

Comment on Article “An Explanation of the Charge at Water’s Surface”

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Abstract

The rationalization of the observed negative charge on the surface of water in terms of accumulation of OH⁻ in the commented article (A. Gray-Weale and J. K. Beattie *Phys. Chem. Chem. Phys.* 2009, 11, 10994-11005) is based on a supposedly uniquely large dielectric decrement of hydroxide solutions. We challenge this rationalization and point to another ion, namely fluoride, which has a comparable dielectric decrement and size and which is repelled from water surface.

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The dielectric decrement, i.e., the decrease of the static dielectric constant upon adding an electrolyte, is an intricate quantity which reflects more than just the response of water to added ions. Namely, it is the sum of solute and solvent contributions.¹ It is true that the former term vanishes for practically fully dissociated electrolytes, such as NaOH or NaCl (but not, for example, for NaF).¹ However, even the second term – called “solvent permittivity” in the Appendix 7.3 of Ref. 1, is not just water response but also a volume effect since water density decreases with added electrolyte. This volume effect, which dominates solutions of weakly hydrated electrolytes, like tetraalkylammonium halides, can be very large and easily produce dielectric decrements, $-d\varepsilon/dc$, which may exceed $-d\varepsilon/dc$ values of strongly hydrated solutes, such as NaOH (see Figure 1).² Therefore, the dielectric decrement is not the most appropriate quantity to build upon a theory of water response to ions.

With the above caveat, let us look more closely on claims made in the commented article.³ On p. 11022, the authors state explicitly: „If an ion could be found that had both a high dielectric decrement and reduced polarisation fluctuations confined to a small enough region (*i.e.* a small value of a), but no surface affinity, then our theory would be disproved.”³ Here is such an ion – fluoride. The solvent dielectric decrement of aqueous NaF is $19.9 \pm 1.0 \text{ M}^{-1}$.¹ For aqueous NaOH the authors of the commented article adopted from Ref. 4 a value of dielectric decrement of $20.9 \pm 0.8 \text{ M}^{-1}$. Thus, these two values are the same within the experimental error, as are the experimental data for the “solvent permittivity” for $c < 0.3 \text{ M}$ (see Figure 2). This leaves aside the fact that the authors of the commented article neglected the non-linear term in Eq. 4 in Ref. 4, which makes the dielectric decrement of NaOH smaller (equal to about 14 M^{-1} for concentrations up to 1M).

Since F^- is isoelectronic with and has the same charge as OH^- , the two anions have also almost identical ionic radii.^{5,6} Consequently, both ions exhibit same positions of peaks on

the ion-water radial distribution function.⁷⁻¹⁰ It is true that the first water shell around hydroxide is somewhat different (more asymmetric) than that around fluoride,⁹ however, this difference cannot be described within the crude model presented in the commented article.³ Thus, the reduced solvent polarization fluctuations around F^- are confined to the same small region as around OH^- ; in other words, these two ions have comparable values of the range parameter a .³ At the same time, there is broad experimental and computational consensus that fluoride has a vanishing affinity for water surface.¹¹⁻¹⁴

Further disproof of the theory outlined in the commented article³ comes from our molecular dynamics of dielectric decrements in aqueous solutions of sodium hydroxide and sodium halides. To this end, we have used the procedure for evaluating static dielectric constants of solutions from the correlation functions of the total dipole moment, as implemented for non-polarizable force fields in the Gromacs program.^{15,16} For water, we adopted the SPC/E model¹⁷ and for Na^+ , OH^- , F^- , and Cl^- we used Lennard-Jones parameters from our previous studies.^{12,18} To check the robustness of our results with respect to the particular choice of potential parameters we also simulated a “small fluoride” with the van der Waals radius of Li^+ , i.e., reduced by about 30 % compared to F^- . The total (i.e., solvent and solute) dielectric decrements $\Delta\epsilon = \epsilon(0) - \epsilon(c)$ calculated for 1 M solutions compare very favorably to experimental values¹ (see Table 1). Note that the comparison is direct since the simulations automatically account for the volume effect and ion pairing.

