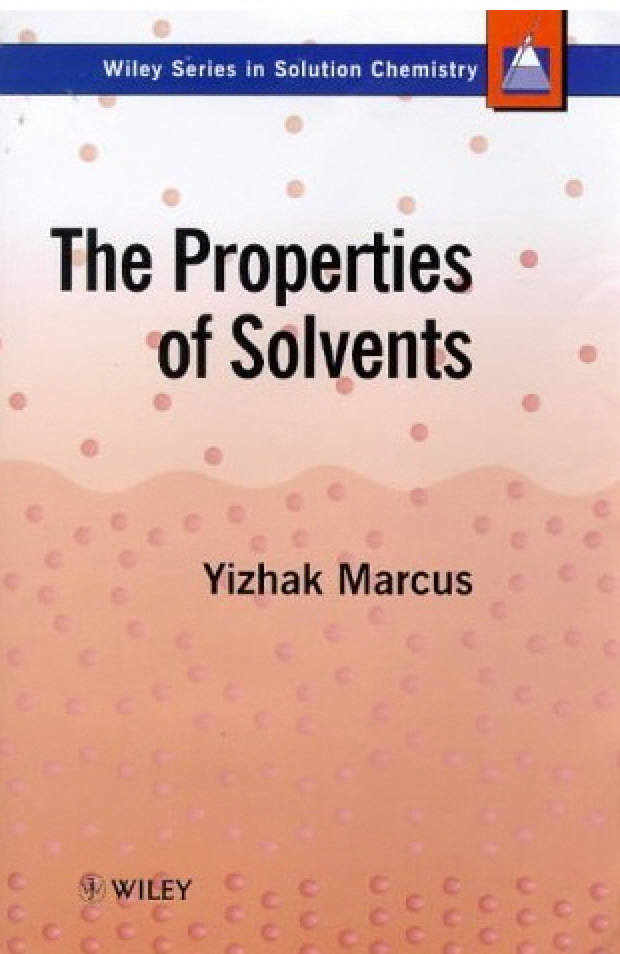

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Contents

Series Preface

There are many aspects of solution chemistry. This is apparent from the wide range of topics which have been discussed during recent International Conferences on Solution Chemistry and International Symposia on Solubility Phenomena. The Wiley Series in Solution Chemistry was launched to fill the need to present authoritative, comprehensive and upto-date accounts of these many aspects. Internationally recognized experts from research or teaching institutions in various countries have been invited to contribute to the Series.

Volumes in print or in preparation cover experimental investigation, theoretical interpretation and prediction of physical chemical properties and behaviour of solutions. They also contain accounts of industrial applications and environmental consequences of properties of solutions.

Subject areas for the Series include: solutions of electrolytes, liquid mixtures, chemical equilibria in solution, acid-base equilibria, vapour-liquid equilibria, liquid-liquid equilibria, solid-liquid equilibria, equilibria in analytical chemistry, dissolution of gases in liquids, dissolution and precipitation, solubility in cryogenic solvents, molten salt systems, solubility measurement techniques, solid solutions, reactions within the solid phase, ion transport reactions away from the interface (i.e. in homogeneous, bulk systems), liquid crystalline systems, solutions of macrocyclic compounds (including macrocyclic electrolytes), polymer systems, molecular dynamic simulations, structural chemistry of liquids and solutions, predictive techniques for properties of solutions, complex and multi-component solutions applications, of solution chemistry to materials and metallurgy (oxide solutions, alloys, mattes etc.), medical aspects of solubility, and environmental issues involving solution phenomena and homogeneous component phenomena.

Current and future volumes in the Series include both single-authored and multi-authored research monographs and reference level works as well as edited collections of themed reviews and articles. They all contain comprehensive bibliographies.

Volumes in the Series are important reading for chemists, physicists, chemical engineers and technologists as well as environmental scientists in academic and industrial institutions.

PETER FOGG
MAY 1996

> endeavored in this book to present as many reliable data as seem to be relevant, without trying to be exhaustive, and to provide these with appropriate annotations. . . . I hope that the long lists of references [following] the extensive tables do not detract too much from the readability of the book. I preferred to have the tables right at the place where the data are discussed or where they can be employed by the reader as an illustration to the points discussed, rather than have them relegated to appendixes.'

Is it necessary to justify further the writing of the present book?

The data collected and shown are from secondary sources—where they have previously been critically evaluated and selected—whenever warranted, but more recent primary sources in research journals have been used to supplement the former or to supersede them if deemed necessary. Access to the primary sources has been through the abstracts up to 1996. The selection of the solvents for which the data are included in this book (the List) is discussed in the Introduction. I am solely responsible for such choices, regarding solvents and data, as have been made. I will be grateful for indications of errors, oversights, and further useful data that may be brought to my attention. Some of the tables are confined to those solvents from the List for which the relevant data have been reported. However, for most of the more extensive tables, many blank spaces have been left, and in some cases entire rows of data have been left blank. This was done with the hope of calling attention to the lack of reliable data, and the expectation that some of these blanks may be filled within the useful lifetime of this book (and its author).

Y. MARCUS
JERUSALEM,
JUNE 1998

List of Symbols

A	surface area of a molecule
A_{vdW}	van der Waals surface area
A, B, C	constants in the Antoine equation
AN	(Gutmann–Mayer) acceptor number
a	activity
a	diameter of ion (distance of closest approach)
a, b	constants in the van der Walls equation
B	(Koppel–Palm) donicity scale
B	second virial coefficient
$b\varepsilon$	non-linear dielectric effect
C_{p}	constant pressure molar heat capacity
C_{V}	constant volume molar heat capacity
c	(volume) concentration (moles per dm^{-3} of solution)
c	specific heat (constant pressure)
c	speed of light, 2.997 92 × 10^{8} ms^{-1}
cmc	critical micelle concentration
D	debye unit of dipole moment, 3.335 64 × 10^{-3} C.m
D	(self) diffusion coefficient
DN	(Gutmann) donor number
D_{S}	(Persson) softness parameter
d	density
d_{C}	critical density
E	electric field strength
E^{o}	standard electrode potential
$E_{1/2}$	polarographic half-wave potential
E_{conf}	configurational energy
$E_{\mathrm{T}}^{\mathrm{N}}$	normalized (Dimroth–Reichardt) polarity index
$E_{\mathrm{T}}(30)$	(Dimroth–Reichardt) polarity index
ΔE_{η}	activation energy for viscous flow
F	Faraday's constant, 96 485 C mol^{-1}

f	fugacity

R	gas constant, 8.3145 J K^{-1} mol^{-1}
R_D	molar refractivity at the sodium D-line
r	radius
r	distance from center of particle
ΔS^*	solvation entropy
ΔS^o	standard entropy change
$\Delta S\neq$	entropy of activation
ΔS_F	(molar) entropy of fusion
S_N1	monomolecular nucleophilic substitution reaction
S_N2	bimolecular nucleophilic substitution reaction
s	molar solubility
T	absolute tmeperature
T_0	ideal glass transition temperature
T_b	(normal, absolute) temperature of boiling
T_C	critical temperature
T_g	(absolute) glass transition temperature
T_m	(absolute) temperature of melting
T_r	reduced temperature, T / T_C
T_t	triple point
t_b	(normal) boiling point (in °C)
t_m	melting temperature (in °C)
$\Delta_V U$	vaporization energy
u	ion mobility
$u(r)$	pair potential
$u^{LJ}(r)$	Lennard–Jones pair potential
ΔV^*	solvation volume
ΔV^o	standard volume change
$\Delta V\neq$	volume of activation
V^E	(excess) molar volume of mixing
V_L	(Leahy) intrinsic volume
V_{vdW}	van der Waals volume
V_X	(McGowan) intrinsic volume

w	mass (weight) fraction
XYZ	generalized solvent-dependent variable
x	mole fraction
Y	(Grunwald–Winstein) solvent polarity parameter
y	packing fraction
Z	(Kosower) polarity index
Z_C	critical compressibility factor
z	(algebraic) charge of ion
[ ]	concentration of the enclosed species
α	polarizability

α	number of solvent molecules sorbed per phenyl group in polystyrene
α	(Kamlet–Taft) hydrogen bond donation ability
α	ultrasound absorption coefficient
α_P	isobaric expansibility
β	(Kamlet–Taft) electron pair donation ability
γ	Ostwald coefficient (for gas solubility)
$\gamma\pm$	mean ionic activity coefficient
${}_w\gamma_s$	transfer activity coefficient from solvent w to solvent s
δ	(Hildebrand) solubility parameter
δ	NMR chemical shift
δ	(Kamlet–Taft) polarizability parameter
ε	(negative of the) depth of the potential well
ε	relative permittivity (dielectric constant)
ε_o	permittivity of free space, 8.8542×10^{-12} C^2 J^{-1} m^{-1}
ε_0	static, low frequency, relative permittivity
ε_∞	relative permittivity at very high ('infinite') frequency
η	(dynamic) viscosity
κ	specific conductance
κ_S	isentropic, adiabatic compressibility
κ_T	isothermal compressibility
λ	equivalent conductivity
λ	thermal conductivity, W K^{-1} m^{-1}
λ_c	critical wavelength
μ	dipole moment
μ	(Marcus) softness parameter
ν	wavenumber
ξ	correlation length
π	group contribution to the 1-octanol/water partition constant
π^*	(Kamlet–Taft) polarity/polarizability parameter
ρ	number density

σ	surface tension
σ	collision diameter of molecules
τ	(orientational) relaxation time
Φ	fluidity
ϕ	volume fraction in actual mixture
φ	volume fraction when volume change on mixing is disregarded
χ	molar volume diamagnetic susceptibility
χ	(Flory–Huggins) interaction parameter
ω	electric field frequency

Chapter 1— Introduction

1—
A Survey of Useful Solvents

Solvents are substances that are liquid under the conditions of application and in which other substances can dissolve, and from which they can be recovered unchanged on removal of the solvent. So many substances conform to this definition—practically all those that can be liquefied under some conditions—that it is not very helpful, unless the word 'application' is stressed, meaning that the solvents and the solutions in them ought to be applicable for some purpose. In the present context, therefore, materials that can be liquefied only under extreme conditions of temperature and presfsure will not be considered extensively. This excludes, for instance, molten salts and slags on the one hand and 'permanent' gases on the other, unless they have found some use as 'supercritical solvents'. Then, again, binary or multi-component liquid mixtures are not dealt with here, although they can be very useful as solvents, since this would have expanded the size of this book enormously. This still leaves a host of organic and many inorganic substances that are liquid at or near ambient conditions, which could be considered to be solvents under the present definition. Of these, a limited number are selected, in order for this book to be useful and handy, rather than trying in vain to be comprehensive and encyclopedic.

The solvents that are included in the extensive compilations of physical and chemical properties shown in this book (the List, referred to as such in this book) have been selected so as to cover the major classes of solvents, and bring several examples of each class. The properties of solvents that have not been included, but that belong to these classes, in particular isomers or higher members of homologous series, can often be inferred from the reported data at least to some extent. One criterion according to which solvents have been selected for inclusion in the List is that most of their physical and chemical properties, among those considered here, should be known. In particular, those chemical properties pertaining to their ability to solvate solutes are stressed as criteria for inclusion, since this book is a part of a series on Solution Chemistry. This solvating ability can be characterized by so-called solvatochromic parameters or similar indices of solvation ability, and some, at least, of the most commonly used of these parameters, ought to be known for inclusion of the solvent in the List.

Water, being the most abundant, extensively employed, and a very useful solvent, has always been accorded very wide attention by chemists of all subdisciplines who have been studying solutions. As an antithesis, the keyword 'non-aqueous' has figured in the titles of many treatments of other solvents. Inorganic solvents have long been considered to be the typical 'non-aqueous solvents', as is manifested in the titles of several books dealing almost exclusively with them, written or edited in the fifties and early sixties by authors such as (Audrieth and Kleinberg 1953; Sisler 1961; Waddington 1965). Only little attention was accorded at the time to organic non-aqueous solvents. In the last few decades, however, this tendency has reversed completely, and a large number of organic, in particular dipolar aprotic, solvents have been dealt with extensively in this context of 'non-aqueous solvents', almost to the exclusion of the traditional inorganic ones, as, for instance, in the books edited by (Coetzee and Ritchie 1969; Lagowski 1966–1978; Covington and Jones 1968). However, the older compilations of physical properties of organic substances (International Critical Tables 1926–1930; Landold–Börnstein Tables 1959 and Timmermann's compilation) do not include most of the now commonly used dipolar aprotic solvents, the relevant data being found only in more recent works, e.g., (Riddick, Bunger and Sakano 1986 and the DIPPR compilation 1997). Then, again, in many books with extensive data, solvents used for electrolytes or ions, polar solvents, whether protic or not, are not always considered together with those used for non-polar commercial materials, such as paints, polymers, etc., or for pharmaceuticals and industrial processes. Here, both kinds are accorded the appropriate space.

A classification scheme for solvents needs, therefore, to reflect to some extent the uses for which the solvents are put. Many classification schemes have been proposed, and a single major property, that may form the basis for the usefulness of solvents for certain applications, can often be employed in order to classify solvents. On the other hand, a few selected properties may advantageously be used to form the basis for the classification. Various solvent classification schemes have been presented (Reichardt 1988) and a common solvent classification scheme is:

(i) non-polar solvents (such as hexane and tetrachloromethane),
(ii) solvents of low polarity (such as toluene and chloroform),
(iii) aprotic dipolar solvents (such as acetone and N,N-dimethylformamide),
(iv) protic and protogenic solvents (such as ethanol and nitromethane),
(v) basic solvents (such as pyridine and 1,2-diaminoethane), and
(vi) acidic solvents (such as 3-methylphenol and butanoic acid).

Some other classification schemes shown below (that differ from the one above only in minor details or in the terminology) are as follows. One classification, (Kolthoff 1974) and (Reichardt 1988), called ***A*** below, is according to the polarity, described by the relative permittivity (dielectric constant) ε the dipole moment μ (in 10^{-30} C.m), and the hydrogen bond donation ability E_T^N (see Chapter 4). Another suggested classification (Parker), called ***B*** below, stresses the acidity and basicity (relative to water) of the solvents. A third one, (Chastrette 1974, 1979), called ***C*** below, stresses the hydrogen bonding and electron pair donation abilities, the polarity, and the extent of self-association. As stated above, the differences among these schemes are mainly semantic ones and are of no real consequence.

Solvent classification scheme ***A***.

Designation	ε	μ	E_T^N	Examples
apolar aprotic	< 15	< 8.3	0.0–0.3	hydrocarbons, halogen substituted hydrocarbons, tertiary amines
weakly polar aprotic	< 15	< 8.3		ethers, esters, pyridine, primary and secondary amines
dipolar aprotic	> 15	> 8.3	0.3–0.5	ketones, nitriles, nitro-compounds, N,N-disubstituted amides, sulfoxides
protic			0.5–1.0	water, alcohols, mono- or unsubstituted amides, carboxylic acids, ammonia

Solvent classification scheme ***B***.

Solvent designation	Relative acidity/basicity	Examples
protic–neutral	fairly strong as either	H_2O, CH_3OH, $(CH_3)_3COH$, C_6H_5OH
protogenic	more acid than water	H_2SO_4, HCOOH
protophilic	more basic than water	NH_3, $HCONH_2$, $H_2NC_2H_4NH_2$
aprotic, protophilic	more basic and less acidic than water	$HCON(CH_3)_2$, CH_3SOCH_3, C_5H_5N, $(C_2H_5)_2O$, tetrahydrofuran
aprotic, protophobic	fairly weak as either	CH_3CN, CH_3COCH_3, CH_3NO_2
aprotic, inert	fairly weak as either	C_6H_{14}, C_6H_6, ClC_2H_4Cl, CCl_4

Solvent classification scheme ***C***.

Solvent class	Examples
apolar, aprotic, electron pair donors	amines, ethers
slightly polar, aprotic, aromatic	chlorobenzene, anisole, acetophenone
apolar, aprotic, aromatic	benzene, substituted aromatic hydrocarbons
aprotic dipolar	nitromethane, acetonitrile, acetone, pyridine
highly polar aprotic	dimethyl sulfoxide, bezonitrile, nitrobenzene
highly polar, polarizable aprotic	sulfolane, hexamethyl phosphoramide
hydrogen bonding	alcohols, ether-alcohols, phenols

highly associated hydrogen bonding	water, ethylene glycol, formamide
miscellaneous	choloroform, carbon disulfide, aniline

In the following, the chemical constitution scheme (Riddick, Bunger and Sakano 1986) is followed, with some minor alterations in their sequence. This sequence is followed in the Tables that constitute the major part of this book and is: aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, phenols, ethers, aldehydes, ketones, carboxylic acids, esters, halogen-substituted hydrocarbons, amines, nitriles and nitro-derivatives, amides, sulfur-containing solvents, phosphorus-containing solvents, and inorganic solvents. Alicyclic solvents are included with the straight-chain ones, and aliphatic solvents precede aromatic and heterocyclic ones. Bifunctional solvents are included with those to which the arbitrarily deemed more important function belongs .Water is considered to be the smallest alkanol, but ammonia, rather than as the shortest amine, is included with the inorganic solvents.

Table 1.1 shows the solvents on the List, that are dealt with in the following sections of the book. An ordinal number in the first column identifies the solvents and can be used for their consistent sequencing. Several alternative names can be assigned to each solvent, and a commonly used one is employed here, without prejudice to other commonly employed ones. Neither is the nomenclature used trying to drive the systematic (IUPAC) nomenclature to its most absurd length. The abbreviations c ≡ cyclo, n ≡ normal, i ≡ iso, and t ≡ tertiary, as well as o ≡ ortho, m ≡ meta, and p ≡ para are used in the names.

Since many solvents have quite common synonyms that are in widespread use, such synonyms are also listed in Table 1.1. Not all common synonyms are shown, and in several cases some permutations of the elements of the name or the Chemical Abstracts name are used as synonyms. In a few cases, Tables and text in other sections of the book refer to these synonyms rather than to the names in the second column, but the serial number shown should prevent any errors of identification.

In order to specify the solvent more clearly, its linear structural formula is given in the fourth column, where in order to save space the common abbreviations Me ≡ methyl and Ph ≡ phenyl are used and c-···- denotes a cyclic compound. (Bicyclic solvents, such as quinoline, could not be illustrated by this device.) The compositional formula in the fifth column follows the convention of alphabetical listing of the atoms in the molecule of the solvent, but with 'C' for carbon being followed first by 'H' for hydrogen, before other kinds of atoms in organic molecules. The entries in this column help in locating the solvent in formula indexes and listings made according to the compositional formula.

A further aid in the location of the solvents and their exact specification is the Chemical Abstracts name, shown in the sixth column of Table 1.1, and the Chemical Abstracts (CAS) Registry Number, shown in the seventh. The Chemical Abstracts name may be the same as the commonly used one or may differ from it considerably, so that it is not always easy to find the solvents in the Chemical Substance Indexes of the Chemical Abstracts. For instance, 'benzene, methyl' is a fairly transparent name for toluene, and 'methanol, phenyl' a slightly

Table 1.1 Nominal data of the solvents on the List

No.	Name	Synonym	Structural Formula	Composition	Chem. Abstr. Name	Cas. Reg. No
10	tetramethylsilane		Me_4Si	$C_4H_{12}Si$	silane, tetramethyl	75-76-3
20	n-pentane		$CH_3(CH_2)_3CH_3$	C_5H_{12}	pentane	109-66-0
30	2-methylbutane	isopentane	$Me_2CHCH_2CH_3$	C_5H_{12}	butane, 2-methyl	78-78-4
40	n-hexane		$CH_3(CH_2)_4CH_3$	C_6H_{14}	hexane	110-54-3
50	c-hexane		c-$(CH_2)_6$-	C_6H_{12}	cyclohexane	110-82-7
60	n-heptane		$CH_3(CH_2)_5CH_3$	C_7H_{16}	heptane	142-82-5
70	n-octane		$CH_3(CH_2)_6CH_3$	C_8H_{18}	octane	111-65-9
80	2,2,4-trimethylpentane	isooctane	$CH_3CMe_2CH_2CHMe_2$	C_8H_{18}	pentane, 2,2,4-trimethyl	540-84-1
90	n-decane		$CH_3(CH_2)_8CH_3$	$C_{10}H_{22}$	decane	124-18-5
100	n-dodecane		$CH_3(CH_2)_{10}CH_3$	$C_{12}H_{26}$	dodecane	112-40-3
110	n-hexadecane	cetane	$CH_3(CH_2)_{14}CH_3$	$C_{16}H_{34}$	hexadecane	544-76-3
120	benzene		C_6H_6	C_6H_6	benzene	71-43-2
130	toluene		PhMe	C_7H_8	benzene, methyl	108-88-3
140	o-xylene		1,2-$PhMe_2$	C_8H_{10}	benzene, 1,2-dimethyl	95-47-6
150	m-xylene		1,3-$PhMe_2$	C_8H_{10}	benzene, 1,3-dimethyl	108-38-3
160	p-xylene		1,4-$PhMe_2$	C_8H_{10}	benzene, 1,4-dimethyl	106-42-3
170	ethylbenzene		PhC_2H_5	C_8H_{10}	benzene, ethyl	100-41-4
180	isopropylbenzene	cumene	$PhCHMe_2$	C_9H_{12}	benzene, 1-methylethyl	98-82-8
190	mesitylene		1,3,5-$C_6H_3Me_3$	C_9H_{12}	benzene, 1,3,5-trimethyl	108-67-8
200	styrene	vinylbenzene	$PhCH=CH_2$	C_8H_8	benzene, ethenyl	100-42-5
210	tetralin	tetrahydronaphthalen	1,2-Ph-c-$(CH_2)_4$-	$C_{10}H_{12}$	naphthalene, tetrahydro	119-64-2

220	cis-decalin	decahydronaphthalen		$C_{10}H_{16}$	naphthalene, decahydro	493-01-6
230	water		HOH	H_2O	water	7732-18-5
240	methanol	methyl alcohol	MeOH	CH_4O	methanol	67-56-1
250	ethanol	ethyl alcohol	C_2H_5OH	C_2H_6O	ethanol	64-17-5
260	1-propanol	n-propyl alcohol	C_3H_7OH	C_3H_8O	1-propanol	71-23-8
270	2-propanol	isopropyl alcohol	Me_2CHOH	C_3H_8O	2-propanol	67-63-0
280	1-butanol	n-butyl alcohol	C_4H_9OH	$C_4H_{10}O$	1-butanol	71-36-3
290	2-methyl-1-propanol	isobutyl alcohol	Me_2CHCH_2OH	$C_4H_{10}O$	1-propanol, 2-methyl	78-83-1
300	2-butanol	s-butyl alcohol	$C_2H_5CH(OH)CH_3$	$C_4H_{10}O$	2-butanol	78-92-2
310	2-methyl-2-propanol	t-butyl alcohol	Me_3COH	$C_4H_{10}O$	2-propanol, 2-methyl	76-65-0
320	n-pentanol	n-pentyl alcohol	$C_5H_{11}OH$	$C_5H_{12}O$	1-pentanol	71-41-0

continued overleaf

***Table 1.1** (continued)*

No.	Name	Synonym	Structural Formula	Composition	Chem.Abstr. Name	Cas. Reg. No
330	i-pentanol	amyl alcohol	$Me_2CHCH_2CH_2OH$	$C_5H_{12}O$	1-butanol, 3-methyl	123-51-3
340	t-pentanol	t-pentyl alcohol	$CH_3CH_2CMe_2OH$	$C_5H_{12}O$	2-butanol, 2-methyl	75-85-4
350	n-hexanol	n-hexyl alcohol	$C_6H_{13}OH$	$C_6H_{14}O$	1-hexanol	111-27-3
360	c-hexanol	cyclohexyl alcohol	$c\text{-}C_6H_{11}OH$	$C_6H_{12}O$	cyclohexanol	108-93-0
370	n-octanol	n-octyl alcohol	$C_8H_{17}OH$	$C_8H_{18}O$	1-octanol	111-87-5
380	n-decanol	n-decyl alcohol	$C_{10}H_{21}OH$	$C_{10}H_{22}O$	1-decanol	112-30-1
390	n-dodecanol	lauryl alcohol	$C_{12}H_{25}OH$	$C_{12}H_{26}O$	1-dodecanol	112-53-8
400	benzyl alcohol		$PhCH_2OH$	C_7H_8O	benzenemethanol	100-51-6
410	2-phenylethanol		$PhCH_2CH_2OH$	$C_8H_{10}O$	ethanol, 2-phenyl	1321-27-3
420	allyl alcohol		$CH_2{=}CHCH_2OH$	C_3H_6O	2-propen-1-ol	107-18-6
430	2-chloroethanol	glycol chlorhydrine	$ClCH_2CH_2OH$	C_2H_5ClO	ethanol, 2-chloro	107-07-3
440	2-cyanoethanol		$NCCH_2CH_2OH$	C_3H_5NO	propanenitrile, 3-hydroxy	109-78-4
450	2,2,2-trifluoroethanol		F_3CCH_2OH	$C_2H_3F_3O$	ethanol, 2,2,2-trifluoro-	75-89-8
460	hexafluoro-i-propanol		$CF_3CH(OH)CF_3$	$C_3H_2F_6O$	2-propanol, 1,1,1,3,3,3-hexafluoro-	920-66-1
470	2-methoxyethanol	methyl cellosolve	$MeOCH_2CH_2OH$	C_3H_8O	ethanol, 2-methoxy	109-86-4
480	2-ethoxyethanol	cellosolve	$C_2H_5OCH_2CH_2OH$	$C_4H_{10}O$	ethanol, 2-ethoxy	110-80-5
490	1,2-ethanediol	ethylene glycol	$HOCH_2CH_2OH$	$C_2H_6O_2$	1,2-ethanediol	107-21-1
500	1,2-propanediol	1,2-propylene glycol	$HOCH_2CH(OH)CH_3$	$C_3H_8O_2$	1,2-propanediol	57-55-6
510	1,3-propanediol	1,3-propylene glycol	$HOCH_2CH_2CH_2OH$	$C_3H_8O_2$	1,3-propanediol	504-63-2
520	1,2-butanediol	1,2-butylene glycol	$HOCH_2CH(OH)CH_2CH_3$	$C_4H_{10}O_2$	1,2-butanediol	584-03-2

530	2,3-butanediol (meso)	2,3-butylene glycol	$CH_3CH(OH)CH(OH)CH_3$	$C_4H_{10}O_2$	2,3-butanediol	5341-95-7
540	1,4-butanediol	1,4-butylene glycol	$HOCH_2CH_2CH_2CH_2OH$	$C_4H_{10}O_2$	1,4-butanediol	110-63-4
550	1,5-pentanediol	1,5-pentylene glycol	$HO(CH_2)_5OH$	$C_5H_{12}O_2$	1,5-pentanediol	111-29-5
560	diethyleneglycol	diglycol	$HOC_2H_4OC_2H_4OH$	$C_4H_{10}O_3$	ethanol, 2,2′-oxybis-	111-46-6
570	triethyleneglycol	triglycol	$HOC_2H_4OC_2H_4OC_2H_4OH$	$C_6H_{14}O_4$	ethanol, 2,2′[1,2-ethanediylbis(oxy)]	112-27-6
580	glycerol	glycerin	$HOCH_2CH(OH)CH_2OH$	$C_3H_8O_3$	1,2,3-propanetriol	56-81-5
590	phenol		PhOH	C_6H_6O	phenol	108-95-2
600	2-methylphenol	o-cresol	2-MePhOH	C_7H_8O	phenol, 2-methyl	95-48-7
610	3-methylphenol	m-cresol	3-MePhOH	C_7H_8O	phenol, 3-methyl	108-39-4
620	4-methylphenol	p-cresol	4-MePhOH	C_7H_8O	phenol, 4-methyl	106-44-5
630	2-methoxyphenol	o-hydroxyanisole	2-MeOPhOH	$C_7H_8O_2$	phenol, 2-methoxy-	90-05-1
640	2,4-dimethylphenol	2,4-xylenol	$2,4\text{-}Me_2PhOH$	$C_8H_{10}O$	phenol, 2,4-dimethyl	105-67-9

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No.	Name	Synonym	Structural Formula	Composition	Chem. Abstr. Name	Cas. Reg. No
650	3-chlorophenol		3-ClPhOH	C_6H_5ClO	phenol, 3-chloro-	108-43-0
660	diethyl ether	ether	$C_2H_5OC_2H_5$	$C_4H_{10}O$	ethane, 1,1′-oxybis-	60-29-7
670	di-n-propyl ether	propyl ether	$C_3H_7OC_3H_7$	$C_6H_{14}O$	propane, 1,1′-oxybis-	111-43-3
680	di-i-propyl ether	isopropyl ether	$Me_2CHOCHMe_2$	$C_6H_{14}O$	propane, 2,2′-oxybis-	108-20-3
690	di-n-butyl ether	butyl ether	$C_4H_9OC_4H_9$	$C_8H_{18}O$	butane, 1,1′-oxybis-	142-96-1
700	di(2-chloroethyl) ether		$ClC_2H_4OC_2H_4Cl$	$C_4H_8Cl_2O$	ethane, 1,1′-oxybis(2-chloro-)	111-44-4
710	1,2-dimethoxyethane		$MeOC_2H_4OMe$	$C_4H_{10}O_2$	ethane, 1,2-dimethoxy	110-71-4
720	bis(methoxyethyl)ether	diglyme	$MeOC_2H_4OC_2H_4OMe$	$C_6H_{14}O_3$	ethane, 1,1′-oxybis(2-methoxy-)	111-96-6
730	furan		$c\text{-}(CH)_4\text{-}O\text{-}$	C_4H_4O	furan	110-00-9
740	tetrahydrofuran	tetramethylene oxide	$c\text{-}(CH_2)_4\text{-}O\text{-}$	C_4H_8O	furan, tetrahydro	109-99-9
750	2-methyl tetrahydrofuran		$c\text{-}(CH_2)_3\text{-}CHMe\text{-}O\text{-}$	$C_5H_{10}O$	furan, tetrahydro, 2-methyl	96-47-9
760	tetrahydropyran	pentamethylene oxide	$c\text{-}(CH_2)_5\text{-}O\text{-}$	$C_5H_{10}O$	pyran, tetrahydro	142-68-7
770	1,4-dioxolane		$c\text{-}O(CH_2)_2\text{-}O\text{-}(CH_2)_2\text{-}$	$C_4H_8O_2$	1,4-dioxane	123-91-1
780	1,3-dioxolane		$c\text{-}OCH_2\text{-}O(CH_2)_2\text{-}O\text{-}$	$C_3H_6O_2$	1,3-dioxolane	646-06-6
790	1,8-cineole			$C_{10}H_{18}O$	2-oxabicyclo [2,2,2]octane, 1,3,3-trimethyl	470-82-6
800	anisole	methoxybenzene	MeOPh	C_7H_8O	benzene, methoxy	100-66-3
810	phenetole	ethoxybenzene	CH_3CH_2OPh	$C_8H_{10}O$	benzene, ethoxy	103-73-1
820	diphenyl ether	phenyl ether	PhOPh	$C_{12}H_{10}O$	benzene, 1,1′-oxybis	101-84-8
830	dibenzyl ether	benzyl ether	$PhCH_2OCH_2Ph$	$C_{14}H_{14}O$	benzene, 1,1′-[oxybis(methylene)bis-]	103-50-4

840	1,2-dimethoxybenzene	veratrole	1,2-Ph(OMe)2	$C_8H_{10}O_2$	benzene, 1,2-dimethoxy	91-16-7
850	trimethyl orthoformate		$HC(OMe)_2$	$C_4H_{10}O_3$	methane, trimethoxy	149-73-5
860	trimethyl orthoacetate		$CH_3C(OMe)_3$	$C_5H_2O_3$	ethane, 1,1,1-trimethoxy	1445-5-0
870	propionaldehyde		$CH_3CH_2CH(O)$	C_3H_6O	propanal	123-38-6
880	butyraldehyde		$CH_3CH_2CH_2CH(O)$	C_4H_8O	butanal	123-72-8
890	benzaldehyde		PhCH(O)	C_7H_6O	benzaldehyde	100-52-7
900	p-methoxybenzaldehyde	anisaldehyde	4-MeOPhCHO	$C_8H_8O_2$	benzaldehyde, 4-methoxy-	123-11-5
910	cinnamaldehyde		PhCH=CHCH(O)	C_9H_8O	2-propenal, 3-phenyl	104-55-2
920	acetone		MeC(O)Me	C_3H_6O	2-propanone	67-64-1
930	2-butanone	methyl ethyl ketone	$MeC(O)C_2H_5$	C_4H_8O	2-butanone	78-93-3
940	2-pentanone	methyl-n-propyl ketone	$MeC(O)C_3H_7$	$C_5H_{10}O$	2-pentanone	107-87-9
950	methyl i-propyl ketone		$MeC(O)CHMe_2$	$C_5H_{10}O$	2-butanone, 3-methyl	563-80-4
960	3-pentanone	diethyl ketone	$C_2H_5C(O)C_2H_5$	$C_5H_{10}O$	3-pentanone	96-22-0
970	c-pentanone		$c\text{-}(CH_2)_4C(O)\text{-}$	C_5H_8O	cyclopentanone	120-92-3

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***Table 1.1** (continued)*

No.	Name	Synonym	Structural Formula	Composition	Chem. Abstr. Name	Cas. Reg. No
980	methyl-i-butyl ketone	hexone	$MeC(O)CH_2CHMe_2$	$C_6H_{12}O$	2-pentanone, 4-methyl	108-10-1
990	methyl t-butyl ketone		$MeC(O)CMe_3$	$C_6H_{12}O$	2-butanone, 3,3-dimethyl	75-97-8
1000	c-hexanone		$c\text{-}(CH_2)_5C(O)\text{-}$	$C_6H_{10}O$	cyclohexanone	108-94-1
1010	2-heptanone	methyl pentyl ketone	$MeC(O)C_5H_{11}$	$C_7H_{14}O$	2-heptanone	110-43-0
1020	3-heptanone	ethyl butyl ketone	$CH_3CH_2C(O)C_4H_9$	$C_7H_{14}O$	3-heptanone	106-35-4
1030	di-t-butyl ketone		$Me_3CC(O)CMe_3$	$C_9H_{18}O$	3-pentanone, 2,2,4,4-tetramethyl	815-24-7
1040	acetophenone	methyl phenyl ketone	PhC(O)Me	C_8H_8O	ethanone, 1-phenyl	98-86-2
1050	propiophenone	ethyl phenyl ketone	$PhC(O)C_2H_5$	$C_9H_{10}O$	1-propanone, 1-phenyl	93-55-0
1060	phenylacetone	benzyl methyl ketone	$PhCH_2C(O)Me$	$C_9H_{10}O$	2-propanone, 1-phenyl	103-79-7
1070	p-methylacetophenone		4-MePhC(O)Me	$C_9H_{10}O$	ethanone, 1-(4-methylphenyl)	122-00-9
1080	p-chloroacetophenone		4-ClPhC(O)Me	C_8H_7ClO	ethanone, 1-(4-chlorophenyl)	99-91-2
1090	benzophenone	diphenyl ketone	PhC(O)Ph	$C_{13}H_{10}O$	methanone, diphenyl	119-61-9
1100	acetylacetone	2,3-pentanedione	$MeC(O)CH_2C(O)Me$	$C_5H_8O_2$	2,4-pentanedione	123-54-6
1110	biacetyl	2,3-butanedione	MeC(O)C(O)Me	$C_4H_6O_2$	2,3-butanedione	431-03-8
1120	formic acid		HCOOH	CH_2O_2	formic acid	64-18-6
1130	acetic acid	ethanoic acid	CH_3COOH	$C_2H_4O_2$	acetic acid	64-19-7
1140	propanoic acid	propionic acid	C_2H_5COOH	$C_3H_6O_2$	propanoic acid	79-09-4
1150	n-butanoic acid	butyric acid	C_3H_7COOH	$C_4H_8O_2$	butanoic acid	107-92-6
1160	n-pentanoic acid	valeric acid	C_4H_9COOH	$C_5H_{10}O_2$	pentanoic acid	109-52-4

1170	n-hexanoic acid	caproic acid	$C_5H_{11}COOH$	$C_6H_{12}O_2$	hexanoic acid	142-62-1
1180	n-heptanoic acid	enanthic acid	$C_6H_{13}COOH$	$C_7H_{14}O_2$	heptanoic acid	111-14-8
1190	dichloroacetic acid		$Cl_2CHCOOH$	$C_2H_2Cl_2O_2$	acetic acid, dichloro-	79-43-6
1200	trifluoroacetic acid		F_3CCOOH	$C_2HF_3O_2$	acetic acid, trifluoro-	76-05-1
1210	acetic anhydride		$CH_3C(O)OC(O)CH_3$	$C_4H_6O_3$	acetic acid, anhydride	108-24-7
1220	benzoyl chloride		$PhC(O)Cl$	C_7H_5ClO	benzoyl chloride	98-88-4
1230	benzoyl bromide		$PhC(O)Br$	C_7H_5BrO	benzoyl bromide	618-32-6
1240	methyl formate		$HC(O)O\ Me$	$C_2H_4O_2$	formic acid, methyl ester	107-31-3
1250	ethyl formate		$HC(O)OC_2H_5$	$C_3H_6O_2$	formic acid, ethyl ester	109-94-4
1260	methyl acetate		$CH_3C(O)O\ Me$	$C_3H_6O_2$	acetic acid, ethyl ester	79-20-9
1270	ethyl acetate		$CH_3C(O)C_2H_5$	$C_4H_8O_2$	acetic acid, ethyl ester	141-78-6
1280	propyl acetate		$CH_3C(O)OC_3H_7$	$C_5H_{10}O_2$	acetic acid, propyl ester	109-60-4
1290	butyl acetate		$CH_3C(O)OC_4H_9$	$C_6H_{12}O_2$	acetic acid, butyl ester	123-86-4
1300	i-pentyl acetate	amyl acetate	$CH_3C(O)OCH_2CH_2CHMe_2$	$C_7H_{14}O_2$	acetic acid, 3-methyl-1-butyl ester	123-92-2

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No.	Name	Synonym	Structural Formula	Composition	Chem. Abstr. Name	Cas. Reg. No
1310	methyl propanoate		$C_2H_5C(O)OMe$	$C_4H_8O_2$	propanoic acid, methyl ester	554-12-1
1320	ethyl propanoate		$C_2H_5C(O)OC_2H_5$	$C_5H_{10}O_2$	propanoic acid, ethyl ester	105-37-3
1330	dimethyl carbonate	methyl carbonate	$(MeO)_2CO$	$C_3H_6O_3$	carbonic acid, dimethyl ester	616-38-6
1340	diethyl carbonate	ethyl carbonate	$(C_2H_5O)_2CO$	$C_5H_{10}O_3$	carbonic acid, diethyl ester	105-58-8
1350	ethylene carbonate		$c\text{-}C_2H_4OC(O)O\text{-}$	$C_3H_4O_3$	1,3-dioxolane-2-one	96-49-1
1360	propylene carbonate		$c\text{-}CH(Me)CH_2OC(O)\text{-}$	$C_4H_6O_3$	1,3-dioxolane-2-one, 4-methyl	108-32-7
1370	diethyl malonate	ethyl malonate	$(C_2H_5OC(O))_2CH_2$	$C_7H_{12}O_4$	propanedioic acid, diethyl ester	105-53-3
1380	methyl benzoate		PhCOOMe	$C_8H_8O_2$	benzoic acid, methyl ester	93-58-3
1390	ethyl benzoate		$PhCOOC_2H_5$	$C_9H_{10}O_2$	benzoic acid, ethyl ester	93-89-0
1400	dimethyl phthalate		$1,2\text{-}Ph(COOMe)_2$	$C_{10}H_{10}O_4$	1,2-benzenedicarboxylic acid, dimethyl ester	131-11-3
1410	dibutyl phthalate		$1,2\text{-}Ph(COOC_4H_9)_2$	$C_{16}H_{22}O_4$	1,2-benzenedicarboxylic acid, dibutyl ester	84-74-2
1420	ethyl chloroacetate		$ClCH_2COOC_2H_5$	$C_4H_7ClO_2$	acetic acid, chloro, ethyl ester	105-39-5
1430	ethyl trichloroacetate		$Cl_3CCOOC_2H_5$	$C_4H_5Cl_3O$	acetic acid, trichloro, ethyl ester	515-84-4
1440	ethyl acetoacetate		$CH_3C(O)CH_2COOC_2H_5$	$C_6H_{10}O_3$	butanoic acid, 3-oxo-, ethyl ester	141-97-9
1450	4-butyrolactone	gamma-butyrolacton	$c\text{-}(CH_2)_3C(O)O\text{-}$	$C_4H_6O_2$	2(3H)-furanone, dihydro	96-48-0
1460	perfluoro-n-hexane		$CF_3(CF_2)_4CF_3$	C_6F_{14}	hexane, tetradecafluoro-	355-42-0
1470	perfluoro-n-heptane		$CF_3(CF_2)_5CF_3$	C_7F_{16}	heptane, hexadecafluoro-	355-57-9
1480	perfluoro-methylcyclohexane		$CF_3\text{-}c\text{-}CF(CF_2)_5\text{-}$	C_7F_{14}	cyclohexane, methyl, tetradecafluoro	355-02-2

1490	perfluoro-decalin			$C_{10}F_{18}$	naphthalene, decahydro, octadecafluoro	306-94-5
1500	fluorobenzene		PhF	C_6H_5F	benzene, fluoro-	462-06-6
1510	hexafluorobenzene		C_6F_6	C_6F_6	benzene, hexafluoro-	392-56-3
1520	1-chlorobutane		$CH_3CH_2CH_2CH_2Cl$	C_4H_9Cl	butane, 1-chloro-	109-69-3
1530	chlorobenzene		PhCl	C_6H_5Cl	benzene, chloro-	108-90-7
1540	dichloromethane	methylene chloride	CH_2Cl_2	CH_2Cl_2	methane, dichloro-	75-09-2
1550	1,1-dichloroethane	ethylidene chloride	Cl_2CHCH_3	$C_2H_4Cl_2$	ethane, 1,1-dichloro-	75-34-3
1560	1,2-dichloroethane	ethylene chloride	$ClCH_2CH_2Cl$	$C_2H_4Cl_2$	ethane, 1,2-dichloro-	107-06-2
1570	tr-1,2-dichloroethylene		tr-CHCl=CHCl	$C_2H_2Cl_2$	ethene, 1,2-dichloro- (Z)	156-60-5
1580	o-dichlorobenzene		1,2-$PhCl_2$	$C_6H_4Cl_2$	benzene, 1,2-dichloro-	95-50-1
1590	m-dichlorobenzene		1,3-$PhCl_2$	$C_6H_4Cl_2$	benzene, 1,3-dichloro-	541-73-1
1600	chloroform	trichloromethane	$CHCl_3$	$CHCl_3$	methane, trichloro	67-66-3
1610	1,1,1-trichloroethane	methyl chloroform	Cl_3CCH_3	$C_2H_3Cl_3$	ethane, 1,1,1-trichloro-	71-55-6

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Table 1.1 *(continued)*

No.	Name	Synonym	Structural Formula	Composition	Chem. Abstr. Name	Cas. Reg. No
1620	1,1,2-trichloroethane		$CHCl_2CH_2Cl$	$C_2H_3Cl_3$	ethane, 1,1,2-trichloro-	79-00-5
1630	trichloroethylene		$CCl_2=CHCl$	C_2HCl_3	ethene, trichloro-	79-01-6
1640	1,2,4-trichlorobenzene		1,2,4-$C_6H_3Cl_3$	$C_6H_3Cl_3$	benzene, 1,2,4-trichloro-	120-82-1
1650	tetrachloromethane	carbon tetrachloride	CCl_4	CCl_4	methane, tetrachloro-	56-23-5
1660	tetrachloroethylene		$CCl_2=CCl_2$	C_2Cl_4	ethene, tetrachloro	127-18-4
1670	1,1,2,2-tetrachloroethane		$CHCl_2CHCl_2$	$C_2H_2Cl_4$	ethane, 1,1,2,2-tetrachloro-	79-34-5
1680	pentachloroethane		$CHCl_2CCl_3$	C_2HCl_5	ethane, pentachloro-	76-01-7
1690	1-bromobutane		$CH_3CH_2CH_2CH_2Br$	C_4H_9Br	butane, 1-bromo-	109-65-9
1700	bromobenzene		PhBr	C_6H_5Br	benzene, bromo-	108-86-1
1710	dibromomethane	methylene bromide	CH_2Br_2	CH_2Br_2	methane, dibromo-	74-95-3
1720	1,2-dibromoethane	ethylene bromide	CH_2BrCH_2Br	$C_2H_4Br_2$	ethane, 1,2-dibromo-	106-93-4
1730	bromoform		$CHBr_3$	$CHBr_3$	methane, tribromo	75-25-2
1740	1-iodobutane		$CH_3CH_2CH_2CH_2I$	C_4H_9I	butane, 1-iodo-	542-69-8
1750	iodobenzene		PhI	C_6H_5I	benzene, iodo-	591-50-4
1760	diiodomethane	methylene iodide	CH_2I_2	CH_2I_2	methane, diiodo-	75-11-6
1770	n-butylamine	1-aminobutane	$CH_3CH_2CH_2CH_2NH_2$	$C_4H_{11}N$	1-butanamine	109-73-9
1780	benzylamine		$PhCH_2NH_2$	C_7H_9N	benzenemethanamine	100-46-9
1790	1,2-diaminoethane	ethylene diamine	$H_2NCH_2CH_2NH_2$	$C_2H_8N_2$	1,2-ethanediamine	107-15-3
1800	diethylamine		$(C_2H_5)_2NH$	$C_4H_{11}N$	ethanamine, N-ethyl	109-89-7
1810	di-n-butylamine		$(C_4H_9)_2NH$	$C_8H_{19}N$	1-butanamine, N-1-butyl	111-92-2
1820	pyrrole	azole			1 H-pyrrole	109-97-7

			c-$(CH)_4$-NH-	C_4H_5N		
1830	pyrrolidine	tetrahydropyrrole	c-$(CH_2)_4$-NH-	C_4H_9N	pyrrolidine	123-75-1
1840	piperidine	hexahydropyridine	c-$(CH_2)_5$-NH-	$C_5H_{11}N$	piperidine	110-89-4
1850	morpholine	tetrahydro-p-oxazine	c-O-$(CH_2)_2$-NH-$(CH_2)_2$-	C_4H_9NO	morpholine	110-91-8
1860	triethylamine		$(C_2H_5)_3N$	$C_6H_{15}N$	ethanamine, N,N-diethyl	121-44-9
1870	tri-n-butylamine		$(C_4H_9)_3N$	$C_{12}H_{27}N$	1-butanamine, N,N-di-1-butyl	102-82-9
1880	aniline		$PhNH_2$	C_6H_7N	benzenamine	62-53-3
1890	o-chloroaniline		2-Ph(Cl)NH_2	C_6H_6ClN	benzenamine, 2-chloro-	95-51-2
1900	N-methylaniline		PhNHMe	C_7H_9N	benzenamine, N-methyl	100-61-8
1910	N,N-dimethylaniline		$PhNMe_2$	$C_8H_{11}N$	benzenamine, N,N-dimethyl	121-69-7
1920	ethanolamine	2-aminoethanol	$H_2NCH_2CH_2OH$	C_2H_7NO	ethanol, 2-amino-	141-43-5
1930	diethanolamine	2,2′-iminodiethanol	$(HOC_2H_4)_2NH$	$C_4H_{11}NO_2$	ethanol, 2,2′-iminobis-	124-68-5

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No.	Name	Synonym	Structural Formula	Composition	Chem. Abstr. Name	Cas. Reg. No
1940	triethanolamine	2,2′,2"-nitrilotriethanol	$(HOC_2H_4)_3N$	$C_6H_{15}NO_3$	ethanol, 2,2′,2"-nitrilotris-	102-71-6
1950	pyridine		c-$(CH)_5N$-	C_5H_5N	pyridine	110-86-1
1960	2-methylpyridine	2-picoline	c-C(Me)$(CH)_4N$-	C_6H_7N	pyridine, 2-methyl	109-06-8
1970	3-methylpyridine	3-picoline	c-CHC(Me)$(CH)_3N$-	C_6H_7N	pyridine, 3-methyl	108-99-6
1980	4-methylpyridine	4-picoline	c-$(CH)_2C(Me)(CH)_2N$	C_6H_7N	pyridine, 4-methyl	108-89-4
1990	2,4-dimethylpyridine	2,4-lutidine	c-C(Me)CHC(Me)$(CH)_2N$	C_7H_9N	pyridine, 2,4-dimethyl	108-47-4
2000	2,6-dimethylpyridine	2,6-lutidine	c-C(Me)$(CH)_3C(Me)N$	C_7H_9N	pyridine, 2,6-dimethyl	108-48-5
2010	2,4,6-trimethylpyridine	2,4,6-collidine		$C_8H_{11}N$	pyridine, 2,4,6-trimethyl	108-75-8
2020	2-bromopyridine		c-CBr$(CH)_4N$	C_5H_4BrN	pyridine, 2-bromo-	109-04-6
2030	3-bromopyridine		c-CHC(Br)$(CH)_3N$-	C_5H_4BrN	pyridine, 3-bromo-	626-55-1
2040	2-cyanopyridine		c-C(CN)$(CH)_4N$-	$C_6H_4N_2$	2-pyridinecarbonitrile	100-70-9
2050	pyrimidine		c-N=CHN=CHCH=CH-	$C_4H_4N_2$	pyrimidine	298-95-2
2060	quinoline			C_9H_7N	quinoline	91-22-5
2070	acetonitrile	cyanomethane	CH_3CN	C_2H_3N	acetonitrile	75-05-8
2080	propionitirle	cyanoethane	CH_3CH_2CN	C_3H_5N	propanenitrile	107-12-0
2090	butyronitrile	cyanopropane	$CH_3CH_2CH_2CN$	C_4H_7N	butanenitrile	109-74-0
2100	valeronitrile	1-cyanobutane	$CH_3(CH_2)_3CN$	C_5H_9N	pentanenitrile	110-59-8
2110	acrylonitrile		CH_2=CHCN	C_3H_3N	2-propenenitrile	107-13-1
2120	benzyl cyanide	phenylacetonitrile	$PhCH_2CN$	C_8H_7N	benzeneacetonitrile	140-29-4
2130	benzonitrile	cyanobenzene	PhCN	C_7H_5N	benzonitrile	100-47-0
2140	nitromethane				methane, nitro-	75-52-5

			CH_3NO_2	CH_3NO_2		
2150	nitroethane		$CH_3CH_2NO_2$	$C_2H_5NO_2$	ethane, nitro-	79-24-3
2160	1-nitropropane		$C_3H_7NO_2$	$C_3H_7NO_2$	propane, 1-nitro-	108-03-2
2170	2-nitropropane		Me_2CHNO_2	$C_3H_7NO_2$	propane, 2-nitro-	79-46-9
2180	nitrobenzene		$PhNo_2$	$C_6H_5NO_2$	benzene, nitro-	98-95-3
2190	formamide		$HC(O)NH_2$	CH_3NO	formamide	75-12-7
2200	N-methylformamide		HC(O)NHMe	C_2H_5NO	formamide, N-methyl	123-39-7
2210	N,N-dimethylformamide		$HC(O)NMe_2$	C_3H_7NO	formamide, N,N-dimethyl	68-12-2
2220	N,N-dimethylthioformamide		$HC(S)NMe_2$	C_3H_7NS	methanethioamide, N,N-dimethyl	758-16-7
2230	N,N-diethylformamide		$HC(O)N(C_2H_5)_2$	$C_5H_{11}NO$	formamide, N,N-diethyl	617-84-5
2240	N-methylacetamide		$CH_3C(O)NHMe$	C_3H_7NO	acetamide, N-methyl	79-16-3
2250	N,N-dimethylacetamide		$CH_3C(O)NMe_2$	C_4H_9NO	acetamide, N,N-dimethyl	127-19-5
2260	N,N-diethyl acetamide		$CH_3C(O)N(C_2H_5)_2$	$C_6H_{13}NO$	acetamide, N,N-diethyl	685-91-6
2270	pyrrolidinone-2	butyrolactam	$c-(CH_2)_3C(O)N(H)-$	C_4H_7NO	2-pyrrolidinone	616-45-5
2280	N-methylpyrrolidinone		$c-(CH_2)_3C(O)N(Me)-$	C_5H_9NO	2-pyrrolidinone, 1-methyl	872-50-4

continued overleaf

***Table 1.1** (continued)*

No.	Name	Synonym	Structural Formula	Composition	Chem. Abstr. Name	Cas. Reg. No
2290	N-methylthiopyrrolidinone		$c\text{-}(CH_2)_3C(S)N(Me)\text{-}$	C_5H_9NS	2-pyrrolidinethione, 1-methyl	10441-57-3
2300	tetramethylurea		$OC(NMe_2)_2$	$C_5H_{12}N_2O$	urea, tetramethyl	632-22-4
2310	tetraethylurea		$OC(N(C_2H_5)_2)_2$	$C_9H_{20}N_2O$	urea, tetraethyl	1187-03-7
2320	dimethylcyanamide		Me_2NCN	$C_3H_6N_2$	cyanamide, dimethyl	1467-79-4
2330	carbon disulfide		CS_2	CS_2	carbon disulfide	75-15-0
2340	dimethyl sulfide	dimethyl thioether	$MeSMe$	C_2H_6S	methane, thiobis-	75-18-3
2350	diethyl sulfide	diethyl thioether	$C_2H_5SC_2H_5$	$C_4H_{10}S$	ethane, 1,1′-thiobis-	352-93-2
2360	di-i-propyl sulfide	diisopropyl thioether	$Me_2CHSHMe_2$	$C_6H_{14}S$	propane, 2,2′-thiobis-	625-80-9
2370	di-n-butyl sulfide	dibutyl thioether	$C_4H_9SC_4H_9$	$C_8H_{18}S$	butane, 1,1′-thiobis-	544-40-1
2380	tetrahydrothiophene	tetramethylene sulfide	$c\text{-}(CH_2)_4S\text{-}$	C_4H_8S	thiophene, tetrahydro-	110-01-0
2390	pentamethylene sulfide		$c\text{-}(CH_2)_5S\text{-}$	$C_5H_{10}S$	2H-thiopyrane, tetrahydro-	1613-51-0
2400	dimethyl sulfoxide		$MeS(O)Me$	C_2H_6OS	methane, sulfinylbis-	67-68-5
2410	di-n-butyl sulfoxide		$C_4H_9S(O)C_4H_9$	$C_8H_{18}OS$	butane, 1,1′-sulfinylbis-	598-04-9
2420	tetramethylene sulfone	sulfone	$c\text{-}(CH_2)_4S(O)_2\text{-}$	$C_4H_8O_2S$	thiophene, tetrahydro, 1,1-dioxide	126-33-0
2430	thiobis(2-ethanol)	thiodiglycol	$HOC_2H_4SC_2H_4OH$	$C_4H_{10}O_2S$	ethanol, 2,2′-thiobis-	111-48-8
2440	diethyl sulfite		$(C_2H_5O)_2SO$	$C_4H_{10}O_3S$	sulfurous acid, diethyl ester	623-81-4
2450	dimethyl sulfate	methyl sulfate	$(CH_3O)_2SO_2$	$C_2H_6O_4S$	sulfuric acid, dimethyl ester	77-78-1
2460	diethyl sulfate	ethyl sulfate	$(C_2H_5O)_2SO_2$	$C_4H_{10}O_4S$	sulfuric acid, diethyl ester	64-67-5
2470	methanesulfonic acid		CH_3SO_3H	CH_4O_3S	methanesulfonic acid	75-75-2
2480	trimethyl phosphate		$(CH_3O)_3PO$	$C_3H_9O_4P$	phosphoric acid, trimethyl	512-56-1

					ester	
2490	triethyl phosphate		$(C_2H_5O)_3PO$	$C_6H_{15}O_4P$	phosphoric acid, triethyl ester	78-40-0
2500	tri-n-butyl phosphate		$(C_4H_9O)_3PO$	$C_{12}H_{27}O_4P$	phosphoric acid, tributyl ester	126-73-8
2510	hexamethyl phosphoramide		$(Me_2N)_3PO$	$C_6H_{18}N_3OP$	phosphoric triamide, hexamethyl	680-31-9
2520	hexamethyl thiophosphoramide		$(Me_2N)_3PS$	$C_6H_{18}N_3PS$	phosphorothioic triamide, hexamethyl	3732-82-9
2530	hydrogen peroxide		H_2O_2	H_2O_2	hydrogen peroxide	7722-84-1
2540	hydrogen fluoride		HF	FH	hydrofluoric acid	7664-39-3
2550	sulfuric acid		H_2SO_4	H_2O_4S	sulfluric acid	7664-93-9
2560	ammonia		NH_3	H_3N	ammonia	7664-41-7
2570	hydrazine		N_2H_4	H_4N_2	hydrazine	302-01-2
2580	sulfur dioxide		SO_2	O_2S	sulfur dioxide	7446-09-5
2590	thionyl chloride		$SOCl_2$	Cl_2OS	thionyl chloride	7719-09-7
2600	phosphorus oxychloride	phosphoryl chloride	$POCl_3$	Cl_3OP	phosphoryl chloride	10025-87-3

less one for benzyl alcohol, but one has to become familiar with the systematics of Chemical Abstracts nomenclature in order to search for diethyl ether under 'ethane, 1,1′-oxybis', for acetophenone under 'ethanone, 1-phenyl', for 4- or (γ-) butyrolactone under '2(3H)-furanone, dihydro', and for dimethylsulfoxide under 'methane, sulfinylbis'. It is expected that with all this information available in Table 1.1 the solvents listed are definitely specified and readily found in the Abstracts and other compilations of information and data.

Many of the solvents on the List are commercial and industrial solvents (those marked as IS in the column 'availability' in Table 1.2 below), and are listed in such works as (Kirk–Othmer 1978; Gerhartz 1985; Flick 1985). Conversely, not all the solvents reported in such works are on the List, partly if they are not well characterized chemically or are mixtures, such as 'rubber solvent', 'mineral spirits', 'aromatic 100', 'polyethylene glycol 400', 'olive oil', (Kirk–Othmer 1978) etc., and partly because many of their essential physical and chemical properties are not known. On the other hand, the List includes many solvents that are hardly of any industrial interest, but still may be useful in laboratory situations or interesting from a theoretical point of view.

2—
Solvent Purity and Purification Methods

Absolute purity cannot be achieved for any material, but high purity can and it is generally desirable and often mandatory for the applications intended for solvents. Commercially available solvents can be obtained in several categories of purity and the desired or required purity depends on the envisaged application. A 'spectrograde' solvent meets the requirement of not absorbing light at specified wavelength ranges. A solvent used for high performance, or pressure, liquid chromatography (HPLC) should in addition to UV-transperancy down to a specified wavelength have a very low residue on evaporation, whereas for electrochemical purposes the solvent should not contain ionizable and electroactive, oxidizable or reducible, impurities. It is, therefore, impractical to specify a solvent that is 'pure' for all possible applications.

There are three aspects of the question of solvent purity that have to be considered: the specification of the purity of the given solvent, its further purification, if necessary, and the testing of the actual purity of the original or purified solvent.

It should be noted that mixtures of isomers are involved in many cases of organic solvents e.g., mixed xylene isomers, mixed cis- and trans-decalin, mixed 1, 1- and 1,2-dichloroethane, or mixed cresols, without obvious detrimental effects on the particular application attempted. However, in the following it is assumed that definite single substances are to be dealt with.

The lowest level of the specification of the purity of a solvent is the statement of the minimal content of the substance in question, such as '98+%' or

'≥99.5%'. The percentage generally pertains to the composition by mass. Further specifications that are generally helpful, and often provided by commercial suppliers, are lists of the actual contents of known impurities, the boiling range at atmospheric or a specified reduced pressure, and/or the density and the index of refraction, usually at 20 or 25°C. Since most solvents have freezing points (t_m/°C) much below room temperature, the specification of the freezing point is not commonly used for solvents. Some solvents, such as *t*-butanol (t_m = 25.62°C), sulfolane (t_m = 28.45°C), N-methylacetamide (t_m = 30.55°C), and ethylene carbonate (t_m = 36.37°C), however, can be specified by this means.

When a boiling point is reported, the boiling range is best determined as the difference between the boiling and condensing temperatures (Swietoslawski 1945, 1959), with a range of 0.5 K denoting a fairly low degree of purity, whereas a range of ≤ 0.1 K denoting high purity. Conformance of the measured boiling point to a value reported in the literature is less well indicative of purity, due to inconsistencies in the temperature and pressure measuring devices employed in different manufacturing plants and laboratories. It is best to specify the purity by more than one criterion, since the effects of impurities on the measured quantity depends on the differences between the values of their properties and those of the principal component. This difference may be low for one method e.g., the density, but higher for another e.g., the refractive index, so that the use of several criteria helps in testing whether the solvent in question conforms to the specifications. Special specifications are sometimes accorded to solvents for specific purposes, as mentioned above: spectral, chromatographic, electrochemical, etc. (Reichardt 1988). More general specifications for solvents used also as reagents (Rosin 1967 and the ACS specifications) are often given by suppliers.

Distillation, and in particular fractional distillation, is the most commonly employed method for the purification of solvents. In order to avoid decomposition at elevated temperatures, distillation at a reduced pressure is often resorted to. It is the usual practice to discard the first and last fractions of the distillate collected and use only the middle fraction, which may constitute no more than some 50–80% of the total amount. The distillation, however, is often the last step that is applied after more specific purification procedures have been applied as described (Riddick, Bunger and Sakano 1986; Perrin, Perrin and Armareyo 1980; Coetzee *et al*. 1982, and Coetzee *et al*. 1985–1990.

An important earlier step in the purification is commonly the removal of the ubiquitous impurity: water. This is present both from its formation in the synthetic procedure during the manufacture of the solvent and because of its ready absorption from the laboratory air. Due to its low molar mass, a millimolar (1 mol m^{-3}) concentration of water may result from only 20 ppm of this impurity. Various drying agents can be used, but porous aluminosilicates known as *molecular sieves* (e.g., the 4A type) have found universal use (Burfield, Gan and Smithers 1978). They must be thermally activated, i.e., pre-dried, for most efficient use. In their pellet-like form they can be kept in the bottom of the storage bottle of a solvent to keep it dry without contaminating it. Also they can be used as well as other drying agents such as calcium hydride for basic solvents, or phosphorus pentoxide for acidic solvents, in the still pot in the final distillation step. Another fairly universal purification method to remove water and other protic impurities from low-polarity solvents is to pass the solvent through a long column of activated alumina or silica gel (Trusell and Diehl 1963).

Table 1.2 lists briefly the purification methods applicable to many of the solvents in the List. The great majority of the solvents listed are commercially available, as indicated (industrial solvents, as listed in the Kirk-Othmer encyclopedia (1978) are marked IS). It should be noted that for many applications the purity of commercially available high quality solvents is such that no further purification is required. The quality shown in Table 1.2 is not necessarily the best available, and the catalogues of several vendors should be consulted if necessary. It is, however, often advisable to guard solvents once their bottles have been opened from the absorption of moisture from the atmosphere, and in the case of basic solvents, also from absorption of carbon dioxide. If purification is deemed to be necessary and no method is specified in Table 1.2, then usually a method noted for a chemically similar solvent can be employed.

Organic solvents ought to be stored in properly sealed glass bottles, since they are not apt to dissolve silica from the glass as water does, when stored over extended periods. When light sensitivity is known or suspected, brown bottles are to be used, or else the bottle should be wrapped by opaque paper. Bottles made of plastic materials are better avoided for storage, since the solvent is capable of leaching a plasticizer out from the bottle. For rapid transfer, however, polyethylene or -propylene pipettes, measuring cylinders, etc. can be used with apparently no detrimental effects.

3—

Tests of Solvent Purity

Testing of solvents, among other laboratory chemicals, for impurities has been discussed in several texts (Riddick, Bunger and Sakano 1986; Rosin 1967; Coetzee 1982 and Coetzee *et al*. 1985–1990). A more or less universal method for solvents should be liquid chromatography, i.e., HPLC or, for the more volatile solvents, gas chromatography. Trace concentrations of heavy metals in solvents such as alcohols can be determined, preferably after pre-concentration by means of, e.g., chelating ion exchangers, by flameless atomic absorption, X-ray fluorescence, or anodic stripping voltammetry (Förster and Lieser 1981). Many other impurities are specific for the solvents discussed, and should be determined according to procedures described with the methods for purification (Riddick, Bunger and Sakano 1986; Rosin 1967; ACS Committee 1993; Perrin, Perrin and Armarego 1980; Coetzee and Coetzee *et al*. (1985–1990)). For example, per-

Table 1.2 Methods for the purification of solvents and their commercial availability

No.	Name	Grade available	Ref	Purification method
10	tetramethylsilane	99.9+%, ACS	[a]	preparative gas chromatography
20	n-pentane	99+%, HPLC IS	[a]	alumina + $AgNO_3$ (to remove olefins, aromatics) and distillation
30	2-methylbutane	99.5+%, HPLC	[a]	silica gel column and distillation
40	n-hexane	99+% IS	[a]	nitration to remove benzene, silica gel column, fractional distillation
50	c-hexane	99+%, ACS IS	[a]	nitration to remove benzene, silica gel column, fractional distillation
60	n-heptane	99+%, HPLC IS	[a]	silica gel column and distillation
70	n-octane	99+% IS	[a]	silica gel column and distillation
80	2,2,4-trimethylpentane	99+%, ACS	[a]	alumina + $AgNO_3$, fractional melting
90	n-decane	99+%	[a]	fractional melting or preparative gas chromatography
100	n-dodecane	99%	[a]	silica gel column and distillation
110	n-hexadecane	99%		
120	benzene	99.9+%, HPLC, ACS	[a]	fractional crystallization, silica gel column, fractional distillation
130	toluene	99.8%, HPLC, ACS	[a]	sodium treatment, then fractional distillation
140	o-xylene	98% IS	[a]	sulfonation and steam hydrolysis, then fractional distillation
150	m-xylene	99% IS	[a]	sulfonation and steam hydrolysis, then fractional distillation
160	p-xylene	99+%, HPLC IS	[a]	sulfonation and steam hydrolysis, then fractional distillation
170	ethylbenzene	available IS	[a]	silica gel column and distillation
180	cumene	99%	[a]	preparative gas chromatography
190	mesitylene	97%	[a]	as for benzene
200	styrene	99%	[a]	inhibitor to prevent polymerization ought to be present
210	tetralin	97%	[a]	H_2SO_4 treatment, then fractional distillation

220	cis-decalin		[a]	fractional crystallization (to separate from trans isomer) and fractional distillation
230	water	99.99+%, ACS		deionization (mixed ion exchanger) and triple distillation
240	methanol	99.9+%, HPLC IS	[b]	drying with molecular sieves, fractionally distill, keep over CaH_2
250	ethanol	99.7%, ACS IS	[b]	drying with CaO, with H_2SO_4 to remove organic impurities, distillation
260	n-propanol	99.5%, ACS IS	[b]	treatment with CaO, distill, keep over CaH_2
270	i-propanol	99.5%, ACS IS	[b]	as for n-propanol
280	n-butanol	99.4%, ACS IS	[a]	as for n-propanol

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No.	Name	Grade available	Ref	Purification method
290	i-butanol	99.0, ACS IS	[a]	as for n-propanol
300	2-butanol	99% IS	[a]	as for n-propanol
310	t-butanol	99%, ACS IS	[b]	as for n-propanol, also fractional crystallization
320	n-pentanol	99%, (98% ACS) IS	[a]	drying and distillation
330	i-pentanol	98.5%, ACS IS	[a]	treat with H_2SO_4, fractionally distill
340	t-pentanol	99%	[a]	fractional distillation
350	n-hexanol	98% IS	[a]	drying and distillation
360	c-hexanol	ACS IS	[a, c]	fractional crystallization and distillation
370	n-octanol	99+%, HPLC, ACS	[a]	drying and distillation
380	n-decanol	98%		
390	n-dodecanol	99%		
400	benzyl alcohol	99%, ACS IS	[a, c]	fractional distillation
410	2-phenylethanol	available		
420	allyl alcohol	99%	[a]	fractional distillation
430	2-chloroethanol	99+%	[a]	drying and fractional distillation
440	2-cyanoethanol			
450	2,2,2-trifluoroethanol	available	[b]	drying (K_2CO_3) and fractional distillation
460	hexafluoro-i-propanol	available		
470	2-methoxyethanol	99.3%, ACS	[a]	drying and fractional distillation
480	2-ethoxyethanol	99%	[a]	drying and fractional distillation
490	1,2-ethanediol	99% IS	[a,c]	drying and fractional distillation
500	1,2-propanediol	99.5%, ACS IS	[a,c]	drying and fractional distillation
510	1,3-propanediol	98%	[a]	drying and fractional distillation
520	1,2-butanediol	98%		

530	2,3-butanediol (meso)	97%	[a]	crystallization from diethyl ether
540	1,4-butanediol	99%		drying and fractional distillation
550	1,5-pentanediol	98%		drying and fractional distillation
560	diethyleneglycol	available IS	[a]	drying and fractional distillation
570	triethyleneglycol	available IS	[a]	drying and fractional distillation
580	glycerol	99.5%, ACS	[a]	drying and fractional distillation
590	phenol	99.5+%, ACS	[a]	fractional crystallization, then fractional distillation

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Table 1.2 *(continued)*

No.	Name	Grade available	Ref	Purification method
600	2-methyl phenol	99+%	[a]	recrystallization from petroleum ether, then fractional distillation
610	3-methylphenol	99% IS	[a]	fractional distillation
620	4-methylphenol	99%	[a]	fractional crystallization, then fractional distillation
630	2-methoxyphenol	98+%		
640	2,4-dimethylphenol	90%	[a]	drying and fractional distillation (8% 2,5-isomer in commercial product)
650	3-chlorophenol	99%		
660	diethyl ether	99+%, ACS IS	[a]	peroxide removal by an alumina column, drying (Na) and fractional distillation
670	di-n-propyl ether	99%	[a]	as for diethyl ether
680	di-i-propyl ether	99.0%, ACS IS	[a]	as for diethyl ether
690	di-n-butyl ether	99% IS	[a]	as for diethyl ether
700	di(2-chloroethyl) ether	99+%	[a]	drying, distillation and preparative chromatography
710	1,2-dimethoxyethane	99.9%, HPLC	[a]	treatment with $LiAlH_4$ and distillation
720	bis(methoxyethyl) ether	99%		
730	furan	available	[a]	drying and fractional distillation
740	tetrahydrofuran	99.0%, ACS IS	[b]	as for diethyl ether
750	2-methyl tetrahydrofuran	99% (stabilized)		
760	tetrahydrofuran	99+%	[a]	drying and fractional distillation
770	1,4-dioxane	99.0%, ACS IS	[b]	as for diethyl ether
780	1,3-dioxolane	99.9%	[a]	treatment with Na and distillation
790	1,8-cineole	available	[a]	fractional crystallization and distillation
800	anisole	available		
810	phenetole	99%		
820	diphenyl ether	99% IS		

830	dibenzyl ether	99%
840	1,2-dimethoxybenzene	available
850	trimethyl orthoformate	99%
860	trimethyl orthoacetate	99%

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No.	Name	Grade available	Ref	Purification method
870	propionaldehyde	available	[a]	drying and fractional distillation
880	butyraldehyde	99%	[a]	drying and fractional distillation
890	benzaldehyde	available	[a, c]	drying and fractional distillation
900	p-methoxybenzaldehyde	available		
910	cinnamaldehyde	99%		
920	acetone	99.9+%, HPLC, ACS	[b]	drying and fractional distillation
930	2-butanone	99.0%, ACS IS	[a]	drying and fractional distillation
940	2-pentanone	97% IS	[a]	drying and fractional distillation
950	methyl i-propyl ketone	99%		
960	3-pentanone	96%, HPLC	[a]	drying and fractional distillation
970	c-pentanone	99%	[a]	drying and fractional distillation
980	methyl i-butyl ketone	98.5%, ACS IS	[a]	drying and fractional distillation
990	methyl t-butyl ketone			
1000	c-hexanone	99.0+%, ACS IS	[a]	drying and fractional distillation
1010	2-heptanone	available IS	[a]	drying and fractional distillation
1020	3-heptanone	available	[a]	drying and fractional distillation
1030	di-t-butyl ketone			
1040	acetophenone	99%	[a]	crystallization, drying and fractional distillation
1050	propiophenone	available		
1060	phenylacetone	available		
1070	p-methylacetophenone	95%		
1080	p-chloroacetophenone	98%		
1090	benzophenone	available		
1100	acetylacetone	available	[c]	drying and fractional distillation

1110	biacetyl	available		
1120	formic acid	99% ACS	[a]	fractional crystallization and distillation (the ACS reagent allows 0.4% acetic acid)
1130	acetic acid	99.7+%, ACS	[a]	drying with P_2O_5, fractional crystallization and distillation
1140	propanoic acid	99.5+%, ACS	[a]	drying with Na_2SO_4 and distillation
1150	n-butanoic acid	99%	[a]	drying and distillation
1160	n-pentanoic acid	99%	[a]	drying and distillation

continued overleaf

***Table 1.2** (continued)*

No.	Name	Grade available	Ref	Purification method
1170	n-hexanoic acid	99%	[a]	drying and distillation
1180	n-heptanoic acid	99%		
1190	dichloroacetic acid	available		
1200	trifluoroacetic acid	available	[a]	drying and fractional distillation
1210	acetic anhydride	97+%, ACS	[a]	treatment with CaC_2 and distillation
1220	benzoyl chloride	98+%, ACS		
1230	benzoyl bromide	97%		
1240	methyl formate	available	[a]	drying and distillation
1250	ethyl formate	available	[a]	drying and distillation
1260	propyl acetate	99% IS	[a]	drying and distillation
1270	butyl acetate	99.5%, ACS IS	[a]	washing with water, drying and distillation
1280	propyl acetate	99+% IS	[a]	washing with water, drying and distillation
1290	butyl acetate	99.5%, ACS IS	[a]	washing with water, drying and distillation
1300	i-pentyl acetate	available IS	[a]	washing with water, drying and distillation
1310	methyl propanoate	available IS	[a]	washing with water, drying and distillation
1320	ethyl propanoate	99% IS	[a]	washing with water, drying and distillation
1330	dimethyl carbonate	99%		
1340	diethyl carbonate	99%		
1350	ethylene carbonate	99%	[a]	fractional crystallization and distillation
1360	propylene carbonate	available IS	[a]	drying and fractional distillation
1370	diethyl malonate	available		
1380	methyl benzoate	99%	[a]	drying and fractional distillation
1390	ethyl benzoate	99%		drying and fractional distillation
1400	dimethyl phthalate	99%		

1410	dibutyl phthalate	available		
1420	ethyl chloroacetate	99%		
1430	ethyl trichloroacetate	99%		
1440	ethyl acetoacetate	available IS	[a]	fractional distillation
1450	4-butyrolactone	available IS		
1460	perfluoro-n-hexane	available		

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No.	Name	Grade available	Ref	Purification method
1470	perfluoro-n-heptane			
1480	perfluoro-methylcyclohexane	available		
1490	perfluoro-decalin	available		
1500	fluorobenzene	available	[a]	fractional distillation
1510	hexafluorobenzene	available	[a]	fractional crystallization and distillation
1520	l-chlorobutane	99.5%, HPLC	[a]	treatment with H_2SO_4, aqueous base, water, drying and fractional distillation
1530	chlorobenzen	99.9%, HPLC, ACS	[a]	drying and fractional distillation
1540	dichloromethane	99.9%, HPLC, ACS	[b]	as for l-chlorobutane
1550	1,1-dichloroethane		[b]	as for l-chlorobutane
1560	1,2-dichloroethane	99.8%, HPLC, ACS	[b]	as for l-chlorobutane
1570	tr-1,2-dichloroethylene	available	[a]	fractional distillation
1580	o-dichlorobenzene	99%, HPLC IS	[a]	passing through alumina column, drying, and distillation
1590	m-dichlorobenzene	98%	[a]	treatment with aqueous base, water, drying and fractional distillation
1600	chloroform	99.9%, HPLC, ACS	[a]	removal of ethanol stabilizer with water, drying and fractional distillation
1610	1,1,1-trichloroethane	98.5%, ACS IS	[a]	drying and fractional distillation
1620	1,1,2-trichloroethane	98% IS	[a]	drying and fractional distillation
1630	trichloroethylene	99.5%, ACS IS	[a]	drying and fractional distillation
1640	1,2,4-trichlorobenzene	99% IS		
1650	tetrachloromethane	99.9+%, HPLC, ACS	[a]	passing through alumina column, drying, and distillation
1660	tetrachloroethylene	99.9+%, HPLC, IS	[a]	treatment with aqueous base, water, drying and fractional distillation
1670	1,1,2,2-tetrachloroethane	97%IS	[a]	as for l-chlorobutane
1680	pentachloroethane	99%	[a]	as for l-chlorobutane

1690	l-bromobutane	98+%		drying and fractional distillation
1700	bromobenzene	available	[a]	drying and fractional distillation
1710	dibromomethane	99%		
1720	1,2-dibromoethane	available IS	[a]	fractional crystallization and distillation
1730	bromoform	available		
1740	l-iodobutane	98% (stabilized)	[a]	treatment with aqueous base, water, drying and fractional distillation
1750	iodobenzene	98%	[a]	treatment with $Na_2S_2O_3$, drying and fractional distillation

continued overleaf

Table 1.2 *(continued)*

No.	Name	Grade available	Ref	Purification method
1760	diiodomethane	available	[a]	drying and fractional distillation
1770	n-butylamine	available IS	[a]	drying and fractional distillation from strong base
1780	benzylamine	available		
1790	1,2-diaminoethane	available	[c, b]	drying and fractional distillation (keep free from CO_2)
1800	diethylamine	available IS	[a]	drying and fractional distillation from strong base
1810	di-n-butylamine	available IS	[a]	drying and fractional distillation from strong base
1820	pyrrole	available	[a]	fractional distillation (avoid contact with air, keep O_2 free)
1830	pyrrolidine	available	[a]	drying and fractional distillation from strong base
1840	piperidine	99%	[a]	pass through alumina column and distill
1850	morpholine	99.0%, ACS IS	[a]	drying and fractional distillation
1860	triethylamine	99+% IS	[a]	drying and fractional distillation from strong base
1870	tri-n-butylamine	99%	[a]	drying and fractional distillation from strong base
1880	aniline	99.5+%, ACS	[a]	fractional crystallization and distillation
1890	o-chloroaniline	98+%	[a]	recrystallization of chloride salt, steam distillation
1900	N-methylaniline	98%		
1910	N,N-dimethylaniline	available	[a, c]	
1920	ethanolamine	98+%, ACS IS	[a]	recrystallization and fractional distillation (keep away CO_2)
1930	diethanolamine	98.5%, ACS IS	[a]	
1940	triethanolamine	98+% IS	[a]	fractional distillation
1950	pyridine	99+%, ACS	[b]	drying and fractional distillation from strong base
1960	2-methylpyridine	98%	[a]	recrystallize salt, liberate with strong base, drying and fractional distillation
1970	3-methylpyridine	99%	[a]	azeotropic distillation with acetic acid, fractional crystallization and distillation
1980	4-methylpyridine	available	[a]	recrystallize salt, liberate with strong base, drying and fractional

				distillation
1990	2,4-dimethylpyridine	available	[a]	fractional crystallization and distillation
2000	2,6-dimethylpyridine	98%	[a]	fractional crystallization and distillation
2010	2,4,6-trimethylpyridine	available	[a]	fractional distillation
2020	2-bromopyridine	99%		

(table continued on next page)

(table continued from previous page)

No.	Name	Grade available	Ref	Purification method
2030	3-bromopyridine	99%		
2040	2-cyanopyridine	99%		
2050	pyrimidine	99%		
2060	quinoline	99%, ACS	[a]	fractional crystallization and distillation
2070	acetonitrile	99.9+%, HPLC, ACS	[b]	passing through alumina column, fractional distillation
2080	propionitrile	99%	[a]	drying (P_2O_5) and distillation
2090	butyronitrile	99% IS	[a]	drying (P_2O_5) and distillation
2100	valeronitrile	99%	[a]	drying (P_2O_5) and distillation
2110	acrylonitrile	99.5+%, IS	[a]	drying ($CaCl_2$) and fractional distillation (amines stabilize against polymerization)
2120	benzyl cyanide	99+%	[a]	treatment with H_2SO_4, water, drying and distillation
2130	benzonitrile	99.9%, HPLC	[b]	drying (P_2O_5) and distillation
2140	nitromethane	96%, HPLC, ACS IS	[a]	fractional crystallization and distillation (impurity: nitroethane)
2150	nitroethane	available	[a]	fractional crystallization and distillation (impurities: nitromethane, 1-nitropropane)
2160	1-nitropropane	98% IS	[a]	fractional crystallization and distillation (impurity: 2-nitropropane)
2170	2-nitropropane	96% IS	[a]	fractional crystallization and distillation (impurities: 1-nitropropane, nitroethane)
2180	nitrobenzene	99.0%, ACS IS	[a]	fractional crystallization and distillation
2190	formamide	99.5+%, ACS	[a]	fractional crystallization and distillation (keep away moisture)
2200	N-methylformamide	available	[a]	drying (P_2O_5) and distillation
2210	N,N-dimethylformamide	99.8+%, ACS IS	[b]	drying and fractional distillation
2220	N,N-dimethylthioformamide	97%		
2230	N,N-diethylformamide	99%		

2240	N-methylacetamide	99+%	[b]	fractional crystallization and distillation
2250	N,N-dimethylacetamide	99+%	[b]	drying and fractional distillation
2260	N,N-diethyl acetamide	99%		
2270	pyrrolidinone-2	available	[a]	fractional distillation
2280	N-methylpyrrolidinone	99+%, HPLC IS	[a]	drying and fractional distillation
2290	N-methylthiopyrrolidinone			
2300	tetramethylurea	available	[a]	drying and fractional distillation

continued overleaf

Table 1.2 *(continued)*

No.	Name	Grade available	Ref	Purification method
2310	tetraethylurea			
2320	dimethylcyanamide	99%		
2330	carbon disulfide	99.9+%, HPLC	[a]	treatment with Hg, drying and fractional distillation
2340	dimethyl sulfide	99+%	[a]	$HgCl_2$ treatment, recrystallization, HCl aq. treatment, drying
2350	diethyl sulfide		[a]	fractional distillation
2360	di-i-propyl sulfide			
2370	di-n-butyl sulfide	99%		
2380	tetrahydrothiophene	98%	[a]	fractional distillation
2390	pentamethylene sulfide			
2400	dimethyl sulfoxide	99.9%, ACS	[b]	drying and fractional distillation
2410	di-n-butyl sulfoxide			
2420	sulfolane	available	[b]	drying and fractional distillation
2430	thiobis(2-ethanol)	99%	[a]	fractional distillation
2440	diethyl sulfite			
2450	dimethyl sulfate	99+%	[c]	
2460	diethyl sulfate	99%		
2470	methanesulfonic acid	99+%		
2480	trimethyl phosphate	98%	[a]	fractional distillation
2490	triethyl phosphate	99%	[a]	drying and fractional distillation
2500	tri-n-butyl phosphate	99%	[a]	wasing with aqueous base and distillation
2510	hexamethyl phosphoramide	99%	[b]	drying with strong base and fractional distillation
2520	hexamethyl thiophosphoramide			

2530	hydrogen peroxide			
2540	hydrogen fluoride	99.99% gas		
2550	sulfuric acid			mixture of fuming H_2SO_4 and 96% H_2SO_4 to produce 100% acid
2560	ammonia	99.99% gas		
2570	hydrazine	available		
2580	sulfur dioxide	99.98% gas		
2590	thionyl chloride	99+%		
2600	phosphorus oxychloride	available	[c]	

Reference: [a] Riddick. Bunger and Sakano 1986; [b] Coetzee 1982 and Coetzee *et al*. 1985-1990; [c] Rosin 1967.

oxides in ethers, that constitute a safety problem, can be determined by their oxidizing power of iodide or of iron(II) in the presence of thiocyanate, and evaluation of the coloration produced. Electroactive impurities, i.e., trace substances that can be oxidized or reduced electrochemically in the operative voltage window of the solvent (see Table 4.8), can be determined by cyclic voltammetry and be removed by pre-electrolysis of the solvent.

A special issue is the determination of the dryness of solvents, i.e., their water content, since water is the most common major impurity found in solvents, apart from isomers in solvents where several of them result in the preparative method. Several older works deal with the determination of water in organic materials (Mitchell and Smith 1948; Tranchart 1968) but these have now been augmented by further methods. The Karl Fischer titration method is still of general utility, and can be applied to samples containing up to 30 mg of water (total amount), and in which down to 5 ppm water, concentration, can be determined precisely. Coulometric generation of the titrant and an electrometric endpoint detection are recommended for this purpose (Lindbeck and Freund 1965). Commercial instruments provided by several vendors are available for this method of determination. Infrared spectrophotometry at 1.9 and/or 3.5 μm can be used for water contents between 0.02 and 1.0 mass % in aprotic solvents (Pearson and Ollerenshaw 1966). Gas chromatography with a non-polar, hydrophobic stationary phase can be used above 0.01 mass % of water in polar solvents (Hollis 1966). Although these references are a few decades old, the principles employed are still valid, although more modern instrumentation is nowadays used.

4—
Toxicity and Other Hazards of Solvents

Special attention must nowadays be given to the hazards involved in the use of solvents, and there is a general tendency to replace solvents that are hazardous, but have long been in use for historical reasons, with less dangerous solvents. For instance, benzene, a very useful solvent but a known carcinogen, ought to be and actually often is replaced by the less hazardous toluene or xylene. Tables 1.3 and 1.4 provide some information concerning the toxicity of solvents on the List as well as their inflammability and the explosive limits of their vapour in air.

The *permissible exposure limit*, PEL in Table 1.3, is given in ppm in the air for an ordinary work shift in the laboratory or in industry (Kirk–Othmer 1978). This quantity is also called the threshold limit (Riddick, Bunger and Sakano 1986). Concentrations that are of *immediate danger to life or health*, called IDLH in Table 1.3, in ppm in the air, may be much higher than the PEL and be tolerated for short periods, say 30 min. The values shown in Table 1.3 are from the Kirk–Othmer encyclopedia (Kirk–Othmer 1978).

