

# Atomistic Simulation of Ion Solvation in Water Explains Surface Preference of Halides

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## Supplementary material

### Surface enhancement factor

The increased ion concentration on the surface for halide ions as compared to the concentration in the bulk was computed from the respective potential of mean force (PMF)  $\Delta G(r)$ . The concentration of the ion between radii  $r_1$  and  $r_2$  is given by

$$C_s(r_1, r_2) = C_b V(r_1, r_2)^{-1} \int_{r_1}^{r_2} e^{-\Delta G(r)/k_B T} 4\pi r^2 dr, \quad (1)$$

with the Boltzmann constant  $k_B$  and the temperature  $T$ .  $V(r_1, r_2) = 4\pi(r_2^3 - r_1^3)/3$  denotes the volume of the shell between  $r_1$  and  $r_2$ , and  $C_b$  is the bulk concentration where  $\Delta G(r)$  was defined to be zero (see Figure 1B/C in the main text). Note that the  $4\pi r^2$  factor is required in this integral because the geometric contribution to the PMFs from the larger number of states at larger  $r$  was explicitly removed from the PMFs  $\Delta G(r)$  via Equation 1 in the main text. We defined the surface as the range  $0.75 \text{ nm} < r < 1.1 \text{ nm}$ . The concentration enhancement at the surface is thus given by  $C(0.75 \text{ nm}, 1.1 \text{ nm})/C_b$ .

The experimental probe depth was incorporated into Equation 1 by assuming that the signal decays exponentially from the droplet surface, that is proportional to  $\exp((r - r_s)/\lambda)$ . Here,  $r_s$  denotes the radius of the droplet surface and  $\lambda$  the decay length. The measured surface concentration is

$$C'_s(r_1, r_2) = C_b \frac{\int_{r_1}^{r_2} e^{(r-r_s)/\lambda} e^{-\Delta G(r)/k_B T} 4\pi r^2 dr}{\int_{r_1}^{r_2} e^{(r-r_s)/\lambda} 4\pi r^2 dr}, \quad (2)$$

and the measured surface concentrations enhancement is given by  $C'_s(r_1, r_2)/C_b$ . As the droplet surface, we used  $r_s = 1.2 \text{ nm}$ , which is located slightly above the Gibbs dividing surface at  $1.12 \text{ nm}$ .  $C'_s(r_1, r_2)/C_b$  turned out to be relatively insensitive to the decay length for values of  $\lambda$  between  $0.5 \text{ nm}$  and  $1.0 \text{ nm}$ .

### Radial distribution functions

Figures S1 and S2 show the radial distribution functions of water oxygens around ions and water respectively, as a function of ion position in the droplet.

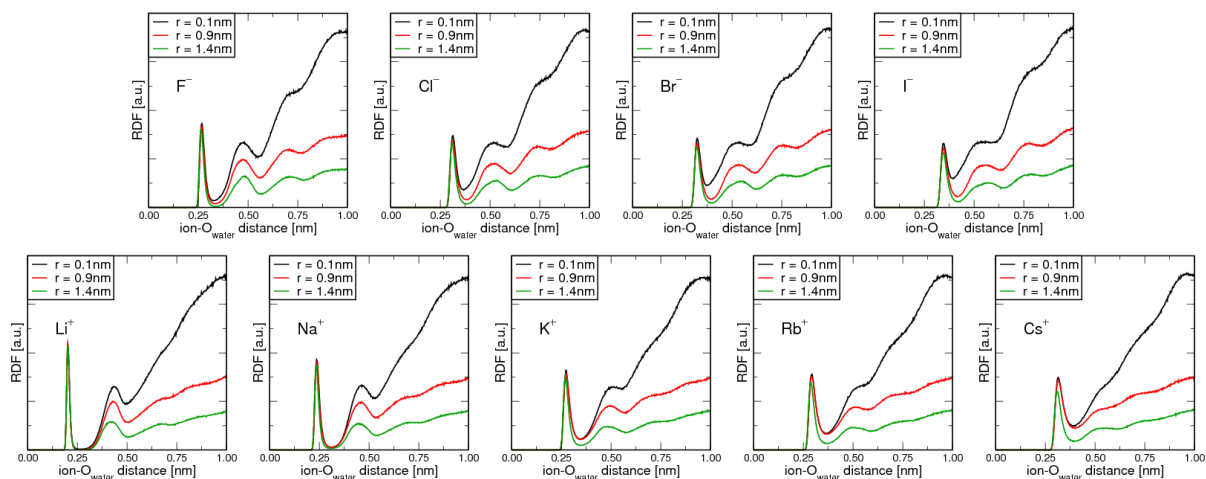


Figure S1: Radial distribution function for water around ions for three positions of the ion with respect to the center of mass of the water cluster.

