

Effect of the Adsorption of Surfactants on the Rheology of Na-Bentonite Slurries

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ABSTRACT: Characteristic rheologic properties, such as shear stress, viscosity, yield point of Na-activated bentonite were studied after adding an anionic surfactant (linear alkyl benzene-sulfonate, LABS) and a cationic surfactant (distearyl dimethyl ammonium chloride, DDAC). The effect of the surfactants also have been investigated at different quantities. The results have been discussed considering the types of additives and their concentrations. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 107–110, 2000

Key words: surfactant; bentonite; slurries

INTRODUCTION

Montmorillonite clays are widely used in various industrial products and processes, such as paper, paints, coatings, ceramics, and drilling fluids, to modify the rheology and control the stability of the system. An extensive literature exists with regard to the structure and chemistry of clay.^{1–5}

Montmorillonite belongs to the 2 : 1 layer clay minerals derived from pyrophyllite. The basic cell unit consists of an octahedral alumina sheet sandwiched between two tetrahedral silica sheets. In the tetrahedral sheets, tetravalent Si is sometimes replaced by trivalent Al, whereas in the octahedral sheet there may be replacement of trivalent by bivalent Fe or Mg. This replacement, which is referred to as isomorphous substitution, results in a deficit of positive charges or excess of negative charges, which are compensated by absorption of a layer of cations that are too large to be accommodated in the crystal. They are either fully expandable, partially expandable, or nonexpandable, depending on the surface charge density and the type and valance of the exchangeable

cations.^{1–5} These cations that exist between the montmorillonite layers are an effective parameter for determining the characteristic properties of montmorillonite clays.^{6–14} Presently, the basic clay mineral is called montmorillonite, and the clays of the smectite group derived from montmorillonite, which contain other clay minerals, are called bentonites.

The rheological properties of bentonite-water systems are not yet fully understood. This complex behavior is due to the unisometric clay particles exposing different crystal faces, on which an electrical double layer can develop, which differs both in the sign and the magnitude of the surface potential. Consequently, different modes of particle-particle and particle-water interactions can occur.

In the presence of salt and in an alkaline medium, clay mineral particles can aggregate in different ways²: association between edge surface of neighboring particles (edge-to-edge, EE); association between flat oxygen planes of two parallel platelets (face-to-face, FF); and association between edge surfaces and a flat oxygen planar surface (edge-to-face, EF). Relatively low salt concentration produce attractive potentials between edges and edges or edges and faces. At certain

conditions of pH and salt concentrations edge-edge and edge-face contacts (card-house structures) may then be formed. At a somewhat higher salt concentration, the potential between the surfaces also becomes attractive. The particles then aggregate face-to-face, in a way that a linked structure throughout the system results.¹⁵⁻¹⁷ "Oriented aggregates" and "book-house" structures are formed.

Cationic and anionic surfactants greatly influence the flow behavior of bentonite slurries. The influence surfactants on bentonite slurries should be more complex than that on other clays. Delamination of bentonite produces very thin particles; because the number of particles is a decisive factor, the flow behavior can change by modest changes in experimental conditions, such as pre-treatment reactions, degree of dispersion, and pH.¹⁵

With cationic polymers, adsorption on negatively charged solid particles and consequent flocculation occur by simple electrostatic attraction. With anionic polymers, it has been proposed that adsorption and flocculation occur via hydrogen bonding between the solid surfaces and the hydroxyl groups on the polymer.

The objective of the present study was to determine the influence of surfactants (cationic, anionic) on the rheological behavior of bentonite slurries.

EXPERIMENTAL

Ore sample taken from Trakya in Turkey have been identified as Ca-montmorillonite clay minerals using X-ray diffraction (XRD) and infrared (IR) analysis methods. The XRD analyses were done using Philips PW Model 1140. IR analyses were done from (400–4000 cm^{-1}) using a Jasco Model 5300 Fourier transform-IR spectroscopy. Chemical analyses were performed by using the Perkin Elmer Model 3030 atomic absorption spectrophotometer.

Peptization process was done mixing 4 wt % NaHCO_3 of the sample with 35% humidity, and this mixture was left for 7-day period in a semi-open stockroom, where it was opened to air circulation, in order to obtain better quality drilling clay.

