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Predicting Sediment Sorption Coefficients for Linear Alkylbenzenesulfonate Congeners from Polyacrylate−Water Partition Coefficients at Different Salinities

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The effect of the molecular structure and the salinity on the sorption of the anionic surfactant linear alkylbenzenesulfonate (LAS) to marine sediment has been studied. The analysis of several individual LAS congeners in seawater and of one specific LAS congener at different dilutions of seawater was carried out after extraction by polyacrylate solid-phase microextraction (SPME) fibers. Sorption isotherms for the tested LAS congeners on marine sediment and at different ionic composition were all nonlinear with a constant Freundlich exponent (n_F) of 0.78 ± 0.05. Differences in LAS sorption of a number of congeners were similar to the differences among the linear partition coefficients (K_{fw}) observed for the polyacrylate SPME fibers in seawater. The sorption of LAS to both the sediment and the SPME fiber significantly decreased in media with lower salinity. Dissolved calcium could fully account for the changed affinity of LAS for the SPME fiber, although the high sorption in seawater was also equaled by a corresponding dissolved concentration of NaCl only. Sediment sorption coefficients of a single LAS congener at varying ionic composition was not as strongly related to the K_{fw} values as the relation observed for different LAS compounds in seawater, likely because sorption mechanisms are different in both phases. In the absence of experimental data for octanol−water coefficients (K_{ow}) of (i) individual LAS congeners at (ii) different ionic compositions, the use of K_{fw} as a tool to predict sorption and other hydrophobicity-related processes is suggested.

Introduction

Sorption to sediment is an important process related to the fate, distribution, and toxicity of organic contaminants in the aquatic environment. Sorption of ionic organic compounds, such as the anionic surfactant linear alkylbenzenesulfonate (LAS), is related to their molecular structure, the sediment characteristics, and the specific ionic composition of the aqueous phase (*1*−*3*). The sorption behavior of LAS is partly a hydrophobicity-driven process, as indicated by the increase of the sorption coefficient values with increasing alkyl chain length (*4*, *5*). Also the relation between the sorption affinity and the organic carbon content of natural sorbents shows that hydrophobic interactions are important (*6*, *7*). On the other hand, several studies have revealed that specific chemical and/or electrostatic interactions may also affect the sorption of LAS (*6*−*8*).

In addition to the sorbent and sorbate properties, the aqueous ionic composition also influences the sorption of ionizable organic compounds, because processes such as ion exchange or ion pair formation are directly influenced by the medium composition (*1*, *2*, *9*). Consequently, the sorption of LAS will be different in freshwater and seawater, and sorption coefficients of LAS to organic phases in the marine environment are generally higher than in freshwater media (*5*). The effect of the aqueous ionic composition on sorption is of particular interest in estuaries. These ecosystems are characterized by large salinity gradients, and they are often the receiving areas for urban, harbor, and industrial effluents that may contain relatively high concentrations of surfactants (*3*, *10*, *11*). While the effect of the sorbent properties on the sorption of LAS has been extensively studied, the effect of the solution chemistry has been mainly tested with simple electrolyte solutions (*6*, *12*). Information about the effect of the composition of aqueous solutions on the sorption of LAS and other anionic organic compounds is thus scarce.

Commercial LAS consists of a mixture of molecules with different alkyl chain lengths (10−14 carbon atoms) and isomers that vary in the position of the benzenesulfonate moiety on the alkyl chain. A typical product contains more than 20 different LAS congeners (*13*). Because it is not feasible to test the sorption of each compound in a whole range of conditions, estimation methods that relate sorption to the molecular structure and other factors that affect sorption of LAS are needed. Although information about the sorption of individual isomers is clearly relevant for a detailed understanding of sorption processes in LAS-exposed sediments, most of the sorption studies have used commercial LAS mixtures. Sorption data for individual LAS congeners have only been reported for a few compounds (*4*, *6*). Several studies have shown that sorption increases with longer alkyl chains in LAS molecules (*4*, *6*, *14*, *15*). One study has shown that the isomers with the most external phenyl positions have a higher sorption affinity to sediments than isomers where the phenyl is attached to the more internal carbon atoms of the alkyl chain (*4*).

In this study, we have used polyacrylate (PA) solid-phase microextraction (SPME) fibers for the analysis of freely dissolved LAS concentrations in sediment sorption tests. The SPME method has been extensively applied for the analysis of freely dissolved concentrations of organic compounds in complex matrixes (see, for instance, refs *16*−*20)*. SPME is considered to be a practical passive sampling procedure, because phase separation and purification steps are not needed (*21*−*23*). Application of this method to ionic organic compounds is more complicated than the SPME analysis of nonionized chemicals, but earlier work has shown that the method is suitable for LAS in seawater solutions (*24*).