It must be stressed that the information summarized in Tables 1.3 and 1.4 is not exhaustive, and where no information is given, this does not mean that a

Table 1.3 The permissible exposure limit (PEL) and the IDLH, the flashpoint and autoignition temperature, and the explosive limits in air of solvents

No.	Name	PEL	Ref	IDLH	Flash	Ref	Autoig.	Expl. lim.	Ref
0	vacuum								
10	tetramethylsilane				-27	[c]	330	1.0–37.9	[c]
20	n-pentane	600	[a]	5000	-40	[a]	243	1.5–7.8	[a]
30	2-methylbutane				-57	[c]	420	1.2–8.2	[c]
40	n-hexane	50	[a]	5000	-22	[a]	225	1.2–7.5	[a]
50	c-hexane	300	[a]	10000	-17	[a]	260	1.3–8.4	[a]
60	n-heptane	400	[a]	4300	4	[a]	204	1.05–6.7	[a]
70	n-octane	500	[a]	3800	13	[a]	206	1.0–6.5	[a]
80	2,2,4-trimethylpentane				12	[c]	411	1.1–6.0	[c]
90	n-decane				46	[c]	201	0.8–5.4	[c]
100	n-dodecane				74	[c]	203	0.6–4.7	[c]
110	n-hexadecane				126	[c]	202	0.5–5.2	[c]
120	benzene	1	[a]	2000	-11	[a]	560	1.3–7.1	[a]
130	toluene	100	[a]	2000	4	[a]	480	1.3–7.1	[a]
140	o-xylene	100	[a]	10000	32	[a]	463	1.0–6.0	[a]
150	m-xylene	100	[a]	10000	29	[a]	465	1.1–7.0	[a]
160	p-xylene	100	[a]	10000	27	[a]	528	1.1–7.0	[a]
170	ethylbenzene	100	[a]	2000	15	[a]	430	1.0–6.7	[a]
180	cumene	50	[b]		44	[c]	424	0.9–6.5	[c]
190	mesitylene				44	[c]	550	0.9–5.2	[c]
200	styrene	100	[b]		32	[c]	490	1.1–6.1	[c]
210	tetralin	25	[b]		71	[c]	384	0.8–5.0	[c]
220	cis-decalin	25	[b]		58	[c]	250	0.7–4.9	[c]

230	water				none			none	
240	methanol	200	[a]	25000	11	[a]	464	6.7–36	[a]
250	ethanol	1000	[a]		13	[a]	423	3.3–19.0	[a]
260	n-propanol	200	[a]	4000	25	[a]	371	2.1–13.5	[a]
270	i-propanol	400	[a]	20000	12	[a]	399	2.0–12.0	[a]
280	n-butanol	100	[a]	8000	35	[a]	343	1.4–11.2	[a]
290	i-butanol	100	[a]	8000	28	[a]	408	1.2–10.9	[a]
300	2-butanol	150	[a]	10000	31	[a]	406	1.7–9.8	[a]
310	t-butanol	100	[a]	8000	11	[a]	478	2.4–8.0	[a]
320	n-pentanol				33	[a]	300	1.2–10.0	[a]
330	i-pentanol	100	[a]	8000	43	[a]	350	1.2–9.0	[a]
340	t-pentanol				37	[c]	435	1.5–9.1	[c]
350	n-hexanol	100	[b]		63	[a]	285	1.2–8.2	[c]
360	c-hexanol	50	[a]	3500	68	[a]	300	1.2–8.2	[c]
370	n-octanol	100	[b]		81	[c]	282	0.9–6.4	[c]
380	n-decanol				82	[c]	288	0.7–5.5	[c]
390	n-dodecanol				127	[c]	275	0.6–5.1	[c]
400	benzyl alcohol				101	[a]	436		
410	2-phenylethanol				96	[c]		1.1–7.0	[c]
420	allyl alcohol	2	[a]	150	21	[a]	378	2.5–18.0	[a]
430	2-chloroethanol	1	[b]		41	[c]	425	4.9–15.9	[c]
440	2-cyanoethanol								
450	2,2,2-trifluoroethanol								
460	hexafluoro-i-propanol								
470	2-methoxyethanol	25	[b]		39	[c]	285	1.8–14.0	[c]
480	2-ethoxyethanol	100	[b]		43	[c]	235	1.7–15.6	[c]

490	1,2-ethanediol	50	[a]	111	[a]	396	3.2–21.6	[c]
500	1,2-propanediol			99	[a]	421	2.6–12.5	[c]
510	1,3-propanediol			122	[c]	378	2.6–16.6	[c]

(table continued on next page)

***Table 1.3** (continued)*

No.	Name	PEL	Ref	IDLH	Flash	Ref	Autoig.	Expl. lim.	Ref
520	1,2-butanediol				90	[c]	392	1.9–13.0	[c]
530	2,3-butanediol (meso)				85	[c]	402	1.9–13.7	[c]
540	1,4-butanediol				134	[c]	357	1.9–13.2	[c]
550	1,5-pentanediol				130	[c]	335	1.5–10.9	[c]
560	diethyleneglycol				149	[a]	224	2.0–17.0	[c]
570	triethyleneglycol				152	[a]	371	0.9–9.2	[c]
580	glycerol				160	[c]	370	2.7–19.0	[c]
590	phenol	5	[b]		80	[c]	715	1.5–	[c]
600	2-methylphenol	5	[b]		81	[c]	599	1.4–7.6	[c]
610	3-methylphenol	5	[a]	250	94	[a]	559	1.1–7.6	[c]
620	4-methylphenol	5	[b]		95	[c]	559	1.1–7.6	[c]
630	2-methoxyphenol								
640	2,4-dimethylphenol				95	[c]	599	1.1–6.4	[c]
650	3-chlorophenol				90	[c]		1.7–8.8	[c]
660	diethyl ether	400	[a]		-45	[a]	160	1.8–36	[a]
670	di-n-propyl ether				21	[c]	215	1.2–9.5	[c]
680	di-i-propyl ether	50	[a]		-28	[a]	443	1.4–7.9	[a]
690	di-n-butyl ether	100	[b]		25	[a]	195	1.5–7.6	[a]
700	di(2-chloroethyl) ether								
710	1,2-dimethoxyethane				-2	[c]	202	1.9–18.7	[c]
720	bis(methoxyethyl) ether				63	[c]		1.3–14.2	[c]
730	furan				-36	[c]		2.3–14.3	[c]

740	tetrahydrofuran	200	[a]		-17	[a]	224	1.8–11.8	[a]
750	2-methyl tetrahydrofuran								
760	tetrahydropyran								
770	dioxane	25	[a]	200	12	[a]	180	2.0–22.2	[a]
780	dioxolane								
790	1,8-cineole								
800	anisole				62	[c]		1.3–9.0	[c]
810	phenetole				62	[c]		1.1–7.8	[c]
820	diphenyl ether	1	[a]		115	[a]	618	0.8–1.5	[a]
830	dibenzyl ether				135	[c]		0.6–6.0	[c]
840	1,2-dimethoxybenzene								
850	trimethyl orthoformate								
860	trimethyl orthoacetate								
870	propionaldehyde				-30	[c]	207	2.6–16.1	[c]
880	butyraldehyde	1	[b]		-7	[c]	216	2.5–12.5	[c]
890	benzaldehyde	5	[b]		65	[c]	192	1.4–7.8	[c]
900	p-methoxybenzaldehyde								
910	cinnamaldehyde								
920	acetone	750	[a]	20000	-18	[a]	465	2.6–12.8	[a]
930	2-butanone	200	[a]	300	-6	[a]	516	1.8–10.0	[a]
940	2-pentanone	200	[a]		7	[c]	452	1.5–8.2	[c]
950	methyl i-propyl ketone				0	[c]	475	1.5–9.0	[c]
960	3-pentanone				13	[c]	452	1.5–8.0	[c]
970	c-pentanone				26	[c]		1.7–10.4	[c]
980	methyl-i-butyl ketone	50	[a]		17	[a]	448	1.4–7.5	[a]
990	methyl t-butyl ketone						461		

1000	c-hexanone	25	[a]	5000	44	[a]	420	1.0–8.0	[c]
1010	2-heptanone	100	[a]	4000	39	[c]	393	1.1–7.9	[c]
1020	3-heptanone				37	[c]	410	1.1–6.8	[c]
1030	di-t-butyl ketone								

continued overleaf

Table 1.3 *(continued)*

No.	Name	PEL	Ref	IDLH	Flash	Ref	Autoig.	Expl. lim.	Ref
1040	acetophenone				82	[c]	571	1.1–6.7	[c]
1050	propiophenone								
1060	phenylacetone								
1070	p-methylacetophenone								
1080	p-chloroacetophenone								
1090	benzophenone (beta)				143	[c]		0.7–5.4	[c]
1100	acetylacetone				34	[c]	340	2.4–11.6	[c]
1110	biacetyl								
1120	formic acid	5	[b]		69	[c]	480	18–57	[c]
1130	acetic acid	10	[b]		43	[c]	427	5.4–16.0	[c]
1140	propanoic acid				55	[c]	475	2.9–14.8	[c]
1150	n-butanoic acid	10	[b]		72	[c]	450	2.2–13.4	[c]
1160	n-pentanoic acid				96	[c]	400	1.6–9.6	[c]
1170	n-hexanoic acid				102	[c]	380	1.3–8.2	[c]
1180	n-heptanoic acid				196	[c]	298	0.4–4.9	[c]
1190	dichloroacetic acid				110	[c]		11.9–43.3	[c]
1200	trifluoroacetic acid								
1210	acetic anhydride	5	[b]		54	[c]	334	2.9–10.3	[c]
1220	benzoyl chloride				72	[c]	85	1.2–4.9	[c]
1230	benzoyl bromide								
1240	methyl formate	100	[b]		-19	[c]	456	5.9–20.0	[c]
1250	ethyl formate	100	[b]		-4	[c]	455	2.7–13.5	[c]

1260	methyl acetate	200	[b]		-10	[c]	502	3.1–16.0	[c]
1270	ethyl acetate	400	[a]	10000	-4	[a]	427	2.2–11.0	[a]
1280	propyl acetate	200	[a]	8000	14	[a]	450	2.0–8.0	[a]
1290	butyl acetate	150	[a]	10000	22	[a]	421	1.7–7.6	[a]
1300	i-pentyl acetate	100	[a]	3000	25	[a]	360	1.0–7.5	[a]
1310	methyl propanoate				-2	[c]	469	2.5–13.0	[c]
1320	ethyl propanoate				12	[c]	477	1.9–11.0	[c]
1330	dimethyl carbonate				17	[c]		3.1–20.5	[c]
1340	diethyl carbonate				25	[c]		1.7–12.4	[c]
1350	ethylene carbonate				152	[c]		3.6–25.1	[c]
1360	propylene carbonate				122	[a]			
1370	diethyl malonate				93	[c]		1.3–7.3	[c]
1380	diethyl benzoate				83	[c]	505	1.2–6.7	[c]
1390	ethyl benzoate				88	[c]	490	1.0–6.1	[c]
1400	dimethyl phthalate				146	[c]	490	0.9–5.8	[c]
1410	dibutyl phthalate	5	[b]		157	[c]	402	0.5–5.9	[c]
1420	ethyl chloroacetate								
1430	ethyl trichloroacetate								
1440	ethyl acetoacetate				57	[c]	295	1.4–9.5	[c]
1450	4-butyrolactone				98	[a]		2.0–12.6	[c]
1460	perfluoro-n-hexane								
1470	perfluoro-n-heptane								
1480	perfluoro-methylcyclohexane								
1490	perfluoro-decalin								
1500	fluorobenzene				-15	[c]		1.6–9.1	[c]
1510	hexafluorobenzene				10	[c]		-13.6	[c]

1520	1-chlorobutane				28	[c]	240	1.8–10.1	[c]
1530	chlorobenzene	75	[a]	2400	30	[a]	638	1.3–7.1	[a]
1540	dichloromethane	500	[a]	5000	none		615	14.8–22.0	[a]
1550	1,1-dichloroethane	50	[a]	1000	13	[a]	458	6.2–15.9	[a]
1560	1,2-dichloroethane	1	[a]		13	[c]	413	6.2–16.0	[c]

(table continued on next page)

***Table 1.3** (continued)*

No.	Name	PEL	Ref	IDLH	Flash	Ref	Autoig.	Expl. lim.	Ref
1570	tr-1,2-dichloroethylene				2	[c]	460	5.6–12.8	[c]
1580	o-dichlorobenzene	50	[a]	1700	66	[a]	648	2.2–9.2	[a]
1590	m-dichlorobenzene				72	[c]	647	1.8–7.8	[c]
1600	chloroform	2	[a]	1000	none				
1610	1,1,1-trichloroethane	350	[a]	1000	none		537	8.0–10.5	[a]
1620	1,1,2-trichloroethane	10	[a]	500	none		460	8.4–13.3	[a]
1630	trichloroethylene	50	[a]	1000	none		410	8.0–10.5	[a]
1640	1,2,4-trichlorobenzene	5	[a]		110	[a]	571	2.9–6.6	[c]
1650	tetrachloroethylene	2	[a]	300	none				
1660	tetrachloroethylene	25	[a]	500	none		none		
1670	1,1,2,2-tetrachloroethane	1	[a]	150	none			20–54	[c]
1680	pentachloroethane				none		none		
1690	1-bromobutane				18	[c]	265	2.6–6.6	[c]
1700	bromobenzene				51	[c]	565	1.5–9.1	[c]
1710	dibromomethane				34	[c]		-27.2	[c]
1720	1,2-dibromoethane	20	[a]	400	none				
1730	bromoform	1	[b]		83	[c]		-35.3	[c]
1740	1-iodobutane								
1750	iodobenzene				66	[c]			
1760	diiodomethane				4	[c]			
1770	n-butylamine	5	[a]	2000	-12	[a]		1.7–9.8	[a]
1780	benzylamine				60	[c]		1.2–7.8	[c]

1790	1,2-diaminoethane	10	[b]		34	[c]	385	4.2–14.4	[c]
1800	diethylamine	25	[a]	2000	-18	[a]		1.8–10.1	[a]
1810	di-n-butylamine				58	[c]	256	1.1–6.1	[c]
1820	pyrrole				39	[c]		2.0–12.0	[c]
1830	pyrrolidine				3	[c]		-12.0	[c]
1840	piperidine				3	[c]		1.4–10.0	[c]
1850	morpholine	20	[a]	8000	38	[a]	310	1.8–10.8	[c]
1860	triethylamine	10	[a]	2000	8	[a]	232	1.2–8.0	[a]
1870	tri-n-butylamine				86	[c]	208	0.6–4.9	[c]
1880	aniline	5	[b]		70	[a]	617	1.3–11.0	[c]
1890	o-chloroaniline				91	[c]		1.5–8.8	[c]
1900	N-methylaniline				78	[c]		1.2–7.4	[c]
1910	N,N-dimethylaniline	5	[b]		63	[c]	370	1.0–6.4	[c]
1920	ethanolamine	3	[a]	6000	93	[a]		3.1–21.6	[c]
1930	diethanolamine	3	[a]		152	[a]	662	1.8–12.4	[c]
1940	triethanolamine				179	[a]		1.2–9.9	[c]
1950	pyridine	5	[b]		20	[c]	482	1.8–12.4	[c]
1960	2-methylpyridine				39	[c]	535	-11.9	[c]
1970	3-methylpyridine				36	[c]	500	1.3–8.7	[c]
1980	4-methylpyridine				57	[c]	500	-11.9	[c]
1990	2,4-dimethylpyridine								
2000	2,6-dimethylpyridine								
2010	2,4,6-trimethylpyridine				57	[c]		1.0–7.2	[c]
2020	2-bromopyridine								
2030	3-bromopyridine								
2040	2-cyanopyridine								

2050	pyrimidine				31	[c]		2.1–11.9	[c]
2060	quinoline				101	[c]	480	1.0–7.8	[c]
2070	acetonitrile	40	[a]	4000	6	[a]	524	4.4–16	[a]
2080	propionitrile				2	[c]	512	3.1–14.0	[c]

continued overleaf

Table 1.3 *(continued)*

No.	Name	PEL	Ref	IDLH	Flash	Ref	Autoig.	Expl. lim.	Ref
2090	butyronitrile				26	[c]	502	1.6–11.4	[c]
2100	valeronitrile				28	[c]		1.5–9.6	[c]
2110	acrylonitrile	20	[b]		0	[c]	481	2.4–17.3	[c]
2120	benzonitrile				101	[c]		1.1–7.0	[c]
2130	benzonitrile				75	[c]		1.3–8.0	[c]
2140	nitromethane	100	[a]	1000	35	[c]	379	7.3–22.2	[c]
2150	nitroethane	100	[b]		28	[c]	360	3.4–17.3	[c]
2160	1-nitropropane	25	[a]		36	[c]	421	2.2–13.8	[c]
2170	2-nitropropane	10	[a]	2300	28	[c]	428	2.6–11.1	[a]
2180	nitrobenzene	1	[a]		88	[a]	482	1.8–	[a]
2190	formamide	20	[b]		175	[c]		7.0–29.3	[c]
2200	N-methylformamide	103	[c]				3.6–18.6	[c]	
2210	N,N-dimethylformamide	10	[a]	3500	58	[a]	445	2.2–15.2	[a]
2220	N,N-dimethylthioformamide								
2230	N,N-diethylformamide								
2240	N-methylacetamide				108	[c]		2.4–13.9	[c]
2250	N,N-dimethylacetamide	10	[b]		63	[c]	354	1.8–13.8	[c]
2260	N,N-diethyl acetamide								
2270	pyrrolidinone-2				130	[c]		-13.8	[c]
2280	N-methylpyrrolidinone				96	[a]	346	2.2–12.2	[a]
2290	N-methylthiopyrrolidinone								
2300	tetramethylurea								
2310	tetramethylurea								

2320	dimethylcyanamide							
2330	carbon disulfide	20	[b]	-30	[c]	90	1.3–50	[c]
2340	dimethyl sulfide			-34	[c]	205	2.2–19.7	[c]
2350	diethyl sulfide			-10	[c]			
2360	di-i-propyl sulfide							
2370	di-n-butyl sulfide							
2380	tetrahydrothiophene			18	[c]		1.5–9.0	[c]
2390	pentamethylene sulfide							
2400	dimethyl sulfoxide			88	[c]	215	2.6–28.5	[c]
2410	di-n-butyl sulfoxide							
2420	sulfolane			177	[c]			
2430	thiobis(2-ethanol)			160	[c]		1.6-	[c]
2440	diethyl sulfite			53	[c]		1.6-	[c]
2450	dimethyl sulfate			83	[c]	188		
2460	diethyl sulfate			104	[c]	436		
2470	methanesulfonic acid							
2480	trimethyl phosphate							
2490	triethyl phosphate			99	[c]	455	1.7–10.0	[c]
2500	tri-n-butyl phosphate							
2510	hexamethyl phosphoramide			106	[c]			
2520	hexamethyl phosphoramide							
2530	hydrogen peroxide							
2540	hydrogen fluoride							
2550	sulfuric acid							

2560	ammonia			651	16–25	[c]
2570	hydrazine	38	[c]	270	4.7–100	[c]
2580	sulfur dioxide	none			none	
2590	thionyl chloride					
2600	phosphorus oxychloride					

Units: (PEL) and IDLH in ppm; flashpoint and autoignition temperature in °C; explosive limits in volume%.
Reference: [a] Krik-Othmer 1978;[b] Riddick, Bunger and Sakano 1986; [c] DIPPR 1997.

solvent is not toxic or flammable. While some solvents are relatively non-toxic regarding their concentrations in the air (at least those having very low vapour pressures), they may still be quite toxic on ingestion or be a strong irritant on skin or eye contact.

The toxic effects on ingestion are commonly reported in terms of LD_{50} in mg kg^{-1} body weight, meaning the lethal dose for 50%, or with some other specified subscript, of the organisms, usually rodents, treated. However, the mode of introduction of the toxic solvent: orally or by subcutaneous or intravenous injection, the duration: acute or chronic, and if the latter, over what time period, and the species of the rodents: whether mice, rats, or rabbits, among other factors, strongly affect the numbers. Such quantities have, moreover, been reported (Riddick, Bunger and Sakano 1986) very non-systematically and some of those available are shown in Table 1.4. For some solvents the minimal lethal doses are reported and for others the LD_{100} values, and few comparisons are readily valid. Handbooks on toxicology (such as Browning 1965) ought to be consulted in this respect. Evidently, total avoidance of ingestion is to be the rule. Harmful effects on skin contact can be expected from strong acids or strong bases or such solvents that can readily hydrolyze to become such materials.

Table 1.4 The 50% lethal dose of solvents (by injection, in rodents) in mg/(kg body weight) (Riddick, Bunger and Sakano 1986)

Solvent	LD_{50}	Solvent	LD_{50}
benzene	4080	ethylene carbonate	11200
ethanol	6.7(?)	propylene carbonate	11100
1-propanol	1870	triethyl phosphate	1370
1-butanol	2680	1-chlorobutane	5600
2-chloroethanol	70	chlorobenzene	3400
phenol	340	tetrachloromethane	5600
3-methylphenol	828	1-bromobutane	6700
allyl alcohol	45	butylamine	360
ethylene glycol	14 (?)	aniline	460
1,2-propanediol	13000	1,2-diaminoethane	1850
1,5-pentanediol	5900	dibutylamine	770
glycerol	19300	piperidine	11000
dibutyl ether	570	2-methylpyridine	670
1,2-dimethoxyethane	7000	nitromethane	950
1,2-dimethoxybenzene	1360	propionitrile	40
benzaldehyde	3260	acrylonitrile	70
3-pentanone	2140	benzyl cyanide	350
cyclohexanone	930	benzonitrile	1400
diisobutyl ketone	5750	formamide	3100
acetophenone	3000	N,N-dimethylacetamide	2580
formic acid	1210	tetramethylurea	1100
acetic acid	3530	sulfolane	2100
propanoic acid	4290	hexamethyl phosphoramide	2650

Acetic acid, acetic anhydride, benzoyl chloride and phosphorus oxycloride can be cited in the latter category.

Further hazards arise from the ability of solvents to ignite or of their vapour to form flammable and even explosive mixtures with air. The flash point is defined as the temperature below which the liquid solvent cannot be ignited, and is reported in Table 1.3 in °C (DIPPR 1997; Kirk–Othmer 1978). The reported flash points, however, depend somewhat on the mode of ignition, and inconsistencies between the sources of the data has been noted. Solvents also have an autoignition temperature (Table 1.3, in °C (DIPPR 1997)), generally well above 200°C (see exceptions in Table 1.3, e.g., some ethers), above which rapid combustion in air takes place even without supply of external heat (Riddick, Bunger and Sakano 1986; Kirk–Othmer 1978). Exceptions are polyhalogenated small hydrocarbons, but these may decompose in a fire fed by other materials to yield very toxic compounds: phosgene and dioxine. Care must, therefore, be used when employing organic solvents at elevated temperatures and even in their storage, when a nearby source could cause ignition.

The vapours of many solvents form with air explosive mixtures, when present at certain concentrations in the air. The lower and upper explosive limits are reported in Table 1.3 in % by volume of the vapours in air, pertaining generally to room temperature (DIPPR 1997; Kirk–Othmer 1978). It should again be stressed that the information provided here is for general guidance only, and that more specific and binding recommendations concerning the hazards involved and precautions to be taken against them should be obtained from the specific regulatory authorities.

References

Audrieth, L. F. and Kleinberg, J. (1953) *Non-Aqueous Solvents*, Wiley, New York.

ACS Committee on Analytical Reagents, *Reagent Chemicals*, American Chemical Society, Washington, 7th ed., 1986, 8th ed., 1993.

Browning, E. (1965) *Toxicity and Metabolism of Industrial Solvents*, Elsevier, Amsterdam.

Burfield, D. R. Gan, G.-H. and Smithers, R. H. (1978) *J. Appl. Chem. Biotechnol*. **28**, 23.

Chastrette, M. (1979) Tetrahedron **35**, 1441.

Coetzee, J. F. and Ritchie, C. D. (eds) (1969) *Solute-Solvent Interactions*, Dekker, New York.

Coetzee, J. F. (ed), *Recommended Methods for the Purification of Solvents and Tests for Impurities*, Pergamon, Oxford, 1982; Coetzee J. F. and other authors in a sequel, *Pure Appl. Chem*. (1985) **57**, 633, 855, 860, (1986) **58**, 1411, 1535, 1541, (1987) **59**, 703, (1990) **62**, 139.

Covington, A. K. and Jones, P. (eds) (1968) *Hydrogen Bonded Solvent Systems*, Taylor & Francis, London.

DIPPR, (1997) *DIPPR Pure Component Data Compilation*, Technical Database Services, New York, Version 12.0 (for Windows).

Flick, E. W. (1985) *Industrial Solvents Handbook*, Noyes Data Corp., Park Ridge, New Jersey.

Förster, M. and Lieser, K. H. (1981) *Fresenius Z. Anal. Chem*. **309**, 352, 355.

Gerhartz, W. ed. (1985) *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, 5th ed.

Hollis, O. L. (1966) *Anal. Chem*. **38**, 309.

Kirk–Othmer, *Encyclopedia of Chemical Technology*, Wiley-Interscience, New York, 3rd ed., 1978 and 4th ed., 1991–7.

Kolthoff, I. M. (1974) *Anal. Chem*. **46**, 1992.

Lagowski, J. J. (ed), *The Chemistry of Non-Aqueous Solvents*, Academic Press, New York, Vol. I (1996), Vol. II (1967), Vol. III (1970), Vol. IV (1976), Vols. Va and Vb (1978).

Landoldt-Börnstein (1959) *Zahlenwerte und Funktionen*, 5th ed.

Lindbeck, M. R. and Freund, H. (1965) *Anal. Chem*. **37**, 1647.

Mitchell, J., Jr., and Smith, D. M. (1948) *Aquametry*, Interscience, New York.

Parker, A. J. (1962) *Quart. Rev. (London)*, **16** (1962) 163; *Chem. Rev*., **69** (1969) 1.

Pearson, B. D. and Ollerenshaw, J. E. (1966) *Chem. Ind*. 370.

Perrin, D. D., Perrin, D. R. and Armarego, W. L. F. (1980) *Purification of Laboratory Chemicals*, Pergamon, Oxford, 2nd ed.

Reichardt, Ch. (1988) *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, 2nd ed.

Riddick, J. A., Bunger, W. B. and Sakano, T. K. (1986) *Organic Solvents*, WileyInterscience, New York, 4th ed.

Rosin, J. (1967) *Reagent Chemicals and Standards*, Van Nostrand, Princeton 5th ed.

Sisler, H. H. (1961) *Chemistry in Non-Aqueous Solvents*, Reinhold, New York.

Swietoslawski, W. (1945) *Ebulliometric Measurements*, Reinhold, New York.

Swietoslawski, W. and Anderson, R. (1959) in: A. Weissberger (ed.) *Physical methods in Organic Chemistry*, Interscience, New York Vol. I, Pt. I, 357.

Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier, New York, Vol. 1 (1950), Vol. 2 (1965).

Tranchant, J. (1968) *Bull. Soc. Chim. France* 2216.

Trusell, F. and Diehl, H. (1963) *Anal. Chem*. **35**, 674.

Waddington, T. C. (ed.) (1965) *Non-Aqueous Solvent Systems*, Academic Press, London.

Washburn, E. W., West, C. J. and Hull, C. (1926–1930) *International Critical Tables*, McGraw-Hill,

Chapter 2—
Solvent Effects

1—
Solvation

The most general effect a solvent may have on a solute dissolved in it, in fact, practically a prerequisite for the solute to dissolve in the first place, is the solvation of the solute. For the most general *solvation process* the solute may not only be a solute foreign to the solvent, but may also be a molecule of the solvent itself, that is, the process of its condensation from the vapour into the liquid also involves solvation. There is no limitation on the concentration of the solute, so that it may dissolve and be solvated in a solution that already contains this solute as well as other ones. In order to permit the consideration of the solvation process in a quantitative manner, it is defined (Ben-Naim and Marcus 1984) as:

> The process in which a particle of the solute is transferred at given temperature and pressure from a fixed position in the ideal gas phase into a fixed position in the liquid phase in which it is solvated.

Once this definition is adopted, the phenomenology and thermodynamics of this process encompass the interactions between the solute particle and its surroundings, as well as all the changes that take place internally in the solute and those accompanying the rearrangements of the solvent molecules and, if present, other solute particles due to the introduction of the solute particle. It is important to stress that not only the direct solute–solvent interactions be taken into account in the solvation process, but also the other changes mentioned. Excluded from consideration, by the insistence on the fixed positions in the two phases, are effects due to translational degrees of freedom of the solute, which are due to the different volumes at the disposal of the solute particle in these phases.

Of particular interest is the solvation process that takes place between the *standard states* of the solute in the ideal gas and in the solution. At a given temperature T the ideal gas standard state is specified by the standard pressure, P^{o} = 0.1 MPa (formerly 0.101 325 MPa = 1 atmosphere was generally specified). The solution standard state is specified as the infinitely dilute solution of the solute in the solvent of interest at T and P^o. Under these standard conditions, only internal solute changes and solute–solvent and solvent–solvent interactions need to be taken into account, but not any solute-solute interactions. Note that the solvation thermodynamics take into account both the *new* solute–solvent interactions and the *changes* in the solvent–solvent interactions caused by the introduction of the solute. The new solute–solvent interactions are taken to include changes in the *internal* degrees of freedom of the solute due to its having a near and constraining environment in the condensed phase, the solution, contrary to its situation in the ideal gas phase, where it is devoid from any interactions with other particles.

The standard thermodynamic functions of solvation defined as above indicated by superscript * differ from the generally tabulated standard thermodynamic functions indicated by superscript ^{o} due to the constraints of fixed positions. They therefore lack the changes in the translational degrees of freedom, due to the compression from the volume of the gaseous state to that in the solution, not relevant to the solvation of the solute. Thus, $\Delta H^* = \Delta H^o + RT\,(\mathrm{l} - \alpha_p T)$, where α_p is the isobaric expansibility of the solvent, $\Delta S^* = \Delta S^o + R(\mathrm{l} - \alpha_p T)$, $\Delta V^* = \Delta V^o - (RT/P^o)(-\mathrm{l} + \kappa_T P^o)$, where κ_T is the isothermal compressibility of the solvent, and so on.

In the present context, the solvation of a solvent molecule in its own liquid (i.e., condensation from the vapour, the opposite of evaporation) is of interest, and molar quantities are employed, rather than quantities pertaining to a single particle (Ben-Naim and Marcus 1984). The Gibbs free energy of solvation of a solvent in itself is:

$$\Delta G^* = RT\ln(pM/RTd) \qquad (2.1)$$

where p is the (saturation) vapour pressure, M is the molar mass, and d is the density. The entropy of solvation is $\Delta S^* = -(\partial\Delta G^*/\partial T)_p$, the enthalpy of solvation is $\Delta H^* = \Delta G^* + T\Delta S^*$, the constant pressure heat capacity of solvation is $(\partial\Delta H^*/\partial T)_p$, the volume of solvation is $\Delta V^* = (\partial\Delta G^*/\partial P)_T$, and so on for higher derivatives.

Strictly speaking, Eq. (2.1) is an approximation, since it should be taken at the constant pressure P^o, but actually is obtained experimentally at the variable pressure p. However, this introduces a negligible error, $\delta\Delta G^* \sim (P^o - p)\Delta V^*$. The volume of solvation of the solvent is given by the molar volume V, corrected for the isothermal compressibility κ_T:

$$\Delta V^* = V - RT\kappa_T \qquad (2.2)$$

Hence, the error $\delta\Delta G^*$ is of the order of 10 to 20 J mol^{-1}, compared to a few times 10^4 J mol^{-1} for ΔG^* (Ben-Naim and Marcus (1984). It is further assumed that the vapour pressure p represents the fugacity f of the of the solvent, since ΔG^* pertains to the process involving the ideal gas phase. However, at temperatures sufficiently remote from the boiling point T_b the vapour pressure of most solvents is sufficiently low for the approximation $p \approx f$ to hold sufficiently well.

Values of ΔG^*, ΔS^*, and ΔH^* of condensation at 298.15 K of a large number of solvents from the List as well as some others have been reported (Ben-Naim and Marcus (1984), and the data are shown in Table 2.1. It is noteworthy that for homologous series $CH_3(CH_2)_nX$, where X is a functional group such as $-CH_3$, $-CH{=}CH_2$, $-C_6H_5$, -OH, -COOH, -OC(O)H, $-OC(O)CH_3$, -O-, -CN, $-CH_2Cl$, among others, ΔG^* is linear with n, the number of methylene groups. The coefficient of n depends little on X and decreases slightly with increasing temperatures. The latter fact, though, makes ΔS^* and ΔH^* definitely non-linear with n, except for a short range of n values. For the condensation process the ΔH^* is invariably larger i.e., more negative, than the $T\Delta S^*$, so that this process is enthalpy dominated. In the context of the present book, however, the *conventional* standard molar heat of evaporation, $\Delta_V H = \Delta H^o$ values for vaporization are presented (Table 3.1), which are smaller than ΔH^*, as mentioned above, by the amount $R\ T(l - \alpha_p T) \approx 1.8$ kJ mol^{-1} at 298.15 K.

The vaporization of solvent molecules from the pure liquid solvent described above should not differ from its vaporization from an infinitely dilute solution of some solute(s) in it, since the vast majority of solvent molecules have other solvent molecules in their surroundings in both cases. As the solute concentration increases in the dilute solution range, it is expected that Raoult's law will be obeyed, that is, the vapour pressure of the solvent will be proportional to its mole fraction in the solution. If this is indeed the case, the solution is an ideal solution. At appreciable concentrations of the solute this will no longer be the case, due to solute–solute interactions and modified solute–solvent ones. The vapour pressure as well as other thermodynamic functions of the solvent and, of course, of the solute will no longer obey ideal solution laws. The consideration of these effects is beyond the scope of this book.

2—
Solution Composition

For a given solute, different solvents show different departures from ideal behaviour, both in terms of the concentration required to observe the onset of such deviations and in terms of their direction and magnitude. It is first necessary to specify the *composition scale* employed. For aqueous solutions the molality scale, moles of solute per kg of water, denoted by m, is frequently used. This scale becomes less useful when several solvents are compared, since in one kg batches of diverse solvents there are a variable number of moles of solvent (l/[M/ kg mol^{-1}]) and they occupy different volumes (l/[d/kg m^{-3}]). Still, the molality scale is in common use for dilute electrolyte solutions in solvents used for electrochemical purposes as it is for their aqueous solutions. However, even the change from water to heavy water, D_2O, requires caution in this respect, and the

Table 2.1 Thermodynamics of solvent condensation from the vapour to the liquid

No.	Name	$-\Delta G^*$	Ref	$-\Delta S^*$	$-\Delta H^*$
0	vacuum				
10	tetramethylsilane	13.01	j	18.3	25.32
20	n-pentane	14.24	[1]	45.2	27.72
30	2-methylbutane	13.48	[1]	42.3	26.09
40	n-hexane	16.96	[1]	53.6	32.93
50	c-hexane	18.51	[1]	53.5	34.46
60	n-heptane	19.64	[1]	62.0	38.12
70	n-octane	22.29	[1]	69.8	43.10
80	2,2,4-trimethylpentane	19.16	[1]	59.0	36.74
90	n-decane	27.74	[1]	85.0	53.08
100	n-dodecane	33.32	[1]	99.7	63.04
110	n-hexadecane	45.51	[1]	125.5	82.92
120	benzene	19.06	[1]	54.9	35.42
130	toluene	21.61	[1]	60.6	39.68
140	o-xylene	24.92	j	68.0	45.21
150	m-xylene	24.32	j	67.4	44.41
160	p-xylene	24.16	j	66.9	44.12
170	ethylbenzene	23.98	[1]	67.1	43.98
180	cumene	25.47	[1]	71.9	46.89
190	mesitylene	27.06	[1]	74.5	49.26
200	styrene	25.15	j	68.9	45.69
210	tetralin	31.59	j	85.8	57.18
220	cis-decalin	29.71	j	78.8	53.19
230	water	26.46	[1]	66.2	46.20
240	methanol	20.33	[1]	62.7	39.03
250	ethanol	21.25	[1]	76.3	43.99
260	n-propanol	23.26	[1]	86.9	49.18
270	i-propanol	21.28	[1]	86.5	47.07
280	n-butanol	25.77	[1]	95.2	54.14
290	i-butanol	24.50	[1]	94.2	52.57
300	2-butanol	23.07	[1]	95.1	51.42
310	t-butanol	20.94	[1]	91.6	48.24
320	n-pentanol	27.76	[1]	104.3	58.84
330	i-pentanol	27.72	[1]	99.8	57.47
340	t-pentanol	23.38	[1]	95.4	51.84
350	n-hexanol	30.01	[1]	112.1	63.45

360	c-hexanol	30.95	j	110.6	63.92
370	n-octanol	35.62	[1]	128.3	73.86
380	n-decanol	40.08	[1]	137.7	81.14
390	n-dodecanol	45.64	[1]	147.7	89.67
400	benzyl alcohol	35.40	j	94.3	63.52
410	2-phenylethanol	37.02	j	111.7	70.31
420	allyl alcohol	22.92	j	78.3	46.26
430	2-chloroethanol	25.15	j	75.5	47.86
440	2-cyanoethanol	37.44	j	69.1	58.05
450	2,2,2-trifluoroethanol.	20.15	j	85.4	45.60

continued overleaf

Table 2.1 *(continued)*

No.	Name	-ΔG*	Ref	-ΔS*	-ΔH*
460	hexafluoro-i-propanol	17.40	j	85.5	42.88
470	2-methoxyethanol	25.01	j	103.3	55.81
480	2-ethoxyethanol	26.00	j	77.1	48.99
490	1,2-ethanediol	37.55	j	85.8	63.12
500	1,2-propanediol	35.84	j	102.4	66.37
510	1,3-propanediol	38.60	j	121.5	74.83
520	1,2-butanediol	36.75	j	114.9	71.00
530	2,3-butanediol (meso)	32.68	j	94.8	60.95
540	1,4-butanediol	41.66	j	123.9	78.60
550	1,5-pentanediol	43.69	j	136.6	84.43
560	diethyleneglycol	43.60	j	135.9	84.12
570	triethyleneglycol	45.73	j	193.2	103.34
580	glycerol	52.68	j	117.5	87.72
590	phenol	32.59	j	90.9	59.69
600	2-methylphenol	32.90	j	112.1	66.31
610	3-methylphenol	34.79	j	96.7	63.63
620	4-methylphenol	35.04	j	114.3	69.12
630	2-methoxyphenol	34.04	j	100.1	63.87
640	2,4-dimethylphenol	34.09	j	112.8	67.73
650	3-chlorophenol	32.14	j	69.9	54.03
660	diethyl ether	14.39	[1]	47.2	28.47
670	di-n-propyl ether	18.94	[1]	61.4	37.24
680	di-i-propyl ether	16.84	[1]	57.5	33.99
690	di-n-butyl ether	23.90	[1]	74.3	46.04
700	di(2-chloroethyl)ether	28.58	j	61.7	46.97
710	1,2-dimethoxyethane	19.45	j	48.2	33.83
720	bis(methoxyethyl) ether	26.17	[1]	62.6	44.84
730	furan	15.00	j	48.3	29.40
740	tetrahydrofuran	17.69	[1]	52.4	33.33
750	2-methyl tetrahydrofuran	18.78	j	51.0	33.99
760	tetrahydropyran	16.31	[1]	68.1	36.61
770	dioxane	21.31	[1]	53.8	37.37
780	dioxolane	20.04	j	57.6	37.21
790	1,8-cineole	27.25	j	34.4	37.50
800	anisole	26.72	j	67.3	46.78
810	phenetole	28.43	j	81.7	52.80

820	diphenyl ether	38.51	j	101.5	68.78
830	dibenzylethe	37.88	j	135.0	78.13
840	1,2-dimehtoxybenzene	31.33	j		
850	trimethyl orthoformate				39.90
860	trimethyl orthoacetate				41.10
870	propionaldehyde	16.57	j	48.5	31.02
880	butyraldehyde	18.50	j	56.3	35.28
890	benzaldehyde	29.45	j	44.0	42.56
900	p-methoxybenzaldehyde	37.72	j	96.9	66.30
910	cinnamaldehyde	38.16	j	122.6	74.70
920	acetone	17.56	[1]	49.8	32.40
930	2-butanone	19.05	[1]	57.8	36.29

(table continued on next page)

Table 2.1 *(continued)*

No.	Name	$-\Delta G^*$	Ref	$-\Delta S^*$	$-\Delta H^*$
940	2-pentanone	21.09	[1]	79.5	44.78
950	methyl i-propyl ketone	23.72	j	47.0	37.73
960	3-pentanone	21.01	[1]	64.0	40.08
970	c-pentanone	27.85	j	52.1	43.38
980	methyl-i-butyl ketone	20.54	[1]	76.4	43.31
990	methyl t-butyl ketone	20.93	j	63.3	39.80
1000	c-hexanone	26.18	[1]	69.5	46.91
1010	2-heptanone	25.88	j	77.3	48.94
1020	3-heptanone	24.96	j	77.9	48.19
1030	di-t-butyl ketone				47.10
1040	acetophenone	32.16	j	77.5	55.26
1050	propiophenone	34.28	j	87.3	60.30
1060	phenylacetone				53.00
1070	p-methylacetophenone				
1080	p-chloroacetophenone	41.54	j	88.0	67.80
1090	benzophenone(beta)	46.66	j	150.0	91.39
1100	acetylacetone	23.50	j	67.0	43.47
1110	biacetyl	20.43	j	67.3	40.50
1120	formic acid	23.17	[1]	-5.2	21.63
1130	acetic acid	24.66	[1]	0.1	24.69
1140	propanoic acid	27.72	[1]	96.8	56.59
1150	n-butanoic acid	30.83	[1]	105.2	62.20
1160	n-pentanoic acid	34.09	[1]	124.0	71.07
1170	n-hexanoic acid	37.94	[1]	142.9	80.53
1180	n-heptanoic acid	41.35	j	116.0	75.94
1190	dichloroacetic acid	33.76	j	84.4	58.92
1200	trifluoroacetic acid	19.11	j	62.0	37.60
1210	acetic anhydride	26.17	j	81.8	50.54
1220	benzoyl chloride	30.88	j	73.5	52.79
1230	benzoyl bromide	33.36	j	90.7	60.40
1240	methyl formate	15.33	[1]	55.5	31.88
1250	ethyl formate	16.87	[1]	55.3	33.37
1260	methyl acetate	17.31	[1]	55.0	33.72
1270	ethyl acetate	18.84	[1]	61.1	37.05
1280	propyl acetate	21.00	[1]	68.0	41.27

1290	butyl acetate	23.36	[1]	74.8	45.65
1300	i-pentyl acetate	24.58	j	76.1	47.26
1310	methyl propanoate	19.17	j	61.9	37.62
1320	ethyl propanoate	20.76	[1]	67.5	40.81
1330	dimethyl carbonate	20.55	j	61.4	38.86
1340	diethyl carbonate	23.69	j	64.0	42.77
1350	ethylene carbonate	39.52	j, d	40.2	52.10
1360	propylene carbonate	38.10	j	97.1	67.06
1370	diethyl malonate	32.28	j	94.6	60.47
1380	methyl benzoate	31.80	j	85.9	57.40
1390	ethyl benzoate	32.28	j	80.9	56.41

continued overleaf

Table 2.1 *(continued)*

No.	Name	$-\Delta G^*$	Ref	$-\Delta S^*$	$-\Delta H^*$
1400	dimethyl phthalate	43.46	j	103.1	74.20
1410	dibutyl phthalate	51.19	j	165.5	100.54
1420	ethyl chloroacetate	26.13	j	84.2	51.22
1430	ethyl trichloroacetate	28.51	j	72.6	50.10
1440	ethyl acetoacetate	27.47	j	94.0	55.49
1450	4-butyrolactone	27.84	j	87.9	54.04
1460	perfluoro-n-hexane	14.98	j	64.7	34.26
1470	perfluoro-n-heptane	17.32	j	68.2	37.67
1480	perfluoro-methylcyclohexane	16.86	j	62.2	35.41
1490	perfluoro-decalin	18.26	j	96.5	47.02
1500	fluorobenzene	19.40	[1]	56.3	36.19
1510	hexafluorobenzene	18.50	j	62.5	37.13
1520	1-chlorobutane	18.20	j	57.7	35.41
1530	chlorobenzene	23.86	[1]	63.3	42.72
1540	dichloromethane	16.10	[1]	47.6	30.30
1550	1,1-dichloroethane	17.03	[1]	50.6	32.12
1560	1,2-dichloroethane	19.65	[1]	57.5	36.79
1570	tr-1,2-dichloroethylene	16.25	j	49.4	30.97
1580	o-dichlorobenzene	28.93	[1]	77.6	52.05
1590	m-dichlorobenzene	27.95	[1]	75.3	50.41
1600	chloroform	17.51	[1]	51.3	32.81
1610	1,1,1-trichloroethane	23.67	[1]	34.5	33.95
1620	1,1,2-trichloroethane	22.53	j	65.4	42.02
1630	trichloroethylene	20.78	j	50.7	35.88
1640	1,2,4-trichlorobenzene	31.68	j	87.0	57.61
1650	tetrachloromethane	18.41	[1]	52.2	33.99
1660	tetrachloroethylene	22.78	j	62.2	41.34
1670	1,1,2,2-tetrachloroethane	25.62	j	73.3	47.47
1680	pentachloroethane	26.38	j	65.6	45.93
1690	1-bromobutane	20.67	j	58.9	38.24
1700	bromobenzene	26.33	[1]	67.2	46.37
1710	dibromomethane	21.52	j	59.2	39.18
1720	1,2-dibromoethane	25.34	j	61.0	43.51
1730	bromoform	25.99	j	68.7	46.48
1740	1-iodobutane	23.22	j	64.2	42.63
1750	iodobenzene	29.86	j	65.6	49.42

1760	diiodomethane	30.16	j	70.7	51.25
1770	n-butylamine	18.80	[1]	61.8	37.22
1780	benzylamine	30.62	j	83.3	55.45
1790	1,2-diaminoethane	24.78	j	79.5	48.50
1800	diethylamine	16.43	[1]	54.4	32.65
1810	di-n-butylamine	26.71	[1]	81.8	51.09
1820	pyrrole	25.75	j	64.5	46.99
1830	pyrrolidine	20.26	j	63.6	39.21
1840	piperidine	21.49	j	64.7	40.77
1850	morpholine	24.69	j	70.7	45.78
1860	triethylamine	18.83	[1]	58.9	34.60
1870	tri-n-butylamine	32.54	j	129.4	71.13

(table continued on next page)

Table 2.1 *(continued)*

No.	Name	$-\Delta G^*$	Ref	$-\Delta S^*$	$-\Delta H^*$
1880	aniline	31.27	j	88.5	57.65
1890	o-chloroaniline	31.82	j	90.1	58.70
1900	N-methylaniline	31.82	j	77.7	54.98
1910	N,N-dimethylaniline	30.34	j	71.4	51.64
1920	ethanolamine	33.86	j	114.5	68.00
1930	diethanolamine	48.22	j, b		50.37
1940	triethanolmine	43.21	j	179.9	104.01
1950	pyridine	23.09	j	63.0	41.88
1960	2-methylpyridine	24.08	j	69.1	44.67
1970	3-methylpyridine	25.66	j	71.6	46.99
1980	4-methylpyridine	25.82	j	69.6	46.58
1990	2,4-dimethylpyridine	27.01	j	75.9	49.64
2000	2,6-dimethylpyridine	25.43	j	75.1	47.81
2010	2,4,6-trimethylpyridine	28.96	j	78.0	52.21
2020	2-bromopyridine				
2030	3-bromopyridine	28.80	j	59.0	46.40
2040	2-cyanopyridine				60.20
2050	pyrimidine				51.63
2060	quinoline	35.80	j	101.4	66.04
2070	acetonitrile	20.44	[1]	47.8	34.69
2080	propionitrile	21.40	[1]	54.1	37.53
2090	butyronitrile	22.61	[1]	61.5	40.95
2100	valeronitrile	25.04	j	69.6	45.78
2110	arylonitrile	19.48	j	51.0	34.69
2120	benzyl cyanide	35.36	j	95.9	53.94
2130	benzonitrile	31.08	j	84.6	56.32
2140	nitromethane	22.67	j	58.8	40.20
2150	nitroethane	23.36	j	62.1	41.88
2160	1-nitropropane	24.59	j	68.9	45.12
2170	2-nitropropane	23.16	j	66.7	43.05
2180	nitrobenzene	33.33	j	78.9	56.86
2190	formamide	39.09	j	78.5	62.49
2200	N-methylformamide	34.83	j	78.0	58.08
2210	NN-dimethylformamide	27.29	j	73.9	49.31
2220	N,N-dimethylthioformamide				

2230	N,N-diethylformamide	28.92	j	73.5	50.84
2240	N-methylacetamide	54.67	j, d	53.7	70.85
2250	N,N-dimethylacetamide	28.80	j	77.8	51.98
2260	N,N-diethyl acetamide				55.95
2270	pyrrolidinone-2	25.08	j		
2280	N-methylpyrrolidinone	32.55	j	78.0	55.80
2290	N-methylthiopyrrolidinone	39.85	j	72.7	61.52
2300	tetramethylurea	29.84	j	70.8	50.94
2310	tetraethylurea	32.53	j	110.1	65.40
2320	dimethylcyanamide	27.82	j	50.5	42.90
2330	carbon disulfide	16.72	j	41.5	29.10

continued overleaf

***Table 2.1** (continued)*

No.	Name	$-\Delta G^*$	Ref	$-\Delta S^*$	$-\Delta H^*$
2340	dimethyl sulfide	15.50	j	45.8	19.17
2350	diethyl sulfide	19.79	j	58.3	37.18
2360	di-i-propyl sulfide	21.82	j	65.6	41.40
2370	di-n-butyl sulfide	29.76	j	85.8	55.30
2380	tetrahydrothiophene	23.16	j	57.8	40.40
2390	pentamethylene sulfide	24.87	j	66.0	44.50
2400	dimethyl sulfoxide	32.28	j	75.2	54.70
2410	di-n-butyl sulfoxide				
2420	sulfolane	43.32	j, b	126.1	81.55
2430	thiobis(2-ethanol)	44.21	j	108.9	76.67
2440	diethyl sulfite	26.57	j	79.4	50.20
2450	dimethyl sulfate	30.32	j	67.1	50.32
2460	diethyl sulfate	36.67	j	73.9	58.71
2470	methanesulfonic acid	50.37	j	66.6	70.24
2480	trimethyl phosphate	30.05	j	59.4	49.01
2490	triethyl phosphate	31.31	j	76.3	59.07
2500	tributyl phosphate	39.96	j	78.0	63.21
2510	hexamethyl phosphoramide	36.32	j	88.3	62.94
2520	hexamethyl thiophosphoramide				
2530	hydrogen peroxide	31.98	j	74.2	54.10
2540	hydrogen fluoride	17.14	j	29.8	25.88
2550	sulfuric acid	55.76	j	111.4	88.97
2560	ammonia	6.62	j, a	48.1	20.97
2570	hydrazine	26.30	j	66.8	46.22
2580	sulfur dioxide	6.40	j, a	57.8	23.64
2590	thionyl chloride	19.00	j	45.6	32.60
2600	phosphorus oxychloride	21.42	j	63.1	40.25

Units: $-\Delta G^*$ and $-\Delta H^*$ in kJ mol^{-1}; $-\Delta S^*$ in JK^{-1} mol^{-1}. Ref: [1] Ben-Naim Marcus (1984); a at 20°C, b at 30°C, d at 40°C, j from eq. (2.1) and data in Table 3.1.

scale frequently used is *aquamolality*, i.e., the number of moles of solute per the same number of moles of the heavy water, or $H_2O + D_2O$ mixtures or some other solvent, as there are in one kg of H_2O, that is, 55.51 moles. For very precise work, the content of ^{17}O and mainly ^{18}O in addition to ^{2}H in ordinary water must also be taken into account, and *standard mean ocean water* (SMOW) is specified.

A commonly used solute concentration scale is the mole fraction one, x, which specifies directly the number of moles of solvent per mol of solute: $(1 - x)/x$. This number is of particular interest in the more concentrated solutions, where a lack of solvent molecules required to surround a solute particle and separate solute particles from one another greatly affects the properties of the solution. However, this scale is useful for the entire composition range, from very dilute solutions to such solutions, mixtures, where it is difficult to designate one component as the solute and the other as the solvent. This scale requires knowledge of the chemical nature of the solute and the solvent in view of the necessity to specify a mole of each. The solvents in out List have no problems in this respect, but polymeric, aggregating, or dissociating solutes may constitute such a problem. The mole fraction scale is still straightforward for solvent mixtures by the specification of the weighted number of moles of the solvent in the mixture. Such commonly used mixtures as 'cresols' or 'decalin isomers' are from the point of view of the specification of the concentration on the mole fraction scale as definite as, say, pure 3-methylphenol or cis-decalin.

Polymeric solvents, such as polyethylene glycol (PEG) of specified mean molar mass, do provide problems in this respect. Thus, whereas triethyleneglycol, $H(OCH_2CH_2)_3OH$ is on our List, the mole fraction in, e.g., PEG-300 (the '300' specifying the mean molar mass, in g mol^{-1}, with six to seven repeating (OCH_2CH_2) groups) cannot be specified precisely—although PEG-300 can be a very useful solvent for many purposes. For such solutions, however, the mass (weight) fraction, *w*, or mass percentage, 100*w*, is the commonly used specification of the composition. When the molecular constitution of both solute and solvent can be specified, and for a single solute, its mole fraction is:

$$x = 1/[1 - (1 - w)M_{\mathrm{solute}}/wM_{\mathrm{solvent}}] \qquad (2.3)$$

If there is more than one solute present, then the mole fraction of solute i is

$$x_{\mathrm{i}} = w_{\mathrm{i}} \Big/ \sum_{\mathrm{j}} w_{\mathrm{j}}(M_{\mathrm{i}}/M_{\mathrm{j}}) \qquad (2.4)$$

where the summation index j comprises the solvent and all the solutes, including solute i. If the composition is specified as (%) w/w, this may correspond to *w*/(l - *w*) rather than to *w* itself and proper caution must be exercised in its numerical interpretation.

For many practical purposes, as well as for some theoretical purposes involving statistical thermodynamics, it is expedient to deal with the volume concentration, denoted by *c* or number density, denoted by ρ, i.e., the number of moles, or molecules, of the solute per unit volume of the solution. It must be realized that once a solution is prepared with a specified concentration *c* at a given temperature *T* and pressure *P*, this value will not remain constant when *T* and/or *P* are changed. It is also necessary to know the density *d* of the solution, not of just the solvent, in order to know the number of moles of solvent per mol of solute if the concentration is appreciable. In dilute solutions the density is usually linear with the concentration, tending to the limiting value of that of the solvent at infinite dilution. A rough estimate of the mole ratio of solvent to solute is obtained from the molar volume of the solvent. Since concentrations *c* are generally specified per l dm^3(1 L) of solution and molar volumes *V* are in cm^3 mol^{-1}, the mole ratio is 1000 *c/V*. It must be realized that there are different numbers of moles of solvent per unit volume in different solvents and at given molarities *c* or number densities ρ also per mol of solute. For solvents on the List there are from 55.5 mol for water down to 3.3 mol for hexadecane in l dm^3. This constitutes nominally a 'solvent effect' that ought not to be neglected.

The relation between the molal and molar scales, *m* and *c* is given by:

$$c = m\,d/(1 + m\,M_{\text{solute}}/1000) \qquad (2.5)$$

$$m = c/(d - c\,M_{\text{solute}}/1000) \qquad (2.6)$$

for densities *d* expressed in g cm^{-3}. It is only for dilute solutions in the particular solvent water at ambient conditions (or a few other solvents with $d \approx$ l g cm^{-3}) that the molar and molal scales nearly coincide and can almost be used interchangeably.

A further method for the specification of the composition of a solution or mixture, related to the molar scale, is the volume fraction of the solute, ϕ. This takes into account any change in the volume of the system that has taken place on the preparation of the solution—the volume (change) of mixing. Therefore for a solute i:

$$\phi_i = c_i v_i \qquad (2.7)$$

where v_i is the partial molar volume of the solute in the solution in $dm^3\ mol^{-1}$. This is an experimentally obtainable quantity, from density measurements, but it is not directly available in tables of the properties of the pure solutes. For instance, for electrolytes, the partial molar volume may be considerably smaller than the volume of the hypothetical liquid, supercooled, electrolyte, due to the phenomenon of electrostriction. For non-electrolytes, the partial molar volume may be smaller or larger than that of the neat solute, when contraction or expansion takes place on their dissolution in or mixing with the solvent. It is common practice, therefore, to specify a modified volume fraction φ:

$$\varphi_i = 1/[1 + (1 - x_i)(V_{\text{solvent}}/V_{\text{solute}})] \qquad (2.8)$$

depending on the molar volumes of the pure solvent and solute. Often the volume composition is specified as (%) v/v, i.e., the volume of the solute mixed with a given volume of the solvent. This corresponds to $\varphi_i/(l - \varphi_i)$. In very dilute solutions the scales φ_i and ϕ_i practically coincide, as they do when the volume of mixing is zero or negligible, i.e., in ideal or nearly ideal solutions. The difference between these two volume fraction scales constitutes another nominal 'solvent effect', due to the different volumes of mixing exhibited by different solvents. Compositions of a solution obtained with several of these composition scales are shown in Figure 2.1 as an illustration.

3—

Solvent Effects on Solubility and Partition

The dissolution of a solute in a solvent always affects the solvent–solvent interactions in the vicinity of the solute particles in addition to the solute–solvent

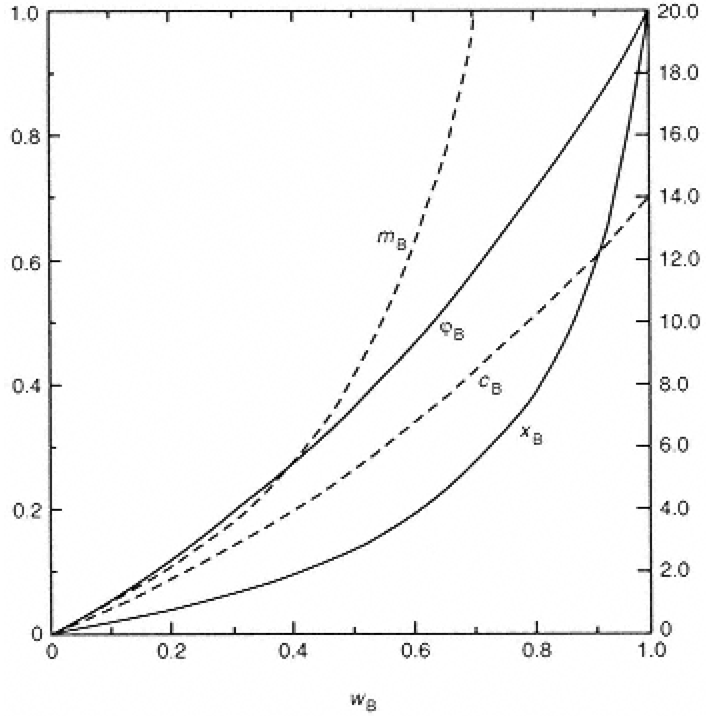


Figure 2.1
Measures of the composition of solutions of a solute B (2-bromoethanol, *d* = 1.7629 g cm^{-3} at 20°C) in a solvent A (water, *d* = 0.9982 g cm^{-3} at 20°C) against the mass fraction W_B: X_B is the mole fraction and φ_B is the volume fraction (assuming negligible volume change on mixing) (left hand ordinate) and m_B is the molality and C_B is the molarity (right hand ordinate).
By permission from Y. Marcus, *Introduction to Liquid State Chemistry*, Wiley, Chichester, 1977.

interactions that take place. Conceptually, one may separate the dissolution into several stages. First, a cavity in the solvent is formed, to accommodate the solute, breaking down the cohesive forces of the solvent. Next dispersion forces are 'switched on', which are universal, in the sense that they apply to non-polar and hardly polarizable solutes and solvents as well as to polar and polarizable ones. Then other forces are 'switched on', providing contributions from interactions of polar molecules with polar or polarizable ones and from donor acceptor interactions, such as electron-pair or hydrogen bond donation and acceptance, whether from or to the solute, the solvent, or both. It is an approximation to separate these conceptual stages into distinct contributions to the overall Gibbs free energy of solvation, but working expressions have been devised that permit accurate predictions of solubilities on this basis.

In the following, the solvent is designated by subscript 1 and the solute by subscript 2. For the purpose of theoretical discussions, solubilities are generally expressed as the mol fraction of the solute, x_2, at a given temperature T and generally the implicit standard pressure P^o, in the saturated solution. The standard molar Gibbs free energy of solution is then:

$$\Delta_{\text{solution}} G^o = -RT \ln x_2 \qquad (2.9)$$

The Gibbs free energy of solution is the difference between the Gibbs free energy of solvation of the solute in the solvent and any Gibbs free energy of interaction in the pure solute that are lost on dissolution, if it is a solid, a liquid, or a non-dilute gas. The latter quantity corresponds to the changing of the solute from a condensed phase, solid or liquid, or high-pressure gaseous phase to the ideal gas state.

The following considerations lead to the thermodynamics of dissolution, to the values of the solubility, and to the solvent effects on solubility. When a gaseous solute dissolves in a solvent, provided that its pressure in the gas phase is low or moderate, then its behaviour in that phase can be taken to be approximately ideal, that is, no interactions in the gas phase are lost on the dissolution. For a solute that is liquid when pure, the interactions among its molecules in the liquid are lost on the dissolution. These lost interactions in the pure liquid are estimated from the enthalpy of vaporization and these are replaced by the solvation enthalpy on dissolution. The corresponding entropy change is estimated from the difference of volume at the disposal of the solute molecules in the solution and the liquid solute and any changes in entropy due to changes in the internal degree of freedom, rotation and vibration. However, such entropy changes are rather small. A solute that is solid in the pure state can be considered first to form a hypothetical undercooled liquid at the temperature of dissolution, with appropriate enthalpy and entropy changes. Then it can be treated as a liquid solute.

When the only effects that have to be taken into account are those of cavity formation in the solvent and the dispersion interactions, i.e., when both the solvent and the solute are non-polar, then Hildebrand's *solubility parameter* concept (Hildebrand and Scott 1950) provides good estimates of the solubility. The mole fraction of a gaseous solute, x_2, in a solution in equilibrium at a partial pressure p_2 of this gas, can be estimated from the following expression:

$$\ln x_2 \approx \ln(p_2/P^o) - V_2\varphi_1^2(\delta_1 - \delta_2)^2/RT \qquad (2.10)$$

where at low solubilities, as are commonly encountered, $\varphi_1^2 \approx 1$, and δ is the solubility parameter. The approximation involved in Eq. (2.10) is the use of the pressure p_2 instead of the fugacity f_2 at low partial pressures. The correction $\ln(f_2/p_2) \approx B_2P^o/RT$, where B_2 is the second virial coefficient of the gaseous solute, can be applied at higher partial pressures. The work required to form the cavity is given by the product of the volume of the solute, V_2, and the cohesive energy density of the solvent, δ^{21}. The larger it is, the lower the solubility, x_2, and the larger the $\Delta_{\text{solution}}G^{o}$ from Eq. (2.9). The effect of the dispersion forces between solute and solvent is manifested in the contribution from δ_2. It is further assumed that the molar volumes and solubility parameters of the gaseous solute can be extrapolated from those of its liquid state at low temperatures to room temperature, and can be seen in Table 2.2, adapted from Shinoda (Shinoda 1978).

On the assumption that the solutions are dilute and that there is no direct association of the solute with the solvent, then the only way that the solvent affects the solubility is via its solubility parameter, δ_1. For a given solute, and since the term involving δ_1 is negative, the more the solubility parameter of the solvent differs from that of the solute, the lower the solubility. Since the term in the solubility parameters is squared, the difference may be either positive or negative to provide the same effect. As already specified above, this behaviour is observed (Shinoda 1978) when only dispersion forces between solute and solvent are operative. If, however, electron-pair donation and acceptance between them come into play, as with CO_2 as the solute in aromatic solvents or tetrachloromethane, then a somewhat higher solubility than Eq. (2.10) predicts is observed.

Other measures of the solubility of a gaseous solute are readily derived from its mole fraction. The *Henry's law constant* is $K_H \approx \lim(p_2/x_2P^{o})$ at $p_2 \to 0$, which becomes on the molal scale $K_m \approx \lim(1000\, p_2/M_1x_2)$ with M_1 the molar mass of the solvent in g mol^{-1} for use in Eq. (2.13) below. The *Ostwald coefficient* is the limit of $\gamma_2 = RT(x_2/p_2)/V_1$ at $p_2 \to 0$ and is related to the mass fraction w_2 by:

$$\gamma_2 = w_2(1 - w_2)^{-1}d_1RT/M_1p_2 \qquad (2.11)$$

Table 2.2 The molar volumes and solubility parameters (as hypothetical liquids at 25° C) of some gaseous solutes (Shinoda 1978)

Gaseous solute	V_2/cm^3 mol^{-1}	δ_2/J$^{1/2}$cm$^{-3/2}$
argon	57.1	10.90
krypton	65.0	13.09
xenon	68*	13.5*
radon	70.0	13.97
hydrogen	35.0	
nitrogen	32.4	5.30
oxygen	33.0	8.18
carbon monoxide	32.1	6.40
carbon dioxide	55.0	12.27
chlorine	74.0	17.80
methane	52.0	11.62
ethylene	65.0	13.50
ethane	70.0	13.50

* Estimated from the relative volumes and energies of vapourization of Kr, Xe, and Rn at the boiling points.

where d is the density and $p_2 = P^o - p_1$, if the solute is a gas, or is the vapour pressure if a liquid.

Returning to the solvation of gaseous or liquid solutes in solvents, the Gibbs free energy of solvation is given by:

$$\Delta G^* = -RT \ln \gamma \qquad (2.12)$$

If the composition is specified in terms of the Henry's law constant K_m on the molal scale, where $p_2 = m_2 K_m$, then the Gibbs free energy of solvation is given by:

$$\Delta G^* = RT \ln(K_m / d_1 RT) \qquad (2.13)$$

with certain highly justifiable approximations (Ben-Naim and Marcus 1984). One should not be confused by noting that various scales of composition lead to seemingly diverse expressions for the same quantity, the Gibbs free energy of solvation. The derivative functions for solvation, discussed above, are readily obtained from the specified experimental data, but care must be taken to note which variables are kept constant in the derivatives. Using these expressions, the nominal solvent effect is manifested also through its molar mass or volume, in addition to its solubility parameter.

A simple expression governs the solubility of a liquid solute in a solvent, provided the solvent is practically insoluble in the liquid solute and that, again, only dispersion forces are operative between them. The first condition yields for the activity of the solute in its practically neat liquid phase, as well as in the saturated solution in equilibrium with it, to $a_2 \approx 1$ and $\ln a_2 \approx 0$. This dispenses effectively with the first term on the right hand side of Eq. (2.10). For a given liquid solute, the solubility parameter of the solvent dictates the solubility and constitutes entirely the solvent effect on it. This fact has found much application in the determination of the solubilities of certain liquid polymers in various solvents, the mole fraction x_2 and volume V_2 then pertain to the monomer of the solute. If, however, the solvent is also soluble in the liquid solute, as is the case when a solvent is capable of swelling a polymer, then the mutual solubility is given by:

$$\ln(x_2''/x_2') = V_2(\varphi_1'^2)(\delta_1 - \delta_2)^2/RT \qquad (2.14)$$

where " and ' designate the two liquid phases. The solvent effect then is manifested not only through δ_1 but also through V_1, which for a given solute volume V_2 determines the volume fraction φ_1 in each phase.

The solubility of a solid, provided that it does not form crystal solvates, or solid solutions, with the solvent but remains as a pure solid, and provided again that only dispersion forces are operative, is given approximately by:

$$\ln x_2 \approx \Delta_F S(T_F - T)/RT - V_2 \varphi_1^2 (\delta_1 - \delta_2)^2/RT \qquad (2.15)$$

Here the solvent effect is given by the second term on the right hand side, the first depending on the solute only, subscript $_F$ denoting fusion. The approximation depends on the mutual cancellation of terms involving the difference between the heat capacity of the solid and the liquid forms of the solute. The ratio $\Delta_F S/R$ can be estimated in various ways. For many molecular solids it varies with the molecular size, being ~ 1.3 per segment. For such solids a segment may be a -CH= (aromatic), a $-CH_2-$, or a $-CH_3$ group or equivalents for oxygen, nitrogen, sulfur, or halogen atoms in the molecule. A better approximation for $\Delta_F S/R$ is obtained from Table 2.3, where the rigidity or flexibility of a molecule is explicitly taken into account.

Solutes that, whatever their state of aggregation, undergo solvation interactions with the solvent beyond those due to dispersion forces, exhibit specific contributions to the solubility, that can be attributed to dipole–dipole and dipole–induced dipole interactions and electron-pair or hydrogen bond donation by the solvent to the solute or *vice versa*. Equations (2.10), (2.14) and (2.15) must then be modified to take these interactions into account by the addition of appropriate terms. Various approaches have been proposed for such additional interactions, and here the following is adopted, following Yalkowski (Yalkowski 1988):

$$\Delta_{\mathrm{solution}} G^{\circ} = \text{cavity term} + A_{s\pi} s_2 \pi_1^* + A_{\beta\alpha}\beta_2\alpha_1 + A_{\alpha\beta}\alpha_2\beta_1 \qquad (2.16)$$

The *A*'s are universal coefficients, taking care of the units involved. The Greek symbols with subscript $_2$ denote the propensities of the solute molecules to undergo specified interactions: polarity-derived ones, s_2, accepting the hydrogen bridges, b_2, and accepting an electron-pair, a_2, to form the corresponding solvates. The Greek letters with subscript $_1$ signify the abilities of the solvent molecules to provide these interactions (see Chapter 4 and Table 4.3). These terms may be many-fold more important than those in Eqs. (2.10), (2.14) and (2.15) in determining the solubilities of a given solute characterized by s_2, a_2 and b_2 in various solvents. In the cases where dipole interactions and electron-pair and hydrogen bond donation are absent, the first two terms on the right hand side of Eq. (2.16) divided by $-RT$ take the place of the right hand sides of Eqs. (2.10), (2.14) and (2.15), the last two terms in Eq (2.16) being then inoperative.

Table 2.3 Approximate values of $\Delta_F S/R$ for solids made up of molecules of various types (Yalkowski 1988)

Molecular type	$\Delta_F S/R$
monoatomic and spherical	1.8
diatomic and small linear triatomic	2.5
nonlinear triatomic	3.5
small rigid	4.5
large rigid	6.8
small flexible	5.5
large flexible*	$6.8 + 2.5(n-5)$

*For flexible alky1 chains with *n* carbon atoms.

A fuller discussion of the quantities π^*, α, and β is given in Chapter 4. The cavity term itself can be expressed either in terms of the Hildebrand solubility parameter, i.e., $A_\delta V_2 \delta_1^2$, where A_δ, is a solute- and solvent-independent quantity, or also by $sA_2\sigma_1$, where A_2 is the surface area of a molecule of solute, σ_1 is the surface tension of the solvent, and s is a coefficient, which may depend on the solute but not on the solvent. Since values of A_2 may not, in general, be available (Bondi 1964), the product sA_2 can be approximated by $s' V_2^{2/3}$. The solvent effect, as far as the cavity term is concerned, is therefore obtained from δ_1^2 (Table 3.1) or σ_1 (Table 3.9).

4—

Solvent Effects on Chemical Equilibria

Consider the equilibrium between reactants A, B, . . . and products M, N, . . . in the gas phase as well as in solution in a given solvent S_I (Figure 2.2). The equilibrium constant in the gas phase, K^g, depends on the properties of the reactants and the products. In very favourable cases it can be estimated from statistical thermodynamics via the relevant partition functions, but for the present purposes it is regarded as given. The problem is to estimate the magnitude of the equilibrium constant in the solution, K^I, and how it changes to K^{II}, when solvent S_{II} is substituted for solvent S_I.

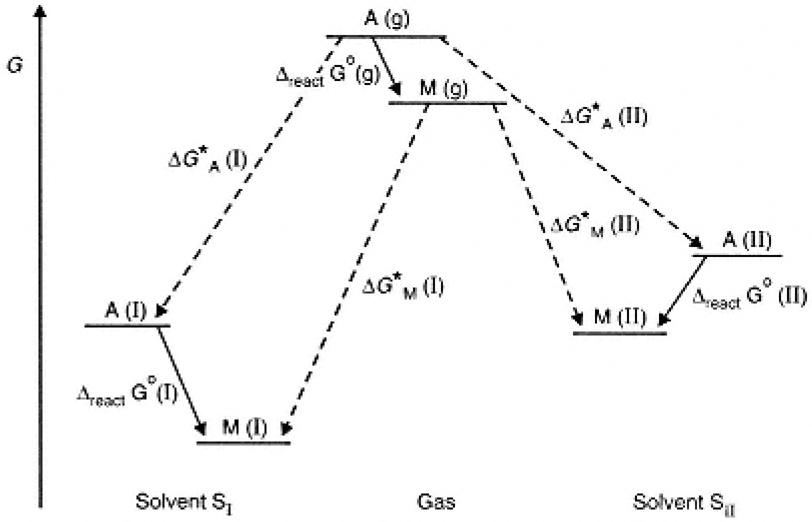


Figure 2.2
Schematic representation of the Gibbs free energies pertaining to the equilibrium between reactant A and product M in the gas phase, g, and in two solvents, S_I and S_{II}, showing the reaction Gibbs free energies $\Delta_{react}G$(g, I, or II) and the solvation Gibbs free energies ΔG^*(A or M, I or II).

By definition, the equilibrium constants do not depend on the concentrations of the reactants and products, and are related to the standard Gibbs free energy of the reaction per mol of reaction as:

$$\Delta_{\text{reaction}} G^{o}(\text{g, I or II}) = -RT \ln K^{(\text{g, I or II})} \qquad (2.17)$$

Rather than the equilibrium constants, the equilibrium quotients:

$$Q^{\text{g}} = p_{\text{M}} p_{\text{N}} \ldots / p_{\text{A}} p_{\text{B}} \ldots \qquad (2.18)$$

and

$$Q^{(\text{I or II})} = [\text{M}][\text{N}] \ldots / [\text{A}][\text{B}] \ldots \qquad (2.19)$$

however, are more readily measurable. Here the p's are partial pressures and the [ ] are concentrations on an appropriate concentration scale e.g., x, m, or c, whence Q may receive the subscripts: Q_x, Q_m, *or* Q_c. These quotients, however, depend on the total pressure, and on the concentrations, respectively. The assumption is made now, that the equilibrium depicted in Figure 2.2 in the gas phase takes place at such low partial pressures and at a constant total pressure P^{o}, that ideal gas conditions can be assumed. Then $-RT \ln Q$ of the reaction in solution can be regarded as made up from $-RT \ln K^{\text{g}}$ and two additional terms, one describing the difference in the solvation of the products and reactants, the other represents the solute–solute interactions among these reactants and products in the solution, expressed by the activity coefficients f: (The activity coefficients are symbolized by f, corresponding to concentrations on the mole fraction scale; for the molality and molarity scales, γ and y should be used.)

$$\begin{aligned} -RT \ln Q^{\text{solution}} = &- RT \ln K^{\text{g}} + [\Delta G^{*}_{\text{M}} + \Delta G^{*}_{\text{N}} + \ldots - \Delta G^{*}_{A} - \Delta G^{*}_{B} - \ldots] \\ &+ RT \ln[f_{\text{M}} f_{\text{N}} \ldots / f_{\text{A}} f_{\text{B}} \ldots] \qquad (2.20) \end{aligned}$$

If the reaction mixture is very dilute in the reactants and the products, the activity coefficients can all be approximated by unity. Then the last term on the right hand side of Eq. (2.20) vanishes, and the left hand side can be written as $\Delta G^{o} = -RT \ln K^{\text{solution}}$, the equilibrium quotient becoming the equilibrium constant. Under ordinary conditions, however, the activity coefficient term must be taken into account, since there are solvent effects on all the terms on the right hand side except $-RT \ln K^{\text{g}}$. The fact that different numbers of solvent molecules may specifically associate with the reactants and the products and that solvent molecules may be released or consumed in the reaction should not be included explicitly, since this effect is already covered by the terms in ΔG^{*}s of solvation of the reactants and products according to our definition of this concept.

In moderately dilute solutions the activity coefficients do depart from unity but to a limited extent. If the reactants and products are all uncharged, of similar sizes, and of equal number i.e., the stoichiometric coefficients for the reaction are the same on both sides, then the logarithm of the activity coefficient quotient, the last term in Eq. (2.20), may still be negligible. This is no longer the case when either the reactants or the products are charged e.g., $CH_3COOH \Leftrightarrow CH_3CO^{-2} + H^+$ or both are charged but with different algebraic charge numbers *z* e.g., for $Cd^{2+} + Br^- \Leftrightarrow CdBr^+$. In such cases solute–solute interactions manifest themselves through the relative permittivity ε of the solvent and this constitutes a clear–cut solvent effect on the equilibrium quotient.

As a very rough approximation, the Debye–Hückel expression can be invoked when charged species are involved. Accordingly, the solvent effect on going from solvent I to II arising from this cause is $[z_M^2 + z_N^2 \ldots - z_A^2 - z_B^2 \ldots] \times (\varepsilon_{II}^{1/2} - \varepsilon_I^{1/2})$. In the acid-base reaction $HA + B \Leftrightarrow A^- + HB^+$ the factor in the square bracket becomes $2(z_M = z_N = l, z_A = z_B = 0)$, whereas for $A^{2-} + H^+ \Leftrightarrow HA^-$ this factor is $-4(z_M = l, z_A = -2, z_B = l)$.

The differences in the solvation of the reactants and the products constitutes in general the major difference between the driving force for the equilibrium reaction in solution and that in the gas phase. In analogy with Eq. (2.16), the molar Gibbs free energy of solvation for any species i that participates in the equilibrium in a given solvent S can be written as:

$$\Delta G_i^* = A_{V\delta} V_i \delta_S^2 + A_{s\pi} s_i \pi_S^* + A_{\beta\alpha} \beta_i \alpha_S + A_{\alpha\beta} \alpha_i \beta_S \qquad (2.21)$$

This expression does not take into account any solvent that is specifically associated with the solute species (see below). It is seen that according to Eq. (2.21) the difference in the Δ*G** values of the product and reactant species is the algebraic sum of products of universal coefficients *A* and the propensities of these species, i.e., V_i, s_i, β_i, and α_i, and the corresponding abilities of the solvent, i.e. δ_S^2, π_S^*, α_S, and β_S to undergo the specified interactions. The molar volume V_i should strictly be taken as the partial molar volume which is normally unknown or the intrinsic volume of the solute species, rather than its molar volume when pure, or as a hypothetical supercooled liquid when the neat solute is a solid at the working temperature. This requirement can seldom be fulfilled and the molar volume of the neat solute is often used as an approximation.

Not shown explicitly in Eq. (2.21) are the number Δn_S of solvent molecules released or consumed in the equilibrium, and in the general case, this can only be roughly estimated, if at all. In some cases many of the solvating molecules are released, as when an uncharged contact ion pair is formed from a cation and an anion of equal formal charge. The dipolar ion pair is assumed to be much less solvated than its separate ionic partners. On the contrary, acid dissociation generally causes solvent molecules to be sequestered, since the resulting hydrogen ion and anion are considerably more solvated than the parent undissociated acid. The solvent effect due to this change of the numbers of solvent molecules involved in the reaction, Δn_S, is in many cases considerable. It should be taken into account beyond what is estimated from the application of Eq. (2.21) to the second term on the right hand side of Eq. (2.20). A term describing this effect is $\Delta n_S \Delta G^*_{\mathrm{cond}}$, where $\Delta G^*_{\mathrm{cond}}$ is the molar Gibbs free energy of condensation of the solvent (see above, Table 2.1). The solvent effects on the entropy and enthalpy of the equilibrium in solution due to this cause can be estimated from the entries in Table 2.1, but there are no values for the corresponding effects incorporated into Eq. (2.21).

Even for a simple reaction, involving just one reactant species and one product species, such as a keto-enol tautomerism or a cis-trans isomerization, Eq. (2.21) for a given solvent is complicated enough, not to speak of a comparison between several solvents. Still, in specific cases it is possible to unravel the solvent effects of cavity formation, if the solute species have different volumes, polarity/polarizability if the solute species differ in their dipole moments or polarizabilities, and solvent Lewis acidity and basicity if the solutes differ in their electron pair and hydrogen bond acceptance abilities. Thus, the enol form has a greater ability than the keto form to accept an electron pair from the solvent to form a hydrogen bond with it, but the keto form may have a larger dipole moment to interact with a polarizable solvent.

For example, according to Reichardt and references quoted by him (Reichardt 1988), the enol form of ethyl acetoacetate, $CH_3C(OH)=CHCOOC_2H_5$, constitutes 65% of it in cyclohexane, 28% in toluene, 11.5% in acetone, and 5% in dimethylsulfoxide, due to competition between intra- and inter-molecular hydrogen bonding of the enol form. When such a competition is precluded, as in 5,5-dimethyl-l,3-cyclohexanedione, the opposite trend is observed: there is 7% enol in toluene, 81% in acetone and 99% in dimethylsulfoxide (Reichardt 1988). In this case, the solvent with a higher electron pair donicity favours the hydrogenbonding enol form.

The *cis/trans* conformational change of the rotamers of chloroacetaldehyde, $ClCH_2C(H)=O$, is another case in point: the *cis*-form has a higher dipole moment and is stabilized by the more polar solvents. Its mole fraction is 45% in cyclohexane, 61% in dichloromethane, 72% in acetone and 84% in dimethyl-sulfoxide (Reichardt 1988).

Other cases where the solvent effects have been unravelled to a certain extent are complex formation equilibria between a metal cation and an anionic ligand. For a given cation, the less strongly an anionic ligand is solvated in a series of solvents, the more readily the complex between them is formed. This is a case of competition of the metal cation, a Lewis acid, and the solvent which may also be a Lewis acid, for the electron-pair donation from the anionic ligand, a Lewis base. Protic solvents solvate anions strongly, but aprotic dipolar solvents permit good complexation while allowing also for reasonable solubilities of the reacting species. On the other hand, for a given anionic ligand, the competition between, say, a hydrogen ion and a metal ion is driven one way or another by the difference in solvation of these positive ions, and this is governed by the electron-pair donation abilities of the solvents.

In order to avoid the contribution to the solvent effect of the changes of the charges on complexation, the third term on the right hand side of Eq. (2.20), as discussed above, the formation of the triiodide anion from iodine and iodide anions can be examined. The large, highly polarizable I_3^- ion is better solvated by highly dipolar aprotic solvents but the smaller I^- anion, a better hydrogen bond acceptor, is better solvated by protic solvents. Thus the logarithms of the formation constants of triiodide increase from 2.85 in water, through 3.7 in formamide and 4.30 in methanol, to 6.6 in nitrobenzene and 7.0 in N,N-dimethylformamide (Alexander 1967).

An example of complexation where the charges are changed between reactants and products is the formation of $ZnBr^+$ from Zn^{2+} and Br^- in various solvents. The logarithms of the formation constant of the complex given (Ahrland 1990) are -0.57 in water, 0.85 in dimethylsulfoxide, 3.82 in pyridine, and 5.67 in acetonitrile. Since the zinc cation is strongly solvated in all these solvents, but to different degrees, the changes in log K cannot be ascribed to the solvation, or lack of it, of the bromide anion alone. The standard molar Gibbs free energies of transfer, $\Delta_{tr}G^o$, of ions between solvents have been compiled critically by (Marcus 1996, 1997). For zinc ions transferring from water to the other solvents the $\Delta_{tr}G^o$ are -45, -2, and 69 kJ mol^{-1}. These are compensated partly by the corresponding values for the singly charged complex $ZnBr^+$, that are not directly known and those of bromide ions are 27, 21, and 31 kJ mol^{-1}, respectively. In this case, the effect of the aprotic solvents versus water can be ascribed to the strong hydration of the bromide anion, but the order among the non-aqueous solvents is due to preferences in the solvation of the zinc and bromozinc cations.

Not only is the extent of the equilibrium reaction, i.e., the ratio of the concentrations of the products to those of the reactants, governed by the initial composition and the equilibrium constant, affected by the solvent, so also is the temperature dependence, i.e., the enthalpy and entropy of the reaction, as should be expected. The standard molar enthalpy is best obtained calorimetrically and the entropy by means of the temperature derivative of the equilibrium constant. As an example of organic reactions, the tautomeric conversion of di(2-quinolyl)-methane to the N-H . . . N hydrogen-bonded species has a reaction enthalpy, $\Delta_r H^o$ /kJ mol^{-1}, that changes from +9.6 for ethanol, through 8.4 for chloroform, -0.4 for benzene, -3.3 for N,N-dimethylformamide to -10.0 in carbon disulfide, (Reichardt 1988). There is again a complicated compensatory interplay in the solvation of the two species between polarity and hydrogen bonding abilities of the solvents. The negative entropies of this reaction, that become more negative along the same sequence, are due more to the solute properties than the solvent ones.

For the complex formation of copper(I) with chloride to form CuCl in solution, the values of $\Delta_r H^o$ /kJ mol^{-1} (Ahrland, 1990) are -6.4 for dimethylsulfoxide, 4.6 for tetrahydrothiophene, 13.0 for pyridine, and 16.8 for acetonitrile. The positive values are explained by the necessity to displace the strongly solvating solvents from the Cu^+ cation, whereas the chloride anion is not solvated appreciably in any of these solvents. The values of the standard molar transfer enthalpies, $\Delta_{tr}H^o$ /kJ mol^{-1}, from water into these solvents for Cu^+ are -42, -91, -127, and -72, and those of Cl^- are 20.0, 25.4, 28, and 19.3, respectively (Marcus 1996, 1997). The unobservable $\Delta_r H^o$ in water, the solvation of the uncharged CuCl in the solution, and electrostatic effects make up the differences between the observed reaction enthalpies, $\Delta_r H^o$ and the sums of the transfer enthalpies $\Delta_{tr}H^o(Cu^+) + \Delta_{tr}H^o(Cl^-)$. Thus, although trends can be explained ad hoc, exact relationships cannot be safely predicted, due to the lack of the additional information.

5—

Solvent Effects of Reaction Rates

The rate constant for a chemical reaction in solution, *k*, is generally expressed in terms of the transition state theory as:

$$k = A_k \exp(-\Delta G^{\neq}/RT) \qquad (2.22)$$

Here the pre-exponential factor A_k is the product of a temperature-dependent constant $(k_B T/h) = 2 \times 10^{10} T\ s^{-1}$, where k_B, and *h* are the Boltzmann and Planck constants, and a solvent-specific coefficient, that relates to both the solvent viscosity η (Table 3.9) and to its orientational relaxation rate τ (Table 3.10). This coefficient may be near unity for very mobile solvent molecules but may be considerably less than unity for viscous or orientationally hindered highly structured solvents see Table 4.1. The exponential factor involves the activation Gibbs energy, $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} = \Delta A^{\neq} + P\Delta V^{\neq}$, that describes the height of the barrier to the formation of the activated complex from the reactants, see Figure 2.3. It also describes temperature and pressure dependencies of the reaction rate, through the $T\Delta S^{\neq}$ and $P\Delta V^{\neq}$ terms. It is assumed that the activated complex is in equilibrium with the reactants, but that its change to form the products is rapid and independent of its environment in the solution.

The barrier that the reaction must overcome in order to proceed is determined by the difference in the solvation of the activated complex and the reactants. The activated complex itself is generally considered to be a transitory moiety, which cannot be isolated for its solvation properties to be studied, but in rare cases it is a reactive intermediate of a finite lifetime. The solvation properties of the activated complex must generally be inferred from its postulated chemical composition and conformation, whereas those of the reactants can be studied independently of the reaction. This is the reason why very little predictive information can be obtained, even though the explanatory power of the transition state theory is very considerable. For organic nucleophilic substitution reactions,

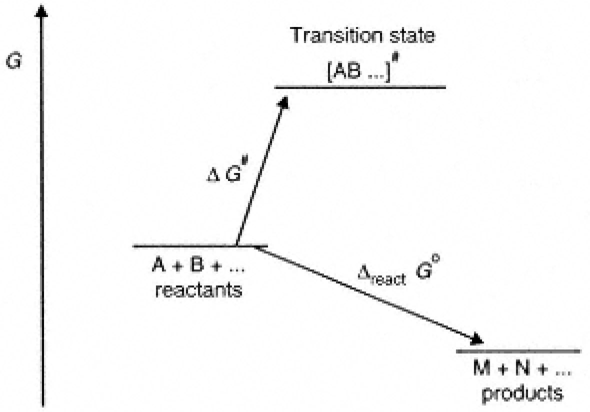


Figure 2.3
Schematic representation of the Gibbs free energies for activation and reaction of reactants A + B+ . . . to form products M + N+ . . . via the transition state [A, B, . . .]$^{\neq}$.

the Hughes–Ingold rules permit to make *qualitative* predictions on the behaviour of the rate when the polarity increases in a series of solvents, as is shown in Table 2.4 (Reichardt 1988).

The general rule is that if net charge is created, or destroyed, in the activated complex relative to the reactants, then there is a large positive, or negative, effect of increasing solvent polarity on the rate, but if the net amount of charge is kept unchanged while it becomes more disperse the effects are relatively small. If no change in the charge distribution takes place upon the formation of the activated complex the change of solvent polarity has but a very small effect.

The rate of solvolysis or de-hydrochlorination of *t*-butyl chloride (2-chloro-2-methylpropane) has been studied very extensively under standardized conditions, and the rate constant has been used as a characterization of solvent polarity. The reaction proceeds according to the scheme:

$$(CH_3)_3C{-}Cl \Leftrightarrow [(CH_3)_3C^{\delta+} \ldots Cl^{\delta-}]^{\neq} \rightarrow (CH_3)_3C^{+} + Cl^{-} \rightarrow \text{products} \qquad (2.23)$$

Table 2.4 Effects of increased solvent polarity on nucleophilic substitutions (Reichardt 1988)

Reactants	Activated complex	Reaction type	Solvent effect on rate
R-X	$R^{\delta+} \ldots X^{\delta-}$	S_N1	large increase
R-X^{+}	$R^{\delta+} \ldots X^{\delta+}$	S_N1	small decrease
Y + R-X	$Y^{\delta+} \ldots R \ldots X^{\delta-}$	S_N2	large increase
Y^{-} +R-X	$Y^{\delta-} \ldots R \ldots X^{\delta-}$	S_N2	small decrease
Y + R-X^{+}	$Y^{\delta+} \ldots R \ldots X^{\delta-}$	S_N2	small decrease
Y^{-} + R-X^{+}	$Y^{\delta-} \ldots R \ldots X^{\delta+}$	S_N2	large decrease

The quantity $Y = \log k - \log k_0$ characterizes the 'ionizing power' of the solvent (Grunwald and Winstein 1948). Here k_0 is the rate constant at 25°C in the reference solvent, 80% v/v ethanol + 20% v/v water, and k is the rate constant in any other solvent studied. Representative values of Y are shown in Table 2.5 (Reichardt 1998; Grunwald and Winstein 1948; Abraham 1972, 1985; and Parker 1978).

The Gibbs energy of activation, $\Delta G^{\neq}$, is (negatively) linearly related to the solvent polarity/polarizability parameter π^* and to its hydrogen bond donation ability α (see Chapter 4), due to the large dipole moment of the activated complex, 8.8 D and the facility of the chlorine atom with its partial negative charge to accept a hydrogen bond (Abraham 1985).

It is tacitly assumed in the Hughes–Ingold rules that the entropy of activation is small relative to the enthalpy of activation, i.e., $\Delta G^{\neq} \approx \Delta H^{\neq}$, and that the temperature effect on the rate follows Eq. (2.22) with an assumed temperature independent value of $\Delta H^{\neq}$. If the number of solvent molecules solvating the activated complex is very different from that solvating the reactants, then this assumption is no longer valid. This is the case in the solvolysis of *t*-butyl chloride in water ($\Delta H^{\neq} = 97$ kJ mol^{-1}, $T\Delta S^{\neq} = 15$ kJ mol^{-1}) compared to, say, ethanol ($\Delta H^{\neq} = 109$ kJ mol^{-1}, $T\Delta S^{\neq} = -4$ kJ mol^{-1}).

When there is no change in the charge distribution in the reaction, as in free radical or isopolar reactions, the Hughes–Ingold rules are inoperative. The solvent polarity may play a minor role only, compared with other effects, such as differences in the volume requirements for cavity formation in highly structured solvents or of the hydrogen bonding abilities of the reactants and the activated

Table 2.5 Solvent polarity parameters Y from rates of solyvolysis of $(CH_3)_3CCL$ (Reichardt 1988)

Solvent	*Y*	Solvent	*Y*
water	3.49	ethyl acetate	-7.70[a]
methanol	-1.09	chlorobenzene	-6.31[b]
ethanol	-2.03	acetonitrile	-3.70[b]
1-propanol	-2.27[a]	nitromethane	-3.09[b]
2-propanol	-2.73	nitrobenzene	-4.69[b]
1-butanol	-2.23[b]	formamide	0.60
2-methyl-2-propanol	-3.26	N,N-dimethylformamide	-3.45[b]
2,2,2-triflouroethanol	1.05	N,N-dimethylacetamide	-3.61[c]
diethyl ether	-7.70[a]	N-methylpyrrolidinone	-3.94[b]
dioxane	-5.57[b]	dimethylsulfoxide	-2.88[a]
acetone	-4.87[b]	benzene	-7.13[b]
formic acid	2.05	pentane	-10.97[b]
acetic acid	-1.68	heptane	-11.06[c]
trifluoroacetic acid	1.91[c]		

[a]Calculated from $Y = [-\delta\Delta G^{\neq} - 4.75]/1.36$, from $\delta\Delta G^{\neq}$/kcal mol^{-1} data relative to N,N-dimethylformadide, (Abraham 1985). [b]Calculated from $Y = 5.03 - \log k$ from log (k/s^{-1} data Abraham (1972). [c]Calculated from $Y = [-\delta\Delta G{\neq}/5.705] - 3.70$, from $\delta\Delta G{\neq}$/kJ mol^{-1} data in Parker (1978).

complex. The former effect, of the 'tightness' of a solvent (see Chapter 4), can be described in terms of its cohesive energy density, $\Delta_V U/V$, which is related to its internal pressure, $P_i = (\partial U/\partial V)_T$, which should be similar to the effect of external pressure (see Chapters 3 and 4). This effect can be described in terms of the activation volume $\Delta V^{\neq}$:

$$(\partial \ln k/\partial P)_T = \Delta V^{\neq}/RT - (n-1)\kappa_T \qquad (2.24)$$

where n is the order of the reaction i.e., the number of reactant molecules making up the activated complex, and κ_T is the compressibility of the solvent (Table 3.1). The activation volume is positive for a unimolecular reaction when bond stretching or cleavage takes place between the reactants and the activation complex and it is negative when bond formation takes place in an associative bimolecular reaction. In a reaction that involves ions and charge neutralization there is an additional effect of volume increase due to the removal of electrostriction caused by the ions. This effect is proportional to $\varepsilon^{-2}(\partial\varepsilon/\partial P)_T$ of the solvent, itself correlated with its compressibility, κ_T, Eq. (3.26).

6—
Solvent Effects on Spectroscopy

The solvent effects on spectroscopic properties i.e., electronic excitation, leading to absorption spectra in the ultraviolet and/or visible range, of solutes in solution are due to differences in the solvation of the ground and the excited states of the solute. Such differences take place when there is an appreciable difference in the charge distribution in the two states, often accompanied by a profound change in the dipole moments. The excited state, in distinction with the transition state discussed above, is not in equilibrium with the surrounding solvent, since the time scale for electronic excitation is too short for the re-adjustment of the positions of the atoms of the solute (the Franck–Condon principle) or of the orientation and position of the solvent shell around it. The consideration of the solvation of the excited state as if it were an equilibrium state of the system is therefore an approximation, which, however, is commonly implicitly made.

The solvent effect is termed solvatochromism and is described in terms of the shifting of the peak position of the lowest energy, longest wavelength, spectral absorption peak. This can be *hypsochromic* (blue shift, negative solvatochromism), when the shift is to lower wavelengths, i.e., to higher energies. The solvent effect is *bathochromic* (red shift, positive solvatochromism) when the shift is to longer wavelengths, i.e., to lower energies. The former effect takes place when the ground state is more dipolar than the excited state, whereas the opposite occurs when the excited state is the more dipolar one. These shifts pertain to the *energy gap* between the ground and excited states, and therefore do not tell directly which of these states (or of both, to different extents) has its potential energy lowered by the better solvation, see Figure 2.4.

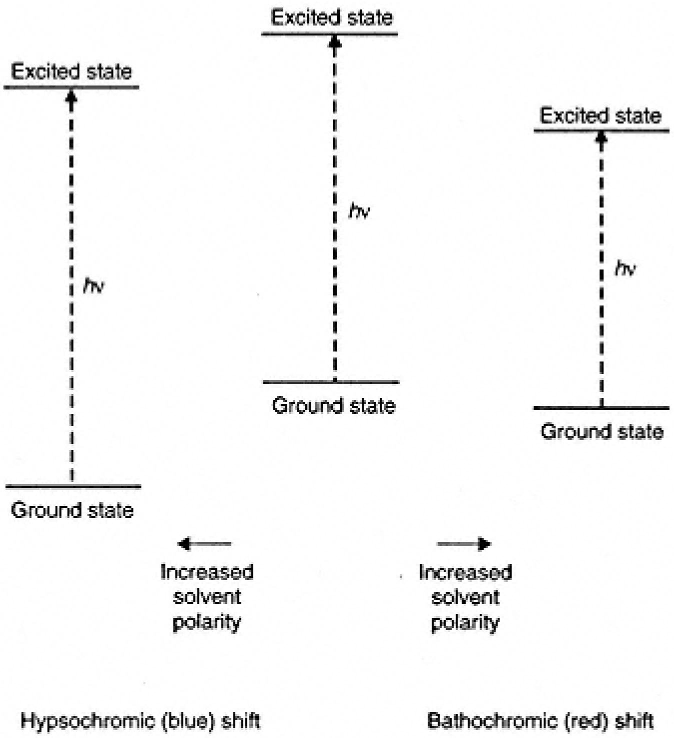


Figure 2.4
The effects of increased solvent polarity on the light absorption energy from the ground to the (Franck–Condon) excited state can be hypsochromic, if the ground state is more stabilized than the excited state or bathochromic if the opposite relative stabilization takes place.

The spectral bands in question are generally due to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and charge transfer electronic transitions. These can arise in molecules with, e.g., an electron-donor group at one end and an acceptor group at the other end of a chain of conjugated double bonds, symbolized as: $\mathrm{D\text{-}[C{=}C\text{-}]}_n\mathrm{A} \Leftrightarrow \mathrm{D}^{\delta+}\text{ - }\mathrm{[C{=}C\text{-}]}_n\mathrm{A}^{\delta-}$. Another possibility is the charge transfer between an ion pair, such as 1-ethyl-4-cyanopyridinium iodide and its excited state, where a part of the charge is transferred from the iodine atom to the pyridine ring. Changes in the spectra of metal complexes due to solvent effects are generally related to changes in the geometry and certain distances of the ligands relative to the central metal atom in the complexes, which are accompanied by electronic transitions between orbitals localized on the metal atom.

When a nonpolar solute is in solution in any solvent, either nonpolar or polar, then mainly dispersive forces operate between them, and any solvent effects are very small and bathochromic (Reichardt 1988), increasing with the polarizability of the solvent. If the solute is dipolar in a nonpolar solvent, then both hypso and bathochromic shifts, increasing with solvent polarizability, are possible, depending on the dipole moments of the ground and excited states. The situation becomes more complicated for a dipolar solute in a dipolar solvent, since then the solvent molecules are properly oriented around the solute in both the ground and excited states (the non-equilibrium of the latter system has been previously mentioned) so that both solvent polarizability and polarity as well as induced polarization of the solute by the solvent play a role. The direction of the spectral shift is again dependent on the relative polarity of the ground and excited states. However, the ground state is no longer that of the isolated solute molecule because of the extensive solvation by dipole–dipole interactions, and the effective dipole moment of the ground state must account also for its induced polarization by the solvent.

The solvatochromic effects on UV/visible spectra of certain solutes are so large, that they can conveniently be employed as probes for certain solvating properties of the solvents. Those that have enjoyed widespread application in this capacity are discussed in Chapter 4. They include 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino)-phenoxide, 4-methoxynitrobenzene, 4-(dimethylamino)-nitrobenzene, for the estimation of the polarity of solvents, acetylacetonato-N,N,N′,N′-tetramethylethylenediamino-copper(II) perchlorate, 4-nitrophenol, and 4-nitroaniline, for the estimation of the electron pair donicity of solvents, 4-carboxymethyl-1-ethylpyridinium iodide, 4-cyano-1-ethylpyridinium iodide, and bis-*cis*-1, 10-phenanthrolinodicyano-iron(II) for the estimation of the hydrogen bond donation abilities of solvents (Marcus 1993).

In the case of fluorescence spectra, it is the emission of the radiation from the excited state that is measured, rather than its absorption. In those cases where the lifetime of the excited state is long relative to the relaxation process, the fluorescence takes place after the atoms of the solute and the solvent molecules have relaxed, so that the solute is now in equilibrium with its surroundings. However, the emission then takes place not to the equilibrium ground state but to a Franck–Condon state, which must itself relax to the ordinary ground state. The differences in solvation of the initial and final states of the light emission then dictate the direction and magnitude of the solvent effect on the fluorescence spectrum. For an example of the fluorescence spectrum of N-ethyl-3-acetylcarbazole in alcohols see (Johnson and Limburg 1984). The emission peak varies from 411 nm for 2-methyl-2-propanol, via 423 nm for 2-propanol, 443 nm for ethanol, 468 nm for methanol, to 493 nm for 2,2,2-trifluoroethanol, in the same direction as the abilities of the alcohols to donate hydrogen bonds (the α parameter in Table 4.3). The fluorescence lifetimes also vary in this series of solvents, between ca. 1.5 ns to ca. 8 ns, but they show a maximum when plotted against α. The system is complicated by there being two solvation steps in the formation of the solvated excited state of the solute.

There are also profound solvent effects on the vibrational, i.e., IR and Raman spectra, of many solutes. A large number of bond vibrations have been studied in this respect, those for stretching of carbonyl (C=O) and hydroxyl, rather, O-D, bonds, perhaps, more extensively than others, involving bond stretching and the bending, rocking, etc. of groups of atoms of solutes in various solvents. Many of the vibrational wavenumbers have also been determined for the isolated solutes in the gaseous state, so that solvent shifts can be reported on an absolute scale. Whereas the stretching vibration v(C=O) of acetone is at 1738 cm^{-1} in the vapour phase, the following solvent shifts, among others, have been noted (Reichardt 1988): *n*-hexane 16.5, tetrachloromethane 20, acetone 23, dimethylsulfoxide 29, aniline 35, and water 40.5 cm^{-1}. For the O-D bond in CH_3OD the corresponding values are 2720 for the vapour, and shifts of 24, 31, 123, 192, and 209 cm^{-1} for the above solvents, respectively. Obviously, there is no value for water, because of the rapid isotope exchange. Both non-specific and specific solvent effects are noted. The former arise from dipole–dipole and dipole–induced dipole interactions on the bond in question, the latter arise from donor–acceptor adduct formation and hydrogen bonding. In the case of acetone, it is the hydrogen bond donating solvents aniline and water that show the largest shifts, and in the case of deuteromethanol the more basic, in the Lewis basicity sense, solvents that do so.

Those solutes for which the solvent shifts are particularly large have been used in the specification of solvent properties, such as electron-pair donation ability, Lewis basicity, or softness. For the former property, the solvent shifts of deuteromethanol or of phenol have served as suitable scales. For the latter property the solvent shifts of the symmetrical stretch of Hg-Br in the Raman spectrum of $HgBr_2$ and of I-CN in the infrared spectrum of ICN have been so employed (see Chapter 4).

Solvent effects on nuclear magnetic resonance (NMR) spectra have been studied extensively, and they are described mainly in terms of the observed chemical shifts, δ, corrected for the solvent bulk magnetic susceptibility (Table 3.5). The shifts depend on the nucleus studied and the compound of which it is a constituent, and some nuclei/compounds show particularly large shifts. These can then be employed as probes for certain properties of the solvents. Examples are the chemical shifts of ^{31}P in triethylphosphine oxide, the ^{13}C shifts in the 2-or 3-positions, relative to the 4-position in pyridine N-oxide, and the ^{13}C shifts in N-dimethyl or N-diethyl-benzamide, for the carbonyl carbon relative to those in positions 2 (or 6), 3 (or 5) and 4 in the aromatic ring (Chapter 4) (Marcus 1993). These shifts are particularly sensitive to the hydrogen bond donation abilities α (Lewis acidity) of the solvents. In all cases there is, again, a trade off between non-specific dipole–dipole and dipole–induced dipole effects and those ascribable to specific electron pair donation of the solvent to the solute or vice versa to form solvates.

