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Rheological Behavior of Pyrophyllite−Water Slurry in the Presence of Anionic, Cationic, and Nonionic Surfactants

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The rheological behavior of pyrophyllite−water clay slurry has been studied in the presence of three different types of surfactants: anionic, cationic, and nonionic. The slurry is non-Newtonian and thixotropic in nature, and the hysteresis area increases with increasing clay concentration. In the presence of acidic pH, surface potential is low and viscosity is high; the opposite is true for alkaline pH. The rheological behavior is different in the presence of three surfactants. The viscosity highly depends on the types of surfactant adsorbed on the clay surface and surface potential after the adsorption. The $d_{(001)}$ lattice spacing of the pyrophyllite clay does not change after the adsorption of surfactants, indicating that the surfactants are not adsorbing inside the clay spacing.

1. Introduction

The rheological behavior of slurries and their characterization has received widespread attention in recent years because of their wide range of industrial applications and academic interest. As an example, the reduction of slurry viscosity can be useful in slurry transportation, easy mixing, and filtering, which can also result in a substantial energy savings. Viscosity or rheological properties of slurry, emulsion, or paste is also important, as it can be used in modifying the physical properties or flow behavior of these materials. Surfactants are one of the essential components in cosmetics, creams, gels, foods, etc. In many of these products, clay is also an important ingredient. The presence of even trace amounts of surfactants can alter the viscosity or rheological properties of these fluids. The interaction between the suspended particles is very important in the rheological behavior of the slurry system. In general, the rheological property depends on different parameters like the solid/water ratio, size, shape, pH,[1,2] surface charge of the particles,[3−5] exchangeable ions of clay particles,[1,5] additive types like surfactants,[6,7] electrolytes,[8] polymers,[9] temperature, etc.

Clays are natural products and have many industrial applications like use as catalysts, in engineering and construction, agriculture, environmental remediation, etc.[10−11] Like the other suspensions, rheological properties of clay−water slurry are also greatly influenced in the presence of surfactants and polymers.[6,7,13−18] Gunister et al.[6,7] have studied the effect of cationic surfactants (benzyldimethyltetradecyl ammonium chloride (BDTAC) and dodecyltrimethyl ammonium bromide (DTAB)) on bentonite clay. They found that, at low solid concentrations (1 or 2%), it exhibits Newtonian behavior, but at high solid concentrations, the flow becomes pseudoplastic. Upon the addition of cationic surfactants at low concentrations, there was no significant change in rheological parameters, but at higher concentrations there was an increase in viscosity and hysteresis area. Between two cationic surfactants, change was sharper for DTAB than that of BDTAC. Isci et al.[13] have studied the rheological properties of Ca-bentonite (CaE), Na-bentonite (NaE), and hectorite (HC) in the presence of a nonionic hydrophilic polymer (polyvinyl alcohol, PVA). When the PVA concentration was increased, the viscosity of CaE and HC increased with a sharp and significant change for CaE, but the same was decreased for NaE. They too performed the XRD analysis to show the increase in viscosity due to an increase in interlayer clay spacing in CaE. The cationic and anionic polyacrylamides' (PAM) effect on the compressive and shear properties of kaolinite suspensions show that cationic PAM based suspensions are less compressible than the anionic and the magnitudes of the yield stress and elastic and viscous modulus are strongly dependent upon the floc structure, with greater values being observed for the cationic PAM than for the anionic PAM due to floc structure-related adsorption.[16] Tunc and Duman[17] have studied the effect of monoethylene glycol (MEG) and different molecular weights of poly(ethylene glycol) (PEG) solutions on the electrokinetic and rheological properties of Na-bentonite suspensions. The Na-bentonite−polymer suspension showed a thixotropic behavior with a hysteresis loop.

