

Surface Affinity of Alkali and Halide Ions in Their Aqueous Solution: Insight from Intrinsic Density Analysis

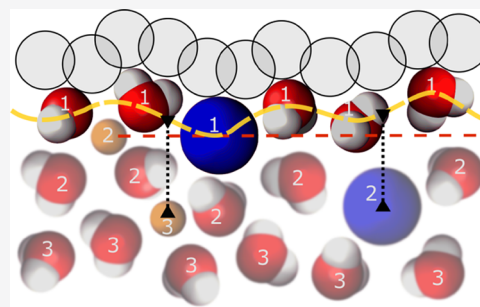
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ABSTRACT: The surface tension of all aqueous alkali halide solutions is higher than that of pure water. According to the Gibbs adsorption equation, this indicates a net depletion of these ions in the interfacial region. However, simulations and experiments show that large, soft ions, such as I^- , can accumulate at the liquid/vapor interface. The presence of a loose hydration shell is usually considered to be the reason for this behavior. In this work, we perform computer simulations to characterize the liquid–vapor interface of aqueous alkali chloride and sodium halide solutions systematically, considering all ions from Li^+ to Cs^+ and from F^- to I^- . Using computational methods for the removal of surface fluctuations, we analyze the structure of the interface at a dramatically enhanced resolution, showing that the positive excess originates in the very first molecular layer and that the next 3–4 layers account for the net negative excess. With the help of a fictitious system with charge-inverted ion pairs, we also show that it is not possible to rationalize the surface affinity of ions in solutions in terms of the properties of anions and cations separately. Moreover, the surface excess is generally dominated by the smaller of the two ions.



1. INTRODUCTION

Aqueous solutions of alkali halide salts are ubiquitous on earth from seawater to the bodies of living organisms, and they also play important roles in a number of processes (e.g., colloidal stability, coagulation kinetics), relevant in pure science as well as in its numerous applications in, e.g., pharmaceutical, food, or cosmetic industry. The interface of such solutions with various apolar phases (including vapor) is also of great importance in a number of fields, such as atmospheric chemistry (involving, e.g., aerosols of seawater droplets), solvent extraction, and the stabilization or denaturation of proteins. Not surprisingly, this field has been the subject of numerous reviews in the past decades.^{1–5}

For almost the entire 20th century, simple ions were thought to be surface inactive solutes, which are effectively repelled from the surface of their aqueous solutions. This view became part of the basic, textbook notions of colloid chemistry⁶ and dates back to the more than 100 years old experiment of Heydweiller, who found that salts increase the surface tension of water.⁷ Experiments have since consistently confirmed that the surface tension of all alkali halide solutions is indeed higher than that of neat water.^{8–10} This finding was rationalized by the theory developed by Onsager and Samaras,¹¹ who applied the Debye–Hückel theory using the law of image charges, i.e., that ions are repelled from the interface as if their mirror images were present at the other side of the interface. This description neglects, among others, the size of the ions, predicting the same distribution for all ions that bear an equal charge. This result is, however, in contrast with the early experiment of Heydweiller, who found that the salt-induced

surface tension increase becomes smaller with the increasing size of the anion.⁷

The classic view that ions are effectively repelled from the water surface has been challenged by experiments, theories, and computer simulations at the turn of the millennium. In the 1990s, photoelectron spectroscopy experiments^{12,13} as well as computer simulations^{14–16} of small aqueous droplets and clusters indicated that Cl^- and heavier halide ions prefer to stay at their surface. In 2004, Liu et al. found by performing sum-frequency generation (SFG) spectroscopy experiments that, contrary to smaller halide anions, Br^- , and I^- ions are present in a non-negligible concentration at the vicinity of the surface of their aqueous solutions.¹⁷ Surface adsorption of iodide¹⁸ as well as of several molecular^{19,20} and complex anions²¹ was observed by second harmonic generation (SHG) spectroscopy, and that of I^- was also evidenced by grazing incidence X-ray fluorescence.²²

To account for these findings, Levin et al. refined the Onsager–Samaras theory by adding the free energy term corresponding to the creation of a suitably large cavity, hosting the ion, in the system. Contrary to the electrostatic forces, this term favors adsorption of the ion at the interface, and this

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effect depends on the size of the cavity (i.e., that of the ion).²³ Properly accounting for the polarizability of the ion further enhances its predicted surface concentration because at the interface the charge distribution inside the ion is shifted to the part that is still solvated, reducing thus further the repelling term.²⁴

The very first result that indicated the adsorption of a simple ion (I^-) at the free surface of its aqueous solution was obtained in the pioneering computer simulation study by Jungwirth and Tobias.²⁵ This work was then followed by several other classical computer simulation^{26–38} and even density functional theory (DFT) studies,³⁹ leading to similar conclusions. Later, Vrbka et al. demonstrated that the surface propensity of the anions depends both on the size and polarizability of the ion,²⁷ in clear accordance with the subsequent theory of Levin et al.^{23,24} It is also clear that the order of the surface affinity of the anions is strongly related to their order in the Hofmeister series.^{40,41} Thus, small, “hard” ions with high charge density, also referred to as kosmotropes or structure makers, form firmly bound (first) hydration shells. The loss of a part of this shell, occurring when the ion approaches the water surface, entails a higher free energy cost than in the case of larger ions with smaller charge density (i.e., chaotropes or structure breakers).^{1,25–27,42–45} Thus, the fact that while the surface affinity increases with increasing size for anions, it is rather insensitive to that of the cations is generally ascribed to the rather small size and polarizability of the alkali cations as compared to those of the halide anions, although the different surface propensity of the positively and negatively charged ions might also correspond to the charge asymmetry of the water molecules.⁵ Our recent results suggest that the hardness of the ions also plays an important role at the surface of ionic surfactant solutions.^{46,47}

In addressing the surface affinity of the different ions by computer simulations, two important issues have to be considered. First, the results depend sensitively on the appropriate parametrization of the potential models used, which are supposed to describe well, among others, the solvation free energy of the individual ions and, hence, also the solubility of the salts.^{5,48–54} A key point in this respect is the treatment of the polarizability of the ions in the simulation: while early studies suggested that adsorption of large anions can only be properly described by polarizable force fields,^{1,25,26} this phenomenon is also seen with simple nonpolarizable models,^{28–30} which, in some cases, were even claimed to better reproduce experimental data than polarizable ones.^{29,35} Not surprisingly, a large number of nonpolarizable^{49,55–61} as well as polarizable^{62,63} force fields were proposed for alkali halides in the past decades, and their performance has been extensively compared in various respects.^{50,52,64,65}

The other important point concerns the definition of the interfacial region in such simulations. Clearly, the liquid surface is corrugated, on the molecular length scale, by thermally activated capillary waves,⁶⁶ and hence, approximating the interfacial region simply by a slab parallel with the macroscopic plane of the surface leads to a serious misidentification of the molecules as being interfacial or noninterfacial ones. This misidentification introduces systematic errors of unknown magnitude when calculating the local properties of the liquid surface,^{67–72} which can even propagate to the computed thermodynamic properties of the system.⁷³ Following the work of Chacón and Tarazona,⁷⁴ a number of methods have been proposed to account for the real, capillary wave corrugated

surface of a liquid phase, often referred to as the “intrinsic” liquid surface, in computer simulations.^{67,75–79} Among these methods, the identification of the truly interfacial molecules (ITIM)⁶⁷ has turned out to be an excellent compromise between computational cost and accuracy.⁷⁷ Since in such an analysis the full set of the particles constituting the first molecular layer at the liquid surface (or any of the subsequent ones) can be identified, surface properties can also be discussed in a layer-by-layer manner.⁸⁰ In particular, in multicomponent systems, the composition of the subsequent molecular layers can be compared with that of the bulk liquid phase, addressing thus unambiguously, in a layer-wise manner, the adsorption of the components.^{68–70,72,81–83} However, in spite of the increasing number of the computer simulation studies of the liquid–vapor interface of aqueous alkali halide solutions, intrinsic analysis of this interface has scarcely been reported.^{32,33,35–38,84}

