Water Structuring and Hydroxide Ion Binding at the Interface between Water and Hydrophobic Walls of Varying Rigidity and van der Waals Interactions

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The interfacial behavior of hydroxide ions has been investigated by means of molecular dynamics simulations of aqueous KOH solutions between hydrophobic carbon-like walls. In agreement with previous calculations, we show that a rigid, attractive wall strongly structures water molecules in neighboring hydration layers, leading to a concentration peak of hydrated OH⁻ ions located about 5 Å from the wall. However, allowing for thermal motion of the wall atoms, as well as suppressing the van der Waals interactions between the wall and water hydrogen atoms, strongly reduces both water structuring and the anionic peak in the interfacial region. We infer that soft hydrophobic environments with weak dispersion interactions with water are not expected to exhibit an appreciable structuring effect on interfacial water molecules. Hence, the mechanism for OH⁻ adsorption operative near a hard attractive wall may not be applicable to soft aqueous interfaces, including the limiting case of the water/air interface.

Introduction

Hydroxide anions together with hydronium cations define the ionic product of water. Despite its literarily basic importance, the hydration structure of OH⁻ in bulk liquid water has only recently been accurately described. Both neutron scattering and ab initio molecular dynamics (MD) simulations are converging to a picture of an asymmetric solvent shell. Here, the hydroxide oxygen acts as an acceptor for strong hydrogen bonds with roughly four neighboring waters, while its hydrogen acts as a donor for a weak hydrogen bond with another water molecule.[1,2] Such a structure is highly dynamic, and molecules from the first solvent shell rapidly exchange with bulk waters. Moreover, the hydroxide ion can accept a proton from a neighboring water molecule, which in turn becomes OH⁻, this mechanism being behind its high diffusion constant.[1]

While the bulk hydration structure of OH⁻ is slowly becoming established, the interfacial behavior of this anion remains controversial. On one hand, classical and ab initio MD simulations of aqueous slabs and large clusters show that hydroxide prefers interior solvation.[3,4] These simulations suggest that OH⁻ is weakly (compared, e.g., to fluoride or alkali cations) repelled from the water/vapor interface. It can be occasionally found at the water surface with its hydrogen, which is less acidic than that of water, pointing into the gas phase. However, hydroxide ions do not accumulate in the topmost layer. The computational results are supported by recent second harmonic generation (SHG) spectra of aqueous NaOH solutions of varying concentrations.[5] Fit of these spectroscopic data to a Langmuir adsorption model reveals no or negligible surface adsorption of OH⁻. Along the same line, vibrational sum frequency generation (VSFG) spectra of basic solutions show little effect of hydroxide

ions on water–water interactions in the interfacial layer.[3,6] Finally, photoelectron spectra (PES) obtained in pure water microjets do not reveal adsorption of OH⁻ in the interfacial layer.[7,8]

On the other hand, a different picture of enhanced surface concentration of hydroxide ions has been reported by colloid and atmospheric chemists. A strong surface adsorption of OH⁻ is invoked in explaining charging effects on sprayed water droplets (the so-called waterfall effect),[9–11] as well as air bubbles,[12,13] oil droplets,[14–16] and bilayer vesicles and droplets (formed from uncharged amphiphiles)[17–20] suspended in water. Typically, these particles acquire in water a negative charge, but its exact chemical origin remains a topic of further inquiry. Since many of these experiments involve oil droplets, classical MD simulations aimed at modeling hydroxide ions at the oil/water rather than the vapor/water interface were performed recently.[21] More precisely, the interface between an aqueous hydroxide solution and a hard attractive hydrophobic wall was investigated. An order of magnitude enhancement of the OH⁻ concentration (compared to its bulk concentration) was observed at about 5 Å from the hydrophobic wall. This was accompanied by density and orientational structuring of water in the vicinity of the wall, as also qualitatively observed in other studies.[22,23] Most recently, ab initio MD simulations of water next to a stiff graphene wall showed interfacial affinity of both hydronium and hydroxide, with the latter being more pronounced.[24]

In this study, we systematically investigate the behavior of hydroxide anion at the interface between water and a hydrophobic environment. To this end, we model a series of hydrophobic walls with varying rigidity and strengths of van der Waals interactions. This allows us to trace the previously observed[21] interfacial adsorption of OH⁻ to water structuring next to a hard attractive wall. Interestingly, for softer hydrophobic environments with weaker van der Waals interactions, this water structuring and, in particular, hydroxide ion adsorption in the interface largely vanishes.

