Efficiency of Egyptian Drilling Muds in the Presence of Cationic Polyethylene imine and Anionic Polyacrylamide

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ABSTRACT: The flow properties of Egyptian bentonite were studied using a combination of anionic polyacrylamide (MW = 1,000,000 g mol^{-1}) and cationic polyethylene imine (MW = 700,000 g mol^{-1}). This combination gave a significant effect on the clay suspensions to be qualified in the field of drilling mud depending on the sequence their addition. It was found that, by adding 50 mg/L cationic polyethylene imine followed by 10 mg/L anionic polyacrylamide, the rheological properties were improved using 6% Egyptian bentonite suspension, especially at 20°C. But, by reversing this addition sequence, the rheological properties of bentonite suspension were declined. The zeta-potential value of bentonite suspension in the presence of 50 mg/L polyethylene imine was −47 mV, while at 10 mg/L polyacrylamide was −55 mV. But, on addition of 10 mg/L polyacrylamide to bentonite suspension followed by 50 mg/L polyethylene imine induced a reduction of the zeta-potential value to −51 mV when compared with that of polyacrylamide alone. By reversing the addition sequence, a very high stable suspension having zeta-potential values of −82 mV was obtained. Potential energy profiles were constructed to investigate the relation between rheological and electrical properties. Potential energy profile at 50 mg/L polyethylene imine followed by 10 mg/L polyacrylamide to bentonite suspension produced a high repulsion potential energy between clay surfaces, i.e. the suspension stability improved. By reversing that sequence, a significant decrease in the energy barrier was observed. The most reliable clay suspension as a drilling mud could be obtained by using 6% clay suspension concentration, with 50 mg/L polyethylene imine followed by 10 mg/L polyacrylamide, at 20°C up to 24 h aging time. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1487–1495, 2007

Key words: anionic polyacrylamide; cationic polyethylene imine; bentonite; rheological properties; drilling mud; zeta-potential; potential energy

INTRODUCTION

Interactions between clays and polymers are rapidly growing in the field of colloid science. Many practical systems for industrial applications contain mixtures of polymers, which are widely used in water-based formulations such as paints, drilling muds, etc. For these applications, polyelectrolytes are of particular interest, because of their interesting rheological properties. These polymers form more extended structures, with effective persistence lengths much larger than those of neutral polymers.[1]

The interaction of clays with polymers has been an important concern in the field of drilling fluid technology.[2] The properties of water-based drilling fluids, in which the key component is often Na$^+$-montmorillonite or bentonite clay, are largely modified by the presence of polymers. 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. In principle, cationic polymers are effective in dealing with negatively charged clay particles, but the use of cationic polymer, in conjunction an anionic polymer, is more effective in flocculation with clay particles.[3]

In addition, from the electrical properties measurements such as zeta-potential, it has been possible to obtain information on the thickness of the adsorbed layer and the configuration of polymers on the clay surfaces.[4–10]

In the present work, the rheological and electrical properties of Egyptian bentonite were investigated in the presence of anionic polyacrylamide (PAM) and cationic polyethylene imine (PEI) concentrations. Also, the effect of polymers addition order on these rheological properties was examined.

EXPERIMENTAL

Egyptian bentonite clay was used in this study. Cation exchange capacity and specific surface area were

TABLE I
Chemical Analysis of Bentonite Clay

Test	Value (wt %)
Ignition loss	8.44
SiO_2	52.52
Al_2O_3 (before ignition)	21.76
Al_2O_3 (after ignition)	23.66
Fe_2O_3	10.72
TiO_2	1.54
CaO	0.42
MgO	3.23
Na_2O	0.82
K_2O	0.40
P_2O_5	0.10

77.3 meq/100 g and 346.7 m^2/g, respectively. Also, the chemical analysis of bentonite clay sample was listed in Table I. X-ray diffraction analysis for this bentonite was performed as shown in Figure 1.

The polymers used were polyacrylamide (PAM) sodium salt of a molecular weight 1,000,000 g mol^{-1} and polyethylene imine (PEI) of a molecular weight 700,000 g mol^{-1}.

The rheological properties of different bentonite clay suspensions (4–8% w/w) in the presence of PEI concentrations (0, 10, 50, 100, and 200 mg/L) after 4 and 24 h aging time were performed.

Also, the rheological properties of different bentonite clay suspensions (4–8% w/w) in the presence of PAM concentrations (0, 5, 10, 20, and 50 mg/L) after 4 and 24 h as aging time were measured.

