Influence of the exchangeable cations on stability and rheological properties of montmorillonite suspensions

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Abstract: The effects of NaCl and CaCl₂ on the colloid stability and rheological properties of Na- and Ca-montmorillonite dispersions were studied. The distribution of cations between the surface and the bulk phase was determined. For both of monocationic montmorillonite, the critical coagulation concentration were 250 mmol NaCl/dm³ and 2 mmol CaCl₂/dm³. The changes in the Bingham yield stresses of Na- and Ca-montmorillonite dispersions as functions of the NaCl and CaCl₂ concentration could be explained in terms of the surface excess amount and equilibrium concentration of the cations, the second electroviscous effect and the formation of a gel structure.

Key words: Aqueous clay suspensions, coagulation, rheology, ion-exchange, montmorillonite.

Introduction

Detailed studies have been reported on the colloid stability of montmorillonite dispersions, their coagulation by different salts, and the dependence of their rheological properties on montmorillonite concentration, pH, and electrolyte concentration [1–6]. The properties of clay dispersions are far from those of monodisperse latex dispersions, which can be regarded as model systems for studying colloid stability and rheology of concentrated dispersions.

These latter model systems can be prepared almost optionally, and in this way the effects of various parameters, e.g., particle size, surface charge density, and the type of surface charged groups can be examined. The effects of particle size, surface charge, volume fraction, salts and pH on the rheological properties of polymer latices have been investigated widely [7–14]. The dependence of the viscosity of latex dispersions on the ionic strength at low electrolyte concentrations is explained by electroviscous effects [7, 8, 11]. Several models exist to describe the flow properties of coagulated colloidal dispersions [7, 12–14]. The single-particle and the hard-floc models must be considered as approximative models. The elastic-floc model provides a consistent physical interpretation of the linear region of the flow curve and the Bingham yield value for plastic-pseudo-plastic systems. A self-consistent field theory has been developed by Russel and Benzing [9, 10] for the interpretation of the viscoelastic properties of ordered latices. This model predicts reasonably the osmotic pressure and shear modulus of ordered monodisperse latices as functions of surface charge density, electrolyte concentration and volume fraction.

Clay suspensions are much more complicated systems than latex dispersions. The particles are anisometric, polydisperse and the properties depend strongly on the origin of the clay. In addition, there is a very important, unique property of montmorillonite and kaolinite particles: the heterogeneous distribution of charges on the platelets. The charge of the basal planes is negative, due to the isomorphous substitutions in the crystal lattice [1], while it is positive on the edge surfaces at acidic pH [1, 3]. The charge of the basal planes is compensated by the exchangeable cations. The structure of the electrical double-layer is determined not only on the ionic strength, but also on specific adsorption affinities of the cations for the silic-
ate layer [15, 16]. Spontaneous ion-exchange reactions take place in all non-homoionic systems. The equilibrium process depends on the surface charge density or surface potential, the salt concentration, and the valency and specific adsorption of cations on the surface and in the bulk [17, 18]. The charge on the edges is pH-dependent. When the positive edge charge is small, it can only be effective when the salt concentration exceeds a certain value, so that there is no longer spillover of the electrical double-layer of the basal planes [19]. The edges can be recharged by the specific adsorption of certain anions [1, 3, 6]. Different types of particle aggregation, mainly edge-to-face and face-to-face, depending on the pH and salt concentration, can occur in dilute and concentrated suspensions [1, 3, 5, 6, 19].

This short survey of the complicating factors involved in clay suspensions shows that not only the interpretation but also the planning of the experiments is rather difficult. An attempt has been made to explain the plastic flow behavior of clay suspensions [20], which gives a satisfactory description of the behavior of rapidly coagulating kaolinite sols. Qualitative explanations have been proposed for the dependence of the flow behavior on the salt concentration and pH based on different types of particle aggregation [1, 2, 5, 6].

In this paper we have investigated colloid stability, sensitivity against salts and dependence of the rheological properties of sodium and calcium montmorillonite dispersions. The charge heterogeneity of the platelets was eliminated by recharging the edges, and the ion-exchange process was followed by determination of the concentrations of both cations in solutions.

