Surfactant/Water Interactions at the Air/Water Interface Probed by Vibrational Sum Frequency Generation

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The molecular structure and orientation of water molecules at an air/water interface has been measured in the presence of cationic and anionic surfactants. We have employed vibrational sum frequency generation to obtain the vibrational spectrum of both the surfactant and water molecules at the water surface. In the presence of the charged surfactant, the water molecules show a high degree of orientation with the directionality dependent upon the anionic or cationic nature of the surfactant headgroup. Relative to the charged surfactants, uncharged surfactants show minimal impact on interfacial water ordering. The results presented here provide valuable new insight into how the interfacial water molecules orient at the air/water interface in the presence of surfactants with different headgroups as well as how the relative order of the surfactants differ for these different amphiphiles.

Introduction

It is well-known that presence of surfactants at a water surface can greatly affect the surface tension of the water. In fact it is this disruption of the relatively high surface tension of water by the surfactant that accounts for the widespread use of surfactants in commercial products such as motor oils, lubricants, detergents, and soaps. Even with the abundant usage of surfactants in these products as well as for use in many industrial processes, little is known on a molecular level about how water and surfactants interact at liquid surfaces and interfaces. Such a lack of information about how the presence of surfactant molecules alter the molecular orientation and intermolecular bonding of surface water molecules places severe limitations on our predictive power for designing surfactants to perform a desired task. However, with recent reports of measurements of the molecular structure of surfactants as they reside at an oil/water[1,2] or air/water[3−8] interface, the future looks promising.

In this letter we provide important new spectroscopic evidence for how different surfactants affect the ordering and orientation of water molecules at the air/water interface. This information is acquired by employing vibrational sum frequency generation (VSFG) to measure the vibrational spectrum of *both* the surfactant *and* the water molecules at the surface as different surfactants are dissolved into the bulk aqueous phase. The unique surface sensitivity of this spectroscopic technique[1−5,9,10] allows us to demonstrate the central role that the presence of charged surfactants plays in the orientation of water molecules.

When a surfactant adsorbs at the air/water interface, the hydrophilic portion, or headgroup, points into the water, whereas the hydrophobic end, or tail, is directed out of the water. For several of the surfactants studied here, the head groups of the surfactant molecules are charged and thus a surface charge is present at the interface. This surface charge induces an electrostatic field in the double-layer region of the interface. At solid/liquid interfaces, previous nonlinear optical studies[11,12] and X-ray scattering studies[13,14] have indicated that the presence of an interfacial charge can strongly orient interfacial water molecules. In pioneering second harmonic studies of water/air interfaces, Eisenthal and co-workers[15] attributed an observed change in the sign of the SH response from the water surface

in the presence of insoluble cationic and anionic surfactants to the differing alignment of water molecules for the oppositely charged surfactants. However, since SHG lacks molecular selectivity under the nonresonant conditions of these earlier studies, little detail pertaining to the origin of the phase shift could be obtained. By being able to probe the vibrational structure of both the water molecules and the surfactant molecules at the air/water interface, we have been able to show that water molecules are indeed highly oriented in the presence of charged surfactants and that the direction of orientation depends upon the surface charge of the surfactant. We find that the sign of the surface charge causes water molecules to align in opposite directions. The opposing alignment is manifested by an interference between CH and OH stretching modes that is constructive for anionic surfactants and destructive for cationic surfactants.

Experimental Section

The laser system employed for the vibrational SFG studies has been described in detail elsewhere.[16,17] Briefly it consists of a titanium:sapphire regenerative amplifier which pumps a two-stage optical parametric amplifier seeded with a small portion of white light continuum. The system produces IR pulses tunable from 2.4 to 4.0 μm at a repetition rate of 1 kHz. The energy of the pulses over this range is approximately 10 μJ with a bandwidth of 18 cm^{-1} and a pulse duration of 1.9 ps. The IR pulses are combined at the interface with approximately 150 μJ of 800 nm light from the Ti:sapphire regenerative amplifier. All spectra presented were obtained under S_{sfg}, S_{vis}, and P_{IR} polarization conditions with the 800 nm and IR beams directed onto the interface at an approximate angle of 56° and 68° from the surface normal, respectively. The generated sum frequency is detected in reflection with a PMT after filtering. The spectra were collected with gated electronics and a computer.