Moreover, the effect of polymers addition order on the rheological properties of bentonite suspensions in the presence of fixed PAM concentration (10 mg/L) and different PEI concentrations was investigated. Also, the rheological properties of constant PEI concentration (50 mg/L) and different PAM concentrations were investigated.

The electrophoretic mobility of the bentonite clay particles in the presence of 10 mg/L PAM as first addition followed by 50 mg/L PEI and the effect of reversing polymer addition order were determined using micro electrophoresis apparatus (Zeta Meter Inc., NY).

RESULTS AND DISCUSSION

Effect of cationic PEI on the rheological properties of bentonite suspension

The rheological properties of bentonite suspensions as a function of PEI concentrations after 24 h aging time at 20°C are shown in Figure 2. A slight increase in the rheological properties of the suspensions is seen as PEI concentrations increase. These results are expected as a strong electrostatic interaction between the clay particles and PEI could be produced. Öztekin et al.[11] stated that the montmorillonite particles have negatively charged faces (F) permanent charges and positively charged edges (E) pH dependant in both neutral and acidic solutions. On the other hand, the all charges of these types become negative at the ambient pH value of bentonite clay dispersions (8.0 ± 0.2). At this pH value, both faces and edges of the bentonite particles are negatively charged.

PEI as a cationic polymer, its imine groups on the chain are protonated and possessed enlarged positive charge. The charge density of PEI strictly depends on the pH of the polymer solution and on its molecular weight. The PEI used in this study has a high molecular weight 700,000 g mol^{-1} of pH 2–3. Since PEI has a net positive charge, and bentonite particles have negative charges, the driving force for the flocculation should be electrostatic.
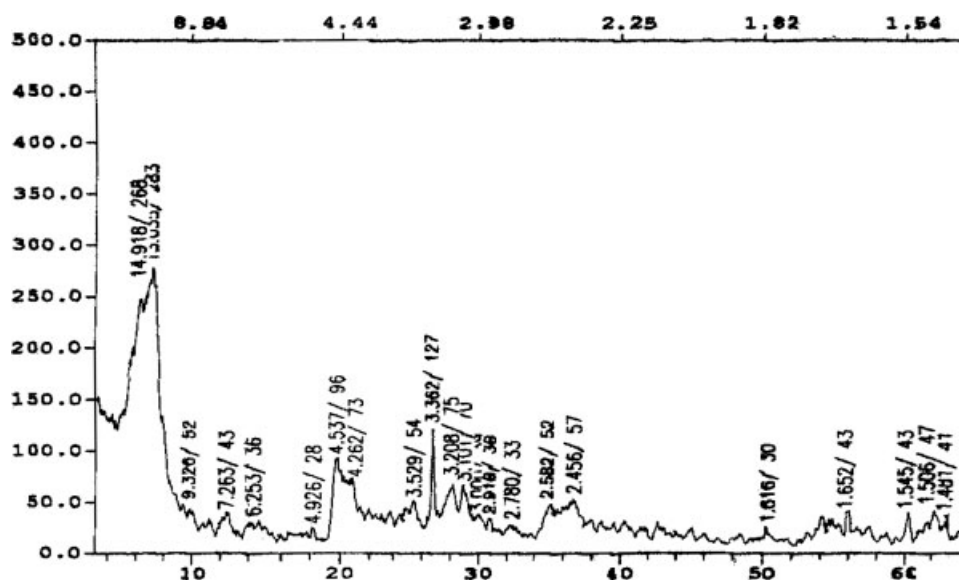

Figure 1 X-ray diffraction analysis of bentonite sample.

Plastic viscosity of bentonite clay at different PEI concentrations after 24 hours at 20 °C

