Solvation Structures for Bromide Ion in Various Solvents by Extended X-Ray Absorption Fine Structure†

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The Br K-edge X-ray absorption spectra have been obtained for bromide ion dissolved in various protic and aprotic solvents. The Br···O distances in protic solvents which are fixed by the hydrogen-bond interaction and Br···C in aprotic solvents by the ion–dipole interaction were determined to be 3.1–3.2 and 3.5–3.6 Å, respectively. The co-ordination numbers of Br^- were found to be widely different, 3–6, from solvent to solvent. In protic solvents the solvation number correlates with the Mayer–Gutmann acceptor number, A_N. Aprotic solvents can be divided into two groups in terms of the solvation structures. The solvation numbers in dimethylformamide, dimethylacetamide, dimethyl sulfoxide, acetone and ethyl methyl ketone are larger than those in other aprotic solvents possibly because of their bonding to Br^- through two methyl groups. The amplitude of the extended X-ray absorption fine structure (EXAFS) oscillation evaluated from the peak intensity in the Fourier-transform spectrum correlates with A_N throughout the series of solvents studied. This correlation is attributed to the similarity between the mechanism determining the amplitude of EXAFS and that of A_N.

The solvation structure of halide anions has been studied by many chemists, and many solvation models have been suggested.[1,2] The most accepted model is a dynamic one. Solvent molecules around the anion are in ceaseless motion. The solvent-exchange rate of the first solvation shell of the halide anion is extremely fast and the anion–solvent interaction is weak. It is, therefore, difficult to determine the solvation structure by any method, though the solvation of halide anions is important in many aspects of chemistry.

The definitive structural studies of aqueous bromide solution by using X-ray diffraction (XRD) or neutron diffraction (ND) have been reviewed.[1,3] The measurements require high concentrations, and the variety of values reported for the co-ordination distance and co-ordination number seem to depend on the technique and the handling of the experimental results. Hydration distances range between 3.12 and 3.43 Å according to XRD;[4] *cf.* also 3.21 Å from ND[5] and 3.43 Å from IR spectroscopy.[6] Some hydration numbers reported are 6[4b,5] and 8–9.4[4c,d] from XRD and 6 from ND.[5] According to NMR or other techniques the hydration number has been reported to be approximately zero because the solvent-exchange rate is too high.[7]

It is difficult to apply the above-mentioned techniques to non-aqueous solvents because of the even weaker anion–solvent interactions than those in water. A variety of co-ordination distances were determined by using NMR spectroscopy[8] and electric conductivity,[9] while the solvation number was evaluated by using thermodynamics.[7,10] Cluster ions in the gas phase have been studied by pulsed high-pressure mass spectrometry,[11] pulsed electron-beam mass spectrometry[12] and gas-phase photoelectron spectroscopy (gas-PES).[13] Some non-aqueous solvents were employed, although it is doubtful whether the model clusters used for the analyses are compatible with the solvation structures in bulk solutions.

Many computer-simulation calculations have also been performed to reveal the solvation structure of halides using the *ab initio* molecular orbital (MO) method,[14] or cluster calculation by Monte Carlo simulation[15] or molecular dynamics.[16] The solvation structure of Br^- has been theoretically calculated,[17] and some of the calculations predicted well the results of gas-PES,[18] XRD[19] or the charge-transfer-to-solvent method.[20] Besides the hydration of halides, a variety of anions[14b] and solvation in non-aqueous solvents[14c] have also been considered. However, it is more difficult to treat the weaker interactions. It has also been believed that halide anions form loose solvation shells and that in equilibrium they have a variety of co-ordination distances and co-ordination numbers.[15a]

Extended X-ray absorption fine structure (EXAFS) has become an important technique for investigating the local structure in solution.[21] It is expected to provide the average co-ordination distance r and the average co-ordination number N for a given element in solution. Synchrotron radiation enables us to study Br most easily among halides by measuring the K-edge absorption and a few studies on Br^- in solution have been reported.[22] However, most studies focused on the interaction between cations and Br^- in water,[21] and there have been no reports involving non-aqueous solvents. Furthermore, the results are somewhat different possibly depending on the counter ion and bromide concentration used (frequently high). This paper reports a study on the EXAFS of Br^- at relatively low concentration in not only water but also in many organic solvents.