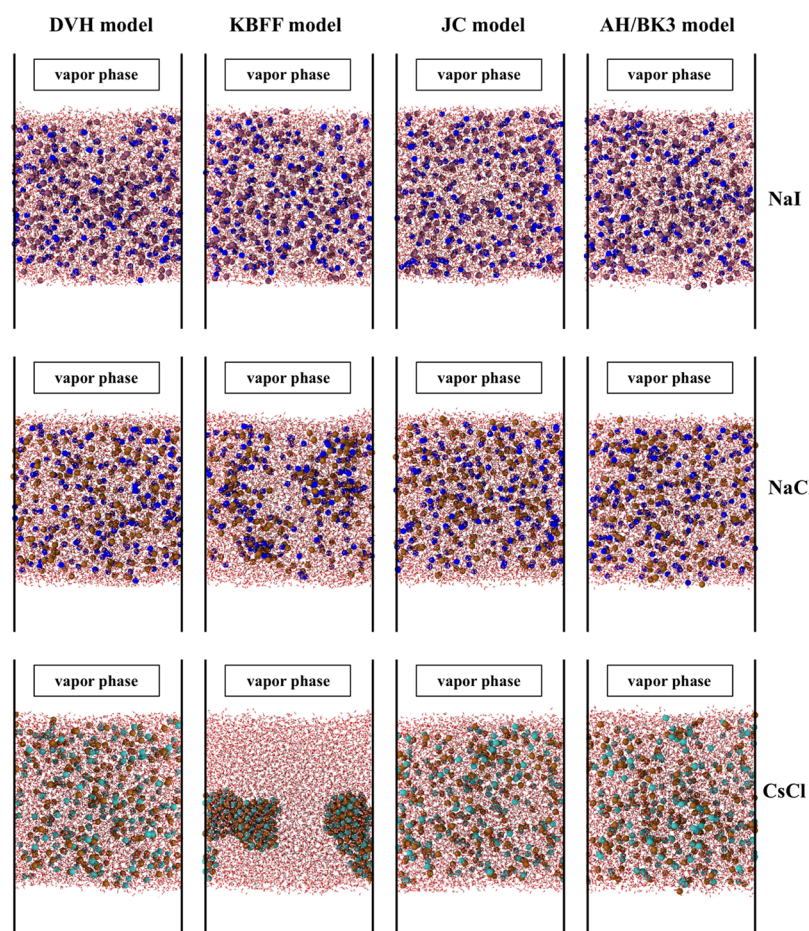
In this study, we report a systematic molecular dynamics simulation study of the intrinsic properties of the liquid–vapor interface of aqueous alkali chloride and sodium halide solutions, considering all ions from Li^+ to Cs^+ and from F^- to I^- . To circumvent the problem of the force field dependence of the results, simulations have been repeated with three widely used nonpolarizable^{58–60} and a polarizable force field.⁶³ It should be emphasized that it is not our goal here to compare the performance of various potential models; the reason for using several force fields is simply to get additional confirmation of the results to be obtained. We check the validity of our simulations by comparing the obtained results (solubility, surface tension, surface excess) with existing experimental data. Furthermore, we also calculate the overall, nonintrinsic density profiles of the ions and compare them with the picture that has emerged from the extensive computer simulation investigation of such systems in the past two decades. The main novelty of this work is the intrinsic analysis of the surface composition, and the investigation of the effect of the sign of the ion charge on the surface propensity. Thus, the main focus of this study is to address (i) how the composition of the subsequent molecular layers beneath the intrinsic liquid surface depends on the type and the polarizability of the cations and anions; (ii) how the different ions are distributed beneath the intrinsic liquid surface, and how these distributions, evidenced by the intrinsic density profiles, are related to the (known) nonintrinsic density profiles; and (iii) how the surface propensity of the ions is related to the sign of their charge.

2. METHODS

2.1. Molecular Dynamics Simulations. Molecular dynamics simulations of the liquid–vapor interface of aqueous Na^+ halide (i.e., F^- , Cl^- , Br^- , and I^-) and alkali (i.e., Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+) chloride solutions have been performed in the canonical (N,V,T) ensemble at 298 K. The X , Y , and Z edges of the rectangular basic simulation box have been 265.0, 62.818, and 62.818 Å, respectively, with X being the macroscopic surface normal axis. The basic box has contained 8000 water molecules and 192 ion pairs in every case. This composition corresponds to the molality of 1.3322 kg/mol (i.e., about 1.3 M salt concentration), well below the experimental solubility⁸⁵ of all of the eight salts considered. The width of the liquid slab has been around 60 Å. To check whether this slab is wide enough to reach the bulk phase composition at its middle part, we have estimated the Debye

Table 1. Diameter of the Various Atoms and Ions (in Å Units), Used in the ITIM Analysis to Determine the Touching Position of the Probe Sphere

model	water		Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	F ⁻	Cl ⁻	Br ⁻	I ⁻
	O	H									
DVH	3.166	0	1.88	1.89	2.77	3.26	3.58	3.66	4.41	4.54	4.78
JC	3.166	0	1.41	2.16	2.84	3.10	3.60	4.02	4.83	4.90	5.20
AH/BK3	3.303	0	1.22	1.80	2.55	2.84	3.21	5.12	4.41	4.30	4.95

**Figure 1.** Instantaneous snapshot of the aqueous solutions of NaI (top row), NaCl (middle row), and CsCl (bottom row), as obtained from the simulations with the DVH (first column), KBFF (second column), JC (third column), and AH/BK3 (fourth column) models. Na⁺, Cs⁺, Cl⁻, and I⁻ ions are shown by dark blue, turquoise, orange, and purple balls, respectively, while water molecules are represented by red sticks.

screening length of the ions, which has turned out to be an order of magnitude smaller than the slab width in every case.

All simulations have been repeated with three non-polarizable force fields of the ions, namely, the Kirkwood-Buff derived force field (KBFF) model of Gee et al.,⁵⁹ as well as the models proposed by Joung and Cheatham (referred to here as JC)⁵⁸ and by Deublein et al. (referred to here as DVH),⁶⁰ generally thought to be among the best non-polarizable models describing the properties of aqueous alkali halide solutions. In these simulations, water molecules have been modeled by the rigid, nonpolarizable SPC/E potential,⁸⁶ as all of the three ion force fields considered have been parameterized using this water model.^{58–60} To address the issue of taking the polarizability of the particles explicitly into account, all simulations have also been performed with the polarizable BK3 water⁸⁷ and AH/BK3 ion models⁶³ of Kiss and Baranyai. In these models, Gaussian charge distributions are used instead of simple point charges, the polarizability of

the particles is described by the charge-on-spring method using harmonic springs, while the short-range repulsion and dispersion interactions are modeled by the Buckingham potential.

All simulations involving nonpolarizable potential models have been performed by the GROMACS 2019.4 simulation package.⁸⁸ The equations of motion have been integrated in time steps of 2 fs. All interactions have been truncated to zero beyond the center-based cutoff distance of 12 Å; the long-range part of both Coulomb and Lennard-Jones interactions has been accounted for by means of the smooth particle mesh Ewald (PME) method.^{89,90} The temperature of the systems has been controlled by the Nosé–Hoover thermostat,^{91,92} using the time constant of 1 ps. The molecular geometry of water has been constrained using the SETTLE algorithm.⁹³ All systems have been equilibrated for 2 ns, followed by a 20 ns long production run, in which 5000 sample configurations,

separated by 4 ps long trajectories each, have been saved for the analyses.

