

Cosolvency effect in subsurface systems contaminated with petroleum hydrocarbons and ethanol

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Received 25 September 2002; received in revised form 19 August 2003; accepted 9 December 2003

Abstract

In Brazil, most gas stations and terminals store tanks containing hydrated ethanol, gasohol and diesel. In case of spills, it is possible that a high aqueous ethanol concentration can facilitate the transfer of hydrocarbons into the aqueous phase, enhancing contaminant concentrations in groundwater, a process called cosolvency. This study investigates the cosolvency effect of ethanol on the aqueous solubility of mono- and polycyclic aromatic hydrocarbons, and presents a simple log-linear model to predict this effect under equilibrium conditions. Cosolvency experiments were carried out in batch reactors under equilibrium conditions for pure mono- and polycyclic aromatic hydrocarbons, gasohol and diesel. A linear relationship between cosolvency power and K_{ow} was determined, which allows predictions of the increase of aromatic hydrocarbon solubility due to the presence of ethanol. Results indicate that cosolvency would be significant only for high aqueous ethanol concentrations (higher than 10%). Under these conditions, cosolvency may be critical only in cases of large gasohol spills or in simultaneous releases of neat ethanol and other fuels. In this way, the hydrophobic and toxic polycyclic aromatic hydrocarbons (PAHs), that are usually present in minor aqueous concentrations in fuel spills without ethanol, may be dissolved in larger amounts in groundwater. © 2003 Elsevier Ltd. All rights reserved.

Keywords: Cosolvency; Ethanol; Gasohol; Petroleum hydrocarbons; Groundwater

1. Introduction

Groundwater plays an important role as water supply for urban and rural areas in Brazil. According to the 2000 National Basic Sanitation Research, more than 60% of the municipalities in the country use groundwater for drinking purpose. However, groundwater quality has deteriorated due to sources such as septic tanks, buried deposits of hazardous wastes, leaking landfills, and spills from transport and storage of petroleum products.

Releases of petroleum products can contaminate groundwater with the more soluble monoaromatic

hydrocarbons, the BTEX compounds (benzene, toluene, ethylbenzene and xylenes), and also with the more hydrophobic polycyclic aromatic hydrocarbons (PAHs) such as naphthalene, phenanthrene, pyrene, and anthracene. Due to their toxicity, these chemicals are present on most lists of drinking water standards. Since in Brazil ethanol is used as the sole fuel or mixed with gasoline (20–26%), in case of a spill, it is expected that ethanol will also be present in groundwater at a gas station or a distribution terminal. In the United States, ethanol presence in groundwater is probably also going to be more frequent, due to the incentives for expanding its use as an automotive fuel oxygenate [1,2].

When spilled gasohol comes into contact with water, the alcohol present in this fuel, being completely miscible in water, will partition preferentially to the water phase. In the case of Brazil, where gas stations

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also have storage tanks containing hydrated ethanol, the same situation may occur in case of simultaneous spills from underground storage tanks containing pure ethanol and diesel. Thus, a high aqueous ethanol concentration can facilitate the transfer of hydrocarbons into the aqueous phase, enhancing contaminants concentration in groundwater, a process called “cosolvency effect” [3,4]. Therefore, associated with the problem related to the inhibition of BTEX biodegradation [5–7], cosolvency can affect the migration and partition of aromatic hydrocarbons in subsurface systems contaminated with mixtures of ethanol and other fuel [1,8].

Considering that one of the main public concerns associated with petroleum hydrocarbon spills is related to groundwater contamination, the possible enhancement of aqueous concentration of mono- and polycyclic aromatic hydrocarbons solubility in water containing high ethanol concentrations must be carefully evaluated. The objective of this study is to determine how important the ethanol cosolvent effect can be, in case of subsurface spills of gasohol, diesel and ethanol, on mono- and polycyclic aromatic hydrocarbons solubility, and to present a simple log-linear model to predict, under equilibrium conditions, the enhancement of aqueous contaminants concentrations due to the presence of ethanol as a cosolvent in groundwater.

