SOLVATION STRUCTURES FOR IODIDE ANIONS IN VARIOUS SOLVENTS BY EXAFS

Halide anions are the most common anions, in existence everywhere, from seawater to our bodies. The solvation structures for such important ions, however, are not well understood owing to their weak interaction with solvent molecules. The weak interaction may be reflected in their various reported hydration numbers, from zero to seven or eight depending upon the methods employed to determine them [1].

The weakening order in interaction with water molecule, Cl^- >Br^- >I^-, has been shown through studies on solvation enthalpy, by solvent extraction or liquid chromatography. It is of great interest to elucidate and compare the differences in solvation structure of these anions.

Our previous EXAFS study on bromide anion [2] verified suitability of the EXAFS method for determining local structures of ions dissolved in water, or in organic solvents where ion-solvent interaction is even weaker. However, the EXAFS method using conventional X-ray conditions has not been ideally suited to chloride and iodide due to the extremely low absorption edge energy of the former and, on the other hand, the very high edge energy (33 keV) of the latter. Therefore, bromide has been the only candidate for EXAFS experiments among the three ions.

Using SPring-8 X-rays, we are now able to explore the XAFS of iodide anions in various solvents and compare the results with those of bromide ions. The beamline **BL01B1** is used to obtain XAFS spectra by a transmission method at the I K-edge. It is equipped with a double-crystal monochromator and a double-mirror system, which effectively removes higher harmonic photons.

EXAFS oscillation signals $k^3\chi(k)$ have been extracted from absorption spectra for 0.1 mol/dm^3 iodide anions dissolved in several solvents and some of them are displayed in Figure 1. The small oscillation amplitudes and noisy spectra are due to two reasons, *i.e.*, first, the weakest interaction of iodide anions with solvents among the three halide anions, and second, the shortest lifetime of its core-hole state. In Fourier transformed (FT) spectra

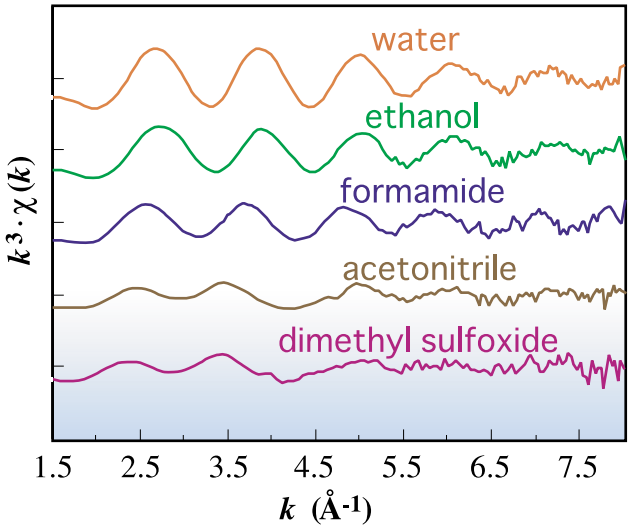

Fig. 1: EXAFS oscillation spectra k^3 χ (k) for iodide anions dissolved in solvents.

of the $k^3\chi(k)$ data, the identification of peaks was easy due to the atom-atom interaction between iodide anions and oxygen or carbon atoms in solvent molecules.

The amplitude of the EXAFS oscillations in Figure 1 can be evaluated by using intensity h of the peak in the FT spectrum. It is interesting that a correlation exists between h and an empirical solvent parameter obtained from NMR measurement, the Mayer-Gutmann acceptor number A_N [3], indicating the strength of interaction between donor solute and acceptor solvent.

The correlation of h with A_N shown in Figure 2 is interpreted as follows. The oscillation amplitude will be greater for ions with a larger number of coordinating atoms N and also with a smaller disorder σ in the atom-atom distance. A larger N leads to greater electrostatic solute-solvent interaction and a smaller σ means a stronger solute-solvent bond. Therefore, h is intimately related to the solute-solvent interaction strength.

The present study suggests that EXAFS has been not only a quantitative tool to determine the geometrical structure, but also can be extended to become a qualitative tool for such complicated systems like a solution for which many empirical parameters are of practical use.