In the present paper, the effect of surfactants on the viscosity of a pyrophyllite−water slurry was studied. Pyrophyllite clay has a broad variety of applications in industry. For example, it is used in the ceramics, paper, paint, plastics, rubber, sealant, adhesive, and chemical industries. It is one of the very common low-cost natural clays with a triclinic crystalline structure. Pyrophyllite is a hydrous aluminum silicate ($Al_2Si_4O_{10}(OH)_2$) with two layers of silica to one of alumina, consisting of chemical composition.[19] Its crystalline structure consists of stacked pairs of tetrahedral silica sheets and octahedral alumina sheets, shown in Figure 1.[20] The absence of a hydroxyl group at the surfaces of the triple layer prevents hydrogen bonding.
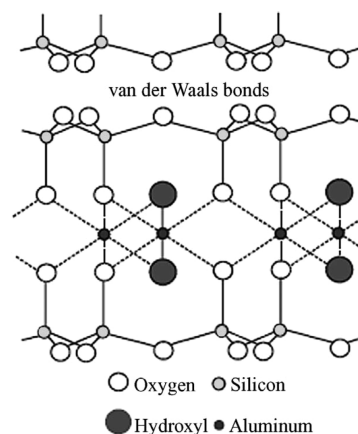

Figure 1. Schematic presentation of the pyrophyllite clay structure.[20]

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The layered structure is held together by van der Waals interactions between the plates. Since the attraction between the layers is weak, the layers can readily be cleaved along the basal planes.

Our main objective of this study is to investigate the effects of solid concentration, pH, and finally surfactants (anionic, cationic, and nonionic) on the viscosity of clay–water slurry. Also, we have attempted to correlate the ζ potential, surfactant adsorption, and lattice spacing with the rheological behavior. From the literature, we have found that most of the studies are concentrated on bentonite clay, and there are a few on pyrophyllite; moreover, the studies are concentrated on low solid content. The novelty of this study is that we used a very high solid concentration of pyrophyllite clay, and the behaviors of three types of surfactants are compared.

2. Experimental Section

2.1. Materials. Pyrophyllite clay and the nonionic surfactant triton X-100 (TX-100) of 99% purity were purchased from Loba Chemie Pvt., Ltd., India. The surfactants cetylpyridinium bromide (CPB) from Rankem, India of 99% purity and sodium dodecylbenzene sulfonate (SDBS) of technical grade (Cat no. 28 995−7) were purchased from Sigma Aldrich chemicals, Germany. Ultrapure water (Sartorius, Germany) of 18.2 MΩ cm resistivity, 71.5 mN/m surface tension, and 6.5−7 pH at 25 °C was used for the measurements.

2.2. Methods. The critical micellar concentration (CMC) of the aqueous solution of surfactants was measured at 25 °C by the Wilhelmy plate technique with a surface tensiometer DCAT 11EC (Data physics, Germany). The CMCs of the surfactants are 1.5 mM, 0.9 mM, and 0.15 mM for SDBS, CPB, and TX-100, respectively. The average particle size of clay was measured by a Malvern particle size analyzer (Mastersizer 2000, Malvern, U.K.), and the average diameter was found to be 8.1 μm. The ζ potential was measured using a ζ potential analyzer (Zeta sizer Nano ZS, Malvern, U.K.) in the presence of a 0.01 mM KCl solution as a background electrolyte. The specific surface area (BET) of the pyrophyllite clay was measured by N$_2$ adsorption−desorption studies at liquid nitrogen temperature (−195.8 °C) using a BET surface area analyzer (Quantachrome, USA, Model No. Autosorb-1). The samples were degassed at 200 °C prior to the analysis.

A cone and plate viscometer (Bohlin Visco-88, Malvern, U.K.) was used for the viscosity measurement. The cone angle is 5.4°, and the diameter is 30 mm. A gap of 0.15 mm was maintained between the cone and plate for all the measurements. A plastic cover was used with a wetted layer of sponge inside to reduce the moisture loss from the slurry during the experiments. All the measurements were carried out at a constant temperature of 30 ± 1 °C maintained using an external water circulator. The viscosity of the slurries without surfactants containing 40%, 45%, 50%, 55%, and 60% (% by wt) clay were measured at variable shear rates from 12 s^{-1} to 99 s^{-1} (up and down cycle). The slurry in the presence of surfactants TX-100, SDBS, and CPB was prepared by adding the desired surfactant solution, and the measurements were carried out after waiting 25−30 min to complete the surfactant adsorption. All the constant shear experiments were performed at a 60 s^{-1} shear rate and at 30 °C.

For the adsorption experiments, a volume of 10 mL of surfactant solution having different concentrations and 0.1 g of pyrophyllite clay was used in 60 mL plastic bottles, for all the experiments. The bottles were shaken for 2 h at 30 °C in a shaker. Pyrophyllite clay was separated from the mixture by

centrifugation at 5000 rpm. The concentrations of the surfactant solution before and after the adsorption were determined by UV−vis spectrophotometer (Jasco, V-530, Japan) at different λ_{max} values of 223 nm, 224 nm, and 258 nm for TX-100, SDBS, and CPB, respectively, using their respective calibration curves (absorbance vs concentration) constructed from the known concentrations. The experiments were repeated at least three times, and the average data were plotted.