The main aim of the present work was to investigate the effect of the molecular structure and the solution chemistry on sorption of LAS to sediment. The effect of the molecular structure on the sorption of LAS to a natural sediment was studied in artificial seawater media using nine individual

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LAS congeners. To our knowledge, this is the first study reporting sorption coefficients for several single LAS compounds at seawater conditions. For one specific LAS structure (C_{12}-2-LAS), the effect of the ionic composition of the medium on sediment sorption was investigated, using dilutions of both standardized freshwater and seawater.

To use the SPME method at different ionic compositions, sorption isotherms for the polyacrylate fiber were generated for several seawater and freshwater dilutions to obtain the appropriate fiber−water partition coefficients (K_{fw}). Because the presence of cations in solution considerably affects the sorption of LAS to natural sorbents (*6, 25*), a second objective was to investigate the effect of Ca^{2+} and Na^+ on the fiber−water distribution using simple electrolyte solutions. Na^+ is the most abundant cation in natural waters. On the other hand, Ca^{2+} is typically the cation influencing environmental processes of anionic surfactants in aquatic systems (*6, 25, 26*). For both the polyacrylate fiber and sediment, sorption data at varying concentrations of these two cations were then compared to data for complex media.

A third objective was to investigate whether the fiber−water partition coefficient could be used as a parameter to predict the sediment sorption for LAS congeners and different medium compositions. Regarding the fact that experimental octanol−water partition coefficients (K_{ow}) are not available for (most) surfactants (*27*−*29*), the experimental fiber−water partition coefficient would represent a valuable and simple tool in structure−activity relationships.

Materials and Methods

Chemicals, Sediment, and Chemical Analysis. Linear alkylbenzenesulfonates are abbreviated as C_n-m-LAS, where n is the length of the alkyl chain and m represents the position of the phenyl group on the alkyl chain. C_{10}-2-, C_{11}-2-, C_{11}-5-, C_{12}-2-, C_{12}-3-, C_{12}-5-, C_{12}-6-, C_{13}-2-, and C_{13}-5-LAS (purity >97%) were synthesized by Dr. J. Tolls as sodium salts in our laboratory (*30*). Stock solutions were made in analytical methanol HPLC grade obtained from Lab-Scan (Dublin, Ireland). GP2 medium (*31*) as seawater (SW) and Dutch standard freshwater (DSW) (*32*), both containing 10 mM NaN_3 (Merck, Darmstadt, Germany), were prepared according to standard procedures in Millipore water from a Milli-Q purification system (resistivity ≥18 MΩ). The ionic composition of both media is presented in Table S1 in the Supporting Information.

The sediment was collected from the North Sea "Friese Front" area. The organic carbon content was 0.27% and the particle size distribution 1.2% clay (<2 μm), 19.2% silt (2 to <63 μm) (11.0% fine silt (<8 μm)), and 79.5% sand (63 to <1000 μm). Additional measured parameters for this sediment have been reported previously (see sediment "North Sea 2" in ref *7*).

LAS extraction and cleanup from water was performed by solid-phase extraction (SPE) using octadecyl reversed-phase silica (C18) columns (Supelclean_ENVI_-18, 0.5 g, Supelco, Bellefonte, PA). LAS was extracted from sediment samples by sonication using methanol as an extraction solvent, and the sediment extracts were concentrated and purified by SPE. A more detailed description of the extraction and cleanup procedures for water and sediment samples is described elsewhere (*7*). Millipore water and ammonium acetate were added to the final solid-phase extracts to make the final composition similar to that of the LC/MS/MS eluents, which consisted of 80:20 methanol/water (v/v) with 10 mM ammonium acetate. Samples were analyzed in an LC/MS/MS system as reported previously (*24*) by screening of the pseudomolecular ion $[M - H]^-$ 339, 325, 311, 297, and 283 m/z and the daughter ion 183 m/z.

SPME Procedure. Disposable SPME fibers were obtained from Polymicro Technologies (Phoenix, AZ) and consisted of glass fibers with a diameter of 108−109 μm coated with 7.5 μm polyacrylate (PA). The fibers were cut into pieces of 40 ± 0.1 mm length, thermally conditioned in a gas chromatography oven overnight at 120 °C under a helium flow, and kept in Millipore water for at least 24 h. Details about the experimental setup as well as the conditioning and extraction procedure of the SPME fiber are given elsewhere (*24*). Briefly: all experiments were conducted at room temperature (19 ± 1 °C). Surfactant solutions were made by adding aliquots of LAS stock in methanol (<1% of the total volume) in 20 mL glass scintillation vials (Perkin-Elmer, Boston, MA). The vials were then completely filled with the corresponding aqueous solution, and one SPME fiber was placed in each vial. Test systems were equilibrated for 48 h. As has been shown in earlier work, this period is sufficient to reach equilibrium for all the LAS congeners tested, including the most hydrophobic ones (e.g., C_{13}-2-LAS) (SI in ref *24*). SPME fibers were extracted and analyzed as explained elsewhere (*24*). Aqueous solutions of the lowest and highest concentrations were extracted by SPE to check whether biodegradation or adsorption of LAS to the glass vial should be considered. For all cases, recoveries were above 93% and averaged 98.4 ± 5.3%. For the rest of the vials, the nominal aqueous concentrations were used. The extraction from the aqueous phase by the SPME fibers was nondepletive for all tested LAS compounds (<5% of the total amount of compound present in the system).

