

# Effects of Solution Chemistry on the Partitioning of Phenanthrene to Sorbed Surfactants

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Solution chemistry effects on surfactant micelle formation, surfactant sorption on kaolinite, and phenanthrene partitioning to surfactant micelles and sorbed surfactants were studied. For the anionic surfactant sodium dodecyl sulfate (SDS), critical micelle concentration (cmc) values decreased with increasing ionic strength but were unaffected by pH changes. For the nonionic surfactant Tween 80, the cmc was unaffected by pH and ionic strength changes. SDS sorption on kaolinite showed strong pH and ionic strength dependency: sorption increased as pH decreased and ionic strength increased, respectively. For Tween 80, only pH changes affected its sorption on kaolinite. Micellar phenanthrene partition coefficients ( $K_{mic}$ ) increased with increasing ionic strength for SDS but were not affected by changes in pH. For Tween 80  $K_{mic}$  values, no pH or ionic strength effect was observed. Phenanthrene distribution coefficients ( $K_D$ ) between the solid and aqueous phases varied as a function of solution chemistry and were primarily dependent on the concentration of surfactant that was sorbed. Organic carbon-normalized partition coefficients ( $K_{oc}$ ) of the sorbed surfactants showed a much greater affinity for phenanthrene than that predicted for natural organic matter. For sorbed SDS aggregates,  $K_{oc}$  values fell into two general regions depending on whether the pH was above or below the point of zero charge (PZC) of kaolinite. Plausible structural differences for sorbed SDS aggregates are discussed to explain these regional  $K_{oc}$  values.

## Introduction

Many studies have demonstrated that surfactant micelles greatly enhance the apparent solubility of hydrophobic organic compounds (HOCs) in water (1–3). Additionally, surfactants that sorb onto solid surfaces can also exhibit HOC partitioning capabilities, presumably because they have micelle-like structures (4). Sorbed surfactants can form local aggregates at aqueous concentrations below their critical micelle concentration (cmc) values; these aggregates are often termed “hemimicelles” (5) or “admicelles” (6) depending on the postulated aggregate layer types and thicknesses. For example, although the term hemimicelle has been used to describe sorbed surfactant aggregates formed by hydrophobic interactions (5), that term is more commonly used only for aggregates having a proposed structure equivalent to monolayer coverage (7). Bilayered aggregates, postulated to occur

at higher surfactant loadings and/or for stronger hydrophobic interactions, are commonly referred to as admicelles (7). Chandar et al. (8) proposed a conceptual model for a sorbed ionic surfactant and suggested that bilayers likely form from the growth of existing aggregates (i.e., monolayers) rather than by forming directly. Because the growth of these bilayered aggregates would be electrostatically hindered, higher surfactant concentrations would be needed to offset this repulsion, and the polar or ionic headgroup of the second layer would be oriented toward the aqueous solution. Yeskie and Harwell (7) studied the sorption of an anionic surfactant onto positively charged mineral surfaces and proposed that electrostatic interactions determine the transition from a hemimicelle structure to an admicelle structure; that is, an admicelle structure becomes more favored as one moves away from a mineral surface's point of zero charge (PZC) to higher charge densities. They also concluded that a heterogeneous mineral surface might have bilayers forming at highly charged areas simultaneously as monolayers are forming at lower charged areas. Additional information on the postulated structures of adsorbed surfactants is available in the literature (9).

Results from previous studies show that hydrophobic interactions between surfactants in aqueous solutions and to previously sorbed surfactants are important and must be understood to describe surfactant sorption to soil minerals. Surfactant sorption typically results from one or more forces (e.g., electrostatic, hydrogen bonding, van der Waals, polarization of  $\pi$  electrons) (4), some of which are affected by the soil solution chemistry. Therefore, it might be expected that the formation and structure of sorbed surfactant aggregates will depend on solution chemistry. Because HOC distributions that develop in surfactant-enhanced remediation (SER) applications may become dependent on the distribution of surfactants between the aqueous and solid phases (10), the effects of solution chemistry must also be considered in SER applications.

Effects of aqueous chemistry on the formation and properties (e.g., cmc, aggregation number, micellar size and shape, microviscosity) of surfactant micelles are relatively well-documented (11, 12) and can be expected to affect HOC solubilization. For example, addition of electrolyte to anionic surfactant solutions not only decreases the cmc and interfacial surface area of the headgroups but also results in an increased partitioning of solubilize due to the increased fraction of surfactant molecules existing in the micellar form (11, 12). In general, studies of pH effects on micellar properties and HOC solubilization have been much less common than those of ionic strength effects.

