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Hydrophobic layered double hydroxides (LDHs): selective adsorbents for liquid mixtures

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Abstract The external and internal surface area of the calcium aluminum double hydroxide $[Ca_2Al(OH)_6]NO_3 \cdot 2H_2O$ were hydrophobized by the anionic surfactants sodium dodecylsulfate and sodium dodecylbenzene sulfonate. The adsorption behavior towards liquid mixtures (benzene/*n*-heptane and *n*-propanol/toluene) was studied by determining the surface excess adsorption isotherms, the heats of immersion in these liquids, and the basal spacing, i.e. the expansion of the interlayer space.

Both hydrophobic layered double hydroxides (LDHs) adsorbed *n*-heptane, benzene, toluene, and *n*-propanol between the layers with considerable increase of the basal spacing. Interlamellar swelling of the hydrophobizised LDHs in *n*-heptane was fundamentally different to the behavior of hydrophobized 2:1 clay minerals (smectites, vermiculites). The surface excess isotherms for benzene/heptane mixtures were U-shaped and indicate preferential adsorption of benzene. Dodecylbenzene sulfonate double hydroxide preferentially adsorbed propanol from *n*-propanol/toluene mixtures but the dodecylsulfate derivative adsorbed both compounds.

Key words Adsorption – anionic surfactants – hydrophobic surfaces – layered double hydroxide – swelling

Introduction

Layered materials with surfactants bound in the interlayer space attract attention for two reasons: (i) Intercalation of organic compounds creates different types of supramolecular structures between the layers. (ii) Hydrophobization of layered materials by ion exchange is an important procedure to gain new types of adsorbents and thickening additives. This type of hydrophobization reactions was extensively studied with 2:1 clay minerals, in particular, montmorillonites [1–4]. In recent years, layered double hydroxides (LDHs) were considered as possible alternatives [5–10]. These readily crystallizing materials consist of positively charged layers. Exchangeable anions and water molecules are bound in the interlayer space. Hydrophobic derivatives are prepared by exchanging the interlamellar anions by anionic surfactants [11–13].

The surface properties of the organic derivatives can be tested by measuring adsorption from mixtures of polar and unpolar liquids [14–20]. Such measurements provide a basis for development or tailoring of adsorbents for liquid mixtures which are often used in practical applications. Clay minerals hydrophobized by cationic surfactants and LDHs modified with anionic surfactants efficiently adsorb various organic solvents on the external and internal surfaces. These processes are often selective, i.e. one component is preferentially adsorbed. The adsorption properties of hydrophobized clay minerals are well documented [14–20]. This first report on liquid adsorption by LDH-derivatives presents the different and somewhat surprising adsorption properties of these layered materials.

Material and methods

Preparation of calcium aluminum double hydroxide $[Ca_2Al(OH)_6]NO_3 \cdot 2H_2O$

Amounts of 25 g NaOH (0.62 mol) and 34.4 g $NaNO_3$ (0.43 mol) were dissolved in 175 ml water. A solution of 68.1 g $Ca(NO_3)_2 \cdot 4H_2O$ (0.29 mol) and 46.8 g $Al(NO_3)_3 \cdot 9H_2O$ (0.125 mol) in 325 ml water was added dropwise under stirring within 90 min. The mixture was aged 12 h at room temperature, then 17 days at 65 °C. The solid was separated by centrifugation, washed with water and dried at 65 °C [12].

The basal spacing of the aged product in contact with the solution was 1.04 nm and decreased to 0.73 nm by drying (100 °C or 65 °C and vacuum). Dispersed in water, the dried sample rehydrated and reached again the spacing of 1.04 nm.

Surfactant adsorption

The adsorption of dodecylsulfate and dodecylbenzene sulfonate on calcium aluminum hydroxide was measured from aqueous solutions. From the concentration changes of the surfactant in solution the specific excess amount $n_i^{\sigma(v)}$ was calculated:

$$n_i^{\sigma(v)} = V^0(c_0 - c_e)/m ,$$

where V^0 is the volume of surfactant solution, c_0, c_e are the initial and equilibrium concentration of surfactant and m the mass of solid.

