094860

SETAC PRESS

Environmental Toxicology and Chemistry, Vol. 15, No. 5, pp. 684–690, 1996
© 1996 SETAC
Printed in the USA
0730-7268/96 $6.00 + .00

SORPTION OF AN ALCOHOL ETHOXYLATE SURFACTANT TO NATURAL SEDIMENTS

MANUEL L. CANO* and PHILIP B. DORN
Westhollow Technology Center, Shell Development Company, Houston, Texas 77251- 1380, USA

(*Received* 24 *April* 1995; *Accepted* 17 *October* 1995)

Abstract—U.S. consumer and industrial use of surfactants results in down the drain disposal and release after treatment in septic fields or sewage plants. Effluent may contain limited concentrations of surfactant, which may remain in receiving waters, and this residual surfactant could become associated with bottom sediments. To assess this phenomenon, we have examined the sorption of a radiolabeled alcohol ethoxylate (C_{15} alcohol with an average of 9 moles of ethylene oxide per mole of alcohol) to natural sediments under sterile conditions to assure that the surfactant was not biodegraded. Control experiments comparing sterilized systems with systems including 1% formalin indicated that formalin could be included in the sediment/surfactant/water mixture to prevent surfactant biodegradation yet not interfere in the sorption process. Four sediments with 0.3–2.2% organic carbon content were used in this study to determine the effect of various sediment properties on the sorption process. Equilibrium sorption was established in 2–4 h. The equilibrium sorption isotherms were determined to be nonlinear and described by the Freundlich model, and distribution ratios (ratio of surfactant concentration on sediment to aqueous concentration) at 1 mg/L surfactant ranged from 350 to 2,100 L/kg. The amount of sorption was better correlated to the percent clay content of the sediment than to the percent organic carbon content of the sediment.

Keywords—Alcohol ethoxylate Sediment Sorption Surfactant

INTRODUCTION

Hundreds of millions of kilograms of nonionic surfactants are used annually in U.S. consumer and industrial markets. In 1991, 842 million kg of nonionic surfactants were produced in the U.S. with the most widely used being linear and essentially linear alcohol ethoxylates (AE), which represented approximately 39% of all nonionics produced [1]. The AEs are rapidly biodegradable and show low aquatic toxicity after biological treatment [2– 6]. Environmental exposure from these surfactants results mainly from residual surfactants remaining after biological treatment in municipal or industrial plants.

Because of this widespread use, residual surfactants remaining after treatment may become associated with bottom sediments after discharge of treated water. While the sorption of many nonionic organic compounds to environmental sorbents has been well studied [7,8], surfactants as a class have not been studied as extensively. Many studies have characterized the sorption of surfactants to minerals and textiles [9,10], but few studies have characterized surfactant adsorption onto environmental sorbents [11– 14]. An understanding of the sorption of surfactants to environmental sorbents is necessary to further our knowledge of the ultimate fate of these residual surfactants.

In this study we characterize the sorption of a model nonionic surfactant (an alcohol ethoxylate) to natural sediments at environmental concentrations. Results of kinetic and equilibrium experiments are used to characterize the nonionic surfactant sorption phenomenon. In addition, factors that affect the sorption process are discussed.

MATERIALS AND METHODS

Surfactant

The surfactant used in this study was a dual radiolabeled AE consisting of a 15-carbon alcohol with an average of 9 moles of ethylene oxide (EO) per mole of alcohol (AE5–9). The ethoxylate distribution was similar to that of the commercially available surfactants, NEODOL® 25-9 or NEODOL 1-9 [15]. Briefly, approximately 93 weight % had between 1 and 18 moles EO/alcohol, 5 weight % had moles EO/alcohol ≥ 19, and 2 weight % was free alcohol (no EO groups). A ^{3}H radiolabel was present primarily on the α and γ carbons of the alkyl portion and a ^{14}C label was present uniformly on the EO portion of the molecule. Figure 1 shows the dual radiolabeled AE5–9 along with the positions of the ^{3}H and ^{14}C labels. The AE5–9 was obtained from the radiolabeled surfactant inventory of Shell Development Company (Houston, TX, USA). The purity of the AE5–9 was 99% (i.e., 99 weight % of the surfactant were molecules with 15 carbons in the alkyl chain and some number of EO groups according to the distribution described above) based on thin layer chromatography methods and the specific activity was 11.5 μCi/g for ^{3}H and 6.4 μCi/g for ^{14}C. Stock solutions of AE5–9 were prepared under sterile conditions in sterile MilliQ water to a nominal concentration of 1,000 ppm. This sterile stock solution was diluted to conduct the experiments. Measured concentrations were determined by radiolabel activity.

The ^{3}H/^{14}C ratio of the AE5–9 surfactant was used to provide additional detail for experimental results. Because all of the surfactant molecules contained exactly 15 carbons in the alkyl chain, the average amount of ^{3}H was constant for each molecule. However, the EO portion of the surfactant can vary in chain length (the average EO chain length is 9). Thus, a molecule with an EO chain length of 9 would have a ^{3}H/^{14}C ratio of 1.80 based on the specific activities of the AE5–9. Changes in this ratio would indicate changes in the ethoxylate distribution. For example, a solution with a ^{3}H/^{14}C ratio of 2.70 would have an average EO chain length of 6 due to the uniform ^{14}C distribution throughout the EO portion of the molecule. This approach has been previously used to determine average EO chain lengths in AE [16].

In addition, an unlabeled AE5–9 surfactant (also obtained

* To whom correspondence should be addressed.

