Environ. Sci. Technol. **1998**, *32,* 2769−2775

Partitioning of Hydrophobic Organic Compounds to Sorbed Surfactants. 1. Experimental Studies

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Partitioning of two hydrophobic organic compounds (HOCs), phenanthrene and naphthalene, to surfactant micelles, kaolinite, and sorbed surfactants was studied to provide further insight on (1) the effectiveness of using sorbed surfactants to remove HOCs from water and (2) the feasibility of surfactant-enhanced remediation (SER) for contaminated subsurface systems. Sorbed surfactant partition coefficients, K_{ss}, showed a strong dependence on the surfactant sorption isotherms: at low sorbed surfactant levels K_{ss} values were at their highest and then decreased with increasing surfactant sorption densities. K_{ss} values for SDS were always larger than the corresponding micellar partition coefficient (K_{mic}) values; for Tween 80, however, K_{ss} values were higher than K_{mic} values only at the lower sorbed surfactant densities. HOC distributions between the immobile and mobile phases varied with surfactant dose because of the competition between sorbed and micellar surfactants for HOC partitioning: distribution coefficients increased initially with increasing surfactant concentrations before decreasing at higher doses. Overall results of this study demonstrate that surfactant sorption to the solid phase can lead to *increases* in HOC retardation when equilibrium conditions are applicable (e.g., slow advection rates). This effect is desirable when the treatment objective is to immobilize HOCs by removing them from water; however, the effect is undesirable in SER applications. Before any surfactant-enhanced mobilization/immobilization process is selected, appropriate consideration of surfactant sorption and HOC partitioning to immobile versus mobile phases pertinent to a specific subsurface system must be contemplated.

Introduction

The widespread occurrence of hydrophobic organic compounds (HOCs) in soils and groundwaters has led to intensive studies of the mobility and fate of these contaminants in subsurface environments and of their remediation potential. Depending on the particular site conditions, two complementary remediation alternatives are often considered: (1) HOC sorption to an immobile phase that subsequently decreases HOC mobility or (2) HOC partitioning to a mobile phase that results in an increase in HOC mobility (and apparent solubility) in water. For the first approach, use of organoclays (e.g., refs *1*−*4*) or organooxides (e.g., refs *5*−*7*) to remove HOCs from water has received much attention. For the second alternative, in-situ surfactant-enhanced remediation (SER) has been suggested as an economically and technically feasible remediation approach (e.g., refs *8*−*11*). An excellent review on the use of surfactants and subsurface remediation has been published recently (*12*).

Enhanced HOC solubility in surfactant systems generally has been quantified by a distribution coefficient that considers only HOC partitioning to the micelles that exist above the critical micelle concentration (cmc); while surfactant monomers have been shown to enhance HOC solubilities in certain systems (e.g., refs *7* and *8*), the effectiveness tends to be less than that of micelles and thus is often assumed to be negligible. Although surfactants can form a mobile micellar pseudophase that leads to the facilitated transport of solubilized HOCs, they also can be adsorbed by the solid matrix and thereby lead to HOC partitioning to immobile sorbed surfactants and, thus, enhanced HOC retardation.

A substantial amount of research on surfactant sorption to soils and minerals has been reported in the literature. For the present study, the work of Fuerstenau and Wakamatsu (*13*) is of particular interest. They investigated the sorption of sodium dodecyl sulfonate to alumina and found that the adsorption isotherms could be divided into four distinct regions. In region I, the surfactant adsorbed primarily as a result of favorable electrostatic forces between the positively charged mineral surface and the negatively charged surfactant, indicating a simple ion exchange of the anionic surfactant with anions in the double layer. Surfactant sorption in region I thus had little effect on the alumina ζ potential. In region II, as the surfactant concentration increased, adsorbed molecules began to associate in the Stern plane through their hydrocarbon chains to form hemimicelles; the slopes of the isotherms in this region increased abruptly and the ζ potential rapidly decreased as the surface charges became neutralized. In region III, further adsorption resulted from continued hydrophobic interactions between surfactant tails that occurred with increasing sorption density; these interactions were opposed by the now unfavorable electrostatic forces as evidenced by the reversal in ζ potential. Finally, when a complete bilayer covered the surface, no further adsorption was observed (region IV). Fuerstenau and Wakamatsu's results and interpretation have been supported by subsequent researchers, including Holsen et al. (*5*), who studied the adsorption of sodium dodecyl sulfate (SDS) on ferrihydrite as a function of pH and observed similar isotherm regions.

Partitioning of HOCs to sorbed surfactants (i.e., hemimicelles, admicelles) has been investigated in a few studies (e.g., refs *5*−*7* and *14*−*16*). Holsen et al. (*5*) examined the sorption of several HOCs on SDS-coated ferrihydrite and found that the ones with lowest solubility had the highest sorption. They also found a linear relationship between HOC sorption and the amount of SDS on the ferrihydrite, suggesting that the adsorbed SDS was primarily responsible for HOC sorption. Sun and Jaffé (*7*) investigated the partitioning of phenanthrene to dianionic monomers and micelles and to the same surfactants sorbed on alumina and found the sorbed surfactants to be generally 5−7 times more effective. Likewise, Nayyar et al. (*15*) reported partition coefficients for several organic contaminants to SDS sorbed on alumina that were higher in value than the corresponding micellar partition coefficients. Similar experiments were performed by Sun et al. (*16*) to obtain partition coefficients for three chlorinated HOCs to silt soils with a sorbed nonionic surfactant (Triton

