Influences of Electrolytes, Polymers and a Surfactant on Rheological Properties of Bentonite–Water Systems

Ö. IŞIK ECE
Istanbul Technical University, Mining Faculty, Mineralogy-Petrography Division, 80626 Maslak, Istanbul, Turkey.

NURFER GÜNGÖR and AYŞE ALEMDAR
Istanbul Technical University, Department of Physics, 80626 Maslak, Istanbul, Turkey.

Abstract. Characteristic rheological properties, such as viscosity, shear stress, yield point, gel strength and thixotropy, of natural Ca-bentonite and Na-peptized bentonite were studied after adding LiCl, KCl, $CaCl_2$, $MgCl_2 \cdot 6H_2O$ electrolytes; $(NaPO_3)_n$, polyvinyl pyrolidone (PVP) polymers and an anionic surfactant (linear alkyl benzene sulphonate, LABS). Changes in flow properties under the influence of various additives at different quantities were investigated in these slurries. The experimental results are discussed in terms of bentonite forms, types and concentrations of additives and influence of exchangeable cations. Bivalent and monovalent cations display entirely different rheological properties in two groups of muds. Furthermore, the difference in the degree of activity of PVP polymer on the viscosity of two mud systems depend on the clay mineral structure. The slurry prepared with Na-bentonite contains a minimum number of tactoids and a maximum number of sheet-bearing clay particles, which reduces the surface area of the clay minerals and increases viscosity by adding PVP polymer.

Key words: bentonite, flow behavior, polyvinyl pyrolidone, linear alkyl benzene sulphonate, rheology

1. Introduction

The term 'rheology' was used for the first time to describe "the study of deformation and flow of matter" by Dr. Bingham of Lafayette College, Indiana. This definition is essential for clay mineralogists and other scientists employed in different fields of academic disciplines. Bentonitic clays are largely composed of the mineral montmorillonite and several parameters determine their rheological properties, such as the size and shape of the particles, layer charge, exchangeability of cations, structure of the particles, water absorption, high swelling ability and edge charge density [1].

The interactions between electrostatically charged clay particles in this system, face/edge combination models, and the formation of a gel structure are not only im-

portant from a scientific point of view; knowledge of such features is important for technological applications, such as drilling mud. These parameters can be changed to gain the desired properties by the addition of various electrolytes, polymers, surfactants and organic matter [2–11].

The viscosity of bentonite dispersions is strongly pH-dependent [12]. At pH < 7, recharging of the edges of clay particles produces a repulsion force between the particles and they move independently. The viscosity increase beyond the minimum reflects the promoted disintegration of the particles in an alkaline medium [13]. Calcium ions, with their strong tendency to form face/face contacts, produce defects in the edge (+)/face (−) network and promote its fragmentation. In the absence of calcium ions, this 'house of cards' breaks down at edge charge densities.

The Na/Ca ratio has a strong influence on the rheological properties of bentonite-based slurries. Based on experimental studies, it is very important to note that the rheological properties of dispersed bentonites depend on the cation originally present in the bentonite [13]. In order to document this idea on the basis of experimental studies, Ca-bentonite in Na-salt solution exhibits different rheological properties from Na-bentonite in Ca-salt solution, even for the same Na/Ca ratio [12].

The unit cell of montmorillonite is between an octahedral sheet of Al—O—OH and two tetrahedral sheets of Si—O. However, sometimes the tetravalent Si in the tetrahedral sheet is replaced by divalent Fe or Mg ions. This replacement, which is referred to as isomorphous substitution [14–16], results in a deficit of positive charges which are compensated by absorption of a layer of cations that are too large to be accommodated in the crystal. These cations are an effective parameter for determining the characteristic properties of montmorillonite clays [17–20]. Today, bentonites are used in different branches of industry, such as in drilling fluids, dyes, pharmaceuticals, paper, cement and ceramics. The type and the abundance of the exchangeable cations; as well as their crystalline structure, give rise to the wide range of uses for these minerals.

The main purpose of this study is to determine the rheological properties of natural Ca-bentonite and Na-peptized bentonite–water systems, and to determine the effects of some electrolytes (LiCl, KCl, CaCl$_2$, MgCl$_2$·6H$_2$O), polymers (polyvinyl pyrolidone, PVP), sodium polyphosphate, (NaPO$_3$)$_n$ and an anionic surfactant (linear alkyl benzene sulphate, LABS), at seven different concentrations, on the rheological behavior of sludges containing various concentrations by weight.

2. Experimental

Samples were taken from the Enez bentonite deposits, close to the Greek border of Turkey. Two samples were washed with distilled water three times and excess water was separated with a porcelain filter (0.15 μm pore size) under reduced pressure. The size fraction less than 2 μm was then separated by sedimentation according to Stoke's law. For XRD analyses, a Philips PW1140 model X-Ray Diffractometer

with CuK_{α} radiation was used. IR analyses (400–4000 cm^{-1}) were performed on 0.1% concentration KBr discs using a Jasco Model 5300 FT/IR spectrometer. Chemical analyses were performed using a Perkin Elmer 3030 Model atomic absorption spectrophotometer.