An SEM analysis was done (JEOL, JSM-6480LB) to show the clay structure. XRD (Phillips, PW 1830HT) analysis was done to confirm the type of clay used and to study the changes in lattice spacing upon surfactant adsorption. The initial surfactant solutions were prepared in proper concentrations such that the equilibrium concentration (after adsorption on the clay) was above CMC, confirmed by UV analysis. For XRD analysis, 4 g of the clay was placed in 50 mL of 16 mM CPB and TX-100 and 40 mM SDBS.

3. Results and Discussion

3.1. Characterization of Clay. The pyrophyllite clay structure was confirmed by XRD analysis (46−1308 from JCPDS PDF Number) with molecular formula Al$_2$Si$_4$O$_{10}$(OH)$_2$. The composition in percent was analyzed by EDX as follows: Na$_2$O = 2.71%, MgO = 1.57%, Al$_2$O$_3$ = 29.78%, SiO$_2$ = 64.78%, K$_2$O = 0.95%, and CaO = 0.21%; the results are comparable with the reported values of chemical analysis done by others.[21,22] Since the K$_2$O present is 0.95% (less than 2%), the sample is a low alkali pyrophyllite. The specific surface area was measured by the BET nitrogen adsorption method and found to be 11.38 m^2/g. The cation exchange capacity (CEC) was determined according to the procedure of Bhattacharyya and Gupta[23] and the value obtained 1.56 mequiv/g is very close (1.24 mequiv/g) to the reported value by others.[24,25]

3.2. ζ Potential of the Pyrophyllite Clay.

3.2.1. Aqueous Media. The ζ potential of the clay at different pH's was measured to know the variation of surface charge with pH and a point of zero charge (pH$_{PZC}$). Pyrophyllite is originally negatively charged in a neutral aqueous media of ζ potential $\sim$−15 mV. Figure 2a shows that the ζ potential in an aqueous media becomes more negative with the increasing pH. The figure also shows that the pH$_{PZC}$ of the clay is $\sim$3.

3.2.2. Surfactant Media. Figure 2b shows the ζ potential of the clay in the presence of CPB, TX-100, and SDBS. In the presence of CPB, first, the cationic surfactant is adsorbed through the headgroups, and the surface becomes more hydrophobic due to the orientation of the tailgroups toward the aqueous media. From the figure, it is clear that, at about 0.01 mM CPB concentration, pyrophyllite shows zero surface potential, which indicates that the monolayer of the surfactant is formed at that concentration. Above that concentration, the surface becomes positively charged due to the formation of a bilayer (hemimicelle) of surfactant molecules. In the presence of SDBS, the curve is not passing through zero potential, but the ζ potential is more negative with the increase in surfactant concentration. The value is higher than that in the presence of pure water, which confirms the occurrence of adsorption of the surfactants on the clay surface, and probably the anionic surfactant molecules adsorb at the clay surface through the tailgroups. The presence of a nonionic surfactant shows almost there is no change in ζ potential with respect to pure water. This may indicate that the adsorption of TX-100 is less on the pyrophyllite surface, changing the surface potential.
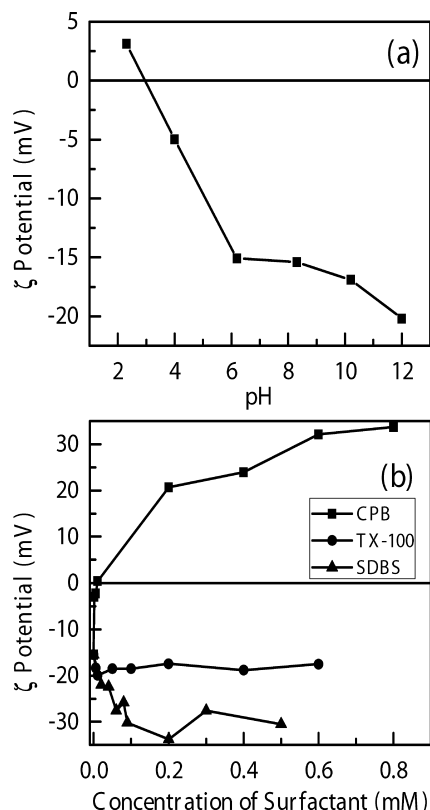
Figure 2. ζ potential of pyrophyllite clay (a) with the variation of pH and (b) with the variation of CPB, TX-100, and SDBS concentrations.
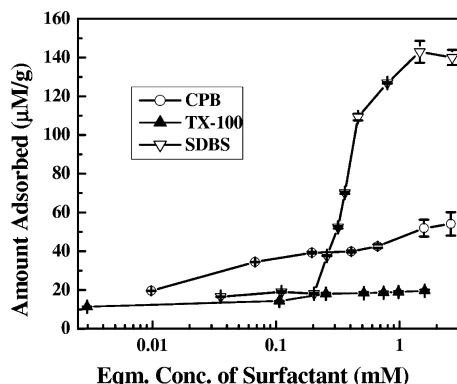

