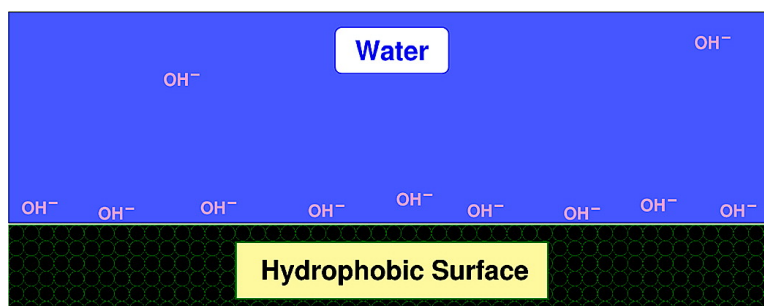


## Physisorption of Hydroxide Ions from Aqueous Solution to a Hydrophobic Surface

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## Physisorption of Hydroxide Ions from Aqueous Solution to a Hydrophobic Surface

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**Abstract:** We present results from detailed molecular dynamics simulations revealing a counterintuitive spontaneous physical adsorption of hydroxide ions at a water/hydrophobic interface. The driving force for the migration of the hydroxide ions from the aqueous phase is the preferential orientation of the water molecules in the first two water layers away from the hydrophobic surface. This ordering of the water molecules generates an electrical potential gradient that strongly and favorably interacts with the dipole moment of the hydroxide ion. These findings offer a physical mechanism that explains intriguing experimental reports indicating that the interface between water and a nonionic surface is negatively charged.

### Introduction

The solvation process of an ion upon transfer from the gas phase into water is characterized by a negative Gibbs energy for all known simple ions.<sup>1</sup> This stabilization upon hydration is a result of the rearrangement of the water molecules in the vicinity of the ion that generates favorable charge-dipole interactions. The ability of water to stabilize ions is reflected by its high dielectric constant. As a consequence of the radial extension of the electrostatic potential, ions in aqueous solution are expected to be repelled from a phase characterized by a low dielectric constant such as a hydrophobic medium. Nevertheless, experimental evidence to the contrary was obtained by measurements (electrophoretic mobility, disjoining pressure isotherms, and atomic force microscopy) which indicated a substantial negative charge at the surface of oil droplets,<sup>2–7</sup> solid hydrophobic polymers,<sup>8–11</sup> hydrophobic assembled structures,<sup>12–17</sup>

gas bubbles,<sup>18,19</sup> and thin-liquid films.<sup>20–24</sup> The negative electric potential measured at the shear plane, the  $\zeta$ -potential, increases strongly with increasing pH, while it is only weakly dependent on the concentration of other electrolytes. For this reason, in the majority of these studies it was concluded that the origin of the negative charge arises from the adsorption of hydroxide ions to the interfacial region. However, this conclusion is met with a great deal of skepticism simply because it is counterintuitive and because there is no physical picture that can support the adsorption process. In fact, the behavior attributed to the hydroxide ions contradicts our picture of ion solvation in which the close approach of an ion to the water/hydrophobic interface is a thermodynamically unfavorable process. In the present study the origin of the OH<sup>−</sup> adsorption to apolar surfaces has been investigated, and a possible explanation is advanced in terms of the specific orientation of water molecules close to the interface.

### Results and Discussion

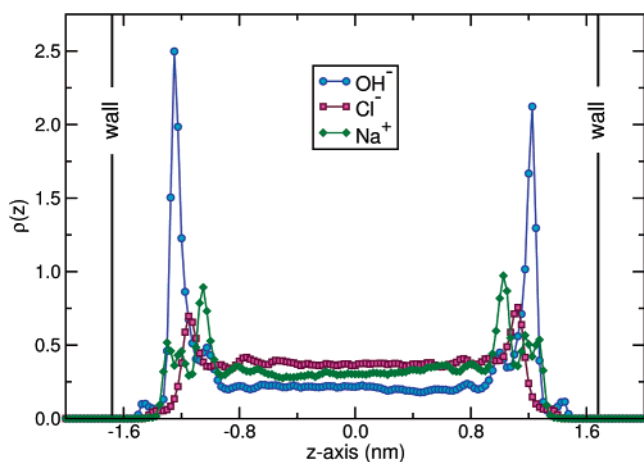
In this study we utilize molecular dynamics (MD) techniques to investigate the behavior of hydroxide ions solvated in water at ambient conditions. The aqueous solution is confined between two immobilized hydrophobic surfaces separated by a distance of 3.60 nm. The TIP5P model was used to describe the water molecules. The behavior of the water molecules along an axis

