

INFLUENCE OF ORGANIC AND INORGANIC SALTS ON THE COAGULATION OF MONTMORILLONITE DISPERSIONS

D. PENNER AND G. LAGALY

University of Kiel, Institute of Inorganic Chemistry, D-24098 Kiel, Germany

Abstract—The colloidal state (stable, coagulated, or gel-like) and the rheological properties of Na-rich montmorillonite (Wyoming) dispersions are strongly influenced by organic cations. This effect is shown for homologous organic cations: alkyl trimethylammonium ions, paraquat, diquat, alkyl bispyridinium ions, and the triphenylmethane dyes crystal violet, methyl green, and tris (tri-methylammonium phenyl) methane chloride. The critical coagulation concentrations, c_K , are small (often <1 mmol/L) because the cations are enriched in the Stern layer and influence the solvent structure near the surface. The strong adsorption of the counterions at the clay-mineral surface causes c_K values to increase with the solid content. Charge reversal (recharging) of the particles was observed with the longer chain alkyl trimethylammonium ions, dodecyl bispyridinium ions, and crystal violet. Other cations reduced the electrophoretic mobility to zero but positive particle charges were not observed.

The plastic viscosity increased sharply at the critical coagulation concentration and showed a minimum slightly below c_K , which was caused by the electroviscous effect. Yield values were developed at concentrations above c_K . In most cases, yield values reached a plateau where the amount of organic cations was ~ 0.5 mmol/g, *i.e.*, about half of the cation-exchange capacity. The c_K values decreased with increasing hydrophobicity of homologous compounds, but the yield value showed maxima at intermediate chain lengths. The yield value of several 0.5% dispersions was high, *e.g.*, dodecyl trimethylammonium ions, 71 Pa; paraquat, 100 Pa; diquat, 42 Pa; hexyl bispyridinium ions, 53 Pa (*vs.* Ca^{2+} , 0.2 Pa; Al^{3+} , 0.7 Pa). The storage modulus as a function of the number of organic cations changed in a similar way as the yield value, and high values were observed (*e.g.*, dodecyl trimethylammonium ions, hexyl bispyridinium ions: 1000 Pa, paraquat: >4000 Pa). Thus, dispersions with high viscosity, yield value, and pronounced viscoelasticity are obtained by coagulating Na-rich montmorillonite dispersions with organic cations.

Key Words—Alkyl Bispyridinium Ions, Alkyl Trimethylammonium Ions, Critical Coagulation Concentration, Colloids, Crystal Violet, Diquat, Flocculation, Methyl Green, Montmorillonite, Paraquat, Rheology, Viscoelasticity.

INTRODUCTION

Organic cations are strongly adsorbed by clay minerals and are very effective destabilizing agents for clay-mineral dispersions, even at very low concentrations. The structure of the aggregates differs from those formed by addition of inorganic salts, and these differences may be observed with the naked eye. Usually, addition of inorganic salts to a clay dispersion yields either more or less dense sediments or gel-like structures (Abend and Lagaly, 2000), whereas flocs and clusters of flocs are observed with organic salts. The lowest salt concentration which causes destabilization is called the critical coagulation concentration, c_K . This concentration can be determined by visual inspection of very dilute clay-mineral dispersions ($<0.1\%$ w/w solid content) after addition of increasing amounts of salt.

The interaction of clay minerals with paraquat (Rau-pach *et al.*, 1979) and diquat was studied in detail because the adsorption was considered to be dependent on the charge-pattern interactions (Lagaly, 1986a), *i.e.*, the fit or misfit of the charge distances in the adsorptive and the silicate layer (Weed and Weber, 1969; Philen *et al.*, 1970, 1971; Haque *et al.*, 1970). Recently, adsorption of paraquat, which is an impor-

tant herbicide, was studied by Rytwo *et al.* (1996a, 1996b).

The adsorption of triphenylmethane dyes (crystal violet, methyl green) on montmorillonite was studied extensively by Margulies and Rozen (1986), Yariv *et al.* (1989), Rytwo *et al.* (1993, 1995, 1996a), and Schramm *et al.* (1997). Cationic surface-active agents like alkylammonium ions and alkyl trimethylammonium ions interact strongly with clay minerals (Lyk-lema, 1994; Xu and Boyd, 1995; Ijodo and Pinnavaia, 1998). The interaction of primary n-alkylammonium ions with 2:1 clay minerals provides a simple and effective method for layer charge determination (Lagaly, 1994). The influence of organic compounds on the flow behavior of clay minerals is important in many practical applications (Lagaly, 1993a). The organic compounds can change the transport of clay minerals in soils and affect the soil mechanics (Wienberg, 1990; Hasenpatt *et al.*, 1989; Schmidt and Lagaly, 1999).

We report the destabilization of colloid dispersions of Na-rich montmorillonites by different types of organic salts: alkyl trimethylammonium chlorides, triphenylmethane dyes, paraquat, and diquat (Figure 1). These salts also showed a strong influence on the flow behavior and rheological properties of the dispersions.

