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Dependence of EXAFS (Extended X-Ray Absorption Fine Structure) Parameters of Iodide Anions in Various Solvents upon a Solvent Parameter

Hajime Tanida* **and Iwao Watanabe**[†]

Experimental Facilities Division, Japan Synchrotron Radiation Research Institute, Sayo, Hyogo 679-5198

†Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043

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X-ray absorption spectra of I *K*-edge have been obtained for iodide ions dissolved in various solvents. Oscillation amplitudes of the extended X-ray absorption fine structure (EXAFS) evaluated from the peak intensities in the Fourier-transform spectra were found to correlate with the Mayer–Gutmann acceptor number (A_N) of solvents studied. The correlation is quite similar to that for bromide ions, which has already been reported by the same authors (H. Tanida, H. Sakane, and I. Watanabe, *J. Chem. Soc., Dalton Trans.*, **1994**, 2321). Such results confirm that the EXAFS method is not only a tool to determine geometrical structures in liquids, but can also be used for evaluating solute–solvent interaction strength, similarly to A_N. The I···O distances in protic solvents and I···C in aprotic solvents were determined to be 3.4—3.5 and 3.7—3.8 Å, respectively. In protic solvents, the larger the A_N values, the shorter the I···O distances and the larger the co-ordination numbers of I^-, which were determined to be 1—4. In aprotic solvents, the co-ordination numbers of I^- were found to be 4—8. It seems that aprotic solvents having two methyl groups in a molecule are able to solvate I^- through two methyl groups, which is similar to the conclusion reported for Br^-.

Although chemists have studied the solvation structures of halide anions and suggested several solvation models for them,[1—3] their solvation structures are not well understood because of their weak anion–solvent interactions. The situation is reflected in the variety of their hydration numbers, reported to be from zero to eight or nine depending upon the methods to determine them.[4] The hydration radii have been reported to be from 3.55 to 3.70 Å for iodide ion by X-ray diffraction method.[4] The diffraction method requires high concentrations and the variety of values reported seem to depend on the way of handling experimental results.

Extended X-ray Absorption Fine Structure (EXAFS) has become an important technique for investigating the local structure in solution.[5] It is expected to provide the average co-ordination distance *r* and the average co-ordination number *N* for a given element in solution. Our previous study on Br^- by EXAFS method concluded that the method is suitable for determining local structure of the anion dissolved at relatively low concentration not only in water but also in many organic solvents.[6]

The new synchrotron radiation facility, SPring-8, provides us with high energy X-rays useful for studying I^- in various solvents by measuring the *K*-edge absorption. Its high energy allows us to ignore the absorption by the solvent. This paper reports a study on EXAFS of I^- in the same solvents as those studied for Br^-.[6] Twelve protic solvents containing OH or NH groups can dissolve ionic species easily because they can participate in hydrogen-bonding anion-solvent and solvent–solvent interactions. Eleven aprotic solvents can also dissolve ionic species with the interaction dominated by electrostatic terms such as the ion-dipole and ion-induced dipole interactions.

We have found a quite interesting dependence of the EXAFS oscillation amplitude for Br^- in various solvents upon an empirical solvent parameter, the Mayer–Gutmann acceptor number A_N.[7] This A_N value is widely used as an indicator of electron-acceptor nature of solvent or the strength of anion-solvent interaction. In the present study we have found a similar correlation between the EXAFS oscillation amplitude and A_N for I^-. We confirm therefore that the EXAFS method provides empirical solvent parameters, which are intimately related with the solvation structures such as co-ordination distance *r* and co-ordination number *N*.

