

# Partitioning of Ethoxylated Nonionic Surfactants in Water/NAPL Systems: Effects of Surfactant and NAPL Properties

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Surfactant-based remediation has received considerable attention as a potential technology for enhancing conventional pump-and-treat remediation processes for aquifers contaminated with organic nonaqueous-phase liquids (NAPLs). In surfactant remediation, NAPL contaminants can be removed by two processes: solubilization and mobilization. Although these processes have been extensively studied, limited information is available regarding the partitioning of nonionic surfactants between aqueous and organic phases. Because surfactants are amphiphilic molecules that have a finite solubility in aqueous phases and NAPL, partitioning between the two phases is expected. The study presented here examines the effect of surfactant and NAPL properties on the partitioning of nonionic surfactants between different aqueous and nonaqueous phases using ethoxylated nonionic surfactants with different chemical structures and mixture distributions and NAPLs covering a wide range of NAPL/water interfacial tensions. In general, surfactant partitioning was found to be strongly correlated with surfactant hydrophobicity, mixture polydispersity, and NAPL/water interfacial tension. Partitioning at the high surfactant concentrations relevant in surfactant remediation (>2% surfactant) was most strongly correlated with surfactant hydrophobicity and NAPL/water interfacial tension whereas low concentration partitioning was more strongly correlated with surfactant mixture polydispersity. A quantitative correlation was developed to predict the high concentration partitioning behavior of surfactant/NAPL systems, given the surfactant critical micelle concentration and the NAPL/water interfacial tension. Implications for aquifer remediation are discussed.

## Introduction

One of the most challenging and persistent problems faced by environmental engineers and scientists today is the remediation of groundwater contaminated with organic nonaqueous-phase liquids (NAPLs). Dense nonaqueous-

phase liquids (DNAPLs), which can be found at residual saturations throughout the porous medium as well as in pools at the bottom of the aquifer, pose the most significant problem due to their location in the aquifer. EPA estimates predict that approximately 60% of the Superfund sites have a medium to high likelihood of containing DNAPLs (1, 2). Because NAPLs have very low aqueous solubilities, they serve as a potential long-term source of contamination, slowly dissolving to form plumes of contaminant that can spread via groundwater flow into regions used for drinking water supply. The most prevalent in-situ method for remediating aquifers contaminated with NAPL is pump-and-treat remediation (1). However, this technique is very inefficient for the removal of NAPLs due to their relatively low aqueous solubilities and, therefore, is mainly used to contain the dissolved contaminant plume. As a result, alternative methods aimed at removing the NAPL source have been sought (3). One alternative that has received widespread attention is surfactant-enhanced pump-and-treat, also known as surfactant-enhanced aquifer remediation (SEAR) (4, 5).

**Surfactants.** Surfactants are amphiphilic molecules containing both hydrophobic and hydrophilic moieties. Due to their amphiphilic nature, dissolved surfactant monomers tend to aggregate above a critical micelle concentration (cmc) to form thermodynamically stable aggregates known as micelles, oriented with the hydrophobic moiety directed into the center of the micelle (6). Hydrophobic contaminant molecules with low aqueous solubilities can partition into the hydrophobic core of aqueous-phase micelles, increasing their apparent aqueous solubility by up to several orders of magnitude and enhancing the efficiency of pump-and-treat to remove NAPL contaminants (4, 5). Removing NAPL by increasing its apparent aqueous-phase solubility via micelle formation is referred to as micellar solubilization.

Ethoxylated nonionic surfactants have received significant attention in surfactant remediation investigations to date due to their relatively high solubilization capacity (e.g., refs 5–7), insensitivity to background electrolyte concentrations (6), and relative ease of biodegradation (8). Ethoxylated nonionic surfactants are generally mixtures of components, with the actual distribution depending on the nature of the starting components in the synthesis. In the synthesis of alcohol ethoxylates, linear alcohols, either pure or commercial-cut, are ethoxylated via reaction with ethylene oxide gas, producing a Poisson distribution of ethoxylate groups (EO) in the mixture (6). Each of the components in these surfactant mixtures has distinct properties, giving rise to a bulk or average cmc and hydrophile:lipophile balance (HLB) for the mixture. HLB is an empirical parameter commonly used as a measure of surfactant hydrophobicity; as HLB increases, surfactant hydrophilicity increases.

**Surfactant Partitioning.** Several researchers have successfully demonstrated the efficiency of micellar solubilization using ethoxylated nonionic surfactants in batch, column, and field studies (5, 7, 9–16). However, one concern with surfactant remediation that has received little attention to date is the partitioning of surfactants between aqueous and organic phases during remediation applications. Because surfactants are amphiphilic molecules, they are soluble in both aqueous and organic phases and can partition between the two phases when both are present. Zimmerman et al. (15) and Butler et al. (12) have shown that partitioning for pure-hydrophobe ethoxylated linear alcohol surfactants can be very significant, leading to a substantial loss of surfactant available for solubilization. In fact, Zimmerman et al. reported near 100% surfactant losses (at 40 g/L of total surfactant

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concentration) due to partitioning into relatively polar organic liquids (e.g., dichloromethane and chloroform). Furthermore, Zimmerman et al. (15) demonstrated that partitioning increases with increasing surfactant mixture hydrophobicity for pure-hydrophobe linear alcohol ethoxylates as well as increasing NAPL polarity. Butler et al. (12) demonstrated that partitioning may result in a significant fractionation of the surfactant mixture, with the more hydrophobic components selectively partitioning into the NAPL, leaving a significantly more hydrophilic surfactant mixture in the aqueous phase. Because solubilization capacity is proportional to surfactant hydrophobicity, selective partitioning of hydrophobic surfactant mixture components may result in a less efficient surfactant system for remediation applications.

