The rheological properties and characterization of bentonite dispersions in the presence of non-ionic polymer PEG

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The effect of poly(ethylene glycol) on the flow behavior of Ca-bentonite and soda activated bentonite dispersions was characterized by the plastic viscosity, the relative viscosity and the yield values. In the range 0.025–12.5 mol/m^3, poly(ethylene glycol) (PEG400, PEG3000, PEG8000) was added to bentonite-water systems in different concentrations. Three layered phases with different basal spacings for each Ca- and Na-bentonites were obtained, as shown by XRD studies. The maximum swelling had a basal spacing at 1.82 nm for both PEG400 containing Ca- and Na-bentonites. In addition, expanded basal spacings are displayed at 1.91 nm for Ca- and 2.08 nm for PEG8000 containing Na-bentonites. After the PEG addition, some significant changes in rheological properties were observed; corresponds changes were also found during XRD and IR studies. The results are interpreted according to the type of bentonites, molecular weight of PEG and their concentrations. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Montmorillonite is a member of the smectite group minerals and has a high swelling ability in water. Smectite group clay minerals exhibit many industrially useful properties due to their unique hydration and dehydration capabilities. These properties make various montmorillonites useful as binders, plasticizers, lubricants and rheological control agents. The general rock name bentonite is given to some clays which contain appreciable quantities of smectite minerals and also have a volcanic origin. Bentonitic clays have large adsorption capacities for polymer compounds and surfactants due to their unique atomic structure [1–3].

The determination of the rheological properties of bentonite-water systems is very important for the characterization of these systems. In order to observe various changes in the flow properties when especially salt, polymer and surfactant are added, it is necessary to describe them to determine their application fields in industry.

The flow behaviours of the bentonite-water systems can be modelled by a pseudoplastic rheological model [3], which depends on concentration, particle shape, particle size distribution and, chemical interactions. The rheological behaviour of the system is determined by the attractive and the repulsive forces between clay particles, which interact with each other through Coulombic and van der Waals forces. The magnitude of the forces is determined by physical and chemical properties of the bentonite-water systems. As a result of these interactions EE (Edge-to-Edge), EF (Edge-to-Face) and FF (Face-to-Face) combinations may be obtained. These simple modes of particle interactions are helpful in understanding the stability and rheological behaviour of a clay-water system.

It is obvious that any additive, when added into the system, changes electrical double layers on surrounding clay particles; consequently, electrostatic behavior between clay particles and rheological properties will be changed. Knowledge of the structure of the interfacial region is very important for better understanding of the stability-flocculation relation of this system. In clay-water dispersions, the interfacial region is modified by addition of electrolytes, surfactants and polymers.

The adsorption of organic polymers on clay minerals has been widely studied [4–10]. Generally, studies have been made of physical properties resulting from the addition of some additives in various clay-water

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systems. In many studies, mostly physical properties such as, particle size, surface structures, basal $d_{(001)}$-spacings, pore-size distribution and surface area [11–14] were taken into consideration. Some studies have investigated the adsorption capacities of several organic compounds on clay minerals and the feasibility of their application to industrial waste water treatment [15, 16]. In these experiments, the same polymers were used, but with different molecular weights and in different concentrations [11].

Non-ionic polymers poly(ethylene glycol) (PEG) and its derivatives are widely used in various industries and are exhausted in wastewater [15–17]. Therefore, PEG was selected to use in this study. The effects of PEG-400, PEG-3000 and PEG-8000 [HO-$(CH_3CHO)_n H$] polymers on rheological properties of natural Ca-bentonite and Na-peptized bentonite were investigated.

2. Experimental

The clay sample was obtained from the bentonite deposits in Enez, Turkey (Bensan Co.). X-ray diffraction and IR techniques were used to determine the clay mineral types. The dominant clay mineral was found to be dioctahedral montmorillonite with minor amounts of illite and kaolinite. Quartz was always present in the clay fraction.

The chemical composition of the sample was determined by atomic adsorption spectroscopy and silica analysis was done by the gravimetric method. The Ca-bentonite (natural sample) has a composition (wt%) of Al_2O_3 19.00, SiO_2 58.80, Fe_2O_3 3.50, CaO 4.60, MgO 2.80, Na_2O 1.00, K_2O 2.76, TiO_2 0.45 and H_2O 7.39. Peptization was done by mixing 4 wt% $NaHCO_3$ with the clay sample at 35% humidity. This mixture was left for a 7-day period in a semi-open stockroom where it was exposed to air circulation in order to obtain a better ion exchange reaction and so better quality drilling clay production. Soda activation is an economic method for changing the natural Ca- to Na-bentonite to obtain stable dispersions in water with both low moisture and low solid contents. Therefore, wide ranges of applications are available in industry, such as suspension oils, binding agents and plasticizers. The Na-peptized bentonite has a composition (wt%) of Al_2O_3 18.73, SiO_2 58.90, Fe_2O_3 3.72, CaO 4.35, MgO 2.63, Na_2O 3.36, K_2O 2.70 and TiO_2 0.49.