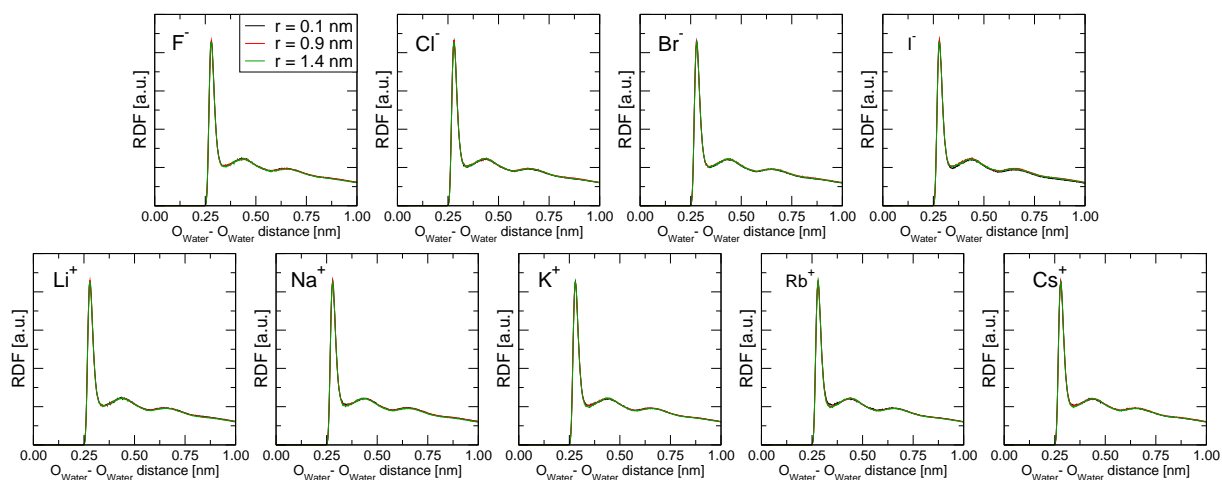


Figure S2: Radial distribution function for water oxygen around water oxygen for three positions of the ion with respect to the center of mass of the water cluster.

## Two-dimensional potentials of mean force

In order to assess whether features of the PMFs are correlated to structural properties, we have computed two-dimensional (2D) PMFs. Figure S3 shows the 2D PMF as a function of two variables: (i) the distance  $r$  from the center of mass and (ii) the coordination number of the ion, defined as the number of water molecules in the first solvation shell, that is until the first minimum in the radial distribution function. The 2D PMF were made, by re-using the individual calculations as displayed in Figure 1 of the main

text, and by making a coordination-number histogram at each distance. For all ions, positive or negative the coordination number decrease slightly when on the surface, as expected. Furthermore it is obvious that the magnitude of the coordination number is correlated to the size of the ion. There does not seem to be a combination of coordination number and distance that correlates to the energy.