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

Yield point of bentonite clay at different PEI concentrations after 24 hours at 20 °C
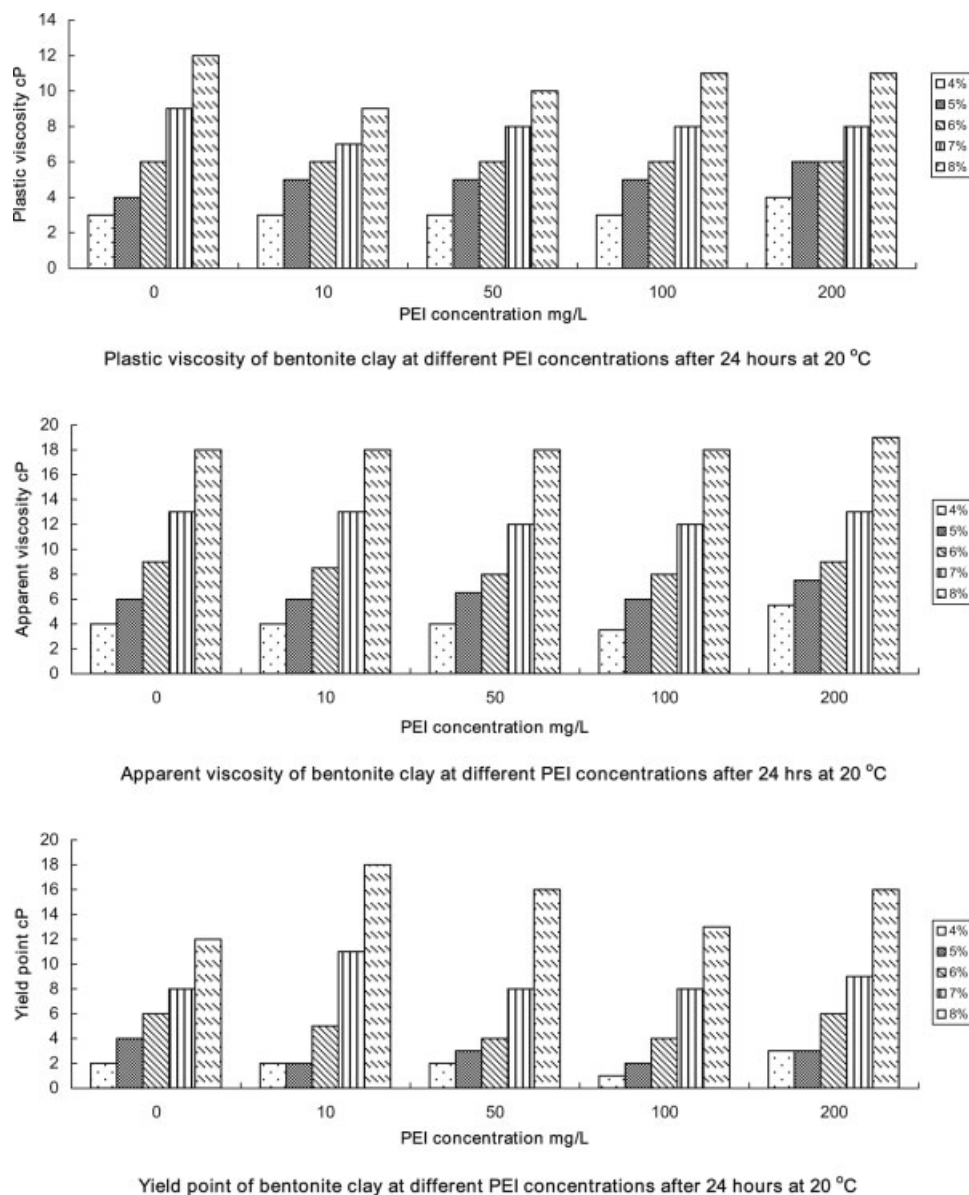
Figure 2 Rheological properties of bentonite clay at different PEI concentrations after 24 h at 20°C.

PEI can increase or decrease the stability of the suspension networks. The PEI as a cationic structure is adsorbed on the surface of the negatively charged bentonite particles by their hydrophilic parts. This will lead to a redistribution of charges in the double layer. Because of the change in the charge position of the solid–liquid system, which reflects the modeled interaction of the particles between each other, the rheologic structure will decrease.

Alemdar et al.[12] studied the adsorption of PEI on bentonite. They gave the same conclusion on its behavior.

Effect of anionic PAM on the rheological properties of bentonite suspension

Anionic polymers are effective flocculants and deflocculants for clays not only for the polymers car-rying negative charges in water, but also for the polymers containing nonionic polar groups such as OH^{-1}, NH_2. The extent of polymers on clay minerals is determined by a number of parameters such as polymer concentration, functional groups of polymer, and bentonite-to-water ratio.[13]