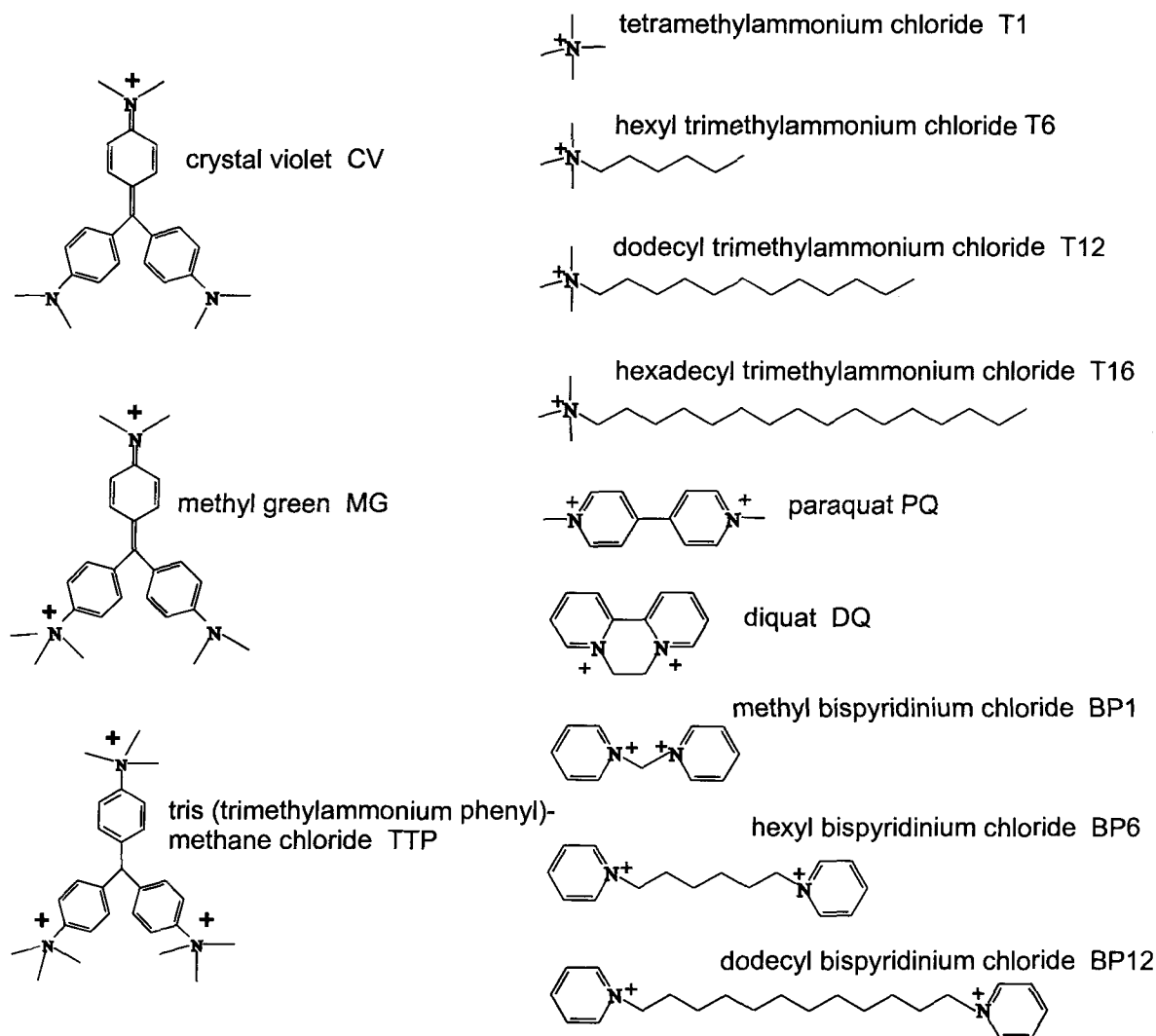


Figure 1. Organic salts which strongly influence the colloidal properties of Na-rich montmorillonite dispersions.

EXPERIMENTAL

Sodium-rich montmorillonite was separated from a Wyoming bentonite ("Greenbond", M40A, obtained from Süd-Chemie, Germany) with the following treatments: dithionite-citrate reduction and oxidation with H_2O_2 . Following these treatments, the bentonite was sodium saturated, size fractionated ($<2\text{-}\mu\text{m}$ fraction), dialyzed, and freeze-dried (Stul and van Leemput, 1982; Tributh and Lagaly, 1986; Permien and Lagaly, 1994a). The mean-layer charge was 0.28 eq/mol (Si, Al) $_4\text{O}_{10}$ (alkylammonium method); the exchange capacity was 0.95 meq/g (by NH_4^+ exchange) (Schmidt and Lagaly, 1999).

Alkyl trimethylammonium chlorides (T1, T6, T12, T16) were obtained from Fluka (Switzerland, "puri-m" quality). Methyl bispyridinium chloride (BP1) was prepared according to Brüdgam and Hartl (1986),

and hexyl and dodecyl bispyridinium chloride (BP6, BP12) by the method of Knight and Shaw (1938). All compounds were transformed into chlorides with an ion-exchange resin (Dowex 1 \times 4, Fluka, Switzerland). Paraquat (PQ), diquat ("Pestanal" quality, DQ), crystal violet (CV), and methyl green (for microscopy, MG) were obtained from Riedel-de-Haen (Germany). Tris (trimethylammonium phenyl) methane chloride (TTP) was synthesized as described by Schneider *et al.* (1992). Sodium, calcium, and aluminum chloride were studied as inorganic reference salts.

A stock dispersion was prepared by mixing an appropriate amount of freeze-dried Na-rich montmorillonite with water, followed by ultrasound treatment (80 W, 40 kHz), shaking for 72 h, and then by additional ultrasound treatment. Aliquots of this solution were mixed with aliquots of electrolyte solutions so that the

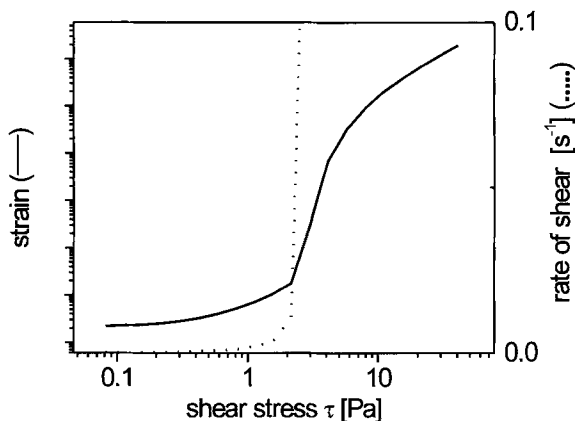


Figure 2. Measurement of the yield value in shear stress-controlled experiments. The yield value, τ_0 , is given by the intersection point.

solid content of the dispersions was 0.5% w/w in the rheological experiments. Electrophoretic mobility measurements were performed with 0.05% w/w dispersions. The dispersions were shaken for 24 h after mixing and then allowed to rest for a further 24 h. Before performing the rheological measurements, the samples were shaken gently for several seconds. The pH of the dispersions was ~ 6.5 .

The flow behavior (rheology) of the Na-rich montmorillonite dispersions containing Na^+ , Ca^{2+} , Al^{3+} , or organic cations was characterized by the plastic viscosity, η , the yield value, τ_0 , the storage modulus, G' , and the loss modulus, G'' . The plate-plate geometry (Physica UDS 200, plate diameter 50 mm, gap 0.5 mm, temperature 15°C) was used because it was more convenient for the investigation of flocculated systems than the cone-plate or Mooney-Ewart arrangement.

Viscosity was determined by recording the shear stress, τ , at shear rates, $\dot{\gamma}$, linearly increasing from 0 to 2000 s^{-1} . The plastic viscosity (Güven, 1992) was derived from the linear section of the flow curves at high shear rates. Yield values were obtained by continuously increasing τ and measuring the resulting deformation, γ , and $\dot{\gamma}$. The intersection of the curves $\gamma = f(\tau)$ and $\dot{\gamma} = f(\tau)$ represented the yield value (Figure 2).

The storage modulus G' was measured by oscillatory shear. Correct values of G' are only obtained at linear viscoelastic behavior and loss angles of $<45^\circ$ (Hochstein and Gleissle, 1995). This condition was checked in stress-controlled experiments by increasing the momentum from 2 to 20 μNm (0.1 to 0.8 Pa) at a frequency of 1 Hz. At momenta of $<10 \mu\text{Nm}$, the modulus remained constant with increasing oscillation frequency (0.5–5 Hz). The reported values of the moduli were measured at a momentum of 3 μNm at 1 Hz.

The critical coagulation concentration, c_K , of the inorganic and organic salts was determined by visual

Table 1. Critical coagulation concentration of 0.025% and 0.5% Na-rich montmorillonite (Wyoming) dispersions. (a) by visual inspection, (b) from viscosity measurements.

