

Correction

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Correction for “Elucidating the mechanism of selective ion adsorption to the liquid water surface,” by Dale E. Otten, Patrick R. Shaffer, Phillip L. Geissler, and Richard J. Saykally, which appeared in issue 3, January 17, 2012, of *Proc Natl Acad Sci USA* (109:701–705; first published January 10, 2012; 10.1073/pnas.1116169109).

The authors note that, due to a printer’s error, on page 703, left column, first paragraph, lines 9–10, “–6.52 kJ/mol” should instead appear as “6.52 kJ/mol.”

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Elucidating the mechanism of selective ion adsorption to the liquid water surface

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Adsorption of aqueous thiocyanate ions from bulk solution to the liquid/vapor interface was measured as a function of temperature by resonant UV second harmonic generation spectroscopy. The resulting adsorption enthalpy and entropy changes of this prototypical chaotrope were both determined to be negative. This surprising result is supported by molecular simulations, which clarify the microscopic origins of observed thermodynamic changes. Calculations reveal energetic influences of adsorbed ions on their surroundings to be remarkably local. Negative adsorption enthalpies thus reflect a simple repartitioning of solvent density among surface, bulk, and coordination regions. A different, and much less spatially local, mechanism underlies the concomitant loss of entropy. Simulations indicate that ions at the interface can significantly bias surface height fluctuations even several molecular diameters away, imposing restrictions consistent with the scale of measured and computed adsorption entropies. Based on these results, we expect an ion's position in the Hofmeister lyotropic series to be determined by a combination of driving forces associated with the pinning of capillary waves and with a competition between ion hydration energy and the neat liquid's surface tension.

air–water interface | electrolyte solutions | Hofmeister effects | nonlinear spectroscopy

The adsorption of ions to aqueous interfaces has been one of the most intensely debated subjects in chemistry for the past century (1, 2). This discussion was reinvigorated by the invocation of strong surface enhancement of halide ions to explain the production of halogens by the reaction of ozone with sea salt aerosols (3, 4). Although positive surface adsorption of several fundamental chaotropic ions has since been verified by the combination of theory (5, 6) and experiment (7–10), the *mechanism* governing relative propensities of ions for aqueous interfaces remains controversial (11–15). This debate is of quite general interest because of the established similarity of ion adsorption to the air/water interface and hydrophobe/water interfaces of proteins, and the corresponding relevance to vital biological phenomena (e.g., protein folding and solubility, enzyme activity) (16, 17), as embodied in the famous Hofmeister series of relative lyotropic ion strength (1, 2, 16, 17).

In this ongoing debate, ion polarizability has been invoked as the essential ionic property by several authors (5, 17, 18). Others have emphasized the importance of ion size (12, 19), dispersion forces (1, 20), interfacial roughness (13), and hydration free energy (15, 17, 21), although these factors are clearly not independent. In any case, it has usually been assumed that there is a positive adsorption enthalpy associated with electrostatic (image charge repulsion) forces and a positive adsorption entropy associated with hydrophobic (volume exclusion) forces, and that the competition between these two determines how ions behave near air–water interfaces. Van der Spoel and coworkers (15) have recently shown that, in simulations, a number of ions in small water droplets actually follow the opposite trend, with negative enthalpies and entropies of adsorption. Here we present a measurement of temperature-dependent adsorption free energy for a prototypical inorganic ion at the liquid water surface, which also

yields considerably negative enthalpy and entropy of adsorption. The signs and magnitudes of these changes provide important constraints on the adsorption process and indicate that the competition between enthalpic and entropic forces underlying adsorption mechanism is resolved in an unanticipated way. Accompanying calculations indicate the generality of this finding and reveal underlying driving forces that have been overlooked in theories of interfacial solvation.

Results and Discussion

The general approach and apparatus used in our resonance-enhanced UV second harmonic generation (SHG) experiments are described elsewhere in connection with our previous studies of thiocyanate as a prototype for the behavior of chaotropic ions (8, 22, 23). For details see *Methods*. Fig. 1 shows the SHG signal collected as a function of bulk concentration of NaSCN (sodium thiocyanate) at five temperatures. Changes in SHG signal with temperature could in general be due to either a change in number of chromophores in the interface, variation in the SHG oscillator strength due to a spectral shift in the resonant (charge transfer to solvent) transition frequency, or a change in interfacial susceptibility corresponding to altered statistics of molecular orientation (23). Measuring the SHG signal as a function of concentration allows us to distinguish among these possibilities.

