

The influence of concentration on the molecular surface structure of simple and mixed aqueous electrolytes

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Abstract

We investigate various mechanisms contributing to the surface ion distributions in simple and mixed aqueous alkali-halide solutions depending on the total salt concentration, using a combination of photoelectron spectroscopy and molecular dynamics simulations. In simple solutions, the surface enhancement of large polarizable anions is reduced with increasing concentration. In the case of a NaBr/NaCl mixed aqueous solution, with bromide as the minority component, the situation is more complex. While the total anion/cation charge separation is similarly reduced with increasing salt content, this alone does not uniquely determine the ion distribution due to the co-existence of two different anions; Br⁻ and Cl⁻. We show that bromide is selectively surface enhanced at higher concentrations, despite the fact that the total anion surface enhancement is reduced. This phenomenon, which can be viewed as “salting out” of bromide by NaCl might have consequences for our understanding of the surface structure of mixed aqueous solutions subjected to concentration increase due to dehydration, such as seawater-born aerosols.

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I. Introduction

Our understanding of the aqueous solution/vapor interface has undergone dramatic changes over the last decades. Surface sensitive experiments¹⁻⁵ and molecular simulations^{6,7} have shown that the surface structure of aqueous solutions is dependent on the identity of the constituent ions to a much larger extent than previously assumed. Contrary to the textbook description,^{8,9} based on classical electrostatic continuum models,¹⁰ it is now well established that large and polarizable anions can be present and even enriched at the surface and locally display very different density profiles than their counter ions. While the main characteristics of this phenomenology are becoming widely accepted, the multi-dimensional parameter space governing the exact surface propensity of a given ionic species for the solution/vapor interface is large, and the possible mutual dependencies therein are still far from fully disentangled. As an example, while the iodide anion has been found to be surface enriched under normal conditions, Krisch *et al.* have recently demonstrated how even moderate concentrations of organic surfactants can dramatically suppress its surface activity,¹¹ illustrative of how multi-component systems may behave very differently from what could be expected from their components in isolation.

In this paper we address concentration dependent effects on the surface composition of simple and mixed aqueous electrolytes. Many naturally occurring saline aqueous systems display significant variations in total salt concentration; e.g., oceanic brine formation can result in supersaturated solutions in shallow coastal areas and evaporation from sea-water aerosols leads to a gradually higher salt content, eventually resulting in crystalline particles.¹² Furthermore, aqueous aerosols of seawater origin are inherently mixed systems; while the dominant solute is NaCl, about 1 out of 650 solvated anions is bromide.¹³ Upon water evaporation, this fraction remains constant, whereas the total concentration of the solution increases. What are the possible effects of increasing the concentration on the molecular surface structure of these abundant aqueous systems? This question may be relevant for obtaining a more detailed molecular-level understanding of bromine chemistry in the atmosphere. An increased scientific interest therein was triggered about twenty years ago by the discovery that tropospheric ozone depletion events (ODEs) in arctic regions are to a large extent governed by bromine oxidation reactions. This was revealed via the observation of a strong anti-correlation between the occurrence of gaseous ozone and filterable bromine compounds.^{14,15} While initially found surprising, given the low abundance of bromide anions in the bulk of arctic snowpack (the main source of bromine in the polar regions), there now exists a growing body of evidence attributing this overrepresentation of bromine's chemical activity to surface specific reactions, where the local concentration can be significantly higher than in the bulk.^{16,17} Ghosal *et al.* have for example shown that the surface propensity of bromide sharply increases as a NaBr-doped NaCl crystal is wetted to its deliquescence point – a

phenomenon attributed to both higher surface propensity of Br^- , as well as the relatively higher solubility of sodium bromide compared to sodium chloride.¹⁸

Using photoelectron spectroscopy (PES) and molecular dynamics (MD) simulations, we will investigate how the ion composition in the interface region evolves with concentration in simple and mixed aqueous alkali-halide solutions. Starting with single salt monovalent electrolytes (LiBr and LiI) we pursue the following line of reasoning. If a system exhibits a structured interface with distinctly different anionic and cationic profiles in the low concentration regime, these differences should eventually be reduced at higher concentration, partly due to the increasing Coulomb energy penalty for maintaining a spatial charge separation with increasing net charge. Further, surface saturation effects¹⁹ as well as reduced electrostatic screening lengths can be expected to weaken the charge separation in the interfacial region at high concentrations. Changes in the relative anion/cation surface composition as function of bulk concentration thus also indirectly carry information about the system in the dilute limit. The considerable surface sensitivity achieved in core-level PES makes this technique ideal to monitor the solution surface region, and the photoemission lines pertaining to each ionic species are easily separated. We experimentally observe a gradual weakening of the I^-/Li^+ separation in the interface region at higher concentrations, while the corresponding situation for Br^-/Li^+ is less clear. MD simulations reveal a qualitatively similar interfacial behavior. While simple systems merely display a weakening of the anion-to-cation surface separation with increasing salt concentration, we further demonstrate that the co-existence of two different anions – as in mixed NaBr/NaCl electrolytes, with bromide as the minority component – actually can cause an *increase* of the Br^- surface coverage with increasing total salt content. This can occur at the expense of the chloride anions being pushed into the solution sub-surface and can hence be viewed as a “salting out” mechanism. This anion-selective layering mechanism at the solution surface provides a further detail to our understanding of the unexpectedly high importance of bromide in atmospheric chemical reactions.

II. Methods

IIa. Experimental details

Liquid soft X-ray photoelectron spectroscopy measurements were conducted at the I411 undulator beamline at the MAX-Lab Swedish national synchrotron facility, Lund. A series of LiBr, LiI and NaBr aqueous solutions at various concentrations (ranging from 0.25 to 6 molar) were prepared from highly de-mineralized water. Further, solutions of co-dissolved NaCl and NaBr were investigated in which the $\text{Br}^-:\text{Cl}^-$ molar ratio was kept fixed at 7:100 while the total salt

concentration was varied (ranging from 0.4 to 4M). To ensure a constant ratio of Br⁻:Cl⁻ in all samples they were prepared from the same 4M solution through varying degrees of dilution. Commercially available salts (>99.5%) were obtained from Sigma-Aldrich and used without further purification.

