Environ. Sci. Technol. **2000**, *34,* 672−679

Sorption of Nonionic Surfactant Oligomers to Sediment and PCE DNAPL: Effects on PCE Distribution between Water and Sediment

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Introduction of surfactant mixtures to the subsurface for the purpose of surfactant-enhanced aquifer remediation requires consideration of the effects of surfactant sorption to sediment and nonaqueous phase liquids. These effects include alteration of the solubilizing properties of the surfactant mixture and alteration of the sorption properties of the stationary phase. Sorption of octylphenol ethoxylate (EO) surfactant oligomers to a low organic carbon content (f_{oc}) aquifer sediment and to dense nonaqueous phase liquid (DNAPL) consisting of tetrachloroethene (PCE) was examined in batch experiments. At aqueous surfactant concentrations far below the critical micelle concentration (CMC) of the mixture, sorption to sediment was characterized by an initial steep isotherm for both high and low EO content oligomers, with somewhat greater uptake of high EO content oligomers. This stage of sorption resulted in mild increases in the equilibrium constant, $K_{d,PCE}$, for distribution of PCE between solution (including surfactant) and sediment (including sorbed surfactant). As the aqueous surfactant concentration increased, surface aggregation of low EO content oligomers on the sediment commenced, and a dramatic increase in $K_{d,PCE}$ was observed. At aqueous surfactant concentrations increasing above the CMC, the formation of solution micelles caused the sorbed surfactant concentrations to plateau and then decrease. This decrease in sorbed surfactant, along with competition by micelles for contaminant, likely contributed to the observed rapid decrease in $K_{d,PCE}$ toward zero. Surfactant sorption to PCE DNAPL was greater relative to sediment by 1−2 orders of magnitude, with much greater uptake of the low EO content oligomers. Sorption of all but the lowest EO content oligomers to the PCE DNAPL was terminated by micellization.

Introduction

The relatively slow dissolution of nonaqueous phase liquid (NAPL) contaminants into groundwater has prompted investigation of nonionic and other surfactants as potential solubilizing agents for enhanced dissolution and removal of NAPL from the subsurface. A major concern in the choice of a solubilizing agent, in addition to its solubilization capacity for the contaminant, is its tendency to sorb to aquifer sediment.

Characterization of the sorption behavior of nonionic surfactants is complicated by the fact that nonionic surfactants are Poisson-distributed mixtures of oligomers of varying chain lengths, such that certain oligomers may undergo stronger sorption to aquifer materials, and these oligomers may or may not be important in solubilization. Above a critical aqueous surfactant concentration, called the critical micelle concentration (CMC), surfactant monomers aggregate in solution to form entities comprised of a hydrophobic core and a hydrophilic shell. These micelles are responsible for the ability of surfactants to solubilize hydrophobic solutes, and they are conceptualized as a phase that is separate from, but in thermodynamic equilibrium with, surfactant monomers in solution (*1*). In the presence of sediment, or other solid sorbents, sorption of surfactant as monomers may occur at low aqueous surfactant concentrations, whereas at higher surfactant concentrations, surfactants may form aggregates at the solid surface, and these surface aggregates have physical properties similar to solution micelles (*2*). These sorbed monomers and surfactant aggregates are considered to exist in thermodynamic equilibrium with solution monomers, such that solution micelles and surface aggregates compete for surfactant monomers added to the system (*3*).

Studies of surfactant sorption to sediment have shown that at nonionic surfactant concentrations well below the CMC of the mixture, the relatively polar oligomers dominate the sorbed population, whereas sorption of relatively nonpolar oligomers dominates at surfactant concentrations at or above the CMC (*4*−*11*). These results also indicate that preferential uptake of less polar or more polar oligomers may depend on the nature (e.g. f_{oc}) of the sediment as well as the oligomer distribution within the surfactant mixture.

Studies examining solubilization of nonaqueous phase liquids (NAPL) by nonionic surfactant mixtures have shown that uptake of nonionic surfactant by NAPL may be dramatic and that lack of accounting for this uptake may result in incorrect values for the solubilization constant (*12, 13*). At the field scale, loss of nonionic surfactant to residual NAPL may be highly detrimental to cleanup efforts in terms of both cost and efficiency of remediation.

It has also been recently shown that surfactant sorption to sediment not only decreases the aqueous surfactant concentration, thereby reducing surfactant solubilizing capacity, but also increases the proportion of contaminant (e.g. dissolved NAPL) that is bound to the stationary phase (*14*). As a result, the equilibrium constant for distribution of contaminant between mobile (dissolved and micellar) and stationary (sediment and sediment-sorbed surfactant) phases, K_d, may actually increase in the presence of surfactant, for aqueous surfactant concentrations below the surfactant CMC (*14*). At aqueous surfactant concentrations above the CMC, contaminant partitioning to micelles has been shown to dramatically decrease the contaminant K_d (*14*). An apparent lag between the observed increase in contaminant K_d and the onset of surfactant sorption was not discussed by the authors (*14*), although the lag suggests that increases in contaminant K_d may depend on the type (more polar versus less polar) and conformation (monomer versus surface aggregate) of sorbed surfactant, rather than simply on the onset of bulk surfactant sorption.

