

# Influence of Nonionic Polymers on the Rheological and Electrical Properties of Egyptian Bentonite

Bassem A. Mostafa,<sup>1</sup> Faiz F. Assaad<sup>2</sup>

<sup>1</sup>Alexandria Company for Petroleum Additives, Alexandria, Egypt

<sup>2</sup>National Research Center, Cairo, Egypt

Received 27 October 2006; accepted 25 May 2007

DOI 10.1002/app.27015

Published online 25 September 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The rheological properties of Egyptian bentonite suspensions in the presence of nonionic polymers were investigated. Two different types of nonionic polymers were studied: poly(ethylene glycol) (molecular weight = 6000 g/mol) and poly(vinyl pyrrolidone) (molecular weight = 40,000 g/mol). The rheological properties (plastic viscosity, apparent viscosity, and yield point) of concentrated clay suspensions (6–8% w/w) at different temperatures after 24 h were determined. As the nonionic polymer concentrations increased, the rheological properties of the bentonite suspensions showed a slight increase, especially at an 8% clay content. The electrical properties (electrophoretic mobility and  $\zeta$  potential) of Egyptian bentonite in the presence of different nonionic polymers were

measured with a  $\zeta$  meter. The results showed that the  $\zeta$  potential of this bentonite was higher with 200 mg/L poly(vinyl pyrrolidone) than with 1000 mg/L poly(ethylene glycol). Potential energy profiles for bentonite suspensions for these nonionic polymers were constructed to show that the net energy barrier for bentonite suspensions followed repulsion or attraction between particles. These profiles showed that the potential energy profile of a bentonite suspension with 200 mg/L poly(vinyl pyrrolidone) produced a high repulsion potential energy between clay surfaces; that is, the suspension stability improved. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 732–743, 2008

**Key words:** adsorption; barrier; rheology; viscosity

## INTRODUCTION

It is an important criterion for many technological applications to know and control the rheological properties of a clay–water system in a colloid structure. The structure of the aqueous clay depends on the clay particles, water molecules, and properties of the ions (counterions). There are several methods to determine the interactions forces between particles and interactions behaviors. One of these methods is to determine the rheological properties of the system.<sup>1,2</sup>

The rheological properties of a bentonite–water system are related to the interactions between the particles of the system. The bentonite particles interact with one another through coulombic and van der Waals forces. As a result of these interactions, edge-to-edge, edge-to-face, and face-to-face combinations may be obtained. These simple modes of particle interactions are rather practical in understanding the stability and rheological behavior of clay–water systems.<sup>3</sup> The addition of a nonionic polymer to a bentonite suspension can induce bridging flocculation, especially at lower concentrations, which leads to improved rheological properties of the suspension. At higher polymer concentrations, the free polymer concentration is

increased, and as a result, bentonite suspension deflocculation is attained. Consequently, the rheological properties of the bentonite suspension decrease.<sup>4–8</sup>

Beside the rheological properties of a bentonite–water system, the electrical properties, such as the  $\zeta$  potential, of clay–colloid systems give information on the thickness of the adsorbed layer and the configuration of polymers on the clay surfaces. At a lower nonionic polymer concentration, the thickness of the double layer increases because of the adsorption of the nonionic polymer onto the surface of more than one particle. Therefore, the suspension stability improves. At higher polymer concentrations, steric stabilization may result in the depletion of double-layer thickness, and consequently, the suspension stability decreases.<sup>9,10</sup>

The aim of this study was to evaluate the influence of nonionic polymers on the rheological and electrical properties of bentonite clay suspensions. Also, the effect of temperature on these rheological properties was examined.

## EXPERIMENTAL

### Materials

Egyptian bentonite clay was used in this study. Nonionic polymers—poly(ethylene glycol) (PEG) of a molecular weight of 6000 g/mol and poly(vinyl pyrrolidone) (PVPy) of a molecular weight of 40,000 g/mol—were used.

Correspondence to: B. A. Mostafa (dr\_bassem2003@yahoo.com).

**TABLE I**  
**Particle Size Analysis of Bentonite Clay**

Particle size (μ m)	Weight (g)	Weight (g)	Average weight (g)	%
>90	0.21	0.13	0.17	0.34
75–90	0.92	1.16	1.04	2.08
63–75	21.63	21.59	21.61	43.22
45–63	18.99	19.66	19.33	38.66
32–45	6.81	6.11	6.46	12.92
20–32	1.28	1.25	1.27	2.54
<20	0.13	0.10	0.12	0.24

Sample weight = 50 g.

**Methods**

The cation exchange capacity and specific surface for the Egyptian bentonite clay were 77.3 mequiv/100 g and 346.7 m<sup>2</sup>/g, respectively. Particle size fractionation and chemical analysis of a bentonite clay sample are listed in Tables I and II. X-ray diffraction analysis for this bentonite sample was performed as shown in Figure 1.

The rheological properties, which include the plastic viscosity, apparent viscosity, and yield point, were determined as follows:

- Plastic viscosity (cP) =  $R_{600} - R_{300}$
- Apparent viscosity (cP) =  $R_{600}/2$
- Yield point (lb/100 ft<sup>2</sup>) =  $R_{300} - \text{Plastic viscosity}$

where  $R_{600}$  is the rotational viscosity at 600 rpm and  $R_{300}$  is the rotational viscosity at 300 rpm.

The rheological properties of different bentonite clay suspensions (6–8% w/w) at different temperatures after 24 h of aging were determined.

The rheological properties of different bentonite clay suspensions (6–8% w/w) in the presence of different PEG concentrations (100, 1000, 2000, and 5000 mg/L) and PVPy concentrations (50, 100, 200, and 500 mg/L) after 24 h of aging were measured.

The effects of temperature on the rheological properties of bentonite suspensions at fixed concentrations of PEG (1000 mg/L) and PVPy (200 mg/L) at 20, 40, 60, and 80°C were investigated.

The electrophoretic mobility of the bentonite clay particles in the presence and absence of PEG (100, 1000, 2000, and 5000 mg/L) and PVPy (50, 100, 200, and 500 mg/L) was determined with a microelectrophoresis apparatus (Zeta Meter, Inc., New York).

