

THE RHEOLOGICAL AND COLLOIDAL PROPERTIES OF BENTONITE DISPERSIONS IN THE PRESENCE OF ORGANIC COMPOUNDS

V. BENTONITE AND SODIUM MONTMORILLONITE AND SURFACTANTS

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Abstract—The influence of surfactants on the flow behavior of sodium montmorillonite dispersions (2% w/w) was studied for a cationic (cetylpyridinium chloride, CPCI) and an anionic surfactant (sodium dodecylsulfate, SDS). When the dispersion pHs were >3.5 and <7 , CPCI concentrations $>10^{-4}$ M increased the shear stress but the Bingham yield value remained virtually unchanged ($\tau_0 \approx 100$ mPa). At $\text{pH} \approx 7$, the shear stress and yield point decreased with increasing CPCI concentration (τ_0 from 430 to 100 mPa). The flow properties of sodium calcium bentonite dispersions were independent of pH and CPCI concentrations $\leq 10^{-4}$ M; they increased modestly at higher concentrations. At $\text{pH} < 4$, SDS addition to the sodium montmorillonite dispersions increased the shear stress and yield value to a maximum value ($\tau_0 = 2100$ mPa) at 10^{-3} M SDS; higher SDS concentrations reduced the shear stress and yield value. At $\text{pH} > 4$, the flow values decreased to a minimum value at 10^{-2} M SDS (τ_0 from 430 to 50 mPa). The flow of the sodium calcium bentonite dispersions at $\text{pH} > 4$ was independent of SDS concentrations $\leq 10^{-3}$ mole/liter; at higher SDS concentrations, the flow values increased more strongly in sodium calcium bentonite than in sodium montmorillonite dispersions.

Surfactants influence the flow behavior of sodium montmorillonite dispersions by their action on the card-house networks in strongly acidic medium and, at higher pH, by the electroviscous effect. At the highest surfactant concentrations without flocculation, the shear stress and yield value are increased by interacting chains of opposed particles.

Addition of the surfactants increases the salt (NaCl) stability of the dispersions because the adsorbed surface active agents influence the counterion distribution between the Stern and the diffuse ionic layer.

Key Words—Bentonite, Cetylpyridinium chloride, Coagulation, Flow behavior, Montmorillonite, Sodium dodecylsulfate (SDS), Surfactants.

INTRODUCTION

Cationic and anionic surfactants greatly influence the flow behavior of kaolinite dispersions. The dependence on the pH value of the dispersion medium reveals different modes of surfactant-kaolinite interactions (Welzen *et al* 1981, Lagaly 1987). At $\text{pH} = 3.3$ and very low concentrations of cetyl trimethylammonium bromide (CTBr), the card-house formation with edge (+)/face(−) contacts (Hofmann and Hausdorf 1945, Fahn *et al* 1953, Hofmann *et al* 1957, van Olphen 1956, 1964, 1977) produces a high Bingham yield stress. At CTBr concentrations $> 10^{-6}$ M, the surfactant cations are bound by negative face charges and decrease the yield point to a minimum. At higher CTBr concentrations, a large part of the counterions on the faces are replaced by the CT^+ cations. The alkyl chains of the surfactants on two opposed faces interact and increase the yield value. At surfactant concentrations between 10^{-4} and 10^{-3} M all sodium counterions are replaced by surfactant cations, and additional ion pairs (cetyl trimethylammonium + bromide ions) are adsorbed. This recharges the particles and eliminates the Bingham yield stress.

When the pH of the dispersion is highly alkaline ($\text{pH} = 10$), a yield value is not observed at CTBr concen-

trations $<10^{-5}$ M and $>10^{-2}$ M. The maximum between 10^{-5} M and 10^{-4} M is again caused by interacting alkyl chains of the surfactant covered particles. Changes in the flow behavior of sodium kaolinite dispersions by an anionic surfactant (sodium dodecylsulfate, SDS) are noticed at $\text{pH} = 3.3$. The high Bingham value caused by the card-house structure remains constant up to SDS concentrations of about 10^{-3} M, then decreases sharply to zero. The surfactant anions attached on the positive edges destroy the edge(+)/face(−) contacts of the card-house. SDS is not adsorbed at a dispersion pH of 10, and no yield value is observed up to 10^{-1} M SDS.

