Partitioning of Ethoxylated Nonionic Surfactants into Nonaqueous-Phase Organic Liquids: Influence on Solubilization Behavior

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The ability of surfactants to enhance the apparent aqueous solubilities of nonaqueous-phase liquid (NAPL) contaminants has increased interest in surfactant-enhanced aquifer remediation (SEAR) applications. This study examines the effect of surfactant partitioning on surfactant solubilization efficiency by analyzing the solubilization of several chlorinated NAPLs by a homologous series of linear alcohol ethoxylate nonionic surfactants. In general, it is found that the partitioning of surfactants can, especially in the cases of polar NAPLs, lead to substantial losses of surfactant, leaving little surfactant remaining in aqueous solution for solubilization. More importantly, it is found that neglecting surfactant partitioning can produce artifacts in the measured solubilization capacities of surfactants for NAPLs. For example, when surfactant partitioning is neglected, measurements of the solubilization capacity for homologous series of surfactants are often observed to produce a maximum solubilization capacity as a function of the surfactant hydrophile–lipophile balance number (HLB). The work described here demonstrates that the observed maximum solubilization capacity can result from neglecting partitioning of the surfactant into the NAPL. When solubilization capacity is calculated based on the amount of aqueous surfactant present after partitioning losses, no maximum is observed. The implications of this work for aquifer remediation are discussed.

Introduction

Dense nonaqueous phase liquids (DNAPLs) are prevalent at many contaminated sites. Due to their high densities, relatively low solubilities, and slow rates of dissolution into groundwater, entrapped DNAPLs cannot be efficiently removed by standard pump-and-treat methods that only treat the aqueous phase (*1–3*). Because surfactants may significantly increase the apparent aqueous solubility of DNAPLs, they have the potential to greatly enhance the efficiency of pump-and-treat remediation technologies (*4*). Laboratory and field experiments with surfactants have demonstrated an increased removal of DNAPLs from contaminated soils (*5*). Investigators have also shown enhanced solubility of nonaqueous phase liquids (NAPLs) such as pesticides, alkanes, chlorinated solvents, polycyclic biphenyls, and

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polycyclic aromatic hydrocarbons in the presence of surfactant solutions (*6–12*).

At aqueous surfactant concentrations above the critical micelle concentration (CMC), surfactant molecules form aggregates known as micelles (*13*). Organic contaminants can partition into surfactant micelles, increasing the apparent aqueous solubility of the contaminants; this process is referred to as solubilization (*13–15*). The solubilization capacity of a surfactant for a particular NAPL can be quantified by the molar solubilization ratio (MSR). The MSR is a ratio of the moles of organic solubilized to the moles of surfactant in micellar form and is often calculated using eq 1 (*16, 17*)

$$\text{apparent MSR} = \frac{C_\text{o} - C_\text{o,sol}}{C_\text{surf} - C_\text{surf,cmc}} \tag{1}$$

where C_o is the molar concentration of the solubilized organic, $C_\text{o,sol}$ is the aqueous solubility of the organic, C_surf is the total molar concentration of the surfactant added, and $C_\text{surf,cmc}$ is the molar concentration of the surfactant at the CMC. One problem with eq 1 is that it does not produce the actual MSR if significant partitioning of the surfactant occurs. When significant partitioning occurs, C_surf will be larger than the actual aqueous surfactant concentration, making the denominator of eq 1 ($C_\text{surf} - C_\text{surf,cmc}$) larger than the quantity of micellar surfactant in solution. As a result, the MSR calculated by Equation [1] will be smaller than the actual MSR. This has been confirmed by Butler and Hayes (*18*), who found that the MSR calculated without accounting for surfactant partitioning gave an erroneous value that was half of the actual MSR for 1,2-DCB in the presence of dodecyl alcohol ethoxylate surfactants.

For systems where surfactant partitioning is not significant, solubilization plots of moles of solubilized organic vs moles of surfactant typically increase linearly at total surfactant concentrations beyond the CMC (*19*). In these systems, eq 1 produces an accurate measure of solubilization capacity (Figure 1A). However, in cases where surfactant partitioning losses are significant, substantial amounts of surfactant may be lost to the NAPL, rendering the surfactant unavailable for solubilization. Surfactant partitioning losses appear as a lag in the solubilization curve, where additional surfactant must be added to the system before the CMC is reached and solubilization begins (Figure 1B). To ensure accurate measurements of MSR in these systems, only data corresponding to conditions where micelles are present in solution (i.e., the aqueous surfactant concentration exceeds the CMC) should be used to calculate MSR values.

The solubilization capacity of a surfactant depends on both surfactant and NAPL characteristics and can be reduced by sorption to solid phases or partitioning into NAPLs. Many investigators have documented the effect of surfactant losses due to sorption to aquifer materials (*5, 20–24*) and the effects of sorbed surfactant on sorption/desorption rates of dissolved organic contaminants (*25, 26*). In addition, several studies have been reported examining partitioning of surfactants into light nonaqueous phase liquids (LNAPLs) and oils (*27–30*). Most of these studies were performed in connection with the enhanced recovery of petroleum products and do not address surfactant partitioning into chlorinated DNAPLs. Furthermore, little work has been reported on the effects of partitioning on the solubilization capacity of a surfactant.

