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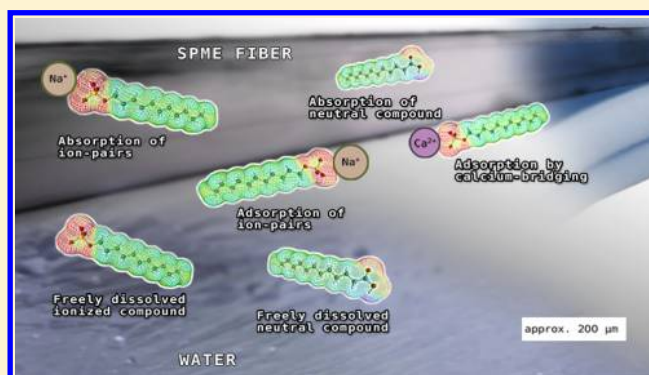
Mechanisms of Neutral and Anionic Surfactant Sorption to Solid-Phase Microextraction Fibers

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Supporting Information

ABSTRACT: Octanol–water partitioning (K_{ow}) is considered a key parameter for hydrophobicity and is often applied in the prediction of the environmental fate and exposure of neutral organic compounds. However, surfactants can create difficulties in the determination of K_{ow} because of emulsification of both water and octanol phases. Moreover, not only is sorption behavior of ionic surfactants related to hydrophobicity, but also other interactions are relevant in sorption processes. A different approach to develop parameters that can be applied in predictive modeling of the fate of surfactants in the environment is therefore required. Distribution between solid-phase microextraction (SPME) fibers and water was used in this study to measure the affinity of surfactants to a hydrophobic phase. Fiber–water sorption coefficients of alcohol ethoxylates, alkyl carboxylates, alkyl sulfates, and alkyl sulfonates were determined at pH 7 by equilibration of the test analytes between fiber and water. Distribution between fiber and water of anionic compounds with $pK_a \sim 5$ (i.e., alkyl carboxylates) was dominated by the neutral fraction. Anionic surfactants with $pK_a \leq 2$ (i.e., alkyl sulfates and alkyl sulfonates) showed strong nonlinear distribution to the fiber. The fiber–water sorption coefficients for alcohol ethoxylates and alkyl sulfates showed a linear trend with bioconcentration factors from the literature. Fiber–water sorption coefficients are promising as a parameter to study the effects of hydrophobicity and other potential interactions on sorption behavior of neutral and anionic surfactants.



INTRODUCTION

Octanol–water partition coefficients (K_{ow}) are often used in environmental risk assessment as a simple measure for hydrophobicity of organic contaminants to predict bioaccumulation, toxicity, and sorption to soil.¹ The K_{ow} value is therefore a key parameter in the prediction of environmental fate and exposure of organic contaminants. As indicated by Goss and Schwarzenbach,² the term hydrophobicity is not always clearly defined. In this publication, they state that “the hydrophobic effect comes from the high amount of free energy that is required to form a cavity in the bulk water phase” as well as the interactions of the compound with water molecules.² Both aspects, cavity formation as well as van der Waals, hydrogen bond, and electrostatic interactions of a compound with water molecules determine the “hydrophobicity” of a compound. Sorption of compounds from the aqueous phase to another phase (for example, passive sampling polymers, organic matter, or lipids) is then the result of hydrophobicity and additional interactions of the compound with this “other” phase.² This concept is also the rationale behind the development of polyparameter LFERs (linear free energy relationships) that are developed as predictive models based on a limited number of basic properties reflecting these major interactions.^{3,4}

For decades, the K_{ow} value has been applied in the development of models for the prediction of partition behavior of organic compounds. One of the reasons for the many successful correlations with K_{ow} is the limited variability in chemical structures of the compounds in these models that mainly consist of nonpolar organic compounds where more specific interactions such as hydrogen bonding are absent or weak. As such, K_{ow} is a reflection of the relative hydrophobicity of nonpolar organic compounds because the specific interactions between these compounds and other phases are considered minimal. However, application of the K_{ow} value as a parameter in predictive models for surfactants, but also for polar and ionized chemicals in general, becomes problematic because of the amphiphilic nature of long carbon-chained surfactants. Compared to neutral organic compounds, environmental distribution of ionized surfactants depends on more specific interactions, but also on solution chemistry variables such as pH and ionic strength. Another fundamental problem with surfactants is that the K_{ow} value is difficult to determine

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experimentally, because surfactants accumulate at interfaces and emulsify both octanol and water phases. Standardized methods like the shake-flask method and likely also the slow stirring method are not considered suitable to measure $\log K_{ow}$ for surface-active compounds.^{5,6}

Alternative methods are therefore required to measure or predict the hydrophobicity of surfactants or to develop parameters that can be applied in quantitative structure–activity relationships (QSARs). QSAR models for more complex compounds are a necessity to meet the regulatory needs of the European legislation on chemicals (i.e., REACH program). Sorption to a hydrophobic phase other than 1-octanol may be used to reflect the hydrophobicity of different surfactants. Promising phases are stationary phases used in liquid chromatography, e.g., C_{18} reversed phase,^{7–9} or polymers used in passive sampling or solid-phase extraction devices.^{10,11} In this study, we have selected a polyacrylate-coated solid-phase microextraction (SPME) fiber as a phase to study sorption of surfactants. The polyacrylate polymer is preferred over polydimethylsiloxane because polyacrylate is more sensitive toward the tested surfactants. Polyacrylate is composed of mostly esterified acrylic copolymer, but the exact composition is not known. The polymer has a high thermal stability and chemical resistance and mostly undergoes nonspecific van der Waals and hydrogen bond interactions with neutral organic sorbates. The SPME method has been mainly applied in environmental studies to measure freely dissolved concentrations of neutral organic compounds.¹² The main advantage of the SPME method is that phase separation is not required. A fiber with some specific coating can be put into a solution and can be easily withdrawn after a certain exposure time. The polyacrylate polymer was recently used to measure polar functionalized molecules such as pharmaceuticals, hormones, and pesticides with moderate to high hydrophobicity ($\log K_{ow} > 2.5$).^{13,14} Furthermore, polyacrylate fibers have been shown to be applicable for the measurement of freely dissolved concentrations of nonionic, anionic, and cationic surfactants.^{15–17} For nonionic and anionic surfactants, fiber–water partition coefficients in seawater medium have been shown to be concentration independent.^{15,16} However, cationic surfactants show nonlinear sorption to polyacrylate fibers because of the presence of acidic functional groups on the surface of the polymer.^{17,18}

