

# Aqueous solvation of charge at hydrophobic liquid surfaces

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## Abstract

The solvation of charge at the interface between an aqueous phase and hydrophobic medium is a key question in the mechanism of a wide range of biomolecular processes. These studies report the direct measurement of the molecular properties of water surrounding an isolated charge at an oil/water interface, and show how the solvating water structure changes with progressive charge build-up. At trace charge concentrations, highly oriented solvating water molecules found in both the aqueous and hydrophobic rich phases have negligible interactions with other water molecules. Water molecules observed within the hydrophobic rich phase are highly oriented by charge–dipole interactions.

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## 1. Introduction

Ion transport across an aqueous/nonaqueous boundary layer is one of the most important and prevalent physical processes that occurs in living systems. The mechanistic role that solvating interfacial water molecules play in this transport process continues to be poorly understood on a molecular-level. The same is true of our understanding of the role that solvating water molecules surrounding bound charge on macromolecules play in three-dimensional structure and assembly.

Obtaining a microscopic understanding of processes such as protein folding, macromolecular assembly and ion transport requires a molecularly sophisticated understanding of how water solvates surface charges, an understanding that to date has largely been derived from theory [1–12].

In this Letter, we have spectroscopically measured the molecular-level characteristics of interfacial water solvating isolated molecular ions adsorbed at a liquid aqueous/nonaqueous interface. These experiments employ vibrational sum frequency spectroscopy (VSFS)

[13–15] to detect the infrared spectrum of water molecules influenced by anisotropic interfacial forces. The results provide detailed information about the H-bonding character and orientation of these solvating water molecules that reside in different portions of the interfacial region both at these isolated concentrations and as charge is progressively added. At trace concentrations the solvating water molecules in the aqueous-rich phase have weaker H-bonding interactions than in bulk water. Those residing in the more hydrophobic region of the interface are preferentially oriented by charge–dipole interactions. Calculations show that the orienting electric field can extend several molecular layers into the organic phase. An enhancement in the vibrational spectrum of solvating water molecules in the vicinity of the interfacial ions allows us to distinguish their properties from those of the more prevalent bulk water molecules.

## 2. Experimental section

The nonlinear laser system and optical configuration employed in these studies has been described in detail elsewhere [13]. Briefly, the laser system consists of a Nd:YAG diode seeded laser that pumps a double pass optical parametric oscillator/optical parametric amplifier

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in series, producing mid-infrared radiation tunable from 2500 to 4000  $\text{cm}^{-1}$ . 532 nm radiation for use at the experiment is generated in a BBO crystal and overlapped spatially and temporally with the infrared pulses at the interface in a total internal reflection geometry (TIR). Under TIR conditions sum frequency signal is enhanced by several orders of magnitude over an externally reflected geometry and allows for the detection of low SF water signal levels [16,17]. SF radiation is collected by a PMT, gated electronics, and computer. Each VSF  $\text{CCl}_4/\text{H}_2\text{O}$  spectrum is obtained with an increment of 2  $\text{cm}^{-1}$  and an average of 50–100 pulses per increment. All spectra were obtained at room temperature.

98%  $d_{25}$ -sodium dodecyl sulfate (SDS) from Cambridge isotope laboratories and dodecyltrimethylammonium chloride (DTAC) from TCI America were used as received. Nanomolar aqueous concentrations of both DTAC and SDS solutions were made by serial dilutions of micromolar stock solutions. The  $\text{CCl}_4/\text{H}_2\text{O}$ /surfactant experiments have been performed using a Kel-F cylindrical cell that is placed on top of an IR grade quartz prism [13]. All glassware and sample cells have been soaked in concentrated sulfuric acid containing No-chromix to remove any organics and surface-active contaminants. After removal from concentrated acid, equipment has been thoroughly rinsed with 17.9 M $\Omega$  cm water from a nanopure filtration system until free from acid residue. Doubly distilled  $\text{CCl}_4$  (Aldrich, 99.9% HPLC grade) was placed in the cell and covered with  $\text{H}_2\text{O}$  (Mallinckrodt ChromAR<sup>®</sup> HPLC Grade)/surfactant solution for equilibration. Surfactant adsorption to the interface and equilibration of the  $\text{CCl}_4/\text{H}_2\text{O}$ /surfactant system was followed by temporally monitoring the VSF signal increase/decrease in the OH stretching spectral region.

