Variation in nitroxide probe chain flexibility within sodium dodecyl sulfate hemimicelles

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apparent as Al content increases.

4. Boron-containing dimers are less stable than their Al-containing analogues. The H form of the boron dimer is the most unstable species. Its hydroxyl group appears less polar than the corresponding one in the Al dimer. These observations support the finding that Brønsted sites in crystalline borosilicates are weak compared to those of their Al analogues. They suggest in addition that tetrahedrally coordinated boron in the hydrogen form of framework borosilicates is unlikely to be highly stable.

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Registry No. Si, 7440-21-3; O_2, 7782-44-7; B, 7440-42-8; Al, 7429-90-5.

Variation in Nitroxide Probe Chain Flexibility within Sodium Dodecyl Sulfate Hemimicelles

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Three nitroxide spin probes (5-, 12-, and 16-doxylstearic acid) were used to investigate the structure of sodium dodecyl sulfate (SDS) micelles and the interfacial layer between water and alumina formed by SDS (hemimicelles of SDS). It was found that whereas the rotational correlation times of the three probes differ in SDS micelles, the effective microviscosities of the probes are the same. In contrast, the microviscosity within the SDS hemimicelles varies according to the distance from the alumina surface: the nitroxide sees a more ordered environment as it is placed closer to the alumina. This represents the first report of variations in flexibility (microviscosity) within a hemimicelle.

The science of the water–solid interfacial layer formed by adsorbed long-chain surfactants on solids has been studied extensively for its value in the fields of enhanced oil recovery,[2] flotation,[3] detergency,[4] lubrication,[5] and microelectronics.[6] Considerable experimental evidence is consistent with the postulate that such surfactants form localized aggregates (termed hemimicelles) on the solid surface.[7] The evidence for hemimicelles has generally been indirect, and hemimicelle structure and dynamics have been inferred from measurements of bulk properties using such techniques as adsorption isotherms, ζ potentials, particle wettability, and heats of adsorption.[8] Recently we reported the use of two types of molecular probes for use in spectroscopic investigations of the hemimicelle microstructure formed by sodium dodecyl sulfate (SDS) adsorbed on alumina. The first involved studies of pyrene and dinaphthylpropane fluorescence,[9] while the second involved the spin probe 16-doxylstearic acid (**1**), a stable nitroxide radical, for use with ESR spectroscopy.[10] The carboxylate functionality of this latter probe adsorbs on the positively charged alumina surface. Our results indicated that at pH 6.5 this probe aggregates mostly by itself on the surface at low SDS concentrations and forms cohemimicelles with the SDS at higher SDS concentrations. The relative anisotropy observed in an ESR spectrum is directly related to the rotational mobility of the probe, a term that can be correlated with the probe's microviscosity.[11] Using this correlation, we were able to deduce that the environment within the SDS hemimicelle is relatively viscous. In both these studies of the microenvironment of the SDS hemimicelle, the data reported represent a single probe position within the hemimicelle (or a time average of many depths from the surface).

Spin probes have been used extensively to study the microviscosity and micropolarity of membranes, multilayers, and micelles.[12] In particular, doxylstearic acid spin probes have been useful in determining these parameters for different probe depths within phospholipid bilayers and micelles. Such studies have provided information on the orientation of the probes within the systems as well as information on the microenvironmental differences within the bilayer or micelle. In this communication, we wish to report the use of three doxylstearic acid derivatives, 16-, 12-, and 5-doxylstearic acids (**1**, **2**, and **3**, respectively) in the ESR investigation of SDS micelles in water and SDS hemimicelles at the water–alumina interface. The results reported here should be viewed as preliminary, bearing in mind the usual

