

## Supporting Information for

### Stern Layer Structure and Energetics at Mica-Water Interfaces

Ian C. Bourg<sup>1</sup>, Sang Soo Lee<sup>2</sup>, Paul Fenter<sup>2</sup>, Christophe Tournassat<sup>3</sup>

<sup>1</sup>*Princeton University, Department of Civil and Environmental Engineering and Princeton Environmental Institute, Princeton, NJ 08544, USA*

<sup>2</sup>*Argonne National Laboratory, Chemical Sciences and Engineering Division, Argonne, IL 60439, USA*

<sup>3</sup>*Université d'Orléans – CNRS/INSU – BRGM, UMR 7327 Institut des Sciences de la Terre d'Orléans, 45071 Orléans, France*

#### XRR analyses

In-situ X-ray reflectivity (XRR) data were fit by (1) conventional model analyses (**Fit<sub>Model</sub>**), i.e., using the structural model for both the solid muscovite and solution<sup>1,2</sup> or (2) using the water profile derived from Molecular Dynamics (MD) simulations (**Fit<sub>MDwater</sub>**)<sup>3</sup> for which only the atoms in the solid mica substrate are modelled using the conventional approach. The model for the mica substrate has the unrelaxed muscovite substrate lattice and relaxed muscovite surface. The model for the solution has the adsorbed solution species and the water above the interfacial region.<sup>1,2</sup> The reflectivity for **Fit<sub>Model</sub>** and **Fit<sub>MDwater</sub>** is expressed as a function of vertical momentum transfer ( $q$ ) as,

$$R(q) \propto (4\pi r_e / q A_{UC})^2 |F_{UC} F_{CTR} + F_{MICA_{surf}} + F_{ADS} + F_{WATER}|^2 \quad (S1)$$

$$R(q) \propto (4\pi r_e / q A_{UC})^2 |F_{UC} F_{CTR} + F_{MICA_{surf}} + F_{MDwater} + F_{WATER}|^2 \quad (S2)$$

where  $r_e$  is the classical electron radius,  $A_{UC}$  is the unit cell area of the muscovite (001) plane (= 46.72 Å<sup>2</sup>),<sup>4</sup> and  $F_{CTR}$  is the structure factor for a semi-infinite crystal along the surface normal

direction ( $= 1/[1-\exp(-iqd/2)]$ )<sup>5,6</sup> where  $d$  is the (001) layer spacing of the mica, which is  $\sim 19.96$  Å.<sup>4</sup> The structure factors for a unit cell of muscovite, the relaxed mica surface, adsorbed species, and bulk water ( $F_{\text{UC}}$ ,  $F_{\text{MICA surf}}$ ,  $F_{\text{ADS}}$ , and  $F_{\text{WATER}}$ , respectively) are calculated as

$$F = \sum_j c_j f_j(q) \exp(iqz_j) \exp[-(qu_j)^2/2] \quad (\text{S3})$$

using the atomic form factor ( $f_j(q)$ ),<sup>7</sup> occupancy ( $c_j$ ), height ( $z_j$ ), and root-mean-square (rms) distribution width ( $u_j$ ) of a  $j^{\text{th}}$  atom. The vertical displacements of  $\text{K}^+$  ions in the interlayers and O atoms in 2:1 (tetrahedral-octahedral-tetrahedral) layers<sup>8</sup> in the top two unit cells (i.e., four 2:1 layers) are allowed to vary independently, while those of  $\text{Si}^{4+}$  (or  $\text{Al}^{3+}$ ) in T sites and  $\text{Al}^{3+}$  in M sites (specifically in two M2 sites, for dioctahedral micas like muscovite) are determined as the average values of those of the coordinating oxygens and a hydroxyl.<sup>1,2</sup> The vertical distribution of adsorbed solution species, including adsorbed cations and water molecules that are ordered at the mica surface, are modeled using two or three Gaussian peaks (Table SI1) followed by a layered-water model.<sup>4,9</sup> Alternatively, the solution structure obtained from the MD simulations is used to calculate  $F_{\text{MD water}}$  for **Fit<sub>MD water</sub>**.<sup>3</sup> In this analysis, parameter  $\Delta z_{\text{MD}}$  (Table SI2) is used to express the vertical displacement of the MD-derived water profile from the ideal (i.e., unrelaxed) location of the surface oxygen atoms.

The  $q$ - and  $E$ -dependent total structure factor,  $F_{\text{tot}}(q, E)$ , for RAXR is expressed as the sum of non-resonant and resonant structure factors,  $F_{\text{NR}}(q) + F_{\text{R}}(q, E)$ . The  $F_{\text{NR}}(q)$  value is calculated on the basis of the best-fit model of the XRR data.<sup>2</sup> The  $F_{\text{R}}(q, E)$  can be divided into  $E$ -dependent anomalous dispersion term,  $f'(E) + if''(E)$ , and  $q$ -dependent partial structure factor of a resonant atom,  $F_{\text{R}}(q)$ , as  $F_{\text{R}}(q, E) = [f'(E) + if''(E)] F_{\text{R}}(q)$ . The  $f'(E) + if''(E)$  value was determined experimentally using X-ray absorption spectrum measured near  $E_0$  in transmission mode through a 0.1  $m$  RbCl solution followed by the differential Kramers-Kronig transform.<sup>2,10</sup> The  $F_{\text{R}}(q)$  values were calculated using a discrete Fourier transform of the element-specific Rb<sup>+</sup> profile derived from the MD simulation as described previously.<sup>3</sup>

The model parameters were optimized using least-squares fitting. The best-fit model was selected based on the smallest  $\chi^2$  ( $= \sum_k [(I_k - I_{\text{calc},k})/\sigma_k]^2 / (N - N_p)$ ), where  $I_k$  and  $I_{\text{calc},k}$  are the measured and calculated intensities, respectively,  $\sigma_k$  is the measured uncertainty of the  $k^{\text{th}}$  data

point, and  $N$  and  $N_p$  are the numbers of data points and parameters used in the model-fit, respectively). The  $R$ -factor ( $= \sum_k (|I_k - I_{\text{calc},k}|/I_k)/N$ ) of the best-fit is also reported for comparison.

Overall, the analyses show excellent agreement between the experimental and simulated data (Fig. 3). However, small differences are observed at  $q > 3 \text{ \AA}^{-1}$  especially with heavier cations (e.g., Rb and Cs). The  $\chi^2$  values between **Fit<sub>Model</sub>** and **Fit<sub>MDwater</sub>** were compared to quantify these differences among the datasets. The fractional deviation ( $f_{\chi^2}$ ) calculated as  $(\chi^2_{\text{MD}} - \chi^2_{\text{model}})/\chi^2_{\text{model}}$  ranges from 1.8 to 4.4, and generally increases as the atomic number increases (Table SI2). This observation does not necessarily indicate that the MD-derived profiles with lighter cations better represent the actual interfacial structures than those with heavier cations. Rather, it most likely results from an increased sensitivity of XRR to heavier elements. That is, the XRR becomes more sensitive to a small difference in the distribution of a heavier cation, e.g., even a few tenths of Ångström difference in height, at the interface.<sup>2,6</sup>

The **Fit<sub>Model</sub>** results show significant displacements of atoms extending into the crystal. The largest magnitudes of displacement are observed in the top surface layer (i.e., within  $\sim 10 \text{ \AA}$  depth) which decrease with depth and become almost negligible below  $\sim 30 \text{ \AA}$  depth. Especially, the displacements of interlayer K clearly show an exponential decay in the magnitude with depth, consistent with previous observations from the muscovite (001) in contact with 3–30 mM alkali metal chloride solutions.<sup>2</sup> The same trend is also observed from the **Fit<sub>MDwater</sub>** results, which generally show atomic displacements with larger magnitude and more scattered pattern over the  $40 \text{ \AA}$  depth than those from **Fit<sub>Model</sub>**.