14601

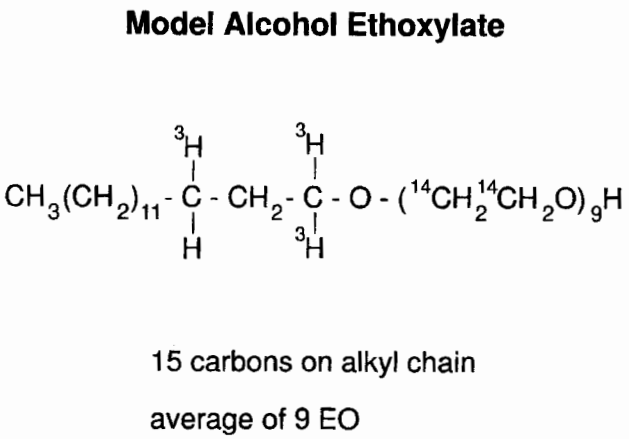

Fig. 1. Model AE used for sediment sorption experiments.

from the Shell Development Company surfactant inventory) was used for some of the desorption experiments.

Sediments and overlying water

Sediment samples were obtained from the University of Mississippi Biological Field Station (Oxford, MS, USA). Samples were collected by mini-ponar grab sampling and shipped to Shell Development Company. Sediments from this site have previously been used in studies concerning the bioavailability of fluoranthene [17]. Upon receipt, the sediments were sieved through a 2-mm sieve [18], thoroughly mixed, and assigned a sediment number. Samples were stored in sealed glass jars at room temperature. Sediment analysis and characterization performed by Soil Analytical Services Inc. (College Station, TX, USA) according to standard procedures [19,20] are shown in Table 1.

Overlying water was collected from some of the sediment sites for use in the sorption experiments. The overlying water was analyzed for pH, total hardness, total alkalinity, and total organic carbon according to standard methods [21] (Table 2).

Sterilization

Because AE are known to biodegrade [22], sterile conditions were used for the sorption experiments to ensure that the surfactant did not biodegrade during the course of an experiment. Sterile conditions represent the most conservative sorption conditions because surfactant loss due to biodegradation does not occur. Several methods of sterility were tested including autoclaving (121°C, 15–20 min for water samples, 1 h for sediment samples), irradiation (7.5 MRad; Neutron Products, Dickerson, MD, USA), and the use of 1% formalin (37% formaldehyde solution; Scientific Products, McGaw Park, IL, USA). When

Table 1. Properties of sediments

Parameter	Unit	Sediment number 1	2	3	4
Moisture	%	91.1	65.6	25.7	19.9
pH	—	4.2	4.8	5.7	4.5
Total organic carbon	%	2.8	1.6	0.3	0.2
Cation exchange capacity	meq/100 g	11.0	8.4	0.8	2.5
Sand	%	29.8	36.1	91.0	54.4
Silt	%	54.4	44.7	8.6	38.4
Clay	%	15.8	19.2	0.4	7.1

Table 2. Overlying water analytical results

Parameter	Unit	Value
pH		8.2
Total hardness	mg/L as $CaCO_3$	7
Total alkalinity	mg/L as $CaCO_3$	7
Total organic carbon	mg/L	1

autoclaving or irradiation were used to sterilize the sediments, overlying water was sterilized by autoclaving and all manipulations were conducted in a sterile hood. Sterility was tested by tube extinction dilution methods [23] using trypticase soy broth (Becton Dickinson Microbiology Systems, Cockeysville, MD, USA). In addition, ^3H and ^{14}C were also used to indicate sterility; when systems were unsterile, the recovery of ^{14}C from solution and sediment was very low due to biodegradation resulting in the formation and loss of $^{14}CO_2$. We were unsuccessful in achieving sterile conditions by autoclaving sediment samples. Irradiation was only successful if the quantity of sediment irradiated in a container was small (<0.5 g). However, the use of 1% formalin always resulted in a sterile system. Experiments using formalin were less difficult because it was not necessary to work in a sterile environment. To test if the presence of formalin would affect the AE5–9 sorption process, we compared the rate and amount of sorption for experiments conducted with 1% formalin or with irradiated sediment and autoclaved water. A sample equilibrium experiment is shown in Figure 2. We did not find a statistically significant difference in the sorption process between the two sterility methods. Thus, most of the results presented are from experiments conducted in the presence of 1% formalin.

Kinetic and equilibrium sorption experiments

Kinetic experiments were carried out in 35-ml glass centrifuge tubes by adding a known mass of sediment (typically 100 mg dry weight) to 25 ml of surfactant solution (10 mg/L AE5–

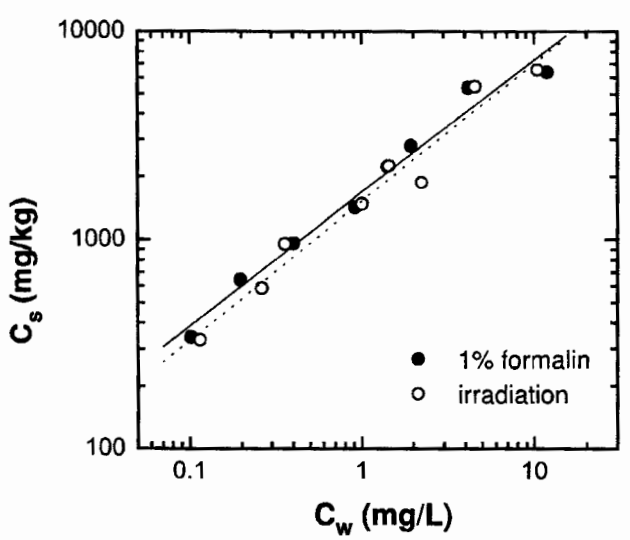

Fig. 2. Equilibrium sorption isotherms for AE5–9 sorption to Sediment 2 using 1% formalin (closed circles) or irradiation (open circles) as the sterilization technique. The Freundlich parameters (and their 95% confidence intervals) for the two fits were K = 3.22 [3.15, 3.29] or 3.17 [3.10, 3.26] and n = 0.64 [0.54, 0.74] or 0.66 [0.54, 0.79] for the experiments with 1% formalin or with irradiation, respectively.