We fit the data in Fig. 1 to a Langmuir adsorption model (22, 23), determining a Gibbs free energy of adsorption (ΔG) at each temperature (see Fig. 2). The linear dependence of ΔG on T allows determination of the adsorption enthalpy change ($\Delta H = -11.9 \pm 0.8 \text{ kJ}\cdot\text{mol}^{-1}$) and entropy change ($\Delta S = -17 \pm 3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) from the intercept and slope, respectively. Like the calculations of ref. 15, these results challenge the presumed adsorption mechanisms on which many theories are based.

Molecular simulations provide support for our experimental conclusion that ion adsorption to interfaces can be driven by negative enthalpies and opposed by negative entropies. We have examined several model systems, ranging from detailed representations of water and solute geometries to simple spherical ions in a schematic polar liquid (the Stockmayer fluid). These diverse systems exhibit very similar mechanistic underpinnings for interfacial adsorption. Here we focus discussion on the simplified but illustrative example of nonpolarizable, fractionally charged ions in a simple-point-charge model of liquid water (SPC/E). In this case, highly soluble ions can be strongly adsorbed to the air–water interface (13) in the absence of complicating factors such as

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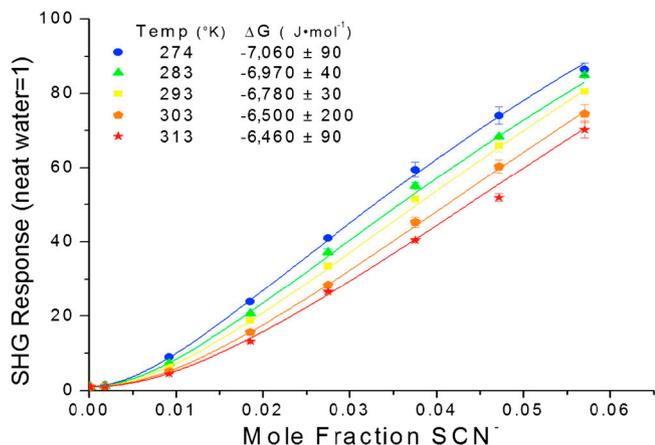


Fig. 1. Measured resonant SHG response of potassium thiocyanate solutions as a function of bulk concentration at five temperatures. The SHG response is fit to a Langmuir adsorption model as previously described (23, 26). Error bars on y axis are one standard deviation. Precision of measured temperatures is $\pm 1^\circ\text{K}$.

polarizability and shape anisotropy. Simulation results for other systems are presented in *SI Text*.

The changes in entropy (S) and average potential energy ($\langle U \rangle$) we compute when reversibly moving these ions through the interfacial region indicate that the thermodynamic behavior observed in our experiments, and in previous simulations (24), is quite general. Fig. 3 shows energy and entropy profiles calculated from simulation, as a function of the ion's height z relative to the Gibbs dividing surface. As in all systems we examined, $TS(z)$ and $\langle U(z) \rangle$ exhibit pronounced minima near the interface, decreasing below their bulk values by many $k_B T$, just as observed in our experiments. Lowering the magnitude of ionic charge increases the depth of these minima and enhances the corresponding maximum in solute surface density.

We have explored the structural origins of these thermodynamic trends by spatially resolving molecular contributions to the total energy $\langle U(z) \rangle = \int d\mathbf{r} \rho(\mathbf{r}; z) \epsilon(\mathbf{r}; z)$. Here, $\rho(\mathbf{r}; z)$ is the average solvent density at position \mathbf{r} (relative to the ion) when the ion is held a distance z above the Gibbs dividing surface. The corresponding energy per molecule, $\epsilon(\mathbf{r}; z) = \epsilon^{(\text{ion})}(\mathbf{r}; z) + \frac{1}{2} \epsilon^{(\text{solv})}(\mathbf{r}; z)$, includes the average interaction energy $\epsilon^{(\text{ion})}(\mathbf{r}; z)$ of a molecule at \mathbf{r} with the ion, and its average energy $\epsilon^{(\text{solv})}(\mathbf{r}; z)$ of interaction with all other solvent molecules. (Both quantities are

