Chemical Fate and Impact of Oxygenates in Groundwater: Solubility of BTEX from Gasoline–Oxygenate Mixtures

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EXECUTIVE SUMMARY

Oxygenate compounds such as ethers and alcohols have been increasingly added to gasoline to improve octane ratings and/or reduce vehicle emissions of pollutants such as carbon monoxide. The increased use of oxygenate additives has raised questions as to the effects of these additives on the water solubility of gasoline constituents such as benzene, toluene, ethylbenzene, and xylenes (collectively referred to as BTEX). In the event of a spill of an oxygenate fuel to groundwater the oxygenate may act as a cosolvent, dissolving higher concentrations of BTEX in the groundwater than would be dissolved from neat gasoline. This laboratory study was conducted to investigate the cosolubility effect of oxygenates. Oxygenates studied include methanol, methyl tertiary-butyl ether (MTBE), ethanol, tertiary-amyl methyl ether (TAME), and isopropyl ether.

This study was conducted as a component of a large-scale research effort to evaluate the fate and impact of oxygenates in groundwater. Other components of the research effort include laboratory experiments on the sorptive properties and biodegradation kinetics of oxygenates and BTEX in gasoline, and natural gradient tracer studies conducted in a shallow sand aquifer at Canada Forces Base Borden, Ontario, Canada. The results of these studies will be published separately.

STUDY OBJECTIVES

The specific objectives of this study were to:

- evaluate through a series of laboratory experiments the effects of water:fuel ratio and oxygenate addition on the aqueous solubility of BTEX;
- develop from cosolvency theory a calibrated model capable of predicting aqueous BTEX concentrations contacting oxygenate fuels; and
- apply this model in a hydrogeological context to characterize dissolved BTEX and oxygenate plumes that could result from fuel spills.

These objectives, and study findings relative to these objectives, are summarized below.

EFFECTS OF WATER:FUEL RATIO AND OXYGENATE ADDITION ON THE AQUEOUS SOLUBILITY OF BTEX

The aqueous solubilities of gasoline constituents such as benzene, toluene, ethylbenzene, and xylene depend on the proportions of gasoline, water, and oxygenate brought into contact (i.e., the mixed composition). For a fuel of fixed composition, such as an oxygenate-free gasoline or a gasoline with fixed oxygenate content, aqueous BTEX solubility (at fixed temperature and pressure) depends only on the proportions of water and fuel brought into contact, conveniently expressed as a water:fuel ratio.*

Determination of Equilibration Time

The term aqueous solubility implies aqueous solubility at equilibrium. Equilibrium solubilities are static and do not change with time. Through a series of batch experiments, an equilibration time of four hours was found to be sufficient to ensure attainment of compositional equilibrium between aqueous and fuel phases. A four hour equilibration time was employed in all subsequent laboratory experiments.

Effect of Water:fuel Ratio on Aqueous BTEX Solubility from Oxygenate-free Gasoline

The first experiments investigated the effect on aqueous BTEX solubility of varying the volume ratio of water brought into contact with an oxygenate-free gasoline. These experiments found that BTEX solubility varied only insignificantly with water:fuel ratio,

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*This water:fuel ratio is the volume ratio of water to fuel prior to mixing. Following mixing and equilibration, the mixture will separate into gasoline and aqueous phases, at a unique **phase volume ratio**. For oxygenate-free gasoline, the water and fuel are mutually insoluble, and the water:fuel ratio and equilibrium phase ratio can be considered equal. For oxygenate gasoline, however, a substantial proportion of the oxygenate is transferred to the water phase upon equilibration. The water:fuel ratio and equilbrium phase ratio are consequently considerably different.

for ratios less than 20:1 (by volume, v/v). The total BTEX concentration remained nearly constant at about 118 mg/L at these ratios. At higher ratios aqueous BTEX solubility was observed to decrease with increasing ratio.

Effect of Oxygenate Addition on Aqueous BTEX Solubility

Subsequent experiments evaluated the effect of oxygenate additives on aqueous BTEX solubility. Oxygenate addition reduces by dilution the proportion of BTEX in gasoline. Consequently for oxygenate fuels, a lower proportion of BTEX is available for dissolution in the aqueous phase. All other physical considerations aside, the presence of oxygenates should tend to reduce the aqueous solubility of BTEX.

Most oxygenates, however, have very high solubilities or are completely miscible in water. At reasonably low equilibrium phase ratios, an aqueous phase in equilibrium with an oxygenate fuel will have a high oxygenate concentration. Gasoline organics such as BTEX are more soluble in concentrated aqueous oxygenate than in water alone. This preferential solubility, referred to in this study as the cosolubility effect, tends to increase the aqueous phase solubility of BTEX from oxygenate fuels.

The presence of oxygenates in gasoline thus tends to decrease BTEX solubility by dilution and increase BTEX solubility by the cosolubility effect. The relative significance of these two offsetting tendencies were investigated in the oxygenate experiments. Methanol and MTBE were selected as the oxygenates for these studies, in part because of their differing solubilities from gasoline. Methanol is hydrophilic and partitions preferentially into the aqueous phase, whereas MTBE is hydrophobic and partitions preferentially into the gasoline phase.

The findings of the laboratory experiments on the effect of oxygenate addition were as follows:

- For an initial (prior to mixing) water:fuel ratio of 10:1 (v/v), the aqueous phase BTEX concentration at equilibrium was found to decrease linearly with increasing initial MTBE content of the gasoline. No cosolubility effect of MTBE was observed.

  For an initial MTBE content of 15% (v/v) in gasoline, contacted with water at an initial water:fuel ratio of 10:1 (v/v), the aqueous BTEX solubility was found to be 121.5 mg/L.

- For an initial water:fuel ratio of 10:1 (v/v), the aqueous phase BTEX concentration at equilibrium was found to remain relatively constant with increasing initial methanol content of the gasoline. The observed BTEX solubility was found to be about 120 mg/L, regardless of the initial methanol content of the gasoline. No cosolubility effect was observed at an initial water:gasoline ratio of 10:1 (v/v).

- Decreasing the initial water:fuel ratio and increasing the initial methanol content of the gasoline will increase the aqueous phase methanol concentration at equilibrium. At an initial water:fuel ratio of 10:1 (v/v), and an initial methanol content of 85% (v/v) in gasoline, the equilibrium aqueous methanol concentration was found to be about 8% (v/v).

- Aqueous BTEX solubility was observed to increase linearly with equilibrium aqueous methanol concentration, for equilibrium aqueous methanol concentrations of 8-25% (v/v). The cosolubility effect was found to be slight over this concentration range; at an equilibrium aqueous methanol concentration of 17% (v/v) the observed aqueous BTEX solubility was found to be 174 mg/L.

- Aqueous BTEX solubility was observed to increase log-linearly with equilibrium aqueous methanol concentration, for equilibrium aqueous methanol concentrations of 25-50% (v/v). The cosolubility effect was found to be marked at equilibrium aqueous methanol concentrations above 25% (v/v). For example, at an equilibrium aqueous methanol concentration of 44% (v/v), the observed aqueous BTEX solubility was found to be 933 mg/L.

Other Oxygenates

Additional experiments were conducted to determine BTEX solubility from gasolines containing:

- 10% ethanol
- 10% tertiary-amyl methyl ether
- 10% isopropyl ether

An initial water:fuel ratio of 10:1 (v/v) was employed. No cosolubility effect was observed for any of these oxygenate fuels at this initial water:fuel ratio. BTEX solubility was found to be the same as for the zero oxygenate case (≈ 120 mg/L).

MODEL DEVELOPMENT AND APPLICATION

Generally, a gasoline spill will affect a large volume of groundwater. Although the actual equilibrium ratio of water to gasoline at any location within a spill site is unknown, equilibrium conditions at any given time probably exist between relatively small volumes of each phase in direct contact along the gasoline-groundwater interface. As groundwater flows through the spill site, compositional equilibrium is continually reapproached or reestablished between the two phases, and the gasoline is gradually stripped of its more soluble constituents.

Partitioning theory and experimental data were employed in developing and applying a theoretical model to simulate dissolved benzene plume formations from spills of gasoline with 0-85% methanol content. Plume formation was simulated by assuming the fuel-groundwater interface acts as a hypothetical batch contactor. In this hypothetical contactor, fuel and fresh groundwater were assumed to be contacted at a prespecified volume ratio and equilibrated. Following equilibration, the contaminated groundwater was assumed to flow out of the contactor. The fuel was assumed to be contacted again with fresh groundwater at the same volume ratio and reequilibrated. This hypothetical batch contacting process was assumed to be carried out indefinitely.

The groundwater composition of each batch was directly inputted to a groundwater transport model. Based on these groundwater composition data and on prespecified hydrogeologic parameters, the transport model then calculated and displayed simulated dissolved benzene and methanol plumes.

Application of the model indicated that for gasolines with high methanol content, benzene solubility in groundwater would be enhanced initially in proportion to the initial methanol content of the gasoline, and in inverse proportion to the aqueous phase:gasoline phase volume ratio at equilibrium. The model predicted that after the initial contacting of the oxygenate fuel with groundwater, the groundwater volume in equilibrium with the gasoline phase would be concentrated in methanol. Owing to the cosolubility effect, the groundwater volume would have higher benzene concentrations than for the zero oxygenate case.

The model predicted that with subsequent contacting, fresh groundwater would progressively deplete the gasoline of its methanol. As the concentration of methanol in the groundwater volume decreases, the cosolubility effect is also diminished. As a consequence, the model predicted that with subsequent contacting, benzene solubility would decrease to the zero methanol value.

The model application characterizes a dissolved BTEX plume formed by a discrete spill of a gasoline-methanol fuel. The front of the plume demonstrates a high methanol content and elevated BTEX concentrations. The remainder of the plume possesses very low methanol content and progressively reduced BTEX concentrations. The distribution and magnitude of the dissolved BTEX concentrations in the plume are controlled by the initial methanol content of the gasoline and the equilibrium aqueous phase:gasoline phase volume ratio.

The total mass of BTEX dissolved in groundwater from a spill of oxygenate gasoline will always be less than from a spill of an equal volume of oxygenate-free fuel, simply because the BTEX content of the oxygenate gasoline is less. Complete dissolution of the available BTEX from a gasoline containing methanol will occur earlier than for an oxygenate-free gasoline, resulting in a smaller dissolved plume. The implications for remediation are that the plume will have a high methanol content, and higher BTEX concentrations than for an oxygenate-free gasoline spill; however, the total BTEX mass loading to the groundwater will be less than for an oxygenate-free gasoline, and the plume size will be smaller.

Section 1

INTRODUCTION

Aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (termed BTEX as a group) are the most water-soluble, mobile, and among the most potentially harmful hydrocarbons found in gasoline. Benzene, the most soluble of these compounds, has a solubility of about 1800 mg/L when present in pure form. Benzene makes up less than 5% (v/v) of most gasolines, hence the maximum benzene concentration in waters affected by gasoline should be less than 90 mg/L. This relatively low solubility could be dramatically increased if a water-soluble cosolvent is present in the gasoline.

Oxygen-containing organic compounds, such as ethers and alcohols, are common gasoline additives and are potential cosolvents. These compounds are termed oxygenates.

The water solubilities of these oxygenate compounds range from a few percent (methyl-tert-butyl-ether, MTBE, for example) to complete miscibility with water (ethanol and methanol). The increasing use of oxygenate additives in gasolines raises concerns that, due to a cosolvent effect of the oxygenates, groundwater impacted by such gasolines could contain higher dissolved BTEX concentrations than previously encountered. The concern about the dissolution of gasoline hydrocarbons and oxygenates into groundwater is addressed in this report. Subsequent reports will address the additional concerns that the presence of oxygenates in gasolines could increase the mobility and persistence of BTEX in groundwaters.

This study aims to:

1. evaluate through a series of laboratory experiments the effect of oxygenate addition on the aqueous solubility of BTEX;

2. develop from cosolvency theory a calibrated model capable of predicting aqueous BTEX concentrations in water contacting oxygenated fuels; and
3. apply this model in a hydrogeological context to characterize dissolved BTEX and oxygenate plumes that could result from fuel spills.

HYDROCARBON SOLUBILITY AND THE EFFECTS OF OXYGENATE COSOLVENTS - PREVIOUS RESEARCH AND THE APPROACH SELECTED

A significant body of literature documents the enhanced solubility of sparsely soluble organics due to the presence of a cosolvent. Munz and Roberts (1986) documented the cosolvency of methanol and 2-propanol for some chlorinated hydrocarbons. Brandini et al. (1985) evaluated the ethanol-benzene-water system, showing the enhanced solubility of benzene in aqueous solutions high in ethanol. Groves (1988) reported enhanced solubility of benzene and hexane when high concentrations (63-267 g/L) of alcohol cosolvents were present in the aqueous phase, but found little enhanced solubility when MTBE was present at lower concentrations (2.6-7.6 g/L). Prediction of the cosolvency effect has been attempted most recently by El-Zoobi et al. (1990) and Pinal et al. (1990) and previously by Groves (1988), Munz and Roberts (1986), Bannerjee (1984), and Yalkowsky and Roseman (1981). The various models appear to be adequate for prediction of aqueous solubilities from the pure phase in the presence of different oxygenates at varying concentrations.

This potential enhancement of solubility has been modelled by Mihelcic (1990) specifically for the case of ethanol and MTBE in gasoline. The existing models, as well as the model developed in this study, are equally capable of addressing oxygenated fuels. None of the current models have, however, demonstrated the hydrogeological factors controlling the BTEX and oxygenate distribution in contaminated groundwaters. This report uses an experimentally-calibrated solubility model to characterize the dissolved plume that could result from the contact of a highly oxygenated fuel with groundwater. A comparison is made between a simulation for normal gasoline and a simulation involving M-85 fuel (a mixture of 85% (v/v) methanol with unleaded gasoline) to demonstrate the impact of the oxygenate. Future reports will address the mobility and fate of contaminants dissolved in groundwater. Two approaches to describing the distribution of components (BTEX and oxygenates) between phases (gasoline and aqueous) are available. One emphasizes the phase relationships and the other emphasizes the distribution of specific organic compounds between phases. The former provides a very useful overview of what happens when oxygenate-bearing gasoline contacts water. Figure 1-1 is the ternary phase diagram for the gasoline-water-methanol system. Mixing of most proportions of gasoline and

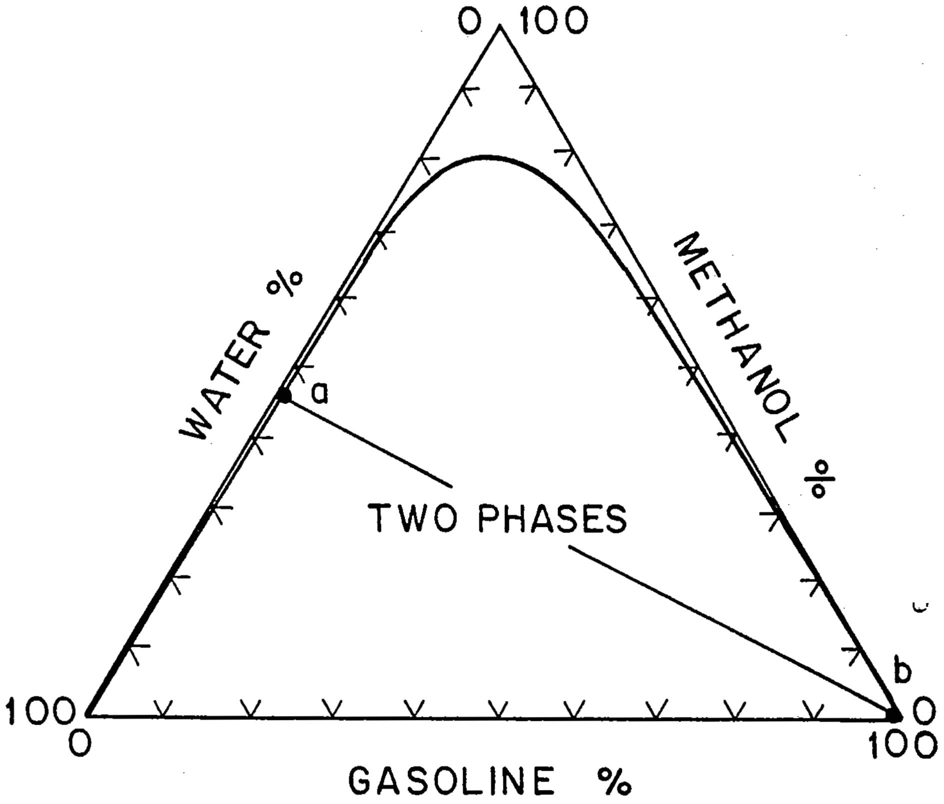

Figure 1-1. Ternary phase diagram for gasoline-water-methanol at 20°C. The curved boundary encloses the two-phase field where the composition of each phase is given as the intersection of the tie lines with the curved boundary (modified from Letcher et al., 1986). For example, a system initially with 50% M-85 and 50% water (v/v) would equilibrate as phases A and B.

water (i.e., a system along the binary water-gasoline side of the ternary phase diagram) produces two phases: gasoline with a small amount of water and water with a small amount of gasoline. The introduction of a water-soluble oxygenate (eg., methanol) adds a significant complexity to the resultant phase compositions. For many mixtures, two phases will still be present, but the composition of the phases at equilibrium will differ markedly from the original phase compositions. For example, in the system illustrated in Figure 1-1, the mixture of a fuel composed of 85% methanol-15% gasoline with > 10% water (v/v) will yield two very different phases: one will be mostly gasoline and the other will be a mixture of water and methanol.

Unfortunately, the phase system approach does not conveniently account for the specific composition of the aqueous phase, which is the key issue addressed in this report. For example, to consider the amount of benzene in the aqueous phase, a benzene-gasoline-oxygenate-water system would have to be considered. Since we are specifically interested in the aqueous concentrations of seven components of gasoline in water (benzene, toluene, ethylbenzene, p-xylene, m-xylene, o-xylene and an oxygenate), working with these multiphase systems becomes unwieldy. Therefore an approach that describes the distribution of the individual compounds between phases has been followed as outlined below.

Work by many researchers (Maijanen <u>et al.</u>, (1984), Reinhard <u>et al.</u> (1984), Stumm and Morgan (1981)) suggests that the aqueous solubility of a particular component of gasoline can be predicted from the aqueous solubility of the pure component and its mole fraction in the gasoline, in accordance with Raoult's Law:

$$C^i_w = s^i * x^b_g \qquad (1\text{-}1)$$

where:

C^i_w = the equilibrium concentration of component i in the water phase
s^i = the solubility of pure component i in water
x^b_g = the molar fraction of component i in the gasoline.

Application of Raoult's Law assumes that the organic phase is ideal. Raoult's Law is probably reliable to within a factor of 2 provided the solubility of component i in water is low (Burris and MacIntyre, 1985, 1986; Leinonen and Mackay, 1973). The molar fractions of individual components in the complex gasoline mixture must be known in order to apply Raoult's Law. Uncertainties in the composition of the gasoline mixture are likely more significant than are the uncertainties associated with the simplifying assumption of ideality inherent in applying Raoult's Law.

Fuels with high oxygenate content will contain less BTEX than unoxygenated fuels. Applying Raoult's Law (Equation 1-1), a decrease in the BTEX content of the gasoline would tend to decrease the BTEX concentration in impacted groundwater. However, the cosolvency effect would increase BTEX solubility by increasing the term (s^b). For example, benzene has a solubility of about 1800 mg/L in pure water. If the water contained 50% methanol (v/v), benzene would be soluble in all proportions (miscible). This report will demonstrate that the actual BTEX concentrations in the impacted groundwaters can be predicted only when both the proportions of BTEX and oxygenates in the gasoline are known, and the gasoline:groundwater phase ratio can be specified.

More complex solubility prediction models include the UNIQUAC/UNIFAC models, the log-linear model (Yalkowsky and Roseman, 1981), the 3-suffix equation, and the near-ideal binary solvent model (Pinal et al., 1990). Because the simple model based upon Raoult's law and partitioning of solutes between phases is not adequate to deal with significant cosolvent effects, the more complex models must be employed. Pinal et al. (1990) reported good agreement between the log-linear and UNIFAC models in some solvent systems, so where the cosolvent effect becomes significant, we feel that the choice of the log-linear model is reasonable. Our purpose in this report is not to improve the available solubility models but to apply an adequate model to experimental data and to establish generalized conclusions on which further research concerning BTEX partitioning from oxygenated gasolines can be based.

One aspect that must be included in any model of enhanced solubility by cosolvents is the requirement to conserve mass. In most spill scenarios, BTEX will be distributed between groundwater and relatively limited volumes of gasoline. When the water phase is relatively large, BTEX depletion in the gasoline phase tends to occur and the maximum predicted aqueous concentration of BTEX is not attained. Such a situation could result from the release of small volumes of gasoline into a large mass of groundwater with rapid mass transfer of components from the organic mixture to the water.

Therefore, we feel that a useful approach to the problem of estimating aqueous concentrations of components such as BTEX in complex mixtures such as gasoline, M-85, and MTBE containing gasoline is that presented by Maijanen et al. (1984) and Shiu et al. (1988). It treats the dissolution of the components of an organic mixture as attaining an equilibrium partitioning between aqueous and organic phases of specified volumes or volume ratios. This approach is more useful than those of Mihelcic (1990), El-Zoobi et al. (1990), and others referenced therein because the ratio of water to gasoline is a variable, as it is in gasoline spills or leaks affecting groundwater. Likewise, the water to gasoline ratio was a variable in our laboratory experiments. This partitioning approach is developed in Section 3 and is shown to be a useful model in generalizing experimental data on the equilibrium dissolution of BTEX from gasolines such as M-85 and predicting dissolved BTEX plumes emanating from simple spills.

Section 2

LABORATORY EXPERIMENTS

A series of laboratory experiments were undertaken to evaluate the aqueous solubility of BTEX from gasoline and oxygenate-gasoline mixtures. The first set of experiments determined the time required for water-gasoline mixtures to reach equilibrium. The second set of experiments determined aqueous BTEX concentrations from varying proportions of water and gasoline. The third set of experiments determined aqueous BTEX concentrations when various proportions of oxygenates were added to the gasoline phase. A final set of experiments measured BTEX concentrations in various water:methanol solutions in equilibrium with gasoline. These experiments were conducted to evaluate the potential for enhanced BTEX solubility with large proportions of methanol. The volume proportions of BTEX in PS-6 gasoline were experimentally determined so that enhanced solubility effects could be recognized.

EXPERIMENTAL METHODS

All laboratory experiments investigating the equilibrium partitioning of BTEX between water and gasoline or gasoline-oxygenate mixtures were completed using the shake-flask batch contacting equilibration procedures of Brookman et al. (1985). PS-6 gasoline supplied by API was used for all experiments except where specified. PS-6 gasoline refers to a standard reference unleaded gasoline, maintained by API for use in API toxicological and environmental research. The designation PS-6 stems from the first use of this reference gasoline in a toxicological study on the rodent carcinogenicity of wholly vaporized unleaded gasoline (MacFarland et al., 1984). Specifications and compositional data for PS-6 gasoline are provided in Appendix A.