9) containing 1% formalin. The sediment concentration was typically 4 g/L. Sorption experiments were performed as follows: mixtures were shaken vigorously and placed on a tumbler for various times (0–24 h) before they were centrifuged for 30 min at 2,500 rpm (864 *g*) in a Sorvall RT6000 centrifuge (Dupont, Newtown, CT, USA) to separate the water from the sediment. After the supernatant was removed, water and sediment samples were analyzed to determine the concentrations of AE5–9 in the water and in the sediment as described below.

Desorption experiments were carried out using a similar procedure. Sediment/water/surfactant (0.1 g, 25 ml, 10 mg/L) samples were first placed on a tumbler for ≥24 h to ensure that equilibrium was established (see Results). The equilibrated surfactant solution was then removed, and desorption was initiated by either adding an equal volume of solution containing a higher concentration (500 mg/L) of unlabeled AE5–9 or by diluting the sediment pellet with a large volume (1 L) of overlying water. These samples were again placed on a tumbler for various times (0–24 h) before they were centrifuged as described above to separate the water from the sediment. After the supernatant was removed, water and sediment samples were analyzed to determine the concentrations of AE5–9 in the water and in the sediment as described below.

Equilibrium experiments (to determine sorption isotherms) were conducted by adding a known mass of sediment (typically 100 mg dry weight) to 25 ml of surfactant solution (0.1–20 mg/L) containing 1% formalin. Mixtures were shaken vigorously and placed on a tumbler for 24–48 h (kinetic experiments indicated equilibrium was achieved within 24 h; see Results) before they were centrifuged as described above to separate the water from the sediment.

All experiments were conducted at ambient temperature (20–23°C). The pH of the experimental systems (surfactant/sediment/water slurries) ranged from 7.9 to 8.2. These values were established when the overlying water containing AE5–9 was mixed with the sediments.

Surfactant measurements

The concentration of AE5–9 in the water was determined by taking an aliquot (4 ml) of the supernatant and combining it with 15 ml Ultima Gold™ scintillation cocktail (Packard Instrument Company, Downers Grove, IL, USA). The resulting solution was counted in a Packard 2500 TR liquid scintillation counter (Packard Instrument Company) and the specific activity of the dual radiolabeled AE5–9 was used to calculate the aqueous concentration. Aqueous concentrations were calculated based on ^{3}H and ^{14}C counts.

The concentration of AE5–9 in the sediment pellet was determined as follows: The sediment pellet was combusted in a Packard 306 oxidizer (Packard Instrument Company) for 3 min. Following combustion, $^{14}CO_2$ formed was trapped using a mixture of 9 ml Carbo-Sorb® solution and 14 ml Permafluor® V scintillation fluid, and the $^{3}H_2O$ formed was trapped using 15 ml Packard Monophase S solution. Carbo-Sorb, Permafluor V, and Monophase S were obtained from Packard Instrument Company. The ^{14}C and ^{3}H activity of these samples was determined by liquid scintillation counting and used to calculate the mass of AE5–9 bound to sediment. Masses were calculated based on ^{3}H and ^{14}C counts. Percent total recovery ranged from 85 to 100% based on ^{3}H or ^{14}C counts.

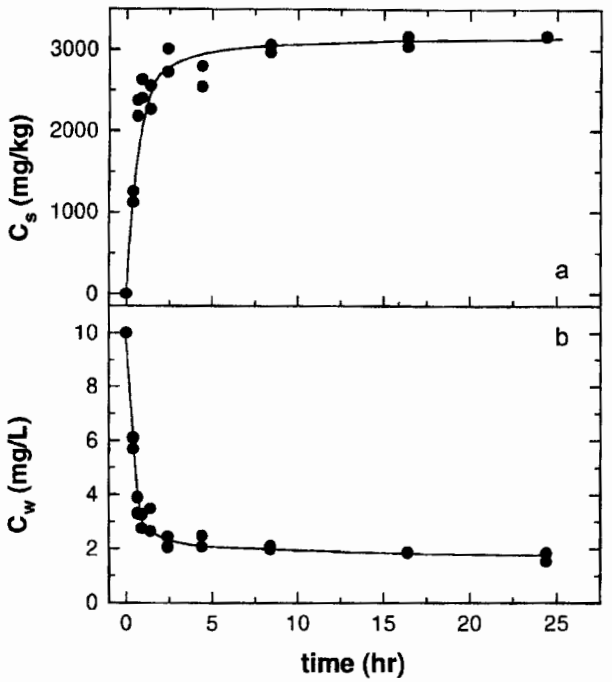

Fig. 3. Sorption kinetics of AE5–9 to Sediment 1. Sorption was measured by following the increase of AE5–9 based on ^{14}C counts on the sediment (**a**) or by following the decrease of AE5–9 based on ^{14}C counts in solution (**b**).

