Structure, Dynamics, and Stability of Water Molecules during Interfacial Interaction with Clay Minerals: Strong Dependence on Surface Charges

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ABSTRACT: Water participates actively in a wide range of interfacial adsorption and reaction processes, and its structure, dynamics, and stability, all of which are crucial to these processes, have been addressed in the present study by means of molecular dynamics simulations. The structure and dynamic behaviors of interfacial water are distinct from those of bulk water and rely strongly on the amounts of surface charges in clay minerals; for example, H-bonds exist predominately among the interfacial water molecules for zero and low surface charges, whereas prevail between the water molecules and clay surfaces for high surface charges. Stabilities of the interfacial water molecules oscillate remarkably during an increase of surface charges that first decline and then are pronouncedly enhanced. Surface charges play a critical role during the interfacial clay/water interaction, and the interfacial water molecules are “liquid-like” at zero and low surface charges but “ice-like” at high surface charges. The present results greatly promote our understanding of clays/water interfaces that exist ubiquitously in environmental conditions.

INTRODUCTION

Water is the most common solvent and participates actively in all types of biological, chemical, and geological processes while people are gradually recognizing it as the most anomalous liquid.1 The situation becomes more complex when forming the water/air and water/solid interfaces. A large number of systems such as proteins, DNA, metal oxides, and clay minerals usually carry an abundance of surface charges, and water molecules over these charged surfaces behave distinctly from their bulk counterparts.2 Surface charges drive the favorable interactions with water molecules,3,4 and the interfacial structures control the subsequent adsorption and reaction processes; however, our knowledge about interfacial water remains very limited.

Recently, Velasco-Velez et al.5 used X-ray absorption spectroscopy and confirmed that the interfacial water over gold electrolytes has a different structure from bulk water. Although with a great deal of experimental efforts, understanding of interfacial water is currently far from clear because the solid/water interfaces are so complicated that direct spectral characterization represents a challenge.2 Instead, computer simulations can provide molecular-level information about the structure and dynamics of the interfacial water that is otherwise almost inaccessible.5 Muscovite mica attracts substantial interest in ecological science as the replacement of AgI in cloud seeding6 and plays a key role in a variety of geological processes such as absorption of nutrients, storage of carbon dioxide, and disposal of nuclear wastes.7 In addition, the mica/water interfaces have been used widely as a prototype in chemistry, biology, and physics3,9–14 because it is very facile to prepare flat mica surfaces at the atomic scale. The first-principles molecular dynamics (MD) calculations (simulation cell with 84 atoms and simulation time of 0.6 ps) showed that the first-layer water molecules condense into a fully connected two-dimensional H-bonding network and the comprising H atoms are oriented preferentially toward the mica surface,10 suggesting the formation of interfacial “ice-like” water films. It is consistent with the results of vibrational sum frequency generation spectroscopy manifesting that no dangling OH groups can be detected at the full monolayer water coverage.15 On the other hand, Bergman and Swenson16 insisted that the interfacial water molecules are disordered and should be ascribed to be “liquid-like”, which was supported by classical molecular dynamics simulations showing high fluidity for the water layers adjacent to the mica surface.11 Despite the controversies, consensus has been reached that the first layer water molecules form strong H-bonds with the mica surface10–16. To resolve the controversies, molecular dynamics (MD) simulations of the mica/water interfaces were conducted in this study, and it was found that the structure, dynamics, and stability of the interfacial water rely strongly on the amount of surface charges. At zero and low surface charges, H-bonds are constructed among the interfacial water molecules, whereas an increase of surface charges causes a gradual transformation, and, at high surface charges, strong H-bonds prevail between the interfacial water molecules and clay surfaces. Surface charges play a critical role during the interfacial clay/water interaction, and the interfacial water molecules over clay minerals are liquid-like at low surface charges but ice-like at high surface charges.
COMPUTATIONAL SECTION

Models of mica consist of 64 unit cells with the lateral dimensions of 41.59 Å × 36.10 Å (8 × 4 unit cells), in line with the previous study. A vacuum slab with the thickness of 10.0 nm was filled by 4933 water molecules (density = 1.0 g·cm⁻³). A wide range of surface charges (Γ = 0, 0.04, 0.08, 0.16, and 0.32 C·m⁻²) were, respectively, generated by Al³⁺/Si⁴⁺ substitutions obeying the Loewenstein rule and then balanced by the interlayer K⁺ ions. Noting that when Γ = 0 C·m⁻², the mica surface is composed solely of Si⁴⁺ sites. Comparisons among the various surface charges (Γ = 0−0.32 C·m⁻²) can discern the differences of interfacial water molecules at Si⁴⁺ sites and Al³⁺ sites and derive the trends of interfacial water properties with increase of surface charges.