Zeta potential measurements were carried out using a PHOTAL, CSA-600 model (Otsuka Electronics Co.), a microelectrophoresis instrument equipped with microprocesser. The measured electrophoretic mobilities were automatically converted to zeta potentials by means of a built-in microprocessor. The zeta potential value for the Ca-bentonite sample was −32.40 mV, and for the Na-peptized sample it was −28.24 mV [18].

The organoclay sample was prepared by modification of bentonitic clay with the non-ionic polymer PEG. The flow behaviour of the dispersions was measured in a Brookfield DVIII + type low-shear viscometer. The sample was dispersed in water (2% w/w) and shaken intensively for 24 h. An adsorption time of 24 h was adopted for the PEG. Flow curves were analyzed using

the Bingham model, where the Bingham yield stress τ is given by the relation

$$\tau = \tau_e + \eta_{pl}\gamma. \qquad (1)$$

Here τ_e is the extrapolated yield value and η_{pl} is the plastic viscosity. Once the curve of shear stress vs. shear rate was obtained for samples under the given experimental conditions, the value of the extrapolated shear stress was determined from the intersection of the extrapolated linear portion of the curve with the axis. The method of least squares was used to determine the values of this intersection. Plastic viscosity was derived from the slope of this linear section.

The X-ray diffraction (XRD) analyses were done using a Philips PW1140 model X-ray difractometer, as shown in Fig. 1 (Güngör and Ece, 1999). IR analyses (400–4000 cm^{-1}) were performed on 0.1% concentration KBr discs using a Jasco Model 5300 FT/IR spectrophotometer. All spectra were obtained in the range 4000–400 cm^{-1}. Spectral outputs were recorded either in the absorbance or transmittance mode as a function of wave number. All chemicals used in this study were pure grade. Polyethylene glycol samples with molecular masses of about 400, 3000 and 8000 were obtained from Fluka Chemical Co.
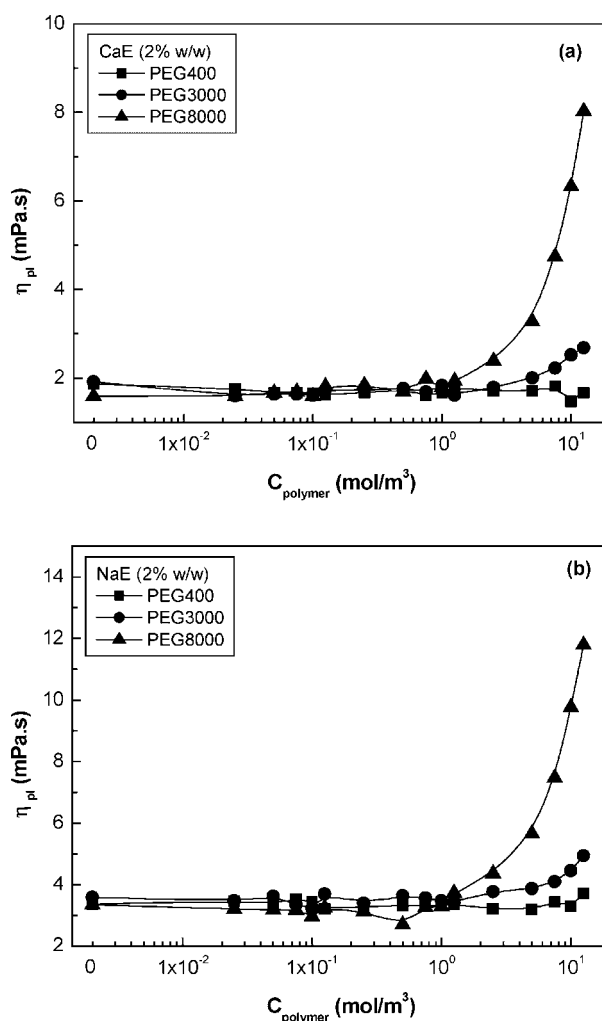

