

Thermodynamics of hydronium and hydroxide surface solvation

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Abstract

The concentration of hydronium and hydroxide at the water-air interface has been under debate for a long time. Recent evidence from a range of experiments and theoretical calculations strongly suggests the water surface is somewhat acidic. Using novel polarizable models we have performed potential of mean force calculations of a hydronium ion, a hydroxide ion and a water molecule in a water droplet and a water slab and we were able to rationalize that hydronium but not hydroxide is slightly enriched at the surface for two reasons. First, because the hydrogen-bond acceptance capacity of hydronium is weaker than water it is more favorable to have the hydronium oxygen on the surface. Second, hydroxide ions are expelled from the surface of droplets, due to the entropy being lower when a hydroxide ion is hydrated on the surface. As a result, the water dissociation constant pK_w increases slightly near the surface. The results are corroborated by calculations of surface tension of NaOH solutions that are in excellent agreement with experiment. The structural and thermodynamic interpretation of hydronium and hydroxide hydration provided by these calculations opens the route to a better understanding of atmospheric and surface chemistry.

Atmospheric chemistry is different from bulk chemistry because reactions can take place in the gas phase or in contact with aerosols. For instance, the air-water interface increases reaction rates for processes in the ozone cycle, like oxidation of halide ions by OH radicals or O₃ [1]. Due to the multitude of different constituents, both natural, e.g. from seawater, volcanic sources, or dust from deserts, and anthropogenic, e.g. from industrial sources, detailed models of the atmospheric composition are very complex [2]. Recent *in situ* measurements of cloud seeding agents have shown that effective ice-nucleation particles are primarily dust or metallic particles [3]. Both the details of reactions under atmospheric conditions and models of the atmosphere as a whole are influenced by the inherent properties of water droplets with dissolved molecules. We have previously shown that the concentration of organic materials and ions may be reduced or enhanced at the water droplet-air interface [4–6]. In this work we revisit the surface p[H] and p[OH] (hydronium resp. hydroxide concentrations) of atmospheric water droplets and, for comparison, water slabs, which are influenced by the presence of organic components, carbon dioxide, ions and indeed dust particles [2]. The composition and pH of aerosols varies with seasons and location on the earth; it has been characterized on many places and is most often acidic [7–9]. This variation has been shown to be important for modeling of clouds [10].

