

Observation of Molecular Ordering at the Liquid–Liquid Interface by Resonant Sum Frequency Generation

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Amphiphilic molecules are known to spontaneously order at liquid–solid¹ and liquid–air interfaces,² forming well-ordered layers, but little is known about the structure of these molecules at the liquid–liquid interface due to experimental inaccessibility. A number of linear and nonlinear spectroscopic studies of surfactants at this interface have been performed,^{3–6} but these studies could not probe alkyl chain ordering. The goal of our work has been to measure the vibrational spectrum of a simple surfactant at an interface between two immiscible liquids in order to understand how such surfactants orient and assemble at this interface. In this communication, we report the first measurement of this type where the vibrational spectrum of sodium dodecyl sulfate (SDS) at the D₂O–CCl₄ interface is obtained. The results provide spectroscopic evidence for interfacial ordering. The success of these studies has come from performing sum frequency generation (SFG) measurements in a total internal reflection geometry (TIR).

Surface SFG is gaining in use as a probe of surfaces and buried interfaces and is thoroughly described in the literature.^{7–15} SFG is more powerful than conventional spectroscopies such as FTIR because of its inherent surface selectivity, and for this reason, SFG is an excellent probe of interfaces. In TIR-SFG, selective probing of the interface between the two phases is obtained with much greater sensitivity than normal SFG much in the way that attenuated total reflectance FTIR gains its sensitivity. Using resonant TIR-SFG, the vibrational spectrum of the surfactant SDS at the D₂O–CCl₄ interface has been obtained, shown in Figure 1. This spectrum of a full monolayer at the interface was obtained using a bulk concentration of 10 mM SDS.

To ascertain the order of SDS as a function of surface concentration, the intensities of the methyl and methylene symmetric stretch peaks in the sum frequency spectra are examined at 10 mM SDS and at several successive lower concentrations. The data in Figure 2 show the symmetric stretch region for methyl (2866 cm⁻¹) and methylene (2840 cm⁻¹) groups as the concentration of SDS is changed from 0.1 to 5 mM. The surface coverage of SDS is determined from the corre-

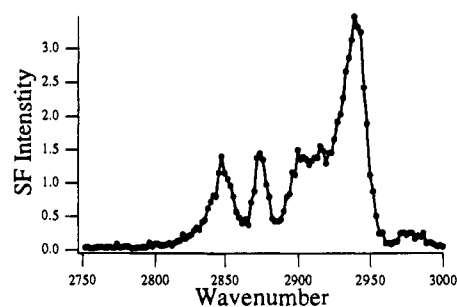


Figure 1. SF spectrum of SDS at the D₂O–CCl₄ interface obtained with a 10 mM concentration of SDS in D₂O. The polarization of light was s output, s visible, p infrared. Peak assignments are as follows: 2840 cm⁻¹ methylene symmetric stretch, 2866 cm⁻¹ methyl symmetric stretch, 2894 cm⁻¹ methylene Fermi resonance, 2928 cm⁻¹ methylene asymmetric stretch, 2960 cm⁻¹ methyl asymmetric stretch.

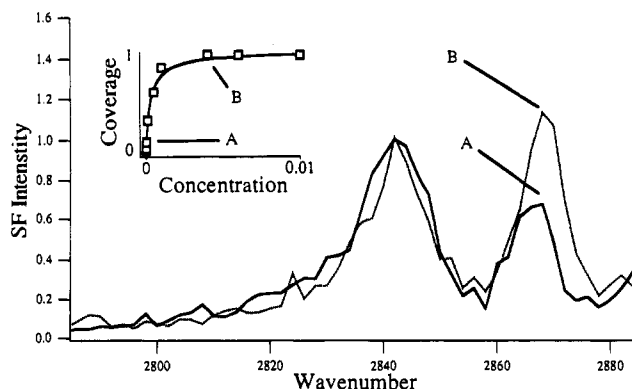


Figure 2. SF spectrum of SDS at the D₂O–CCl₄ interface for various SDS concentrations: —, 0.1 mM; ···, 5.0 mM. Inset: Isotherm data for SDS at the H₂O–CCl₄ interface at 20 °C, concentration in mol/L. The polarization of light was s output, s visible, p infrared. Data are fitted to a Frumkin isotherm which describes adsorption of repulsively interacting adsorbates to an interface.