Figure 1 The plastic viscosity as a function of polymer concentration: (a) Ca-bentonite and (b) Na-bentonite.
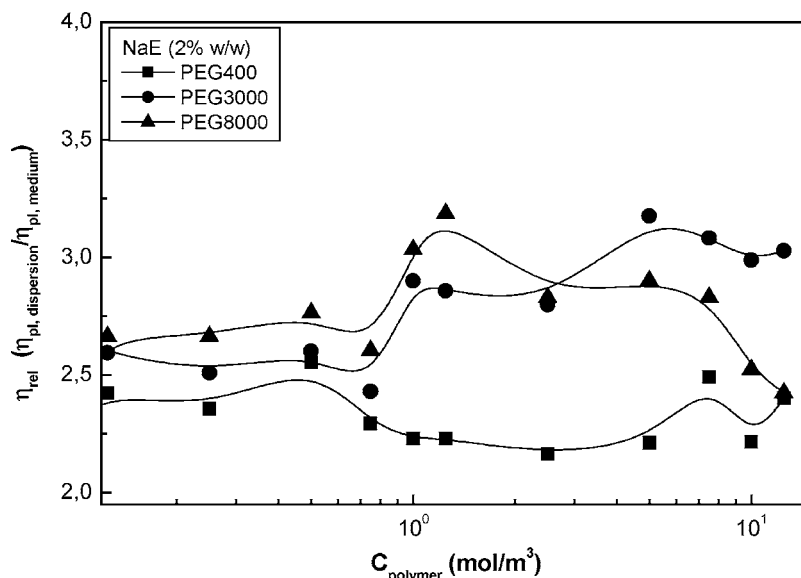
Figure 2 The relative viscosity of Na-bentonite + PEG dispersions.

3. Results

The addition of PEG into bentonite dispersion increased the plastic viscosities (η_{pl}) in both dispersions (Fig. 1a and b). Figures show that viscosity values increase especially after the addition of 1.25 mol/m^3 or more with PEG 8000.

The Na-bentonite sample has naturally a higher plastic viscosity (Fig. 1b), because Na-bentonites have smaller particle size, a greater number of clay particles in dispersion and increased surface area of clay minerals. At the beginning, when η_{pl} values were evaluated, it was thought that polymer addition into the system would cause flocculation. It is possible that PEG forms H-bonds with oxygen atoms on the surface of clay minerals; thus, PEG molecules can attach on various places on clay surfaces. PEG can hold on the clay surfaces and at the same time, some PEG molecules can attach to other clay surfaces and those already attached PEG molecules on the surface of other clay minerals may form bridging flocculation [2, 18, 19]. In this case, this new appearance in slurry could end up with flocculation. For this reason, the relative viscosities of slurries have been measured to decide which alternative is correct. The relative viscosity ($\eta_{rel} = \eta_{pl\,dispersions}/\eta_{pl\,medium}$) is not changed so significantly as η_{pl} with the polymer concentration. However, keeping the relative viscosity values (η_{rel}) in constant together with increasing in polymer concentration showed that an increase in η_{pl} values, after adding of 1.25 mol/m^3 additive, is not related to the flocculation of system, but it is related to swelling of all molecular weights of PEG's in water. Slight increase was observed for soda activated Na-bentonite with PEG3000 and PEG8000 (Fig. 2). On increasing the concentration of PEG8000, an increase occurred in the η_{rel}, up to concentration of 1.25 mol/m^3. This slight increase is more likely due to bridging flocculation formed between the clay particles. Further additions of PEG8000 caused slight decrease in the η_{rel}. The decrease of the viscosity may be attributed to deflocculation of the clay particles. XRD data showed that beyond this concentration,
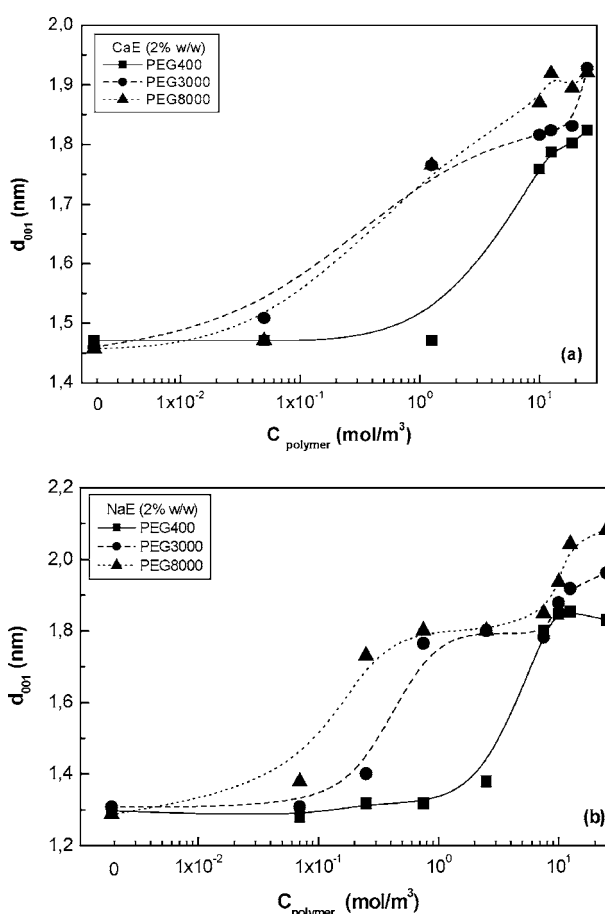

