

Hydration and Distribution of Ions at the Mica-Water Interface

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Molecular-scale structures of mica surfaces in electrolyte solutions reveal how ion and interfacial hydration control cation adsorption. Key differences are obtained for Rb^+ and Sr^{2+} using resonant anomalous x-ray reflectivity: Rb^+ adsorbs in a partially hydrated state and incompletely compensates the surface charge, but Sr^{2+} adsorbs in both fully and partially hydrated states while achieving full charge compensation. These differences are driven by balancing the energy cost of disrupting ion and interface hydration with the electrostatic attraction between the cation and charged surface.

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The distribution of ions near charged surfaces is fundamental to understanding interfacial reactions in electrolyte solutions. It is important in a broad range of phenomena, including transport of aqueous metal ions and colloids in the natural environment [1], colloidal and macromolecular interactions in physiological environments [2], and electrostatically controlled preparation of catalyst precursors on support oxides [3].

Perhaps the simplest charged solid-liquid interface is that between an aqueous solution and the basal surface of mica, which has a fixed lattice charge. Measurements using the surface force apparatus (SFA) demonstrated fundamental differences in the interactions between muscovite mica sheets separated by monovalent and divalent cation solutions [4,5]. Repulsive forces observed at large separations in the presence of divalent cations were weaker than expected compared to those observed in the presence of monovalent cations. Furthermore, an unexpected difference in the interaction of the like-charged mica sheets was observed at small separations at submolar concentrations, with net repulsion in the presence of monovalent cations, and net attraction in the presence of divalent cations. The results were interpreted as strong vs weak adsorption of monovalent and divalent cations, respectively, and thought to reflect the relative magnitudes of hydration energies, such that weakly hydrated cations are strongly adsorbed and strongly hydrated cations are weakly adsorbed to mica.

Recent theoretical studies suggest that multivalent cations can induce attraction between like-charged surfaces at small surface separations due to ion-ion correlations [6–8]. Ion-ion correlations also have been predicted to lead to an ion condensation transition that depends strongly on cation charge [9]. These concepts, however, are based on models that use point charges interacting through a continuous medium with fixed dielectric permittivity, but exclude the critical molecular features of ion-hydration and water structure at the charged interface. Understanding how cations interact with charged surfaces beyond the continuum and point-charge approximation is presently limited by our

knowledge of the actual molecular-scale structures at the solid-aqueous solution interface.

In order to address the critical molecular features underlying the different adsorption behaviors, we probed the distribution of cations at the basal surface of muscovite mica in contact with aqueous electrolyte solutions. Previous *in situ* characterization of this interface by high-resolution x-ray reflectivity (XR) showed systematic and substantial changes to the structures that vary with atomic number, charge, and solution concentration of the cation [10]. Although this previous study also indicated that both monovalent and divalent cations may adsorb in a partially hydrated state, its lack of elemental specificity did not allow a unique determination of interfacial cation distributions. Here, we use an element-specific interfacial probe (resonant anomalous x-ray reflectivity, or RAXR) to obtain the specific cation distributions and the associated changes in hydration layer structure for Rb^+ and Sr^{2+} at the muscovite (001)-electrolyte solution interface. The key revelation is that hydrated ions compete with interfacial water for sorption sites resulting in molecular-scale structures that depend explicitly on balancing ion and interface hydration energies with the electrostatic attraction between the cation and charged surface.

Laterally averaged total and element-specific electron density profiles in 0.01 M RbCl and $\text{Sr}(\text{NO}_3)_2$ at a *pH* of approximately 5.5 were determined with $<1 \text{ \AA}$ spatial resolution along the muscovite (001) surface-normal direction using XR (i.e., reflectivity vs momentum transfer, Fig. 1) and RAXR (i.e., reflectivity vs x-ray energy, Fig. 2). The XR data were measured using monochromatic (19 keV) synchrotron radiation x-rays (Advanced Photon Source, beam line 11-ID-D and 12-BM-B, Argonne National Laboratory, U.S.A.). Total interfacial density profiles [Fig. 3(a) and 3(b)] were obtained by model-independent inversion [11] and standard model-dependent data analysis [12]. Multiple RAXR spectra were measured near the cation's *K*-absorption edge (15.211 and 16.113 keV for Rb^+ and Sr^{2+} , respectively) at fixed momentum transfer ranging from $q = 0.2$ to 4.9 \AA^{-1} , with 15

