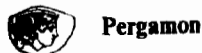**Pergamon**

PII: S0045-6535(96)00240-8

SORPTION OF TWO MODEL ALCOHOL ETHOXYLATE SURFACTANTS TO SEDIMENTS

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ABSTRACT

We have examined the sorption of two radiolabeled alcohol ethoxylate surfactants (AE) (C13 alcohols with exactly 3 or 9 moles of ethylene oxide (EO) per mole of alcohol) to natural sediments. Formalin was included in the sediment/surfactant/water mixtures to prevent biodegradation. Four sediments with 0.3 to 2.2 % organic carbon content were used in equilibrium experiments to determine the effect of various sediment properties and EO chain length on the sorption process. The equilibrium sorption isotherms were determined to be non-linear 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 110 to 590 L/kg. These distribution ratios indicated that the AEs did not sorb strongly to the tested sediments. 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.

INTRODUCTION

Hundreds of millions of kilograms of nonionic surfactants are used annually in U.S. consumer and industrial markets. In 1991, 842 million kilograms 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]. 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 [11-15]. An understanding of the sorption of surfactants to environmental sorbents is necessary to further our knowledge of the ultimate fate of these residual surfactants. Since AEs represent such a large fraction of the surfactant market, it is important to characterize these processes for AEs in order to better understand their environmental fate. A previous study characterized the sorption of another model AE (C15 alcohol with an average of 9 moles of ethylene oxide (EO) per mole of alcohol; AE5-9) to natural sediments [15]. To further understand the AE sorption process in the sediment compartment, we have conducted additional experiments described below.

In this study we examine the effect of EO chain length on sorption by comparing two model AE surfactants with different EO chain lengths (3 or 9 EO per mole of alcohol). Equilibrium sorption isotherms were determined for these interactions. In addition, factors which affect the sorption process are discussed.

MATERIALS AND METHODS

Surfactants

The surfactants used in this study were radiolabeled alcohol ethoxylates (AE) consisting of 13 carbon alcohols with exactly 3 or 9 moles of ethylene oxide (EO) per mole of alcohol (AE-3 or AE-9). These surfactants have been used in a previous sediment sorption study [11]. The molecular weights are 332 and 596 daltons for the AE-3 and AE-9 respectively. A ^{14}C label was present uniformly on the EO portion of each molecule. Fig. 1 shows the radiolabeled AE-3 and AE-9 along with the position of the ^{14}C label. The AE-3 and AE-9 were obtained from the radiolabeled surfactant inventory of Shell Development Company (Houston, TX). The purity of these surfactants was 95-98% based on thin liquid chromatography methods and the specific activity was 6.9 mCi/mmole for AE-3 and 6.6 mCi/mmole for AE-9. Stock solutions were prepared under sterile conditions in sterile MilliQ water to a nominal concentration of 1000 mg/L. These sterile stock solutions were diluted to conduct the experiments. Measured concentrations were determined by radiolabel activity.

Sediments and overlying water

Sediment samples were obtained from the University of Mississippi Biological Field Station (Oxford, MS). Samples were collected by mini-ponar grab sampling and shipped to Shell Development Company. Sediments from

AE-3   MW = 332   AE-9   MW = 596

$$CH_3(CH_2)_{12}\text{-}O\text{-}(^{14}CH_2{}^{14}CH_2O)_3H \qquad CH_3(CH_2)_{12}\text{-}O\text{-}(^{14}CH_2{}^{14}CH_2O)_9H$$

Figure 1: Model alcohol ethoxylates used for sediment sorption experiments.

this site have previously been used in studies concerning the bioavailability of fluoranthene [16]. Upon receipt, the sediments were sieved through a 2 mm sieve [17], 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) according to standard procedures [18,19] are shown in Table 1.

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

Overlying water was collected from one 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 [20] (Table 2).

Sterilization

Since alcohol ethoxylates are known to biodegrade [21], 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.

Table 2: Overlying water analytical results.

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

Previous experiments with the AE5-9 surfactant indicated that the use of 1% formalin (37% formaldehyde solution, Scientific Products, McGaw Park, IL) resulted in a sterile system without altering the sorption of the surfactant [15]. Thus, the results presented in this study are from experiments conducted in the presence of 1 % formalin.