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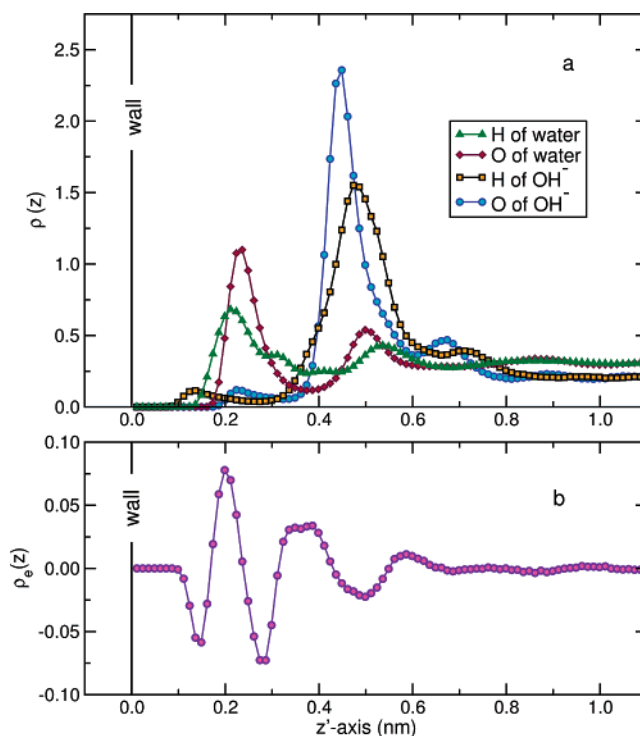
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**Figure 1.** Density profile of hydroxide (calculated according to the position of the oxygen atom), chloride and sodium ions solvated in water next to hard hydrophobic walls. The simulations with different ions were performed separately. The value of the integral of all distributions is normalized to one.

