Rheological and Electrical Properties of Bentonite in Anionic Polystyrene Sulfonate and Nonionic Poly(vinyl alcohol)

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ABSTRACT: The flow properties of bentonite were studied with a combination of anionic polystyrene sulfonate (molecular weight = 70,000 g/mol) and nonionic poly(vinyl alcohol) (molecular weight = 50,000 g/mol). This combination had a significant effect on clay suspensions depending on the sequence of the polymer addition. The addition of 50 mg/L anionic polystyrene sulfonate followed by 200 mg/L nonionic poly(vinyl alcohol) improved the rheological properties with a 7% bentonite suspension, especially at 20°C and after 24 h of aging. However, by the reversal of this addition sequence, the rheological properties of bentonite suspensions were reduced. The ζ potential of bentonite suspensions of the individual polymers at the same concentration was −42 mV for polystyrene sulfonate and −63 mV for poly(vinyl alcohol). The combined effect of anionic polystyrene sulfonate followed by nonionic poly(vinyl alcohol) noticeably changed the ζ potential (−95 mV). With the reversal of the addition sequence, this parameter did not change. Potential energy profiles were constructed to investigate the suspension stability. Potential energy profiles of polystyrene sulfonate added to bentonite suspensions and followed by poly(vinyl alcohol) produced high repulsion potential energy between clay surfaces, reflecting high suspension stability. By the reversal of this sequence, a significant reduction of the energy barrier was observed. On the basis of the rheological and electrical properties of this system, the addition of polystyrene sulfonate followed by poly(vinyl alcohol) provides a promising tendency for a 7% clay concentration to meet desirable drilling mud properties. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3886–3894, 2007

Key words: additives; clay; colloids; density; polystyrene; rheology

INTRODUCTION

The interaction of clays with polymers has been an important concern in the field of drilling fluid technology.[1,2] 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. When nonionic polymers are added to suspensions at low concentrations, an increase in the rheological parameters, such as the yield stress and viscosity, can be observed. Alternatively, if suspensions are stabilized by polymers, a reduction of these parameters results. A higher concentration of a polymer leads to a stabilizing effect or deflocculation of a clay suspension. This behavior has been observed mainly for clay suspensions containing high-molecular-weight polymers, such as poly(vinyl alcohol) (PVA).[3] The addition of only a few percent of PVA to Na^+ montmorillonite suspensions leads to a pronounced increase in the static yield stress, after which the suspension is deflocculated with a further increase in PVA.[4]

The polyvalent ions act as bridges between the anionic groups on the polymer and the negative sites on the clay. The extent of anionic polymer adsorption is far below and much less dependent on the molecular weight than that of uncharged polymers. It is currently believed that polyanions are adsorbed by relatively few train segments in aqueous solutions and do not enter the interlamellar region.[5]

In addition, from the measurements of electrical properties such as the ζ potential, it has been possible to obtain information on the thickness of adsorbed layers and the configuration of polymers on clay surfaces.[6]

In this work, the rheological and electrical properties of Egyptian bentonite were investigated in the presence of polystyrene sulfonate (PSS) and PVA. Also, the effect of the polymer addition order on these rheological properties was examined.

EXPERIMENTAL

Egyptian bentonite clay was used in this study. The cation-exchange capacity and specific surface area were 77.3 mequiv/100 g and 346.7 m^2/g, respectively. Also, a chemical analysis of a bentonite clay sample is listed in Table I. X-ray diffraction analysis for this bentonite was performed as shown in Figure 1.

The polymers were PSS sodium salt with a molecular weight of 70,000 g/mol and PVA with a molecular weight of 50,000 g/mol.

The rheological properties of different bentonite clay suspensions (4–8% w/w) in the presence of PSS (0, 30, 50, 100, and 200 mg/L) after 4 and 24 h of aging were determined.

Also, the rheological properties of different bentonite clay suspensions (4–8% w/w) in the presence of PVA (0, 50, 100, and 200 mg/L) after 4 and 24 h of aging were measured.

Moreover, the effects of the polymer addition order on the rheological properties of bentonite suspensions in the presence of a fixed PVA concentration (200 mg/L) and different PSS concentrations were investigated. Also, the rheological properties of a constant PSS concentration (50 mg/L) and different PVA concentrations were investigated.

The electrophoretic mobility of the bentonite clay particles in the presence of 200 mg/L PVA as the first addition followed by 50 mg/L PSS and the effect of reversing the polymer addition order were determined with a microelectrophoresis apparatus (Zeta Meter, Inc., New York, NY).

RESULTS AND DISCUSSION

Effect of anionic PSS on the rheological properties of bentonite suspensions

The rheological properties of bentonite suspensions as a function of the PSS concentration after 24 h of aging at 20°C are illustrated in Figure 2. With an increase in the polymer concentration, the rheological properties (the plastic and apparent viscosities as well as the yield point) of the bentonite suspensions showed a slight increase, especially with 7 or 8% bentonite.

