Strong surface adsorption of aqueous sodium nitrite as an ion pair

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1. Introduction

The study of ion adsorption to aqueous interfaces and its myriad consequences is currently a very active field that impacts many areas of science. Motivated by the postulated high concentration of halide ions at the surface of sea salt aerosol particles, simulations first predicted surface enhancement of selected anions and experiments subsequently verified these predictions for several simple systems, thus revising standard textbook descriptions of ion-depleted electrolyte surfaces. The focus of recent efforts has been on establishing the mechanism of this selective ion adsorption phenomenon, which has been shown to correlate strongly with the famous Hofmeister Effects of biochemistry, including protein solubility and protein denaturation. Much attention has focused on ion polarizability as an order parameter for surface activity, and the importance of interfacial fluctuations has recently been demonstrated. However, few studies have addressed the details of interfacial solvation with explicit consideration of the counterion, mainly noting that simple cations tend to remain buried under the outermost liquid surface layers. Here we present results of resonant UV-second harmonic generation experiments on aqueous solutions of sodium nitrite, demonstrating that the anion and cation adsorb strongly to the interface as a correlated ion-pair at concentrations as low as 0.1 M. The large adsorption free energy (ΔG = −17.8 kJ/mol) resembles that for the ‘Jones–Ray salts’ found to exhibit anomalous surface tension behavior at millimolar concentrations. These unusual interfacial properties may have important consequences for nitrite chemistry, considering its ubiquitous presence in natural environments.

We have developed a general approach to the quantitative study of interfacial anion adsorption, exploiting the surface-specific technique of second-harmonic generation (SHG) spectroscopy to directly probe anions in the interface via strong ultraviolet resonance features, usually charge-transfer-to-solvent (CTTS) transitions. The experimental preparations and procedures used here are similar to those reported for a previous study of sodium nitrate. Selected concentrations of sodium nitrite (>99% purity) ranging from 0 to 6 M were prepared by successive volumetric dilutions of stock 6 or 1 M solutions. The SHG response of these solutions was observed at 255, 247, and 200 nm, generated by incident probes of 1 kHz, 140 fs light pulses at 510, 485, and 400 nm. Focusing onto the sample surface resulted in a diffraction-limited spot diameter of ~140 μm, with average power densities generally ranging from 1 to 30 mJ cm -2 per pulse. Our earlier experiments were interpreted in terms of an adapted Langmuir isotherm model, which omitted explicit consideration of the cation, primarily because these simple cations are usually unobservable by SHG owing to their inherent molecular centrosymmetry, low polarizability, and predicted deep partitioning within the interface. However, straightforward changes to the model facilitate their explicit inclusion, as detailed in Section 2. This yields four different models for the dependence of the surface ion concentration on bulk electrolyte concentration, as summarized in Table 1.
The adapted Langmuir surface adsorption models described in Section 2 can each be solved for the concentration of adsorbate (e.g., nitrite anion) present in the interface ($N_s$) as a function of bulk concentration, as summarized in Table 1. The SHG signal is then expressed as a function of surface-bound adsorbate as [9]

$$\frac{I_{2L}}{I_{2s}} = \left( A + BN_s \right)^2 + (CN_s)^2,$$

(1)

where $I_{2L}$ is the intensity of the second-harmonic response normalized by the square of the incident laser intensity. The parameters $A$, $B$, and $C$ are proportional to the wavelength-dependent molar second-harmonic susceptibility of water, and the real and imaginary molar susceptibility components of the anion, respectively. Substitution of the appropriate expressions from Table 1 results in an equation describing the SHG signal as a function of bulk concentration, which can be fit to the observed signal to determine four parameters $A$, $B$, $C$, and the equilibrium constant $K$, allowing for the determination of the free energy of adsorption for the processes described [9,19].

The relative abilities of the models described in Section 2 to describe our SHG data provide a useful indicator of the probable mechanism for nitrite adsorption to the interface. In our earlier resonant SHG studies [9,19], only the solute anion or cation was the candidate for adsorption to the interface. However, nitrite is a weak base and in this study, other evolved species were considered as possible participants in the adsorption process, assuming a $pK_a$ of 3.3 [21]. Water concentration was approximated as being constant at 55.5 M and measurements taken at bulk concentrations over 4 M were excluded because of the noted incipient decrease in the SHG signal.

Applying any of the models in Table 1 to possible secondary species present due to the acid–base reactions of nitrite failed to replicate the data. This included using permutations of Na+, $H_3O^+$, $NO_2^-$, and $OH^-$ concentrations as participating cations and anions, ion-pairs or unimolecular adsorbates in these models. In these cases, either the fits failed to converge or were otherwise unacceptably poor, an example of which is presented in Figure 1a.

Only Model 4, describing concerted ion-pair surface adsorption, successfully fit the data (Figure 1a), and then only when sodium and nitrite were the species considered to be explicitly involved in the pairing. The singular agreement of the ion-pair Model 4 using $Na^+/NO_2^-$ concentrations indicates that the adsorption of nitrite anions to the interface is coupled to the adsorption of sodium cations in a manner that generates a single ion-paired species, rather than two translationally independent surface ions.