Sorption isotherms between SPME fibers and aqueous solutions with different ionic compositions were obtained for C_{12}-2-LAS. Seawater dilutions were prepared by mixing the seawater with the DSW medium at different ratios. For the freshwater dilutions, the DSW medium was mixed with Millipore water. All solutions contained NaN_3 at 10 mM to avoid LAS biodegradation. The specific effects of Ca^{2+} and Na^+ on the affinity of LAS for PA-coated SPME fibers was tested in 10 mM NaN_3 solutions with a reagent grade salt, $CaCl_2 \cdot H_2O$ or NaCl, from Merck (Darmstadt, Germany). Concentrations ranged from 0.14 to 8.98 mM for Ca^{2+} and from 11 to 418 mM for Na^+, which correspond to the Ca^{2+} and Na^+ concentrations for the seawater and freshwater dilutions tested. LAS concentrations tested ranged from 0.01 to 65 mg/L depending on the salt composition of the solutions. The pH of every equilibrated solution was determined with a 761 Calimatic pH meter (Knick, Germany).

Sorption Experiments. Sorption to sediment in seawater was measured for the nine LAS congeners. C_{12}-2-LAS was used to test the effect of the solution chemistry on the sorption of LAS to sediments. The LAS concentration tested ranged from 0.02 to 3 mg/L depending on the salt composition of the solutions and the LAS congener. Equilibrated LAS concentrations in all tests were well below the precipitation limits (see ref *24*) and the critical micelle concentration (cmc) (ca. 650 mg/L for an LAS commercial mixture (*13*)). Sorption tests were performed similarly to those reported previously (*7*). Briefly, sorption experiments were carried out by adding 0.2 g (ww) of the sediment to 20 mL scintillation vials filled with the LAS solutions. The system was equilibrated for 24 h; this time was sufficient to reach equilibrium in the system, and it is in agreement with other sorption studies with LAS compounds and sediments or soils (*4, 6, 8*). After the equilibration period, one fiber was introduced into each vial. The test systems were then placed on a shaking device for at least 48 h to equilibrate the fibers with the sediment suspension. Next SPME fibers were extracted and analyzed, and the aqueous concentrations were determined using the K_{fw} values. The K_{fw} values needed to calculate the freely dissolved concentration in the sorption tests with seawater are taken from an earlier publication (*24*), while K_{fw} values for C_{12}-2-LAS at the different ionic compositions are derived

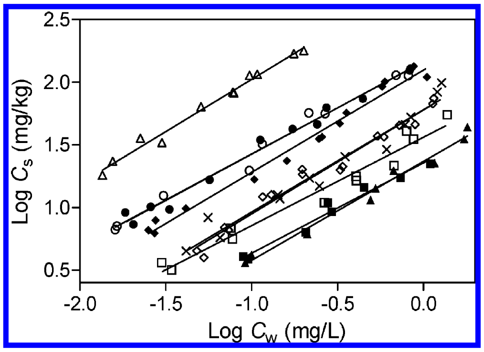

FIGURE 1. Sediment−water sorption isotherms for the LAS compounds tested at seawater salinity: C_{10}-2-LAS (■), C_{11}-2-LAS (□), C_{11}-5-LAS (▲), C_{12}-2-LAS (○), C_{12}-3-LAS (◆), C_{12}-5-LAS (◇), C_{12}-6-LAS (×), C_{13}-2-LAS (△) and C_{13}-5-LAS (●). Data points represent single measurements.

TABLE 1. Freundlich Parameters[a] of the Sediment−Water Isotherms (K_F and n) and Sediment−Water Distribution Coefficients for the Individual LAS Compounds in Seawater

compd	log K_F	n	log K_d at 10 mg/kg
C_{10}-2-LAS	1.36 ± 0.03	0.72 ± 0.05	1.49
C_{11}-5-LAS	1.37 ± 0.02	0.79 ± 0.04	1.47
C_{11}-2-LAS	1.56 ± 0.04	0.70 ± 0.04	1.80
C_{12}-6-LAS	1.78 ± 0.04	0.82 ± 0.05	1.96
C_{12}-5-LAS	1.78 ± 0.03	0.83 ± 0.04	1.94
C_{12}-3-LAS	2.10 ± 0.03	0.82 ± 0.03	2.34
C_{12}-2-LAS	2.16 ± 0.04	0.73 ± 0.03	2.59
C_{13}-5-LAS	2.16 ± 0.03	0.74 ± 0.03	2.58
C_{13}-2-LAS	2.86 ± 0.04	0.83 ± 0.03	3.24

[a] Taken from the Freundlich isotherms in Figure 1, with the Freundlich constant (K_F) at C_a = 1 mg/L.

from the experimental fiber−water isotherms given in the present paper.