The simulations involving the polarizable BK3 and AH/BK3 models have been done with the program MACSIMUS.⁹⁴ The exp-6 part of the potential has been cut off at 12 Å and smoothed. Slab cutoff corrections have been calculated from the Fourier series (32 terms) of the X-density profile. In addition, the Yeh–Berkowitz⁹⁵ correction has been added to the slab geometry. The long-range part of the electrostatic forces has been evaluated by Ewald summation^{96,97} with a direct calculation in the reciprocal space, using the real space cutoff of 18 Å, the separation parameter of 0.1953 Å⁻¹, and the maximum reciprocal space vector of 0.1955 Å⁻¹, corresponding to the estimated errors in the forces on the maximum charge (1.168 e) of 6.9 and 69 fN in the real and reciprocal space terms, respectively.⁹⁸ The equations of motion have been integrated using the leap-frog method with the time step of 1.67 fs; the water geometry has been constrained by the SHAKE algorithm.⁹⁹ The induced dipoles have been integrated by the ASPC method.¹⁰⁰ The optimized damping parameters have ranged from 0.701 for NaI (corresponding to the worst convergence of the self-consistent field) to 0.719 for KCl (best). The one-step error of the induced dipole moment has been approximately 0.0012 D; the integration error was few times larger. The temperature has been controlled using the Nosé–Hoover thermostat with the time constant of 0.3 ps. The equilibration and production parts of the simulations have been 70 ps (starting from equilibrium configurations of previous nonpolarizable runs) and 10 ns long, respectively; in the latter phase, 10 000 sample configurations, separated by 1 ps each, have been saved for further evaluation.

2.2. ITIM Analyses. In ITIM analysis, the molecules that are at the intrinsic liquid surface are identified by moving a probe sphere of a given radius from the bulk opposite phase toward the surface along grid lines parallel with the macroscopic surface normal.⁶⁷ Once the probe hits a particle, this particle is marked as being at the surface (as it is “seen” by the probe from the opposite phase), and the probe is moved along the next grid line. Once all grid lines are considered, the full list of the interfacial molecules is determined. Disregarding the set of particles that are already identified as forming the surface layer and repeating the entire procedure enable the identification of the molecules that form the next subsurface layer.⁶⁷ The procedure involves a free parameter, i.e., the size of the probe; however, the use of such a free parameter is unavoidable in an intrinsic surface analysis, as it sets the length scale on which the surface is looked at.⁷⁷

In this study, the intrinsic surface of the liquid phase of the systems simulated has been determined by the ITIM method⁶⁷ using the freely available¹⁰¹ PYTIM software¹⁰² and the MDAnalysis package.¹⁰³ In accordance with previous suggestions,^{67,77} the probe sphere radius of 2 Å and the grid spacing of the test lines of 0.4 Å have been used in the analyses. In determining the contact position of an atom with the probe, the size of the individual atoms has been approximated by the distance at which the non-Coulomb part of their homonuclear interaction becomes zero (in the case of the nonpolarizable models, this distance equals the Lennard-Jones diameter). The atomic diameters used in the ITIM analyses are summarized in Table 1. For every system simulated, the lists of the particles that form the first four individual subsurface molecular layers have been determined.

3. RESULTS AND DISCUSSION

3.1. Solubility. Figure 1 shows instantaneous snapshots of the NaI, NaCl, and CsCl solutions, as obtained from the production phase of our simulations with all of the four salt potentials considered. These snapshots have always been taken from the production part of the simulations. The snapshot obtained for the CsCl solution, described by the KBFF model, is rather striking, as it shows the salt being in the crystalline phase, fully separated from water. The fact that no hydrated Cs⁺ or Cl⁻ ion is seen at the snapshot suggests that the KBFF model of CsCl is practically insoluble in SPC/E water. This tendency for aggregation is also seen in the KBFF model of NaCl, where the ions form clusters rather than being more or less uniformly distributed in the solution, like in all other systems shown in the snapshots.

To systematically analyze which of the alkali halide salts, described by the four potential models considered, are not soluble in the corresponding model of water at the roughly 1.3 M concentration used in our simulations, we have calculated the cation–anion radial distribution function (rdf) in all of the 32 systems simulated. The resulting rdfs corresponding to the NaCl and CsCl solutions are shown in Figure 2, while the rdfs obtained in all systems simulated are

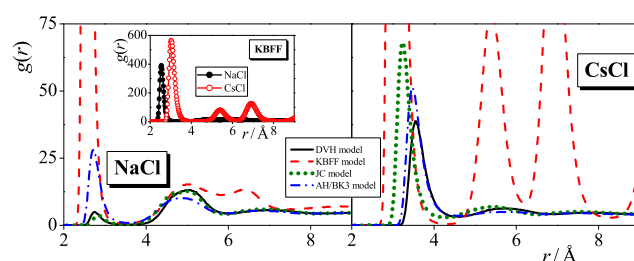


Figure 2. Anion–cation radial distribution function in the NaCl (left panel) and CsCl (right panel) solutions simulated with the DVH (solid black lines), KBFF (red dashed lines), JC (green dotted lines), and AH/BK3 (blue dash-dotted lines) salt models. The inset shows the functions obtained for NaCl (black line with filled symbols) and CsCl (red line with open symbols) with the KBFF model on a different scale.

plotted in Figure S1 of the Supporting Information. All functions exhibit a peak between 2 and 4 Å, followed by a clear second peak between 4 and 6 Å. These peaks correspond to the contact and solvent-separated cation–anion pairs, respectively. The amplitude of the first peak scatters between about 2 and 80 in every case, depending on the salt and the potential model used, with the exception of the NaCl and CsCl solutions of the KBFF model (see the inset of Figure 2). In these systems, the heights of the first, contact peak are around 400 and 600, respectively. In the case of CsCl, the entire rdf, exhibiting high peaks separated by deep minima, is characteristic of a crystalline phase, in accordance with the corresponding snapshot of Figure 1. In the case of NaCl, the rdf is still liquidlike, but the extremely high first peak, in accordance with the corresponding snapshot, indicates that far too many ion pairs are formed, suggesting that NaCl is probably undergoing crystallization. Thus, probably already sufficiently large crystal nuclei of NaCl are formed; and hence a longer simulation run would likely lead to the formation of a NaCl crystal that is separated from the saturated solution. It should be emphasized that the experimental solubilities of NaCl and CsCl (being about 6.1 M¹⁰⁴ and 11.3 M,¹⁰⁵

respectively), similarly to those of all other salts considered in this study, are well above the roughly 1.3 M concentration used in our simulations. The apparent failure of the KBFF model in describing the solubilities of various alkali chloride salts in water, being strikingly severe in the case of CsCl, is probably related to the fact that in parametrizing this model the properties of the hydrated ions were only fitted at infinite dilution,⁵⁹ which led to crystals of too low lattice energy. Similar severe underestimation of the aqueous solubility of alkali halide⁵² and alkali dodecylsulfate⁴⁷ salts by the KBFF model has also been reported previously. For this reason, here, we refrain from analyzing the surface behavior of the KBFF model of salts and consider only the other three salt potential models in the following analyses.

