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Spatial Distribution of Nitrate and Nitrite Anions at the Liquid/Vapor Interface of Aqueous Solutions

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The photochemistry of nitrate anions in sea salt aerosols is a topic of great interest to the atmospheric science community. At present, there is little experimental data regarding the nitrate anion spatial distribution at solution interfaces. This fundamental information is essential for developing an understanding of the complex interfacial chemistry/photochemistry that has been suggested to occur at the liquid−vapor interface of sea salt aerosols.[1]

The debate over the surface propensity of nitrate anions began in 2003, when molecular dynamics (MD) simulations predicted that nitrate anions prefer interfacial to bulk solvation in aqueous solutions.[2] In contrast, subsequent simulations in 2006 indicated that the probability of finding nitrate anions at the aqueous interface is quite small.[3] The most recent simulations using extended-slab models predict a decreased interfacial nitrate anion concentration.[4] The back-and-forth nature of the simulations leaves the debate over the surface propensity of nitrate anions unresolved, and quantitative experimental results have been slow to follow. Sum-frequency generation studies identified structural changes in the interfacial hydrogen-bonding network of water in the presence of nitrate anions but were unable to extract an anion concentration profile.[5] UV second-harmonic generation experiments qualitatively indicated that nitrate anions have a weak propensity for the interface.[6] In addition, an analysis of surface tension data suggested that the concentration of nitrate ions at the surface is the same as in the bulk.[14]

Our previous studies of alkali halide salt solutions using depth-resolved X-ray photoemission spectroscopy (XPS) of deliquesced single-crystal samples have provided the most quantitative determination of ion concentration profiles at the liquid−vapor interface available to date.[7−10] In addition, those studies served as an important experimental validation of the theoretical models of alkali halide ion distributions at the liquid−vapor interface of aqueous solutions.[11] Here we extend our studies to aqueous solutions of sodium nitrate, sodium nitrite, and mixtures of these two salts. This study provides experimental results to quantitatively address the surface propensity of molecular nitrate and nitrite anions in aqueous solution. As such, this is our first publication of the surface versus bulk propensity of polarizable *molecular* ions at the liquid−vapor interface.

Our XPS measurements used a 15 μm aqueous liquid jet of 3 M $NaNO_3$, 3 M $NaNO_2$, or a mixture of the two (3 M each) at 4 °C with tunable synchrotron radiation from the U41-PGM undulator beamline of the BESSY facility in Berlin. Details of the experimental setup have been recently reviewed.[12] The incident photon energy was tuned to generate photoelectrons of N 1s and O 1s at photoelectron kinetic energies (eKEs) over the range 150−820 eV. Over this energy range, the depth from which the photoelectrons escape the aqueous solution and contribute to the main photoemission peaks varies [it is controlled by the inelastic mean free path (IMFP)], allowing us to change the probe depth of the experiment. In aqueous ionic solutions, photoelectrons from the outermost ∼1.2−1.5 nm contribute to the signal at 150 eV (with an exponential weighting for electrons generated closest to the surface), whereas at 800 eV, the outermost ∼5.0 nm of the solution is probed.[13]

Figure S1 in the Supporting Information (SI) shows the photoemission spectra of the N 1s region for 3 M aqueous solutions of $NaNO_3$, $NaNO_2$, and an equimolar mixture of the two solutions. These spectra show that the N 1s binding energies of the two anions differ by 3.8 eV and can be easily resolved in an aqueous solution containing both anions.

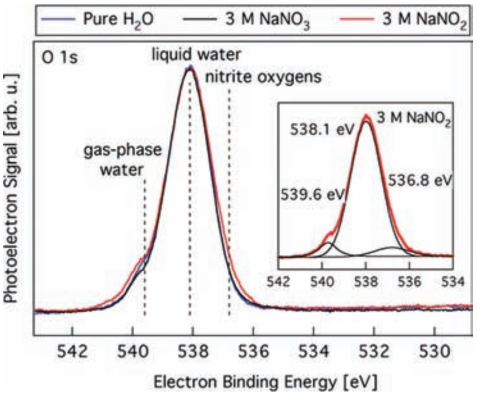

Figure 1. O 1s region of neat water, 3 M $NaNO_3$, and 3 M $NaNO_2$. The nitrate O 1s envelope is identical to that of neat water, whereas the nitrite envelope shows a broadening on the lower-energy side. The inset shows three different Gaussian peaks used to fit the O 1s region of aqueous $NaNO_2$.