sponding bulk concentration as shown by the adsorption isotherm for SDS at the H₂O–CCl₄ interface in the inset of Figure 2. This data reveals a distinct change in the methyl symmetric stretch intensity with increasing surface coverage. Methyl peak intensity is determined by the average orientation of the methyl group symmetric stretch transition dipole component perpendicular to the surface. The number of gauche defects in the alkyl chain affects the intensity of the methyl peaks, as large numbers of gauche defects cause random methyl group orientation.¹⁶ These results show that the closer packing of the alkyl chains at high concentrations allows for fewer gauche defects within the alkyl chain. The increase in methyl peak intensity is thus indicative of an ordering of the alkyl chains, as the methyl groups possess an average orientation that is more closely perpendicular to the surface with higher surface coverages. This has been observed in other self-assembling systems in which the tighter molecular packing at higher surface coverages induces ordering of the alkyl chains through chain–chain interactions.^{15–17} With the increase in surface concentration, a reduction in gauche defects takes place within the alkyl chain, shown schematically in Figure 3. To more completely examine the effect of concentration on monolayer order, the ratio of methyl to methylene intensity is plotted as a function of the bulk concentration in Figure 4. From this graph, it is confirmed that the intensity ratio reflects a chain ordering that occurs as surface coverage of the surfactant increases. A

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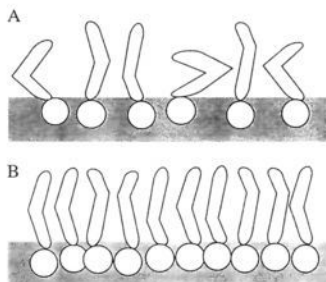


Figure 3. Schematic illustration of SDS monolayers at the water-carbon tetrachloride interface at (A) low and (B) high surface concentrations.

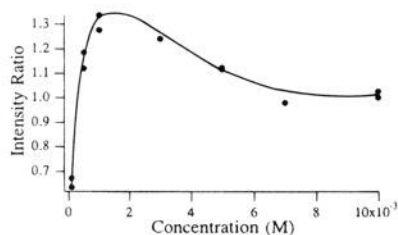


Figure 4. Plot of ratio of the methyl to methylene symmetric stretch intensities as a function of bulk concentration. The ratio was calculated from sum frequency data taken with s output, s visible, and p infrared light polarizations. The solid line is presented as a guide to the eye.

reduction in chain order at higher concentrations is also observed as manifested in the decrease in methyl to methylene ratio for higher bulk concentrations. This may be due to a disruption of the layer possibly caused by electrostatic interactions of the head groups, ion pair formation, or local micelle-type structure at the interface. Contributions arising from an increase in

interfacial roughness at higher concentrations¹⁸ may also contribute to the relative decrease in the methyl to methylene intensity ratio.

Another significant result is the apparent disorder of SDS at this interface relative to other amphiphilic molecules at the liquid-air and solid-liquid interfaces. It is known that the symmetry of molecules at an interface plays a crucial role in determining the induced nonlinear polarization at that interface.¹⁶ Sum frequency spectra from layers containing well-ordered alkyl chains typically display resonances due only to the terminal methyl group.¹⁹ In systems with a high degree of order within the alkyl chain, the resonant signal from the methylene groups vanishes through nearly complete cancellation of the induced field. In the presence of gauche defects within the chain, methylene resonances appear in the spectra, this being indicative of less ordered alkyl chain packing. It is because of the methylene resonances that remain at bulk concentrations greater than that needed to form a full monolayer at the interface that it can be concluded that SDS does not form well-ordered layers. Similar results were obtained by Bain et al.^{20,21} for SDS adsorption onto hydrophobic substrates from water. It is most likely that this disorder exists due to the ionic nature of this surfactant which prevents formation of closely packed layers.

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