An amount of 0.5 g LDH was dispersed in 50 ml water. Various volumes of 0.1% surfactant solutions were added. After an equilibration period of 48 h the solid was separated by centrifugation (6000 rpm). The concentration of surfactant in the equilibrium solution was determined by two-phase titration [29].

Preparation of the surfactant-LDHs

The surfactant-LDHs used as adsorbents for the liquid mixtures were prepared by anion exchange of the LDH with sodium dodecylsulfate (DS) and sodium dodecylbenzene sulfonate (DBS), both from Fluka AG, Swiss, in p.a. quality. An amount of the surfactant twice the theoretical anion exchange capacity (1 eq/mol LDH; 1 mol LDH = 310.1 g) was added to the dispersion of 10 g calcium aluminum hydroxide in 100 ml water. The concentration of surfactant was 0.1 M. The dispersion was allowed to stand for one week at 50 °C. After separation of the solid, the procedure was repeated twice. The separated sample was washed several times and dried at 60 °C in vacuum. Determination of the surface excess isotherms required careful purification of the adsorbents. The hydrophobic LDH derivatives were extracted in *n*-propanol/water (1:1 per volume) in a Soxhlet apparatus for one week until anionic surfactants were no longer removed from the samples. After drying at 60 °C the samples were ground to a fine powder. The surfactant content of the samples was calculated from the thermal weight loss and the carbon content.

Adsorption excess isotherms

Adsorption measurements were carried out in benzene/*n*-heptane and *n*-propanol/toluene mixtures at 25 °C. Mixtures containing methanol or ethanol could not be studied because they dissolved the organic derivatives. Liquid mixtures with composition $0 < x_1^0 < 1$ were prepared (x_1^0 molar fraction of component 1, i.e. benzene or n-propanol). The adsorbents, calcium aluminum hydroxide and both organic derivatives, were dried at 60 °C in vacuum for 24 h. Amounts of $m = 0.2–0.5$ g adsorbent were added to 8 cm^3 of the liquid mixtures (total molar amount n^0) with composition x_1^0. After 24 h, the equilibrium composition of the bulk, x_1, was determined in a Zeiss liquid interferometer. The specific surface excess was calculated from $\Delta x_1 = x_1^0 - x_1$:

$$n_1^{\sigma(n)} = n^0 \Delta x_1/m .$$

The adsorption excess isotherms (composite isotherms) were constructed by plotting $n_1^{\sigma(n)}$ versus x_1.

Enthalpy of immersion

The specific enthalpy of immersion, $\Delta_w H$, was measured in an isothermal microcalorimeter (LKB 2107, batch sorption cell; Bromma, Sweden) at 25 ± 0.1 °C.

X-ray diffraction

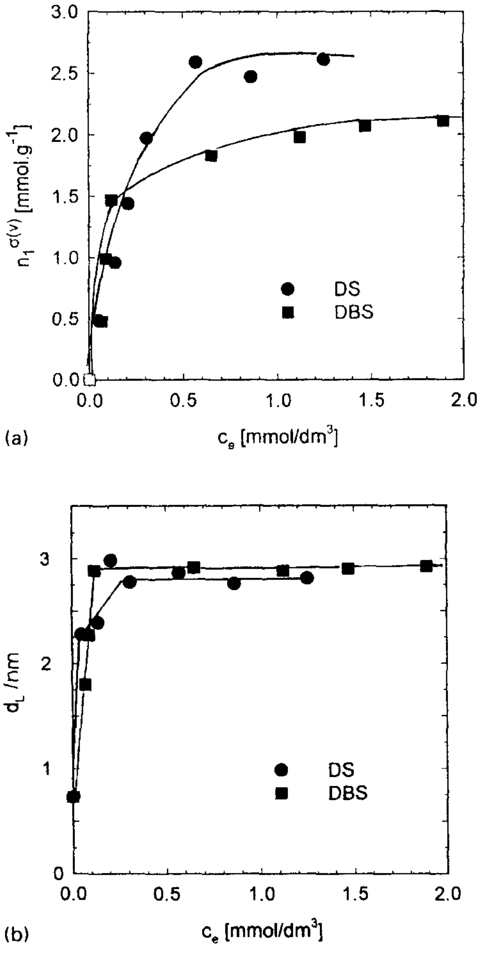
The powder diagrams of the calcium aluminum double hydroxide and its organic derivatives were taken with a Philips powder diffractometer (Cu K_α, Ni filter, 40 kV, 35 mA) at 25 °C. To minimize evaporation of the liquids, the sample was coated by a Mylar film. The basal spacing was calculated from the d-value of the first, intense basal reflection. Generally, a few more, less intense basal reflections were observed. The basal spacings is $d_L = l d_{001}$.