Previous studies of surfactant solubilization have not typically accounted for surfactant losses due to partitioning, sometimes leading to erroneous conclusions about the
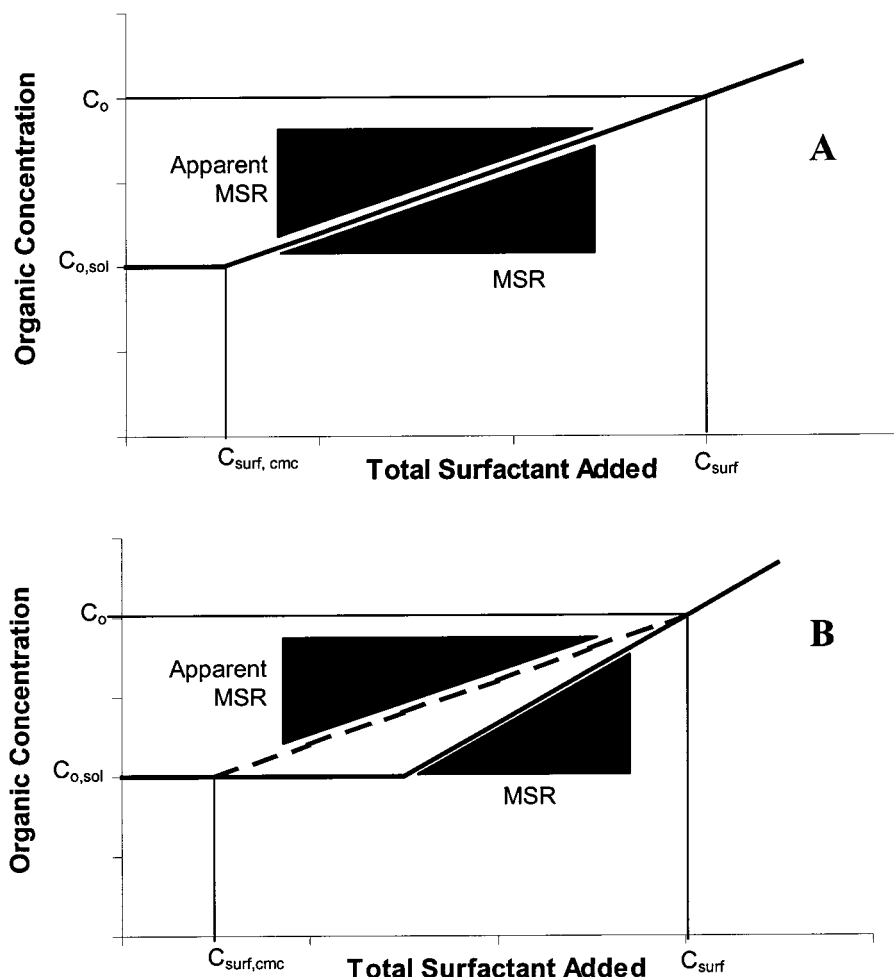
FIGURE 1. (A) Solubilization behavior in a system where surfactant does not partition into NAPL. (B) Solubilization behavior in a system where surfactant partitions into NAPL to a significant extent.

optimum surfactant for a given remediation application. For example, some researchers have observed a maximum apparent MSR (eq 1) when plotting apparent MSR vs either the hydrophile−lipophile balance (HLB) or number of ethoxylate (EO) units (*9, 11, 31, 32*). The HLB of a surfactant is an empirical measure of surfactant hydrophilicity and for alcohol ethoxylates is equal to the weight percent of the hydrophilic group divided by 5 (*19*). Both increasing HLB and increasing number of EO units within a homologous series of surfactants are indicative of an increase in the relative hydrophilic character of the surfactant. The maximum that is observed when apparent MSR is plotted against HLB or EO units has been attributed to several different phenomena. For example, Diallo et al. (*9*) ascribed the maximum apparent MSR to the net result of two effects: (i) decreasing micellar core volume and (ii) increasing solubilization volume in the ethylene oxide shell of the surfactant micelles as the number of EO units per molecule increases. However, Saito and Shinoda (*32*) and Pennell et al. (*11*) associated the apparent maximum MSR with a reduction in cloud point of the surfactant to room temperature when organic compounds are present.

The existence of a maximum apparent MSR suggests the existence of an optimum surfactant HLB for solubilization of a given contaminant. Fountain et al. (*31*) state that "[o]nce the appropriate HLB is determined, surfactants from different chemical families may be compared at this HLB to determine the chemical type which is the most effective solubilizer". This implies that surfactant selection for SEAR design should be based on the HLB corresponding to the maximum

apparent MSR for the contaminant of interest. As mentioned previously, however, because the apparent MSR calculation (eq 1) does not consider surfactant partitioning into NAPLs, it will not provide an accurate measure of the solubilization capacity of the surfactant in a system where partitioning losses to NAPLs are great. As will be discussed in this paper, neglecting partitioning can lead to a maximum apparent MSR when no maximum is observed in the actual MSR.

