No. 202413

Structure of Salt Water Solutions

Osamu Takahashi

Research Institute for Synchrotron Radiation Science, Hiroshima University

Summary

How does the interaction between ions and water in aqueous solution change the microstructure of water? Gas molecules are basically single molecules, and solid systems are orderly and well-ordered, forming crystalline structures or amorphous structures if they are irregular. What about liquids? Also, when a salt dissolves in water, it becomes an ion, but what is the hydration structure around the ion? In the present study, we aim to model the hydration structure of salts and the surrounding water structure by first-principles theoretical calculations and clarify the microscopic picture.

Molecular dynamics (MD) simulations were performed in the NPT ensemble using the code GROMACS for 1 M to 4 M NaCl and $MgSO_4$ aqueous solutions. The radial distribution functions and diffusion coefficients were in good agreement with those of previous studies. To understand the structure of water around ions, the order parameter Tetrahedrality and the diffusion constant were applied. Compared to the structure of bulk water, the first hydration shell for ions is highly disordered, whereas the second hydration shell and above show similar trends to bulk water.

XES spectral calculations were performed using the structures obtained MD simulations. A cluster of about 20 molecules was constructed around a randomly selected water molecule, and spectra were produced when the central molecule was core-excited. In the spectra of the first hydration sphere, both cations and anions tended to peak at the $1b_1'$ state on the low energy side. This is because the X...H-O (where X is a cation or anion) is more linear than the hydrogen bonds in bulk water, which accelerates the dynamics induced by the formation of the inner-shell hole of the hydrogen atom.

As a further application, XES spectral calculations of water in liquid crystal film pores were performed. The study was performed for two types of liquid crystal membranes: triethylammonium-based and imidazolium-based. In water in the membranes, the relative intensity of the two peaks is independent of the concentration of water (experimentally corresponding to the water pressure in the membrane). In the case of the triethylammonium system, the intensity between the two peaks tends to be higher at 3 M. This reflects the difference in the dynamics derived from the various hydrogen bonding modes. The calculated spectra obtained reflect differences in the hydrophilicity of the functional groups.

Our XES spectral calculations reveal that the XES spectra truly reflect the molecular orientation around the excited molecules.