

Attraction between like-charged monovalent ions

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Ions with like-charges repel each other with a magnitude given by the Coulomb law. The repulsion is also known to persist in aqueous solutions albeit factored by the medium's dielectric constant. In this paper, we report results from molecular dynamics simulations of alkali halides salt solutions indicating an effective attraction between some of the like-charged monovalent ions. The attraction is observed between anions, as well as between cations, leading to the formation of dimers with lifetimes on the order of few picoseconds. Two mechanisms have been identified to drive this counterintuitive attraction. The first is exhibited by high-charge density ions, such as fluoride, at low salt concentrations, yielding effective attractions with magnitude up to the order of $1-2 kT$. In this case, the stronger local electric field generated when the two ions are in contact augments the alignment of neighboring waters toward the ions. This results in a gain of substantial favorable ion-water interaction energy. For fluorides, this interaction constitutes the major change among the different energy components compensating for the anion-anion repulsion, and therefore, rendering like-charge association possible. The second mechanism involves mediation by counterions, the attractions increase with salt concentration and are characterized by small magnitudes. In particular, clusters of ion triplets, in which a counterion is either bridging the two like-charged ions or is paired to only one of them, are formed. Although these two mechanisms may not yield net attractions in many cases, they might still be operational and significant, explaining effective repulsions between like-charged ions with magnitudes much smaller than expected based on continuum electrostatics. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4705692>]

I. INTRODUCTION

Particles carrying like-charges repel each other. This is one of the fundamental laws of physics by which nature operates. The interaction between like-charged ions can also occur in water. Although, water is known to exhibit many anomalies, can it effectively change the character of this interaction from repulsion to attraction?

A well known example of like-charge attraction is found between macroions in aqueous solutions. A necessary condition to observe this attraction is the presence of multivalent counterions. Despite the lack of full understanding of the underlying mechanism, it known to be induced by the accumulation (or condensation) of the counterions at the macroions' surface.^{1,2} Such condensation can lead to charge inversion at different regions of the surface of the (or even on the entire) macroions.³⁻⁶ Two such macroions can feel attraction if the regions of the counterion accumulation are anti-correlated.^{7,8} Another example of like-charge attraction is given by the pairing of polyatomic ions such as guanidinium groups.⁹ By adopting a particular configuration of the dimer, atoms with partial negative charge on one cation can interact favorably with atoms with partial positive charge on the other cation, optimizing the quadrupole-quadrupole interactions.¹⁰ Furthermore, polyatomic ions with hydrophobic residues, such as

tetraalkylammonium, can also attract each other, and even exhibit some degree of aggregation, in aqueous solution.¹¹

Nevertheless, is it possible that two, single-atom, like-charged ions attract each other in aqueous solution without the possibility of counterion condensation, or any impact at all from the counterions? The answer is to be found in the behavior of the water molecules. If we approximate the water molecules as a continuum medium, their effect on the interaction between the like-charged ions is to scale down the repulsion by the corresponding dielectric constant. However, at short distances of nearly contact, there is no dielectric screening to the electrostatics and repulsion with a magnitude on the order of that observed in vacuum is expected. Indeed, describing the solvent by a continuum model is known to be inappropriate especially for interactions at short distances,¹² and solvent-induced interactions, such as the hydrophobic effect, can be understood only by including the atomic degrees of freedom of the solvent.¹³

The first theoretical argument for like-charge attraction came from predictions based on the integral equation theory.¹⁴⁻¹⁸ These different studies utilized different approximations and models to describe the system. In the majority of the investigations, attraction between chlorides was reported with a magnitude of few kJ/mol. These predictions stimulated several scientists to test the results through molecular dynamics and Monte Carlo simulations. In one of the earliest studies,^{19,20} a clear attractive minimum at contact in the chloride-chloride potential of mean force (PMF) was found,

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while the PMF for a pair of sodium cations was found to be repulsive. Subsequent studies found similar results^{21–23} but the magnitude of the attraction was argued to depend on the potential parameters employed in the calculations.^{24,25} More recently, Monte Carlo simulations in the gas phase were employed to study the PMF between two like-charged ions as a function of the number of surrounding water molecules.²⁶ The results indicate that with an appropriate number of waters, attraction between both anions, as well as cations, is possible. Furthermore, computer simulations of ionenes found that fluorides can attract each other, and this attraction is stronger in the presence of the more hydrophobic ionenes.²⁷ Weak attraction between iodides was also observed; however, it was argued that it is a consequence of the high accumulation of these large anions around ionenes.

In all the previously mentioned studies, the driving force for the like-charge attraction, if reported, was argued to be a water molecule simultaneously bounding to (i.e., bridging) the two ions. Although bridging waters were mostly observed between two anions, this argument has also been invoked for cations.²⁶ Nevertheless, it is not clear at all what are the enthalpic or entropic gain for the system when a water molecule is bridging the two like-charged ions that can overcome the large electrostatic repulsion between the ions. In addition to bridging waters, bridging counterions, as well as counterions that are bound to only one of the paired ions, have been also observed.²⁷

A different interpretation based on the fact that the solvent molecules can exhibit induced polarizability has been proposed.²⁸ In this case, it is argued that the induction energy due to the field of the two ions can stabilize the like-charged ion pair. As expected, the polarization energy becomes larger in magnitude (more negative) as the polarizability of the solvent increases, and above a critical value this energy can overcome the repulsion between the ions. In another study, it was argued that the process of bringing two like-charged ions together leads to a higher local charge density and this generates a more favorable solvation enthalpy.²⁹

The most direct experimental method to study particle correlations in liquids is by neutron or x-ray diffractions. While the theoretical studies were applied to low or medium range concentrations, the applicability of neutron and x-ray diffractions is limited to very high concentrations (e.g., 10 M). In this range of concentrations, the solution display structural features similar to the molten state of the salt. Correlation of like-charged ions in the molten state can be reminiscent to the structure of the crystal (or crystal hydrates), in which anion-anion associations have been argued to form.^{30,31} Taking the high concentration issue into consideration, the correlation between chloride ions has been reported to exhibit a peak at close distance.^{32–35} The interchloride contact distance appears to depend on the counterion and experimental conditions.

Arguably, the most convincing experimental report of attraction between like-charged simple ions is obtained by F¹⁹ NMR relaxation rates of alkali metal fluoride solutions in D₂O.³⁶ Large deviations, toward lower rates, of F¹⁹ magnetic relaxation were observed with the increase in the salt concentration. This increase in relaxation times could only be explained due to a close contact between two fluorides. Fur-

ther analysis of the results indicated that the closest fluoride-fluoride separation is approximately 0.3 nm.

In this paper, we study the effective interactions between like-charged monovalent ions in alkali-halides solutions. It is found that anions, as well as cations, can attract each other with magnitudes up to the order of kT and lifetimes on the order of few picoseconds. Two different mechanisms that allow like-charge attractions are identified. The first operates between high-charge density ions and is driven by enthalpy. The attraction originates from the stronger ordering of the water molecules around the like-charged ionic dimer (a consequence of a stronger local electric field) relative to the individually hydrated ions. For some ions, e.g., fluorides, the strength of this gain in energy can overcompensate the strong electrostatic repulsions. The second mechanism involves mediation by counterions. Both, bridging counterions, as well as counterions that are paired to only one of the like-charged ions, are observed. In this case, the attractions are weaker and increase with the salt concentrations. We argue that these mechanisms for attraction operate between like-charge ions in many cases, even in those where the overall interaction between the ions is repulsive. The effect in this case is to reduce the magnitude of the repulsion at contact, where the dielectric screening of the solvent is not relevant.

II. METHODS

We study the effective interaction between two like-charged ions in different alkali halides salt solutions. To this end, we performed two types of simulations. The first is a series of simulations of one aqueous alkali-halide salt solution at different concentrations, and the second is a series of simulations designed to obtain the potential of mean force between two halide ions.

The molecular dynamics package GROMACS version 4.0.5 (Ref. 37) was used to perform all of the computer simulations with a time step of 0.002 ps. The electrostatic forces were evaluated by the Particle-Mesh Ewald method (with real-space cutoff of 1.0 nm, grid spacing of 0.12 nm, and quadratic interpolation) and the Lennard-Jones (LJ) forces by a cutoff of 1.0 nm (with long range dispersion corrections for the energy and pressure). The system was maintained at a constant temperature of 300 K by the velocity rescaling thermostat³⁸ with a coupling time of 0.1 ps, and at a pressure of 1.0 bar by the Berendsen thermostat³⁹ with a compressibility of 1×10^{-5} 1/bar and a coupling time of 1.0 ps.

The LJ parameters for the alkali metal and halide ions were taken from the OPLS force field^{40–43} and are given in Table I. The water molecules were represented by the TIP4P-Ew model.⁴⁴ Their bond distances and angle were constrained using the SETTLE algorithm.⁴⁵ To describe the LJ potential between different particles, we used the geometric combination rule.

