Mechanism of ion adsorption to aqueous interfaces: Graphene/water vs. air/water

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The adsorption of ions to aqueous interfaces is a phenomenon that profoundly influences vital processes in many areas of science, including biology, atmospheric chemistry, electrical energy storage, and water process engineering. Although classical electrostatics theory predicts that ions are repelled from water/hydrophobe (e.g., air/water) interfaces, both computer simulations and experiments have shown that chaotropic ions actually exhibit enhanced concentrations at the air/water interface. Although mechanistic pictures have been developed to explain this counterintuitive observation, their general applicability, particularly in the presence of material substrates, remains unclear. Here we investigate ion adsorption to the model interface formed by water and graphene. Deep UV second harmonic generation measurements of the SCN− ion, a prototypical chaotrope, determined a free energy of adsorption within error of that for air/water. Unlike for the air/water interface, wherein repartitioning of the solvent energy drives ion adsorption, our computer simulations reveal that direct ion/graphene interactions dominate the favorable enthalpy change. Moreover, the graphene sheets dampen capillary waves such that rotational anisotropy of the solute, if present, is the dominant entropy contribution, in contrast to the air/water interface.

Results

Fig. 1 diagrams the experimental setup and shows the SHG signal versus the bulk mole fraction of thiocyanate anions in solution. The data were fit to a simple Langmuir model, to extract the free energy of ion adsorption: ΔGads,gra = −8.5 ± 1.1 kJ/mol (SEs are quoted, and a more detailed description of how they are calculated is in SI Appendix). This is within error of the free energy of adsorption to the air/water interface (ΔGads,vap = −6.78 ± 0.03 kJ/mol). We note that the model used does not account for any surface potential caused by the electrical double layer. We attempted to use a model that does include the surface potential, as detailed in SI Appendix. However, the parameter errors and parameter correlations were too large to draw conclusions from.

Significance

The Gibbs free energy of adsorption of a prototypical anion to a graphene/water interface is determined by surface-sensitive spectroscopy and interpreted via molecular dynamics simulations to establish the adsorption mechanism, which is found to be qualitatively different from that operative for the air/water interface and probably representative of a general water/hydrophobe interface.


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To elucidate the molecular details underlying the lack of change in $\Delta G_{\text{ads}}$, we performed MD simulations of ion adsorption to the graphene/water interface. Previous studies have shown that iodide and thiocyanate exhibit very similar behavior (9). Although the effects of thiocyanate anisotropy are more significant at graphene/water than for the air/water interface (SI Appendix), the general conclusions drawn from the iodide simulations are the same, and we therefore focus our discussion on this simpler model. The simulation box contained a graphene/water interface on one end and an air/water interface on the other (Fig. 2A). The potential of mean force (PMF; Fig. 2B, black curve) for an iodide ion above the graphene was constructed using umbrella sampling, wherein the height of the ion was biased with a harmonic potential. As discussed in SI Appendix, computing $\Delta G_{\text{ads}}$ directly from the PMF requires the size of an adsorption site for an ion at the air/water interface to be defined. This is avoided by comparing the difference of values, $\Delta \Delta G_{\text{ads}}$ (SI Appendix, Eq. S17), for the graphene/water and air/water interfaces. Also as discussed in SI Appendix, there is some freedom in choosing the model parameters. We have found that our results are surprisingly insensitive to varying the flexibility of graphene but that $\Delta \Delta G_{\text{ads}}$ does depend on the choice of interaction strength between the ion and the graphene. We have chosen this interaction to reproduce the experimental free energy difference, which yields an adsorption energy for iodide at graphene in vacuum (no waters) in reasonable agreement with density functional theory (21, 22). This is similar in spirit to the approach of Williams et al. (23), who capture the effects of the graphene–ion polarization interaction (as measured by density functional theory calculations) by empirically adjusting the interaction strength between the ion and the carbon atoms. Despite the similarity in the adsorption free energies at the two interfaces, there are qualitative differences in the PMFs between the two interfaces.

The enthalpy was calculated directly from the total potential energy of the simulations (Fig. 2B, red curve), and the entropy was calculated by subtracting the enthalpy from the free energy (Fig. 2B, blue curve) (Materials and Methods). The air/water interface has a more favorable enthalpy change than does the graphene/water interface, but this is offset by an accompanying unfavorable entropy change, whereas the graphene/water interface exhibits an entropy contribution near zero. To clarify the enthalpy contributions, Fig. 3A, B compares the total potential energy to the direct interaction of iodide with graphene in vacuum. Comparison of the two curves reveals that the potential energy at the graphene/water interface is primarily due to the direct interaction and not to the solvent repartitioning energy, as found for the air/water interface, which exhibits no equivalent direct interaction. Fig. 4 depicts this situation, displaying spatial maps of water–water interactions (Fig. 4A) and iodine–water interactions (Fig. 4B), as first described in ref. 9. Notice in Fig. 4A (especially Fig. 4A, Middle) that the water–water interactions are less disrupted at the graphene interface than at the air interface. This leads to a less favorable enthalpy change when these interfacial waters are repartitioned back into the bulk solution. To better understand the entropy contributions, Fig. 3B shows the height fluctuations of the two interfaces relative to the instantaneous interface (24), an important contribution to the entropy at the air/water interface (9). The graphene sheet itself severely dampens these fluctuations (Fig. 3B, Left, cyan curve), and the iodide ion actually slightly enhances the fluctuations when it approaches the interface (Fig. 3B, Left, red curve). In contrast, at the air/water interface, large height fluctuations are dampened when the ion approaches the interface (Fig. 3B, Right).