**RESULTS AND DISCUSSION**

**Effect of temperature on the rheological properties of bentonite clay suspensions**

The effect of temperature on the rheological properties of bentonite suspensions was examined. The

rheological properties of bentonite suspensions at different temperatures (20, 40, 60, and 80°C) after 24 h are shown in Figure 2. The plastic viscosity decreases as the temperature increases. The plastic viscosity measures the contribution of fluid viscosity under dynamic flow conditions. With an increase in the temperature, bentonite platelet flow becomes more non-Newtonian and shear-thinning. Exposure to high temperatures for a long time makes bentonite more dispersed, and this increases the number of individual platelets in the suspension; consequently, the plastic viscosity decreases (Fig. 2). In the study, the temperature increased up to 80°C, and this led to higher yield stresses and lower plastic viscosities.<sup>11</sup>

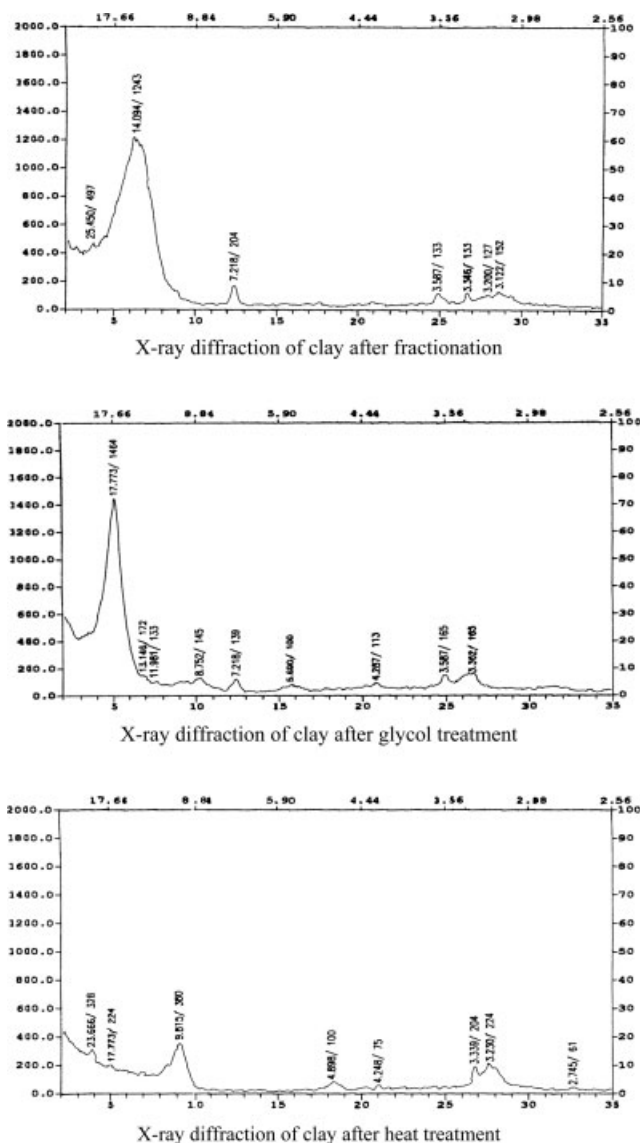
Also, Figure 2 shows the apparent viscosity and yield point. The apparent viscosity describes fluid flowing through a particular geometry. The yield point expresses the force required to initiate flow. Therefore, these properties increase as the temperature increases, and they are related to the clay suspension percentage. At higher temperatures, the internal energy of the clay–water system increased. The more such interactions there are, the more swelling there is. Consequently, these properties increase.<sup>12</sup>

**Rheological properties of bentonite–PEG suspensions**

The effect of PEG on the rheological properties of bentonite suspensions after 24 h of aging was exam-

**TABLE II**  
**Chemical Analysis of Bentonite Clay**

Test	wt %
Ignition loss	8.44
SiO <sub>2</sub>	52.52
Al <sub>2</sub> O <sub>3</sub> (before ignition)	21.76
Al <sub>2</sub> O <sub>3</sub> (after ignition)	23.66
Fe <sub>2</sub> O <sub>3</sub>	10.72
TiO <sub>2</sub>	1.54
CaO	0.42
MgO	3.23
Na <sub>2</sub> O	0.82
K <sub>2</sub> O	0.40
P <sub>2</sub> O <sub>5</sub>	0.10



**Figure 1** X-ray diffraction analysis of a bentonite sample.

ined. The results show slight variations in the rheological properties as a function of concentration (Fig. 3). The rheological properties of the bentonite suspensions in the absence of PEG increase with increasing bentonite clay content from 6 to 8%. The addition of different concentrations (100, 1000, 2000, and 5000 mg/L) of PEG to bentonite suspensions has clearly no effect on the rheological properties. Therefore, the rheological properties increase with increasing clay content and aging time. The best rheological properties of bentonite suspensions to be used as drilling mud according to the Oil Companies Materials Association (OCMA) are as follows:

- Apparent viscosity = 15 cP min
- Yield point/plastic viscosity = 6 maximum

The rheological properties fulfilling the required OCMA specifications were reached with 8% bentonite content and 24 h of aging in the presence of 2000 mg/L PEG. The effect of the PEG layer on the bentonite particle surface has been studied.<sup>13</sup> PEG does not interact electrostatically with charged clay particles. Such behavior can be attributed to the magnitude of the attractive forces, which is reduced by the fact that the smallest possible distance between the particles is increased. This effect is due to the construction of the steric barrier by PEG layers between the clay particles. Also, the interaction between the adsorbed PEG layers gives rise to a repulsive force between the particles that leads to a significant modification of the charge distribution of the electrical double layers. This type of double layer makes the viscosity of these suspensions decrease. A bentonite dispersion is stabilized by an adsorbed PEG layer; a repulsive force being caused by the interaction between PEG layers, the dispersion is sterically stabilized. This phenomenon is in agreement with the rheological properties of bentonite suspensions in this study; that is, the effect of PEG on the rheological properties of bentonite suspensions is limited.<sup>14</sup>

Nonionic PEG was added to bentonite suspensions at different temperatures after 24 h of aging. The rheological properties of bentonite suspensions in the presence of 2000 mg/L PEG as a function of temperature after 24 h of aging are given in Figure 4. The plastic viscosity appears to decrease, especially for 7 and 8% bentonite suspensions. The decrease in the plastic viscosity with the temperature rising is due to the reduction of the attractive forces between the polymer (PEG) and clay particles.<sup>15</sup> The interaction between an adsorbed polymer and clay surfaces depends on two factors:

1. The internal energy, increased by temperature, leads to more separation distance between the clay surfaces.
2. Contrary to that, the presence of a nonionic polymer links the clay surfaces.

The product of these two opposite factors depends on the clay concentration, polymer concentration, and temperature. With an increase in the temperature, the network structure becomes weaker, and consequently, the plastic viscosity is reduced.

