

# UNIFAC Modeling of Cosolvent Phase Partitioning in Nonaqueous Phase Liquid-Water Systems

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**Abstract:** In this study, an existing thermodynamic model was used to predict equilibrium phase partitioning behavior of a cosolvent in a two-phase nonaqueous phase liquid (NAPL)–water system. The activity coefficients are calculated using the universal quasichemical functional group activity coefficient (UNIFAC) method. We examined an assortment of cosolvent–NAPL pairs of environmental interest and compared the UNIFAC-predicted ternary phase diagrams against published experimentally derived ternary phase diagrams. Results show that the UNIFAC model is a promising method for predicting equilibrium cosolvent partitioning behavior in NAPL–water systems, and thus can be useful in estimating the potential for NAPL solubilization and mobilization in remediation processes. The cosolvent partitioning behavior is interpreted with regard to changes in the physical properties of the NAPL–water system. Changes in interfacial tension between the two phases were estimated using an existing correlation. A viscosity experiment was conducted for selected mixtures of ethanol, toluene, and water; and the viscosity was found to increase with increasing amounts of the cosolvent.

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## Introduction

Groundwater contamination from nonaqueous phase liquids (NAPLs) is a serious environmental problem. Common NAPLs have low aqueous solubilities, thus they may serve as long-term sources of groundwater contamination. Recently, the use of a cosolvent in remediating NAPL contaminated aquifers has received attention for its promising results, as has been demonstrated by experimental studies at the laboratory scale (Brandes and Farley 1993; Imhoff et al. 1995; Lunn and Kueper 1997; Grubb and Sitar 1999; Harmon et al. 1999; Ramsburg and Pennell 2002) and at the field scale (Rao et al. 1997; Falta et al. 1999). Depending on the phase partitioning behavior, a cosolvent may: (1) reduce the NAPL–water interfacial tension thus enhancing NAPL mobilization as a discrete phase; (2) enhance NAPL solubility in the aqueous phase allowing for NAPL transport as an aqueous solute; and/or (3) alter the NAPL phase volume, density, and viscosity.

In this study, an existing thermodynamic model was used to demonstrate how cosolvent phase partitioning can be predicted and how this partitioning behavior is interpreted with respect to changes in NAPL solubility and physical properties. The equilibrium phase partitioning of a cosolvent in a two-phase NAPL–water system was calculated using the universal quasichemical functional group activity coefficient (UNIFAC) method (Freden-

slund et al. 1977). Universal quasichemical functional group activity coefficient is a semiempirical model based on the group-contribution theory, such that the compounds in a liquid mixture are composed of functional groups and the mixture is described by its functional group composition. The main advantage of the UNIFAC method over other semiempirical thermodynamic models (Peters and Luthy 1994) is that activity coefficients can be estimated for systems where little or no experimental data are available. The UNIFAC method has been used for the prediction of NAPL solubility in the aqueous phase (Broholm and Feenstra 1995; Lee and Chrysikopoulos 1995, 1998; Kan and Tomson 1996; Chrysikopoulos and Lee 1998) and activity coefficients in multicomponent NAPLs (Wang et al. 1998; Peters et al. 1999).

We examined an assortment of NAPLs of environmental interest [benzene, toluene, and tetrachloroethylene (PCE)] and potentially useful cosolvents, and used ternary phase diagrams to compare the UNIFAC-derived phase equilibria against published experimental data. We also used the phase equilibrium predictions and an existing correlation to predict changes in interfacial tension between the two phases. Furthermore, for one of the ternary systems (ethanol–toluene–water), we conducted a two-phase viscosity experiment to simultaneously determine the viscosity of each phase in the presence of a cosolvent.