Controls without sediment were used to confirm initial aqueous concentrations. Water samples and the sediment phase were analyzed for at least two samples from every test series, and a closed mass balance was confirmed (96 ± 8%). For sorption data, sediment concentrations were determined by a mass balance approach, using the aqueous concentration derived from SPME samples. All sediment sorption experimental data were measured for individual compounds.

Results and Discussion

Influence of the Molecular Structure on the Sorption of LAS to Sediment and Polyacrylate Fibers. Sorption data from the sediment suspension experiments were fitted to the Freundlich isotherm:

$$\log C_s = \log K_F + n_F \log C_w \tag{1}$$

where C_s (mg/kg) and C_w (mg/L) are the surfactant concentrations in the sediment and in the water phase, respectively. log K_F is the Freundlich constant or the distribution coefficient at a fixed C_w of 1 mg/L, and n_F is the Freundlich exponent as a measure of the degree of nonlinearity.

The sediment sorption isotherms for all the tested LAS compounds in seawater are presented in Figure 1, and the Freundlich exponents (n_F) and the Freundlich coefficients (K_F) are listed in Table 1. The K_F of C12-2-LAS is very close to the value that was measured and reported in a previous publication (*7*). Sorption isotherms to this marine sediment, with a relatively low OC content compared to that of freshwater sediments, are clearly nonlinear for all tested compounds. The Freundlich exponents (n_F) do not differ significantly from each other, with a mean value of 0.78 ± 0.05. In general, the magnitude of the Freundlich coefficient (K_F values) is notably influenced by both the alkyl chain length and the position of the benzenesulfonate moiety (Table 1). The higher sorption affinity with longer alkyl chain length has also been shown for LAS in sorption studies with freshwater sediments (*4*, *6*, *14*). Data from marine monitoring studies also show a preferential accumulation of longer alkyl chain lengths in sediment (*33*−*35*). The sorption affinity to the marine sediment also clearly increases for LAS isomers with a more external position of the benzenesulfonate moiety, as was also found for freshwater sediment (*4*). The most external isomers (2-phenyl) of each *n*-alkylbenzenesulfonate series have a sorption similar to that of the most internal isomers of its homologue with an additional methyl group. This is the case for the K_F values obtained for C_{13}-5-LAS and C_{12}-2-LAS and for C_{11}-5-LAS and C_{10}-2-LAS. The same trends have also been reported for the K_{ow} and vapor pressure of the neutral internal and external isomers of linear alkylbenzenes (*36*). However, differences between the external and internal isomers are not constant for all homologues, and therefore, interpretation of the obtained data and/or extrapolation to other LAS congeners has to be done carefully.

Similar effects of alkyl chain length and the position of the benzenesulfonate group have recently been observed for the partitioning of LAS between seawater and PA-coated SPME fibers for the same set of nine LAS congeners as used in this study (*24*). In contrast to the nonlinear sediment−water sorption isotherms, the reported fiber−water isotherms of all LAS compounds were linear over the whole tested concentration range up to their maximum solubility. As shown in an earlier publication, competition effects were not observed when a mixture of different LAS congeners in the same system was tested (*24*). The observed nonlinearity in sediment sorption suggests that sorption sites in sediment are heterogeneous, where likely additional adsorption processes play a role besides partitioning into a single organic phase. To compare the sorption affinity at a comparable loading of the sediment sorption sites, the sediment−water distribution coefficient ($K_d = C_s/C_w$) at a fixed sorbed concentration is calculated from the Freundlich parameters (Table 1).

Figure 2A shows the sediment−water distribution coefficient at 10 mg/kg for all tested LAS compounds plotted against their respective fiber−water partition coefficients (K_{fw}) in 100% seawater, taken from ref *24*. A good correlation between these two parameters is obtained, as shown by the small standard errors and the slope close to unity (regression coefficient r^2 = 0.97). This strong correlation indicates that differences in the sediment sorption coefficient between the tested LAS homologues and isomers are closely predicted by the fiber−water partition coefficients (K_{fw}). Although the nonlinearity of sediment sorption is not yet accounted for by this correlation, the nearly identical isotherm nonlinearity suggests that differences in sorption affinity between LAS structures are mainly related to hydrophobicity and can be estimated by the measured K_{fw} values.

