Solid-liquid interface structure of muscovite mica in CsCl and RbBr solutions

Stelian PINTEA^{a,b}, Wester de POEL^a, Aryan E.F. de JONG^{a,b}, Vedran VONK^{a,c}, Pim van der ASDONK^a, Jakub DRNEC^b, Olivier BALMES^b, Helena ISERN^b, Thomas DUFRANE^b, Roberto FELICI^b, Elias VLIEG^{a*}

^aRadboud University, Institute for Molecules and Materials, Nijmegen, The Netherlands

^bEuropean Synchrotron Radiation Facility, Grenoble, France

^cDeutsch Elektronen Synchrotron DESY, Hamburg, Germany

*corresponding author: e.vlieg@science.ru.nl (E. Vlieg)

ABSTRACT

The solid-liquid interface formed by single terminated muscovite mica in contact with two different ionic solutions is determined using surface x-ray diffraction. Specular and non-specular crystal truncation rods of freshly cleaved mica immersed in CsCl or RbBr aqueous solution were measured. The half monolayer of surface potassium ions present after the cleavage is completely replaced by the positive ions (Cs^+ or Rb^+) from the solution. These ions are located in the ditrigonal surface cavities with small outward relaxations with respect to the bulk potassium position. We find evidence for the presence of a partly ordered hydration shell around the surface Cs^+ or Rb^+ ions as well as partly ordered negative ions in the solution. The lateral liquid ordering induced by the crystalline surface is vanishing at distances larger than 5 Å from the surface.

3.1. INTRODUCTION

Muscovite, the most common form of mica mineral, has an interesting bulk and surface crystal structure for scientific and technological applications. Its atomically flat surface¹ is a perfect substrate for the growth of macromolecular (mono) layers^{2,3,4,5}, the study of DNA molecules^{6,7} or for being functionalized by exchanging the surface ions^{8,9}. The cleaved (001) muscovite surface is also often used as a model surface for studying the crude oil-mineral reservoir interaction^{10,11,12} in order to improve the efficiency of the oil recovery process.

The muscovite surface is suitable for most surface science techniques, although it sometimes plays only a secondary role in the experiment: atomic force microscopy (AFM)¹³, scanning tunneling microscopy (STM)¹⁴, X-ray photoelectron spectroscopy (XPS)^{8,15}, Auger electron spectroscopy (AES)¹⁶, low energy electron diffraction (LEED)¹⁷, X-ray reflectivity (XRR)¹⁸, surface X-ray diffraction (SXRD)⁵ and transmission electron microscopy (TEM)¹⁹. A major scientific application of mica is in the surface force apparatus (SFA)^{20,21} where its flatness and transparency play a crucial role.

On such a well-studied system several structural details are already known. According to the XRR measurements of Schlegel et al.²², Cs⁺ is adsorbed at 2.16 Å from the topmost crystalline oxygen layer for both concentrations of the aqueous solution that were used: 0.01 and 0.5 m. Two partly out-of-plane ordered solution layers were reported: the first one at a height of 4.0 Å and the second at 6.33 and at 6.72 Å for the two concentrations, respectively. Perfect surface charge compensation is achieved for the lower concentration while the presence of more concentrated solution leads to surface charge overcompensation according to their study. Perfect charge compensation occurs if the cation coverage is 0.5 monolayer (ML), where we define 1 monolayer as the number of cations corresponding to a full K⁺ layer in the bulk mica structure (see Figure 1).

The adsorption of Rb⁺ ions was studied using resonant anomalous X-ray scattering by Fenter et al.²³. They found a Rb⁺ ion height of 2.33 Å and a surface charge compensation of only 73 %. Two partly out-of-plane ordered solution layers, covering the Rb-terminated muscovite, were found to be located at a height of 4.1 and 8.9 Å from the oxygen layer forming the surface ditrigonal cavities. Both cations, Cs⁺ and Rb⁺, are adsorbed as partly hydrated species, where the classical inner-sphere is a combination of the water molecules of the solution and the topmost crystalline oxygen atoms.

Although investigated with many techniques, the full structure of Cs- or Rb-terminated muscovite is not completely elucidated. The most important structural studies are providing ambiguous or incomplete answers regarding the surface-interface structure of the muscovite in these ionic aqueous solutions. Previous XRR^{22,24} and resonant anomalous XRR²³ studies have the drawback of being only sensitive to the structure along the surface normal direction and, consequently, the in-plane location of the adsorbed species is only assumed, not determined. The molecular dynamics study of Sakuma and Kawamura²⁵ is stressing another issue: the role and the level of ordering (if any) of the negative ions also present in the solution. The XPS measurements of Xu and Salmeron⁸ conclude that the Cl⁻ from a CaCl₂ solution cannot be completely removed from the surface by

rinsing it with water, while $(\text{SO}_4)^{2-}$ from a CaSO_4 solution can be removed, making the situation even more complicated.

This research aims to fully characterize the solid-liquid interface made by crystalline muscovite mica in contact with aqueous solutions of CsCl or RbBr. To achieve this we obtain extensive in situ surface X-ray scattering data sets containing not only the specular but also non-specular rods using single-terminated surfaces. This enables the determination of both the out-of-plane and the in-plane ordering of the species present at the interface. We find that the surface K^+ ions are completely exchanged by 0.5 ML of Cs^+ or Rb^+ ions located in the ditrigonal cavities. These ions exhibit a small outwards relaxation. Near the interface we find limited water ordering and evidence for negative ions.

3.2. EXPERIMENTAL METHODS AND MATERIALS

The side and top view of the bulk muscovite structure are depicted in Figure 1. The monoclinic unit cell (C2/c space group) has the following cell parameters: $a = 5.1906 \text{ \AA}$, $b = 9.008 \text{ \AA}$, $c = 20.047 \text{ \AA}$ and $\beta = 95.757^\circ$. High quality muscovite mica sheet (S&J Trading Inc., Glen Oaks, New York), was cut in pieces of about $45 \times 45 \text{ mm}^2$. The large sample size minimizes edge effects and gives a large flat area for accurate experiments. For each sample preparation a freshly cleaved surface was used. Cleavage was initiated using a knife¹.

Figure 1. Left: side view of the muscovite structure. The colored part is showing our choice for the bulk unit cell. The pink plane is the c-glide plane that symmetrically connects the two possible K^+ cleavage planes (arbitrarily named surface termination 1 at $c = 0.25$ and surface termination 2 at $c = 0.75$). Right: top view of a single terminated muscovite surface depicting the random half occupancy of the ditrigonal cavities by K^+ ions after cleavage.