The rheological properties of bentonite suspensions (4–8%) as a function of PAM sodium salt concentration (5, 10, 30, 50 mg/L) after 24 h aging time at 20°C are shown in Figure 3. This figure indicated that plastic and apparent viscosity values generally increase up to 10 mg/L of PAM 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 that can be considered for the interaction between PAM molecules and clay particles. First, it
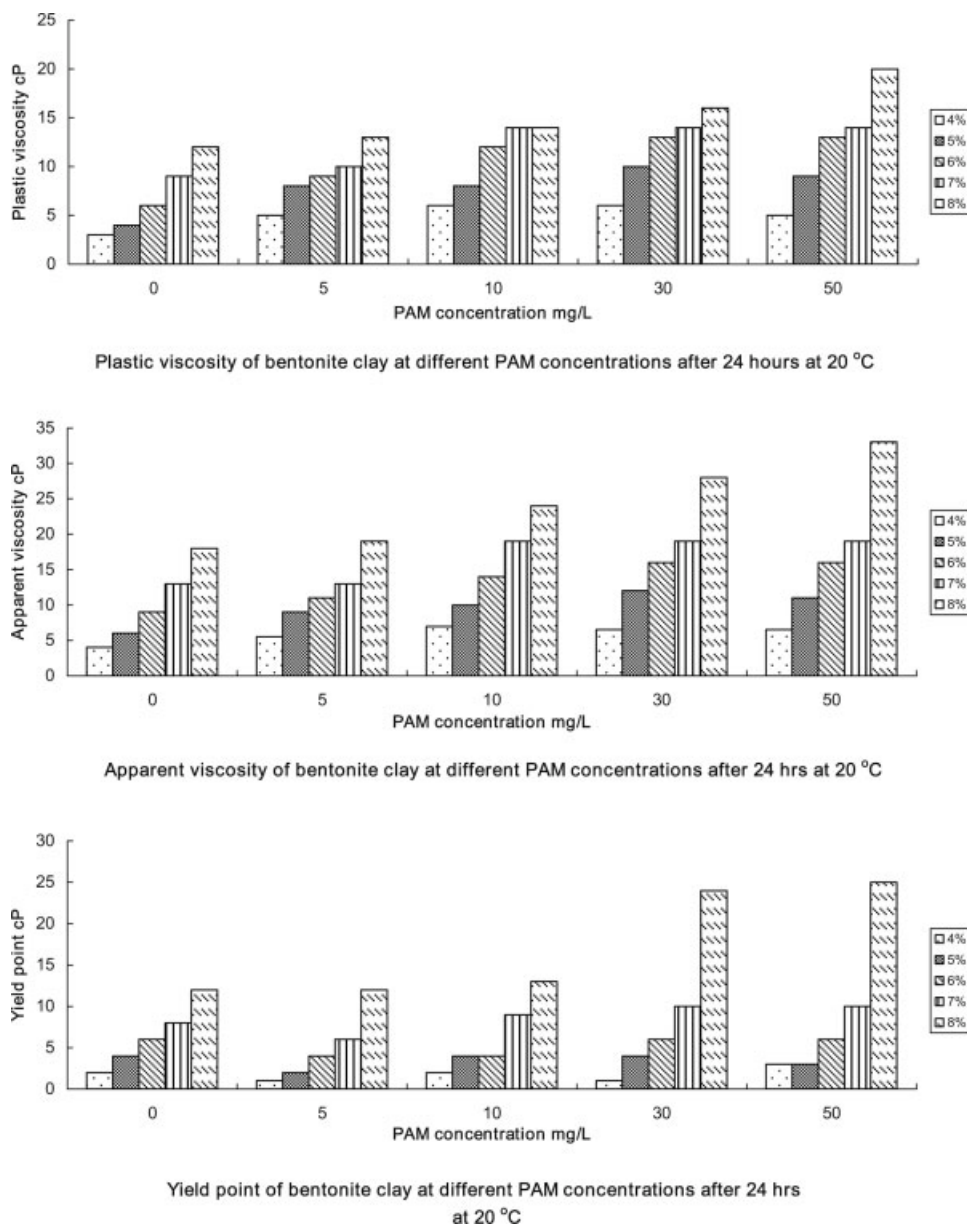
Plastic viscosity of bentonite clay at different PAM concentrations after 24 hours at 20 °C

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

Yield point of bentonite clay at different PAM concentrations after 24 hrs at 20 °C

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

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.[14]

The rheological properties of bentonite–water system without polymer are increased by increasing the bentonite 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 and as a result viscosity increases. Addition of anionic PAM to the clay suspension gives more effective bridging. So, the viscosity of bentonite suspensions obey Oil Companies Materials Association (OCMA).[15,16]