## Molecular dynamics (MD) simulations

Newton's equations of motion were solved with the Verlet algorithm. Water molecules were modeled as rigid entities using the SHAKE algorithm. Each simulation contained a mica slab consisting of six 2:1 layer-type phyllosilicate (tetrahedral-octahedral-tetrahedral) layers with 500 potassium ions in its anhydrous interlayers and 100 alkali metal ions (Li, Na, K, Rb, or Cs) on its external basal surfaces, 9616 water molecules, and 18 alkali chloride ion pairs in the water region, for a total of 41,484 atoms.

## Thermodynamic integration (TI) calculations

The TI calculations involved varying the size ( $\sigma_i$ ) and well-depth ( $\epsilon_i$ ) parameters describing the Van der Waals interaction energy  $\phi$  between two ions of type  $i$  on the Lennard-Jones 6-12 interaction model  $[\phi(r_i) = 4 \epsilon_i [(\sigma_i/r_i)^{12} - (\sigma_i/r_i)^6]$  from the value for Cs to the value for Li in a series of small steps. We used a thermodynamic path along which  $\sigma_i$  and  $\epsilon_i$  were adjusted linearly from the values for Cs to Rb in 10 steps, then from Rb to K in 5 steps, from K to Na in 15 steps, and finally from Na to Li in 35 steps. Progress along the overall transformation from Cs to Li is quantified by the parameter  $\lambda$ , which increases regularly from 0 to 1 with each transformation step. Each small transformation step was followed by 0.2 ns of equilibration and 0.8 ns of simulation (for the ions on mica) in the  $NP_zT$  ensemble. After each transformation step, 8 snapshots of the coordination of all 100 adsorbed ions (sampled with a 100 ps interval) were used to calculate the ensemble average value of  $\langle \partial \mathcal{H} / \partial \lambda \rangle_\lambda$  for adsorbed ions, where  $\mathcal{H}$  is the Hamiltonian. Simultaneously, 80 snapshots of the coordination of all ions located  $> 2$  nm from the surface (sampled with a 10 ps interval) were used to calculate the ensemble average value of  $\langle \partial \mathcal{H} / \partial \lambda \rangle_\lambda$  for ions in bulk-liquid-like water. Finally, the free energy difference for the transformation of Cs to Li was calculated as  $\Delta F = \int_0^1 \langle \partial \mathcal{H} / \partial \lambda \rangle_\lambda d\lambda$ . The free energy difference associated with intermediate transformation steps was obtained by calculating the same integral to  $\lambda$  values smaller than 1 (Fig. SI3). Our TI calculations show that the transformation of Cs to Li is less favorable on the mica surface than in bulk liquid water (Fig. SI3). The free energy of the cation exchange reaction was obtained with the relation:  $\Delta F_{\text{ex}}^{\text{Cs}/i} = \Delta F_{\text{ads}}^{\text{Cs}/i} - \Delta F_{\text{aq}}^{\text{Cs}/i}$ . For TI simulations carried out in the  $NPT$  or  $NVT$  ensembles (i.e., at constant pressure or constant volume), the free energy difference  $\Delta F$  corresponds to the difference in Gibbs free energy ( $\Delta G$ ) or in Helmholtz free energy ( $\Delta A$ ), respectively. Since our TI simulations were carried out in the  $NP_zT$  ensemble (constant pressure in the  $z$  direction, but fixed simulation cell size in the  $x$  and  $y$  directions), we simply refer to our calculated free energy difference as  $\Delta F$ . Our predicted values of  $\Delta F_{\text{aq}}^{\text{Cs/Rb}} = 26.6 \pm 0.2 \text{ kJ mol}^{-1}$ ,  $\Delta F_{\text{aq}}^{\text{Cs/K}} = 42.5 \pm 0.3 \text{ kJ mol}^{-1}$ ,  $\Delta F_{\text{aq}}^{\text{Cs/Na}} = 113.4 \pm 0.9 \text{ kJ mol}^{-1}$  and  $\Delta F_{\text{aq}}^{\text{Cs/Li}} = 242.8 \pm 1.4 \text{ kJ mol}^{-1}$  are close to the experimental values of  $\Delta G_{\text{aq}}^{\text{Cs}/i}$  (25, 45, -115, and -225  $\text{kJ mol}^{-1}$ , respectively)<sup>11</sup> except in the case of Li.

## Surface complexation model

Our surface complexation model is based on a simplified version of the three plane model (TPM) formalism,<sup>12</sup> an extension of the well known triple layer model (TLM) of ion adsorption at mineral-water interfaces.<sup>13</sup> To develop a triple plane model (TPM) of ion adsorption at the mica-water interface, we assigned the specific adsorption of ions to three planes (planes 0, 1, and 2) located at  $z = 1, 2$ , and  $4 \text{ \AA}$ . Each cation, then, forms three types of surface complexes:



where  $\text{Mica}^-$  is a negative charge site on the mica surface,  $\text{M} = \text{Li, Na, K, Rb, or Cs}$ , and  $K_{\text{M},p}$  is the equilibrium constant associated with the adsorption of alkali metal  $\text{M}$  in adsorption plane  $p$ . On the TPM model, activities of a surface species are defined as equal to the surface concentration of the species times a Boltzmann factor,  $\exp\left(\frac{zF\psi_{0,1,2}}{RT}\right)$  where  $z$  is the net charge transferred to the planes in the corresponding chemical equation, and where  $\psi_{0,1,2}$  is a surface potential assigned to planes 0, 1 and 2. Intrinsic affinity coefficients  $K_{\text{M},p}$  are, then, related to the activities of dissolved species  $a_i$  and concentrations of surface species  $c_i$  according to:<sup>12,14</sup>

$$K_{\text{M},0} = \frac{a_{\text{MicaM}}}{a_{\text{M}^+} \cdot a_{\text{Mica}^-}} = \frac{c_{\text{MicaM}}}{a_{\text{M}^+} \cdot c_{\text{Mica}^-}} \exp\left(\frac{F\psi_0}{RT}\right) \quad (\text{S7})$$

$$K_{\text{M},1} = \frac{a_{\text{Mica-M}}}{a_{\text{M}^+} \cdot a_{\text{Mica}^-}} = \frac{c_{\text{Mica-M}}}{a_{\text{M}^+} \cdot c_{\text{Mica}^-}} \exp\left(\frac{F\psi_1}{RT}\right) \quad (\text{S8})$$

$$K_{\text{M},2} = \frac{a_{\text{Mica}\cdots\text{M}}}{a_{\text{M}^+} \cdot a_{\text{Mica}^-}} = \frac{c_{\text{Mica}\cdots\text{M}}}{a_{\text{M}^+} \cdot c_{\text{Mica}^-}} \exp\left(\frac{F\psi_2}{RT}\right) \quad (\text{S9})$$

where  $R$  is the ideal gas constant and  $T$  is absolute temperature. Surface potentials values are calculated according to the following charge-potential relationships:

$$\psi_0 - \psi_1 = \frac{\sigma_0}{c_1} \quad (\text{S10})$$

$$\psi_1 - \psi_2 = \frac{\sigma_0 + \sigma_1}{C_2} \quad (\text{S11})$$

where  $C_1$  and  $C_2$  are interfacial capacitance densities (in  $\text{F}\cdot\text{m}^{-1}$ ), and  $\sigma_0$  and  $\sigma_1$  are the charge residing in planes 0 and 1 (in  $\text{C}\cdot\text{m}^{-2}$ ). The relationship between  $\sigma_2$  and  $\psi_2$  is obtained from the Gouy-Chapman relation:

$$\sigma_2 = -2\sqrt{2\varepsilon_w\varepsilon_0RT1000I} \sinh\left(\frac{F\psi_2}{2RT}\right) \quad (\text{S12})$$

where  $\varepsilon_w$  is the water dielectric constant (78.4 at 25 °C), and  $I$  is the ionic strength (expressed here in  $\text{mol}\cdot\text{dm}^{-3}$ ). At last, the following charge balance constraint makes it possible to calculate  $\psi_{0,1,2}$  values:

$$Q_0 + Q_1 + Q_2 + Q_d = 0 \quad (\text{S13})$$

Calculations were carried out with the geochemical code PHREEQC v.3 in which the TPM is implemented.<sup>15</sup> The activities of species in solution were calculated with the Debye-Huckel activity model. The resulting values of the equilibrium constants  $K_{M,p}$  are reported in Table SI4. The PHREEQC input file that calculates the results shown in Figure 9 is given at the end of this electronic annex.