Figure 3 Basal spacing (d_{001}) as a function of PEG concentration: (a) Ca-bentonite and (b) Na-bentonite.

PEG8000 preferentially entered into the clay platelets instead attaching on the surface (Fig. 3). This caused swelling of the dispersion and increased η_{pl} of the dispersion. Beyond 1.25 mol/m^3 PEG concentration, η_{rel} continued to increase for PEG3000. This showed that small molecular weight of PEG still was attaching on to the clay surfaces at higher polymer concentrations. However, polymer contacts formed on the surface of clay minerals are not strong enough to develop yield
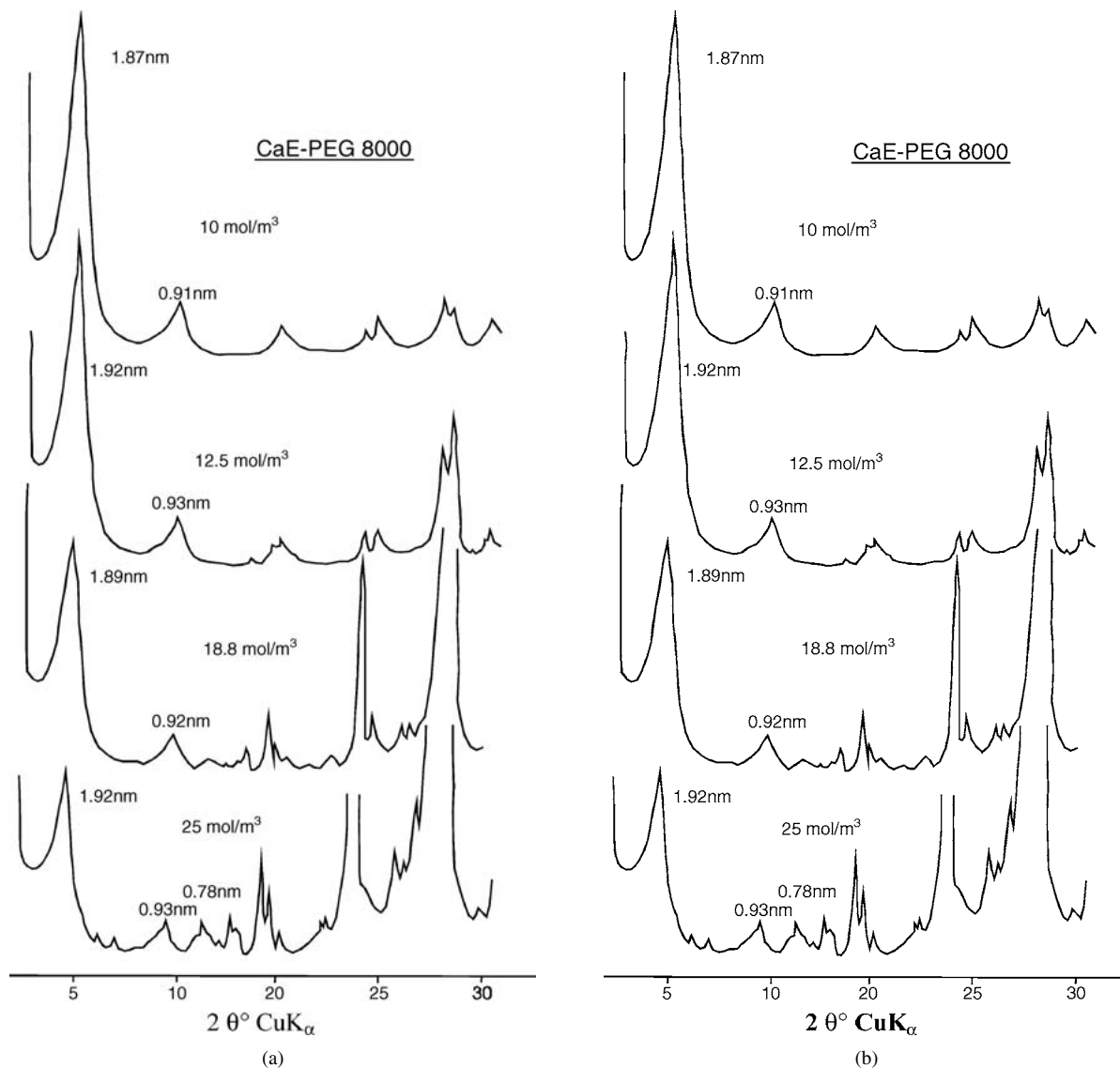
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Figure 4 X-ray diffraction patterns of PEG treated clay samples: (a) Ca-bentonite and (b) Na-bentonite.