The Na-peptization process was accomplished by mixing 4 wt.% NaHCO$_3$ with the natural Ca-bentonites of 35% humidity and this mixture was left for 7 days in a semi-opened stockroom where it was open to air circulation in order to obtain better quality drilling clay [21]. After this well-controlled interaction process, clay samples do not contain excess NaHCO$_3$ in the system. However, zeta potential values for KCl solution were measured in 10^{-3} M concentration. The particle size distribution and the zeta potential of the samples have been determined by a method using laser light reflection by the particles (Zetasizier-3, Malvern). Calgon solution (0.5 wt.%) was used as a dispersive medium. The instrument uses a 5 mV He–Ne laser, which gives the percentage of particle size in a given interval. The median particle size diameter of Ca-bentonite is 366.8 nm and the Na-peptized bentonite sample measured 291.7 nm.

KCl stock solution (1 M) was used as electrolyte in the zeta potential measurements. Its concentration in clay slurries was diluted to 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4} and 10^{-5} M and the zeta potential was measured for each concentration. At pH = 9, the zeta potential value for the natural sample is -31.60 mV and for the Na-peptized sample it is -32 mV.

The surface areas of the samples were determined by BET nitrogen adsorption; the surface area of Ca-smectite ranges between 77 to 83 m^2/g and peptized clays range within the same limits. All chemicals used in this study were pure grade and the molecular weight of (NaPO$_3$)$_n$ was 6000–7000, PVP (NC$_2$H$_4$C$_2$OH$_2$) was 360,000 and LABS (R—⬡—SO$_3^-$Na$^+$; R = linear alkyl chain) is a mixture.

The viscosity, gel strength and thixotropy values of natural and peptized samples were determined with a Fann type (model 35SA) viscometer. This has a rotating cup (i.d. = 1.841 cm) which is coaxial with an inner rotor (o.d. = 1.724 cm). The cup can be rotated at speeds which produce shear rates of 10.2, 17.0, 170.4, 340.8, 511.2, and 1022.4 s^{-1}. The rotor is connected to a torsion spring, which measures the torque acting on it. Calibration of the Fann viscometer was accomplished at 20°C by using glycerol solutions of known viscosity.

The bentonite slurries were prepared by dispersing the clay in distilled water (22.5 g clay/350 mL water) with a mechanical mixer at 1800 rpm for 20 min. The slurry was then allowed to stand for 24 h before making measurements at 1800 rpm while mixing for 5 min. The measurements were performed for six values of shear rate, starting from a high shear rate (1021.8 s^{-1}). The gel strength of bentonite slurries were measured by the Fann viscometer giving the rotational movement as 3 cycle/min. Between each subsequent measurement, the slurry was left to stand for 10 min in order to regain the gel structure.

3. Discussion of Results

3.1. DESCRIPTION OF SAMPLES

The main non-clay mineral in the bulk samples is dolomite and the approximate structural formula of natural Ca-bentonite was determined as; $(Si_{7.79}Al_{0.21})(Al_{2.70}Fe_{0.22}Mg_{0.17}Ti_{0.09})(Ca_{0.63}K_{0.13}Na_{0.34})O_{20}(OH)_4$. The major differences between natural Ca-bentonite and Na-peptized bentonite are that CaO ranges from 4–4.5 to 3.25 wt.% and Na_2O ranges from 1.25–1.35 to 2.62–2.70 wt.%, respectively. The flow properties of a bentonite–water system are related to the interactions between the clay particles. The clay particles with a net negative charge interact with each other through Coulombic and van der Waals forces. As a result of these interactions, EE (Edge-to-Edge), EF (Edge-to-Face) and FF (Face-to-Face) combinations may be obtained. Consequently, the above combinations will affect the concentration by weight (bentonite/water ratio), particle size and shape of the bentonite minerals, the type of exchangeable cations, their quantities and shear stress. The calcium ions present in the bentonite–water system form strong face-to-face contacts and stabilize an extended band-like structure throughout the whole system, which imparts considerable plasticity to the system [13, 22].

XRD studies revealed that Ca-bentonite is very poorly crystallized, but it shows excellent crystallization after 4 wt.-% $NaHCO_3$ treatment (Figure 1). Also, XRD data indicate that both samples are pure smectite and there is no other clay or non-clay mineral in the samples. The Na-peptized bentonite sample shows excellent expansion from 12.44 to 16.66 Å after ethylene glycol treatment and a sharp (001) diffraction peak indicates good crystallization after the peptization process.

IR spectra of natural and peptized samples are shown in Figure 2. FT/IR spectroscopy can be used as a fundamental tool for studying bonding of water molecules on clay mineral surfaces. Water exhibits three vibrational modes: a symmetric stretch of $\nu_1 = 3633$ cm^{-1} (strong, broad), an asymmetric stretch of $\nu_3 = 3433$ cm^{-1} (weak) and H—O—H bend of $2\nu_2$ (2×1633) $= 3200$ cm^{-1}, where ν_1, ν_2 and ν_3 are distinct vibrational modes and $2\nu_2$ is the bending overtone (Figure 1).