The first series of simulation covered 6×20 ns (thus, 120 ns) of data collection, after 8 ns of equilibration time, for 20 different salt solutions, composed by each of the alkali cation (Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺) and each of the halide anion (F⁻, Cl⁻, Br⁻, and I⁻). The trajectories were

TABLE I. The OPLS parameters for the alkali metal and halide ions used in this work.

Cation	σ (nm)	ϵ (kJ/mol)	Anion	σ (nm)	ϵ (kJ/mol)
Li ⁺	0.1260	$2.615 \times 10^{+1}$	F ⁻	0.2733	3.012×10^0
Na ⁺	0.3330	1.160×10^{-2}	Cl ⁻	0.4417	4.928×10^{-1}
K ⁺	0.4935	1.372×10^{-3}	Br ⁻	0.4624	3.766×10^{-1}
Rb ⁺	0.5622	7.155×10^{-4}	I ⁻	0.5400	2.929×10^{-1}
Cs ⁺	0.6716	3.389×10^{-4}			

saved every 10 ps. For each alkali halide salt solution, we performed simulations at four different concentrations of 0.89, 1.84, 2.85, and 3.93*m*, consisting of $N_{\text{cations}} = N_{\text{anions}} = 32, 64, 96,$ and 128 ions, respectively, solvated in $2064 - N_{\text{cations}} - N_{\text{anions}}$ water molecules. In order to calculate the average lifetimes of the anionic dimers in NaF and NaI solutions, we performed two additional simulations of 7.2 ns, at each concentration, where the trajectories were saved every 0.2 ns.

In the second series of simulations, we calculated the PMF between two identical halide anions neutralized by two potassium cations and surrounded by 1936 water molecules. This setup corresponds to a salt concentration of 0.056*m*. The PMF was computed from the mean force acting on each of the halide ions whose positions were held fixed in space.^{46,47} Then the mean force acting between the anions along their axis of separation (the *z* axis) was integrated as a function of their interparticle distance, *d*, to yield the Gibbs energy profile. As the PMF represents only relative values, it was shifted such that the Gibbs energy of the state at the largest separation (*d* = 2.50 nm) corresponds to zero. To obtain the PMF between each halide anion pair, we performed 58 simulations with different values of *d*, ranging from 0.37 to 2.50 nm. At each distance, the system was equilibrated for 8.0 ns and data collected for an additional 40.0 ns. The error in determining the change in Gibbs energy, ΔG , between the associated (*d* = 0.40–0.57 nm depending on the anion) and dissociated (*d* = 2.50 nm) states is obtained by integrating the mean forces plus/minus their errors. We checked our determination of the potential of mean force on KCl solution at 1.84*m* (64 anions, 64 cations, and 1936 water molecules). In this case, the positions of two chlorides were held fixed while those of the others were not. The resulting curve of the PMF from the direct force calculations was compared with that obtained from simulations, where the positions of all the chlorides were not fixed (i.e., first series of simulations). In the latter, the potential of mean force between the chlorides was obtained from the radial distribution function (RDF)⁴⁸ through the relation $w(r) = -RT \ln[g(r)]$. The comparison indicates a very good agreement, with maximum discrepancy on the order of 0.1 kJ/mol.

In order to achieve accurate thermodynamic analyses of the system at the associated and dissociated states, we performed 12 additional simulations at each of these points for 120.0 ns (thus, a combined trajectory of 1.44 μ s) for the KF and KI salt solutions. This was necessary since the change in enthalpy, which is approximated by the change in the potential energy of the system, is obtained by subtracting a large number from a similar large number. These 12 simulations were

considered statistically independent and, therefore, the error estimate in this case was determined by the standard error of the mean (obtained from the 12 simulations). To analyze dynamical properties of the KF and KI solutions, we performed 12 additional simulations for 2.4 ns each, for the associated and dissociated states, where the trajectories were saved every 1.0 ps.

A water molecule was considered to form a bridge between two ions in contact with each other if it simultaneously formed a hydrogen bond with these ions. A hydrogen bond is defined by a donor–acceptor cutoff distance of 0.35 nm and a donor–hydrogen–acceptor angle larger than 150°. Two anions, or two cations, are regarded in contact with each other if their interparticle distance is smaller than the position of the first minimum in the corresponding RDF. Similar criteria, based on a distance cutoff at the first minimum in the RDF, were applied to define bridging anions and cations.

Because we calculated the electrostatics using Ewald summation, the decomposition of the energy into different terms requires the recalculation of the potential energy by simple direct evaluation of the interparticle distances from the trajectories. Recalculating the potential energy this way ignores the electrostatic potential due to periodic image boxes. This is the main reason why the sum of all components in Table IV does not recover the corresponding ΔH shown in Table III. Furthermore, since the trajectories were saved every 10 ps, the associated errors of the energy components are significantly larger than those for ΔH .

III. RESULTS AND DISCUSSION

A. Attraction between anions

Figures 1(a) and 1(b) present the RDF between halide anions for different sodium and cesium halide salt solutions at concentration of 0.89*m*. Except for NaI solution, the propensity of all the halides to form anion-anion contact pair (dimer) is larger than random. For chlorides, bromides, and iodides, the height of the first peak (thus, the probability to form the contact pair) is in the range of 1 and 2. However, fluorides behave distinctively different in that the probability to form dimers is markedly larger, where the height of the first maximum is approximately 5 and 4 for NaF and CsF solutions, respectively. This is very counterintuitive since, if anything, one would have expected the low-charge density anions, such as iodides with smaller direct anion-anion repulsion at contact, to have larger propensity to form contact pairs relative to high-charge density ions such as fluorides. Note that the locations of the first peaks of the RDFs are just larger than the corresponding diameters of the anions (see Table I), indicating that these peaks correspond to configurations at contact and not to solvent separated pairs. The largest difference is observed for fluoride, where the first maximum is around 0.40 nm while $\sigma = 0.273$ nm. In Figs. 1(c) and 1(d), the halide-halide RDFs for sodium fluoride and sodium iodide are plotted for different concentrations. The height of the first maximum decreases with increasing concentration for sodium fluoride, whereas it increases for sodium iodide solutions. This opposite behavior exhibited by the two salts indicates that the mechanism

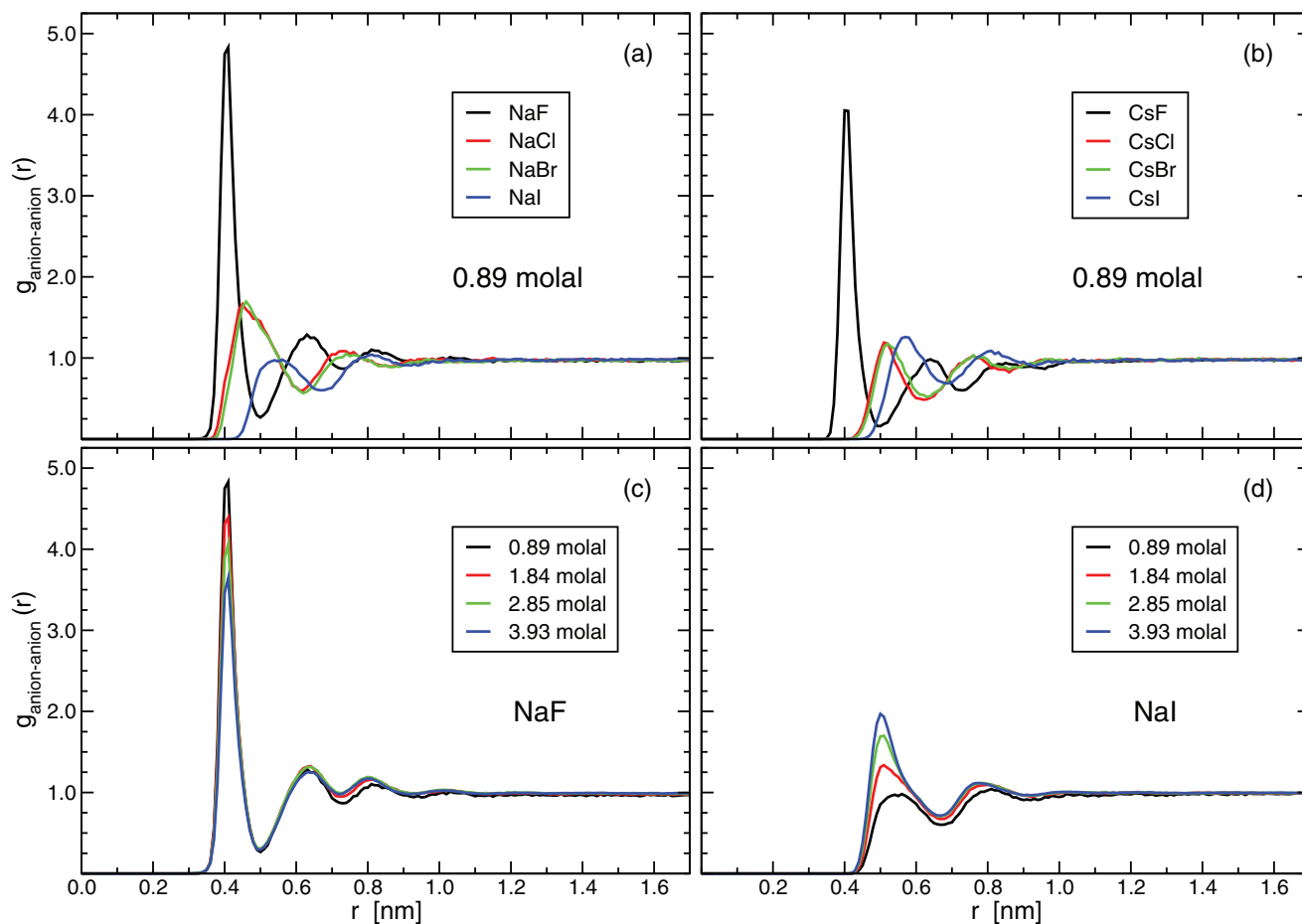


FIG. 1. The radial distribution function between halide anions. (a) In a 0.89*m* sodium halide and (b) cesium halide salt solutions. (c) In different concentrations of sodium fluoride and (d) sodium iodide salt solutions.