After the cleavage the surface K^+ ions were exchanged by either Cs^+ or Rb^+ by immersing the sample in 56 mM aqueous solution of CsCl or 11 mM aqueous solution of RbBr. Both salts, CsCl and RbBr, were high purity (Sigma Aldrich, code 203025 and 336149, respectively) and were dissolved in ultrapure water (resistivity $\geq 18.2 \text{ M}\Omega\cdot\text{cm}$). Although the exchange of the surface K^+ with Cs^+ (or Rb^+) from the solution should take a few minutes⁸, the muscovite was kept in solution for two hours, in order to make sure that the exchange was complete. After removal from the

solution, the sample was placed on the plateau of an environment cell. A thin mylar foil (13 μm ; Lebow Company, Goleta, California) was used to cover the sample after some additional solution was dropped onto the muscovite surface in order to create the liquid environment in which the SXRD experiment was performed. No degradation of the liquid film or of the bulk part of the muscovite was observed during the whole experiment. Similar measurements we performed in a dry environment (air or nitrogen flow) revealed small changes in the reflectivity curve as a function of exposure time, but this is not the case in the wet environment.

Surface X-ray diffraction (SXRD) is a well-known technique to determine the structure of (buried) interfaces^{26,27,28}. The modulation of the reflected intensity along the l direction of reciprocal space is measured as a function of the momentum transfer $Q = h \cdot \vec{a}^* + k \cdot \vec{b}^* + l \cdot \vec{c}^*$, where $\vec{a}^*$, $\vec{b}^*$, $\vec{c}^*$ are the reciprocal lattice vectors and (hkl) the diffraction indices. SXRD data were measured on the vertical z-axis diffractometer of the ID03 beam line of the European Synchrotron Radiation Facility (ESRF) using monochromatic X-rays of 15 keV energy ($\lambda = 0.8266 \text{ \AA}$). The beam size at the sample position was chosen to be $1.00 \times 0.02 \text{ mm}^2$ (horizontal x vertical), giving a constant footprint of $1 \times 2 \text{ mm}^2$ at the angle of incidence of 0.6° that was used for all the non-specular rods. The beam characteristics were selected to minimize the attenuation of the signal when passing through the water and mylar film, to avoid the presence of absorption edges of the chemical elements involved in the experiment and to minimize radiation damage. The diffracted intensities were recorded using a Maxipix 2x2 area detector and all the crystal truncation rods (CTRs) were measured in the stationary geometry²⁹, which made the data acquisition time two orders of magnitude smaller than when using a point detector that requires rocking scan measurements. In order to obtain the structure factor amplitudes, a specially written script that applies all the necessary correction factors was used. To account for the variation in absorption of the x-rays when passing through the water and mylar film covering the sample, an incident and exit angle dependent correction factor was applied. This correction uses the 13 μm thickness of the mylar foil and a 15 μm water film thickness as estimated by weighting the amount of solution dropped onto the surface.

It is important to have proper error bars in the data analysis. In the case of SXRD there are two main errors: statistical and systematic errors. The statistical errors are very small in our case due to the high value of photon counts and therefore do not determine the real error. In order to estimate the systematic errors, symmetry equivalent reflections are often used. On muscovite mica a mirror symmetry (due to the glide plane of the crystal structure) along the h direction will be present in the surface reflections from normal samples with a random mixture of the two possible surface terminations. In our case, however, this symmetry is absent because we performed the measurements on single terminated surfaces (as explained below). Systematic errors of 5-15% are typical for this type of experiments. We assumed here an error of 5% for the entire data set consisting of the (00), (11), ($1\bar{1}$), (13), ($1\bar{3}$), (33), ($3\bar{3}$), (02), ($0\bar{2}$), (20) and (40) rods. This small error was found to be consistent with the spread in data between nearly-equivalent rods as found in the full analysis. During the analysis we increase the error bars near

bulk Bragg peaks to 20% in order to give more relative weight to the surface-sensitive data during fitting.

Model structure fitting to the data was done using the ROD software³⁰. In the calculations the ionic scattering coefficients³¹ for Cs^+ , Rb^+ , Cl^- and Br^- , averaged scattering coefficients that take into account the 25 % replacement of the bulk Si by Al atoms and the theoretical values of the anomalous dispersion coefficients at 15 keV were used³². For the bulk structure of muscovite atom positions from the Inorganic Crystal Structure Database (ICSD) were used³³. The use of Cs^+ or Rb^+ ions facilitates the X-ray analysis owing to the strong scattering power of these ions.

3.3. RESULTS AND DISCUSSION

3.3.1. Single surface termination: theory and experiment

The glide plane along the c -axis present in the bulk structure of muscovite symmetrically relates the two K^+ cleavage planes situated at $c = 0.25$ and at $c = 0.75$ in the conventional bulk unit cell, leading to two different surface terminations as shown in Figure 1. The terminations have a different rod profile, but the glide plane symmetry means that the (hkl) reflection of termination 1 is the same as the $(h\bar{k}l)$ reflection of termination 2. Assuming a size of the cleaved terraces of the order of micrometers, the large footprint of the X-ray beam on the sample is expected to probe a region that contains equal amounts of the two terminations. This would give rise to a mirror plane along the h -axis of the reciprocal space that would symmetrically relate the rods located on either side of the mirror plane. In this way the (11) and $(1\bar{1})$ rods would be equivalent. We found, however, that by using a high quality muscovite mica and by careful cleaving, terraces larger in size than the X-ray beam footprint can be achieved¹.

The presence of steps and the size of the terraces can easily be checked by mapping the intensity of a reflection that is sensitive to the surface termination. We chose the $(1\ 1\ 1.3)$ reflection for this and the map over an area of $35 \times 20\text{ mm}^2$ is shown in Figure 2. This shows a single step near $x = 5$ and large, single-terminated terraces from which a measuring condition with a single termination is easily selected.

A full SXRD data set on the $x = -3$ and $y = 1$ spot was recorded in the case of Cs-terminated muscovite. Note that the name of the termination is arbitrary since the shape of the (11) rod corresponding to termination 1 is the same as the $(1\bar{1})$ rod shape corresponding to termination 2. The same method was applied to find a single terminated area of the Rb-terminated muscovite. The use of a single termination avoids uncertainties in the ratio of the two terminations and leads to a data set with a larger number of unique reflections.

Figure 2. The 2D plot of the (1 1 1.3) diffracted intensities. Based on these data a single terminated spot for the complete data set was selected.

3.3.2. Fitting and surface models

A large number of different models was tested in order to select a model that could accurately fit the data while being as simple as possible, i.e. having as few fitting parameters as possible. Figure 3 shows the side view of this model. Each atomic layer has its own independent set of parameters indicated on the right side of the figure: *occ.* – occupancy; *d(axis)* – displacement along the specified axis; $B_{||}$ – in-plane and $B_{\perp}$ – out-of-plane Debye-Waller parameter accounting in our case also for the level of ordering³⁴. The fixed part of the bulk crystal is highlighted by the yellow shaded region.

