

all surface charge densities and aggregate radii studied. Moreover, for divalent counterions, Figure 9 shows that the surface polarization may cause at most an increase of  $D/D_0$  by a factor of 10, but the effect of ion-ion correlations is a decrease of  $D/D_0$  by 1000 to 10000. This more dramatic consequence on the diffusion due to the correlation effect found for divalent counterions is mainly connected with the reduction of  $g(r)$  at large  $r$  (see, e.g.,  $g(R_c)$  in Table II and in Figure 5) and leads to a lower potential of mean force at the micellar surface and to a larger potential barrier between the micelle and the cell boundary.

### Conclusions

Expressions for the reaction field in systems with spherical dielectric discontinuities have been casted into an image charge form by defined approximations. The image approximation in spherical symmetry has been tested in a cell model of ionic micellar systems by Monte Carlo simulations.

The influence of the surface polarization, compared with the direct ionic interaction, increases with decreasing surface charge density and with increasing counterion charge. However, the magnitude of the polarization effect is very sensitive to the location of the dielectric boundary. If the dielectric discontinuity is more

than a few angstroms within the micellar hard core radius, the effect is almost negligible. But, on the other hand, when the dielectric discontinuity and the micellar hard core superimpose there is an appreciable shift of the maximum of the counterion distribution away from the micellar surface and the fluctuations of the counterion distribution from the spherical symmetry are decreased. The lower degree of counterion accumulation around the micelle leads to a higher osmotic pressure and a higher self-diffusion of the counterions.

The large uncertainty of the location of the dielectric radius in a continuum model impedes a more direct comparison of the polarization effects with experimental data. However, some recent NMR data by Kahn et al.<sup>25</sup> indicate that divalent counterions do not replace monovalent counterions to the extent which is predicted by the PB equation or by simulations in the primitive model. Kahn et al. suggest that these experimental results could be understood in terms of dielectric effects.

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## Use of a Nitroxide Spin Probe To Study the Structure of the Adsorbed Layer of Dodecyl Sulfate at the Alumina-Water Interface

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A nitroxide spin probe is used to examine the process of hemimicelle formation of the anionic surfactant sodium dodecyl sulfate (SDS) adsorbed on alumina by ESR spectroscopy of the slurry. It is found that, at low SDS concentrations, the probe itself aggregates on the surface. As the SDS concentration is raised such that SDS hemimicelles form, the probe aggregates are broken up, and the resulting ESR spectrum is consistent with the nitroxide being within the SDS hemimicelles with a local viscosity of 120–165 cP.

The adsorption of surfactants on charged particulate solids is a process of fundamental importance in the fields of flotation,<sup>2</sup> detergency,<sup>3</sup> enhanced oil recovery,<sup>4</sup> and lubrication.<sup>5</sup> Adsorbed surfactants create unique chemical microenvironments that differ in many respects from the properties of either the bulk solution or the adsorbed solvent around the solid. It has been established that the adsorbed layer consists of localized aggregates, termed hemimicelles.<sup>6</sup> Conventional methodology for the study of such systems has involved the measurement of bulk properties<sup>7</sup> (adsorption isotherms,  $\zeta$  potentials, particle wettability, and heats of adsorption) that do not give direct information on the molecular structure and dynamics of the adsorbed surfactant layer. Other common methods involve procedures that are likely to alter the system in question (e.g., freezing). Recently, we reported the use of pyrene and dinaphthylpropane (DNP) excimer fluorescence as probes of the molecular structure of sodium dodecyl sulfate (SDS) on alumina.<sup>8</sup>

Nitroxide spin probes have been widely used in the field of biology to study the structure of membranes, enzymes, and nucleic acids.<sup>9</sup> Spin probes have also been useful in the study of micelles in solution.<sup>10</sup> For these studies the anisotropy of the ESR spectra due to hindered rotational freedom of the spin probe has provided not only rotational time constants for the probe but also information on the dynamic nature of the binding itself. The ESR

spectrum provides information on the local viscosity and the local polarity of the microenvironment of the probe. In this paper, we report the use of a nitroxide spin probe for study of the structure of an alumina-bound surfactant, SDS. The information obtained from this relatively simple and convenient technique complements

