

## Coadsorption of Anionic and Nonionic Surfactant Mixtures at the Alumina–Water Interface

P. Somasundaran,\* E. Fu, and Qun Xu

Langmuir Center for Colloids and Interfaces, Henry Krumb School of Mines,  
Columbia University, New York, New York 10027

Received June 27, 1991. In Final Form: December 5, 1991

The adsorption of monodispersed, isomerically pure anionic surfactant, *p*-octylbenzenesulfonate, and nonionic surfactant, dodecyloxyheptaethoxyethyl alcohol, and their mixtures on alumina was investigated to determine interactions between such surfactants. In a single surfactant system, only the anionic sulfonate was found to adsorb to any appreciable extent. In the mixed surfactant system, the sulfonate was found to induce significant coadsorption of the nonionic surfactant. This was attributed to hydrophobic interaction between the sulfonate and the alcohol at the mineral/solution interface. Adsorption of the sulfonate was also enhanced due to both hydrophobic interaction and the reduction of electrostatic repulsion between sulfonate head groups which are shielded from each other by the nonionic surfactant molecules.

### Introduction

Adsorption of surfactants on solids has major industrial applications in areas ranging from froth flotation to detergency. Commercial surfactants used in various processes invariably consist of mixtures of compounds which can have a marked effect on the interfacial behavior of the system. However, there has been very little fundamental work on such systems, and an overwhelming majority of the research on adsorption has been performed with systems containing a single surfactant. Since surfactant mixtures generally do not behave like single surfactants, there is a need to conduct studies with well-defined surfactant mixtures in order to elucidate mechanisms by which surfactants interact and to model the behavior in actual systems.

Mixtures of anionic and nonionic surfactants have demonstrated enhanced surface activity in many cases.<sup>1–5</sup> Literature on the solution behavior of anionic/nonionic surfactant mixtures suggests significant deviations in their behavior from ideal behavior<sup>6,7</sup> in contrast to mixtures of similarly charged surfactants.<sup>8,9</sup> However, there is very little information on interactions of such mixtures at solid/liquid interfaces. In this study, isomerically pure alcohol and sulfonate surfactants have been synthesized and their adsorption on alumina has been investigated. Surface tension and zeta potential measurements have been performed for the information needed for developing mechanisms.

### Materials and Methods

**Alumina.** Linde A alumina was purchased from Union Carbide Corp. It was specified to be 90%  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and 10%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and to have a mean diameter of 0.3  $\mu$ m. The specific surface area was measured to be 14 m<sup>2</sup>/g by N<sub>2</sub> BET adsorption using a Quantasorb system.

**Anionic Surfactant.** Sodium *p*-octylbenzenesulfonate, C<sub>8</sub>H<sub>17</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na, or C<sub>8</sub>PhS, was synthesized in our laboratory, and high-performance liquid chromatographic analysis of this compound showed it to be more than 97% isomerically pure.

**Nonionic Surfactant.** Dodecyloxyheptaethoxyethyl alcohol, C<sub>12</sub>H<sub>25</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>6</sub>OH, or C<sub>12</sub>EO<sub>6</sub>, was purchased from Nikko Chemicals, Japan, and was specified to be monodispersed and at least 97% pure.

NaCl, used for controlling ionic strength, was purchased from Aldrich Chemical Co. and was of ultrapure grade (99.99%). HCl and NaOH, used for regulating the pH, were purchased from Fisher Scientific Co. and were of A.R. grade. Water used for preparing all solutions was distilled 3 times in a glass still. Conductivity was measured to be in the range of (1–2)  $\times 10^{-6}$   $\Omega^{-1}$ .

**Adsorption.** Adsorption experiments were conducted in capped 50-mL centrifuge tubes. First, 4 g of alumina and 20 mL of 0.03 M NaCl solution were mixed and allowed to equilibrate at the test temperature for 1 h to achieve a steady pH value. A total of 20 mL of 0.03 M NaCl solution containing surfactant at the test temperature was then added, and the sample was allowed to equilibrate for at least 2 h. pH measurements were then made and, if necessary, adjusted using 0.1 N HCl or NaOH. The pH was monitored twice daily for 3 days, and the samples were allowed to equilibrate for at least 12 h after the final pH adjustment. The sample was then centrifuged for 30 min at 4500 rpm inside an incubator set at the test temperature and 20 mL of supernatant pipetted out for analysis.