## Model Development

For a three-component two-phase system to be at equilibrium, the product of each component's mole fraction multiplied by its activity coefficient must be identical in both phases, such that (Reid et al. 1987)

$$x_i^N \gamma_i^N = x_i^W \gamma_i^W \quad (1)$$

where  $x$  = mole fraction;  $\gamma$  = activity coefficient with respect to the pure liquid reference state; superscripts  $N$  and  $W$  indicate the NAPL (nonaqueous) and water (aqueous) phase, respectively; and subscript  $i$  = component indicator. In most semiempirical models, the activity coefficient is assumed to have two components

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$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (2)$$

where superscripts *C* and *R* represent the combinatorial and residual parts, respectively. The combinatorial part considers the size and shape of the molecules while the residual part considers group interactions between the molecules. The UNIFAC equations for calculating the combinatorial and the residual parts are widely published (Fredenslund et al. 1977; Lyman et al. 1982) and thus are not listed in this paper. In this study the required UNIFAC interaction parameters were obtained from Hansen et al. (1991).

A *FORTRAN* computer program was developed to calculate phase equilibrium in a ternary two-phase system by simultaneously solving Eq. (1) for all three components. Because Eq. (1) must hold true for all three components, the following function (3) is minimized in order to compute mole fractions of every component in each phase

$$F = \sum_{i=1}^3 \text{ABS}(x_i^N \gamma_i^N - x_i^W \gamma_i^W) \quad (3)$$

The BCPOL function subroutine of the IMSL *FORTRAN* numerical libraries (Visual Numerics, Houston) is utilized for minimization of Eq. (3), which is subject to the following constraints:

$$\sum_{i=1}^3 x_i^N = 1 \quad (4)$$

$$\sum_{i=1}^3 x_i^W = 1 \quad (5)$$

and

$$0 \leq x_i \leq 1 \quad (6)$$

The computer program was designed to construct an entire ternary phase diagram by initially determining, in the absence of any cosolvent, the equilibrium mole fractions of the NAPL component in the aqueous phase and the water component in the NAPL phase. Once this baseline is established, the computer program incrementally increases the cosolvent mole fraction in the aqueous phase and calculates new equilibrium mole fractions for all remaining components in both phases. The computer program repeats the calculation process until the two phases converge to the plait point.

