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ORIGINAL CONTRIBUTION

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Interaction of sodium dodecylsulfate (SDS) with homoionic montmorillonites: adsorption isotherms and metal-ion release

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Abstract The interaction of dodecylsulfate anions (DS^-) with homoionic Ca-, Mg-, Ni-, Cu-, Cd-, Pb- and Fe-montmorillonites were investigated. Mg- and Cd-montmorillonite do not adsorb DS^-, and an anion exchange at the edges of the clay mineral does not take place. Three different adsorption processes are identified on the other montmorillonites: i) Fe-montmorillonite is covered with amorphous iron hydroxide, and DS^--anions are bound at positively charged sites. ii) On Ca- and Pb-montmorillonite DS^- is precipitated as $Me(DS)_2$. iii) On Ni- and Cu-montmorillonite DS^- forms ion pairs with the cations on the surface. In all cases DS^- is not bound above the CMC but the metal ions are mobilized from the surface either by solubilization of the precipitates or by formation of mixed micelles.

Key words Sodium dodecylsulfate – adsorption – precipitation – montmorillonite

Introduction

Surfactants belong to the most produced organic compounds. They are widely used in domestic and technical processes. After their use they reach sewage plants and are accumulated in sewage sludge. By their application in agriculture, the surfactants are washed into the soils where they interact with the solid–liquid interfaces, and thus they may alter the adsorption properties with respect to organic contaminants. For this reason it is important to understand the binding mechanisms of surfactants at the interface between water and soil minerals. Cationic surfactants are predominantly adsorbed by ion exchange [1, 2], whereas different binding modes are found for anionic surfactants. Different mechanisms are known:

i) At interfaces with low or variable positive and negative charges (organic matter, iron- and aluminum oxides and hydroxides) surfactants are bound by physisorption and/or ion pairing or ion exchange. With increasing concentration, associates (admicelles, hemimicelles) are formed and at high concentration the interface can be covered by a double layer [3–10].

ii) Anionic surfactants can also interact with negatively charged surfaces. They associate with multivalent surface cations or are precipitated. Examples are the adsorption of alkylsulfonates at quartz and kaolinite [11], the interaction of dodecyl benzenesulfonate with kaolinite [12], of octyl benzenesulfonate with kaolinite, illite and chlorite [13], of dodecylsulfate with fluorite [14], of hexadecylsulfate with zeolite-A [15], and of oleate with scheelite and calcite [16]. Other publications [17, 18] interpret the adsorption of anionic surfactants like dodecylsulfate, dodecylbenzenesulfate and dodecylbenzenesulfonate at minerals qualitatively as precipitation at the mineral surfaces. The results are in good agreement with the known precipitation process of anionic surfactants with metal ions in aqueous solutions [19, 20]. Missing are detailed investigations on the interaction of anionic surfactants with montmorillonites, which are important soil constituents. However, some hints exist that anionic surfactants are precipitated on calcium bentonites [21, 22].

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Other publications prove the existence of precipitated calcium di-dodecylsulfate at the surface of bentonite [23] and Ca-montmorillonite [24] by x-ray diffractometry. By increasing the concentration of the anionic surfactant above the critical micelle concentration (CMC), the precipitates can be dissolved or resolubilized in the micellar phase [13, 20]. However, the mechanism of this dispersion process is not yet investigated with pure homoionic montmorillonites.

The aim of this work is to investigate the interaction of an important anionic surfactant, sodium dodecylsulfate (SDS) at concentrations below and above its CMC with purified, homoionic montmorillonites. The metal ions Ni^{2+}, Cu^{2+}, Mg^{2+}, Cd^{2+}, Ca^{2+} and Pb^{2+} are chosen on the basis of their decreasing solubility product with DS^-, a quantity that corresponds roughly to their ionic radii. The Fe^{3+}-ion is included in this study since it is completely hydrolyzed even in slightly acidic solution.

Theory

Anionic surfactants precipitate in aqueous solutions with metal ions:

$$Me^{2+} + 2DS^- \rightleftharpoons Me(DS)_{2\,(\mathrm{solid})} \,. \tag{1}$$

The solubility product K_S is:

$$K_S = a_{Me} a_{DS}^2 = m_{Me} m_{DS}^2 \cdot \gamma_{Me} \gamma_{DS}^2 \tag{2}$$

with a: activity in the bulk phase; m_i: molarity in the bulk phase; γ: activity coefficient.

By measuring m_{Me} and m_{DS} in the saturated solution, the solubility product can be calculated when the activity coefficients are known and calculated by Davis' equation [25].