The yield point of bentonite–PAM system decreases by increasing the polymer concentration as shown in Figure 3. The explanation of this behavior is given below:
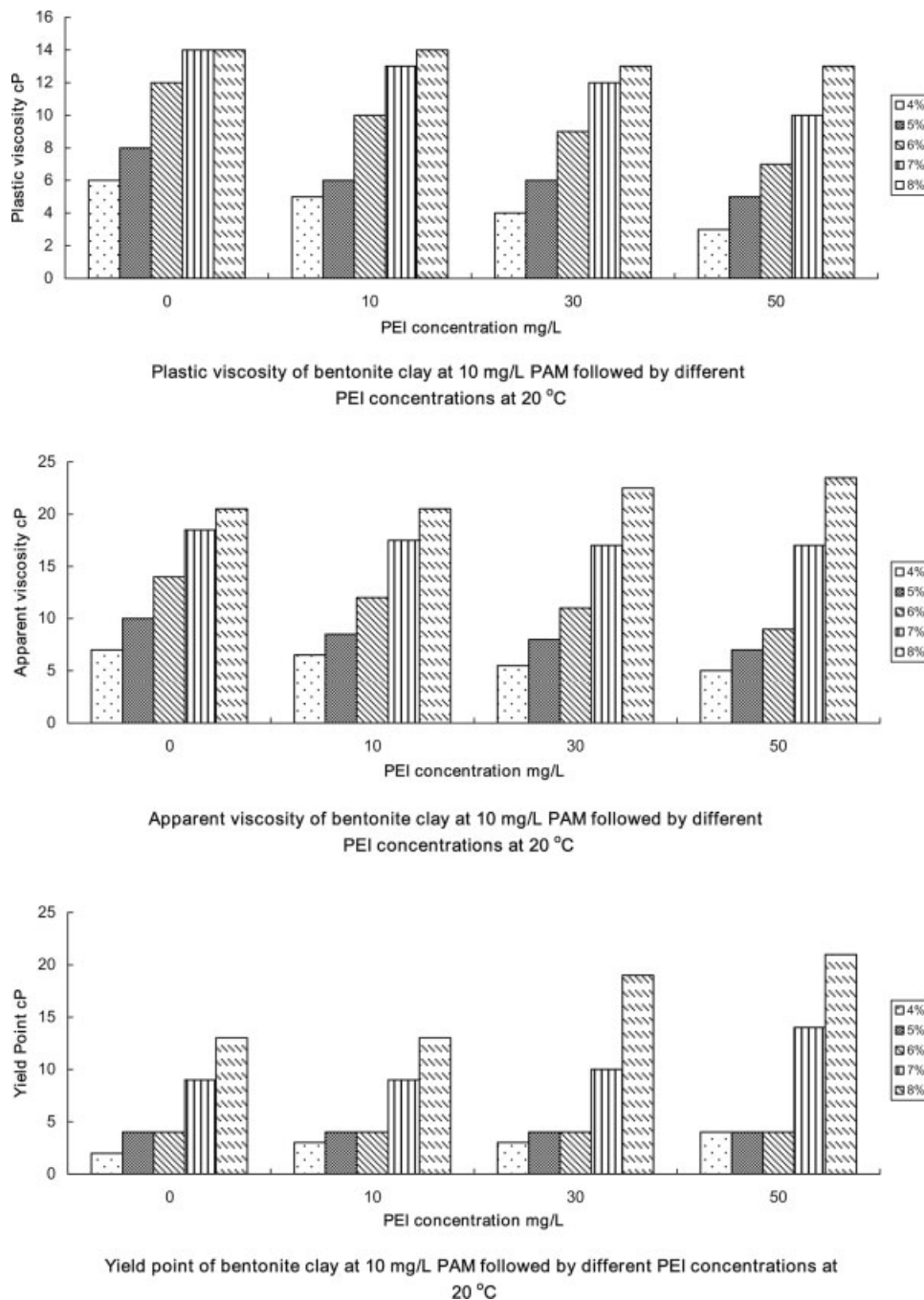
Plastic viscosity of bentonite clay at 10 mg/L PAM followed by different
PEI concentrations at 20 °C

Apparent viscosity of bentonite clay at 10 mg/L PAM followed by different
PEI concentrations at 20 °C

Yield point of bentonite clay at 10 mg/L PAM followed by different PEI concentrations at
20 °C

Figure 4 Rheological properties of bentonite clay at 10 mg/L PAM followed by different PEI concentrations at 20°C.

