Ions at Hydrophobic Aqueous Interfaces: Molecular Dynamics with Effective Polarization

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Abstract

The affinity of halide anions to the water/oil interface is investigated using molecular dynamics simulations effectively accounting for polarization effects by an electronic continuum correction, which is practically realized via rescaling of the ionic charges. This simple and computationally efficient correction to non-polarizable simulations is suited for electronically homogeneous media and we show that it works well also for the water/oil interface, which exhibits practically no electronic discontinuity. Consequently, for this interface the current simulations give interfacial affinities of halide anions which are consistent with experiment and previous explicitly polarizable calculations. For the water/vapor interface, however, the present method overestimates the anionic surface affinities, which can be traced back to the abrupt change in the electronic part of the relative permittivity upon moving from the liquid to the gas phase.

TOC Graphics
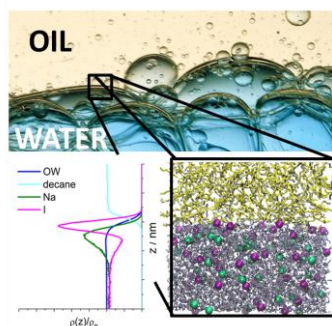
Keywords: ions, aqueous interface, charge scaling, molecular dynamics, polarizability.

It is now reasonably well established, both by computer simulations and spectroscopic experiments, that soft inorganic anions (such as iodide, bromide, thiocyanate, etc.) exhibit affinity for hydrophobic aqueous interfaces.[1-14] The molecular mechanism behind this phenomenon, which is at odds with simple electrostatic considerations,[15, 16] is rather complex, involving both enthalpic and entropic contributions from the solute and the solvent.[7, 12-14, 17, 18] One of the forces that drive soft (polarizable) ions to hydrophobic aqueous interfaces originates from the ability of water molecules to polarize the ion and vice versa.[17, 19] The effect of the stabilizing polarization interaction can be seen, e.g., from comparison between polarizable and non-polarizable molecular dynamics (MD) simulations, with the latter yielding as a rule weakened interfacial propensities of soft ions.[19, 20]

It has been suggested recently that in order to compensate for the lack of polarization in non-polarizable models of aqueous electrolytes, the ions should be assigned charges which are scaled by a factor of $1/\sqrt{\varepsilon_e}$. Here, ε_e is the part of the relative permittivity, which is due to electronic degrees of freedom and which can be taken as the high frequency dielectric permittivity (ε_e =

2

1.78 for water).[21, 22] In this way, the electronic polarization effects in the whole system are accounted for effectively within an electronic continuum correction (ECC), as evidenced from Eq. 2.8 in Ref. 21. Note that the partial charges on water oxygen and hydrogen atoms have already been effectively scaled when developing common non-polarizable water force fields by fitting to experimental properties of water.[21, 22] Our recent results show that ECC significantly improves properties of bulk aqueous salt solutions compared to non-polarizable simulations, yielding agreement with experimental structural data comparable to explicitly polarizable force fields.[23, 24] However, the applicability of ECC to aqueous interfaces has not been systematically examined yet. Encouragingly, recent simulations[14] of iodide with its charge scaled (however, without any reference to the effective polarization method) by $0.75 - 0.8$, i.e., accidentally almost exactly by the ECC factor, showed enhanced surface affinity compared to that from non-polarizable simulations with a full charge on the ion. It is, however, questionable, if ECC, which assumes homogeneous electronic solvent environment, is justified for the description of the approach of an ion to the water/vapor interface with ε_e sharply dropping to 1. A more consistent with the spirit of ECC would be modeling ions at the water/oil interface, since the values of ε_e are comparable in the two media (e.g., $\varepsilon_e = 2$ for decane).[21, 22, 25] The water/oil interface thus does not represent an appreciable discontinuity in the electronic polarization properties of the system. In this study we explore the behavior of halide anions at the aqueous solution/decane interface employing non-polarizable MD simulations with ECC. We show that in these cases the simulations yield reliable results in quantitative agreement with experiment,[26, 27] while at the aqueous solution/vapor interface the ionic propensities are overestimated due to the discontinuity in the electronic part of the relative permittivity upon moving from the aqueous bulk to the vapor.