### 3. Results and discussion

The studies involve two charged surfactants, SDS and DTAC adsorbed at the  $\text{CCl}_4/\text{H}_2\text{O}$  interface. The OH stretch modes of water are measured, modes that are sensitive in frequency, phase and lineshape to the bonding environment and orientation of the measured water molecules [13,18–20]. The experiments are configured to probe vibrational modes in the water molecules that have their dipole transition components perpendicular to the interfacial plane. Fig. 1a–c shows the spectra of the OH stretch region of interfacial water molecules at the neat  $\text{CCl}_4/\text{H}_2\text{O}$  interface and the same interface with trace amounts of anionic (SDS) and cationic (DTAC) surfactant adsorbed at the interface from nanomolar aqueous phase surfactant concentrations. Relative to the neat interface (Fig. 1a), the presence of trace amounts of SDS at the interface (Fig. 1b) produces a large dip in VSF intensity near 3600  $\text{cm}^{-1}$  and slightly

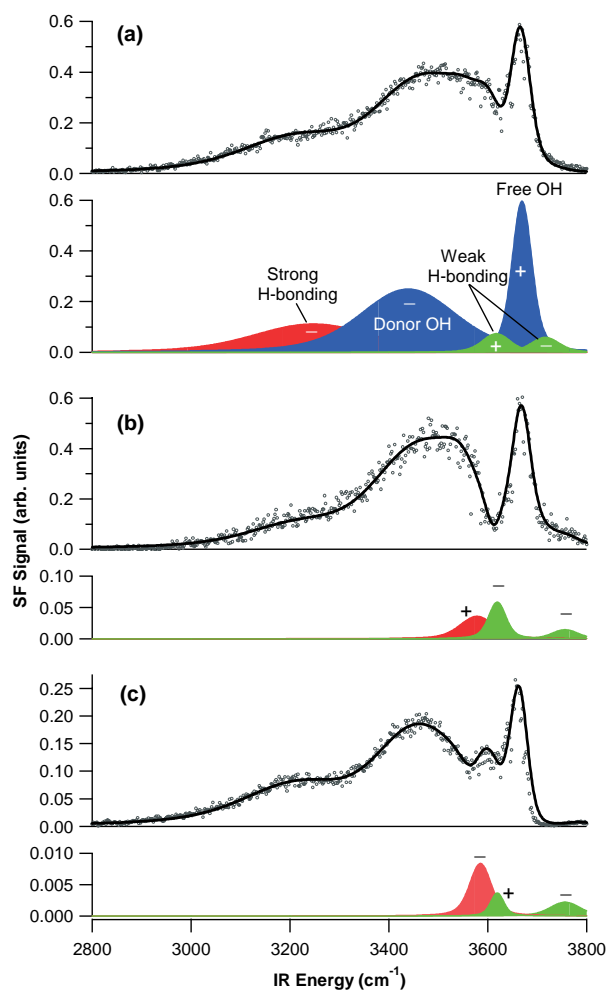


Fig. 1. (a) VSF spectrum of  $\text{H}_2\text{O}$  at the neat  $\text{CCl}_4/\text{H}_2\text{O}$  interface with least squares fit to the data superimposed as a solid line. Shown directly below are peaks contributing to the spectrum for the neat  $\text{CCl}_4/\text{H}_2\text{O}$  interface as determined previously [13,20]. (b) VSF spectrum of the  $\text{CCl}_4/\text{H}_2\text{O}$  interface at 10 nM SDS bulk aqueous phase concentration. The solid line is the fit to the data upon inclusion of contributing peaks (shown directly below) for OH modes of water molecules solvating the cationic head group of SDS at the  $\text{CCl}_4/\text{H}_2\text{O}$  interface. (c) VSF spectrum of the  $\text{CCl}_4/\text{H}_2\text{O}$  interface at 47 nM DTAC bulk aqueous phase concentration. The solid line is the fit to the data upon inclusion of contributing peaks (shown directly below) for OH modes of water molecules solvating the cationic head group of DTAC at the  $\text{CCl}_4/\text{H}_2\text{O}$  interface. All spectra are taken with S,S,P polarization. The shading of the solvating peaks corresponds to the water molecules displayed in Fig. 2 with similar shading. The positive/negative sign associated with each solvating  $\text{H}_2\text{O}$  peak corresponds to the phase (amplitude sign) of the vibrational mode.

increased intensity near 3700  $\text{cm}^{-1}$ . For DTAC (Fig. 1c), adsorption produces increased intensity near 3600  $\text{cm}^{-1}$  and a decrease near 3700  $\text{cm}^{-1}$ . As the concentration of these two surfactants increase up to bulk concentrations of  $\sim 200$  nM, the observations become more pronounced, but the spectral regions affected remain the same.