The CLAYFF force field was developed especially for mica and other clay minerals, and its combination with flexible simple point charge water model has been verified sufficiently to describe the interfacial interactions between clay minerals and water. Gromacs 4.6.5 software was used. The Ewald electrostatic summation and van der Waals interactions were defined with the cutoff radii of 12.0 Å, and the long-range electrostatic interactions were handled by the particle-mesh-Ewald method. The V-rescale thermostat and Parrinello−Rahman barostat were used to control the simulation temperature (300.0 K) and pressure (1.0 bar). Twenty nanosecond MD simulations were run for each system, and the Newton’s equations of motion were resolved using the leapfrog algorithm with a 2.0 fs time step. The three-dimensional diffusion coefficients (D) of water molecules were calculated using the Einstein relation

\[ D = \lim_{t \to \infty} \frac{\langle r(t)^2 \rangle}{6t} \]

where \( \langle r(t)^2 \rangle \) refers to the mean-square displacement of the center of mass for water molecules over a time interval (t).

RESULTS AND DISCUSSION

Orientation of Interfacial Water. The density profiles of water oxygen (Ow) and hydrogen (Hw) atoms have been plotted as a function of distances from the mica surface (Figures 1 and 2). The interfacial water layers are strongly affected by the mica surface, and increase of surface charges greatly enhances the interaction between the water molecules and the mica surface, resulting in significant reduction of distances. According to the Ow density profiles, the first layer water falls at 0.284, 0.271, 0.259, 0.252, and 0.246 nm away from the mica surface for Γ = 0, 0.04, 0.08, 0.16, and 0.32 C·m⁻², respectively. In addition, when the surface charge density increases up to 0.08 C·m⁻², a shoulder peak emerges at around 0.185 nm, and this shoulder peak becomes more significant with further increase of surface charges. Consequently, increase of surface charges causes a larger portion of water molecules to reorient at the interface, and, at Γ = 0.32 C·m⁻², the ratio of water molecules at 0.185 vs 0.246 nm is as large as 34.5%, suggesting the formation of the compact interfacial water layers at higher surface charges. Perturbation of water molecules by surface charges decays rapidly with the distances away from the mica surface, and the Ow density profiles of the fourth layer water are similar for all surface charges (Γ = 0−0.32 C·m⁻²).

It is indicated from the results of density profiles that surface charges may cause the reorientation of interfacial water molecules, as corroborated by the analyses of cos Ψ (Figure 3). Note that Ψ stands for the angle between the opposite vector of water dipole and the normal vector of the mica surface.

