

# Modeling Sorption of Anionic Surfactants onto Sediment Materials: An a priori Approach for Perfluoroalkyl Surfactants and Linear Alkylbenzene Sulfonates

CHRISTOPHER P. HIGGINS<sup>†,‡</sup> AND RICHARD G. LUTHY<sup>\*,†</sup>

Department of Civil and Environmental Engineering, Stanford University, Stanford, California 94305-4020

A mechanistically derived model predicting the sorption of anionic surfactants to sediments was developed and evaluated for three classes of surfactants: perfluoroalkyl carboxylates, perfluoroalkyl sulfonates, and linear alkylbenzene sulfonates. The model includes both hydrophobic and electrostatic components and estimates the contribution of each to the sediment–water distribution coefficient ( $K_d$ ) using Gibbs free energy terms. The hydrophobic free energy term was calculated from the aqueous solubilities of non-charged alkylbenzene or perfluoroalkane analogs and prior observations of increases in  $K_d$  values with increasing chain lengths. The electrostatic term was calculated from aqueous solution measurements using the non-ideal competitive adsorption Donnan (NICA-Donnan) model. The NICA-Donnan calculations were performed using parameters previously derived for generic humic acids. These two terms were coupled by multiplying by the fraction of organic carbon in the sediment,  $f_{oc}$ , and a single fitting parameter,  $F_{access}$ , the volumetric fraction of organic carbon accessible to the sorbing surfactant. The combined model accurately predicted the sediment–water distribution coefficients for all three classes of anionic surfactants. In its current formulation, the model was unable to capture the slight degree of isotherm nonlinearity observed for these surfactants.

## 1. Introduction

One of the most useful tools for modeling the fate of hydrophobic organic compounds (HOCs) in aquatic systems recognizes that the sorption of HOCs to sediments and soils is dominated by the fraction of organic carbon ( $f_{oc}$ ) of the sorbent and the hydrophobicity of the sorbate. Thus, knowing only the  $f_{oc}$  of the sorbent and an indicator of the hydrophobicity of the sorbate, relatively accurate estimations of the sediment–water partition coefficient ( $K_d$ ) can be made for dilute aqueous solutions (ref 1; p 292). These estimations rely on several key assumptions, namely that natural humus-like organic matter is the dominant phase into which HOCs sorb and that parameters such as the octanol–water partition coefficient ( $K_{ow}$ ) are accurate indicators of the hydrophobicity

of the sorbate. While this implicitly ignores the fact that some forms of organic carbon present in sediments (such as black carbon) may act as strong sorbents, this approach has proven quite robust. Unfortunately, this paradigm typically breaks down if the sorbate's chemical structure includes any charged or potentially charged moieties that either dramatically affect the indicators of hydrophobicity (i.e., aqueous solubility) or interact with specific functional groups present in the sediment. Such is the case for anionic surfactants such as perfluorochemical (PFC) surfactants and linear alkyl benzene sulfonates (LAS).

The role of organic matter in the sorption of anionic surfactants to sediments and soils has not always been clear. Previous work on LAS sorption at moderate aqueous concentrations ( $\leq 1 \text{ mg}\cdot\text{L}^{-1}$ ) suggested that positively charged surfaces such as iron oxides can adsorb the anionic surfactants, with some evidence suggesting a specific orientation of the sorbed LAS molecule (mechanism A in Figure 1) (2). This electrostatically driven sorption paradigm was supported by several previous studies examining LAS sorption onto different soils (3) and pure-phase minerals (4). However, these previous studies employed fairly high aqueous concentrations (ppm range) and thus may have been complicated by micelle formation in the bulk phase or at least hemimicelle formation at the interface. A recent study of LAS sorption (performed at sub-ppm concentrations) concluded that the flotation effects observed were due to monolayer coverage of the pure-phase minerals, which was also consistent with the sorption isotherms observed (2). Though high concentration releases of LAS or PFC surfactants are possible (e.g., through the direct discharge of fire-fighting foams), the aqueous concentrations of LAS and PFC surfactants in the environment are more typically in the  $\mu\text{g}\cdot\text{L}^{-1}$  and  $\text{ng}\cdot\text{L}^{-1}$  ranges, respectively (5, 6). Thus, it is possible that the sorption mechanism inferred by data collected at much higher concentrations is not applicable to dilute solution conditions typically found in the environment.

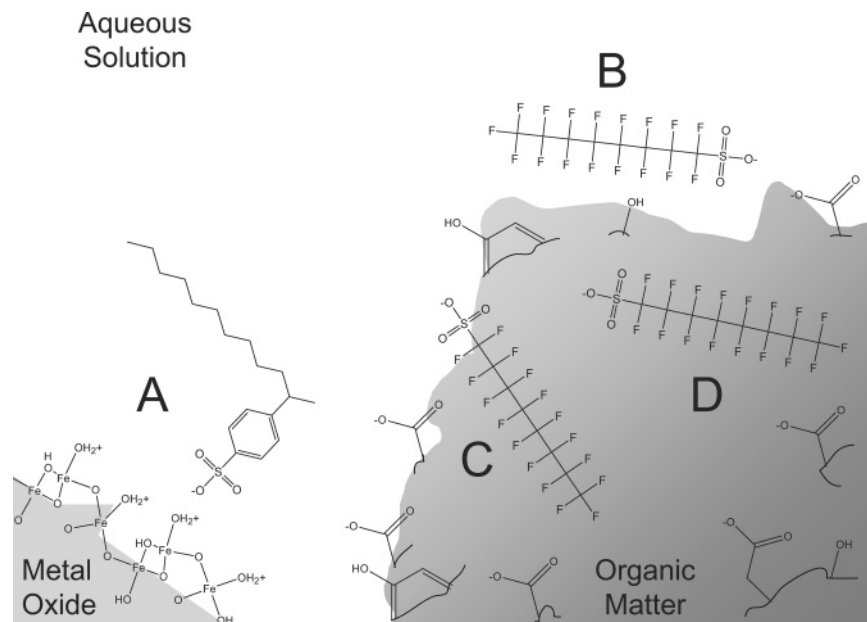
Other investigators, working at somewhat lower aqueous concentrations, have observed weak correlations of LAS sorption with  $f_{oc}$  or % silt, suggesting that organic matter may play a role in anionic surfactant sorption (7, 8), and others have measured distribution coefficients for LAS and dissolved organic matter (9). While not concluding that organic matter was responsible for sorption, Westall et al. noted a general increase in LAS sorption with the  $f_{oc}$  of the sediment (10). In a previous study, we determined that sediment organic carbon was the dominant sorbent-specific parameter affecting sorption of PFC surfactants in the dilute solution range (11), and these results are consistent with the limited data from PFC manufacturers (12, 13). However, while these observations allow for organic-carbon normalized partition coefficients (i.e.,  $K_{oc}$  values) to be calculated, these values are empirically derived and do not account for the effects of pH and aqueous  $[\text{Ca}^{2+}]$  observed for either LAS or PFC surfactants (10, 11). Such effects may be particularly important for modeling of groundwater plumes of PFC surfactants from landfills, where groundwater chemistry will likely vary substantially from site to site. Thus, attempts to estimate the sorption of anionic surfactants a priori must account not only for the hydrophobicity of the sorbate and the organic carbon content of the sorbent, but also for the effects of solution-specific parameters that may impact the observed  $K_d$  value.