Nonionic surfactant sorption to natural low organic carbon aquifer sediment has been examined in only a few studies, hence examination of this interaction was one goal

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10.1021/es990886a CCC: $19.00
Published on Web 01/08/2000

TABLE 1. Chemical and Physical Properties of Surfactants and Model Contaminant

name	MW[a]	average chemical structure[b]	CMC[c]	HLB[d]
Igepal CA-720	734.89	$C_8H_{17}-C_6H_5O-(CH_2CH_2O)_{11.7\pm0.3}OH$	0.25	14.6
Igepal CA-887	1527.76	$C_8H_{17}-C_6H_5O-(CH_2CH_2O)_{29.9\pm0.1}OH$	1.6	17.4
1:2 mixture	1096.10	$C_8H_{17}-C_6H_5O-(CH_2CH_2O)_{20.2\pm0.1}OH$	0.6	N/A
tetrachloroethylene	165.83	$Cl_2C{=}CCl_2$		

[a] Average molecular weight of surfactant mixture, g mol^{-1}. [b] From experimentally determined EO average ($\pm$ represents SD of data). [c] g L^{-1}, experimentally determined by drop weight method (*16*). [d] Hydrophile−lipophile balance data from manufacturer (N/A represents data not available).

of this study. Another goal of this study was to compare surfactant sorption by dense NAPL (DNAPL) to surfactant sorption by a natural low organic carbon content aquifer sediment. This comparison shows the relative impact of these two sorbents on the oligomer distribution within a nonionic surfactant mixture. Tetrachloroethene (PCE), a common chlorinated solvent, was chosen to represent the DNAPL since it is a common DNAPL constituent. The sorption of individual oligomers within the surfactant mixture was also monitored in a three-component system containing surfactant, solubilized PCE, and sediment in order to determine whether increases in the equilibrium constant describing distribution of PCE between mobile (dissolved and micellar) and stationary (sediment and sediment-sorbed surfactant) phases, $K_{d,PCE}$, coincided with the onset of sorption of particular oligomers to, or particular surfactant conformations on, the sediment.

Methods

Materials. Octylphenol ethoxylate nonionic surfactant mixtures Igepal CA-620, CA-720, and CA-887, with experimentally determined average ethoxylate (EO) chain lengths of 7.1 $\pm$ 0.1, 11.7 $\pm$ 0.3, and 29.9 $\pm$ 0.2 EO units, respectively, were donated by Rhodia Inc., Cranbury, NJ. Purified octylphenol and octylphenol ethoxylate standards, with 1 and 3 EO units per molecule, were donated by Dr. Jennifer Field, Oregon State University. Alkylphenol ethoxylate surfactants are more toxic relative to other surfactants being considered as remediation agents (*15*). However, alkylphenol ethoxylates were used in this study due to relative ease of measurement and as representatives of other less toxic nonionic surfactants in terms of their solubilization and sorption behaviors. Reagent grade tetrachloroethylene (PCE) (99% pure, Aldrich, Milwaukee, WI) was used as the model DNAPL. All chemicals were used as received from the manufacturer without further purification. Selected physical and chemical properties for the surfactants and model contaminant used in the experiments are found in Table 1. All experiments were conducted at controlled room temperature (22 °C).

Natural aquifer sediment quarried from Pleistocene lacustrine deposits was obtained from Monroc Incorporated (Salt Lake City, UT). The sediment was dry-sieved to remove fractions larger than 2 mm and smaller than 106 μm. The sediment was also rinsed with Milli-Q (Millipore Corp., Bedford, MA) ultrapure water (18 MΩ) to further remove fines. The sediment surface area (3.273 $m^2\ g^{-1}$) was determined by N_2 BET multipoint analysis (Porous Materials, Inc., Ithaca, NY). The sediment organic carbon content (f_{oc} = 0.0033) was determined by total organic carbon analysis (American West Analytical Laboratories, Salt Lake City, UT). Petrographic microscopy indicated that the sediment was composed of approximately 80% quartz, 15% granite clasts, and 5% carbonate clasts. Iron oxide coatings were visible on the quartz grains.

Artificial groundwater (AGW) was used in all experiments and was prepared according to Scholl et al. (*17*) as follows: 1.5E-5 M KNO_3, 1.4E-4 M $MgSO_4{\cdot}7H_2O$, 7.0E-5 M $CaSO_4{\cdot}2H_2O$, 8.0E-5 M NaCl, 1.4E-5 M $NaHCO_3$, pH ~6.8, and ionic strength equal to 3.0E-3 M.

Surfactant Sorption to Sediment. Surfactant sorption to sediment was examined in 20 mL liquid scintillation vials (Fisher Scientific, Hampton, NH). Two layers of aluminum foil were placed over the vial openings prior to capping. Each vial contained 25 g of sediment and 14 mL of solution, yielding a solid concentration of 1785.7 g L^{-1}. A 1:2 by weight mixture of Igepal CA-720 and CA-887 was used at total surfactant concentrations ranging from 0.05 to 2.0 g L^{-1}. The samples were allowed to equilibrate by slow rotation (15 rpm) for 48 h on a lab rotator (Glas-Col Laboratory Products, Terra Haut, CA). Sample equilibration time (48 h) was determined in preliminary batch tests using 0.1, 1.0, and 2.0 g L^{-1} nominal (initial) surfactant concentrations sampled daily over a period of 5 days. After equilibration, the samples were centrifuged at 1500 rpm for 45 min using a Beckman Instruments (Fullerton, CA) Avanti 30 centrifuge to settle the fines before sampling. Some blank (sediment-free) samples were not centrifuged in order to compare results to centrifuged samples to determine possible effects of centrifugation on surfactant concentration in the supernatant, which were found to be negligible. Surfactant concentrations in the supernatant were analyzed as described below.

PCE Sorption to Sediment. Sorption of PCE to the sediment was examined using the same protocol (vials, foil cover, solids concentration, and numbers of blanks and replicates) as described above. Sample equilibration time was determined in preliminary batch tests with 95 and 190 mg L^{-1} dissolved PCE (50% and 100% normal water solubility) sampled daily over a period of 4 days. Blank (no sediment) samples were utilized to account for PCE sorption to container and PCE loss to headspace, both of which were determined to be negligible. Both blanks and samples with sediment were duplicated at all concentrations. Prior to sampling, the vials were centrifuged to settle the fines as described above. PCE concentrations in the supernatant were analyzed as described below.

Solubilization of, and Surfactant Sorption to, PCE DNAPL. PCE solubilization experiments were conducted in 50 mL sealed glass ampules (Wheaton Scientific Products, Millville, NJ). A 50:1 volume ratio of aqueous solution to nonaqueous PCE was used within a total volume of 51 mL. Headspace (~10 mL) in the sealed ampules was inconsequential in the presence of the PCE droplet. The same surfactant mixture and concentrations that were used in the surfactant sorption experiments were used in the solubilization experiments. The sealed glass ampules were equilibrated by rotation (20 rpm) for 100 h. Four replicates were used for each surfactant concentration (including zero surfactant). Sample equilibration time was determined by batch tests using 0.1, 1.0, and 2.0 g L^{-1} surfactant concentrations sampled daily over 7 days. Surfactant and PCE concentrations in the supernatant above the PCE droplet were analyzed as described below.