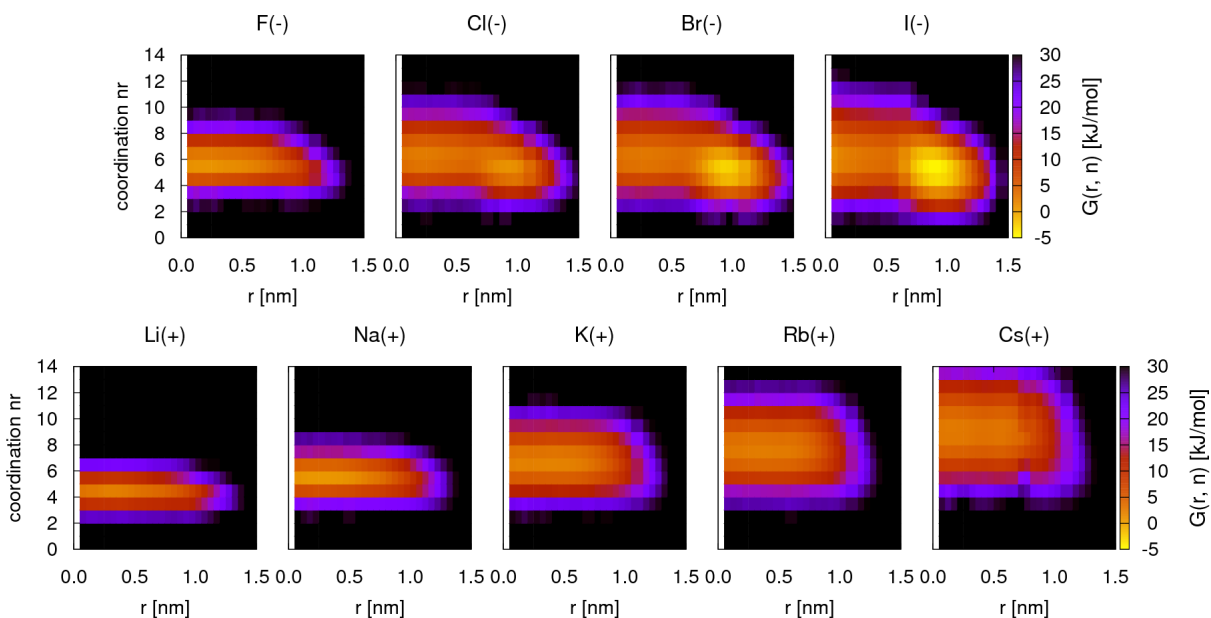


Figure S3: Two-dimensional potential of mean force. The PMF as a function of distance and ion-coordination number

Figure S4 shows 2D PMF as a function of the orientation of the water molecules in the first solvation shell, prepared in the same manner as Figure S3. For negative ions there is a preferential orientation where a water hydrogen points towards the ion, leading to an angle of about 120 degrees. For the positive ions the optimal angle is zero. The smaller ions coordinate the water better as seen from the narrower angle distribution. It seems superficially that the distribution of angles for the negative ions (except fluorine) is somewhat wider close to the surface, which could be interpreted as leading to higher entropy, and hence explain the surface preference. This is however incorrect. Figure 3 in the main text clearly shows that for the negative ions the heavier ones loose more entropy on moving to the surface than the lighter ones. In other words, the energy analysis presented in the main text is the only correct way to include effects of both water and ion. A limited focus on the ion only may lead to the wrong

conclusion on surface preference due to neglect of the water-water interactions.

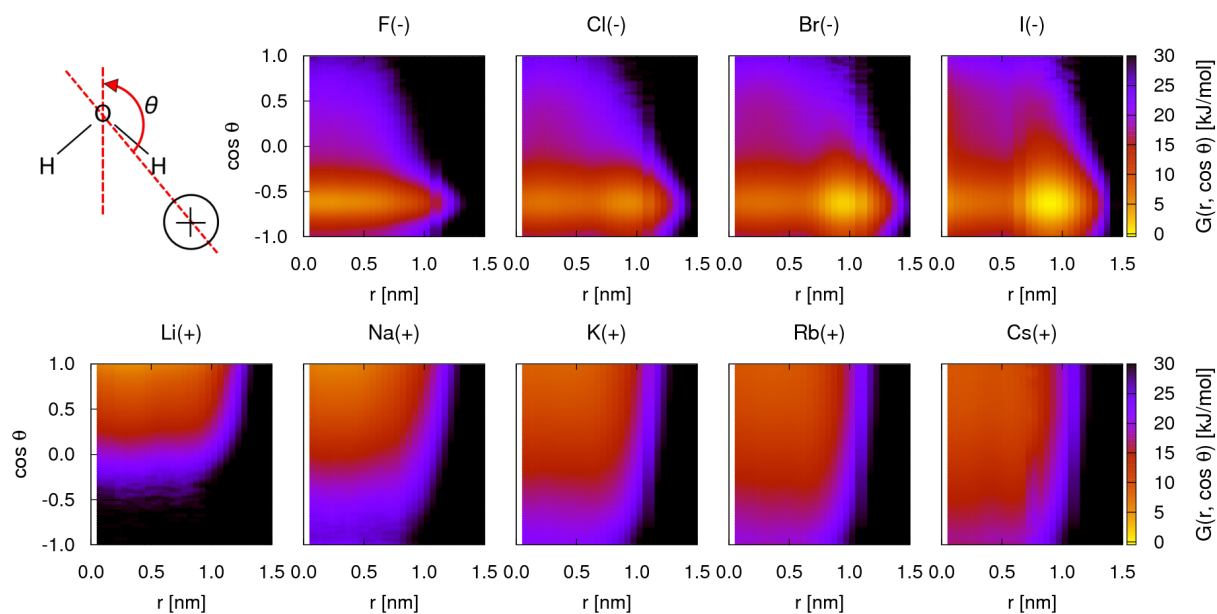


Figure S4: 2D potential of mean force. The PMF as a function of angle of the water bisector (illustrated in figure) with the ion-water oxygen vector.

