

Increased Propensity of I_{aq}^- for the Water Surface in Non-Neutral Solutions: Implications for the Interfacial Behavior of $H_3O_{\text{aq}}^+$ and OH_{aq}^-

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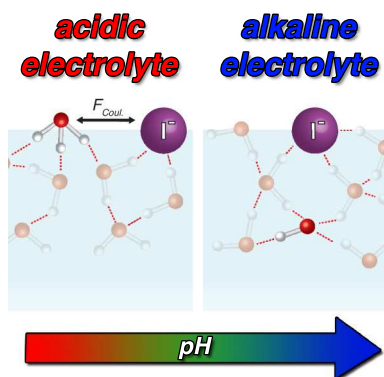
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Abstract

By a combination of surface sensitive photoelectron spectroscopy and molecular dynamics simulations we characterize the surface propensity of the iodide anion in aqueous solutions at acidic, neutral and basic conditions (pH = 1, 6.8 and 13). In both experiments and simulations an increased surface concentration of I^- is found in non-neutral solutions. We interpret these findings in terms of I^- surface co-adsorption with hydronium at low pH and "salting out" of iodide by hydroxide from the bulk solution to the surface at high pH. The present study is thus in accord with the picture of a weak surface adsorption of hydronium and surface depletion of hydroxide, being in sharp contradiction with the interpretation of electrophoretic and titration measurements in terms of strong surface enrichment of OH^- .



Keywords: Water surface, Hydroxide, Hydronium, Photoelectron spectroscopy, MD simulations

The interfacial properties of the inherent ions of water, hydronium (H_3O^+) and hydroxide (OH^-), have recently been under intense discussion. On one hand, classical, effective valence bond, and *ab initio* molecular dynamics (MD) simulations,¹⁻⁹ as well as different surface selective spectroscopic experiments¹⁰⁻¹² and surface tension measurements¹³ point to a modest surface propensity of H_3O^+ and no or very weak surface adsorption of OH^- . On the other hand, results from electrophoretic and titration measurements have been interpreted in terms of an extremely strong surface adsorption of hydroxide ions.¹⁴⁻¹⁶ This interpretation has been supported

by aqueous droplet electrospray experiments,¹⁷ as well as by simulations^{18,19} and sum-frequency vibrational spectroscopy²⁰ of different hydrophobic aqueous interfaces. Electrospray, however, provides information about small and charged droplets containing a very limited number of water molecules, which are only indirectly correlated with the bulk solution.²¹ The only molecular calculations showing appreciable interfacial affinity of OH^- were done for rigid hydrophobic interfaces,^{18,19} while soft interfaces, such as the water/oil or water/vapor interface, exhibited no or very weak hydroxide adsorption.^{8,22} In addition, a recent sum-frequency scattering study on oil emulsions in water by Roke and co-workers excluded strong hydroxide adsorption and a new interpretation of the interfacial charge in terms of charge transfer between water molecules has been suggested (unpublished results).

Given this situation, where conflicting interpretations of the molecular origin of the charge at aqueous interfaces exist, more experimental evidence is clearly needed. One powerful and promising technique in this context is photoelectron spectroscopy (PES), which could only recently be applied to the aqueous phase with the invention of the liquid micro-jet technique.^{23,24} Furthermore, due to the short inelastic mean free path of electrons in the condensed phase, the method is highly surface sensitive.^{25,26} The shortest probing depth achieved in liquid-jet PES of aqueous samples is thought to be approximately 1 nm.²⁶ While this is deeper than the information depth stemming from the surface-specific non-linear response utilized in sum-frequency generation (SFG) and second-harmonic generation (SHG) experiments²⁷ it is important to realize that the sensitivity in PES decays as an exponential function with depth in the sample, meaning that the outermost surface layer will still contribute to a much larger extent than the sub-surface. The technique can thus be used to identify species present at the interface and quantify their surface propensities, which has been exploited in several recent investigations of ion specific adsorption at the water surface.²⁸⁻³⁰