Polar solvents containing OH or NH groups, called protic solvents, which dissolve ionic species easily, can participate in hydrogen-bond anion–solvent and solvent–solvent interactions. The ionic species can also be dissolved in polar solvents called aprotic solvents, in which the interactions are dominated by electrostatic terms, *i.e.* the ion–dipole and ion–induced dipole interactions. In this paper the values of r, N and the other parameters concerning the solvation of Br^- in 12 protic and 11 aprotic solvents are reported. We have found a quite interesting dependence of the EXAFS amplitude upon an empirical solvent parameter, the Mayer–Gutmann acceptor number, A_N.[23] This is widely used as an indicator of electron-acceptor nature of the solvent and of the strength of anion solvation. We believe that the EXAFS method provides some empirical solvent parameters which are intimately related with the solvation structure.

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† *Non-SI unit employed:* eV ≈ 1.60×10^{-19} J.

Table 1 EXAFS curve-fitting results and the Mayer–Gutmann acceptor number A_N

Solvent	Scattering atom	r/Å	N	σ/Å	$-\Delta E_0$/eV	A_N
1 1,1,1,3,3,3-Hexafluoropropan-2-ol	O	3.11	4.7	0.106	7.6	61.6
2 Water	O	3.19	6[a]	0.126	8.0	54.8
3 2,2,2-Trifluoroethanol	O	3.12	4.4	0.099	7.7	53.3
4 Acetic acid[b]						
first shell	O	3.14	6.4	0.186	6.5	52.9
second shell	C	3.79	3.2	0.027		
5 Ethylene glycol	O	3.14	3.3	0.079	8.3	42.8
6 Methanol	O	3.15	3.7	0.089	7.8	41.5
7 Formamide	N	3.26	4.9	0.136	9.3	39.8
8 Ethanol	O	3.14	3.1	0.076	8.6	37.1
9 Isopropyl alcohol	O	3.12	2.5	0.075	10.3	33.6
10 Propanol	O	3.13	2.9	0.069	8.7	31.0
11 Butyl alcohol	O	3.12	2.7	0.063	8.8	30.0
12 *tert*-Butyl alcohol[c]						
first shell	O	3.18	2.6	0.097	8.0	27.1
second shell	C	3.66	7.8	0.248		
13 Nitromethane	C	3.43	4.3	0.154	9.8	20.5
14 Acetonitrile	C	3.48	4.7	0.162	9.1	19.3
15 Dimethyl sulfoxide	C	3.53	5.6	0.177	8.9	19.3
16 Propylene carbonate	C	3.50	3.1	0.124	8.1	18.3
17 Dimethylformamide	C	3.61	6.3	0.192	8.1	16.0
18 Nitrobenzene	C	3.49	4.6	0.161	8.9	14.8
19 Pyridine	C	3.52	5.1	0.172	8.7	14.2
20 Dimethylacetamide	C	3.56	6.3	0.198	9.1	13.6
21 *N*-Methylpyrrolidin-2-one	C	3.55	2.9	0.161	8.4	13.3
22 Acetone	C	3.57	5.8	0.203	8.1	12.5
23 Ethyl methyl ketone	C	3.56	5.4	0.184	8.2	

[a] The Br^- in water is used as a reference for the solutions of protic solvents and its N value is assumed to be six. [b] The result of a two-shell model. The N value ratio for O to C is fixed at 2:1. [c] The result of a two-shell model. The N value ratio for O to C is fixed at 1:3.

Experimental

Chemicals.—Bromide solutions were prepared from the tetra-*n*-butylammonium salt (ion-pair chromatography grade, Nacalai Tesque, Kyoto). The solvents (Table 1) were also from Nacalai Tesque and purified before use according to the standard procedures.[24] Their water contents were determined to be less than 40 mmol dm^{-3} by Karl–Fisher titration at Osaka University a few days after the EXAFS measurements at Tsukuba.