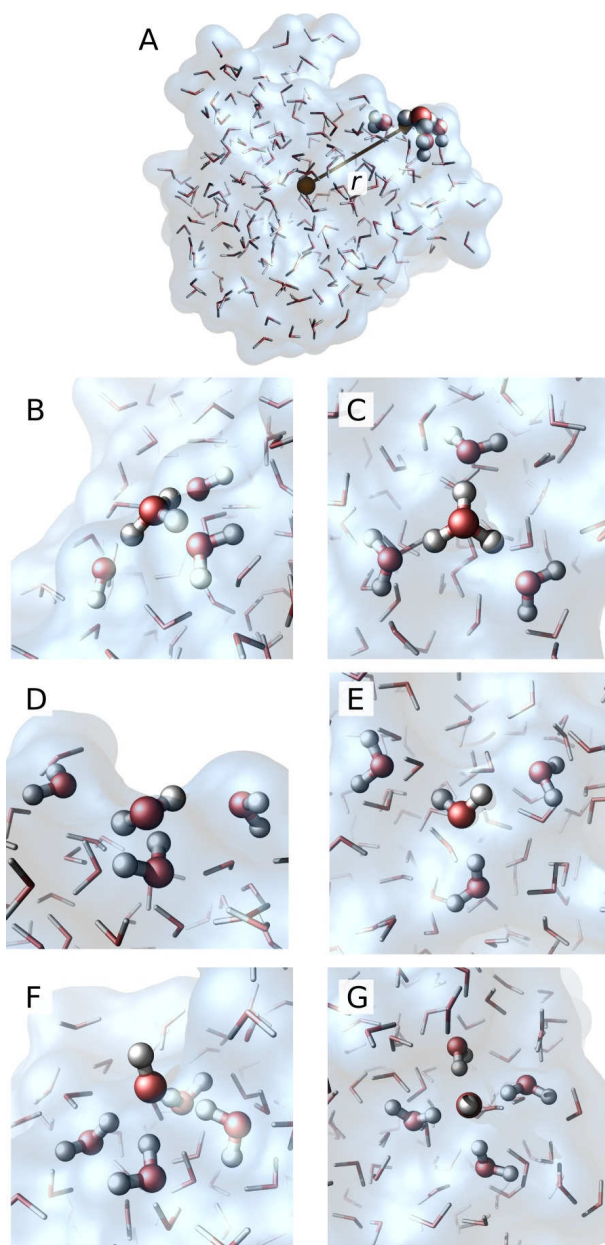


Figure 1: A) Simulation snapshot of a water droplet with a hydronium ion at the surface. Orientation on the droplet surface in side view and top view for B,C) hydronium, D,E) water and F,G) hydroxide. Water molecules that form a hydrogen bond to the solute are shown as ball-and-stick models, visualizing the coordination number of the solute at the surface.

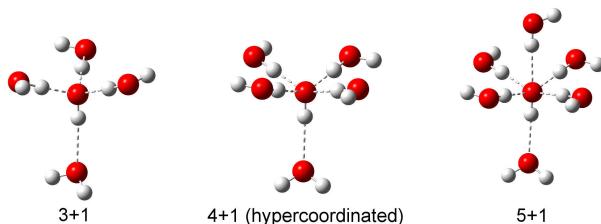


Figure 2: Hydroxide complexed by 3, 4, or 5 water molecules. The numbers refer to the number of hydrogen bonds with O^* and H^* , respectively.

During the last few years a number of experimental [11–15] and theoretical [12, 16–20] studies have shown that there is an enhancement of H_3O^+ on water surfaces. The answer to why this is the case has not yet been fully addressed. By focusing on small water droplets (1A), we describe here why the outermost surface (the first few Ångström) is slightly positively charged in droplets. Existing molecular models are not able to reproduce the structure of hydroxide in water correctly, yielding too large coordination numbers or inaccurate radial distribution functions [21–24]. *ab initio* simulations, in contrast, yield the correct solvation but they do not provide converged free energies and enthalpies due to higher computational cost. To obtain the appropriate solvation structure with a reduced computational cost, we therefore developed state-of-the-art polarizable models for hydroxide and hydronium that work in conjunction with the SWM4-NDP water model [25]. Details on the new models are given in the supporting information.

The hydroxide ion predominantly forms a hypercoordinated structure in dilute aqueous solutions [21, 26–35] (2). The hydroxide oxygen (O^*) accepts four hydrogen bonds in a square planar configuration. In addition, the hydroxide hydrogen (H^*) can donate a weak hydrogen bond [21, 26–31, 36]. Occasionally, the O^* coordination changes to 3-fold [21, 22, 27, 28, 30, 34, 35, 37] or 5-fold [22, 34]. For the hydronium the dominant structure in bulk is a dynamically distorted Eigen complex [38–46]. The coordination of the hydroxide observed in bulk simulations using our model is very similar to what was obtained in Car-Parinello MD (CPMD) simulations (1). Further validation of the hydronium and hydroxide models showed excellent agreement to *ab initio*, Fourier transform infrared (FTIR), neutron diffraction and X-ray structural data (see supporting information).

With these new models we studied the hydronium and hydroxide ions in a water droplet, and, for comparison also a water molecule (1). Earlier studies

Table 1: Population (in %) of various hydroxide complexes in bulk water using our new model. In the notation (X+Y) X and Y refer to the number of hydrogen bonds with O* and H*, respectively. CPMD data from ref[22].

Model	3+0	3+1	4+0	4+1	5+0	5+1
Our model	< 1	< 1	50	43	3	3
CPMD	6	9	30	45	4	5

of pure water droplets [47] and water droplets containing alkali or halide ions [4, 5] have shown that the simulated properties of such systems critically depend on the model used. Using state of the art polarizable models [25, 48] we recently disentangled the complex energetics underlying surface solvation preferences of the halide ions [5].