All experiments were conducted at 10°C. Dissolved BTEX concentrations were measured by the hexane micro-extraction technique described by Patrick et al. (1985). Oxygenate concentrations were determined by direct aqueous injection onto a Hewlett

Packard 5840A gas chromatograph with a flame ionization detector. Details of the analytical methods and quality assurance/quality control data are presented in Appendix B.

TIME-TO-EQUILIBRIUM EXPERIMENTS

The time required for water-gasoline systems to reach equilibrium was determined so that gasoline-saturated conditions could be assumed in subsequent experiments. Regular unleaded gasoline obtained from a service station was used in place of PS-6 gasoline in the time-to-equilibrium experiments. Equilibrium aqueous concentrations of each organic component in the time-to-equilibrium experiments differed from equilibrium aqueous concentrations obtained in subsequent experiments due to the differences in the composition of regular unleaded gasoline and the PS-6 gasoline used in subsequent experiments.

Saturated solutions of gasoline and water were prepared without headspace in 60 mL hypovials filled with 10 parts groundwater--obtained from the aquifer at the Canadian Forces Base Borden, Ontario, Canada experimental site (Patrick et al.,1985)--and 1 part gasoline (v/v). Samples were then rotated at 40 rpm in a 10°C refrigerator for 0.5, 1, 2, 4, 8, 16, 24, 40, or 50 hours. Triplicate samples were prepared for each time interval. After each sampling interval the hypovials were placed upside down in a GSA® rotor head and centrifuged for 15 minutes at 2000 rpm inside a 10°C SORVALL® centrifuge to separate the gasoline and water phases. The separated water phase was removed by glass syringe and dispensed into 18 mL glass hypovials (containing 0.2 mL of sodium azide (NaN_3) bactericide) in preparation for BTEX analysis by gas chromatography.

The results of the time-to-equilibrium experiments are presented in Figure 2-1. An equilibrium condition is apparently reached within 1 hour. A conservative equilibration time of 4 hours was allowed in all subsequent laboratory investigations into gasoline solubility.

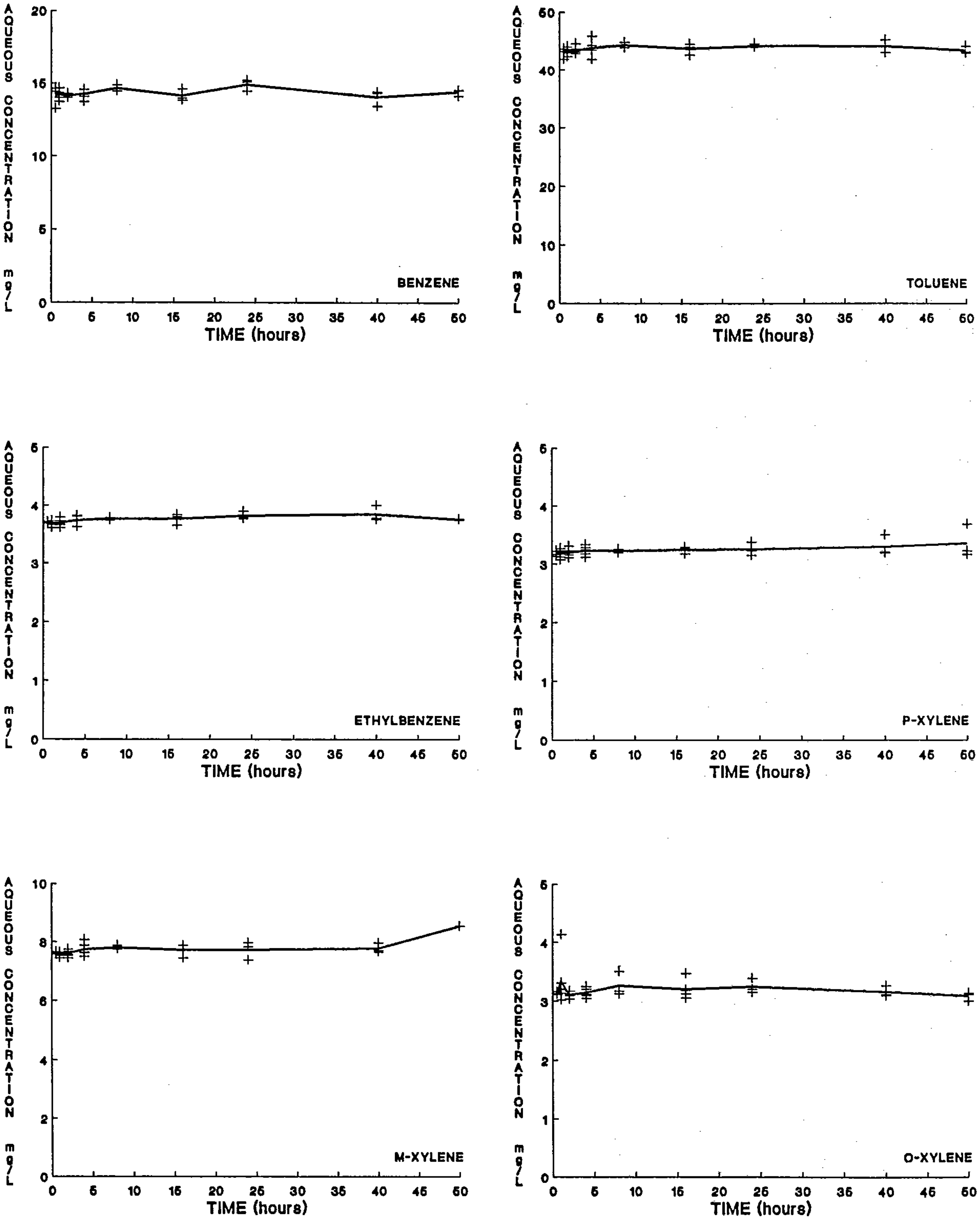

Figure 2-1. Results of time-to-equilibrium experiments for dissolved BTEX from gasoline.

EFFECT OF VARYING AQUEOUS:GASOLINE PHASE RATIOS

The effect of varying water:gasoline ratios on the equilibrium aqueous BTEX concentrations was examined. These experiments addressed water volume (V_w) to gasoline volume (V_g) ratios between 1:1 and 1000:1. Triplicate samples of each water:gasoline ratio were prepared following the procedures previously outlined.

The average equilibrium aqueous BTEX concentrations of each triplicate set are summarized in Table 2-1a. The lower set of data in Table 2-1a (V_w/V_g = 1 to 1000) were analyzed at a later date using gasoline that may have experienced some evaporation during storage. Differences in the aqueous BTEX concentrations between these two sets of data are likely due to differences in the initial gasoline composition.

Table 2-1a data suggest that the aqueous benzene concentrations are constant for water:gasoline ratios up to 20:1 (v/v). At higher ratios depletion of the available benzene and toluene in the gasoline results in lower aqueous concentrations. Similar reduction of aqueous toluene, ethylbenzene and xylene concentrations is observed at water:gasoline ratios greater than 60:1 and 100:1 (v/v), respectively.

This experiment was repeated using pure benzene in place of gasoline. The average equilibrium benzene concentrations of each triplicate set are summarized in Table 2-1b.

Table 2-1a. Average aqueous BTEX concentrations for various water:gasoline volume ratios.

Water: Gasoline Ratio (v/v)	Benzene (mg/L)	Toluene (mg/L)	Ethyl-Benzene (mg/L)	p-Xylene (mg/L)	m-Xylene (mg/L)	o-Xylene (mg/L)	Total BTEX (mg/L)
10:1	59.7	31.3	3.7	3.8	9.4	5.8	113.6
15:1	58.9	31.3	3.7	3.8	9.3	5.8	112.9
20:1	57.3	30.2	3.6	3.6	9.0	5.5	109.2
30:1	51.1	30.0	3.7	3.7	9.4	5.9	103.8
40:1	50.3	30.3	3.8	3.8	9.5	5.8	103.4
50:1	45.2	29.4	3.7	3.8	9.4	5.8	97.4
60:1	47.6	29.9	3.7	3.8	9.5	5.8	100.4
1:1	64.7	46.4	6.1	6.2	15.2	8.9	147.4
10:1	63.0	46.8	6.3	6.3	15.7	9.4	147.4
100:1	42.9	43.6	6.4	6.5	16.4	9.5	125.3
1000:1	11.5	19.3	4.0	4.1	10.3	5.9	55.0

Table 2-1b. Average dissolved benzene concentrations for various water:benzene volume ratios.

Water:Benzene Ratio (v/v)	Benzene (mg/L)
1:1	2113.2
10:1	2068.2
100:1	2042.2
1000:1	917.8*

*NOTE: all benzene dissolved (single phase).

AQUEOUS BTEX CONCENTRATIONS FROM OXYGENATE-GASOLINE MIXTURES

The aqueous solubility of BTEX from gasoline containing variable concentrations of oxygenates was examined. Triplicate samples of each gasoline-oxygenate:water combination were prepared following procedures outlined in Section 2.1. The initial water:gasoline-oxygenate ratio for all cases was 10:1 (v/v). The following combinations of gasoline and oxygenate (v/v) were evaluated:

1. 100 % PS-6 gasoline, no oxygenates
2. 90 % PS-6 gasoline, 10 % ethanol
3. 95 % PS-6 gasoline, 5 % methanol
   90 % PS-6 gasoline, 10 % methanol
   85 % PS-6 gasoline, 15 % methanol
   50 % PS-6 gasoline, 50 % methanol
   15 % PS-6 gasoline, 85 % methanol
4. 95 % PS-6 gasoline, 5 % MTBE
   90 % PS-6 gasoline, 10 % MTBE
   85 % PS-6 gasoline, 15 % MTBE
5. 90 % PS-6 gasoline, 10 % tertiary amyl methyl ether (TAME)
6. 90 % PS-6 gasoline, 10 % isopropyl ether (IPE)

The average aqueous BTEX concentrations of each triplicate set are presented in Table 2-2. The aqueous benzene concentrations are about the same for equilibrium with gasoline-methanol mixtures as for pure gasoline. Slightly lower aqueous benzene concentrations were observed for equilibrium with MTBE, TAME, and IPE. Apparently, at a 10:1 initial water:fuel ratio the lower BTEX contents of the gasoline-oxygenate systems were sufficient to offset the cosolvency effects of the oxygenates.

Table 2-2. Average experimental aqueous oxygenate and BTEX concentrations for various gasoline-oxygenate mixtures. Initial water:gasoline ratio = 10:1 (v/v).

Initial Oxygenate Content of Gasoline	Oxygenate (mg/L)	Benzene (mg/L)	Toluene (mg/L)	Ethyl-Benzene (mg/L)	p-Xylene (mg/L)	m-Xylene (mg/L)	o-Xylene (mg/L)	Total BTEX (mg/L)
0% (PS-6)	0.0	65.5	33.1	3.9	3.9	10.2	6.2	122.8
10% Eth	6707.8	65.5	31.3	3.9	3.9	9.9	6.1	120.6
5% Meth	4111.1	63.4	33.5	4.0	4.0	10.5	6.3	121.7
10% Meth	8001.5	67.0	33.0	4.1	4.1	10.5	6.5	125.2
15% Meth	11291.3	64.9	32.4	3.9	3.9	10.1	6.2	121.5
50% Meth	43041.3	60.6	31.6	4.0	3.9	9.9	6.2	116.2
85% Meth	61500.2	55.2	35.4	4.7	4.7	11.7	7.4	119.0
5% MTBE	1755.5	60.1	31.7	3.8	3.8	9.9	6.0	115.4
10% MTBE	3647.1	60.5	30.5	3.7	3.7	9.6	5.9	114.0
15% MTBE	5142.0	57.2	28.7	3.5	3.5	9.0	5.5	107.4
10% TAME	1259.0	59.0	27.4	3.4	3.4	8.6	5.3	107.2
10% IPE	1374.6	56.1	27.8	3.5	3.5	9.0	5.6	105.6

(Eth = Ethanol; Meth = Methanol; TAME = Tertiary-amyl-methyl-ether;
IPE = Isopropyl ether)

COSOLUBILITY EFFECTS OF HIGH METHANOL CONTENTS

Additional experiments were carried out to study the effect of high methanol concentrations on the aqueous solubility of BTEX from gasoline. These high methanol concentrations were achieved by contacting concentrated aqueous methanol with oxygenate-free gasoline.

Since the aqueous solubility of BTEX depends only on the proportions of gasoline, water, and oxygenate (methanol) brought into contact, contacting oxygenate-free gasoline with concentrated aqueous methanol at a specified aqueous methanol:gasoline ratio is entirely equivalent to contacting oxygenate gasoline with water at a different (lower) water:fuel ratio. For example, contacting oxygenate-free gasoline with 75% (v/v) aqueous methanol at an aqueous methanol:gasoline ratio of 10:1 (v/v) is entirely equivalent to contacting an oxygenate gasoline of 88.2% (v/v) methanol content with water at a water:fuel ratio of 0.29:1 (v/v).

Three experiments were conducted. Two of the experiments examined the effect of methanol on the aqueous solubility of BTEX from gasoline, and one examined the effect of methanol on the aqueous solubility of benzene from an immiscible benzene phase. The desired aqueous methanol concentrations were created by mixing methanol and water prior to addition of the gasoline phase. The three experiments examined:

1. initial aqueous methanol content = 0 - 90% (v/v)
   initial aqueous methanol:gasoline ratio = 10:1 (v/v),
2. initial aqueous methanol content = 0 - 90% (v/v)
   initial aqueous methanol:benzene ratio = 10:1 and 1:1 (v/v), and
3. initial aqueous methanol content = 50% (v/v)
   initial aqueous methanol:gasoline ratio = 1:1 to 1000:1 (v/v).

The results of these experiments are summarized in Tables 2-3, 2-4, and 2-5.

Table 2-3. Average aqueous BTEX concentrations with varying methanol content of the aqueous phase (v/v) at equilibrium. Initial aqueous methanol:gasoline phase ratio 10:1 (v/v).

Initial Aqueous Methanol Content (% v/v)	Equilibrium Aqueous Methanol Content (% v/v)	Benzene (mg/L)	Toluene (mg/L)	Ethyl-Benzene (mg/L)	p-Xylene (mg/L)	m-Xylene (mg/L)	o-Xylene (mg/L)	Total BTEX (mg/L)
0	0.00	50.3	39.7	5.4	5.1	12.7	7.0	120.2
2	0.63	52.3	41.7	5.9	5.4	13.7	7.9	126.9
5	4.20	54.2	44.2	6.2	5.9	14.9	8.3	133.6
10	8.24	56.7	49.7	7.1	6.5	16.8	9.6	146.5
20	17.04	63.0	58.8	9.1	8.5	21.7	13.0	174.2
50	43.60	216.8	306.5	68.6	67.9	168.3	105.3	933.4
75	62.82	661.4	1758.8	662.2	670.4	1670.7	907.5	6331.0
90*	70.60	1031.2	3371.8	1658.3	1739.0	4430.7	2221.8	14452.8

*NOTE: Only a single phase present at equilibrium.

Table 2-3 illustrates that, for an aqueous methanol:gasoline ratio of 10:1, aqueous BTEX concentrations increase dramatically when the aqueous methanol content at equilibrium exceeds about 20% (v/v). A similar increase in aqueous benzene solubility from pure benzene is observed in Table 2-4. Complete dissolution of the benzene phase was noted for initial aqueous methanol contents greater than 75% (v/v). Table 2-5 illustrates the dependence of the equilibrium aqueous BTEX concentrations on the aqueous methanol:gasoline ratio. The results in Table 2-5 can be compared with Table 2-1 to observe the effect of adding methanol to the aqueous phase. For volume ratios of less than 100:1, the aqueous BTEX concentrations are greater for the case with 50% initial methanol content (v/v). For volume ratios greater than 100:1, the aqueous BTEX concentrations are slightly lower for the 50% methanol case. This effect is due to the depletion of the limited amount of BTEX in the gasoline phase at high volume ratios.

Table 2-4. Average aqueous benzene concentration with varying methanol content of the aqueous phase at equilibration. Initial aqueous methanol:benzene ratio = 10:1 (v/v).

Initial Aqueous Methanol Content (% v/v)	Equilibrium Aqueous Methanol Content (% v/v)	Benzene (mg/L)
0	0.00	1659.8
2	1.67	1701.7
5	4.22	1703.9
10	8.54	2038.3
20	17.46	2213.4
50	43.50	10259
75	59.04	79470*
90	70.11	78063*

*NOTE: All benzene dissolved

Table 2-5. Effect of initial aqueous methanol:gasoline ratio on aqueous BTEX concentrations. Initial aqueous methanol consisted of 1:1 water:methanol mixture (v/v).

Aqueous Methanol: Gasoline Ratio (v/v)	Benzene (mg/L)	Toluene (mg/L)	Ethyl-Benzene (mg/L)	p-Xylene (mg/L)	m-Xylene (mg/L)	o-Xylene (mg/L)	Total BTEX (mg/L)
1:1	263.1	217.6	40.1	40.4	98.7	59.2	719.1
10:1	273.2	258.4	50.5	50.6	124.9	74.8	832.3
100:1	60.3	104.1	32.8	33.8	84.0	45.8	360.8
1000:1	7.5	13.4	4.8	5.0	12.5	6.4	49.6

VOLUME PROPORTIONS OF BTEX

Five samples of PS-6 gasoline were analyzed using gas chromatography/mass spectrometry (GC/MS) techniques to determine the relative volume proportions of each BTEX component in the gasoline. The results of this determination are presented in Table 2-6. These values are used in subsequent sections to calculate aqueous BTEX concentrations for aqueous solutions in equilibrium with gasoline.

Table 2-6. BTEX composition of PS-6 gasoline (volume percent).

Run #	Benzene %	Toluene %	Ethyl-Benzene %	p-Xylene %	m-Xylene %	o-Xylene %	Total BTEX %
1	2.117	3.740	1.580	2.030	4.222	1.970	15.659
2	1.905	3.301	1.235	1.826	3.940	1.969	14.176
3	2.141	3.691	1.503	1.899	4.169	2.071	15.474
4	2.087	3.437	1.763	1.614	3.935	2.185	15.021
5	2.159	3.425	1.768	1.674	4.094	2.243	15.363
Average	2.082	3.519	1.570	1.809	4.072	2.088	15.139
Rel. Std. Dev.	5.06%	5.23%	14.52%	9.83%	3.5%	6.31%	4.04%

NOTE:

1. The BTEX volume percent measurements for runs 1, 2, and 3 were made by vapor injection and selected ion monitoring on a Hewlett-Packard GC/MS. The injection comprised 100 µl of vapor from the equilibration of 3 µL of gasoline in a 1 L bottle (external standard technique).

2. Runs 4 and 5 were performed by split solvent injection of gasoline diluted in hexane with an MFT internal standard onto a GC with an FID detector to confirm the results of the vapor analyses.

Section 3

PREDICTING AQUEOUS CONCENTRATIONS OF BTEX FROM PS-6 GASOLINE

The following sections describe the parameters and relationships that describe the aqueous solubility of BTEX compounds from a gasoline mixture. A simple equilibrium partitioning model to describe BTEX distributions is reviewed and applied. This approach is well-suited for considering cases where the gasoline:aqueous phase ratio is variable. The following sections present the partitioning theory and discuss the effects on BTEX solubility of changing the volumes of water and gasoline in equilibrium.

PARTITIONING THEORY

The following section outlines the theory developed by Maijanen et al. (1984). The most significant assumptions are noted. For more detailed discussion of this theory refer to Maijenen et al. (1984) and Shiu et al. (1988).

A mass balance expression can be written to describe the equilibrium partitioning of each component (eg., benzene) in a two phase system, namely gasoline and water.

$$y^b_g * V^i_g * p^b = c^b_g * V_g + c^b_w * V_w \tag{3-1}$$

where:

y^b_g = the volume proportion of benzene in the gasoline,
V^i_g = the initial volume of the gasoline (m^3),
p^b = the density of benzene (g/m^3),
c^b_g = the equilibrium concentration of benzene in the gasoline phase (g/m^3),
V_g = the volume of the gasoline phase at equilibrium (m^3),
c^b_w = the equilibrium concentration of benzene in the water phase (g/m^3), and
V_w = the volume of the water phase at equilibrium (m^3).

The left hand side of Equation 3-1 represents the initial mass of benzene, and the right hand side expresses the partitioning of this mass between the gasoline and the water.

The distribution of benzene between the two phases can be described in terms of a gasoline-water partitioning coefficient, K^b_{gw}, where:

$$K^b_{gw} = c^b_g / c^b_w \tag{3-2}$$

We will assume that Raoult's Law applies to the system, then:

$$c^b_w = x^b_g * s^b \tag{3-3}$$

where:
x^b_g = the molar fraction of benzene in gasoline, and
s^b = the solubility of pure benzene in water (g/m^3).

The initial concentration of benzene in gasoline is:

$$c^b_g = y^b_g * p^b \tag{3-4}$$

If the amount of benzene dissolved in the aqueous phase is much smaller than the initial amount of benzene in the gasoline, we can assume that the change in benzene concentration in the gasoline phase is negligible. The gasoline-water partitioning coefficient (K^b_{gw}) can then be expressed as:

$$K^b_{gw} = (y^b_g \bullet p^b) / (x^b_g * s^b) \tag{3-5}$$

In a mixture such as gasoline, the molar fraction of the individual components (x^b_g) is difficult to determine accurately. The assumption that the volume fraction (y^b_g) is equivalent to the molar fraction (x^b_g). was found to be invalid for predicting the aqueous benzene concentrations in equilibrium with gasoline, as discussed in Appendix A. Experimentally determined volume fractions of BTEX in PS-6 gasoline are presented in Table 2-6. The molar fractions of BTEX in PS-6 gasoline were approximated from a characterization of PS-6 gasoline reported by Brookman et al., 1985. The approximation method is described in Appendix A.

This expression for K^b_{gw} (Equation 3-5) can be substituted into Equation 3-1 to obtain a value for the benzene concentration in the aqueous phase.

$$y^b_g * V^i_g * p^b = c^b_g \bullet V_g + c^b_w \bullet V_w \tag{3-1}$$

$$y^b_g * V^i_g \bullet p^b = K^b_{gw} * c^b_w \bullet V_g + c^b_w * V_w \qquad (3\text{-}6)$$

or: $$c^b_w = (y^b_g \bullet V^i_g * p^b) / (K^b_{gw} \bullet V_g + V_w) \qquad (3\text{-}7)$$

By dividing by V_g, c^b_w can also be expressed as:

$$c^b_w = y^b_g \bullet (V^i_g/V_g) \bullet p^b / (K^b_{gw} + V_w/V_g) \qquad (3\text{-}8)$$

For the case of pure gasoline the relative volumes of the gasoline and water phases were not observed to change during equilibration, hence, V_g is equal to V^i_g. Significant changes in the volume of the gasoline phase upon equilibration with water are expected when the gasoline contains oxygenate compounds that will preferentially partition into the aqueous phase.