These solvent effects change the electron shielding around the nucleus in question, hence its response to the applied magnetic and electrical fields. The shifts can be both downfield, expressed as a positive shift (in ppm), as well as upfield, expressed as a negative shift, increasing with solvent polarity, basicity, or acidity. For example, for acetone as a probe, a downfield shift takes place for $\Delta\delta(^{13}C{=}O)$ and an upfield shift is found for $\Delta\delta(C{=}^{17}O)$, relative to $\delta = 0$ in neat acetone. It should be noted that the time scale of the nuclear magnetic resonance phenomena is of the order of μs, so that faster reactions, such as proton isotope exchange between water and hydroxyl groups of alcohols, cause the averaging of the observed ^{1}H NMR signal between the weighted individual responses of the protons in the two species.

There are many more solvent effects on spectroscopic quantities, that cannot be even briefly discussed here, and more specialized works on solvent effects should be consulted, e.g, Reichardt's book (Reichardt 1998). These solvent effects include effects on the line shape and particularly line width of the nuclear magnetic resonance signals and their spin-spin coupling constants, solvent effects on electron spin resonance (ESR) spectra, on circular dichroism (CD) and optical rotatory dispersion (ORD), on vibrational line shapes in both the infrared and the UV/visible spectral ranges, among others.

7—

Solvent Effects in Electrochemistry

Solvent effects in electrochemistry are relevant to those solvents that permit at least some ionic dissociation of electrolytes, hence conductivities and electrode reactions. Certain electrolytes, such as tetraalkylammonium salts with large hydrophobic anions, can be dissolved in non-polar solvents, but they are hardly dissociated to ions in the solution. In solvents with relative permittivities (see Table 3.5) $\varepsilon < 10$ little ionic dissociation takes place and ions tend to pair to neutral species, whereas in solvents with $\varepsilon > 30$ little ion pairing occurs, and electrolytes, at least those with univalent cations and anions, are dissociated to a large or full extent. The Bjerrum theory of ion association, that considers the solvent surrounding an ion as a continuum characterized by its relative permittivity, can be invoked for this purpose. It considers ions to be paired and not contributing to conductivity and to effects of charges on thermodynamic properties even when separated by one or several solvent molecules, provided that the mutual electrostatic interaction energy is $< 2\,k_{B}T$. For ions with a diameter of a nm, the parameter b is of prime importance:

$$\log b = \log|z_{+}z_{-}| + 1.746 - \log\varepsilon - \log(a/\mathrm{nm}) \qquad (2.25)$$

and the degree of association, $1 - \alpha$, of the ions, α designates commonly the degree of dissociation of the electrolyte, is given by:

$$1 - \alpha = 4000\pi N_{\mathrm{Av}} c u^{3} Q(b) \qquad (2.26)$$

where c is the concentration of the electrolyte in mol dm^{-3}, $u = |z_{+}z_{-}|e^{2}/$

$\varepsilon_o \varepsilon k_B T$ and $Q(b)$ is the integral $\int_2^b t^{-4} \exp(t)\,\mathrm{d}t$, t being an auxiliary variable. The number of ions per unit volume (l dm^3) in such a solution, acting as charge carriers, is $N_A \alpha C$. One of the most important of the solvent effects in electrochemistry is, therefore, on the premise of the consideration of the solvent as a continuum, directly related via b and u to the magnitude of the relative permittivity ε (Marcus 1977).

Together with the relative permittivity, that is responsible for the number of charge carriers per unit volume of the solution as seen above, the solvent viscosity, η, (see Table 3.9) must also be mentioned among the bulk properties that are responsible for the differences of the conductivities of electrolyes in different solvents. The mobilities u_i^∞ of the ions of a given electrolyte at infinite dilution in an electrical field, when compared in a series of solvents, depend to a major degree on the viscosities of the solvents, other things remaining constant. The latter condition implies constant sizes of the ions, implying either that they are not solvated i.e., the very large tetraalkylammonium cations, or that the size of the solvated ion depends only slightly on the solvent. Under such conditions Walden's rule and Stokes' law hold, i.e., that:

$$u_i^\infty \eta = (|z_i|F)^{-1} \lambda_i^\infty \eta = (F/6\pi N_{Av})/r_i = constant \qquad (2.27)$$

where F is the Faraday constant, $|z_i|$ is the absolute charge number, λ_i^∞ is the limiting equivalent conductivity, and r_i, is the radius of the ion. The number 6 in the denominator of the third expression in Eq. (2.27) signifies that slipping of the moving ion in the solvent takes place, otherwise, if sticking occurs, this number is 4. Table 2.6 shows that for many solvents Walden's law is indeed fairly well obeyed for the large tetrabutylammonium cation, but much less so for the sodium cation, since the size of such a solvated ion depends on the different sizes of the solvents and their number in the solvation shell. Walden's and Stokes' rules can, therefore, be employed as a rough guide to the mobilities of ions in solvents, in which knowledge of the conductivities is required for the envisaged application.

A solvent, in addition to permitting the ionic charges to separate and the electrolyte solution to conduct an electrical current, also solvates the discrete ions, firstly by ion-dipole or ion-induced dipole interactions and secondly by more direct interactions, such as hydrogen bonding to anions or electron pair donation to cations. The latter interactions, thus, depend on the Lewis acidity and basicity, respectively, of the solvents (Table 4.3). The redox properties of the ions at an electrode therefore depend on their being solvated, and the solvent effects on electrode potentials or polarographic half wave potentials, or similar quantities in voltammetry are manifested through the different solvation abilities of the solvents.

The relevant quantities are the transfer activity coefficients, ${}_{w}\gamma^{os}$, related to the standard molar transfer Gibbs free energies by:

$$\Delta_{tr} G^o(X^\pm, W \rightarrow S) = RT \ln {}_{w}\gamma^{o}{}_{s} \qquad (2.28)$$

Table 2.6 The limiting equivalent conductivities, λ^{∞}, and the Walden products, $\lambda^{\infty}\eta$, of tetrabutylammonium and sodium ions in various solvents at 25°C (Kratochvil and Yeager 1972, Marcus 1997)

Solvent	$\lambda^{\infty}(Bu_4N^+)$	$\lambda^{\infty}\eta$	$\lambda^{\infty}(Na^+)$	$\lambda^{\infty}\eta$
water	19.5	17.4	50.1	44.7
heavy water (D_2O)	15.6	17.2	41.6	45.9
methanol	39.1	21.5	45.23	24.9
ethanol	19.4	21.0	20.31	22.0
1-propanol	11.0	21.4	10.17	19.8
2,2,2-trifluoroethanol	12.1	21.2		
acetone	66.4	20.1	70.2	21.3
ethylene carbonate (40°C)	10	19.3	13	25.1
propylene carbonate	9.44	23.9	9.13	23.5
4-butyrolactone	13.6	23.1	14.43	24.5
dichloroethane	38	15.6		
1,2-dichloroethane	27.1	21.1		
pyridine	22.7	20.1	26.6	23.6
acetonitrile	61.7	21.0	76.8	26.1
nitromethane	34.9	20.9	56.8	34.0
nitrobenzene	11.8	21.1	16.6	29.7
formamide	6.54	21.6	9.88	32.6
N,N-dimethylformamide	26.9	21.6	30.0	24.1
N,N-dimethylthioformamide	16.6	32.9		
N-methylacetamide (40°C)	7.8	28.6	8.2	30.1
N,N-dimethylacetamide	23.0	21.3	25.69	23.8
dimethylsulfoxide	10.9	21.8	13.94	27.9
sulfolane (40 (C)	2.80	22.5	3.61	29.0
hexamethylphosphoric triamide	6.15	19.1	6.15	19.1

Units: λ^{∞}, in $cm^2\ S\ mol^{-1}$; $\lambda^{\infty}\eta$, in $cm^2\ S\ mol^{-1}\ Pa\ s$.

for a given ion $X^{\pm}$, cation or anion, transferring at infinite dilution from a reference solvent W commonly, water, but also methanol, acetonitrile or others, to the target solvent S. Note that in Eq. (2.28) as written, both $\Delta_{tr}G^{o}$and ${}_{w}\gamma^{os}$ pertain to the molal mol kg^{-1} scale. Since $\Delta_{tr}G^{o}$ is generally quoted in tables (Marcus 1997) on the molar (mol dm^{-3}) scale, the appropriate symbol on the right hand side is ${}_{w}\gamma^{os}$, while some authors use the mole fraction scale for $\Delta_{tr}G^{o}$, so that conversions among the scales is required. The standard electrode potential E^{o} involving $X^{\pm}$ in solvent S will differ from that in the reference solvent W by $\Delta E^{o} = \Delta_{tr}G^{o}(X^{\pm}, W \rightarrow S)/nF$, where n is the number of electrons involved in the electrode reaction.

The thermodynamic functions of transfer of individual ions cannot, of course, be studied experimentally, since only complete electrolytes are thermodynamic components, so that an extrathermodynamic assumption is needed in order to split the measurable quantity into the contributions from the individual ions. A commonly employed assumption is that for a reference electrolyte with large, univalent, nearly spherical cation and anion of nearly equal sizes the measured quantity can be split evenly between the cation and anion. A widely used reference electrolyte is tetraphenylarsonium tetraphenylborate, the ions of which are supposed to be equally (and only to a minor extend) solvated in all solvents.

On the basis of this extrathermodynamic assumption such thermodynamic quantities of transfer as $\Delta_{tr}G^o$ ($X^\pm$, W → S), and the derived functions $\Delta_{tr}H^o(X^\pm, W \rightarrow S)$ and $\Delta_{tr}S^o(X^\pm, W \rightarrow S)$ have been evaluated for a large number of ions in a large number of solvents with various chemical functional groups (Marcus 1997). On this basis, the standard electrode potentials and their temperature derivatives in many solvents have been reported (Marcus 1985). The standard molar Gibbs free energy and enthalpy of transfer have been related to properties of the solvents, for given classes of ions, in a way that permitted the successful prediction of such values. The solvent properties involved include the cohesive energy density (Table 3.1), the polarizability or molar refractivity (Table 3.5), and the electron pair and hydrogen bond donation ability (Table 4.2). It is surprising, perhaps, that the relative permittivity and the dipole moment of the solvents do not appear to play any role in this respect, but this behavior has been rationalized (Marcus, Kamlet and Taft 1988; Marcus 1998).

At finite concentrations the effect of the solvent on the ion–ion interactions are superimposed on the solvent effect discussed above for infinite dilution. The former effect can be expressed as the mean ionic activity coefficient, $\gamma_\pm$ again, expressed conventionally on the molal scale, relative to infinite dilution in the solvent in question, which in dilute solutions, where the extended Debye–Hückel expression is deemed to hold, is:

$$\ln \gamma_\pm = A(\varepsilon) I^{1/2} / [1 + B(\varepsilon) I^{1/2}] \qquad (2.29)$$

where $I = \sum c_i z_i^2$ is the ionic strength, the summation extends over all ionic species in the solution, of concentration c_i, and charge z_i. The coefficients $A(\varepsilon)$ and $B(\varepsilon)$ are quantities that depend on the relative permittivity and temperature. The coefficient $B(\varepsilon)$ depends also on the mean distance of approach of the ions in the solution, which may depend on the solvent, if the ions are well solvated, hence separated by solvent shells. In not so dilute solutions there are additional solvent effects. Ion pairing, already discussed briefly above, sets in, and at higher concentrations in solutions with bulky solvents a lack of sufficient solvent molecules to solvate the ions to the extent that they are solvated at infinite dilution may take place. In such a case neighboring ions will share solvent molecules.

References

Abraham, M. H. (1972) *J. Chem. Soc*. Perkin Trans. **2** 1343.

Abraham, M. H. (1985) *Pure Appl. Chem*. **57**, 1055.

Ahrland, S. (1990) *Rev. Inorg. Chem*. **11**, 195.

Alexander, R., Ko, E. C. F., Mac, Y. C. and Parker, A. J. (1967) *J. Am. Chem Soc*. **89**, 3707.

Ben-Naim, A. and Marcus, Y. (1984) *J. Chem. Phys*. **81**, 2016.

Bondi, A (1964) *J. Phys. Chem* **68**, 441.

Grunwald, E. and Winstein, S. (1948) *J. Am. Chem. Soc*. **70**, 2700.

Hildebrand, J. H. and Scott, R. L. (1950) *The Solubility of Nonelectrolytes*, Reinhold, New York, 3rd ed.

Johnson, G. E. and Limburg, W. W. (1984) *J. Phys. Chem.* **88**, 2211.

Kratochvil, B. and Yeager, H. L. (1972) *Topics in Current Chemistry* **27**, 1; also Marcus (1997), Chapter 18.

Marcus, Y. (1977), *Introduction to Liquid State Chemistry*, Wiley, Chichester, p. 243, 244.

Marcus, Y. (1985) *Pure Appl. Chem*. **57**, 1103.

Marcus, Y. (1993) *Chem. Soc. Rev*. **22**, 409.

Marcus, Y. (1996) in Volkov, A. G. and Deamer, D. W. eds., *Liquid-Liquid Interfaces*, CRC Press, Boca Raton, p. 39; (1997) *Ion Properties*, Dekker, New York.

Marcus, Y. (1997) *Ion Properties*, Dekker, New York.

Marcus, Y., Kamlet, M. J. and Taft, R. W. (1988) *J. Phys. Chem*. **92**, 3613; Marcus, Y. (1998) *Electrochim. Acta*, in the press.

Parker, A. J., Mayer, U. and Gutmann, V. (1978) *J. Org. Chem*. **43**, 1843.

Reichardt, Ch. (1988) *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, 2nd ed., pp. 92, 100, 110, 139, 295, 315, 352.

Shinoda, K. (1978) *Principles of Solution and Solubility*, Dekker, New York.

Yalkowsky, S. H. and Banerjee, S. (1988) *Aqueous Solubility*, Dekker, New York.

Chapter 3—
Physical Properties of Solvents

The proper choice of a solvent for a particular application depends on several factors, among which its physical properties are of prime importance. The solvent should first of all be liquid under the temperature and pressure conditions at which it is employed. Its thermodynamic properties, such as the density and vapour pressure, and their temperature and pressure coefficients, as well as the heat capacity and surface tension, and transport properties, such as viscosity, diffusion coefficient, and thermal conductivity also need to be considered. Electrical, optical and magnetic properties, such as the dipole moment, dielectric constant, refractive index, magnetic susceptibility, and electrical conductance are relevant too. Furthermore, molecular characteristics, such as the size, surface area and volume, as well as orientational relaxation times have appreciable bearing on the applicability of a solvent or on the interpretation of solvent effects. These properties are discussed and presented in this Chapter.

For the majority of the solvents considered in the List many of these properties have been listed and annotated in the compilations (Riddick, Bunger and Sakano 1986; DIPPR 1997). Further sources of such data are provided (Lide 1994; Landolt–Börnstein 1959). In addition to these more general sources, data have been obtained from a large number of other sources, as noted by lower case letters in square brackets in the Tables included in this Chapter.

Temperature-dependent data have been selected for 25°C as far as available in these sources, unless the solvent is not liquid at this temperature. Such solvents, from among the List, are *t*-butanol (No. 310), *c*-hexanol (No. 360), *n*-dodecanol (No. 390), 1,4-butanediol (No. 540), phenol (No. 590), 2-methylphenol (No. 600), 4-methyl- phenol (No. 620), 2-methoxyphenol (No. 630), 3-chlorophenol (No. 650), phenyl-acetone (No. 1060), *p*-methylacetophenone (No. 1070), benzophenone (No. 1090), ethylene carbonate (No. 1350), diethanolamine (No. 1940), 2-cyanopyridine (No. 2040), N-methylacetamide (No. 2240), di-*n*-butylsulfoxide (No. 2410), sulfolane (No. 2420) hexamethyl thiophosphoramide (No. 2520), hydrogen fluoride (No. 2540), ammonia (No. 2560), and sulfur dioxide (No. 2580). Several of these have melting points sufficiently close to 25°C, so that they are readily used in the slightly supercooled state, and values for this temperature can be assigned. In all cases, temperatures other than 25°C have been designated by letter codes in the reference columns as follows: a ≤ 20°C, b 30°C, c 35°C, d 40°C, e 45°C, f ≥ 50°C, and Tb for the normal boiling point. Temperatures (in °C) that are not multiples of 5 have been denoted by the letter code closest to the one for such temperatures. Other codes in these columns are: j for values obtained from principles, from entries in other Tables in this book, or from homology, k for data pertaining to the gaseous phase, and m for values estimated from a correlation expression with other properties.

1—
The Liquid Range of Solvents

Under ambient conditions solvents are liquid between their freezing point and their normal boiling point. When equilibrium conditions are established, the freezing point of the liquid solvent is the same as the melting point of the solidified solvent, T_m. If the gaseous phase in equilibrium with the melting or freezing solvent consists entirely of the vapour of this solvent, then the three phases, vapour, liquid, and solid, of this single component co-exist at the triple point, T_t, that is generally very close to T_m, for water the respective temperatures are $T_t = 273.16$ K and $T_m = 273.15 \text{ K} \equiv 0°\text{C}$. The value of the melting point can be determined with an accuracy of 0.01 K, provided that the solvent is very pure, since impurities decrease the melting point, and that supercooling can be prevented. An impurity of molar mass of 50 g mol^{-1} at a level of 0.01% wt causes a depression of the freezing point of < 0.01 K for solvents such as water or diethyl ether, but one of 0.02–0.03 K for solvents such as hexamethyl phosphoramide, 1,2-dibromoethane, and bromoform, of 0.06 K for tetrachloromethane, and of 0.13 K for sulfolane (tetramethylene sulfone). For most purposes values given to 0.1 K are sufficiently accurate. Solvents with melting points above 25°C are listed on p. 67 except hydrogen fluoride, ammonia and sulfur dioxide, but they are liquids near enough to ambient conditions to be useful as solvents.

The liquid solvent is in equilibrium with its vapour alone along the saturation curve (denoted by subscript σ), but when an external pressure is imposed, the liquid boils only when its vapour pressure equals the external pressure. The normal boiling point, T_b, is reached at standard atmospheric pressure, $P^o = 101.325$ kPa ($\equiv$ 1 atm). At reduced pressures the solvent boils at $T < T_b$. Such pressures are caused, for instance, by the elevation of the place above sea level (in Jerusalem, at an elevation of ca. 800 m, water boils at ~ 97°C), by certain weather conditions, or on the application of a partial vacuum. Since the boiling point is strongly pressure dependent, and since the usual determination with a mercury-in-glass thermometer suspended in the vapour depends on the position of the thermometer, corrections to P^o and for the thermometer stem-length have to be applied. If the solvent boils at the temperature T when the external pressure is P, then the pressure correction leads for many solvents to:

$$T_b = T[1 + 9.0 \times 10^{-4}(P^o - P)/\mathrm{kPa}] \qquad (3.1)$$

Impurities raise the boiling point, although the effect is smaller than for the melting point. Few solvents, with an impurity of molar mass of 50 g mol^{-1} at the level of 0.01% wt, have their boiling point raised by > 0.01 K, examples of such solvents being nitrobenzene and quinoline. However, the accuracy with which normal boiling points are reported for most solvents is not better than 0.1 K. Note that for three solvents on the List (hydrogen fluoride, ammonia, and sulfur dioxide) the normal boiling point is below 25°C, but they have nevertheless been used as solvents.

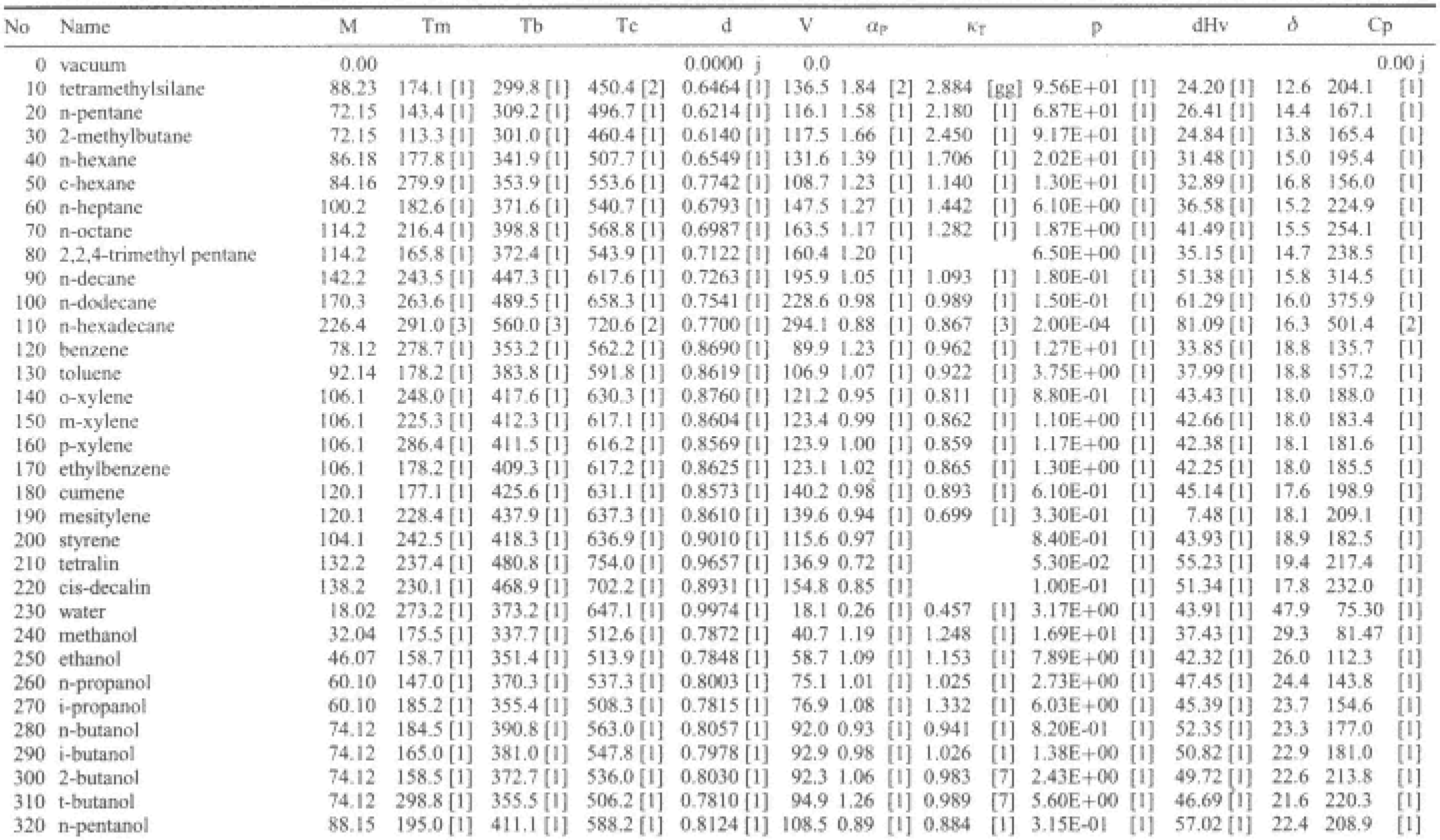
The freezing and normal boiling points of the solvents on the List are shown in Table 3.1. They have been rounded to the nearest 0.1 K, but in the cases where the decimal is reported as '.2', this is generally because the values have been taken from lists of data (Riddick, Bunger and Sakano 1986; DIPPR 1997; Lide 1994) where they are shown as integral Celsius temperatures (to which 273.15 has been added to obtain the temperature in K), and only rarely when these values have their decimals between '.00' and '.09'.

A solvent may, however, remain in the liquid state outside of the limits imposed by the freezing and normal boiling points. A solvent may be supercooled below T_m when it is pure (does not contain crystallization nuclei, such as dust particles) and cooled rapidly. It may exist in the supercooled condition indefinitely, but a slight disturbance may induce rapid crystallization, i.e., freezing. As the solvent is cooled its viscosity increases and eventually it may become so high that the substance becomes a glass. For many purposes a glass is defined as a homogeneous and isotropic liquid-like state of matter that is not in internal equilibrium and has a viscosity $\geq 10^{10}$ Pa·s. The temperature at which this glass transition takes place, T_g, is not necessarily precisely defined and may have a range of a few degrees, since the vitrification process is notoriously slow. Values of the glass transition temperature of some solvents are shown in Table 3.2 (Angell, Sare and Sare 1978).

Some solvents are reluctant to crystallize before turning into a glass, including allyl alcohol (2-propen-1-ol), ethylene glycol (1,2-ethanediol), and hexylene glycol (2-methyl-pentane-2,4-diol). Some common solvents may be liquid below their freezing points if they contain impurities, in particular small amounts of water. Thus, *t*-butyl alcohol (2-methyl-2-propanol), acetic acid, and phenol can appear liquid at or below ambient temperatures (i.e., < T_m) due to this cause.

On the contrary, a liquid can be prevented from boiling at and above T_b by the application of an elevated external pressure, $P > P^o$. The temperature can then be raised beyond T_b with the solvent remaining a liquid and a distinct phase from its vapour up to its critical point, T_C. Beyond this temperature, however, the liquid and vapour become indistinguishable, and constitute a supercritical fluid

Table 3.1 Thermophysical properties of solvents (temperature dependent properties at 25°C, unless otherwise noted)



No	Name	M	Tm	Tb	Tc	d	V	α_P	κ_T	p	dHv	δ	Cp
0	vacuum	0.00				0.0000 j	0.0						0.00 j
10	tetramethylsilane	88.23	174.1 [1]	299.8 [1]	450.4 [2]	0.6464 [1]	136.5	1.84 [2]	2.884 [gg]	9.56E+01 [1]	24.20 [1]	12.6	204.1 [1]
20	n-pentane	72.15	143.4 [1]	309.2 [1]	496.7 [1]	0.6214 [1]	116.1	1.58 [1]	2.180 [1]	6.87E+01 [1]	26.41 [1]	14.4	167.1 [1]
30	2-methylbutane	72.15	113.3 [1]	301.0 [1]	460.4 [1]	0.6140 [1]	117.5	1.66 [1]	2.450 [1]	9.17E+01 [1]	24.84 [1]	13.8	165.4 [1]
40	n-hexane	86.18	177.8 [1]	341.9 [1]	507.7 [1]	0.6549 [1]	131.6	1.39 [1]	1.706 [1]	2.02E+01 [1]	31.48 [1]	15.0	195.4 [1]
50	c-hexane	84.16	279.9 [1]	353.9 [1]	553.6 [1]	0.7742 [1]	108.7	1.23 [1]	1.140 [1]	1.30E+01 [1]	32.89 [1]	16.8	156.0 [1]
60	n-heptane	100.2	182.6 [1]	371.6 [1]	540.7 [1]	0.6793 [1]	147.5	1.27 [1]	1.442 [1]	6.10E+00 [1]	36.58 [1]	15.2	224.9 [1]
70	n-octane	114.2	216.4 [1]	398.8 [1]	568.8 [1]	0.6987 [1]	163.5	1.17 [1]	1.282 [1]	1.87E+00 [1]	41.49 [1]	15.5	254.1 [1]
80	2,2,4-trimethyl pentane	114.2	165.8 [1]	372.4 [1]	543.9 [1]	0.7122 [1]	160.4	1.20 [1]		6.50E+00 [1]	35.15 [1]	14.7	238.5 [1]
90	n-decane	142.2	243.5 [1]	447.3 [1]	617.6 [1]	0.7263 [1]	195.9	1.05 [1]	1.093 [1]	1.80E-01 [1]	51.38 [1]	15.8	314.5 [1]
100	n-dodecane	170.3	263.6 [1]	489.5 [1]	658.3 [1]	0.7541 [1]	228.6	0.98 [1]	0.989 [1]	1.50E-01 [1]	61.29 [1]	16.0	375.9 [1]
110	n-hexadecane	226.4	291.0 [3]	560.0 [3]	720.6 [2]	0.7700 [1]	294.1	0.88 [1]	0.867 [3]	2.00E-04 [1]	81.09 [1]	16.3	501.4 [2]
120	benzene	78.12	278.7 [1]	353.2 [1]	562.2 [1]	0.8690 [1]	89.9	1.23 [1]	0.962 [1]	1.27E+01 [1]	33.85 [1]	18.8	135.7 [1]
130	toluene	92.14	178.2 [1]	383.8 [1]	591.8 [1]	0.8619 [1]	106.9	1.07 [1]	0.922 [1]	3.75E+00 [1]	37.99 [1]	18.8	157.2 [1]
140	o-xylene	106.1	248.0 [1]	417.6 [1]	630.3 [1]	0.8760 [1]	121.2	0.95 [1]	0.811 [1]	8.80E-01 [1]	43.43 [1]	18.0	188.0 [1]
150	m-xylene	106.1	225.3 [1]	412.3 [1]	617.1 [1]	0.8604 [1]	123.4	0.99 [1]	0.862 [1]	1.10E+00 [1]	42.66 [1]	18.0	183.4 [1]
160	p-xylene	106.1	286.4 [1]	411.5 [1]	616.2 [1]	0.8569 [1]	123.9	1.00 [1]	0.859 [1]	1.17E+00 [1]	42.38 [1]	18.1	181.6 [1]
170	ethylbenzene	106.1	178.2 [1]	409.3 [1]	617.2 [1]	0.8625 [1]	123.1	1.02 [1]	0.865 [1]	1.30E+00 [1]	42.25 [1]	18.0	185.5 [1]
180	cumene	120.1	177.1 [1]	425.6 [1]	631.1 [1]	0.8573 [1]	140.2	0.98 [1]	0.893 [1]	6.10E-01 [1]	45.14 [1]	17.6	198.9 [1]
190	mesitylene	120.1	228.4 [1]	437.9 [1]	637.3 [1]	0.8610 [1]	139.6	0.94 [1]	0.699 [1]	3.30E-01 [1]	7.48 [1]	18.1	209.1 [1]
200	styrene	104.1	242.5 [1]	418.3 [1]	636.9 [1]	0.9010 [1]	115.6	0.97 [1]		8.40E-01 [1]	43.93 [1]	18.9	182.5 [1]
210	tetralin	132.2	237.4 [1]	480.8 [1]	754.0 [1]	0.9657 [1]	136.9	0.72 [1]		5.30E-02 [1]	55.23 [1]	19.4	217.4 [1]
220	cis-decalin	138.2	230.1 [1]	468.9 [1]	702.2 [1]	0.8931 [1]	154.8	0.85 [1]		1.00E-01 [1]	51.34 [1]	17.8	232.0 [1]
230	water	18.02	273.2 [1]	373.2 [1]	647.1 [1]	0.9974 [1]	18.1	0.26 [1]	0.457 [1]	3.17E+00 [1]	43.91 [1]	47.9	75.30 [1]
240	methanol	32.04	175.5 [1]	337.7 [1]	512.6 [1]	0.7872 [1]	40.7	1.19 [1]	1.248 [1]	1.69E+01 [1]	37.43 [1]	29.3	81.47 [1]
250	ethanol	46.07	158.7 [1]	351.4 [1]	513.9 [1]	0.7848 [1]	58.7	1.09 [1]	1.153 [1]	7.89E+00 [1]	42.32 [1]	26.0	112.3 [1]
260	n-propanol	60.10	147.0 [1]	370.3 [1]	537.3 [1]	0.8003 [1]	75.1	1.01 [1]	1.025 [1]	2.73E+00 [1]	47.45 [1]	24.4	143.8 [1]
270	i-propanol	60.10	185.2 [1]	355.4 [1]	508.3 [1]	0.7815 [1]	76.9	1.08 [1]	1.332 [1]	6.03E+00 [1]	45.39 [1]	23.7	154.6 [1]
280	n-butanol	74.12	184.5 [1]	390.8 [1]	563.0 [1]	0.8057 [1]	92.0	0.93 [1]	0.941 [1]	8.20E-01 [1]	52.35 [1]	23.3	177.0 [1]
290	i-butanol	74.12	165.0 [1]	381.0 [1]	547.8 [1]	0.7978 [1]	92.9	0.98 [1]	1.026 [1]	1.38E+00 [1]	50.82 [1]	22.9	181.0 [1]
300	2-butanol	74.12	158.5 [1]	372.7 [1]	536.0 [1]	0.8030 [1]	92.3	1.06 [1]	0.983 [7]	2.43E+00 [1]	49.72 [1]	22.6	213.8 [1]
310	t-butanol	74.12	298.8 [1]	355.5 [1]	506.2 [1]	0.7810 [1]	94.9	1.26 [1]	0.989 [7]	5.60E+00 [1]	46.69 [1]	21.6	220.3 [1]
320	n-pentanol	88.15	195.0 [1]	411.1 [1]	588.2 [1]	0.8124 [1]	108.5	0.89 [1]	0.884 [1]	3.15E-01 [1]	57.02 [1]	22.4	208.9 [1]

(table continued on next page)

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330	i-pentanol	88.15	156.0 [2]	401.9 [1]	579.5 [2]	0.8072 [1]	109.2	0.82	[1]	0.952	[7]	3.16E-01	[1]	55.60 [1]	22.1	211.3	[1]
340	t-pentanol	88.15	264.4 [1]	375.2 [1]	545.0 [1]	0.8050 [1]	109.5	1.14	[1]	1.112	[7]	2.23E+00	[1]	50.20 [1]	20.5	244.3	[1]
350	n-hexanol	102.1	228.6 [1]	430.2 [1]	610.0 [1]	0.8161 [1]	125.2	0.87	[1]	0.837	[1]	1.09E-01	[1]	61.61 [1]	21.8	241.3	[1]
360	c-hexanol	100.1	298.3 [1]	434.3 [1]	625.0 [1]	0.9687 [1]	103.4	0.77	[1]	0.570	[7]	9.07E-02	[2]	62.01 [1]	23.3	202.4	[1]
370	n-octanol	130.2	258.2 [1]	468.3 [1]	652.5 [1]	0.8222 [1]	158.4	0.84	[1]	0.764	[1]	1.00E-02	[1]	72.00 [1]	20.9	305.5	[1]
380	n-decanol	158.2	280.0 [3]	502.0 [3]	690.0 [2]	0.8287 [1]	191.0	0.84	[2]	0.690	[7]	1.00E-03	[2]	79.28 [2]	19.9	370.9	[2]
390	n-dodecanol	186.3	299.0 [3]	532.0 [3]	721.0 [2]	0.8307 [1]	224.3	0.83	[2]	0.630	[7]	1.00E-04	[2]	87.70 [2]	20.6	437.7	[2]
400	benzyl alcohol	108.1	257.9 [1]	478.6 [1]	677.0 [2]	1.0408 [1]	103.9	0.69	[1]	0.497	[1]	1.50E-02	[1]	61.55 [1]	23.8	215.9	[1]
410	2-phenylethanol	122.1	246.0 [3]	492.0 [3]	684.0 [2]	1.0232 [3]	119.4	0.73	[2]			6.78E-03	[c]	8.37 [c]	23.9	250.3	[2]
420	allyl alcohol	58.08	144.0 [1]	370.0 [1]	545.1 [2]	0.8466 [1]	68.6	1.27	[2]			3.48E+00	[2]	44.72 [2]	24.1	161.4	[1]
430	2-chloroethanol	81.59	205.7 [1]	401.8 [1]	585.0 [2]	1.2629 [1]	101.8	0.90	[1]	0.620	[7]	9.57E-01	[2]	45.85 [2]	20.1	110.1	[2]
440	2-cyanoethanol	71.08	227.0 [1]	493.0 [1]		1.0407 [1]	68.3	0.72	[1]			1.00E-02	[1]	56.10 [1]	28.0		
450	2,2,2-trifluoroethanol	100.0	229.7 [1]	347.2 [1]	499.3 [h]	1.3818 [1]	72.4	1.19	[1]	1.220	[7]	1.01E+01	[1]	44.00 [1]	23.9	155.8	[cc]
460	hexafluoro-i-propanol	168.0	263.2 [a]	331.2 [a]		1.6064 [a]	104.6	1.59*	[a]			2.12E+01	[a]	41.58 [a]	19.3		
470	2-methoxyethanol	76.10	188.1 [1]	397.8 [1]	564.0 [2]	0.9596 [1]	79.3	0.91	[1]	0.620	[7]	1.30E+00	[1]	54.00 [1]	25.5	174.9	[1]
480	2-ethoxyethanol	90.12	173.0 [b]	408.8 [1]	569.0 [2]	0.9253 [1]	97.4	0.93	[1]	0.680	[7]	7.10E-01	[1]	47.20 [1]	20.3	210.8	[1]
490	1,2-ethanediol	62.07	260.6 [2]	470.7 [1]	645.0 [2]	1.1104 [1]	55.9	0.62	[1]	0.392	[1]	1.17E-02	[1]	61.10 [1]	32.4	150.5	[1]
500	1,2-propanediol	76.10	213.0 [1]	460.8 [1]	626.0 [2]	1.0326 [1]	73.7	0.69	[1]	0.487	[7]	1.77E-02	[1]	64.40 [1]	25.8	188.7	[1]a
510	1,3-propanediol	76.10	246.5 [1]	487.6 [1]	658.0 [2]	1.0497 [1]	72.5	0.61	[1]			5.90E-03	[2]	72.80 [1]	33.0	246.1	[2]
520	1,2-butanediol	90.12	220.0 [2]	467.0 [3]	680.0 [2]	0.9991 [k]	90.2	0.78	[k]			1.00E-02	[2]	69.10 [2]	27.2	248.9	[2]
530	2,3-butanediol (meso)	90.12	280.8 [1]	449.9 [1]	611.0 [2]	0.9871 [1]	91.3	0.99	[2]			5.10E-02	[1]	59.20 [u]	24.9	248.9	[2]
540	1,4-butanediol	90.12	307.6 [1]	455.5 [1]	667.0 [2]	1.0126 [1]	89.0	0.65	[1]	0.440	[7]	1.4E-03	[2]	76.60 [1]	24.7	202.2	[2]
550	1,5-pentanediol	104.1	257.6 [1]	515.6 [1]	673.0 [2]	0.9862 [1]	105.6	0.61	[1]	0.458	[7]	5.20E-04	[2]	82.40 [u]	27.9	225.5	[2]
560	diethyleneglycol	106.1	265.4 [1]	518.8 [1]	680.0 [2]	1.1159 [1]	95.1	0.67	[1]	0.363	[7]	6.00E-04	[1]	82.14 [2]	29.1	242.7	[1]a
570	triethyleneglycol	150.1	268.9 [1]	561.2 [1]	700.0 [2]	1.1198 [1]	134.1	0.71	[1]			1.80E-04	[1]	101.3 [2]	27.2	324.8	[1]a
580	glycerol	92.10	291.3 [1]	563.2 [1]	723.0 [2]	1.2582 [1]	73.2	0.49	[1]	0.246	[7]	2.00E-05	[2]	85.60 [1]	33.7	223.3	[1]
590	phenol	94.11	314.1 [1]	455.0 [1]	694.3 [1]	1.0719 [1]	87.9	0.80	[1]	0.542	[7]	5.50E-02	[1]	57.80 [1]	25.1	201.4	[1]d
600	2-methylphenol	108.1	304.1 [1]	464.2 [1]	697.6 [1]	1.0398 [1]	104.0	0.76	[1]	0.480	[7]	4.10E-02	[1]	64.39 [1]	21.9	232.9	[1]b
610	3-methylphenol	108.1	285.4 [1]	475.4 [1]	705.8 [1]	1.0299 [1]	105.0	0.76	[1]			1.90E-02	[1]	61.71 [1]	22.1	224.9	[1]
620	4-methylphenol	108.1	307.9 [1]	475.1 [1]	704.6 [1]	1.0202 [1]	106.0	0.75	[1]			1.70E-02	[1]	67.20 [1]	22.1	227.4	[1]c
630	2-methoxyphenol	124.1	301.8 [3]	478.2 [3]		1.1285 [3]	110.0	0.89	[1]			2.45E-02	[c]	62.05 [c]	23.8		
640	2,4-dimethylphenol	122.1	297.7 [1]	484.1 [1]	707.6 [1]	1.0164 [1]	120.2	0.82	[1]			2.20E-02	[1]	65.86 [1]	23.0	245.7	[2]f
650	3-chlorophenol	128.5	306.0 [3]	489.0 [3]	729.0 [2]	1.2679 [3]	101.4	0.82	[1]			1.21E-01	[2]	52.16 [2]	18.2		
660	diethyl ether	74.12	156.9 [1]	307.6 [1]	466.7 [1]	0.7079 [1]	104.7	1.61	[1]	1.967	[3]	7.16E+01	[1]	27.18 [1]	15.4	172.5	[1]
670	di-n-propyl ether	102.1	150.0 [1]	363.2 [1]	530.6 [1]	0.7420 [1]	137.7	1.27	[1]	1.320	[7]	8.33E+00	[1]	35.70 [1]	15.5	221.6	[1]

continued overleaf

***Table 3.1** (continued)*

No	Name	M	Tm	Tb	Tc	d	V	α_P		κ_T		p		dHv	δ	Cp	
680	di-i-propyl ether	102.1	187.7 [1]	341.7 [1]	500.3 [1]	0.7181 [1]	142.3	1.48	[1]	1.610	[7]	1.88E+01	[1]	32.60 [1]	14.6	216.1	[1]
690	di-n-butyl ether	130.2	178.0 [1]	413.4 [1]	581.0 [2]	0.7643 [1]	170.4	1.13	[1]			8.98E-01	[1]	44.40 [1]	15.9	251.9	[1]
700	di(2-chloroethyl)ether	143.0	226.4 [1]	451.9 [1]		1.2130 [1]	117.9	0.96	[1]	0.740	[7]	2.07E-01	[1]	45.20 [1]	18.8	220.9	[1]b
710	1,2-dimethoxyethane	90.12	204.0 [1]	357.7 [1]	536.0 [1]	0.8624 [1]	104.5	1.02	[1]	0.990	[7]	9.27E+00	[2]	32.10 [1]	16.8	193.3	[1]
720	bis(methoxyethyl)ether	134.1	209.2 [1]	432.9 [1]	608.0 [2]	0.9383 [1]	143.0	1.07	[a]			4.50E-01	[1]	43.15 [1]	19.3	226.0	[1]
730	furan	68.08	187.5 [1]	304.5 [1]	490.2 [1]	0.9313 [1]	73.1	0.73	[1]			8.00E+01	[2]	27.46 [1]	18.6	114.8	[1]
740	tetrahydrofuran	72.11	164.8 [1]	339.1 [1]	540.2 [1]	0.8837 [1]	81.6	1.29	[1]	0.953	[7]	2.35E+01	[1]	31.80 [1]	19.0	123.9	[1]
750	2-methyltetrahydrofuran	86.13	136.0 [1]	353.1 [1]	537.0 [1]	0.8536 [1]	100.9	1.12	[1]			1.26E+01	[c]	32.34 [1]	17.1		
760	tetrahydropyran	86.13	228.0 [1]	361.0 [1]	572.2 [1]	0.8771 [1]	98.2	1.04	[1]	0.956	[7]	3.55E+01	[1]	34.90 [1]	18.2	156.5	[1]
770	1,4-dioxane	88.11	285.0 [1]	347.5 [1]	587.0 [1]	1.0281 [1]	85.7	1.10	[1]	0.738	[1]	4.95E+00	[1]	35.70 [1]	19.7	150.6	[1]
780	1,3-dioxolane	74.08	175.9 [1]	348.8 [1]		1.0644 [1]	69.6	1.18	[m]			1.10E+01	[1]	35.60 [1]	21.8		
790	1,8-cineole	154.2	274.0 [1]	447.0 [1]		0.9192 [1]	167.8	0.92	[ee]			2.50E-01	[1]	35.72 [c]	14.6		
800	anisole	108.1	235.7 [1]	426.8 [1]	645.6 [1]	0.9894 [1]	109.3	0.95	[1]	0.686	[3]	4.72E-01	[1]	45.00 [1]	19.7	208.6	[1]b
810	phenetole	122.1	243.6 [1]	443.0 [1]	647.2 [1]	0.9605 [1]	127.2	0.97	[1]			2.04E-01	[1]	51.04 [1]	19.5	227.9	[1]a
820	diphenyl ether	170.2	300.0 [1]	531.2 [1]	766.8 [1]	1.0712 [1]	158.9	0.81	[1]			2.80E-03	[1]	66.90 [1]	20.7	268.4	[1]
830	dibenzyl ether	198.2	276.8 [1]	561.5 [1]	777.0 [2]	1.0289 [1]	190.7	0.56	[1]			3.00E-03	[1]	76.06 [2]	19.2	299.0	[2]
840	1,2-dimethoxybenzene	138.1	295.7 [1]	479.4 [1]		1.0820 [1]	127.7	0.93	[1]			6.30E-02	[1]	48.38	18.9		
850	trimethylorthoformate	106.1		375.0 [3]		0.9431 [3]	112.5							38.10 [u]	16.7		
860	trimethylorthoacetate	120.1		382.0 [3]		0.8846 [3]	135.8							39.30 [u]	14.2		
870	propionaldehyde	58.08	193.0 [1]	321.2 [1]	496.0 [2]	0.7913 [1]	73.4	1.47	[1]			4.23E+01	[1]	29.63 [1]	19.3	137.2	[1]
880	butyraldehyde	72.11	176.8 [1]	348.0 [1]	525.0 [2]	0.7968 [1]	90.5	1.19	[1]			1.57E+01	[1]	33.68 [1]	18.4	164.0	[1]
890	benzaldehyde	106.1	217.6 [1]	451.9 [1]	695.0 [1]	1.0436 [1]	101.7	0.25	[1]	0.230	[7]	1.69E-01	[1]	39.60 [1]	19.1	172.0	[1]
900	p-methoxy-benzaldehyde	136.1	275.7 [3]	522.7 [3]		1.1197 [3]	121.6					5.02E-03	[r]	64.50 [u]	22.6		
910	cinnamaldehyde	132.1	265.7 [3]	526.0 [3]		1.0497 [3]	125.9					4.07E-03	[r]	72.92 [c]	24.1		
920	acetone	58.08	178.5 [1]	329.2 [1]	508.1 [1]	0.7849 [1]	74.0	1.45	[1]	1.324	[1]	3.08E+01	[1]	30.99 [1]	22.1	124.9	[1]
930	2-butanone	72.11	186.5 [1]	352.7 [1]	536.8 [1]	0.7884 [1]	90.2	1.32	[1]	1.188	[1]	1.26E+01	[1]	34.79 [1]	18.7	158.9	[1]
940	2-pentanone	86.13	196.3 [1]	375.4 [1]	561.1 [1]	0.8012 [1]	107.5	1.13	[1]	1.092	[1]	1.62E+00	[1]	43.14 [1]	18.2	184.3	[1]
950	methyl i-propyl ketone	86.13	181.0 [1]	368.0 [1]	553.0 [2]	0.8050 [1]	107.0	1.17	[2]	1.080	[7]	6.96E+00	[2]	36.90 [u]	17.9	180.0	[2]
960	3-pentanone	86.13	234.2 [1]	375.1 [1]	561.5 [1]	0.8095 [1]	106.4	1.24	[1]	1.073	[1]	4.80E+00	[1]	38.52 [1]	18.0	190.1	[1]
970	c-pentanone	84.12	221.9 [1]	403.9 [1]	626.0 [1]	0.9452 [1]	89.1	1.02	[1]			1.54E+00	[1]	42.63 [1]	21.3	154.5	[1]
980	methyl i-butyl ketone	100.1	189.0 [1]	390.6 [1]	571.5 [1]	0.7968 [1]	125.7	1.18	[1]			2.51E+00	[1]	41.70 [1]	17.2	215.8	[1]
990	methyl t-butyl ketone	100.1	220.7 [3]	379.0 [3]	565.8 [h]	0.8013 [1]	125.0					4.27E+00	[c]	38.00 [4]	17.4	207.3	[z]

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1000	c-hexanone	98.15	241.1 [1]	428.8 [1]	654.0 [1]	0.9419 [1]	104.2	0.95	[1]	0.662	[7]	5.40E-01	[1]	45.13 [1]	19.7	179.3	[1]
1010	2-heptanone	114.1	238.2 [1]	424.2 [1]	611.5 [1]	0.8110 [1]	140.8	1.06	[1]			5.14E-01	[1]	47.24 [1]	17.4	243.6	[1]
1020	3-heptanone	114.1	234.2 [1]	420.6 [1]	606.0 [2]	0.8110 [1]	140.8	0.98	[1]			7.46E-01	[1]	46.44 [v]	17.4	245.7	[2]
1030	di-t-butyl ketone	142.2		424.0 [3]		0.8198 [3]	173.5							45.30 [u]	15.7		
1040	acetophenone	120.1	292.8 [1]	475.2 [1]	729.0 [1]	1.0234 [1]	117.4	0.84	[1]	0.560	[7]	4.90E-02	[1]	53.40 [1]	20.8	204.6	[1]
1050	propiophenone	134.1	291.8 [3]	491.0 [3]		1.0104 [1]	132.8					1.84E-02	[c]	58.50 [u]	20.5		
1060	phenylacetone	134.1	300.0 [3]	489.7 [3]		1.0157 [3]	132.1							51.20 [u]	19.2		
1070	p-methylacetophenone	134.1	301.0 [3]	499.0 [3]		1.0051 [1]	133.5										
1080	p-chloroacetophenone	154.6	291.6 [3]	546.0 [3]		1.1920 [1]	129.7			0.670	[dd]	1.01E-03	[r]	65.97 [c]	22.6		
1090	benzophenone	182.2	299.0 [3]	579.1 [3]	830.0 [2]	1.1077 [1]	164.5	0.66	[2]			1.01E-04	[c]	89.40 [u]	23.0	302.2	[2]e
1100	acetylacetone	100.1	250.0 [1]	411.5 [1]	602.0 [2]	0.9720 [1]	103.0	1.09	[n]			1.84E+00	[2]	41.80 [1]	19.5	208.2	[2]
1110	biacetyl	86.09	270.8 [c]	363.0 [3]		0.9805 [3]	87.8					7.45E+00	[c]	38.70 [u]	20.3		
1120	formic acid	46.03	281.4 [1]	373.7 [1]	580.0 [2]	1.2145 [1]	37.9	1.02	[1]	0.647	[1]	5.75E+00	[1]	19.90 [1]	21.4	99.0	[1]
1130	acetic acid	60.05	289.8 [1]	391.0 [1]	592.7 [1]	1.0443 [1]	57.5	1.07	[1]	0.918	[1]	2.08E+00	[1]	23.00 [1]	18.9	123.1	[1]
1140	propanoic acid	74.08	252.5 [1]	414.3 [1]	612.7 [1]	0.9877 [1]	75.0	1.07	[1]	1.050	[1]	4.51E-01	[1]	30.97 [2]	26.4	152.8	[1]
1150	n-butanoic acid	88.11	268.0 [1]	436.9 [1]	628.2 [1]	0.9536 [1]	92.4	1.05	[1]	0.800	[7]	1.02E-01	[1]	40.18 [2]	25.1	177.7	[1]
1160	n-pentanoic acid	102.1	239.5 [1]	458.7 [1]	651.0 [1]	0.9344 [1]	109.3	0.96	[1]	1.068	[7]	1.90E-02	[1]	51.17 [2]	24.7	197.0	[1]
1170	n-hexanoic acid	116.1	269.7 [1]	478.2 [1]	662.0 [c]	0.9226 [1]	125.9	1.01	[1]	0.820	[7]	5.00E-03	[1]	61.79 [2]	24.6	248.1	[1]
1180	n-heptanoic acid	130.1	263.0 [3]	496.0 [3]	679.0 [c]	0.9188 [1]	141.7	0.73	[o]			9.96E-04	[r]	76.50 [2]	22.5	265.6	[2]
1190	dichloroacetic acid	128.9	284.0 [3]	466.0 [3]	686.0 [2]	1.5629 [1]	82.5	0.98	[2]			3.66E-02	[r]	57.17 [c]	26.3	184.0	[2]
1200	trifluoroacetic acid	114.0	257.9 [1]	344.9 [1]	491.3 [1]	1.4789 [1]	77.1	1.59	[1]	1.350	[7]	1.44E+01	[1]	36.30 [1]	20.9		
1210	acetic anhydride	102.0	200.1 [1]	413.2 [1]	569.0 [1]	1.0746 [1]	95.0	1.13	[1]	0.870	[7]	6.80E-01	[1]	48.90 [1]	22.1	191.5	[1]b
1220	benzoyl chloride	140.5	272.0 [3]	370.0 [3]	697.0 [2]	1.2108 [1]	116.1	0.82	[2]			8.30E-02	[2]	50.92 [2]	20.4		
1230	benzoyl bromide	185.0	249.0 [3]	492.0 [3]		1.5694 [3]	117.9					3.01E-02	[c]	58.60 [u]	21.8		
1240	methyl formate	60.05	174.2 [1]	304.9 [1]	487.2 [1]	0.9670 [1]	62.1	1.61	[1]			7.81E+01	[1]	30.59 [1]	20.9	119.7	[1]
1250	ethyl formate	74.08	193.6 [1]	327.5 [1]	508.5[1]	0.9157 [1]	80.9	1.42	[1]	1.205	[1]	3.40E+01	[1]	31.94 [1]	20.9	144.3	[1]
1260	methyl acetate	74.08	175.1 [1]	330.0 [1]	506.6 [1]	0.9283 [1]	79.8	1.42	[1]	1.138	[7]	2.90E+01	[1]	32.29 [1]	19.3	143.9	[1]
1270	ethyl acetate	88.11	189.6 [1]	350.3 [1]	523.3 [1]	0.8945 [1]	98.5	1.38	[1]	1.207	[7]	1.26E+01	[1]	35.59 [1]	18.2	167.7	[1]
1280	propyl acetate	102.1	178.2 [1]	374.7 [1]	549.7 [1]	0.8827 [1]	115.7	1.27	[1]	1.149	[7]	4.51E+00	[1]	39.73 [1]	18.0	196.2	[1]a
1290	butyl acetate	116.1	199.7 [1]	399.2 [1]	579.2 [2]	0.8767 [1]	132.5	1.17	[1]	1.048	[7]	1.53E+00	[1]	44.04 [1]	17.6	228.4	[1]
1300	i-pentyl acetate	130.1	194.7 [1]	415.3 [1]	599.0 [2]	0.8662 [1]	150.3	1.04	[1]			8.14E-01	[2]	45.55 [2]	16.6	249.9	[1]a
1310	methyl propanoate	88.11	185.7 [3]	351.9 [3]	530.6 [2]	0.9084 [4]	97.0	1.31	[2]			1.12E+01	[2]	36.11 [2]	18.6	177.8	[2]
1320	ethyl propanoate	102.1	1993. [1]	372.3 [1]	546.1 [1]	0.8842 [1]	115.5	1.25	[1]	1.304	[7]	4.97E+00	[1]	39.25 [1]	17.2	196.1	[1]
1330	dimethyl carbonate	90.08	272.0 [3]	363.0 [3]	548.0 [2]	1.0698 [4]	84.2	1.19	[2]			7.38E+00	[2]	37.26 [4]	20.3	170.4	[2]

continued overleaf

Table 3.1 *(continued)*

No	Name	M	Tm	Tb	Tc	d	V	α_P	κ_T	p	dHv	δ	Cp
1340	diethyl carbonate	118.1	230.2 [1]	400.0 [1]	576.0 [2]	0.9691 [1]	121.9	1.10 [1]	1.000 [7]	1.44E+00 [2]	41.10 [1]	17.8	212.4 [1]
1350	ethylene carbonate	88.06	309.5 [1]	521.4 [1]	790.0 [2]	1.3312 [2]	66.2	0.74 [1]	0.530 [7]	1.01E-02 [1]	50.10 [1]	25.9	134.3 [2]d
1360	propylene carbonate	102.0	218.2 [1]	514.9 [1]	778.0 [2]	1.1981 [1]	85.2	0.95 [1]	0.590 [1]	6.16E-03 [2]	65.28 [1]	21.8	160.2 [2]
1370	diethyl malonate	160.1	224.3 [1]	472.5 [1]	653.0 [2]	1.0496 [1]	152.6	1.00 [1]		3.59E-02 [2]	58.73 [2]	18.5	285.0 [1]a
1380	methyl benzoate	136.1	261.1 [1]	472.7 [1]	711.0 [1]	1.0840 [1]	125.6	0.88 [1]	0.445 [7]	5.30E-02 [1]	55.57 [1]	21.5	221.3 [1]
1390	ethyl benzoate	150.1	238.5 [1]	485.6 [1]	698.0 [2]	1.0422 [1]	144.1	0.89 [1]		3.81E-02 [2]	54.59 [2]	20.0	246.0 [1]
1400	dimethyl phthalate	194.1	272.2 [2]	558.0 [3]	766.0 [2]	1.1906 [1]	163.1	0.78 [2]		4.00E-04 [2]	72.30 [2]	20.7	285.0 [2]
1410	dibutyl phthalate	278.3	238.0 [1]	613.2 [1]	781.0 [2]	1.0425 [1]	267.0	0.86 [1]		1.00E-05 [2]	98.70 [2]	16.7	498.00 [1]a
1420	ethyl chloroacetate	122.5	247.0 [3]	417.0 [3]	618.0 [2]	1.2569 [1]	97.5	1.00 [2]		6.73E-01 [r]	49.48 [4]	22.0	
1430	ethyl trichloroacetate	191.4		441.0 [3]		1.3832 [1]	138.4			1.81E-01 [r]	48.34 [4]	18.2	
1440	ethyl acetoacetate	130.1	234.0 [1]	454.0 [1]	673.0 [1]	1.0215 [1]	127.4	0.95 [1]		3.00E-01 [1]	53.71 [c]	20.1	250.2 [1]
1450	4-butyrolactone	86.09	229.8 [1]	477.0 [1]	709.0 [1]	1.1254 [1]	76.5	0.86 [1]	0.610 [7]	4.30E-01 [1]	52.20 [1]	25.5	141.4 [1]
1460	perfluoro-n-hexane	338.0	187.2 [d]	331.2 [d]	447.7 [d]	1.6783 [4]	201.4	1.26 [d]	2.880 [d]	2.92E+01 [d]	31.97 [d]	12.1	240.20 [z]a
1470	perfluoro-n-heptane	388.0	222.2 [d]	355.7 [d]	474.9 [d]	1.7276 [d]	224.6	1.64 [p]	2.280 [d]	1.02E+01 [d]	36.40 [u]	12.3	322.20 [z]a
1480	perfluoro-methyl-cyclohexane	350.0	235.2 [d]	349.2 [d]	486.8 [d]	1.7879 [4]	195.8	1.38 [d]	2.115 [d]	1.41E+01 [d]	33.95 [4]	12.7	
1490	perfluoro-decalin	462.1	262.0 [d]	415.2 [d]	565.2 [d]	1.9465 [4]	237.4	1.16 [q]		6.60E+00 [s]	45.40 [4]	13.4	
1500	fluorobenzene	96.10	230.9 [1]	357.9 [1]	560.1 [1]	1.0191 [1]	94.3	1.18 [1]	0.942 [7]	1.02E+01 [1]	34.58 [1]	18.1	146.3 [1]
1510	hexafluorobenzene	186.0	278.3 [1]	353.4 [1]	516.8 [1]	1.6123 [1]	115.8	1.41 [1]	1.180 [27	1.23E+01 [2]	35.69 [1]	16.9	221.61 [1]
1520	1-chlorobutane	92.57	150.1 [1]	351.6 [1]	542.2 [1]	0.8808 [1]	105.1	0.80 [1]		1.53E+01 [2]	33.52 [1]	17.1	174.6 [1]a
1530	chlorobenzene	112.5	227.6 [1]	404.8 [1]	632.4 [1]	1.1014 [1]	102.2	0.99 [1]	0.771 [1]	1.60E+00 [1]	40.97 [1]	19.8	148.8 [1]
1540	dichloromethane	89.93	178.2 [1]	312.8 [1]	510.0 [1]	1.3943 [1]	64.5	1.35 [1]	1.026 [1]	5.83E+01 [1]	28.82 [1]	20.2	177.0 [1]
1550	1,1-dichloroethane	98.96	176.2 [1]	330.5 [1]	523.2 [1]	1.1684 [1]	84.7	1.33 [1]	1.148 [1]	3.03E+01 [1]	30.62 [1]	18.3	126.2 [1]
1560	1,2-dichloroethane	98.96	237.5 [1]	356.6 [1]	561.0 [1]	1.2463 [1]	79.4	1.15 [1]	0.816 [1]	1.06E+01 [2]	35.16 [1]	20.0	128.9 [1]
1570	tr-1,2-dichloroethylene	96.94	223.4 [1]	320.8 [1]	516.5 [1]	1.2460 [1]	77.8	1.36 [1]	1.119 [3]	4.53E+01 [1]	29.50 [1]	18.4	112.7 [2]a
1580	o-dichlorobenzene	147.0	256.1 [1]	453.6 [1]	697.3 [1]	1.2998 [1]	113.1	0.85 [1]	0.610 [7]	1.71E-01 [1]	50.20 [1]	20.5	221.6 [1]
1590	m-dichlorobenzene	147.0	248.4 [1]	446.2 [1]	684.0 [1]	1.2828 [1]	114.6	0.88 [1]		2.52E-01 [1]	48.58 [1]	20.0	161.6 [2]
1600	chloroform	119.3	209.6 [1]	334.3 [1]	536.6 [1]	1.4793 [1]	80.7	1.29 [1]	1.033 [1]	2.63E+01 [1]	31.28 [1]	19.5	117.0 [1]
1610	1,1,1-trichloroethane	133.4	242.8 [1]	347.2 [1]	545.0 [1]	1.3301 [1]	100.3	1.25 [1]		1.65E+01 [1]	32.39 [1]	19.6	144.4 [1]
1620	1,1,2-trichloroethane	133.4	236.6 [1]	387.0 [1]	612.0 [1]	1.4314 [1]	93.2	1.00 [1]		3.00E+00 [1]	40.28 [1]	20.1	148.5 [1]a
1630	trichloroethylene	131.3	186.8 [1]	360.3 [1]	571.0 [1]	1.4599 [1]	90.0	1.17 [1]	0.857 [3]	6.31E+00 [1]	34.27 [1]	19.0	120.5 [1]
1640	1,2,4-trichloro-benzene	181.4	290.1 [1]	442.5 [2]	725.0 [2]	1.4540 [1]	124.8	0.80 [2]		5.74E-02 [2]	55.72 [2]	20.7	183.9 [2]

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1650	tetrachloromethane	153.8	250.3 [1]	349.8 [1]	556.6 [1]	1.5841 [1]	97.1	1.25	[1]	1.080	[1]	1.52E+01	[1]	32.43 [1]	17.6	131.3	[1]
1660	tetrachloroethylene	165.8	250.8 [1]	394.2 [1]	620.3 [1]	1.6147 [1]	102.7	1.02	[1]	0.791	[7]	2.46E+00	[1]	39.61 [1]	19.0	146.4	[1]
1670	1,1,2,2-tetrachloroethane	167.8	229.4 [1]	418.3 [1]	645.0 [2]	1.5865 [1]	105.8	0.97	[1]	0.617	[7]	7.60E-01	[1]	45.71 [1]	20.2	165.7	[1]
1680	pentachloroethane	202.3	244.2 [1]	433.0 [1]	646.2 [1]	1.6733 [1]	120.9	0.90	[2]			4.89E-01	[2]	44.12 [2]	19.2	195.4	[1]
1690	1-bromobutane	137.0	160.8 [1]	374.8 [1]	577.0 [2]	1.2687 [1]	108.0	1.14	[1]	1.026	[1]	5.50E+00	[1]	36.60 [1]	17.8	168.1	[1]
1700	bromobenzene	157.0	242.3 [1]	429.1 [1]	670.2 [2]	1.4882 [1]	105.5	0.88	[1]	0.668	[3]	5.50E-01	[1]	44.54 [1]	20.2	154.2	[1]
1710	dibromomethane	173.8	221.0 [1]	370.0 [1]	611.0 [2]	2.4907 [1]	69.8	1.02	[2]	0.697	[3]	6.03E+00	[2]	37.45 [2]	22.4	104.9	[2]
1720	1,2-dibromoethane	187.8	282.9 [1]	404.5 [1]	583.0 [1]	2.1693 [1]	86.6	0.94	[1]	0.641	[1]	1.04E+00	[1]	41.73 [1]	19.8	136.0	[1]
1730	bromoform	252.7	281.2 [1]	422.4 [1]	696.0 [2]	2.8785 [1]	87.8	0.91	[1]	0.549	[7]	7.90E-01	[1]	44.67 [1]	21.9	132.8	[1]a
1740	1-iodobutane	184.0	170.2 [1]	403.7 [1]		1.6072 [1]	114.5	1.02	[1]			1.85E+00	[1]	40.63 [1]	18.3		
1750	iodobenzene	204.0	241.8 [1]	461.5 [1]	721.2 [2]	1.8231 [1]	111.9	0.83	[1]	0.582	[7]	1.30E-01	[1]	47.55 [1]	20.7	158.8	[1]
1760	diiodomethane	267.8	279.3 [1]	455.0 [1]	747.0 [2]	3.3230 [1]	80.6	0.83	[1]			1.60E-01	[1]	49.38 [1]	24.1	133.9	[1]
1770	n-butylamine	73.14	224.1 [1]	350.2 [1]	561.1 [1]	0.7366 [1]	99.3	1.35	[1]	1.142	[7]	1.22E+01	[1]	35.74 [1]	17.8	188.0	[1]
1780	benzylamine	107.1	283.2 [c]	458.0 [3]	684.0 [2]	0.9812 [3]	109.2	0.85	[2]			9.82E-02	[r]	53.60 [u]	21.6	213.7	[2]
1790	1,2-diaminoethane	60.10	284.5 [1]	390.1 [1]	593.0 [1]	0.8891 [1]	67.6	0.79	[1]	0.508	[1]	1.67E+00	[2]	46.60 [1]	25.5	172.5	[1]
1800	diethylamine	73.14	223.4 [1]	328.7 [1]	497.0 [1]	0.7019 [1]	104.2	1.56	[1]	1.514	[7]	3.11E+01	[1]	31.32 [1]	16.4	176.7	[1]a
1810	di-n-butylamine	129.2	211.0 [1]	432.8 [1]	495.8 [1]	0.7576 [1]	170.6	1.12	[1]	1.065	[7]	3.04E-01	[1]	49.44 [1]	16.6	292.8	[2]
1820	pyrrole	67.09	249.7 [1]	402.9 [1]	639.7 [1]	0.9653 [1]	69.5	0.87	[2]	0.652	[7]	1.10E+00	[1]	45.15 [1]	24.8	128.2	[1]
1830	pyrrolidine	71.12	215.3 [1]	359.7 [1]	568.6 [1]	0.8538 [1]	83.3	1.13,	[1]	0.814	[7]	8.39E+00	[2]	37.57 [1]	20.5	156.5	[2]
1840	piperidine	85.15	262.7 [1]	379.4 [1]	594.1 [1]	0.8566 [1]	99.4	1.35	[1]	0.917	[7]	4.28E+00	[2]	39.29 [1]	17.8	186.4	[1]
1850	morpholine	87.12	268.4 [1]	402.1 [1]	618.0 [2]	0.9957 [1]	87.5	0.95	[1]	0.615	[7]	1.34E+00	[1]	44.00 [1]	21.8	174.3	[2]
1860	triethylamine	101.1	158.5 [1]	362.0 [1]	535.4 [1]	0.7228 [1]	140.0	1.30	[1]	1.379	[1]	9.04E+00	[1]	34.88 [1]	15.2	224.4	[1]
1870	tri-n-butylamine	185.3	203.2 [1]	487.2 [1]	638.4 [1]	0.7742 [1]	239.4	1.07	[b]			2.06E-02	[c]	69.44 [c]	15.8		
1880	aniline	93.13	267.2 [1]	457.6 [1]	699.0 [1]	1.0178 [1]	91.5	0.85	[1]	0.471	[1]	9.00E-02	[1]	55.80 [1]	24.1	191.0	[1]
1890	o-chloroaniline	127.5	271.2 [1]	482.0 [1]	722.0 [2]	1.2080 [1]	105.6	0.79	[1]	0.450	[7]	3.40E-02	[1]	56.80 [1]	22.7	198.3	[2]
1900	N-methylaniline	107.1	216.0 [1]	469.4 [1]	701.0 [1]	0.9822 [1]	109.1	0.81	[1]	0.500	[7]	6.04E-02	[2]	53.10 [1]	21.5	191.6	[2]
1910	N,N-dimethylaniline	121.1	275.6 [1]	467.2 [1]	687.0 [1]	0.9527 [1]	127.2	0.86	[1]			9.43E-02	[2]	49.80 [1]	19.3		
1920	ethanolamine	61.08	283.7 [1]	444.1 [1]	614.5 [1]	1.0129 [1]	60.3	0.78	[1]	0.426	[7]	4.93E-02	[2]	66.10 [1]	31.8	127.2	[1]b
1930	diethanolamine	105.1	301.1 [1]	541.5 [1]	715.3 [1]	1.0947 [1]	96.4	0.59	[1]	0.260	[7]	1.28E-04	[2]	48.30 [1]	26.3	233.5	[1]b
1940	triethanolamine	149.1	294.7 [1]	608.5 [1]	787.5 [1]	1.1192 [1]	133.3	0.48	[1]	0.360	[7]	5.00E-04	[2]	101.8 [2]	21.6	310.0	[1]b
1950	pyridine	79.10	231.6 [1]	388.4 [1]	617.2 [1]	0.9778 [1]	80.9	1.02	[1]	0.715	[7]	2.77E+00	[2]	40.15 [1]	21.7	135.6	[1]a
1960	2-methylpyridine	93.13	206.4 [1]	402.6 [1]	621.1 [1]	0.9398 [1]	99.1	0.99	[1]			1.51E+00	[2]	42.92 [1]	20.2	159.2	[1]b
1970	3-methylpyridine	93.13	255.1 [1]	417.3 [1]	644.9 [1]	0.9533 [1]	97.8	0.97	[1]			8.10E-01	[2]	45.23 [1]	20.9	159.0	[1]
1980	4-methylpyridine	93.13	276.8 [1]	418.5 [1]	646.3 [1]	0.9503 [1]	98.0	0.96	[1]	0.700	[7]	7.57E-01	[1]	44.81 [1]	20.8	159.0	[2]
1990	2,4-dimethylpyridine	107.1	209.2 [1]	431.6 [1]	647.0 [1]	0.9270 [1]	115.6	0.84	[1]			3.97E-01	[t]	47.78 [1]	19.8	184.6	[ff]

continued overleaf

Table 3.1 *(continued)*

No	Name	M	Tm	Tb	Tc	d	V	α_P	κ_T	p	dHv	δ	Cp
2000	2,6-dimethylpyridine	107.1	267.1 [1]	417.2 [1]	623.8 [1]	0.9183 [1]	116.7	0.98 [1]		7.44E-01 [1]	46.06 [1]	19.3	184.9 [2]
2010	2,4,6-trimethylpyridine	121.1	229.0 [3]	444.2 [3]	645.0 [i]	0.9104 [1]	133.1	0.83 [2]		1.57E-01 [t]	50.34 [4]	19.0	214.0 [2]
2020	2-bromopyridine	158.0		467.0 [3]		1.6562 [4]	95.4				51.08 [w]	22.6	
2030	3-bromopyridine	158.0		443.0 [3]		1.6407 [4]	96.3			2.32E-01 [r]	44.66 [c]	21.5	
2040	2-cyanopyridine	104.1	301.0 [e]			1.0811 [4]	96.3				58.45 [e]	24.6	
2050	pyrimidine	80.09	295.0 [3]	396.9 [2]	397.0 [1]	1.0164 [4]	78.8	0.89 [2]		2.25E+00 [2]	49.81 [4]	24.5	133.7 [2]
2060	quinoline	129.1	258.3 [1]	510.3 [1]	794.5 [1]	1.0900 [1]	118.5	0.73 [1]	0.440 [7]	1.12E-02 [1]	64.10 [1]	22.8	200.0 [1]
2070	acetonitrile	41.05	229.3 [1]	354.8 [1]	545.5 [1]	0.7760 [1]	52.9	1.38 [1]	1.070 [7]	1.22E+01 [1]	33.23 [1]	24.1	91.4 [1]
2080	propionitrile	55.05	180.4 [1]	370.5 [1]	564.4 [1]	0.7764 [1]	70.9	1.33 [1]	1.113 [7]	6.37E+00 [1]	36.03 [1]	21.8	119.7 [1]
2090	butyronitrile	69.11	161.3 [1]	390.8 [1]	582.3 [1]	0.7862 [1]	87.9	1.16 [1]	1.004 [7]	2.62E+00 [1]	39.33 [1]	19.8	155.8 [2]
2100	valeronitrile	83.13	177.0 [2]	414.5 [2]	603.0 [2]	0.7944 [2]	104.6	1.06 [2]		9.72E-01 [2]	44.08 [2]	19.9	189.7 [2]
2110	acrylonitrile	53.06	189.6 [2]	350.5 [2]	535.0 [2]	0.8011 [2]	66.2	1.42 [2]		1.45E+01 [2]	33.26 [2]	21.6	108.6 [2]
2120	benzyl cyanide	117.1	249.4 [1]	506.7 [1]	732.0 [2]	1.0125 [1]	115.7	0.59 [1]		1.23E-02 [2]	51.90 [1]	20.7	
2130	benzonitrile	103.1	260.4 [1]	464.3 [1]	699.4 [1]	1.0003 [1]	103.1	0.83 [1]	0.621 [1]	8.64E-02 [2]	54.45 [1]	22.7	190.3 [1]f
2140	nitromethane	61.04	244.6 [1]	374.4 [1]	588.0 [1]	1.1304 [1]	54.0	1.22 [1]	0.716 [7]	4.89E+00 [1]	38.62 [1]	25.7	105.8 [1]
2150	nitroethane	75.07	183.6 [1]	387.2 [1]	557.0 [1]	1.0441 [1]	71.9	1.14 [1]	0.790 [7]	2.79E+00 [1]	40.24 [1]	22.7	138.5 [1]
2160	1-nitropropane	89.09	169.2 [1]	404.3 [1]	675.2 [1]	0.9954 [1]	89.5	1.01 [1]	0.800 [7]	1.36E+00 [1]	43.39 [1]	21.5	175.3 [1]
2170	2-nitropropane	89.09	181.8 [1]	393.4 [1]	617.9 [1]	0.9833 [1]	90.6	1.04 [1]	0.891 [7]	2.40E+00 [1]	41.34 [1]	20.3	170.2 [2]
2180	nitrobenzene	123.1	278.9 [1]	484.0 [1]	732.0 [1]	1.1987 [1]	102.7	0.85 [1]	0.508 [7]	3.50E-02 [1]	55.01 [1]	22.1	177.2 [1]b
2190	formamide	45.04	275.7 [1]	483.7 [1]	771.0 [2]	1.1288 [1]	39.9	0.75 [1]	0.399 [7]	8.82E-03 [2]	60.57 [1]	39.6	107.6 [1]
2200	N-methylformamide	59.07	269.4 [1]	472.7 [1]	721.0 [2]	0.9995 [1]	59.1	0.88 [1]	0.560 [7]	3.38E-02 [2]	56.25 [1]	31.1	123.8 [1]
2210	N,N-dimethylformamide	73.10	212.7 [1]	426.2 [1]	596.6 [1]	0.9433 [1]	77.4	1.00 [1]	0.642 [7]	5.30E-01 [1]	47.57 [1]	24.1	148.3 [1]
2220	N,N-dimethylthioformamide	89.16	264.7 [f]			1.0465 [4]	85.2						
2230	N,N-diethylformamide	101.1		451.0 [3]		0.9081 [4]	111.4	0.86 [1]		1.91E-01 [c]	49.00 [1]	20.4	
2240	N-methylacetamide	73.10	303.7 [1]	479.0 [1]	690.0 [1]	0.9494 [1]	77.0	0.88 [1]	0.630 [7]	1.24E-05 [1]	69.00 [1]	29.4	151.4 [1]
2250	N,N-dimethylacetamide	87.12	253.0 [1]	439.3 [1]	637.0 [1]	0.9368 [1]	93.0	0.98 [1]	0.630 [7]	2.40E-01 [1]	50.23 [1]	23.3	176.0 [1]a
2260	N,N-diethylacetamide	115.1		459.0 [3]		0.9048 [1]	127.3	0.87 [1]			54.11 [x]	18.3	
2270	pyrrolidinone-2	85.11	298.0 [1]	518.0 [1]	802.0 [2]	1.1069 [1]	76.9	0.90 [1]		1.30E+00 [1]		30.1	
2280	N-methylpyrrolidinone	99.13	248.8 [1]	475.0 [1]	724.0 [2]	1.0283 [1]	96.4	0.86 [1]	0.620 [7]	5.10E-02 [1]	53.96 [1]	23.6	166.1 [1]a
2290	N-methylthiopyrrolidinone	115.36	276.0 [2]	557.0 [2]	869.0 [2]	1.3451 [2]	85.6	0.69 [2]		3.02E-03 [2]	59.55 [2]	25.8	
2300	tetramethylurea	116.16	272.0 [1]	448.4 [1]		0.9656 [1]	120.3	1.41 [1]	0.910 [7]	1.22E-01 [2]	45.50 [1]	18.9	229.6 [jj]
2310	tetraethylurea	172.2	253.0 [g]	488.0 [3]		0.9064 [g]	190.0			2.61E-02 [41	63.61 [41	17.9	345.7 [jj]

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2320	dimethylcyanamide	70.09		436.7 [3]		0.8675 [4]	80.8			4.10E-01 [r]	41.14 [c]	21.9	
2330	carbon disulfide	76.13	161.6 [1]	319.4 [1]	552.0 [1]	1.2563 [1]	60.6	1.22 [1]	0.950 [1]	4.82E+01 [1]	27.52 [1]	20.3	76.0 [1]
2340	dimethyl sulfide	62.13	174.9 [1]	310.5 [1]	503.1 [1]	0.8419 [1]	73.8	1.30 [1]		6.47E+01 [1]	27.65 [1]	18.5	118.1 [1]
2350	diethyl sulfide	90.18	169.2 [1]	365.3 [1]	557.0 [1]	0.8312 [1]	108.5	1.45 [1]		7.78E+00 [1]	35.77 [1]	17.5	171.4 [1]
2360	di-i-propyl sulfide	118.2	195.1 [c]	393.6 [3]	585.7 [j[	0.8138 [4]	145.3			2.57E+00 [c]	39.64 [4]	16.4	202.6 [ii]
2370	di-n-butyl sulfide	146.2	198.1 [1]	462.1 [1]	717.0 [1]	0.8383 [1]	174.5			8.68E-02 [2]	53.60 [1]	17.1	281.2 [1]a
2380	tetrahydrothiophene	88.17	177.0 [1]	394.1 [1]	632.0 [1]	0.9940 [1]	88.7	0.95 [1]		2.45E+00 [1]	38.62 [1]	20.5	139.8 [2]
2390	pentamethylene sulfide	102.20	292.0 [3]	415.0 [3]	657.1 [j]	0.9846 [4]	103.8			1.05E+00 [c]	42.80 [u]	19.7	
2400	dimethyl sulfoxide	78.13	291.7 [1]	462.2 [1]	729.0 [2]	1.0958 [1]	71.3	0.91 [1]	0.524 [7]	7.70E-02 [1]	52.89 [1]	26.6	153.1 [1]
2410	di-n-butyl sulfoxide	162.3	305.0 [3]			0.8319 [1]	195.1						
2420	sulfolane	120.1	301.6 [1]	560.5 [1]	849.0 [2]	1.2610 [1]	95.3	0.62 [2]	0.430 [7]	9.02E-04 [2]b	79.50 [u]	27.2	180.0 [1]b
2430	thiobis(2-ethanol)	122.1	263.0 [1]	555.0 [1]	731.0 [2]	1.1805 [f]	103.5	1.10 [f]		4.30E-04 [2]	75.00 [1]	26.5	253.5 [2]
2440	diethyl sulfite	138.1		431.2 [2]	624.0 [2]	1.0830 [1]	127.6			4.30E-01 [c]	48.50 [u]	19.0	211.6 [2]d
2450	dimethyl sulfate	126.1	241.4 [3]	461.7 [3]	716.0 [2]	1.3333 [4]	94.6	0.89 [2]		1.28E-01 [c]	48.50 [u]	22.6	
2460	diethyl sulfate	154.1	248.7 [3]	481.0 [3]	749.0 [2]	1.1770 [1]	131.0	0.90 [2]		7.12E-03 [c]	56.90 [u]	20.4	
2470	methanesulfonic acid	96.11	292.8 [2]	561.0 [2]		1.4775 [2]	65.1	0.68 [2]		5.70E-05 [2]	68.26 [2]	31.8	
2480	trimethyl phosphate	140.0	227.1 [1]	470.4 [1]	722.0 [2]	1.2142 [1]	115.3	1.04 [1]	1.320 [7]	1.17E-01 [2]	47.30 [1]	21.1	
2490	triethyl phosphate	182.1	216.0 [2]	489.0 [3]	750.0 [2]	1.0696 [1]	170.3	0.96 [1]	1.490 [7]	4.76E-02 [2]	57.30 [1]	16.4	
2500	tri-n-butyl phosphate	266.3	193.0 [1]	562.0 [3]		0.9727 [1]	273.8	0.93 [1]	1.620 [7]	9.04E-04 [1]	61.42 [y]	15.3	456.80 [y]
2510	hexamethyl phosphoramide	179.2	280.4 [1]	506.0 [1]		1.0199 [1]	175.7	0.86 [1]	0.790 [7]	6.11E-03 [2]	61.1 [1]	19.1	321.30 [1]
2520	hexamethyl thiophosphoramide	195.2	302.2 [f]										
2530	hydrogen peroxide	34.02	272.7 [2]	423.4 [2]	730.2 [2]	1.4415 [2]	23.6	0.80 [2]		2.62E-01 [2]	52.2 [2]	45.9	85.53 [2]
2540	hydrogen fluoride	20.01	189.8 [2]	292.7 [2]	461.2 [2]	0.9529 [2]	21.0	2.64 [2]	4.800 [bb]	1.22E+02 [2]	25.3 [2]	33.0	50.16 [2]a
2550	sulfuric acid	98.08	283.5 [2]	610.0 [2]	925.0 [2]	1.8333 [2]	53.5	0.67 [2]		7.90E-06 [2]	86.9 [2]	25.6	139.09 [2]
2560	ammonia	17.03	195.4 [2]	239.7 [2]	405.7 [2]	0.6812 [2]	25.0	1.85 Tb		1.00E+03 [2]	19.8 [2]	29.2	82.26 [2]
2570	hydrazine	32.05	274.7 [2]	386.7 [2]	653.2 [2]	1.0047 [2]	31.9	0.86 [2]		1.92E+00 [2]	44.3 [2]	36.2	98.90 [2]
2580	sulfur dioxide	64.06	200.0 [2]	263.1 [2]	430.8 [2]	1.4626 [2]	43.8	1.80 Tb		4.00E+02 [2]	22.4 [2]	12.3	87.30 [2]
2590	thionyl chloride	118.9	172.0 [2]	348.8 [2]	567.0 [2]	1.6297 [2]	73.0	1.17 [2]		1.59E+01 [2]	30.9 [2]	19.8	119.46 [2]
2600	phosphorus oxychloride	153.3	274.3 [2]	378.7 [2]	602.2 [2]	1.6666 [2]	92.0	1.10 [2]		4.77E+00 [2]	38.5 [2]	19.8	138.83 [2]

Units: M in g mol^{-1}; T_m, T_b, T_c in K; d in g cm^{-3}; V in cm^3 mol^{-1}; α_P in 10^{-3} K^{-1}; κ_T in GPa^{-1}; p in kPa; $\Delta_V H$ in kJ mol^{-1}; δ in J$^{1/2}$ cm$^{-3/2}$; C_P in J K^{-1} mol^{-1}.

References: [1] Riddick, Bunger and Sakano 1986. [2] DIPPR 1997. [3] Lide 1994. [4] Landoldt-Börnstein 1959, 1967, 1969. [7] Marcus and Hefter 1997. [a] Kötzsch 1966; Kivinen, Murto and Lehtonen 1967; Murto *et al.* 1967; Murto, Kivinen and Lindell 1970; Rochester and Symonds 1973; Rochester and Symonds 1974; Macdonald, Dolan and Hyne 1976. [b] Klofutar, Paljk and Malneršič 1982. [c] Stephenson and Malanowski 1987. [d] Reed 1964; Banks 1970; Kirk-Othmer 1994; Hudlicky 1976; Joyner 1986. [e] Bickerton, Pilcher and G. Al-Takhin 1984. [f] Diggle and Bogsanyi 1974 (HMThPT, DMThF); Gritzner, Rechberger and Gutmann 1977 (NMThPy); V. Gutmann, Danksagmüller and Duschek 1974 (DMThF); Ikeda (1971) (S(EtOH)$_2$). [g] Kozyro *et al.* 1990. [h] Baehr, Klobasa and Scharf (1989). [i] Lin *et al.* 1980. [j] Yaws *et al.* 1989. [k] Czechowski, Zywucki and Jadzyn 1988. [l] Ksiazczak 1981; with density at 25°C from Lide 1994. [m] Inglese, Grolier and Wilhelm 1983. [n] Dallos and Ratkovics 1991. [o] Bernardo-Gil, Esquivel and Ribeiro 1990. [p] Serratrice, Delpuech and Diguet 1982. [q] Fischer and Weiss 1986. [r] Jordan 1954. [s] Lawson 1980. [t] Lencka (1990). [u] Pedley, Naylor and Kirby 1986. [v] Stephenson and Fuchs 1985. [w] Abboud and Notario 1997. Values of dHv are marked as $(\Delta H_V^o)_b$. [x] Barone *et al.* 1985. [y] McKay and Healy, 1960. [z] Domalski and Hearing 1990. [aa] Shehatta 1993. [bb] Karger, Vardag and Lüdemann 1994 (at 0°C). [cc] Tagaki and Noguchi 1992. [dd] Reddy, Naidu and Prasad 1994 (at 35°C, calculated from the reported ultrasound velocity and data in this Table for acetophenone). [ee] Barata and Serrano 1994. [ff] Chirico *et al.* 1994. [gg] Takagi *et al.* 1989. [hh] Basarova, Svoboda and Kolska 1993. [ii] C. L. Yaws and X. Pan 1992. [jj] G. J. Kabo, A. A. Kozyto, V. V. Diky and V. V. Simirsky 1995.

Table 3.2 Glass transition temperatures of some solvents, T_g in K (Angell, Sare and Sare 1978)

Solvent	T_g/K	Solvent	T_g/K
2-methylbutane	68.2	Phenol	198
benzene	131	diethyl ether	92.5
toluene	117.2	anisole	122
water	136	acetone	93
methanol	102.7	chloroform	105.9
ethanol	97.2	tetrachloromethane	130.6
1-propanol	98	pyridine	116
benzyl alcohol	171.9	acetonitrile	93
2,2,2-trifluoroethanol	144.2	nitrobenzene	161
1,2-ethanediol	154.2	N,N-dimethylformamide	129
glycerol	189.5	dimethyl sulfoxide	150

(SCF). This fluid does not any more have a free surface, that characterizes a liquid as opposed to a vapour, but may serve as a useful solvent just the same. Some substances that are gases at ambient conditions can be compressed by high pressures to become supercritical fluids and solvents, a well-known example being carbon dioxide, used extensively as an extractant for foodstuffs and pharmaceuticals. Some physical properties—the critical temperature T_C, pressure P_C, and density d_C—of supercritical solvents are shown in Table 3.3.

Contrary to the convention of reporting the properties of liquid solvents at the standard thermodynamic conditions of 298.15 K (25°C) and 0.1 MPa, there are generally no agreed conditions for the properties of supercritical solvents. These fluids are normally employed at a reduced temperature, i.e., a given fraction of the critical temperature, $T_r = T/T_C$, between 1.0 and 1.1 and at a reduced

Table 3.3 Critical properties of some 'supercritical solvents'

Supercritical solvent	T_C/K	P_C/MPa	d_C/g cm^{-3}
nitrogen	126.20	3.40	0.157
xenon	289.8	5.88	1.105
methane	190.65	4.64	0.162
ethylene	282.65	5.1	0.218

ethane	308.15	4.88	0.203
propane	369.95	4.26	0.219
n-butane	425.115	3.80	0.228
dichlorodifluoromethane	385.0	4.13	0.558
carbon dioxide	304.20	7.39	0.468
water	647.30	22.12	0.315
dinitrogen oxide	309.60	4.26	0.450
ammonia	405.55	11.4	0.236
sulfur dioxide	430.35	7.87	0.525
sulfur hexafluoride	318.70	3.76	0.736

pressure, $P_r = P/P_C$, between 1 and 2 (and corresponding reduced densities). The ratio of the critical parameters:

$$Z_C = P_C M / d_C R T_C = P_C V_C / R T_C \qquad (3.2)$$

where M is the molar mass and V the molar volume, is called the critical compressibility factor. For so-called van der Waals fluids, the P-V-T properties of the vapours of which obey the van der Waals equation, with a and b being the van der Waals constants: $(P - aV^2(V - b) = RT$, Z_C should be a universal constant (0.375), but actual fluids, as readily derived from Table 3.3, do not conform to this expectation (see DIPPR 1997) for Z_C data of liquids that are not considered supercritical solvents).

It has been found that certain solvents behave very similarly in physicochemical terms when compared at corresponding states, i.e., at the same reduced temperature, T_r. Therefore the value of T_C may be used as an important parameter of the solvent. The critical temperatures of the solvents in our List are generally not known to better than 0.1 K, and those that are known are shown in Table 3.1. There, as for the melting and boiling points, the decimal '.2' is generally a sign that the source value (Riddick, Bunger and Sakano 1986; DIPPR 1997; Lide 1994) was reported as an integral Celsius temperature.

2—
The *P-V-T* Properties of Solvents

The mutual dependence of the pressure, volume, and temperature of a substance is described by its equation of state. Many such equations have been proposed for the description of the actual properties of substances (and mixtures) in the gaseous and liquid states. The van der Waals expression is just one of these and of limited applicability. The virial equation of state:

$$PV = RT + B_2(T)P + B_3(T)P_2 + \cdots \qquad (3.3)$$

used for gases and vapours has the required flexibility of empirically describing real substances, B_2, B_3, . . . being the second, third, . . . virial coefficients. For liquids, however, the equation of state depends in a more complicated form on the intermolecular potential energy $u(r)$ and the pair correlation function $g(r)$:

$$PV = RT - (N_A RT/6V)\int r[\mathrm{d}u(r)/\mathrm{d}r]g(r)\,\mathrm{d}r \qquad (3.4)$$

but a discussion of this subject is outside the scope of this book.

The density, d, of a solvent depends on both the temperature and the pressure and its value at ambient conditions is an important characteristic. Most solvents at 25°C and 0.1 MPa have densities between those of n-pentane (0.62319 g cm^{-3}) and of tetrachloromethane

(1.58436 g cm^{-3}). The ratio of the molar mass and the density is the molar volume of the solvent: $V = M/d$, depending on the temperature and pressure in a similar, but reciprocal, manner as the density. Molar masses M of the solvents are known to 3 decimal places when expressed in g mol^{-1}, i.e., to better than 1 in 10^4, but are shown to only 2 places in Table 3.1. The densities, in g cm^{-3} at 25°C, unless otherwise noted, are shown in Table 3.1. The SI values of the densities are in kg m^{-3}, with numerical values 1000 times larger than those in g cm^{-3}. They are known to at least 4 decimal places i.e., generally again to better than 1 in 10^4, so that molar volumes could be given to at least 2 decimal places. For most purposes, however, values of V appear as factors in expressions, not in differences, so that the second decimal is not important and the values pertaining to 25°C and 0.1 MPa are shown in Table 3.1, having been rounded to the nearest 0.1 cm^3 mol^{-1}. The SI values of the liquid molar volumes are in m^3 mol^{-1}, i.e., 10^{-6} times the numerical values shown in the Table. The molar volumes of solvents on the List range from the smallest, 18.07 cm^3 mol^{-1} for water to the largest, 294.1 cm^3 mol^{-1} for *n*-hexadecane, but for most of these solvents they are within a factor of two from 100 cm^3 mol^{-1}.

The value of the molar volume of a solvent at other temperatures and pressures, not too far from the ambient, can be obtained by employing the isobaric thermal expansibility, α_p, and the isothermal compressibility, κ_T. The former of these expresses the relative increase in volume on raising the temperature at a constant pressure and the latter expresses the relative decrease of the volume on raising the pressure at a constant temperature. These quantities are also temperature and pressure dependent, but over a limited range of these variables near ambient conditions they can be taken as being constant.

The isobaric thermal expansibility is defined as:

$$\alpha_p = (\partial \ln V/\partial T)_P = V^{-1}(\partial V/\partial T)_P = -(\partial \ln d/\partial T)_P = -d^{-1}(\partial d/\partial T)_P \tag{3.5}$$

being within 30% of 1×10^{-3} K^{-1} for most solvents. This quantity is readily measured with adequate precision by measuring the density at two temperatures 10 K apart, but can be measured to a high precision with a dilatometer, that measures directly the volume expansion of a given quantity of solvent when the temperature is raised. The values of $10^3\ \alpha_p$/K^{-1} to 2 decimals are shown in Table 3.1, being often obtained as $(\Delta d/\Delta T)/d$(25°C) from data at 15 or 20 and 30°C (Riddick, Bunger and Sakano 1986).

The isothermal compressibilities are defined as:

$$\kappa_T = -(\partial \ln V/\partial P)_T = -V^{-1}(\partial V/\partial P)_T \tag{3.6}$$

and have been measured for fewer solvents than the expansibilities. High pressures are generally required in order to obtain significant changes in the volume or density. The Tait equation:

$$[1 - V(P)/V(P^\circ)] = C \log[(B + P)/(B + P^\circ)] \tag{3.7}$$

is often invoked for this purpose, from which $\kappa_T = (\ln 10)C/(B + P^{o})$ is obtained, where B and C are empirical, generally temperature-dependent, constants. Alternatively, the adiabatic, isentropic, compressibility:

$$\kappa_S = -V^{-1}(\partial V/\partial P)_S = (u^2 d)^{-1} \qquad (3.8)$$

can be used, obtained from measurements of the ultrasound velocity u and the density d at ambient pressure. This quantity can be converted to the isobaric compressibility by the addition of $TV\alpha_P^2 C_P^{-1}$, where C_p is the molar constantpressure heat capacity. Values of κ_T/GPa^{-1} from such sources, ranging from 0.25 to 2.50 GPa^{-1} for the solvents in our List and reported in Table 3.1 for 25°C are generally accurate to 3 decimals. Note that for solvents with oblate molecules (see below), such as aromatic ones, the compressibilities are generally lower than for chain-like molecules of similar molecular masses, and that there is a general decrease of κ_T as the molecules become larger. The temperature dependence of κ_T is ~ 0.7% K^{-1} at ambient conditions, but κ_T diverges to infinity at the critical temperature.

Additional values of the isothermal compressibility can be estimated for the many solvents for which no values of k_T or k_S have been determined experimentally from a correlation with other solvent properties (Marcus and Hefter 1997):

$$\begin{aligned}\kappa_T/\mathrm{GPa}^{-1} &= 0.024 + 0.0235(V/\mathrm{cm}^3\,\mathrm{mol}^{-1}) - 0.0266(V_X/\mathrm{cm}^3\,\mathrm{mol}^{-1}) \\ &\quad + 564(\alpha_P/\mathrm{K}^{-1}) + 5.25(p/\mathrm{MPa}) \qquad (3.9)\end{aligned}$$

where V_x is a measure of the intrinsic volume and p is the vapour pressure (see below for both quantities), with all the variable values being those for 25°C. Figure 3.1 shows the applicability of this expression. Such values have been estimated (Marcus and Hefter 1997) and are shown in Table 3.1, marked by m, and are considered to be accurate to 2 decimals only, so that the zero in the third decimal is insignificant. Further values can similarly be estimated by means of Eq. (3.9), with corrections possibly being required (Marcus and Hefter 1997) for long aliphatic chains in the solvent molecules.

