

$\partial r)_r$  of  $\sim 4$  D./Å. However, care should be taken since we initially assumed that  $\Psi_A$  and  $\Psi_B$  are orthogonal and in this case the homopolar dipole vanishes. If we had included the overlap integral, then the primary moments would have changed somewhat.

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## Mechanisms of Alkyl Sulfonate Adsorption at the Alumina-Water Interface

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Adsorption isotherms of sodium dodecyl sulfonate on alumina were determined at controlled ionic strength, pH, and temperature. Electrophoretic mobilities of the alumina were also measured for the same conditions. The results indicate that at a certain critical concentration or critical pH, adsorption increases markedly through association of the hydrocarbon chains of the adsorbed sulfonate ions to form hemimicelles at the solid-liquid interface. The dependence of the isotherms on surfactant concentration and on pH is interpreted in terms of the Stern-Grahame model of the electrical double layer.

### Introduction

In previous papers<sup>1,2</sup> it was shown that such interfacial parameters as  $\zeta$  potential and flotation response depend upon the number of carbon atoms in the hydrocarbon chain of a surfactant and upon the concentration of the surfactant in solution. Correlation of the various interfacial parameters showed that marked changes in each of the parameters occur at some critical concentration of the surfactant. It was postulated that these abrupt changes are due to the association of adsorbed surfactant ions to form two-dimensional aggregates or hemimicelles at the solid-solution interface. From the dependence of the flotation and electrokinetic behavior on the chain length of the surfactant, the van der Waals cohesive energy responsible for lateral interaction between surfactant ions at the interface was calculated on a molar basis to be  $-0.6$  kcal. for each  $\text{CH}_2$  group in the chain. A direct test of the proposed adsorption mechanisms is best obtained through the measurement of the adsorption of the surfactant itself and that is the purpose of this study.

Indications of interactions at the interface can be found in the work by Wayman and co-workers<sup>4-7</sup> on the adsorption of surfactants on clay minerals. Adsorption isotherms of surfactants on silica and alumina determined by other workers<sup>8-10</sup> do exhibit marked changes at certain critical concentrations. However, these investigations have not been extensive and no

- (1) Based in part on the Ph.D. dissertation of P. Somasundaran, University of California, Berkeley, Calif., 1964.
- (2) D. W. Fuerstenau, T. W. Healy, and P. Somasundaran, *Trans. AIME*, 229, 321 (1964).
- (3) P. Somasundaran, T. W. Healy, and D. W. Fuerstenau, *J. Phys. Chem.*, 68, 3562 (1964).
- (4) C. H. Wayman, *Proc. Intern. Clay Conf.*, 1, 329 (1963).
- (5) C. H. Wayman, J. B. Robertson, and H. G. Page, U. S. Geological Survey Professional Paper 475-B (1963).
- (6) C. H. Wayman, *ibid.*, 450-C (1962).
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- (8) I. W. Wark and A. B. Cox, *Trans. AIME*, 112, 189 (1934).
- (9) K. Shinoda, et al., "Colloidal Surfactants," Academic Press, New York, N. Y., 1963, Chapter 3.
- (10) M. J. Jaycock and R. H. Ottewill, *Bull. Inst. Mining Met.*, 72, 497 (1963).

quantitative description of the adsorption process has been presented to account for the breaks in the isotherms or for the significance of the slope of the isotherms. Tamamushi and Tamaki<sup>11</sup> attempted to explain such isotherms in terms of a Brunauer-Emmett-Teller (B.E.T.) type of equation, but the validity of their approach is questionable because of their neglect of electrical effects. Also, adsorption isotherms generally have not been determined over a sufficiently wide range or with a precise control of such variables as ionic strength, pH, and temperature which affect the adsorption processes.

The objective of this paper is to present the results of detailed studies of the adsorption isotherms of sodium dodecyl sulfonate on alumina in aqueous media. These isotherms together with the electrophoretic behavior of alumina suggest mechanisms of adsorption of surfactant ions at the solid-liquid interface.