This treatment is useful because it permits calculation of the aqueous BTEX concentrations by considering both the phase volume ratio (V_w/V_g) and the partitioning between the gasoline and aqueous phase (K^b_{gw}). The results of the laboratory experiments are discussed in terms of these calculations. As will be seen in later sections, when the experimentally observed aqueous BTEX concentrations significantly exceed concentrations predicted using the equilibrium partitioning model, the discrepancy is attributable to the cosolvency effect.

EFFECT OF AQUEOUS:GASOLINE PHASE RATIO ON BTEX SOLUBILITY

The effect of changing aqueous:gasoline phase ratios on dissolved BTEX concentrations was evaluated using the theory and equations developed at the beginning of Section 3. Values for the parameters used in these calculations are summarized in Appendix C.

The calculated dissolved BTEX concentrations resulting from varying the aqueous:gasoline phase volume ratio are presented on Table 3-1. The interest in this exercise is to demonstrate that the calculations reproduce trends observed in the experimental data. For this reason, the calculated values presented on Table 3-1 are normalized to the average experimental value for $V_w/V_g = 10$ (Table 1-1a). The normalized calculated trend is shown as the bold line in Figure 3-1. The rationale for this normalization is discussed in more detail in Section 4, and the relationship between normalized and unnormalized data is discussed in Appendix D.

Table 3-1. Calculated dissolved BTEX concentrations for varying aqueous:gasoline phase ratios.

Vw/Vg*	Benzene (mg/L)	Toluene (mg/L)	Ethyl-benzene (mg/L)	p-Xylene (mg/L)	m-Xylene (mg/L)	o-Xylene (mg/L)
K_{gw}*:	346.2	1348.7	5267.8	3476.5	5960.4	5360.9
0.01	61.42	31.53	3.71	3.80	9.40	5.81
0.1	61.41	31.53	3.71	3.80	9.40	5.81
1	61.25	31.51	3.71	3.80	9.40	5.81
10	59.70	31.30	3.70	3.79	9.39	5.80
15	58.87	31.19	3.70	3.78	9.38	5.79
20	58.07	31.07	3.69	3.78	9.37	5.79
30	56.53	30.85	3.69	3.77	9.35	5.78
40	55.06	30.62	3.68	3.76	9.34	5.77
50	53.67	30.40	3.67	3.75	9.32	5.76
60	52.35	30.19	3.67	3.74	9.31	5.75
70	51.09	29.98	3.66	3.73	9.29	5.74
100	47.66	29.36	3.64	3.69	9.25	5.70
200	38.93	27.46	3.57	3.59	9.10	5.60
500	25.13	23.00	3.39	3.32	8.67	5.32
1000	15.79	18.11	3.12	2.95	8.05	4.90
10000	2.06	3.75	1.28	0.98	3.51	2.03
100000	0.21	0.42	0.19	0.13	0.53	0.30
1000000	0.02	0.04	0.02	0.01	0.06	0.03

*NOTE: V_w/V_g = aqueous:gasoline phase volume ratio.
K_{gw} calculated from Equation 3-5.

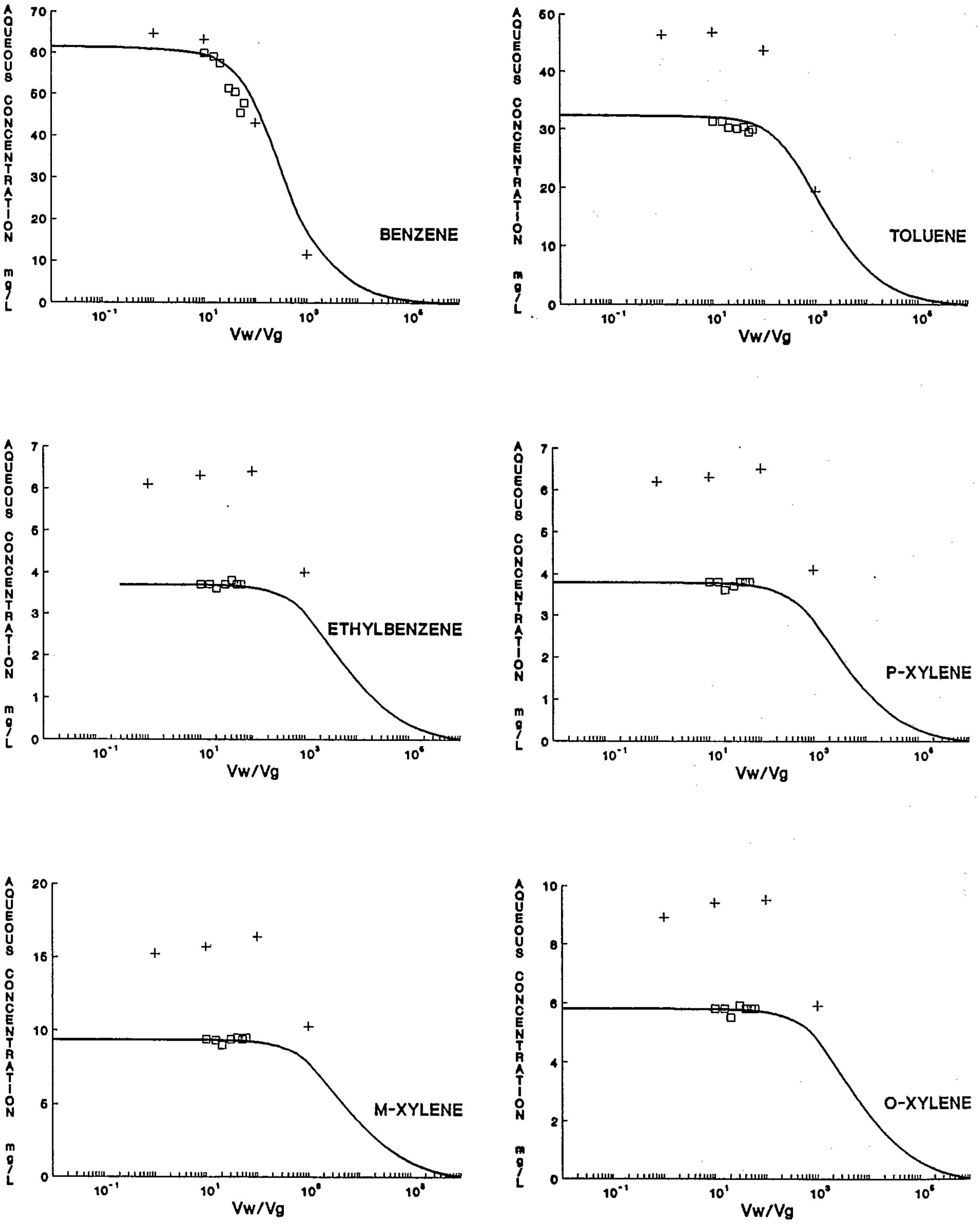

Figure 3-1. Effect of varying aqueous:gasoline phase ratio (V_w/V_g) on aqueous BTEX concentrations. Curve represents normalized calculated trend, squares represent experimental data for primary date, and crosses represent experimental data for secondary date.

Note that the experimental data from different dates (shown as crosses in Figures 3-1) follow a parallel trend with different (higher) initial value. These data were not considered in the normalization procedure, although a second normalized curve could be calculated to fit the trend of these data. The differences between these two data sets suggest that the composition of the gasoline had changed during storage, possibly by evaporation of the more volatile constituents. This would result in increased volume fractions of the less volatile BTEX components (toluene, ethylbenzene and xylenes), and hence higher aqueous TEX concentrations. Similarly, the composition of the gasoline may have varied between the determination of the BTEX volume fractions (Table 2-6) and the other solubility experiments.

Figure 3-1 demonstrates that the aqueous BTEX concentrations are relatively constant for aqueous:gasoline phase ratios of less than approximately 20:1 (v/v). At greater dilutions the observed aqueous BTEX concentrations diminish as the BTEX pool in the gasoline phase is depleted. The partitioning theory adequately reproduces the effects of this depletion on the aqueous BTEX concentrations. An aqueous:gasoline phase ratio of 10:1 (v/v) was used in subsequent experiments investigating the aqueous solubility of BTEX from oxygenate-gasoline mixtures.

Section 4

PREDICTING AQUEOUS BTEX CONCENTRATIONS FROM GASOLINE CONTAINING OXYGENATE ADDITIVES

The possibility of enhanced solubility of BTEX due to the presence of oxygenated hydrocarbons in gasoline is a concern in potential contamination situations. Most oxygenates have high solubilities and some are miscible with water. Oxygenates that partition preferentially into the aqueous phase will be termed hydrophilic, while oxygenates that partition preferentially into the organic phase will be termed hydrophobic.

In equilibrium experiments the final volumes, densities, and molecular compositions of the gasoline mixtures may change significantly depending on whether the oxygenate partitions towards the aqueous or organic phase. A simple equilibrium experiment was performed in a calibrated container to evaluate the partitioning of methanol between gasoline and water. A 9 mL volume of a 15% PS-6 gasoline and 85% methanol mixture (v/v, 1.45 mL gasoline; 7.65 mL methanol) was added to 8 mL of water. After equilibrium the volume of the aqueous phase was 15.8 mL, while the gasoline phase was reduced to 1.2 mL. This demonstrates that methanol partitions preferentially towards the aqueous phase. Methanol is slightly more dense than the pure gasoline mixture (Appendix C). Hence, the gasoline will be slightly less dense at equilibrium. The molar and volume fractions of BTEX will increase due to the partitioning of the methanol but should approximate the values for pure gasoline.

The lower aqueous solubility and higher hydrophobicity of MTBE (Appendix C) suggest that MTBE will partition preferentially into the organic phase.

The aqueous concentrations of BTEX for various oxygenate:gasoline ratios at a constant water:gasoline ratio of 10:1 were calculated for a hydrophilic oxygenate (methanol) using theories developed in Section 3. A similar calculation was performed for a hydrophobic oxygenate (MTBE). For each case, these theoretical calculations were compared against data obtained in experiments described in Section 2. In addition, the theory for calculation of aqueous BTEX concentrations under the conditions where cosolvency is significant was further developed and the results of these theoretical calculations were compared with experimental data from Section 2. Aqueous BTEX concentrations calculated using the theory described in this section were used as input into a groundwater flow model to produce dissolved benzene and methanol plumes that would simulate different spill conditions. Variables in this modelling exercise were the initial methanol content of the gasoline and the relative ratios of gasoline and water in equilibrium.

EFFECT OF A HYDROPHILIC OXYGENATE ON THE AQUEOUS CONCENTRATIONS OF BTEX

For the purposes of this calculation it is assumed that the oxygenate is completely partitioned into the aqueous phase at equilibrium. The value of K^{b}_{gw} at equilibrium is then assumed to be equivalent to the value for pure gasoline. The ratio V^{i}_{g}/V_{g} will increase as the concentration of oxygenate is increased.

The calculated aqueous BTEX concentrations for gasolines with varying methanol content are presented in Table 4-1 for an initial water:gasoline ratio of 10:1 (v/v). These calculated concentrations have been normalized to the experimentally determined BTEX concentrations at zero methanol content, from Table 2-2.

The effects of this normalization are illustrated in Figure 4-1. On this diagram, the symbols represent the experimentally determined aqueous benzene concentrations, the lower line represents the trend calculated using data from Appendix C, and the upper, bold line represents the calculated trend normalized to the zero oxygenate content. In general, the calculated values (lower line on Figure 4-1) underestimate the experimental values, however, similar trends are apparent. The discrepancy is

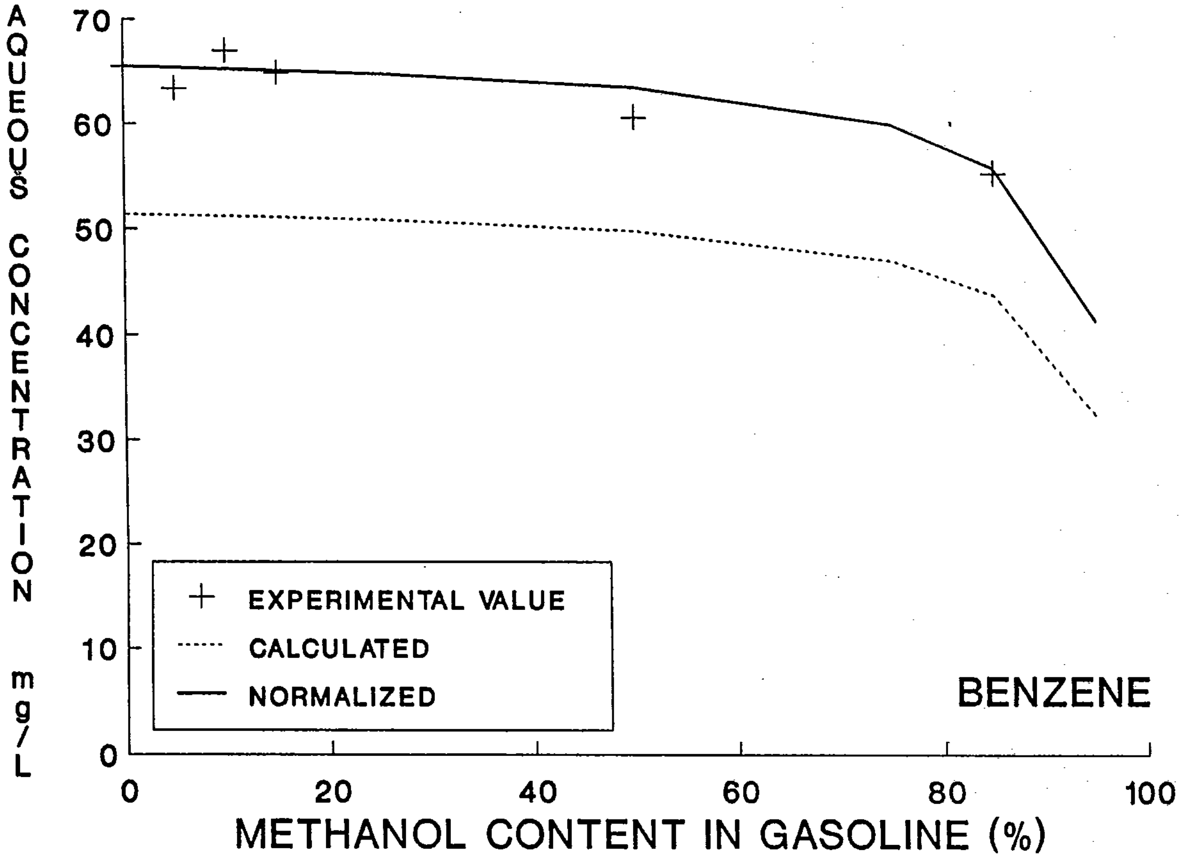

Figure 4-1. Effect of methanol content on aqueous benzene concentration. Calculated trends normalized to experimentally determined BTEX concentrations at zero methanol content (Table 2-2). Initial water:gasoline ratio is 10:1 (v/v).

Table 4-1. Calculated aqueous methanol and BTEX concentrations for gasoline with varying methanol content. Initial water:gasoline volume ratio = 10:1.

Initial Methanol Content of Gasoline (% v/v)	Methanol (% v/v)	Benzene (mg/L)	Toluene (mg/L)	Ethyl-benzene (mg/L)	p-Xylene (mg/L)	m-Xylene (mg/L)	o-Xylene (mg/L)
0.0	0.00	65.50	33.10	3.90	3.90	10.20	6.20
5.0	0.50	65.39	33.09	3.90	3.90	10.20	6.20
10.0	0.99	65.28	33.07	3.90	3.90	10.20	6.20
15.0	1.48	65.14	33.05	3.90	3.90	10.20	6.20
25.0	2.44	64.83	33.01	3.90	3.90	10.19	6.20
50.0	4.76	63.54	32.83	3.89	3.89	10.18	6.19
75.0	6.98	59.95	32.32	3.88	3.86	10.14	6.16
85.0	7.83	55.74	31.65	3.85	3.83	10.09	6.13
95.0	8.68	41.28	28.69	3.75	3.68	9.86	5.97

relatively small and probably reflects uncertainties in the determinations of the volume composition or the molar composition estimate, uncertainties in the temperature-dependent aqueous solubilities, or the assumption that Raoult's Law is applicable. For example, increasing the molar fraction of benzene in the initial gasoline by 28% yields a calculated curve that fits the experimental data fairly well.

The calculation is based upon the assumption that all of the oxygenate partitions into the aqueous phase. The aqueous methanol concentrations from Table 2-2 show that approximately 99% of the methanol partitions towards the aqueous phase. For an initial water:gasoline ratio of 10:1 (v/v), the normalized, calculated relationship between aqueous BTEX concentration and initial methanol content of the gasoline (% v/v) is illustrated in Figure 4-2. For benzene, the aqueous concentrations are observed to be roughly constant for methanol contents less than 50% (v/v). The aqueous benzene concentrations are lower for methanol contents greater than 50% (v/v) due to depletion of the available benzene in the gasoline phase. The aqueous concentrations of other BTEX compounds remain relatively constant for methanol contents up to 90% (v/v). The averaged experimental data are generally well represented by the

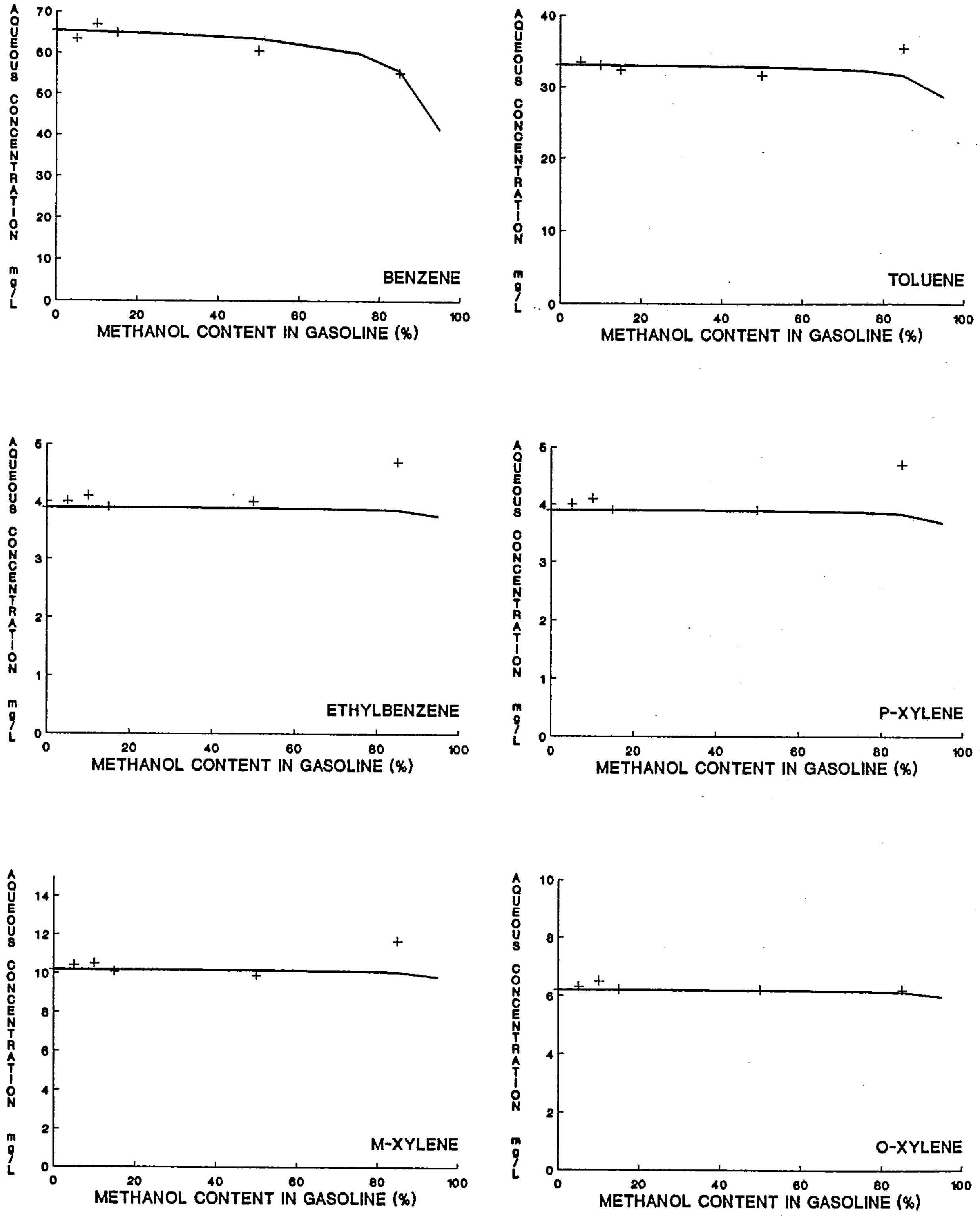

Figure 4-2. Effect of initial methanol content in gasoline on aqueous BTEX concentrations. Initial water:gasoline ratio is 10:1 (v/v). Curve represents calculated normalized trend; crosses represent experimental data.

calculated trends. This suggests that the potential for enhanced BTEX solubility due to the presence of methanol in the gasoline is minimal for the situation that produces low aqueous methanol contents.

EFFECT OF A HYDROPHOBIC OXYGENATE ON THE AQUEOUS CONCENTRATIONS OF BTEX

For the purpose of this calculation it is assumed that the oxygenate remains within the gasoline phase at equilibrium. As all of the oxygenate remains within the gasoline phase, the value of the equilibrium constant K^b_{gw} remains constant as the oxygenate content of the gasoline is changed.

The theory of Section 3 was applied to calculate aqueous BTEX concentrations resulting from contacting water and gasolines with varying MTBE content. The results of these calculations are presented in Table 4-2. These calculated values were normalized to the experimental values for zero MTBE content. The calculated relationships between aqueous BTEX concentration and MTBE content of the gasoline (percent v/v) from Table 4-2 and the experimental data from Table 2-2 are shown on Figure 4-3.

Table 4-2. Calculated aqueous BTEX concentrations for gasoline with varying MTBE content. Initial water:gasoline ratio = 10:1 (v/v).

