Rheological and Electrical Properties of Egyptian Bentonite as a Drilling Mud

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ABSTRACT: The flow properties of Egyptian bentonite as a drilling mud were studied using anionic polyacrylamide as an additive (MW 1,000,000 g/mol). The rheological properties (plastic viscosity, yield point, thixotropy) of bentonitepolyacrylamide mud were investigated at different concentrations (5–20 mg/L). It was found that, as polyacrylamide concentration increases, rheological properties increase after 24-h aging time and up to 40°C. By increasing temperature, rheological properties become nearly constant. Electrical properties (electrophoretic mobility and zeta potential) of Na bentonite/PAM mud were measured using zeta meter. The results showed that zeta potential of Egyptian bentonite/ PAM mud increased at low PAM concentrations up to 10 mg/L. At high polyacrylamide concentrations, these prop-

INTRODUCTION

The interaction of clays with polymers has been an important concern in the field of drilling fluid technology.^{1,2} The key component of water-based drilling fluids is often Na⁺-montmorillonite or bentonite clay. Polymers are used as additives to reduce filtration, stabilize clays, flocculate drilled solids, increase carrying capacity, and serve as emulsifiers and lubricants. In some cases, they may adsorb strongly onto the clay particle and prevent flocculation at high electrolyte concentration.

Anionic polymer, polyacrylamide sodium salt (PAM), has been found to either act as flocculants at low concentrations, or to enhance the stability of the suspension at higher concentrations when they are exposed to high temperatures.³ High molecular weight polymers have been used to improve the "yield" and plastering properties of the clay.^{4–6}

When anionic polymers are added to the suspension at low concentrations, an increase in the rheological parameters such as the yield stress and viscosity is observed. Alternatively, if the suspension is stabilized by the polymer, a decrease of these parameters is the result. This behavior has been observed mainly

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erties decreased. To investigate the relation between rheological and electrical properties, potential energy profiles were constructed. Potential energy profile at 10 mg/L polyacrylamide–clay showed a high repulsion potential energy between clay surfaces, i.e., suspension stability attained. The most reliable clay suspension to meet the desired properties could be reached using 6% clay suspension concentration, 10 mg/L polyacrylamide, and temperature 40°C up to 24-h aging time. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1496–1503, 2007

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for clay suspensions containing high molecular weight polymers.⁴ In the former study, the solid volume fraction, polymer concentration, and temperature were parameters that modified the viscosity and sedimentation of clay suspensions. However, the effect of the polymer on the suspension viscosity was monitored by increasing the amount of polymer added in the bulk without taking into account the clay particle–particle interactions, as these were gradually covered.^{7–11}

Beside the rheological properties, measurement of the electrical properties as zeta potential has been possible to obtain information on the thickness of the adsorbed layer and the configuration of polymers on the clay surfaces.^{9,10,12–16}

In the present work, the rheological and electrical properties of Egyptian bentonite were investigated under different polyacrylamide concentrations. Also, the effect of temperature on these rheological properties was examined.

EXPERIMENTAL

Egyptian bentonite clay was used in this study. CEC and specific surface of Egyptian bentonite clay were 77.3 mequiv/100 g and 346.7 m^2/g , respectively. Chemical analysis of bentonite clay sample was listed in Table I. X-ray diffraction analysis for this bentonite sample was performed as shown in Figure 1.

The polymer used was polyacrylamide sodium salt of molecular weight 1,000,000 g/mol.

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TABLE I Chemical Analysis of Bentonite Clay

Test	Value (% wt)
Ignition loss	8.44
SiO ₂	52.52
Al ₂ O ₃ (before ignition)	21.76
Al_2O_3 (after ignition)	23.66
Fe ₂ O ₃	10.72
TiO ₂	1.54
CaO	0.42
MgO	3.23
Na ₂ O	0.82
K ₂ O	0.40
P_2O_5	0.10

The rheological properties of different bentonite clay suspensions (4-8%, w/w) after 4- and 24-h aging times were measured.

Also, the rheological properties of different bentonite clay suspensions (4–8%, w/w) in the presence of different polyacrylamide concentrations (5–20 mg/L) after 4- and 24-h aging times were measured.

Moreover, the effect of temperature on rheological properties of bentonite suspensions at fixed polyacrylamide concentration (10 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 polyacrylamide (5–20 mg/L) was determined with microelectrophoresis apparatus (Zeta Meter, NY).