Figure 3. The side view of the model used to determine the surface/interface structure. The yellow shaded part highlights the fixed crystalline region. The ditrigonal surface cavities were filled by Cs⁺, (Rb⁺) or water. The model is completed by a hydration shell around the cavity (modeled by two hydration rings) and three water layers.

On top of the rigid muscovite mica region we used four crystalline layers that are allowed to relax out-of-plane and have fitted in-plane and out-of-plane Debye-Waller parameters. The $d(\alpha)$ displacement accounts for the possible variation in the tetrahedral rotation angle of the topmost silicon/aluminum oxide structure³⁵. It is modeled as an in-plane displacement of the topmost oxygen layer along the a and b axes as shown in Figure 4 by the orange arrows originating from the topmost oxygen atoms. All four layers have a fixed occupancy of 100 % because there is no exchange process affecting these layers.

The most important modification expected at the surface is the replacement of the K^+ with Cs^+ or Rb^+ ⁸. The exchange ions are expected to fill half of the surface ditrigonal cavities (i.e. they replace the half K^+ monolayer expected at the surface after cleavage) in order to fully compensate for the surface charges. This is modelled by allowing the presence of the exchange ion in both cavities and fitting its occupancy using 50 % as starting value. These positive ions have the occupancy, two relaxations (out-of-plane and along the a axis) and the two independent Debye-Waller parameters as fitted parameters. The displacement along the a axis, shown in Figure 4 by the red arrows originating from the ions in the ditrigonal cavity, is introduced in order to allow a compensation for the tilted c axis with respect to the a axis ($\beta=95.757^\circ$). The vacant cavities are filled with a water molecule with the constraint that the total occupancy of the cavity equals 1. Each ion in the cavity is expected to build up a hydration shell around it, similar to their hydration shell in solution³⁶. This is modeled by allowing in principle several hydration rings centered on the positive ion in the cavity. The hydration ring is modelled as a continuous charge density surrounding the ion by using 12 equally spaced oxygen atoms. For each hydration ring independent occupancy, c – displacement, radius and in- and out-of-plane Debye-Waller parameters are fitted. Although we allowed for several hydration rings (at variable heights; on top of each other) around each cavity

Figure 4. Top view of the surface fit model. Only the two topmost crystalline layers, the ions in the cavity and their hydration ring are shown for clarity. The orange arrows in the magnified image denote the directions of allowed relaxation in order to check for the changes in the tetrahedral rotation angle. The red arrows on the positive ion depict its in-plane relaxation direction in order to compensate for the tilted c axis of the muscovite crystalline structure.

center, in practice one ring per cavity was already sufficient for the Rb-terminated sample, while for the Cs-terminated muscovite there is also a second ring much weaker in occupancy than the first one. The second half of the surface ditrigonal cavities was filled with water molecules having similar independent variable parameters as the positive ions in the cavity.

The possibility of having the negative ions co-adsorbed at the surface is mentioned by other authors²⁵, and therefore the presence of Cl⁻ or Br⁻ at a position above the ditrigonal cavities was allowed. These ions have the same amount and type of variable parameters as the positive ions present in the cavities.

The highly ordered crystalline structure is expected to induce (limited) ordering of the water from the solution film that covers the sample. This was modeled by allowing several water layers on top of the whole model described until now. It turned out that the minimum number of water layers needed to get a good fit was three in the case of Cs-terminated muscovite and two for the Rb-terminated sample. Each layer is modeled by a single water molecule per surface unit cell. The occupancy of these layers was allowed to go above 100 % in order to be able to generate the ~4.6 (or more) water molecules contained in the bulk water monolayer per surface unit cell. Partial ordering in the liquid layer is modelled using anisotropic Debye-Waller parameters. A high value for the Debye-Waller parameter (i.e. $B > 2000$) means in our case a completely disordered liquid layer. The Debye-Waller parameter is related to the root mean square of the vibration amplitude (shown in the tables) through the formula: $B = 8\pi^2 \langle u^2 \rangle$. It is important to mention that all the water molecules were modeled using a single oxygen atom, because X-rays are not sensitive to the two hydrogen atoms. From the electron density of these oxygen atoms it is easy to derive the equivalent water density.

3.3.3. The Cs-terminated surface/interface structure

As mentioned above, several different models were tried. The models that give a good fit were found to yield similar electron densities at the solid-liquid interface and we selected the simplest model giving a good fit. The final results for the muscovite mica - CsCl solution interface are presented in Table 1 and depicted in Figures 5-7.

The non-specular data points together with the best fit (solid line) are presented in Figure 7. The comparison between the (11) and (1 $\bar{1}$) rods proves that the choice of the single terminated surface was correct. The normalized χ^2 value for the best fit model was 2.62 and we consider this value as satisfactory if we take into account the large number of data points (more than 4200) and the relatively good (5 %) agreement factor used for the error calculations.

During the fitting process trends in the variations of different parameters, ranging from relatively small to large variations, were observed. Based on this behavior, three main interface regions can be defined: the crystalline region, the interface charged region and the liquid region.

Table 1. Structure of the muscovite mica - CsCl solution interface.

Element		z - height [Å]	Occupancy [%] per surface unit cell	In-plane vibration ($u_{ }$) [Å]	Out-of-plane vibration ($u_{\perp}$) [Å]
Water _{third layer}		8.9 ± 0.5	27 ± 3	∞	9 ± 3
Water _{second layer}		6.2 ± 0.5	5 ± 2	∞	3.3 ± 2.0
Water _{first layer}		5.2 ± 0.3	0.5 ± 0.2	∞	0.4 ± 0.2
Hydration ring 2		3.9 ± 0.2 ($R = 2.2 \pm 0.3$)	0.40 ± 0.20	9.9 ± 2.0	0.9 ± 0.5
Cl ⁻ _{cavity}		2.97 ± 0.20 ($\Delta\alpha = 0.35 \pm 0.20$)	$25 \pm 10 \%$	1.4 ± 0.4	0.2 ± 0.2
Hydration ring 1		1.87 ± 0.20 ($R = 3.0 \pm 0.3$)	2.1 ± 0.3	0.2 ± 0.1	0.7 ± 0.3
Ditrigonal Cavity	Water	0.51 ± 0.05 ($\Delta\alpha = -0.19 \pm 0.10$)	$43 \pm 10 \%$	0.48 ± 0.10	0.28 ± 0.10
	Cs ⁺	0.43 ± 0.05 ($\Delta\alpha = 0.02 \pm 0.01$)	$57 \pm 10 \%$	0.21 ± 0.1	0.26 ± 0.1
O _{bulk-top}		$\Delta\alpha = 0.57 \pm 0.20^\circ$	100 % (fixed)	0.12 ± 0.05	0.24 ± 0.10
Si/Al _{bulk}		Fixed	100 % (fixed)	0.10 ± 0.05	0.14 ± 0.05

The crystalline region is characterized by very small relaxations and consists of the top four crystalline layers. The out-of-plane relaxations in this region are negligible within the error bars (< 0.03 Å) and were fixed to zero in the final model. The most noticeable variation comes from the out of plane Debye-Waller parameter of the topmost oxygen layer that gives $u_{\perp} = 0.24$ Å. This strong increase with respect to the bulk isotropic value of 0.1 Å is likely caused by the removal of the second half of the crystal during the cleavage process. This increases the vibrational freedom of the topmost oxygen atoms in the out-of-plane direction where they are in contact with a liquid phase. The small relaxation values in this region prove the rigidity of the crystalline muscovite mica structure.