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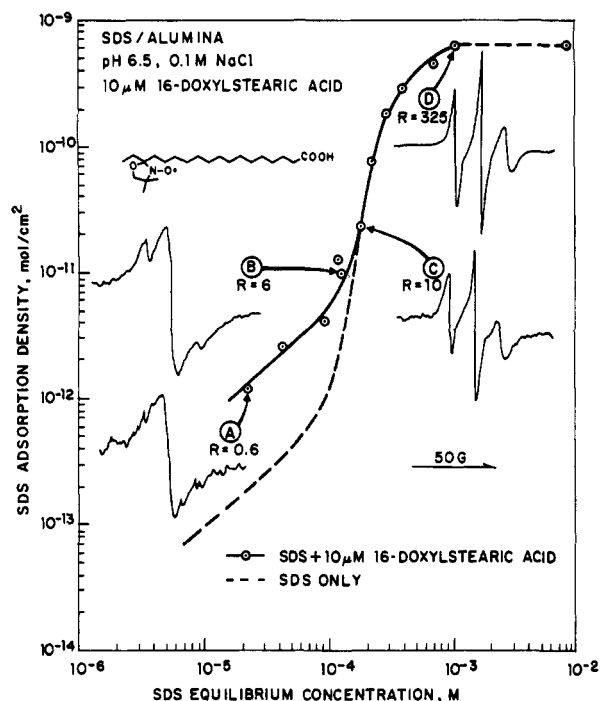
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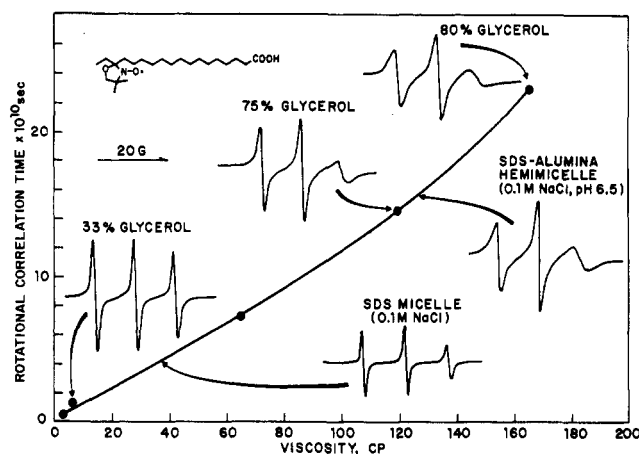
**Figure 1.** Adsorption isotherm of SDS on alumina in the absence and presence of **1** together with representative ESR spectra of **1**.  $R$  is [adsorbed SDS]/[adsorbed probe].

our work using fluorescence methods as well as classical methods.<sup>8</sup>

The spin probe used in these studies was 16-doxylostearyl acid (**1**) which has been used extensively in studies on membrane structure<sup>11</sup> and was chosen because its long-chain alkyl group and polar carboxyl functionality should allow it to form cohemimicelles with SDS. The anionic sulfate moiety of SDS and the carboxylate function of the spin probe adsorb electrostatically to the positively charged (at neutral pH) alumina surface.<sup>12</sup>

Our first investigation involved determining how much of a perturbation the probe makes on the system we are studying. For this purpose, we measured the adsorption isotherm for binding of the SDS on alumina in the presence of the probe **1**. As can be seen in Figure 1, the shape of the adsorption isotherm is similar to that found for the system in the absence of the probe. Significant deviations do occur, however, at low SDS concentrations where an enhancement in SDS adsorption is observed. This enhancement can be attributed to the synergistic coadsorption of the surfactant with **1**.

