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Interactions of polyacrylamide polymer with bentonite in aqueous systems

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Abstract

The flow properties of natural Ca bentonite and Na bentonite–water systems were studied after adding an anionic polyacrylamide (PAM) polymer. The effect of the PAM has also been investigated at different quantities. The experimental results are discussed in terms of bentonite forms and concentration of PAM. Besides, measurement of rheological properties of Ca bentonite + PAM and Na bentonite + PAM systems have been examined in detail through XRD, FT-IR and DTA analyses. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Clays, the active mineral portion of soils, are dominantly colloidal and crystalline. Montmorillonites are members of the smectite clay family of minerals. The structure of montmorillonites and other similar smectite clays consists of two tetrahedral sheets (Si–O) separated by an octahedral sheet (Al–O–OH). However, sometimes, the tetravalent Si in the tetrahedral sheet is replaced by divalent Fe²⁺ or Mg²⁺ ions. This replacement, which is referred to as isomorphous substitution [1,2], 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 [1–11]. The general name given to clays that contain appreciable quantities of montmorillonite minerals is bentonite.

Bentonites show a colloidal structure and small particle size. The particles of montmorillonite have a net negative charge. The industrial application of bentonite–water systems is very widespread, such as paper, paints, coatings, and drilling fluids, to modify the rheology and control the stability of the system. The knowledge of rheological behaviour of these systems is very important for technology.

The literature contains various publications on the rheological properties of bentonite–water systems [12–19]. There are many studies concerning the effects of exchangeable cations upon rheological properties of the bentonite clays [3–11]. Besides, there are also various studies on the distinct effects, upon these properties, of different salts, polymers and

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surfactants materials added to the bentonite–water systems [7–11]. Clay flocculation is general, a process that is found to be important in many systems, since clays are universally present in deposits, oil reservoirs and marine and agricultural systems. The effect of PAM on clay is a widely studied phenomenon [21–23].

The purpose of this work is to determine the rheological properties of Ca bentonite and Na-activated bentonite–water systems and to study the effects of PAM in different concentrations.

2. Experimental study

Samples were taken from the Enez clay deposits, close to the Greek border of Turkey. X-rays and infrared (IR) techniques were used to determine the clay mineral types. The dominant clay mineral was found to be dioctahedral motmorillonite with minor amount of illite and kaolinite. Quartz was always present in clay fraction. There is no other clay or non-clay mineral in the samples. Chemical analysis was performed by using the Perkin Elmer 3030 Model atomic absorption spectrophotometer. The sample has a composition (wt.%) of: Al₂O₃ 19.00, SiO₂ 62.80, Na₂O 1.00, K₂O 0.76, CaO 4.60, MgO 1.80, Fe₂O₃ 2.20, TiO₂ 0.45 and H₂O 7.39. Specific surface determined by N₂ adsorption was 88.69 m²/g, based on the BET method.

The peptization process was done by mixing 4 wt.% NaHCO₃ and 35% clay sample with 35% humidity and this mixture was left for 7-day period in semi-opened stockroom where it was exposed to air circulation [20].

For XRD analyses, a Philips PW1140/90 model X-ray Diffractometer with CuK_α radiation was used. For DTA analyses a Rigagu Thermoflex was used. FT-IR spectra of their KBr pellets, (1/300) were taken. Bentonite samples and PAM were mixed in different composition. FT-IR analyses (400–4000 cm⁻¹) were performed using a Unicomp Wattson 1000 style Spectrophotometer. Spectra outputs have been recorded either in absorbance or transmittance mode as a function of the wave number.

The medium particle size diameter of Ca bentonite is 366.8 nm and that of Na-peptized sample 291.7 nm [11].

The viscosities of the dispersions was measured in a Brookfield DVI type low-shear viscometer, under room conditions. The bentonite was dispersed in water (2%, w/w) and shaken intensively for 24 h. An adsorption time of 2 h was adopted for the PAM.