Also, the apparent viscosity and yield point of bentonite suspensions in the presence of 2000 mg/L PEG are affected at different temperatures. It is obvious from Figure 4 that these properties increase as the temperature increases. PEG can attach to the particle surfaces and to the interlayers, and this leads to increased clay swelling. As the temperature increases, the penetration of the polymer into the interlayers of clay particles increases, and conse-

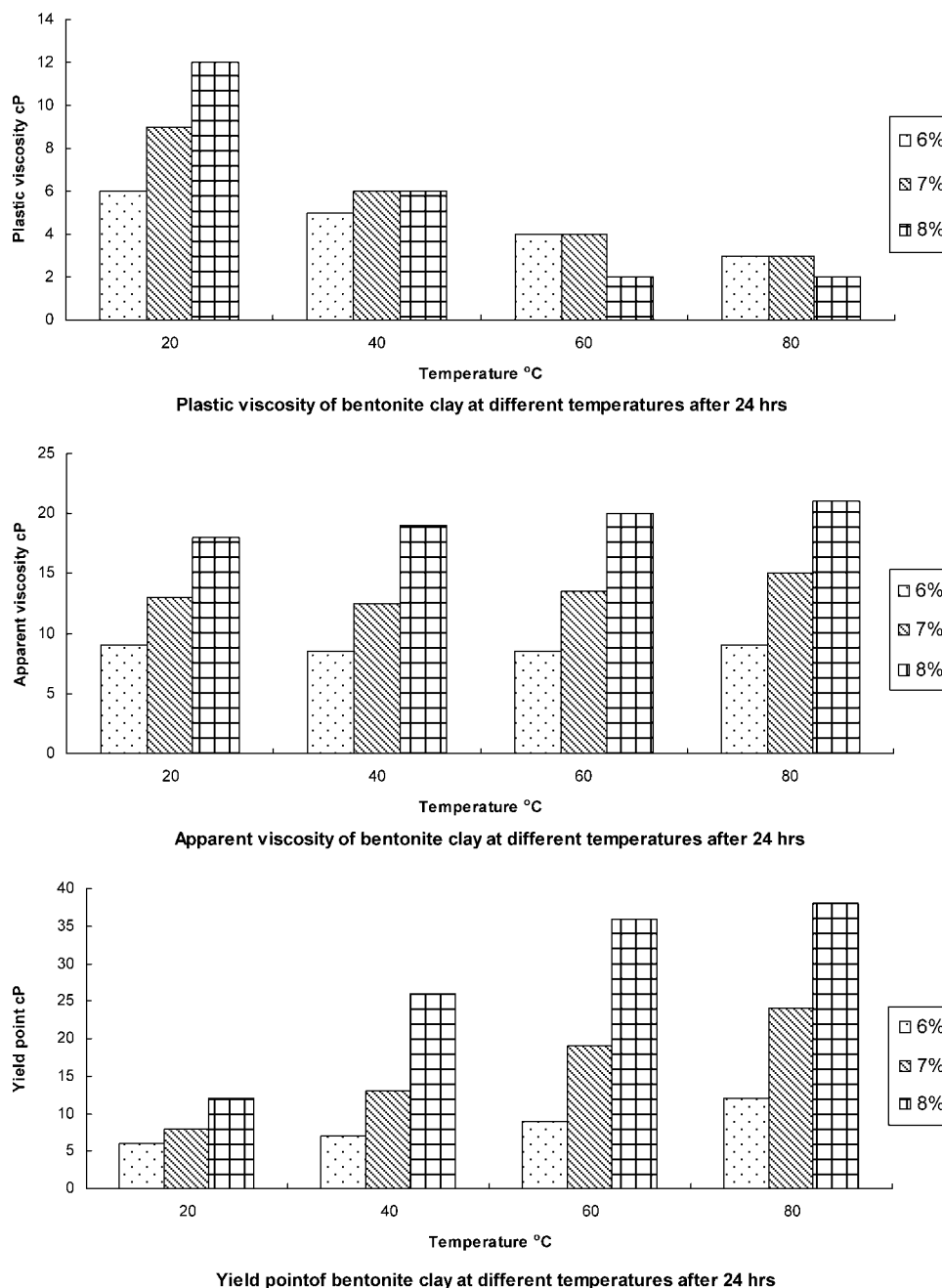


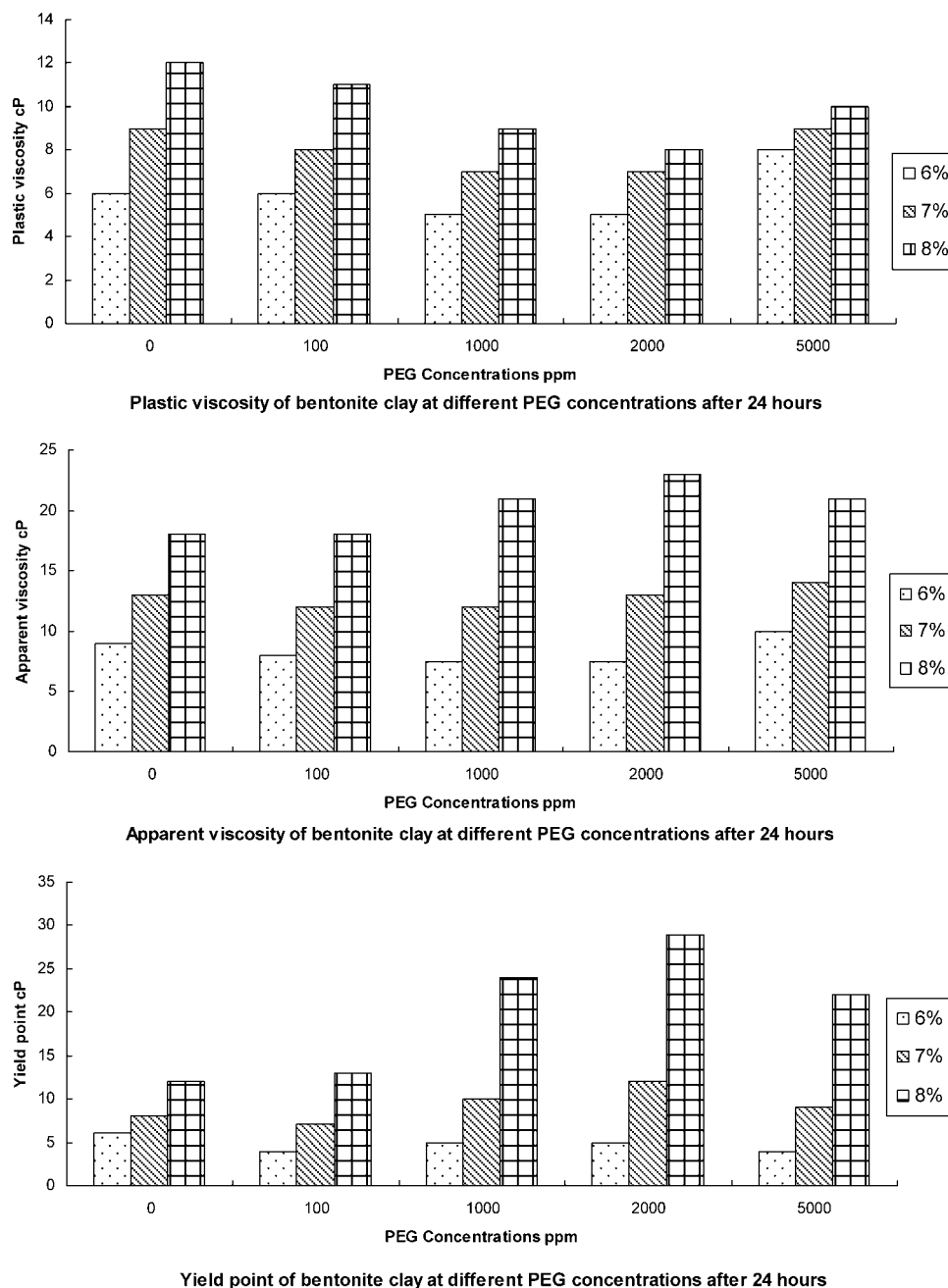
Figure 2 Rheological properties of bentonite clay at different temperatures after 24 h.