The goal of this study was to develop tools for estimating the sorption of anionic surfactants to sediments and soils using limited data on the sorbate, sorbent, and aqueous

\* Corresponding author phone: (650) 723–3921; fax: (650) 725–8662; e-mail: luthy@stanford.edu.

<sup>†</sup> Stanford University.

<sup>‡</sup> Current Affiliation: Johns Hopkins Bloomberg School of Public Health, Baltimore, Maryland 21205.



**FIGURE 1. Potential sorption mechanisms of anionic surfactants in sediments and soils. Adsorption of C12 LAS onto metal oxides (A), adsorption of perfluorooctane sulfonate (PFOS) onto organic matter (B), limited penetration absorption of PFOS into organic matter (C), and the traditional conceptualization of a compound fully absorbed into organic matter (D). As discussed in the text, modeling efforts suggest mechanism C is most likely.**

conditions. The modeling approach described here accounts for the hydrophobicity of the surfactant, the organic matter present in the sediments and soils, and the effects of solution parameters on sorption. These latter effects are accounted for by invoking a Coulombic free energy contribution to the partition coefficient in the form of a Donnan electrostatic potential for the organic matter. Thus, changes in  $K_d$  values with different aqueous solutions are modeled as changes in this electrostatic potential.

## 2. Modeling Approach

Consistent with previous observations discussed above, we begin with the assumption that at low concentrations (i.e., dilute solution), the sorption of anionic surfactants to soils and sediments can be described as a phase transfer process between the bulk aqueous solution and the sediment or soil organic matter. As depicted in Figure 1, it is possible that the anionic surfactant is fully absorbed into the organic matter (mechanism D) or that the charged head group is at or near the organic matter–water interface (mechanism C). Because the Donnan potential does not necessarily fall to zero at the organic matter–water interface (to the extent such an interface can be accurately defined), (14) electrostatic effects may impact anionic surfactant sorption for both mechanisms C and D, as depicted in Figure 1. As will be discussed, our conceptual model is that of mechanism C, where the surfactant monomers interact with the organic matter in a micelle-like configuration. Regardless of which mechanism is more applicable, the anionic surfactant molecule sorption can be explained as a phase transfer process.

The sediment–water distribution coefficient ( $K_d$ ) can be written as follows:

$$K_d (\text{L} \cdot \text{kg}_{\text{sed}}^{-1}) = f_{\text{oc}} K_{\text{oc}} \quad (1)$$

with  $K_{\text{oc}}$  the organic-carbon normalized distribution coefficient and  $f_{\text{oc}}$  the fraction organic carbon present in the sediment ( $\text{kg}_{\text{oc}} \cdot \text{kg}_{\text{sed}}^{-1}$ ). This phase-transfer process has an associated Gibbs free energy change ( $\Delta G_{\text{sorption}}$ ), given by

$$\Delta G_{\text{sorption}} = -RT \ln K_{\text{oc}} + \text{constant}_{\text{oc}} \quad (2)$$

with  $R$  the ideal gas constant ( $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ), and  $T$  the temperature (K). The second term ( $\text{constant}_{\text{oc}}$ ) allows  $K_{\text{oc}}$  to be related to the true thermodynamic distribution coefficient by accounting for the reference states. Using the Flory–Huggins theory of polymer dissolution as developed by Chiou (15), Zhu and Pignatello (16) approximated this constant by relating the volumetric distribution coefficient ( $K_{\text{vol,oc,i}}$ ) for an ideal solute to a simplified expression of the activity of the solute in the solid phase:

$$\ln K_{\text{vol,oc,i}}^{\text{ideal}} = \ln \frac{\bar{V}_w}{\bar{V}_i} - 1 \quad (3)$$

with  $\bar{V}_w$  the molar volume of water ( $0.018 \text{ L} \cdot \text{mol}^{-1}$ ) and  $\bar{V}_i$  the molar volume of the sorbate.  $\bar{V}_i$  can be calculated from atomic volumes using the approach of Abraham and McGowan (17) and the recommended modifications (18). The volumetric distribution coefficient ( $K_{\text{vol,oc}}$ ) can then be related to the standard mass-based distribution coefficient by accounting for the fraction of organic carbon accessible to the sorbate ( $F_{\text{access}}$ ) and the organic matter density ( $\rho_{\text{oc}}$ ; estimated to be  $\sim 0.5 \text{ kg}_{\text{oc}} \cdot \text{L}_{\text{oc}}^{-1}$ ). As discussed by Zhu and Pignatello (16), because  $\Delta G_{\text{sorption}} = 0$  for an ideal solute, the constant can thus be expressed as

$$\frac{\text{constant}_{\text{oc}}}{RT} = \ln \left( \frac{F_{\text{access}}}{\rho_{\text{oc}}} \cdot \frac{\bar{V}_w}{\bar{V}_i} \right) - 1 \quad (4)$$

This approximation can subsequently be used for nonideal sorbates, where  $\Delta G_{\text{sorption}} \neq 0$ .

Because anionic organic surfactants contain both hydrophobic and charged moieties, the free energy change with sorption ( $\Delta G_{\text{sorption}}$ ) must account for both hydrophobic and Coulombic effects:

$$\Delta G_{\text{sorption}} = \Delta G_{\text{hydrophobic}} + \Delta G_{\text{Coulombic}} \quad (5)$$

Implicit in this formulation is the absence of a free energy contribution due to any specific chemical binding of the surfactant molecule to any particular functional groups present in the organic matter. Given the very similar sorption

observed for both perfluoroalkyl sulfonates and perfluoroalkyl carboxylates (11) and the general lack of chemical reactivity of these molecules, we feel this omission is justified. In addition, while the Coulombic term arises solely due to the head group's charge, the magnitude of the hydrophobic term is not entirely dependent on the surfactant tail: as will be discussed, minor differences in the size of the surfactant head groups may aid in explaining the very slight differences in sorption observed for perfluorosulfonates when compared to perfluorocarboxylates. Furthermore, though we recognize the greater utility in differentiating between the various contributions to the hydrophobic free energy term (e.g., dipole effects, hydrogen-bonding effects, cavity effects), we have not attempted to discern the relative contributions of these processes to the overall "hydrophobic" free energy term.