MTBE in Gasoline (% v/v)	Benzene (mg/L)	Toluene (mg/L)	Ethyl-benzene (mg/L)	p-Xylene (mg/L)	m-Xylene (mg/L)	o-Xylene (mg/L)
0.00	65.50	33.10	3.90	3.90	10.20	6.20
5.00	62.93	31.98	3.77	3.68	9.91	6.03
10.00	60.36	30.85	3.64	3.45	9.61	5.86
15.00	57.79	29.73	3.51	3.23	9.32	5.69
25.00	52.66	27.49	3.26	2.78	8.73	5.34
50.00	39.82	21.87	2.61	1.67	7.25	4.49
75.00	26.98	16.26	1.97	0.55	5.78	3.63
85.00	21.84	14.02	1.71	0.10	5.19	3.29
95.00	16.70	11.77	1.45	-0.34	4.60	2.95

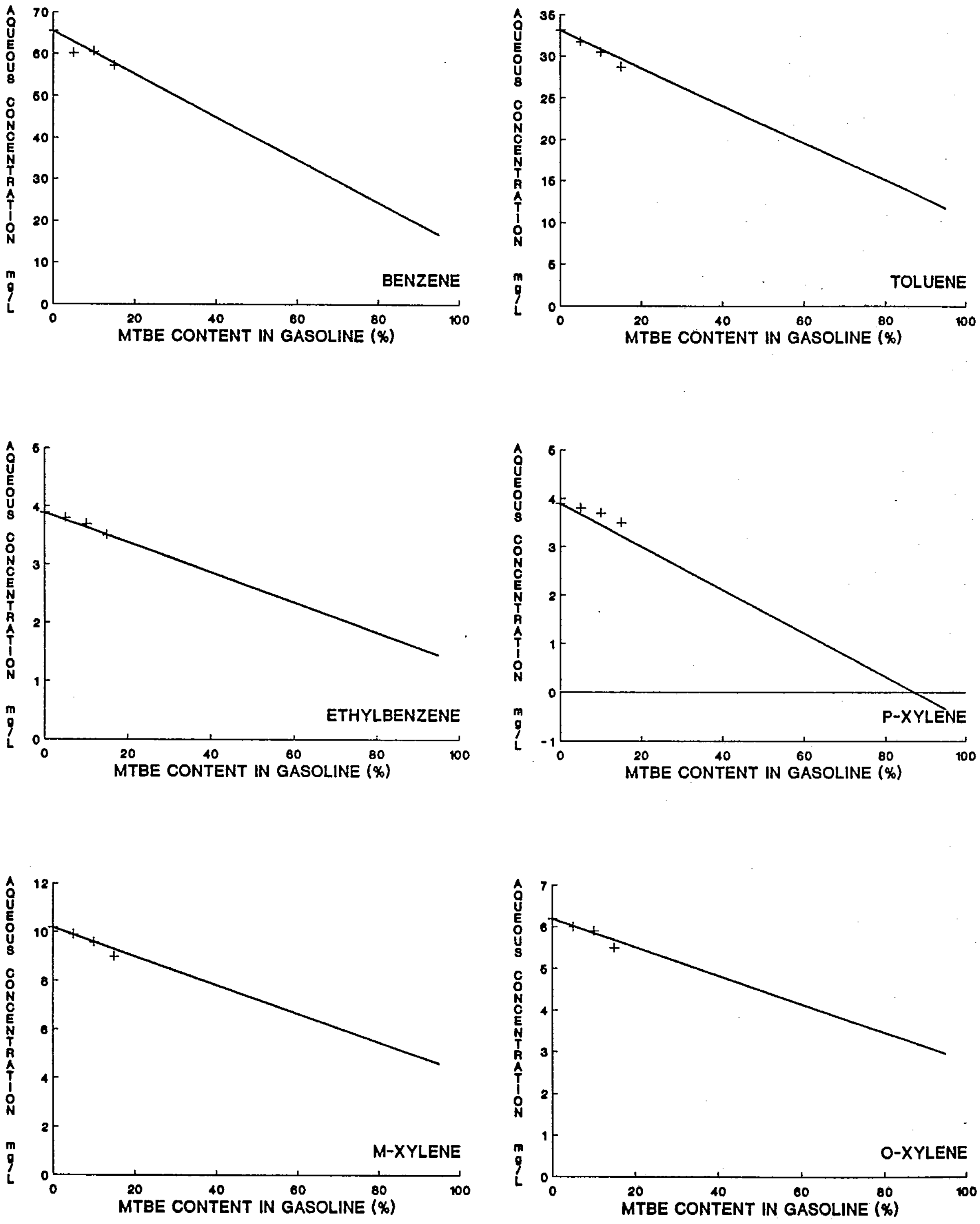

Figure 4-3. Effect of MTBE content on aqueous BTEX concentrations. Initial water:gasoline ratio = 10:1 (v/v). Curve represents calculated and normalized trend; crosses represent experimental data.

The experimental data are generally observed to follow a trend similar to that for the normalized values. There does not appear to be any enhanced solubility of BTEX due to the presence of MTBE in the gasoline. The calculation also assumed that all of the oxygenate remained within the gasoline phase. The experimental results suggest that approximately 46% (v/v) of the available MTBE partitioned into the aqueous phase.

ENHANCED SOLUBILITY OF BTEX BY HYDROPHILIC SOLVENTS

Our research demonstrated that high methanol contents in gasoline would not produce unexpectedly high aqueous BTEX concentrations for water:gasoline ratio of 10:1. Under these conditions the maximum aqueous methanol concentration is on the order of 8% (v/v) (for M-85). It is conceivable that situations might arise where larger volumes of gasoline with high methanol content (M-85) may come into contact with smaller volumes of water. This could result in aqueous methanol contents in excess of 50% (v/v). The following sections investigate the effects of such high aqueous methanol contents on the solubility of BTEX components from gasoline. The theory that describes the effects of high aqueous methanol content is developed and comparisons with experimental data for benzene-methanol-water and gasoline-methanol-water systems are presented. The benzene-methanol-water system was considered separately to demonstrate that the theory is applicable for cosolvency of a component from a pure phase. The effects of changing water:gasoline ratios on the aqueous BTEX concentrations for high aqueous methanol contents were further investigated and the results are summarized at the end of this section.

Cosolvency Theory

In aqueous solutions of a completely water-miscible cosolvent the solubility of hydrophobic organic compounds is believed to increase exponentially with increasing cosolvent volume fraction (Pinal et al., 1989; Rao, 1989; Banerjee, 1989; and Banerjee and Yalkowski, 1988). This relationship is expressed as:

$$\log S_m = \log S_w + \beta * f_c \qquad (4\text{-}1)$$

where:

S_m = solubility in water-cosolvent mixture
S_w = solubility in water
f_c = volume fraction of cosolvent in the aqueous phase
β = a measure of the relative ability of the cosolvent to solubilize hydrophobic organic compounds (cosolvency power) as expressed by:

$$\beta = \log (S_c / S_w) \qquad (4\text{-}2)$$

where:

S_c = solubility in pure cosolvent.

The parameter β is also a measure of the hydrophobicity of the solute (Rao, 1989) as expressed by:

$$\beta = a \log (K_{ow}) + b \qquad (4\text{-}3)$$

where:

K_{ow} = octanol-water partitioning coefficient, and
a, b = constants applying to a group of compounds (for example, BTEX).

The following expression is obtained by substituting the expression for β from Equation 4-2 into 4-1:

$$\log S_m = f_c \log S_c + (1 - f_c) \log S_w \qquad (4\text{-}4)$$

It is assumed that the total solubility is simply the sum of the solubilities in the individual solvent components.

This assumption is not valid for the case where the cosolvent is present in infinite dilution. In this case, the individual cosolvent molecules will be fully hydrated and should possess different properties than the bulk cosolvent (Banerjee, 1989; Banerjee and Yalkowski, 1988). In dilute solutions the solute is believed to contact only one hydrated cosolvent molecule at a time. Therefore, the solubility of a hydrophobic compound should be a linear rather than logarithmic function of the cosolvent fraction (Banerjee, 1989).

For example, for cosolvent contents less than 20% by volume, Banerjee and Yalkowski (1988) observed the linear relationship:

$$S_m = f_c * V_H * S_c^i + (1 - f_c * V_H) * S_w \tag{4-5}$$

where:

V_H = ratio of the hydration shell volume to cosolvent volume, and
S_c^i = solubility within the hydration shell of the cosolvent.

For toluene solubility in methanol-water mixtures with less than 20% methanol Banerjee and Yalkowski (1988) estimated $V_H = 6.7$ and $S_c^i = 1.4 * S_w$ from experimental results.

With cosolvent contents greater than 20% by volume, the conventional exponential behavior was observed. The breakpoint appears to be the region where the hydration shells of the cosolvent molecules begin to interact (Banerjee, 1989).

BTEX are miscible with methanol. If a pure BTEX phase were added to a solution with very high aqueous methanol contents, the final system would consist of a single phase and no separate BTEX phase would be present at equilibrium. In our experiments with gasoline, water, and methanol, a separate gasoline phase was always in equilibrium with the aqueous phase. The aqueous concentrations of BTEX are determined by partitioning of the solute between the two phases. This partitioning is controlled by the hydrophobicity of the solute as expressed by Equation 4-3.

Since the log-linear relationship starts at the breakpoint $(f'_{oc}, S_m(f'_{oc}))$, rather than at the point of water solubility $(0, S_w)$, Equation 4-1 should be modified to:

$$\log S_m = \log S_m(f'_c) + \beta (f_c - f'_c) \tag{4-6}$$

where:

f'_c = the methanol content at the breakpoint.

If no experimental values are available, f'_c can be estimated to be 0.25, and S_m (f'_c) can be calculated by Equation 4-5.

Effect of Methanol on Benzene Solubility

The experimentally determined aqueous benzene concentrations for aqueous phases with various methanol contents in equilibrium with pure benzene (Table 2-4) are presented graphically in Figures 4-4 and 4-5. Figure 4-4 presents the results for low aqueous methanol contents on a linear scale, while Figure 4-4 shows the entire range on a logarithmic scale. Essentially all of the benzene was dissolved into the aqueous phase for equilibrium methanol contents greater than approximately 55% (v/v) at an equilibrium aqueous methanol:benzene phase volume ratio V_w/V_b of 10. The experiments were repeated with $V_w/V_b = 1$ and the results are included in Figure 4-4. Examination of Figure 4-4 suggests that a breakpoint between linear and logarithmic behavior exists at an aqueous methanol content between 25% and 30% (v/v).

Aqueous concentrations of benzene for low methanol contents were calculated using Equations 4-5, 3-5, and 3-8. The values of V_H and S_c^l/S_w estimated by Banerjee and Yalkowski (1988) were used in solving (4-5). The results of this calculation are presented in Table 4-3 and the trends are plotted in Figure 4-4 for comparison with the experimental results.

A relatively good fit was observed between the calculated and experimental results shown in Figure 4-4 for aqueous methanol contents less than 25% (v/v). This indicates that the linear model adequately describes the partitioning of BTEX when sufficient methanol is present to cause enhanced cosolvency of BTEX.

The experimental results presented in Figure 4-5 suggest that a log-linear relationship exists between benzene concentration and methanol content for methanol contents greater than 25 to 30% (v/v). Aqueous benzene concentrations were calculated for methanol contents greater than 30% (v/v) using Equations 4-6, 4-3, 3-5, and 3-8.

Table 4-3. Calculated aqueous benzene concentration in water-methanol mixtures contacting pure benzene.

a) Low Methanol Content

f_c	$V_w/V_b = 10$ Benzene (mg/L)	$V_w/V_b = 1$ Benzene (mg/L)
0	1744.66	1776.40
0.1	2200.51	2251.26
0.2	2651.57	2725.60
0.25	2875.32	2962.58
0.3	3097.90	3199.43

V_w/V_b = aqueous methanol:benzene phase volume ratio

b) High Methanol Content ($f'_c = 0.25$)

f_c	$V_w/V_b = 10$ Benzene (mg/L)	$V_w/V_b = 1$ Benzene (mg/L)
0.3	3789.1	3942.1
0.35	4975.7	5242.9
0.4	6505.2	6969.6
0.45	8456.8	9258.8
0.5	10915.3	12289.3
0.55	13962.9	16293.2
0.6	17666.1	21569.0
0.65	22058.2	28496.8
0.7	27120.4	37552.2
0.75	32766.0	49318.2
0.8	38835.4	64488.1
0.85	45108.6	83852.4
0.9	51334.3	108258.2
0.95	57268.3	138529.3

V_w/V_b = aqueous methanol:benzene phase volume ratio

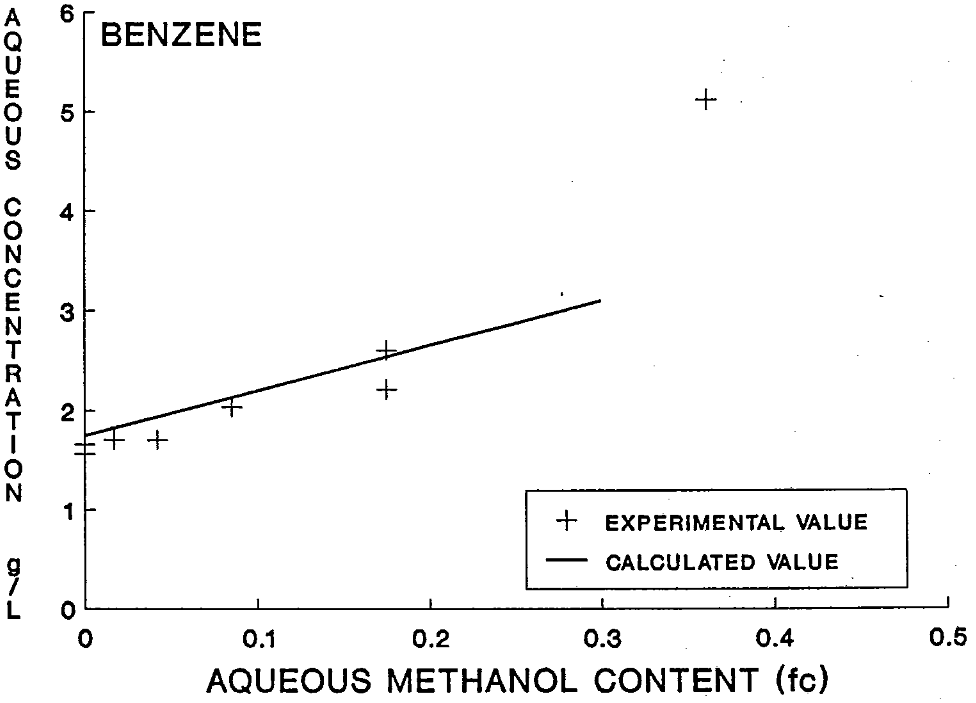

Figure 4-4. Cosolvency effect of methanol on aqueous benzene concentration (linear scale) at an aqueous methanol:benzene phase volume ratio of 10.

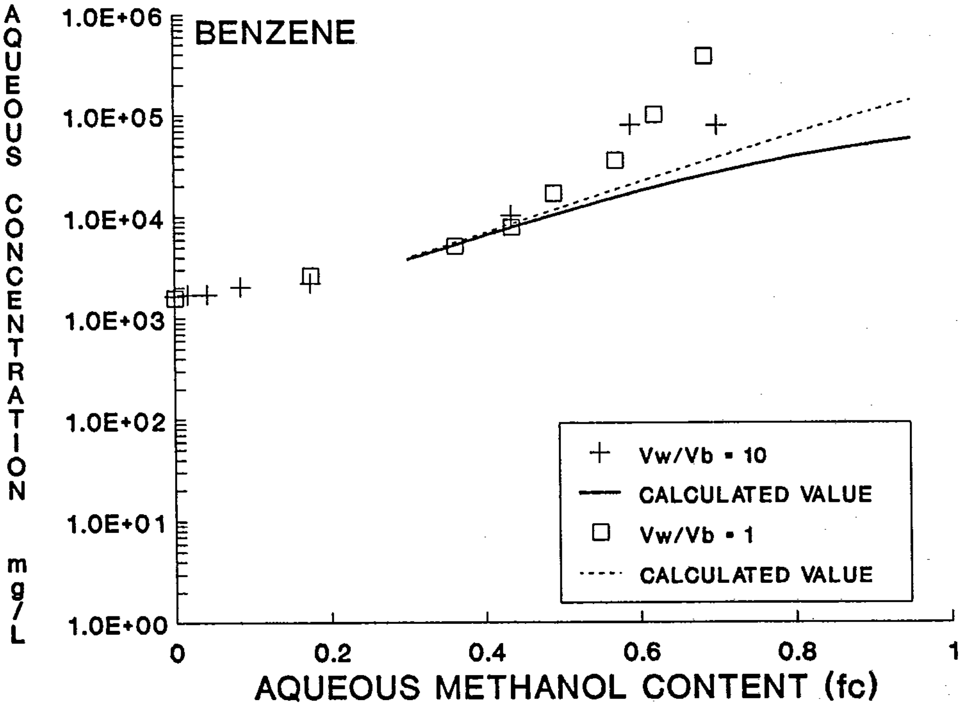

Figure 4-5. Cosolvency effect of methanol on aqueous benzene concentration (logarithmic scale) at aqueous methanol:benzene phase volume ratios of 10 and 1.

Values for a and b in Equation 4-3 were derived and the breakpoint (f'_c) was considered to be 25% (v/v). The results of this calculation are presented in Table 4-3 and illustrated in Figure 4-2. The calculated benzene concentrations agree with the experimental values for equilibrium aqueous methanol contents up to 55% (v/v). At higher methanol contents the experimental values are higher than the calculated values. The trend of the calculated curve in Figure 4-5 for $V_w/V_b = 10$ diverges from the log linear trend at higher methanol contents due to complete dissolution of the benzene phase.

The above discussion demonstrates that the partitioning model and the cosolvency theory can reproduce the experimentally determined aqueous benzene concentrations in equilibrium for a benzene-methanol-water system. The theory will now be applied to the more complex gasoline-methanol-water system.

Effect of Methanol on BTEX Solubility From Gasoline

The experimentally determined aqueous BTEX concentrations for aqueous phases with various methanol contents in equilibrium with gasoline (Table 2-3) are plotted in Figures 4-6 and 4-7. Figure 4-6 presents the results for low methanol contents on a linear scale, while Figure 4-7 displays the entire range of methanol contents on a logarithmic scale. Breakpoints are observed at aqueous methanol contents between 20 and 30% (v/v). The linear relationship is valid at methanol contents below 20% (v/v), while the log-linear relationship is better above 30% (v/v).

The relative increase in solubility with methanol content (β) for aqueous methanol contents greater than 30% (v/v) increased corresponding to the hydrophobicity of the solute. This suggests that the cosolvency effect is greater for the xylenes than for benzene. A linear relationship between β and $\log(K_{ow})$ is observed in Figure 4-8, which demonstrates the applicability of Equation 4-3. The values of a and b, as derived from Figure 4-8, are 2.57 and -3.01, respectively.

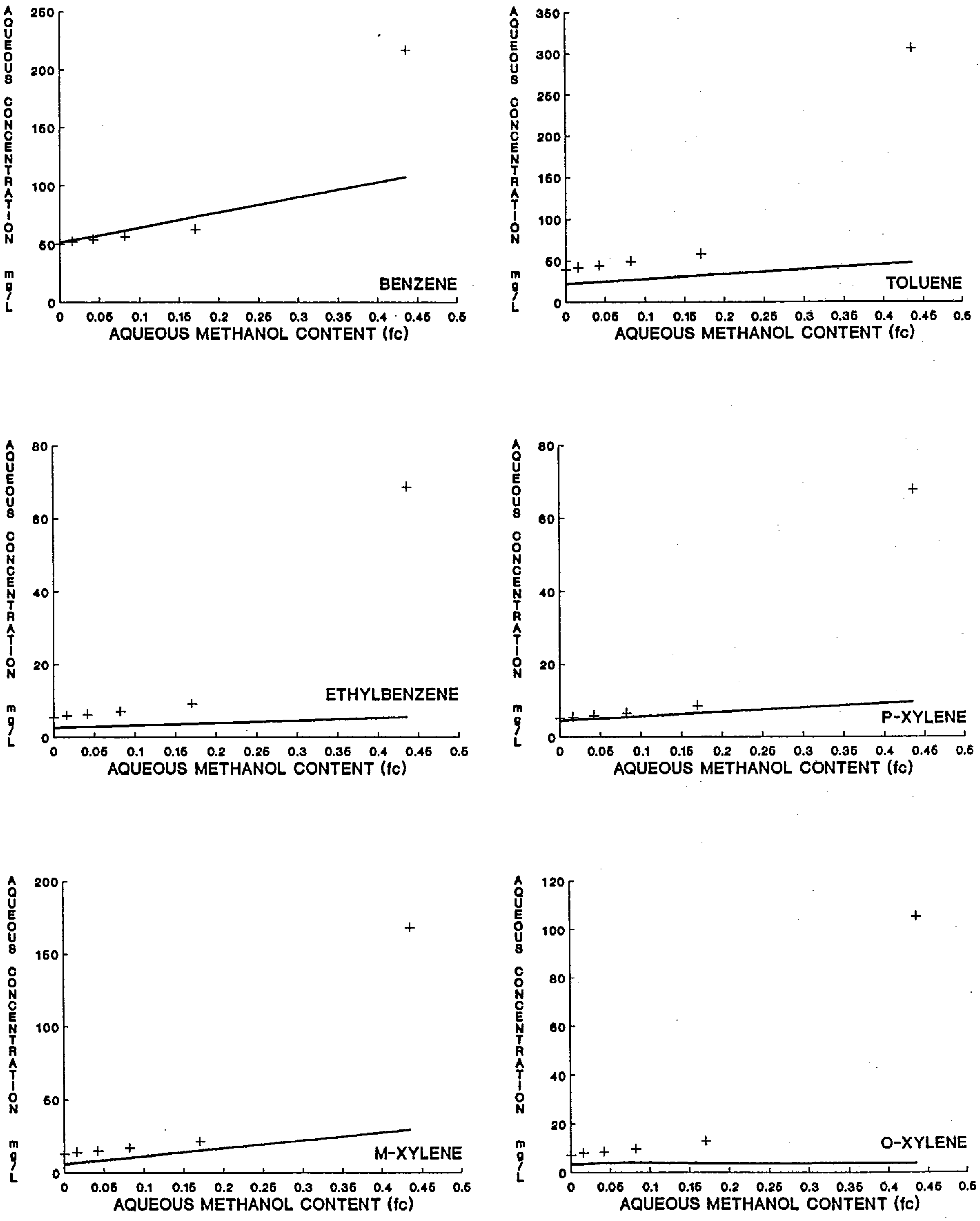

Figure 4-6. Cosolvency effect of methanol on aqueous BTEX concentrations (linear scale). Line represents calculated linear trend from Equation 4-5; crosses represent experimental data.