3—

Vaporization Properties of Solvents

The vapour pressure, p, of a solvent at 25°C is an important quantity and varies considerably among common solvents, some being very volatile, such as *n*- pentane and diethyl ether, with $p = 68.7$ and 71.6 kPa, respectively at this temperature, whereas others are quite non-volatile, such as *n*-hexadecane and dibutyl phthalate, with $p = 2 \times 10^{-4}$ and 1×10^{-5} kPa, respectively. The values of the vapour pressure of the solvents in our List at 25°C (or where otherwise noted, for solvents not liquid at 25°C), p/kPa in exponential notation ('E ± k' ≡ $10^{\pm k}$), are shown in Table 3.1 and pertain to the saturation value,

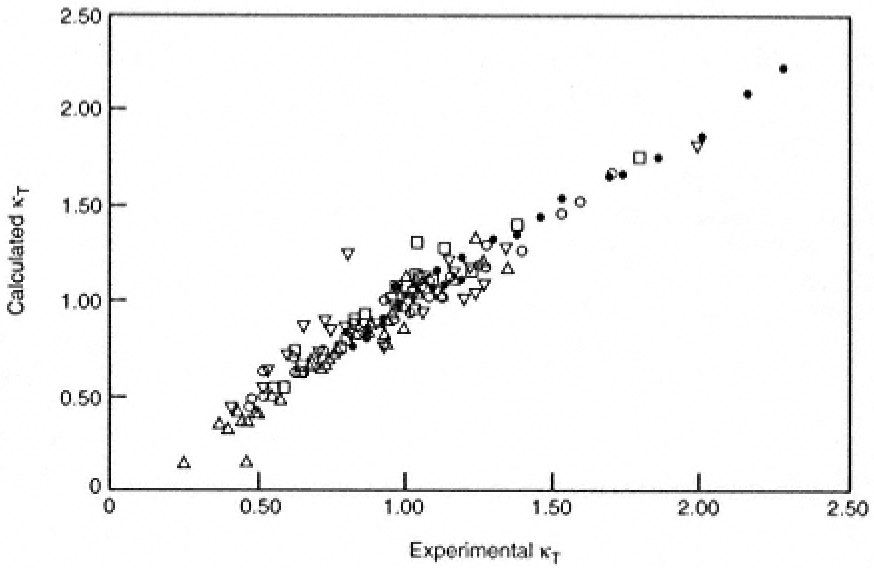

Figure 3.1
The isothermal compressibilities (in GPa^{-1}) of solvents calculated from Eq. (3.8) plotted against the experimental values. Dots (●) pertain to hydrocarbons upright triangles (Δ) to hydroxy compounds, circles (○) to oxy-compounds, squares (□) to halogen substituted compounds, and downward pointing triangles (∇) to nitriles and amines

since 25°C is generally below T_b. For the three solvents where this is not the case, the vapour pressures quoted are at 20°C for hydrogen fluoride, and at 25°C but at $p > P^o$ for ammonia and sulfur dioxide.

Of course, the vapour pressure is very temperature dependent, and reaches $P^o = 101.325$ kPa at the normal boiling point, T_b. The isochoric thermal pressure coefficient, $\partial p/\partial T)_V = \alpha_p/\kappa_T$, can be obtained from the two quantities on the right hand side listed in Table 3.1. Except at T_c, it does not equal the coefficient along the saturation line, $(\partial p/\partial T)_\sigma$, which is the normal vapour pressure curve. The latter temperature dependence is often described by means of the Antoine equation:

$$\log p = A - B/(T - C) \qquad (3.10)$$

The constant A depends on the units of p, often quoted in torr, 1 torr = 1 mmHg = 133.3 Pa, and the constant C is zero for many solvents, while the numerical values of A, B, and C may be different in different temperature ranges (Riddick, Bunger and Sakano 1986). Another way to obtain the temperature dependence of the vapour pressure, $(\partial p/\partial T)_\sigma$, is by means of the enthalpy of vaporization.

In general, the molar enthalpy of vaporization is obtained from the Clausius–Clapeyron equation, representing the difference per mole of the enthalpy of the vapour and of the liquid at equilibrium with it:

$$\Delta_V H = RT^2(\partial \ln p/\partial T)_\sigma(1 + B_2 V^g) \approx RT^2(\partial \ln p/\partial T)_\sigma \qquad (3.11)$$

where B_2 is the second virial coefficient of the vapour and V^g is its molar volume. The approximation due to neglecting the volume of the liquid relative to that of the vapour is completely justified, but that due to the treating of the latter as an ideal gas neglecting the B_2V^g term, the second expression on the right hand side, can lead to errors, when $\Delta_V H$ is to be derived from data near the boiling point. For example, for benzene at 353 K (~ T_b) $V^g = 29.0$ m^3 mol^{-1}, $V = 0.096 \times 10^{-3}$ m^3 mol^{-1}, $B_2 = -0.96 \times 10^{-3}$ m^3 mol^{-1}, so that the error in neglecting the term in the second virial coefficient is ca. 3% of $\Delta_V H$. However, if the approximation is applied at T_b - 100 K, the error is < 0.1%. If the values of B and C of the Antoine equation are known at about 25°C, then the molar latent heat of vaporization at this temperature can be obtained from:

$$\Delta_V H \approx -R \ln 10 BT^2/(T - C)^2 \qquad (3.12)$$

to the same degree of approximation. The enthalpy of vaporization depends on the temperature, and is approximately constant only over short temperature intervals. The values of the molar heat of vapourization of the solvents in our List at 25°C, except where otherwise noted, $\Delta_V H$/kJ mol^{-1}, are shown in Table 3.1. If the second decimal is zero, then the value quoted is known to no better than 0.1 kJ mol^{-1}, otherwise it is known to 0.01 kJ mol^{-1} or better. The values of $\Delta_V H$/kJ mol^{-1} vary from 19.9 for ammonia and formic acid to 101 for triethylene glycol and triethanolamine. For a homologous series they increase with the size of the molecules of the solvents, and they are appreciably higher for strongly molecularly associated solvents, except where the vapour is also associated, as for the lower carboxylic acids and hydrogen fluoride, than for non-associated ones of similar size. In only a few cases are these data lacking, but in some of them $\Delta_V H$ at T_b is known (Riddick, Bunger and Sakano 1986; DIPPR 1997), or can be estimated for non-associated liquids from Trouton's rule (see Table 4.1):

$$\Delta_V H(T_b) = T_b \Delta_V S(T_b) \qquad (3.13)$$

with the entropy of vaporization $\Delta_V S(T_b) = (11.0 \pm 0.6)R$ being Trouton's constant for non-associating solvents.

The inverse of the thermal pressure coefficient, $(\partial p/\partial T)_\sigma$ along the saturation line $(\partial T_b/\partial P)_\sigma$, determined at the boiling point, is the pressure coefficient of the boiling temperature, which has been given in Eq. (3.1) as ~ 9.0×10^{-4} KkPa^{-1} (valid within ± 20%) for many solvents.

A quantity that is closely related to the molar enthalpy of vaporization is the molar energy of vaporization:

$$\Delta_V U = \Delta_V H - P\Delta V \cong \Delta_V H - RT \qquad (3.14)$$

This equals the negative of the internal (configurational) energy of the solvent, E_{conf}, which is related to its pair potential *u(r)* (see Eq. (3.18)) and pair correlation function *g(r)* on the molecular level (Marcus 1977):

$$E_{conf} = 2\pi N_{Av}^2 V^{-1} \int_0^\infty u(r) g(r) r^2 \, dr \qquad (3.15)$$

The pair correlation function is a short range quantity in liquids, decaying to unity after a few molecular diameters, the correlation length ξ. However, in supercritical fluids *g(r)* has a much longer range and ξ becomes considerably larger than the mean inter-molecular separation at the critical density. For instance, for carbon dioxide $\xi = 5.5$ nm at T_C compared to the mean intermolecular separation of 0.55 nm (Eckert, Knutson and Debenedetti 1996).

From the configurational energy of the solvent are derived several other significant properties. One is the internal pressure (see Chapter 4), $P_i = \partial\Delta_V U/\partial V)_T = T(\partial p/\partial T)_V - P \cong T\,\alpha_P/\kappa_T$. The ambient pressure term *P* is generally negligible, the internal pressures being of the order of 100 to 1000 MPa. Another derived quantity is the cohesive energy density, $\Delta_V U/V$, measuring the energy that has to be input into unit volume of the solvent in order to bring all its molecules contained in this volume to the ideal gas state, i.e., to be at infinite distances from and not interacting with one another. Its square root, the (Hildebrand) solubility parameter:

$$\delta = (\Delta_V U/V)^{1/2} = [(\Delta_V H - RT)/V]^{1/2} \qquad (3.16)$$

is used a great deal in the estimation of the mutual solubilities of liquids, the solubilities of solutes in solvents, and other purposes. Values of the solubility parameters, $\delta/\mathrm{J}^{1/2}\ \mathrm{cm}^{-3/2}$ equiv; $\delta/\mathrm{MPa}^{1/2}$, of the solvents in our List are shown in Table 3.1, having been calculated from $\Delta_V H$ and V values from the same Table, hence are not annotated. The values of $\delta/\mathrm{J}^{1/2}\ \mathrm{cm}^{-3/2}$ for non-associated solvents are generally between 12 and 22, whereas they are considerably higher for associated ones, the maximal value noted being 47.9 for water, due to its very small molar volume. The values of δ are, in principle, temperature dependent, and the listed values pertain to 25°C, at which they are generally employed, unless the $\Delta_V H$ and V values pertain to a different temperature as noted for the *d* values. For supercritical fluids, the expression:

$$\delta = 1.25 P_C^{1/2} \qquad (3.17)$$

was proposed, possibly modified by the ratio of the reduced densities of the supercritical fluid and the corresponding liquid, where P_C is the critical pressure, see Table 3.3 (K. Giddings, M. N. Myers and J. W. King 1969).

4—

The Heat Capacity of Solvents

When a solvent is heated at constant pressure it absorbs the energy both in its internal degrees of freedom, vibrations and rotations, and by letting its temperature increase, kinetic energy, i.e., translation. The measure of the energy input required for raising the temperature of a mole of solvent by a unit is the molar heat capacity (at constant pressure), C_p. This quantity has been measured for a large number of solvents to a good accuracy, and the values at 25°C, in J K^{-1} mol^{-1}, given to 2 decimals, are shown in Table 3.1. Values with '00' or '0' as the last decimals have been given in the original with fewer valid digits. The heat capacity at constant volume, C_V is much less readily measured, and if required can be calculated as: $C_V = C_P - \alpha_P^2 VT/\kappa_T$, i.e., from the expansibility, compressibility, and molar volume. The heat capacity itself depends on the temperature, although not strongly at temperatures remote from the critical point. It figures in many thermodynamic derivations, as also in a measure of the structuredness of the solvents (see Chapter 4). Sometimes the mass specific heat is required and is readily calculated from the data in Table 3.1, $c = C_p/M$, in J K^{-1} g^{-1}. The molar heat capacities vary from 50 for hydrogen fluoride to ~ 500 J K^{-1} mol^{-1} for *n*-hexadecane and dibutyl phthalate, increasing in general with the number of bonds in the molecules of the solvents.

5—

The Molecular Sizes of Solvents

The molecular size of a solvent can be characterized in several ways. One of them is to assign the solvent a 'molecular diameter', as if its molecules were spherical. From a different aspect, this diameter characterizes the 'cavity' occupied by a solvent molecule in the liquid solvent. From a still further aspect, this is the mean distance between the centers of mass of two adjacent molecules in the liquid. The diameter plays a role in many theories pertaining to the liquid state, not least to those treating solvent molecules as hard spheres, such as the scaled particle theory (SPT, see below). Similar quantities are the 'collision diameters' σ of gaseous molecules of the solvent, or the distance characterizing the minimum in the potential energy curve for the interaction of two solvent molecules. The latter quantity may be described, e.g., according to the Lennard–Jones potential (Marcus 1977) (Fig. 3.2):

$$u^{LJ}(r) = 4\varepsilon[(r_0/r)^{12} - (r_0/r)^6] \qquad (3.18)$$

where r_o is the equilibrium distance, $r_0 = 2^{1/6}\sigma$ and $u^{LJ}(\sigma) = 0$, while $u^{LJ}(r(r_0) = -\varepsilon$ is the depth of the potential well. It is not to be expected that these various 'diameters' obtained from experimental data or theory are close to each other for a given solvent, since most solvents are not particularly spherical, being more prolate or oblate in molecular shape.

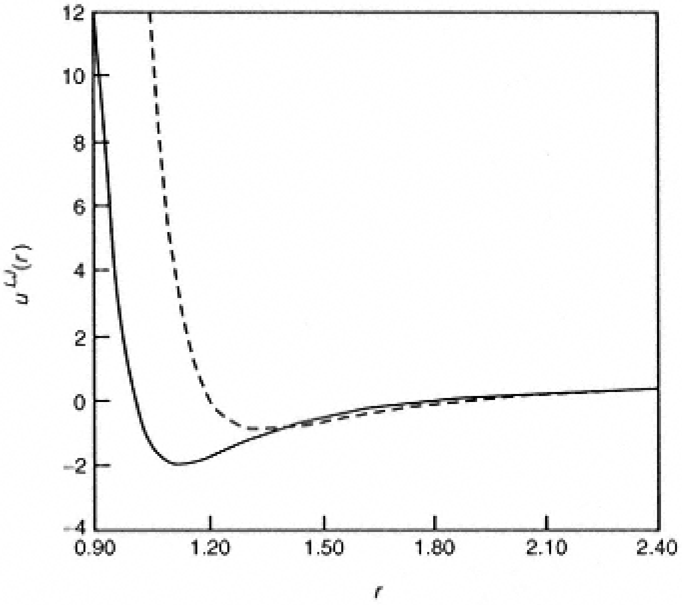

Figure 3.2
The Lennard–Jones pair interaction energy, $u^{\mathrm{LJ}}(r)$ as a function of the intermolecular distance r. The continuous curve has the values in Eq. (3.18) of $\varepsilon = 8$ and $r_0 = 1.0$ and the dashed curve of $\varepsilon = 4$ and $r_0 = 1.2$ in arbitrary units

A quantity obtained from the molar volume, $\sigma_{\mathrm{V}} = [(6/\pi)V / N_{\mathrm{Av}}]^{1/3}$ is sometimes used in lieu of a better value of the molecular diameter. This has the drawback that it makes the diameter temperature-dependent, although much more moderately than is V itself because of the cube-root dependence, but mainly because it ignores the packing of the molecules in the liquid, i.e., the necessary existence of void volume in it. A packing factor, $k_{\mathrm{p}} = 1.725$, valid for the close packing of spheres obtained empirically with steel balls of uniform size can be introduced to yield $\sigma'_{\mathrm{V}} = [(6/\pi)V/K_{\mathrm{p}}N_{\mathrm{Av}}]^{1/3} = 0.834\sigma_{\mathrm{V}}$ as a more realistic value. For values of V in cm^3 mol^{-1} and &sgr$'_{\mathrm{V}}$ in nm this becomes: $\sigma'_{\mathrm{V}} = 0.1225V^{1/3}$. An empirical value, still based on the molar volume, that has been obtained from a fit to some 50 solvents (Kim 1978) is:

$$\sigma'_{\mathrm{V}} = 0.1363V^{1/3} - 0.085 \qquad (3.19)$$

with the quantities in the same units as above.

The packing fraction, y (the reciprocal of the cube root of the packing factor k_{p}), need not be the same for all solvents; indeed it is expected to depend on the deviation of the shape of the solvent molecule from sphericity. The scaled particle theory, SPT, relates the packing fraction in a solvent, with near spherical molecules, to some of its thermophysical properties (Marcus 1986) as follows:

$$y = -0.0469 + 0.4418(\log Y) - 0.0520(\log Y)^2 \qquad (3.20)$$

where $Y = [\Delta_v H/RT) - 1]/T\alpha^P$. The assigned diameter is then $\sigma_{SPT} = 0.14692 Y^{1/3} V^{1/3}$, again with the diameter in nm and the volume in cm^3 mol^{-1}. The values shown in Table 3.4 have all been obtained in this way from the data in Table 3.1, where missing data of α_p have arbitrarily been assigned the value 0.001 K^{-1}, with a minimal effect on σ_{SPT} due to the logarithm and cube root in the expressions.

A quite different approach to the molecular size of solvents is the estimation of its molecular surface area and volume from the van der Waals radii of the constituent atoms and the manner and geometry of their mutual bonding (Bondi 1964). The necessary calculations are quite involved, and the values shown in Table 3.4 have been taken from a single source (DIPPR 1997), in order to be consistent. The reported molar van der Waals surface areas, A_{vdW}, are in 10^4 m^2 mol^{-1} and the molar van der Waals volumes, V_{vdW}, are in cm^3 mol^{-1}, the latter in order to be comparable with the molar volumes (in Table 3.1) and the intrinsic volumes, defined below, also reported in Table 3.4.

The ratio of the van der Waals surface area to the van der Waals volume, A_{vdW}/V_{vdW}, is a measure of the shape of the molecules: whether oblate ($A_{vdW}/V_{vdW} \leq 1.33$), globular ($1.33 \leq A_{vdW}/V_{vdW} \leq 1.40$), or prolate ($1.40 \leq A_{vdW}/V_{vdW}$), the numerical values being in 10^{10} m^{-1}. Aromatic solvents as well as alicyclic and heterocyclic solvents are, as expected, oblate, with typical A_{vdW}/V_{vdW} values of 1.24–1.28. Chain-like aliphatic molecules are prolate, with A_{vdW}/V_{vdW} decreasing with the chain length from ~ 1.56 for 2-carbon solvents down to ~ 1.37 for 10-carbon solvents, probably due to folding of the longer alkyl chains. Very small molecules, such as water, hydrogen fluoride, ammonia, and chloroform have values of this ratio > 1.75.

For various purposes it is necessary to know the intrinsic volume of a mole of the solvent molecules as they are in the liquid solvent, which should be a temperature- and pressure-independent quantity, since only the amount of void space is taken to increase on thermal expansion and decrease on compression. The van der Waals volume is one measure of the intrinsic volume, but several ways of its calculation lead to somewhat different results. In particular, this calculated volume should depend on the conformation of the molecules in the liquid, whether extended or folded, and if the latter, to what average shape. This problem can be circumvented by the calculation of V_X (McGowan 1978, 1984; Abraham and McGowan 1987), that depends additively and solely on the numbers N_i and kinds i of atoms constituting the solvent and the number of bonds between these atoms, N_{bonds}. The following values of V_{Xi}/cm^3 mol^{-1} have been assigned to the atoms to be found in the solvents in our List:

C 16.35, H 8.71, O 12.43, N 14.39, F 10.48, Cl 20.95, Br 26.21, I 34.53, S 22.91, P 24.87, and Si 26.83, and to a bond: -6.56 (irrespective of whether single, double or triple).

Table 3.4 The sizes of solvent molecules (or prorated per mole)

No.	Name	Diameter	VdW surf.	VdW vol.	Intrin. volume
10	tetramethylsilane	0.596	88.7	64.3	91.8
20	n-pentane	0.546	82.9	58.0	81.3
30	2-methylbutane	0.542	82.8	58.0	81.3
40	n-hexane	0.587	96.4	68.3	95.4
50	c-hexane	0.559	81.0	61.4	84.5
60	n-heptane	0.623	109.9	78.5	109.5
70	n-octane	0.655	123.4	88.7	123.6
80	2,2,4-trimethylpentane	0.641	125.2	88.7	123.6
90	n-decane	0.711	150.4	109.2	151.8
100	n-dodecane	0.761	177.4	129.6	179.9
110	n-hexadecane	0.845	231.4	170.6	236.3
120	benzene	0.526	60.0	48.4	71.6
130	toluene	0.568	74.2	59.5	85.7
140	o-xylene	0.601	88.4	70.7	99.8
150	m-xylene	0.604	88.4	70.7	99.8
160	p-xylene	0.605	88.4	70.7	99.8
170	ethylbenzene	0.602	88.0	69.7	99.8
180	cumene	0.634	101.4	80.0	113.9
190	mesitylene	0.637	102.6	81.8	113.9
200	styrene	0.593	82.7	66.3	95.5
210	tetralin	0.648	91.2	81.0	117.1
220	cis-decalin	0.666	113.7	94.3	125.7
230	water	0.343	22.6	12.4	16.7
240	methanol	0.408	35.8	21.7	30.8
250	ethanol	0.469	49.3	31.9	44.9
260	n-propanol	0.515	62.8	42.2	59.0
270	i-propanol	0.516	62.7	42.2	59.0
280	n-butanol	0.558	76.2	52.4	73.1
290	i-butanol	0.557	76.2	52.4	73.1
300	2-butanol	0.552	76.2	52.4	73.1
310	t-butanol	0.548	76.2	52.3	73.1
320	n-pentanol	0.594	89.8	62.6	87.2
330	i-pentanol	0.597	89.7	62.6	87.2
340	t-pentanol	0.582	91.7	62.6	87.2
350	n-hexanol	0.627	103.3	72.9	101.3

360	c-hexanol	0.592	87.8	64.8	90.4
370	n-octanol	0.685	130.3	93.3	129.5
380	n-decanol	0.727	157.3	113.8	157.6
390	n-dodecanol	0.770	184.3	134.2	185.8
400	benzyl alcohol	0.596	81.1	64.1	91.6
410	2-phenylethanol	0.626	94.6	74.3	105.6
420	allyl alcohol	0.490	57.5	38.7	54.7
430	2-chloroethanol	0.555	59.6	40.1	57.2
440	2-cyanoethanol	0.505			60.4
450	2,2,2-trifluoroethanol*	0.501	57.9		41.5
460	hexafluoro-i-propanol	0.551			69.6
470	2-methoxyethanol	0.533	68.8	45.9	67.0

(table continued on next page)

***Table 3.4** (continued)*

No.	Name	Diameter	VdW surf.	VdW vol.	Intrin. volume
480	2-ethoxyethanol	0.565	82.3	56.1	81.1
490	1,2-ethanediol	0.487	56.2	36.5	50.8
500	1,2-propanediol	0.533	69.6	46.8	64.9
510	1,3-propanediol	0.537	69.7	46.8	64.9
520	1,2-butanediol	0.569	83.1	57.0	79.0
530	2,3-butanediol (meso)	0.559	83.0	57.0	79.0
540	1,4-butanediol	0.574	83.2	57.0	79.0
550	1,5-pentanediol	0.612	96.7	67.2	93.1
560	diethyleneglycol	0.575	79.2	60.7	84.8
570	triethyleneglycol	0.664	122.0	84.9	118.9
580	glycerol	0.547	76.5	51.3	70.7
590	phenol	0.557	67.9	53.8	77.5
600	2-methylphenol	0.595	81.8	65.0	91.6
610	3-methylphenol	0.595	81.8	65.0	91.6
620	4-methylphenol	0.601	81.8	65.0	91.6
630	2-methoxyphenol	0.600			97.5
640	2,4-dimethylphenol	0.623	93.3	73.8	105.7
650	3-chlorophenol	0.580	78.7	63.4	89.8
660	diethyl ether	0.529	75.4	51.5	73.1
670	di-n-propyl ether	0.607	102.2	72.0	101.3
680	di-i-propyl ether	0.601	102.2	71.9	101.3
690	di-n-butyl ether	0.669	128.8	91.9	129.5
700	di(2-chloroethyl) ether	0.599			97.6
710	1,2-dimethoxyethane	0.558	81.4	55.2	79.0
720	bis(methoxyethyl) ether	0.635	114.4	79.4	113.0
730	furan	0.502	43.5	36.4	53.6
740	tetrahydrofuran	0.504	54.3	43.5	62.2
750	2-methyl tetrahydrofuran	0.553			76.3
760	tetrahydropyran	0.550			76.3
770	dioxane	0.524	59.0	46.6	68.1
780	dioxolane	0.492			54.0
790	1,8-cineole	0.660			135.9
800	anisole	0.584	79.3	62.4	91.6
810	phenetole	0.619	92.8	72.6	105.7

820	diphenyl ether	0.684	112.6	95.4	138.3
830	dibenzyl ether	0.744	139.6	115.8	166.5
840	1,2-dimethoxybenzene	0.619			119.8
850	trimethyl orthoformate	0.581			84.8
860	trimethyl orthoacetate	0.620			98.9
870	propionaldehyde	0.478	58.4	39.0	54.7
880	butyraldehyde	0.528	71.9	49.3	68.8
890	benzaldehyde	0.607	77.0	61.0	87.3
900	p-methoxybenzaldehyde	0.617			107.3
910	cinnamaldehyde	0.629			111.2
920	acetone	0.482	58.4	39.0	54.7

continued overleaf

***Table 3.4** (continued)*

No.	Name	Diameter	VdW surf.	VdW vol.	Intrin. volume
930	2-butanone	0.525	71.9	49.3	68.8
940	2-pentanone	0.573	85.4	59.5	82.9
950	methyl i-propyl ketone	0.563	85.3	59.5	82.9
960	3-pentanone	0.562	85.4	59.5	82.9
970	c-pentanone	0.541	70.0	52.6	72.0
980	methyl-i-butyl ketone	0.600	98.8	69.7	97.0
990	methyl t-butyl ketone	0.602			97.0
1000	c-hexanone	0.575	83.5	62.9	86.1
1010	2-heptanone	0.633	112.4	80.0	111.1
1020	3-heptanone	0.636	112.4	80.0	111.1
1030	di-t-butyl ketone	0.679			139.2
1040	acetophenone	0.610	89.3	70.4	101.4
1050	propiophenone	0.635			115.5
1060	phenylacetone	0.626			115.5
1070	p-methylacetophenone				115.5
1080	p-chloroacetophenone	0.632			120.2
1090	benzophenone	0.709	136.2	106.4	148.1
1100	acetylacetone	0.564	87.9	61.0	84.5
1110	biacetyl	0.535			70.4
1120	formic acid	0.381	36.3	22.7	32.4
1130	acetic acid	0.442	51.8	33.3	46.5
1140	propanoic acid	0.518	65.3	43.6	60.6
1150	n-butanoic acid	0.560	78.8	53.9	74.7
1160	n-pentanoic acid	0.600	92.3	63.9	88.8
1170	n-hexanoic acid	0.632	105.8	74.3	102.8
1180	n-heptanoic acid	0.666	119.3	84.3	116.9
1190	dichloroacetic acid	0.539	72.7	51.0	64.4
1200	trifluoroacetic acid	0.492	65.1	41.1	51.8
1210	acetic anhydride	0.554	86.4	54.4	76.2
1220	benzoyl chloride	0.606	90.1	68.6	99.5
1230	benzoyl bromide	0.608			104.8
1240	methyl formate	0.450	50.9	32.5	46.5
1250	ethyl formate	0.499	64.4	42.7	60.6
1260	methyl acetate	0.497	64.4	42.5	60.6

1270	ethyl acetate	0.539	77.9	52.8	74.7
1280	propyl acetate	0.578	91.4	63.0	88.8
1290	butyl acetate	0.613	104.9	73.2	102.9
1300	i-pentyl acetate	0.646	117.8	83.5	117.0
1310	methyl propanoate	0.539	77.9	52.8	88.8
1320	ethyl propanoate	0.578	91.4	63.0	102.9
1330	dimethyl carbonate	0.520	70.4	46.2	66.4
1340	diethyl carbonate	0.596	97.4	66.7	94.6
1350	ethylene carbonate	0.535	49.3	38.2	55.6
1360	propylene carbonate	0.550	57.0	45.2	69.7
1370	diethyl malonate	0.662	126.9	88.4	124.4
1380	methyl benzoate	0.623	95.3	73.9	113.8
1390	ethyl benzoate	0.651	108.8	84.1	127.9

(table continued on next page)

Table 3.4 *(continued)*

No.	Name	Diameter	VdW surf.	VdW vol.	Intrin. volume
1400	dimethyl phthalate	0.695	130.6	99.5	171.1
1410	dibutyl phthalate	0.827	211.6	160.8	253.7
1420	ethyl chloroacetate	0.564	88.2	60.9	86.9
1430	ethyl trichloroacetate	0.633			111.4
1440	ethyl acetoacetate	0.622	107.4	74.7	104.4
1450	4-butyrolactone	0.527	62.5	45.9	63.8
1460	perfluoro-n-hexane	0.683			120.2
1470	perfluoro-n-methylcyclohexane	0.693			110.3
1470	perfluoro-n-heptane	0.701			137.8
1490	perfluoro-decalin	0.755			161.9
1500	fluorobenzene	0.537	63.1	50.8	73.4
1510	hexafluorobenzene	0.568	78.6	63.2	82.3
1520	l-chlorobutane	0.571	79.7	56.0	79.5
1530	chlorobenzene	0.566	71.4	57.8	83.9
1540	dichloromethane	0.460	49.9	34.7	49.4
1550	l,l-dichloroethane	0.507	63.3	44.9	63.5
1560	1,2-dichloroethane	0.509	63.0	43.7	63.5
1570	tr-1,2-dichloroethylene	0.491	57.6	40.1	59.2
1580	o-dichlorobenzene	0.599	84.6	65.7	96.1
1590	m-dichlorobenzene	0.599	84.6	65.7	96.1
1600	chloroform	0.502	76.6	43.5	61.7
1610	1,1,1-trichloroethane	0.542	75.8	53.7	75.8
1620	1,1,2-trichloroethane	0.548	73.6	53.1	75.8
1630	trichloroethylene	0.529	71.3	49.5	71.5
1640	1,2,4-trichlorobenzene	0.625	123.3	101.0	108.4
1650	tetrachloromethane	0.537	72.8	52.3	73.9
1660	tetrachloroethylene	0.564	85.0	59.0	83.7
1670	1,1,2,2-tetrachloroethane	0.578	84.2	62.5	88.0
1680	pentachloroethane	0.605	96.7	71.3	100.2
1690	1-bromobutane	0.566	82.5	58.8	104.4
1700	bromobenzene	0.580	73.4	60.2	89.1
1710	dibromomethane	0.495	55.3	38.4	60.0
1720	1,2-dibromoethane	0.538	68.6	49.3	74.0
1730	bromoform	0.544	68.1	50.0	77.5

1740	1-iodobutane	0.586			112.7
1750	iodobenzene	0.596	77.2	64.7	97.5
1760	diiodomethane	0.535	64.3	50.9	76.6
1770	n-butylamine	0.542	79.1	54.9	77.2
1780	benzylamine	0.595	84.0	66.6	95.7
1790	1,2-diaminoethane	0.505	96.6	41.5	59.0
1800	diethylamine	0.537	79.3	55.8	77.2
1810	di-n-butylamine	0.675	133.3	96.8	133.6
1820	pyrrole	0.501	53.1	42.0	57.7
1830	pyrrolidine	0.520	63.9	49.0	66.3
1840	piperidine	0.546	77.4	59.2	80.4

continued overleaf

***Table*3.4** *(continued)*

No.	Name	Diameter	VdW Surf.	VdW Vol.	Intrin. volume
1850	morpholine	0.542	69.9	52.7	72.2
1860	triethylamine	0.608	106.4	76.0	105.4
1870	tri-n-butylamine	0.774	187.4	137.4	189.9
1880	aniline	0.562	70.4	56.4	81.6
1890	o-chloroaniline	0.593	90.9	66.4	93.9
1900	N-methylaniline	0.596	84.1	67.6	95.7
1910	N,N-dimethylaniline	0.622	96.8	76.7	109.8
1920	ethanolamine	0.496	59.0	39.0	54.9
1930	diethanolamine	0.578	93.1	65.1	88.9
1940	triethanolamine	0.674	127.1	89.8	123.0
1950	pyridine	0.522	66.5	45.5	67.5
1960	2-methylpyridine	0.562	81.2	56.7	81.6
1970	3-methylpyridine	0.562	81.2	56.7	81.6
1980	4-methylpyridine	0.563	81.2	56.7	81.6
1990	2,4-dimethylpyridine	0.602			95.7
2000	2,6-dimethylpyridine	0.597	86.0	67.8	95.7
2010	2,4,6-trimethylpyridine	0.627	110.7	79.0	109.8
2020	2-bromopyridine	0.561			85.0
2030	3-bromopyridine	0.558			85.0
2040	2-cyanopyridine	0.568			83.0
2050	pyrimidine	0.529	45.6	42.6	63.4
2060	quinoline	0.623	76.4	71.1	104.4
2070	acetonitrile	0.436	43.1	28.4	40.4
2080	propionitrile	0.485	56.6	38.6	54.5
2090	butyronitrile	0.531	70.1	48.8	68.6
2100	valeronitrile	0.571	83.6	59.1	82.7
2110	acrylonitrile	0.468	51.3	35.1	50.2
2120	benzyl cyanide	0.617	88.7	70.8	101.2
2130	benzonitrile	0.585	75.2	60.5	87.1
2140	nitromethane	0.449	46.9	30.5	42.4
2150	nitroethane	0.498	60.2	40.7	56.5
2160	1-nitropropane	0.543	73.7	50.9	70.6
2170	2-nitropropane	0.542	73.6	50.9	70.6
2180	nitrobenzene	0.584	77.6	61.8	89.1

2190	formamide	0.431	41.1	25.5	36.5
2200	N-methylformamide	0.485	54.8	36.5	50.6
2210	N,N-dimethylformamide	0.521	68.4	46.8	58.1
2220	N,N-dimethylthioformamide				75.2
2230	N,N-diethylformamide	0.595			92.9
2240	N-methylacetamide	0.536	68.3	47.1	64.7
2250	N,N-dimethylacetamide	0.557	81.9	57.0	78.8
2260	N,N-diethyl acetamide	0.618			105.0
2270	pyrrolidinone-2		66.4	50.5	67.9
2280	N-methylpyrrolidinone	0.570	80.0	60.4	82.0
2290	N-methylthiopyrrolidinone	0.558	94.8	65.8	92.6
2300	tetramethylurea	0.587			102.8
2310	tetraethylurea	0.716			159.2

(table continued on next page)

Table 3.4 *(continued)*

No.	Name	Diameter	VdW surf.	VdW vol.	Intrin. volume
2320	dimethylcyanamide	0.523			64.5
2330	carbon disulfide	0.453	47.5	31.2	49.1
2340	dimethyl sulfide	0.481	55.4	38.1	55.4
2350	diethyl sulfide	0.555	82.4	58.6	83.6
2360	di-i-propyl sulfide	0.634			111.8
2370	di-n-butyl sulfide	0.689			140.0
2380	tetrahydrothiophene	0.539	67.0	51.7	72.7
2390	pentamethylene sulfide	0.570			86.8
2400	dimethyl sulfoxide	0.513	61.4	41.8	61.3
2410	di-n-butyl sulfoxide				145.8
2420	sulfolane	0.590	80.0	61.2	84.5
2430	thiobis(2-ethanol)	0.587	96.2	68.8	95.3
2440	diethyl sulfite	0.616	100.8	70.7	101.2
2450	dimethyl sulfate	0.562	76.4	62.4	78.9
2460	diethyl sulfate	0.632	103.4	82.9	107.1
2470	methanesulfonic acid	0.513	61.8	42.0	58.9
2480	trimethyl phosphate	0.593	94.6	66.8	72.2
2490	triethyl phosphate	0.688	135.0	97.5	114.5
2500	tri-n-butyl phosphate	0.810			199.0
2510	hexamethyl phosphoramide	0.702	135.1	97.4	126.8
2520	hexamethyl thiophosphoramide				137.3
2530	hydrogen peroxide	0.358	29.2	16.1	22.6
2540	hydrogen fluoride	0.290	18.3	9.1	12.6
2550	sulfuric acid	0.487	64.2	43.8	50.7
2560	ammonia	0.310	24.5	13.8	20.8
2570	hydrazine	0.390	34.8	21.1	30.8
2580	sulfur dioxide	0.382	40.3	25.7	34.7
2590	thionyl chloride	0.489	55.4	37.7	57.6
2600	phosphorus oxychloride	0.540	75.2	52.1	73.9

Units: diameter in nm; vdW surface in 10^4 m^2 mol^{-1}; vdW volume in cm^3 mol^{-1}, intrinsic volume in cm^3 mol^{-1}.

[*] For trifluoroethanol the value 57.9 × 10^4 m^2 mol^{-1} is from Murray *et al.* 1993, compared with 52.5 for ethanol, 39.0 for methanol, and 57.9 for trifluoroacetic acid from this source and the values in this Table from (DIPPR 1997).

Accordingly, the following simple expression is used for the calculation of V_x:

$$V_X/\mathrm{cm}^3\ \mathrm{mol}^{-1} = \sum_i N_i V_{xi} - 6.56 N_{\mathrm{bonds}} \qquad (3.21)$$

A drawback of the resulting intrinsic volume is that it does not distinguish between isomers, not only geometrical ones, such as 1,1-dichloro- and 1,2- dichloroethane, both having $V_x = 63.5$ cm^3 mol^{-1}, but also structural ones, such as 1-butanol and diethyl ether, both having $V_x = 73.1$ cm^3 mol^{-1}. The V_x values, shown in Table 3.4, are nearly proportional to the van der Waals intrinsic molar volumes, and since they are much more readily calculated they can be employed in their stead. The linear correlation expression

$$V_{\mathrm{vdW}} = 1.8 + 0.674 V_X \ \mathrm{cm^3\,mol^{-1}} \ (\text{within } \pm 1 \ \mathrm{cm^3\,mol^{-1}}) \qquad (3.22)$$

has been established (Marcus 1991) for many solvents of diverse kinds. Another estimate of the intrinsic volume, V_L, requires elaborate computations, but is related to V_X by:

$$V_L = 59.7 + 0.682 V_X \ \mathrm{cm^3\,mol^{-1}} \ (\text{within } \pm 1 \ \mathrm{cm^3\,mol^{-1}}) \qquad (3.23)$$

as found for over 200 solid, liquid, and gaseous substances (Leahy 1986).

6—

Electrical and Optical Properties

The response of a solvent to an electrical field depends on the intrinsic dipole moment of its molecules, but depends also on cooperative effects of adjacent dipoles, when these are correlated in the liquid. The dipole moment μ is the measure of the separation of the positive and negative centers of charge in the molecule, and is measured best for the solvent vapour e.g., by microwave spectroscopy, where such cooperative effects are absent. When this is impractical, because of low volatility, for instance, then the dipole moment may be measured for a dilute solution of the solvent as a solute in an inert diluent, c-hexane, tetrachloromethane, and benzene being mostly used for this purpose. The less polarizable the diluent, the less interaction of the solute with the diluent takes place and the more representative is the measured dipole moment of that for the isolated solvent molecule. The intrinsic dipole moments of molecules can also be calculated by *ab initio* or semi-empirical molecular quantum mechanical calculations, the latter if bond distances and angles are known. If the solvent molecules can undergo conformational changes, then the dipole moment becomes temperature-dependent and in solutions it is also dependent on the molecular environment. The values are generally reported in Debye units (D), 1 D = 3.33564 × 10^{-30} C.m. The values are known to 0.01 D and are shown for the solvents on our List in Table 3.5.

Solvents with highly symmetrical molecules have zero dipole moments, as have also alkanes, but electronegative atoms connected to aliphatic or aromatic skeletons cause the molecules to have finite dipole moments. Several of the solvents on the List are outstandingly polar, i.e., have dipole moments ~ 4 D or larger: triethylene glycol, glycerol, ethylene carbonate, propylene carbonate, 4- butyrolactone, 2-cyanopyridine, aceto-, propio-, butyro- and benzonitriles, nitrobenzene, N,N-dimethylthioformamide, N,N-diethylformamide, N-methylpyrrolidinone, N-methylthiopyrrolidinone, dimethylsulfoxide, sulfolane, dimethyl sulfate, hexamethyl phosphoramide and hexamethyl thiophosphoramide. Many others have dipole moments approaching this value, but on the whole, the

Table 3.5 Electric, optical, and magnetic properties of solvents

No.	Name	Mu		Epsilon		-d ln ε / dT		nD	-dnD / dT		α	Conductivity		-Chi	
0	vacuum	0.00	j	1.00	j	0.00	j	1.0000		j		0.00E+00	j	0.0	j
10	tetramethylsilane	0.00	[1]	1.92	[1]			1.3582		[1]a	12.0			74.8	[3
20	n-pentane	0.00	[1]	1.84	[1]	2.00	[m]	1.3547	0.552	[1]	10.2			63.0	[3
30	2-methylbutane	0.00	j	1.83	[1]	0.70	[c]	1.3509	0.570	[1]	10.2			64.4	[3
40	n-hexane	0.09	[1]	1.88	[1]	1.90	[m]	1.3723	0.520	[1]	11.9			74.1	[3
50	c-hexane	0.00	j	2.02	[1]	1.82	[m]	1.4235	0.538	[1]	10.5			68.2	[3
60	n-heptane	0.00	[1]	1.92	[1]	1.68	[m]	1.3851	0.506	[1]	13.8			85.4	[3
70	n-octane	0.00	[1]	1.95	[1]	1.54	[m]	1.3951	0.476	[1]	15.6			96.6	[3
80	2,2,4-trimethylpentane	0.00	j	1.96	[1]	1.67	[m]	1.3890	0.494	[1]	15.4			98.3	[3
90	n-decane	0.00	[1]	1.99	[1]	1.50	[m]	1.4097	0.444	[1]	19.2			119.5	[3
100	n-dodecane	0.00	[1]	2.00	[1]	1.38	[m]	1.4195	0.430	[1]	22.9			142.0	[3
110	n-hexadecane	0.00	j	2.05	i	0.65	[c]	1.4325		[2]	30.3			187.6	[3
120	benzene	0.00	[1]	2.27	[1]	2.03	[m]	1.4979	0.640	[1]	10.4			54.8	[3
130	toluene	0.31	[1]	2.38	[1]	2.35	[m]	1.4941	0.560	[1]	12.3			66.1	[3
140	o-xylene	0.45	[1]	2.57	[1]	2.38	[m]	1.5030	0.500	[1]	14.2			77.8	[3
150	m-xylene	0.30	[1]	2.37	[1]	1.89	[m]	1.4946	0.516	[1]	14.3			76.6	[3
160	p-xylene	0.00	[1]	2.27	[1]	1.62	[m]	1.4933	0.514	[1]	14.2			76.8	[3
170	ethylbenzene	0.37	[1]	2.40	[1]			1.4932	0.536	[1]	12.7			77.2	[3
180	cumene	0.39	[1]	2.38	[1]			1.4889	0.510	[1]	16.0			89.3	[3
190	mesitylene	0.00	[1]	2.28	[1]			1.4968	0.506	[1]	16.2			92.3	[3
200	styrene	0.13	[1]	2.43	[1]			1.5440	0.519	[1]	14.5			68.0	[3
210	tetralin	0.60	[1]	2.77	[1]	2.40	[m]	1.5392	0.432	[1]	17.0			93.0	[3
220	cis-decalin	0.00	j	2.20	[1]	1.15	[m]	1.4788	0.440	[1]	17.4			106.7	[3

230	water	1.85	[2]	78.36	[1]	4.53	[1]	1.3325	0.644	[1]	1.5	5.89E-06	[1]	12.9	[3
240	methanol	2.87	[1]	32.66	[1]	6.08	[m]	1.3265	0.383	[1]	3.3	1.50E-07	[1]	21.4	[3
250	ethanol	1.66	[1]	24.55	[1]	6.22	[m]	1.3594	0.400	[1]	5.1	1.35E-07	[1]	33.5	[3
260	n-propanol	3.09	[1]	20.45	[1]	6.50	[m]	1.3837	0.372	[1]	7.0	9.17E-07	[1]	45.2	[3
270	i-propanol	1.66	[1]	19.92	[1]	7.14	[m]	1.3752	0.410	[1]	7.0	5.80E-06	[1]	45.7	[3
280	n-butanol	1.75	[1]	17.51	[1]	7.71	[m]	1.3974	0.390	[1]	8.8	9.12E-07	[1]	56.1	[3
290	i-butanol	1.79	[1]	17.93	[1]	8.60	[m]	1.3939	0.390	[1]	8.8	1.30E-06	[1]	57.2	[3
300	2-butanol	1.66	[2]	16.56	[1]	9.90	[c]	1.3953	0.364	[1]	8.8			57.3	[3

continued overleaf

Table 3.5 *(continued)*

No.	Name	Mu		Epsilon		-d ln ε/dT		nD	-dnD/ dT		α	Conductivity		-Chi	
310	t-butanol	1.66	[1]	12.47	[1]	14.60	[c]	1.3852	0.740	[1]	8.8	2.66E-06	[1]	57.4	[3
320	n-pentanol	1.70	[1]	13.90	[1]	5.30	[m]	1.4080	0.420	[1]	10.6			67.4	[3
330	i-pentanol	1.82	[1]	15.19	[1]	7.98	[c]	1.4052	0.370	[1]	10.6	1.40E-07	[1]	69.0	[3
340	t-pentanol	1.70	[1]	5.78	[1]	10.09	[c]	1.4020	0.560	[1]	10.6			70.9	[3
350	n-hexanol	1.55	[1]	13.30	[1]	8.06	[m]	1.4157	0.375	[1]	12.5			79.2	[3
360	c-hexanol	1.86	[1]	15.00	[1]	10.06	[m]	1.4648	0.374	[1]	11.3			73.4	[3
370	n-octanol	1.76	[1]	10.34	[1]	9.94	[m]	1.4276	0.400	[1]	16.1	1.39E-05	[1]	102.2	[3
380	n-decanol	1.62	[2]	8.10	[3]			1.4350		[2]	19.8				
390	n-dodecanol	1.70	[2]	5.70	[c]	8.63	[c]	1.4413		[2]	23.5			148.4	[3
400	benzyl alcohol	1.66	[1]	12.70	[1]	4.89	[n]	1.5384	0.396	[1]	12.9			71.8	[3
410	2-phenylethanol	1.66	[2]	12.31	[c]a	11.60	[c]	2.3310		[2]	14.5			68.1	[3
420	allyl alcohol	1.77	[1]	21.60	[1]			1.4113	0.450	[1]	6.8			36.7	[3
430	2-chloroethanol	1.88	[1]	25.80	[1]			1.4421	0.390	[2]	10.6			72.2	[3
440	2-cyanoethanol													54.6	[3
450	2,2,2-trifluoroethanol	2.52	[a]c	26.67	[f]	7.24	[f]	1.2907		[1]a	5.2	3.90E-05			
460	hexafluoro-i-propanol	2.05	[b]	16.62	[b]	20.20	[b]	1.2770		[b]	7.2				
470	2-methoxyethanol	2.04	[1]	16.93	[1]	11.58	[n]	1.4002	0.380	[1]	7.6	1.09E-04	[1]a	60.3	[3
480	2-ethoxyethanol	2.08	[1]	29.60	[1]			1.4057	0.400	[1]	9.5	9.30E-06	[1]		
490	1,2-ethanediol	2.31	[2]	37.70	[1]	5.16	[m]	1.4306	0.240	[1]	5.7	1.16E-04	[1]	38.9	[3
500	1,2-propanediol	2.25	[1]	32.00	[1]a	6.22	[m]	1.4314	0.300	[1]	7.6				
510	1,3-propanediol	2.55	[1]	35.00	[1]a	5.30	[m]	1.4386	0.200	[1]	7.6			50.2	[3
520	1,2-butanediol	2.18	[a]					1.4360		[2]	9.3			67.0	[3
530	2,3-butanediol (meso)	2.1	[2]	21.53	[g]	3.65	[g]	1.4372	0.340	[2]	9.4			62.0	[3

540	1,4-butanediol	2.5	[1]	30.20	[1]b	5.35	[t]	1.4443	0.700	[1]	9.3			61.5	[3]
550	1,5-pentanediol	2.51	[1]					1.4484	0.608	[1]	11.2			73.5	[3
560	diethyleneglycol	2.31	[1]	31.69	[1]a	13.67	[n]	1.4461	0.280	[1]	10.1	5.86E-05	[1]		
570	triethyleneglycol	5.58	[1]a	23.69	[1]a			1.4541	0.340	[1]	14.4	8.40E-06	[1]		
580	glycerol	4.21	[2]	42.50	[1]	4.79	[m]	1.4730	0.800	[1]	8.1	6.00E-06	[1]	57.0	[3
590	phenol	1.59	[1]b	11.60	[1]d	7.37	[m]	1.5427	0.450	[1]	11.0	2.68E-06	[1]	60.2	[3
600	2-methylphenol	1.45	[1]	11.50	[1]	22.00	[m]	1.5442	0.500	[1]	12.8	1.27E-07	[1]	73.0	[3
610	3-methylphenol	1.48	[1]a	12.44	[1]	9.44	[m]	1.5396	0.450	[1]	13.0	1.40E-06	[1]	72.0	[3
620	4-methylphenol	1.48	[1]a	11.07	[1]d	9.32	[n]	1.5391	0.420	[1]	13.2	1.38E-06	[1]	70.1	[3
630	2-methoxyphenol	2.40	[a]								13.6			79.1	[3

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No.	Name	Mu		Epsilon		-d ln ε / dT		nD	-dnD/dT		α	Conductivity		- Chi	
640	2,4-dimethylphenol	1.70	[1]a	6.16	[1]b			1.5254	0.480	[1]	14.5	8.00E-08	[1]e	83.5	[q
650	3-chlorophenol	2.14	[a]					1.5632		[2]	12.9			77.6	[3
660	diethyl ether	1.15	[1]a	4.20	[1]	5.00	[m]	1.3495	0.560	[1]	8.9	3.00E-14	[1]	55.1	[3
670	di-n-propyl ether	1.32	[1]	3.39	[1]			1.3780	0.490	[1]	12.6			79.4	[3
680	di-i-propyl ether	1.22	[1]a	3.88	[1]	10.70	[m]	1.3655	0.500	[1]	12.6			79.4	[3
690	di-n-butyl ether	1.17	[1]a	3.08	[1]a			1.3968	0.450	[1]	16.3				
700	di(2-chloroethyl) ether	2.58	[1]	21.20	[1]a			1.4553	0.430	[1]	12.6				
710	1,2-dimethoxyethane	1.71	[1]	7.20	[1]	5.69	[n]	1.3781	0.304	[1]	9.6			55.2	[r]
720	bis(methoxyethyl) ether	1.97	[1]	5.80	[4]			1.4058	0.408	[1]	13.9			85.8	[r]
730	furan	0.71	[1]	2.94	[1]			1.4187	0.538	[1]	7.3			43.1	[3
740	tetrahydrofuran	1.75	[1]	7.58	[1]	3.94	[n]	1.4050	0.440	[1]	7.9	9.30E-06	[1]		
750	2-methyl tetrahydrofuran	1.38	[c]	5.26	[s]	4.14	[s]	1.4051	0.481	[1]	9.8				
760	tetrahydropyran	1.63	[1]	5.61	[1]			1.4186	0.444	[1]	9.8				
770	dioxane	0.45	[1]	2.21	[1]	1.80	[m]	1.4203	0.460	[1]	8.6	5.00E-13	[1]	51.1	[3
780	1,3-dioxolane	1.47	[1]					1.3992		[1]	6.7				
790	1,8-cineole	1.58	[c]	4.57	[1]			1.4555	0.400	[1]	18.1			114.5	[3
800	anisole	1.25	[1]	4.33	[1]	5.90	[m]	1.5143	0.500	[1]	13.0	1.00E-13	[1]	72.2	[3
810	phenetole	1.36	[1]	4.22	[1]a	4.90	[m]	1.5049	0.500	[1]	15.0			84.5	[3]
820	diphenyl ether	1.17	[1]	3.60	[1]	4.50	[m]	1.5781	0.476	[2]	20.9			108.1	[3]
830	dibenzyl ether	1.39	[2]	3.86	[4]			1.5385	0.412	[1]	23.7				
840	1,2-dimethoxybenzene	1.29	[1]	4.09	[1]			1.5323		[1]	15.7			87.4	[3
850	trimethyl orthoformate	1.70	[a]					1.3790		[3]	10.3				
860	trimethyl orthoacetate	1.46	[a]					1.3810		[3]	12.5				

870	propionaldehyde	2.54	[1]a	18.50	[1]a			1.3593	0.518	[1]	6.4	9.50E-03	[1]	34.3	[3
880	butyraldehyde	2.45	[1]d	13.40	[1]			1.3766	0.505	[1]	8.2			46.1	[3
890	benzaldehyde	2.77	[1]a	17.80	[1]a			1.5437	0.360		12.7			60.8	[3
900	p-methoxybenzaldehyde	3.85	[a]	15.50	[c]a			1.5730			15.9			78.0	[3]
910	cinnamaldehyde	3.62	[a]	16.90	[3]						17.5			74.8	[3]
920	acetone	2.69	[1]a	20.56	[1]	4.72	[m]	1.3560	0.544	[1]	6.4	4.90E-07	[1]	34.0	[3
930	2-butanone	2.76	[1]	18.11	[1]	4.77	[m]	1.3769	0.480	[1]	8.2	3.60E-07	[1]	45.6	[3
940	2-pentanone	2.70	[1]a	15.38	[1]a	4.49	[m]	1.3885	0.469	[1]	10.1			57.4	[3
950	methyl i-propyl ketone	2.77	[2]	15.87	[4]	4.84	[m]		1.3857	[2]	10.0			58.5	[3
960	3-pentanone	2.82	[1]	17.00	[1]a	5.18	[m]	1.3900	0.450	[1]	10.0			57.3	[3
970	c-pentanone	2.93	[2]	14.45	[4]	2.23	[c]	1.4354	0.412	[4]	9.2			51.6	[3
980	methyl-i-butyl ketone	2.70	[2]a	13.11	[1]a	5.07	[c]	1.3936	0.430	[1]	11.9	5.20E-06	[1]	70.0	[3

continued overleaf

Table 3.5 *(continued)*

No.	Name	Mu		Epsilon		-d ln ε/dT		nD	-dnD/dT		α	Conductivity		-Chi	
990	methyl t-butyl ketone	2.75	[a]	12.60	[c]a			1.3950		[3]	11.9			69.9	[3]
1000	c-hexanone	3.08	[1]	15.50	[c]	3.73	[c]	1.4500	0.212	[1]	11.1	5.00E-16	[1]	62.0	[3]
1010	2-heptanone	2.97	[1]a	11.98	[1]a	4.61	[m]	1.4066	0.428	[1]	13.7			80.5	[3]
1020	3-heptanone	2.78	[1]a	12.88	[1]a			1.4066	0.440	[1]	13.7			80.7	[3]
1030	di-t-butyl ketone	2.51	[a]	14.50	[c]			1.4200		[3]	17.4			104.1	[3]
1040	acetophenone	2.95	[1]	17.39	[1]	5.30	[m]	1.5321	0.450	[2]	14.4	3.10E-07	[1]	72.6	[3]
1050	propiophenone			15.50	[c]a			1.5270		[3]	16.2				
1060	phenylacetone							1.5170		[3]	15.8			83.2	[3]
1070	p-methylacetophenone	3.16	[a]					1.5340		[3]	16.4				
1080	p-chloroacetophenone	2.48	[a]	9.60	[x]			1.5550		[3]	16.5			86.5	[3]
1090	benzophenone (beta)	2.98	[2]	11.40	[3]			1.6060		[3]	22.5			110.0	[3]
1100	acetylacetone	2.78	[1]a	25.70	[1]a			1.4465		[2]	11.0			54.9	[3]
1110	biacetyl	1.03	[a]					1.3930		[3]a	8.3				
1120	formic acid	1.82	[1]b	58.50	[1]	6.41	[n]	1.3694	0.420	[1]	3.4	6.08E-05	[1]	19.9	[3]
1130	acetic acid	1.68	[1]b	6.15	[1]	-2.62	[m]	1.3698	0.380	[1]	5.2	1.00E-07	[1]	31.7	[3]
1140	propanoic acid	1.68	[1]b	3.37	[1]			1.3843	0.440	[1]	7.0	1.00E-07	[1]	43.4	[3]
1150	n-butanoic acid	1.65	[1]b	2.90	[1]	-1.83	[m]	1.3958	0.382	[1]	8.8			55.1	[3]
1160	n-pentanoic acid	1.61	[1]a	2.66	[1]a			1.4060	0.400	[1]	10.6			66.8	[3]
1170	n-hexanoic acid	1.13	[1]	2.63	[1]			1.4148	0.388	[1]	12.5			78.5	[3]
1180	n-heptanoic acid	1.68	[2]	2.71	[c]f			1.4210		[2]	14.3			88.6	[3]
1190	dichloroacetic acid			8.20	[3]a			1.4658		[2]	9.1			58.2	[3]
1200	trifluoroacetic acid	2.28	[1]	8.55	[1]a	-1.35	[m]	1.2850		[1]a	5.4			42.9	[r]
1210	acetic anhydride	2.82	[1]	20.63	[1]	-13.64	[n]	1.3904	0.410	[1]	8.9	5.00E-07	[1]	52.8	[3]

1220	benzoyl chloride	3.16	[2]	23.00	[3]a			1.5508		[2]	14.7			75.8	[3]
1230	benzoyl bromide														
1240	methyl formate	1.77	[1]	8.50	[1]a	13.50	[m]	1.3415	0.440	[1]	5.2	1.92E-06	[1]		
1250	ethyl formate	1.94	[1]	7.16	[1]			1.3575	0.460	[1]	7.0	1.45E-07	[1]		
1260	methyl formate	1.68	[2]	6.68	[1]	7.60	[m]	1.3589	0.500	[1]	7.0	3.40E-04	[1]	42.2	[3]
1270	ethyl acetate	1.78	[2]	6.02	[1]	5.70	[m]	1.3698	0.490	[1]	8.8	1.00E-07	[1]	54.1	[3]
1280	propyl acetate	1.78	[1]	6.00	[1]	3.10	[m]	1.3828	0.480	[1]	10.7	2.20E-05	[1]	65.9	[3]
1290	butyl acetate	1.84	[2]	5.01	[4]	6.50	[m]	1.3918	0.470	[1]	12.4	1.60E-06	[1]	77.4	[3]
1300	i-pentyl acetate	1.86	[1]	4.63	[1]b	6.50	[m]	1.3981	0.480	[1]	14.4			89.4	[3]
1310	methyl propanoate	1.70	[2]	6.23	[4]			1.3742		[2]	8.8			54.1	[3]

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No.	Name	Mu		Epsilon		-d ln ε/ dT		nD	-dnD/ dT		α	Conductivity		-Chi	
1320	ethyl propanoate	1.74	[1]a	5.65	[1]a	7.30	[m]	1.3814	0.460	[1]	10.6			65.8	[3]
1330	dimethyl carbonate	0.87	[4]	3.17	[4]			1.3690		[4]	7.5				
1340	diethyl carbonate	0.90	[1]	2.82	[1]a			1.3829	0.390	[1]	11.3	9.10E-08	[1]	75.4	[3]
1350	ethylene carbonate	4.87	[1]	89.78	[1]d	4.55	[n]	1.419	0.370	[1]d	6.6	1.00E-06	[1]		
1360	propylene carbonate	4.94	[4]	64.92	[1]	3.63	[n]	1.419	0.375	[1]	8.6	2.00E-06	[1]	54.5	[r]
1370	diethyl malonate	2.54	[1]	7.87	[1]	8.80	[m]	1.413	0.390	[2]	15.1			93.3	[3]
1380	methyl benzoate	1.94	[1]	6.59	[1]a	3.20	[m]	1.514	0.460	[1]	15.0	1.37E-03	[1]a	81.6	[3]
1390	ethyl benzoate	1.99	[1]	6.02	[1]a	8.10	[m]	1.503	0.400	[1]	16.9	1.00E-07	[1]	93.3	[3]
1400	dimethyl phthalate	2.66	[c]	8.50	[3]			1.516		[4]	19.5				
1410	dibutyl phthalate	2.82	[1]a	6.44	[1]b	7.10	[m]	1.490	0.500	[1]	30.6	4.20E-06	[1]b	175.1	[3]
1420	ethyl chloroacetate	2.63	[4]	12.78	[4]			1.421		[4]	9.8			72.3	[3]
1430	ethyl trichloroacetate	2.54	[4]	9.03	[4]	7.10	[m]	1.450		[4]	14.7			99.5	[3]
1440	ethyl acetoacetate	2.93	[4]	16.55	[4]			1.419		[4]	12.8				
1450	4-butyrolactone	4.12	[1]	39.00	[1]a	3.17	[p]	1.434		[1]	7.9				
1460	perfluoro-n-hexane			1.57	[c]			1.251		[h]	12.7				
1470	perfluoro-n-heptane			1.77	[h]			1.262		[h]	14.7				
1480	perfluoro-methylcyclohexane	0.00	[d]	1.85	[h]	1.13	[v]	1.278		[h]	13.5				
1490	perfluoro-decalin	0.15	[d]	1.98	[d]			1.313		[h]	18.3				
1500	fluorobenzene	1.48	[1]	5.42	[1]			1.462	0.500	[2]	10.4			58.3	[3]
1510	hexafluorobenzene	0.00	[1]	2.05	[c]			1.374	0.558	[1]	10.5				
1520	1-chlorobutane	1.90	[1]	7.39	[1]a	4.00	[m]	1.400	0.510	[1]	10.1	1.00E-08	[1]	67.1	[3]
1530	chlorobenzene	1.69	[2]	5.62	[1]	3.00	[m]	1.521	0.592	[1]	12.4	7.00E-09	[1]	69.6	[3]

1540	dichloromethane	1.14	[1]	8.93	[1]	8.50	[m]	1.421	0.600	[1]	6.5	4.30E-09	[1]	46.6	[3]
1550	1,1-dichloroethane	1.82	[1]	10.00	[1]a	14.30	[m]	1.413	0.520	[1]	8.4	2.00E-07	[1]	57.4	[3]
1560	1,2-dichloroethane	1.83	[1]	10.36	[1]	5.08	[c]	1.442	0.540	[1]	8.3	4.00E-09	[1]	59.6	[3]
1570	tr-1,2-dichloroethylene	0.70	[1]	2.14	[1]			1.446	1.138	[2]	8.2			48.9	[3]
1580	o-dichlorobenzene	2.50	[1]	9.93	[1]	4.47	[m]	1.549	0.458	[1]	14.3	3.00E-09	[1]	84.4	[3]
1590	m-dichlorobenzene	1.54	[1]	5.04	[1]	2.76	[m]	1.543	0.498	[1]	14.3		[1]	84.1	[3]
1600	chloroform	1.15	[1]	4.89	[4]	3.68	[m]	1.442	0.590	[1]	8.5	1.00E-08	[1]	59.3	[3]
1610	1,1,1-trichloroethane	1.70	[1]	7.25	[1]a	11.40	[m]	1.435	0.420	[1]	10.4	7.30E-07	[1]		
1620	1,1,2-trichloroethane	1.55	[1]	7.29	[1]a			1.468	0.524	[1]	10.3				
1630	trichloroethylene	0.80	[1]	3.42	[1]a			1.475	0.568	[1]	10.0	8.00E-10	[1]	65.8	[3]
1640	1,2,4-trichlorobenzene	1.26	[2]	4.15	[4]			1.571		[4]	16.3			106.5	[3]
1650	tetrachloromethane	0.00	[1]	2.24	[1]a	2.06	[m]	1.457	0.558	[1]	10.5	4.00E-16	[1]	66.8	[3]
1660	tetrachloroethylene	0.00	[1]	2.28	[1]	2.02	[m]	1.503	0.530	[1]	12.0			81.6	[3]

continued overleaf

***Table 3.5** (continued)*

No.	Name	Mu		Epsilon		-d ln ε/dT		nD	-dnD/dT		α	Conductivity		-Chi	
1670	1,1,2,2-tetrachloroethane	1.71	[1]	8.20	[1]a			1.491	0.520	[1]	12.3			89.8	[3
1680	pentachloroethane	0.94	[1]	3.73	[1]a			1.500	0.460	[1]	14.1			99.2	[3
1690	1-bromobutane	1.96	[1]	7.10	[1]a	0.49	[m]	1.437	0.460	[1]	11.2			71.0	[3
1700	bromobenzene	1.56	[1]	2.65	[1]	2.65	[m]	1.557	0.490	[1]	13.5	1.20E-09	[1]	78.1	[3
1710	dibromomethane	1.43	[2]	6.68	[3]d	12.50	[m]	1.538		[2]	8.7			65.1	[3
1720	1,2-dibromoethane	1.19	[1]	4.75	[1]b	2.91	[m]	1.536	0.580	[1]	10.7	2.00E-08	[1]	78.8	[3
1730	bromoform	0.99	[1]	4.39	[1]a	2.42	[m]	1.595	0.550	[1]	11.8	2.00E-06	[1]	82.6	[3
1740	l-iodobutane	1.93	[1]	6.29	[1]a	3.11	[m]	1.497	0.560	[1]	13.3			93.6	[3
1750	iodobenzene	1.40	[1]	4.49	[1]a	0.78	[c]	1.617	0.560	[1]	15.5	2.40E-08		92.0	[3
1760	diiodomethane	1.08	[1]	5.32	[1]			1.738	0.620	[1]	13.1			93.1	[3
1770	n-butylamine	1.37	[1]	4.88	[1]a			1.398	0.434	[1]	9.5			58.9	[3
1780	benzylamine	3.11	[a]	4.60	[c]a			1.538		[2]	13.6			75.3	[3
1790	1,2-diaminoethane	1.90	[1]	12.90	[1]	17.90	[m]	1.454	0.547	[1]	7.3	9.00E-06	[1]	45.5	[3
1800	diethylamine	1.20	[1]	3.78				1.382	0.410	[1]	9.7			56.8	[3
1810	di-n-butylamine	0.98	[1]	2.98	[1]a			1.415	0.500	[1]	16.9			103.	[3
1820	pyrrole	1.80	[1]	8.13	[1]			1.507	0.472	[1]	8.2			48.6	[3
1830	pyrrolidine	1.57	[1]					1.440	0.530	[1]	8.7			54.8	[3
1840	piperidine	1.20	[1]	5.80	[1]a	11.84	[n]	1.452	0.480	[2]	10.6			64.2	[3
1850	morpholine	1.56	[1]	7.42	[1]			1.452	0.440	[2]	9.3			55.0	[3
1860	triethylamine	0.66	[2]	2.42	[1]a	1.71	[o]	1.398	0.600	[1]	13.5			82.3	[3
1870	tri-n-butylamine	0.78	[1]	2.29	[4]	1.16	[o]	1.428	0.100	[1]	24.3			156.	[3
1880	aniline	1.51	[1]	6.98		3.41	[m]	1.583	0.528	[1]	12.1	2.40E-06	[1]	62.4	[3
1890	o-chloroaniline	1.77	[1]	13.40	[1]			1.585	0.442	[1]	14.0			78.9	[3

1900	N-methylaniline	1.73	[c]	6.06	[1]			1.568	0.527	[1]	14.2			73.3	[3
1910	N,N-dimethylaniline	1.68	[2]	4.91	[1]a	9.40	[m]	1.556	0.504	[1]	16.2			85.1	[3
1920	ethanolamine	2.27	[1]	37.72	[1]			1.452	0.340	[1]	6.5	1.10E-03	[1]	42.1	[3
1930	diethanolamine	2.81	[1]	25.19	[e]	4.31	[e]	1.473	0.250	[1]	10.7				
1940	triethanolamine	3.57	[1]	29.36	[1]			1.483	0.200	[1]	15.1				
1950	pyridine	2.37	[1]	12.91	[1]	4.88	[n]	1.507	0.550	[1]	9.6	4.00E-06	[1]	48.5	[3
1960	2-methylpyridine	1.97	[1]	9.80	[1]a	4.84	[i]	1.498	0.520	[1]	11.5			60.3	[3
1970	3-methylpyridine	2.40	[1]	11.35	[i]	3.97	[i]	1.506		[1]	11.5			62.2	[3
1980	4-methylpyridine	2.60	[1]	11.86	[i]	3.67	[i]	1.503	0.488	[1]	11.5			61.8	[3
1990	2,4-dimethylpyridine	2.30	[1]	9.60	[1]a			1.498		[1]	13.4			71.5	[3

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No.	Name	Mu		Epsilon		-d lnε/dT		nD	-dnD/dT		α	Conductivity		-Chi	
2000	2,6-dimethylpyridine	1.66	[1]	7.33	[1]a			1.495	0.440	[1]	13.5			71.7	[3
2010	2,4,6-trimethylpyridine	2.05	[1]	12.02	[4]			1.495	0.440	[1]	15.4			83.2	[3
2020	2-bromopyridine	3.11	[4]	24.02	[4]			1.571		[4]	12.4				
2030	3-bromopyridine	1.99	[4]	9.85	[4]			1.571		[4]	12.5				
2040	2-cyanopyridine	5.24	[4]b	93.80	[j]b	4.34	[y]	1.529		[4]	12.5	5.00E-07	[j]b		
2050	pyrimidine	2.00	[4]					1.499		[2]	9.2			43.1	[3
2060	quinoline	2.18	[1]	8.95	[1]	8.44	[n]	1.624	0.453	[1]	16.6	2.20E-06	[1]	85.9	[3
2070	acetonitrile	3.92	[2]	35.94	[1]	4.16	[p]	1.341	0.496	[1]	4.4	6.00E-08	[1]	27.6	[3
2080	propionitrile	4.02	[2]	28.26	[1]	4.21	[n]	1.363	0.450	[1]	6.3	8.51E-08	[1]	38.8	[3
2090	butyronitrile	4.07	[2]	24.83	[1]b			1.382	0.430	[1]	8.1			50.4	[3
2100	valeronitrile	3.57	[1]	19.71	[1]			1.395	0.400	[1]	9.9	1.20E-08	[1]		
2110	acrylonitrile	3.67	[1]	33.00	[1]b			1.388	0.539	[1]	6.2				
2120	benzyl cyanide	3.47	[1]	18.70	[1]			1.520	0.482	[1]	14.0	5.00E-06	[1]	76.6	[3
2130	benzonitrile	4.18	[2]	25.20	[1]	3.62	[m]	1.525	0.506	[1]	12.5	5.00E-06	[1]	65.2	[3
2140	nitromethane	3.56	[1]	35.87	[1]b	4.35	[m]	1.379	0.450	[1]	5.0	5.00E-07	[1]	20.9	[3
2150	nitroethane	3.60	[1]	28.06	[1]b	9.35	[m]	1.389	0.439	[1]	6.8	5.00E-05	[1]b	33.6	[3
2160	1-nitropropane	3.59	[1]	23.24	[1]			1.399	0.405	[1]	8.6	3.30E-03	[1]	44.8	[3
2170	2-nitropropane	3.73	[1]	25.52	[1]			1.392	0.411	[1]	8.6	5.00E-03	[1]	45.2	[3
2180	nitrobenzene	4.22	[2]	34.78	[1]	5.18	[m]	1.550	0.460	[1]	13.0	2.05E-08	[1]	61.8	[3
2190	formamide	3.37	[1]	109.50	[1]	15.10	[m]	1.446	0.144	[1]	4.2	2.00E-05	[1]	23.1	[3
2200	N-methylformamide	3.86	[1]	182.40	[1]	8.88	[c]	1.430	0.380	[1]	6.1	8.00E-05	[1]	34.3	[r]
2210	N,N-dimethylformamide	3.82	[2]	36.71	[1]	5.12	[c]	1.428	0.460	[1]	7.8	6.00E-06	[1]	38.8	[r]
2220	N,N-dimethylthioformamide	4.74	[a]a	47.50	[e]	2.90	[e]	1.576		[4]	11.2				

2230	N,N-diethylformamide	3.97	[a]	29.02	[4]			1.434		[4]	11.5				
2240	N-methylacetamide	3.85	[a]	191.30	[1]b	7.97	[c]	1.425	0.470	[1]c	7.8	2.00E-05	[1]d	45.2	[3
2250	N,N-dimethylacetamide	3.72	[1]	37.78	[1]	6.09	[c]	1.435	0.560	[1]	9.6			56.1	[3
2260	N,N-diethyl acetamide	3.75	[4]	31.33	[4]			1.439		[4]	13.3			77.5	[3
2270	pyrrolidinone-2	3.55	[1]	27.79	[k]	2.50	[k]	1.486	0.400	[1]	8.8				
2280	N-methylpyrrolidinone	4.09	[1]	32.20	[1]			1.467	0.500	[1]	10.6	1.00E-06	[1]	61.7	[r]
2290	N-methylthiopyrrolidinone	4.86	[e]	47.50				1.583		[e]	11.4				
2300	tetramethylurea	3.47	[1]	23.60	[1]			1.449		[1]	12.8	6.00E-06	[1]	75.7	[3
2310	tetraethylurea	3.83	[4]	14.74	[4]			1.446		[4]	20.1			122.4	[3
2320	dimethylcyanamide	4.35	[w]	37.23	[4]			1.409		[4]	7.9				
2330	carbon disulfide	0.06	[1]	2.64	[1]b	2.34	[m]	1.624	0.674	[1]	8.5			42.2	[3
2340	dimethyl sulfide	1.45	[1]	6.20	[1]a			1.432	0.628	[1]	7.6			44.9	[3

continued overleaf

Table 3.5 *(continued)*

No.	Name	Mu		Epsilon		-d Inε/dT		nD	-dnD/dT		α	Conductivity		-Chi	
2350	diethyl sulfide	1.61	[1]	5.72	[1]			1.440	0.558	[1]	11.3			67.9	[3
2360	di-i-propyl sulfide	1.67	[c]	5.81	[4]			1.438		[4]	15.1			91.8	[3
2370	di-n-butyl sulfide	1.61	[1]	4.41	[c]			1.450	0.462	[1]	18.6			113.	[3
2380	tetrahydrothiophene	1.90	[1]	8.61	[4]			1.502	0.521	[1]	10.4			63.5	[3
2390	pentamethylene sulfide	1.71	[4]	6.58	[c]			1.510		[4]	12.3				
2400	dimethyl sulfoxide	4.06	[4]	46.45	[1]			1.477	0.358	[1]	8.0	2.00E-07	[1]	43.9	[r]
2410	di-n-butyl sulfoxide	3.99	[a]												
2420	sulfolane	4.81	[1]	43.26	[1]			1.481	0.340	[1]b	10.8	2.00E-06	[1]b		
2430	thiobis(2-ethanol)			27.84	[e]	5.92	[e]	1.519	0.322	[1]	12.5				
2440	diethyl sulfite	3.09	[a]	15.60	[c]a			1.415		[3]a	12.7			75.5	[3
2450	dimethyl sulfate	4.09	[a]	50.28	[4]			1.386		[4]	8.8			62.2	[3
2460	diethyl sulfate	2.99	[4]	16.20	[4]	5.53	[m]	1.414		[4]	13.0			86.9	[3
2470	methanesulfonic acid							1.432		[2]	6.7	5.00E-06	[u]		
2480	trimethyl phosphate	3.18	[1]	16.39	[1]			1.395	0.260	[1]	10.9				
2490	triethyl phosphate	3.12	[1]	10.79	[1]			1.403	0.374	[1]	16.6	1.19E-06	[1]	111.	[r]
2500	tri-n-butyl phosphate	3.07	[1]	8.91	[1]	7.08	[m]	1.422	0.480	[1]	26.7			181.	[r]
2510	hexamethyl phosphate	5.54	[1]	29.30	[1]a	20.60	[k]	1.457	0.360	[1]	18.9	1.90E-05	[1]	118.	[r]
2520	hexamethylthiophosphoramide	4.47	[a]	39.50	[e]b			1.507		[e]b		3.10E-05	[e]b		
2530	hydrogen peroxide	2.26	[2]	70.70	[3]	6.51	[3]	1.407		[2]	2.3			17.0	[3
2540	hydrogen fluoride	1.82	[2]	84.00	[1]	12.00	[1]0	1.340		[2]	0.8	1.00E-04	[1]0	8.6	[3
2550	sulfuric acid	2.72	[2]	100.00	[1]			1.4184		[2]	5.3	1.04E+00	[1]	38.8	[3
2560	ammonia	1.47	[2]	22.38	[1]T	3.30	[1]	1.325		[2]	2.0	1.00E-09	[1]	16.3	[3

2570	hydrazine	1.75	[2]	52.90	[c]a	4.95	[n]	1.469	[2]	3.5				
2580	sulfur dioxide	1.63	[2]	11.90	[1]	12.40	[1]	1.357	[2]	3.8	3.00E-06	[1]	18.2	[3
2590	thionyl chloride	1.45	[2]	9.25	[3]a			1.516	[2]	8.7			44.3	[3
2600	phosphorus oxychloride	2.42	[2]	13.90	[1]			1.484	[2]	10.4	2.00E-06	[1]	67.8	[3

Units: mu (μ) in D (1 D = 3.33564 × 10^{-30} C.m); eps (ε) is dimensionless; -1000(d ln ε/dT) is in K^{-1}; n_D is dimensionless; Cond (&kgr) is in ohm^{-1} m^{-1}; Chi ($-\chi$) is in 10^{-6} cm^3 mol^{-1}; 1000dn_D/dT is in K^{-1}; α is in 10^{-30} m^3.

References: [1] Riddick, Bunger and Sakano 1986; [2] DIPPR 1997; [3] Lide 1994; [4] Landoldt-Börnstein 1959, 1967; [a] McClellan 1989. [b] Kötzsch (1966); Kivinen, Murto and 10144Lehtonen 1967; Murto *et al*. 1967; Murto and Lindel 1970; Rochester and Symonds 1973; Rochester and Symonds 1974; Macdonald, Dolan and Hyne 1976. [c] Abboud and Notario 1997. [d] Varushchenko *et al*. 1980. [e] Diggle and Bogsanyi 1974 (HMThPT, DMThF); Gritzner and Gutmann 1977 (NMThPy); Gutman Danksagmüller and Duschek 1974 (DMThF); lkeda 1971 (S(EtOH)$_2$). [f] Murto and Heino 1966. [g] Venkatesewara Rao and Bhanumathi 1978. [h] Reed 1964; Banks 1970; Kirk-Othmer 1994; Hudlicky 1976; Joyner 1986. [i] Botros *et al*. 1983. [j] Lemire and Sears 1981. [k] Pirilä-Honkanen and ruostesuo 1991. [l] Jander and Lafrenz 1970. [m] Maryott and Smith 1951; Buckley and Maryott 1958. [n] Fialkov 1990. [o] Klofutar, Paljk and Malnersic; 1982. [p] Côté *et al*. 1996. [q] Baliah and Jeyanthy 1989. [r] Gerger, Mayer and Gutmann 1977; Baetman and Baudet 1967. [s] Streck and Richert 1994. [t] Grineva and Zhuravlev 1996. [u] Paul *et al*. 1980. [v] Lifanova, Usacheva and Zhuravlev 1992. [w] Herail, Berthelot and Proutiere 1995. [x] Puranik, Kumbharkhane and Mehrotra 1994. [y] Ponomarenko, *et al*. 1993.

'polarity' of a solvent—as far as it pertains to its ability to solvate solutes—is in general more of a chemical property, as discussed in Chapter 4, than measurable by the dipole moment alone.

When a non-conductor is placed between the plates of a capacitor, the electric field between the plates is diminished because of the dielectric properties of the non-conductor. If the molecules of the latter have no permanent dipoles, then the only effect is the electronic and atomic polarization. When the applied electric field changes its direction at a high frequency, the electrons in the molecule can rapidly adapt their average localizations (actually, the mean density of the electron cloud) to follow the field. The 'infinite frequency' permittivity of a medium relative to that of free space, ε_∞, i.e., that measured at very high frequencies (> 10 GHz), is therefore a measure of the electronic polarization. Light can be considered as a rapidly varying electric field, hence the short wavelength, high frequency, refractive index squared, n_∞^2, is an equivalent measure of this quantity. This is approximated by the refractive index squared measured at the D-line of sodium (589.3 nm is the mean wavelength of the doublet), n_D^2, or better by 1.1 n_D^2. The refractive index, i.e., the ratio of the velocity of light in vacuum to that in the transparent medium, is a dimensionless, and unitless, quantity. Values of n_D are between 1.2 and 1.8 for most liquids and can be readily measured to 4 decimals, or more with greater care, but are temperature and pressure dependent. The values of n_D at 25°C at ambient pressure, rounded to 4 decimals, are shown in Table 3.5 for the solvents in our List. The temperature dependence of the refractive index is $dn_D/dT \sim 0.45 \times 10^{-3}\ K^{-1}$ (within ±20%) for many solvents is also shown in Table 3.5 (when given in Riddick, Bunger and Sakano (1986)), but the pressure derivative is small and not extensively documented.

The molar refractivity R of the solvent is derived from the Lorentz–Lorenz expression, and at the D-line:

$$R_D = V(n_D^2 - 1)/(n_D^2 + 2) \qquad (3.24)$$

The molar refractivity is expressed in $cm^3\ mol^{-1}$ as is V. It is fairly temperature independent and is additive in the constituent atoms of the molecules of the solvents, and some structural features, with good accuracy. The infinite frequency value of the molar refractivity is 1–2% smaller than R_D. The polarizability α of the solvent is generally expressed as:

$$\alpha = (3/4\pi N_{Av})R_D \qquad (3.25)$$

hence, being proportional to R_D, is also temperature independent. Since both R_D and α can be readily calculated from the V values in Table 3.1 and n_D^2 values from Table 3.5, only α is displayed there specifically. The values of $\alpha/10^{-30}\ m^3$ vary from 1.46 for very small molecules, such as water, and increase with molecular size through 4.45 for acetonitrile and 6.33 for acetone, to 8.73 for diethyl ether, 10.5 for tetrachloromethane 12.92 for nitrobenzene, and 26.72 for tri-*n*-butyl phosphate. For molecules of the same size they are larger for aromatic ones and those containing double and triple bonds or the heavier halogen atoms than for aliphatic molecules with single bonds only. The R_D and α values do not convey much more information than V does, because the function (n_D^2 - 1)/(n_D^2 + 2), at least for the solvents on the List, is within 25% of 0.25.

If the molecules of the solvent are devoid of permanent dipoles, then on reduction of the frequency of the electric field it is still only the electronic and atomic polarization that follow the direction of the field. The static relative permittivity of such a solvent, ε_0, is therefore the same as ε_∞ and is practically the same as n_D^2. However, if the molecules of the solvent do have a permanent dipole, the molecule as a whole, subject to its random thermal motion, orients itself in the direction of the field. The resulting relative permittivity ε (called also the dielectric constant, the subscript zero being dropped, since the static, low frequency, < 1 MHz relative permittivity is henceforth meant) is therefore larger than n_D^2. It may reach high values if cooperative interactions between dipoles take place, behaviour that is enhanced at low temperatures, with $\varepsilon = 348$ being attained by N-methylpropanamide at -40°C (Bass *et al*. 1964). The values of ε are dimensionless and unitless, and must be multiplied by $4\pi\varepsilon_o$, where ε_o is the permittivity of vacuum = 8.8542×10^{-12} C^2 J^{-1} m^{-1}, in order to obtain the dielectric constant of the liquid medium in electrostatic calculations. Values of ε of hydrocarbons and other non-polar solvents, being in the range of 1.9–4, are known to 3–4 decimals or better, those for polar solvents, with $\varepsilon > 4$, commonly to 2 decimals only. The values of ε at 25°C are shown to 2 decimals in Table 3.5 for the solvents in our List.

Solvents with values of $\varepsilon \leq 10$ may be either non-polar or polar but are considered as low dielectric constant solvents, since electrolytes are not appreciably dissociated to ions in them. These include hydrocarbons, many halogen-substituted hydrocarbons, and many ethers and amines. Solvents with values of $\varepsilon \geq 30$ are necessarily highly polar and permit almost complete dissociation of electrolytes. These include water, methanol and polyols, formic acid, the cyclic ethylene- and propylene- carbonates, 4-butyrolactone, ethanolamine, 2-cyanopyridine, nitromethane and -benzene, amides, dimethyl sulfoxide, sulfolane, hydrogen fluoride, sulfuric acid, and hydrazine among the solvents on the List. Solvents with in between values of ε permit some ionic dissociation but extensive ion-pairing is the dominant effect in them. The solvation properties of the solvents (see Chapter 4), on the other hand, are only poorly related to the dielectric properties, hence the use of solvents for specific purposes must take into account all the relevant properties. Many useful supercritical fluids are non-polar, a notable exception is water, and few data about their dielectric properties are known. The relative permittivity of carbon dioxide increases strongly with its density but is hardly affected by temperature (50, 100°C) at given densities: $\varepsilon = 1.05$ at $d = 0.1$ g cm^{-3}, increasing to 1.28 at $d = 0.5$ and to 1.55 at $d = 1.0$ g cm^{-3} (Rosset, Mourier and Caude 1986). It increases in an s-shaped manner as the pressure is increased through the critical value at a temperature (40°C) above T_C (Fedotov *et al*. 1996).

The molar polarization of the solvent, P, is given by the Clausius–Mosotti expression $P = V(\varepsilon - 1)/(\varepsilon + 2)$, similar to the expression for the molar refraction. It is the molar polarization that relates the relative permittivity to the dipole moment μ and the polarizability α:

$$P = (4\pi N_{Av}/3)(\alpha + g\mu^2/3k_B T) \qquad (3.26)$$

where g is the Kirkwood dipole angular correlation parameter. This function describes the angular correlation between the dipoles in the following way:

$$g = 1 + Z\,|\cos\theta| \qquad (3.27)$$

where Z is the average number of nearest neighbours (coordination number) and θ is the angle between the dipoles of the molecules in the solvent. The values of g are presented and discussed further in Chapter 4, since they relate to the way the solvents are structured. In practice, g cannot be readily estimated from the molecular constitution of the solvent and is obtained by means of an empirically modified Kirkwood expression from reaction field theory. It depends on the relative permittivity, the refractive index, the dipole moment, and the molar volume as:

$$g = (9k_B\varepsilon_o/4\pi N_{Av})VT\mu^{-2}(\varepsilon - 1.1n_D^2)(2\varepsilon + 1.1n_D^2)/\varepsilon(2 + 1.1n_D^2)^2 \qquad (3.27)$$

The empirical factor 1.1 multiplying n_D^2 is an estimate of the relation of ε_∞ to it, but other values, e.g., 1.05, have also been suggested.

The molar refraction R_D and molar polarization P per unit volume, i.e., the functions f $(n_D) = (n_D^2 - 1)/n_D^2 + 2)$ and $g(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 2)$, or similar functions with 1 replacing 2 and/or 2 multiplying n_D and ε in the denominators, have often been employed in correlations of chemical properties of solvents with their physical, optical, and electrical properties.

The temperature dependence of the relative permittivity is generally negative and quite marked, mainly due to the increased thermal randomization, hence diminished cooperativity between the dipoles, as the temperature is raised. The relative change with the temperature, $-(1/\varepsilon)d\varepsilon/dT = -d\ln\varepsilon/dT$ at 25°C is given in Table 3.5 in 10^{-3} K^{-1} to two decimals, which is a realistic estimate of its accuracy (a zero in the second decimal can be ignored, the value being known to only one decimal). Over moderate temperature ranges the coefficient $d\ln\varepsilon/dT$ itself is temperature independent, but it does change over larger ranges. A few solvents (carboxylic acids) have positive values of the temperature derivative of the relative permittivity, since they are associated to dimers with antiparallel orientation of their intrinsic dipoles in the neat liquid, the extent of this association diminishing with increasing temperatures.

The pressure dependence of the relative permittivity has been determined for relatively few solvents only, although it is an important quantity in theoretical treatments of the partial molar volumes of electrolyte solutions and other quantities involving charged particles in solution. The values of $(\partial \ln \varepsilon/\partial P)_T$ in GPa^{-1} are shown in Table 3.6. Many solvents follow the expression:

$$(\partial \ln \varepsilon/\partial P)_T = 0.39 + [(\varepsilon - 1)/3\varepsilon][2.9743 + 0.0257\varepsilon](0.70\kappa_T - 0.22) \quad (3.28)$$

where the numerical constants are independent of the temperature, the pressure, and the specific liquid (Marcus and Hefter 1997; Schadow and Steiner 1969).

The relative permittivity of a solvent depends also on the electric field *E*, but ordinary fields employed in the laboratory are rarely strong enough to cause an appreciable change of ε. The phenomenon is called the non-linear dielectric effect. A relevant expression (Grahame 1953) is:

Table 3.6 The pressure dependence of the relative permittivity, $(\partial \ln \varepsilon/\partial P)_T/\mathrm{GPa}^{-1}$

Solvent	25°C		30°C		Solvent	25°C		30°C	
2-methylbutane	0.83	[a]			3-methyl-2-pentanone			1.02	[c]
n-pentane	1.09	[i]	0.76	[e]	c-hexanone			0.86	[m]
c-hexane	0.71	[h]^{a}			2-octanone			1.12	[c]
n-hexane	0.92	[i]	0.60	[e]	γ-butyrolactone	0.43	[n]		
n-heptane	0.71	[b]	0.73	[b]	propylene carbonate	0.50	[n]		
n-octane	0.76	[k]			1-chlorobutane			1.49	[m]
n-noane	0.69	[k]			dichloromethane	1.49	[d]		
n-decane	0.65	[k]			1,1-dichloroethane			1.63	[m]
benzene	0.69	[h]^{a}			1,2-dichloroethane			1.82	[m]
toluene	0.54	[a]			o-dichlorobenzene			0.96	[m]
water	0.59	[e]			m-dichlorobenzene			0.77	[m]
methanol	1.20	[d]	0.96	[c]	chloroform	1.21	[d]		
ethanol	0.96	[e]	0.77	[c]	1,1,1-trichloroethane			1.54	[m]
1-propanol	0.86	[f]			tetrachloromethane	0.61	[a]		
1-butanol	0.76	[e]			fluorobenzene			1.25	[m]
2-butanol	1.14	[f]			chlorobenzene			0.64	[e]
2-methyl-1-propanol	0.98	[g]	0.79	[c]	bromobenzene			0.50	[e]
2-methyl-2-propanol			4.68	[e]	iodobenzene			0.44	[m]
3-methyl-1-butanol	0.88	[e]			aniline			0.49	[c]
c-pentanol			1.09	[j]	pyridine	0.83	[e]^{b}		
1-hexanol	0.66	[e]			acetonitrile	1.07	[d]		
1-heptanol	0.80	[l]			propionitrile			1.14	[m]
benzyl alcohol	0.68				benzonitrile			0.63	[m]

		[m]^a							
1,2-ethanediol			0.44	[c]	nitromethane			0.89	[m]
glycerol			0.33	[c]	nitrobenzene			0.58	[c]
diethyl ether	2.03	[e]			N-methylpyrrolidinone	0.72	[o]		
1,2-dimethoxyethane	1.78	[n]			carbon disulfide	0.68	[a]		
acetone	1.60	[d]	1.11	[c]					
2-butanone			1.01	[c]					

[a] Mopsik 1969; [b] Scaife 1971; [c] Schadow and Steiner 1969; [d] Swaddle 1990; [e] Landol-Börnstein 1959; Chen, Dannhauser and Johari 1969; [g] Owen and Brinkley 1943; [h] Kasprowicz and Kielich 1967; [i] Srinivasan and Kay 1977; [j] Würflinger 1982; [k] Scaife and Lyons 1980; [l] Vij, Scaife and Calderwood; [m] Isaacs 1981; [n] Côté *et al*. 1996; [o] Uosaki, Kawamura and Moriyoshi 1996.

^{a}At 20°C. ^{b}at 15°C.

$$\varepsilon(E) = n_D^2 + [\varepsilon(E = 0) - n_D^2]/(1 + bE^2) \qquad (3.29)$$

but this can be simplified into a power series in E^2, truncated after the second term. The values generally used for the non-linear dielectric effect (*NDE*) are $b = -[\varepsilon(E - \varepsilon(E = 0)]/\varepsilon(E = 0)E^2$ or $NDE = [\varepsilon(E - \varepsilon(E = 0)]/E^2$. The non-linear dielectric effect is of the order of $10^{-18}\,V^{-2}m^2$ and has been determined for a limited set of solvents only, both positive and negative values of $b\varepsilon(E = 0)$ having been reported, Table 3.7. The older values (not shown), i.e., those reported before say 1950, are generally incorrect, partly due to impure solvents, partly due to inaccurate instrumentation and insufficiently high fields, manifested in ε not depending strictly on the second power of the electric field. The non-linear dielectric effect has been related to association of the solvent molecules, by dipole-dipole interactions for aprotic solvents, and is negatively

Table 3.7 The relative permittivity field dependence coefficient $b\varepsilon/10^{-18}\,V^{-2}\,m^2$

Solvent	*b*ε		Solvent	*b*ε	
n-pentane	0.081	[a]	fluorobenzene	-1.01	[d]
n-hexane	0.121	[a]	chlorobenzene	-1.6	[k]
n-heptane	0.109	[a]	1,1-dichloroethane	-28	[n]30°C
n-ocane	0.124	[a]	1,2-dichloroethane	-34	[h]
n-nonane	0.127	[a]	chloroform	-1.6	[f,k]
n-decane	0.100	[a]	1,1,1-trichloroethane	-0.7	[m]
				7.8	[k]
c-hexane	0.150	[a]	tetrachloromethane	0.19	[a]
benzene	0.166	[a]	1,1,2,2-tetrachloroethane	-12.0	[l]
water	-1080	[b]20°C	bromobenzene	0.66	[d]
methanol	-660	[b,c]	1,2-dibromoethane	1.0	[i]
ethanol	-385	[b,c]	iodobenzene	1.00	[d]
1-propanol	-330	[b,c]	aniline	-110	[e]
1-butanol	-240	[b,c]	nitrocyclohexane	25	[j]
t-butanol	80	[b]	nitrobenzene	-315	[j]
1-pentanol	-180	[d]	carbon disulfide	0.27	[a]
t-pentanol	8.6	[m]			
1-hexanol	-140	[b]			
1-octanol	-67	[d]			
1-decanol	18	[b]			
1-dodecanol	54	[b]			
benzyl alcohol	-600	[d]			
glycerol	-650	[d]			
diethyl ether	-0.32	[i]			
	1.5	[k]			

1,2-dimethoxyethane	-6.0	[l]
veratrole	3	[g]
acetone	-84	[b]

[a] Krupowski, Parry, Jones and Davies 1974 [b] Parry Jones 1975 [c] Brown and Parry Jones 1975 [d] Dutkiewicz and Dutkiewicz 1993; [e] Malsch 1929; [f] Thiebaut, Weisbecker and Ginet 1968. [g] Dutkiewicz and Koput 1995 [h] Nowak *et al*. 1980. [i] Piekara 1962. [j] Dutkiewicz 1981 [k] Böttcher 1973. [l] Dutkiewicz 1994 [m] Nowak 1972 [n] Nowak and Malecki 1985.

correlated with the polarity of the solvents, e.g., the $E_T(30)$ index (Chapter 4) (Dutkiewicz and Dutkiewicz 1993), although only for alkanols and halobenzenes.

A further dependence of the relative permittivity is on the frequency ω of an alternating electrical field. As mentioned above, the limits are the high frequency (>10 GHz) value, ε_∞, corresponding to n_∞^2 (approximately 1.1 n_D^2), and the static (low frequency, < 1 MHz) value, ε_0, but at inbetween frequencies the dependence is quite complicated. The complex permittivity is given by the Cole–Cole expression (Cole and Cole 1941):

$$\varepsilon(\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/(1 + \omega^2\tau^2) + \mathrm{i}(\varepsilon_0 - \varepsilon_\infty)\omega\tau/(1 + \omega^2\tau^2) \qquad (3.30)$$

where τ is the relaxation time, provided that there is a single relaxation time, see also below, and i ≡ √-1. Proper evaluation of this function yields the required quantities ε_0, ε_∞, and τ, see Figure 3.3. Values of the relaxation times are presented and discussed further below.

