Interaction of Surfactants With Alumina-Based Thickening Agents[1]

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This work reports on the rheological properties of alumina dispersions and how those properties change in the presence of alcohol ethyoxylate, sodium ether sulfate, sodium alcohol sulfate and sodium linear alkylbenzene sulfonate. The following conclusions were reached: alumina dispersions are pseudoplastic, that is, the viscosity decreases with increasing shear rate, and they are also thixotropic, that is, the viscosity decreases with time if the shear rate is held constant. When shearing is stopped, the viscosity gradually recovers. At pH 9, the alumina dispersion studied consisted of suspended aluminum hydroxide flocs. The hindered flow of flocs past one another gave the dispersion a high viscosity. When surfactants were added to the dispersion, the viscosity decreased.

Because of their use as commercial thickeners, aqueous clay suspensions have been studied extensively (1). Besides thickening, aqueous clay suspensions can also be used to make a product that is convenient for the consumer because of its rheology. A product thickened by a clay suspension is easily dispensed because it becomes more fluid as it passes through the dispensing nozzle. Once the product has been dispensed it "sets up" so the product remains in place. Alumina suspensions are rheologically similar to clay suspensions (2). Unlike clays, however, alumina can be obtained in high purity and is chemically simpler. Because thickened products often contain surfactants, we wanted to see what the effect of adding various types of surfactants would be on the rheology of alumina dispersions.

EXPERIMENTAL

Preparation of alumina dispersions. The dispersions used in this work were prepared from Catapal® D alumina (Vista Chemical Co., Ponca City, Oklahoma). Catapal® D alumina consists of agglomerates of relatively large boehmite crystallites (pseudoboehmite). The size of the agglomerates and crystallites that make up the agglomerates is given in Table 1. Because of the large crystallite size, Catapal® D alumina is readily dispersible.

TABLE 1

Composition of Catapal® D Alumina

Crystallite size (angstroms)		020	021
		40	64
Agglomerate size	% < 45 microns	% > 90 microns	Average
	40	20	65
Surface Area (m^2/g): 235 (calcined 3 hr @ 500 C)			

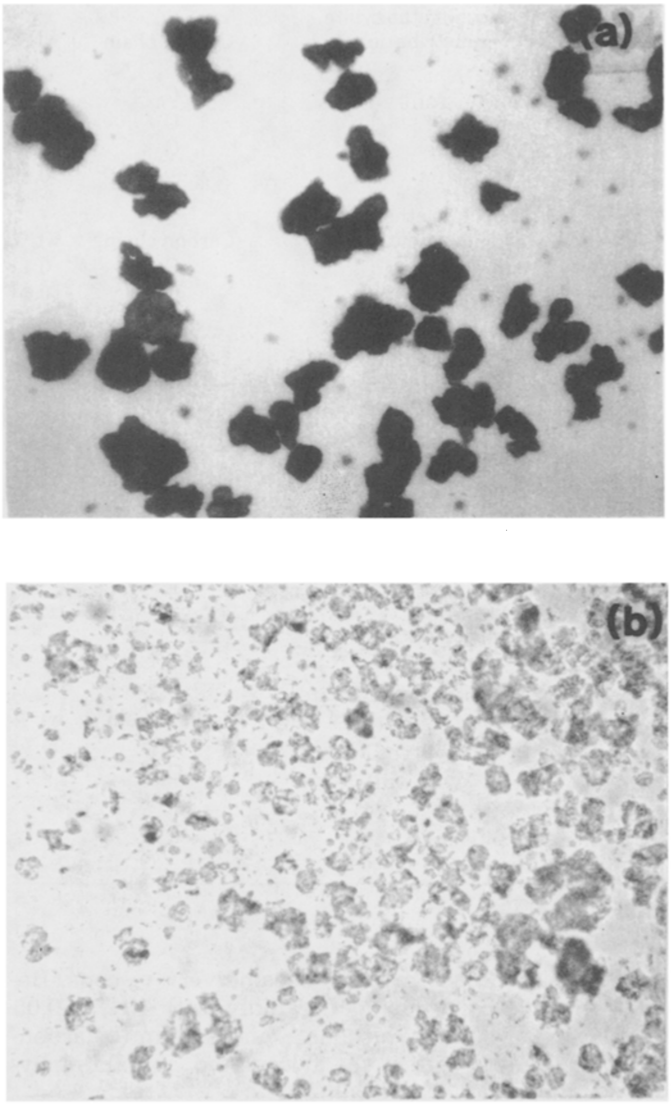

FIG. 1. Deagglomeration of alumina particles in 12 M hydrochloric acid. Photomicrographs taken (a) before, and (b) 1 second after, addition of acid (60 ×).