Alcohol concentrations were measured by high-performance liquid chromatography (HPLC) with a reverse-phase HPLC column and a refractive index detector. Integrated peak areas were used for calibration. Reproducibility of the peak areas was within 5%. The solvent used for HPLC analysis was a 90:10 (v/v) mixture of acetonitrile and water.

Sulfonate concentration above  $2 \times 10^{-4}$  kmol/m<sup>3</sup> was measured by a two-phase titration technique.<sup>10</sup> Dilute solutions below  $2 \times 10^{-4}$  kmol/m<sup>3</sup> were analyzed by UV absorbance using a Beckman DU-8 UV-visible spectrophotometer. Wavelength scans of C<sub>8</sub>PhS solutions showed an absorbance peak at 223 nm.

Surface tension measurements were made using a water-jacketed Fisher Model 20 ring tensiometer set at the test temperature. A 15–20-mL portion of solution at the test temperature is poured into a 25-mL beaker, which is placed inside a water bath within the water jacket. Five minutes was allowed for surface tension equilibration before measurements began.

Zeta potential measurements were made using a Zeta Meter Model D system.

### Results and Discussions

Surface tension curves for various mixtures of dodecyloxyheptaethoxyethyl alcohol (C<sub>12</sub>EO<sub>6</sub>) and sodium

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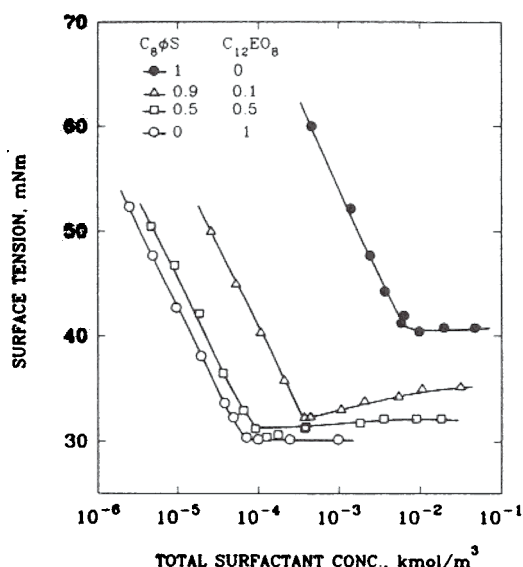


Figure 1. Surface tension vs total surfactant concentration for  $C_8$ -benzenesulfonate and  $C_{12}EO_8$  alcohol and their mixtures of different compositions: 50 °C, 0.03 M NaCl.

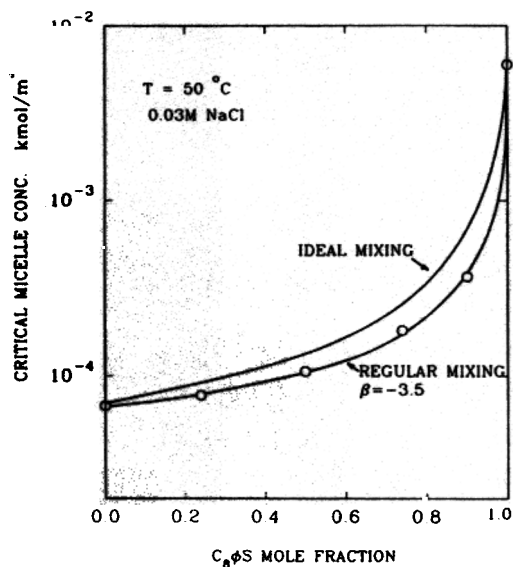


Figure 2. Measured cmc and theoretical cmc calculated from ideal mixing and regular mixing for  $C_8$ -benzenesulfonate and  $C_{12}EO_8$  alcohol and mixtures as a function of composition.

$p$ -octylbenzenesulfonate ( $C_8PhS$ ) are given in Figure 1. Surface activity is greater for the nonionic species and decreases as the percentage of sulfonate is increased. Critical micelle concentrations of the mixtures determined by surface tension measurements plotted in Figure 2 as a function of surfactant composition suggests a regular solution behavior with an interaction parameter of  $-3.5$ . Literature values for the interaction parameter between ethoxylated alcohols and anionic surfactants range from  $-2$  to  $-5$ <sup>11-13</sup> and the interaction parameters for the present system are within this range.