Measurements.—The Br K-edge absorption measurements were performed at BL-6B and 10B of the Photon Factory of the National Laboratory for High Energy Physics in Tsukuba. X-Ray transmission spectra at 0.1 mol dm^{-3} were obtained by using a 1 cm cell with polyethylene or polytetrafluoroethylene windows at room temperature (25 ± 3 °C). A 5 mm cell was used for dimethyl sulfoxide solution because of its large background absorption.

The concentration dependence of the spectra was checked by measuring at different concentrations. All of the solutions were also measured at 0.05 as well as 0.1 mol dm^{-3}, though the results were the same. In the presence of a few mol dm^{-3} tetra-*n*-butylammonium bromide the spectra of aqueous solutions displayed slight differences from those at lower concentrations. Since ion-pair formation is known in some solvents,[25] additional measurements were performed. A 2 mol dm^{-3} methanol solution (1 mm path) gave a similar spectrum to that for a 0.1 mol dm^{-3} solution, and the same was true for nitrobenzene solution of 5 mmol dm^{-3} (20 mm path), although it has been reported that ion-pair formation must be considerable in 2 mol dm^{-3} methanol solution[25a] and in 0.1 mol dm^{-3} nitrobenzene solution[25b], while it may be negligible in 0.1 mol dm^{-3} methanol and 5 mmol dm^{-3} nitrobenzene solutions. Therefore, as far as the tetra-*n*-butylammonium bromide solution is concerned, the EXAFS of Br^- is not sensitive to ion-pair formation.

Data Analyses

Subtracting the Background.—In this study we found that the spectra of Br^- in solution display strong multielectron excitation structure (MEES) in the EXAFS energy region.[26] Thus the MEES had to be removed in advance. The procedures have been reported in detail[27] and only the essential part is given here.

The normalized EXAFS interference function $\chi(k)$ in k space is defined as in equations (1) and (2) where k is the photoelectron

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

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

wave vector, m the electron mass, E is 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 Br atom and $\mu_b(k)$ is the background contribution to the whole absorption $\mu(k)$ from the other shells and atoms in the solution. The term $\mu_b(E)$ was calculated by least-squares fitting using the formula $aE^{-3} - bE^{-4} - c$, which comprises of Victoreen's formula and a constant term c. The parameters a, b and c were determined by using not only the pre-edge region but also the highest-energy region, so that the fitting of $\alpha E^{-3} - \beta E^{-4}$ to $\mu(E) - \mu_b(E)$ gave the same β/α value as reported.[28]

The final $\mu_0(k)$ containing the MEES was determined by the following method.[27] First, a temporary $\mu_0(k)$ [denoted as $\mu_t(k)$ here] and then a temporary $\chi_t(k)$ were calculated as usual. The dotted line in Fig. 1 is $\chi_t(k)$ showing the EXAFS and the MEES. Next, smoothing calculations were applied to $k^3\chi_t(k)$ until all the higher-frequency components (EXAFS due to further scattering and noise) disappeared, although the EXAFS due to the nearest neighbour clearly remained. Then, two cubic spline

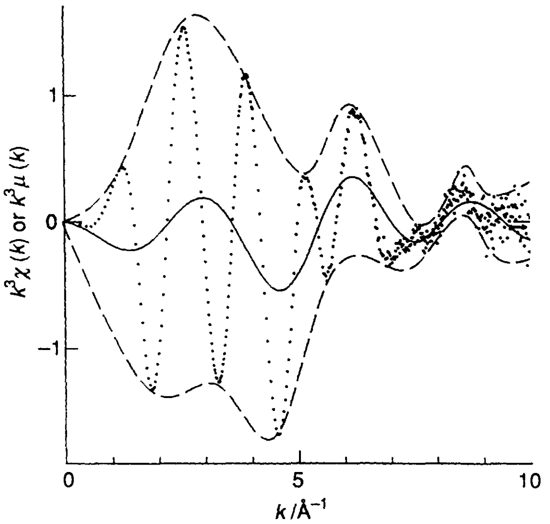


Fig. 1 The tentative Br K-edge EXAFS spectrum $k^3\chi_t(k)$ for Br^- aqueous solution (dotted line). The $k^3\mu_0$ spectrum (solid line) is the average of two spline curves (broken lines) connecting the maxima and minima of a spectrum obtained by smoothing the $k^3\chi_t(k)$ spectrum