The molecular weight of PAM (CH₂=CH–C=ONH₂) was 80,000–100,000.

3. Results and discussion

XRD studies revealed that Ca bentonite is very poorly crystallized, but it shows excellent crystallization after 4 wt.% NaHCO₃ treatment (Fig. 1). The Na-peptized bentonite sample shows in particular a sharp and intense peak which corresponds to an interplanar distance $d_{(001)}$ of 12.44 Å. After treatment by ethylene glycol this peak is shifted to 16.66 Å. The intensity and the linewidth of these (001) peaks indicate good crystallization after the peptization process [10]. The pattern of PAM-treated Ca bentonite and Na-peptized bentonite are shown in Fig. 2. Considerable shifts are observed in XRD lines, particularly with PAM-treated bentonites. This

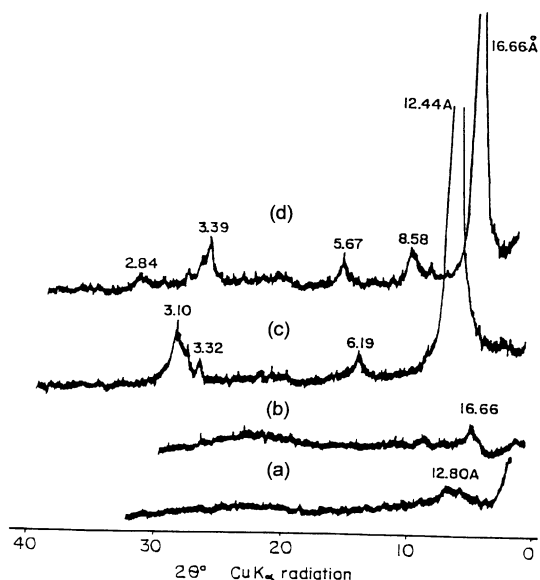


Fig. 1. XRD data of natural Ca bentonite and Na-peptized bentonite: (a) Ca bentonite, air-dried; (b) Ca bentonite, ethylene glycol treated; (c) Na bentonite, air-dried; (d) Na bentonite, ethylene glycol treated.