The influence of surfactants on sodium montmorillonite dispersions should be more complex than on kaolinite. First of all, delamination of sodium montmorillonite produces very thin particles and the degree of delamination is highly dependent on the experimental conditions. As the number of particles is a decisive factor, the flow behavior can change dramatically by modest changes in experimental conditions such as pretreatment reactions, degree of dispersion, and pH. The secondary electroviscous effect becomes very important in dispersions of large, but very thin particles. It is caused by the extended diffuse ionic layers around the particles which restrict the translational and rota-

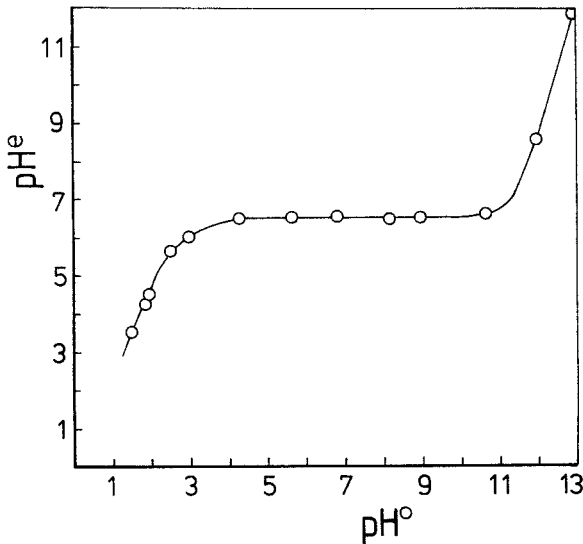


Figure 1. Buffering action of sodium montmorillonite dispersions (4% w/w). pH° and pH^e are the values of the aqueous solution (adjusted with 0.1 M HCl or 0.1 M NaOH) before and after montmorillonite addition. pH^e was measured 5 days after clay addition.

tional motion of the particles and, therefore, increase viscosity and yield value. Salt addition decreases the double layer thickness, thereby increases the mobility of the particles and reduces the flow values (cf. Figure 4 in Permien and Lagaly 1994a) (Norrish 1954, Callaghan and Ottewill 1974, Rand *et al.* 1980, Permien and Lagaly 1994a).

Another consequence of the extreme aspect ratio of the delaminated particles is the preferential face-to-face aggregation and formation of band-type networks (Weiss and Frank 1961, Weiss 1962, Fitzsimmons *et al.* 1970, O'Brien 1971, Fukushima 1984, Keren *et al.* 1988, Keren 1989, Quirk 1986, Quirk and Murray 1991, Ramsay and Lindner 1993, Permien and Lagaly 1994a, 1994b). Card-house structures are less important in montmorillonite than in kaolinite dispersions because the positive charging of the montmorillonite edges only occurs in strongly acidic milieu (Permien and Lagaly 1994c, 1994d).

A montmorillonite dispersion shows a pronounced buffering action at $\text{pH} \approx 6.5$ (Figure 1). Considerable quantities of acid or base must be added to reach a pH far from 6.5. The reaction proceeds slowly; the dispersion pH changes within hours or days which results in changes in the flow behavior. In acidic milieu, the clay mineral particles are attacked by the acid. The release of octahedral cations from the structure influences the flow behavior (Permien and Lagaly 1994d). Therefore, the flow properties often show considerable differences from experiment to experiment and are highly dependent on the way the pH is adjusted.

The paper attempts to clarify the influence of a cat-

ionic (cetylpyridinium chloride, CPCl) and an anionic surfactant (sodium dodecylsulfate, SDS) on the flow behavior of homoionic sodium montmorillonite dispersions at dispersion pHs between 2 and 12. The study also comprises measurements with the original bentonite which was used to prepare the sodium montmorillonite. These measurements reveal the influence of the surfactants on the flow behavior of the dispersion in the presence of a certain amount of calcium ions.

EXPERIMENTAL

Two types of clays were used in the experiments:

(i) an original Wyoming bentonite "Greenbond" ("Na, Ca-bentonite" in the following). It contained 79% montmorillonite (determined by alkylammonium exchange; Lagaly 1994a). The main impurities were quartz, feldspars and mica. Most important is that the montmorillonite contained sodium and calcium ions on exchange positions. Chemical analysis indicated a molar ratio $\text{Na}^+/\text{Ca}^{2+} = 6.5$. The layer charge determined by alkylammonium exchange was 0.28 eq/(Si,Al)₄O₁₀. Corresponding to an interlayer exchange capacity of 0.78 meq/g (Lagaly 1994a).

(ii) The Na-montmorillonite was obtained from the bentonite by size fractionation (<2 μm fraction) after dithionite-citrate treatment and H₂O₂ oxidation (Permien and Lagaly 1994a).

Na, Ca-bentonite and Na-montmorillonite were dispersed in water so that the solid content was about 2.2% (w/w). The dispersions were shaken intensively for 12 h, then ultrasonicated (38 W, 3 min), and again shaken for 24 h. Aliquots of 1800 μl of these dispersions were mixed with 100 μl of surfactant solution and 100 μl hydrochloric acid or sodium hydroxide solution of different concentrations, so that the required pH (between $\text{pH} = 2$ and 12) and surfactant concentrations from 10^{-5} M to $5 \cdot 10^{-2}$ M were obtained.