Experimental

Iodide solutions were prepared from tetra-*n*-butylammonium and potassium salts for non-aqueous solvents and water, respectively. Salts and solvents (Table 1) were of guaranteed grade from Nacalai Tesque, Kyoto. The I *K*-edge absorption measurements were performed at BL01B1 of SPring-8 in Hyogo, Japan, running at the ring current of 70 mA and the energy of 8 GeV.[8] Transmission spectra were obtained with the use of a Si (311) double crystal monochromator, two Rh-coated mirrors at the grazing incidence angle of 1.5 mrad which removed the higher harmonics, and two gas ionization chambers. The I_0 chamber was 17 cm long filled with Ar and the *I* chamber was 31 cm filled with Kr. X-ray transmission spectra at 0.1 mol dm^{-3} concentration were obtained by using a 2 cm cell with polyethylene or poly(tetrafluoroethylene) film windows at room temperature (25±3 °C). More than two scans were recorded

Table 1. EXAFS Curve-Fitting Results

	Solvent	Scattering atom	r/Å	N	σ/Å	$-\Delta E_0$/eV	R
1	1,1,1,3,3,3-Hexafluoropropan-2-ol	O	3.40	4.1	0.110	2.7	0.12
2	Water	O	3.50	6[a]	0.141	2.8	0.10
3	2,2,2-Trifluoroethanol	O	3.42	3.8	0.113	2.5	0.10
4	Acetic acid[b]						
	first shell	O	3.45	1.1	0.063	−2.3	0.08
	second shell	C	4.81	0.5	0.087		
5	Ethylene glycol	O	3.46	2.6	0.106	2.2	0.13
6	Methanol	O	3.48	2.8	0.110	1.6	0.19
7	Formamide	N	3.64	3.0	0.116	2.4	0.16
8	Ethanol	O	3.47	2.4	0.104	2.3	0.14
9	Isopropyl alcohol	O	3.51	1.5	0.091	1.6	0.19
10	Propanol	O	3.47	2.2	0.103	2.2	0.12
11	Butyl alcohol	O	3.49	1.9	0.099	1.1	0.16
12	*tert*- Butyl alcohol[c]						
	first shell	O	3.58	1.2	0.090	1.8	0.30
	second shell	C	4.77	3.5	0.251		
13	Nitromethane	C	3.72	4.7	0.162	7.0	0.20
14	Acetonitrile	C	3.74	4.5	0.159	8.2	0.20
15	Dimethyl sulfoxide	C	3.73	6.3	0.176	10.2	0.20
16	Propylene carbonate	C	3.72	4.6	0.156	7.9	0.18
17	Dimethylformamide	C	3.77	8.7	0.217	9.6	0.40
18	Nitrobenzene	C	3.75	4.7	0.154	6.9	0.20
19	Pyridine	C	3.79	4.5	0.143	6.8	0.20
20	Dimethylacetamide	C	3.74	6.6	0.193	10.0	0.21
21	*N*-Methylpyrrolidin-2-one	C	3.71	5.1	0.163	9.8	0.19
22	Acetone	C	3.71	6.5	0.188	10.3	0.19
23	Ethyl methyl ketone	C	3.76	5.8	0.178	8.3	0.20

a) The I^- in water is used as a reference and its N value is assumed to be six. b) The results of a two-shell model is a tentative one. The N value ratio for O to C is fixed at 2:1. Refining the analysis is in progress. c) The results of a two-shell model is a tentative one. The N value ratio for O to C is fixed at 1:3. Refining the analysis is in progress.

for each sample and no differences among them were observed. The energy was calibrated using copper foil, and the reproducibility of the monochromator around the I K-edge region was confirmed by obtaining the spectrum of 0.1 mol dm^{-3} NaI aqueous solution once a day during the measurements.