With these assumptions, the Coulombic term can then be expressed in terms of an electrostatic potential:

$$\Delta G_{\text{sorption},i} = \Delta G_{\text{hyd},i} + z_i F \Psi \quad (6)$$

and by incorporating eqs 2 and 4:

$$-RT \ln K_{\text{oc},i} + RT \left( \ln \left( \frac{F_{\text{access}} \bar{V}_w}{\rho_{\text{oc}} \bar{V}_i} \right) - 1 \right) = \Delta G_{\text{hyd},i} + z_i F \Psi \quad (7)$$

where  $\Psi$  is the organic matter's electrostatic potential (V),  $F$  is the Faraday constant ( $\text{C}\cdot\text{mol}^{-1}$ ), and  $z_i$  is the charge of the surfactant. Because  $\Psi$  is typically negative for organic matter and  $z_i$  is also negative for anionic surfactants, this Coulombic term is typically positive. Thus, sorption of anionic surfactants to natural organic matter can be regarded as a competition between hydrophobic and Coulombic effects, and only when the free energy change due to the hydrophobe is sufficiently negative will the surfactant molecule be substantially absorbed into the organic matter phase. To predict anionic surfactant partition coefficients (i.e.,  $K_{\text{oc}}$ ), accurate estimations of both the hydrophobic and Coulombic free energy terms must be made.

**2.1. Hydrophobic Free Energy Term Estimations.** As noted in previous studies of both LAS and PFC surfactant sorption (10, 11), sediment-water partition coefficients for anionic surfactants increase with increasing chain length of the hydrophobe, with the  $\log K_d$  values regularly increasing for each additional  $\text{CF}_2$  or  $\text{CH}_2$  moiety. For PFC surfactants the free energy change of  $\sim 3.3 \text{ kJ}\cdot\text{mol}^{-1}$  per  $\text{CF}_2$  group is very similar to the free energy change for transfer of a  $\text{CF}_2$  moiety from the bulk aqueous phase to a micelle (19). In addition, this free-energy change per  $\text{CF}_2$  moiety is very close to that predicted by others for absorption of fluorotelomer olefins and alcohols into humic acid from water ( $\sim 3.4 \text{ kJ}\cdot\text{mol}^{-1}$ ) (18).

In comparison, examining the solubilities of a series of  $n$ -perfluoroalkanes (20) reveals a change in free energy for transferring a  $\text{CF}_2$  group from the gas phase to the aqueous phase of approximately  $5.3 \text{ kJ}\cdot\text{mol}^{-1}$  (Table 1). Thus, the transfer of a  $\text{CF}_2$  group from the organic matter to the bulk aqueous phase requires approximately 60% of the energy needed to transfer a  $\text{CF}_2$  group from the gas phase to the bulk aqueous phase. Similarly, for LAS, the change in solubility per  $\text{CH}_2$  group (i.e., for linear alkyl benzenes) translates to a change in free energy of  $\sim 3.5 \text{ kJ}\cdot\text{mol}^{-1}$  (Table 1), whereas the change in free energy due to sorption (either to sediment or dissolved humic substances) is  $\sim 2.1 \text{ kJ}\cdot\text{mol}^{-1}$  (Table 1). This suggests that for both LAS and anionic PFC surfactants, the free energy of transferring the hydrophobic component of the molecule from the aqueous solution to

**TABLE 1. Relevant Gibbs Free Energy Changes at 25 °C**

	phase transfer (from → to)	per $-\text{CF}_2-$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )	per $-\text{CH}_2-$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )
$\Delta\Delta G_{\text{sol}}(\text{gas})$	gas → water	5.3 <sup>a</sup>	0.68 <sup>b</sup>
$\Delta\Delta G_{\text{sol}}(\text{L})$	liquid → water	7.8 <sup>a</sup>	3.5 <sup>a</sup>
$\Delta\Delta G_{\text{sorption}}$	sediment/soil → water	3.3 <sup>c</sup>	2.1 <sup>e</sup> 2.6 <sup>f</sup> 2.1 <sup>g</sup>
$\Delta\Delta G_{\text{absorption}}$	organic matter → water	3.4 <sup>d</sup>	2.4 <sup>h</sup>
$\Delta\Delta G_{\text{adsorption}}$	montmorillonite → water		0.78 <sup>i</sup>

<sup>a</sup> Calculated from data in Table 2. <sup>b</sup> Calculated from  $\log K_{\text{ow}}$  of  $n$ -alkanes in Schwarzenbach et al. (ref 1; p 1198). <sup>c</sup> Calculated from PFC-sediment data in Higgins and Luthy (17). <sup>d</sup> Predicted by Goss et al. (18). <sup>e</sup> Calculated from LAS-sediment data measured by Westall et al. (10). <sup>f</sup> Calculated from LAS-sediment data measured by Hand and Williams (8). <sup>g</sup> Calculated from LAS-DHS data measured by Traina et al. (9). <sup>h</sup> Calculated from  $\log K_{\text{ow}}$  of  $n$ -alkanes and eq 9-26a in Schwarzenbach et al. (ref 1; p 1198 and p 302). <sup>i</sup> Calculated from data of Cowan and White (21) by Schwarzenbach et al. (ref 1; p 435).

the organic matter phase can be estimated from the excess free energy of aqueous solution for the corresponding organic molecule, in a manner similar to that previously described (ref 1; p 436). Briefly, by calculating the aqueous activity coefficient ( $\gamma_{\text{sat}}^{\text{w}}$ ) of the hydrophobe, we can relate that directly to the excess free energy in solution (see footnote b in Table 2). For the perfluoroalkanes, the solubilities used were the solubilities of the "superheated liquid" phase (i.e.,  $C_{\text{sat}}^{\text{w}}(\text{L})$ ), calculated using the approach discussed in Schwarzenbach et al. (ref 1; p 139).

**2.2. Size of Terminal Functional (Head) Group.** In the foregoing, we have essentially deconstructed the surfactant molecules into a hydrophobic tail and a point-charged functional group subject to electrostatic repulsion in the organic matter, as will be discussed. This conceptual model omits, however, the identity and size of the functional group (i.e., the sulfonate and carboxylate moieties). Initially, one might be tempted to simply treat these functional groups as point charges, as differences in sorption between them would generally not be expected unless specific chemical interactions exist between the functional groups and specific sites (ref 1; p 433). Our conceptual model does not incorporate any specific chemical interactions, and yet, we previously observed stronger sorption for sulfonates as compared to carboxylates of equal perfluorocarbon chain length (11). Given the general propensity for cation complexation by carboxylates and the fact that sulfonates are known to be poor ligands, if a specific chemical interaction was responsible (i.e., cation bridging via complexation of calcium, etc.), one would have expected exactly the opposite trend, with the carboxylate sorbing more strongly than the sulfonate.