Finally, it should be noted that the solubility of the AH/BK3 model of NaCl in BK3 water was also shown previously to be somewhat below the concentration considered here.⁵³ This is reflected in the disproportionately high first peak of the rdf, which is apparent not only for NaCl, but also for the majority of the salts simulated using the AH/BK3 model, as well as for the DVH model of NaF. Despite this unphysically high presence of contact ion pairs,¹⁰⁶ neither the snapshots nor the rdfs indicate the onset of crystallization, probably because the oversaturation in these systems is not high enough.

3.2. Surface Tension and Surface Excess. The surface tension of all systems simulated has been calculated through the pressure route as

$$\gamma = \frac{L_X}{2} \left\langle p_{XX} - \frac{p_{YY} + p_{ZZ}}{2} \right\rangle \quad (1)$$

where p_{XX} , p_{YY} , and p_{ZZ} are the corresponding elements of the pressure tensor, L_X is the length of the X edge (being perpendicular to the macroscopic plane of the surface) of the basic box, and the brackets $\langle \dots \rangle$ denote averaging over the equilibrium trajectory. The obtained values are collected and compared with experimental data in Table 2. Further, the

Table 2. Comparison of the Surface Tension (in mN/m Units) of the Various Systems Simulated with Experimental Data

	DVH	JC	AH/BK3	experiment
neat water	62.7 ± 0.2	62.7 ± 0.2	69.8 ± 0.2	72.0 ^{a,b}
NaF	65.1 ± 0.3	64.9 ± 0.4	71.5 ± 0.4	
NaCl	65.2 ± 0.4	65.2 ± 0.3	71.9 ± 0.3	73.6 ^a 74.1 ^b
NaBr	65.6 ± 0.3	64.9 ± 0.3	71.3 ± 0.4	75.0 ^b
NaI	65.2 ± 0.1	63.9 ± 0.2	69.5 ± 0.3	73.6 ^b
LiCl	65.7 ± 0.2	64.4 ± 0.1	71.2 ± 0.3	73.7 ^a
KCl	64.4 ± 0.2	64.6 ± 0.4	71.0 ± 0.4	74.6 ^a 74.2 ^b
RbCl	64.4 ± 0.3	64.5 ± 0.2	71.5 ± 0.3	
CsCl	64.8 ± 0.3	63.7 ± 0.2	71.4 ± 0.3	

^aRef 9. ^bRef 10.

surface excess of the salts, Γ , determined from the simulations as

$$\Gamma = \int_0^{L_X/2} \left[\rho_s(X) - \frac{\rho_s^0}{\rho_w^0} \rho_w(X) \right] dX = \frac{1}{2A} \left[N_s - \frac{\rho_s^0}{\rho_w^0} N_w \right] \quad (2)$$

is collected in Table 3. In this equation, ρ_s and ρ_w stand for the number density of the salt and water, respectively, determined along the axis, X , ρ_s^0 , and ρ_w^0 are the corresponding values in

Table 3. Surface Excess of the Ions (in $\mu\text{mol}/\text{m}^2$ Units) as Obtained in the Different Systems Simulated

	DVH	JC	AH/BK3
NaF	−0.73	−0.97	−0.74
NaCl	−0.57	−0.46	−0.50
NaBr	−0.62	−0.48	−0.13
NaI	−0.41	−0.28 (−0.35)	−0.04
LiCl	−0.53	−0.36	−0.16
KCl	−0.70	−0.53	−0.34
RbCl	−0.58	−0.39	−0.34
CsCl	−0.55	−0.52	−0.37

^aThe shown values hold both for the cations and for the anions. The value in parenthesis refer to charge-inverted NaI. Error bars are on the order of 0.1 $\mu\text{mol}/\text{m}^2$.

the bulk liquid phase (determined in the 10 Å wide slab in the middle of the liquid slab), while N_s and N_w are the total number of the corresponding particles in the basic box, and $A = L_Y L_Z$. It should be noted that, since the bulk liquid density of the cations has to be equal (in the thermodynamic limit) with that of the anions (and, evidently, the total number of the oppositely charged ions in the entire system is also equal in the simulation), the surface excesses of the two ions also have to be the same. Thus, in eq 2, ρ_s can equally stand for the cations or for the anions.

As is seen in Table 2, the surface tension of the salt solutions is always noticeably higher than that of neat water. This increase is typically 2–3% for the polarizable AH/BK3 model, being in a somewhat better agreement with the experimental trend of an about 2–4% increase than the roughly 3–5% increase shown by the two nonpolarizable models. The only exception in this respect is that the surface tension of the NaI solution agrees, within error bars, with that of neat water in the case of the AH/BK3 model; however, this behavior is not supported by the experimental data. (The deviation of the surface tension values from the experimental data simply reflects the performance of the water models considered in this respect, and hence, they are of little relevance themselves here.) It is also seen that, besides the aforementioned increase with respect to neat water, the surface tension values obtained from the simulations of the various salt solutions do not show any particular trend in any case.

Consistently with the observed increase of the surface tension, the surface excess of the salts turns out to be negative, indicating net negative adsorption of the ions at the liquid surface in every case. This finding is consistent with the classical textbook picture of capillary inactive salts.⁶ Again, no particular trend of these values is seen with the systematic change of the cations or anions. In general, the values obtained with the DVH and AH/BK3 models are somewhat larger and smaller, respectively, than those of the JC model, indicating that the effective repulsion of the ions by the liquid surface is the strongest with the DVH and weakest with the polarizable AH/BK3 potential.

3.3. Surface Affinity of the Various Ions. **3.3.1. Non-intrinsic Density Profiles.** The nonintrinsic (i.e., relative to the external frame set to the basic simulation box) number density profiles of the water molecules, alkali cations, and halide anions along the macroscopic surface normal axis, X , are shown in Figure 3a,b, as obtained with the AH/BK3 salt model in the Na⁺ halide and alkali Cl[−] solutions, respectively. The profiles obtained with all potential models considered are collected in

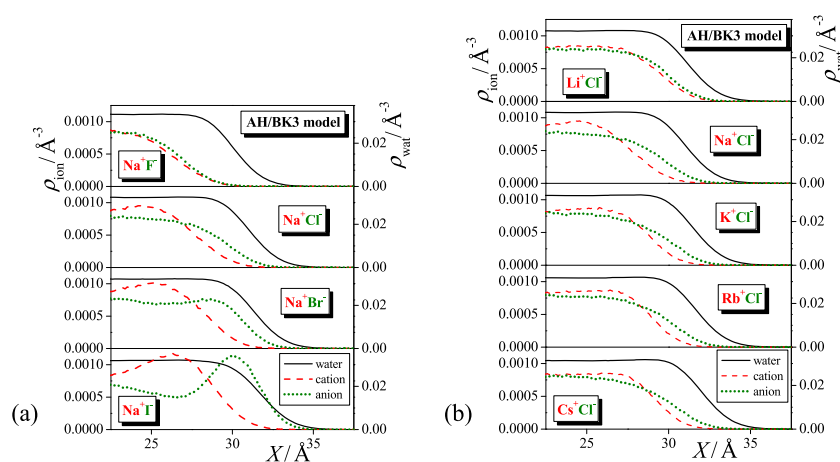


Figure 3. Nonintrinsic number density profiles of the water molecules (solid black lines), cations (red dashed lines), and anions (green dotted lines) along the macroscopic surface normal axis, X , as obtained from the simulations of (a) sodium halide and (b) alkali chloride solutions, using the AH/BK3 model of the salts. The zero value of X corresponds to the middle of the liquid phase. Scales on the left and right refer to the densities of the ions and water molecules, respectively.