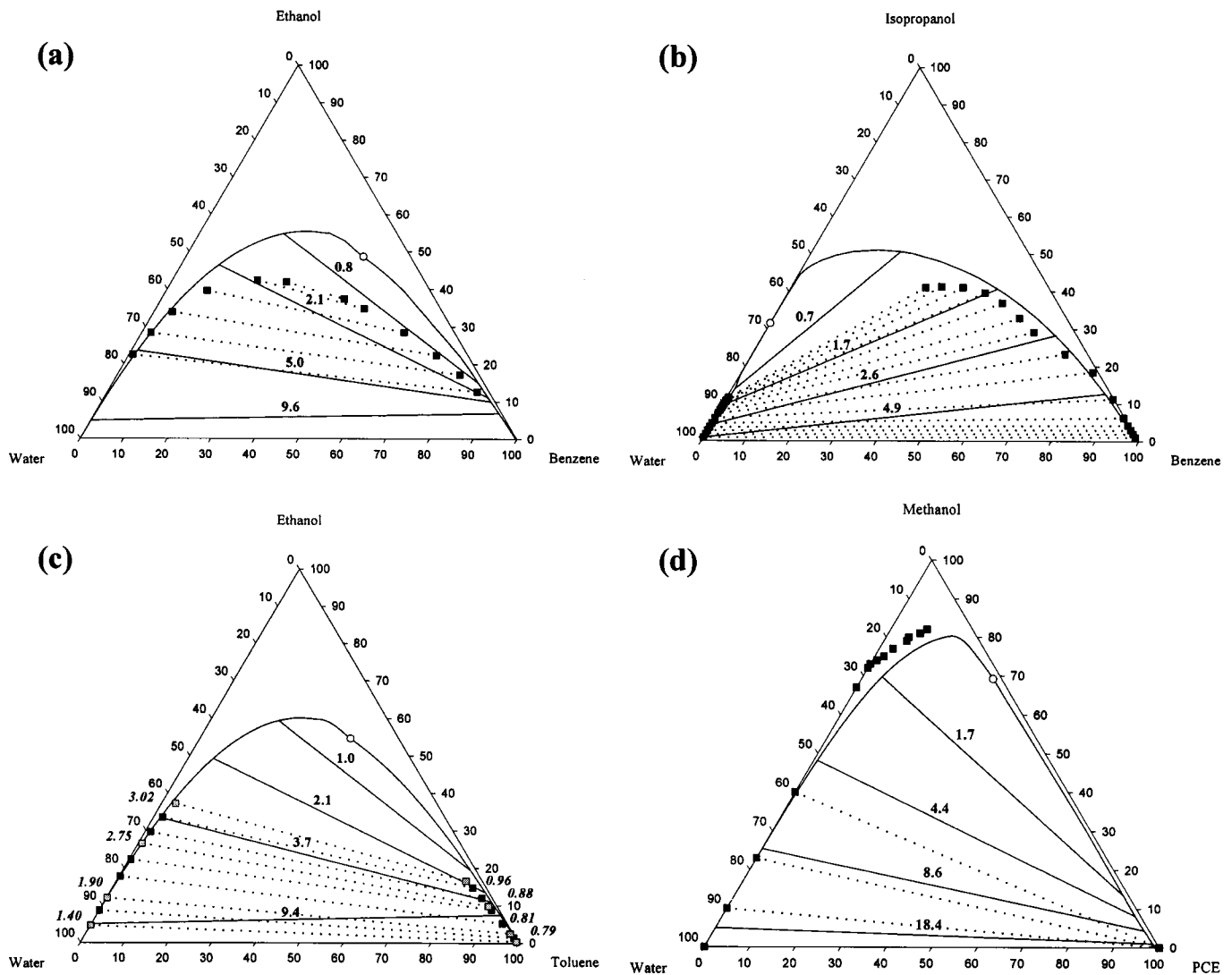
Ternary diagrams depicting phase equilibria for cosolvent partitioning in NAPL-water systems have been described by Peters and Luthy (1993). The binodal curve separates overall system compositions that exist as a single phase from those that exist as two phases. Each point on the binodal curve indicates the composition (expressed in mole percent) in one of the phases. In the ternary diagrams presented in this paper, points on the binodal curve on the left side represent the aqueous phase and points on the right represent the NAPL phase. Within the two-phase region, the straight line connecting points on the binodal curve is the tie line. Points along this line represent overall system compositions corresponding to the liquid-liquid phase equilibria represented by the tie line end points. When the system contains enough cosolvent such that the system is single phase, the point is called the plait point (open circle). For a description of how ternary phase diagrams are used to predict NAPL behavior in solvent extraction remediation process, the reader is referred to the work of Falta (1998).

## Results and Analysis

For this study, we considered several two-phase, three-component systems. The selection of cosolvent-NAPL pairs was based on environmental relevance and the availability of experimental results for comparison. Two of the NAPLs considered, benzene and toluene, would not typically occur as environmental contaminants in pure form. Peters and Luthy (1993, 1994) have demonstrated how cosolvent partitioning can be described for NAPLs that are complex chemical mixtures. Despite the added complexity of hydrocarbon mixtures, it is possible that a single component, such as benzene or toluene, may serve as a representative chemical to describe the overall phase partitioning behavior of some mixtures. The ternary diagrams in Fig. 1 show the predicted tie lines (solid lines) and binodal curve for cosolvent-NAPL pairs consisting of: (a) ethanol-benzene, (b) isopropanol-benzene, (c) ethanol-toluene, and (d) methanol-PCE, respectively. The temperature used for UNIFAC activity coefficient calculations is 25°C. The experimental data for each system are superimposed on the ternary diagram as squares, and the experimental tie lines are represented by dotted lines. The experimental results plotted in Figs. 1(a-c) are from Sørensen and Arlt (1979), and in Fig. 1(d) are from Imhoff et al. (1995). In general, for the systems depicted in Fig. 1, there is fairly good agreement between the UNIFAC-derived and experimentally derived ternary diagrams with regard to the slopes of the tie lines and the phase compositions at lower cosolvent concentrations. The UNIFAC model has mixed performance in its ability to predict phase compositions at higher cosolvent concentrations and consequently the size of the two-phase region may be underestimated or overestimated. Additional research is needed to address the performance of the UNIFAC model at higher cosolvent concentrations, but is beyond the scope of the current work.