The bentonite suspension of this study could be regarded as consisting of flocs whose average size was determined by the bentonite suspension and polymer concentration. These flocs were, of course, much larger than the flow units that determined the plastic viscosity. Therefore, the bentonite particles were coagulated into flocs, which were grouped together into units known as aggregates, producing a continuous network throughout the suspension. The variation in the rheological properties, brought about by changes in the PSS concentration in the suspension, resembled quite closely the variation of the plastic viscosity, which was explained in terms of flow units, under high shear conditions.[7] However, because the internal structures of both were determined largely by the nature of the particle–particle bonds, their variations with the PSS concentration should have been similar. When PSS was attached to one positive edge site of a bentonite clay particle, the negative charge density at this edge increased. This reaction generally increased the viscosity and increased the stability of the colloidal dispersion, as discussed later in this study.[8,9]

Effect of nonionic PVA on the rheological properties of bentonite suspensions

PVA as a nonionic polymer was used as an additive to examine the rheological properties of bentonite suspensions. Figure 3 shows that there was no effect of PVA addition to 6% bentonite on the initial value of the viscosity. When the clay content was increased (7 or 8%), the viscosity increased significantly. The viscosity of the suspension was monitored by increases in the amount of the polymer added in the bulk without the clay particle–particle interactions being taken into account, as these were gradually covered. The addition of different PVA concentrations to the bentonite suspensions led to a pronounced increase in some rheological properties, such as the plastic viscosity, apparent viscosity, and yield point.[10] Also, when a higher PVA concentration (>100 mg/L) was added to denser clay, a stabilizing effect or deflocculation of the clay suspension was observed. This behavior has been observed mainly for clay suspensions containing high-molecular-weight polymers, such as PVA (molecular weight = 50000 g/mol). These statements reveal that PVA modifies the viscosity of clay suspensions.[11,12]
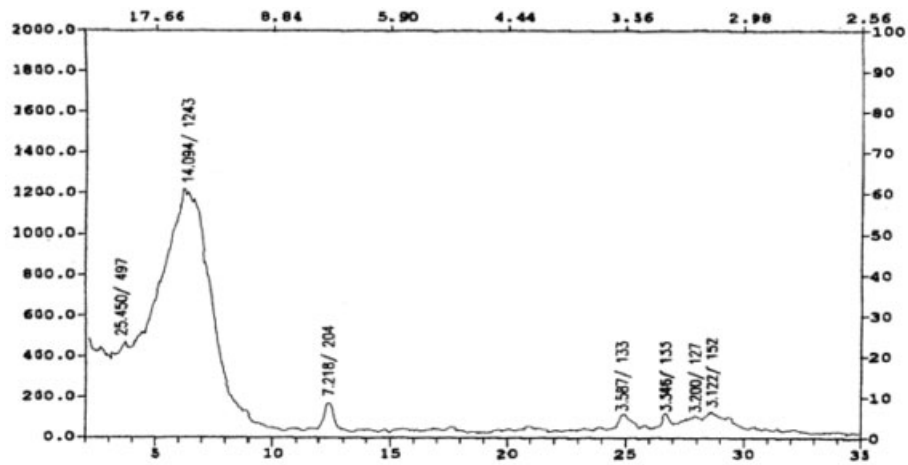
This phenomenon is in agreement with the rheological properties of the bentonite suspensions in this study.

Effect of anionic PSS and nonionic PVA on the rheological properties of bentonite suspensions
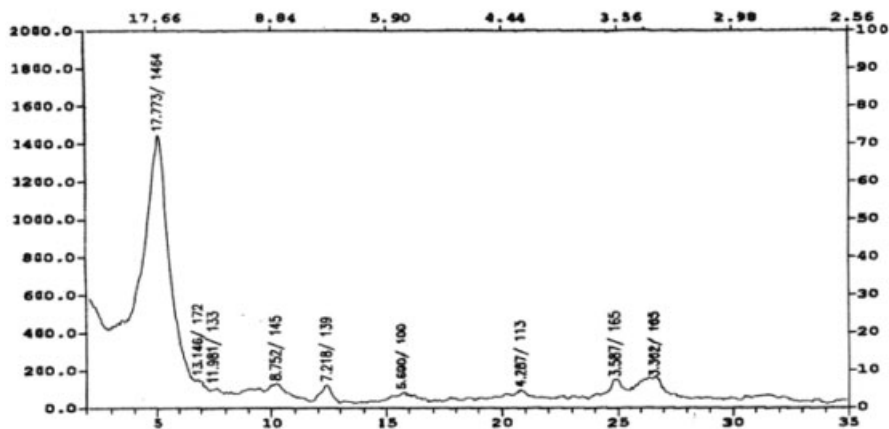
The rheological properties of bentonite clay suspensions in the presence of 50 mg/L PSS in conjunction

