

## Concentration Dependence of Hydration Structures in Aqueous Salt Solutions Revealed by Soft X-ray Absorption Spectroscopy

Masanari Nagasaka

Institute for Molecular Science

### Summary

Microscopic properties of aqueous salt solutions such as viscosity, boiling point, and melting point, are influenced by the interaction between solute ions and solvent water molecules. Soft X-ray absorption spectroscopy (XAS) is an element specific method for light elements, where the electronic structures of ions are separately observed from those of solvent water molecules in aqueous salt solutions. Recently, we have realized XAS of liquid samples in transmission mode by developing the precise thickness control method (20 ~ 2000 nm). In this study, we have investigated the concentration dependence of solvation structures of  $\text{Li}^+$  ions in aqueous LiCl solutions by using O K-edge XAS. The experiments were performed at soft X-ray beamline BL3U at the UVSOR-III Synchrotron. From O K-edge XAS of aqueous LiCl solutions, the peaks related to water molecules in the first coordination shells of  $\text{Li}^+$  ions show lower energy shifts by increasing the salt concentrations until 8 M, but they show higher energy shifts above 8 M. For revealing two concentration regions, we have performed molecular dynamics (MD) simulations of aqueous LiCl solutions at different concentrations. The radial distribution functions (RDF) between  $\text{Li}^+$  ions and water molecules show lower distance shifts by increasing the salt concentrations. The RDF  $\text{Li}^+ - \text{Cl}^-$  shows a higher distance shift by increasing the salt concentration. On the other hand, the RDF  $\text{Li}^+ - \text{Li}^+$  is not nearly changed below 8 M and shows higher distance shifts above 8 M. These changes of RDF would be related to two concentration regions observed by XAS. In the future, we will discuss the concentration dependence of solvation structures of ions by using inner-shell calculations. We have also developed the ultrathin liquid cell including membranes with no Si atoms for measuring XAS spectra of aqueous LiCl solutions at Li K-edge and Cl L-edge. The hydration shell of  $\text{Li}^+$  ions will be investigated from both  $\text{Li}^+$  ions and hydrating water molecules by XAS at the Li and O K-edges.