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Electrical Aspects of Adsorbing Colloid Flotation. XIV. Adsorption of Lauryl Sulfate on $Fe(OH)_3$ and $Al(OH)_3$

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Abstract

The adsorption of lauryl sulfate (LS) ion on ferric hydroxide and aluminum hydroxide flocs was investigated. Hemimicelle formation on $Fe(OH)_3$ begins at supernatant LS concentrations of about 20 mg/L; on $Al(OH)_3$ it begins at about 8 mg/L. Added salts interfere with the adsorption of LS on these flocs. For $Fe(OH)_3$ the order of strength in interference is $NO_3^- < SO_4^{2-} < H_2PO_4^-$; for $Al(OH)_3$ the order is $NO_3^- < C_2O_4^{2-}$. The results observed for $Fe(OH)_3$ were consistent with zeta potential measurements.

INTRODUCTION

In foam flotation of particulates, at optimal surfactant concentration a monolayer (hemimicelle) of surfactant ions is adsorbed onto the solid surface. The hydrocarbon tails present a hydrophobic surface, allowing the attachment of bubbles and flotation. If the concentration of surfactant is further increased, the exposed hydrocarbon tails may permit a second layer of surfactant to adsorb, forming a micellar layer on the solid surface. This second monolayer will be attached by van der Waals forces to the first layer and will present an ionic or hydrophilic surface, preventing bubble attachment and flotation (*1*). Hemimicelle and micelle formation are illustrated in Fig. 1. This theory implies that flotation takes place only over a finite range of surfactant concentration; concentrations above and below this range yield hydrophilic surfaces to which bubbles cannot attach. Previously it has been shown that longer times are necessary for the removal of ferric hydroxide by flotation at concentrations of sodium lauryl sulfate (NLS) above the

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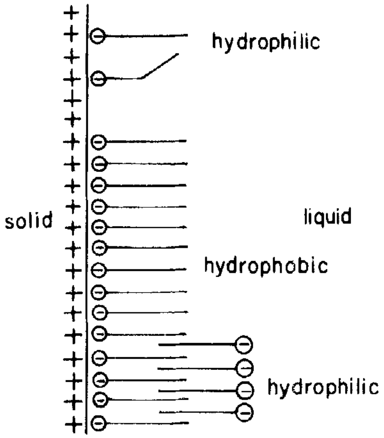

FIG. 1. Surface phases present at various surfactant concentrations in the bulk phase.

optimum concentration but well below the critical micelle concentration (*1*).

If anions other than surfactant ions are present in solution, these anions may compete for the surface sites, displacing surfactant ions. The resulting surface may appear as in Fig. 2. Particles of this type are much less hydrophobic than those coated with a hemimicelle formed from only surfactant ions, and bubble attachment and flotation of such particles may be inhibited. The effects of several competing anions on the flotation of ferric hydroxide have been studied previously (*1*, *2*). A statistical mechanical analysis of adsorption isotherms for surfactant ions and competing anions

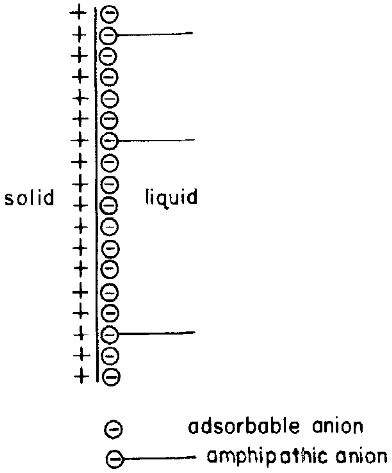

FIG. 2. Surface phase present in the presence of a competing anion and surfactant.

onto a positively charged surface has been done by Currin et al. (*3*). Currin also showed that surfactant can be displaced from the solids in a ferric hydroxide sludge by the addition of salts. This technique may permit development of an efficient method for surfactant recovery from collapsed foamate.

In the present work the amount of surfactant adsorbed onto ferric hydroxide particles was determined experimentally. The adsorption isotherms were determined in the absence of added competing anions and in the presence of various quantities of added nitrate, sulfate, and phosphate. The zeta potentials of these particles were also measured.