Counterion (see Figure 1)	Charge	c_K (mmol/L)		
		0.025% a	0.5% a	0.5% b
Na ⁺	1	5	15–30	18
Ca ²⁺	2	0.4	2–6	2.8
Al ³⁺	3	0.08	1.5	0.65
T1	1	5	12	5.8
T6	1	0.3	2	2
T12	1	0.15	0.8	0.76
T16	1	0.09	0.2	0.35
PQ	2	0.08	0.4	0.40
DQ	2	0.1	0.5	0.45
BP1	2	0.2	1	0.85
BP6	2	0.2	0.6	0.62
BP12	2	0.1	0.1	0.18
CV	1	0.1	1	0.9
MG	2	0.2	1.5	1
TTP	3	0.05	0.1	0.09

inspection of the behavior of 0.025% Na-rich montmorillonite dispersions (Permien and Lagaly, 1994b, Lagaly *et al.*, 1997). With more highly concentrated dispersions, $\leq 0.5\%$ w/w, a clear distinction between the stable and the coagulated sol was often difficult, in particular when inorganic salts were used.

The electrophoretic mobility of the montmorillonite particles in the presence of inorganic and organic salts was measured by microelectrophoresis (PenKem 501). The error in measurement increased to about $\pm 3.5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when the particles began to aggregate near the zero point of charge. Owing to the deep color of the 0.5% montmorillonite-dye dispersions, the electrophoretic mobility could not be measured with this optical detection method. Schramm *et al.* (1997) reported the electrophoretic mobility of 0.07% dispersions of homoionic montmorillonites in the presence of crystal violet.

RESULTS

Critical coagulation concentration

The c_K value of 0.025% w/w Na-rich montmorillonite dispersions decreased from 5 mmol/L for NaCl to 0.4 mmol/L for CaCl_2 and 0.08 mmol/L for AlCl_3 (Table 1). Na-rich montmorillonite dispersions typically have c_K values of 5–10 mmol/L NaCl (Lagaly, 1993b; Permien and Lagaly, 1994b). A similar value was observed for tetramethylammonium counterions. The c_K values of the dispersions with organic cations were distinctly smaller.

The c_K value is usually measured at very low solid contents (Lagaly *et al.*, 1997, Chap. 11), because it often changes with the solid concentration. Visual evaluation of the critical salt concentration of 0.5% w/w dispersions was not clear in each case, in particular with the inorganic ions, although the increase with sol-

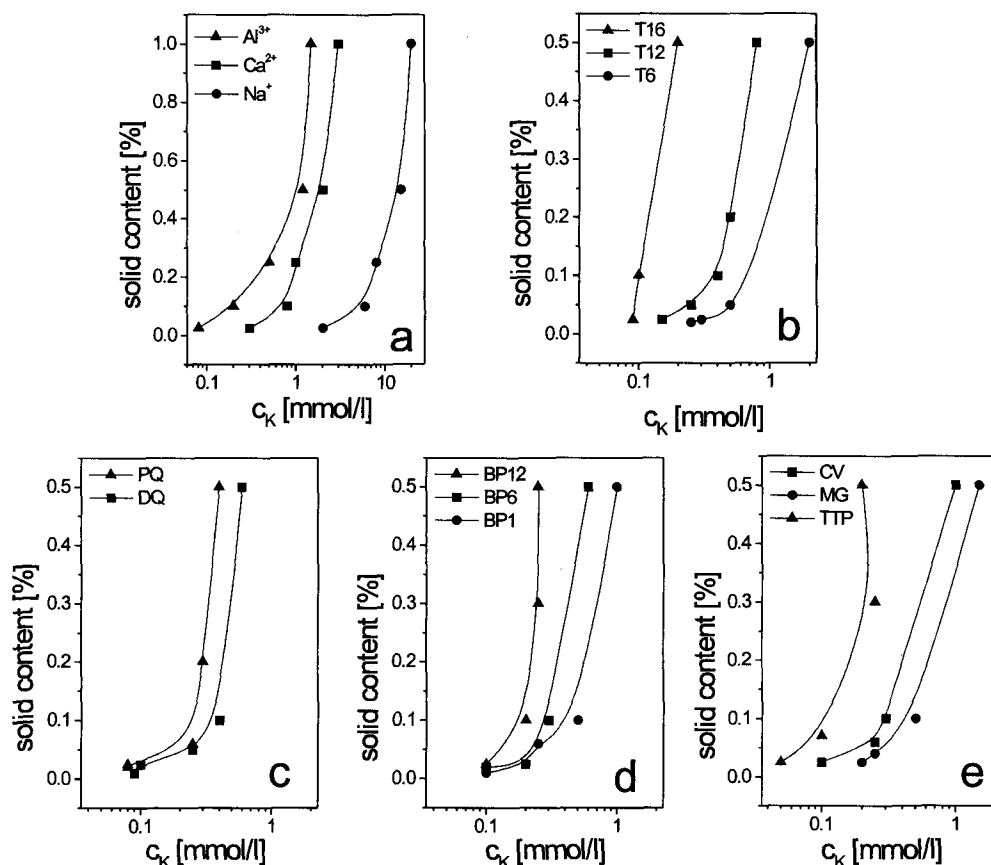


Figure 3. Variation of c_K of Na-rich montmorillonite dispersions (visual inspection) with the solid content: a) with sodium, calcium, and aluminum as counterions; b) with alkyl trimethylammonium ions T6, T12, T16; c) with PQ and DQ; d) with alkyl bispyridinium cations BP1, BP6, BP12; and e) with CV, MG, and TTP.

id content was evident (Table 1). Reliable c_K values were obtained from the steep increase of the viscosity at a certain salt concentration. The salt concentration where the viscosity of the 0.5% dispersion exceeded 1.6 mPas was taken as the critical coagulation concentration. The salt-free dispersion of 0.5% w/w Na-rich montmorillonite had a viscosity of 1.51 ± 0.03 mPas.

The c_K value decreased with increasing chain length of the alkyl trimethylammonium and alkyl bispyridinium ions. This behavior is typical of surface-active counterions (Lagaly *et al.*, 1997, Chap. 3). The different distance between the charges in paraquat and diquat did not affect c_K . This corresponded to the influence of alkyl bispyridinium cations. Increasing chain length from methyl to hexyl reduced the critical concentration (0.5% dispersion) slightly from 0.85 mmol/L to 0.62 mmol/L. The effect of an increasing charge separation became stronger with longer alkyl chains: c_K of the dodecyl derivative was 0.18 mmol/L. The ionic charge increasing from crystal violet to methyl green did not influence c_K , but the trivalent cation TTP reduced this value strongly and, among all systems, showed the lowest critical coagulation concentration.

The variation of c_K with solid content is illustrated in Figure 3. In the presence of sodium, calcium, and aluminum ions, cationic surfactants, and triphenyl methane dyes, the c_K values were clearly different even at the lowest solid contents. In contrast, the critical concentrations of BP6, BP12, PQ, and DQ were identical at the lowest particle concentrations.