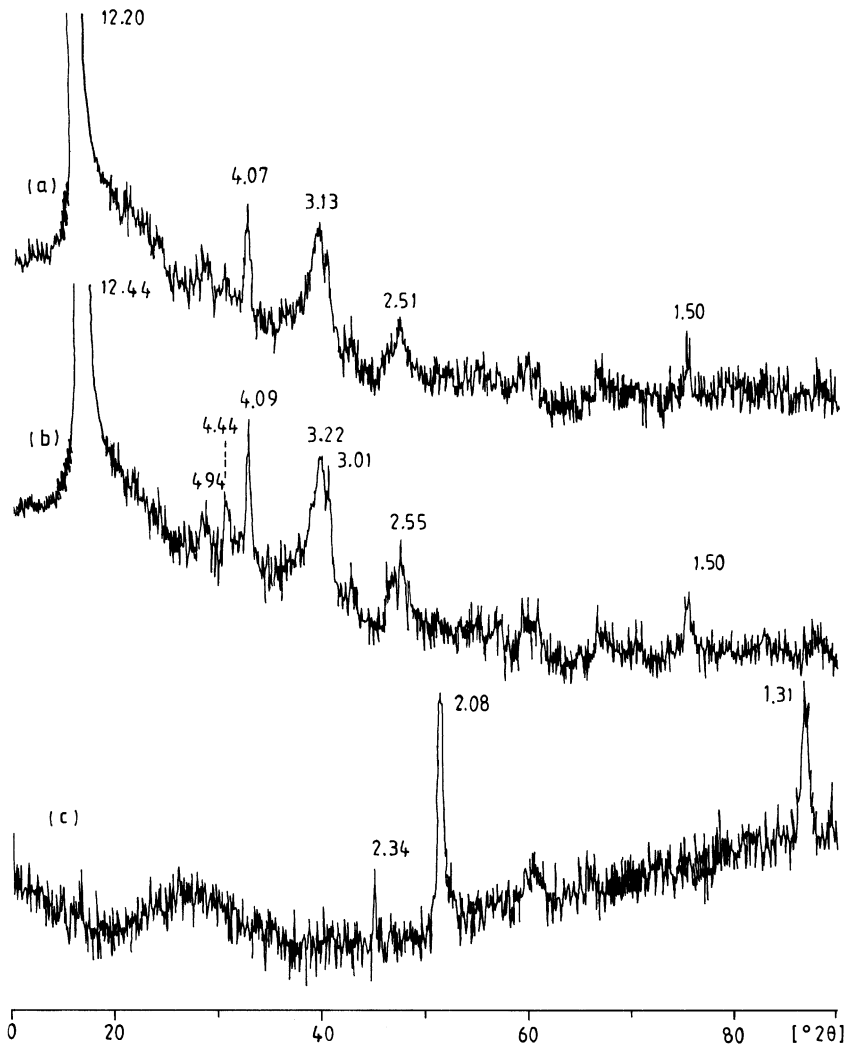


Fig. 2. XRD patterns of (a) Ca bentonite–water system containing PAM (w/w, 18%), (b) Na bentonite–water system containing PAM (w/w, 16%), (c) PAM.

result shows that the PAM molecules and clay particles interact with each other. In the diagram of differential thermal analysis and infrared spectrophotometric analysis studies of PAM adulterated samples, the main characteristics of the natural Ca bentonite samples are also observed. Only some shiftings are detectable in DTA thermogram peaks and in FT-IR absorption bands (Figs. 4–8).

The FT-IR spectra of natural and peptized samples are shown in Fig. 3. FT-IR spectroscopy can be used as a fundamental tool for studying bonding of

water molecules on clay mineral surfaces. Water exhibits different vibrational modes: a symmetric stretch of $\nu_1 = 3633 \text{ cm}^{-1}$ (strong, broad), an asymmetric stretch of $\nu_3 = 3433 \text{ cm}^{-1}$ (weak) and H–O–H bending of $\nu_2 = 1633$ and 1655 cm^{-1} . ν_1 , ν_2 and ν_3 are distinct vibrational modes.

The absorption band at 3433 cm^{-1} in Fig. 3 is assigned to the H–O–H stretching vibration of firmly bonded H_2O , and those at 1655 and 1633 cm^{-1} to the H–O–H bending vibration. The IR absorption bands due to structural O–H in montmo-

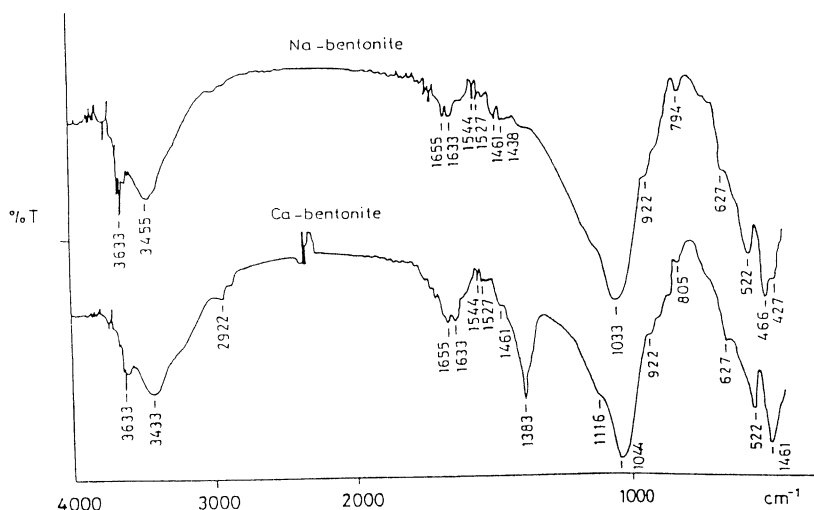


Fig. 3. IR spectra of natural Ca bentonite and Na-peptized bentonite.

rillonite include the O–H stretching vibration at 3633 cm^{-1} and in-plane vibrations at 922 cm^{-1} (Al_2OH) and $794\text{--}805\text{ cm}^{-1}$ (MgAlOH) [10]. 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} .