Results and discussion

Adsorption of anionic surfactants on calcium aluminum hydroxide

The specific surface excess amounts of dodecylsulfate (DS) and dodecylbenzene sulfonate (DBS) were measured up to surfactant equilibrium concentrations of 2 mmol/dm^3 (Fig. 1a). In this range of concentrations the specific excess amount $n_1^{\sigma(v)}$ increases to 2.70 mmol DS/g and 2.10 mmol DBS/g. As the adsorption is measured in very diluted solution, the specific excess amount is equal to the amount of surfactant adsorbed.

Fig. 1 Adsorption of dodecylsulfate (●) and dodecylbenzene sulfonate (■) by calcium aluminum hydroxide in aqueous solution: (a) surface excess, $n_1^{\sigma(v)}$, as a function of the equilibrium concentration of surfactant, c_e; (b) basal spacing, d_L, as a function of c_e



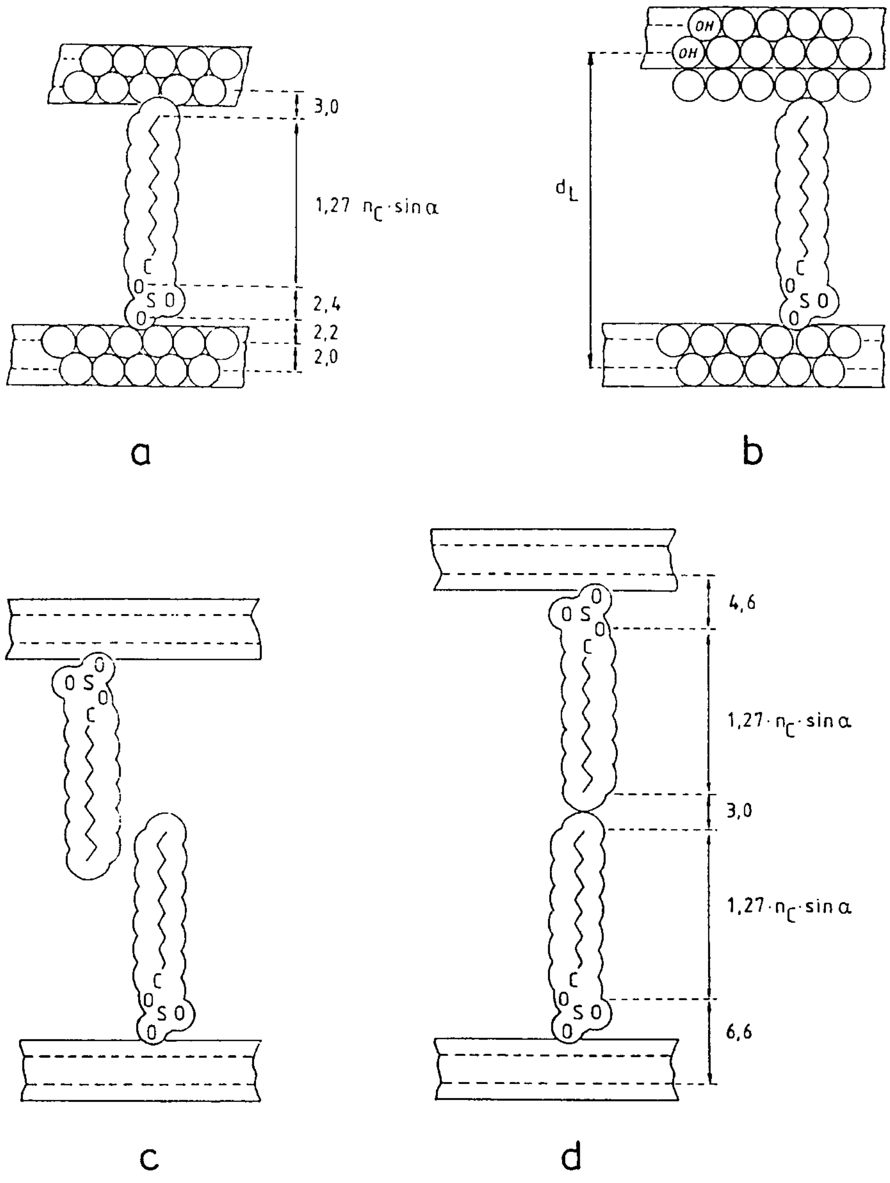
The molar mass of the adsorbent $[Ca_2Al(OH)_6]NO_3 \cdot 2H_2O$ is 310.14. The value $n_1^{\sigma(v)} =$ 2.70 mmol DS/g corresponds to 0.84 mol DS/mol LDH and $n_1^{\sigma(v)} = 2.10$ mmol DBS/g to 0.65 mol DBS/mol LDH. The exchange capacity related to the interlamellar anions is 1 mol/mol. Thus, only 84% and 65% of the exchangeable sites were occupied by anionic surfactants. Quantitative exchange is attained in more highly concentrated solutions (see below).

