The Effect of Some Salts and $(NaPO_3)_n$ Polymer on Viscosity of Na-Montmorillanite Slurry

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Summary: The rheological properties of the slurry that have been prepared Na-montmorillonite clay have been determined, the effects of NaCl, KCl, LiCl, $CaCl_2$ and $MgCl_2.6H_2O$ salts and $(NaPO_3)_n$ polymer have also been investigated at different concentrations. The changes in rheological properties of Na-montmorillonite slurry when salts have been added to concentration have been commented. Information on the vander waals and electrostatical interaction between the colloidal clay the bentonite-water systems is given.

Introduction

Montmorillonites are members of the smectite' family of minerals. The structure of montmorillonites and other similar smectite clays consists of two tetrahedral sheets separated by an octahedral sheet. The tetrahedral sheets contain tetravalent silicon and trivalent aluminium cations. The apeces of these tetrahed point toward one another and the oxygen anions at the tip of these tetrahedra form part of the octahedral sheet, which contains mostly trivalent aluminum with varying amounts of Fe^{2+}, Mg^{2+}. These units of tetrahedral and octahedral sheets are separated by layers of such hydrated exchangeable cations as Na^+ and Ca^{2+}. These cations are present to counterbalance a weak net negative charge on the structure resulting from internal chemical substitutions in the tetrahedral and octahedral sheets. This inter-unit layer is responsible for the properties and uses of various montmorillonites [1-3]. The exchangeable cations that exist between the montmorillonite layers are the effectible parameter on all characteristic properties.

The knowledge of rheological behaviour of montmorillonite-water systems is very important for technology and the analysis of great differences in the rheological behaviour of montmorillonite slips if different salts have added [4,5]. But there has been only a few publications on the rheological properties of Turkish montmorillonite despite the fact that there are very many montmorillonite blends in Turkey [6-11]. Describing their rheological properties would be useful for industrial which use montmorillonite, throughout the world.

The present work had two objectives: First, the determination of the fluidity of one prepared using a, Na-montmorillonite. Secondly, the development of a system with the desired fluidity by using salts and $(NaPO_3)_n$ polymers of various concentrations. In addition, the extent of the effects such as that of the type of montmorillonite and salt as well as of the concentration changes were studied and evaluated.

Results and Discussion

The zeta potential values determined for solutions with various concentrations are given in Figure 1. When electrolytes are added, if the cation in the electrolyte is sodium, the zeta potential increases for concentration values between 10^{-2} - 10^{-5}. If the cation in the electrolyte is calcium, for the same concentration values a decrease in zeta potential is observed. A more effective increase in zeta potential is obtained with increasing concentrations of Na-containing electrolytes which have relatively more active anions [12].

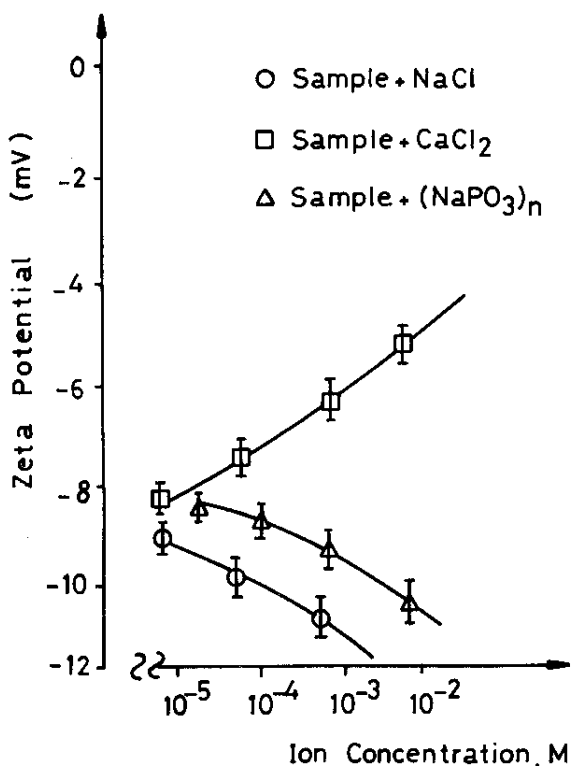The $\tau=f(\gamma)$ curve (Figure 2) for the sample, which are consistent with the Bingham platic flow model [13,14].

The change of the apparent viscosity of the montmorillonite slurry is given Figure 3 as a function of shear rate. The curve show sudden decrease at small shear rates indicating thixotropic properties of the sample.

