

RHEOLOGICAL PROPERTIES AND THIXOTROPIC BEHAVIOUR OF KAOLINITE SUSPENSIONS

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The rheological properties of Ca-Na-kaolinite and of monocationic Na-kaolinite were investigated as a function of the concentration of the suspension and of the electrolyte used as coagulating agent. The structure of aggregates of both types is changed by bivalent cations present in the electrolyte, as reflected by rheological curves and hysteresis loop.

Introduction

Structure formation of particles and rheological properties of suspensions of clay minerals, such as kaolinite, can be varied between wide limits by modifying the interactions between the particles. In connection with the formation of structure, VAN OLPHEN [1] supposes aggregated or flocculated states and their combinations. He defines the aggregated state as coming about by face-to-face interaction, whereas in flocculation edge-to-face or edge-to-edge associations are characteristic. He takes into account the double layers of positive charge formed at the edges under suitable conditions. The changes of rheological properties are explained — especially in the case of sols and gels of montmorillonite — by changes in character and strength of the interactions between the double layers of positive charge at the edges and those of negative charge present at basic faces. MICHAELS and BOLGER [2] consider the flocs as stable flow units forming larger aggregates. At low shear rates the aggregates form a loose network, which determines the plastic and structural properties of the suspension. At high shear rates the aggregates break down into individual flocs. FLEGMANN, GOODWIN and OTTEWILL [3] stated that the yield stress of monocationic kaolinite suspensions, plotted as a function of pH, changes according to a maximum curve. The maximum observed appeared to occur at a zero point of charge of the kaolinite edges.

Materials and methods

For preparing the material, Zettlitz kaolin was desaggregated with Na_2CO_3 . On the basis of our earlier investigations, addition of 0.2 g Na_2CO_3 to 100 g kaolin was found optimal. The material treated with Na_2CO_3 solution was dried over water bath. A suspension of 4% concentration was prepared from the sample and

the particles of $d \leq 2 \mu\text{m}$ were separated by sedimentation. The fraction to be used was separated from the supernatant containing particles of colloidal dimensions by centrifugating only once. The sample obtained can be considered as Ca-Na-kaolinite, as according to our earlier experiences no total ion exchange occurs with Na_2CO_3 [4].

From the Ca-Na-kaolinite, monocationic Na-kaolinite was obtained by acidic and subsequent NaCl treatment as follows. The pH of the suspension was adjusted with HCl to $\text{pH}=4$, thus decomposing the Na_2CO_3 . Then the material was treated with $2N$ NaCl and purified by centrifugation until the Cl^- ion concentration of the supernatant decreased to $1.5 \cdot 10^{-3}$ mole. The rheological properties and thixotropic behaviour of both Ca-Na- and monocationic Na-kaolinite were studied in suspensions of different concentrations, as well as with constant kaolinite concentration in the presence of different quantities of coagulating electrolyte.

The measurements were made with a viscometer type "Rotovisco". The Bingham yield stresses τ_B were obtained by extrapolating the linear sections of the flow curves in the usual way. We used principally these data for rheological characterization of the materials.

Results and discussion

Na-kaolinite suspension of relatively lower concentration (20%) exhibits a low yield stress ($\tau_B=20$ dynes/cm²) without showing a hysteresis loop (Fig. 1). With increasing concentrations the yields stress increases; from 30% concentration this increase is more important and a hysteresis loop appears, the area of the latter also increases with concentration.

In the case of Ca-Na-kaolinite the hysteresis loop can be observed already at 20% concentration, but is of opposite sense. The τ values obtained with decreasing r.p.m. being higher then those increasing r.p.m. (Fig. 2), the system exhibits "anti-

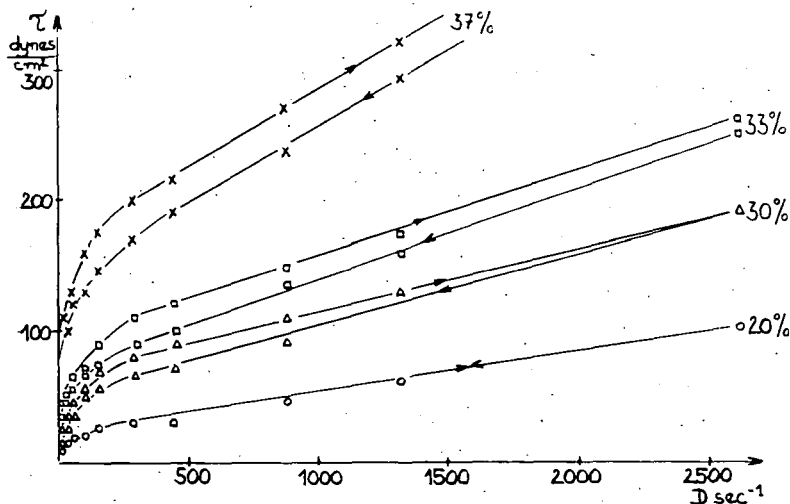


Fig. 1. Flow curves of Na-kaolinite suspensions of different concentration

thixotropy". With increasing concentration, this phenomenon becomes more pronounced. In suspensions of this type the effect of prolonged shear on flow properties was also studied. After determining the flow curves in the usual way (lower curves in