RESULTS

Kinetics of sorption and desorption

Experiments were conducted to quantify the rate with which the AE5–9 surfactant would sorb to natural sediments. A sorption time course for an experiment with Sediment 1 is shown in Figure 3. The sorption process was followed by measuring increases in AE5–9 concentration on the sediment (Fig. 3a) as well as the corresponding losses in solution (Fig. 3b). Sorption occurred rapidly, with greater than 90% of the equilibrium sorption occurring within 2–4 h. Equilibrium sorption was established within 24 h. Rapid equilibrium times have been observed for nonionic surfactants binding to sediments and soils [11,24].

Desorption of AE5–9 from natural sediments was also studied to determine if the sorption process was reversible. Two types of desorption experiments were performed: (1) competition experiments with unlabeled AE5–9 and (2) dilution experiments. Results from a competition experiment are shown in Figure 4. After equilibrium sorption was established by mixing the sediment/water/surfactant slurries for 24 h, the equilibrated surfactant solution was removed, and a solution containing a 50-fold excess of unlabeled AE5–9 was added to the centrifuge tubes. The large excess of unlabeled AE5–9 was able to displace the bound labeled AE5–9 indicating that the original AE5–9 was not irreversibly bound. More than 90% of the equilibrium amount sorbed was desorbed from the sediment within 2–4 h. Dilution experiments were performed by diluting the sediment/water/surfactant slurry 10-fold with pond water. These results were similar to those of Figure 4. These two types of experiments indicate that the sorption/desorption process is rapid and reversible.

Equilibrium sorption isotherms

Equilibrium sorption experiments were conducted with all four sediments. Sediment/water/surfactant slurries were allowed

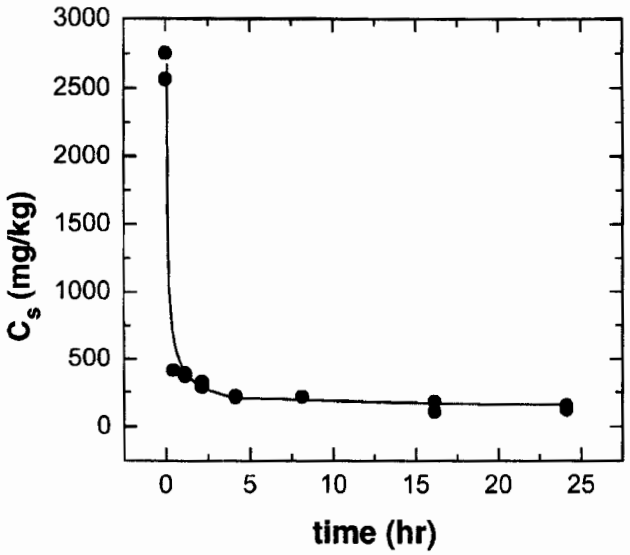

Fig. 4. Desorption kinetics of AE5–9 from Sediment 1. After equilibrium was established by mixing the sediment/water/surfactant slurries for 24 h, the equilibrated surfactant solution was removed and a solution containing a 50-fold excess of unlabeled AE5–9 was added to the system. Desorption was measured by following the decrease in radiolabeled AE5–9 on the sediment.

to equilibrate for at least 24 h before the waters and the sediments were separated by centrifugation. AE5–9 concentrations were measured in the water and on the sediment to determine equilibrium sorption isotherms based on ^{3}H and ^{14}C counts. In all cases, the sorption isotherms were best described by a Freundlich isotherm model [25]:

$$C_s = KC_w^n \quad (1)$$

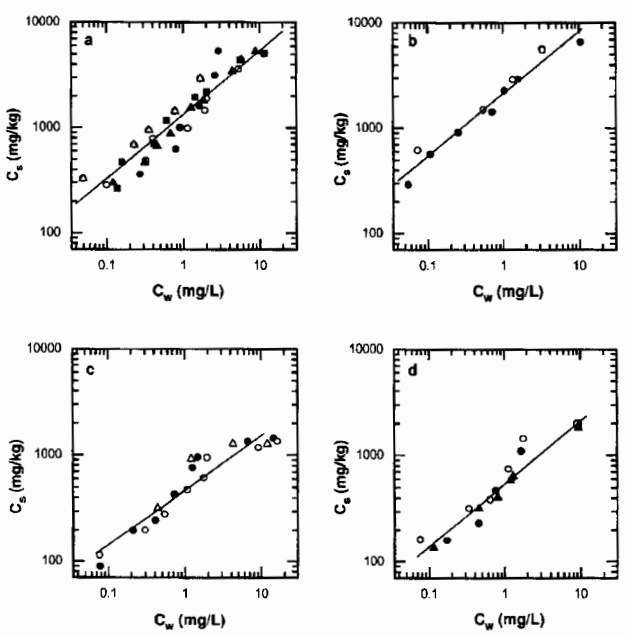

Fig. 5. Equilibrium sorption isotherms for AE5–9 sorbing to Sediments 1 (**a**), 2 (**b**), 3 (**c**), and 4 (**d**). Data are plotted based on ^{3}H counts and the lines represent the Freundlich parameter fits summarized in Table 3. For each sediment, different symbols indicate separate experiments. All of these experiments were conducted with a particle concentration of 4 g/L.

Table 3. Summary of Freundlich parameters[a] for equilibrium sorption isotherms

Basis[b]	Sediment number	K (L/kg)	n	r[c]
^{3}H	1	1,300	0.61	0.96
	2	2,100	0.59	0.98
	3	470	0.51	0.95
	4	540	0.59	0.98
^{14}C	1	990	0.69	0.97
	2	1,700	0.65	0.99
	3	350	0.58	0.92
	4	510	0.53	0.97

[a]Parameters, K and n, were determined by least-squares fitting using Equation 1.
[b]Surfactant concentrations were calculated using either ^{3}H or ^{14}C specific activity as a basis.
[c]Correlation coefficient from least-squares fit of Equation 1.

where C_s is the concentration of AE5–9 on the sediment (mg AE5–9/kg dry sediment), C_w is the concentration of AE5– 9 in solution (mg/L), K is a Freundlich constant (L/kg), and n represents the nonlinearity of the sorption isotherm. For linear sorption isotherms $n = 1$.