Extensive research has also been performed on the low concentration partitioning of nonionic ethoxylated alkyl-phenol surfactants into saturated hydrocarbon organics, with implications in emulsion formation and phase behavior (17–29). Most of these studies were conducted using surfactant concentrations below the cmc to estimate the partition coefficient  $K_p$  [the ratio of the equilibrium organic-phase surfactant monomer concentration ( $C_m^o$ ) to the equilibrium aqueous-phase surfactant monomer concentration ( $C_m^w$ )]. For pure monodisperse surfactants (i.e., single-surfactant component), Harusawa et al. (20) demonstrated a linear increase in  $C_m^o$  with increasing total aqueous surfactant concentration up to the cmc, at which point they observed a sharp break in the partitioning curve and a plateau in the nonaqueous-phase surfactant concentration. Because aqueous micelle formation limits the aqueous surfactant monomer concentration for monodisperse surfactants and partitioning is a monomer process, micelle formation limits surfactant partitioning.

For mixtures of surfactant components, many researchers have shown a slight increase in partitioning beyond the aqueous-phase cmc rather than a sharp break or plateau, resulting from changes in the relative concentration of individual surfactant monomers (18, 20–22). These changes have been reported to arise from the selective partitioning of hydrophobic mixture components into the nonaqueous phase, resulting in a more hydrophilic aqueous-phase monomer distribution. As micelles begin to form above the cmc, they are enriched in the hydrophilic surfactant mixture components, relative to the initial surfactant distribution, as a result of the selective partitioning of hydrophobic surfactant components into the organic phase. It is important to note that surfactant molecules in micellar aggregates above the cmc are generally more thermodynamically stable than surfactant molecules existing in monomeric form, resulting in a leveling off of the aqueous- and nonaqueous-phase surfactant monomer concentration. The leveling off can be gradual, however, depending on the disparity between the micellar and the initial surfactant component distributions. As the total concentration increases, the micellar surfactant distribution asymptotically approaches the initial surfactant distribution, coinciding with the nonaqueous-phase surfactant concentration asymptotically approaching a plateau value (20).

In comparing surfactants of varying hydrophobicity, Greenwald et al. (18) and Crook et al. (19) demonstrated an increase in the partitioning coefficients for octyl phenol ethoxylates with increasing hydrophobicity (e.g., decreasing number of EO units) caused by a greater affinity for the organic phase. Crook et al. (19) also demonstrated that polydisperse (multicomponent) surfactants have higher partition coefficients for isooctane than monodisperse (single-component) surfactant mixtures at HLBs > 9, likely due to the selective partitioning of lower HLB oligomers within the mixture (19). Ysambert et al. (28) demonstrated an increase in the partitioning coefficient with increasing

organic-phase polarity using an *n*-heptane/benzene organic mixture. Furthermore, as the benzene content was increased (increasing the polarity), they also observed a decrease in the selective partitioning of hydrophobic surfactant mixture components into the *n*-heptane/benzene mixture (28).

Although these studies provide insight into the partitioning of surfactants into organic liquids at concentrations near the cmc, to our knowledge little work has been reported investigating the effect of surfactant structure or mixture polydispersity on partitioning at concentrations relevant for surfactant remediation applications (~40 g/L). Furthermore, partitioning has not been thoroughly investigated with any of the relatively polar chlorinated organics commonly found as separate phase contaminants in groundwater (e.g., trichloroethylene, chlorobenzene, etc.). As discussed above, surfactant partitioning can have two primary effects: (i) a significant loss of bulk surfactant due to partitioning, resulting in surfactant concentrations potentially below optimum levels for remediation operations, and (ii) a significant change in the bulk properties of the surfactant mixture due to selective partitioning, potentially resulting in a less efficient surfactant mixture in the aqueous phase. Because these effects can have very serious implications for aquifer remediation, partitioning needs to be well understood before implementing surfactant remediation in the field. Furthermore, the ability to predict equilibrium surfactant partitioning losses could be a critical factor in the design of appropriate surfactant remediation schemes. Therefore, the objective of the work presented here was to examine the relationship between surfactant partitioning behavior and surfactant/NAPL properties for ethoxylated nonionic surfactants spanning several surfactant classes and chlorinated NAPLs covering a wide range of polarities and NAPL/water interfacial tensions (IFT). The overall goal was to develop an understanding of the physicochemical properties affecting surfactant partitioning and incorporate this understanding into a quantitative correlation utilizing surfactant/NAPL properties to predict partitioning losses.