Data Analysis

The analysis procedure has been reported in detail.[6,9,10] Figure 1 shows some of the X-ray absorption spectra for iodide solutions. Their EXAFS oscillation spectra are given in Fig. 2. The normalized EXAFS interference function $\chi(k)$ in k space is defined as in Eqs. 1 and 2 where k is the photoelectron wave vector, m the electron mass, E the incident X-ray energy, E_0 the threshold energy which is tentatively determined to be the midpoint of the edge jump, $\mu(k)$ the total absorption coefficient, $\mu_0(k)$ the absorption due only to the K-shell excitation of a hypothetical isolated I atom and $\mu_b(k)$ the background contribution to the whole absorption $\mu(k)$ from the other shells and the atoms in the solution.

$$\chi(k) = [\mu(k) - \mu_0(k) - \mu_b(k)]/\mu_0(k) \qquad (1)$$

$$k = [(2m/\hbar^2)(E - E_0)]^{1/2} \qquad (2)$$

As shown in Figs. 1 and 2, the EXAFS oscillations appear only in the low k region and are even weaker than those for Br^-, thus the EXAFS analysis is very difficult. The weaker EXAFS structures for I^- are reflecting the weaker I-solvent interaction and are also characteristic of higher atomic number elements.

The Fourier Transform (FT) calculations were performed over the ranges of k = 3.5—8 and 3.1—6 Å^{-1}, for protic and aprotic solvents, respectively. The FT spectra are shown in Fig. 3. The parameters of the phase shift $\psi(k)$ and the back-scattering amplitude $F(k)$ are generated by FEFF version 6.01[11] for r = 3.45 and 3.6 Å for protic and aprotic solvents, respectively. The scattering atoms are O (or N for formamide) and C in protic and aprotic solvents, respectively. Since the scattering amplitude for hydrogen is negligible, the EXAFS method detects the $I^-\cdots O$ (or N) or $I^-\cdots C$ interaction.

The EXAFS spectra $k^3\chi(k)$ were fitted with equations (3) and (4); where the subscript j indicates the co-ordination shell number.

$$k^3\chi(k) = k^3 \sum_j \frac{B_jF_j(k_j)}{k_jr_j}\exp(-2\sigma_j^2k_j^2)\sin[2k_jr_j + \psi_j(k_j)] \qquad (3)$$

$$k_j = [k^2 - (2m/\hbar^2)\Delta E_{0j}]^{1/2} \qquad (4)$$

The variable parameters in the curve-fitting calculation are r, the amplitude factor B_j ($B_j = S_jN_j$, where S is the amplitude

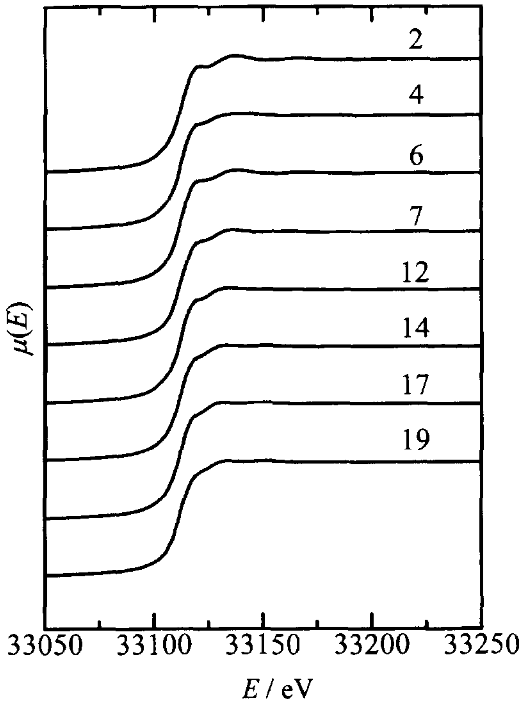


Fig. 1. The I K-edge X-ray absorption spectra of I^- in several solvents (numbered as in Table 1).