The rigidity of mica is also revealed by the tetrahedral rotation angle, α . For the bulk structure, the value of α is 8.13° ^{37,38}. This value was calculated using the formula: $\alpha = \frac{\Delta(\text{Å})}{0.047}$, where Δ is the difference (in Å) between the mean high and mean low distances from the bulk K⁺ to the oxygen atoms forming the two ditrigonal cavities around it. For the surface tetrahedral blocks only the oxygen atoms on one side of the cleavage plane are taken into account, leading to an angle of 7.56° . The angle thus changes by only 0.57° .

Figure 5. Side view of the muscovite – CsCl aqueous solution interface depicting both ionic entities – Cs^+ and Cl^- – at the interface. The projected electron density is shown by the black curve; the red curve shows the (11) Fourier component of this density

Figure 6. The experimental data and the best fit (black solid line) of the specular rod of the muscovite – 56 mM CsCl aqueous solution interface. The red and blue solid curves are fits using models in which one and two water layers are removed, respectively.

Figure 7. The best fit (solid line) and the data for the measured crystal truncation rods. The clear difference between the red and blue rods proves that the mica is singly terminated.

The interface charged region includes the hydrated ionic species at the surface/interface and the partly ordered hydration water present there: the Cs^+ , the hydration ring and Cl^- layers from Table 1. The Cs^+ occupancy is found to be 57 ± 10 %, leaving a 43 ± 10 % water occupancy. Here we only considered the eight electrons of the oxygen atoms from the water molecule as taking part in the diffraction process, while the two electrons of the hydrogen atoms are only contributing to the background as diffuse scattering. We cannot make a distinction between the water and hydronium in this experiment, thus a combination of the two is also possible. The charged Cs^+ or H_3O^+ in the cavity is surrounded by a hydration ring with radius $R = 3.0$ Å, containing 2.1 H_2O molecules per surface unit cell (calculated as a continuous charge density from the twelve oxygen atoms used to model the hydration ring).

The z-projected electron density as seen in the (00) rod is shown in the black curve on the right side of Figure 5. This curve drops below the expected density of bulk water because the disordered bulk water is invisible in the region of the (00) rod that was measured and the applied

scattering geometry with a solution thickness that is effectively infinite. The electron density has a peak around $z=3.0$ Å that consistently shows up in the different fitting models we tested. This points to the presence of Cl^- at the interface, because water is not expected to give density above that of bulk liquid water. This Cl^- is located on top of the cavities with an occupancy of 25 ± 10 %. We cannot distinguish between a lateral position of this possible Cl^- ion above the Cs-occupied or the water-occupied cavity, because these sites are crystallographically equivalent. However, if the Cl^- would be directly above the Cs^+ ion, their distance would be 2.55 Å according to our fit and this is much smaller than the sum of the two ionic radii of 3.50 Å ($R_{\text{Cs}^+} = 1.86$ Å; $R_{\text{Cl}^-} = 1.64$ Å)³⁹. While the large lateral vibration amplitude of 1.4 Å of the Cl^- makes this distance somewhat uncertain, it seems more likely that the Cl^- is located above the cavity without Cs^+ . In that case the Cs-Cl distance is 5.8 Å. The out-of-plane vibration parameter ($u_z = 0.2$ Å) of Cl^- denotes a well-defined layer in the out-of-plane direction. The Cl^- occupancy has a large error bar because different combinations of Cl^- and water yield the same z -projected electron density.

We therefore find that the Cs^+ is adsorbed in a partly hydrated state at the muscovite surface. The 2.1 H_2O molecules / surface unit cell (equivalent to 2.1 $\text{H}_2\text{O}/\text{Cs}^+$) from the hydration shell, combined with the six oxygen atoms forming the ditrigonal cavity of the crystalline muscovite mica ~~and the Cl^-~~ , are together very close to the eight-fold coordination of the Cs^+ in aqueous solution reported by Mahler and Persson³⁶. A schematic of the structure in this region is shown in Figure 8. The mean distance from the Cs^+ to the hydration water molecules is about 3.33 Å, somewhat bigger than the 3.07 Å reported by Mahler and Persson. The mean distance from the Cs^+ to the bulk ditrigonal oxygen atoms is about 3.31 Å and is larger because of the other bonds that the bulk oxygen atoms have within the crystalline lattice of muscovite.

Figure 8. A schematic of the ionic region structure showing the distances between the Cs^+ , the substrate and the hydration shell.

The partially ordered liquid region of the solid-liquid interface consists of the topmost four water layers (there are of course more bulk water layers, but these are invisible in the rods as measured in our geometry). The values of the parameters corresponding to these layers were fluctuating during the fitting procedure, but they gave the same electron density projected on the **z**-direction as the one presented in Figure 5. These fluctuations strongly affect the error bars of these parameters. The limited in-plane ordering at the interface is illustrated by the small electron density projected along the z-direction when using the (11) Fourier component³⁴. This is depicted by the red curve in Figure 5.

The water layers only affect the low *l* values of the specular rod as visible in Figure 6 where the variation of the shape of the specular rod as a function of the presence of different water layers is shown. Removing one layer has only a small (but significant) effect, removing two layers clearly yields a much worse fit.

3.3.4. The Rb-terminated surface/interface structure

The model and the fitting procedure for the muscovite – RbBr aqueous solution interface are similar to that for the CsCl solution. The fitted values for the structural parameters are presented in Table 2. Also in this case different models were tried, but all lead to a similar electron density projected on the z axis. The final result contains two water layers (instead of three for CsCl) and yields a normalized χ^2 value of 3.47 for the 2700 structure factors. An agreement factor of 5 % was used for the error bars calculation. Figures 9-11 show the obtained projected electron density (for both the (00) and (11) Fourier components) and the different rod profiles.

Table 2. Structure of the muscovite – RbBr solution interface.

