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Potential Dependent Alignment and Hydrogen Bonding of Water Molecules at Charged Air/Water and CCl_4/Water Interfaces

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Abstract: We observe potential dependent alignment and hydrogen bonding of interfacial water molecules at a charged air/water and CCl_4/water interface. The interfacial potential is a result of the presence of charged soluble surfactant adsorbed to the interface. We vary the interface potential by changing the surface charge density, the ionic strength, and the temperature while monitoring OH stretching modes sensitive to the structure and hydrogen bonding of interfacial water molecules. As the potential is increased at the air/water interface we observe a progression from a waterlike and less hydrogen bond ordered structure to an icelike and more hydrogen bond ordered structure. This progression is a direct consequence of the induced alignment of the interfacial water molecules resulting from the large electrostatic field produced in the interfacial region by the charged surfactant. Temperature dependence measurements confirm the conclusion that there is a potential dependent alignment of the interfacial water molecules. In comparison, at the CCl_4/water interface we observe only the icelike structure both in the presence and absence of a charged surfactant. The structural difference observed at the air/water and CCl_4/water interfaces is discussed within the context of the structure imposing effect the nonpolar CCl_4 molecules have on the interfacial water molecules.

Introduction

Surfactants or amphiphiles are composed of a hydrophobic and a hydrophilic moiety. This unique combination of chemical properties in a single molecule results in the partitioning of surfactants to water surfaces. The presence of surfactants at an air/water or oil/water interface greatly affects the surface tension of the water. In fact, this reduction of the relatively high surface tension of water by a surfactant accounts for the widespread use of surfactants in commercial products such as motor oils, lubricants, detergents, and soaps. In addition, many of the processes essential to the evolution and maintenance of life are dependent on the surface free energy lowering effect of surfactants. Processes ranging from the stabilization of globular proteins to the formation of complex organelles and membranous structures are intimately coupled to the interface modifying characteristics of surfactants.[1] Despite the technological and biological importance of surfactants, little is known on a molecular level about how water and surfactants interact at liquid surfaces and interfaces. Specifically, the presence of charged surfactants at an interface results in a large surface charge and thus a large electrostatic field in the interfacial region. The effect this electrostatic field has on the structure and hydrogen bonding of interfacial water molecules is not fully understood, yet it is essential to a full description of the surface modifying effects of charged surfactants. In this paper we report on changes in the alignment and hydrogen bonding of water molecules induced by the presence of a charged surfactant at the air/water and CCl_4/water interface.

Over the past 20 years extensive theoretical work has been conducted in an effort to better understand the structure and hydrogen bonding of interfacial water molecules at charged interfaces.[2−6] The bulk of this work has been conducted with simulations employing metal electrodes as the source of the surface charge at the electrode/water interface. Experimental confirmation of these theoretical studies has been slow to follow due, in part, to the limited number of techniques suitable for interfacial investigations. With the development of FTIR spectroscopy as a tool capable of discriminating surface molecules from bulk molecules, the potential dependent vibrational spectroscopy of water molecules at the charged electrode/water interface has been obtained.[7,8] These studies have been, for the most part, in agreement with the theoretical studies. Recent results from X-ray scattering studies[9,10] of water at a charged electrode surface are in agreement with some theoretical results and in disagreement with others.[5] Within the past decade laser based nonlinear optical techniques such as second harmonic generation (SHG)[11−14] and vibrational sum frequency generation (VSFG)[15−19] have become powerful tools for the study of

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interfaces. In particular, charged interfaces such as the quartz/water interface[12,20] as well as the charged-surfactant-air/water interface[11,17,21] have been investigated with SHG and VSFG. In the work presented here we employ VSFG to explore the effects surface charge density, ionic strength, and temperature have on the alignment and hydrogen bonding of water molecules at both the air/water and CCl_4/water interfaces.

In a recent publication[17] we showed that there is a large enhancement in the sum frequency response in the OH stretching spectral region when a charged surfactant is adsorbed to the air/water interface. We attribute this enhancement to an alignment of the interfacial water molecules induced by the large electrostatic field present in the interfacial region resulting from the surface charge produced by the charged surfactant. A similar alignment of interfacial water molecules has been observed at the electrode/water interface with X-ray scattering[9,10] and FTIR experiments.[7,8] In addition, molecular dynamics simulations suggest that water molecules between two charged platinum plates not only align with the electrostatic field but also hydrogen bond in a tetrahedral network much like the structure of cubic ice.[4−6] In the present paper we further characterize the alignment of water molecules at the air/water and CCl_4/water interfaces induced by the presence of a charged surfactant. By examining OH stretching modes sensitive to the local hydrogen bonding environment of interfacial water molecules we observe a progression from a waterlike and less hydrogen bond ordered structure to an icelike and more hydrogen bond ordered structure with increasing interfacial potential. We also find that the water molecules at the air/water interface achieve maximum orientation at a potential of approximately 260 mV, whereas the maximum in the orientation of water molecules at the CCl_4/water interface occurs at approximately 160 mV. VSFG spectra from both interfaces obtained as a function of temperature are also presented and shown to agree with our observation that interfacial water molecules are aligned by the presence of charged surfactants. Finally, we show that the structure and hydrogen bonding of water molecules at the air/water and CCl_4/water interfaces is markedly different both in the absence and presence of charged surfactant.

Background

Vibrational sum frequency generation (VSFG) is a nonlinear optical technique that has been extensively used in the study of surfaces and interfaces.[15,16,18,19,21,22] VSFG is a second-order process and therefore under the dipole approximation is forbidden in media that possess inversion symmetry. At the interface between two centrosymmetric media there is no inversion center and thus VSFG is allowed in this region. The asymmetric nature of interfaces allows one to specifically probe the interfacial region using VSFG. Typically, one combines a visible laser beam and a tunable infrared laser beam at the interface with the energy range of the tunable IR laser overlapping with the energies of vibrational modes of molecules present at the interface. By scanning the energy of the IR laser and monitoring the generated sum frequency signal one obtains a vibrational spectrum of the interfacial molecules. The VSFG intensity is proportional to the square of the surface nonlinear susceptibility $\chi_s^{(2)}(\omega_{sfg} = \omega_{vis} + \omega_{ir})$ as

$$I_{sfg} \propto |P_{sfg}|^2 \propto \chi^{(2)}_{NR} + \sum_v |\chi^{(2)}_R v| e^{i\gamma_v}|^2 \, I_{vis} I_{ir} \tag{1}$$

where P_{sfg} is the nonlinear polarization at ω_{sfg}, χ_{NR}, and χ_{R_v} are the nonresonant and resonant parts of $\chi_s^{(2)}$, γ_v is the relative phase of the vth vibrational mode, and I_{vis} and I_{ir} are the visible and IR intensities. Since the susceptibility is in general complex, the resonant terms in the summation are associated with a relative phase γ_v which is used to account for any interference between two modes which overlap in energy. $\chi^{(2)}_R v$ is also proportional to the number density of molecules, N, and the orientationally averaged molecular hyperpolarizability, β_v, as follows

$$\chi^{(2)}_{R_v} = \frac{N}{\epsilon_0}\langle\beta_v\rangle \tag{2}$$

Thus the square root of the measured SF intensity is proportional to the number density of molecules at the surface or interface. The molecular hyperpolarizability, β_v, is enhanced when the frequency of the IR field is resonant with a SF-active vibrational mode from a molecule at the surface or interface. This enhancement in β_v leads to an enhancement in the nonlinear susceptibility $\chi^{(2)}_R v$ which can be expressed as

$$\chi^{(2)}_R v \propto \frac{A_v}{\omega_v - \omega_{ir} - i\Gamma_v} \tag{3}$$

where A_v is the intensity of the vth mode and is proportional to the product of the Raman and the IR transition moments, ω_v is the resonant frequency, and Γ_v is the line width of the transition. Since the intensity term, A_v, is proportional to both the IR and Raman transition moments, only vibrational modes which are both IR and Raman active will be SF-active. Thus molecules or vibrational modes which possess an inversion center will not be SF-active.