A negatively sloped tie line [e.g., Fig. 1(d): methanol cosolvent with PCE NAPL] indicates that the cosolvent preferentially partitions to the aqueous phase relative to the NAPL phase. Such a cosolvent would have a limited effect on the physical properties of the NAPL phase, but may be effective in enhancing the aqueous solubility of the NAPL. Conversely, a positively sloped tie line [e.g., Fig. 1(b): isopropanol cosolvent with benzene NAPL] indicates that the cosolvent preferentially partitions to the NAPL phase relative to the aqueous phase. Large amounts of this type of cosolvent would be needed to enhance NAPL solubility, but it may beneficially cause the NAPL phase to swell in volume, and it may significantly alter its density and viscosity. For example, consider two different cosolvents in the benzene-water system [Figs. 1(a and b)]. If ethanol is added such that the overall mole percentages are 40% benzene, 40% water, and 20% ethanol, the aqueous phase contains approximately 28% ethanol and has dissolved benzene up to a concentration of 2%. Conversely for a system with the same proportions but in which the cosolvent is isopropanol, the aqueous phase contains only about 5% isopropanol and 0.2% benzene. However, the benzene phase contains approximately 29% isopropanol and its volume would increase by a similar amount. Furthermore, the model predictions shown in Figs. 1(a and c) show that at low cosolvent concentrations, the ethanol tends to favor the NAPL phase but at higher cosolvent concentrations the ethanol favors the aqueous phase. This predicted behavior, however, is not verified by the experimental tie lines.

As noted earlier, the main advantage of the UNIFAC method is that activity coefficients can be estimated for systems where little or no experimental data are available. As such, depending on the remediation objective, the UNIFAC method can be used to pre-



**Fig. 1.** Comparison between universal quasichemical functional group activity coefficient derived ternary phase diagrams (solid lines) and experimental results (squares) for cosolvent-nonaqueous phase liquid pairs: (a) ethanol–benzene, (b) isopropanol–benzene, (c) ethanol–toluene, and (d) methanol–tetrachloroethylene. Bold number on top of each universal quasichemical functional group activity coefficient-generated tie line is predicted interfacial tension (dyne/cm). For (c), italic bold numbers represent viscosity measurements (cp). Axes are in mole percents