quently, the rheology of the suspension increases.<sup>16</sup> Therefore, the best conditions used to achieve OCMA specifications were an 8% clay content and 2000 mg/L PEG at 80°C.

**Rheological properties of bentonite-PVPy suspensions**

The rheological properties of bentonite suspensions in the presence of different PVPy concentrations (50, 100, 200, and 500 mg/L) after 24 h were examined. The results show slight variations in the rheological

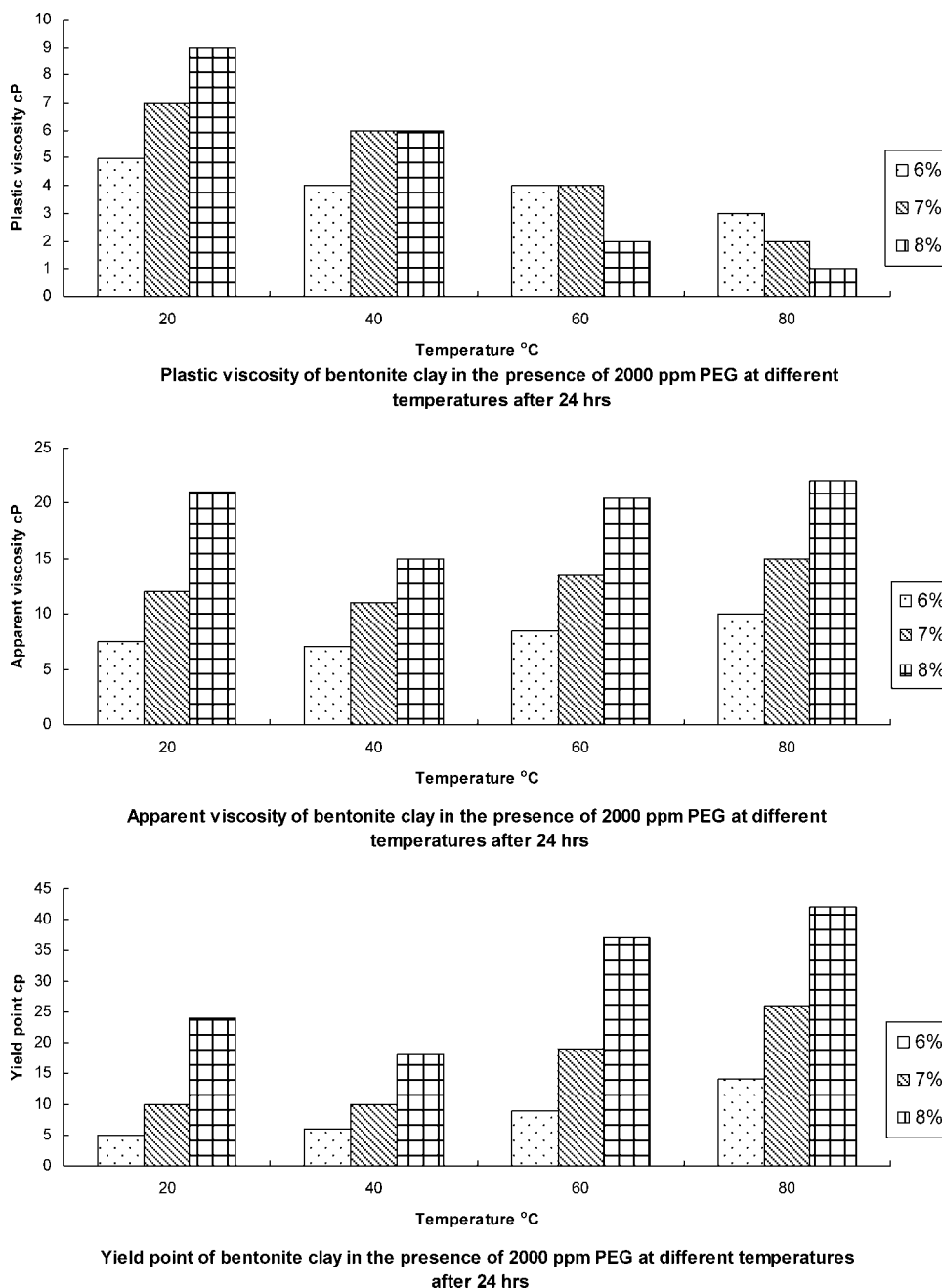
properties as the PVPy concentration increases (Fig. 5). At an 8% clay content, the rheological properties of the bentonite suspensions decrease as the PVPy concentration increases from 0 to 200 mg/L and then increase as the PVPy concentration increases (500 mg/L). The adsorption of PVPy onto clay surfaces competes with the preferential affinity to water molecules. PVPy adsorption alters the structure of a suspension in the vicinity of the clay surfaces. Bridging is considered to be a result of the adsorption of segments of individual polymeric flocculant molecules onto the surface of more than one particle.