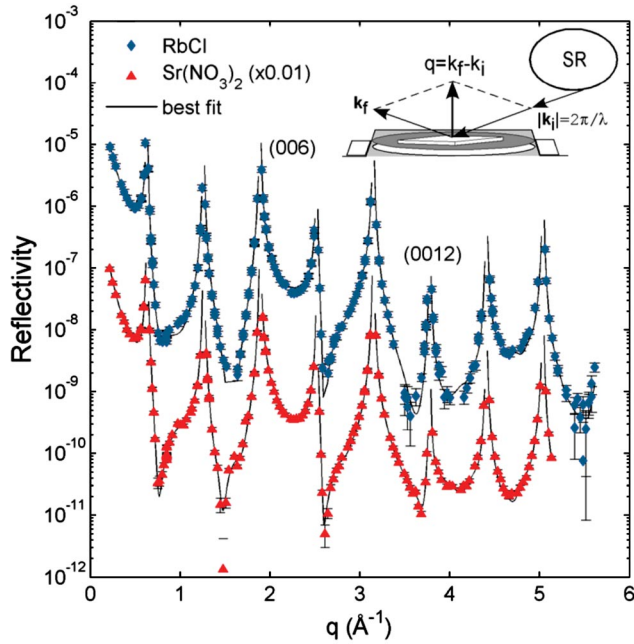


FIG. 1 (color). High-resolution XR as a function of momentum transfer, $q = 4\pi/\lambda \cdot \sin(\alpha)$, where α is the incident and outgoing angle of x rays reflected by the surface in a specular geometry (inset). The Sr data are shifted by factor of 0.01 for clarity.

and 14 spectra for Rb^+ and Sr^{2+} , respectively (selected data sets are shown in Fig. 2). The RAXR data were analyzed with traditional model-dependent approaches as in Ref. [13]. For direct comparison of total and ion-specific profiles in the model-dependent analysis, the total profiles were broadened by the same experimental resolution (FWHM = 0.64 Å corresponding to $q_{\text{max}} = 4.9 \text{ \AA}^{-1}$ of the Sr^{2+} RAXR spectra).

Comparison of the total and ion-specific electron density profiles for aqueous Rb^+ and Sr^{2+} on the muscovite (001) surface is shown in Fig. 3(a) and 3(b). For each ion, the difference in the two profiles gives the net interfacial hydration profile, because specific adsorption of anions is expected to be negligible under these solution conditions. The distributions of Rb^+ and Sr^{2+} are fundamentally different: Rb^+ adsorbs as a single discrete layer while Sr^{2+} adsorbs over a broader region with sorption maxima at two distinct heights above the muscovite surface. The residual interfacial hydration structures are also different: a distinct hydration layer is observed in the presence of Rb^+ , whereas a less distinct hydration structure is observed in the presence of Sr^{2+} . Both hydration profiles are dissimilar to that in pure deionized water [14], revealing that the adsorbed cations play critical roles in altering the hydrogen bonding network near the mica surface.

Pictorial models of adsorbed and hydrated Rb^+ and Sr^{2+} ions [Fig. 3(c) and 3(d), respectively] combine the measured interfacial structures with the normal coordination geometry of the aqueous cations: sixfold coordination for Rb^+ forming a distorted octahedron [15] and eightfold