## Materials and Methods

**Reagents.** Several surfactants were used in this study, representing a range of hydrophobicities and interfacial properties. They included pure-hydrophobe primary alcohol ethoxylates (AE) and a commercial Witconol SN-120 primary alcohol ethoxylate supplied by Witco Corporation (New York, NY), commercial Tergitol 15-S series secondary alcohol ethoxylates (Union Carbide, Danbury, CT), commercial Tagat series ethoxylated glyceryl ethers (Goldschmidt Chemical Corporation, Hopewell, VA), and commercial Myrj and Tween series ethoxylated fatty acid esters and ethoxylated sorbitan fatty acid esters, respectively (ICI Surfactants, Wilmington, DE). The surfactants were used without further purification. Relevant physical properties of the surfactants can be found in Table 1.

The DNAPLs studied were chosen based on their frequency of occurrence in the environment and were selected to cover a range of polarities and aqueous solubilities. They included two chlorinated alkenes [tetrachloroethylene (PCE) and trichloroethylene (TCE)], two chlorinated aromatics [chlorobenzene (CB) and 1,2-dichlorobenzene (DCB)], and a chlorinated alkane [1,1,2-trichloroethane (TCA)]. All of the chlorinated organics were obtained from Sigma (St. Louis, MO) except for TCA, which was obtained from Aldrich (Milwaukee, WI). The organic compounds were 99%+ pure and were used without further purification. Relevant physical properties of the chlorinated organics can be found in Table 2.

**Methods.** Batch experiments were run to investigate the partitioning of surfactants in the presence of NAPL. Surfactant solutions (2 mL) with concentrations ranging from 200 to

**TABLE 1. Selected Physical Properties of Ethoxylated Nonionic Surfactants Used in Partitioning Experiments**

Surfactant	Surfactant Class	Surfactant Structure	Chain Length	EO groups	HLB <sup>b</sup>	CMC <sup>c</sup> (mg/L)
C <sub>12</sub> E <sub>10</sub>	Primary AE <sup>a</sup>		12	10	14.2	68.5 <sup>e</sup>
C <sub>12</sub> E <sub>14</sub>			12	14	14.9	123.2 <sup>e</sup>
C <sub>12</sub> E <sub>16</sub>			12	16	15.1	158.6 <sup>e</sup>
C <sub>12</sub> E <sub>20</sub>			12	20	16.6	240 <sup>d</sup>
C <sub>12</sub> E <sub>30</sub>			12	30	17.6	560 <sup>d</sup>
Witconol SN-120			9-11	9	14.0	54 <sup>f</sup>
Tergitol 15-S-20	Secondary AE		12-14	20	16.4	280 <sup>g</sup>
Tergitol 15-S-30			12-14	30	17.5	710 <sup>g</sup>
Myrj 52	Ethoxylated Fatty Acid Ester		18	40	16.9	N/A
Tagat L2	Ethoxylated Glyceryl Ester		12	20	15.7	N/A
Tween 20	Ethoxylated Sorbitan Fatty Acid Ester		12	20	16.7	181.8 <sup>h</sup>

<sup>a</sup> AE, alcohol ethoxylate. <sup>b</sup> Hydrophile:lipophile balance. <sup>c</sup> Critical micelle concentration; N/A, not available. <sup>d</sup> Measured by Witco Corp. <sup>e</sup> Estimated by polynomial regression of cmc values measured by Witco Corp. <sup>f</sup> Reported by Pennell et al. (17). <sup>g</sup> Measured by Union Carbide. <sup>h</sup> Measured in this work.

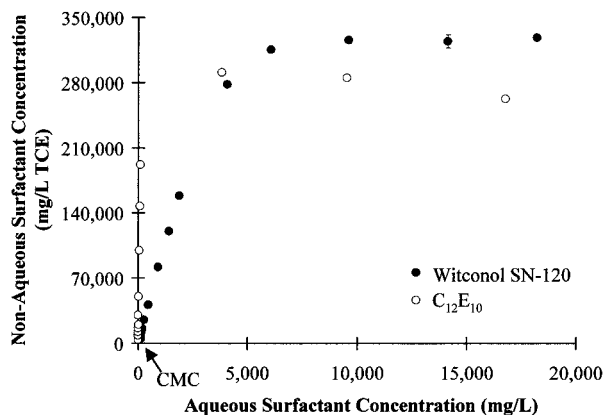
**TABLE 2: Selected Physical Properties of Chlorinated Organics Used for Partitioning Experiments**

NAPL	abbrev	molecular formula	IFT <sup>a</sup> (dyn/cm)	aq solubility <sup>c</sup> (10 <sup>-4</sup> mol/L)
tetrachloroethylene	PCE	C <sub>2</sub> Cl <sub>4</sub>	47.5	9.1
1,2-dichlorobenzene	DCB	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	40.1 <sup>b</sup>	11
chlorobenzene	CB	C <sub>6</sub> H <sub>5</sub> Cl	37.4	43
trichloroethylene	TCE	C <sub>2</sub> HCl <sub>3</sub>	34.5	100
1,1,2-trichloroethane	TCA	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	29.6	330

<sup>a</sup> Interfacial tension, reported by Demond et al. (32). <sup>b</sup> Measured in this work. <sup>c</sup> Reported by Riddick et al. (33).