The adsorption isotherms of sodium  $p$ -octylbenzenesulfonate ( $C_8PhS$ ) and dodecyloxyheptaethoxyethyl al-

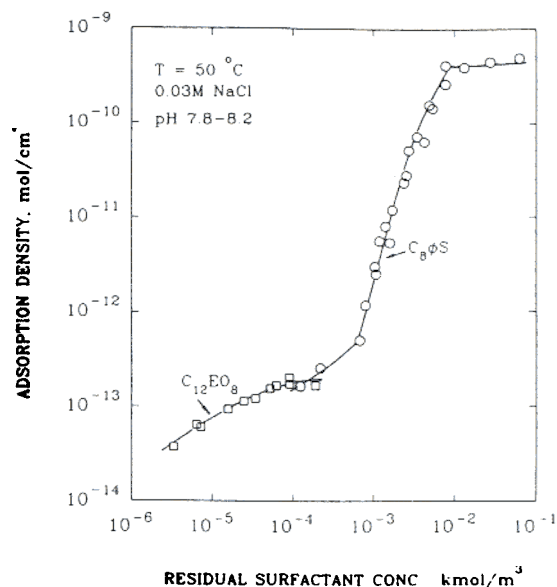


Figure 3. Adsorption of  $C_8$ -benzenesulfonate and  $C_{12}EO_8$  alcohol on alumina.

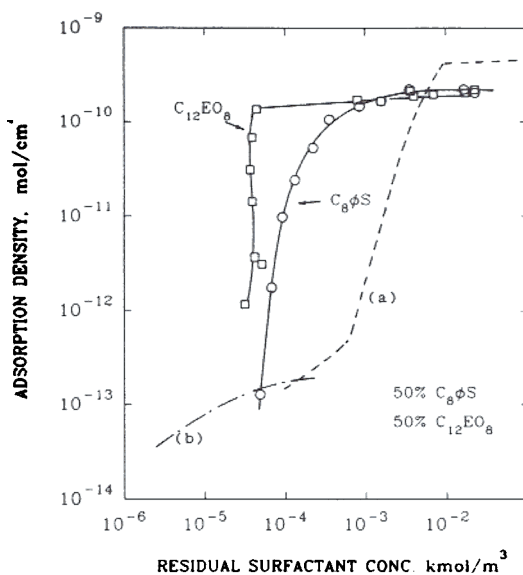


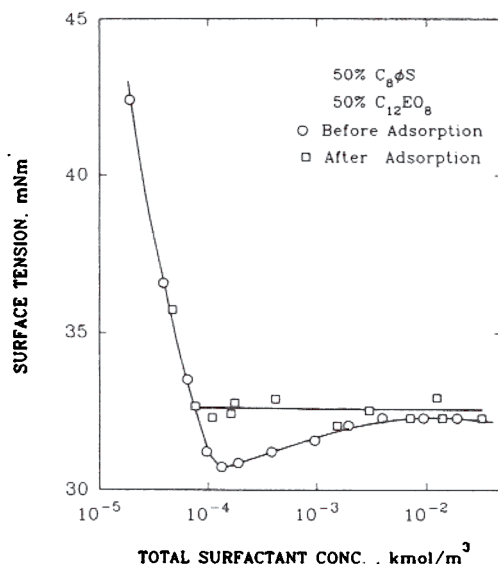
Figure 4. Adsorption of  $C_8$ -benzenesulfonate and  $C_{12}EO_8$  alcohol from mixtures at initial composition of 50 mol % sulfonate-50 mol % alcohol as a function of individual residual surfactant concentrations: (a) adsorption of 100%  $C_8$ -benzenesulfonate, (b) adsorption of 100%  $C_{12}EO_8$  alcohol; 50 °C; 0.03 M NaCl.

cohol ( $C_{12}EO_8$ ) on alumina are given in Figure 3. The shape of  $C_8PhS$  adsorption isotherm is typical of that obtained for long-chain alkanesulfonates on mineral oxides.<sup>14</sup> Above a concentration of  $4.5 \times 10^{-4}$  kmol/m<sup>3</sup>, hemimicellization occurs and this region of accelerated adsorption extends to a concentration of  $6.5 \times 10^{-3}$  kmol/m<sup>3</sup>, which corresponds to the critical micelle concentration (cmc). Compared to the adsorption of sulfonate, the plateau adsorption level of the nonionic  $C_{12}EO_8$  is more than 3 orders of magnitude lower. It is apparent that hemimicellization does not occur in this system, as a region of accelerated adsorption is absent.