### PMFs for halide ions with inverted charge

To assess if the size of the halide ions, in combination with the respective polarizability fully accounts for the surface preference, we have, in addition to the PMFs reported in the main text, computed PMFs for hypothetical cations. The polarization of these hypothetical cations as well as their size, as given by the Lennard-Jones parameters, were taken from the halide ions, but the hypothetical cations carry an inverted charge of +1. These cations are denoted as  $F^+$ ,  $Cl^+$ ,  $Br^+$ , and  $I^+$ .

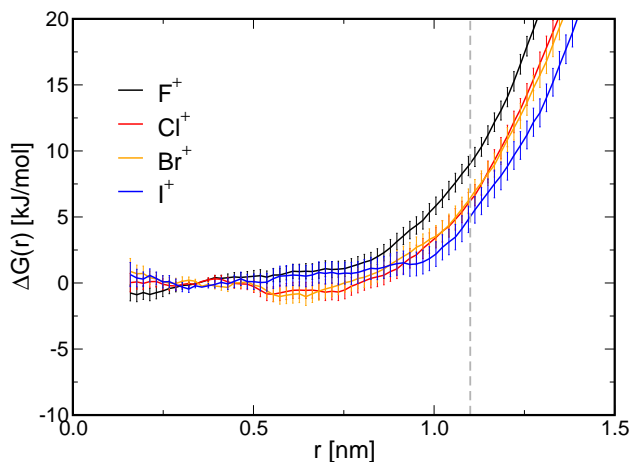


Figure S5: Potentials of mean force for hypothetical cations, with size and polarizability taken from the halide ions, but with inverted (positive charge). These “cations” are denoted as  $F^+$ ,  $Cl^+$ ,  $Br^+$ , and  $I^+$ . The grey line indicates the droplet surface in the absence of an ion. In contrast to the large halide ions, none of these hypothetical cations shows any surface preference, demonstrating that even size in combination with polarizability of an ion are not sufficient to explain surface/bulk preference.

PMFs for halide ions with inverted charge were computed using umbrella sampling simulations. Umbrella sampling is an alternative to the constraint simulations technique described in the main text and is equally suitable to compute PMFs. Accordingly, the radius was split in the range  $0.2 \text{ nm} \leq r \leq 2 \text{ nm}$  in 33 equidistant sections, where each section represents an umbrella center. For each umbrella simulation, the respective ions was placed into the respective section along  $r$ , and subsequently restrained with respect to the COM of the water droplet with a harmonic force. A force constant of  $k = 1000 \text{ kJ mol}^{-1} \text{ nm}^{-2}$  was applied for  $r \leq 1.35 \text{ nm}$ , and a gradually increasing  $k$  up to  $3000 \text{ kJ mol}^{-1} \text{ nm}^{-2}$  for larger  $r$ . After energy minimization, umbrella windows for  $r \leq 1.5 \text{ nm}$  were simulated for 1 ns, the other umbrella windows for 250 ps. The first 50 ps was removed from all simulations for equilibration, and the PMFs were computed using the weighted histogram analysis method (WHAM) [1]. The statistical uncertainty in the PMFs was derived using bootstrap analysis by generating hypothetical trajectories based on the respective umbrella histogram and the autocorrelation time. For more details on the bootstrapping procedure we refer to reference [2].

The potentials of mean force for  $F^+$ ,  $Cl^+$ ,  $Br^+$ , and  $I^+$  are presented in Figure S5. In contrast to the large halide anions (Figure 1B in the main text), none of these hypothetical cations displays any surface preference, demonstrating that even size in combination with polarizability of an ion are not sufficient to

explain surface/bulk preference.

## References

- [1] Kumar, S., Bouzida, D., Swendsen, R. H., Kollman, P. A., Rosenberg, J. M. The weighted histogram analysis method for free-energy calculations of biomolecules. i. the method. *J. Comp. Chem.* 13:1011–1021, 1992.
- [2] Hub, J. S., de Groot, B. L., van der Spoel, D. g\_wham – a free weighted histogram analysis implementation including robust error and autocorrelation estimates. *J. Chem. Theor. Comput.* 6:3713–3720, 2010.