Confirmation of enhanced anion concentration at the liquid water surface

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Abstract

The textbook view of the liquid electrolyte surfaces as being devoid of ions have recently been challenged by molecular dynamics simulations, which predict a surface enhancement of highly polarizable anions. Here we present the first direct experimental verification of this prediction. Enhanced azide (N$_3^-$) concentrations were measured at the liquid surface by femtosecond second harmonic generation (SHG) experiments exploiting the charge-transfer-to-solvent (CTTS) resonance of N$_3^-$, yielding a surface excess free energy of $-9.9 \pm 0.3$ kJ/mole. Such surface-enhanced concentrations of anions could have important consequences for the chemical reactions taking place on atmospheric aerosols and at the ocean-air interface.

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1. Introduction

Theoretical models of electrolyte solutions have until recently been limited to a description of the solvent as a continuum dielectric medium and the interface as a discontinuous change in dielectric constant. The earliest model, by Onsager and Samaras [1] described the ions as point charges and employed image charge repulsion as the dominant interfacial force, as first suggested by Wagner [2]. Since then, several improvements to the original model have been made, taking into account finite ion size, dispersion forces, hydrophobicity and polarizability, as described in recent review articles [3, 4]. These models extend the agreement with surface tension experiments, but incorporate empirical and even unphysical parameters, such as a cut-off distance of closest approach for ions that are attracted to the surface. Moreover, they cannot describe the molecular interactions between ions and water molecules that account for the different solvation of negative and positive charges in water, or the molecular-level structure of the liquid–vapor interface. An alternative approach is to use MD simulations that explicitly incorporate molecular water–ion interactions and molecular surface structure, at the cost of longer calculation time and loss of analytical expressions. These simulations are very sensitive to the potentials used. Those employing non-polarizable potentials [5, 6] generally predict all ions to be repelled from the surface, whereas those using polarizable potentials [7, 8, 9] predict that large polarizable anions are actually attracted to the outermost surface layers, while small unpolarizable ions are repelled from the surface, as in the early models. This is consistent with both experiments and theoretical calculations on aqueous clusters, which show the polarizable anions to reside at the surface, whereas the cations and non-polarizable anions remain in the interior of the clusters [10, 11].

Experimental investigations have similarly been limited to macroscopic thermodynamic methods such as

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surface tension and surface potential measurements. The surface tension of electrolyte solutions increases linearly with concentration above 0.01 M [12]. A surface tension increase is linked to a surface deficit by the Gibbs adsorption equation [13]. Linear optical methods have only been applicable for surfactants rigorously confined to the surface, as light necessarily penetrates at least wavelength dimensions into the solution, probing hundreds of molecular layers. Indirect experiments have alluded to the presence of ions at the interface by measuring chemical reaction dynamics that could only be explained by reactions involving surface ions [14,15]. Recent technological advances have made it possible to directly and selectively probe the liquid water surface and soluble surfactants on a molecular level using nonlinear optical and photoelectron techniques. Recent studies by the Richmond [16] and Allen [17] groups have addressed the local water structure of the interface of halide salt solutions in the 0.5–2 M concentration range by the very similar surface selective technique of sum-frequency generation (SFG) spectroscopy. Their results indicate only a minor perturbation of the water structure at the interface, but reveal an increased interfacial thickness for bromide and iodide solutions. However, these indirect experiments were not able to establish or exclude the existence of an enhanced ion concentration in the outermost surface layers. Photoelectron emission experiments have been able to directly detect iodide at the interface in the presence of large hydrophobic counter-ions [18] and concentrations of sodium iodide solutions higher than 0.1 M [19]. These results show surface saturation above 2 moles/kg, resembling a traditional Langmuir isotherm, which indicates an enhanced surface concentration. However, the authors conclude that the surface is instead depleted of ions, in agreement with the Gibbs adsorption equation, but they were unable to exclude an enhancement in the outmost surface layers because the probing depth of their experiment (several nm), is much larger than the thickness of a water layer (about 3 Å). The recent theoretic and experimental findings have received much attention, engendering debate over possible violation of the Gibbs adsorption equation [20–22].

