Molecular Dynamics Simulations of Ion Adsorption at Mica-Water Interfaces

IAN C. BOURG[1]

[1]Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA, icbourg@lbl.gov

The structure electrical double layer (EDL) on charged mineral surfaces—the manner in which ion adsorption screens interfacial charge—is a recurrent theme in geochemical modeling. It plays important roles, for example, in studies of ion adsorption, colloidal aggregation, water film thickness in unsaturated porous media, and chemo-mechanical coupling in clayey media. Current theories of EDL structure are based primarily on macroscopic-scale measurements, mean-field theories such as the Gouy-Chapman model, and implicit-solvent theories and calculations (e.g., Brownian dynamics simulations) [1]. A more detailed atomistic-level of EDL structure is emerging from all-atom theoretical calculations [2], X-ray reflectivity experiments [3,4], and molecular dynamics (MD) simulations of charged mineral-water interfaces [5,6]. However, these techniques have not yet been applied in parallel to elucidate the structure of the EDL in a same system.

Here, I describe MD simulations of the structure of the EDL formed by alkali chloride electrolytes at muscovite mica-water interfaces, in conditions similar to those examined in recent X-ray reflectivity experiments [3,4]. The simulations reveal the existence of three types of adsorbed species (inner-sphere surface complexes, outer-sphere surface complexes, diffuse layer ions), in agreement with the X-ray reflectivity results. The identity of the three species is consistent with the tenets of the well-known triple layer model (TLM) [7]. Ion density profiles in the diffuse ion swarm are consistent with the Gouy-Chapman model, suggesting that they are adsorbed primarily through long-range electrostatic interaction with the charged mineral surface.

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