**Figure 3** Rheological properties of bentonite clay at different PEG concentrations after 24 h at 20°C.

Such bridging links the particles together into loose aggregates, which often sediment rapidly. This consequently reduces the rheological properties of the bentonite suspensions.<sup>17</sup> Also, PVPy can flocculate clay particles. The floc-aggregated particles produced with polymers are much stronger than those formed by the addition of electrolytes. The particles are held together by elastic bonds, rather than van der Waals forces. Nevertheless, above a critical shear rate, the flocs are broken down. Effective bridging flocculation requires that the adsorbed polymer extend far enough from the particle surface to attach to other

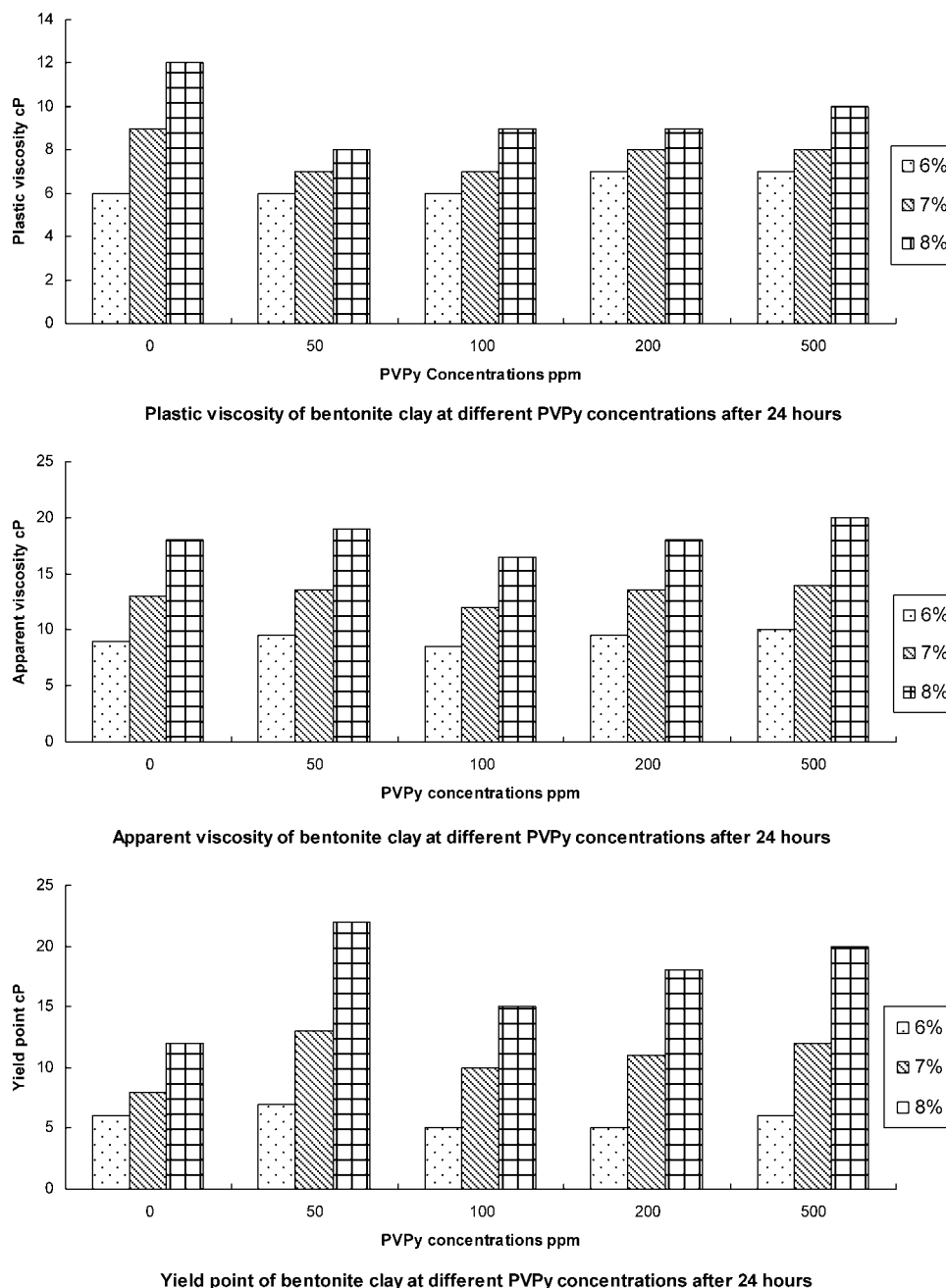
particles and that sufficient free surface be available for the adsorption of segments of the extended chains. To achieve bridging aggregation of a polymeric flocculant, the adsorption of macromolecules onto the clay particle surfaces is not enough; in addition, the loops of adsorbed polymer molecules on surfaces must interact with one another, or it is necessary that the loops should extend to surfaces of other particles. This requires the spatial extension of the loops of the polymeric flocculants to span at least the distance over which the electrostatic repulsion between particles is operative. This distance deter-



**Figure 4** Rheological properties of bentonite clay in the presence of 2000 ppm PEG at different temperatures after 24 h.

mines the degree of flocculation. If this distance is small, clay particle flocculation increases, and consequently, viscosity increases, whereas if this distance is large, electrostatic repulsion between clay particles is operative, and as a result, viscosity decreases.<sup>18</sup> Moreover, PVPy forms a gel-like structure together with bonded water molecules and absorbed clay minerals. Sodium bentonite has the ability to form a gel because of its high swelling property. The swollen particles can be disintegrated after sometime giving numerous small particles and thus a large surface area. If a sodium bentonite–water system is pre-

pared as a slurry (7 and 8%), which provides large interaction between the particles, the viscosity and binding 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 an equilibrium state, contribute to gel formation. This phenomenon can be explained from a chemical composition point of view: PVPy resembles a gel structure, and it is a linear protein that is made of various pyrrolidone rings. It dissolves in water, exhibiting various hydrophilic structures, and can be curled like a ball. PVPy adheres onto clay sur-



**Figure 5** Rheological properties of bentonite clay at different PVPy concentrations after 24 h at 20°C.

faces when added to a bentonite–water system and absorbs water by swelling in bentonite, and consequently, gels of bentonite suspensions are nearly constant for each bentonite content, even if the PVPy concentration increases and also after a long aging time.<sup>19</sup> Therefore, the addition of 200 mg/L PVPy to a bentonite suspension is considered the best concentration to obtain the desired rheological properties.