Equation 2 can be modified to take into account the interaction of surfactant ions at the interface by separating  $W_\delta$  into electrostatic and interaction terms

$$\Gamma_\delta = 2rC \exp\left[\frac{-zF\psi_\delta - n\phi}{RT}\right] \quad (3)$$

where  $\epsilon$  is the dielectric constant of the medium,  $R$  is the gas constant,  $T$  is the absolute temperature,  $z$  is the valence of counterions including the sign,  $F$  is the Faraday constant, and  $C$  is the moles of ions/cm.<sup>3</sup> in the bulk solution. Based on the Stern-Grahame treatment of the double layer, expression for the adsorption of counterions at the plane  $\delta$  is given by the equation

$$\Gamma_\delta = 2rC \exp\left[\frac{-zF\psi_\delta - n\phi}{RT}\right] \quad (2)$$

where  $\Gamma_\delta$  is the adsorption density in moles/cm.<sup>2</sup> at the plane  $\delta$ ,  $r$  is the effective radius of the adsorbed ion in centimeters,  $C$  is the concentration of ions in the bulk in moles/cm.<sup>3</sup>, and  $W_\delta$  is the work required to bring the ions to the plane  $\delta$ .

culated by taking the average of the area occupied by cubic packing and by hexagonal close-packing of ions of 5.9-Å. diameter (the diameter of the sulfonate head). Sodium dodecyl sulfonate used was prepared from high-purity dodecyl sulfonic acid by treating it with sodium hydroxide, and the resulting sodium salt was purified by recrystallization from hot absolute ethyl alcohol. Triply distilled conductivity water was used for adsorption and electrokinetic studies.

Adsorption of sodium dodecyl sulfonate under various conditions was measured by determining the difference in concentration of the surfactant in solution before and after adding alumina. Experiments were carried out at a constant temperature of  $25 \pm 0.2^\circ$ , and an atmosphere of purified nitrogen was maintained in the adsorption cell. Total ionic strength was also kept constant at  $2 \times 10^{-3} M$  by additions of decinormal solutions of sodium chloride and hydrochloric acid and sodium hydroxide which were used for pH adjustment. The adsorption cell, which was stirred magnetically, normally contained 200 ml. of solution and 4 g. of alumina for each experiment, but for cases where the adsorption was lower, 8 g. of alumina and 150 ml. of solution were used. The lowest point was obtained using 16 g. of alumina and 100 ml. of solution. Although equilibrium was attained in much less than 1 hr. under the conditions used, each sample was agitated for 2 hr. (but more vigorous agitation was found to decrease the equilibrium time appreciably). After the equilibrium was attained, samples were collected for determination of the equilibrium concentration of sodium dodecyl sulfonate and for electrophoresis experiments. Determinations of pH were made after allowing the suspension to settle for at least 30 min.

The sulfonate concentration was determined by a variation of the methylene blue method described by Jones.<sup>20</sup> It is based on the principle that the anionic dodecyl sulfonate in water combines with the cationic methylene blue to give a blue complex that is soluble in chloroform. Hence, the concentration of sodium dodecyl sulfonate in any aqueous solution can be determined by extracting the methylene blue sulfonate complex with chloroform and evaluating the concentration colorimetrically by comparison with the color produced by known quantities of sodium dodecyl sulfonate. The possible experimental errors have been examined by Wayman.<sup>21</sup> Since the readings could vary from one dye to another, the same type of dye was used through each set of analyses. Absorption by the methylene blue sulfonate complex was determined from 640 to 660  $m\mu$  in a Cary Model 14 spectrophotometer. The maximum optical density ob-