The basal spacing d_L of the organic derivatives in contact with the equilibrium solution increased sharply at very low equilibrium concentrations of surfactants (Fig. 1b). It reached the maximum value ($d_L = 2.78$ nm for DS, $d_L = 2.96$ nm for DBS) at amounts adsorbed as low as $n_1^{\sigma(v)} = 1.7$ mmol DS/g or 0.53 mol DS/mol LDH and $n_1^{\sigma(v)} = 1.5$ mmol DBS/g or 0.47 mol DBS/mol LDH. Only 50% of the exchangeable sites are needed to be occupied by the surfactants to jack the layers apart. This noticeable result illustrates the pillaring action of the alkyl chains.

The equivalent area available to an anion in the interlayer space is 0.287 nm^2. (The lattice of calcium aluminum hydroxide is described by a hexagonal cell with $a = 0.332$ nm which contains 0.333 charges per layer [21]. As the area of the basal plane in the unit cell is $a^2\sqrt{3}/4 = 0.0955$ nm^2, the equivalent area is $0.0955/0.33 = 0.287$ nm^2.) When only 50% of the exchangeable sites are occupied, an area of $0.287/0.50 =$ 0.57 nm^2 is available to each surfactant. The packing density of the chains is similar to that in fully exchanged, highly charged smectites. The cross-sectional area of an alkyl chain in all-trans conformation is about 0.24 nm^2 [22].

The basal spacing indicates that the alkyl chains are oriented normally to the layers (Fig. 2a, b). Kopka et al. [11] and Meyn et al. [12] calculated the basal spacings of the LDHs after intercalation of different acid anions. The calculated spacing for a perpendicular arrangement of dodecylsulfate anions was 2.48 nm, for the dodecylbenzene sulfonate derivative 2.69 nm. The maximum spacings observed in contact with the equilibrium solution (2.78 and 2.96 nm, resp.) were about 0.3 nm higher. As discussed for alkylammonium vermiculites [17] and alkylammonium montmorillonites [18], formation of such expanded monolayers (Fig. 2b) is typical of the adsorption of polar liquids between the interlamellar alkyl chains. The water molecules form clusters between the surfactant anions [18, 23–25]. The surfactant anions may be evenly distributed in the interlayer space or may be aggregated in bundles.

Fig. 2 Arrangement of dodecylsulfate ions between the layers of double hydroxides; alkyl chains perpendicular to the surface: (a) monolayers, (b) expanded monolayers, (c) bilayers with interdigitating chains, and (d) bilayers



Adsorption of benzene/*n*-heptane

For the liquid adsorption measurements calcium aluminum double hydroxide was fully exchanged by repeated treatments with 0.1 M surfactant solutions. Excess of surfactant had to be carefully removed by long-time Soxhlet extraction because dissolved compounds interfere with the interferometric determination of the liquid composition. The extracted samples contained 1.18 mmol DS/g and 2.03 mmol DBS/g, resp. The theoretical surfactant content (1 mol/mol LDH) is 1000/(212.14 + 265.07) = 2.10 mmol DS/g and 1000/(212.14 + 325.07) = 1.86 mmol DBS/g (molar mass of $[Ca_2Al(OH)_6]^+ = 212.14$; of DS = 265.07; of DBS = 320.07). The values indicate that the DS-derivative lost a considerable amount of surfactant during extraction whereas the DBS-derivative remained in fully exchanged state, even the excess of sodium dodecylbenzene sulfonate was not removed quantitatively.