The rheological properties of a bentonite suspension as a function of temperature in the presence of 200 mg/L PVPy after 24 h of aging are shown in Figure 6. As the temperature increases, the plastic

viscosity decreases, especially for 7 and 8% clay suspensions. This property could be due to the polymer's preferential affinity for the clay surface in comparison with the affinity of the water molecules. In fact, there is a competition between these two interactions present in the system to reach the clay surface. With an additional increase in temperature (80°C), the affinity of the polymer to water molecules is much more than that to the clay surface; therefore, flocculation increases, and as a result, the plastic viscosity decreases.<sup>20</sup> Moreover, the apparent viscosity and yield point of bentonite suspensions increase

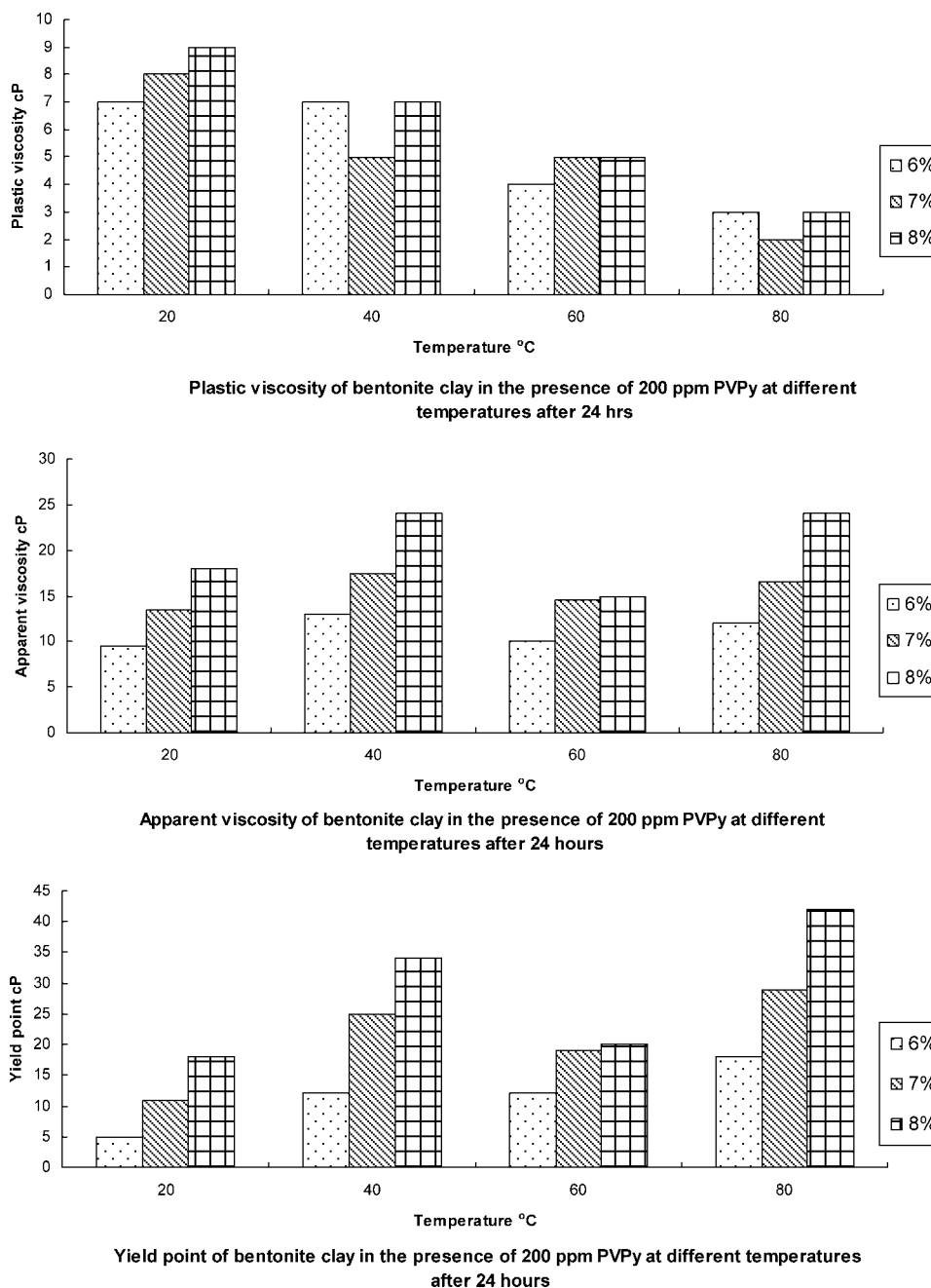


Figure 6 Rheological properties of bentonite clay in the presence of 200 ppm PVPy at different temperatures after 24 h.

with rising temperature. This increase reflects the nature of PVPy and its ability to adhere to the clay surface as the temperature increases.<sup>21</sup>

**Electrokinetic properties of bentonite suspensions in the presence of PEG**

The stability of bentonite suspensions in the presence of a nonionic polymer was investigated. The  $\zeta$  potentials of bentonite suspensions as a function of PEG concentrations (100, 1000, 2000, and 5000 mg/L) are given in Table III. Experimental data show that as the PEG concentration increases (0–2000 mg/L),  $\zeta$

becomes more negative with respect to the suspension without PEG addition, and this means that a stable suspension is obtained and that the repulsive forces of the clay particles precede the attraction. This behavior correlates with the trend of rheological properties observed in Figure 3. 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 one another during the particle collisions, and the dispersion flocculates. To show that the net energy barrier for bentonite suspensions follows repulsion or attraction between particles, potential