responsible for the attraction between two fluoride anions is different than that for the attraction between two iodide anions. The results for all other alkali halide solutions are given in Fig. S1 of the supplementary material.⁴⁹ In this figure, the height of the first maximum of the halide-halide RDF is given as a function of concentration. Negative slopes are evident only for the alkali fluoride solutions suggesting that the driving force for the attractions between chlorides, as well as between bromides, are similar to that between iodides (however, especially for chlorides, contribution from both mechanisms is possible). The results for salt solutions with lithium cations are not shown, since for LiF, we observed precipitation at all concentrations and for the other halides solutions convergence was not well achieved (except for LiI solutions). This is likely due to the strong interactions lithium can make with water molecules and high-charge density ions (because of its small σ value) impeding frequent exchanges with its first solvation shell.

In order to characterize the attraction between two fluorides versus that operating between two iodides, we plot in Fig. 2(a) the number of water molecules bridging (i.e., hydrogen bonded to) the two halides at contact as a function of concentration. For NaI salt solutions, there is no significant number of bridging waters. However, for NaF solutions, there are 1.55 such bridging waters per fluoride dimer at 0.89*m*,

which slightly decreases with concentration and reaches 1.44 at 3.93*m* (see below for a snapshot of such bridging water). The number of cations that are simultaneously in contact with (bridging) the two anions are shown in Fig. 2(b). In contrast to the number of bridging waters, the number of bridging cations is insignificant for NaF solutions, but substantial for NaI solutions. In the latter, the number of cations bridging the two iodides increases from 0.28 at 0.89*m* to 0.49 at 3.93*m*. Such formation of triplets, of anion dimer with a “gluing” cation, is a reasonable explanation for an effective attraction between the anions. Nevertheless, the probability of observing this configuration indicates that at least half of the iodide-iodide dimers are formed without this “gluing” cation. We find that there are also significant amounts of halide dimers where only one of the anions is paired to the cation. This is shown in Fig. 2(c). Such ion pairing is also observed for NaF solutions; however, it is much more evident for NaI and again increases with concentration. To demonstrate that such pairing to only one of the anions contributes uniquely for the ability of the two anions to approach each other and is not just a mere consequence of a cutoff consideration, we plotted in Fig. S2a of the supplementary material,⁴⁹ the distribution of the anion-cation-anion angle observed for both cases. It is clear that the two curves belong to different distributions; whereas the bridging cations form a well-defined angle around 110°, the paired

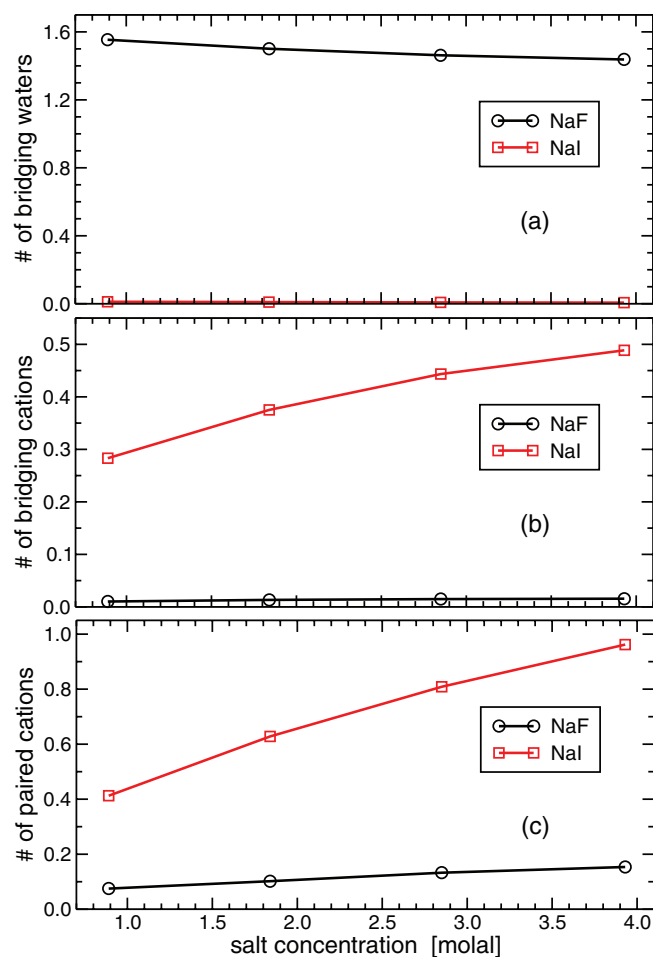


FIG. 2. (a) Number of water molecules, per anion dimer, that are simultaneously hydrogen bonded with both anions as a function of concentration. (b) and (c) Same as in (a) but for the number of cations that are simultaneously bound to (bridging) the two anions (b), and for the number of cations bound only to one of the paired anions (c).

cations forms a wider distribution with much smaller values. By pairing to a cation, the direct electrostatic repulsion between the two anions is reduced and likely to be viewed more as a charge-dipole interaction than as a charge-charge interaction.

For cases in which the attraction is correlated to the number of bridging or paired cations, it is reasonable to assume that anions will attract each other more when the cation and anion bind each other stronger. The propensity of a cation to form a contact pair with an anion can be physically understood by the Collins law of matching water affinities.^{50,51} However, the results shown in Fig. S1 of the supplementary material for chloride, bromide, and iodide salt solutions do not fully support this argument. For example, for bromide, the strongest attraction is observed in NaBr and decreases with the size of the cation. For iodide solutions, a maximum around the potassium cation is observed. This is probably a result of additional competing effects. For example, when the cations are small (e.g., sodium), they bind the water molecules tightly and can contribute to an effective attraction between anions, reminiscent of the salting-out effect. However, the ability of the anion and cation to form a contact pair is also important,

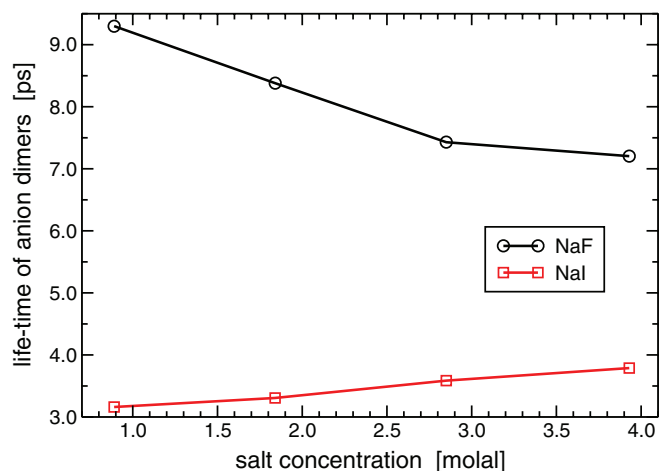


FIG. 3. The average time the anions spend at contact (interanion distances smaller than the first minimum in the corresponding RDF) before separating.

as evident from the alkali iodide solutions, possibly explaining the maximum observed for potassium iodide.

In Fig. 3, we plot the average time the anions exist as dimers for NaF and NaI solutions as a function of concentrations. This kinetic stability of the anionic dimers correlates with their thermodynamic stability. Thus, the lifetimes for the fluoride anions are larger than those for iodides. In addition, while for fluorides the lifetimes reduce with concentrations, for iodides they increase, reflecting the same tendency as the formation propensity shown in Figs. 1(c) and 1(d).