Details of the experimental setup have been described elsewhere.¹⁴ Briefly, the sample was injected into a vacuum chamber through a glass nozzle, forming a 15 μm liquid micro-jet at 4° C at roughly 100 m/s. Both the nozzle and the pump generating the necessary backing pressure were obtained from Microliquids GmbH.²⁰ The electron detection was made at an angle of 54.7° (the so-called magic angle²¹) relative to the polarization plane of the synchrotron light polarization vector and perpendicular to the flow of the liquid jet. The photoelectrons emitted from the liquid surface entered the differentially pumped electron analyzer through a skimmer with a diameter of 500 μm . The total experimental resolution at the photon energy range used in the current experiment (140-270 eV) was better than 200 meV, determined from the width of the 1b₁ water gas-phase line. This is significantly narrower than the natural width of the photoelectron lines here investigated.

All measured Li⁺ 1s, Na⁺ 2s, Br⁻ 3d and I⁻ 4d photoelectron lines were fitted using Voigt line shapes. Energy positions of each spin-orbit doublet component were free parameters in the fitting procedure, but their relative intensity was fixed to the ratio found at high concentration. This provides a robust constraint on the coefficients of the spline interpolation function, needed to handle the slightly non-linear background under the LiI spectral features in the low concentration regime. The Gaussian width was free for each doublet, but the constituent components were forced to take the same value.

Due to the slightly different BEs of the levels here considered, the absolute probing depth will not be exactly the same for the respective cations and the anions. Since the photon energy is the same in all measurements of a certain system, the photoelectron probing depth for each ionic species will however be constant as well as the photoionization cross section. This means that at a given photon energy, any concentration dependent variations in the relative anion/cation signals must signify real changes in the surface composition.

Iib. Computational details

Molecular dynamics simulations were performed with the aim of obtaining ionic distributions of simple and mixed sodium halide salt solutions of increasing concentration next to the air/water interface. Only sodium salts were modeled, while experimentally both sodium and lithium salts were investigated, since more reliable parameterization exists for the former and the

nature of the alkali cation has only a weak effect on the anionic density profiles.⁷ Two different concentrations – 2 and 4M – were investigated for single salt solutions of NaCl, NaBr, and NaI and for mixed solutions with 92% of NaCl and 8% of NaBr (Br:Cl = 6:70).

A unit cell with dimensions of 33 x 33 x 150 Å³ contained 898 water molecules and 76 NaX molecules for 4M salt solution or 38 NaX molecules for 2M salt solutions (X stands for halide anions). 3D periodic boundary conditions were applied, which yielded a slab geometry. Long range electrostatic interactions beyond the non-bonded cutoff of 9 Å were accounted for using the Particle Mesh Ewald (PME) method.²² The Berendsen temperature (300 K) and pressure (1 atm) couplings were employed²³ and all O-H bonds were constrained using the SHAKE algorithm.²⁴ Polarizable models for water (POL3²⁵) and ions²⁶⁻²⁸ was employed with the induced dipoles converged in each step by a self-consistent procedure. For each system, minimization and 1 ns equilibration was followed by a 20 ns production run with a time step of 1 fs. Such a simulation length provided sufficiently converged results. All simulations were performed using the AMBER 10 program package.²⁹

The trajectories were used to obtain density profiles, i.e., averaged distributions of ions and water molecules along the z-coordinate, normal to the slab surface. From these density profiles, the corresponding experimental PE response was simulated,³⁰ which enables a more direct comparison with experimental data.

III. Results and discussion

In the following section we present photoemission and molecular dynamics data on how the surface structure aqueous alkali-halide solutions evolves with concentration. We begin with two simple systems, and then consider a mixed system.

IIIa. Concentration dependent surface structure of simple alkali-halide solutions

Figure 1 shows photoelectron spectra of LiI and LiBr aqueous solutions at concentrations ranging from 0.25 M to 6 M. Trace a), taken from LiBr solutions, displays Li⁺_{aq} 1s and Br⁻_{aq} 3d_{5/2,3/2} features at 60.1 and 73.2/74.3 eV BE, respectively. The lithium cations in the LiI solutions (trace b) are again monitored through the Li⁺_{aq} 1s line but this time contrasted against the I⁻_{aq} 4d_{5/2,3/2} feature at 53.8/55.5 eV BE, a unique signature of the iodide anions. These values are consistent with previous reports¹⁷ and no concentration dependence on the BEs was observed. In the present work, all spectra of the simple solutions were recorded at 140 eV photon energy, result-

ing in kinetic energies around the minimum of the photoelectron mean free path leading to an appreciable surface sensitivity.^{16,30}

The different anion and cation PE intensities at given salt and concentration primarily arise from differences in atomic photoionization cross sections.³¹ The main concentration dependent effect, as expected, is that the absolute PE signal intensities of the respective anion and cation features in figure 1 increase monotonously, while non-stoichiometric variations in the surface structure with concentration will be manifested in varying anion/cation signal intensity ratios. To quantitatively evaluate how the surface composition of simple LiBr and LiI solutions varies with total salt concentration, the respective photoemission features in figure 1 were fitted according to the methods described in the section on experimental details. The relative anion/cation PE signal intensity ratios obtained from integration of the fits at each concentration are shown in figure 2. The Y-axis values are arbitrarily chosen to be 1 for the observed ratio at the lowest studied concentration (0.25 M). The PE ratio of the two salt solutions evolves very differently as function of concentration; while no significant change is observed in the Br⁻/Li⁺ ratio (filled squares), the I⁻/Li⁺ ratio (open circles) decreases by approximately 17% when going from 0.25M to 6M.³² These findings strongly indicate that iodide is adsorbed on the surface as the decreasing I⁻/Li⁺ ratio indicates a weakening of the anion-to-cation surface separation at high concentrations, which can only be expected if the separation is pronounced in the dilute limit. The almost constant PE ratio (showing only a small decrease, almost within the experimental uncertainty) for LiBr indicates that bromide is adsorbed to a lesser degree.