The samples were again shaken and measured in the viscosimeter at 20°C about 24 h after preparation. The viscosimeter was a Low Shear rotational viscosimeter (Contraves LS 30, Zurich) which allowed measurements of the shear stress up to 1250 mPa and of the shear rate $\dot{\gamma}$ up to 120 s^{-1} . The flow behavior of the dispersions was mostly non-Newtonian (Güven 1992). It is characterized by the shear stress at $\dot{\gamma} = 94.5 \text{ s}^{-1}$, τ^* , and the Bingham yield point, τ_0 . The yield value is defined as the shear stress extrapolated from the linear or almost linear section of the flow curves at the highest shear rates ($\dot{\gamma} \rightarrow 120 \text{ s}^{-1}$) to $\dot{\gamma} = 0$ (Güven 1992).

As mentioned above, the pH of the dispersions changed with time when $\text{pH} \neq 6.5$. Therefore we recorded two pH values, e.g., $\text{pH} = 4 \rightarrow 5.5$. The first value, $\text{pH} = 4$, is the pH of the control solution containing the surfactant and acid or base but no clay. The second value, $\text{pH} = 5.5$, is the pH of the clay dispersion at the moment of rheological measurement. The pH-values of the dispersions (and also of the control so-

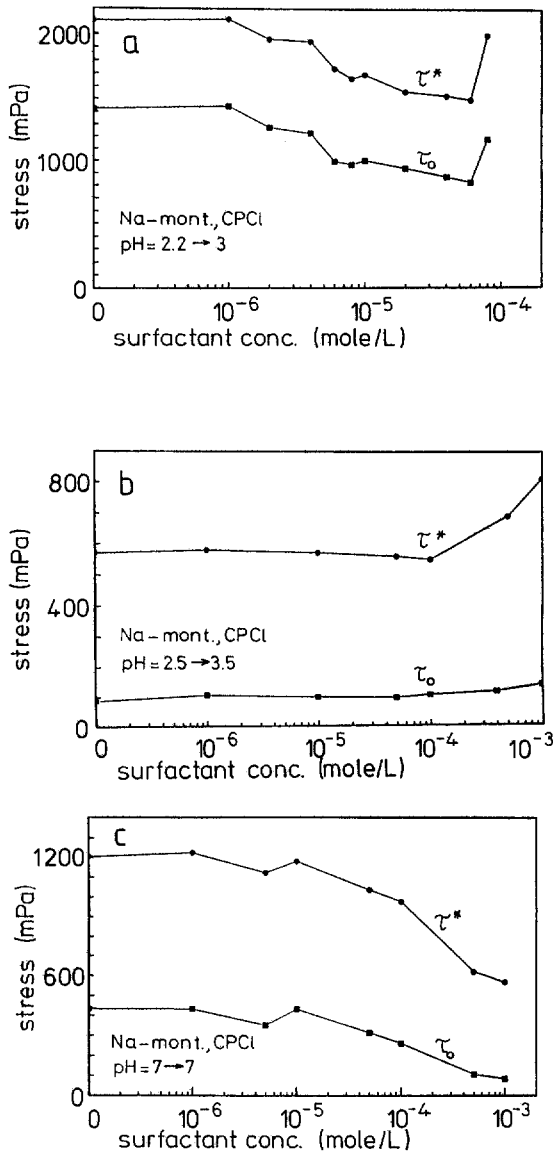


Figure 2. Shear stress τ^* and yield value τ_0 of the sodium montmorillonite dispersion (2% w/w) vs. the amount of cetylpyridinium chloride added. (a) pH = 2.2 → 3, (b) pH = 2.5 → 3.5, (c) pH = 7 → 7.

lutions) were measured with colorimetric test papers because glass-electrode methods do not give reliable pH values, even in visually clear supernatant liquids (Keller and Matlack 1990). The pH changes of the sodium calcium bentonite dispersions were greater than those of the sodium montmorillonite dispersions.

The salt stability of the sodium montmorillonite dispersions in the presence of the surfactants was measured by test tube experiments with sodium chloride at room temperature (Permien and Lagaly 1994c). The solid mass content of the dispersions was 0.025 percent (w/w), and the pH was 6.5.

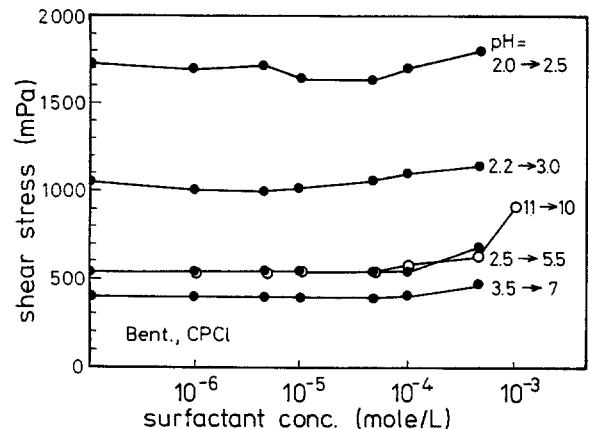


Figure 3. Shear stress τ^* of the sodium calcium bentonite dispersion (2% w/w) vs. amount of cetylpyridinium chloride added at different dispersion pH.