Surfactants were dissolved in either HPLC grade water from Mallinckrodt or deuterium oxide from Cambridge Laboratories with a pH of approximately 6 and 5.5, respectively. A VSFG spectrum was obtained for each neat solvent at the air/solvent interface. The surface of the neat solvent at the air/solvent interface was determined to be relatively free of organic contaminant by absence of peaks in the CH stretching region

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of the VSFG spectra. Sodium dodecyl sulfate (SDS) was obtained from Fluka and dodecylammonium (DDA) was obtained from Kodak. Both DDA and SDS were studied at the critical micelle concentration which is 8.1 mM for SDS and 14 mM for DDA. Surface tension studies in this lab have shown monolayers of both these molecules to form at these bulk concentrations with molecular areas of 35 and 45 Å^2/molecule for DDA and SDS respectively. Pentadecanoic acid (PDA) from Sigma was spread at the air/water interface by placing 1 drop of 1 mg/mL PDA in methanol on either a H_2O or D_2O surface with an area of 19.6 cm^2 which should place the monolayer in the liquid condensed (LC) phase. Further, at monolayer coverage in the LC region PDA has been shown to have a molecular area of approximately 25 Å^2/molecule.[18]

Results and Discussion

Vibrational sum frequency generation (VSFG) is a nonlinear optical technique that has been extensively used in the study of surfaces and interfaces. Since VSFG is a second-order nonlinear process, it is inherently surface sensitive. By employing a tunable infrared beam, the technique can also be sensitive to molecular structure. These two aspects of VSFG allow one to obtain a vibrational spectrum of molecules at an interface. The VSFG intensity is proportional to the square of the surface nonlinear susceptibility $\chi_s^{(2)}$ ($\omega_{sfg} = \omega_{vis} + \omega_{IR}$) as follows:

$$I_{SFG} = |P_{SFG}|^2 \propto |\chi_{NR}^{(2)} + \sum_v |\chi_{R_v}^{(2)}| e^{i\gamma_v}|^2 I_{vis} I_{IR} \qquad (1)$$

where χ_{NR} and χ_{R_v} are the nonresonant and resonant parts of $\chi_s^{(2)}$, the sum is taken over all sum-frequency active vibrational modes v, and I_{vis} and I_{IR} are the intensities of the incident laser beams. Since the susceptibility is in general complex, the resonant terms in the summation have associated with them a relative phase γ_v which is used to account for any interference between two modes which overlap in energy. The resonant term χ_{R_v} can be further expressed as follows:

$$\chi_{R_v}^{(2)} \propto \frac{A_v}{\omega_v - \omega_{IR} - i\Gamma_v} \qquad (2)$$

where A_v is the intensity of the vth vibrational mode and is proportional to the product of the Raman transition moment and the IR moment, ω_v is the resonant frequency, and Γ_v is the line width. At an interface where there is a large electrostatic field, E_0, a third-order effect or a $\chi^{(3)}$ interaction between the optical fields and the electrostatic field can contribute to the nonlinear polarization from the interface as follows:

$$P_{SFG} = \chi^{(2)}:E_{vis}E_{IR} + \chi^{(3)}:E_{vis}E_{IR}E_0 \qquad (3)$$

The third-order term, $\chi^{(3)}$, can also be broken down into resonant and nonresonant contributions as is discussed above for $\chi^{(2)}$. For the systems studied here the electrostatic field E_0 resides in the double-layer region, and thus any $\chi^{(3)}$ contributions to the nonlinear polarization that arises from this region which is made up primarily of water molecules. Conversely, $\chi^{(2)}$ contributions to the nonlinear polarization come from the surface layer where the surfactant concentration is much higher. SHG studies at the charged insoluble surfactant air/water interface have shown that the $\chi^{(3)}$ contributions to the nonlinear polarization cannot be neglected and in fact dominate at low ionic strengths.[15]

Figure 1 shows the VSFG spectra from a monolayer of pentadecanoic acid (PDA) on H_2O and D_2O at the air/water interface. Films of PDA at the air/water interface have been
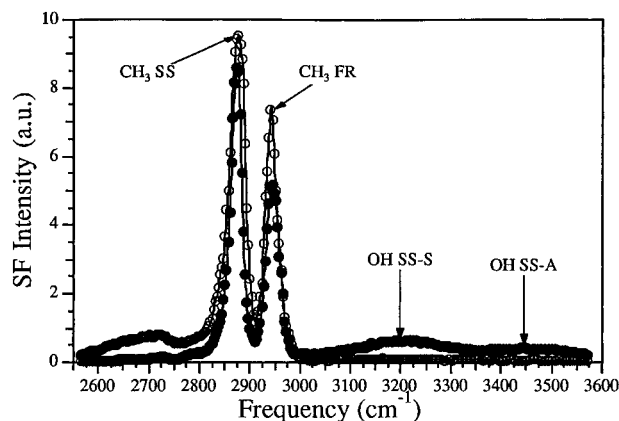