The surface excess isotherms for benzene/*n*-heptane mixtures (benzene = compound 1) were U-shaped (Fig. 3a), which indicates that only benzene is adsorbed for $x_1 > 0$. The amount of benzene adsorbed, $n^s_{1,0}$, was obtained from the composite isotherm by the graphical procedure of Schay and Nagy [15, 23, 26]. Extrapolation of the linear section of the isotherm to $x_1 = 0$ yielded $n_1^{\sigma(n)} = n^s_{1,0} = 0.17$ mmol benzene/g LDH for unmodified calcium aluminum hydroxide. As the basal spacing of the sample was not changed after dispersion in benzene/*n*-heptane (Table 1), benzene molecules were not intercalated and were adsorbed solely on the external surface. Hydrophobization strongly increased the adsorption of benzene. The amount adsorbed raised to $n^s_{1,0} \approx 0.70$ mmol/g (Table 2).

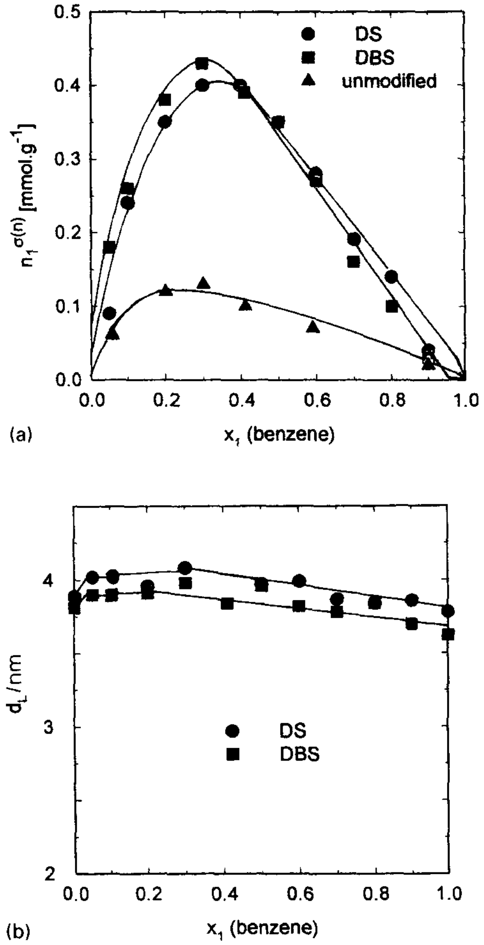


Fig. 3 Adsorption of benzene/n-heptane on dodecylsulfate (●) and dodecylbenzene sulfonate (■) LDH: (a) surface excess isotherms, $n_1^{\sigma(n)}$ vs. x_1, x_1 = molar fraction of benzene in the equilibrium liquid mixture; (b) basal spacing d_L as a function of x_1

The amounts adsorbed can also be expressed by the volume occupied of the adsorptive:

$$V^s = n^s_{1,0} \cdot V_{m,1} ,$$

where $V_{m,1} = M/\rho$ is the molar volume of benzene (78.12/0.8765 = 89.13 cm^3/mol). V^s increases from 0.014 cm^3/g for the original LDH to about 0.1 cm^3/g for the hydrophobized derivatives (Table 2).

Adsorption of benzene proceeded into the interlayer spaces (Fig. 4). The basal spacing of the dried hydrophobic LDH was 2.41 nm (for DS) and 2.62 nm (for DBS) (Table 1). These values are identical with the calculated spacing for perpendicular chains (2.48 nm for DS; 2.69 nm for DBS, see above). Adsorption of benzene from heptane/benzene mixtures jacks the layers apart to spacings of 3.7–4.1 nm (Figs. 3b, 4). In mixtures rich on heptane the spacing is slightly higher than in pure benzene and pure heptane.