The absorption at 3433 cm^{-1} is assigned to the H—O—H stretching vibration of firmly bonded H_2O, and those at 1655 and 1633 cm^{-1} are due to the H—O—H bending vibration. The IR absorptions due to structural OH in montmorillonite include the O—H stretching vibration at 3633 cm^{-1} and in-plane vibrations at 922 cm^{-1} (Al_2OH) and 794–805 cm^{-1} (MgAlOH) [24, 25]. The major difference between Ca- and Na-bentonites appear in the 1383 cm^{-1} stretching vibration, which almost disappears on Na-smectite, with a minor difference also appearing at 427 cm^{-1}.
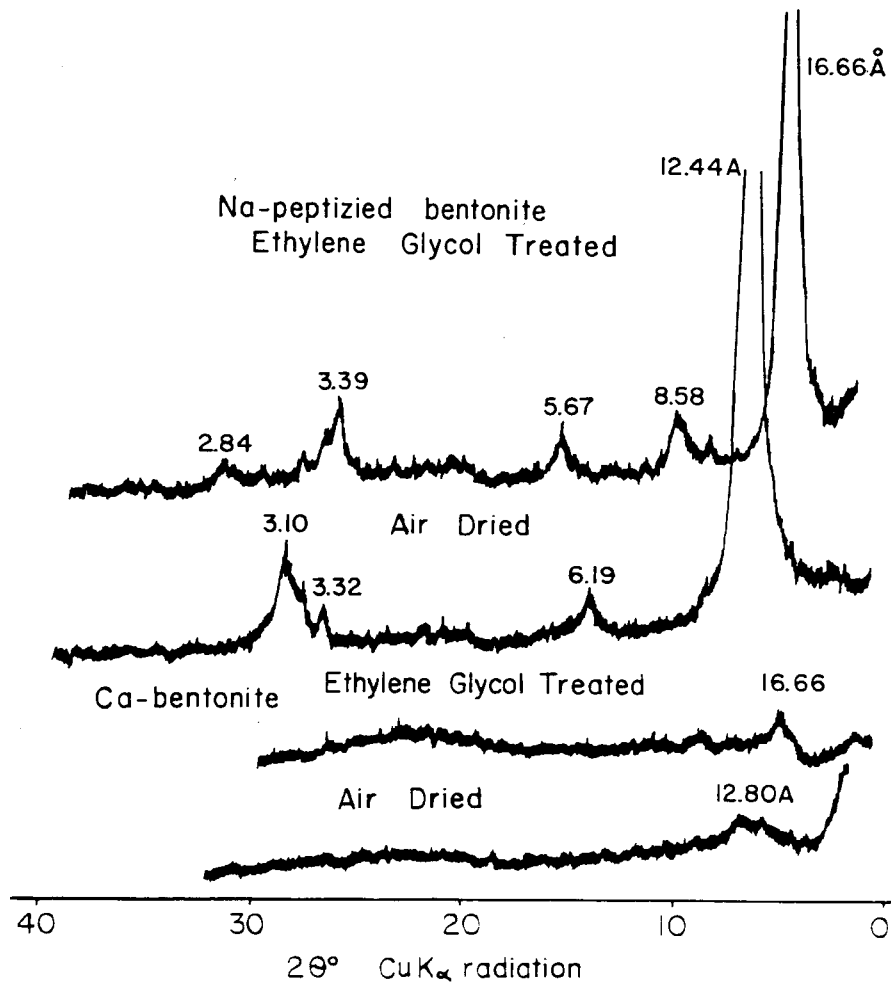
Figure 1. XRD data of Ca-bentonite and Na-peptized bentonite.

3.2. RHEOLOGICAL PROPERTIES

The increase of viscosity and consistency of calcium bentonite slurries after addition of soda is a direct consequence of the opposite effect of sodium and calcium ions. When soda is added to bentonite, the aqueous dispersion becomes alkaline and the sodium ions become exchangeable interlayer cations and initiate disintegration of the particles. Calcium ions are enriched in the contact regions and stabilize the contacts (Ca-bentonite $+ 4$ wt.% $NaHCO_3 = $ Na-bentonite $+ CaCO_3$ at pH $= 8.6$). The stable three-dimensional network forms and the dispersion obtains a considerable consistency.

The shear stress curves of natural and activated bentonite slurries are presented in Figure 3a as a function of shear rate. Since they all possess one yield point, and their shear stress changes linearly with the shear rate, it is understood that
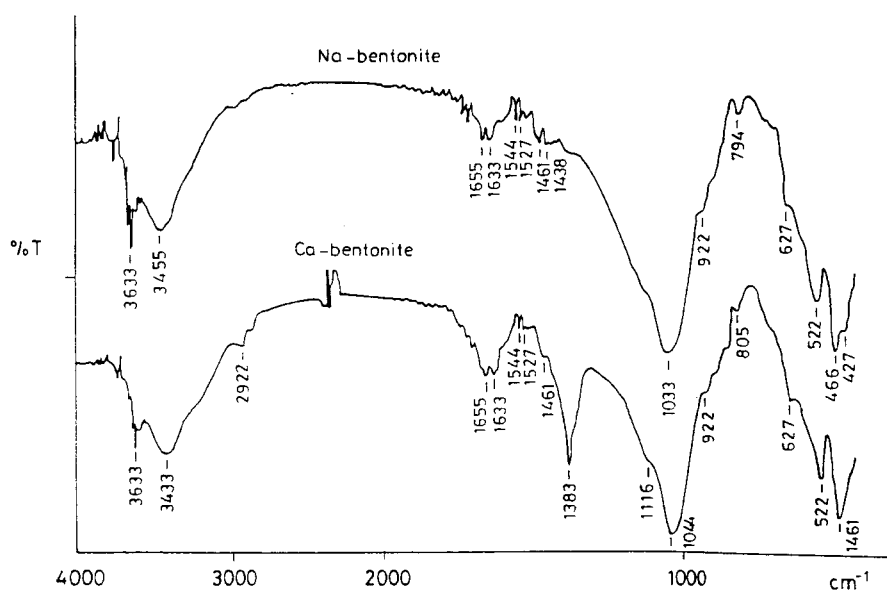
Figure 2. IR spectra of natural Ca-bentonite and Na-peptized bentonite.