Influence of the Ionic Composition on the Sorption of C_{12}-2-LAS to Sediment and Polyacrylate Fibers. SPME calibration curves were needed to measure the aqueous concentrations in sediment sorption tests. Fiber−water partition studies in 100% seawater are reported elsewhere (*24*), but because we needed partition coefficients in other media, sorption isotherms were made at all aqueous compositions (diluted seawater, freshwater, and diluted freshwater). Linear sorption isotherms could be fitted to the fiber−water sorption data for C_{12}-2-LAS at different seawater and freshwater solutions (Figure S1 in the Supporting Information). Table 2 lists the calculated log K_{fw} values. The standard errors in log K_{fw} are small in all cases (≤0.03 log

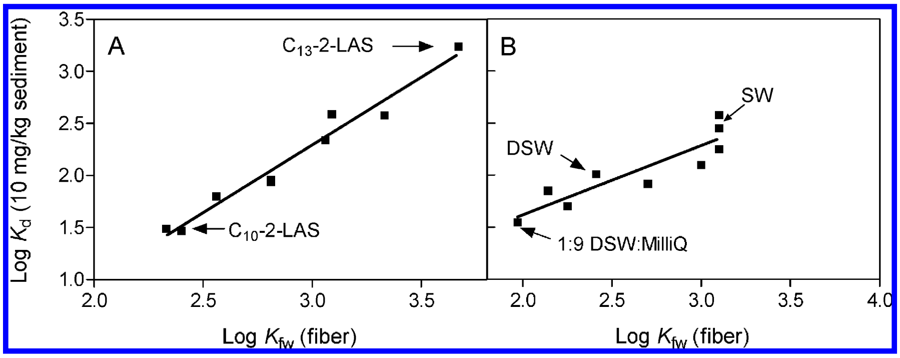

FIGURE 2. Sediment−water distribution coefficient (K_d, at C_s = 10 mg/kg) plotted against the fiber−water partition coefficient (K_{fw}) for (A) all the LAS tested compounds in seawater and (B) C_{12}-2-LAS at different ionic compositions. The fitted regression lines are log K_d = (1.30 ± 0.09) log K_{fw} − (1.61 ± 0.27), r^2 = 0.97, and se = 0.11 in (A) and log K_d = (0.49 ± 0.08) log K_{fw} + (0.51 ± 0.22), r^2 = 0.84, and se = 0.10 in (B). K_{fw} values in (A) (100% seawater) are from ref *24*. K_{fw} values in (B) are from Table 2.

TABLE 2. Freundlich Parameters of the Sediment−Water Isotherms (K_F and n), Sediment−Water Distribution Coefficient (K_d), and Fiber−Water Sorption Coefficients (K_{fw}) for C_{12}-2-LAS at the Dilutions Tested

	sediment			SPME fiber		
solution composition[a]	log K_F	n	log K_d (at 10 mg/kg)	log K_{fw}[b]	log K_{fw}[c] ($CaCl_2$ solution)	log K_{fw}[d] (NaCl solution)
SW	2.16 ± 0.04	0.73 ± 0.03	2.58	3.0 ± 0.02[e]	2.9 ± 0.06	3.0 ± 0.08
3:1 SW−DSW	2.15 ± 0.03	0.79 ± 0.04	2.45	3.1 ± 0.03	3.0 ± 0.03	2.9 ± 0.04
1:1 SW−DSW	1.95 ± 0.01	0.76 ± 0.02	2.25	3.1 ± 0.02	2.9 ± 0.06	3.0 ± 0.09
1:3 SW−DSW	1.87 ± 0.04	0.79 ± 0.05	2.10	3.1 ± 0.01	2.8 ± 0.04	2.9 ± 0.05
DSW	1.73 ± 0.03	0.80 ± 0.05	1.92	2.7 ± 0.03	2.7 ± 0.02	2.5 ± 0.05
3:1 DSW−Milli-Q	1.79 ± 0.05	0.78 ± 0.05	2.01	2.4 ± 0.03	2.5 ± 0.02	
1:1 DSW−Milli-Q	1.59 ± 0.04	0.85 ± 0.06	1.70	2.3 ± 0.03	2.4 ± 0.03	
1:3 DSW−Milli-Q	1.61 ± 0.04	0.71 ± 0.11	1.85	2.1 ± 0.03	2.3 ± 0.03	
1:9 DSW−Milli-Q	1.46 ± 0.03	0.85 ± 0.07	1.55	2.0 ± 0.01	2.2 ± 0.05	