In the dried samples the surfactant anions are aggregated in monolayers (Fig. 2a). Bilayer arrangements (Figs. 2c, d) may be formed by swelling. The basal spacing should be 4.44 nm (DS) and 4.87 nm (DBS), resp. for perpendicularly arranged chains (Fig. 2d). The observed spacings indicate bilayers with interdigitating chains (Fig. 2c).

Table 2 Adsorption from binary liquid mixtures

Adsorbent[a]	n^s_1	n^s_2 (mmol/g)	n^s (mmol/g)	V^s (cm^3/g)
benzene/*n*-heptane[b]				
LDH	0.17	–	0.17	0.014
DS-LDH	0.70	–	0.70	0.096
DBS-LDH	0.69	–	0.69	0.101
n-propanol/toluene[b]				
DS-LDH	0.74	0.54	1.28	0.173
DBS-LDH	1.32	–	1.32	0.161

[a] See Table 1.
[b] Component 1 = benzene and *n*-propanol, resp.

Table 1 Basal spacing of calcium aluminum double hydroxides (LDHs)

Adsorbent[a]	Basal spacing (nm)					
	Dried	In water	In *n*-heptane	In benzene	In toluene	In *n*-propanol
LDH	0.80	1.01	0.80	0.80	0.80	3.92
DS-LDH	2.41	2.78	3.89	3.78	4.02	3.07
DBS-LDH	2.62	2.96	3.81	3.65	3.70	2.98

[a] DS-LDH = dodecylsulfate derivative; DBS-LDH = dodecylbenzenesulfonate derivative.

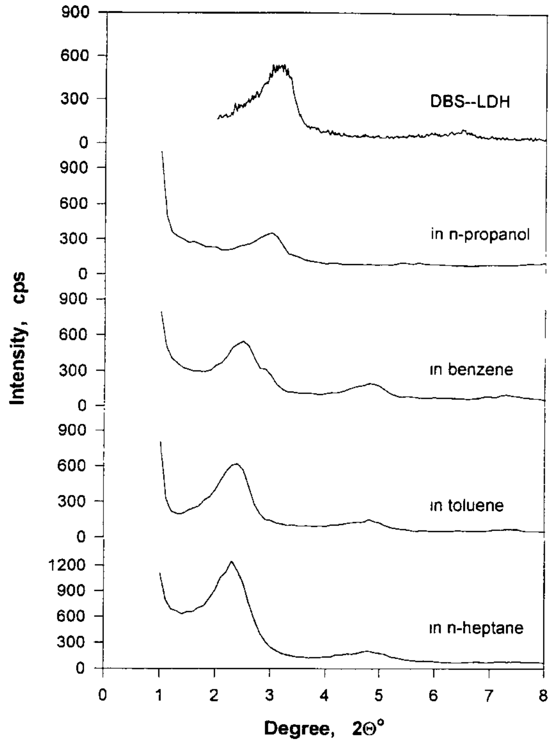


Fig. 4 X-ray powder diagrams showing the basal reflections of dodecylbenzene sulfonate LDH after dispersion in several liquids