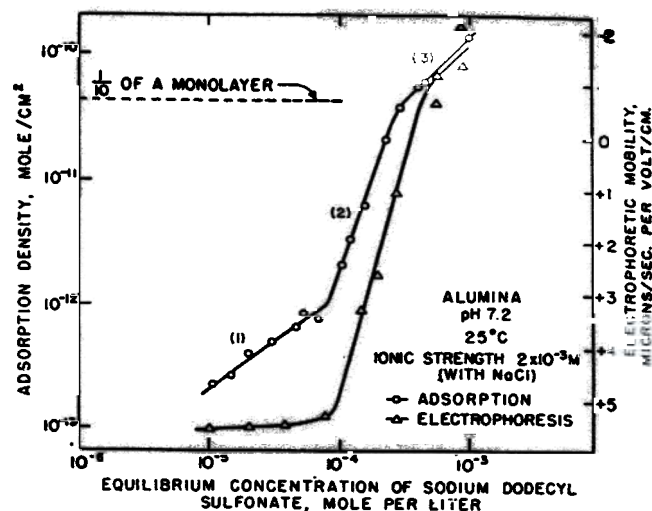


Figure 1. Adsorption density of dodecyl sulfonate ions on alumina and the electrophoretic mobility of alumina as a function of the concentration of sodium dodecyl sulfonate at pH 7.2 and at constant temperature and ionic strength.

tained was used for evaluation of the sulfonate concentration. The lowest concentration that could be measured was  $10^{-5} M$  in the aqueous solution.

The electrophoretic mobility of the alumina particles was determined by means of a Zeta-Meter. This method was necessary if the measurement of electrokinetic behavior was to be determined with the same small particles that were used in the adsorption experiments. In addition, this method has the advantage over the streaming potential technique in that it gives an indication of the distribution of charges among the particles rather than only a net value for the charge of the particles in the system.

## Results

The adsorption isotherm of sodium dodecyl sulfonate by alumina at pH 7.2 and  $25^\circ$  is given in Figure 1. Electrophoretic mobilities of the particles under the same conditions are also given in Figure 1.

The adsorption isotherm consists of three regions: region 1, characterized by a low increase in adsorption with surfactant concentration; region 2 by an abrupt increase in the slope of the isotherm; and region 3 again by a lower dependence of adsorption on surfactant concentration. The electrophoretic mobility exhibits an almost negligible dependence on sulfonate addition in region 1, but it decreases abruptly through region 2. The end of region 2 is characterized by the

(20) J. H. Jones, *J. Assoc. Agr. Chemists*, 28, 398, 409 (1945).

(21) C. H. Wayman, U. S. Geological Survey Professional Paper 450-B (1962).

mobility becoming zero. In region 3, the mobility is opposite in sign. Moreover, in region 3 a number of particles were observed to have a positive charge, and those particles with a negative charge have a wide distribution of electrophoretic mobilities. This probably results from a distribution of particles with varying surface activities, thereby giving rise to a distribution of adsorption densities. However, the net electrophoretic mobility is characterized by a slower change in region 3.

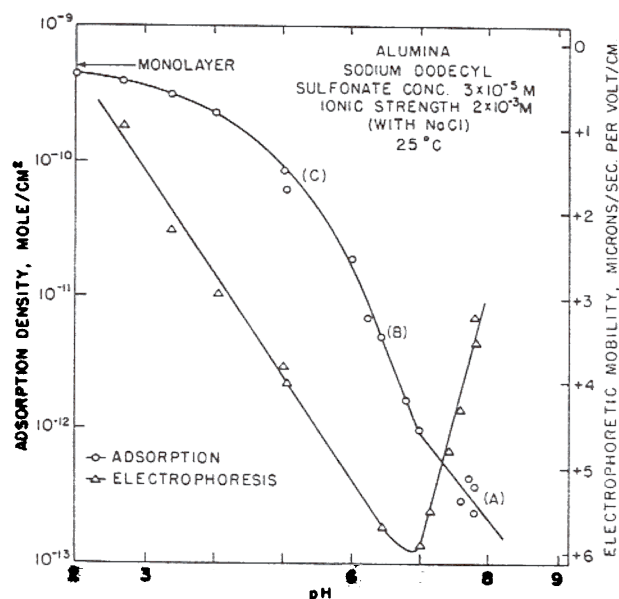


Figure 2. Adsorption density of sodium dodecyl sulfonate on alumina and the electrophoretic mobility of alumina as a function of pH at constant residual sodium dodecyl sulfonate concentration, ionic strength, and temperature. The ionic strength for the point at pH 1.98, however, exceeds  $2 \times 10^{-3} N$ .