Viscosity

The plastic viscosity as a function of the salt concentration changed in a similar way for all dispersions: an initial decrease to a minimum, then a steep increase. Increasing valency of the inorganic cations strongly reduced the critical salt concentration (Figure 4). The curves for the dispersions containing cationic surfactants were shifted to lower values with increasing chain length (Figure 5). Paraquat and diquat yielded almost identical viscosity curves, and the minimum was very weak (Figure 6). The minimum was pronounced in the presence of the bispyridinium cations. At higher concentrations the viscosity reached the values of paraquat and diquat. The monovalent and divalent dyes exerted the same influence on the viscos-

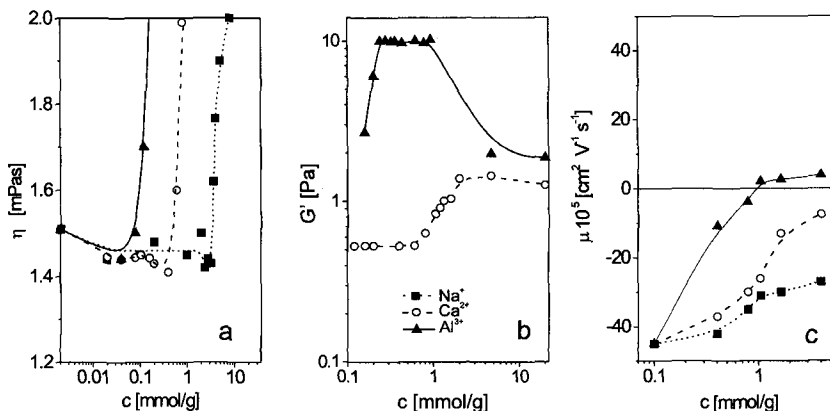


Figure 4. Plastic viscosity, η , storage modulus, G' , and electrophoretic mobility, μ , of 0.5% dispersions of Na-rich montmorillonite in the presence of sodium, calcium, and aluminum ions. c = added amount of counterions per g Na-rich montmorillonite (1 mmol/g = 5 mmol/L).

ity; the trivalent cation TTP raised the viscosity at much lower concentrations (Figure 7).

Yield values

The yield value τ_0 of most dispersions with organic salts increased steeply at low salt concentrations and remained constant at higher concentrations. Figure 8 serves as an example. Table 2 shows the yield values of the plateaus and the salt concentration at which the plateau was reached. The yield values were very small in the presence of calcium chloride and aluminum chloride (0.2 Pa for Ca²⁺ and 0.7 Pa for Al³⁺ at the maximum) but large when organic salts were added. Increasing chain length of the alkyl trimethylammonium ions increased the yield value from 2 Pa (T1) to 71 Pa (T12). The hexadecyl derivative (T16) reached 36 Pa, but decreased to 0.6 Pa at higher concentration (Figure 8a). Extremely high yield values were measured after addition of paraquat (100 Pa) and diquat (42 Pa) (Figure 8b). Dispersions with bispyridinium

ions showed the maximum yield value for the hexyl derivative. The yield value of dispersions with crystal violet (maximum of τ_0 : 18 Pa) disappeared above 2 mmol/g; with methyl green and TTP, τ_0 remained at a plateau of ~ 8 Pa. In most cases, τ_0 reached the plateau at salt concentrations around or below 1 mmol/g.

Storage modulus

The storage modulus of the 0.5% dispersions of Na-rich montmorillonite in NaCl solutions was very small ($<10^{-2}$ Pa) and the linear viscoelastic condition was not attained (Lagaly *et al.*, 1999). Calcium and aluminum ions increased G' to ~ 1 and 10 Pa, respectively (Figure 4; Table 2). These values were small compared with the high moduli in the presence of organic cations.

Tetramethylammonium ions yielded a storage modulus between 10–20 Pa (Figure 5). With the longer chain derivatives, G' increased steeply with the concentration and reached high plateau values (560 Pa for

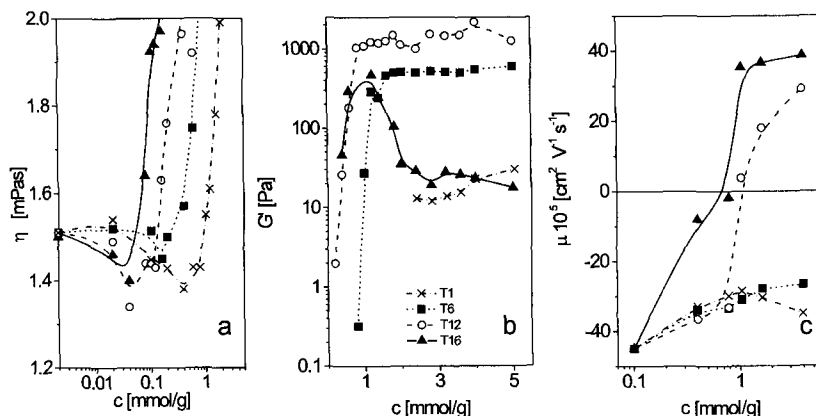


Figure 5. Plastic viscosity, η , storage modulus, G' , and electrophoretic mobility, μ , of 0.5% dispersions of Na-rich montmorillonite after addition of c (mmol/g) of alkyl trimethylammonium ions T1, T6, T12, T16.

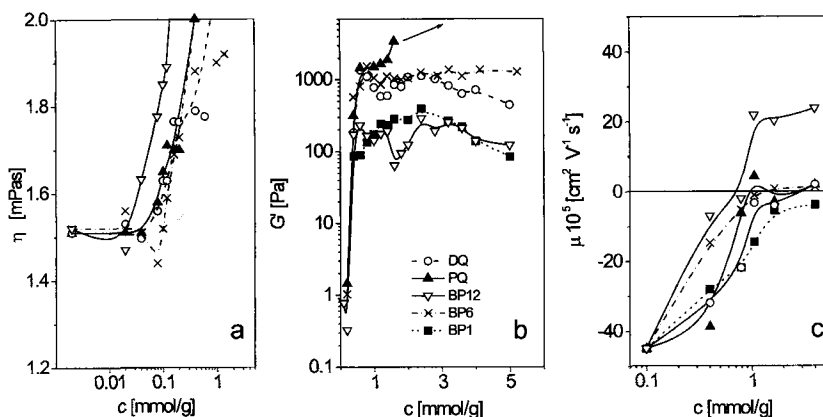


Figure 6. Plastic viscosity, η , storage modulus, G' , and electrophoretic mobility, μ , of 0.5% dispersions of Na-rich montmorillonite after addition of c (mmol/g) PQ, DQ, and alkyl bispyridinium ions BP1, BP6, BP12.