The artifact of a maximum apparent MSR can be avoided by conducting experiments at very low NAPL/water phase volume ratios such that the influence of partitioning on aqueous surfactant concentration will not be significant. However, without measuring surfactant partitioning for a given system, it is not possible to know in advance how small a NAPL/water ratio is necessary such that partitioning losses will be negligible. A more straightforward approach is to calculate actual MSR directly, by determining the slope of the solubilization curve at *aqueous* surfactant concentrations beyond the CMC. This approach provides an accurate picture of the solubilization capacity of surfactant remaining in solution.

Previous results from our laboratory indicate that partitioning may be substantial for certain nonionic surfactant/NAPL systems (*18*). It was proposed that partitioning could influence the solubilization process, and may in some cases produce the appearance of a maximum apparent MSR under conditions where solubilization capacity (actual MSR) was not a maximum. As such, the objectives of this work were (i) to assess the extent to which surfactant partitioning can influence observed solubilization behavior and (ii) to de-

TABLE 1. Selected Properties of NAPLs Used in Solubilization and Partitioning Experiments

chemical name	abbrev	IFT[a] (dynes/cm)	aqueous solubility[c] (% weight)
tetrachloroethylene	PCE	47.5	0.015
1,2-dichlorobenzene	1,2-DCB	40.1[b]	0.0156
chlorobenzene	CB	37.4	0.0488
trichloroethylene	TCE	34.5	0.137
chloroform	CF	32.8	0.815
1,1,2-trichloroethane	1,1,2-TCA	29.6	0.44
dichloromethane	DCM	28.3	1.30

[a] IFT values (38). [b] Determined by pendant drop analysis. [c] Aqueous solubility (39).

TABLE 2. Selected Properties of Nonionic Surfactants Used in Solubilization and Partitioning Experiments

name	av molecular formula	av MW (g/mol)	HLB[a]	CMC[b] (mg/L)
$C_{12}E_{10}$	$C_{12}H_{25}(OCH_2CH_2)_{10}OH$	626	14.1	75[c]
$C_{12}E_{16}$	$C_{12}H_{25}(OCH_2CH_2)_{16}OH$	890	15.8	171[c]
$C_{12}E_{20}$	$C_{12}H_{25}(OCH_2CH_2)_{20}OH$	1066	16.5	240
$C_{12}E_{30}$	$C_{12}H_{25}(OCH_2CH_2)_{30}OH$	1506	17.6	560

[a] Hydrophile-lipophile balance, calculated as HLB = wt % EO/5 (19). [b] Witco Corp. [c] Estimated by polynomial regression of CMC values provided by Witco for the C_{12} series.

termine the effect of different surfactant and DNAPL properties on the amount of surfactant lost due to partitioning.

Experimental Section

Two chlorinated alkenes, tetrachloroethylene (PCE) and trichloroethylene (TCE), three chlorinated alkanes, dichloromethane (DCM), chloroform (CF), and 1,1,2-trichloroethane (1,1,2-TCA), and two chlorinated aromatic compounds, chlorobenzene (CB) and 1,2-dichlorobenzene (1,2-DCB), were examined in this study. These compounds are representative of environmental contaminants and cover a range of polarities and NAPL/water interfacial tensions. Table 1 presents selected properties of the NAPLs used in this study. PCE, TCE, DCM, CB, and 1,2-DCB were purchased from Sigma (St. Louis, MO), while CF and 1,1,2-TCA were obtained from Aldrich (Milwaukee, WI). All NAPLs were 99%+ pure and used as received.

Each organic compound was studied in the presence of up to four different linear alcohol ethoxylate nonionic surfactants with average numbers of ethoxylate (EO) units of approximately 10, 16, 20, and 30. Table 2 gives the formulas of these surfactants as well as average molecular weights (MW), HLBs, and CMCs. These linear alcohol ethoxylate nonionic surfactants were supplied by Witco Corp. (New York, NY). Linear alcohol ethoxylate nonionic surfactants were chosen for this study because they have significant potential for environmental remediation applications due to their nontoxic and biodegradable nature (33) and have been studied for such purposes in laboratory and field experiments (34–37).

For each surfactant and chlorinated hydrocarbon pair, batch experiments were conducted to determine partitioning losses and NAPL solubilization. Samples were prepared by contacting 100 μL of pure organic liquid (unless otherwise noted, e.g., Figure 7) with 2 mL of surfactant solution in 4 mL glass vials equipped with open-top screw caps and Teflon-backed septa. The samples were vigorously mixed using a VWR (Philadelphia, PA) Vortexer 2. Experiments with lightly mixed samples showed that for the systems of interest, vigorous mixing did not change the ultimate equilibrium

but accelerated the approach to equilibrium. The contents of each vial were allowed to equilibrate for 3 days on a LabQuake shaker (LabIndustries, Berkeley, CA) in a 25 °C temperature-control room. Mixing time for all of these experiments was at least 3 days and was found to be sufficient for equilibrium solubilization values to be achieved. Samples were centrifuged at 3000 rpm for 1 h to separate the NAPL from the aqueous phase.