If the concentration of surfactant in the bulk phase exceeds the critical micelle concentration (CMC), the precipitate is resolubilized in the micellar phase. By the methods employed we cannot distinguish whether the metal ions are associated at the outer surface of a micelle or if the insoluble salt $M(DS)_2$ is incorporated in the core of the micelles. X_{ass} is the association constant, which is the fraction of DS^- anions in the micelles that are neutralized by divalent metal ions:

$$X_{ass} = 2\,\frac{m_{\mathrm{micelle},\,M^{2+}}}{m_{\mathrm{micelle},\,DS^-}} \,. \tag{3}$$

The CMC is related to the metal ion concentration by Eq. (4) [26], where α and β are empirical constants, and $m_{0,\,Me}$ is the total (analytical) molarity of the metal salt. Equation (1) to (4) are combined

$$m_{DS} = \mathrm{CMC} = \beta m_{0,\,Me}^{-\alpha} \tag{4}$$

under the assumption that the molarities of the DS^--monomer and the free metal ion are controlled by Eq. (2) and (4) [20]:

$$m_{0,\,DS} = \beta m_{0,\,Me}^{-\alpha} + \frac{2}{X_{ass}} \left\{ m_{0,\,Me} - K_S \frac{m_{0,\,Me}^{2\alpha}}{\gamma_{Me} \gamma_{DS}^2} \right\} ; \tag{5}$$

X_{ass} is obtained by fitting Eq. (5) to experimental values of the total molarity of metal ions and DS^- in the bulk phase ($m_{0,\,Me}$, $m_{0,\,DS}$), if α, β, and the activity coefficients are known.

Any binding process, irrespective of whether it is precipitation or ion pairing at the surface, can be regarded as an adsorption of DS^-. This adsorption isotherm is obtained by a plot of the specific surface excess, n_{DS}^{σ}, versus the equilibrium concentration of DS^-:

$$n_{DS}^{\sigma(V)} = \frac{V}{M}\,(m_{0,\,DS} - m_{eq,\,DS}) \tag{6}$$

with $n_{DS}^{\sigma(V)}$: specific surface excess of DS^-, $\mathrm{mol \cdot g^{-1}}$; V: volume of the equilibrium phase, L; M: mass of adsorbent, g; $m_{0,\,DS}$: initial concentration of DS^-, $\mathrm{mol \cdot dm^{-3}}$; $m_{eq,\,DS}$: equilibrium concentration of DS^-, $\mathrm{mol \cdot dm^{-3}}$.

Materials and methods

Materials

The homoionic montmorillonites were prepared from Ca^{2+}-bentonite from Südchemie AG, Germany as folows. A 20 g/L dispersion was treated with 7.5% H_2O_2/0.1 M Na-acetate for the oxidation of organic compounds and then allowed to sedimentate for 48 h in a 60 cm glass cylinder. The supernatant, containing the size fraction below 2 μm, was separated and treated with a two-fold surplus (resp. to total c.e.c) of metal nitrate salts and subsequent washing with Millipore-water. This procedure was repeated three times. Then the dispersion was dialyzed until the conductivity of the washing-water became less than 3 $\mu\mathrm{S \cdot cm^{-1}}$. Finally, the products were freeze-dried to constant weight with the exception of Fe-montmorillonite, which was stored as a stock dispersion of 40 $\mathrm{g\,dm^{-3}}$ at pH = 6. The characteristic data of these montmorillonites are given in Table 1. The cation exchange capacity (c.e.c.) was determinated by the NH_4^+-technique [1, 27] and the external surfaces were obtained from the BET adsorption isotherm of N_2. The basal spacing was determined from the (0 0 1)-reflection in the x-ray power diagram. Sodium dodecylsulfate (SDS) was supplied by Fluka AG at a purity grade of 98%, the metal salts were purchased as nitrates of p.A. grade from Merck AG.

Table 1 Homoionic montmorillonites

	Cation exchange capacity (c.e.c)/meq · g^{-1}	BET m^{2} · g^{-1}	d_{011}/Å dried sample[1]
Na^{+}-montmorillonite	0.98	88.7	10.9
Ca^{2+}- ”	0.97	82.9	14.9
Mg^{2+}- ”	0.91	25.6	14.6
Cd^{2+}- ”	0.90	55.8	14.8
Pb^{2+}- ”	0.89	54.9	12.7
Ni^{2+}- ”	0.9[2]	41.0	14.9
Cu^{2+}- ”	0.9[2]	45.0	12.9
Fe^{3+}- ”	–[3]	41.0	15.1

[1] Three droplets of each 15 μL of a 15 g dm^{-3} dispersion were placed on a microscope slide and airdried.

