

## Application of a compact synchrotron radiation facility to studies on the structure of solvated chloride and iodide ions in various solvents\*

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*Abstract:* A beamline equipped on the compact superconductive synchrotron radiation (SR) facility at Ritsumeikan University was designed for performing extended X-ray absorption fine structure (EXAFS) analyses of solutions and solids. The introduction of three different crystals, Si(220), Ge(220), and InSb(111), as the monochromator of the EXAFS spectrometer covers the K-edge absorption energy range of elements with low atomic numbers from silicon (atomic number 14) through zinc (30). The L<sub>III</sub>-edge of the iodide ion could be measured by Si(220) and Ge(220). It is, however, not possible to measure the absorption of the bromide ion with this equipment. Using this spectrometer, the solvation structure of Cl<sup>-</sup> and I<sup>-</sup> ions was investigated in water, methanol, and ethanol under atmospheric pressure.

### INTRODUCTION

The extended X-ray absorption fine structure (EXAFS) method has been widely employed by a number of investigators for various materials, such as solids, liquids, inorganic complexes, biomaterials, etc. However, the use of the EXAFS method was restricted to middle heavy atoms with atomic numbers larger than 19 (K), and atoms lighter than potassium were hardly investigated by the method under atmospheric pressure. Ritsumeikan University, a private university in Japan, has had a compact superconductive synchrotron radiation (SR) facility since 1995 [1], and one of the 16 beamlines (two of which are used for monitoring) has been devoted to EXAFS investigations of various materials. In the EXAFS spectrometer, a Si(220) crystal has been used since 1996 and a Ge(220) crystal has also been used since 1998, both of which have been widely accepted for measurements of middle heavy atoms heavier than potassium. The SR facility supplies intense X-rays over a range of 1–3 keV. An extension of the measurable energy range of the X-rays is strongly expected to cover a range of elements of lower atomic numbers. Thus, the introduction of a new crystal InSb(111) has been successfully proposed in 2002, and measurements of EXAFS spectra of atoms of low atomic numbers from silicon (atomic number 14) through zinc (30) became possible.

Ionic solvation is one of the most fundamental subjects to be investigated in solution chemistry, and a number of ions in solutions have been studied with respect to their structural and dynamic properties by various methods; the results have been summarized in books and reviews [2–10]. Although diffraction (X-ray and neutron), NMR, and other methods are valuable for investigations of ionic solvation, the EXAFS method is a convenient and useful method for studies of local structure of solvated ions in aqueous and nonaqueous solutions. However, the method has difficulties for the determination of the structure of solvated light ions such as lithium, sodium, fluoride, and chloride. Although it is still

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\*Lecture presented at the European Molecular Liquids Group (EMLG) Annual Meeting on the Physical Chemistry of Liquids: Novel Approaches to the Structure, Dynamics of Liquids: Experiments, Theories, and Simulation, Rhodes, Greece, 7–15 September 2002. Other presentations are published in this issue, pp. 1–261.

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generally not possible to study atoms lighter than silicon by the EXAFS method, the solvation structure of chloride ions in solution became accessible in the present work after improvement of the EXAFS spectrometer.

Since the solvation of anions is weaker than that of cations, except for the fluoride ion, EXAFS oscillations resulting from anionic solvation are usually less pronounced than the ones originating from cationic solvation. Therefore, high-quality EXAFS spectra with little noise should be obtained for the analysis of the solvation structure of anions. The solvation structure of heavy anions such as bromide and iodide ions in methanol and ethanol has already been investigated by the EXAFS method [11,12], but no report has been published for the chloride ion by the EXAFS method. No investigation has been made for the solvation structure of chloride ions in organic solvents except in DMSO [13].

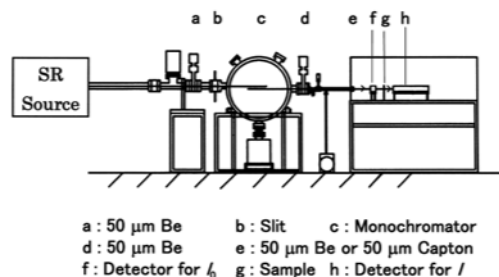
For EXAFS studies on light atoms, the measurements have to be carried out under vacuum in order to avoid absorption of incident X-rays by air. However, by using a suitable combination of crystals, strong X-ray beams in the soft X-ray range are obtainable, and thus, the K-edge EXAFS spectra of solutions containing chloride ions can be measured under atmospheric pressure.

