

Understanding cation adsorption on mica using X-ray reflectivity and molecular dynamics simulations

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Phyllosilicates act as major adsorbents for nutrients and toxic contaminants in natural water systems. Understanding their surface reactivity relies on both theoretical predictions and experimental observations on the mechanism and structure at the atomic level. However, a consistent approach between computational simulations and experiments for the interfacial structure has not been fully established.^[1]

Here, we describe combined efforts to utilize molecular dynamics (MD) simulations and in-situ high-resolution X-ray reflectivity (XR) data to understand cation adsorption processes at the muscovite (001) – 0.1 M alkali metal chloride solution interface. The interfacial structures obtained from MD simulations were used to calculate XR signals that were compared directly with the experimental XR data. The MD simulations showed the influence of the size of the adsorbed cation on the adsorption states. Larger cations (e.g., Rb or Cs) adsorb mostly in the ditrigonal sites of the surface whereas smaller cations (e.g., Li or Na) adsorb mostly on top of the oxygen triads in Al-substituted tetrahedra. The XR signals calculated from the MD-derived structure showed excellent agreement with the experiment data, including the heights of adsorbed cations and changes in interfacial hydration structures caused by the cations. However, some discrepancies were also observed; in particular, the simulations overestimated the fractions of inner-sphere cation complexes with respect to outer-sphere complexes.

In summary, this method allows us to test our understanding of XR data using fully atomistic simulations without any assumed models. In addition, the agreement between XR and MD results characterizes the accuracy of the input parameters used in the MD simulations, which can help developing more realistic theories to explain the surface reactivity of phyllosilicates in aqueous conditions.

References

- [1] Sakuma *et al.* (2011) *J Phys Chem C*, **115**, 15959-15964; Fenter *et al.* (2013) *J Phys Chem C*, **117**, 5028-5042.