A typical infrared absorption spectrum of PAM has the following characteristic absorption bands: strong bands at 1660 and 3450 cm^{-1} (N–H, stretch); broad bands at 770 , 1200 and 3200 cm^{-1} (C–H, stretch); medium bands at 2925 , 2883 (aliphatic, asymp. C–H, stretch), 1130 , 1325 , 1355 , 1420 , 1460 and 2950 cm^{-1} , and a shoulder at 1620 cm^{-1} [24]. The FT-IR spectra of PAM-treated Ca bentonite and Na-peptized bentonite are shown in Figs. 4 and 5. Considerable shifts are observed in vibrational frequencies, particularly with PAM-treated bentonites. These results show that the PAM molecules and clay particles interact with each other. Thus, PAM is loosely bound and interacts near the surface and/or into the interlayers of the bentonites.

While standard PAM shows peaks at 1660 and 3450 cm^{-1} (N–H, strong bonds), the infrared spectrum of PAM on Ca bentonite and Na bentonite (Figs. 4 and 5) showed additional peaks.

The DTA thermograms of natural Ca bentonite and peptized Na bentonite samples are shown in Fig. 6. The position, the form and the size of the first endothermic peak due to the loss of physical water

between the layers on differential thermal analysis thermograms vary according to the kind of exchangeable cations and, therefore, according to their hydration energies. Fig. 6 shows no obvious difference in the thermograms of the two samples. The thermograms of Ca bentonite–water and Na bentonite water systems containing PAM (w/w, 14%) are shown in Fig. 7. The differences with the curves in Fig. 6 are as follows:

- (i) a shift of the first endothermic peak from 90°C to 71°C and 92°C to 76°C for the Ca and Na bentonite–water systems, respectively;
- (ii) almost disappearance of the shoulder observed after the first endothermic at 157°C and 161°C , in the Ca- and peptized Na bentonite, respectively;
- (iii) at higher temperatures ($900\text{--}1000^\circ\text{C}$), the less pronounced endothermic–exothermic peak system in PAM-adulterated bentonites.

The flow properties of a bentonite–water system is related to the interactions between particle–particle and particle–water molecules of the system. The exchangeable cations that exist between the bentonite layers are the effective parameter on rheological properties. In the bentonite–water system, like many other characteristic features, the rheological properties are dependent on cation types and their quantities.