EXPERIMENTAL PROCEDURES, FERRIC HYDROXIDE

Ferric hydroxide slurries were prepared by dissolving ferric nitrate in distilled water and adjusting the pH to 5.0 with 0.1 *N* NaOH. The addition of NLS generally raised the pH, which was then readjusted to 5.0 with 0.1 *N* HNO_3. The method outlined in *Standard Methods* (*4*) was used to analyze the supernatant of the slurries for NLS. This method consists of diluting a known volume of the solution and adding a buffered methylene blue solution. A complex of methylene blue–anionic surfactant is formed which can be quantitatively extracted from the aqueous solution with chloroform. The organic phase is washed with a buffered solution to remove any uncomplexed methylene blue which may be present and then diluted 100.0 mL. The absorbance of this solution at 652 nm was then measured. In this work a Bausch & Lomb Spectronic 20 was used for absorbance measurements. A calibration curve was found to be linear and easily reproduced.

In an attempt to prepare more reproducible slurries, a dry ferric hydroxide was prepared by separating the solid (before addition of NLS) from ferric hydroxide slurries by centrifuging and drying this solid at 70°C for 24 h. The dry particles were finely ground and used in preparing additional slurries.

RESULTS ON FERRIC HYDROXIDE

Slurries were prepared containing 500 mg Fe/L. Known amounts of a concentrated NLS solution were added to the slurries and the supernatant was analyzed for NLS concentration after equilibrating for at least 30 min. This procedure allowed sufficient time for the particulates to settle and resulted in supernatants containing no visible iron. The volume of the NLS solution added and the volume of reagents added for pH adjustment were at first neglected in the calculation of nominal NLS concentrations. A control experiment was done using the same procedure with no iron present to indicate the error introduced by these approximations and to determine if a significant amount of NLS was adsorbed onto the walls of the beaker. The middle curve in Fig 3a indicates the expected line for the control if these

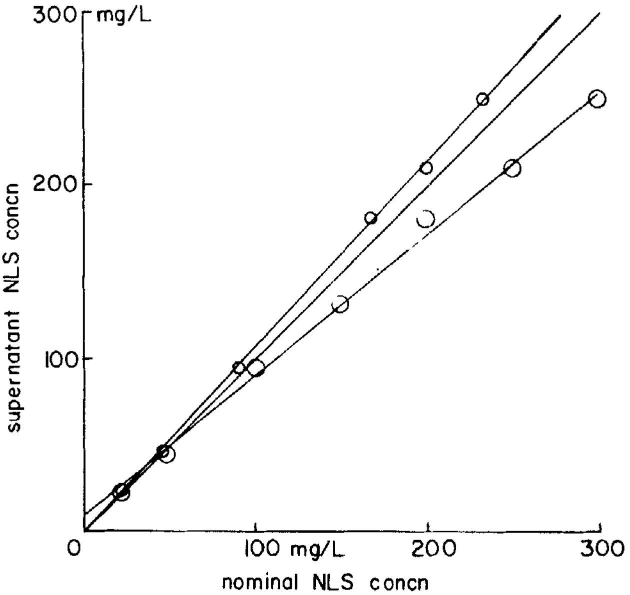

FIG. 3a. Control experiment: (middle) theoretical curve, (upper) neglecting NLS solution volume, (lower) taking NLS solution volume into account.

approximations are 100% valid and no NLS is adsorbed onto the walls of the beaker. The upper curve represents a least squares analysis on the actual experimental data for this control. Comparison of the middle and upper curves indicates that some error is introduced by the approximations made and that this error is largest at the higher concentrations. The data have been replotted including the volume of NLS solution in the calculation of nominal NLS concentration. A least squares analysis of these data is shown by the upper curve in Fig 3a. This appears to be the major source of error with these approximations. There is no indication of appreciable absorption of NLS on the beaker walls. The lower curve in Fig. 3b illustrates the results from the experiments containing iron. The control data are replotted in the upper curves. These data indicate that a large amount of surfactant is adsorbed onto the ferric hydroxide particles, with adsorption occurring at NLS concentrations as low as 20 mg/L. The first monolayer appears to begin forming at this point, but the concentrations at which hemimicelle formation is complete is not clearly shown because of the scatter in the data at higher NLS concentrations. This scatter seems to result from the inability to reproducibly prepare slurries since the analytical procedure for NLS is more accurate than these data indicate.