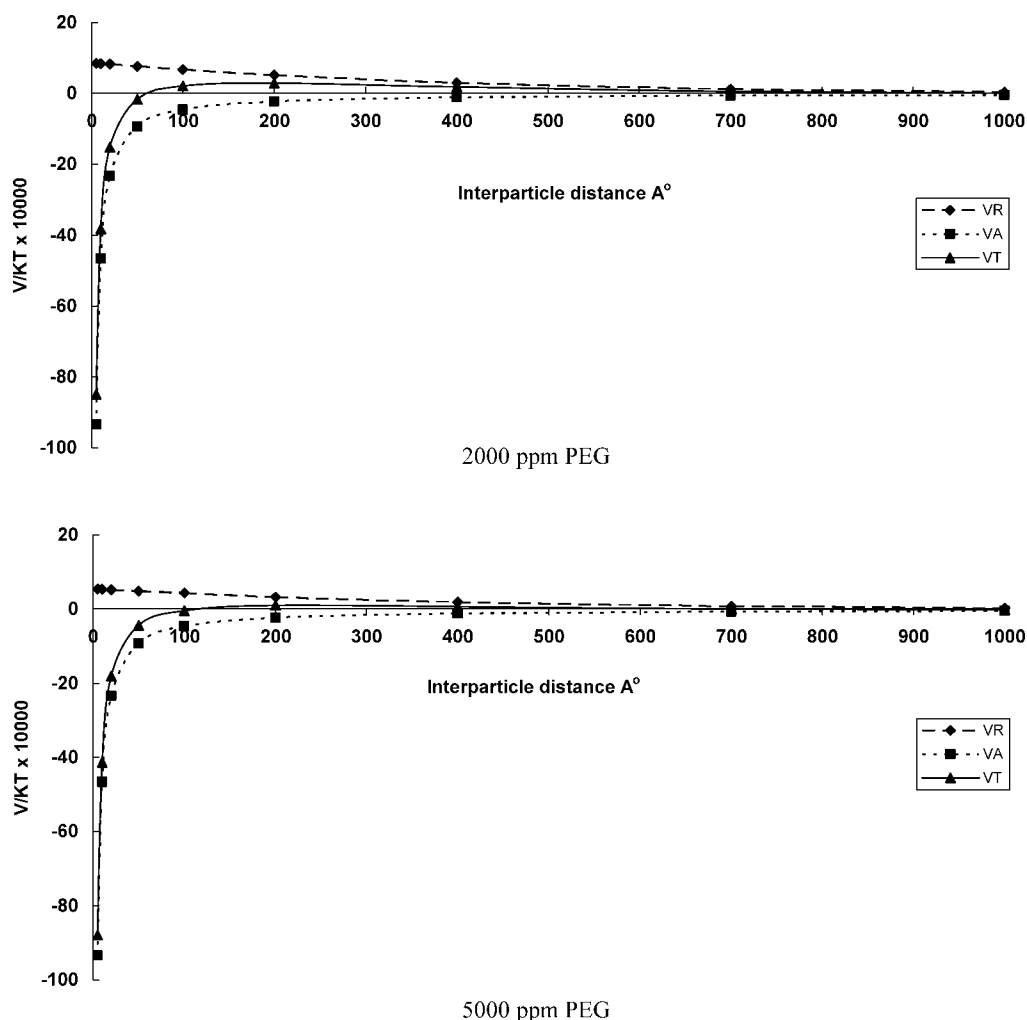
**TABLE III**  
Electrokinetic Properties of Bentonite Suspensions  
in the Presence of PEG

Polymer concentration (mg/L)	Mobility ( $\mu\text{m/s/V/cm}$ )	$\zeta$ potential (mV)
0	2.4	-32
500	3.5	-40
1000	3.8	-45
2000	3.0	-47
5000	2.5	-33

energy profiles for bentonite suspensions in the presence of PEG should be demonstrated.<sup>22</sup>

Figure 7 shows potential energy profiles of bentonite suspensions at two PEG concentrations (2000 and 5000 mg/L). As the PEG concentration increases, the potential energy barrier decreases from  $2.87 \times 10^4$  to  $1.0 \times 10^4$  KT; that is, the potential barrier decreases 3 times more than that of the bentonite suspension without PEG. This decrease in the energy barrier

reflects a reduction of the repulsion energy. Therefore, the attraction energy overcomes the repulsion energy, and the clay particles become close to one another. This means that the systems under these conditions are destabilized. 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 steric hindrance through the adsorbed polymer layer. The reduction in the  $\zeta$  potential with increasing PEG concentrations (Table III) produces a compression in the electrical double layer. This causes a reduction of the repulsive forces between the particles, and as a result, the  $\xi$  values decrease.<sup>23</sup> This behavior can be also explained through a screening effect on the electrical edge charge particles. These cause a decrease in electrostatic interactions between particles. As a result of the screening of the surface charge by the addition of PEG, electrostatic interactions become less, and there is also a decrease in  $\xi$ . Therefore,



**Figure 7** Potential energy profile for a bentonite suspension in the presence of different PEG concentrations ( $V_R$  = repulsion energy;  $V_A$  = attraction energy).  $V_T$  is total potential energy,  $V_R$  is repulsive potential energy and  $V_A$  is attractive potential energy.

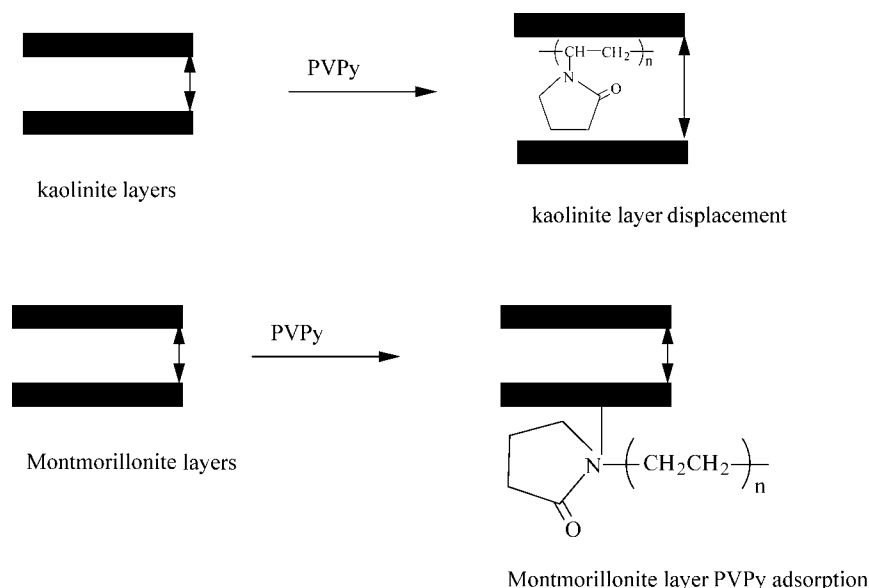
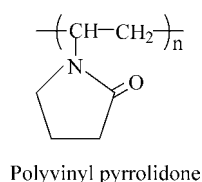
**TABLE IV**  
Electrokinetic Properties of Bentonite Suspensions in the Presence of PVPy

Polymer concentration (mg/L)	Mobility ( $\mu\text{m/s/V/cm}$ )	$\zeta$ potential (mV)
0	2.4	-32
50	2.4	-32
100	4.8	-63
200	5.4	-70
500	2.2	-29

there is no clear effect on the rheological properties of bentonite suspensions after the addition of different PEG concentrations.<sup>24</sup>

**Electrokinetic properties of bentonite suspensions in the presence of PVPy**

PVPy as a nonionic polymer was also used. The data show its effect on the stability of bentonite suspensions. At a low polymer concentration range (50, 100, and 200 mg/L),  $\xi$  increases as PVPy increases (Table IV). This behavior is in good agreement with the rheological properties (Fig. 5). There is a slight change in the rheological properties as the PVPy concentration increases from 50 to 200 mg/L. This phenomenon could be due to the irregular form of the polymer:



The irregular form of PVPy makes it able to penetrate between kaolinite interlayer surfaces, where they have separated particles as the van der Waals forces predominate. Contrary to that, the montmorillonite surfaces are held together through electrostatic attraction forces. Under this condition, PVPy molecules are not able to be accommodated on the interlayer of montmorillonite surfaces. This explanation is clearly illustrated in Figure 8.

