CROATICA CHEMICA ACTA CCACAA **71** (4) 983–1004 (1998)

ISSN-0011-1643
CCA-2543
Original Scientific Paper

Surface Modification of Bentonites.
II. Modification of Montmorillonite with Cationic Poly(ethylene oxides)

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Received January 29, 1988; accepted May 2, 1998

Surface modification of clay minerals has become increasingly important for optimizing the practical application of bentonites, kaolins, and clays. We describe the reaction of montmorillonite, an important mineral in bentonites, with cationic poly(ethylene oxides). Poly(ethylene oxides), PEOs, with molecular masses between 1550 and 35000, were modified by substituting the OH end groups by bromine, then replacing Br by trimethylammonium (TMA) groups. Mono-endcapped PEOs were prepared from poly(ethylene oxide)monomethyl ethers. These cationic PEOs were strongly adsorbed by montmorillonite and bound by cation exchange. The cationic end groups of the PEOs displaced external and internal exchangeable cations. The macrocations did not flocculate sodium montmorillonite dispersions but stabilized them by forming lyospheres around the particles (steric stabilization). They impeded settling of dispersed calcium montmorillonite particles, even at a 1 percent solid content, and a gel was formed that stiffened within a certain period. This is caused by a certain degree of delamination of the calcium montmorillonite particles that are split at some given break points. The initial stages of gel formation were studied with low shear viscosimetry. An interesting aspect is the temperature dependence of the flow values. The viscosity of calcium montmorillonite dispersed in solutions of di-endcapped PEOs decreased above 40–50 °C but the yield value rose sharply.

This article is dedicated to Professor Egon Matijević on the occasion of his 75th birthday.

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INTRODUCTION

Many colloid scientists avoid studying clay mineral dispersions because of the complex behavior of the anisometric particles with pronounced unequal charge distribution, but Egon Matijević contributed to the basic knowledge of the colloidal behavior of clay minerals.[1–3]

Large amounts of colloidal bentonite dispersions are used as drilling fluids, for slurry walling and in geotechnical applications. As thickening and thixotropic agents they are added to paints, lubricants, adhesives, pharmaceutical products and many other dispersed systems. Bentonite addition in paints minimizes sagging. The mineral that makes bentonites suitable for these uses is montmorillonite.[4]

Many of these applications require a high degree of dispersion. Highly dispersed bentonites are only obtained in the presence of sufficient amounts of sodium ions in slightly alkaline conditions. Thus, industrial bentonite activation requires addition of sodium ions, mostly in the form of soda ($Na_2CO_3 \cdot 10\ H_2O$). When sodium bentonites or soda-activated bentonites are dispersed in water, the montmorillonite particles are not only separated but also delaminate into single silicate layers or doublets, triplets ... (Figure 1).[4] Due to this delamination, bentonites used as thickening and thixotropic agents are superior to other clay minerals.

The highest degree of delamination is only attained in the absence of divalent cations. Other minerals, particularly iron oxides, amorphous materials such as silica, and organic substances can reduce the degree of delami-

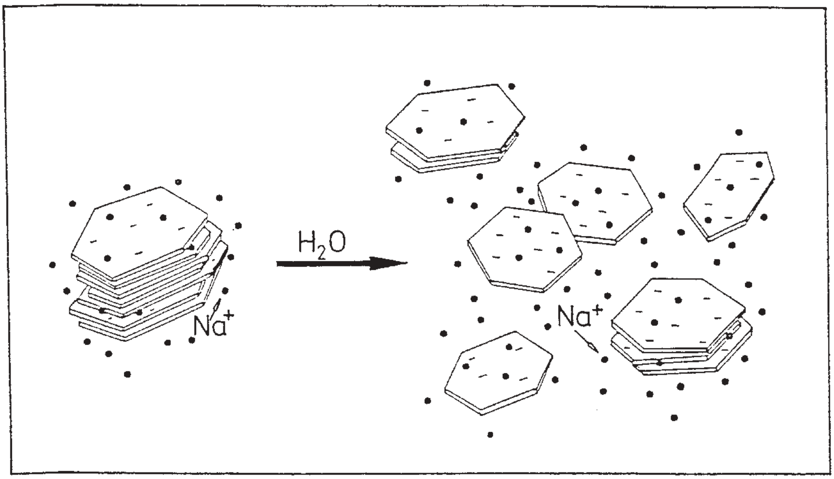

Figure 1. Delamination of sodium montmorillonite particles in water.

nation. These admixtures and the fact that the divalent cations are not removed from the system during soda activation reduce the optimal degree of delamination in technical dispersions.

Calcium and magnesium ions have a pronounced effect on clay mineral dispersions. Even small amounts of calcium ions added to a colloidal dispersion of sodium montmorillonite cause the particles to coagulate and to form a sediment. The coagulating power of divalent ions is stronger than predicted by the DLVO theory because of a considerable contribution of ion-ion correlation.[5,6]

The desired effect of sodium bentonite addition in concretes and adhesives or for civil engineering is often destroyed in the presence of considerable amounts of calcium ions. One possible way to overcome this problem is steric stabilization when macromolecules are attached to the clay mineral particles. To attach poly(ethylene oxide) chains tightly to the clay mineral surface, cationic derivatives of PEO were prepared by introducing trimethylammonium groups at one end or at both ends of poly(ethylene oxides). These cationic PEOs greatly changed the colloidal properties of calcium montmorillonite dispersions. Mosquet *et al.*[7] used the same procedure to stabilize $CaCO_3$ dispersions by PEOs with anionic end groups.

EXPERIMENTAL

Sodium and Calcium Montmorillonite

We used Wyoming bentonite (Greenbond, sample M 40A) as starting material. Iron oxides were removed by sodium citrate and sodium dithionate. Organic material was oxidized by hydrogen peroxide. The < 2 μm fraction was separated by sedimentation. The sodium montmorillonite dispersion was then coagulated with 1 M NaCl solution. The coagulate was separated by centrifugation, then dialyzed in water until chloride ions could no longer be detected by precipitation with $AgNO_3$. The dispersion was freeze-dried, and the dried loose material of flaky pastry appearance was homogenized by gentle low-energy ball-milling. For details see Refs. 8, 9.

Homoionic calcium montmorillonite was prepared by dispersing 60 g freeze-dried sodium montmorillonite in 400 ml water before 500 ml 0.5 M calcium chloride solution was added. The dispersion was held at 65 °C for 24 h before the solution was decanted. This procedure was twice repeated. After three washings with water, the dispersion was dialyzed and freeze-dried.

The montmorillonite layer charge was determined by the alkylammonium method.[10] Mean layer charge: 0.28 charges/$(Si, Al)_4O_{10}$ unit (≡ eq/mol); limits of charge distribution: 0.25 and 0.33 charges/unit; equivalent area 0.75 nm^2/charge; interlayer cation exchange capacity: 0.78 meq/g; total exchange capacity: 0.95 meq/g (from carbon content of alkylammonium derivatives.[10] As the amount of exchangeable cations at the edges is in the order of 15–20 percent of the total exchange capacity. These values indicate that the montmorillonite fraction contains ≥ 96 percent montmorillonite.[11]

Poly(ethylene oxides)

Poly(ethylene oxides) with molecular masses of about 1550, 4000, 20000 and 35000 (suppliers' information) were obtained from Hüls AG, Germany (Polywachs 1550, 4000, 20000) and Hoechst AG, Germany (Polyglycol 35000 S). Samples PEO 2000 M and PEO 5000 M were poly(ethylene oxide) monomethyl ethers $HO\text{-}(CH_2\text{-}CH_2\text{-}O\text{-})_n\text{-}CH_3$ (Polyethylene glycol 2000-monomethyl ether, Polyethylene glycol 5000-monomethyl ether, Fluka Comp., Switzerland).