Why is the relative anion/cation separation reduced at higher concentrations? We can identify two principally different mechanisms leading to such a behavior. First, the net ion surface excess can be reduced due to saturation of the available solution surface “sites”, which primarily should act to reduce the anion surface excess as it is more surface active in the dilute limit. Secondly, the distribution of the cations is sensitive to the characteristic length scale of charge separation (the screening length) of the electrolyte solution, which decreases with increasing concentration.⁹ The cations required to neutralize the charge of adsorbed anions thus on average moves closer to the surface in more concentrated solutions. As a consequence they become more visible in the PE spectra, resulting in gradually smaller anion/cation PE ratios; the mechanism is illustrated in figure 3. As the screening length also influences the electrostatic free energy penalty associated with bringing anions to the surface, it is not a trivial task to separate the respective influences of saturation effects and changes of the screening length on the PE ratio. Fortunately, both mechanisms lead to the conclusion that a decrease in the anion/cation PE ratio with increasing salt concentration signifies adsorption of anions; if there is no enrichment of anions in the surface region neither saturation nor redistribution of excess cations can occur.³³

To aid the interpretation of the photoemission data, figure 4 shows converged density profiles obtained from MD simulations of 2 and 4M NaX (X = Cl (a), Br (b) and I (c)) aqueous solutions. Consistent with previous results²⁷, these alkali-halide solutions display a structured surface with an anion enriched and sodium depleted surface layer, followed by a sodium enriched and anion depleted sub-surface region. This is mainly a consequence of the difference in ion-water interactions in the surface and bulk regions for the varying ionic species. The magnitude of this effect is known to scale with the anion size and polarizability¹⁹, which is clear from figure 4. While the NaCl interface shows a weak anion/cation surface separation the NaI interface is heavily structured, with NaBr found as an intermediate between these two. While this behavior is generic for polarizable force fields, the exact values of the anionic surface peaks depend on a particular choice of potential parameters.

In the present context we are primarily interested in how the surface region is affected by total concentration changes. As seen for all traces (a-c) of figure 4, the anion-to-cation separation clearly diminishes when going from 2 to 4M. While this effect is subtle for NaCl, since the degree of charge separation is small for this salt at any concentration, the weakening of the anion-to-cation separation upon doubling the concentration becomes more pronounced for NaBr and even more so for NaI. We note that both effects discussed above indeed can be observed, most clearly for the NaI solutions; while the iodide surface peak is reduced in intensity there is also a redistribution of the counter ions toward the surface, in excellent agreement with the prediction based on reduced screening lengths (see figure 3). The density profiles show certain oscillations in the interior of the slab for the 4M concentrations. This behavior is qualitatively reminiscent of the concentration profiles in molten salts.³⁴ As the total amount of water in the solution at 4M is comparable to the amount of water required to solvate the ions this is not entirely surprising.

In order to strengthen the connection between the photoemission data and the MD results, we have evaluated the anion/cation PE response from the density profiles in figure 4 (the details on this procedure have been given elsewhere³⁰) – the results are presented in figure 5. The dotted blue lines show the respective anion/sodium PE ratios as function of the electron attenuation length for 2 and 4M concentrations, respectively. The solid thick red lines show the corresponding PE ratios for 4M/2M, which is the relevant quantity to compare with the experimental data. In agreement with the experimental decrease of the I⁻/Li⁺ PE ratio as function of concentration, shown in figure 2, we see that the curve of the simulated 4M/2M ratio for NaI (figure 4c) lies well below unity at short attenuation values and grows with increasing attenuation lengths, which corresponds to going from exclusively probing the surface region to including more and more sub-surface/bulk contributions. For large attenuation lengths the ratio should approach 1, which is not fully reached in the present simulations due to the lack of a proper infinite bulk – an

surface enhancement in finite systems inevitably occurs at the expense of bulk depletion. However, the evolution of the 4M/2M curves for the different halides clearly shows that the anion surface propensity in the dilute limit ($I^- > Br^- > Cl^- > F^-$) correlates with a decrease in the anion/cation PE ratio with increasing concentration. Yet, a fully quantitative comparison between the simulated and the experimental PE ratios would be hampered by uncertainties in the real attenuation lengths for photoelectrons originating from the aqueous phase as function of KE, an issue we have recently addressed in detail.³⁰ As the minimum effective attenuation length from an aqueous cylindrical surface (such as our liquid micro-jet target) probably exceeds 10 Å we expect, based on the simulated data, to see contrast in the anion/cation PE ratio in going from 2 to 4M for iodide salts (figure 5, trace c). However, this effect should hardly be visible for chloride and bromide salts (trace a and b), consistent with the experimental results (figure 1 and 2), exhibiting concentration dependent changes of the anion/cation PE ratio for LiI but not for LiBr.

IIIb. Concentration dependent surface structure of mixed alkali-halide solutions

Using the same methodology we now investigate the surface structure of mixed salt solutions at varying concentrations. We have chosen a system similar to that studied previously in connection to atmospheric aerosols formed from sea spray near the deliquescence point,¹⁸ namely NaBr/NaCl mixtures with sodium bromide as the minority component. Figure 6(a) displays PE spectra of mixed NaBr/NaCl solutions ($Br^-:Cl^- = 7:100$) at three different concentrations; 0.4, 2 and 4M, taken at 271 eV photon energy. This is contrasted against the analogous measurement of pure NaBr solutions, shown in figure 6(b), at 0.4 and 4M concentrations. The spectra contain the $Na^+_{aq} 2s$ at 68.0 eV BE and $Br^-_{aq} 3d_{3/2,5/2}$ features and the respective trace have been normalized to the sodium 2s line intensity. In figure 7 the corresponding $Br^-_{aq} 3d_{3/2,5/2}/Na^+_{aq} 2s$ PE ratios are shown, obtained from integrals of fits of the respective features in figure 6, plotted as function of concentration. The ratios have been normalized to the value obtained at the lowest concentration, i.e. 0.4M. We only monitor bromide and sodium, since no suitable chloride photoelectron line lies in the vicinity of $Br^-_{aq} 3d_{3/2,5/2}$ and $Na^+_{aq} 2s$. Through a combination of what we learned from the simple systems and the observation of the behavior of the Br^- and Na^+ PE signals for the mixed system we can however also infer the behavior of Cl^- .