TABLE I
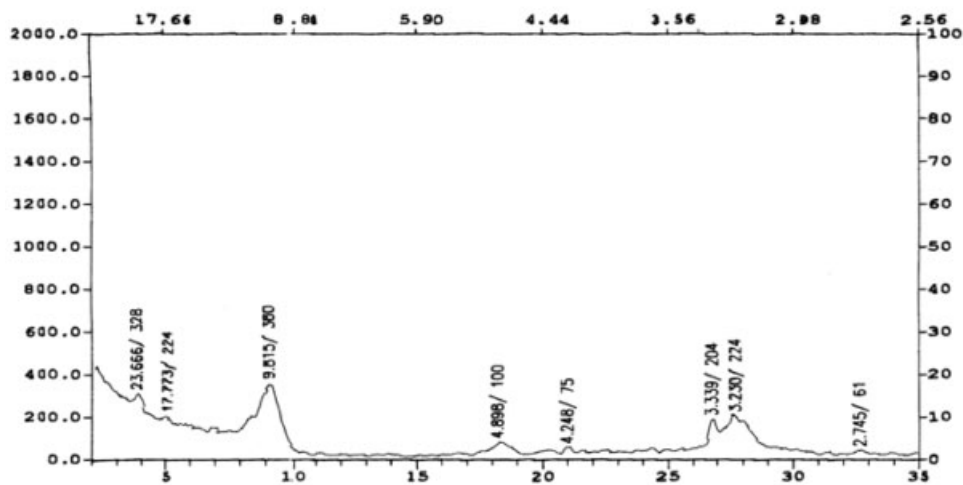### Chemical Analysis of Bentonite Clay

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

Figure 1 X-ray diffraction analysis of bentonite samples.