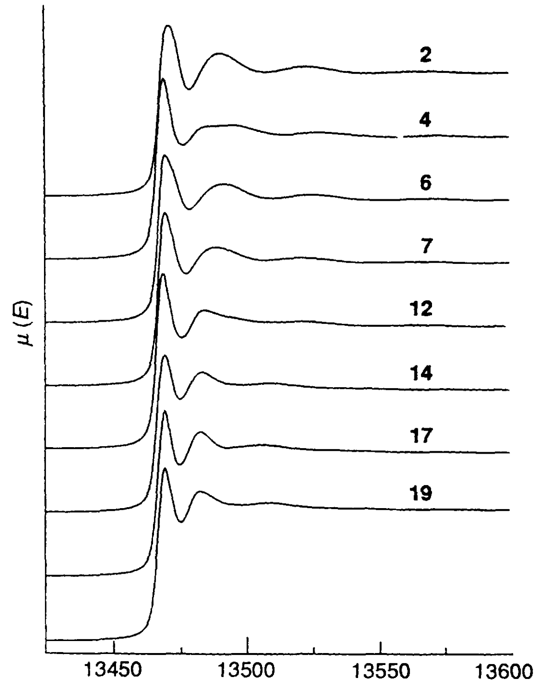


Fig. 2 The Br K-edge X-ray absorption spectra of Br^- in several solvents (numbered as in Table 1)

interpolation curves, $\mu_{max}(k)$ connecting the maxima and $\mu_{min}(k)$ connecting the minima, of the smoothed $k^3\chi_t(k)$ are calculated as shown in Fig. 1 (broken lines). The final $\mu_0(k)$ was obtained from equation (3) and is represented in Fig. 1 by the solid line.

$$\mu_0(k) = \mu_t(k) + \tfrac{1}{2}[\mu_{max}(k) + \mu_{min}(k)] \qquad (3)$$

The MEES onset energies correspond to the minima at 1.5, 4.5 and 7.8 Å^{-1} appearing in $\mu_0(k)$. The details of the MEES have been discussed elsewhere.[26]

Fig. 2 shows typical examples of the X-ray absorption spectra for bromide solutions. The use of $\mu_0(k)$ obtained above leads to the $k^3\chi(k)$ spectra shown in Fig. 3, in which one still observes the MEES at around 7.5 Å^{-1} for some solutions.

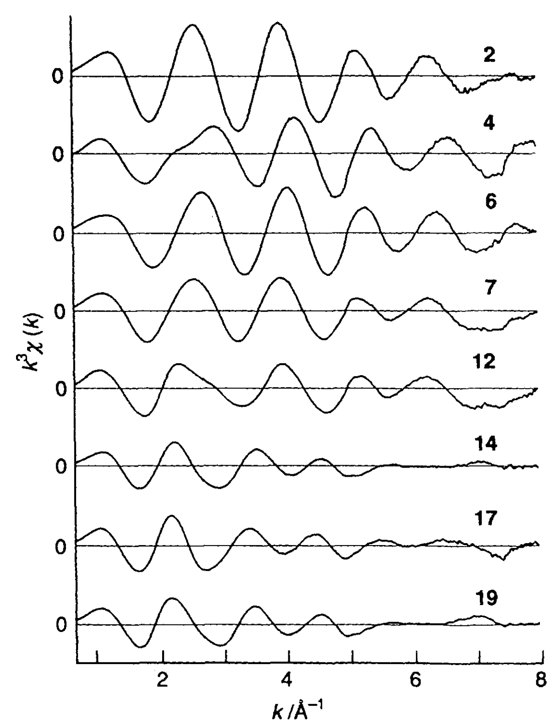


Fig. 3 The Br K-edge EXAFS $k^3\chi(k)$ spectra of Br^- in several solvents

Curve-fitting Calculation.—The EXAFS spectra $k^3\chi(k)$ were fitted by the equations (4) and (5);[28] where subscript j indicates