In general the surface susceptibility $\chi_s^{(2)}$ is a 27 element tensor; however, it can often be reduced to several nonvanishing elements by invoking symmetry constraints. Liquid surfaces and interfaces as well as monolayers on liquid surfaces are isotropic in the plane of the surface. The symmetry constraints for an in-plane isotropic surface reduces $\chi_s^{(2)}$ down to the following four independent nonzero elements

$$\chi^{(2)}_{zzz};\chi^{(2)}_{xxz} = \chi^{(2)}_{yyz};\chi^{(2)}_{xzx} = \chi^{(2)}_{yzy};\chi^{(2)}_{zxx} = \chi^{(2)}_{zyy} \tag{4}$$

where z is defined to be the direction normal to the surface. These four independent elements contribute to the VSFG signal under the four different polarization conditions SSP, SPS, PSS, and PPP where the polarizations are listed in the order of decreasing frequency (sf,vis,ir). Which vibrational modes are present under a certain polarization condition depends on the polarization of the IR field and the direction of the IR and Raman transition moments. The SSP polarization condition accesses vibrational modes with transition moments which have components perpendicular to the surface plane, whereas the SPS and PSS polarization conditions access modes which have transition moments with components parallel to the surface plane. The intensity under PPP polarization conditions contains

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contributions from all of the tensor elements thus vibrational modes with components both perpendicular and parallel to the surface plane will be present in the PPP polarized VSFG spectra. For the systems in this study, the crucial vibrational modes of the interfacial water molecules all possess transition moments with components out of the plane of the surface. Consequently, we confine our discussion to the SSP polarization condition. However, verification of the peak assignments has been made from spectra using all of the polarization combinations.

At an interface where charged surfactant is adsorbed a significant surface charge exists which produces a large electrostatic field E_0. This electrostatic field can make an additional contribution to the nonlinear polarization induced at the interface by the optical fields E_{vis} and E_{ir} through a third-order polarization term $\chi^{(3)}$ as follows

$$P_{\mathrm{sfg}} = \chi^{(2)} :\ E_{\mathrm{vis}}E_{\mathrm{ir}} + \chi^{(3)} :\ E_{\mathrm{vis}}E_{\mathrm{ir}}E_0 \qquad (5)$$

The second term in eq 5 is the third-order polarization term, $P^{(3)}_{\mathrm{sfg}}$, and contains the electrostatic field dependence of the nonlinear polarization induced at the interface. Both $\chi^{(3)}$ and $\chi^{(2)}$ have resonant and nonresonant portions as described above, and, in fact, the overall SF response can be represented by an effective surface susceptibility which is a combination of $\chi^{(3)}$ and $\chi^{(2)}$. In the absence of a large electrostatic field one would expect the interfacial water molecules to be randomly oriented after a few water layers and thus not contribute to the nonlinear polarization. The presence of a large electrostatic field aligns the interfacial water molecules beyond the first few water layers and thus removes the centrosymmetry over this region allowing more water molecules to contribute to the nonlinear polarization. The depth of the asymmetric region is on the order of the Debye length or 3 nm at an ionic strength of 10 mM and 10 nm at an ionic strength of 1.0 mM corresponding to approximately 10−30 water layers, respectively. Previous studies have shown that this alignment of the interfacial water molecules is manifested in the VSFG spectra as a large enhancement in the SF response in the OH stretching spectral region.[17,21] This electrostatic field dependent enhancement results from a combination of an increased number of water molecules interacting with the optical fields and an alignment of the transition dipole moments of the OH modes with the polarization vector of the IR light.

Second harmonic studies[11] at the air/water interface with an insoluble charged surfactant present have shown that the SHG intensity is dependent on the interfacial potential which, in turn, is dependent on the surface charge density and the ionic strength of the surfactant solution. The relationship between the nonlinear polarization for VSFG and the interfacial potential can be obtained by integrating $P^{(3)}_{\mathrm{sfg}}$ over the region where the electrostatic field, E_0, is present. Assuming $\chi^{(3)}$ is constant over the interfacial region and using the relationship between the electrostatic field $E(z)$ and the interfacial potential $\Phi(z)$ one obtains

$$\begin{aligned} P_{\mathrm{sfg}} &= \chi^{(2)}E_{\mathrm{vis}}E_{\mathrm{ir}} + \chi^{(3)}E_{\mathrm{vis}}E_{\mathrm{ir}}\Phi(0) \\ &= [\chi^{(2)} + \chi^{(3)}\Phi(0)]E_{\mathrm{vis}}E_{\mathrm{ir}} \qquad (6) \end{aligned}$$

where $\Phi(0)$ in the potential at the interface where $z = 0$. Equation 6 demonstrates the linear dependence of the nonlinear polarization on the interfacial potential.

In the work presented here we monitor the structure and hydrogen bonding of interfacial water molecules as the interfacial potential is varied. The Gouy−Chapman model has been shown to accurately characterize the interfacial potential as a function of surface charge density and ionic strength.[11,23] Using this model the interfacial potential is expressed as

$$\Phi(0) = \frac{2kT}{ze}\sinh^{-1}\left(\sigma\sqrt{\frac{\pi}{2\epsilon kTI}}\right) \qquad (7)$$

where σ is the surface charge density, z is the sign of the charged surfactant molecule, ϵ is the permittivity of free space, and I is the ionic strength of the bulk solution. We obtain the surface charge density from surface tension measurements employing a Wilhelmy balance. Within the confines of the Gouy−Chapman model, the depth of the interfacial region, called the double layer region or the Debye−Hückel screening length, over which the electrostatic field is present can be expressed as

$$\frac{1}{\kappa} = \left(\sqrt{\frac{1000DRT}{8\pi N^2\epsilon^2 I}}\right) = 0.3/\sqrt{I} \quad \text{(nm)} \qquad (8)$$

where D is the dielectric constant and I is the ionic strength of the bulk solution in mol/L. Increasing the bulk surfactant concentration increases the surface concentration and the surface charge density thereby resulting in an increased interfacial potential. Varying the ionic strength of the solution has a 2-fold effect on the electrostatic field created by the soluble charged surfactants used in this study. One effect is a change in the Debye−Hückel screening length, eq 8, brought about by a change in the number of ions present at the interface. For example, as the ionic strength increases the number of ions at the interface increases and the surface charge is screened in a smaller distance. The smaller Debye−Hückel screening length means that fewer interfacial water molecules interact with the electrostatic electric field which in turn produces a smaller nonlinear polarization. The other effect is a reduction in the interfacial potential, eq 7, that accompanies increasing ionic strength. Also pertinent to consider is that the surface concentration of soluble surfactants and thus the surface charge density are dependent on the ionic strength of the solution. For a bulk SDS concentration of 4.00 mM the surface concentration increases by 10−15% over the range of ionic strengths studied here with most of the increase achieved before an ionic strength of 0.05 M.