The electrical conductivity of a solvent is generally very low, and is very sensitive to its purity. For instance, the absorption of carbon dioxide from the air

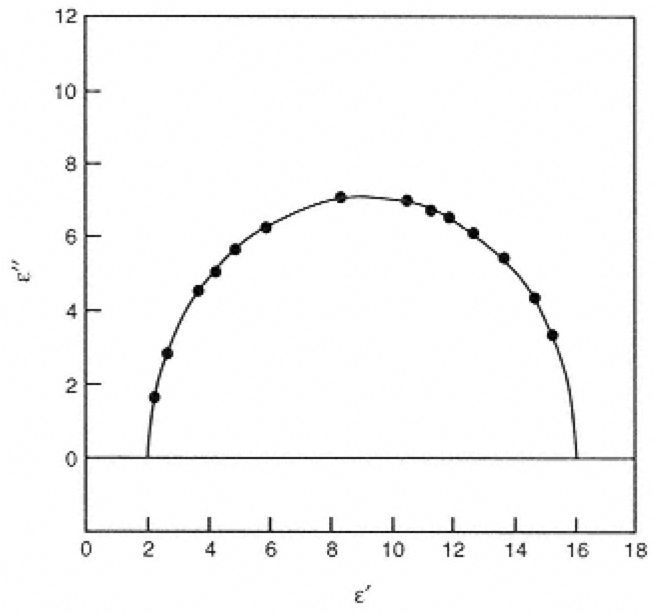

Figure 3.3
Cole–Cole plot in the complex plane of the loss factor (the imaginary part) ε'' against the real part ε′ in Eq. (3.30), for a solvent with the high frequency relative permittivity $\varepsilon_\infty = n_\infty^2 = 2$ and the low frequency value $\varepsilon_0 = 16$ and a single relaxation time τ. These data correspond approximately to trimethyl phosphate, but the plotted points are fictitious, just to show that a semicircle describes experimental data such as these

in water causes the latter to conduct 200 times better than pure water, because of the slight ionic dissociation of the carbonic acid formed. Still, the conductivity can be measured with adequate accuracy for carefully purified solvents. The values of the specific conductances of the solvents in our List at 25°C in $\text{ohm}^{-1}\ \text{m}^{-1}$ are shown in Table 3.5 in exponential notation ('E-*k*' $\equiv 10^{-k}$). The conductivity of the purified solvents can be traced to their autosolvolysis discussed in Chapter 4. If the mobility of the resulting ionic species is estimated, e.g., from the self diffusion coefficients (see below), then the concentrations of these species can be obtained from the conductivity, hence also could the autosolvolysis constant. However, this connection cannot in general be made.

7—

Magnetic Properties of Solvents

A further property of solvents that should be presented here is their magnetic susceptibility. Solvents are diamagnetic, i.e., they have the property of being pushed from a region of high magnetic flux to one of lower flux in an inhomogeneous magnetic field or out of the field entirely. The quantity reported in Table 3.5 is the negative of the molar (volume) diamagnetic susceptibility, $-\chi$, in $10^{-6}\ \text{cm}^3\ \text{mol}^{-1}$. This quantity is field-independent and hardly temperaturedependent, and is additive in the diamagnetic susceptibilities of the constituent atoms and some structural features. For instance, the increment per methylene group in a straight alkyl chain is $11.5 \times 10^{-6}\ \text{cm}^3\ \text{mol}^{-1}$. It is not surprising, therefore, that the molar, volume, diamagnetic susceptibility is proportional to the molar refractivity:

$$-\chi = 2.46 \times 10^{-5} R_D \qquad (3.31)$$

for most organic solvents. Table 3.8 lists some of the additive atomic and structural contributions to the diamagnetic susceptibility, from which also those of the molar refractivity can be estimated according to the above expression.

One use of the magnetic susceptibility is the correction of nuclear magnetic resonance chemical shifts of solutes measured in various solvents so as to be on

Table 3.8 Atom and group increments to the diamagnetic susceptibility, $-\chi$ in $10^{-6}\ \text{cm}^3\ \text{mol}^{-1}$ (Selwood 1956)

Atom	$-\chi$	Atom	$-\chi$	Atom	$-\chi$
H	2.93	O in ether, ROH	4.61	I	40.5
C	6.00	O, carbonyl	-1.73	S	15.0
N in ring	4.61	O,carboxyl	3.36	P	26.3
N in chain	5.57	F	6.3	H_2O	13.0
N, monoamide	2.54	Cl	17.0	C, aromatic*	-0.24
N, diamide	2.11	Br	26.5	-C=C-*	-5.5

*A correction to be applied for each occurrence.

a common basis. The bulk magnetic susceptibility correction for the nuclear magnetic resonance chemical shift measured for a solute in two solvents placed in two coaxial cylinders in the magnetic field is $\Delta\delta = (2\pi/3) \times 10^6\Delta\chi$ in ppm.

8—
Surface and Transport Properties of Solvents

The surface tension, σ, also symbolized by γ, of a solvent is the work that has to be applied in order to increase its surface area by one unit and is defined as the force acting at right angles per unit length. The quantity depends, in principle, on the second phase against which the surface exists, and it is implied to be the vapour at the saturation pressure. Practically, the surface tension is measured against air at constant atmospheric pressure, the difference being negligible in most circumstances. The surface tension is measurable by the capillary rise or the bubble pressure methods, and is moderately temperature dependent. The values of σ at 25°C, in mN m^{-1}, are shown in Table 3.9 to 1 decimal, although for many solvents it is known with better accuracy. The surface tension generally decreases linearly with the temperature.

The values of the surface tension vary only moderately among the solvents on the List, most of the values being between 20 and 40 mN m^{-1}, notable exceptions being the lighter aliphatic hydrocarbons with lower values. On the other hand, higher values characterize water, polyols, and other strongly hydrogen bonded solvents such as alkanolamines, thiobisethanol, hydrogen peroxide, sulfuric acid and some highly substitited halocarbons as trichlorobenzene, bromoform, diiodomethane, and some substituted aromatic solvents like benzophenone, aniline, quinoline and nitrobenzene.

The dynamic viscosity, η, of a solvent is the resistance that it presents to laminar flow, and varies considerably among solvents, some, such as diethyl ether, having a low viscosity (0.242 mPa s) whereas others, such as glycerol, have a very high viscosity (945 mPa s). A less often used value is the kinematic viscosity, $v = \eta/d$, that is commonly the quantity directly measured in a flow viscosimeter, being proportional to the time required for a certain volume of liquid to flow out of it. The kinematic viscosity of supercritical fluids is very low, of the order of 10^{-7} J s kg^{-1}, one to two orders of magnitude lower than for ordinary liquids, since the viscosity decreases much more rapidly than the density as the temperature is raised near the critical point (Eckert, Knutson and Debenedetti 1996). The fluidity of a solvent is the reciprocal of its (dynamic) viscosity. The temperature-dependent dynamic viscosities η are shown in Table 3.9 at 25°C, in mPa s (equal numerically in the non-SI unit of cP, centi-Poise), to 3 or 4 significant figures.

The viscosity of a solvent depends strongly on the temperature, and Table 3.9 shows the values of $-100\ \mathrm{d}\ln\eta/\mathrm{d}T$ in K^{-1} at 25°C unless otherwise noted. The

Table 3.9 Transport and surface properties of solvents

No.	Name	sigma		eta		-d ln η/dT		D		lambda	
10	tetramethylsilane	12.3	[2]	0.236	[ee]	0.75	[ee]	3.89	[ee]	0.1148	[2]
20	n-pentane	15.5	[1]	0.225	[1]	0.84	[2]	5.62	[4]	0.1125	[2]
30	2-methylbutane	14.5	[1]	0.215	[1]	0.93	[2]	4.85	[4]	0.1096	[2]
40	n-hexane	17.9	[1]	0.294	[1]	0.86	[2]	4.21	[4]	0.1196	[2]
50	c-hexane	24.6	[1]	0.898	[1]	1.75	[2]	1.41	[4]	0.1234	[2]
60	n-heptane	19.7	[1]	0.397	[1]	1.05	[2]	3.11	[4]	0.1247	[2]
70	n-octane	21.2	[1]	0.515	[1]	1.23	[2]	2.75	[4]	0.1277	9[2]
80	2,2,4-trimethylpentane	18.3	[1]	0.475	[1]	1.20	[2]	2.42	[h]b	0.0982	[2]
90	n-decane	23.4	[1]	0.861	[1]	1.48	[2]	1.31	[4]	0.1318	[2]
100	n-dodecane	24.9	[1]	1.378	[1]	1.75	[2]	0.93	[i]	0.1354	[2]
110	n-hexadecane	27.1	[2]	2.831	[2]	2.08	[2]	0.38	[y]	0.1421	[2]
120	benzene	28.2	[1]	0.603	[1]	1.27	[2]	2.16	[4]	0.1433	[2]
130	toluene	27.9	[1]	0.553	[1]	1.15	[2]	2.59	[j]b	0.1323	[2]
140	o-xylene	29.5	[1]	0.756	[1]	1.36	[2]	1.61	[h]b	0.1313	[2]
150	m-xylene	28.1	[1]	0.581	[1]	1.19	[2]	2.56	[j]d	0.1302	[2]
160	p-xylene	27.8	[1]	0.605	[1]	1.21	[2]	2.75	[j]d	0.1297	[2]
170	ethylbenzene	28.5	[1]	0.637	[1]	1.24	[2]			0.1289	[2]
180	cumene	27.7	[1]	0.739	[1]	1.35	[2]	1.68	[h]b	0.1232	[2]
190	mesitylene	28.3	[1]	1.039	[1]	1.54	[2]			0.1351	[2]
200	styrene	31.6	[1]	0.696	[1]	1.42	[2]			0.1365	[2]
210	tetralin	34.5	[1]	2.14	[1]	1.96	[2]			0.1296	[2]
220	cis-decalin	31.6	[1]	3.034	[1]	2.23	[2]	0.46	[h]b	0.1130	[2]
230	water	71.8	[1]	0.8903	[1]	2.21	[2]	2.13	[4]	0.6063	[2]
240	methanol	22.3	[1]	0.551	[1]	1.32	[2]	2.32	[4]	0.1999	[2]
250	ethanol	21.9	[1]	1.083	[1]	1.91	[2]	1.01	[4]	0.1681	[2]

Table 3.9 *(continued)*

No.	Name	sigma		eta		$-d \ln \eta/dT$		D		lambda	
290	i-butanol	22.5	[1]	3.333	[1]	3.24	[2]			0.1318	[2]
300	2-butanol	23.0	[1]	2.998	[1]	3.96	[2]			0.1344	[2]
310	t-butanol	20.1	[1]	4.438	[1]	2.80	[2]	0.51	[4]c	0.1158	[2]
320	n-pentanol	25.2	[1]	3.513	[1]	2.87	[2]	0.26	[aa]	0.1528	[2]
330	i-pentanol	23.9	[1]	3.738	[1]	3.11	[2]			0.1407	[2]
340	t-pentanol	22.3	[1]	3.548	[1]	4.51	[2]			0.1213	[2]
350	n-hexanol	25.7	[1]	4.592	[1]	3.14	[2]			0.1537	[2]
360	c-hexanol	33.8	[1]	41.06	[1]b	69.90	[2]b			0.1341	[2]
370	n-octanol	26.9	[1]	7.363	[1]	3.59	[2]	0.14	[4]	0.1598	[2]
380	n-decanol	28.4	[2]	11.32	[2]	3.93	[2]			0.1615	[2]
390	n-dodecanol	29.4	[2]	15.72	[2]	4.05	[2]			0.1496	[2]
400	benzyl alcohol	39.5	[1]	6.54	[1]	3.30	[2]			0.1603	[2]
410	2-phenylethanol	40.6	[2]	1.43	[d]a	4.59	[2]			0.1627	[2]
420	allyl alcohol	25.3	[1]	1.333	[1]	2.08	[2]			0.1546	[2]
430	2-chloroethanol	38.9	[1]	3.046	[1]	2.65	[2]			0.1332	[2]
440	2-cyanoethanol										
450	2,2,2-trifluoroethanol			1.755	[1]	2.57	[1]				
460	hexafluoro-i-propanol	16.1	[a]	1.579	[a]						
470	2-methoxyethanol	30.8	[1]	1.61	[1]	2.53	[2]			0.1880	[2]
480	2-ethoxyethanol	28.2	[1]	1.85	[1]	2.70	[2]			0.1757	[2]
500	1,2-propanediol	36.5	[1]	42.2	[1]	6.26	[2]			0.2004	[2]
510	1,3-propanediol	45.2	[1]	46.6	[1]a	3.60	[2]			0.2226	[2]
520	2-butanediol	35.3	[2]	50	[2]	6.22	[2]			0.1730	[2]

530	2,3-butanediol (meso)	30.6	[1]	65.8	[1]c	4.93	[2]				
540	1,4-butanediol	44.2	[1]	71.5	[1]	4.96	[2]			0.2059	[2]
550	1,5-pentanediol	43.4	[1]	114.66	[1]a	5.10	[2]			0.2000	[2]
560	diethyleneglycol	48.5	[1]	30	[1]	4.69	[2]			0.2037	[2]
570	triethyleneglycol	45.2	[1]	49	[1]a	4.56	[2]			0.1931	[2]
580	glycerol	63.3	[1]	945	[1]	8.53	[2]	0.00	[k]b	0.2918	[2]
590	phenol	38.8	[1]	3.5	[1]e	2.70	[2]	0.78	[j]7	0.1565	[2]f

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(table continued from previous page)

No	Name	sigma		eta		$-d \ln \eta/dT$		D		lambda	
600	2-methylphenol	35.0	[1]	7.608	[1]	2.68	[2]b	0.58	[u]	0.1517	[2]c
610	3-methylphenol	37.0	[1]	9.807	[1]b	5.48	[2]	0.55	[u]	0.1493	[2]
620	4-methylphenol	34.6	[1]	9.402	[1]c	4.29	[2]b	0.61	[u]	0.1426	[2]c
630	2-methoxyphenol							0.73	[u]		
640	2,4-dimethylphenol	31.2	[1]	68.5	[2]	3.42	[2]	0.58	[u]	0.1612	[2]
650	3-chlorophenol			11.55	[3]	3.08	[2]				
660	diethyl ether	16.5	[1]	0.242	[1]a	1.01	[2]	6.1	[j]a	0.1282	[2]
670	di-n-propyl ether	19.9	[1]	0.339	[1]	1.16	[2]			0.1266	[2]
680	di-i-propyl ether	17.2	[1]	0.379	[1]	1.11	[2]			0.1093	[2]
690	di-n-butyl ether	22.5	[1]	0.645	[1]	1.35	[2]			0.1279	[2]
700	di(2-chloroethyl) ether	37.0	[1]	2.14	[1]	2.52	[1]				
710	1,2-dimethoxyethane	24.6	[1]	0.455	[1]	1.06	[2]			0.1405	[2]
720	bis(methoxyethyl) ether	30.4	[2]	0.989	[1]	1.57	[2]				
730	furan	23.4	[1]	0.361	[1]	1.01	[2]			0.1262	[2]
740	tetrahydrofuran	26.4	[1]	0.462	[v]	1.04	[2]			0.1200	[2]
750	2-methyl tetrahydrofuran			0.473	[v]	1.01	[v]				
760	tetrahydropyran			0.764	[1]	1.62	[1]	1.84	[1]		
770	1,4-dioxane	32.8	[1]	1.194	[1]	1.77	[2]	1.01	[4]	0.1588	[2]
780	1,3-dioxolane			0.6	[1]a						
790	1,8-cineole	31.1	[1]	2.303	[dd]	3.42	[dd]				
800	anisole	34.6	[1]	0.984	[1]	1.51	[2]	1.35	[h]b	0.1560	[2]
810	phenetole	32.9	[1]	1.138	[1]	1.71	[2]			0.1397	[2]
820	diphenyl ether	39.4	[1]	2.6	[1]	2.26	[2]	0.35	[h]b		

830	dibenzyl ether	38.2	[1]	4.654	[1]	2.69	[2]			0.1249	[2]
840	1,2-dimethoxybenzene			3.281	[1]						
850	trimethyl orthoformate										
860	trimethyl orthoacetate										
870	propionaldehyde			0.318	[1]	1.00	[2]			0.1601	[2]
880	butyraldehyde	29.9	[1]	0.43	[1]	1.06	[2]			0.1451	[2]
890	benzaldehyde	38.3	[2]	1.321	[1]	1.52	[2]			0.1525	[2]
900	p-methoxybenzaldehyde			4.22	[d]						

continued overleaf

***Table 3.9** (continued)*

No.	Name	sigma		eta		-d ln η/dT		D		lambda	
910	cinnamaldehyde			5.4	[d]						
920	acetone	22.7	[1]	0.303	[1]	0.95	[2]	4.77	[4]	0.1605	[2]
930	2-butanone	23.7	[1]	0.378	[1]	1.09	[2]			0.1450	[2]
940	2-pentanone	24.5	[1]	0.463	[1]	1.13	[2]			0.1420	[2]
950	methyl i-propyl ketone	24.8	[2]	0.429	[2]	1.18	[2]			0.1424	[2]
960	3-pentanone	24.8	[1]	0.442	[1]	1.08	[2]			0.1439	[2]
970	c-pentanone	33.2	[1]	1.307	[1]	1.48	[2]			0.1484	[2]
980	methyl-i-butyl ketone	23.2	[1]	0.546	[1]	1.34	[2]			0.1439	[2]
990	methyl t-butyl ketone			0.713	[d]a	1.31	[2]			0.1384	[2]
1000	c-hexanone	35.0	[1]	2.003	[1]	2.01	[2]	0.89	[l]	0.1403	[2]
1010	2-heptanone	26.1	[1]	0.76	[1]	1.36	[2]				
1020	3-heptanone	25.5	[1]	0.743	[2]	1.47	[2]			0.1360	[2]
1030	di-t-butyl ketone										
1040	acetophenone	38.8	[1]	1.66	[1]	1.82	[2]			0.1471	[2]
1050	propiophenone										
1060	phenylacetone										
1070	p-methylacetophenone										
1080	p-chloroacetophenone										
1090	benzophenone	45.1	[3]	13.61	[d]	2.16	[2]f	0.46	[j]7		
1100	acetylacetone	30.3	[1]	0.767	[2]	1.27	[2]			0.1533	[2]
1110	biacetyl										
1120	formic acid	37.0	[1]	1.966	[1]	2.02	[2]			0.2698	[2]

1130	acetic acid	26.9	[1]	1.131	[1]	1.48	[2]	0.99	[j]a	0.1593	[2]
1140	propanoic acid	26.2	[1]	1.024	[1]	1.43	[2]			0.1465	[2]
1150	n-butanoic acid	26.2	[1]	1.529	[1]	1.65	[2]			0.1466	[2]
1160	n-pentanoic acid	26.1	[1]	1.975	[1]	1.99	[2]			0.1420	[2]
1170	n-hexanoic acid	27.5	[1]	2.826	[1]	2.19	[2]			0.1420	[2]
1180	n-heptanoic acid	27.8	[2]	3.84	[2]	2.36	[2]			0.1426	[2]
1190	dichloroacetic acid	35.4	[3]	5.91	[2]	1.95	[2]			0.1869	[2]
1200	trifluoroacetic acid	13.5	[1]	0.855	[1]	1.54	[2]			0.1621	[2]

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No.	Name	sigma		eta		$-d \ln \eta/dT$		D		lambda	
1210	acetic anhydride	31.9	[1]	0.841	[1]	1.37	[2]	1.61	[1]	0.1640	[2]
1220	benzoyl chloride	38.7	[2]	1.137	[2]	1.42	[2]			0.1041	[2]
1230	benzoyl bromide										
1240	methyl formate	23.9	[1]	0.328	[1]	0.94	[2]			0.1851	[2]
1250	ethyl formate	24.0	[1]	0.377	[1]	1.05	[2]			0.1603	[2]
1260	methyl acetate	24.1	[1]	0.364	[1]	1.02	[2]	3.28	[4]	0.1534	[2]
1270	ethyl acetate	23.1	[1]	0.426	[1]	1.10	[2]	2.77	[4]	0.1439	[2]
1280	propyl acetate	23.7	[1]	0.551	[1]	1.16	[2]			0.1409	[2]
1290	butyl acetate	24.5	[1]	0.689	[1]	1.34	[2]			0.1367	[2]
1300	i-pentyl acetate	24.2	[1]	0.789	[1]	1.42	[2]			0.1304	[2]
1310	methyl propanoate	24.4	[2]	0.431	[2]	1.09	[2]			0.1453	[2]
1320	ethyl propanoate	23.7	[1]	0.502	[1]	1.18	[2]			0.1387	[2]
1330	dimethyl carbonate	28.5	[2]	0.585	[d]	1.44	[2]			0.1617	[2]
1340	diethyl carbonate	26.0	[1]	0.748	[1]	1.34	[2]				
1350	ethylene carbonate	41.4	[2]	1.93	[1]d	1.41	[2]				
1360	propylene carbonate	41.4	[2]	2.53	[1]	2.22	[2]			0.2124	[2]
1370	diethyl malonate	31.1	[1]	1.94	[1]	2.05	[2]			0.1503	[2]
1380	methyl benzoate	37.5	[1]	1.859	[1]	2.09	[2]			0.1536	[2]
1390	ethyl benzoate	34.8	[1]	1.947	[1]	2.00	[2]			0.1443	[2]
1400	dimethyl phthalate	40.4	[2]	14.36	[2]	4.76	[2]			0.1487	[2]
1410	dibutyl phthalate	33.4	[1]	15.4	[1]	4.70	[2]			0.1361	[2]
1420	ethyl chloroacetate	31.3	[1]	1.11	[2]	1.59	[2]			0.1362	[2]
1430	ethyl trichloroacetate			0.4334	[d]a						

1440	ethyl acetoacetate	31.3	[1]	1.508	[g]	1.83	[2]			0.1515	[2]
1450	4-butyrolactone	38.5	[2]	1.717	[2]	1.91	[v]			0.1613	[2]
1460	perfluoro-n-hexane	11.0	[s]	0.662	[f]						
1470	perfluoro-n-heptane	11.9	[s]	0.8892	[f]						
1480	perfluoro-methylcyclo-hexane	14.0	[w]	0.873	[f]						
1490	perfluoro-decalin	15.0	[t]	5.14	[d]						
1500	fluorobenzene	27.1	[1]	0.549	[1]	1.25	[2]			0.1260	[2]
1510	hexafluorobenzene	21.6	[1]	0.86	[1]	2.05	[2]	1.61	[m]	0.0882	[2]

continued overleaf

Table 3.9 *(continued)*

No.	Name	sigma		eta		$-d \ln \eta/dT$		D		lambda	
1520	1-chlorobutane	23.4	[1]	0.426	[1]	1.11	[2]			0.1187	[2]
1530	chlorobenzene	32.5	[1]	0.758	[1]	1.15	[2]	2.35	[j]	0.1269	[2]
1540	dichloromethane	27.2	[1]	0.411	[1]	0.93	[2]	3.78	[l]	0.1390	[2]
1550	1,1-dichloroethane	24.2	[1]	0.505	[1]	1.07	[2]			0.1110	[2]
1560	1,2-dichloroethane	31.5	[1]	0.779	[1]	1.27	[2]	1.72	[4]	0.1347	[2]
1570	tr-1,2-dichloroethylene	27.8	[2]	0.385	[2]	0.93	[2]			0.1120	[2]
1580	o-dichlorobenzene	36.2	[1]	1.324	[1]	1.44	[2]			0.1211	[2]
1590	m-dichlorobenzene	35.5	[1]	1.028	[1]	1.27	[2]			0.1172	[2]
1600	chloroform	26.5	[1]	0.536	[1]	1.00	[2]	2.31	[4]	0.1175	[2]
1610	1,1,1-trichloroethane	24.9	[1]	0.795	[1]	1.39	[2]	0.71	[x]	0.1012	[2]
1620	1,1,2-trichloroethane	33.0	[1]	1.101	[1]	1.40	[2]			0.1328	[2]
1630	trichloroethylene	28.8	[1]	0.532	[1]	0.91	[2]			0.1150	[2]
1640	1,2,4-trichlorobenzene	44.7	[2]	2.669	[2]	1.83	[2]			0.1117	[2]
1650	tetrachloromethane	26.1	[1]	0.901	[1]	1.42	[2]	1.32	[4]	0.0997	[2]
1660	tetrachloroethylene	31.3	[1]	0.841	[1]	1.04	[2]			0.1100	[2]
1670	1,1,2,2-tetrachloro-ethane	35.4	[1]	1.575	[1]	1.67	[2]			0.1127	[2]
1680	pentachloroethane	34.2	[1]	2.276	[1]	1.72	[2]			0.0940	[2]
1690	1-bromobutane	24.8	[1]	0.597	[1]	1.09	[2]			0.1037	[2]
1700	bromobenzene	35.5	[1]	1.069	[1]	1.38	[1]	1.12	[4]	0.1108	[2]
1710	dibromomethane	40.1	[2]	0.981	[2]	1.05	[2]	1.55	[n]	0.1085	[2]
1720	1,2-dibromoethane	38.3	[1]	1.611	[1]	1.51	[2]			0.1011	[2]
1730	bromoform	45.0	[1]	1.868	[1]	1.29	[2]	1.58	[l]	0.0994	[2]
1740	1-iodobutane	28.7	[1]	0.826	[1]						

1750	iodobenzene	38.8	[1]	1.517	[1]	1.57	[2]			0.1000	[2]
1760	diiodomethane	50.0	[1]	2.592	[1]	1.53	[2]	0.56	[n]	0.0980	[2]
1770	n-butylamine	23.5	[1]	0.578	[1]	1.40	[2]			0.1607	[2]
1780	benzylamine	39.5	[3]	1.59	[3]	1.76	[2]			0.1669	[2]
1790	1,2-diaminoethane	40.1	[1]	1.54	[1]	2.55	[2]			0.2322	[2]
1800	diethylamine	19.4	[1]	0.289	[1]	1.28	[2]			0.1341	[2]
1810	di-n-butylamine	24.1	[1]	0.946	[1]	1.70	[2]			0.1334	[2]

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No.	Name	sigma		eta		-d In η/dT		D		lambda	
1820	pyrrole	37.1	[1]	1.233	[1]	1.88	[2]			0.1641	[2]
1830	pyrrolidine	29.2	[1]	0.702	[1]	1.51	[2]			0.1592	[2]
1840	piperidine	29.4	[1]	1.362	[1]	1.70	[2]	0.97	[o]	0.1789	[2]
1850	morpholine	36.9	[1]	2.011	[1]	2.19	[2]			0.1643	[2]
1860	triethylamine	20.1	[1]	0.363	[1]	1.03	[2]	2.97	[o]	0.1187	[2]
1870	tri-n-butylamine	24.3	[1]	1.313	[1]	1.85	[2]			0.1204	[2]
1880	aniline	42.8	[1]	3.77	[1]	3.36	[2]	0.62	[u]	0.1722	[2]
1890	o-chloroaniline	43.1	[1]	2.916	[1]a	2.34	[2]	0.72	[u]	0.1523	[2]
1900	N-methylaniline	39.7	[1]	2.01	[1]	2.41	[2]			0.1577	[2]
1910	N,N -dimethylaniline	25.6	[1]	1.288	[1]	1.55	[2]			0.1419	[2]
1920	ethanolamine	48.3	[1]	19.346	[1]	4.14	[2]	0.05	[cc]	0.2366	[2]
1930	diethanolamine	49.0	[2]	351.9	[1]b	7.64	[2]				
1940	triethanolamine	45.2	[2]	613.6	[1]	7.78	[2]			0.1964	[2]
1950	pyridine	36.3	[1]	0.884	[1]	1.53	[2]	1.49	[o]	0.1624	[2]
1960	2-methylpyridine	32.8	[1]	0.753	[1]	1.33	[2]			0.1465	[2]
1970	3-methylpyridine	34.5	[1]	0.872	[1]	1.35	[2]			0.1368	[2]
1980	4-methylpyridine	35.5	[1]	0.866	[2]	1.45	[2]			0.1388	[2]
1990	2,4-dimethylpyridine	33.2	[1]	0.887	[1]a		[2]				
2000	2,6-dimethylpyridine	31.0	[1]	0.869	[1]a	1.37	[2]			0.1302	[2]
2010	2,4,6-trimethylpyridine	31.8	[2]	0.806	[e]	2.35	[2]			0.1463	[2]
2020	2-bromopyridine										
2030	3-bromopyridine										
2040	2-cyanopyridine										

2050	pyrimidine	30.3	[2]							0.1521	[2]
2060	quinoline	45.2	[1]	3.145	[1]	2.56	[2]			0.1492	[2]
2070	acetonitrile	28.3	[1]	0.341	[1]	0.96	[2]	4.85	[j]	0.1877	[2]
2080	propionitrile	26.7	[1]	0.405	[1]	1.06	[2]			0.1677	[2]
2090	butyronitrile	26.8	[1]	0.549	[1]	1.18	[2]			0.1673	[2]
2100	valeronitrile	27.0	[2]	0.692	[2]	1.24	[2]			0.1650	[2]
2110	acrylonitrile	26.7	[2]	0.339	[2]	0.91	[2]			0.1651	[2]
2120	benzyl cyanide	40.8	[1]	1.961	[1]	1.78	[2]			0.1245	[2]

continued overleaf

***Table 3.9** (continued)*

No.	Name	sigma		eta		-d In η/dT		D		lambda	
2130	benzonitrile	38.5	[1]	1.237	[1]	1.51	[2]			0.1485	[2]
2140	nitromethane	36.3	[1]	0.614	[1]	1.17	[2]	2.11	[4]	0.2068	[2]
2150	nitroethane	32.1	[1]	0.638	[1]	1.16	[2]			0.1631	[2]
2160	1-nitropropane	30.1	[1]	0.791	[1]	1.35	[2]			0.1542	[2]
2170	2-nitropropane	29.3	[1]	0.721	[1]	1.21	[2]			0.1408	[2]
2180	nitrobenzene	42.4	[1]	1.784	[1]	1.80	[2]			0.1480	[2]
2190	formamide	58.2	[1]	3.302	[1]	2.62	[2]			0.3529	[2]
2200	N-methylformamide	39.5	[1]	1.65	[1]	1.58	[2]	0.85	[p]	0.2127	[2]
2210	N,N-dimethylformamide	36.4	[1]	0.802	[1]	1.22	[2]	1.61	[p]	0.1840	[2]
2220	N,N-dimethylthioformamide	45.4	[b]	1.98	[b]						
2230	N,N-diethylformamide			1.254	[d]						
2240	N-methylacetamide	32.9	[1]	3.65	[1]b	2.08	[2]				
2250	N,N-dimethylacetamide	31.7	[1]	0.927	[1]	1.19	[2]			0.1672	[2]
2260	N,N-diethyl acetamide										
2270	pyrrolidinone-2	46.3	[2]	13.3	[1]	3.14	[2]			0.1943	[2]
2280	N-methylpyrrolidinone	40.7	[1]	1.666	[1]	1.88	[2]	0.78	[z]	0.1340	[2]
2290	N-methylthiopyrrolidinone	97.5	[2]	4.25	[b]					0.1344	[2]
2300	tetramethylurea			1.395	[1]						
2310	tetraethylurea										
2320	dimethylcyanamide										
2330	carbon disulfide	31.5	[1]	0.363	[1]a	0.72	[2]	4.11	[4]	0.1513	[2]
2340	dimethyl sulfide	23.8	[1]	0.279	[1]	0.86	[2]			0.1407	[2]
2350	diethyl sulfide	24.5	[1]	0.417	[1]	1.04	[2]			0.1324	[2]

2360	di-i-propyl sulfide										
2370	di-n-butyl sulfide	26.8	[1]	978	[1]	1.55	[1]				
2380	tetrahydrothiophene	35.0	[1]	0.971	[1]	1.31	[2]			0.1409	[2]
2390	pentamethylene sulfide										
2400	dimethyl sulfoxide	43.0	[1]	1.991	[1]	1.93	[2]	0.76	[1]	0.2223	[2]
2410	di-n-butyl sulfoxide										
2420	sulfolane	35.5	[1]	10.286	[1]b	2.27	[2]			0.1986	[2]

(table continued on next page)

(table continued from previous page)

No.	Name	Sigma		eta		-d ln η/dT		D		lambda	
2430	diethyl sulfite	29.0	[2]	0.839	[d]	1.28	[2]			0.1187	[2]
2430	thiobis(2-ethanol)	52.9	[2]	50.9	[b]	4.23	[2]			0.2061	[2]
2450	dimethyl sulfate	40.1	[3]	1.76	[d]					0.1337	[2]
2460	diethyl sulfate	34.6	[3]	1.6	[d]					0.1106	[2]
2470	methanesulfonic acid	50.0	[2]	10.52	[r]						
2480	trimethyl phosphate	36.9	[1]	2.03	[l]	1.75	[2]				
2490	triethyl phosphate	29.6	[1]	2.147	[l]	1.67	[2]				
2500	tri-n-butyl phosphate	27.2	[1]	3.39	[l]	1.83	[1]				
2510	hexamethyl phosphoramide	33.8	[1]	3.11	[l]	2.39	[1]				
2520	hexamethyl thiophosphoramide	28.7	[b]	5.55	[b]						
2530	hydrogen peroxide	73.7	[2]	1.15	[2]	1.85	[2]			0.4883	[2]
2540	hydrogen fluoride	8.4	[2]	0.256	[c]	0.88	[2]	8.41	[bb]	0.4274	[2]
2550	sulfuric acid	52.4	[2]	23.55	[2]	3.84	[2]	0.07	[q]	0.3351	[2]
2560	ammonia	21.1	[2]	0.131	[2]	0.99	[2]	5.71	[4]T	0.4791	[2]
2570	hydrazine	65.6	[2]	0.967	[2]	1.64	[2]			0.8936	[2]
2580	sulfur dioxide	21.7	[2]	0.265	[2]	1.38	[2]			0.1957	[2]
2590	thionyl chloride	32.3	[2]	0.633	[2]	0.79	[2]			0.1390	[2]
2600	phosphorus oxychloride	32.0	[2]	1.043	[2]	1.24	[2]			0.1236	[2]

Units: σ in mN m^{-1}; η in mPa·s; d ln η/dT in -10^{-2} K^{-1}; D in 10^{-5} cm^2 s^{-1}; λ in W m^{-1} K^{-1}.

References: [1] Riddick, Bunger and Sakano 1986. [2] DIPPR 1997. [3] Lide 1994. [4] Landoldt-Börnstein 1969. [a] Kötzsch 1966; Kivinen, Murto and Lehtonen 1967; Murto *et al*. 1967; Murto, Kivinen and Lindell 1970; Rochester and Symonds 1973; Rochester and Symonds 1974; Macdonald, Dolan and Hyne 1976 [b] Diggle and Bogsanyi 1974 (HMThPT, DMThF); Gritzner, Rechberger and Gutmann 1977 (NMThPy); Gutmann, Danksagmüller and Duscheck 1974 (DMThF); Ikeda 1971 ($S(EtOH)_2$). [c] Jander and Lafrenz 1970. [d] Abboud and Notario 1997. [e] Inglese, Grollier and Wilhelm 1983. [f] Reed 1964; Banks 1970; Kirk-Othmer 1994; Hudlicky 1976; Joyner 1986 [g] Marcus 1985 [h] Dobis 1976 [i] Iwahashi *et al.* 1990. [j] Samigullin 1973. [k] Fiorito and Meister 1972 [l] Claessens *et al.* 1984. [m] Hogenboom, Krynicki and Sawyer 1990. [n] Sandhu 1971. [o] Neronov and Chviruk 1968. [p] Easteal and Woolf 1985 [q] Harris 1982

[r] Paul *et al*. 1980. [s] Skripov and Firsov 1968 [t] Wesseler, Iltis and Clark, Jr. 1977. [u] Sharma and Kalia 1977 [v] Ponomarenko *et al*. 1994 [w] Fernandez, Williamson and McLure 1994 [x] Grochulski, Pszczolkowski and Kempka 1992 [y] Dymond and Harris 1992. [z] Ambrosone *et al*. 1995 [aa] Karger *et al*. 1995 [bb] Karger, Vardag and Lüdemann 1994 [cc] Rodnikova *et al*. 1994. [dd] Barata and Serrano 1994 [ee] Pankhurst, Jr. and Jonas 1975. [ff] Brüsewitz and Weiss 1993.

viscosity has generally an Arrhenius-type exponential dependence on the temperature:

$$\eta(T) = A_\eta \exp(-\Delta E_\eta / RT) \qquad (3.32)$$

but in the case of glass-forming solvents, a dependence that can be related to the free volume of the solvent (the difference between the molar and intrinsic volume), of the form $\eta(T)=A'_\eta \exp[-B'_\eta/(T-T_0]$, appears to represent the data better. In the former expression $\Delta E_\eta = -RT^2 \mathrm{d} \ln \eta/\mathrm{d}T$ is the activation energy for viscous flow, ranging from about 6 to 20 kJ mol^{-1}, and in the latter expression T_0 is the ideal glass transition temperature (see Table 3.2 for some experimental glass transition temperatures, T_g). The mechanism of viscous flow of a liquid involves the jumping of the molecules from their positions into nearby vacancies, hence depends on the free (void) volume in the liquid and on the bonding of the moving molecule to its neighbours that is disrupted in the jumping process before being formed again. It is, therefore, not surprising that there exists a definite relationship between ΔE_η and the enthalpy of vaporization, $\Delta_v H$, the former constituting a fraction between 0.2 and 0.3 of the latter, as is readily obtained from the data in Tables 3.1 and 3.9. The pressure dependence of the viscosity is also closely related to the free volume of the solvent. The fluidity ($\Phi = 1/\eta$) is proportional to the ratio between the free and the occupied volume, the former, as mentioned above, being the difference between the actual molar volume and the intrinsic molar volume (Tables 3.1 and 3.4) (Hildebrand 1978). In fact, the logarithm of the viscosity of liquids was found (Marcus 1998) to be described well for some 300 liquids by the empirical relationship:

$$\log(\eta/\mathrm{mPa\cdot s}) = -3.44(1 - V_X/V) + 0.081(\Delta_V H/RT \ln 10) + 0.46 n_{OH} \quad (3.33)$$

where n_{OH} is the number of hydroxy1 groups in the molecule.

Self diffusion coefficients can be obtained from the rate of diffusion of isotopically labeled solvent molecules as well as from nuclear magnetic resonance band widths. The self-diffusion coefficient of water at 25°C is $D = 2.27 \times 10^{-5}$ cm^2 s^{-1}, and that of heavy water, D_2O, is 1.87×10^{-5} cm^2 s^{-1}. Values for many solvents at 25°C, in 10^{-5} cm^2 s^{-1}, are shown in Table 3.9. The diffusion coefficient for all solvents depends strongly on the temperature, similarly to the viscosity, following an Arrhenius-type expression: $D = A_D \exp(\Delta E_D/RT)$. In fact, for solvents that can be described as being globular (see above), the Stokes-Einstein expression holds:

$$D = kT/S\pi\eta(\sigma/2) \qquad (3.34)$$

where $S = 6$ for slipping flow and $S = 4$ for sticky flow and σ is the diameter of the molecule. Provided that this diameter is temperature-independent, then $D\eta$ ought to be proportional to the temperature, as actually found for many solvents.

Non-globular molecules are not expected to obey this relationship. The self diffusion in supercritical fluids is an order of magnitude faster than in ordinary liquids with molecules of similar sizes (Eckert, Knutson and Debenedetti 1996).

The thermal conductivity of solvents, λ, is an important property of solvents with respect to the removal of heat generated in exothermal reactions and in their uses as heat exchange fluids. When convection is the mechanism of thermal conductance, it depends on the mobility of the molecules of the solvent and therefore increases the smaller these molecules are. For globular molecules in the gaseous phase the thermal conductivity is proportional to the viscosity: $\lambda/\eta = (5/2)R/M$, where M is the molar mass, but this relationship does not hold in liquids. For the latter, the potential energy is also involved, and the expression that fits the data for over 270 solvents is (Marcus 1998):

$$\begin{aligned}\lambda/W\ \mathrm{K^{-1}\,m^{-1}} &= 0.0695\,\mathrm{H}(C_\mathrm{P}/\mathrm{J\,K^{-1}\,mol^{-1}})/(V/\mathrm{cm^3\,mol^{-1}}) \\ &\quad + 0.00205\,\mathrm{H}(M/\mathrm{kg\,mol^{-1}})^{-1} \qquad (3.35)\end{aligned}$$

without involvement of the viscosity. However, in solvents associated by hydrogen bonds in a three-dimensional network energy can also be dissipated by means of vibrational coupling of adjacent bonds, so that such solvents exhibit relatively large thermal conductivities, beyond what is predicted by Eq. (3.35). Values of $\lambda/\mathrm{W\ m^{-1}\ K^{-1}}$ for most of the solvents on the List are shown in Table 3.9 (DIPPR 1997).

Two further quantities are relevant to the ability of the molecules of the solvents in the liquids to move are their rotational relaxation time and the absorption of ultrasound waves. The orientational relaxation rate is obtainable from nuclear magnetic resonance and vibrational spectroscopic, infrared and Raman, band widths, and from dielectric and ultrasound measurements. The orientational relaxation time, τ, is the reciprocal of the relaxation rate, and is measured in ps. The values obtained from different techniques are not necessarily the same, partly because different mechanisms govern the relaxation times, and partly because the rotations around different axes may have different rates and the techniques have different sensitivities to such effects. The values of τ obtained mainly from dielectric relaxation rates (see Eq. (3.30)), or rather from the critical wavelength $\lambda_c = 2\pi c\tau$ (Maryott and Smith 1955; Buckley and Marriott 1958), where c is the speed of light, are known for many solvents at 20 or 25°C and are summarized in Table 3.10. Solvents composed of rigid molecules have a single relaxation rate and yield a single semicircular Cole-Cole plot (Figure 3.3). Some solvents have more than one relaxation rate, due to different mechanisms for the relaxation taking place when internal rotations of parts of the molecule are possible or when intermolecular association occurs. Thus, *c*-hexanol, *n*-hexanol and *n*-decanol have the shorter relaxation times of 160, 21, and 53 ps, respectively, in addition to the longer ones shown in

Table 3.10 Orientational relaxation times and ultrasound absorption characteristic of solvents

No.	Name	Relaxation time		Ultrasound absorption	
40	n-hexane	7.4	[a]a	60	[e]
50	c-hexane	10	[f] (1990)	192	[e]
120	benzene	16	[b]	850	[e]
130	toluene	7.4	[a]a	86	[e]
140	o-xylene	9.6	[a]a	63	[e]
170	ethylbenzene			71	[e]
180	cumene			65	[e]
220	cis-decalin			124	[e]
230	water	9.45	[a]a	21	[e]
240	methanol	53	[a]a	30	[e]
250	ethanol	143	[a]a	52	[e]a
260	n-propanol	430	[a]a		
270	i-propanol	290	[a]a		
280	n-butanol	480	[a]	81	[e]
290	i-butanol	800	[a]a	153	[e]
300	2-butanol	500	[a]a		
320	n-pentanol	820	[a]a	97	[e]
330	i-pentanol			131	[e]
350	n-hexanol	1046	[a]a		
360	c-hexanol	2430	[a]		
370	n-octanol	1360	[a]		
380	n-decanol	1660	[a]a		
400	benzyl alcohol			79	[e]
420	allyl alcohol			44	[e]

430	2-chloroethanol			59	[e]
490	1,2-ethanediol	205	[h]a		
500	1,2-propanediol	675	[h]a		
510	1,3-propanediol	562	[h]a		
520	1,2-butanediol	1073	[h]a		
530	2,3-butanediol	2050	[h]a		
540	1,4-butanediol	1282	[h]a		
560	diethyleneglycol	470	[h]a		
580	glycerol	2604	[h]a		
660	diethyl ether	2.18	[a]	45	[e]
670	di-n-propyl ether				
680	di-i-propyl ether			53	[e]
710	1,2-dimethoxyethane	3.6	[f]		
730	furan	1.75	[a]a		
740	tetrahydrofuran	2.87	[a]a		
770	1,4-dioxane			117	[e]
800	anisole	9.6	[a]	44	[e]
820	diphenyl ether	5.9	[a]d		
900	p-methoxybenzaldehyde			64	[e]
910	cinnamaldehyde			96	[e]
920	acetone	3.34	[a]a	26	[e]
930	2-butanone	10	[c]		
1000	c-hexanone	10.4	[a]a	73	[e]

(table continued on next page)

Table 3.10 *(continued)*

No.	Name	Relaxation time		Ultrasound absorption	
1010	2-heptanone	11.2	[a]		
1040	acetophenone	39	[a]a		
1070	p-methylacetophenone	13	[k]b		
1090	benzophenone	82	[a]f		
1130	acetic acid	23	[c]	104	[e]
1140	propanoic acid			131	[e]
1190	dichloroacetic acid			105	[e]
1210	acetic anhydride			58	[e]
1240	methyl formate			49	[e]
1250	ethyl formate			50	[e]
1260	methyl acetate			36	[e]
1270	ethyl acetate	4.35	[a]a		
1280	propyl acetate			43	[e]
1300	i-pentyl acetate	8.5	[a]a		
1360	propylene carbonate	43.1	[f]		
1400	dimethyl phthalate			188	[e]
1410	dibutyl phthalate			250	[e]
1430	ethyl trichloroacetate	30	[g]b		
1500	fluorobenzene	5.6	[a]a		
1510	hexafluorobenzene	42	[b]		
1520	1-chlorobutane	7.9	[a]		
1530	chlorobenzene	10.3	[a]	147	[e]

1540	dichloromethane	8	[c]	779	[e]
1560	1,2-dichloroethane	6.9	[a]		
1580	o-dichlorobenzene			132	[e]
1590	m-dichlorobenzene				
1600	chloroform	7.4	[a]	363	[e]
1610	1,1,1-trichloroethane	5.5	[a]a	436	[e]
1640	1,2,4-trichlorobenzene			110	[e]
1650	tetrachloromethane	4.5	[a]a	546	[e]
1690	1-bromobutane	8.7	[a]		
1700	bromobenzene	16.4	[a]	144	[e]
1720	1,2-dibromoethane	11.6	[a]		
1730	bromoform			262	[e]
1740	1-iodobutane	18.6	[a]		
1750	iodobenzene	27.2	[a]a		
1800	diethylamine			36	[e]
1820	pyrrole	7.8	[a]a		
1830	pyrrolidine	12.9	[a]a		
1860	triethylamine			206	[e]
1870	tri-n-butylamine			96	[e]
1880	aniline	19.6	[a]a		
1890	o-chloroaniline			56	[e]
1920	ethanolamine			166	[e]
1950	pyridine	7.27	[a]a		
1970	3-methylpyridine			66	[e]

continued overleaf

Table 3.10 *(continued)*

No.	Name	Relaxation time		Ultrasound absorption	
1980	4-methylpyridine	13.3	[a]a		
2010	2,4,6-trimethylpyridine	40.4	[a]a		
2060	quinoline	44.6	[a]a		
2070	acetonitrile	3.21	[f]		
2130	benzonitrile	37.9	[a]a		
2180	nitrobenzene	46	[a]	74	[e]
2190	formamide	37.3	[f]	39	[e]
2200	N-methylformamide	128	[f]	33	[e]
2210	N,N-dimethylformamide	10.4	[f]		
2240	N-methylacetamide	9	[d]		
2250	N,N-dimethylacetamide	16	[f]		
2330	carbon disulfide	4.5	[a]a	2068	[e]
2400	dimethyl sulfoxide	4.7	[k]b		
2480	trimethyl phosphate	37	[e]a		
2550	sulfuric acid	480	[a]a		

Units: τ in ps; α/f^2 in 10^{-15} s^2 m^{-1}.
References: [a] Maryott and Smith 1951; Buckley and Maryott 1958. [b] Heasell and Lamb 1956. [c] Jenkins and Marcus 1995. [d] Bass *et al*. 1969. [e] Heasall and Lamb 1956; Krebs and Lamb 1958. [f] Buchner and Barthel 1995 [g] Srivastava and Srivastava 1997 [h] Lux and Stockhausen 1993. [j] Fawcett 1992 [k] Singh and Sharma 1996. [l] Becker *et al*. 1995.

Table 3.10. For tetrachloromethane and carbon disulfide the times shown in the Table are lower limits. The relaxation time for heavy water, D_2O is some 25% longer than for ordinary water, H_2O. The relaxation time of water depends strongly on the temperature, conforming to the quartic expression (Kaatze 1989):

$$\tau/\mathrm{ps} = 17.56 - 0.5780(t/^{\circ}\mathrm{C}) + 0.01043(t/^{\circ}\mathrm{C})^2 - 9.860 \times 10^{-5}(t/^{\circ}\mathrm{C})^3 + 3.743 \times 10^{-7}(t/^{\circ}\mathrm{C})^4 \tag{3.36}$$

The absorption of ultrasonic energy is also influenced by relaxation effects. At the frequencies of near 100 MHz that are employed, the relaxation times are of the order of ns, rather than the ps for dielectric relaxation. The relevant quantity is the absorption coefficient, α, divided by the square of the frequency, f^2. Values of α/f^2 in 10^{-15} s^2 m^{-1} have been measured for many solvents near 25°C at the frequency of 104 to 107 MHz (Heasall and Lamb 1956; Krebs and Lamb 1958) and are shown in Table 3.10, being considered accurate within ±2%. For a few solvents the ratio α/f^2 depends strongly on the frequency as it decreases somewhat for all solvents, e.g., for carbon disulfide $\alpha/f^2/$ $(10^{-15}$ s^2 $m^{-1})$ = 2068 at 104 MHz and 776 at 189 MHz and for dichloromethane it decreases from 779 at 107 MHz to 550 at 193 MHz

9—
Water and Heavy Water

Due to the importance of water as a solvent it merits a specific tabulation of its properties, although most are shown in Tables 3.1, 3.4, 3.5, 3.6, 3.9, and 3.10, where they can be compared with those of solvents, such as methanol, hydrogen peroxide, ethylene glycol, ammonia, and hydrogen fluoride, that share some features (structure, hydrogen bonding ability, etc.) with water (Marcus and Hefter 1997). It is also instructive to compare the properties of ordinary, light water, H_2O, with those of its isotopically substituted analog, deuterium oxide or heavy water, D_2O. Table 3.11 shows this comparison for general properties, those of

Table 3.11 Comparison of the properties of light and heavy water (DIPPR 1997; Marcus 1985)

Property	water (H_2O)	deuterium oxide (D_2O)
molar mass, M/g mol^{-1}	18.015	20.031
melting point, T_m/K	273.15	276.96
normal boiling point, T_b/K	373.15	374.55
critical point, T_C/K	647.13	643.89
critical pressure, P_C/MPa	22.055	21.941
critical volume, V_C/cm^3 mol^{-1}	55.9	56.3
van der Waals volume, V_{vdW}/cm^3 mol^{-1}	12.4	12.4
van der Waals surface, A_{vdW}/10^4 m^2 mol^{-1}	22.6	22.6
magnetic susceptibility, χ/10^{-6} cm^3 mol^{-1}	-12.9	
values at 298.15 K		
density, d/g cm^{-3}	0.997 047	1.104 48
molar volume, V/cm^3 mol^{-1}	18.069	18.133
isobaric expansibility, α_p/10^{-3} K^{-1}	0.255	0.218
isothermal compressibility, κ_T/GPa^{-1}	0.4525	0.4678
molar heat capacity, C_p/J K^{-1} mol^{-1}	75.384	84.52
vapour pressure, p/kPa	3.170	2.740
molar heat of vaporization, $\Delta_v H^o$/kJ mol^{-1}	43.869	46.375
relative permittivity, ε	78.46	78.06
$-1000(\partial \ln \varepsilon/\partial T)_p$, K^{-1}	4.59	4.64
$(\partial \ln \varepsilon/\partial P)_T$, GPa^{-1}	0.471	
refractive index, n_D	1.332 50	1.328 41
conductivity, κ/10^{-6} S m^{-1}	5.89	
	0.912	1.121

viscosity, η/mPa s		
$-1000(\partial \ln \eta/\partial T)_p$, K^{-1}	22.4	27.1
surface tension, σ/mN m^{-1}	71.96	71.85
self diffusion coefficient, D 10^{-5} cm^2 s^{-1}	2.272	2.109
thermal conductivity, λ/W m^{-1} K^{-1}	0.6063	0.5962
ideal gas heat capacity, C_p^o (ig)/J K^{-1} mol^{-1}	33.578	34.238
ideal gas entropy, S^o(ig)/J K^{-1} mol^{-1}	188.72	198.23
relaxation time (20°C), τ/ps	9.55	12.3

continued overleaf

***Table 3.11** (continued)*

Property	water (H_2O)	deuterium oxide (D_2O)
molecular parameters		
O-H(D) bond length, pm	95.72	95.75
bond angle, °	104.523	104.474
moment of inertia, $I_A/10^{-30}$ kg m^{-2}	0.102 20	0.183 84
moment of inertia, $I_B/10^{-30}$ kg m^{-2}	0.191 87	0.383 40
length of hydrogen bond, pm	276.5	276.6
dipole moment, μ/D	1.834	1.84
electrical quadrupole moment, $\theta/10^{-39}$ C m^2	1.87	
polarizability, $\alpha/10^{-30}$ m^3	1.456	1.536
collision diameter, σ/pm	274	
potential energy minimum, (u/k_B)/K	732	
chemical properties		
heat capacity density, $[C_p(1)-C_p(\mathrm{ig})]/V$/J K^{-1} cm^{-3}	2.31	2.77
solubility parameter, δ/$J^{1/2}$ $cm^{-3/2}$	49.4	48.7
normalized polarity index, E_T^N	1.000	0.991
polarity/polrizability, π^*	1.09	
electron pair donicity, β	0.47	
hydrogen bond donation ability, α	1.17	

the liquids at 298.15 K, those of the isolated molecules, and some chemical properties, pertaining to Chapter 4. The data are taken mostly from (DIPPR 1997; Marcus 1985).

The molecular properties that do not depend on the masses of the atoms are seen to be very similar for the two isotopic species. This point is made use of in discussions of the structure of water (see Chapter 4). It is also noteworthy that although the boiling point of heavy water is higher than that of light water, the vapour pressure of the former being less than that of the latter, the vapour pressure curves intersect, at higher outside pressures, near 198°C, and the critical point of heavy water is *lower* than that of light water (Marcus 1998). Heavy water does show the density anomaly near the freezing point just as light water does: the volume increase on freezing is 1.632 cm^3 mol^{-1} for H_2O and 1.561 cm^3 mol^{-1} for D_2O (positive! contrary to most liquids, the volumes of which diminish on freezing). The thermal expansivities of the two ices are the same, but just above the melting points the liquids contract by 0.0059% for H_2O and 0.0032% for D_2O, reaching maximal density at 3.98°C and 11.19°C, respectively.

References

Abboud, J.-L. M. and Notario, R. (1997) *Critical Compilation of Scales of Solvent Effects*, report to IUPAC Commission on Phys. Org. Chem. (private communication).

Ambrosone, L., D'Errico, G., Sartorio, R. and Vitagliano, V. (1955) *J. Chem. Soc., Faraday Trans*. **91**, 1339.

Angell, C. A., Sare, J. M. and Sare, E. J. (1978) *J. Phys. Chem*. **82**, 2622.

Baetman, N. and Baudet, J. (1967) *Compt. Rend*. **265C**, 288.

Baliah, V. and Jeyanthy, J. J. D. (1989) *Indian J. Chem*. **28A**, 472.

Banks, R. E. (1970) *Fluorocarbons and their Derivatives*, Macdonald, London, 2nd ed.

Barata, P. A. and Serrano, M. L. (1994) *J. Chem. Eng. Data* **39**, 289.

Barone, G., Castronuovo, G., Della Gatta, G., Elia, V. and Iannone, A. (1985) *Fluid Phase Equil*. **21**, 157.

Basarova, P., Svoboda, V. and Kolska, Z. (1993) *Fluid Phase Equil.* **89**, 253.

Bass, S. J., Nathan, W. I., Meighan, R. M. and Cole, R. H. (1964) *J. Phys. Chem.* **68**, 509.

Becker, U., Wessels, V., Turky, G., Ghoneim, A. and Stockhausen, M. (1995) *Z. Phys. Chem. (Munich)* **191**, 251.

Bernardo-Gil, G., Esquivel, M. and Ribeiro, A. (1990) *J. Chem. Eng. Data* **35**, 252.

Bickerton, J., Pilcher, G. and Al-Takhin, G. (1984) *J. Chem. Thermodyn*. **16**, 373.

Bondi, A. (1964) *J. Phys. Chem*. **68**, 441.

Botros, M. G., Naoum, M. M., Shinouda, H. G. and Rizk, H. A. (1983) *J. Chim. Phys*. **80**, 441.

Böttcher, C. J. F. (1973) *Theory of Electric Polarization*, Elsevier, Amsterdam, 2nd ed., vol. 1, 296.

Brown, B. L. and Parry Jones, G. (1975) *J. Chem. Soc., Faraday Trans. 2* **71**, 1657.

Brüsewitz, M. and Weiss, A. (1993) *Ber. Bunsengesell. Phys. Chem*. **97**, 1.

Buchner, R. and Barthel, J. (1995) *J. Mol. Liq*., **65**, 55; (1992) *Chem. Soc. Rev*. **21**, 263.

Chen, T., Dannhauser, W. and Johari, J. (1969) *J. Chem. Phys*. **50**, 2046.

Chirico, R. D., Hossenlopp, I. A., Gammon, B. E., Knipmeyer, S. E. and Steele, W. V. (1994) *J. Chem. Thermodyn*. **26**, 1187.

Claessens, M., Fiasse, P., Fabre, O., Zimmermann, D. and Reisse, J. (1984) *Nouv. J. Chim.* **8**, 357.

Cole, K. S. and Cole, R. H. (1941) *J. Chem. Phys*. **9**, 341.

Côté, J.-F., Brouillette, D., Desnoyers, J. E., Rouleau, J.-F., St. Artaud, J.-M. and Perron, G. (1996) *J. Solution Chem*. **25**, 1163.

Czechowski, G., Zywucki, B. and Jadzyn, J. (1988) *J. Chem. Eng. Data* **33**, 55.

Dallos, A. and Ratkovics, F. (1991) *J. Chem. Thermodyn*. **23**, 207.

Diggle, J. W. and Bogsanyi, D. (1974) *J. Phys. Chem*. **78**, 1018.

DIPPR, (1997) *The DIPPR Pure Component Data Compilation*, Technical Database Services, Inc., New York, version 12.4 (for Windows).

Dobis, O. (1976) *J. Chem. Phys*. **65**, 4264.

Domalski, S. and Hearing, E. D. (1990) *J. Phys. Chem. Ref. Data* **19**, 881.

Dutkiewicz, M. (1981) *J. Chem. Soc., Faraday Trans. 2* **77**, 1301.

Dutkiewicz, M. (1994) *J. Mol. Struct*. **318**, 171.

Dutkiewicz, M. and Dutkiewicz, E. (1993) *J. Solution Chem*. **22**, 787.

Dutkiewicz, M. and Koput, J. (1995) *J. Mol. Struct*. **354**, 153.

Dymond, J. H. and Harris, K. R. (1992) *Mol. Phys*. **75**, 461.

Easteal, A. J. and Woolf, L. A. (1985) *J. Chem. Soc., Faraday Trans. 1* **81**, 2821.

Eckert, C. A., Knutson, B. L. and Debenedetti, P. G. (1996) *Nature* **383**, 313.

Fawcett, W. R. (1992) *Chem. Phys. Lett*. **199**, 153.

Fedotov, A. N., Simonov, A. P., Popov, V. K. and Bagratashvili, V. N. (1996) *Zh. Fiz. Khim*. **70**, 166; (1996) *Russ. J. Phys. Chem*. **70**, 156.

Fernandez, J., Williamson, A.-M. and McLure, I. A. (1994) *J. Chem. Thermodyn*. **26**, 897.

Fialkov, Yu. Ya. (1990) *Rastvoritel' kak Sredstvo Upravleniya Khimicheskim Protsessom (Solvents as Factors Regulating Chemical Processes)*, Khimiya, St. Petersburg.

Fiorito, R. B. and Meister, R. (1972) *J. Chem. Phys*. **56**, 4605.

Fischer, T. and Weiss, A. (1986) *Ber. Bunsenges. Phys. Chem*. **90**, 896.

Gerger, W., Mayer, U. and Gutmann, V. (1977) *Monatsh. Chem*. **108**, 417.

Giddings, J. C., Myers, M. N. and King, J. W. (1969) *J. Chromatogr. Sci*. **7**, 276; King, J. W. (1989) *J. Chromatogr. Sci*. **27**, 355; Yang, J. and Griffiths, P. R. (1996) *Anal. Chem.* **68**, 2353.

Grahame, D. C. (1953) *J. Chem. Phys*. **21**, 1054.

Grineva, O. V. and Zhuravlev, V. I. (1996) *J. Chem. Eng. Data* **41**, 604.

Gritzner, G., Rechberger, P. and Gutmann, V. (1977) *J. Electroanal. Chem*. **75**, 739.

Grochulski, T., Pszczolkowski, L. and Kempka, M. (1992) *Phys. Rev. Lett*. **68**, 3635.

Gutmann, V., Danksagmüller, K. and Duschek, O. (1974) *Z. Phys. Chem. (NF)* **92**, 199.

Harris, K. R. (1982) *J. Chem. Soc., Faraday Trans. 1* **78**, 1629.

Heasall, E. L. and Lamb, J. (1956) *Proc. Phys. Soc*. **B69**, 869; (1956) *Proc. Roy. Soc.* **A237**, 233; Krebs, K. and Lamb, J. (1958) *Proc. Roy. Soc.* **A244**, 558.

Herail, M., Berthelot, M. and Proutiere, A. (1995) *J. Phys. Org. Chem*. **8**, 421.

Hildebrand, J. (1978) *Disc. Faraday Soc*. **66**, 151.

Hogenboom, D. L., Krynicki, K. and Sawyer, D. W. (1990) *Mol. Phys*. **40**, 823.

Hudlicky, M. (1976) *Organic Fluorine Chemistry*, Plenum, New York, 2nd ed.

Ikeda, E. (1971) *J. Phys. Chem*. **75**, 1240.

Inglese, A., Grolier, J.-P.E. and Wilhelm, E. (1983) *J. Chem. Eng. Data* **28**, 124.

Isaacs, N. S. (1981) *Liquid Phase High Pressure Chemistry*, Wiley, Chichester.

Iwahashi, M., Yamaguchi, Y., Ogura, Y. and Suzuki, M. (1990) *Bull. Chem. Soc. Jpn*. **63**, 2154.

Jander, J. and Lafrenz, Ch. (1970) *Ionizing Solvents*, Verlag Chemie/Wiley, Weinheim.

Jenkins, H. O B. and Marcus, Y. (1995) *Chem. Rev*. **95**, 2695.

Jordan, T. E. (1954) *Vapor Pressure of Organic Compounds*, Interscience, New York.

Joyner, B. D. (1986) *J. Fluorine Chem*. **33**, 337.

Kaatze, U. (1989) *J. Chem. Eng. Data* **34**, 371.

Kabo, G. J., Kozyro, A. A., Diky, V. V., and Simirsky, V. V. (1995) *J. Chem. Eng. Data* **40**, 371.

Karger, N., Vardag, T. and Lüdemann, H.-D. (1994) *J. Chem. Phys*. **100**, 8271.

Kasprowicz, B. and Kielich, S. (1967) *Acta Phys. Polon*. **31**, 787.

Kirk-Othmer (1994) Encyclopedia of Chemical Technology Wiley, New York, 4th ed. **11**, 501.

Kim, J. I. (1978) *Z. Phys. Chem. (Frankfurt)* **113**, 129.

Kivinen, A., Murto, J. and Lehtonen, M. (1967) *Suomen Kemist*. **40B**, 336.

Klofutar, C., Paljk, S. and Malneršič, R. (1982) *J. Chem. Soc., Faraday Trans. 1* **78**, 3693.

Kötzsch, H. J. (1966) *Chem. Ber*. **99**, 1143.

Kozyro, A. A., Simirskii, V. V., Kabo, G. Ya., Frenkel, M. L., Krasulin, A. P., Sevruk, M. V. and Sokolov, N. A. (1990) *Zh. Fiz. Khim*. **64** 2360; (1990) *Russ. J. Phys. Chem*. **64**, 1274.

Krupowski, T., Parry Jones, G. and Davies, M. (1974) *J. Chem. Soc., Faraday Trans. 2* **70**, 1348.

Ksiazczak, A. (1981) *Pol. J. Chem*. **55**, 1629.

Landoldt-Börnstein Zahlenwerte und Funktionen (1959) **II/6**, p. 618 ff (relative permittivities); *ibid*. (1967) **II/10**, p. 66 ff (diamagnetic susceptibilities); *ibid*. (1969), **II/5**, p. 148 ff. (viscosities); **II/5a**, p. 588 ff (diffusion coefficients).

Lawson, D. D. (1980) *Appl. Energy* **6**, 241.

Leahy, D. (1986) *J. Pharm. Sci*. **75**, 629; Leahy, D. E., Carr, P. W., Pearlman, R. S., Taft, R. W. and Kamlet, M. J. (1986) *Chromatographia* **21**, 473.

Lemire, R. J. and Sears, P. G. (1981) *J. Solution Chem*. **10**, 511.

Lencka, M. (1990) *J. Chem. Thermodyn*. **22**, 473.

Lide, D. (1994/5) ed., *Handbook of Chemistry and Physics*, CRC, Boca Raton, 75th ed.

Lifanova, N. V., Usacheva, T. M. and Zhuravlev, V. I. (1992) *Zh. Fiz. Khim*. **66**, 237; (1992) *Russ. J. Phys. Chem*. **66**, 125.

Lin, C. T., Young, F. K., Brulé, M. R., Lee, L. L., Starling, K. E. and Chao, J. (1980) *Hydrocarbon Process*. **59** (8), 117.

Lux, A. and Stockhausen, M. (1993) *Phys. Chem. Liq*. **26**, 67.

Macdonald, D. D., Dolan, B. and Hyne, J. B. (1976) *J. Solution Chem*. **5**, 405.

Malsch, J. (1929) *Phys. Z.* **29**, 770; **30**, 837.

Marcus, Y. (1984) *J. Solution Chem*. **13**, 599.

Marcus, Y. (1985) *Ion Solvation*, Wiley, Chichester, Chapter 5.

Marcus, Y. (1991) *J. Phys. Chem*. **95**, 8886.

Marcus, Y. (1977) *Introduction to Liquid State Chemistry*, Wiley, Chichester, Chapter 2.

Marcus, Y. (1998) to be published.

Marcus, Y. and Hefter, G. T. (1997) *J. Mol. Liquids* **73, 74**, 61.

Marcus, Y. and Hefter, G. T. (1997) unpublished results (presented in part at the 30th Intl. Conf. Solution Chem., Vichy, August 1997).

Maryott, A. A. and Smith, E. R. (1955) *Dielectric Constants of Pure Liquids*, NBS Circular 514; Buckley, F. and Mariott, A. M. (1958) *Dielectric Relaxation of Liquids*, NBS Circular 589.

McClellan, A. L. (1989) *Tables of Experimental Dipole Moments*, Rahara Enterprises El Cerrito, CA, Vol. 3.

McGowan, J. C. (1978) *J. Appl. Chem. Biotechnol*. **28**, 599; idem., (1984) *ibid*. **34A**, 38; Abraham, M. H. and McGowan, J. C. (1987) *Chromatographia* **23**, 243.

McKay, H. A. C. and Healy, T. V. (1960) *Progr. Nucl. Chem*. **III/2**, 546.

Mopsik, F. I. (1969) *J. Chem. Phys*. **50**, 2559.

Murto, J. and Heino, E.-L. (1966) *Suomen Kemist*. **39B**, 263.

Murray, J. S., Lane, P., Brinck, T., Paulsen, K., Grice, M. E. and Politzer, P. (1993) *J. Phys. Chem*. **97**, 9369.

Murto, J., Kivinen, A. and Lindell, E. (1970) *Suomen Kemist*. **43B**, 28.

Nowak, J. (1972) *Acta Phys. Polon*. **41A**, 617.

Nowak, J. and Malecki, J. (1985) *Chem. Phys*. **95**, 331.

Nowak, J., Malecki, J., Thiebaut, J.-M. and Rivail, J.-L. (1980) *J. Chem. Soc., Faraday Trans. 2* **76**, 197.

Neronov, Yu. I. and Chviruk, O. V. (1968) *Zh. Fiz. Khim*. **42**, 1612; (1968) *Russ. J. Phys. Chem*. **42**, 845.

Owen, B. B. and Brinkley, S. R. Jr. (1943) *Phys. Rev*. **64**, 32.

Pankhurst, H. J. Jr. and Jonas, J. (1975) *J. Chem. Phys*. **63**, 2698, 2705.

Parry Jones, G. (1975) in M. Davies, (ed.) *Dielectric and Related Molecular Processes* **2**, 198.

Paul, R. C., Kapila, V. P., Kumar, R., Gupta, S. K. and Sharma, S. K. (1980) *Z. Anorg, Allgem. Chem.* **471**, 203.

Pedley, J. B., Naylor, R. D. and Kirby, S. P. (1986) *Thermochemical Data of Organic Compounds* 2nd ed., Chapman & Hall, London.

Piekara, A. (1962) *J. Chem. Phys*. **36**, 2145.

Pirilä-Honkanen, P. and Ruostesuo, P. (1991) *Thermochim. Acta* **184**, 65.

Ponomarenko, S. P., Borovikov, Yu. Ya, Dul'nev, P. G., Borovikova, E. S., Makovetskii, V. P., and Nikolaenko, T. K. (1993) *Zh. Obshch. Khim*. **63**, 2312.

Ponomarenko, S. M., Mushtakova, S. P., Demakhin, A. G., Faifel', B. L. and Kalmanovich, D. G. (1994) *Zhur. Obshch. Khim.* **65**, 190, (1995) *J. General Chem*. **65**, 160.

Puranik, S., Kumbharkhane, A. C. and Mehrotra, S. (1994) *J. Mol. Liq.* **59**, 173.

Reddy, N. Y., Naidu, P. S. and Prasad, K. R. (1994) *Indian J. Pure Appl. Phys*. **32**, 958.

Reed, T. M. (1964) in J. H. Simons, (ed.) *Fluorine Chemistry*, Academic Press, New York, **5**, pp. 133 ff.

Riddick, J. A., Bunger, W. B. and Sakano, T. K. (1986) *Organic Solvents*, Wiley-Interscience, New York, 4th ed.

Rochester, C. H. and Symonds, J. R. (1973) *J. Chem. Soc., Faraday Trans. 1* **69**, 1267.

Rochester, C. H. and Symonds, J. R. (1974) *J. Fluorine Chem*. **4**, 141.

Rodnikova, M. N., Privalov, V. I., Samigullin, F. N. and Zhakova, V. V. (1994) *Zh. Fiz. Khim*. **68**, 2235; (1994) *Russ. J. Phys. Chem*. **68**, 2032.

Rosset, R. H., Mourier, P. and Caude, M. (1986) *Actual Chim*. **7**, 17.

Samigullin, F. M. (1973) *Zh. Strukt. Khim*. **14**, 611, (1973) *J. Struct. Chem*. **14**, 569.

Sandhu, H. S. (1971) *Can. J. Phys*. **49**, 1069.

Scaife, W. G. S. (1971) *J. Phys. A* **4**, 413.

Scaife, W. G. S. and Lyons, C. G. R. (1980) *Proc. Roy. Soc.* **A370**, 193.

Schadow, E. and Steiner, R. (1969) *Z. Phys. Chem. (NF)* **66**, 105.

Selwood, P. W. (1956) *Magnetochemistry* Interscience, New York, 2nd ed.

Serratrice, G., Delpuech, J.-J. and Diguet, R. (1982) *Nuov. J. Chim.* **6**, 489.

Sharma, C. A. and Kalia, R. K. (1977) *J. Chem. Eng. Data* **22**, 39.

Shehatta, I. (1993) *Thermochim. Acta* **213**, 1.

Singh, P. J. and Sharma, K. S. (1996) *Indian J. Pure Appl. Phys*. **34**, 1.

Skripov, V. P. and Firsov, V. V. (1968) *Zh. Fiz. Khim*. **42**, 1253, (1968) *Russ. J. Phys. Chem*. **42**, 653.

Srivastava, S. K. and Srivastava, S. L. (1977) *Indian J. Phys*. **51B**, 26.

Stephenson, W. K. and Fuchs, R. (1985) *Can. J. Chem*. **63**, 336.

Stephenson, R. M. and Malanowski, S. (1987) *Handbook of Thermodynamics of Organic Compounds*, Elsevier, New York.

Streck, C. and Richert, R. (1994) *Ber. Bunsenges. Phys. Chem*. **98**, 619.

Srinivasan, K. R. and Kay, R. L. (1977) *J. Solution Chem*. **6**, 357.

Srivastava, S. K. and Srivastava, S. L. (1977) *Indian J. Phys*. **51B**, 26.

Swaddle, T. W. (1990) *Inorg. Chem*. **29**, 5017.

Tagaki, T. and Noguchi, M. (1992) *Thermochim. Acta* **195**, 239.

Takagi, T., Teranishi, H., Yokogama, C. and Takahashi, S. (1989) *Thermochim. Acta* **142**, 291.

Thiebaut, J. M., Weisbecker, A. and Ginet, C. (1968) *Compt. Rend*. **267**, 661.

Uosaki, Y., Kawamura, K. and Moriyoshi, T. (1996) *J. Chem. Eng. Data* **41**, 1525.

Varushchenko, R. M., Bulgakova, L. L., Druzhinina, A. I., Mirzabekyants, N. S. and Makarov, K. N. (1980) *Perftoiro. Uglerody Biol. Med*. 30.

Venkatsewara Rao, A. and Bhanumathi, A. (1978) *Indian J. Pure Appl. Phys*. **16**, 553.

Vij, J. K., Scaife, W. G. and Calderwood, J. H. (1978) *J. Phys., D* **11**, 545.

Wesseler, E. P., Iltis, R. and Clark, L. C. Jr. (1977) *J. Fluorine Chem*. **9**, 137.

Würflinger, A. (1982) *Ber. Bunsenges. Phys. Chem*. **86**, 172.

Yaws, C. L., Chen, D., Yang, H.-C., Tan, L. and Nico, D. (1989) *Hydrocarbon Processing Intl. Ed*. **68** (7), 61.

Yaws, C. L. and Pan, X. (1992) *Chem. Eng*. (4) 130.

Chapter 4—
Chemical Properties of Solvents

The chemical properties of solvents have obviously a strong bearing on their applicability for various purposes. The solvents should selectively dissolve the desired solutes and not some others, they should be inactive in the chemical reactions undergone by the solutes, but solvate, again selectively, reactants, transition states, intermediates, and products. These aspects of the behaviour can be achieved by the proper blend of the chemical properties of structuredness, polarity, electron-pair and hydrogen bond donation and acceptance ability, softness, acidity and basicity, hydrophilicity or hydrophobicity, and redox properties, among others. Such chemical characteristics can often be derived from physical properties, but in other cases must be obtained from chemical interactions, for instance by the use of chemical probes ('indicators').

Most of these properties have been obtained for ambient conditions for a large number of solvents, and those available for those on the List in Chapter 1 are presented and discussed in this Chapter. Values not pertaining to 25°C have been marked with the same temperature codes as in Chapter 3 in the references columns outside the square brackets in the Tables of this Chapter, with j denoting quantities calculated for this book from the data in the sources indicated.

1—
The Structuredness of Solvents

The volatility, viscosity, diffusion coefficient and relaxation rates of solvents are closely connected with the self-association of the solvents, described quantitatively by their structuredness. This property has several aspects that can be denoted by appropriate epithets (Bennetto and Caldin 1971). One of them is 'stiffness' expressible by the internal pressure, the cohesive energy density, the square of the solubility parameter, see Chapter 3, or the difference between these two. Another aspect is 'openness' expressible by the compressibility or the fluidity, the reciprocal of the viscosity, of the solvent (see Chapter 3). A further aspect is 'ordering', expressible by the deficit of entropy of the liquid solvent relative to the solvent vapour or the dipole orientation correlation, in the case of polar solvents (see Chapter 3).

An earlier expression for the structuredness as expressed by the 'ordering' of the solvent derives from Trouton's rule. This rule states that the entropy of vaporization at the normal boiling point, i.e., under isobaric conditions, of non-structured solvents is a constant. This entropy is the ratio of the corresponding enthalpy and the boiling point, since the Gibbs free energy change at this point is zero, the liquid and the vapour being at equilibrium. Specifically (cf. Eq. (3.12)),

$$\Delta_V S^\circ(T_b, P^\circ)/R = \Delta_V H^\circ(T_b, P^\circ)/T_b \lesssim 11.6 \qquad (4.1)$$

describes such non-structured solvents. On the contrary, solvents with $\Delta_V S^o(T_b, P^o)/R \geq 12$ are structured, and those inbetween these limits are borderline cases (Marcus 1992). Values of $\Delta_V S^o(T_b, P^o)/R$ are shown in Table 4.1.

This measure, however, pertains to the normal boiling point rather than to ambient conditions. The deficit of the entropy of the liquid solvent relative to the solvent vapour and to a similar non-structured solvent at any temperature, such as 25°C, has also been derived (Marcus 1996). An alkane with the same skeleton as the solvent, i.e., with atoms such as halogen, O, N, etc. being exchanged for CH_3, CH_2, and CH, etc., respectively, can be taken as the non-structured solvent. Since the vapour may also be associated, the temperature dependence of the second virial coefficient, B, of the vapour of both the solvent and the corresponding alkane, must also be taken into account. The entropy of vaporization at the temperature T, where $p \neq P^o$, is given by:

$$\Delta_V S^\circ(T, P^\circ) = \Delta_V H^\circ(T, P^\circ)/T + R\ln[p(T)/P^\circ] \qquad (4.2)$$

where P^o is the standard pressure of 0.1 MPa. The structuredness of the solvent can therefore be expressed by the non-dimensional quantity:

$$\Delta\Delta_V S^\circ(T, P^\circ)/R = [\Delta_V S^\circ_{\mathrm{solvent}}(T, P^\circ) - \Delta_V S^\circ_{\mathrm{alkane}}(T, P^\circ)]/R + (P^\circ/R)\mathrm{d}[B_{\mathrm{solvent}} - B_{\mathrm{alkane}}]/\mathrm{d}T \qquad (4.3)$$

A solvent with $\Delta\Delta_V S^o(T, P^o)/R>2$ is considered structured, or ordered, according to this criterion, whereas solvents with this entropy deficit lower than 2 are considered unstructured. Values of $\Delta\Delta_V S^o(T, P^o)/R$ of solvents at 25°C are shown in Table 4.1, and further values, for 60°C, 333.15 K, have also been published (Marcus 1996).

A different measure for the structuredness of solvents in terms of order, relevant to polar solvents only, is their dipole orientation correlation parameter (see Chapter 3):

$$g = (9k\varepsilon_o/4\pi N_{\mathrm{Av}})VT\mu^{-2}(\varepsilon - 1.1n_D^2)(2\varepsilon + 1.1n_D^2)/\varepsilon(2 + 1.1n_D^2)^2 \qquad (3.25)$$

Table 4.1 The structuredness of solvents, measured by their Trouton's constant, the entropy deficit, the dipole orientation correlation coefficient, and the heat capacity density

No.	Name	Trouton		$\Delta\Delta_V S$		g		$\Delta C_p/V$	
10	tetramethylsilane	9.7	[a]					0.4	[a]j
20	n-pentane	10.0	[a]	0.00	[d]			0.4	[a]j
30	2-methylbutane	10.0	[a]	-0.84	[d]			0.4	[d]
40	n-hexane	10.2	[a]	0.00	[d]			0.4	[a]j
50	c-hexane	11.2	[a]	0.07	[d]			0.4	[a]j
60	n-heptane	10.3	[a]	0.00	[d]			0.4	[a]j
70	n-octane	10.4	[a]	0.00	[d]			0.4	[a]j
80	2,2,4-trimethylpentane	9.9	[a]					0.3	[a]j
90	n-decane	10.6	[a]	0.00	[d]			0.4	[a]j
100	n-dodecane	11.0	[c]	0.00	[d]			0.4	[a]j
110	n-hexadecane	10.9	[c]	0.00	[d]			0.4	[b]j
120	benzene	10.5	[a]	0.56	[d]			0.4	[d]
130	toluene	10.4	[a]	0.74	[d]			0.6	[d]
140	o-xylene	10.6	[a]	1.67	[d]			0.5	[d]
150	m-xylene	10.6	[a]	1.49	[d]			0.4	[d]
160	p-xylene	10.5	[a]	1.51	[d]			0.4	[d]
170	ethylbenzene	10.3	[a]	0.78	[d]	1.03	j	0.4	[d]
180	cumene	10.6	[a]	0.99	[d]			0.4	[d]
190	mesitylene	10.7	[a]	0.98	[d]			0.3	[d]
200	styrene	11.1	[a]					0.4	[d]
210	tetralin	11.0	[a]			0.42	j	0.4	[a]j
220	cis-decalin	10.5	[a]					0.4	[a]j

230	water	13.1	[b]	7.82	[d]	2.57	[b]	2.3	[d]
240	methanol	12.5	[b]	6.26	[d]	2.82	[b]	0.9	[d]
250	ethanol	13.5	[b]	7.45	[d]	2.90	[b]	0.8	[d]
260	n-propanol	13.4	[b]	6.67	[d]	2.99	[b]	0.7	[d]
270	i-propanol	13.5	[b]	6.28	[d]	3.08	[b]	0.8	[d]
280	n-butanol	13.3	[b]	7.83	[d]	3.10	[b]	0.7	[d]
290	i-butanol	13.7	[b]	8.15	[d]	3.32	[b]	0.7	[d]
300	2-butanol	13.2	[b]	5.98	[d]	2.94	[b]	0.9	[d]
310	t-butanol	13.6	[b]	5.00	[d]	2.22	[b]	1.1	[d]
320	n-pentanol	13.1	[b]	6.27	[d]	2.67	[b]	0.7	[d]
330	i-pentanol	13.0	[b]			2.64	[b]	0.7	[d]
340	t-pentanol	12.9	[b]			0.92	j	0.5	[a]j
350	n-hexanol	12.8	[b]	5.37	[d]	3.07	[b]	0.6	[d]
360	c-hexanol	12.7	[b]			2.13	[b]	0.7	[b]j
370	n-octanol	12.7	[b]			2.85	[b]	0.6	[d]
380	n-decanol	12.5	[b]			2.63	[b]		
390	n-dodecanol	12.3	[b]			2.06	[b]		
400	benzyl alcohol	13.0	[b]			1.80	[b]	1.0	[d]
410	2-phenylethanol	12.5	[c]						
420	allyl alcohol	13.0	[b]			3.04	[b]	0.8	[b]j
430	2-chloroethanol	12.5	[b]			2.78	[b]		
440	2-cyanoethanol								

continued overleaf

***Table 4.1** (continued)*

No.	Name	Trouton		$\Delta\Delta_V S$		g		$\Delta C_p/V$	
450	2,2,2-trifluoroethanol.	12.6	[b]			2.38	[b]		
460	hexafluoro-i-propanol					2.65	j		
470	2-methoxyethanol	11.9	[b]	5.81	[d]	1.70	[b]		
480	2-ethoxyethanol	12.0	[b]	5.87	[d]	3.61	j		
490	1.2-ethanedio	13.4	[b]	21.20	[d]	2.08	[b]	0.9	[d]
500	1,2-propanediol	14.2	[b]	18.20	[d]	2.43	j	1.2	[d]
510	1,3-propanediol	14.3	[b]	22.50	[d]	2.06	[b]	2.0	[d]
520	1,2-butanediol	13.7	[c]					1.1	j
530	2,3-butanediol (meso)	14.8	[c]					1.3	j
540	1,4-butanediol	15.0	[b]			2.06	[b]	0.8	[b] j
550	1,5-pentanediol	15.3	[b]			2.47	[b]	0.7	[b] j
560	diethyleneglycol	14.3	[b]			0.51	[b]	1.1	[b] j
570	triethyleneglycol	14.0	[b]			0.50	[b]		
580	glycerol	14.1	[b]	39.50	[d]	2.13	[b]	1.4	[d]
590	phenol	12.5	[b]			1.92	[b]	1.1	[b]d, j
600	2-methylphenol	11.7	[a]			2.30	j	0.9	[d]
610	3-methylphenol	12.3	[b]			2.09	[b]	0.9	[a] j
620	4-methylphenol	12.0	[b]			2.15	[b]	0.9	[a]c, j
630	2-methoxyphenol								
640	2,4-dimethylphenol	11.7	[a]			0.86	j		
650	3-chlorophenol	11.4	[c]						
660	diethyl ether	10.6	[b]			1.39	[b]	0.5	[d]
670	di-n-propyl ether	10.7	[b]			0.94	[b]	0.4	[a] j

680	di-i-propyl ether	10.4	[b]			1.54	[b]	0.4	[d]
690	di-n-butyl ether	10.9	[b]			0.90	[b]	0.2	[d]
700	di(2-chloroethyl) ether	12.0	[b]			1.84	[b]		
710	1,2-dimethoxyethane	11.0	[c]			1.23	[b]		
720	bis(methoxyethyl) ether	11.4	[b]			0.89	[b]		
730	furan	10.7	[a]			0.80	j	0.6	[a] j
740	tetrahydrofuran	10.7	[b]			1.07	[b]	0.5	[a] j
750	2-methyl tetrahydrofuran	11.0	[a]			1.66	j		
760	tetrahydropyran					0.83	j	0.5	[d]
770	1,4-dioxane	11.0	[b]					0.6	[a] j
780	1,3-dioxolane							0.6	[d]
790	1,8-cineole					0.99	j		
800	anisole	11.1	[b]			0.66	[b]		
810	phenetole	11.1	[b]			0.70	[b]		
820	diphenyl ether	10.9	[a]			0.61	j	0.6	[b]b, j
830	dibenzyl ether	11.5	[c]			0.77	j	0.5	[b]b, j
840	1,2-dimethoxybenzene	12.1	[b]			0.71	[b]		
850	trimethyl orthoformate								
860	trimethyl orthoacetate								
870	propionaldehyde	10.6	[b]			1.19	[b]	0.8	[a] j
880	butyraldehyde	10.9	[b]			1.08	[b]	0.7	[a] j
890	benzaldehyde	11.2	[b]			0.98	[b]	0.5	[a] j
900	p-methoxybenzaldehyde					0.50	j		
910	cinnamaldehyde					0.60	j		
920	acetone	10.9	[b]	2.36	[d]	1.05	[b]	0.6	[d]

(table continued on next page)

***Table 4.1** (continued)*

No.	Name	Trouton		$\Delta\Delta_V S$		g		$\Delta C_p/V$	
930	2-butanone	10.6	[b]	1.96	[d]	1.18	[b]	0.6	[d]
940	2-pentanone	10.7	[b]	2.02	[d]	1.19	[b]	0.5	[d]
950	methyl i-propyl ketone	11.0	[b]			1.19	[b]		
960	3-pentanone	10.8	[b]	2.01	[d]	1.22	[b]	0.5	[a] j
970	c-pentanone	11.2	[b]			0.69	[b]	0.5	[d]
980	methyl-i-butyl ketone	11.1	[b]			1.17	[b]	0.5	[a] j
990	methyl t-butyl ketone					1.17	j		
1000	c-hexanone	10.9	[b]			0.86	[b]	0.6	[d]
1010	2-heptanone	10.9	[b]			1.24	[b]	0.4	[b]j
1020	3-heptanone	11.0	[c]			1.19	j	0.5	[b]j
1030	di-t-butyl ketone					2.01	j		
1040	acetophenone	11.2	[b]			0.95	[b]	0.7	[b]j
1050	propiophenone								
1060	phenylacetone								
1070	p-methylacetophenone								
1080	p-chloroacetophenone								
1090	benzophenone	11.3	[c]			0.75	j		
1100	acetylacetone	11.9	[b]			1.69	[b]		
1110	biacetyl								
1120	formic acid	7.1	[b]	-3.9	[d]	6.47	[b]	1.4	[d]
1130	acetic acid	7.2	[b]	-4.50	[d]	0.54	[b]	1.0	[d]
1140	propanoic acid	9.6	[b]	-3.80	[d]	0.25	[b]	0.8	[d]
1150	n-butanoic acid	12.5	[b]	-1.50	[d]	0.39	[b]	0.6	[d]

1160	n-pentanoic acid	11.6	[b]	6.60	[d]	0.16	[b]	0.6	j
1170	n-hexanoic acid	13.1	[b]			0.33	[b]	0.6	[d]
1180	n-heptanoic acid	13.7	[b]			0.20	[b]		
1190	dichloroacetic acid	12.8	[c]						
1200	trifluoroacetic acid	11.8	[b]			0.74	[b]		
1210	acetic anhydride	11.9	[b]			1.36	[b]	0.9	[b]j
1220	benzoyl chloride	11.2	[b]			1.13	j		
1230	benzoyl bromide								
1240	methyl formate	11.1	[b]			0.90	[b]	0.8	[b]j
1250	ethyl formate	10.9	[b]			0.77	[b]	0.7	[b]j
1260	methyl acetate	11.1	[b]			0.92	[b]	0.6	[b]j
1270	ethyl acetate	11.1	[b]			0.85	[b]	0.5	[d]
1280	propyl acetate	11.1	[b]			0.96	[b]	0.5	[b]j
1290	butyl acetate	11.0	[b]			0.79	[b]	0.5	[b]j
1300	i-pentyl acetate	10.9	[b]			0.81	[b]	0.5	[b]j
1310	methyl propanoate	11.1	[b]			0.95	j	0.7	[b]j
1320	ethyl propanoate	10.8	[b]			0.93	[b]	0.5	[b]j
1330	dimethyl carbonate	11.1	[b]			0.97	j		[b]j
1340	diethyl carbonate	11.4	[c]			0.86	j		
1350	ethylene carbonate	12.2	[b]			1.59	[b]	0.6	[b]j
1360	propylene carbonate	11.6	[b]			1.23	[b]		
1370	diethyl malonate	11.7	[b]			0.85	[b]		
1380	methyl benzoate	11.0	[a]			0.78	j		

continued overleaf

Table 4.1 *(continued)*

No.	Name	Trouton		$\Delta\Delta_V S$		g		$\Delta C_p/V$	
1390	ethyl benzoate	11.1	[c]			0.76	j		
1400	dimethyl phthalate	12.0	[c]			0.76	j		
1410	dibutyl phthalate	15.5	[a]			0.79	[b]		
1420	ethyl chloroacetate					0.89	j		
1430	ethyl trichloroacetate					0.86	j		
1440	ethyl acetoacetate	11.6	[c]			1.25	j		
1450	4-butyrolactone	10.8	[b]	3.57	[d]	1.07	[b]	0.7	[a]j
1460	perfluoro-n-hexane								
1470	perfluoro-n-heptane								
1480	perfluoro-methylcyclohexane								
1490	perfluoro-decalin								
1500	fluorobenzene	10.5	[b]			0.83	[b]	0.5	[a]j
1510	hexafluorobenzene	10.8	[a]					0.5	[a]j
1520	1-chlorobutane	10.3	[b]	1.57	[d]	0.99	[b]	0.6	[d]
1530	chlorobenzene	10.6	[b]	0.90	[d]	0.64	[b]	0.5	[d]
1540	dichloromethane	10.9	[b]	2.55	[d]	1.04	[b]	0.7	[d]
1550	1,1-dichloroethane	10.6	[b]	1.84	[d]	0.78	[b]	0.5	[d]
1560	1,2-dichloroethane	10.9	[b]	2.44	[d]	1.13	j	0.6	[d]
1570	tr-1,2-dichloroethylene	10.6	[b]					0.5	[a]j
1580	o-dichlorobenzene	10.7	[b]			0.68	[b]	0.9	[d]
1590	m-dichlorobenzene	10.4	[a]			0.68	j	0.4	[a]j
1600	chloroform	10.7	[b]	2.01	[d]	1.30	[b]	0.6	[d]
1610	1,1,1-trichloroethane	10.3	[b]			0.99	[b]	0.5	[a]j

1620	1,1,2-trichloroethane	10.8	[b]			1.75	[b]	0.6	[a]j
1630	trichloroethylene	10.6	[b]			1.07	[b]	0.4	[a]j
1640	1,2,4-trichlorobenzene	9.8	[c]			0.66	j	0.4	[a]j
1650	tetrachloromethane	10.3	[b]	1.03	[d]			0.4	[d]
1660	tetrachloroethylene	10.6	[a]					0.5	[a]j
1670	1,1,2,2-tetrachloroethan	11.1	[a]	2.99	[d]	1.19	j	0.6	[d]
1680	pentachloroethane	10.3	[a]			1.12	j	0.6	[a]j
1690	1-bromobutane	10.2	[a]			0.85	j	0.5	[a]j
1700	bromobenzene	10.6	[b]			0.67	[b]	0.5	[a]j
1710	dibromomethane	11.0	[c]			0.76	j	0.7	[a]j
1720	1,2-dibromoethane	10.8	[a]			0.78	j	0.7	[a]j
1730	bromoform	11.1	[b]			0.80	[b]	0.7	[b]j
1740	1-iodobutane	10.0	[a]			0.69	j		
1750	iodobenzene	10.3	[a]			0.50	j	0.5	[a]j
1760	diiodomethane	11.2	[a]			0.59	j	0.9	[a]j
1770	n-butylamine	11.0	[b]			0.97	[b]	0.7	[d]
1780	benzylamine	11.5	[c]					0.8	[b]j
1790	1,2-diaminoethane	12.9	[b]			1.13	[b]		
1800	diethylamine	10.6	[a]	1.09	[d]	0.90		0.5	[d]j
1810	di-n-butylamine	11.2	[b]			0.90	[b]		
1820	pyrrole	11.6	[a]			0.68	j	0.8	[b]j
1830	pyrrolidine	11.7	[b]			0.65	[b]	0.9	[b]j
1840	piperidine	10.6	[b]			1.54	[b]	0.8	[d]
1850	morpholine	11.4	[b]	2.90	[d]	1.14	[b]		
1860	triethylamine	10.3	[b]	-0.07	[d]	0.71	[b]	0.4	[d]

(table continued on next page)

***Table 4.1** (continued)*

No.	Name	Trouton		$\Delta\Delta_V S$		g		$\Delta C_p/V$	
1870	tri-n-butylamine	11.6	[a]						
1880	aniline	11.6	[b]			0.81	[b]	0.9	[d]
1890	o-chloroaniline	11.6	[b]			1.72	[b]		
1900	N-methylaniline	11.6	[c]					0.8	
1910	N,N-dimethylaniline	11.1	[b]			0.58	[b]		
1920	ethanolamine	13.5	[b]			2.25	[b]	0.6	[d]
1930	diethanolamine	14.5	[b]			1.49	j	0.9	[d]
1940	triethanolamine	13.9	[b]			1.45	[b]	0.8	[d]
1950	pyridine	11.1	[b]			0.93	[b]	0.6	[d]
1960	2-methylpyridine	10.8	[b]			1.04	[b]	0.5	[d]
1970	3-methylpyridine	10.8	[b]			0.79	[b]	0.6	[b]j
1980	4-methylpyridine	10.9	[b]			0.67	[b]	0.6	[b]j
1990	2,4-dimethylpyridine					0.86	j		
2000	2,6-dimethylpyridine	10.9	[a]			1.19	j	0.4	[b]j
2010	2,4,6-trimethylpyridine	10.9	[c]			1.65	j		
2020	2-bromopyridine					0.98	j		
2030	3-bromopyridine					0.87	j		
2040	2-cyanopyridine					1.52	j		
2050	pyrimidine	13.3	[c]						
2060	quinoline	11.1	[b]			0.65	[b]	0.5	[a]j
2070	acetonitrile	10.3	[b]	4.38	[d]	0.74	[b]	0.7	[d]
2080	propionitrile	10.7	[b]	4.47	[d]	0.73	[b]	0.6	[d]

2090	butyronitrile	10.6	[b]	3.18	[d]	0.73	[b]	0.6	[d]
2100	valeronitrile	10.8	[c]			0.87	j		
2110	acrylonitrile	11.2	[a]			0.77	j		
2120	benzyl cyanide	12.5	[b]			0.79	[b]		
2130	benzonitrile	11.0	[b]			0.66	[b]	0.7	[d]
2140	nitromethane	11.3	[b]	3.36	[d]	0.92	[b]	0.9	[d]
2150	nitroethane	11.2	[b]	2.86	[d]	0.84	[b]	0.7	[d]
2160	1-nitropropane	11.2	[b]	2.62	[d]	0.84	[b]	0.7	[d]
2170	2-nitropropane	10.9	[b]	1.95	[d]	0.91	[b]	0.7	[d]
2180	nitrobenzene	11.0	[b]			0.88	[b]	0.4	[d]
2190	formamide	11.8	[b]	7.58	[d]	1.67	[b]	1.5	[d]
2200	N-methylformamide	12.0	[b]	6.10	[d]	3.97	[b]	0.8	[d]
2210	N,N-dimethylformamide	11.1	[b]	4.00	[d]	1.03	[b]	0.7	[d]
2220	N,N-dimethylthioformamide					0.77	j		
2230	N,N-diethylformamide					1.06	j		
2240	N-methylacetamide	14.4	[b]			4.41	[b]	0.9	[b]j
2250	N,N-dimethylacetamide	11.1	[b]	3.34	[d]	1.26	[b]	0.7	[d]
2260	N,N-diethyl acetamide					1.46	j		
2270	pyrrolidinone-2	12.3	[b]	5.48	[d]	1.03	[b]	1.0	[d]
2280	N-methylpyrrolidinone	11.3	[b]	3.36	[d]	0.92	[b]	0.6	[d]
2290	N-methylthiopyrrolidino					0.72	j		
2300	tetramethylurea	13.7	[b]			1.16	[b]		
2310	tetraethylurea					0.92	j		
2320	dimethylcyanamide								

continued overleaf

***Table 4.1** (continued)*

No.	Name	Trouton		$\Delta\Delta_V S$		g		$\Delta C_p/V$	
2330	carbon disulfide	10.2	[b]					0.5	[a]j
2340	dimethyl sulfide	10.5	[a]			0.89	j	0.6	[a]j
2350	diethyl sulfide	10.5	[a]			0.92	j	0.5	[a]j
2360	di-i-propyl sulfide					1.17	j		
2370	di-n-butyl sulfide	10.7	[a]			0.94	j		
2380	tetrahydrothiophene	10.6	[b]			0.84	j	0.5	[a]j
2390	pentamethylene suflide					0.83	j		
2400	dimethyl sulfoxide	11.1	[b]	5.07	[d]	1.04	[b]	0.8	[d]
2410	di-n-butyl sulfoxide								
2420	sulfolane	11.6	[b]			0.92	[b]	0.4	[a]j
2430	thiobis(2-ethanol)	14.5	[c]						
2440	diethyl sulfite	11.1	[c]			1.16	[b]		
2450	dimethyl sulfate	10.5	[c]			1.61	j		
2460	diethyl sulfate	11.8	[c]			1.22	j		
2470	methanesulfonic acid								
2480	trimethyl phosphate	10.8	[c]			1.00	[b]		
2490	triethyl phosphate	11.0	[c]			0.94	[b]		
2500	tri-n-butyl phosphate	13.1	[b]			1.02	[b]		
2510	hexamethyl phosphorictriamide	13.4	[b]			1.39	[b]		
2520	hexamethyl thiophosphorictriamide								
2530	hydrogen peroxide	13.2	[c]					1.8	[b]j
2540	hydrogen fluoride	3.1	[c]			4.29	j	0.9	[b]a, j

2550	sulfuric acid					3.95	j	1.0	[b]j
2560	ammonia	11.7	[b]			1.68	[b]	1.8	[b]a, j
2570	hydrazine	12.7	[b]			2.75	[b]	1.5	[b]j
2580	sulfur dioxide	11.5	[c]			1.07	j	1.0	[b]a, j
2590	thionyl chloride	9.9	[c]			1.27	j	0.7	[b]j
2600	phosphorus oxychloride	10.9	[c]			0.98	j	0.5	[b]j

Units : $\Delta_v S_o(T_b, P^o)/R$, $\Delta\Delta_v S^o(T, P^o)/R$, and g are dimensionless; $[C_p(l) - C_p(g)]/V$ is in JK^{-1} cm^{-3}.
References:[a] Riddick, Bunger and Sakano 1986. [b] marcus 1992. [c] DIPPR 1997. [d] Marcus 1996.