B. Attraction between cations

In Sec. III A, it was shown that anions can effectively attract each other in aqueous solution. Is a similar attraction possible between cations? Figures 4(a) and 4(b) display the alkali-alkali RDF for different alkali fluoride and alkali iodide solutions, respectively, at 0.89*m*. For the alkali fluoride salts, only in KF solution the first peak is (slightly) above one. In addition, the maximum in NaF solution is observed for the solvent separated configuration at $r = 0.64$ nm (second peak). For the alkali iodide salts, the cations slightly attract each other to a contact configuration in KI and RbI solutions, while they slightly repel each other in NaI solution. In Figs. 4(c) and 4(d) we plot these cation-cation RDFs for different concentrations for NaBr and CsBr solutions. In both cases, the attraction between the cations increases with concentration. This is similar to the behavior found for the halide-halide attraction correlated to the number of bridging or paired cations. Figure S3 in the supplementary material⁴⁹ exhibits the height of the first maximum of the alkali-alkali radial distribution functions in all salt solutions. The strongest attraction between the sodium cations is when the counter anion is chloride and between potassium cations it is for bromide counter anions. For both rubidium and cesium cations, the cation-cation attraction increases with the size of the counter anion. Although it depends on the identity of the anions, it seems that, in general, stronger attraction can be displayed between

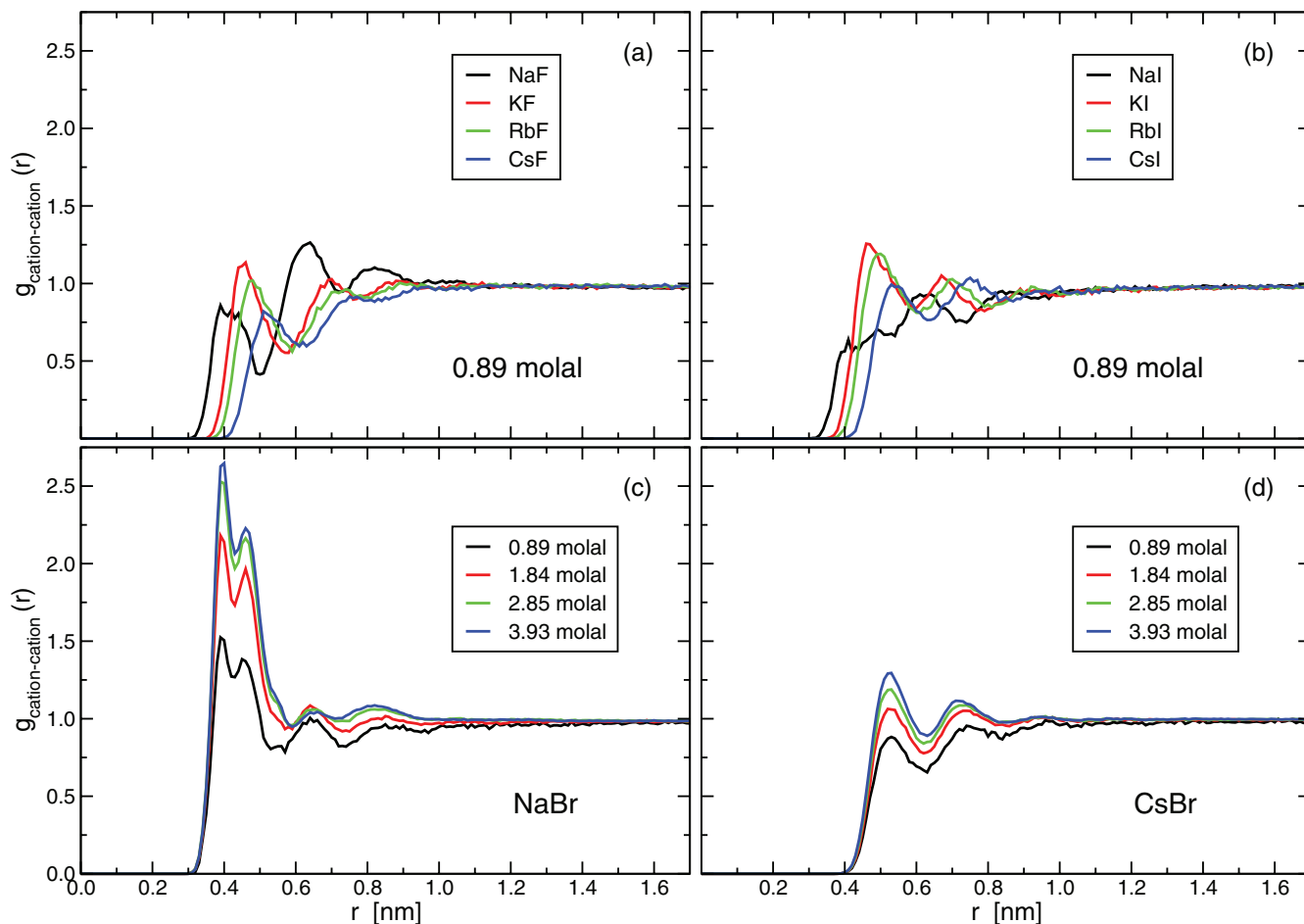


FIG. 4. The radial distribution function between alkali cations. (a) In 0.89*m* alkali fluoride and (b) alkali iodide salt solutions. (c) In different concentrations of sodium bromide and (d) cesium bromide salt solutions.

cations with smaller size. For example, the cesium halide salts display the weakest attractions, suggesting that a weak ion-water interaction, characterizing large ions, do not play a major role in the attraction, as was previously argued.¹⁷

Although the simulations with the lithium cations did not converge well, for LiCl and LiBr solutions, it was noticeable that lithium cations can also attract each other and they exhibit similar behavior, as found for the attraction between fluoride anions. Thus, the attraction increases with decreasing concentrations, however, without water molecules bridging the two cations. Stronger attraction is found to correlate with smaller size counter anions, and in fact for LiI solutions, no attraction between the lithium cations was detected at any concentration.

As expected from the behavior of NaBr and CsBr solutions as a function of concentration (Figs. 4(c) and 4(d)), we did not find any bridging waters for the cation dimers. Figure 5(a) displays the number of anions bridging the two cations for NaBr and CsBr solutions as a function of concentration. In line with the stronger cation-cation attraction observed for NaBr, there are more bromides bridging the sodium dimers than that bridging the cesium dimers, and this number increases with concentration in both cases. The number of anions that are in contact with only one of the cations is shown in Fig. 5(b). Again, larger numbers are detected for NaBr but

the difference, compared with the number of bridging anions, is smaller. The normalized distributions of the cation-anion-cation angle for bridged and paired anions configurations are plotted in Fig. S2b of the supplementary material. As is the case for the formation of anions dimers, also here the bridging and the paired counterions are distinct from a geometric point of view; the paired anions form wider distribution with smaller values. However, in the case of an anion bridging two cations, there is a significant amount of linear configurations ($\theta = 180^\circ$) not observed for the case of a cation bridging two anions. Note that the first peak of the RDF for NaBr shown in Fig. 4(c) is split. This is a result of two different angles that the bridged bromide forms with the two sodium cations. Figure 5(c) displays this bimodal distribution in NaBr contrasted by the unimodal distribution observed for CsBr salt solution.

The energetics involved in the attraction between like-charged ions “glued” by, or just paired with, counterion may not be so peculiar. However, the attraction between high-charge density ions, such as that observed between fluorides, not mediated by counterions is not so trivial; one would think that when separated, the sum of the interactions of each of the fluorides with the surrounding water molecules is stronger than when they are associated. And obviously, in the separated state the fluoride-fluoride repulsion is much weaker.

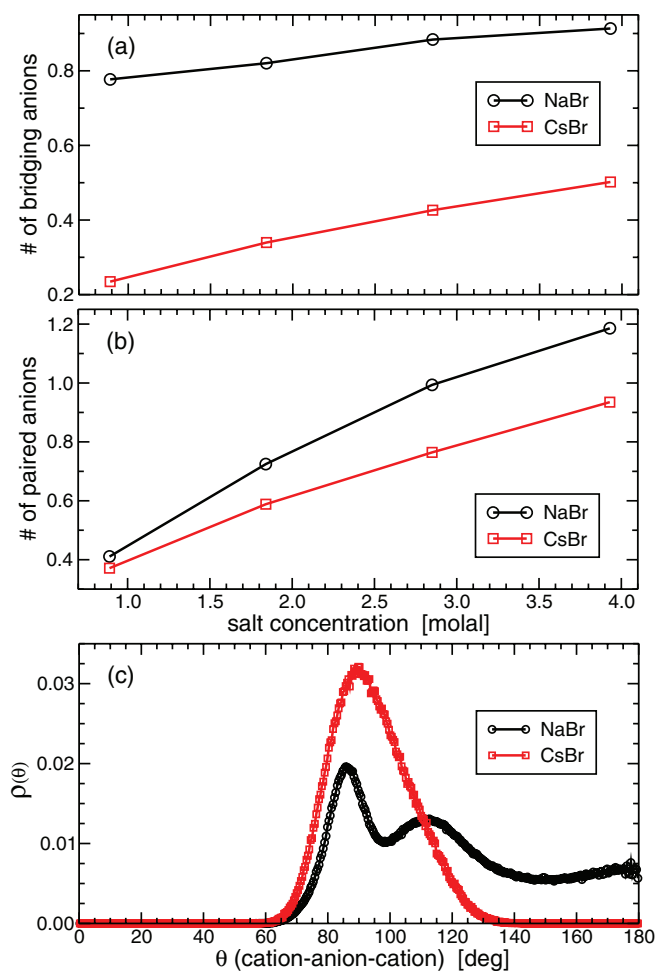


FIG. 5. (a) Number of anions, per cation dimer, that are simultaneously bounded to the two cations as a function of concentration. Note that in contrast to the case of paired anions (shown in Fig. 2), here no bridged water molecules were found for any salt at any concentration. (b) Same as in (a) but for the number of anions bound to only one of the paired cations. (c) Normalized probability distribution of the angle the bridging anion forms with the paired cations (cation–anion–cation) at concentration of 3.93 m. The two maxima observed at 86° and 113° in the curve for NaBr rationalize the double maxima of the first peak in the corresponding RDF shown in Fig. 4(c).