Experimental Section

The laser system employed for the vibrational SFG studies has been described in detail elsewhere.[24,25] 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 generated in ethylene glycol. The system produces IR pulses tunable from 2.4−4.0 μm at a repetition rate of 1 kHz. The energy of the pulses over this range is approximately 8 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}, P_{ir} polarization conditions which picks out the vibrational modes with components of the transition dipole moment perpendicular to the plane of the interface. Spectra from the air/water interface were obtained in an external reflection geometry with the 800 nm and IR beams directed onto the interface in a copropagating arrangement at

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angles of 56 and 68 deg from the surface normal, respectively. The beam diameters of the tunable IR and 800 nm laser beams used in the air/water studies were approximately 300 and 800 μm, respectively. Spectra from the CCl_4/water interface were obtained in a total internal reflection geometry with the 800 nm and tunable IR beams coincident on the interface from the CCl_4 side at the critical angle for each wavelength (66.5 and 73.2 deg, respectively). The beam diameter of the tunable IR and 800 nm laser beams for the CCl_4/water studies was approximately 300 μm and 4 mm, respectively. Generation of fluorescence and continuum in the CCl_4 by the 800 nm beam necessitated the beam expansion (as compared to the air/water studies) to 4 mm. Previous studies[18,22] have shown that operating in a total internal reflection geometry produces an enhancement of several orders of magnitude in the generated nonlinear polarization. For both geometries the generated sum frequency light is detected in reflection with a PMT after filtering. Individual spectra were collected with gated electronics and a computer while, the IR frequency was scanned from 2750 to 3700 cm^{-1}. Each scan was obtained with an increment of 4 cm^{-1} and an average of 300 laser shots per increment and each spectra presented is an average of at least two scans. We obtain peak intensities, bandwidths, areas, and positions from least-squares fits to the spectral data using eqs 1 and 3.

Both 18 MΩ water from a Nanopure filtration system and HPLC grade water from Mallinckrodt were used with no detectable difference in the VSFG spectra or in surface tension measurements performed with a Wilhelmy balance. HPLC grade carbon tetrachloride (99.9+%) from Sigma-Aldrich was used as received. Atom d-25 sodium dodecyl sulfate (98%) from Cambridge isotope laboratories was used as received. The bulk concentration of SDS in the aqueous phase was increased by additions of a stock solution followed by gentle stirring. After each addition 20−30 min was allowed for the interfacial adsorption of SDS to occur before a spectral scan was obtained. From surface tension measurements performed with a Wilhelmy balance and the Gibbs equation for adsorption we calculate the surface density of SDS. The surface density measurements were consistent with literature measurements conducted at the same ionic strength.[26,27] The surface potential is then calculated using Gouy−Chapman theory and the assumption that each SDS molecule is charged. Absorption of the tunable IR beam in the OH stretching region by the CCl_4 was determined to be negligible with FTIR and by monitoring the IR energy from the laser system after the beam had traversed a 1 cm path length of CCl_4. All glassware and experimental apparatus which came into contact with the aqueous or organic phases were soaked in concentrated sulfuric acid containing No−Chromix for at least 3 h and then were thoroughly rinsed with 18 MΩ water.

Results

A. SDS at the Air/Water Interface. Figure 1 shows the VSFG spectra from water molecules at the air/water interface with varying bulk concentrations of deuterated SDS and an ionic strength of 10 mM. The solid lines in Figure 1 are a fit to the data using eqs 1 and 3 from which we obtain the position, area, width, and intensity (height) of each peak. As the bulk concentration is increased we observe an enhancement in the OH peaks from the interfacial water molecules. As mentioned above this enhancement is a result of the alignment of the interfacial water molecules which accompanies the interfacial electrostatic field produced by the charged surfactant. We observe this enhancement at bulk concentrations corresponding to very small surface coverages, approximately 200−300 Å^2/molecule, and find that a maximum in the enhancement is observed well before the maximum surface coverage is reached at 2−3 mM. This first observation illustrates the high sensitivity of VSFG to the presence of charged surfactants at the interface and from the second observation we infer that the interfacial water molecules achieve their greatest degree of alignment before maximum surface coverage is attained.

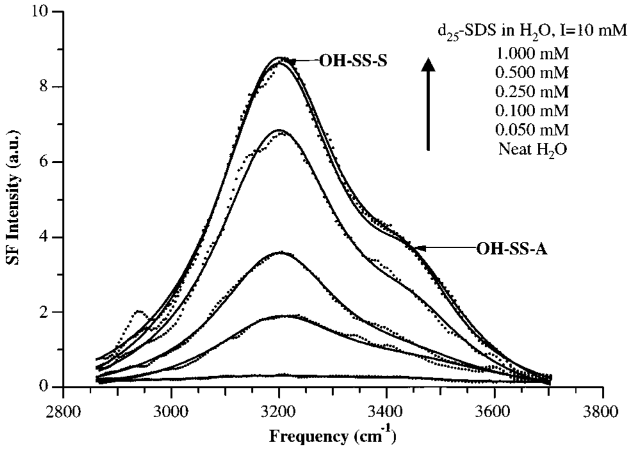

Figure 1. VSFG spectra from the air/water interface under S-sf, S-vis, P-ir polarization conditions for various bulk concentrations of SDS and an ionic strength of 10 mM. Solid lines are a least-squares fit to the data using eqs 1 and 3.

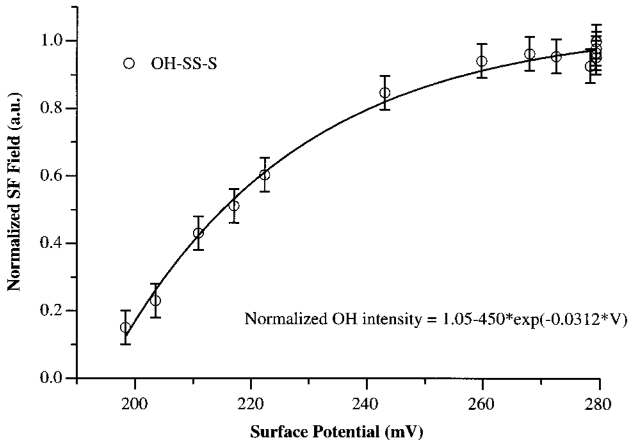

Figure 2. Normalized SF field at the position of the OH−SS−S peak from the fitted spectra in Figure 1 plotted as a function of the surface potential for the air/water interface. Surface potential determined from surface tension measurements and the Gibbs and Gouy−Chapman equations. Solid line is a least-squares fit to the data using an exponential function with the functionality included on the figure.