Figure 1. Sum frequency spectra of pentadecanoic acid on H_2O and D_2O with S_{sfg}, S_{vis}, P_{IR} polarizations. Open circles are for D_2O and closed circles are for H_2O. Solid lines are a guide to the eye.

studied previously by the VSFG technique and have been shown to readily form well-ordered monolayers,[18-20] consistent with what is observed here. Both spectra in Figure 1 are dominated by the CH_3 symmetric stretch, CH_3–SS at 2875 cm^{-1}, and the CH_3 Fermi resonance, CH_3–FR at 2935 cm^{-1}, with no contribution observed from CH_2 stretching modes. For amphiphilic molecules which form well-ordered monolayers, predominantly trans conformation, the CH_2 bonds will be on opposing sides of the carbon backbone. This orientation produces a cancellation of the CH_2 stretching vibrational modes, and thus a monolayer with no or few gauche defects will exhibit only CH_3 vibrational modes in the SF spectrum.[1,18] Conversely, the presence of the CH_2 vibrational modes in a particular spectrum implies a lesser degree of order or more gauche defects. The dominance of the CH_3–SS over negligible contributions from the CH_2–SS for the PDA spectra suggests considerable ordering of the monolayer.

In addition to the CH_3 stretching modes, we find two small peaks in the PDA–H_2O spectrum at higher frequency (Figure 1) which were previously not measured for this system. We attribute the first peak, located at 3200 cm^{-1} and designated OH–SS–S in Figure 1, to the coupled OH symmetric stretch from tetrahedrally coordinated water molecules at the interface. This peak has been observed to have a strong intensity in the spectrum of ice, and thus its strength is indicative of tetrahedral bond ordering in the molecular arrangement of water molecules or an "icelike" structure.[11] The second peak, designated OH–SS–A and located at 3450 cm^{-1}, can be attributed to one of two possible modes. The first possibility is the OH symmetric stretch of asymmetrically hydrogen-bonded water molecules.[11] The other possibility is that it is due to molecules with bifurcated hydrogen bonds.[21] The assignment of this mode is not crucial to the studies here since either assignment is indicative of bond disorder in the molecular arrangement or a more "waterlike" molecular arrangement.[11] The corresponding OD stretches, in the 2600–2700 cm^{-1} range, are present in the spectrum of PDA on D_2O. However, since the IR power from the OPA is decreasing rapidly in this region, these peaks are not easily resolvable and will not be discussed further.

Figure 2 shows the VSFG spectra from the air/water interface of 14 mM dodecylammonium solutions in both H_2O and D_2O. Upon comparison of the DDA–H_2O spectrum with the PDA–H_2O spectrum, one immediately notices the large enhancement of the OH peaks from the interfacial water molecules in the DDA spectrum. We attribute this enhancement to the large electrostatic field present in the double-layer region arising from separation of the cationic headgroup and chloride ions (present at the interface as counterions). At monolayer concentrations
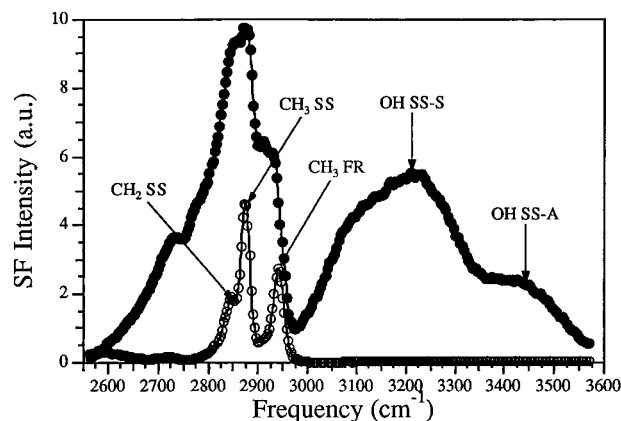
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Figure 2. Sum frequency spectra of 14 mM dodecylammonium in H$_2$O and D$_2$O with S_{sfg}, S_{vis}, and P_{IR} polarizations. Open circles are for D$_2$O and closed circles are for H$_2$O. Solid lines are a guide to the eye.