Table SI1. Best-fit model parameters for the adsorbed solution species with **FIT<sub>Model</sub>**.

| Samples | $\chi^2$ (R-factor) | First peak |                    |           | Second peak |                    |           | Third peak |                    |           |
|---------|---------------------|------------|--------------------|-----------|-------------|--------------------|-----------|------------|--------------------|-----------|
|         |                     | $z_1$ (Å)  | $c_1$ ( $W_{eq}$ ) | $u_1$ (Å) | $z_2$ (Å)   | $c_2$ ( $W_{eq}$ ) | $u_2$ (Å) | $z_3$ (Å)  | $c_3$ ( $W_{eq}$ ) | $u_3$ (Å) |
| LiCl    | 3.01 (0.067)        | 0.94(f)    | 0.05(11)           | 0.10(f)   | 2.33(4)     | 6.54(44)           | 0.86(6)   | 5.27(15)   | 4.68(99)           | 1.03(16)  |
| NaCl    | 2.20 (0.051)        | 1.07(4)    | 0.29(5)            | 0.10(f)   | 2.58(2)     | 6.61(15)           | 0.87(2)   | 5.34(6)    | 3.09(23)           | 0.82(4)   |
| KCl     | 3.21 (0.064)        | 1.99(7)    | 3.46(50)           | 0.48(6)   | 3.51(8)     | 3.28(57)           | 0.53(8)   | 5.88(9)    | 4.30(92)           | 1.08(14)  |
| RbCl    | 4.41 (0.088)        | 2.06(2)    | 2.30(6)            | 0.10(f)   | 3.17(12)    | 7.52(97)           | 1.34(13)  |            |                    |           |
| CsCl    | 3.15 (0.061)        | 2.25(1)    | 4.89(12)           | 0.25(1)   | 3.49(8)     | 3.68(58)           | 1.08(7)   |            |                    |           |

$z_j$ ,  $c_j$ , and  $u_j$ : height from the muscovite surface, occupancy, and distribution width of the  $j^{\text{th}}$  peak ( $j=1,2$ , and  $3$ ). Occupancies ( $c_j$ ) are expressed in the dimensionless unit of water equivalents,  $W_{eq}$ , the effective number of water molecules required to obtain the electron density of a peak (i.e., the electron density normalized to the number of electrons in  $H_2O$  molecules per  $A_{UC}$ ).

f: fixed during fit

The number in parentheses after each parameter indicates the  $1\sigma$  standard deviation of the last digit(s).

Table SI2. XRR data fit with the MD-derived water profiles (**Fit<sub>MDwater</sub>**).

| Samples                                                    | LiCl    | NaCl    | KCl     | RbCl    | CsCl    |
|------------------------------------------------------------|---------|---------|---------|---------|---------|
| $\chi^2$                                                   | 8.41    | 7.77    | 10.71   | 17.34   | 16.97   |
| (R-factor)                                                 | (0.102) | (0.091) | (0.151) | (0.160) | (0.109) |
| $f_{\chi^2}$                                               | 1.8     | 2.5     | 2.3     | 2.9     | 4.4     |
| $\Delta z_{\text{MD}}$ (Å)                                 | 0.13(2) | 0.05(1) | 0.21(1) | 0.32(2) | 0.24(1) |
| $\rho_{\text{solution}}$ (e <sup>-</sup> /Å <sup>3</sup> ) | 0.336   | 0.338   | 0.341   | 0.343   | 0.345   |

$f_{\chi^2} = (\chi^2_{\text{MD}} - \chi^2_{\text{model}}) / \chi^2_{\text{model}}$  where  $\chi^2_{\text{MD}}$  and  $\chi^2_{\text{model}}$  are the  $\chi^2$  values from **Fit<sub>MDwater</sub>** and **Fit<sub>Model</sub>**, respectively.

$\Delta z_{\text{MD}}$ : vertical displacement of the MD-derived water profile

$\rho_{\text{solution}}$ : calculated electron density of each 0.1 M alkali metal chloride solution

The number in parentheses after each parameter indicates the 1 $\sigma$  standard deviation of the last digit(s).



Table SI3. Cation and water density peak coordinates predicted here and in previous MD or MC simulations of mica-water interfaces. Values reported in bold font are peak coordinates predicted in the present study. Values reported in italics are the fraction of surface charge balanced by ISSC1 and ISSC2 counter-ions and the relative contribution of sub-layers W1.1, 1.2, and 1.3 to the first water layer.