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S0013-936X(97)01075-4 CCC: $15.00

TABLE 1. Selected Properties of the HOCs and Surfactants Used in This Study[a]

compound	formula	MW	solubility in distilled water	log K_{ow}	cmc[b]
phenanthrene	$C_{14}H_{10}$	178.23	7.2 μM	4.57	
naphthalene	$C_{10}H_8$	128.17	240 μM	3.36	
SDS	$C_{12}H_{25}SO_4Na$	288.38	complete		1.45 mM[c]
Tween 80	$C_{18}S_6E_{20}$[d]	1310	complete		9.92 μM[e]

[a] HOC data from ref *17*. Surfactant data from supplier unless noted. [b] 0.1 M NaCl. [c] Reference *32*. [d] Reference *33*. [e] Reference *10*.

X-100). They observed that the sorbed surfactant increased HOC partitioning relative to the untreated soils; however, when the aqueous surfactant concentration was greater than the cmc, the micelles competed against the sorbed surfactant for HOC partitioning and led to an overall decrease in HOC distribution coefficients.

Many previous studies of HOC partitioning to sorbed surfactants examined conditions favorable for the formation of surfactant bilayers resulting from high adsorption densities. In these studies, a single HOC sorbed surfactant partition coefficient was often observed. However, for many expected surfactant remediation applications, a surfactant solution would likely be pumped into or near the contaminated subsurface environment, and thus aqueous surfactant concentrations would vary spatially and temporally from zero to the applied concentration. Also, because soil−surfactant and surfactant−surfactant interactions lead to highly nonlinear sorption isotherms, the transport of surfactant monomers and micelles would exhibit very complex behavior. Correspondingly, the HOC distribution between immobile and mobile phases would also be expected to show complex behavior depending on the surfactant mass in each phase. Therefore, a quantitative evaluation of any potential surfactant remediation approach must consider the distribution of surfactant and subsequent HOC partitioning to each phase to maximize efficiency and minimize remediation costs.

The objectives of this study were to (1) study the sorption characteristics of an anionic surfactant (SDS) and a nonionic surfactant (Tween 80) to kaolinite, a common soil mineral; (2) examine the partitioning of two related HOCs (phenanthrene and naphthalene) to the adsorbed surfactants within the context of the first objective; and (3) develop overall HOC distribution coefficients that consider sorbed surfactant amounts and the presence of micelles as a function of surfactant dose. Results from this investigation provide additional insight into the role that sorbed surfactant structure plays in HOC partitioning.

Experimental Section

Materials. Phenanthrene (Aldrich, 99.5+%), naphthalene (Aldrich, 99+%), SDS (Sigma, 99.5+%), and Tween 80 (Aldrich, no purity reported) were used as received; selected physicochemical properties for these compounds are shown in Table 1. Tween 80 (polyoxyethylene [20] sorbitan monooleate), a food-grade surfactant having both a low toxicity and a high potential for biodegradation, has been suggested as a good candidate for subsurface SER applications (*10*). Concentrated HOC stock solutions were prepared in HPLC-grade methanol and stored in the dark at 4 °C in amber borosilicate bottles to minimize photodegradation and/or volatilization. Fresh surfactant stock solutions were prepared monthly in 0.1 M NaCl and stored in the dark at room temperature. Kaolinite, a nonswelling 1:1 layer phyllosilicate clay generally formed from the weathering of granitic rocks and a common constituent of many soils, was used as received from Sigma. The BET specific surface area (Quantasorb Jr., Quantachrome Co.) of duplicate kaolinite samples was 14.3 ± 0.2 m^2/g. All other reagents were of analytical grade or better and were used without further treatment.

Analytical Methods. Aqueous phenanthrene and naphthalene concentrations were quantified by fluorescence (PTI, Inc.) at the excitation/emission wavelengths of 250/364 and 278/322 nm, respectively; slits were set for bandwidths of 4 and 0.5 nm on the excitation and emission sides, respectively. No attempts were made to control oxygen levels. Absorbance measurements (HP 8452A) were also made at the above wavelengths. Aqueous SDS and Tween 80 concentrations were quantified by total organic carbon (TOC) analysis (Shimadzu 5050) and UV absorbance ($\lambda = 234$ nm), respectively. All analytical determinations utilized standard external calibration curves over their linear response regions and were made well above the instrumental and method detection limits. Relative precisions of 1 and 3% were routinely obtained for absorbance/fluorescence and TOC measurements, respectively.

Micellar Solubilization of HOCs. Fluorescence techniques were used to determine surfactant cmc values and micellar partition coefficients (K_{mic}) at pH 4 in 0.1 M NaCl solutions. These techniques monitor changes in fluorescence that result from alterations in the microenvironment (e.g., polarity, viscosity) around a fluorescence probe (e.g., refs *18*−*20*). In addition to their high precision and sensitivity, fluorescence techniques have the advantage of being useful at low solute concentrations. For example, partition coefficients as a function of solute concentration can be determined below solute solubility, whereas other techniques such as enhanced solubility methods work only above the "true" aqueous saturation limit. The interested reader should consult the references cited above; additional details on the specific techniques used here are presented in the Supporting Information to this paper. In addition to using fluorescence to determine K_{mic} values at different concentrations below aqueous HOC solubility limits, we also conducted solubility enhancement experiments to compare K_{mic} values obtained at saturation conditions. General procedures for obtaining molar solubilization ratios and their corresponding K_{mic} values using solubility enhancement were adapted from Diallo et al. (*21*) and Nayyar et al. (*15*).

