XAFS analysis of triiodide ion in solutions

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Iodine K-edge XAFS of triiodide ions in various solvents were measured at SPring-8 BL01B1 and analyzed. Though the anion takes a linear and symmetric form, the second peak expected from enhanced multiple scatterings can be hardly observed because of its large vibrations. The bond distances and the Debye-Waller factors for the I–I couple vary when protic solvents were used and they were similar when aprotic solvents were used. It was indicated that the larger the Mayers' acceptor number of the solvent is, the larger the Debye-Waller factor is. It was also found that among the aprotic solvents, the larger the Gutmann's donor number is, the smaller the Debye-Waller factor is.

Keywords: Iodine K-edge, Triiodide ion, Solute structure, Solvent effect.

1. Introduction

Iodine makes variety of polyanions. Many investigations have been made about the polyanions because of their interests about the maximum number of polymerization, electronic characters, electric conductivity, polarizer for visual light, etc.. Triiodide ion is the most fundamental polyiodide ion. The formation constant of triiodide ion from iodine molecule and iodide ion in solutions varies from $10^{2.9}$ to $10^{8.3}$ mol/L depending on the characters of solvent used (Bienvenue, Msika & Dubois, 1980). This difference may affect the solute structure of triiodide ion. In this study, iodine K-edge XAFS for triiodide ion in solutions are analyzed to reveal the influence of solvent characters on the solute structure.

2. Experimental

Solutions of 0.01 mol/L I_3^- were prepared from equimolar of NaI and I_2 (NaI$_3$ solution) or tetra-*n*-propylammonium triiodide (TPAI$_3$ solution). Tetra-*n*-propylammonium triiodide (TPAI$_3$) was synthesized according to the method described by Tebbe & Gilles (1996). The two counter cations were selected to check the effect of the difference on ion-pair formation. Solvents used were acetone, *N*, *N*-dimethylacetamide, nitromethane, *N*, *N*-dimethylformamide, tetrahydrothiophen-1, 1-dioxide, methanol, acetonitrile, dimethylsulfoxide, ethanol, and water. All of the solvents were used to prepare NaI$_3$ solutions and acetone, *N*, *N*-dimethylacetamide, acetonitrile, dimethylsulfoxide, and methanol were used for TPAI$_3$ solutions. Aqueous solution of 0.01 mol/L NaI$_3$ could not be prepared owing to the small solubility of I_2 and rather low stability of I_3^- in water. Therefore, NaI of 0.04 mol/L and I_2 of 0.01 mol/L were dissolved in water. Anhydrous sodium sulfate was used to keep the solutions dry except for the aqueous solution.

Iodine K-edge X-ray absorption spectra were obtained in transmission mode at room temperature at BL01B1 beamline of SPring-8 of Japan Synchrotron Radiation Research Institute at Hyogo, Japan. A silicon double crystal monochromator was used in Si(311) diffraction mode. For the higher harmonics rejection a Rh-coted quartz mirror was used. Solution samples were filled in glass cells whose path length was 5 – 20 cm according to the background absorption of solvent (and the total iodine concentration for aqueous solution). I_2 and TPAI$_3$ powders were also measured as reference standards. The spectrum for TPAI$_3$ was also measured at 10 K.

EXAFS analyses were performed by Xanadu software (Sakane *et al.*, 1993). Theoretical phase shifts and scattering amplitude for TPAI$_3$ structure reported by Tebbe & Gilles (1996) were calculated with FEFF 6.01a (Zabinsky *et al.*, 1993). Fourier transforms were performed with *k*-range of 3.6 – 15.4 Å^{-1} unless otherwise noted. To reduce ripples, Hamming window function was used for truncation of the *k*-range. To avoid false peaks creation, phase shifts and backscattering amplitude were corrected as the I–I nearest neighbor during the transformations. Curve fitting calculated with *k*-range of 3.75 – 13.95 Å^{-1}. A one-shell model was used except the aqueous solution for which a two-shell model including solvated I$^-$ and I$_3^-$ was adopted. Every solution samples were measured twice and analyzed separately. The errors on the results are estimated from the difference of the two results and are within 0.004 Å for the I–I distance and 0.003 Å for its Debye-Waller factor except for dimethylsulfoxide and aqueous solutions. The differences in the distance were 0.014 Å and 0.007 Å and those in the Debye-Waller factor were 0.005 Å and 0.0001 Å for dimethylsulfoxide and aqueous solutions, respectively,