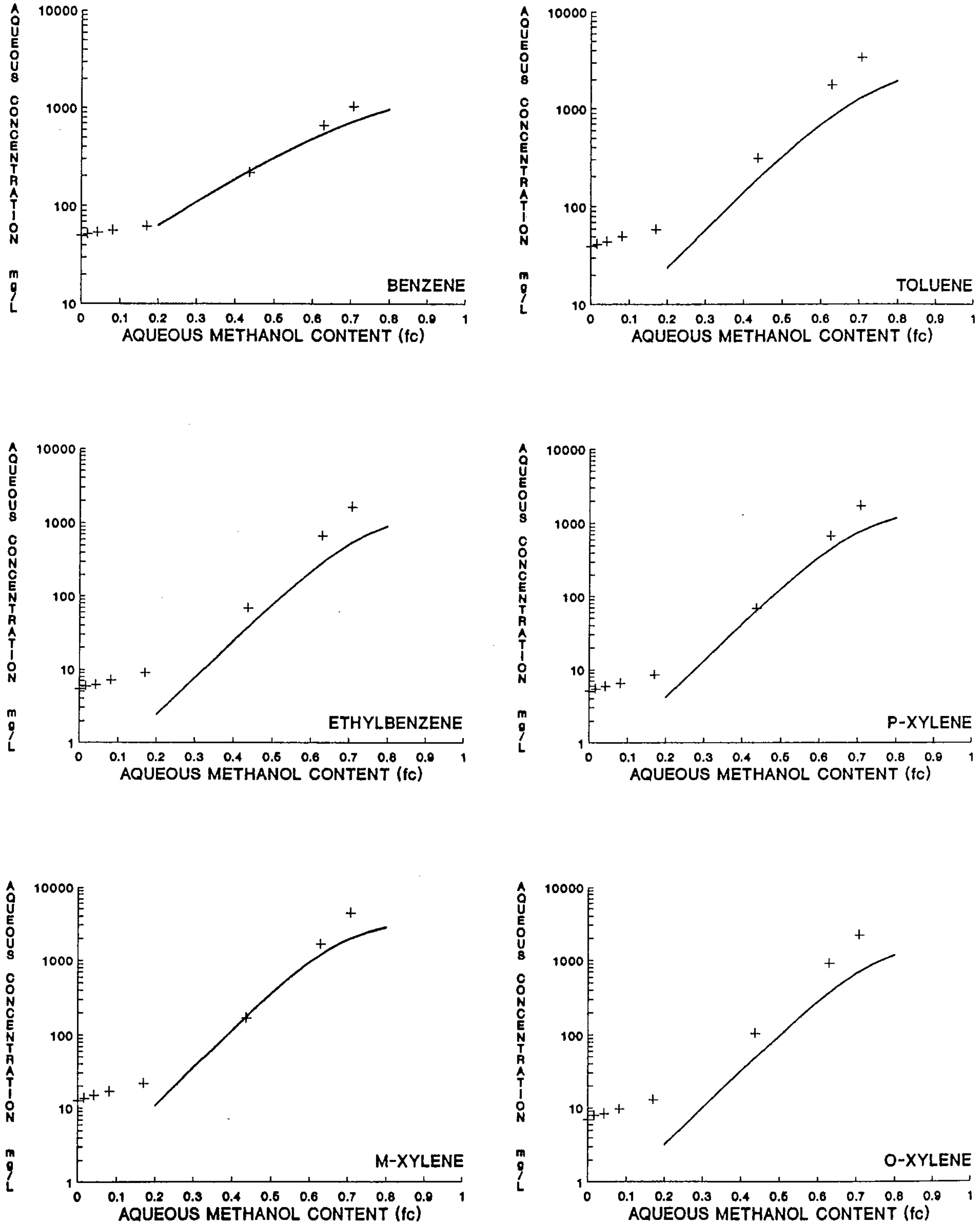

Figure 4-7. Cosolvency effect of methanol on aqueous BTEX concentrations (logarithmic scale). Curve represents calculated log-linear trend from Equation 4-6; crosses represent experimental data.

Aqueous concentrations of BTEX for aqueous methanol contents less than 25% (v/v) were calculated using Equation 4-5. The values used for V_H and S_c^l were estimated for toluene by Banerjee and Yalkowski (1988). The results of this calculation are presented in Table 4-4, and the trend is plotted in Figure 4-6. There is generally good agreement between the calculated and experimentally determined values.

Table 4-4. Calculated aqueous BTEX concentrations in water-methanol mixtures contacting gasoline (low methanol content).

Methanol Content (Equilibrium) f_c	Benzene (mg/L)	Toluene (mg/L)	Ethyl-benzene (mg/L)	p-Xylene (mg/L)	m-Xylene (mg/L)	o-Xylene (mg/L)
0.00	51.4	22.5	2.6	4.5	5.9	3.4
0.016	53.5	23.4	2.7	4.7	6.8	3.6
0.042	57.0	25.0	2.9	5.0	8.2	3.8
0.082	62.3	27.3	3.1	5.4	10.4	4.2
0.17	73.8	32.6	3.8	6.5	15.3	3.6
0.436	107.8	48.3	5.6	9.7	29.8	3.8

For aqueous methanol contents greater than 25% (v/v) the aqueous BTEX concentrations were calculated using Equations 4-3, and 4-6 followed by 3-3 and 3-8. The molar fractions, volume fractions, and relative phase volumes change as the system approaches equilibrium. These changes have little effect on the aqueous solute concentrations as long as the equilibrium methanol content is used in the calculations. If experimentally determined aqueous methanol contents are not available, the methanol content can be determined from the gasoline-water partitioning coefficient. The results of these calculations are summarized in Table 4-5, and plotted in Figure 4-7. The calculated results correspond well with the experimentally determined values. The trends of the calculated curves diverge from the log linear trend at higher methanol contents due to depletion of available BTEX in the gasoline.

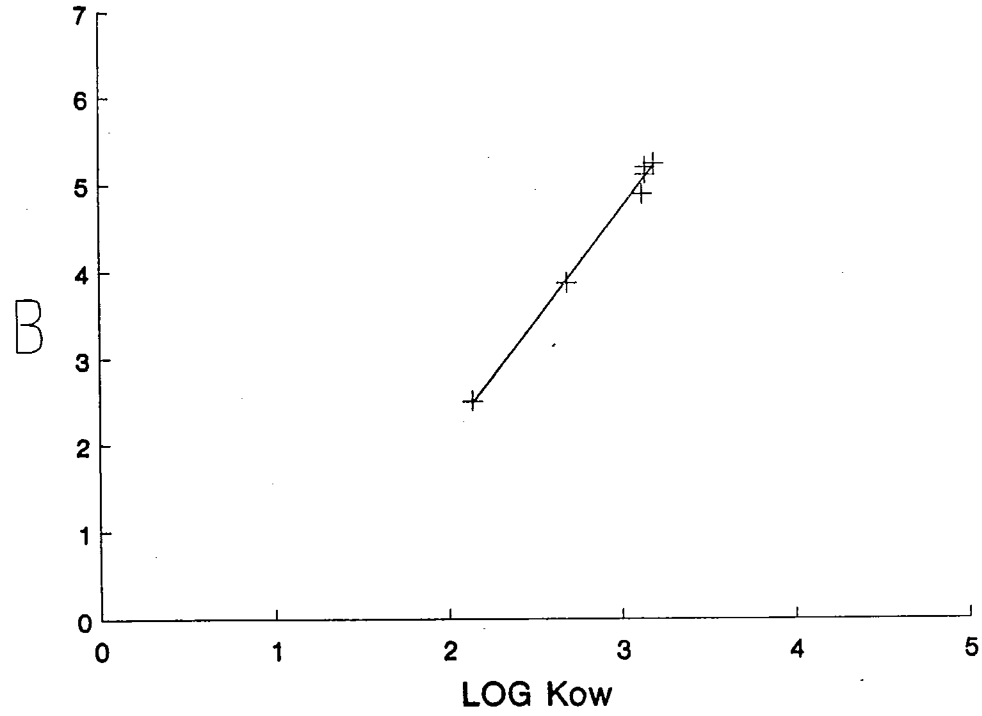

Figure 4-8. β as a function of K_{ow}.

Table 4-5. Calculated aqueous BTEX concentrations in water-methanol mixtures contacting gasoline (high methanol content).

Methanol Content (Equilibrium) f_c	Benzene (mg/L)	Toluene (mg/L)	Ethylbenzene (mg/L)	p-Xylene (mg/L)	m-Xylene (mg/L)	o-Xylene (mg/L)
0.20	63.9	23.9	2.4	4.2	10.8	3.2
0.25	84.2	37.3	4.3	7.5	19.6	5.7
0.30	110.5	58.1	7.7	13.3	35.6	10.2
0.35	144.2	90.0	13.8	23.8	64.4	18.0
0.40	187.2	138.8	24.6	42.2	115.6	32.0
0.45	241.2	212.1	43.5	74.2	205.1	56.3
0.50	307.8	319.8	76.1	128.4	356.8	98.2
0.55	388.2	473.1	130.9	216.4	600.2	168.2
0.60	483.1	681.6	218.4	349.9	959.4	280.2
0.65	591.6	948.1	347.8	533.1	1428.3	446.8
0.70	711.6	1263.2	519.1	752.4	1951.6	669.8
0.75	839.4	1603.3	715.1	976.0	2442.7	929.7
0.80	970.2	1935.7	905.6	1169.6	2833.9	1187.9

Effect of Aqueous:Gasoline Phase Ratios at Higher Methanol Contents

Aqueous BTEX concentrations were calculated using Equations 4-3, 4-6, 3-5 and 3-8, assuming that the aqueous methanol content at equilibrium was 43.6%. This was the experimentally determined value for the case where $V_w/V_g = 10$ (Table 2-3). The molar fractions, volume fractions and relative phase volumes change as equilibrium is approached. These changes have relatively little effect on the aqueous BTEX concentrations.

The results of these calculations are summarized in Table 4-6. This trend and the experimentally determined aqueous BTEX concentrations for an initial 1:1 water:methanol mixture in equilibrium with gasoline at various gasoline:aqueous phase volume ratios (Table 2-5) are plotted in Figure 4-9. The calculated trend roughly corresponds with the experimental results, confirming the reliability of the calculation. Depletion of the available BTEX was observed to occur at lower aqueous phase:gasoline phase ratios than for similar experiments without cosolvents. This is due to the higher solubilities of BTEX in the water-methanol mixture.

Table 4-6. Effect of aqueous:gasoline phase ratio on aqueous BTEX concentrations for gasoline contacted with 50% aqueous methanol by volume.

Aqueous: Gasoline Ratio	Benzene (mg/L)	Toluene (mg/L)	Ethyl-benzene (mg/L)	p-Xylene (mg/L)	m-Xylene (mg/L)	o-Xylene (mg/L)
1:1	244.4	189.3	35.4	61.4	170.5	46.0
2.5:1	239.6	187.5	35.3	61.0	169.3	45.8
5:1	232.0	184.7	35.1	60.4	167.3	45.5
7.5:1	224.9	181.9	34.9	59.9	165.3	45.2
10:1	218.2	179.2	34.6	59.3	163.4	45.0
25:1	185.1	164.7	33.4	56.1	152.7	43.4
50:1	147.7	145.1	31.4	51.5	137.8	40.9
75:1	122.9	129.7	29.7	47.5	125.5	38.8
100:1	105.2	117.2	28.2	44.2	115.2	36.8
250:1	56.5	74.4	21.5	31.0	77.3	28.3
500:1	31.9	46.2	15.4	20.7	49.9	20.4
750:1	22.2	33.5	12.0	15.5	36.8	16.0
1000:1	17.0	26.3	9.8	12.4	29.2	13.1

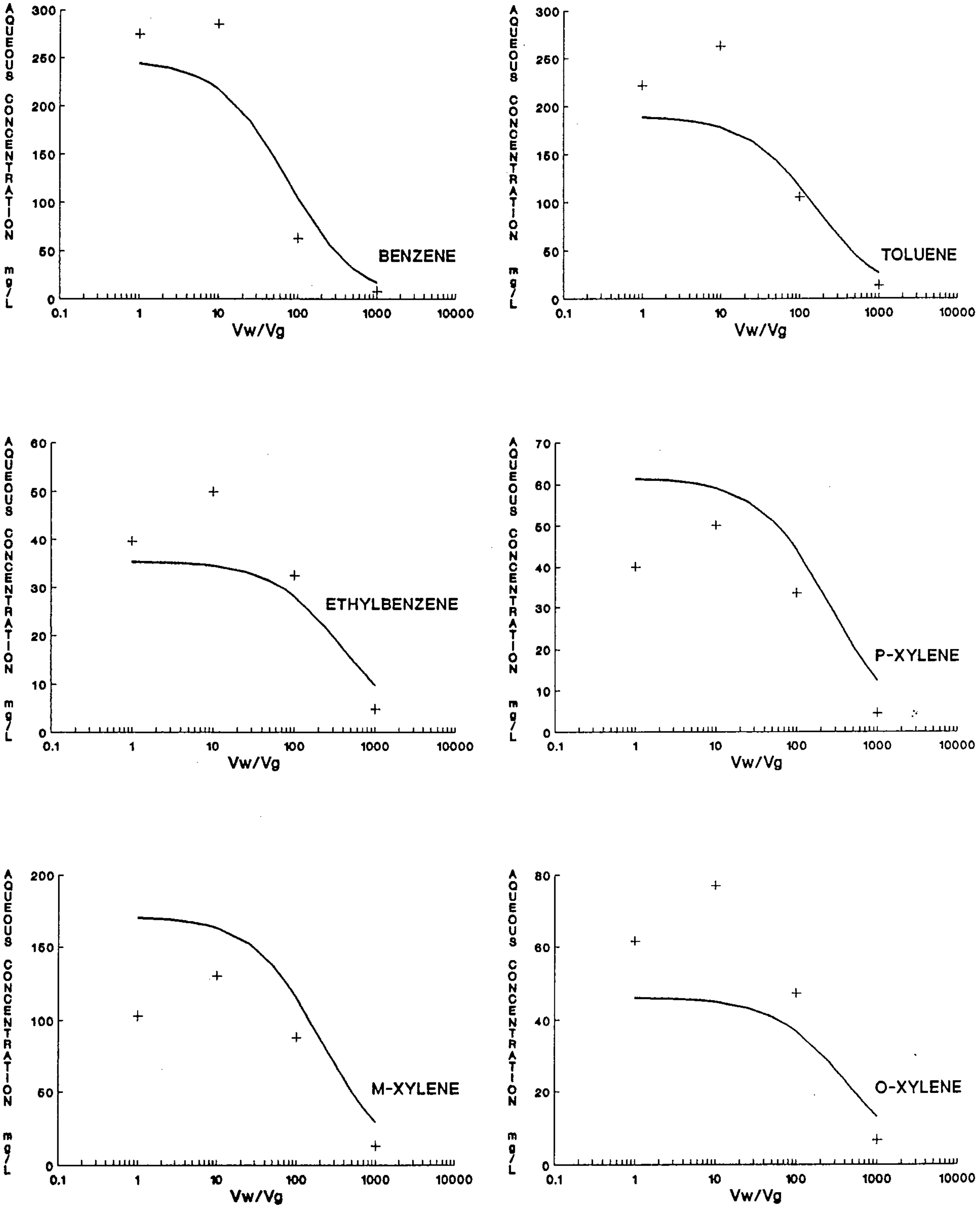

Figure 4-9. Effect of aqueous:gasoline phase ratio (V_w/V_g)on BTEX concentration for gasoline contacted with 50% aqueous methanol (v/v). Curve represents calculated log-linear trend from Equation 4-6; crosses represent experimental data.

Summary of Cosolvency Effects

Hydrophilic oxygenate additives such as methanol can potentially enhance the solubility of BTEX compounds in gasoline mixtures. The partitioning and cosolvency theories developed in the previous sections suggest that this effect will be greatest when the aqueous phase has a methanol content of greater than approximately 20% (v/v). This implies that when gasoline containing methanol is introduced into a water phase the relative proportions of the two phases control the resultant aqueous BTEX concentrations. For example, a spill of M-85 fuel into a smaller volume of water would create an aqueous phase with a relatively high methanol content, which would be characterized by higher aqueous BTEX concentrations than for a spill of gasoline. If the water volume were much larger than the initial fuel volume, then the resultant aqueous BTEX concentrations would be lower than for a spill of gasoline.

DISSOLVED BTEX PLUMES RESULTING FROM SPILLS OF METHANOL-GASOLINE MIXTURES

The following sections apply the theories developed above to investigate the effect of methanol content in gasoline on dissolved BTEX plumes in groundwater. The effects of methanol partitioning between the gasoline and groundwater phases, the calculation methods used to obtain concentration input for the groundwater transport model, and the results of the modelling exercise are discussed.

Methanol Partitioning

As a spill of gasoline containing methanol contacts the groundwater the methanol will partition preferentially into the aqueous phase. For a gasoline with high methanol content (M-85), the following mass balance expression is derived from Equation 3-8:

$$c^m_w = y^m_g * V^i_g * p^m / (K^m_{gw} * V_g + V_w) \qquad (4\text{-}7)$$

Assuming that methanol and water form ideal mixtures, methanol will partition into the aqueous phase resulting in significant changes to the phase volumes according to:

$$V_w = V^i_w + (c^m_w * V_w) / p^m \qquad (4\text{-}8)$$

$$V_w = (V^i_w * p^m) / (p^m - c^m_w) \qquad (4\text{-}9)$$

$$V_g = V^i_g + V^i_w - V_w \qquad (4\text{-}10)$$

The following relationship is obtained by substituting Equations 4-9 and 4-10 into 4-7:

$$c^m_w = y^m_g * V^i_g * p^m \; / \; (K^m_{gw} * (V^i_g + V^i_w) + (1 - K^m_{gw}) * V_w) \qquad (4\text{-}11)$$

The aqueous concentration of methanol and the volume of the aqueous phase can be calculated from Equations 4-9 and 4-11 by iteration. Equation 4-10 can be used to calculate V_g if the initial volumes of water and gasoline that will be in equilibrium are known. These values can then be substituted into Equations 4-5 and 4-6 to calculate the aqueous BTEX concentrations.

Successive Batches

In all of the examples considered this far we have been concerned only with the equilibrium BTEX concentrations from contacting fixed volumes of water and gasoline. In a real spill situation fresh groundwater will continually flow past the gasoline spill. As the groundwater flows, small volumes of each phase will likely reach equilibrium. Because the composition of the gasoline phase will change due to dissolution of the soluble components (BTEX), the aqueous concentrations of successive groundwater volumes will also change.

This situation can be simulated by considering a series of successive batches in which quantities of water and gasoline are brought into equilibrium, then the water is removed and replaced with fresh water. This process can be repeated numerous times. The composition of the gasoline will change with each successive batch in response to dissolution of the BTEX into the water. A set of equations that can be used to complete a sample simulation is included in Appendix E. The simulation was repeated for various methanol contents of gasoline and various initial gasoline volume to water volume ratios. These calculations were made using the octanol-water partitioning coefficient of methanol, $K^m_{ow} = 0.178$, in approximation of the gasoline-water partition coefficient.

Cline et al. (1991) report a gasoline-water partition coefficient for methanol of $K^{m}_{gw} = 0.0051$. The differences in these values do not significantly change the findings of the batch simulations and subsequent modelling. The results of these simulations for benzene are summarized in Tables 4-7 and 4-8 respectively. Table 4-7 demonstrates that the lower partitioning value of Cline et al., estimates more methanol in the aqueous phase, and less benzene. After batch 3, however, little effect is noted. Similarly in Table 4-8, the lower partitioning coefficient estimates more methanol in the aqueous phase for the initial batches, with less BTEX partitioning into the aqueous phase.

Modelling was used to calculate the composition of the batches for input into a transport model. The data were calculated with the octanol-water partitioning coefficient for methanol rather than the recently-reported gasoline-water partitioning coefficient. As demonstrated in Tables 4-7 and 4-8, this substitution does not significantly change the results.

Table 4-7. Aqueous benzene concentrations (mg/L) in successive batches of water exposed to gasoline pools with varying methanol content.

	Initial Methanol Content (v/v):							
Batch	0	0.3	0.4	0.5	0.6	0.7	0.8	0.85
1	52.70	109.36	148.47	230.34	353.55	531.86	741.13	793.36
1*	52.70	116.39	169.58	261.60	396.36	585.09	790.36	829.08
2	52.70	57.64	58.54	59.05	59.15	58.93	57.91	56.60
2*	52.70	52.80	52.78	52.73	52.63	52.42	51.80	50.79
3	52.70	53.17	53.15	53.05	52.87	52.57	51.86	50.82
3*	52.70	52.63	52.59	52.53	52.43	52.23	51.60	50.54
4	52.69	52.69	52.64	52.57	52.46	52.25	51.63	50.58
5	52.69	52.63	52.59	52.53	52.43	52.23	51.59	50.48
6	52.69	52.63	52.59	52.53	52.42	52.22	51.56	50.38
7	52.69	52.62	52.58	52.52	52.42	52.21	51.53	50.26
8	52.69	52.62	52.58	52.52	52.42	52.20	51.50	50.14
9	52.69	52.62	52.58	52.52	52.41	52.19	51.47	50.00
10	52.69	52.62	52.58	52.52	52.41	52.19	51.43	49.84
10*	52.69	52.62	52.58	52.52	52.41	52.17	51.36	49.61

Note: Initial water:gasoline volume ratio = 1:1 for all simulations. Batches with * are values calculated with methanol $K^{m}_{gw} = 0.0051$.

Table 4-8. Aqueous benzene concentrations (mg/L) in successive batches of water exposed to M-85 fuel pools of varying size.

	Initial Gasoline Volume:								
Batch	10	5	2	1	0.8	0.5	0.2	0.1	0.01
1	2571.56	2178.39	1395.06	793.36	641.87	405.68	233.56	156.91	25.29
1*	2564.60	2202.29	1443.82	829.08	669.79	420.52	236.47	157.78	25.29
2	86.04	73.28	61.68	56.60	55.20	52.61	45.35	35.42	1.86
2*	53.04	52.17	51.43	50.79	50.49	49.55	44.28	34.96	1.86
3	58.54	54.06	51.76	50.82	50.45	49.38	42.99	29.88	0.07
3*	51.95	51.56	51.09	50.54	50.24	49.25	42.90	29.78	0.07
4	53.41	51.99	51.24	50.58	50.24	49.11	41.22	22.40	0.00
5	52.35	51.73	51.17	50.48	50.11	48.84	38.81	12.56	0.00
6	52.11	51.67	51.11	50.38	49.97	48.54	35.41	3.65	0.00
7	52.05	51.65	51.05	50.26	49.81	48.19	30.46	0.27	0.00
8	52.03	51.62	50.99	50.14	49.64	47.78	23.23	0.00	0.00
9	52.02	51.59	50.93	50.00	49.44	47.30	13.54	0.00	0.00
10	52.00	51.56	50.86	49.84	49.22	46.73	4.29	0.00	0.00
10*	51.83	51.30	50.59	49.81	48.99	46.47	3.90	0.00	0.00

Note: Initial water volume = 1 for all simulations.
Initial methanol content of gasoline = 0.85 (v/v) for all simulations.
Batches with * are values calculated with methanol $K^{m}_{gw} = 0.0051$.

BTEX Plumes

The results of selected successive batch simulations were used as input into a groundwater transport model to simulate dissolved benzene and methanol plumes. Comparisons of the resultant plumes were made for a range of methanol contents and for various equilibrium volume ratios of the two phases.