Preparation of bromopoly(ethylene oxides)

First, poly(ethylene oxide) was reacted with $SOBr_2$ or PBr_3 in toluene to substitute the OH groups at both ends or at one end (PEO 2000 M, 5000 M) by bromine:[12]

$$HO(CH_2CH_2O)_nCH_2CH_2OH + SOBr_2 \xrightarrow{N(C_2H_5)_3} Br(CH_2CH_2O)_nCH_2CH_2Br + H_2O + SO_2$$

and

$$3\ HO(CH_2CH_2O)_nCH_3 + PBr_3 \xrightarrow{N(C_2H_5)_3} 3\ Br(CH_2CH_2O)_nCH_3 + H_3PO_3$$

50 g PEO 4000 (about 12.5 mmol) was dissolved in 300 ml toluene (dried over molecular sieve 3–4 Å). Water adhering to the poly(ethylene oxide) was removed with about 50 ml toluene using a water separator. After cooling, 8.7 ml (62.5 mmol) triethylamine was added. An amount of 3.9 ml (50 mmol) thionylbromide in 20 ml toluene was dropped into this solution, held under stirring at 35 °C. After 1 hour in refluxing conditions, the solution was filtered through a layer of kieselguhr (2 cm thick, Hyflo Super Cel, Fluka Comp.). The filtrate was bleached with 10 g activated charcoal at 50 °C and again filtered through kieselguhr. The bromo derivative was crystallized at 4 °C. It was separated, dried and dissolved in 120 ml ethanol, again treated with 5 g charcoal and filtered through kieselguhr. After cooling, the bromo-PEO was precipitated by adding 100 ml ether and dried in vacuum. We used 22 ml (1 ml) triethylamine and 10 ml (0.5 ml) thionyl bromide to prepare the bromo derivative of 50 g PEO 1550 (35000).

The bromo-PEO monomethyl ether was prepared from 35 g (about 17.5 mmol) PEO 2000 M, dissolved in 400 ml dried toluene. About 100 ml toluene was separated to remove the water. The solution was reacted with 1.7 ml (about 20 mmol) phosphorous tribromide under refluxing for 8 hours. The solution was concentrated by evaporation and cooled down to crystallize the bromo derivative. The product was twice recrystallized from about 50 ml toluene, then dried at 50 °C in vacuum.

Preparation of Cationic Poly(ethylene oxides)

The cationic PEOs were obtained by reacting the bromo derivative with trimethylamine:[13]

$$\mathrm{Br(CH_2CH_2O)}_n\mathrm{CH_2CH_2Br} + 2\mathrm{N(CH_3)_3} \rightarrow$$
$$\mathrm{Br^-(CH_3)_3N^+(CH_2CH_2O)}_n\mathrm{CH_2CH_2N^+(CH_3)_3Br^-}$$

or

$$\mathrm{Br(CH_2CH_2O)}_n\mathrm{CH_3} + \mathrm{N(CH_3)_3} \rightarrow \mathrm{Br^-(CH_3)_3N^+(CH_2CH_2O)}_n\mathrm{CH_3}$$

40 g (about 10 mmol) bromo-PEO 4000 was dissolved in 100 ml ethanol (dried over CaO by refluxing) and reacted with 8 ml (70 mmol) $N(CH_3)_3$ in 25 ml dried ethanol. (Gaseous trimethylamine was obtained from its aqueous solution with concentrated NaOH solution and condensed in acetone-dry ice). The solution was placed in a gas-tight vessel and held at 75 °C in a drying cupboard for 38 hours at 75 °C. Then, nitrogen was passed through the solution to remove excess of trimethylamine. After addition of 15 g charcoal, the solution was heated under reflux for 2 hours, then immediately filtered through kieselguhr. The filter cake was washed three times with ethanol. The volume of the collected filtrates was reduced to 75 ml by evaporation. The trimethylammonium derivative crystallized after cooling and was dried in vacuum. The trimethylammonium derivatives of the other bromo-PEOs were prepared by the same procedure. The amount of trimethylamine was 6 to 8 mol/mol PEO.

The bromide content of the cationic PEOs was determined by precipitation of the bromide ions with silver ions (Fajans titration with eosin sodium salt as adsorption indicator). Table I gives the bromide contents and, calculated from these data, the average molecular mass. The molecular masses derived from the bromide content are in good agreement with the nominal molecular masses with the exception of TMA PEO 5000 M. Probably, the original sample had a molecular mass distinctly smaller than that given by the supplier.

TABLE I

Molecular mass of cationic PEOs derived from bromide content

Sample	Bromide content	Molecular mass	
	μmol/g	exp.	theor.*
$(TMA)_2$ PEO 1550	880.2	2272	1794
$(TMA)_2$ PEO 4000	525.2	3808	4244
$(TMA)_2$ PEO 35000	55.6	35960	35244
TMA PEO 2000 M	406.7	2459	2122
TMA PEO 5000 M	355.5	2813	5122

* Substituting one OH group by $N^+(CH_3)_3Br^-$ increases the molecular mass by 122.

Adsorption Experiments

A stock dispersion of sodium montmorillonite was prepared by dispersing 14 g sodium montmorillonite (freeze-dried) in 750 g water by shaking. 24 hours later, the dispersion was ultrasounded (Sonorex, 80 W) for 15 min. The dispersion volume was adjusted to 1 l. An Ultra Turrax must be used to disperse calcium montmorillonite in water (14 g/750 ml). The dispersion was shaken for 24 h, then treated with ultrasound for 15 min. Finally, the volume was adjusted to 1 l. As the calcium montmorillonite particles settle rapidly, the stock dispersion was carefully shaken before samples were taken.

In adsorption experiments, amounts of 0.1 to 2 ml polymer solution (concentration in the range of 40–60 g/l) were placed into small vessels. Water was added to reach a volume of 2 ml before 5 ml montmorillonite dispersion was added. The final solids content was 1%. The amount of polymer adsorbed was calculated from the depletion in the solution. Correctly, depletion gives the specific surface excess, $n_1^{\sigma(n)}$, which, for preferential adsorption from diluted solution, approximates the amounts adsorbed, n_1^s (Ref. 14). Polymer concentration was determined by measuring the refractive index (differential refractometer, Knauer Comp., Germany).

The amounts of sodium and calcium ions displaced by the cationic PEOs were measured by emission spectroscopy (Spectra Span IV, Beckman Instruments).

Rheological Measurements

Flow curves (shear stress τ against shear rate $\dot{\gamma}$) were determined with a Low Shear Couette viscosimeter (Contraves, Zürich). Maximal shear rate was $\dot{\gamma} = 128.5\ \mathrm{s}^{-1}$. Flow curves were recorded of the samples prepared for adsorption measurements.

Reproducible results could only be obtained when, after mixing the montmorillonite dispersion with the polymer solution, the samples were shaken for a constant period (24 hours) before 1 ml of the dispersion was placed into the rheometer cup. Before starting measurements, the dispersion was sheared for one minute at $\dot{\gamma} = 100\ \mathrm{s}^{-1}$. After resting 15 s, measurements were started, increasing $\dot{\gamma}$ to $128.5\ \mathrm{s}^{-1}$, then going back to $\dot{\gamma} = 0$.

