Thermodynamics of hydronium and hydroxide surface solvation†

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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 pKw increases slightly near the surface. The results are corroborated by calculations of surface tension of NaOH solutions that are in reasonable 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.

1 Introduction

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 condi-

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tions 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 pH 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

During the last few years a number of experimental11–15 and theoretical12,16–20 studies have shown that there is an enhancement of H3O+ on water surfaces. The answer to why this is the case has not yet been fully addressed. Here, we address the bulk/surface solvation of hydronium and hydroxide using a highly reduced system, that is, a single ion in a water droplet (Fig. 1A), and we describe why the outermost surface (the first few Ångström) is slightly positively charged in droplets.

2 Results and Discussion

Existing molecular models are not able to reproduce the structure of hydroxide in water correctly, yielding too large coordination numbers or inaccurate radial distribution func-
...ions 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 (Fig. 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 (Fig. 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).

**Fig. 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.

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

With these new models we studied the hydronium and hydroxide ions in a water droplet, and, for comparison also a water molecule (Fig. 1). Earlier studies 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 Fig. 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 (Fig. 1A). The inside (bulk) of the droplet is taken as the reference point where the energy was defined to zero. Fig. 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 (Fig. 3B,C), demonstrating that the surface preference of hydronium is an enthalpic effect. Hence, the thermodynamics for hydronium solvation is different from small hydrophobic

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**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.
particles, which are expelled from bulk water mainly by an entropic effect at room temperature.\textsuperscript{6,49} For hydroxide the enthalpic contribution is almost flat, whereas entropy favors the bulk, similar to the case of the fluoride ion\textsuperscript{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 (Fig. 4A), which, remarkably, is not counterbalanced by any increased hydronium-water interaction (Fig. 4B). The mechanistic 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\textsuperscript{8} due to strong ion-water interactions. The energetics of hydronium solvation is qualitatively similar to what was found for the negative halide ions, Cl\textsuperscript{−}, Br\textsuperscript{−} and I\textsuperscript{−} (but not F\textsuperscript{−}). For hydronium, 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. It is important to note, however, that the energetics of bulk/surface solvation may alter at high salt concentration due to interactions with nearby counter ions.

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.\textsuperscript{50–52} They estimated that the hydroxide surface affinity should be on the order of 20 kJ/mol, or 50 kJ/mol at room temperature. These values are an order of magnitude larger than the effects seen here and in previous experiments.\textsuperscript{11,13–15} \textsuperscript{16–20} Mundy et al. have performed ab initio MD simulations\textsuperscript{53} and find a surface preference of OH\textsuperscript{−} of just 1kJ/mol. While ab initio simulations are in principle more general than classical simulations, they cannot provide the same 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.\textsuperscript{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), (Fig. 3). These find-
ings are in agreement with a large body of evidence\textsuperscript{11–20}. This surface enhancement of H$_3$O$^+$ in a neat water droplet corresponds to a slightly lower surface p[H], which coincides with an increased surface p[OH] (Fig. 3A, right y-axis). As a net result, the autodissociation constant p$K_w$ is slightly increased near the surface, which might affect the protonation state of pH indicator dyes (Fig. 3D, details in the supporting information). The concentration of H$_3$O$^+$ in atmospheric water droplets will be further enhanced by the hydrolysis of carbon dioxide to carboxylic acid, or due to the presence of dust particles\textsuperscript{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$_3$O$^+$, 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$^+\)$. In addition, inverting the charge of the large halide ions in silico eliminates their surface preference\textsuperscript{3}. 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.\textsuperscript{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 Fig. 5 that presents the probability for the orientational angle $\theta$ 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 ($r < 0.5$ nm). On the surface ($r \approx 1$ nm), in contrast, hydronium is strongly oriented with the dipole pointing to the droplet center (that is, with the oxygen on the outside, Fig. 1B/C). Water molecules at the surface display only a weak preference for the oxygen pointing slightly inwards (Fig. 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 (Fig. 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 (Fig. 3C, red) is due to the reduced rotational freedom (Fig. 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.

\begin{figure}
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\caption{Fig. 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 Fig. 1A. $\theta$ 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.}
\end{figure}

3 Conclusions

The results presented here, in conjunction with earlier results on alkali- and halide ions\textsuperscript{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 are of importance\textsuperscript{36,57}. 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 \textit{et al.}\textsuperscript{11,13}, probing the water surface at the molecular scale, should be regarded as definite proof in this matter.

The presence of H$_3$O$^+$ at the surfaces of aerosol particles might influence the production of bromine atoms, which in
turn are involved in the depletion of stratospheric ozone. By rationalizing the hydronium and hydroxide concentration at the water droplet surface using PMF calculations, and by previous work on droplet composition, we hope to contribute to improving models of the atmosphere in turn can contribute to more accurate predictions from climate models.

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