C. Why do fluorides attract each other relatively strongly?

In order to elucidate the origin of the attraction between high-charge density, like-charged ions, we calcu-

TABLE II. The number of waters, and cations, bridging the halide dimer as well as the number of paired cations bound to only one of the anions of the halide dimer. The results were analyzed from the simulations at 0.056 m of the corresponding potassium halides. In the second column, the halide-halide equilibrium contact distance (HH-CD), defining the halide dimer, is given.

Salt	HH-CD (nm)	No. of bridged waters	No. of bridged cations	No. of paired cations
KF	0.40	1.93	0.00	0.01
KCl	0.51	0.93	0.03	0.03
KBr	0.52	0.75	0.05	0.06
KI	0.57	0.02	0.13	0.08

lated the PMFs between two halide anions (fluorides, chlorides, bromides, and iodides), surrounded by two potassium cations at a concentration of 0.056 m. Table II summarizes the number of bridging waters, bridging cations, and paired cations at the equilibrium contact distance between the halide anions. The table indicates that there are almost two (1.93) waters interacting simultaneously with the two fluorides and this number decreases with the size of the halide anions, being insignificant for iodide. The number of bridged or paired cations, although increasing for larger halides, is small for all salts. This is due to the low salt concentration used. For iodide, the numbers obtained are similar to those extrapolated from the curves in Figs. 2(b) and 2(c). Instantaneous configurations displaying two water molecules bridging a fluoride dimer, as well as a potassium cation bridging two or paired to only one of the iodides, are shown in Fig. 6. Also shown in this figure is the configuration of the waters around an iodide dimer without any bridging waters or any bridging or paired cations.

The potentials of mean force between the halide anions are shown in Fig. 7. In this low concentration salt solutions, only fluorides attract each other (relative to the dissociated state at $d = 2.50$ nm), while the other halides display a repulsive local minimum with a magnitude of approximately +1.2 kJ/mol. The well-depth at contact between the fluorides is -2.5 kJ/mol, around the magnitude of thermal fluctuations (kT). For comparison, the well depth of the PMF between these anions in the 0.89 m NaF solution shown in Fig. 1(a) is -4.0 kJ/mol. This means that although the attraction increases with decreasing the concentration from 3.93 to 0.89 m,

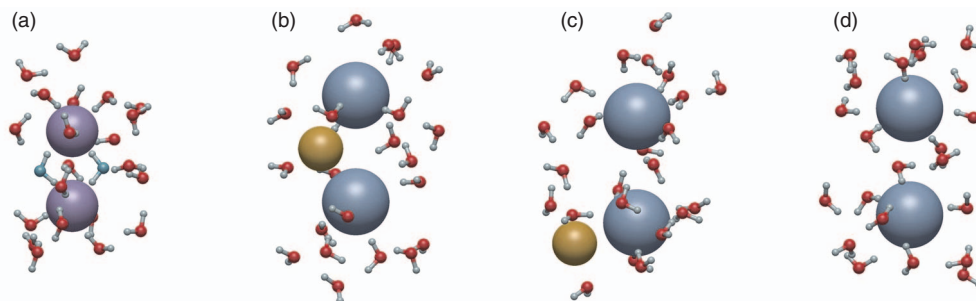


FIG. 6. Snapshots of the water molecules and potassium cations (yellow) in the vicinity of two halide anions at contact from the simulations at a concentration of 0.056 m. (a) Around fluoride dimer (purple). Around iodide dimer (gray-blue) with a bridging potassium (b), paired to only one of the iodides (c), and without any bridging waters or any bridging or paired cations (d). The oxygen atoms of the two water molecules bridging the fluoride anions are denoted by blue color.

TABLE III. Thermodynamic data for the association of two halide anions at a concentration of 0.056*m* of the corresponding potassium halide salt. All values are given in kJ/mol.

Salt	ΔG	ΔH	$T\Delta S$
KF	-2.5 ± 0.3	-5.7 ± 0.5	-3.2 ± 0.8
KI	$+1.2 \pm 0.3$	-1.8 ± 0.6	-3.0 ± 0.9

a further decrease in concentration leads to a maximum below which the attraction becomes weaker. Table III presents the results of the thermodynamics of the association process of two fluorides and two iodides. The table indicates that for both anions, the process of bringing the two halides together involves an enthalpic gain but with an entropic penalty. However, for iodides, the gain in enthalpy does not compensate for the entropic penalty, while for fluorides, it does rendering the contact pair more stable. Why ΔH is negative and why is it more negative for fluorides than for iodides? In order to address these questions, we decomposed, in Table IV, the change in enthalpy (which, for these simulations, are almost identical to the change in potential energy) into different terms. As expected, the anion-anion repulsion between the halide anions is large and is larger for KF because the contact equilibrium distance of fluorides (0.40 nm) is smaller than for iodides (0.57 nm). The repulsion between the potassium cations is very similar in both cases. The remaining four energetic terms differ between KF and KI; however, the changes in anion-water and water-water interactions are the most significant. It is known that around ions, the structure of the surrounding water molecules change relative to that in bulk.⁵² However, if the structure around individually hydrated ion is the same as that around the dimer, then the process of anion association is expected to be accompanied by weakening of the anion-water attractive interactions. This is because in the anion dimeric state, there are less first and second shell waters around the two anions. Table IV indicates exactly the opposite; the anion-water interaction for the two halides contacting each other is significantly stronger than when they are separated. This is true for fluorides and iodides and likely to be the reason why ΔH is negative. The only way this is possible is if the structure of the waters around the anions changes between the separated and associated states. Why does the structure of water changes? Around anions, the water molecules orient their hydrogens toward the anions yielding a favorable interaction energy. The magnitude of this orientational order correlates with the intensity of the local electric field experienced by the water molecules. For KF and KI, it seems that the electric field acting on neighboring waters is stronger when the anions are in contact, and the gain in the interaction en-

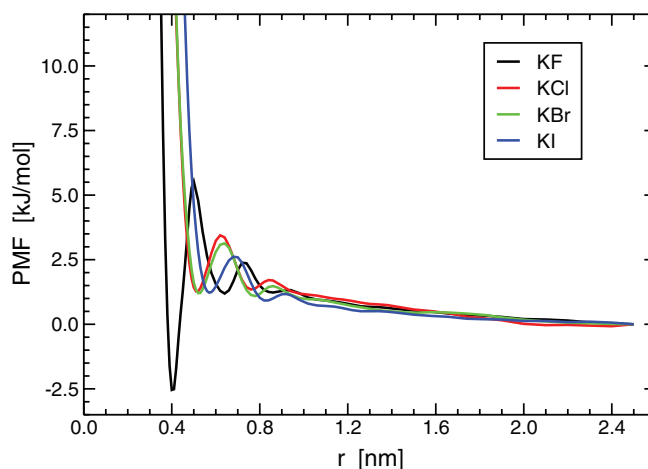


FIG. 7. Potential of mean force between two halides ions surrounded by 1936 waters and 2 potassium counterions (thus, at a concentration of 0.056*m*).

ergy compensates for the smaller number of waters in the surrounding shells. Apparently, the change in ΔH , and thereby in water ordering, is stronger for fluoride than for iodide. This is because at anionic contact, the electric field around the fluoride dimer is stronger (since the charge density is higher) than around the iodide dimer, inducing a larger change in the re-orientation of the neighboring water molecules. When water molecules are aligned by the application of an external electric field, there is a disruption of the interaction between the water molecules,⁵³ analogous to the weakened water-water interactions observed around high-charge density ions compared with the interactions in bulk.⁵² This is indicated in Table IV, where larger disruption is found for KF, than for KI, solution.

