Neutron Reflectivity Studies of Surfactants at Electrode Surfaces

Knowledge of the forces that control the assembly of surfactant molecules at the solid-liquid interface is vital for traditional fields such as detergency, flotation, oil recovery and tribology [1]. Thin organic films deposited at solid surfaces also find application in the fabrication of optoelectronic devices, sensors, biosensors, and chemically modified electrodes [2]. It has long been established that the assembly of surfactants at the solid-liquid interface depends on the charge at the solid surface [3, 4]. For example, the spreading of vesicles into a phospholipid bilayer requires that the surface of the solid be negatively charged and hydrophilic.

However, the present understanding of the role played by charge on the interaction of a surfactant molecule with the electrified solid surface is far from being complete. Electrochemistry provides a unique opportunity to study the effect of the charge on the properties of amphiphilic and ionic surfactants at the charged solid-liquid interface [5]. When an organic film is deposited on a gold electrode, the charge density at the metal surface may be varied from about 30 μC/cm^2 to about 40 μC/cm^2. This magnitude of charge generates electric fields on the order of 10^{10} V/m. Such a field interacts with polar molecules in the membrane. By changing the sign of the charge one can use attractive or repulsive forces. In this manner, by turning a knob on a control instrument one can force phase transitions in the film of organic molecules or force surfactants to desorb or re-adsorb on the surface.

We have recently employed electrochemical techniques, atomic force microscopy, and neutron reflectivity to study the field driven transformations of thin films formed by a model anionic surfactant, sodium dodecyl sulfate (SDS), at the surface of a gold electrode [6]. Figure 1 shows how the surface concentration of SDS at the Au electrode surface changes with the electrode potential. A convenient way to interpret these data is to look at the electrode potential as an operational variable that can be easily adjusted using a control instrument.

Figure 1 shows that the character of SDS adsorption is strongly influenced by the charge on the metal. At sufficiently negative potentials SDS molecules are totally desorbed from the electrode surface. At moderate negative charge densities SDS forms a film characterized by a limiting surface concentration 4.0 x 10^{-10} mol cm^{-2}. When the metal surface is positively charged the surface concentration of SDS increases to 8.1 x 10^{-10} mol cm^{-2}.

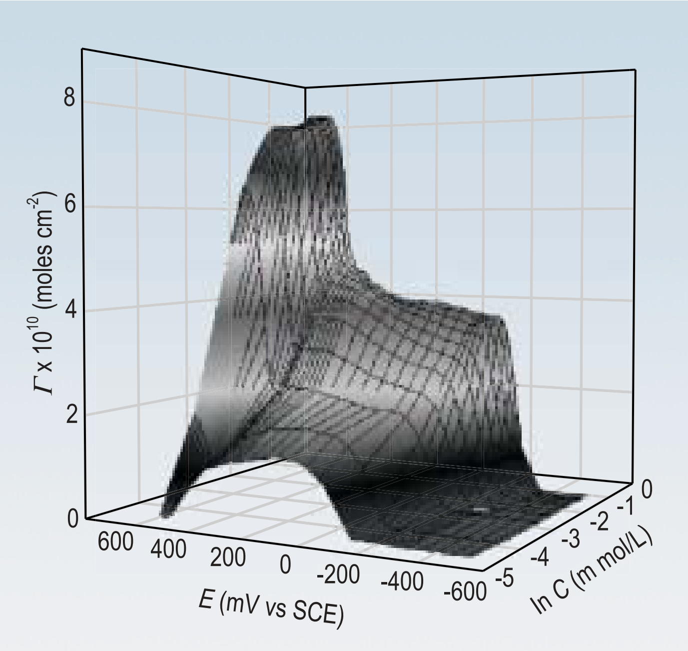

FIGURE 1. Three dimensional plots of the surface concentration of SDS as a function of electrode potential measured versus the calomel reference electrode (SCE) and the logarithm of the bulk SDS concentration.

Neutron reflectivity experiments carried out on the NG-7 reflectometer were employed to determine the structure of the film formed by SDS at different charge densities at the gold surface. Thin layers of chromium (≈ 20 Å) and gold (≈ 80 Å) were sputtered onto the crystal quartz substrate. After cleaning, the crystal was mounted on a specially constructed Teflon® cell [7]. The cell had ports for the counter (gold foil) and reference electrodes (Ag/AgCl, $E \approx -40$ mV versus SCE). D$_2$O (99.9 % molecular fraction) was used as a solvent in reflectivity studies.