In this Letter, we report verification of the predicted surface anion enhancement in the outermost molecular layers of aqueous solutions of sodium azide through the use of surface-specific and molecule-selective resonant second harmonic generation (SHG) spectroscopy. The measured concentration profiles yield a Langmuir adsorption isotherm for surface versus bulk azide concentrations, from which the corresponding negative surface free energy ($\Delta G_{\text{ads}} = -9.9 \pm 0.3 \text{ kJ/mol}$) is extracted. The azide anion has previously been investigated both in the gas phase [23] and the bulk liquid, showing a charge-transfer-to-solvent (CTTS) band around 200 nm [24]. A recent paper characterizes small azide-containing water clusters by both photoelectron spectroscopy and MD simulations as well as azide at the extended water surface by MD simulations [9]. In all cases, they find the azide anion strongly adsorbing to the surface. The extended surface simulation was carried out with 1 azide anion and 556 water molecules, corresponding to a ~0.1 M solution. Using the surface specific technique of SHG, we directly probe the azide adsorption through the resonance structure of the surface CTTS band at three different wavelengths: 200, 225 and 250 nm. The bulk CTTS band is shown in Fig. 1.

2. Experimental

The laser system will be described in detail in a future publication and only a brief description is presented here. A homebuilt Ti:sapphire oscillator is used to seed a regenerative amplifier (Spectra Physics, Spitfire). The amplifier is used to pump two OPA’s (Light Conversion, TOPAS). The three probing wavelengths used in this Letter are generated by doubling the 800 nm directly (400 nm), by fourth harmonic generation of the idler from the TOPAS (450 nm) and by sum-frequency of the 800 nm with the signal beam from the TOPAS (500 nm).

All glassware in contact with the solutions are soaked in hot chromic acid and rinsed thoroughly with 18 MΩ water (Millipore, Milli-Q) before use. The sodium azide solutions were prepared with 18 MΩ water and 99.99% pure sodium azide obtained from Aldrich and used without further purification.
3. Results and discussion

Like other even-order nonlinear processes, SHG is forbidden in bulk centro-symmetric media within the dipole approximation [25]. Bulk liquid water exhibits inversion symmetry due to the randomized orientation of the water molecules, but at the liquid–air interface, the symmetry is necessarily broken and the top few molecular layers exhibit a net orientation due to the interface and generate a weak SHG response. For the pure air–water interface, the majority of the SHG signal is generated in the top liquid layer with a small contribution from the second layer, according to MD simulations [26]. SHG, as well as the similar technique of SFG, have become a widely used surface-selective probe for liquid surfaces [27].

The SHG intensity is expressed by the second order susceptibility $\chi^{(2)}$, that in turn is the sum of the contributions from the water background and the azide anions:

$$I_{\text{SHG}} \propto |\chi^{(2)}|^2 \times I_{\text{Fundamental}}^2,$$  
(1)

$$\chi^{(2)} = \chi_{\text{water}}^{(2)} + \chi_{\text{azide}}^{(2)}.$$  
(2)

The susceptibilities are in general complex quantities but non-resonant contributions, such as the water background, are real. The norm square of the total susceptibility in Eq. (1) leads to interference between the different contributions. Both constructive and destructive interference with the water background have previously been observed [28]. The azide susceptibility is proportional to the surface concentration, $N_S$, and the orientationally averaged molecular susceptibility (hyperpolarizability, $\beta$)

$$\chi_{\text{azide}}^{(2)} = N_S \times \beta_{\text{Orientation}}.$$  
(3)

Assuming the orientation of the azide molecules does not change significantly over the concentration range, the change in the azide response is from surface concentration changes.

The surface adsorption is modeled by the standard Langmuir adsorption model

$$N_S = \frac{\lambda_S^{\text{max}} \times x}{x + 55.5 \text{ moles/liter} \times \exp(\Delta G_{\text{Ads}}/RT)}.$$  
(4)

Here $x$ is the bulk electrolyte concentration, $\lambda_S^{\text{max}}$ is the maximum surface concentration and $\Delta G_{\text{Ads}}$ is the Gibbs free energy of adsorption. The Langmuir model is incorporated in the expression for the SHG intensity assuming the water background to be constant and the orientation of the azide ions stay constant

$$I_{\text{SHG}} \propto |A + (B + iC) \times N_S|^2$$

$$= (A + B \times N_S)^2 + (C \times N_S)^2$$

$$= \left( A + \frac{B^2 \times x}{x + D} \right)^2 + \left( \frac{C^2 \times x}{x + D} \right)^2.$$  
(5)