Medium particle size diameter of Na-activated bentonite is measured at 291.7 nm (Zetasizer-3, Malven). The surface area was determined by

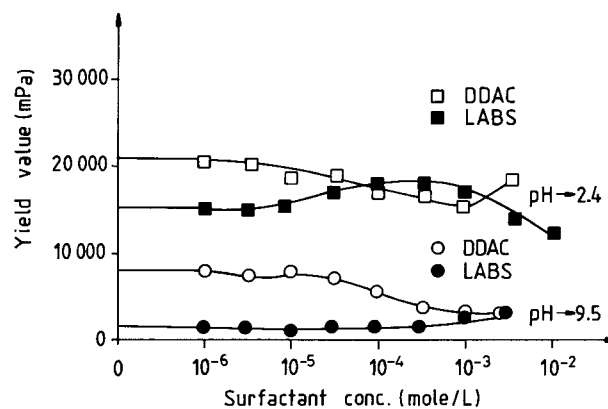


Figure 1 Yield value of the sodium bentonite slurries (6% w/w) versus the amount of DDAC and LABS.

BET (Quanto Chrome, autosorb-1 model) nitrogen adsorption technique. It has been found 54.56 m^2/g .

The viscosity, shear stress and yield point values of Na-activated sample was determined with a Fann type (Model 35 SA) viscometer. This instrument is fully described by Van Wazer et al.¹⁸

The bentonite-water systems were prepared by dispersing the clay in distilled water (22.5 g clay/350 mL water) with a mechanic mixer at 1800 rpm for 20 min. The slurry was then allowed to stand for 24 h, and it become ready for the measurement at 600 rpm while mixing for 5 min. The measurements were performed for six values of shear rate.

RESULTS

Flow curves of bentonite-water systems respond sensitively to the different types of interaction between the particles. The bentonite particles with a net negative charge interact with each other (Coulombic and van der Waals forces). Formation of the different networks (EE, EF, FF) depends on volume concentration (bentonite/water ratio), particle size and shape, pH, and exchangeable cations. Organic compounds can increase or decrease the stability of the networks.

It is generally, more useful to control flocculation of clay suspensions by the addition of surface-active ions rather than by adjusting the pH.

The cationic and anionic surfactants distearyl dimethyl ammonium chloride (DDAC) and linear alkyl benzene sulfonate (LABS) were used.

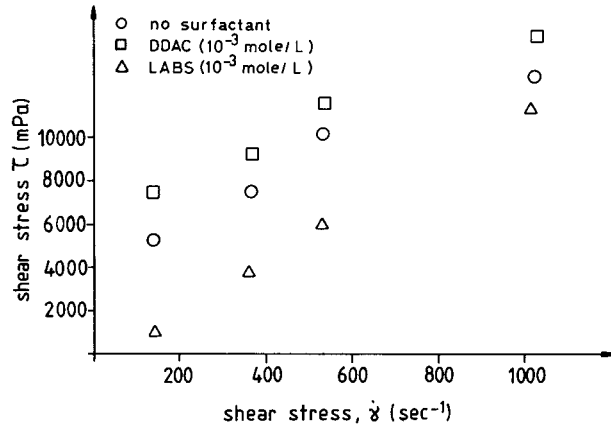


Figure 2 The shear stress (τ)–shear rate ($\dot{\gamma}$) rheogram.

The values of yield stress (τ_y) as a function of DDAC and LABS adsorbed, which are plotted in Figure 1, show marked changes in both the degree and mode of the flocculation of the clay particles. The distearyl dimethyl ammonium ion was adsorbed on the negative faces only at low pH values, (pH \sim 2.4) and reduced the charge, there by decreasing the heteropolar (face-edge) interaction and so lowering the value of τ_y . Many edge-face contacts are destroyed, and the shear stress is reduced. When a mechanical force acts on the card-house, a certain number of edge-face contacts are broken. The homopolar interaction, face-face, was reduced when a low value was reached. At higher DDAC concentrations, the particles bristling with alkyl chains are held together by the interpenetrating alkyl chains and the extrapolated shear stress is increased.