Equilibrium sorption experiments

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 (a range of 0.01 to 20 mg/L) containing 1 % formalin. Mixtures were shaken vigorously and placed on a tumbler for 24 to 48 hr. Kinetic experiments from a previous study [15] indicated equilibrium was achieved within 24 hr. The samples were then centrifuged for 30 min at 2500 RPM (864 x g) in a Sorvall RT6000 centrifuge (Dupont, Newtown, CT) to separate the water from the sediment. After the supernatant was removed, water and sediment samples were analyzed to determine the concentrations of surfactant in the water and in the sediment as described below.

All experiments were conducted at ambient temperature (20 to 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 AE-3 or AE-9 was mixed with the sediments.

Surfactant measurements

The concentration of AE-3 or AE-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). The resulting solution was counted in a Packard 2500 TR liquid scintillation counter (Packard Instrument Company, Downers Grove, IL) and the specific activity of the radiolabeled AE-3 or AE-9 was used to calculate the aqueous concentration. Aqueous concentrations were calculated based on ^{14}C counts.

The concentration of AE-3 or AE-9 in the sediment pellet was determined as follows: The sediment pellet was combusted in a Packard 306 oxidizer (Packard Instrument Company, Downers Grove, IL) 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. Carbo-Sorb® and Permafluor® V were obtained from Packard Instrument Company (Downers Grove, IL). The ^{14}C activity of these samples was determined by liquid scintillation counting and used to calculate the mass of AE-3 or AE-9 bound to sediment.

Percent total recovery ranged from 85-110% based on ^{14}C counts.

RESULTS

Equilibrium sorption isotherms

Equilibrium sorption experiments were conducted with both surfactants and four sediments. Sediment/water/surfactant slurries were allowed to equilibrate for at least 24 hr before the waters and the sediments were separated by centrifugation. Surfactant concentrations were measured in the water and on the sediment to determine equilibrium sorption isotherms based on ^{14}C counts. In all cases, the sorption isotherms were best described by a Freundlich isotherm model [22]:

$$C_s = KC_w{}^n \tag{1}$$

where C_s is the concentration of AE-3 or AE-9 on the sediment (mg surfactant/kg dry sediment), C_w is the concentration of AE-3 or AE-9 in solution (mg/L), K is a Freundlich constant (L/kg), and n represents the non-linearity of the sorption isotherm. For linear sorption isotherms n = 1.

Equilibrium sorption isotherms for AE-3 sorbing to all four sediments are shown in Fig. 2. All of the data for one sediment (3 experiments per sediment) were used to determine a sorption isotherm (by least squares fitting of Equation (1)) for that sediment (Figs. 2a-d). All of the isotherms were slightly non-linear (n = 0.83-0.97). The Freundlich constant, K, ranged from 110 to 500 L/kg while n ranged from 0.83 to 0.97. All of the parameters for the Freundlich isotherms for AE-3 sorption are given in Table 3.