Equilibrium sorption isotherms for AE5–9 sorbing to all four sediments are shown in Figure 5. All of the data (two to five experiments per sediment) were used to determine a sorption isotherm (by least squares fitting of Eqn. 1) for each sediment (Fig. 5a–d). All of the isotherms were nonlinear (n = 0.51–0.69). Because a dual radiolabeled surfactant was used in these studies, it was possible to calculate Freundlich parameters using least-squares fitting based on concentrations determined from either ^{3}H counts or ^{14}C counts. Only data based on ^{3}H counts are shown in Fig. 5 (data based on ^{14}C counts is slightly shifted); however, all of the parameters (based on ^{3}H or ^{14}C counts) are given in Table 3. The Freundlich constant, K, ranged from 470 to 2,100 L/kg based on ^{3}H and from 350 to 1,700 L/kg based on ^{14}C while n ranged from 0.51 to 0.61 based on ^{3}H and from 0.53 to 0.69 based on ^{14}C.

As mentioned in the Materials and Methods, the ratio of ^{3}H to ^{14}C provides an indication of the average EO chain length of the surfactant. Average EO chain lengths in solution and sorbed to the sediment based on ratios of ^{3}H/^{14}C are given in Table 4. Based on the isotherms described by the parameters in Table 3, after equilibrium had been established, the average EO chain length for sorbed surfactant was 8.3 and the average EO chain length remaining in solution was 11.4. The characteristics of the sediment had little effect on the distribution of EO groups between the solution and the sediment; however, there was a measurable change in the average distributions. The more hydrophilic compounds that had longer EO chain lengths (smaller

Table 4. Average EO chain lengths of the AE in solution and sorbed to sediment under equilibrium conditions

Sediment	Average number of EO groups per AE molecule in solution	Average number of EO groups per AE molecule sorbed to sediment
1	11.4	8.1
2	12.7	8.4
3	11.3	8.1
4	10.1	8.5

$^3H/^{14}C$) tended to sorb less. This preferential sorption for the shorter EO chain lengths should be taken into account when considering the sorption of a surfactant with a range of EO chain lengths.

A distribution ratio, D, can be defined for any sorption equilibrium condition:

$$D = \frac{C_s}{C_w} \quad (2)$$

Because the equilibrium sorption isotherms were nonlinear, D varies with C_w, thereby complicating the comparison of isotherms for various sediments. Equations 1 and 2 may be combined to express the distribution ratio as a function of the aqueous surfactant concentration:

$$D = KC_w^{n-1} \quad (3)$$

To make comparisons for sorption to different sediments, a specific distribution ratio, D_1, can be defined when $C_w = 1$ mg/L. Equation 3 indicates that $D_1 = K$. This specific ratio, D_1, will be used for the comparison described below.

Sediment characteristics affecting sorption

The four sediments used in this study spanned a wide range of sediment characteristics. The organic carbon content ranged from 0.2 to 2.8%, the percent sand ranged from 29.8 to 91.0, the percent silt ranged from 8.6 to 54.4, and the percent clay ranged from 0.4 to 19.2. These sediments are representative of many of the sediments found in the United States [26].

We examined the effect of sediment organic carbon and percent clay on the sorption of AE5–9. For many nonionic chemicals, the amount of sorption correlates very well with the percent organic carbon for sediments having ≥0.2% organic carbon. This process has been studied extensively [7,8] and has become the basis for the equilibrium partitioning approach, which is currently being applied in the determination of sediment quality criteria [27]. However, the amount of AE5–9 sorption (as defined by D_1) to this set of natural sediments did not correlate with the percent organic carbon (correlation coefficient, $r = 0.61$; $p = 0.38$; Fig. 6). This suggests that the sorption of this nonionic AE surfactant may not follow the equilibrium partitioning model and another model may be more suitable to describe this process.

The amount of sorption (as defined by D_1) did correlate with the percent clay in the sediment ($r = 0.93$; $p = 0.06$; Fig. 7). This result has been previously observed in the studies of Brownawell et al. [11]. The forces involved in this type of interaction may facilitate the sorption of the surfactant to sediments with higher amounts of clay.

Effect of particle concentration

The effect of particle concentration on the sorption process has been studied by many investigators [8,12,14,28,29]. Generally, they conclude that under some conditions, the amount of sorption is less when the particle concentration increases. These results may be due to a greater frequency of particle–particle interactions, which may lead to a lower sorption equilibrium. Severtson and Banerjee [30] provide a mechanism and thermodynamic support for a collision model, which leads to increased desorption from particle–particle interactions.

