

Influences of Nonionic Poly(ethylene glycol) Polymer PEG on Electrokinetic and Rheological Properties of Bentonite Suspensions

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ABSTRACT: The determination of the electrokinetic properties of colloidal systems is very important for the characterization of these systems. Colloidal systems have high adsorption performance due to the carrying of negative charges and the colloid structure. The control of the electrokinetic properties of the bentonite–water system are important not only from a technological point view; they are also important from a scientific point of view. Knowing the electrokinetic and rheological properties of bentonite minerals is important for the estimation of the behavior of clays under various environmental conditions. The purpose of this study was to interpret the effect of the nonionic poly(ethylene

glycol) (PEG) polymer on electrokinetic and rheological properties. Zeta potential and viscosity measurements were done as a function of PEG molecular weights (400, 3000, and 8000) and their concentrations (2.5×10^{-5} to 1.25×10^{-2} mol/L). We interpreted the experimental data, taking into account these two parameters. X-ray diffraction studies were done together with the electrokinetic and rheological measurements. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 341–346, 2002

Key words: rheology; zeta potential; viscosity; bentonite–water system; nonionic surfactant; poly(ethylene glycol)

INTRODUCTION

Bentonitic clay, with a large amount of montmorillonite mineral, shows a colloidal structure because of its internal structure and small particle size. However, because of its particle structure, shape, charge distribution, and ion exchangeability, the behavior of colloidal bentonitic clay suspensions is much more difficult to interpret and to predict than those of most other clay minerals. Bentonite–water systems are generally more complex. The estimation of the zeta potential (ζ) from electrophoretic mobility measurements in clay colloid systems is complicated because it has two very different types of surfaces and charges exposed by the particles in suspensions. Bentonite particles contain negative and positive charges in large surfaces and narrow edges, respectively. Because of this structural feature, electrostatic interactions can play roles as both attractive and repulsion forces, and therefore, the interpretation of interactions becomes more difficult. Such properties lead to discrepancies among the results of electrokinetic and

rheological experiments and make their interpretation more difficult.^{1,2}

ζ is an electrical potential in the double layer at the interface between clay particles and the surrounding liquid in which particles move, and it is the measurement of the stability of a clay solution, which has a great importance in many of the industrial processes with respect to flocculation or deflocculation phenomena. Today, ζ measurements are used especially in medicine, in biomedical determinations, and in metallurgy for the determination of the flocculent nature of the media used in flotation of mineral oxides.^{3,4}

There are many published studies on the microelectrophoretic behavior of colloidal suspensions other than clay–water systems.^{5–13} In a previous article,¹⁴ we only evaluated the rheologic properties of bentonite–water systems in the presence of nonionic poly(ethylene glycol) (PEG). In this study, we investigated differential changes in electrokinetic properties of the same colloidal system and Ca-Enez, peptized Enez, and a purified natural montmorillonite (SNaM) sample, which were used to prepare suspensions by the addition of PEG additives of different molecular weights (400, 3000, and 8000) and different concentrations.

EXPERIMENTAL

The clay sample was obtained from bentonite deposits in Enez, Turkey (courtesy of Bengan Co.). A

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Philips PW 1040 model X-ray diffractometer was used to determine the clay mineral types. X-ray diffraction (XRD) analyses are shown in Figure 1.¹⁴ The dominant clay mineral was dioctahedral montmorillonite with a minor amount of illite and kaolinite. Quartz was always present in the clay fraction. There was no other clay or nonclay mineral in the samples.¹⁴

CaE indicates natural Ca-bentonite collected from Enez area, and NaE indicates the peptized version of CaE with 5% NaHCO₃. For the purification procedure (SNaM sample), we used soda-activated bentonite. First, iron oxides were removed by a sodium citrate and sodium dithionate buffering technique. To remove carbonate, we mixed bentonite dispersion with a NaCl/HCl solution and then washed it three times with these solutions. Organic material was oxidized with hydrogen peroxide solution at 80°C. The 2 μm fraction was separated by sedimentation with Stoke's law, and after sedimentation, a large amount of montmorillonite dispersion was obtained. This sodium montmorillonite dispersion was coagulated with a NaCl solution. The coagulate was separated by centrifugation and then dialyzed in monodest water until the conductivity of system was 7–8 mS/cm. The dispersion was freeze dried, and the dried material was powdered in a ball.^{15,16}