The spectra clearly show that, the adsorption of charged surfactants at the  $\text{CCl}_4/\text{H}_2\text{O}$  interface at

nanomolar aqueous phase surfactant concentrations results in a significant modification of the interfacial water behavior. Wilhelmy balance surface pressure measurements [21] shows that at these concentrations, (headgroup areas of  $>4000 \text{ \AA}^2/\text{molecule}$ ) the water molecules responsible for the observed spectral changes solvate *isolated* interfacial surfactant head groups. The inverse spectral changes observed in  $3600\text{--}3700 \text{ cm}^{-1}$  regions for these two differently charged surfactants represent the opposite orientation of the solvating water molecules as influenced by the different electrostatic field orientation.

To understand the bonding environment of these solvating water molecules we rely on previous VSF studies of the neat  $\text{CCl}_4/\text{H}_2\text{O}$  interface [13,20] that have identified peaks in this region associated with different types of water bonding species. For discussion purposes, these peaks and assignments are shown in Fig. 1a (below spectrum). The peak position and bandwidth provide information about the H-bonding environment of interfacial water molecules [22]. The relative sign (phase) of the peaks derived from the fits assist in determining the average orientation of the dipole moment of contributing modes and therefore, an average molecular orientation [23]. The lowest energy broad peak ( $3247 \text{ cm}^{-1}$ ) corresponds to the collection of interfacial water molecules that participate in the tetrahedral H-bonding similar to that in bulk water [13,22,24]. The two largest peaks at  $3669$  and  $3439 \text{ cm}^{-1}$  are due to water molecules that straddle the interface. The higher energy peak corresponds to the free OH bond that orients into and weakly bonds with the  $\text{CCl}_4$  phase [25]. The lower energy peak (donor OH) corresponds to the adjoining but energetically uncoupled OH bond of the same  $\text{H}_2\text{O}$  molecule that orients into the aqueous phase and act as a hydrogen donor to other water molecules [13,20]. The two peaks at  $3617 \text{ cm}^{-1}$  ( $\nu_1$ ) and  $3716 \text{ cm}^{-1}$  ( $\nu_3$ ) are due to a small number of weakly bonding water molecules at the interface that are oriented on the average with both hydrogens pointed into the  $\text{CCl}_4$  phase [13,20].

The spectral changes observed in Fig. 1b and c demonstrate that the solvating water molecules participate in the weakest water–water interactions found at this interface. These results are consistent with the understanding that when charge–dipole interactions are strong the tetrahedral bonding of  $\text{H}_2\text{O}$  molecules is partially broken down, therefore, reducing the hydrogen bonding interactions between water molecules and leading to a vibrational shift to higher energies [26]. This behavior is contrary to water observed at higher surfactant concentration where stronger hydrogen bonding is induced by additional interfacial charge [19]. The different orientation (phase) of these solvating water molecules induced by the opposite sign of the electrostatic field produced by SDS (anion) and DTAC (cation) accounts for the different trends observed in Fig. 1b and c in  $3600\text{--}3700$

$\text{cm}^{-1}$  region of the spectrum. This electrostatic field is also responsible for the enhanced VSF signal from the solvating water molecules [19]. In conjunction with experiments described herein, VSF studies with various aqueous salt solutions at the  $\text{CCl}_4/\text{H}_2\text{O}$  interface indicate that counterions play no role in the spectral changes observed herein.