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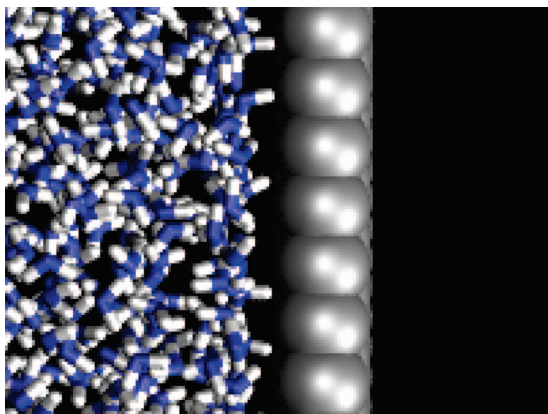
Figure 1. A snapshot of one of the water/wall interfaces. Color coding: water oxygens − blue, water hydrogens − white, and carbon atoms − grey spheres.

Methods

Classical MD simulations were used to investigate water–water hydrogen bonding and distribution of hydroxide anions next to hydrophobic environments of varying properties. The basic system configuration (i.e., unit cell composition, water and ion potentials, cutoffs, and accounting for long-range electrostatics via Ewald summation) was similar to that of a previous study.[21] The system consisted of two hydrophobic carbons walls, each of 418 carbon-like atoms in a closed packed layer, between 1960 TIP5P water molecules[25] with two potassium cations and two hydroxide anions. The unit cell was a rectangular prism (elongated in the z-direction perpendicular to the interface) of dimensions of $42 \times 43 \times 100 \text{ Å}^3$. After application of periodic boundary conditions, this arrangement yielded an infinite water slab surrounded by carbon walls.[21] A snapshot of one of the water/wall interfaces is presented in Figure 1. Simulations were carried out for 38 ns after a sufficiently long equilibration of 2 ns within the NVT ensemble at 300 K with a 2 fs time step. All MD simulations were performed using the program package Gromacs, version 3.3.2.[26]

The focus of the present study was on modeling the effect of different hydrophobic environments. The wall was either kept rigid (i.e., with all carbon atoms permanently fixed in their initial positions) or its atoms were moving in a harmonic potential with a realistic force constant in the z-direction in order to give the wall the possibility to thermally oscillate and deform without letting water molecules penetrate through it. The force constants of this harmonic potential were chosen to be 1000 kJ mol^{-1} nm^{-2} along the x and y axes and 500 kJ mol^{-1} nm^{-2} along the z-axis, allowing for certain "softness", typical for hydrophobic environments. We denote the former as a rigid wall, while the later is denoted as a thermal wall. In addition, we assumed two types of van der Waals interactions between the wall and water. First, we employed the van der Waals interactions between the wall and water derived from the previous simulation study (denoted here as the attractive wall).[21] In this case, Lennard-Jones parameters between water hydrogens and the wall were included to avoid possible nonphysical situations of hydrogens penetrating into the wall. However, this also has the effect of increasing the attractive interactions between water molecules and wall atoms. Nevertheless, since only one layer of hydrophobic particles is considered with a vaccum phase on top of it, the interfacial water molecules do not interact with as many hydrophobic sites as they would if the hydrophobic phase is pure oil. This smaller number of interaction sites for the single-layer wall has the effect of reducing the attractive wall−water interaction. Overall, on the basis of simulations of the water/oil interface reported in the literature, it seems that the present potential for the attractive wall has a slightly stronger attractive interaction between water and a hydrophobic phase.[27] Second, we derived water−wall interactions using standard combination rules, which means zero van der Waals interaction between water hydrogens and wall atoms.