Slurries were also prepared from dried ferric hydroxide (see experimental section). In these slurries the volume of NLS solution added was considered

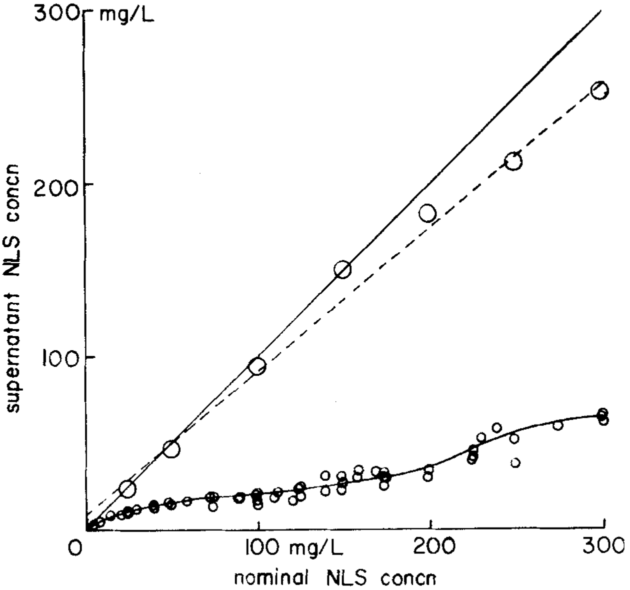

FIG. 3b. Absorption of NLS on ferric hydroxide particles at pH 5.0: (lower) 500 ppm Fe, (upper) no iron present.

in the calculation of Fe(III) and nominal NLS concentrations. Slurries were prepared containing 500 or 2000 ppm Fe(III) and various concentrations of NLS. The results of these experiments are shown in Fig. 4. The slurry containing 2 g Fe/L adsorbed almost all the surfactant even at very high NLS concentrations. Two plateaus (indicating hemimicelle and micelle formation) were observed once in the data from slurries containing 500 mg Fe/L (these data are not shown), but the second plateau could not consistently be found. A hemimicelle appears to be present at a nominal NLS concentration range of 10–90 mg/L. At higher NLS concentrations very little additional adsorption is occurring.

Additional work was done by preparing similar slurries containing 500 ppm Fe from dried ferric hydroxide and adding sodium nitrate, sodium sulfate, or dibasic sodium phosphate solutions. NLS was also added and the supernatants analyzed for NLS concentrations. The results of these experiments are shown in Figs. 5, 6, and 7. The nitrate added as nitric acid for pH adjustment has been considered negligible in calculating nitrate concentration. Nitrate concentrations as low as 0.02 *M* reduce the amount of NLS adsorbed, but some NLS adsorption occurs in slurries with as much as 0.1 *M* nitrate present. Sulfate concentrations of 2.5×10^{-4} *M* and higher substantially inhibit adsorption of NLS on ferric hydroxide, as shown in Fig. 6. In the presence of 5×10^{-3} *M* sulfate, no NLS is adsorbed. Phosphate

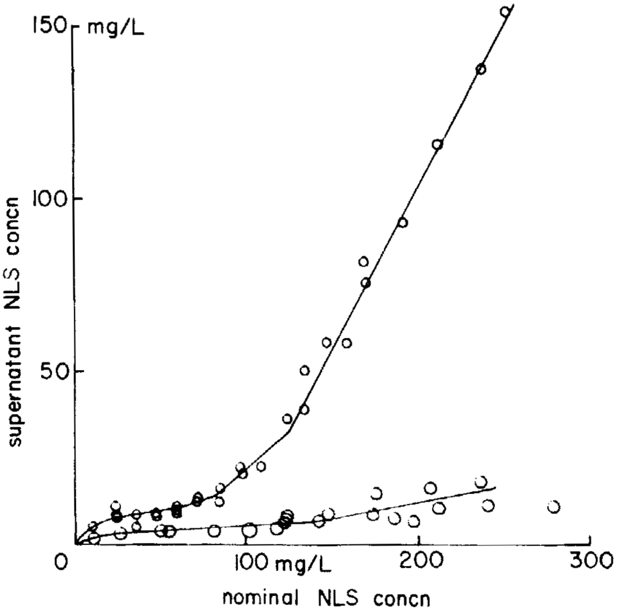

FIG. 4. Adsorption of NLS on ferric hydroxide particles which have been previously dried: (upper) 500 ppm Fe, (lower) 2000 ppm Fe.