Figure 3. Adsorption isotherms of SDBS, CPB, and TX-100 on pyrophyllite clay.

3.3. Adsorption of Surfactants on the Pyrophyllite Clay Surface. Before studying the rheological behavior, we have studied the adsorption isotherm of three surfactants on the clay surface, and the isotherms are shown in Figure 3. Figure 3 clearly shows that the natures of the curves are not exactly similar for the three surfactants studied here, whereas there is a difference in the amount adsorbed at the plateau level. The order of amount adsorbed at the plateau level is SDBS > CPB > TX-100. By observing the isotherms, it seems that TX-100 is following a monolayer adsorption. Initially, there is an almost linear increase in the amount adsorbed (Henry's region) with the increase in surfactant concentration; after that region, there is a gradual decrease in slope, finally reaching a plateau level nearly at 0.25 mM concentration. The TX-100 is probably adsorbed at the hydrophobic sites present on the clay surface, attaching through the tailgroup. During the grinding process of producing pyrophyllite powder, some surfaces result from the easy cleavage between the layers, whereas lateral surfaces

(edges) are formed by the fracture of the ionic and covalent bonds. Therefore, the basal surfaces where the interlayer space is devoid of the hydrated counterions are hydrophobic.[20] The adsorption isotherm of CPB shows initially there is a linear increase in the amount adsorbed, and at about 0.2 mM concentration, the amount adsorbed reaches a primary saturation level. Subsequently, at ~0.4 mM concentration, again there is an increase in the amount adsorbed, maybe due to the formation of hemimicelle, and finally reaches a secondary saturation level at nearly 1.5 mM concentration. Similar to CPB, the isotherm of SDBS is also a bit complex: the amount adsorbed reaches a primary saturation approximately at 0.1 to 0.2 mM concentration. Then, there is an increase in the amount adsorbed, finally reaching a secondary saturation level at ~1.5 mM concentration. The adsorbed amount of SDBS being higher than CPB is attributed probably to the presence of bivalence calcium ions in the solution dissolute from the clay. That may also lead to the formation of a hemimicelle for SDBS adsorption. To corroborate, further, we have analyzed the supernatant of the clay−water suspension using atomic absorption spectrometry (AAS) and found the presence of Ca^{2+} ions in the solution. So, the increased amount adsorbed can be attributed to the reduction in surface potential of the clay, as well as the headgroup repulsion between the adsorbed surfactant molecules.

3.4. Effect of Clay Concentration on Viscosity. The rheological behavior was studied for five different concentrations (40%, 45%, 50%, 55%, and 60% by wt) of clay−water slurry, and the hysteresis curves were obtained by varying the shear rate from 17 to 99 s^{-1}. It is observed that the shear stress increases with an increase in the shear rate and that the viscosity decreases at higher values of shear. Also, the upward curve cycle shows a higher viscosity than the downward curve; as a result, there is a presence of a hysteresis loop for all the concentrations. The slurry shows non-Newtonian and thixotropic (shear thinning) behavior; i.e., viscosity is a function of the shear rate and time. Thixotropy is usually evaluated by measuring the area enclosed between the up- and down-curve obtained with a linear increasing and decreasing shear rate over time. The reason for thixotropy is slow deformation of the internal structure under shear. Figure 4f shows that the area under the hysteresis loop increases nonlinearly with an increase of the solid content in the system. The change in hysteresis area is significant between 40% and 60% solid concentration.