T6, >1000 Pa for T12; Figures 5 and 9a). G' of the dispersion with hexadecyl trimethylammonium chloride rose to a maximum (480 Pa), then decreased to a plateau at ~ 20 Pa. The highest modulus (>4000 Pa) was observed with PQ (Figure 6); dispersions with DQ showed smaller values which decreased at higher concentrations (Figures 6 and 9b). The storage modulus of the dispersions containing bispyridinium salts was highest with BP6 (1300 Pa) (Figure 6). G' of the dispersions containing MG or TTP reached maximum values of 90 and 110 Pa, respectively, then decreased to 30–50 Pa. The elasticity of the dispersion collapsed at crystal violet concentrations of 2 mmol/g (Figures 7, 9c, and 9d).

Increasing concentration of the organic cations changed G'' in the same way as G' . The plateau values were distinctly smaller (Figure 9), for instance, T6: $G' = 560$ Pa, $G'' = 50$ Pa; PQ: $G' \sim 2000$ Pa, $G'' \sim 100$ Pa (at 1.5 mmol/g paraquat); BP6: $G' \sim 1300$ Pa, $G'' \sim 130$ Pa; MG: $G' = 50$ Pa, $G'' = 3$ Pa. The loss

angle, $\delta = \tan^{-1}(G''/G')$, was smaller than 5° , also indicating the high elasticity of the network structure. The dispersions with CaCl_2 showed a maximum G' of 1.4 Pa, $G'' = 0.9$ Pa, and $\delta = 35^\circ$. With aluminum ions, G' increased to 10 Pa ($G'' = 3.6$ Pa, $\delta = 20^\circ$) and decreased to $G' \approx G'' \sim 1.5$ Pa ($\delta = 41^\circ$) at concentrations >10 mmol/g.

Recharging of the particles

The compression of the diffuse layer at increasing salt concentration decreases the electrophoretic mobility of the particles (Lagaly, 1986b; Lagaly *et al.*, 1997, Chap. 10). The zeta potential became slightly positive in the presence of larger numbers of aluminum ions (Figure 4). The effect was not sufficiently strong to reprecipitate the coagulated montmorillonite, but the elasticity of the particle network was distinctly reduced (Figure 4). Recharging is typical of surfactants (Lagaly, 1986b; Böhmer and Koopal, 1992; Lyklema, 1994; Lagaly *et al.*, 1997) and was pronounced for T12, T16, and BP12 (Figures 5 and 6), also causing

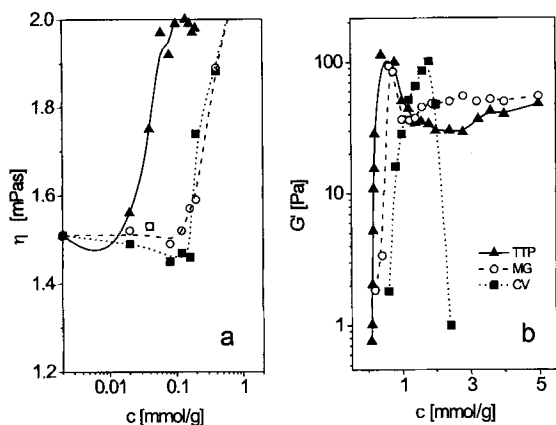


Figure 7. Plastic viscosity, η , and storage modulus, G' , of 0.5% dispersions of Na-rich montmorillonite after addition of c (mmol/g) triphenylmethane dyes CV, MG, and TTP.

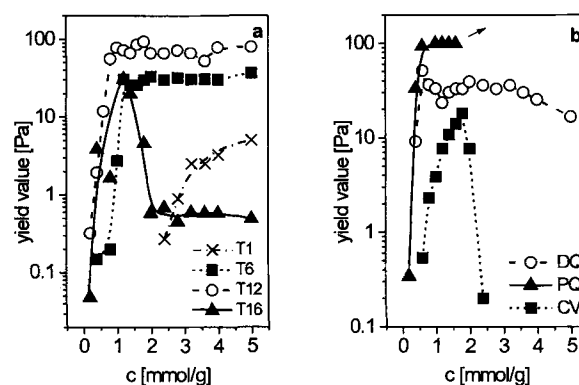


Figure 8. Yield value of 0.5% dispersions of Na-rich montmorillonite in the presence of c (mmol/g) alkyl trimethylammonium ions T1, T6, T12, T16 (a) and DQ, PQ, CV (b).

Table 2. Yield value (plateau value) and maximum storage modulus of 0.5% Na-rich montmorillonite dispersions at 20°C. c is the amount of salt (per g montmorillonite) at which the plateau yield values are reached (by extrapolation). c_K from viscosity measurements, in mmol/g (from Table 1).

Counterion (see Figure 1)	c_K mmol/g	c mmol/g	Yield Value Pa	Storage Modulus Pa
Na ⁺	3.6	—	—	—
Ca ²⁺	0.56	2.67	0.2	1.4
Al ³⁺	0.13	0.27	0.7	10
T1	1.16	3.1	2.4	24
T6	0.4	1.27	28.8	560
T12	0.15	0.79	71.2	2000
T16	0.07	0.99	36	480
PQ	0.08	0.6	99.6	>4000
DQ	0.09	0.6	42.4	1400
BP1	0.19	1	16	400
BP6	0.12	0.51	53	1300
BP12	0.036	0.57	13	300
CV	0.18	1.71	18	105
MG	0.2	0.49	8.2	90
TTP	0.018	0.3	9.3	110

repeptization. Paraquat, diquat, and the bispyridinium salts, BP1 and BP6, reduced the mobility, and the particles appeared to be virtually uncharged at amounts of ≥ 1 mmol/g (Figure 6). Recharging by crystal violet caused repeptization of the particles (Yariv *et al.*, 1990; Schramm *et al.*, 1997).

DISCUSSION

Critical coagulation concentration

Many practical applications involving bentonites are based on the colloidal behavior of dispersions: stable,

coagulated, or gel-like (Abend and Lagaly, 2000). Na-rich montmorillonite dispersions are coagulated by NaCl concentrations of ~ 5 mmol/L (Table 1) (Lagaly 1993b; Permien and Lagaly, 1994b). This value is extremely small compared with many other colloidal dispersions which show c_K values > 50 mmol/L (Lagaly *et al.*, 1997, Chap. 3). The small value is caused by the interaction between the negative edges and negative faces of the clay-mineral particles at low salt and solid content (Permien and Lagaly, 1994b; Abend and Lagaly, 2000).