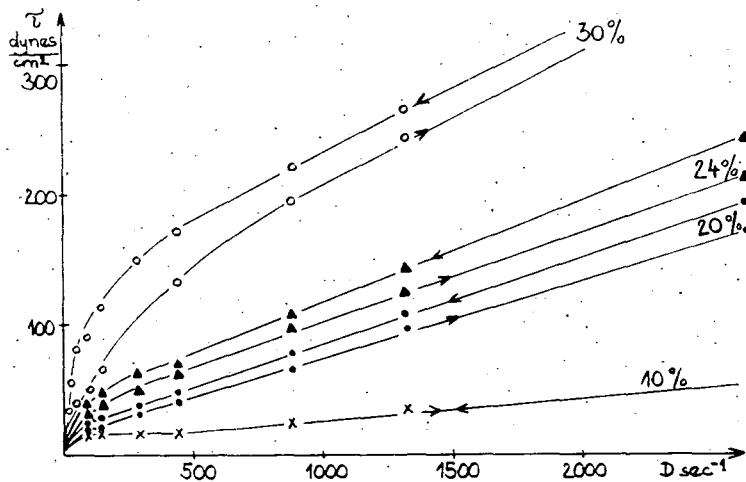


Fig. 2. Flow curves of Ca-Na-kaolinite suspensions of different concentration

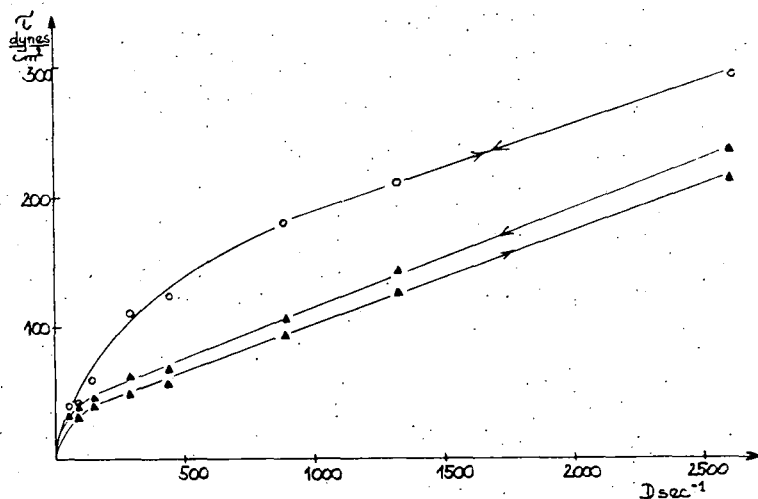


Fig. 3. Effect of shear on the flow curves of 24% Ca-Na-kaolinite suspension

Fig. 3), the suspension was sheared with the highest r.p.m. ($D=2620 \text{ sec}^{-1}$) for 30 minutes, and the flow curves were recorded again (upper curve in the figure). As a result, the τ values become significantly higher, whereas the hysteresis loop disappeared.

This difference in behaviour can be explained with the different rates of aggregation and differences in the interactions (adhesive forces) between the particles. The bonds between the particles of the Na-kaolinite suspension, in which the adhesion is low, can be more easily interrupted by shearing and regenerate more slowly, thus giving a regular hysteresis loop. In contrary, in the Ca-Na-kaolinite suspensions, the adhesive forces between the particles being higher, the system will be in more aggregated state. On the mechanical impact of the shearing, disaggregation, possibly also orientation of the particles will occur. At the same time, while the number of the particles is increased by the shear, the tendency of the system to rebuild the structure is comparatively high; thus higher τ values are obtained in the descending branch of the curve than in the ascending branch. The significant increase of the τ values after shearing with the maximum r.p.m. shows that the disaggregation proceeded further. The number of the particles forming the structure having thus reached a maximum, no further increase can be found in the descending branch, and thus the hysteresis loop disappears.