It is immediately seen that the bromide anions in the mixed and the pure solutions behave very differently upon changes in the total salt concentration. While no significant changes are observed in the $Br^-_{aq} 3d_{3/2,5/2}/Na^+_{aq} 2s$ PE ratio for the pure NaBr solutions (similar to LiBr in figure 1 and 2), an *increase* is observed for the mixed solutions at higher concentrations. At first glance, this might seem to be in conflict with our conclusions drawn from the single component systems, namely that higher salt concentration acts to reduce the anion/cation PE signal near the

surface. This apparent contradiction is reconciled when we realize that the present system contains two different anions, each associated with a respective density profile that do not have to be identical. Then, bromide can be gradually enriched at the surface by replacement of chloride ions without necessarily giving rise to an increase in the total anion surface density. In the mixed solutions, an enrichment of any one species of anion, therefore, does not have to imply charge separation. Concentration-driven weakening of the total anion/cation separation (where the anion profile is the sum of the Br^- and Cl^- contributions) can thus still occur if the adsorption of bromide is strong enough. Bromide is thus selectively surface enhanced at the expense of the chloride anions. The absence of strong concentration dependence in the pure chloride and bromide solutions, as discussed above in section IIIa, indicates that the charge separation is relatively modest in those solutions. In the mixed solutions the charge separation should be much smaller for a given total salt concentration due to the much lower concentration of bromide. The concentration dependence of the PE ratio for the mixed solutions is thus interpreted primarily in terms of replacement of chloride by bromide in the surface region.

Converged density profiles from MD simulations of mixed NaBr/NaCl solutions ($\text{Br}:\text{Cl}^- = 6:70$) at 2 and 4M concentration are shown in figure 8. Comparison with the corresponding simulations for pure solutions (figure 4b) indicate that bromide now shows more surface enrichment, as expected due to replacement of chloride by bromide in the surface region. Such replacement does not result in an energetic penalty due to charge separation that is inevitably associated with adsorption from the pure solutions. Because of the much larger concentration of chloride than bromide, a considerable amount of chloride is present in the surface region even though chloride does not have any appreciable surface preference.

We have multiplied the simulated ionic density profiles in the mixed solution with a decaying exponential function, with the IMFP in the exponent, in order to mimic the experimental signal.³⁰ The integrals thereof, resulting in simulated bromide and sodium PE signals, together with the ratio of the two, are plotted in Figure 9 as a function of the assumed value of IMFP. In agreement with the above interpretation of the experimental data, the simulated 4M/2M bromide/sodium signal ratio indeed lies above 1 and decreases slightly toward unity for higher values of the electron attenuation length.

While the effects are rather subtle, one can indeed see that the simulated bromide surface density peak becomes more pronounced when going from 2 to 4M of the mixed solutions, which is consistent with the experimental observations. The mechanistic explanation for this behavior is not obvious at first sight; if the differences in free energy associated with bringing an ion to the surface from the bulk solution were constant for both bromide and chloride one would expect a constant ratio of their concentrations in the interfacial region. That this is not the case thus

means that this free energy difference is concentration dependent for either or both species of ions. Such a concentration dependence does not necessarily reflect changes in the surface region only; it may equally well be caused by changes in the bulk solution, since it is the free energy difference in populating the two regions that governs surface segregation phenomena. As the magnitude of the difference in free energy that is required to explain the observed change in PE ratio is small, it is difficult to disentangle the respective contributions from the surface and bulk regions.

The excess free energy of mixing equimolar solutions of sodium chloride and sodium bromide is slightly positive for ~ 1 M solutions, and more so for even higher concentrations.³⁵ This means that there is a thermodynamic driving force toward segregation of bromide and chloride in the bulk solutions due to ion-ion interactions (though it is much weaker than the entropic driving force toward mixing, therefore, bulk demixing does not occur). The existence of such a driving force leads to the conjecture that bromide may be “salted out” from the bulk solution to the surface region due to slightly unfavorable interactions between bromide and chloride ions.

On a microscopic level, we can also find aspects of halide hydration that offers further mechanistic explanations to the observed phenomenon. Due to its smaller size – and hence its larger surface charge density – chloride anions are more strongly hydrated than bromide. This might be one of the differentiating factors between Br^- and Cl^- in the surface region when the number of water molecules available per ion to form hydration shells is gradually reduced at higher concentrations. For concentrations of several moles per liter, the total amount of water in the solution is comparable to the amount required to solvate the ions. This means that the anions effectively compete for solvating water molecules. Due to the stronger hydration of Cl^- relative to Br^- , the total energy of the system should be lowered if the more strongly hydrated species, i.e. Cl^- , is preferentially in the bulk enabling full hydration. Populating the hydration-wise less favorable surface sites preferentially with the more weakly hydrated but polarizable Br^- therefore both lowers the total bulk free energy and leads to a more favorable surface configuration, due to the favorable polarization bromide in outermost surface region. There are thus aspects of the observed phenomenon that can be qualitatively understood in a way similar to surface segregation in solids.³⁶ Furthermore, at high concentrations the solvated anions are on average relatively close to each other for purely steric reasons. It is easy to imagine that short-range repulsive interactions between solvated anions, which are inconsequential for low concentration where electrostatic repulsion keeps the anions apart, then may become important.

IV. Conclusions

From photoemission experiments and molecular dynamics simulations we have provided a consistent picture on how the molecular surface structure of simple and mixed inorganic electrolytes evolves with concentration. Some aqueous salts, such as LiI, display a pronounced anion/cation surface separation at low concentrations, which gradually collapses at higher concentrations. This concentrational weakening is less pronounced for the smaller halides, and already for LiBr and NaBr we could not observe an appreciable concentration dependence of the surface ionic structure using PES. These observations have been shown to be compatible with MD simulations employing polarizable force fields, predicting that the charge-separation is weaker for bromide salts than for iodide salts (and even weaker for chloride salts). We have discussed this phenomenon both in terms of surface saturation as well a gradual reduction of the electrostatic screening length— clearly, explicit ion-ion interactions are also becoming more important in the high concentration regime.