Surfactant and PCE Sorption to Sediment in a Three-Component Experiment. An aliquot of supernatant from each of the four replicate ampules in the PCE solubilization experiment was removed immediately following sampling for PCE and surfactant concentrations. These aliquots were transferred to four 20 mL scintillation vials, two of which contained 25 g sediment (yielding the same solids concentration as in the sediment sorption experiments). Aliquots (14 mL) were transferred to the vials containing sediment, whereas 24 mL aliquots were transferred to sediment-free vials in order to minimize headspace. The same protocol was used (vials, foil cover, solids concentration, and numbers

of blanks and replicates) as in the two-component surfactant sorption experiments described above. Samples were equilibrated with slow rotation (15 rpm) for 48 h, as determined from the above experiments. Samples were centrifuged as described above. Surfactant and PCE concentrations in the supernatant were analyzed as described below.

HPLC Analyses. Prior to analyses, aliquots (1 mL) of supernatant were removed from the reaction ampules or vials and were placed into 2 mL vials (screwtop with PTFE-lined septa) with 0.25 mL of methanol added to prevent surfactant sorption to the vial. Surfactant was analyzed using a Shimadzu Scientific Instruments (Columbia, MD) 10Avp HPLC system with a 70-vial autosampler, fluorescence detection, and CLASS-VP v.5 software. The analytical method utilized permitted underivatized aqueous injections and was modified from a method developed by Kibbey et al. (*18*). A flow gradient from 0.3 to 1.0 mL min^{-1} over a period of 35 min held at 1.0 mL min^{-1} for an additional 13 min, and a solvent gradient from 100% acetonitrile to 30% water/70% acetonitrile over a period of 48 min was utilized. Separations were carried out on a Supelco (Bellefonte, PA) Supelcosil LC-Si (5μm, 2.5 cm × 46 cm ID) with a Hypersil (Cheshire, UK) ODS C18 (*4 mm*) pre (guard)-column. Sample injections (8 μL) were analyzed using fluorescence detection (λ_{ex} = 202 nm, λ_{em} 311 nm). Due to the length of HPLC analysis, individual sample analyses were not replicated.

Chromatogram peak areas were related to surfactant concentration (M) using a response factor, RF, which varied over the duration of the analysis due to changes in flow rate, solvent fraction, and oligomer ethoxylation. RF was regressed against oligomer EO content (using EO chain length as a surrogate for the three variables described above) using data from analysis of pure octylphenol and octylphenol ethoxylates with 1 and 3 EO units per molecule as well as Igepal CA-620, CA-720, and CA-887. The surfactant solutions were mixed in borosilicate glass vials with 20% MeOH to prevent sorption to the vials. The observed linear decrease in RF with EO chain length was described using the following equation

$$RF_i = RF_{OP} - m \cdot i$$

where RF_i is the response factor for the individual oligomers, RF_{OP} is the response factor for pure octylphenol (determined to be 1.30×10^{11}), m is the slope relating the response factor to EO chain length, and i is the number of EO units in the oligomer (EO chain length). The experimentally determined value of m (1.64×10^9) was optimized by minimizing the sum of the squares of error between known surfactant concentrations and calculated surfactant concentrations (R^2 = 0.999) using the RF value.

GC Analyses. PCE concentrations were determined by gas chromatography (Shimadzu GC-17A, with FID detection) immediately after opening the ampule or vial (within 10 s) and capping the container with foil between subsequent (triplicate) analyses. The method used was modified from Fountain et al. (*19*) and utilized a stainless steel column (3 ft × 1/8th in.) packed with 1% AT-1000 on Graphpac-GB (Alltech Associates, Inc., Deerfield, IL), 225 °C injection port temperature, 200 °C column temperature, 300 °C detector temperature, and a flow rate of 40 mL min^{-1}. Aliquots (2 μL) were direct injected and required 2.25 min for analysis. A calibration curve was developed (R^2 = 0.999) using PCE standards in methanol over a linear calibration range of 0−1.0 g L^{-1} PCE.

Data Analysis. Sorbed concentrations of PCE and surfactant were determined by the difference between averaged aqueous concentrations from samples with sediment and without sediment (blanks). Sorbed surfactant concentrations in the three-component experiments were determined by the difference in surfactant concentration between the sample with sediment and the supernatant from the two-component experiment (the solution which was added to the sediment in the three-component experiment). The average EO chain length of sorbed and solution oligomers was determined according to the methods of Kibbey and Hayes (*7*). The solubilizing capacity of the surfactant mixture was quantified using the molar solubilization ratio (MSR) (*20*). $K_{d,PCE}$, the equilibrium distribution constant, was calculated by dividing the concentration of PCE sorbed to the sediment and sorbed surfactant ($mg_{PCE}\ kg_{sed}^{-1}$) by the concentration of the PCE in the bulk solution (dissolved plus micellar) ($mg_{PCE}\ L_{solution}^{-1}$) in the three-component experiments.

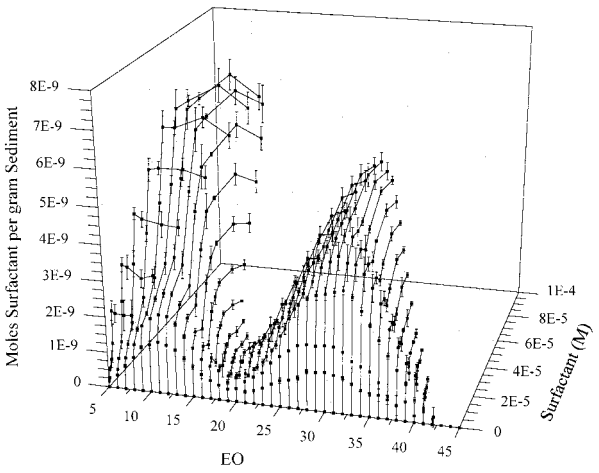

FIGURE 1. Individual surfactant oligomer isotherms for sorption to sediment in the two-component experiment for nominal bulk surfactant concentrations ranging from 0 to 2.0 g L^{-1}. Initial strong sorption is followed by surface aggregation (second steep rise) of surfactant monomers, particularly low EOs, on the sediment surface. Sorption ceases with micellization (isotherm slopes level and decrease).