value. There was no change on the yield value of either bentonite dispersions after the addition of PEG400 and PEG3000 polymers. In contrast, there was a slight change in the yield value of both bentonite dispersions on the addition of PEG8000.

How does the addition of PEG interact with clay minerals? In order to understand whether added PEG can enter into the interlayer of clay minerals or not, XRD analyses were done to measure $d_{(001)}$-spacings. Basal $d_{(001)}$-spacings of the films are shown as a function of PEG concentrations in Fig. 3. The study of $d = f(C)$ curves indicates that the Na-bentonite unit cell $d_{(001)}$ spacing increased from 1.29 nm (natural) to 2.12 nm in the PEG8000 added sample. In some samples, Na^+ is weakly bonded between the interlayers of the clays, therefore the polymer can easily move into the interlayer to swell the crystal structure. This is an expected result, because the displacement of Ca^{++} atoms, which are electrostatically bonded strongly to the layers, is rather difficult. Therefore, Na-smectite samples provide higher swelling properties at 2.12 nm with respect to Ca-smectite at 1.92 nm (Figs 3, 4a and b). The rheological properties were measured for the concentra-

tion interval of 0.025–12.5 mol/m^3, however, d-spacing measurements were done using XRD techniques up to 25 mol/m^3 concentration in order to better examine the swelling properties of bentonite-PEG suspensions (Fig. 4a and b). The PEG8000 enhances swelling properties most among the three polymers due to its higher molecular weight. PEG8000 increases the basal spacing of bentonites by 32 and 62% of their initial value for CaE and NaE respectively. Comparing these data with PEG400 and PEG3000 including lower molecular weight, these increases are 24 and 41% for PEG400 for CaE and NaE respectively and 32 and 50% for PEG3000 for CaE and NaE, respectively. The results show that PEG8000 increases the basal spacing most effectively.