$$k^3\chi(k) = k^3\sum_j \frac{B_jF_j(k_j)}{k_jr_j^2}\exp(-2\sigma_j^2k_j^2)\sin[2k_jr_j + \varphi_j(k_j)] \qquad (4)$$

$$k_j = [k^2 - (2m/\hbar^2)\Delta E_{0j}]^{\frac{1}{2}} \qquad (5)$$

the co-ordination shell number. The variable parameters in the curve-fitting calculation are r, the Debye–Waller-like factor σ, the amplitude factor B ($B_j = S_jN_j$, where S is the amplitude reduction factor) and the absorption-edge shift ΔE_0. The back-scattering amplitude $F(k)$ and the phase shift $\varphi(k)$ are generated by the computer program FEFF version 5.05[29] for r = 3.2 and 3.6 Å for protic and aprotic solvents, respectively.

The non-linear least-squares curve-fitting calculations were applied to the unfiltered $k^3\chi(k)$ data at k 1.5–5 and 1.3–4.4 Å^{-1} for protic and aprotic solvents, respectively. The scattering atoms are O (or N for formamide) and C, in protic and aprotic solvents, respectively. The spectra were fitted with a single-shell model except for those of acetic acid **4** and *tert*-butyl alcohol **12** which were fitted with a two-shell model.

The S value for aprotic solvents **13–23** was determined to be 0.6 by using a tetra-*n*-propylammonium bromide crystal as a reference compound, the structure of which has been reported.[30] For protic solvents **1–12** the value was determined to be 1.4 by using the spectra for aqueous solutions, the solvation number being assumed to be six according to a number of studies.[1] The results are given in Table 1.

We did not use the Fourier filtering method which has frequently been used to reduce the number of contributing shells and thus of the parameters to be optimized. This is because the distortions caused by it could be significant when applied to systems with weak EXAFS as in the present bromide solutions exhibiting only a few oscillations. In any case, the contributions from the second or higher shells are negligible in the present samples.

Results and Discussion

As is shown in Fig. 2, the EXAFS oscillations appear only in the low *k* region. Such a quick reduction in the EXAFS amplitude with *k* makes the MEES very distinct, thus the EXAFS analysis is difficult. The oscillations look simple except for acetic acid and *tert*-butyl alcohol solutions. The frequencies indicate that the *r* values for protic solvents are smaller than those for aprotic solvents. The *k* ranges where the oscillations are observed in this study are usually considered to be the XANES (X-ray absorption near-edge structure) regions, where multiple scattering predominates. However, the multiple scattering seems not to contribute much to the spectra as indicated in Fig. 3. This must be due to the large disorders in *r* and to the relatively large *r* values for the present samples, both of which tend to destroy the multiple scattering structures faster than the single scattering structures.

EXAFS Amplitude and the Acceptor Number.—The spectra for aqueous solutions shown in Figs. 2 and 3 exhibit a few times stronger EXAFS oscillations compared to those for aprotic solutions such as acetonitrile or pyridine. The amplitudes were evaluated from the peak heights *h* in the Fourier-transform (FT) spectra shown in Fig. 4. The FT calculations were performed over the ranges *k* 1–8 and 1–6 Å^{-1} for protic and aprotic solvents, respectively. The phase shift and the back-scattering amplitude parameters used in the FT calculations were the same as those used for curve-fitting calculations. The main peaks in the FT spectra in Fig. 4 correspond to the Br$\cdots$O (or Br$\cdots$N) and the Br$\cdots$C interactions, in protic and aprotic solvents, respectively. We noticed that the oscillations are stronger for solutions with greater anion–solvent interactions, which could be evaluated by the Mayer-Gutmann acceptor number A_N of the solvent. Fig. 5 shows the linear correlation between *h* and A_N. The acceptor number indicates the ability of the solvent to accept electrons and thus the anion solvation strength. The A_N values are obtained by NMR spectroscopy from the relative ^{31}P chemical shifts for triethylphosphine oxide dissolved in the various solvents.