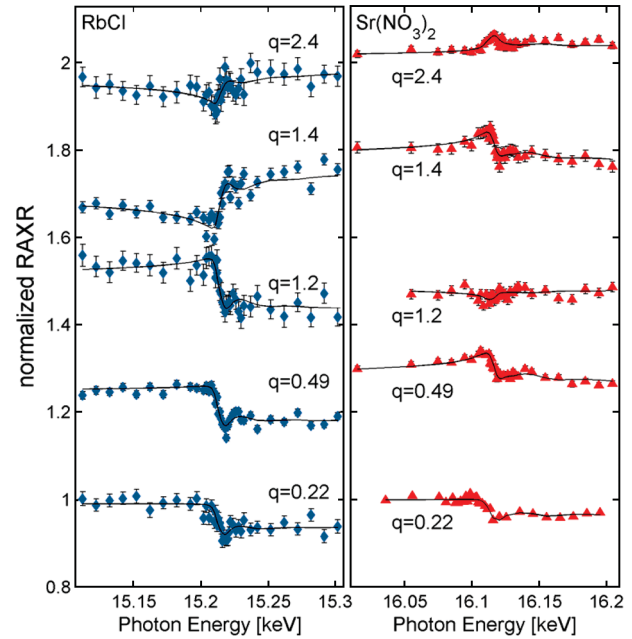


FIG. 2 (color). Selected RAXR spectra of Rb^+ and Sr^{2+} on the muscovite (001) surface, measured near the *K*-absorption edges of each ion (15.211 and 16.113 keV, respectively). The spectra are expressed in normalized form $|F(q, E)/F_{\text{NR}}(q)|^2 = 1 + |F_{\text{R}}(q, E)/F_{\text{NR}}(q)|^2 + 2|F_{\text{R}}(q, E)/F_{\text{NR}}(q)| \cos[\Phi_{\text{NR}}(q) - \Phi_{\text{R}}(q, E)]$, where $F(q, E)$ is the total structure factor, $F_{\text{NR}}(q)$ is the nonresonant (NR) structure factor, $F_{\text{R}}(q)$ the resonant structure factor, and Φ is the phase [13]. Each spectrum is shifted by 0.25, and data are shown over a limited E range for better visibility.

coordination for Sr^{2+} forming a distorted antiprismatic cube [16,17]. For the derived single layer of Rb^+ [Fig. 3(a)], the height ($2.33 \pm 0.10 \text{ \AA}$) above the basal surface oxygen plane of mica indicates that adsorption takes place by ligand exchange, i.e., water in the Rb-hydration shell is replaced by surface oxygens to form what is classically termed an inner-sphere species [Fig. 3(c)]. This agrees with the previous assessment derived from XR measurements of monovalent cations (e.g., K^+ vs Cs^+) on the muscovite (001) surface [10]. The average $\text{Rb-O}_{\text{surf}}$ bonding distance ($3.24 \pm 0.14 \text{ \AA}$) deduced from the measured height is somewhat larger than that for the aqueous hydration shell ($\text{Rb-O}_{\text{hyd}} = 2.93 \text{ \AA}$) [15] and the observed distribution width (FWHM = $1.74 \pm 0.14 \text{ \AA}$) is broader than the experimental resolution (0.64 Å). The distribution width should reflect the intrinsic distribution which might include thermal vibrations and structural variations resulting from Rb exchange. The high symmetry of the Rb octahedral shell coupled with the tridentate adsorption geometry of the ditrigonal site might induce a discrete hydration layer containing at least three water molecules per ion, consistent with observation of a hydration layer at a height of $\sim 4 \text{ \AA}$.

The interfacial structures for Sr^{2+} are distinct from those observed for Rb^+ . The height of the first adsorbed Sr^{2+}