[2] Estimated from the c.e.c. of the Ca-bentonite (containing about 50% Ca- and 45% Mg-montmorillonite) used for the ion exchange.

[3] Fe-montmorillonite carries predominantly pH-dependent charges, therefore a c.e.c. cannot be given.

Methods

The adsorption experiments were performed by the batch-technique. To the dispersions of the montmorillonites an amount of SDS from a stock-solution was added, the total volume of the aliquots was 10 ml, and the tubes were shaken for 24 h in a head-over-head-rotor. After this the samples were centrifugated 30 min at 20 000 r.p.m. and the supernatant was analyzed for the metal ions by atomic absorption spectroscopy (Hitachi 180-80) and for SDS by the two-phase titration technique [28]. The equilibrium concentrations of the montmorillonite in the dispersions were 15 g dm^{-3} for Ca-, Mg-, Cd- and Pb-montmorillonite and 9.5 g dm^{-3} for Cu-, Ni- and Fe-montmorillonite for the determination of adsorption isotherms. For the determination of the mobilization isotherms of the metal ions separate experiments were performed with a dispersion concentration of 0.5 g dm^{-3} for Ca-, Mg-, Cd- and Pb-montmorillonite, since otherwise the total metal concentrations and therefore the dilution errors were too high. For Cu-, Ni- and Fe-montmorillonite dispersion concentrations of 9.5 g dm^{-3} were convenient to minimize dilution errors for the AAS analytics. The x-ray powder diagrams were measured with the XRD theta/theta-diffractometer (Seifert GmbH, Germany). The samples were prepared by drying a droplet of about 20 μl of the dispersion on a microscope slide at 40 °C. This procedure was repeated three times to obtain a film of sufficient thickness, yielding reproducible intensities and positions of the reflections.

Results and discussion

Binary system

Precipitation and micellar solubilization of Ca(DS)$_2$ and Mg(DS)$_2$ in the binary systems (without a mineral phase) is well understood ($\log K_S = -9.67$ and -8.51, respectively, [20]) but no information exists on the behavior of the other metal-surfactant systems. However, the precipitation of Ca(DS)$_2$ and Mg(DS)$_2$ are not investigated at low concentrations of metal ions as used in this study. Therefore, we have studied the reaction of the metal ions (exception Fe^{3+}) with SDS in aqueous solution at the same metal ion concentrations used for the adsorption experiments at the homoionic montmorillonites.

Figure 1 shows the precipitation – solubilization diagram for an initial metal ion concentration of 2.2×10^{-4} mol · dm^{-3} with increasing concentration of DS$^-$. The initial metal ion concentration corresponds to the total c.e.c. of the montmorillonite in the dispersions used for the mobilization experiments with Ca-, Pb-, and Cd-montmorillonite (0.5 g dm^{-3}, see *materials and methods*). Shown are only the data for the precipitating ions Ca^{2+} (△) and Pb^{2+} (□) and for Cd^{2+} (▼) as representative for not precipitating ions (Cd^{2+}, Ni^{2+}, Mg^{2+}, Cu^{2+}). At these metal ion concentrations, Cd^{2+}, Ni^{2+}, Mg^{2+} and Cu^{2+} are not precipitated with DS$^-$, because the solubility product is too high, and the CMC is reached before any precipitation occurs. The consequence is that the data points for Cd^{2+} lie on a straight line, i.e. the analytical molarity, corresponding to the free metal ion concentration, is equal to the total molarity in the samples. In contrast to Cd^{2+} (and Ni^{2+}, Mg^{2+}, Cu^{2+}, not shown here), the concentrations of free Ca^{2+} and Pb^{2+} decrease linearly with increasing molarity of DS$^-$ above the points “a” in Fig. 1, i.e. these metal ions are precipitated by DS$^-$. The solubility products are calculated by fitting Eq. (2) to the precipitation boundaries (straight lines in Fig. 1). For Ca^{2+} we obtain $\log K_S = -9.2 \pm 0.1$ and for Pb^{2+} $\log K_S = -9.8 \pm 0.1$. The value for Ca(DS)$_2$ is higher than that obtained by Kallay and coworkers [20] who applied much higher metal concentrations.