two slurries behave as Bingham plastics (Figure 3a). The changes of the apparent viscosities of the two bentonite slurries are given in Figure 3b as a function of shear rate. These curves show a sudden decrease at small shear rates, indicating thixotropic properties of the samples. The curve of natural Ca-bentonite resembles that of Na-peptized bentonite, but it decreases comparatively slowly. The natural sample has a low apparent viscosity (2.5 mPa sec), whereas the Na-peptized sample has a higher apparent viscosity (28 mPa sec). The apparent viscosities of the samples decrease with an increase in the Na content. This result can be expected because more water will penetrate into the interlayers and the medium water will reduce.

Gel strength measurements were obtained as a function of time. In forming gel structures with bentonitic clays and water, it is well known that the most effective parameter is the exchangeable cations. The stability of the gel structure formed in a slurry is related to the nature of the exchangeable cations; the adjoining particles of a Na-bentonite slurry exhibit a net-like appearance. The variation in gel strength with time has been determined by periodic recesses of the slurry (Figure 4). As observed in the peptized sample, there is a continuous increase, whereas there is a progressive deterioration in the natural bentonite. The peptized bentonite system tends to be dispersed, while the natural bentonite system becomes aggregated. Furthermore, it is difficult to recover the gel strength of a swelling bentonite slurry after a certain time compared to the non-swelling bentonite slurry. The swelled particles disintegrate after a certain time, giving numerous small particles and consequently a large surface area. If the slurry is prepared with Na-bentonite, this provides
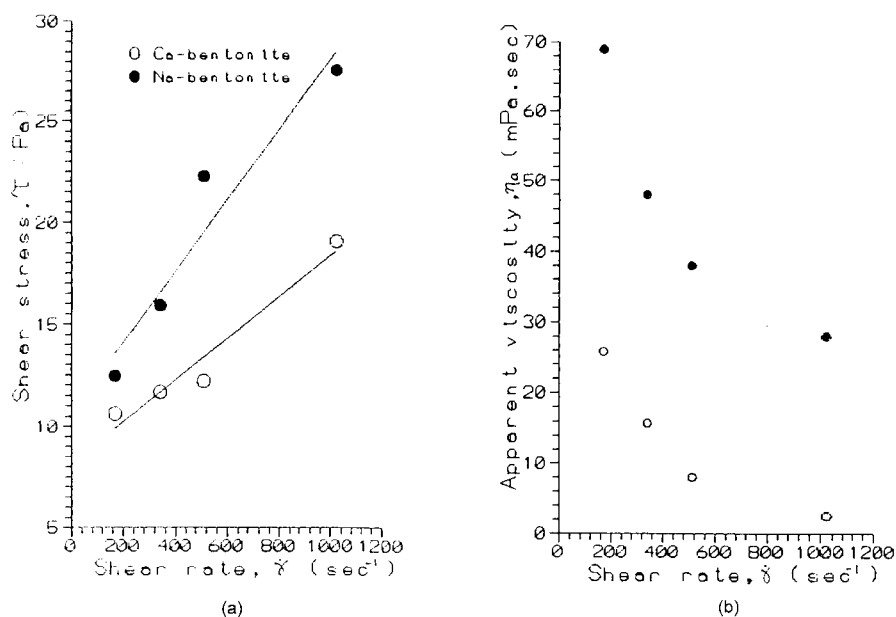
Figure 3. (a) The shear stress (τ) vs. shear rate (γ) rheogram. Two straight lines were drawn according to the least squares method. Ca-bentonite: $y = 0.0102257x + 8.15821$ and Na-peptized bentonite: $y = 0.0175656x + 10.5682$. (b) The apparent viscosity (η_a) vs. shear rate (γ) rheogram.

larger numbers of clay particles in the system and, consequently, better interactions between water and clay due to the increase in surface area. As a result of this phenomenon, viscosity and binding water increase, and considering the physical properties, a reversible gel structure forms as a cluster. In addition, the repulsive electrostatic and van der Waals forces bring the particles to an equilibrium state, which contributes to gel formation [10, 16, 22].

The changes of the apparent viscosity depending on the electrolyte type and concentrations are shown in Figure 5a (natural) and 5b (Na-peptized). Rheological properties of the studied electrolytes in different clay–water systems have been reported. However, the influences of the same electrolytes on the rheological properties of original Enez Ca-bentonites and Na-peptized bentonites, and how much they are changed, have not been studied.