Whereas the ESR spectrum of **1** in aqueous solution shows the typical isotropic three-line spectrum characteristic of nitroxides, the spectrum in an aqueous slurry of alumina and adsorbed SDS is distinctly different from the solution spectrum and changes markedly as a function of SDS concentration.<sup>13</sup> Three types of ESR spectra are observed, corresponding to different regions in the adsorption isotherm. At low SDS concentrations ( $<150 \mu\text{M}$ ; surface coverage of  $17 \times 10^{-12} \text{ mol/cm}^2$ ), the probe aggregates heavily on the surface, leading to a spin-exchange narrowed spectrum consisting of one broad peak (Figure 1A). The interpretation of this spectrum as resulting from spin exchange is consistent with similar spectra reported with nitroxide aggregates.<sup>10</sup> It should be noted that this spectrum differs from the frozen



**Figure 2.** ESR spectra and calculated rotational correlation time constants (as in ref 18) in ethanol-glycerol mixtures, SDS micelles, and SDS-alumina hemimicelles (point D in Figure 1).

spectrum of nitroxides obtained when such probes are rigidly bound to surfaces;<sup>14</sup> however, we cannot rule out the possibility of the probe being rigidly bound to the surface as well as aggregated.<sup>15</sup> The role of the alumina surface in promoting aggregation is clear in this case since no probe aggregation is noted in aqueous solution at this concentration ( $10 \mu\text{M}$ ). As the SDS concentration is raised sufficiently to allow significant surface aggregation of the SDS (hemimicelle formation), a sharper, anisotropic spectrum is obtained. In the second region (Figure 1B) the spectrum consists of components due to surface-bound and solubilized probe. In the third region (Figure 1C) SDS hemimicelle formation leads to the complete breakup of the surface aggregates of the probe; therefore, each nitroxide no longer interacts strongly enough with other nitroxides to result in exchange narrowing of the spectrum. In the absence of spin exchange, the spectrum that is obtained is anisotropic due to the high local viscosity. A calibration curve of relative rotational time constants for **1** in mixtures of ethanol/glycerol (Figure 2) shows that the hemimicelle spectrum is similar to that obtained in 75–80% glycerol (120–165-cP viscosity).<sup>16</sup> This spectral similarity can be used operationally to define a microviscosity, that is, the local viscosity of the heterogeneous environment is the homogeneous viscosity that results in a similar ESR spectrum of the probe. This value is similar to the value determined for SDS hemimicelles using DNP excimer fluorescence measurements (90–120 cP).<sup>8</sup> This viscosity is markedly higher than that obtained for the probe in SDS micelles using this ESR technique (approximately 45 cP with 0.1 M NaCl). The change between the two types of ESR spectra occurs over a relatively sharp region of SDS concentrations and is consistent with the location of the two major regions of the adsorption isotherm (Figure 1): the spectrum is exchange narrowed until the onset of hemimicellization where an anisotropic, solution spectrum is obtained. At higher SDS concentrations, the spectrum remains essentially unchanged (Figure 1D). This suggests that the aggregate structure does not change appreciably as a function of SDS surface coverage.

The  $^{14}\text{N}$  hyperfine splitting constant ( $A_N$ ) obtained for the spectrum shown in Figure 1D was 15.0 G. This value can be compared to those obtained for **1** in ethanol (14.6 G) and in water (16.0 G). The smaller  $A_N$  value for **1** in the SDS hemimicelle compared to **1** in water is consistent with the nitroxide being in the less polar environment of a hemimicelle. However, the relative polarity is still higher than that of a hydrocarbon environment (14.1 G for **1** in dodecane<sup>17</sup>).

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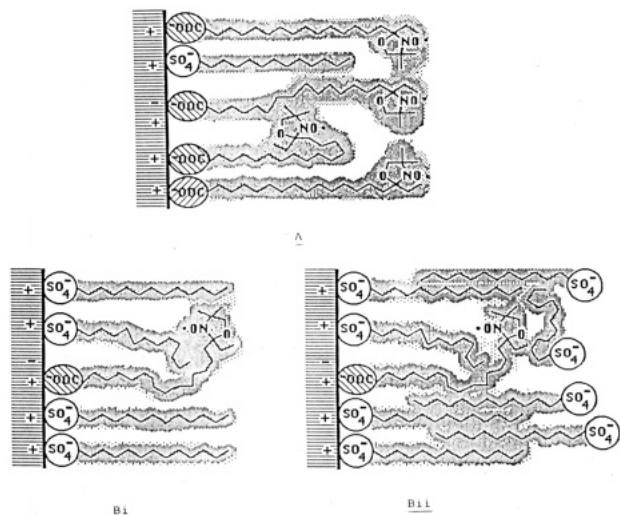
(13) Samples were prepared by addition of a known volume of 0.1 M SDS (Fluka Chemicals) solution containing  $10 \mu\text{M}$  **1** (Aldrich) to 0.5 g of alumina (Linde A grade, Union Carbide Corp.  $0.3 \mu\text{m}$ ,  $15 \text{ m}^2/\text{g}$  surface area). Sufficient NaCl was added to bring the salt concentration to 0.1 M (total volume of 15 mL). HCl (aqueous) was added to bring the pH to 6.5. The mixture was then stirred for 12 h. The ESR spectra were recorded on a Bruker 100D ESR X-band spectrometer using a quartz flat cell for the measurements.