1.1. Cosolvency theory

Cosolvency is generally modeled based on a log-linear equation, where the increasing cosolvent concentration causes a logarithmic increase of the hydrophobic organic compound (HOC) solubility [9–12]:

$$\log S_m = \log S_w + \sigma f. \quad (1)$$

The log-linear model describes a logarithmic increase in HOC solubility related to its aqueous solubility as a function of the cosolvent concentration, where S_m is the solubility of the solute in the water–cosolvent mixture, S_w is the solubility in pure water, f is the cosolvent volume fraction in the aqueous phase, and σ is the cosolvency power.

The HOC solubility in water (S_w) can be obtained by Raoult’s Law [9,13,14], which describes the behavior of solutes in an ideal mixture of two phases in thermodynamic equilibrium. This equation can be expressed as follows:

$$S_w = X_i \gamma_i S_i^w, \quad (2)$$

where X_i is the molar fraction in the organic phase, γ_i is the coefficient of solute activity in the organic phase, and S_i^w is the solubility of the pure solute in water. For dissolution of petroleum hydrocarbons, γ_i is considered equal to unity, since interactions among the compounds with similar chemical structures are considered to be insignificant [15,16]. For solid solutes, such as naphtha-

lene, the supercooled liquid solubility is used to account for the effect of crystal structure upon solubility [12].

The cosolvency power can be determined for a group of HOC by the relationship [17]

$$\sigma = a \log K_{ow} + b, \quad (3)$$

where the coefficients a and b are empirical constants, unique to a cosolvent for a class of aromatic organic solutes. For a given solvent system, this equation shows that the cosolvency power (σ) is proportional to the HOC’s octanol–water partition coefficient K_{ow} . By knowing the values of σ for a range of mono- and polycyclic aromatic hydrocarbons, it is possible to determine the cosolvency power for other petroleum hydrocarbons. Note that Morris et al. [17] determined values from solubility data measured over a cosolvent concentration (f) range of 0–90% in binary mixtures. For BTEX (and other liquid constituents), complete miscibility may be noted at cosolvent concentrations (f) greater than $\sim 70\%$.

2. Methodology

2.1. Monoaromatic hydrocarbons in the Brazilian commercial gasoline

A series of experiments with batch reactors was done to evaluate first the effect of BTX compounds in the presence of ethanol. The reactors consisted of 60-mL glass vials with Teflon septum and aluminum seal. In these experiments, the cosolvency power (σ) was initially obtained for pure benzene, toluene, and *o*-xylene in an ethanol–water system. Afterwards, cosolvency experiments were carried out with ethanol-free gasoline and with Brazilian commercial gasoline (containing 22% ethanol) to validate the log-linear cosolvency model.

Experiments with pure BTX were done in triplicates with a water–BTX ratio of 10:1 (experiments done in the presence of one hydrocarbon at a time). Samples containing the hydrocarbon–water mixtures were placed into a shaker at $25 \pm 1^\circ\text{C}$, until complete equilibrium between the phases. Equilibrium was reached in 48, 72 and 120 h for benzene, toluene and *o*-xylene, respectively. After this period, the vials were placed upside down in a centrifuge for 20 min at 3000 rpm to completely separate the hydrocarbon and water phases. These experiments were conducted for ethanol–sole BTX–water systems in ethanol volumetric fractions of 1.0%, 2.2%, 4.0%, 10.0%, 16.0% and 22.0%. Experiments with ethanol-free gasoline and with the Brazilian commercial gasoline were prepared with gasoline–distilled water ratios of 1:1, 1:2, 1:5, 1:10 and 1:20, which were kept in equilibrium for 120 h. Since the Brazilian commercial gasoline used in the experiments contained 22% ethanol, these ratios represented ethanol

fractions of 15.8%, 8.47%, 3.62%, 1.81% and 0.93%, respectively.

2.2. Mono- and polycyclic aromatic hydrocarbons in the Brazilian commercial diesel

Naphthalene, anthracene and pyrene were selected to represent the 16 PAHs of the EPA priority list. Experiments with pure PAHs were prepared in triplicate 20 mL vials with a water–hydrocarbon volume ratio of 40:1. Each experiment with pure PAHs was prepared similarly to the experiments with BTX described above. Equilibrium was reached in 15 days for naphthalene and pyrene, and 24 days for anthracene. The same experiments were repeated for a PAH–water–ethanol system in ethanol volumetric contents of 1%, 5%, 10%, and 20%.

