Anion exclusion in hydrated smectite studied by molecular dynamics simulations

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In the characterization of geochemical systems, molecular dynamics (MD) simulations and other atomistic simulation techniques can provide invaluable insights into the dynamics and structure of complex and highly anisotropic molecular environments. The aim of this study is to quantify anion-exclusion in the nanopores of hydrated smectite clay minerals and provide a molecular scale understanding of this phenomenon. In particular, our research aimed to re-examine earlier and seemingly contradictory MD simulation studies on anion exclusion in the two- and three-layer hydrates of Na-montmorillonite [1] [2]. In this research we report the Helmholtz free energy barrier of Cl^- entry from bulk-liquid-like pore water into montmorillonite interlayer nanopores for a range of hydration states (one- to five-layer hydrates), counter-ion types (Na^+, Ca^{2+}), ionic strengths, and montmorillonite edge structures. Montmorillonite edge surfaces were modelled using the so-called *A*-*C* and *B*-type edge models [3]. Interatomic interactions were modelled using the CLAYFF forcefield [4] and the SPC/E water model. Simulation were performed with Gromacs [5] and the free energy barriers were calculated from both regular MD simulations (500 ns) and from constrained MD simulations using umbrella sampling.

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