It is often suggested that sorbed surfactant aggregates have micelle-like characteristics (4); therefore, they might be expected to show similar responses to changes in solution chemistry. Of even more importance, however, may be the effect of aqueous chemistry on the interactions between surfactant molecules and sorbent surfaces. Fuerstenau and Wakamatsu (5) observed a strong pH dependence on the adsorption isotherms of sodium dodecyl sulfonate to alumina and concluded that pH affects the electrostatic interactions between a charged solid surface and a charged surfactant headgroup, thus changing the critical concentration limit required for hemimicelle formation. Their results were later supported by the work of Holsen et al. (13), who showed that the adsorption of sodium dodecyl sulfate (SDS) on ferrihydrite varied with solution pH due to changes in electrostatic and molecular interactions. Cummins et al. (14) studied the sorption of nonionic surfactants on silica and observed strong

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TABLE 1. Micellar Partition Coefficients ( $K_{mic}$ ) for Phenanthrene with Varying Solution Chemistry Conditions<sup>a</sup>

NaCl (M)	SDS			Tween 80		
	cmc (mM)	$K_{mic} \times 10^{-3} (M^{-1})$	$K_{oc} (L/g)$	cmc ( $\mu M$ )	$K_{mic} \times 10^{-3} (M^{-1})$	$K_{oc} (L/g)$
0	8.1	$1.48 \pm 0.12$	$10.28 \pm 0.83$	9.92	$47.4 \pm 2.15$	$66.02 \pm 2.99$
0.001	8.0	$1.67 \pm 0.15$	$11.59 \pm 1.04$	nd <sup>b</sup>	nd	nd
0.01	5.6	$2.12 \pm 0.26$	$14.72 \pm 1.81$	9.92	$54.6 \pm 2.23$	$76.04 \pm 3.11$
0.1 <sup>c</sup>	1.5	$2.28 \pm 0.41$	$15.83 \pm 2.84$	9.92	$55.0 \pm 1.33$	$76.60 \pm 1.85$
0.1	1.5	$2.17 \pm 0.17$	$15.07 \pm 1.18$	9.92	$48.7 \pm 3.43$	$67.83 \pm 4.78$
0.1 <sup>d</sup>	1.5	$2.23 \pm 0.14$	$15.49 \pm 0.97$	9.92	$51.3 \pm 7.55$	$71.45 \pm 10.52$

<sup>a</sup> Obtained by nonlinear regression analysis of fluorescence data using the method from ref 18. Values for  $K_{mic}$  and  $K_{oc}$  are  $\pm$  SD. The pH value was 6 unless otherwise noted. <sup>b</sup> nd, not determined. <sup>c</sup> pH 4. <sup>d</sup> pH 10.

pH-dependent sorption, presumably because of pH-dependent hydrogen bonding between surfactant and surface groups. Xu and Boyd (15, 16) investigated ionic strength effects on cationic surfactant sorption to negatively charged clay soils and observed increased sorption at higher ionic strengths. They postulated that the effective size of the sorbed ionic surfactant headgroups decreases as the counterion concentration increases, leading to a decrease in the electrostatic repulsion between the headgroups in the sorption layer, analogous to micelles in solution.

We are aware of only two studies that have investigated HOC partitioning to sorbed surfactants as a function of aqueous chemistry. Holsen et al. (13) examined the sorption of several HOCs on SDS-coated ferrihydrite as a function of pH. Their results for a limited pH range (i.e., all values were below the PZC of ferrihydrite) showed that partition coefficients normalized by the amount of sorbed SDS were very similar for each HOC. These results suggest that pH variations primarily affected the interactions between the surface and surfactant molecules but did not alter the physicochemical properties of sorbed SDS aggregates that might have led to different partitioning effects. Similar results were obtained by Kibbey and Hayes (17), who investigated phenanthrene partitioning to silica coated with cetylpyridinium chloride (CPC); they found that carbon-normalized phenanthrene partition coefficients ( $K_{oc}$ ) to the CPC-coated silica at pH 5 and pH 7.8 were similar and concluded that the sorptive capacity of the sorbed CPC did not change significantly with pH.

To better understand the importance of solution chemistry on the distribution of HOCs between aqueous and solid phases in SER applications, more detailed studies of the interactions between surfactants and soil minerals and the subsequent partitioning of HOCs as a function of aqueous chemistry are necessary. The objectives of this work were to systematically investigate the effects of pH and ionic strength on (i) micellar cmc values, (ii) surfactant sorption to a common soil mineral, (iii) HOC solubilization by surfactant micelles, and (iv) HOC partitioning to sorbed surfactant aggregates.

## Experimental Section

Physicochemical characteristics of the materials utilized in this study and detailed experimental procedures have been previously reported (18); therefore, they are only briefly mentioned here. Phenanthrene, kaolinite, SDS, and Tween 80 were selected as the model HOC, soil mineral, and anionic and nonionic surfactants, respectively. Solution pH and ionic strength values were adjusted as necessary with 0.5 M HCl and/or 0.5 M NaOH and NaCl, respectively; these and other reagents were of analytical grade or better and were used without further treatment. Aqueous phenanthrene, SDS, and Tween 80 concentrations were determined by fluorescence, total organic carbon (TOC) analysis, and UV absorbance, 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.

Fluorescence techniques (18–23) were used to determine cmc values and phenanthrene micellar partition coefficients ( $K_{mic}$ ) for the surfactants as a function of solution pH and ionic strength. Surfactant sorption rates, equilibrium isotherms, and sorption envelopes on kaolinite were determined in triplicate batch experiments for the appropriate solution chemistry conditions; sorbed surfactant concentrations ( $q$ ,  $\mu\text{mol/g}$ ) were calculated by mass balance. Subsequent phenanthrene sorption to the sorbed surfactants at these solution chemistry conditions were performed in triplicate batch experiments; phenanthrene concentrations were measured in the aqueous phase after centrifugation, and sorbed amounts were calculated by mass balance.