The yield value τ_B was obtained by extrapolating the linear section of the flow curves at the highest shear rates to $\dot{\gamma} = 0$. Plastic viscosity was derived from the slope of this linear section. The relative viscosity η_{rel} was defined as the ratio of the plastic viscosity of the dispersion to that of the dispersion medium, *i.e.* the serum obtained by centrifugation.

RESULTS

Adsorption and Cation Exchange

The adsorption isotherms of cationic PEO on sodium and calcium montmorillonite increased steeply at low polymer equilibrium concentrations (<0.5 g/l, Figure 2a, b). This behavior was also typical of unmodified PEO.[15–17]

PEO adsorption reached a plateau after a sharp turn of the curve whereas the amounts of cationic PEO adsorbed increased slightly at higher polymer concentrations. Saturation was not reached for $(TMA)_2$ PEO 35000 on sodium montmorillonite and $(TMA)_2$ PEO 1550 on calcium montmorillonite. The scattering of data for calcium montmorillonite resulted from the incomplete distribution of calcium montmorillonite in water because the calcium montmorillonite particles in stock solution settled rapidly.

The maximum amounts of cationic PEOs adsorbed (estimated from Langmuir approximation of the data at low polymer equilibrium concentrations, Table II) corresponded to the pseudoplateau values in Figure 2a, b. The

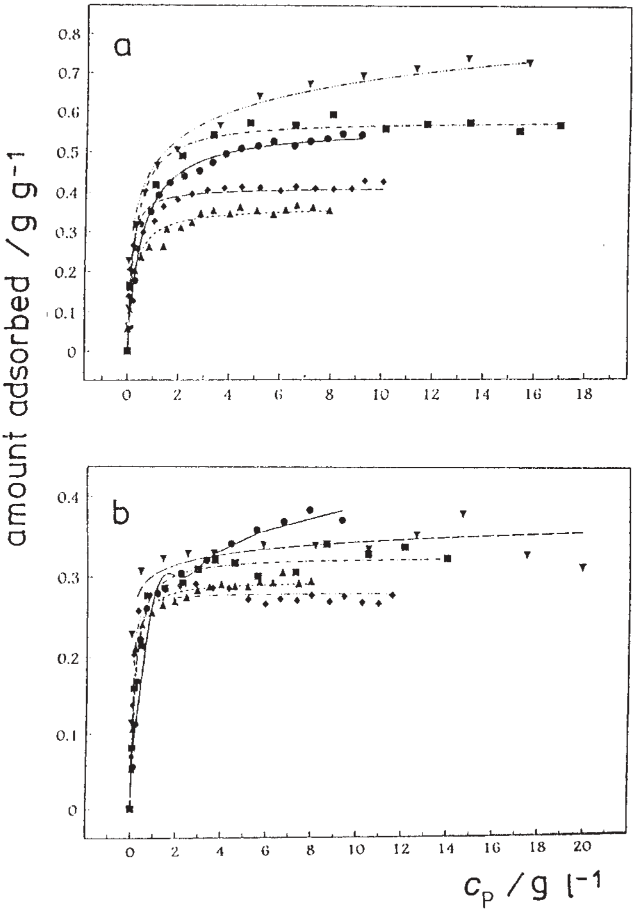

Figure 2. Adsorption isotherms of cationic PEOs on (a) sodium and (b) calcium montmorillonite. c_p is the polymer equilibrium concentration. ● $(TMA)_2$ PEO 1550, ■ $(TMA)_2$ PEO 4000, ▼ $(TMA)_2$ PEO 35000, ▲ TMA PEO 2000 M, ◆ TMA PEO 5000 M.

saturation values expressed in g/g increased with the molecular mass of cationic PEOs for sodium montmorillonite and were nearly constant for calcium montmorillonite. The number of $(TMA)_2$ PEO cations adsorbed (in meq/g) decreased with the molecular mass for both montmorillonites and was constant for both mono-endcapped PEOs. At saturation smaller amounts of these PEOs were adsorbed, as compared to divalent macrocations.

Increasing amounts of cationic PEOs displaced increasing amounts of sodium and calcium ions (Figure 3a, b). The amounts of cations displaced

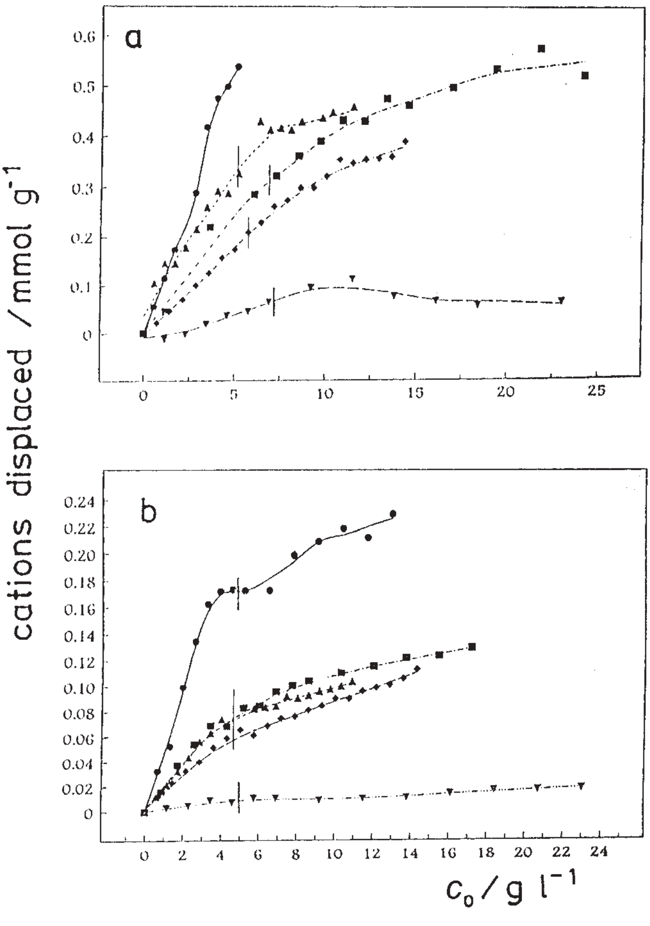

Figure 3. Amounts of cations displaced from montmorillonite by cationic PEOs. c_0 is the initial polymer concentration. The lines correspond to c_p = 2 g/l in Figure 2. ● $(TMA)_2$ PEO 1550, ■ $(TMA)_2$ PEO 4000, ▼ $(TMA)_2$ PEO 35000, ▲ TMA PEO 2000 M, ◆ TMA PEO 5000 M; a) sodium ions displaced from sodium montmorillonite, b) calcium ions displaced from calcium montmorillonite.

still increased when PEO adsorption reached the pseudoplateau. Evidently, cation exchange lagged behind adsorption. At low polymer concentrations most, but not all, PEO cations were bound by cation exchange. The degree of cation exchange increased with increasing polymer addition. The maximum amounts of cations displaced (at the end points of the curves shown in Figure 3) are somewhat higher than the amounts of cationic PEO adsorbed. It was not possible to remove the solid completely by centrifugation. Small amounts of the clay mineral could always be detected by laser light scattering. These dispersed particles carried certain amounts of sodium and calcium ions into the solution and may pretend to somewhat higher levels of cation exchange. The main cause may be that, under the influence of the adsorbed poly(ethylene oxide), small amounts of the interlayer cations were exchanged by protons. The general result is that the cationic PEOs are bound by cation exchange, and both cationic end groups of $(TMA)_2$ PEO displace exchangeable cations.