The major elements of some samples were determined with X-ray fluorescence (XRF; RIGAKU 3070) with the rock standards of the Geological Survey of Japan. The samples (0.6 g) were fused with 6 g of XRF-grade flux, a 4:1 mix of lithium metaborate and lithium tetraborate, for 20 min at 1100°C with intermittent swirling to ensure thorough mixing; the resultant melt was poured into the crucible (80% Pt + 20% Zr) to form glass beads. The analytical precision and accuracy of the ICP-MS method were checked with the Geological Survey of Japan rock standards (JR-3, JG-3, JH-1). The results of the chemical analyses of these samples are given in Table I.

The particle size distribution (PSD) of the bentonitic clays was measured by the sedimentation technique method. A photocentrifugal particle size analyzer (SACP4L, Shimazu Corp.) was used.¹⁷ Samples were put in distilled water and dispersed ultrasonically for 10 min under 50 W. No dispersing reagents were used. The preliminary measurement of the instrument is in the range 20–0.02 μm. After adjusting to the proper concentration and 30-s ultrasonic vibration again, we measured the PSD of three samples in the range of 40 to 0.04 or 0.03 μm. The PSD data are shown in Figure 1. The results show that the particle size of the SNaM sample was smaller than the other bentonite samples.

ζ measurements were carried out with a PHOTAL model CSA-600 (Otsuka Electrokinetic Co.), a microelectrophoresis instrument equipped with a microprocessor. The electrophoretic mobilities measurements were automatically converted to ζ by means of the

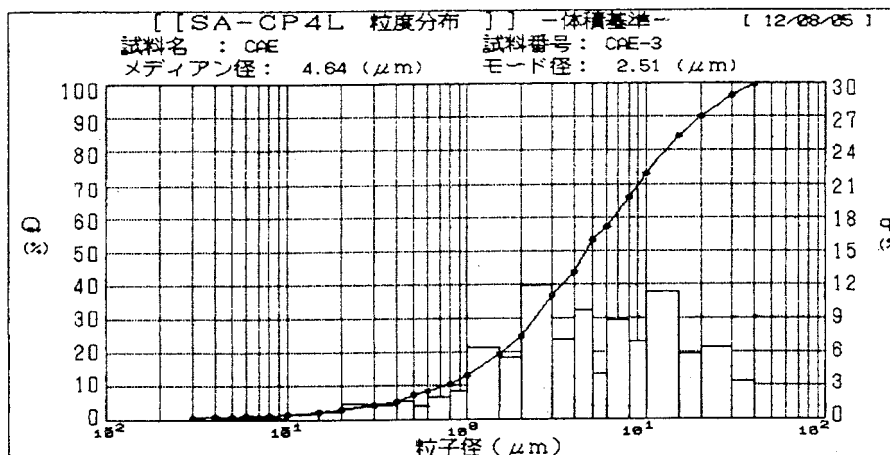
built-in microprocessor. ζ value for CaE was –32.40, for NaE, it was –28.24, and for SNaM, it was –44.70 mV.

The organoclay sample was prepared by the modification of bentonitic clay with the nonionic PEG. The flow behavior 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. The adsorption time of 24 h was adopted for the PEG, and all the suspensions exhibited Bingham plastic behavior.