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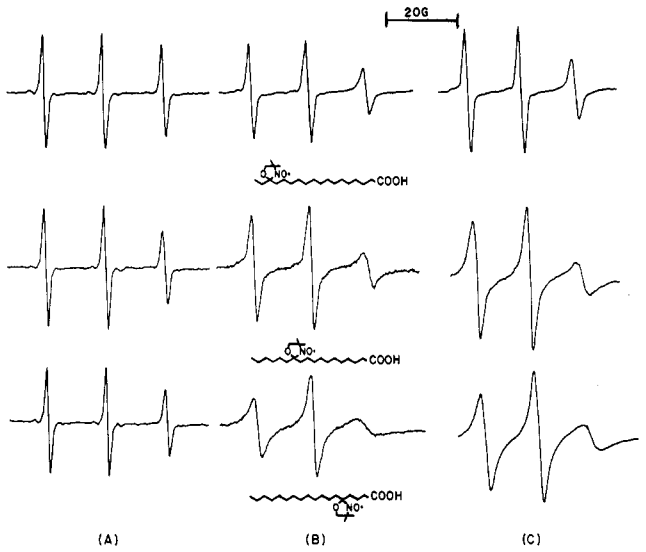

Figure 1. ESR spectra of three probes (10 μM) in (A) submicellar SDS solution (4×10^{-4} M SDS, 0.1 M NaCl), (B) SDS micelles (5.2×10^{-2} M SDS, 0.1 M NaCl) and (C) 60% glycerol, 40% ethanol.

caveat about the possibility of specific probe–substrate interactions being present (distortions of the system by introduction of a probe). However, the fact that these probes form cohemimicelles with SDS on alumina suggests that the probes interact with SDS in a fashion similar to the SDS–SDS interactions present in the absence of probe.

These three probes show very similar ESR spectra in dilute aqueous solution (10 μM) as can be seen in Figure 1A; however, the probes show differences on addition of SDS at concentrations greater than the critical micelle concentration (Figure 1B). The hyperfine splitting (A_N) can be related to the micropolarity of the probe. Previous workers have noted the change in rotational correlation times on going from **1** to **3** yet also found that the micropolarity did not vary.[12c] The variation in rotational correlation times was assumed to reflect the different environments seen by the two probes (**1** and **3**) within the SDS micelle. The micropolarities were originally explained by assuming that water molecules are present in the hydrocarbon core of the SDS micelles;[12c] however, this was later questioned based on a visible spectroscopy study that also showed that the nitroxides of different probes sense the same, polar environment.[13] The authors of this latter study suggested that both the nitroxide and carboxyl moieties of the probes remain in the water–SDS interfacial layer, but this study did not rationalize the variation in rotational correlation times for the different probes. Rather than using rotational correlation times directly to obtain data on the probe microviscosities, we were able to immitate the ESR spectrum of each probe in SDS micelles with spectra in mixtures of ethanol/glycerol of measured viscosities.[14] The ESR spectra of the probes in SDS micelles (Figure 1C) resemble the spectra of the probes in a mixture of 40% ethanol and 60% glycerol (45 cP). The rotational correlation times vary differently as a function of viscosity for the three probes. The result is that although the ESR spectra appear different for **1**, **2**, and **3** in SDS micelles, the viscosity that each probe senses is essentially the same. This then supports the suggestion that all three nitroxide moieties reside in the interfacial (Stern) layer of the micelle.

It was our aim to apply this spin probe technique to the SDS/alumina system in order to determine whether the microviscosity and hence the flexibility of the hemimicellar hydrophobic chains vary within the adsorbed layer. The ESR spectra obtained on addition of the probes to alumina/SDS solutions at SDS concentrations above the critical hemimicelle concentration (chc) are shown in Figure 2A.[15] As can be seen in these spectra, the