Thermodynamically (and via our experimental approach), the net process described by Model 4 of ion-pairing and subsequent ion-pairing to the interface,

$$M_{aq}^+ + X_{aq}^- \rightleftharpoons MX_{aq} \rightleftharpoons MX_{surface},$$

(2)

is indistinguishable from independent cation/anion adsorption and subsequent ion-pairing within the interface:

$$M_{aq}^+ + X_{aq}^- \rightleftharpoons K_{aq}MX_{surface} \rightleftharpoons K_{surf} MX_{surface}.$$  

(3)

The mechanism described by (3), should be highly disfavored compared to that in (2) due to the large image charge repulsion engendered in the approach of two independent ions to the lower interfacial dielectric in the first step of (3), and is therefore discounted. This leaves Eq. (2) to describe the stepwise process of ion-pair adsorption to the interface given in Model 4. Simonin et al. [22] have semi-empirically calculated the ion-pair association constant for sodium nitrite to be 0.209 under the mean spherical approximation, which can be used as the equilibrium constant $K_{2a}$ of Eq. (2) to determine ion-pair concentrations as a function of nominal sodium nitrite concentrations in the regime studied. The ion-pair concentrations are comparable to free ion concentrations in the studied regime, further justifying the likely dominance of the mechanism described by (2) over that of (3). The data are then fit as a function of the calculated bulk ion-pair concentration using Model 1, wherein the surface adsorbate concentration of Eq. (1) ($N_s$) is that of the interfugal ion-pair.

This approach is employed for the fit in Figure 2, and reveals that adsorption of the ion-pair to the interface under such a mechanism, represented by the second step of Eq. (2), is accompanied by the large free energy change of $-17.8 \pm 0.3$ kJ/mol. This fit

Table 1

<table>
<thead>
<tr>
<th>Model</th>
<th>Equilibrium expression</th>
<th>Surface concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$K = \frac{[MNO_2]}{[M][NO_2]}$</td>
<td>$N_s = \frac{[K_{surf}]}{[M][NO_2]}$</td>
</tr>
<tr>
<td>2</td>
<td>$K = \frac{[NO_2[M]NO]}{[M][NO_2]}$</td>
<td>$N_s = \frac{[K_{surf}]}{[M][NO_2]}$</td>
</tr>
<tr>
<td>3</td>
<td>$K = \frac{[NO_2[M]NO]}{[M][NO_2]}$</td>
<td>$N_s = \frac{[K_{surf}]}{[M][NO_2]}$</td>
</tr>
<tr>
<td>4</td>
<td>$K = \frac{[NO_2[M]NO]}{[M][NO_2]}$</td>
<td>$N_s = \frac{[K_{surf}]}{[M][NO_2]}$</td>
</tr>
</tbody>
</table>

Figure 1. SHG responses at 200 nm (red/triangle), 247 nm (green/circle) and 255 nm (blue/square), as a function of bulk electrolyte concentration (error bars represent one standard deviation). The lines in panel a is the fit of the data to Model 1 (independent $NO_2^-$ adsorption) while panel b is the fit of the data to Model 4 (concerted $NO_2^-$ and Na+).
is little guidance available in the literature as to the interfacial behavior of nitrite, except for the study of Brown et al., which concluded that nitrite and nitrate exhibit similar interfacial distributions, which are depleted relative to bulk concentrations, but these did not consider the possible effects of counterions [30]. The absorption spectrum of bulk aqueous sodium nitrite is presented in Figure 3, overlaid with the surface sodium nitrite SHG measurements at 6 M presented in this Letter. The interfacial nitrite anions exhibit a strong shift in resonance enhancement energy from that observed in the bulk CTTS spectra, indicating that this interfacial species exists in a much different electronic environment than it does in the bulk. Although this resonance shift may be due to direct perturbation by ion-pairing, typically CTTS energy shifts as a function of increasing salt concentration are quite small [31], suggesting that interfacial solvation is the dominant reason for the large shift in resonance. Strong CTTS shifts have been noted for other surface-solvated species [19], and apparently the surface-bound sodium nitrite moieties are no exception to this trend.

In summary, analysis of the surface SHG response of aqueous sodium nitrite as a function of bulk concentration in terms of several proposed models of adsorption suggests that nitrite ions reside in the interface predominately as ion-pairs, even at bulk concentrations as low at 100 mM. These ion-pairs are likely to be preferentially adsorbed relative to independently solvated ions, owing to both the zero net charge of the pair and the weaker dielectric of the interfacial region. This finding suggests that explicit consideration of cations in the general mechanism of anion adsorption to the aqueous interfaces may be required. This is supported by the simulation results obtained very recently by Wick and Cummings [32].

Considering the ubiquitous presence of nitriles in atmospheric aerosols and terrestrial water bodies, the observed surface enhancement and probable ion-pair speciation may engender significant and presently unrecognized interfacial chemistry in aqueous systems, since surface-active halogens have already been shown to have dramatic effects on aqueous molecular bromine and chlorine production rates on aerosol surfaces in the presence of ozone [2].