1. Bridging occurs 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 this 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.[17]

2. Na–bentonite has the ability to form a gel because of its high swelling property. The swelled particles can be disintegrated after sometime, 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 this condition, viscosity and water binding increases, and as a result, reversible gel can be formed as a cluster, which decrease yield point values. Moreover, the repulsive electrostatic and van der Waals forces bring the bentonite particles to
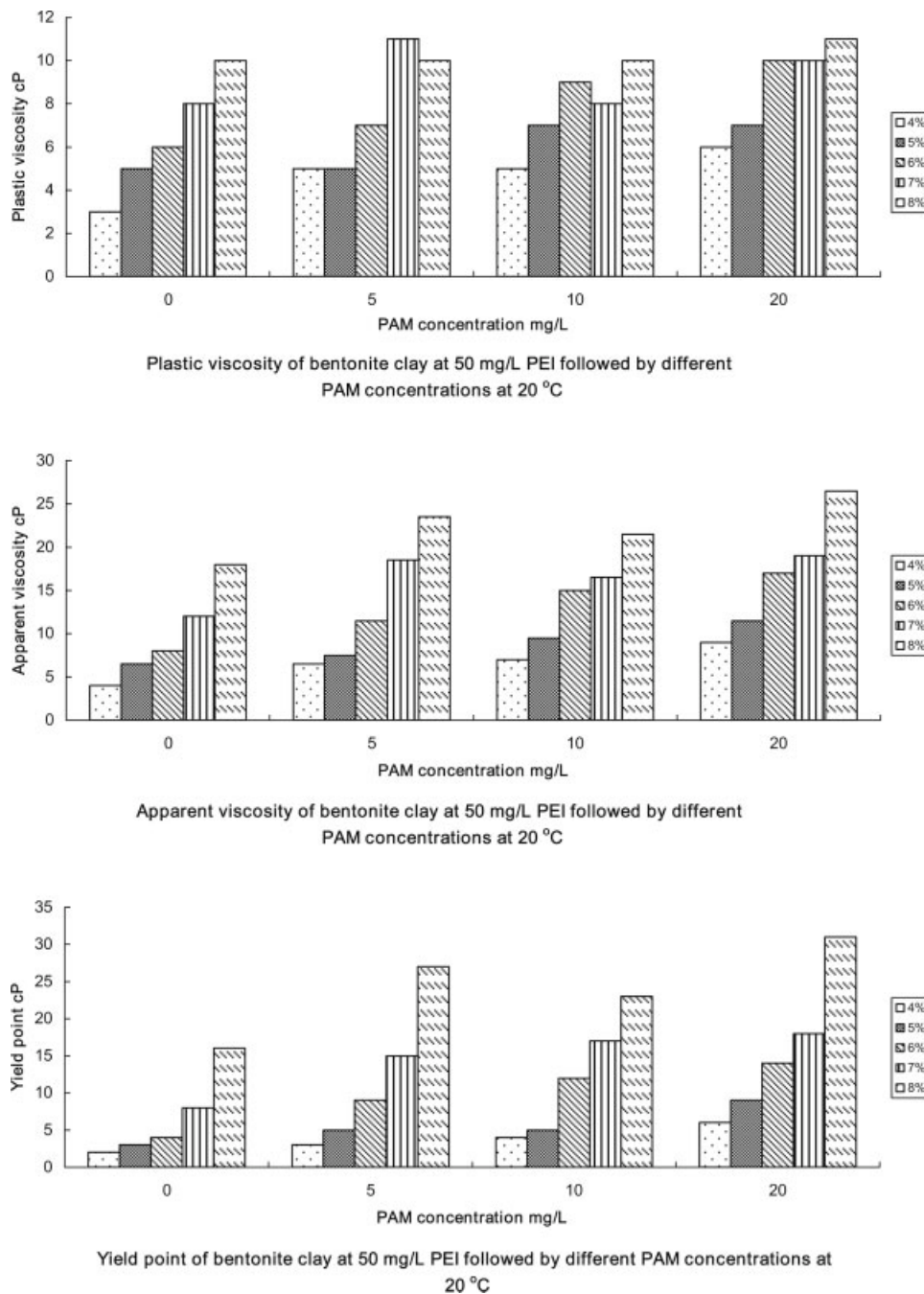
Plastic viscosity of bentonite clay at 50 mg/L PEI followed by different PAM concentrations at 20 °C

Apparent viscosity of bentonite clay at 50 mg/L PEI followed by different PAM concentrations at 20 °C

Yield point of bentonite clay at 50 mg/L PEI followed by different PAM concentrations at 20 °C

Figure 5 Rheological properties of bentonite clay at 50 mg/L PEI followed by different PAM concentrations at 20°C.

equilibrium state; it contributes to decrease gel formation in the presence of PAM. So, the yield point becomes constant as PAM concentration increases.[18]