Element		z – height [Å]	Occupancy [%] (per surface unit cell)	In-plane vibration ($u_{ }$) [Å]	Out-of-plane vibration ($u_{\perp}$) [Å]
Water _{second layer}		8.3 ± 0.5	13.7 ± 3.0	∞	5.0 ± 1.0
Water _{first layer}		4.9 ± 0.3	1.6 ± 0.5	∞	1.1 ± 0.5
Br ⁻ _{cavity}		3.1 ± 0.2 ($\Delta\alpha = -0.47 \pm 0.05$)	19 ± 10 %	1.6 ± 0.2	0.13 ± 0.02
Hydration ring		1.7 ± 0.2 (R = 2.7 ± 0.2)	2.2 ± 0.3.	0.42 ± 0.2	0.32 ± 0.2
Ditrigonal cavity	Water	0.77 ± 0.05 ($\Delta\alpha = -0.08 \pm 0.20$)	44 ± 10 %	1.76 ± 0.30	0.13 ± 0.10
	Rb ⁺	0.21 ± 0.05 ($\Delta\alpha = 0.01 \pm 0.05$)	56 ± 10 %	0.27 ± 0.10	0.28 ± 0.10
O _{bulk-top}		$\Delta\alpha = 0.50 \pm 0.10^\circ$	100 % (fixed)	0.13 ± 0.05	0.28 ± 0.10
Si/Al _{bulk}		Fixed	100 % (fixed)	0.12 ± 0.05	0.12 ± 0.05

Figure 9. Side view of the muscovite – RbBr aqueous solution interface structure. The projected electron density is shown by the black curve; the red curve shows the (11) Fourier component of this density.

Figure 10. The (00) rod for the muscovite – RbBr solution sample. The solid line is the best fit and the circles are the data points.

Figure 11. The best fit (solid lines) and the data for the measured crystal truncation rods.

As for CsCl, the whole surface/interface can be divided in three regions: the crystalline fitted region, the interface charged region and the liquid region.

The parameters of the fitted crystalline region have similar behavior as in the case of CsCl solution – muscovite interface, with the tetrahedral rotation angle changing by 0.50° , from 8.13° to 7.63° .

For the interface charged region several trends can be noticed. First, the occupancy for the Rb^+ ion was found to be approximately 56 %. The remaining 44 % of the cavities are occupied with water. The water filling the cavity is located at $z = 0.77 \pm 0.05 \text{ \AA}$ from the surface.

The Rb^+ ion in the cavity is surrounded by a hydration ring at $z = 1.7 \text{ \AA}$ with a radius of $2.7 \text{ \AA}$ and $2.2 \text{ H}_2\text{O}$ molecules/surface unit cell. The negative Br^- ion is located at $z = 3.1 \text{ \AA}$ and occupies about 19 % of the ditrigonal surface cavities. The lateral location of these ions is ambiguous because of the high value of their in-plane vibration parameter, $u_{\parallel} = 1.6 \pm 0.2 \text{ \AA}$, but the small value for the out-of-plane vibration parameter, $u_{\perp} = 0.13 \pm 0.2 \text{ \AA}$, is evidence for a well-defined layer in the out-of-plane direction. The presence of the negative ions in this layer is deduced from the high

electron density in this region, which exceeds the normal value of the bulk water (about $334 \text{ e}^-/\text{nm}^3$; shown in the right side of Figure 9 by the blue dashed line). As in the case of CsCl, we expect the Br^- to be located above the empty cavity, because if it would be directly above the Rb^+ ion their distance would be $2.97 \text{ \AA}$, which is smaller than the sum of the ionic radii ($R_{\text{Rb}^+} = 1.86 \text{ \AA}$; $R_{\text{Br}^-} = 1.64 \text{ \AA}$). The mean distance from the Rb^+ ion to the topmost crystalline oxygen atoms is $3.17 \text{ \AA}$ and to the oxygen from the hydration water molecule is about $3.08 \text{ \AA}$. Both values are close to the radius of the hydrated Rb^+ ion of $2.98 \text{ \AA}$ ³⁶.

Figure 12. The schematic of the ionic region depicting the distances between the adsorbed Rb^+ , the substrate and the hydration water molecules.

A complete (hydration) shell is built around the Rb^+ by the six bulk oxygen atoms, the hydration water molecules, as shown in Figure 12.

The liquid region, in this case containing the two water layers, has similar characteristics as in the CsCl case and only affects the low l value of the specular rod.

3.3.5. Discussion

The most accurate result of our analysis is the determination of the coordinates of the adsorbed Cs^+ and Rb^+ ions inside the ditrigonal cavities, since these cations have a high charge density and are well-ordered. Previous XRR results had the drawback of being sensitive only to the height of the adsorbed ions, although the authors were also assuming the ions to be at this location. Both ions are adsorbed at heights with outwards relaxation with respect to the initial crystalline K^+ position: $0.43 \pm 0.05 \text{ \AA}$ and $0.21 \pm 0.05 \text{ \AA}$ for Cs^+ and Rb^+ respectively. The difference of $0.22 \text{ \AA}$ between the two relaxations is in good agreement with the difference in ionic radii of these ions, although a unique value for ionic radii does not exist since it depends on the chemical surrounding³⁶. **Error! Bookmark not defined.**⁴⁰. Moreover, the same good agreement is obtained if we compare the out-of-plane relaxations with the difference in radius between the adsorbed ion and the K^+ normally present at the surface after the cleavage.

For both CsCl and RbBr the cation coverage is about 0.5 ML. These cations could form a regular pattern, e.g. in an occupied-unoccupied arrangement, but the measured rods are not sensitive to that. Only when such a pattern would have significant long-range order, superstructure reflections would occur, but we have not found any evidence for this. The cations have quite large vibration amplitudes, so it's likely that the location of the cations is not static and no long-range order occurs.

The first column of Table 3 shows a direct comparison between our results and the adsorption height obtained by other authors using XRR and MD simulation studies. While in the case of Cs⁺ there is a good agreement between our value and the previous literature, for Rb⁺ our result only agrees with the study of Lee et al.³⁵ and is very different from the earlier results of Park et al.⁴¹ Although the concentration of the solution is different for each of these studies, this fact seems insufficient to explain the discrepancy.

When the cations are the only charged species involved in charge compensation, a coverage of 50% is expected for a charge neutral interface. The values we find, $57 \pm 10 \%$ for Cs⁺ and $56 \pm 10 \%$ for Rb⁺, agree within the error bars with this charge compensation, but leave room for a slight overcompensation. The actual coverage will depend on the electrolyte concentration⁴², but this dependence has not been determined for CsCl or RbBr. For RbCl nearly full compensation has been found for concentrations above 5 mM. We have used 56 mM and 11 mM for CsCl and RbBr respectively, and thus indeed full charge compensation is expected. Schlegel et al.²² do not report a Cs⁺ coverage for their CsCl system. For RbCl, total Rb⁺ coverages were reported of $43 \pm 3 \%$ for 3 mM³⁵ and $36 \pm 8 \%$ for 10 mM⁴¹. This partial compensation does not fully agree with the values reported above. We note that both the found coverages for Cs⁺ and Rb⁺ and their relaxation confirm the fact that these cations have fully exchanged with the K⁺ on the starting mica surface^{8,9}.