Here $A$ is the real water background, $B$ and $C$ are the real and imaginary component of the azide susceptibility and $D$ is the Langmuir constant 55.5 M × exp(Δ$G_{\text{Ads}}$/RT). The constants $A$, $B^2$ and $C^2$ are allowed to change with the wavelength but the constant $D$ is fitted simultaneously to all three wavelengths. The magnitude of the azide susceptibility ($B^2$) + ($C^2$), for the different wavelengths are shown in Fig. 2. The Gibbs free energy of adsorption is extracted from Fig. 1. The obtained fit parameters are shown in Table 1.

The SHG intensity measured as a function of concentration for the three selected wavelengths is shown in Fig. 2. The SHG intensity is observed to increase monotonically with azide concentration at the resonant wavelength 200 nm. At the near-resonant wavelengths, 225 and 250 nm, the SHG intensity shows a small initial decrease due to the partly destructive interference between the azide resonance and background water response [28]. The concentration dependence at the three wavelengths is fit simultaneously to the standard Langmuir adsorption equation, as described in the methods section. The fit yields a Gibbs free energy of adsorption of ~9.9 ± 0.3 kJ/mole, corresponding roughly to the energy of half a water hydrogen bond. The rest of the fitting parameters are shown in Table 1. The negative value of the free energy is in accord with surface enhancement of the azide anion at the air–water interface predicted by Joungwirth [9]. However, their theoretical prediction does not include the Gibbs free energy.

We believe this is the first direct measurement of enhanced ion concentration at the liquid water–air interface. It should be noted that due to the very shallow probing depth of the SHG experiment [26], the measured Gibbs free energy is for adsorption to the outermost molecular layers of liquid density. Different surface probes have different probing depths and

Table 1
Parameters obtained in the fit of the SHG data to the Langmuir model in Fig. 2

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>$A$</th>
<th>$B^2$</th>
<th>$C^2$</th>
<th>$(B^2)^2 + (C^2)^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.988 ± 0.006</td>
<td>0.30 ± 0.27</td>
<td>3.66 ± 0.12</td>
<td>13.5 ± 1.9</td>
</tr>
<tr>
<td>225</td>
<td>0.902 ± 0.006</td>
<td>-0.82 ± 0.12</td>
<td>2.84 ± 0.16</td>
<td>8.7 ± 1.7</td>
</tr>
<tr>
<td>250</td>
<td>0.991 ± 0.006</td>
<td>-0.58 ± 0.12</td>
<td>1.87 ± 0.14</td>
<td>3.8 ± 1.3</td>
</tr>
</tbody>
</table>

The constant $D$ is fitted globally to yield the value 0.92 ± 0.12.
accordingly measure different surface properties. The distribution of ions at the interface could also be highly non-monotonic along the surface normal, as predicted for bromide and iodide, wherein the surface enhancement at the outermost layer is followed by a depletion in subsequent layers [7]. In these cases, the surface concentration integrated through the entire interfacial region should be lower than the bulk concentration, in agreement with the Gibbs adsorption equation and the observed surface tension increase, even though the top surface layer is enhanced.

4. Conclusion

Using femtosecond second harmonic generation we have directly measured an enhanced azide \((N_3^-)\) concentration at the liquid water–air interface as predicted by recent computer simulations [9]. The concentration profile yield a Langmuir isotherm with a Gibbs free energy of adsorption of \(-9.9 \pm 0.3\) kJ/mole.

These recent findings highlight the need for new theoretical models of the liquid–vapour interfaces of aqueous electrolytes, explicitly incorporating the molecular structure of the solvent that engenders the specific solvation of negative and positive charges and the local structure of the water surface, such as those obtained in MD simulations. For these, the effective potentials used are of central importance and reliable direct experimental measurements, such as those presented here, are essential to develop realistic models.

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References

[22] L. Vrbka et. al., Curr. Opin. Colloid In., available online 3 July 2004.