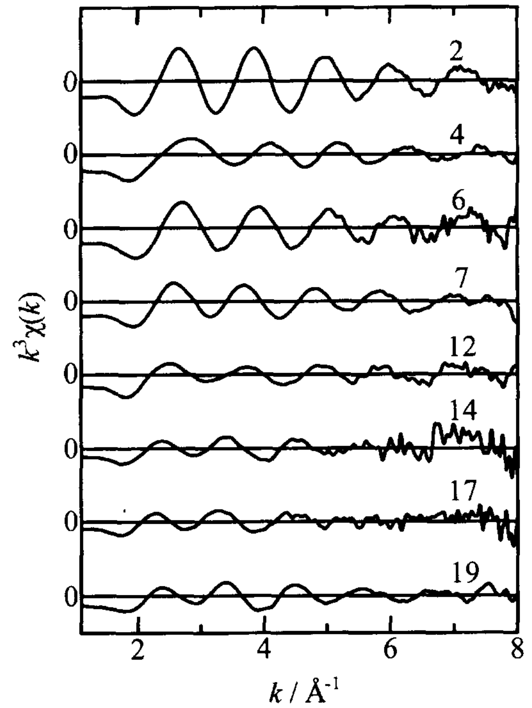


Fig. 2. The I K-edge EXAFS $k^3\chi(k)$ spectra of I^- in several solvents.

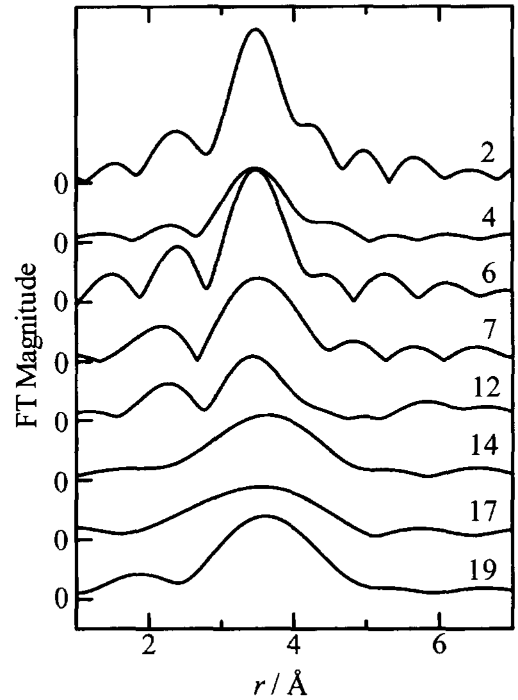


Fig. 3. The I K-edge EXAFS FT spectra of I^- in several solvents.

reduction factor), the Debye–Waller like factor σ and the absorption-edge shift ΔE_0. The S value was determined by using the spectrum for aqueous solution, for which the solvation number was assumed to be six according to a number of studies.[3]

The non-linear least-squares curve-fitting calculations were applied to the unfiltered $k^3\chi(k)$ data at k 3.5—5.8 and 3.1—5.5 Å^{-1} for protic and aprotic solvents, respectively. The spectra were fitted with a single-shell model except for those of acetic acid and *tert*-butyl alcohol, which were fitted with a two-shell model. The two shell models had also been adopted for the previous analysis for Br^-. In the model the first shell was composed of O and the second shell of C, and the ratios of the N values for the first and the second shell were assumed to be 2 : 1 for acetic acid and 1 : 3 for *tert*-butyl alcohol. The ΔE_0 values for two shells were kept equal. The results are given in Table 1.

We did not use the Fourier filtering method either for the analysis of I^- spectra or for Br^-, because the distortion caused by the method could be significant when applied to the systems exhibiting weak EXAFS oscillation such as from solvated anions. In any case, the contributions from the second or higher shells are negligible in the present samples. We have tried to include the third order coefficient term C_3 in the curve-fitting calculation. However, when the term C_3 containing the information about asymmetrical distribution and anharmonic potential of surrounding atoms was included in the fitting calculations, we could fit the spectra only with negative values for the Debye–Waller like factor σ. Then we discarded the use of the C_3 term. R values in Table 1 are the residuals of the fitting calculation. Although the R values were large due to poor spectral features in the EXAFS spectra, the analyses gave reproducible results.