The optical density ($=\lg I_0/I$) of the dispersions was measured in cells with an optical path length of 0.1 cm at a wavelength of 400 nm (Shimadzu photometer, UV-120-02).

The cationic and anionic surfactants cetylpyridinium chloride (CPCI) (from Merck, Germany) and sodium dodecylsulfate (SDS) (from Fluka, Switzerland) were used.

RESULTS

The shear stress and yield value of the acidic sodium montmorillonite dispersion (pH = 2.2 → 3.0, Figure 2a) were high. Increasing concentrations of CPCI decreased τ^* and τ_0 . At concentrations $\geq 10^{-4}$ M ($\geq 10^{-3}$ M at the other pH values) the dispersion formed flocs and could not be measured. At slightly higher pH, the stresses remained constant up to 10^{-4} M CPCI (Figure 2b). The curves for the neutral dispersion (Figure 2c) were almost identical to those for sodium montmorillonite dispersed in sodium chloride solutions (Figure 6 in Permien and Lagaly 1994d, cf. Figure 4b).

In the presence of calcium ions (Na, Ca-bentonite) the shear stress and yield value remained constant up to CPCI concentrations of 10^{-4} M at all pH values (from 2.5–10), then increased slightly (Figure 3).

When the anionic surfactant SDS was added, and pH was between 4 and 10, the dependence of the stresses τ^* and τ_0 is similar to that in Figure 2c and also to the behavior of Na-montmorillonite dispersed in NaCl solution. The stress curves for pH = 7 → 6.5 are shown as an example (Figure 4b). The shear stress and yield value at the minimum are virtually independent on pH ($\tau^* \approx 350$ mPa, $\tau_0 \approx 50$ mPa).

Significantly different curves were observed with SDS in the more strongly acidic media (at pH = 3.0 → 3.5 and pH = 2.2 → 3.0) (Figure 4a). In spite of the high shear stress and yield value at pH = 2.2 → 3.0, SDS

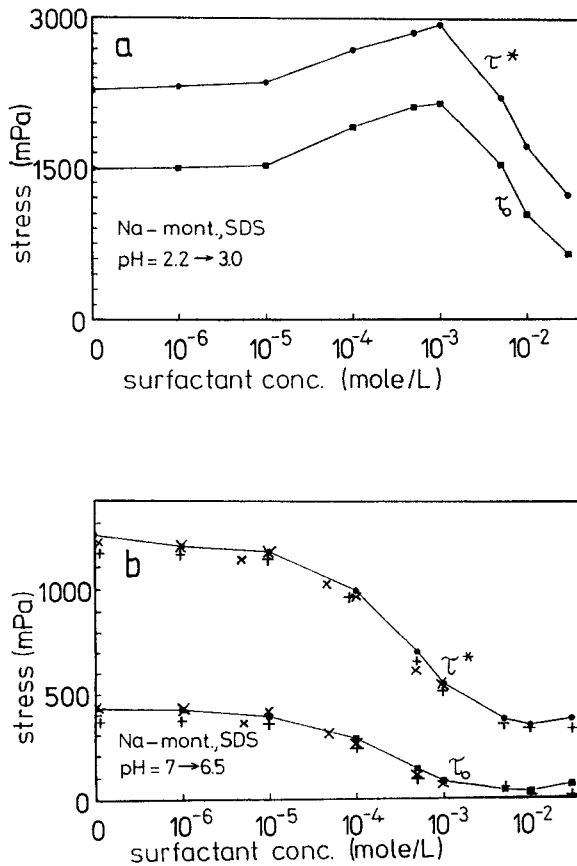


Figure 4. Shear stress τ^* and yield value τ_0 of the sodium montmorillonite dispersion (2% w/w) vs. the amount of sodium dodecylsulfate added. (a) pH = 2.2 → 3.0, (b) pH = 7 → 6.5 (for comparison: * τ^* and τ_0 for CPCI against CPCI concentration; + for NaCl against NaCl concentration).

addition increased these values further to a maximum at about 10^{-3} M SDS and reduced τ^* and τ_0 below the values of the surfactant free dispersion. At pH = 3.0 → 3.5, the maximum was sharper and was shifted to about $5 \cdot 10^{-3}$ M; τ^* and τ_0 at the highest SDS concentration ($5 \cdot 10^{-2}$ M) remained higher than in the surfactant free dispersion.

