

Metal adsorption at mica-water interfaces

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The structure of the electrical double layer (EDL) on charged mineral surfaces 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 (XRR) 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, we describe efforts to combine XRR measurements, MD simulations, and ion exchange isotherms to examine the EDL formed by metal chloride solutions at the muscovite mica-water interface. In particular, we determine the influence of the size of the adsorbed cation (for alkali metals), its valence (mono-, di-, or trivalent), the surface occupancy (for mixtures of Na- and Rb-exchanged mica) and the concentration of the background electrolyte (from 0 M to 1.0 M) on the structure of the EDL and on the structure and dynamics of interfacial water (including its dielectric constant). We also use our results to characterize the accuracy of the input parameters used in our MD simulations of mica-water (and clay-water) systems and of the methodologies used in interpreting our XRR results. Finally, we compare our results with recent second harmonic generation (SHG) and atomic force microscopy (AFM) data on the adsorption of metals at mica-water interfaces.

[1] Sposito G., *The Surface Chemistry of Natural Particles*, Oxford University Press (2004). [2] Woelki S., Kohler H.-H., Krienke H., *J. Phys. Chem. B* **112**, 3365 (2008). [3] Lee S.S., Fenter P., Park C., Sturchio N.C., Nagy K.L., *Langmuir* **26**, 16647 (2010). [4] Lee S.S., Fenter P., Nagy K.L., Sturchio N.C., *Langmuir* **28**, 8637 (2012). [5] Tournassat C., Chapron Y., Leroy P., Bizi M., Boulahya F., *J. Colloid Interface Sci.* **339**, 533 (2009). [6] Bourg I.C., Sposito G., *J. Colloid Interface Sci.* **360**, 701 (2011).