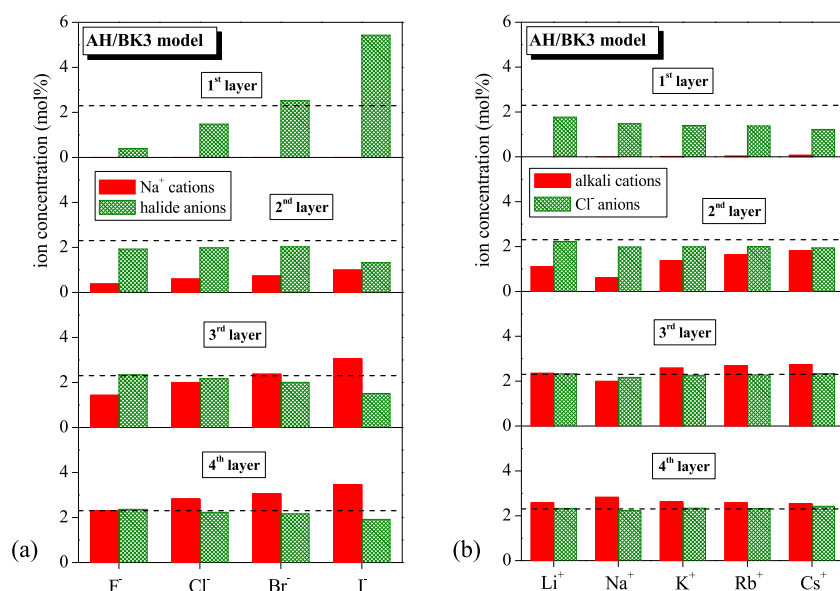


Figure 4. Mole fraction of the cations (red filled bars) and anions (green checkered bars) in the first (top panels), second (second panels), third (third panels), and fourth (bottom panels) molecular layers, as obtained from the simulations of (a) sodium halide and (b) alkali chloride solutions, using the AH/BK3 model of the salts.

Figures S2 and S3 of the Supporting Information. The nonintrinsic density profiles typically change smoothly between the bulk liquid and the vapor phase, reflecting, besides the real surface behavior of the particles, also the smoothing effect of the capillary waves. With a few exceptions, the ion profiles damp to zero several angstroms before the water profile, with the anion and cation profiles being rather similar to each other. This finding suggests that, in these systems, the ions are effectively repelled from the interface, and there is no characteristic difference between the surface propensities of the oppositely charged ions. This trend is seen for the NaF, NaBr, and all alkali Cl^- solutions of the two nonpolarizable models and also for the NaF and LiCl solutions of the polarizable AH/BK3 model. In the other systems, the profile of the anions extends noticeably closer to the liquid surface than that of the cations, and the excess negative charge at the vicinity of the surface is compensated by a positively charged layer, reflected in a peak of the cation density profile

roughly 5 Å beneath the negatively charged layer. Finally, in the case of the nonpolarizable JC and polarizable AH/BK3 models, the profile of the I^- ions in the NaI solution exhibits a clear peak at the vicinity of the surface, suggesting surface adsorption of the I^- ions. This peak is followed by a depletion layer of the I^- ions, coinciding with the peak of the Na^+ profile. The corresponding surface excess values (Table 3) reveal that this minimum overcompensates the effect of the surface peak, and hence, in spite of the enrichment of the I^- ions close to the water surface, the surface excess of the I^- ions is still negative. Considering that the surface excess of the cations has to be equal to that of the anions, an equivalent explanation of the negative surface excess is that the density peak of the Na^+ ions at the position of the I^- depletion layer does not fully compensate the effect of the depletion of the Na^+ ions at the vicinity of the surface. Interestingly, no density peak of the I^- ions is seen at the vicinity of the liquid surface with the nonpolarizable DVH model.

The picture seen from these results is in accordance with that of the earlier simulations,^{25–38} showing that (i) larger ions have higher surface affinity, (ii) polarizability also contributes to the surface affinity of the ions, (iii) I^- is enriched at the vicinity of the surface of its solution, while other ions are effectively repelled from there, and (iv) some of the nonpolarizable models can reproduce this I^- enrichment, while others do not show it, and accounting for the polarization in the model increases this enrichment.

3.3.2. Layer Composition. The above picture can be refined in several respects by analyzing the composition of the subsequent molecular layers beneath the liquid surface and the intrinsic density profiles. The mole percentages of the alkali and halide ions in the first four molecular layers are shown in Figure 4a,b, as obtained with the AH/BK3 salt model in the Na^+ halide and alkali Cl^- solutions, respectively. The values obtained with all potential models considered are shown in Figures S3 and S4 and collected in Tables S1–S3 of the Supporting Information. As is seen, while the first layer always contains a noticeable amount of anions (with the exception of F^- in the case of the nonpolarizable models), this layer is practically free from cations in every case. Further, anions are typically in an excess concentration with respect to the cations even in the second layer. Thus, anions have a clearly higher surface propensity than cations in every case, even if their nonintrinsic density profiles (Figure 3 and also Figures S2 and S3 of the Supporting Information) do not show this difference. This fact can, at least partly, be attributed to the smearing effect of the capillary waves. The markedly different concentration of the oppositely charged ions in the first two layers, together with their very similar nonintrinsic density profiles (see, e.g., the case of LiCl), stresses that two particles that are at the same distance from the macroscopic plane of the liquid surface (i.e., the Gibbs dividing surface) might well belong to different molecular layers. In particular, among the anions and cations that are at the same distance from the Gibbs dividing surface, anions are typically closer to the real, capillary wave corrugated liquid surface than cations. This finding suggests that anions prefer to stay at the negatively curved, locally concave positions (troughs) while cations at the locally convex, positively curved crests of the subsurface layer they belong to. This finding is illustrated in the sketch of Figure 5.

3.3.3. Intrinsic Density Profiles. The intrinsic (i.e., relative to the molecularly rough, capillary wave corrugated liquid surface) number density profiles of the water molecules, alkali cations, and halide anions along the macroscopic surface normal axis, X , are shown in Figure 6a,b, as obtained with the AH/BK3 salt model in the Na^+ halide and alkali Cl^- solutions, respectively. The profiles obtained with all potential models considered are collected in Figures S6 and S7 of the Supporting Information. It should be emphasized that the intrinsic liquid surface is defined as a surface going through the centers of the particles identified as being interfacial (see Figure 5),^{67,77} and hence, the intrinsic distance of the first layer particles is zero by definition. As a consequence, their contribution to the intrinsic density profile appears as a Dirac delta peak at zero distance,⁷⁷ which is indicated by arrows in Figure 6. These profiles, being already free from the smearing effect of the capillary waves, clearly show the layering structure of the particles beneath the liquid surface. In particular, the profiles of the water molecules exhibit clear peaks corresponding to the second and third subsurface layers.

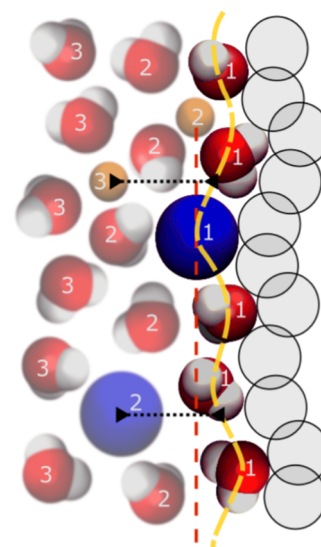


Figure 5. Schematic illustration of the situations (i) when a large Cl^- anion (blue sphere), marked by (1) and a small Li^+ cation (orange sphere), marked by (2) are at the same distance from the macroscopic plane of the liquid surface (as they are both located in the plane marked by the red dashed line); yet, the large ion is part of the first, while the smaller ion is only of the second layer and (ii) when a large Cl^- anion (blue sphere), marked by (2) and a small Li^+ cation (orange sphere), marked by (3) are at the same distance from the real, capillary wave corrugated liquid surface (marked by the orange dashed line); yet, the large ion is part of the second, while the smaller ion is only of the third layer. Gray spheres represent the probe sphere in its touching positions with the surface particles, numbers indicate to which layer the given particle belongs to, bright particles form the first layer, while pale particles are beneath this layer.