In total, we have thus modeled four different hydrophobic environments denoted as rigid wall, thermal wall, attractive rigid wall, and attractive thermal wall, the latter two employing the additional van der Waals interaction between water hydrogens and wall atoms.

Results and Discussion

The principle results of the present study of hydroxide ions at the water/hydrophobic wall interface are summarized in
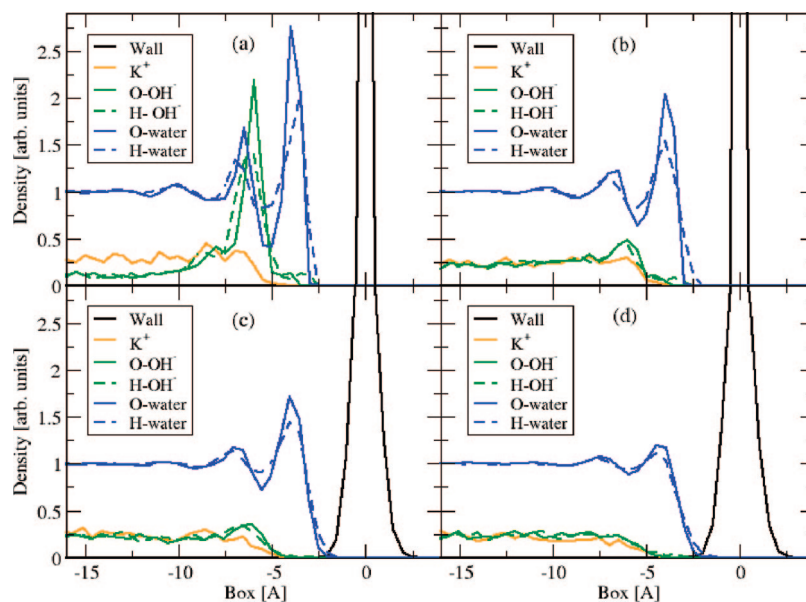
Figure 2. Number density profiles of individual species along the z-direction averaged over the simulation. The profiles were normalized as follows: water bulk density is unity, the signal from water hydrogens was divided by two, and the ion densities were multiplied by a factor of 200 for better visibility in the plots. (a) Attractive rigid wall, (b) rigid wall, (c) attractive thermal wall, and (d) thermal wall.