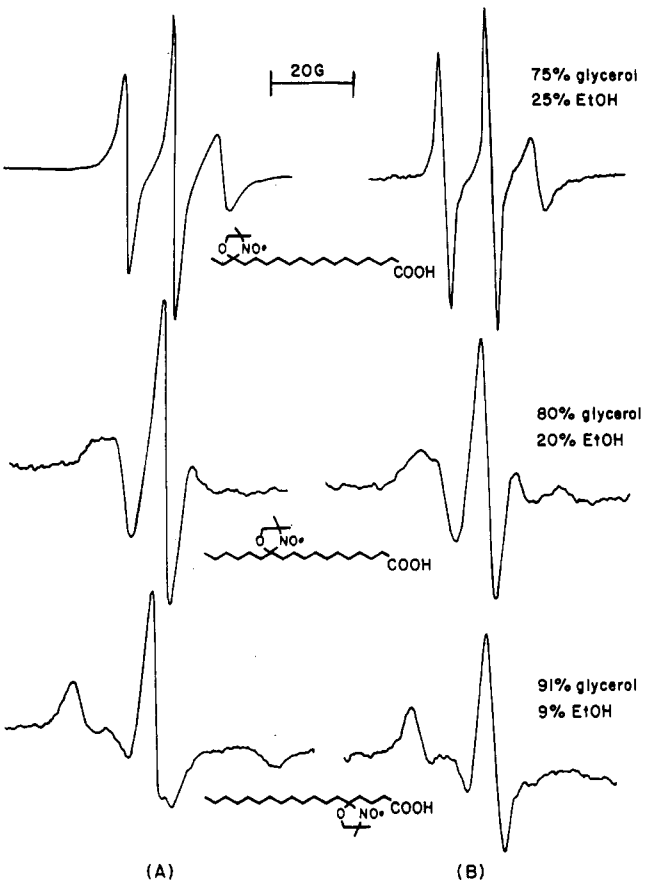

Figure 2. ESR spectra of three probes (10 μM) in (A) SDS/alumina (pH 6.5, 0.1 M NaCl, adsorption density = 4.5×10^{-10} mol/cm^2) and (B) mixtures of glycerol/ethanol.

nitroxides show marked decreases in mobility as compared to the spectra for the probes in SDS micelles (Figure 1B). In both micelles and hemimicelles, the carboxylate termini of the probes can be viewed as immobilized on the time scale of the measurements. As was seen in the SDS micelles, the probes show different spectra as a function of the distance from the immobilized carboxylates; however, whereas the equivalent ESR spectra of the probes in the micelles could be obtained from solutions of the probes at a single EtOH/glycerol ratio, the equivalent ESR spectra for the probes in hemimicelles require different ratios of EtOH/glycerol (75%, 80%, and 91% glycerol for **1**, **2**, and **3**, respectively). For greater distances of nitroxide functionality from the alumina-bound carboxylate, the probe has a greater ability to rotate, suggesting that the probe spends more time in environments of lower viscosity.[16] This indicates that the SDS alkyl chains are more ordered near the alumina–SDS interface than at the SDS–H_2O interface. This represents the first reported indication of variations in microviscosity within a hemimicelle. We suggest that the probe mobility changes reflect the relative ordering of the SDS alkyl chains within the hemimicelle (and analogous ordering of the stearic acid alkyl chain of the probe). Near the alumina surface, packing of SDS alkyl chains is relatively

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(14) Measured by the capillary flow method.

(15) Samples were prepared by adding a known volume of 0.1 M SDS (Fluka Chemicals) solution containing 10 μM probe (Aldrich) to 0.5 g of alumina (Line A grade, Union Carbide Corporation, 0.3 μm, 15 m^2/g surface area). Sufficient NaCl was added to bring the salt concentration to 0.1 M (total volume 15 mL). HCl was added to bring the pH to 6.5 and then the mixture was stirred for 12 h. ESR spectra were recorded on a Bruker Model 100D X-band spectrometer.

(16) It is possible that the nitroxide moieties of the probes are not reflecting the SDS chain mobility but rather the alkyl chain flexibility of the bound probe. However, since the binding behavior of either the carboxyl of the probe or the sulfate of the SDS and the interaction of their long-chain alkyl functions should be similar, we suggest that the variation in the rotational mobility between **1**, **2**, and **3** can be expressed as a model (rather than as a probe) for the SDS hemimicelle. The essential conclusions remain the same, however.