Based upon our computational results, we suggest that it is the strong electric field around the fluoride dimer, inducing strong orientations of neighboring waters, and as a result strong favorable anion-water interaction, that drives the attraction between the two fluorides. This favorable anion-water interaction is the major energy component compensating the strong repulsion between the fluorides at contact. A similar mechanism operates around iodide dimer also; however, the change in the induced orientations is not as strong and thereby the change in anion-water interaction is much smaller. Note that the water molecules bridging the two fluorides are not the driving force for the attraction, but a consequence of the anion dimer configuration.

We analyzed the structure of water molecules around the anions in the separated state and compared it with that around the associated state. The translational order, as represented by the RDF between the anions and the oxygen atom of waters,

TABLE IV. Components of the change in energy for the association process of the two halide anions. All values are given in kJ/mol.

Salt	Anion-anion	Anion-water	Water-water	Anion-cation	Cation-water	Cation-cation
KF	$+290.7 \pm 0.0$	-456 ± 5	$+191 \pm 6$	-129 ± 5	$+78 \pm 4$	11 ± 1
KI	$+187.9 \pm 0.0$	-205 ± 9	$+45 \pm 8$	-167 ± 9	$+113 \pm 4$	11 ± 1

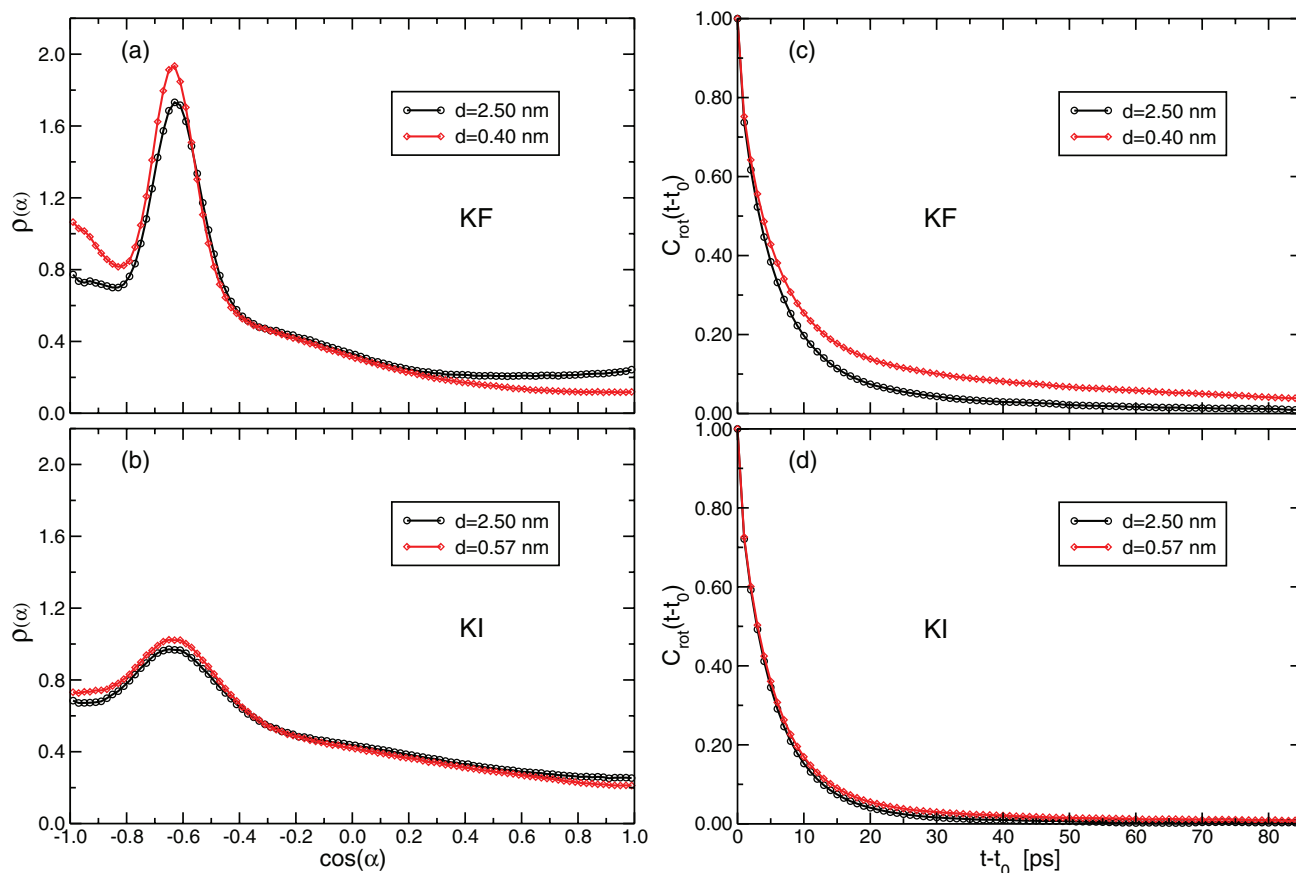


FIG. 8. (a) Normalized distribution of the angle between the water molecule dipole moment and the oxygen(water)-anion vector for KF and (b) for KI. (c) The rotational autocorrelation function (normalized by its value at $t - t_0 = 0$) of the water molecules dipole moment in KF and (d) KI salts. In all cases, the analysis was performed in the associated and dissociated states for the simulations at $0.056m$, and only water molecules within the first two solvation shells around the anions were considered.

did not exhibit significant difference between the two states (see Fig. S4 in the supplementary material⁴⁹). However, the orientational order does differ. In Figs. 8(a) and 8(b), we plot the distribution of the angle formed between the dipole moment of the surrounding (first and second solvation shells) water molecules and the water-anion vector in KF and KI solutions, respectively. In both cases, there is more structure (deviation from horizontal line) in the associated state. However, whereas this difference, or change in structure, is quite small around iodides, it is much larger around fluorides. The enhancement is evident for angles larger than 114° (alignment of the dipole moment toward the anion) on the expense of angles smaller than 72° (alignment of the dipole moment away from the anion). This indeed corresponds to a more favorable interaction energy between the anions and the water molecules when the two anions are in contact. We also plotted the rotational autocorrelation function of these water molecules in Figs. 8(c) and 8(d). Relative to the separated state, there is a slight retardation in the rotation of the water molecules around the iodide dimer, but substantial slowing down around the fluoride dimer. Another example of slower dynamics of the water molecules around the anionic dimer is seen in their mean-squared displacement (Fig. 9). The retardation in the diffusion of the water molecules around

the fluoride dimer is larger than that around the iodide dimer. This is again a consequence of a stronger change in the electric field experienced by the water molecules in the case of KF.

As shown in Fig. 1(c), for salt concentrations above $0.89m$, the attraction between fluoride anions decreases with concentration. Given the explanation above, the reason for the decreased attraction is that at higher concentrations, there are less water molecules available to react to the change in the electric field induced by the fluoride association. With an increase in the salt concentration, many of the water molecules are already structurally adapted to the field generated by other nearby ions.

It is not clear to what extent the two mechanisms for attraction between like-charged ions described in this paper can be accounted by continuum electrostatic models. The case in which a third oppositely charged ion mediates the attraction (especially, via bridging the like-charged dimer) is likely to be easier to model. In the case where the attraction is driven because the water polarization is significantly increased around the like-charged dimer, the dielectric constant of the solvent considered in the continuum model has to be a function of the distance between the two like-charged ions.

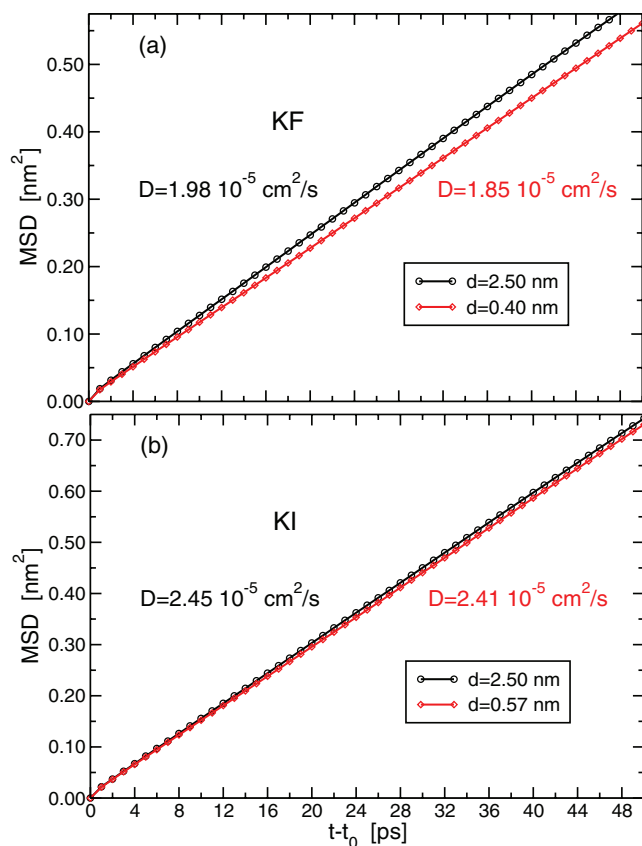


FIG. 9. The mean-squared displacement of the water molecules around the halide anions (thus, at time $t - t_0 = 0$ were found in the first or second solvation shells), and the corresponding diffusion constant in the associated and separated states of the anions for (a) KF and (b) KI salt solutions.

