

## Can Ion Pairs Adsorb on a Negatively Charged Mica Surface in Aqueous Solution?

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### 1 Introduction

Ion adsorptions on a mineral surface are important to develop an interfacial double layer theory. The phenomena are also critical to remove toxic elements in water. A comparison of molecular dynamics (MD) simulations and x-ray crystal truncation rods (CTR) scattering measurements implied an excess adsorption of  $\text{Cs}^+$  on a muscovite surface more than the number to compensate the negatively charged muscovite surface in water [1]. This could be explained by the co-adsorption of  $\text{Cs}^+$  and  $\text{Cl}^-$  in the aqueous solution. Such an ion-pair adsorption enhances the maximum number of cations adsorption on a mineral surface and therefore it is important to know the mechanism of the ion-pair adsorption. Here we investigated the interfacial structures of aqueous KCl and KI solutions on muscovite surfaces using the x-ray CTR scattering measurements and discussed the possibility of potassium-monovalent anion pair adsorption on a negatively charged mineral surface.

### 2 Experiment

Mica (Muscovite:  $\text{KAl}_2(\text{OH})_2(\text{AlSi}_3\text{O}_{10})$ ) belongs to the group of 2:1 layer silicates and consists of an octahedral  $[\text{AlO}_6]$  sheet sandwiched between two tetrahedral  $[(\text{Si,Al})\text{O}_4]$  sheets. One of the four Si atoms in the tetrahedron is replaced by an Al atom because of which there exists an overall negative charge on the layers. This charge is compensated for and the layers are bonded together by an interlayer of  $\text{K}^+$  ions. The mica crystals were cut into  $1 \times 1 \text{ cm}^2$  squares and glued on flat silica glass lenses. A peeling procedure was employed to prepare fresh and clean (001) mica planes. The surface was immediately immersed in a 0.5 M KCl or KI solution and kept in it for at least a few hours. Just prior to the CTR measurements, the mica was mounted on a thin-film liquid cell and the liquid cell was covered using a polyester film  $6 \mu\text{m}$  thick to prevent the solution from evaporating. The x-ray CTR scattering intensities were corrected by the scattering area, Lorentz, polarization, attenuation factors, and rod interception. The experiments were carried out at Photon Factory, KEK, Japan (BL-4C) by using monochromatic x-rays of 11.0 keV. The CTR refers to scattering with a momentum transfer vector perpendicular to the interface  $Q$ . The CTR profile was obtained in the range  $Q = 1.3\text{--}4.4 \text{ \AA}^{-1}$  with individual rocking scans at given  $Q$  values. The resolution of the data was approximately equal to  $\pi/Q_{\text{max}}$ , where  $Q_{\text{max}}$  is the highest  $Q$  value at which data were obtained. In these measurements, the resolution was  $0.72 \text{ \AA}$ .

### 3 Results and Discussion

The x-ray CTR scattering profiles of KCl and KI solutions on mica surfaces were shown in Fig. 1. The Bragg reflection points (00*l*) (*l* = 4, 6, 8, 10, 12, and 14) of the mica surface were at  $Q \approx 1.2, 1.9, 2.5, 3.2, 3.8,$  and  $4.4 \text{ \AA}^{-1}$ , respectively. The intensities between the Bragg reflection points reflect the scattering from the aqueous salt solution/mica interfaces. There was no distinct difference between the scattering profiles of the KCl and KI solutions on mica surfaces, indicating that these interfacial electron densities should be similar between them. Since the number of electron of an iodide is much larger than a chloride, no difference of the CTR scattering profiles implied that ion-pair (K-Cl or K-I) adsorption was minor on a mica surface.

The ion-pair adsorption would depend on the energy balance among the hydration energies of ions, attractive interaction between cations and anions, and interactions of ions with a negatively charged mica surface. Low hydration energy of cations would be most important factor to realize the ion-pair adsorption on a mica surface. The adsorption behaviour of  $\text{Cs}^+$  ions with various monovalent anions should be investigated in the future works.

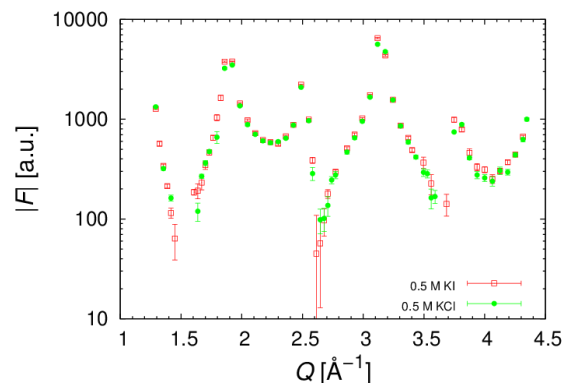


Fig. 1: X-ray CTR scattering profiles of 0.5 M KI and KCl solutions on muscovite surfaces. The normal axis is absolute value of the structure factor  $F$  of the interfaces.

### Acknowledgement

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### References

- [1] H. Sakuma and K. Kawamura, *Geochim. Cosmochim. Acta* **75** (2011) 63.

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