Generally, ion profiles in aqueous solution are reported as anion-to-cation ratios,[7−10] as quantifying the photoemission signals to extract absolute ion profiles is a difficult challenge requiring an accurate knowledge of both the incident photon flux and the cross sections for ionization in solution. In the present study, we overcame these problems, allowing us to report the first quantitative absolute anion profiles in solution from aqueous sodium nitrate and nitrite, by measuring the O 1s region (Figure 1) as a function of eKE, which for the nitrite system provides an internal calibration. For the NO_2^- solution (Figure 1 inset), the O 1s contribution of the anion (536.8 eV) can be resolved from that of gas-phase water (539.6 eV) and liquid water (538.1 eV). The ratio of the nitrite anion O 1s peak area to that of the solvent water O 1s peak area can be used to determine an absolute ion concentration that we report in units of molarity. In contrast, the O 1s contribution from the nitrate ion in solution cannot be resolved from that of the liquid water signal, so the absolute ion profile can be

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extracted only by using the energy-dependent ratio of N 1s photoelectron peak areas in the equimolar solution containing both NO_3^- and NO_2^- (Figure S1c). This approach assumes that the profiles of nitrate and nitrite anions are not affected in going from the pure 3 M solutions to that of the mixture. Using this systematic approach, we generated the absolute nitrate anion density as a function of depth into solution, as shown in Figure 2.

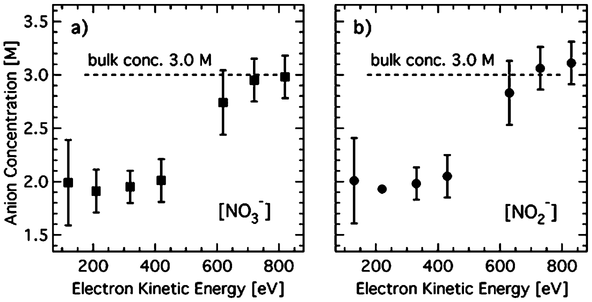

Figure 2. Anion experimental depth profiles into solution for aqueous solutions of (a) 3 M $NaNO_3$ and (b) 3 M $NaNO_2$. In both cases, the interface was depleted in anions relative to the bulk. At high eKEs (>600 eV), the bulk concentration was recovered.

Figure 2 shows the eKE-dependent depth profiles of NO_3^- and NO_2^- in aqueous solution. The absolute concentration of NO_2^- was directly measured from the O 1s spectrum by taking the ratio of the nitrite oxygen atom peak area (divided by 2 to account for the oxygen atom stoichiometry) to the liquid water peak area. In converting the result to molarity units, we assumed the density of water to be constant at all probe depths. In both cases, there was a near-surface depletion of anions extending to an energy of 400 eV, after which the bulk 3.0 M concentrations were recovered. These studies present two important results. First, while the anions preferred bulk solvation, we still observed some anions in the volume of our shallowest probe depth. NO_3^- and NO_2^- anions in this volume may experience a reduced solvent cage, as predicted by theory,[4] and have already been suggested to play increased roles in photochemistry.[1] Second, the interfacial region over which anion concentrations differed from that of the bulk extended to experimental probe depths associated with eKEs of 400−500 eV. At these energies, we probed the outermost 2.5−3.0 nm of solution, indicating that the interface of these systems appears to be substantially broader than that observed for alkali halide solutions.[7−10]

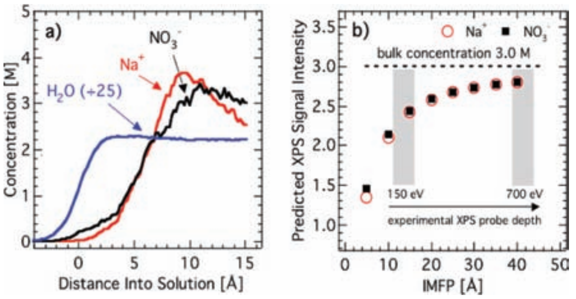

Figure 3. (a) Density profiles from MD simulation[4] of aqueous $NaNO_3$. (b) Ion concentrations predicted using the density profiles in (a) (see the SI for details).