100 000 mg/L were prepared in 4-mL glass vials equipped with open-faced screw caps and Teflon-backed rubber septa, followed by injection of 100–500  $\mu$ L of organic liquid. The samples were then allowed to equilibrate in a constant-temperature room at 25 °C either quiescently or with mixing using a VWR (Philadelphia, PA) Vortexer 2 and a LabQuake shaker (Lab Industries, Berkeley, CA). Previous experimental results showed 3 days mixing time to be sufficient for obtaining equilibrium partitioning values under mixing conditions. Samples in quiescent partitioning experiments were allowed to equilibrate for at least 3 weeks. After being equilibrated, the samples were centrifuged at 4000 rpm for 1.5 h to separate the aqueous and organic phases for analysis. It should be noted that cloudy mesophases formed in most of the systems studied here. Analysis of both aqueous and organic phases in the quiescent experiments, however, indicated that the mesophases were primarily oil-in-water macroemulsions with surfactant compositions very similar to the bulk NAPL. Additional optical microscopy work supported this conclusion. As a result, the oil-in-water macroemulsions were treated as part of the NAPL in this analysis.

Following equilibration, the aqueous phase was sampled and analyzed by high-performance liquid chromatography (HPLC) and gas chromatography (GC) using methods described in Zimmerman et al. (15). The separation and analysis of mixed surfactant systems was achieved using an HPLC method detailed in Kibbey and Hayes (34). In quiescent partitioning experiments, the nonaqueous phase was also sampled, diluted with methanol, and measured directly for



**FIGURE 1. Partitioning curves for a commercial ethoxylated linear alcohol and a pure-hydrophobe ethoxylated linear alcohol in the presence of TCE.**

surfactant concentration using the above methods. Non-aqueous-phase surfactant concentrations were either determined by difference from the total surfactant added or by direct measurement of the organic phase. Error bars on all of the figures represent 95% confidence intervals attributed to instrumental and sampling error.

**Determination of Partitioning Plateau Values.** Plots of the nonaqueous-phase surfactant concentration (mg/L) versus the aqueous-phase surfactant concentration (mg/L) were generated. Mass units were used for the surfactant concentrations due to the mixed nature of the surfactants used and the use of the ELSD, a mass detector, for surfactant detection. Plateaus of the partitioning curves were estimated by averaging the concentration points on the plateau. In the case of single-point quiescent partitioning experiments, which were run at sufficiently high concentrations such that partitioning had leveled off, plateaus were estimated by averaging the nonaqueous-phase concentrations of triplicate samples. Error bars for average plateau values represent 95% confidence intervals. Because the solubilization of NAPL and the partitioning of surfactant between aqueous and non-aqueous phases can significantly change the respective phase volumes, nonaqueous-phase surfactant concentrations calculated by difference from aqueous-phase concentrations must be corrected for NAPL volume changes. Since it is not possible to directly measure the NAPL volume in these experiments due to macroemulsion formation, the partitioned surfactant concentrations were corrected by calculating the approximate NAPL volume change due to surfactant partitioning and NAPL solubilization.

## Results and Discussion

### Effect of Surfactant Mixture Polydispersity on Partitioning.

Figure 1 demonstrates the effect of mixture polydispersity on partitioning well beyond the cmc by comparing the partitioning of Poisson distributed pure-hydrophobe C<sub>12</sub>E<sub>10</sub> into TCE with that of Witconol SN-120, a more broadly distributed commercial surfactant mixture with an average structure of C<sub>9-11</sub>E<sub>9</sub>. Note that the partitioning of the commercial surfactant mixture continues to increase at concentrations well above its cmc (54 mg/L), whereas the pure-hydrophobe surfactant appears to plateau near its cmc (68.5 mg/L). The increase in partitioning of Witconol SN-120 beyond the cmc is likely due to the deviation of the total surfactant distribution (monomer + micelle) in the aqueous and organic phases from the initial surfactant distribution at concentrations above the cmc, caused by the selective partitioning of hydrophobic surfactant mixture components into the NAPL. To quantitatively investigate this hypothesis, an experiment was run with two well-defined mixtures of

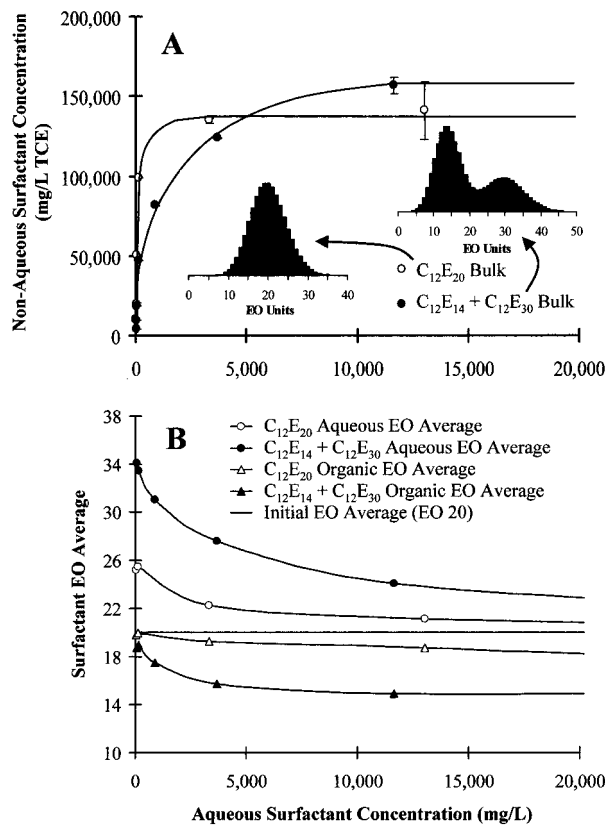


FIGURE 2. (A) Bulk partitioning curves and theoretical molar ethoxylate group (EO) distribution of  $C_{12}E_{20}$  (av EO = 20) and  $C_{12}E_{14} + C_{12}E_{30}$  (av EO = 20). (B) Surfactant EO distributions for  $C_{12}E_{20}$  and  $C_{12}E_{14} + C_{12}E_{30}$  in the presence of TCE.

