ELSEVIER

Marine Chemistry 54 (1996) 171–177

MARINE CHEMISTRY

Sorption of linear alkylbenzenesulfonates (LAS) on marine sediment

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Received 11 July 1994; accepted 22 April 1996

Abstract

The sorption of a commercial-grade linear alkylbenzenesulfonate (LAS) and of its constituent homologous compounds was characterized in marine sediments from the Bay of Cadiz (southwestern Spain).

Experimental data were fitted to a Freundlich model. The sorption coefficient K ranged from 96 for the homologue C_{10}-LAS to 1112 for the homologue C_{13}-LAS, with sorption expressed as $\mu g\,g^{-1}$ LAS of sediment and equilibrium LAS concentration as $mg\,l^{-1}$. LAS sorption on marine sediment was found to be an irreversible process.

K increased substantially with increasing salinity. The relation was linear for the homologue C_{11}-LAS, with a threefold increase in the value of K as salinity increased from 0 to 75.

Keywords: marine sediment; sorption; linear alkylbenzenesulfonates; isotherms

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1. Introduction

Knowledge of the processes involved in distributing organic microcontaminants among ecosystem compartments is essential to an understanding of their behavior in the environment. This is particularly important in the case of linear alkylbenzenesulfonates (LAS), due to their frequent use (as much as 5.5 g per head per day in some developed countries) as surfactants in detergents and other cleaning products.

LAS sorption on natural sediments is known to occur widely. Most published studies have been carried out using either riverine sediments (Hon-nami and Hanya, 1980; Urano et al., 1984; Amano et al., 1992; Amano and Fukushima, 1993) or soil components, principally metallic oxides and clays (Matthijs and De Henau, 1985). Similar studies have been performed with non-ionic surfactants (Kronberg et al., 1986; Liu et al., 1992). These studies have provided answers to many important questions: thus, the relation between the chemical structure of LAS and its sorption capacity is known (Hand and Williams, 1987) and the influence of the nature of the sediment on LAS sorption has been determined. A theoretical model for sorption has been proposed (Di Toro et al., 1990) and validated in field studies (Hand et al., 1990).

In addition to the theoretical interest, quantitative information about the process of LAS sorption is of great ecological significance. For example, modelling the phenomenon may allow one to estimate

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PII S0304-4203(96)00040-0

the proportion of discharged surfactant that is removed from the water column and accumulated in compartments where its degradation rate is substantially different (Takada and Ogura, 1992). Knowing the sorption isotherms may also allow one to estimate the distribution of the surfactant in the soluble fraction and in the fraction associated with suspended solids. This is an important step in quantifying the total amount of LAS that is dispersed in aquatic systems. It should be borne in mind that direct determination of the amount of surfactant associated with the particulate phase is extremely laborious, involving the filtration or centrifugation of large volumes of water.

Sorption of LAS on sediments in the marine environment has received little attention so far, despite the fact that LAS concentrations in sediments, especially those from coastal areas, can be high. Kikuchi et al. (1986) found LAS concentrations ranging from 0.2 to 69 $\mu g\,g^{-1}$ in sediments from the Bay of Tokyo; Marcomini et al. (1988) reported values of 2 to 20 $\mu g\,g^{-1}$ for the Venice Lagoon; and Takada and Ogura (1992) found concentrations between 0.5 and 24 $\mu g\,g^{-1}$ in sediments from the Tamagawa Estuary in the Bay of Tokyo. It is known that coastal areas experience great variability in physicochemical conditions; variation in parameters such as salinity may have large effects on sorption processes.

The present study provides, for the first time, data on LAS sorption on marine sediments. The study was carried out using a commercial LAS and, separately, its constituent homologues between C_{10}-LAS and C_{13}-LAS. An attempt was made to determine the effect of salinity on sorption.

2. Experimental

2.1. Materials

The sediment used in the sorption experiments was taken from a salt pond in the Bay of Cadiz (southwestern Spain), at a recently dredged location which had received a low LAS input. The sediment was dried at 80°C and sieved through a 300 μm mesh. A sample was used to perform a BET isotherm, in order to determine the specific surface and mean pore volume of the sediment. These results are shown in Table 1, together with some other physical and chemical characteristics of the sediment.