A  $\zeta$ -potential analyzer (ZetaPlus, Brookhaven Instruments) was used to determine the apparent  $\zeta$ -potential of kaolinite particles with and without sorbed surfactants; the instrument calculates apparent  $\zeta$ -potential values by converting measured electrophoretic mobility data using the Smoluchowski equation. To measure the  $\zeta$ -potential as a function of solution pH and surfactant dose, samples used in the sorption isotherm or envelope tests were gently agitated to resuspend some of the particles in the supernatant (to achieve a solid-phase concentration between  $10^{-5}$  and  $10^{-2}$  mass ratio) before taking a 2-mL aliquot for analysis. Relative standard deviations for  $\zeta$ -potential measurements were generally less than 5% and never more than 10%.

## Results and Discussion

**Aqueous Chemistry Effects on Micellar Solubilization. (A) cmc Determinations.** Surfactant titrations of aqueous solutions containing a hydrophobic fluorescent probe result in two distinct fluorescence regions that can provide relatively well-defined surfactant cmc values when using nonlinear fitting procedures (18). The influence of ionic strength (as added NaCl) on the cmc of SDS at pH 6 was dramatic (Table 1). Note that the “true” ionic strength of each solution would be slightly greater than the amount of added NaCl because the free sodium ion concentration from SDS contributes to the total ionic strength. However, considering the degree of micellar ionization ( $\alpha$ ) to be about 0.2 (22), the effect of free sodium ion from SDS is small and thus neglected in our determination of cmc values and in all of our other ionic strength calculations, consistent with the literature (24, 25). The cmc values we obtained for SDS and the trend observed for increasing ionic strength agree well with the results of previous studies for similar ionic strength conditions (11, 12, 18, 24). As the ionic strength increases in SDS solutions, the repulsive electrostatic force between the headgroups decreases and the interfacial hydrophobic force between hydrocarbon chains increases, thereby resulting in a decrease

in the headgroup area and interfacial free energy per molecule that leads to increased bond energies between SDS molecules in the aggregate structure (11, 12); stronger bonding energies of SDS molecules result in lower cmc values. More detailed information on the thermodynamics of micelle formation is available in the literature (11, 12).

No pH effect (4–10) on the cmc of SDS was observed; this was expected because of the low  $pK_a$  value ( $\sim 2.3$ ) for SDS (11). Likewise, cmc values for Tween 80 as a function of ionic strength and pH also showed negligible differences. A few studies have reported decreases in the cmc of nonionic surfactants upon increasing addition of electrolytes (nitrates of sodium and potassium); however, the magnitude of these decreases was much smaller than the decreases typically observed for ionic surfactants (11).

**(B) Micellar Partition Coefficients.** Solution chemistry effects on the micellar solubilization of phenanthrene are summarized in Table 1.  $K_{mic}$  values were determined from experimental fluorescence measurements using nonlinear regression analysis of the following equation (18):

$$F_t = \frac{F_w + F_{mic}K_{mic}(S_{surf} - cmc)}{1 + K_{mic}(S_{surf} - cmc)} \quad (1)$$

where  $S_{surf}$  is the total aqueous surfactant concentration, and  $F_t$ ,  $F_w$ , and  $F_{mic}$  are phenanthrene-normalized fluorescence intensities in the total system, aqueous phase, and micellar phase, respectively.

An increase in the phenanthrene partition coefficient to SDS micelles is observed with increasing ionic strength at a fixed pH of 6 (Table 1). A conceptual model has been proposed to describe the effects of electrolyte addition on the partitioning of nonpolar compounds such as phenanthrene into the core (or deep region within the palisade layer) of ionic surfactant micelles (11). For example, displacement of the cmc to lower values as a result of electrolyte addition leads to increased partitioning overall because of the increased fraction of surfactant molecules existing in the micellar form (11, 12); however, this does not explain the increase in  $K_{mic}$  observed here. "Salting out" effects can lead to increases in HOC partition coefficients; however, using a Setschenow constant of  $0.28 \text{ M}^{-1}$  for phenanthrene (26), we calculate that the  $K_{mic}$  value should have increased about 6% for the 0.1 M NaCl solution, which is much smaller than the relative difference (47%) we observed. Therefore, it appears that the differences in  $K_{mic}$  values for phenanthrene are caused primarily by changes in SDS micellar properties with ionic strength.

No significant effects of solution pH were observed for SDS solubilization of phenanthrene (Table 1). Again, this can be attributed to the fact that SDS molecules have strong dissociation characteristics (i.e., low  $pK_a$  of  $\sim 2.3$ ). For Tween 80, little to no effects on phenanthrene solubilization were observed with changing solution chemistry conditions. A few studies, however, have reported increases in the solubilization of organic compounds by nonionic micelles at ionic strength values much higher than the range used here (11).