A polymeric flocculation bridging mechanism is proposed to explain the stability of colloidal particles. PVPy adsorbs only on the clay surface, not into interlayers of bentonite. Bridging is considered to be a result of the adsorption of segments of individual polymeric flocculant molecules onto the surface of more than one particle, which leads to a stable suspension.<sup>25</sup>

By increases in the polymer concentrations (>200 mg/L), such bridging links the particles together into loose aggregates, which often sediment rapidly, and as a result, the  $\xi$  value decreases (Table IV). This behavior is reflected in the rheological properties shown in Figure 5. As the PVPy concentration increases more than 200 mg/L, there is a reduction in the rheological properties. Not only is the bridging aggregation of a polymeric flocculant obtained from the adsorption of macromolecules onto clay particle surfaces, but the loops of adsorbed polymer molecules on surfaces also can interact with one another, or they extend to surfaces of other particles.

The bridging aggregation of PVPy to bentonite particles was investigated through the study of the potential energy profiles of bentonite suspensions in the presence of this nonionic polymer. Figure 9

**Figure 8** Schematic view of intercalation of PVPy into kaolinite by guest displacement and into montmorillonite by adsorption on the surface.

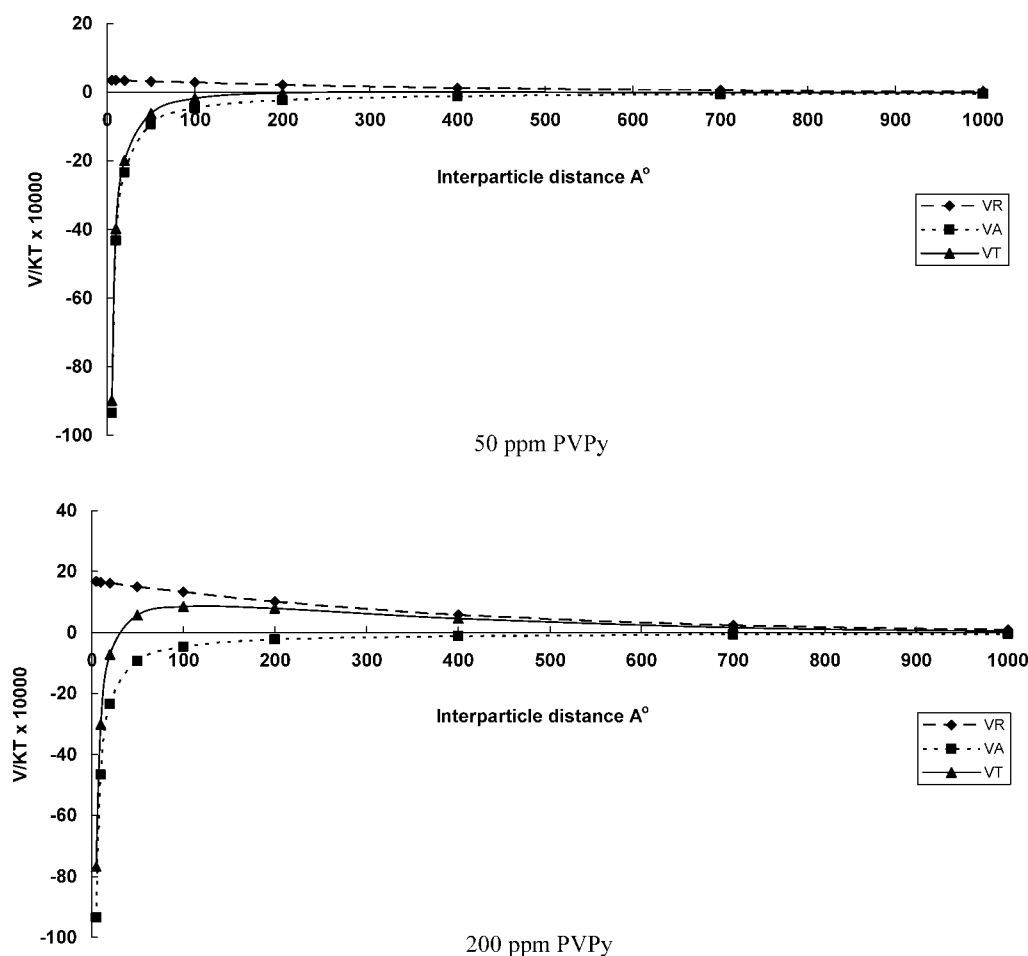


Figure 9 Potential energy profile for a bentonite suspension in the presence of different PVPy concentrations.

presents the potential energy profiles of bentonite suspensions in the presence of different PVPy concentrations (50 and 200 mg/L). The potential energy barrier increases from  $0.05 \times 10^4$  KT at the interparticle distance (400 Å) to  $8.58 \times 10^4$  KT at the interparticle distance (100 Å) as the PVPy concentration increases from 50 to 200 mg/L; that is, the potential barrier increases 160 times as the PVPy concentration increases from 50 to 200 mg/L. This phenomenon agrees with the polymeric bridging flocculation mechanism, in which the interparticle distance decreases from 400 to 100 Å as a result of the bridging of PVPy to bentonite particles, and consequently, a stable suspension is attained. With an increase in the PVPy concentration ( $>200$  mg/L), the potential energy barrier decreases from  $8.58 \times 10^4$  KT at the interparticle distance (100 Å) to  $-0.17 \times 10^4$  KT at the interparticle distance (400 Å); that is, the potential barrier decreases 40 times as the polyvinyl concentration increases beyond 200 mg/L. Under this condition, the attraction energy overcomes the repulsion energy, and the clay particles become close to one another. This requires the spatial exten-

sion of the loops of the polymeric flocculants to span at least the distance over which the electrostatic repulsion between particles is operative. This distance is equal to the sum of the thicknesses of the electrostatic double layers surrounding the approaching colloidal particles. Therefore, the  $\xi$  value of the suspension decreases. Consequently, the systems are destabilized.<sup>17</sup>

## CONCLUSIONS

1. The rheological properties of bentonite suspensions are affected by an increase in the temperature.
2. Nonionic polymers have a limited effect on the rheological properties of bentonite suspensions.
3. The best rheological properties of bentonite suspensions in the presence of PEG that achieved OCMA specifications were attained with an 8% clay content and 2000 mg/L PEG at 80°C.
4. The rheological and electrical properties of bentonite suspensions in the presence of PVPy were higher than those of PEG.

5. The best rheological and electrical properties of bentonite suspensions that achieved OCMA specifications were attained by the addition of 200 mg/L PVPy to an 8% clay content at 80°C.

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