A large batch of 5 wt percent alumina dispersion was prepared by adding Catapal® D to distilled water. The alumina-water mixture was mechanically stirred while the pH was lowered to pH 3 by adding a few drops of concentrated hydrochloric acid (J.T. BAKER ANALYZED®). While stirring, the pH was monitored with a Corning pH/ion meter model 135 fitted with a Corning glass electrode. The mixture was stirred for 0.5 hr. During stirring, the pH tended to drift above pH 3, so additional drops of acid were used to lower it. The purpose of lowering the pH was to break down alumina agglomerates. An early stage of this breakdown is shown in the photomicrographs of Figure 1.

After the mixture was stirred 0.5 hr, a few drops of ca. 14 M sodium hydroxide (Mallinkrodt AR grade) were added to it. As the pH rose, aluminum hydroxide

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TABLE 2

Composition of Surfactants

Alfonic® 810-60 alcohol ethoxylate		
Alcohol homolog distribution	Carbon chain	wt %
	C_4	—
	C_6	0.4
	C_8	42.0
	C_{10}	57.1
	$C_{12} + < C_{12}$	0.5
Alfonic® 1412-S sodium ether sulfate		
Alcohol homolog distribution	Carbon chain	wt %
	C_8	0.1
	C_{10}	0.6
	C_{12}	37.9
	C_{14}	59.6
	C_{16}	1.9
Sample used was 82.93% active		
$Na_2SO_4 < 0.15\%$		
Unsulfated ethoxylate (free oil): 0.91%		
Alfol® 12 sodium alcohol sulfate		
Homolog Distribution	Carbon chain	wt %
	C_{12}	99.85
	C_{14}	0.15
Active: 99.3%		
Unsulfated alcohol: 0.02%		
Na_2SO_4: nil		
Sodium linear alkylbenzene sulfonate:		
Alkyl distribution:	Carbon chain	wt %
	C_{12}	99.7
	C_{10}	0.3
Active: 99.7%		
Unsulfonated alkylate: 0.94%		
Na_2SO_4: < 1%		

precipitated and the mixture became very viscous. Because the viscosity changed rapidly with pH, a 0.05 M mixture of sodium carbonate and sodium bicarbonate was used to buffer the flocculated aluminum hydroxide dispersion at pH 9.9.

An alumina dispersion was also prepared to show the effect of pH and alumina content. For this dispersion, the mixture was made acidic with nitric acid and aluminum hydroxide was precipitated with ammonium hydroxide. Experience has shown us that the choice of acid and base does not affect the rheology of the dispersion over the pH range we studied.

Surfactants used in this work. An alcohol ethoxylate, sodium alcohol ether sulfate, sodium alcohol sulfate and sodium linear alkylbenzene sulfonate were each added to samples of the alumina dispersion to determine their effect on viscosity. Compositions of the surfactants are presented in Table 2.

The alcohol ethoxylate used was Alfonic® 810-60. This surfactant is a blend of primarily octyl and decyl linear alcohols with an average of two moles of ethylene oxide attached to the alcohol.

The sodium alcohol ether sulfate used was a deoiled and desalted sample of Alfonic® 1412-S. This ether sulfate is based on a blend of primarily dodecyl and tetradecyl linear alcohols with an average of three mol of ethylene oxide attached to the alcohol.

The ethoxylate blend was sulfated and neutralized to form the sodium salt.

The sodium alcohol sulfate used was a deoiled and desalted sample prepared by sulfating lauryl alcohol.

The sodium linear alkylbenzene sulfonate used was also deoiled and desalted. The alkyl portion of this sample was analyzed to be 99.7% dodecyl alkyl with the remainder decyl alkyl.

Viscosity measurements. To measure viscosity, a Haake Rotovisco RV 12 viscometer fitted with a concentric cylinder measuring head was used. A small sample of the dispersion was placed between the walls of the concentric cylinders, and the resistance to rotation of the inner cylinder was measured at various rotation rates.