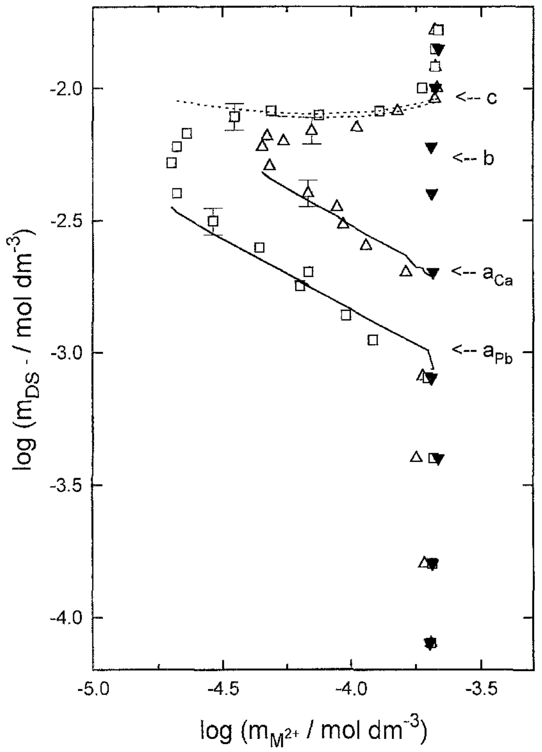


Fig. 1 Precipitation-solubilization diagram of DS^- with Ca^{2+} (△), Pb^{2+} (□) and Cd^{2+} (▼), initial metal ion concentration: $2.2 \cdot 10^{-4}$ mol·dm^{-3}. The lines are calculated according to Eqs. (2) and (5) for the precipitation (—) and the solubilization (---) boundaries. "a_{Ca}, a_{Pb}": beginning of the precipitation of $Ca(DS)_2$ and $Pb(DS)_2$, respectively; "b": beginning of the solubilization; "c"; complete solubilization

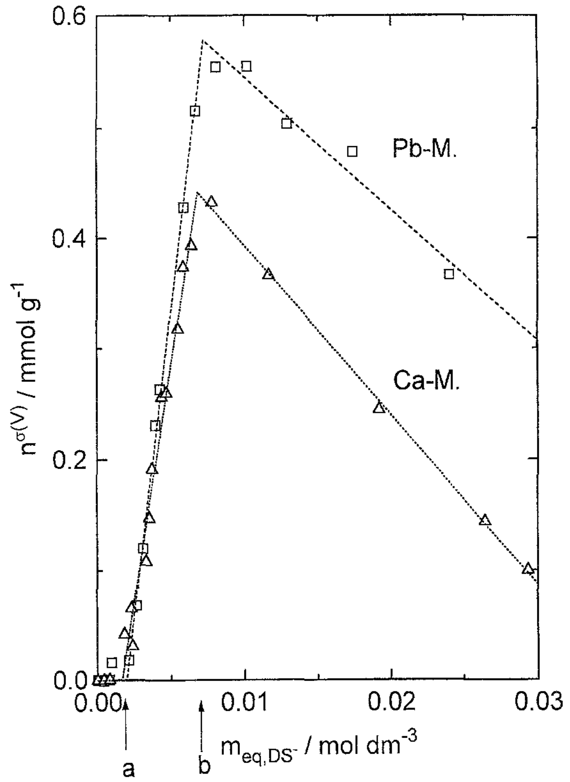


Fig. 2 Specific surface excess $n_{DS}^{\sigma(V)}$, Eq. (6), for Ca- and Pb-montmorillonite at a concentration of 15 g dm^{-3}. "a" and "b" denote the beginning of the precipitation and the solubilization, respectively

Above the point "b" in Fig. 1 the CMC of SDS is exceeded and the precipitates are solubilized in the micellar phase. The association constants X_{ass} for Ca^{2+} and Pb^{2+} are obtained by fitting Eq. (5) to the solubilization boundaries between "b" and "c" (dotted lines). We obtain $X_{ass} = 0.11 \pm 0.01$ for Pb^{2+} and $X_{ass} = 0.10 \pm 0.01$ for Ca^{2+}. The latter value is smaller than that obtained in ref. [20], this is due to the much lower total concentration of Ca^{2+} (2.2×10^{-4} mol dm^{-3}) employed in this work. At metal ion concentrations smaller than 5×10^{-5} mol dm^{-3} the experimental data for Ca^{2+} (△) and Pb^{2+} (□) deviate significantly from the by Eq. (5) calculated curves (dotted curves) between the points "b" and "c" in Fig. 1. This is the consequence of the fact that Eq. (4) overestimates the CMC at these low total metal salt concentrations.