| ISSC1       | ISSC2                    | OSSC                     | W1.1               | W1.2               | W1.3                     | W2          | W3          | Salinity     | Model                         |
|-------------|--------------------------|--------------------------|--------------------|--------------------|--------------------------|-------------|-------------|--------------|-------------------------------|
| Li-mica     |                          |                          |                    |                    |                          |             |             |              |                               |
| 0.5         | 2.0                      | 3.7                      | 2.1                | 2.7                | —                        | 5.7         | ~ 9         | 0 M          | KFF <sup>c</sup>              |
| <b>1.37</b> | <b>1.83</b>              | <b>~ 3.3<sup>b</sup></b> | <b>1.65</b>        | <b>2.91</b>        | —                        | <b>5.51</b> | <b>9.05</b> | <b>0.1 M</b> | <b>CLAYFF+SPC/E</b>           |
| <i>0.33</i> | <i>0.64</i>              |                          | <i>0.35</i>        | <i>0.65</i>        | —                        |             |             |              |                               |
| Na-mica     |                          |                          |                    |                    |                          |             |             |              |                               |
| 1.4         | —                        | —                        | 2.0                | ~ 2.9 <sup>a</sup> | 3.2                      | 5.8         | 9.7         | 0 M          | KFF <sup>c</sup>              |
| 1.5         | —                        | —                        | ~ 1.9 <sup>a</sup> | 3.2                |                          | 5.9         | 9.5         | 0.5 M        | KFF <sup>c</sup>              |
| 0.5/1.8     | —                        | —                        | n.r.               | n.r.               | n.r.                     | n.r.        | n.r.        | 1 M          | CLAYFF+SPC <sup>d</sup>       |
| <b>1.05</b> | <b>2.05</b>              | <b>~ 4.1<sup>b</sup></b> | <b>1.77</b>        | <b>2.61</b>        | <b>~ 3.1<sup>a</sup></b> | <b>5.63</b> | <b>9.07</b> | <b>0.1 M</b> | <b>CLAYFF+SPC/E</b>           |
| <i>0.63</i> | <i>0.33</i>              |                          | <i>0.13</i>        | <i>~ 0.44</i>      | <i>~ 0.43</i>            |             |             |              |                               |
| K-mica      |                          |                          |                    |                    |                          |             |             |              |                               |
| 1.5         | —                        | —                        | 2.0                | 2.8                | 3.3                      | 5.9         | 9.5         | 0 M          | KFF <sup>c</sup>              |
| 2.1         | 2.5                      | —                        | 1.6                | 2.8                | —                        | 5.1         | n.r.        | 0 M          | SFF+MCY <sup>e</sup>          |
| —           | 2.3                      | —                        | 1.9                | 2.6                | —                        | 5.0         | 7.7         | 0 M          | SFF+TIP4P <sup>f</sup>        |
| —           | 2.1                      | —                        | 1.7                | 2.7                | —                        | 5.0         | n.r.        | 0 M          | SFF+TIP4P <sup>g</sup>        |
| 1.5         | —                        | —                        | n.r.               | n.r.               | n.r.                     | n.r.        | n.r.        | 0 M          | CLAYFF+SPC <sup>d</sup>       |
| 1.7         | —                        | —                        | 1.7                | 2.7                | 3.6                      | 6.3         | ~ 9.5       | 0 M          | CLAYFF+SPC <sup>h</sup>       |
| 1.4         | —                        | —                        | 1.8                | 2.7                | 3.5                      | 6.1         | ~ 9.2       | 0 M          | CLAYFF+SPC <sup>i</sup>       |
| n.r.        | n.r.                     | n.r.                     | 1.7                | 2.7                | 3.6                      | n.r.        | n.r.        | 0 M          | CLAYFF+TIP4P2005 <sup>j</sup> |
| <b>1.53</b> | <b>~ 2.4<sup>a</sup></b> | <b>~ 4.6<sup>b</sup></b> | <b>1.75</b>        | <b>2.63</b>        | <b>3.55</b>              | <b>6.13</b> | <b>9.19</b> | <b>0.1 M</b> | <b>CLAYFF+SPC/E</b>           |
| <i>0.91</i> | <i>0.08</i>              |                          | <i>0.11</i>        | <i>0.37</i>        | <i>0.53</i>              |             |             |              |                               |
| Rb-mica     |                          |                          |                    |                    |                          |             |             |              |                               |
| <b>1.67</b> | <b>2.53</b>              | <b>~ 5.3<sup>b</sup></b> | <b>1.73</b>        | <b>2.63</b>        | <b>3.69</b>              | <b>6.29</b> | <b>9.05</b> | <b>0.1 M</b> | <b>CLAYFF+SPC/E</b>           |
| <i>0.89</i> | <i>0.07</i>              |                          | <i>0.12</i>        | <i>0.36</i>        | <i>0.52</i>              |             |             |              |                               |
| Cs-mica     |                          |                          |                    |                    |                          |             |             |              |                               |
| 2.0         | —                        | —                        | 2.0                | 2.8                | 4.0                      | 6.3         | —           | 0 M          | KFF <sup>c</sup>              |
| 2.0         | —                        | —                        | 1.8                | 2.5                | —                        | 5.0         | n.r.        | 0 M          | SFF+TIP4P <sup>g</sup>        |
| 2.0         | —                        | ~ 5.5 <sup>b</sup>       | 2.3                | 3.2                | 4.0                      | 6.7         | ~ 10.0      | 0 M          | CLAYFF+SPC <sup>k</sup>       |
| <b>1.93</b> | <b>2.87</b>              | <b>~ 5.5<sup>b</sup></b> | <b>1.69</b>        | <b>2.61</b>        | <b>~ 3.9<sup>a</sup></b> | <b>5.11</b> | <b>8.95</b> | <b>0.1 M</b> | <b>CLAYFF+SPC/E</b>           |
| <i>0.83</i> | <i>0.07</i>              |                          | <i>0.15</i>        | <i>0.42</i>        | <i>0.43</i>              |             |             |              |                               |

<sup>a</sup>Interatomic potential models include the MCY,<sup>16</sup> SPC and SPC/E,<sup>17</sup> TIP4P,<sup>18</sup> and TIP4P2005<sup>19</sup> water models, the SFF<sup>20</sup> and CLAYFF<sup>21</sup> clay models, and the KFF<sup>22</sup> model of clay and water. n.r.: not reported. <sup>b</sup>Approximate position of a very low peak or a shoulder on a nearby peak. <sup>c</sup>Sakuma et al.<sup>22-24</sup> (reported  $z$  values were decreased by 0.1 Å to account for the fact that the authors set  $z = 0$  at the outermost basal O atoms, not the average position of basal O atoms). <sup>d</sup>Teich-McGoldrick et al.<sup>25</sup> <sup>e</sup>Park and Sposito<sup>26</sup> (data obtained with a rigid mica structure; water density peak positions were read from a figure and incremented by 0.2 Å based on the authors' statement that their reported values were "offset by 0.2 Å from their absolute position"). <sup>f</sup>Leng et

al.<sup>27,28</sup> g Meleshyn<sup>29,30</sup> (data obtained with a rigid mica structure).<sup>h</sup> Wang et al.<sup>31</sup> i Dequidt et al.<sup>32</sup> j Song et al.<sup>33</sup>  
(data obtained with mica coated by only ~1.5 water monolayers).<sup>k</sup> Kerisit et al.<sup>34</sup>

Table SI4. Values of the equilibrium constants  $K_{M,p}$  for the adsorption of the five alkali metals ( $M = \text{Li, Na, K, Rb, Cs}$ ) in the three adsorption planes ( $p = 0, 1, 2$ ) on our three plane model (TPM).

| Metal               | Li    | Na    | K     | Rb    | Cs   |
|---------------------|-------|-------|-------|-------|------|
| $\log_{10} K_{M,0}$ | -1.20 | -0.95 | -0.17 | -0.64 | -99  |
| $\log_{10} K_{M,1}$ | 0.40  | -0.20 | 1.18  | 1.56  | 1.40 |
| $\log_{10} K_{M,2}$ | -0.40 | -0.45 | 0.45  | 0.76  | 1.05 |