Solution/decane interface. Density profiles, i.e., averaged densities from MD simulations with ECC of halide anions along the normal to the solution/decane interface are depicted in Figures 1.
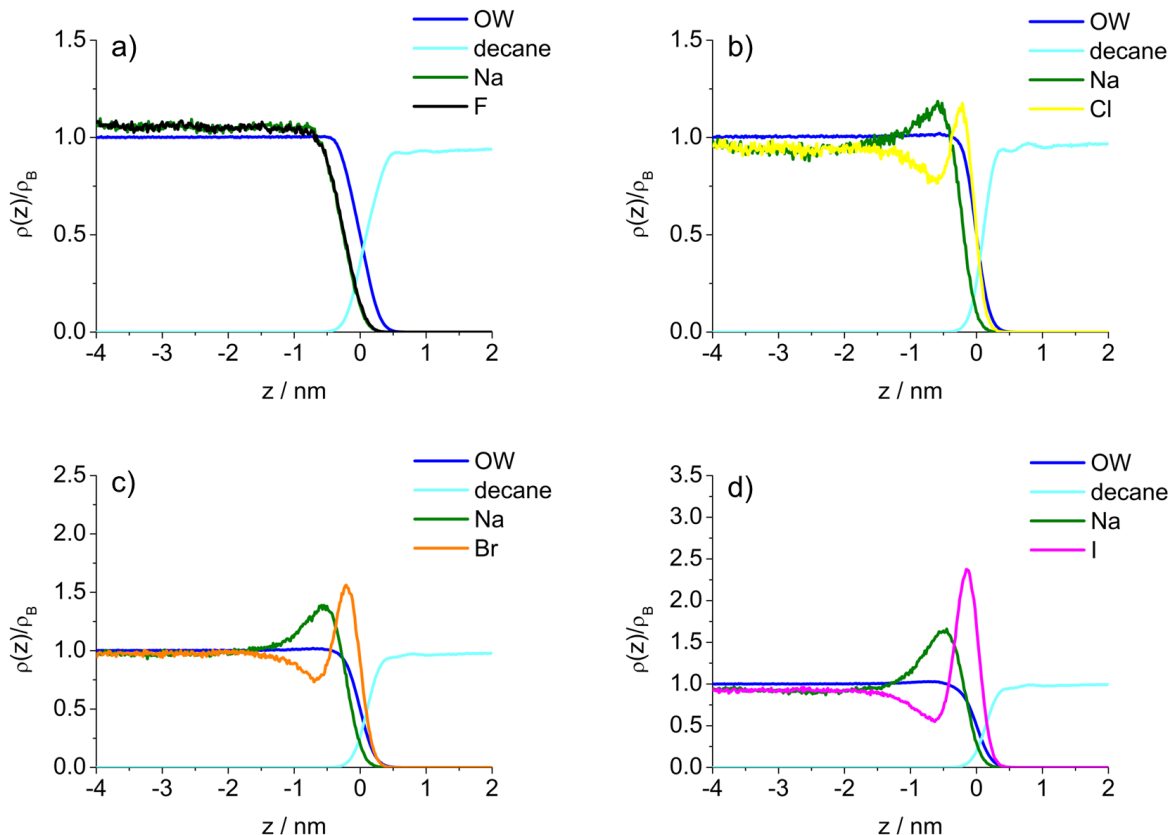
Figure 1 *Symmetrized number density profiles $\rho(z)$ with the ECC charges of water oxygen (blue), decane CH_n groups (cyan), sodium (olive green), and various ions: (a) - fluoride (black), b) chloride (yellow), c) bromide (orange) and d) iodide (magenta), respectively, plotted vs. slab distance z and normalized by the bulk density of water ρ_B at the solution/decane interface. Ion densities have been scaled by water/ion concentration ratio of 55.56. The Gibbs dividing surface for water is taken as the origin of the z-coordinate in all cases.*

These results demonstrate that propensities of the anions for the interface follow the series $F^- <$ $Cl^- < Br^- < I^-$. Fluoride is directly repelled from the solution/decane interface, while the heavier halides exhibit an increasing interfacial concentration peak, followed by a depletion zone just below the interface. In these cases, the charge compensating counter-ion, i.e., sodium exhibits a peak in the anion depletion zone, which leads to a formation of an effective electric double layer at the interface.[7] The net interfacial excesses of ions (with respect to the bulk) and the corresponding changes in interfacial tension compared to the neat water/decane interface are shown in Table 1.

Table 1 *Interfacial excesses (in ions/nm^2) calculated from ionic density profiles and changes in interfacial tension with respect to pure water $\Delta\gamma$ (in mN/m/M) from MD simulations with the ECC of different ionic solutions at the solution/decane interface.*

	NaF	NaCl	NaBr	NaI
interfacial excess	-0.15	0.00	0.06	0.24
$\Delta\gamma$	0.9 ± 0.9	0.0 ± 0.9	-0.9 ± 0.7	-3.2 ± 1.0