Cosolvency experiments with Brazilian commercial diesel oil were done the same way as described above, for a diesel–water ratio of 1:10. Vials were prepared with 1000 mg L⁻¹ sodium azide bactericide, and kept under agitation until equilibrium between phases was achieved. Previous experiments indicated that the water–diesel mixture was equilibrated in 30 days. The same conditions were repeated for the ethanol–diesel–water system for ethanol volumetric fractions of 1%, 5%, 10% and 20%.

2.3. Analytical methods

Ethanol and BTEX were analyzed directly using a gas chromatograph (GC-FID), Hewlett-Packard 5890 model, coupled with static automatic sampling Headspace (EPA, method 8015A). Analyses were performed with a fused-silica mega-bore column (length 30 m, internal diameter 0.53 mm and 2.65 μm film of cross-linked 100% dimethyl polysiloxane), using helium as the carrier gas.

Two methods were used for PAHs quantification. Samples from experiments with pure PAHs were analyzed using a high-performance liquid chromatograph (HPLC), Hewlett-Packard 1050 model with a quaternary pump, fitted with a fluorescence detector (FLD) for naphthalene, and ultraviolet detector (UVD) for anthracene and pyrene (EPA Method 8310), and separated on a reversed-phase C18 column (Vydac 201 TP) of 25 cm × 4.6 mm ID and 5 μm film thickness. The eluent was delivered at a flow rate of 1 mL min⁻¹, with isocratic elution program of acetonitrile/water (9:1). PAHs analyses for experiments with diesel–ethanol–water systems were performed using a Finnigan GC/MS quadrupole spectrometer (EPA, Method 8270B), fitted with a fused-silica capillary column (30 m length, ID 0.25 mm and 0.25 μm film of cross-linked 5% diphenyl dimethylpolysiloxane). Prior to the analyses, PAHs were

extracted from liquid samples with methylene chloride (EPA, method 3510B).

3. Results and discussion

3.1. Cosolvency power determination

Results of the pure BTX and PAHs log solubility in relation to ethanol volumetric fraction increase in aqueous phase are shown in Fig. 1. With the increase of aqueous ethanol fraction, an increase of BTX and PAHs solubility was observed. The ethanol-free aqueous solubility for pure benzene, toluene, *o*-xylene, naphthalene, anthracene and pyrene were 1757, 567, 202, 36, 0.06 and 0.22 mg L⁻¹, respectively. In the presence of a 10% ethanol volumetric fraction, the aqueous solubility of benzene, toluene, *o*-xylene, naphthalene, anthracene and pyrene increased by 20%, 40%, 50%, 73%, 116% and 127%, respectively. The HOC cosolvency power (σ) is obtained from the slope of log S_m , as a function of the cosolvent fraction in Fig. 1. The σ values obtained for the aromatic hydrocarbons tested indicate that the cosolvency power increases according to the hydrocarbon hydrophobicity (Table 1). In Table 1, the results presented in [17] for ethanol–water systems with cosolvent fraction ranges of 0–90% are also included for comparison. Cosolvency values obtained in our experiments are smaller, but expected since the slope of the log-solubility curves is smaller for lower ranges of f . Due to the cosolvency effect, highly hydrophobic compounds such as the polycyclic aromatic hydrocarbons can be present in larger concentrations in ground-water contaminated by petroleum hydrocarbon–ethanol

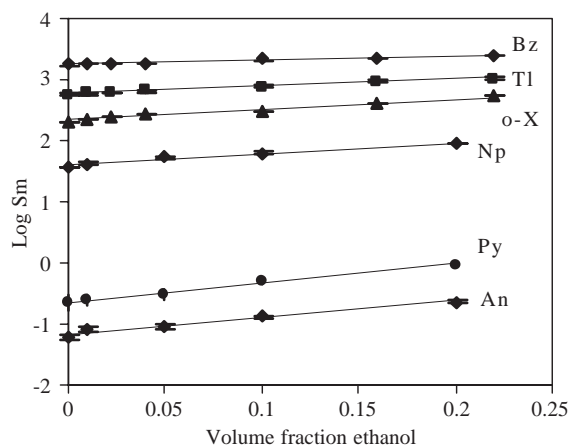


Fig. 1. Aromatic hydrocarbons log solubility increase due to the effect of aqueous ethanol concentration in pure hydrocarbon–ethanol–water systems. Benzene (Bz); toluene (Tl); *o*-xylene (o-X); naphthalene (Np); pyrene (Py); anthracene (An).