IV. CONCLUSIONS

In this paper, we showed that attraction between like-charged ions is possible in different aqueous salt solutions. The ions we studied are monovalent single-atom ions, in contrast to the macroions for which like-charge attraction can also be observed due to, multivalent, counterion condensation. The type of like-charge attractions we report here are induced by two different mechanisms. In both cases, the resulting attraction is not very strong, but the effect is substantial because it eliminates the, large, direct electrostatic repulsion acting between the ions. This leads to the formation of contact pairs (dimers) with maximum relative stability of $1-2 kT$ and, consequently, with lifetimes on the order of few picoseconds. The first mechanism operates between high-charge density ions and is driven by the stronger favorable interaction between the ionic dimer and the surrounding water molecules relative to the corresponding favorable interaction for the separated state of the ions. The necessity for high-charge density ions, such as fluorides or possibly lithium cations, is because only in this case the ordering of the water molecules around the ions in the dimeric state will be significantly different from that in the separated state. The concomitant change in the ion-water interaction energy is the major energy term that compensates the ion-ion repulsion allowing the two like-charged ions to attract each other (see Fig. 10). Thus, it is the ability of the water molecules to reorganize around the dimer differently from that around the individually hydrated ions that drives this attraction, and therefore, this attraction is (predominantly) strengthened for lower salt concentrations. This may be related to the reason why at concentrations above 0.1M, fluoride salt solutions are non-ideal and the composition of the species existing in solution is difficult to identify.⁵⁴ The

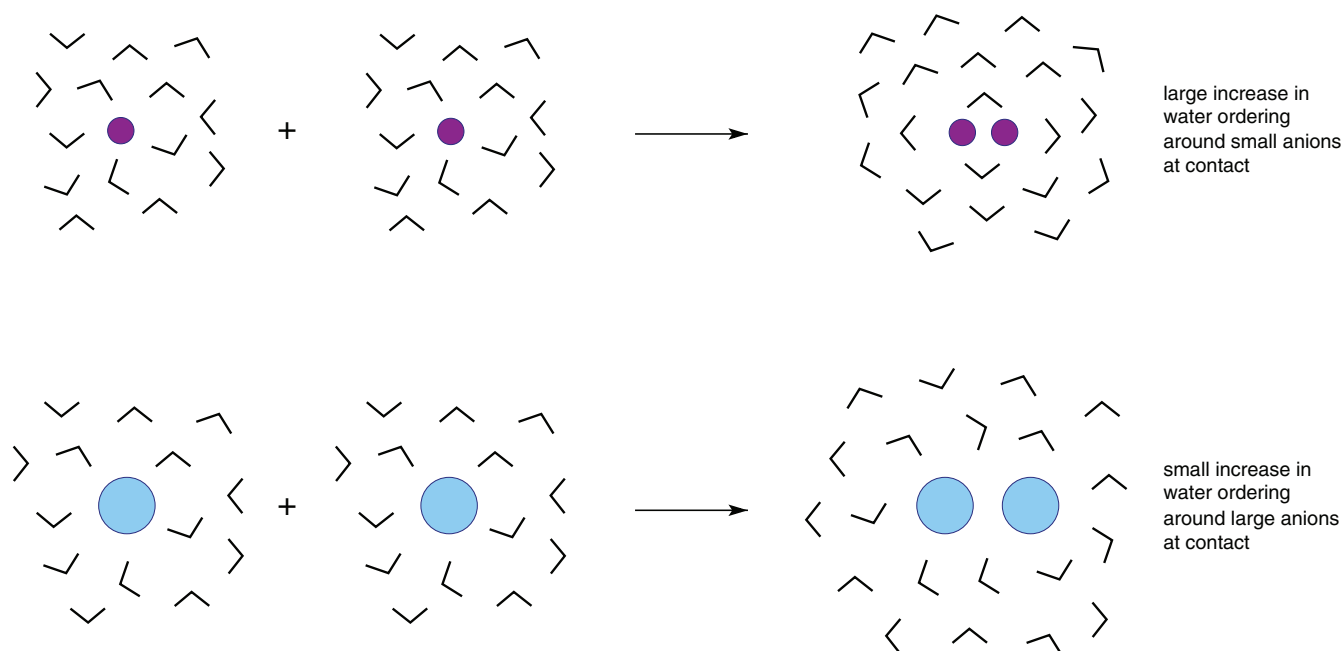


FIG. 10. Illustration of why high-charge density ions (fluorides) can attract each other relatively strong, while such attraction is not observed for low-charge density ions (iodides). In the former, there is a strong increase in the alignment of the water molecules dipole moments toward the ions at contact, on the expense of the ordering between the water molecules (upper panel). Whereas, in the latter, there is a much smaller increase in the orientation of the water dipoles toward the ionic dimer and, therefore, the water-water order can be maintained (lower panel).

second mechanism for the attraction between like-charged ions involves the association of a third oppositely charged ion. Here, the magnitude of the attraction is smaller, the lifetimes of the contact pairs are shorter, and both increase with the concentration of the salt. Both, bridging counterions, which are simultaneously bound to the two like-charged ions, as well as counterions that are paired to only one of the like-charged ions are observed. The identity of the counterions plays a role, however, a general trend is difficult to identify. In some cases, e.g., in the attraction between chlorides or between bromides, larger attractions are observed for a smaller size counterions. These counterintuitive results add to reports of an effective repulsion in aqueous solution between ions of opposite charge. This, for example, operates between magnesium divalent cation and chloride anion.⁵⁵ Thus, the behavior of the water molecules around the ions has the power to overturn an electrostatic repulsion to an attraction, and vice versa.

ACKNOWLEDGMENTS

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Supplementary Material:
Attraction between Like-Charged Monovalent Ions

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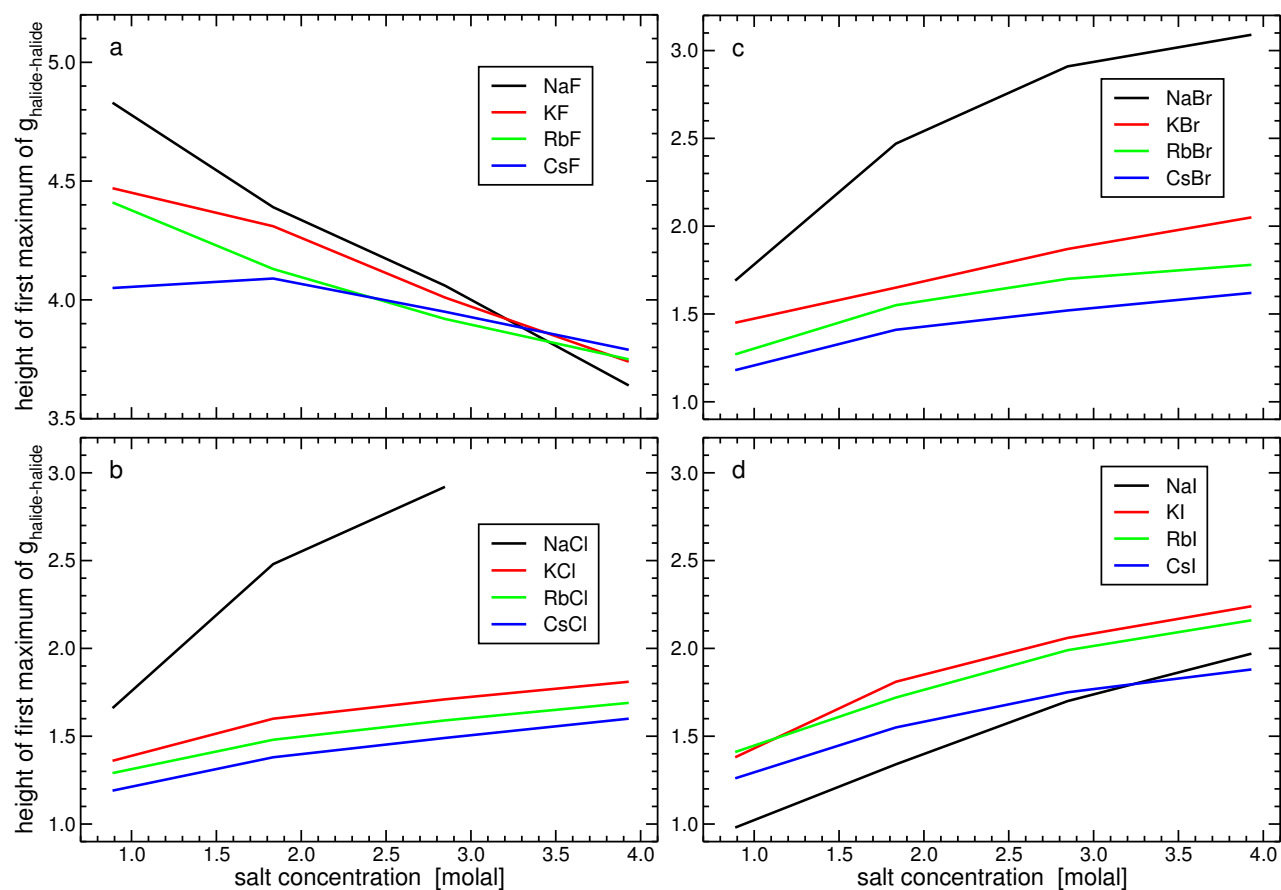


Figure S1: The value of the halide-halide radial distribution function at its (first) maximum as a function of concentration for (a) alkali fluoride, (b) alkali chloride, (c) alkali bromide, and (d) alkali iodide. Note the values of the y -axis in (a) are different than in the other graphs. The value for sodium chloride at the largest concentration is not reported since the salt in this case exhibited precipitation.

