

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

**HEALTH AND ENVIRONMENTAL SCIENCES
API PUBLICATION NUMBER 4531
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Health and Environmental Sciences Department

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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,

* 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 equilibrium 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.

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

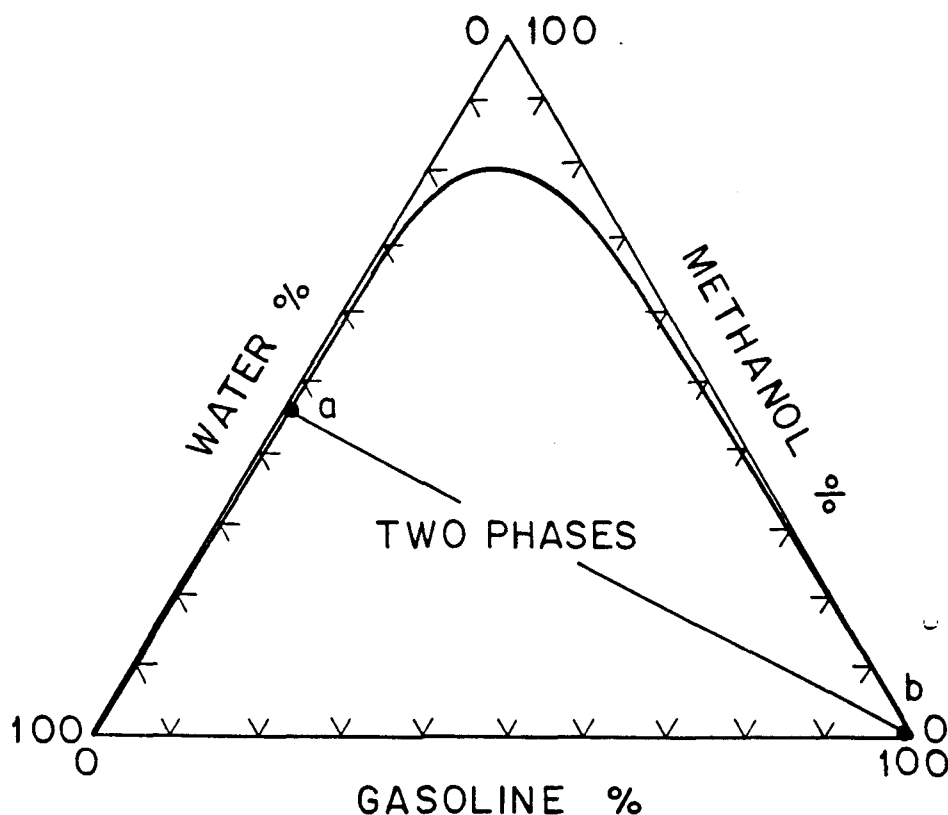


Figure 1-1. Ternary phase diagram for gasoline-water-methanol at 20°C. The curved boundary encloses the two-phase field where the composition of each phase is given as the intersection of the tie lines with the curved boundary (modified from Letcher *et al.*, 1986). For example, a system initially with 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 et al., (1984), Reinhard et al. (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:

$$C_w^i = s^i * x_g^b \quad (1-1)$$

where:

- C_w^i = the equilibrium concentration of component i in the water phase
- s^i = the solubility of pure component i in water
- x_g^b = 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 unoxxygenated 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.

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.