**Aqueous Chemistry Effects on Surfactant Sorption to Kaolinite. (A) Ionic Strength.** The influence of ionic strength on surfactant sorption is shown in Figure 1. Both SDS sorption isotherms exhibit "S-shaped" curves, indicative of aggregate-forming interactions between SDS molecules on the surface in addition to sorbate-sorbent interactions. In general, SDS sorption at 0.1 M NaCl was greater than for no added NaCl, consistent with previous observations (15). Increased SDS sorption at the higher ionic strength can be explained by a decrease in the electrostatic repulsion (i.e., screening) between sorbed SDS molecules as well as between SDS and kaolinite; it is important to note that, at the condition studied here (pH 4.6), both the kaolinite surface and SDS

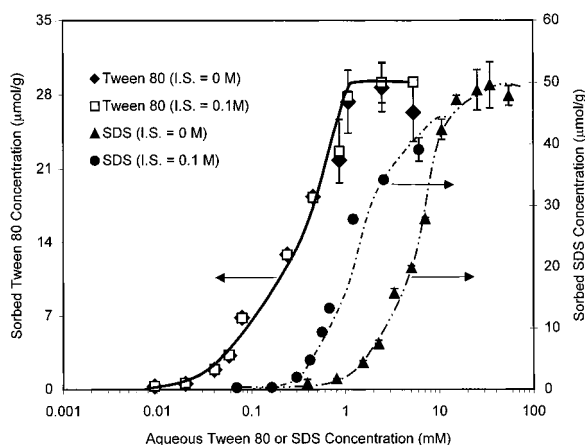


FIGURE 1. Surfactant sorption on kaolinite for two ionic strength conditions (as added NaCl) at pH 4.6. Kaolinite concentration was 100 g/L. Lines are provided to show the general trends.

have net negative charges. The initial enhancement that occurs with increasing ionic strength at low SDS concentrations most likely results from the screening effect between SDS and kaolinite that allows SDS molecules to first sorb; enhancement at higher SDS concentrations most likely results from decreasing repulsions between sorbed SDS headgroups when hydrophobic forces become more important.

Tween 80 sorption isotherms for 0 and 0.1 M NaCl (Figure 1) show that differences in sorption are minor for the ionic strength conditions studied, in agreement with Brownawell et al. (27). Consistent with previous reports (3, 18), the majority of Tween 80 sorption occurs well above its cmc value ( $9.2 \mu\text{M}$ ). The sharp rise in sorption can be interpreted as being a change from surfactant monomer sorption to surface coverage by surfactant aggregates that form hemimicelles and/or admicelles (18).

**(B) pH.** pH effects on SDS sorption to kaolinite are summarized in Figure 2. A wide range of pH values at fixed ionic strength were investigated for both sorption versus dose experiments (Figure 2a) and sorption envelope tests (Figure 2b). In Figure 2a, SDS sorption decreases with increasing pH over the entire dose region. All sorption curves exhibit the classic S-shape, indicating the formation of sorbed surfactant aggregates (due to hydrophobic interactions between SDS tails) at all pH values. The pH dependency of SDS sorption on kaolinite is more dramatically shown in the sorption envelope test results (Figure 2b). Here, the sorbed amount of SDS on kaolinite versus solution pH is shown for an SDS dose of 2 mM. Again, it is obvious that SDS sorption decreases as the pH increases. Increasing pH values increase the negative charge density on the kaolinite surface and thus increase the repulsive force between the kaolinite surface and negative headgroups of anionic surfactants such as SDS, thereby decreasing overall sorption. When the solution pH is below the overall PZC of kaolinite (pH 4.1–4.3), the net surface charge of kaolinite becomes positive, and thus more SDS molecules can be sorbed due to the attraction between the surface and the SDS headgroup.

The Tween 80 sorption envelope for an initial dose of 1.67 mM is also shown in Figure 2b. Tween 80 sorption generally decreases as the pH increases, most likely because of the corresponding increase of net negative charge on the kaolinite surface above its PZC (i.e., pH-dependent surface sites). For example, hydrogen bonding has been suggested as the mechanism responsible for the sorption of nonionic surfactants on mineral surfaces (14, 27). Depending on the solution pH relative to the PZC, surface hydroxyl groups ( $\text{S-OH}$ ) of kaolinite can be either protonated to positively charged species ( $\text{S-OH}_2^+$ ) or deprotonated to negatively charged



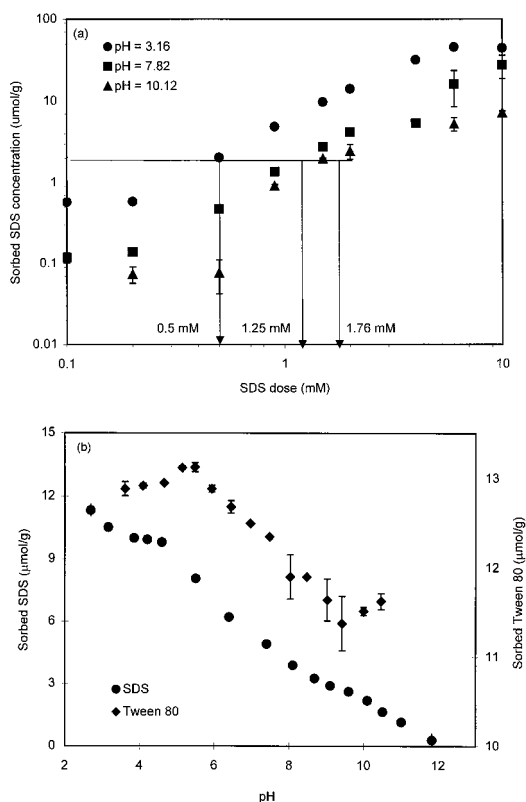


FIGURE 2. Surfactant sorption on kaolinite for 0.1 M NaCl. Error bars for some data points are smaller than the symbols. Kaolinite concentration was 100 g/L. (a) SDS sorption curves for three pH values. The solid lines identify the pH-dependent doses necessary to obtain equivalent SDS loadings (see text). (b) Sorption envelopes. The SDS dose was 2 mM, and the Tween 80 dose was 1.67 mM.