Equilibrium sorption isotherms for AE-9 sorbing to all four sediments are shown in Fig. 3. All of the data for one sediment (3 experiments per sediment) were used to determine a sorption isotherm (by least squares fitting
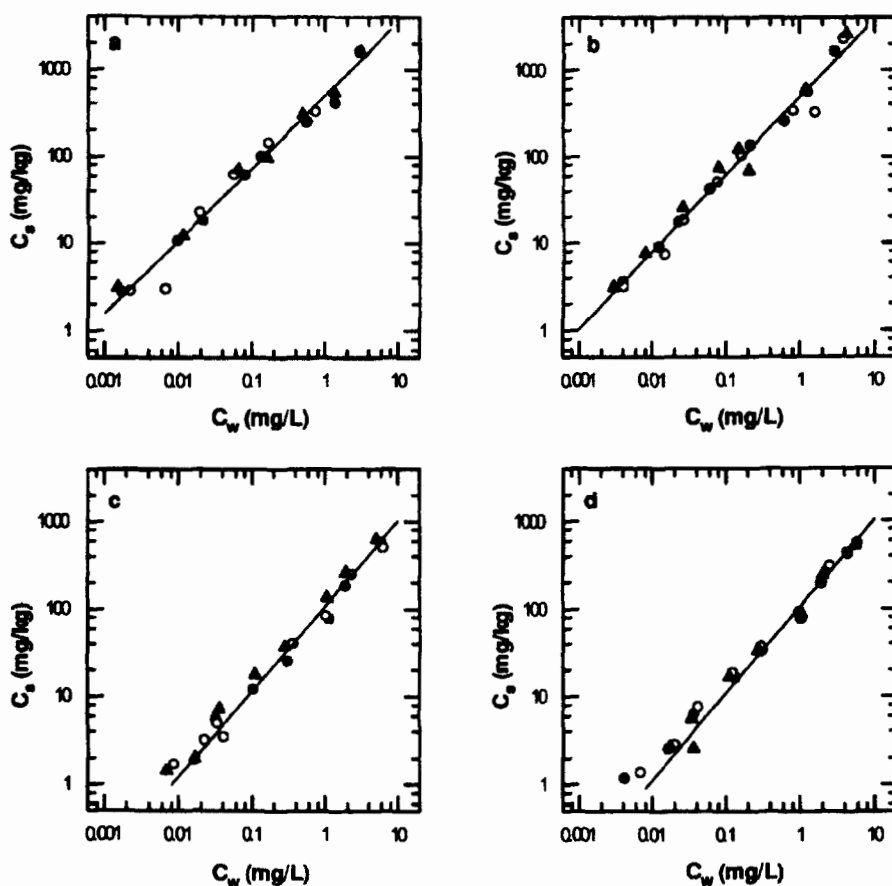
Figure 2: Equilibrium sorption isotherms for AE-3 sorbing to Sediments 1 (a), 2 (b), 3 (c), and 4 (d). Data are plotted based on ^{14}C counts and the lines represent the Freundlich parameter fits summarized in Table 3. For each sediment, different symbols indicate separate experiments. All of these experiments were conducted with a particle concentration of 4 g/L.

of Equation (1)) for that sediment (Figs. 3a-d). All of the isotherms were non-linear (n = 0.45-0.66). The Freundlich constant, K, ranged from 110 to 590 L/kg while n ranged from 0.45 to 0.66. All of the parameters for the Freundlich isotherms for AE-9 sorption are given in Table 3. The sorption isotherms for AE-9 sorption were much more nonlinear than those for AE-3 sorption. This is consistent with AE-3 being the more hydrophobic of the two and thus more like the typical nonionic compounds that sorb to sediments with linear isotherms at low concentrations.

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

Surfactant	Sediment Number	K (L/kg)	n	r[b]
AE-3	1	500	0.83	0.99
	2	490	0.89	0.99
	3	110	0.97	0.98
	4	110	0.89	0.99
AE-9	1	450	0.66	0.99
	2	590	0.56	0.98
	3	110	0.53	0.99
	4	160	0.45	0.98

[a] Parameters, K and n, were determined by least squares fitting using Equation (1).
[b] Correlation coefficient from least squares fit of Equation (1).

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

$$D = \frac{C_s}{C_w} \tag{2}$$

Because the equilibrium sorption isotherms were non-linear, 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:

$$D = KC_w{}^{n-1} \tag{3}$$

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 [23].
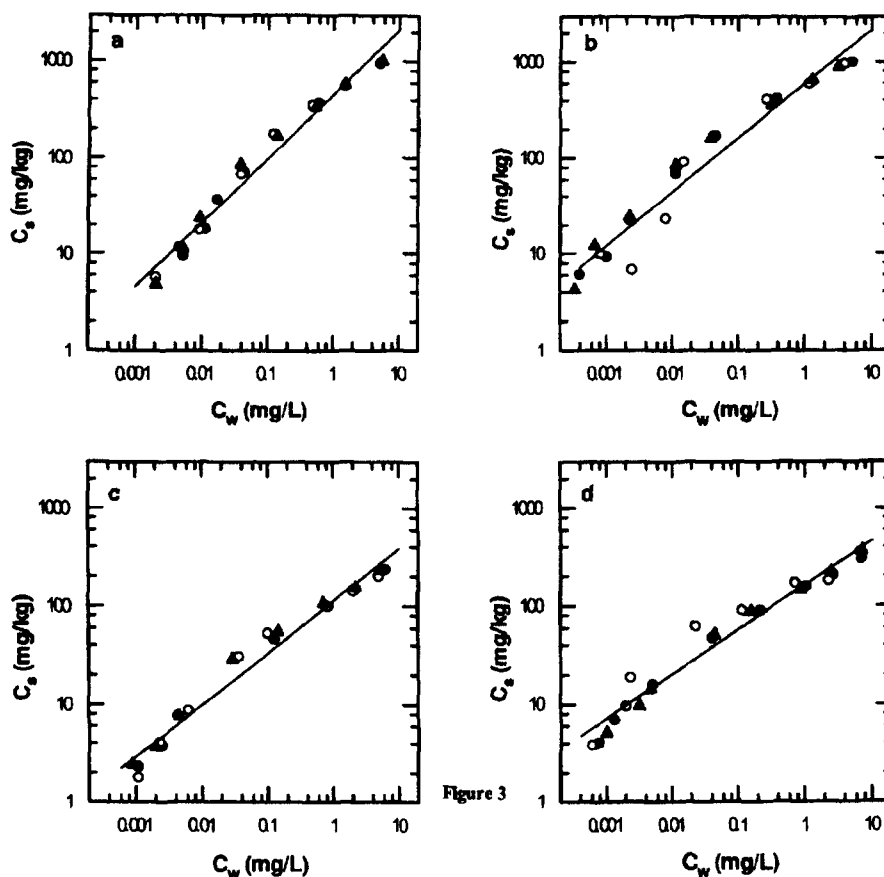
Figure 3: Equilibrium sorption isotherms for AE-9 sorbing to Sediments 1 (a), 2 (b), 3 (c), and 4 (d). Data are plotted based on ^{14}C counts and the lines represent the Freundlich parameter fits summarized in Table 3. For each sediment, different symbols indicate separate experiments. All of these experiments were conducted with a particle concentration of 4 g/L.

We examined the effect of sediment organic carbon and percent clay on the sorption of AE-3 and AE-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 [24]. However, the amount of AE-3 or AE-9 sorption (as defined by D_l) to this set of natural sediments did not correlate very well with the percent organic carbon (see Table 4 and Fig. 4).

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Table 4: Summary of statistical parameters for correlations of sorption with percent organic carbon or percent clay in the sediment.

Parameters	R [a]	p [b]
AE-3, organic carbon	0.93	0.07
AE-9, organic carbon	0.78	0.21
AE-3, clay	0.93	0.07
AE-9, clay	0.97	0.03

[a] The parameter R is the correlation coefficient
[b] The parameter p is the probability the R is zero.

This suggests that the sorption of these nonionic alcohol ethoxylate surfactants may not follow the Equilibrium Partitioning model and another model may be more suitable to describe their sorption. Similar results were obtained in the previous study with AE5-9 [15].

The amount of sorption (as defined by D_1) correlated better with the percent clay in the sediment (see Table 4 and Fig. 5). This result has been previously observed in other studies [11,15]. The forces involved in this type of interaction may facilitate the sorption of these surfactants to sediments with higher amounts of clay.