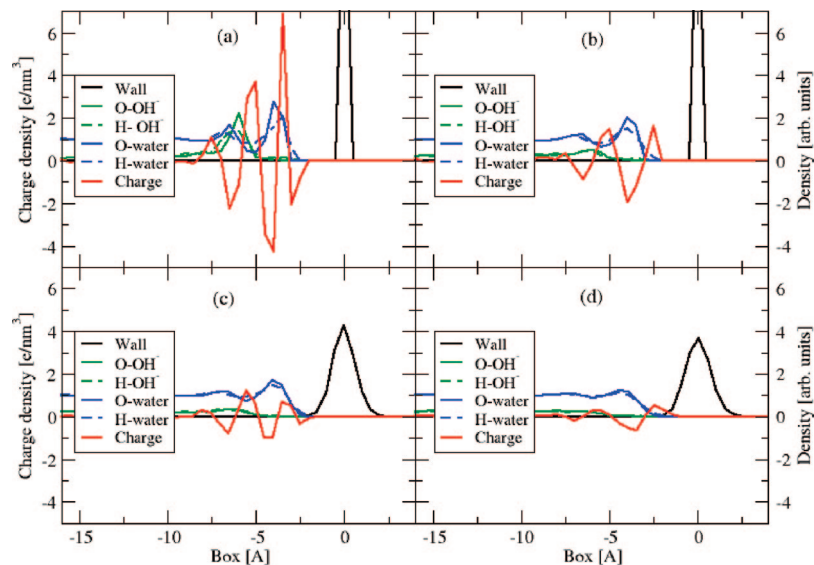
Figure 3. Water charge density profiles of the systems with the number density profiles taken from Figure 2 for easier comparison: (a) attractive rigid wall, (b) rigid wall, (c) attractive thermal wall, and (d) thermal wall. Note that, despite water hydrogens being oriented toward the wall, there is a small negative charge next to the wall in panels a and c due to the lone pair charges of the TIP5P water molecules.
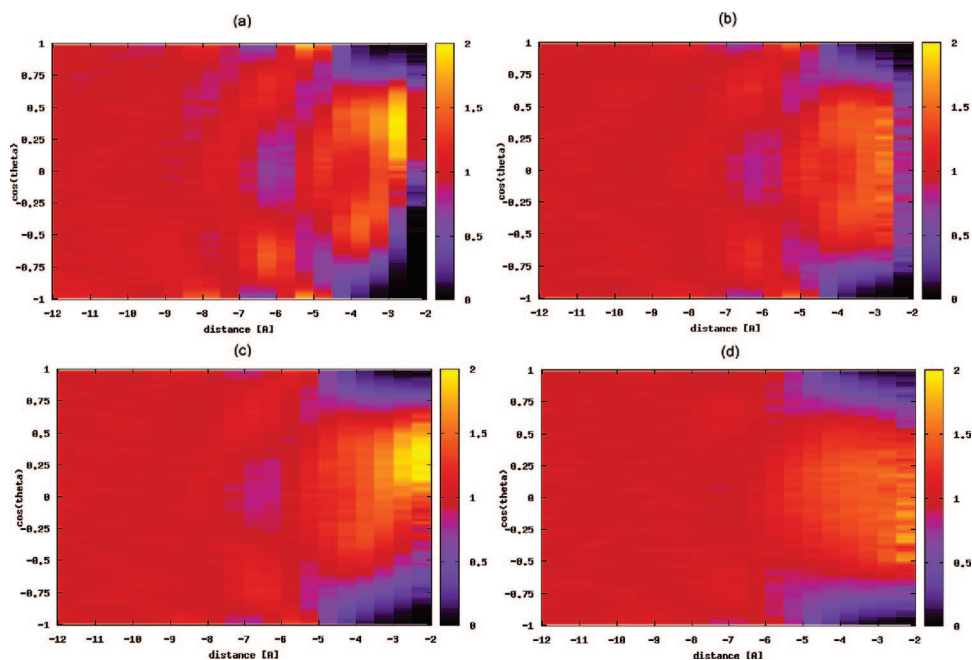
Figure 4. Orientations of water molecules in layers parallel to the hydrophobic interface. The distribution of the angle θ between the water dipole and the normal to the interface is represented in the color scheme. (a) Attractive rigid wall, (b) rigid wall, (c) attractive thermal wall, and (d) thermal wall.