Table 3. Comparison of the interface charged region with results from literature.

	Cation adsorption layer		Solution layer		Solution layer (2)	
	z [Å]	Element	z [Å]	Element	z [Å]	Element
Muscovite - CsCl solution interface (this study) – SXRD	2.13	Cs⁺	3.6	H₂O	4.7	Cl⁻+H₂O
Muscovite - CsCl solution interface (Schlegel, 2006 ²²) – XRR	2.16	Cs ⁺	4.0	H ₂ O	6.3 ÷ 6.7	H ₂ O
Cs ⁺ exchanged muscovite (Sakuma, 2011 ²⁵) – MD	2.1	Cs ⁺	4.2	H ₂ O	6.5	H ₂ O
Muscovite - CsCl solution interface (Lee, 2012 ³⁵) – RA-XRR	2.26	Cs ⁺	3.53	H ₂ O	8.74	H ₂ O
Muscovite - RbBr solution interface (this study) – SXRD	1.91	Rb⁺	3.4	H₂O	4.8	Br⁻+H₂O
Muscovite - RbCl solution interface (Park, 2006 ⁴¹) – RA-XRR	2.33	Rb ⁺	4.1	H ₂ O	9.0	H ₂ O
Muscovite - RbCl solution interface (Lee, 2012 ³⁵) – RA-XRR	1.97	Rb ⁺	3.6	H ₂ O	6.3	H ₂ O
Height is calculated with respect to the mean height of topmost oxygen layer from the crystal. MD = molecular dynamics simulation. (RA-)XRR = (resonant anomalous -) X-ray reflectivity.						

Even when taking into account the fact that the accuracy of the structural parameters decreases when probing the more disordered solution layers, we find evidence for Cl^- ($25 \pm 10 \%$) and Br^- ($19 \pm 10 \%$) in the interface region, a possibility also included in Molecular Dynamics simulations²⁵. The presence of these negative charges in the interface region appears to indicate a charge uncompensated interface because the charge is larger than the small excess from the cations, but we should take into account all the atoms and ions of the crystal, solution and interface when considering charge neutrality. We should also keep in mind, when estimating the global and local charge of the sample, that SXRD is not capable of distinguishing between the charge neutral water molecule and the negatively charged hydroxyl or the positively charged hydronium that can naturally occur in solution by water self-ionization process or induced by the hard X-rays probing the sample. We may thus assume overall charge neutrality is maintained, even if we cannot directly measure this.

We cannot directly identify the species that causes the enhanced density in both the CsCl and RbBr solutions and that we attribute to anions. An alternative explanation would be the presence of a small amount of Cs or Rb at that location, similar to the outer-sphere Rb reported by Lee et al.³⁵ (at a greater distance from the interface, however). The fact that the enhanced density is stronger in the case of RbBr compared with CsCl is consistent with the stronger scattering power of Br compared with Cl and inconsistent with the stronger scattering power (and higher concentration) of Cs compared with Rb. This therefore points to the anions as the cause of the enhanced density. Note that we cannot directly infer the presence of outer-sphere Rb adsorption, since these are expected to occur in the parts of the interface that are too disordered to distinguish these from other species.

As already noted by Odelius et al.⁴³, the random replacement of 25% of the bulk Si by Al leaves some ditrigonal cavities with two Al ions, while others have one (a fully random distribution will not occur, because otherwise some cavities could have three or more Al ions, leading to a very high local charge). One would expect that the cations are preferably located in those cavities that have two Al ions. This would mean that the (fixed) Si-Al-O structure determines the preferred location of the cations. In the future, a local probe like AFM might find this correlation of the cation location with the cavity structure.

In general, the highly ordered crystal induces stronger ordering in the out-of-plane direction than in the in-plane direction for the layers above the hydration ring, except the first hydration ring ($z=1.87 \text{ \AA}$) for the Cs – terminated sample. This is clearly visible in the much higher in-plane vibration parameter for the negative ions than their out-of-plane vibration parameters, which indicates that these ions are very mobile in the lateral direction.

As illustrated in Figures 8 and 12, the coordination number of the cation is completed by the six oxygen atoms forming the ditrigonal surface cavities and by the layer containing the negative ions.

In this way we arrive at coordination numbers for the cation that are similar to the values in its hydrated form.

The presence of both specular and non-specular rods in the data set helps in distinguishing the layers with and without in-plane ordering^{28,34}. The degree of ordering in the solution near the crystal surface is most conveniently visualized as the projected electron density, shown in Figures 5 and 9 for the CsCl and RbBr solutions, respectively. The (11) Fourier component depicted in these figures indicates the amount of in-plane ordering for each layer. Consistent with other solid-liquid interfaces reported in literature, beyond the ions and water molecules located in the ditrigonal cavities, only two additional solution layers show limited lateral ordering. Whether the cations are part of the crystal or not is almost a matter of semantics. From our XRD perspective, these ions are well ordered, with a well-defined position and small vibration parameters. One still expects these ions to be mobile on a timescale of seconds, but beyond what XRD can probe. Thus the cations have both solidlike and liquidlike properties.

A direct comparison between the projected charge densities with other XRR and MD simulation studies is presented in Figure 13 and listed in Table 3. There is a relatively good agreement in most of the cases for the crystal part including the surface cations, but the disagreement increases as we go to the layers that are further away from the surface. This disagreement might partly originate from the different experimental conditions, in particular the concentration of the solution and the quality of the crystal used, but the details of the data analysis and model refinement should also be considered. The structural information about the solution layers away from the interface, for example, is only visible at the low l values of the specular data, a region where we find that the angle-dependent correction for the X-ray absorption has a significant effect. Considering the poor consistency found between the results obtained by different experimental methods, it is difficult to identify the most accurate results.

Recent developments in AFM make it possible for this technique to be used for probing the ordering of the solution near an interface¹³. Such measurements, performed on the muscovite mica – water interface, revealed also the out-of-plane layering structure of the water in contact with the crystal as well as the rapid decrease of the degree of ordering when probing solution layers further away from the interface¹³. However, because the electron density cannot be derived from AFM measurements yet and because of the different experimental conditions, a direct comparison with our results is not possible.

Figure 13. The z-projected electron density as seen in the (00) rod for muscovite – CsCl solution interface (left) and for muscovite – RbBr solution interface (right) and results from literature: molecular dynamics (MD) simulations²⁵, 0.49 M and 0.01 M CsCl solution XRR measurements²², resonant anomalous XRR for 0.01 M⁴¹ and for 0.003 M³⁵ RbCl solution.