Let us now use the above simulations to reinvestigate the propensity of fluoride for the surface. In Figure 3 we show the free energy profiles of bringing fluoride (both within the original parameterization and the “small F^- ”) across the vapor/water interface. This results come from our molecular dynamics simulations of a single ion in aqueous slab geometry, which explicitly account for the water dipole fluctuations both in the bulk and at the interface.

Figure 3 clearly demonstrates that fluoride (and also the “small F⁻”) is repelled from the water surface. Also note that in this case inclusion of polarization would change little on the present conclusion since F⁻ is a hard, non-polarizable ion, as shown in previous simulations with a polarizable force field.¹² To reiterate and conclude, the observed repulsion of fluoride from water surface is in contradiction with the predictions of the model presented in the commented article.³

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Table 1: Simulated and experimental (interpolated to 1 M) total solvent dielectric decrements, $\Delta\epsilon = \epsilon(0) - \epsilon(c)$ of investigated $c = 1$ M aqueous solutions.

Solute	$\Delta\epsilon$ MD simulation	$\Delta\epsilon$ experiment ^{1,4}
NaOH	12 ± 1	13.8 ± 1
NaF	13 ± 1	10.1 ± 0.7
NaF (small F ⁻)	9 ± 1	---
NaCl	14 ± 2	-12.8 ± 0.3

Figure captions

Figure 1: Fit curves for the “solvent permittivities” (according to the terminology of Ref. 1 of aqueous solutions of tetramethyl, tetrapropyl and tetrabutyl ammonium bromide obtained from the data of Ref. 2 compared with the corresponding data (●) and fit curve for NaOH(aq).⁴

Figure 2: Experimental solvent dielectric decrements of aqueous solutions of NaOH and NaF as functions of solute molarity.^{1,4}

Figure 3: Free energy profiles of fluoride (black) and “small F⁻” (red) as they move across the vapor/water interface. We see that in both cases there is the same repulsion of the anion from the surface (with the Gibbs dividing surface situated at $z = 0$) into the aqueous bulk. The inset shows the ion – water oxygen radial distribution functions demonstrating the different sizes of the two simulated anions.