In this study, polyacrylate fibers were used to derive an empirical parameter that reflects the hydrophobicity for a selection of neutral and anionic surfactants. Fiber–water sorption coefficients may then be used as a parameter to predict sorption, bioaccumulation, or toxicity for neutral and anionic surfactants although we realize that adsorption coefficients should not be used for absorption processes and vice versa. Considering that more interactions are involved in environmental sorption and bioconcentration processes, additional sorption phases may be needed in the future to predict the environmental behavior of neutral and anionic surfactants. Homologous series of nonionic and anionic surfactants (same headgroup but varying carbon chain length) and chemicals with different polar headgroups were selected in this study as test compounds. The selected surfactant classes include alcohol ethoxylates, alkyl carboxylates, alkyl sulfates, and alkyl sulfonates. Solution chemistry variables such as pH and ionic strength are considered important variables for the speciation of anionic surfactants and are taken into account. Note that polyacrylate is a phase that will also have certain interactions

with surfactants that need interpretation, but the strength of the approach is that it presents a set of experimentally determined sorption coefficients for a large number of surfactants from different classes to the same defined sorption phase. The possibility of using an alternative for octanol–water partitioning has important consequences for the regulatory evaluation of surfactants. New estimation methods for surfactants are urgently needed, because it is simply impossible to generate experimental data for all existing surfactants that are produced.

MATERIALS AND METHODS

Chemicals and Materials. Alcohol ethoxylates, C_xEO_y ($C_{10}EO_4$, $C_{12}EO_4$, $C_{12}EO_5$, $C_{12}EO_6$, $C_{12}EO_7$, $C_{12}EO_8$, $C_{13}EO_4$, $C_{14}EO_8$, and $C_{16}EO_8$), and sodium salts of linear alkyl carboxylates, C_xCO_2 ($C_{11}CO_2$, $C_{13}CO_2$, and $C_{14}CO_2$), were obtained from Sigma-Aldrich (Zwijndrecht, The Netherlands). The compound $C_{13}EO_8$ was synthesized by Roy Sheppard, Unilever, Port Sunlight Research Laboratory.¹⁹ Sodium salts of linear alkyl sulfates (C_xSO_4) and linear alkyl sulfonates (C_xSO_3) were obtained from Sigma-Aldrich ($C_{12}SO_4$) and from Research Plus (South Plainfield, NJ; $C_{13}SO_4$, $C_{15}SO_4$, $C_{16}SO_4$, $C_{17}SO_4$, $C_{14}SO_3$, $C_{15}SO_3$, and $C_{16}SO_3$). An alkyl benzenesulfonic acid, C_{12} -2-LAS was synthesized as sodium salt by Zhu et al.²⁰ All organic compounds had purities higher than 98%, except for $C_{10}EO_4$ and C_{12} -2-LAS (both $\geq 97\%$). All inorganic salts (NaH_2PO_4 , H_2O , $Na_2HPO_4 \cdot 12H_2O$, NaN_3 , $CaCl_2 \cdot 2H_2O$, $MgSO_4 \cdot 7H_2O$, $NaHCO_3$, $KHCO_3$, and $NaCl$) and glacial acetic acid were obtained from Merck Chemicals (Amsterdam, The Netherlands). Ammonium acetate and sodium acetate were purchased from Sigma-Aldrich. Methanol was obtained from Biosolve (Valkenswaard, The Netherlands). Ultrapure water was obtained from a Millipore water purification system (resistivity $> 18 \text{ M}\Omega/\text{cm}$, Merck Chemicals).

Glass optical fibers coated with polyacrylate were obtained from Polymicro Industries (Phoenix, AZ). Fibers with different thicknesses were used in this study: $7 \mu\text{m}$ ($V_{\text{fiber}} = 3.3 \mu\text{L}/\text{m}$) and $35 \mu\text{m}$ polyacrylate fiber ($V_{\text{fiber}} = 15.0 \mu\text{L}/\text{m}$). Fibers were cut to an appropriate length (varying from 4 to 8 cm), conditioned at 120°C for 16 h under a nitrogen flow,¹⁶ and stored in ultrapure water until further use. Glass scintillation vials of 20 mL with polyethylene-lined caps were obtained from PerkinElmer (Waltham, MA).

Optimization of Experimental Test Conditions. Alkyl sulfates were selected as model compounds to optimize experimental test conditions, i.e., influence of headspace volume and medium composition on recovery of analytes from water (no fibers were added in both experiments), and desorption of analytes from the fiber. The influence of headspace volume was tested by spiking alkyl sulfates (C_{15} to $C_{18}SO_4$) dissolved in methanol into increasing volumes of ultrapure water (v/v 0.2%; $V = 20$ to 24.5 mL). No biocide was added in this experiment. The available headspace volume was estimated by measuring the internal glass surface unexposed to water with a ruler. For all experiments, the test vials were shaken in the dark at $20 \pm 1^\circ\text{C}$ and 150 rpm on a Laboshake reciprocal shaker from Gerhardt (Königsberg, Germany). After 1 day of shaking, water samples were taken for direct analysis with LC-MS/MS. The remaining water volume was divided over two vials, and methanol was subsequently added (methanol/water, 50/50) to measure the recovery of the test analytes.