Another very interesting AFM study⁴² performed at the same 10mM concentration for a RbCl aqueous solution in contact with a mica surface shows full Rb⁺ coverage of the surface for areas bigger than 20x20 nm². The big change in observed surface occupancy for Rb⁺ might be induced by the use of different anion (Cl⁻ instead of Br⁻) or by the formation of surface domains in the presence of the AFM tip.

The use of a large data set including non-specular rods makes it easier to distinguish the partial ordering of the solution from crystal relaxations near the interface. In rods with large in-plane momentum transfer, like rod (33) or (40) in our data, the disordered solution is essentially invisible and exclusive sensitivity to the crystal structure is obtained. Since X-ray diffraction works best for the ordered parts, we are confident about our finding that the relaxations in the crystal are small/negligible (< 0.03 Å). In comparison, in the XRR analyses of Schlegel et al.²² and Lee et al.³⁵ relaxations for layers up to 40 Å deep in the crystal were included and systematic differences as a function of ion species and concentration inferred. Considering the structure of muscovite mica, however, it seems unlikely that the relaxations would propagate beyond the first bulk crystalline K⁺ layer from the surface, i.e. beyond a depth of 10 Å because bonds at this cleavage plane are very weak. If we limit our analysis to the specular rod, we find similar deep relaxations as Schlegel et al. and Lee et al., but these relaxations disagree with the many non-specular rods. This shows the advantage of a more extended data set to experimentally limit the number of the relevant fitting parameters. Despite the different treatment of the deep relaxations, the values for the most significant relaxation, that of Cs⁺, are in good agreement. This is a consequence of the heavy Cs⁺ that dominates many of the features in the specular rod.

3.4. CONCLUSIONS

The present study precisely determines the adsorption site of the Cs⁺ and Rb⁺ to be the surface ditrigonal cavities of muscovite mica exposed to CsCl and RbBr solution. The out-of-plane relaxations of these cations, 0.43 ± 0.05 Å for Cs⁺ and 0.21 ± 0.05 Å for the Rb⁺, agree with their ionic radii and with the ionic radius of the K⁺ that they replace.

We find evidence for the presence at the interface of hydrated negatively charged ions, ordered in the out-of-plane direction and highly disordered in the lateral direction. A hydration shell is shared by these surface cations and anions. The ordering in the solution is limited to the first two/three layers. The important solid-liquid interface interactions are taking place in the 10 Å interface containing the topmost bulk crystal layers of the muscovite and the 5-6 Å above it.

The use of single-terminated mica surfaces enables the acquisition of a large data set with unique reflections. Such a large data set helps distinguishing the out-of-plane ordering from the ordering in the lateral direction and is limiting the number of free parameters used in data analysis. The use of heavy elements, with strong scattering power in the X-ray regime, Cs⁺ and Rb⁺, enhanced our surface sensitivity and the accuracy of the final results, although limited agreement was found with other XRR, resonant anomalous XRR and MD simulation results reported in literature. Studies using a range of conditions and combining different methods may be needed to clarify these issues.

Acknowledgements

We thank the ESRF and the beam line staff for using the facilities of ID03.

References

- ¹ de Poel, W.; Pinte, S.; Drnec, J.; Carla, F.; Felici, R.; Mulder, P.; Elemans, J.A.A.W.; van Enckevort, W.J.P.; Rowan, A.E.; Vlieg, E. *Muscovite mica: Flatter than a pancake*. *Surf. Sci.* **2014**, *619*, 19–24.
- ² Peanasky, J.; Schneider, H.M.; Granick, S. Self-Assembled Monolayers on Mica for Experiments Utilizing the Surface Forces Apparatus. *Langmuir* **1995**, *11*, 953–962.
- ³ Lowack, K.; Helm, C.A. Polyelectrolyte Monolayers at the Mica/Air Interface: Mechanically Induced Rearrangements and Monolayer Annealing. *Macromolec.* **1998**, *28*, 2912–2921.
- ⁴ van den Bruele, F.J.; de Poel, W.; Sturmans, H.W.M.; Pinte, S.; de Gelder, R.; Wermeille, D.; Juricek, M.; Rowan, A.E.; van Enckevort, W.J.P.; Vlieg, E. Monolayer and aggregate formation of a modified phthalocyanine on mica determined by a delicate balance of surface interactions, *Surf. Sci.* **2012**, *606*, 830–835.
- ⁵ de Poel, W.; Pinte, S.; de Jong, A.; Drnec, J.; Carla, F.; Felici, R.; op den Camp, H.J.; Elemans, J.A.; van Enckevort, W.J.; Rowan, A.E.; Vlieg, E. Dibenzo-crown-ether layer formation on muscovite mica. *Langmuir* **2014**, *30*, 12570–12577.
- ⁶ Pastre, D.; Hamon, L.; Mechulam, A.; Sorel, I.; Baconnais, S.; Curmi, P.A.; Le Cam, E.; Pietrement, O. Atomic Force Microscopy Imaging of DNA under Macromolecular Crowding Conditions. *Biomacromolecules* **2007**, *8*, 3712–3717.
- ⁷ Tang, T.-C.; Amadei, C.A.; Thomson, N.H.; Chiesa, M. Ion Exchange and DNA Molecular Dip Stick: Studying the Nanoscale Surface Wetting of Muscovite Mica. *J. Phys. Chem. C* **2014**, *118*, 4695–4701.
- ⁸ Xu, L.; Salmeron, M. An XPS and Scanning Polarization Force Microscopy Study of the Exchange and Mobility of Surface Ions on Mica. *Langmuir* **1998**, *14*, 5841–5844.
- ⁹ Gaines, G.L. The Ion-exchange Properties of Muscovite Mica. *J. Phys. Chem.* **1957**, *61* (10), 1408–1413.
- ¹⁰ Drummond, C.; Israelachvili, J. Fundamental studies of crude oil-surface water interactions and its relationship to reservoir wettability. *J. Pet. Sci. Eng.* **2004**, *45*, 61–81.
- ¹¹ Lord, D.L.; Buckley, J.S. An AFM study of the morphological features that affect wetting at crude oil-water-mica interface. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2002**, *206*, 531–546.
- ¹² Buckley, J.S.; Lord, D.L. Wettability and morphology of mica surfaces after exposure to crude oil. *J. Pet. Sci. Eng.* **2003**, *39*, 261–273.
- ¹³ Kimura, K.; Ido, S.; Oyabu, N.; Kobayashi, K.; Hirata, Y.; Imai, T.; Yamada, H. Visualizing water molecule distribution by atomic force microscopy. *J. Chem. Phys.* **2010**, *132*, 194705.
- ¹⁴ Bahamondes, S.; Donoso, S.; Henriquez, R.; Flores, M. Morphological and electrical study of gold ultrathin films on mica. *Thin Solid Films* **2013**, *548*, 646–649.
- ¹⁵ Bhattacharyya, K.G. XPS study of mica surfaces. *J. Electron. Spectrosc. Relat. Phenom.* **1993**, *63*, 289–306.
- ¹⁶ de Cooman, B.C.; Vankar, V.D.; Vook, R.W. AES studies of palladium films formed on copper and mica. *Surf. Sci.* **1983**, *128*, 128–144.
- ¹⁷ Pesty, F.; Garoche, P. Low-energy electron beam on an insulator surface: Impact of the charging process on the diffraction by mica muscovite. *Surf. Sci.* **2005**, *580*, 153–162.
- ¹⁸ Briscoe, W.H.; Speranza, F.; Li, P.; Konovalov, O.; Bouchenoire, L.; van Stam, J.; Klein, J.; Jacobs, R.M.J.; Thomas, R.K. Synchrotron XRR study of soft nanofilms at the mica-water interface. *Soft Matter* **2012**, *8*, 5055.
- ¹⁹ Bell, I.A.; Wilson, C.J.L. Deformation of biotite and muscovite: TEM microstructure and deformation model. *Tectonophysics* **1981**, *78*, 201–228.
- ²⁰ Israelachvili, J.; Adams, G. E. Measurement of Forces Between Two Mica Surfaces in Aqueous Electrolyte Solutions in the Range 0–100 nm. *J. Chem. Soc., Faraday Trans.* **1978**, *174*, 975–1001.
- ²¹ Israelachvili, J.; Min, Y.; Akbulut, M.; Alig, A.; Carver, G.; Greene, W.; Kristiansen, K.; Meyer, E.; Pesika, N.; Rosenberg, K.; Zeng, H. Recent advances in the surface forces apparatus (SFA) technique. *Rep. Prog. Phys.* **2010**, *73*, 036601.