Figure 1

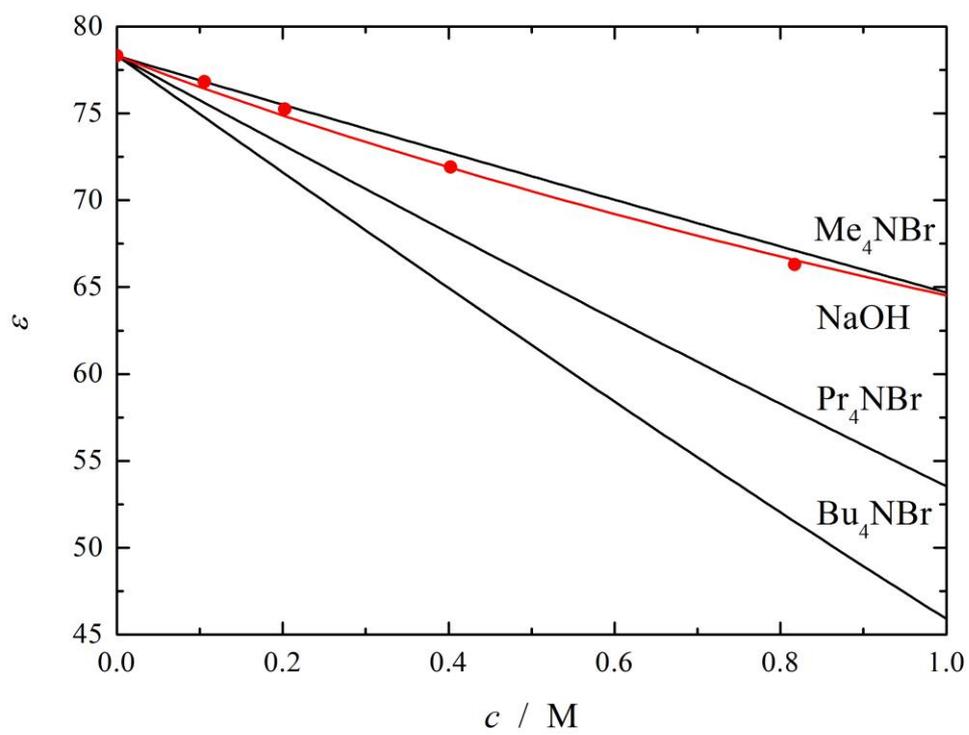


Figure 2

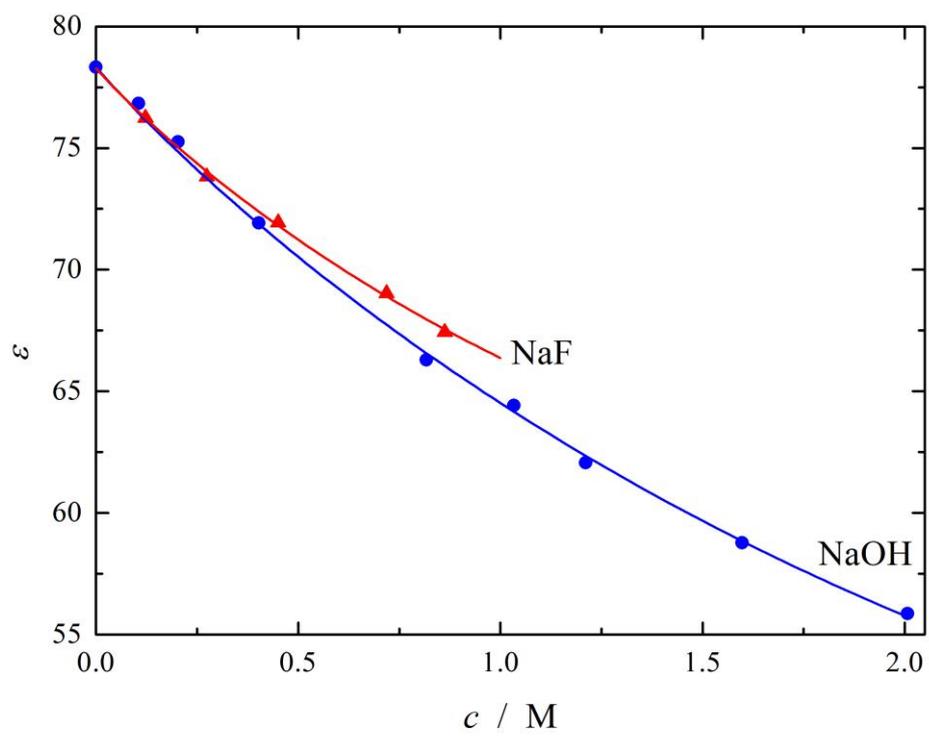
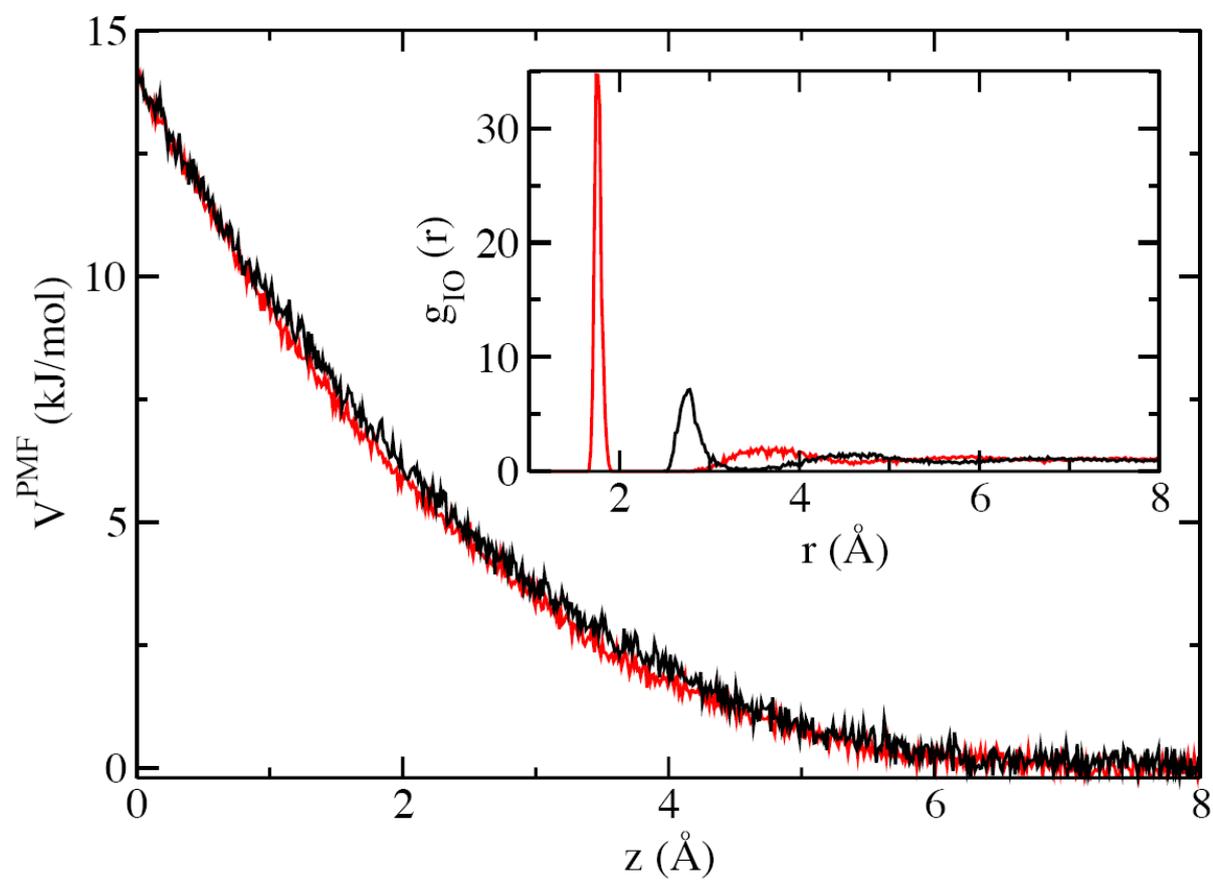


