STABILIZATION OF KAOLINITE SUSPENSIONS BY ANIONIC-NONIONIC SURFACTANT MIXTURES

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ABSTRACT

Kaolinite dispersion in aqueous solutions of a nonionic ethoxylated alcohol (C_{12}EO_8) was found to be enhanced significantly by the addition of anionic sodium dodecyl sulfate (SDS). The adsorption of C_{12}EO_8 with the ethylene oxide chains protruding into the bulk liquid is proposed to cause steric stabilization of the suspension. Such an oriented adsorption would render the surface hydrophilic, an interpretation which is supported by skin flotation data which show a marked decrease in flotation with increased C_{12}EO_8 adsorption. Correlation of settling rate with zeta potential data showed the increase in zeta potential caused by added SDS to play only a minor role in the observed increase in suspension stability.

INTRODUCTION

Stabilization of fines resulting from surfactant adsorption can affect processes such as enhanced oil recovery since the mobilization of the fines in porous media can lead to drastic changes in the permeability of oil reservoirs (1). On the other hand, such stabilization is desired in colloidal processing.

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employed, for example, in the fabrication of advanced ceramic materials (2).

It is known that the adsorption of ionic surfactants at the solid-liquid interface can lead to stabilization of colloidal suspensions. This is usually explained by the increased electrostatic repulsion caused by surfactant adsorption on particles (3). Stabilization of particles by polymer adsorption, on the other hand, has often been reported to result from steric hindrance between tail segments of the adsorbed polymer molecules (4,5). However, information on stabilization using anionic-nonionic surfactant mixtures is very limited in the literature (6). Since mixed surfactant systems have the potential for achieving a better performance than a single surfactant in processes such as enhanced oil recovery (7), it is necessary to have information on stabilization of fines caused by such systems.

In this work, the adsorption of mixtures of anionic sodium dodecylsulfate (SDS) and nonionic octaethylene glycol mono-n-dodecyl ether (C₁₂EO₈) on kaolinite has been studied and an attempt has been made to understand the mechanism of the dispersion of fines by the adsorbed surfactants.

EXPERIMENTAL

Materials

Mineral: Well-crystallized Georgia kaolinite was purchased from the clay repository at the university of Missouri and converted to Na-kaolinite by an ion-exchange method (8). Surface area of the sample, as determined by our BET measurement using nitrogen, was 8.2 m²/g.

Reagents: Sodium dodecyl sulfate of over 99% purity was purchased from Fluka Chemicals. The nonionic surfactant, octaethylene glycol mono-n-dodecyl ether [CH₃(CH₂)₁₁(OCH₂CH₂)₈OH or C₁₂EO₈], purchased from Nikko Chemicals, Japan, was specified to be >97% pure. No minimum was observed in the surface tension vs. concentration curves of these two surfactants, indicating absence of surface active impurities, and therefore they were used as received.

STABILIZATION

Methods

Procedure: Tl of 0.03M NaC teflon stoppers desired concen hours with per suspension was tests. The heig the cylinder wa vs time curve settling rate of portion of the and the residu supernatant an was used for t system. Under observed during volumetric cyli and a major pc retained in th weighed. This particles.

Analysis: SD method(9,10). performance I column and a was a mixture of nylon membranes.

RESULTS AN

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STABILIZATION OF KAOLINITE SUSPENSIONS

METHODS

Procedure: Three gram samples of Na-kaolinite were contacted with 15 ml of 0.03M NaCl solution for two hours at room temperature (25 °C) in a teflon stoppered glass vial. Following this, 15 ml of the surfactant solution of desired concentration was added and the contents allowed to stand for 72 hours with periodic manual shaking for one minute after every 8 hours. The suspension was then transferred to a 20 mm diameter cylinder for the settling tests. The height of the suspension/supernatant interface from the bottom of the cylinder was recorded as a function of settling time. The interface height vs time curve showed an initial linear part and the slope was defined as settling rate of the suspension. After completion of the settling test a small portion of the supernatant was decanted, centrifuged to remove any fines and the residual concentration of surfactant determined. The remaining supernatant and the sediment were then mixed and the resulting suspension was used for the zeta potential measurements using a Zeta Meter Model D system. Under certain experimental conditions skin flotation of kaolinite was observed during the settling test. In such cases, the contents of the volumetric cylinder were transferred to a separating funnel and the sediment and a major portion of the liquid were drained out. The skin floated fraction retained in the funnel was removed by washing with water, dried and weighed. This fraction provided a measure of the wettability of kaolinite particles.