The present result implies that both A_N and *h* are subject to the same physical quantities such as *N* and *r* in a similar way. If A_N is considered simply as reflecting the strength of interaction between PEt_3O and the solvent and if such interactions as those between Br^- and the solvents have similar mechanisms, it is reasonable to expect a correlation between *h* and A_N because the larger is *N* or the smaller *r* the larger are the A_N and the *h* values. The infrared absorption studies of Mayer *et al.*[31] and Robinson and Symons[32] revealed that PEt_3O has three primary solvent molecules in water and one or two in alcohols. Thus the average *N* values in protic solvents must be the most important factor determining their A_N values. The same is true for *h*.

There is another factor, the disorder in *r* or the Debye–Waller-like factor σ, which is strongly reflected in *h*. The larger the σ value the weaker the interaction strength must be, thus the smaller are the A_N and the *h* values. However, the present study revealed that σ is not correlated with A_N.

The value of *h* may be treated semiquantitatively as a function of *N*, *r* and σ. If the FT is performed over the range *k* 0–∞ Å^{-1} and if the electron mean free path λ is independent of *k*, the *h* value is theoretically derived as in equation (6).[33] Although the

$$h \propto \frac{SN}{r^2\sigma}\exp\left(\frac{-2r}{\lambda}\right) \qquad (6)$$

h values were 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 are included for the FT calculations.

Co-ordination Structures in Protic Solvents.—Protic solvents form hydrogen bonds with Br^- through $Br^-\cdots$H–O (or $Br^-\cdots$H–N for formamide) interaction. Since the scattering amplitude for hydrogen is negligible, the EXAFS method detects the Br$\cdots$O interaction. As expected, the σ values are rather large reflecting the highly disordered solvation structures.

The most reliable results which the present EXAFS study provides are the relative co-ordination distances of Br^-. The *r* value for water, 3.19 Å, is consistent with some results from XRD[4d,e] and ND.[5] As indicated in Figs. 6 and 7, the *r* values for alcohol solutions are similar to each other, although the *N* values are quite different. The *r* values for protic solvents are around 3.1 Å except those for water and formamide (and for Bu^{t}OH which will be discussed later). The longer distances for these two solvents 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 from Br^-, leading to large *r* values. This interpretation is also supported