The shear stress, τ^* , and the yield point, τ_0 , in the acidic Na, Ca-bentonite dispersion (pH = 2.2 → 3.5, Figure 5a) were distinctly smaller than for Na-montmorillonite (Figure 4a). The maximum was only weakly outlined. At higher pH, the curves for the Na, Ca-bentonite dispersions were very different from those of the calcium free dispersions (Figure 5b and Figure 4b). The stresses were constant up to about $5 \cdot 10^{-4}$ M, then increased. Similar curves as in Figure 5b for pH = 3.5 → 7 were found for pH = 2.5 → 5 and pH = 11 → 9. The step at $5 \cdot 10^{-3}$ M SDS was observed in all cases.

As mentioned above, the montmorillonite is slowly

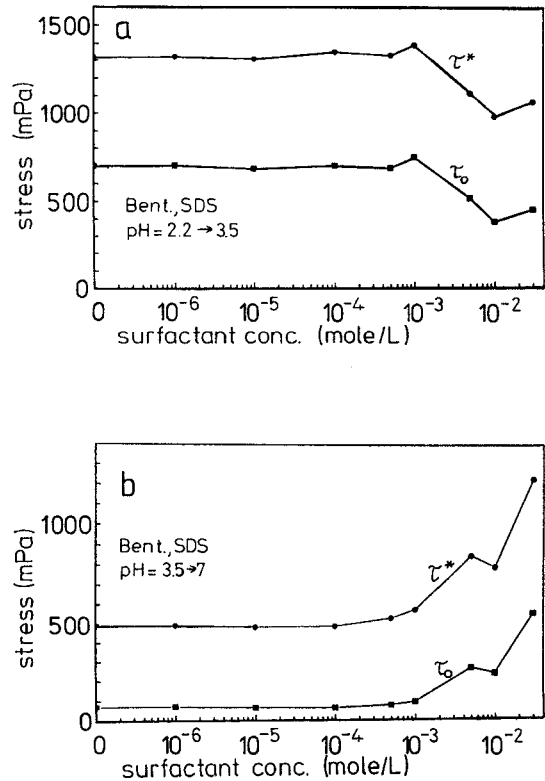


Figure 5. Shear stress τ^* and yield value τ_0 of the sodium calcium bentonite dispersion (2% w/w) vs. the amount of sodium dodecylsulfate added. (a) pH = 2.2 → 3.5, (b) pH = 3.5 → 7.0.

attacked in acidic medium. The removal of multivalent cations from the octahedral sheet had only a weak influence on the flow behavior of the dispersion (Permien and Lagaly 1994d). The changes were insignificant compared with the effect of surfactant addition. This was also seen when the measurements of the flow curves were repeated a few days later.

The optical density of the sodium montmorillonite dispersion was about 0.6. In most cases, it remained unchanged up to 10^{-3} M CPCI and $2 \cdot 10^{-2}$ M SDS, in spite of changes of the flow behavior. For instance, the increase of τ^* in Figure 2b was not seen in the optical density. Also, the maximum of the curves in Figure 4a or the decrease of τ^* and τ_0 to the minimum in Figure 4b were not accompanied by changes of the optical density up to $5 \cdot 10^{-2}$ M SDS.

The influence of pH on the flow behavior of the surfactant free dispersions can be derived from the curves in Figures 2–5 and supplementary diagrams (not shown). In a strongly acidic medium, the shear stress τ^* and the yield value τ_0 of the Na-montmorillonite dispersions were high but decreased dramatically with increasing pH (Figure 6). At higher pH, τ^* and τ_0 increased again. The occurrence of a minimum in the