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

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

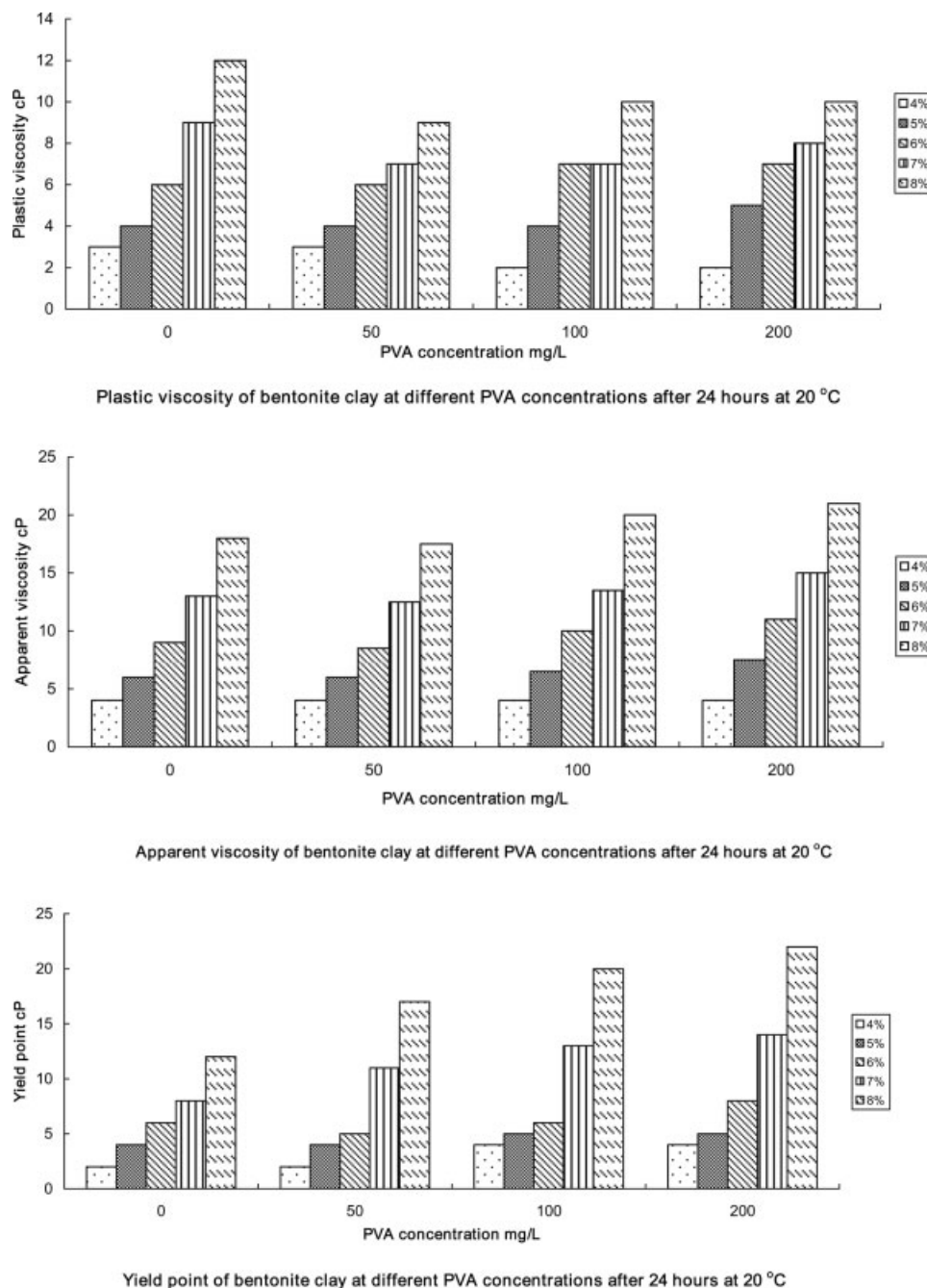Yield point of bentonite clay at different PSS concentrations after 24 hours at 20 °C
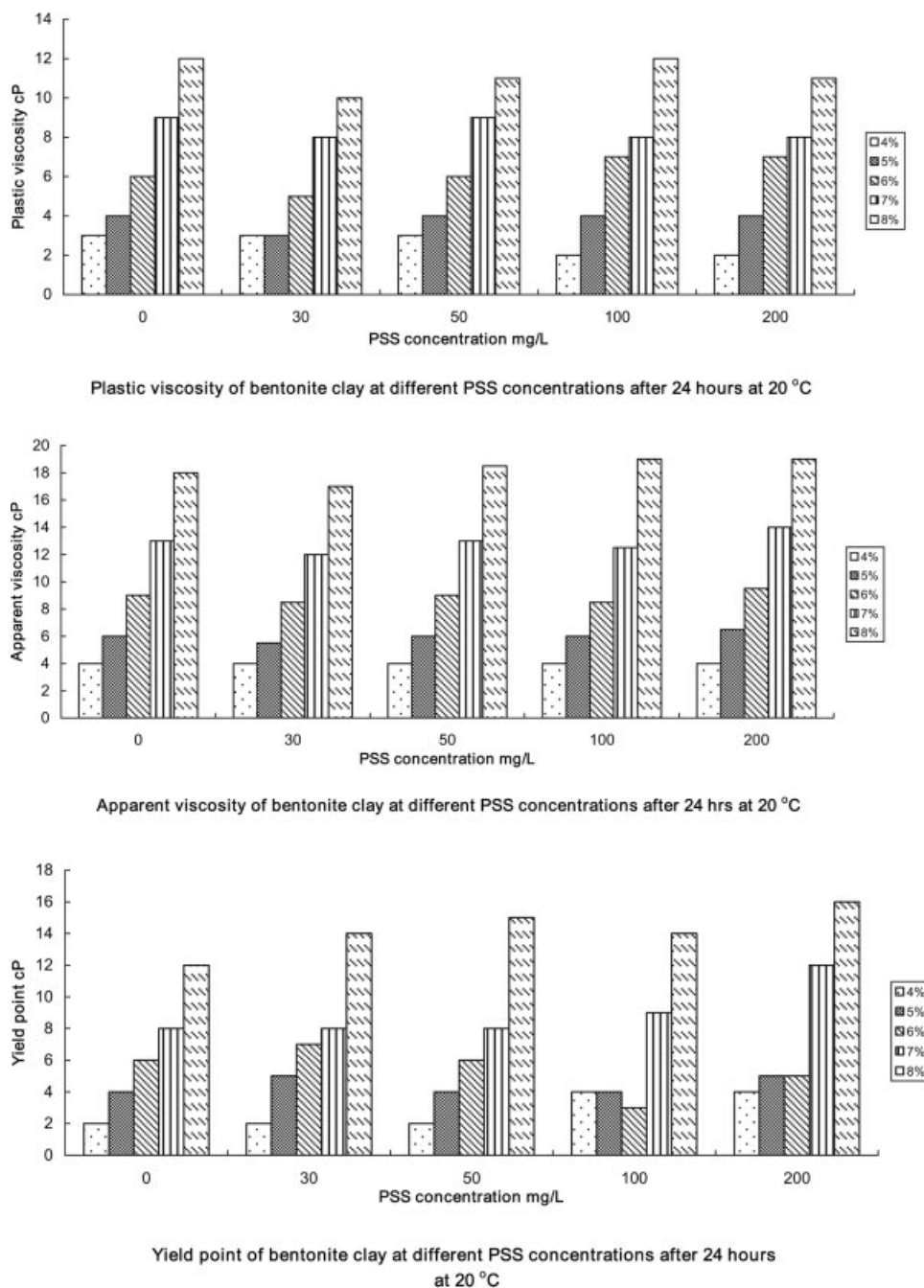
Figure 2 Rheological properties of bentonite clay with different PSS concentrations after 24 h at 20°C.

with different concentrations of PVA (50, 100, and 200 mg/L) at 20°C after 24 h of aging are shown in Figure 4. By comparing the rheological properties of the bentonite suspensions in the presence of PVA alone, as illustrated in Figure 3, and in the presence of dual-component systems with PSS and PVA, we found that there was no difference in the rheological properties between the dual components and PVA alone.