In the present work, the solvation structures of chloride (K-absorption edge is 2.820 keV) and iodide (K- and  $L_{III}$ -absorption edges are 33.163 and 4.558 keV, respectively) ions in water (as reference), methanol, and ethanol were determined, and the results for the latter ion were compared with those previously obtained [11,12]. An investigation of the solvation structure of the bromide ion (K- and  $L_{III}$ -absorption edges are 13.478 and 1.552 keV, respectively) was not possible by the present equipment.

### EXAFS SPECTROMETER AT THE SR CENTER OF RITSUMEIKAN UNIVERSITY, KUSATSU, JAPAN

The beamline used in the present study is depicted in Fig. 1. It consists of three windows, a slit, a double-crystal monochromator, and two detectors. An X-ray beam with a broad energy range emitted from the SR ring passes through the first Be window (a), which eliminates low-energy X-rays and prevents the crystal in the monochromator from the heat caused by irradiation. The size of the incident beam is controlled by the slit (b). Then, monochromatized X-rays are obtained through the monochromator (c) equipped with Si(220), Ge(220), or InSb(111) double crystals. This part of the beamline is evacuated to  $(1-4) \times 10^{-6}$  Pa. The monochromatized X-rays enter a low vacuum part (2-3 Pa) and the second Be window (d) separates the high vacuum part from that of low vacuum. The third window (e) separates the low vacuum part from the atmospheric environment. A beryllium foil or a Capton film is used for the third window. Then, the X-rays pass through the sample (g) and the X-ray absorption spectrum measured is recorded in a computer.

The double-crystal monochromator used is of Golovchenko type [14]. The monochromator can move over the angle range of the double crystals from  $15^\circ$  to  $75^\circ$ . The InSb(111) crystal can extract the X-rays having energies corresponding to the K-edge absorption range from 1.7 to 6.4 keV, which

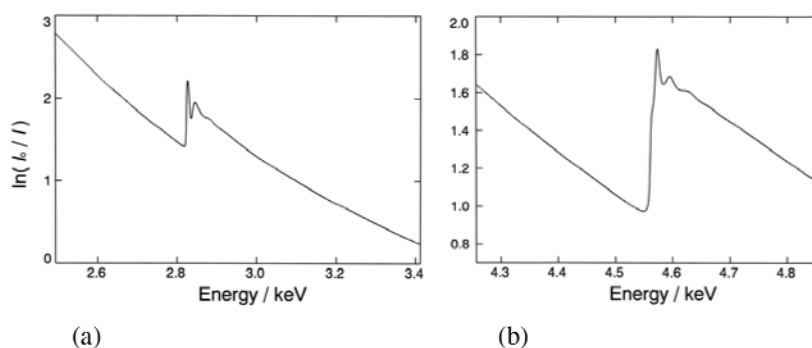


**Fig. 1** The outline of EXAFS spectrometer at the SR Center of Ritsumeikan University. The two detectors (f and h) are almost in contact with each other and sample (g) is attached to f for the measurements of K-edge EXAFS spectra of chlorine.

includes Si, P, S, Cl, Ar, K, Ca, Sc, Ti, and V atoms (atomic numbers from 14 to 23). However, since the L-edge absorption of In and Sb appears in the range of 3.7–4.7 keV, X-ray absorption spectra of potassium, calcium, and scandium are difficult to be measured using the InSb(111) monochromator. Crystals of Si(220) and Ge(220) can cover, on the other hand, the X-ray energy range of 3.4–12.4 and 3.2–12.0 keV, respectively. However, since the intensity of X-rays emitted from the compact SR source steeply drops above 11 keV [1], the Si(220) and Ge(220) crystals are practically used for elements from potassium (atomic number 19) up to zinc (30).

## SOLVATION STRUCTURE OF CHLORIDE AND IODIDE IONS IN METHANOL AND ETHANOL

For the measurement of the EXAFS spectra of sample solutions for  $\text{Cl}^-$ , the ionization chamber for the measurement of the X-ray intensity after absorption,  $I$ , was placed just behind the chamber for measuring  $I_0$  and the sample. The distance between the two chambers was about 5 mm. The sample was absorbed on a small piece of a paper (CLEAN WIPW-P, Asahi Kasei, Co. Ltd., Tokyo) and sealed in a thin Mylar bag, and it was attached on the window of the latter chamber. The K- and  $\text{L}_{\text{III}}$ -edge EXAFS absorption spectra of  $1 \text{ mol dm}^{-3}$   $(\text{C}_2\text{H}_5)_4\text{NCl}$  and  $0.5 \text{ mol dm}^{-3}$  NaI aqueous solutions obtained are shown in Fig. 2.