RESULTS AND DISCUSSION

Rheological properties of bentonite clay suspensions

Bentonite, as natural smectite clay, has typical characteristics such as negative electric charge, very high specific surface, high sensitivity to the hydration, and high plasticity which explains why this clay is employed as drilling mud.

The rheological properties of different bentonite suspension concentrations (4–8% weight of ovendried bentonite/total weight of suspension) after 4, 8, 16, 24 h aging times were shown in Figure 2. It was found that as bentonite concentration increases, rheological properties increase after a certain aging time, depending on the clay concentration. The flow properties of a bentonite–water system is related to the interactions between particle–particle and particle–water molecules of the system.¹⁷

In aqueous dispersion, water can penetrate into the interlayer space and cause swelling between clay particles. Therefore, a relationship between rheological properties and swelling is expected. The strength of bentonite gel has been attributed to the repulsive forces of the interactive double layers or/and to the formation of three dimensional band-like structures, and thus the formation of the effective double layers are a result of swelling.¹⁸ Thus, the rheological properties were increased as bentonite concentration increased. The rheological properties of this bentonite are in good agreement with the results recorded by other works.¹⁹

Rheological properties of bentonite-polyacrylamide suspensions

Anionic polymers are effective flocculants and deflocculants for clays, for polymers not only carry negative charges in water but also contains nonionic polar groups such as OH⁻, NH₂. The extent of polyacrylamide on bentonite is determined by a number of parameters such as polymer concentration and bentoniteto-water ratio.²⁰

The rheological properties of bentonite suspensions (4–8%) as a function of polyacrylamide sodium salt concentration (5, 10, 30, 50 mg/L) after 24-h aging



Figure 1 X-ray diffraction analysis of bentonite sample.



Plastic viscosity of bentonite clay at different aging times at 20 °C



Apparent viscosity of bentonite clay at different aging times at 20 °C



Yield point of bentonite clay at different aging times at 20 °C

Figure 2 Rheological properties of bentonite clay at different aging times at 20°C.

time at 20°C were shown in Figure 3. These results indicated that plastic and apparent viscosity values generally increase up to 10 mg/L of polyacrylamide sodium salt, and then become constant by increasing the polymer concentration. Such behavior can be explained through the polymer-clay interactions. There are three possibilities which can be considered for the interaction between PAM molecules and clay particles: first, it is possible that anionic exchange can take place between the surface hydroxyls of the mineral and the carboxylic anions of the polymer. Second, hydrogen bonds can form between the surface hydroxyls and the C=O of the polymer. Third, it is possible that divalent ions can establish electrostatic bridges between the anionic part of the polymer and the surface of the clay particles.²¹

The rheological properties of bentonite–water system without polymer are increased by increasing ben-

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tonite suspension concentration. This phenomenon can be explained by a screening effect on the electrical charges of faces and edges of bentonite particles. The net electrostatic interaction between particles decreases and, as a result, mechanical coupling in the system increases and, consequently, the viscosity values increase. By introducing the polymer, this effect increases in relation to the amount of polymer. The values of plastic and apparent viscosity as observed in Figure 3 increases with increasing PAM in the clay suspension. There is a direct relationship between the amount of clay-polymer-water interactions (bridging) and the viscosity. By increasing the clay percent, the bridging increases. By adding the anionic PAM to the clay suspensions, this phenomenon becomes more effective.22

The yield point of bentonite–PAM system decreases by increasing the polymer concentration as shown in



Plastic viscosity of bentonite clay at different PAM concentrations after 24 hours at 20 $^{\circ}\mathrm{C}$



Apparent viscosity of bentonite clay at different PAM concentrations after 24 hrs at 20 °C



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

Figure 3. The explanation of this behavior is given below:

- 1. Bridging can occur only at low polymer coverage because free surfaces are available on which adsorption of a molecule attached to another particle can take place. This bridging cannot be reached unless the loops are longer than the thickness of the double layer. Under that condition, flocculation will be effective. The newly formed network increases the resistance of the system that leads to strong interaction between the clay particles and, consequently, the mechanical coupling becomes longer ranged and fixed. Thus, the yield point becomes steady.²³
- Na-bentonite has the ability to form a gel because of its high swelling property. The swelled particles can be disintegrated after some time giving numerous small particles; thus, a large surface

area was produced. If the Na–bentonite PAM system is prepared as slurry, it provides a large interaction between the particles. Under that condition, viscosity and water binding increase and, as a result, reversible gel can be formed as a cluster which decreases yield point values. Moreover, the repulsive electrostatic and van der Waals forces which bring the bentonite particles to equilibrium state are contributed to decrease gel formation in the presence of PAM. So, the yield point becomes constant as polyacrylamide concentration increases.²⁴