From the resistance, the speed of rotation and the cylinder geometry, the apparent viscosity was calculated at various shear rates. Because viscosity was found to decrease with time, viscosity measurements were taken after the shear rate had been constant for five min, enough time to give a constant viscosity.

To illustrate the time dependence of the viscosity, some measurements were done by linearly increasing the shear rate with time. For these measurements, the shear rate was scanned from zero to 474 sec^{-1} in five min, and the viscosity was calculated at several shear rates in the scanned range.

For all viscosity measurements, the temperature was controlled by a circulating water bath (Haake F3 digital circulating bath). The temperature was 25 C unless indicated otherwise.

RESULTS

Rheology of alumina dispersions without surfactants. An overview of the rheology of a 5 wt percent alumina dispersion is shown in Figure 2. Viscosity is plotted vs pH along one axis and vs shear rate along the other axis. The highest viscosity was found around pH 8–9.5. At a constant pH, the viscosity decreased with increasing shear rate.

The effect of pH on viscosity at a constant shear rate is seen in Figure 3. Two peaks were present in the pH range studied. The smaller peak was at approximately pH 7 and the larger peak at approximately pH 9. The effect of alumina content is also seen in Figure 3. The viscosity of a 2.5 wt percent alumina dispersion was much lower than the viscosity of a 5 wt percent alumina dispersion.

Viscosity decreased with increasing shear rate at pH 9.9, as shown in Figure 4. Decreasing viscosity with increasing shear rate means the dispersion was pseudoplastic.

Besides being pseudoplastic, the dispersion was also thixotropic, that is, the viscosity depended on time. This was demonstrated by the following experiment. A sample of the dispersion was sheared in a small lab mixer for 30 min. The mixer was stopped and 2.5 min later the viscosity of dispersion was measured as the shear rate was scanned from rest to 474 sec^{-1}. Twenty-five min after the mixer was stopped, another sample was taken and the viscosity measured again. The results are shown in Figure 5. As seen in the figure, the "25-min" viscosity was higher than the

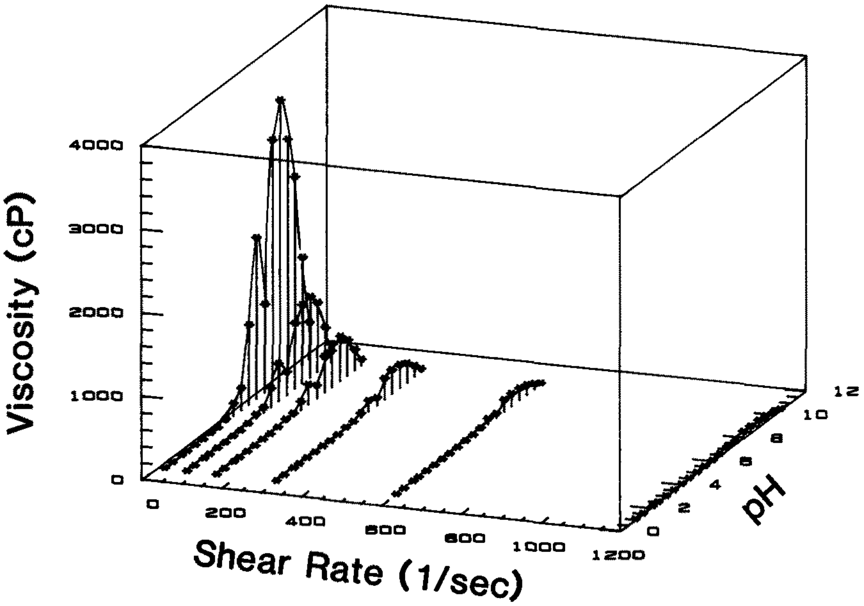

FIG. 2. Viscosity dependence on pH and shear rate for a 5 wt percent alumina dispersion. T = 25 C.

"2.5-min" viscosity. The increase in viscosity with time was larger at low shear rates. A measurement 12 hr after the mixture had been sheared gave a viscosity vs shear rate curve identical to the "25-min" data.