Poisson-distributed pure-hydrophobe surfactants ( $C_{12}E_{20}$ , 0.475 mol fraction of  $C_{12}E_{14} + 0.525$  mol fraction of  $C_{12}E_{30}$ ). The two mixtures were chosen to have similar bulk properties (average of  $\sim 20$  EO units; cmc  $\sim 240$  mg/L) with different degrees of polydispersity. The theoretical EO distributions of the mixtures calculated from the molar Poisson distributions are shown in Figure 2A along with a plot of the bulk partitioning of each mixture into TCE. Note that the more broadly distributed mixture ( $C_{12}E_{14} + C_{12}E_{30}$ ) continues to partition above the cmc to a greater extent than does the single pure-hydrophobe mixture ( $C_{12}E_{20}$ ). This is also accompanied by significantly more selective partitioning of hydrophobic (low EO) surfactant mixture components in the broadly distributed mixture, demonstrated in Figure 2B by an increase in the aqueous-phase EO average (20  $\rightarrow$  34 EO units) and decrease in the nonaqueous-phase EO average (20  $\rightarrow$  15 EO units). From these data, it is apparent that as surfactant mixture polydispersity increases, selective partitioning of hydrophobic mixture components increases as well, resulting in continual partitioning at concentrations well above the aqueous cmc. Previous researchers have attributed post-cmc increases in partitioning to the changing micellar and monomer surfactant distribution with increasing concentration (21, 22). As micelles begin to form, both the aqueous-phase surfactant monomers and the micelles are enriched in hydrophilic surfactant components relative to the initial distribution. As the aqueous concentration increases, the surfactant distributions in micellar and monomeric form become increasingly hydrophobic, asymptotically approaching the initial distribution and coinciding with partitioning asymptotically approaching a plateau concentration.

**Effect of NAPL Properties on Surfactant Partitioning.** Figure 3 is a plot of the partitioning of a pure-hydrophobe

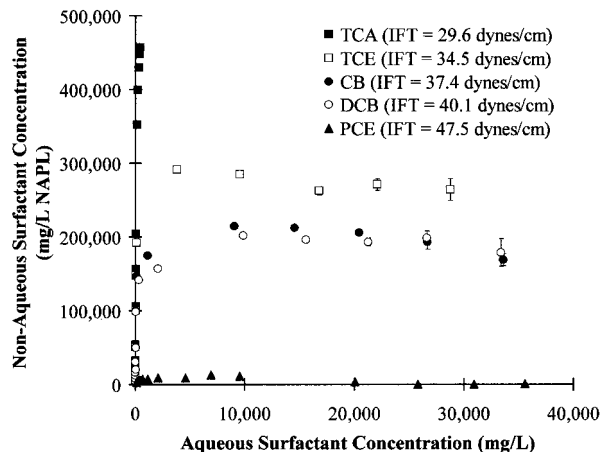


FIGURE 3. Effect of NAPL polarity (as measured by NAPL/water interfacial tension) on the partitioning of  $C_{12}E_{20}$  ethoxylated linear alcohol.

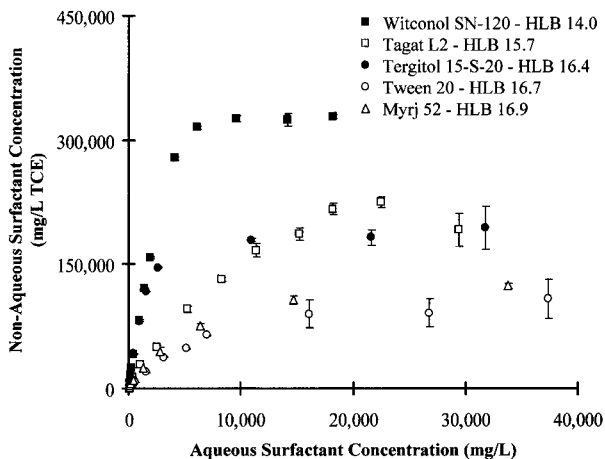


FIGURE 4. Effect of surfactant hydrophobicity on the partitioning of ethoxylated nonionic surfactants in the presence of TCE.

