Intrinsic Complexities of Ion Adsorption Structures at the Muscovite (001)–Brine Interface

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We investigated the distribution of ions adsorbed on the negatively-charged muscovite (001) surface in solutions containing a wide range of concentrations of RbCl (50 μM to ~7 M) and RbI (20 mM to ~1 M) to understand systematically the effect of the solution composition on ion adsorption in brine conditions. *In situ* observations using high-resolution X-ray reflectivity revealed non-classical variations in adsorbed Rb coverage as a function of dissolved Rb concentration ([Rb]). A series of measurements at low RbCl concentrations ([Rb] ≤ 20 mM) showed an increase in Rb coverage with increasing [Rb] that reached a plateau when [Rb] ≥ 1 mM. This saturated coverage was consistent with full compensation of the muscovite surface charge (Park et al., 2008). In the high [Rb] regime ([Rb] ≥ 20 mM) for both RbCl and RbI, we found that the Rb coverage started to increase again until it eventually reached a second saturation state when [Rb] ≥ 1 M. This non-monotonic variation can be explained by a Langmuir isotherm model having two distinct sites with different adsorption constants. The second saturation corresponds to the Rb coverage required to occupy all available ditrigonal sites of the surface. This Rb overcompensation in the high [Rb] regime seems to lead to anion co-adsorption. Significant changes in interfacial structure other than adsorbed Rb were observed, including the formation of an ordered film with d-spacing matching the (111)-lattice spacing of the cubic RbI crystal. The formation of this RbI film was presumably induced by the epitaxy between the muscovite (001) and the RbI (111) planes. In contrast, interfacial changes were less pronounced for RbCl, mainly reflecting a large (≥10%) lattice mismatch of the crystallographic planes of RbCl to the muscovite (001) plane. Overall, these results demonstrate intrinsic complexities of ion adsorption structures in brine conditions, which need to be incorporated in geochemical models in many natural conditions.

Reference: Park, C., Fenter, P.A., Sturchio, N.C., and Nagy, K.L. (2008) *Langmuir*, **24**, 13993-14004.