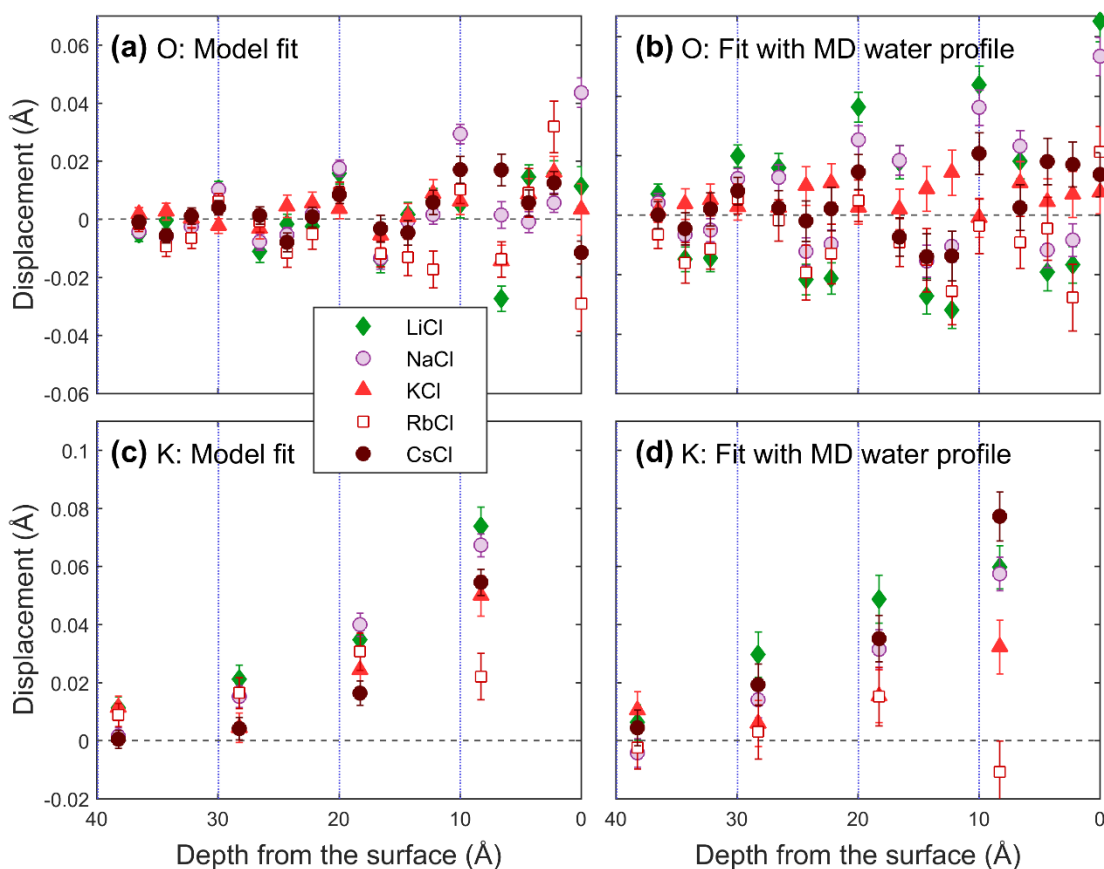


Figure S11. Vertical displacements of O atoms and interlayer K in the top two unit cells of muscovite below the (001) surface in contact with 0.1 M alkali metal cation chloride solutions. **a** and **b**: O displacements derived from **Fit<sub>Model</sub>** and **Fit<sub>MDwater</sub>**. **c** and **d**: K displacements derived from **Fit<sub>Model</sub>** and **Fit<sub>MDwater</sub>**. A positive displacement indicates movement of an atom toward the solution. Blue vertical lines show the top oxygen plane of each half unit cell.

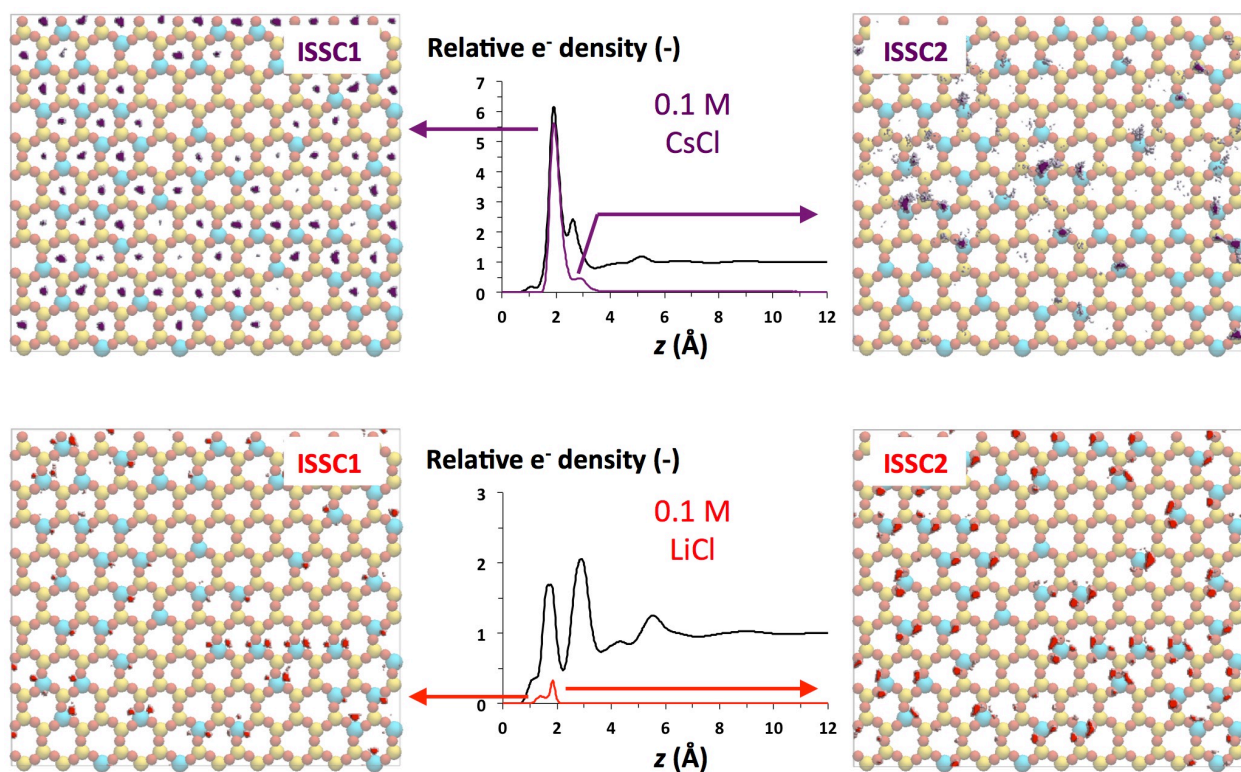


Figure SI2. Central column: electron density profiles as a function distance from the mica surface (black lines) and contribution from the counter-ion (colored lines) predicted by MD simulation in the case of Cs- and Li-bearing mica (upper and lower figures). The figures of the left and right sides show  $xy$  density maps of ISSC1 and ISSC2 species on one of the mica surfaces, overlain on an image of surface O atoms (red spheres) and underlying Si and Al atoms (yellow and blue spheres). Light and dark colors (purple and red for Cs and Li, respectively) indicate regions where cation atomic density is  $> 0.5$  times or  $> 3$  times greater than the density of O atoms in liquid water.

Figure SI3. Difference in free energy ( $\text{kJ mol}^{-1}$ ) associated with the transformation of Cs to Li at the mica-water interface (pink squares) or in bulk-liquid-like water (light blue diamonds) predicted with the TI technique, plotted as a function of the progress of the transformation.