Figure 1. Snapshot for the interfacial contact of the mica surface (Γ = 0.08 C·m⁻²) with water. Color scheme: Si (yellow), Al (pink), O (red), H (white), and K (purple).
Transformation of H-Bonding Networks. With no surface charges (Γ = 0 C·m⁻²), the tetrahedral surface of mica is composed solely of Si⁴⁺ sites and the first layer water molecules are inclined to construct H-bonds among themselves. Silica and undoped zeolites that contain only the silica (≡Si–O–Si≡) linkages are known to be hydrophobic. The tetrahedral surface of the electroneutral mica (Γ = 0 C·m⁻²) is also comprised of siloxane linkages and hence assumed to be hydrophobic, as testified by the positive cos Ψ. Hydrophobic surfaces repel water, whereas hydrophilic surfaces attract water. The positive cos Ψ values indicate that a majority of H atoms of the first layer water molecules point away from the mica surface and accordingly the mica surface of the electroneutral mica (Γ = 0 C·m⁻²) is hydrophobic. The H-bonding networks are well structured (Figure 4A), resulting in the small standard deviations for Ψ values (σ = 0.67). Introduction of surface charges disrupts the H-bonding networks among water molecules and causes the first layer water to reorient toward the mica surface (Figure 4B,C). Accordingly, the standard deviations for Ψ(σ) become significantly larger, amounting to 5.15 and 4.63 for Γ = 0.04 and 0.08 C·m⁻². The sign of cos Ψ turns to be negative, and it implies that the mica surface is getting hydrophilic. However, the regulation of hydrophobic/hydrophilic properties is local and takes place mainly at substituted sites, consistent with the observations that a majority of the first layer water molecules still form H-bonds among themselves. It suggests that for no and low surface charges, the first layer water molecules are liquid-like rather than ice-like. The continuing increase of surface charges causes an obviously larger portion of water molecules to further rotate and approach the mica surface. For Γ = 0.16 C·m⁻², the second H atoms of the first layer water molecules (referred to as H₂, see Figure 4D) begin to contact with the mica surface, and Figure 2B indicates that an obviously larger portion of H atoms in the first layer water molecules emerges at around 0.161 nm than for Γ = 0.04, 0.08 C·m⁻², in line with the results of cos Ψ and σ. Meanwhile, a reversal of standard deviations for Ψ(σ) has been detected, and the σ values for Γ = 0.16 and 0.32 C·m⁻² are lower than those for Γ = 0.08 C·m⁻² and amount to 1.01 and 0.43, respectively. The very negative cos Ψ and low σ values for Γ = 0.32 C·m⁻² manifest that a majority of the first layer water molecules use

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Figure 2. Density profiles for (A) oxygen (O₆) and (B) hydrogen (O₃) atoms of water to interact with mica surface.

Figure 3. Orientation of water molecules at the mica surface, where the definition of Ψ is given as an inset.

Figure 4. Schematic illustration for the orientation of water molecules at the mica/water interfaces: (A) Γ = 0 C·m⁻²; (B) Γ = 0.04 C·m⁻²; (C) Γ = 0.08 C·m⁻²; (D) Γ = 0.16 C·m⁻²; and (E) Γ = 0.32 C·m⁻². Color scheme: Si (yellow), Al (pink), O (red), and H (white).

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surface. In bulk water, cos Ψ is averaged at 0.28. When interacting with the electroneutral mica surface (Γ = 0 C·m⁻²), cos Ψ of the first layer water becomes slightly positive and it implies that the interfacial water molecules prefer to form H-bonds among themselves rather than with the mica surface. Introduction of surface charges causes cos Ψ to be negative, and cos Ψ becomes more negative with further increase of surface charges, suggesting that higher surface charges correspond to the larger extent of water reorientation. The more negative cos Ψ manifests a higher tendency for both H atoms in water to point toward the mica surface, and at, Γ = 0.32 C·m⁻², cos Ψ can amount to −0.87, where a considerable portion of interfacial water molecules use both H atoms to form H-bonds with the mica surface (Figure 4E). The results are consistent with those of H_W density profiles (Figure 2B). With no surface charges (Γ = 0 C·m⁻²), the first peak of H_W is centered at 0.296 nm, and its abundance reduces substantially (1.00:0.76 for 0:0.32 C·m⁻²) due to the introduction of surface charges, although only slight alteration is caused to its position. In addition, introduction of surface charges produces a noticeable peak at a distance very close to the mica surface (around 0.161 nm) because water reorientation greatly facilitates the formation of H-bonds with the mica surface.
two H atoms to form H-bonds with the surface-O atoms (Figure 4E), where the interfacial water should be ascribed an ice-like structure.\textsuperscript{10,15} The H-bonds are stronger than those at the hydrophilic Mg(OH)\textsubscript{2} surface,\textsuperscript{31} hence, alteration of surface charges can regulate the hydrophobic/hydrophilic properties of the mica surface in a wide range, from hydrophobic to highly hydrophilic. The results are further supported by the $\Gamma_W$ density profiles (Figure 2B). The abundances of H atoms corresponding to the peak at around 0.16 nm are pronouncedly enlarged with increase of surface charges, and the ratios for 0.04:0.08:0.16:0.32 C \textcdot m\textsuperscript{-2} are 0.29:0.35:0.75:1.00. Consequently, increase of surface charges causes more H atoms of the first layer water molecules to point toward the mica surface and the higher extent of reorientation for the first layer water molecules (see Figure 4) ($\Gamma = 0$–0.32 C \textcdot m\textsuperscript{-2}). At $\Gamma = 0.32$ C \textcdot m\textsuperscript{-2}, a large portion of the first layer water molecules use two H atoms to construct H-bonds with the mica surface and the H-bond networks between the interfacial water molecules and the mica surface have been constructed, different from the situation of $\Gamma = 0$ C \textcdot m\textsuperscript{-2} where the H-bond networks exist mainly among the interfacial water molecules.