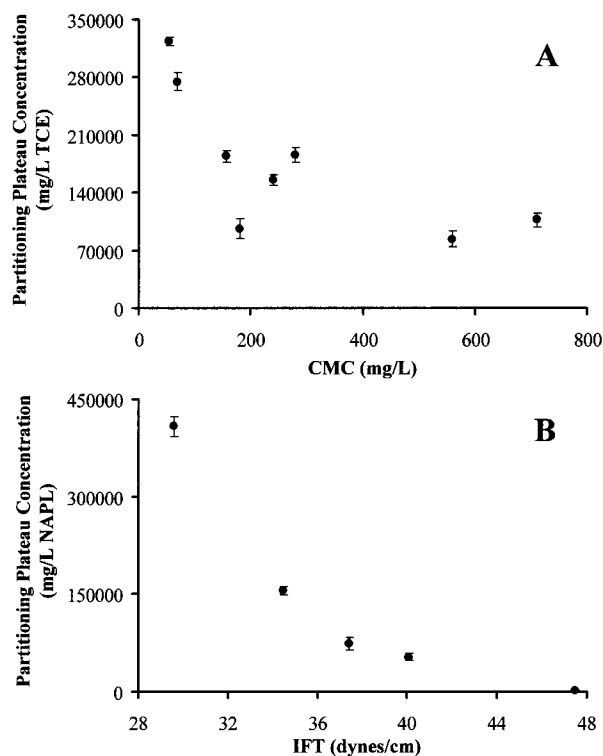
ethoxylated primary alcohol,  $C_{12}E_{10}$ , in the presence of NAPLs of varying aqueous solubilities and IFTs, used here as measures of NAPL polarity. As shown, partitioning is most significant with the most polar NAPL (TCA) and decreases with decreasing NAPL polarity or increasing NAPL/water IFT. In fact, the partitioning of  $C_{12}E_{10}$  in the presence of TCA has not yet reached a plateau at 40 000 mg/L of total surfactant, suggesting that the aqueous-phase cmc (68.5 mg/L) has not yet been reached. Although TCA is likely too water-soluble to exist as a pure separate phase in an aquifer for a long period of time, mixtures of TCA with other less soluble solvents may result in pools of NAPL with a high-partitioning capacity.

Partitioning curves were also generated for Tergitol commercial secondary alcohol ethoxylates and Tween commercial ethoxylated sorbitan fatty acid esters in the presence of PCE, TCE, CB, and DCB. As with the ethoxylated primary alcohols, the most significant partitioning was exhibited in the presence of the most polar NAPL, in this case TCE, followed by decreases in the partitioning of surfactant in the presence of NAPLs of decreasing polarity.

**Effect of Surfactant Properties on Partitioning.** Figure 4 is a plot of the partitioning of five commercial ethoxylated alcohol surfactants in the presence of TCE including a primary alcohol ethoxylate, a secondary alcohol ethoxylate, an ethoxylated fatty acid ester, an ethoxylated glyceryl ester, and an ethoxylated sorbitan fatty acid ester. As shown, the partitioning of ethoxylated nonionic surfactants correlates fairly well with relative surfactant hydrophobicity, as evi-

**TABLE 3: Summary of Partitioning Plateau Concentrations for Surfactant/NAPL Systems Tested**

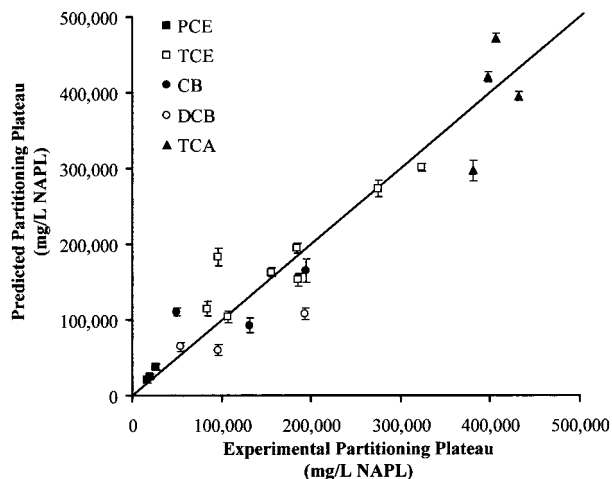
surfactant	NAPL	partitioning plateau (g/L of NAPL)	SD (g/L of NAPL)
C <sub>12</sub> E <sub>10</sub>	PCE	26	4
Tergitol 15-S-20	PCE	17	4
Tween 20	PCE	20	4
C <sub>12</sub> E <sub>10</sub>	DCB	194	8
C <sub>12</sub> E <sub>20</sub>	DCB	54	5
Tergitol 15-S-20	DCB	96	7
C <sub>12</sub> E <sub>10</sub>	CB	190	16
Tergitol 15-S-20	CB	130	10
Tween 20	CB	50	5
Witconol SN-120	TCE	323	5
C <sub>12</sub> E <sub>10</sub>	TCE	270	11
C <sub>12</sub> E <sub>16</sub>	TCE	184	7
C <sub>12</sub> E <sub>20</sub>	TCE	156	6
C <sub>12</sub> E <sub>30</sub>	TCE	80	10
Tergitol 15-S-20	TCE	185	9
Tergitol 15-S-30	TCE	107	8
Tagat L2	TCE	250	33
Tween 20	TCE	100	12
C <sub>12</sub> E <sub>20</sub>	TCA	398	6
C <sub>12</sub> E <sub>30</sub>	TCA	380	14
Tergitol 15-S-20	TCA	431	6
Tween 20	TCA	406	6



**FIGURE 5. (A) Plot of partitioning plateau concentration versus surfactant cmc for partitioning in the presence of TCE. (B) Plot of partitioning plateau concentration versus NAPL/water IFT for C<sub>12</sub>E<sub>20</sub>.**

denced by the increases in partitioning with decreasing HLB. The plateaus of the partitioning curves, in particular, correlate well with surfactant hydrophobicity whereas the initial slope of the partitioning curves are highly dependent on the polydispersity of the surfactants, as discussed above. Table 3 lists the partitioning plateau values and standard deviations (SD) for all of the surfactant/NAPL systems tested.