Effect of temperature on bentonite suspensions in the absence of anionic polyacrylamide

The effect of temperature on rheological properties of bentonite suspensions was examined. The rheological properties of bentonite suspensions at different tem-



Plastic viscosity of bentonite clay at different temperatures after 24 hrs



Apparent viscosity of bentonite clay at different temperatures after 24 hrs



Yield point of bentonite clay at different temperatures after 24 hrs

Figure 4 Rheological properties of bentonite clay at different temperatures after 24 h.

peratures (20, 40, 60, 80°C) after 24 h was shown in Figure 4. The plastic viscosity was decreased as temperature increased. By increasing the temperature, bentonite platelets flow becomes more non-Newtonian and shear-thinning. The exposure to high temperatures for long times makes the bentonite more dispersed, which increases the number of individual platelets in the suspension and, consequently, plastic viscosity decreases (Fig. 4). In a previous study, the temperature increased up to 80°C, displaying higher yield stresses and lower plastic viscosities.²⁵

Also, Figure 4 showed that the apparent viscosity and yield point were increased as temperature increased. These properties are related to the clay suspension percentage. At higher temperatures, the internal energy of the system increased, which provides the clay–water interactions. The more of such interaction, the more would be the swelling. Consequently, these properties will be increased.²⁶

Effect of temperature on bentonite suspensions in the presence of anionic polyacrylamide

The rheological properties of bentonite suspensions in the presence of 10 mg/L polyacrylamide at different temperatures (20, 40, 60, 80°C) were examined. Figure 5 showed plastic viscosity of bentonite suspensions as a function of temperature after 24-h aging time. It was found that plastic viscosity begins to decrease rapidly till 40°C, and then it decreases slowly up to 80°C regardless to bentonite concentration. These results could be explained through the hydrophobic association between the suspension particles. As the temperature increases, weakening of the hydrophobic association increases, and thereby the strength of the suspension network. Also, the weakness of the hydrophobic suspensions may be due to the increased mobility of the polymer chains, which disrupts intermolecular associations, and/or an increase in polymer solubil-



Plastic viscosity of bentonite clay in the presence of 10 mg/L PAM at different temperatures after 24 hrs



Apparent viscosity of bentonite clay in the presence of 10 mg/L PAM at different temperatures after 24 hrs



Figure 5 Rheological properties of bentonite clay in the presence of 10 mg/L polyacrylamide at different temperatures after 24 h.

ity as the temperature increases, and thus, plastic viscosity decrease.²⁷

The other rheological properties were shown in Figure 5. These figures showed an increase in apparent viscosity and yield point of bentonite suspensions in the presence of 10 mg/L polyacrylamide as the temperature reached 60°C and then decreased at higher temperature. Figure 5 showed that in the absence of the PAM, these rheological properties have the same behaviors. But in its presence, at temperatures more than 60°C, these rheological properties were lower than the recorded values in its absence. As temperature increases to 60°C, the polymer induced bridging with clay particles, which encourage water molecules to penetrate into bentonite layers and increase swelling. Consequently, yield point and apparent viscosity increased. Increasing the temperature to more than 60°C showed a decrease in these rheological properties. At these temperatures the bentonite particles become more dispersed as the activation energy of these clay particles increases. This energy increases the probability of collisions between clay particles and the polymer molecules. So, the increase of repulsions between clay particles and the anionic molecules decrease these rheological properties.²⁸

Electrokinetic properties of bentonite suspensions in the presence of anionic polymer

The stability of bentonite suspensions in the presence of PAM was examined. Zeta potential as a parameter to illustrate the magnitude of particles attraction– repulsion was taken as index to examine the suspension stability. The zeta potential is computed from the electrophoretic mobility of the sol particles as given from the following equation:

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Electrokinetic Properties of Bentonite Suspensions in the Presence of Polyacrylamide Sodium Salt		
Polymer concentration (mg/L)	Mobility (µm/s per V/cm)	Zeta potential (mV)
0	2.4	-32
5	3.7	-50
10	4.2	-55
15	3.5	-47
20	3.0	-40
50	2.2	-29

TABLE II

 $V_{\rm el} = \epsilon \xi E / 4 \pi \eta$

where V_{el} is the electrophoretic velocity in µm/s, ε is the dielectric constant of the medium, *E* is the applied electric field in V/cm, η is the viscosity of the medium in poise, and ξ is the zeta potential in mV.