species ( $\text{S-O}^-$ ). Therefore, as the solution pH decreases, favorable hydrogen bonding between the oxyethylene group of Tween 80 and sorbed protons on the surface occurs. Conversely, increasing solution pH values result in deprotonation of surface hydroxyl groups and therefore less hydrogen bonding between Tween 80 and kaolinite, resulting in decreased Tween 80 sorption.

**(C)  $\zeta$ -Potential.**  $\zeta$ -potential measurements of kaolinite from the SDS sorption isotherms of Figure 1 exhibited similar S-shaped curves when plotted versus aqueous surfactant concentration (data not shown), consistent with the formation of surfactant aggregates at the surface. As shown in Figure 3a, sorbed SDS directly influences the  $\zeta$ -potential of kaolinite (i.e.,  $\zeta$ -potential becomes more negative as SDS sorption increases). Similar to results from previous studies (5, 8, 28), the  $\zeta$ -potential of kaolinite is relatively constant at low SDS sorption levels but becomes more negative as surfactant aggregates (i.e., hemimicelles and/or admicelles) form. Ultimately, the  $\zeta$ -potential reaches a constant value again as the kaolinite surface becomes saturated with SDS molecules. Considering the electrostatic repulsion between SDS headgroups and negatively charged surface sites, it follows that a significant fraction of SDS molecules must initially sorb via anion exchange at the edge sites of kaolinite, which have an apparent PZC of about 7.3 (29). In addition, SDS may displace some loosely bound water molecules from the relatively hydrophobic basal plane of kaolinite, thereby sorbing in a horizontal orientation that takes advantage of the interaction between the hydrophobic SDS chain and the surface. As the SDS surface density increases, lateral interactions between sorbed SDS molecules become more important and lead to a vertically oriented SDS surface layer.

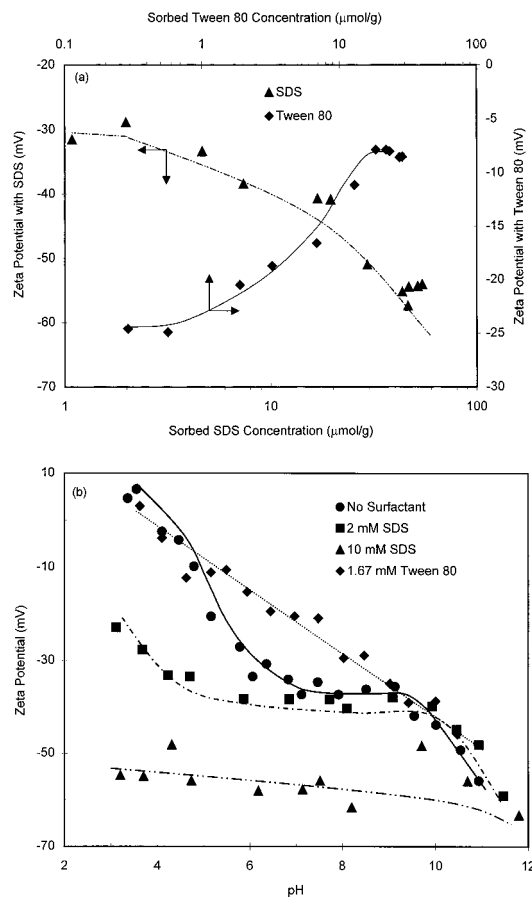


FIGURE 3.  $\zeta$ -potential of kaolinite for 0 M NaCl. Lines are provided to show the general trends. (a) Dependence on sorbed surfactant concentrations at pH 4.6. (b) Dependence on pH for finite surfactant doses.

$\zeta$ -potential measurements of kaolinite with sorbed Tween 80 are also shown in Figure 3a; opposite to SDS, increasing concentrations of sorbed Tween 80 lead to less negative  $\zeta$ -potentials. The formation of nonionic surfactant aggregates at the surface generally leads to a lowering of the mobility of the particles, probably due to a shift in the position of shear plane or change in adsorption characteristics of the ions present (including potential determining ions) (30).