Figure 3:



Supplementary information

The dielectric decrements were calculated using molecular dynamics simulations, employing the GROMACS program package.¹ Each simulated system contained 783 water molecules, 14 sodium cations, and 14 anions, corresponding to 1M solution of NaF, NaCl, and NaOH. Water was constrained with SETTLE algorithm.² Production runs of 19 ns were carried out with a 2 fs time step after 1 ns of equilibration. The system was kept at pressure of 1 atm and temperature of 300 K using the Berendsen barostat and thermostat.³ Barostat scaling time was 2 ps with compressibility of $4.5 \cdot 10^{-5} \text{ bar}^{-1}$, while the thermostat time constant was set to 1.0 ps. The van der Waals and Coulomb interactions were cut-off at 1.1 nm and the long-range Coulomb interactions were accounted for using the Particle Mesh Ewald (PME) Method⁴ with Fourier spacing grid of 0.12 nm. Details concerning calculation of free energy profiles of ions moving across the air/water interface are given in our previous study.⁵ We just note here that the size of the unit cell, $3 \times 3 \times 9 \text{ nm}$ is large enough to make the interactions between periodic images of the aqueous slabs negligible.⁶

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Graphical abstract

The dielectric decrement of fluoride, which is repelled from water surface, coincides with that of hydroxide at low concentrations.