Following centrifugation, 1 mL of supernatant was removed, half was analyzed on a Hewlett-Packard (Palo Alto, CA) Series 5880 gas chromatograph (GC) to determine solubilized organic concentration, and the other half was analyzed on a Hewlett-Packard Series 1050 high performance liquid chromatograph (HPLC) to determine aqueous phase surfactant concentration. The GC was equipped with a 30 m DB624 column with 0.53 mm inner diameter (J&W Scientific, Folsom, CA), a Hewlett-Packard 7672A autosampler, and flame ionization detector. The GC was fitted with a Hewlett-Packard split liner packed with PorePak P 80-100 (AllTech, Deerfield, IL) to prevent the surfactant from interfering with analytical measurements. Samples for the GC were prepared by adding 0.5 mL of the supernatant to 0.5 mL of HPLC-grade methanol in glass autosampler vials. Autosampler vials were immediately sealed with Teflon-lined aluminum crimp-seal caps and analyzed to prevent organic losses due to volatilization. Standards of each organic were prepared and analyzed in series with the samples on the GC. A standard calibration curve was generated for each chlorinated hydrocarbon using a linear, least squares regression technique.

Analysis of the aqueous surfactant concentration was performed on a Hewlett-Packard 1050 Chemstation HPLC using a Hypersil (Shandon Scientific Ltd., England) silica precolumn. For the HPLC surfactant analysis, methanol was pumped through the precolumn at a rate of 1 mL/min. Detection was performed by a Sedere (Richard Scientific, Novato, CA) SEDEX 55 evaporate light scattering detector (ELSD) operated at 40 °C. A standard calibration curve was generated for each surfactant by generating 12 standards of varying concentration over a range that incorporated concentrations below the CMC to above the maximum sample concentration. Surfactant standards were analyzed in series with the samples, and the resulting standard curve was fit to a quadratic log–log expression using a linearized polynomial least-squares fit as described in Kibbey and Hayes (24). The concentration of surfactant in the NAPL was determined by difference from the known total and measured aqueous surfactant concentration. Micellar solubilization was quantified by measuring the aqueous concentration of organic liquid solubilized. Partitioning isotherms and solubilization curves were generated for total surfactant concentrations ranging from 0.01% to 4 wt % with a water/NAPL ratio of 20:1 unless otherwise noted (e.g., Figure 7). Error bars on all figures represent 95% confidence intervals for instrumental analysis error.

Results and Discussion

Surfactant Partitioning. Partitioning isotherms are shown in Figure 2 for a linear dodecyl ethoxylate surfactant with an EO average of 16 ($C_{12}E_{16}$) in the presence of selected chlorinated hydrocarbons. Partitioning curves correspond to total surfactant additions up to 20 g/L. It is apparent from the figure that the extent of surfactant partitioning increases with decreasing NAPL/water interfacial tension (IFT) as shown in Table 1. Partitioning is also found to increase with increasing NAPL solubility in water (Table 1). For organic compounds with relatively low IFTs, such as CF, 1,1,2-TCA, and DCM, the amount of surfactant partitioning loss can be significant with as much as 95% of the total amount of surfactant in the system partitioning into the NAPL for the conditions used in this experiment. For NAPLs with inter-
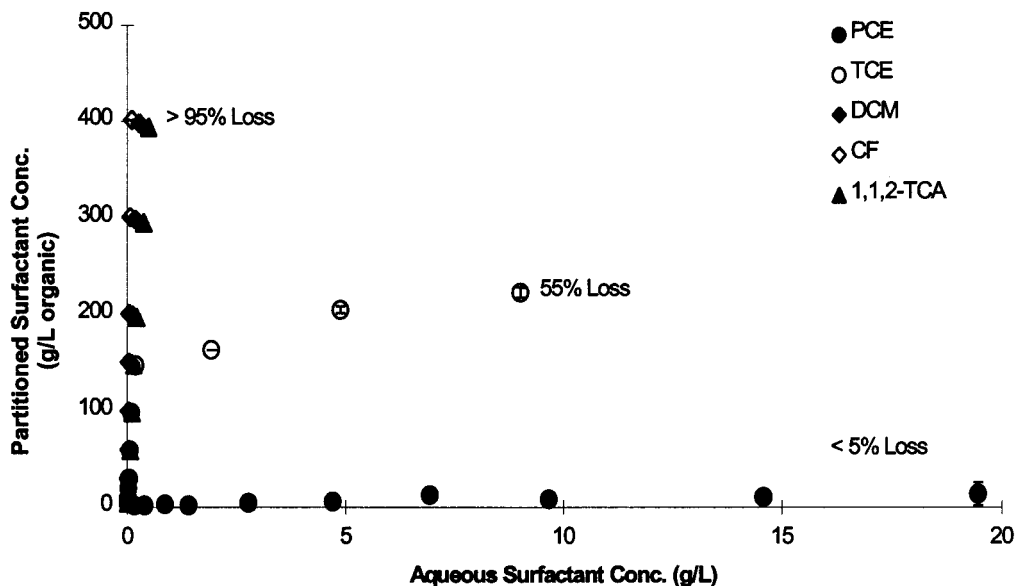
FIGURE 2. Partitioning of $C_{12}E_{16}$ into chlorinated hydrocarbons. In all cases, the total amount of surfactant added is 20 g/L. The percentages on the figure correspond to the amount of surfactant lost due to partitioning at the highest surfactant concentration. Note: DCM, 1,1,2-TCA, and CF overlap and are difficult to distinguish.
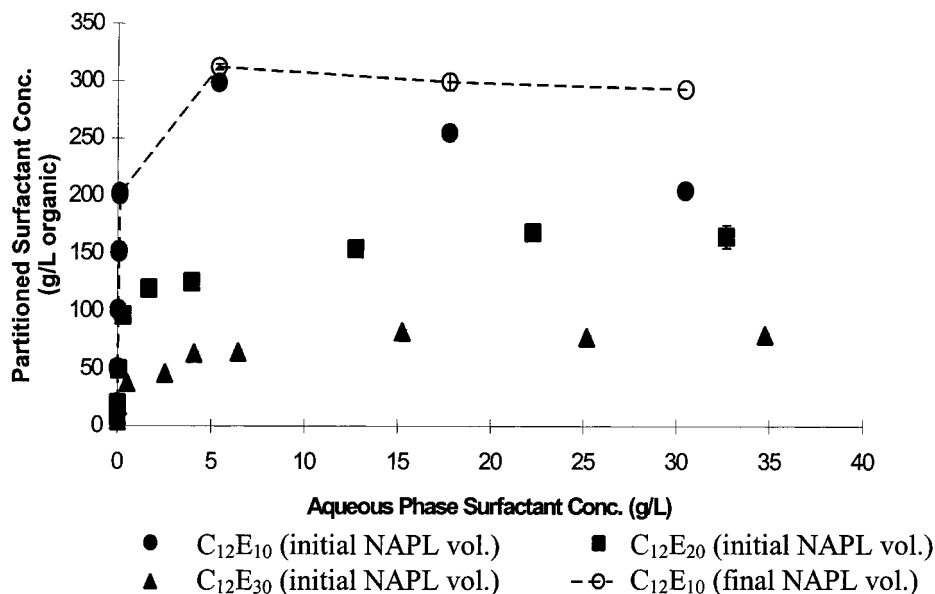