3.5. Effect of pH on Viscosity. To study the pH effect, the viscosities were measured for a 55% clay−water slurry at different pH's, and the changes are shown in Figure 5. The viscosity is found to decrease with increasing pH, which can be explained using the ζ potential values. The measurement of ζ potential mentioned in the previous section shows that it is positive at pH ~ 2, and then it becomes zero (pH ~ 3) and finally negative. The maximum change in ζ potential is between pH 2 and 6; after pH = 6, the change in the ζ potential value is not significant (Figure 2). At acidic pH, lower ζ potential values can be attributed to the adsorption of H$^+$ ions on the negatively charged clay surface as well as on the Al−OH group and the formation of Al-(OH$_2$)$^+$. Whereas, in the presence of OH$^-$ ions, Al−OH formed negatively charged Al−O$^-$ after the release of H$^+$, and thus, the surface became more negative. Finally, at lower pH, the surface charge of the clay is less. Thus, interparticle electrostatic repulsion is also less, and the agglomeration tendency is more due to van der Waals forces of attraction; as a result the viscosity is more. Above pH 6, the change in viscosity is less, which is also consistent with the ζ potential data.
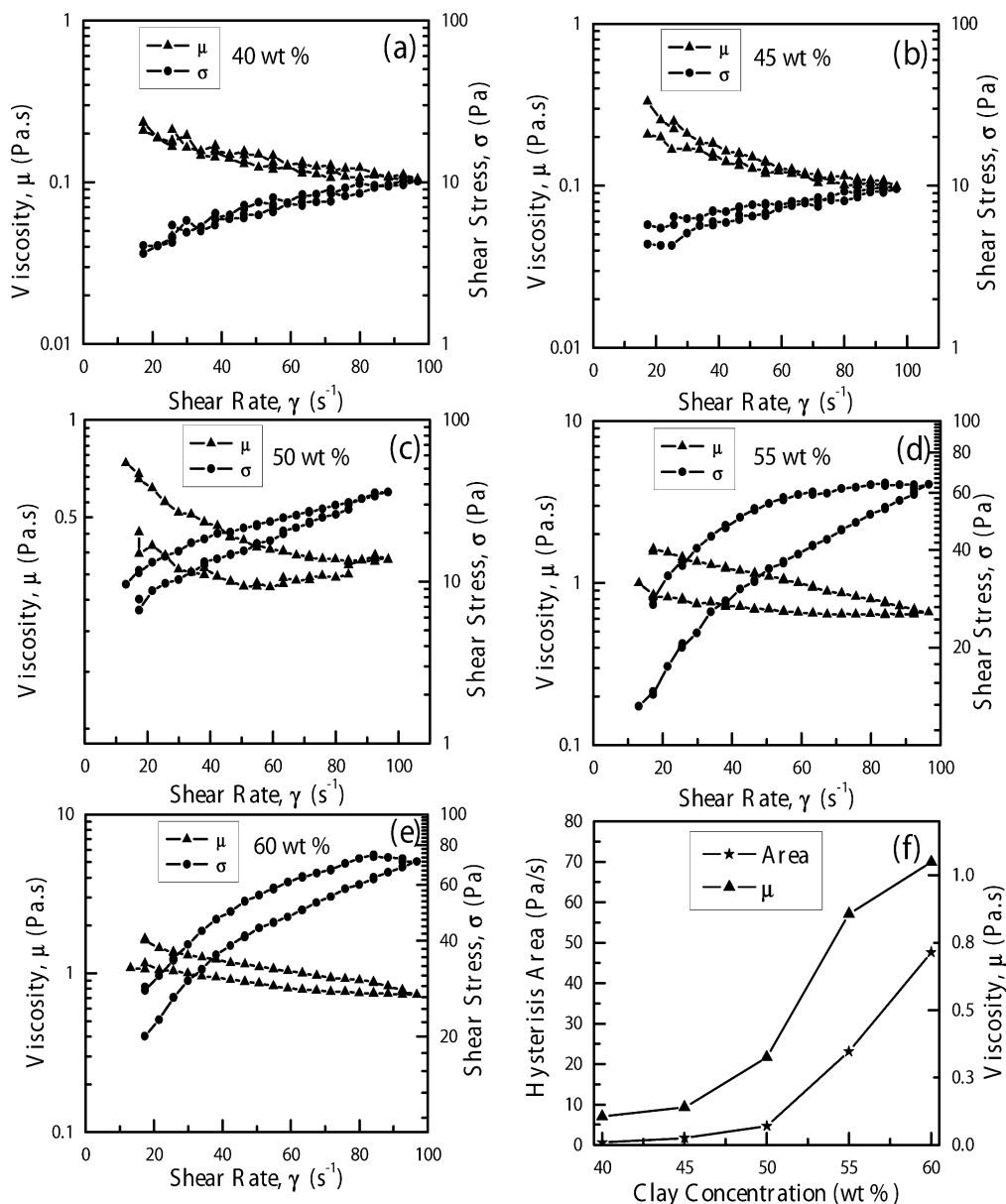
Figure 4. (a−e) Plot of shear rate vs viscosity and shear stress. (f) The change in hysterisis area and viscosity with the increasing concentration of clay in pure water. The viscosity was measured at a 60 s^{-1} constant shear rate.
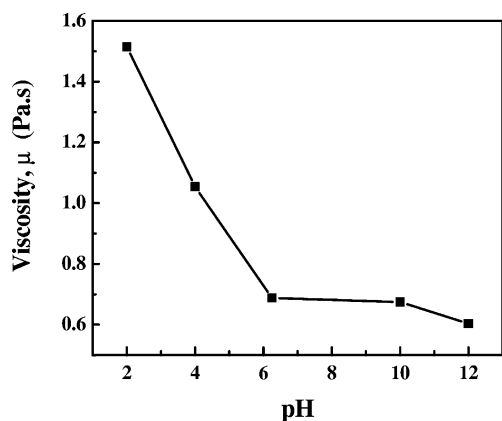