Interestingly, the intrinsic density profiles are much more sensitive to the type of the cations than of the anions. Thus, while the anion profiles in the various Na^+ halide solutions are rather similar to each other (Figure 6a and also Figure S6 of the Supporting Information), a clear peak of the cation profile emerges in the various alkali Cl^- solutions at about 3 Å from the intrinsic liquid surface, which becomes higher with the increasing cation size (Figure 6b and also Figure S7 of the Supporting Information). This peak can be attributed to the cations of the second subsurface layer, as illustrated by Figure 6b. The reason for the different behavior of the cations and anions in this respect can probably be explained by the different distribution of these ions in the first two subsurface molecular layers of their solutions. Clearly, the anion concentration shows a marked size dependence in the first layer only (the contribution of which is not seen in the intrinsic density profiles), while, from the second layer on, it is largely independent of the anion type (see Figure 4a and also Figure S4 of the Supporting Information). On the other hand, since the first molecular layer is practically free from cations, the first cation-containing layer is the *second* one. It is precisely in this second molecular layer where the concentration of the cations shows (with the exception of Li^+) a noticeable increase with their size. This size dependence then vanishes from the third layer on (see Figure 4b and also Figure S5 of the Supporting Information).

Another clear difference between the distribution of the differently charged ions with respect to the intrinsic liquid surface is that the intrinsic density profile of the Cl^- ions is practically independent of the type of the cations, while the

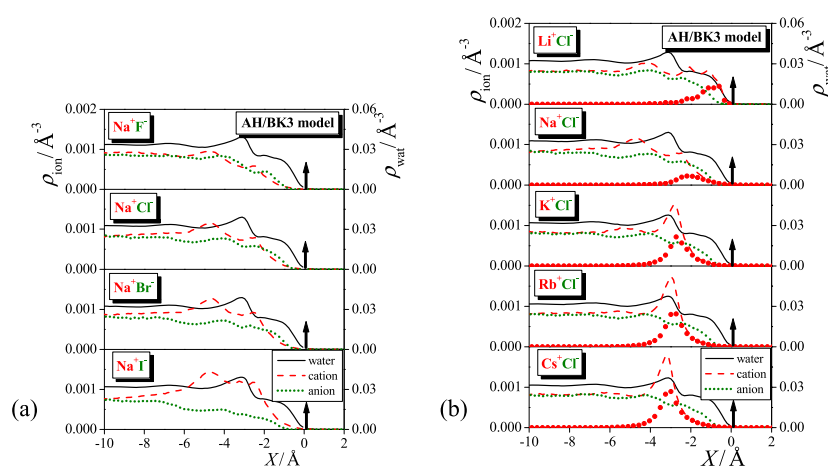


Figure 6. Intrinsic number density profiles of the water molecules (solid black lines), cations (red dashed lines), and anions (green dotted lines) along the macroscopic surface normal axis, X , as obtained from the simulations of (a) sodium halide and (b) alkali chloride solutions, using the AH/BK3 model of the salts. In panel (b), the contributions of the cations that belong to the second subsurface layer are also shown (full red circles). The zero value of X corresponds to the position of the intrinsic liquid surface. Up arrows indicate the Dirac delta functions corresponding to the densities of the first layer particles. Scales on the left and right refer to the densities of the ions and water molecules, respectively.

Na^+ profile exhibits a marked increase in the X range of the second and third molecular layers with the increasing size of the anions. This finding is illustrated in Figure 7 on the

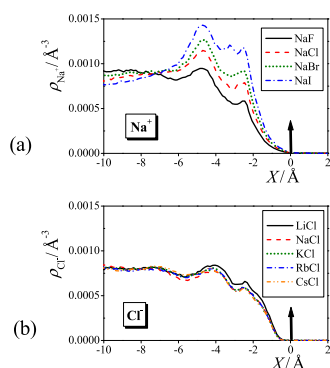


Figure 7. Intrinsic number density profiles (a) of the Na^+ ions in the aqueous solutions of NaF (solid black lines), NaCl (red dashed lines), NaBr (green dotted lines), and NaI (blue dash-dotted lines) and (b) of the Cl^- ions in the aqueous solutions of LiCl (solid black lines), NaCl (red dashed lines), KCl (green dotted lines), RbCl (blue dash-dotted lines), and CsCl (orange dash-dot-dotted lines) along the macroscopic surface normal axis, X , as obtained with the AH/BK3 model of the salts. The zero value of X corresponds to the position of the intrinsic liquid surface. Up arrows indicate the Dirac delta functions corresponding to the densities of the first layer particles.

example of the profiles obtained with the AH/BK3 model. This difference can again be explained by the different affinity of the cations and anions to the surface layer. Thus, the surface layer, being free from cations, contains larger anions in higher concentration. This negative surface charge is compensated by an excess amount of cations in the subsequent molecular layers. The cation concentration in the second and third layers thus increases with increasing negative surface charge density, which is implied by the increasing size of the anions. On the other hand, since the surface layer is always free from cations, there is no such driving force on the anion density in the subsequent layers.

A rather striking feature of the intrinsic density profiles is that, in many cases, the cation density exceeds the anion

density in the entire interfacial region, apart from the first molecular layer (which gives the Dirac delta contribution at zero distance). Considering the fact that the first layer always contains significantly more anions than cations, this behavior is understandable, since the net negative charge of the surface layer has to be compensated in the subsequent layers. However, in the layer composition, the number of anions typically exceeds that of the cations even in the second layer (Figure 4); yet, the intrinsic profiles show higher cation than anion density even at the immediate vicinity of the surface (Figure 6). This is not an error in our calculations and can be explained by analyzing in detail, for the sake of definiteness, the case of the LiCl solution simulated with the AH/BK3 model.

In this case, the Li^+ density clearly exceeds the Cl^- density up to about 8 Å from the intrinsic surface (see the top panel of Figure 6b and also Figure 8), while there are twice as many Cl^- than Li^+ ions in the second subsurface layer, and the concentration of the two ions is almost the same in the third layer (see the top panel of Figure 4b and Table S3 of the Supporting Information). It should also be recalled that the

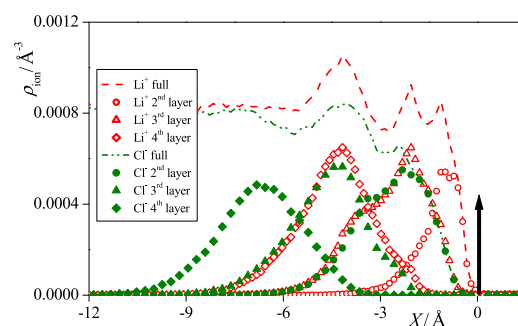


Figure 8. Intrinsic number density profiles of the Li^+ cations (red dashed lines) and Cl^- anions (green dash-dot-dotted lines) along the macroscopic surface normal axis, X , as obtained from the simulation with the AH/BK3 model. The contributions of the Li^+ (red open symbols) and Cl^- (green filled symbols) ions that belong to the second (circles), third (triangles), and fourth (diamonds) subsurface molecular layers are also shown. The up arrow indicates the Dirac delta function corresponding to the density of the first layer particles.