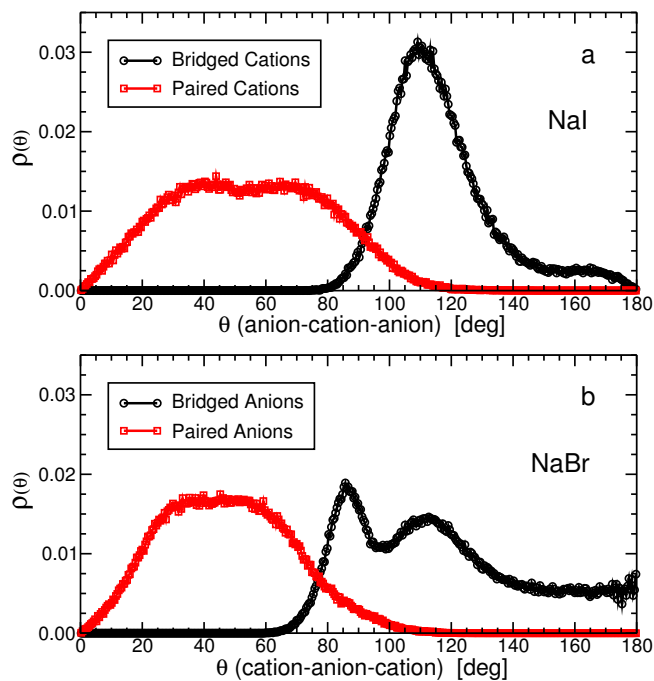


Figure S2: (a) Normalized probability distribution of the anion-cation-anion angle for NaI salt solution at concentration of 1.84 molal. The curves are plotted for cations bridging the two anions (black) as well as for cations that are paired to only one of the anions (red). (b) Same as (a) but for the cation-anion-cation angle in NaBr solution at 1.84 molal. In both cases, the plots for other concentrations are similar.

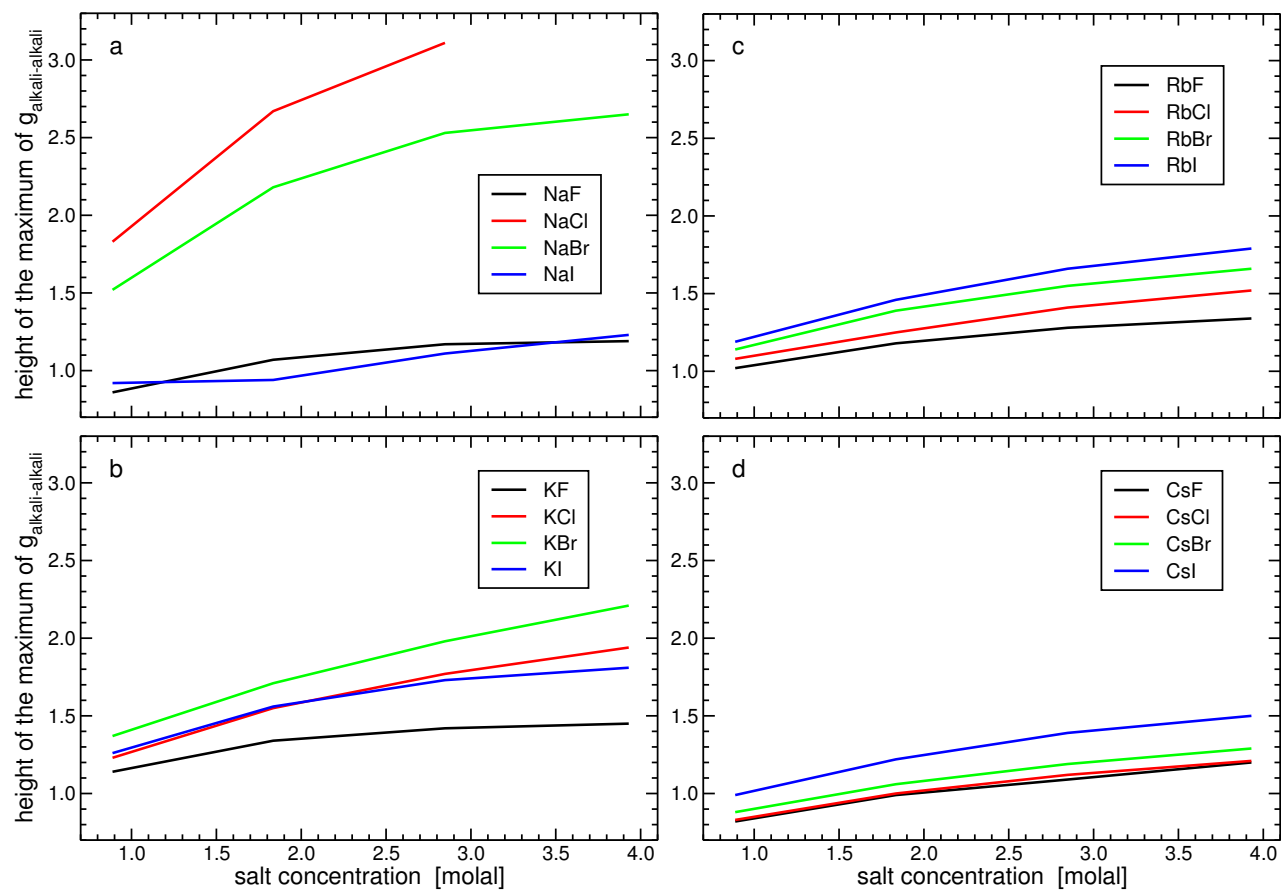


Figure S3: The value of the alkali-alkali radial distribution function at its maximum as a function of concentration for (a) sodium halides, (b) potassium halides, (c) rubidium halides, and (d) cesium halides. For sodium halides the first peak is split, so the reported values correspond to the largest maximum. As is the case for Fig. S1, the value for sodium chloride at the largest concentration is not reported.

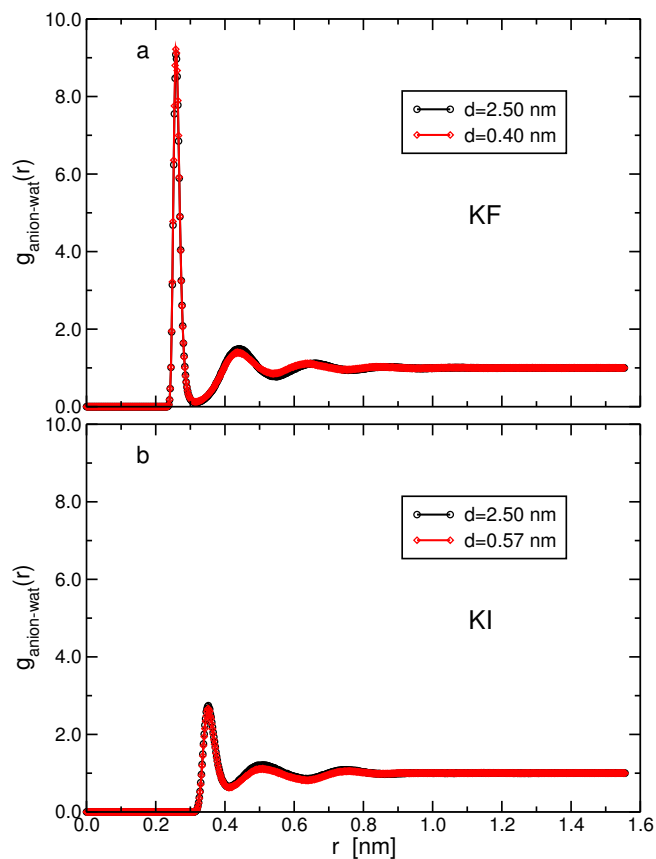


Figure S4: The radial distribution function between the anions and the oxygen atom of the water molecules for the associated and dissociated states in the simulations at 0.056 molal for (a) potassium fluoride, and (b) potassium iodide.