The behavior of PSS/PVA on bentonite particles is determined by flocculation and the precipitation. A mechanism for PSS/PVA adsorption on bentonite particles is proposed.[13] In this mechanism, which is

shown in Figure 5, as PSS is added first, it partially adsorbs onto bentonite particles. Upon the addition of PVA, it interacts with adsorbed PSS on bentonite particles to form a soluble complex, which is adsorbed onto the bentonite particles to give bridging flocculation. Unlike flocculation with just PSS, the presence of the second polymer (PVA) can bind the particles, which are coated with the adsorbed polymer, and as a result, effective flocculation is present.

On the other side, Figure 6 shows the rheological properties of bentonite clay suspensions in the presence of 200 mg/L PVA followed by the addition of

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

Apparent viscosity of bentonite clay at different PVA concentrations after 24 hours at 20 °C

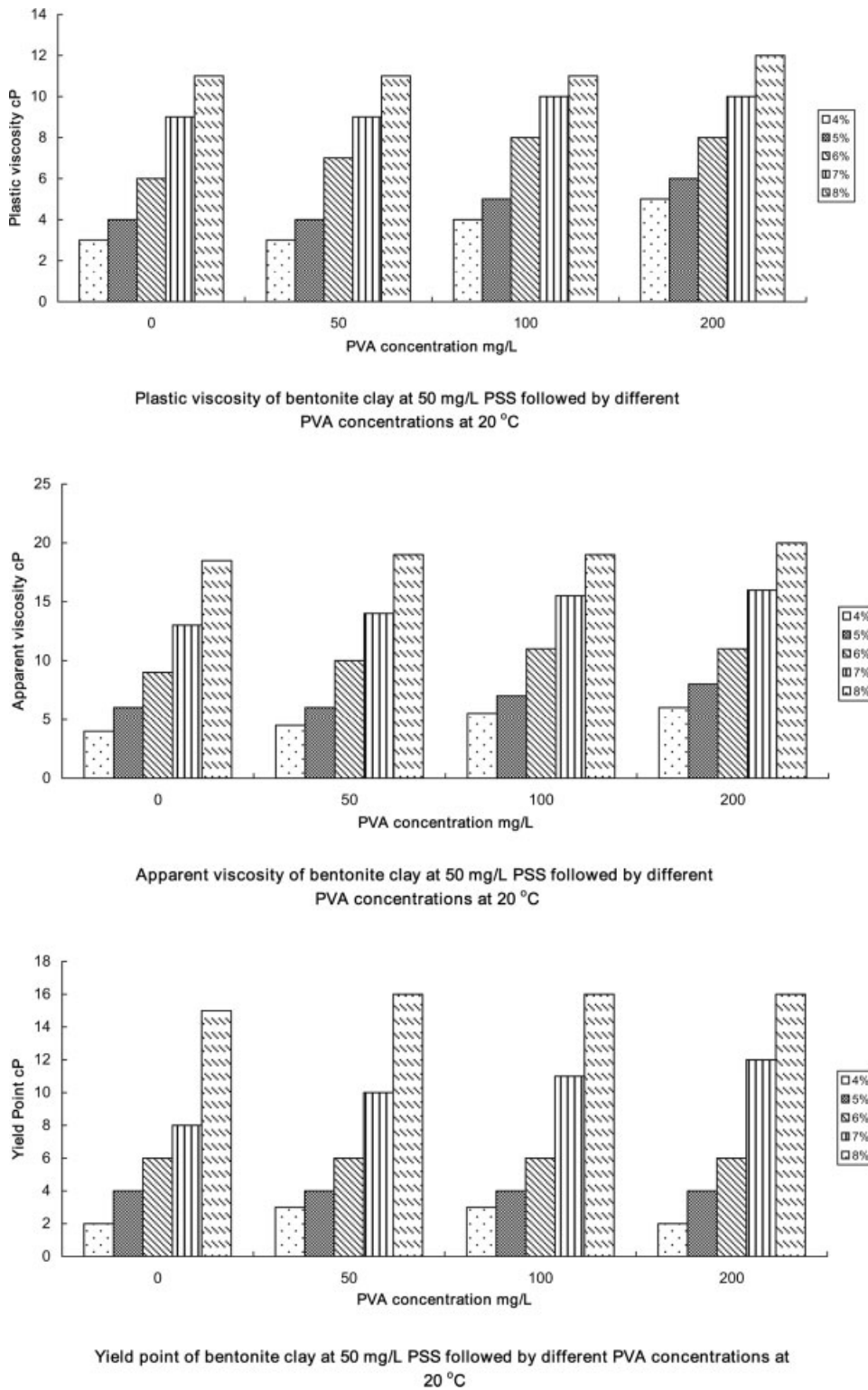Yield point of bentonite clay at different PVA concentrations after 24 hours at 20 °C