We examined whether the particle concentration effect occurred in our experimental system by conducting equilibrium sorption experiments with Sediment 1 at sediment concentrations ranging from 2 to 24 g/L. These isotherms are plotted in Figure 8. The AE5–9 partitioned to a higher degree in the sediment at the lower particle concentrations. This result is demonstrated in Figure 9, which shows the specific distribution ratio (D_1) resulting from a Freundlich model fit to the data in Figure 8 as a function of the sediment concentration in the experiment. The specific distribution ratio (D_1) decreases as the particle concentration increases. While this effect may have been due to particle–particle interactions, it is also possible that it may have been caused by the presence of colloidal materials in the experimental systems. These colloids may have not been effectively separated by centrifugation. Nevertheless, particle effects

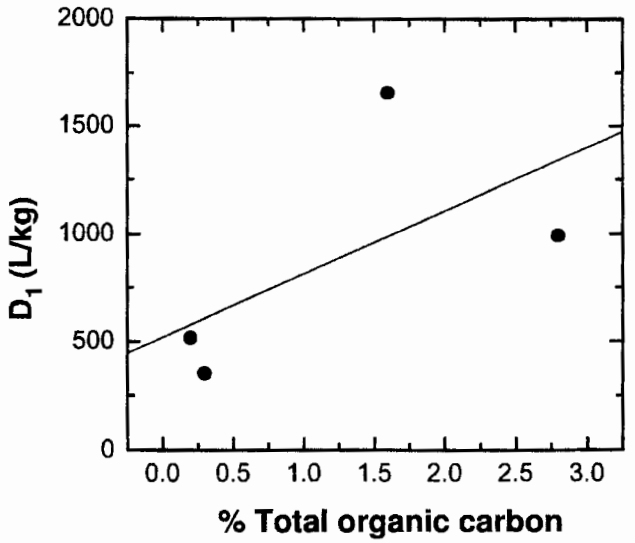

Fig. 6. Effect of sediment organic carbon on the sorption of AE5–9 to four natural sediments. The specific distribution ratios (D_1) from the Freundlich parameters for the four sediments are plotted as a function of sediment organic carbon. The line represents the best fit linear least-squares model for D_1 as a function of sediment organic carbon.

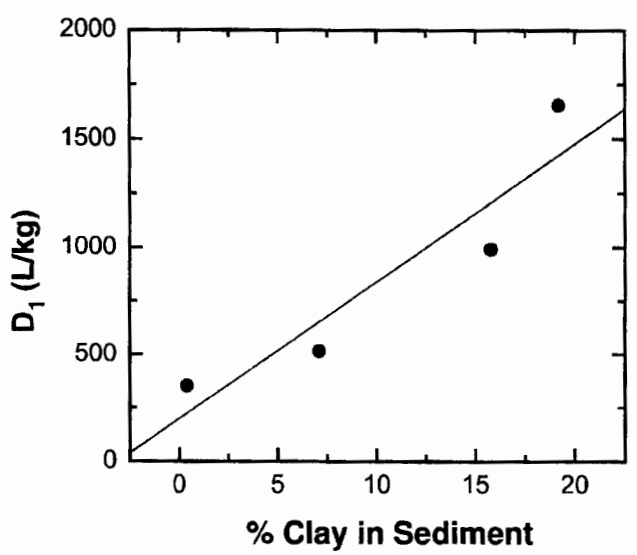

Fig. 7. Effect of sediment clay content on the sorption of AE5–9 to four natural sediments. The specific distribution ratios (D_1) from the Freundlich parameters for the four sediments are plotted as a function of sediment clay content. The line represents the best fit linear least squares model for D_1 as a function of sediment clay content.

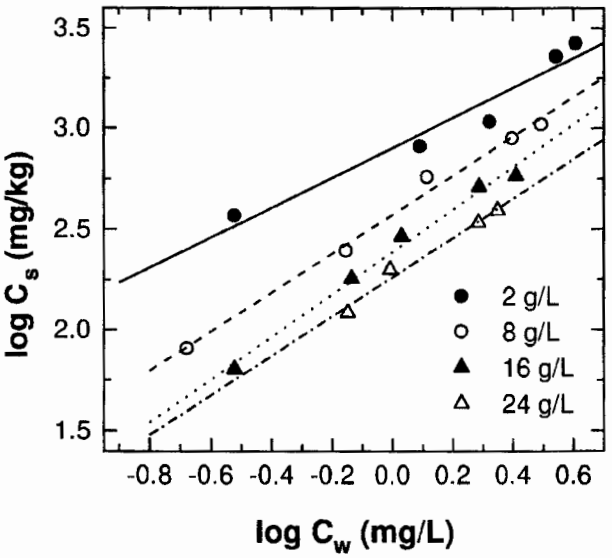

Fig. 8. Equilibrium sorption isotherms for AE5–9 sorbing to Sediment 1 at varying particle concentrations. Equilibrium experiments were carried out using four different particle concentrations (2, 8, 16, and 24 g/L sediment). Data and the best fit Freundlich isotherms are plotted for each particle concentration.

may result in varying distribution ratios for surfactant sediment sorption.

Particle concentrations in the environment can range from 10 mg/L for solids in suspension in rivers and estuaries to 10 g/L for the lower limits in the beds of natural water systems [28]. Thus, the concentrations used in our experiments are similar to those observed for the lower limits in the beds of natural water systems. Higher particle concentrations may result in even less sorption. This particle interaction effect should be considered and may make it difficult to model sorption under actual field conditions.

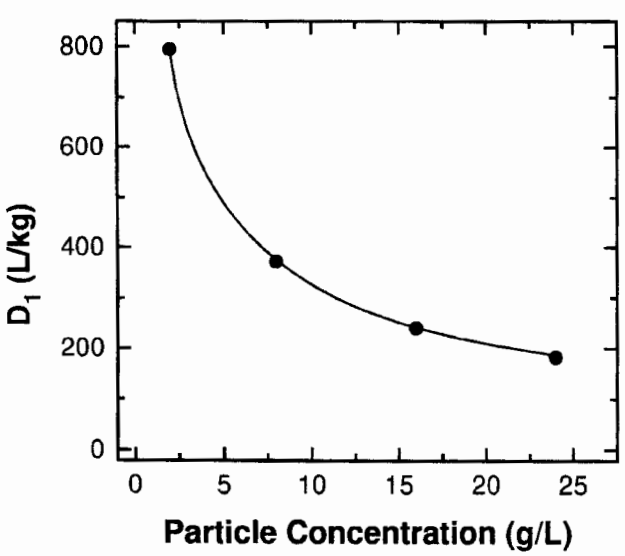

Fig. 9. Effect of particle concentration on the sorption of AE5–9 to Sediment 1. The specific distribution ratio (D_1) from each of the isotherms of Figure 8 is plotted as a function of the particle concentration.