To obtain more detail about the bonding character of the solvating water molecules, established spectral fitting procedures were employed [23]. For the lowest concentrations of these surfactants studied, the solvating water peaks contributing to the spectral changes induced by the surfactants are shown in Fig. 1b and c (below spectra) along with the fit to the data (Fig. 1b and c) obtained by the inclusion of these peaks. We use the term solvating  $\text{H}_2\text{O}$  molecules to include those directly hydrating the charged surfactant head group ( $1^\circ$  solvation shell) or  $\text{H}_2\text{O}$  molecules not directly interacting with the head group ( $2^\circ$  solvation shell) but perturbed by the electric field gradient [12].

Fig. 2 is a schematic representation of the orientation and environment of the solvating water molecules assigned to the peaks shown in Fig. 1b and c. For SDS, we attribute the peaks at  $3619 \pm 1$  and  $3756 \pm 10 \text{ cm}^{-1}$  to solvating water molecules that lie in the  $\text{CCl}_4$  rich portion of the interface. The assignment is facilitated by our previous neat interfacial studies [13,20]. The negative amplitude of the  $3619 \text{ cm}^{-1}$  peak for SDS indicates that these water molecules are oriented by the electrostatic field to have their H atoms directed towards the aqueous phase. For DTAC, the OH modes of solvating water

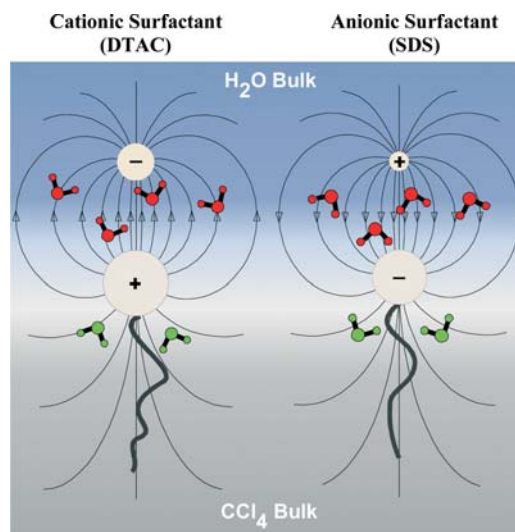


Fig. 2. Schematic of solvating  $\text{H}_2\text{O}$  molecules displaying charge dependent orientation due to charge–dipole interactions with anionic/cationic surfactants adsorbed at the  $\text{CCl}_4/\text{H}_2\text{O}$  interface. Solvating  $\text{H}_2\text{O}$  molecules in a  $\text{CCl}_4$  rich environment are shown to orient in opposing directions corresponding to the charge on the surfactant head group.  $\text{H}_2\text{O}$  molecules in an aqueous rich environment are shown to orient similarly.

molecules that lie in the  $\text{CCl}_4$  rich portion occur at the same frequencies but, as indicated by the sign derived for these peaks, these solvating water molecules are oriented in the opposite direction with their H atoms pointed in the direction of the  $\text{CCl}_4$  phase. The lower energy and broader peaks at  $3577 \pm 2$  (SDS) and  $3585 \pm 2 \text{ cm}^{-1}$  (DTAC) are due to solvating  $\text{H}_2\text{O}$  molecules in an aqueous rich environment. These measured frequencies are coincident with those observed in previous spectroscopic studies of solvating  $\text{H}_2\text{O}$  molecules in aqueous salt solutions and are in general agreement with frequency shift trends observed for halides and oxyanions in aqueous solutions [27–31]. These lower energy peaks are of opposite phase (orientation) consistent with the different charge on SDS and DTAC which orients these water molecules in opposite direction in the aqueous phase. Furthermore, these solvating water molecules in the aqueous environment are of opposite orientation to their counterparts residing in the organic rich phase. To reiterate, all of these water molecules show minimal bonding interactions with other water molecules at these low concentrations.

Interestingly, the intensity of the free OH peak, the H-donor OH peak and the peak representing tetrahedral bonding among water molecules are not affected to any significant extent by the presence of the surfactant for the concentrations depicted in Fig. 1b and c, or for bulk concentration up to  $\sim 200 \text{ nM}$  (L.F. Scatena, G.L. Richmond, in preparation). The CH stretch modes near  $2800\text{--}3000 \text{ cm}^{-1}$  are also not apparent at these low concentrations. Fig. 3a and b shows that this behavior changes with higher surfactant concentrations. Near  $300 \text{ nM}$ , ( $\sim 500 \text{ \AA}^2/\text{molecule}$ ) the intensity of the free OH mode ( $3669 \text{ cm}^{-1}$ ) begins to decline indicating that at this point a measurable portion of free OH bonds are either bonding to the surfactant or are reoriented by the surfactant charge. Accompanying this decrease in in-

tensity of the free OH mode is a progressively large increase in intensity near  $3200\text{--}3400 \text{ cm}^{-1}$ , indicative of stronger hydrogen bonding interactions between water molecules and the onset of an interfacial double layer. The SF response at this point begins to sample an increased volume of oriented interfacial water, as shown in previous higher concentration studies [19,32].