Results

Surfactant Sorption to Sediment. A steep initial sorption isotherm was observed for all oligomers at low aqueous oligomer concentrations (Figures 1and 2a,b), with decreasing slope as the aqueous oligomer concentration increased. Greater uptake of high EO content oligomers was observed within the steep initial portion of the isotherms (Figure 1), as also shown by the solution EO average (Figure 2b), which was initially below that of the stock solution. The steep initial isotherm slope represents high-energy sorption sites on the sediment (*5*, *6*, *9*, *11*, *21*). The higher initial uptake of high EO content oligomers may suggest a polar character of the high-energy sorption sites. However, it has also been shown that hydrophobic moieties on sediment can increase the slope of the initial portion of the isotherm (*6*, *21*).

At intermediate aqueous oligomer concentrations, a second steep rise in sorbed concentration was observed, presumably representing sorption to a newly formed surface phase. The rise was steepest for the lowest EO content oligomers, and its slope decreased with increasing oligomer EO content (Figures 1 and 2). This rise started at lower aqueous concentrations for the low EO content oligomers relative to the high EO content oligomers (Figures 1 and 2). Since the oligomer concentrations differed from one another in the Poisson-distributed surfactant mixture, the isotherms would not show a simultaneous second steep rise (with respect to aqueous oligomer concentration) even if all oligomers were incorporated into this surface phase at the same mixture concentration. Examination of nominal (initial)

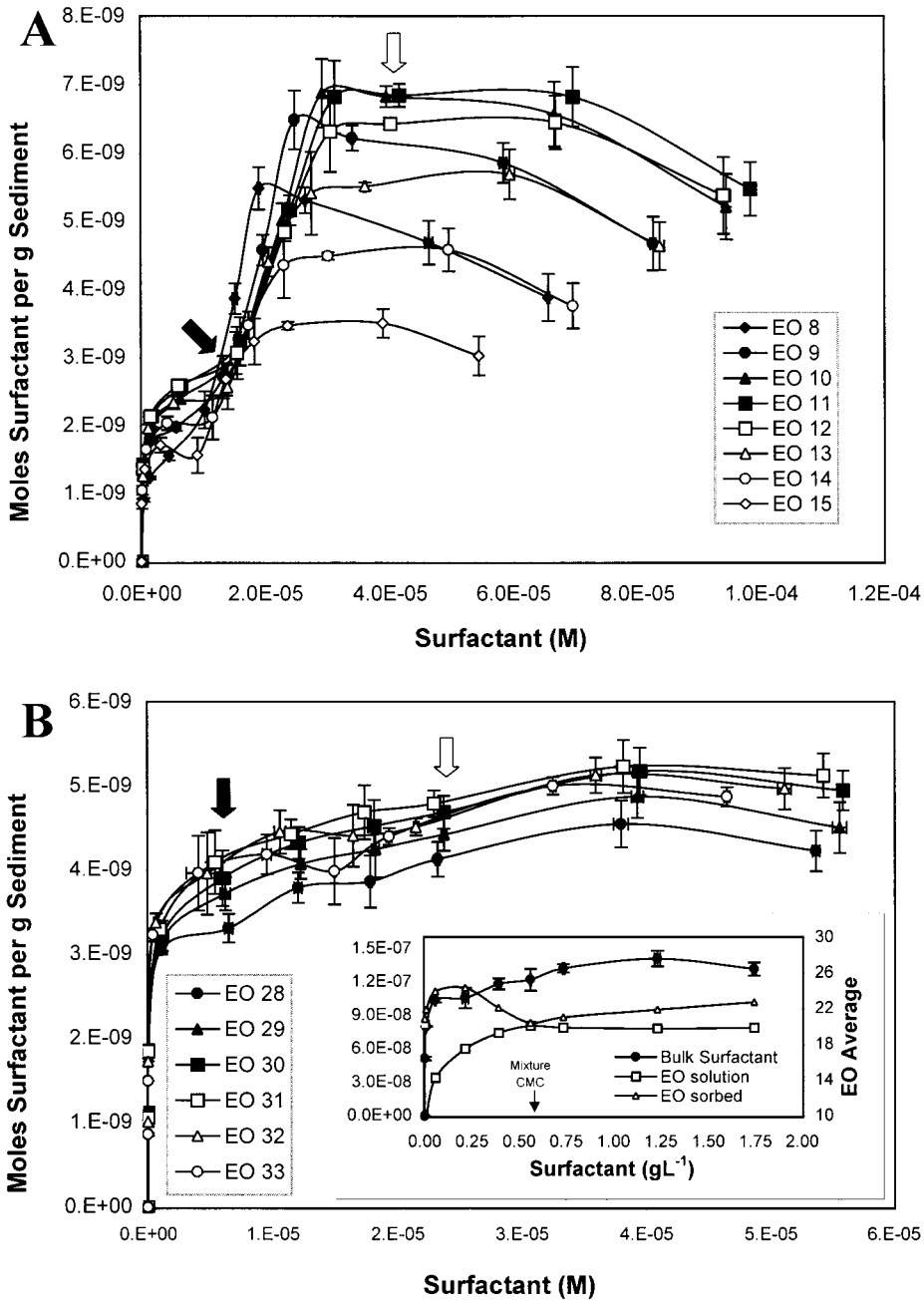

FIGURE 2. Individual surfactant oligomer isotherms for sorption to sediment in the two-component experiment. Data are represented in two dimensions to allow quantitative comparison of the sorption of low EO content oligomers (a) and high EO content oligomers (b). Bulk surfactant (total mixture) sorption to sediment (left ordinate axis) is shown in the inset (b) with sorbed and solution EO averages (right ordinate axis).

