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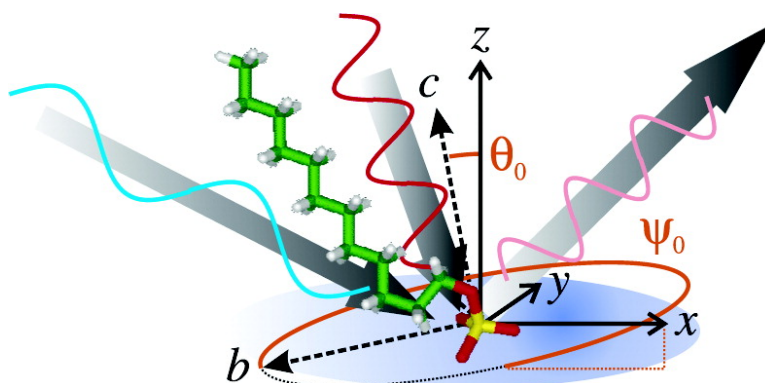
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Surfactant Headgroup Orientation at the Air/Water Interface

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Surfactants are prevalent in consumer products, biological systems, and industrial processes.[1−3] Consequently, a molecular-level understanding of how surfactants bond and orient at surfaces has ramifications for many of the economic, health, and environmental issues of today. Some of the most common surfactants used in commercial products consist of a charged headgroup and an extended hydrophobic alkyl chain. The behavior of such charged surfactants at an interface is largely dependent on the molecular characteristics of the polar headgroup and its structure, orientation, solvation, and interaction with adjacent surfactants. To date, much has been learned about surfactant behavior at aqueous surfaces using spectroscopic methods, such as vibrational sum-frequency spectroscopy. While these studies[4−7] have provided information about the ordering of the alkyl chains and the surrounding interfacial water structure, no information has been obtained about the headgroup structure and orientation.

In this communication, we provide the first measurement of the spectroscopy and orientation of a charged alkyl surfactant headgroup at the air/water interface using sum-frequency spectroscopy. The viability and success of these experiments are a result of our recent demonstration of sum-frequency generation using infrared frequencies down to 900 cm^{-1}.[8] Sodium dodecyl sulfate (SDS) has been used as a prototype system in this study, providing the first account of vibrational sum-frequency measurements of sulfate modes in the 1100 cm^{-1} region and demonstrating how polarization experiments can be used to determine its interfacial orientation. Our results consolidate previous findings of the structure of these monolayers to enable, for the first time, a comprehensive picture of the orientation and conformation of this surfactant at the air/water interface.

Vibrational sum-frequency spectroscopy[9,10] is an ideal probe of adsorbed monolayer structure since, being a second-order nonlinear optical technique, it is inherently selective of noncentrosymmetric environments and, thereby, excludes surfactant molecules in solution below the monolayer. In this experiment, a fixed-frequency visible beam ($\omega_{vis} = 12\,500$ cm^{-1}) and tunable infrared beam ($\omega_{IR} = 940-1160$ cm^{-1}) are spatially and temporally overlapped at the liquid surface. The sum-frequency beam ($\omega_{SF} = \omega_{vis} + \omega_{IR}$) generated at the interface is collected in reflection geometry. The intensity of the sum-frequency signal is proportional to that of the incident visible and IR beams, and also to the square of the second-order nonlinear susceptibility $\chi^{(2)}$ as

$$I_{SF} \propto |\chi^{(2)}|^2 I_{vis} I_{IR} \qquad (1)$$

In addition to the surface-specificity of this technique, $\chi^{(2)}$ is a very sensitive probe of molecular orientation. Structural information is obtained by probing the solution surface using different polarizations (s or p) for each of the three beams. In the ssp scheme, the s-polarized component of the sum-frequency beam is detected, while the s-polarized visible and p-polarized infrared beams are incident at the solution surface. In the ppp scheme, all beams are p-polarized.
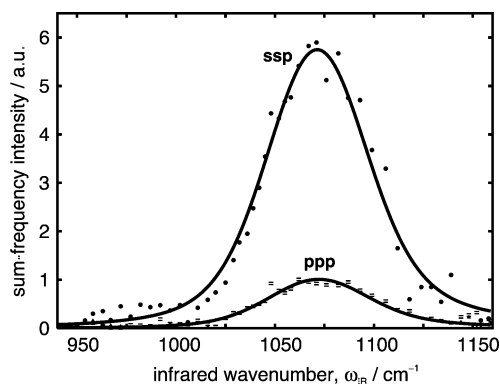

Figure 1. Sum-frequency spectra of the SO$_3$ symmetric stretch, obtained using different polarization schemes to probe elements of the second-order susceptibility for SDS adsorbed at the air/water interface.

Figure 1 shows room-temperature spectra of the SDS solution/air interface collected in these two polarization schemes. SDS (Aldrich) was dissolved in 18.2 MΩ Nanopure water to achieve a bulk concentration of 6.2 mM. At this concentration, a well-ordered monolayer forms at the interface.[7] It is sufficiently below the CMC (8.1 mM[11]) to minimize complications due to micelles at the surface. We have identified this vibrational mode at 1070 cm^{-1} as the SO$_3$ symmetric stretch[12−14] and fit the sps and ppp spectra to a peak profile that accounts for homogeneous and inhomogeneous line broadening. These different polarization schemes allow various elements of the $\chi^{(2)}$ tensor to be accessed. Fitting the ssp spectrum gives $\chi^{(2)}_{yyz}$; the ppp spectrum contains contributions from $\chi^{(2)}_{xxz}$, $\chi^{(2)}_{xzx}$, $\chi^{(2)}_{zxx}$, and $\chi^{(2)}_{zzz}$. The negligible signal obtained with sps polarization indicates that $\chi^{(2)}_{yzy} \approx 0$.