Figure 4 shows the isotherms for adsorption of sodium  $p$ -octylbenzenesulfonate ( $C_8PhS$ ) and dodecyloxyhepta-

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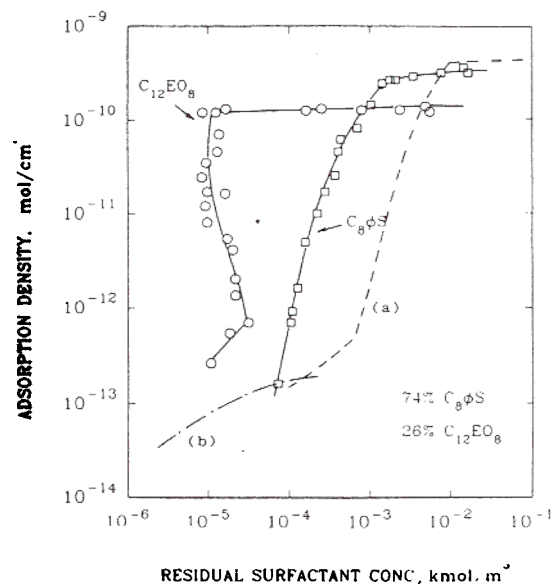


**Figure 5.** Surface tension vs total surfactant concentration for mixtures of  $C_8$ -benzenesulfonate and  $C_{12}EO_8$  alcohol before and after contact with alumina: initial composition 50 mol % sulfonate–50 mol % alcohol; 50 °C; 0.03 M NaCl.

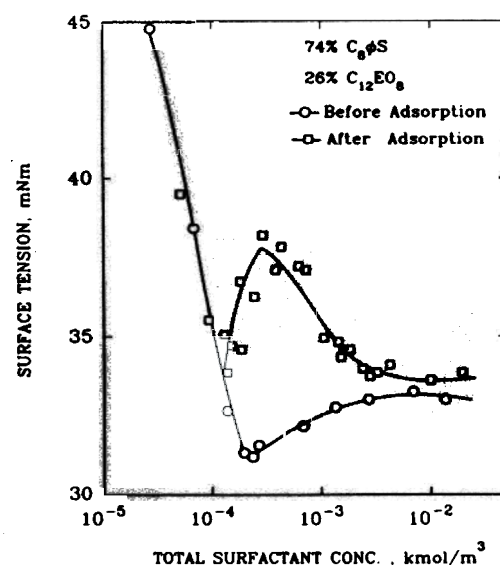
ethoxyethyl alcohol ( $C_{12}EO_8$ ) on alumina from their 1:1 mixtures. It is seen that the ethoxylated alcohol adsorbs to a much greater extent than the sulfonate, even though it exhibited only trace adsorption in the absence of the sulfonate. The preferential adsorption of  $C_{12}EO_8$  from the mixture is also reflected in the surface tension results (Figure 5) where the higher surface tension after adsorption can be considered to be the result from the preferential depletion of nonionic surfactant from the solution.

As a result of the synergism, adsorption of the sulfonate is also markedly increased. The data show that the onset of hemimicellization is lowered by more than an order of magnitude in concentration. The presence of the nonionic surfactant between the sulfonate ions in the hemimicelles should enhance sulfonate adsorption by reducing the lateral electrostatic repulsion between the ionic sulfonate head groups. The effect of synergism is also apparent from a comparison of the slopes of sulfonate adsorption isotherms in the initial hemimicellar region. Coadsorption of the nonionic surfactant leads to an increase of the slope to 6.6 from 3.7 for the pure sulfonate adsorption.

Individual component adsorption isotherms for a surfactant mixture initially consisting of 74 mol % sulfonate and 26 mol % alcohol are given in Figure 6. The general shape of the curves and relative surface activities are similar to the results discussed above for the 1:1 system. However, one striking feature of this system is the increased curvature of the alcohol adsorption isotherm. The slope changes sign between  $2 \times 10^{-5}$  and  $3 \times 10^{-5}$  kmol/m³ and residual concentrations are reduced to  $1 \times 10^{-5}$  kmol/m³ before the onset of adsorption plateau. The surface tension results obtained with the solutions after contact with the mineral clearly support these results. The maximum in surface tension as shown in Figure 7 is caused by the excess depletion of the alcohol from solution. A similar trend is also apparent in Figure 5 for the 50 mol % sulfonate system, but to a much lesser extent. Such behavior indicates an increase in the adsorption energy of the nonionic species relative to that of the anionic one. As adsorption of sulfonate increases, the surface becomes more negative and further adsorption of sulfonate becomes unfavorable. The change in the curvature of  $C_{12}EO_8$  isotherm in Figure 6 indicates that incremental sulfonate adsorption requires