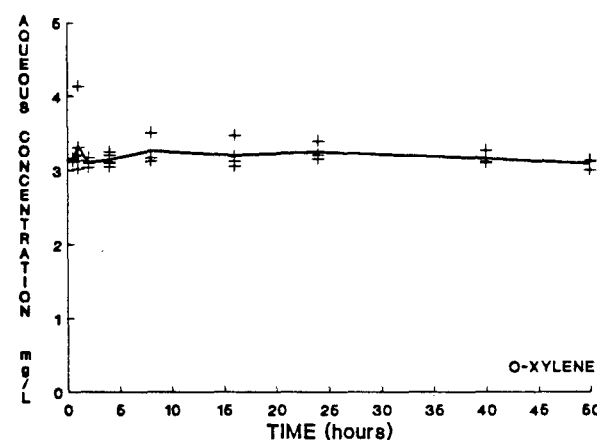
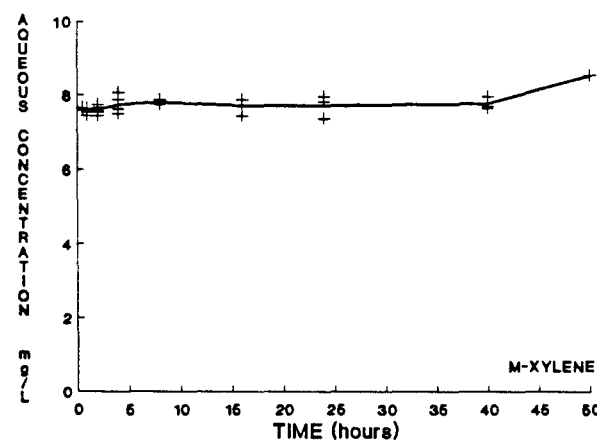
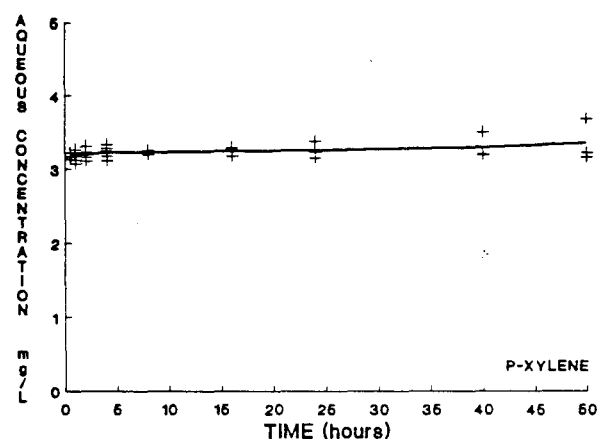
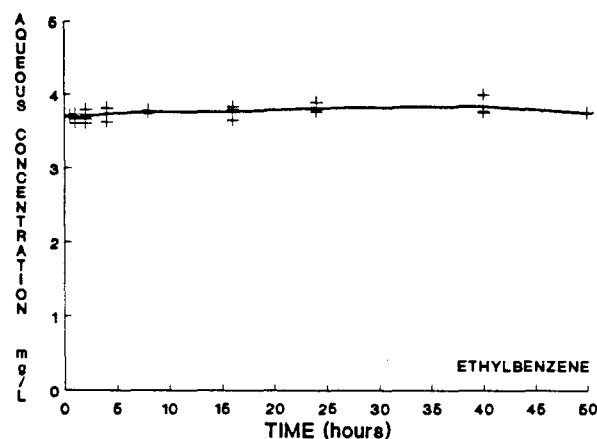
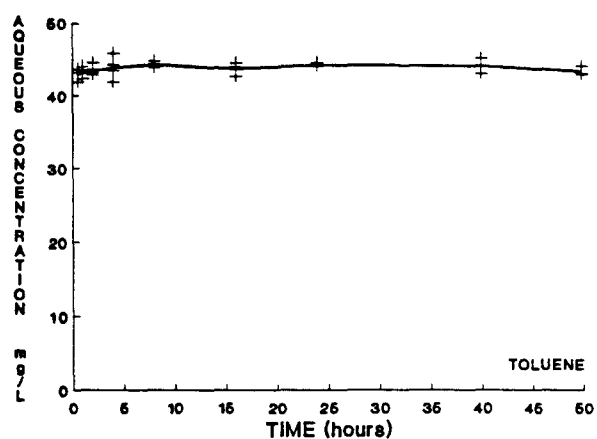
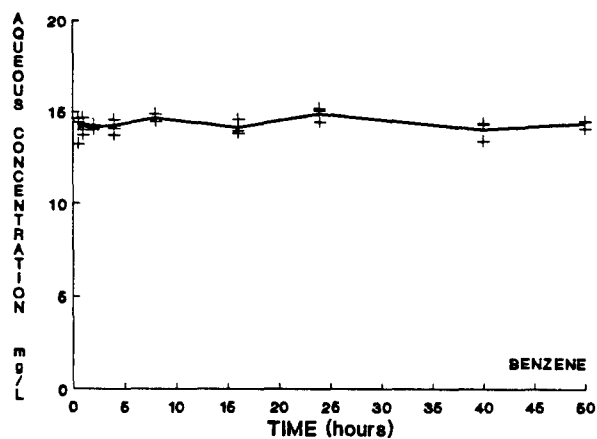


Figure 2-1. Results of time-to-equilibrium experiments for dissolved BTEX from gasoline.

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 μ l of vapor from the equilibration of 3 μ L 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.