To further examine this latter point the SF field at the position of the OH−SS−S peak, normalized to unity at maximum intensity, is plotted in Figure 2 as a function of the surface potential calculated from surface tension measurements. As will be discussed further below the OH−SS−S peak results from OH vibrations from water molecules that are in a tetrahedral arrangement with a high degree of hydrogen bond order much like the structure of ice. From Figure 2 we find that the intensity reaches a maximum at a surface potential of approximately 260 mV. Equation 6 would predict that the SF field should be linear with the surface potential where we find that the SF field has an exponential dependence on the surface potential. The deviation from the linearity predicted by eq 6 is a result of the alignment of the dipole moments of the interfacial water molecules which results in a lesser degree of cancellation of the transition moments of the OH stretches as the surface potential increases. The maximum enhancement observed at 260 mV then corresponds to maximum alignment of the interfacial water molecules with further increases in the potential having minimal effect on the alignment of the water molecules. Potential dependent alignment of the interfacial water molecules has been observed previously at the charged electrode/water interface with FTIR[7,8] and X-ray scattering experiments.[9,10]

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Table 1. Labels, Structural Designations, and Peak Frequencies of the OH Peaks Used in This Study to Elucidate Structural Information from the VSFG Spectra

OH peak label	structural designation	peak freq (cm^{-1})
OH−SS−S, H_2O	icelike, high H-bond order	3200−3250
OH−SS−A, H_2O	waterlike, low H-bond order	3400−3450

Table 1 lists the labels, structural designations, and peak positions of the two peaks observed in the VSFG spectra from interfacial water molecules shown in Figure 1.[28−30] It is important to note here that the vibrational spectra of liquid water is extremely complex, due to coupling across hydrogen bonds and energetic coupling of many normal modes, and thus the exact assignment of the normal modes responsible for each peak is exceedingly difficult. However, from the two peaks present in the spectra of Figure 1 and a qualitative assignment of the structural environment of the water molecules contributing to each peak, we can obtain information concerning the hydrogen bonding between interfacial water molecules. The first peak (OH−SS−S) occurs at 3200 cm^{-1} and is attributed to the in-phase coupled OH vibrations from water molecules that are in a tetrahedral arrangement with a high degree of hydrogen bond order.[19,30,31] This peak has been described as being indicative of an "icelike" structure and dominates the IR and Raman spectra from bulk water below room temperature. The peak located between 3400 and 3450 cm^{-1} is attributed to the coupled vibrations from water molecules that have incomplete tetrahedral coordination with one strong and one weaker hydrogen bond or to water molecules with bifurcated hydrogen bonds.[19,30−32] The OH−SS−A peak has been described as being indicative of a lesser degree of hydrogen bond order and a more "waterlike" structure. We have shown through isotopic dilution studies[33,34] that the square root area under the OH peaks in the VSFG spectra of surface water is a good indicator of the relative number of oscillators (water molecules) contributing to the OH peaks. Figure 3 shows the relative percent of OH oscillators contributing to each peak calculated from the fitted data of Figure 1 plotted versus the surface potential. Figure 3 shows that there is an increase in the degree of hydrogen bond order with an increase of the surface potential as evidenced by the increase in the proportion of water molecules contributing to the OH−SS−S peak. In fact, the partitioning of water molecules into the more hydrogen bond ordered structure increases from 50% at approximately 200 mV to 70% at approximately 230 mV.

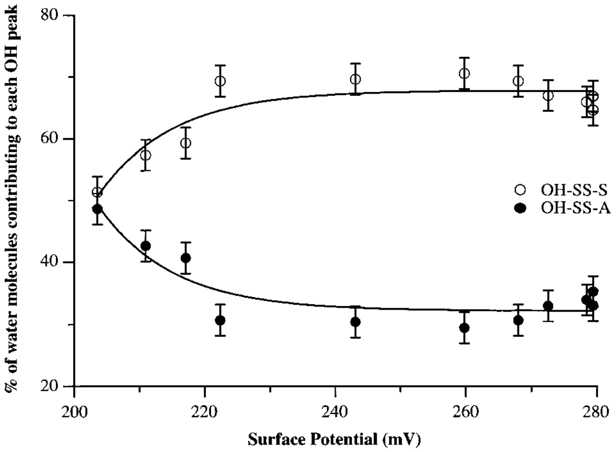

Figure 3. Relative percent of the OH oscillators contributing to each OH peak as determined from the fitted spectra in Figure 1 plotted versus the surface potential. Solid line is a least-squares fit to the data using an exponential function.

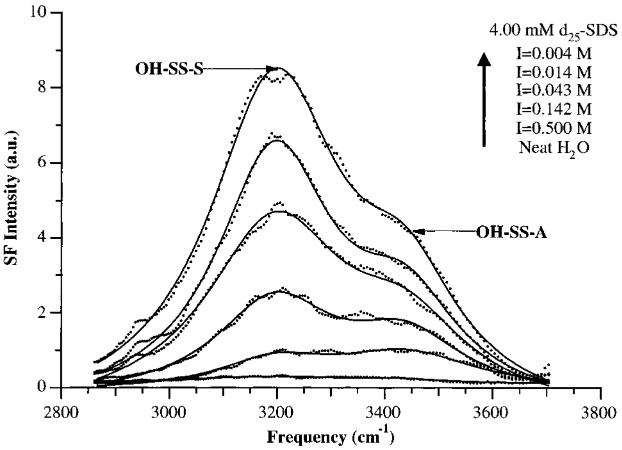

Figure 4. VSFG spectra from the air/water interface under S-sf, S-vis, P-ir polarization conditions for various ionic strength and a bulk SDS concentration of 4.00 mM. Solid lines are a least-squares fit to the data using eqs 1 and 3.

Figure 4 shows the VSFG spectra from the air/water interface for a 4.00 mM bulk SDS concentration at varying ionic strengths. The solid lanes in Figure 4 are a fit to the data using eqs 1 and 3. As the ionic strength is increased from 4.00 mM to 0.5 M we observe a dramatic decrease in the enhanced OH peaks in the VSFG spectra. The decrease in the enhancement with increasing ionic strength results from both a decrease in the surface potential and a decrease in the double layer depth. The decreased surface potential diminishes the alignment of the interfacial water molecules, while the decreased double layer depth reduces the number of water molecules interacting with the optical fields. The range of ionic strengths studied results in the double layer changing from a few angstroms to a few nanometers which corresponds to a variation from a few water layers to tens of water layers. Figure 5 shows the relative percent of OH oscillators contributing to each peak calculated from the fitted data in Figure 4 plotted versus the surface potential determined from surface tension measurements. As the interfacial potential is increased by decreasing the ionic strength Figure 5 shows that there is a progression from a less hydrogen bond ordered structure to a more hydrogen bond ordered structure. The partitioning of water molecules into the more hydrogen bond ordered structure increases from 40% at approximately 180 mV to 65% at approximately 230 mV which is in good agreement with the similar data in Figure 3 obtained by varying the bulk concentration.