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

different PSS concentrations (10, 30, and 50 mg/L) at 20°C after 24 h of aging. A comparison of the data obtained with PSS alone in Figure 2 and with the dual-component systems shows that there is no big difference in the obtained rheological properties. Also, Figure 5 shows that when PVA is added first to colloidal particles, it forms a primary complex. The addition of PSS to the primary complex leads to precipitation. Therefore, as effective flocculation is obtained, the rheological properties of bentonite suspensions increase.[14,15]

Synergy between PSS and PVA with respect to the stability of bentonite suspensions

The stability of bentonite suspensions in the presence of PSS and PVA was examined. The ζ potential of bentonite suspensions in the presence of 50 mg/L PSS was −42 mV, whereas for 200 mg/L PVA, it was −63 mV.

The addition of 200 mg/L PVA to a bentonite suspension followed by 50 mg/L PSS gave a ζ potential of −63 mV, which was similar to that obtained by the addition of PVA alone. However, by the reversal of

Plastic viscosity of bentonite clay at 50 mg/L PSS followed by different PVA concentrations at 20 °C

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

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

Figure 4 Rheological properties of bentonite clay with 50 mg/L PSS and different PVA concentrations at 20°C.

the addition sequence, a very highly stable suspension having a ζ potential of -95 mV was produced.

There was a decrease in the ζ potential for the PVA/PSS bentonite system compared with that of the reverse sequence of addition. The maximum adsorption of PVA was reached (200 mg/L). The lowest value of the ζ

potential for this type of PVA/PSS system corresponded to a jump or sudden decrease in the absolute value of the ζ potential. This lowest value could be approached at the maximum adsorbed amount of PVA.[16]

Also, the adsorbed PVA layer thickness increased with increasing polymer concentration because the

PSS adsorbed on colloidal particles   PVA adsorbed on colloidal particles
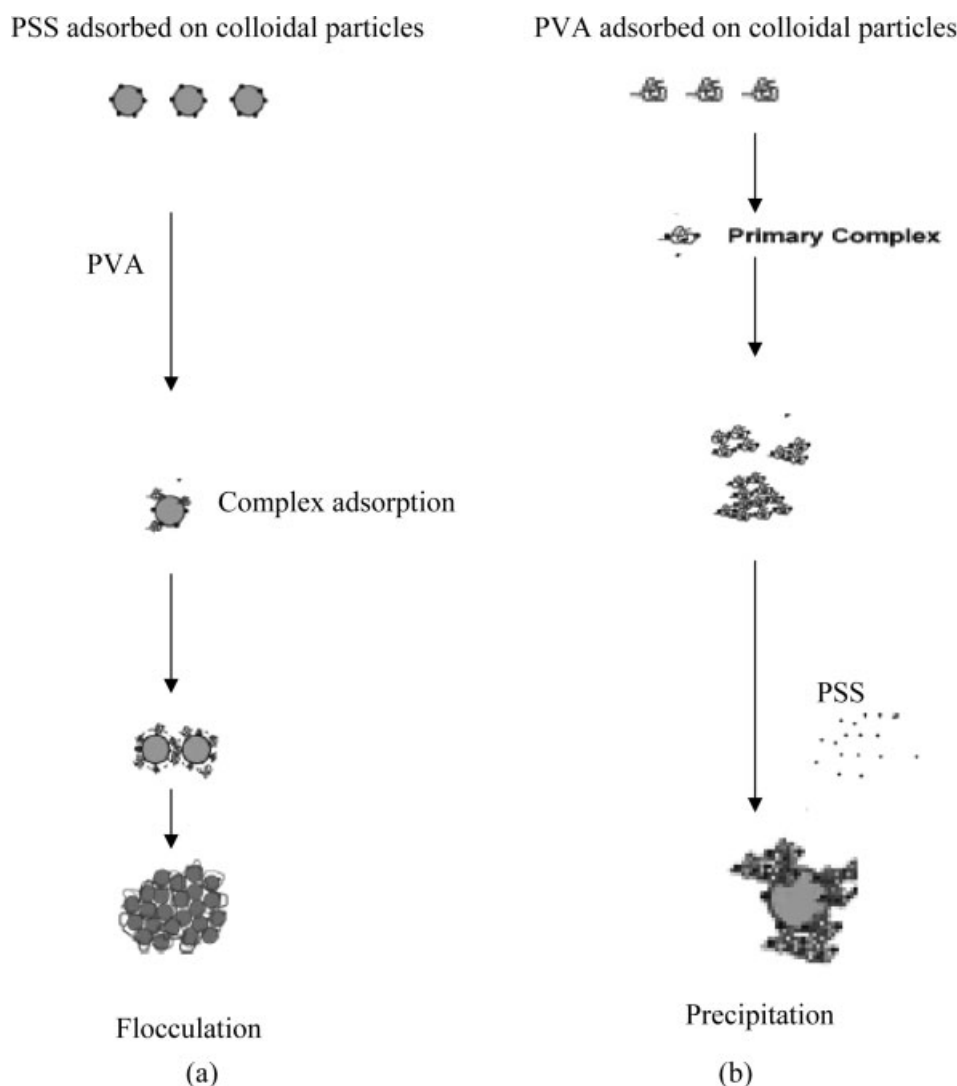
Figure 5 Proposed mechanism for the flocculation of bentonite particles by a PSS/PVA complex: (a) flocculation and (b) precipitation.