Figure 2a shows the neutron reflectivity data determined for SDS adsorption at various electrode potentials, and Fig. 2b shows the scattering length density profiles calculated from the reflectivity curves. The neutron reflectivity data are consistent with electrochemical measurements. They show that at very negative potentials the gold solution interface is free from hydrogenated species. When

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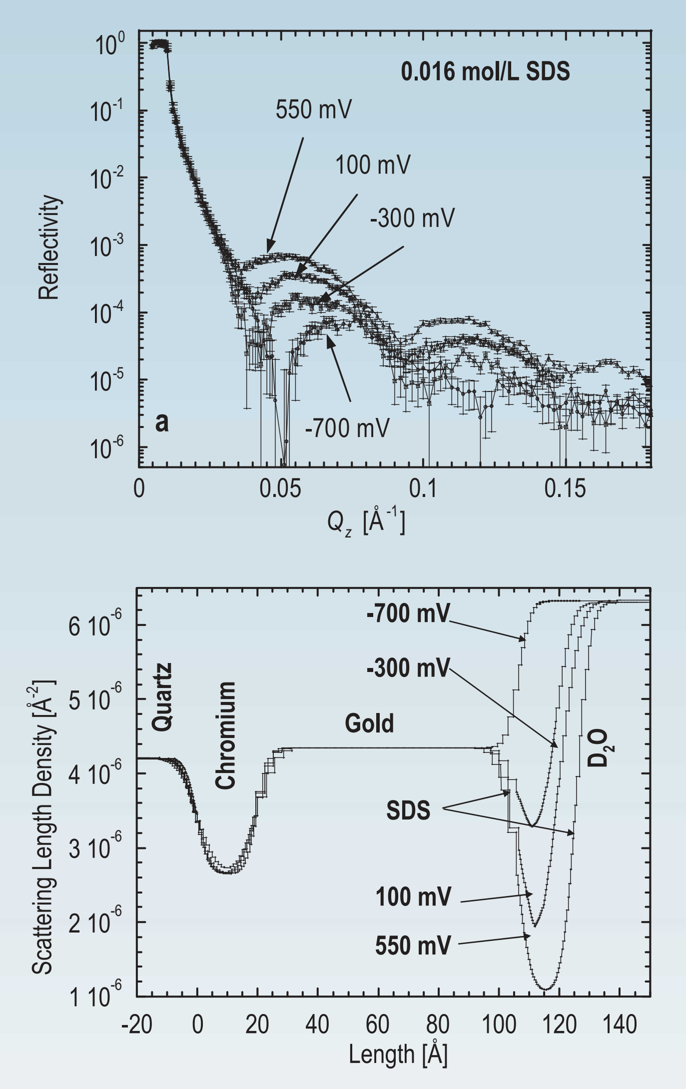

FIGURE 2. (a) Normalized neutron reflectivity curves for a Au/Cr-coated quartz substrate in 0.016 mol/L SDS in D_2O. (b) Scattering length density profiles of the interface as determined from the fitting procedure.

the potential increases, the film of hydrogenated species appears at the electrode surface. The thickness of this film increases, and the scattering length density progressively decreases, with increasing potential. When combined with the results of electrochemical measurements and atomic force imaging, the neutron reflectivity data allow the determination of the structure of the film formed at different charge densities. At small or moderate negative charge densities SDS molecules form a hemimicellar film that consists of hemicylindrical stripes, as first observed by Manne [4]. The packing of SDS molecules in a cross section of that hemicylinder is shown schematically in Fig. 3 (top). At positive charge densities the hemimicellar state is transformed into the interdigitated bilayer schematically shown in Fig. 3 (bottom).

The results of this study demonstrate the need for the use of neutron reflectometry to study adsorption and phase transitions in films of surfactants adsorbed at the solid-solution interface. Specifically, they show that when neutron reflectivity measurements are combined with electrochemical studies and atomic force microscopy, they provide unique opportunities to study different stages involved in the interaction of surfactants with solid surfaces.

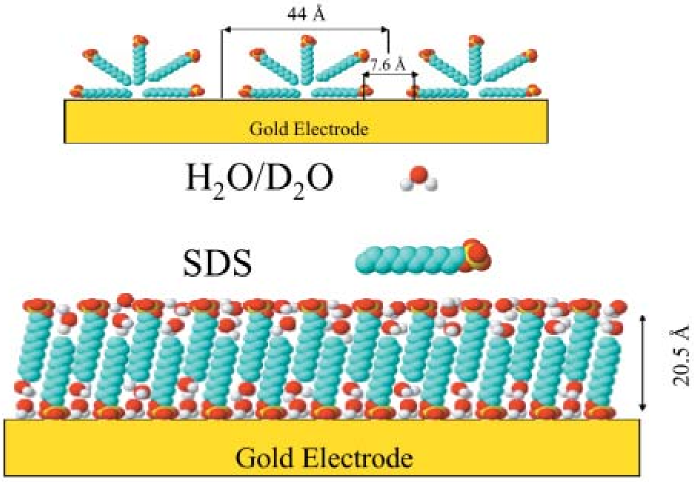

FIGURE 3. Models of SDS adsorption at the Au-solution interface: (top) cross section of hemicylindrical aggregates observed at moderately negative charge densities; (bottom) interdigitated bilayer observed at positive charge densities.

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