TABLE II

Maximum amounts of cationic PEOs adsorbed on sodium and calcium montmorillonite (from Langmuir plots)

Sample	Charge density*	Maximum amounts adsorbed			
		Na^+		Ca^{2+}	
	meq/g	g/g	meq/g	g/g	meq/g
$(TMA)_2$ PEO 1550	0.8802	0.570	0.502	0.374	0.329
$(TMA)_2$ PEO 4000	0.5252	0.582	0.306	0.326	0.171
$(TMA)_2$ PEO 35000	0.0556	0.713	0.040	0.329	0.018
TMA PEO 2000 M	0.4067	0.362	0.147	0.318	0.129
TMA PEO 5000 M	0.3555	0.411	0.146	0.281	0.100

* From bromide content, equivalents refer to the amounts of charges.

Colloid Stability

When cationic PEOs were added to the sodium montmorillonite dispersions (1% solid content), the colloidal distribution remained stable, the particles were not flocculated. The most remarkable observation was made with calcium montmorillonite dispersions (1% solid content, Figure 4). A pure calcium montmorillonite dispersion settled very rapidly. $(TMA)_2$ PEO 1550 and 4000 addition produced a turbid, viscous dispersion, which did not form a sediment. After some days, the dispersion with $(TMA)_2$ PEO 1550 became so stiff that the test tubes could be turned over without the dispersion

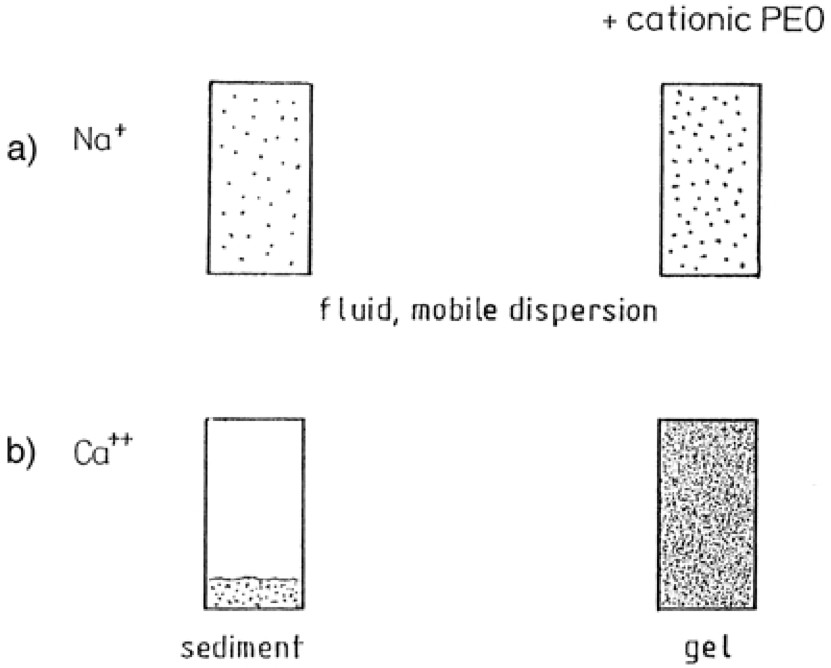

Figure 4. Influence of cationic PEOs on the colloidal stability of sodium and calcium montmorillonite: a) stabilization of colloidal sodium montmorillonite, b) stiffening and gel formation of calcium montmorillonite dispersions.

flowing out. The gel of $(TMA)_2$ PEO 35000 dispersions showed some synaeresis. Thus, the cationic PEOs stabilized the colloidal dispersion of calcium montmorillonite particles.

Flow Behavior

The influence of cationic PEOs on the flow behavior of dispersions was compared with the effect of unsubstituted PEOs. PEO addition slightly increased the plastic viscosity of sodium montmorillonite dispersions (Figure 5a); yield values were not created. Plastic viscosity η_p is interesting for practical applications; relative viscosity η_{rel} (plastic viscosity of the dispersion / plastic viscosity of the serum) reveals the influence of the clay mineral. Changes of η_{rel} with the polymer concentration were modest. The position of the maximum depended on the molecular mass (Figure 5b). Plastic viscosity of PEO/Ca^{2+} dispersions (Figure 5c) was smaller than that of PEO/Na^+ dispersions. Relative viscosity increased with polymer concentra-

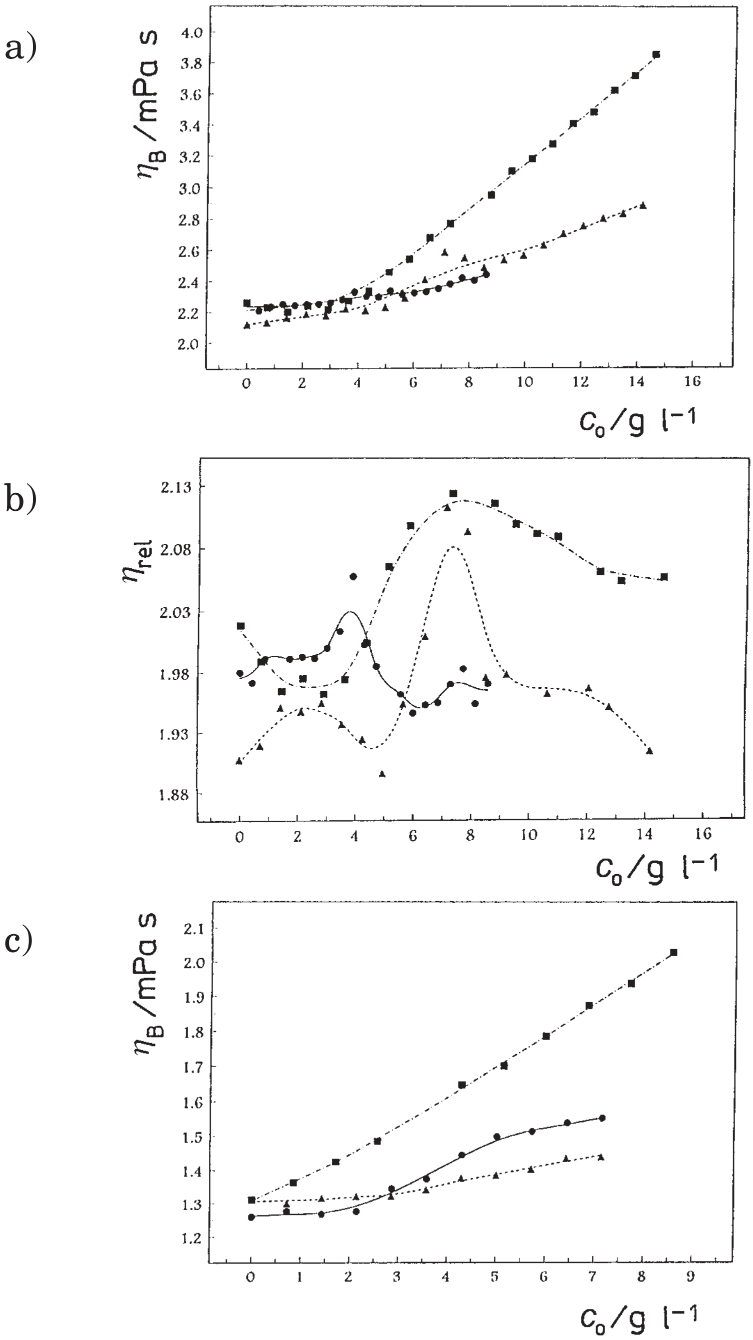

Figure 5. Continued on the next page.