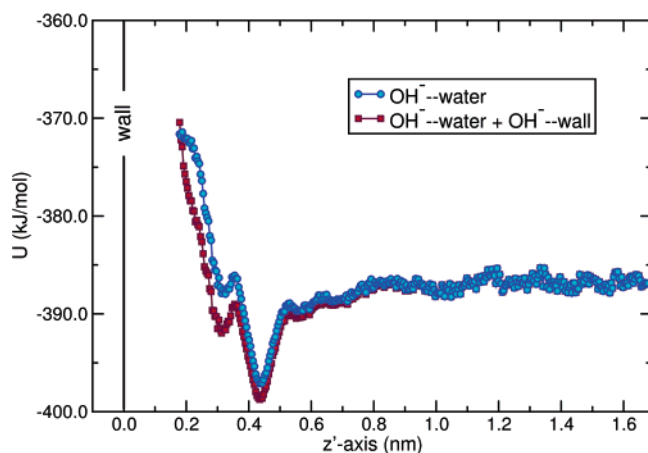
perpendicular to the surfaces, the  $z$ -axis, indicates that they exhibit bulk properties in the range  $-0.8 \leq z \leq 0.8$  nm (the mid-plane is at  $z = 0$ ). In this region the density of the water molecules is 1.00 g/mL. Figure 1 displays the density distribution of the hydroxide ions along the  $z$ -axis. It is shown that the density of the hydroxide ions is much higher in the proximity of the surfaces than in the bulk region. The concentration of the hydroxide ions in the simulations that were performed to calculate the density profile shown in Figure 1 was 0.06 M. The same behavior was also obtained at concentrations of 0.03, 0.11, 0.17, and 0.25 M. For comparison we also calculated the density profiles of other ions. In some experimental studies, the difference in the behavior of a solution containing hydroxide ions was compared with that of a solution containing sodium chloride. These ions usually represent a borderline case between kosmotropic (structure-maker) and chaotropic (structure-breaker) ions and probably reside in the middle of the Hofmeister series. The density distribution of chloride and sodium ions (with concentrations set to 0.11 M) along the  $z$ -axis is also plotted in Figure 1. These ions show a much weaker tendency to adsorb at the surface. In addition, the maximum of the distribution of the chloride ions is shifted away from the surface (by a distance of 0.11 nm), and for the sodium ions it is shifted even further (by a distance of 0.20 nm). Figure 2a displays the density distributions of the oxygen and hydrogen atoms of the hydroxide ions superimposed onto the density distributions of the oxygen and hydrogen atoms of the water molecules. The hydroxide ions are clearly adsorbed at a location near the *second* layer of the interfacial water molecules but shifted by about 0.06 nm toward the first layer. They are, however, almost completely excluded from the first layer. In addition, the density profile exhibits a second, albeit much smaller, peak at around 0.67 and 0.72 nm for the oxygen and hydrogen atoms, respectively. Similar density profiles for the atoms of the water molecules were obtained from the simulations with chloride and sodium ions as well as from simulations in the absence of ions. Note that the maximum of the density profile of the sodium ions shown in Figure 1 appears outside the region where the water molecules display an inhomogeneous density profile. Therefore, it is likely that these positive ions are not physically bound to the surfaces. The density profile of the sodium ions displays also a split peak



**Figure 2.** (a) Density profile of the oxygen and hydrogen atoms of the hydroxide ions and the water molecules and (b) net charge density distribution due to the water molecules as a function of the distance from the surface. The distributions are averaged over the two surfaces and the  $z$ -axis is translated so that the location of the wall is at  $z' = 0$  nm. Note, that in the TIP5P water model the negative charge is located on the lone-pair electrons sites and not on the oxygen atom.

before (closer to the wall) the main density maximum. This split peak is present at a location where the net charge density distribution due to the water molecules, shown in Figure 2b, displays a negative minimum (around 0.5 nm away from the wall). However, the negative minima (of the net charge density distribution) occurring at ca. 0.14 and ca. 0.28 nm do not induce similar density maxima. This is likely due the loss of attractive charge-dipole interaction energy since the complete first solvation shell around the ion can no longer exist.

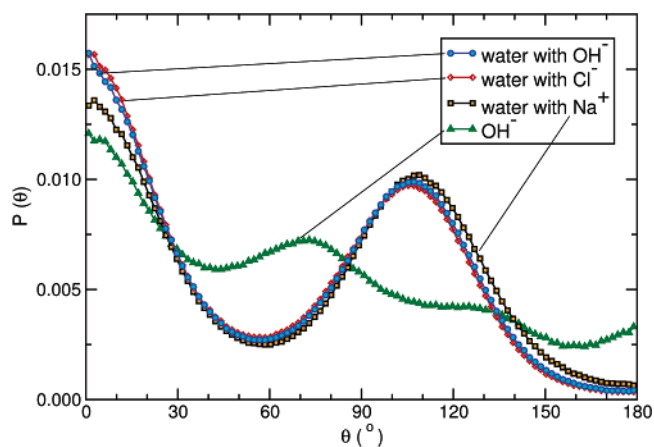
To estimate the equilibrium constant of the adsorption of the hydroxide ions from the bulk to the surface, the value of the integral of the density distribution of the main maximum of the oxygen atoms, shown in Figures 1 and 2a (in the range  $0.39 \leq z' \leq 0.60$  nm), divided by the integral over the same length in the bulk was calculated. This yielded an estimate of 5.2 for the equilibrium constant of OH<sup>-</sup> binding, corresponding to a Gibbs energy of  $-4.1$  kJ/mol. Since an adsorption process is associated with a loss of entropy, the interaction energy of a hydroxide ion with its environment near the surface should not only stabilize the ion more than do bulk water molecules but also compensate for the loss of entropy associated with the adsorption. The magnitude of the dispersion forces between the hydroxide ion and the surface is very small compared to the magnitude of the electrostatic forces acting between the hydroxide ion and the water molecules (see below). As a consequence, the stabilization energy required for the adsorption must be due to the interactions of the hydroxide ion with the water molecules next to the surface. Figure 3 displays the potential energy of a hydroxide ion with its environment as a function the distance of the ion from the surface. It also displays