Only when the functional groups are not treated as simple point charges can this difference between the sulfonate and carboxylate functional groups be explained. Using the molecular volume approach of Abraham and McGowan (17) and the recommended modifications (18), slightly different molecular volumes can be calculated for replacing the terminal fluorine of a perfluoroalkane with either a sulfonate or a carboxylate (Table 2). Translating this slight difference into a difference in solubility using an average  $a$  factor of 0.04 (ref 1; p 148), a difference in the excess free energy of aqueous solution can be calculated. Using the relationship between the excess free energy of aqueous solution and the free energy of sorption described above (Tables 1 and 2), we calculate that based on size alone, the sulfonate moiety should sorb slightly more strongly to the organic matter, by a factor of  $\sim 1.6$ . While alternative explanations are possible for such a minor difference in partitioning, the estimated difference is remarkably consistent with the observed average difference of  $\sim 1.7$  (11).

**TABLE 2. Chemical-Specific Model Inputs**

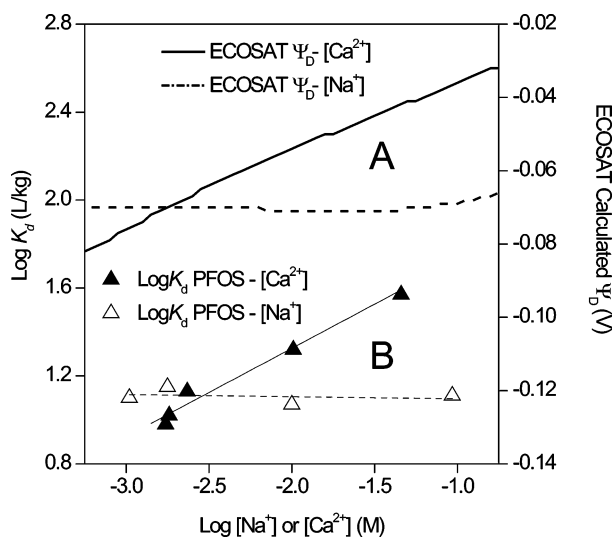
surfactant	formula	tail			uncharged head group		
		$\log C_{\text{sat}}^{\text{w}} \text{ (M)}$	$\log P \text{ (kPa)}$	$\log C_{\text{sat}}^{\text{w}} \text{ (L)}$	formula	$\Delta \bar{V} \text{ (cm}^3\text{/mol)}^a$	$-\Delta G_{\text{hyd}} \text{ (kJ/mol)}^b$
PFOA [PFHpS] <sup>c</sup>	C <sub>7</sub> F <sub>15</sub> -X	-7.49 <sup>d</sup>	1.02 <sup>f</sup>	-8.47	-[CO]-	9.74	25.5
					-[SO <sub>2</sub> ]-	22.17	26.7
PFNA PFOS	C <sub>8</sub> F <sub>17</sub> -X	-8.41 <sup>d</sup>	0.57 <sup>g</sup>	-9.84	-[CO]-	9.74	28.8
					-[SO <sub>2</sub> ]-	22.17	30.0
PFDA [PFNS] <sup>c</sup>	C <sub>9</sub> F <sub>19</sub> -X	-9.33 <sup>e</sup>	0.11 <sup>g</sup>	-11.22	-[CO]-	9.74	32.2
					-[SO <sub>2</sub> ]-	22.17	33.4
PFUnA PFDS	C <sub>10</sub> F <sub>21</sub> -X	-10.26 <sup>e</sup>	-0.34 <sup>f</sup>	-12.60	-[CO]-	9.74	35.5
					-[SO <sub>2</sub> ]-	22.17	36.7
PFDoA [PFUnS] <sup>c</sup>	C <sub>11</sub> F <sub>23</sub> -X	-11.17 <sup>e</sup>	-0.79 <sup>f</sup>	-13.96	-[CO]-	9.74	38.8
					-[SO <sub>2</sub> ]-	22.17	40.0
C10 LAS	C <sub>16</sub> H <sub>25</sub> -X	-7.07 <sup>h</sup>	N/A	-7.07	-[SO <sub>2</sub> ]-	25.94	34.8
C12 LAS	C <sub>18</sub> H <sub>29</sub> -X	-8.30 <sup>h</sup>	N/A	-8.30	-[SO <sub>2</sub> ]-	25.94	39.2
C14 LAS	C <sub>20</sub> H <sub>33</sub> -X	-9.52 <sup>h</sup>	N/A	-9.52	-[SO <sub>2</sub> ]-	25.94	43.5

<sup>a</sup> Estimated using approach of Abraham and McGowan (17) with recommended modification (18). <sup>b</sup> Calculated via  $-\Delta G_{\text{hyd}} = RT \cdot n \cdot \ln \gamma_{\text{sat}}^{\text{w}}(L)$ , with  $n = 0.42$  for perfluoroalkanes,  $n = 0.62$  for hydrocarbons, and  $\log \gamma_{\text{sat}}^{\text{w}}(L) = \log 55.6 - \log C_{\text{sat}}^{\text{w}}(L) + 0.04 \Delta \bar{V}$ . <sup>c</sup> For predictive purposes only. No sorption data available for this surfactant. <sup>d</sup> Obtained from Horvath and Getzen (20). <sup>e</sup> Estimated from shorter chain analog data provided in Horvath and Getzen (20). <sup>f</sup> Estimated from analog data provided in Dias et al. (22) and Dias et al. (23). <sup>g</sup> Obtained from Dias et al. (22) or Dias et al. (23). <sup>h</sup> As estimated by Sherblom et al. (24).

**2.3. Coulombic Free Energy Term Estimations.** Though the effects of pH and aqueous solution composition on anionic surfactant sorption have been reported previously (10, 11), a mechanistic explanation for these phenomena remains unclear. Both studies interpret these presumably Coulombic effects with respect to changes in a potential,  $\Psi$ . Given the apparent importance of organic matter in anionic surfactant sorption, it is logical to consider this to be the potential of the organic matter. Previous investigations on the binding of metals with humic substances have modeled these organic phases as heterogeneous Donnan gels (25). The charge present in these gels gives rise to a Donnan potential,  $\Psi_D$ , which is considered to be independent of position in the gel. Related efforts incorporate nonideal competitive adsorption (NICA) models, which allow for metal-metal and metal-proton competition for specific sites within the gel (26).