mixture concentrations shows that the low EO content oligomers were preferentially incorporated into this surface phase. For a 0.4 g L^{-1} nominal mixture concentration (represented by the 5th symbol from the lowest in each isotherm, as indicated by closed arrows in Figure 2a,b), only oligomers containing 20 EO units or less were incorporated into this surface phase (Figures 1 and 2). Oligomers containing 30 EO units or more were incorporated only above the 1.0 g L^{-1} nominal mixture concentration (the third symbol from the highest in each isotherm, as indicated by open arrows in Figure 2a,b). The sorbed EO average decreased from a maximum value during the second steep rise in sorption, also indicating that the low EO content oligomers were preferentially incorporated into this phase (Figure 2b). It appears that the second steep rise represents surface aggregation (*3*, *6*), since the surface phase showed the highest affinity (steepest isotherms) for, and preferential incorporation of, the lowest EO content oligomers, which would be least compatible with the aqueous phase and most likely to aggregate on the surface.

At higher aqueous surfactant concentrations, sorbed concentrations leveled, indicating cessation of sorption of the corresponding oligomer (Figures 1 and 2). As was observed in surface aggregation, cessation of sorption was initiated at lower bulk surfactant concentrations for the lower EO content oligomers. For a nominal mixture concentration of 0.8 g L^{-1} (the fourth symbol from the highest in each isotherm), the oligomers containing 14 EO units or less reached sorption plateaus. In contrast, oligomers containing 25 EO units or more did not reach sorption plateaus until the 1.5 g L^{-1} nominal mixture concentration (second symbol from highest in each isotherm) (Figures 1 and 2).

The sorption plateaus occurred at lower bulk concentrations for oligomers with lesser numbers of EO units. Since oligomers with lower numbers of EO units are known to form micelles at lower aqueous concentrations (*22*), it appears that incorporation of the oligomers into solution micelles resulted in the termination of sorption to the sediment, as has been previously observed by others (*2*, *5*, *23*−*25*). The sorbed EO average reached a minimum value upon micellization of low EO content oligomers (Figure 2b). Beyond this minimum, the sorbed EO average curve rose due to continued sorption of high EO content oligomers, which were not incorporated into solution micelles until higher mixture concentrations. The aqueous mixture concentration corresponding to the minimum in sorbed EO average was about 0.6 g L^{-1} (Figure 2b), matching the CMC determined for the stock mixture using surface tension measurements (Table 1), further indicating that micellization terminated the sorption of low EO oligomers to the sediment.

At the highest nominal mixture concentration (2 g L^{-1}), the sorbed concentrations decreased somewhat for the low EO content oligomers (Figures 1 and 2a). The observed decrease in sorbed concentration at the 2.0 g L^{-1} bulk surfactant concentration was replicated in all experiments and was statistically significant (Figure 2a).

Decreased sorption to sediment at high mixture concentrations has been observed by others (*26*) and has been explained by the enrichment of high-CMC oligomers in the monomer phase as the solution concentration increases beyond the CMC of the low-CMC oligomers. This explanation assumes that the high-CMC oligomers display a lower affinity for the sediment relative to the low-CMC oligomers. Although this assumption holds at the concentration range of concern, the model's simplification of oligomer sorption isotherms to a single affinity constant makes uncertain the applicability of this model to the work described here. The decrease in sorbed concentration at the highest mixture concentrations may result from the enhanced compatibility of the relatively hydrophobic low EO content oligomers with the micellar solution phase. Since only the low EO content oligomers experienced decreased sorption, the sorbed EO average increased during this stage of sorption.

The highest sorbed concentration for a given aqueous oligomer concentration was achieved by the oligomers that dominated the mixture (e.g. EOs 10−13 and 29−31) (Figures 1 and 2). This trend cannot be attributed to higher affinities of the dominant oligomers for the sediment, since one would expect higher affinities to trend either toward the nonpolar or polar ends of the spectrum rather than to intermediate values, let alone two of them. This result indicates that the differences in oligomer affinities for the sediment were less significant than their relative concentrations within the mixture.

Surfactant Sorption to PCE DNAPL. Surfactant loss to the PCE was highest for the low EO oligomers (Figures 3 and 4a) and resulted in NAPL-sorbed concentrations over 2 orders of magnitude greater than the corresponding sediment-sorbed concentrations. Sorbed concentrations and isotherm slopes decreased with increasing EO content of the oligomer, indicating that in contrast to sediment sorption, the differences in oligomer affinities for PCE DNAPL were more significant than differences in their respective concentrations within the mixture.

Isotherm plateaus indicated the onset of micellization of the associated oligomer in the aqueous phase. The isotherms for oligomers EO5 through EO7 did not plateau, even at the highest aqueous concentrations (Figure 3 and 4a), indicating that these low EO content oligomers continued to be incorporated into the PCE DNAPL in the presence of solution micelles. In contrast, sorption of low EO content oligomers to sediment (and surface aggregates) was reduced at the highest aqueous surfactant concentrations (Figure 1). These results indicate that high surfactant concentrations may yield reduced surfactant sorption to sediment but not to PCE DNAPL.

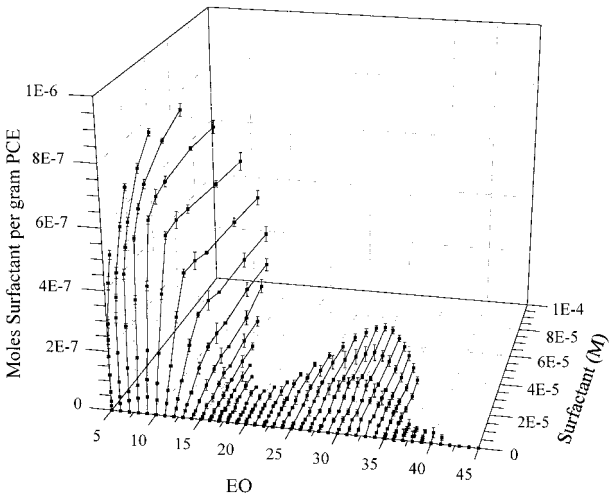

FIGURE 3. Individual surfactant oligomer isotherms for sorption to PCE DNAPL in the two-component experiment for nominal bulk surfactant concentrations ranging from 0 to 2.0 g L^{-1}.