The influence of medium composition on the recovery of alkyl sulfates (C_{15} to $C_{18}SO_4$) was tested with ultrapure water, 5 mM NaH_2PO_4/Na_2HPO_4 pH 7 buffer, and Dutch Standard Water (containing 1.36 mM $CaCl_2 \cdot 2H_2O$, 0.73 mM $MgSO_4 \cdot 7H_2O$, 1.19 mM $NaHCO_3$, and 0.20 mM $KHCO_3$) with minimum headspace volume (small air bubble of <1 cm was visible). A biocide was added to this experiment and all subsequent experiments to inhibit biodegradation of the analytes (1 mM sodium azide). After 1 week, the samples were extracted with a similar procedure as described above. The vial caps were extracted separately.

Desorption of analytes from fibers was tested by exposing fibers for 1 week to water (only containing 1 mM sodium azide) spiked with alkyl sulfates (C_{15} to $C_{18}SO_4$). The fibers were sequentially desorbed into methanol with or without 10 mM ammonium acetate (two times). Finally, the fibers were extracted overnight in the same solvent composition.

Fiber–Water Equilibration of Neutral and Anionic Surfactants. Equilibration of the test analytes between fiber and water was measured by exposing fibers in sodium phosphate buffer at pH 7. Five different mixtures of surfactants were used: mixture A containing $C_{10}EO_4$, $C_{12}EO_5$, $C_{12}EO_6$, $C_{12}EO_7$, $C_{12}EO_8$, and $C_{13}EO_8$; mixture B containing $C_{12}EO_4$, $C_{13}EO_4$, $C_{14}EO_8$, and $C_{16}EO_8$; mixture C containing $C_{11}CO_2$, $C_{13}CO_2$, and $C_{14}CO_2$; mixture D containing $C_{15}SO_4$, $C_{16}SO_4$, $C_{17}SO_4$, and $C_{18}SO_4$; and mixture E containing $C_{14}SO_3$, $C_{15}SO_3$, and $C_{16}SO_3$. Fiber and water samples were taken in duplicate over a period of 7 days for mixtures A to C and 21 days for mixtures D and E. Fibers were desorbed in 800 μ L of methanol containing 10 mM ammonium acetate. The fibers were allowed to desorb for 1 day at room temperature. Both fiber and water samples were reconstituted to the desired mobile phase composition for LC-MS/MS analysis (80/20 methanol/water).

Fiber–Water Distribution of Anionic Surfactants. The effect of pH on distribution of $C_{11}CO_2$ between fiber and water was tested in buffered solutions at pH 3/4/5 (5 mM acetic acid/sodium acetate buffer) and at pH 6/7/8 (5 mM sodium phosphate buffer) at a single aqueous concentration of $C_{11}CO_2$ (triplicate samples). To ensure detectable concentrations of $C_{11}CO_2$ in fiber and water samples, total concentrations in water were increased in samples with higher pH values: 1800 μ g/L at pH 8, 1000 μ g/L at pH 7, and 300 μ g/L at pH 3/4/5/6. The fiber–water equilibration time was 7 days.

The effect of pH and ionic strength on distribution of $C_{12}SO_4$ between fiber and water was tested at pH 4/5/6/7 (using the same buffers mentioned above) with increasing concentrations in water (500 to 23 000 μ g/L; triplicate samples). Parallel to the buffered treatments (containing 8 mM Na^+), sodium concentrations were increased at pH 7 to levels occurring in seawater (469 mM $NaCl$). The effect of calcium (10 mM $CaCl_2$; pH 8.1) on the distribution of $C_{12}SO_4$ was tested in a nonbuffered treatment (because of calcium precipitation in a sodium phosphate buffer). Distribution of alkyl sulfates and alkyl sulfonates with longer chain lengths ($C_{13}SO_4$, $C_{15}SO_4$, $C_{16}SO_4$, $C_{17}SO_4$, $C_{14}SO_3$, $C_{15}SO_3$, and $C_{16}SO_3$) between fiber and water was measured for individual compounds at pH 7 in 5 mM sodium phosphate (50 to 4000 μ g/L; triplicate samples). The fiber–water equilibration time was 17 to 21 days.

Chemical Analysis. All compounds were analyzed on a PerkinElmer (Norwalk, CT) liquid chromatographic system (PE200 series LC) coupled to a triple quadrupole mass

spectrometer (MDS Sciex API 3000 MS/MS System, Applied Biosystems, Foster City, CA). The interface was a Turbo Ion spray source operated at 250 to 400 °C (Applied Biosystems). All compounds were optimized for MS by direct infusion of standard solutions of the analytes. A solvent delay switch (Da Vinci, Rotterdam, The Netherlands) was used to prevent the inorganic constituents in water samples (sodium azide and sodium phosphate) from interfering with the ionization of the compounds and entering the mass spectrometer. The column used in the separation of test analytes was Gracesmart C_{18} column (150 \times 2.1 mm; 5 μ m particle size; Grace Discovery Sciences, Breda, The Netherlands). The analytes were separated using an isocratic method with an eluent composition of 90:10 methanol–water containing 10 mM ammonium acetate. The mass spectrometer settings used in the detection of the analytes are shown in Table S1. Chromatograms were integrated with Analyst 1.4.2 (Applied Biosystems).

Data Analysis. A first-order one-compartment model was fitted to the concentrations in fiber versus time with Graphpad Prism version 5.00 (Graphpad Software, San Diego, CA):

$$c_{\text{fiber}} = \frac{k_1}{k_2} c_{\text{total}} (1 - e^{-k_2 t}) \quad (1)$$

where c_{fiber} is the concentration in the fiber (in mg/L), k_1 and k_2 are uptake and elimination rate constants (in hour⁻¹), c_{total} is the total measured concentration in water (in mg/L), and t is time (in hours). In case the test analyte concentration in the aqueous solution was depleted more than 5%, eq 1 changed into:²¹

$$c_{\text{fiber}} = \frac{k_1}{k_1 \frac{V_{\text{fiber}}}{V_{\text{water}}} + k_2} c_{\text{total}} (1 - e^{-[k_1 \frac{V_{\text{fiber}}}{V_{\text{water}}} + k_2] t}) \quad (2)$$

The effect of pH on fiber–water distribution of $C_{11}CO_2$ was fitted with the following equation:

$$\log D_{\text{fiber}} = \log K_{\text{fiber}} + \log f_{\text{neutral}} = \log K_{\text{fiber}} + \log \left(\frac{1}{1 + 10^{\text{pH} - \text{pK}_a}} \right) \quad (3)$$

where D_{fiber} is the fiber–water distribution coefficient (in L/L), K_{fiber} is the fiber–water partition coefficient (in L/L), f_{neutral} is the neutral fraction, and pK_a is the acid dissociation constant.