Table 1
Characteristics of sediments and water used in sorption experiments. Seawater characteristics are for the experiment shown in Fig. 1

Sediment:	
Organic C (%)	0.144
Organic N (%)	0.161
PO_4^{3-} ($\mu g\,g^{-1}$)	1.67
Fe (%)	4.05
Mn ($\mu g\,g^{-1}$)	235
LAS ($\mu g\,g^{-1}$)	< 0.2
Specific surface ($m^2\,g^{-1}$)	14.9
Mean pore diameter (nm)	3.5
Porosity	0.76
Clay (%)	3.0
Silt (%)	35.5
Sand (%)	61.5
Water:	
Salinity	36.2
pH	7.9
Alkalinity (mM)	2.18
LAS ($\mu g\,l^{-1}$)	n.d.
HPO_4^{3-} (μM)	0.2
Ca^{2+} (mM)	10.5
Mg^{2+} (mM)	80.2

n.d. = not detected.

The seawater used was taken from a deep well close to the coast, and thus was almost free from LAS. Some of the main characteristics of the seawater are shown in Table 1. The seawater was evaporated at temperatures up to 60°C until the salinity approached 75. Hypersaline water was then filtered through a 0.45 μm filter, and the required salinities obtained by subsequent dilution with Milli-Q water.

Table 2
Percentage of active matter (A.M.) and percentage composition of homologues in the LAS standards and commercial LAS used

Standard	A.M.	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
C_{10}	12.00	99.49	–	–	–	–
C_{11}	26.35	5.50	93.61	0.79	–	–
C_{12}	25.18	0.62	14.21	84.38	0.79	–
C_{13}	21.10	0.21	0.52	9.93	75.11	–
Commercial LAS	6.62	3.90	37.40	35.40	23.10	0.20

The commercial LAS and its constituent homologues were supplied by Petroquímica Española S.A. Table 2 indicates the proportion of active matter and the proportional composition of the different homologues in the standards used.

The concentration of dialkyltetraline sulfonates (DATS) in the commercial LAS is less than 0.2% and practically zero in the standards of the various homologues.

2.2. *Determination of sorption and desorption of* LAS

Sorption was determined in Teflon-stoppered Pyrex bottles by placing about 0.4 g of sediment in 100 ml of a LAS solution of the appropriate salinity. The range of LAS concentrations used was from 0 to 1000 ppb. The system was equilibrated in a thermostated bath provided with orbital agitation. The experiments were carried out at 25 ± 0.5°C and each one lasted 19–20 h. Under these conditions the systems all achieved equilibrium within 4 h. These results is according to obtained by Matthijs and De Henau (1985). Phases were separated by filtration through a 0.45 μm filter. The first portion of the filtrate was discarded, and a 50 ml volume was then taken to determine the equilibrium LAS concentration.

Desorption experiments were carried out in stoppered 100 ml glass centrifuge tubes (Pyrex), using 0.2 g of sediment and 50 ml of LAS solution. After reaching equilibrium, the sediment was separated from the LAS solution by centrifuging at 3300 g for 20 min at 25°C. An aliquot was subsequently taken for LAS analysis and the rest of the solution was gently aspirated with a Pasteur pipette to remove it from the tube. The sediment was resuspended in 50 ml of seawater free of LAS and the procedure continued as in the sorption experiments. This operation was repeated twice.

A control solution of LAS without sediment was used during the sorption experiments in order to check for the absence of LAS biodegradation. The results obtained demonstrated that biodegradation was not significant during the time the sediment remained in contact with the solutions of LAS. Another possible cause of the loss of the surfactant, the sorption on the walls of the receptacle and the centrifuges tubes, is negligible owing to its small value (in the least favorable case, 200 cm^2 against the approx. 6 m^2 of the 0.4 g of sediment).

2.3. LAS *analysis*

The procedure used to isolate and preconcentrate the LAS was based on solid-phase extraction using octadecyl reversed-phase silica (C_{18}) columns and strong anion exchange (SAX) columns.