3.2.1. *Effect of LiCl and KCl*

It is observed that, upon addition of LiCl and KCl, there is an initial decrease in viscosity followed by an increase (Figures 5a and 5b). The effectiveness of the two electrolytes on natural and peptized samples is quite different and the Na-peptized slurry is much more affected by addition of electrolytes. The values of η_a decrease with increasing salt concentration and reveal that contacts between protonated edges and the negative faces, and formation of card-house structures
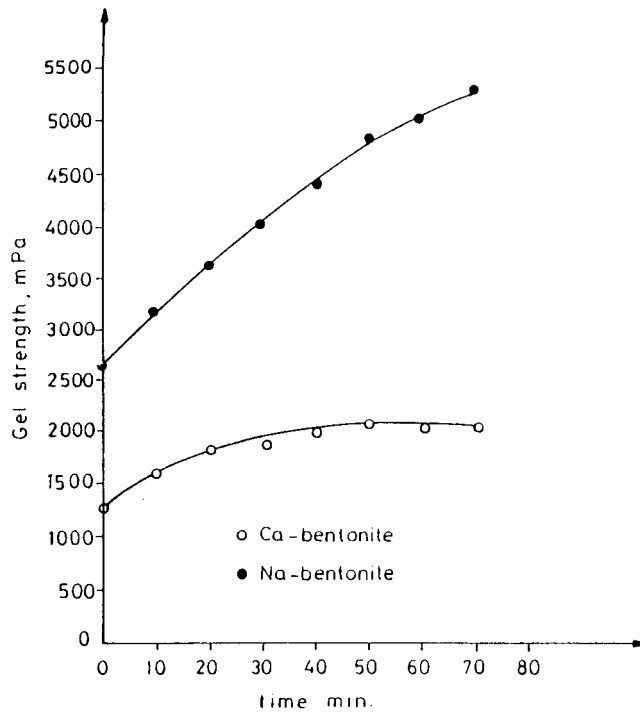
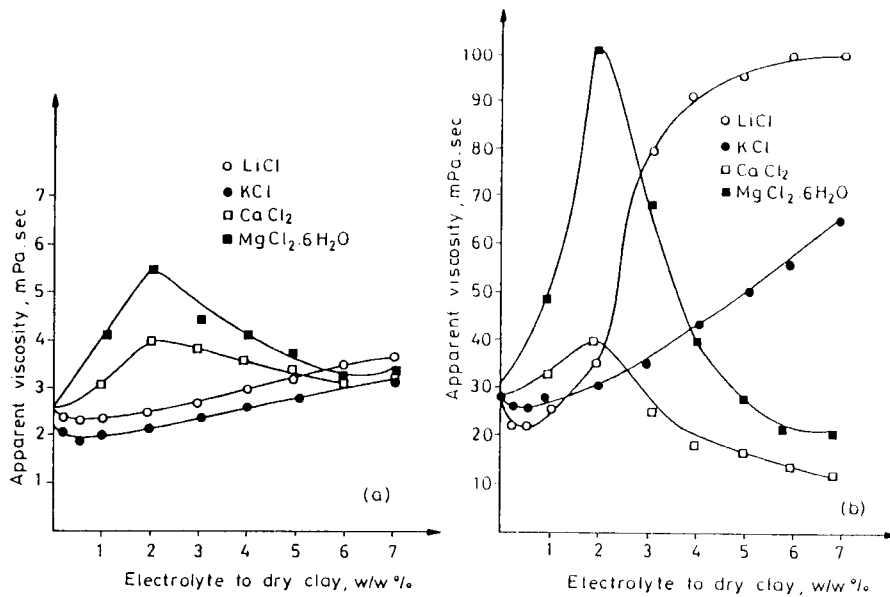*Figure 4.* Variation of gel strength with time.

Figure 5. (a) The changes of the apparent viscosity of the natural Ca-bentonites. (b) The changes of the apparent viscosity of the Na-peptized bentonites.

are not important at these salt concentrations. With the addition of small amounts of LiCl, KCl, the Li^+ and K^+ are attracted to the negatively charged faces of the clay particles, whereas the Cl^- ions migrate to the positively charged edges. These phenomena can be explained by a screening effect on the electrical charges of faces and edges of particles; the net electrostatic interactions between particles decrease. van der Waals forces are much weaker, therefore it cannot compensate. As a result, the mechanical coupling in the system reduces and the viscosity decreases. When salt concentrations are further increased, the interaction between the faces of the clay particles becomes more attractive and η_a increases sharply (Figure 5b). As the amount of LiCl and KCl in the slurry increases, the Li^+ (or K^+) ions start to penetrate between the layers of the smectite. It is also well known that the mobilites of the Li^+ and K^+ ions are much faster than the other ions, and their contributions to binding of layers are very weak [4, 13, 16, 22]. Therefore, layers cause the smectite to dissociate into smaller platelets, each of these platelets being negatively charged on the flat surfaces and positively charged on the edges. The electrostatic interactions between clay particles are capable of leading to the card-house networks that characterize gel formation in clay slurries. The thickening of the slurry results from the interaction between the protonated edges and the negative faces, and also, very likely, from formation of card-house structures.