Freundlich sorption isotherms were fitted to nonlinear fiber–water sorption isotherms with

$$\log c_{\text{fiber}} = \log K_F + N \times \log c_{\text{water}} \quad (4)$$

where K_F is the Freundlich sorption coefficient (intercept) and N is the nonlinearity exponent (slope).

RESULTS AND DISCUSSION

Optimization of Experimental Test Conditions. A series of alkyl sulfates (C_{15} to $C_{18}SO_4$) were chosen as model compounds for optimization of the experimental conditions for the sampling of water (headspace volume and medium composition) and fiber (desorption conditions). The effect of headspace volume of the used 20 mL vials on the measured concentration in the aqueous phase was tested in order to check for possible losses from the experimental system (no fibers were added). The volume of water (without added salts) was varied from 20 to 24.5 mL. With increasing headspace volume, increased losses were observed with increasing chain length of alkyl sulfates; see Figure S1. These losses were attributed either to sorption to the glass wall or to the air–

water interface. Hardly any effect of headspace volume was observed for $C_{15}SO_4$, but losses up to 67% were observed for $C_{18}SO_4$. Subsequent experiments were therefore performed with minimum headspace volume. Previously, recoveries of alcohol ethoxylates were also increased by minimization of the headspace volume.¹⁵

The effect of medium composition on the recovery of alkyl sulfates (C_{15} to $C_{18}SO_4$) from the water phase was subsequently tested (no fibers were added). Recoveries from ultrapure water and 5 mM sodium phosphate buffer at pH 7 were about 100%, but recoveries decreased with increasing chain length of alkyl sulfates in water containing divalent cations such as calcium and magnesium; see Figure S2. The losses were attributed to the formation of calcium/magnesium-bridging complexes between alkyl sulfates and the glass wall. The compounds also sorbed to the vial cap (lined with polyethylene) in the presence of divalent cations. The sorbed amount to the vial cap increased with increasing chain length of the alkyl sulfates (ranging from 2% to 6%). From these results, it was decided that the medium composition for subsequent experiments should only contain monovalent cations to prevent losses of alkyl sulfates to vial surfaces (i.e., 5 mM of sodium phosphate buffered at pH 7).

Finally, the organic solvent used to desorb alkyl sulfates (C_{15} to $C_{18}SO_4$) from 35 μ m polyacrylate fibers was evaluated. Extraction of fibers with 90/10 methanol/water without ammonium acetate resulted in slow desorption of the test analytes; see Figure S3. However, extraction of the fiber in methanol containing 10 mM ammonium acetate resulted in instantaneous desorption of the analytes. This suggests that ammonium acetate functions as an ion-pairing reagent in the extraction of alkyl sulfates from the fiber.²² Ammonium acetate was therefore used in all experiments to ensure complete desorption of anionic surfactants from fibers.

Fiber–Water Equilibration of Neutral and Anionic Surfactants. Equilibrium profiles of partitioning/distribution of alcohol ethoxylates, alkyl carboxylates, alkyl sulfates, and alkyl sulfonates between 35 μ m polyacrylate fibers and water were determined; see Figures S4 to S6. Representative equilibrium profiles of $C_{11}CO_2$, $C_{18}SO_4$, and $C_{12}EO_7$ are shown in Figure 1. Fiber–water partition or distribution coefficients (K_{fiber} or $D_{\text{fiber}} = k_1/k_2$) were calculated from the

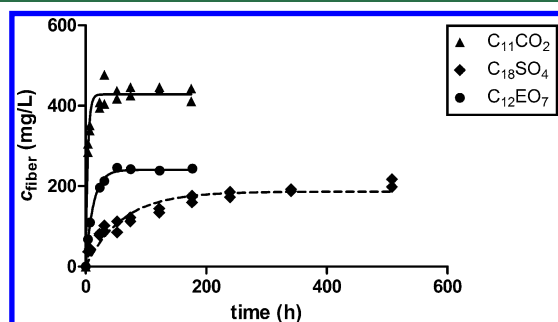


Figure 1. Concentrations of dodecyl carboxylic acid ($C_{11}CO_2$), octadecyl sulfate ($C_{18}SO_4$), and dodecyl heptaethylene glycol ($C_{12}EO_7$) in 35 μ m polyacrylate fibers versus time. The data were fitted with a one-compartment model assuming first-order kinetics. Depletion of the water phase was taken into account. A replicates test showed a poor fit for $C_{18}SO_4$ (indicated with the dashed line). The medium was buffered with 5 mM sodium phosphate at pH 7 and contained 1 mM sodium azide.

ratio of uptake (k_1) and elimination (k_2) rate coefficients obtained by fitting a one-compartment model to the data assuming first-order kinetics; see eq 1 and Table S2. The aqueous phase was depleted by more than 5% for the following compounds, i.e., $C_{12}EO_4$ (6%), $C_{13}EO_4$ (16%), $C_{16}EO_8$ (25%), $C_{13}CO_2$ (14%), and $C_{14}CO_2$ (40%). For these compounds, the kinetic model was adjusted to take depletion of the aqueous phase into account; see eq 2. Recoveries were close to 100%, except for $C_{12}EO_4$ and $C_{12}EO_5$ (66% and 74%) which may be caused by sorption of these compounds to the glass wall of the vials. Note that fiber–water partitioning of alcohol ethoxylates decreases with increasing ethoxylation (see below).