Figure 3. Sum frequency spectra of 8.1 mM sodium dodecyl sulfate in H$_2$O and D$_2$O with S_{sfg}, S_{vis}, and P_{IR} polarizations. Open circles are for D$_2$O and closed circles are for H$_2$O. Solid lines are a guide to the eye.

the electrostatic field can be as large as 10^7 V/m and extend in to the bulk water as much as 100 water molecule diameters. The field has a 2-fold effect on the OH stretches as compared to the OH stretches present in the noncharged PDA on H$_2$O spectrum. First, the field can enhance the SFG signal through a $\chi^{(3)}$ effect or a coupling of the static field to the optical fields present. Second, the field can align the interfacial water molecules producing an enhanced SFG signal in the OH stretching region through alignment of the OH bonds. The observed enhancement is certainly a combination of each of these effects and is consistent with the behavior of water molecules observed at the charged quartz/water interface[11,12] and the charged insoluble surfactant air/water interface.[15] Further, the peak at 3200 cm^{-1} dominates over the peak at 3450 cm^{-1} in the DDA−H$_2$O spectrum which indicates a tetrahedral arrangement or "icelike" structure of the interfacial water molecules. Another notable difference in the comparison of the PDA−H$_2$O and DDA−H$_2$O spectra is the dip in the DDA spectra at approximately 2970 cm^{-1} indicative of a destructive interference between the CH$_3$−FR and the OH−SS−S modes. This interference is not present in the DDA−D$_2$O spectrum which provides further evidence that the OH bonds are involved.

The relative order of the DDA monolayer can be ascertained by comparing the DDA spectrum with the PDA spectrum in the CH stretching region. For the case of DDA−D$_2$O, the spectrum is dominated by the CH$_3$−SS and CH$_3$−FR with the CH$_2$−SS present as a much smaller peak. This is indicative of a fairly well ordered monolayer, with few gauche defects, but not as well ordered as the carboxylic acid containing surfactant, PDA. The DDA−H$_2$O spectrum is also dominated by the CH$_3$− SS but characterization of the CH$_3$−FR is not as straightforward as with the case of DDA−D$_2$O due to the aforementioned interference that occurs in this region. The interference diminishes the CH$_3$ Fermi resonance but enhances a shoulder on the CH$_3$ symmetric stretch which could be attributed to the CH$_2$ Fermi resonance (CH$_2$−FR) and/or the CH$_2$ asymmetric stretch (CH$_2$−AS). Further, it should be noted that the laser bandwidth is approximately 18 cm^{-1} which makes resolving the peaks in this region difficult. An additional peak is observed near 2700 cm^{-1} in the DDA−H$_2$O and DDA−D$_2$O spectra which is likely due to an NH Fermi resonance.

Figure 3 shows the VSFG spectra from solutions of 8.1 mM SDS in H$_2$O and D$_2$O at the air/water interface. Inspection of the SDS−H$_2$O spectrum in the OH stretching region shows some similarities to the DDA−H$_2$O spectrum, namely, the OH peaks are greatly enhanced as a result of the field present in the double-layer region due this time to separation of the *negatively* charged headgroup of SDS and the *positively* charged sodium ions
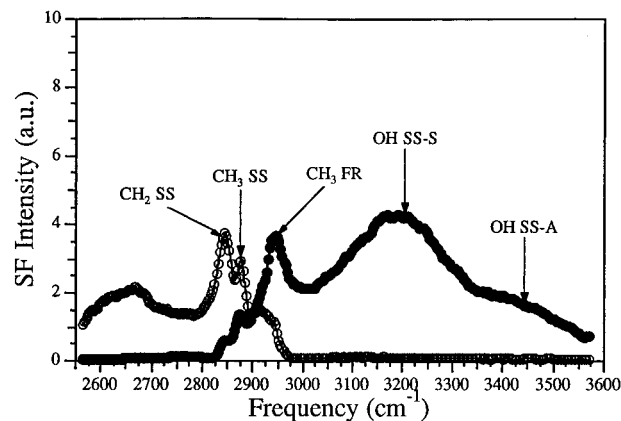
(present at the interface as counterions). In addition, like DDA, the OH peak at 3200 cm^{-1} dominates over the peak at 3450 cm^{-1} indicating a tetrahedral arrangement of the interfacial water molecules. Upon further inspection however, one finds that the destructive interference in the DDA−H$_2$O spectrum located at 2970 cm^{-1} is replaced by an enhancement or constructive interference for the SDS−H$_2$O spectrum. In fact the CH$_3$ Fermi resonance is enhanced so much that it now dominates the CH stretching spectral region. This situation is not observed for the SDS−D$_2$O spectrum which is dominated by the CH$_2$−SS and a much smaller signal from CH$_3$−FR. This behavior can be explained by the fields present at these interfaces which are in opposite directions for DDA and SDS. The fields will align the dipoles of the interfacial water molecules in opposite directions and thus the OH stretching modes will have moments in opposite directions. The difference in directionality of the OH bonds for the two surfactants gives rise to the difference in the interference between the CH$_3$−FR and the OH−SS−S at 3200 cm^{-1}. This flip in the molecular arrangement of interfacial water molecules at oppositely charged surfaces has been observed at the charged electrode/water interface[14] and proposed to occur at the charged insoluble surfactant air/water interface by SHG experiments.[15]