The interfacial excess is negative for F^-, roughly zero for Cl^- and Br^-, and positive for I^-. This is inversely connected with the change in interfacial tension compared to neat water,[7, 28] which is positive for F^-, close to zero for Cl^- and Br^-, and negative for I^-. Semiquantitatively and within the statistical error, the calculated results agree with earlier measurements showing that iodide (unlike the lighter halides) indeed behaves as a weak surfactant at the solution/decane interface,

decreasing the interfacial tension.[26] The present ECC results are also consistent with earlier explicitly polarizable simulations showing a weak free energy minimum at the interface between water and another hydrophobic liquid – dichloromethane, which, however, has a larger dielectric constant than decane.[29] In contrast, test calculations without the ECC correction, i.e., non-polarizable simulations with full ionic charges yielded, inconsistently with experiment,[26] negative interfacial excesses and, correspondingly, increase in surface tension, for all halides (including iodide). This further underlines the importance of inclusion of polarization effects for accurate description of interfacial behavior of soft ions.[1, 3, 17, 19]

Solution/vapor interface. Unlike the water/oil interface, which is electronically almost homogeneous (since the electronic part of the relative permittivity is of comparable value in water and in alkenes[21, 22, 25]), the water/vapor interface exhibits a discontinuity in the electronic relative permittivity from 1.78 to 1. A straightforward application of ECC, which assumes an electronically homogeneous medium, should thus lead to an overestimation of the ionic surface affinity, since the ionic charges are too small ("overscaled") as if the electronic part of the relative permittivity was the same in vapor and water. Overestimation of the charge scaling and, consequently, of the ionic surface affinity indeed happens in the present simulations. This is demonstrated in Figure 2 and Table 2 which (analogously to Figure 1 and Table 1 for the solution/decane interface) show the ion density profiles, surface excesses, and changes in surface tension for the alkali halide solution/vapor interfaces. Except for fluoride, all the heavier halides exhibit a significant surface affinity, which is also reflected in large positive surface excesses and, consequently, negative changes in surface tension, increasing in absolute value in the order $Cl^- < Br^- < I^-$. This surface affinity is larger than that observed previously using explicitly polarizable force   fields[1-3, 7, 9] (which themselves tend to overestimate the surface ion effect,

but for a different reason connected with an undamped polarization response in most models[30])
and it is not consistent with measured positive surface tension increments.[31] In principle, one
could try to introduce a reduced scaling of the ionic charges to account for the lower electronic
relative permittivity of the vapor phase compared to water. This would correctly lead to reduced
ionic surface affinities, however, potentially at the expense of stretching the ECC approach
beyond its range of applicability, which encompasses electronically homogeneous (or at least
approximately homogeneous) environments.
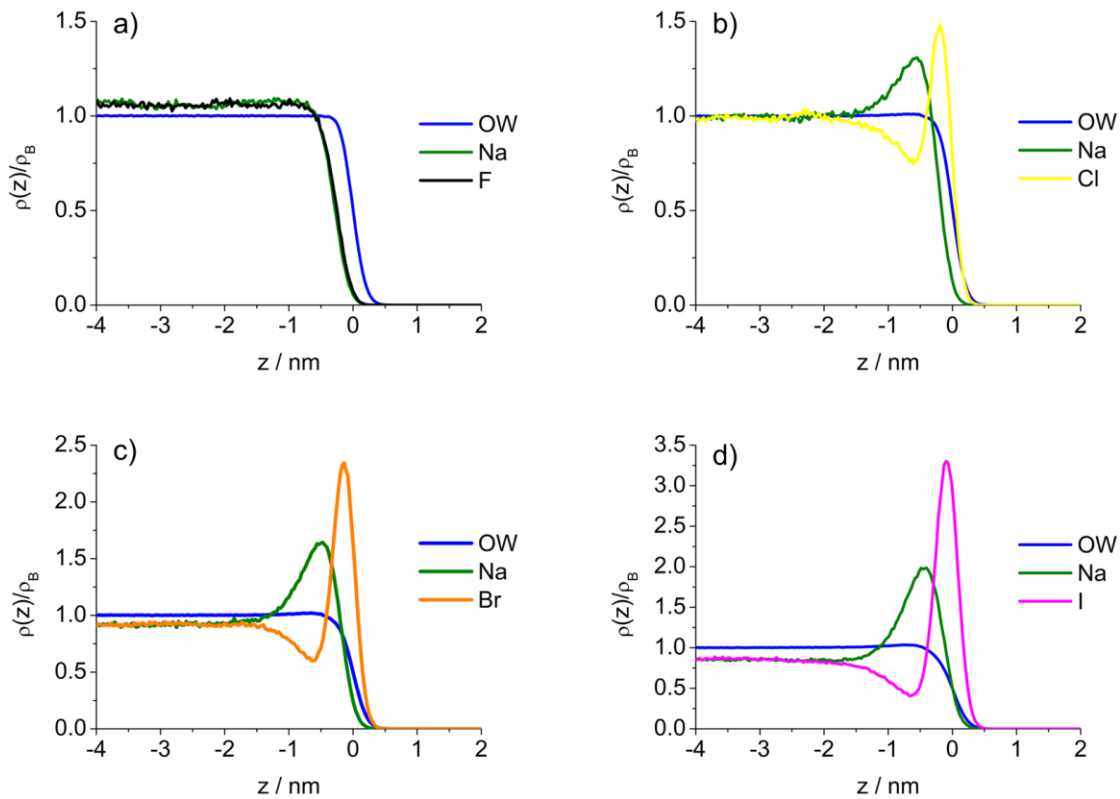
Figure 2 *Symmetrized number density profiles $\rho(z)$ with the ECC charges of water oxygen (blue),*

sodium (olive green), and various ions: (a) - fluoride (black), b) chloride (yellow), c) bromide