Calculation of the dimension of electric field penetration on either side of the interface due to the surfactant charge provides an estimate of the dimension with which the observed field effects would influence the orientation of these observed solvating water molecules at trace surfactant concentrations. A simple point charge calculation [33] places this distance at several angstroms, consistent with molecular dynamics simulations of the  $\text{CCl}_4/\text{H}_2\text{O}/\text{SDS}$  system where sulfate–water correlations persist beyond  $\sim 7 \text{ \AA}$  [7]. Conversely, on the  $\text{CCl}_4$  rich side of the interface, the relatively low dielectric constant of liquid  $\text{CCl}_4$  ( $\epsilon_{\text{CCl}_4} \approx 2$ ) compared to liquid  $\text{H}_2\text{O}$  ( $\epsilon_{\text{H}_2\text{O}} \approx 79$ ) results in reduced screening of the electric field and consequently solvating  $\text{H}_2\text{O}$  molecules that penetrate or exist in the saturated ( $\sim 10 \text{ mmole/l H}_2\text{O}$  in  $\text{CCl}_4$ ) [34] organic phase are likely to be oriented to a dimension approximately 5 times the value calculated for liquid  $\text{H}_2\text{O}$ . Although a quantitative measure of the specific interfacial location and number of water molecules being examined can not be ascertained within these experiments, the VSF technique probes those water molecules that are preferentially oriented by the penetrating field.

#### 4. Conclusion

Water solvating a charge at a hydrophobic surface plays a fundamental role in governing the structure, dynamics and thermodynamics of numerous biological macromolecules and membranes. These spectroscopic results provide a more detailed molecular picture of the solvation of an isolated charge and progressive charge increase at an oil/water interface than has previously been measured. The weak H-bonding character of the water molecules in the vicinity of the interfacial amphiphilic charge, particularly those in the aqueous-rich phase, suggests that the transport of an ion across a fluid hydrophobic–aqueous interface would not be hindered by strong hydrogen bonding in the more aqueous rich region. Furthermore, the charge also impacts the structuring of water that penetrates into the organic phase. Water molecules that penetrate into the organic phase are highly oriented by electrostatic fields that are capable of extending further into the organic liquid than in liquid water. Our ability to characterize the solvation at trace charge concentrations and to monitor the solvation with progressive addition of charge is important information for those developing models of water sol-

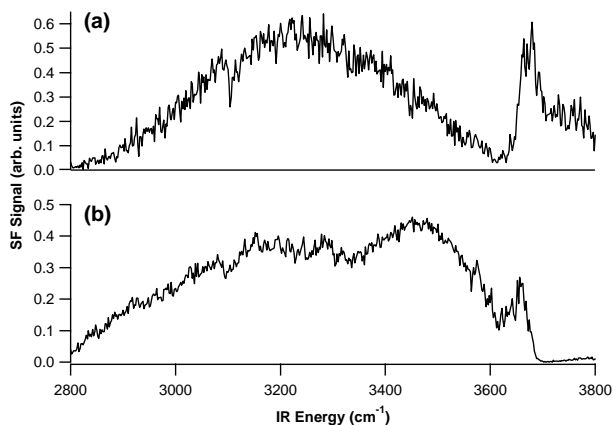


Fig. 3. (a) VSF spectra of the  $\text{CCl}_4/\text{H}_2\text{O}$  interface at  $292 \text{ nM}$  aqueous phase concentration SDS. (b) VSF spectra of the  $\text{CCl}_4/\text{H}_2\text{O}$  interface with  $399 \text{ nM}$  aqueous phase concentration DTAC.

vation at protein surfaces and other hydrated macromolecular assemblies.

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