The first step of the extraction procedure consisted of the preconditioning of the solid-phase extraction resins to ensure uniform wetting of the minicolumns. This was achieved by passing 10 ml of methanol through each C_{18} and SAX column. Washing was done with 10 ml of Milli-Q water at pH 3 (C_{18} column) or pH 7 (SAX column).

Filtered samples from the sorption experiments were adjusted to pH 3 and passed at a flow rate of 2 $ml\,min^{-1}$ through a 3 ml C_{18} column, which contained octadecylsilica (Supelclean LC-18 SPE). The column was then rinsed with 6 ml of methanol–water (30:70). Adsorbed LAS in the column was then eluted with 10 ml methanol in a SAX column (Supelclean LC-SAX SPE). The SAX resin was rinsed with 5 ml of 2% acetic acid in methanol solution, followed by 5 ml of methanol. LAS was finally eluted from the SAX column by successively passing 3 ml volumes of 2 *N* HCl in methanol. The hydroalcoholic solution of hydrochloric acid was dried by heating under a nitrogen stream. The residue was dissolved in 1 ml methanol–water (80:20) and between 10 and 50 μl were taken for LAS analysis by high-performance liquid chromatography (HPLC).

LAS was analyzed in a Waters high-performance liquid chromatograph equipped with a fluorescence detector ($\lambda_{exc} = 225$ nm and $\lambda_{em} = 295$ nm). Homologues were separated using a Lichosorb RP-8-DB column of 250 mm length and 4.0 mm internal diameter, with a particle size of 10 μm, and precolumns of the same stationary phase. Sodium perchlorate (10 $g\,l^{-1}$) in methanol–water (80:20), at a flow rate of 1.0 $ml\,min^{-1}$, was used as an eluent. LAS was determined based on the peak area, using external standards. These standards were treated in the same way as the samples. Peak areas were calculated using the Waters software "Baseline 810".

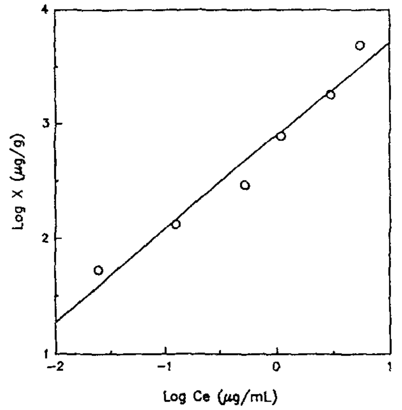

Fig. 1. Linearization of Freundlich's isotherm for the sorption of a commercial LAS on a marine sediment at 25°C and salinity = 36. X = amount of LAS sorbed per unit of adsorbent; C_e = equilibrium concentration of LAS in solution.

The mean recovery of LAS in the phase extraction step was 98% and the average relative standard deviation ($n = 5$) was found to be 3% (González-Mazo, 1994).

3. Results and discussion

Fig. 1 shows sorption of a commercial LAS at a salinity of 36 and a temperature of 25°C, with the initial range of LAS concentrations lying between 30 and 1000 ppb. Data were fitted to a linear Freundlich isotherm of the type:

$$\log X = \log K + n \log C_e$$

where X is the amount of LAS adsorbed per unit of adsorbent ($\mu g\, g^{-1}$), C_e is the equilibrium concentration of LAS in solution ($mg\, l^{-1}$), K is a constant, related to the bounding energy, which can be defined as the distribution or sorption coefficient and represents the amount of LAS adsorbed into sediments per unit equilibrium concentration ($\mu g\, g^{-1}$), and n is a measure of sorption intensity.

Hand and Williams (1987) have reported on a similar result (with $n = 1$), using riverine sediments and similar concentrations of LAS to those used in the present study. Even with higher initial concentrations of LAS (0.3–9 ppm), using sediments and suspended solids from rivers and lakes, Amano et al. (1989) derived a similar model to that of Freundlich ($n = 1.75$). Results obtained by other authors for riverine sediments could be satisfactorily described by Langmuir and Freundlich isotherms (Matthijs and De Henau, 1985). However, these isotherms, as well as those of Urano et al. (1984), were obtained using LAS concentrations appreciably higher.

