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Effects of substrate structure and composition on the structure, dynamics, and energetics of water at mineral surfaces: A molecular dynamics modeling study

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Abstract

Molecular dynamics computer simulations of the molecular structure, diffusive dynamics and hydration energetics of water adsorbed on (0 0 1) surfaces of brucite $Mg(OH)_2$, gibbsite $Al(OH)_3$, hydrotalcite $Mg_2Al(OH)_6Cl\cdot 2H_2O$, muscovite $KAl_2(Si_3Al)O_{10}(OH)_2$, and talc $Mg_3Si_4O_{10}(OH)_2$ provide new insight into the relationships between the substrate structure and composition and the molecular-scale structure and properties of the interfacial water. For the three hydroxide phases studied here, the differences in the structural charge on the octahedral sheet, cation occupancies and distributions, and the orientations of OH groups all affect the surface water structure. The density profiles of water molecules perpendicular to the surface are very similar, due to the prevalent importance of H-bonding between the surface and the water and to their similar layered crystal structures. However, the predominant orientations of the surface water molecules and the detailed two-dimensional near-surface structure are quite different. The atomic density profiles and other structural characteristics of water at the two sheet silicate surfaces are very different, because the talc (0 0 1) surface is hydrophobic whereas the muscovite (0 0 1) surface is hydrophilic. At the hydrophilic and electrostatically neutral brucite and gibbsite (0 0 1) surfaces, both donating and accepting H-bonds from the H_2O molecules are important for the development of a continuous hydrogen bonding network across the interfacial region. For the hydrophilic but charged hydrotalcite and muscovite (0 0 1) surfaces, only accepting or donating H-bonds from the water molecules contribute to the formation of the H-bonding network at the negatively and positively charged interfaces, respectively. For the hydrophobic talc (0 0 1) surface, H-bonds between water molecules and the surface sites are very weak, and the H-bonds among H_2O molecules dominate the interfacial H-bonding network. For all the systems studied, the orientation of the interfacial water molecules in the first few layers is influenced by both the substrate surface charge and the ability by the surfaces to facilitate H-bond formation. The first layer of water molecules at all surfaces is well ordered in the *xy* plane (parallel to the surface) and the atomic density distributions reflect the substrate crystal structure. The enhanced ordering of water molecules at the interfaces indicates reduced orientational and translational entropy. In thin films, water molecules are more mobile parallel to the surface than perpendicular to it due to spatial constraints. At neutral, hydrophilic substrates, single-monolayer surface coverage stabilizes the adsorbed water molecules and results in a minimum of the surface hydration energy. In contrast, at the charged and hydrophilic muscovite surface, the hydration energy increases monotonically with increasing water coverage over the range of coverages studied. At the neutral and hydrophobic talc surface, the adsorption of H_2O is unfavorable at all surface coverages, and the hydration energy decreases monotonically with increasing coverage.

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1. Introduction

Interaction between water and solid surfaces can substantially affect the properties of both phases, including the structure and dynamics of the near surface water and the

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reactivity and functionality of the substrate surface (Thiel and Madey, 1987; Hochella and White, 1990; Brown, 2001; Henderson, 2002). These interactions are, thus, of significant interest in many geochemical, technological and biological systems. In geochemistry and environmental science, water–mineral interactions are important factors controlling such processes as surface ion adsorption and ion exchange, which are crucial for the mobility of contaminants in surface and groundwater systems, weathering, soil development, soil moisture behavior, water composition and quality, and removal and sequestration of atmospheric CO_2 (Davis and Kent, 1990; Hochella and White, 1990; Brown et al., 1999; Brown, 2001; Brown and Parks, 2001). Mineral–water interactions are largely controlled by the substrate structure, composition, and surface charge distribution, which vary widely among minerals. The substrate surface structure provides the basic framework for water adsorption. Local variation of near-surface structural charge (electron density) due to structural substitutions or defects provides negatively or positively charged surface sites which can orient the H_2O dipoles and which can significantly influence formation of donating or accepting hydrogen bonds with the surface.