● $C_{12}E_{10}$ (initial NAPL vol.)   ■ $C_{12}E_{20}$ (initial NAPL vol.)
▲ $C_{12}E_{30}$ (initial NAPL vol.)   - ⊖ - $C_{12}E_{10}$ (final NAPL vol.)

FIGURE 3. Partitioning of linear dodecyl alcohol ethoxylates into trichloroethylene (TCE).

mediate IFTs, such as TCE, the amount of surfactant lost due to partitioning appears to level off above solution concentrations near the CMC. The leveling off trend can be attributed to the micellization of the surfactant which limits the concentration of monomers present above the CMC. Since partitioning is believed to be an interaction between surfactant monomers and NAPL (32), the formation of micelles limits the amount of partitioning that can occur at solution concentrations above the CMC. Due to the high surfactant affinity for the lower IFT NAPLs (CF, 1,1,2-TCA, DCM), the CMC was not attained in the aqueous solution for the total amount of surfactant added in this experiment (20 g/L). Though no direct evidence is available, it is possible that in the case of low IFT NAPLs, such as CF, 1,1,2-TCA, and DCM, reverse micelles (nonpolar exterior, polar interior) may form in the NAPL, leading to the very substantial surfactant loses observed (16).

Figure 3 shows the partitioning isotherms for a range of surfactants in the presence of TCE. This figure illustrates that surfactants with fewer EO units tend to partition to a greater extent than those with greater numbers of EO units. This can be explained by the fact that low-EO surfactants are more hydrophobic and as such have a greater driving force to leave the aqueous phase and partition into the NAPL. Note that although the low-EO surfactants are more hydrophobic than high-EO surfactants, they are still relatively polar and water soluble. As a result, even low-EO surfactants do not partition to a significant extent into the most nonpolar NAPLs studied, such as PCE (Figure 2).

