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The vibrational spectrum of an amphiphilic surfactant, sodium dodecyl sulfate (SDS) at the interface between two immisicible liquids, D_2O/CCl_4, has been obtained for the first time by resonant sum frequency generation. The vibrational spectra obtained offer spectroscopicevidence for interfacial ordering of the alky chain as a function of surface coverage. Analysis of the ratio of the methyl/methylene peak intensities as a function of bulk aqueous phase concentration of SDS suggests that unlike the liquid-air and solid-liquid interfaces SDS is considerably more disordered at the liquid-liquid interface.

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

by

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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 - solid[1] 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 CCl_4 - D_2O 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.

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 D_2O - CCl_4 interface has been obtained and is 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 10mM 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 mM to 5mM. The surface coverage of SDS is determined from the corresponding bulk concentration as shown by the adsorption isotherm for SDS at the H_2O - CCl_4 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 and this 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 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 is 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.

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 [18]. In systems with a high degree of order within the alkyl chain, the resonant signal from the methylene groups vanish 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.[19 20]for SDS adsorption onto hydrophobic substrates from water. It is most likely that this disorder exits due to the ionic nature of this surfactant which prevents formation of closely packed layers.

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Figure Captions

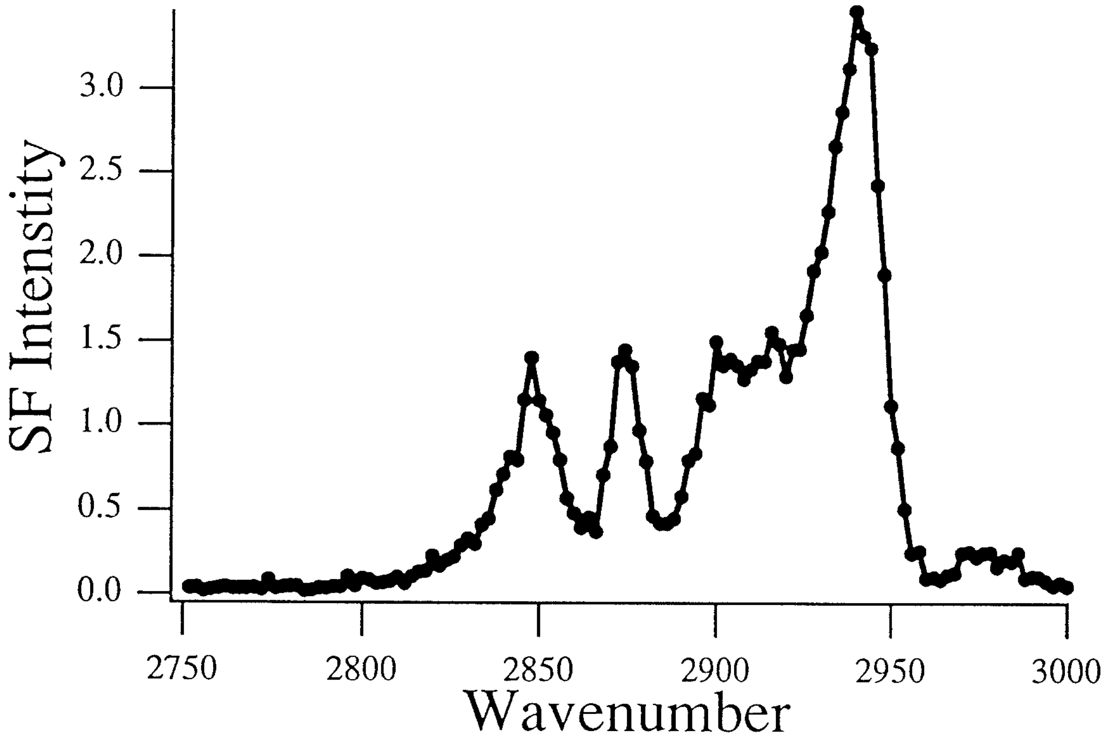
Figure 1. SF spectrum of SDS at the D_20 - CCl_4 interface obtained with a 10mM concentration of SDS in D_2O. The polarization of light was s output, s visible, p infrared. Peak assignments are as follows: 2840 cm^{-1} methylene symmetric stretch, 2866 cm^{-1} methyl symmetric stretch, 2894 cm^{-1} methylene fermi resonance, 2928 cm^{-1} methylene asymmetric stretch, 2960 cm^{-1} methyl asymmetric stretch.