maximum adsorbed amount of PVA (200 mg/L) possessed a larger double-layer thickness. The linear relationship between the two supports indicated that the length of the PVA tail determined the length of the adsorbed layer thickness. This result coincided with the relationship between the area occupied by PSS and PVA. Thus, the estimated double-layer thickness was described as the largest distance up to which the segments extended away from the surface. Hence, the larger values for the thickness obtained in this study suggested a different orientation at the surface.

Changes in the thickness of the double layer of bentonite suspensions could be calculated through potential energy profiles in the presence of 50 mg/L PSS together with 200 mg/L PVA, as illustrated in Figure 7. These profiles showed that the clay particles possessed a very high potential energy barrier of about 19.7×10^4 KT at an intermediate distance of 100 Å. Thus, the repulsion between the clay particles was very high under this

condition; the clay particles were separated from one another, and this meant that the system was stable.

By the reversal of the order of addition of these polymers, a decrease in the potential energy barrier from 19.7×10^4 to 6.07×10^4 KT at an intermediate distance of 100 Å was observed, as shown in Figure 8. This decrease in the energy barrier indicated that the attraction energy overcame the repulsion energy and that the clay particles become close to one another. This meant that the system under this condition was destabilized. This system should be avoided when we think about a bentonite suspension as drilling mud.