**Figure 3.** Potential energy (electrostatic and Lennard-Jones interactions) between a hydroxide ion and its environment (water molecules and surface atoms) as well as with only the water molecules as a function of the distance from the surface. The simulations were performed with only one ion solvated in water, i.e., at concentrations of 0.03 M.

the interaction only with the water molecules which is the major component of the total potential energy. The location of the adsorption of the hydroxide ion (approximately at 0.44 nm away from the surface) is characterized by a sharp global minimum of the potential energy curve. However, at shorter distances there is a sharp increase in the potential energy, corresponding to the very small values found for the density distribution shown in Figures 1 and 2a. The potential energy difference between the adsorbed state and the bulk state is approximately  $-12$  kJ/mol. This value can serve as an approximation for the enthalpy change from which the change in entropy,  $-27$  J/K·mol, is obtained through the relation  $\Delta G_b^0 = \Delta H_b^0 - T\Delta S_b^0$ . The mean squared displacement as a function of time of the hydroxide ions along the surface normal is very small and exhibits irregular jumps as expected for adsorbed particles (the diffusion coefficient is not defined in this case). However, the mean squared displacement in the plane parallel to the surface is found to be a linear function of time; therefore, it exhibits a diffusive behavior. The associated lateral diffusion coefficient is calculated to be  $1.38 \times 10^{-5}$  cm<sup>2</sup>/s which is similar to the diffusion coefficient of a hydroxide ion in bulk liquid water ( $1.67 \times 10^{-5}$  cm<sup>2</sup>/s). (This value was obtained from 2.0 ns simulation of a single hydroxide ion solvated in 1960 TIP5P water molecules at  $T = 300$  K and  $P = 1$  atm. In this case, periodic boundary conditions were applied in all directions.) Thus, a main contribution to the entropy loss is the retarded motion perpendicular to the surface.

As shown in Figure 3, the interaction energy of a hydroxide ion with the water molecules near the surface is stronger than that in the bulk. This is possible only if the hydrogen-bonded structure of the water molecules next to the surface is different from that in the bulk. In the density distributions shown in Figure 2a for the water molecules, the curve of the oxygen atoms next to the surface, in the first two layers, does not overlap with the curve of the hydrogen atoms. This indicates that the orientation of the water molecules in this region is not isotropic. There exists a preferential orientation that generates, as shown in Figure 2b, an alternating net charge distribution along the surface normal. We contend that the favorable adsorption of hydroxide ions to a hydrophobic surface originates from the interaction energy of this electrical potential gradient with the permanent



**Figure 4.** Probability density of the angle between the covalent O–H bond vector and the surface normal of the interfacial (first layer away from the surface) water molecules (with hydroxide, chloride, and sodium ions) and hydroxide ions. Thus, an O–H bond that is parallel to the surface normal and points toward the bulk corresponds to an angle of 0°.

dipole moment of the hydroxide ion. Note that, although the electrical potential gradient is larger in magnitude at the first water layer, the hydroxide ions are hardly adsorbed there. This is because adsorption at the first water layer will prevent a complete formation of hydrogen bonds between the ion and the surrounding water molecules. Thus, the electrical potential gradient is not strong enough to break the first hydration shell around the ions.