The groundwater transport model used for these simulations was DPORTRAN (Sudicky, 1990). This model solves for flow in two-dimensions using the Galerkin finite element method and for mass transport using the Laplace-Transform Galerkin technique. The transport simulations for each case were performed using a homogeneous anisotropic porous medium and average horizontal and vertical velocities equal to 0.067 m/day and 0.000862 m/day (downward), respectively. The parameter values for the modelled flow system are presented in Table 4-9. The hydraulic conductivity and dispersivity values are typical of a sandy aquifer similar to the aquifer at Borden, Ontario (Sudicky, 1986). The dimensions of the model field were 50 x 3 m. Concentrations of benzene or methanol were input over a 5 m length of the upper boundary. This would represent a gasoline or M-85 fuel spill with a width of 5 m. A stepped concentration input was used with each step of 10 days representing successive batch concentrations. The remainder of the upper boundary was a third-type boundary that permits infiltration of uncontaminated water. The model output was contoured to illustrate the solute concentration distributions at 150, 250 and 350 days. Contour intervals of 5 mg/L and 200 mg/L were used for the benzene and methanol cases, respectively. The two solutes were assumed to behave independently during transport and were modelled as separate cases. Benzene was assumed to migrate at about 90% of the groundwater velocity as per field observations in the Borden aquifer (Patrick et al. 1985). Methanol was assumed to migrate at the groundwater velocity as observed in field observations (Barker et al. 1990). No biological or chemical mass loss was considered. This will be addressed in a subsequent report (Hubbard et al., in prep.).

Table 4-9. Transport parameters for groundwater flow modelling.

Length of Flow System	50 m
Aquifer Thickness	3 m
Length of Solute Input Zone	5 m
Number of Nodes in X-Direction	101
Number of Nodes in Z-Direction	51
Longitudinal Dispersivity	0.5 m
Transverse Dispersivity	0.002 m
Benzene Diffusion Coefficient	4.305×10^{-5} m^2/day
Methanol Diffusion Coefficient	7.548×10^{-5} m^2/day
Horizontal Hydraulic Gradient	3.0×10^{-3}
Vertical Hydraulic Gradient	5.0×10^{-5}
Porosity	0.35
Mean X - Hydraulic Conductivity	7.78 m/day
Mean Z - Hydraulic Conductivity	6.04 m/day
Mean X - Velocity	6.667×10^{-2} m/day
Mean Z - Velocity	-8.62×10^{-4} m/day
Benzene Retardation Factor	1.1
Methanol Retardation Factor	1.0

The effects of increasing the initial methanol content of the gasoline on the resultant dissolved benzene and methanol plumes are illustrated in Figures 4-10 and 4-11, respectively.

Figure 4-10 shows that the shape of the dissolved benzene plume changes significantly with increasing methanol content. For the case with high methanol content (85% v/v), elevated benzene concentrations are observed near the leading edge of the plume. The effects of dispersion cause a longer and broader plume to develop. The gasoline phase remains as a continuous source of dissolved benzene.

The shapes of the dissolved methanol plumes are considerably different from the dissolved benzene plumes (Figure 4-11). The methanol content of the gasoline is depleted quickly, resulting in a discrete elliptical plume. The center of mass of this plume is initially identical to the benzene plume, however, the methanol plume will advance at a greater velocity due to the lack of retardation of methanol.

The effects of changing the equilibrium aqueous:gasoline phase volume on the resultant dissolved benzene plumes are illustrated on Figure 4-12. Initial aqueous:gasoline phase ratios of 0.1, 1, and 10 (v/v) were modelled. The case with low aqueous:gasoline phase ratio clearly illustrates the formation of a pulse with high benzene concentrations near the front of the plume with the remaining benzene in the gasoline serving as a long term source of dissolved benzene. The case with a high aqueous:gasoline phase ratio illustrates complete dissolution of the benzene from the gasoline due to the cosolvency effects of the methanol. The benzene then travels as a small elliptical pulse. Dispersion causes the maximum concentrations of the plume to decrease, while increasing the area of impact over time. Note that lowest benzene concentration contour is 5 mg/L for all of these simulations. The actual volume in which the groundwater concentrations exceed the drinking water standard for benzene is much larger.

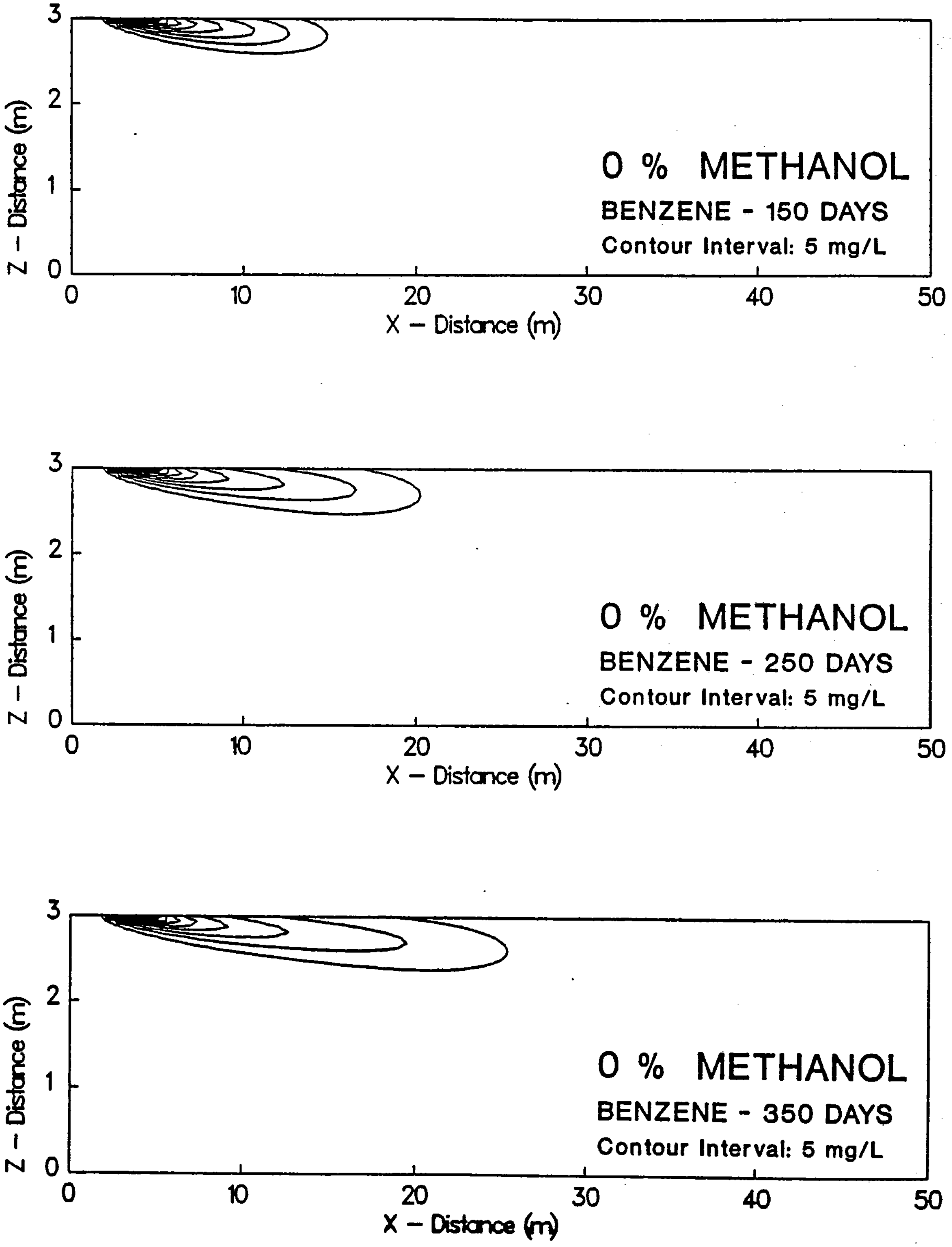

Figure 4-10. Examples of dissolved benzene plumes arising from spills of gasoline with no methanol.

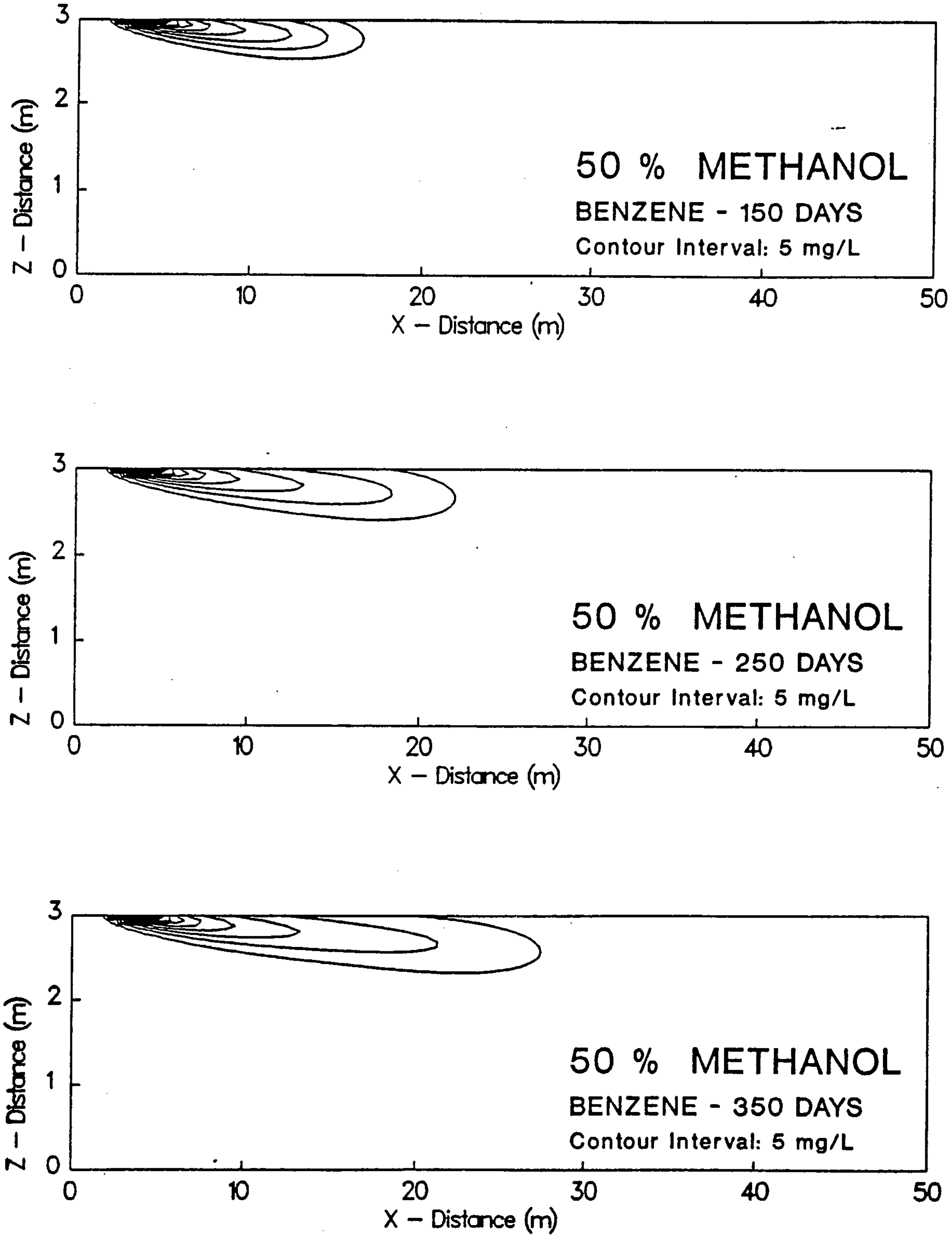

Figure 4-11. Examples of dissolved benzene plumes arising from spills of gasoline with 50% methanol.

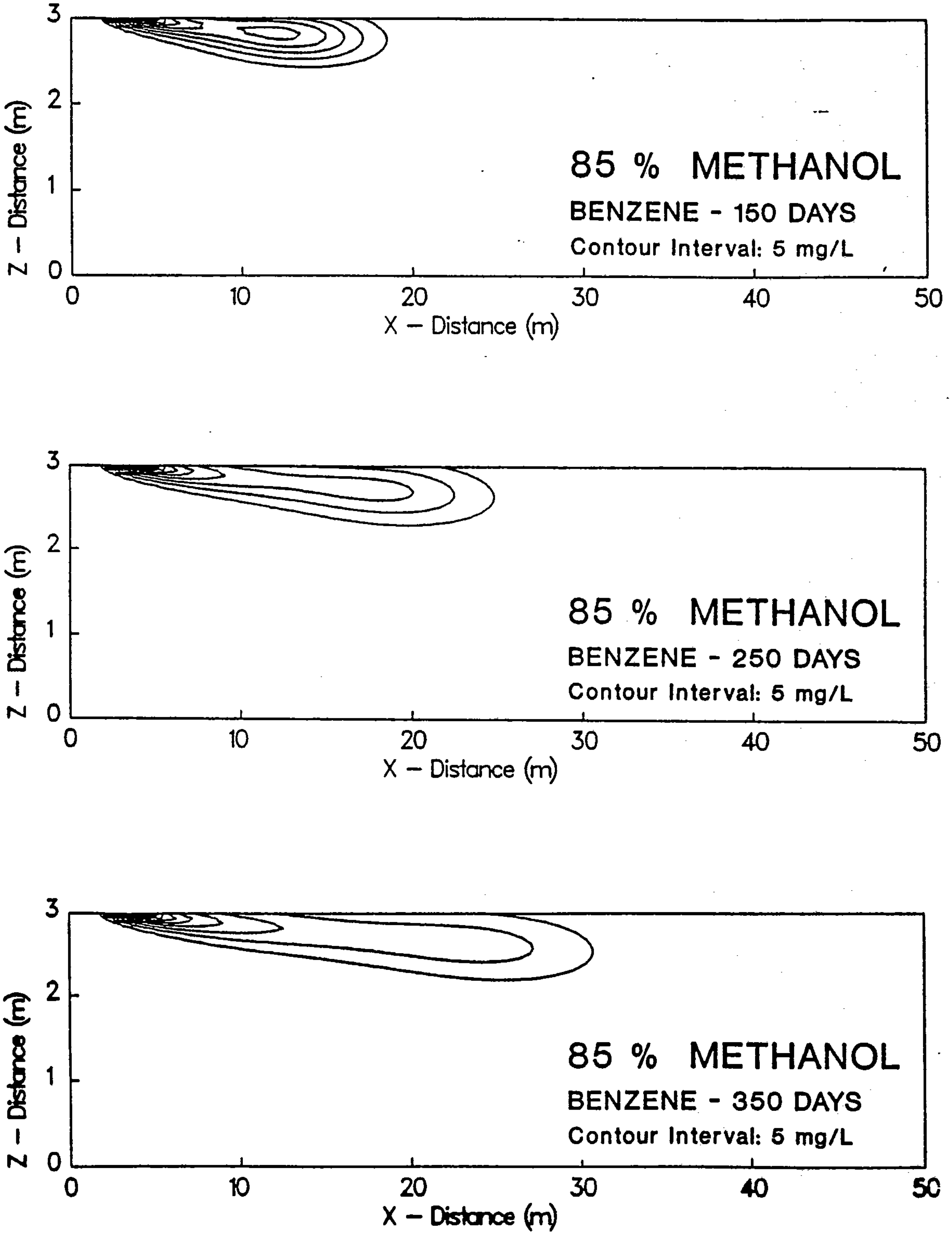

Figure 4-12. Examples of dissolved benzene plumes arising from spills of gasoline with 85% methanol.

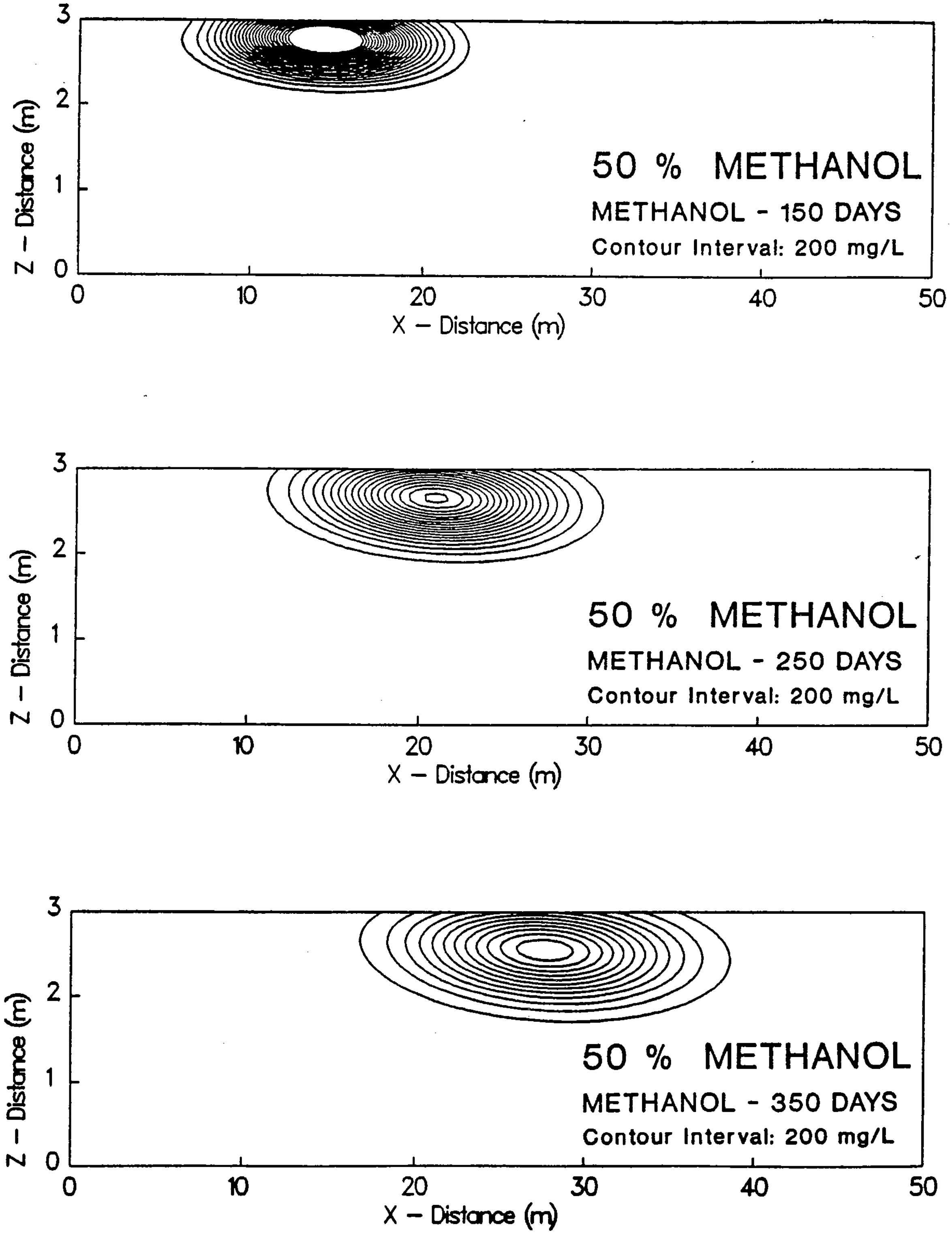

Figure 4-13. Examples of dissolved methanol plumes arising from spills of gasoline with 50% methanol.

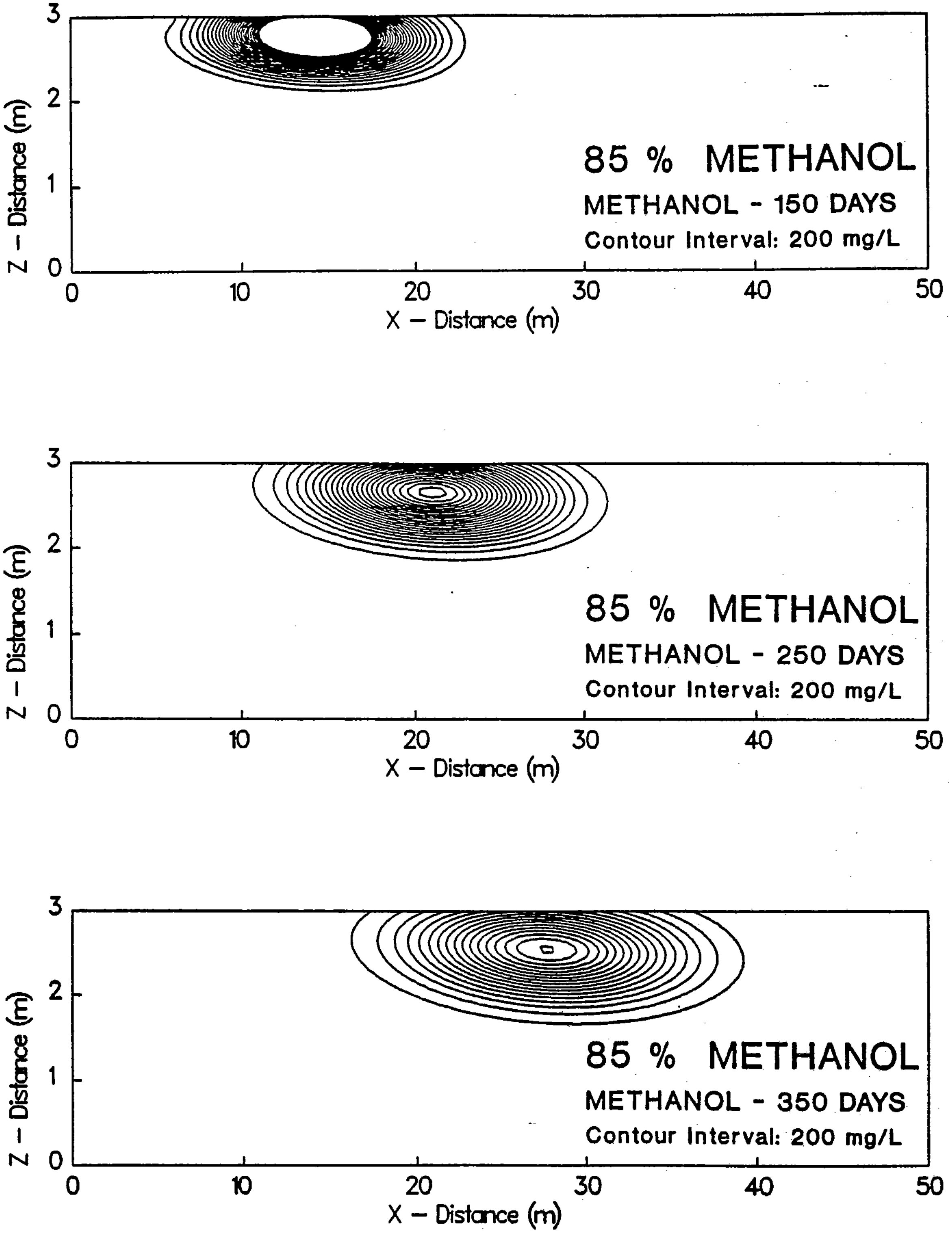

Figure 4-14. Examples of dissolved methanol plumes arising from spills of gasoline with 85% methanol.