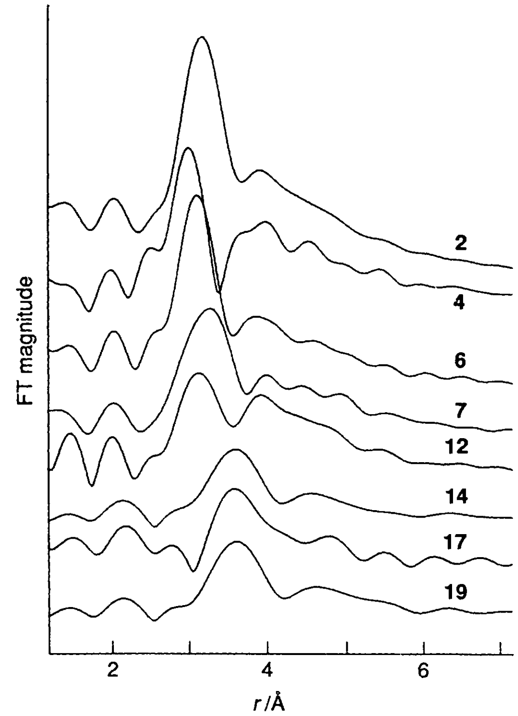


Fig. 4 The Br K-edge EXAFS FT spectra of Br^- in several solvents

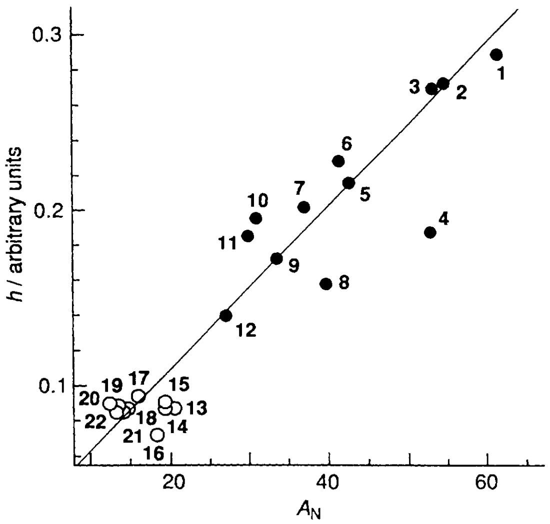


Fig. 5 Correlation of the peak height *h* of the FT spectrum for Br^- with the acceptor number A_N of the solvent: (●) protic and (○) aprotic solvents

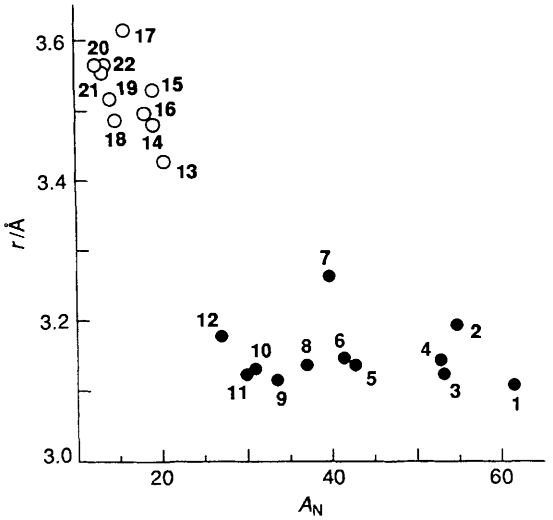


Fig. 6 Correlation of the co-ordination distance r with the solvent acceptor number A_N: (●) protic and (○) aprotic solvents

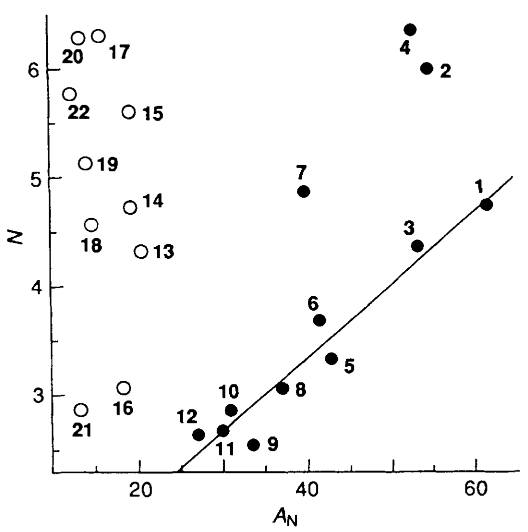


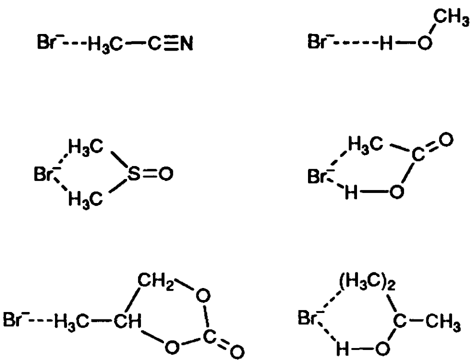
Fig. 7 Correlation of the co-ordination number N with the solvent acceptor number A_N: (●) protic and (○) aprotic solvents

by a preliminary study of highly concentrated aqueous bromide solutions which indicates that the r value becomes small at the highest concentration where almost no second solvation shell water exists.