The peak corresponding to structural hydroxyl stretching at 3627 cm^{-1} was attributed to Ca-smectite (Fig. 5). Hydrogen vibration, indicated by a broad peak centered on 3465 cm^{-1} was assigned to O—H stretching and an H—O—H deformation peak at 1641 cm^{-1} was also present in the FTIR spectrum of Ca smectite. The sharp peak due to Si—O stretching at 1043 cm^{-1}, and other sharp peaks due to Si—O bending at 523 and
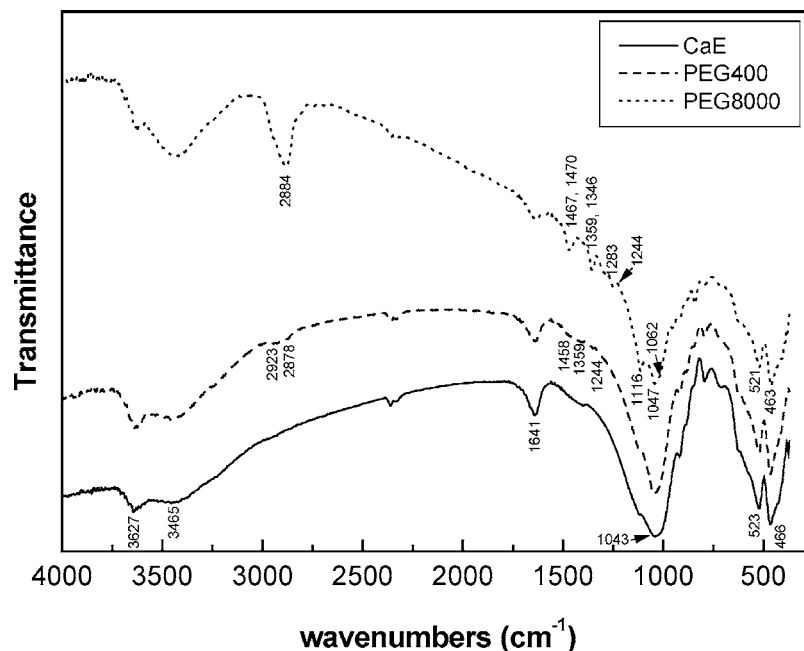
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Figure 5 FTIR spectra of Ca-bentonite, in addition of PEG400 and PEG8000 (1.25 mol/m^3).
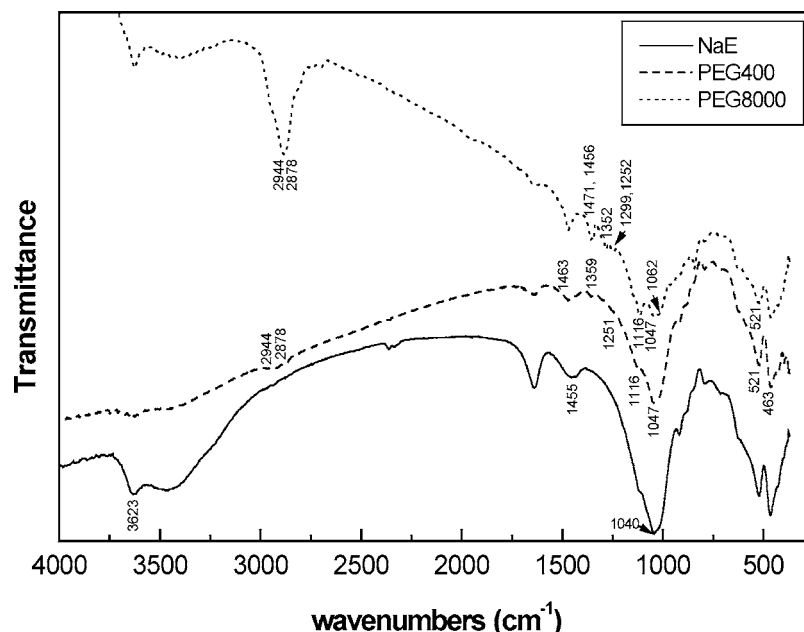

Figure 6 FTIR spectra of Na-bentonite in addition of PEG400 (2.5 mol/m^3) and PEG8000 (0.75 mol/m^3).

466 cm^{-1} were also observed. After NaHCO$_3$ activation, the FTIR spectra peaks of Ca-smectite were transformed to the hydroxyl peak and the results (Fig. 6) are seen more clearly at 3623 cm^{-1}. In addition, the Si—O stretching peak that appeared at 1043 cm^{-1} in Ca-smectite had moved to 1039 cm^{-1} in Na-smectite (Fig. 6). An additional peak also occurred at about 1455 cm^{-1}, due to the presence of calcite.

While standard PEG400 showed spectral peaks at 2882 cm^{-1} (alkyl CH stretching), 1457, 1352 1298, and 1250 cm^{-1} (alkyl CH deforming), 1109 cm^{-1} (C—O—C stretching), the FTIR spectra of PEG400 adsorbed on Ca-smectite showed additional peaks, including 2923, 2878 cm^{-1} (alkyl CH stretching), 1458, 1359, 1283, and 1244 cm^{-1} (CH deforming). The hydroxyl stretching frequencies were broadened on

PEG400 adsorbed Na-smectite. The FTIR spectra of PEG 400 adsorbed on Na-smectite was similar to that obtained for PEG400 adsorbed on Ca-smectite, with bands due to alkyl CH vibration at 2944, 2878, 1463, 1359, 1299, and 1251 cm^{-1}. For both PEG400 adsorbed on Ca- and Na-bentonites, the Si—O stretching peaks were broadened and gave two maxima at 1116 and 1047 cm^{-1}, respectively. The result of FTIR spectra in 12.5 mol/m^3 PEG400 adsorbed Ca-smectite was similar to 2.5 mol/m^3 PEG400 adsorbed Na-smectite.