To further explore the sensitivity of the VSFG experiments to the orientation of interfacial water molecules we have performed temperature dependent measurements. Figure 6 shows the VSFG spectra from the air/water interface with a bulk SDS concentration of 4.00 mM and an ionic strength of 10 mM for varying temperatures. The spectra in Figure 6 shows that the intensities of the OH peaks are very dependent on the temperature. The decrease in the intensity of the OH peaks with increasing temperature results from the increased random-

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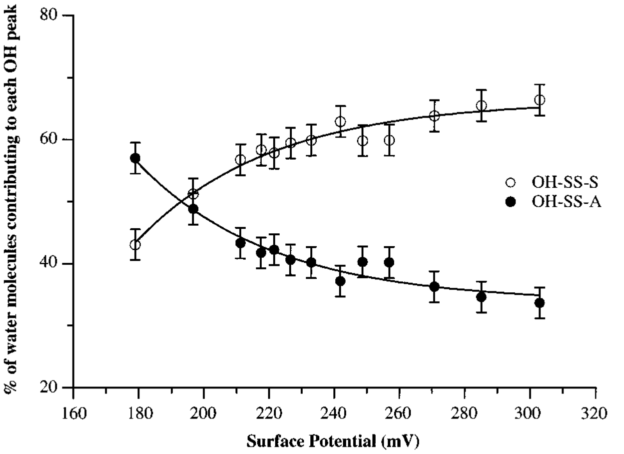

Figure 5. Relative percent of the OH oscillators contributing to each OH peak as determined from the fitted spectra in Figure 4 plotted versus the surface potential. Solid line is a least-squares fit to the data using an exponential function.

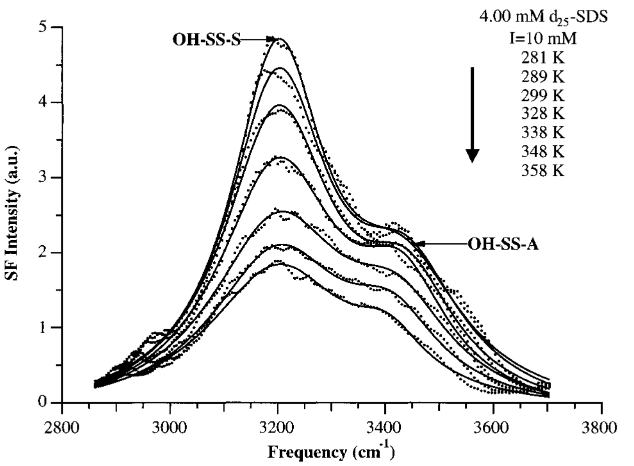

Figure 6. VSFG spectra from the air/water interface under S-sf, S-vis, P-ir polarization conditions for various temperatures and a bulk SDS concentration of 4.00 mM and an ionic strength of 10 mM. Solid lines are a least-squares fit to the data using eqs 1 and 3.

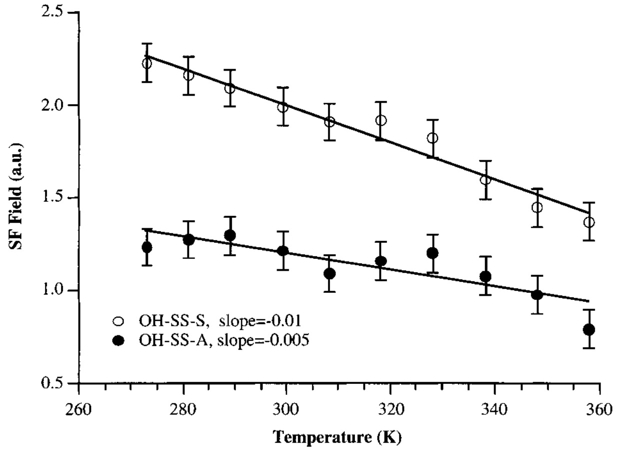

Figure 7. SF field from the fitted spectra in Figure 6 plotted as a function of the temperature. Solid lines are a linear least-squares fit to the data.

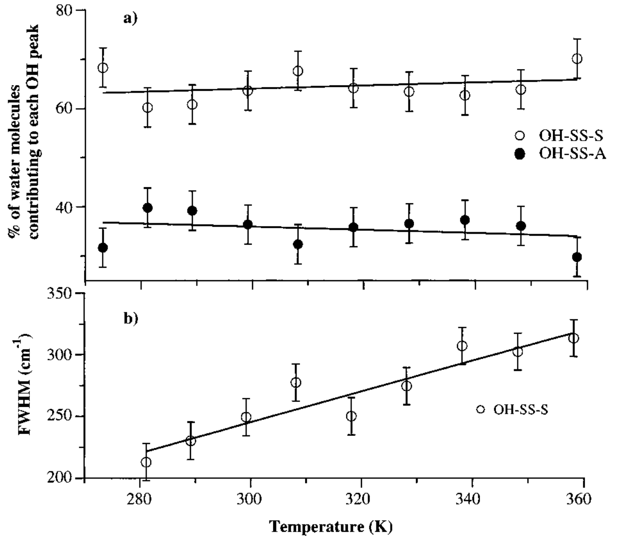

Figure 8. (a) Relative percent of the OH oscillators contributing to each OH peak as determined from the fitted spectra in Figure 6 and (b) fwhm of the OH−SS−S peak from the fitted spectra in Figure 6 plotted versus temperature. Solid lines are a linear least-squares fit to the data.

ization of the interfacial water molecules afforded by the increased thermal energy. Figure 7 shows the SF field at the peak positions of the OH−SS−S and OH−SS−A peaks obtained by taking the square root of the peak intensity from the fitted spectra in Figure 6 plotted as a function of the temperature. These data illustrate the temperature dependence of the OH peaks, and the steeper slope obtained for the OH−SS−S peak implies that this peak is more temperature dependent than the OH−SS−A peak. Figure 8a shows the relative percent of OH oscillators contributing to each peak calculated from the fitted data in Figure 6 plotted versus the temperature. As the temperature is increased from near freezing to near boiling we observe very little change in the partitioning of water molecules between the two peaks with the relative percent of oscillators in each peak remaining constant at approximately 65% and 35% for the OH−SS−S and OH−SS−A peaks, respectively. The observation that the peak intensity decreases with increasing temperature whereas the partitioning between the icelike and water like peaks remains constant is a result of the increasing bandwidth of the OH−SS−S peak with increasing temperature as shown in Figure 8b. As the temperature is increased the OH−SS−S peak intensity decreases while the bandwidth increases, these opposing effects cause the relative area of the OH−SS−S peak to remain constant. We see a similar effect occurs in the OH−SS−A peak but to a much lesser degree since the decrease in peak intensity from this peak is much smaller.