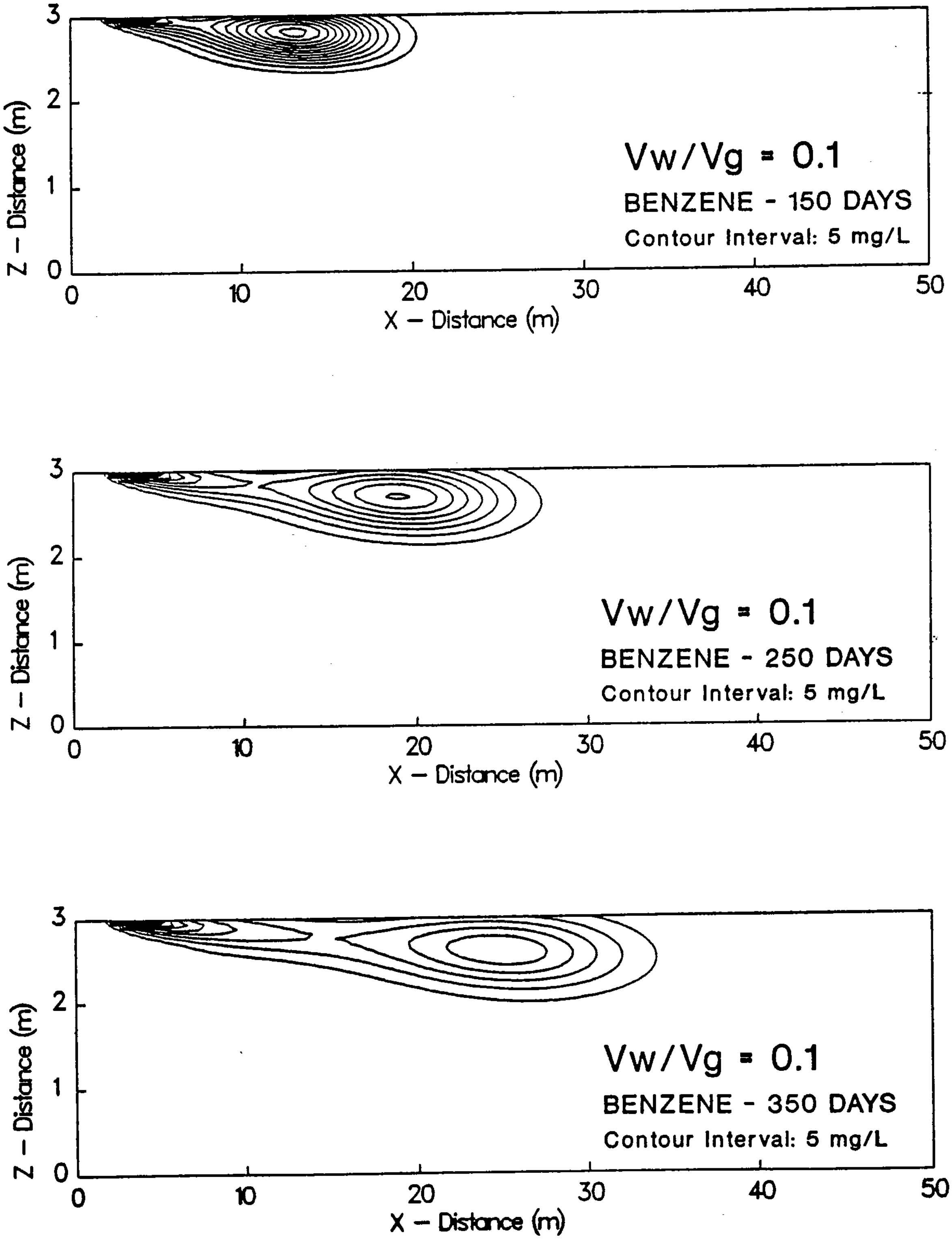

Figure 4-15. Examples of dissolved benzene plumes arising from spills of gasoline with 85% methanol content for initial water:gasoline volume ratio (V_w/V_g) = 0.1.

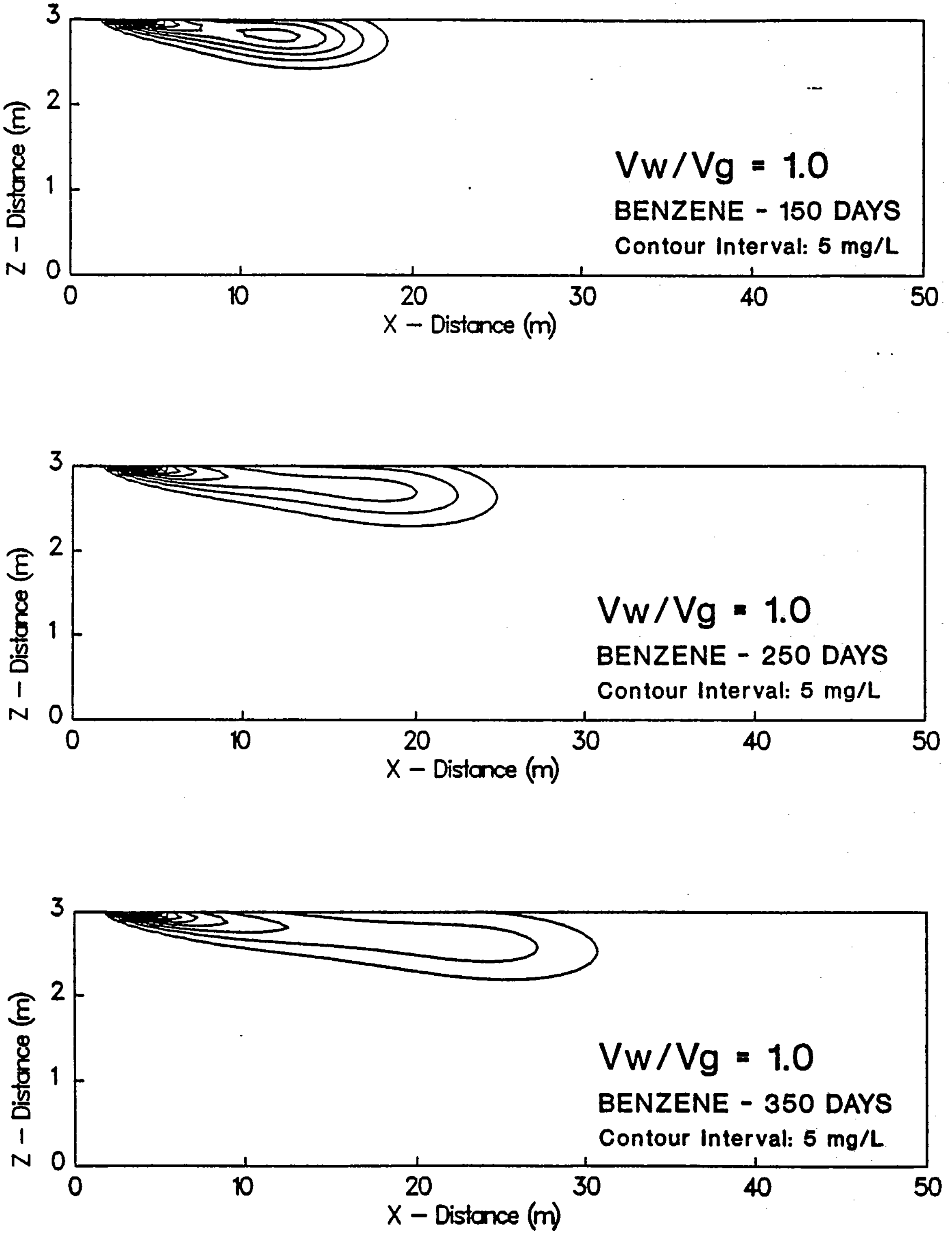

Figure 4-16. Examples of dissolved benzene plumes arising from spills of gasoline with 85% methanol content for initial water:gasoline volume ratio (V_w/V_g) = 1.0.

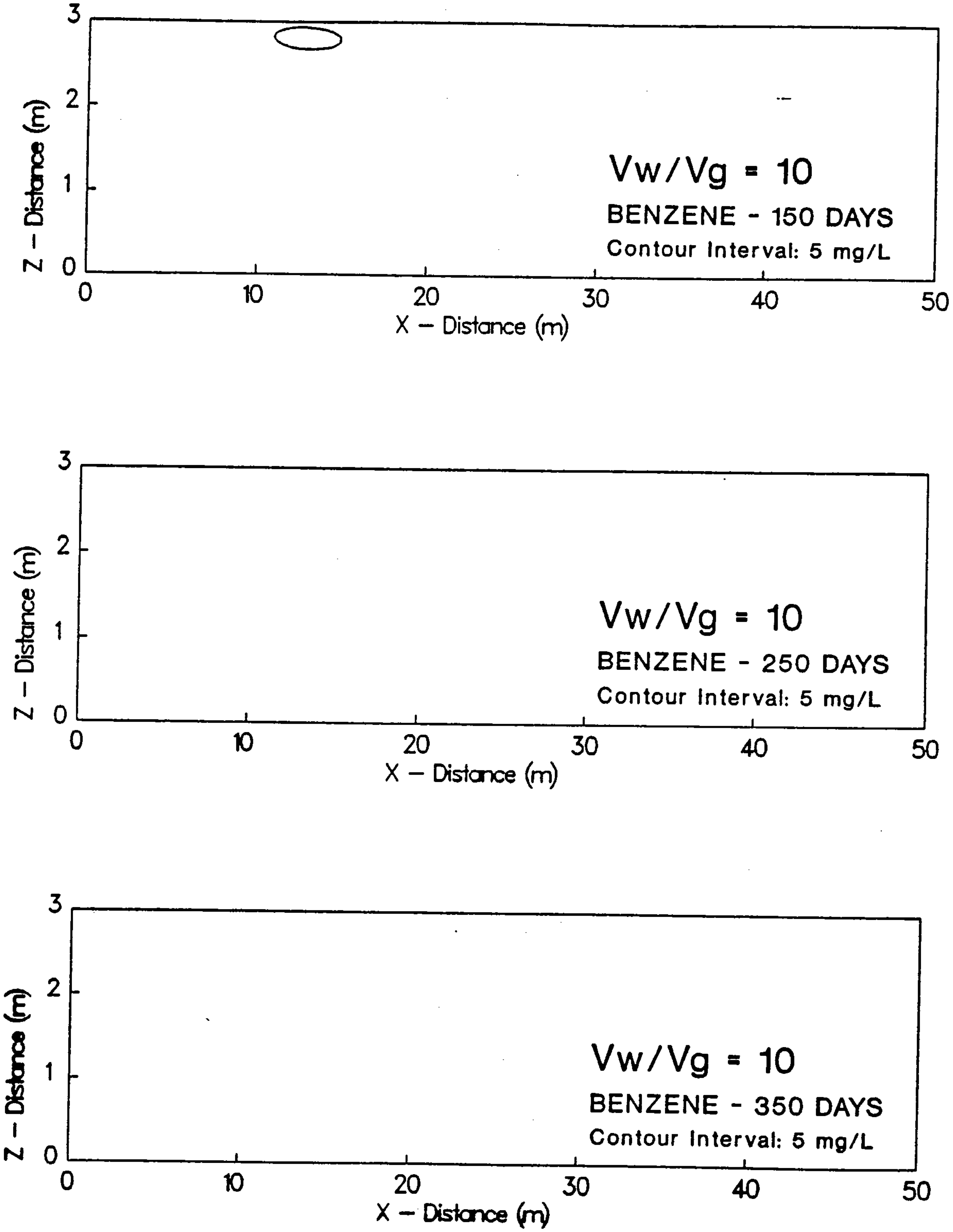

Figure 4-17. Examples of dissolved benzene plumes arising from spills of gasoline with 85% methanol content for initial water:gasoline volume ratio (V_w/V_g) = 10.

The equilibrium aqueous:gasoline phase ratio which would be observed in a real spill is unknown. The modelling demonstrates that changing this ratio can have a profound effect on the shape and concentrations of the resultant dissolved benzene plume.

The implication of this modelling exercise is that releases of gasoline with high methanol content may result in larger dissolved BTEX plumes having higher concentrations near the leading edge of the plume. However, the resultant plumes may also be smaller and demonstrate lower but not insignificant dissolved benzene concentrations. The actual situation appears to be very dependant upon the equilibrium aqueous and gasoline phase volumes at the source of the plume.

Section 5

CONCLUSIONS

1. Laboratory experiments indicate that equilibrium of gasoline and water mixtures occurs rapidly, and that four hours is a sufficient equilibration time for BTEX solubility experiments.
2. The aqueous BTEX concentrations resulting from contacting gasoline and water remain constant as the water:gasoline ratio is increased up to about 20:1 (v/v). At higher water:gasoline ratios, the aqueous BTEX concentrations are reduced due to depletion of the available BTEX in the gasoline phase.
3. The addition of oxygenates to gasoline will reduce the amount of BTEX in the gasoline, and thereby reduce the total amount of BTEX available to potentially contaminate a soil or groundwater.
4. For an oxygenate that partitions into the aqueous phase, such as methanol, the observed aqueous BTEX concentrations will remain constant, or decrease slightly, with increasing initial oxygenate content of the gasoline, at high water:gasoline volume ratios.
5. For an oxygenate that partitions into the gasoline phase, such as MTBE, the observed aqueous BTEX concentrations decrease linearly with increasing initial oxygenate content of the gasoline, at all water:gasoline volume ratios.
6. Experiments with gasoline containing 85% methanol (v/v) (M-85 fuel) or 15% MTBE (v/v) in contact with 10 volumes of water did not produce higher dissolved BTEX concentrations than similar experiments conducted using pure gasoline. No consolubility effects were noted at this water:gasoline ratio.
7. Aqueous BTEX concentrations increase in proportion to increasing methanol content of the aqueous phase. This relationship appears to be linear up to aqueous methanol contents between 20 and 30% (v/v), and log linear for higher aqueous methanol contents. In cases of high methanol content all of the BTEX in the gasoline phase may partition into the aqueous phase.
8. In real spill situations equilibrium between gasoline and aqueous phases may occur, but only along the interface between the two phases. The actual volumes of the two phases which are in equilibrium are unknown. Simulation of the resultant dissolved BTEX concentrations for equilibration of successive batches of water with gasoline containing methanol indicate that the initial batch will have a high aqueous methanol content and higher aqueous BTEX concentrations than the case with pure gasoline. Subsequent batches will have a low methanol content and lower aqueous BTEX concentrations than the pure gasoline case.

9. Releases of gasoline with high methanol content (eg., M-85 fuel) may produce dissolved plumes with high aqueous methanol and elevated aqueous BTEX concentrations near the plume front. Dispersion causes these plumes to be slightly longer than for the case of gasoline without methanol. Varying the ratio of the aqueous and gasoline phase volumes in equilibrium creates dramatic changes in the plume shape and concentration distributions. For low aqueous:gasoline phase equilibrium volume ratios the resultant dissolved BTEX plume may be larger and include a discrete pulse with higher aqueous BTEX concentrations near the plume front. At high aqueous:gasoline phase equilibrium volume ratios the available BTEX in the gasoline would be depleted, resulting in a shorter, discrete pulse of dissolved BTEX. The simulations suggest that changes in the ratio of phase volumes at equilibrium are more important in defining the resultant plume shape and concentration distribution than is the initial methanol content of the gasoline phase.

Section 6

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APPENDIX A

SPECIFICATIONS AND COMPOSITION OF PS-6 GASOLINE

PS-6 gasoline refers to a standard reference unleaded gasoline, maintained by API for use in API toxicological and environmental research. The designation PS-6 stems from the first use of this reference gasoline in a toxicological study on rodent carcinogenicity of wholly vaporized unleaded gasoline (MacFarland et al., 1984). Specifications for PS-6 gasoline, as cited in MacFarland et al. (1984), are provided in Table B-1.

PS-6 gasoline may contain more than 1200 compounds (Brookman et al., 1985). Identification of 151 compounds were completed by Brookman et al. (1985), of which 42 were determined to account for approximately 75% of the gasoline volume. The identified compounds and their measured volume and weight fractions are listed in Table B-2. The weight fractions were assumed to be equivalent to the volume fractions for the rest of the compounds. For aromatic hydrocarbons, which have relatively high densities, and low molecular weights, the molar fraction:volume fraction ratio will be greater than 1. Hence, the assumption that the molar fractions and volume fractions are equal is not valid for these compounds. This would result in a high estimate of the partitioning coefficient (K_{gw}), and a low estimate of the dissolved concentrations for these compounds. For the aromatic hydrocarbons the weight fraction was estimated to be slightly greater than the volume fraction.

The reciprocal of the molar weight of gasoline can be expressed as the sum of the weight fraction to molar weight ratios for each constituent. The molar weight and the weight percentage to molar weight ratio for each compound are listed on Table B-3. The molar weight of gasoline was thus estimated to be 96.8 g/mole. The BTEX molar fractions were then calculated as the weight percentage to molar weight ratio for the compound multiplied by the molar weight of gasoline. The calculated molar fractions are presented on Table B-3.

The molar fraction estimates for BTEX used to calculate dissolved BTEX concentrations in this study were made by multiplying the molar fraction:volume fraction ratio from Table B-4 by the experimentally determined volume fractions of BTEX in PS-6 gasoline. These results are summarized on Table B-4.

Table B-1. Specifications of PS-6 Gasoline (from MacFarland et al., 1984).

Research octane number	92.0
Motor octane number	84.1
(R + M)/2	88.1
Reid vapor pressure, psia	9.5
Distillation, ASTM D-86	
Initial boiling point, °F	93
5% distilled, °F	105
10% distilled, °F	116
20% distilled, °F	138
30% distilled, °F	164
40% distilled, °F	190
50% distilled, °F	216
60% distilled, °F	238
70% distilled, °F	256
80% distilled, °F	294
90% distilled, °F	340
95% distilled, °F	388
100% distilled, °F	428
Recovery, %	97
10% evaporated, °F	112
50% evaporated, °F	211
90% evaporated, °F	331
API gravity	60.6
Gum, ASTM D-381, g/gal	1
Sulfur, ppm	97
Phosphorus, g/gal	<0.005
Lead, g/gal	<0.05
Stability, hrs	>24

Table B-2. Molecular composition of PS-6 Gasoline. (from Brookman et al., 1985).

COMPOUNDS	VOLUME %	WEIGHT %	MOLAR WEIGHT (g/mole)	WEIGHT % / MOLAR WEIGHT (moles/100g)
n-PARAFFINS				
n-butane		3.83	58	0.0660
n-pentane	10.19	3.11	72	0.0432
n-hexane		1.58	86	0.0184
C3,C7-C10, n-alkanes	1.21	1.21 e	121 a	0.0100
ISO-PARAFFINS				
isobutane	1.14	1.14 e	58	0.0197
isopentane	10.26	8.72	72	0.1211
2-methylpentane		3.93	86	0.0457
3-methylpentane	8.81	2.36	86	0.0274
2,3-dimethylbutane		1.66	86	0.0193
C6-isoalkane	0.18	0.18 e	86	0.0021
2-methylhexane		1.08 e	100	0.0108
3-methylhexane	4.54	1.30	100	0.0130
2,3-dimethylhexane		1.08 e	100	0.0108
2,4-dimethylpentane		1.08 e	100	0.0108
C7-isoalkanes	0.23	0.23	100	0.0023
2,2,4-trimethylpentane		5.22	114	0.0458
2,3,4-trimethylpentane	11.74	2.99	114	0.0262
2,3,3-trimethylpentane		2.85	114	0.0250
2,2,3-trimethylpentane		0.68 e	114	0.0060
C8-isoalkanes	4.98	4.98 e	114	0.0437
2-methyloctane			128	0.0000
3-methyloctane	1.51	1.51 e	128	0.0118
4-methyloctane			128	0.0000
2,2,5-trimethylhexane			128	0.0000
C9-isoalkanes	0.50	0.50 e	128	0.0039
C10 - C13-isoalkanes	2.65	2.65 e	163 a	0.0163

(cont'd)

Table B-2. (cont'd)

COMPOUNDS	VOLUME %	WEIGHT %	MOLAR WEIGHT (g/mole)	WEIGHT % / MOLAR WEIGHT (moles/100g)
CYCLOPARAFFINS				
cyclopentane	0.15	0.15 e	70	0.0021
methylcyclopentane	0.97	0.97 e	84	0.0115
cyclohexane	0.08	0.08 e	84	0.0010
methylcyclohexane				
1,trans,3-dimethylcyclopentane	0.77	0.77 e	98	0.0079
1,cis,3-dimethylcyclopentane				
C7-cycloalkanes	0.32	0.32 e	98	0.0033
C8-cycloalkanes	0.74	0.74 e	112	0.0066
C9-cycloalkanes	1.03	1.03 e	126	0.0082
C10 - C13-cycloalkanes	0.62	0.62 e	161 a	0.0039
MONO-OLEFINS				
propylene	0.03	0.03 e	42	0.0007
trans-butene-2	0.75	0.75 e	56	0.0134
cis-butene-2			56	0.0000
C4-alkenes	0.15	0.15 e	56	0.0027
pentene-1			70	0.0000
trans-pentene-2	1.22	1.22 e	70	0.0174
cis-pentene-2			70	0.0000
C5-alkenes	0.07	0.07 e	70	0.0010
C6-alkenes	0.14	0.14 e	84	0.0017
2-methylpentene-1	1.26	1.26 e	84	0.0150
2-methylpentene-2			84	0.0000
C7 - C12-alkenes	5.34	5.34 e	133 a	0.0402

(cont'd)

Table B-2. (cont'd)

COMPOUNDS	VOLUME %	WEIGHT %	MOLAR WEIGHT (g/mole)	WEIGHT % / MOLAR WEIGHT (moles/100g)
AROMATICS				
benzene	1.69	1.94	78	0.0249
toluene	3.99	4.73	92	0.0514
ethylbenzene	1.69 e	2.00	106	0.0189
o-xylene	1.91 e	2.27	106	0.0214
m-xylene	4.78 e	5.66	106	0.0534
p-xylene	1.45 e	1.72	106	0.0162
1-methyl-3-ethylbenzene		1.54	120	0.0128
1-methyl-4-ethylbenzene	5.33	1.56	120	0.0130
1,2,4-trimethylbenzene		3.26	120	0.0272
C9-alkylbenzenes	2.40	2.51 e	120	0.0209
C10-alkylbenzenes	2.11	2.21 e	134	0.0165
C11-alkylbenzenes	0.52	0.57 e	148	0.0039
C12-alkylbenzenes	0.21	0.21 e	162	0.0013
C9 - C13-indans/tetralins	1.54	1.59 e	147 a	0.0108
C10 - C12-naphthalenes	0.74	0.74 e	144 a	0.0051
TOTAL	99.94	100.02		1.0334

MOLAR WEIGHT OF PS-6 GASOLINE = 96.77 g

NOTES:

e - weight % estimated as equivalent to volume %
a - assumed average group molecular weight

Table B-3. Molar fraction to volume fraction ratios for BTEX in PS-6 gasoline.