For high EO content oligomers, the isotherms showed a continuous slow rise with aqueous oligomer concentration (Figure 3 and 4b), giving DNAPL-sorbed concentrations that were nearly an order of magnitude higher for PCE DNAPL than sediment. However, the total mass of high EO surfactant sorbed to the PCE DNAPL was quite small due to the relatively low PCE-solution ratio used in the study, resulting in scatter that obscured any indication of a sorption plateau, which presumably occurred upon incorporation of these oligomers into solution micelles at the highest mixture concentrations.

Micellization, as indicated by the plateaus in the low EO content oligomer isotherms (Figure 4a), began at an aqueous mixture concentration ∼0.6 g L^{-1} (Figure 4a), matching the value determined from surface tension measurements (Table 1), and from sediment sorption (Figure 2b). This indicates that the upward shift in EO average of the solution from 20.3 to 23.5 had negligible effect on the CMC of the mixture. The solution EO average (∼23) remained high above the sorbed EO average (∼9) indicating that even at the highest aqueous concentrations examined, insufficient high EO content oligomer sorption occurred to reverse the enrichment of low EO oligomers in the DNAPL (Figure 4b).

Solubilization of PCE. PCE solubilization by the surfactant mixture (Figure 4b) also started at an aqueous mixture concentration of 0.6 g L^{-1}, the mixture CMC value indicated by sorption experiments (Figures 2b and 4b) and surface tension measurements (Table 1). Slope linearity of the enhanced solubility curve indicated that the solubilizing capacity of the micellar solution changed negligibly as the mixture concentration increased and the solution EO average dropped from 23.5 to 21.5 (Figure 4b). An increasing enhanced solubility slope might be expected if relatively polar micelles result from higher solution EO averages, since polar micellar solutions show lower solubilization capacities for hydrophobic compounds such as PCE (*12*). However, the solution EO average may not reflect micelle polarity since preferential incorporation of low EO content oligomers into micelles may occur even at the low aqueous mixture concentrations that showed elevated EO averages (Figures 3 and 4).

The value of the molar solubilization ratio, MSR, for PCE solubilization by the 1:2 mixture was 0.887 ± 0.003. This value compares favorably to values ranging from 1.8 to 0.6 obtained for solubilization of PCE by other surfactants falling