Figure 2. This composite picture shows density profiles along the direction perpendicular to the interface of individual species (i.e., oxygen and hydrogen atoms of hydroxide anions, potassium cations, water oxygens and hydrogens, and the carbon atoms of the wall) averaged over MD trajectories. Comparison of the situation for the four hydrophobic environments under investigation – rigid wall, thermal wall, attractive rigid wall, and attractive thermal wall – directly reveals the two causes of water structuring and consequent OH⁻ adsorption next to the hydrophobic wall.

Let us start the discussion with results for the attractive rigid wall (Figure 2a) which show strong density oscillations of water and a density peak of hydroxide ions in the vicinity of the interface. Note that the parameters of this particular system, and, consequently, the results, are very similar to those observed in

the previous study.[21] Such water density fluctuations, albeit weaker, were also observed in earlier simulations[22,23] and related to the strength of the attractive interaction between the wall and water molecules.[23] The density peak of OH⁻ overlaps with the second water peak about half a nanometer from the wall. Hydroxide ions thus do not accumulate at the topmost layer of water but rather stay beneath it in the region of the second hydration layer. In other words, hydroxide remains fully hydrated and does not behave like a hydrophobic solute. The density peak of OH⁻ near the interface is caused by the stabilization of its dipole in the oscillating charge distribution due to the solvent structuring near the wall (Figure 3a). Figure 4a shows the orientations of water molecules in thin layers parallel to the interface. For this purpose, we have plotted the distributions of cos θ, where θ is the angle between the water

dipole and the normal to the interface. The attractive hard wall strongly orients water molecules in its vicinity with an average θ value of about 0.2, i.e., with water hydrogens pointing preferentially toward the wall (Figure 4a). This preferential water orientation weakens upon moving toward the aqueous bulk and disappears at about 7 Å from the wall.

Allowing for thermal motion of the wall (attractive thermal wall) or turning off the additional van der Waals interaction between the wall and hydrogen atoms (rigid wall) have a similar effect. We find that water becomes less structured, and the hydroxide peak significantly decreases in the vicinity of the interface (Figure 2b,c). At the same time, the oscillations of the water electric field near the wall become strongly damped (Figure 3b,c). Also, the preferential orientation of the interfacial water molecules with hydrogens pointing toward the wall disappears upon turning off the additional van der Waals term (Figure 4b,c). Nevertheless, there is still a small excess of OH^- in the interface relative to K^+ or to the density of hydroxide ion in the bulk.

Combining these two effects, i.e., letting the wall atoms thermally move and not introducing a special van der Waals term between wall and hydrogen atoms (thermal wall), leads to a complete disappearance of the density peak of hydroxide ion in the vicinity of the interface (Figure 2d). This distribution of ions thus resembles that obtained from simulations of the hydroxide solution/vapor interface.[3,4,28] At the same time, density oscillations of water near this hydrophobic environment almost disappear, and the density profile of water becomes similar to the smooth monotonic curve reported previously for the water/hydrocarbon, water/halocarbon, and water/vapor interfaces.[29–31] This is accompanied by further damping of the electric field oscillations near the wall (Figure 3d). From this point of view, the thermal wall is less "structured" than the attractive thermal wall. Orientation of interfacial water molecules (Figure 4d), with the dipole moment broadly peaking parallel to the interface, also resembles that observed at the previously investigated interfaces.[29,31–33]

Within a broader perspective, the present comprehensive results for four different interfaces with varying rigidity and van der Waals interactions are not only important for a better understanding of the conditions for adsorption of hydrated hydroxide ions to hydrophobic surfaces, but also allow for gaining deeper insight into the mechanism of hydrophobic interactions. Currently, simulations are under way that go beyond the model of a single layer of hydrophobic atoms, addressing the above issues for realistic water/alkane interfaces.

Conclusions

We investigated the distribution of hydroxide ions and water structuring next to a hydrophobic environment of varying properties. When the hydrophobic wall is kept rigid and additional van der Waals interactions between the wall and the water hydrogen atoms are introduced, a strong peak of OH^- is found. This density peak, which occurs about half a nanometer from the wall, is not a consequence of dehydration of hydroxide but rather originates from the oscillating density and electric field of water in the vicinity of the rigid attractive wall.

Introducing thermal motions of wall atoms, as well as turning off the additional van der Waals term, significantly reduces both the hydroxide peak and water structuring. Still a small excess of OH^- at the interface compared to its bulk concentration or to the denisty of potassium countercations is observed. However, in the case of a thermal wall with no additional van der Waals term between the wall and the hydrogen atoms, no density peak of OH^- is observed, and there is only very weakly structured water in the vicinity of the wall. We note that this interface thus behaves similarly to the water/vapor interface in terms of a lack of appreciable OH^- adsorption.[3,4,28]

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