Compounds with increasing carbon chain length showed increasing $\log k_1$ and constant $\log k_2$ values indicating that the diffusive resistance in the polyacrylate polymer is the rate-limiting step in the partition process;^{23,24} see Figure S7. The rate-limiting step changed from diffusion into the polymer to diffusion across an unstirred boundary layer (surrounding the fiber) at a $\log K_{\text{fiber}}$ or $\log D_{\text{fiber}}$ value of 3.5.²⁴ Below this value, equilibration of compounds between fiber and water only depended on diffusion of test analytes into the fiber coating resulting in similar equilibration times (~ 2 days). Above a $\log K_{\text{fiber}}$ or $\log D_{\text{fiber}}$ value of 3.5, equilibration times for more hydrophobic compounds increased to 3–4 days; see the time to reach 95% of equilibrium ($t_{95\%}$) for $C_{14}EO_4$, $C_{16}EO_8$, and $C_{14}CO_2$ in Table S2. This breaking point at $\log K_{\text{fiber}}$ of around 3.5 corresponds very well with earlier data for neutral organics with the same fiber coating.^{23,24} The $t_{95\%}$ values ranged from 23 to 101 h for alcohol ethoxylates and from 11 to 57 h for alkyl carboxylates.

Fiber–Water Distribution of Anionic Surfactants. The effect of pH on the fiber–water distribution of $C_{11}CO_2$ was tested with 35 μ m polyacrylate fibers; see Figure 2. The

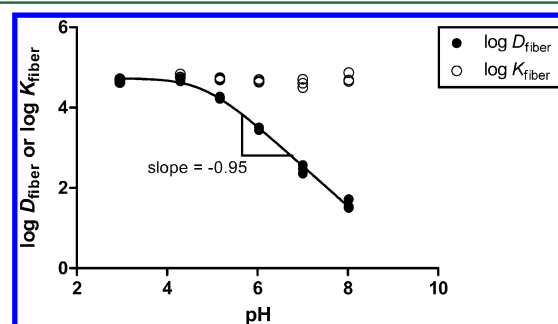


Figure 2. Logarithmic 35 μ m polyacrylate fiber–water partition (K_{fiber}) and distribution (D_{fiber}) coefficients of dodecyl carboxylic acid ($C_{11}CO_2$) versus pH of the medium. The medium was buffered with 5 mM sodium acetate (pH 3/4/5) or 5 mM sodium phosphate (pH 6/7/8) and contained 1 mM sodium azide.

concentrations in the fiber increased with decreasing pH of the medium. A constant partition coefficient was obtained when the neutral fraction approached 1 at pH values lower than 2 log units below the pK_a value. A $\log K_{\text{fiber}}$ value of 4.73 ± 0.04 for the neutral form of $C_{11}CO_2$ was calculated with eq 3. After normalization of the separate $\log D_{\text{fiber}}$ values with the neutral fraction of the compound ($K_{\text{fiber}} = D_{\text{fiber}}/f_{\text{neutral}}$), a constant $\log K_{\text{fiber}}$ value of 4.70 ± 0.02 was calculated; see Figure 2 (open symbols). In addition, a pK_a value of 4.82 was calculated with eq 3. After correction for ionic strength, the pK_a value decreased to 4.78.²⁵ This value is close to an average pK_a value of 4.86 ± 0.02 ($N = 8$) calculated for a series of alkyl carboxylic

acids, i.e., from propanoic to nonanoic acid in dilute aqueous solutions.²⁶ These data provide evidence that only the neutral fraction of $C_{11}CO_2$ partitions to the fiber ($f_{\text{neutral}} = 0.007$ at pH 7). Because sorption of $C_{11}CO_2$ is dominated by the neutral fraction, linear distribution was observed for this compound (unpublished results). Similar pH-dependent polyacrylate fiber–water distribution coefficients have also been observed for small organic acids like chlorophenols,²⁷ estradiol, and triclosan.¹³

Equilibration times for alkyl sulfates and alkyl sulfonates were much longer compared to those for alcohol ethoxylates and alkyl carboxylates; see Figure S6. The equilibration time for 35 μm polyacrylate fiber–water distribution of alkyl sulfates and alkyl sulfonates was nearly 3 weeks (concentrations in the fiber did not increase further with longer equilibration times). This may be an indication for another sorption mechanism to the fiber (see below) compared to alcohol ethoxylates and alkyl carboxylates. A one-compartment model was fitted to these data, but a replicates test showed a poor fit for $C_{15}SO_3$ and all tested alkyl sulfates.

The effect of pH on the fiber–water distribution of $C_{12}SO_4$ (35 μm polyacrylate fibers) is shown in Figure S8 and Table S3. Initially, it was hypothesized that sorption of $C_{12}SO_4$ to the fiber would become linear near the pK_a value of the compound ($pK_a = 1.9$),²⁸ similar to the pH dependence of $C_{11}CO_2$. However, the nonlinearity of the fiber–water sorption isotherms of $C_{12}SO_4$ increased with decreasing pH (N decreased from 0.38 to 0.09 from pH ~ 7 to ~ 4 ; see eq 4). Increasing sorption of $C_{12}SO_4$ to the fiber was observed with decreasing pH, analogous to the effect of pH on sorption of $C_{11}CO_2$ to the fiber. Sorption affinity or Freundlich coefficients ($\log K_F$) of $C_{12}SO_4$ increased with a factor of 6 \times at pH ~ 6 , 40 \times at pH ~ 5 , and 63 \times at pH ~ 4 compared to the sorption affinity of $C_{12}SO_4$ at pH ~ 7 . Note that the surface charge on the fiber also decreases with decreasing pH; see below.