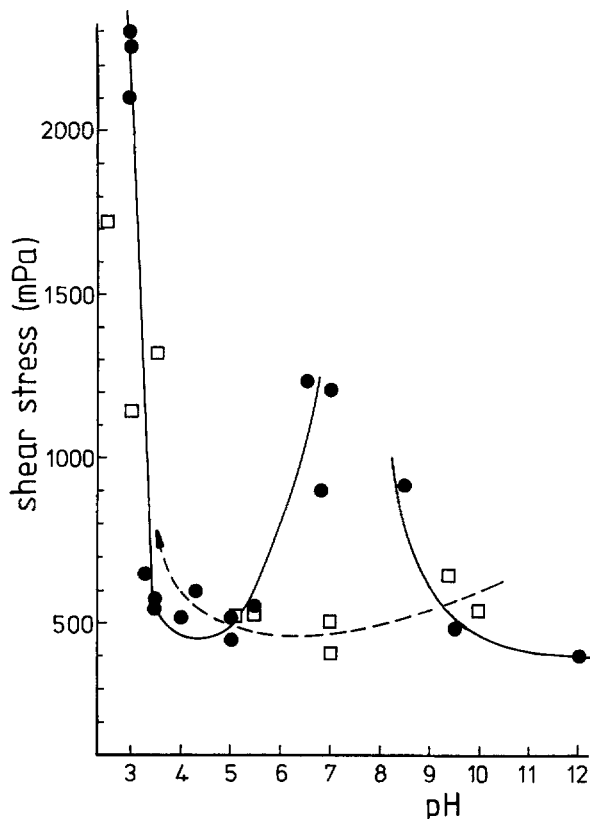


Figure 6. Dependence of the shear stress τ^* on the dispersion pH for the sodium montmorillonite dispersion (\bullet , —) and the sodium calcium bentonite dispersion (\square , ---). Plotted are the pH values of the dispersion medium just before the rheological measurements.

flow parameters of clay dispersions is well-known (Rand *et al* 1980, Brandenburg and Lagaly 1988, Permien and Lagaly 1994d). The shear stress and yield value decreased again at higher pH. The minimum values were around 300–400 mPa. In the presence of calcium ions (Na, Ca-bentonite dispersions) τ^* and τ_0 also decreased sharply in acidic milieu and showed a very shallow minimum at $\text{pH} \approx 6$.

An unexpected result was the influence of the surfactants on the critical coagulation concentration, c_K , with sodium chloride (Table 1). CPCI addition to the Na-montmorillonite dispersion enhanced c_K from 8 to 16 mmole/liter. The anionic surfactant increased the critical coagulation concentration to 135 mmole/liter at 10^{-1} M SDS.

DISCUSSION

Cetylpyridinium chloride

In strongly acidic media, CP^+ ions decreased the shear stress τ^* and yield value τ_0 (Figure 2a) but the minimum stress values were still high. The cetylpyridinium ions on the faces of the clay mineral particles

Table 1. Critical sodium chloride concentration for the coagulation of a sodium montmorillonite dispersion (0.025% w/w) in the presence of cetylpyridinium chloride (CPCI) and sodium dodecylsulfate (SDS) at $\text{pH} = 6.5$ and room temperature.

Surfactant conc. (M)	c_K (mmole/L)	
	CPCI	SDS
0	8	
5×10^{-7}	9.5	
10^{-6}	9	10
10^{-5}	7	10
2×10^{-5}	11	
10^{-4}	13	10
2×10^{-4}	16	
10^{-3}	1)	12
10^{-2}	1)	81
10^{-1}	1)	136

¹ Coagulation by CPCI itself.

make it difficult to form the edge(+)/face(-) contacts of the card-house structure. When a mechanical force acts on the card-house, a certain number of edge-to-face contacts are broken. However, the particles can easily shift into neighboring contact positions (Hofmann 1962). This latching mechanism is disturbed when organic cations are adsorbed on the faces. The large cations restrain gliding of an edge along the face into a neighboring site where the edge can again engage into a new contact position.

At $\text{pH} = 2.5 \rightarrow 3.5$ (Figure 2b) the card-house network breaks apart. The electroviscous effect is suppressed by the acid added to adjust the pH and cause τ^* and τ_0 to acquire their minimum values (Figure 6). Therefore, CPCI addition (up to 10^{-4} M) did not further decrease τ^* and τ_0 . The increase of the yield value at $>10^{-4}$ M CPCI is probably caused by interacting alkyl chains of approaching particles. As in many other cases, the beginning of aggregation was not recognized in the optical density up to 10^{-3} M CPCI.

At $\text{pH} \approx 7$, the flow values changed with the CPCI concentration (Figure 2c) in the same way as for sodium montmorillonite dispersed in NaCl solutions (Figure 4b). Thus, the behavior is governed by the electroviscous effect. At CPCI concentrations $>10^{-3}$ M the particles settled as flocs because the exchange of the counterions by CP^+ cations made the particles less hydrophilic.

Sodium dodecylsulfate

Dodecylsulfate anions were not adsorbed by the clay mineral particles from very dilute solutions and did not influence the flow behavior of the acidic dispersions at concentrations $\leq 10^{-5}$ M (Figure 4a). Because of card-house structure formation, τ^* and τ_0 values were high. Somewhat unexpected was the increase of τ^* and τ_0 at higher SDS concentrations. The addition of an electrolyte, in this case SDS, increases the edge(+)/

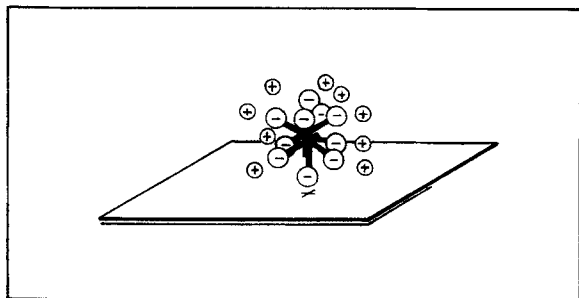


Figure 7. Small surface aggregates (Rupprecht and Gu 1991): one surfactant anion is anchored at a surface site and other surfactant anions together with their gegen ions are clustered around it.

face(-) attraction between the particles (heterocoagulation, see, for instance, Hogg *et al* 1966) and reduces the electrostatic repulsion between the faces at larger distances. Both effects increase the mechanical stability of the network.