While standard PEG3000 showed adsorption peaks at 2890 cm^{-1} (alkyl CH stretching), 1469, 1361, 1344, 1282, and 1242 cm^{-1} (alkyl CH deforming), 1113 cm^{-1} (C—O—C stretching) and 1062 cm^{-1} (C—OH stretching), the FTIR spectra of PEG3000 adsorbed on Ca-smectite showed additional peaks including:

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2884 cm^{-1} (alkyl CH stretching), 1467, 1470, 1359, 1346, 1283, and 1244 cm^{-1} (CH deforming), 1062 cm^{-1} (C—O—C-stretching) and 1116cm^{-1} (C—O—C stretching). The FTIR spectrum of PEG 3000 adsorbed on Na-smectite was similar to that obtained for PEG3000 adsorbed on Ca-smectite, with bands due to alkyl CH bending vibrations at 2878, 1471, 1352, 1299, and 1252 cm^{-1} and C—O—C and Si—O—C stretchings at 1103 cm^{-1}. Also, 1.25 mol/m^{3}PEG3000 adsorbed Ca-smectite FTIR spectra results were similar to 0.75 mol/m^3 PEG3000 adsorbed Na-smectite. Thus, it appears that PEG3000 does not present an organized structure in the interlamellar structure of smectite. PEG8000 adsorbed Ca- and Na-smectite samples also displayed similar peaks as PEG3000 adsorbed Ca- and Na-smectites.

While standard PEG8000 showed peaks at 3482 cm^{-1} (O—H stretching), 2888 cm^{-1} (alkyl CH stretching), 1469, 1361, 1344, 1282, and 1242 cm^{-1} (alkyl CH deforming), 1113 cm^{-1} (C—O—C stretching), 1060 cm^{-1} (C—OH stretching), the FTIR spectra of PEG8000 adsorbed on Ca-smectite showed additional peaks including: 3436 cm^{-1} (O—H stretching), 2888 cm^{-1} (alkyl CH stretching), 1472, 1361, 1346, 1281, and 1244 cm^{-1} (CH deforming), 1116 cm^{-1} (C—O—C stretching) and 1062 cm^{-1} (C—OH stretching) (Fig. 7). The FTIR spectrum of PEG 8000 adsorbed on Na-smectite was similar to that obtained for PEG8000 adsorbed on Ca-smectite, with bands due to O—H vibration at 3458 cm^{-1}, alkyl CH vibration at 2879, 1471, 1352, 1283, and 1252 cm^{-1} and C—O—C and Si—O—C stretching at 1105 cm^{-1} (Fig. 8).
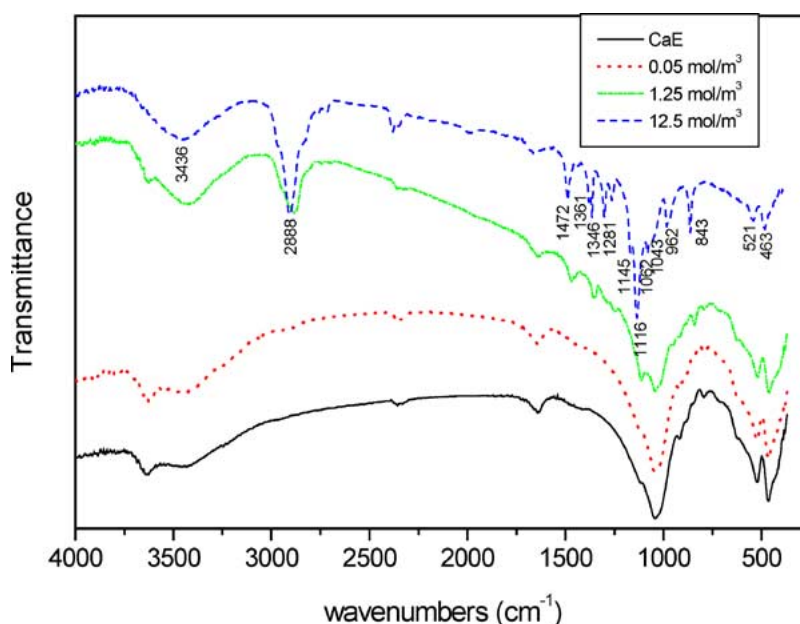