Figure 5. Effect of pH on slurry (55% by wt) viscosity at a 60 s^{-1} constant shear rate.

3.6. Effect of Surfactants on Viscosity. The viscosity of the slurry in the presence of an increasing concentration of all the surfactants was studied at a constant shear rate of 60 s^{-1}.

The viscosities obtained in the presence of varying concentrations of TX-100 are given in Figure 6a. It is observed that, with the increasing concentration of the surfactant in the slurry, the viscosity increases from 0.856 Pa·s to 2.233 Pa·s. Initially, the rise in viscosity is more with the surfactant concentration, but after 1 mM of TX-100 concentration, the viscosity change is not significant probably due to reaching toward an adsorption plateau region. The change in viscosity is attributed to the adsorption of surfactants. The nonionic surfactant may adsorb on the solid surface by attaching either a tail- or headgroup on the surface. The adsorption of nonionic surfactants through the headgroup by hydrogen bonding may show the following changes: (i) increasing surface hydrophobicity (ζ potential close to zero) and (ii) formation of a hemimicelle in the adsorption isotherm. The absence of these two characteristics indicates that adsorption may occur by attaching the tailgroup on the solid surface. Hence, although the change in ζ potential is negligible, after the adsorption of surfactant molecules, there will be an enhanced hydration layer on the clay surface, and that may be the reason for increasing viscosity.[26]
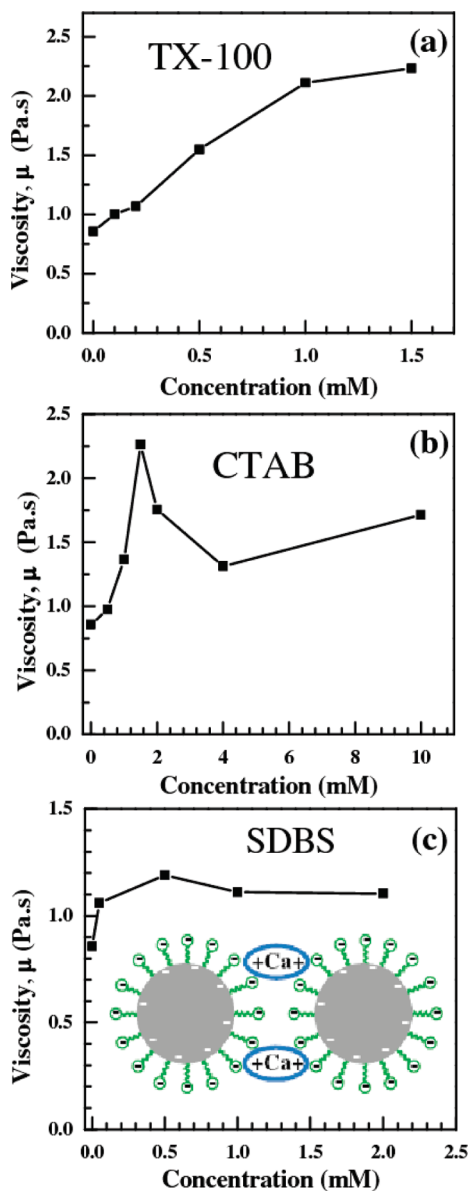
Figure 6. Viscosity of 55% pyrophyllite−water slurry at a 60 s^{-1} constant shear rate in the presence of (a) TX-100, (b) CPB, and (c) SDBS. Inset of c shows the schematic presentation of bridging of two clay particles in the presence of SDBS and a Ca^{2+} ion.