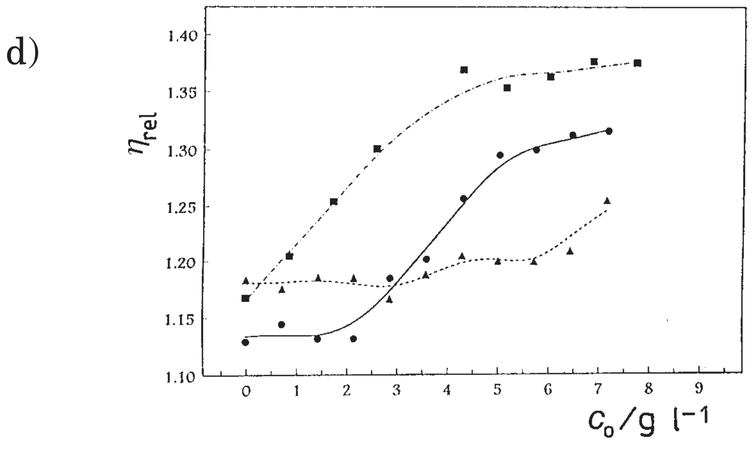

Figure 5. Flow behavior of sodium and calcium montmorillonite dispersions (1 percent solid content) in the presence of ● PEO 1550, ▲ PEO 20000, ■ PEO 35000, at 20 °C. c_0 is the initial polymer concentration. a, b) Plastic viscosity η_B and relative viscosity η_{rel} (plastic viscosity of the dispersion/plastic viscosity of the serum) of sodium montmorillonite dispersions; c, d) plastic viscosity η_B and relative viscosity η_{rel} of calcium montmorillonite dispersions.

tion but remained below the values of sodium montmorillonite dispersions (Figure 5d). No yield value was required to make the dispersions flow.

The viscosity of sodium montmorillonite dispersions in the presence of most cationic PEOs remained constant at 2–2.5 mPa s; the relative viscosity decreased slightly (Figure 6). When $(TMA)_2$ PEO 35000 was added, η_B increased with polymer concentration and η_{rel} showed a maximum. Yield values were not observed. Both viscosity values, η_B and η_{rel}, of calcium montmorillonite dispersions increased with the polymer concentration (Figure 7a, b). Bingham yield values τ_B were recorded with $(TMA)_2$ PEO 1550 (Figure 7c). A detailed rheological study of the gels (oscillatory and creeping experiments) will be reported in a separate paper.

Hysteresis effects were observed for $(TMA)_2$ PEO 35000/Na^+ (antithixotropic behavior) and all calcium montmorillonite dispersions. The flow behavior of the $(TMA)_2$ PEO 1550/Ca^{2+} dispersions changed from antithixotropic to thixotropic at a polymer concentration of c_0 = 4 g/l. The antithixotropic behavior of the $(TMA)_2$ PEO 4000/Ca^{2+} dispersion, as expressed by the hysteresis loop of the flow curves, increased between c_0 = 3 and 5 g/l PEO and remained constant at higher polymer dosages. The weak antithixotropic behavior in the presence of other cationic PEOs was slightly strengthened with increasing polymer addition.

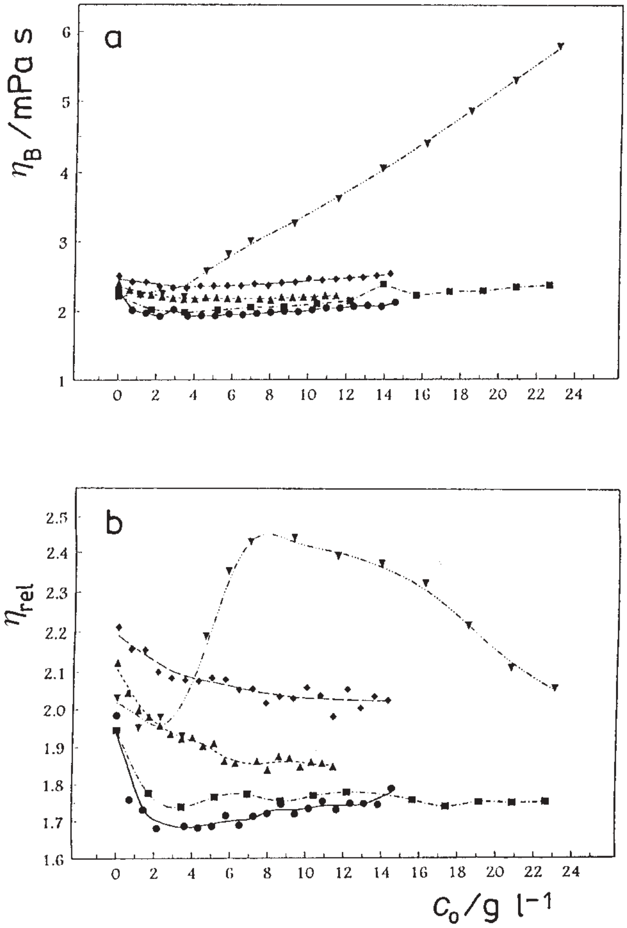

Figure 6. Influence of cationic PEOs on the flow behavior of sodium montmorillonite dispersions (1 percent solid content) at 20 °C. c_0: initial polymer concentration. ● $(TMA)_2$ PEO 1550, ■ $(TMA)_2$ PEO 4000, ▼ $(TMA)_2$ PEO 35000, ▲ TMA PEO 2000 M, ◆ TMA PEO 5000 M; a) plastic viscosity η_B, b) relative viscosity η_{rel}.

Influence of Temperature

The viscosity of sodium and calcium montmorillonite dispersions in the presence of unmodified PEO decreased with rising temperature. This behavior was also observed for sodium montmorillonite dispersions and cationic polymers but calcium montmorillonite dispersions behaved differently (Figure 8). At $(TMA)_2$ PEO 1550 concentrations above c_0 = 3 g/l, the plastic viscosity decreased with increasing temperature whereas the yield value τ_B