The effect of temperature on the viscosity of the 5 wt percent alumina dispersion is shown in Figure 6. The viscosity decreased about 11% as the temperature increased from 25 to 45 C. The biggest decrease was seen at low shear rates.

Effect of addition of surfactants. Adding 5 × 10^{-6} mol of either Alfonic® 1412-60 sodium ether sulfate or Alfonic® 810-60 alcohol ethoxylate to 50 g of the dispersion decreased the viscosity. This is shown in Figure 7. The viscosity decreased 10–15% at a shear rate of 7 sec^{-1}.

The decrease in viscosity on adding 5 × 10^{-6} mol of sodium linear alkylbenzene sulfonate or sodium lauryl sulfate to 50 g of the dispersion is shown in Figure 8. Adding these surfactants decreased the viscosity 40–45% at a shear rate of 7 sec^{-1}.

DISCUSSION

Before discussing the decrease in viscosity of the dispersion on adding surfactants, we will discuss the rheology of alumina dispersions without surfactants. Because rheology depends on pH, our discussion is based on pH ranges.

pH 1–5. In the pH range 1–5, the viscosity of the aqueous alumina mixture is less than 50 centipoise at all shear rates. In this pH range, alumina agglomerates break down as shown in Figure 1. It is also likely that complex aluminum hydroxo ions are formed by dissolving some of the agglomerates. Brossett (3) iden-

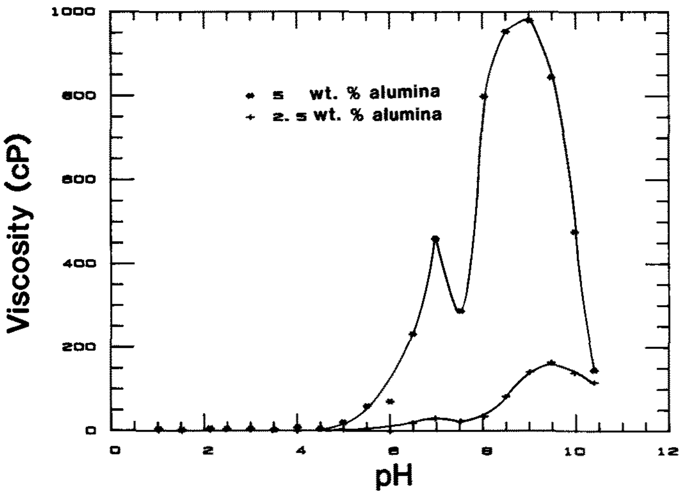

FIG. 3. Viscosity vs pH for 5 wt percent and 2 wt percent alumina dispersion. T = 25 C, shear rate = 74 sec^{-1}.

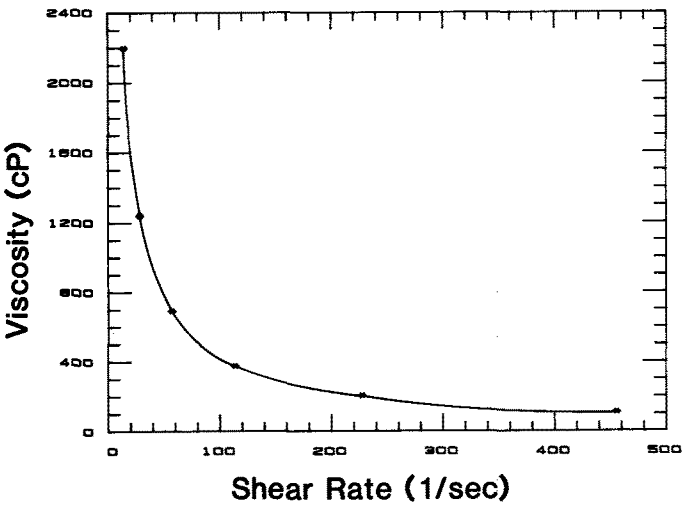

FIG. 4. Viscosity dependence on shear rate for a 5 wt percent alumina dispersion. T = 25 C, pH = 9.9.