As expected on the basis of electrostatic stabilization (Lagaly *et al.*, 1997, Chap. 3.1), the critical calcium and aluminum concentration, 0.4 and 0.08 mmol/L, is distinctly smaller than the critical sodium concentration. The difference between the critical concentrations results from the compression of the diffuse ionic layer with increasing ionic charge of the counterions. The relation between c_K (1), *i.e.*, the critical coagulation concentration of Na⁺, c_K (2), and c_K (3) corresponding to the values for Ca²⁺ and Al³⁺, respectively, is (Table 1, 0.025% dispersions): c_K (1) ~ 12 c_K (2) = 63 c_K (3). This ratio of the c_K values may be compared with the ratio predicted by the DLVO theory (Overbeek, 1980; Lagaly *et al.*, 1997; Chap. 3.1): c_K (1) = (4–64) c_K (2) = (9–729) c_K (3). The smaller value corresponds to low surface potentials (≤ 50 mV) and the large value to surface potentials ≥ 150 mV. As the surface potentials calculated from the surface charge density are distinctly higher, the observed c_K ratio confirms the strong Stern-layer adsorption of the inorganic counterions (Chan *et al.*, 1984; Goldberg,

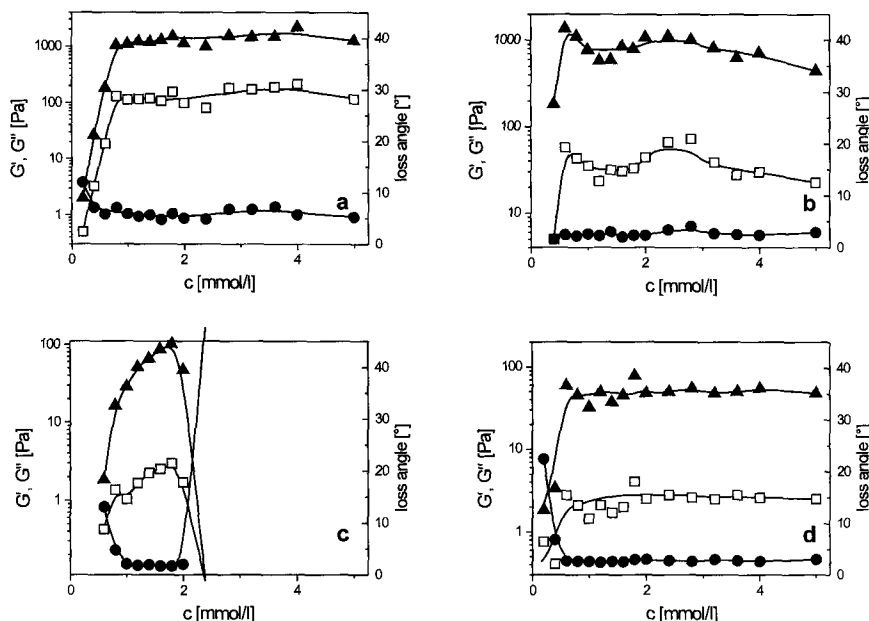


Figure 9. Storage modulus G' (\blacktriangle), loss modulus G'' (\square), and loss angle δ (\bullet) of 0.5% dispersions of Na-rich montmorillonite in the presence of c (mmol/g) organic salts. a) dodecyl trimethylammonium chloride (T12), b) DQ, c) CV, and d) MG.

1992; Gan and Low, 1993; Permien and Lagaly, 1994a, 1994b; Quirk and Marčelja, 1997).

The monovalent organic cations are adsorbed more strongly than the inorganic ions. They strongly reduce the surface potential, and the c_K values drop below 1 mmol/L (Table 1, 0.025% dispersions). The c_K values for divalent organic cations are in the range of the critical concentrations of the monovalent organic cations. The c_K values of Al^{3+} and TTP are comparable.

The ionic charge of the organic counterions is distinctly less important than for inorganic ions, because even the monovalent cations strongly reduce the surface potential. This implies that the discreteness of the charges must be considered. The charges of the 2:1 layers are clearly separated (surface charge density $\sigma_0 \sim 0.1 \text{ C/m}^2$). The 0.025% dispersion of the montmorillonite with a cation-exchange capacity of 0.95 meq/g contains $0.95 \times 0.25 = 0.24 \text{ mmol/L}$ counterions. Therefore, the amount of monovalent cations for charge compensation is $\geq 0.24 \text{ mmol/L}$. The c_K values are of this order of magnitude if the cations do not have hydrophobic tails that are too long. Certainly, not all surface charges must be compensated to destabilize the dispersion (see also Schramm *et al.*, 1997). At small potentials, c_K becomes very dependent on the Stern potential (Lagaly, 1986b; Lagaly *et al.*, 1997, Chap. 3). The consequence is that even a weak increase in adsorption reduces c_K strongly.

Complete charge compensation of the 0.025% dispersion requires 0.12 mmol/L divalent cations. In fact, the critical concentrations are $\sim 0.1 \text{ mmol/L}$ but higher values were also observed. A proportion of divalent cations, in particular with short distances between the charges (chain lengths ≤ 6 carbon atoms), do not compensate two negative surface charges but are attached to one surface site only.

Within a homologous series, for instance, trimethyl alkylammonium or bispyridinium ions, c_K decreases with increasing molecular size. This effect is not a part of DLVO theory and is caused (a) by the van der Waals attraction between the hydrophobic parts of the organic cations attached to different particles and (b) by the influence of the organic cations on the solvent (water) structure near the surface (Lagaly and Witter, 1982; Lagaly *et al.*, 1983; Lagaly, 1987). The disturbance of the water structure enhances the adsorption of the counterions and decreases the Stern potential and the electrostatic repulsion. In some cases, the water structure reduces the repulsive hydration forces which contribute to the dispersion stability (Israelachvili, 1994).

When the salts solely regulate the thickness of the diffuse ionic layers (DLVO theory), c_K is independent of the solid content. The critical coagulation concentration increases with the solid content when the counterions are adsorbed in the Stern layer (Stumm *et al.*, 1970; Rooy *et al.*, 1980; Lagaly *et al.*, 1997, Chap.

11). This behavior of c_K is observed for Na-rich montmorillonite dispersions in the presence of inorganic and organic counterions. The c_K values increase considerably with the particle concentration (Figure 3; Table 1). When the solid content is raised to 5 g/L, complete charge compensation would require $0.95 \times 5 = 4.8 \text{ mmol}$ monovalent organic cations per liter. In most cases, the coagulation concentrations are distinctly smaller, because of the formation of tactoids at these relatively high particle concentrations. The distance between the 2:1 silicate layers within the tactoids is smaller than the distance between the tactoid units. Coagulation starts when the forces between the external surfaces of neighboring tactoids become attractive (Schramm and Kwak, 1982; Schramm *et al.*, 1997), more precisely, when the barrier of the potential curve becomes smaller than $\sim 20 \text{ kT}$ (Permien and Lagaly, 1994a).

Rheological properties

The appearance of attractive forces at c_K steeply increases the viscosity of the dispersions (Figures 4–7). This behavior can be used to measure the coagulation concentration of more highly concentrated dispersions ($\geq 0.1\% \text{ w/w}$).

The plastic viscosity increases at c_K but the interactions between the particles are too weak to create a yield value. Somewhat higher salt concentrations are required to build a network which resists the shearing forces below a threshold value. In most cases, the yield value increases rapidly after addition of small amounts of salt and reaches plateau values at $\sim 0.5 \text{ mmol/g}$ salt (Figure 8; Table 2). This indicates that complete charge compensation (which requires 0.95 mmol/g) is not required to establish the maximum yield value.