When co-solvated with NaCl, bromide was found to display a different concentration dependent surface behavior than in single salt solutions. The gradual saturation of the weak surface adsorption observed in simple solution does not occur in the mixed system containing bromide as the minority component. On the contrary, in the mixed solution the relative surface preference of bromide increases with growing concentration of the solution. In this case, Br⁻ can replace Cl⁻ in the interfacial layer without additional charging of the interface. There is also a weak tendency for demixing of the two anions and, effectively, NaCl is “salting out” bromide to the surface. These effects can have consequences for tropospheric bromine chemistry, where the source of bromide is aqueous sea salt particles.

Acknowledgments

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Figure and table captions

Figure 1) Surface sensitive photoelectron spectra of aqueous (a) LiBr and (b) LiI solutions at concentrations ranging from 0.25 to 6M. The photon energy was 140 eV, which produces photoelectrons with kinetic energies in the range of approximately 65-90 eV. The $\text{Li}_{\text{aq}}^+ 1s$, $\text{Br}_{\text{aq}}^- 3d$ and $\text{I}_{\text{aq}}^- 4d$ photoelectron lines uniquely identify the lithium cation and the respective anions.

Figure 2) Concentration dependent I^-/Li^+ and Br^-/Li^+ PE signal ratios as obtained from integrals of the spectra shown in figure 1. The ratios were normalized to the lowest concentration, i.e. 0.25 M.

Figure 3) Qualitative illustration of the distribution of positive counter charge to a constant region of fixed excess negative charge for three different screening lengths. The negative charge distribution is constructed from an arbitrary functional form, and the counter charge profile decays exponentially for large distances from the surface. Due to the requirement of charge neutrality, the integral of the curves – including the full exponential tail not shown in the figure – is zero in all cases. For shorter screening lengths, i.e. at higher electrolyte concentrations, a larger portion of the positive counter charge is close to the surface. In a PE experiment this is manifested as a stronger cation signal relative to that of the anion.

Figure 4) Converged MD density profiles obtained for pure a) NaCl, b) NaBr and c) NaI aqueous solutions at 2 and 4M concentrations.

Figure 5) Calculated anion/sodium PE signal ratios obtained from convolution of the MD density profiles in figure 4 as function of assumed electron attenuation length. Curves are shown for 4 and 2M concentrations, as well as the ratios between these (4M/2M). The magnitude of the latter at a given attenuation length indicates how strongly affected the surface structure is by varying the total salt concentration. While the ratios decreases for all salts the effect is significantly increases in the order $\text{NaCl} < \text{NaBr} < \text{NaI}$.

Figure 6) $\text{Br}_{\text{aq}}^- 3d$ and $\text{Na}_{\text{aq}}^+ 2s$ photoelectron spectra of a) mixed solution NaCl/NaBr solutions with the $\text{Br}:\text{Cl}$ number ratio fixed at 7:100 while the total salt concentration was varied from 0.4 to 4M. Trace b) shows the analogous measurements from a pure NaBr solution.

Figure 7) Concentration dependent Br^-/Na^+ PE signal ratios as obtained from integrals of the data given in figure 6. The ratios were normalized to the lowest concentration, i.e. 0.4M.

Figure 8) Converged MD density profiles obtained for a mixed solution of NaBr/NaCl at total concentrations 2 and 4M. The bromide-to-sodium ratio was kept at 6:70 in both cases.

Figure 9) Calculated bromide/sodium PE signal ratios obtained from convolution of the MD density profiles in figure 8, analogous to that obtained for the single-salt systems in figure 5. Again, the anion/cation PE ratios for 4 and 2M concentrations, as well as the ratios between these (4M/2M), are given as function of attenuation. In agreement with the experimental observations, an increase in the relative surface coverage of bromide is observed upon going from 2 to 4M (resulting in positive values of the 4M/2M curve for short attenuation lengths).