Results and Discussion

EXAFS Amplitude and the Acceptor Number. The spectra for iodides in water and alcohols shown in Figs. 1 and 2 exhibit a few times stronger EXAFS oscillations than those in aprotic solvents. The main peaks in the FT spectra in Fig. 3 correspond to the I···O (or I···N) and the I···C interactions in protic and aprotic solvents, respectively. The EXAFS oscillation amplitudes are evaluated from the peak height *h* in Fourier-transformed (FT) spectra shown in Fig. 3. We previously reported in the study on Br^- that the oscillations were stronger with greater anion-solvent interactions or the acceptor number A_N of the solvent by Mayer and Gutmann. A linear correlation between *h* and A_N was found. Here again the same linear correlation between *h* and A_N is found for I^-, as shown in Fig. 4. The A_N values have been obtained by NMR spectroscopy from relative ^{31}P chemical shift values for triethylphosphine oxide (PEt_3O) dissolved in various solvents. We confirm that both *h* and A_N are subject to the same physical quantities such as *r* and *N* in similar ways. The large deviations from the linear correlation for acetic acid (**4**) and formamide (**7**) are similar to those for Br^-.

The value of *h* may be treated semi-quantitatively as a function of *N*, *r* and σ. If the FT is performed over the range from 0 to ∞ $Å^{-1}$ for *k* and if the electron mean free path λ is approximated to be independent of *k*, the *h* value is theoretically derived as follows.[12]

$$h \propto \frac{SN}{r^2\sigma}\exp\left(\frac{-2r}{\lambda}\right) \qquad (5)$$

Although the *h* values are obtained from limited *k*-range data in the present study, this may not introduce serious errors since the most significant part of the EXAFS oscillations is included for the FT calculation.

We previously reported that the *N* values for Br^- in protic solvents must be most important factor determining their A_N values and the same is true for *h*. The infrared absorption studies of Mayer et al.[13] and Robinson and Symons[14] revealed that PEt_3O has three primary solvent molecules in water and one or two in alcohols. Not only the previous study on Br^- but also the present study on I^- supports the idea. Equation 5 predicts that the variation of *r* values for I^- is too small to cause the variation of the experimental *h* values. As shown in Fig. 5, in protic solvents the larger the A_N values, the smaller the *r* values although the change is small, while for Br^- almost constant *r* values were found. Figure 6 shows the difference in *r* values between Br^- and I^-. The ionic radii r_{X^-} are 2.16 and 1.95 Å for I^- and Br^-, respectively.[15] The ordinate scale in Fig. 6 takes into account of the difference in r_{X^-}, and then the zero level corresponds to the non-specific co-ordination distance to the kind of solvent. The smaller electric charge density on the surface of I^- than that on Br^- leads to the weaker attraction of solvents to I^-. The result in Fig. 6 indicates that in protic solvents with weaker anion-solvent interaction the interactions become even weaker for I^- compared to the case of Br^-.

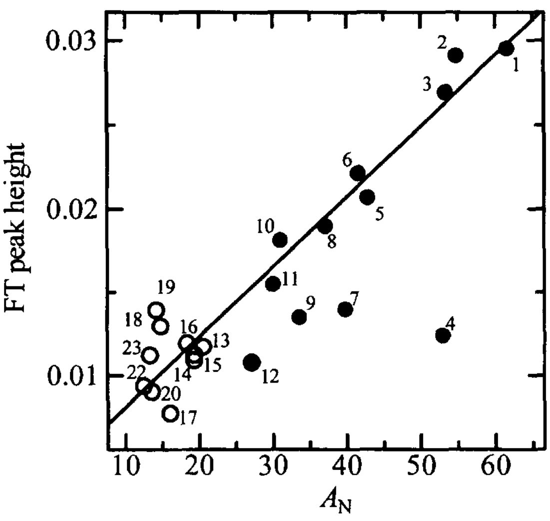


Fig. 4. Correlation of the peak height *h* of the FT spectrum for I^- with the acceptor number A_N of the solvent: (●) protic and (○) aprotic solvents.