Figure 2. Sum Frequency spectrum of SDS at the D_20 - CCl_4 interface for various SDS concentration. —— 0.1 mM, ········ 5.0 mM. Inset: Isotherm data for SDS at the H_20 - CCl_4 interface at 20°. The polarization of light was s output, s visible, p infrared. Data is fit to a Frumkin isotherm which describes adsorption of repulsively interacting adsorbates to an interface.

Figure 3. A 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 polarizationsThe solid line is presented as a guide to the eye.

FIG 1



SF Intenstity
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2750
2800
2850
2900
2950
3000
Wavenumber

FIG 2

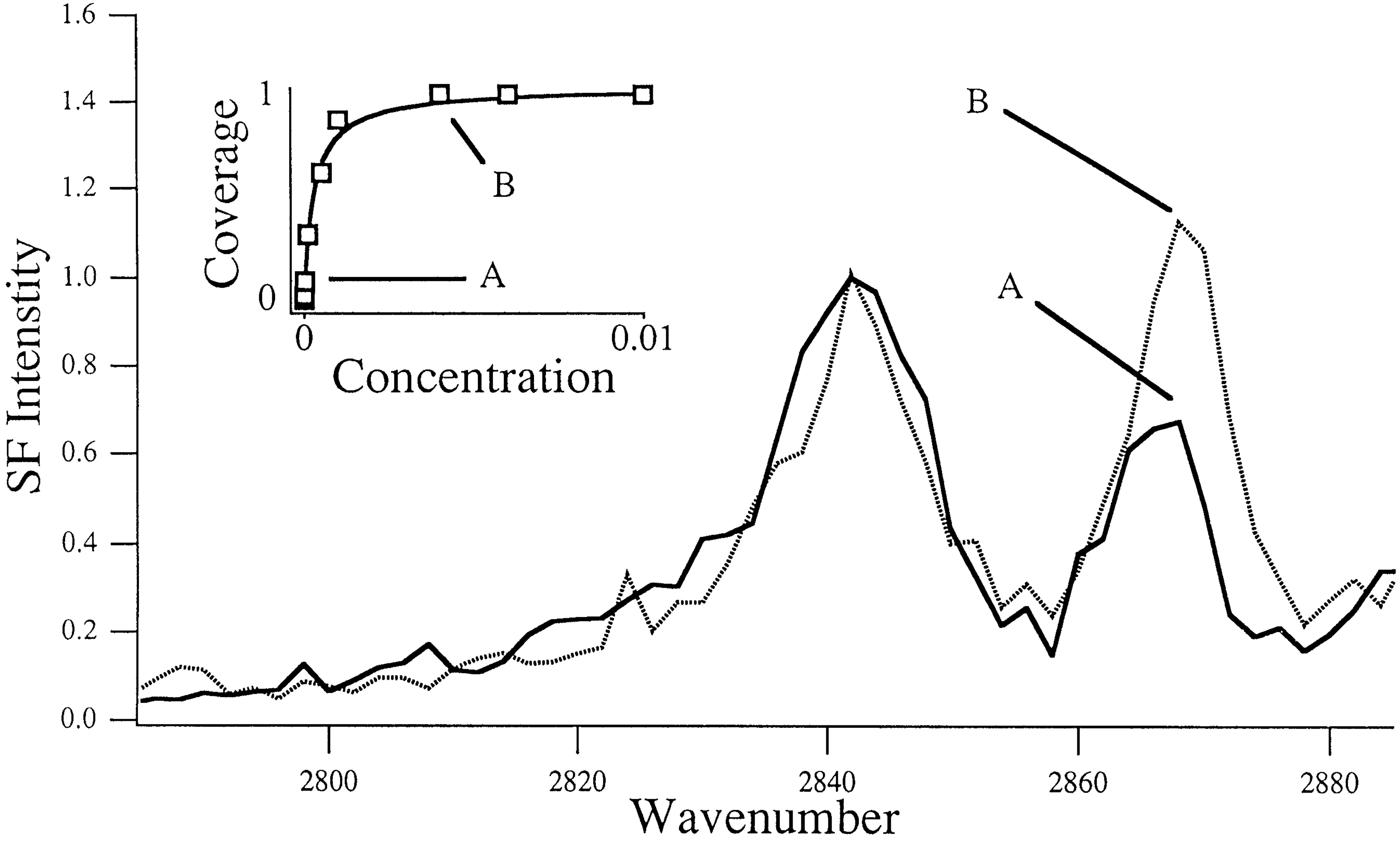

SF Intenstity
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
2800
2820
2840
2860
2880
Wavenumber
B
A
Coverage
1
0
0
0.01
Concentration
B
A