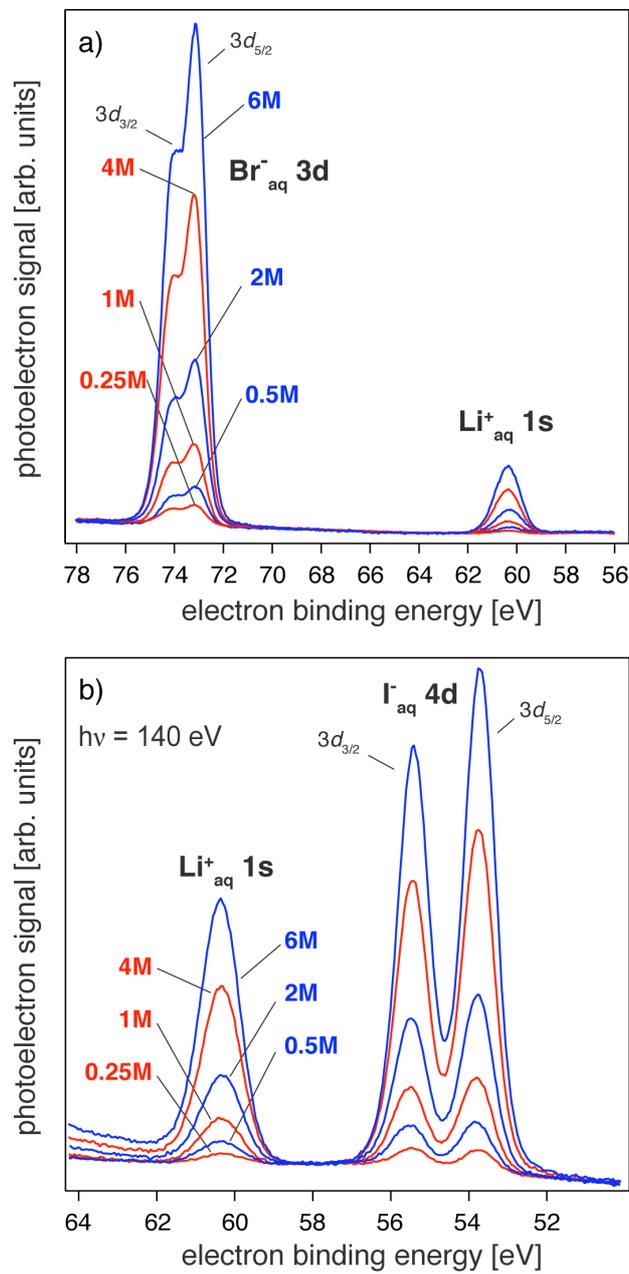


Figure 1

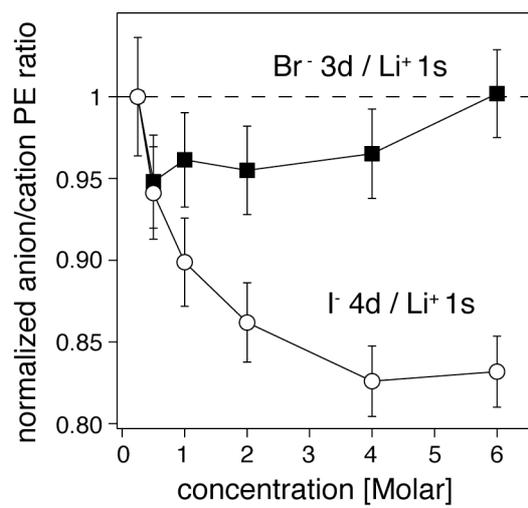


Figure 2

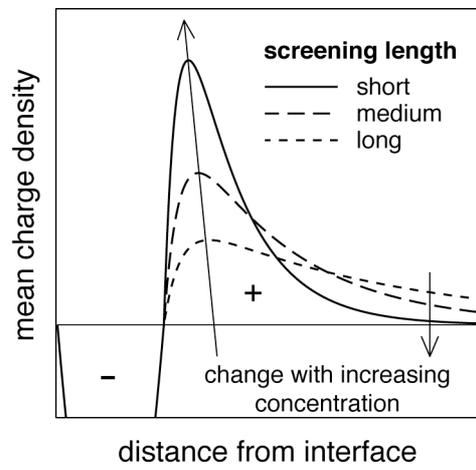


Figure 3

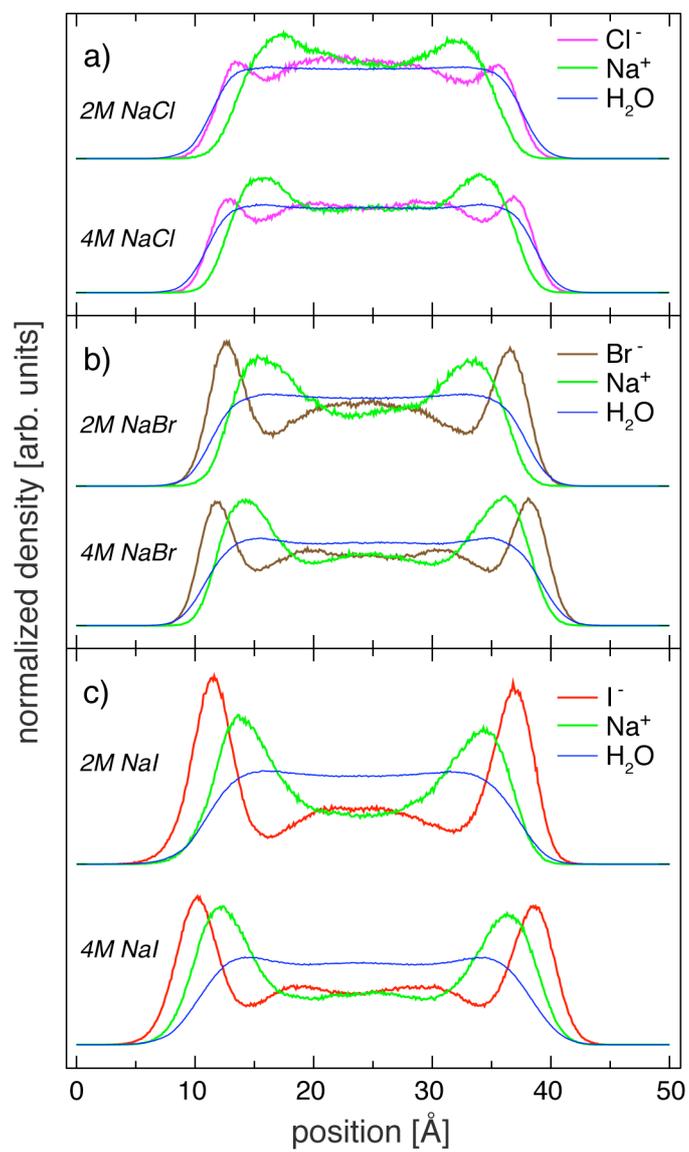


Figure 4

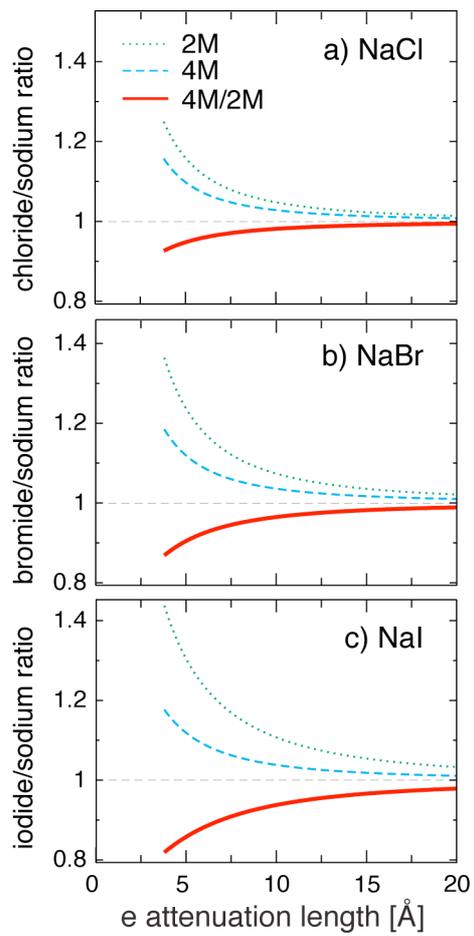


Figure 5

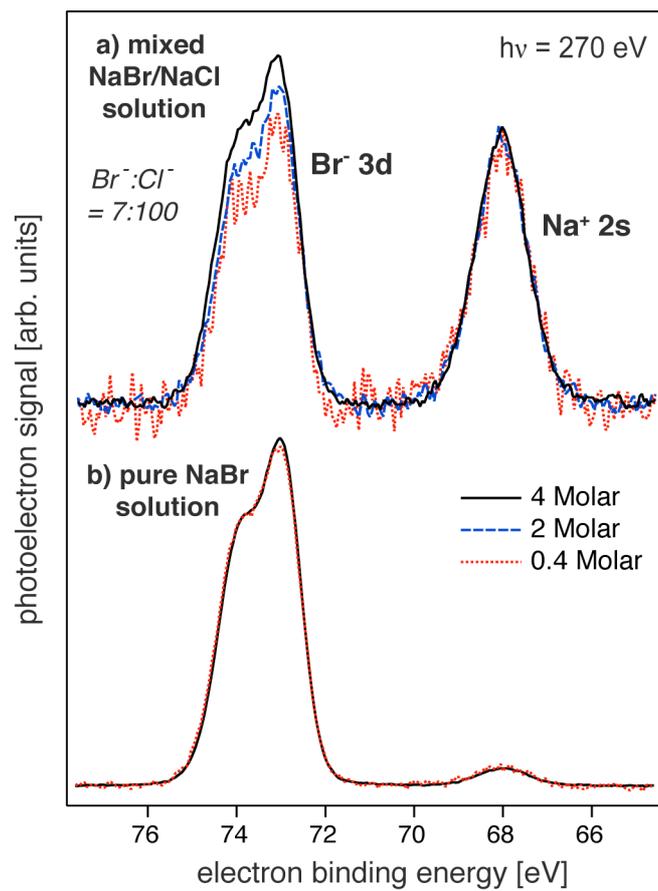


Figure 6

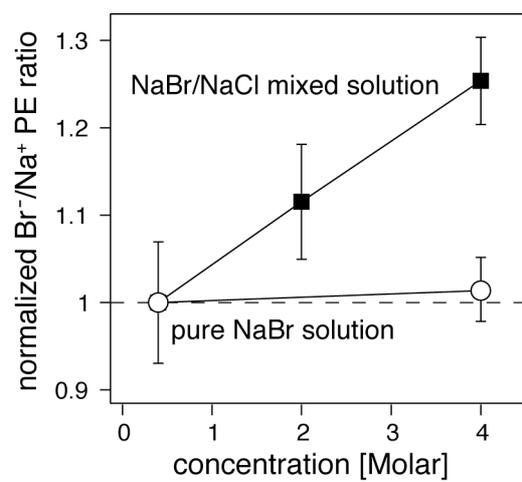


Figure 7

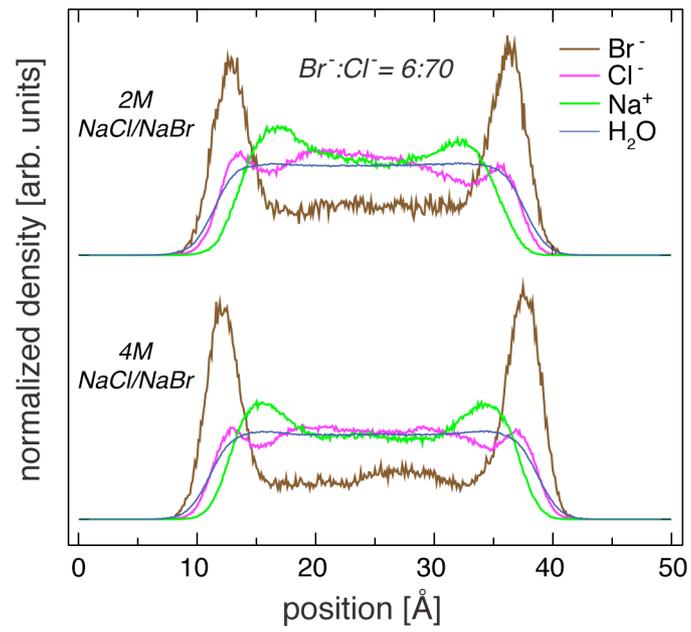


Figure 8

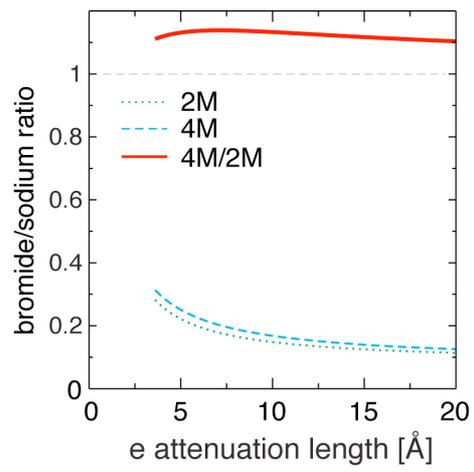


Figure 9

References

- (1) Petersen, P. B.; Saykally, R. J.; Mucha, M.; Jungwirth, P. *J Phys Chem B* **2005**, *109*, 10915.
- (2) 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.
- (3) Ottosson, N.; Vacha, R.; Aziz, E. F.; Pokapanich, W.; Eberhardt, W.; Svensson, S.; Öhrwall, G.; Jungwirth, P.; Björneholm, O.; Winter, B. *J Chem Phys* **2009**, *131*.
- (4) Winter, B.; Weber, R.; Hertel, I. V.; Faubel, M.; Vrbka, L.; Jungwirth, P. *Chem Phys Lett* **2005**, *410*, 222.
- (5) Winter, B.; Faubel, M. *Chemical Reviews* **2006**, *106*, 1176.
- (6) Chang, T. M.; Dang, L. X. *Chemical Reviews* **2006**, *106*, 1305.
- (7) Jungwirth, P.; Tobias, D. J. *Chemical Reviews* **2006**, *106*, 1259.
- (8) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*; 6th edition ed.; Wiley: New York, 1997.
- (9) Fawcett, W. R. *Liquids, Solutions, and Interfaces*; Oxford University Press: Oxford, UK, 2004.
- (10) Onsager, L.; Samaras, N. N. T. *J. Chem. Phys.* **1934**, *2*, 528.
- (11) Krisch, M. J.; D'Auria, R.; Brown, M. A.; Tobias, D. J.; Hemminger, J. C.; Ammann, M.; Starr, D. E.; Bluhm, H. *J Phys Chem C* **2007**, *111*, 13497.
- (12) Finlayson-Pitts, B. J.; Hemminger, J. C. *Journal of Physical Chemistry A* **2000**, *104*, 11463.
- (13) Morris, A. W.; Riley, J. P. *Deep Sea Research and Oceanographic Abstracts* **1966**, *13*, 699.
- (14) Spicer, C. W.; Plastringe, R. A.; Foster, K. L.; Finlayson-Pitts, B. J.; Bottenheim, J. W.; Grannas, A. M.; Shepson, P. B. *Atmos Environ* **2002**, *36*, 2721.
