

Supporting Information

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

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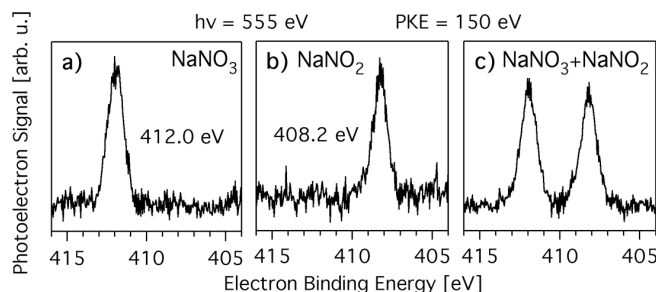


Figure S1. X-ray photoemission spectra from the N1s region of (a) 3 M NaNO₃, (b) 3 M NaNO₂ and (c) a mixture of 3 M NaNO₃ and 3 M NaNO₂. These spectra were taken with incident photon energy of 555 eV and a corresponding photoelectron kinetic energy of approximately 150 eV. The peaks are separated by 3.8 eV, which allows the individual components of the mixture to be quantified. The ratio of the two components in (c) is used to determine the absolute concentration of nitrate in the pure solution (see main text for further details).

Convolution Integral:

The depth dependent photoemission results presented in this study are an integrated quantity (we collect photoelectrons from a range of sample depths varying up to the maximum accessible escape depth at any given energy) that cannot be directly compared with the density profiles generated by molecular dynamics simulations. The inelastic scattering of the photoelectrons as they escape the solution means that the experiment exponentially weights photoelectrons that are generated closer to the surface. For example for a sample with a uniform solute distribution into the bulk, even for photoelectrons with kinetic energy such that the inelastic mean free path (IMFP) is of 1.0 nm, 40% of the photoelectrons we measure would originate from the top 0.5 nm of the surface. A quantitative comparison between the experimental profiles and the simulation requires the convolution of the theoretical density profiles with an experimental probe depth characteristic of photoemission from aqueous media. Theoretical ion densities may be converted into predicted XPS signals for a given solute ion at a given photoelectron kinetic energy $S_{ion}(KE)$ by using the integral:

$$S_{ion}(KE) = \int_0^{-z} e^{\frac{-z}{IMFP(KE)}} \rho(z) dz \quad \text{Equation S-1}$$

for each ion, where z is the distance into the sample from the aqueous vapor interface, $\rho(z)$ is the ion density (actually the atom in question (e.g., the O atom when comparing to the O(1s) spectrum)) as a function of depth into solution, obtained from the results of the molecular dynamics simulation, and $IMFP(KE)$ is the kinetic energy dependent inelastic mean free path of the photoelectrons as they exit the sample and are collected in the energy analyzer. There are a number of assumptions built into this representation of the convolution. We assume, for example, the dominant origin of the inelastic scattering of a photoelectron produced at a depth z as it moves through the liquid is due to the water density between z and the surface, and that the water density is essentially constant as a function of depth into the solution. Since the water

density is an order of magnitude larger than any other component of the solution this would seem to be reasonable.

In the simulations of Thomas, et al.¹ the size of the simulation box limits the maximum distance from the interface into the solution to 1.5 nm. At high photoelectron kinetic energy, the experiment collects some electrons that originate from solution depths that exceed this value. Since the simulation of the solution exhibits bulk behavior at depths of 1.5 nm, we have extended the simulation data to 5.0 nm using an average density value of the last 5 data points from the simulation. Extending the data in this manner allows us to carry out the convolution appropriate to high kinetic energies (eg., 700 eV, where IMFP \approx 4 nm). In front of the Gibbs dividing surface (the point in the simulation at which the density of water is half that of its bulk value) there is essentially no attenuation of photoelectrons as they leave the sample since this is the top molecular layer of the solution. To accommodate this, the experimental probe depth function

used in these calculations, $e^{\frac{-z}{\text{IMFP}(KE)}}$, is assumed to have a value of 1.0 up to the Gibbs dividing surface and then attenuates towards the bulk. Thus, this function accounts for the attenuation of the photoelectrons that are generated deeper into the bulk but recognizes that electrons generated in the first layer of the solution are not attenuated. This last point has a minor impact on the present study since the nitrate anion density in the surface region is depleted compared to the bulk.

Using the above mentioned convolution integral and the details presented here the density profiles from the MD simulations of Thomas et al. have been convoluted to generate predictions of the measured ion concentrations presented in Figure 3 of the main text.

References:

- (1) Thomas, J. L.; Roeselova, M.; Dang, L. X.; Tobias, D. J. *J. Phys. Chem. A* **2007**, *111*, 3091.