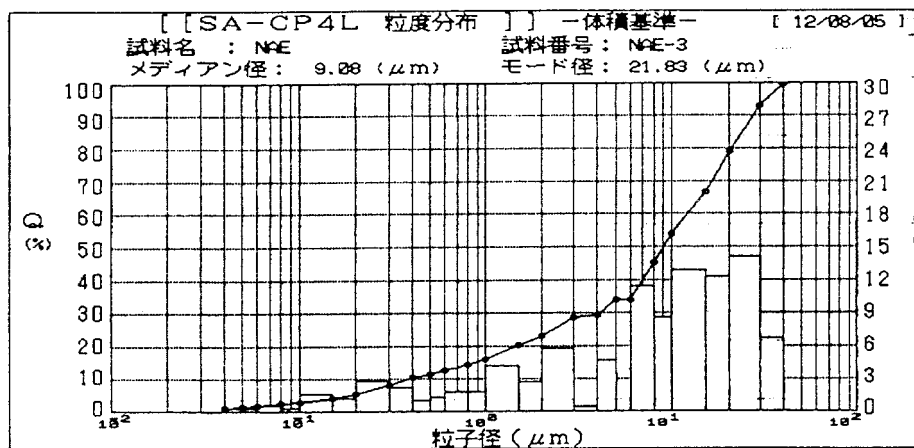
RESULTS

When colloidal clay minerals are added into water, different effects on the rheological and electrokinetic properties will occur due to the interactions between particles and water molecules, particles and particles, and particles and ions. The particles interact with each other through Coulombic and van der Waals forces. Clay particles move randomly in the suspension, and this motion, which is called *Brownian motion*, causes particle-to-particle collisions. The stability of the dispersion is directly dependent on how the particles interact during the collision moments. If the attractive van der Waals forces dominate, the particles attract each other during the particle collisions, and the dispersion flocculates. To achieve stable dispersions, the repulsive forces must exceed the attractive forces. The repulsive forces are caused by electrostatic interactions between the particles or by a steric hindrance through the adsorbed polymer layer. At high polymer concentrations, the electrical double layers are compressed, which causes a reduction of the repulsive forces between the particles. Through the adsorption of a polymer (PEG) layer onto the particle surface, a steric barrier is obtained between the particles. The magnitude of the attractive forces is reduced by the fact that the smallest possible distance between the particles is increased by the polymer (PEG) layers. The interaction between the adsorbed polymer layers also gives rise to a repulsive force between the particles. When a dispersion is stabilized by an adsorbed polymer layer, causing a repulsive force by the interaction between polymer layers, the dispersion is sterically stabilized.

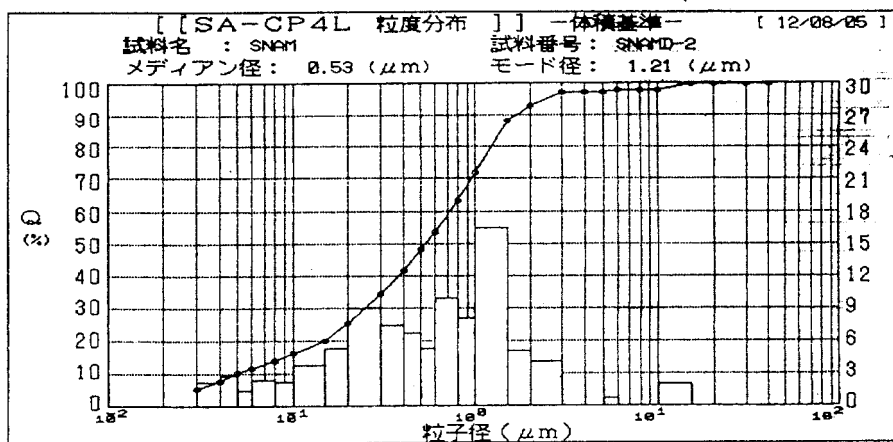
Chemical additives (electrolytes, polymers, surface active agents, etc.) will interact with clay particles when added into a water system. The extent of the interaction of clay particles and additives is determined by a number of parameters. These are particle size and shape, the surface charge of clay particles, solid/water ratio, additive type, the degree of hydrolysis of additive, concentration and molecular weight of additives, pH, and temperature.^{14,18–20} Different polymers have different effects on bentonite suspensions. The effects of the polymers on the rheological



(a)



(b)



(c)

Figure 1 PSD graphics: (a) CaE sample, (b) NaE sample, and (c) SNaM sample.