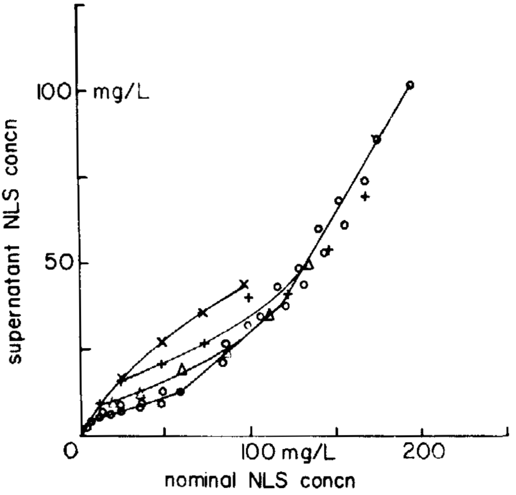

FIG. 5. Nitrate competition for adsorption sites on previously dried ferric hydroxide particles: (○) 0.10 M $NaNO_3$, (△) 0.02 M $NaNO_3$, (+) 0.05 M $NaNO_3$, (×) 0.10 M $NaNO_3$.

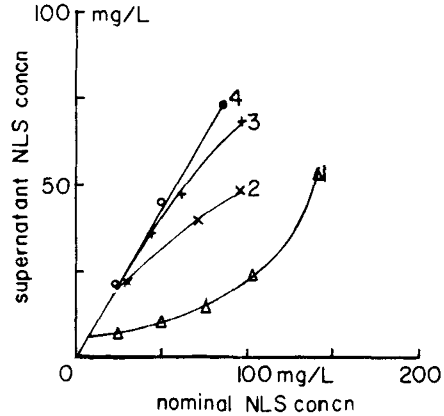

FIG. 6. Sulfate competition for adsorption sites on previously dried ferric hydroxide particles: (1) 1 × 10^{-4} *M* Na_2SO_4, (2) 2.5 × 10^{-4} *M* Na_2SO_4, (3) 5 × 10^{-4} *M* Na_2SO_4, (4) 5 × 10^{-3} *M* Na_2SO_4.

concentrations as low as 10^{-4} *M* decrease the amount of NLS adsorbed. All of our work was done at pH 5.0, where the predominant form (>99%) of phosphate is $H_2PO_4^-$ ($K_{a1} = 7.5 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$, and $K_{a3} = 2.2 \times 10^{-13}$) and the predominant form of sulfate is SO_4^{2-} ($K_{a2} = 1.2 \times 10^{-2}$) (5). At higher pH's the effect of phosphate is expected to be greater. Foam flotation studies by Clarke, Wilson, and Clarke (2) with 100 ppm Fe(III), 50 ppm NLS, at pH 5.0, and with added salts, indicate

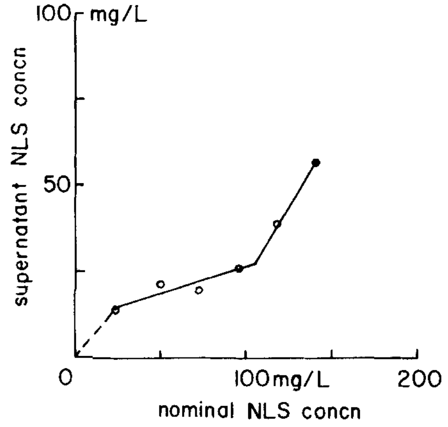

FIG. 7. Phosphate competition for adsorption sites on previously dried ferric hydroxide particles: 1 × 15^4 *M* Na_2HPO_4.

efficient removal of ferric hydroxide with 0.1 *M* $NaNO_3$, slow removal with 5×10^{-3} *M* Na_2SO_4, no removal with 0.03 *M* Na_2SO_4, and no removal with 2.5×10^{-3} *M* Na_2HPO_4 present.