At SDS concentrations $> 10^{-3}$ M, the surfactant anions break up the edge(+)/face(-) contacts, and τ^* and τ_0 decrease. The constancy of the optical density again indicated that discrete particles were not formed up to $5 \cdot 10^{-2}$ M SDS.

The type of flow curves changed when pH was increased from 3.0 \rightarrow 3.5 to 4 \rightarrow 5.5. The curves for SDS, CPCI and NaCl at pH \approx 7 are virtually identical (Figure 4b) and reveal the influence of the electroviscous effect. As the degree of dispersion, i.e., the number of particles did not distinctly change, the optical density remained constant over the whole concentration range.

One can conclude from the drastic changes in the flow curves at pH $>$ 3.5 that above this pH value positive edge charges are no longer important for the flow behavior of montmorillonite dispersions.

Effect of calcium ions

The shear stress and yield point of the surfactant free dispersions of Na-montmorillonite decreases sharply in acidic milieu (Figure 6) when the card-house network is disintegrated. The increase in shear stress at pH $>$ 5 results from the higher degree of delamination and, therefore, the higher number of particles in the dispersion. Raising the pH above 7 requires increased amounts of NaOH which reduce the degree of delamination and the electroviscous effect, and τ^* and τ_0 decrease again.

The shear stress τ^* and yield value τ_0 of strongly acidic dispersions of Na, Ca-bentonite were distinctly lower than of the Na-montmorillonite dispersions (Figure 2a, 3 and 6). Calcium ions induce face/face aggregations within the card-house network which enlarge the aperture size, and τ^* and τ_0 are reduced. The "stair-step card-house" shown in Figure 8 of O'Brien (1971)

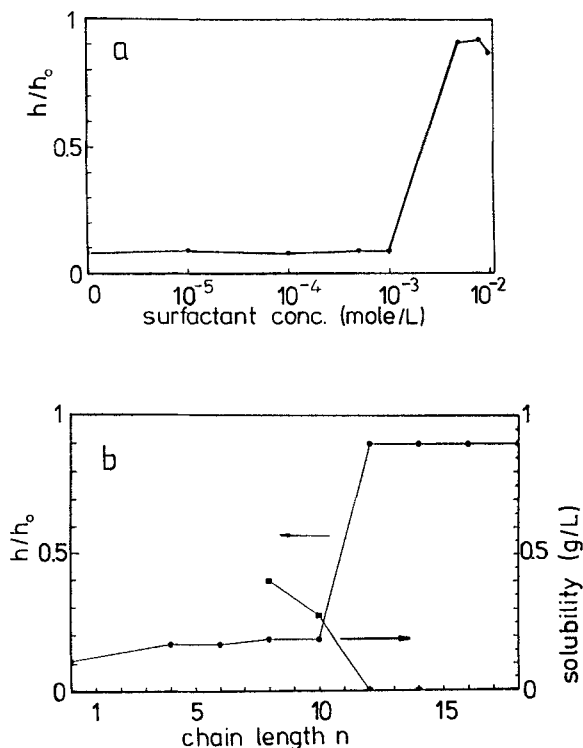


Figure 8. Sedimentation of sodium calcium bentonite dispersions (1% w/w). h/h_0 is the ratio of the sediment height to the total height of the dispersion. (a) h/h_0 (after 60 days) vs. the concentration of dodecylsulfate; pH \approx 6.5, (b) h/h_0 (after 60 days) vs. the number of carbon atoms in the alkyl chain of sodium alkylsulfates; surfactant concentration $5 \cdot 10^{-2}$ M, pH \approx 6.5. The solubility of the calcium alkylsulfates in water at 25°C (Stache 1981, p. 143) is also shown.

very well represents a card-house structure containing band-type aggregations of clay mineral platelets. The thickening effect of calcium ions, which is very important for practical uses, occurs when the amount of salts (NaCl, CaCl_2 , Na_2CO_3 , etc.) in the dispersion is $> 10^{-3}$ M (Permien and Lagaly 1994b).