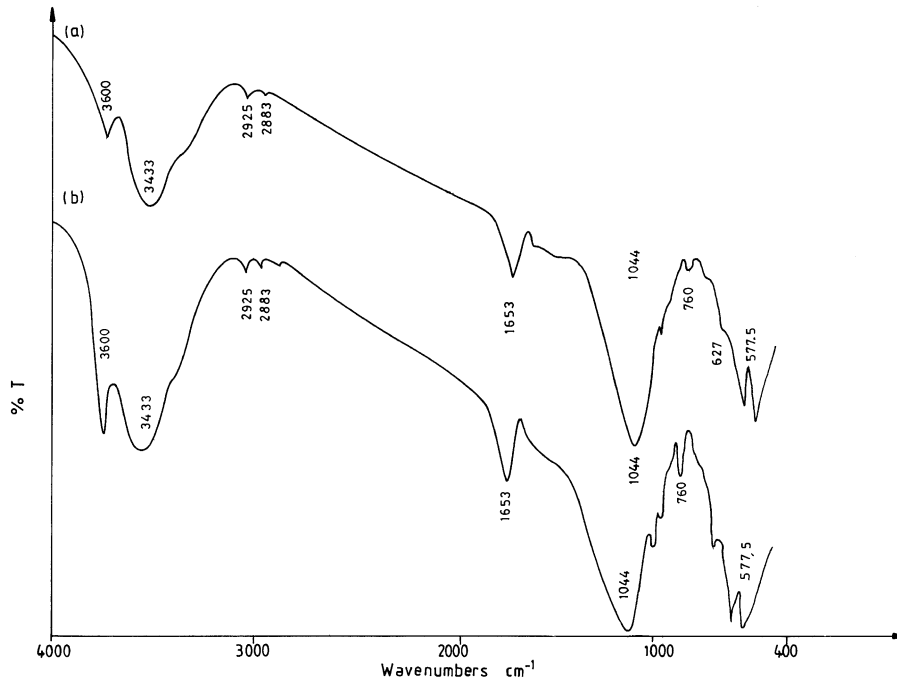


Fig. 4. IR spectra of (a) Ca bentonite–water system containing PAM (w/w, 2%), (b) Ca bentonite–water system containing PAM (w/w, 14%).

The extent of polymers on clay minerals is determined by a number of parameters such as molecular weight, polymer concentration, degree of hydrolysis

of polymer, functional groups of polymer and bentonite-to-water ratio, pH. Besides, in the bentonite–water system, like many other characteristic features,

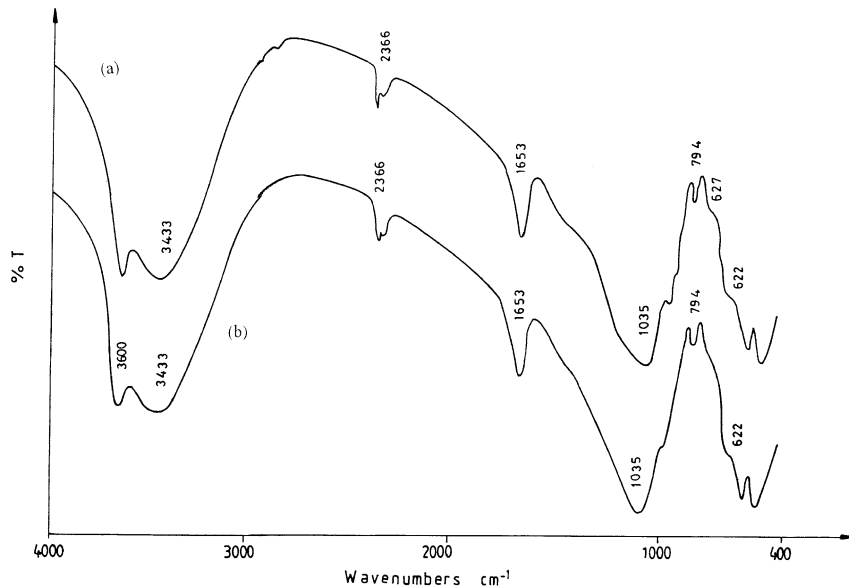


Fig. 5. IR spectra of (a) Na bentonite–water system containing PAM (w/w, 8%), (b) Na bentonite–water system containing PAM (w/w, 14%).