Addition of 469 mM sodium ions (equal to levels in seawater) to the medium at pH ~ 7 increased the linearity of the sorption process to the fiber ($N = 0.51$) compared to the treatment containing only 5 mM sodium phosphate buffer ($N = 0.38$); see Figure S8 and Table S3. The recovery of the treatments containing high sodium concentrations decreased to $\sim 80\%$, probably because of sorption of $C_{12}SO_4$ to the test vial. Fiber–water sorption isotherms of alkyl sulfates and alkyl sulfonates with longer chain lengths than $C_{12}SO_4$ ($C_{13}SO_4$, $C_{15}SO_4$, $C_{16}SO_4$, $C_{17}SO_4$, $C_{14}SO_3$, $C_{15}SO_3$, and $C_{16}SO_3$) showed an increased affinity for the fiber with increasing chain length and nonlinear sorption isotherms ($0.29 < N < 0.65$); see Figure S9 and Table S4.

Possible Sorption Mechanism of Anionic Surfactants.

Previously, linear partitioning of alkyl benzenesulfonates to 7 μm polyacrylate fibers was observed in seawater medium by Rico-Rico et al.¹⁶ In this study, nonconditioned fibers showed nonlinear distribution of alkyl benzenesulfonates whereas temperature-conditioned fibers (at 120 $^{\circ}\text{C}$ for 16 h under a helium stream) resulted in linear “partitioning” of alkyl benzenesulfonates to 7 μm polyacrylate fibers. It was concluded that the polyacrylate polymer underwent a change in sorption properties because the glass transition temperature was exceeded during the temperature-conditioning treatment (going from a glassy to a rubbery state).¹⁶ Earlier results from Rico-Rico et al.¹⁶ were repeated in seawater medium to check for possible inconsistencies in the currently adopted method. Sorption of increasing concentrations of an alkyl

benzenesulfonate (C_{12} -2-LAS) was measured to 7 μm polyacrylate fibers that were originally used in that study (purchased in May 2001). This resulted in nearly linear fiber–water sorption isotherms ($N = 0.83$; data not shown) and an average $\log D_{\text{fiber}}$ value of 3.40 which is a factor of two higher than the reported $\log K_{\text{fiber}}$ value of 3.1.¹⁶ This suggests that high concentrations of sodium and calcium ions along with the specific sorption properties of this polymer contributed to the linearity of the sorption process of anionic surfactants with a low pK_a value ($pK_a = 2.55$ for dodecyl benzenesulfonic acid).²⁹ Previously, the observed linearity of sorption isotherms for alkyl benzenesulfonates was also suggested to be caused by the presence of calcium ions in seawater medium.³⁰

The 7 μm polyacrylate fiber originally used by Rico-Rico et al.¹⁶ and the more recently purchased 7 and 35 μm polyacrylate fibers (in January 2012) were used to measure sorption isotherms of $C_{12}SO_4$ in 10 mM calcium chloride (at pH 8.1). Addition of 10 mM calcium chloride increased the linearity of the 35 μm fiber–water distribution of $C_{12}SO_4$ at pH ~ 8 ($N = 0.49$ vs $N = 0.38$ at pH ~ 7 in 5 mM sodium phosphate buffer); see Figure S10 and Table S3. The 7 μm fiber used by Rico-Rico et al.¹⁶ showed more linear distribution ($N = 0.87$) compared to the recently purchased 7 μm fiber ($N = 0.48$). Interestingly, both 7 μm fibers showed a higher response compared to 35 μm fibers. Normalization of the concentration of $C_{12}SO_4$ in the fiber to the fiber surface area resulted in similar sorption isotherms for both 7 and 35 μm fibers (only for new batch of fibers); see Figure S11. This suggests that sorption of $C_{12}SO_4$ in a medium containing calcium chloride is probably determined by surface adsorption. However, sorption isotherms in a medium containing 5 mM sodium phosphate did not show overlapping sorption isotherms for 7 and 35 μm fibers; see Figure S12. No plausible explanation could be found for the different response of both fibers in a medium containing sodium phosphate. Sorption of calcium bridging complexes of $C_{12}SO_4$ to the fiber or reduction of the fiber surface charge (i.e., less electrostatic repulsion) may occur in the treatment containing calcium.³¹ Calcium bridging complexes with anionic surfactants may involve charged carboxylic acid groups which are believed to occur on the fiber surface of the polyacrylate polymer.^{17,18} In previous experiments, two permanently charged cationic surfactants showed a maximum sorption level on 7 μm polyacrylate fibers that corresponded to the cation exchange capacity experimentally determined for this fiber.¹⁷ In addition, the basic pharmaceutical chlorpromazine ($f_{\text{neutral}} = 0.005$; $pK_a = 9.3$) showed a dual-mode uptake to 35 μm polyacrylate fibers with nonlinear adsorption of the cationic species to the cation exchange sites on the fiber and linear absorption of the neutral species to the fiber.¹³

The reason for the nonlinearity of the sorption of alkyl sulfates to polyacrylate fibers is not completely clear. The longer observed equilibration time for alkyl sulfates points to a rate-limiting sorption process to the fiber. An increase in the sorption affinity with decreasing pH may be related to an increase in the neutral fraction of $C_{12}SO_4$. However, the nonlinearity of the distribution process cannot be explained by mere sorption of the neutral fraction which is negligibly low for alkyl sulfates at pH 7. Another sorption mechanism may therefore contribute to the sorption of anionic surfactants with a low pK_a value. At high sodium ion concentrations, the sorption affinity for the fiber is probably increased due to higher sorption of ion-pairs of $C_{12}SO_4$ and sodium ions. The long equilibration time may also suggest slow sorption of ion-pairs.

Partitioning of ion-pairs of organic anions and inorganic cations also occur in octanol–water systems,^{32,33} whereas ion-pairs are assumed to contribute less in partitioning of organic anions to phospholipid membranes.^{34,35} The sorption affinity of $C_{12}SO_4$ to the fiber may also be increased by salting-out of $C_{12}SO_4$. However, salting-out effects in ionic strength equal to seawater are less than a factor of 2 for long-chained neutral compounds like dialkyl phthalates,³⁶ whereas the sorption affinity of $C_{12}SO_4$ to the fiber increased with a factor of 10. A salting-out effect is, therefore, unlikely in our experiments.