Another possible contributing factor in the interfacial water alignment could arise from the chemical nature of the solvation shell of the charged headgroup. While this type of alignment certainly occurs in the solvation sphere of the charged head-groups, one would expect these effects to align only the water molecules in the double-layer region neighboring the surfactant headgroups. Since the alignment of so few water molecules would probably not produce the large enhancements observed here, we conclude that the dominate contribution in these studies is the field-induced orientation. More evidence for this will be presented in a later publication involving mixed cationic and anionic surfactants and ionic strength studies.

Comparison of the CH stretching modes of SDS with those of PDA should allow one to gauge the relative order of the monolayer. However, the constructive interference observed for SDS in the Fermi resonance region makes such a comparison difficult. Thus one must look to the SDS−D$_2$O spectrum to assess the order of the monolayer. For SDS−D$_2$O one finds that the CH spectral region is dominated by the CH$_2$−SS with the CH$_3$−SS present as a slightly smaller peak. This pattern is indicative of a monolayer that is less ordered, with more gauche defects, than both the DDA and PDA monolayers. These findings are consistent with studies of SDS and DDA at the oil/water interface performed in this laboratory.[22]

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The directionality of the electrostatic field present in the double-layer region at the air/water interfaces of SDS and DDA in H₂O manifests itself in the VSFG spectra. This field leads to an enhancement in the OH stretching modes as well as a constructive interference between the OH−SS−S mode of water molecules and the CH₃−FR modes of the anionic surfactant SDS, and a destructive interference between same modes for the cationic surfactant DDA. The pH of the D₂O and H₂O used in the experiments here could be sufficiently acidic to deprotonate some of the PDA molecules at the interface. However, since the OH vibrational modes in the VSFG spectra from PDA are not significantly enhanced over what is observed for the neat air/water interface the fraction of deprotonated molecules should be negligible. Further, negligible interference is observed between the water vibrational modes and the CH stretching vibrations for the carboxylic acid surfactant PDA. The CH₃−FR and OH−SS−S peaks, as with all others under SSP polarization conditions, are out-of-plane vibrational modes and contribute to the spectra only when the IR light has an out-of-plane component or is P-polarized. S-polarized IR sum frequency experiments have been conducted and neither of these peaks nor the interference are present.

Summary and Conclusions

We conclude that the observed interference in the VSFG spectra presented here is indicative of a flip in orientation of the interfacial water molecules when comparing the molecular arrangement of water molecules at interfaces with cationic and anionic surfactants. The X-ray scattering work by Gordon et al.[14] at the charged electrode/water interface has shown that water molecules at a negatively (positively) charged interface are aligned with their protons (oxygen atoms) directed toward the negative (positive) charge. We have observed a similar effect at the charged soluble surfactant air/water interface for cationic and anionic surfactants. At the air/water interface with a cationic surfactant present, the water molecules in the double-layer region will align with their oxygen atoms pointing toward the air. The reverse is true for an anionic surfactant where the water molecules will orient with their oxygen atoms pointed into the solution. We have performed other studies with surfactant molecules such as dodecyltrimethylammonium bromide (positive headgroup) and sodium dodecyl sulfonate (negative headgroup) as well as studies in which we have varied the ionic strength and bulk surfactant concentration and find the ordering of interfacial water molecules to be consistent with the data presented here.[23] Further, this interference is observed over a range of submonolayer concentrations and thus is not an artifact of bulk micelle formation.

The study of simple surfactants at the air/water interface has allowed us to lay the groundwork for studying more complicated systems. We are currently studying several systems where the ordering of interfacial water molecules may be less intuitive. The first of these systems is mixed, cationic and anionic, surfactant solutions where one might expect the interfacial water molecules to align in both orientations or to be randomized. Another system is aqueous solutions of zwitterionic molecules where one might expect the water molecules to be less ordered. These studies are being conducted at the air/water interface with future extension to oil/water interfaces.

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