Atomistic Simulations of Smectite Hydration Processes

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Molecular simulations have emerged as a useful tool for obtaining detailed insights into the structure, thermodynamics and dynamics of hydrated smectite clay minerals and other geochemical systems[1]. In this work, we present our most recent research efforts from molecular dynamics (MD) simulations using the Gromacs suite of programs and the Matlab ATOM scripts [2-3], along with the CLAYFF and INTERFACE forcefields. The specific aim of this study was to complement experimental data on the montmorillonite hydration and microstructure, by predicting the hydration energetics of the Wyoming type (USA) montmorillonite for a wide range of water contents (up to 60 w% H2O) and interlayer solutes (Li^+, Na^+, K^+, Cs^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Cl^-). We report several dynamical, thermodynamical and structural properties at different water loadings, for instance ion/water/clay atom coordination environments and residence times, hydrogen bonding behavior, diffusion coefficients, as well as immersion energies and the swelling free energy (PMF) profiles during montmorillonite hydration. Furthermore, we scrutinize the main driving forces behind clay hydration, by decomposing the overall hydration energy in terms of: long-range and short-range interactions, electrostatic and VdW interactions, as well molecular component specific interactions.

Several recent studies have also shown that atomistic simulations in combination with mixed layer modeling of *00l* powder XRD reflections [4], can aid in the interpretation of experimental diffraction data, significantly improving the atomistic understanding of the interlayer solute and water structure. With this in mind, we also compare the consistency of different combinations of mechanistic forcefields (CLAYFF and INTERFACE) and water models (SPC/SPC/E/TIP3P/TIP4P/TIP5P) commonly used in atomistic simulations of clay minerals, with the previously reported and semi-empirical data and structure factors for different clay lattices and hydration states.

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