At distances larger than the second layer away from the surface, both the density profile and orientation of the water molecules are isotropic, i.e., the same as in the bulk. Thus, the changes imposed on the structural nature of the water molecules due to the presence of the surface are short ranged. However, because it induces inhomogeneous density distributions of negative and positive ions, it can give rise to long-range phenomena.

The anisotropy at the interface can also be seen in Figure 4. This figure displays the probability density of the angle between the covalent O–H bond and the surface normal for the first layer of water molecules from the simulations with hydroxide, chloride, and sodium ions. The curves are bimodal with a prominent peak at 0° (corresponding to the O–H bond pointing toward the bulk) and a complementary peak at approximately 107° (which is obtained due to the molecular H–O–H angle given that the other O–H bond is aligned with the surface normal). This behavior is similar to the orientation of water molecules next to an uncharged extended hydrophobic wall obtained from integral equation theory.<sup>25</sup> It should be pointed out that, at the interface, the number of hydrogen bonds per molecule slightly decreases while the magnitude of the distortion from ideal hydrogen-bond geometry increases.<sup>26–28</sup> This behavior was also obtained when the interfacial water molecules were exposed to the influence of an external electric field.<sup>29</sup> It is evident from Figure 4 that the orientation of the water molecules in the simulations with the hydroxide ions is almost identical to that with the chloride ions. In the simulations with the sodium ions the distribution is only slightly shifted due to

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the influence of the cations. Thus, it seems that the sign of the charge of the ions has a small effect in determining the overall orientation of the water molecules next to the surface (at least for low ion concentrations). Moreover, the same preferential orientation is found in simulations of water in the absence of ions (figure not shown). This behavior raises a question regarding the origin of the broken symmetry exhibited by the water molecules at the interface. If only the dipole moment of the water molecule is considered, the orientation of the dipoles at the interfacial layer can point either toward or away from the surface. Nevertheless, if the water-surface interaction energies of the two orientations are degenerate, as for example, for a hydrophobic surface, then no preferential orientation at the surface is possible. However, if the quadrupole moment of the water molecule is also taken into account, then one of these orientations will be favored.<sup>30</sup> Thus, the apparent broken symmetry at the interface is possible due to the existence of a quadrupole moment of the water molecule. By describing the water molecules as a multipolar solvent of at least a dipole and a quadrupole in a region of dielectric inhomogeneity, it was predicted that the molecules are oriented so as to place their hydrogens in the high-dielectric side of the interface,<sup>31,32</sup> consistent with the orientation observed in this study. Note that, although the angular anisotropy of the interfacial water molecules has been addressed in previous studies, to the best of our knowledge, this is the first report that demonstrates the ability of this anisotropic environment at the interface to specifically and physically bind hydroxide ions.

As a result of this preferential orientation of the water molecules at the interface, the adsorbed hydroxide ions are also oriented in such a way that the hydrogen atoms point away from the surface toward the bulk. This can be seen in the density distribution plotted in Figure 2a and from the probability density of the O–H bond angle shown in Figure 4. The latter exhibits multiple maxima. The maximum with the highest intensity occurs at an angle of 0°. This is a result of a second-layer hydroxide ion accepting a hydrogen from the first-layer water molecules. Other maxima with decreasing intensities occur at angles of 73, 133, and 180°. The value at  $\theta = (180 - 107) = 73^\circ$  corresponds to the formation of a hydrogen bond with a water molecule present in the second layer and has an O–H bond orientation of 107°. The other two maxima at  $\theta = 133$  and 180°, which are smaller in magnitude, are probably due to hydrogen bond donation to water molecules present in the first layer. The driving force for pointing the hydrogen atom toward the wall is likely to be the small negative net charge density distribution at the wall due to the lone-pair electrons (see Figure 2b). Therefore, the resulting orientational preference of the hydroxide ions is due to the orientation of the water molecules in the first layer that are part of their first solvation shell (short-range effect) and due to the electrical potential gradient next to the surface (long-range effect).