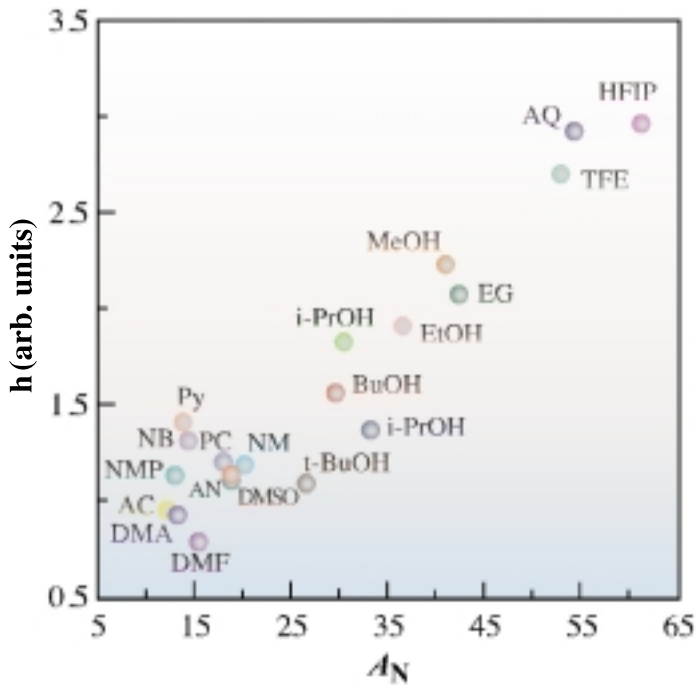

Fig. 2. Correlation of the first shell peak height h in an FT spectrum with acceptor number A_N of the solvent. HFIP for 1,1,1,3,3,3-hexafluoroisopropanol, AQ for water, TFE for 2,2,2-trifluoroethanol, EG for ethylene glycol, MeOH for methanol, EtOH for ethanol, i-PrOH for isopropanol, PrOH for n-propanol, BuOH for n-butanol, t-BuOH for t-butanol, NM for nitromethane, AN for acetonitrile, DMSO for dimethyl sulfoxide, PC for propylene carbonate, DMF for N,N-dimethylformamide, NB for nitrobenzene, Py for pyridine, DMA for N,N-dimethylacetamide, NMP for N-methyl-2-pyrrolidone and AC for acetone.

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References

[1] H. Ohtaki and T. Radnai, *Chem. Rev.* **93** (1993) 1157.
[2] H. Tanida *et al., J. Chem. Soc. Dalton Trans.* **2321** (1994).
[3] V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum, New York, 1978.

EXAFS STUDY ON LIQUID SELENIUM UNDER HIGH-PRESSURE

High-pressure XAFS enables structural information difficult to obtain through conventional high-pressure X-ray diffraction studies to be accessed. We have successfully measured XAFS spectra of crystalline and liquid Se at pressure of 2.5 GPa and temperatures up to 1223K at the beamline **BL01B1** [1].

Liquid Se is a typical liquid semiconductor at atmospheric pressure and its main constituents are two-fold coordinated chain molecules. Recently, study on the semiconductor-to-metal transition of liquid Se in the pressure range from 1 GPa to 4 GPa showed that the transition has some features of a first-order transition [2]. We focus on how structural changes of the Se system associate with the changes in its electronic properties.

A large-volume Paris-Edinburgh press was used to generate high-pressure, high-temperature conditions. A mixture of Se powder and BN powder was put in a BN capsule, which was surrounded by a gasket made of Boron and epoxy. The sample was heated using two graphite disk-type heaters inside the gasket. The beam was focused vertically by a mirror. The size of the X-ray beam was reduced to 0.3(H) x 0.2(V) mm^2 by slits to adjust to the small sample size. The intensities of the incident and transmitted X-rays were measured with ionization chambers.

Figure 1 shows an example of XAFS spectra for liquid Se measured at pressure of 2.5 GPa and temperature of 773 K. Clear EXAFS oscillations were observed in spite of experimental difficulties. Figure 2 shows the temperature dependence of radial distribution function, $|F(r)|$, obtained by the Fourier transform of EXAFS function $\chi(k)$ multiplied by k, for crystalline and liquid Se at 2.5 GPa. The main peak corresponds to the covalent bonds. The peak height decreases continuously with increasing temperature due to the thermal factor. The radial distribution function changes little upon melting; this indicates that the two-fold chain structure is largely preserved in the liquid. A steep