B. SDS at the CCl_4/Water Interface. Figure 9 shows the VSFG spectra from the CCl_4/H_2O interface in the OH stretching spectral region with varying bulk concentrations of the charged soluble surfactant SDS present in the aqueous phase and an ionic strength of 10 mM. Inspection of the spectra in Figure 9 shows that similar to the air/water case there is a large enhancement in the intensity from the OH peaks as the bulk surfactant concentration is increased. This increase with increasing bulk concentration is again a result of the fact that the interfacial concentration, and thus the surface charge density and magnitude of the electrostatic field, is a function of the bulk concentration. We find that this enhancement reaches a maximum value a bulk concentration of approximately 0.5 mM, while surface tension measurements show that the maximum surface coverage occurs around 1−2 mM. From this observation we infer that the water molecules have achieved their highest degree before maximum surface coverage is reached. Further, we observe an enhancement in the SF response at submicromolar bulk concentrations which correspond to surface concentrations several orders of magnitude below the maximum surface concentration. The

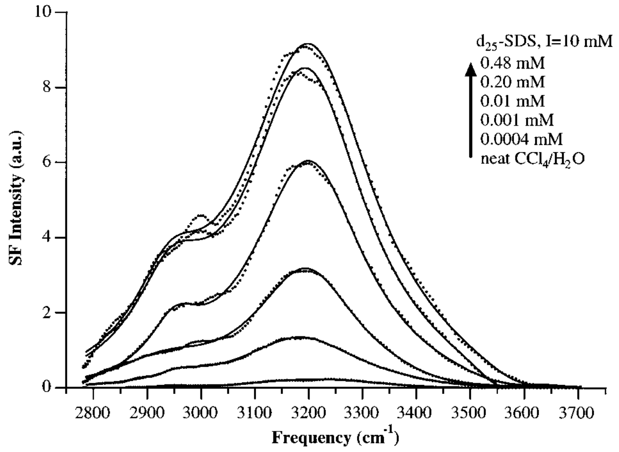

Figure 9. VSFG spectra from the CCl_4/water interface under S-sf, S-vis, P-ir polarization conditions for various bulk concentrations of SDS and an ionic strength of 10 mM. Solid lines are a least-squares fit to the data using eqs 1 and 3.

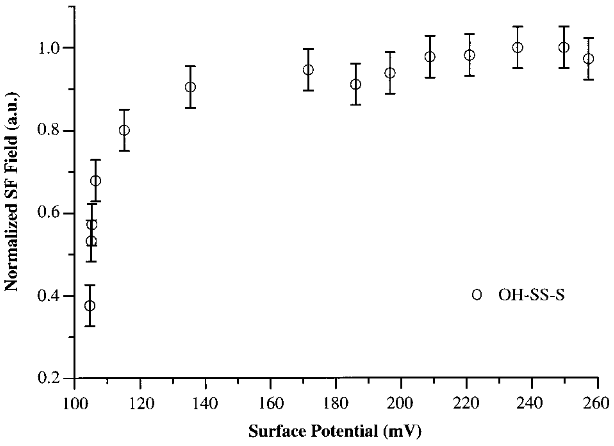

Figure 10. Normalized SF field at the position of the OH−SS−S peak from the fitted data of Figure 9 plotted versus the interfacial potential. The interfacial potential is calculated from surface tension measurements and the Gibbs equation.

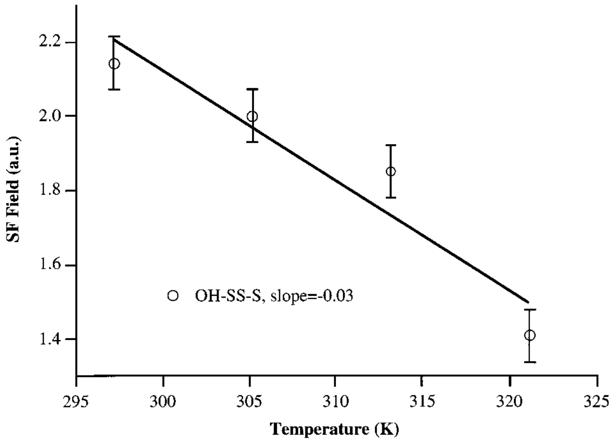

Figure 11. SF field at the OH−SS−S peak position from fitted VSFG spectra plotted versus the temperature. Solid line is a linear least-squares fit to the data.

ability to detect a very low surface concentration of SDS again illustrates the high sensitivity of this experimental technique. The presence of CCl_4 has some effect on the SDS present at the interface, most notable is an increased surface activity which results in more SDS at the interface in comparison to the air/water interface for a certain bulk concentration.

Inspection of Figure 9 shows that the dominant feature in the VSFG spectra from the CCl_4/SDS/water interface is the OH−SS−S (icelike) peak, while there is little or no evidence for intensity from the OH−SS−A (waterlike) peak. This observation is markedly different from what was observed at the air/water interface where the waterlike (OH−SS−A) peak gave rise to a prominent shoulder on the icelike (OH−SS−S) peak. The shoulder in the 2900−3050 cm^{-1} region in the spectra from Figure 9 arises from a small amount of contaminant, CH stretches, present at the neat interface riding on the large OH−SS−S peak. The fact that a small amount of contaminant is visible in the VSFG spectrum from the CCl_4/water interface and not the air/water interface is a result of the enhancement in the VSFG signal obtained in the total internal reflection (TIR) geometry which we have found from previous studies[18,22] to be as much as 4 orders of magnitude. Adding to our increased sensitivity in the TIR geometry is the fact that many trace bulk impurities will preferentially adsorb at the CCl_4/water interface and thus result in small signals in the VSFG spectrum. From the dominance of the OH−SS−S peak we infer that the prevailing structure of water molecules at the CCl_4/water interface in the presence of SDS is a tetrahedral arrangement much like the structure of ice. This observation is in striking contrast to the IR and Raman spectra from bulk water at room temperature for which there is approximately equal distribution between each mode.[31] As will be discussed below, this difference is a result of the structure inducing influence the nonpolar CCl_4 molecules have on the interfacial water molecules.

Figure 10 shows the normalized SF field from the OH−SS−S peak obtained from the spectra in Figure 9 plotted against the interfacial potential determined from surface tension measurements. As was the case for the air/water data we find that at the CCl_4/water interface the dependence of the SF field on the potential deviates from the linear relationship predicted by eq 6. Again this deviation is a result of the alignment of the transition dipole moments of the interfacial water molecules with the polarization vector of the IR light. At the CCl_4/water interface we find that the water molecules achieve their maximum alignment at an interfacial potential of approximately 160 mV somewhat below what was observed from the air/water interface. We again have verified the alignment of the interfacial water molecules with temperature dependent measurements shown in Figure 11 where we plot the SF field at the OH−SS−S peak versus temperature. Figure 11 shows that as the temperature is increased the SF field diminishes as a result of the increased thermal energy and the increased randomization of the OH transition dipole moments. In comparison to the complimentary data from the air/water interface we find that at the CCl_4/water interface the dependence of the SF field on the temperature is approximately three times larger.