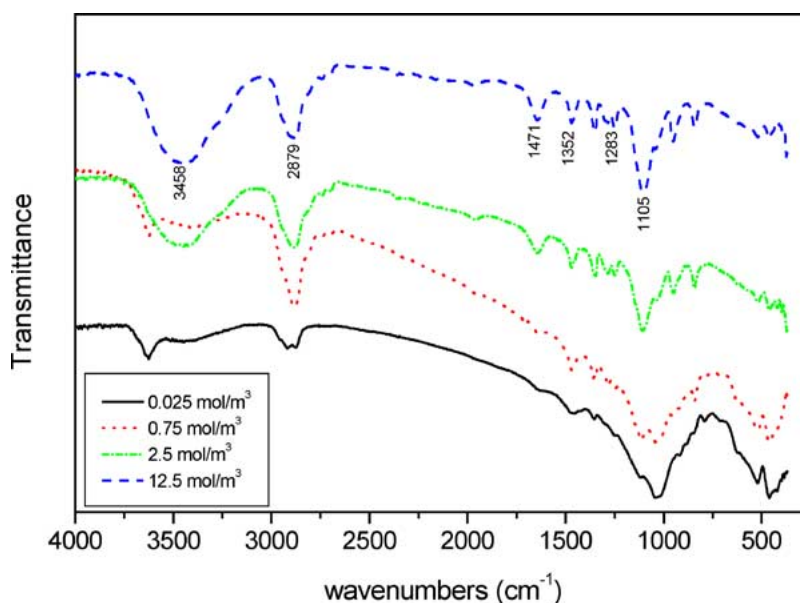
Figure 7 FTIR spectra of Ca-bentonite, in addition of PEG8000.

Figure 8 FTIR spectra of Na-bentonite in addition of PEG8000.

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4. Discussion

When clay minerals are added into water, an adsorption process will proceed together with swelling and dispersion. Colloidal clay particles dispersed in a continuous medium are in constant Brownian movement. The combination of interaction energies determines whether the particles remain separate, so that the dispersion is stable in the colloidal sense, or stick together, in which case destabilization (coagulation or flocculation) occurs. Clay particles generally interact with electrical double-layer repulsion or attraction, Van der Waals attraction and steric effects.

The viscosity of bentonite-water systems increases with an increase in Na content. The Na-peptized bentonite has a high plastic viscosity (3.42 mPas), whereas the Ca-bentonite (natural sample) has a lower plastic viscosity (1.79 mPas). This difference may be caused by the difference in swelling and dispersion mechanisms of these two bentonitic clays [17]. Exchangeable cations, which determine orientation of many physical properties of bentonitic clays, such as particle size, surface charge, surface area and particle number per unit volume, also have a strong influence on the dispersion mechanisms. The increase of viscosity and consistency of Ca-bentonite dispersions after addition of sodium ion is a direct consequence of the opposite effect of Na^+ and Ca^{++} ions. When clays are dispersed in water, Na-peptized bentonite has unique crystal layers in very fine colloidal particles from tens to hundreds of microns because the electrostatic attraction among the crystal layers is weaker. On the other hand, for the Ca-bentonite, the mean particle size is kept at several μm in water, because the electrostatic attraction among the crystal layers is stronger.

The chemical additives (electrolytes, polymers, surface active agents, etc.,) will interact with clay particles when added to a water-clay system. All these interactions are affected by the pH and type and concentrations of additives added in solution. As a result, depending on various different parameters, which are related to the differences in structures of clay particles and compositions of additives, more tight and closed or more loose and open layers can be observed.

Non-ionic polymers influence flocculation and deflocculate clays, which normally have negative charges in water. Non-ionic polymer does not interact electrostatically with charged clay particles. The polymer molecules can attach or anchor on the particle surfaces and into the interlayers. Adsorption of polymer onto the charged surface of clay particles leads to significant modification of the charge distribution in the electrical double layers. PEG is a non-ionic structural polymer that is dissolvable in water and it can be viewed as an extended glycol.

An increase in d-spacing after the addition of PEG elucidated that ion exchange reaction had occurred between PEG polymer and exchangeable cations in the interlayer of clay minerals. Penetration of organic compound into the interlayer space can change the thickness of the bentonite platelets. Network structures collapse when displaced by less polar compounds. It is well known that bentonitic clay forms intercalated compounds with various organic and inorganic compounds. This phenomenon is strongly related to the swelling behaviour of smectite with water molecules [15].

These results show that the PEG molecules and clay particles interact with each other. Thus, PEG is loosely bound and interacts near the surface and/or into the interlayers of smectites. In the exchangeable Na^+ cation containing samples, the XRD data revealed that polymers more easily introduce into the interlayers and replacement of Ca^{++}, which has electrostatically more tight bonds than Na^+ between interlayers, is more difficult than Na^+ ($d_{Na} > d_{Ca}$). The OH stretching frequencies in the bentonite-PEG's adsorption products were broadened and displaced to lower frequencies by about 20–40 cm^{-1}. These shifts may be attributed to formation of hydrogen bonds. For further studies, zeta potential values of bentonite-PEG suspensions will be useful to interpret the interaction of PEG molecules with clay particles.

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