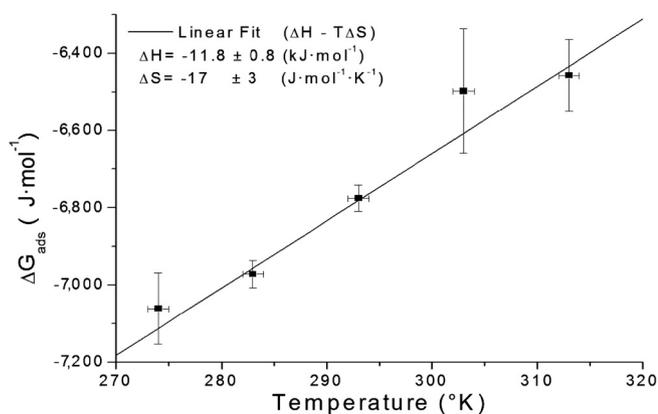


Fig. 2. Linear fit of the free energy of thiocyanate adsorption to the interface as a function of temperature. The relationship indicates negative standard enthalpy and negative entropy changes of $-11.8 \pm 0.8 \text{ kJ}\cdot\text{mol}^{-1}$ and $-17 \pm 3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively. Error bars on y axis are propagated from the inverse variance of the data presented in Fig. 1. Error on x axis is the maximum range of temperatures measured for a nominal temperature ($\pm 1^\circ\text{K}$).

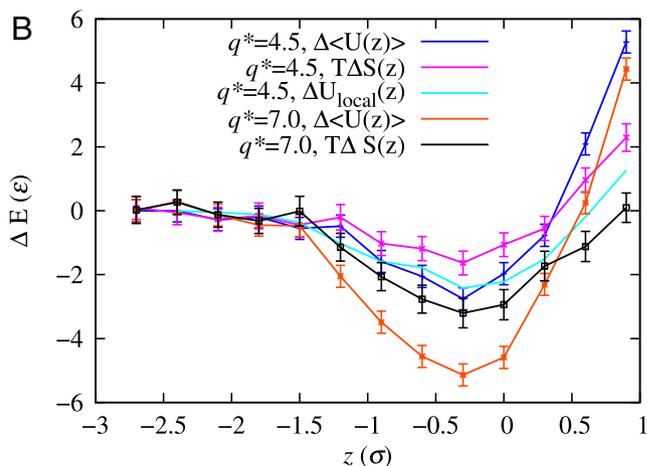
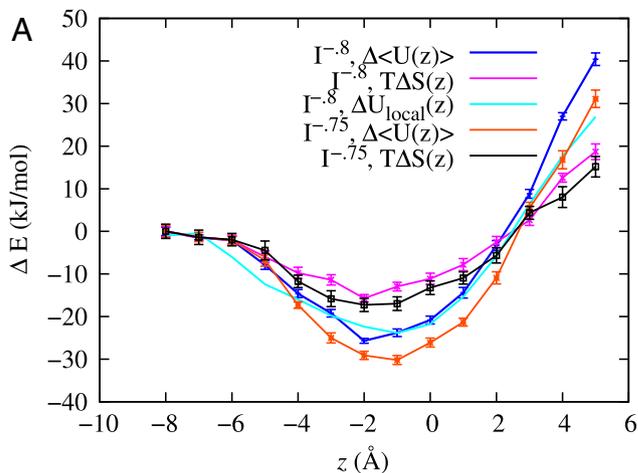


Fig. 3. Computed entropy $T\Delta S(z)$ and average total potential energy $\Delta\langle U(z) \rangle$ as functions of ion height z , relative to their values when the ion lies near the center of a simulated liquid slab. Results are shown in *A* for an iodide-sized ion, with fractional charges of $-0.8e$ and $-0.75e$, in liquid SPC/E water. Results for the Stockmayer liquid, at reduced temperature $T^* = 0.7$, are plotted in *B*. These solutes are moderately larger than solvent molecules, with reduced diameters $\sigma^* = 1.5$ and $\sigma^* = 1.25$, and carry charges of reduced magnitude $q^* = 7$ and $q^* = 4.5$, respectively. Also shown are the results of the local approximation to the average energy described in the text (Eq. 1).

strongly dominated by electrostatic contributions.) Fig. 4 shows these interaction energies, for an iodide-sized anion in water, as functions of lateral and vertical distance from the ion. Similar results for the Stockmayer system are presented in *SI Text*.