Discussion

A. Surface Potential Effects. The presence of charged surfactant at the air/water interface induces an electrostatic field in the double layer region. This field is on the order of 10^8 V/m at maximum surface coverage and can induce an alignment of the interfacial water molecules which is manifested in the VSFG spectra. The depth of the field and thus the region probed by VSFG is on the order of the double layer which, within the confines of Gouy−Chapmann theory, depends on the solution ionic strength. The dependence of the SF field in the OH stretching region on the surface potential is illustrated in Figure 2. As the surface potential is increased by increasing the bulk concentration of SDS while holding the ionic strength constant at 10 mM we observe an increase in the intensity from the OH−SS−S peak. The functionality of this increase follows an exponential which agrees well with previous experiments conducted at the metal electrode/water interface.[8] At the air/water interface we find that the interfacial water molecules attain the highest degree of alignment at a potential of 260 mV, whereas for the metal electrode/water interface maximum alignment was observed at a potential of 500 mV. The difference in the potential at which maximum alignment is achieved at the SDS-air/water interface in comparison to the metal electrode/water interface is possibly due to extended hydrogen bonding between the interfacial water molecules and the SDS headgroup. At the SDS-air/water interface the water molecules are oriented by the electrostatic field with their hydrogens pointed toward the air. Hydrogen bonding between SDS headgroups and water molecules aligns the water molecules such that the hydrogens are directed toward the headgroup[35] which is essentially the same orientation produced by field alignment. Extended hydrogen bonding between water molecules and the SDS headgroups would act to enhance the field alignment of the interfacial water molecules thus causing maximum alignment to occur at a lower surface potential. Hydrogen bonding of the water molecules in the solvation sphere of the surfactant headgroup also may contribute to the enhancement. However, theoretical studies[35] of SDS at the air/water and CCl_4/water interfaces have shown that these waters are contained within several angstroms from the headgroup, whereas the double layer region extends several nanometers and thus contains many more water molecules. The fact that there are fewer water molecules in the solvation sphere means that the dominant contribution to the enhanced SF response arises from water molecules not necessarily participating in solvation of the headgroup.

The structural properties of bulk water have been previously characterized in numerous studies through inspection of the OH peaks in Raman and IR spectra.[8,28−31] In addition, both FTIR[7,8,30] and VSFG[17,19−21,36,37] have been used to study the structure of surface water molecules in a variety of systems. The OH−SS−S peak located between 3200 and 3250 cm^{-1} is attributed to the coupled stretching vibration from water molecules that have complete tetrahedral coordination with two strong hydrogen bonds much like the structure of ice.[19,30,31] The OH−SS−A peak occurs at approximately 3400 cm^{-1} and two different assignments have been suggested for this peak. The first assignment is from coupled OH vibrations of water molecules that are asymmetrically hydrogen bonded with incomplete tetrahedral coordination and a lesser degree of hydrogen bond order.[19,30,31] Other authors[32] have attributed this peak to the OH stretch from water molecules with bifurcated hydrogen bonds; this assignment also implies a molecular arrangement with a lesser degree of hydrogen bond order than the OH−SS−S peak. Raman and IR spectroscopic studies have shown that the peak at 3200 cm^{-1} dominates the spectra of bulk liquid water at low temperatures, whereas the peak at 3450 cm^{-1} dominates the spectra at elevated temperatures.[31] The temperature dependence of these spectral features gives rise to the characterization of these two peaks as being indicative of "icelike" (OH−SS−S) and "waterlike" (OH−SS−A) structures with the icelike peak corresponding to a higher degree of hydrogen bond ordering and the waterlike peak corresponding to a lower degree of hydrogen bond ordering.

A third OH peak observed in previous studies of bulk and surface water is located at approximately 3680 cm^{-1} and is attributed to the free OH stretch from water molecules that have hydrogen atoms not participating in hydrogen bonding.[28,36] The laser system employed limits our ability to obtain spectra in the 3600−4000 cm^{-1} region thus we confine our discussion to the two OH peaks located at 3200 and 3400 cm^{-1}. The red-shift of the peak position of the OH peaks with increased intermolecular hydrogen bonding as is seen in the three aforementioned peaks has been thoroughly examined.[28,29,38] The shift occurs because hydrogen bonding actually "steals" bond strength from the OH bond and thus stronger hydrogen bonds result in weaker OH covalent bonds and vibrational modes at lower energy. A comparison of the peak positions with the degree of hydrogen bonding illustrates the well-known trend that the peak position of the OH peak is red-shifted with increased hydrogen bonding. Accompanying the red-shift of the peak frequency with increased hydrogen bonding is a large increase in the bandwidth of the OH peak. This increase in the bandwidth results from dynamic dipole−dipole coupling between neighboring water molecules which produces a distribution of low- and high-frequency stretching modes.[29,39] The nature of this distribution also has an effect on the position of the peak frequency of the OH peak. Deconvolution of these two effects, hydrogen bonding and intermolecular coupling, on the energetics of the OH stretching peaks in the vibrational spectra is difficult and generally requires the study of HOD in H_2O or D_2O which eliminates the intermolecular coupling effect. However, the extent of hydrogen bonding can be inferred through a comparison of the relative amount of each peak, OH−SS−S and OH−SS−A, present in the vibrational spectra. This comparison is possible since the icelike (OH−SS−S) peak is indicative of more complete or extensive hydrogen bonding than the waterlike (OH−SS−A) peak.

Figures 3 and 5 illustrate how the intermolecular hydrogen bonding changes as a function of the surface potential at the air/water interface. The observed increase in the relative percent of oscillators contributing to the more strongly hydrogen bonded peak (OH−SS−S) with increasing surface potential provides us with direct evidence that the intermolecular hydrogen bonding increases with increasing surface potential. Theoretical studies[5,6] of water molecules between two platinum electrodes with surface charge densities covering the same range of values as those determined here from the SDS-air/water interface have shown a similar trend. We observe this trend in two separate cases; first by increasing bulk SDS concentration to increase the surface potential (Figure 3) and second by decreasing the ionic strength to increase the surface potential (Figure 5). The functionality shown in the two figures is somewhat different with the plot in Figure 3 rising at a faster rate than the plot in Figure 5. This phenomena is due to the fact that as the ionic strength is varied (Figure 5) *both* the surface potential *and* the double layer depth change, whereas as the bulk concentration is varied (Figure 3) while holding the ionic strength constant only the surface potential changes. Low surface potentials in Figure 5 correspond to high ionic strength and thus a small double layer thereby producing a larger electrostatic field and greater alignment than the equivalent surface potential in Figure 3. Complicating the situation even more is the fact that as the double layer decreases with decreasing ionic strength there are

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fewer water molecules interacting with the optical fields. We have had little success deconvoluting each effect in the data in Figure 5, thus the data are presented as a function of the surface potential and only qualitatively compared to Figure 3.

X-ray scattering experiments[10] of the electrode/water interface suggest that there is a substantial increase in the density of interfacial water molecules as compared to bulk water caused by destruction of the hydrogen bonded network when a large electrostatic field is applied across the interface. The work presented here as well as theoretical studies[5,6] show the opposite behavior in that there is actually an increase in the intermolecular hydrogen bonding when a large electrostatic field is applied across the interface. This observation is inferred from Figures 3 and 5 which show that as the interfacial potential is increased the partitioning into the more extensively hydrogen bonded and icelike peak also increases. Further inspection of Figures 3 and 5 show that a maximum in the partitioning of water molecules into the more hydrogen bond ordered structure occurs at approximately 230 mV. The fact that this potential is somewhat smaller than the 260 mV potential required to achieve maximum alignment of the water dipoles as shown in Figure 2 shows that increased dipole alignment with increased surface potential continues to occur after maximum hydrogen bonding is achieved.