The flow behavior of Na, Ca-bentonite dispersions remained unchanged at concentrations $< 10^{-3}$ M CPCI (Figure 3). The calcium ions reduce τ^* and τ_0 values of the acidic dispersion (Figures 2a, 3 and 6). Very likely, low concentrations of the surfactant cations do not disturb the band-type fragments created by the calcium ions and, therefore, do not decrease the flow values. At higher pH, the attenuation of the electroviscous effect by the calcium ions is so strong that the contribution of the surfactant cations is also insignificant. The increased value of τ^* near 10^{-3} M CPCI reveals the stiffening effect of the calcium ions at salt concentrations $> 10^{-3}$ M. This could not be measured in detail because the hydrophobic cetylpyridinium montmorillonite particles began to settle in flocs.

SDS decreases the stability of the network structure

of the Na, Ca-bentonite only at concentrations $>10^{-3}$ M and at low pH (pH < 4) (Figure 5a). At higher pH, the effect of calcium ions is predominant. The values of τ^* and τ_0 remain constant up to 10^{-3} M SDS (Figure 5b). The step at about 10^{-2} M SDS is probably related to the precipitation of calcium dodecylsulfate.

The partial replacement of calcium ions by sodium ions on the clay mineral particles and the precipitation of calcium dodecylsulfate enhances the degree of delamination. The increase of τ^* and τ_0 at $>10^{-3}$ M SDS (Figure 5b) corresponds to a steep increase in the sediment volume (Figure 8a). Precipitation of the calcium salt of the surfactant is required for this volume increase. The sediment volume remained small (Figure 8b) in the presence of the more soluble, short chain calcium alkylsulfates.

Precipitated calcium dodecylsulfate was identified by its X-ray powder diffraction pattern. This salt has a layer structure with a basal spacing of 30 Å which has sometimes been misinterpreted as calcium montmorillonite intercalated with SDS.

Salt stability

One expects that the addition of a cationic surfactant will reduce the Stern potential and decrease the critical coagulation concentration of sodium chloride in Na-montmorillonite dispersions. However, the c_K value was increased (Table 1). Cetylpyridinium ions near the surface may change the distribution of the sodium counterions between the Stern layer and the diffuse ionic layer. The long hydrophobic alkyl chains at the surface would influence the structure of the dispersion medium near the surface. Sodium ions would be displaced from the surface and the Stern potential would increase to a higher negative value. Because the Stern potential at the coagulation point is low (Miller and Low 1990, Chan *et al* 1984, Permien and Lagaly 1994c), even modest changes of the absolute value of the potential would have a significant effect on the stability (Figure 13 in Lagaly 1986). Increased salt stability was also observed in the presence of several neutral organic compounds, for instance, Triton X 100 (t-octylphenyl polyethylene oxide).

The stabilizing effect of the anionic surfactant was stronger than that of cetylpyridinium chloride (Table 1). Adsorption of anionic surfactants on sodium clay minerals was detectable in an acidic milieu in which the edges of the particles are positively charged. Nevertheless, a few anions were also adsorbed at higher pH by interaction with sporadically occurring positively charged edge sites or by complex formation between the head group and octahedral cations on the edges. The adsorption of modest amounts of anionic surfactants is difficult to measure by the concentration changes in solution because of the pronounced volume exclusion effect for anions (cf. Permien and Lagaly 1994d and references there, see also Chou Chang and

Sposito 1994). Binding of dodecylsulfate on sodium montmorillonite could be recognized by a LAMMA technique (=laser microprobe material analyser).

Isolated surfactant anions sporadically anchored on the particle edges act as nuclei for the clustering of additional surfactant anions (Rupprecht and Gu 1991, see also Lagaly 1994b) (Figure 7). Formation of these small surface aggregates increases the negative charge density at the edges. This is less important for the flow behavior but has a significant influence on the stability of diluted colloidal dispersions. Coagulation of Na-montmorillonite dispersions at pH ≈ 6.5 occurs between negative edges and faces. Anionic surfactants bound in the form of small surface aggregates (Figure 7) on the edges can increase the Stern potential, and thereby enhance the salt stability. The Stern potential at the coagulation point is on the order of 20–30 mV (cf. Permien and Lagaly 1994c).

CONCLUSION

Cationic and anionic surfactants influence the flow behavior of sodium montmorillonite dispersions by several mechanisms. In strongly acidic media (pH < 4) the surfactants affect the stability of the card-house structure. The cationic surfactant promotes disintegration of the card-houses. This also occurs at higher concentrations of the anionic surfactant ($>10^{-3}$ M), whereas lower SDS concentrations stiffen the network. At pH > 4 , the surfactants act as 1:1 electrolytes which reduce the shear stress and yield value by the electroviscous effect. At high surfactant concentrations, the alkyl chains of opposed particles interact and flocs are formed. Still higher concentrations cause repeptization by recharging the particles.

In the presence of calcium ions, band-type structures predominate and weaken the influence of surfactant ions on the flow behavior.

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