Using generic parameters for humic acids derived from extensive data sets (27, 28), a NICA-Donnan model (as formulated in the computer program ECOSAT, version 4.8) allows for straightforward calculation of a  $\Psi_D$  given specific aqueous conditions (i.e., pH, [Ca<sup>2+</sup>], [Na<sup>+</sup>], etc.) (29). While these generic parameters do not account for natural variability in the charging behavior of organic matter, in the absence of site-specific data, they should work well as a first approximation. Figure 2 indicates that calculated changes in  $\Psi_D$  with varying salt concentrations (A) are parallel to the changes observed in the  $\log K_d$  values for PFC surfactants (B). Furthermore, because ECOSAT's calculation of  $\Psi_D$  takes into account both the pH and [Ca<sup>2+</sup>] of the solution simultaneously, it can account for the vast majority of variation in PFC surfactant sorption for a given sediment (Figure 3). In other words, ECOSAT's calculation of  $\Psi_D$  does not require one to differentiate between pH and [Ca<sup>2+</sup>] effects. In previous work, both pH and [Ca<sup>2+</sup>] affected the sorption of LAS and PFC surfactants (10, 11), though given the difficulty in varying only one parameter at a time in natural systems, it was unclear whether the changes in sorption with pH were due to actual pH effects or due to covarying [Ca<sup>2+</sup>]. ECOSAT's calculation of  $\Psi_D$  suggests that the majority of the pH effect observed (at least for PFC surfactants) was actually due to the increase in [Ca<sup>2+</sup>] with decrease in pH.

**2.4. Relating  $K_{oc}$  to  $K_d$ .** Once both the hydrophobic and Coulombic free energy contributions were estimated, it was



**FIGURE 2. Effects of solution composition on ECOSAT-calculated  $\Psi_D$  (A), and experimentally determined  $\log K_d$  for PFOS (B).  $\log K_d$  data are from Higgins and Luthy (11).**

necessary to relate the total free energy change due to sorption ( $\Delta G_{\text{sorption}}$ ) to the measured sediment-water partition coefficient ( $K_d$  in  $L \cdot \text{kg}_{\text{sed}}^{-1}$ ). This conversion is performed by including the constant  $_{oc}$  term, as detailed in eqs 4 and 7. However, if we assume that  $F_{\text{access}} = 1$ , as was assumed by Zhu and Pignatello (16), this implies that all organic matter present in the sediment behaves and can be modeled as a humus-like Donnan gel. While the majority of organic matter present in soils and sediments may be humus-like, previous observations of hydrophobic organic compound sorption into organic matter indicate that organic matter heterogeneities may have very significant impacts on partitioning behavior (30). Thus, describing the entire pool of organic matter as a homogeneous phase may not adequately represent realistic conditions. When using the same NICA-Donnan model employed in this study to estimate the relative contribution of individual sorbents to the sorption of heavy metals in a sandy soil, Weng et al. found that the site density within the soil organic matter needed to be adjusted to approximately 30% of the generic humic acid site density to

arrive at realistic estimations of aqueous activities of the metals (31). By estimating the reactive humic acid fraction, these authors essentially implied that the remaining fraction was nonreactive or minimally reactive with respect to metal binding. While the same may not necessarily be true for anionic surfactants, to allow for the possibility that not all of the organic matter is accessible for anionic surfactant sorption,  $F_{\text{access}}$  was allowed to be a fitted parameter. Though this parameter would likely vary with differing sediments, as a first approximation, we assumed that  $F_{\text{access}}$  was less than 1 and was constant for all sediments.

### 3. Materials and Methods

For model development, we relied on sorption data from two primary studies in which PFC surfactant sorption (11) and LAS sorption (10) was measured for several different sediments and aqueous solution compositions. In both studies, sediment–water partition coefficients were measured for surfactants of differing chain lengths. Previously measured or calculated literature values for the aqueous solubilities and vapor pressures of perfluoroalkanes (20, 22, 23) and estimated solubilities of linear alkylbenzenes (24) were used for calculation of the hydrophobic free energy term (Table 2).

Calculation of the NICA-Donnan potential ( $\Psi_D$ ) was performed using the ECOSAT model (29), using model parameters previously described for generic humic acid (27, 28). To validate the model, reported partition coefficients for individual PFC surfactants were compared to those predicted by the model (12, 13). For model development and validation, actual aqueous solution measurements of pH,  $[\text{Ca}^{2+}]$ , and  $[\text{Na}^+]$  were used when possible, but in some cases were estimated from available information. A complete set of sediment and solution-specific model inputs (derived from literature sources) is provided as Supporting Information.

Attempts were also made to construct isotherms for LAS sorption onto various sediments previously described (10), to allow for an evaluation of the possibility that the Coulombic term could be responsible for nonlinear isotherms. For this isotherm modeling, the initially calculated potential was allowed to increase with increasing sorbed surfactant using a constant capacitance (change in  $\Psi_D$  per unit charge in the gel) calculated from the ECOSAT output.

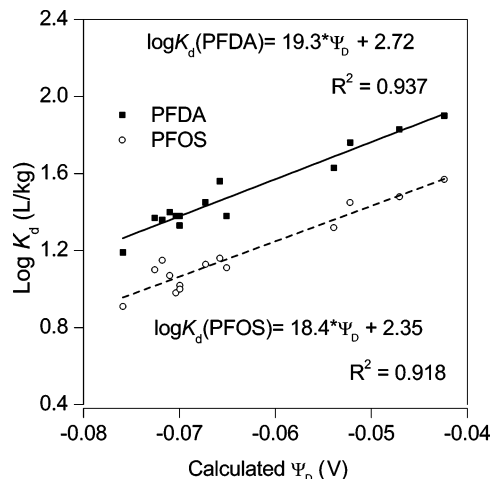
Combining eqs 1 and 7, the overall model equation was

$$K_d (\text{L} \cdot \text{kg}_{\text{sed}}^{-1}) = f_{\text{oc}} \frac{F_{\text{access}} \bar{V}_w}{\rho_{\text{oc}} \bar{V}_i} \exp(-1) \exp\left(\frac{-\Delta G_{\text{hyd},i} - z_i F \Psi_D}{RT}\right) \quad (8)$$

with the chemical-specific parameters provided in Table 2, all sediment and solution-specific parameters provided in the Supporting Information, and all other values listed or estimated as above. Model optimization was performed using OriginPro 7.5.

### 4. Results and Discussion

As apparent in Figure 4, the model provides a very good fit, generally within a factor of 2, of the measured partition coefficients for both PFC surfactants and LAS when the  $F_{\text{access}}$ , the fraction of the organic matter chiefly responsible for surfactant sorption, is approximately 0.34. Given that experimentally derived  $K_{\text{oc}}$  values are accurate only within a factor of 2 and the many sources of experimental uncertainty, we believe this a priori approach for predicting sorption of anionic surfactants performs quite well. Moreover, deviations from the predicted values appear to be strongly dependent on the sediment, rather than randomly distributed (see the Supporting Information). When  $F_{\text{access}}$  was optimized for each sediment, the resulting values range from 0.09 to 0.9. This



**FIGURE 3. Correlation between ECOSAT-calculated Donnan potential ( $\Psi_D$ ) and  $\log K_d$  for PFOS and perfluorodecanoate (PFDA). Data are from Higgins and Luthy (11).**

is consistent with our expectation that the fraction of organic matter responsible for sorption should be somewhat variable, though variations in the hydrophobic and Coulombic interactions between the sorbing surfactants and the organic matter would also vary somewhat from sediment to sediment.