3. Results and discussion

EXAFS Fourier transforms for some solution samples are shown in Fig. 1. They are low signal to noise ratio and only one peak appears at almost identical position among them. The peak height changes with solvents. It is clear from Raman spectra for some solution that I$_3^-$ in these solutions take symmetrical linear form. Therefore, a second peak should be enhanced by multiple scattering effect and is expected to appear around 5.8 Å. In Fig. 1, the second peak is, though, hardly observed. There may be two
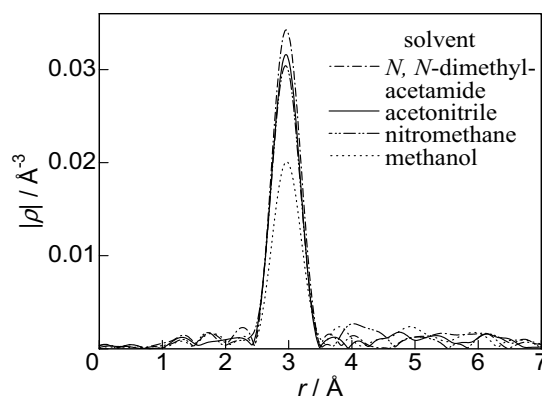

Figure 1
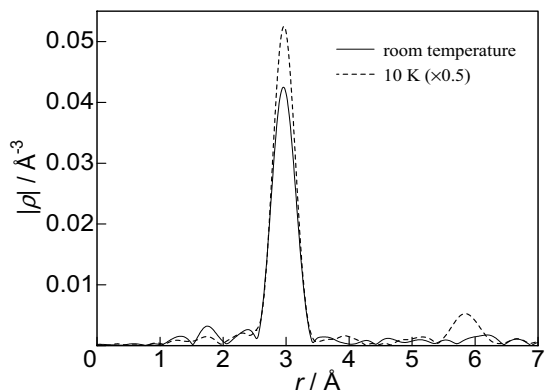Iodine K-edge EXAFS Fourier transforms for I$_3^-$ solutions of some organic solvents.

Figure 2
Iodine K-edge EXAFS Fourier transforms for $(n\text{-}C_3H_7)_4NI_3$ powder.

reasons why the second peak cannot be observed. One is the insufficient energy resolution of absorption spectra at such a high energy region, and the other is the large thermal vibration within the molecular ion. In the spectrum for the aqueous solution, there appears a fine structure just above the edge that is assigned as hydrated I^- XANES structure. From this fine structure the energy resolution including that of both the monochromator and from the shortness of the core hole lifetime is less than about 5 eV. On the other hand, the signal component of 5.8 Å in the Fourier transform corresponds to the shortest cycle of 7 eV in energy space. Therefore, the spectral resolution is high enough for detecting a component with such a distance at the iodine K-edge region. To reduce thermal vibrations within I_3^-, $TPAI_3$ powder was cooled until about 10 K and its XAFS was analyzed. Figure 2 shows EXAFS Fourier transforms with k-range of $2.7 - 17.5$ Å^{-1} for $TPAI_3$ at room temperature and at about 10 K. At room temperature the second peak does not appear, too, while at 10 K, it appear clearly. It is resulting that the disappearance of the second peak in the solution samples does not result from spectral resolution but from large thermal vibration of I_3^-. Provided that much lower noise spectra are observed for solution samples, then the second peak appears in Fourier transform. A summarized compound spectrum was made up from 12 independent spectra of several solution samples that have little difference in those EXAFS $\chi(k)$ and then transformed as shown in Fig. 3. In Fig. 3 noise level is decreased and a small second peak appears. In the previous papers for polyiodine
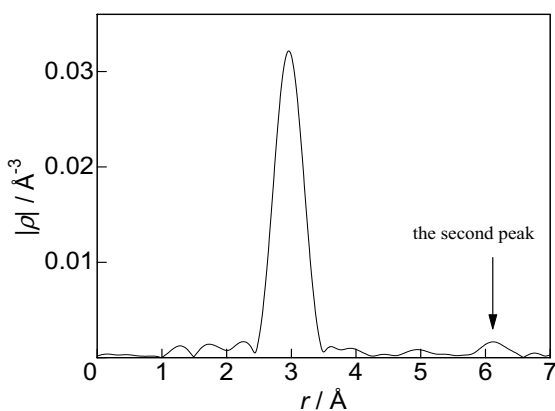