nonintrinsic density profiles of the two ions coincide with each other (see the top panel of Figure 3b), indicating that the ions do not form a noticeable double layer at the liquid surface. Figure 8 shows that, from the second molecular layer on, the cations are considerably closer to the surface than the anions in each layer. Moreover, the density profiles of the Li^+ ions in the third and fourth layers almost perfectly coincide with those of the Cl^- ions in the second and third layers, respectively. Since the first layer is practically free from Li^+ ions, this result reveals that there is a clear, one-layer shift between the anions and cations that are at the same distance from the capillary wave corrugated, intrinsic liquid surface. The fact that two particles that are at the same intrinsic distance might still belong to different subsurface layers is also illustrated in the sketch of Figure 5. The key point in this respect is the large size difference between the two particles, which also implies a much stronger bound first hydration shell around the small than around the large ions. (In this particular case, the Cl^- ion is almost four times larger than the Li^+ ion; see Table 1.) Thus, the smaller Li^+ ion, being surrounded by water molecules, will never be directly exposed to the surface and will, therefore, belong to the second (or farther) molecular layer. On the other hand, the larger Cl^- ion can occupy the same range of intrinsic distances itself as the Li^+ ion together with its first hydration shell, and hence it may well belong to the same layer as the outer waters around the Li^+ ion. This has the effect that larger Cl^- ions can easily be found one molecular layer closer to the surface than smaller Li^+ ions that are located at the same intrinsic distance from the surface.

Although this argument seems to be rather technical, concerning details of the definition of the intrinsic surface and of the subsurface molecular layers, in fact it concerns deeply the physics that is behind the different surface propensities of different ions. Thus, for purely geometrical reasons, small ions are always better shielded by their hydration shell than larger ones. Namely, the water molecules can approach the center of smaller ions closer, forming thus a more compact shell than around larger ions (see also the sketch of Figure 5: small Li^+ ions are surrounded by four water molecules, while the first layer Cl^- ion has five water neighbors, yet its hydration shell is not compact enough to cover it entirely). This geometric difference is then exacerbated by an energetic one: as the water molecules can approach closer the charge carried by a smaller ion, they are also attached more strongly to smaller ions than to larger ones. It is known that smaller, “harder” ions are more strongly repelled (effectively) from the liquid surface than larger, “softer” ones.^{1,25–27,42–45} Our present results show clearly the effect of this combination of geometric and energetic factors: smaller ions are located in farther layers from the intrinsic surface than larger ones, even if they correspond to very similar nonintrinsic distributions and even if their intrinsic density, from the second layer on, exceeds that of the larger ion.

3.4. Role of the Sign of the Ion Charge. Our results show, in accordance with previous studies,^{25–38} that halide anions clearly have a higher affinity to the water surface than alkali cations. This difference can, at least partly, be attributed to the different size of these ions.²³ However, there are also some indications that simply the effect of the ion size might not be enough to explain this difference. For example, relatively large differences in their size do not imply marked differences in the behavior of different cations (see, e.g., Li^+ and Cs^+ , even in the lack of polarization), while the roughly 30% difference in

the diameter of Cs^+ and Cl^- corresponds to much stronger changes in this respect. All of these results suggest that the surface affinity of the ions might well depend also on the sign of their charge. In the frame of continuum theories, such as the Born model, the behavior of the ions should, in the lack of an external electric field, be independent of the sign of their charge.⁵ However, as long as water molecules are explicitly treated in the calculation, the different distributions of their positive and negative fractional charges might well lead to different behavior of the oppositely charged solvated ions. To investigate this point in detail, we have repeated the simulation of the NaI solution, done with the JC model, with the only difference that charges of the opposite sign have been assigned to the ions. This fictitious system, consisting of hypothetical Na^- and I^+ ions, is referred to here as the charge-inverted NaI solution. Since, apart from the sign of the ion charges, this system is identical with the real NaI solution, any difference found between the two systems can be attributed to the sign of the ion charge.

The nonintrinsic density profiles of the ions in these systems are compared in Figure 9. As is evident, although the larger ion

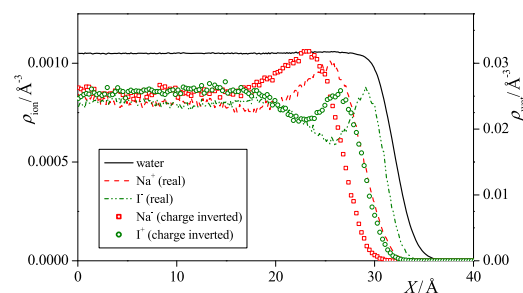


Figure 9. Nonintrinsic number density profiles of the water molecules (solid black line), Na^+ (red dashed lines) and I^- (green dash-dot-dotted lines) ions, and the charge-inverted fictitious Na^- (red open squares) and I^+ (green open circles) ions, as obtained from the simulation with the real and charge-inverted JC model, respectively. The zero value of X corresponds to the middle of the liquid phase. Scales on the left and right refer to the densities of the ions and water molecules, respectively.

can approach the surface closer in both cases, the charge-inverted I^+ ion has a considerably weaker affinity to the water surface than the real, negatively charged I^- ions, as its density peak appears about 3 Å farther from the surface, and this peak is lower than the bulk liquid phase density of the I^+ ion. The above shift of the iodide profile is accompanied by a similar shift of the sodium profile. Consistently, while the concentration of the real I^- ions is 3.41, 1.80, and 1.76 mol % in the first three molecular layers, respectively (see Table S2 of the Supporting Information), these values are 1.80, 2.75, and 2.11 for the charge-inverted I^+ ions. Further, the (negative) surface excess of charge-inverted NaI is 25% larger in magnitude than that of the real NaI (see Table 3).

Although these results clearly reveal that the sign of the charge of the ions has a non-negligible influence on their surface affinity, the physical reason laying behind this finding might not be obvious at first sight. Thus, negative ions are more strongly hydrated than positive ones, simply because positively charged H atoms of a water molecule can approach the hydrated anion closer than the negatively charged O atom (being also the center of the short-range repulsive interaction) can a cation of the same size.⁵ Further, positively charged, less

strongly hydrated ions can more easily lose a part of their hydration shell and can thus be more easily exposed to the opposite phase than more strongly hydrated negative ones.^{1,25–27,42–45} These considerations seem to contradict our finding that the charge-inverted I^+ ions are located farther from the interface than the real, negatively charged I^- ions.

One may argue that the higher surface affinity of the negatively charged ions than their positive counterparts is related to the surface potential of water. Indeed, there is an about 0.5 V potential difference across the liquid–vapor interface of neat water, with the potential being more positive at the vapor than at the liquid side, which arises from the surface orientation of the water molecules. This surface potential is often claimed to be, at least partly, responsible for the higher surface affinity of anions than cations.^{107,108} However, it has been demonstrated several times that such orientational preferences are exhibited solely by the water molecules forming the first molecular layer at the surface of the aqueous phase, and no orientational preference prevails beyond this layer.^{67–69,71,109} Since the different surface affinities of the real I^- and charge-inverted I^+ ions affect several subsurface molecular layers, this explanation does not seem to be able to account for the observed differences.