Surfactant Sorption on Kaolinite. Batch experiments were conducted in triplicate to determine surfactant sorption rates and equilibrium isotherms using centrifuge tubes with Teflon-lined screw caps (Corex, 25 mL). Solid-to-water mass ratios (r_{sw}) of 1:10 were generally used for both surfactants. Tubes containing weighed amounts of kaolinite were filled with 25 mL of a 0.1 M NaCl solution of pH 4.6. Surfactant stock solutions were then added such that the concentration ranged from zero to well above the cmc (i.e., 10 and 7.6 mM for SDS and Tween 80, respectively). The samples were placed on an end-over-end tumbler for 24 h to equilibrate; preliminary rate studies showed this time to be adequate for equilibration (see Supporting Information). The solids were separated from aqueous solution by centrifugation at 7000 rpm for 30 min, and aliquots (4 mL) of the supernatant were taken for analysis. Sorbed surfactant concentrations in the solid phase (S_{sorb}, μmol/g) were calculated by mass balance from the aqueous concentrations (S_{surf}, mM) after dilution factors and system losses had been accounted for.

HOC Partitioning to Sorbed Surfactants. Equilibrium experiments were conducted in triplicate using centrifuge tubes (Corex, 25 mL) with Teflon-lined caps having lead foil faces. Tubes containing kaolinite were filled with a 0.1 M NaCl solution followed by the addition of surfactant stock solutions. The same amount of surfactant used in the surfactant sorption tests was added, and the pH was adjusted such that identical conditions were maintained. The samples were placed on a tumbler for 24 h to achieve surfactant sorption equilibrium. The HOCs were then added in an appropriate amount such that the initial phenanthrene and naphthalene concentrations were 4.49 and 78 μM, respectively. The samples were mixed on an end-over-end tumbler for 3 days and then centrifuged at 7000 rpm for 30 min to separate the aqueous and solid phases; preliminary rate studies (Supporting Information) showed equilibration was complete within this time period. HOC concentrations in aliquots (3 mL) taken from the supernatant were determined by fluorescence and absorbance using external standards in appropriate surfactant solutions. HOC amounts partitioned to the sorbed surfactants were calculated by mass balance. In addition to the fixed HOC concentration experiments described above (i.e., various surfactant doses), varying HOC concentration experiments were conducted (i.e., fixed surfactant dose) to determine the linearity of sorption isotherms for various sorbed surfactant concentrations and to test the reliability of the results obtained by using only one HOC concentration as a function of multiple surfactant concentrations.

Results and Discussion

Micellar Solubilization of HOCs. K_{mic} values for phenanthrene and naphthalene below their aqueous solubility limits were determined from the equation

$$F_{\mathrm{t}} = \frac{F_{\mathrm{w}} + F_{\mathrm{mic}}K_{\mathrm{mic}}(S_{\mathrm{surf}} - \mathrm{cmc})}{1 + K_{\mathrm{mic}}(S_{\mathrm{surf}} - \mathrm{cmc})} \qquad (1)$$

where S_{surf} is the total aqueous surfactant concentration and F_{t}, F_{w}, and F_{mic} are the fluorescence intensities per unit HOC concentration in the total system, aqueous phase, and micellar phase, respectively; derivation of eq 1 is shown in the Supporting Information. cmc values for SDS and Tween 80 in 0.1 M NaCl were determined to be 1.35 mM and 9.16 μM, respectively (see Supporting Information). Using these values, phenanthrene and naphthalene partition coefficients were then determined by nonlinear least-squares fitting of eq 1 to the experimental measurements for F_{t} (Figure 1; Table 2); K_{mic} values obtained by this method were similar to those obtained from the linearized (i.e., inverse) form of eq 1 that is commonly used for the determination of micellar partition coefficients (*18, 20*).

General results show that the more hydrophobic compound, phenanthrene, has a larger partition coefficient than naphthalene and that the nonionic surfactant (Tween 80) has larger K_{mic} values than does the anionic surfactant (SDS), agreeing with previous observations (8, *15, 22*). As can be seen in Table 2, K_{mic} values obtained by fluorescence generally decreased with increasing HOC concentration. Although the deviations were not large and some values had more relative uncertainty associated with them, the decrease appears to be significant at the 95% confidence level. The dependence of micellar partition coefficients on solute concentration has been critically reviewed by Dunaway et al. (*23*); for example, they reported a large dependence for alkane and highly polar amphiphilic compound partitioning with K_{mic} values increasing with increasing aqueous alkane mole fraction, whereas polar amphiphiles showed the opposite behavior. Dunaway et al. explained the phenomena using a two-site model whereby a solute partitions either to hydrophobic micelle cores or to the vicinity of hydrophilic headgroups, depending on the solute type. For aromatic compounds such as benzene, however, a more complicated behavior and less dependence on solute concentration were observed (*23*). For Tween 80, micellar partition coefficients obtained by the solubility enhancement method agreed qualitatively with the solute concentration trends observed for fluorescence-determined K_{mic} values. For SDS, however, the solubility enhancement values tended to deviate upward from the established trends, particularly for phenanthrene. Reasons for this apparent discrepancy are not presently known; studies to further investigate these general phenomena are ongoing.