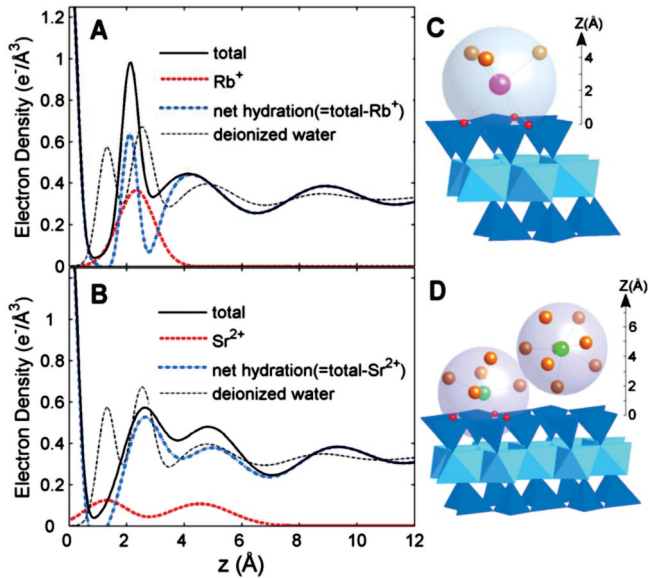


FIG. 3 (color). Total and ion-specific electron density profiles along the surface-normal direction above the muscovite (001) surface for (a) Rb^+ and (b) Sr^{2+} at concentrations of 0.01 M and $\text{pH} \sim 5.5$. Net interfacial hydration profiles (blue dash-dot lines) obtained by subtracting the derived cation adsorption profiles (red dashed lines) from the total interfacial electron density profiles (black solid lines) are compared to the original interfacial hydration structure in deionized water (thin black dashed line) [14]. The origin is chosen at the mean position of the (001) surface oxygen layer in the muscovite. Pictorial models of (c) Rb^+ and (d) Sr^{2+} aqueous complexes on the muscovite surface based on the measured ion adsorption profiles and known ion-hydration structures in bulk solution. Magenta: Rb^+ , green: Sr^{2+} , orange: water, red: surface oxygen. The dashed lines represent cation-oxygen bonds in the coordination shell (indicated by the large spheres). Additional water in the surface hydration layer is not included in these pictorial models.

layer [Fig. 3(b)] ($1.26 \pm 0.22 \text{ \AA}$) is lower than the Rb^+ height, but indicates that Sr^{2+} also adsorbs in the ditrigonal cavity [Fig. 3(d)]. The $\text{Sr-O}_{\text{surf}}$ distance ($2.58 \pm 0.45 \text{ \AA}$) is comparable to that of the aqueous hydration shell ($\text{Sr-O}_{\text{hyd}} = 2.63 \text{ \AA}$) [17] within error, indicating classical inner-sphere sorption. The second adsorbed Sr^{2+} layer [Fig. 3(b)] is at a significantly larger height ($4.52 \pm 0.24 \text{ \AA}$). Structural models suggest that this height corresponds to adsorption of Sr^{2+} as a fully hydrated ion [i.e., a classical outer-sphere species; Fig. 3(d)]. The distribution width of the fully hydrated species ($\text{FWHM} = 3.14 \pm 0.29 \text{ \AA}$) is $\sim 50\%$ larger than that of the partially hydrated species ($\text{FWHM} = 2.00 \pm 0.29 \text{ \AA}$) suggesting that the fully hydrated species is more mobile. The larger width may be due to changes in the ion height as the cation moves laterally through the interfacial hydration layer. The net interfacial hydration layer in the presence of Sr^{2+} is also more diffuse than that observed in the presence of Rb^+ . This reflects the superposed hydration structures of the two sorbed Sr^{2+} species. While adsorption of Sr^{2+} as a

fully hydrated species might be expected due to its large hydration energy ($-1445 \text{ kJ mol}^{-1}$ as compared to -296 kJ mol^{-1} for Rb^+) [18], the coexistence of fully and partially hydrated Sr^{2+} is a key difference with respect to the simpler behavior observed for Rb^+ .

The adsorbed ion coverages derived from the RAXR spectra give additional insight into aqueous cation-surface interactions. The derived Rb^+ coverage of $0.72 \pm 0.16 \text{ Rb}^+ / A_{\text{uc}}$ (where $A_{\text{uc}} = 46.72 \text{ \AA}^2$) compensates 72% of the fixed surface charge ($1.0e^- / A_{\text{uc}}$) and is similar to that derived from SFA measurements [4]. The remaining charge presumably is compensated by a diffuse Rb^+ layer (to which the present measurements are insensitive). In contrast, the total coverage of Sr^{2+} ($0.64 \pm 0.16 \text{ Sr}^{2+} / A_{\text{uc}}$, with 0.28 ± 0.12 and 0.36 ± 0.12 in the first and second sorption layers, respectively) indicates full compensation of the surface charge [19].