Our observation that at the CCl_4/SDS/water interface the OH−SS−S peak dominates the OH stretching spectral region provides direct evidence that there is more extensive hydrogen bonding between neighboring interfacial water molecules when compared to bulk water molecules. This difference is a result of the effect that the nonpolar CCl_4 molecules have on the water molecules in the interfacial region. This effect can be explained in terms of the ability of water to solvate a nonpolar molecule such as CCl_4 and the corresponding decrease in entropy associated with the solvation of nonpolar molecules. This decrease in the entropy of the system overrides the enthalpy of solvation and causes the solvation of nonpolar molecules in water to be energetically unfavorable. The decrease in entropy results from water molecules rearranging into a tetrahedral structure in order to maximize hydrogen bonding in the presence of a nonpolar solute.[1] Our observation that the VSFG spectrum is dominated by the icelike peak at the CCl_4/SDS/water interface is a direct consequence of the structure inducing influence of CCl_4 molecules on the interfacial water molecules. This observation is also consistent with previous calculations[40] of hydrogen bonding at an oil/water interface which suggests that there is an increase in the strength of the hydrogen bonding among the water molecules near a hydrophobic surface. As was mentioned earlier we are probing specifically the asymmetric interfacial region which for the studies discussed here, ionic strength of 10 mM, corresponds to at most 10−20 water layers. In the bulk aqueous phase the water molecules are not influenced by the presence of a nonpolar molecule and thus the waterlike peak accompanies the icelike peak. In a recent publication[37] we showed that at the neat CCl_4/water interface the dominant peak is the icelike OH−SS−S, peak while at the neat air/water interface we observed an equal distribution between the OH−SS−S peak and the less hydrogen bond ordered waterlike OH−SS−A peak. The similarity of the water structure at the CCl_4/water interface both in the presence and in the absence of a charged soluble surfactant further allows us to infer that the presence of the surfactant and counterions in the aqueous phase does not disrupt the hydrogen bond ordering of the interfacial water molecules.

B. Temperature Effects. Previous temperature-dependent SHG studies[13,14] at the neat air/water interface suggest that there are two types of interactions which produce a net orientation of surface water molecules. One interaction is strongly temperature dependent and is attributed to hydrogen bonding, while the other is less temperature dependent and attributed to orientation due to the permanent dipole of water. These SHG experiments probe the overall changes in the nonlinear polarizability from the water surface and do not contain the molecular specificity afforded by VSFG. Previous VSFG measurements from the neat air/water interface[36] show little or no temperature dependence in all of the OH peaks which is in contradiction with the SHG experiments. The fact that we observe a strong temperature dependence at the air/SDS/water interface whereas little dependence was observed in VSFG studies from the neat air/water interface provides further support that the presence of SDS does indeed align the surface water molecules. At the air/water interface in the presence of SDS we observe that both OH peaks are dependent on temperature; however, the icelike and waterlike peaks have somewhat different temperature dependencies. From the slopes of the linear fits to the data in Figure 7 we conclude that the icelike peak is more temperature dependent, while the waterlike peak is less temperature dependent. This observation is in good agreement with the previous SHG studies from the neat air/water interface[13,14] since the more temperature-dependent peak (OH−SS−S) results from more strongly hydrogen bonded water molecules and the less temperature-dependent peak (OH−SS−A) is less strongly hydrogen bonded.

The temperature dependence of the OH−SS−S peak at the CCl_4/water interface is larger than both the OH−SS−S and OH−SS−A peaks at the air/water interface as evidenced by the larger negative slope shown in Figure 11. Earlier we concluded that the intermolecular hydrogen bonding was stronger at the CCl_4/water interface than at the air/water interface and thus the VSFG spectra from the CCl_4/water interface should be more strongly temperature dependent. The fact that this trend is observed in the temperature dependent measurements provides further support that the intermolecular hydrogen bonding is greatest at the CCl_4/water interface where the nonpolar CCl_4 molecules induce hydrogen bonding between water molecules. Equation 7 shows that the surface potential increases with increasing temperature thus the fact that the SF field decreases with increasing temperature provides evidence that the increased randomization of interfacial water molecules by the increased thermal energy outweighs any alignment produced by increased surface potential.

At the SDS-air/water interface we observe that the partitioning of water molecules into icelike and waterlike structures is relatively temperature independent (Figure 8a) with 65% and 35% of the oscillators contributing to the OH−SS−S and OH−SS−A peaks, respectively. The fact that in the presence of SDS the intermolecular hydrogen bonding of interfacial water molecules is relatively independent of the temperature while the alignment is strongly temperature dependent can be explained by the increased bandwidth that accompanies the increased temperature. As the temperature is increased the distribution of hydrogen bonded states increases and thus the energy range of OH oscillators increases as evidenced by the increased bandwidth shown in Figure 8b. The increased bandwidth is a result of more states energetically accessible to the interfacial water molecules but still within the two OH peaks. Thus the relative number of water molecules contributing to each peak does not change; however, the distribution of environments in which the water molecules exist does change.

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The spectral broadening of vibrational peaks with increasing temperature is well studied[28,29,31] and results from a decrease in the net alignment of the transition dipole moments of the molecules with the polarization vector of the optical field.

Conclusions

We have performed unique experiments exploring the influence that a charged surfactant has on the alignment and hydrogen bonding of water molecules at the air/water and CCl_4/water interface. The alignment of interfacial water molecules is evidenced by an enhancement in the OH stretching peaks of the VSFG spectra. The exponential dependence of this enhancement agrees well with FTIR studies from the charged metal electrode/water interface. By employing the interface specific technique of VSFG to monitor OH stretches sensitive to hydrogen bonding we observe a progression from a less hydrogen bonded and waterlike structure to a more hydrogen bonded and icelike structure as the surface potential is increased at the air/water interface. We can control the extent of hydrogen bonding by either increasing the bulk concentration of charged surfactant or decreasing the solution ionic strength. The observed formation of an icelike structure with increased applied potential agrees well with molecular dynamics simulations of water molecules between two platinum electrodes.[5,6] At the CCl_4/water interface the water molecules are predominantly in the icelike arrangement as evidenced by no observable contribution from the waterlike peak in the VSFG spectra. The difference in the hydrogen bonding of water molecules observed at the air/water and CCl_4/water interface is a direct result of the structure imposing effect the nonpolar CCl_4 molecules have on the interfacial water molecules. VSFG measurements at various temperatures from both the air/water and CCl_4/water interface confirm our sensitivity to the alignment of interfacial water molecules. The relationship between the temperature dependence of the VSFG measurements and intermolecular hydrogen bonding is in good agreement with previous SHG measurements from the neat air/water interface. We find that the temperature dependence of the SF response increases in the order air/water OH−SS−A, air/water OS−SS−S, and CCl_4/water OH−SS−S which follows the order of increased intermolecular hydrogen bonding. These studies provide new insight into the effects charged surfactants have on the structure and hydrogen bonding of interfacial water molecules and have particular relevance to theoretical studies examining water molecules between two charged electrodes.

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