**Development of a Partitioning Correlation.** Figure 5, panels A and B, shows plots of the partitioning plateau



**FIGURE 6. Partitioning correlation fit.**

concentration versus surfactant cmc and NAPL/water IFT, respectively. Note that these physical properties are used here as relative measures of surfactant hydrophobicity ( $\downarrow$  cmc =  $\uparrow$  hydrophobicity) and NAPL polarity ( $\downarrow$  IFT =  $\uparrow$  polarity). On the basis of the high degree of correlation between the partitioning plateau and the cmc and IFT, a correlation was developed to predict the mass-partitioning plateau concentrations for the wide range of surfactant/NAPL combinations studied here. These two parameters, cmc and IFT, were chosen as representative and easily measurable physical properties of the surfactants and NAPLs used in this study, respectively. Only two properties were used in the correlation to minimize the number of adjustable parameters and to facilitate the use of the correlation by using readily available properties. Several other physical and empirically determined properties were investigated in the development of this correlation, such as surfactant HLB, surface tension,  $\Delta G^\circ$  of surfactant monomer transfer between aqueous and nonaqueous phases, molecular weight, and NAPL dielectric constant, dipole moment, specific conductance, and aqueous solubility. However, surfactant partitioning was found to correlate the most strongly with surfactant cmc and NAPL/water IFT. On the basis of the trends exhibited in Figure 5, where partitioning was found to be inversely proportional to surfactant cmc and NAPL/water IFT, the form of the empirical correlation is

$$C_p = \frac{\kappa}{\text{cmc}^\alpha \text{IFT}^\beta} \quad (1)$$

where  $C_p$  is the partitioning plateau concentration (mg/L of NAPL); cmc is the aqueous surfactant critical micelle concentration (mg/L); IFT is the organic/water interfacial tension (dyn/cm); and  $\kappa$ ,  $\alpha$ , and  $\beta$  are empirical constants. The empirical constants  $\kappa$ ,  $\alpha$ , and  $\beta$  were determined by performing a least squares nonlinear regression on the experimental data using Microsoft EXCEL and SYSTAT statistical software. Values of the constants, including confidence intervals, are as follows:  $\kappa = 5.3 \times 10^{15}$  ( $\pm 5 \times 10^{14}$ ),  $\alpha = 0.4$  ( $\pm 0.1$ ), and  $\beta = 6.2$  ( $\pm 0.2$ ) with an  $R^2$  of 0.963. This correlation has been tested for ethoxylated nonionic surfactants with aqueous cmc values ranging from 54 to 710 mg/L and for chlorinated NAPLs with organic/water IFTs ranging from 29.6 to 47.5 dyn/cm. Figure 6 demonstrates the fit of the correlation with a plot of the predicted versus experimental partitioning plateau concentrations for the surfactant/NAPL combinations tested. As shown, the correlation adequately captures the partitioning behavior for surfactants of different classes and hydrophobicities and NAPLs of varying IFTs. The correlation can also be refined

for a particular organic (i.e., constant IFT and  $\beta$ ) to provide an excellent fit versus surfactant cmc. It is interesting to note that the functional form of the correlation may apply to other surfactant/NAPL processes in SEAR, including micellar solubilization and macroemulsion formation. As the surfactant cmc and NAPL/water IFT increase, solubilization and the extent of macroemulsion formation both decrease, just as partitioning does (unpublished data). The extension of these concepts to emulsion formation and solubilization is currently underway and will be reported soon.

### Implications for Aquifer Remediation

Surfactant partitioning was found to be strongly correlated to three properties: (i) surfactant mixture polydispersity, (ii) surfactant hydrophobicity, and (iii) NAPL/water IFT. As surfactant mixture polydispersity increased, selective partitioning of hydrophobic mixture components into NAPL increased as well, resulting in significant changes in the surfactant mixture distribution as well as increasing partitioning at surfactant concentrations well above the cmc. At high concentrations, surfactant partitioning appeared to be correlated more strongly to the bulk properties of the surfactant/NAPL system. In particular, as surfactant hydrophobicity and NAPL polarity increased (as represented by decreasing cmc and IFT, respectively), partitioning increased as well. An empirical correlation was developed to predict the partitioning plateau concentrations of surfactant/NAPL systems given the surfactant cmc and the NAPL/water IFT. The correlation, valid for a fairly wide range of ethoxylated nonionic surfactant cmc values (50–710 mg/L) and chlorinated NAPL/water IFTs (29.6–47.5 dyn/cm), fits the data very well.

Because partitioning can be very significant for particular surfactant/NAPL systems, partitioning must be taken into account when designing surfactant remediation schemes. The correlation developed here could be particularly useful for such purposes by predicting equilibrium surfactant partitioning losses and aiding in transport modeling and surfactant selection.