Effect of EO chain length

The effect of EO chain length on the sorption of AE to these natural sediments can be determined by comparing the sorption isotherms for AE-3 and AE-9. If D_1 is used to compare the amount of surfactant that sorbs to a given sediment, it can be seen that the mass of AE-3 and AE-9 that sorb to these sediments is approximately the same. However, it is important to note that the two surfactants have substantially different molecular weights. Thus, when equal masses of the surfactants are sorbed, there is approximately 1.8 times more AE-3 sorbed on a molar basis. This indicates that there are 1.8 times as many AE-3 molecules sorbed than AE-9 molecules. If we assume that the same sorption sites are used by both surfactants, then 1.8 times more sites are covered by the AE-3; however, the surface area coverage differences may not be this large. Thus, on a molar basis, the AE-3 sorbs more strongly than the AE-9 while on a mass basis, the amounts of sorption are similar.
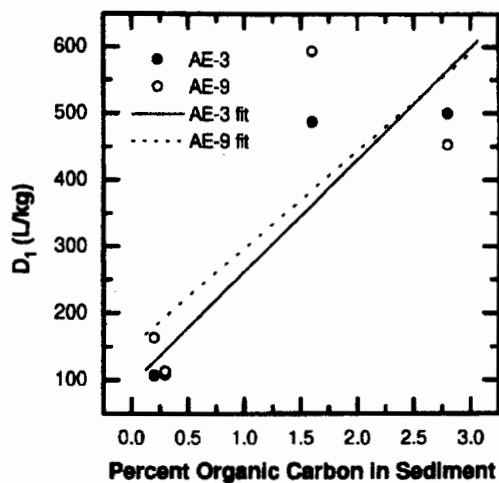
Figure 4: Effect of sediment organic carbon on the sorption of AE-3 or AE-9 to four natural sediments. The specific distribution ratios (D_1) from the Freundlich parameters for the four sediments are plotted as a function of sediment organic carbon. The lines represents the best fit linear least squares model for D_1 as a function of sediment organic carbon.
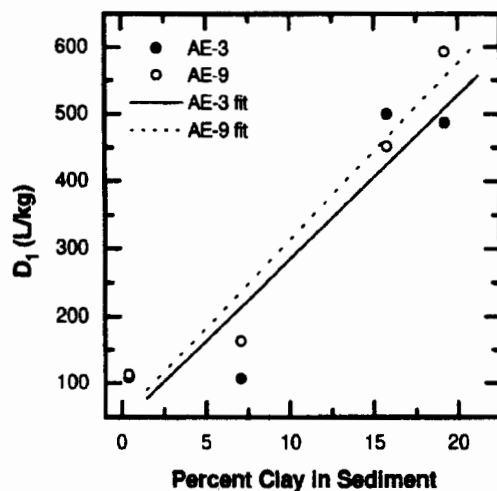

Figure 5: Effect of sediment clay content on the sorption of AE-3 or AE-9 to four natural sediments. The specific distribution ratios (D_1) from the Freundlich parameters for the four sediments are plotted as a function of sediment clay content. The lines represents the best fit linear least squares model for D_1 as a function of sediment clay content.

DISCUSSION

Equilibrium sorption isotherms are non-linear

The sorption isotherms determined from the equilibrium experiments in this study were non-linear and could be described by the Freundlich model. Other investigators [11,13] have also observed non-linear sorption isotherms for AEs sorbing to natural sediments. The amount of sorption (as measured by D_1) ranged from 110 to 590 L/kg in this study and from 2.2 to 2100 L/kg in other studies [11,13,15]. The non-linearity of the isotherms is described by the Freundlich parameter, n. We observed n in the range of 0.45 to 0.97 while other investigators [11,13] observed 0.51 to 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 [24-26]. Our data [15, this study] and that of others [11,13] suggest that this simplified approach may not be 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 non-linearity 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.

EO chain length affects equilibrium sorption

We observed the sorption of AE-3 to be stronger than AE-9 on a molar basis. This is consistent with the results of Brownawell et al. [11] who conducted similar experiments. However, the data in our study indicate that on a mass basis, the amount of sorption observed under equilibrium conditions for AE-3 and AE-9 were not significantly different. Since sorption phenomena are typically described on a mass basis, these data suggest that the EO chain length (at least in the range of 3 to 9) may not be very important in determining the mass of surfactant that will sorb to a given sediment. The properties of the sediment are probably more important in determining the amount of surfactant that will sorb.

In summary, we have measured the sorption of two model alcohol ethoxylates to a series of natural sediments under sterile conditions. Data from these sorption experiments indicated the equilibrium sorption isotherms were non-linear and best described by the Freundlich model. The AE-3 and AE-9 did not sorb strongly to the tested sediments. Sorption was better correlated to the percent clay content of the sediment than to the percent organic carbon content of the sediment. Finally, EO chain length (in the range of 3 to 9) did not effect the amount of sorption on a mass basis.

ACKNOWLEDGMENT

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