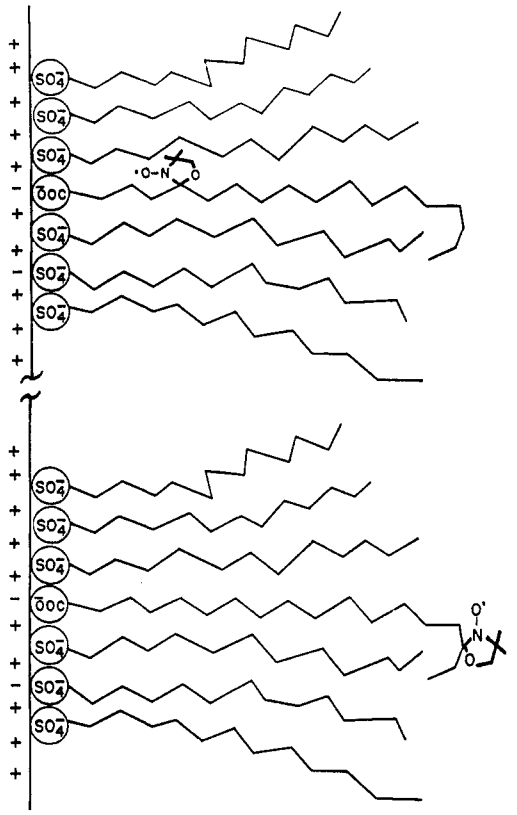

Figure 3. Schematic representation showing the SDS hemimicelle flexibility differences in two probe positions (modeling **1** and **3**).

tight so that rotational mobility is severely restricted. Further from the solid surface the alkyl chains can spread out such that the flexibility of the system increases. This is shown pictorially in Figure 3. It should also be noted that there is no tendency for the nitroxide moiety to bind to the alumina surface as was demonstrated by adding Tempo (2,2,6,6-tetramethylpiperidino-1-oxy) to an alumina suspension. In this case, the ESR spectrum of this probe was clearly that of the probe in aqueous solution. Centrifugation of the mixture further demonstrated this point.

Because of the highly anisotropic nature of the spectra in the hemimicelles, it is difficult to determine hyperfine coupling constants for the probes **2** and **3**. With **1**, a relatively high value is obtained for the hyperfine splitting (15.0 G). This supports the model shown in Figure 3 where the nitroxide of **1** resides at the water–SDS interface.

ESR spectroscopy with nitroxide spin probes represents a facile method for probing microenvironments. It is possible to determine microviscosities by calibration of the ESR spectra of the probes in solvent mixtures of known viscosities. This method avoids the complications involved in comparing rotational correlation times for different probes, which can vary differently as a function of the solution viscosity, since the response of the probe to solution viscosity is accounted for explicitly. Indeed, the microviscosity can effectively be defined as the homogeneous solution viscosity which results in the same spectrum as that in the microenvironment. With this methodology, while the spin probes **1**, **2**, and **3** were found to be in similar microenvironments in SDS micelles, they sense different microviscosities in SDS hemimicelles as a function of distance from the alumina surface. The flexibility variations indicated by these results provides a more detailed picture of the structure of hemimicelles than that obtainable by classical bulk property measurements.

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Registry No. **1**, 53034-38-1; **2**, 29545-47-9; **3**, 29545-48-0; SDS, 151-21-3.

Cadmium Sulfide/Poly(vinylferrocene)/Gold and Cadmium Sulfide/Polypyrrole/Gold Solid-State Cells

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The fabrication and electrical behavior of solid-state CdS/poly(vinylferrocene)$^{0/+}$(PVF$^{0/+}$)/Au and CdS/polypyrrole$^{0/n+}$(PP$^{0/n+}$)/Au cells are described. Both polymers contact CdS to yield normal Schottky-like (semiconductor/metal) behavior, in the dark and under illumination, when the polymer layers are in the partially oxidized and charged state, PVF$^{0/+}$ and PP$^{0/n+}$. Photocurrent generation in these cells depends strongly upon oxidation state of the dry polymer film. In the partially oxidized state, CdS/PVF$^{+/0}$/Au, photocurrents increase linearly with increasing light intensity. When the polymer film is in the fully reduced and neutral state, CdS/PVF^{0}/Au, the observed photocurrents are ca. 2 orders of magnitude smaller and nearly independent of incident light intensity. A similar dependence of photocharacteristics on oxidation state is observed for the CdS/PP/Au cell. An analysis of the photovoltaic cell response under redox polymer charge-transport control is presented.

Introduction

A difficulty with photoelectrochemical cells for the conversion of solar to electrical or chemical energy is the tendency of the photoactive cathode or anode to passivate or dissolve in solution.[1-3] These corrosion reactions are especially deleterious in aqueous solutions where water plays a key role in the solvation of electrode lattice ions or supplies oxygen for forming passive oxide layers. Recently, several reports have described solid-state photovoltaic devices constructed by sandwiching a thin and dry electroactive polymer film between semiconductor and metal electrodes.[4-7] In

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