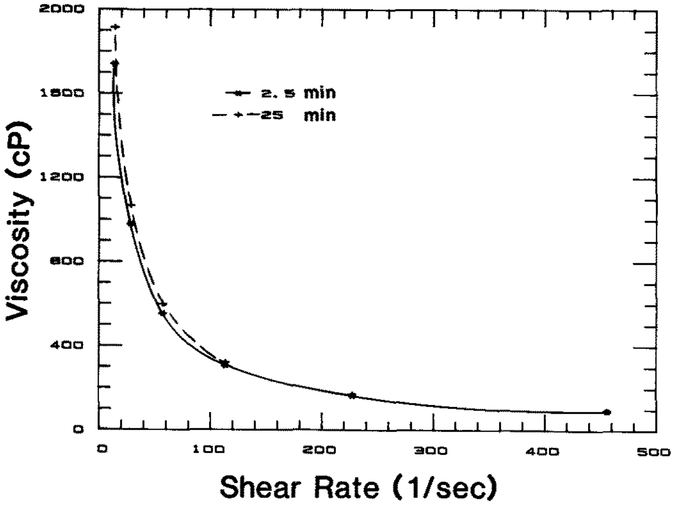

FIG. 5. Dependence of viscosity on time and shear rate. Viscosity 2.5 min after shearing shown as solid line. Viscosity 25 min after shearing shown as dashed line. T = 25 C, pH = 9.9, 5 wt percent alumina suspension.

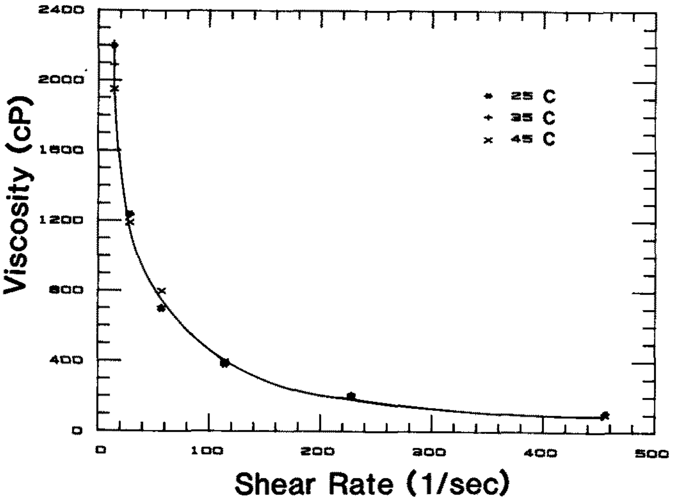

FIG. 6. Dependence of viscosity on temperature. pH = 9.9, 5 wt percent alumina suspension.

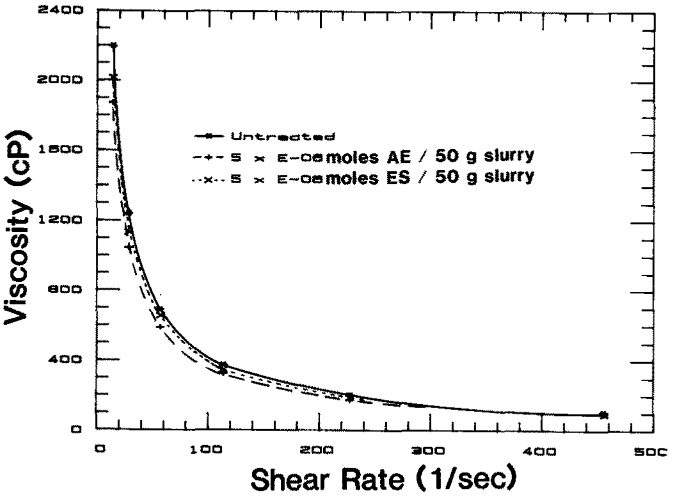

FIG. 7. Decrease in viscosity on addition of 5 × 10^{-6} mol of either Alfonic® 1412-S sodium ether sulfate or Alfonic® 810-60 alcohol ethoxylate/50 g dispersion. T = 25 C, pH = 9.9, 5 wt percent alumina suspension.