FIG 2

FIG-3

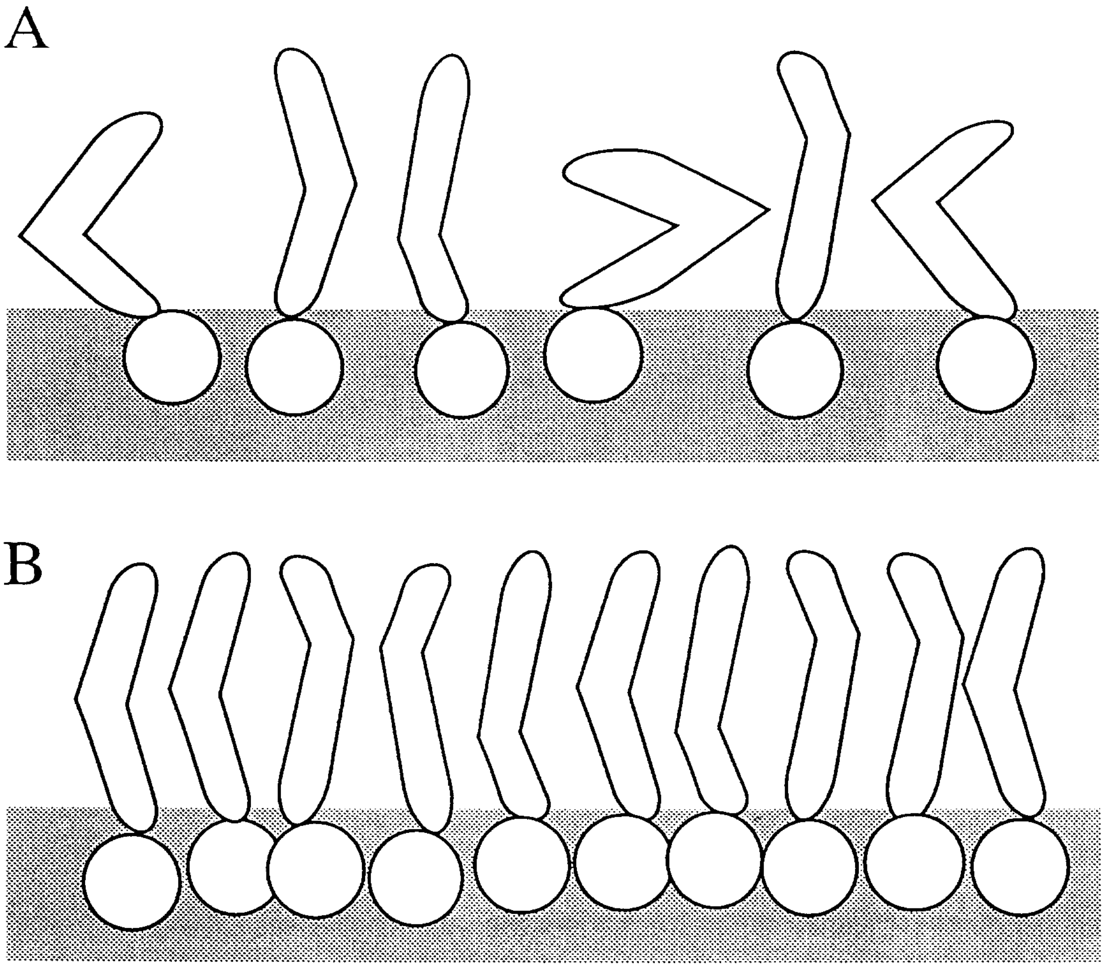
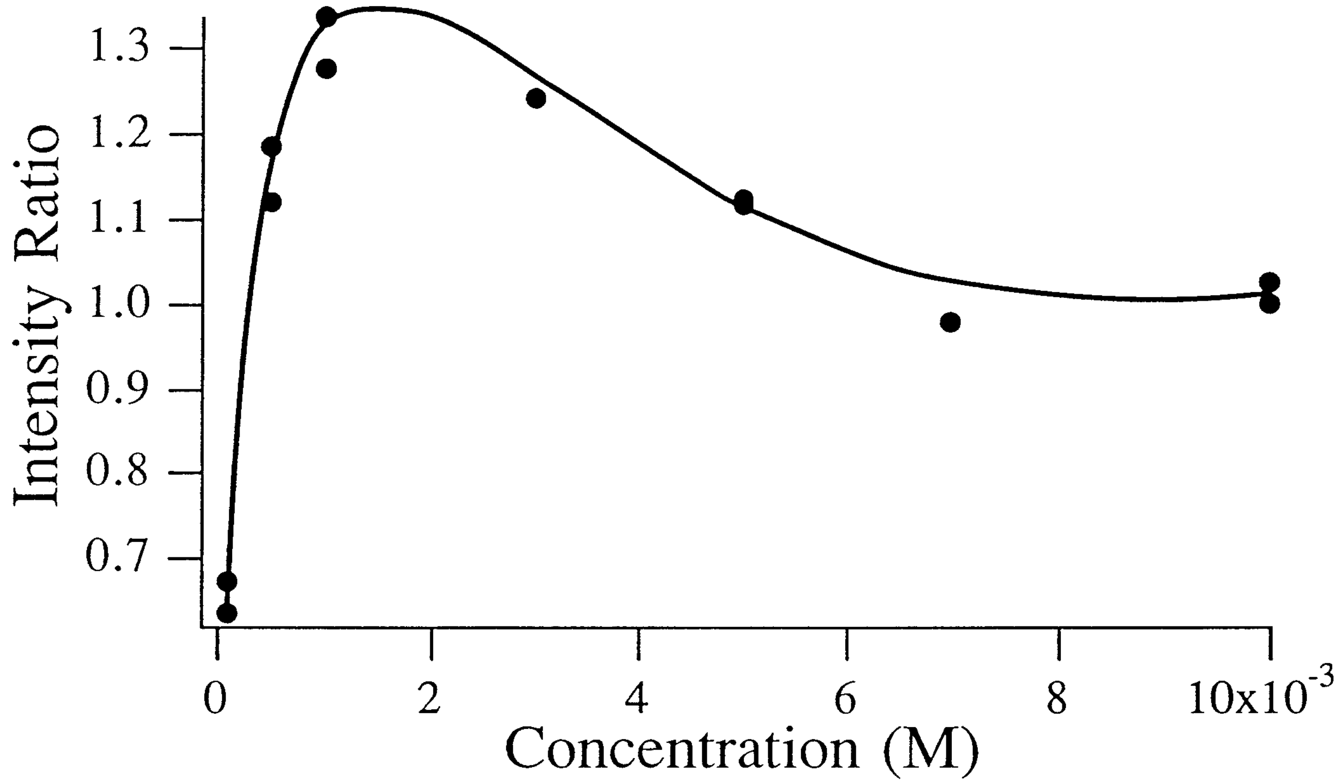


FIG 4



Intensity Ratio
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0
2
4
6
8
10×10^{-3}
Concentration (M)