TABLE I
Chemical Analyses (wt %) of Bentonite Samples

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	CaO	K ₂ O	MgO	MnO	TiO ₂	P ₂ O ₈
CaE	60.18	18.49	5.65	1.41	4.60	2.32	2.40	0.11	0.68	0.37
NaE	58.90	18.73	3.71	3.36	4.35	2.70	2.63	0.09	0.50	0.34
SNaM	62.66	19.31	6.10	2.36	0.22	0.72	2.48	0.01	0.78	0.04

and colloidal properties vary with increasing in concentration. The importance of the surface properties of bentonites, such as adsorption, adjoining character, and high colloidal water content, increases while the particle size decreases. When the particle size of clay minerals in suspension decreases, they will interact better with each others because they have larger surface areas, and then particle-to-particle interaction abilities will be enhanced.^{8,20}

PEG is a nonionic structural polymer that is dissolvable in water. The chemical composition of PEG can be viewed as extension glycols. Nonionic polymers are macromolecular with a number of polar functional groups, which are distributed along the chains. A nonionic 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 the polymer on the charged surface of clay particles leads to a significant modification in the charge distribution of the electrical double layers.

Figures 2–4 show the variations in the plastic viscosities (η_p) and ζ as a function of concentration. The viscosity of the bentonite–water systems increased with an increase in the montmorillonite content. The η_p values of CaE, NaE, and SNaM were 1.79, 3.42, and 6.50 mPas, respectively. This difference may have been caused by the difference in the swelling and dispersion mechanisms of montmorillonite. PEG-400

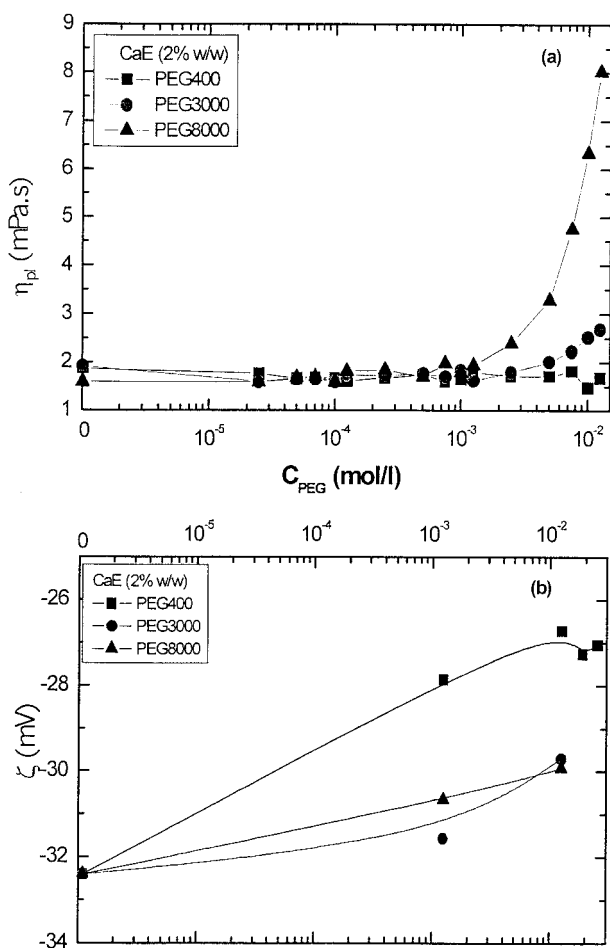


Figure 2 Influence of PEG on the viscosity (at $\gamma = 100$ rpm) and ζ of 2% (w/w) CaE bentonite suspensions.

