**Summary**

Solid-liquid interfaces are hosting many important physical and chemical phenomena

occurring in nature. The transport and mobility of cations and anions dissolved in

aqueous solutions are influenced by the minerals the solution comes in contact with.

This thesis is using muscovite mica as a model mineral surface in contact with water

and different ionic aqueous solutions in order to determine the structure of these

solid-liquid interfaces at the atomic scale. Surface X-ray diffraction is used for our

study; this is a powerful technique for the structure determination of surfaces and

interfaces. State-of-the art surface X-ray diffraction measurements, including both

specular and non-specular crystal truncation rods, were performed on muscovite mica

that was especially prepared to have only one of the two possible surface terminations.

Data sets containing more than 2000 unique reflections were measured for each

sample, which means a significant improvement in terms of dataset size with respect

to other similar studies limited to specular reflectivity curves. This improvement was

possible thanks to the use of area detectors.

The third chapter describes the surface structure of muscovite in 56 mM CsCl

solution and in 11 mM RbBr solution. The use of the heavy monovalent cations of

Cs+ and Rb+ enhances the surface sensitivity and the results show that the ions replace

the surface K+ ions and an out-of-plane relaxation of these ions with respect to the

bulk muscovite crystal position of K+ that depends on the ionic radius. Both cations

are located on the top of the center of the ditrigonal surface cavities and are

compensating (within the error bars) for the muscovite surface charge. The adsorbed

cations are forming inner-hydration complexes. The negatively charged ions, naturally

present in the solution, are forming outer-hydration complexes and they are present

with higher probability in the vicinity of the interface than in solution. The surface

induced lateral ordering of the liquid phase is limited to the first 2-3 Å of the solution,

while in the out-of-plane direction the ordering is visible up to about 10 Å.

With respect to Cs+ and Rb+, the detection of the much lighter K+ ion is more

difficult. The experimental conditions for the muscovite mica – water and muscovite

mica – 10-4 M aqueous KOH solution were carefully selected in order to limit the

amount of hydronium ions we can have in the liquid phase. As described in chapter

four, the results for both conditions, show the presence of unrelaxed surface

potassium cations. The surface charge of the freshly cleaved muscovite is fully

compensated in water environment, while the presence of low concentration KOH

solution leads to overcompensation of these charges. There is strong evidence of

inner-hydration complex formed by the surface ions. The ordering in the lateral

direction is restricted to the first two interface atomic layers from the topmost

crystalline oxygen (forming the surface cavities). In the out-of-plane direction there is

a decreasing level of ordering as we go further away the surface and the ordering is

limited to the first 10 Å.

The structure of the solid-liquid interface formed by muscovite mica in contact with

aqueous solution of divalent ions is presented in the fifth chapter. SrCl2 and BaCl2

salts were used to prepare 10-2 M aqueous solutions. Like in the case of the

monovalent ions, the compensation for the surface charges resulting after the cleavage

of muscovite is the main mechanism in the adsorption process of the cations.

Although these divalent ions have smaller ionic and covalent radii than the K+ they

are replacing, they still show out-of-plane relaxations, likely due to their relatively

strong and well-defined inner-hydration shell. Clear evidence for the presence of

negative ions, forming outer-hydration complexes in the vicinity of the interface, was

found. The coordination distance at the interface suggests the presence at the surface

of SrCl+ or BaCl+, but using surface X-ray diffraction is difficult to distinguish these

from the charge neutral salts of SrCl2 or BaCl2.