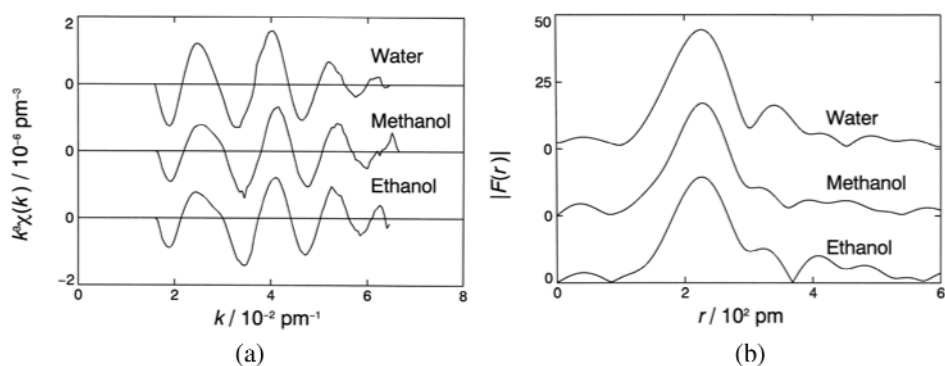


**Fig. 2** (a) The K-edge EXAFS spectrum of aqueous  $1 \text{ mol dm}^{-3}$   $(\text{C}_2\text{H}_5)_4\text{NCl}$  solution. (b) The  $\text{L}_{\text{III}}$ -edge EXAFS spectrum of aqueous  $0.5 \text{ mol dm}^{-3}$  NaI solution.

For the EXAFS study,  $1 \text{ mol dm}^{-3}$  tetraethylammonium chloride was used in all the solvents. On the other hand,  $0.5 \text{ mol dm}^{-3}$  sodium iodide was used for the aqueous system, while  $0.5 \text{ mol dm}^{-3}$   $(n\text{-C}_5\text{H}_9)_4\text{NI}$  was dissolved for methanol and ethanol.

The extracted oscillations and their Fourier transformed structure functions for the chloride solutions are shown in Fig. 3. The bands appearing around 230 pm in Fig. 3b are mainly due to  $\text{Cl}^-$ -O interactions (no phase-shift correction was made). The oscillations  $k^3\chi(k)$  showed shoulders around  $3 \times 10^{-2}$  pm in the functions of the methanol and ethanol systems, which were not observed in the aqueous system. The appearance of the shoulders in the  $k^3\chi(k)$  functions suggested that more than one kind of atom-pairs should contribute.

The solvation structure of the chloride ion in water has been extensively investigated by X-ray and neutron diffraction methods [8,9] and most investigators have reported that the average hydration number of the chloride ion in water is six and the  $\text{Cl}^-$ -O distance is 320–330 pm [9]. For the evaluation of the numbers of interatomic interactions and interatomic distances in methanol and ethanol solutions, the structural data in the aqueous solution was used as the reference.



**Fig. 3** (a) The extracted oscillations  $\chi(k)$  weighted by  $k^3$  of chloride ion in water, methanol, and ethanol. (b) The Fourier transformed radial distribution curves, uncorrected for the phase shift.

In a first attempt, the  $k^3\chi(k)$  functions in the methanol and ethanol systems were analyzed under the assumption of a single atom-pair involved. When the peak analyses were carried out under the assumption of only one type of  $\text{Cl}^-$ -O interaction in the solvated chloride ion, the coordination numbers of the chloride ion were found to be 3.4 and 3.8, respectively, with a  $\text{Cl}^-$ -O interatomic distance of 316–319 pm. These results are close to the values previously reported [11,12]. However, the solvation numbers of the chloride ion in the alcohol solutions thus obtained are unrealistically small compared with six coordination in water. It should be noted that the Hamilton  $R$ -factors thus obtained in the methanol and ethanol systems are fairly large compared with that found in the aqueous solution (see Table 1).

**Table 1** The number of interaction,  $n$ , the bond length,  $r$ , the Debye–Waller factor,  $\sigma$ , and the Hamilton  $R$ -factor for the solvated chloride ion in 1 mol  $\text{dm}^{-3}$  water, methanol, and ethanol solutions of  $(\text{C}_2\text{H}_5)_4\text{NCl}$  and the solvated iodide ion in 0.5 mol  $\text{dm}^{-3}$  NaI aqueous solution and 0.5 mol  $\text{dm}^{-3}$   $(n\text{-C}_4\text{H}_9)_4\text{NI}$  methanol and ethanol solutions at 25 °C.