Ternary systems

In the ternary systems of metal ions, surfactant ions, and montmorillonite, a similar precipitation process may take place, if the solubility products are low enough. This is expected for $Ca(DS)_2$ and $Pb(DS)_2$. When the CMC is reached, the precipitate will be solubilized in the micellar phase. Because the precipitation takes place at a surface, it is formally treated as an adsorption process, described by Eq. (6). Figure 2 shows the specific surface excess $n_{DS}^{\sigma(V)}$ as a function of the equilibrium concentration m_{DS} for Ca- and Pb-montmorillonite. We can distinguish two different processes. With increasing concentration of DS^- $Ca(DS)_2$ and $Pb(DS)_2$ are precipitated at the surface when m_{DS} is greater than "a". The surface excess increases until the CMC is reached at "b". The slope of the line between "a" and "b" is slightly steeper for Pb-montmorillonite than for Ca-montmorillonite and the maximum value is higher. This indicates that the affinity of Pb^{2+} to sodium dodecylsulfate is higher than that of Ca^{2+}. Above "b" the surface excess decreases due to the solubilization of $Ca(DS)_2$ and $Pb(DS)_2$ in the micellar phase. This process is promoted by the enhanced exchange of the divalent ions with sodium ions provided by the surfactant added. The Me^{2+}-montmorillonites are continuously transformed to Na-montmorillonite which do not bind the surfactant anion. This excludes the possible binding of DS^- by anion exchange at

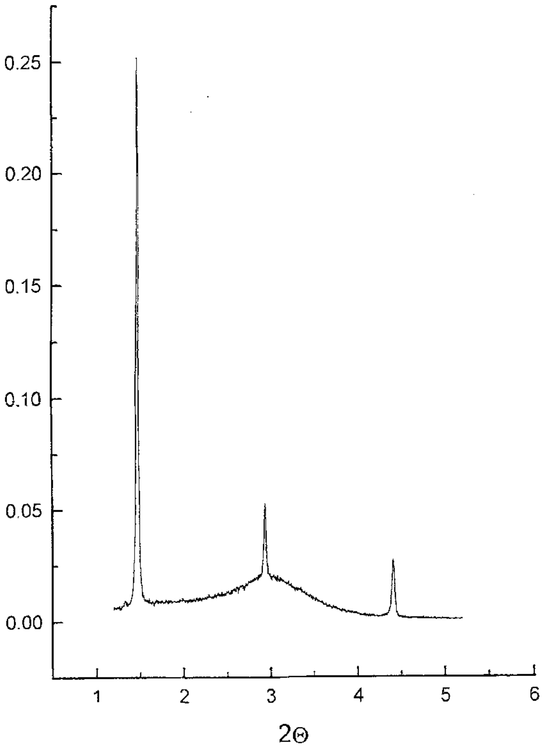


Fig. 3 X-ray diffractogram of a dried sample of Ca-montmorillonite with precipitated Ca-dodecylsulfate (precipitated from a dispersion of 15 g montmorillonite/dm^3 and 4.4 mmol SDS/dm^3, then air dried)

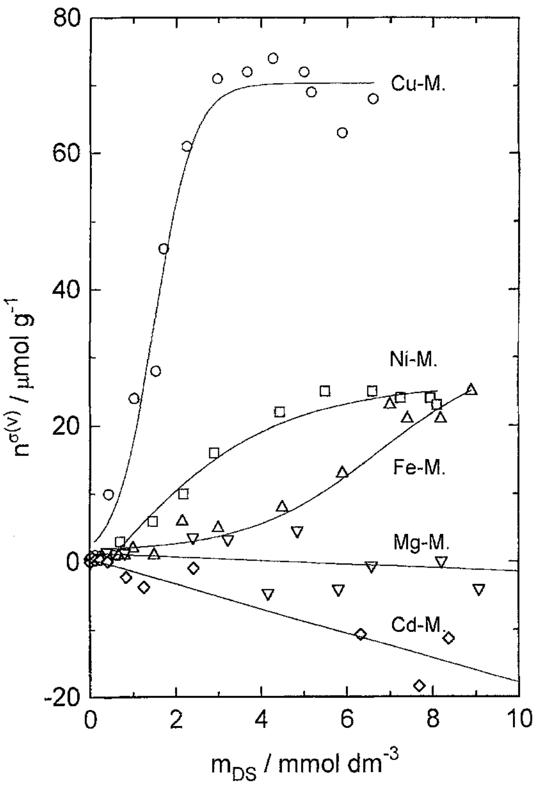


Fig. 4 Specific surface excess $n_{DS^-}^{\sigma(V)}$, for Cu-, Ni-, and Fe-montmorillonite (dispersion concentration 9.5 g dm^{-3}) and Mg- and Cd-montmorillonite (dispersion concentration 15 dm^{-3})

the edges, since in that case Na-montmorillonite should also adsorb dodecylsulfate. This result coincides with that reported in the literature [29].