The adsorption isotherm for sodium dodecyl sulfonate on alumina is given in Figure 2 as a function of pH at constant ionic strength of  $2 \times 10^{-3} N$  and an equilibrium concentration of approximately  $3 \times 10^{-5}$  mole/l. This curve also consists of three parts: region A showing a low increase in adsorption with lowering of pH, region B with a greater increase in adsorption, and region C with a constantly decreasing rate of increase of adsorption with lowering of pH.

Figure 3 presents the adsorption density and electrophoretic mobility as a function of sulfonate concentration at pH 6.9 under conditions of constant temperature and constant ionic strength. This set of curves is similar to that given in Figure 1 for pH 7.2. The adsorption isotherms at pH 6.9 and 7.2 are now put together in Figure 4 for comparative purposes.

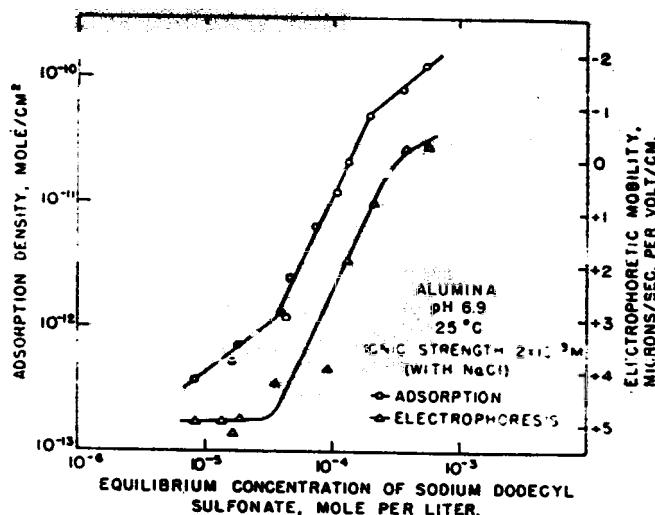


Figure 3. Adsorption density of dodecyl sulfonate ions on alumina and the electrophoretic mobility of alumina as a function of the concentration of sodium dodecyl sulfonate at pH 6.9 and at constant temperature and ionic strength.

### Discussion of Results

In interpreting these results, we shall consider that sulfonate ions are adsorbed at the alumina-water interface as counterions in the electrical double layer. Furthermore, since sulfonate ions are not chemisorbed they are adsorbed appreciably only below the zero-point-of-charge of alumina, namely below pH 9.

**Effect of Surfactant Concentration on Adsorption.** The shape of the adsorption isotherm supports the adsorption mechanism mentioned earlier. In region 1 of Figure 1 or in region A of Figure 2, at low concentrations of surfactants or at low surface potentials, the surfactant ions are adsorbed individually and adsorption results primarily from electrostatic forces between surfactant ions and the charged solid surface. However, when the concentration of the reagent reaches the hemimicelle concentration or hemimicelle pH, that is the pH at which hemimicelles start forming at the solid-liquid interface at constant equilibrium concentration of surfactant, the ions begin to associate with each other. This association enhances the adsorption of sulfonate ions considerably and, hence, the rapid rise in the adsorption isotherms result. Thus, in region 2, the adsorption is due to the electrostatic attraction between the ions and the charged solid surface and hemimicelle association of hydrocarbon chains. When sulfonate ions equivalent in number to the surface sites have been adsorbed, the contribution due to the electrostatic attraction disappears, and the further increase in adsorption will be only due to association between the hydrocarbon chains. Thus, in region 3,



the slope of the adsorption isotherm decreases. The reason mentioned above for the decrease in slope from region 2 to region 3 is supported by the electrophoretic mobility curve which shows that the net charge on the particles becomes close to zero at the concentration where the adsorption isotherm changes its slope.