Fig. 2A shows the sorption isotherms obtained in the same experiment for each of the homologues C_{10}-LAS, C_{11}-LAS and C_{12}-LAS. Data for C_{13}-LAS are not reported due to imprecise quantification within the concentration range used. This was a consequence of its high sorption capacity.

The sorption experiment was repeated using equimolecular solutions of the different LAS homologues. These solutions were prepared after adequately mixing and diluting stock solutions of the

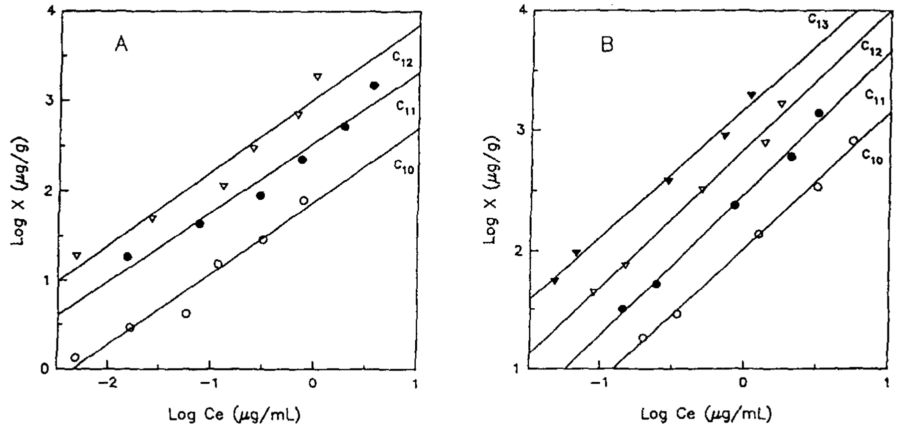

Fig. 2. Linearization of Freundlich's isotherm for the sorption of LAS homologues: (A) solution of a commercial LAS; and (B) equimolecular solution of the homologues C_{10}-LAS to C_{13}-LAS (X = amount of LAS sorbed per unit of adsorbent; C_e = equilibrium concentration of LAS in solution).

available standards (Table 1). The isotherms obtained are shown in Fig. 2B.

The results indicated that, even when each homologue was represented in equal proportion, *K* increased with the length of the aliphatic chain (Table 3). Both experiments resulted in different values for *n*.

The present results are qualitatively in agreement with those obtained by Hand and Williams (1987) for non-marine sediments, and support the suggested mechanism for surfactant sorption on natural sediments (Di Toro et al., 1990). According to this mechanism, both competitive and cooperative processes coexist during sorption. The former takes place through hydrophobic interactions, with the different homologues competing for the preferential sorption sites. The changes in the value of *K* with increasing length of the aliphatic chain (which is a measure of the energy bound between adsorbent and adsorbate) agrees with the way other, related properties change with the degree of hydrophobicity (e.g., the octanol/water partition coefficient; Hand and Williams, 1987).

Fig. 3 shows the sorption isotherms for the homologues C_{11}-LAS, C_{12}-LAS and C_{13}-LAS, in experiments carried out separately with each one. It was found that the variation of *K* between one homologue and the other was similar to that obtained when sorption occurred jointly. The observed tendency for the value of *n* to decrease from C_{11}-LAS to C_{13}-LAS (Table 3, experiment C) may be related to the effect of chain length on some of the processes implicated in the cooperative sorption mechanism. However, this hypothesis must remain tentative since the parameters derived for the Freundlich equation were affected by appreciable error (Table 3). The magnitude of the errors is due to the uncertainty produced when working at low LAS concentrations, close to environmental values.

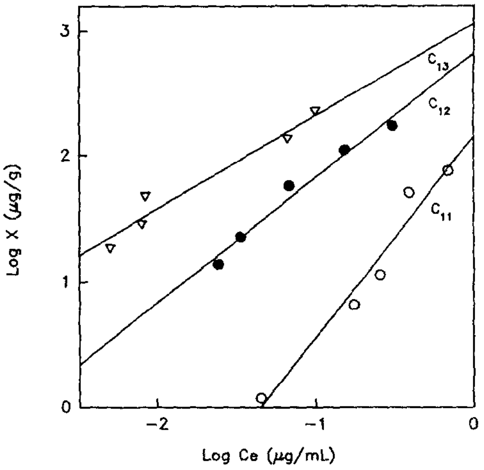

Fig. 3. Linearization of Freundlich's isotherm for the sorption of three individual LAS homologues in separate experiments. X = amount of LAS sorbed per unit of sorbent; C_e = equilibrium concentration of LAS in solution.