**Experimental**

Montmorillonite was obtained from Kuzmice (Czechoslovakia) bentonite. After peptization with Na$_2$CO$_3$ (2.5 g/100 g bentonite), the $<1 \mu$m fraction was separated by sedimentation. Residual Na$_2$CO$_3$ was removed by acidifying (HCl) up to pH 4. Homionic sodium and calcium forms were prepared by dispersion of the montmorillonite in NaCl or CaCl$_2$ solutions. The final salt concentration of the dilute suspensions was 1 mol/dm$^3$. After standing for 1 day, the suspensions were centrifuged (4 000 rpm, 10 min). This treatment was repeated three times in order to obtain homoionic samples. Excess electrolyte was removed by washing with distilled water, and then by dialysis against distilled water. The final concentration of chloride ions in the suspensions was less than $10^{-3}$ mol/dm$^3$. Suspensions were concentrated by evaporation of a given amount of water (sodium montmorillonite) or by centrifugation (calcium montmorillonite). The cation-exchange capacity of the montmorillonite, 0.80 ± 0.01 meq/g, was determined by the method of Fraser and Russel [21]. Montmorillonite pastes were stored in a refrigerator at 2$^\circ$–3$^\circ$C.

Samples for coagulation and rheological measurements were made by the dilution of montmorillonite pastes with calculated amounts of NaCl or CaCl$_2$ solutions, and a specific amount of 50 $\mu$mol (NaPO$_3$)$_6$ per gram montmorillonite was added to all samples to recharge the positive edges [3]. Suspensions were homogenized by means of repeated ultrasonication during 5 min. The coagulation values of 2 g/dm$^3$ Na- and Ca-montmorillonite suspensions were determined by visual inspection of coagulation series with increasing NaCl or CaCl$_2$ concentrations after standing for 24 h.

Rheological measurements were made with a Searle-type Rotovisco test-2 (GDR) rotational viscometer. The shear rate was gradually increased and then decreased between 5 and 1312 s$^{-1}$. 50 g/kg Na- and Ca-montmorillonite suspensions containing 0 to 300 mmol/kg NaCl or 0 to 100 mmol/kg CaCl$_2$ were measured at 25 ± 0.5 $^\circ$C. After preparation, the suspensions were left for 2 days to reach the equilibrium state of ion-exchange. Before the rheological measurements all samples were sheared for 2 min from shear rate 5 to 1312 s$^{-1}$, and were then left at rest for 5 min.

The concentrations of Na$^+$ and Ca$^{2+}$ in all suspensions were measured with ion-selective electrodes (OP-Ca- and Na-0711P, Radelkis, Hungary) and a precision pH-meter (OP-205/1, Radelkis, Hungary). After ultracentrifugation (20 000 rpm, 30 min, UCF-3180 MOM, Hungary), the Na$^+$ and Ca$^{2+}$ contents of the supernatants were also determined with an atomic absorption spectrometer (Zeiss AAS 1, GDR). The equilibrium concentrations of Na$^+$ determined by both methods agreed relatively well. The deviations from their averages were between 0.2% and 12%. Greater differences were found for the Ca$^{2+}$ concentrations.

**Results and discussion**

**Colloid stability**

The salt stability of two systems was measured: i) homoionic systems in which no ion-exchange is apparent (i.e., Na-montmorillonite + NaCl, and Ca-montmorillonite + CaCl$_2$), and ii) non-homoionic systems in which an ion-exchange occurs (i.e., Na-montmorillonite + CaCl$_2$, Ca-montmorillonite + NaCl) (Table 1). It is surprising that the coagulation values depend only on the coagulating salts and not on the cations originally present in the montmorillonite samples.

The coagulation values for the homoionic systems agree relatively well with literature data [1, 3, 6] and

<table>
<thead>
<tr>
<th>Homionic samples</th>
<th>Coagulation value, mmol/dm$^3$</th>
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<tbody>
<tr>
<td></td>
<td>NaCl</td>
</tr>
<tr>
<td>Na-montmorillonite</td>
<td>250</td>
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<tr>
<td>Ca-montmorillonite</td>
<td>250</td>
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Table 1. Coagulation values for different montmorillonite-salt systems