These energy maps reveal important contributions to adsorption thermodynamics that are spatially local in character. Water molecules engage in interactions whose average energies deviate appreciably from bulk values only when they reside very near the ion or very near the interface. Furthermore, the spatial pattern of these energies in the vicinity of the ion changes little as it breaches the interface (except in regions of low solvent density). As a result, the total energy of adsorption can be rationalized in terms of changes in the average number of solvent molecules in three distinct environments: near the ion (within a coordination distance ℓ_{coord}), near the undisturbed interface (within a distance ℓ_{surf} of the Gibbs dividing surface but at least ℓ_{coord} away from the ion), and in the bulk liquid. Defining these populations as n_{coord} , n_{surf} , and n_{bulk} , respectively, we have

$$U_{\text{local}}(z) = \bar{\epsilon}_{\text{coord}} n_{\text{coord}}(z) + \bar{\epsilon}_{\text{surf}} n_{\text{surf}}(z) + \bar{\epsilon}_{\text{bulk}} n_{\text{bulk}}(z), \quad [1]$$

The most prominent soft collective modes at fluid interfaces are capillary waves, undulations in surface topography on length scales greater than a molecular diameter. We find from simulations that ions at interfaces can act to restrict such fluctuations, to a degree commensurate with measured adsorption entropies. Applying the coarse-graining procedure of ref. 26 to each of a large ensemble of configurations sampled in our aqueous simulations, we determined the surface height $h(\mathbf{x})$ above a grid of points \mathbf{x} in the plane parallel to the average interface. The mean-square amplitude of height fluctuations, $\langle \delta h^2(\mathbf{x}) \rangle$, is plotted in Fig. 5 as a function of lateral distance x from the ion, for the same two ion locations as in Fig. 4. Ion-induced modulations of local interfacial flexibility, which are strongly restrictive in the adsorbed state, extend many molecular diameters away from the solute. To estimate the resulting changes in entropy, we adopt a simple model, harmonic in a collection of $\delta h(\mathbf{x}) = h(\mathbf{x}) - \langle h(\mathbf{x}) \rangle$ variables with couplings selected to reproduce observed correlations $\langle \delta h(\mathbf{x}) \delta h(\mathbf{x}') \rangle$ (see *Methods*). The precise thermodynamic predictions of this model depend on how fine a grid of \mathbf{x} values is used. A resolution of 2.5 Å, comparable to a water molecule's diameter, yields an adsorption entropy, $\Delta S \approx -8 k_B$ for $\text{I}^{-0.8}(\text{aq})$, which is consistent in sign and magnitude with values from experiment and simulation.

Concluding Remarks

The importance of explaining the microscopic origin and mechanism of small ions' adsorption propensities for the air/water interface is twofold. First, this behavior serves as a prototype for selective adsorption in numerous chemical and biological contexts. Indeed, the ordering of cations and anions in Hofmeister's series is mirrored by the strength of their effects on some 40 different phenomena, ranging from protein folding to dielectric relaxation (17).

More fundamentally, the lack of a compelling molecular explanation for this apparently very general behavior highlights a profound gap in our physical understanding of ion solvation in heterogeneous environments. Theoretical descriptions, dating from the work of Onsager and Samaras (27) in 1934 to recent work by Levin et al. (12) and Netz and coworkers (11), have achieved agreement with certain data, but do not capture all essential trends and features revealed by modern experiments and computer simulations. By contradicting expectations common to all of these approaches, our thermodynamic measurements confound the long-standing problem. Together with our computational results, however, these experiments point to specific shortcomings in previous theoretical approaches and suggest a different view of the molecular ingredients underlying ion adsorption.

Our results highlight the importance of energy contributions that are neglected in typical applications of dielectric continuum theory. In particular, placing a charged solute at the interface effectively reduces the contact area between liquid and vapor, offering an energetic benefit beyond the scope of conventional reaction field calculations. Although interaction of an ion with the solvent polarization it induces tends to strongly disfavor adsorption, the concomitant transfer of solvent molecules from the surface region into bulk liquid more than compensates in the systems we have studied. For the case of aqueous solvent, this effect could alternatively be viewed as an advantage of ions scavenging unsatisfied hydrogen bonds at the interface, rather than disrupting favorable intermolecular arrangements in bulk solution.

For adsorption entropies, our results highlight the nonlocal response of interfacial shape fluctuations. Early theoretical approaches, based on dielectric continuum theory, included entropic effects only implicitly through temperature dependence of the dielectric constant, making no statement on their microscopic origins. More recent calculations have explicitly included entropy increases due to releasing orientational constraints on nearby

solvent molecules when an ion is partially desolvated. Constraints on interfacial shape imposed by an ion at the surface, however, have been essentially overlooked. These collective contributions, neglected in any theory featuring a quiescent liquid surface, dominate the entropy of adsorption in our analysis.