At pH \approx 9.5, the flow values changes with the DDAC concentration. Thus, the behavior is governed by the electroviscous effect. At DDAC concentrations $> 10^{-4}$ the particles settled as flocs because the exchange of the counterions by DDA⁺ cations made the particles less hydrophilic.

Linear alkyl benzene sulfonate anions were not adsorbed by the clay particles from very dilute solutions and did not influence the flow behavior of the acidic dispersions at concentrations $\leq 10^{-5}M$ (at pH \approx 2.4). Because of card-house structure formation, τ_y values were high. At LABS concentrations $> 10^{-3}M$, the surfactant anions break up the edge-face contacts, and τ_y decrease. At pH 9.5, the stresses were constant up to about $5 \times 10^{-4}M$ and then increased.

When DDAC and LABS surfactants were added in a ratio of between 10^{-6} to 10^{-2} mol/L of

the Na-bentonite, variation of shear stress with shear rate may be given as in Figure 2 (at pH \approx 9.5). After addition of DDAC surfactant, flow properties of Na-bentonite still follow the Bingham plastic model. However, an increase at yield point value is observed after addition, because viscosity increases together with increasing gel strength.

It has been observed that, the addition of LABS (for 10^{-3} mol/L); Newtonian flow (at pH \approx 9.5).

Additional a surfactants show more effectiveness in Na-activated clays, because Na-activated clays have smaller particle sizes and greater number of clay particles in slurry, and increased surface area of clay minerals is more effective in clay water additives systems. The repulsive forces, which are caused by electrostatic interactions of clay particles, are relatively dominant in Na-activated samples, because Na-exchangeable cation can better deflocculate the system.

The results indicate that surfactant type and concentration can be adjusted to yield any desired system rheology. In conclusion, it can be stated that the rheological properties of bentonites are such that the formation of gel structures with water can be altered by the addition of electrolytes and that, in this process, the following factors are influential, in the order given: (1) the type of bentonite, (2) the type of the electrolyte, and (3) the concentration. However, it is also believed that in order to understand whether or not a mechanism other than the electrostatic and van der Waals interactions exists in the modeling of particles, the structures of the samples in sludge form should further be clarified by an examination of particle size, using an electron microscope.

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REFERENCES

1. Searle, A. B.; Grimshaw, R. W. *The Chemistry and Physics of Clays*; Enest, Benn Limited: London, 1986.
2. Olphen Van, H. *An Introduction to Clay Colloid Chemistry*, 2nd ed.; Interscience: New York, 1977.
3. Worrall, W. E. *Clays and Ceramic Row Materials*; Elsevier: London, 1986.
4. Reed, J. S. *Introduction to the Principles of Ceramic Processing*; John Wiley and Sons: New York, 1988.

5. Miller, R. W. Soils, An Introduction to Soils and Plant Growth; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1990.
6. Brandenburg, U.; Lagaly, G. Appl Clay Sci 1988, 3, 263.
7. Keren, R.; Shainberg, I.; Klein, E. Soil Sci Soc Am J 1988, 52, 76.
8. Keren, R. Soil Sci Soc Am J 1989, 53, 25.
9. Erzan, A.; Güngör, N. J Colloid Interface Sci 1995, 176, 301.
10. Güngör, N.; Tulun, T. Research Industry 1996, 55, 268.
11. Güngör, N. Powder Handl Process 1996, 8, 4.
12. Güngör, N.; Ece, I. Bull Tech Univ Istanbul 1996, 49.
13. Güngör, N.; Dilmaç, Ş. J Inclusion Phenom Mol Recognition Chem 1996, 26, 93.
14. Güngör, N. Arab Gulf J Scientific Res 1994, 15, 551.
15. Vali, H.; Bachman, L. J Colloid Interface Sci 1988, 126, 278.
16. Lagaly, G. Appl Clay Sci 1989, 4, 105.
17. Permien, T.; Lagaly, G. Clays Clay Min 1995, 43, 229.
18. van Wazer, J. R.; Lyons, J. W.; Kim, K. Y.; Colwell, R. E. Viscosity and Flow Measurement; Interscience: New York, 1963.