In a previous PES study the lack of appreciable surface adsorption of OH^- could be inferred from the linear dependence of the valence and core PES signals from hydroxide on its bulk concentration.¹² Here, we probe the interfacial behavior of hydronium and hydroxide using a different

strategy: From previous PES measurements^{26,31} and MD simulations^{32–34} of pH neutral iodide solutions of varying concentration it follows that iodide is present (weakly adsorbed) at the water surface. This is commonly rationalized in terms of the anion's polarizability which enables the formation of a stabilizing surface dipole. Recent work also suggest that the polarizability of I^- can be important for its bulk hydration motifs,³⁵ an effect which conceivably can be influential also for its surface behavior. In this study, we follow the intensity of the I^- PES signal – which is a measure of its surface affinity – as a function of pH. We show that the iodide surface propensity increases both upon raising and lowering the pH compared to the neutral solution. Using simple electrostatic arguments and molecular dynamics simulations we interpret this observation in terms of surface co-adsorption of hydronium and iodide at low pH, and "salting out" of iodide by hydroxide from the bulk solution to the surface at high pH.

The liquid-jet photoelectron experiments of 0.5M LiI solutions as function of pH were performed at the Swedish national synchrotron facility MAX-lab, Lund, at the soft X-ray undulator beamline I411. The experimental setup has been described in detail previously³⁶ and further details are given in the Supplementary Information. The samples were prepared freshly from highly de-mineralized water (18.2 MOhm, Millipore Direct-Q) and commercially available salts (Sigma Aldrich, >99%). The pH was subsequently adjusted to the desired value (1, 6.8 or 13) by adding concentrated HCl and NaOH solutions and was monitored using a calibrated pH meter (Hanna pH 212) equipped with a Mettler Toledo Inlab Routine electrode.

Polarizable classical force fields were employed in the MD simulations, since solutions of polarizable ions (iodide in particular) are studied. A periodic simulation box of $2.9 \times 2.9 \times 13 \text{ nm}^3$ containing 700 water molecules, along with the ions, in a slab geometry was employed. The number of ions was chosen such as to provide a 1 M solution of NaI. Na^+ , which is similarly repelled from water surface as Li^+ , was used as counterion to I^- . An additional 1 M of either Na^+ and OH^- , or H_3O^+ and Cl^- was added to simulate a strongly basic (pH ~ 14) or acidic (pH ~ 0) system. The basicity/acidity of the solutions was thus 1 pH unit stronger than that in the experiment in order to improve the statistics of the simulated data by increasing the number of ions.

Calculations were performed employing the Gromacs 4.0.7 software suite.³⁷ Further simulation details are given in the Supplementary Information.

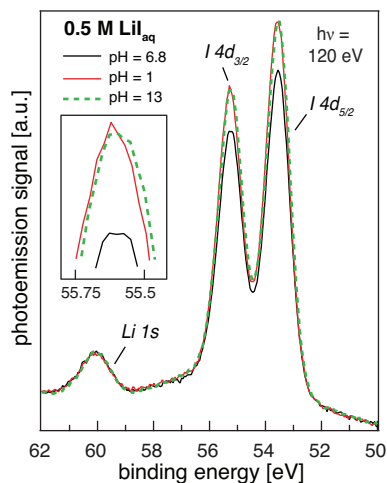


Figure 1: Surface sensitive photoelectron spectra of 0.5 M LiI aqueous, obtained at a photon energy of 120 eV. The Li 1s and I 4d_{5/2,3/2} photoemission features uniquely identify the lithium cations and iodide anions. The inset shows a magnification of the I 4d_{3/2} region, revealing an increased surface propensity of I⁻ in non-neutral solutions.

Figure 1 shows the photoelectron spectra of a 0.5 M LiI aqueous solutions at pH = 1, 6.8, and 13 in the binding energy range of 50-63 eV. This region contains the Li 1s line at 60.1 eV BE, pertaining to the hydrated lithium cations, as well as well as the I 4d_{5/2,3/2} spin-orbit doublet at 53.8/55.5 eV BE, identifying the iodide anions. These values are in good agreement with those reported in the literature.³⁸ The spectra were taken under identical circumstances and in direct sequence, so that intensity variations of any spectral features reflect genuine differences in surface propensity of the corresponding species.