Non-structured solvents have g values near unity, say $0.7 \le g \le 1.3$. Structured polar solvents have $g > 1.7$ (Marcus 1992), if their dipoles are arranged, on the average, in the head-to-tail configuration. There are a few strongly doubly hydrogen bonded solvents where the configuration is such that the dipoles cancel each other and they have very low g values although they are highly structured: these are, for example, the lower carboxylic acids. Values of g at 25°C and 0.1 MPa from (Marcus 1992) are shown in Table 4.1, and values for further solvents can be calculated from the data in Tables 3.1 and 3.5. The temperature and pressure dependencies of V, n_D, and ε must be known in order to evaluate g at other conditions, but these are available only for some of the solvents in this Table (see Tables 3.1, 3.5 and 3.6 for the T and P dependencies of V and ε, the dependence of n_D being not very important for polar liquids).

A simpler criterion for structuredness to apply is the heat capacity density of the solvent, i.e., the constant pressure heat capacity of the liquid solvent minus that of the corresponding ideal gas per unit volume of the liquid solvent (Marcus 1996): $[C_p(\mathrm{l}) - C_p(\mathrm{g})]/V$. The idea behind this empirical measure is that more energy must be introduced into a unit volume of a substance when in an ordered liquid state than is accommodated by the translational, vibrational and rotational degrees of freedom of the molecules of this substance in the ideal gaseous state, in order to raise its temperature and partly destroy this ordering. The quantity $[C_p(\mathrm{l}) - C_p(\mathrm{g})]/V$ is shown in Table 4.1 for 25°C in $\mathrm{JK^{-1}\ cm^{-3}}$, and the criterion for denoting structuredness (ordering) of a solvent is its being larger than 0.6.

It can be seen in Table 4.1 that some solvents are considered to be structured according to all the above criteria, others are considered to be non-structured in conformity to all of them, but that there are solvents that are structured following some of these criteria but not according to the others. Self-association by hydrogen bonding generally leads to structuredness being recognized by all these criteria, whereas self-association by dipole interactions is weaker, and may not be manifested universally. It is obvious that different aspects of structuredness or 'ordering' are described by these criteria, but that they can still be used as useful guides to the expected behaviour of the solvents in this respect.

Water, of course, is highly structured according to all the above criteria, but by no means is the most structured in conformity with all of them. The entropy deficit $\Delta\Delta_\mathrm{V} S^\mathrm{o}(T, P^\mathrm{o})/R$ of polyhydric alcohols is larger than that of water, even after division by the number of hydroxyl groups. The dipole orientation correlation parameter g of water and its Trouton constant $\Delta_\mathrm{V} S^\mathrm{o}(T_\mathrm{b}, P^\mathrm{o})/R$ are reasonably high, but lower than those of several monohydric-alcohols. Only the heat capacity density of water, $[C_p(\mathrm{l}) - C_p(\mathrm{g})]/V$, is higher than any of the solvents on the List. The lower carboxylic acids have low structuredness parameters according to criteria that depend on the entropy of vaporization, due to the association of both the liquid and vapour to hydrogen bonded cyclic dimers, and this is manifested also in their values of $g << 1$. The structuredness of solvents is expected to decrease with increasing temperatures, as was demonstrated in the case of the entropy deficit (Marcus 1996), so that poor association at ambient temperatures should be inferred with care, when dealing with high boiling solvents with a relatively low Trouton constant.

The 'stiffness' aspect of the structuredness of solvents is expressed by the cohesive energy density, $\Delta_\mathrm{V} U/V$, equalling the square of the solubility parameter δ reported in Table 3.1. The work that must be done against this stiffness in order to create cavities that are able to accommodate a solute of given size in a series of solvents is proportional to this quantity. This work is also given by the product of surface tension σ of the solvent (Table 3.9) and the surface area of this cavity. (This holds strictly for macroscopic cavities, but is apparently extendable also to molecular sized ones.) For non-associated solvents another measure of their stiffness is the internal pressure, P_i (see Table 4.2), that equals

Table 4.2 The internal pressure P_i and cohesive energy density $\Delta_\mathrm{V}U/V$ of solvents, and the difference $\Delta_\mathrm{V}U - P_\mathrm{i}$ if larger than 50 J cm^{-3}

Solvent	Ref.	P_i/J cm^{-3}	$\Delta_\mathrm{v}\ U/V$/J cm^{-3}	$(\Delta_\mathrm{v}\ U/V - P_\mathrm{i})$/J cm^{-3}
n-hexane	[c, d]	239	225	
c-hexane	[d]	413	364	
n-heptane	[a]	254	231	
2,2,4-trimethylpentane	[c,d]	236	200	
n-decane	j	286	250	
benzene	[a, b]	369	353	
toluene	[c, d]	355	337	
p-xylene	j	347	322	
water	[b]	151	2294	2143
methanol	[b]	288	858	570
ethanol	[b]	293	676	383
1-propanol		280	595	315
2-propanol	j	242	558	316
1-butanol	[c, d]	300	485	185
2-methyl-2-propanol		339	467	128
2,2,2-trufluoroethanol	j	291	573	282
ethylene glycol	[b]	502	1050	548
glycerol	j	594	1135	541
2-methylphenol	j	472	595	123
diethylether	[c, d]	264	251	
1,2-dimethoxyethane	j	307	283	
tetrahydrofuran	j	404	359	
1,4-dioxane	[b]	494	388	

acetone	[a, b]	331	488	157
3-pentanone	j	345	339	
c-hexanone	[c, d]	413	364	
acetophenone	[c, d]	457	456	
acetic acid	j	348	357	
n-butanoic acid	j	391	628	237
methyl acetate	[b]	372	372	
ethyl acetate	[b]	356	331	
propylene carbonate	[b]	544	475	
4-butyrolactone	j	420	647	227
perfluoro-*n*-heptane	[a]	215	151	
perfluoromethyl-*c*-hexane	[a]	228	161	
fluorobenzene	j	373	340	
chlorobenzene	j	383	377	
dichloromethane	[c, d]	408	414	
1,2-dichloroethane	[a]	419	400	
chloroform	[c, d]	370	362	
tetrachloromethane	[a, b]	339	310	
1,2-dibromoethane	[a]	447	392	
bromoform	[a]	451	480	
n-butylamine	j	352	335	
di-*n*-butylamine	j	314	275	
piperidine	j	439	369	
aniline	j	538	583	

(table continued on next page)

***Table 4.2** (continued)*

Solvent	Ref.	P_i/J cm^{-3}	Δ_v U/V/J cm^{-3}	(Δ_v U/V - P_i)/J cm^{-3}
2-ethanolamine	j	546	1055	509
pyridine	j	425	466	
acetonitirle	[b]	395	581	186
nitromethane	j	508	669	161
nitrobenzene	j	499	511	
formamide	[b]	554	1568	1014
N-methylformamide	j	469	910	441
N,N -dimethylformamide	[b]	480	581	101
carbon disulfide	[a]	372	412	
dimethylsulfoxide	[b]	521	708	187
tri-*n*-butyl phosphate	j	171	215	
hexamethyl phosphoramide	[b]	403	365	

References: [a] Westwater, Frantz and Hildebrand 1928; Hildebrand and Carter 1932; Alder *et al*. 1954; Smith and Hildebrand 1959; [b] Dack 1975; [c] Allen, Gee and Wilson 1960; [d] Barton 1983.

approximately (within ca. 50 J cm^{-3}) the cohesive energy density. The values of P_i shown are mainly those that have been reported directly and many further values can be obtained from $P_i = T\,\alpha_p/\kappa_T - P$ (the subtrahend P being negligible), see Table 3.1, some of them being shown in Table 4.2. For associated solvents $\Delta_V U/V - P_i$, >> 50 J cm^{-3}, whether their stiffness as measured by P_i is large e.g., dioxane, or small e.g., water. This difference is therefore an important characteristic of a solvent, denoting whether it is associated or not, see Figure 4.1. It is noteworthy that for hydrocarbons and ethers, among non-associated solvents, $\Delta_V U/V - P_i < 0$, *whereas for ketones, esters, and halogen substituted hydrocarbons, although this inequality still generally holds, the difference is smaller.*

The 'openness' of the solvent depends on its so-called free volume, that can be approximated by the difference between its molar and intrinsic volumes:

$$V_{\text{free}} = V - V_{\text{intrinsic}} \qquad (4.4)$$

The latter can be taken as either V_x, or V_{vdW}, or V_{L}, related by Eqs. (3.19), (3.20), and (3.21), respectively, to the constitution of the solvents. It is obvious that the free volumes defined according to these choices of the intrinsic volume are not the same, and caution must be exercised when this notion is applied to concrete problems. The fluidity $\Phi = 1/\eta$ of solvents depends on the free volume: $\Phi = B[(V - V_0)/V_0]$*, according to (Hildebrand 1978), where* B is a temperature-independent constant and V_0 is the 'occupied volume', that may be equated with the intrinsic volume, see also Eq. (3.33). As mentioned in Chapter 3, the compressibilities of solvents appear to depend mainly on their free volumes, according to Eq. (3.8), so that there exists a relationship between the compressibilities of solvents and their fluidities (Marcus 1998). Two non-linear curves result from plots of log Φ ν *s* κ_T, one for non-associated liquids and the e.g., by the molar refraction R_D, may contribute to the chemical aspect of polarity.

From the chemical standpoint, polarity is understood as 'the sum of all the molecular properties responsible for all the interaction forces between solvent and solute molecules' (Reichardt 1965) that lead to the overall solvation ability of the solvent (Reichardt 1988). For the estimation of solvent polarities, resort is taken to empirical parameters obtained for certain standard substances used as probes, by the measurement of some suitable property that exhibits a large solvent-sensitivity. The idea is that the standard substance can act as a stand-in for the 'general solute' i.e., that any solute will experience the solvent polarity measured by this standard substance in the same manner as the latter (Marcus 1993). This is, of course, impossible to achieve in a rigorous and completely general way, and the success of the proposed empirical parameters depends on their ability to approximate this requirement. One way to overcome this difficulty is to employ as probes several standard substances with different functional groups, that produce convergent i.e., highly mutually correlated values of such a polarity parameter, and employ its average value. This will result in some 'fuzziness' of this parameter, but it will be able to describe the solvent polarity towards diverse solutes better than a parameter based on a single standard substance with a single kind of operative functional group (Marcus 1993). Furthermore, solvent effects usually depend on more than a single property of a series of solvents, so that correlations with such a single parameter are often quite poor, whereas a dependence on two or a few mutually independent parameters describes the solvent effects much better.

Of the many empirical polarity parameters or indexes that have been proposed, only a few remain viable, in the sense that they are currently more or less widely used to describe the polarity of solvents for various purposes. Some such parameters that are commonly used describe better other, more specific, properties than polarity: e.g., hydrogen bond or electron-pair donation ability. Thus, only two polarity parameters have been employed in recent years: Dimroth and Reichardt's $E_T(30)$ (Dimroth *et al*. 1966) and Kamlet and Taft's π^* (Kamlet, Abboud and Taft 1977) solvatochromic parameters. These are based on the solvent-induced shifts of the lowest energy absorption bands of certain solvatochromic indicators in the ultraviolet-visible spectral region. They are readily measured by using dilute solutions of specified probes in the solvents in question, but describe somewhat different aspects of solvent polarity.

Values of $E_T(30)$ are known for several hundred solvents, and are obtained from the peak wavenumber $\tilde{\nu}$ of the longest wavelength charge transfer absorption band of the betaine indicator 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino)-phenoxide in dilute solution in the solvent. This indicator, which was number 30 in a series of compounds studied, hence the designation $E_T(30)$, exhibits a very high sensitivity to solvent polarity, i.e., a very wide range of wavelengths of the hypsochromic or blue-shift effect in solvents of increasing polarities. It is soluble in most solvents without chemical reaction, hence is eminently suitable to act as the polarity probe. The energy of the transition as measured in kcal mol^{-1} (1 cal = 4.184 J) is:

$$E_T(30) = hcN_A\tilde{\nu} = 2.859 \times 10^{-3}(\tilde{\nu}/cm^{-1}) = 28590/(\lambda/nm) \qquad (4.5)$$

A cognate quantity is the normalized value:

$$\begin{aligned} E_T^N &= [E_T(\text{solvent}) - E_T(\text{TMS})]/[E_T(\text{water}) - E_T(\text{TMS})] \\ &= [E_T(\text{solvent}) - 30.7]/32.4 \qquad (4.6) \end{aligned}$$

where TMS is tetramethylsilane, considered a solvent with minimal polarity i.e., E_T^N = 0, whereas water is considered a solvent with maximal polarity i.e., E_T^N = 1. The values of $E_T(30)$ are strictly valid for 25° C, when they are known to within ±0.1 kcal mol^{-1}, but are often measured at room temperature near this value without strict thermostating, and are used as if they do not depend on the temperature, which is an approximation that should be kept in mind. Values of $E_T(30)$ and of E_T^N of the solvents on our List are shown in Table 4.3.

A few of the values were obtained indirectly from correlations with other indicators, because of either insolubility of the betaine in certain solvents or its reaction with them. Thus, the penta-*t*-butyl-substituted betaine on the five phenyl groups, para to their attachment to the pyridine and the phenoxide groups, is more soluble in aliphatic hydrocarbons than the standard unsubstituted betaine, that is practically insoluble in them. However, the E_T' values of this substituted betaine can be readily converted to those of the standard indicator (Laurence, Nicolet and Reichardt 1987):

$$E_T(30) = [E_T' - 1.81]/0.9424 \qquad (4.7)$$

Furthermore, the standard betaine is protonated by highly acidic solvents (that have p*K* values lower than that of this betaine in water, 8.65 (Kessler and Wolfbeis 1991), so that secondary values for such solvents have to be obtained, e.g., from its relation with Kosower's *Z* parameter (Hormadaly and Marcus 1979) (see below and Figure 4.2):

$$E_T(30) = 0.752Z - 7.87 \qquad (4.8)$$

As is shown below, the polarity measured by $E_T(30)$ for a protic solvent shows its ability to donate a hydrogen bond to a solute in addition to its polarity *per se*. A different solvatochromic polarity parameter, that is devoid of this complication (but has others), is Kamlet and Taft's π^* (Kamlet, Abboud and Taft 1977). This is based on the average of values of the $\pi \to \pi^*$ transition energies for several nitro-substituted aromatic indicators. The quantities are normalized to give π^* = 0 to cyclohexane and π^* = 1 to dimethylsulfoxide. The use of multiple probes is designed to eliminate specific interactions and spectral anomalies, but, as mentioned before, can cause some 'fuzziness' of the resulting values. More-

Table 4.3 Solvatochromic and other measures of solvent polarity and coordinative bonding ability

No.	Name	α		β		π^*		E_T30	E_T^N		SB	DN		AN		Z		μ	
0	vacuum	0.00	[a]	0.00	[a]	−1.2	[f]	27.1	−0.111	[o]	0.000	0.0		0.0					
10	tetramethylsilane	0.00	[a]	0.02	[h]	−0.12	[m]	30.7	0.000	[o]									
20	n-pentane	0.00	[a]	0.00	[a]	−0.15	[f]	31.1	0.009	[o]	0.073								
30	2-methylbutane	0.00	[a]	0.01	[h]	−0.15	[m]	30.9	0.006	[o]	0.053								
40	n-hexane	0.00	[a]	0.00	[a]	−0.11	[f]	31.0	0.009	[o]	0.056	0.0	[i]	0.0	[s]				
50	c-hexane	0.00	[a]	0.00	[a]	0.00	[b]	30.9	0.006	[o]	0.073	0.0	[i]	1.6	[t]	60.1	[x]		
60	n-heptane	0.00	[a]	0.00	[a]	−0.06	[m]	31.1	0.012	[o]	0.083	0.0	[i]	0.0	[s]				
70	n-octane	0.00	[a]	0.00	[a]	0.01	[f]	31.1	0.012	[o]	0.079	0.0	[i]						
80	2,2,4-trimethylpentane	0.00	[a]	0.00	[a]	0.01	[m]				0.044					60.1	[x]		
90	n-decane	0.00	[a]	0.00	[a]	0.03	[f]	31.0	0.009	[o]	0.066								
100	n-dodecane	0.00	[a]	0.00	[a]	−0.01	[m]	31.1	0.012	[o]	0.086			1.6	[t]				
110	n-hexadecane	0.00	[a]	0.00	[a]	0.08	[f]				0.086								
120	benzene	0.00	[a]	0.10	[d]	0.55	[f]	34.3	0.111	[o]	0.124	0.1	[i]	8.2	[s]	54.0	[x]	−0.02	[aa]
130	toluene	0.00	[a]	0.11	[d]	0.49	[f]	33.9	0.099	[o]	0.128	0.1	[i]	6.8	[t]				
140	o-xylene	0.00	[a]	0.12	[f]	0.51	[f]	34.7	0.123	[p]	0.157								
150	m-xylene	0.00	[a]	0.12	[i]	0.47	[d]	34.6	0.120	[p]	0.162	5.0	[i]						
160	p-xylene	0.00	[a]	0.12	[i]	0.45	[f]	33.1	0.074	[o]	0.160	5.0	[i]						
170	ethylbenzene	0.00	[a]	0.12	[f]	0.53	[f]	34.1	0.105	[p]	0.152	6.0	[i]						
180	cumene	0.00	[a]	0.18	[i]	0.41	[d]	34.6	0.120	[p]		6.0	[i]						
190	mesitylene	0.00	[a]	0.13	[i]	0.45	[f]	32.9	0.068	[o]	0.190	10.0	[i]						
200	styrene	0.00	[a]	0.12	[i]			34.8	0.127	[o]		5.0	[i]						
210	tetralin	0.00	[a]					33.5	0.086	[o]	0.156								
220	cis-decalin	0.00	[a]	0.08	[h]	0.09	[f]	31.2	0.015	[o]	0.056								
230	water	1.17	[b]	0.47	[f]	1.09	[b]	63.1	1.000	[o]		18.0	[i]	54.8	[s]	94.6	[x]	0.00	[bb]
240	methanol	0.98	[c]	0.66	[f]	0.60	[d]	55.4	0.762	[o]	0.545	30.0	[i]	41.5	[s]	83.6	[x]	0.02	[bb]
250	ethanol	0.86	[c]	0.75	[f]	0.54	[d]	51.9	0.654	[o]	0.658	32.0	[i]	37.1	[s]	79.6	[x]	0.08	[bb]
260	n-propanol	0.84	[c]	0.90	[f]	0.52	[d]	50.7	0.617	[o]	0.727	30.0	[i]	33.7	[u]	78.3	[x]	0.16	[bb]
270	i-propanol	0.76	[c]	0.84	[c]	0.48	[d]	48.4	0.546	[o]	0.762	36.0	[i]	33.5	[s]	76.3	[x]		
280	n-butanol	0.84	[c]	0.84	[c]	0.47	[d]	49.7	0.586	[o]	0.809	29.0	[i]	32.2	[u]	77.7	[x]	0.18	[bb]
290	i-butanol	0.79	[c]	0.84	[c]	0.40	[c]	48.6	0.552	[o]		37.0	[i]	35.5	[r]	77.7	[x]		
300	2-butanol	0.69	[c]	0.80	[c]	0.40	[c]	47.1	0.506	[o]	0.888			30.5	[r]	75.4	[x]		

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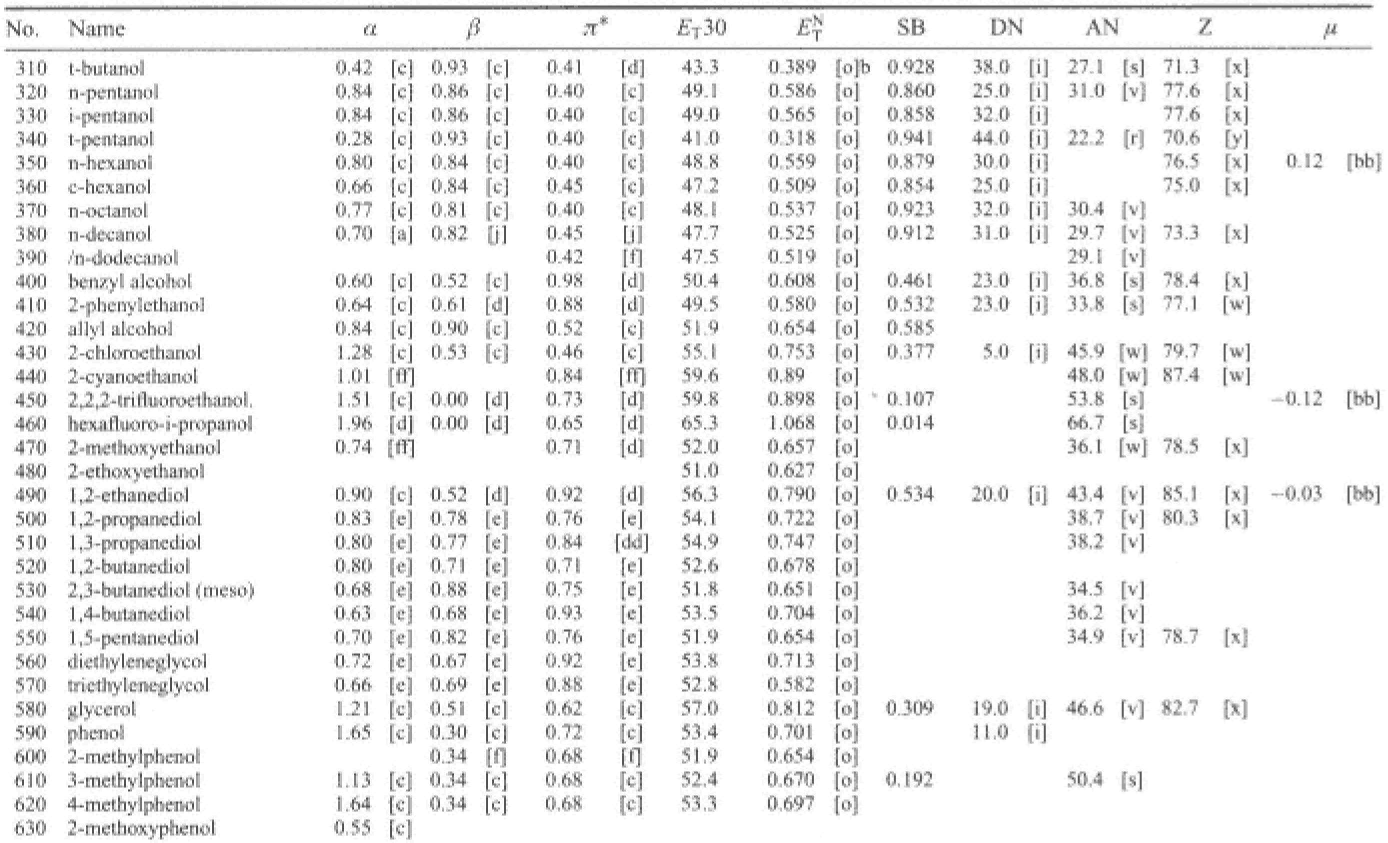
Table 4.3 *(continued)*



No.	Name	α		β		π^*		E_T30	E_T^N		SB	DN		AN		Z		μ	
310	t-butanol	0.42	[c]	0.93	[c]	0.41	[d]	43.3	0.389	[o]b	0.928	38.0	[i]	27.1	[s]	71.3	[x]		
320	n-pentanol	0.84	[c]	0.86	[c]	0.40	[c]	49.1	0.586	[o]	0.860	25.0	[i]	31.0	[v]	77.6	[x]		
330	i-pentanol	0.84	[c]	0.86	[c]	0.40	[c]	49.0	0.565	[o]	0.858	32.0	[i]			77.6	[x]		
340	t-pentanol	0.28	[c]	0.93	[c]	0.40	[c]	41.0	0.318	[o]	0.941	44.0	[i]	22.2	[r]	70.6	[y]		
350	n-hexanol	0.80	[c]	0.84	[c]	0.40	[c]	48.8	0.559	[o]	0.879	30.0	[i]			76.5	[x]	0.12	[bb]
360	c-hexanol	0.66	[c]	0.84	[c]	0.45	[c]	47.2	0.509	[o]	0.854	25.0	[i]			75.0	[x]		
370	n-octanol	0.77	[c]	0.81	[c]	0.40	[c]	48.1	0.537	[o]	0.923	32.0	[i]	30.4	[v]				
380	n-decanol	0.70	[a]	0.82	[j]	0.45	[j]	47.7	0.525	[o]	0.912	31.0	[i]	29.7	[v]	73.3	[x]		
390	/n-dodecanol					0.42	[f]	47.5	0.519	[o]				29.1	[v]				
400	benzyl alcohol	0.60	[c]	0.52	[c]	0.98	[d]	50.4	0.608	[o]	0.461	23.0	[i]	36.8	[s]	78.4	[x]		
410	2-phenylethanol	0.64	[c]	0.61	[d]	0.88	[d]	49.5	0.580	[o]	0.532	23.0	[i]	33.8	[s]	77.1	[w]		
420	allyl alcohol	0.84	[c]	0.90	[c]	0.52	[c]	51.9	0.654	[o]	0.585								
430	2-chloroethanol	1.28	[c]	0.53	[c]	0.46	[c]	55.1	0.753	[o]	0.377	5.0	[i]	45.9	[w]	79.7	[w]		
440	2-cyanoethanol	1.01	[ff]			0.84	[ff]	59.6	0.89	[o]				48.0	[w]	87.4	[w]		
450	2,2,2-trifluoroethanol.	1.51	[c]	0.00	[d]	0.73	[d]	59.8	0.898	[o]	0.107			53.8	[s]			−0.12	[bb]
460	hexafluoro-i-propanol	1.96	[d]	0.00	[d]	0.65	[d]	65.3	1.068	[o]	0.014			66.7	[s]				
470	2-methoxyethanol	0.74	[ff]			0.71	[d]	52.0	0.657	[o]				36.1	[w]	78.5	[x]		
480	2-ethoxyethanol							51.0	0.627	[o]									
490	1,2-ethanediol	0.90	[c]	0.52	[d]	0.92	[d]	56.3	0.790	[o]	0.534	20.0	[i]	43.4	[v]	85.1	[x]	−0.03	[bb]
500	1,2-propanediol	0.83	[e]	0.78	[e]	0.76	[e]	54.1	0.722	[o]				38.7	[v]	80.3	[x]		
510	1,3-propanediol	0.80	[e]	0.77	[e]	0.84	[dd]	54.9	0.747	[o]				38.2	[v]				
520	1,2-butanediol	0.80	[e]	0.71	[e]	0.71	[e]	52.6	0.678	[o]									
530	2,3-butanediol (meso)	0.68	[e]	0.88	[e]	0.75	[e]	51.8	0.651	[o]				34.5	[v]				
540	1,4-butanediol	0.63	[e]	0.68	[e]	0.93	[e]	53.5	0.704	[o]				36.2	[v]				
550	1,5-pentanediol	0.70	[e]	0.82	[e]	0.76	[e]	51.9	0.654	[o]				34.9	[v]	78.7	[x]		
560	diethyleneglycol	0.72	[e]	0.67	[e]	0.92	[e]	53.8	0.713	[o]									
570	triethyleneglycol	0.66	[e]	0.69	[e]	0.88	[e]	52.8	0.582	[o]									
580	glycerol	1.21	[c]	0.51	[c]	0.62	[c]	57.0	0.812	[o]	0.309	19.0	[i]	46.6	[v]	82.7	[x]		
590	phenol	1.65	[c]	0.30	[c]	0.72	[c]	53.4	0.701	[o]		11.0	[i]						
600	2-methylphenol			0.34	[f]	0.68	[f]	51.9	0.654	[o]									
610	3-methylphenol	1.13	[c]	0.34	[c]	0.68	[c]	52.4	0.670	[o]	0.192			50.4	[s]				
620	4-methylphenol	1.64	[c]	0.34	[c]	0.68	[c]	53.3	0.697	[o]									
630	2-methoxyphenol	0.55	[c]																

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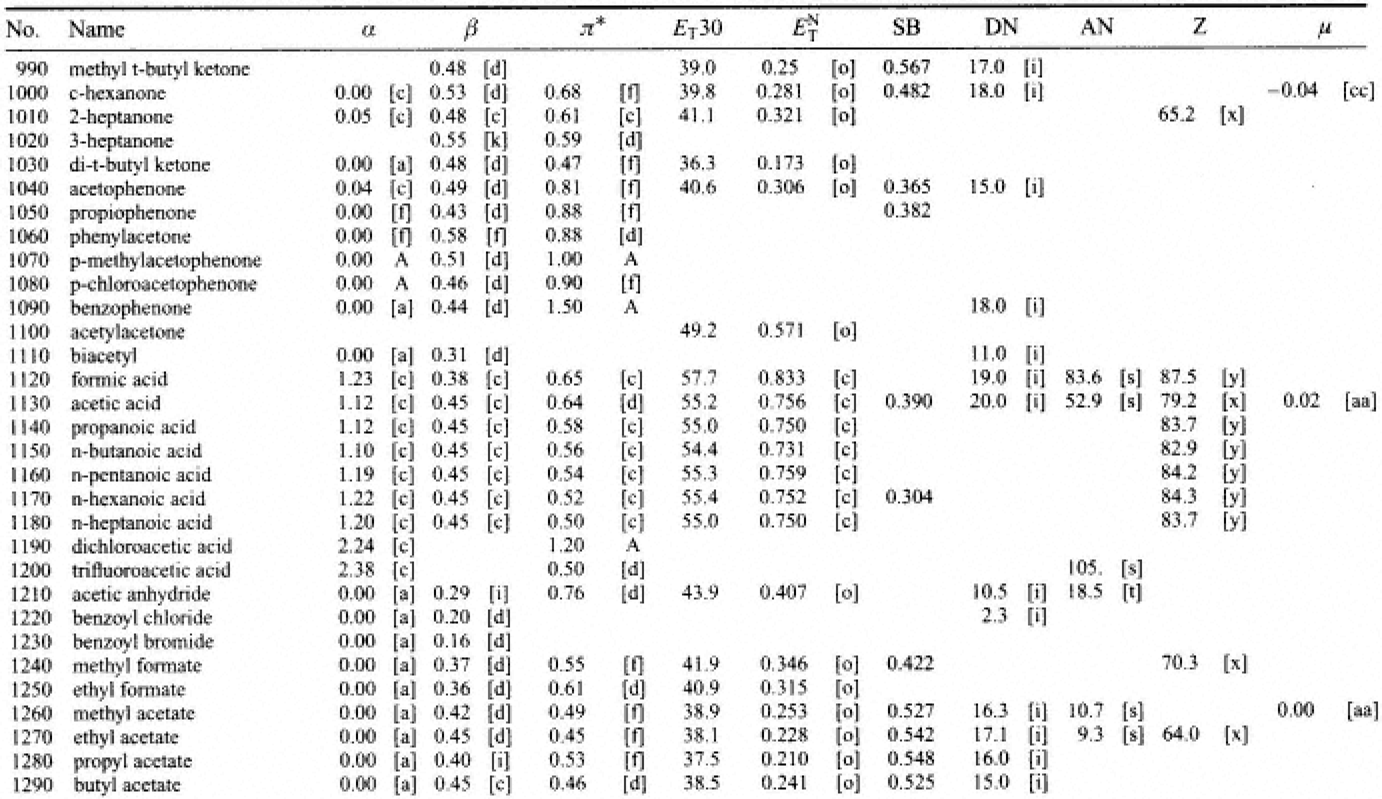
640	2,4-dimethylphenol			0.35	[f]	0.64	[f]	50.3	0.605	[o]				44.8	[s]				
650	3-chlorophenol	1.57	[c]	0.23	[c]	0.77	[c]	60.8	0.929	[o]									
660	diethyl ether	0.00	[a]	0.47	[d]	0.24	[f]	34.5	0.117	[o]	0.562	19.2	[i]	3.9	[s]			0.00	[aa]
670	di-n-propyl ether	0.00	[a]	0.46	[d]	0.27	[d]	34.0	0.102	[o]	0.666	18.0	[i]						
680	di-i-propyl ether	0.00	[a]	0.49	[d]	0.19	[f]	34.1	0.105	[o]	0.657	19.0	[i]						
690	di-n-butyl ether	0.00	[a]	0.46	[d]	0.18	[f]	33.0	0.071	[o]	0.137	19.0	[i]			60.1	[x]		
700	di(2-chloroethyl) ether	0.00	[a]	0.40	[i]	0.77	[f]	41.6	0.336	[o]		16.0	[i]						
710	1,2-dimethoxyethane	0.00	[a]	0.41	[d]	0.53	[d]	38.2	0.231	[o]	0.636	20.0	[i]	10.2	[s]	59.1	[x]		
720	bis(methoxyethyl) ether	0.00	[a]			0.64	[d]	38.6	0.244	[o]	0.623			9.9	[s]				
730	furan	0.00	[a]	0.14	[i]	0.48	[f]	36.0	0.164	[o]	0.107	6.0	[i]	3.3	[t]			−0.01	[aa]
740	tetrahydrofuran	0.00	[a]	0.55	[d]	0.55	[f]	37.4	0.207	[o]	0.591	20.0	[i]	8.0	[s]	58.8	[x]	0.00	[bb]
750	2-methyl tetrahydrofuran	0.00	[a]	0.45	[i]	0.48	A	36.5	0.179	[o]	0.584	18.0	[i]			55.3	[x]		
760	tetrahydropyran	0.00	[a]	0.54	[c]	0.48	[f]	36.2	0.170	[o]	0.591	22.0	[i]						
770	1,4-dioxane	0.00	[a]	0.37	[d]	0.49	[f]	36.0	0.164	[o]	0.444	14.8	[i]	10.8	[s]	64.5	[x]	0.07	[aa]
780	1,3-dioxolane	0.00	[a]	0.45	[h]	0.63	[f]	43.1	0.383	[o]		21.2	[ee]						
790	1,8-cineole	0.00	[a]	0.61	[i]	0.36	[f]	34.0	0.102	[o]	0.737	24.0	[i]						
800	anisole	0.00	[a]	0.32	[c]	0.70	[f]	37.1	0.198	[o]	0.299	9.0	[i]					−0.02	[aa]
810	phenetole	0.00	[a]	0.30	[c]	0.65	[f]	36.6	0.182	[o]	0.295	8.0	[i]			58.9	[x]		
820	diphenyl ether	0.00	[a]	0.13	[d]	0.66	[d]	35.3	0.142	[o]b									
830	dibenzyl ether	0.00	[a]	0.41	[d]	0.80	[f]	36.3	0.173	[o]	0.330	19.0	[i]						
840	1,2-dimethoxybenzene	0.00	[a]					38.4	0.238	[o]	0.340								
850	trimethyl orthoformate	0.00	[a]			0.58	[d]												
860	trimethyl orthoacetate	0.00	[a]			0.35	[d]												
870	propionaldehyde	0.00	[f]	0.40	[d]	0.65	[f]												
880	butyraldehyde	0.00	[f]	0.41	[d]	0.63	[f]												
890	benzaldehyde	0.00	[a]	0.44	[d]	0.92	[d]				0.290	16.0	[i]	12.8	[t]				
900	p-methoxybenzaldehyde	0.00	[a]	0.49	[d]														
910	cinnamaldehyde	0.00	[a]	0.53	[d]														
920	acetone	0.08	[c]	0.48	[d]	0.62	[f]	42.2	0.355	[o]	0.475	17.0	[i]	12.5	[s]	65.7	[x]	0.03	[bb]
930	2-butanone	0.06	[c]	0.48	[d]	0.60	[f]	41.3	0.327	[o]	0.520	17.4	[i]			64.0	[x]		
940	2-pentanone	0.05	[c]	0.50	[d]	0.65	[f]	41.1	0.321	[o]						63.3	[x]		
950	methyl i-propyl ketone	0.00	A	0.48	[d]	0.64	[n]	40.9	0.315	[o]	0.540	17.1	[i]						
960	3-pentanone	0.00	[c]	0.45	[d]	0.57	[f]	39.3	0.265	[o]	0.557	15.0	[i]						
970	c-pentanone	0.00	[a]	0.52	[d]	0.71	[f]	39.4	0.269	[o]	0.465	18.0	[i]						
980	methyl-i-butyl ketone	0.02	[f]	0.48	[f]	0.65	[f]	39.4	0.269	[o]		16.0	[i]			62.0	[x]		

continued overleaf

***Table 4.3** (continued)*



No.	Name	α		β		π^*		E_T30	E_T^N		SB	DN		AN		Z		μ	
990	methyl t-butyl ketone			0.48	[d]			39.0	0.25	[o]	0.567	17.0	[i]						
1000	c-hexanone	0.00	[c]	0.53	[d]	0.68	[f]	39.8	0.281	[o]	0.482	18.0	[i]					−0.04	[cc]
1010	2-heptanone	0.05	[c]	0.48	[c]	0.61	[c]	41.1	0.321	[o]						65.2	[x]		
1020	3-heptanone			0.55	[k]	0.59	[d]												
1030	di-t-butyl ketone	0.00	[a]	0.48	[d]	0.47	[f]	36.3	0.173	[o]									
1040	acetophenone	0.04	[c]	0.49	[d]	0.81	[f]	40.6	0.306	[o]	0.365	15.0	[i]						
1050	propiophenone	0.00	[f]	0.43	[d]	0.88	[f]				0.382								
1060	phenylacetone	0.00	[f]	0.58	[f]	0.88	[d]												
1070	p-methylacetophenone	0.00	A	0.51	[d]	1.00	A												
1080	p-chloroacetophenone	0.00	A	0.46	[d]	0.90	[f]												
1090	benzophenone	0.00	[a]	0.44	[d]	1.50	A					18.0	[i]						
1100	acetylacetone							49.2	0.571	[o]									
1110	biacetyl	0.00	[a]	0.31	[d]							11.0	[i]						
1120	formic acid	1.23	[c]	0.38	[c]	0.65	[c]	57.7	0.833	[c]		19.0	[i]	83.6	[s]	87.5	[y]		
1130	acetic acid	1.12	[c]	0.45	[c]	0.64	[d]	55.2	0.756	[c]	0.390	20.0	[i]	52.9	[s]	79.2	[x]	0.02	[aa]
1140	propanoic acid	1.12	[c]	0.45	[c]	0.58	[c]	55.0	0.750	[c]						83.7	[y]		
1150	n-butanoic acid	1.10	[c]	0.45	[c]	0.56	[c]	54.4	0.731	[c]						82.9	[y]		
1160	n-pentanoic acid	1.19	[c]	0.45	[c]	0.54	[c]	55.3	0.759	[c]						84.2	[y]		
1170	n-hexanoic acid	1.22	[c]	0.45	[c]	0.52	[c]	55.4	0.752	[c]	0.304					84.3	[y]		
1180	n-heptanoic acid	1.20	[c]	0.45	[c]	0.50	[c]	55.0	0.750	[c]						83.7	[y]		
1190	dichloroacetic acid	2.24	[c]			1.20	A												
1200	trifluoroacetic acid	2.38	[c]			0.50	[d]							105.	[s]				
1210	acetic anhydride	0.00	[a]	0.29	[i]	0.76	[d]	43.9	0.407	[o]		10.5	[i]	18.5	[t]				
1220	benzoyl chloride	0.00	[a]	0.20	[d]							2.3	[i]						
1230	benzoyl bromide	0.00	[a]	0.16	[d]														
1240	methyl formate	0.00	[a]	0.37	[d]	0.55	[f]	41.9	0.346	[o]	0.422					70.3	[x]		
1250	ethyl formate	0.00	[a]	0.36	[d]	0.61	[d]	40.9	0.315	[o]									
1260	methyl acetate	0.00	[a]	0.42	[d]	0.49	[f]	38.9	0.253	[o]	0.527	16.3	[i]	10.7	[s]			0.00	[aa]
1270	ethyl acetate	0.00	[a]	0.45	[d]	0.45	[f]	38.1	0.228	[o]	0.542	17.1	[i]	9.3	[s]	64.0	[x]		
1280	propyl acetate	0.00	[a]	0.40	[i]	0.53	[f]	37.5	0.210	[o]	0.548	16.0	[i]						
1290	butyl acetate	0.00	[a]	0.45	[c]	0.46	[d]	38.5	0.241	[o]	0.525	15.0	[i]						

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1300	i-pentyl acetate	0.00	[a]	0.45	[c]	0.49	[f]				0.481								
1310	methyl propanoate	0.00	[a]	0.27	[i]	0.48	[f]	38.0	0.225	[o]		11.0	[i]						
1320	ethyl propanoate	0.00	[a]	0.42	[d]	0.47	[d]					17.1	[i]	6.7	[t]				
1330	dimethyl carbonate	0.00	[a]	0.38	[d]	0.47	[f]	38.2	0.232	[o]	0.433	17.2	[i]			64.7	[x]		
1340	diethyl carbonate	0.00	[a]	0.40	[d]	0.40	[f]	36.7	0.185	[o]	0.340	16.0	[i]			64.6	[x]		
1350	ethylene carbonate	0.00	[a]	0.41	[i]			48.6	0.552	[o]d		16.4	[i]d						
1360	propylene carbonate	0.00	[a]	0.40	[d]	0.83	[f]	46.0	0.472	[o]	0.341	15.1	[i]	18.3	[s]	72.4	[x]	−0.09	[bb]
1370	diethyl malonate	0.00	[a]	0.42	[k]	0.64	[d]												
1380	methyl benzoate	0.00	[a]	0.39	[d]	0.75	[f]	38.1			0.378								
1390	ethyl benzoate	0.00	[a]	0.41	[d]	0.68	[f]	38.1	0.228	[o]	0.417	15.0	[i]						
1400	dimethyl phthalate	0.00	[a]	0.78	[c]	0.82	[c]	40.7	0.309	[o]									
1410	dibutyl phthalate	0.00	[a]	0.45	[k]	0.72	[n]	39.5	0.272	[o]									
1420	ethyl chloroacetate	0.00	[a]	0.35	[d]	0.67	[f]	39.4	0.269	[o]		13.0	[i]						
1430	ethyl trichloroacetate	0.00	[a]	0.25	[d]	0.56	[f]	38.7	0.247	[o]									
1440	ethyl acetoacetate			0.43	[k]	0.61	[d]	49.4	0.577	[o]									
1450	4-butyrolactone	0.00	[a]	0.49	[d]	0.85	[f]	44.3	0.420	[o]	0.399	18.0	[i]	17.3	[s]			0.02	[bb]
1460	perfluoro-n-hexane	0.00	[a]	−0.08	[h]	−0.48	[f]				0.057								
1470	perfluoro-n-heptane	0.00	[a]	0.00	[d]	−0.39	[d]												
1480	perfluoro-methylcyclohexane	0.00	[a]	−0.06	[h]	−0.48	[f]												
1490	perfluoro-decalin	0.00	[a]	−0.05	[h]	−0.40	[f]												
1500	fluorobenzene	0.00	[a]	0.07	[c]	0.62	[d]	37.0	0.194	[o]	0.113	3.0	[i]			60.2	[x]		
1510	hexafluorobenzene	0.00	[a]	0.02	[h]	0.27	[f]	34.2	0.108	[o]	0.119								
1520	1-chlorobutane	0.00	[a]	0.00	[d]	0.40	[f]	36.9	0.191	[o]	0.138								
1530	chlorobenzene	0.00	[a]	0.07	[d]	0.68	[f]	36.8	0.188	[o]	0.182	3.3	[i]	11.9	[t]	58.0	[x]		
1540	dichloromethane	0.13	[c]	0.10	[c]	0.82	[d]	40.7	0.309	[o]	0.178	1.0	[i]	20.4	[s]	64.7	[x]	−0.02	[aa]
1550	1,1-dichloroethane	0.10	[c]	0.10	[f]	0.48	[f]	39.4	0.269	[o]				16.2	[s]	62.1	[x]	0.07	[bb]
1560	1,2-dichloroethane	0.00	[a]	0.10	[c]	0.73	[f]	41.3	0.327	[o]	0.126	0.0	[i]	16.7	[s]	64.3	[x]	0.03	[bb]
1570	tr-1,2-dichloroethylene	0.00	[a]	0.00	[d]	0.44	[d]	41.9	0.346	[o]									
1580	o-dichlorobenzene	0.00	[a]	0.03	[c]	0.77	[f]	38.0	0.225	[o]	0.144	3.0	[i]			60.0	[x]		
1590	m-dichlorobenzene	0.00	[a]	0.03	[c]	0.65	[f]	36.7	0.185	[o]		2.0	[i]						
1600	chloroform	0.20	[c]	0.10	[c]	0.58	[d]	39.1	0.259	[o]	0.071	4.0	[i]	23.1	[s]	63.2	[x]		
1610	1,1,1-trichloroethane	0.00	[a]	0.00	[d]	0.44	[f]	36.2	0.170	[o]	0.085								
1620	1,1,2-trichloroethane	0.00	[a]	0.13	A	0.72	[f]	40.3	0.296	[o]									
1630	trichloroethylene	0.00	[a]	0.05	[c]	0.48	[f]	35.9	0.160	[o]									
1640	1,2,4-trichlorobenzene	0.00	[a]	0.00	[c]	0.66	[f]	36.2	0.170	[o]									

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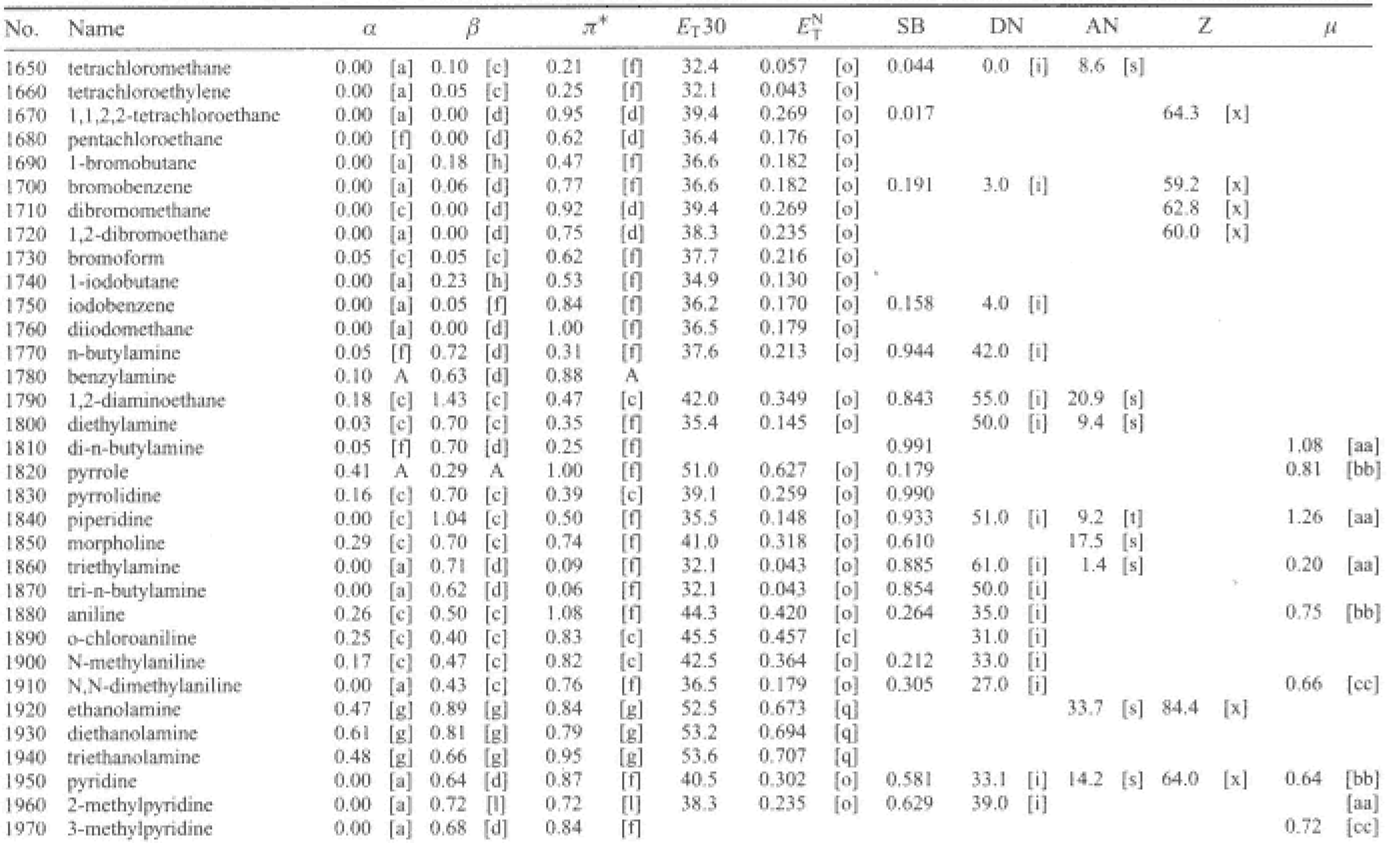
***Table 4.3** (continued)*



No.	Name	α		β		π^*		E_T30	E_T^N		SB	DN		AN		Z		μ	
1650	tetrachloromethane	0.00	[a]	0.10	[c]	0.21	[f]	32.4	0.057	[o]	0.044	0.0	[i]	8.6	[s]				
1660	tetrachloroethylene	0.00	[a]	0.05	[c]	0.25	[f]	32.1	0.043	[o]									
1670	1,1,2,2-tetrachloroethane	0.00	[a]	0.00	[d]	0.95	[d]	39.4	0.269	[o]	0.017					64.3	[x]		
1680	pentachloroethane	0.00	[f]	0.00	[d]	0.62	[d]	36.4	0.176	[o]									
1690	1-bromobutane	0.00	[a]	0.18	[h]	0.47	[f]	36.6	0.182	[o]									
1700	bromobenzene	0.00	[a]	0.06	[d]	0.77	[f]	36.6	0.182	[o]	0.191	3.0	[i]			59.2	[x]		
1710	dibromomethane	0.00	[c]	0.00	[d]	0.92	[d]	39.4	0.269	[o]						62.8	[x]		
1720	1,2-dibromoethane	0.00	[a]	0.00	[d]	0.75	[d]	38.3	0.235	[o]						60.0	[x]		
1730	bromoform	0.05	[c]	0.05	[c]	0.62	[f]	37.7	0.216	[o]									
1740	1-iodobutane	0.00	[a]	0.23	[h]	0.53	[f]	34.9	0.130	[o]									
1750	iodobenzene	0.00	[a]	0.05	[f]	0.84	[f]	36.2	0.170	[o]	0.158	4.0	[i]						
1760	diiodomethane	0.00	[a]	0.00	[d]	1.00	[f]	36.5	0.179	[o]									
1770	n-butylamine	0.05	[f]	0.72	[d]	0.31	[f]	37.6	0.213	[o]	0.944	42.0	[i]						
1780	benzylamine	0.10	A	0.63	[d]	0.88	A												
1790	1,2-diaminoethane	0.18	[c]	1.43	[c]	0.47	[c]	42.0	0.349	[o]	0.843	55.0	[i]	20.9	[s]				
1800	diethylamine	0.03	[c]	0.70	[c]	0.35	[f]	35.4	0.145	[o]		50.0	[i]	9.4	[s]				
1810	di-n-butylamine	0.05	[f]	0.70	[d]	0.25	[f]				0.991							1.08	[aa]
1820	pyrrole	0.41	A	0.29	A	1.00	[f]	51.0	0.627	[o]	0.179							0.81	[bb]
1830	pyrrolidine	0.16	[c]	0.70	[c]	0.39	[c]	39.1	0.259	[o]	0.990								
1840	piperidine	0.00	[c]	1.04	[c]	0.50	[f]	35.5	0.148	[o]	0.933	51.0	[i]	9.2	[t]			1.26	[aa]
1850	morpholine	0.29	[c]	0.70	[c]	0.74	[f]	41.0	0.318	[o]	0.610			17.5	[s]				
1860	triethylamine	0.00	[a]	0.71	[d]	0.09	[f]	32.1	0.043	[o]	0.885	61.0	[i]	1.4	[s]			0.20	[aa]
1870	tri-n-butylamine	0.00	[a]	0.62	[d]	0.06	[f]	32.1	0.043	[o]	0.854	50.0	[i]						
1880	aniline	0.26	[c]	0.50	[c]	1.08	[f]	44.3	0.420	[o]	0.264	35.0	[i]					0.75	[bb]
1890	o-chloroaniline	0.25	[c]	0.40	[c]	0.83	[c]	45.5	0.457	[c]		31.0	[i]						
1900	N-methylaniline	0.17	[c]	0.47	[c]	0.82	[c]	42.5	0.364	[o]	0.212	33.0	[i]						
1910	N,N-dimethylaniline	0.00	[a]	0.43	[c]	0.76	[f]	36.5	0.179	[o]	0.305	27.0	[i]					0.66	[cc]
1920	ethanolamine	0.47	[g]	0.89	[g]	0.84	[g]	52.5	0.673	[q]				33.7	[s]	84.4	[x]		
1930	diethanolamine	0.61	[g]	0.81	[g]	0.79	[g]	53.2	0.694	[q]									
1940	triethanolamine	0.48	[g]	0.66	[g]	0.95	[g]	53.6	0.707	[q]									
1950	pyridine	0.00	[a]	0.64	[d]	0.87	[f]	40.5	0.302	[o]	0.581	33.1	[i]	14.2	[s]	64.0	[x]	0.64	[bb]
1960	2-methylpyridine	0.00	[a]	0.72	[l]	0.72	[l]	38.3	0.235	[o]	0.629	39.0	[i]						[aa]
1970	3-methylpyridine	0.00	[a]	0.68	[d]	0.84	[f]											0.72	[cc]

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1980	4-methylpyridine	0.00	[a]	0.67	[d]	0.80	[f]	39.5	0.272	[o]		34.0	[i]					0.73	[aa]
1990	2,4-dimethylpyridine	0.00	[a]	0.74	[d]	0.82	[f]											0.60	[cc]
2000	2,6-dimethylpyridine	0.00	[a]	0.76	[d]	0.67	[f]	36.9	0.191	[o]	0.708							0.54	[cc]
2010	2,4,6-trimethylpyridine	0.00	[a]	0.78	[d]	0.66	[f]	36.4	0.176	[o]								0.55	[cc]
2020	2-bromopyridine	0.00	[a]	0.53	[h]	0.98	[f]	41.3	0.327	[o]									
2030	3-bromopyridine	0.00	[a]	0.60	[h]	0.90	[f]	39.7	0.278	[o]								0.37	[cc]
2040	2-cyanopyridine	0.00	[a]	0.29	[h]	1.20	[f]	44.2	0.417	[o]b									
2050	pyrimidine	0.00	[a]	0.48	[d]	0.87	[f]												
2060	quinoline	0.00	[a]	0.64	[d]	0.93	[f]	39.4	0.269	[o]	0.526	32.0	[i]					0.52	[cc]
2070	acetonitrile	0.19	[c]	0.40	[c]	0.66	[f]	45.6	0.460	[o]	0.286	14.1	[i]	18.9	[s]	71.3	[x]	0.34	[bb]
2080	propionitrile	0.00	[a]	0.37	[d]	0.64	[f]	43.6	0.398	[o]	0.365	16.1	[i]	19.7	[t]	67.2	[x]	0.36	[bb]
2090	butyronitrile	0.00	[a]	0.45	[i]	0.63	[f]	42.5	0.364	[o]	0.384	16.6	[i]			67.8	[x]	0.37	[bb]
2100	valeronitrile	0.00	[a]			0.63	[f]	42.4	0.361	[o]	0.408					63.2	[x]		
2110	acrylonitrile	0.00	[a]	0.25	[u]			46.7	0.494	[o]									
2120	benzyl cyanide	0.00	[a]	0.41	[c]	0.93	[f]	42.7	0.370	[o]		15.1	[i]	17.7	[t]			0.38	[bb]
2130	benzonitrile	0.00	[a]	0.37	[c]	0.88	[f]	41.5	0.333	[o]	0.281	11.9	[i]	15.5	[s]	65.0	[x]	0.34	[bb]
2140	nitromethane	0.22	[c]	0.06	[c]	0.75	[f]	46.3	0.481	[o]	0.236	2.7	[i]	20.5	[s]	71.2	[x]	0.03	[bb]
2150	nitroethane	0.00	[a]	0.15	[i]	0.77	[f]	43.6	0.398	[o]	0.234	5.0	[i]						
2160	1-nitropropane	0.00	[a]	0.34	[f]	0.78	[f]												
2170	2-nitropropane	0.00	[a]	0.34	[f]	0.66	[f]	42.0	0.349	[o]									
2180	nitrobenzene	0.00	[a]	0.30	[c]	0.86	[f]	41.2	0.324	[o]	0.240	4.4	[i]	14.8	[s]			0.23	[bb]
2190	formamide	0.71	[c]	0.48	[c]	0.97	[d]	55.8	0.775	[o]	0.414	24.0	[i]	39.8	[s]	83.3	[x]	0.09	[bb]
2200	N-methylformamide	0.62	[c]	0.80	[c]	0.90	[c]	54.1	0.722	[o]		27.0	[i]	32.1	[s]			0.17	[bb]
2210	N,N-dimethylformamide	0.00	[a]	0.69	[d]	0.88	[f]	43.2	0.386	[o]	0.613	26.6	[i]	16.0	[s]	68.4	[x]	0.11	[bb]
2220	N,N-dimethylthioformamide	0.00	[a]	0.35	[z]			44.0	0.410	[o]				18.8	[s]			1.35	[bb]
2230	N,N-diethylformamide	0.00	[a]	0.79	[i]	0.80	[f]	41.8	0.343	[o]	0.614	30.9	[i]					0.09	[bb]
2240	N-methylacetamide	0.47	[c]	0.80	[c]	1.01	[c]	52.0	0.657	[o]b	0.735			23.7	[t]	77.9	[x]		
2250	N,N-dimethylacetamide	0.00	[a]	0.76	[d]	0.85	[f]	42.9	0.377	[o]	0.650	27.8	[i]	13.6	[s]	66.9	[x]	0.17	[bb]
2260	N,N-diethyl acetamide	0.00	[a]	0.78	[d]	0.80	[f]	41.4	0.330	[o]	0.660	32.2	[i]					0.17	[bb]
2270	pyrrolidinone-2	0.36	[c]	0.77	[c]	0.85	[c]	47.9	0.531	[o]									
2280	N-methylpyrrolidinone	0.00	[a]	0.77	[d]	0.92	[f]	42.2	0.355	[o]	0.613	27.3	[i]	13.3	[s]			0.13	[bb]
2290	N-methylthiopyrrolidinone	0.00	[a]					42.8	0.373	[o]				17.7	[s]			1.35	[bb]
2300	tetramethylurea	0.00	[a]	0.80	[d]	0.79	[f]	40.9	0.315	[o]	0.624	29.6	[i]	9.2	[s]			0.14	[bb]
2310	tetraethylurea	0.00	[a]	0.71	[d]	0.66	[f]	43.1	0.383	[o]									
2320	dimethylcyanamide	0.00	[a]	0.64	[h]	0.72	[h]	43.8	0.404	[o]		17.0	[i]						

continued overleaf

***Table 4.3** (continued)*

No.	Name	α		β		π^*		E_T30	E_T^N		SB	DN		AN		Z		μ	
2330	carbon disulfide	0.00	[a]	0.07	[i]	0.51	[f]	32.8	0.065	[o]	0.104	2.0	[i]	7.5	[t]				
2340	dimethyl sulfide	0.00	[a]	0.34	[h]	0.50	[f]	26.8	0.188	[o]		40.0	[i]						
2350	diethyl sulfide	0.00	[a]	0.37	[h]	0.44	[f]	35.7	0.154	[o]		41.0	[i]					0.68	[cc]
2360	di-i-propyl sulfide	0.00	[a]	0.38	[h]	0.35	[f]	34.9	0.130	[o]									
2370	di-n-butyl sulfide	0.00	[a]	0.38	[h]	0.34	[f]	34.9	0.130	[o]								0.82	[aa]
2380	tetrahydrothiophene	0.00	[a]	0.44	[h]	0.60	[f]	36.8	0.185	[o]	0.436							0.80	[bb]
2390	pentamethylene sulfide	0.00	[a]	0.36	[h]	0.55	[f]	35.9	0.160	[o]									
2400	dimethyl sulfoxide	0.00	[a]	0.76	[d]	1.00	[d]	45.1	0.444	[o]	0.647	29.8	[i]	19.3	[s]	70.2	[x]	0.22	[bb]
2410	di-n-butyl sulfoxide	0.00	[a]	0.83	[d]			38.4	0.238	[o]		31.0	[i]			61.6	[x]		
2420	sulfolane	0.00	[a]	0.39	[c]	0.90	[f]	44.0	0.410	[o]	0.365	14.8	[i]	19.2	[s]	70.6	[x]	0.00	[bb]
2430	thiobis(2-ethanol)							54.5	0.735	[o]								0.73	[aa]
2440	diethyl sulfite	0.00	[a]	0.45	[d]	0.73	[h]	41.5	0.333	[0]									
2450	dimethyl sulfate	0.00	[a]	0.33	[h]	0.70	[f]												
2460	diethyl sulfate	0.00	[a]	0.45	[d]	0.62	[f]												
2470	methanesulfonic acid													126.3	[s]			0.00	
2480	trimethyl phosphate	0.00	[a]	0.77	[c]	0.73	[f]	43.6	0.398	[o]	0.522	23.0	[i]	16.3	[s]			0.02	[bb]
2490	triethyl phosphate	0.00	[a]	0.77	[d]	0.69	[f]	41.7	0.324	[o]	0.614	26.0	[i]			64.6	[x]	0.09	[cc]
2500	tributyl phosphate	0.00	[a]	0.80	[j]	0.63	[f]	38.9	0.253	[o]		23.7	[i]	9.9	[s]	61.3	[x]	0.17	[aa]
2510	hexamethyl phosphoramide	0.00	[a]	1.00	[d]	0.87	[f]	40.9	0.315	[o]	0.813	38.8	[i]	9.8	[t]	62.8	[x]	0.29	[bb]
2520	hexamethyl thiophosphoramide	0.00	[a]	1.05	[b]			39.5	0.272	[o]				10.6	[s]			1.57	[aa]
2530	hydrogen peroxide																		
2540	hydrogen fluoride																		
2550	sulfuric acid																		
2560	ammonia							39.5	0.272	[r]		59.0	[i]					0.86	[bb]
2570	hydrazine											44.0	[i]						
2580	sulfur dioxide																		
2590	thionyl chloride											0.4	[i]						
2600	Phosphorus oxychloride					0.70	[f]					11.7	[i]	11.0	[t]				

Units: α, β, π^*, E_T^N, *AN*, and μ are dimensionless; $E_T(30)$, *DN*, and *Z* are in kcal mol^{-1} (1 cal = 4.184 J).

References: [a] Reichardt, VCH, 1988. [b] Bekarek 1981; Stolarova, Buchtova and Bekarek 1984, [c] Marcus 1991, [d] Kamlet, *et al.* 1983, [e] Gonçalves *et al.* 1993, [f] Marcus, Kamlet and Taft 1988, Kamlet *et al.* 1988, Marcus 1991, Laurence *et al.* 1994, [g] Labban and Marcus 1997, [h] Nicolet and Laurence 1986 Laurence, Nicolet, and Helbert 1986, [i] Marcus 1984, [j] Migron and Marcus 1991, [k] Koppel and Paju 1976, Makitra and Pirig 1979, [l] Berthelot *et al.* 1984, [m] Godfrey 1972, [n] Abraham *et al.* 1989, [o] Reichardt 1994, [p] Laurence *et al.* 1994, [q] Marcus 1993, [r] Laurence *et al.* 1989, [s] Mayer, Gutmann, and Gerger, 1975 Mayer, 1983, [t] Schmid 1983, Symons and Pena-Nunez, 1985, [u] Abboud and Notario 1997, [v] Spange *et al.* 1984, [w] Elias *et al.* 1982, [x] Griffith and Pugh 1979, Griffith and Pugh 1979, [y] Hormadaly and Marcus 1979, Medda, Pal, and Bagchi 1988, Medda *et al.* 1992, [z] Taft *et al.* 1985, Kamlet *et al.* 1987, Kamlet *et al.* 1988, Abboud *et al.* 1988, [aa] Persson 1986, Johnsson and Persson 1987, Persson, Sandström, and Goggin 1987, [bb] Marcus 1994, [cc] Laurence *et al.* 1981, [dd] Krieger 1984, [ee] Ponomarenko 1994, [ff] Spange and Keutel 1992.

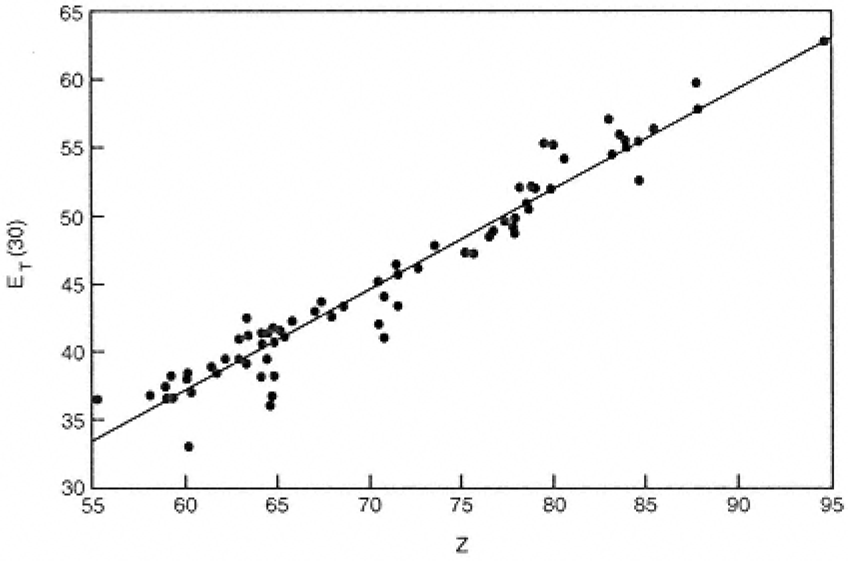

Figure 4.2
The correlation between the Dimroth-Reichardt $E_T(30)$ and the Kosower Z solvent polarity parameters, Eq. (4.8), both in kcal mol^{-1}

over, π^* measures a certain blend of polarity and polarizability of the solvents, that is not necessarily the same for all uses: for non-spectroscopic considerations of solvent polarity/polarizability, such as solubilities, a further parameter, δ, is introduced, taking values of 0.5 for polychlorinated aliphatic solvents, 1.0 for aromatic solvents, but 0.0 for all others. The quantity that has to be employed for such uses is then $\pi^*(1 - d\delta)$, with $d = 0.4$ for several applications. The development of the concept and use of π^* has recently been discussed and its values for over two hundred solvents compiled (Laurence *et al*. 1994), shifting from the use of the average of values of several probes to the use of a single primary probe, S = 4-nitroanisole (and a secondary probe, 4-nitro-N,N-dimethylanilinie) These more recent values, obtained from $\bar{\nu}(S)$, lead to $\pi^* = [(\bar{\nu}(S)/cm^{-1}) - 34\,120]/2400$ (the constants normalizing as above to yield $\pi^* = 0$ for cyclohexane and $\pi^* = 1$ for dimethylsulfoxide), are close to but not identical with the original Kamlet and Taft values (Kamlet, Abboud and Taft 1977; Kamlet *et al*. 1983). The $\pi^*(S)$ values at 25°C for the solvents in our List are shown in Table 4.3, and it must also be recognized that π^* is temperature-dependent and that the precision of the determination of $\bar{\nu}(S)$ is about ± 10 cm^{-1} (Laurence *et al*. 1994).

There are certain rules, according to which π^* values can be estimated for solvents for which they have not been measured (Kamlet *et al*. 1983). As a generalization, π^* values of solutes can be obtained from multivariate linear free energy correlations involving these solutes (e.g., partitioning between 1-octanol

and water) and the assumption is that a liquid substance that can act as a solvent has the same π^* value as when it acts as a solute. Thus for polar aliphatic solvents with dipole moments μ, expressed in Debye units, $\pi^* \approx 0.03 + 0.23(\mu/\mathrm{D})$ and for aromatic ones $\pi^* \approx 0.56+0.11(\mu/D)$.

Furthermore, in a homologous series such as aliphatic ketones, esters, carboxylic acids and amides (and also side chains of aromatic solvents), 0.02 is to be subtracted from an initial π^* value for each additional methylene group added. For alkanols, however, this methylene decrement does not apply. When this methylene group is added directly to an aromatic ring (replacing -H by $-CH_3$) the decrement to π^* is 0.04 units. If there are two polar substituents on an aromatic ring, 0.10 is added to the higher π^* value of the monosubstituted derivative if the second group is in the ortho position, 0.05 is added if in the meta position, and nothing is added if in the para position.

The two polarity parameters, E_T^N and π^*, are related also in a general manner to certain physical properties of the solvents beyond the dipole moment mentioned above, namely functions of their refractive index and relative permittivity (Bekarek 1981) (cf. Chapter 3): $\mathrm{f}(n) = (n_\mathrm{D}^2 - 1)/(2n_\mathrm{D}^2 + 1)$ and $\mathrm{f}(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$. The expressions employed are:

$$E_\mathrm{T}^\mathrm{N} = -0.026 + 2.223[\mathrm{f}(\varepsilon)]^2 - 0.898\,\mathrm{f}(n)\mathrm{f}(\varepsilon) \qquad (4.9)$$

and

$$\pi^* = 15.45\,\mathrm{f}(n)\mathrm{f}(\varepsilon) - 0.573 \qquad (4.10)$$

These expressions should serve for the estimation of so far unknown E_T^N and π^* values, the second one replacing earlier expressions, where the coefficient of $\mathrm{f}(n)\mathrm{f}(\varepsilon)$ was 14.65 for aliphatic solvents, whereas for aromatic ones the expression was $\pi^* = 8.08\,\mathrm{f}(n)\mathrm{f}(\varepsilon) - 0.058$ (Kamlet *et al*. 1983; Bekarek 1981).

The polarity of some supercritical solvents has been determined in terms of the π^* parameter by means of 2-nitroanisole (Yonker *et al*. 1986). It is necessary to specify the temperature and pressure, provided they are $> T_\mathrm{C}$ and $> P_\mathrm{C}$, or the density of the solvent to which the values pertain as these can be varied over wide ranges. Table 4.4 shows some relevant data.

3—
Electron Pair Donicity

The solvating ability of solvents depends not only on their general polarity, which is a non-specific property, but in a large part to their ability to interact in a specific manner with the solute. This may take place by the donation of a nonbonding pair of electrons from a donor atom of the solvent towards the formation of a coordinate bond with the solute, therefore exhibiting Lewis basicity, or the acceptance of such a pair from a solute, an exhibition of Lewis acidity of a protic or protogenic solvent towards the formation of a hydrogen bond between it and

Table 4.4 The polarity (π^*) of some 'supercritical solvents' (Yonker *et al*. 1986)

'supercritical solvent'	T/K	P/MPa	d/g cm^{-3}	π^*
xenon	299	10	1.66	-0.35
ethane	314		0.50	-0.25
carbon dioxide	323	7.4	0.20	-0.48
	323	10.5	0.44	-0.22
	323	15.7	0.68	-0.09
	323	20.4	0.77	-0.05
	323	34.3	0.92	0.00
	313		0.70	0.00
	296	27	0.95	0.04
dinitrogen oxide	323	18	0.68	-0.12
	296	27	0.95	-0.03
ammonia	418		0.25	0.25
	296	27	0.62	0.80
sulfur hexafluoride	323		1.02	-0.60

the solute. Such a direct solvation is often much stronger than non-specific polar interactions, based on dispersion forces and multipole and induced dipole interactions.

The ability of a solvent to donate a pair of electrons of one of its donor atoms towards the formation of a coordinate bond with an acceptor atom of a solute is a measure of its Lewis basicity. Several methods have been proposed over the years to express this donor ability or donicity, but only few of them have proved to be viable and of any real usefulness.

One of them is Gutmann's donor number, *DN*, (Gutman and Vychera 1966) defined as the negative of the standard molar heat of reaction (expressed in kcal mol^{-1}, 1 cal = 4.184 J) of the solvent with antimony pentachloride to give the 1:1 complex, when both are in dilute solution in the inert diluent 1,2-dichloroethane. This quantity needs to be determined calorimetrically, as was done for a considerable number of solvents at that time (Gutman and Vychera 1966). There are several problems with the *DN* scale. One is the fact that calorimetric equipment

The correlation between the Koppel and Palm, Shorter, and Kagiya $B_{\text{O-D}}(\text{CH}_3\text{OD})/\text{cm}^{-1}$ (circles), Eq. (4.11), and the Koppel and Paju $B_{\text{O-H}}(\text{C}_6\text{H}_5\text{OH})/\text{cm}^{-1}$ (triangles), Eq. (4.12) and the Lewis basicity scales with the Gutmann $DN/\text{kcal mol}^{-1}$ scale

Values of *DN* obtained either directly or via the spectroscopic parameters are listed in Table 4.3.

A solvatochromic scale, based on the ultraviolet-visible, rather than the infrared, spectral band of suitable probes is that based on the Kamlet-Taft β parameter. This is again an averaged quantity, for which the wavenumber shifts of several protic indicators relative to structurally similar but aprotic homomorphs are used (Kamlet *et al*. 1983; Kamlet and Taft 1976). It is assumed that the nonspecific effect of a solvent on the protic probe is the same as that on the aprotic one, and that it can be expressed in terms of the π* parameter for the solvent, so that the donicity of the solvent, if it is a Lewis base, causes the difference between the responses of the two probes towards the solvent. The probes originally employed were 4-nitrophenol (vs 4-nitroanisole) and 4-nitroaniline (vs 4-nitroN,N-diethylaniline), but once a π* scale is known, the need for the specific aprotic homomorph values no longer exists, since the general expression:

$$\beta = b(\bar{\nu}_0 - \bar{\nu}) + s(\pi^* - d\delta) \qquad (4.13)$$

can be employed. Here $\bar{\nu}_0$ is the wavenumber of the probe in the gas phase or in cyclohexane and *b* and *s* are solvent-independent coefficients, selected for the normalization making β = 0 for cyclohexane and β = 1 for hexamethyl phosphoric triamide. The probes are selected in view of the fact that the larger the ratio *b/s* the less is the effect of the non-specific interactions. In this respect the probe acetylacetonato-N,N,N′,N′-tetramethylethylenediaminocopper(II) perchlorate (Soukup and Schmid 1985) is favorable, since it is substantially independent of π* (i.e., *b/s* ≈ ∞) with β = 0.358($\bar{\nu}$ - 18.76).

It was later shown by Laurence and coworkers that there are significant systematic differences between β values of solvents obtained with indicators with an oxygen donor atom and those with a nitrogen donor atom (Nicolet and Laurence 1986). These authors recommended the use of a single indicator, preferably 4-nitrophenol relative to 4-nitroanisole or else 4-nitroaniline relative to 4-nitro-N,N-di*methyl*aniline (rather than 4-nitro-N,N-di*ethyl*aniline used by Kamlet and Taft 1976), to establish a basicity scale. The main point of difference is with respect to solvents that do not have an oxygen donor atom, such as amines, pyridines, and sulfides. In order to 'save' the β scale, Kamlet and Taft proposed a family-dependent covalency parameter, ξ, equal to -0.20 for P=O bases, 0.00 for C=O, S=O, and N=O bases, 0.20 for -O- bases, 0.60 for pyridines, and 1.00 for amines, for use in linear free energy relationships (Kamlet *et al*. 1985).

The further question arises, whether β values of compounds in bulk, acting as solvents, are the same as when they are in dilute solutions, acting as solutes. This question was answered in the affirmative in the case of non-associated solvents (Abraham *et al*. 1989), the solute values having been obtained from hydrogen bonding equilibrium constant data, e.g., for interactions of the solvents as solutes with phenol or 4-fluorophenol in tetrachloromethane diluent. Notwithstanding these difficulties, again with the understanding that the β scale has a built-in 'fuzziness', the values given (Kamlet and Taft 1976) augmented by values obtained by others (not necessarily averaged over several probes) are shown in Table 4.3.

Some estimation rules have been established for β in the cases where it has not been determined. These generally pertain to the substances used as solutes, but if they are non-associating, it was shown above that the values can be used for solvents too. The β values of acyclic ketones and of esters appear to be the same as for acetone (0.48) and ethyl acetate (0.45), respectively, those for chloro- and polychloroalkanes are between 0.00 and 0.10. For the first to third substitution of a methyl group on an aromatic ring, 0.01 is to be added to β, as for the substitution of an ethyl for a methyl group. For the addition of a chlorine or bromine atom to an aromatic ring subtract 0.10 from β, for a fluorine atom subtract 0.05 (Taft *et al*. 1985). In general, when large molecules have two functional groups that are well separated from one another, the resulting β is the sum of the two individual β values, calculated as if the other did not exist. It must be remembered that on the whole the average β values for solvents have an uncertainty of ca. ±0.04 units.

The *DN* and β electron pair donicity scales are closely related to each other, as is to be expected. The correlation expression, established for 25 solvents for which both measures were known at the time, was $DN = -0.9 + 39.18\beta$ (Kamlet *et al*. 1985). A correlation involving many more solvents has since been established:

$$DN = 0.5 + 38.2\beta \qquad (4.14)$$

valid for 107 solvents (Marcus 1993), see Figure 4.4.

A problem with the quantitative measures of the Lewis base strength according to the above scales, that has not so far been resolved satisfactorily, is the relative basicities of oxygen- and nitrogen-donor bases. An example that has been discussed by several authors is the case of triethylamine (Marcus 1984; Maria and Gal 1985), which according to the *DN* scale is a very strong base (considerably stronger than, say, pyridine and dimethylsulfoxide) but according to the β scale is only a moderately strong base, with β values comparable to pyridme and dimethylsulfoxide. The family-dependent covalency parameter ξ (see above) has been introduced by Kamlet and Taft as a partial solution of this problem (Kamlet *et al*. 1985). A recent recommendation (Abboud and Notario 1997) is to employ for the Lewis basicity scale only values obtained with the probe 4-nitrophenol, designated β_{OH}, rather than the average of values based on several probes, including 4-nitroaniline, due to the relative weakness of the latter as a hydrogen bond donor and its having two acceptor hydrogen atoms. According to the β_{OH} scale the tertiary amines, such as triethylamine, are indeed very strong Lewis bases, as indicated by the original *DN* scale.

Another problem concerns the basicity of hydroxylic solvents, such as water

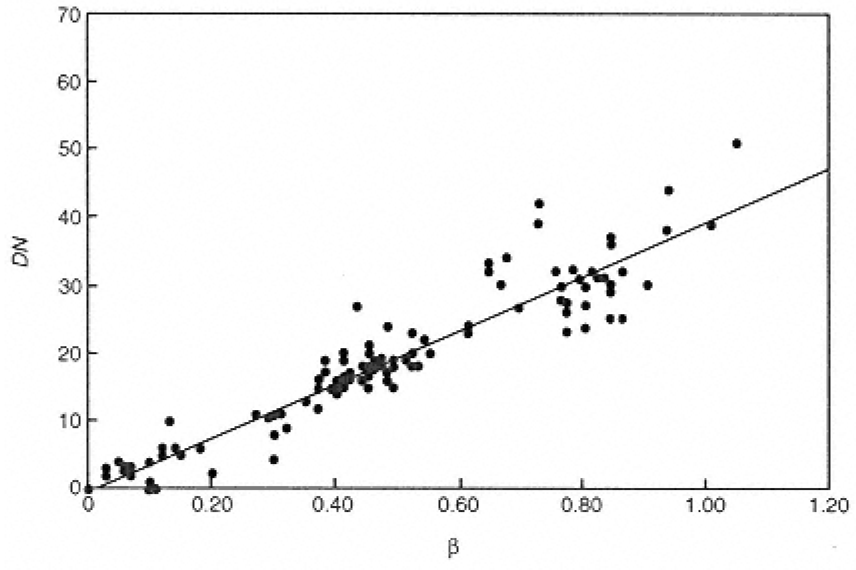

Figure 4.4
The correlation between the Gutmann *DN*/kcal mo^{-1} scale and the Taft and Kamlet β Lewis basicity scales, Eq. (4. 13)

and alkanols. Their isolated molecules in dilute solutions in inert solvents have lower β values than the bulk solvents, contrary to the case of the non-associated solvents as mentioned above (Abraham *et al*. 1989). However, the cooperative effect of the hydrogen bonds in the networks or chains produced by association cause these solvents to have larger β values than the monomers: for water β = 0.47—as high as for ethers—compared with 0.18 for the monomer, for methanol 0.66 compared with 0.41, for ethanol 0.75 compared with 0.47, etc. The same difficulty has been observed for the *DN* values: these have been determined calorimetrically for the monomers, leading to values of 18 for water and 19 for methanol, whereas indirect methods lead to higher values, such as 30 for methanol and 32 for ethanol (Marcus 1984). Note that as the alkyl chain lengthens, the Lewis basicity increases, up to about four or five carbon atoms in the chain, and then decreases slowly for longer alkyl chains, as the cooperative effect of the association decreases.

Many other scales of electron-pair donation abilities have been proposed over the years, which are in general in good correlation with *DN* e.g., the heat of complexation of the solvent molecules with boron trifluoride in dichloromethane (Maria and Gal 1985), and β e.g., *SB*, the solvatochromism of 5-nitroindoline compared with 1-methyl-5-nitroindoline in neat solvents (Catalan *et al*. 1996) scales. The latter, the *SB* scale, has the advantage that the N–H acid function of the 5-nitroindoline probe has only a single hydrogen atom, contrary to the nitroanilines used for the β scale, that have two. It was devised quite recently for

201 solvents, the major part of which are on the List, and the values are reported in Table 4.3. These scales have not found much application so far, and are not discussed any further here.

4— Hydrogen Bonding Ability

Protic solvents are those that have a hydrogen atom bonded to an electronegative atom, and which can either be dissociated from it in acid-base reactions or at least form a hydrogen bond or bridge to another electronegative atom of a second molecule, or the same one for an internal hydrogen bond. In certain solvents a tautomeric equilibrium is established between a form that is protic and another that is not e.g., in β-diketones such as acetylacetone, whereas in others only strongly basic solutes can induce the formation of a hydrogen bond with a certain hydrogen atom of such solvents, called protogenic. These include, e.g., chloroform or nitromethane, in fact several solvents that have a methyl group adjacent to groups such as C=O, C≡N, or NO_2. A number of scales for the hydrogen bonding ability of solvents have been proposed over the years, and a few of them are still viable, in the sense that they are in continued use.

The acceptor number, *AN*, introduced by (Mayer, Gutman and Gerger 1975), expresses the ability of a solvent to form a hydrogen bond by accepting an electron-pair of a donor atom from a solute molecule. It is defined as the limiting value of the NMR chemical shift δ of the ^{31}P atom in triethylphosphine oxide at infinite dilution in the solvent, relative to n-hexane, corrected for the diamagnetic susceptibility of the solvent, and normalized so as to make $AN = 2.348(\delta/\text{ppm})$ (Mayer, Gutman and Gerger 1975). A secondary measure uses tributyl phosphate as the probe: $AN = 1.131\delta^{31}_{\text{corr}}\text{P}(\text{Bu}_3\text{PO}_4) + 0.8$ (Elias *et al*. 1982.) The coefficient arises from the assignment of the value $AN = 100$ to the interaction of triethylphosphine oxide with the Lewis acid antimony pentachloride dissolved in 1,2-dichloroethane, the basis for the *DN* scale. Since aprotic, and non-protogenic, solvents have non-vanishing acceptor numbers, < 10 for apolar and 10 to 20 for dipolar aprotic solvents, it is clear that *AN* includes a non-specific polarity effect. However, protic solvents have considerably higher *AN* values, in the range 25–130, as is seen in Table 4.3 where the values are collected. The acceptor numbers are linearly correlated to the 'polarity' parameter $E_T(30)$, which also has a non-specific dependence on the solvent properties, see Figure 4.5:

$$AN = -59.9 + 1.850E_T(30) \qquad (4.15)$$

established for 51 solvents (Marcus 1993). Further correlations have led to additional *AN* values: $AN = 12.73 \log \varepsilon - 0.056DN - 2.33$ (Schmid 1983), $AN = -681 + 0.03157[\tilde{\nu}_{\max}(\text{di-}t\text{-butyl-amine oxide})/\text{cm}^{-1}]$ (Schmid 1983), and $AN = (\tilde{\nu}_{\max}[\text{Fephen}_2(\text{CN})_2]/10^3\ \text{cm}^{-1} - 15.06)/0.077$ (Spange *et al*. 1984).

Another measure of the hydrogen bonding ability of solvents is Kosower's Z

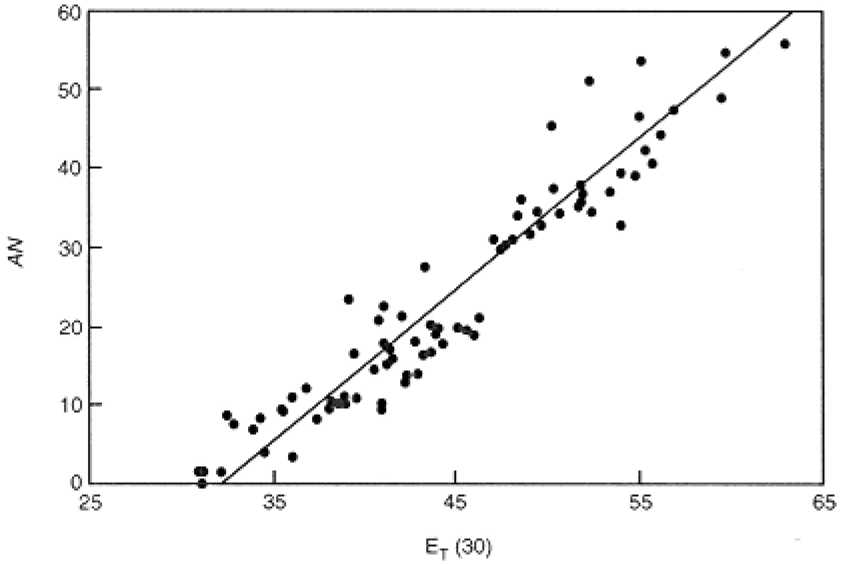

Figure 4.5
The correlation between the Gutmann-Mayer *AN* scale and the Dimroth-Reichardt $E_T(30)$/kcal mol^{-1} polarity/Lewis acidity scales, Eq. (4.14)

parameter (Kosower 1958), defined as the transition energy, in kcal mol^{-1} (1 cal = 4.184 J) of the lowest energy ultraviolet-visible absorption band of 4-carboxymethyl-1-ethylpyridinium iodide dissolved in the solvent, $Z = 2.859 \times 10^{-3}(\tilde{\nu}\ /\mathrm{cm}^{-1})$. A subsidiary measure, called Z' in the following, is the similar transition energy of 4-cyano-1-ethylpyridinium iodide (Kosower 1958; Hormadaly and Marcus 1979), which unlike the former probe can also be used in fairly strong acids, and is closely related to its values by $Z' = 1.011\ Z - 4.8$ (Marcus 1993). The *Z* scale has been expanded (Griffith and Pugh 1979) and can be further expanded by incorporation of values obtaine via Z'. These values were not normalized, hence vary from ca. 60 for aprotic solvents to ca. 95 for water, as shown in Table 4.3. The *Z* and Z' values necessarily include contributions from the polarity as well as electron pair donicity of the solvents, although the main sensitivity is to the hydrogen bonding ability. In fact, *Z* was originally designed to be a measure of the polarity, as was $E_T(30)$, and the latter is also a sensitive measure of the hydrogen bond donating ability, if the non-specific polarity is taken into account. The two scales are linearly related to one another by (cf. Eq. (4.8):

$$Z = 14.7 + 1.236 E_T(30) \qquad (4.16)$$

as found for 61 solvents for which both parameters were available (Marcus 1993). Obviously, *Z* and *AN* are also well linearly correlated

(Marcus 1993).

A measure of the hydrogen bonding ability of solvents that was designed to be devoid of contributions from the polarity and electron-pair donicity is the Kamlet-Taft α scale (Kamlet and Taft 1976). This scale too is based on solvatochromic parameters, averaged for several probes, so that it has a built-in 'fuzziness', but should measure the ability to donate hydrogen bonds of the solvent molecules to a 'general solute', rather than be specific for the probe employed to define it. It turns out that one probe, the ^{13}C NMR chemical shift δ of the 2- and the 3-carbon atoms of pyridine-N-oxide relative to the 4-atom, yields values that are independent of the solvent polarity and basicity and are sensitive only to its hydrogen bonding ability (Schneider *et al*. 1993), i.e., $\alpha = 2.43 - 0.162[\delta(C2) - \delta(C4)]/\mathrm{ppm} = 0.40 - 0.174[\delta(C3) - \delta(C4)]/\mathrm{ppm}$. It may be noted that pyridine-N-oxide can also be used as a solvatochromic indicator for the hydrogen bond donation ability, but then it is also sensitive to π^*, but with a fairly high discrimination: $\alpha = [(\tilde{\nu}/1000\ \mathrm{cm}^{-1}) - 35.42 - 0.61\pi^*]/2.49]$ (Vorkunova and Levin 1983). Other probes, such as the ^{13}C NMR chemical shifts δ of the ring carbon atoms of N,N-dimethyl-(or diethyl-)benzamide relative to the C=O carbon atom, e.g., $\alpha = 0.541[\delta(C3) - \delta(C = O)]/\ \mathrm{ppm} - 0.21\pi^*$ and the wavenumber $\tilde{\nu}$ of the light absorption peak of *cis*-bis(1,10-phenanthrolino)-dicyanoiron(II): $\alpha = 0.375[(\tilde{\nu}/1000\ \mathrm{cm}^{-1}) - 15.636] - 0.45\pi^* + 0.27\beta$, can be employed. Furthermore, linear correlations with Z (or Z'), AN, and E_T^N, taking into account the non-specific interactions by means of the π^* values of the solvents can be used (Marcus 1993):

$$\alpha = 0.0485Z - 2.75 - 0.46\pi^* \qquad (4.17)$$

$$\alpha = 0.0337AN - 0.10 - 0.47\pi^* \qquad (4.18)$$

$$\alpha = 2.13E_T^N - 0.03 - 0.76\pi^* \qquad (4.19)$$

Values of α either reported in (Kamlet *et al*. 1983) or obtained by these means are shown in Table 4.3. On the whole, the α values are expected to involve an uncertainty of ±0.08, due to the averaging process of results from several probes (Kamlet *et al*. 1983).

