Thermodynamics of Confined Water in Swelling of Clays: Role of Competetive Cation Hydration

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The swelling capacity and stability of clay play a crucial role in various areas ranging from cosmetics to oil extraction; hence change in their swelling behaviour is important for their efficient utilization. Here we focus on understanding the role of different hydration properties of cation on the thermodynamics of clay swelling by water adsorption. We have used mica as the reference clay, Na+ , Li+ , and H+ ions as the interstitial cations, and performed grand canonical Monte Carlo simulations of water adsorption in mica pores (of widths d = 4 − 40 Å). The disjoining pressure, swelling free energy, and several structural properties of confined water and ions were calculated. We expected higher water density in H-mica pores (ρH) due to the smaller size of H+ ions having higher hydration energy. However, the counter-intuitive trend of ρLi > ρNa > ρb (bulk density) > ρH was observed. The swelling free energy for Na-mica is characterized by global minima at d = 6 Å corresponding to crystalline swelling with significant and multiple barriers for crystalline swelling to osmotic swelling (d > 12 Å). A shift in the location of global minima of swelling free energy as well at it becoming more repulsive is observed in the increasing order of Na+ , Li+ , and H+ ions. We found that the competition between surface atoms and water molecules to hydrate the Na+ ions favour the non-swelling nature, whereas, it changes significantly in the Li+ ions and H+ ions case thus favouring clay swelling.

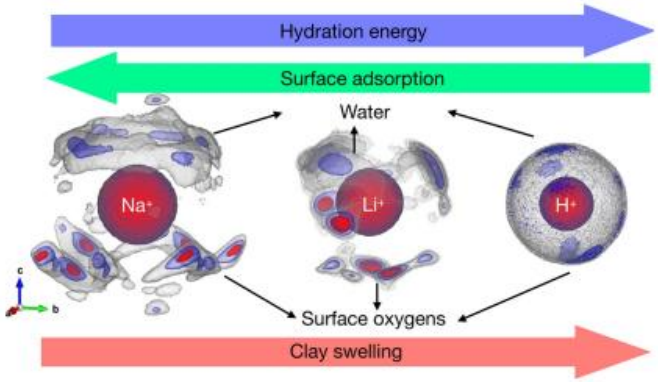

Figure 1: Three-dimensional pair-correlation function illustrating cation (central atom) hydration by oxygen of water molecules (top-side) and surface (bottom side) for various cations.

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