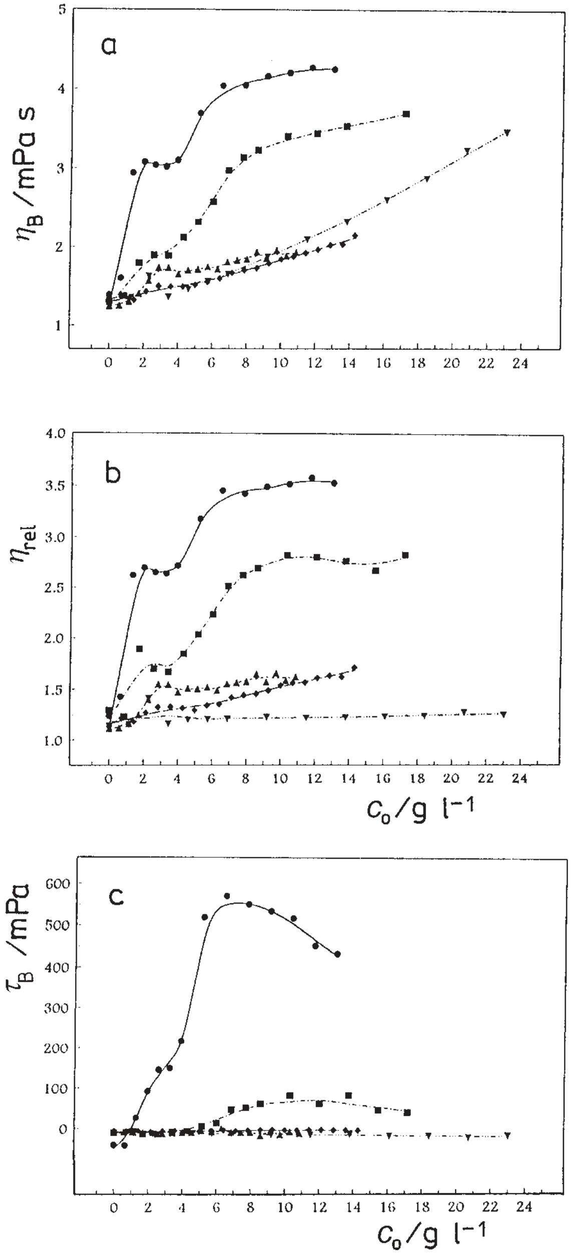

Figure 7. Influence of cationic PEOs on the flow behavior of calcium montmorillonite dispersions (1 percent solid content) at 20 °C. c_0: initial polymer concentration. ● (TMA)$_2$ PEO 1550, ■ (TMA)$_2$ PEO 4000, ▼ (TMA)$_2$ PEO 35000, ▲ TMA PEO 2000 M, ◆ TMA PEO 5000 M; a) plastic viscosity η_B, b) relative viscosity η_{rel}, c) Bingham yield value τ_B.

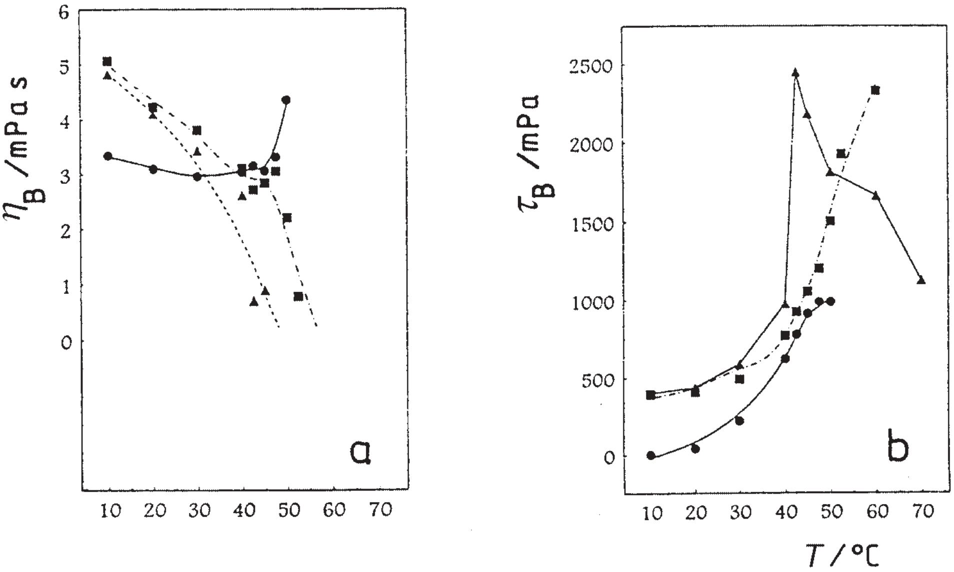

Figure 8. Temperature dependent changes of plastic viscosity η_B (a) and yield value τ_B (b) of $(TMA)_2$ PEO 1550 / calcium montmorillonite dispersions (montmorillonite content: 1 percent). c_o: initial polymer concentration, c_p: polymer equilibrium concentration; ● $c_o = 2.60$ g/l; $c_p = 0.37$ g/l; ▲ $c_o = 6.49$ g/l, $c_p = 3.29$ g/l; ■ $c_o = 10.29$ g/l, $c_p = 7.85$ g/l.

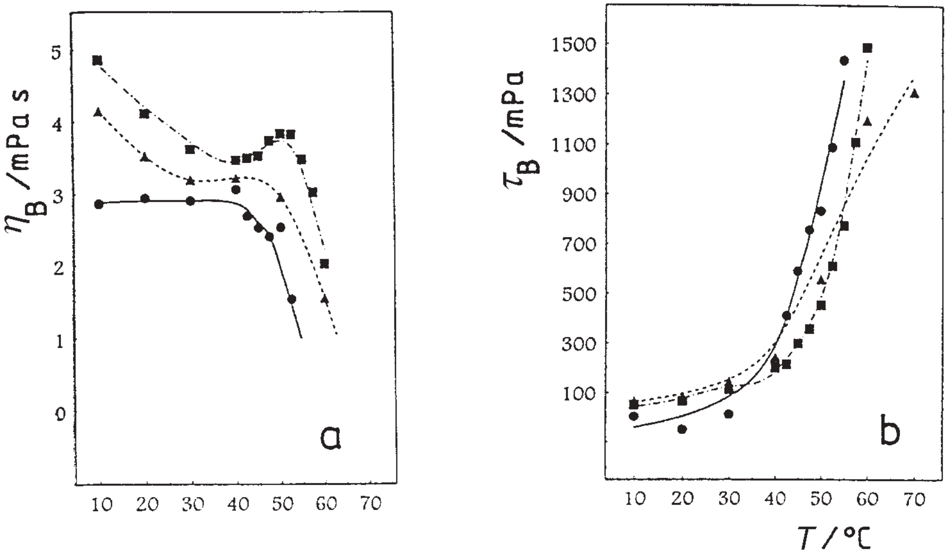

Figure 9. Temperature dependence of η_B (a) and τ_B (b) of $(TMA)_2$ PEO 4000 / calcium montmorillonite dispersions (montmorillonite content: 1 percent); ● $c_o = 5.15$ g/l, $c_p = 2.22$ g/l; ▲ $c_o = 8.58$ g/l, $c_p = 5.57$ g/l; ■ $c_o = 17.16$ g/l, $c_p = 13.92$ g/l.

rose steeply above 40 °C. At polymer additions of 6.49 g/l, τ_B reached a sharp maximum at 43 °C. Probably, a maximum of τ_B was also formed at higher polymer concentrations but the decreasing branch was outside the measuring range. Above 40 °C, the weak antithixotropic behavior changed into strong thixotropic flow. Dispersions containing $(TMA)_2$ PEO 4000 also showed a steep increase of the yield value above 40 °C (Figure 9) and a switch from antithixotropic to thixotropic behavior. $(TMA)_2$ PEO 35000 did not produce this effect, η_P decreased with temperature, and yield value and hysteresis effects were absent (Figure 10).