\textbf{Stability Oscillation of Interfacial Water.} The diffusion coefficients of water layers ($D$) in vicinity of the mica surface are plotted in Figure 5. With no surface charges ($\Gamma = 0$ C \textcdot m\textsuperscript{-2}), the diffusion coefficients ($D$) of the first, second, third, and fourth layer water are, respectively, $3.08 \pm 0.20 \times 10^{-9}$, $3.41 \pm 0.40 \times 10^{-9}$, $3.31 \pm 0.26 \times 10^{-9}$, and $3.21 \pm 0.26 \times 10^{-9}$ m\textsuperscript{2} \textcdot s\textsuperscript{-1}, which are less than the value of bulk water ($4.02 \times 10^{-9}$ m\textsuperscript{2} \textcdot s\textsuperscript{-1})\textsuperscript{32,33} and manifest the stabilization effects of the mica surface to the interfacial water molecules. In spite of its hydrophobic nature, the mica surface exhibits the stabilization effects to the first layer water molecules. The $D$ values of the first layer water increase to $3.17 \pm 0.28 \times 10^{-9}$ and $4.04 \pm 0.22 \times 10^{-9}$ m\textsuperscript{2} \textcdot s\textsuperscript{-1}, respectively, for $\Gamma = 0.04$ and 0.08 C \textcdot m\textsuperscript{-2}. Accordingly, stabilities of the first layer water decline due to the introduction of surface charges and confirm the liquid-like characteristics at low surface charges.\textsuperscript{11,16} At low surface charges, stabilities of the first layer water molecules rely strongly on the H-bonding networks among themselves, and $\Gamma = 0.08$ C \textcdot m\textsuperscript{-2} rather than $\Gamma = 0.04$ C \textcdot m\textsuperscript{-2} causes a larger perturbation to the H-bonding networks among the interfacial water molecules that result in the more significant loss of stabilities. The $D$ values of the first layer water molecules are calculated to be $3.28 \pm 0.02 \times 10^{-9}$ and $2.28 \pm 0.28 \times 10^{-9}$ m\textsuperscript{2} \textcdot s\textsuperscript{-1}, respectively, for $\Gamma = 0.16$ and 0.32 C \textcdot m\textsuperscript{-2}, which are less than those of $\Gamma = 0.08$ C \textcdot m\textsuperscript{-2} and imply the reversal for the trend of stabilities with further elevation of surface charges.

As mentioned above, increase of surface charges causes the transformation of H-bonding networks from among water molecules to between water molecules and the mica surface. When compared to $\Gamma = 0.08$ C \textcdot m\textsuperscript{-2}, stabilities of the first layer water molecules have been substantially improved for $\Gamma = 0.16$ C \textcdot m\textsuperscript{-2} but are still lower than those for $\Gamma = 0$ C \textcdot m\textsuperscript{-2}, corroborating that the H-bonding transformation from among water molecules to between water molecules and the mica surface is not beneficial to the stability of interfacial water molecules. When surface charges increase up to 0.32 C \textcdot m\textsuperscript{-2}, the H-bonding transformation has finished and the H-bonds between water molecules and the mica surface predominate. The ordered array of the first layer water results in the superior stabilities and verifies the formation of ice-like water.\textsuperscript{10,15}

\section*{CONCLUSIONS}

In this work, we have shown that the structure, dynamics, and stability of water molecules at the mica/water interfaces are distinct from those of bulk water and rely strongly on the surface charges in clay minerals. For example, the H-bonding networks are reconstructed during the gradual increase of surface charges and transformed from among water molecules to between water molecules and clay surfaces. Surface charges play a critical role during the interfacial clay/water interaction. As compared to the condition of zero surface charges, the interfacial water molecules over clay surfaces exhibit decreased stability and are liquid-like at low surface charges but show pronounced stability enhancement and are ice-like at high surface charges, thus reconciling the previous controversies.

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The authors declare no competing financial interest.

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