-
- ²² Schlegel, M. L.; Nagy, K. L.; Fenter, P.; Cheng, L.; Sturchio, N. C.; Jacobsen, S. D. Cation sorption on the muscovite (001) surface in chloride solutions using high-resolution X-ray reflectivity. *Geochimica et Cosmochimica Acta* **2006**, 70, 3549-3565.
- ²³ Fenter, P.; Park, C.; Nagy, K. L.; Sturchio, N. C. Resonant anomalous X-ray reflectivity as a probe of ion adsorption at solid-liquid interfaces. *Thin Solid Films* **2007**, 515, 5654-5659.
- ²⁴ Cheng, L.; Fenter, P.; Nagy, K.L.; Schlegel, M.L.; Sturchio, N.C. Molecular-Scale Density Oscillations in Water Adjacent to a Mica Surface. *Phys. Rev. Lett.* **2001**, Vol. 87, 15, 156103.
- ²⁵ Sakuma, H.; Kawamura, K. Structure and dynamics of water on Li⁺-, Na⁺-, K⁺-, Cs⁺-, H₃O⁺-exchanged muscovite surfaces: A molecular dynamics study. *Geochimica et Cosmochimica Acta* **2011**, 75, 63-81.
- ²⁶ Feidenhans'l, R. Surface structure determination by X-ray diffraction. *Surf. Sci. Rep.* **1989**, 10, 105-188.
- ²⁷ Robinson, I. K.; Tweet, D.J. Surface X-ray diffraction. *Rep. Prog. Phys.* **1992**, 55, 599-651.
- ²⁸ Vlieg, E. X-ray diffraction from surfaces and interfaces. *Chapter 3.4.2. in Surface and Interface Science*, Vol. 1: Concepts and Methods, Ed. K. Wandelt, 2012, Wiley-VCH.
- ²⁹ Vlieg, E. Integrated Intensities Using a Six-Circle Surface X-ray Diffractometer. *J. Appl. Cryst.* **1997**, 30, 532.
- ³⁰ Vlieg, E. ROD: a program for surface X-ray crystallography. *J. Appl. Cryst.* **2000**, 33, 401.
- ³¹ Prince, E. (editor) International tables for crystallography 3rd ed. *Kluwer Academic Publishers* **2004**, Volume C, p. 578-579.
- ³² Cromer, D.T.; Liberman, D.A. Anomalous dispersion calculations near to and on the long-wavelength side of an absorption edge. *Acta Cryst.* **1981**, A37, 267.
- ³³ Gueven, N. The crystal structure of 2M1 phengite and 2M1 muscovite. *Z. Kristallogr.* **1971**, 134, 196.
- ³⁴ Reedijk, M. F.; Arsic, J.; Hollander, F.F.A.; de Vries, S.A.; Vlieg, E. Liquid Order at the Interface of KDP Crystals with Water: Evidence for Icelike Layers. *Phys. Rev. Lett.* **2003**, Vol. 90, 6, 066103.
- ³⁵ Lee, S.S.; Fenter, P.; Nagy, K.L.; Sturchio, N.C. Monovalent Ion Adsorption at the Muscovite (001) – Solution Interface: Relationships among Ion Coverage and Speciation, Interfacial Water Structure, and Substrate Relaxation. *Langmuir* **2012**, 28, 8637
- ³⁶ Mahler, J.; Persson, I. A Study of the Hydration of the Alkali Metal Ions in Aqueous Solution. *Inorg. Chem.* **2012**, 51, 425-438.
- ³⁷ McCauley, J.M.; Newnham, R.E. Origin and predictions of ditrigonal distortions in micas. *American Mineralogist* **1971**, 56, 1626-1638.
- ³⁸ Tatayema, H.; Shimoda, S.; Sudo, T. The crystal structure of synthetic MgIV mica. *Zeitschrift für Kristallographie* **1974**, Bd. 139, S. 196-206.
- ³⁹ Volkov, A.G.; Paula, S.; Deamer, D.W. Two mechanisms of permeation of small neutral molecules and hydrated ions across phospholipid bilayers. *Bioelectrochemistry and Bioenergetics* **1997**, 42, 153-160.
- ⁴⁰ Shannon, R.D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Cryst.* **1976**, A32, 751.
- ⁴¹ Park, C.; Fenter, P.A.; Nagy, K.L.; Sturchio, N.C. Hydration and Distribution of Ions at the Mica-Water Interface. *Phys. Rev. Lett.* **2006**, 97, 016101.
- ⁴² Ricci, M.; Spijker, P.; Voitchovsky, K. Water-induced correlation between single ions imaged at the solid-liquid interface. *Nat. Commun.* **2014**, 5, 4400.
- ⁴³ Odelius, M.; Bernasconi, M.; Parrinello, M. Two Dimensional Ice Adsorbed on Mica Surface, *Phys. Rev. Lett.* **1997**, 78, 2855.