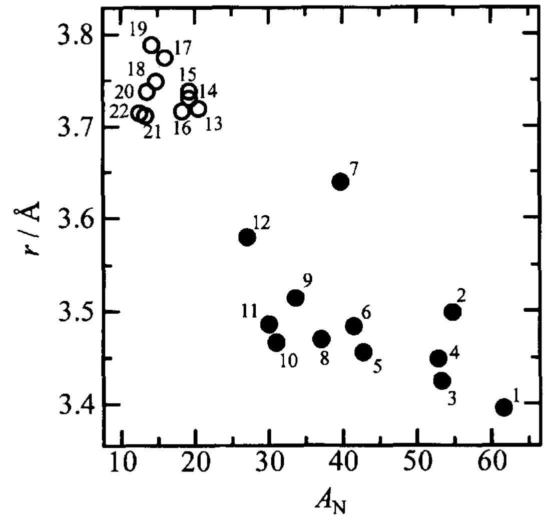


Fig. 5. Correlation of the co-ordination distance *r* for I^- with the solvent acceptor number A_N: (●) protic and (○) aprotic solvents.

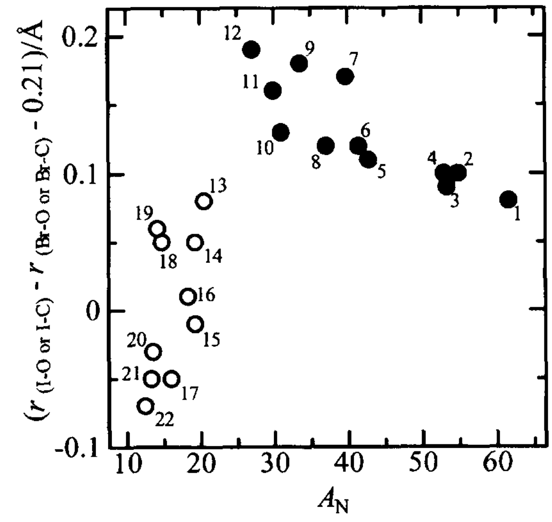


Fig. 6. The differences in the co-ordination distances $r_{(I-O or I-C)}$ and $r_{(Br-O or Br-C)}$ with respect to the difference in ionic radius, $2.16Å(r_{I^-})-1.95Å(r_{Br^-}) = 0.21$ Å, plotted against the solvent acceptor number A_N.

The Debye–Waller like factor σ can be strongly reflected in *h*. As expected, the σ values are rather large, reflecting the highly disordered solvation structures. However studies on both Br^- and I^- revealed almost no correlation or only slight increase in σ with A_N. Therefore we conclude that the *N* term in protic solvents predominates in *h*. This is supported by the correlation of the *N* value of I^- in protic solvents with the A_N value in Fig. 7. Smaller *h* values in aprotic solvents compared to the protic ones are mainly due to larger *r* and σ values.

Co-ordination Structures in Protic Solvents. Protic solvents form hydrogen bonds with I^- through $I^- \cdots H\text{–}O$ (or $I^- \cdots H\text{–}N$ for formamide) interaction. As indicated in Figs. 5 and 7, the *r* values for alcohol solutions are similar to each other or slightly decrease with A_N value, although the *N* values slightly increase with A_N value. Figure 8 shows the differences in *N* values between Br^- and I^-. The differences among protic solvents are almost constant (except for acetic acid). This implies similar mechanisms working on the solvation of Br^- and I^-. It was our experience that the EXAFS spectrum of Br^- in acetic acid was complicated and not able to be fitted with a single-shell model. The EXAFS for I^- is again found to be difficult to be analyzed with a simple model. The EXAFS oscillation for acetic acid solution (**4**) is exceptionally weak compared to other protic solvents, e.g. water (**2**) or methanol (**6**), as shown in Fig. 2. The EXAFS analyses with a two-shell model or even larger-shell-models were not successful. Therefore, the tentative results obtained with a two-shell model given in Table 1 and Scheme 1, and the points in figures for acetic acid solution should be considered as being tentative at present and need to be refined in future.