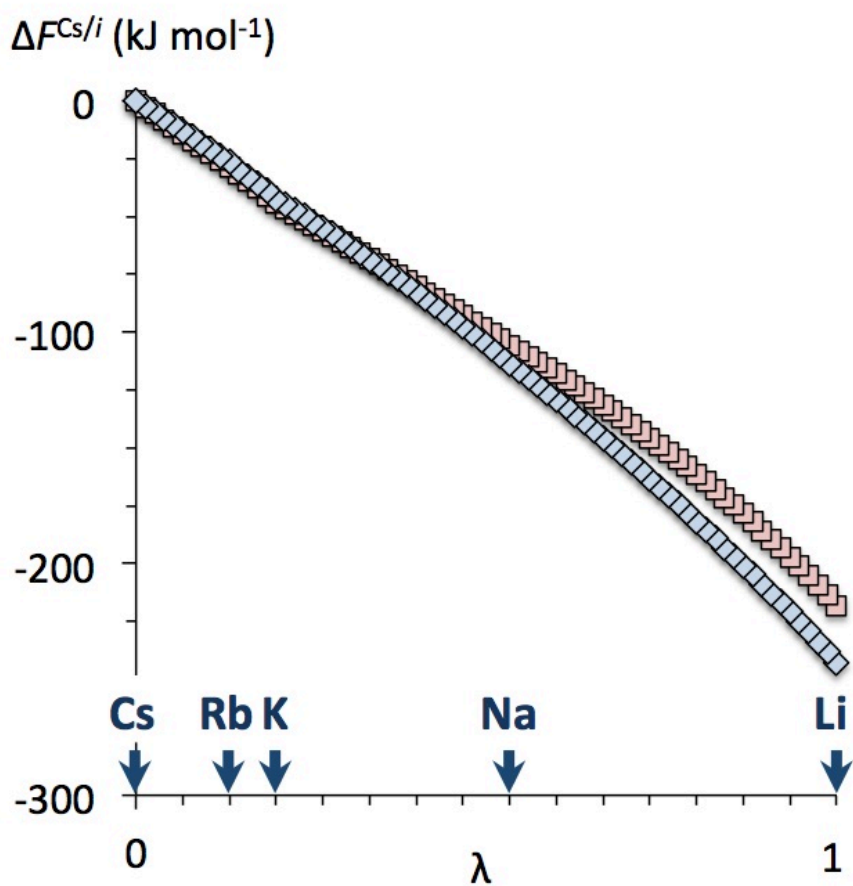
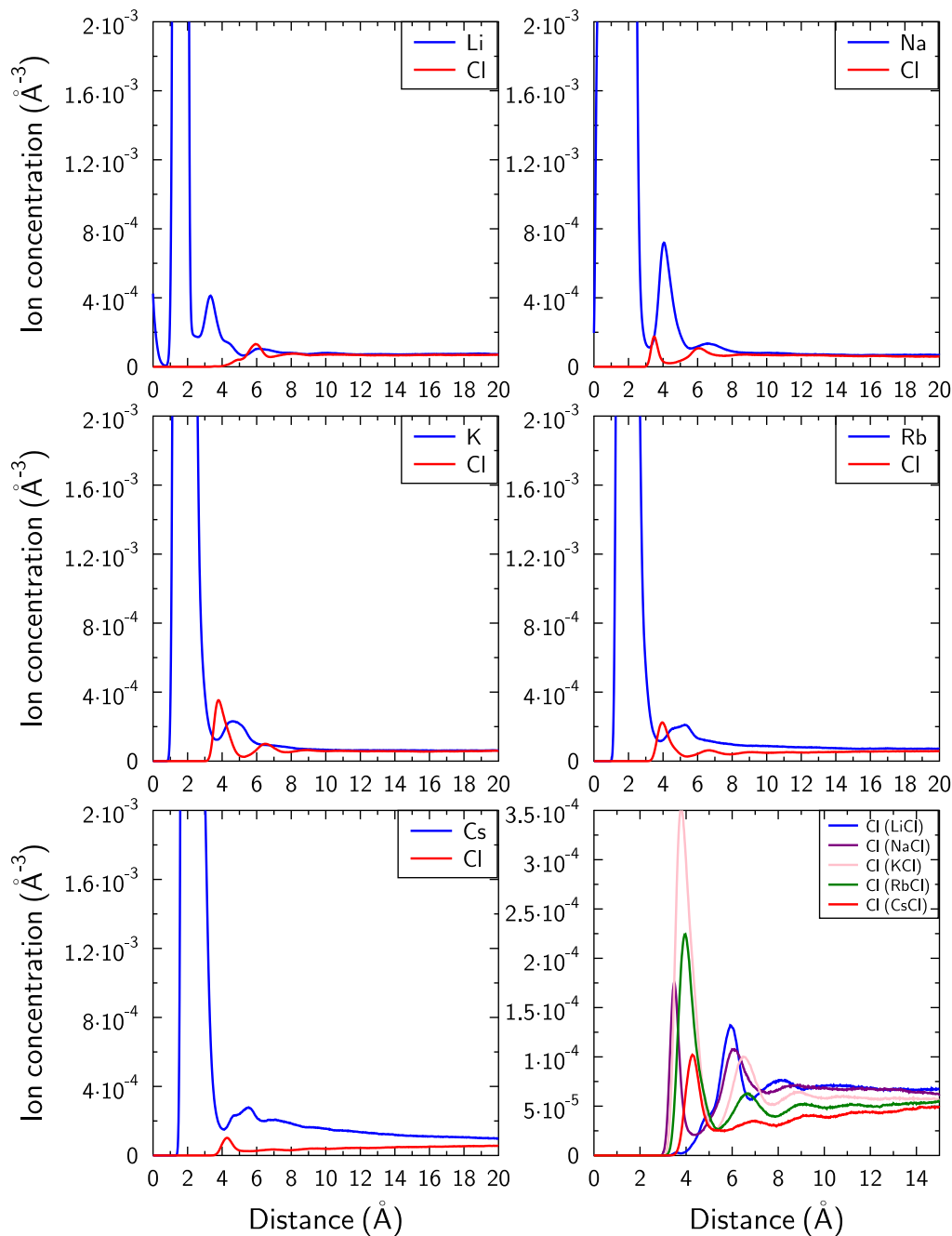


Figure SI4. Comparison of alkali metal (blue line) and chloride (red line) density profiles predicted by MD simulations for muscovite mica in contact with 0.1 M alkali chloride solutions. The figure in the lower right corner compares chloride density profiles obtained with the five different alkali metals.



## PHREEQC input file

```
DATABASE ThermoChimie_PHREEQC_v9.dat
#9616 water molecules
#18 alkali chloride ion pairs --> 0.104 mol/L

# C = eps*eps0/x
# if eps = 78.3 then C = 78.3*8.85419e-12/x =0.693 / x with x in nm
# if eps = 39.2 then C = 39.2*8.85419e-12/x =0.347 / x with x in nm

SURFACE_MASTER_SPECIES
Mica Mica-

SURFACE_SPECIES
Mica- = Mica-
log_k 0
-cd_music 0 0 0

Mica- + Na+ = NaMica
log_k -0.95
-cd_music 1 0 0

Mica- + Na+ = MicaNa
log_k -0.2
-cd_music 0 1 0

Mica- + Na+ = (Mica)Na
log_k -0.45
-cd_music 0 0 1

Mica- + Li+ = LiMica
log_k -1.2
-cd_music 1 0 0

Mica- + Li+ = MicaLi
log_k 0.4
-cd_music 0 1 0

Mica- + Li+ = (Mica)Li
log_k -0.4
-cd_music 0 0 1

Mica- + K+ = KMica
log_k -0.17
-cd_music 1 0 0
```



```
Mica- + K+ = MicaK
log_k 1.18
-cd_music 0 1 0
```

```
Mica- + K+ = (Mica)K
log_k 0.45
-cd_music 0 0 1
```

```
Mica- + Rb+ = RbMica
log_k -0.635
-cd_music 1 0 0
```

```
Mica- + Rb+ = MicaRb
log_k 1.555
-cd_music 0 1 0
```

```
Mica- + Rb+ = (Mica)Rb
log_k 0.755
-cd_music 0 0 1
```

```
Mica- + Cs+ = CsMica
log_k -99
-cd_music 1 0 0
```

```
Mica- + Cs+ = MicaCs
log_k 1.4
-cd_music 0 1 0
```

```
Mica- + Cs+ = (Mica)Cs
log_k 1.05
-cd_music 0 0 1
```

```
SELECTED_OUTPUT
-reset false
-user_punch true
-file Mica_Li_pragmatic.prn
USER_PUNCH
-headings "n°" "Elem" "%DL" "%Na0_n" "%Na1_n" "%Na2_n"
-start
3 PUNCH 1
5 PUNCH "Li"
10 PUNCH (3.524e-3-MOL("LiMica")-MOL("MicaLi")-
MOL("(Mica)Li"))/3.524e-3
20 Ch0=MOL("LiMica")/(MOL("LiMica")+MOL("MicaLi")+MOL("(Mica)Li"))
25 PUNCH Ch0
30 Ch1=MOL("MicaLi")/(MOL("LiMica")+MOL("MicaLi")+MOL("(Mica)Li"))
35 PUNCH Ch0+Ch1
```

```

40 Ch2=MOL("(Mica)Li")/(MOL("LiMica")+MOL("MicaLi")+MOL("(Mica)Li"))
45 PUNCH Ch0+Ch1+Ch2
-end

SOLUTION 1
-water 1
Li 104
Cl 104 charge
Surface 1
-equilibrate 1
Mica 3.524e-3 1000 1 #0.34 C/m2 -> 3.52e-6 mol/m2 ; 1000 m2 => 3.52e-3
mol site
-cd_music
-donnan 2e-9 # 0.104 mol/L, two debye lengths ~2nm
-capacitance 3.47 1.74
# Plane 0 at 1
# Plane 1 at 2 A = 1+1 --> C1=3.47 F m-1
# Plane 2 at 4 A = 2+1 --> C2=1.74 F m-1
END

SELECTED_OUTPUT
-reset false
-user_punch true
-file Mica_Na_pragmatic.prn
USER_PUNCH
-headings "n°" "Elem" "%DL" "%Na0_n" "%Na1_n" "%Na2_n"
-start
3 PUNCH 2
5 PUNCH "Na"
10 PUNCH (3.524e-3-MOL("NaMica")-MOL("MicaNa")-
MOL("(Mica)Na"))/3.524e-3
20 Ch0=MOL("NaMica")/(MOL("NaMica")+MOL("MicaNa")+MOL("(Mica)Na"))
25 PUNCH Ch0
30 Ch1=MOL("MicaNa")/(MOL("NaMica")+MOL("MicaNa")+MOL("(Mica)Na"))
35 PUNCH Ch0+Ch1
40 Ch2=MOL("(Mica)Na")/(MOL("NaMica")+MOL("MicaNa")+MOL("(Mica)Na"))
45 PUNCH Ch0+Ch1+Ch2
-end

SOLUTION 1
-water 1
Na 104
Cl 104 charge
Surface 1
-equilibrate 1
Mica 3.524e-3 1000 1 #0.34 C/m2 -> 3.52e-6 mol/m2 ; 1000 m2 => 3.52e-3
mol site
-cd_music