The strength of the network against shearing forces, *i.e.*, the yield value, increases from T1 to T12 owing to the increasing attractive forces between the particles. The decrease of the yield value for T16, despite a distinctly smaller c_K , suggests that the longer chains held the particles at larger distances so that disruption of the contacts by the mechanical force is facilitated.

The divalent organic cations can bridge between neighboring 2:1 silicate layers and create a network of high mechanical stability. One expects the highest yield values for paraquat and hexyl bispyridinium chloride, which is observed. Both cationic charges in BP1 are too close to enable effective bridging. This geometric influence also reduces the stiffening effect of diquat compared with paraquat. The smaller yield value with BP12 may be caused by adsorption of a part of the cations in a way that both ionic end groups are attached at the same particle so that the number of interparticle contacts is reduced.

The yield value of the CV-containing dispersions increases at distinctly higher concentrations than MG and TTP, but reaches a higher maximum value. The

decrease at 2 mmol/g CV results from recharging of the particles by CV cations adsorbed in excess to cation-exchange capacity (Schramm *et al.*, 1997). Rytwo *et al.* (1995) showed that the plane of the monovalent CV cations lies at slight inclination relative to the 2:1-layer silicate surface, whereas the divalent MG cations are oriented with their plane parallel to the surface (Margulies and Rozen, 1986). The van der Waals contact between the inclined CV cations of two adjacent 2:1 layers creates a larger yield value than the interactions between the flat-lying and more highly charged MG and TTP cations.

The yield value indicates the stability of the network structure against shearing forces. Information on the elasticity of the network structure is provided by G' . This value changes with increasing salt concentration in the same way as the yield value. Thus, the T12 dispersion has the highest storage modulus (maximum 2000 Pa) (Table 2). Like the yield value, G' decreases with increasing loading. The bispyridinium cations reveal the same trend, and G' is highest for BP6. The divalent paraquat cations are the most effective strengthening agents; G' of the 0.5% dispersion increases to several thousand Pa (Figure 6). As discussed above, bridging of neighboring particles by DQ and BP1 is less effective and the storage modulus is smaller.

Recharging of the particles by adsorbed CV cations causes the collapse of G' at ≥ 2 mmol/g. G' of the MG- and TTP-containing dispersions increases to a maximum value at ~ 0.5 mmol/g then decreases to 30–50 Pa (Figure 7) because the particles are not redispersed. The yield value also shows a maximum. A simple model to explain the behavior is that two and three positive charges distributed over the adsorbed triphenyl methane ions interact with the negative charges of unoccupied sites of neighboring 2:1 layers (like in the mosaic model of charge neutralization by polymers; Gregory, 1973; Lagaly *et al.*, 1997, p. 123) which increases G' and τ_0 . If the surface coverage by MG and TTP cations increases, these additional interactions are weakened, and G' and τ_0 decrease to a lower plateau value.

ACKNOWLEDGMENT

We thank the German-Israeli-Foundation for financial support.

REFERENCES

- Abend, S. and Lagaly, G. (2000) Sol-gel transitions of bentonite dispersions. *Applied Clay Science*, **16**, 201–227.
- Böhmer, M.R. and Koopal, L.K. (1992) Adsorption of ionic surfactants on variable-charge surfaces. 1. Charge effects and structure of the adsorbed layer. *Langmuir*, **8**, 2649–2659.
- Brüdgam, I. and Hartl, H. (1986) Dipyrindiomethan-Diiodid. *Acta Crystallographica C*, **42**, 866–868.
- Chan, D.Y.C., Pashley, R.M., and Quirk, J.P. (1984) Surface potentials derived from co-ion exclusion measurements on homoionic montmorillonite and illite. *Clays and Clay Minerals*, **32**, 131–138.
- Gan, H. and Low, F. (1993) Spectroscopic study of ionic adjustments in the electric double layer of montmorillonite. *Journal of Colloid and Interface Science*, **161**, 1–5.
- Goldberg, S. (1992) Use of surface complexation models in soil chemical systems. *Advanced Agronomy*, **47**, 233–329.
- Gregory, J. (1973) Rates of flocculation of latex particles by cationic polymers. *Journal of Colloid and Interface Science*, **42**, 448–456.
- Güven, N. (1992) Rheological aspects of aqueous smectite suspensions. In *Clay-Water Interface and its Rheological Implications*, N. Güven and R.M. Pollastro, eds., CMS Workshop Notes Volume 4, The Clay Minerals Society, Boulder, Colorado, 81–126.
- Haque, R., Lilley, S., and Coshov, W.R. (1970) Mechanism of adsorption of diquat and paraquat on montmorillonite surface. *Journal of Colloid and Interface Science*, **33**, 185–188.
- Hasenpatt, R., Degen, W., and Kahr, G. (1989) Flow and diffusion in clays. *Applied Clay Science*, **4**, 179–192.
- Hochstein, B. and Geissle, W. (1995) Linear viscoelastic region exhibited by pure fluids and their suspensions. *Rheology*, **5**, 72–79.
- Ijdo, W.L. and Pinnavaia, T.J. (1998) Staging of organic and inorganic gallery cations in layered silicate heterostructures. *Journal of Solid State Chemistry*, **139**, 281–289.
- Israelachvili, J. (1994) *Intermolecular and Surface Forces*. Academic Press, London, 450 pp.
- Knight, G.A. and Shaw, B.D. (1938) Long chain alkylpyridines and their derivatives. New examples of liquid crystals. *Journal of the American Chemical Society*, **121**, 682–683.
- Lagaly, G. (1986a) Smectite clays as ionic macromolecules. In *Developments in Ionic Polymers, Volume 2*, A.D. Wilson and H.J. Prosser, eds, Elsevier Applied Science Publication Ltd., London, 77–140.
- Lagaly, G. (1986b) Colloids. In *Ullmann's Encyclopedia of Industrial Chemistry, Volume A7*, VCH Verlagsgesellschaft, Weinheim, 341–367.
- Lagaly, G. (1987) Water and solvents on surfaces bristling with alkyl chains. In *Interaction of Water in Ionic and Non-Ionic Hydrates*, H. Kleeberg, ed., Springer-Verlag, Berlin, 229–239.
- Lagaly, G. (1993a) Praktische Verwendung und Einsatzmöglichkeiten von Tonen. In *Tonminerale und Tone—Struktur, Eigenschaften, Anwendungen und Einsatz in Industrie und Umwelt*, K. Jasmund and G. Lagaly, eds., Steinkopff-Verlag, Darmstadt, 358–420.
- Lagaly, G. (1993b) From clay minerals to colloidal clay mineral dispersions. In *Coagulation and Flocculation. Theory and Applications*, B. Dobias, ed., Marcel Dekker Inc., New York, 427–494.
- Lagaly, G. (1994) Layer charge determination by alkylammonium ions. In *Layer Charge Characteristics of 2 : 1 Silicate Clay Minerals*, A.R. Mermut, ed., CMS Workshop Notes, Volume 6, The Clay Minerals Society, Boulder, Colorado, 1–46.
- Lagaly, G. and Witter, R. (1982) Clustering of liquid molecules on solid surfaces. *Berichte der Bunsengesellschaft für Physikalische Chemie*, **86**, 74–80.
- Lagaly, G., Witter, R., and Sander, H. (1983) Water on hydrophobic surfaces. In *Adsorption from Solution*, R.H. Ottewill, C.H. Rochester, and A.L. Smith, eds., Academic Press, London, 65–77.
- Lagaly, G., Schulz, O., and Zimehl, R. (1997) *Dispersionen und Emulsionen. Eine Einführung in die Kolloidik feinverteilter Stoffe einschließlich der Tonminerale (mit einem his-*