In region 3, the surfactant ions are probably adsorbed by a slightly different mechanism. After the net charge becomes zero, the surfactant ions that associate with those ions that are already adsorbed might adsorb with the polar head away from the surface since this reduces the repulsion between the ionic heads. This type of adsorption of the ions leads to a less hydrophobic surface and, hence, probably is the reason for the decrease in flotation and contact angle observed by some workers.

Region 1 of the adsorption isotherm can be examined with the help of an exact form of Gouy-Chapman equation<sup>17</sup> for the diffuse layer charge by considering an ion-exchange process between the dodecyl sulfonate ions and the chloride ions. The total adsorption density of negatively charged counterions in moles/cm<sup>2</sup>,  $\Gamma_-$ , can be evaluated from eq. 1 as

$$\Gamma_- = \frac{\sigma_d}{zF} = 6.1 \times 10^{-11} \sqrt{C_-} [(\exp 19.46\psi_s) - 1] \quad (4)$$

The total concentration of negative ions in the bulk,  $C_-$ , has been kept constant at  $2 \times 10^{-3} M$  throughout the experiment by the addition of NaCl and HCl. Changes in  $\zeta$  potential and hence  $\psi_s$  are very small as seen from the electrophoretic mobility curve in Figure 1. Thus, in region 1,  $\Gamma_-$  is constant. The increase in adsorption density of dodecyl sulfonate as the bulk concentration of the dodecyl sulfonate is increased is due to the exchange between the chloride ions and sulfonate ions and governed by the following simple law if there is no preference of sulfonate ( $R^-$ ) over chloride ( $Cl^-$ ) for the surface

$$\Gamma_{R^-}/\Gamma_{Cl^-} = C_{R^-}/C_{Cl^-} \quad (5)$$

Equation 5 predicts a slope of 1 for the adsorption isotherm in the region 1. The experimental value of 0.8 is in approximate agreement with the prediction, especially considering the slight change in electrophoretic mobility which would only decrease the slope from the theoretical value of 1. This value is also in agreement with that obtained by Jaycock and Ottewill for ion exchange between dodecyl sulfate and chloride ions on stannic oxide.<sup>22</sup>

In region 2, however, specific adsorption due to the association of hydrocarbon chains at the solid-liquid interface takes place and hence, the adsorption density of dodecyl sulfonate alone increases. The increased

slope in the second region is due to this specific adsorption. Equation 5 can be modified in the following manner to take this into account. At any particular value of  $\psi_s$

$$\Gamma_{R^-}/\Gamma_{Cl^-} = f_{R^-}C_{R^-}/f_{Cl^-}C_{Cl^-} \quad (6)$$

where  $f_{R^-}$  and  $f_{Cl^-}$  are specific adsorption coefficients for  $RSO_3^-$  and  $Cl^-$ . The coefficients can be expressed in terms of the difference in free energy of adsorption

$$\frac{\Gamma_{R^-}}{\Gamma_{Cl^-}} = \frac{C_{R^-}}{C_{Cl^-}} \exp[(\mu_{Cl^-} - \mu_{R^-})/RT] \quad (7)$$

Assuming the specific adsorption potential of chloride ions negligible compared to that of alkyl sulfonate ions and differentiating eq. 7 in the logarithmic form with respect to  $\ln C_{R^-}$  yields

$$\frac{d \ln \Gamma_{R^-}}{d \ln C_{R^-}} + \frac{d \ln \frac{C_{Cl^-}}{\Gamma_{Cl^-}}}{d \ln C_{R^-}} = 1 - \frac{d\mu_{R^-}}{d \ln C_{R^-}} \frac{1}{RT} \quad (8)$$

Substituting  $\mu_{R^-} = n\phi$

$$\frac{d \ln \Gamma_{R^-}}{d \ln C_{R^-}} = 1 - \frac{d \ln (C_{Cl^-}/\Gamma_{Cl^-})}{d \ln C_{R^-}} - \frac{\phi}{RT} \frac{dn}{d \ln C_{R^-}} \quad (9)$$

At constant  $\psi_s$ , the slope of the isotherm will be given by eq. 9. However, the actual slope of the adsorption isotherm will be less because  $\psi_s$  is decreasing slightly. An experimental value higher than 1 indicates the strong influence of the van der Waals cohesive energy term,  $(\phi/RT)(dn/d \ln C_{R^-})$ . Remember that  $\phi$  is  $-0.6$  kcal./mole of  $CH_2$  groups, or  $-RT$ .