Table 1
Cosolvency power (β) for aromatic hydrocarbons in ethanol–water systems (regression analysis at the 95% confidence level, $n = 3$)

Compound	Benzene	Toluene	<i>o</i> -Xylene	Naphthalene	Anthracene	Pyrene
σ^a	0.65 ± 0.05	1.27 ± 0.13	1.66 ± 0.29	1.85 ± 0.68	2.72 ± 0.78	3.14 ± 0.58
σ^b	2.05	—	—	3.48	4.29	—

^aFrom our experiments (ethanol volume fraction from 0 to 20%).

^bFrom [17] (ethanol volume fraction from 0 to 90%).

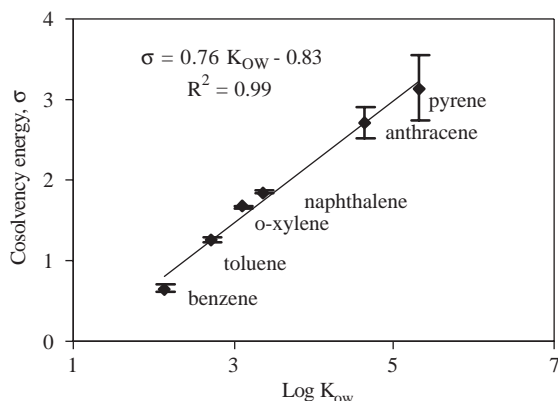


Fig. 2. Correlation between cosolvency power and log octanol–water partition coefficient for aromatic hydrocarbons (slope = 0.76 ± 0.12 and intercept = -0.83 ± 0.44 regression analysis at the 95% confidence level).

mixtures. Using Eq. (3), it is possible to determine values of σ for other fuel constituents. Coefficients a and b for this equation are determined from the cosolvency power (σ) values obtained for benzene, toluene, *o*-xylene, naphthalene, anthracene and pyrene and their respective octanol–water partition coefficient (K_{ow}) (Fig. 2). Thus, the values of the cosolvency power for other fuel hydrocarbons can be calculated using the following equation (regression analysis at the 95% confidence level, $n = 6$):

$$\sigma = 0.76(\pm 0.12)\log K_{ow} - 0.83(\pm 0.44),$$

$$R^2 = 0.99. \quad (4)$$

The high R^2 obtained for Eq. (4), over orders of magnitude of K_{ow} , makes this empirical equation useful to predict the cosolvency for other PAHs in ethanol–water systems under equilibrium conditions. Deviations from the log-linear equation above are presented in the literature for low and high cosolvent fractions, because of different solubility mechanisms. Banerjee and Yalkowsky [18] used a linear relation at lower cosolvent concentrations and a log-linear relation at higher cosolvent concentrations. Li and Yalkowsky [10] used the log-linear model for low and high cosolvency fractions, but incorporated two cosolvency power values

for each range of f . In our experiments, we also tested a linear solubility model, but a better model accuracy [19], given by the root mean square error, was obtained for the majority of the aromatic compounds studied with the log-linear equation.

The slope of Eq. (4) obtained in Morris et al. [17] (0.85) is statistically equal to the value obtained in our study, but the intercept is different (0.81). This difference is related to the larger aqueous ethanol fractions used in their experiments. Eq. (4), presented above for $f < 20\%$, is probably more accurate to predict the aromatic hydrocarbon solubility, since it is unlikely that ethanol concentrations exceed 20% in sites contaminated with gasohol or even in cases of neat ethanol spills. Therefore, if high concentrations of ethanol were present in the aquifer, the possible increase of PAHs solubility in groundwater could expand these plumes more rapidly, thus, bringing more difficulties for remediation of sites contaminated with petroleum hydrocarbons and ethanol mixtures.