DISCUSSION

Equilibrium sorption isotherms are nonlinear

The sorption isotherms determined from our equilibrium experiments were nonlinear and could be described by the Freundlich model. Other investigators [11,13] have also observed nonlinear sorption isotherms for AEs sorbing to natural sediments. Urano et al. [13] did not attempt to sterilize their systems while Brownawell et al. [11] used azide as a sterilizing agent. The amount of sorption (as measured by D_1) ranged from 350 to 2,100 L/kg in this study and from 2.2 to 720 L/kg in other studies [11,13]. The nonlinearity of the isotherms is described by the Freundlich parameter, n. We observed n in the range of 0.51–0.69 while other investigators [11,13] observed 0.63–0.91. These other studies were conducted using different sediments and different AE surfactants. Even though all of these studies were conducted with a wide range of experimental systems, the data indicate that the sorption of AE to natural sediments cannot be described by a linear adsorption isotherm even at very low AE concentrations. In addition, AE do not appear to sorb strongly to natural sediments under any of these conditions. These data, however, may be used to estimate the amount of surfactant that may become associated with bottom sediments under conditions where biodegradation will not occur.

Equilibrium partitioning theory does not describe the sorption of AE to natural sediments

For many nonionic chemicals, the amount of sorption correlates with the percent organic carbon in sediments having ≥0.2% organic carbon. Many investigators have studied this process [7,8]. This phenomenon has been used to derive the equilibrium partitioning approach, which attempts to use organic carbon normalization to describe the sorption of nonionic compounds to sediments in order to account for the sorption variability observed when using different sediments. This approach has been applied and used to determine sediment quality criteria for several nonionic compounds [27,31,32]. Our data and that of others [11,13] suggest that this simplified approach is not suitable for AE surfactants. The sorption process appears to be much more complicated. Rather than sorption simply being correlated to the percent organic carbon of the sediment, other factors such as the nonlinearity of the sorption isotherm and the percent clay of the sediment may affect the amount of sorption. In addition, the heterogeneity of typical AE surfactants also complicates the sorption process. Thus, it may not be appropriate to use the equilibrium partitioning approach to model the sorption of AE surfactants.

AE surfactants in the sediment environment

We observed the sorption of this AE to natural sediments to be rapid and reversible. These sorption properties suggest that AE surfactants are not likely to accumulate in the sediment environment although this may not be true for AE with a low number of EO groups. The AEs have been shown to be rapidly degradable and evidence exists for three degradation pathways: central fission, separating the hydrophilic and hydrophobic groups; attack at the terminal end of the alcohol chain; and attack at the terminal end of the EO chain [6,22]. Only one of these pathways could result in AE with shorter EO chain lengths that may bind tightly to sediments.

Biodegradation of AE is known to occur in solution, but it is not clear if sorbed surfactant can biodegrade. Because the sorption process appears to be reversible, in the environment,

as the AE in solution naturally degrades, a driving force would be established for the sorbed AE to desorb from the sediment. This AE would then be able to biodegrade. Dilution of sediments could also lead to desorption, which would enable the AE to biodegrade in solution. Additional experimental work would be necessary to quantify the competition between the sorption and biodegradation processes. These types of experiments could be conducted under nonsterile conditions to determine that sorbed AE can biodegrade either on the sediment or in solution following desorption from sediments.

In summary, we have measured the sorption of a model AE to a series of natural sediments under sterile conditions. Data from our sorption experiments indicated that the sorption process was rapid and reversible with equilibrium being established in 2–4 h. The equilibrium sorption isotherms were nonlinear and best described by the Freundlich model and the amount of sorption was better correlated to the percent clay content of the sediment than to the percent organic carbon content of the sediment.

Acknowledgement—We thank Tim E. Vipond, Sharon R. Fruge, and Jay Postlewaite for technical assistance with the experimental work and Lou Kravetz for many helpful discussions. We also thank the University of Mississippi for providing us with the sediment and overlying water samples.