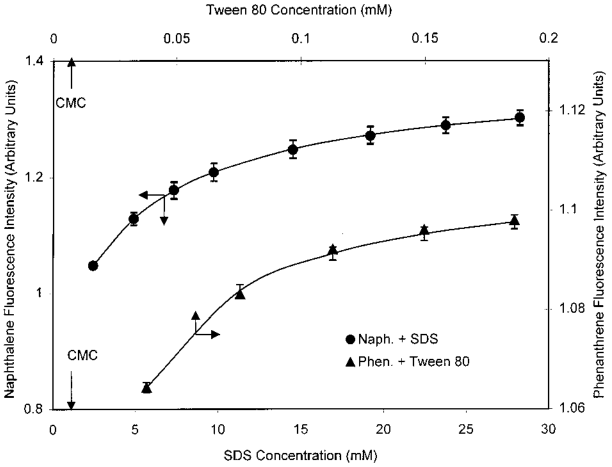

FIGURE 1. Determination of micellar partition coefficients for naphthalene and phenanthrene to SDS and Tween 80, respectively. Symbols are the experimental data and solid lines are the nonlinear regression fits of eq 1 to the data. Total HOC concentrations were 195 μM for naphthalene and 4.49 μM for phenanthrene.

Surfactant Sorption on Kaolinite. SDS sorption on kaolinite was relatively quick, requiring ~6 h to reach equilibrium (Supporting Information), and no significant differences were observed for r_{sw} values of 1:10 and 1:4 (Figure 2). SDS isotherms exhibited the characteristic S-shaped curves as previously reported (*5, 13, 24*); those studies generally used positively charged mineral surfaces (ferrihydrite or alumina), and the sorption isotherms clearly showed three or four distinct regions, indicative of the varying importance of sorption interactions between solid surfaces and surfactant molecules as described in the Introduction. Our results for SDS sorption on negatively charged kaolinite appear to show only three distinct regions. In region I, SDS sorption is low because of electrostatic repulsions between the anionic headgroup (sulfate ion) of SDS molecules and the kaolinite surface; any sorption that does occur in this region likely results from interactions between the hydrophobic SDS tails and the relatively hydrophobic basal plane and/or by anion exchange to the small number of positively charged sites that exist. In region II, the sharp rise in the isotherm indicates increasing associations between SDS molecules at the surface, presumably through lateral interactions of their hydrophobic tails, and the formation of hemimicelles and/or admicelles (*25*). The sorption plateau that is observed in region III is generally thought to correspond to either an increase in electrostatic repulsion between the anionic headgroups, complete surface coverage, and/or the attainment of a constant surfactant monomer concentration in the aqueous phase; it is noteworthy that the sorption of SDS begins to level out near its cmc but that the isotherm becomes flat at ~40 μmol/g only above the cmc.

Similarly to SDS, Tween 80 sorption also showed a high degree of nonlinearity and an S-shaped curve that plateaued

TABLE 2. HOC Partition Coefficients to Surfactant Micelles (K_{mic}) and Sorbed Surfactants (K_{ss})[a]

		SDS						Tween 80					
HOC	C_t (μM)	K_{mic}[b] (M^{-1})	R^2	N[c]	K_{ss}[d] (M^{-1})	R^2	N	K_{mic}[b] (M^{-1})	R^2	N	K_{ss}[d] (M^{-1})	R^2	N
phenanthrene	1.68	2693 ± 42	0.993	15	nd[e]			63495 ± 1982	0.999	15	nd		
	2.81	2282 ± 610	0.998	15	nd			55011 ± 1337	0.996	15	nd		
	4.49	1635 ± 72	0.998	15	13804 ± 621	0.990	27	51507 ± 2810	0.999	15	58606 ± 384	0.971	30
	6.73	3467 ± 156[f]	0.998	27	nd			35481 ± 807[f]	0.999	15	nd		
naphthalene	39	381 ± 5.1	0.999	24	nd			nd			nd		
	117	315 ± 22	0.998	24	525 ± 24[g]	0.959	27	2754 ± 408	0.996	18	8323 ± 579[g]	0.960	30
	195	152 ± 27	0.999	24	nd			nd			nd		
	241	245 ± 5.1[f]	0.998	24	nd			2239 ± 289[f]	0.986	15	nd		

[a] From experiments using fixed HOC concentrations (C_t) and varying surfactant concentrations. Values are ± SD. Ionic strength = 0.1 M NaCl and pH 4.0 (K_{mic}) or 4.6 (K_{ss}). [b] Determined by nonlinear regression of eq 1 except as noted. [c] N, number of data points. [d] Determined by nonlinear regression of eq 2. [e] nd, Not determined. [f] Obtained by linear regression of solubility enhancement data. [g] Naphthalene concentration was 78 μM.

