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Probing the intermolecular hydrogen bonding of water molecules at the CCl₄/water interface in the presence of charged soluble surfactant

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The molecular structure and hydrogen bonding of water molecules at the CCl₄/water interface in the presence of a charged soluble surfactant has been explored in this study using vibrational sum frequency generation. By examining OH stretching modes that are highly sensitive to the local hydrogen bonding environment it is found that water molecules at the CCl₄/water interface both in the presence and absence of a charged soluble surfactant are predominantly in a tetrahedral arrangement much like the structure of ice. Isotopic dilution studies have been employed to further characterize this icelike interfacial structure. A blueshift of approximately 120 cm⁻¹ of the icelike OH stretching mode is observed upon dilution with D₂O. The first vibrational spectra of the OH stretching mode from uncoupled HOD molecules at the CCl₄/water interface is also reported. © 1997 American Institute of Physics. [S0021-9606(97)03346-1]

The interactions between water and charged amphiphiles at surfaces can play a dominant role in many processes including micellization, stabilization of membranes, and protein activity. At an oil/water interface an amphiphile alters the hydrogen bonding of water at the junction, resulting in a lowering of the interfacial tension. How these changes in hydrogen bonding with surfactant adsorption are manifested in the nonlinear vibrational spectroscopy of interfacial water at the CCl₄/H₂O interface is the focus of this paper.

Total internal reflection sum frequency generation (TIR-VSFG) is employed here in a unique set of experiments which characterize in detail the hydrogen bonding between interfacial water molecules at the liquid/liquid interface in the presence of a simple charged soluble surfactant. The combination of the surface sensitivity of VSFG and the enhancement afforded by operating in a total internal reflection geometry makes TIR-VSFG a powerful tool in studies such as these. The spectroscopy of the OH stretching modes of interfacial water molecules has been used in this study as a diagnostic of interfacial water structure and hydrogen bonding. These modes are particularly sensitive to the hydrogen bonding environment of water molecules as shown by numerous IR and Raman studies of bulk water. For bulk water, these studies have shown that water molecules partition into icelike and waterlike structures. We report that at the CCl₄/water interface both in the presence and in the absence of surfactant, nearly all interfacial molecules are in a tetrahedral arrangement much like the structure of ice with little or no evidence for a waterlike structure.

Further explorations of the icelike character of the interfacial water molecules in the presence of surfactants is obtained through isotopic dilution experiments. Isotopic dilution studies in which the OH stretching vibrations are progressively decoupled by additions of D₂O have been invaluable in studies of hydrogen bonding in bulk water and ice but this is the first study in which such experiments have been applied to liquid surfaces. The shift in energy observed in the icelike O–H peak with uncoupling of the OH symmetric stretching vibration has provided us with a quantitative means of comparing the hydrogen bonding at this interface with that measured for bulk ice and supercooled liquid water. Through isotopic dilution studies we have also obtained the first vibrational spectra of the uncoupled OH stretching mode from HOD molecules at the CCl₄/water interface. This mode has been shown to be an excellent indicator of the local hydrogen bonding environment in bulk studies.

Figure 1 shows the VSFG spectra from the CCl₄/water interface with the aqueous phase having a bulk sodium dodecyl sulfate (SDS) concentration of 1.0 mM. All spectra presented were obtained under S₄fg, Svis, Pir polarization conditions which pick out vibrational modes with components of the transition dipole moment perpendicular to the plane of the interface. The series of spectra were taken with various mixtures of H₂O and D₂O ranging from a mole fraction of 1.00 to 0.10. The mole fraction of H₂O, D₂O, and HOD were calculated by assuming complete isotopic exchange. The presence of SDS at the interface is evidenced by the C–H stretching modes of the alkyl chain and is also verified by interfacial tension measurements. Because these modes have been examined in detail in previous studies from this laboratory under higher spectral resolution, further discussion is not warranted here. The shoulder in the spectra near 3000 cm⁻¹ has not been studied in any detail here but could be due to the OH stretch from water molecules that are hydrogen bonded to the charged sulfate head group with the large redshift presumably a result of the strong hydrogen

Higher degree of hydrogen bond order and the waterlike hedral coordination and a more waterlike structure. These modes at a lower degree of hydrogen bond order. From the “waterlike” modes with the icelike mode corresponding to a position of the OH stretching modes with increased intramolecular hydrogen bonding as is seen in the three aforementioned modes has been thoroughly examined. The shift in the vibrational bandwidths, and integrated areas.

The VSFG spectra from the CCl4/H2O interface with 1.0 mM SDS in 100% H2O, the dominant feature in the OH stretching spectral region is centered around 3200 cm⁻¹. We attribute the observed peak at 3200 cm⁻¹ to the OH–SS–S mode, which corresponds to the in-phase coupled symmetric stretch from water molecules that have complete tetrahedral coordination much like the structure of ice. In contrast, for SDS at the air/water interface the VSFG spectrum shows two peaks, one corresponding to the OH–SS–S mode and an additional peak located between 3400 and 3450 cm⁻¹, which is attributed to water molecules that have incomplete tetrahedral coordination and a more waterlike structure.

These two peaks are commonly referred to as the “icelike” and “waterlike” modes with the icelike mode corresponding to a higher degree of hydrogen bond order and the waterlike mode to a lower degree of hydrogen bond order. From the dominance of the icelike mode in the VSFG spectra from SDS at the CCl4/H2O interface we infer that the prevailing structure of the interfacial water molecules in the presence of a charged surfactant is a tetrahedral arrangement much like the structure of ice. As will be described in a later publication, relative to the neat CCl4/H2O interface, the addition of surfactant results in increased intensity in the icelike mode due to electrostatic field induced orientation of water molecules in the double-layer region.