Effect of cationic PEI and anionic PAM on the rheological properties of bentonite suspension

Effect of PEI concentrations

In these tests, anionic PAM dosage was maintained constant (10 mg/L), and PEI was added at various

dosage levels 10, 50, 100, and 200 mg/L. Comparison of the rheological properties of bentonite suspensions in the presence of PEI alone after 24 h aging time is shown in Figure 2 and that of the rheological properties of bentonite suspensions in a sequence addition of 10 mg/L PAM in conjunction with different concentrations of cationic PEI after 24 h aging time is shown in Figure 4. It was found that the dual-component systems perform much better than PEI alone. Xiao et al.[19] suggests that clay flocculation increases with an increase in anionic PAM dosage, since more effective bridging, via charge interaction,

TABLE II
Electrokinetic Properties of Bentonite Suspension in the Presence of 50 mg/L Polyethylene imine (PEI) and 10 mg/L Polyacrylamide (PAM) at 20°C

Polymer concentration	Mobility μm/s per V/cm	Zeta potential (mV)
10 mg/L PAM 50 mg/L PEI	3.8	−51
50 mg/L PEI 10 mg/L PAM	6.2	−82

would be expected between clay and anionic polymer. Addition of PEI to the interacted clay–PAM decrease bridging efficiency between clay particles and PAM as a result of charge neutralization between anionic PAM and PEI. Consequently, the rheological properties of bentonite suspensions in the presence of PAM and PEI were decreased when compared those of with PAM alone (10 mg/L). At higher PEI dosage (more than 50 mg/L), not all the PEI will be adsorbed. The excess will be free in suspension and will interact with anionic polymer, so impeding interaction between the anionic PAM and the small clay flocs that have already formed.[20]

Effect of PAM concentrations

The influence of anionic PAM dosage on clay flocculation at a constant dosage of PEI (50 mg/L) was also investigated. Figure 5 shows the rheological properties of bentonite suspensions in the presence of 50 mg/L PEI in conjunction with different concentrations of PAM (5, 10, 20 mg/L). Comparison of the rheological properties of bentonite suspensions in the presence of PAM alone after 24 h aging time is shown in Figure 3 and that of the rheological properties of bentonite suspensions in a sequence addition of 50 mg/L PEI followed by different concentrations of an anionic PAM after 24 h aging time is shown in Figure 4. It was found that the dual-component systems give more valuable yield point than the same results obtained from Figure 3. Rushmere[21] suggests that the most effective flocculation for anionic PAM alone was found at the lowest dosage level (lower than 10 mg/L). From the above-men-

tioned statement, it is obvious to expect the effect of PEI and anionic PAM combination systems. It seems that a substantial reduction for anionic PAM dosage (10 mg/L) is required for an effective flocculation in conventional polymeric flocculation systems. Svending[22] showed that the deterioration of flocculation at high anionic PAM dosage was also reflected on the rheological properties. From Figure 5, it was found that 50 mg/L of PEI followed by addition of 10 mg/L PAM was the best dosage to give the required rheological properties of bentonite suspension.

Effect of polymer addition order

The order of polymers addition is often crucial, particularly for dual-component flocculation systems. Xiao et al.[23] investigated the effect of PEI and PAM addition order. Apparently, effect of PAM addition order changed with PEI where it gave better results when it was added first, whereas by reversing the sequence of addition, the rheological properties were decreased. It was found that the floc formed by anionic polymer is sensitive to shear stress, which implies the bonding between the clay and the polymers is weak. The presence of PEI may make the flocs more robust and shear-resistant. These results agreed well with those of Xiao et al.[23] Therefore, addition of anionic PAM after PEI makes the bridging occurs not only between anionic polymer chains and cationic PEI, but also between unoccupied negative surfaces of clay via charge interaction of PEI-clay, and consequently, the rheological properties were increased.