This precipitation process can also be investigated by x-ray diffractometry. Figure 3 shows a x-ray diffractogram of a thin film of Ca-montmorillonite with precipitated dodecylsulfate (15 g dm^{-3} and $m_{DS} = 4.4$ mmol dm^{-3}). The broad reflection centered at $2\Theta = 2.84°$ corresponds to the basal spacing of the montmorillonite ($d_{001} = 14.1$ Å) and the sharp reflections at $2\Theta = 1.48°, 2.94°$ and $4.41°$ are assigned to the d_{001} d_{002} and d_{003} values of the Ca(DS)$_2$ precipitate. Pure Ca(DS)$_2$ gives the same reflections (not shown here). Similar diffractograms are found for Pb-montmorillonite, proving again the existence of precipitated Pb(DS)$_2$. In the presence of Mg^{2+}, Cd^{2+}, Cu^{2+}, and Ni^{2+} as exchanged cations no reflections of precipitates were found, indicating that the interaction of DS$^-$ with these homoionic montmorillonites is of different nature. In all cases the basal spacing of the montmorillonites did not increase, the anionic surfactant is not intercalated into the interlayer space.

Figure 4 shows the isotherms for the other systems. Due to the higher solubility product DS$^-$ is not precipitated on Cu-, Ni- and Fe-montmorillonite. The slopes and the maximum values of the isotherms are much smaller than observed for Ca- and Pb-montmorillonite. The s-shape of the isotherms indicates a weak cooperative interaction: Mg-montmorillonite does not bind DS$^-$. For Cd-montmorillonite $n_{DS}^{\sigma(V)}$ becomes negative. A similar behavior is observed for Na-montmorillonite (not shown here). The reason is the anion exclusion effect (negative adsorption) [30, 31] from the negatively charged surface of the montmorillonite. For the other homoionic montmorillonites the exclusion of the surfactant anions is overcompensated by the attractive interaction with the exchangeable metal ions. This observation indicates that the binding of DS$^-$ on Cu- and Ni-montmorillonite is not caused by anion exchange at the edges, since this reaction should also take place on Mg- and Cd-montmorillonite. We propose the binding as ion pair with the Me^{2+} at the surface of montmorillonite. Figure 5 shows models of ion-pairing and precipitation. Above the CMC no further binding of DS$^-$ is observed.

Fe-montmorillonite was prepared as described in the *Materials and methods* section in slightly acidic dispersion, where no free Fe^{3+} ions may exist. Under these conditions (rapid neutralization of Fe(III) containing solutions) the first precipitation product is amorphous ferrihydrite [32]

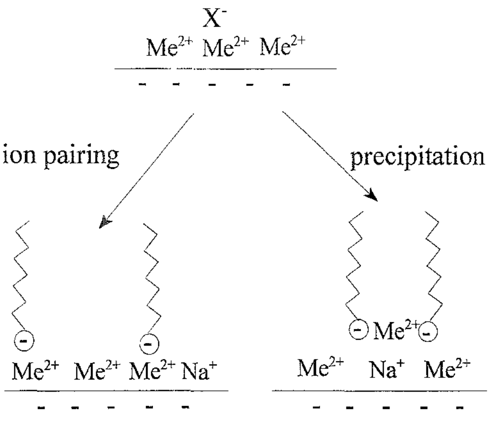


Fig. 5 Schematic representation of the ion-pairing and precipitation model

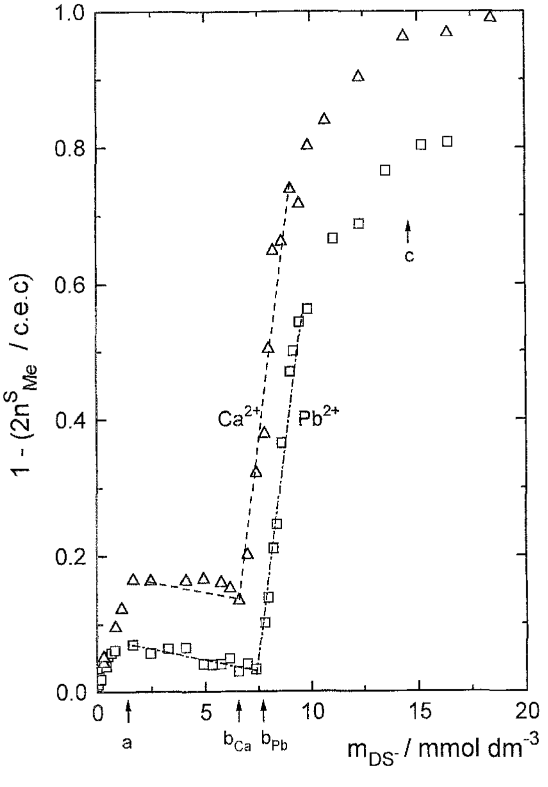
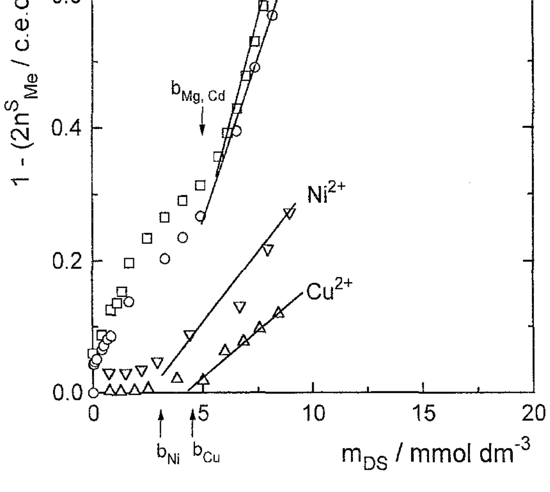