The potentials of mean force (PMF) in a water droplet are shown in 3 along with a breakdown into enthalpy $\Delta H(r)$ and entropy $-T\Delta S(r)$. Here, the distance r between the center-of-mass (COM) of the droplet and the COM of the solute was taken as reaction coordinate (1A). The inside (bulk) of the droplet is taken as the reference point where the energy was defined to zero. 3A confirms earlier experimental [11–15] and theoretical[12, 16–20] work showing that hydronium is preferentially solvated at the water surface. The enthalpic contribution to the PMF for hydronium solvation is stronger than the unfavorable entropic contribution (3B,C), demonstrating that the surface preference of hydronium is an enthalpic effect. Hence, the thermodynamics for hydronium solvation is different from small hydrophobic particles, which are expelled from bulk water mainly by an entropic effect at room temperature.[6, 49] For hydroxide the enthalpic contribution is almost flat, whereas entropy favors the bulk, similar to the case of the fluoride ion [5]. As expected, the PMF curve for water is approximately zero until it gets outside the droplet, and it therefore lies in between the hydroxide and hydronium curves. A similar plot of the free energy profile for a hydronium and a hydroxide ion in a water slab is given in Figure S6 of the supporting information.

By decomposing the enthalpy into water-water and water-ion interaction energies we are able to further rationalize the causes underlying surface solvation. The diffusion of hydronium from surface to bulk leads to a rupture of favorable water-water interactions (4A), which, remarkably, is not counter-balanced by any increased hydronium-water interaction (4B). The mechanis-

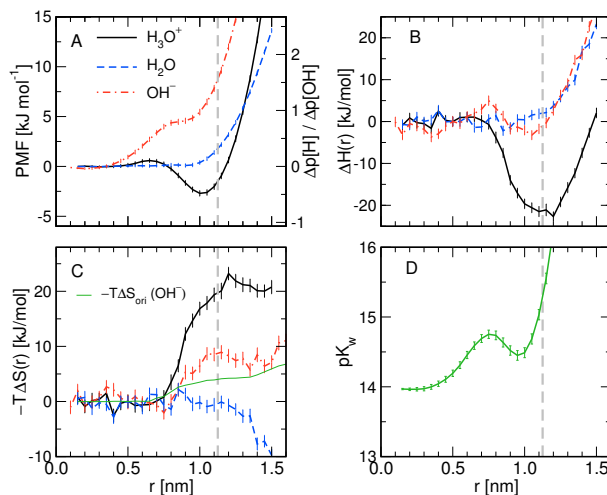


Figure 3: A) potential of mean force (PMF), B) enthalpy and C) entropy as a function of position r in a water droplet (visualized in 1) for hydronium (black/solid line), water (blue/dashed) and hydroxide (red/dot-dashed). (C, green) Orientational entropy of hydroxide. D) pK_w as a function of position in the droplet. The grey dashed line indicates the Gibbs dividing surface.

tic reason for this being that hydronium is a weaker hydrogen bond acceptor than water. This behavior contrasts that of positive alkali ions that are solvated inside droplets [5] due to strong ion-water interactions. The energetics of hydronium solvation is qualitatively similar to what was found for the *negative* halide ions, Cl^- , Br^- and I^- (but not F^-). For hydroxide, weakening of ion-water and strengthening of water-water interactions near the interface exactly cancel, demonstrating that the bulk preference is a purely entropic effect. The enthalpy components for solvation of water in a water droplet also cancel each other.

Gray-Weale and Beattie suggested that hydroxide ions are surface-bound (or rather slightly below the surface) based on surface-tension data and Poisson-Boltzmann calculations [50–52]. They estimated that the hydroxide surface affinity should be on the order of $20 k_B T$, or 50 kJ/mol at room temperature. These values are an order of magnitude larger than the effects seen here and in previous experiments [11, 13–15] and calculations [16–20]. Mundy *et al.* have performed *ab initio* MD simulations [53] and find a surface preference of OH^- of just $1 k_B T$. While *ab initio* simulations are in principle more general than classical simulations, they cannot provide the same