[a] SW = artificial seawater; DW = artificial Dutch standard freshwater. [b] K_{fw} from the complex seawater and freshwater dilutions. [c] K_{fw} from the experiments with $CaCl_2$ solutions at the same $CaCl_2$ concentration as used for the seawater and freshwater dilutions. [d] K_{fw} from the experiments with NaCl solutions at the same NaCl concentration as used for the seawater and freshwater dilutions. [e] The K_{fw} value at 100% seawater is from ref *24*.

unit). Only small differences in K_{fw} values are observed between seawater and 4-fold diluted seawater solution (1:3 SW−DSW). The K_{fw} value for the freshwater solution (log value of 2.7) is a factor of 2 lower compared to those of the seawater solutions (log K_{fw} values of 3−3.1) and clearly decreased, with an additional factor of 6, upon further 10-fold dilution with pure water (log K_{fw} = 2 for 1:9 DSW−Milli-Q solution).

Linear isotherms were also obtained when the SPME fibers were exposed to solutions of NaCl or $CaCl_2$ at electrolyte concentrations comparable to those of the seawater and freshwater dilutions (Figure S2 in the Supporting Information, Table 2). Although no buffer was added, the pH did not change dramatically, varying from 7.31 to 7.5 and from 7.02 to 7.51 from the highest to the lowest $CaCl_2$ and NaCl concentrations, respectively. Obtained K_{fw} values of C_{12}-2-LAS in the sodium solution systems are not different at concentrations of 112 mM Na^+ and higher, corresponding to the Na^+ concentrations in the seawater dilutions (Figure 4 and Figure S2). Interestingly, the average K_{fw} value for the higher Na^+ concentrations is very close to the value obtained for the complex seawater dilutions (Table 2). K_{fw} was notably lower for the solution containing 11 mM Na^+.

Fiber−water isotherms at different Ca^{2+} concentrations show a pattern similar to those obtained for the complex seawater and freshwater dilutions (Table 2, Figure 4, and Figure S2 in the Supporting Information). At Ca^{2+} concentrations above 3 mM, K_{fw} remains constant, while for the lower Ca^{2+} concentration range, K_{fw} decreases by a factor of 3 with 10 times lower Ca^{2+} concentrations. One should keep in mind that, due to the addition of NaN_3, Na^+ is present at 10 mM at the lowest tested Ca^{2+} concentrations of 0.14 mM. The K_{fw} values at high Ca^{2+} concentrations are again very similar to K_{fw} for the reported seawater dilutions and the single electrolyte systems with the highest Na^+ concentrations.

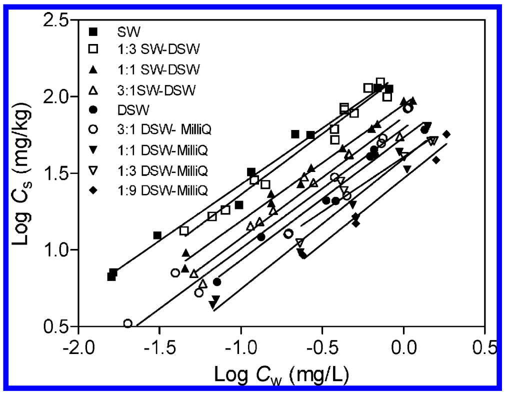

FIGURE 3. Sediment−water sorption isotherms for C_{12}-2-LAS at different seawater and freshwater dilutions. Data points represent single measurements.

Figure 3 presents the marine sediment sorption isotherms at different ionic compositions. Again, as observed for tests in seawater (*24*), the sediment−water isotherms are all nonlinear while the fiber−water isotherms are linear. The degree of nonlinearity is constant for all sediment−water isotherms, with a mean Freundlich exponent n_F of 0.79 ± 0.05 (Table 2). Sorption of C_{12}-2-LAS to sediment systematically increased with the salt concentration in solution, as presented in Figure 4. The increasing sorption affinity to natural sorbents with increasing salt content in solution has been reported for LAS and other anionic surfactants

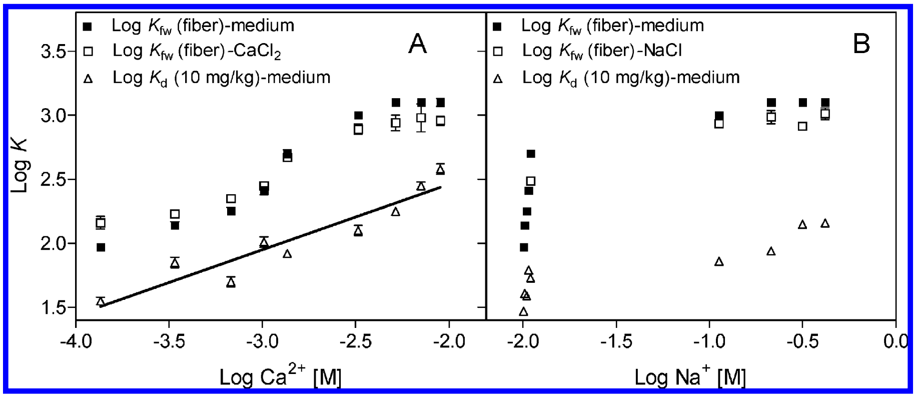

FIGURE 4. Sediment−water distribution coefficient (K_d, at C_s = 10 mg/kg) or fiber−water partition coefficient (K_{fw}) as a function of the Ca^{2+} concentration (A) and Na^+ concentration (B). In the case of the dilutions of seawater and freshwater media, sorption coefficients are related to the concentration of either Ca^{2+} or Na^+. K_d and K_{fw} are from Table 2.