In addition to the above-mentioned sorption mechanisms, alkyl sulfates may adsorb on the surface of the fiber (as anion or ion-pair). Assuming that alkyl sulfates have a surface area per molecule of 0.4 to 0.7 nm²,³⁷ a total number of molecules on the fiber surface (22.18 mm² for 4 cm fiber) can be calculated, i.e., 3.2 to 5.5×10^{13} surfactant molecules. The highest concentration of alkyl sulfates measured in the fiber at pH 7 is only about 5 to 20 times higher than the calculated amount based on (monolayer) surface coverage. However, an adsorption mechanism does not fully explain the increased affinity of $C_{12}SO_4$ for the fiber with decreasing pH (in case only monolayers of surfactants are formed). In addition, $C_{12}SO_4$ shows different affinities for 7 and 35 μ m fibers when concentrations in the fiber are normalized for fiber surface area; see Figure S12). None of the described sorption mechanisms, absorption of neutral fraction, absorption of ion-pairs, or adsorption of ion-pairs or anions, can therefore be mutually excluded on the basis of these results.

Effects of Structure on Fiber–Water Partitioning/Distribution. The measured $\log D_{\text{fiber}}$ values for alkyl carboxylates and $\log K_{\text{fiber}}$ values for alcohol ethoxylates with constant ethoxylate unit length correlate well with the number of aliphatic carbon atoms; see Figure 3. The $\log D_{\text{fiber}}$ or \log

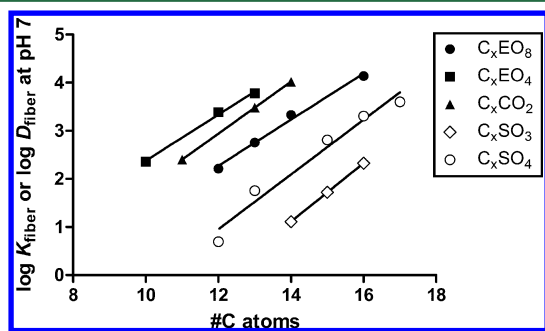


Figure 3. Logarithmic 35 μ m polyacrylate fiber–water partition ($\log K_{\text{fiber}}$) or distribution coefficients ($\log D_{\text{fiber}}$) versus amount of carbon atoms (#C atoms) for alcohol ethoxylates (with 4 and 8 ethoxylate units; C_xEO_4 and C_xEO_8), alkyl carboxylates (C_xCO_2), alkyl sulfonates (C_xSO_3), and alkyl sulfates (C_xSO_4). The medium was buffered with 5 mM sodium phosphate at pH 7 and contained 1 mM sodium azide.

K_{fiber} values at pH 7 increased by about 0.5 log units with every increase in carbon atoms (pooled slope for alkyl carboxylates and alcohol ethoxylates). A regression with the number of carbon atoms and ethoxylate units showed that $\log K_{\text{fiber}}$ or $\log D_{\text{fiber}}$ values at pH 7 of alcohol ethoxylates and alkyl carboxylates increase with 0.47 to 0.54 log units per carbon atom and decrease with 0.27 log units per ethoxylate unit; see eqs 5 and 6 (see also Figure S13). Note that the increment per carbon atom or decrement per ethoxylate unit can have different values for other hydrophobic phases. For example, a C_{18} HPLC stationary phase does not distinguish between

different ethoxymers using a mobile phase composition of methanol and water.⁸ The increment per carbon atom is in line with earlier publications for fiber–water partitioning of alcohol ethoxylates and alkyl benzenesulfonates performed in seawater with 0.47–0.51 log units^{15,16} and sediment–water partitioning of alkyl benzenesulfonates with ~ 0.4 –0.44 log units.^{31,38} The increment is also comparable to the fragment used in calculating $\log K_{\text{ow}}$ values with KowWin (v. 1.68), 0.49 log units,³⁹ and to the increase in $\log K_{\text{ow}}$ or $\log K_{\text{fiber}}$ (polyacrylate) values calculated for a series of alkanes (C_5 to C_{18}) with polyparameter LFERs, 0.54 or 0.46 log units, respectively.^{40,41} This shows that partitioning per CH_2 group to different phases is mainly related to the energy required to create a cavity in water (i.e., hydrophobic effect).

Alcohol ethoxylates:

$$\log K_{\text{fiber}} = (0.47 \pm 0.01)\#C - (0.27 \pm 0.01)\#EO - 1.326 \pm 0.15$$

$$R^2 = 0.996; \quad \text{SER} = 0.056; \quad N = 10$$
(5)

Alkyl carboxylates:

$$\log D_{\text{fiber}} = (0.54 \pm 0.00)\#C - 3.52 \pm 0.01$$

$$R^2 = 1.000; \quad \text{SER} = 0.001; \quad N = 3$$
(6)

For anionic surfactants with a pK_a value ≤ 2 such as alkyl sulfates and alkyl sulfonates, no constant D_{fiber} was determined because of nonlinear sorption to the fiber. Another method to determine D_{fiber} for nonlinear sorption isotherms is to calculate D_{fiber} at a constant fiber loading. This approach seems more reasonable considering that sorption properties of the fiber are only dependent on the solute loading of the fiber and are not directly related to the concentration in water.⁴² The sorption coefficients of alkyl sulfates and alkyl sulfonates were therefore compared at the same solute loading on the fiber. Concentrations in water were calculated with a Freundlich sorption isotherm at a constant fiber loading of 0.5 mM. This is an average concentration in the fiber where all fiber–water sorption isotherms overlapped, except for $C_{14}SO_3$ and $C_{15}SO_3$. The Freundlich models of the two latter compounds were therefore extrapolated. Fiber–water distribution coefficients ($D_{\text{fiber}} = c_{\text{fiber}}/c_{\text{water}}$) were subsequently calculated at the constant fiber loading of 0.5 mM and the calculated concentration in water. The calculated increment in $\log D_{\text{fiber}}$ per carbon atom is 0.57 and 0.61 log units for alkyl sulfates and alkyl sulfonates, respectively; see eqs 7 and 8 and Figure 3. The calculated fiber–water distribution coefficients for all tested anionic surfactants now increase with increasing neutral fraction of the surfactants, i.e., alkyl carboxylates ($pK_a = 4.86$) > alkyl sulfates ($pK_a = 1.9$)²⁸ > alkyl sulfonates ($pK_a = -1.9$),⁴³ although no linear trend of the $\log D_{\text{fiber}}$ values with neutral fraction was observed (data not shown).