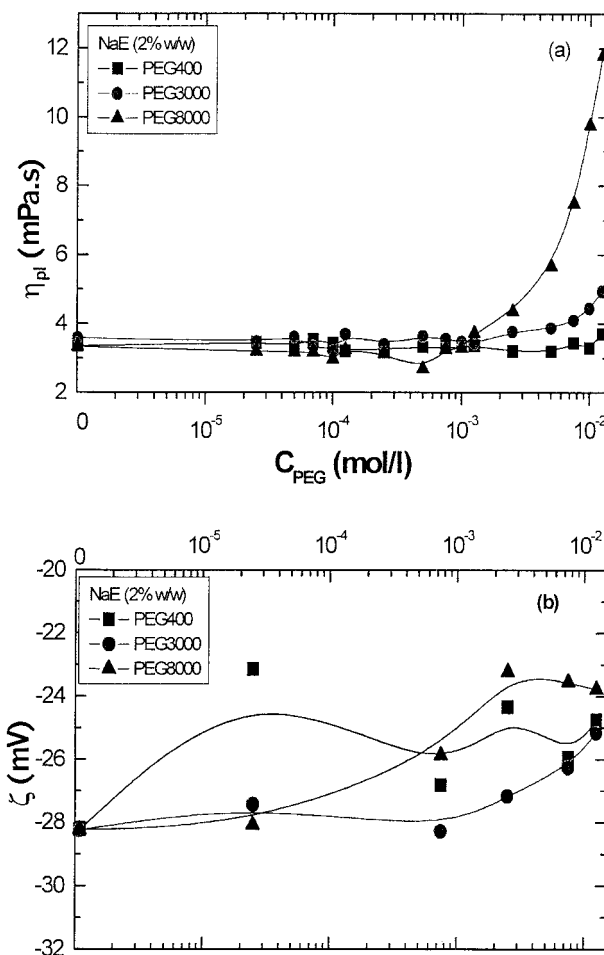


Figure 3 Influence of PEG on the viscosity (at $\gamma = 100$ rpm) and ζ of 2% (w/w) NaE bentonite suspensions.

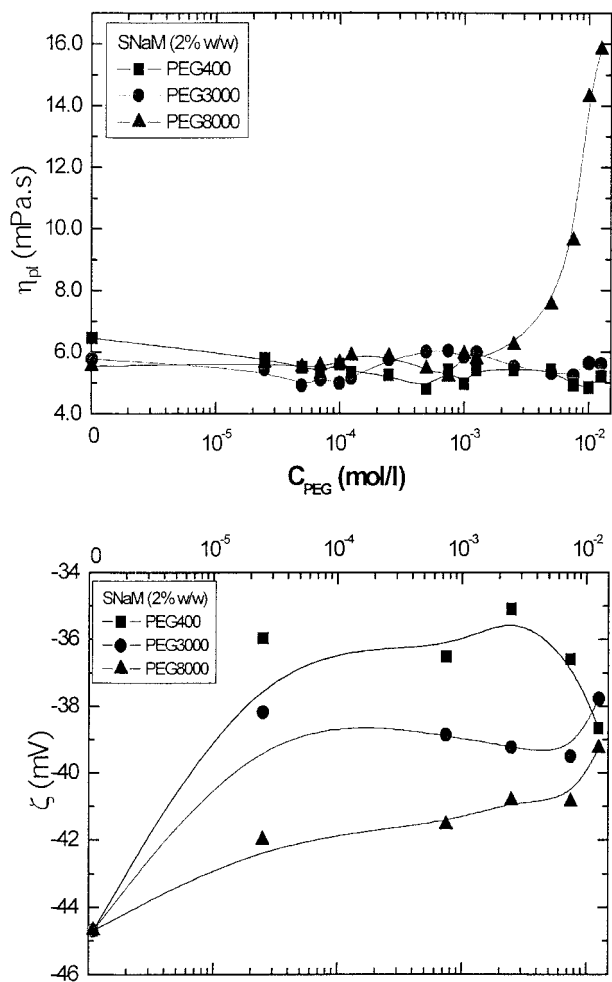


Figure 4 Influence of PEG on the viscosity (at $\gamma = 100$ rpm) and ζ of 2% (w/w) SNaM bentonite suspensions.

and PEG-3000 polymers were clearly not effective for the η_p values. As the amount of montmorillonite in the bentonite increased (Table I), the effect of the PEG also increased, and the greatest interaction occurred in the SNaM sample.