To understand this behavior, we have investigated both the structural and the energetic properties of the regular and charge-inverted systems. To characterize the structure of the hydrating water, we have calculated the cosine distribution of the angle γ , formed by the vector pointing from the ion to the O atom of a neighboring water molecule, and the dipole vector of this water molecule. In this analysis, a water molecule is considered to be the neighbor of the ion if its O atom is closer to the ion than the first minimum position of the corresponding radial distribution function. The resulting distributions are shown in Figure 10. As is seen, in the case

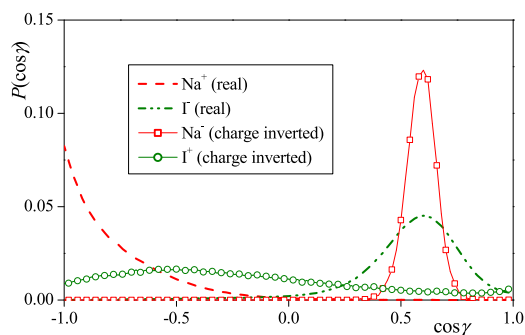


Figure 10. Cosine distribution of the angle γ , formed by the vector pointing from the ion to the O atom of its first shell water neighbor and by the dipole vector of this water molecule, as obtained for the Na^+ (red dashed lines) and I^- (green dash-dot-dotted lines) ions in the real NaI solution and for the fictitious Na^- (red open squares) and I^+ (green open circles) ions in the charge-inverted system, simulated by the JC salt model.

of the negatively charged ions, the peak of the $P(\cos \gamma)$ distribution occurs at around 0.6, indicating that one of the two H atoms of the water molecule points preferentially straight to the ion, while the other H atom, pointing roughly along the tangent of the ion, presumably participates in a H-bond with another first shell water molecule. Further, this preference is clearly stronger for the smaller Na^- than for the larger I^- ion. In the case of the real, positively charged Na^+ ion,

the peak of the $P(\cos \gamma)$ distribution is at -1 , indicating that here the O atom of a first shell water molecule points preferentially to the ion, while the dipole vector of the water molecule coincides with the ion–oxygen axis. On the other hand, no marked orientational preference is seen for the water molecules hydrating the charge-inverted I^+ ions.

Next, we have calculated the average interaction energy of the ions with the entire aqueous phase. To calculate this energy without allowing the interface as well as the other ions present in the system influencing its value, we have simulated the infinitely dilute bulk aqueous solutions of both the real and charge-inverted NaI (considering 998 water molecules and one ion pair, the latter being fixed at the maximum possible distance from each other). Further, the entire calculation has also been repeated with the AH/BK3 model. The obtained values, collected in Table 4, confirm that, among the pairs of

Table 4. Average Interaction Energy of the Ions with All Water Molecules in the System (in kJ/mol Units), as Obtained in Infinitely Dilute Real and Charge-Inverted NaI Solutions with the JC and AH/BK3 Models

model	real NaI solution		charge inverted NaI solution	
	Na^+	I^-	Na^-	I^+
JC	−758	−562	−1269	−390
AH/BK3	−640	−461	−975	−337

real and charge-inverted ions, the negatively charged ion always interacts considerably stronger with the hydrating water molecules than its positively charged counterpart. Further, this difference is clearly far larger for the smaller Na^+/Na^- than for the larger I^-/I^+ ions. This is not surprising considering the $1/r$ decay of the charge–charge interaction, which makes the above difference, originating in the closer approach of the H than the O atoms of the water molecules to the ion, stronger at smaller distances. It should also be emphasized that this qualitative picture is seen in the case of both the non-polarizable JC and the polarizable AH/BK3 model, although in this latter case the hydration energy values are always somewhat, by about 15–25%, smaller in magnitude than in the lack of the explicit treatment of the polarization.

Both the structural and energetic information, when considered for the anions and for the cations separately, corroborates the picture that negative ions are more strongly hydrated than positive ones. However, by considering pairs of ions, it is clear that the energy lost by switching iodide's charge from negative to positive is clearly overcompensated by the energy gain of switching sodium's charge from positive to negative. The total thermodynamic force is then driving all ions in the charge-inverted system away from the interface, no matter whether, singularly, they are more strongly or more weakly hydrated. Thus, the smaller surface affinity of the charge-inverted I^+ than the real I^- ion originates from the global energetic change dominated by the sign of the charge of the smaller Na^+/Na^- ion.

4. CONCLUSIONS

In this paper, we have presented a systematic computer simulation investigation of the surface affinity of alkali and halide ions in the aqueous solutions of alkali chlorides and sodium halides, considering three simple nonpolarizable and a polarizable potential model. We have found, in accordance with earlier claims,^{47,52} that the KBFF model severely

underestimates the aqueous solubility of at least some of these salts, while the DVH model, in contrast with other simulations^{25–38} as well as with experimental evidence,^{17,18,22} does not show enrichment of Γ^- at the liquid surface.

The results obtained from the present simulations are, in general, consistent with the picture established in the past two decades, showing that (i) the majority of the ions are effectively repelled from the water surface; (ii) the surface affinity of the anions increases with increasing size, while the surface layer is practically free from cations in every case; and (iii) Γ^- ions are enriched at the water surface; this enrichment can be described even without taking the polarizability of the particles into account, but polarization clearly enhances this effect, and this enrichment does not contradict the negative surface excess of the Γ^- ion because of the presence of a depletion layer below the surface.²⁷

However, by analyzing the intrinsic properties of the liquid surface, we have also refined the above picture in several respects. Thus, our results point out that, in discussing the adsorption of a certain species, a clear distinction has to be made between adsorption in its thermodynamic sense (as described in terms of the surface excess and the change of the surface tension) and its structural sense, discussed in terms of surface enrichment. A clear example for this difference is the adsorption of the Γ^- ions at the aqueous surface. Thus, the concentration of Γ^- in the surface layer well exceeds that in the bulk liquid phase, as obtained with both the JC and AH/BK3 models; yet, its surface excess is negative, and the surface tension of the solution is higher than that of neat water for the JC model, and, within error bars, both the surface excess and the change of the surface tension are zero for AH/BK3. In other words, in spite of its enrichment, in the thermodynamic sense, Γ^- is still not or negatively adsorbed at the surface of its aqueous solution. This seeming contradiction can be resolved by considering that, besides the positive contribution of the first layer, the subsequent layers give negative contributions to the surface excess (see Figure 4b and also Figure S4b,c of the Supporting Information), and this depletion overcompensates the enrichment of the surface layer. A similar explanation was suggested earlier by Vrbka et al.²⁷

It is also well established that smaller, more strongly hydrated ions have a smaller surface affinity than larger, weakly hydrated ones.^{1,25–27,42–45} We have demonstrated that the reason for this is partly geometric and partly energetic: better hydrated small ions might belong to the next subsurface layer than larger, less strongly hydrated ones even if they are located at the same intrinsic distance from the surface. As we have shown in the example of LiCl, the difference in the hydration of the two ions in such cases results in a one-layer shift of their contribution, without being accompanied by a similar shift in their density profiles. As a consequence, the larger concentration of the anions than cations in the surface layer does not necessarily involve separation of the oppositely charged ions and thus their formation of a noticeable double layer.

Finally, we have shown, in accordance with earlier claims,⁵ that negative ions are more strongly hydrated than positive ions of the same size because of the charge asymmetry of the water molecules. However, this stronger hydration can be accompanied by an increase rather than a decrease in the surface excess of large anions, simply because the same but opposite effect is stronger on the smaller cations. The lesson learned is that it makes little sense to consider the properties of anions or cations separately from each other in trying to

predict their surface affinity. Instead, one always has to consider the combined effect of ion pairs and, as a rule of thumb, due to the $1/r$ decay of the charge–charge Coulomb interaction the smaller of the two ions guides this effect.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcb.0c05547>.

Figures showing the ion–ion rdfs, water and ion intrinsic and nonintrinsic density profiles, and ion concentrations in the first four subsurface layers. Numerically, the concentration of the different ions in the first four subsurface layers of their aqueous solutions, as obtained for all systems with the three potential models considered in the analyses (PDF)

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Notes

The authors declare no competing financial interest.

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