The observed coverage of Sr^{2+} provides a simple explanation for the SFA-based observations that only weak long-range forces were observed at and above $\sim 10^{-2} \text{ M}$ concentration in divalent cation solutions [5]. It contrasts, however, with the interpretation of the SFA results in terms of a relatively weak interaction between the divalent cations and muscovite surface (i.e., low surface coverage) with charge compensated mainly by adsorption of hydronium ions (H_3O^+). The present results suggest instead that the weak forces measured by SFA are the result of nearly full compensation of the interfacial charge by a two-component Stern layer, due to strong interaction between the divalent cations and muscovite surface. Strong adsorption is supported by our experimental observation that Sr^{2+} does not desorb rapidly upon rinsing with deionized water, conditions under which Rb^+ readily desorbs (data not shown).

The distribution of Sr^{2+} in two different interfacial sites involves a balance between the energy needed to remove water molecules from the ion's hydration shell and the energy released by compensating the surface charge. Given the probable rapid exchange rate of water in the Sr^{2+} hydration shell ($> 10^8 \text{ sec}^{-1}$, inferred from the value for Ca^{2+} [2]), we surmise that the total structure represents a dynamic equilibrium between partially and fully hydrated species of Sr^{2+} . Therefore, the comparable occupancies of the two adsorbed Sr species indicate that the adsorption strengths for these species must be comparable, contrary to the common assumption that outer-sphere adsorption is inherently weaker than inner-sphere adsorption [1]. The exact behavior, however, will be system dependent since the tendency to form fully hydrated species would increase with the cation's hydration energy and the separation between the adsorbed cation and surface charge.

Ion-hydration energies alone are not able to explain our results if we consider the electrostatic energy difference between the two adsorbed divalent cation species. The reduction in electrostatic energy by shifting Sr^{2+} from the fully hydrated to the partially hydrated position is

only ~ 15 kJ mol $^{-1}$, assuming a constant electrostatic field in a medium with a dielectric constant of bulk liquid water (i.e., $\epsilon_r \sim 80$) [20]. Given the large ion-hydration energy for Sr $^{2+}$, this suggests that stabilization of the partially hydrated species may require a substantially larger electrostatic energy contribution which could be achieved through a significant reduction of the interfacial dielectric constant from that of bulk water [21] and/or strong electrostatic coupling of counterions with localized surface charges [22]. A low dielectric constant for interfacial water agrees with the presence of an ordered interfacial hydration layer, as observed here and previously [14,23–26]. Consequently, while the large difference in hydration energies for Rb $^{+}$ and Sr $^{2+}$ can explain their contrasting interfacial ion distributions, the estimated energy balance demonstrates the critical role that the interfacial hydration structure must play in stabilizing the distributions.

These results explain known trends showing that the hydration state of adsorbed cations depends on the location and magnitude of surface charge. Cations tend to partially dehydrate upon adsorption when charge is located at the surface (e.g., simple oxides [27]) but instead tend to adsorb as fully hydrated species when the charge is deeper in the lattice (e.g., some clays [28]), with adsorption on muscovite being intermediate between these two regimes. Also, the lower surface charge that is often found in clays perturbs the interfacial dielectric constant less, thus favoring adsorption of hydrated cations. While the distribution and hydration of interfacial ions have long been known to be critical aspects of these phenomena [29], the direct determination of the interfacial structure demonstrates that explicit incorporation of these key molecular-scale features into theoretical descriptions is necessary.

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- [20] The energy change due to displacing a point charge in the surface-normal direction near a flat charged surface is given by $\Delta E = \Delta z N_A Z Q e^2 / 2 \epsilon_r \epsilon_0$ (Δz : charge displacement, N_A : Avogadro's number, Z : ion valence, Q : surface charge density, e : electron charge, ϵ_0 : dielectric permittivity of vacuum). The quoted change in energy is much smaller than the energy required to remove even a single water molecule from the Sr $^{2+}$ hydration shell ($1445/8 = 181$ kJ mol $^{-1}$). Assuming an extreme case of $\epsilon_r \sim 6$ (Ref. [21]) for ordered water near solid surfaces, the electrostatic energy is reduced by ~ 200 kJ mol $^{-1}$, which is comparable to the energy required to remove one water molecule from the hydration shell.
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