As is immediately clear from Fig. 1, the general appearance of the photoelectron spectrum does not dramatically change with pH. The background almost perfectly overlaps in all the three spectra, and so do the Li 1s photolines – note that the spectra has been neither shifted nor offsetted. These observations show that the overall electronic structure of the solute ions is not strongly perturbed by pH variations and that the interfacial behavior of Li⁺ remains unaffected. What does change, however, is the intensity of the I 4d_{5/2,3/2} lines; relative to the neutral solution the intensity increases by ~13% at both pH = 1 and 13, revealing a larger propensity of I⁻ anions for

the aqueous solution surface at non-neutral pHs.

What causes the increased iodide surface propensity under acidic and basic conditions? One parameter that is changed upon addition of HCl/NaOH to the LiI solutions is the ionic strength of the electrolyte. In a recent study of the concentration dependent surface structure of LiI aqueous solutions we have shown, however, that the surface propensity of iodide relative to its lithium counterions is actually *reduced* at higher concentration.³⁹ A factor contributing to the weakening of the anion/cation surface separation at higher salt concentrations is the reduced electrostatic screening length, which decreases with increasing ionic strength. Since this effect goes in the opposite direction of what is observed in Fig. 1, we can conclude that the increased surface propensity of I^- upon addition of HCl/NaOH cannot be explained in terms of changes in the total ionic strength of the solution. Similarly, we can exclude the possibility that the co-solvation of the Cl^- and Na^+ ions significantly influence the surface propensity of I^- . This is so because measurements of a 0.5 M LiI + 0.1 M NaCl solution (corresponding to approximately the same concentration of Cl^- and Na^+ as in the solutions with pH = 1 and 13, respectively) yielded indistinguishable photoelectron spectrum from that of the pure 0.5 M LiI solution in the binding energy region shown in Fig. 1.

Since the experimental observations cannot be explained by changed ionic strength or effects of the Cl^- and Na^+ ions we have to consider the direct interactions of iodide with the co-solvated H_3O^+ and OH^- ions. We start with solutions at low pH, which can be interpreted along the lines outlined in ref.¹⁰ From previous studies of alkali-halide salt solutions⁴⁰ it is well understood that the preferential adsorption of iodide is counteracted by the free energy penalty associated with moving the alkali counterion to the interface in order to maintain net charge neutrality in the interfacial region. This leads to a spatial structuring of the interface where an iodide-enriched/cation-depleted surface layer is counterbalanced by an iodide-depleted/cation-enriched subsurface.⁴¹ In contrast, such structured density profiles are not observed for aqueous solutions containing small, surface-repelled cations, such as F^- , given the similar surface repulsion of such solvated anions and cations.²⁸ These results show that at molar concentrations anionic and cationic interfacial distributions are strongly correlated, due to their Coulombic interaction. A straightforward inter-

pretation of the experimentally observed increase of the I^- signal upon decrease of the solution pH is thus that hydronium ions exhibit an increased surface propensity compared to alkali cations, which indeed has been suggested from a number of recent studies.^{3,10} Interfacial H_3O^+ thus electrostatically pulls co-solvated I^- towards the surface. In this way the iodide surface coverage can increase without affecting the Li^+ distribution, hence removing the free energy penalty associated with alkali cation surface-repulsion. This finding is in accord with a recent second harmonic generation (SHG) study, showing that iodide is more strongly adsorbed at the water surface in aqueous solutions of hydriodic acid (HI) compared to potassium iodide.¹⁰

Turning to the high pH solutions it is clear that the same mechanism as discussed above cannot be invoked to explain the experimental finding of the increased I^- signal. If OH^- was preferentially adsorbing at the interface one would expect to see a reduced surface propensity of iodide in basic solutions due to the Coulomb repulsion between the two negatively charged species in the anion-enriched surface layer. This is, however, just the opposite of what is experimentally observed. Instead, the phenomenon strongly resembles the previously observed situation in highly concentrated mixed aqueous NaCl/NaBr solutions.³⁹ When two monovalent anions are co-solvated in an aqueous solution the more strongly hydrated species, i.e., the one with the lower surface propensity (Cl^-), tends to "salt out" the other ion (Br^-) toward the surface layer.³⁹ Such an ion exchange, which does not change the electrostatic balance within the surface region since the two species are of identical charge, is energetically favorable given the differences in the surface propensities of the two species. This effect should scale with the difference in surface adsorption energy of the two anions. It is hence natural to interpret the present photoemission data, showing an increased surface coverage of iodide in basic solutions, in terms of "salting out" of I^- by OH^- . This strongly suggests that the surface propensity of OH^- is much lower than that of I^- , and even of Cl^- , since we do not see such a strong "salting out" behavior of I^- in solutions in which LiI is co-solvated with 0.1 M NaCl.