Solvent	Interaction	Chloride solution				$R$	Iodide solution			
		$n$	$r/\text{pm}$	$\sigma/\text{pm}$	$R$		$n$	$r/\text{pm}$	$\sigma/\text{pm}$	$R$
Water	$\text{Cl}^-$ -O	6 <sup>a</sup>	320 <sup>a</sup>	$20.7 \pm 0.1$	0.028	$\text{I}^-$ -O	8 <sup>a</sup>	360 <sup>a</sup>	$20.1 \pm 0.1$	0.044
Methanol	$\text{Cl}^-$ -O	$3.4 \pm 0.3$	$316 \pm 1$	$15.9 \pm 0.6$	0.153	$\text{I}^-$ -O	$3.9 \pm 0.3$	$353 \pm 1$	$20.0 \pm 0.7$	0.190
	$\text{Cl}^-$ -O	$3.2 \pm 0.2$	$317 \pm 1$	$16.6 \pm 0.2$		$\text{I}^-$ -O	$3 \pm 1$	$361 \pm 1$	$17 \pm 3$	
	$\text{Cl}^- \cdots \text{C}$	$3.2 \pm 0.2$	$389 \pm 1$	$19.7 \pm 0.1$	0.018	$\text{I}^- \cdots \text{C}$	$3 \pm 1$	$405 \pm 1$	$20 \pm 3$	0.046
Ethanol	$\text{Cl}^-$ -O	$3.8 \pm 0.4$	$319 \pm 1$	$16.8 \pm 0.7$	0.183	$\text{I}^-$ -O	$3.5 \pm 0.4$	$352 \pm 1$	$17.7 \pm 0.7$	0.171
	$\text{Cl}^-$ -O	$3.9 \pm 0.5$	$320 \pm 1$	$18.1 \pm 0.7$		$\text{I}^-$ -O	$3 \pm 1$	$358 \pm 1$	$17 \pm 2$	
	$\text{Cl}^- \cdots \text{C}$	$3.9 \pm 0.5$	$391 \pm 1$	$19.6 \pm 0.4$	0.056	$\text{I}^- \cdots \text{C}$	$3 \pm 1$	$404 \pm 1$	$20 \pm 5$	0.059

<sup>a</sup>Fixed during the calculation.

Thus, two scatterers around the ion were assumed: the oxygen atom of the hydroxyl group and carbon atom in the methyl or methylene group in the alcohol molecules. The Hamilton  $R$ -factors were remarkably improved, and the values were comparable with that in the aqueous system. The numbers of  $\text{Cl}^-$ -O and  $\text{Cl}^- \cdots \text{C}$  pairs were assumed to be the same in the least-squares refinements;  $\text{Cl}^- \cdots \text{CH}_2$  and  $\text{Cl}^- \cdots \text{CH}_3$  interactions were not distinguished in the analysis of the structure functions in the ethanol system. The total numbers of interacting atoms with the chloride ion became 6.7 and 7.8 for methanol and ethanol, respectively, which were close to the hydration number of the chloride ion in water.

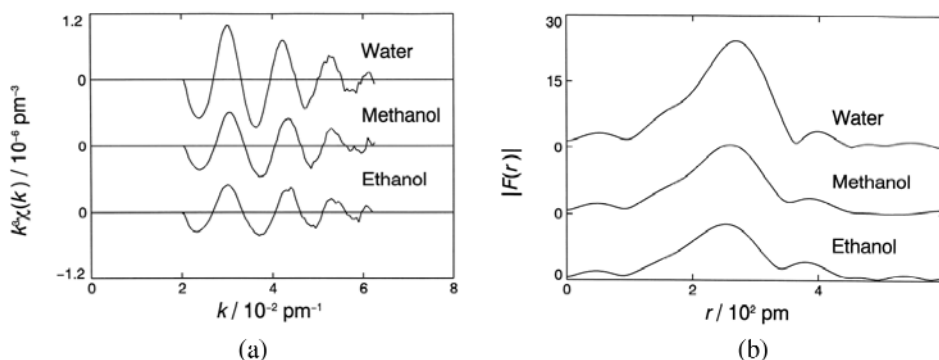
Independent variations of the  $n$ -values for the  $\text{Cl}^-$ -O and  $\text{Cl}^- \cdots \text{C}$  interactions were not possible in the present investigation due to poor convergence of the least-squares refinements of the data. Therefore, the same values of  $n$  for the two interactions found in the methanol and ethanol systems do not definitely mean that all the solvating alcohol molecules combine with the chloride ion through both hydroxyl and methyl (or methylene) groups. We could not confirm from the present study whether or not all alcohol molecules in the solvation shell of the anion form chelate rings, and monodentate solvation of some alcohol molecules in the solvation shell is not excluded.