- torischen Beitrag über Kolloidwissenschaftler von Klaus Beneke*). Steinkopff Verlag, Darmstadt, 560 pp.
- Lagaly, G., Reese, M., and Abend, S. (1999) Smectites as colloidal stabilizers of emulsions. II. Rheological properties of smectite-laden emulsions. *Applied Clay Science*, **14**, 279–298.
- Lyklema, J. (1994) Adsorption of ionic surfactants on clay minerals and new insights in hydrophobic interactions. *Progress in Colloid and Polymer Science*, **95**, 91–97.
- Margulies, L. and Rozen, H. (1986) Adsorption of methyl green on montmorillonite. *Journal of Molecular Structure*, **141**, 219–226.
- Overbeek, J.T.G. (1980) The rule of Schulze and Hardy. *Pure and Applied Chemistry*, **52**, 1151–1161.
- Permien, T. and Lagaly, G. (1994a) The rheological and colloidal properties of bentonite dispersions in the presence of organic compounds. I. Flow behaviour of sodium montmorillonite in water-alcohol. *Clay Minerals*, **29**, 751–760.
- Permien, T. and Lagaly, G. (1994b) The rheological and colloidal properties of bentonite dispersions in the presence of organic compounds. III. The effect of alcohols on the coagulation of sodium montmorillonite. *Colloid and Polymer Science*, **272**, 1306–1312.
- Philen, O.D., Jr., Weed, S.B., and Weber, J.B. (1970) Estimation of surface charge density of mica and vermiculite by competitive adsorption of diquat vs paraquat. *Soil Science Society of America Proceedings*, **34**, 527–531.
- Philen, O.D., Jr., Weed, S.B., and Weber, J.B. (1971) Surface charge characterization of layer silicates by competitive adsorption of two organic divalent cations. *Clays and Clay Minerals*, **19**, 295–302.
- Quirk, J.P. and Marčelja, S. (1997) Application of double-layer theories to the extensive crystalline swelling of Li⁺-montmorillonite. *Langmuir*, **13**, 6241–6248.
- Raupach, M., Emerson, W.W., and Slade, P.G. (1979) The arrangement of paraquat bound by vermiculite and montmorillonite. *Journal of Colloid and Interface Science*, **69**, 398–408.
- Rooy, N. de, Bryn, P.L. de, and Overbeek, J.T.G. (1980) Stability of dispersions in polar organic media. I. Electrostatic stabilization. *Journal of Colloid and Interface Science*, **75**, 542–554.
- Rytwo, G., Nir, S., and Margulies, L. (1993) Competitive adsorption of methylene blue and crystal violet to montmorillonite. *Clay Minerals*, **28**, 139–143.
- Rytwo, G., Nir, S., Margulies, L. (1995). Interactions of monovalent organic cations with montmorillonite: Adsorption studies and model calculations. *Soil Science Society of America Journal*, **59**, 554–564.
- Rytwo, G., Nir, S., and Margulies, L. (1996a) A model for adsorption of divalent organic cations to montmorillonite. *Journal of Colloid and Interface Science*, **181**, 551–560.
- Rytwo, G., Nir, S., and Margulies, L. (1996b) Adsorption and interactions of diquat and paraquat with montmorillonite. *Soil Science Society of America Journal*, **60**, 601–610.
- Schmidt, C.U. and Lagaly, G. (1999) Surface modification of bentonites. I. Betaine montmorillonites and their rheological and colloidal properties. *Clay Minerals*, **34**, 447–458.
- Schneider, H.J., Schiestel, T., and Zimmermann, P. (1992) The incremental approach to nonvalent interactions: Coulomb and van-der-Waals effects in organic ion pairs. *Journal of the American Chemical Society*, **114**, 7698–7703.
- Schramm, L.L. and Kwak, J.C.T. (1982) Interactions in clay suspensions: The distribution of ions in suspension and the influence of tactoid formation. *Colloids and Surfaces*, **3**, 43–60.
- Schramm, L.L., Yariv, S., Ghosh, D.K., and Hepler, L.G. (1997) Electrokinetic study of the adsorption of ethyl violet and crystal violet by montmorillonite clay particles. *Canadian Journal of Chemistry*, **75**, 1868–1877.
- Stul, M.S. and van Leemput, L. (1982) Particle-size distribution, cation exchange capacity and charge density of de-ferrated montmorillonites. *Clay Minerals*, **17**, 209–215.
- Stumm, W., Huang, C.P., and Jenkins, S.R. (1970) Specific chemical interaction affecting the stability of dispersed systems. *Croatia Chemica Acta*, **42**, 223–244.
- Tributh, H. and Lagaly, G. (1986) Aufbereitung und Identifizierung von Boden- und Lagerstättentonen. *GIT Fachzeitschrift für das Laboratorium*, **30**, 524–529, 771–776.
- Weed, S.B. and Weber, J.B. (1969) The effect of cation exchange capacity on the retention of diquat and paraquat by three-layer type clay minerals. I. Adsorption and release. *Soil Science Society of America Proceedings*, **33**, 379–382.
- Wienberg, R. (1990) Zum Einfluß organischer Schadstoffe auf Deponietone. *Abfallwirtschaftsjournal*, **6**, 393–403.
- Xu, S. and Boyd, S.A. (1995) Cationic surfactant adsorption by swelling and nonswelling layer silicates. *Langmuir*, **11**, 2508–2514.
- Yariv, S., Müller-Vonmoos, M., Kahr, G., and Rub, A. (1989) Thermal analytical study of the adsorption of crystal violet by laponite. *Journal of Thermal Analysis*, **35**, 1941–1952.
- Yariv, S., Nasser, A., and Baron, P. (1990) Metachromasy in clay minerals. Spectroscopic study of the adsorption of crystal violet by laponite. *Journal of the the Chemical Society Faraday Transactions*, **86**, 1593–1598.

E-mail of corresponding author: h.mittag@email.uni-kiel.de
 (Received 18 March 1999; accepted 25 November 1999;
 Ms. 323; A.E. David A. Laird)