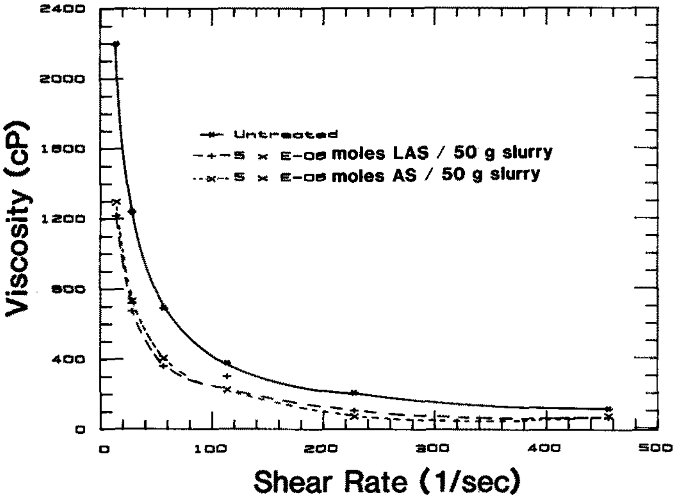

FIG. 8. Decrease in viscosity on addition of 5 × 10^{-6} mol of either sodium linear alkylbenzene sulfonate or sodium lauryl sulfate/50 g of dispersion. T = 25 C, pH = 9.9, 5 wt percent alumina suspension.

tifies the most likely ionic species in solution at low pH but high total aluminum concentration as $(Al_6[OH]_{15})^{+3}$. We believe that in the pH range 1-5 the solution consists of complex aluminum hydroxo ions and undissolved alumina particles.

Complex aluminum hydroxo complex ions are not polymeric in the pH range 1-5 and apparently do not interact enough to increase viscosity. Undissolved alumina particles are not likely to interact either because they are positively charged by adsorbed H^+ ions (2). Because neither complex aluminum hydroxide ions nor alumina particles are likely to interact, the viscosity is low in the pH range 1-5.

pH 5-7. As the pH increases, other polynuclear aluminum hydroxide complexes form and grow (4). These complexes are planar with hydroxide bridges connecting aluminum cations. Because the mixture contains small particles of alumina, it is possible that some polymeric ions grow from the surface of alumina particles. The combination of polymeric ions in solution and polymeric ions growing from alumina particles could explain the increase in viscosity between pH 5 and 7.

pH 7-8. The viscosity sharply decreases between pH 7 and 7.5. If the formation of polynuclear aluminum hydroxide complexes causes the increase in viscosity between pH 5 and 7, the destruction of these ions could explain a decrease in viscosity. Above pH 7, the chains may be destroyed by base (5). A proposed reaction given in reference (5) is:

$$[(H_2O)_2(OH)_3\,\text{Al-OH-Al}\,(OH)_3\,(H_2O)_2]^- \\ + OH^- \rightarrow 2[Al(OH)_4\,2H_2O]^-$$

pH 8-9. Viscosity increases to a maximum in the pH range 8-9. There are probably two reasons for this increase. First, aluminum hydroxide is precipitated in this pH range. As the amount of precipitate increases, flow becomes more hindred and the viscosity increases. Second, electrostatic repulsion between the precipitated aluminum hydroxide flocs may decrease as the pH approaches pH 9. The point of zero charge for Catapal® D alumina is ca. pH 9. If aluminum hydroxide flocs also have a point of zero charge near pH 9, then the repulsion between the flocs will decrease as the pH approaches pH 9. As electrostatic repulsion decreases, interaction between flocs would increase and the viscosity would increase. Both an increase in the number of precipitated aluminum hydroxide flocs and a decrease in the repulsion between them may explain the viscosity increase in the pH range 8—9.

pH 9—11. In the range 9—11, the viscosity again decreases sharply. As the pH increases above pH 9, alumina is increasingly negatively charged by adsorption of OH^- ions. Aluminum hydroxide flocs may also become increasingly negatively charged above pH 9. If the flocs become increasingly negatively charged, then their interaction will decrease and the viscosity will decrease.

Structure and rheology of the dispersion at pH 9.9. Both pseudoplasticity and thixotropy can be explained if the dispersion at pH 9.9 consists of negatively charged aluminum hydroxide flocs that form a structured suspension.

In Figure 4, the pseudoplasticity of the dispersion is shown by the decrease in viscosity with increasing shear rate. Pseudoplastic flow is common, and several models have been proposed to explain it (6—8). In these models, a decrease in viscosity with increasing shear rate is attributed to the breakdown of solution structure. In the present case, either the flocs or a structure formed between the flocs may be broken down by shearing (9—13). The structure formed between the flocs arises because of a balance of van der Waals attractive and electrostatic repulsive forces. When these forces are balanced, the flocs have a fixed separation, like the fixed separation of atoms in a crystal. A discussion of colloidal structures that arise because of a balance of attractive and repulsive forces is available (14). If the structure is sheared, the balance of forces is disrupted and the structure breaks down, decreasing the viscosity.