Table 3
Parameters (± standard error) for the Freundlich isotherm in the different experiments

Homologous	Experiment	*K*	*n*	r^2
C_{10}-LAS	A	78 ± 18	0.81 ± 0.08	0.98
C_{11}-LAS	A	350 ± 52	0.77 ± 0.08	0.98
C_{12}-LAS	A	1084 ± 256	0.81 ± 0.09	0.97
C_{10}-LAS	B	96 ± 10	1.15 ± 0.10	0.99
C_{11}-LAS	B	377 ± 28	1.20 ± 0.10	0.99
C_{12}-LAS	B	640 ± 99	1.15 ± 0.13	0.98
C_{13}-LAS	B	1112 ± 267	0.99 ± 0.16	0.95
C_{11}-LAS	C	142 ± 59	1.38 ± 0.29	0.92
C_{12}-LAS	C	655 ± 131	0.99 ± 0.09	0.99
C_{13}-LAS	C	1145 ± 263	0.74 ± 0.08	0.98

A = sorption of commercial LAS; B = sorption of an equimolecular solution of homologues; C = sorption of homologues in separate experiments. To calculate *K* and *n*, sorption was expressed as μg LAS/g of sediment and equilibrium LAS concentration as mg l^{-1}.

LAS sorption on riverine sediments was found to be a largely reversible process (Hand and Williams, 1987; Marin et al., 1994). LAS recovery from sediment in our experiments, after successive seawater treatments, was less than 6% of the adsorbed amount of a homologue with a low sorption capacity (C_{10}-LAS) in the above two studies. Such disagreement may have two reasons: (i) the sorption constant increases with the ionic strength of the medium (see below); and (ii) our sorption experiments were carried out at low LAS concentrations (< 1000 ppb) in comparison to previous works, and with sediments of high specific surface and elevated organic matter content. Both factors would affect LAS sorption capacity.

However, bearing in mind that desorption may be a slow process, the quantity desorbed may well have

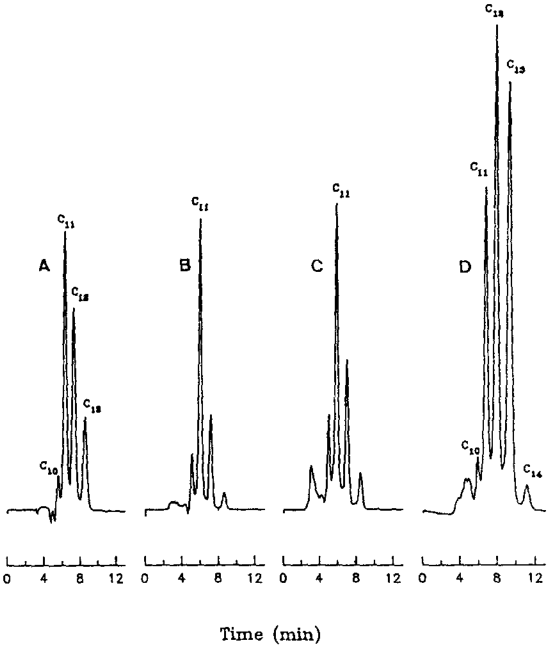

Fig. 4. Chromatograms for: (A) an LAS standard; (B) water in equilibrium with sediment after a sorption experiment; (C) water in a tidal channel close to the Bay of Cadiz; and (D) extract in methanol of a superficial sediment sample from the same location.

been greater, had the desorption experiment been extended over a longer period of time.