$\zeta$ -potential measurements as a function of pH for fixed surfactant doses and no added NaCl are shown in Figure 3b; it can be seen that the PZC of kaolinite occurs when the pH is approximately 4.2. Again, kaolinite with sorbed SDS exhibits a more negative  $\zeta$ -potential than the bare mineral surface, because of the original negative kaolinite charge plus the negative charge due to sorbed SDS headgroups. Even at pH values below the PZC, sorption of SDS reverses the surface charge of kaolinite and results in an overall net negative charge, consistent with previous observations (5). For a 2 mM SDS dose, the  $\zeta$ -potential is more negative relative to bare kaolinite for all pH values below 8. Above pH 8 (i.e., above the surface edge PZC) SDS sorption is relatively low (Figure 2b); therefore,  $\zeta$ -potentials of kaolinite with sorbed SDS are similar to those without SDS present above pH 8, demonstrating the small effect of SDS on the  $\zeta$ -potential. At a higher SDS dose (10 mM), kaolinite surfaces become saturated with SDS molecules. Under these conditions, sorbed SDS is the primary contributor to the relatively high negative surface charge, and the  $\zeta$ -potential is relatively independent of pH. When Tween 80 is added to kaolinite suspensions, the  $\zeta$ -potential decreases with increasing pH but to a lesser extent than the bare kaolinite (Figure 3b). This observation is particularly dramatic in the pH range from 5

TABLE 2. Phenanthrene Distribution ( $K_D$ ) and Organic Carbon-Normalized Partition ( $K_{oc}$ ) Coefficients to Sorbed Surfactants on Kaolinite for Varying Solution Chemistry Conditions<sup>a</sup>

	pH	$S_{\text{sorb}}$ ( $\mu\text{mol/g}$ )	$K_D^b$ (L/g)	$R^2$	$N^c$	$f_{oc}^d$ (%)	$K_{oc}$ (L/g)
SDS	3.38	10.51	$0.556 \pm 0.012$	0.976	18	0.1509	$368 \pm 7.6$
	3.85	9.99	$0.383 \pm 0.010$	0.992	15	0.1434	$264 \pm 5.9$
	4.32	9.80	$0.222 \pm 0.005$	0.988	18	0.1406	$155 \pm 3.5$
	5.25	8.07	$0.100 \pm 0.002$	0.999	15	0.1156	$86.5 \pm 1.4$
	5.87	7.79	$0.098 \pm 0.008$	0.991	18	0.1122	$87.6 \pm 7.4$
	6.50						
	IS = $1 \times 10^{-3}$ M	0.84	$0.0144 \pm 0.002$	0.996	18	0.0121	$119 \pm 14.1$
	IS = $1 \times 10^{-2}$ M	0.87	$0.0168 \pm 0.001$	0.999	15	0.0125	$135 \pm 9.6$
	IS = $1 \times 10^{-1}$ M	3.51	$0.0727 \pm 0.003$	0.983	18	0.0505	$144 \pm 5.9$
	7.85	3.26	$0.068 \pm 0.004$	0.992	15	0.0470	$145 \pm 10.4$
Tween 80	8.40	2.91	$0.055 \pm 0.005$	0.997	18	0.0410	$131 \pm 10.4$
	9.11	2.62	$0.051 \pm 0.002$	0.991	15	0.0369	$138 \pm 5.6$
	4.60	12.90	$0.1301 \pm 0.0015$	0.994	18	0.926	$90.9 \pm 2.1$
	6.25	12.13	$0.0289 \pm 0.0008$	0.987	18	0.871	$71.2 \pm 3.4$
	7.85	9.47	$0.0157 \pm 0.0005$	0.973	15	0.679	$89.6 \pm 2.7$

<sup>a</sup> Values for  $K_D$  and  $K_{oc}$  are  $\pm$  SD. Ionic strength = 0.1 M unless noted. Dose was 2 and 1.527 mM for SDS and Tween 80, respectively. <sup>b</sup> Obtained from linear regression analysis of experimental isotherms. <sup>c</sup> Number of data points. <sup>d</sup> For SDS,  $f_{oc}$  was calculated from the theoretical carbon content specified by the chemical formula. For Tween 80, the carbon content was determined by TOC measurements.

to 9. Above pH 9, differences in  $\zeta$ -potential become small because the sorbed Tween 80 amounts are lower and are relatively constant as shown in Figure 2b.

**Aqueous Chemistry Effects on Phenanthrene Partitioning to Sorbed Surfactants. (A) Ionic Strength.** The influence of ionic strength (as added NaCl) on phenanthrene partitioning to sorbed SDS was investigated at pH 6.5 (Table 2). As discussed previously, SDS sorption increases with increasing ionic strength; therefore, one would logically expect phenanthrene sorption to the solid phase (which includes sorbed SDS aggregates) to correspondingly increase with ionic strength. To determine whether SDS molecules sorbed under different ionic strength conditions exhibit different partitioning characteristics, carbon-normalized partition coefficients ( $K_{oc}$ ) were calculated from the linear distribution coefficients ( $K_D$ ). The organic carbon fraction ( $f_{oc}$ , % in mass sorbed C/sorbent mass) was calculated from SDS sorption results for the same pH and dose (i.e., 2 mM).  $K_{oc}$  values for sorbed SDS were approximately 10 times greater than those for SDS micelles (Tables 1 and 2), indicating a higher affinity of the sorbed SDS molecules for phenanthrene (18). Sorbed SDS  $K_{oc}$  values increased with increasing ionic strength; although the percentage increase in phenanthrene partitioning was slightly less than that observed for SDS micelles (i.e., 20% versus 30% for a NaCl increase from 0.001 to 0.1 M), the increase was larger than the estimated 6% increase expected due to salting out.