The influence of Ca^{2+} ions on the rheological properties of Ca-Na- and Na-kaolinite was also studied. The Bingham yield stress of 20% suspensions of different CaCl_2 concentrations is shown in Fig. 4. The τ_B values of the Ca-Na-kaolinite,

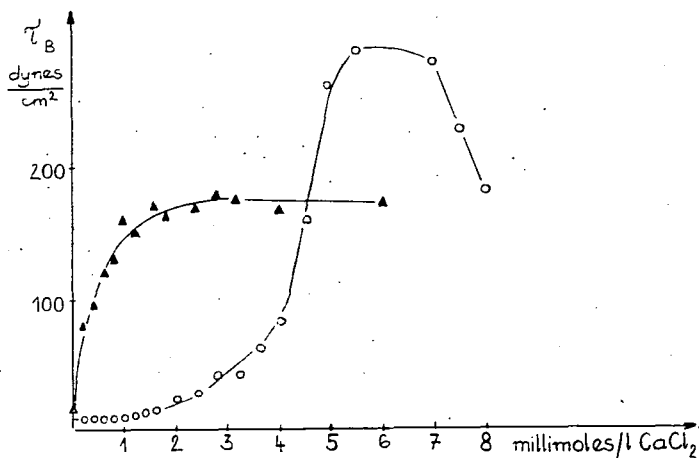


Fig. 4. Bingham yield stress of 20% Ca-Na-kaolinite and Na-kaolinite suspensions of different CaCl_2 concentrations. ▲ Ca-Na-kaolinite, ○ Na-kaolinite

which is, as we have seen, in a slightly aggregated state, increase steeply in the presence of small quantities of CaCl_2 , but reach a constant value at 2 mmole/l CaCl_2 concentration. The flow curves show antithixotropy at all CaCl_2 concentrations studied. At the same time, the effect of the CaCl_2 on a thoroughly washed Na-kaolinite suspension (of $0.3 \cdot 10^{-3}$ mole Cl^- ion concentration) is minimal up to 2 mmole/l concentration added. With further increasing CaCl_2 concentrations the τ_B values show, however, a steep increase exceeding the maximum observed

with Ca-Na-kaolinite. The τ_B vs. CaCl_2 concentration curve of a Na-kaolinite suspension of 40% washed in a usual way (of $1.5 \cdot 10^{-3}$ mole Cl^- ion concentration) shows an essentially similar curve (Fig. 5). Some difference can be observed in the beginning of the curve, a well expressed minimum at low CaCl_2 concentrations being observable in the latter case.

The differences in the effect of the Ca^{2+} ions on the rheological behaviour of the samples can be interpreted by taking into account the different states of aggregation of the starting material. The strength of the network of the Ca-Na-kaolinite suspensions, more aggregated from the beginning, will be increased by the influence of small quantities of CaCl_2 , resulting in a steep τ_B curve. The increase of the adhesion may be attributed to a decrease of the thickness of the double layer rather than to ion exchange. In Na-kaolinite suspensions the flocculation process expressed by the increase of the yield stress starts at comparatively higher CaCl_2 concentrations. The minimum of the curve shown in Fig. 5 can be interpreted with changes of the charges (+) at the edges and (-) on the faces, caused by electrolyte, as presented by VAN OLPHEN in connection with montmorillonite. The steep ascension of the curve after the minimum represents the flocculation process as a result of increasing van der Waals forces.

We studied also the effect of CaCl_2 on the thixotropic behaviour of a 40% Na-kaolinite suspension. The thixotropy found at low CaCl_2 concentrations increases at higher concentrations, as shown by the broadening of the hysteresis loop at 3.3 mmole/l concentration (Fig. 6). Maximum thixotropy seems to be connected with a mild flocculating effect. With further increasing CaCl_2 concentration, the interactions between the particles become more intense and the breadth of hysteresis loop decreases; finally the loop disappears at 13.4 mmole/l concentration (Fig. 7). So no thixotropy is found in the system with maximum τ_B values. At CaCl_2 concentrations exceeding that corresponding to the maximum of τ_B , anti-thixotropy appears, similarly as in Ca-Na-kaolinite suspensions. The character of thixotropy or antithixotropy and their degree can be systematically varied by changing the interactions (adhesive forces) between the particles.