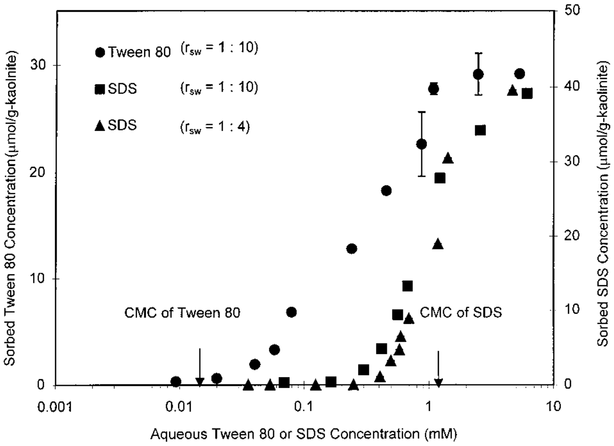

FIGURE 2. Surfactant sorption isotherms on kaolinite (pH 4.6, IS = 0.1 M). Error bars for some data points are smaller than the symbols. Kaolinite to water mass ratios (r_{sw}) were 1:10 (SDS, Tween 80) or 1:4 (SDS).

at ~29 μmol/g; however, most of the Tween 80 sorption occurred above the cmc (Figure 2). This latter observation is in agreement with some previous studies (e.g., refs *10*, *26*, and *27*) that found nonionic surfactant sorption occurring above the cmc but contrasts with other studies (e.g., refs *28* and *29*) that found the sorption of nonionic surfactants to plateau near their cmc values. It generally has been thought that surfactant sorption should reach a limiting maximum value at the cmc if the sorbing species are surfactant monomers because the concentration of monomers is constant above the cmc. Although no satisfactory explanation for the contrasting observations above is yet available, a comparison of the quantity of native organic matter present in the sorbents is noteworthy: those studies using sorbents with relatively low organic carbon mass fractions ($f_{oc} < 0.06\%$, refs *10* and *26* and the present study) observed nonionic surfactant sorption above the cmc, whereas the studies using sorbents with much larger amounts of native organic matter ($0.76\% < f_{oc} < 3.04\%$, refs *28* and *29*) did not.

HOC Partitioning to Sorbed Surfactants. HOC partitioning to sorbed surfactants reached equilibrium within ~48 h (Supporting Information). Figure 3 shows phenanthrene and naphthalene sorption isotherms to kaolinite covered with various levels of sorbed surfactant; these levels of surfactant coverage correspond to the different regions existing in the surfactant sorption isotherms as discussed earlier (Figure 2). The linearity of each HOC isotherm was evaluated using Freundlich and linear sorption models. It is obvious from Figure 3 and Table 3 that HOC partitioning to kaolinite with (i.e., K_{ss}) and without (i.e., K_{min}) adsorbed surfactants resulted in linear or nearly linear isotherms; for our particular systems, Freundlich n values ranged from 0.93 to 1.08 for phenanthrene and from 1.03 to 1.12 for naphthalene sorption to kaolinite surfaces covered with sorbed SDS or Tween 80. As the amount of surfactant adsorbed on the kaolinite surface increased, the sorption of phenanthrene and naphthalene to the solid phase also increased. However, when normalized by the amount of sorbed surfactant present, K_{ss} values decreased with increasing sorbed surfactant amounts (Table 3).

The effectiveness of a treatment/remediation scheme utilizing surfactants will depend on the distribution of an HOC between immobile phases (e.g., HOC sorbed to aquifer solids) and mobile phases (e.g., water and micelles), which is commonly quantified by a distribution coefficient (K_D). Phenanthrene and naphthalene partitioning between immobile and mobile phases as a function of aqueous surfactant concentration is shown in Figure 4. These experiments were conducted by holding total HOC concentrations constant and varying the surfactant doses; K_D values were then determined directly after centrifuging to remove kaolinite. At low aqueous SDS concentrations, K_D values increased with increasing surfactant concentration (Figure 4a,b) because the amount of SDS adsorbed to kaolinite increases rapidly in this region (Figure 2) and because the sorbed SDS is very effective for HOC partitioning (*30*, *31*). When the aqueous phase SDS concentration reaches its cmc, SDS sorption to kaolinite plateaus and micelles begin competing for HOC molecules, thereby causing a decrease in K_D. For Tween 80, all but one data point is above the cmc; thus, the HOCs are partitioning to both surfactant phases (sorbed surfactant and micelles) over the majority of the concentration range examined (Figure 4c,d). K_D values initially increase at lower concentrations because the affinity of sorbed Tween 80 for the two HOCs is greater than that of the micellar Tween 80 in this region. As the amount of micellar Tween 80 becomes larger relative to the sorbed Tween 80, K_D values begin to decrease. Note that this decrease in K_D occurs even though the Tween 80 sorption to kaolinite has not yet reached a plateau (Figure 2).