**(B) pH.** Phenanthrene sorption isotherms for varying pH conditions at 0.1 M NaCl were observed to be linear (data not shown); therefore, distribution coefficients were determined using linear regression analysis (Table 2).  $K_D$  values decreased with increasing pH, which can be attributed primarily to decreased SDS sorption at high pH (13).  $K_{oc}$  values for phenanthrene partitioning to sorbed SDS were calculated as before, and these values were then compared to the value predicted from a correlation using the phenanthrene octanol–water partition coefficient ( $K_{ow}$ ) (26). In all cases, our measured  $K_{oc}$  values were larger than the predicted value with relative effectiveness of sorbed SDS to natural organic carbon ranging from 10 to 40 times greater (Figure 4). Holsen et al. (13) obtained similar results for the partitioning of several HOCs to SDS-coated ferrihydrite over a limited pH range (i.e., pH values all below ferrihydrite's PZC). Results from both studies clearly show that sorbed SDS provides a more effective medium for HOC partitioning than does the same amount of natural organic matter on a carbon basis.

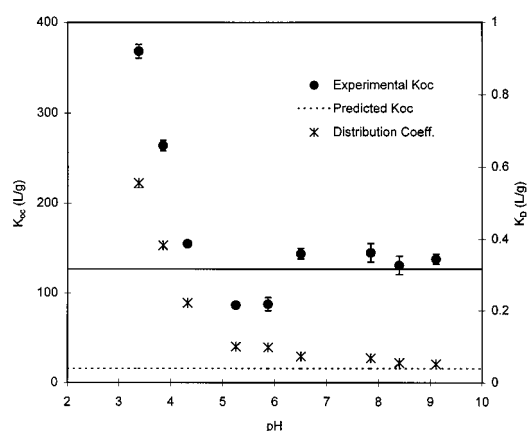


FIGURE 4. Effect of pH on phenanthrene distribution ( $K_D$ ) and organic carbon normalized partition ( $K_{oc}$ ) coefficients for sorbed SDS. The ionic strength was 0.1 M NaCl, and the kaolinite concentration was 100 g/L. Error bars for some data points are smaller than the symbols. The solid line is the average  $K_{oc}$  value for pH values above the PZC of kaolinite. The predicted  $K_{oc}$  value is from ref 26.

Interestingly, Figure 4 and Table 2 show that sorbed SDS  $K_{oc}$  values can be divided into two distinct regions depending on whether the solution pH is above or below the PZC of kaolinite;  $K_{oc}$  values below the PZC (i.e., pH 3.4 and pH 3.9) are much greater than those above the PZC. This observation contrasts with the results of Ko et al. (18), who found that phenanthrene  $K_{oc}$  values decreased as the amount of sorbed SDS increased under fixed solution chemistry conditions where the pH > PZC. However, that study showed that higher partition coefficients for sorbed SDS are obtained in region I of the SDS sorption isotherm (18), whereas the sorbed SDS here exists as aggregates for the particular dose used (i.e., 2 mM was the SDS dose used, which would correspond to sorption in region II and possibly region III as shown in Figures 1 and 2a).

To further examine differences in partitioning to sorbed SDS aggregates, we conducted phenanthrene sorption tests on kaolinite loaded with the same amount of SDS under different pH conditions (i.e.,  $q = 1.95 \mu\text{mol/g}$  as shown in Figure 2a). Ideally, phenanthrene isotherms and distribution coefficients should have been identical regardless of pH because of the constant  $f_{oc}$  value. However, it is obvious from Figure 5 that the  $K_D$  value for the isotherm below the PZC of kaolinite (i.e., the one conducted at pH 3.2) is much greater than those two conducted above the PZC (i.e., pH 7.8

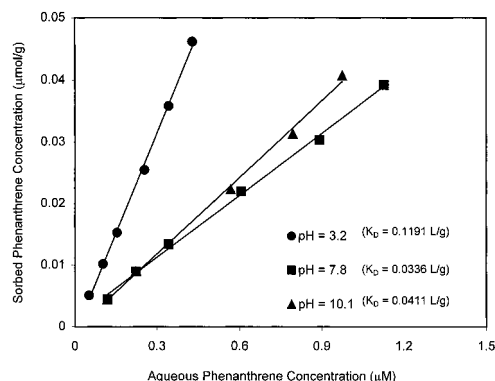


FIGURE 5. Phenanthrene sorption isotherms on kaolinite loaded with the same amount (1.95  $\mu\text{mol/g}$ ) of sorbed SDS under different pH conditions. The ionic strength was 0.1 M NaCl, and the kaolinite concentration was 100 g/L. Error bars are smaller than the symbols. Solid lines are the best fits from linear regression and represent the  $K_D$  values.

and pH 10.1).  $K_{oc}$  values calculated from the  $K_D$  values and sorbed SDS amounts were  $435 \pm 9.5$ ,  $122 \pm 2.1$ , and  $150 \pm 3.0$  L/g for pH 3.2, pH 7.8, and pH 10.1, respectively. These values agree well with those obtained using a constant SDS dose of 2 mM (Table 2); additionally, the values fall into the same two regions described above. These results suggest that sorbed SDS aggregates formed at pH values below and above the PZC of a mineral surface will have different HOC partitioning characteristics.