3.2.2. *Effect of CaCl₂ and MgCl₂·6H₂O*

Upon the addition of a small amount of $CaCl_2$ or $MgCl_2 \cdot 6H_2O$, rather than the initial electrostatic neutralization, which takes place in the case of LiCl or KCl, two and single valent cations have opposite behaviors. The exchange of $2Na^+$ with Ca^{2+} or Mg^{2+} does not affect the charge balance, whereas two Cl ions are free to migrate to the edges and neutralize the positive charges there. This results in the smectite becoming more negatively charged than it was before the addition of the salt into the slurry causing the greater stabilization of the colloid (Figures 5a and 5b). The interaction between the clay particles becomes stronger, the mechanical coupling becomes longer ranged and the viscosity increases. The major increase in viscosity of Na-peptized bentonite samples is evidence of an increase in the mechanical coupling among the clay particles. The strong mechanical coupling between these like-charged particles is provided by the cations that are present in solution.

What happens with increased concentration of $CaCl_2$ or $MgCl_2 \cdot 6H_2O$ in the slurry? We have already remarked that unlike the mobile Li^+ and K^+, the interstitial Ca^{2+} or Mg^{2+} act to bond the layers even closer together, so that with increasing concentration, there is no dissociation into platelets as observed in the previous case. However, once the interstitial salts are saturated, there will be no more exchangeable cations left to displace, then Ca^{2+} or Mg^{2+} start attaching themselves to the negatively charged surfaces of the smectites and start neutralizing them. Thus, the same scenario as in the initial addition of LiCl or KCl applies, only for larger concentrations of $CaCl_2$ or $MgCl_2 \cdot 6H_2O$. The combined effects of weaker

electrostatic interactions between relatively neutral particles, with more water dispelled from the layers of each particle, leads to a lowering of the viscosity. The strong decrease in viscosity reflects the decreasing stability of the card-based on edge/face contacts.

The idea of edge-to-face association was discussed and direct observations on the microstructure of clay flocs were recently made using SEM [4]. The smectite lamellae displayed face-to-face associations in the flocs that formed at neutral pH conditions. The microstructure of the smectite flocs was found to consist of bonds (ribbons) that were made of marginally overlapping smectite lamellae. A ribbon-like arrangement of overlapping smectite lamellae in smectite flocs has also been described [4, 8, 10, 14] and it was proposed that smectite particles form flocs consisting of irregular chains of marginally overlapping thin smectite platelets in sheared suspensions of <0.01 M NaCl solution. SEM studies presented face-to-face association rather than edge-to-face association. The increasing stiffness of gels with increasing clay concentrations seems not to be primarily the result of a more close-packed 'card-house' structure, but it is caused mainly by the increased thickness of the face-to-face associated sheets [4].

3.2.3. *Effect of Polymers*

The most important parameters that govern the extent of adsorption of polymers are molecular weight, polymer concentration, the functional groups of the polymer, the degree of hydrolysis of polymers, surface charge, the material of the adsorbent, the solid-to-liquid ratio, pH and temperature. The organic and inorganic polymers polyvinyl pyrolidone (PVP) and sodium polyphosphate $(NaPO_3)_n$ were used. Figures 6a and 6b show the effect of addition of polymers to natural and peptized bentonite slurries. It is observed that the addition of polymers does not show enough effective changes in the viscosity values of natural samples and the quantity of $(NaPO_3)_n$ decreases when the PVP viscosity values increase slightly. The influences of polymers on Na-peptized and natural clay samples (one decreases while another increases) are similar; however, the difference between the degree of influences is also obvious.

Polymer adsorption involves only the clay surface, not the interlayers. This phenomenon is due to the irregular forms of the polymers. The non-localised, negative charge on the clay structure is immediately compensated in the zone closest to it by positive ions in the slurry. The next zone outward from the clay surface is composed of both positive and negative ions in decreasing abundance [26, 27].

As with simpler organic molecules, the initiation of the process is through hydrogen ion exchange or cation interaction with the polymer. Polymer adsorption is conditioned by such effects as pH or exchange cation concentrations. The ideal situation is to coat the clay particles with a polymer, thus producing a stable suspension of clay-polymer in the slurry [27].

Increasing the PVP concentration increases the viscosity of Na-peptized clays. From a chemical composition point of view, PVP resembles a gel structure and it is
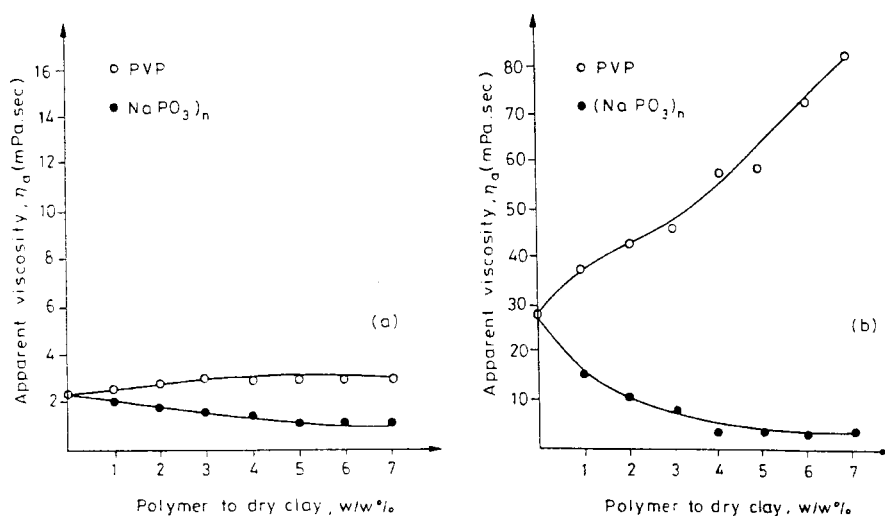
Figure 6. (a) The change of the apparent viscosity of the natural Ca-bentonites with $(NaPO_3)_n$ and polymers added to slurries. (b) The change of the apparent viscosity of the Na-peptized bentonites with $(NaPO_3)_n$ and PVP polymers added to slurries.