Our results for HOC partitioning in the presence of sorbed surfactant and micelles demonstrate that large differences can exist in the HOC sorption capacity of surfactant aggregates in micellar versus sorbed forms. This can be seen quite readily by calculating sorbed surfactant partition constants as a function of surfactant dose from the experimental HOC distribution coefficients. The distribution coefficient defines the HOC mass balance and can be expressed as

$$K_D = \frac{C_{immob}}{C_{mob}} = \frac{S_{sorb}K_{ss} + K_{min}}{1 + S_{mic}K_{mic}} \qquad (2)$$

where C_{immob} (mol/g of kaolinite) and C_{mob} (mol/L) are the immobile and mobile HOC concentrations, respectively, and

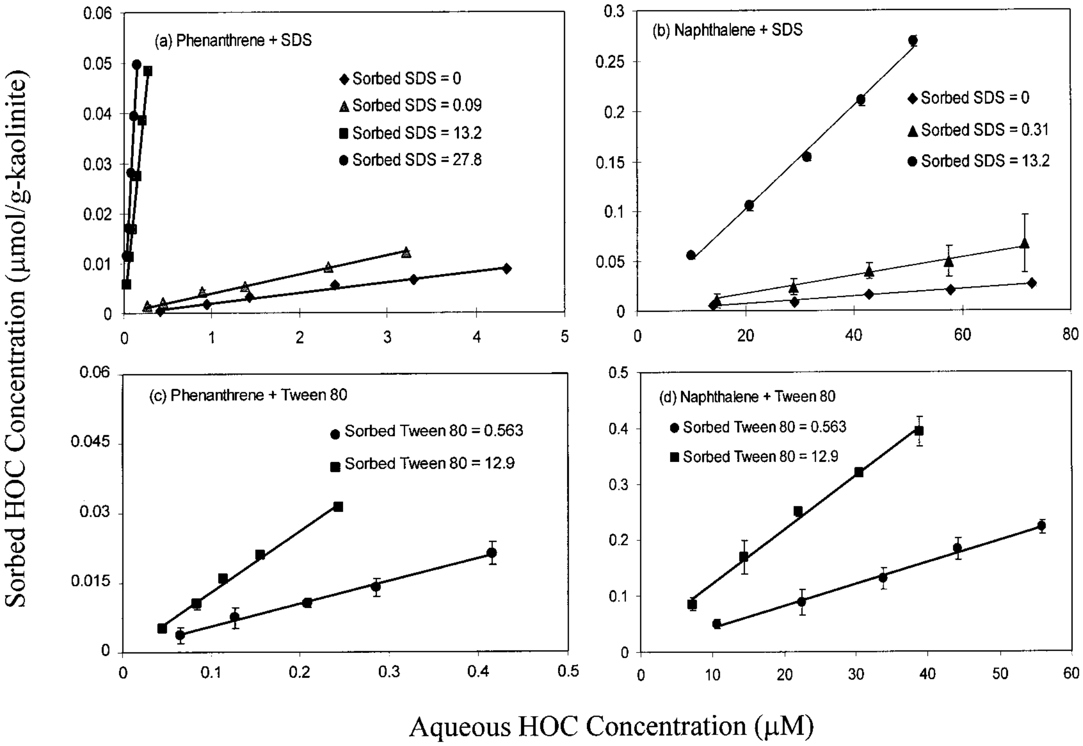

FIGURE 3. HOC sorption isotherms on kaolinite with various concentrations of sorbed surfactant (units of μmol/g of kaolinite). Error bars for some data points are smaller than the symbols. $r_{sw} = 100$ g/L except for naphthalene sorption to bare kaolinite, where it was 300 g/L.

TABLE 3. Parameters of the HOC Sorption Isotherms for Sorbed Surfactants[a]

			Freundlich model[c]			linear model[d]	
	S_{sorb}[b] (μmol/g)	N[e]	K_{ss} (M^{-1})	n	R^2	K_{ss} (M^{-1})	R^2
phenanthrene							
SDS	0.0	18	0.002 ± 2E−4[f]	0.996 ± 0.107	0.994	0.002 ± 5E−5[f]	0.986
	0.09	21	51503 ± 2540	0.972 ± 0.067	0.995	51111 ± 641	0.991
	13.2	18	13149 ± 1134	0.992 ± 0.029	0.999	13497 ± 584	0.999
	27.8	15	11480 ± 1229	0.992 ± 0.026	0.992	11934 ± 231	0.999
Tween 80	0.563	15	123027 ± 3844	1.083 ± 0.035	0.994	162885 ± 7994	0.992
	12.9	15	85113 ± 2201	0.932 ± 0.011	0.995	65228 ± 1477	0.994
naphthalene							
SDS	0.0	15	3.04E−4 ± 8.3E−6[f]	1.091 ± 0.111	0.996	3.64E−4 ± 1.9E−5[f]	0.992
	0.31	15	2319 ± 229	1.121 ± 0.096	0.992	2932 ± 338	0.985
	13.2	15	367 ± 44	1.0325 ± 0.015	0.995	385 ± 8.7	0.996
Tween 80	0.563	15	8511 ± 841	1.091 ± 0.209	0.989	7304 ± 772	0.993
	12.9	15	1122 ± 104	1.107 ± 0.125	0.991	977 ± 68	0.982

[a] From experiments using varying HOC concentrations and fixed sorbed surfactant concentrations (S_{sorb}). Values for K_{ss} and n are ± SD. Ionic strength = 0.1 M NaCl and pH 4.6. [b] Maximum sorption plateaus for SDS and Tween 80 were approximately 40 μmol/g and 29 μmol/g, respectively. [c] Model parameters determined from nonlinear regression analysis of $q_{HOC} = K_{ss}C_{HOC}^{n}$. [d] Model parameters determined from linear regression analysis of $q_{HOC} = K_{ss}C_{HOC}$. [e] N, number of data points. [f] Values are K_{min} (L/g of kaolinite).