Depending on the surface charge of kaolinite, the following conceptual interactions between SDS and kaolinite can be postulated. When the pH is above the overall PZC of kaolinite, SDS sorption is inhibited by electrostatic repulsion between the net-negative surface and the negative SDS headgroup (5). For these conditions, sorption most likely occurs through interactions between the hydrophobic SDS tails and the relatively hydrophobic basal plane, although some additional sorption likely occurs via anion exchange (e.g., on edge sites of kaolinite below pH 8 as discussed above). With increasing SDS dose, the sorbed molecules reorient from a relatively flat-lying position to more condensed configurations as adjacent SDS tails begin to interact. As a result, the anionic headgroups become oriented toward the aqueous phase, and formation of a bilayer (i.e., vertical interaction between SDS molecules) becomes inhibited due to electrostatic repulsion. Instead, the lateral interactions between SDS molecules form a compact monolayer structure that leads to a decrease in the  $\zeta$ -potential as observed in Figure 3a (5). At very high SDS doses, it is conceivable that a bilayer could ultimately form above the PZC; however, the aggregate structure formed under these conditions most likely would not be as compact as that for the monolayer. Conversely, at pH values below the overall kaolinite PZC, the original net surface charge is positive, and the attractive forces between anionic SDS headgroups and positively charged surface sites allow for formation of a sorbed SDS structure in which the hydrophobic tails are directed toward the aqueous phase. With increasing dose, the hydrophobic tails of sorbed SDS molecules begin to interact via hydrophobic forces to form hemimicelles (8), and the overall aggregate structure would be relatively compact with most of the hydrophobic tails directed toward the aqueous phase. As the SDS dose is further increased, bilayers can begin to form by the vertical interaction between tails (11); however, the total number of molecules in the second layer is expected to be lower than that in the first layer which contacts the kaolinite surface because of repulsion between the free headgroups. For sorbed SDS aggregates, the overall number of headgroups oriented toward the aqueous phase will be determined by the initial interac-

tions between the kaolinite surface and SDS monomers; when the solution pH is greater than the overall PZC, the fraction of headgroups oriented in this manner should be greater than when the pH is below the PZC.

Considering the SDS-kaolinite interactions described above, our sorbed surfactant partitioning results can be interpreted as partitioning to the different structures (i.e., SDS monolayers and bilayers) that likely exist on the surface. For example, SDS hemimicelles formed at pH values below the PZC have their hydrophobic tails oriented predominantly toward the aqueous phase; this results in a stronger affinity for HOCs than when the headgroups are oriented toward the aqueous phase (i.e., pH values above the PZC). As SDS doses increase and bilayers begin to form at pH values below the PZC, the number of headgroups oriented toward the aqueous phase increases, leading to less favorable interactions with HOCs. This interpretation is consistent with Edwards et al. (31), who suggested that sorbed surfactants will have a greater affinity for HOC partitioning if the hydrophobic regions are in direct contact with the bulk solution with no intervening hydrophilic groups. If our interpretation is correct, then variations in  $K_{oc}$  values for SDS will be entirely dependent on the different configurations that surface aggregates can form.

The influence of pH on phenanthrene partitioning to sorbed Tween 80 is summarized in Table 2. The Tween 80 dose for these experiments was 1.527 mM, which is well above the cmc value; therefore, Tween 80 micelles contributed to the overall phenanthrene distribution. As can be seen in Table 2,  $K_D$  values decrease with increasing pH; this trend was expected because of the decrease in Tween 80 sorption with increasing pH and the concurrent increase in the number of Tween 80 micelles. Similarly to sorbed SDS, the affinity of sorbed Tween 80 for phenanthrene can be evaluated by calculating  $K_{oc}$  values. Because of the presence of micelles, however, a mass balance that includes micelles and sorbed surfactant was required to calculate the partitioning capacity of sorbed Tween 80, expressed below as  $K_{ss}$  ( $M^{-1}$ ) (18):

$$K_D = \frac{S_{\text{sorb}}K_{ss} + K_{\text{min}}}{1 + S_{\text{mic}}K_{\text{mic}}} \quad (2)$$

where  $K_D$  is the experimental phenanthrene distribution coefficient (L/g) between the solid and apparent aqueous phases,  $S_{\text{sorb}}$  is the sorbed surfactant concentration (mol/g), and  $K_{\text{min}}$  (L/g) is the phenanthrene sorption constant to the bare kaolinite surface. Values for  $K_{ss}$  calculated from the above equation were converted to  $K_{oc}$  values using the average carbon fraction of Tween 80 (i.e., 0.548 as determined by TOC analysis). As shown in Table 2,  $K_{oc}$  values for sorbed Tween 80 are similar in magnitude to those for Tween 80 micelles (Table 1) and are approximately 10 times greater than those for natural organic matter, consistent with the results of Edwards et al. (32), who obtained relative effectiveness factors ranging from 10 to 26 for nonionic surfactants sorbed on sand.  $K_{oc}$  values for the pH conditions investigated here showed no significant differences, implying that the sorbed Tween 80 aggregates had similar structures and/or physicochemical characteristics. Further studies utilizing a wider range of pH values including those below the PZC will be necessary to verify whether this is a general property of Tween 80.

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