(orange) and d) iodide (magenta), respectively, plotted vs. slab distance z and normalized by the

bulk density of water ρ_B at the solution/vapor interface. Normalization of the graphs is the same as in Figure 1.

Table 2 *Surface excesses (in ions/nm^2) calculated from ionic density profiles and changes in surface tension with respect to pure water $\Delta\gamma$ (in mN/m/M) from MD simulations with the ECC of different ionic solutions at the solution/vapor interface.*

	NaF	NaCl	NaBr	NaI
surface excess	-0.35	0.06	0.44	1.04
$\Delta\gamma$	1.3 ± 0.8	-0.1 ± 0.9	-2.4 ± 1.0	-6.8 ± 1.1

Conclusions. We have shown that MD simulations which account for electronic polarization effects in an effective continuum-like way via rescaling ionic charges describe reasonably well the affinities of heavier halides for the water/oil interface. The simple and computationally cheap ECC correction thus works well not only in bulk electrolytes,[21-24] but also at aqueous interfaces with hydrophobic liquids, where charge scaling leads to increased ionic interfacial affinities. This is not only an important methodological finding but also a support for the physical fundamentals of the effective way of accounting for polarization effects. At the water/vapor interface, which is (unlike the oil/water interface) strongly discontinuous in terms of the electronic part of the relative permittivity, the ECC approach is, however, reaching limits of its applicability and, consequently, tends to overestimate the ionic surface affinities.

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Methods. We performed 50 ns molecular dynamics (MD) simulations of a series of 1m aqueous solutions of alkali halides (fluoride, chloride, bromide and iodide) at the solution/decane and solution/vapor interfaces. All systems were first equilibrated for at least 50 ns (solution/decane interface) or 1 ns (solution/vapor interface). For solution/vapor interfaces, MD simulations were performed at a constant temperature of 298 K employing the velocity-rescale thermostat.[32] The unit cell contained 207 cations, 207 anions and 11502 SPC/E[33] water molecules. The size of the unit cell was 6 nm × 6 nm × 30 nm, with the thickness of the aqueous phase being 10 nm. To generate solution/decane interfaces, additional 650 decane molecules were placed symmetrically at both solution/vapor interfaces. These MD simulations were also performed at 298 K, with an anisotropic pressure coupling applied in the z-direction and constant pressure of 1 bar maintained by the Berendsen barostat.[34] The size of the unit cell for solution/decane simulations was roughly 6×6×16.2 nm with the same thickness of the aqueous phase as for the solution/vapor simulations.

Surface excesses of ions were calculated from the ion density profiles taking the water surface excess equal to zero, consistent with our previous work,[35] Surface tension was calculated from the asymmetry of the pressure tensor[7] as $\gamma = \frac{1}{2} L_z \left\langle P_{zz} - \frac{1}{2}(P_{xx} + P_{yy}) \right\rangle$, where L_Z is the dimension of the unit cell in the direction perpendicular to the interface and P_{xx}, P_{yy}, and P_{zz} are the diagonal components of the pressure tensor. For simulations involving solution/decane interfaces, the pressure tensors were calculated from auxiliary MD simulations without pressure coupling within NVT ensemble with average box size obtained from MD simulations with the anisotropic pressure coupling.

Parameters for the ions were taken from Ref. [36], while decane was represented by the TraPPE united atom force field.[37] Electronic polarization effects were accounted for in an

effective way by introducing ECC,[21, 22] which is practically realized by rescaling all ionic charges

by $\dfrac{1}{\sqrt{\varepsilon_{el}}}$, where $\varepsilon_{el}=1.78$ is the electronic part of the static relative permittivity of water (i. e., the

scaling factor equals to 0.75).[21, 22] 3D periodic boundary conditions were used with long range

electrostatic interactions beyond the non-bonded interaction cutoff of 1.0 nm being accounted for

using the particle-mesh Ewald procedure.[38] The LINCS algorithm was employed to constrain all

bonds containing hydrogen atoms.[39] Equations of motion were integrated using the leap-frog

algorithm with a timestep of 2 fs. All MD simulations were performed using the program

GROMACS 4.0.7.[40]

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