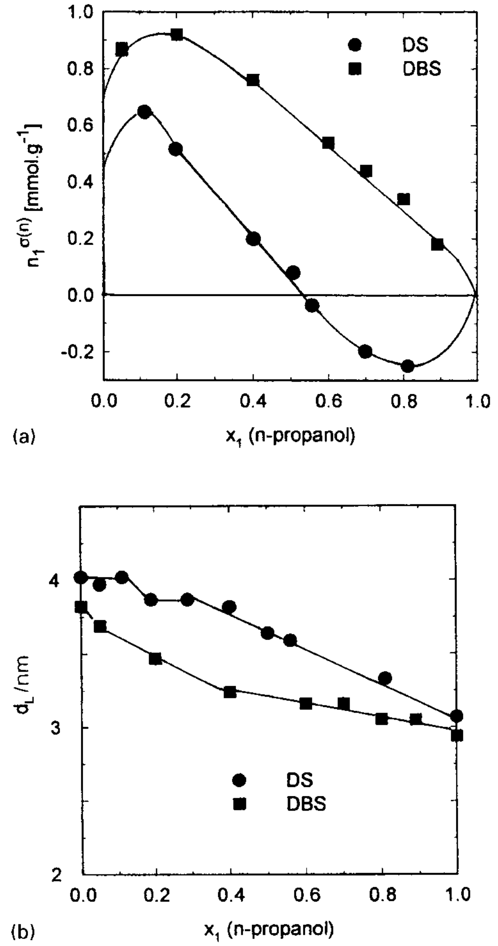


Fig. 5 Adsorption of n-propanol/toluene on dodecylsulfate (●) and dodecylbenzene sulfonate (■) LDH: (a) surface excess $n_1^{\sigma(n)}$ vs. x_1, x_1 = the molar fraction of propanol; (b) basal spacing d_L vs. x_1

Only benzene is adsorbed from mixtures of *n*-heptane/benzene with $x_1 > 0$. When the hydrophobized samples are dispersed in n-heptane ($x_1 = 0$), the basal spacing increases strongly and is even slightly higher than in benzene (Figs. 3b, 4, Table 1). This is a very noticeable result, because hydrophobized montmorillonites and vermiculites do not swell in aliphatic hydrocarbons (cf. Fig. 14 in [20]).

Adsorption of propanol/toluene

The dodecylsulfate derivative showed a type-IV isotherm (Fig. 5a) with a linear section between $x_1 \approx 0.1$ and $x_1 \approx 0.6$ and an azeotropic point at $x_1^a = 0.5$. At x_1^a the composition of the adsorption phase, x_1^s, is the same as in the bulk liquid mixture, x_1. In the range of the linear section of the isotherm, the composition of the adsorption phase is $x_1^s = x_1^a = 0.55$. Therefore, almost equal molar amounts of propanol ($x_1^s = 0.55$) and toluene ($x_2^s = 0.45$) were adsorbed. The basal spacing decreased from 4.0 nm in toluene to 3.1 nm in propanol (Fig. 5b) in spite of the constant composition of the adsorption layer between $x_1 \approx 0.1$ and $x_1 \approx 0.6$. Thus, the degree of interdigitation of the chains (Fig. 2b, c) increased with polarity of the liquid mixture.

The fundamentally different behavior of the dodecylbenzene sulfonate derivative was unexpected. The surface excess isotherm was of type II with a linear section between $x_1 \approx 0.2$ and $x_1 \approx 0.9$. In this range of equilibrium bulk composition only propanol is adsorbed. The basal spacing decreased from 3.6 nm in toluene ($x_1 = 0$) to 2.9 nm in propanol ($x_1 = 1$). With increasing polarity of the liquid mixture the bilayers of interpenetrating chains (Fig. 2c) collapsed to slightly expanded monolayers (Fig. 2b).

The reason of the unexpected exclusion of the hydrocarbon from the adsorption layer is seen in the tendency of the alcohol molecules to form distinct clusters [23–25] which push aside the toluene molecules. Enough adsorption sites are available in the dodecylsulfate derivative, and toluene and propanol are adsorbed. The higher surfactant density of dodecylbenzene sulfonate LDH reduces the number of surface sites for adsorption. Anchoring of the propanol clusters on the surface do not admit space for adsorbing toluene molecules.

Lattice expansion and adsorptive volume

The volume of the adsorption phase, $V^s = n_1^s + n_2^s$, is about 0.1 cm^3/g for the adsorption from benzene/heptane and about 0.17 cm^3/g in propanol/toluene. In the hydrocarbon mixture the basal spacing increased from about 2.5 nm (dried sample) to more than 3.5 nm. As the area per charge is 0.287 nm^2, an expansion of the lattice by 1 nm corresponds to $0.287 \cdot 1 \times 10^{-21} \cdot 6.023 \times 10^{23} =$ 173 cm^3/mol. With one anion DBS per mol double layer hydroxide the molar mass is 537 (see above). An increase of the spacing by 1 nm corresponds to a volume of $173/537 = 0.32$ cm^3/g. The expansion of the lattice in benzene/heptane is distinctly higher than the volume $V^s \approx 0.1$ cm^3/g occupied by the adsorption phase. A similar result is obtained for the dodecylsulfate derivative.