Fig. 6 Normalized amount of metal ions desorbed into the bulk phase (1–2 n^S_M/c.e.c) as a function of DS$^-$ concentration for Ca-(□) and Pb-(△) montmorillonite. "a": beginning of the precipitation; "b": beginning of the solubilization; "c": complete solubilization. (Dispersion concentration: 0.5 g dm^{-3})

and in this case it is assumed that ironhydroxide is precipitated on the surface of the montmorillonite. Also the nearly unchanged interlayer distance (see Table 1) indicates that there are no defined Fe-species in the interlayer space. Therefore it is assumed that the clay mineral is coated by amorphous $FeO_x(OH)_y$ which carries pH-dependent binding sites. The point of zero charge of such iron-hydroxides is usually above pH = 8, thus their surface is positively charged and may bind anions like DS$^-$.

Additional information is obtained from the concentration of the metal ions which are desorbed into the solution under the influence of the surfactant. Figure 6 shows the normalized amount of the free metal ions in the bulk phase (1–2n^S_{Me}/c.e.c., where n^S_M is the amount of metal ions on the montmorillonite) as a function of m_{DS}. From m_{DS} = 0 to "a", the mobilization of Ca^{2+} and Pb^{2+} due to formation of soluble complexes, probably of the type MeDS follows a linear curve. From "a" to "b" the concentration of Ca^{2+} and Pb^{2+} decreases due to precipitation of the corresponding DS$^-$ salts. Above "b" a strong metal ion mobilization occurs which decreases gradually when approaching the limit at (1–2n^S_{Me}/c.e.c) ≈ 1. Thus nearly 100% of the Ca^{2+} ions and about 80% of the Pb^{2+} ions are mobilized from the montmorillonite surface. From this plot the solubility products K_S and the micellar association coefficients X_{ass} are obtained. We yield $\log K_S = -9.9 \pm 0.1$ and $X_{ass} = 0.09$ for $Ca(DS)_2$ and

Fig. 7 Mobilization of Mg^{2+}, Cd^{2+}, Ni^{2+} and Cu^{2+} by DS$^-$. (1–2 n^S_M/c.e.c) is the normalized amount of the metal ions desorbed into the bulk phase. The lines indicate the enhanced mobilization above the CMC "a": beginning of the precipitation; "b": beginning of the mobilization (dispersion concentrations: 0.5 g dm^{-3} for Mg- and Cd-montmorillonite and 9.5 g dm^{-3} for Ni- and Cu-montmorillonite)



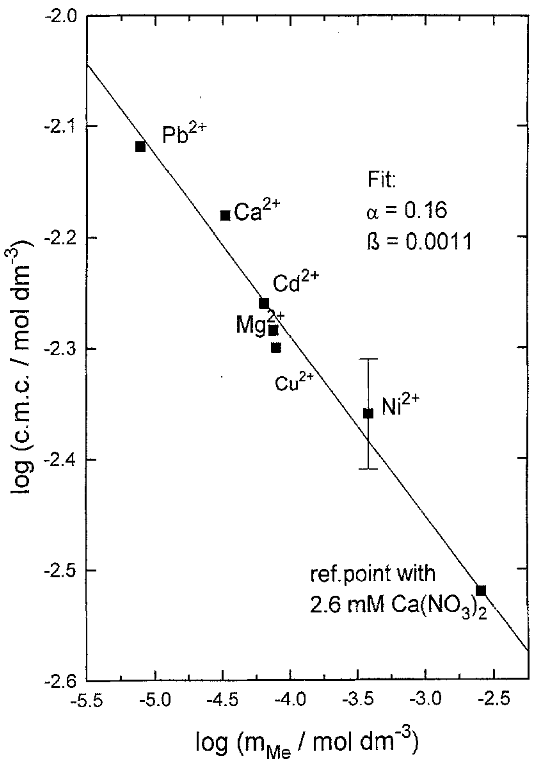


Fig. 8 Critical micelle concentration as a function of free metal ion concentration according to Eq. (4). The line is calculated with $\alpha = 0.16$ and $\beta = 1.1 \times 10^{-3}$