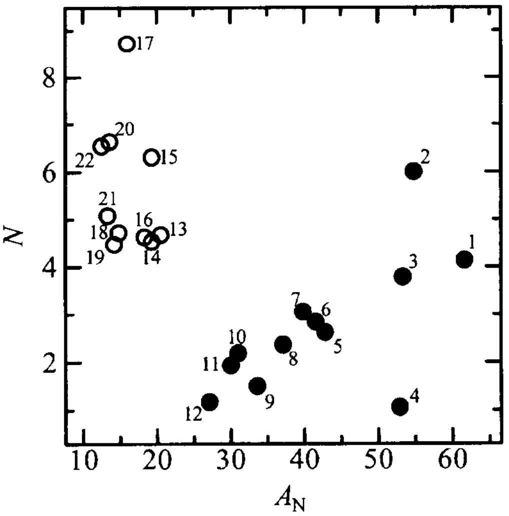


Fig. 7. Correlation of the co-ordination number *N* for I^- with the solvent acceptor number A_N: (●) protic and (○) aprotic solvents.

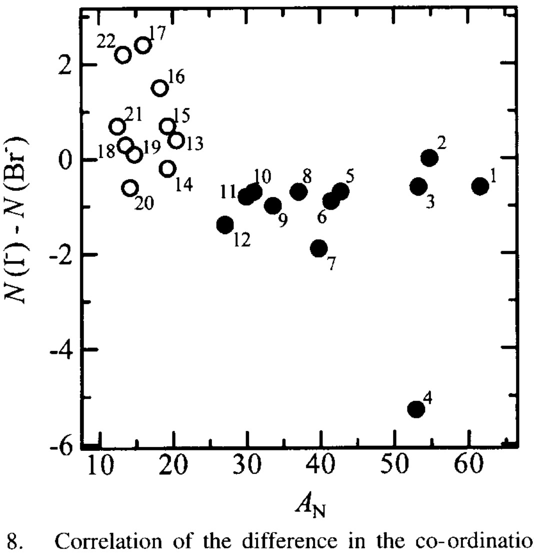


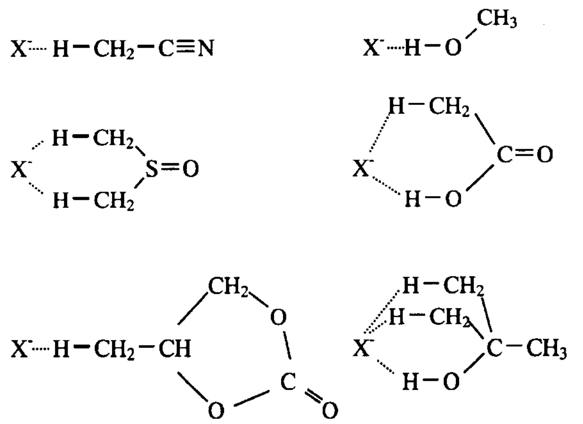
Fig. 8. Correlation of the difference in the co-ordination number *N* between I^- and Br^- with the solvent acceptor number A_N: (●) protic and (○) aprotic solvents.

The larger *r* values for water and formamide are a consequence of their strong structure-making character in the bulk. The strong hydrogen-bond network between solvent molecules in the first and second solvation shells pulls the first-shell solvent molecules out from I^-, leading to larger *r* values. The similar results were also observed in the previous study on Br^-.