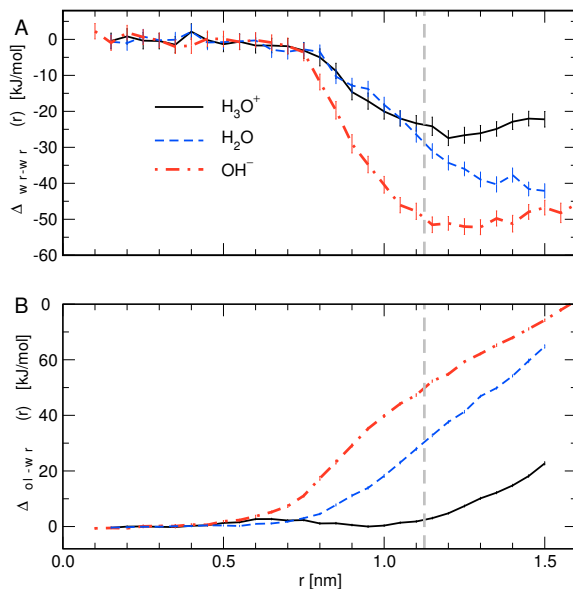


Figure 4: Decomposition of enthalpy (3B) into interaction energies for each of three solutes as a function of distance r from the droplet center (visualized in 1). The grey dashed line indicates the Gibbs dividing surface.

rigorous sampling. We have computed the surface tension for sodium hydroxide solutions at five concentrations (Table S3). The increase in surface tension upon addition of salt is about 0.88 mN/m (Figure S7), smaller than the experimental value of 2 mN/m [54]. However, in line with the PMFs, the density profile (Figure S7C) shows that hydroxide and sodium ions predominantly reside in the bulk, suggesting that an increased surface tension is not an indicator for surface affinity. In summary we find that the hydroxide surface affinity is approximately +4 kJ/mole – hence preferring the bulk – where it is -3 kJ/mole for hydronium – preferring the surface), (see 3). These findings are in agreement with a large body of evidence[11–20]. This surface enhancement of H_3O^+ in a neat water droplet corresponds to a slightly lower surface $\text{p}[\text{H}]$, which coincides with an increased surface $\text{p}[\text{OH}]$ (3A, right y-axis). As a net result, the autodissociation constant pK_w is slightly increased near the surface, which might affect the protonation state of pH indicator dyes (3D, details in the supporting information). The concentration of H_3O^+ in atmospheric water droplets will be further enhanced by the hydrolysis of carbon dioxide to carbonic acid, or due to the presence of dust particles[2].

Can our present results be generalized to other ions in order to predict their bulk/surface preference? There are both positive as well as negative ions that are preferentially solvated on the droplet surface (e.g., H_3O^+ , Cl^- , Br^- , I^-) while there are other positive as well as negative ions that are solvated in the bulk (e.g., OH^- , F^- , alkali ions and the ammonium ion[4]). In addition, inverting the charge of the large halide ions *in silico* eliminates their surface preference[5]. Neither the sign, nor the polarizability of the ion is sufficient to explain the surface preference and it is therefore unlikely that surface/bulk preference can be rationalized using continuum descriptions of water such as Poisson-Boltzmann calculations, since a) water is an inherently asymmetric molecule and b) entropic effects play a significant role as well. Experiments that do not probe the molecular scale, might not give conclusive evidence about surface acidity [55]. In the best of worlds a theoretical model should be able to reconcile the available measurements, and developing models that find the right balance between accuracy and computational tractability was one of the goals of this work.

Structural insight into the bulk/surface hydration is given in 5 that presents the probability for the orientational angle θ between molecular dipole and the axis between the droplet center and the center of mass of the solute. The probabilities are normalized by the PMF for the respective solute, thus presenting the two-dimensional probability $P(r, \cos(\theta))$. All three solutes are isotropically distributed inside the droplets ($r < 0.5 \text{ nm}$). On the surface ($r \approx 1 \text{ nm}$), in contrast, hydronium is strongly oriented with the dipole pointing to the droplet center (that is, with the oxygen on the outside, 1B/C). Water molecules at the surface display only a weak preference for the oxygen pointing slightly inwards (1D/E). The second orientational vector of the water molecule connecting the two hydrogen atoms is nearly randomly oriented at the surface (not shown). The hydroxide ion, if located at the surface, is oriented parallel to the distance axis as well, but in this case with the oxygen on the inside (1F/G). Analysis of the Shannon entropy of $P(r, \cos(\theta))$ shows that only 50% of the reduced entropy for OH^- being at the surface (3C, red) is due to the reduced rotational freedom (3C, green), suggesting that alterations in the water entropy are important as well. These structures are consistent with the notion that hydronium is a weak hydrogen bond acceptor whereas hydroxide is a weak hydrogen bond donor.