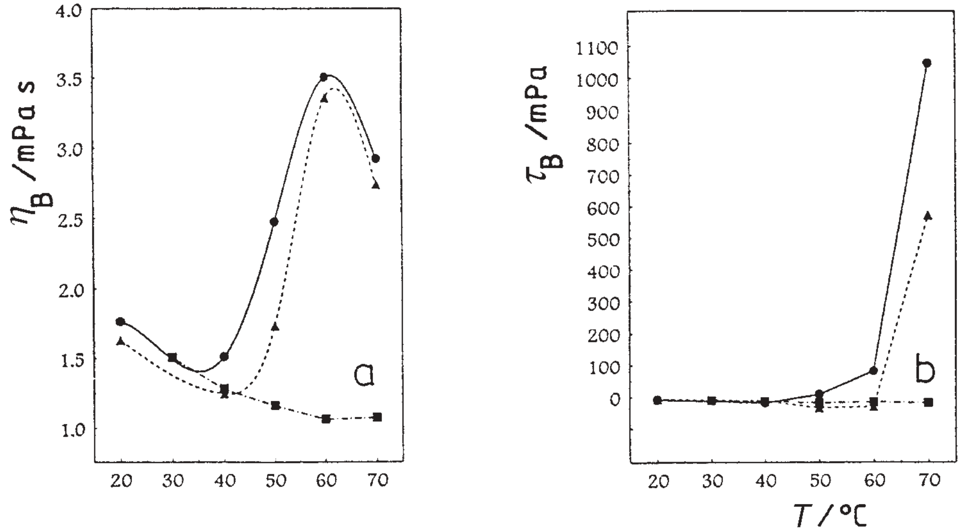

Figure 10. Temperature dependence of η_B (a) and τ_B (b) of cationic PEOs / calcium montmorillonite dispersions (montmorillonite content: 1 percent). ■ $(TMA)_2$ PEO 35000: c_o = 9.21 g/l, c_p = 5.44 g/l; ● TMA PEO 2000 M: c_o = 6.00 g/l, c_p = 2.99 g/l; ▲ TMA PEO 5000 M: c_o = 6.07 g/l, c_p = 3.18 g/l.

Viscosity of calcium montmorillonite dispersions in solution of TMA PEO 2000 M and 5000 M increased strongly above 40 °C to a maximum at 60 °C. The yield value was zero below 60 °C but rose steeply at higher temperature (Figure 10). The increase of τ_B lagged behind the steep increase of viscosity. Hysteresis was not observed below 40 °C, but a sharp maximum of thixotropy was found at 60 °C.

DISCUSSION

Adsorption and Cation Exchange

Displacement of considerable amounts of exchangeable cations reveals that adsorption of cationic PEOs mainly proceeds by cation exchange. The total exchange capacity of Wyoming montmorillonite is 0.95 meq/g. The maximum amount of macromolecules bound (Table II) and interlayer cations displaced (Figure 3), about 0.5 meq/g, is reached with the shortest di-endcapped PEO. Because of the space requirement of the poly(ethylene oxide) chain, not all inorganic cations are replaced by trimethylammonium groups and the number of $(TMA)_2$ PEO cations adsorbed (in meq/g) decreases with increasing molecular mass. As the amount of cations displaced corresponds to the amounts (in meq/g) of macrocations adsorbed, each trimethylammonium end group must be attached to a negative surface charge, that is, both end groups of the divalent macrocation are in contact with the surface. As the colloidal dispersion of sodium montmorillonite particles is not flocculated by cationic PEOs, bridging between particles is excluded. The way the samples were prepared (adding slowly the diluted montmorillonite dispersion to the solution of modified PEO) contributed to the enhanced stability because all silicate layers were surrounded and immediately covered by the macrocations (Figure 11a). The colloidal distribution is stabilized by envelopes of poly(ethylene oxide) around the silicate layers or thin packets of them. In addition to steric stabilization, electrostatic repulsion contributes to the stability because only a certain amount of sodium and calcium ions is replaced by trimethylammonium groups (Table II). As the envelopes (lyospheres)[18] contain considerable amounts of water, the van der Waals attraction is reduced and the electrostatic repulsion becomes more dominant.[19]

An interesting aspect is that the absorbed amounts of TMA PEO monocations are distinctly smaller than the amounts of dications of similar molecular mass. This seems to have kinetic reasons. A large molecule with only one charged group, probably buried in the coil, will be adsorbed more slowly than a macromolecule with two charges.

A sodium montmorillonite dispersion consists of separated silicate layers or thin packets of them (Figure 1). All sodium ions can be easily displaced by trimethylammonium groups (Figure 11a). In contrast, the calcium montmorillonite dispersion consists of particles composed of many silicate layers. These particles settle rapidly and form a sediment. Macrocations penetrate between the particles, and macromolecular bridges are easily formed. Most of the exchangeable calcium ions are constrained in the interlayer space of the particles. Nevertheless, large amounts of cations are displaced by cationic PEOs with molecular masses ≤ 5000. Therefore, inter-

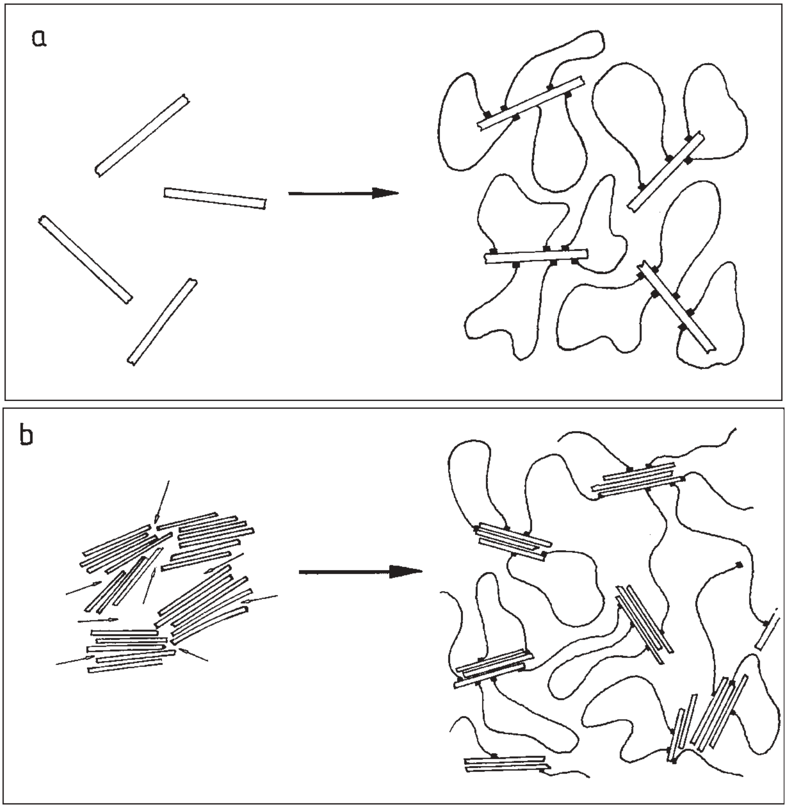

Figure 11. Schematic representation of the influence of cationic PEOs on the colloidal distribution of sodium and calcium montmorillonite.
a) Sodium montmorillonite: the macrocations adsorb onto the dispersed silicate layers and contribute to stabilization of the colloidal distribution.
b) Calcium montmorillonites: the macrocations are adsorbed on the particles and penetrate between the silicate layers at many points (arrows). A part of these macromolecules form bridges and create a voluminous network, which is expanded by the repulsion between the particles.

layer cations must be exchanged by trimethylammonium groups. The macrocations penetrate to some extent into interlayer spaces. The particles are split at zones of weak contacts and at dislocations between coherent domains (arrows in Figure 11b)[20–22] and a certain degree of delamination is attained. When the $(TMA)_2$ PEO cations penetrate between silicate layers, their end groups get attached to adjacent silicate layers and, by splitting the particles, they bridge the fragments (Figure 11b). This reaction proceeds slowly, and the dispersion stiffens within certain time periods. In particular, the large cation $(TMA)_2$ PEO penetrates very slowly into the narrow slits between particles and into some disordered interlayer spaces.