REFERENCES

1. **U.S. International Trade Commission.** 1991. Synthetic organic chemicals, United States production and sales, 1991. USITC Publication 2607. Washington, DC.
2. **Turner, A.F., F.S. Abram, V.M. Brown** and **H.A. Painter.** 1985. The biodegradability of two primary alcohol ethoxylate nonionic surfactants under practical conditions, and the toxicity of the biodegradation products to rainbow trout. *Water Res.* **19**:45–51.
3. **Maki, A.W., A.J. Rubin, R.M. Sykes** and **R.L. Shank.** 1979. Reduction of nonionic surfactant toxicity following secondary treatment. *J. Water Pollut. Control Fed.* **51**:2301–2313.
4. **Yoshimura, K.** 1986. Biodegradation and fish toxicity of nonionic surfactants. *J. Am. Oil Chem. Soc.* **63**:1590–1596.
5. **Dorn, P.B., J.P. Salanitro, S.H. Evans** and **L. Kravetz.** 1993. Assessing the aquatic hazard of some branched and linear nonionic surfactants by biodegradation and toxicity. *Environ. Toxicol. Chem.* **12**:1751–1762.
6. **Talmadge, S.S.** 1994. *Environmental and Human Safety of Major Surfactants: Alcohol Ethoxylates and Alkylphenol Ethoxylates.* Lewis, Boca Raton, FL, USA.
7. **Karickhoff, S.W.** 1984. Organic pollutant sorption in aquatic systems. *J. Hydraul. Eng.* **110**:707–735.
8. **DiToro, D.M.** 1985. A particle interaction model of reversible organic chemical sorption. *Chemosphere* **14**:1503–1538.
9. **Hough, D.B.** and **H.M. Rendall.** 1983. Adsorption of ionic surfactants. In G.D. Parfitt and C.H. Rochester, eds., *Adsorption from Solution at the Solid/Liquid Interface.* Academic, New York, NY, USA, pp. 247–319.
10. **Clunie, J.S.** and **B.T. Ingram.** 1983. Adsorption of nonionic surfactants. In G.D. Parfitt and C.H. Rochester, eds., *Adsorption from Solution at the Solid/Liquid Interface.* Academic, New York, NY, USA, pp. 105–152.
11. **Brownawell, B.J., H. Chen, W. Zhang** and **J.C. Westall.** 1991. Adsorption of surfactants. In R. Baker, ed., *Organic Substances in Sediments and Water.* Lewis, Chelsea, MI, USA, pp. 127–147.
12. **DiToro, D.M., L.J. Dodge** and **V.C. Hand.** 1990. A model for anionic surfactant sorption. *Environ. Sci. Technol.* **24**:1013–1020.
13. **Urano, K., M. Saito** and **C. Murata.** 1984. Adsorption of surfactants on sediments. *Chemosphere* **13**:293–300.
14. **Hand, V.C., R.A. Rapaport** and **R.H. Wendt.** 1990. Adsorption of dodecyltrimethylammonium chloride (C_{12}TMAC) to river sediment. *Environ. Toxicol. Chem.* **9**:467–471.
15. **Shell Chemical Company.** 1994. NEODOL® product guide for alcohols, ethoxylates, and derivatives. SC 7-94, Houston, TX, USA.
16. **Gordon, B.E.** and **W.T. Shebs.** 1969. Sorption and rinsability of a nonionic surfactant under realistic laundering conditions. A radiotracer approach. *Proceedings,* International 5th Congress on Surface Active Substances, Vol. 3, Barcelona, Spain, September 9–13, 1968, pp. 155–168.
17. **Suedel, B.C., J.H. Rodgers, Jr.** and **P.A. Clifford.** 1993. Bioavailability of fluoranthene in freshwater sediment toxicity tests. *Environ. Toxicol. Chem.* **12**:155–165.
18. **American Society for Testing and Materials.** 1980. Standard practice for preparation of sediment samples for chemical analysis. D 3976-80. In *Annual Book of ASTM Standards,* Vol. 11.02—Water(II). Philadelphia, PA, USA, pp. 625–627.
19. **Plumb, R.H., Jr.** 1981. Procedures for handling and chemical analysis of sediment and water samples. Technical report. EPA/CE-81-1. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS, USA.
20. **Page, A.L.** 1982. *Methods of Soil Analysis. Part 1: Chemical and Microbiological Properties,* 2nd ed. Agronomy Monograph 9. American Society of Agronomy and Soil Science Society of America, Madison, WI, USA.
21. **American Public Health Association, American Water Works Association, and Water Pollution Control Federation.** 1989. *Standard Methods for the Examination of Water and Wastewater,* 17th ed. American Public Health Association, Washington, DC, USA.
22. **Swisher, R.D.** 1987. *Surfactant Biodegradation,* 2nd ed. Marcel Dekker, New York, NY, USA, pp. 476–497.
23. **Meynell, G.G.** and **E. Meynell.** 1970. *Theory and Practice in Experimental Bacteriology,* 2nd ed. Cambridge University Press, London, UK, pp. 185–196.
24. **Valoras, N., J. Letey** and **J.F. Osborn.** 1969. Adsorption on nonionic surfactants by soil materials. *Soil Sci. Soc. Am. Proc.* **33**: 345–348.
25. **Freundlich, H.** 1925. *The Elements of Colloidal Chemistry.* (Translated by G. Barger.) Methuen & Col, London, UK.
26. **Suedel, B.C.** and **J.H. Rodgers, Jr.** 1991. Variability of bottom sediment characteristics of the continental United States. *Water Res. Bull.* **27**:101–109.
27. **DiToro, D.M., et al.** 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ. Toxicol. Chem.* **10**:1541–1583.
28. **O'Connor, D.J.** and **J. Connolly.** 1980. The effect of concentration of adsorbing solids on the partition coefficient. *Water Res.* **14**:1517–1523.
29. **Scamehorn, J.F., R.S. Schechter** and **W.H. Wade.** 1982. Adsorption of surfactants on mineral oxide surfaces from aqueous solutions I: Isomerically pure anionic surfactants. *J. Colloid Interface Sci.* **85**:463–478.
30. **Severtson, S.J.** and **S. Banerjee.** 1993. Mechanistic model for collisional desorption. *Environ. Sci. Technol.* **27**:1690–1692.
31. **U.S. Environmental Protection Agency.** 1993. Guidelines for developing site-specific sediment quality criteria for the protection of benthic organisms. EPA-822-R-93-017. Office of Water, Washington, DC.
32. **U.S. Environmental Protection Agency.** 1993. Technical basis for deriving sediment quality criteria for nonionic organic contaminants for the protection of benthic organisms by using equilibrium partitioning. EPA-822-R-93-011. Office of Water, Washington, DC.