3.2. Experiments with Brazilian commercial gasoline and diesel—cosolvency predictions

Experiments with Brazilian commercial gasohol, with pure gasoline (ethanol-free) and diesel were used to evaluate the fraction of ethanol that would be significant to increase BTEX and PAHs solubility and to validate the cosolvency log-linear model for petroleum hydrocarbons and ethanol mixtures. The cosolvency log-linear model is based on the hydrocarbon solubility in water and on the enhancement caused by the ethanol presence in the aqueous system. According to Raoult's law, hydrocarbon solubility in water without the cosolvent can be estimated by knowing the target contaminant mole fraction in gasohol and diesel. Results of the BTEX and PAHs mole fractions in Brazilian commercial diesel oil and gasoline without ethanol showed that the mass of monoaromatics present in both fuels is similar (Table 2).

Experiments with pure gasoline without ethanol showed that the average equilibrium concentrations of benzene, toluene and total xylenes in a water–gasoline system were, respectively, 10.5, 28.4 and 11.7 mg L^{-1} . Cosolvency results for the Brazilian gasohol showed an enhancement of BTX aqueous concentration with an

Table 2

Mole fractions of some mono- and polycyclic aromatic hydrocarbons present in commercial diesel and gasoline in Brazil

Compounds	Diesel mole fraction	Gasoline ^a mole fraction
Benzene	5.51×10^{-3}	7.80×10^{-3}
Toluene	3.93×10^{-2}	4.20×10^{-2}
<i>o</i> -Xylene	2.80×10^{-2}	1.70×10^{-2}
Ethylbenzene	4.54×10^{-2}	1.11×10^{-2}
1-Methylnaphthalene	2.85×10^{-3}	ND ^b
2-Methylnaphthalene	4.33×10^{-3}	ND ^b
Naphthalene	1.26×10^{-3}	6.00×10^{-3}
Acenaphthene	3.14×10^{-5}	ND ^b
Fluorene	1.52×10^{-4}	ND ^b
Fenanthrene	4.05×10^{-4}	ND ^b

^a Brazilian gasoline without ethanol.

^b ND—not determined.

increase in ethanol fraction. Comparing the data between the smallest and the largest ratio of water–gasoline mixture, where the aqueous ethanol fraction ranged from 0.93% to 15.8%, it was observed that the solubility of benzene, toluene, and total xylenes increased by 67%, 89% and 90%, respectively. BTX concentrations estimated with the log-linear model in the ethanol–water mixtures showed a reasonable agreement with the experimental data (Fig. 3). BTX mole fractions were estimated based on the original composition of the gasoline without ethanol, because it was assumed that ethanol was quickly transferred to the aqueous phase. An error analysis for the evaluation of this model [19] indicated that the log-linear model predicts 90% the effect of BTX solubility enhancement due to the increase of the ethanol fraction, which is represented by the slopes in Fig. 3. However, the model accuracy, where 100% indicates a perfect estimate, ranged from 105% to 150%. Differences between experimental and predicted concentrations were mainly caused by an error in the intercept of the log-linear model equation, which is caused from incorrect estimations of the BTX mole fractions in gasoline.

The aqueous concentration of some monoaromatics and PAHs equilibrated with commercial diesel containing different volume fractions of ethanol and log-linear model predictions are presented in Fig. 4. In pure water–diesel systems without ethanol, the average aqueous concentration of benzene, toluene, *o*-xylene, naphthalene and phenanthrene were, respectively, 8.58, 18.23, 3.62, 0.15 and 0.005 mg L⁻¹. Albeit the aqueous phase concentrations of monoaromatics are much higher than naphthalene and phenanthrene, the relative increase in solubility due to cosolvency is more significant for the PAHs. The solubility enhancement of benzene, toluene, *o*-xylene, naphthalene and phenanthrene in an ethanol