Synergy between PEI and anionic PAM on Bentonite suspension stability

The stability of bentonite suspension in the presence of PEI and PAM was examined. It was found that zeta-potential value of bentonite suspension in the presence of 50 mg/L PEI was −47 mV, while in the presence of 10 mg/L PAM was −55 mV. The addition of 10 mg/L PAM to bentonite suspension followed by 50 mg/L PEI induced a reduction of the zeta-potential to become −51 mV when compared with that of PAM alone. But, by reversing the addi-
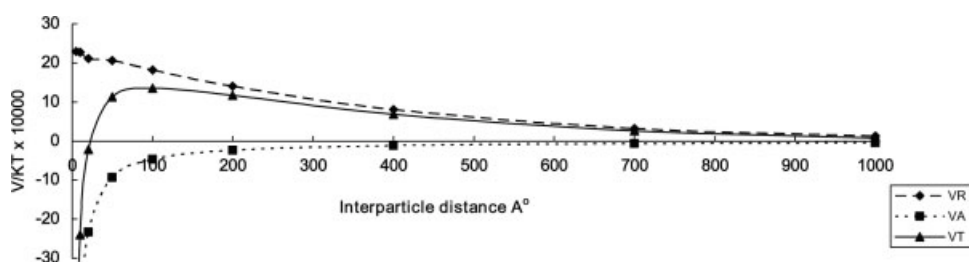

Figure 6 Potential energy profile for bentonite suspension in the presence of 50 mg/L PEI and 10 mg/L PAM.
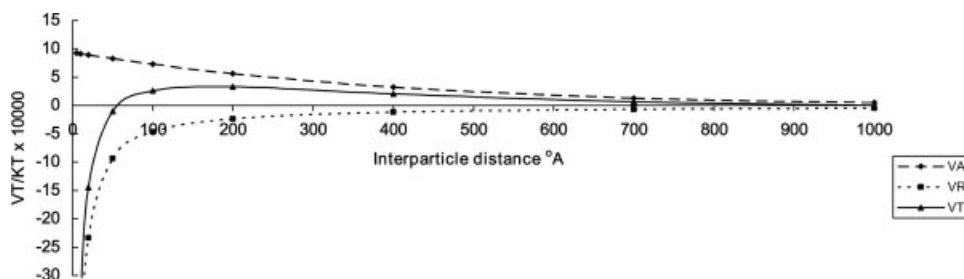
Figure 7 Potential energy profile for bentonite suspension in the presence of 10 mg/L PAM and 50 mg/L PEI.

tion sequence, a very high stable suspension having −82 mV zeta-potential was produced as mentioned in Table II.

The reasons of the above phenomenon could be explained through such mechanism. When the anionic polymer was added first, small flocs were formed. The floc size was significantly increased with the addition of PEI as a second component. When the PEI was added first, the floc sizes were relatively smaller than those formed by anionic polymer alone. However, after PAM was added, the electrical stability was increased. The reason for this could be due to bridging had occurred not only between anionic polymer chains, which were already located on the preflocculated bentonite flocs, but also between unoccupied negative surfaces of bentonite via charge interaction between PEI and bentonite. This explanation concerning the effectiveness of addition orders of these two polymers was also observed by Churchman.[24]

The electrical stability of bentonite suspension in the presence of 50 mg/L PEI and 10 mg/L PAM was investigated by drawing the potential energy profiles. Figure 6 shows the potential energy profiles for bentonite suspensions in the presence of 50 mg/L PEI followed by 10 mg/L PAM. From this energy profile, it can be seen that the clay particles possess very high potential energy barrier of about 13.52×10^4 KT at intermediate distance of 100 Å. This energy barrier value depends upon the value of zeta-potential. As the zeta-potential of bentonite suspension is high (about −82 mV), the repulsion between clay particles will be high and the clay particles separated from each other, which means the system is more stable.

On the other hand, Figure 7 shows the potential energy profiles for bentonite suspensions in the presence of 10 mg/L PAM followed by 50 mg/L PEI. After this treatment of bentonite suspension, a significant decrease in the energy barrier was observed. The energy barrier values decreased from 13.52×10^4 at intermediate distance 100 Å to 3.3×10^4 KT at intermediate distance 200 Å. The lower value for the energy barrier reflects that the repulsion energy V_R decreased and the attraction energy V_A between them increased. Therefore, the attraction energy overcomes the repulsion energy and the clay particles become close to each other. It means that the system under this condition is destabilized.

CONCLUSIONS

1. The rheological properties of Egyptian bentonite suspensions in the presence of 50 mg/L cationic PEI followed by 10 mg/L anionic PAM at 20°C after 24 h aging time give the best rheological properties as a drilling mud.
2. The electrical double layer properties of the clay could be used to investigate the interrelation between clay surfaces and polymers. Its indication determines the suitability of bentonite suspension to be a good drilling mud.
3. Addition order of PEI and PAM to the bentonite suspension should be taken into consideration to obtain a highly stable bentonite suspension.
4. Addition of 50 mg/L PEI followed by 10 mg/L PAM to bentonite suspensions produced highly stable bentonite suspension when compared with the addition of PAM alone or PEI to the bentonite suspensions.

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