Figure 3
Iodine K-edge EXAFS Fourier transform for the compound spectrum made up from 12 independent spectra for organic solvent solutions.
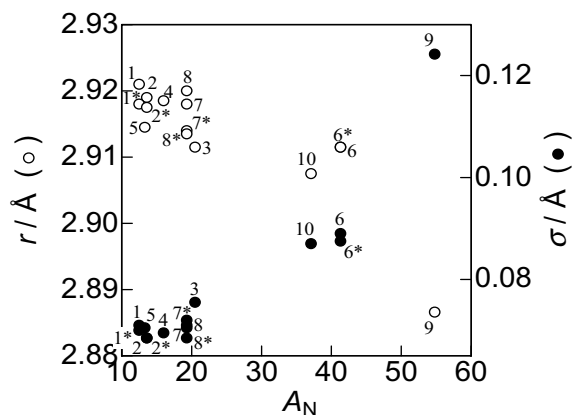

Figure 4
Plots of the nearest I–I distance r and the Debye-Waller factor σ as a function of the Mayers' acceptor number A_N of the solvents. Solvents are acetone (**1**), N, N-dimethylacetamide (**2**), nitromethane (**3**), N, N-dimethylformamide (**4**), tetrahydrothiophen-1, 1-dioxide (**5**), methanol (**6**), acetonitrile (**7**), dimethylsulfoxide (**8**), water(**9**) and ethanol(**10**). Counter cations are Na$^+$ unless otherwise noted as, e.g., **1***, for which tetra-n-propylammonium salt were used.

species of Yokoyama *et al.* (1995) and Coppens *et al.* (1986), the multiple scattering peak can be hardly observed in XAFS. In this study the second peak can be observed because of the high quality of the spectra and the proper analysis treatments.

Except the aqueous and the methanol solutions, the I–I distance and the Debye-Waller factor for solution samples showed no dependence on the formation constant. There are few differences between two counter cations indicating no ion-pair formation or no effect on the triiodide structure with ion-pair formation. The formation constants were related to solvent parameters by Bienvenue, Msika & Dubois (1980), i.e., Gutmann's donor number (Gutmann, 1967), Kamlet-Taft's basicity parameter β (Taft & Kamlet, 1980), and Mayers' acceptor number (Mayer, Gutmann & Gerger, 1975). The acceptor number is also known to have relations to the degree of solvation of anions (Tanida, Sakane & Watanabe, 1994, Tanida, 2000). Figure 4 plots the distances and the Debye-Waller factors as a function of the acceptor number. In aqueous and alcohol solutions, the structural parameters indicate correlation of decrease of the distance and increase of the Debye-Waller factor with increasing the acceptor number. Other solvents have small acceptor number and no relations to these structural parameters among them. The group of these solvents also lies on the correlation with water and alcohols.