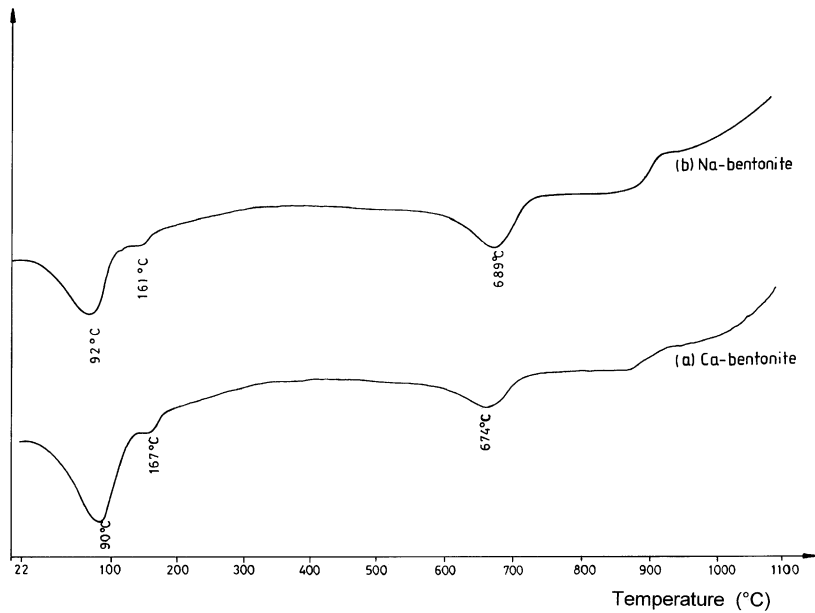


Fig. 6. DTA thermogram of natural Ca bentonite and Na-peptized bentonite.

rheological properties are dependent on cation types and their quantities.

Anionic polymers are effective flocculants and deflocculants for clays which normally carry negative charges in water only when the polymer also

contains nonionic polar groups (such as OH^{-1} , NH_2) or if the anion is carboxyl (COO^{-}).

The adsorption of non-ionic or weakly ionic polymers is the consequence of physical forces (Van der Waals forces or hydrogen bonding) between adsor-

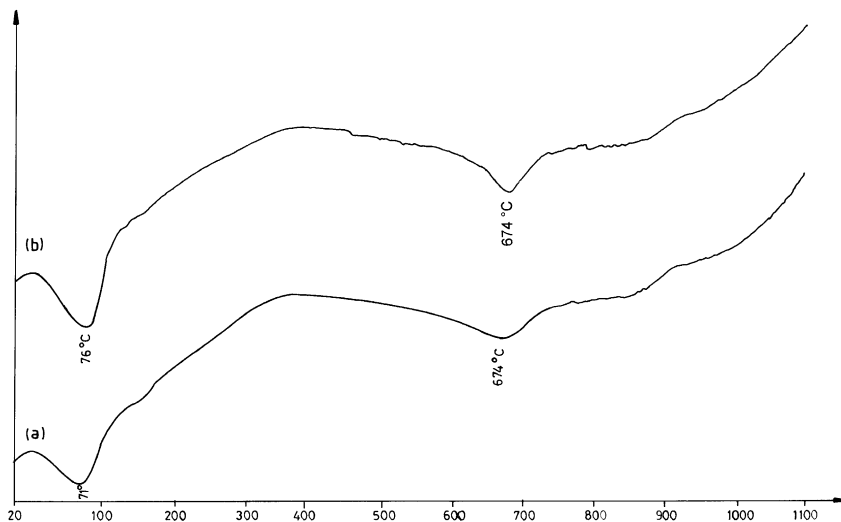


Fig. 7. DTA thermogram of (a) Ca bentonite–water system containing PAM (w/w, 14%), (b) Na bentonite–water system containing PAM (w/w, 14%).

bent (polymer) and adsorbate (clay). The molecules adsorbed initially are taking up a flat configuration. With the continuation of adsorption, the molecules are assuming a configuration with more loops protruding out from the surface to enable more material to adsorb. This process involves the adsorption of segments.

The polymer studied in this work was polyacrylamide (PAM). PAM is an anionic structured polymer that can be dissolved in water. It displays a more anionic structure when its hydrolysis goes up. The nature and the quality of the PAM are determined by the molecular weights and by the degree of hydrolysis. It is commonly used as a very dilute solution, which causes rapid agglomeration and sedimentation.