Zeta potentials of ferric hydroxide particles were measured with a Zeta Meter consisting of a cell across which a potential can be applied which will cause the charged particles to move. The average velocity of the particles is measured at a known applied voltage to determine zeta potential. A graph prepared from the Helmholtz-Smoluchowski formula was used to determine the zeta potential (*6*)

$$\mathrm{ZP} = 113{,}000 \frac{V_t}{D_t} \mathrm{EM}$$

where ZP = the zeta potential of the particle in mV
V_t = the viscosity of the suspending liquid in P
D_t = the dielectric constant of the suspending liquid
EM = electrophoretic mobility in μm/s per V/cm

Slurries containing 10 ppm Fe at pH 5.0 were prepared from ferric nitrate. The zeta potentials of these particles at various NLS concentrations are shown in Fig. 8. The surface charge is positive ($z = +15$ mV) in the absence of NLS, and decreases rapidly with the addition of small amounts of surfactant. The zeta potential reaches a minimum of −22 mV at about 70 ppm NLS. The particles were also examined in the presence of nitrate, sulfate, and phosphate. Ferric hydroxide particles in slurries containing 0.01 *M* $NaNO_3$, 0.10 *M* $NaNO_3$, 5×10^{-4} *M* Na_2SO_4, or 1×10^{-3} *M* Na_2SO_4 at pH 5.0 have positive zeta potentials; those containing 3×10^{-3} to 6×10^{-3} *M* Na_2SO_4 or 1×10^{-4} *M* Na_2HPO_4 have negative zeta potentials.

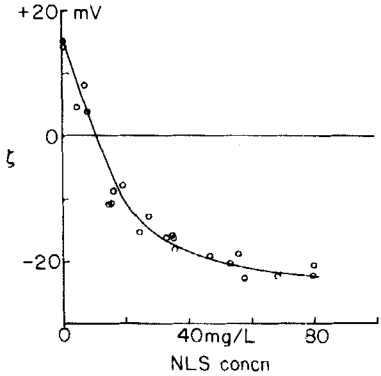

FIG. 8. Zeta potentials of ferric hydroxide in the presence of NLS. 10 ppm Fe(III), pH 5.0.

TABLE 1

Competing anion present	Concentration (*M*)	ζ(mV)
NO_3^-	0.01	$\sim+17$
	0.10	>0
SO_4^{2-}	5×10^{-4}	>0
	1×10^{-3}	>0
	2×10^{-3}	~0
	3×10^{-3}	<0
	4×10^{-3}	<0
	5×10^{-3}	<0
	6×10^{-3}	<0
PO_4^{2-}	1×10^{-4}	~-15

Because of the high ionic strength of some of these solutions, accurate zeta potentials were more difficult to obtain. Zeta potentials close to zero are also more difficult to measure since the particles are moving very slowly. Therefore only the sign and not the magnitude of the zeta potential was observed for many cases. These results are summarized in Table 1.

WORK ON ALUMINUM HYDROXIDE

The adsorption of NLS by freshly prepared aluminum hydroxide slurries was also studied, and the effects of addition of nitrate and oxalate on this adsorption were determined. [Aluminum hydroxide, like ferric hydroxide, has been found to be a useful floc for adsorbing colloid flotation (*7*).]

Aluminum hydroxide slurries were prepared from a solution of AR grade $Al(NO_3)_3 \cdot 9H_2O$ in distilled water; these contained 500 mg/L of Al(III). One hundred milliliters of this solution was heated to 90°C and treated with 1 *M* NaOH solution until the pH was 6.0. The desired quantity of NLS was added as a 1 g/L solution and the pH readjusted back to 6.0 by addition of 0.1 *M* HNO_3. The solution was stirred for 3 min, then allowed to settle for 1 h. The supernatant liquid was analyzed for NLS by the Methylene Blue method described earlier in this paper.