2. Methods

In the Langmuir model used to analyze our similar earlier experiments [9,19,20], anions are attracted or repelled from the surface with an effective potential characterized by a Gibbs free energy of adsorption ($\Delta G_{\text{ads}}$). The overall adsorption is characterized by the equilibrium expression

$$
\mu_1 = \mu_2 + RT \ln \left( \frac{\alpha}{1 - \alpha} \right)
$$

where $\mu_1$ is the chemical potential of the adsorbed species, $\mu_2$ is the chemical potential of the bulk phase, $R$ is the gas constant, $T$ is the temperature, and $\alpha$ is the surface coverage. This equation relates the chemical potential of the adsorbed species to the chemical potential of the bulk phase and the entropy change associated with the adsorption process.

Figure 2. SHG responses at 200 nm (red/triangle), 247 nm (green/circle) and 255 nm (blue/square), as a function of bulk electrolyte concentration (error bars represent one standard deviation). Lines are the fit using Model 1 as a function of bulk sodium nitrite ion pairs, assuming an association constant of 0.209. The fit yields an adsorption free energy of $-17.8 \pm 0.3$ kJ/mol.

Figure 3. Bulk absorption spectrum [21] (line) overlaid with relative SHG susceptibility (dots/error bars) of 6 M aqueous sodium nitrite. Both are normalized to maximum observed values. The strongly shifted (+35 nm) resonance features of the surface species indicate a strikingly different chemical environment between bulk and surface nitrite.
SW + X⁻ ⇌ W + SX⁻, \quad \text{(Model 1)}

wherein surface sites (S) accommodate either water molecules (W) or anions (X⁻). The usual assumptions of non-interacting surface species and a conserved number of surface sites apply, augmented by the constraint that surface sites are always occupied. This model’s underlying assumptions are retained from these previous experiments to maintain quantitative comparability while conserving the simplicity of the Langmuir-type model.

The concentration of anions at the liquid surface as a function of bulk electrolyte concentration asymptotically approaches a maximum surface coverage (saturation), characterized by $S_{\text{max}}$. This describes the incrementally weakening adsorption tendency as a function of concentration due to the physical effect of crowding, viz. fewer water-bound surface sites are available for a bulk anion to occupy as more sites become populated by other anions.

In our earlier studies, this model omitted explicit consideration of the cation [9,19], primarily because these simple cations are usually unobservable by SHG owing to their inherent molecular centro-symmetricity, low polarizability, and predicted deep partitioning within the interface [5,19]. However, a straightforward change to the model facilitates their explicit inclusion. On the assumption that cations (M⁺) and anions partition to the same surface site, the resulting equilibrium expression is:

\[
2SW + M⁺ + X⁻ \rightleftharpoons 2W + SX⁻ + SM⁺ \quad \text{(Model 2)}
\]

If the cations and anions partition to distinct interfacial regions, as suggested by simulations that predict a sublayer of cations buried beneath a layer of anions, they will occupy separate interfacial sites:

\[
5SW + S_W^X + M⁺ + X⁻ \rightleftharpoons 2W + S_W^X + S_M^M⁺ \quad \text{(Model 3)}
\]

For simplicity, we assume that the two surface site types have the same maximum surface coverage ($S_{\text{max}}$).

Finally, we can also allow for the possibility that these ions do not explore the interfacial region independently once adsorbed, but instead translate in concert as an ion-pair. In such a scenario, we can again adopt a Langmuir model, except that we assume an adsorbate replaces a single interfacial water molecule as an ion-pair rather than adsorbing as two independent ions, effectively adsorbing both anion and cation to a single surface site:

\[
5W + M⁺ + X⁻ \rightleftharpoons W + 5MX \quad \text{(Model 4)}
\]

Table 1 lists the equilibrium expressions for surface anion concentrations in each of these scenarios, subject to the constraint of interfacial electroneutrality ($[SX] = [SM]$). As a function of bulk concentrations, Models 2 and 3 yield nearly identical behavior, and in the case of Model 3, we find that the functional dependence is identical to that in Model 1, excepting a factor of two difference in the adsorption free energies (reflected in the exponent of the equilibrium constant K). We thus have three models that include a counterion as an explicit interfacial species (Models 2–4), one of which (Model 4) has a very distinct functional form with respect to bulk concentration, and a fourth model (Model 1) that considers the independent adsorption of a solute as a single species to the interface.

While these simple changes to the model allow for a functional diagnostic of mechanism, increasingly complicated models and assumptions can certainly be invoked. The nature and consequences of altering the assumptions underlying these simple Langmuir-type models, and their application to SHG studies of this type, are discussed elsewhere [33]. In this Letter, we describe the use of these simple models as diagnostics to elucidate the nature of adsorption of sodium nitrite to the aqueous/air interface, as observed via resonance-enhanced UV-SHG.

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