The EXAFS χ spectra for I^- in not only acetic acid but also *tert*-butyl alcohol (**12**) need be fitted with a two-shell model, was the case for Br^-. Their EXAFS spectra do not look simple as shown in Fig. 2. We suggested in the previous study on Br^- that not only the OH group of their solvent molecules but also the methyl group, which is positively charged, directly co-ordinate to anion X^-, as illustrated in Scheme 1; thus the first shell is comprised of O and the second shell of C atoms from OH and CH_3, respectively.

The model of the solvation structure for I^- in *tert*-butyl alcohol gave us the tentative results after the curve-fitting calculation, in a similar way to the Br^- case; thus the first shell is expected to be comprised of O and the second shell of three C atoms from $(CH_3)_2C$. However this should be refined in future.

Co-ordination Structures in Aprotic Solvents. Anions in aprotic solvents must be stabilized through the ion-dipole interaction. The *r* and σ values are larger than those for protic



Scheme 1. The solvation structures proposed for halide anion X^- in several solvents. Those for I^- in acetic acid and *tert*-butyl alcohol are tentative and should be refined in future.

solvents. These are reasonable consequences of the solvation being weaker than that of hydrogen bonding. As shown in Fig. 6, the average difference in r values between Br^- and I^- in aprotic solvents is around 0.21 Å, the difference in their ionic radii.

We found a quite interesting result, that the solvents having the largest N values can provide two methyl groups for the Br-solvent interaction. This model again explains the large N values for I^- in dimethylformamide (**17**), approximately twice as large as those in other solvents. Nitromethane (**13**), acetonitrile (**14**), propylene carbonate (**16**), nitrobenzene (**18**), and *N*-methylpyrrolidin-2-one (**21**) may provide one carbon atom per molecule for the anion-solvent interaction. Dimethyl sulfoxide (**15**), dimethylacetamide (**20**), and acetone (**22**) and ethyl methyl ketone (**23**) can be classified as the intermediate solvents. The negative values in Fig. 6 for dimethylformamide (**17**), acetone (**22**), and *N*-methylpyrrolidin-2-one (**21**) seem to be due to their bulky size which sterically prevents closer access to smaller ion Br^- than to larger ion I^-.

The shapes and sizes of acetonitrile (**14**) and nitromethane (**13**) seem to allow them to access to anions closely, leading to larger N and smaller r values than those for nitrobenzene (**18**) and pyridine (**19**). However, as indicated in values of N and r and also in comparison of Br^- and I^- data, the four solvents, (**13**), (**14**), (**18**), and (**19**), behave quite similarity concerning the solvation. Both Br^- and I^- may be solvated by contacting to the aromatic molecules at the edges of the planer ring.

It is important to know whether the EXAFS method is capable to differentiate the co-ordinating atom S from C(in methyl groups). Our fitting calculations on the spectra for I^- in dimethyl sulfoxide using the $\psi(k)$ and $F(k)$ parameters for S atom did not lead to acceptable N, ΔE_0, or σ values, but the use of the parameters for C did; thus it is concluded that the co-ordinating atom to I^- in dimethyl sulfoxide is carbon.

Conclusion

In the present study, EXAFS spectroscopy proved to be a powerful tool for determining the local structures of iodide ions in various solvents at relatively low concentrations, even though the I *K*-edge EXAFS oscillation amplitudes are small due to the weak I-solvent interaction and to the short life time of excited states inherent to high atomic number elements. The r and N values for I^- are compared with those for Br^-. They could be discussed in relation to the microscopic shapes and sizes of solute and solvent molecules. The almost linear correlations of A_N of solvent with the EXAFS oscillation amplitude h found for both Br^- and I^- indicate that the EXAFS data for anions can be well interpreted in terms of another solvent parameter similar to A_N. The values of empirical parameters for solvation structure such as r, N, and σ obtained from the EXAFS method are also found to be intimately related with the solute–solvent interactions.

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