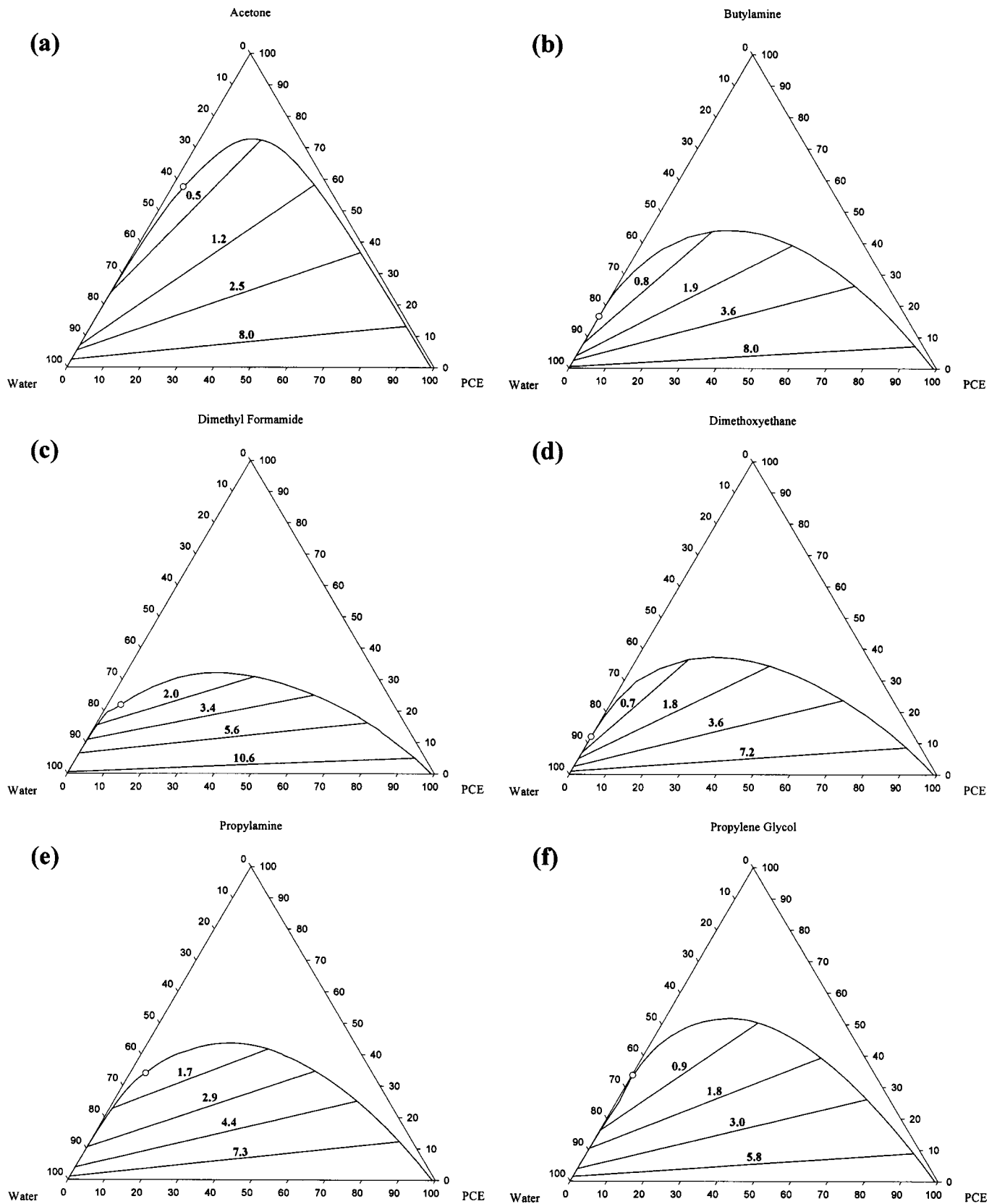
screen cosolvent selection. Fig. 2 illustrates the flexibility of the UNIFAC method by showing the UNIFAC-derived ternary diagrams for a wide variety of cosolvents in a PCE–water system. This figure shows a diversity of cosolvent partitioning behavior. With the exception of methanol [Fig. 1(d)], the predicted tie lines show that each of the cosolvents in Fig. 2 has higher affinity for the NAPL phase than for the aqueous phase. These findings suggest that remediation of a PCE-contaminated aquifer would best be achieved with a design that targets PCE phase swelling and modification rather than a design aimed at PCE dissolution in the aqueous phase. The size of the two-phase region of the ternary phase diagram is a measure of the amount of cosolvent required to completely solubilize two phases. Assuming the UNIFAC predictions in Fig. 2 are accurate, the most effective cosolvent, with regard to solubilization, is dimethyl formamide, and the least effective cosolvent is acetone.