The interaction energy of a charged dipolar particle with the surrounding water molecules is weaker as the thermal motion of the latter increases, (i.e., for a more isotropic orientation of the solvent molecules). Therefore, it is the preferential orientation of the interfacial water molecules, which generates more

favorable interactions, that acts as the driving force for the adsorption of the hydroxide ions to a hydrophobic surface. The remarkably strong adsorption of hydroxide ions is most likely due to their geometric dipole size which matches the oscillation length of the charge distribution next to the surface. This mechanism does not require that the surface be purely hydrophobic. It can be any nonionic surface that will induce the same preferential orientation of the interfacial water molecules.<sup>33</sup> As revealed experimentally, the negative charge at the interface is also measured in pure water, indicating that the source of the hydroxide ions is from the autodissociation of water. Although the bulk concentration of hydroxide ions is very low, their concentration at the interface can be substantial. Thus, the results presented in this contribution are relevant to a large variety of phenomena involving nonionic surfaces in contact with aqueous solutions. These include, inter alia, interactions between lipid bilayers,<sup>14</sup> stability of surfactant-free, oil-in-water emulsions<sup>2–7</sup> and interactions between proteins and self-assembled monolayers.<sup>13,16</sup>

## Conclusions

In this contribution we presented results from molecular dynamics simulations indicating that hydroxide ions are physically adsorbed at the water/hydrophobic interface. The driving force for the adsorption is the preferential orientation of the water molecules in the first two layers away from the hydrophobic surface. There exists a preferential orientation that generates an alternating net charge distribution along the surface normal. The interaction energy of this electrical potential gradient with the permanent dipole moment of the hydroxide ion renders the adsorption process possible. These findings demonstrate the importance of explicit representation of solvent molecules in studies of adsorption phenomena.

## Methods

The MD computer simulations were performed using GROMACS package version 3.1. The time step used for integrating Newton's equations of motion was 0.002 ps. To maintain the system at a constant temperature of 300 K, a Berendsen thermostat was applied using a coupling time of 0.1 ps. The system was also coupled to a lateral pressure of 1 bar with a coupling time of 1.0 ps and an isothermal compressibility of  $5 \times 10^{-5} \text{ bar}^{-1}$ . The evaluation of the electrostatic forces was performed using the particle-mesh Ewald method (with grid spacing of 0.12 nm and cubic interpolation). The evaluation of the Lennard-Jones (LJ) interactions was performed using a twin range cutoff of 0.9 and 1.4 nm. Interactions within the shorter cutoff were updated every step, while longer-range interactions were updated every five steps.

To check the sensitivity of the results to the choice of the water model, we performed simulations with three different water models. The results reported in this study were performed with the TIP5P<sup>34</sup> potential. We chose to use the TIP5P water model because of its accuracy in reproducing the structural and thermodynamic properties of water in the liquid phase at ambient conditions. However, the same qualitative results were obtained with SPC<sup>35</sup> and SPC/E,<sup>36</sup> in which

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case, the equilibrium constant for the hydroxide-ion adsorption was estimated to be 4.0 and 3.9, respectively. We note that MD simulations with a polarizable water model have shown that polarization effects are of secondary importance compared to the electrostatic interactions in determining the properties of interfacial water at a hydrophobic surface.<sup>37</sup>