**4.1. Isotherm Linearity.** Even when using values of  $F_{\text{access}}$  specifically fitted for each sediment, the sorption isotherms generated by the model displayed minimal degrees of nonlinearity (Figure 5). This is somewhat inconsistent with previous observations (10, 11). The lack of nonlinearity was likely due to the fact that even when the sorbed molecules were restricted to a fraction of the organic matter ( $F_{\text{access}}$ ), the additional charge generated by the sorbing molecules was insufficient to change the total charge (and thereby the  $\Psi_D$ ) of the organic matter. While electrostatic repulsion is still the most likely explanation for the nonlinear isotherms observed for LAS and PFC surfactants, the charge density in the organic matter would need to be much lower than that calculated by ECOSAT to predict the degree of nonlinearity that has been observed. Given that the generic parameters used to calculate  $\Psi_D$  were developed from humic acids rather than solid-phase organic matter (into which we assume the surfactants are absorbing) is lower than that calculated from ECOSAT. Additional efforts are needed to determine the mechanism and underlying cause of nonlinear anionic surfactant isotherms.

**4.2. Model Optimization.** As with any modeling effort, the larger the number of fitted parameters, in general, the better the fit. At present, we are left to evaluate the meaning of the most obvious fitted parameter,  $F_{\text{access}}$ . Clearly, without varying this parameter, the model would overpredict the distribution coefficients by a factor of 3. If the value of this parameter truly is one (as was assumed by Zhu and Pignatello) (16), then one of the other model components is in error if the conceptual model is accurate. While some parameters such as  $\rho_{\text{oc}}$  and  $\bar{V}_i$  were estimated, these estimates were either identical in value or approach to similar estimates described previously (16). Aside from these estimates, the two other components to examine are the hydrophobic free energy term and the calculated Donnan potential.

With respect to the excess free energy term, while the change in free energy (per  $\text{CF}_2$  or  $\text{CH}_2$ ) is likely correct, we limited our treatment of the free energy associated with the head group to the volume contribution to the excess free energy of solution. Though this described quite well the difference in sorption observed for the perfluorocarboxylates and perfluorosulfonates, it explicitly does not include any

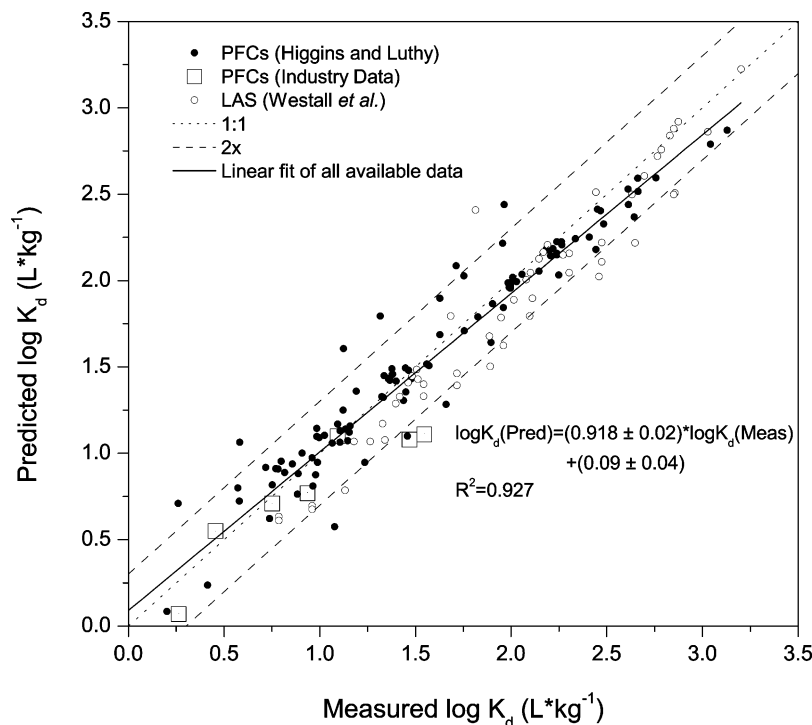


FIGURE 4. Predicted versus measured distribution coefficients for PFCs and LAS using  $F_{\text{access}}$  of 0.34.

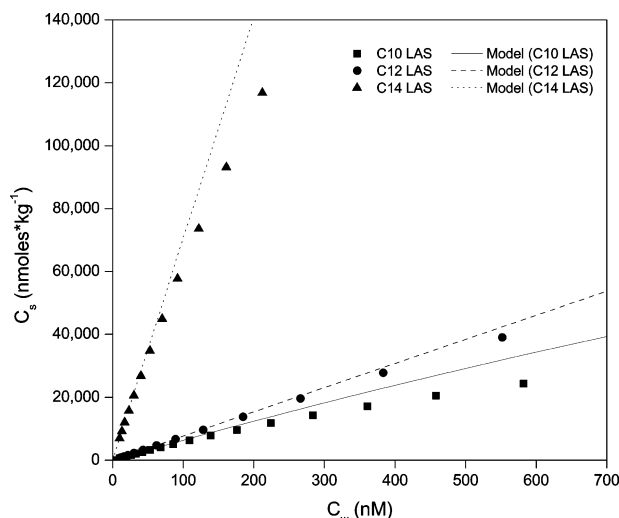


FIGURE 5. Comparison of C10 LAS, C12 LAS, and C14 LAS sorption isotherms on EPA Sediment 12 using the charged organic matter model described here versus fitted virial isotherms, as described by Westall et al. (10).

other effects these molecular fragments might have on  $\Delta G_{\text{sorption}}$ . Given their polar nature, it seems logical that including additional energetic terms (such as those described by Abraham et al.) (32) would likely decrease the excess free energy of solution, thereby bringing our predictions closer to that observed. As only  $2.7 \text{ kJ}\cdot\text{mol}^{-1}$  would need to be subtracted for both the carboxylates and the sulfonates to arrive at a reasonable fit, it is entirely possible that inclusion of an additional term would bring the model's predictions (assuming  $F_{\text{access}} = 1$ ) closer to measured values.

With respect to calculated Donnan potential, given the very analogous behavior in the variation of  $\Psi_D$  (when compared to the  $\log K_d$  values, as shown in Figures 2 and 3), it seems likely that the variation in  $\log K_d$  with changing solution parameters is also correct. However, it is still possible that the absolute potential is incorrect, as the potential would

only need to be 28 mV more negative to explain the factor of 3 difference. Furthermore, if the nonlinear isotherms that have been observed for PFC surfactant and LAS sorption are truly electrostatically derived, then this term must be re-evaluated, as the current model formulation only predicts near-linear sorption at these low concentrations of sorbed surfactants. However, a more negative potential would likely be the result of a higher charge density, exactly the opposite of what would need to change for more nonlinearity to be observed. Clearly, additional efforts are needed to evaluate the utility of organic matter charge models (such as that employed by ECOSAT) in explaining the sorptive behavior of anionic surfactants to natural organic matter.