Discussion
Given the electronic properties of graphene and the qualitative differences in the molecular details underlying aqueous ion adsorption to graphene and air, it is surprising that the experimental free energies are within error of each other. Furthermore, using UV SHG spectroscopy, Onorato et al. (25) measured similar free energies for SCN$^-$ adsorption to the dodecanol/water interface. Based on interfacial affinities alone, it would appear that the effect of a hydrophobic boundary is generic, regardless of whether the boundary is a rigid material like graphene or instead a coexisting vapor phase. Our more detailed results suggest, however, that the underlying mechanism of adsorption to the graphene/water interface is qualitatively different from that for air/water.

Before presenting a mechanistic interpretation, we note that the net change in free energy due to solvation is a path-independent quantity that can be parsed in many different (yet exact) ways, each highlighting contributions from different physical factors, such as the entropic costs of solute volume exclusion (26–29), the energetic consequences of charging a microscopic cavity (12, 13, 28, 29), intrinsic polarization of an aqueous interface (7, 8), or surface tension and solute-induced deformations and fluctuations of such interfaces (9, 11, 30). The complexity of aqueous solvation limits the simple insight that can be gained from any one analysis of this kind. In particular, the statistics of solvent–solute interactions are strongly yet subtly shaped by interactions among solvent molecules, and the entropy of solvation cannot be rigorously decomposed into contributions from distinct degrees of freedom [indeed, the entropy that notionally cancels contributions from solvent–solvent energetics in approaches like that of ref. 13 is not a measurable entropy at all (31)]. Here we focus on the influence
of our simulated graphene substrate on two factors we have previously emphasized in the context of air–water interfaces, namely, the entropic cost associated with capillary wave pinning and enthalpic gain associated with repartitioning undercoordinated water molecules at the interface to the bulk. In other parsings of solvation free energy, contributions from these factors might appear only implicitly, e.g., through the effect of capillary waves on the range of fluctuations in the solvent–solute interaction energy.

Below, we also discuss how our results may be interpreted in the context of cavity formation at the interface and how electrostatic interactions with the solvent differ at the two interfaces.

Solvation of SCN\(^{-}\) at the air/water interface exhibits a large enthalpic contribution, which Otten et al. (9) have attributed to favorable solvent repartitioning, and a large unfavorable entropic contribution, attributed to the dampening of capillary waves. Because previous work has shown that the interface between liquid water and a hydrophobic substrate is similar to the air/water interface at the molecular level (24), one might intuitively expect that the similar adsorption free energies arise due to similar molecular adsorption mechanisms. However, we show here that the similarity of adsorption affinities actually reflects a subtle cancellation in differences in adsorption enthalpy and entropy. In particular, our simulations clearly show that the graphene/water interface exhibits a smaller enthalpic contribution dominated by the direct interaction of the iodide and graphene (Fig. 3A) and a much reduced entropic contribution, consistent with the fact that the capillary waves are already suppressed by the graphene (Fig. 3B). In this mechanistic interpretation, we would expect the role of graphene to generalize to other material substrates where capillary fluctuations are suppressed relative to the air/water interface. Indeed, our results are consistent with the simulation studies of Iuchi et al. (32) and Kumar et al. (33), who investigated the adsorption of an excess proton to the air/water interface and a hydrophobic wall. In both cases, a similar well depth in the PMF as the ion moved to the interface was observed, and the enthalpic gain and entropic cost was reduced in the presence of the hydrophobic wall. Further studies on other atomically thin, uncharged monolayers are necessary to fully understand the role of graphene in the context of solvation dynamics.
needed to confirm the extent to which this cancellation effect holds in general.

To explore interfacial ion solvation from a different mechanistic perspective, we have examined a solvation pathway that first creates an uncharged volume-excluding solute and then introduces the ion’s charge. For the air/water interface this route emphasizes the strong aversion of a neutral solute for the liquid phase and a competing preference for liquid due to electrostatic interactions. In the case of graphene, both these biases are substantially weakened, highlighting again the dominant importance of direct interaction between the ion and graphene (Fig. 5). Further results and discussion of these calculations are given in SI Appendix.