Alkyl sulfonates ($c_{\text{fiber}} = 0.5 \text{ mM}$)

$$\log D_{\text{fiber}} = (0.61 \pm 0.00)\#C - 7.40 \pm 0.02$$

$$R^2 = 1.000; \quad \text{SER} = 0.002; \quad N = 3$$
(7)

Alkyl sulfates ($c_{\text{fiber}} = 0.5 \text{ mM}$)

$$\log D_{\text{fiber}} = (0.57 \pm 0.06)\#C - 5.87 \pm 0.89$$

$$R^2 = 0.967; \quad \text{SER} = 0.251; \quad N = 5$$
(8)

Fiber–Water Sorption as a Hydrophobicity Parameter. Sorption coefficients of neutral and anionic surfactants for polyacrylate fibers could be useful as an empirical parameter that reflects differences in hydrophobicity and that could be applied for example as a descriptor in correlations with sorption, toxicity, or bioaccumulation of surfactants. Only a few literature references are available about bioconcentration of surfactants. These literature data were compared to measured or estimated fiber–water sorption coefficients. Bioconcentration factors (BCF) of surfactants were found in literature for 7 alcohol ethoxylates⁴⁴ and 3 alkyl sulfates for common carp (*Cyprinus carpio*).⁴⁵ The logarithmic BCF values were subsequently correlated with the measured fiber–water sorption coefficients; see Figure 4. For one alcohol ethoxylate

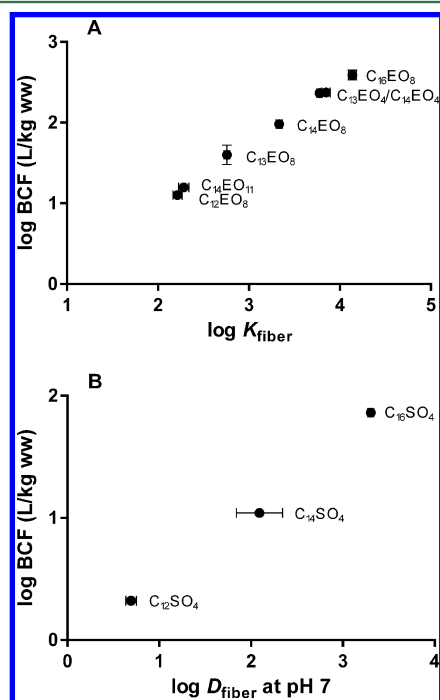


Figure 4. Logarithmic bioconcentration factors (BCF) from literature^{44,45} versus logarithmic 35 μm polyacrylate fiber–water partition/distribution coefficients at pH 7 of (A) alcohol ethoxylates (C_xEO_y) and (B) alkyl sulfates (C_xSO_4).

($C_{14}EO_{11}$) and one alkyl sulfate ($C_{14}SO_4$), fiber–water sorption coefficients were predicted with eqs 5 and 8, while for the other compounds experimental data from this study were used. For alcohol ethoxylates, the linear trend of BCF versus fiber–water partition coefficients is evident; see Figure 4A. Both parameters increase with the number of carbon atoms and decrease with the number of ethoxylate units. Alkyl sulfates follow a similar trend as the alcohol ethoxylates (see Figure 4B). Fiber–water distribution coefficients of alkyl sulfates depend on the (selected) constant fiber loading as well as on the pH and ionic strength of the exposure medium, and these correlations between log BCF and log D_{fiber} will be different under other circumstances. However, on a relative scale, such correlations can be useful for predicting BCF of related compounds. It is expected that bioconcentration of neutral and anionic surfactant classes will have completely different mechanisms depending on the type of headgroup, charge, and substitution of the carbon chain (e.g., perfluorinated compounds). For example, organic anions partition less to biological membranes

than the neutral forms, but they retain a relatively strong membrane affinity compared to either octanol–water or fiber–water distribution of organic anions.^{27,46}

In summary, the polyacrylate fiber shows linear partition/distribution properties for alcohol ethoxylates and alkyl carboxylates (with $pK_a \sim 5$). For alkyl carboxylates, fiber–water distribution at pH 7 is dominated by the low neutral fraction of these compounds and sorption of anionic species is probably negligible compared with the total sorption observed. However, nonlinear distribution to the fiber occurs for alkyl sulfates and alkyl sulfonates with pK_a values much lower than 5. For these anionic surfactants, the linearity of the sorption process is dependent on the pH of the medium, the solution chemistry of the medium providing ion-pairs with sodium ions or bridging complexes with calcium ions, and the sorption properties of the polymer.

As mentioned in the previous paragraph, sorption coefficients of surfactants to polyacrylate fibers could be useful as a parameter that reflects differences in hydrophobicity and as a parameter to predict sorption to other phases. However, sorption to polyacrylate and sorption to organic matter, whole sediment particles, and lipids will not be governed by exactly the same sorption mechanism and types of interaction. Therefore, a single parameter or a single polymer or hydrophobic phase will not be sufficient in predictive modeling of sorption phenomena of surfactants to environmental phases. Likely, we would need a series of phases that correspond with specific types of interaction. Our future research will focus on a systematic study of different interaction types of surfactant classes with “model phases”.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b02901.

Supplementary graphs and tables (PDF)

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Notes

The authors declare no competing financial interest.

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