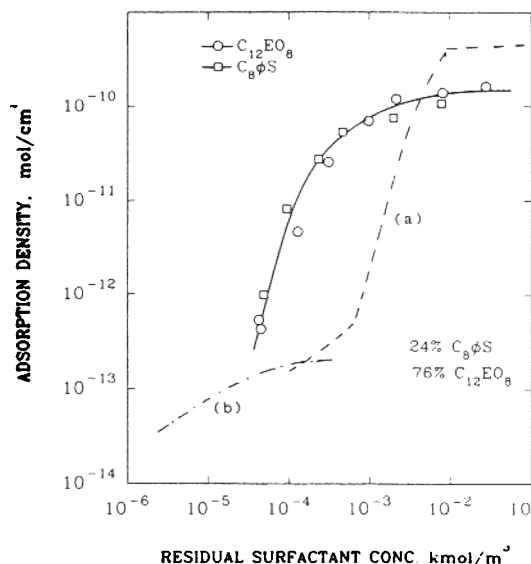
**Figure 6.** Adsorption of  $C_8$ -benzenesulfonate and  $C_{12}EO_8$  alcohol from mixtures at initial composition of 74 mol % sulfonate–26 mol % alcohol as a function of individual residual surfactant concentration: (a) adsorption of 100%  $C_8$ -benzenesulfonate, (b) adsorption of 100%  $C_{12}EO_8$  alcohol; 50 °C; 0.03 M NaCl.



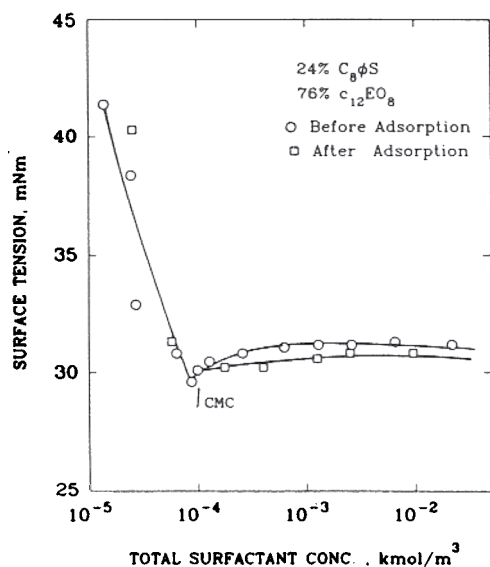
**Figure 7.** Surface tension vs total surfactant concentration for mixtures of  $C_8$ -benzenesulfonate and  $C_{12}EO_8$  alcohol before and after contact with alumina: initial molar composition 74 mol % sulfonate–26 mol % alcohol; 50 °C; 0.03 M NaCl.

additional nonionic surfactant to reduce electrostatic repulsion, such that the concentration of the nonionic  $C_{12}EO_8$  can actually decrease.

Component adsorption isotherms for 24 mol % sulfonate/76 mol % alcohol compositions are given in Figure 8. It is apparent that the relative surface activities of the species are closer to each other and the slope of the adsorption isotherm less than those of the two mixtures discussed previously. The reason for these differences becomes obvious upon examining the surface tension curve of this system given in Figure 9. Surface tension results show the cmc to be below  $1 \times 10^{-4}$  kmol/m³, which corresponds to a point in the initial hemimicellar region. Therefore, adsorption through most of the concentration range occurs from micellar solutions. The variation in monomer concentrations for each component in this



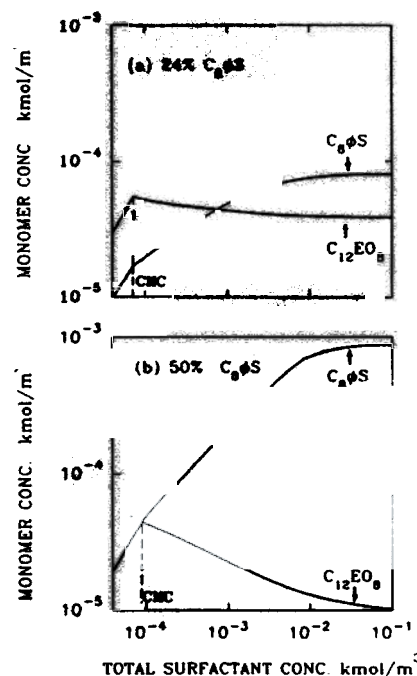
**Figure 8.** Adsorption of  $C_8$ -benzenesulfonate and  $C_{12}EO_8$  alcohol on alumina from mixtures at initial molar composition of 24 mol % sulfonate–76 mol % alcohol: (a) adsorption of 100%  $C_8$ -benzenesulfonate, (b) adsorption of 100%  $C_{12}EO_8$  alcohol; 50 °C; 0.03 M NaCl.