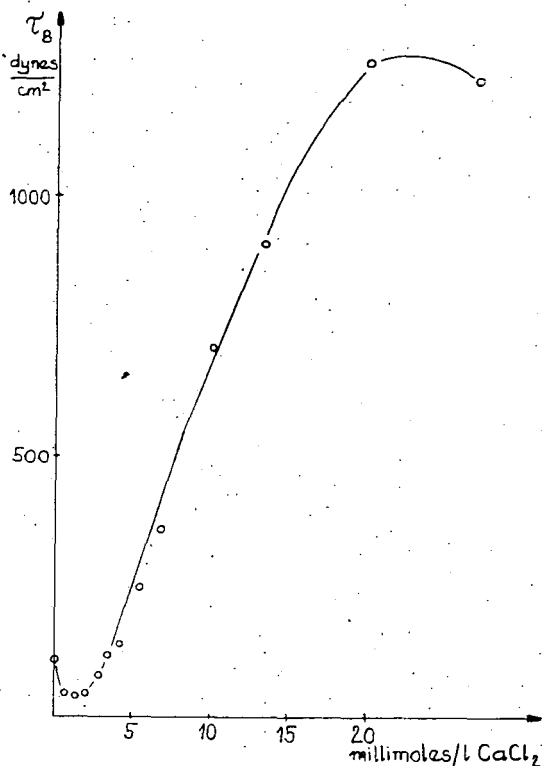


Fig. 5. Bingham yield stress of 40% Na-kaolinite suspensions of different CaCl_2 concentration

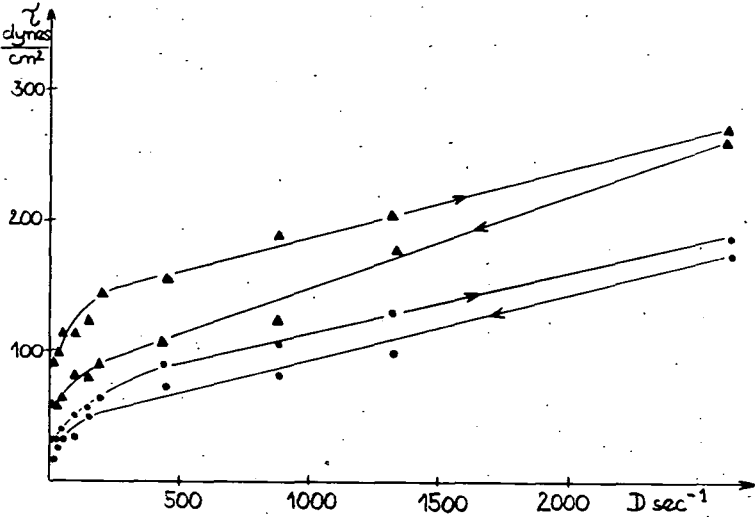


Fig. 6. Effect of CaCl₂ on the thixotropic behaviour of 40% Na-kaolinite suspension. CaCl₂ concentration: ● 0.67 mmole/l; ▲ 3.3 mmole/l

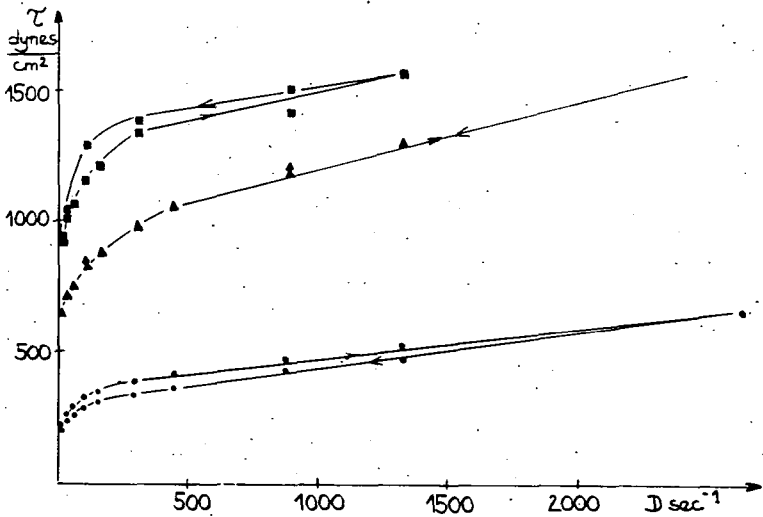


Fig. 7. Effect of CaCl₂ on the thixotropic behaviour of 40% Na-kaolinite suspension. CaCl₂ concentration: ● 6.7 mmole/l; ▲ 13.4 mmole/l; ■ 26.8 mmole/l

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РЕОЛОГИЧЕСКИЕ СВОЙСТВА И ТИКСОТРОПИЯ
КАОЛИНИТОВЫХ СУСПЕНЗИЙ

Ф. Санто, М. Гильде

Изучены реологические свойства Са-Na-каолинита и монокатионного Na-каолинита в зависимости от концентрации суспензии и коагулирующего электролита. Структура агрегатов, образующихся из образцов обоих типов, изменялась под влиянием двухвалентного катиона прибавляемого электролита. Происходящие изменения отразились в реологическом поведении и на виде гистерезисных петель.