Constructing a predictive theory from the physical picture we have developed will require quantitative understanding of the influences of small ions on their coordination environment and on the statistics of capillary wave fluctuations. The local energy changes we have emphasized describe not only the rupture of solvent-solvent hydrogen bonds induced by an ion, but also straining of hydrogen bonds between its first and second solvation shells. A simple but accurate accounting for these latter effects (e.g., as a function of solute size) is not yet available. Similarly, it is not yet clear why the suppression of interfacial fluctuations we observe in simulations should be weaker for more highly charged solutes. Recent advances in the thermodynamics of bulk ion solvation (28, 29) and of surface shape changes (26) should provide useful guides for this effort.

Methods

Experimental Details. The surface-selective UV (193 nm) SHG response, resonant with the charge-transfer-to-solvent (CTTS) transition of the ion, was generated by focusing an incident laser beam (386 nm, 100 fs pulses, $<5 \text{ mJ}\cdot\text{cm}^{-2}$) onto the surface of a sample solution contained in a Petri dish. The emitted SHG was then collimated, steered, and spectrally filtered from the incident beam before detection with a photomultiplier. A thermoelectrically stabilized aluminum block kept in contact with the base and sides of the sample dish maintained a constant solution temperature that was monitored with K-type thermocouples inserted to the middle of the solution bulk (approximately 5 mm deep). Room temperature ($19.5 \pm 0.5 \text{ }^\circ\text{C}$) dry nitrogen was flowed across the adjacent optics to prevent condensation on the optical faces at higher temperature measurements. The environment local to the sample was controlled with a jacketing atmosphere of 0% humidity room temperature ($19.5 \pm 1 \text{ }^\circ\text{C}$) nitrogen. Further details are as given in ref. 22.

All solutions and dilutions were prepared gravimetrically and stored for no more than 24 h in airtight, ambered, or opaque glass containers, cleaned with Nochromix solution. Potassium thiocyanate (>99% purity) solutions were prepared with >18 MW water (<5 ppb oxidizable carbon) and passed by syringe through a 0.22 μm filter (Millipore; Durapore GVWP02500) that had been previously rinsed thrice with water and then thrice with the solution of interest.

The measured SHG response vs. concentration is shown for five temperatures in Fig. 1. We show the variation of the SHG oscillator strength, $[B^2 + C^2]^{1/2}$, where B and C are, respectively, the real and imaginary components of the anion susceptibility, with temperature. Although the observed increase in effective oscillator strength with temperature is in agreement with the measured bathochromic shift of CTTS D-band transition energy (increasing resonant character with respect to the SHG energy) (8), separation of the effect of a spectral shift and a change in net orientation requires knowledge of the SHG susceptibility tensor element changes as a function of temperature. This information can typically be obtained via configuration and polarization analysis experiments, but these are not performed in the present study. Nonetheless, we can infer that the observed increase in effective oscillator strength with temperature is dominated by the spectral shift, because increased thermal motion should have a randomizing orientational effect, thus reducing the effective SHG susceptibility.

Simulation Details. All simulations included a single charged solute, a uniform neutralizing background charge, and solvent molecules arranged in a slab geometry (with periodic boundary conditions applied in all three Cartesian directions). Configurational sampling of the canonical ensemble was performed with standard Monte Carlo methods. Several million Monte Carlo trial moves (corresponding, in the case of water, to 3–4 ns of sampling by molecular dynamics) were attempted in each of the runs described below.

Aqueous solvent comprised 252 molecules interacting via the SPC/E potential with Ewald summation. All water simulations were performed at temperature $T = 300 \text{ K}$, with a simulation cell of size $20 \times 20 \times 40 \text{ \AA}$. Stockmayer solvent comprised 240 particles with Lennard-Jones diameter σ and energy ϵ , and with dipole moment $\mu^* = \mu / \sqrt{(4\pi\epsilon_0\sigma^3\epsilon)} = 1.25$. All Stockmayer simulations were performed at temperature $T^* = k_B T / \epsilon = 0.7$, with a simulation cell of size $6.7 \times 6.7 \times 13.4\sigma$, and with Ewald summation.