Two immobile walls confined the water molecules to a slab with a thickness of 3.36 nm. Each wall was composed of a monolayer of atoms constrained to a triangular arrangement with a lattice spacing of 0.23 nm. The water–wall interactions (for the case of the TIP5P water model) were represented by a 6–12 LJ potential with the parameters:  $\sigma_{(O_w-W)} = 0.352$ ,  $\sigma_{(H_w-W)} = 0.319$  nm and  $\epsilon_{(O_w-W)} = 0.572$ ,  $\epsilon_{(H_w-W)} = 0.286$  kJ/mol. These parameters were calculated using a geometric combination rule between the parameters of TIP5P water model and the parameter of a CH<sub>2</sub> group taken from the GROMOS96 force-field.<sup>38</sup> United atom representation is used to describe the methylene group, therefore, no partial charges were applied to the surface. Since the LJ parameters of the water hydrogens are equal to zero,  $\sigma_{(H_w-W)}$  was estimated from the ratio of the van der Waals (vdW) radius between oxygen and hydrogen. The value of  $\epsilon_{(H_w-W)}$  was taken as half the corresponding value associated with oxygen. The LJ parameters between the water hydrogens and the wall were included to avoid the nonphysical situation of the hydrogens penetrating into the wall. In addition, experimental evidence suggests that the vdW radius of a water molecule is better represented in terms of a small, but significant, degree of nonsphericity.<sup>39</sup> There was no interaction between the two lone-pair sites of water and the wall. These water–wall interactions yield a potential that is almost isoenergetic for the case where the dipole moment of the water molecule points toward or away from the surface. Similar procedures were applied for the calculation of the water–wall interactions when using the SPC and SPC/E water models. There were no interactions between the atoms of the surface. We also performed test simulations where the parameters  $\epsilon_{(O_w-W)}$  and  $\epsilon_{(H_w-W)}$  were smaller to represent weaker water–wall interactions. We find that if the water–wall interactions are weak enough, no structuring of the interfacial water molecules occurs and thereby no adsorption of hydroxide ions is observed. The density oscillations of the water molecules next to the hydrophobic surface reported in this contribution are similar to those reported in other studies<sup>25,40,41</sup> including simulations with a polarizable water model.<sup>37</sup> The effect of the attractive water–solute forces on the density at the interface was addressed in previous theoretical studies.<sup>42,43</sup>

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The hydroxide ion was generated from an SPC water by removing one hydrogen and setting the charge on the oxygen atom to  $-1.41$ .<sup>44,45</sup> We also performed simulations where the charges on the oxygen and hydrogen atoms of the hydroxide ion were set to  $-1.2$  and  $+0.2$ , respectively. The same qualitative behavior of the adsorption of the hydroxide ions to the surface was observed. However, the equilibrium constant of the adsorption was estimated to be 4.2 which is smaller than the value obtained from the simulations where the dipole moment of the hydroxide ion was larger. The parameters describing Na<sup>+</sup> and Cl<sup>-</sup> were taken from the GROMOS96 force field.<sup>38</sup>

The starting configuration of all the simulations was prepared by placing 1962 water molecules between the two surfaces and simulating for at least 5 ns. Then the  $n$  hydroxide ions replaced the position of  $n$  water molecules present around the midpoint between the two surfaces ( $z = 0.0$  nm). The system was then equilibrated for 4 ns before a data collection stage of 36 ns. The coordinates of the ions were saved every 0.1 ps, while the coordinates of the water molecules were saved every 20.0 ps. This procedure was performed for four (two for the simulations with chloride and sodium ions) independent (different initial velocities) simulations. Since a fewer number of independent simulations were performed in the case of chloride and sodium ions, we increased the concentration of these ions in the solution. Thus, more ions were included in the simulations because, essentially, the same number of water molecules was used, allowing comparable statistical averaging. However, we do expect to obtain similar results with lower concentration of chloride and sodium ions as was obtained in the case of the hydroxide ions when simulating at different concentrations in the range of 0.03–0.25 M.

The charge density distribution displayed in Figure 2b was calculated by the equation:  $\rho_e(z) = \rho_H(z) \cdot e_H + \rho_l(z) \cdot e_l$ , where  $\rho_H(z)$  and  $\rho_l(z)$  are the density profiles and  $e_H(z)$  and  $e_l(z)$  are the partial charges of the hydrogen atoms and the lone-pair electrons, respectively. To calculate the potential energy between a hydroxide ion and its environment (Figure 3), eight additional simulations were performed with only one hydroxide ion (to prevent any ion–ion interactions) for 10 ns with data collected every 0.02 ps.

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