$\log K_S = -10.6$ and $X_{ass} = 0.11$ for $Pb(DS)_2$ on the montmorillonite. The values of the solubility products are smaller in the dispersion than in aqueous solution. The montmorillonite surface induces a precipitation of $Me(DS)_2$ probably due to the enhanced metal ion concentration near the surface.

Mg^{2+}, Cd^{2+}, Ni^{2+} and Cu^{2+} are not precipitated by DS^-. Therefore, these ions are continuously mobilized from the montmorillonite surface by the anionic surfactant (Fig. 7), whereas no mobilization of iron is observed due to the precipitation as iron oxide-hydroxide. For Mg^{2+} and Cd^{2+} a mobilization is observed already at surfactant concentrations between zero and "b". The reason is presumably the formation of premicellar aggregates combined with a displacement by sodium ions, but it is not clear why Ni^{2+} and Cu^{2+} do not show such an effect. At surfactant concentrations above the points denoted with "b" the slopes of the mobilization curves are steepest. It should be noted that the surfactant concentrations at the points "b" correspond to the CMC of SDS in the presence of divalent metal ions (see below). The reason for the enhanced mobilization is the association of the metal ions at the negatively charged micelles, the association parameter X_{ass} is calculated by Eq. (3) as 0.05, 0.04, 0.34 and 0.20 for Mg^{2+}, Cd^{2+}, Ni^{2+} and Cu^{2+}, respectively. Since these data vary over nearly one decade it may be assumed that the interaction between SDS micelles and the metal cations is of specific and not of simply electrostatic nature. However, such an effect should be investigated separately.

A proof that the metal ions are associated with the dodecylsulfate micelles is given in Fig. 8, where the critical micelle concentration, derived from the points "b" in Fig. 6 and 7, is plotted versus the free metal ion concentrations at these points. A linear relationship with $\alpha = 0.16$ and $\beta = 1.1 \times 10^{-3}$ is obtained as expected from Eq. (4). This indicates that the formation of micelles really controls the release of the metal ions and not some premicellar aggregates. These values differ slightly from published data ($\alpha = 0.23$ and $\beta = 8 \times 10^{-4}$, [20]). With respect to the different situation in the dispersion and presence of the clay mineral, this difference does not contradict the above statement.

Summary

The interaction of sodium dodecylsulfate with different homoionic montmorillonites has been studied in order to understand the binding mechanism. The adsorption isotherms and the concentration of the metal ions in the bulk phase have been measured. Three types of interactions have been identified:

(i) On Fe-montmorillinite Fe^{3+} ions are not free but form amorphous iron-oxidehydroxide. These coatings are positively charged and may bind the DS^- anions directly.

ii) If the solubility product of a metal ion with dodecylsulfate is small enough, $Me(DS)_2$ precipitates. This is found for Ca- and Pb-montmorillonite. Probably the solubility products are smaller in the dispersion than in aqueous solution as the precipitation process is influenced by the surface of the montmorillonite. No intercalation into the interlayer space is observed, the interlayer distance is not increased. When the CMC is exceeded, the precipitates are solubilized in the micelles of the bulk solution. This coincides with a strong release of the metal ions from the surface and the amount of DS^- adsorbed is reduced since the montmorillonites are transformed into their sodium forms, which does not adsorb DS^-. The CMC can be calculated from the mobilization isotherm.

iii) If there are specific interactions of the metal ions with DS^-, ion pairs are bound by the surface as found at Ni- and Cu-montmorillonite. The s-shaped forms of the isotherms indicate a small degree of cooperativity below the CMC. Above the CMC no further binding takes places, rather the metal ions are released from the montmorillonites by association with the micelles. The CMC can also be calculated from the points "b" of the mobilization isotherms.

Mg- and Cd-montmorillonites do not adsorb DS^-, i.e., no ion pairs are formed on the surface. The interface excess is zero or even below zero due to the anion exclusion effect of the negatively charged montmorillonite. These investigations prove that an anion exchange at the montmorillonite edges is not responsible for the adsorption of DS^-, since in that case Mg- and Cd-montmorillonite should bind DS^-.

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