In order to validate the above interpretation of the PES measurements we have performed MD simulations of slabs of aqueous NaI solutions at varying pH induced by adding HCl or NaOH.

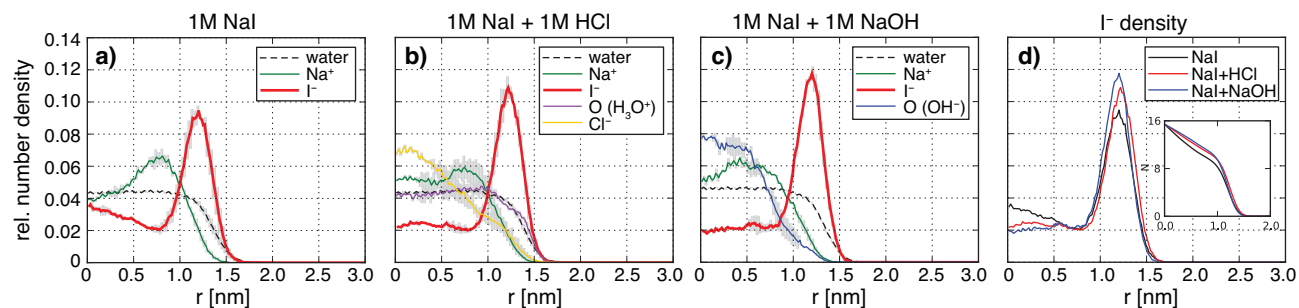


Figure 2: Density profiles of simulated neutral (a), acidic (b), and basic (c) NaI solution. Comparison of I^- density profiles and number of I^- (inset) as a function of the distance from the center of the simulation box is presented in (d).

Density profiles of water and ions for neutral, acidic, and basic NaI solution are depicted in Fig. 2a-c. At neutral pH the surface propensity of iodide is evident; the iodide's peak at the air/water interface coincides with the depletion in the density of Na^+ , and is followed by increased density of the cation in the subsurface region (Fig. 2a). The corresponding density profiles for the acidic and basic solutions are shown in Fig. 2b and c, respectively. The I^- density profiles in the three systems are plotted next to each other, together with their integrated values, in Fig. 2d. In excellent agreement with the PES measurements an increased number of interfacial I^- ions with respect to the pH neutral solution is evident both in the acidic and basic systems. Furthermore, the proposed rationalization of the experimental data in terms of ion-ion electrostatic interactions is in accord with the MD simulated ionic profiles. Namely, in the acidic system, adsorption of hydronium ions leads to an increase of the iodide surface density peak, while in the basic system the low surface propensity of hydroxide results in a "salting out" of I^- toward the aqueous surface.

To summarize, using surface sensitive photoelectron spectroscopy we have shown that the surface concentration of I^- in LiI aqueous solutions is increased at non-neutral pH values. These observations are consistent with the presence of hydronium at the water surface and with surface repulsion of hydroxide. This interpretation is supported by MD simulations, which reproduce well the experimental observed pH-dependent behavior of iodide.

In this study, the increased surface propensity of I^- in solutions of non-neutral pH has been used as a tool to probe the surface affinity of H_3O^+ and OH^- . Nevertheless, the present findings

may have direct implications for the surface structure of naturally occurring salt solutions containing large polarizable halides at non-neutral pHs. Partially dehydrated aqueous droplets of seawater origin can reach high concentrations of inorganic salts and may also be rather acidic due to the presence of atmospherically occurring acids, such as H_2SO_4 or HNO_3 .⁴² Our data suggest that such natural pH variations may further increase the surface activity of large polarizable anions, providing thus an additional part of the puzzle of the anomalous importance of bromine chemistry in the troposphere.^{43,44}

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Supporting Information Available: Further experimental and computational details. This material is available free of charge via the Internet <http://pubs.acs.org>

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