S_{sorb} is the sorbed surfactant concentration (mol/g of kaolinite). From our previously determined values for micellar solubilization (K_{mic}), surfactant distribution (S_{sorb} and S_{mic}), and HOC sorption to kaolinite (K_{min}), K_{ss} values can be calculated for each distribution data point using eq 2. Alternatively, an overall average K_{ss} value can be calculated by fitting eq 2 to the distribution data using nonlinear regression analysis.

Average K_{ss} values determined by the above procedure are shown in Table 2. As expected, these values are intermediate of the ones calculated for each individual data point (Figure 4). In all cases, K_{ss} values were larger for the more hydrophobic HOC (phenanthrene) and for the nonionic surfactant (Tween 80). For both SDS and Tween 80, the average K_{ss} values calculated for phenanthrene and naphthalene were always larger than the K_{mic} values at equivalent HOC concentrations (Table 2). When all K_{mic} values in Table 2 are considered, only one (i.e., Tween 80 for a phenanthrene concentration of 1.68 μM) is larger than the corresponding K_{ss}. Previous studies have also reported sorbed surfactant partition coefficients that were generally larger than the micellar partition coefficients (*7, 14, 15, 27*). No convincing explanation for this observation has yet been advanced; presumably it results from geometric differences between sorbed and dissolved surfactant aggregate structures.

K_{ss} values for SDS calculated directly from each HOC distribution data point clearly show distinct ranges that generally correspond well with the locations of the different surfactant sorption regions (i.e., compare Figure 4a,b with Figure 2). For both phenanthrene and naphthalene, as the amount of surfactant sorbed to kaolinite increased, the respective K_{ss} values decreased. In addition, these individual K_{ss} values showed excellent agreement with the isotherm K_{ss} values. For phenanthrene, all individual and isotherm K_{ss}

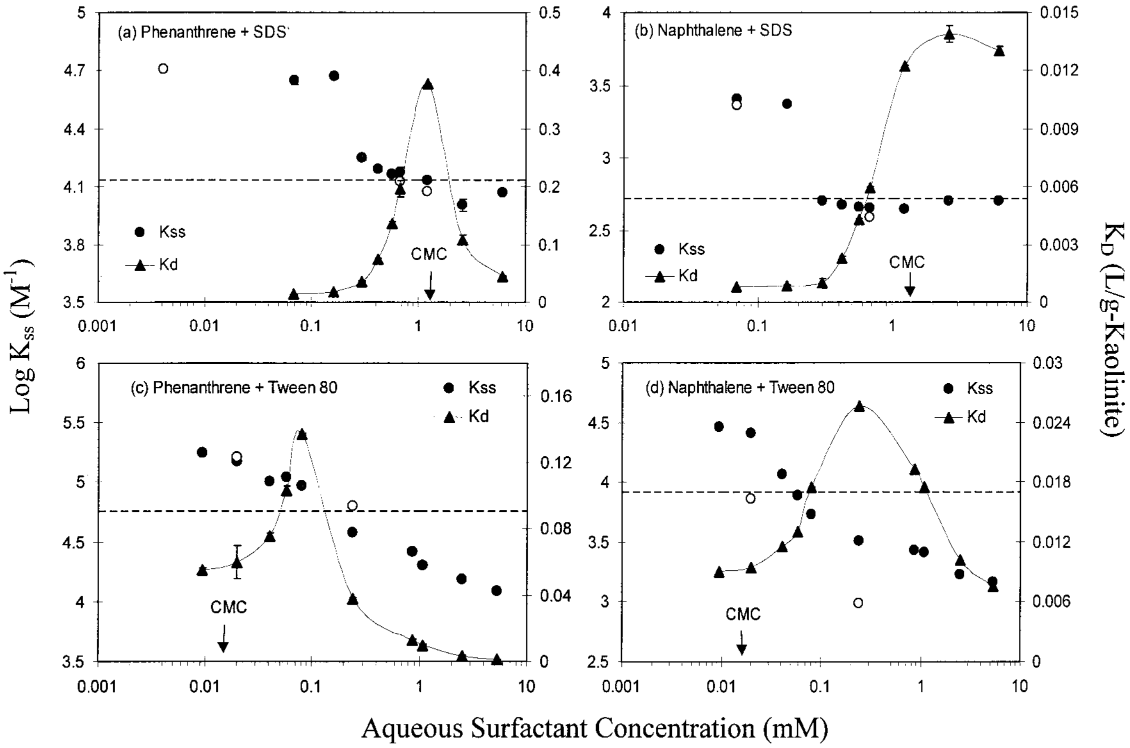

FIGURE 4. HOC distribution (K_D, right axes) and sorbed surfactant partition (K_{ss}, left axes) coefficients. Error bars for some data points are smaller than the symbols. $r_{sw} = 100$ g/L. Total HOC concentration was 4.49 μM (phenanthrene) or 78 μM (naphthalene). Individual K_{ss} values (solid circles) were determined from the K_D values using eq 2 and the micellar partition (K_{mic}) and kaolinite sorption (K_{min}) coefficients below. Isotherm K_{ss} values (open circles) are from Table 3 (linear values). Average K_{ss} values (dashed lines) are from Table 2. (a) $K_{mic} = 1635$ M^{-1}. $K_{min} = 0.002$ L/g. (b) $K_{mic} = 280$ M^{-1}. $K_{min} = 0.0003$ L/g. (c) $K_{mic} = 51507$ M^{-1}. $K_{min} = 0.002$ L/g. (d) $K_{mic} = 2496$ M^{-1}. $K_{min} = 0.0003$ L/g.

values obtained for SDS were much larger than any of the K_{mic} values observed (Figure 4a and Table 2). Although all K_{ss} values for naphthalene and SDS were also larger than the K_{mic} values, the difference was much smaller; in fact, K_{ss} values approached K_{mic} as sorbed SDS levels increased.