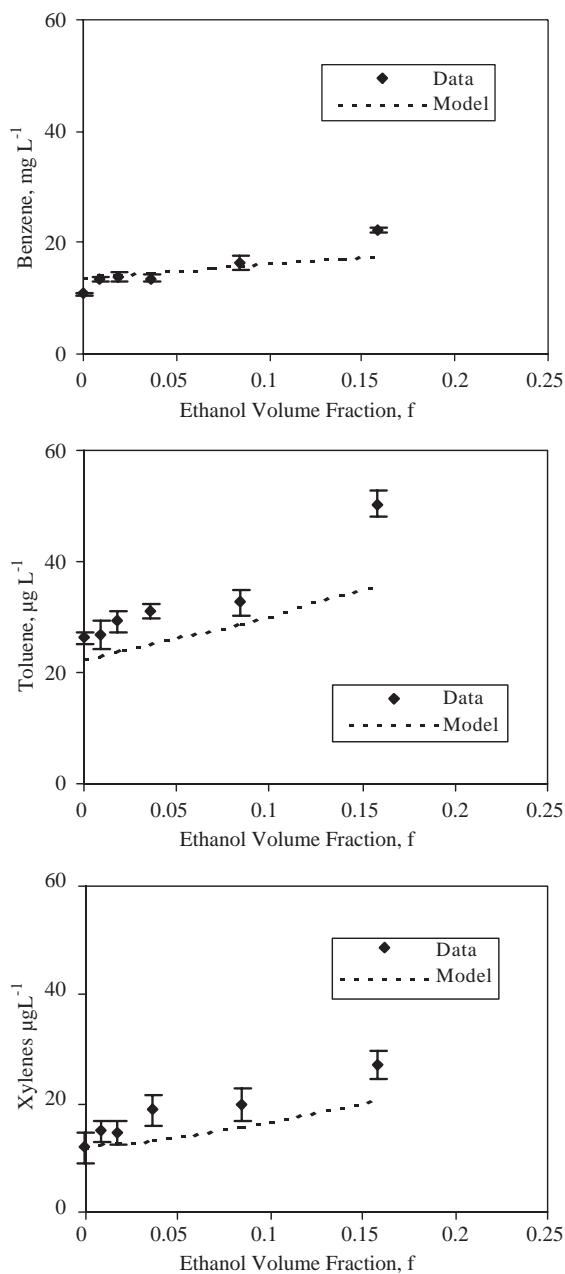


Fig. 3. Monoaromatic hydrocarbon solubility increase in gasoline–ethanol–water systems and log-linear model predictions.

volume fraction of 20% were, respectively, 29%, 34%, 80%, 135% and 230%. These results show the importance of cosolvency effect for the more hydrophobic PAHs present in diesel.

The log-linear model was also applied to the data obtained for the Brazilian commercial diesel–water–ethanol systems. The model predictions made for