Zeta potential values of bentonite suspensions in the presence of different PAM concentrations (5, 10, 15, 20,

50 mg/L) were recorded in Table II. It was found that, as PAM concentration increased, zeta potential increased up to 10 ppm and then it decreased as PAM increased.

It has been shown that the suspension without polymer addition has zeta potential value -32 mV, but the same suspension becomes more dispersed by adding this anionic polymer (-55 mV). The charge distribution could be changed in the system after the addition of 10 ppm PAM. Addition of 10 ppm polyacrylamide makes the PAM/bentonite system more dispersed, which leads to increased zeta potential values. This phenomenon is attained because the screening effect of edge charges of clay minerals with anionic polymer makes these negative charges repel each other. This behavior correlates well with the trend of viscosity values after the addition of the polymer as observed in Figure 3. Zeta potential values decreased 30 mV units as the concentration of the PAM changed from 10 to 50 mg/L. This decrease in zeta potential is due to the hydrophobic tails of anionic polymer mole-



Figure 6 Potential energy profile for bentonite suspension in the presence of different polyacrylamide concentrations.

cules, which are attached to the positive edges of clay particles, which interact with one another. This creates clusters of bridging flocculation having less mobility compared with small particles.²⁹

The interaction energies of the double layer around the clay particles were showed by using the zeta potential values of the clay throughout the potential energy profiles. Figure 6 showed the potential energy profiles for bentonite suspensions in the presence of 5, 10, 20 mg/L polyacrylamide. The repulsion V_R and attraction V_A energies between the surfaces of two bentonite particles are calculated as a function of distance from the clay surface.

Attraction energy $(V_A) = Aa/12H$

Repulsion energy $(V_R) = \varepsilon a \zeta^2 \ln(1 + e^{-kH})$

Total interaction energy $(V_T) = V_A + V_R$

where *A* is the Van der Wall's force in erg/cm^2 , *a* is the radius of clay particle in cm, *H* is the interparticle distance in cm, ε is the dielectric constant of the medium, ξ is the zeta potential in esu, and *k* is the Boltzman constant.

By adding these components V_R and V_A , the total interaction free energy V_T is obtained. At intermediate distance (200 Å) of the energy profile as shown in Figure 6, the clay particles in the presence of 10 mg/Lpolyacrylamide possess a high potential energy barrier for repulsion of nearly about 3.97×10^4 kT. As the zeta potential of bentonite suspension is high at 10 mg/L polyacrylamide (about -55 mV), the repulsion between clay particles is very high and clay particles are separated from each other which means that the system is stable. By increasing polyacrylamide concentration to 20 mg/L, the energy barrier values decreased from 3.97×10^4 to 1.0×10^4 /kT which explains why the zeta potential value is decreased at this level of concentration. Consequently, the attraction energy overcomes the repulsion energy and the clay particles become close to each other. This means that the systems under these conditions are destabilized, i.e., lower zeta potential could be obtained (Table II). The lower value for the potential energy barrier is due to the reduction in the repulsion energy V_R , while the attraction energy V_A between clay particles increased.

CONCLUSIONS

- Electrokinetic properties of Egyptian bentonite showed an optimum dose of polyacrylamide 10 mg/L, which gives the best rheological and colloidal properties.
- 2. The rheological properties of Egyptian bentonite were affected by temperature. The temperature

range from 40 to 60°C in the presence of 10 mg/ L polyacrylamide gives the most reliable bentonite suspension as a drilling mud.

- 3. The electrical double layer properties of the clay could be used to investigate the interrelation between clay surfaces and polymers.
- 4. A close relation was existed between the electrical and rheological properties. So, the quality of a drilling mud could be determined through its electrical properties.
- 5. Finally, by using 10 mg/L anionic polyacrylamide, the drilling mud suspension was reduced from 8 to 6%.

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