To compare our results to the most recent theoretical models in the literature, the density profiles from MD simulations[4] (Figure 3a) were used to generate convoluted, simulated (predicted) photoelectron signal strengths (Figure 3b) as a function of experimental probe depth that can be compared to the experimental results in Figure 2a. At an experimental probe energy of 150 eV, corresponding to an exponentially weighted depth of ∼1.2−1.5 nm, the MD simulation predicted a nitrate molarity of 2.4. The ion concentration of 2.1 M predicted assuming an IMFP of 10 Å for escaping photoelectrons gave a better overlap with the experimental results of this study at 150 eV. The slight difference between theory and experiment at 150 eV could be a result of the finite size of the simulation or of the estimated IMFP values for photoelectrons in aqueous media.[13] At higher eKEs, the predicted ion concentrations converged on 2.8 M, which is better than 90% of the bulk concentration and within the present accuracy of the experimental measurements. Details of the procedure for comparing the experimental results with the simulation are given in the SI.

We have provided for the first time quantitative information on the surface versus bulk propensity of molecular anions in aqueous solution. These results clearly demonstrate the preference of nitrate and nitrite anions for bulk solvation in aqueous solution. However, the top surface layers of 3 M NO_3^- and NO_2^- solutions are only partially depleted of anions. We have shown that the interface of these systems is broad, extending up to 3.0 nm into the solution; this is substantially broader than what we observed previously for alkali halide solutions.[7−10] This is possibly due to the more specific and directional solute−solvent bonding interactions expected for a molecular ion solute as compared with an atomic ion solute.[15] The nitrate ion depletion at the interface does not support the previously mentioned surface tension analysis. A similar discrepancy (in an opposite direction) exists for our previously published direct measurements of Br^- surface enhancement for aqueous solutions of KBr,[7] where the surface tension analysis indicated a slight surface depletion.[14]

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Supporting Information Available: N 1s spectra with binding energy assignments and a summary of how the MD simulations were convoluted with the experimental probe depth for comparison with experiment. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Wingen, L. M.; Moskun, A. C.; Johnson, S. N.; Thomas, J. L.; Roeselova, M.; Tobias, D. J.; Kleinman, M. T.; Finlayson-Pitts, B. J. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5668.
(2) Salvador, P.; Curtis, J. E.; Tobias, D. J.; Jungwirth, P. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3752.
(3) Dang, L. X.; Chang, T. M.; Roeselova, M.; Garrett, B. C.; Tobias, D. J. *J. Chem. Phys.* **2006**, *124*, 066101.
(4) Thomas, J. L.; Roeselova, M.; Dang, L. X.; Tobias, D. J. *J. Phys. Chem. A* **2007**, *111*, 3091.
(5) Schnitzer, C.; Baldelli, S.; Shultz, M. J. *J. Phys. Chem. B* **2000**, *104*, 585.
(6) Otten, D. E.; Petersen, P. B.; Saykally, R. J. *Chem. Phys. Lett.* **2007**, *449*, 261.
(7) Ghosal, S.; Hemminger, J. C.; Bluhm, H.; Mun, B. S.; Hebenstreit, E. L. D.; Ketteler, G.; Ogletree, D. F.; Requejo, F. G.; Salmeron, M. *Science* **2005**, *307*, 563.
(8) Krisch, M. J.; D'Auria, R.; Brown, M. A.; Ammann, M.; Starr, D. E.; Bluhm, H.; Tobias, D. J.; Hemminger, J. C. *J. Phys. Chem. C* **2007**, *111*, 13497.
(9) Brown, M. A.; D'Auria, R.; Kuo, I.-F. W.; Krisch, M. J.; Starr, D. E.; Bluhm, H.; Tobias, D. J.; Hemminger, J. C. *Phys. Chem. Chem. Phys.* **2008**, *10*, 4778.
(10) Ghosal, S.; Brown, M. A.; Bluhm, H.; Krisch, M. J.; Salmeron, M.; Jungwirth, P.; Hemminger, J. C. *J. Phys. Chem. A* **2008**, *112*, 12378.
(11) Jungwirth, P.; Tobias, D. J. *Chem. Rev.* **2006**, *106*, 1259.
(12) Winter, B.; Faubel, M. *Chem. Rev.* **2006**, *106*, 1176.
(13) Ottosson, N. Master's Thesis, Department of Physics, Göteburg University, Göteburg, Sweden, 2007; http://www.physics.gu.se/english/.
(14) Pegram, L. M.; Record, M. T. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 14278.
(15) Tobias, D. J.; Hemminger, J. C. *Science* **2008**, *319*, 1197.

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