```

```

-donnan 2e-9 # 0.104 mol/L, two debye lengths ~2nm
-capacitance 3.47 1.74
# Plane 0 at 1
# Plane 1 at 2 A = 1+1 --> C1=3.47 F m-1
# Plane 2 at 4 A = 2+1 --> C2=1.74 F m-1

END

SELECTED_OUTPUT
-reset false
-user_punch true
-file Mica_K_pragmatic.prn
USER_PUNCH
-headings "n°" "Elem" "%DL" "%Na0_n" "%Na1_n" "%Na2_n"
-start
3 PUNCH 3
5 PUNCH "K"
10 PUNCH (3.524e-3-MOL("KMica")-MOL("MicaK")-MOL("(Mica)K"))/3.524e-3
20 Ch0=MOL("KMica")/(MOL("KMica")+MOL("MicaK")+MOL("(Mica)K"))
25 PUNCH Ch0
30 Ch1=MOL("MicaK")/(MOL("KMica")+MOL("MicaK")+MOL("(Mica)K"))
35 PUNCH Ch0+Ch1
40 Ch2=MOL("(Mica)K")/(MOL("KMica")+MOL("MicaK")+MOL("(Mica)K"))
45 PUNCH Ch0+Ch1+Ch2
-end

SOLUTION 1
-water 1
K 104
Cl 104 charge
Surface 1
-equilibrate 1
Mica 3.524e-3 1000 1 #0.34 C/m2 -> 3.52e-6 mol/m2 ; 1000 m2 => 3.52e-3
mol site
-cd_music
-donnan 2e-9 # 0.104 mol/L, two debye lengths ~2nm
-capacitance 3.47 1.74
# Plane 0 at 1
# Plane 1 at 2 A = 1+1 --> C1=3.47 F m-1
# Plane 2 at 4 A = 2+1 --> C2=1.74 F m-1
END

```

```

SELECTED_OUTPUT
-reset false
-user_punch true
-file Mica_Rb_pragmatic.prn
USER_PUNCH
-headings "n°" "Elem" "%DL" "%Na0_n" "%Na1_n" "%Na2_n"
-start

```

```

3  PUNCH 4
5  PUNCH "Rb"
10 PUNCH (3.524e-3-MOL("RbMica")-MOL("MicaRb")-
MOL("(Mica)Rb"))/3.524e-3
20 Ch0=MOL("RbMica")/(MOL("RbMica")+MOL("MicaRb")+MOL("(Mica)Rb"))
25 PUNCH Ch0
30 Ch1=MOL("MicaRb")/(MOL("RbMica")+MOL("MicaRb")+MOL("(Mica)Rb"))
35 PUNCH Ch0+Ch1
40 Ch2=MOL("(Mica)Rb")/(MOL("RbMica")+MOL("MicaRb")+MOL("(Mica)Rb"))
45 PUNCH Ch0+Ch1+Ch2
-end
SOLUTION 1
-water 1
Rb 104
Cl 104 charge
Surface 1
-equilibrate 1
Mica 3.524e-3 1000 1 #0.34 C/m2 -> 3.52e-6 mol/m2 ; 1000 m2 => 3.52e-3
mol site
-cd_music
-donnan 2e-9 # 0.104 mol/L, two debye lengths ~2nm
-capacitance 3.47 1.74
# Plane 0 at 1
# Plane 1 at 2 A = 1+1 --> C1=3.47 F m-1
# Plane 2 at 4 A = 2+1 --> C2=1.74 F m-1
END

```

```

SELECTED_OUTPUT
-reset false
-user_punch true
-file Mica_Cs_pragmatic.prn
USER_PUNCH
-headings "n°" "Elem" "%DL" "%Na0_n" "%Na1_n" "%Na2_n"
-start
3  PUNCH 5
5  PUNCH "Cs"
10 PUNCH (3.524e-3-MOL("CsMica")-MOL("MicaCs")-
MOL("(Mica)Cs"))/3.524e-3
20 Ch0=MOL("CsMica")/(MOL("CsMica")+MOL("MicaCs")+MOL("(Mica)Cs"))
25 PUNCH Ch0
30 Ch1=MOL("MicaCs")/(MOL("CsMica")+MOL("MicaCs")+MOL("(Mica)Cs"))
35 PUNCH Ch0+Ch1
40 Ch2=MOL("(Mica)Cs")/(MOL("CsMica")+MOL("MicaCs")+MOL("(Mica)Cs"))
45 PUNCH Ch0+Ch1+Ch2
-end
SOLUTION 1
-water 1
Cs 104
Cl 104 charge
Surface 1
-equilibrate 1

```

```

Mica 3.524e-3 1000 1 #0.34 C/m2 -> 3.52e-6 mol/m2 ; 1000 m2 => 3.52e-3
mol site
-cd_music
-donnan 2e-9 # 0.104 mol/L, two debye lengths ~2nm
-capacitance 3.47 1.74
# Plane 0 at 1
# Plane 1 at 2 A = 1+1 --> C1=3.47 F m-1
# Plane 2 at 4 A = 2+1 --> C2=1.74 F m-1
END

# END of Calibration based on MD data
PRINT
-selected_out false # PRINT

# Start of exchange isotherms

INCREMENTAL_REACTIONS true

SOLUTION 1
-water 1
Rb 3
Cl 3 charge
Surface 1
-equilibrate 1
Mica 3.524e-3 1000 1 #0.34 C/m2 -> 3.52e-6 mol/m2 ; 1000 m2 => 3.52e-3
mol site
-cd_music
-donnan 2e-9 # 0.104 mol/L, two debye lengths ~2nm
-capacitance 3.47 1.74
# Plane 0 at 1
# Plane 1 at 2 A = 1+1 --> C1=3.47 F m-1
# Plane 2 at 4 A = 2+1 --> C2=1.74 F m-1
SAVE SOLUTION 1
SAVE SURFACE 1
END

PRINT
-reset false
-selected_out true

SELECTED_OUTPUT
-reset false
-user_punch true
-file Exchange_Rb_K_pragmatic.prn
USER_PUNCH
-headings "E_K_mica" "Rbsol" "K_CsRb" "Rb in Stern layer"
-start
10 K_exch=MOL("KMica")+MOL("MicaK")+MOL("(Mica)K")
20 Rb_exch=MOL("RbMica")+MOL("MicaRb")+MOL("(Mica)Rb")
90 PUNCH K_exch/(K_exch+Rb_exch)
100 PUNCH TOT("Rb")*1000