Three possibilities can be considered for the interaction between PAM molecules and clay particles: (i) an anionic exchange between the surface hydroxyls of the mineral and the carboxylic anions of the polymer; (ii) the formation of hydrogen bonds between the surface hydroxyls and the C=O of the polymer; (iii) the establishment of bridges involving divalent ions, originating from electrostatic forces [25–29].

In Fig. 8, the viscosity of Ca- and Na bentonite–water systems is plotted vs. PAM concentration for a 2% Ca and Na bentonite–water systems. The rheological properties of bentonite–water system are quite

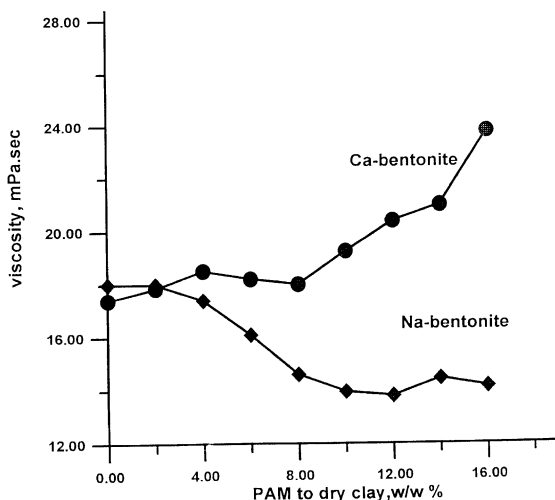


Fig. 8. The influence of (a) PAM on the viscosity (at $\gamma = 100$ rpm) of 2% (w/w) Ca bentonite–water system, (b) Na bentonite–water system.

variable depending on the structure of the mineral, its particle size and the pH of the environment. The Ca bentonite (natural sample) has a low apparent viscosity (16 mPa s), whereas the Na-peptized sample has a higher apparent viscosity (18 mPa s) at 100 rpm. The apparent viscosities of the samples increase with an increase in the Na content [10].

The effectiveness of PAM on natural and peptized samples is quite different. The values of apparent viscosity decrease with increasing PAM concentration in Na bentonite–water system and reveal that contacts exist between protonated edges and the negative faces. The formation of cardhouse structures is not important at these PAM concentrations. These phenomena can be explained by a screening effect on the electrical charges of faces and edges of particles; the net electrostatic interaction between particles decreases. As a result, mechanical coupling in the system reduces and the viscosity decreases. This effect increases in relation to the amount of PAM concentration.

PAM makes a flocculation effect on Ca–water system (Fig. 8). This effect increases with the concentration of the PAM. PAM endures on the clay particles. Ca ion shows an increasing effect on bridging flocculation. The newly formed network increases the resistance of the system. The interaction between the clay particles becomes stronger, the mechanical coupling becomes longer ranged and the viscosity increases.

A third bonding possibility would originate from the interaction between polyvalent cations (Ca^{2+}), acting as cross-linking agents between the solid surface and the polymer. The interaction between the polyacrylamide and the clay micelles is attended by a co-flocculation, characterized by the formation of polymer bridges between several mineral particles [26].

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 change densities.

4. Conclusions

In this study, same amounts of PAM have been added to the bentonite–water systems in the same

conditions. The different results show the importance of the changeable cations that bentonite includes, on the interaction of the clay particles and PAM molecules. Whereas PAM has a flocculation effect in Ca bentonite–water system, it has a deflocculation effect in Na bentonite–water system. Ca^{2+} ions advance the formation of bridging flocculation. PAM molecules are being adsorbed at the particle surfaces instead of going into the layers of Ca bentonite systems.

The deviations that have been observed in the vibration frequencies spectrums of PAM added Ca and Na bentonites is an indicator of the interaction between the PAM molecules and clay particles.

In summary, our results conclude the following: the rheological properties of bentonites and the formation of gel structures with water are altered by the addition of PAM. The type of bentonite and the concentration of PAM are influential factors in the order given.

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