a linear protein, which is made of various pyrolidone rings. It dissolves in water exhibiting various hydrophilic structures and can be curled like a ball. PVP molecules adsorb on clay surfaces when added into a bentonite–water system, because of the cationic charges of PVP, which can adsorb on the negatively charged clay surfaces with electrostatic interaction and consequently, electrostatic stabilization observed. Regardless of the presence of PVP in the system, the possibility of forming a card-house structure should not be forgotten when negatively charged clay surfaces interact with positively charged edges. PVP adsorbs medium water by swelling in the slurry and consequently, the viscosity of the system increases while fluidity decreases.

The difference in the behaviours of activity degrees of PVP polymers on the viscosity of two mud systems depend on the clay mineral structure (Figure 6a and 6b). Regardless of polymer, adsorption not being between interlayers of the clay structure, the adsorption takes place on the surface of clays, also the type of exchangeable cations and their quantities are important during the clay-polymer interaction. Because Na-peptized bentonite disperses in the slurry in the form of relatively minimum numbers of sheet-bearing and maximum numbers of tactoid-containing structures compared to Ca-bentonite in slurry [27]. For this reason, it has a higher surface area. In this way, an increase in viscosity of this system should be much higher, because the reaction of PVP with clay particles would be more effective. PVP forms a gel-like structure together with water molecules bound to it and absorbed clay minerals. In contrast, the slurry prepared with Ca-bentonite contains a minimum number of tactoids and a maximum number of sheet-bearing

clay particles. Consequently, the surface area of clay minerals will be reduced and its reaction with added PVP will be at a minimum level.

An inorganic and non-ionic polymer $(NaPO_3)_n$ exhibits a flocculant effect on the viscosities of bentonite–water systems. As in the addition of PVP, Na-activated bentonite has been more affected than the natural sample. The clay–polymer interaction is more effective due to there being more clay particles and a higher surface area in the system. This phosphate component, which adheres to clay particles, shows a flocculant effect that helps precipitation of particles in a glass beaker. In some cases, many clay particles can suddenly be adhered with polymer molecules and clay particles also adhere to each other (bridging flocculation); the previously occurring gel structure breaks down. Under this condition, medium water shows its effect and fluidity increases when viscosity decreases.

3.2.4. *Effect of Surfactant*

The influence of surfactants on the flow behaviour of bentonite slurries was studied for an anionic surfactant (linear alkyl benzene sulphonate, LABS) (Figure 7). It is a powerful surfactant and de-flocculant. Surfactants greatly influence the flow behaviour of clay slurries. However, the influence of surfactants on montmorillonite (especially Na-montmorillonite) slurries should be more complex than on other clays. First of all, Na-bentonite produces very thin particles and the degree of delamination is highly dependent on the experimental conditions. As the number of particles is a decisive factor, the flow behaviour can change dramatically by modest changes in experimental conditions such as pre-treatment reactions, degree of dispersion, and pH [27, 28].

The surfactant anions attached on the positive edges destroy the edge–face contacts of the card-house. The surfactant anions break up the edge–face contacts, and shear stress and apparent viscosity decrease (Figure 7).

Sulphonate (SO_3^-) is a polar group and those surfactants which contain this group are strong de-flocculants. When LABS is slowly added into slurry, negatively charged hydrophilic edges bond with positively charged edges. Under these conditions, those bonds that develop under electrostatic attraction will be avoided and interactions between clay particles are not observed; the solution will be more stable. At higher LABS concentration, free hydrophilic edges come together to develop bridge flocculation; consequently, the viscosity values increase.