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**Figure 3.** Schematic representation of (A) probe aggregates on alumina at low (subhemimicellar) concentrations, (B) probe incorporated in SDS-alumina hemimicelles [(i) monolayer, (ii) bilayer].

Several control experiments were also performed. At both the subhemimicellar and hemimicellar regions, centrifuging the slurry demonstrated that no probe is present in the supernatant. As the pH of the aqueous slurry is raised, the alumina surface no longer is cationic and consequently will no longer electrostatically attract the sulfate or carboxyl moieties. Under conditions of high pH,

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the ESR spectra of slurries both above and below the critical hemimicelle concentration are identical with those obtained from solution spectra, and centrifugation of the slurries indicated that all the probe is in the liquid phase.

The use of ESR spin probes to study the microenvironment of adsorbed surfactants on surfaces represents a simple yet valuable method for obtaining a considerable amount of information on the system. This work suggests a model shown schematically in Figure 3. The probe head groups bind to the surface in aggregate groups such that the nitroxide functions interact strongly (Figure 3A). As SDS hemimicellization occurs, the probe aggregates are dispersed. The nitroxide moieties are in a locally viscous environment (on a time average), consistent with a more densely packed surface aggregate layer of SDS hemimicelles than found with SDS solution micelles. Since the polarity measurements indicate that the nitroxide moieties are not in an aqueous environment, this suggests either that the alkyl chain of **1** curves such that the nitroxide sits in a region partly shielded from the aqueous environment (Figure 3B) or the SDS forms bilayers at the alumina surface such that the nitroxide is present in a hydrophobic region (Figure 3C). Alternatively, a mixture of both aggregation modes may be present at the surface. Since only one type of ESR spectrum is observed at SDS concentrations above the critical hemimicelle concentration, these data suggest that the aggregate structure does not change significantly throughout the adsorption isotherm. Work is currently in progress to address this question and to determine more precisely the nature of the adsorbed layer.

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## Shear Viscosity of Monolayers at the Air-Water Interface

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The in-plane shear viscosity of monomolecular surfactant layers at the air-water interface was measured with high accuracy. For this purpose a simple but sensitive technique was developed. It is applicable to study lipids and long-chain fatty acids that are concentrated at the air-water interface. Measurements are presented for *L*- $\alpha$ -dimyristoylphosphatidylcholine (DMPC), *L*- $\alpha$ -dipalmitoylphosphatidylcholine (DPPC), and palmitic acid in the surface pressure range from 0 to 40 mN/m. At high pressures where DPPC and palmitic acid are known to be largely or completely solid the measured surface viscosities are large. At low pressures all three substances reduce the surface viscosity of water. The above changes in viscosity are in the range in which a connected coverage of the surface is observable for DPPC and DMPC. Upon further expansion of the monolayer the surfactant films undergo a second transition leading to what appears to be a discontinuous coverage of the surface. This is reflected by an abrupt increase of the surface viscosity to that of pure water. This step in surface viscosity is attributed to a change of state of the monomolecular film from one in which the fluid lipid is continuous over the surface to one in which it is discontinuous.

### Introduction

Three methods have been used previously to study the viscosity of surfactant monolayers at the air-water interface. These methods include the barrier-gap flow through system,<sup>1,2</sup> oscillating cylinders,<sup>3</sup> and the damping of capillary waves<sup>4</sup> or surface motion.<sup>5</sup> The method reported here has a significantly higher sensitivity, which makes possible the observation of novel changes in surface viscosity of monolayers at the air-water interface as a function

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