Fig. 1: Zeta potential of sample as a function of NaCl, $CaCl_2$ and $(NaPO_3)_n$ concentration.
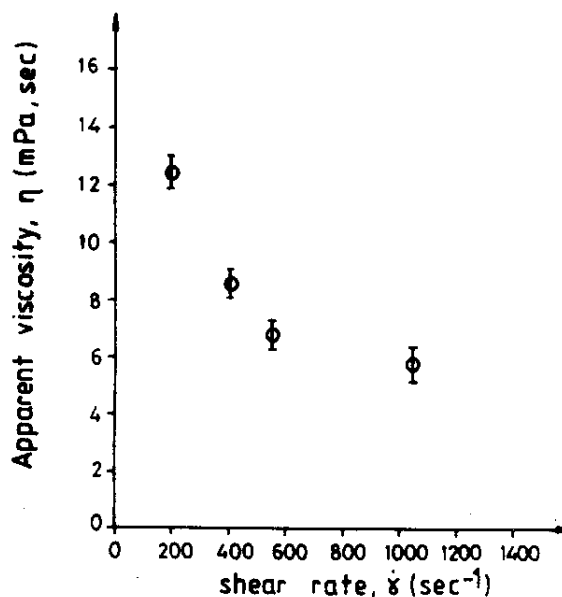

Fig. 3: Apparent viscosity versus shear stress.

The variation in gel strength with time has been determined by periodical recesses of the slurry (Fig. 4). As is observed in the sample, there is a continuous increase. Sodium-montmorillonite has the ability to form gel formation because of its high swelling property. The swelled particles can be disintegrated after some time giving numerous small particles thus, giving a large surface area. If the sodium-montmorillonite water system is prepared as slurry which provides the large water increase and a physical, reversible gel can be formed as a cluster. Besides, the repulsive electrostatic and van der Waals forces which bring the particles to equilibrium state contribute to gel formation.

In the second part of the study, the changes in the rheological properties of montmorillonite slips when various electrolytes have been added are examined by considering the effect of salt type and the electrolyte concentration separately. The change of the apparent viscosity depending on the electrolyte type are shown in Figure 5 as function

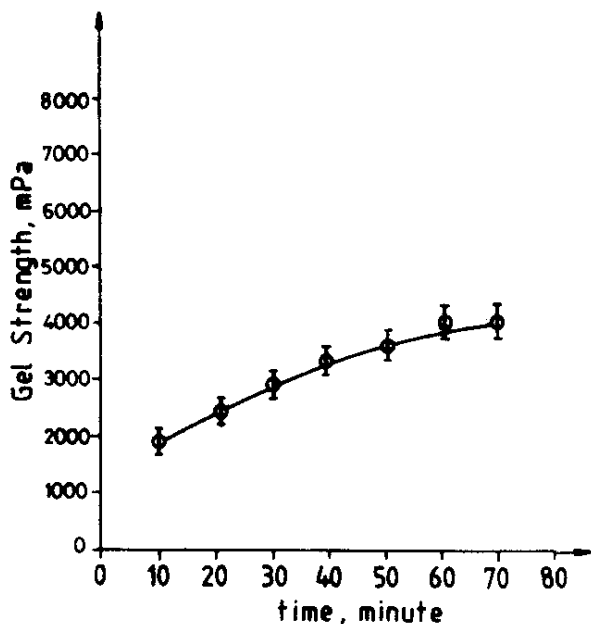Fig. 2: Shear rate-shear stress curves of sodium-montmorillonite slurry.

Fig. 4:   Variation of the gel strength with time.

of electrolyte concentration. According to this figure, the following observations would be obtained.

The major changes observed in the rheological properties of the electrolyte containing montmorillonite slip are results of the small ionic diameter and the very large ion-exchange capacity of sodium cation. The electrolytes, in order of decreasing effects, which cause changes in viscosity are listed below:

$$KCl > LiCl = MgCl_2.6H_2O > NaCl > CaCl_2$$

As shown in Fig. 5, an increase in the concentration of electrolyte (up to 3%) causes an increase in the observed viscosity for all types of electrolytes because of the long-range electrostatic repulsions between the interacting double layers [15]. Depending on the type of electrolyte, the increase in viscosity may continue, remain constant, or decrease.
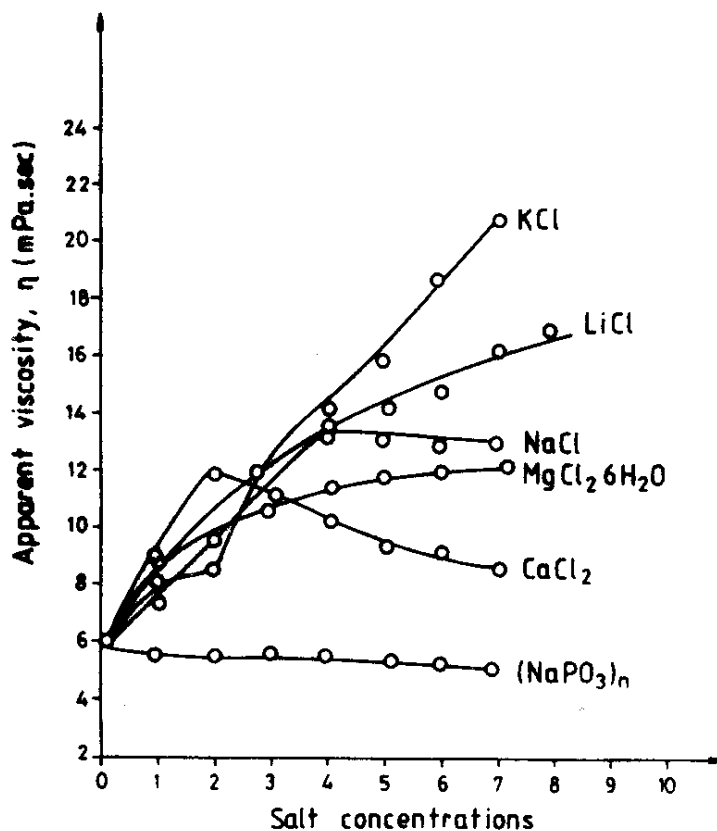