Analysis: SDS concentration was measured using a two phase titration method(9,10). C_{12}EO_{8} concentration was determined using high performance liquid chromatography (HPLC) with a reverse phase C_{18} column and a refractive index detector. The mobile solvent used in HPLC was a mixture of 90% acetonitrile and 10% water filtered through 0.4 micron nylon membrane.

RESULTS AND DISCUSSION

Settling Rate and Zeta Potential Measurements:

The effect of adding sodium dodecylsulfate and octaethylene glycol mono-n-dodecyl ether, both individually and as a mixture, on the settling
rates and zeta potentials of kaolinite suspensions are shown in Figures 1 and 2 respectively. It can be seen from Figure 1 that, in the absence of C$_{12}$EO$_{8}$ addition of 0.43 x 10$^{-3}$ kmol/m$^{3}$ of SDS results in a decrease in settling rate from 1.45 to 1.22 cm/min. The corresponding increase in absolute zeta potential value was 6.5 mV. Increase in SDS concentration from 0.43 to 1.0 x 10$^{-3}$ kmol/m$^{3}$ did not cause any further reduction in the settling rate although the accompanying increase in zeta potential is significant (from -19 to -37 mV). These results indicate the limited contribution of electrostatic repulsion to the suspension stability.

The effect of octaethylene glycol mono-n-dodecyl ether on the suspension stability is more pronounced than that of sodium dodecyl sulfate.
The lowest settling rate obtained upon C\textsubscript{12}EO\textsubscript{8} addition (0.73 cm/min) was about 40 percent lower than that achieved with SDS (1.23 cm/min.). Electrokinetic measurements carried out as a function of C\textsubscript{12}EO\textsubscript{8} concentration showed that the absolute zeta potential decreased slightly with increasing C\textsubscript{12}EO\textsubscript{8} concentration although the corresponding suspension stability showed sharp increase. This observation suggests that steric factors, rather than electrostatic repulsion, govern the stability in this case.

The settling rates obtained using SDS - C\textsubscript{12}EO\textsubscript{8} mixtures were lower than that achieved using individual surfactants (Fig.1). As already shown, the contribution of electrostatic repulsion to the overall stability is limited and therefore the major contribution can be considered to be due to steric effect caused by C\textsubscript{12}EO\textsubscript{8} adsorption. This inference was also supported by the results obtained from electrokinetic experiments conducted with mixed surfactants and C\textsubscript{12}EO\textsubscript{8} alone, which showed that enhancement in stability
obtained with C_{12}EO_{8} addition was not accompanied by any increase in absolute zeta potential value. A close examination of settling rate curves in Figure 1 shows that the enhanced stability obtained using mixed surfactants is more synergistic than additive. For example, the difference between the lowest settling rate at 0 and 1.0 kmol/m^3 SDS, in the presence of C_{12}EO_{8} is about three times the difference at same SDS concentrations in the absence of C_{12}EO_{8}.

**Adsorption Studies:**

Adsorption studies were conducted to understand the mechanism of synergism between the two surfactants in enhancing the stability of kaolinite suspension. Adsorption tests were carried out with both individual surfactants and their mixtures and the results obtained are discussed in the following sections.

Adsorption of C_{12}EO_{8} and SDS on kaolinite: The isotherms for the adsorption of SDS and C_{12}EO_{8} on kaolinite are shown in Figure 3. Plotted on a logarithmic scale, the SDS isotherm has a slope of 1 in the entire region below plateau, indicating absence of lateral interactions between adsorbed molecules (11). Below the plateau adsorption level, stabilization of kaolinite was not observed and this is possibly due to insufficient charge induced by the adsorbed surfactant. The C_{12}EO_{8} adsorption isotherm was characterized by an initial shoulder region (I) with a small slope and a second region (II) in which the adsorption density increased more sharply till the plateau (III) was approached. The adsorption behavior was similar to that observed by Levitz (12) and Partyka (13) for the nonionic surfactant Triton X-100 - silica system. Since the structure of C_{12}EO_{8} is similar to that of Triton X-100 it is reasonable to assume that the mechanism for C_{12}EO_{8} adsorption on kaolinite is likely to be similar to that of Triton X-100 adsorption on silica. Adsorption of C_{12}EO_{8} in the low concentration region (I) can be attributed to hydrogen bonding of the ethoxylated groups of the surfactant to the kaolinite surface with the hydrocarbons chain lying flat on the surface. Adsorption of SDS and C_{12}EO_{8} in Figures 4 at different fixed concentrations indicating synergism can be seen.
Stabilization of kaolinite suspensions

