Structure, Energetics, and Dynamics of Smectite Clay Interlayer Hydration: Molecular Dynamics and Metadynamics Investigation of Na-Hectorite

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Abstract:

This paper presents a classical molecular dynamics (MD) and metadynamics investigation of the relationships between the structure, energetics, and dynamics of Na-hydroxyhectorite and serves to provide additional, molecular-scale insight into the interlayer hydration of this mineral. The computational results support a model for interlayer H2O structure and dynamics based on 2H NMR spectroscopy and indicate
that H2O molecules undergo simultaneous fast librational motions about the H2O C2 symmetry axis and site hopping with C3 symmetry with respect to the surface normal. Hydration energy minima occur at one-, one-and-one-half-, and two-water-layer hydrates, which for the composition modeled correspond to 3, 5.5, and 10 H2O/Na+, respectively. Na+ ions are coordinated by basal O atoms (OMIN) at the lowest hydration levels and by H2O molecules (OH2O) in the two-layer hydrate, and H2O molecules have an average of three H-bonds at the greatest hydration levels. The metadynamics calculations yield activation energies for site hopping of H2O molecules of ~6.0 kJ/mol for the one-layer structure and ~3.3 kJ/mol for hopping between layers in the two-layer structure. Computed diffusion coefficients for water and Na+ are substantially less than in bulk liquid water, as expected in a nanoconfined environment, and are in good agreement with previous results.

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