The logarithmic form of eq. 3 can be differentiated to give

$$\frac{d \ln \Gamma_s}{d \ln C} = 1 - \frac{d(zF\psi_s/RT)}{d \ln C} - \frac{\phi}{RT} \frac{dn}{d \ln C} \quad (10)$$

This equation can now be used for the evaluation of the rate of change of adsorption density in the presence of specific adsorption. In addition, based on the assumption that adsorption in the Stern layer is proportional to the total adsorption in the double layer and, hence, that both change in a similar manner, eq. 10 can be used for the analysis under conditions where the adsorption is mainly outside the Stern layer. It should be noted that eq. 10 describes the relation between adsorption density of any particular kind of ion and the bulk concentration of these ions. In region 1,

(22) M. J. Jaycock, R. H. Ottewill, and I. Tar, *Bull. Inst. Mining Met.*, 73, 256 (1964).

$$\frac{d \ln \Gamma_s}{d \psi_s} = \frac{-zF}{RT} - \frac{\phi}{RT} \frac{dn}{d \psi_s} \quad (11)$$

This equation can be used to study the variation of adsorption as a function of pH by putting it in the form

$$\frac{d \ln \Gamma_s}{d \text{pH}} = \frac{-d \psi_s}{d \text{pH}} \frac{zF}{RT} - \frac{d \psi_s}{d \text{pH}} \frac{dn}{d \psi_s} \frac{\phi}{RT} \quad (12)$$

Upon substitution of the value  $-1$  for the valence of dodecyl sulfonate ion, eq. 12 becomes

$$\frac{d \ln \Gamma_s}{d \text{pH}} = \frac{F}{RT} \frac{d \psi_s}{d \text{pH}} - \frac{\phi}{RT} \frac{dn}{d \psi_s}$$

In region A,  $dn/d \text{pH}$  is nil and the change of adsorption density with pH should then be determined by the change of  $\psi_s$  with pH. Since the  $\zeta$  potential is directly proportional to the electrophoretic mobility at constant temperature,  $d \psi_s/d \text{pH}$  will be determined by the slope of the mobility-pH curve. In region A,  $d \psi_s/d \text{pH}$  is negative and  $d \ln \Gamma_s/d \text{pH}$  must also be negative, as can be seen in Figure 2.

The transition point from region A to B corresponds to the hemimicelle pH for that particular equilibrium concentration and association between the hydrocarbon chains begins to take place at that point. Hence, in region B, the second term ( $dn/d \text{pH}$ ) also becomes effective. The term  $dn/d \text{pH}$  is negative, whereas  $d \psi_s/d \text{pH}$  is positive in region B. It can be seen that the magnitude of the second term,  $dn/d \text{pH}$ , due to hemimicelle association is very high so that the slope of the adsorption isotherm  $d \ln \Gamma_s/d \text{pH}$  is negative. The drop in  $\zeta$  potential in region B is indicative of the strong effect of this rapid hemimicelle association.

As the pH is further increased, the effect of sudden hemimicelle formation diminishes and the slope of the isotherm decreases. In region C, the association of a new ion going to the surface with a hemimicelle probably still takes place, but its effect will be very small compared to that of the association of a number of individually adsorbed ions to form a new hemimicelle. In other words, in region C,  $dn/d \text{pH}$  diminishes and, correspondingly, the rate of increase in adsorption decreases continuously.