The interfacial tension between an aqueous phase and a NAPL phase is an important determinant in the potential for NAPL mobilization as a discrete phase (Demond and Lindner 1993). For a three-component system, it can be estimated using the correlation

developed by Fu et al. (1986). The correlation was developed from an interfacial layer model and has been proven to give satisfactory results for a large number of ternary systems. The correlation for estimating the interfacial tension for a ternary mixture is

$$\sigma' = \frac{KRTX}{A_{wo} \exp(X)(x_1q_1 + x_2q_2 + x_3q_3)} \left( \frac{\text{dyne}}{\text{cm}} \right) \quad (7)$$

where  $A_{wo} = 2.5 \times 10^9 \text{ cm}^2/\text{mol}$  = van der Waals area of a standard segment;  $K = 0.9414$  = fitted constant;  $R$  = gas constant;  $T$  = temperature in kelvin,  $X = -\ln(x_1 + x_2 + x_3)$ ;  $x_i$  = mole fractions of the  $i$ th component in the phase where that component is a solute;  $x_{3r}$  = mole fraction for the third component in the phase where it is richer; and  $q_i$  = pure component area parameter defined by the model UNIQUAC (Universal Quasi Chemical) for vapor–liquid and liquid–liquid equilibria. For ternary or higher systems, the interfacial tension correlation of Fu et al. generally provides the best predictions (Seo and McCray 2002). The predicted interfacial tensions are shown in dyne/cm for each predicted tie line in Figs. 1 and 2. As expected, the interfacial tension



**Fig. 2.** Universal quasichemical functional group activity coefficient-derived ternary phase diagrams for tetrachloroethylene–water system and various cosolvents including: (a) acetone, (b) butylamine, (c) dimethyl formamide, (d) dimethoxyethane, (e) propylamine, and (f) propylene glycol. Bold number on top of each tie line is predicted interfacial tension (dyne/cm)

between the NAPL and aqueous phases has a maximum value when no cosolvent is present and decreases as more cosolvent is added to the system. At the plait point, the interfacial tension is zero.

Currently, there are no suitable correlations to predict viscosity of ternary liquid mixtures, especially aqueous mixtures (Reid et al. 1987). For this work, a two-phase viscosity experiment was conducted to simultaneously measure the viscosity of each phase in the presence of a cosolvent. A commercially available falling-ball viscometer (Gilmont Instruments, Barrington, IL) was modified to measure simultaneously the NAPL phase viscosity and the water phase viscosity in the presence of a cosolvent. The ethanol-toluene-water ternary system was selected due to availability of the experimental phase diagram (Sørensen and Arlt 1979). The viscosity of each phase for four different experimental tie lines (gray shaded squares) was measured and the results are presented in Fig. 1(c). The viscosity experiments were conducted at 25°C and the density of each component is assumed to be invariant. Results show that for the ethanol-toluene-water system, the viscosity of each phase increases as the cosolvent mole fraction increases.

## Summary

In this study, an existing thermodynamic model was used to predict the equilibrium phase partitioning of a cosolvent in a variety of NAPL-water systems. The activity coefficients were calculated using the UNIFAC method. The main advantage of the UNIFAC method is that activity coefficients can be estimated for systems where little or no experimental data are available. For the cosolvent-NAPL combinations selected for this study, the UNIFAC-derived ternary diagrams show fairly good agreement with published experimental data. This work demonstrates how the UNIFAC model can be used to predict cosolvent-enhanced NAPL solubilization as well as cosolvent partitioning into the NAPL phase (which can lead to alterations in volume, density, and viscosity of that phase). Using the estimated phase compositions, an existing correlation was used to predict cosolvent-induced decreases in interfacial tension between the two phases. An experiment was conducted to measure the viscosity of each phase for a ternary system consists of ethanol, toluene, and water; and the viscosity was found to increase with increasing cosolvent concentration.

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