Interactions of methyl groups with halide ions have been confirmed in alkali halide solutions of dimethyl sulfoxide [13,15]. A slightly positively charged methyl or methylene group in alcohol molecules can interact with halide ions.

Similar experiments were carried out for  $0.5 \text{ mol dm}^{-3}$  NaI aqueous solution as a reference and  $0.5 \text{ mol dm}^{-3}$   $(n\text{-C}_4\text{H}_9)_4\text{NI}$  methanol and ethanol solutions. The structure functions  $k^3\chi(k)$  and the Fourier transforms  $|F(r)|$  for the three solutions are shown in Fig. 4.

The hydration number for the iodide ion determined by the X-ray diffraction and EXAFS methods was rather widely spread from 6 to 9 [9] or 6.8 to 8.2 [16], whereas the values found by the molecular dynamics simulations were 7.3 to 9.8 [9]. According to the results of MD simulations, the hydration number of large anions cannot be a unique value but an average of widely distributed hydration numbers over a range from, here, 7 to 16 [17]. Finally, the value of 8 for the hydration number of the iodide in water was adopted as a reference value of the present EXAFS analysis. The  $\text{I}^-$ -O distance of 360 pm [16] found from X-ray diffraction studies was taken as the reference value.

Refinements of the data under the assumptions of one- and two-scatterers were examined. The results are summarized in Table 1. As has been seen in the case of the chloride ion, calculations with two-scatterers gave better results than those with one-scatterer. The total numbers of interacting atoms, oxygen and carbon atoms, are  $6 \pm 2$  for both methanol and ethanol systems. The differences between  $\text{I}^-$ -O and  $\text{I}^- \cdots \text{C}$  distances are 44 and 46 pm, respectively, for methanol and ethanol. The values are much smaller than those for  $\text{Cl}^-$ -O and  $\text{Cl}^- \cdots \text{C}$  (72 and 71 pm for methanol and ethanol, respectively). The shortening of these distances in the iodide case suggests easier accommodation of alcohol molecules around the iodide ion, it having a larger surface area than the chloride ion. The smaller solvation numbers of the halide ions in methanol and ethanol, compared to those in water, may be caused by the ligand–ligand repulsive interactions in the solvation shell of the anions due to the larger volumes of the alcohol molecules compared to water. The error involved in the numbers of  $\text{I}^-$ -O and  $\text{I}^- \cdots \text{C}$  interactions are rather large, which may in part arise from a large fluctuation in the position of the coordinating alcohol molecules and a wide distribution of numbers of solvating molecules around the large iodide ions. A possibility of monodentate interactions of some alcohol molecules with the iodide ion in the solvation shell can, again, not be excluded.



**Fig. 4** (a) The extracted oscillations  $\chi(k)$  weighted by  $k^3$  of iodide ion in water, methanol, and ethanol. (b) The Fourier transformed radial distribution curves, uncorrected for the phase shift.

## CONCLUDING REMARKS

Introduction of Si(220), Ge(220), and InSb(111) as the monochromator of the EXAFS spectrometer could cover the K-edge absorption energy range of elements with low atomic numbers from silicon (atomic number 14) through zinc (30). By using the spectrometer, the solvation structure of  $\text{Cl}^-$  and  $\text{I}^-$  ions was investigated in water, methanol, and ethanol under an atmospheric pressure. The EXAFS measurements of the chloride ion had not been possible to be made so far.

The solvation structure of the chloride and iodide ions in methanol and ethanol was determined by the EXAFS method, and it was found that the chloride ion is solvated with 3.4 methanol and 3.8 ethanol molecules through the alcoholic hydroxyl group and methyl group in methanol and methyl or methylene group in ethanol. On the other hand, the iodide ion interacts with  $3 \pm 1$  molecules in both methanol and ethanol. A possibility of monodentate interactions of some alcohol molecules with the chloride and iodide ions in the solvation shell could not be fully excluded. The  $\text{Cl}^-$ -O and  $\text{Cl}^- \cdots \text{C}$  distances were determined to be  $317 \pm 1$  and  $389 \pm 1$  pm, respectively, for methanol and  $320 \pm 1$  and  $391 \pm 1$  pm, respectively, for ethanol. The  $\text{I}^-$ -O and  $\text{I}^- \cdots \text{C}$  distances, on the other hand, were found to be  $361 \pm 1$  and  $405 \pm 1$  pm, respectively, for methanol and  $358 \pm 1$  and  $404 \pm 1$  pm, respectively, for ethanol.

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