The data from Figure 1 are used to obtain $\chi^{(2)}$, the macroscopic nonlinear quantity pertaining to the interface. The desired orientation information comes from a comparison of the relevant macroscopic and microscopic quantities in

$$\chi^{(2)} = \frac{N}{\epsilon_0} \langle \beta \rangle \qquad (2)$$

where N is the surface molecular number density; ϵ_0 is the vacuum permittivity; β is the molecular hyperpolarizability, and the angular brackets denote an ensemble average over participating orientations. Values for the vibrational hyperpolarizability tensor elements are obtained using ab initio methods (at the RHF/6-311G+(d,p) level) that extend established procedures for determining β elements for diatomics[15] and simple polyatomic molecules.[16] In brief, displacements of all the atoms along the normal mode coordinate are used to generate a set of input geometries describing the SO$_3$ symmetric stretch. For each of these structures, polarizability tensor and dipole moment vector elements are calculated. Derivatives of these quantities with respect to the normal mode coordinate are then determined and subsequently used to construct the necessary elements of β; details will appear in a forthcoming paper.
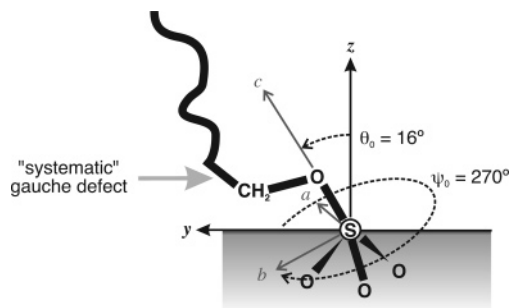
Figure 2. The determined orientation of the SDS headgroup at the air/water interface, showing the tilt of the reference S−O bond and the twist of the S−O−C plane.

Quantitative determination of the molecular orientation proceeds by taking ratios of eq 2 obtained for different polarization schemes ($\chi^{(2)}_{ppp}/\chi^{(2)}_{ssp}$ and using $\chi^{(2)}_{sps}/\chi^{(2)}_{ssp} \approx 0$). This approach also removes the dependence of these expressions on the surface number density and eliminates the need to determine $\chi^{(2)}$ and β elements to absolute scale.

Assuming a sharply peaked distribution for the tilt and twist angles, we have determined that the average tilt angle is $\theta_0 = 16°$ and that the S−O−C plane is, on average, twisted at $\psi_0 = 270°$, as shown in Figure 2. This geometry for the S−O−C plane creates an initial alkyl chain orientation that is largely in the plane of the water surface. It is implausible for the chain to continue along this direction since (1) this would create a very short monolayer, contrary to what is observed from neutron reflectivity studies;[17] (2) this would result in an extremely large effective area per headgroup, contrary to the value of 48 Å reported by surface tension studies;[11,17] (3) orientation analyses of the terminal methyl groups have shown them to be directed primarily along the surface normal.[5]

Infrared measurements[11,14] indicate that SDS at near-monolayer concentration contains a large number of gauche defects; this has previously been attributed to a lack of order in the chains. Vibrational sum-frequency generation studies of the alkyl chains of SDS at the air/water interface have shown a very large contribution from the CH_2 band,[6,7,18] also indicative of significant gauche defects. On the basis of our determination of the S−O−C plane orientation and knowledge that the alkyl chain is primarily extended in a direction normal to the interface, we propose a refined structural interpretation of the gauche defects. In addition to the randomly distributed gauche defects along the chain, a *systematic* one occurs near the headgroup. This would cause the alkyl chain, initially oriented nearly parallel to the air/water interface, to twist up and adopt a more vertical orientation as it extends away from the interface. To better account for the reported layer thickness and surface area per molecule, the necessary gauche defect must occur early in the chain, perhaps between the first few methylene groups, as depicted in Figure 2. Our results are consistent with molecular dynamics simulations[19,20] of an SDS monolayer at the air/water interface. Dominguez and Berkowitz have used the results of their

MD simulations to analyze the conformation of the alkyl chains by reporting the likelihood of finding a gauche defect at each position along the chain.[20] The authors have found less than 5% probability of a gauche defect in the $S-O-C_1-C_2$ dihedral, 45% probability at the next position along the chain (where it is drawn in Figure 2), and roughly 25% likelihood for each of the remaining positions leading to the methyl chain end. The significantly higher gauche probability between the first two methylenes from the headgroup lends strong support to our conclusions, which arrive at the same surfactant structure, but based on experimental results.

In summary, we have made the first vibrational sum-frequency measurement of the molecular structure and orientation of the headgroup of a charged alkyl surfactant. The results provide a detailed picture of the orientation of this important molecule at the air/water interface. In addition, they support theoretical predictions on the conformational order of the alkyl chain close to the headgroup. These studies demonstrate the feasibility and value of future investigations in this spectral region for understanding surfactant behavior at liquid and solid interfaces.

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