4. Conclusion

Electrolytes, polymers and a surfactant containing two groups of mud show important effects on rheological properties depending on bentonite types and their exchangeable cations during clay–water interaction. In the bentonite–water system, like many other characteristic features, rheological properties are dependent on cation types and their quantities. Added chemicals show more effectiveness in Na-peptized clays, because Na-peptized clays have smaller particle sizes, a greater
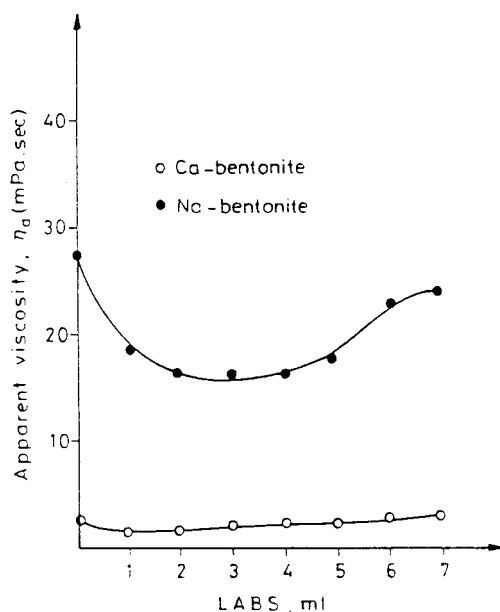
Figure 7. The change of the apparent viscosity of the natural Ca- and Na-peptized bentonites with LABS surfactant added to slurries.

number of clay particles in the slurry and increased surface area of clay minerals are more effective in clay–water–additives systems. The repulsive forces, which are caused by electrostatic interactions of clay particles, are relatively dominant in Na-peptized samples because a Na exchangeable cation can deflocculate the system better.

The experiments carried out in this work have shown that the rheological properties of the bentonite can be brought to desired values by the use of suitable electrolytes, polymers or a surfactant. When LiCl, KCl and PVP are added to the slurries, the apparent viscosity increases; on the other hand when $CaCl_2$, $MgCl_2 \cdot 6H_2O$ and $(NaPO_3)_n$ are added, the apparent viscosity decreases. The addition of LiCl and KCl, at first slightly decreases the viscosity, followed by an increase; whereas the variation after addition of similar amounts of $CaCl_2$ and $MgCl_2 \cdot 6H_2O$ is exactly the opposite. The initial increases in this case are followed by a gradual decrease, the extremum of these curves in both Ca- and Na-bentonites are occurring at about the same weight percent. As the result of this study, LiCl and KCl can be used as flocculants (even suitable for gelation) at 6.43 wt.-% of dry bentonite; $CaCl_2$ and $MgCl_2 \cdot 6H_2O$ can also be used as deflocculants after adding electrolytes at 3 wt.% of dry bentonite.

References

1. N. Güven: *CMS Workshop Lectures* **4**, 81 (1992).
2. D. Heath and T.F. Tadros: *J. Colloid Interface Sci.* **93**, 307 (1982).
3. D. Heath and T.F. Tadros: *J. Colloid Interface Sci.* **93**, 320 (1982).
4. H. Vali and L. Bachmann: *J. Colloid Interface Sci.* **126**, 278 (1988).
5. T.F.P. Akae: *J. Colloid lnterface Sci.* **124**, 624 (1988).
6. N. Güngör and T. Dilmaç: *Second International Ceramics Congress*, Istanbul, 24–28 October, p. 197 (1994).
7. N. Güngör: *Powder Handling and Processing* **7**, 317 (1995).
8. N. Güngör and T. Tulun: *Res. Ind.* **55**, 268 (1996).
9. N. Güngör: *Powder Handling and Processing* **8**, 367 (1996).
10. N. Güngör and Ö.I. Ece: *Bulletin of the Technical University of Istanbul* **49**, 351 (1996).
11. N. Güngör and T. Dilmaç: *International Ceramic Review* **41**, 22 (1997).
12. U. Branderburg and G. Lagaly: *Appl. Clay Sci.* **3**, 263 (1988).
13. G. Lagaly: *Appl. Clay Sci.* **4**,105 (1989).
14. R.K. Khandal and T.F. Tadros: *J. Colloid Interface Sci.* **25**,122 (1988).
15. P.K. Singh, V.P. Sharma, R. Caenn and G.V. Chlingarian; *J. Petr Sci. Engin.* **6**, 349 (1992).
16. A. Takeo and P.E. Low: *J. Colloid Interface Sci.* **124** (1988).
17. B.A. Searle and R.W. Grimshaw: *The Chemistry and Physics of Clays and Other Ceramic Materials*, Ernest Bern Limited, London (1960).
18. H. Van Olphen: *An Introduction to Clay Colloid Chemistry*, John Wiley and Sons, New York, p. 301 (1963).
19. W.E. Worral: *Clays and Ceramic Raw Materials*, Elsevier Applied Sci. Publishers, London and New York, p. 127 (1986).
20. S.J. Reed: *Introduction to the Principles of Ceramic Processing*, John Wiley and Sons, New York, p. 486 (1988).
21. F. Labedenko and D. Plee: *Appl. Clay Sci.* **3**, 1 (1988).
22. J.S. Chen, J.M. Cusman, and P.F. Low: *Clays Clay Min.* **38**, 57 (1990).
23. N. Güngör: *Arab Gulf J. Sci. Res.* **15**, 261 (1997).
24. V.C. Farmer: *The Infrared Spectra of Minerals*, Mineralogical Society, London (1974).
25. J.D. Russel and V.C. Farmer: *Clay. Min. Bull.* **5**, 443 (1964).
26. L.L. Schramn and J.C.K. Kwak: *Clays Clay Min.* **30**, 40 (1982).
27. T. Permien and G. Lagaly: *Appl. Clay Sci.* **9**, 251 (1994).
28. T. Permien and G. Lagaly: *Clays Clay Min.* **43**, 229 (1995).