Figure 5 indicates the structural parameters as a function of the donor number. One may find there is no relation in Fig. 5. Nevertheless, ignoring all the protic solvents, water and alcohol solutions, in Fig.5 leads a small but clear linear correlation between the Debye-Waller factors and the donor numbers. The Debye-Waller factors for aprotic solvent solutions are plotted again in Fig.6 as functions of the donor number and the Kamlet-Taft basicity parameter β. Figure 6 shows both of the functions are quite similar and declining line with the solvent parameters. Adopting the relations indicated in Figs. 4 and 6 for the protic and the aprotic solvents only, respectively, they can be unified as the more the electron of I_3^- is withdrawn by solvent molecules and the lower the electron density on the anion, the
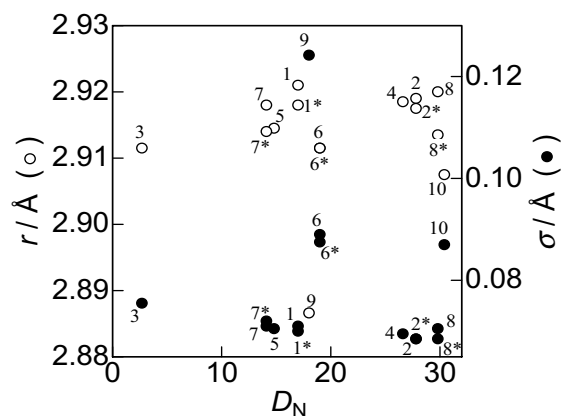
Figure 5

Plots of the nearest I–I distance r and the Debye-Waller factor σ as a function of the Gutmann's donor number D_N of the solvents. Specification of each plots are the same as Fig. 4.

larger its Debye-Waller factor becomes and then the weaker the bond in the anion is. According to the pictures of simple molecular orbital interpretations (Mizuno, Tanaka & Harada, 1981, Kertész & Vonderviszt, 1982), HOMO of triiodide ion has antibonding character. Nevertheless, from this study HOMO should have bonding character. A problem of this unified interpretation is the limited application scope of the each solvent parameters. The classification in which a solvent is protic or aprotic has been found for Br⁻ and I⁻ solvation studies by XAFS (Tanida, Sakane & Watanabe, 1994, Tanida, 2000). It may reflect a feature of anion-solvent interactions. In Figs. 4 and 5, the I–I distances become smaller when its Debye-Waller factors become larger. It is a phenomenon that cannot be understood by common knowledge. For the aqueous solution, the Debye-Waller factor is so large that solution the thermal vibration of I_3^- would not be approximated with the Debye-Waller factor alone. Higher order cumulants should be considered in the aqueous solution. It is concluded that the other solutions that the solvent effects affect the I–I bond strength in the triiodide ion in a complex manner.
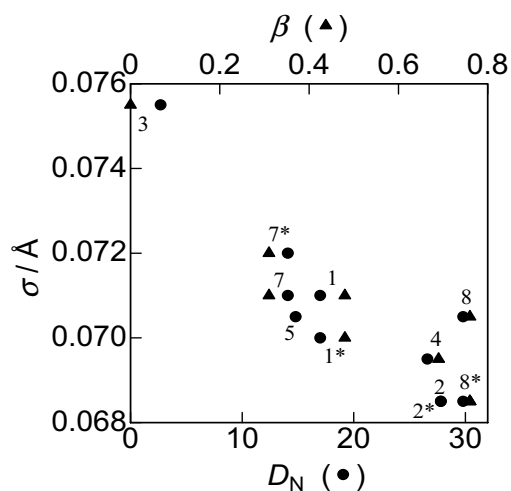
X-Ray absorption spectra measurements were performed under the approval of the JASRI (Proposal No. 1999B0208-NX -np).

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Figure 6

Plots of the nearest I–I distance r and the Debye-Waller factor σ as a function of the Gutmann's donor number D_N or the Kamlet-Taft's basicity parameter β of the aprotic solvents. Specification of each plots are the same as Fig. 4.