Only a certain fraction of poly(ethylene oxides) form bridges. Other macrocations adsorb on one particle only, probably in the form of loops with both charged end groups attached to negative surface charges of the same layer. These poly(ethylene oxides) contribute to the repulsion between the particles and keep apart the strands or bands of bridged particles so that voluminous networks form.

Probably, the TMA PEOs stiffen the calcium montmorillonite dispersion by the same mechanism. The positive end groups of mono-endcapped PEOs are bound by the surface charges. Methyl end groups are adsorbed on the silicate surface by van der Waals forces and dip between the surface oxygen atoms.[23,24]

Flow Behavior

The plastic viscosity of sodium montmorillonite dispersed in cationic PEO solutions (Figure 6) changes in a similar way as in the presence of pure PEO (Figure 5a). The different type of interaction with the clay mineral is expressed by relative viscosity. The τ_{rel} maxima in the PEO solutions are probably caused by interparticle bridging at intermediate polymer concentrations. The relative viscosity of the dispersions with cationic PEOs decreases at smaller polymer concentrations, then remains constant because the interactions are always repulsive. It shows a maximum in the presence of $(TMA)_2$ PEO 35000. Probably, a few bridges form between the particles. However, the contacts are not strong enough to create a yield value.

The most important aspect is the stiffening of calcium montmorillonite dispersions by cationic PEOs. In pure PEO, τ_{rel} increases slightly (Figure 5d) because of a certain complex formation between calcium ions and poly(ethylene oxide) segments.[25–27] Viscosity is much more enhanced when $(TMA)_2$ PEO 1550 and 4000 are added (Figure 7). The data in Figure 7 represent initial states of stiffening. As mentioned above, the dispersions stiffen within days and, eventually, become rigid gels. Rheological measurements, however, were performed with samples shaken 24 hours after mixing the components. As macrocations penetrate between particles and into some interlayer spaces between incoherent domains, the flow behavior of the polymer/calcium montmorillonite dispersions is antithixotropic because shearing promotes delamination and thus increases the gel strength.

Several systems used in practical applications show long-term stiffening when bentonites or synthetic hectorites[28] are added. The main cause is also seen in the slowly proceeding disarticulation of the particles.

There are two further interesting aspects of the flow behavior. One is the influence of salts, which will be discussed in a further paper, the other is the influence of temperature on the viscosity of the calcium montmorillonite dispersions (Figures 8–10).

The changes of viscosity and yield values with rising temperature reveal the interplay between (i) increased delamination of the particles and, therefore, increased gel strength at zero or low shear rates and (ii) fragmentation of the network at high shear forces which, depending on the numbers of flowing units produced, increases or decreases viscosity. The apparent viscosity of calcium montmorillonite in $(TMA)_2$ PEO 1550 and 4000 solutions decreases with rising temperature but the yield value increases steeply at 40 °C. Higher temperatures promote penetration of the macrocations between and into calcium montmorillonite particles. The number of bridges and, therefore, the yield value increases. At higher temperature and shear rates the network is fragmentated more easily into smaller units and plastic viscosity becomes smaller than at room temperature. The steeper decrease above 50 °C to 60 °C may result from the reduced immobilization of water when hydrogen bridges between water and CH_2CH_2O-segments are broken.

The viscosity increase in the presence of the mono-endcapped TMA PEO (Figure 10) is more difficult to explain. When, at enhanced temperature and high shear rates, a cationic end group of $(TMA)_2$ PEO spanning the distance between two particles loses contact with the surface, the positive charge is attracted by another negative surface site at the same particle (forming a loop) or at a neighboring particle (forming a bridge). More and more loops are formed during shearing so that the network is fragmented and viscosity decreases. In the case of monocations, one chain end is in weak contact with the silicate layer. When this group is desorbed by shearing, the interaction is too weak to form a second contact at the surface of the same or another particle. The network is decomposed into a large number of small units. Also, the macromolecules point into the solution and increase the viscosity more strongly than loops do. Both effects increase the viscosity with rising temperature. The behavior of TMA PEO and $(TMA)_2$ PEO montmorillonite particles may be compared with that of hairy lattices. The particles with the hairs extended into the solution show a higher viscosity than the particles with collapsed hair after heating.[29,30]

The switching of antithixotropic to thixotropic behavior at higher temperature is a direct consequence of these processes. After fragmentation of the network, a number of cationic end groups of $(TMA)_2$ PEO may remain free during shearing but can anchor at a neighboring particle when the dispersion remains in rest so that viscosity increases. In contrast, the methyl end groups of TMA PEOs interact only weakly with the silicate surface and latching of the methyl end groups between surface oxygen atoms is promoted by shearing: antithixotropic behavior is more pronounced above 40 °C.

CONCLUSION

The colloidal stabilization of calcium montmorillonite by cationic poly(ethylene oxides) may be of practical interest. Addition of these polymers impedes settling of the particles, which is often undesirable in practical applications of bentonites. Even calcium montmorillonite dispersions with a solid content as small as 1 percent are stiffened and form gels. Another interesting aspect is the strongly increasing yield value, but decreasing viscosity above 40 °C, in the presence of di-end-capped poly(ethylene oxides) with lower molecular masses.

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SAŽETAK

Površinska modifikacija bentonita. II. Modifikacija montmorilonita s kationskim poli(etilen-oksidima)

Jörn Dau i Gerhard Lagaly

Poli(etilen-oksidi), PEO, s molekularnim masama između 1550 i 35000 modificirani su zamjenom završnih OH grupa bromom i nakon toga, zamjenom broma trimetilamonijevim skupinama. Poli(etilen-oksidi) s jednom završnom OH skupinom pripravljeni su iz poli(etilen-oksid)-monometil-etera. Tako pripravljeni kationski PEO snažno se adsorbiraju na montmorilonit i vežu putem kationske zamjene. Kationske završne grupe poli(etilen-oksida) istiskuju vanjske i unutarnje zamjenljive katione. Makrokationi nisu flokulirali disperziju montmorilonita, već su je stabilizirali putem nastajanja liosfera oko čestica (sterička stabilizacija). Nastale liosfere usporavaju taloženje dispergiranih čestica kalcijevog montmorilonita čak i u slučaju 1 %-tnog sadržaja čvrste faze; gel koji pri tome nastane, zgusne se nakon stanovitog vremena. To je uzrokovano razdvajanjem čestica montmorilonita pri čemu se do određenog stupnja, zbiva proces delaminacije montmorilonita. Početna faza nastajanja gela proučavana je mjerenjem viskoziteta (low-shear viscosimetry). Interesantan je aspekt temperaturna ovisnost vrijednosti protoka. Viskoznost kalcijeva montmorilonita dispergiranog u otopini PEO s dvije završne skupine smanjuje se iznad 40°C – 50 °C dok se vrijednost iscrpka naglo smanjuje u istom temperaturnom području.