```

```

110 PUNCH Rb_exch/K_exch*act("K+")/act("Rb+")
120 PUNCH Rb_exch/3.524e-3
-end

```

```

USE SOLUTION 1
USE SURFACE 1
REACTION 1
Rb -1
K +1
6.523e-3 moles in 1000 steps
END

```

```

SELECTED_OUTPUT
-reset false
-user_punch true
-file Exchange_Rb_Na_pragmatic.prn
USER_PUNCH
-headings "E_Na_mica" "Rbsol" "Na_CsRb" "Rb in Stern layer"
-start
10 Na_exch=MOL("NaMica")+MOL("MicaNa")+MOL("(Mica)Na")
20 Rb_exch=MOL("RbMica")+MOL("MicaRb")+MOL("(Mica)Rb")
90 PUNCH Na_exch/(Na_exch+Rb_exch)
100 PUNCH TOT("Rb")*1000
110 PUNCH Rb_exch/Na_exch*act("Na+")/act("Rb+")
120 PUNCH Rb_exch/3.524e-3
-end

```

```

USE SOLUTION 1
USE SURFACE 1
REACTION 1
Rb -1
Na +1
6.523e-3 moles in 1000 steps
END

```

```

SELECTED_OUTPUT
-reset false
-user_punch true
-file Exchange_Rb_Li_pragmatic.prn
USER_PUNCH
-headings "E_Li_mica" "Rbsol" "Li_CsRb" "Rb in Stern layer"
-start
10 Li_exch=MOL("LiMica")+MOL("MicaLi")+MOL("(Mica)Li")
20 Rb_exch=MOL("RbMica")+MOL("MicaRb")+MOL("(Mica)Rb")
90 PUNCH Li_exch/(Li_exch+Rb_exch)
100 PUNCH TOT("Rb")*1000
110 PUNCH Rb_exch/Li_exch*act("Li+")/act("Rb+")

```

```
120 PUNCH Rb_exch/3.524e-3
-end
```

```
USE SOLUTION 1
USE SURFACE 1
REACTION 1
Rb -1
Li +1
6.523e-3 moles in 1000 steps
END
```

```
SELECTED_OUTPUT
-reset false
-user_punch true
-file Exchange_Rb_Cs_pragmatic.prn
USER_PUNCH
-headings "E_Cs_mica" "Rbsol" "Cs_CsRb" "Rb in Stern layer"
-start
10 Cs_exch=MOL("CsMica")+MOL("MicaCs")+MOL("(Mica)Cs")
20 Rb_exch=MOL("RbMica")+MOL("MicaRb")+MOL("(Mica)Rb")
90 PUNCH Cs_exch/(Cs_exch+Rb_exch)
100 PUNCH TOT("Rb")*1000
110 PUNCH Rb_exch/Cs_exch*act("Cs+")/act("Rb+")
120 PUNCH Rb_exch/3.524e-3
-end
```

```
USE SOLUTION 1
USE SURFACE 1
REACTION 1
Rb -1
Cs +1
6.523e-3 moles in 1000 steps
END
```

##### Exchange Cs-Me for DeltaG calculation

```
SOLUTION 1
-water 1
Cs 3
Cl 3 charge
Surface 1
-equilibrate 1
Mica 3.524e-3 1000 1 #0.34 C/m2 -> 3.52e-6 mol/m2 ; 1000 m2 => 3.52e-3
mol site
-cd_music
-donnan 2e-9 # 0.104 mol/L, two debye lengths ~2nm
-capacitance 3.47 1.74
# Plane 0 at 1
```

```
# Plane 1 at 2 A = 1+1 --> C1=3.47 F m-1
# Plane 2 at 4 A = 2+1 --> C2=1.74 F m-1
SAVE SOLUTION 1
SAVE SURFACE 1
END
```

```
PRINT
-reset false
-selected_out true
```

```
SELECTED_OUTPUT
-reset false
-user_punch true
-file Exchange_Cs_K_pragmatic.prn
USER_PUNCH
-headings "E_Cs" "K_CsK" "E_Cssol"
-start
10 Cs_exch=MOL("CsMica")+MOL("MicaCs")+MOL("(Mica)Cs")
20 K_exch=MOL("KMica")+MOL("MicaK")+MOL("(Mica)K")
30 ECssol=TOT("Cs")/(TOT("Cs")+TOT("K"))
100 PUNCH Cs_exch/(Cs_exch+K_exch)
110 PUNCH K_exch/Cs_exch*act("Cs+")/act("K+")
120 PUNCH ECssol
-end
```

```
USE SOLUTION 1
USE SURFACE 1
REACTION 1
Cs -1
K +1
6.523e-3 moles in 1000 steps
END
```

```
SELECTED_OUTPUT
-reset false
-user_punch true
-file Exchange_Cs_Na_pragmatic.prn
USER_PUNCH
-headings "E_Cs" "K_CsNa" "E_Cssol"
-start
10 Cs_exch=MOL("CsMica")+MOL("MicaCs")+MOL("(Mica)Cs")
20 Na_exch=MOL("NaMica")+MOL("MicaNa")+MOL("(Mica)Na")
30 ECssol=TOT("Cs")/(TOT("Cs")+TOT("Na"))
100 PUNCH Cs_exch/(Cs_exch+Na_exch)
110 PUNCH Na_exch/Cs_exch*act("Cs+")/act("Na+")
120 PUNCH ECssol
-end
```

```
USE SOLUTION 1
USE SURFACE 1
```



```

REACTION 1
Cs -1
Na +1
6.523e-3 moles in 1000 steps
END

```

```

SELECTED_OUTPUT
-reset false
-user_punch true
-file Exchange_Cs_Rb_pragmatic.prn
USER_PUNCH
-headings "E_Cs" "Rb_CsRb" "E_Cssol"
-start
10 Cs_exch=MOL("CsMica")+MOL("MicaCs")+MOL("(Mica)Cs")
20 Rb_exch=MOL("RbMica")+MOL("MicaRb")+MOL("(Mica)Rb")
30 ECssol=TOT("Cs")/(TOT("Cs")+TOT("Rb"))
100 PUNCH Cs_exch/(Cs_exch+Rb_exch)
110 PUNCH Rb_exch/Cs_exch*act("Cs+")/act("Rb+")
120 PUNCH ECssol
-end

```

```

USE SOLUTION 1
USE SURFACE 1
REACTION 1
Cs -1
Rb +1
6.523e-3 moles in 1000 steps
END

```

```

SELECTED_OUTPUT
-reset false
-user_punch true
-file Exchange_Cs_Li_pragmatic.prn
USER_PUNCH
-headings "E_Cs" "K_CsLi" "E_Cssol"
-start
10 Cs_exch=MOL("CsMica")+MOL("MicaCs")+MOL("(Mica)Cs")
20 Li_exch=MOL("LiMica")+MOL("MicaLi")+MOL("(Mica)Li")
30 ECssol=TOT("Cs")/(TOT("Cs")+TOT("Li"))
100 PUNCH Cs_exch/(Cs_exch+Li_exch)
110 PUNCH Li_exch/Cs_exch*act("Cs+")/act("Li+")
120 PUNCH ECssol
-end

```

```

USE SOLUTION 1
USE SURFACE 1
REACTION 1
Cs -1
Li +1
6.523e-3 moles in 1000 steps
END

```

## References

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