Water, as expected, has a very high hydrogen bond donation ability or Lewis acidity as a solvent: $\alpha = 1.17$. However, there are several solvents with a stronger ability to donate hydrogen bonds: certain phenols and halogen-substituted alcohols and carboxylic acids. The largest value have been established for hexafluoro-*i*-propanol: $\alpha = 1.96$, dichloroacetic acid: $\alpha = 2.24$, and trifluoroacetic acid: $\alpha = 2.38$, but in the case of the carboxylic acids proton donation rather than hydrogen bonding may have been involved, these being, in aqueous solutions, quite strong acids, see Table 4.4 below. According to another measure of the Lewis acidity, AN, again hexafluoro-*i*-propanol: $AN = 66.7$ and trifluoroacetic acid: $AN = 105.3$ are stronger than water, $AN = 54.8$, and so are also methanesulfonic acid, $AN = 126.3$ (no α value is available) and formic acid, *AN* = 83.6, and the highest value belongs to trifluoromethanesulfonic acid, *AN* = 131.7 (Mayer, Gutman and Gerger 1975).

On the other side of the scale, very moderate, but not negligible, Lewis acidities are ascribed, according to their α parameters, to C-H acids, such as chloroform and bromoform, primary and secondary acyclic amines, such as *n*-butylamine and diethylamine, and protogenic solvents, such as methyl-alkyl ketones, acetonitrile, and nitromethane. It can be expected that liquid 1-alkynes (not on the List), having the grouping H-C≡C-R, also have non-negligible α values, being C-H Lewis acids. It can be safely concluded, however, that aprotic solvents other than those of the classes noted above have no Lewis acid character, with $\alpha \approx 0$ for all intents and purposes.

It has been established (Kamlet and Taft 1985) that a large number of solvent effects involving a given solute and a series of solvents can be described by the general linear solvation energy relationship (LSER):

$$XYZ = XYZ_0 + h\delta^2 + s\pi^* + b\beta + a\alpha \qquad (4.20)$$

Here *XYZ* is the observed quantity; solubility, partition coefficient, light absorption peak, NMR chemical shift, toxicity, etc., XYZ_0 is the value of this quantity in the absence of a solvent i.e., in the gas phase, or in a reference solvent with $\pi^* = \beta = \alpha = 0$, e.g., *c*-hexane, and *h, s, b*, and *a* are solute-dependent but solvent-independent coefficients. A term describing solvent properties additional to those described by the solvatochromic parameters is generally required, i.e., $h\delta^2$, related to the work done in the formation of a cavity to accommodate the solute, where δ is the solubility parameter of the solvent, Table 3.1. Obviously, the terms in Eq. (4.20) can be replaced by equivalent terms involving other solvent parameters, such as $E_T(30)$, *DN*, *AN*, etc., with due changes to the numerical values of the coefficients and of XYZ_0. In many cases it is found that not all five terms on the right hand side of Eq. (4.20) are required, i.e., when restricted kinds of solvents are employed, such as aprotic and non-protogenic solvents, so that the term $a\alpha$ is unnecessary.

5—
Solvent Softness

Another property that characterizes solvents is their softness, in terms of the HSAB concept (Pearson 1963), according to which the interactions of soft solvents are strongest with soft solutes, of hard solvents with hard solutes, but are weaker for hard solvents with soft solutes and vice versa. The applicability of the softness property takes into account that it is superimposed on the more general electron pair donation property discussed above. In fact, it can replace (Marcus 1987) the notion of the family dependence of the β scale, expressed by the ξ parameter (Kamlet *et al*. 1985). A few quantitative scales have been proposed for this solvent property; scales for solute, in particular ion, softness are also available (Marcus 1972).

A solvent softness scale, dependent on the thermodynamics of transfer of ions from water to the target solvent, has been proposed (Marcus 1987). Since soft ions prefer soft solvents and hard ions hard solvents, and since silver ions are soft, whereas sodium and potassium ions are hard, the difference:

$$\mu = \{\Delta_{tr}G^{o}(Ag^{+}) - 0.5[\Delta_{tr}G^{o}(Na^{+}) + \Delta_{tr}G^{o}(K^{+})]\}/(100\ kJ\ mol^{-1}) \qquad (4.21)$$

constitutes this solvent softness scale. The standard molar Gibbs free energies of transfer, $\Delta_{tr}G^{o}$, for these ions have been reported for many solvents on the mol dm^{-3} scale for 25°C (Marcus 1997). Values of $\Delta_{tr}G^{o}$/kJ mol^{-1} are generally know to ±6 units, so that the accuracy of μ values should be ±0.08. The average of the standard molar Gibbs free energies of transfer of sodium and potassium is used, since the radius of the silver ions at 0.115 nm is in between those of the alkali metal ions, 0.102 and 0.138 nm, respectively (Marcus 1997), in order to eliminate electrostatic effects on the Gibbs free energy of transfer that represent hard-hard interactions. Although single ion Gibbs free energies of transfer are used in μ, the resulting values are independent of any extrathermodynamic assumption employed to derive them, because the difference between the values of the singly charged cations is employed.

Another measure of solvent softness proposed is based on Raman spectroscopic measurements. It is the wavenumber shift $\Delta\tilde{\nu}$ of the Raman band for the symmetrical stretching of Br-Hg-Br in the solvent relative to that of gaseous mercury bromide (Persson 1986). A solvent softness scale, called $D_S = [\Delta\tilde{\nu}$ (Hg-Br)/cm^{-1}] has accordingly been established. An extension of this scale to further solvents is difficult in those cases where the solubility of mercury bromide is insufficient for the ca. 0.2 mol dm^{-3} required for the Raman spectral measurements.

Iodoacetylenes as well as iodine cyanide are soft Lewis acids (Laurence *et al*. 1981), which interact with basic solvents yielding characteristic wavenumber shifts $\Delta\tilde{\nu}$ (C-I) (e.g., for ICN relative to the wavenumber in CCI_4 solutions). These shifts differ for soft solvents, with sulfur or selenium donor atoms or π systems, and hard solvents, with oxygen or nitrogen donor atoms. However, these authors have not converted this observation and their data to a solvent softness scale. In fact, if prorated values of $\Delta\tilde{\nu}$ (O-H), for phenol, relative to CCI_4 solutions, see $B_{O\text{-}H}$ above, representing the hard basicity of the solvents, are subtracted, the remainder measures the solvent softness. Quantitatively,

$$\Delta\Delta\tilde{\nu}(CI) = [\Delta\tilde{\nu}(CI)/cm^{-1}] + 6 - 0.121[\Delta\tilde{\nu}(OH)/cm^{-1}] \qquad (4.22)$$

can be set as a measure of solvent softness (Marcus 1998). Slightly negative (≥ -10) values of $\Delta\Delta\tilde{\nu}(CI)$ signify hard solvents, slightly positive values (≤ 7) signify borderline solvents, and those with this difference > 7 are soft.

The three scales, μ, D_s, and $\Delta\Delta\tilde{\nu}(\mathrm{CI})$ are mutually correlated, though not linearly:

$$\mu = 6.95 \times 10^{-4} D_S^2 - 8.4 \times 10^{-3} D_S \qquad (4.23)$$

for 34 solvents for which both μ and D_s values are known, and

$$\mu = -0.1556 + 0.01445\Delta\Delta\tilde{\nu}(\mathrm{CI}) + 0.0039\Delta\Delta\tilde{\nu}(\mathrm{CI})^2 \qquad (4.24)$$

but it should be noted that there are only eleven solvents for which both μ and $\Delta\Delta\tilde{\nu}(\mathrm{CI})$ values are available. Table 4.3 includes the μ values either determined directly from the ion transfer data or via these correlation expressions, as noted by the references shown.

Solvent effects that can be described by an LSER such as Eq. (4.20), but where soft solvents are involved, are better accounted for if a term *m*μ is added (Marcus 1987).

6—
Solvent Acidity and Basicity

The Lewis basicity, electron-pair donicity, and acidity, hydrogen bond donation ability, discussed above pertain to the bulk solvents and their solvating properties, in which coordinate bonds are formed with solutes, and among the solvent molecules themselves, but no net chemical reaction takes place. The acidity and basicity discussed in the present section, on the contrary, deal with the propensity of solvents to undergo complete proton transfer reactions, which are of great importance to the characterization of solvents and their utility for various purposes. Although this book deals with the properties of solvents in the bulk, it is important to consider also some properties of isolated molecules of the solvents, since these can throw some light on the bulk behaviour. The proton affinity of solvent molecules and their acidity in the gas phase describe the tendency of these molecules to form the protonated ion by accepting a proton on the one hand and to lose a proton to form the anion on the other.

The proton affinity, *PA* in kJ mol^{-1} at 298 K, of a solvent S is the negative of the standard molar enthalpy change of the process S + H$^+$ → SH$^+$ in the gaseous phase. The process is often carried out as an equilibrium competition process with some other base B, the *PA* of which is known:

$$\mathrm{BH^+ + S \rightleftarrows B + SH^+} \qquad (4.25)$$

with the equilibrium constant K_{eq} measured over a range of temperatures, and the enthalpy change is obtained from the van't Hoff relationship, $\Delta H^\circ_{eq} = RT^2 \mathrm{d}\ln K_{eq}/\mathrm{d}T$. Ammonia is often employed as the reference base B, with *PA* = 854.0 kJ mol^{-1} (the decimal is uncertain), so that the proton affinity of the solvent S can be obtained from $\Delta H^{\circ}_{\mathrm{eq}}$. Most of the data available are from (Lias *et al*. 1988). There exist relationships between the gaseous phase basicity of solvents, *PA*, and their solvation abilities, i.e., basicities in solution (Taft 1975).

The compilation (Lias *et al*. 1988) is also the source of most of the data for the gas phase acidity, ΔG_A in kJ mol^{-1} at 298 K. This is the standard molar Gibbs free energy of proton dissociation according to $S(H) \rightarrow S^- + H^+$ in the gas phase. Again, the equilibrium constant K_{eq} of a competition reaction,

$$S(H) + A^- \rightleftarrows S^- + AH \qquad (4.26)$$

is used, with $\Delta G_A = -RT \ln K_{eq}$. Gaseous hydrogen chloride is often employed as the reference acid, AH, with $\Delta G_A = 1535.1$ kJ mol^{-1}. Relationships also exist between the gaseous phase acidity of solvents and their acidities in solution, e.g. in dimethyl sulfoxide (Taft and Bordwell 1988) or in water (see below).

Several techniques contribute to such data, mass spectrometry being a frequently used one, where fragment appearance potentials are measured. Pulsed ion cyclotron resonance or else photoionization or laser photodetachment are also often applied, with careful control of the ion or photon energies. In a few cases it was not possible to measure equilibrium constants and their temperature dependence, and it was necessary to bracket the reaction between two reference systems, in one of them the reaction taking place and in the other not. When it is desired to convert from enthalpies to Gibbs free energies or vice versa, the entropy change is approximated by that arising from the change in the number of participating particles and the symmetry numbers of the gaseous species. This does not take into account changes in vibrational modes, but these often have only negligible effects at 298 K. The values of *PA* and of ΔG_A at 298.15 K of the solvents on our List, generally reliable to ±8 kJ mol^{-1}, are shown in Table 4.5.

Just as the gas phase acidity and basicity can throw some light on the bulk behaviour of solvents, so can the corresponding aqueous phase quantities. The abilities of a solvent molecule to either dissociate a proton to form the hydrated anion and the hydrated hydronium cation, or to associate a proton to form the 'onium' cation are indicators of its acidity or basicity, that reflect to some degree also the behaviour of the bulk solvent. It must be noted, however, that these abilities are not equivalent to the Lewis acidity and basicity discussed above, that describe the abilities of the solvent molecules in the environment of the bulk solvent to form hydrogen bonds with solute Lewis bases and acids, respectively. Nor are they equivalent to the abilities to dissociate a proton or accept it in the gaseous state. The hydration of the species involved in the reactions in an aqueous phase plays a profound role, determining the extent to which they can proceed, see Fig. 2.2. In the following 'S' designates a generalized solvent molecule.

The acid dissociation of the protic or protogenic solvent S(H) in a dilute aqueous solution proceeds according to

$$S(H)(aq) + H_2O \rightleftarrows S^-(aq) + H_3O^+(aq) \qquad (4.27)$$

The constant concentration of the water in the infinitely dilute aqueous solutions

Table 4.5 The acidic and basic properties of solvents and their autoprotolysis

No.	Name	PA	ΔGa	pKa	pKb	pKs
0	vacuum					
10	tetramethylsilane		1635 [a]			
20	n-pentane					
30	2-methylbutane					
40	n-hexane					
50	c-hexane	707 [a]	1665 [a]			
60	n-heptane					
70	n-octane					
80	2,2,4-trimethylpentane					
90	n-decane					
100	n-dodecane					
110	n-hexadecane					
120	benzene	759 [a]	1636 [a]			
130	toluene	794 [a]	1564 [a]			
140	o-xylene	809 [a]				
150	m-xylene	820 [a]	1564 [a]			
160	p-xylene	803 [a]	1568 [a]			
170	ethylbenzene	802 [a]	1562 [a]			
180	cumene	804 [a]	1560 [a]			
190	mesitylene	840 [a]				
200	styrene	838 [d]				
210	tetralin	815 [a]				
220	cis-decalin					

230	water	697 [a]	1607 [a]			17.51 [j]
240	methanol	761 [a]	1569 [a]	15.09 [f]	16.0 [m]	16.91 [j]
250	ethanol	788 [a]	1551 [a]	15.90 [f]	15.9 [m]	19.10 [j]
260	n-propanol	798 [a]	1546 [a]	16.10 [f]		19.40 [j]
270	i-propanol	800 [a]	1543 [a]		17.2 [m]	21.08 [j]
280	n-butanol	800 [a]	1543 [a]	16.10 [f]	17.3 [n]	20.89 [j]
290	i-butanol	805 [a]	1540 [a]	16.10 [f]		21.08 [j]
300	2-butanol	816 [a]	1538 [a]		17.2 [n]	
310	t-butanol	810 [a]	1540 [a]	19.00 [j]	17.6 [n]	26.80 [j]
320	n-pentanol		1537 [a]			20.81 [j]
330	i-pentanol		1535 [a]			
340	t-pentanol		1533 [a]	19.00 [j]	17.3 [n]	
350	n-hexanol		1533 [a]			
360	c-hexanol	835 [b]				
370	n-octanol		1528 [a]			19.44 [r]
380	n-decanol					
390	n-dodecanol					
400	benzyl alcohol	794 [c]	1520 [a]	18.00 [j]		
410	2-phenylethanol	789 [a]	1525 [e]	15.44 [f]		
420	allyl alcohol		1534 [e]	15.52 [f]		
430	2-chloroethanol			14.31 [f]		
440	2-cyanoethanol			14.03 [f]		
450	2,2,2-trifluoroethanol.	707 [a]	1482 [a]	12.37 [f]		

continued overleaf

***Table 4.5** (continued)*

No.	Name	PA	ΔGa	pKa	pKb	pKs
460	hexafluoro-i-propanol	690 [a]		9.30 [g]		
470	2-methoxyethanol	846 [b]	1535 [a]	14.82 [f]		20.70 [j]
480	2-ethoxyethanol			15.12 [f]		
490	1,2-ethanediol	829 [b]		15.07 [f]		15.84 [j]
500	1,2-propanediol	828 [b]		14.80 [k]		17.21 [j]
510	1,3-propanediol	856 [b]		15.10 [j]		
520	1,2-butanediol	829 [b]				
530	2,3-butanediol (meso)	834 [b]		14.90 [k]	14.4 [j]	
540	1,4-butanediol	886 [b]		14.50 [k]		
550	1,5-pentanediol	886 [b]				
560	diethyleneglycol					
570	triethyleneglycol			14.50 [k]		
580	glycerol	829 [b]		14.10 [k]		
590	phenol	821 [a]	1432 [a]	9.67 [j]		
600	2-methylphenol		1431 [a]	10.29 [j]		
610	3-methylphenol		1434 [a]	10.09 [j]		
620	4-methylphenol		1437 [a]	10.26 [j]		
630	2-methoxyphenol		1429 [f]	9.98 [z]		
640	2,4-dimethylphenol			10.63 [j]		
650	3-chlorophenol		1399 [f]	9.13 [v]		
660	diethyl ether	838 [a]			16.0 [o]	
670	di-n-propyl ether	846 [a]			15.9 [o]	

680	di-i-propyl ether	862 [a]			15.8 [o]	
690	di-n-butyl ether	852 [a]			16.0 [j]	
700	di(2-chloroethyl) ether				17.8 [o]	
710	1,2-dimethoxyethane	857 [a]			16.9 [j]	
720	bis(methoxyethyl) ether					
730	furan	804 [a]				
740	tetrahydrofuran	835 [c]			14.8 [o]	35.50 [s]
750	2-methyl tetrahydrofuran	852 [a]				
760	tetrahydropyran	836 [a]			15.1 [o]	
770	1,4-dioxane	811 [a]			15.6 [o]	
780	1,3-dioxolane				17.8 [j]	
790	1,8-cineole					
800	anisole	838 [a]			18.0 [o]	
810	phenetole				17.9 [o]	
820	diphenyl ether				18.2 [o]	
830	dibenzyl ether				17.0 [o]	
840	1,2-dimethoxybenzene					
850	trimethyl orthoformate					
860	trimethyl orthoacetate					
870	propionaldehyde	793 [a]	1504 [g]			
880	butyraldehyde	801 [a]				
890	benzaldehyde	838 [a]			21.1 [j]	
900	p-methoxybenzaldehyde	893 [a]				
910	cinnamaldehyde					
920	acetone	823 [a]	1513 [g]	24.20 [j]	16.8 [m]	32.50 [j]
930	2-butanone	826 [d]	1512 [f]	20.50 [1]	21.2 [1]	25.94 [j]

(table continued on next page)

***Table 4.5** (continued)*

No.	Name	PA	ΔGa	pKa	pKb	pKs
940	2-pentanone					25.62 [j]
950	methyl i-propyl ketone	841 [a]	1508 [f]	21.00 [1]		
960	3-pentanone	843 [a]	1512 [f]	19.90 [1]		
970	c-pentanone	832 [a]			21.5 [j]	
980	methyl t-butyl ketone					
1000	c-hexanone	843 [a]		17.80 [1]	20.8 [j]	
1010	2-heptanone					
1020	3-heptanone					
1030	di-t-butyl ketone	864 [a]				
1040	acetophenone	859 [a]	1491 [g]	21.55 [j]	17.5 [p]	
1050	propiophenone		1488 [g]			
1060	phenylacetone		1445 [g]	18.30 [1]		
1070	p-methylacetophenone	873 [a]			17.2 [p]	
1080	p-chloroacetophenone				17.7 [p]	
1090	benozophenone					
1100	acetylacetone		1409 [h]	8.93 [j]		19.30 [j]
1110	biacetyl	815 [a]	1463 [i]			
1120	formic acid	748 [a]	1415 [a]	3.75 [j]		5.77 [j]
1130	acetic acid	796 [a]	1429 [a]	4.76 [j]		14.45 [j]
1140	propanoic acid	802 [a]	1424 [a]	4.87 [j]		
1150	n-butanoic acid		1420 [a]	4.82 [j]		
1160	n-pentanoic acid		1419 [a]	4.86 [j]		

1170	n-hexanoic acid		1418 [a]	4.88 [j]	
1180	n-heptanoic acid				
1190	dichloroacetic acid		1342 [h]	1.30 [f]	
1200	trifluoroacetic acid		1323 [a]	0.23 [f]	
1210	acetic anhydride				9.85 [j]
1220	benzoyl chloride				
1230	benzoyl bromide				
1240	methyl formate	788 [a]			
1250	ethyl formate	808 [a]			
1260	methyl acetate	828 [a]	1524 [g]		22.50 [j]
1270	ethyl acetate	840 [a]			22.83 [j]
1280	propyl acetate	839 [a]			
1290	butyl acetate				23.28 [j]
1300	methyl-i-butyl ketone	846 [a]			
1300	i-pentyl acetate				18.80 [j]
1310	methyl propanoate	838 [a]			
1320	ethyl propanoate				
1330	dimethyl carbonate				
1340	diethyl carbonate				
1350	ethylene carbonate				
1360	propylene carbonate				
1370	diethyl malonate		1432 [a]	13.30 [j]	
1380	methyl benzoate	852 [a]			
1390	ethyl benzoate				

continued overleaf

Table 4.5 *(continued)*

No.	Name	PA	ΔGa	pKa	pKb	pKs
1400	dimethyl phthalate					
1410	dibutyl phthalate					
1420	ethyl chloroacetate					
1430	ethyl trichloroacetate					
1440	ethyl acetoacetate			10.68 [j]		
1450	4-butyrolactone					7.88 [j]
1460	perfluoro-n-hexane					
1470	perfluoro-n-heptane					
1480	perfluoro-methylcyclohexane					
1490	perfluoro-decalin					
1500	fluorobenzene	764 [a]				
1510	hexafluorobenzene	743 [a]				
1520	1-chlorobutane					
1530	chlorobenzene	760 [a]				
1540	dichloromethane					
1550	1,1-dichloroethane					
1560	1,2-dichloroethane					
1570	tr-1,2-dichloroethylene					
1580	o-dichlorobenzene					
1590	m-dichlorobenzene					
1600	chloroform		1461 [a]			
1610	1,1,1-trichloroethane					

1620	1,1,2-trichloroethane					
1630	trichloroethylene					
1640	1,2,4-trichlorobenzene					
1650	tetrachloromethane					
1660	tetrachloroethylene					
1670	1,1,2,2-tetrachloroethane					
1680	pentachloroethane					
1690	1-bromobutane					
1700	bromobenzene	763 [a]				
1710	dibromomethane					
1720	1,2-dibromoethane					
1730	bromoform		1514 [a]			
1740	1-iodobutane					
1750	iodobenzene					
1760	diiodomethane					
1770	n-butylamine	914 [a]			10.7 [j]	
1780	benzylamine	907 [a]			9.7 [q]	
1790	1,2-diaminoethane	945 [a]			10.1 [q]	15.20 [t]
1800	diethylamine	945 [a]			10.9 [q]	
1810	di-n-butylamine	956 [a]			11.2 [q]	
1820	pyrrole	868 [a]	1468 [a]	-3.80 [j]?		
1830	pyrrolidine	942 [a]			11.2 [j]	
1840	piperidine	947 [a]			11.1 [j]	
1850	morpholine	918 [a]			8.49 [j]	
1860	triethylamine	972 [a]			10.7 [j]	
1870	tri-n-butylamine	982 [a]			10.8 [q]	

(table continued on next page)

Table 4.5 *(continued)*

No.	Name	PA	ΔGa	pKa	pKb	pKs
1880	aniline	876 [a]	1502 [a]		18.6 [j]	
1890	o-chloroaniline				16.6 [j]	
1900	N-methylaniline	913 [a]	1496 [a]		18.8 [j]	
1910	N,N-dimethylaniline	935 [a]			19.1 [j]	
1920	ethanolamine	926 [a]			9.50 [j]	5.70 [t]
1930	diethanolamine				8.88 [j]	
1940	triethanolamine				7.76 [j]	
1950	pyridine	924 [a]	1602 [a]		5.17 [j]	
1960	2-methylpyridine	942 [a]			6.00 [j]	
1970	3-methylpyridine	938 [a]			5.75 [j]	
1980	4-methylpyridine	942 [a]			6.06 [j]	
1990	2,4-dimethylpyridine	951 [a]			6.63 [j]	
2000	2,6-dimethylpyridine	955 [a]			6.72 [j]	
2010	2,4,6-trimethylpyridine				7.43 [j]	
2020	2-bromopyridine	898 [d]				
2030	3-bromopyridine	900 [d]				
2040	2-cyanopyridine	871 [a]				
2050	pyrimidine	882 [a]	1569 [a]			
2060	quinoline	948 [a]			4.94 [j]	
2070	acetonitrile	787 [a]	1525 [g]		24.1 [j]	32.20 [j]
2080	propionitrile	806 [a]	1532 [g]			33.54 [j]
2090	butyronitrile	810 [a]				

2100	valeronitrile					
2110	acrylonitrile					
2120	benzyl cyanide	816 [b]	1440 [g]			
2130	benzonitrile	820 [a]				
2140	nitromethane	750 [a]	1473 [g]	10.21 [j]		
2150	nitroethane	773 [a]	1472 [g]	8.46 [j]		
2160	1-nitropropane			8.98 [j]		
2170	2-nitropropane		1474 [g]	7.67 [j]		
2180	nitrobenzene	809 [a]				
2190	formamide	830 [a]			15.2 [o]	16.80 [t]
2200	N-methylformamide	861 [a]			15.6 [o]	10.74 [j]
2210	N,N-dimethylformamide	884 [a]	1640 [a]		15.6 [o]	23.10 [j]
2220	N,N-dimethylthioformamide	904 [y]	1561 [e]			
2230	N,N-diethylformamide					
2240	N-methylacetamide				16.5 [o]	
2250	N,N-dimethylacetamide	905 [a]	1535 [g]			23.95 [j]
2260	N,N-diethyl acetamide					
2270	pyrrolodinone-2				15.6 [o]	
2280	N-methylpyrrolidinone	907 [a]			14.7 [o]	25.60 [j]
2290	N-methylthiopyrrolidinone					
2300	tetramethylurea	933 [aa]				
2310	tetraethylurea					
2320	dimethylcyanamide	858 [a]				
2330	carbon disulfide					

continued overleaf

***Table 4.5** (continued)*

No.	Name	PA	ΔGa	pKa	pKb	pKs
2340	dimethyl sulfide	839 [a]	1615 [a]		20.9 [m]	
2350	diethyl sulfide	858 [a]				
2360	di-i-propyl sulfide					
2370	di-n-butyl sulfide	873 [a]				
2380	tetrahydrothiophene	856 [a]			18.5 [j]	
2390	pentamethylene sulfide					
2400	dimethyl sulfoxide	834 [a]	1533 [a]		15.5 [m]	31.80 [j]
2410	di-n-butyl sulfoxide					
2420	sulfolane				15.3 [j]	25.45 [j]
2430	thiobis(2-ethanol)					
2440	diethyl sulfite					
2450	dimethyl sulfate					
2460	diethyl sulfate					
2470	methanesulfonic acid	770 [x]	1318 [y]	-1.92 [w]		
2480	trimethyl phosphate	887 [a]				
2490	triethyl phosphate	910 [a]				
2500	tri-n-butyl phosphate					
2510	hexamethyl phosphoramide	948 [c]				20.56 [t]
2520	hexamethyl thiophosphoramide	932 [c]				
2530	hydrogen peroxide		1542 [a]			
2540	hydrogen fluoride		1530 [a]			12.50 [j]
2550	sulfuric acid		1281 [a]			3.33 [t]

2560	ammonia	854 [a]	1657 [a]		9.25 [n]	32.50 [t]
2570	hydrazine	856 [a]				
2580	sulfur dioxide					
2590	thionyl chloride					
2600	phosphorus oxychloride					13.30 [u]

Units: *PA* and ΔG_A in kJ mol^{-1}; pK_a, pK_b and pK_s, are dimensionless (but the *K* pertain to species concentrations in mol dm^{-3}).

References: [a] Lias *et al*. 1988 [b] Guenat *et al*. 1985 [c] Gasteiger and Hutchings 1984 [d] Ford and Scribner 1983 [e] Grual, Schnute and Squires 1990 [f] McMabon and Kebarle 1977, Cumming and Kebarle 1978 [g] Bartmess, Scott and Mclver 1979 [h] Taft, Caldin and Gold 1975 [i] Nogaj *et al*. 1990 [j] Riddick, Bunger and Sakano 1986 [k] Wooley and George 1974 [l] Ingemann and Nibbering 1985 [m] Perdoncin and Scorrano 1977 [n] Deno and Turner 1966 [o] Levitt and Levitt 1979 [p] Azzaro *et al*. 1982 [q] Frenna *et al*. 1985 [r] Kreshov, Aldarova and Smolova 1969 [s] Rosés 1993 [t] Weber and Houriet 1988 [u] Gutmann 1959 [v] Ernst and Herring 1965 [w] Guthrie 1978 [x] de Petris, Fornarini and Occhiuccini 1992 [y] Decouzon *et al*. 1994 [z] Biggs [aa] Abboud *et al*. 1993.

is generally ignored in the expression for the equilibrium constant, or rather absorbed into this constant. The acid dissociation equilibrium constant $K_a = [S^-][H_3O^+]/[HS]$, or the negative decadic logarithm of this quantity, pK_a, are generally used, the latter being shown in Table 4.5 for 25°C (Riddick, Bunger and Sakano 1986). It must be remembered that in aqueous solutions the self dissociation equilibrium of the water takes place concurrently with the dissociation of the (acidic) solvent:

$$2H_2O \rightleftarrows OH^-(aq) + H_3O^+(aq) \qquad (4.28)$$

described by the autoprotolysis constant of water (see below), pK_S = 17.51 on the mol dm^{-3} scale at 298 K. This value differs from the commonly quoted value pK_w = 14.00, which is the negative decadic logarithm of the ion product [OH$^-$][H$_3$O$^+$], because of the latter not taking the concentration of water in bulk water, 55.5 mol dm^{-3}, into account. It should also be noted that some of the entries found in the literature do not pertain directly to the acid dissociation process given above, and had to be converted appropriately.

The base protonation process is the opposite of the acid dissociation, with the difference that the conjugate base is the neutral solvent, not its anion. Some solvents can be protonated sufficiently in their dilute aqueous solutions:

$$\mathrm{S(aq)} + \mathrm{H_2O} \rightleftarrows \mathrm{SH^+(aq)} + \mathrm{OH^-(aq)} \qquad (4.29)$$

so that pK_b, the negative of the decadic logarithm of the equilibrium constant K_b = [SH$^+$][OH$^-$]/[S], is given (on the mol dm^{-3} scale at 25°C). For others, a stronger acid than water is required to protonate the solvent, and aqueous 0.1 mol dm^{-3} sulfuric acid is generally employed. Then the constants reported, pK_{BH+}, are for the equilibrium

$$\mathrm{S(aq)} + \mathrm{H_3O^+(aq)} \rightleftarrows \mathrm{SH^+(aq)} + \mathrm{H_2O} \qquad (4.30)$$

These values are converted here to pK_b values by the addition of 14.00 (for pK_w), but the reference is marked with an asterisk, denoting that the medium is actually dilute H_2SO_4 rather than water. The values of pK_b on the mol dm^{-3} scale at 25°C are also shown in Table 4.5, most of the data being, again, from (Riddick, Bunger and Sakano 1986) supplemented with data from other sources.

Returning now to the bulk solvents, their relevant acid-base reaction is their autoprotolysis, if protic or protogenic, according to:

$$2\mathrm{SH} \rightleftarrows \mathrm{SH_2^+} + \mathrm{S^-} \qquad (4.31)$$

with the equilibrium constant K_s. Some confusion exists in the literature on whether this constant is the ion product [SH$_{2+}$][S$_-$] or whether it includes also the concentration of the bulk solvent, 1000 times the reciprocal of the molar volume, squared: [SH$_{2+}$]/[HS]$_2$. Care must be taken when data from different sources are compared. Here, in Table 4.5, the second mode is employed. Further care has to be taken in ascertaining that the data used pertain to a very thoroughly dried solvent sample, since trace amounts of water can cause erroneous results (too low pK_S values). The data shown are dimensionless and pertain to 25°C (Riddick, Bunger and Sakano 1986).

In the few cases where data are available for solvents that are neither protic nor protogenic, the constant for the autosolvolysis equilibrium is recorded instead of that for the autoprotolysis. This pertains, for instance, to the equilibrium $2\,\mathrm{POCl_3} \rightleftarrows \mathrm{POCl_2^+} + \mathrm{POCl_4^-}$.

7—

Aqueous Solubility and Partition

Water is, of course, a very commonly used solvent, and in many cases it is used in aqueous mixtures with other solvents. Hence an important aspect of the chemical properties of solvents pertaining to their applicability is their mutual solubility with water. Mixtures of solvents with water are used in such chemical applications as synthesis and separation, as well as in order to bring solutes into solution for making physical measurements on them, for example spectroscopic ones. On the other hand, for the purpose of liquid-liquid distribution, negligible or minimal mutual solubility with water is generally required. There are many solvents that are completely miscible with water, at least at room temperature, although they may have an upper or lower consolute temperature, above or below which they separate into two liquid phases. Examples of this phenomena are phenol and triethylamine respectively. Generally, the solubility of water in solvents with which it is not completely miscible is considerably larger than that of the solvent in water, because water consists of very small molecules that are readily accommodated among the molecules of the other solvent. Data for the solvents on our List at 25°C (unless otherwise noted) on the mole fraction scale, *x*, are shown in Table 4.6.

Conversion of solubilities from the *x*-scale to the mol dm^{-3} scale, *c*, and vice versa requires knowledge of the volume change on mixing the components (the excess volume of mixing, V^E). If this is ignored, then the approximate relationships:

$$c_{\text{solvent}} \sim x_{\text{solvent}}/[V_{\text{water}} + x_{\text{solvent}}(V_{\text{solvent}} - V_{\text{water}})] \qquad (4.32)$$

and

$$x_{\text{solvent}} \sim c_{\text{solvent}} V_{\text{water}}/[1 - c_{\text{solvent}}(V_{\text{solvent}} - V_{\text{water}})] \qquad (4.33)$$

are followed, with the corresponding solubility values for water in the solvent being obtained by exchanging the subscripts $_{\text{solvent}}$ and $_{\text{water}}$ in Eqs. (4.32) and (4.33). The molar volumes in these expressions should be given in $\text{dm}^3\ \text{mol}^{-1}$ in view of the units used for *c*. Values of V^E are generally of the order of $\pm 1\ \text{cm}^3\ \text{mol}^{-1}$ for equimolar mixtures and smaller at other compositions, so that the above approximations are generally fairly well obeyed. The solubility of a solvent in water, when expressed in the units of mol dm^{-3}, cannot be larger than $1000/(V_{\text{solvent}}/\text{cm}^3\ \text{mol}^{-1})$, corresponding to trace amounts of water in the nearly neat solvent, even for completely water-miscible solvents.

Most of the solvents on the List are stable in the presence of water for long periods, but there are a few solvents that react with water. They do so either rather slowly but more rapidly in the presence of basic or acidic catalysts, such as certain esters, or rapidly, such as acetic anhydride or phosphorus oxychloride. These are noted by 'reacts' in Table 4.6. Many solvents, on the other hand, are quite hygroscopic, and unless kept over a drying agent, such as molecular sieves

Table 4.6 The mole fraction solubilities of the solvents in water and of water in the solvents, the octanol/water partition constant, log *P*, and the miscibility index

No.	Name	In water		Water in		log *P* O/W		Miscibilty
0	vacuum							
10	tetramethylsilane	4.00e-6	[a]			3.85	[d]	29
20	n-pentane	9.50e-6	[a]	4.80e-4	[a]	3.39	[d]	
30	2-methylbutane	1.20e-5	[a]	3.88e-4	[a]a			
40	n-hexane	2.57e-6	[a]	5.31e-4	[a]a	3.90	[d]	29
50	c-hexane	2.14e-5	[a]a	2.57e-4	[a]	3.44	[d]	28
60	n-heptane	6.42e-7	[a]	5.06e-4	[a]	4.66	[d]	29
70	n-octane	1.04e-9	[a]	6.02e-4	[a]	5.18	[d]	29
80	2,2,4-trimethylpentane	3.79e-7	[a]	3.49e-4	[a]			
90	n-decane	6.6e-11	[a]	5.7e-6	[a]			29
100	n-dodecane	3.9e-12	[a]	6.1e-6	[a]	6.80	[g]	29
110	n-hexadecane	4.45e-10		6.8e-4				30
120	benzene	4.13e-4	[a]	2.75e-3	[a]	2.13	[d]	21
130	toluene	1.01e-4	[a]	1.71e-3	[a]	2.69	[d]	23
140	o-xylene	2.97e-5	[a]	2.53e-3	[a]	3.12	[d]	23
150	m-xylene	2.48e-5	[a]	2.36e-3	[a]a	3.20	[d]	23
160	p-xylene	2.65e-5	[a]	2.68e-3	[a]	3.15	[d]	24
170	ethylbenzene	2.58e-5	[a]	2.53e-3	[a]	3.15	[d]	24
180	cumene	9.79e-6	[a]	2.01e-3	[a]a	3.66	[d]	24
190	mesitylene	7.22e-6	[a]	1.94e-3	[a]a	3.84	[d]	24
200	styrene	5.36e-5	[a]	3.80e-3	[a]	2.95	[g]	22
210	tetralin	1.16e-7						24
220	cis-decalin	<2.6e-5	[b]	2.74e-3	[b]a			29
230	water	miscible		miscible				

***Table 4.6** (continued)*

No.	Name	In water		Water in		log *P* O/W		Miscibility
270	i-propanol	miscible		miscible		0.13	[d]	15
280	n-butanol	1.92e-2	[a]	5.15e-1	[a]	0.75	[d]	15
290	i-butanol	2.6e-2	[a]	4.56e-1	[a]	0.75	[d]	
300	2-butanol	3.36e-2	[a]a	7.64e-1	[a]	0.71	[d]	16
310	t-butanol	miscible		miscible		0.36	[d]	16
320	n-pentanol	4.56e-3	[a]	2.83e-1	[a]	1.40	[d]	17
330	i-pentanol	5.58e-3	[a]	3.42e-1	[a]	1.42	[d]	
340	t-pentanol	2.46e-2	[a]	6.00e-1	[a]	0.91	[d]	16
350	n-hexanol	1.25e-3	[a]a	3.13e-1	[a]a	2.03	[d]	17
360	c-hexanol	6.96e-3	[a]	4.26e-1	[a]a	1.23	[d]	16
370	n-octanol	4.4e-5	[a]	2.75e-1	[e]	3.15	[f]	17
380	n-decanol	2.4e-5	[g]	2.44e-1	[g]			18
390	n-dodecanol	3.4e-5	[g]	1.06e-1	[g]	5.13	[d]	18
400	benzyl alcohol	1.33e-4	[a]a	3.54e-1	[a]a	1.08	[d]	13
410	2-phenylethanol	3.6e-3	[g]	7.40e-2	[g]	1.36	[d]	
420	allyl alcohol	miscible		miscible		0.17	[d]	14
430	2-chloroethanol	miscible		miscible		-0.06	[g]	11
440	2-cyanoethanol	miscible		miscible				
450	2,2,2-trifluoroethanol	miscible		miscible		0.41	[f]	
460	hexafluoro-i-propanol	miscible		miscible		1.66	[g]	
470	2-methoxyethanol	miscible		miscible		-0.60	[f]	13
480	2-ethoxyethanol	miscible		miscible		-0.05	[f]	14
490	1,2-ethanediol	miscible		miscible		-2.27	[f]	2

500	1,2-propanediol	miscible	miscible	-1.41	[f]	4
510	1,3-propanediol	miscible	miscible			3
520	1,2-butanediol					6
530	2,3-butanediol(meso)	miscible	miscible	-0.92	[f]	
540	1,4-butanediol	miscible	miscible	-1.38	[f]	3
550	1,5-pentanediol	miscible	miscible	-0.99	[f]	
560	diethyleneglycol	miscible	miscible	-1.98	[f]	5

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No.	Name	In water		Water in		log *P* O/W		Miscibility
570	triethyleneglycol	miscible		miscible		-2.08	[f]	6
580	glycerol	miscible		miscible		-2.56	[f]	1
590	phenol	1.78e-2	[a]	6.78e-1	[a]	1.49	[d]	
600	2-methylphenol	5.27e-3	[a]d			1.95	[f]	
610	3-methylphenol	4.27e-3	[a]d	4.84e-1	[b]	1.96	[d]	
620	4-methylphenol	3.84e-3	[a]d			1.94	[d]	14
630	2-methoxyphenol	3.6e-3	[h]			1.31	[f]	
640	2,4-dimethylphenol	1.17e-3	[a]			2.30	[g]	
650	3-chlorophenol	4.17e-3	[c]	6.05e-1	[c]	2.49	[d]	
660	diethyl ether	1.54e-2	[a]	5.76e-2	[a]	0.89	[d]	23
670	di-n-propyl ether	8.67e-4	[a]	2.50e-2	[a]	2.03	[d]	
680	di-i-propyl ether	2.14e-3	[a]a	3.15e-2	[a]a	2.03	[d]	26
690	di-n-butyl ether	4.15e-5	[a]a	1.36e-2	[a]a	3.21	[g]	26
700	di(2-chloroethyl) ether	1.30e-3	[a]a	8e-3	[a]a			20
710	1,2-dimethoxyethane	miscible		miscible				17
720	bis(methoxyethyl) ether	miscible		miscible				15, 17
730	furan	2.7e-3	[a]	1.1e-2	[a]			20
740	tetrahydrofuran	miscible		miscible		0.46	[d]	17
750	2-methyl tetrahydrofuran	3.26e-2	[a]	2.36e-1	[a]			
760	tetrahydropyran	1.79e-2	[a]	1.34e-1	[a]	0.95	[g]	
770	1,4-dioxane	miscible		miscible		-0.42	[f]	17
780	1,3-dioxolane	miscible		miscible				
790	1,8-cineole	4.10e-4	[a]a			2.11	[d]	20

800	anisole	1.75e-3	[a]			2.51	[d]	20
810	phenetole	1.77e-4	[a]			4.36	[f]	22
820	diphenyl ether	4.14e-4	[a]					
830	dibenzyl ether	3.6e-6	[a]c					
840	1,2-dimethoxybenzene	9.3e-2	[g]	9.6e-2	[g]	2.21	[d]	
850	trimethyl orthoformate							
860	trimethyl orthoacetate							
870	propionaldehyde	1.20e-1	[a]	3.25e-1	[a]	0.38	[f]	

continued overleaf

***Table 4.6** (continued)*

No.	Name	In Water		Water in		log *PO*/W		Miscibility
880	butyraldehyde	1.87e-2	[a]	1.10e-1	[a]	0.88	[d]	
890	benzaldehyde	5.1e-4	[a]a			1.48	[d]	15, 19
900	p-methoxybenzaldehyde							
910	cinnamaldehyde	1.9e-4						
920	acetone	miscible		miscible		-0.24	[d]	15, 17
930	2-butanone	7.31e-2	[a]a	3.08e-1	[a]a	0.29	[d]	17
940	2-pentanone	1.31e-2	[a]a	1.40e-1	[a]a	0.91	[d]	
950	methyl i-propyl ketone	1.343-2	[c]	1.12e-1	[c]	0.84	[g]	
960	3-pentanone	7.3e-3	[a]a	1.13e-1	[a]a	0.82	[g]	18
970	c-pentanone	6.54e-2	[d]			0.38	[g]	
980	methyl-i-butyl ketone	3.10e-3	[a]	9.72e-2	[a]	1.31	[g]	19
990	methyl t-butyl ketone	3.4e-3	[a]	9.8e-2		1.20	[g]	
1000	c-hexanone	4.3e-3	[a]a	3.21e-1	[a]a	0.81	[d]	17
1010	2-heptanone	6.81e-4	[a]	8.31e-2	[a]	1.98	[d]	
1020	3-heptanone	2.28e-3	[a]a	4.75e-2	[a]a			22
1030	di-t-butyl ketone					3.00	[g]	
1040	acetophenone	8.2e-4	[d]	1.04e-1	[e]	1.58	[d]	15, 18
1050	propiophenone	4.1e-4	[g]	4.9e-2	[g]	2.20	[d]	
1060	phenylacetone					1.44	[d]	
1070	p-methylacetophenone					2.19	[d]	
1080	p-chloroacetophenone					2.35	[d]	
1090	benzophenone(beta)					3.18	[f]	
1100	acetylacetone	3.46e-2	[a]a	2.08e-1	[a]a	2.14	[f]	12, 18

1110	biacetyl	8.6e-2	[g]	2.06-e1	[g]			12, 17
1120	formic acid	miscible		miscible		-0.54	[d]	5
1130	acetic acid	miscible		miscible		-0.24	[d]	14
1140	propanoic acid	miscible		miscible		0.32	[d]	15
1150	n-butanoic acid	miscible		miscible		0.86	[d]	16
1160	n-pentanoic acid	4.32e-3	[a]a	4.59e-1	[a]a	1.39	[d]	
1170	n-hexanoic acid	1.50e-3	[a]a			1.95	[d]	17

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No.	Name	In water		Water in		log P O/W		Miscibility
1180	n-heptanoic acid	3.05-e4	[c]					
1190	dichloroacetic acid	miscible		miscible		1.29	[f]	
1200	trifluoroacetic acid	miscible		miscible				12, 19
1210	acetic anhydride	reacts		reacts				12, 19
1220	benzoyl chloride	reacts		reacts				
1230	benzoyl bromide	reacts		reacts				
1240	methyl formate	8.2e-2	[a]			-0.26	[g]	14, 19
1250	ethyl formate	3.15e-2	[a]	4.57e-1	[a]a	0.27	[g]	15, 19
1260	methyl acetate	7.31e-2	[a]a	2.69e-1	[a]a	0.18	[d]	15, 17
1270	ethyl acetate	1.77e-2	[a]	1.29e-1	[a]	0.73	[d]	19
1280	propyl acetate	4.1e-3	[a]a	1.45e-1	[a]	1.24	[d]	19
1290	butyl acetate	1.06e-3	[a]a	7.3e-2	[a]a	1.82	[d]	22
1300	i-pentyl acetate	2.8e-4	[a]a	6.8e-2	[a]a	2.17	[g]	
1310	methyl propanoate	1.01e-3	[d]a			0.82	[g]	
1320	ethyl propanoate	3.44e-3	[a]a	6.54e-2	[a]a	1.21	[d]	21
1330	dimethyl carbonate	2.80e-2	[g]	1.30e-1	[g]			14, 19
1340	diethyl carbonate	2.77e-3	[g]	6.09e-2	[g]			21
1350	ethylene carbonate	miscible	d	miscible	d			6, 17
1360	propylene carbonate	3.61e-2	[a]	3.39e-1	[a]			9, 17
1370	diethyl malonate	3.1e-3	[a]a	<1.47e-1	[a]			
1380	methyl benzoate	2.78e-4	[a]a	5.33e-2	[a]a	2.16	[d]	
1390	ethyl benzoate	6e-5	[a]a	4e-2	[a]a	2.64	[d]	21
1400	dimethyl phthalate	3.7e-4	[d]			1.56	[g]	12, 19

1410	dibutyl phthalate	<6e-6	[a]a	6.7e-2	[a]a			22
1420	ethyl chloroacetate	2.93e-3	[g]	4.83e-2	[g]			
1430	ethyl trichloroacetate							21
1440	ethyl acetoacetate	1.85e-2	[a]	2.71e-1	[a]	1.23	[f]	13, 19
1450	4-butyrolactone	miscible		miscible		-0.64	[g]	10
1460	perfluoro-n-hexane							
1470	perfluoro-n-heptane							
1480	perfluoro-methylcyclohexane							

continued overleaf

Table 4.6 *(continued)*

No.	Name	In Water		Water in		log *PO*/W		Miscibility
1490	perfluoro-decalin							
1500	fluorobenzene	2.87e-4	[a]b	1.68e-3	[a]	2.27	[d]	20
1510	hexafluorobenzene					2.22	[f]	
1520	1-chlorobutane	2.1e-4	[a]a	4.1e-3	[a]a	2.64	[d]	23
1530	chlorobenzene	7.83e-5	[a]b	2.03e-3	[a]	2.84	[d]	21
1540	dichloromethane	2.79e-3	[a]	9.27e-3	[a]	1.15	[d]	20
1550	1,1-dichloroethane	9.55e-4	[a]a	5.25e-3	[a]	1.79	[g]	20
1560	1,2-dichloroethane	1.48e-3	[a]a	1.02e-2	[a]	1.63	[d]	20
1570	tr-1,2-dichloroethylene	1.18e-3	[a]	2.89e-2	[a]	2.09	[d]	21
1580	o-dichlorobenzene	1.91e-5	[a]	2.47e-2	[a]	3.28	[d]	21
1590	m-dichlorobenzene	1.36e-5	[a]a			3.48	[d]	
1600	chloroform	1.24e-3	[a]b	6.1e-3	[a]	1.94	[d]	19
1610	1,1,1-trichloroethane	1.78e-4	[a]a	2.51e-3	[a]	2.36	[d]	22
1620	1,1,2-trichloroethane	5.96e-4	[a]a	8.67e-3	[a]	1.89	[g]	19
1630	trichloroethylene	1.88e-4	[a]	2.29e-2	[a]	2.35	[d]	20
1640	1,2,4-trichlorobenzene					3.98	[d]	24
1650	tetrachloroethylene	9.05e-5	[a]	1.15e-3	[a]b	2.63	[d]	24
1660	tetrachloroethylene	1.63e-5	[a]	9.7e-4	[a]	2.88	[d]	25
1670	1,1,2,2-tetrachloroethane	3.09e-4	[a]a	1.02e-2	[a]	2.39	[d]	19
1680	pentachloroethane	4.5e-5	[a]	3.9e-3	[a]	3.20	[d]	
1690	1-bromobutane	8.0e-5	[a]b			2.75	[g]	23
1700	bromobenzene	5.12e-5	[a]b	3.68e-3	[a]	2.99	[d]	21
1710	dibromomethane	1.20e-3	[c]					19
1720	1,2-dibromomethane	4.13e-4	[a]b	7.35e-3	[a]	1.74	[g]	20

1730	bromoform	2.27e-4	[a]b					
1740	1-iodobutane	1.2e-5	[a]a			3.08	[g]	
1750	iodobenzene	3.00e-5	[a]b	3.12e-3	[a]	3.25	[d]	22
1760	diiodomethane	8.35e-5	[a]b			2.30	[g]	
1770	n-butylamine	miscible		miscible		0.86	[d]	
1780	benzylamine					1.09	[f]	

(table continued on next page)

(table continued from previous page)

No.	Name	In water		Water in		log *PO*/W		Miscibility
1790	1,2-diaminoethane	miscible		miscible				
1800	diethylamine	miscible		miscible		0.50	[d]	
1810	di-n-butylamine	6.6e-4	[a]a	3.22e-1	[a]a	2.75	[d]	
1820	pyrrole	1.25e-2	[a]			0.75	[f]	
1830	pyrrolidine	miscible		miscible				
1840	piperidine	miscible		miscible		0.85	[f]	
1850	morpholine	miscible		miscible		-1.08	[f]	14
1860	triethylamine	1.03e-2	[a]a	2.13e-1	[a]a	1.36	[d]	26
1870	tri-n-nutylamine	4e-6	[a]a	1.23e-2		1.52	[f]	28
1880	aniline	6.72e-3	[a]	2.05e-1	[a]	0.90	[d]	12
1890	o-chloroaniline	1.25e-3	[a]	3.8e-2	[a]a	1.91	[d]	
1900	N-methylaniline							
1910	N,N-dimethylaniline	1.64e-4	[d]	8.43e-2		2.28	[d]	
1920	ethanolamine	miscible		miscible		-1.31	[f]	2
1930	diethanolamine	7.8e-1	[a]a	miscible		-1.43	[f]	1
1940	triethanolamine	miscible		miscible		-1.75	[f]	2
1950	pyridine	miscible		miscible		0.65	[d]	16
1960	2-methylpyridine	miscible		miscible		1.06	[f]	16
1970	3-methylpyridine	miscible		miscible		1.20	[d]	
1980	4-methylpyridine	miscible		miscible		1.22	[d]	
1990	2,4-dimethylpyridine	miscible		miscible				
2000	2,6-dimethylpyridine	miscible		miscible				

2010	2,4,6-trimethylpyridine	4.53e-3	[c]	8.24e-1	[c]	1.72	[f]	
2020	2-bromopyridine					1.42	[f]	
2030	3-bromopyridine					1.60	[d]	
2040	2-cyanopyridine					0.50	[d]	
2050	pyrimidine	miscible		miscible		-0.40	[f]	
2060	quinoline	8.5e-4	[a]a			2.03	[d]	
2070	acetonitrile	miscible		miscible		-0.34	[d]	11,17
2080	propionitrile	3.62e-2	[a]			0.10	[d]	13,17
2090	butyronitrile	8.8e-3	[a]	2.3e-2	[ff]	0.53	[g]	14,19

continued overleaf

Table 4.6 *(continued)*

No.	Name	In water		Water in		log*P* *O*/W		Miscibility
2100	valeronitrile							
2110	acrylonitrile	2.62e-2	[a]b	8.61e-2	[a]b			
2120	benzyl cyanide					1.56	[d]	12, 19
2130	benzonitrile	3.5e-4	[a]	5e-2	[a]b	1.56	[d]	15, 19
2140	nitromethane	3.55e-2	[a]	6.74e-2	[a]	-0.34	[d]	10, 19
2150	nitroethane	1.16e-2	[a]	4.23e-2	[a]	0.18	[g]	13, 20
2160	1-nitropropane	3.07e-3	[a]	2.99e-2	[a]	0.18	[d]	
2170	2-nitropropane	3.51e-3	[a]	2.57e-2	[a]	0.87	[d]	15, 20
2180	nitrobenzene	2.78e-4	[a]a	1.62e-2	[a]a	1.85	[d]	14, 20
2190	formamide	miscible		miscible		-1.67	[f]	3
2200	N-methylformamide	miscible		miscible		-0.97	[g]	
2210	N,N-dimethylformamide	miscible		miscible		-1.01	[d]	12
2220	N,N-dimethylthioformamide							
2230	N,N-diethylformamide	miscible		miscible				
2240	N-methylacetamide	miscible		miscible		-1.05	[f]	
2250	N,N-dimethylacetamide	miscible		miscible		-0.77	[d]	13
2260	N,N-diethyl acetamide					0.34	[d]	14
2270	pyrrolidinone-2	miscible		miscible				10
2280	N-methylpyrrolidinone	miscible		miscible				13
2290	N-methylthipyrrolidinone							
2300	tetramethylurea	miscible		miscible				15
2310	tetraethylurea					1.79	[f]	
2320	dimethylcyanamide					0.18	[f]	

2330	carbon disulfide	4.98e-4	[a]a	6.00e-4	[a]			26
2340	dimethyl sulfide	5.9e-3	[a]	1.4e-2	[a]			
2350	diethyl sulfide	6.4e-4				1.95	[f]	
2360	di-i-propyl sulfide							
2370	di-n-butyl sulfide							26
2380	tetrahydrothiophene							21
2390	pentamethylene sulfide							

(table continued on next page)

(table continued from previous page)

No.	Name	In water		Water in		log*P* *O*/W		Miscibility
2400	dimethyl sulfoxide	miscible		miscible		-1.35	[d]	9
2410	di-n-butyl sulfoxide							
2420	sulfolane	miscible	b	miscible	b			9, 17
2430	thiobis(2-ethanol)	miscible		miscible				4
2440	diethyl sulfite					2.80	[g]	
2450	dimethyl sulfate	4.0e-3	[c]a					
2460	diethyl sulfate							12, 21
2470	methanesulfonic acid	miscible		miscible				
2480	trimethyl phosphate					-0.52	[f]	10
2490	triethyl phosphate					0.80	[g]	14
2500	tri-n-butyl phosphate	2.6e-5	[a]	4.2e-1	[a]			18
2510	hexamethyl phosphoramide	miscible		miscible		0.28	[f]	15
2530	hydrogen peroxide	miscible		miscible		-1.14	[f]	
2540	hydrogen fluoride					-0.44	[f]	
2550	sulfuric acid	miscible		miscible				
2560	ammonia	miscible		miscible		-1.49	[f]	
2570	hydrazine					-1.23	[f]	
2580	sulfur dioxide	reacts		reacts				
2590	thionyl chloride	reacts		reacts				
2600	phosphorus oxychloride	reacts		reacts				

Units: All the quantities are dimensionless.
References: [a] Riddick, Bunger and Sakano 1986. [b] Marcus 1977 [c] Stephen and Stephen 1963 [d] Taft *et al*. 1985, Kamlet *et al*. 1987 Kamlet *et al*. 1987 Kamlet *et al*. 1988 Abboud *et al*. 1998 [e] Kamlet *et al*. 1985 [f] Leo, Hansch and Elkins 1971 [g] Stephenson and Stuart 1986, Stephenson 1992 [h] Varhanickova, Shiu and Mackay 1995.

(see Chapter 1) will absorb water from the atmosphere. There is some correlation between the mutual solubility with water and the hygroscopicity of the solvents.

In a homologous series, in which the members differ from each other by the number of methylene groups, the solubility in water at a given temperature decreases by a constant factor of ca. 4 or 5 per methylene increment. This is the case without regard to the functional group at the end of the alkyl chain: -Ph, -OH, -C(O)Me, -COOH, -COOR, $-NH_2$, -CN, etc. Branching increases the aqueous solubility relative to the corresponding straight chain solvent.

The dependence of the mutual solubility with water on the temperature cannot be described by a simple expression, since it is the result of opposing effects. Many solvents experience a shallow minimum in the solubility near room temperature, but this is by no means a universal behaviour.

Hildebrand's solubility parameter $\delta = \{[\Delta_v H^o - RT]/V\}^{1/2}$ is a useful guide for the solubility of nonpolar solutes in nonpolar solvents, but a poor predictor for solubilities in water. In general, the more polar a solvent, or solute, the better it dissolves in water, but again, there is no clear relationship between any single polarity parameter, such as the dipole moment, μ, the relative permittivity, ε, the E_T^N polarity index, etc) and the solubility of a solvent in water. A multivariable relationship has been found to be successful for this purpose (Yalkowski, Pinal and Banerjee 1988; Cohen *et al*. 1993):

$$\log(s/\mathrm{mol\,dm^{-3}}) = 0.75 - 0.0642V_X + 1.59\alpha + 4.9\beta \qquad (4.34)$$

where V_X is the intrinsic volume shown in Table 3.4 and α and β are the solvatochromic hydrogen bond and electron pair donicities shown in Table 4.3. The larger the volume of the solvent molecules, the more work has to be done against the cohesive energy of the highly structured water, hence the smaller the solubility, but the better the hydrogen bonding and/or the electronpair donation abilities of the solvent molecules, the stronger are the interactions with water, hence the larger the solubility. The solubilities of solvents in water that are not shown in Table 4.6 can, therefore, be estimated from Eq. (4.34).

A solvent property that is closely related to the aqueous solubility is its hydrophobicity or lipophilicity. This is generally described by log *P*, the logarithm of the partition constant of the solvent as a solute at infinite dilution between 1-octanol and water, these two solvents being mutually saturated with each other. This system is said to represent the physiological conditions at biological membranes, the octanol, having both polar and nonpolar parts, playing the role of the membrane (Leo, Hansch and Elkins 1971). The values of log *P* are additive to a good extent in the constituting atoms, groups, and structural features i of the solute (in our case: solvent) molecules: $\log P = \Sigma n_i\pi_i$, where the n_i are their frequency of occurrence in the molecule and the π_i are their additive substituent constants. For a functional group X:

$$\pi_X = \log P(\mathrm{R-X}) - \log P(\mathrm{R-H}) \qquad (4.35)$$

with values listed in Table 4.7 for atoms or groups X substituting H on an alkyl or aryl skeleton. Corrections have to be applied for chain branching, -0.20, and for ring formation, -0.09. The distribution ratios depend on the temperature mildly, $d \log P/dT \sim 0.009\ \mathrm{K}^{-1}$, and the values of π_i are valid for 25°C.

Distribution ratios between other solvents than 1-octanol and water, or rather their logarithms, are linearly related to the log *P* values, so when these have not been determined directly, they can be obtained from those for the other solvents. In the cases of acidic or basic solvents that dissociate or associate with a proton in aqueous solutions a dilute buffer is used to keep the solvent molecules in their neutral form, and extrapolation to zero ionic strength should be applied in order to obtain accurate results. The log *P* data for the 1-octanol/water partition obtained either directly or indirectly by means of correlations with data for other

Table 4.7 Substituent Constants π for the Octanol/Water Partition Constants (Leo, Hansch and Elkins 1971)

Substituent	aliphatic	aliphatic and aromatic	aromatic
methyl, $-CH_3$		0.50	
methylene, $-CH_2$		0.50	
-CH (saturated)		0.50	
-CH (unsaturated)		0.35	
-C (saturated)		0.50	
-C (unsaturated)		0.35	
$-CH=CH_2$		0.70	
phenyl, $-C_6H_5$		2.13	
phenylene, $-C_6H_4$		2.13	
$-C_{63}$		2.13	
pyridyl, $-C_5H_4N$		0.65	
fluoro, -F	-0.17		0.13
chloro, -Cl	0.39		0.76
bromo, -Br	0.66		0.94
iodo, -I	1.00		1.15
thio, -S-	-0.05		1.12
oxo, -O-	-0.98		-0.52
hydroxy, -OH	-1.16		-0.67
methoxy, $-OCH_3$	-0.47		-0.02
keto, -C=O	-1.21		-1.05

carboxy, -C(O)O-	-0.77	-0.55
amino, $-NH_2$	-1.19	-1.23
nitro, $-NO_2$	-0.82	-0.28
amido, $-C(O)NH_2$	-1.71	-1.49
nitrilo, -C≡N	-0.84	-0.57
trifluoromethyl, $-CF_3$	0.88	

solvents, mostly taken from (Taft *et al*. 1985; Leo, Hansch and Elkins 1971), are shown in Table 4.6.

The more hydrophobia a solvent, i.e., the larger log P, the less is its solubility in water, log s, and in fact linear relationships have been obtained for these quantities. For 140 solvents of various classes (Hansch, Quinlan and Laurence 1968):

$$\log(s/\text{mol dm}^{-3}) = -1.214 \log P + 0.850 \qquad (4.36)$$

The fragment additive π_i values can therefore serve to estimate the solubility of solvents (and solutes in general) in water, with a standard error of ~ 30%, see Figure 4.6.

The mutual miscibility of solvents that does not involve water has been reported on an empirical basis by assigning to each solvent a miscibility number, on a scale of standard solvents ranging from 1 for the very hydrophilic glycerol to 31 for the very lipophilic petrolatum. If the miscibility numbers of two solvents differ by ≤ 15 they are probably miscible, whereas if they differ by ≥ 17 they are probably immiscible. Those that have a miscibility number of 16 ought to be miscible with all solvents, hence act as 'universal solvents'. The miscibility numbers are shown in Table 4.6, where, in the cases where two numbers are shown, the first pertains to miscibility with solvents of high lipophilicity and the second to miscibility with solvents of high hydrophilicity (Godfrey 1972).

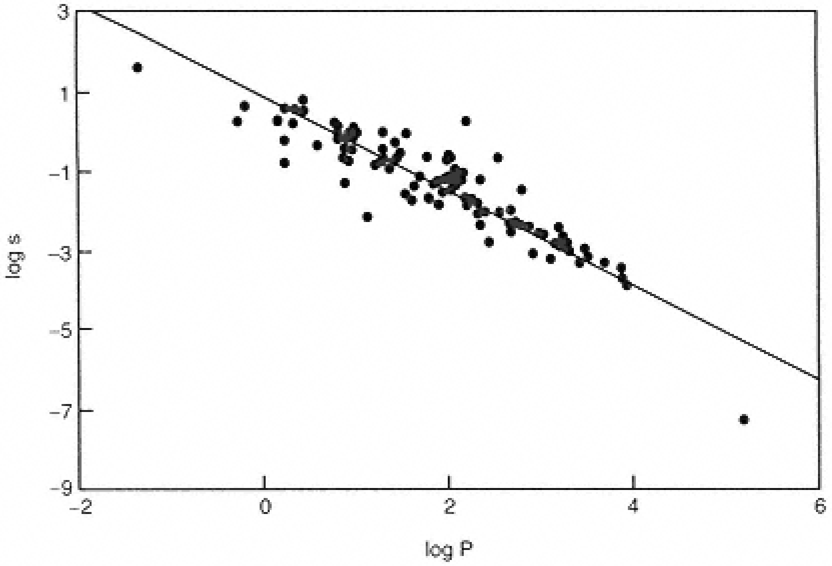

Figure 4.6
The correlation between the molar aqueous solubility of solvents $\log(s/\text{mol dm}^{-3})$, and the 1-octanol/water distribution ratio, log P

8—
Windows for Spectroscopy and Electrochemistry

Solvents may have properties that make them non-available for certain applications. Obviously, outside their liquid range they cannot be employed as liquid solvents, so that under ambient conditions, the freezing point and the normal boiling point constitute the 'temperature window' for the use of the solvents. These quantities are presented in Table 3.1 in K, but are repeated in Table 4.8 in °C for the sake of convenience. Solvents have normally such a high vapour pressure some 20° below the normal boiling point to make it inconvenient to use them at or above (t_b/°C) - 20, and a higher boiling solvent, possibly a higher homologue, is generally preferred. On the other hand, if a solvent is to be removed after its useful employment by evaporation or distillation, a low boiling solvent is to be chosen.

Solvents for spectroscopic use need to be transparent in the wavelength or wavenumber ranges where the desired spectral information is to be obtained. All liquids have an ultraviolet cutoff, meaning that at and below some wavelength in the ultraviolet they absorb so much of the UV light that they cannot be used as solvents for spectroscopic purposes in this range.

The common commercial instruments for UV spectroscopy in solutions themselves become ineffective at < 180 nm and require flushing by dry nitrogen to remove light-absorbing water vapour at < 220 nm. Therefore a cutoff at, say, 190 nm makes a solvent an excellent one from this point of view (provided, of course, that the solutes of interest are soluble in it). Table 4.8 provides the UV cutoff points of the solvents in the List, defined as the point where their absorbance in a 1.0 cm light-path-length cell against dry air is 1.0. The solvents do absorb at wavelengths above this cutoff, but the absorbance decreases steeply, to a value of, say, < 0.1 at 10–20 nm beyond the cutoff point. The values in Table 4.8, in nm, have been rounded to the nearest 5 nm (Reichardt 1988; Krieger 1984). The solvents in the List are generally colorless when pure or, if slightly yellowish, they exhibit a high UV cutoff, say 380 nm, hence they do not absorb light in the visible spectral range, 400–700 nm. Wavelengths beyond the cutoff point thus constitute the 'UV-visible windows' of the solvents.

However, all molecular solvents have strong absorption bands in the infrared range, so that they can be used as solvents for spectroscopic purposes in this range only at wavenumbers exterior to these intense bands. The IR range normally used in commercial instruments with organic solvents, whether FTIR or not, is from 625–5000 cm^{-1} (16–2 μm), since outside this range special windows are required and mulls or salt pellets or disks are employed instead of solutions in liquid solvents. Even so, rather thin layers of the solutions, 0.1 mm, are generally used. The useful 'IR windows' for the solvents under conditions where the transmittance for infrared light is at least about 70%, (Sadtler 1983; Reichardt 1988), are shown in Table 4.8. These IR-transparent windows are

Table 4.8 The temperature, UV, infrared, and potential windows in which solvents can be used

No.	Name	Liquid range		Spectroscopic windows		Electrochemical windows				
		t_m	t_b	UV	IR	Work Elec.	Ref. Elec.	Electrolyte	Range	Ref.
10	tetramethylsilane	-99.1	26.6							
20	n-pentane	-129.8	36.0	200	< 1350, 1500–2800, > 3000					
30	2-methylbutane	-159.9	27.8		< 1350, 1500–2800, > 3000					
40	n-hexane	-95.4	68.7	200	780–1330, 1500–2600, > 3000					
50	c-hexane	6.7	80.7	195	< 850, 900 –1430, 1470–2800					
60	n-heptane	-90.6	98.4	195	< 1370, 1460–2700, > 3000					
70	n-octane	-56.8	125.6		< 1370, 1460–2700, > 3000					
80	2,2,4-trimethylpentane	-107.4	99.2	205	700–1180, 1500–2700, > 2900					
90	n-decane	-29.7	174.1		730–1380, 1500–2800, > 3030					
100	n-dodecane	-9.6	216.3		730–1380, 1500–2800, > 3030					
110	n-hexadecane	17.8	286.8	190	< 880, 1660–2660, > 3100					
120	benzene	5.5	80.0	280	740–1000, 1050–1470, > 1550					
130	toluene	-95.0	110.6	285	780–1400, 1500–2800, > 3000					
140	o-xylene	-25.2	144.4	290	780–1020, 1050–1430,					
150	m-xylene	-47.9	139.1	290	800–1300, 1500–2700, > 3000					

(table continued from previous page)

No.	Name	Liquid range		Spectroscopic windows		Electrochemical windows				
		t_m	t_b	UV	IR	Work Elec.	Ref. Elec.	Electrolyte	Range	Ref.
170	ethylbenzene	-95.0	136.1		800–1430, 1520–2800, > 3100					
180	cumene	-96.1	152.4		1620–2820, > 3100					
190	mesitylene	-44.8	164.7		850–1370, 1650–2820, > 3020					
200	styrene	-30.7	145.1							
210	tetralin	-35.8	207.6							
220	cis-decalin	-43.1	195.7	200	< 1420, 1470–2800, > 3000					
230	water	0.0	100.0	190		C[Hg]	SCE	$HClO_4$ [Et4NOH]	+1.4--2.3	[a]
240	methanol	-97.7	64.5	205	1520–2760, > 3600	DME	Hg pool	Et4NBr	-2.2	[b]
250	ethanol	-114.5	78.2	205	1500–2800, > 3600	DME	Ag/Ag(I)	$LiClO_4$		[b]
260	n-propanol	-126.2	97.1	210	1460–2800, > 3400					
270	i-propanol	-88.0	82.2	210	1540–2600, > 3500					
280	n-butanol	-88.7	177.6	205	1480–2820, > 3500					
290	i-butanol	-108.2	107.8	220	1500–2800					
300	2-butanol	-114.7	99.5	260	1420–2800					
310	t-butanol	25.6	82.3	215	1500–2840					
320	n-pentanol	-78.2	137.9		1500–2800					
330	i-pentanol	-117.2	128.7	215	1500–2800					
340	t-pentanol	-8.8	102.0		1500–2800					
350	n-hexanol	-44.6	157.0		1460–2800					

360	c-hexanol	25.1	161.1		1440–2800
370	n-octanol	-15.0	195.1	215	2500–2750
380	n-decanol	6.8	228.8		
390	n-dodecanol	25.8	258.8		
400	benzyl alcohol	-15.3	205.4		1500–2800
410	2-phenylethanol	-27.2	218.8		
420	allyl alcohol	-129.2	96.8		1500–2600
430	2-chloroethanol	-67.5	128.6		1480–2800
440	2-cyanoethanol	-46.2	219.8		630–1020, 1460–2220, 2240–2860
450	2,2,2-trifluoroethanol.	-43.5	74.0	190	

continued overleaf

Table 4.8 *(continued)*

No.	Name	Liquid range		Spectroscopic windows		Electrochemical windows				
		t_m	t_b	UV	IR	Work Elec.	Ref. Elec.	Electrolyte	Range	Ref.
460	hexafluoro-i-propanol	-10.0	58.0							
470	2-methoxyethanol	-85.1	124.6	210	< 820, 1460–2800					
480	2-ethoxyethanol		135.6	210	1460–2660					
490	1,2-ethanediol	-66.6	197.5		1500–2600	DME	BBCr	Bu_4NClO_4	+1.2--1.0	[e]
500	1,2-propanediol	-60.2	187.6		1500–2600					
510	1,3-propanediol	-26.7	214.4		1500–2600					
520	1,2-butanediol		193.8							
530	2,3-butanediol (meso)	7.6	176.7							
540	1,4-butanediol	34.4	182.3							
550	1,5-pentanediol	-15.6	242.4							
560	diethyleneglycol	-7.8	245.6		1460–2600					
570	triethyleneglycol	-4.3	288.0							
580	glycerol	18.1	290.0	205	1500–2700, > 3600	DME	Ag/Ag(I)	LiCl		[b]
590	phenol	40.9	181.8		1640–3000					
600	2-methylphenol	30.9	191.0		1640–2900					
610	3-methylphenol	12.2	202.2		1640–2840					
620	4-methylphenol	34.7	201.9		1640–2840					
630	2-methoxyphenol	28.6	205.0							
640	2,4-dimethylphenol	24.5	210.9							
650	3-chlorophenol	32.8	215.8							
660	diethyl ether	-116.3	34.4	215	1080,1450–2760,		Ag/Ag(I)		+1.3--0.6	[b]

					> 3000			$LiAlcl_4$		
670	di-n-propyl ehter	-123.2	90.0		1000,1460–2780, > 3000					
680	di-i-propyl ether	-85.5	68.5		< 980, 1480–2800, > 3000					
690	di-n-butyl ether	-95.2	140.2	210						
700	di(2-chloroethyl)ether	-46.8	178.7		1470–2820, > 3000					
710	1,2-dimethoxyethane	-69.2	84.5	220	< 830, 1500–2800, > 3000	Hg/Pt	Ag/Ag(I)	Bu_4NPF_6	+0.9--3.6	[b]

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No.	Name	Liquid range		Spectroscopic windows		Electrochemical windows				
		t_m	t_b	UV	IR	Work Elec.	Ref. Elec.	Electrolyte	Range	Ref.
720	bis(methoxyethyl) ether	-64.0	159.7	220	< 1070, 1200–2800, > 3000					
730	furan	-85.7	31.3		> 1600					
740	tetrahydrofuran	-108.4	65.9	220	< 850, 1200–2780, > 3040	Pt	Ag/Ag(I)	$LiClO_4$	+1.8--3.6	[b]
750	2-methyl tetrahydrofuran	-137.2	79.9							
760	tetrahydropyran	-45.2	87.8		< 820, 1480–2700, > 3000					
770	dioxlane	11.8	74.3	220	700–850, 920–1000, 1500–2700	DME		Hg pool		-2.3
780	dioxolane	-97.3	75.6		1460–2700, > 3000					
790	1,8-cineole	0.8	173.8		< 960, 1460–2820, > 3000					
800	anisole	-37.5	153.6		1640–2820, > 3100					
810	phenetole	-29.6	169.8		1640–2820, > 3100					
820	diphenyl ether	26.8	258.0		1600–3000, > 3100					
830	dibenyl ether	3.6	288.3		1500–2800, > 3100					
840	1,2-dimethoxybenzene	22.5	206.2		1640–2820, > 3100					
850	trimethyl orthoformate		101.8							
860	trimethyl orthoacetate		108.8							
870	propionaldehyde	-80.2	48.0		< 830, 1760–2560, > 3000					
880	butyraldehyde	-96.4	74.8		1760–2560, > 3000					
890	benzaldehyde	-55.6	178.7		1800–2700, > 3100					

900	p-methoxybenzaldehyde	2.5	249.5							
910	cinnamaldehyde	-7.5	252.8							
920	acetone	-94.7	56.0	330	700–1050, 1800–3000	DME	SCE	$\mathrm{N_aclo_4}$ [Et4NPF6]	+1.6-.4	[b]
930	2-butanone	-86.7	79.5	330	< 1150, 1740–2840					
940	2-pentagon	-76.9	102.2	330	<1150, 1740 –2800					
950	methyl i-propyl ketone	-92.2	94.8							
960	3-pentanone	-39.0	101.9	330	<920, 1760–2800					
970	c-pentanone				1800–2800	51.3		130.7	1800–2800	
980	methyl-i-butyl ketone	-84.2	117.4	335						

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Table 4.8 *(continued)*

No.	Name	Liquid range		Spectroscopic windows		Electrochemical windows				
		t_m	t_b	UV	IR	Work Elec.	Ref. Elec.	Electrolyte	Range	Ref.
990	methyl t-butyl ketone	-52.5	105.8		< 1150, 1750–2820, > 3000					
1000	c-hexanone	-32.1	155.6		1750–2800, > 3000					
1010	2-heptanone				< 1350, 1750–2820, 3000					
1020	3-heptanone	-39.0	147.4		< 1350, 1750–2820, > 3000					
1030	di-t-butyl ketone		150.8							
1040	acetophenone	19.6	202.0		> 1720					
1050	propiophenone	-18.6	217.8							
1060	phenylacetone	26.8	216.5							
1070	p-methylacetophenone	27.8	225.8							
1080	p-chloroacetophenone	18.4	272.8							
1090	benzophenone(beta)	25.8	305.9							
1100	acetylacetone	-23.2	138.3		< 1200, > 1750					
1110	biacetyl	-2.4	89.8							
1120	formic acid	8.2	100.5		870–1120, 1700–2460	DME	SCE	NaOOCH	+0.2--0.8	[b]
1130	acetic acid	16.6	117.8		1800–2450	Pt	SCE	$NaClO_4$	+2.0--1.7	[b]
1140	propanoic acid	-20.7	141.1							
1150	n-butanoic acid	-5.2	163.7							
1160	n-pentanoic acid	-33.7	185.5		1760–2500					
1170	n-hexanoic acid	-3.5	205.0		< 970, 1740–2500					

1180	n-heptanoic acid	-10.2	222.8							
1190	dichloroacetic acid	10.8	192.8							
1200	trifluoroacetic acid	-15.3	71.7		< 1100, 1270–1720, 1830–2900	Au	Ag/Ag(I)	$NaClO_4$	+2.1--0.9	[c]
1210	acetic anhydride	-73.1	140.0		< 970, > 1960	Pt	Ag/Ag(I)	$LiClO_4$	+2.1--1.1	[b]
1220	benzoyl chloride	-1.2	96.8							
1230	benzoyl bromide	-24.2	218.8							
1240	methyl formate	-99.0	31.7	260	< 1160, 1220–1670,	>1760				

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No.	Name	Liquid range		Spectroscopic windows		Electrochemical windows				
		t_m	t_b	UV	IR	Work Elec.	Ref. Elec.	Electrolyte	Range	Ref.
1250	ethyl formate	-79.6	54.3		870–950, 1800–2800, > 3000					
1260	methyl acetate	-98.1	56.8		1800–2900, > 3050					
1270	ethyl acetate	-83.6	77.1	255	700–770, 1800–2800, > 3000					
1280	propyl acetate	-95.0	101.5							
1290	butyl acetate	-73.5	126.0	255	1800–2800, > 3000					
1300	i-pentyl acetate	-78.5	142.1							
1310	methyl propanoate	-87.5	78.7							
1320	ethyl propanoate	-73.9	99.1		< 1020, 1500–1680,					
1330	dimethyl carbonate	-1.2	89.8							
1340	diethyl carbonate	-43.0	126.8	255	< 780, 1500–1700, 1770–2900					
1350	ethylene carbonate	36.3	248.2		< 700, > 1880					
1360	propylene carbonate	-55.0	241.7	280		Pt	SCE	Et_4NPF_6	+1.7 --1.9	[b]
1370	diethyl malonate	-48.9	199.3		< 1000, 1400–1700, 1780–2900					
1380	methyl benzoate	-12.1	199.5		1750–2920, > 3030					
1390	ethyl benzoate	-34.7	212.4		1750–2920, > 3080					
1400	dimethyl phthalate		284.8		< 700, 1720–2900					
1410	dibutyl phthalate	-35.2	340.0		< 700, 1720–2900					
1420	ethyl chloroacetate	-26.2	143.8		< 760, 1430–1700, 1800–2900					

1430	ethyl trichloroacetate		167.8						
1440	ethyl acetoacetate	-39.2	180.8	< 1000, 1760–2900					
1450	4-butyrolactone	-43.4	203.8	1500–1700, 1880–2880	DME	BBCr	Bu_4NClO_4	+1.4 --2.1	[e]
1460	perfluoro-n-hexane	-86.0	58.0						
1470	perfluoro-n-heptane	-51.0	82.5						
1480	perfluoro-methyl-cyclohexane	-38.0	76.0						
1490	perfluoro-decalin	-11.2	142.0						
1500	fluorobenzene	-42.3	84.7	1620–3030, > 3100					
1510	hexafluorobenzene	5.1	80.2	< 970, 1060–1380, > 1600					

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***Table 4.8** (continued)*

No.	Name	Liquid range		Spectroscopic windows		Electrochemical windows				
		t_m	t_b	UV	IR	Work Elec.	Ref. Elec.	Electrolyte	Range	Ref.
1520	1-chlorobutane	-123.1	78.4	220	1480–2820, > 3000					
1530	chlorobenzene	-45.6	131.6	285	< 670, 1130–1430, > 1580					
1540	dichloromethane	-95.0	39.6	230	800–1200, > 1300	Pt	SCE	Bu_4NPF_6	+1.8--1.7	[b]
1550	1,1-dichloroethane	-97.0	57.3		720–960, > 1450	Pt	SCE	Bu_4NClO_4	+1.7--1.8	[d]
1560	1,2-dichloroethane	-35.7	83.4	230	780–1200, > 1500	DME		neutral	+0.4--2.6	[c]
1570	tr-1,2-dichloroethylene	-49.8	47.6	230						
1580	o-dichlorobenzene	-17.1	180.4	295						
1590	m-dichlorobenzene	-24.8	173.0							
1600	chloroform	-63.6	61.1	245	800–1200, > 1300					
1610	1,1,1-trichloroethane	-30.4	74.0		> 1460					
1620	1,1,2-trichloroethane	-36.6	113.8							
1630	trichloroethylene	-86.4	87.1	275						
1640	1,2,4-trichlorobenzene	16.9	213.5	310						
1650	tetrachloromethane	-22.9	76.6	260	> 800					
1660	tetrachloroethylene	-22.4	121.0	290	> 940					
1670	1,1,2,2-tetrachloroethane	-43.8	145.1							
1680	pentachloroethane	-29.0	159.8							
1690	1-bromobutane	-112.4	101.6		750–1200, 1460–2850, > 3000					
1700	bromobenzene	-30.9	155.9							
1710	dibromomethane	-52.2	96.8							

1720	1,2-dibromoethane	9.7	131.3		< 1170, > 1440
1730	bromoform	8.0	149.2	330	780–1100, > 1200
1740	1-iodobutane	-103.0	130.5		
1750	iodobenzene	-31.4	188.3		
1760	diiodomethane	6.1	181.8		720–1080, 1130–3050
1770	n-butylamine	-49.1	77.0		< 730, 920–1370, 1660–2800
1780	benzylamine	10.0	184.8		

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No.	Name	Liquid range		Spectroscopic windows		Electrochemical windows				
		t_m	t_b	UV	IR	Work Elec.	Ref. Elec.	Electrolyte	Range	Ref.
1790	1,2-diaminoethane	11.3	116.9		1700–2560	DME	NCE	Bu_4NI	--1.3	[b]
1800	diethylamine	-49.8	55.5		750–1120, 1470–2620, > 3000					
1810	di-n-butylamine	-62.2	159.6		< 1120, 1470–2620, > 2980					
1820	pyrrole	-23.5	129.7		1600–3100, > 3500					
1830	pyrrolidine	-57.9	86.5							
1840	piperidine	-10.5	106.2		1470–2500					
1850	morpholine	-4.8	128.9		1450–2620, > 2980	DME	NCE	Bu_4NI	-0.6--3.0	[b]
1860	triethylamine	-114.7	88.8		< 1050, 1480–2620, > 3000					
1870	tri-n-butylamine	-70.0	214.0							
1880	aniline	-6.0	184.4		1650–3000					
1890	o-chloroaniline	-2.0	208.8		1670–3000					
1900	N-methylaniline	-57.2	196.2							
1910	N,N-dimethylaniline	2.4	194.0							
1920	ethanolamine	10.5	170.9		1630–2400					
1930	diethanolamine	27.9	268.3		1480–2440					
1940	triethanolamine	21.5	335.3		1500–2500					
1950	pyridine	-41.6	115.2	305	800–970	C[DME]	Ag/Ag(1) [H	$LiClO_4$	+1.4 -	[b]
1960	2-methylpyridine	-66.8	129.4		1600–2900, > 3100					
1970	3-methylpyridine	-18.1	144.1		1600–2900, > 3100					

1980	4-methylpyridine	3.6	145.3							
1990	2,4-dimethylpyridine	-64.0	158.4							
2000	2,6-dimethylpyridine	-6.1	144.0							
2010	2,4,6-trimethylpyridine	-44.2	171.0							
2020	2-bromopyridine		193.8							
2030	3-bromopyridine		169.8							
2040	2-cyanopyridine	27.8								
2050	pyrimidine		21.8							
2060	quinoline	-14.9	237.1		1630–2980, > 3100					
2070	acetonitrile	-43.9	81.6	195	< 1050, 1500–2220, > 2240	Pt	Ag/Ag(1)	NaClO$_4$	+2.4--2.0	[b]
2080	propionitrile	-92.8	97.3		1500–2220, 2240–2820, > 3100	DME	BBCr	Bu$_4$NClO$_4$	+1.2--1.9	[e]

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***Table 4.8** (continued)*

No.	Name	Liquid range		Spectroscopic windows		Electrochemical windows				
		t_m	t_b	UV	IR	Work Elec.	Ref. Elec.	Electrolyte	Range	Ref.
2090	butyronitrile	-111.9	117.6			DME	SCE	$LiCIO_4$ (isobutyro)	=0.6--2.8	[b]
2100	valeronitrile	-96.2	141.3							
2110	acrylonitrile	-83.6	77.3							
2120	benzyl cyanide	-23.8	233.5		< 680, 720–1400, 1500–2200,> 2300	DME	BBCr	Bu_4NCIO_4	+1.4--1.8	[e]
2130	benzonitrile	-12.8	191.1	300	760–1480, 1500–2200	Pt	SCE	Bu_4NCIO_4	+1.8--1.9	[d]
2140	nitromethane	-28.6	101.2	280	670–1350, > 1620	Pt	SCE	$LiCIO_4$	+0.9--2.6	[b]
2150	nitroethane	-89.6	114.0		630–1080, 1620–2830, >3020					
2160	1-nitropropane	-104.0	131.1		< 1300, 1600–2830, >3000					
2170	2-nitropropane	-91.4	120.2		< 1090, 1600–2860, >3020					
2180	nitrobenzene	5.7	210.8		1630–3060, > 3120	DME	BBCr	Bu_4NCIO_4	+1.6--0.2	[e]
2190	formamide	2.5	210.5		790–1200, 1750–3040	DME	BBCr	Bu_4NCIO_4	+1.0--0.5	[e]
2200	N-methylformamide	-3.8	199.5			DME	BBCr	Et_4NCIO_4	+1.1--2.0	[e]
2210	N,N-dimethylformamide	-60.5	153.0	270	740–950, 1800–2700 Pt		SCE	Et_4NPF6	+1.6--2.1	[b]
2220	N,N-dimethylthioformamide	-8.5				DME	BBCr	Bu_4NCIO_4	+0.3--1.5	[e]
2230	N,N-diethylformamide		177.8			DME	BBCr	Bu_4NCIO_4	+1.0--1.9	[e]
2240	N-methylacetamide	30.5	205.8		760–1270, 1700–2840	DME	Hg pool	Et_4NPF_6	+0.3--2.7	[b]
2250	N,N-dimethylacetamide	-20.2	166.1	270	610–980, 1760–2800	DME	BBCr	Bu_4NCIO_4	+1.1--2.2	[e]

2260	N,N-diethyl acetamide		185.8			DME	BBCr	Bu_4NCIO_4	+1.1--2.3	[e]
2270	pyrrolidinone-2	24.8	244.8		1740–2820					
2280	N-methylpyrrolidinone	-24.4	201.8	260		Pt	$Hg/Hg_2(I)$	$LiCIO_4$	+1.2--3.9	[e]
2290	N-methylthiopyrrolidinone	-19.3			< 1120, 1140–1340, 1680–2840	DME	BBCr	Bu_4NCIO_4	-0.4--1.6	[e]
2300	tetramethylurea	-1.2	175.2			DME	SCE	$NaNO_3$	+0.3--1.8	[b]
2310	tetraethylurea	-20.2	214.8							
2320	dimethylcyanamide		163.5							

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No.	Name	Liquid range		Spectroscopic windows		Electrochemical windows				
		t_m	t_b	UV	IR	Work Elec.	Ref. Elec.	Electrolyte	Range	Ref.
2330	carbon disulfide	-111.6	46.2	380	< 1300, 2200–2800					
2340	dimethyl sulfide	-98.3	37.3		< 960, 1040–1400, 1460–2820					
2350	diethyl sulfide	-104.0	92.1		< 1230, 1460–2820, > 3000					
2360	di-i-propyl sulfide	-78.1	120.4							
2370	di-n-butyl sulfide	-75.1	188.9							
2380	tetrahydrothiophene	-96.2	120.9		1440–2820, > 3000	DME	BBCr	Bu_4NCIO_4	+0.7--0.8	[e]
2390	pentamethylene sulfide	18.8	141.8							
2400	dimethyl sulfoxide	18.5	189.0	265	< 940, 1090–1400, 1450–2900	DME	SCE	Et_4NCIO_4	-0.4--2.8	[a]
2410	di-n-butyl sulfoxide	31.8								
2420	sulfolane	28.4	287.3		1450–2850	DME	Ag/Ag(I)	$NaCIO_4$	+1.2--2.3	[b]
2430	thiobis(2-ethanol)	-10.2	281.8		1470–2800	DME	BBCr	Bu_4NCIO_4	+0.9--1.3	[e]
2440	diethyl sulfite									
2450	dimethyl sulfate	-13.8	188.5							
2460	diethyl sulfate	-24.5	207.8							
2470	methanesulfonic acid	19.7	288.0							
2480	trimethyl phosphate	-46.1	197.2			DME	BBCr	Et_4NCIO_4	+1.2--1.4	[e]
2490	triethyl phosphate		215.8							
2500	tri-n-butyl phosphate	-193.0	288.8		1500–2840, > 3000					
2510	hexamethyl phosphoramide	72.0	232.8			DME	Ag/Ag(I)	$NaCIO_4$	+0.7--2.4	[b]

2520	hexamethylthiophos. amide thiophosphoramide	29.0		DME	BBCr	Bu_4NCIO_4	+0.5--2.2	[e]
2530	hydrogen peroxide	-0.5						
2540	hydrogen fluoride	-84.0	19.5					
2550	sulfuric acid	10.3	336.8					
2560	ammonia	-77.8	-33.5	Pt	Ag/Ag(I)	KI	+0.5--2.3	[c]
2570	hydrazine	1.5	113.5					
2580	sulfur dioxide	-73.2	-10.1	Pt	Ag/Ag(I)			[b]
2590	thionyl chloride	-101.2	75.6					
2600	phosphorus oxychloride	-29.9	105.5					

Units: t_m and t_b in °C; UV cutoff in nm; IR windows in cm^{-1}; potential range in V.
References: [a] Sawyer and Roberts, 1974 [b] Mann 1969 [c] Badoz-Lambling and Cauquis 1974 [d] Kadish and Anderson 1987 [e] Gritzner 1990

'framed' by prominent absorption bands, which may be rather narrow or quite broad. Since the functional groups have characteristic, more or less invariant, absorption bands, not all the homologues have their windows recorded in Table 4.8. Often more than one IR-window is available, and solvents can generally be selected for IR spectroscopy that have the required transparency for any solute that is soluble in them.

For electrochemical work it is important to know the limiting potentials that may be applied in oxidative, anodic, or reductive, cathodic, scans of solutions in which solutes can undergo redox reactions without the solvent being oxidized or reduced. These limits constitute the 'electrochemical window' for the solvent. However, the breadth of this window, in terms of the applicable voltages, depends not only on the solvent itself, but also on the material of the working electrode involved, the reference electrode against which the potentials are measured, and the nature of the supporting electrolyte present.

This electrolyte provides the required conductivity to the solution, but its ions may themselves undergo redox reactions before the solvent does. The choice of the supporting electrolyte, in turn, depends not only on the resistance of its ions to being reduced or oxidized but also on its solubility in the solvent in question. Tetraalkylammonium ions are generally the preferred cations, otherwise alkali metal ions such as lithium or sodium may be employed, and perchlorate or hexafluorophosphate are commonly the anions of choice.

The aqueous saturated calomel electrode (SCE) is generally employed as the reference electrode though in a few cases as the normal calomel electrode (NCE), connected to the solution in the non-aqueous solvent by means of a salt bridge involving the latter solvent, in order to avoid contamination of the solution to be studied with water. Otherwise, an Ag/Ag^+ or an Hg/Hg_2^{2+} electrode or an inert electrode with the bis(biphenyl)chromium(I)/(0) redox couple (BBCr) directly in the non-aqueous solution, or a mercury pool, in combination with a dropping mercury electrode (DME) as the working electrode, are employed as the reference electrode. In order to compare different solvents, however, it is necessary to consider the quoted potentials against a common reference electrode eg, the SHE: standard hydrogen electrode. Either the junction potentials, when an external aqueous SCE with a salt bridge is used, or the transfer activity coefficient of such ions as Ag^+ or Hg_2^{2+} must then be taken into account, the latter having been reported in (Marcus 1997) for many solvents on the List employed for electrochemical purposes. As the working electrode, a DME or a platinized, black platinum electrode is generally used, but gold or graphite, glassy or pyrolytic carbon are also employed.

It turns out that water has an overall rather narrow electrochemical window :~ 3.5 V, compared with ~ 4.5 V for solvents such as nitromethane and dimethylsulfoxide, ~ 5 V for acetonitrile, and ~ 6 V for propylene carbonate. More positive potentials than in water i.e., stronger oxidizing agents, can be applied, for instance, in nitromethane, acetonitrile, propylene carbonate, and acetic acid, and more negative ones i.e., stronger reducing agents, in N,N-dimethylformamide, dimethylsulfoxide, propylene carbonate, acetonitrile, liquid ammonia, hexamethyl phosphoramide, tetrahydrofuran, and other ethers.

In view of the multitude of combinations of working electrode, reference electrode, and supporting electrolyte that can be successfully used in non-aqueous solvents for electrochemical work, it is impossible to present the 'electrochemical window' with all this information in a single table comprising all the solvents of interest. Instead, Table 4.8 shows a selection of combinations, which strives to show the widest 'electrochemical window' that has been reported. This is not to exclude other combinations for use where either the cathodic or the anodic limit beyond those reported in Table 4.8 has to be preferred. Even between the stated limits given in V in the column 'range' other combinations can work as well as those shown, so that the purpose of the entries in Table 4.8 is illustrative rather than exhaustive. In a few cases more than one example of the working electrode, reference electrode, and/or supporting electrolyte are given, since no single combination is useful for both the anodic and the cathodic side, and then the second example is placed in square brackets [].

References

Abboud, J.L.-M., Mo, O., DePaz, J. J. G. *et al*. (1993) *J. Am. Chem. Soc*. **115**, 12468.

Abboud, J.-L. M. and Notario, R. (1997) *Critical Compilation of Scales of Solvent Effects*, report to IUPAC Commission on Phys. Org. Chem., private communication.

Abraham, M. H., Buist, G. J., Grellier, P. L., McGill, R. A., Prior, D. V., Oliver, P. S., Turner, E., Morris, J. J., Taylor, P. J., Nicolet, P., Maria, P.-C., Gal, J.-F., Abboud, J.-L. M., Doherty, R. M., Kamlet, M. J., Shuely, W. J. and Taft, R. W. (1989) *J. Phys. Org. Chem*. **2**, 540, 661.

Aider, J., Haycock, E. W., Hildebrand, J. H. and Watts, H. (1954) *J. Chem. Phys*. **22**, 1060.

Allen, G., Gee, G. and Wilson. G. J. (1960) *Polymer* **1**, 456.

Azzaro, M., Gal, J.-F., Geribaldi, S. and Luopi, A. (1982) *J. Org. Chem*. **47**, 4981.

Badoz-Lambling, J. and Cauquis, G. (1974) in H. W. Nürnberg, (ed), *Advances in Analytical Chemistry and Instrumentation* Wiley, London, Vol. 10 *Electroanalytical Chemistry*, Chapter 5.

Bartmess, J. E., Scott, J. A. and McIver, R. T., Jr. (1979) *J. Am. Chem. Soc*. **101**, 6046.

Barton, A. F. M. (1983) *Handbook of Solubility Parameters and other Cohesion Parameters*, CRC Press, Boca Raton, FL, p. 118.

Bekarek, V. (1981) *J. Phys. Chem*. **85**, 722; Stolarova, M., Buchtova, M. and Bekarek, V. (1984) *Acta Univ. Palac. Olom*. **79**, 77.

Bennetto, H. P. and Caldin, E. F. (1971) *J. Chem. Soc. A* 2191.