Similarly, the effect of CPB is shown in Figure 6b. It is observed that, with the increasing concentration of the surfactant in the slurry, the viscosity increases very rapidly up to 1.5 mM concentration (2.262 Pa·s) and then starts decreasing sharply to a value of 1.715 Pa·s at 10 mM concentration. This behavior may be explained in terms of the surfactant adsorption behavior on oppositely charged surfaces,[27] as we have mentioned before. Since the clay is negatively charged, the cationic surfactant (CPB) adsorbs initially on the surface using the headgroups toward the solid surface, and the surface becomes hydrophobic. The hydrophobicity of the pyrophyllite clay increases the coagulation tendency and ultimately shows higher viscosity. Further, with the increase in surfactant concentration, surfactants form a bilayer (hemimicelle) by attaching the tail groups toward the solid surface, and the surface becomes more hydrophilic (positively charged). The ζ potential values shown in Figure 2b also support this behavior. This study may also explain the decreasing behavior of viscosity at higher surfactant concentrations.
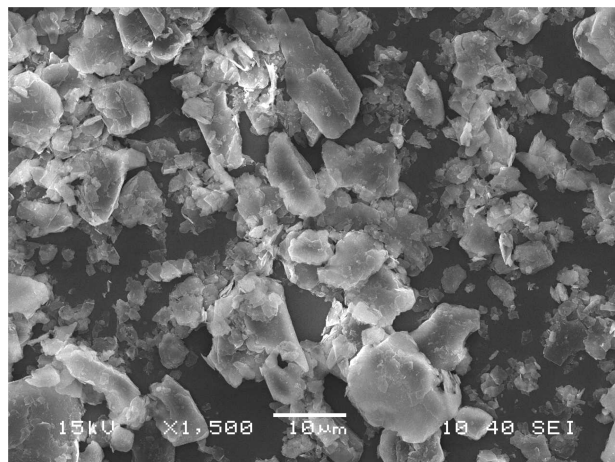

Figure 7. SEM micrograph of pyrophyllite clay.

Finally, Figure 6c shows the effect of SDBS in a similar way. The rheological behavior of clay slurry in the presence of SDBS at a constant shear rate shows initially that the viscosity decreases with time. This highly time dependent shear thinning property in the presence of anionic surfactants may be due to the development of a high repulsive force between the clay layers; as a result, there will be slipping of the layers under the shear force. The change in viscosity in the presence of SDBS as presented in Figure 6c shows initially, at very low surfactant concentrations, that there is a small increase in viscosity (0.856 Pa·s to 1.104 Pa·s); further, there is almost no change with increasing SDBS concentration. The ζ potential values also show initially at very low surfactant concentrations that the change in ζ potential occurs; after that with the increasing surfactant concentration, the change in ζ potential is less. Similar to the pH effect, the lesser change in ζ potential may be the reason why there is no change in viscosity with the change in surfactant concentration. Initially, although the ζ potential is negative, a small increase in viscosity may be attributed to the formation of bridges between two particles in the presence of Ca^{2+} ions, as well as an increase of the hydration layer. When the surfactants are adsorbed on the clay surface, it becomes more negative; then, there may be the chance of connecting two particles by the bivalence calcium ion. The schematic presentation is shown in Figure 6c, in the inset. It is also important to note that the final viscosity in the presence of SDBS is lower than those of the other two surfactants studied here.