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### Literature Cited

- (1) MacDonald, J. A.; Kavanaugh, M. C. *Environ. Sci. Technol.* **1994**, *28*, 362A–368A.
- (2) U.S. EPA. *Evaluation of the Likelihood of DNAPL Presence at NPL Sites*; 9355.4-13, EPA 15401R-93-073, PB93-963343; U.S. Environmental Protection Agency: Washington, DC, 1993.

- (3) Mackay, D. M.; Cherry, J. A. *Environ. Sci. Technol.* **1989**, *23*, 630–636.
- (4) West, C. C.; Harwell, J. H. *Environ. Sci. Technol.* **1992**, *26*, 2324–2330.
- (5) Pennell, K. D.; Abriola, L. M.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1993**, *27*, 2332–2340.
- (6) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; John Wiley & Sons: New York, 1989.
- (7) Fountain, J. C.; Klimek, A.; Beikirch, M. G.; Middleton, T. M. *J. Hazard. Mater.* **1991**, *28*, 295–311.
- (8) Swisher, R. D. *Surfactant Biodegradation*; Surfactant Science Series, Vol. 18; Marcel Dekker Inc.: New York, 1987.
- (9) Abdul, A. S.; Gibson, T. L.; Rai, D. N. *Ground Water* **1990**, *28*, 920–926.
- (10) Shiau, B.-J.; Sabatini, D. A.; Harwell, J. H. *Ground Water* **1994**, *32*, 561–569.
- (11) Pennell, K. D.; Adinolfi, A. M.; Abriola, L. M.; Diallo, M. S. *Environ. Sci. Technol.* **1997**, *31*, 1382–1389.
- (12) Butler, E. C.; Hayes, K. F. *Water Res.* **1998**, *32*, 1345–1354.
- (13) Diallo, M. S.; Abriola, L. M.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1994**, *28*, 1829–1837.
- (14) Pennell, K. D.; Jin, M.; Abriola, L. M.; Pope, G. A. *J. Contam. Hydrol.* **1994**, *16*, 35–53.
- (15) Zimmerman, J. B.; Kibbey, T. C. G.; Cowell, M. A.; Hayes, K. F. *Environ. Sci. Technol.* **1999**, *33*, 169–176.
- (16) Abriola, L. M.; Condit, W. E.; Cowell, M. A. *J. Environ. Eng.* **2000**, *126*, 39–46.
- (17) Ozdeger, E.; Sudol, E. D.; El-Aasser, M. S.; Klein, A. J. *Polym. Sci. A* **1997**, *35*, 3813–3825.
- (18) Greenwald, H. L.; Kice, E. B.; Kenly, M.; Kelly, J. *Anal. Chem.* **1961**, *33*, 465–468.
- (19) Crook, E. H.; Fordyce, D. B.; Trebbi, G. F. *J. Colloid Sci.* **1965**, *20*, 191–204.
- (20) Harusawa, F.; Saito, T.; Nakajima, H.; Fukushima, S. *J. Colloid Interface Sci.* **1980**, *74*, 435–440.
- (21) Harusawa, F.; Tanaka, M. *J. Phys. Chem.* **1981**, *85*, 882–885.
- (22) Warr, G. G.; Grieser, F.; Healy, T. W. *J. Phys. Chem.* **1983**, *87*, 4520–4524.
- (23) Brooks, B. W.; Richmond, H. N. *J. Colloid Interface Sci.* **1994**, *162*, 59–66.
- (24) Brooks, B. W.; Richmond, H. N. *J. Colloid Interface Sci.* **1994**, *162*, 67–74.
- (25) Marquez, N.; Anton, R.; Graciaa, A.; Lachaise, J.; Salager, J. L. *Colloids Surf. A* **1995**, *100*, 225–231.
- (26) Salager, J. L.; Marquez, N.; Anton, R. E.; Graciaa, A.; Lachaise, J. *Langmuir* **1995**, *11*, 37–41.
- (27) Ravera, F.; Ferrari, M.; Liggieri, L.; Miller, R.; Passerone, A. *Langmuir* **1997**, *13*, 4817–4820.
- (28) Ysambertt, F.; Anton, R.; Salager, J. L. *Colloids Surf. A* **1997**, *125*, 131–136.
- (29) Bourrel, M.; Schechter, R. S. *Microemulsions and Related Systems*; Surfactant Science Series, Vol. 30; Marcel Dekker Inc.: New York, 1988.
- (30) Shiau, B. J.; Sabatini, D. A.; Harwell, J. H. *Environ. Sci. Technol.* **1995**, *29*, 2929–2935.
- (31) Becher, P. In *Non-ionic Surfactants*; Schick, M. J., Ed.; Marcel Dekker Inc.: New York, 1967; p 481.
- (32) Demond, A. H.; Lindner, A. S. *Environ. Sci. Technol.* **1993**, *27*, 2318–2331.
- (33) Riddick, J. A.; Bunger, W. B.; Sakano, T. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; John Wiley and Sons: New York, 1986.
- (34) Kibbey, T. C. G.; Yavaraski, T. P.; Hayes, K. F. *J. Chromatogr. A* **1996**, *752*, 155–165.

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