Compound	Molar Fraction	Volume Fraction	Molar Fraction/ Volume Fraction
benzene	0.024	0.0169	1.42
toluene	0.050	0.0399	1.25
ethylbenzene	0.018	0.0169	1.08
o-xylene	0.021	0.0191	1.09
m-xylene	0.052	0.0478	1.08
p-xylene	0.016	0.0145	1.08

Table B-4. Experimentally determined volume fractions and calculated molar fractions for BTEX in PS-6 gasoline.

Compound	Volume Fraction yg	Molar Fraction xg
benzene	0.02082	0.02965
toluene	0.03519	0.04388
ethylbenzene	0.01570	0.01696
o-xylene	0.02088	0.02266
m-xylene	0.04072	0.04402
p-xylene	0.01809	0.01959
TOTAL	0.15140	0.17676

APPENDIX B

ANALYTICAL METHODS / QUALITY CONTROL RESULTS

Hexane Micro-Extraction for the Determination of Purgeable Aromatics in Groundwater

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A hexane liquid-liquid micro-extraction/gas chromatographic technique has been devised as a rapid alternative to the slower purge and trap and conventional solvent extraction methods for the determinations of benzene, toluene, and the three xylene isomers at trace levels in groundwater. Split injection isothermal capillary column chromatography permits a run time of five minutes without the loss of baseline resolution. Method detection limits in ug/L were as follows: benzene, 1.8; toluene, 1.4; p-xylene, 0.6; m-xylene, 0.8; o-xylene, 1.2. Replicate analyses of an in-house quality control standard containing approximately 85 ug/L of each compound were accumulated during a typical 8-day session. The means of the determinations differed no more than 1% from the true values with relative standard deviations averaging 2.9% overall. Evaluation of a USEPA quality control standard spiked into a typical organic-free groundwater matrix gave similar results.

INTRODUCTION

A gas chromatographic technique is described to determine several aromatic components of gasoline in groundwater samples. The components are: benzene, toluene, ethyl benzene and the p,m,o-xylenes. The samples analyzed were recovered from a controlled field injection experiment where possible interferents were known not to be present in the aquifer. Usually these compounds are determined by purge and trap techniques (1). However, because the hydrogeologist may require many analyses to define the shape, movement and attenuation of a trace contaminant plume, purge and trap methods are too time consuming to use on a routine basis. Separatory funnel or continuous solvent extraction techniques are not only slow and labour intensive but can suffer from volatilization losses as well. The methodology presented here was derived from a pentane liquid-liquid extraction (LLE) technique previously described by Glaze et al., which requires that the partitioning of an analyte be at equilibrium between the two phases, as opposed to being exhaustively extracted from the water (2). Pentane was replaced with hexane since the chromatographic column used easily affords complete separation of the analytes from the solvent peak. This helps to reduce the solvent vapour pressure in the sample vials thereby improving the precision of the method.

EXPERIMENTAL

APPARATUS. Samples and aqueous standards were extracted in Supelco 18-ml crimp-top hypo-vials with teflon-faced silicone septa. The determinations were performed on an isothermal gas chromatograph equipped with a split injection port, capillary column, and FID. The column used was a 0.32mm x 6m fused quartz type with a 0.25 µm bonded CARBOWAX 20M stationary phase. The chromatographic conditions were as follows: injection port temperature: 200x C; oven temperature: 90x C; detector temperature: 300x C; carrier gas: Helium; column flow rate: 5 ml/min.

REAGENTS. The following reagents were used: glass distilled hexane and methanol; organic-free reagent water; 10% aqueous sodium azide solution; reagent grade benzene, toluene, m-fluorotoluene, p,m,o-xylenes.

PROCEDURE. SAMPLE BOTTLE PREPARATION. Bottles and other glassware were soaked in a commercial alkaline cleaning solution for several hours, then rinsed with deionized water, dilute nitric acid, and more deionized water. The bottles were then baked overnight at 110x C. Upon removal from the oven, the bottles were covered with foil. Because the septa can be a major source of contamination, they were boiled in water for one hour, then baked overnight at 110x C in an oven.

SAMPLE COLLECTION AND HANDLING. Sample vials were filled to overflowing with no aeration, quickly crimped, then stored on ice until needed. Prior to capping, 100 ul of the sodium azide preservative was injected directly into the water. The same treatment was given to the aqueous standards. To solvent extract a sample or standard, a vent needle was inserted through the septum, then one ml of water was removed with a syringe. With the vent still in place, 500 ul of hexane, containing the internal standard m-fluorotoluene, was added. The vent was then removed and the bottle agitated on its side at maximum speed on a platform shaker for 10 min. The bottle was inverted and the phases allowed to separate for 10 to 30 minutes before the sample was analyzed. The bottle was then set upright and approximately 4 ul of the hexane phase was removed, while venting, for injection into the chromatograph.

QUALITY CONTROL. Samples and standards were equilibrated to room temperature before extraction. The gas chromatograph was calibrated at the start of each working day by averaging the runs for three standard replicates at approximately 3000 ug/L for each compound. Two stock standards, one approximately an order of magnitude more concentrated than the other, were independently prepared. The higher concentration was used to calibrate the instrument; the lower one was used as a check, and was routinely run after every tenth sample. The standard checks were initially prepared at several concentrations in water to establish linearity and detection limits. Subsequently, during a sampling session they were run at a fixed concentration comparable to that of the unknowns. A stock standard was prepared gravimetrically, injecting the various pure compounds through a septum into one 60 ml aliquot of methanol. This solution was then further diluted volumetrically by injecting through a septum into one litre of reagent water.

An upper limit of 1% (v/v) methanol in water has been previously recommended; however, it was not necessary to exceed 0.05% for the present study (2). The aqueous standard dilution was mixed on a magnetic stirrer to avoid aeration, and then quickly distributed into hypovials with an all-glass and teflon repipette. The methanolic standards were stored in a freezer when not in use and discarded after 3 months. Aqueous standards were stored no longer than two days. The hexane extraction solution and reagent water blanks were checked on a daily basis.

RESULTS AND DISCUSSION

METHOD DETECTION LIMIT (MDL). Table I shows detection limits for the analytical procedure. It does not take into account field sampling errors, sample matrix, or analyte losses due to long term volatilization. These values were determined by the procedure recommended by USEPA/EMSL which defines MDL as the minimum concentration measurable with 99% confidence that it is greater than zero (3).

ACCURACY AND PRECISION. Near the detection limit, it can be seen that for the six compounds, the average absolute error is approximately +13%. The overall standard deviation at this level is 9.4%. Table II summarizes the results of replicate analyses of in-house quality control samples accumulated during a typical sampling session (approximately 8 days in duration, n = 31). As was expected, at these higher concentrations the overall standard deviation has improved to 2.9%, while accuracy is virtually 100%. To further evaluate the method, and its applicability to field samples, a USEPA quality control standard (WP 879 #1) was analyzed in a typical groundwater matrix. Calibration standards were prepared as previously described using laboratory reagent water. The results shown in Table III display standard deviations comparable to those obtained previously with errors which are generally larger, but still acceptable. It is quite likely that this increase in error was a result of experimenter bias, not matrix effects, as the ionic strength of the groundwater used was much lower than the 1.0 required to affect extraction efficiencies, while the pH was neutral (1).

CONCLUSIONS

The hexane micro-extraction method has a sensitivity approaching that of a purge and trap system, but can be used routinely, with a much shorter turnaround time. This allows the analyst to work with larger batches of samples at a faster rate. Detection limits are adequate with a simple split injection, eliminating the need to employ more elaborate splitless or cryogenic schemes. These limits can be lowered somewhat by increasing the water to hexane ratio.

The column used is capable of resolving the p- and m-xylene isomers in a 5 minute isothermal run. Separation of these two isomers is impossible with the less polar capillary columns commonly employed. Furthermore, the method can easily be extended to include ethylbenzene and various halogenated aromatics.

Samples containing organic interferents, e.g. waste water, landfill leachate, require the replacement of the FID with a detector which is more specific to the compounds of interest, e.g. an MSD..

(1) "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater", EPA-600/4-82-057; Longbottom, James E., Lichtenberg, James J., Eds.; USEPA/EMSL: Cincinatti, OH, 1982; Method 602.

(2) Glaze, William H.; Lin, C.C.; Burleson, J.L.; Henderson, J.E.; Mapel, D.; Rawley, R.; Scott, D.R., "Optimization of Liquid-Liquid Extraction Methods for Analysis of Organics in Water", Project Report, Contract No's. CR-805472, CR-808561; USEPA/EMSL: Cincinatti, OH, 1983.

(3) "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater", EPA-600/4-82-057; Longbottom, James E., Lichtenberg, James J., Eds.; USEPA/EMSL: Cincinatti, OH, 1982; Appendix A.

TABLE I. METHOD DETECTION LIMIT

	ug/L					
Compound	N	S%	X	Xo	E%	MDL
benzene	7	13	4.3±0.7	3.7	+16	1.8
toluene	7	13	3.2±0.5	3.6	-11	1.4
p-xylene	7	5.8	3.1±0.2	3.6	-14	0.6
m-xylene	7	5.7	4.4±0.3	3.7	+19	0.8
o-xylene	7	9.7	3.8±0.4	3.7	+3	1.2

N: number of replicate determinations; S%: relative standard deviation; X: mean of replicate determinations, 99% confidence level, background subtracted; Xo: true value; E%: average relative error; reagent water matrix.

TABLE II. ACCURACY AND PRECISION AT TYPICAL SAMPLE CONCENTRATIONS

	ug/L				
Compound	N	S%	X	Xo	E%
benzene	31	4.2	84.5±1.9	85.2	-1
toluene	31	2.9	83.8±0.9	83.7	0
p-xylene	31	2.4	83.3±1.5	83.5	0
m-xylene	31	2.8	86.2±1.5	85.6	+1
o-xylene	31	2.0	86.6±1.6	85.7	+1

reagent water matrix

TABLE III. ANALYSIS OF USEPA QUALITY CONTROL SAMPLE WP 879 #1

			ug/L		
Compound	N	S%	X	Xo	E%
benzene	7	3.0	30.6±1.1	30.7	0
toluene	7	6.1	5.6±0.4	4.1	+37
p-xylene	7	1.8	20.5±0.4	19.1	+7
m-xylene	7	1.7	45.3±0.9	42.6	+6
o-xylene	7	2.5	12.1±0.4	10.6	+14

Xo: EPA value; groundwater matrix

DIRECT AQUEOUS INJECTION PROCEDURE

OXYGENATES:		
MtOH	-	Methanol
EtOH	-	Ethanol
MTBE	-	Methyl Tertiary Butyl Ether
TAME	-	Tertiary Amyl Methyl Ether
IPE	-	Iso-propyl Ether

SAMPLE PREPARATION

A 1.0ml aqueous sample (removed from a 18.0ml hypovial for BTEX analysis) is placed in a 1.5ml screw cap septum vial and sealed with a teflon lined septa and screw cap. A 4ul aliquot of the aqueous solution is sampled for chromatographic analysis using a 10ul syringe equipped with a chaney adapter to enhance repeatability.

CHROMATOGRAPHIC ANALYSIS

The aqueous samples are run on a Hewlett Packard 5840A gas chromatograph with a FID detector. The column is 10ft. X .125 in. i.d., packed with 3% SP1500 on Carbopack B (80/100 mesh). The analyses are run isothermally at 100, 190 or 200°C, depending on oxygenate (see chart). A helium carrier gas at a flow rate of 20 ml/min is used. The detector temperature is 300°C and the injection temperature is 200°C.

Quantitative results are determined using an ESTD method of calibration and method detection limits for some of the compounds are found to be <250ug/L, using the EPA procedure for method detection limit (MDL).

GC COLUMN TEMPERATURES (ISOTHERMAL)

Oxygenate	Column Temp °C	Retention Time
MTBE	190	3.0
IPE	190	4.0
EtOH	120	1.8
TAME	200	4.0
MtOH	100	1.4

DIRECT AQUEOUS INJECTION - OXYGENATES

METHOD DETECTION LIMIT

Oxygenate	N	X mg/L	Xo	S%	E%	MDL
MtOH	12	.760+/-.039	.988	5.13	-23.1	.106
MTBE	12	.533+/-.093	.740	17.4	-28.0	.249

* MDL for the other oxygenates are estimated to be in the same range as those reported.

ACCURACY AND PRECISION AT TYPICAL CONCENTRATION

OXYGENATE	N	X mg/L	Xo	S%	E%
MtOH	21	409.92+/-8.73	395.00	2.13	+3.78
MTBE	21	71.95+/-1.31	74.0	1.81	-2.77

N : number of replicate determinations

X : mean of replicate determinations, 99% confidence level

Xo : true value

S% : relative standard deviation

E% : relative error

MDL : method detection limit

APPENDIX C

PARAMETER VALUES USED IN CALCULATIONS

ORGANIC CHEMICAL PROPERTIES

Chemical	Molecular Weight (g)	Density (g/m^3)	Solubility (@ 20°C) (g/m^3)	$\log(K_{ow})$	yg [1] Volume Fraction in PS-6 Gasoline	xg [2] Molar Fraction in PS-6 Gasoline
GASOLINE (PS-6)			750100		1.0	1.0
BENZENE	78.12	878650	1780	2.14	0.02082	0.02969
TOLUENE	92.15	866900	515	2.69	0.03519	0.04392
ETHYL-BENZENE	106.17	867000	152	3.15	0.01570	0.01700
p-XYLENE	106.17	861100(3)	198	3.15	0.01809	0.02263
m-XYLENE	106.17	864200(4)	134	3.20	0.04072	0.04406
o-XYLENE	106.17	880200	175	3.13	0.02088	0.01959
MTBE	102.18	751900			varied	varied
METHANOL	32.04	791400	miscible	-0.75 (5)	varied	varied

All data values from Verscheuren, 1983 except as noted.

(1) measured (see Section 2)
(2) estimated (see Appendix B)
(3) solubility at 25°C
(4) solubility from Kebe et al., 1984
(5) from Lyman et al., 1982

APPENDIX D

RELATIONSHIP BETWEEN NORMALIZED AND UNNORMALIZED DATA

The data normalization procedure entails multiplying theoretically calculated aqueous phase concentrations by a fixed constant, referred to here as the normalizing factor, NF. The normalizing factor consists of the ratio of an experimentally determined concentration to a corresponding theoretical concentration at the same fixed volume ratio. In this report, all normalizing factors were based on concentrations at the 10:1 water:fuel volume ratio. This empirical normalization procedure allows theoretical trends to more closely match experimentally determined data.

The relationship between normalized and unnormalized data is determined as follows:

Unnormalized and normalized water phase concentrations are, from Equation 3-8:

$$C_{wu} = \frac{y_g (V_g^l / V_g) p}{K_u + (V_w / V_g)} \tag{D-1}$$

$$C_{wn} = C_{wu}\ NF = \frac{y_g (V_g^l / V_g) p}{K_u + (V_w / V_g)}\ NF \tag{D-2}$$

where the subscripted u refers to unnormalized data, and the subscripted n refers to normalized data. From Equation D-2,

$$\frac{V_w}{V_g} = \frac{y_g (V_g^l / V_g) p}{C_{wn}}\ NF - K_u \tag{D-3}$$

Solving equation 3-8 for the normalized data partition coefficient and substituting for the volume ratio from Equation D-3:

$$K_n = \frac{y_g(V_g^l/V_g)p}{C_{wn}} - \frac{V_w}{V_g} \tag{D-4}$$

$$K_n = \frac{y_g(V_g^l/V_g)p}{C_{wn}} - \frac{y_g(V_g^l/V_g)p}{C_{wn}} NF + K_u \tag{D-5}$$

Finally, from Equation 3-2 for normalized data,

$$C_{gn} = K_n C_{wn} \tag{D-6}$$

$$C_{gn} = K_n C_{wn} = \left[\frac{y_g(V_g^l/V_g)p}{C_{wn}} - \frac{y_g(V_g^l/V_g)p}{C_{wn}} NF + K_u\right] C_{wn} \tag{D-7}$$

$$C_{gn} = K_u C_{wn} + (1 - NF)\, y_g(V_g^l/V_g)p \tag{D-8}$$

For a given fixed gasoline phase composition:

$$C_{gu} = C_{gn} \tag{D-9}$$

$$K_u C_{wu} = K_u C_{wn} + (1 - NF)\, y_g(V_g^l/V_g)p \tag{D-10}$$

or,

$$C_{wu} = C_{wn} + \frac{(1 - NF)\, y_g (V_g^i / V_g) p}{K_u} \qquad \text{(D-11)}$$

Equation D-8 expresses the phase relationship for normalized data in terms of the unnormalized partitioning coefficient K_u. From Equation D-8, the slope of the phase relationship for normalized data is K_u, the same as for unnormalized data.

Equation D-11 quantifies the difference between normalized and unnormalized data. If the second term on the right-hand side of this equation is constant, the normalized trend mirrors the unnormalized trend at all volume ratios, differing only by this fixed constant term.

Strictly speaking, Equation D-8 is inconsistent in that at a zero normalized aqueous phase concentration a nonzero gasoline phase concentration would be calculated. This observation is important in confining consideration of normalized data and trends only to those volume ratios for which experimental data are provided.

APPENDIX E

SUCCESSIVE BATCH SIMULATIONS

The following calculations were used to determine the resultant benzene concentrations from contacting successive batches of fresh water with a known volume of gasoline. The parameters used in these calculations are summarized at the end of this section.

The calculations have been performed using an IBM PC and LOTUS 1-2-3. The initial step requires an iterative calculation to solve two equations for the equilibrium aqueous methanol concentration, and the equilibrium aqueous phase volume, beginning with an estimate of the equilibrium aqueous phase volume.

$$C^m{}_w(n) = (y^m{}_g(n) \bullet V^i{}_g(n) \bullet p^m) \ / \ (K^m{}_{ow} \bullet (V^i{}_g(n) + V^i{}_w) + (1-K^m{}_{ow}) * V_w(n))$$

$$V_w(n) = (V^i{}_w \bullet p^m) \ / \ (p^m - C^m{}_w(n))$$

$$V_g(n) = V^i{}_g(n) + V^i{}_w - V_w(n)$$

Subsequent calculations determine the volume of the gasoline phase, and the volume fraction of methanol in the gasoline, and in the aqueous phase.

For the first batch:

$$V^i{}_g(n) = V^i{}_g(1)$$

$$y^m{}_g(n) = y^m{}_g(1)$$

For following batches:

$$V^i{}_g(n) = V_g(n-1)$$

$$y^m{}_g(n) = ((V^i{}_g(n-1) \bullet y^m{}_g(n-1)) - (V_w(n-1) * (C^m{}_w(n-1) / p^m))) \ / \ (V_g(n-1))$$

$$f_c(n) = (V_w(n) - V^i{}_w) \ / \ V_w(n)$$

The next series of calculations evaluates the solubility of benzene for the aqueous methanol solution determined above. This calculation is linear below the experimentally determined breakpoint, and logarithmic above it.

For $f_c(n) \leq 0.25$

$$S^{b}_{m}(n) = f_{c}(n) * V_{H} \bullet S^{\infty b}_{c} + (1 - f_{c}(n) \bullet V_{H}) * S_{w}$$

For $f_{c}(n) > 0.25$

$$\log S^{b}_{m}(n) = \log(S^{b}_{m}(fc{=}0.25)) + \beta \bullet (f_{c}\,(n) - 0.25)$$

$$\beta = a * \log\,(K^{b}_{ow}) + b$$

With this value it is then possible to determine the volume fraction of benzene in the gasoline phase, and hence the gasoline-water partitioning coefficient for benzene under the calculated conditions.

$$K^{b}_{gw}(n) = (y^{b}_{g} * p^{b}) / (x^{b}_{g} * S^{b}_{m}(n))$$

For the first batch:

$$y^{b}_{g}(n) = y^{b}_{g}(1) = y^{b}_{g0} * (1 - y^{m}_{g}(1))$$

For the following batches:

$$y^{b}_{g}(n) = (y^{b}_{g}(n-1) - (((C^{b}_{w}(n-1) * V_{w}(n-1)) / (p^{b} * V^{i}_{g}(n-1))) * (V^{i}_{g}(n-1) / V_{g}(n-1))$$

The dissolved benzene concentration in the aqueous phase of each batch can then be determined by:

$$C^{b}_{w}(n) = (y^{b}_{g}(n) * (V^{i}_{g}(n)/V_{g}(n))* p^{b}) \; / \; (K^{b}_{gw}(n) + (V_{w}(n) / V_{g}(n)))$$

LIST OF PARAMETERS:

n = batch number

$C^m_w(n)$ = aqueous concentration of methanol in nth batch,

$y^m_g(n)$ = volume fraction of methanol in gasoline for nth batch,

$V^i_g(n)$ = initial volume of gasoline prior to exposure to the nth batch,

$V_g(n)$ = equilibrium volume of gasoline for nth batch,

V^i_w = initial volume of water (constant),

$V_w(n)$ = equilibrium volume of aqueous phase for nth batch,

p^m = density of methanol,

K^m_{ow} = octanol-water partitioning coefficient for methanol,

K^m_{gw} = gasoline-water partitioning coefficient for methanol,

$f_c(n)$ = cosolvent fraction of aqueous phase for nth batch,

S_w = solubility of benzene in water

$S^b_m(n)$ = solubility of benzene in water-methanol mixture for nth batch,

$S^{\infty b}_c$ = solubility of benzene within the hydration shell of the methanol,

$S^b_m(fc{=}0.25)$ = solubility of benzene in water-methanol mixture at breakpoint (observed),

β = a measure of the relative ability of methanol to solubilize benzene, and ofthe hydrophobicity of benzene,

a,b = experimentally determined constants for BTEX,

$K_{ow}{}^b$ = octanol-water partitioning coefficient for benzene,

$K^b_{gw}(n)$ = gasoline-water partitioning coefficient for benzene in nth batch,

y^b_g/x^b_g = volume fraction to molar fraction ratio for benzene in gasoline,

p^b = density of benzene,

$y^b_g(n)$ = volume fraction of benzene in gasoline phase prior to exposure of the nth batch,

y^b_{g0} = initial volume fraction of benzene in gasoline,

$c^b_w(n)$ = concentration of benzene in aqueous phase for nth batch.

The values of constants, and experimentally determined parameters used in these calculations are presented in Appendix C.

Order No. 841-45310

1-0620—10/91—5C (5A)

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