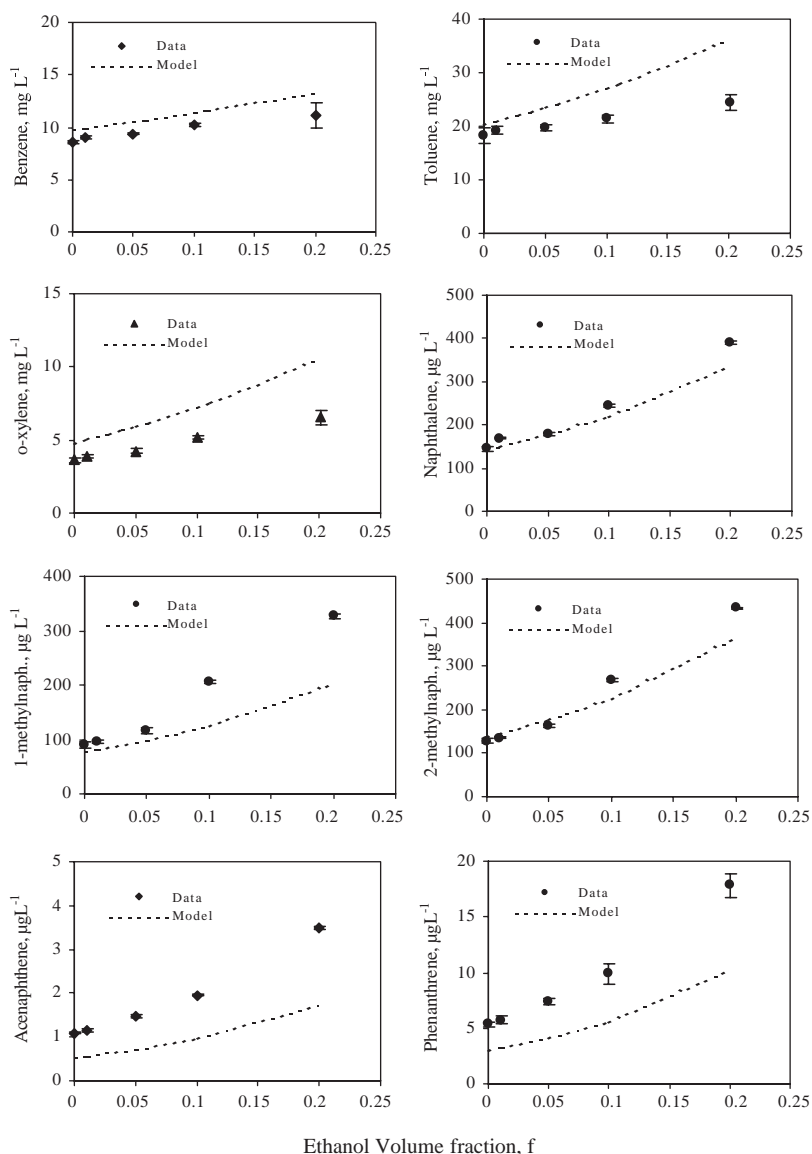


Fig. 4. Mono- and polycyclic aromatic hydrocarbon solubility increase in diesel–ethanol–water systems and log-linear model predictions.

aqueous concentrations of some mono- and polycyclic aromatic hydrocarbons provide an estimation of the highest aqueous concentration that these compounds can achieve in mixed spills of diesel and ethanol. Measured concentrations of these hydrocarbons in the diesel–water–ethanol mixtures showed good agreement with the log-linear model (Fig. 4). Error analysis of the model predictions [19] for the diesel experiments ranged between 90% and 140% for the slope of Eq. (1) and between 120% and 210% for the model accuracy. Deviations between experimental data and model predictions are related to incorrect determination of the mole fractions of the simulated contaminants (*o*-

xylene, acenaphthene and phenanthrene), or due to cosolvency power under- or over-predictions (toluene and 1-methylnaphthalene). These errors can be related to analytical uncertainties, contaminants non-ideal behavior and estimations of diesel molecular weight and density [16].

4. Conclusions

This study indicates that spills and leaks of gasohol or of simultaneous petroleum hydrocarbons and neat ethanol releases in the subsurface may increase the

effective solubility of mono- and polycyclic aromatic hydrocarbons in groundwater. This effect will be more pronounced for aqueous ethanol concentrations higher than 10%. For minor gasohol spills, it is not expected that concentrations of ethanol in groundwater will achieve these high levels. Results of a gasohol controlled release field experiment, performed in a sandy aquifer with a 100 L spill [20], showed that the highest ethanol concentration in groundwater near the source zone was below 1%. However, cosolvency may be critical in cases of large spills of gasohol or in simultaneous releases of neat ethanol and other fuels. This last case should be carefully evaluated in Brazil because hydrated ethanol is sold as sole fuel and, consequently, stored in gas stations and terminals with other petroleum products. Then, if the ethanol mass spilled in the aquifer is significant, higher BTEX concentrations will be expected in groundwater, and the more hydrophobic PAHs, that are usually present in minor aqueous concentrations in fuel spills without ethanol, may be dissolved in larger amounts in groundwater. Note that the cosolvency effect would only occur at or near the source zone where ethanol concentrations can be high. Since ethanol is a non-sorbing solute, it will migrate faster than the BTEX and PAHs in groundwater and would eventually be chromatographically separated from the aromatic hydrocarbons. It is also important to observe that ethanol can also drastically alter the biodegradation pattern of these contaminants in the groundwater plume due to the preferential consumption of electron acceptors and nutrients.

The simulations carried out with the log-linear model to evaluate the solubility enhancement of petroleum hydrocarbons in the presence of ethanol showed that this model is adequate to predict the co-solvency effect. A linear relationship between cosolvency power and K_{ow} was determined that allows predictions of the increase of aromatic hydrocarbon solubility due to the presence of ethanol under equilibrium conditions. However, due to mass transfer resistances, caused by hydrogeologic factors, contaminant concentrations in groundwater are likely to be smaller than predicted with the cosolvency model. Additional studies are needed to evaluate dissolutions of fuels in the presence of ethanol, which incorporate the effect of mass transfer limitations.

Acknowledgements

The authors wish to thank the funds provided to this project from Petrobras, Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Financiadora de Estudos e Projetos (Finep/CTPETRO). We also would like to thank the comments and suggestions given by an anonymous reviewer.

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