Berthelot, M., Gal, J.-F., Laurence, C. and Maria, P.-C. (1984) *J. Chem. Phys*. **81**, 327.

Biggs, A. I. (1956) *Trans. Faraday Soc*. **52**, 35.

Catalan, J., Diaz, C., Lopez, V., Perez, P., de Paz, J.-L. G. and Rodriguez, J. G. (1996) *Liebigs Ann*.

1785.

Cohen, S., Marcus, Y., Migron, Y., Dikstein, S. and Shafran, A. (1993) *J. Chem. Soc., Faraday Trans*. **89**, 3271.

Cumming, J. B. and Kebarle, P. (1978) *Can. J. Chem*. **56**, 1.

Dack, M. R. J. (1975) *Chem. Soc. Rev*. **4**, 211; (1975) *Aust. J. Chem*. **28**, 1643.

Decouzon, O., Exner, O., Gal, J,-F., Maria, P.-C. and Waisser, K. (1994) *J. Phys. Org. Chem*. **7**, 511.

Deno, N. C. and Turner, J. O. (1966) *J. Org. Chem*. **31**, 1969.

Dimroth, K., Reichardt, C., Siepmann, T. and Bohlmann, F. (1966) *Liebigs Ann. Chem*. **661**, 1.

DIPPR (1997) *The DIPPR Pure Component Data Compilation*, Technical Database Services, Inc., New York, version 12.4 (for Windows).

Elias, H., Dreher, M., Neitzel, S. and Volz, H. (1982) *Z. Naturforsch*. **37B**, 684.

Ernst, Z. L. and Herring, F. G. (1965) *Trans. Faraday Soc*. **61**, 454.

Ford, G. P. and Scribner, J. D. (1983) *J. Comput. Chem*. **4**, 594.

Frenna, V., Vivona, N., Consiglo, G. and Spinelli, D. (1985) *J. Chem. Soc. Perkin Trans 2*, 1865.

Gasteiger, J. and Hutchings, M. G. (1984) *J. Am. Chem. Soc*. **106**, 6489.

Godfrey, N. B. (1972) *Chem. Technol*. **2**, 359.

Gonçalves, R. M. C., Simões, A. M. N., Albuquerque, L. M. P. C., Rosés, M., Rafols, C. and Bosch, E. (1993) *J. Chem. Res. (S)* 214.

Graul, S. T., Schnute, M. E. and Squires, R. R. (1990) *Int. J. Mass Spectrom. Ion Proc*. **96**, 181.

Griffith, T. R. and Pugh, D. C. (1979) *J. Solution Chem*. **8**, 247; Griffith, T. R. and Pugh, D. C. (1979) *Coord. Chem. Rev*. **29**, 129.

Gritzner, G. (1990) *Pure Appl. Chem*. **62**, 1839.

Guenat, C., Houriet, R., Stahl, D. and Winkler, J. (1985) *Helv. Chim. Acta* **68**, 1647.

Guthrie, J. P. (1978) *Can. J. Chem*. **56**, 2342.

Gutmann, V. (1959) *J. Phys. Chem*. **63**, 378.

Gutmann, V. and Vychera, E. (1966) *Inorg. Nucl. Chem. Lett*. **2**, 257.

Gutmann, V. (1968) *Coordination Chemistry in Non-aqueous Solutions*, Springer, Vienna.

Hansch, C., Quinlan, J. E. and Laurence, G. L. (1968) *J. Org. Chem*. **33**, 347.

Hildebrand, J. H. (1978) *Disc. Faraday Soc*. **66**, 151.

Hildebrand, J. H. and Carter, J. M. (1932) *J. Am. Chem. Soc*. **54**, 3592.

Hormadaly, J. and Marcus, Y. (1979) *J. Phys. Chem*. **83**, 2843; Medda, K., Pal, M. and Bagchi, S. (1988) *J. Chem. Soc., Faraday Trans. 1* **84**, 1501; Medda, K., Chatterjee, P., Chandra, A. K. and Bagchi, S (1992) *J. Chem. Soc., Perkin Trans*. 343.

Ingemann, S. and Nibbering, N. M. M. (1985) *Acta Chem. Scand*. **39B**, 697.

Kadish, K. M. and Anderson, J. E. (1987) *Pure Appl. Chem*. **59**, 703.

Kamlet, M. J. and Taft, R. W. (1976) *J. Am. Chem. Soc*. **98**, 2886.

Kamlet, M. J. and Taft, R. W. (1976) *J. Am. Chem. Soc*. **98**, 377.

Kamlet, M. J. and Taft, R. W. (1985) *Acta Chem. Scand*. **B39**, 611.

Kamlet, M. J., Abboud, J.-L. and Taft, R. W. (1977) *J. Am. Chem. Soc*. **99**, 6027; Abboud, J.-L., Kamlet, M. J. and Taft, R. W. (1977) *J. Am. Chem. Soc*. **99**, 8325.

Kamlet, M. J., Abboud, J.-L. M., Abraham, M. H. and Taft, R. W. (1983) *J. Org. Chem*. **48**, 2877.

Kamlet, M. J., Gal, J-F., Maria, P.-C. and Taft, R. W. (1985) *J. Chem. Soc., Perkin Trans. 2* 1583.

Kessler, M. A. and Wolfbeis, O. (1991) *Spectrochim Acta A* **A47**, 187.

Koppel, I. and Palm, V. (1972) in N.B. Chapman, (ed), *Advances in Linear Free Energy Relationships*, Plenum, London, 203; Burden, A. G., Collier, G. and Shorter, J. (1976) *J. Chem. Soc., Perkin Trans. 2*, 1627.

Koppel, I. and Paju, A. (1976) *Organic React. (Tartu)* **11**, 121; Makitra, R. G. and Pirig, Ya. N. (1979) *Organic React. (Tartu)* **16**, 103.

Kosower, E. M. (1958) *J. Am. Chem. Soc*. **80**, 3253 and following papers quoted in (Laurence 1987).

Kreshov, A. P., Aldarova, N. S. and Smolova, N. T. (1969) *Zh. Fiz. Chim*. **43**, 2846; (1969) *Russ. J. Phys. Chem*. **43**, 1599.

Krieger, P. A. (1984) *High Purity Solvents Guide* Burdick & Jackson, McGraw-Hill Park, IL.

Labban, A.-K. S. and Marcus, Y. (1997) *J. Chem. Soc., Faraday Trans*. **93**, 77.

Laurence, C., Nicolet, P. and Reichardt, C. (1987) *Bull. Soc. Chim. Fr*. 125.

Laurence, C., Nicolet, P., Lucon, M., Dalati, T. and Reichardt, Ch. (1989) *J. Chem. Soc., Perkin Trans 2* 873.

Laurence, Ch, Nicolet, P., Dalati, M. T., Abboud, J.-L. M. and Notario, R. (1994) *J. Phys. Chem*. **98**, 5807.

Laurence, Ch., Queignec-Cabanetos, M., Dziembowska, T., Queignec, R. and Wojtkowiak, B. (1981) *J. Am. Chem. Soc*. **103**, 2567.

Leo, A., Hansch, C. and Elkins, D. (1971) *Chem. Rev*. **71**, 525.

Levitt, L. S. and Levitt, B. W. (1979) *Z. Naturforsch*. **B34**, 614.

Lias, S. G., Bartmess, J. E., Liebman, J. F., Holmes, J. L., Levin, R. D. and Mallard, W. G. (1988) *J. Phys. Chem. Ref. Data* **17**, Suppl. 1.

McHahon, T. B. and Kebarle, P. (1977) *J. Am. Chem. Soc*. **99**, 2222.

Mann, C. K. (1969) in A. J. Bard, (ed), *Electroanalytical Chemistry*, Dekker, New York, Vol. 3, p. 57 ff.

Marcus, Y. (1972) *Israel J. Chem*. **10**, 659; Marcus, Y. (1986) *Thermochim. Acta* **104**, 389.

Marcus, Y. (1977) *Introduction to Liquid State Chemistry*, Wiley, Chichester, Ch. 5.

Marcus, Y. (1984) *J. Solution Chem*. **13**, 599.

Marcus, Y. (1987) *J. Phys. Chem*. **91**, 4422; (1994) *J. Chem. Soc., Perkin Trans. 2* 1751.

Marcus, Y. (1991) *J. Solution Chem*. **20**, 929.

Marcus, Y. (1991) *J. Phys. Chem*. **95**, 8886.

Marcus, Y. (1992) *J. Solution Chem*. **21**, 1217.

Marcus, Y. (1993) *Chem. Soc. Rev*. **22**, 409.

Marcus, Y. (1996) *J. Solution Chem*. **25**, 455.

Marcus, Y. (1997) *Ion Properties*, Dekker, New York.

Marcus, Y. (1998) to be published. Unpublished results.

Marcus, Y., Kamlet, M. J. and Taft, R. W. (1988) *J. Phys. Chem*. **92**, 3613.

Maria, P.-C. and Gal, J.-F. (1985) *J. Phys. Chem*. **89**, 1296.

Mayer, U., (1983) *Stud. Phys. Theor. Chem*. **27**, 219.

Mayer, U., Gutmann, V. and Gerger, W. (1975) *Monatsh. Chem*. **106**, 1235;

Migron, Y. and Marcus, Y. (1991) *J. Chem. Soc., Faraday Trans*. **87**, 1339.

Nicolet, P. and Laurence, C. (1986) *J. Chem. Soc., Perkin Trans. 2* 1071; Laurence, C., Nicolet, P. and Helbert, M. (1986) *ibid*. 1081.

Nogaj, B., Dulewicz, E., Brycki, B., Hrynio, A., Barczynsi, P., Dega-Szafron, Z., Kozial, P. and Katritzky, A. R. (1990) *J. Phys. Chem*. **94**, 1279.

Pearson, R. G. (1963) *J. Am. Chem. Soc*. **85**, 3533.

Perdonan, G. and Scorrano, G. (1977) *J. Am. Chem. Soc*. **99**, 6983.

Persson, I. (1986) *Pure Appl. Chem*. **58**, 1153; Johnsson M. and Persson, I. (1987) *Inorg. Chim. Acta*, **127**, 15; Persson, I., Sandström, M. and Goggin, P. L. (1987) *Inorg. Chim. Acta*, **129**, 183.

de Petris, G., Fornarini, S. and Occhiuccini, G. (1992) *Int. J. Mass Spec. Ion Proc*. **112**, 231.

Ponomarenko, S. M., Mushtakova, S. P., Demakhin, A. G., Faifel, B. L. and Kalmanovich, D. G. (1994) *Zhur. Obshch. Khim.* **65**, 190.

Reichardt, C. (1965) *Angew. Chem*. **77**, 30; Kovats, E. Sz. (1968) *Chimia* **22**, 459.

Reichardt, Ch. (1988) *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, 2nd ed.

Reichardt, Ch. (1994) *Chem. Rev*. **94**, 2319.

Riddick, J. A., Bunger, W. B. and Sakano, T. K .(1986) *Organic Solvents*, Wiley-Interscience, New York, 4th ed.

Rosés, M. (1993) *Anal. Chem. Acta* **276**, 223.

Sadtler, (1983) *Infrared Spectra Handbook of Common Organic Solvents* Sadtler, Philadelphia.

Sawyer, D. T. and Roberts, J. L. Jr., (1974) *Experimental Electrochemistry for Chemists*, Wiley, New York.

Schmid, R. (1983) *J. Solution Chem*. **12**, 135; Symons M. C. R. and Pena-Nunez, A. S. (1985) *J. Chem. Soc., Faraday Trans. l* **81**, 2421.

Schneider, H., Badrieh, Y., Migron, Y. and Marcus, Y. (1993) *Z. Phys. Chem*. **177**, 143.

Smith, E. B. and Hildebrand, J. H. (1959) *J. Chem. Phys*. **31**, 145.

Soukup, R. W. and Schmid, R. (1985) *J. Chem. Educ*. **62**, 459; Migron, Y. and Marcus, Y. (1991) *J. Phys. Org. Chem*. **4**, 310.

Spange, S. and Kevtel, D. (1992) *Liebigs Ann. Chem*. 423.

Spange, S., Meissner, H., Hotzel. H. and Heublein, G. (1984) *Z. Chem*. **24**, 257.

Stephenson, R. M. (1992) *J. Chem. Eng. Data* **37**, 80; (1993) *J. Chem. Eng. Data* **38**, 634.

Stephenson, R. M. and Stuart, J. (1986) *J. Chem. Eng. Data* **31**, 56.

Taft, R. W. (1975) in *Proton Transfer Reactions*, E.F. Caldin and V. Gold, (eds), Chapman and Hall, London.

Taft, R. W., Abraham, M. H., Famini, G. R., Doherty, R. M., Abboud, J.-L. M. and Kamlet, M. J. (1985) *J. Pharm. Sci*. **74**, 807; Kamlet, M. J., Doherty, R. M., Abraham, M. H., Carr, P. W., Doherty, R. F. and Taft, R. W. (1987) *J. Phys. Chem*. **91**, 1996; Kamlet, M. J., Doherty, R. M., Abraham, M. H., Marcus, Y. and Taft, R. W. (1988) *J. Phys. Chem*. **92**, 5244; Abboud, J.-L. M., Roussel, Ch., Gentric, E., Sraidi, Kh., Lauransan, J., Guiheneuf, G., Kamlet, M. J. and Taft, R. W. (1988) *J. Org. Chem*. **53**, 1545.

Taft, R. W. and Bordwell, F. G. (1988) *Acct. Chem. Res*. **21**, 463.

Varhanickova, D., Shiu, W.-Y. and Mackey, D. (1995) *J. Chem. Eng. Data* **40**, 448.

Vorkunova, E. I. and Levin, Ya. A. (1983) *Zhur. Obshchei Khim*. **54**, 1349 (1983) (*J. General Chem*. **54**, 1206).

Weber, J. and Houriet, R. (1988) *J. Phys. Chem*. **92**, 5926.

Westwater, W., Frantz, H. W. and Hildebrand, J. H. (1928) *Phys. Rev*. **31**, 135.

Wooley, E. M. and George, R. E. (1974) *J. Solution Chem*. **3**, 119.

Yalkowski, S. H., Pinal, R. and Banerjee, S. (1988) *J. Pharm. Sci*. **77**, 74; Kamlet, M. J., Doherty, R. M., Abraham, M. H., Carr, P. W., Doherty, R. F. and Taft, R. W. (1987) *J. Phys. Chem*. **91**, 1996.

Yonker, C. R., Frye, S. L., Kalkwarf, D. R. and Smith, R. D. (1986) *J. Phys. Chem*. **90**, 3022; Smith, R. D., Frye, S. L., Yonker, C. R. and Gale, R. W. (1987) *J. Phys. Chem*. **91**, 3059.

Chapter 5— Applications

1— A Survey of Typical Applications

Some of the solvents on the List have no widespread applications, but can be employed for specialized needs. However, most of the solvents have found uses in many fields, and a great deal of these, as shown in Table 1.2 and marked IS for 'industrial solvent' in the column 'grade available', are bulk commercial solvents. Table 5.1 surveys typical applications of the solvents on the List, without implying exhaustiveness, or that solvents not shown are devoid of important applications. The listing is alphabetical, not implying the order of importance of the uses.

Some comments on and explanations of the applications listed are in place here. As is seen below, not all applications are of the solvents as such: in many cases they are added to other materials to improve their properties, to initiate reactions and accelerate their rates, and as reagents that are consumed by transforming other compounds to more useful ones. Following is an alphabetical lexicon with brief definitions of the key words used in Table 5.1.

An absorbent is used to absorb gases from industrial processes or power plants, in particular acidic gases, when used as an acid absorber. An alkylator, also acetylator, aminator, benzoylator, methylator, etc. is used as a reagent, rather than as a solvent, in order to transfer an alkyl group, acetyl, amine, benzoyl, methyl, etc. groups, respectively, to other compounds. An antifreeze is added to radiator fluids of motor vehicles to prevent freezing at low outside temperatures. A binder is used in composite materials to achieve cohesiveness. A bleacher reacts with coloured materials or impurities in them by either oxidizing or reducing them, causing the colour to fade. A blood substitute is able to carry oxygen and haemoglobin through the arteries, veins, and capillaries of living animals. A blowing agent is used in polymer manufacture to create porosity. A catalyst initiates reactions and accelerates their rate, without being consumed. In some cases it may do so by means of its acidic or basic properties, but must then be regenerated before reuse. A chelator forms stable chelates with metal ions,

Table 5.1 Typical applications of solvents in the laboratory and in industry

No.	Name	Typical applications
0	vacuum	removal of gases
10	tetramethylsilane	NMR reference
20	n-pentane	blowing agent, solvent
30	2-methylbutane	blowing agent
40	n-hexane	blowing agent, extractant, eluant, solvent
50	c-hexane	blowing agent, extractant, solvent
60	n-heptane	fuel, extractant, solvent
70	n-octane	solvent
80	2,2,4-trimethylpentane	fuel, microemulsions, solvent
90	n-decane	microemulsions, solvent
100	n-dodecane	microemulsions, solvent
110	n-hexadecane	lubricant, microemulsions
120	benzene	extractant, solvent
130	toluene	diluent, extractant, solvent
140	o-xylene	diluent, extractant, solvent
150	m-xylene	diluent, extractant, solvent
160	p-xylene	diluent, extractant, solvent
170	ethylbenzene	solvent
180	cumene	
190	mesitylene	solvent
200	styrene	monomer, crosslinking agent
210	tetralin	coal liquefaction, solvent
220	cis-decalin	solvent
230	water	absorbent, blowing agent, coolant, electrochemistry eluant, extractant,*
240	methanol	cleaner, coal liquefaction, electrochemistry, eluant, fuel, reductant, solvent
250	ethanol	cleaner, dispersant, electrochemistry, extractant, fuel, solvent
260	n-propanol	solvent
270	i-propanol	catalyst, cleaner, developer, solvent
280	n-butanol	catalyst, extractant, solvent
290	i-butanol	extractant, solvent
300	2-butanol	solvent
310	t-butanol	catalyst, solvent
320	n-pentanol	extractant, solvent

330	i-pentanol	extractant, solvent
340	t-pentanol	
350	n-hexanol	extractant, solvent
360	c-hexanol	
370	n-octanol	extractant, solvent
380	n-decanol	liquid crystals
390	n-dedecanol	extractant, lubricant
400	benzyl alcohol	catalyst, solvent
410	2-phenylethanol	
420	allyl alcohol	
430	2-chloroethanol	
440	2-cyanoethanol	

(table continued on next page)

***Table 5.1** (continued)*

No.	Name	Typical applications
450	2,2,2-trifluoroethanol.	
460	hexafluoro-i-propanol	
470	2-methoxyethanol	solvent
480	2-ethoxyethanol	solvent
490	1,2-ethanediol	antifreeze, coating agent, electrochemistry, plasticizer,
500	1,2-propanediol	antifreeze, plasticizer, solvent
510	1,3-propanediol	
520	1,2-butanediol	
530	2,3-butanediol (meso)	
540	1,4-butanediol	
550	1,5-pentanediol	
560	diethyleneglycol	antifreeze, plasticizer, solvent
570	triethyleneglycol	solvent
580	glycerol	cryoprotectant, humectant, lubricant, plasticizer, soldering
590	phenol	catalyst, solvent
600	2-methylphenol	
610	3-methylphenol	solvent
620	4-methylphenol	catalyst
630	2-methoxyphenol	
640	2,4-dimethylphenol	
650	3-chlorophenol	
660	diethyl ether	extractant, solvent
670	di-n-propyl ether	
680	di-i-propyl ether	extractant, solvent
690	di-n-butyl ether	
700	di(2-chloroethyl) ether	extractant
710	1,2-dimethoxyethane	electrochemistry, solvent,
720	bis(methoxyethyl) ether	solvent
730	furan	
740	tetrahydrofuran	electrochemistry, solvent,
750	2-methyl tetrahydrofuran	electrolytes
760	tetrahydropyran	

770	dioxane	solvent
780	dioxolane	electrolytes
790	1,8-cineole	catalyst
800	anisole	solvent
810	phenetole	
820	diphenyl ether	
830	dibenzyl ether	
840	1,2-dimethoxybenzene	
850	trimethyl orthoformate	
860	trimethyl orthoacetate	
870	propionaldehyde	
880	butyraldehyde	

continued overleaf

Table 5.1 *(continued)*

No.	Name	Typical applications
890	benzaldehyde	
900	p-methoxybenzaldehyde	
910	cinnamaldehyde	
920	acetone	cleaner, coatings, eluant, extractant, solvent
930	2-butanone	coatings, extractant, solvent
940	2-pentanone	
950	methyl i-propyl ketone	
960	3-pentanone	
970	c-pentanone	
980	methyl-i-butyl ketone	extractant, solvent
990	methyl t-butyl ketone	
1000	c-hexanone	extractant, solvent
1010	2-heptanone	
1020	3-heptanone	
1030	di-t-butyl ketone	
1040	acetophenone	catalyst, solvent
1050	propiophenone	
1060	phenylacetone	
1070	p-methylacetophenone	
1080	p-chloroacetophenone	
1090	benzophenone	catalyst, photoinitiator, photosensitizer
1100	acetylacetone	catalyst, chelator, extractant
1110	biacetyl	
1120	formic acid	catalyst, electrochemistry, solvent
1130	acetic acid	buffer, catalyst, electrochemistry, etchant, solvent
1140	propanoic acid	
1150	n-butanoic acid	
1160	n-pentanoic acid	
1170	n-hexanoic acid	extractive distillation
1180	n-heptanoic acid	extractive distillation
1190	dichloroacetic acid	catalyst
1200	trifluoroacetic acid	catalyst
1210	acetic anhydride	acetylator

1220	benzoyl chloride	benzoylator
1230	benzoyl bromide	
1240	methyl formate	
1250	ethyl formate	
1260	methyl acetate	
1270	ethyl acetate	extractant, solvent
1280	propyl acetate	
1290	butyl acetate	solvent
1300	i-pentyl acetate	
1310	methyl propanoate	
1320	ethyl propanoate	
1330	dimethyl carbonate	methylator
1340	diethyl carbonate	
1350	ethylene carbonate	electrolytes
1360	propylene carbonate	electrolytes, solvent

(table continued on next page)

Table 5.1 *(continued)*

No.	Name	Typical applications
1370	diethyl malonate	
1380	methyl benzoate	
1390	ethyl benzoate	catalyst
1400	dimethyl phthalate	plasticizer, solvent
1410	dibutyl phthalate	binder, catalyst, plasticizer, solvent
1420	ethyl chloroacetate	alkylator
1430	ethyl trichloroacetate	
1440	ethyl acetoacetate	alkylator
1450	4-butyrolactone	electrolytes, solvent
1460	perfluoro-n-hexane	
1470	perfluoro-n-heptane	
1480	perfluoro-methylcyclohexane	
1490	perfluoro-decalin	blood substitute
1500	fluorobenzene	
1510	hexafluorobenzene	
1520	l-chlorobutane	alkylator
1530	chlorobenzene	solvent
1540	dichloromethane	blowing agent,electrochemistry, extractant, solvent
1550	1,1-dichloroethane	
1560	1,2-dichloroethane	extractant, solvent
1570	tr-1,2-dichloroethylene	
1580	o-dichlorobenzene	solvent
1590	m-dichlorobenzene	
1600	chloroform	extractant, solvent
1610	1,1,1-trichloroethane	cleaner, degreaser, solvent
1620	1,1,2-trichloroethane	
1630	trichloroethylene	cleaner, solvent
1640	1,2,4-trichlorobenzene	
1650	tetrachloromethane	extractant, solvent
1660	tetrachloroethylene	cleaner, solvent
1670	1,1,2,2-tetrachloroethane	
1680	pentachloroethane	
1690	l-bromobutane	alkylator

1700	bromobenzene	
1710	dibromomethane	
1720	1,2-dibromoethane	
1730	bromoform	
1740	l-iodobutane	alkylator
1750	iodobenzene	
1760	diiodomethane	
1770	n-butylamine	catalyst
1780	benzylamine	catalyst
1790	1,2-diaminoethane	catalyst, chelator, crosslinker
1800	diethylamine	catalyst
1810	di-n-butylamine	aminator, catalyst
1820	pyrrole	electrolytes

continued overleaf

Table 5.1 *(continued)*

No.	Name	Typical applications
1830	pyrrolidine	catalyst
1840	piperidine	catalyst
1850	morpholine	catalyst, corrosion inhibitor
1860	triethylamine	acid absorber, catalyst
1870	tri-n-butylamine	catalyst
1880	aniline	catalyst
1890	o-chloroaniline	
1900	N-methylaniline	
1910	N,N-dimethylaniline	catalyst
1920	ethanolamine	acid absorber, catalyst, cleaner, corrosion inhibitor
1930	diethanolamine	acid absorber, catalyst
1940	triethanolamine	acid absorber, catalyst, cleaner, corrosion inhibitor
1950	pyridine	catalyst, corrosion inhibitor, electrochemistry, extractant
1960	2-methylpyridine	catalyst
1970	3-methylpyridine	catalyst
1980	4-methylpyridine	catalyst
1990	2,4-dimethylpyridine	catalyst
2000	2,6-dimethylpyridine	catalyst
2010	2,4,6-trimethylpyridine	
2020	2-bromopyridine	
2030	3-bromopyridine	
2040	2-cyanopyridine	
2050	pyrimidine	
2060	quinoline	catalyst, solvent
2070	acetonitrile	electrochemistry, electrolytes
2080	propionitrile	
2090	butyronitrile	
2100	valeronitrile	
2110	acrylonitrile	monomer
2120	benzyl cyanide	
2130	benzonitrile	
2140	nitromethane	electrochemistry, solvent
2150	nitroethane	

2160	l-nitropropane	
2170	2-nitropropane	
2180	nitrobenzene	solvent, extractant
2190	formamide	electrolytes
2200	N-methylformamide	electrolytes
2210	N,N-dimethylformamide	absorbent, catalyst, electrolytes, electrochemistry, solvent
2220	N,N-dimethylthioformamide	
2230	N,N-diethylformamide	catalyst
2240	N-methylacetamide	
2250	N,N-dimethylacetamide	catalyst, solvent
2260	N,N-diethyl acetamide	
2270	pyrrolidinone-2	solvent
2280	N-methylpyrrolidinone	absorbent, catalyst, electrolytes, electrochemistry

(table continued on next page)

Table 5.1 *(continued)*

No.	Name	Typical applications
2290	N-methylthiopyrrolidinone	
2300	tetramethylurea	catalyst, solvent
2310	tetraethylurea	
2320	dimethylcyanamide	
2330	carbon disulfide	solvent
2340	dimethyl sulfide	
2350	diethyl sulfide	
2360	di-i-propyl sulfide	
2370	di-n-butyl sulfide	
2380	tetrahydrothiophene	
2390	pentamethylene sulfide	
2400	dimethyl sulfoxide	electrochemistry, electrolytes, extractant, solvent
2410	di-n-butyl sulfoxide	
2420	sulfolane	electrolytes, solvent
2430	thiobis(2-ethanol)	
2440	diethyl sulfite	
2450	dimethyl sulfate	alkylator
2460	diethyl sulfate	
2470	methanesulfonic acid	catalyst
2480	trimethyl phosphate	electrolytes
2490	triethyl phosphate	catalyst
2500	tri-n-butyl phosphate	extractant, plasticizer, solvent
2510	hexamethyl phosphoramide	catalyst, electrolytes, solvent
2520	hexamethylthiophosphoramide	
2530	hydrogen peroxide	bleacher, catalyst, etchant, oxidant
2540	hydrogen fluoride	catalyst, electrochemistry, etchant, solvent
2550	sulfuric acid	catalyst, dehydrator, electrochemistry, etchant, leaching agent
2560	ammonia	coolant
2570	hydrazine	propellant, reductant
2580	sulfur dioxide	bleacher, electrolytes
2590	thionyl chloride	catalyst, electrochemistry
2600	phosphorus oxychloride	catalyst

Further applications: *leaching agent, neutron moderator and reactor coolant, solvent, working that may be used in analytical chemistry or for separations, e.g., by solvent extraction. A cleaner acts as a solvent that removes grease and other impurities from mechanical parts, cloth, etc. A solvent may be used in coal liquefaction in order to disperse the coal dust and permit its reactions. A coating agent wets the material immersed in it and permits other reagents to coat the material with a suitable layer. A coolant acts by removing heat from systems through the medium of its heat capacity. A corrosion inhibitor can protect materials covered by it from corrosion by an aggressive atmosphere. A cryoprotectant used with tissues or living organisms permits their temperature to be lowered considerably without causing irreversible damage. A degreaser is a cleaner that specifically removes grease and oily materials. A dehydrator removes water from materials. A developer is used in photoresist materials in order to bring out the imprinted pattern. A diluent is used in mixtures with other solvents in order to improve their chemical or physical characteristics. A dispersant forms suspensions of materials in it without dissolving them. A solvent is used in electrochemistry by dissolving the electrolyte in order to permit current to flow between a cathode and an anode, without itself thereby being reduced or oxidized (see below). It may be used in electrolytes employed in an electrical battery as their solvent, again without itself being reduced or oxidized when current is drawn from it. A solvent is used as an eluant in chromatographic columns, either for analytical or for preparative use. An etchant reacts with the surface of materials, dissolving away layers that are not protected by a non-reactive covering, and may be used in electropolishing and similar processes. An extractant, either alone, as a solvent, or diluted with a diluent, is used with another liquid phase normally an aqueous solution, in order to separate solutes by their partitioning between the two liquid phases (see below). When used as a fuel, the chemical energy stored in the intramolecular bonds is liberated by combustion in air. A humectant is a hygroscopic material that avidly retains water sorbed from a humid atmosphere, and may be used in cosmetics and pharmaceuticals. A leaching agent is able to dissolve desired substances out of solid materials. A lubricant is used by virtue of its rheological properties i.e. viscosity, to reduce friction between moving parts in machinery. A solvent may be used in liquid crystals by virtue of its long chains. Use in microemulsions implies participation in multi-component systems, generally involving also water, an alcohol, and a surface active agent, to produce an agent useful, e.g., in bringing up crude oil from nearly exhausted drillings. An oxidant, or reductant, is used as a reagent to remove, or supply, electrons in reactions. A plasticizer is used to confer on polymers suitable mechanical elastic properties. A propellant is used as a rocket fuel, being oxidized by a suitable substance, producing a large volume of hot gases, hence a large thrust. A working fluid is used in order to transmit mechanical forces, a required property being low compressibility. Finally, a solvent, if nothing else is mentioned, is used in order to bring into solution many kinds of material, inorganic, organic, or biochemical, and this implies generally that it is produced as an industrial solvent in large bulk quantities.

2—
Applications in Solvent Extraction

Solvent extraction, or liquid—liquid distribution, is the process in which one or more solutes partition selectively between two immiscible liquid phases (Rydbery, Musikas and Choppin 1992). The process is applied industrially in hydrometallurgy e.g., recovery of copper and nickel from ores, in nuclear fuel reprocessing to separate uranium and plutonium from fission products; in treatment of fermentation liquors e.g., recovery of citric acid; in treatment of waste waters e.g., removal of phenolic compounds, and many other applications. The process is also widely used in the laboratory, in organic synthesis to recover the product or to purify it from impurities, and in analytical chemistry to separate analytes or as a pre-concentration step, and has, mainly in the past, been used in coordination chemistry to study complex formation in solution.

In the vast majority of cases one of the phases is aqueous, but this is not an absolute requirement. Liquid—liquid distribution has been studied between molten salts and metals (Marcus 1967), between molten salts and organic liquids, and with a few other completely anhydrous systems. When reversed phase chromatography is used, one organic solvent is adsorbed on the surface of an inert carrier in a column and another solvent, which may be anhydrous, is used as the mobile phase, eluting solutes selectively (Kertes, Zangen and Schmuckler 1992). On the other hand, liquid—liquid distribution is sometimes applied in cases where both phases are highly aqueous but still immiscible. If solvents such as 1-butanol or tri-*n*-butyl phosphate are used, then the organic-rich liquid phase contains 1.06, respectively 0.72 moles of water per mol of organic compound (Table 4.6). Even well water-soluble organic liquids, such as polyethylene glycol (PEG-2000) can be used in so called aqueous biphasic systems, provided that a highly soluble salt, such as potassium hydroxide or ammonium sulfate, is used as a salting out agent (Rogers and Zhang 1997).

An application has been found in which a system that exhibits an upper, or lower, critical consolute point, UCST or LCST, respectively, is utilized. At a temperature above or below this point, the system is one homogeneous liquid phase and below or above it, at suitable compositions, it splits into two immiscible liquids, between which a solute may distribute. Such a system is, for instance, the propylene carbonate - water one: at 25°C the aqueous phase contains a mole fraction of 0.036 propylene carbonate and the organic phase a mole fraction of 0.34 of water. The UCST of the system is 73°C (Murata, Yokoyama and Ikeda 1972), and above this temperature the system coalesces into a single liquid. Temperature cycling can be used in order to affect the distribution of the solutes e.g. alkaline earth metal salts or transition metal chelates with 2-thenoyl trifluoroacetone (Murata, Yokayama and Ikeda 1972).

Still, in most liquid—liquid distribution systems one of the liquid phases is more aqueous while the other is mainly non-aqueous. Therefore, a major consideration of the choice of the solvent for solvent extraction is its immiscibility with water and the expected losses of the solvent to the aqueous phase. In many solvent extraction applications the solvent is used as a diluent for an active extractant, which may be either a solid or a liquid when neat. In these cases, where a separate active extractant is used, the chemical processes taking place in the selective extraction of the desired solute or solutes and their recovery in the stripping stage are of prime importance, but a discussion of which is outside the scope of this book (Rydberg, Musikas and Choppin 1992). However, whether used as the solvent-extractant itself or as the diluent, solvent losses due to solubility in the aqueous phase ought to be minimized. There are other losses, due to entrainment of droplets, volatility, etc., that depend on the equipment used for the extraction. Table 4.6 may be used as a guide for the solubility losses to be expected. As a general rule, the more unlike water in its properties a solvent is, the less its solubility in water will be, but its ability to extract hydrophilic solutes from an aqueous phase will also be lessened. This is illustrated by log P, the logarithm of the partition constant of the solvent molecules between 1-octanol and water, the log P O/W column in Table 4.6, which is a measure of the hydrophobicity of these molecules when >0, see Figure 4.6. Very hydrophobic and non-polar solvents, such as hydrocarbons and halocarbons, can generally be only used as diluents, whereas polar solvents are useable as extractants for solutes from aqueous solutions. It is not very easy to balance between low water solubility of the solvent on the one hand and high polarity and extractive capacity for solutes that reside in the aqueous phase, primarily, due their hydrophilicity, on the other.

There are other criteria for the choice of a solvent, besides the chemistry of the extraction involved and the miscibility with water. One set of criteria concern the physical properties of the solvent: its density, viscosity, surface tension, volatility, etc. The density d in Table 3.1, and its temperature dependence, given by α_p, determine whether it is the lower or the upper liquid phase in extractions from aqueous solutions, except when the latter are very dense due to high concentrations of the solutes. Chloroform and tetrachloromethane are examples of solvents/diluents much denser than water, whereas hexane and diisopropyl ether are examples of low density solvents/diluents. The viscosity η and surface tension σ in Table 3.9 are of importance for the disengagement of the liquid phases after they are brought into equilibrium. The higher the former and the lower the latter, the more the two phases will tend to remain in intimate contact as quasi-emulsions, and the more difficult the desired phase separation will be. The volatility of the solvent may be a nuisance due to its possible losses, but may be of great advantage when the solvent is to be recovered and recycled by being distilled away from the extracted solute. See the vapour pressure p and the heat of vaporization $\Delta_v H$ in Table 3.1

Further criteria for the choice of a solvent are its availability, cost, toxicity, hazardousness, and other aspects of environmental acceptability. The availability of solvents on the List is summarized in Table 1.2. Other industrial solvents are dealt with where the tonnage produced and the costs are also listed (Kirk-Othmer 1997). The toxicity of the solvents and hazards due to flammability and explosiveness of their vapours in air are listed in Tables 1. 3 and 1.4, which should be regarded as general guides only, not as sources of binding data, for which the original literature about the specific solvent in question should be consulted.

Several examples of the use of solvents in solvent extraction processes follow.

Because of cost factors, solvent extraction applied to large scale hydrometallurgical processes, such as the recovery of copper from acidic ore leach solutions, is carried out with the most selective reagent for e.g., copper versus iron, which is not itself a liquid solvent, in a petroleum diluent that confers on the mixture the desired physical properties. For the particular case of copper recovery, commercial hydroxyoxime reagents have been used on a very large scale, but their discussion is outside the scope of this book.

Nuclear fuel reprocessing depends almost exclusively on the PUREX process. This devolves on the use of tri-*n*-butyl phosphate (TBP) in a hydrocarbon diluent, say *n*-dodecane, the properties of both being specified in the various Tables in this book. The diluent is added in order to reduce the viscosity (Table 3.9) and density (Table 3.1) of the organic phase as mentioned later. The uranium, in the form of the uranyl cation, UO_2^{2+} , is extracted accompanied by two nitrate anions from the aqueous solution that contains a high concentration of nitrate salt and nitric acid and is solvated by the TBP. The aqueous nitrate is required partly for the complexation of the uranium and partly for the salting-out of the uranyl nitrate-TBP complex. The main property of the TBP solvent that comes into play here is its high Lewis basicity, described by its β value (Table 4.3), making it able to solvate the uranyl nitrate complex effectively (Marcus 1986). The low solubility of TBP in water (Table 4.6) reduces solubility losses, and this reduced loss is enhanced by the presence of the dodecane, lowering the activity of the TBP in the organic phase. It does so both by diminishing its concentration and by interacting with it by dispersion forces, by virtue of the alkyl chains in both components. This system is an example of the use of a solvent mixture, but since dodecane alone does not extract the uranium at all whereas neat TBP does, the solvent can be regarded as a diluent-modified solvent rather than as a mixture. The successful application of TBP in the PUREX process depends, of course, also on the strongly preferential extraction of uranium(VI) and plutonium(IV), compared with plutonium(III) and practically all fission products, on the ability to strip the organic phase and recycle it, and on the relative radiation stability of the TBP.

Another industrial solvent extraction process used on a large scale is the selective extraction of hydrochloric acid and phosphoric acid, resulting from the attack of phosphate ores by the former acid, from the aqueous calcium chloride formed in this attack (Baniel and Blumberg 1959). The solvent employed in this process is an isomer of butanol or pentanol, the choice depending on their immiscibility with water (Table 4.6) on the one hand and a high concentration of the active hydroxyl group, compared with higher alcohols, on the other. The hydroxyl group solvates the acids: it readily accepts the proton on the oxygen atom, the solvents having a high β value, to form the oxonium cation. It also donates a hydrogen bond to the chloride and dihydrogenphosphate anions, due to the high α value of the solvent (Table 4.3). The calcium ions being more strongly hydrated than solvated, and hence are not extracted, and the calcium chloride serves to salt the acids out. Some water, of course, is co-extracted with the acids, and the properties of the organic phase are those of the 'wet' solvent. For instance, the relative permittivity of this phase is higher than that of the neat alcohols and permits ionic dissociation of the extracted and solvated acids to some extent. Subsequent treatment of the organic extract with water removes the acids, due to the absence of the salting-out calcium chloride. The acids can be separated by vaporization of the hydrogen chloride, leaving a concentrated phosphoric acid behind, and the alcohol is recycled.

Extraction of organic compounds is illustrated by the production of citric acid from an aqueous fermentation broth by means of tertiary amines. Contrary to the lower molecular weight amines on the List, amines with altogether 24 or more carbon atoms in their alkyl chains are virtually water insoluble. They are generally used in a hydrocarbon diluent modified by an alcohol, say, dodecane and 1-octanol, in order to provide the desired physical properties, such as low viscosity and fast phase disengagement. The particular trick employed in this case is the extraction of the citric acid from the fermentation broth at a low temperature into the organic solvent phase and the stripping of the latter by water at a high temperature, where the transfer of the citric acid is reversed. In this manner the product solution can be made more concentrated than the feed (Baniel and Blumberg 1957). Another example is the recovery of ethanol from carbohydrate fermentation in an aqueous biphasic system constituted of aqueous polyethylene glycol (PEG 6000) as the upper phase that is collecting the ethanol, and the fermentation broth which is an aqueous mixture of dextran, glucose, and yeast cells as the lower phase, (Kühn 1980). Although PEG 6000, which is a waxy solid at room temperature, of mean molar weight of 6000 g mol^{-1}, is not one of the solvents in our List, its chemical properties are similar to those of triethyleneglycol, which is (Table 4.3). The ethanol, that inhibits the fermentation at higher concentrations, is removed by the upper phase as it is formed. An alternative for the continuous removal of the ethanol is its extraction by a long chain, water immiscible, alcohol e.g., oleyl alcohol (Job *et al*.1989). Another typical application of solvent extraction in the field of fermentation is the removal of penicillin from the fermentation broth by extraction with butyl or isopentyl acetate. The extraction is carried out at pH 2.0–2.5 in the broth, and stripping takes place by water at a pH of 6.0 (Edler 1970). The solvents have been chosen partly because of their low toxicity (Tables 1.3 and 1.4), low cost, immiscibility with water, and chemical nature - polarity, absence of Lewis acidity and a moderate Lewis basicity (Table 4.3) - that is conducive to the extraction.

In a quite different field, that of petroleum chemistry, solvent extraction is being used extensively for the separation of aromatic and aliphatic hydrocarbons. The preferred solvents are all very polar: sulfolane (Beardmore and Kosters 1963), dimethylsulfoxide, and N-methylpyrrolidinone. The polar solvents (Tables 3.5 and 4.3) have a higher affinity to the aromatic hydrocarbons and remove them from the mixture. Additional features in favour of, e.g., sulfolane, employed at 120°C, are its high heat capacity and density and chemical stability, whereas dimethylsulfoxide has a lower viscosity than sulfolane, permitting its use at ambient temperatures, and a low toxicity, which are an advantage (Tables 1.3, 3.1, 3.9). Selective recovery of *p*-xylene from its mixture with its isomers and other hydrocarbons has been effected by the use of liquid anhydrous hydrogen fluoride, with boron trifluoride added as an isomerization catalyst. The high acidity of the hydrogen fluoride causes it to protonate the aromatic compounds and extract them from mixtures with aliphatic hydrocarbons, with which the hydrogen fluoride is immiscible (Mackor *et al*. 1958). The components of the heavy fraction of petroleum have been separated on an industrial scale by supercritical pentane (Eckert, Knutson and Debenedetti 1996).

A final application of solvent extraction mentioned here is the recent use of supercritical carbon dioxide (Tables 3.3 and 4.4), beyond the well-known decaffeination process, used to extract essential and fatty oils from plant materials (Simandi *et al*. 1993). The temperature range used is 40–70°C and the applied pressure is 8–30 MPa. The higher the pressure, the better the yield. The supercritical solvent has the advantage of being readily removed from the extract by lowering the pressure, being non-toxic, and applicable under mild conditions that do not harm the products. The use of dense gases in conjunction with ordinary organic solvents has also been considered (Brunner and Peter 1982), again in relation to the extraction of oils from natural sources but also for other purposes. For instance, acetone plus carbon dioxide at 70°C can raise the triglyceride concentration in an extract to 10%, compared to only 1% with pure carbon dioxide.

3—
Applications in Electrochemistry

Although many electrochemical processes, such as electroplating, charging and discharging of batteries, and electroanalytical determinations, are carried out in aqueous solutions, the application of non-aqueous solvents continuously grows in importance. Water, of course, is a nearly ideal medium for carrying out such processes: it has a high relative permittivity (Table 3.5), allowing essentially complete ionic dissociation of many electrolytes, it has a reasonable liquid range (Table 3.1), and a wide enough electrochemical window, so that it resists electroreduction and -oxidation (Table 4.8). The autoprotolysis constant of water (Table 4.5) and specific conductance (Table 3.5) are sufficiently low for the resulting hydronium and hydroxide ions not to interfere too strongly with processes involving strong electrolytes. The viscosity of water (Table 3.9) is fairly low, so that the mobilities of ions, unless strongly hydrated or intrinsically large, is fast. Water has a very good solvating, or hydrating, ability of ions: cations by virtue of the lone pairs on its oxygen atom which are donated to them due to having a substantial β value (Table 4.3) and anions by virtue of the hydrogen bonds formed with them by having a high α value (Table 4.3). It has the particular advantage of having very small molecules (Table 3.4), so that many of them can find their place around an ion without excessive crowding, each contributing its bonding ability. When the lattice energy of a salt is not too high, these properties of water lead to a sufficient gain in enthalpy on dissolution to counterbalance loss of entropy of the solvating water molecules due to their partial immobilization, and yield high solubilities of many salts. Water is readily available, at low cost at the quantities required for electrochemical processes, is non-toxic, non-hazardous, and can be readily purified, e.g., by deionization in mixed bed ion exchange columns with subsequent multi-stage distillation, in quartz equipment, to produce a very pure solvent.

However, for certain applications non-aqueous solvents have their advantages. Uni-univalent electrolytes dissolved at low to moderate concentrations in solvents with a relative permittivity larger than, approximately, 30 are completely dissociated into ions. Of the solvents on the List, methanol, glycols, glycerol, formic acid, ethylene and propylene carbonate, 4-butyrolactone, ethanolamine, 2-cyanopyridine, acetonitrile, nitromethane and -benzene, the amides, whether N-substituted or not, dimethyl sulfoxide, sulfolane, dimethyl sulfate, and hexamethyl phosphoramide have $\varepsilon \geq 30$ at ambient conditions (Table 3.5). Most of these solvents have, indeed, been used in electrochemical processes.

Consider, for instance, high energy density batteries. They have a light metal anode usually lithium, but also sodium, magnesium, calcium, and aluminum, with equivalent weights of 6.94, 22.99, 12.16, 20.04, and 8.99 g equiv.$^{-1}$, respectively, have been used, and a transition metal halide, sulfide, or oxide cathode. The electrolyte for a lithium anode is a lithium salt with a large anion e.g., perchlorate, tetrafluoroborate, hexafluorophosphate or trifluoromethylsulfonate (Marcus 1997). The charge carriers, ions in the electrolyte, should be at the highest concentration and mobility as possible, in order to achieve a good performance-to-size ratio of the battery. Since the anode metal is very reactive, water or a protic solvent must be excluded, so the choice of solvents is limited to dipolar aprotic solvents, capable of solvating the electrolyte so that it is well soluble. Other criteria for its choice are:

(i) a long liquid range (Table 3.1 or 4.8), say from -50-+50°C, and many applications focus on the lower part of this range;

(ii) a low vapour pressure (Table 3.1) up to the maximal temperature of application, so as to avoid loss and the danger of explosion;

(iii) a high relative permittivity (Table 3.5), so that the number density of charge carriers is given directly by the nominal concentration of the electrolyte;

(iv) good solvating power for both cation (high β) and anion (high α, but see below) of the electrolyte (Table 4.3), to ensure good solubility, > 0.3 mol dm^{-3}, at all temperatures employed;

(v) low viscosity (Table 3.9) and small molar volume (Table 3.1), in order to ensure high mobilities of the (solvated) ions;

(vi) chemical stability against attack by the electrode materials and depolarizers, if present. This stability may be manifested kinetically, rather than thermodynamically, so that this may involve passivation;

(vii) ready availability at low cost, ease of purification (Table 1.2) and non-toxicity nor involvement of other hazards (Tables 1.3 and 1.4).

In criterion (iv) the requirement of high α cannot be realized, since protic solvents are excluded, so that large anions, that are only weakly solvated and confer a low lattice energy on the electrolyte salt, have to be used.

Solvents that meet all or most of the criteria are propylene carbonate, dimethylsulfoxide, 4-butyrolactone, acetonitrile, sulfur dioxide, thionyl chloride, and phosphorus oxychloride. Certain other solvents, with fairly low ε values, such as tetrahydrofuran, dimethoxyethane, and 1,3-oxolane are used in conjunction with a high ε solvent, in order to reduce the viscosity without impairing excessively the other desirable properties of the co-solvent. All these solvents are on the List, with properties shown in the tables mentioned. Commercial implementation of such batteries has been highly successful, with energy densities of primary dischargeable batteries of 0.3 W h g^{-1} or 0.5 W h cm^{-3} and a self discharge rate of < 2% per year of the open-circuit battery being achieved.

Perhaps contrary to the conception derived from the properties of solvents desirable for batteries, solvents for certain other electrochemical applications need have neither high relative permittivities nor particularly good ion solvating abilities. Such applications are those involving organic or organometallic solutes to be studied electrochemically with respect to their redox reactions. An example is benzonitrile, with a moderate ε (Table 3.5) and low α and β values (Table 4.3), but a wide electrochemical window (Table 4.8). It has been used for the study of mono- and dinitrosyliron(II) porphyrins, five reversible single electron transfer steps having been found for them (Kadish and Anderson 1987). Other examples are certain haloalkanes: dichloromethane and 1,1- and 1,2-dichloroethane. These, again, have fairly low ε, α, and β values (Tables 3.5 and 4.3) but are useful electrochemical solvents nevertheless. These solvents have low freezing temperatures, so that they can be employed for low temperature studies of solutes that are themselves, their oxidation or reduction products decomposed at ambient conditions. The freezing point of 1,2-dichloroethane is not as low as those of the other two haloalkanes, but its boiling point is higher and its vapour pressure lower, so that the advantages and disadvantages have to be balanced according to the envisaged use. All three have been used in the electrochemical study of porphyrins (Kadish and Anderson 1987). Solvents with relative permittivities lower than 5 such as benzene, toluene, xylene, and anisole, among solvents on the List, as well as polyaromatic solvents, such as naphthalene, phenanthrene, biphenyl and terphenyl, have also found applications, since they are electrochemically very inert, with electrochemical windows (see Chapter 4) of 4 V (Abbott 1993).

Polarography and voltammetry have been very widely used in electroanalytical methods for the determination of the concentrations of inorganic, organic, and organometallic compounds. Whereas many inorganic compounds are being studied in aqueous solutions, non-aqueous solvents are finding ever widening uses for such determinations, in particular for complexes and chelates, organometallic species, and organic compounds. Solubility considerations are major causes for preferring the non-aqueous solvents, as well as avoidance of undesirable hydrolysis reactions that may take place when aqueous solutions are employed. Although some poorly solvating solvents have been used, as mentioned above, the major applications are of strongly solvating solvents. Some of the more popular solvents, each having its advantages and drawbacks, are: methanol, ethanol, glycerol, 1, 2-dimethoxyethane, tetrahydrofuran, 1,4-dioxane, acetone, formic acid, acetic acid, propylene carbonate, 4-butyrolactone, 1,2-diaminoethane, pyridine, morpholine, acetonitrile, nitromethane, formamide, N-methylformamide, N,N-dimethylformamide, acetamide, N-methylacetamide, N-methylpyrrolidinone, tetramethylurea, dimethylsulfoxide, sulfolane, hexamethyl phosphoramide, ammonia, and sulfur dioxide, among the solvents on the List. Their properties, with respect to their electroanalytical uses, have been discussed (Mann 1969). In particular, the half-wave potentials of cations in a large number of non-aqueous solvents, including most of the above as well as the sulfur donor atom containing solvents on the List, such as N-methylthiopyrrolidinone, N,N-dimethylthioformamide, hexamethyl thiophosphoramide, and 2,2′-thiobisethanol, have been reported (Gritzner 1986). Table 5.2 lists the half-wave potentials. $E_{1/2}$ in V, for 8 representative cations and the standard electrode potentials, E^{o}, for Ag^{+} and Hg^{2+}, against the bis(biphenyl)chromium(I)/(0) reference electrode and with a 0.01 mol dm^{-3} tetrabutylammonium perchlorate supporting electrolyte (0.1 mol dm^{-3} for Ag^{+} and Hg^{2}) at 25°C.

The solvents used for electroanalytical determinations vary widely in their physical properties: liquid ranges (e.g., acetamide, N-methyl-acetamide and sulfolane are liquid only above ambient temperatures), vapour pressures (Table 3.1), relative permittivities (Table 3.5), viscosities (Table 3.9), and chemical properties, such as electron pair and hydrogen bond donicities (Table 4.3), dissolving ability of the required supporting electrolyte to provide adequate conductivity, and electrochemical potential windows (Table 4.8). A suitable solvent can therefore generally be found among them that fits the electroanalytical problem to be solved.

4—
Applications in Organic Chemistry

Perusal of Table 5.1 shows that for many applications, substances that are nominally solvents are employed as reagents or as catalysts, but they may fulfill their function as solvents at the same time. Such applications are not discussed

Table 5.2 Polarographic half-wave potentials, $E_{1/2}$ in V, against the bis(biphenyl)-chromium(I)/(0) reference electrode and with a tetrabutylammonium perchlorate supporting electrolyte at 25 °C (Gritzner 1986)

No.	Name	Li^+	Na^+	K^+	Cu^+	Ag^+	Cu^+	Zn^{2+}	Cd^{2+}	Hg^{2+}	Pb^{2+}
240	methanol	-1.49	-1.22	-1.24		1.34	0.96	-0.40	0.28		0.47
250	ethanol	-1.46	-1.17	-1.18		1.28	0.94	-0.18	0.22	1.35	0.52
260	1-propanol	-1.43	-1.12	-1.13		1.29	1.00		0.29		0.54
280	1-butanol	-1.40	-1.09	-1.10		1.33	1.02		0.45		0.62
350	1-hexanol	-1.41	-1.10			1.34			0.37		0.51
410	2-phenylethanol					1.33	1.09	0.19	0.45		0.65
450	2,2,2-trifluoroethanol					1.75	1.60		0.90		0.98
490	1,2-ethanediol					1.22	0.65	-0.36	0.27		0.41
740	tetrahydrofuran	-1.44	-1.25	-1.20		1.30	0.82	-0.05	0.32	1.37	0.51
890	benzaldehyde					1.44	1.21	0.29	0.60		0.65
920	acetone	-1.40	-1.22	-1.28	1.02	1.32	1.23	0.13	0.51		0.71
1120	formic acid					1.56	1.42		0.72		0.84
1130	acetic acid					1.49	1.28		0.57		0.72
1360	propylene carbonate	-1.25	-1.07	-1.19		1.51	1.25	0.21	0.64	1.61	0.69
1450	4-butyrolactone	-1.34	-1.17	-1.26		1.36	1.13	0.14	0.51		
1540	dichloromethane					1.56	1.36				0.80
1560	1,2-dichloroethane					1.50					0.71
1820	pyrrole	-0.76	-1.75	-0.76	0.85	0.97		0.18	0.55		0.66
1880	aniline	-1.04	-0.87		0.55	0.89		0.00	0.28		0.49
1950	pyridine	-1.43	-1.20	-1.23		0.61		-0.31	0.03	0.78	0.34
2070	acetonitrile	-1.20	-1.12	-1.22	0.42	1.03		0.10	0.46	1.34	0.69
2080	propionitrile		-1.03		0.41	1.03			0.47	1.42	0.67

2090	butyronitrile		-1.10		0.44	1.06	0.14	0.47	1.43	0.69
2120	benzyl cyanide	-1.11	-1.05	0.51	0.51	1.14	0.20	0.56	1.47	0.73
2130	benzonitrile	-1.12	-1.04	-1.13	0.50	1.11	0.24	0.54	1.45	0.70
2140	nitromethane				1.03	1.57	0.50	0.82	1.69	0.85

continued overleaf

***Table 5.2** (continued)*

No.	Name	Li^+	Na^+	K^+	Cu^+	Ag^+	Cu^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}	Pb^{2+}
2180	nitrobenzene					1.55	1.39	0.59	0.78	1.60	0.81
2190	formamide				0.72	1.20	0.86		0.16		0.39
2200	N-methylformamide	-1.66	-1.32	-1.33		1.12	0.72	-0.39	0.13		0.28
2210	N,N-dimethylformamide	-1.62	-1.35	-1.37		1.11	0.71	-0.29	0.13	1.14	0.27
2220	N,N-dimethylthioformamide	-0.97	-0.91	-1.02	-0.00	0.26		-0.24	0.05	0.50	0.28
2230	N,N-diethylformamide	-1.62	-1.33	-1.35		1.14	0.72	-0.29	0.14		0.27
2250	N,N-dimethylacetamide	-1.69	-1.38	-1.40		1.03	0.73	-1.23	0.13		0.26
2260	N,N-diethyl acetamide	-1.77	-1.38	-1.38		1.03	0.74	-0.23	0.11		0.27
2280	N-methylpyrrolidinone	-1.70	-1.37	-1.41		1.03	0.75	-0.25	0.12	1.12	0.27
2290	N-methylthiopyrrolidinone	-1.03	-0.94	-1.03	-0.1	0.18		-0.25	0.06	0.45	0.27
2300	tetramethylurea	-1.76	-1.39	-1.40	0.77	1.04	0.95	-0.14	0.25		0.22
2400	dimethyl sulfoxide	-1.86	-1.37	-1.40	0.60	0.96	0.72	-0.37	0.02	1.02	0.18
2420	sulfolane (at 303 K)	-1.26	-1.15	-1.25		1.35	1.23	0.28	0.58		0.64
2430	thiobis(2-ethanol)					0.69	0.41	-0.01	0.32	0.98	0.44
2480	trimethyl phosphate	-1.72	-1.37	-1.36		1.18	0.93	-0.12	0.21	1.29	0.34
2510	hexamethyl phosphoramide		-1.52	-1.42		0.89	0.55	-0.70	0.05	0.93	0.16
2520	hexamethylthiophosphoramide	-1.07	-0.81		0.20	0.44	0.55	-0.33	0.25	0.70	0.44

further here. What is discussed is the use of solvents in order to bring reactants into solution, constituting the reaction medium, and permitting subsequent isolation of the products, without themselves being consumed or modified. A major source of information on this subject is the book by (Reichardt 1988), and only some aspects of it are discussed here.

The choice of the solvent as the reaction medium depends on its ability to allow sufficient concentrations of the reactants to be achieved (solubility requirements) solvating them to an extent commensurate with the desired reactivity of the reactants. At the same time it also depends on the solvent being inert with respect to them and the reaction products, so that it is not itself attacked. Further considerations are the ease with which the products are liberated from excess reactants, if present, and from the solvent itself, possible effects on the relative yields of desired products and undesired by-products, and effects on the rates at which the reactions proceed, see Chapter 2.

The general rule for organic or non-electrolyte inorganic solutes, whether gaseous, liquid, or solid, is that they would show adequate solubilities when their solubility parameters δ are within 4 $J^{1/2}$ $cm^{-3/2}$ of that of the solvent. Values of the latter for the solvents on the List are shown in Table 3.1. Expressions for the estimation of solubilities are presented in Chapter 2. The effects on the rate of reactions have also been discussed there, and it is instructive to compare rates of reactions in various classes of solvents. For instance, the rates of bimolecular aromatic nucleophilic substitutions S_N2 of 4-fluoronitrobenzene with the azide anion (Miller and Parker 1961) in protic and aprotic solvents are shown in Table 5.3. The protic or protogenic solvents with appreciable values of α (Table 4.3), solvate the incoming azide anion strongly and decrease its reactivity, so that the reaction proceeds slowly, whereas the aprotic solvents, solvating the anion only through ion-dipole interactions, permit a much faster reaction. The solvation of the negatively charged transition state must, of course, also be taken into

Table 5.3 Rate constants for bimolecular reactions of $FC_6H_4NO_2$ with N^{-3} in various solvents (Miller and Parker 1961)

Solvent	$k_2 \times 10^4$ mol^{-1} s^{-1} at 25°C	$k_2 \times 10^4$ mol^{-1} s^{-1} at 100°C
methanol	0.00067	2.28
N-methylformamide		36.0
nitromethane	1.84	
acetonitrile	5.4	
dimethylsulfoxide	5.68	
benzonitrile	12.5	
nitrobenzene	16.3	
N,N-dimethylformamide	16.3	11 100
N,N-dimethylacetamide	59.0	
acetone	>48	

account, whereas that of the organic substrate, being less polar than the transition state, may be less important.

The stronger the solvating ability of a solvent is, the more it decreases the thermodynamic activity of the reactants and their reactivity, i.e., their availability for the reaction. A linear correlation has been found between the activation Gibbs free energy (Figure 2.2) of a series of S_N2 reactions and the acceptor number *AN* of the solvents involved (Table 4.3) (Parker *et al*. 1978), see Figure 5.1. Similar considerations apply to the choice of a solvent for S_N1 solvolysis reactions, e.g., the solvolysis of *t*-butyl halides. Here a negative linear correlation between the activation energies of reactions in series of solvents and the acceptor numbers *AN* of the latter has been established (Parker *et al*. 1978) (Figure 5.1). In these cases, the transition state does not have a net charge, but it is highly polar and the leaving group is an anion.

If a salt with a large organic cation e.g., tetraethylammonium rather than a small cation e.g., sodium, can be used, the importance of the solubility consideration becomes smaller (Miller and Parker 1961). A balance must be struck between the solubility of the reactant salt and the availability of the anion for the reaction: the former decreasing, the latter increasing, as the hydrogen bond donation ability of the solvent diminishes.

The choice of solvents as reaction media thus depends, through their solvating

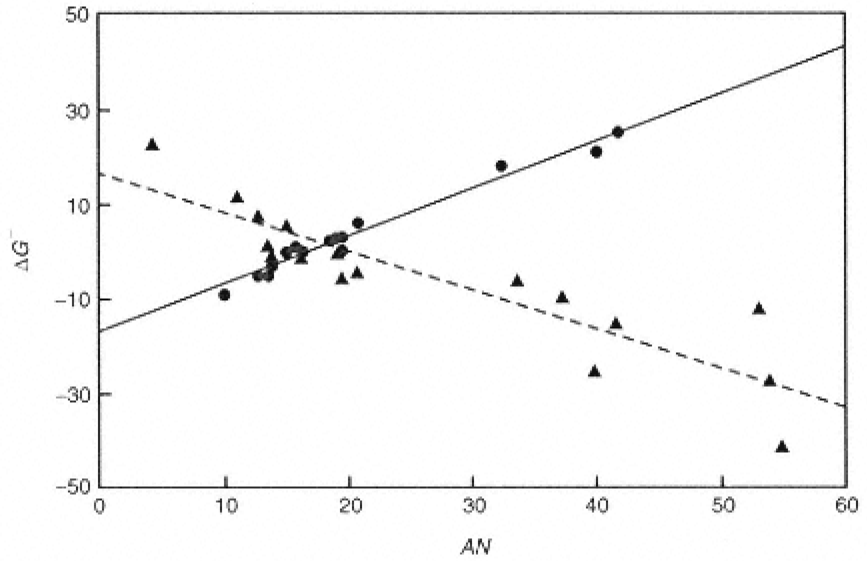

Figure 5.1
The activation energy, $\Delta G^{\neq}$/kJ mol^{-1}, of the S_N2 replacement of fluoride by azide on 4-nitrofluorobenzene (circles, continuous line) and the S_N1 solvolysis of *t*-butyl chloride (triangles, dashed line) as a function of the acceptor number, *AN*, of the solvent (Parker *et al*. 1978)

abilities, on solubilities, effects on reaction rates and positions of equilibria. When inert solvents are to be used, the choice is on the aliphatic hydrocarbons, mainly *n*-hexane and *c*-hexane, due to their convenient physical characteristics. Non-polar organic substances are soluble in these hydrocarbons to some extent, polar ones much less so. The latter e.g., long-chain alkylammonium salts, may aggregate in such solvents to inverted micelles or other structures. The alternatives, providing higher solubilities but still low or moderate solvation, are aromatic hydrocarbons or halogen-substituted aliphatic hydrocarbons. Among the former, benzene is no longer employed much as a solvent due to the carcinogenic properties ascribed to it, so alkylbenzenes are the solvents used. The higher polarizabilities, n_D in Table 3.5 or π^* in Table 4.3, as well as the higher solubility parameters δ (Table 3.1) of these solvents permit the dissolution of polar substances as described in Chapter 2. Still, these solvents have sufficiently low electron-pair donicities (β in Table 4.3) and negligible hydrogen bond donation abilities (α in Table 4.3, except for chloroform and a few similar solvents) to cause only weak solvation, leaving reactants to be relatively reactive.

Reagents that are themselves too polar, or of electrolytic nature, to be dissolved in such non-polar or slightly polar solvents can often be employed by the use of a phase-transfer catalyst. The reagent is dissolved in a second, immiscible, and polar solvent, generally water, in contact with the reaction medium, and the catalyst is used to convey it to the non-polar organic phase for the reaction. Such phase-transfer catalysts consist mostly of salts with long-alkyl-chain-substituted ammonium cations with altogether 12–28 carbon atoms in the 1 to 4 chains, that are soluble both in water and in the non-polar organic phase. Phase-transfer catalysis has also been applied to reactions in supercritical solvents, for instance for bromination of benzyl chloride with potassium bromide in supercritical carbon dioxide with acetone cosolvent using tetraheptylammonium bromide as the catalyst (Eckert, Knutson and Debenedetti 1996).

The use of various solvents as reaction media for diverse reactions is summarized in Table 5.4 (after Reichardt 1988).

Further considerations pertain to the recovery of the reaction products after its completion. Crystallization of the reaction product may be induced if to the reaction medium, in which it is well soluble, a co-solvent is added in which the product is insoluble. Such combinations may also be used for the recrystallization of the crude product. Since for the latter purification method the solubility should be high at high temperatures but much lower at low temperatures, the temperature coefficient of the solubility becomes an important criterion for the employment of a solvent. Little general guidance on this point can be given, in view of the temperature T appearing in the denominators of both terms of opposite signs in expressions such as (2.15). The impurities need to be retained in the solution at all temperatures. The solvent should be either well volatile, so that it is readily removed from the purified crystals, or else washable away by means of a further, volatile, solvent, in which the crystals remain insoluble. None

Table 5.4 Solvents as reaction media (after Reichardt 1988)

Reaction	Suggested solvents
halogenation	acetic acid, o-dichlorobenzene, CCl_4, nitrobenzene
nitration	acetic acid, CH_2Cl_2, o-dichlorobenzene, CCl_4, nitrobenzene, sulfuric acid
sulfonation	heptane, 1,4-dioxane, acetic acid, chloroform, CCl_4, nitrobenzene, sulfuric acid
diazotization	benzene, water, ethanol, acetic acid, DMF[a], sulfuric acid
ozonization	methanol, acetic acid, ethyl acetate, CH_2Cl_2, 1,2-dichloroethane, chloroform, CCl_4
epoxidation	benzene, diethyl ether, 1,4-dioxane, acetone, acetic acid, chloroform, CCl_4
oxidation	benzene, water, t-butanol, 1,4-dioxane, acetic acid, ethyl acetate, CH_2Cl_2, $CHCl_3$, pyridine, nitrobenzene, sulfolane, sulfuric acid
hydride reduction	benzene, toluene, diethyl ether, DME[b], tetrahydrofuran, 1,4-dioxane
hydrogenation	c-hexane, heptane, water, methanol, ethanol, tetrahydrofuran, 1,4-dioxane, acetic acid, ethyl acetate, DMF[a]
aldol reaction	benzene, toluene, water, methanol, ethanol, diethyl ether, DME[b], tetrahydrofuran, acetic acid, pyridine, dimethylsulfoxide
Wittig reaction	benzene, toluene, methanol, ethanol, t-butanol, diethyl ether, DME[b], tetrahydrofuran, acetic acid, CH_2Cl_2, pyridine, acetonitrile, DMF[a], dimethylsulfoxide
Diels-Alder reaction	benzene, toluene, water, methanol, ethanol, diethyl ether, tetrahydrofuran, 1,4-dioxane, acetone, CH_2Cl_2, 1,2-dichloroethane, o-dichlorobenzene, chloroform, acetonitrile,
Grinard reaction	diethyl ether, tetrahydrofuran
Friedel-Crafts reaction	heptane, CH_2Cl_2, 1,2-dichloroethane, o-dichlorobenzene, nitrobenzene, carbon disulfide, sulfolane
S_N1 reactions	water, methanol, ethanol, t-butanol, acetic acid,
S_N2 reaction	acetone, acetonitrile, DMF[a], dimethylsulfoxide, sulfolane

[a]N,N-dimethylformamide, [b]1,2-dimethoxyethane

of the solvents should form crystal solvates with the product. Although Table 4.6 pertains to solvents, the 'miscibility' column can provide a guide to the solubility of organic substances with quite diverse functional groups, whether liquid or crystalline. A further guide is the fact that substances tend to dissolve in solvents with similar polarities, so that a solvent and co-solvent for the recrystallization of a given product can be selected according to the polarities in Table 4.3 (as well as the solubility parameters in Table 3.1).

A further major application of solvents in organic chemistry is in HPLC, for the chromatographic separation of solutes, be it for preparative or analytical purposes. The effectivity of a solvent as an eluant in HPLC depends on its competition with the solutes for active sites on the stationary phase. If the latter is an oxide, such as silica or alumina, then the more polar the solvent, the better is its competitive power. The polarity is measured by $E_T(30)$ or E_T^N (Table 4.3), and solvents can be ordered in an 'eluotropic series' according to increasing values of these parameters. If the stationary phase is charcoal or silanized silica the eluotropic series is reversed. Among further solvent properties that ought to be considered when a solvent for HPLC is selected is its viscosity (Table 3.9), which should be low, and its suitability for the monitoring of the progress of the elution, e.g., by UV spectrometry, for which method a suitable window where the solvent itself does not absorb must be available (Table 4.8). Also supercritical fluids have been used in HPLC separations, where the properties of the eluant can be fine-tuned to the needs (Schoenmakers and Uunk 1989).

5—
Applications in Polymer Science and Technology

Many of the considerations discussed above in connection with organic chemistry are, of course, also valid for polymer technology. The aspects to be discussed here are solvents for polymers, used in such materials as paints and lacquers, and media for the polymerization reaction. A final deliberation pertains to certain biopolymers and polyelectrolytes, where the natural solvent is water, but where other solvents may also be useful in their study.

When polymers are used as constituents of coatings, paints, and lacquers they require solvents as dispersing agents. Whether true solutions are formed or emulsions, the solvents used have to conform to environmental specifications, but should be sufficiently volatile so as to permit rapid drying of the applied polymer and pigment, if present. If the polymers are to be present in a true, molecularly dispersed solution, they cannot have an excessively high molecular weight nor be extensively crosslinked. For the specification of the composition of polymer solutions the mass fraction w or volume fraction φ, ignoring volumes of mixing, is used (see Section 2) instead of the mole fraction, since the latter is negligible due to the high molar mass of the polymer relative to that of the solvent. If the mass fraction is > 5% it is better to consider the 'solvent' as dissolved in the polymer rather than vice versa, so that a swollen polymer or a gel results.

Due again to the high molar mass M_2 of the polymers, the entropy of their dissolution is given by the Flory-Huggins expression:

$$\Delta S_2 = -R[\ln \varphi_2 + \varphi_1(1 - V_2/V_1)] \qquad (5.1)$$

where as in Section 2 the subscripts 1 and 2 pertain to the solvent and solute, respectively, and V_2 can be approximated by M_2/d_{monomer}. The heat of solution is given by a regular-solution-type expression:

$$\Delta_{\mathrm{solution}} H_2 = \chi V_2 \varphi_1^2 \qquad (5.2)$$

where χ is the interaction parameter. As a result of these considerations, a valid guide to the solubility of polymers is their solubility parameters, since according to Eq. (2.15) the solubility decreases with increasing differences of the δ values of the solute and solvent. Table 5.5 lists solubility parameters of common polymers (Shinoda 1978), from non-polar to highly polar, and those of solvents on the List are given in Table 3.1.

Polymers of sufficiently high molecular weight, and in particular if they are crosslinked, are insoluble in the common solvents but they do swell in them. That is, the liquid solvent enters the macromolecular network, being adsorbed on any functional groups the latter contains, and stretching the network against its elastic forces to an equilibrium state. Following is a discussion of the swelling of polystyrene crosslinked by divinylbenzene that constitutes a mole fraction x of the copolymer. The average number of carbon atoms in the polymer backbone between crosslinking points is $\lambda = (1 + x)/x$, and beyond or below a limiting value of this number, λ_0, no more solvent can be imbibed by the tightly crosslinked polymer. It has been shown (Errede 1989) that the relative swelling power C (in cm^3 g^{-1}) is given by the expression:

$$C = S/(\lambda^{1/3} - \lambda_0^{1/3}) \qquad (5.3)$$

where S is the volume of solvent (in cm^3 g^{-1}) sorbed by the styrene-divinylbenzene copolymer at saturation. The number α of moles of solvent sorbed per phenyl group in the copolymer is given by:

$$\alpha = 104C/V \qquad (5.4)$$

where 104 g mol^{-1} is the molar mass of styrene and V is the molar volume of the swelling solvent. Values of α can be determined to ±0.01, varying between 0 and 3.5, and reflect the affinity of the functional group of the solvent to the phenyl ring on the one hand and the steric hindrance due to the molecular bulk of the solvent on the other. It was also shown (Errede 1989) that the Flory-Huggins interaction parameter χ at solvent volume fractions φ in the solvent-copolymer system is given by:

$$\chi = 1.50 - 1.01\varphi - 0.005\,87V\alpha(1 - \varphi) \qquad (5.5)$$

Table 5.5 The solubility parameters, δ/J$^{1/2}$ cm$^{-3/2}$, of polymers (Shinoda 1978).

Polymer	δ	Polymer	δ
polytetrafluoroethylene	12.3	polymethylmethacrylate	19.4
polydimethylsilicone	14.9	polyvinyl acetate	19.6
polyethylene	16.1	polyglycol terephthalate	21.9
polyisobutene	16.5	polymethacrylonitrile	21.9
polybutadiene	17.4	cellulose diacetate	22.3
polystyrene	18.6	poly-1,6-diaminohexane adipamide	27.8
polyvinyl acetate	19.2	polyacrylonitrile	31.5

is valid for these particular copolymers. The thermodynamic functions of the system may be deduced from this expression, giving the parameter χ. The smaller the interaction parameter, the more nearly ideally the system behaves. The limiting value of the Flory-Huggins parameter at low solvent volume fractions is $\chi_0 = 1.50 - 0.00587V\alpha$. Hence the values of α are seen to be important quantities for the swelling and thermodynamic behaviour of the copolymersolvent systems, and Table 5.6 shows α and χ_0 value at 23°C for solvents on the List. The values of the swelling power, *C*, are linear functions of the square of the difference of the solubility parameters of styrene and the solvent in question, but the coefficients of this expression depend on the solvent class (Errede 1989).

Polymerization of suitable monomers takes place according to one or more of several catalyzed mechanisms: anionic, cationic, free radical, or with Ziegler-Natta catalysts. The steps involved are initiation of the polymerization, propagation by the addition of monomers to shorter, reactive polymers or oligomers, and termination of the polymer chain growth. Appropriate media are employed: the bulk liquid monomer or its melt, a solution of it, or its suspension/emulsion. In the cases where a solution is used, the solvent should dissolve the monomer as well as the growing oligomers to a high degree, but the polymer may become insoluble when it reaches a sufficient molecular weight. This is the case for the polymerization of perfluorinated monomers in supercritical carbon dioxide (Eckert, Knutson and Debenedetti 1996). When a solvent is used its main roles are to decrease the viscosity of the reaction mixture and to remove the heat evolved in the reaction by virtue of its heat capacity and heat transfer properties. Some examples of solution polymerizations are those of ethylene in liquid alkanes or in supercritical fluid ethylene (Table 3.3), polycarbonates prepared in dichloromethane, polyimides prepared in N,N-dimethyl- acetamide or N-methyl-pyrrolidinone, or polymethacrylates prepared in esters, ketones, or aromatic or chloro-hydrocarbons. These solvents are specified in view of the solubilities and reactivities of the polymerizing species and take into account the mechanisms according to which chain initiation, propagation, and termination proceed.

For instance, in cases where the mechanism of the propagation of the polymer chain is by means of cationic polymerization, the rate increases with the polarity of the solvent. Thus, when the boron trifluoride-diethyl ether complex is used as the catalyst for styrene polymerization, then at 0°C the rate equation for a series of solvents takes the simple form of dependence on the solvent polarity (Heublein 1985):

$$\log k = -5.9 + 0.1E_T(30) \qquad (5.6)$$

and in the copolymerization of isobutene with *p*-chlorostyrene with aluminium tribromide catalyst the r_1 rate values are 1.1 in *n*-hexane, 1.14 in styrene, 2.80 in dichloroethylene, 14.9 in nitrobenzene, and 22.2 in nitromethane (Overberger and Kamath 1963).

The solvent of choice for biopolymers - polymeric carbohydrates, proteins,

Table 5.6 The number α of solvent molecules sorbed per phenyl group and the limiting Flory-Huggins parameter χ_0 for polystyrene-divinylbenzene copolymers-solvent systems (Errede 1989)

Solvent	α	χ_0
n-hexane	< 0.10	> 1.42
cyclohexane	0.56	1.18
n-decane	< 0.01	1.50
benzene	2.50	0.20
toluene	1.98	0.27
o-xylene	1.74	0.27
m-xylene	1.53	0.40
p-xylene	1.46	0.44
ethylbenzene	1.55	0.39
cumene	1.23	0.49
tetralin	1.69	0.15
cis-decalin	0.68	0.89
1-hexanol	< 0.01	1.50
cyclohexanol	0.47	1.21
benzyl alcohol	0.83	1.00
ethylene glycol	0	1.50
diethyl ether	0.64	1.11
di-n-bytyl ether	0.30	1.19
tetrahydrofuran	2.57	0.28
tetrahydropyran	2.21	0.23
1,4-dioxane	2.10	0.43
anisole	1.84	0.28
2-butanone	1.28	0.82
2-pentanone	1.35	0.66
3-pentanone	1.50	0.57
cyclopentanone	2.29	0.31
2-heptanone	1.09	0.67
acetophenone	1.68	0.35
methyl acetate	1.13	0.97
ethyl acetate	1.20	0.81
propyl acetate	1.20	0.69
butyl acetate	1.16	0.61
fluorobenzene	2.19	0.29
1-chlorobutane	1.55	0.65

chlorobenzene	2.23	0.17
dichloromethane	3.24	0.29
1,1-dichloroethane	2.10	0.52
1,2-dichloroethane	2.39	0.41
o-dichlorobenzene	1.80	0.31
m-dichlorobenzene	1.87	0.25
chloroform	2.99	0.08
1,1,2-trichloroethane	2.28	0.25
tetrachloromethane	2.12	0.30
1,1,2,2-tetrachloroethane	2.28	0.10
tetrachloroethylene	2.02	0.30

(table continues on next page)

***Table 5.6** (continued)*

Solvent	α	χ_0
1-bromobutane	1.68	0.44
bromobenzene	2.04	0.24
iodobenzene	1.75	0.36
aniline	1.70	0.59
N,N-dimethylaniline	1.84	0.13
pyridine	2.11	0.50
nitrobenzene	1.14	0.47
carbon disulfide	3.37	0.31

nucleic acids, etc., is of course water. This is also the solvent of choice for synthetic polyelectrolytes. The special features of water for such applications are discussed in the next section. However, such polymers, although highly hydrophilic and possibly carrying charges in polyelectrolytes, such as polymethymethacrylic acid, and in proteins in the $-NH_3^+$ or $-CO_2^-$ side groups, can also be dissolved in polar solvents, such as N,N-dimethylformamide or dimethylsulfoxide. In fact, the backbone of a protein consists of repeating -C(=O)N(H)-groups and can be likened to a monosubstituted amide solvent, in which the side groups, whether ionogenic e.g., of glutamic acid or arginine, polar e.g., of serine, or nonpolar e.g., of isoleucine, are dissolved. In view of the paucity of water in the interior or coiled proteins, and therefore the unimportance of the water structure that is the main cause of hydrophobicity, the 'CONHphobicity' of apolar side chains of the protein appears to play a more important role than their hydrophobicity in determining the structure (Bloemendal *et al*. 1989).

A polyelectrolyte shows a 'polyelectrolyte effect' when there is an increase in the reduced viscosity of its solution, $(\eta - \eta_0)/c$, when its is diluted. This effect is due to ionized groups repelling each other in the dilute solution, causing elongation of the polyelectrolyte, i.e., extension of its coiled form, thus causing increased viscosity. At higher concentrations the ion pairing of the ionic groups fixed on the polymer backbone with the counter ions causes shielding of the charges, as is attained by the addition of a simple salt, and a lowering of the reduced viscosity. It was shown that for the sodium salt of lightly sulfonated, 1.7 to 6.0 mol%, polystyrene, NaSPS, the polyelectrolyte effect is manifested in solutions of the more polar solvents dimethylsulfoxide, N,N-dimethylformamide (DMF), and 2-methoxyethanol, but not in the less polar ones cyclohexanone, tetrahydrofuran (THF) and 1,4-dioxane. This behaviour was explained in terms of the former solvents solvating the ions well, hence causing electrostatic repulsion and chain elongation, whereas the latter solvating them less well, permitting ion pairing and shielding of the charges (Lundberg and Phillips 1982). Similar effects were shown by NaSPS in DMF whether the degree of sulfonation was high or low and irrespective of the molecular weight of the polymer (3500–400000 g mol^{-1}), but in THF the effect was observed in the more highly sulfonated high molecular weight samples of 40–200 ionic groups per chain (Hara, Wu and Lee 1988). Short polymers with ionic groups only at the two ends of the chain also exhibit such behaviour in DMF and in 1-butanol, and small angle light and neutron scattering, in xylene solutions of NaSPS showed an equilibrium between intra- and intermolecular association due to ion pairing (Pedley *et al*. 1990).

6—
Special Features of Water As Solvent

The physical and some chemical properties of water are shown in Table 3.11 and in many other tables in this book where it is possible to compare them with those of other solvents. It is clear that water has some features that make its use as a solvent fairly unique. It has a very small size, Table 3.4, that enables many water molecules to surround a given solute and solvate it without crowding. It has a large polarity index $E_T(30)$, polarity/polarizability parameter π^*, and hydrogen bond donation ability α, Table 3.5, that permit it to solvate strongly polar solutes, especially those carrying a negative charge or having a large Lewis basicity. It is highly structured by a network of hydrogen bonds, Table 3.1, that demands a high input of work for the creation of a cavity to accommodate a solute. It has a high relative permittivity ε, that enables electrolytes to dissociate completely. It must be realized, however, that in all these features water, among the solvents on the List, does not necessarily have the extreme values of the properties. Hydrogen fluoride is smaller than water, phenols, and fluoroalkanols have larger α values, ethylene carbonate, formamide, and N-methyl formamide have larger ε values, and alkanepolyols have larger entropy deficits, denoting structuredness, than water. Other properties of water are far from extreme: the liquid range, between the freezing and normal boiling point, the electrochemical window, Table 4.8, density, volatility, molar heats of vaporization and heat capacity, Table 3.1, and viscosity, Table 3.9, the electron pair donicity (Lewis basicity) β or *DN*, Table 3.5, gas phase proton affinity and acidity as well as autoprotolysis constant, Table 3.6. It is its readily availability and its relative ease of purification as well as its non-toxicity and non-flammability, and of course its unique role in physiological processes, in addition to the properties listed above, that make water such a widely used solvent. It is, therefore, justified to have listed in this book the acid and base dissociation constants in aqueous solutions, Table 4.5, the mutual solubilities with other solvents, Table 4.6, and the octanol/water distribution constants, Table 4.6, all pertaining specifically to water as the solvent.

A class of solutions where the combined properties of water make it a rather unique solvent is micellar solutions. These solutions arise from the dissolution of surfactants in water at above a certain concentration (the critical micelle concentration, *CMC*). The micelles are structures that contain a few tens to a few hundreds of surfactant molecules, arranged so as to have the hydrophobic long chains, 'tails', directed towards the inside of the micelle and the hydrophilic 'heads' pointing outwards, constituting the surface of the micelle. The surfactants in question may be non-ionic, such as polyoxyethylene alkylethers $H(CH_2)_n(OC_2H_4)_mOH$ with n typically 6–16 and m 4–6, and dimethylalkylamine oxides, $H(CH_2)_nN(CH_3)_2O$ with n typically 10–14. They may also be ionic, either cationic, such as alkyl sulfates $H(CH_2)_{12}SO_4^-M^+$, alkylsulfonates $H(CH_2)_{12}SO_3^-M^+$, or *p*-alkylbenzenesulfonates $H(CH_2)_{12}C_6H_5SO_3^-M^+$, or alkyl caboxylates $H(CH_2)_nCO_2^-M^+$ with n typically 7–15 and M^+ an alkali metal cation, generally sodium, or they may be anionic, such as $H(CH_2)_{12}NH_3^+Cl^-$ or $H(CH_2)_{12}N(CH_3)_3^+Cl^-$. The alkyl chains need not be normal i.e., they may be branched, and may be fluorine-substituted. Some natural surfactants are also of importance: e.g., lecithins such as 1,2-diacyl glycero-3-phosphate, with the acyl groups being $H(CH_2)_nCO$ and n typically 12–18, the latter possibly oleyl, i.e., unsaturated.

The micelles are generally spherical when containing a few tens of surfactant molecules but rod-like, prolate, or disc-like, oblate, when their number exceeds one hundred, due to crowding of the 'tails' in the interior of a spherical micelle. Generally micelles in aqueous solutions can be considered as microdispersed separate phases, in the thermodynamic sense, since they are formed as it were in a single step to give the average aggregation number, rather than in a gradual stepwise manner. This is deduced from the existence of the *CMC* and the abrupt change of properties, such as the surface tension of the solution, beyond that concentration of surfactant, to become independent of the concentration. That is, the number of micelles increases when more surfactant is added to the solution, but the concentration of monomers remains constant, so that its chemical potential, the thermodynamic activity of the surfactant, does so too. On the other hand, the aggregation number, a few tens to a few hundreds, is finite, so that no true phase separation takes place, and the solution is macroscopically homogeneous, transparent and isotropic. Micelles are capable of solubilizing hydrophobic, that is, lipophilic, substances in their interior, permitting their microdispersion in the solution. All these properties of micelles are, on the whole, unique for water as the solvent, due to its high cohesive energy density and structuredness (Chapter 4).

It may be expected that other, highly structured solvents with a tri-dimensional network of strong hydrogen bonds, would also permit micelle formation by surfactants, but little evidence of such occurrences has been reported. On the other hand, surfactants in non-polar solvents, aliphatic or aromatic hydrocarbons and halocarbons tend to form so-called inverted micelles, but these aggregate in a stepwise manner rather than all at once to a definite average size. In these inverted micelles, formed, e.g., by long-chain alkylammonium salts or dinonyl-naphthalene sulfonates, the hydrophilic 'heads' are oriented towards the interior, the alkyl chains, 'tails', towards the exterior of the micelles (Shinoda 1978). Water and hydrophilic solutes may be solubilized in these inverted micelles in nonpolar solvents, such as hydrocarbons.

Another feature, unique to water as a solvent, is the formation of clathrate-like structures around hydrophobic solutes, when they dissolve to yield very dilute solutions. These structures, of course, are not as robust as the crystalline clathrates of the noble gases and the light hydrocarbons, but have average lifetimes longer than clathrate-like water clusters in neat bulk water. Pentagonal dodecahedra are the geometric form that the structures take, for instance in the crystalline methane clathrate, CH_4 ((23/4)H_2O, and such structures are said to be present also in liquid water and in solutions of methane in water (Pauling 1957). This notion has been criticized as being oversimplified, certainly being so in terms of the number of water molecules involved and their precise structure. However, the qualitative depiction of such an assembly of water molecules around hydrophobic solutes in dilute solution may be valid. In the formation of such structures water appears to be unique.

Finally, in its acid-base behaviour water shows some special features. Water is like other protic solvents, mainly alkanols and polyols, in being amphoteric. It is able to deliver protons to more basic solutes and accept them from more acidic ones, as well as donate hydrogen bonds to and accept them at the same time from suitable solutes. However, it differs from, say, methanol, in how much more 'free hydroxyl' groups it contains. The evidence comes from infrared and proton NMR studies of basic probes that are Lewis bases i.e. anions and aprotic solvents (Luck 1967). This issue of 'free hydroxyl' groups is controversial, however, as regards whether they exist at all and if they do, what their concentration is. A corollary of 'free hydroxyl' groups is the existence of 'free lone pairs' of electrons at the ends of the cooperative hydrogen bonded chains. There, again, the evidence comes from infrared and NMR studies with cations as probes. Water appears not to have more 'free lone pairs' than methanol (Luck 1967).

References

Abbott, A. (1993) *Chem. Soc. Rev*. **22**, 435.

Baniel A. and Blumberg, R. (1959) *Dechema Monographs* **33** 57; Baniel, A., Blumberg, R., Alon, A., El-Roy, M. and Goniadski, D. (1962) *Chem. Eng. Progr*:, **58** (11), 100 (phosphoric acid). Baniel, A. M., Blumberg, R. and Hajdu, K. *British Patent* 1 426 018 (1973); *European Patent* 0 049 429 (1982) (citric acid).

Beardmore F. S. and Kosters, W. C. G. (1963) *J. Inst. Petrol*. **49**, 1.

Bloemendal, M., Marcus, Y., Sijpkes, A. H. and Somsen, G. (1989) *Int. J. Peptide Protein Res*. **34**, 405.

Brunner G. and Peter, S. (1982) *Ger. Chem. Eng*. **5**, 181; Brunner, G. (1983) *Fluid Phase Equil.* **10**, 289; Brunner, G. (1988) in J. A. Marinsky and Y. Marcus, (eds.), *Ion Exchange and Solvent Extraction*, Dekker, New York, Vol. 10, p. 105.

Eckert, C. A., Knutson, B. L. and Debenedetti, P. G. (1996) *Nature* **383**, 313 (a review, see references therein).

Edler, A. L. (ed.), (1970) *Chem. Eng. Progr. Symp. Ser*., **66** (cf. Kirk-Othmer (1978)

Encyclopedia of Chemical Technology Wiley-Interscience, New York, 4th ed., vol. 10, p. 166).

Errede, L. A. (1989) *J. Phys. Chem*. **93**, 2668; Errede, L. A. (1992) *Polymer* **33**, 2168.

Gritzner, G. (1986) *J. Phys. Chem*. **90**, 5478; Gritzner, G. (1990) *Pure Appl. Chem*. **62**, 1839; Hörzenberger F. and Gritzner, G. (1993) *J. Chem. Soc., Faraday Trans*. **89**, 3557 (corrigenda: *ibid*. (1996) **92** 1083); Gritzner G. and Hörzenberger, F. (1995) *J. Chem. Soc., Faraday Trans*. **91**, 3843.

Hara, M., Wu, J.-L. and Lee, A. H. (1988) *Macromol*. **21**, 2214.

Heublein, G. (1985) *J. Macromol. Sci.-Chem*. **A22**, 1277.

Job, C., Schertler, C., Staudenbauer, W. L. and Blass, E. (1989) *Biotechnol. Tech*. **3**, 315.

Kadish K. M. and Anderson, J. E. (1987) *Pure Appl. Chem*. **59**, 703; Lançon D. and Kadish, K. M. (1983) *J. Am. Chem. Soc*. **105**, 5610.

Kertes, A. S., Zangen, M. and Schmuckler, G. (1992) in *Principles and Practices of Solvent Extraction*, J. Rydberg, C. Musikas and G. R. Choppin (eds.), Dekker, New York, pp. 520.

Kirk-Othmer, (1978) *Encyclopedia of Chemical Technology*, Wiley-Interscience, New York, 3rd ed., 1978 and 4th ed., 1991-7, vol. 22.

Kühn, I. (1980) *Biotechnol. Bioeng*., **22**, 2393.

Luck, W. A. P. (1967) *Disc. Faraday Soc*. **43**, 115; Oaks, J., Slater, J. and Symons, M. C. R. (1970) *Trans. Faraday Soc*. **66**, 546; Symons, M. C. R., Thomas, V. K., Fletcher, N. J. and Pay, N. G. (1981) *J. Chem. Soc., Faraday Trans. 1* **77**, 1899; Symons, M. C. R. (1983) *ibid*. **79**, 1273; Robinson H. L. and Symons, M. C. R. (1985) *ibid*. **81**, 2131.

Lundberg R. D. and Phillips, R. R. (1982) *J. Polym. Sci., Polym. Phys.* **20**, 1143.

Mackor, E. L., Hofstra, A. and van der Waals, J. H. (1958) *Trans. Faraday Soc*. **54**, 186; MacLean C. and Mackor E. L. (1962) *Disc. Faraday Soc*. **34**, 165; Marcus, Y., Shamir J. and Soriano, J. (1970) *J. Phys. Chem*., **74**, 133–139.

Marcus, Y. (1967) in *Solvent Extraction Chemistry* D. Dyrssen, J.-O. Liljenzin and J. Rydberg, (eds.), North-Holland Publ. Co. Amsterdam, pp. 555–580.

Marcus, Y (1986) *Ion Solvation*, Wiley Chichester, pp. 262–4.

Marcus, Y. (1997) *Ion Properties* Dekker, New York.

Mann, C. K. (1969) in A. J. Bard, (ed.), *Electroanalytical Chemistry*, Dekker, New York, Vol.3.

Miller J. and Parker, A. J. (1961) *J. Am. Chem. Soc.* **83**, 117; Alexander, R., Ko, E. C. F., Parker, A. J. and Broxton, T. J. (1968) *J. Am. Chem. Soc*. **90**, 5049.

Murata, K., Yokoyama, Y. and Ikeda, S. (1972) *Anal. Chem.*, **44**, 805; Hong, C.-S., Finston, H. L., Williams, E. T. and Kertes, A. S. (1979) *J. Inorg. Nucl. Chem*., **41**, 420.

Overberger C. G. and Kamath, V. G. (1963) *J. Am. Chem. Soc*. **85**,446.

Parker, A. J., Mayer, U., Schmid, R. and Gutmann, V. (1978) *J. Org. Chem*. **43**, 1843.

Pauling, L. (1957) *Trans. Intl. Conf. on the Hydrogen Bond*, Ljubljana; Pauling, L. (1960) *The Nature of the Chemical Bond*, 3rd ed., Cornell Univ. Press, Ithaca, N. Y.; Claussen, W. F. (1951) *J. Chem. Phys*. **19**, 1425; Claussen W. F. and Polglase, M. F. (1952) *J. Am. Chem. Soc*. **74**, 4817.

Pedley, A. M., Higgins, J. S., Peiffer, D. G. and Burchard, W. (1990) *Macromol*. **23**, 1434; Pedley, A. M., Higgins, J. S., Peiffer, D. G. and Rennie, A. R. (1990) *Macromol*. **23**, 2494; Hara, M., Wu, J.-L, Jerome, R. J. and Granville, M. (1988) *Macromol.* **21**, 3330; Hegedus R. D. and Lenz, R. W. (1988) *J. Polym. Sci., Polym. Chem*. **26**, 367.

Reichardt, Ch. (1988) *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, 2nd ed.

Rogers R. D. and Zhang, J. (1997) in J. A. Marinsky and Y. Marcus, (eds.), *Ion Exchange and Solvent Extraction* Dekker, New York, Vol. 13, 141.

Rydberg, J., Musikas, C. and Choppin, G. R. (eds.), (1992) *Principles and Practices of Solvent Extraction* Dekker, New York.

Schoenmakers P. J. and Uunk, L. G. M. (1989) in *Advances in Chromatography*, J. C. Giddings, E. Grushka, and P. R. Brown, (eds.), Dekker, New York, **30**, 1.

Shinoda, K. (1978) *Principles of Solution and Solubility* Dekker, New York.

Simandi, B., Sawinsky, J., Deak, A., Kemeny, S., Fekete, J., Kery, A., Then, M. and Lemberkowics, L. and Shibuya, Y., Ohinata, H., Yonei, Y. and Ono, T. (1993) *Solvent Extraction in the Process Industries*, D. H. Logsdail and M. J. Slater, (eds.), Elsevier, London, Vol. 2, 676 and 684.

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