Fig. 5:   The change of the apparent viscosities of the sample, with concentrations of NaCl, KCl, LiCl, CaCl₂, MgCl₂ 6H₂O, (NaPO₃)ₙ polymer.
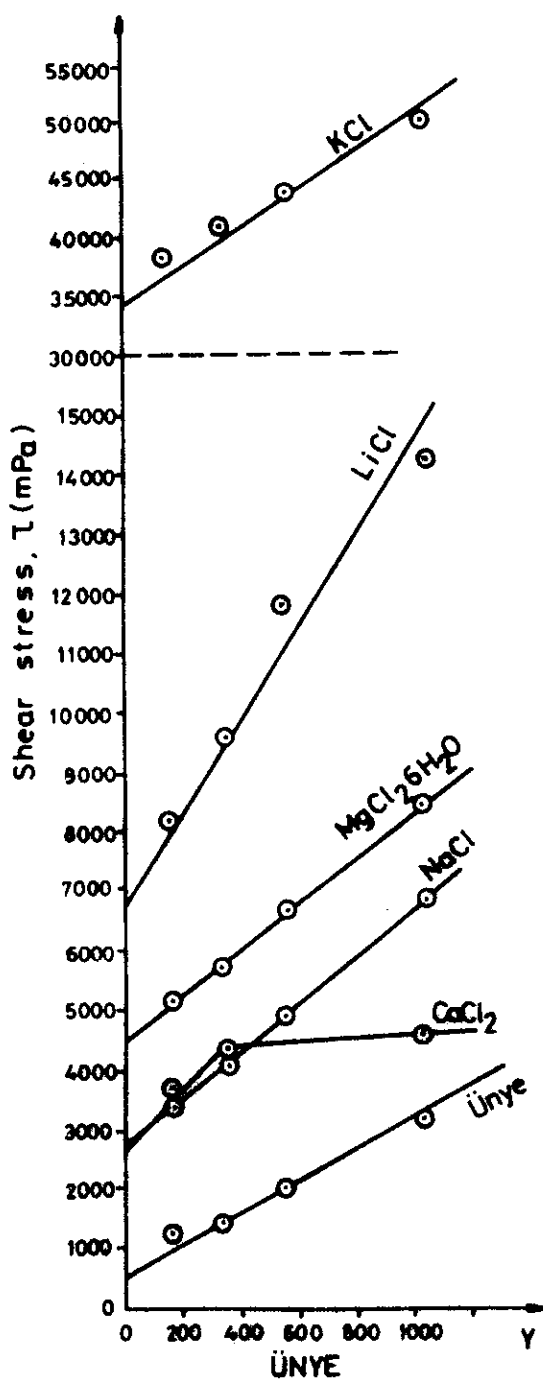
Fig. 6:   Shear stress (mPa) vs shear rate (sec⁻¹)
          after electrolytes and $(NaPO_3)_n$ added into
          slurries.

Sodium-montmorillonite is very sensitive towards the cation of the salt. When the cation is changed, the effect of the salt also changes. When the cation is Sodium and Magnesium, no change in the gel structure with an increase in concentration is observed and the viscosity increase which occurs at low concentrations remains constant. The rate of increase in viscosity diminishes when the cation is litsium, but continues to increase if the cation is potassium. The slip loses its fluid nature at high concentrations of KCl. This may be interpreted in terms of the face-to-edge conglomerations at high potassium ion concentrations. However, it is certain that the best combination is that of sodium montmorillonite with KCl. When very high viscosities are desired. The best concentration for obtaining the desired viscosity value can be determined experimentally. However, the concentration curve given in Fig. 4 may also be useful.