Although partitioning levels off near the CMC in the $C_{12}E_{20}$ and $C_{12}E_{30}$ plots in Figure 3, the $C_{12}E_{10}$ partitioning curve appears to reach a maximum and then decrease. The decrease occurs in this case because a significant fraction of the TCE present is solubilized by the surfactant, reducing the volume of organic liquid available for surfactant partitioning at higher surfactant concentrations. When the amount of $C_{12}E_{10}$ partitioned is plotted based on the actual volume of NAPL present (calculated from solubilization data), as shown by the dashed line in Figure 3, the partitioned surfactant concentration levels off, following the same trend as $C_{12}E_{20}$
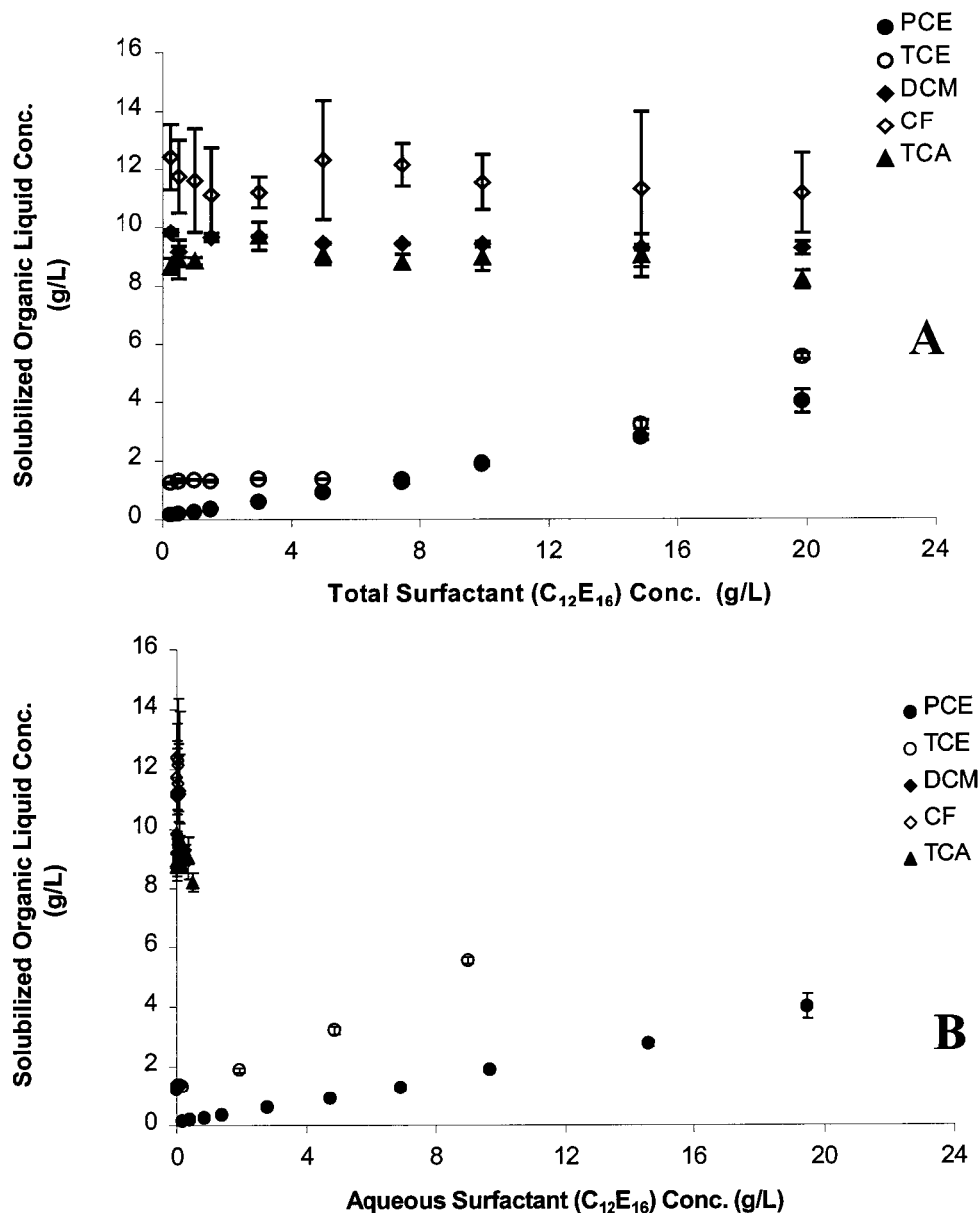
FIGURE 4. Solubilization of selected NAPLs by $C_{12}E_{16}$. (A) Solubilized organic vs total surfactant concentration and (B) solubilized organic vs aqueous surfactant concentration. Note: DCM, 1,1,2-TCA, and CF overlap and are difficult to distinguish in (B).

and $C_{12}E_{30}$. Of the systems investigated, only $C_{12}E_{10}$ had sufficient solubilization capacity to solubilize a substantial fraction of the TCE initially present in NAPL form. The solubilization capacities of $C_{12}E_{20}$ and $C_{12}E_{30}$ were lower, producing negligible changes in the volume of separate-phase TCE under the conditions examined.

II. Surfactant Enhanced NAPL Solubilization. Figure 4 shows solubilization of selected organic liquids using $C_{12}E_{16}$, the same surfactant for which partitioning behavior was shown in Figure 2. The effects of partitioning on solubilization are demonstrated in the plots of DCM, 1,1,2-TCA, and CF by the fact that no solubilization is observed (i.e., no increase in aqueous organic concentration is observed with increasing total surfactant addition in Figure 4A). In the cases of DCM, 1,1,2-TCA, and CF, the CMC of the surfactant is never attained in solution (Figure 4B) because nearly all of the surfactant added to the system is lost due to partitioning into the organic liquid phase. The horizontal lag that occurs in the solubilization plot of TCE in Figure 4A is indicative of partitioning losses; when solubilization is plotted as a function of surfactant remaining in the aqueous solution after partition-

ing (Figure 4B), the lag is not observed. NAPLs are solubilized when sufficient surfactant is added to the system such that the surfactant remaining in solution after partitioning exceeds the CMC. In the case of TCE (Figure 4A), the solution surfactant concentration would exceed the CMC of $C_{12}E_{16}$ after 0.17 g/L (Table 2) were added if no partitioning to the NAPL occurred; however, the aqueous surfactant concentration does not, in fact, reach the CMC until more than 5 g/L have been added. This behavior is less noticeable for PCE, because partitioning losses into PCE are less significant. As a result, plots of PCE solubilization in Figure 4A,B are similar.