In summary, we used DUV–SHG spectroscopy to determine the free energy of adsorption of thiocyanate to the graphene/water interface as $-8.5 \pm 1.1$ kJ/mol, which is within error of $-6.78 \pm 0.03$ kJ/mol for the air/water interface (9). Molecular dynamics simulations show that although the free energies are similar, the corresponding mechanisms are not. For the graphene/water interface, the enthalpy is dominated by the direct interaction of the ion and graphene. Entropy changes are negligible in our simulations of an isotropic solute; for a linear molecule we find them to be accounted for by the solute’s rotational anisotropy (SI Appendix). This suggests that even though hydrophobe/water interfaces are similar at the molecular scale (24), there are subtle, but important, differences that need to be considered when treating interfacial ion adsorption. Other studies, both theoretical and experimental, suggest that similar atomically thin, uncharged interfacial layers may also exhibit this cancellation effect between enthalpy and entropy (25, 32, 33).

Materials and Methods

Experimental Details. Fig. 1A depicts the experiment, wherein 100-fs laser pulses at 386 nm incident on the surface of CVD graphene (three to five layers) suspended on top of solutions of NaSCN generate 193 nm second harmonic radiation, which is resonant with the charge transfer to solvent transition of thiocyanate (9). A more detailed explanation of the procedure is given in SI Appendix. In the dipole approximation, such even-order nonlinear processes are inherently surface specific due to symmetry constraints (34); thus, the resonance-enhanced SHG selectively probes thiocyanate ions at the graphene/water interface. Fig. 1B diagrams the interfacial structure, whereas Fig. 1C shows the actual SHG signal collected (normalized to the nonresonant SHG signal).
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2. Verreault D, Allen HC (2013) Bridging the gap between microscopic and macroscopic descriptions of ion dynamics as implemented in the LAMMPS simulation package (38) (available at lammps.sandia.gov), with a time step of 1.0 fs and a damping constant of 1 ps. For each window, a simulation of 7 ns was performed. To reconstruct the PMF, the multistate Bennett acceptance ratio (39) method was used. At ambient conditions, it is reasonable to ignore contributions due to pressure–volume work, and contributions from kinetic energy are independent of z. We therefore equate the changes in enthalpy to the changes in potential energy. Potential energy profiles were measured directly from the umbrella sampling simulations by binning the samples according to the z coordinate of the ion, with a bin width of 0.1 nm. The autocorrelation time of the potential energy in each window was used to construct uncorrelated data sets, and the SE for each height was computed as

\[ s = \sigma / \sqrt{n - 1} \]

where \( \sigma \) is the SD of the potential energy at a given height, and n is the number of samples. The entropy profiles were calculated by subtracting the potential of mean force from the enthalpy \( \Delta E(z) = U(z) - \Delta(z) \), and error bars were calculated by simple propagation of errors. Long-ranged Coulomb interactions were computed using the particle–particle particle-mesh solver (40) with an interpolation order S, a neutralizing background charge, a k-space grid of 18 × 16 × 30, and a screening parameter of 2.95 nm\(^{-1}\). Short-range Lennard–Jones (LJ) interactions were also defined between atomic species i and j.

\[ U_{LJ}(r_{ij}) = 4\epsilon \left( \frac{\sigma_{ij}^1}{r_{ij}} - \frac{\sigma_{ij}^6}{r_{ij}^{12}} \right) \]

with parameters given in SI Appendix, Table S4 (35, 41, 42). There were no Coulomb interactions between graphene carbon atoms and other species. Furthermore, because their equations of motion were not integrated, no interaction potential between carbon atoms was defined (although tests with a flexible graphene model were performed; SI Appendix). Similarly, because only a single iodide ion was present, no iodide–iodide LJ parameters were defined.

[3] 

where z is the instantaneous height of the iodide above the graphene sheet. A total of 23 windows with \( z_{\text{min}} = 0.3, 0.4, \ldots, 2.5 \) nm were used, with \( k_{\text{bias}} = 836.8 \text{kJ/ mol nm}^2 \). Dynamics were propagated at a temperature of 298 K using Langevin dynamics (36, 37) as implemented in the LAMMPS simulation package (38) (available at lammps.sandia.gov), with a time step of 1.0 fs and a damping constant of 1 ps. For each window, a simulation of 7 ns was performed. To reconstruct the PMF, the multistate Bennett acceptance ratio (39) method was used. At ambient conditions, it is reasonable to ignore contributions due to pressure–volume work, and contributions from kinetic energy are independent of z. We therefore equate the changes in enthalpy to the changes in potential energy. Potential energy profiles were measured directly from the umbrella sampling simulations by binning the samples according to the z coordinate of the ion, with a bin width of 0.1 nm. The autocorrelation time of the potential energy in each window was used to construct uncorrelated data sets, and the SE for each height was computed as

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