The addition of $CaCl_2$ to the sample in concentrations greater than 3% causes a decrease in viscosity. This also can be explained by the replacement of sodium with calcium in highly concentrated $CaCl_2$ solutions which results in the exclusion of water, trappede between layers, into the medium. However, the electrostatic repulsive force and the increase in viscosity observed at low concentrations, due to excessive amount of sodium ions, are so large that the viscosity value remains above that of the sludge even at a 7% concentration.

Different salts have different effects on the sample. The salt which increase viscosity at a fast rate is KCl. Constant viscosity values are obtained with highly concentrated NaCl and $MgCl_2$. $6H_2O$ solutions. The only salt which causes a decrease in viscosity is $CaCl_2$.

The experiments carried out in this work have shown that the rheological properties of the sample can be thought to desired values by the use of suitable salts. With the wide range of montmorillonite and salt types, it has been possible to make various generalizations based on the experimental results. High viscosities can be obtained using the Na-montmorillonites with KCl. If slight increases in viscosity are desired, lithium with sodium-montmorillonite could be used.

For a constant viscosity increase independent of concentration, Na-montmorillonite

with 4% or more NaCl or $MgCl_2.6H_2O$ may be used.

It has been observed that, although the addition of an salt causes an increase in the yield point and the shear stress values, the conformation to the Bingham model does not change. It is only when $CaCl_2$ is added to the sample, while is acceptable as a sodium-montmorillonite, that the slip containing the salt shows a pseudoplastic behaviour with a yield point.

The addition of sodium metaphosphate showed no effect on the viscosity value. The nonionic polymer attaches itself to the negatively charged clay through hydrogen-bonding and then by polymer bridges. The polymer may inhibit the diffusion of water by being adsorbed on the particles. When salts are added, due to the charged nature of the particles in the sludge, the cluster model and the dilation properties are altered, and as a result, rheological properties is obtained.

In this study, the experimental results have shown that the viscosity of sodium-montmorillonite slurries can be altered to some extent by the use of various salts. The sodium-montmorillonite being much more sensitive towards salts. On the other hand, the addition of a polymer shows no effect on the viscosity value.

Experimental

Ore sample taken from Anatolia (Unye site) have been identified as montmorillonite clay minerals using XRD, DTA-TG and IR analysis methods.

The sample had the chemical composition (wt %): SiO_2 70.30; Al_2O_3 15.00; Fe_2O, 1.10; CaO 1.60; Na_2O 1.45; K_2O 1.20; TiO_2 0.30. In addition, a trace elemental analysis on the sample was performed using the neutron activation technique. For irradiations the Triga Mark II reactor at ITU Nuclear Energy Institute (250 kW, 1.66×10^{12} neutrons/cm².) The irradiation sample was then removed unto a Canberra Nuclear Inc. model Gx2018 Hp-Ge dedector cooled by liquid nitrogen. As the result [153]Sm, [219]Np, [169]Yb, [181]Hf, [141]Ce, [47]Sc, ^{59}Fe, [233]Pa, [140]La, [122]Sb, [134]Cs, [82]Br trace elements were identified.

Particle size distribution were measured by using Micrometrics Model 5000D Sedigraph, for sample dispersed in water, with calgon and subjected to magnetic mixing: The average particle size of sample have been found as 0.50 μm.

The specific surface area of the sample were determined by dye absorption technique [11]. The calculated values of the specific surface are 120 m²/g.

Elektrokinetic measurements

Zeta potential measurements were done using zeta meter 3.0 (zetameter Inc., USA, a microelectrophoresis instrument equipped with micro-processing, 100 mg samples shifted through 325 mesh sieves were stirred in 100 mL solutions (NaCl, $CaCl_2$, or sodium-metaphosphate, ion concentration 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2} M) for 10 minutes using a magnetic stirer. They were let to stand for 5 minutes and were, the placed in the instrument. The Smoluchowski equation was used to calculate zeta potentials from electrophoretic mobilities. The maximum ionic strength used in all measurements was below 0.1 M which corresponds to a double-layer thickness (1/K) of about 10A. Since the particle sizes used for the measurement of zeta potentials are a few micrometers in size, and the solubility of cations in clay minerals is over 10^{-3} M, the condition of Ka>>1 is obeyed under almost all conditions and the Smoluchowski equation is valid [12]. At each measurement, the motions of a minimum of 20 particles were followed and the average zeta potential value was determined. The experiments were carried out at room temperature.

Rheological properties

Viscosity, gel strength and yield point of bentonite slurries were determined with a Fann type (model 35 SA) viscometer slurries of the samples were obtained by disperisng. The weighted amount of sample in distilled water (22.5 g/350 mL water) with a mechanical stirring at 1800 rpm for 5 minutes. Then, the slurries were let to stand for 24 hours. The measurements were performed for six value of shear rate starting from high shear rate ($1021 s^{-1}$).

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