We see from Fig. 9 that a large amount of NLS is adsorbed by the floc. Hemimicelle formation begins at a nominal NLS concentration of about 40 mg/L (about 8 mg/L actual concentration), and it appears that adsorption is essentially complete for this run when the nominal concentration of NLS is about 200 mg/L (about 10 mg/L actual concentration). Figure 10 shows the results of a similar experiment carried out using 100 mL of a solution containing 250 mg Al(III)/L; hemimicelle formation is again seen to occur at an actual NLS concentration of about 8 mg/L. The results of making the

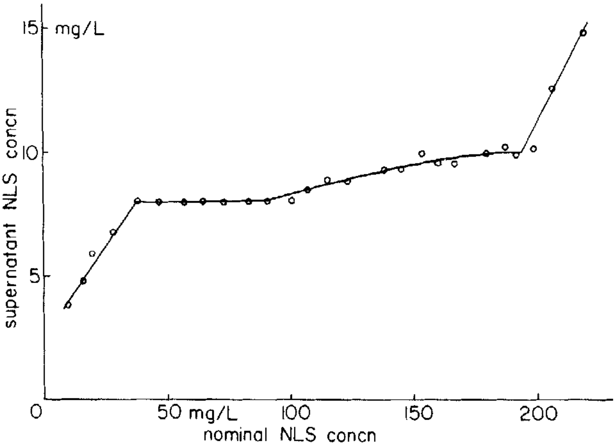

FIG. 9. Adsorption of NLS on aluminum hydroxide floc at pH 6.0. 500 mg/L of Al(III) is present.

solution 0.1 M in NO_3^- by adding $NaNO_3$ are shown in Fig. 11. We see that the nominal concentration of NLS at which hemimicelle formation takes place is increased to about 13 mg/L by the addition of this much nitrate. Making the solution 10^{-3} M in sodium oxalate increases the nominal concentration of NLS at which hemimicelle formation takes place to about 14 mg/L, as shown in Fig. 12. At a nominal concentration of 10^{-2} M oxalate, much less NLS was adsorbed and no plateau in the NLS adsorption

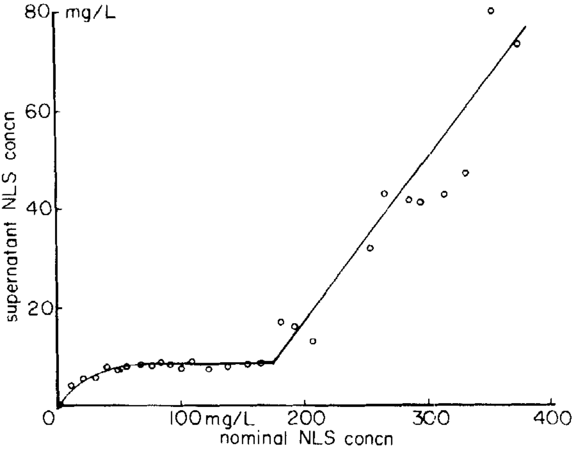

FIG. 10. Adsorption of NLS on $Al(OH)_3$ floc at pH 6.0. 250 mg/L of Al(III) is present.

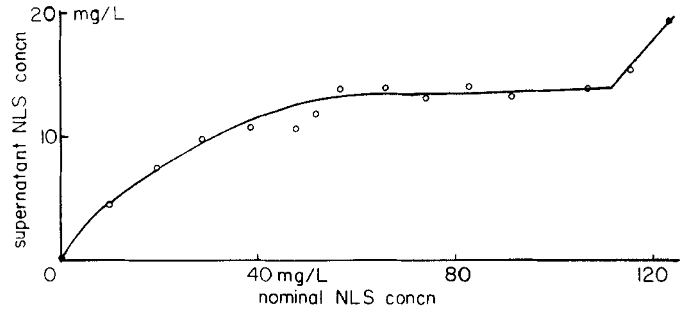

FIG. 11. Adsorption of NLS on $Al(OH)_3$ floc at pH 6.0 in the presence of 0.1 M NaNO. 500 mg/L of Al(III) is present.

isotherm was observed—evidently no surface phase transition is occurring under these conditions as seen in Fig. 13. It was not possible to go to higher nominal oxalate concentrations because the $Al(OH)_3$ precipitate redissolved under these conditions.