The results presented here, in conjunction with earlier results on alkali- and halide ions [5], show first of all that water is a complex material, which can not be described by macroscopic models if effects on the molecular scale

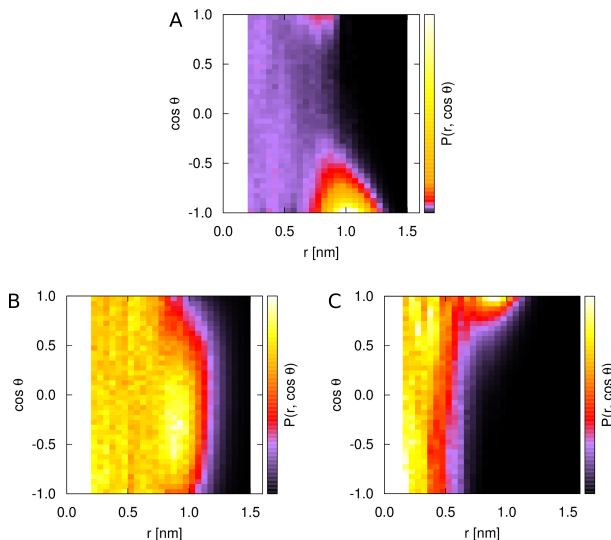


Figure 5: Orientation distribution for A) hydronium, B) water and C) hydroxide in a water droplet as a function of distance from the center of the droplet r , as in 1A. θ is the angle between the dipole vector of the solute and the vector from the center of the droplet to the oxygen atom of the solute.

are of importance. The hydroxide model devised in this work is probably the first simulation model to have the correct solvation structure and henceforth it yields a significant improvement in the ability to model subtle phenomena. It is demonstrated here that hydronium is surface bound and hydroxide is not. Much of the debate in the literature on whether the surface of water is basic or acidic involves ionic solutions or water at non-neutral pH, and we do not want to extrapolate our work to systems we have not tested explicitly. Nevertheless, it seems valid to infer that at neutral pH and low ionic strength, where the concentration of hydronium and hydroxide is very low, the surface of water is characterized by a slight hydronium enhancement. Beyond that, only direct experimental evidence, for instance in the fashion demonstrated by Petersen *et al.* [11, 13], probing the water surface at the molecular scale, should be regarded as definite proof in this matter.

The presence of H_3O^+ at the surfaces of aerosol particles might influence the production of bromine atoms, which in turn are involved in the depletion of stratospheric ozone [56, 57]. By rationalizing the hydronium and hydroxide concentration at the water droplet surface using PMF calculations, and

by previous work on droplet composition [4–6] we hope to contribute to improving models of the atmosphere [2] which in turn can contribute to more accurate predictions from climate models.

Methods Potential of mean forces (PMFs) were computed according to the protocol in refs. [5, 6] using constrained molecular dynamics simulations. Approximately 30 positions along the reaction coordinate r – the distance between COM of the solute and the COM of the water droplet (see 1) – were selected in the range $0.15 \text{ nm} \leq r \leq 1.5 \text{ nm}$ (1.7 nm for OH^-), with a distance of 0.05 nm between adjacent positions. Each position was simulated for 20 ns at a temperature of 293.15 K , where the first 50 ps of the trajectories was removed for equilibration. The PMFs were computed by integration of the mean force on the solute.

Statistical errors for all properties were computed using a binning analysis, and the errors in the PMFs using standard error propagation. The analytical entropy correction due to Neumann for spherical systems was applied to the PMFs [58], as in our previous work [5, 6].

$\Delta H(r)$ was computed from the average potential energy of the system relative to the same central region. Because the volume was constant (infinite) and the temperature was controlled the constant contribution from the temperature was considered not to affect the relative enthalpies. The entropic contribution the PMFs was henceforth computed as

$$-T\Delta S(r) = G(r) - H(r), \quad (1)$$

where $G(r)$ denotes the PMF. The interaction energies were computed by averaging of the sum of the respective Lennard-Jones and Coulomb interactions. Here, the polarization energy of solute and water were attributed to solute-water and water-water interactions, respectively. Simulations were carried out using the efficient GROMACS simulation software [59, 60], further details are given in refs. [5, 6] and in the supporting information. Water was described by the polarizable SWM4-NDP water model[61], in conjunction with the hydronium and hydroxide models developed here. The new models are available from the GROMACS Molecule and Liquid database [62] at <http://virtualchemistry.org>.

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