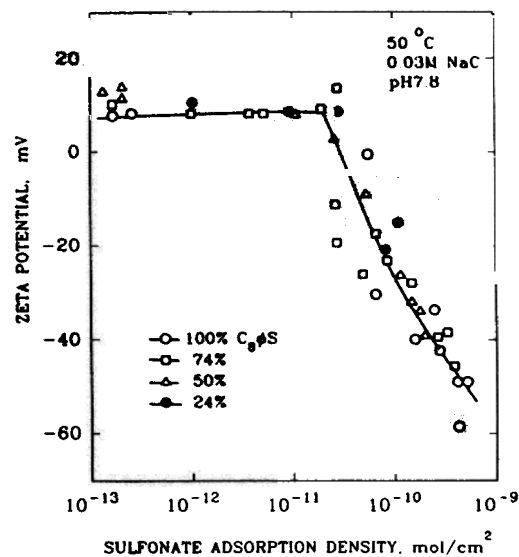
**Figure 9.** Surface tension vs total surfactant concentration for mixtures of  $C_8$ -benzenesulfonate and  $C_{12}EO_8$  alcohol before and after contact with alumina: initial composition 24 mol % sulfonate–76 mol % alcohol; 50 °C, 0.03 M NaCl.

system is calculated in Figure 10a using the “best fit” regular solution interaction parameter of  $-5.0$ . The figure indicates that sulfonate monomer concentration increases by 1 order of magnitude above the cmc as compared to 2 orders of magnitude above cmc for 50% sulfonate system (Figure 10b). Thus, an increase in sulfonate adsorption with concentration should be expected to occur in this system, but at a reduced rate. Since adsorption of the nonionic surfactant is dependent on the generation of a hydrophobic microdomain by the sulfonate species, the reduced sulfonate adsorption rate leads to a slow increase of adsorption of the nonionic  $C_{12}EO_8$ .

Figure 11 compares the zeta potential of alumina for various surfactant compositions as a function of the sulfonate adsorption density. Results indicate that a single curve is adequate for fitting the data, although the levels



**Figure 10.** Monomer concentrations calculated from regular mixing theory for mixtures of (a) 24%  $C_8$ -benzenesulfonate–76%  $C_{12}EO_8$  alcohol and (b) 50%  $C_8$ -benzenesulfonate–50%  $C_{12}EO_8$  alcohol; 50 °C; 0.03 M NaCl.



**Figure 11.** Zeta potential of alumina after adsorption of  $C_8$ -benzenesulfonate and  $C_{12}EO_8$  alcohol as a function of sulfonate adsorption density for various surfactant compositions: 50 °C, 0.03 M NaCl.

of alcohol adsorption differ substantially among these systems. Thus, the data indicate that the eight ethoxyl groups are insufficient to mask or even partially mask the alumina surface and the synergism for mixture adsorption mainly arises from the hydrophobic interaction of the surfactants at the alumina–water interface as well as in the bulk solution.

### Conclusions

Results obtained with mixtures of a nonionic/anionic surfactant system have shown more complex behavior compared to those of single surfactant systems. Ethoxylated alcohol itself showed only trace adsorption on

alumina, but it was clear that the adsorption can be enhanced by orders of magnitude by the introduction of the anionic sulfonate. It is suggested that the initial electrostatic adsorption of sulfonate provides a sufficient number of hydrophobic sites for hemimicellar type adsorption of ethoxylated alcohol to occur. Such a mechanism is analogous to the surface nucleation phenomenon, where the primary adsorbing species acts as a catalytic agent for the adsorption of the secondary species. The inclusion of nonionic surfactant in the adsorbed layer can be expected to reduce the electrostatic repulsion between the sulfonate head groups in the layer and enhance

markedly the hydrophobic interaction among the hydrocarbon chains of the adsorbed nonionic and ionic surfactant molecules and thus increase their adsorption markedly.

**Acknowledgment.** Financial support of the National Science Foundation (CTS-89-21570), Department of Energy, Unilever Research, and BP America is gratefully acknowledged.

**Registry No.**  $C_{12}E_8$ , 3055-98-9;  $Al_2O_3$ , 1344-28-1;  $C_8H_{17}C_6H_4SO_3Na$ , 6149-03-7.