Figure 5 is a plot of actual MSR vs HLB for PCE, TCE, CB, and 1,2-DCB, calculated based on slopes of solubilization curves and measured aqueous surfactant concentrations. This figure only contains data for PCE, TCE, CB, and 1,2-DCB because it was not possible to obtain MSR values for the more polar organics, DCM, 1,1,2-TCA, and CF for the concentrations and volume ratios studied, as discussed previously. It is apparent from the figure that no maximum actual MSR exists in the range of HLBs examined. This is in contrast to the apparent maxima that have been observed
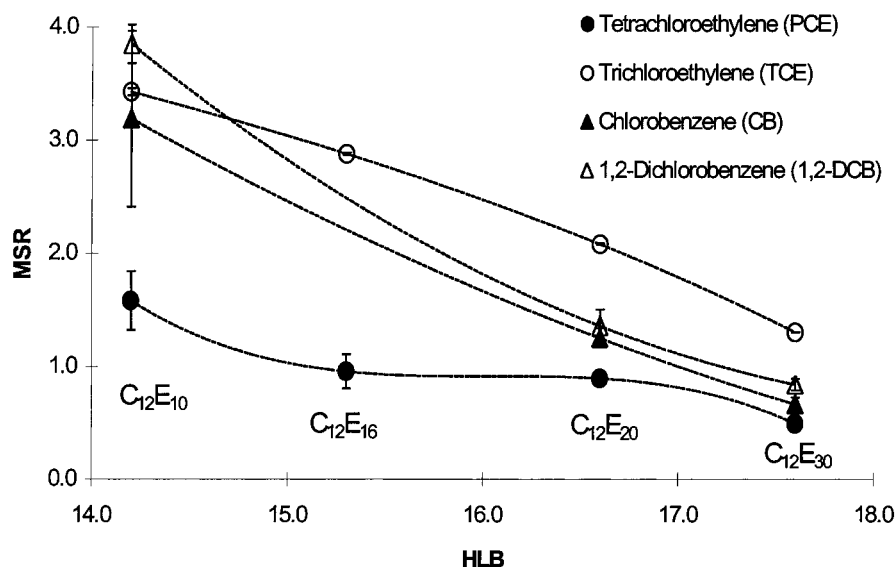
FIGURE 5. Plot of MSR vs HLB with surfactant losses due to partitioning taken into account for calculation of MSR (actual MSR).
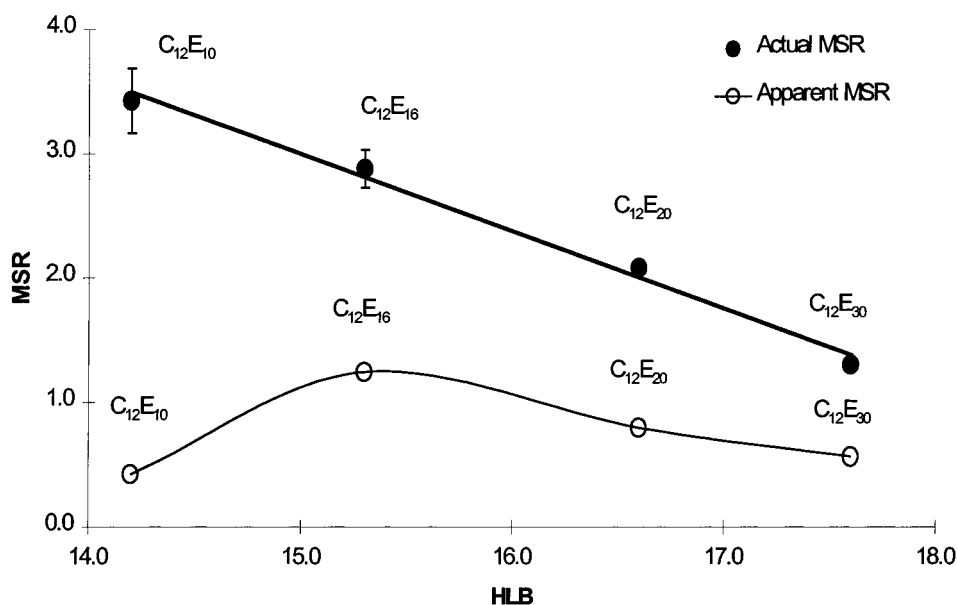

FIGURE 6. Actual MSR and apparent MSR vs HLB for linear alcohol ethoxylates in the presence of TCE. Apparent MSR values correspond to total surfactant addition of 10 g/L and were calculated using eq 1.

by others for these systems (CB, 1,2-DCB) under similar conditions when partitioning has not been taken into account (*9, 11*). It should be noted, however, that for sufficiently low-EO surfactants a dramatic decrease in solubilization capacity may be observed due to the formation of a separate surfactant/organic phase as a result of the relative hydrophobicity of the surfactant. Selected experiments conducted with $C_{12}E_6$ produced a surfactant/organic phase which could be centrifuged out of solution, leaving very little surfactant or organic in the supernatant. This phenomenon is consistent with the measurements of Saito and Shinoda (*34*), who found that surfactant cloud point temperature was decreased by solubilization, with the effect most pronounced for relatively hydrophobic surfactants with few EO units.