The importance of sorption as one of the mechanisms involved in LAS removal from the marine water column may be inferred from the chromatograms shown in Fig. 4. Chromatograms B and C correspond, respectively, to water in equilibrium with the sediment after a sorption experiment, and a seawater sample from a tidal channel close to the Bay of Cadiz. Both chromatograms are similar and, in comparison with that of a commercial LAS (Fig. 4A), show a significant reduction in the presence of long-chain homologues. Taking into acount that the chromatogram C is the result of both field biodegradation and sorption, can be concluded that both processes are responsible for the greater removal of homologues.

Fig. 4D shows a chromatogram for an extract in methanol (Soxhlet, 24 h) of a sediment sample collected at the same location as the water sample in Fig. 4C. This sediment, which is under reducing conditions (Eh ≈ -180 mV), shows higher concentrations of C_{12}-LAS and C_{13}-LAS than of C_{11}-LAS. The presence of the C_{14}-LAS homologue can even be detected, despite its very low concentration in commercial detergents (Table 2).

From an environmental point of view, the trends followed by the different homologues during the sorption process imply that those which are more easily degradable during dissolution are removed from the water column. These compounds are then stored in a compartment of the ecosystem where the LAS degradation rate, under anoxic conditions, is extremely low. This is supported by the presence of appreciable amounts of C_{14}-LAS in the sediment.

The sorption constant (K) is highly dependent on salinity. If one considers that the effect of salinity on the process of LAS sorption may be described in terms of a variation from the ideal behaviour of the adsorbate in solution, then it may be deduced from the expression of Freundlich's isotherm, in agreement with Brönsted–Bjerrum, that:

$$K_0 C_e^n = K(C_e \gamma)^n$$

where C_e is the equilibrium concentration of LAS, K_0 is the sorption constant in pure water, K is the sorption constant in water of salinity S, and γ is the activity coefficient of the LAS ion at this salinity S.

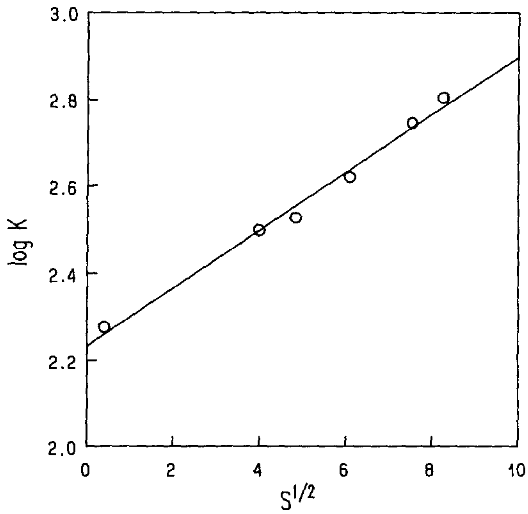

Fig. 5. Variation of the logarithm of the sorption constant against the square root of the salinity, for the homologue C_{11}-LAS ($r^2 = 0.99$).

Taking the logarithms and considering that γ could be related to the ionic strength of the medium in accordance with the limit law of Debye–Hückel, the preceding equation becomes:

$$\log K = \log K_0 + nA(I)^{1/2}$$

Bearing in mind the relationship between ionic strength and salinity (Charnock and Crease, UNESCO, 1966; Millero and Sohn, 1992), and assuming a value of 0.51 for A (water at 25°C), the result is:

$$\log K = \log K_0 + 7.20 \times 10^{-2} n S^{1/2}$$

Fig. 5 shows the variation of log K against $S^{1/2}$ for the different tests carried out. By comparing this with the previous equation, a value of 0.92 can be deduced for n, which agrees with the values obtained from other tests.

For the C_{11}-LAS homologue, K varied by more than 300% within the range of salinities studied, whose extremes corresponded on the one hand to fresh water and on the other to the maximum reached in summer in the salt ponds of the Bay of Cadiz ($S \approx 75$). In the absence of other factors controlling the presence of LAS in the environment (degradation or dispersion), it is concluded that LAS tends to accumulate in sediments in locations with more stagnant, hypersaline waters.

Acknowledgements

This work was carried out as part of a joint research program of Petroquímica Española S.A., the Consejo Superior de Investigaciones Científicas (No. 3897/91) and the University of Cádiz (No. 9/91).

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