(*3, 6, 14, 26*). The aqueous metal content and salts that may dissolve from the sediment during the sorption experiments were not measured. In principle, such a release may affect the aqueous composition and thereby also the fiber−water partition coefficients. However, the changes in composition will likely be very minor. In Figure 4, the relation between K_{fw} (fiber) as well as K_d (at 10 mg/kg sediment) and the Ca^{2+} concentration in the seawater and freshwater dilutions is presented. Although this does not account for the nonlinearity of the isotherms for different sediments, or heterogeneity of sorption sites, a comparison with other studies can be made.

An average increase of (0.51 ± 0.04) log K_d per log [Ca^{2+}] is obtained. This factor is considerably higher than the value of 0.23 given by Westall et al. (*6*) for specific LAS congeners, who used only $CaCl_2$ solutions between $10^{-3.8}$ and $10^{-2.7}$ M and freshwater sediments that varied in their organic carbon, clay, and metal oxide contents, but closer to the 0.37 value obtained by García et al. (*12*) for mixtures of LAS homologues sorbing to sludge. Moreover, this factor is also comparable to the one obtained for the effect of Ca^{2+} concentration on the sorption of perfluorinated surfactants to freshwater sediments (*26*). Consequently, the increase of the sorption of LAS to sediment when the salt concentration is increased seems to be related to the Ca^{2+} concentration in solution. The relation between K_d values and K_{fw} values for C_{12}-2-LAS at varying aqueous ionic compositions, in Figure 2B, is not as strong as the relation observed for different LAS compounds in seawater in Figure 2A. Although both affinity parameters increase with increasing salinity, this is much stronger for the SPME fiber. The affinity for the SPME fiber also reaches a maximum at a certain salinity of the aqueous phase, while the affinity coefficients for sediment at 10 mg/kg tend to increase further (Figure 4A).

Effect of the Ionic Composition on K_{fw} and K_d. The effect of the ion concentration (Ca^{2+}, Na^+, K^+, etc.) on sorption processes of ionizable compounds has been examined in several studies with sediment (*2, 6, 26*), octanol (*2*), and membranes (*37, 38*). Three mechanisms can explain this effect. The first one is sorption into the organic phase of ion pairs of LAS molecules with the cations in solution, thereby maintaining electroneutrality (*2*). In that case, sorption will increase with increasing electrolyte concentrations of cations in the water. A second explanation is related to the effect of the cations on the sorbent phase itself. Westall et al. (*6*) suggest that the reduction of a negatively charged surface with increased cations in solution may result in reduced repulsion of the LAS anion, which would favor sorption in the case of an adsorptive process. Divalent cations such as calcium will shield the surface more efficiently on a molar basis than monovalent cations, which may explain the stronger effects of calcium. Third, the formation of a positively charged LAS complex with Ca^{2+} ($Ca(LAS)^+$) may sorb to negatively charged sites in an ion exchange process.

The first mechanism (ion pairing) is probably the most plausible explanation for the effects of the different ionic compositions on the SPME K_{fw} values. The linear isotherms for the fibers are a further indication that an absorption process dominates the sorption of LAS to the PA-coated SPME fiber, as was noted before (*24*). In addition, the relationship between K_{fw} and the Ca^{2+} concentration from data in the fresh- and seawater solution as well as in the $CaCl_2$ solutions (Figure 4) is similar to typical complexation curves of ionic compounds (*2, 39*). This curve shape was not observed for Na^+, likely because the tested concentration range does not cover the entire LAS^-Na^+ "complexation curve" (Figure 4B). This topic is briefly further discussed in section 1 of the Supporting Information.