The dependence of K_{ss} on sorbed SDS levels appears to be qualitatively consistent with proposed surfactant structures at mineral surfaces (*5*, *13*, *24*). For example, the configuration of adsorbed SDS in region I is expected to be different from that in regions II and III, where micelle-like structures are thought to exist at these relatively higher sorption densities. Apparently, these differences in sorbed surfactant structure that result from regional sorption mechanisms and sorption densities lead to regional differences in K_{ss} values. To our knowledge, there have been no previous reports of K_{ss} values that decreased with increasing SDS sorption for nonpolar HOC compounds such as naphthalene and phenanthrene; Nayyar et al. (*15*) reported a similar observation for the polar compound naphthol in SDS−alumina systems but did not see the effect for naphthalene.

In contrast to SDS, the calculated individual K_{ss} values for Tween 80 did not show distinct ranges but instead decreased monotonically over the surfactant concentration range examined (Figure 4c,d). In addition, although the decreasing trend exhibited by individual K_{ss} values agreed qualitatively that observed for the isotherm K_{ss} values (Table 3), there was not the same good agreement in values as was obtained for SDS. Some complications with Tween 80 were expected because micelles existed throughout the concentration ranged studied; conversely, for SDS the close agreement resulted primarily because, with the exception of region III, HOC partitioning to sorbed SDS did not have to compete with partitioning to SDS micelles over the majority of the SDS sorption regions examined (Figure 4a,b). Although average K_{ss} values for Tween 80 were larger than corresponding K_{mic} values, some of the individual and isotherm K_{ss} values actually fell below K_{mic}. Whether this proves to be a general observation for nonionic surfactants or is merely a result of the complications from working with Tween 80 will be investigated in future studies.

Implications for Treatment/Remediation Alternatives Using Surfactants. Depending on the desired treatment objective, addition of surfactants to a subsurface system should either increase HOC distribution coefficients (i.e., immobilization objective) or decrease them (i.e., mobilization objective as in many SER applications). For example, distribution coefficients for phenanthrene and naphthalene to kaolinite are 0.002 and 0.0003 L/g, respectively (Table 3); thus, addition of a surfactant to a similar system would have to bring the distribution coefficients below these values if mobilization was desired. However, as shown in Figure 4, all HOC distribution coefficients for the surfactant doses investigated are larger than these values even when the dose and subsequent aqueous concentration are well above the cmc; this is a direct result of surfactant sorption followed by HOC partitioning to the sorbed surfactant. For example, the K_D value of naphthalene for an initial Tween 80 dose of 7.63 mM is 0.0075 L/g (i.e., the last point in Figure 4d corresponding to $S_{surf} = 5.32$ mM), which greatly exceeds the value without surfactant present. In other words, the addition of Tween 80 leads to an increase in the retardation of naphthalene instead of decreasing the value as desired. Because the plateau for Tween 80 sorption occurs near the above dose (i.e., 770 × cmc, Figure 2), it is expected that much higher doses would be needed to overcome the enhanced retardation effects caused by its sorption. A more useful approach, therefore, would be to utilize the Tween 80 to increase retardation in this particular system; the optimum dose to use would correspond to a maximum K_D value.

In any evaluation of a treatment/remediation scheme utilizing surfactants, the effect of dose on the HOC distribution coefficient must be quantified. Very often, only one coefficient value for HOC partitioning to sorbed surfactants has been reported in the literature, presumably because that experimental sorption data mainly covers the sorption regions where the surfactant molecule interactions dominate at the surface (*15*, *22*). However, all of the characteristic sorption regions likely will develop during an in-situ application as the surfactant front (i.e., mass transfer zone) advances through the porous medium. Therefore, the relative role of regional HOC partition coefficients to sorbed surfactant should be considered in remediation/treatment processes. Also, the porosity (or r_{sw}) for the particular system must be taken into account when the surfactant sorption is quantified. Finally, in addition to the equilibrium aspects discussed above, all rate processes including HOC sorption, micellar solubilization, partitioning to sorbed surfactants, and surfactant sorption may need to be quantified.

Acknowledgments

We gratefully acknowledge two reviewers who provided constructive comments for improving the manuscript. Preliminary funding for this work was provided by the Office of the Vice President for Research and Associate Provost for Graduate Studies, through the Center for Energy and Mineral Resources, Texas A&M University, and the National Science Foundation (Grant CTS-9630577). Additional funding was provided by the Gulf Coast Hazardous Substance Research Center, which is supported under cooperative agreement R822721-01-4 with the U.S. Environmental Protection Agency. The contents of this paper do not necessarily reflect the views and policies of the U.S. EPA nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

Supporting Information Available

Detailed information on the fluorescence techniques used in this study and preliminary rate data is available (9 pages). Ordering information is given on any current masthead page.

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Received for review December 12, 1997. Revised manuscript received June 9, 1998. Accepted June 29, 1998.

ES971075E