The effects of the PEG-400 on ζ were larger, as shown in Figures 2–4. The behavior of ζ as a function of concentration was the same in all three PEG-containing bentonite suspensions. ζ decreased with increasing amounts of PEG. This could be explained by a screening effect on the electrical charges of edges of particles, which caused a decrease in electrostatic interactions between particles. As a result of the screening of surface charge by the addition of PEG, electrostatic interactions would become less, and there would also be a decrease in ζ . SNaM gave more defloccule suspension than the other bentonite samples, based on ζ measurements (Fig 4).

XRD studies revealed that the expansion of $d_{(001)}$ spacings up to 17.6 Å after the addition of the additives was good indication for the introduction of PEG molecules into the interlayer structures (Fig. 5). However, the viscosity of the suspension did not change too much after water molecules between interlayers were left out. Similar observations were done, and slight changes were found in ζ measurements after the addition of the same quantity of polymer. Besides, the numerical difference and the effects on the rheological and electrokinetic properties of PEG on the three samples were alike.

In the CaE and NaE suspensions, it was proven with monitoring the changes in relative viscosity that the large proportion of the fast and continuous increase in viscosity, after the addition of about 10 g/L of PEG-

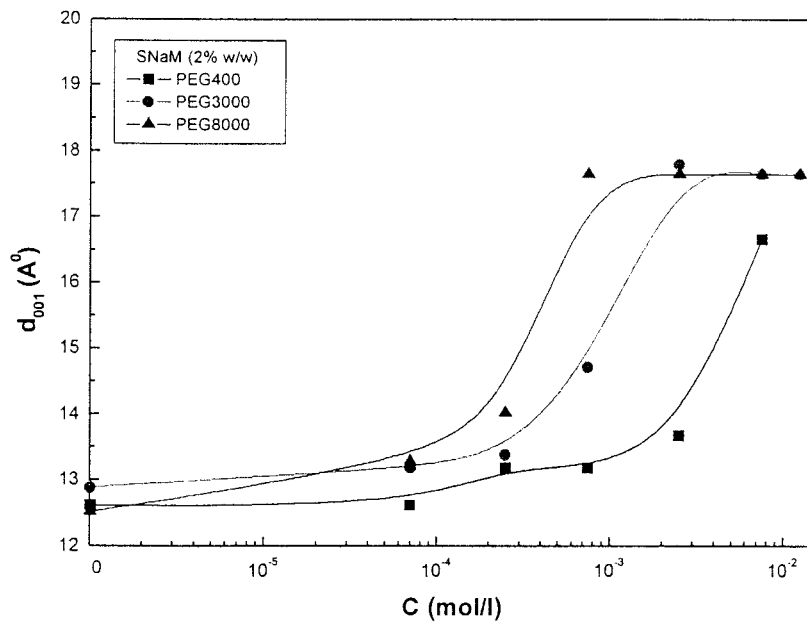


Figure 5 Basal spacing (d_{001}) as a function of PEG concentration for SNaM suspensions.

8000 was due to the flocculation of polymer molecules among each other.¹⁴ Figures 2–4 show an increase in PEG concentration together with a decrease in ζ values, which indicate that the system became more flocculated. A small decrease in ζ values created screening effects on some charges of clay particles with polymer molecules that caused a decrease in repulsive forces between particles. However, if this decrease was bigger, in this case, structure of the system should have changed, causing bridging flocculation of PEG molecules, and the whole system could be flocculated.

As a result, the experimental studies on the suspensions prepared with the CaE, NaE, and SNaM samples and treated with three different PEG molecules of different molecular weights and concentrations documented that expanding $d_{(001)}$ spacing indicated the introduction of PEG molecules into the interlayer, and a decrease in ζ values indicate a part of the PEG molecules were attached on the clay surfaces, especially in the SNaM sample. Rheological properties showed that viscosity and yield values increased with an increase in the molecular weight of nonionic polymers.

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