Figure 6 compares MSR vs HLB curves generated from the same samples, both neglecting and accounting for the partitioning process (apparent MSR and actual MSR, respectively). The apparent MSR was calculated based only on the solubilization achieved at a total surfactant concentration of 10 g/L for each surfactant/TCE system. When partitioning is taken into account, no maximum MSR is observed.

However, when partitioning is neglected, an apparent MSR maximum is observed. The maximum in the apparent MSR curve is an artifact of neglecting surfactant losses due to partitioning. Because the total amount of surfactant partitioning depends on the amount of NAPL present, the position of the maximum will also depend on the amount of NAPL present. When greater amounts of NAPL are present, partitioning losses of low-EO surfactants (which partition to a greater extent) will be increased, and position of the apparent MSR maximum will shift to higher HLBs.

The dependency of the maximum on the NAPL/water ratio is illustrated in Figure 7, which shows apparent MSR (eq 1) vs HLB for a 0.01 M surfactant initial concentration and 1,2-DCB/water ratios of 1:20, 1:40, and 1:200. The 0.01 M surfactant initial concentration and 1:40 condition were chosen to mimic that of Diallo et al. (*9*). In the 1:20 NAPL/water ratio curve where the most 1,2-DCB is present, the apparent MSR maximum occurs at an HLB greater than 17, while in the 1:40 NAPL/water ratio curve, the maximum MSR occurs at an HLB near 15. No visible apparent MSR maximum occurs in the 1:200 NAPL/water ratio curve, which is similar
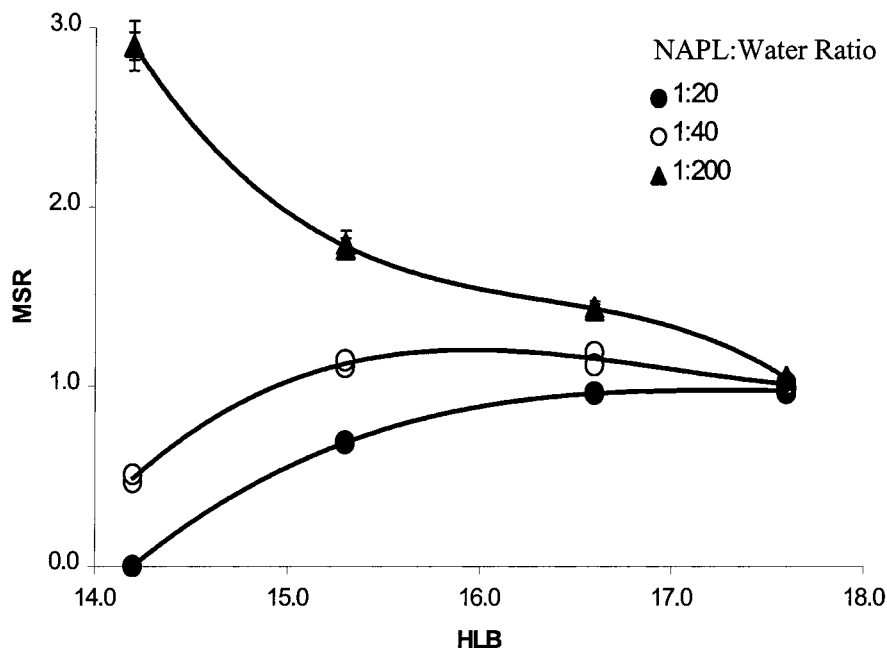
FIGURE 7. Apparent MSR (eq 1) vs HLB for linear alcohol ethoxylate surfactants in the presence of 1,2-DCB at three phase volume ratios. Total surfactant concentration is 0.01 M for all data points.

to the plot of actual MSR vs HLB in Figure 5 indicating that losses are not very significant when relatively little NAPL is present relative to the water volume.

Implications for Aquifer Remediation. The work presented here demonstrates that partitioning of surfactant into nonaqueous phase liquid contaminants may be significant for some contaminant and surfactant combinations. As a result, surfactant partitioning should be considered while selecting a surfactant for a particular remediation application to minimize surfactant losses due to partitioning. Partitioning may greatly reduce surfactant recovery in post-groundwater-extraction recycling operations (*18*). In addition, it is apparent that neglecting surfactant partitioning behavior can produce anomalous observations of surfactant solubilization capacity, causing the solubilization capacity of a surfactant that partitions into a NAPL to appear lower than its actual value. If this effect is not considered when surfactants are being screened for a remediation operation, it is possible that a sub-optimum surfactant may be selected over a more efficient surfactant that partitions into the NAPL contaminant of interest. Because the extent of partitioning is dependent on the amount of NAPL volume present, the optimum surfactant for remediating contaminated sites with relatively small amounts of contamination may actually be a surfactant which can partition to a significant extent, but which has a high solubilization capacity for the contaminant of interest. For highly contaminated sites, considering surfactant partitioning behavior will be essential for accurately modeling surfactant movement and the solubilization process.

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