CONCLUSIONS

A monolayer of NLS is adsorbed onto ferric hydroxide particles at pH 5.0 in the concentration range of 10–90 ppm NLS. The surface is positively charged when no surfactant is adsorbed and negatively charged in the presence of >10 ppm NLS due to the negatively charged lauryl sulfate ions adsorbed onto the surface. Some additional adsorption of NLS occurs in the range 90–120 ppm but a well-defined second plateau is not formed. This evidence does not indicate an abrupt surface phase change when a second layer of surfactant is adsorbed. Flotation has been shown to be inhibited in this concentration range (*1*).

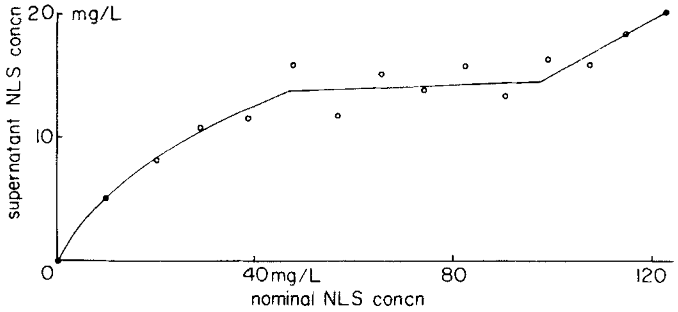

FIG. 12. Adsorption of NLS on $Al(OH)_3$ floc at pH 6.0 in the presence of 10^{-3} M $Na_2C_2O_4$. 500 mg/L of Al(III) is present.

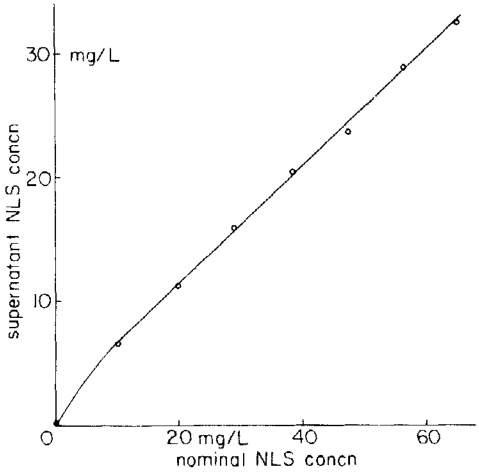

FIG. 13. Adsorption of NLS on $Al(OH)_3$ floc at pH 6.0 in the presence of 10^{-2} *M* $Na_2C_2O_4$. 500 mg/L of Al(III) is present.

The zeta potential of ferric hydroxide at pH 5.0 has been found to be positive in the presence of up to 0.1 *M* nitrate. Previous work (*2*) indicates that rapid removal of iron by flotation with 50 ppm NLS occurs at these nitrate concentrations. The zeta potential of ferric hydroxide at pH 5.0 is positive in the presence of up to 0.002 *M* sulfate and negative in the presence of 0.003 *M* or greater concentrations of sulfate. Clarke et al. report rapid removal of ions by flotation with sulfate present at up to 0.0025 *M* and slow, incomplete, or no removal at higher sulfate concentrations. They report no visible removal at phosphate concentrations 0.0025 *M* and greater; lower concentrations of phosphate were not examined. We found a negative zeta potentials for ferric hydroxide particles in the presence of 0.001 *M* phosphate. These data imply that positive zeta potentials are necessary for efficient flotation of ferric hydroxide with NLS, and indicate that zeta potential measurements may be useful in anticipating interferences in foam flotation separations.

Our data for the adsorption of NLS on aluminum hydroxide exhibit the same general pattern as seen for ferric hydroxide—a surface phase transition forming a hemimicelle of surfactant on the floc, interference with surfactant adsorption as other adsorbable anions are added, and no indication of a phase transition as additional surfactant is adsorbed onto the hemimicellar layer.

Acknowledgments

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