- (15) Simpson, W. R.; von Glasow, R.; Riedel, K.; Anderson, P.; Ariya, P.; Bottenheim, J.; Burrows, J.; Carpenter, L. J.; Friess, U.; Goodsite, M. E.; Heard, D.; Hutterli, M.; Jacobi, H. W.; Kaleschke, L.; Neff, B.; Plane, J.; Platt, U.; Richter, A.; Roscoe, H.; Sander, R.; Shepson, P.; Sodeau, J.; Steffen, A.; Wagner, T.; Wolff, E. *Atmos Chem Phys* **2007**, *7*, 4375.
- (16) Finlayson-Pitts, B. J. *Chem. Rev.* **2003**, *103*, 4801.
- (17) Thomas, J. L.; Jimenez-Aranda, A.; Finlayson-Pitts, B. J.; Dabdub, D. *J Phys Chem A* **2006**, *110*, 1859.
- (18) Ghosal, S.; Brown, M. A.; Bluhm, H.; Krisch, M. J.; Salmeron, M.; Jungwirth, P.; Hemminger, J. C. *J Phys Chem A* **2008**, *112*, 12378.
- (19) Petersen, P. B.; Saykally, R. J. *Annu. Rev. Phys. Chem.* **2006**, *57*, 333.
- (20) Microliquids GmbH, <http://www.microliquids.com>.
- (21) Hüfner, S. *Photoelectron Spectroscopy*; Springer-Verlag Berlin Heidelberg, 1995.
- (22) Essmann, U.; Perera, L.; Berkowitz, M. L.; Darden, T.; Lee, H.; Pedersen, L. G. *Journal of Chemical Physics* **1995**, *103*, 8577.
- (23) Berendsen, H. J. C.; Postma, J. P. M.; Vangunsteren, W. F.; Dinola, A.; Haak, J. R. *Journal of Chemical Physics* **1984**, *81*, 3684.
- (24) Ryckaert, J. P.; Ciccotti, G.; Berendsen, H. J. C. *Journal of Computational Physics* **1977**, *23*, 327.
- (25) Caldwell, J. W.; Kollman, P. A. *Journal of Physical Chemistry* **1995**, *99*, 6208.
- (26) Hrobarik, T.; Vrbka, L.; Jungwirth, P. In *230th National Meeting of the American-Chemical-Society*; Elsevier Science Bv: Washington, DC, 2005, p 238.
- (27) Jungwirth, P.; Tobias, D. J. *J Phys Chem B* **2001**, *105*, 10468.
- (28) Wick, C. D.; Dang, L. X.; Jungwirth, P. *Journal of Chemical Physics* **2006**, *125*, 4.