Swelling in propanol/toluene mixtures increased the spacing of the DBS derivative by about 1 nm in toluene rich mixtures. The volume of the adsorption layer, $V^s = 0.16$ cm^3/g, is again smaller than the volume increment by the expansion of the interlayer space. At high propanol contents ($0.5 < x_1 < 0.8$) the spacing raised by 0.4–0.6 nm, the volume of the interlayer space, by $0.32 \cdot 0.4 = 0.13$ cm^3/g and $0.32 \cdot 0.6 = 0.19$ cm^3/g, resp. The expansion of the interlayer space is now comparable to V^s.

A value of V^s smaller than the real expansion of the interlayer space was often observed in the course of adsorption studies on swelling hydrophobic clay minerals [17, 18]. When the interlayer spaces are opened in the first step of the adsorption process, an additional amount of bulk liquid (i.e. liquid with the same composition as in the bulk) penetrates between the layers: the total amount of liquid in the expanded interlayer space becomes larger than V^s. Probably, the driving force is a gain of conformational entropy of the alkyl chains when the layers are pried open. This effect is not dominant in case of highly polar liquids when the interlayer separation is determined by clustering of intercalated molecules [23, 24].

A comment must be made to the decreasing basal spacing of the dodecylsulfate derivative in propanol/toluene in spite of a constant composition of the adsorption phase (for $0.1 < x_1 < 0.7$, Fig. 5b). With x_1 increasing, the composition of the total interlamellar liquid (i.e. adsorption phase + bulk-type liquid) becomes richer in propanol. The van der Waals attraction between the alkyl chains increases because the difference between the Hamaker constant of the alkyl chains and that of the medium becomes larger [27]. The expansion of the interlayer space is, therefore, reduced. This mechanism also operates in the presence of the dodecylbenzene sulfonate anions. The adsorption phase only contains propanol but a certain amount of bulk-like liquid is also taken up at $x_1 < 0.5$. In fact, the spacing decreases more steeply between $x_1 \approx 0$ and $x_1 \approx 0.4$ where the total interlamellar expansion is distinctly larger than V^s.

Table 3 Enthalpy of immersion of calcium aluminum double hydroxides (LDHs)

Adsorbent[a]	$-\Delta_w H$(J/g)			
	n-Heptane	Benzene	Toluene	*n*-Propanol
LDH	3.20	4.10	4.00	8.20
DS-LDH	6.47	14.3	15.2	24.60
DBS-LDH	6.12	10.53	10.02	26.75

[a] See Table 1.

Enthalpy of immersion

The exothermic heats of immersion (Table 3) reveal strong interactions with the interlamellar surfaces primed with surfactant anions. As expected, they increased in the order: heptane < aromatic hydrocarbons < propanol. A quite different series was observed for microporous, pillared montmorillonite: heptane < ethanol < benzene [28].

The heats of immersion of the DBS-derivative in benzene and toluene but not in heptane and propanol were smaller than those of DS-LDH. The amounts adsorbed from the pure liquids ($n_{i,0}^s$ at $x_1 = 0$ and $x_1 = 1$) are not exactly known. It is questionable [20] if these values can be derived from V^s: $n_{i,0}^s \approx V^s/V_{m,i}$($V_{m,i}$ molar volume of component i). When this approximation holds, equal amounts of pure liquids would be adsorbed by DS- and DBS-LDH. The smaller wetting enthalpies of DBS-LDH in benzene and toluene then indicate that the energetically most favored adsorption sites for benzene and toluene are the uncovered internal surfaces between the alkyl chains. Due to the higher surfactant density, this area is smaller for the DBS-LDH compared with the dodecylsulfate derivative.

Conclusions

When the surface of double layer hydroxides is hydrophobized, the adsorption capacity towards organic liquids is strongly enhanced. The examples reported here (calcium aluminumhydroxide with dodecylsulfate and dodecylbenzene sulfonate) attract attention because the adsorption behavior is fundamentally different from the well-known behavior of hydrophobic clay minerals. One striking effect is the interlamellar swelling of both derivatives in *n*-heptane which was never observed with alkylammonium clay minerals. Another point of interest is the preferential adsorption of propanol by the dodecylbenzene sulfonate derivative, whereas the dodecylsulfate derivative adsorbs propanol and toluene in almost equal amounts.

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