CONCLUSIONS

Egyptian bentonite suspensions in the presence of 50 mg/L anionic PSS followed by 200 mg/L nonionic PVA at 20°C after 24 h of aging gave the best rheological properties as drilling mud.
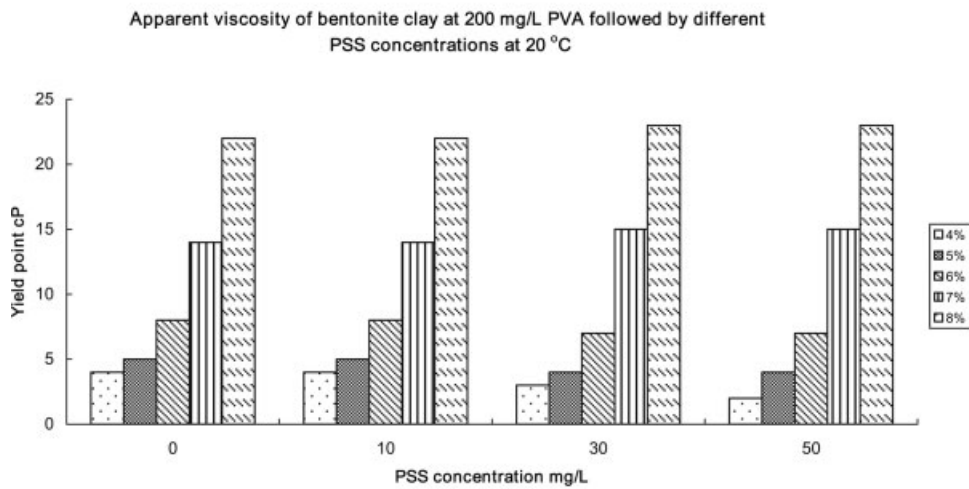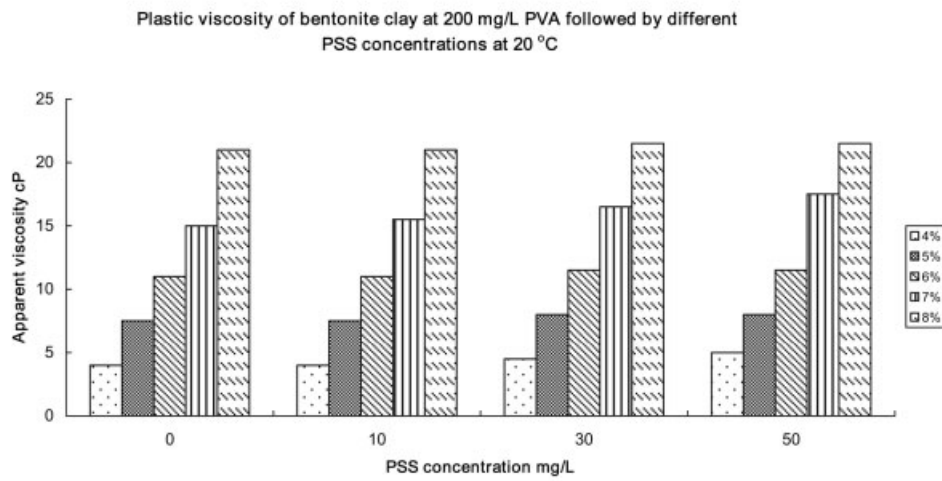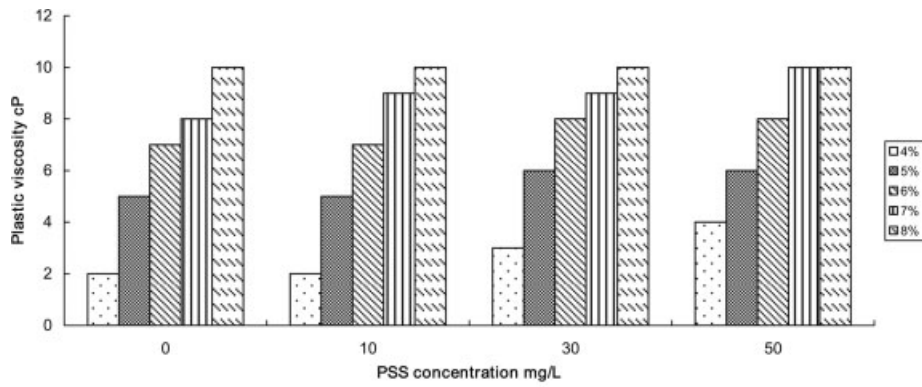
Figure 6 Rheological properties of bentonite clay with 200 mg/L PVA and different PSS concentrations at 20°C.
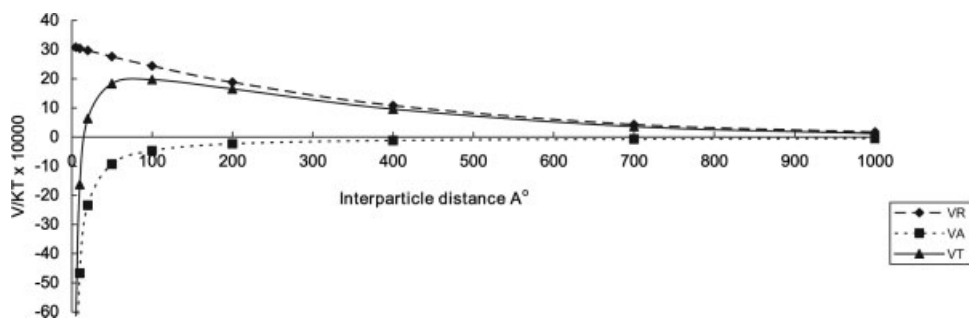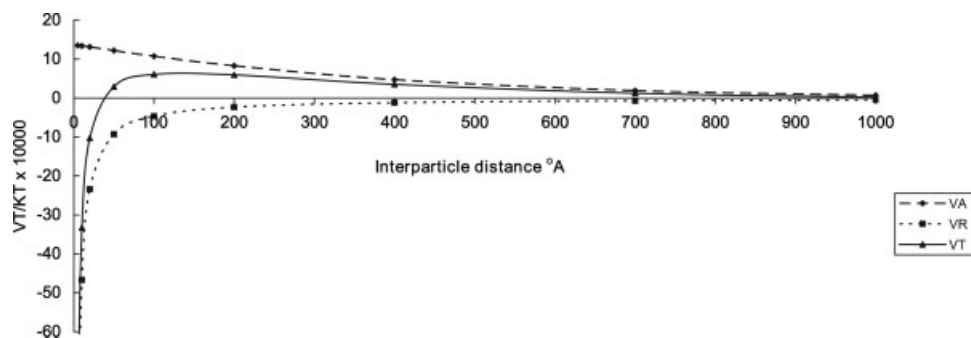

Figure 7 Potential energy profile for bentonite suspensions in the presence of 50 mg/L PSS and 200 mg/L PVA.

Figure 8 Potential energy profile for bentonite suspensions in the presence of 200 mg/L PVA and 200 mg/L PSS (V_A = attraction energy; V_R = repulsion energy; V_T = total energy).

The electrical double-layer properties of the clay could be used to investigate the interrelation between the clay surfaces and polymers. It determined the suitability of bentonite suspensions as good drilling mud.

The addition order of PSS and PVA to the bentonite suspension should be taken into consideration to obtain a highly stable bentonite suspension.

The addition of 50 mg/L PSS followed by 200 mg/L PVA to bentonite suspensions produced highly stable bentonite suspensions in comparison with the addition of PVA alone or PSS to bentonite suspensions.

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