The nonlinearity of all the sediment−water isotherms suggests that partitioning is not the only process occurring in sediments and the functional sulfonate group might contribute by either specific or nonspecific chemical interactions of an adsorption process. Contrary to the pattern observed for the fiber−water coefficient K_{fw}, the affinity for sediment (K_d) systematically increases when the concentration of Ca^{2+} is increased (Figure 4). The relation between K_d and [Ca^{2+}] does not follow the shape of a complexation curve. It remains unclear whether the observed dependency of the sorption on the cation concentration is only related to a change in the sorbing phase or is a combination of more than one mechanism. The sorption of anionic substituted phenols to a clayish freshwater sediment was not influenced by different Na^+ concentrations, while strong effects of [Ca^{2+}] were observed (*2*). This suggests that for sediment specific effects of divalent cations, such as changes in the surface charge by shielding or ion exchange of positively charged complexes, may be more important than increased partitioning as ion pairs or as free ions with counterions.

Fiber−Water Partition Coefficients as a Measure for Hydrophobicity and a Parameter To Predict Sediment Sorption: A Brief Evaluation. The effect of hydrophobicity on sorption processes is often modeled with the octanol−water partition coefficient (K_{ow}), and numerous studies for nonpolar compounds have reported a strong relation between the sorption coefficient (K_p) and the octanol−water partition coefficient K_{ow} (*40−42*). Although K_{ow} is used for the estimation of the hydrophobicity of organic compounds, the measurement or estimation of this parameter is not straightforward for ionic compounds such as LAS. The experimental determination of K_{ow} for surfactants is complicated (*43*), because of the tendency of these compounds to accumulate at surfaces and to readily emulsify both phases (*44−46*). Other parameters such as the cmc are used as a hydrophobicity measure for surfactants, but this is not a good parameter when comparing different surfactant classes (*47*). Roberts et al. (*48*) have proposed an algorithm for the calculation of K_{ow} values for LAS compounds, and also the KowWIN software from the EPI-suite (version 3.20) package supplies estimates of K_{ow} for LAS homologues. It is questionable whether octanol or models calibrated for neutral compounds capture the molecular interactions between ionized compounds and organic matter. Robert's algorithm and the KowWIN software as estimation routines for K_{ow} are furthermore not ideal, since (i) both estimation routines are not based on direct experimental data, (ii) the estimates from both methods differ by more than 0.5 log unit, and (iii) no isomer-specific K_{ow} values are calculated by the KowWIN program. Moreover, this study shows that the hydrophobicity of surfactants such as LAS depends on the solution chemistry, and estimation programs do not take that into account. The polyacrylate-coated SPME fiber is the first hydrophobic phase for which distribution coefficients have been experimentally determined for individual LAS congeners, both single and in mixtures (*24*), over a broad concentration range and at varying salinity.

Although the sorption test for the marine sediment in seawater showed a strong relation between sediment−water distribution coefficients and K_{fw} values (Figure 2A), that relationship was not so straightforward for a single LAS compound at varying ionic composition (Figure 2B). Together with the linear sorption isotherms to polyacrylate SPME and nonlinear isotherms for sediments, this suggests that the sorption mechanisms to the fiber and the sediment are not completely similar. Partitioning is the process governing the uptake of LAS in the SPME fibers, while adsorption processes can also take place in the sorption of LAS to sediment. However, the differences among the sorption of LAS isomers to sediment and to SPME fiber seem to be well explained by the hydrophobicity of the LAS molecule, and this is well predicted by the K_{fw} data.

To get an idea of the feasibility of the K_{fw} values to predict other hydrophobicity-driven processes than sorption to sediment, we have employed the experimental bioconcentration factors (BCFs) for different LAS congeners in fish obtained by Tolls et al. (*49*) (Figure S3, Supporting Information). In another study, the same authors showed that water hardness affects the bioconcentration of LAS congeners (*9*). Even though biotransformation rate differences between LAS congeners may cloud a direct relationship, Figure S3 shows a strong correlation between the BCF values (artificial freshwater, 1.2 mM hardness) and the K_{fw} values (100% artificial seawater). This again indicates that differences in BCF values for the different LAS congeners are well predicted by the polyacrylate−water partition coefficients.

Hence, the excellent agreements obtained from the sediment sorption and bioconcentration coefficients with the K_{fw} values reveal that the polyacrylate−water partition coefficients obtained with the SPME method might represent a suitable parameter for hydrophobicity differences of LAS congeners. For more precise estimates that include the effect of the ionic composition, we would suggest to test one congener as a reference chemical in that particular solution. The sorption and bioconcentration coefficients for other congeners in the same solution can then be predicted from a correlation with the fiber−water partition coefficient.

Supporting Information Available

Discussion on sorption of LAS congeners to polyacrylate SPME fiber, a table with the ion composition of the artificial GP2 seawater (SW) and Dutch standard water (DSW), fiber−water isotherms for C_{12}-2-LAS at different seawater and freshwater dilutions, fiber−water isotherms for C_{12}-2-LAS at different Na^+ and Ca^{2+} concentrations, and a figure representing bioconcentration factors versus fiber−water partition coefficients for different LAS congeners. This material is available free of charge via the Internet at http://pubs.acs.org.

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