Another OH mode often observed in bulk and surface water studies but not observed here 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. The laser system employed limits our ability to detect this mode. The redshift of the peak position of the OH stretching modes with increased intermolecular hydrogen bonding as is seen in the three aforementioned modes has been thoroughly examined. 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 stretching mode is redshifted with increasing hydrogen bonding. Accompanying the redshift of the peak frequency with increased hydrogen bonding is a large increase in the bandwidth of the OH stretch. 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. The nature of this distribution also has an effect on the position of the peak frequency of the OH stretching mode. 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 H2O or D2O, which eliminates the intermolecular coupling effect. However, the extent of hydrogen bonding can be inferred through a comparison of the relative number of water molecules contributing to the icelike and waterlike modes. This comparison is possible since the icelike mode is indicative of more complete hydrogen bonding than the waterlike mode.

Our observation that at the CCl4/water interface the icelike mode dominates the OH stretching spectral region provides direct evidence that there is more complete hydrogen bonding between neighboring water molecules at the interface than in the bulk. This observation is a consequence of the hydrophobic effect which causes the interfacial water molecules to rearrange into a tetrahedral structure thus maximizing the intermolecular hydrogen bonding in the presence of a nonpolar solute such as CCl4. We are probing specifically the asymmetric interfacial region which for an ionic strength of 1.0 mM corresponds to at most 30 water layers (see Ref. 12), thus one might expect CCl4 to be present in this region. In the bulk aqueous phase the water molecules are not influenced by the presence of a nonpolar molecule and the waterlike peak accompanies the icelike peak. At the near CCl4/water interface we also find that the icelike mode dominates the VSFG spectrum. The similarity of the water structure at the CCl4/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 counter ions in the aqueous phase does not disrupt to any measurable degree the hydrogen bond ordering of the interfacial water molecules.

Further information about the interfacial water hydrogen bonding structure can be extracted from the spectra of the isotopic mixtures shown in Figs. 1 and 2 where the latter corresponds to spectra from the lowest H2O concentrations depicted on an expanded scale for clarity. Numerous IR and Raman studies of H2O/D2O mixtures have been conducted in the past to gain a better understanding of the structure of water in both bulk liquid water and bulk ice. As D2O (H2O) is added to H2O (D2O) the intermolecular coupling between the OH (OD) oscillators decreases as a result of the difference in hydrogen bonding between H2O and D2O and the difference in energy of the OH and OD stretches.
The intermolecular decoupling as D$_2$O (H$_2$O) is added to H$_2$O (D$_2$O) manifests itself in the IR and Raman spectra as a blueshift in the spectral position of the OH (OD) stretching vibrations. This blueshift occurs as the mole fraction of H$_2$O (D$_2$O) is decreased and results from the decreased intermolecular coupling of the OH oscillators. Experiments conducted on cubic and amorphous ice$^9$ as well as supercooled liquid water$^{15}$ have shown a blueshift in the OH–SS–S peak of approximately 100–120 cm$^{-1}$ as the mole fraction of H$_2$O varies from 1.00 to 0.01.

Close inspection of the spectra in Fig. 1 shows a similar blueshift of the OH–SS–S peak position with decreasing H$_2$O mole fraction. The peak position goes from 3200 cm$^{-1}$ at a mole fraction of 1.00 to 3230 cm$^{-1}$ at a mole fraction of 0.05. The blueshift in the peak frequency of the OH–SS–S with decreasing H$_2$O mole fraction is a result of the intermolecular decoupling of the OH oscillators by the addition of OD oscillators as previously mentioned. The magnitude of the blueshift that we observe for the CCl$_4$/H$_2$O–SDS system varies from 1.00 to 0.2 mole fraction over the range from 1.0 to 0.2. Beyonda mole fraction of 0.05, the blueshift in the peak frequency of the OH–SS–S mode varies from 3200 to 3230 cm$^{-1}$ as the mole fraction of H$_2$O decreases.

FIG. 2. VSFG spectra from the CCl$_4$/H$_2$O interface with 1.0 mM SDS in the aqueous phase for low mole fractions of H$_2$O under S-sf, S-vis, P-ir polarization conditions.

FIG. 3. Plot of the peak position of the OH–SS–S mode from the spectral data fits as a function of the mole fraction of H$_2$O.

Our VSFG studies of the hydrogen bonding and struc-
ture of water molecules at the CCl₄/water interface in the presence of a charged soluble surfactant provide new insight into differences between interfacial and bulk water molecules. We find that water molecules at the CCl₄/water interface both in the presence and absence of a charged soluble surfactant are predominantly in a tetrahedral arrangement much like the structure of ice whereas water molecules in the bulk are equally partitioned into waterlike and icelike modes at room temperature. Isotopic dilution studies have been used for the first time to understand the hydrogen bonding of water molecules at a liquid surface. A blueshift of approximately 120 cm⁻¹ in the icelike peak is observed upon dilution which we attribute to intermolecular uncoupling of the OH oscillators. The similarity in the magnitude of this frequency shift with that of bulk amorphous and cubic ice as well as supercooled liquid water further confirms our conclusion that the interfacial water molecules are in an ice-like arrangement. At low H₂O mole fractions we find that we are sensitive to the OH stretching mode from uncoupled HOD at the CCl₄/water interface. This mode has been shown to be essential in the full characterization of the structure of bulk water in both liquid and solid phases from IR and Raman spectroscopic studies. Our future endeavors will include exploiting this mode to probe the interfacial hydrogen bonding environment as a function of temperature and the presence of structure making and breaking ions as well as to probe structural dependencies on the interfacial potential.

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1 M. N. Jones and D. Chapman, Micelles, Monolayers, and Biomembranes (Wiley–Liss, New York, 1995).