If, instead, we assume that all estimated and calculated values are correct and that  $F_{\text{access}}$  has a physical meaning (and is not simply a correction term), this would suggest that the sorption mechanism is more likely mechanism C than mechanism D (Figure 1). Thus, if the phase into which the surfactants are absorbing is only the outermost layer of organic matter (and no true absorption occurs), then one would expect that only a fraction of the organic matter (on a mass basis) associated with the outermost layer would be important for anionic surfactant sorption. This Donnan-gel "rind" fraction would be highly dependent on the surface-to-volume ratio of the organic matter, and would likely vary substantially from sediment to sediment. Moreover, this might aid in explaining the observation that the estimated dissolved organic carbon-normalized distribution coefficient (i.e.,  $K_{\text{doc}}$ ) for a fluorotelomer alcohol was an order of magnitude larger than the measured soil  $K_{\text{oc}}$  values (33). A close examination of the LAS literature suggests a similar phenomena may be occurring: though it is also possible that some of this difference may be due to differing experimental conditions (namely  $[\text{Ca}^{2+}]$ ), the average  $\log K_{\text{oc}}$  value calculated for C12 LAS data collected by Westall et al. (10) is 3.88 for sediments, while the average  $\log K_{\text{doc}}$  value for C12 LAS observed by Traina et al. (9) is 4.88 for dissolved humic substances. Presumably, the ratio of the surface area (in contact with the aqueous phase) to the volume or mass of organic matter is much higher in dissolved humic substances than particulate organic matter and/or organic

matter adsorbed to mineral surfaces. If it is this organic matter fraction into which the anionic surfactants absorb, then a higher ratio would lead to larger organic carbon-normalized distribution coefficients when the organic matter is in the dissolved phase as opposed to the particulate phase. In addition, if the physical orientation depicted in mechanism C (Figure 1) is correct, this could lead to a deviation from the Donnan potential term calculated by ECOSAT, as the charge would no longer be evenly distributed within the gel. The charge density would instead be higher closer to the organic-matter-water interface, perhaps leading to a higher potential (and more sorption nonlinearity) as more surfactants are sorbed. Additional efforts are needed to determine whether this interpretation of  $F_{\text{access}}$  is, in fact, correct. Interestingly, though our physical interpretation of this reactive or accessible organic matter fraction is different than that of Weng et al. (31), the average fitted value we obtained (0.34) is very close to that obtained by these authors (average relative site density of 31%) using an entirely different approach.

**4.3. Absorption Versus Adsorption.** As discussed above, it has not always been clear that absorption into organic matter is the dominant mechanism by which anionic surfactants (in dilute solutions) are retained in sediments and in soils. Much of the earlier work on LAS sorption suggested that adsorption to mineral surfaces was the most important mechanism. Inasmuch as PFC surfactants have generally been described as both hydrophobic and oleophobic, one might initially assume that organic matter would not be important for PFC surfactant sorption.

However, additional mechanistic insight is provided by examining the relative free energy changes with sorption. The potential utility of using free energy changes (per  $\text{CF}_2$  or  $\text{CH}_2$  moieties) to discern the differences between adsorption and absorption was recently discussed by Goss and Bronner (34). For example, as discussed above, the change in free energy of sorption per  $\text{CH}_2$  group for LAS is approximately  $2.1 \text{ kJ}\cdot\text{mol}^{-1}$  (Table 1). This free energy change is greater than the free energy change (per  $\text{CH}_2$  group) of  $\sim 0.8 \text{ kJ}\cdot\text{mol}^{-1}$  calculated for a clearly adsorptive process (alkylammonium ions adsorbing onto montmorillonite; Table 1). Conversely, if one uses the  $\log K_{\text{ow}}$  data for  $n$ -alkanes and  $\log K_{\text{ow}} - \log K_{\text{oc}}$  LFERs provided by Schwarzenbach et al. (ref 1; p 302), one calculates a free energy change per  $\text{CH}_2$  of  $2.4 \text{ kJ}\cdot\text{mol}^{-1}$  (Table 1) for this clearly adsorptive process. As the free energy change per  $\text{CH}_2$  for LAS sorption is much closer to that predicted for absorption, this suggests that absorption (i.e., mechanisms C or D in Figure 1) is the dominant process. Mechanistically, the smaller free energy change for adsorption is likely due to the partial relief of the "cavity" term of the excess free energy in solution. In absorption, this free energy difference would be greater due to complete relief of the aqueous "cavity" term and the additional interactions (i.e., van der Waals, etc.) with the sorbing phase. While the approach to modeling anionic surfactant sorption presented here is built on the assumption that absorption of the type depicted by mechanism C (or possibly D) in Figure 1 is the dominant mechanism, it is clear that additional studies, such as  $^{19}\text{F}$  NMR, would be needed to confirm this mechanism.

## Acknowledgments

We thank Phil Gschwend of MIT and Sandy Robertson of Stanford for insightful comments on early drafts of the manuscript. We acknowledge funding for this research from the National Science Foundation's Division of Bioengineering and Environmental Systems both for the project work (BES-0201955) as well as instrumentation (BES 0216458). C.H. was supported by the National Defense Science and Engineering

Graduate Fellowship Program and the National Science Foundation Graduate Research Fellowship Program.

## Supporting Information Available

Sediment and solution-specific model inputs, a complete listing of predicted vs measured distribution coefficients, and a plot depicting sediment-specific data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## Literature Cited

- Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, 2nd ed; John Wiley & Sons: Hoboken, NJ, 2003.
- Kristiansen, I. B.; de Jonge, H.; Nornberg, P.; Mather-Christensen, O.; Elsgaard, L. Sorption of linear alkylbenzene sulfonate to soil components and effects on microbial iron reduction. *Environ. Toxicol. Chem.* **2003**, *22*, 1221–1228.
- Fink, D. H.; Thomas, G. W.; Meyer, W. J. Adsorption of anionic detergents by soils. *J. Water Pollut. Control Fed.* **1970**, *42*, 265–271.
- Volk, V. V.; Jackson, M. L. Alkyl benzene sulfonate and linear alkylate sulfonate adsorption by hydroxy iron and aluminum systems. *J. Water Pollut. Control Fed.* **1968**, *40*, 205–215.
- McAvoy, D. C.; Eckhoff, W. S.; Rapaport, R. A. Fate of linear alkylbenzene sulfonate in the environment. *Environ. Toxicol. Chem.* **1993**, *12*, 977–987.
- Simcik, M. F.; Dorweiler, K. J. Ratio of perfluorochemical concentrations as a tracer of atmospheric deposition to surface waters. *Environ. Sci. Technol.* **2005**, *39*, 8678–8683.
- Urano, K.; Saito, M.; Murata, C. Adsorption of surfactants on sediments. *Chemosphere* **1984**, *13*, 293–300.
- Hand, V. C.; Williams, G. K. Structure-activity-relationships for sorption of linear alkylbenzenesulfonates. *Environ. Sci. Technol.* **1987**, *21*, 370–373.
- Traina, S. J.; McAvoy, D. C.; Versteeg, D. J. Association of linear alkylbenzenesulfonates with dissolved humic substances and its effect on bioavailability. *Environ. Sci. Technol.* **1996**, *30*, 1300–1309.
- Westall, J. C.; Chen, H.; Zhang, W.; Brownawell, B. J. Sorption of linear alkylbenzenesulfonates on sediment materials. *Environ. Sci. Technol.* **1999**, *33*, 3110–3118.
- Higgins, C. P.; Luthy, R. G. Sorption of perfluorinated surfactants on sediments. *Environ. Sci. Technol.* **2006**, *40*, 7251–7256.
- du Pont Adsorption/Desorption of Ammonium Perfluorooctanoate to Soil (OECD 106), E.I. du Pont de Nemours and Company EMSE report no. 17-03, U.S. Environmental Protection Agency docket OPPT-2003-0012-0401, 2003.
- 3M Soil Adsorption/Desorption Study of Potassium Perfluorooctane Sulfonate (PFOS), 3M Laboratory report no: E00-13 11. U.S. Environmental Protection Agency docket AR 226-1030a030, 2000
- Koopal, L. K.; Saito, T.; Pinheiro, J. P.; van Riemsdijk, W. H. Ion binding to natural organic matter: General considerations and the NICA-Donnan model. *Colloids Surf. A* **2005**, *265*, 40–54.
- Chiou, C. T. *Partition and Adsorption of Organic Contaminants in Environmental Systems*; John Wiley and Sons: Hoboken, NJ, 2002.
- Zhu, D. Q.; Pignatello, J. J. A concentration-dependent multi-term linear free energy relationship for sorption of organic compounds to soils based on the hexadecane dilute-solution reference state. *Environ. Sci. Technol.* **2005**, *39*, 8817–8828.
- Abraham, M. H.; McGowan, J. C. The use of characteristic volumes to measure cavity terms in reversed phase liquid-chromatography. *Chromatographia* **1987**, *23*, 243–246.
- Goss, K. U.; Bronner, G.; Harner, T.; Monika, H.; Schmidt, T. C. The partition behavior of fluorotelomer alcohols and olefins. *Environ. Sci. Technol.* **2006**, *40*, 3572–3577.
- La Mesa, C.; Sesta, B. Micelles in perfluorinated surfactant solutions. *J. Phys. Chem.* **1987**, *91*, 1450–1454.
- Horvath, A. L.; Getzen, F. W. IUPAC-NIST solubility data series 68. Halogenated aliphatic hydrocarbon compounds C-3-C-14 with water. *J. Phys. Chem. Ref. Data* **1999**, *28*, 647–778.
- Cowan, C. T.; White, D. The mechanism of exchange reactions occurring between sodium montmorillonite and various  $n$ -primary aliphatic amine salts. *Trans. Faraday Soc.* **1958**, *54*, 691–697.
- Dias, A. M. A.; Caco, A. I.; Coutinho, J. A. P.; Santos, L. M. N. B. F.; Pineiro, M. M.; Vega, L. F.; Costa Gomes, M. F.; Marrucho, I. M. Thermodynamic properties of perfluoro- $n$ -octane. *Fluid Phase Equilib.* **2004**, *225*, 39–47.

- (23) Dias, A. M. A.; Goncalves, C. M. B.; Caco, A. I.; Santos, L. M. N. B. F.; Pineiro, M. M.; Vega, L. F.; Coutinho, J. A. P.; Marrucho, I. M. Densities and vapor pressures of highly fluorinated compounds. *J. Chem. Eng. Data* **2005**, *50*, 1328–1333.
- (24) Sherblom, P. M.; Gschwend, P. M.; Eganhouse, R. P. Aqueous solubilities, vapor pressures, and 1-octanol-water partition coefficients for C9–C14 linear alkylbenzenes. *J. Chem. Eng. Data* **1992**, *37*, 394–399.
- (25) Benedetti, M. F.; van Riemsdijk, W. H.; Koopal, L. K. Humic substances considered as a heterogeneous donnan gel phase. *Environ. Sci. Technol.* **1996**, *30*, 1805–1813.
- (26) Kinniburgh, D. G.; Milne, C. J.; Benedetti, M. F.; Pinheiro, J. P.; Filius, J.; Koopal, L. K.; van Riemsdijk, W. H. Metal ion binding by humic acid: Application of the NICA-Donnan model. *Environ. Sci. Technol.* **1996**, *30*, 1687–1698.
- (27) Milne, C. J.; Kinniburgh, D. G.; Tipping, E. Generic NICA-Donnan model parameters for proton binding by humic substances. *Environ. Sci. Technol.* **2001**, *35*, 2049–2059.
- (28) Milne, C. J.; Kinniburgh, D. G.; van Riemsdijk, W. H.; Tipping, E. Generic NICA-Donnan model parameters for metal-ion binding by humic substances. *Environ. Sci. Technol.* **2003**, *37*, 958–971.
- (29) Keizer, M.; van Riemsdijk, W. *Equilibrium Calculation of Speciation and Transport (ECOSAT)*, version 4.8; Department of Soil Quality, Wageningen University: The Netherlands, 2005.
- (30) Luthy, R. G.; Aiken, G. R.; Brusseau, M. L.; Cunningham, S. D.; Gschwend, P. M.; Pignatello, J. J.; Reinhard, M.; Traina, S. J.; Weber, W. J.; Westall, J. C. Sequestration of hydrophobic organic contaminants by geosorbents. *Environ. Sci. Technol.* **1997**, *31*, 3341–3347.
- (31) Weng, L.; Temminghoff, E. J. M.; van Riemsdijk, W. H. Contribution of individual sorbents to the control of heavy metal activity in a sandy soil. *Environ. Sci. Technol.* **2001**, *35*, 4436–4443.
- (32) Abraham, M. H.; Andonianhaftvan, J.; Whiting, G. S.; Leo, A.; Taft, R. S.; Hydrogen-bonding .34. The factors that influence the solubility of gases and vapors in water at 298-K, and a new method for its determination. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1777–1791.
- (33) Liu, J. X.; Lee, L. S. Solubility and sorption by soils of 8:2 fluorotelomer alcohol in water and cosolvent systems. *Environ. Sci. Technol.* **2005**, *39*, 7535–7540.
- (34) Goss, K.-U.; Bronner, G. What is so special about the sorption behaviour of highly fluorinated compounds? *J. Phys. Chem. A* **2006**, *110*, 9518–9522.

*Received for review October 12, 2006. Revised manuscript received January 11, 2007. Accepted February 7, 2007.*

ES062449J