For the common oxides, hydroxides and silicates of the Earth's near-surface environment, the surface chemistry is strongly affected by the pH-dependent surface protonation/deprotonation (Davis and Kent, 1990; Hochella and White, 1990; Brown, 2001; Rustad, 2001). For a given mineral, the bulk properties of the near-surface aqueous solutions, such as pH, can affect the structure and properties of the interfacial water by modifying the substrate surface (Du et al., 1994; Yeganeh et al., 1999; Ostroverkhov et al., 2004). For water on sapphire (Al_2O_3) (Yeganeh et al., 1999) and crystalline or fused quartz (SiO_2) (Du et al., 1994; Ostroverkhov et al., 2004) surfaces, sum frequency vibrational spectroscopy suggests that the H_2O dipoles flip 180° when the solution pH crosses the iso-electric point of the surface. At the water–quartz interface at both low ($\sim$2) and high ($\sim$12) pH, interfacial water molecules are well ordered and yield spectroscopic features similar to those of the ice–quartz interface. At intermediate pHs the surface water is expected to be less ordered (Du et al., 1994; Ostroverkhov et al., 2004).

Minerals in geochemical environments often have particle sizes as small as few nanometers and expose several surfaces simultaneously, possibly with non-stoichiometric surface compositions (Trainor et al., 2004). Surface defects, absorbents including inorganic and organic ions and molecules, and solution chemistry can complicate the interfacial interactions. The involvement of microbes adds one more level complexity. In most geochemical systems, however, water is the ubiquitous solvent and also participates directly or indirectly in the interfacial chemical reactions. In order to adequately understand and ultimately predict the effects of interaction of aqueous solutions with rocks, sediments, soils, and other natural and synthetic materials, a detailed knowledge of the structure and properties of interfacial water is prerequisite and essential (Thiel and Madey, 1987; Hochella and White, 1990; Brown et al., 1999; Brown, 2001; Henderson, 2002).

The effects of mineral surface structure and composition on the structure and dynamics of the near-surface aqueous fluids are, however, difficult to study and incompletely understood. In addition to the natural complexity of near-surface fluids discussed above, the aqueous phase is statically and dynamically disordered, and there are fewer applicable experimental techniques to probe its properties in situ than are available for probing mineral surfaces (Du et al., 1994; Williams et al., 1998; Teschke et al., 2000; Cheng et al., 2001; Fenter and Sturchio, 2004; Ostroverkhov et al., 2004, 2005; Ruan et al., 2004). It is, thus, instructive to first attempt to understand somewhat idealized systems, starting with the interaction of pure liquid water with perfect mineral surfaces without considering, for instance, chemical reactivity. Molecular computer simulations are extremely efficient in obtaining detailed fundamental information about the behavior of such well-defined systems on the molecular time- and length-scales (e.g., Cygan, 2001). Such insight into the structure of interfacial water is essential to improved understanding of surface-specific experimental data obtained by, for instance, X-ray reflectivity (Cheng et al., 2001), X-ray crystal truncation rod diffraction experiments (Trainor et al., 2004), and sum-frequency vibrational spectroscopy (Ostroverkhov et al., 2004, 2005).

It has long been known that different surfaces affect the structure, dynamical behavior and physical and chemical properties of interfacial water in different ways (Packer, 1977; Beaglehole and Christenson, 1992; Du et al., 1994; Lee and Rossky, 1994; Israelachvili and Wennerströn, 1996; Akiyama and Hirata, 1998; Yeganeh et al., 1999; Joseph et al., 2000; Brown, 2001; Scatena et al., 2001; Michot et al., 2002). Computational studies of different oxide and hydroxide surfaces show quite different near-surface water structures and suggest that different surface functional groups can play different roles in developing the interfacial hydrogen bonding networks that are key to understanding near-surface water structure (e.g., Lee and Rossky, 1994; Rustad et al., 2003; Wang et al., 2004b). For instance, molecular modeling shows that the interfacial water molecules at the magnetite (001) surface accept and donate H-bonds from and to several different surface functional groups (Rustad et al., 2003). For water at the portlandite or brucite (001) surfaces, MD models show that $Ca_3{}^{VI}OH$ or $Mg_3{}^{VI}OH$ surface functional groups serve as both H-bond donors and acceptors (Kalinichev and Kirkpatrick, 2002; Wang et al., 2004b). For water at a hydroxylated silica surface, simulation results show that interfacial water molecules have two different preferred orientations with different H-bonding configurations (Lee and Rossky, 1994). Detailed and systematic investigation of these issues are essential to further advance our understanding of the ways in which the competing molecular-scale phenomena control the structural and dynamic properties of interfacial water.