Figure 3: Adsorption of C_{12}EO_{8} and SDS on kaolinite. pH=5, s/l=0.1, I=0.03 M NaCl.

Adsorption of C_{12}EO_{8}-SDS mixture on kaolinite: Adsorption tests were carried out in this case as a function of C_{12}EO_{8} concentration at two different fixed SDS concentrations. Equilibrium adsorption densities of C_{12}EO_{8} and SDS are shown as a function of residual C_{12}EO_{8} concentration in Figures 4 and 5 respectively. It can be seen from these figures that adsorption of each surfactant is enhanced by the presence of the other indicating synergism between the two surfactants. In the case of C_{12}EO_{8}, it can be seen that in addition to a two fold increase in plateau adsorption density the slope of the adsorption isotherm also increased upon sodium dodecylsulfate addition. These results indicate adsorption of sodium dodecylsulfate provides a energetically more favorable environment for the surface. In region II, the adsorption is dominated by cooperative adsorbate-adsorbate interactions to form solloid clusters of the adsorbed molecules. Under these conditions, the adsorbed C_{12}EO_{8} with the ethylene oxide chains in the outside region could result in steric hindrance for aggregation of the particles (4, 15).

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FIG. 4 Adsorption of C₁₂EO₈ on kaolinite from SDS/C₁₂EO₈ mixtures. pH = 5, s/l = 0.1, I = 0.03 M NaCl.

FIG. 5 Adsorption of SDS on kaolinite from SDS/C₁₂EO₈ mixtures.

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C₁₂EO₈ adsorption at the interface. In the case of SDS, its adsorption density passes through a maximum. The decrease in adsorption density beyond the maximum is attributed to the formation of mixed micelles which results in a reduction in the concentration of available SDS monomers since total SDS dosage is fixed. Since both SDS and C₁₂EO₈ can adsorb on kaolinite by themselves, enhanced adsorption of SDS and C₁₂EO₈ from mixtures suggests a possibility that the adsorption sites of C₁₂EO₈ and SDS are adjacent to each other on kaolinite surface. These clusters, in addition to providing more sites for possible second layer adsorption, can form a hydrophobic pool into which abstraction of molecules from the bulk solution is favored with increased enthalpic contribution. Such a bilayer formation would also render the surface hydrophilic since C₁₂EO₈ molecules in the second layer will have their hydrophilic groups oriented towards the bulk solution. This possibility is supported by the skin flotation response plotted in Figure 6 which shows a decrease in floatation with C₁₂EO₈ adsorption.
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The enhanced $C_{12}EO_8$ adsorption in the presence of SDS, with the hydrophilic ethyleneoxide chains protruding into bulk, is proposed to result in steric hindrance for the aggregation of the particles.

CONCLUSION

Stabilization of aqueous kaolinite suspensions by ethoxylated alcohol ($C_{12}EO_8$) is found to occur due to steric hindrance between the ethylene oxide chains of $C_{12}EO_8$ adsorbed on particles. The stability obtained using $C_{12}EO_8$ was enhanced significantly by sodium dodecylsulfate addition. Adsorption studies clearly showed cooperative interactions between SDS and $C_{12}EO_8$ adsorbed at the interface. Such interactions apparently result in the formation of local hydrophobic clusters which enhance the adsorption of $C_{12}EO_8$ by abstracting its hydrocarbon chains into the clusters and leaving the ethylene oxide chains in the bulk solution. Such an orientation of adsorbed $C_{12}EO_8$ renders kaolinite surface hydrophilicity, as tested by skin flotation, and results in enhanced stabilization of the suspension through steric hindrance to aggregation of the particles.

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