3.7. Effect of Surfactant Adsorption on Pyrophyllite Lattice Spacing (d$_{(001)}$). The scanning electron microscope (SEM) micrograph of fine pyrophyllite clay shown in the Figure 7 indicates that the clay particles are not spherical, but they are, as expected, of the plate type. It has been established by earlier researchers that the dioctahedral structure of pyrophyllite consists essentially of neutral (electrically balanced) tetrahedral−octahedral−tetrahedral layers held together by van der Waals forces. In general, the surfactants are adsorbed on the layer surfaces and change the layer spacing depending on the amount of surfactant adsorbed, hydrocarbon chain length, etc. To see the change in d$_{(001)}$ lattice spacing of the clay, an XRD analysis was done before and after adsorption of the surfactants. In the presence of surfactants, the clay was treated above the CMC of the surfactants to get the saturated adsorbed layer of the surfactants on the clay surface. XRD patterns under different conditions are shown in the Figure 8.

It can be seen from the Table 1 that the d$_{(001)}$ spacing of the pyrophyllite clay decreases upon washing compared to that of raw clay. This may be attributed to, as in the presence of water,
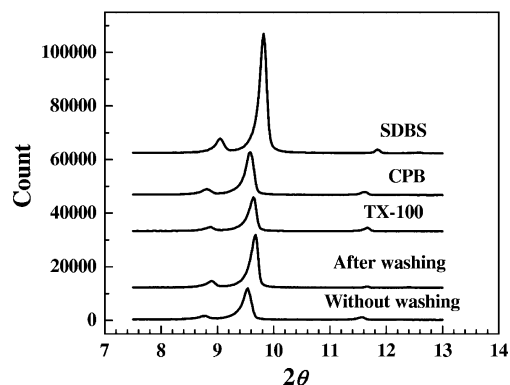
Figure 8. XRD pattern of pyrophyllite clay under different conditions.

Table 1. The d(001) Lattice Spacing Obtained from the XRD Data

pyrophyllite	$d_{(001)}$ spacing (Å)
without washing	9.27
after washing	9.12
SDBS	9.06
TX-100	9.16
CPB	9.21

some soluble ions dissolved in water, reducing the lattice spacing, but the change is not significant enough to compare. The reported $d_{(001)}$ spacing value of pyrophyllite clay is 9.19 Å[28] and is very close to our value. In the presence of surfactants, we can observe that the spacing did not change significantly (between 9.06 to 9.21 Å). In the previous studies,[6,29] it has been shown that, after the adsorption of surfactants, the increase in $d_{(001)}$ spacing is approximately above 3 Å depending on the type of clay and surfactant used. This value is generally about the minimum thickness of a surfactant molecule. In our study, with respect to the thickness of a surfactant molecule (~3 Å), the change in spacing is not significant. Thus, from the results, we can conclude that the surfactant molecules are not adsorbing inside the pyrophyllite clay spacing, but they are adsorbing only on the surface. This may be attributed to the low CEC of pyrophyllite clay compared to the other clays.

Finally, by comparing all the results, we can conclude that more surface charge leads to a decrease in viscosity of the slurry. The change in viscosity of the pyrophyllite−water slurry in the presence of surfactants is mainly due to the change in surface charge of the clay and an increase in hydration, after adsorption of the surfactants, but not due to a change in clay spacing.

4. Conclusion

The rheological behavior of the pyrophyllite−water slurry is non-Newtonian and thixotropic in nature. The viscosity at a constant shear rate and the hysteresis area under the variable shear stress increase with increasing solid concentration. The change in viscosity with pH follows a similar trend to that of the change in ζ potential with pH. In the presence of TX-100 and SDBS, there is an increasing trend in viscosity with the increase in surfactant concentration, but the change is more with TX-100. Whereas, in the presence of CPB, first there is an increase in viscosity; after a certain value, again there is a decrease with the increase in surfactant concentration due to the formation of a bilayer of adsorbed surfactant molecules. The presence of SDBS increases the viscosity of the pyrophyllite−water slurry more than the pure water alone, in spite of there being an increase in surface charge (more negative), maybe due to the formation of bridges between two particles in the presence of Ca^{2+} ions, as well as an increase of the hydration layer. In the presence of CPB, the surface charge changes from negative to positive, passing through the isoelectric point; the viscosity also increases with increasing surfactant concentration. Finally, again, there is a decrease in viscosity due to formation of the surfactant bilayer, leading to more positive charge on the surface. At a high surfactant concentration, although the surface charge is more positive, the viscosity at that point is more than that of water alone. The adsorption of surfactants seems to be occurring at the surface of the clay, so the clay spacing does not change significantly after the adsorption.

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