

Resolving Cation Speciation at Charged Mineral – Solution Interfaces Using Resonant Anomalous X-ray Reflectivity

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Electrostatic interactions at a charged interface in aqueous solutions are mediated by formation of an electrical double layer (EDL). The atomic-scale distributions and adsorption free energies of cations in the EDL were determined using specular and resonant anomalous x-ray reflectivity. Experiments were conducted at the muscovite (001) surface in contact with solutions containing a variety of metal cations. Measurements were made at beamlines 6-ID-B, 11-ID-D, and 33-ID-D of the Advanced Photon Source, Argonne National Laboratory.

In situ observations reveal that cations adsorb in three distinct species: inner-sphere, adsorbed outer-sphere, and extended outer-sphere species, whose sorption heights are determined by the number of hydration layers (0, 1, and 2, respectively) between the cation and the surface [1]. These species coexist at the interface, and their partitioning is controlled in part by cation hydration enthalpy. The adsorption strength of cations also depends on the hydration enthalpy: among ions with the same charge, ones with larger hydration enthalpies adsorb more weakly to the surface. The results strongly suggest that both EDL and thermodynamic models need to incorporate a more explicit description of ion solvation in order to achieve a more predictive and realistic understanding of electrostatic processes at charged interfaces.

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[1] Lee, S.S. et al., *Langmuir*, 26, 16647-16651 (2010).