Figure 4 shows a very strong dependence of the adsorption of sulfonate ions on the pH of the system. The interesting feature of this set of curves is the change in hemimicelle concentration with pH. Hemimicelle concentration at pH 7.2 is  $8 \times 10^{-6}$  mole/l. and at pH 6.9 it is  $3.5 \times 10^{-6}$  mole/l. At a lower pH, the

(23) D. W. Fuerstenau and H. J. Modi, *J. Electrochem. Soc.*, 106, 336 (1959).

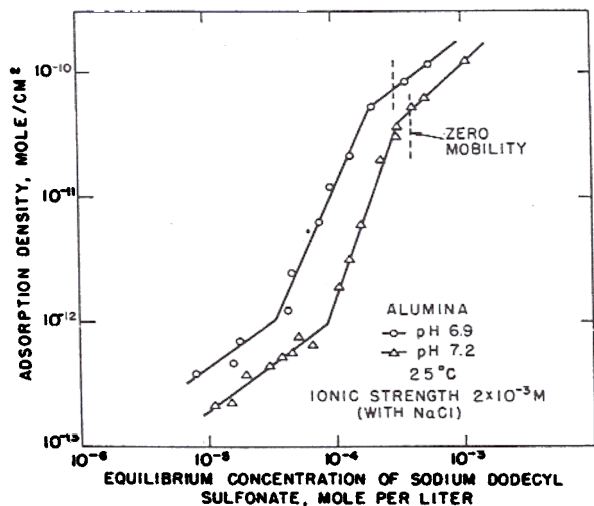


Figure 4. Comparison of adsorption isotherms of dodecyl sulfonate ions on alumina at pH 6.9 and 7.2.

particles are more positive and, hence, there is an increase in adsorption at the lower pH. Greater charge on the particle at lower pH will need a greater adsorption density of sulfonate before the  $\zeta$  potential is brought to zero and this can be observed in Figure 4 by the change in adsorption density at the transition between region 2 and region 3.

**Surface Coverage.** From surface area measurements, assuming that saturation adsorption of stearic acid on alumina corresponds to a monolayer, maximum adsorption in Figure 2 approaches a calculated monolayer of dodecyl sulfonate on alumina. At the lowest pH value studied (pH 1.98), the ionic strength exceeds the value used for all the other experiments, that is  $2 \times 10^{-3} M$ . At these low pH values where the surface charge will be high, the amount of sulfonate adsorbed approaches monolayer coverage.

Data on adsorption of the sulfonate ions at pH 7.2 show that association of the adsorbed ions begins at a coverage of about  $10^{-12}$  mole/cm<sup>2</sup> (based on the area of the sulfonate head) and that zero mobility (the transition from region 2 to region 3) occurs at about  $3 \times$

$10^{-11}$  mole/cm<sup>2</sup>, or at a coverage of only about one-tenth of a monolayer. The much higher coverage at about pH 2 as compared to pH 7 may result partly from the presence of and coadsorption of sulfonic acid molecules which occur in appreciable concentration at low pH values since the  $pK$  of sulfonic acid is about 1.5. Extensive adsorption of the sulfonic acid molecules would occur through interaction of hydrocarbon chains, but without electrostatic repulsion because the polar heads are uncharged.

### Summary

Detailed adsorption measurements of sodium dodecyl sulfonate ions on alumina together with electrophoretic mobility measurements at constant ionic strength and pH indicate that sulfonate ions are adsorbed individually as counterions in the electrical double layer at low sulfonate concentrations. Adsorption under these conditions occurs by an ion-exchange process. The adsorption of sulfonate ions was found to be exceedingly dependent upon the pH of the liquid with no adsorption occurring above the zero-point-of-charge of alumina (pH 9), which suggests that chemisorption does not exist in this system. At a certain critical concentration or critical pH, adsorption increases rapidly through the formation of two-dimensional aggregates of the surfactant ions or hemimicelles at the solid-solution interface. At still greater adsorption densities, the increase in adsorption with increasing sulfonate concentration decreases because the sign of the net electrical charge at the interface is reversed by the adsorbed surfactant ions. The dependence of the adsorption isotherms on surfactant concentration and on pH is interpreted in terms of the Stern-Grahame model of the electrical double layer.

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