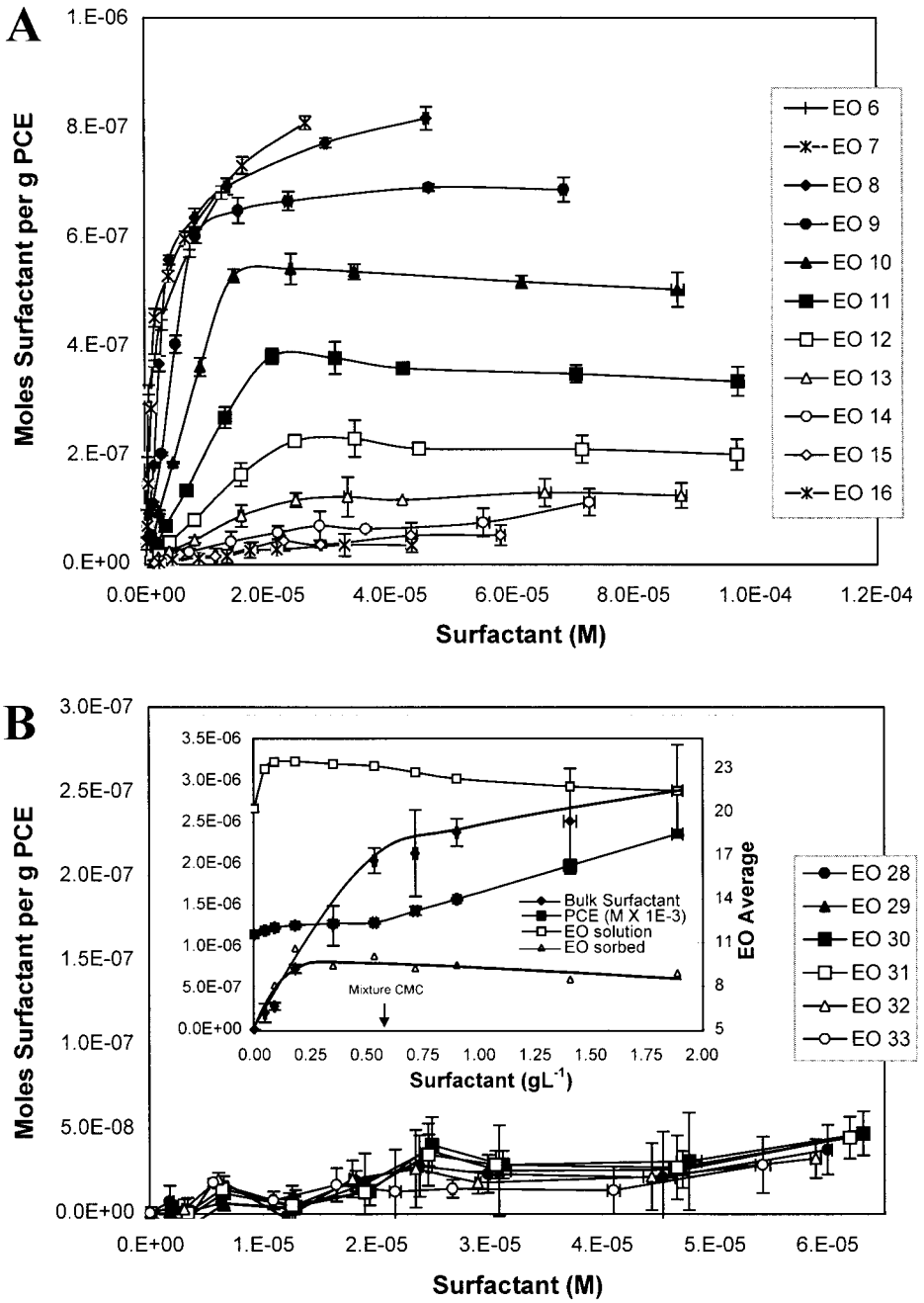

FIGURE 4. Individual surfactant oligomer isotherms for sorption to PCE DNAPL in the two-component experiment. Data are represented in two dimensions to allow quantitative comparison of the sorption of low EO content oligomers (a) and high EO content oligomers (b). Sorption to PCE DNAPL was 2 and 1 orders of magnitude greater than sorption to sediment for low and high EO oligomers, respectively. Bulk surfactant (total mixture) sorption to PCE DNAPL (left ordinate axis) is shown in the inset (b) with sorbed and solution EO averages (right ordinate axis), and PCE solubilization (left ordinate axis) by the surfactant mixture is shown in the inset (b).

in the hydrophile−lipophile (HLB) range between 14 and 18 (*12*, *27*).

PCE-Sediment Interaction. The isotherm for PCE sorption to the sediment (not shown) indicated a value of the equilibrium constant for distribution of PCE between sediment and water, $K_{d,PCE}$, of 0.034 ± 0.004 mL g^{-1}. This low value for K_d indicates mild interaction of dissolved PCE with this sediment, consistent with the low organic carbon content of the sediment ($f_{oc} = 0.0033$) and the low hydrophobicity of PCE, which has an octanol−water partition constant, K_{ow}, of $10^{2.88}$ (*28*).

Surfactant and PCE Sorption to Sediment in a Three-Component Experiment. Surfactant sorption to sediment in the three-component system (not shown) showed the same behavior that was observed in the two-component system (Figures 1 and 2), due to the low PCE:solution ratio (50:1) used in the solubilization study. The equilibrium constant, $K_{d,PCE}$, for distribution of PCE between solution (including aqueous surfactant) and sediment (including sediment-sorbed surfactant) increased from 0.034 mL g^{-1} (the value in the absence of surfactant) to 0.14 mL g^{-1} (a 4-fold increase) upon surfactant addition to the system (Figure 5). A maximum value was reached as the mixture concentration reached its CMC (0.6 g L^{-1}). As the surfactant concentration increased beyond the CMC, $K_{d,PCE}$ decreased dramatically toward zero.

This study corroborates the work of Ko et al. (*14*) who examined sorption of two hydrophobic organic contaminants (naphthalene and phenanthrene) to sediment in the presence

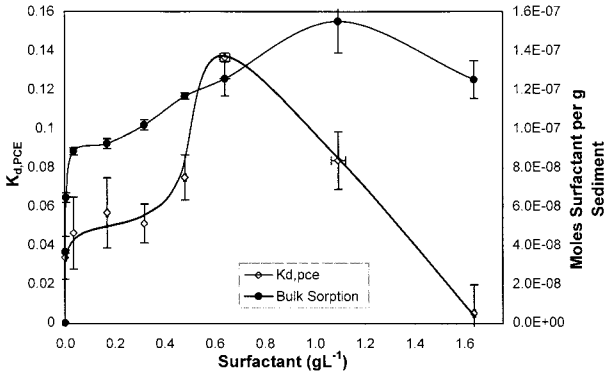

FIGURE 5. $K_{d,PCE}$ (equilibrium distribution constant between bulk sediment and bulk solution) and bulk surfactant sorption to sediment, in the three-component experiment. $K_{d,PCE}$ is initially weakly affected by monomer sorption but steeply rises with onset of surfactant surface aggregation. A rapid drop in $K_{d,PCE}$ toward zero occurs with micellization.

of two surfactants (sodium dodecyl sulfate and Tween-80) as a function of surfactant concentration. In the work of Ko et al. (*14*) as well as in this study, a lag was observed between the onset of surfactant sorption to sediment and significant increases in contaminant K_d (Figure 5). Comparison of Figures 1, 2, and 5 indicates that the significant increase in $K_{d,PCE}$ was associated with the onset of surfactant surface aggregation, rather than the onset of surfactant sorption in general. Prior to surface aggregation, the sorption of oligomers to the sediment surface had little effect on $K_{d,PCE}$, corroborating the suggestion that surfactant sorption at low aqueous surfactant concentrations is largely in the form of monomers (*7*, *29*). It has been observed that the sorption capacity of sorbed surfactant for a particular hydrophobic solute may exceed that of micellar surfactant from the same mixture (*14*). This may be attributed to the initial incorporation of primarily low EO content oligomers into surface aggregates (Figure 1), since micellar solutions of lower EO content oligomers yield greater solubilization of hydrophobic compounds relative to micellar solutions of higher EO content oligomers (*12*). Ko et al. (*14*) also observed that the sorption capacity of sorbed surfactant for a particular hydrophobic compound decreased with increased sorbed concentration of the surfactant. Our work indicates that this may be due to increased polarity of the surface aggregate upon incorporation of higher EO content oligomers as the aqueous surfactant concentration is increased. The rapid decrease in $K_{d,PCE}$ toward zero upon micellization in the aqueous phase may be attributed largely to competition between micelles and surface aggregates for the solute, but the decrease may also be in part due to decreased surface aggregation upon micellization in the solution (Figure 1). Although our results closely resemble those of Ko et al. (*14*) for sodium dodecyl sulfate, it is interesting to note that in the case of Tween-80, Ko et al. (*14*) observed the most dramatic increase in contaminant K_d after aqueous Tween-80 concentrations had increased beyond the CMC. A decrease in contaminant K_d below the initial value (in the absence of surfactant) was not observed even at aqueous Tween-80 concentrations over 2 orders of magnitude above the CMC. Apparently sorption of Tween-80 to sediment continued well beyond the CMC of the mixture, as may be expected for some surfactant mixtures (*26*).

