Molecular modeling of the structure and dynamics of the interlayer and surface species of mixed-metal layered hydroxides: Chloride and water in hydrocalumite (Friedel’s salt)

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ABSTRACT

The dynamical behavior of Cl− and H2O molecules in the interlayer and on the (001) surface of the Ca-aluminate hydrate hydrocalumite (Friedel’s salt) over a range of temperatures from –100 to 300 °C was studied using isothermal-isobaric molecular dynamics computer simulations. This phase is currently the best available model compound for other, typically more disordered, mixed-metal layered hydroxides. The computed crystallographic parameters and density are in good agreement with available X-ray diffraction data and the force field developed for these simulations preserves the structure and density to within less than 2% of their measured values. In contrast to the highly ordered arrangement of the interlayer water molecules interpreted from the X-ray data, the simulations reveal significant dynamic disorder in water orientations. At all simulated temperatures, the interlayer water molecules undergo rapid librations (hindered hopping rotations) around an axis essentially perpendicular to the layers. This results in breaking and reformation of hydrogen bonds with the neighboring Cl− anions and in a time-averaged nearly uniaxial symmetry at Cl−, in good agreement with recent 35Cl NMR measurements. Power spectra of translational, librational, and vibrational motions of interlayer and surface Cl− and H2O were calculated as Fourier transforms of the atomic velocity autocorrelation functions and compared with the corresponding spectra and dynamics for a bulk aqueous solution. The ordered interlayer space has significant effects on the motions. Strong electrostatic attraction between interlayer water molecules and Ca atoms in the principal layer makes the Ca···OH2− bond direction the preferred axis for interlayer water librations. The calculated diffusion coefficient of Cl− as an outer-sphere surface complex is almost three times that of inner-sphere Cl−, but is still about an order of magnitude less than that of Cl− in bulk aqueous solution at the same temperature.

INTRODUCTION

Mixed-metal layered hydroxides (MMLHs), also called layered double hydroxides (LDHs) and “anionic clays,” are among the few oxide-based materials with permanent anion exchange capacity developed through isomorphous substitution. They occur in many natural environments, are readily synthesized, and are receiving rapidly increasing attention for a wide variety of applications in catalysis, environmental remediation, and medicine (e.g., Ulibarri et al. 1995; Newman and Jones 1998, Schmassmann et al. 1993). They also play a key role in cement medicine (e.g., Ulibarri et al. 1995; Newman and Jones 1998, Schmassmann et al. 1993). They also play a key role in cement chemistry, due to their importance in controlling the chemical behavior of anionic species (Taylor 1997). MMLHs have a layered structure typically based on that of brucite or portlandite. Substitution of 3+ cations (often Al) for 2+ cations (often Mg or Ca) in the principal hydroxide layer leads to a permanent positive charge. This charge is compensated by anions, which have associated water molecules, in the interlayer space and on the particle surfaces.

Hydrocalumite, [Ca3Al(OH)6]Cl·2H2O, also known as Friedel’s salt, is unique among MMLHs, because it has not only an ordered Ca-Al distribution in the hydroxide layer, but well ordered Cl− and water in the interlayer space. The interlayer order is due to coordination of the water molecules to Ca in the hydroxide layer, which results in an unusual sevenfold-coordinated Ca environment. This phase occurs naturally (Fischer et al. 1980; Passaglia and Sacerdoti 1988; Sacerdoti and Passaglia 1988) and also forms by reaction of Cl-containing deicing salts with the calcium aluminates of Portland cement (Birnin-Yauri and Glasser 1998).

Because of its structural order and occurrence as relatively large crystals, hydrocalumite is the only MMLH for which a single crystal structure refinement is available (Terzis et al. 1987). Thus, it is currently the best model compound for understanding the structure and dynamical behavior of surface and interlayer water and anions in MMLHs. Such understanding is essential for exploitation of the unique anion exchange capabilities of this important class of compounds. Recent 35Cl NMR spectroscopic study of hydrocalumite in our laboratory is broadly consistent with the structure determined by XRD, but has provided important new insight into the dynamical be-