Thixotropy, the gradual recovery of viscosity when shearing is stopped, can also be explained if a structured suspension is formed by precipitated aluminum hydroxide. If shearing is stopped, attractive and repulsive forces will reestablish the structure destroyed by shearing. As the structure is reestablished, the viscosity will increase. This is our explanation for the gradual increase of viscosity with time shown in Figure 5.

Temperature can also break down the structure. The effect of temperature on the viscosity is shown in Figure 6. The decrease is less at higher shear rates. Apparently the structure is already broken down by shearing at high shear rates, and so the effect of temperature is less as the shear rate increases.

Effect of surfactants on viscosity. We believe that the high viscosity of our alumina dispersion around pH 9 arises from hindered flow of aluminum hydroxide flocs past one another. Because the dispersions are pseudoplastic and thixotropic, we also believe that the aluminum hydroxide flocs form a structured suspension. The decrease in viscosity when surfactants are added to the suspension can be explained if surfactants adsorb on the flocs, change the attractive and repulsive forces between the flocs, and alter the structure of the suspension.

We are not aware of data on the adsorption of surfactants on aluminum hydroxide. There are, however, numerous studies of the adsorption of anionic surfactants on alumina (15—18). Anionic surfactants are electrostatically adsorbed on alumina at pH < 9 because alumina is positively charged. Even when alumina is negatively charged, at pH > 9, a small adsorption of sodium alkylbenzene sulfonate has been reported (19). We therefore believe that anionic surfactants can absorb on aluminum hydroxide flocs, even though the flocs are negatively charged.

TABLE 3

Estimate of Solubility Product

Aluminum salt	Ksp
$Al(C_{12}\ LAS)_3$	1.8×10^{-9}
$Al(C_{12}\ AS)_3$	3.2×10^{-9}
$Al(C_{13}\ ES)_3$	$> 10^{-1}$

Alcohol ethoxylates are uncharged and therefore must physically adsorb on substrates (20). Because physically adsorbed molecules are not strongly bound to substrates, we predict that alcohol ethoxylates will not decrease the viscosity as much as anionic surfactants. The alcohol ethoxylate we tested decreased the viscosity about 15%. This compares to either sodium linear alkylbenzene sulfonate or sodium lauryl sulfate, which decreased the viscosity 40—45%. The other anionic surfactant, sodium ether sulfate, decreased the viscosity of the dispersion only about 10%. Our conclusion is that sodium ether sulfate does not adsorb as readily on the aluminum hydroxide flocs as do either sodium lauryl sulfate or sodium linear alkylbenzene sulfonate.

If anionic surfactants adsorb on negatively charged flocs, they cannot be attracted to the entire floc but must adsorb at specific sites. Aluminum atoms on the surface of the flocs are possible adsorption sites.

The tendency of anionic surfactants to interact with aluminum ions can be measured by the aluminum ion-surfactant solubility product. To estimate the solubility product, surfactant solutions of increasing concentration were added to a 0.01 M solution of aluminum nitrate until precipitate formed. Precipitation of surfactants was measured at pH 3.5 because precipitation of aluminum hydroxide at higher pH masked thep precipitation of aluminum-surfactant salts. The estimated solubility products are given in Table 3.

A small solubility product indicates surfactant readily forms a complex with aluminum. Sodium lauryl sulfate and sodium linear alkylbenzene sulfonate have small solubility products. They adsorb strongly on alumina. The solubility product for sodium ether sulfate was more than eight orders of magnitude greater than sodium lauryl sulfate or sodium linear alkylbenzene sulfonate. Sodium ether sulfate does not adsorb strongly on alumina. We therefore explain the small decrease in viscosity of the alumina dispersion on adding sodium ether sulfate to the low interaction with aluminum. Conversely, the large decrease in viscosity on adding either sodium lauryl sulfate or sodium linear alkylbenzene sulfonate is attributed to these surfactants' greater interaction with aluminum.

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