This work corroborates previous observations regarding the dominant type (polar versus nonpolar) and conformation (monomer versus surface aggregate) of surfactant sorbed to low f_{oc} aquifer sediment with increasing aqueous mixture concentration. This work also showed that DNAPL can be expected to have a much greater impact than low f_{oc} sediment on loss of both polar and nonpolar oligomers from solution, with greater loss of the nonpolar oligomers. High aqueous mixture concentrations were shown to decrease surfactant loss to sediment but not to DNAPL. Sorption of nonpolar oligomers to DNAPL continued despite micellization. Significant rises in $K_{d,PCE}$ were shown to coincide with surface aggregation rather than with the onset of bulk surfactant sorption, and it was speculated that decreased surfactant sorption at high aqueous mixture concentrations contributed, along with competition for contaminant by micelles, to decreases in contaminant K_d. The significance of increased contaminant K_d at the scale of a contaminated site depends on the ability to flush super-CMC surfactant concentrations through the entirety of the site.

Acknowledgments

The authors thank Dr. Jennifer Field for supplying purified alkylphenol ethoxylate standards for calibration and for helpful conversations during the course of this work. The authors would also like to thank Dr. Tohren C. G. Kibbey for many helpful discussions. Thanks are also extended to Eila Burr, Applied Research Associates, for assistance with analytical instrumentation, and Rebecca Kessler for sediment characterization. This research was supported by a grant from the United States Environmental Protection Agency, Grant R826650-01, to Dr. William P. Johnson. This work was also partially supported by the Air Force Research Laboratory Summer Faculty Program at Tyndall Air Force Base, FL. Although the research described in this article has been funded by the United States Environmental Protection Agency, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

Literature Cited

(1) Harwell, J. H.; Helfferich, F. G.; Schechter, R. S. *AIChE J.* **1982**, *28*, 448−459.
(2) Levitz, P.; Van Damme, H.; Keravis, D. *J. Phys. Chem.* **1984**, *88*, 2228−2235.
(3) Harwell, J. H.; Schechter, R. S.; Wade, W. H. *AIChE J.* **1985**, *31*, 415−427.
(4) Kibbey, T. C. G.; Hayes, K. F. *J. Contam. Hydrol.* **2000**, *41*, 1−22.
(5) Kibbey, T. C. G.; Hayes, K. F. *J. Colloid Interface Sci.* **1998a**, *197*, 198−209.
(6) Kibbey, T. C. G.; Hayes, K. F. *J. Colloid Interface Sci.* **1998b**, *197*, 210−220.
(7) Kibbey, T. C. G.; Hayes, K. F. *Environ. Sci. Technol.* **1997**, *31*, 1171−1177.
(8) Yuan, C.; Jafvert, C. T. *J. Contam. Hydrol.* **1997**, *28*, 311−325.
(9) Brownawell, B. J.; Chen, H.; Zhang, W.; Westall, J. C. *Environ. Sci. Technol.* **1997**, *31*, 1735−1741.
(10) Desbene, P. L.; Portet, F.; Treiner, C. *J. Colloid Interface Sci.* **1997**, *190*, 350−356.
(11) Somasundaran, P.; Snell, E. D.; Xu, Q. *J. Colloid Interface Sci.* **1991**, *144*, 165−173.
(12) Zimmerman, J. B.; Kibbey, T. C. G.; Cowell, M. A.; Hayes, K. F. *Environ. Sci. Technol.* **1999**, *33*, 169−176.
(13) Bulter, E. C.; Hayes, K. F. *Water Res.* **1998**, *32*, 1345−1354.
(14) Ko, S.; Schlautman, M. A.; Carraway, E. R. *Environ. Sci. Technol.* **1998**, *32*, 2769−2775.
(15) Weinheimer, R. M.; Varineau, P. T. In *Nonionic Surfactants: Organic Chemistry*; van Os, N. M., Ed.; Surfactant Science Series, Marcel Dekker: New York, 1998; Vol. 72, pp 39−85.
(16) Adamson, A. W. *Physical Chemistry of Surfaces*, 4th ed; John Wiley and Sons: New York, 1982; pp 20−23.
(17) Scholl, M. A.; Mills, A. L.; Herman, J. S.; Hornberger, G. M. *J. Contam. Hydrol.* **1990**, *6*, 331−336.
(18) Kibbey T. C. G.; Yavaraski, T. P.; Hayes, K. F. *J. Chromatogr.* **1996**, *752*, 155−165.
(19) Fountain, J. C.; Starr, R. C.; Middleton, T.; Beikirch, M.; Taylor, C.; Hodge, D. *Ground Water* **1996**, *34*, 910−916.
(20) Edwards, D. A.; Luthy, R. G.; Liu, Z. L. *Environ. Sci. Technol.* **1991**, *25*, 127−133.

(21) Clint, J. H. *Surfactant Aggregation*; Chapman and Hall: New York, 1992; pp 192−220.
(22) Meguro, K.; Ueno, M.; Esumi, K. In *Nonionic Surfactants: Physical Chemistry*; Schick, M. J., Ed.; Surfactant Science Series, Marcel Dekker: New York, 1987; Vol. 23, pp 109−183.
(23) Cases, J. M.; Villieras, F. *Langmuir* **1992**, *8*, 1251−1264.
(24) Denoyel, R.; Rouquerol, J. *J. Colloid Interface Sci.* **1990**, *143*, 555−572.
(25) Gao, Y.; Du, J.; Gu, T. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 2671−2679.
(26) Trogus F. J.; Schechter, R. S.; Wade, W. H. *J. Colloid Interface Sci.* **1979**, *70*, 293−305.
(27) Diallo, M. S.; Abriola, L. M.; Weber, W. J. *Environ. Sci. Technol.* **1994**, *28*, 1829−1837.
(28) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; John Wiley & Sons: New York, 1993; p 622.
(29) West, C. C.; Harwell, J. H. *Environ. Sci. Technol.* **1992**, *26*, 2324−2330.

Received for review August 2, 1999. Revised manuscript received November 29, 1999. Accepted December 1, 1999.

ES990886A