Molecular Simulations of Hydration and Swelling in Clay Minerals

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Swelling clay minerals play a significant role in a variety of environmental and engineering processes. Our research involves using molecular computer simulations to investigate hydration and ion-exchange properties of clays. It is well established that short-range (crystalline) swelling in clay minerals is a discrete process, occurring through the sequential formation of integer-layer hydrates. Grand canonical ensemble Monte Carlo simulations have been used to characterize the thermodynamics underlying these swelling transitions as well as to investigate their structural origins. Results indicate that ion hydration thermodynamics play a fundamental role in determining swelling mechanisms. Swelling free energies have been decomposed into energetic and entropic components, indicating that energetic effects are dominant. The results may be helpful in characterizing the origins of hysteresis in both adsorption isotherm and ion exchange experiments.