- (29) Case, D. A. D., T. A.; Cheatham, III, T. E.; Simmerling, C. L.; Wang, J.; Duke, R. E.; Luo, R.; Crowley, M.; Walker, R. C.; Zhang, W.; Merz, K. M.; Wang, B.; Hayik, S.; Roitberg, A.; Seabra, G.; Kolossvary, I.; Wong, K. F.; Paesani, F.; Vanicek, J.; Wu, X.; Brozell, S. R.; Steinbrecher, T.; Gohlke, H.; Yang, L.; Tan, C.; Mongan, J.; Hornak, V.; Cui, G.; Mathews, D. H.; Seetin, M. G.; Sagui, C.; Babin, V.; Kollman, P. A.; Amber 10, University of California, San Francisco: San Francisco, 2008.
- (30) Ottosson, N.; Faubel, M.; Bradforth, S. E.; Jungwirth, P.; Winter, B. *J. El. Spec. Rel. Phen.* **2010**, *177*, 60.
- (31) Yeh, J. J.; Lindau, I. *At. Data Nucl. Data Tables* **1985**, *32*, 1.
- (32) It should be noted that in a pioneering PES study of aqueous NaI solutions, no concentration dependence was observed in the anion/cation signal evolution [Weber et al., *J. Phys. Chem. B* **2004**, *108*, 4729-4736]. However, the result should be treated with

some care due to the quite low signal-to-noise ratios in the spectra, which is greatly improved in the present study.

- (33) We note that a simple adsorption isotherm such as the Langmuir one is of limited use in quantifying this phenomenon. An inherent feature of such a model is that the adsorbing species are non-interacting and the saturation of the surface sites should thus suppress the surface signal from the anionic and cationic species in the same way. This is clearly not the case, e.g., for the LiI solutions (in that was really the case the Γ/Li^+ PE ratio would have be constant for all concentrations). This is however hardly surprising as the respective ion-ion interactions become increasingly important at high concentrations, changing the character of the ionic interfacial double layer.
- (34) Lanning, O. J.; Madden, P. A. *J. Phys. Chem. B* **2004**, *108*, 11069.
- (35) Covington, A. K.; Lilley, T. H.; Robinson, R. A. *J. Phys. Chem.* **1968**, *72*, 2759.
- (36) Zangwill, A. *Physics at Surfaces*; Cambridge University Press, 1988.