The N values for alcohols **1**, **3**, **5**, **6** and **8**–**12** depend almost linearly on their A_N values as indicated in Fig. 7. This seems to indicate that the solvation mechanisms for Br^- in alcohols are similar and that only the solvation numbers are different and thus the A_N value reflects only the average solvation number.

The EXAFS χ spectra for acetic acid and *tert*-butyl alcohol in Fig. 3 have unique structure at around k 2–3 $Å^{-1}$. They could be fitted with a two-shell model. We suggest that not only the OH group of acetic acid, but also the methyl group, which is highly positively charged, co-ordinate Br^- as illustrated in Scheme 1 and thus the rather large N value is due to the first solvation shell comprised of O and C atoms from OH and CH_3, respectively. The second shell at around 3.8 Å could be assigned to the C atom of the C=O group.

The spectrum for Bu^tOH was also fitted with the two-shell model. We suggest here that the two methyl groups approach Br^- as illustrated in Scheme 1; thus the first shell is comprised of O and the second shell of three C atoms from $(CH_3)_2C$. The curve-fitting calculations were performed according to the models given above, *i.e.* the ratios of the N values of the first and the second shell were fixed at 2:1 for acetic acid and 1:3 for Bu^tOH. The ΔE_0 values for the two shells were kept equal. From the results it is concluded that both acetic acid and *tert*-butyl alcohol solvate Br^- ion with roughly three solvent molecules. The primary models of the solvation structures for the two solvents are derived from semiempirical MO calculations[34] for clusters consisting of a Br^- ion and several co-ordinating solvent molecules. The most stable solvation structures given by the calculations are taken into consideration for the interpretations of the EXAFS spectra.



Scheme 1 The solvation structures proposed for Br^- in several solvents

The N value of isopropyl alcohol is the same as that for *tert*-butyl alcohol, *i.e.* the smallest among the alcohols studied, while it has a typical r value for the alcohols. Although the difference in the solvation structures for these two alcohols is not known, the perfect correlation of h *vs.* A_N for these two alcohols (**9** and **12** in Fig. 5) must result not from the solvation numbers but from the longer distance for Bu^tOH and its larger disorder.

Co-ordination Structures in Aprotic Solvents.—The main solvation mechanism in aprotic solvents must be the ion–dipole interaction. The r values are 3.4–3.6 Å, which are larger than those for protic solvents. The σ values are also larger than those for protic solvents. These are reasonable consequences of the weaker solvation through the ion–dipole interaction than that through hydrogen bonding. The r values seem to correlate slightly with A_N, *i.e.* the smaller the r, the larger is A_N.

It is quite interesting to find that the solvents having largest N values, dimethylformamide, dimethylacetamide, acetone, dimethyl sulfoxide and ethyl methyl ketone, can all provide two methyl groups for the bromide–solvent interaction. The large N values of around six for these bulky solvents seem to indicate that there are approximately three solvent molecules in the primary solvation shell just like the cases of N-methylpyrrolidin-2-one and propylene carbonate, the former (**17**, **20**, **22**, **15** and **23**) orienting two methyl groups to Br^- and the latter (**21** and **16**) a single methyl group.

Acetonitrile and nitromethane are smaller in size. Their shapes allow them to access Br^- closely, thus larger N and shorter r result. Pyridine and nitrobenzene have larger N values of around five. The values could be explained if Br^- is solvated either by facing the ring of a solvent molecule or by contacting the edges of five molecules similarly to the solvation structure in acetonitrile or nitromethane.

Conclusion

In the present study EXAFS spectroscopy proved to be a powerful tool for determining the local solvation structures of bromide ion in various organic solvents at relatively low concentrations. The r and N values can be related to the microscopic shapes of the solvent molecules. The r values for protic solvents are smaller than those for aprotic solvents. This is the reasonable consequence of the stronger solvation through hydrogen bonding than that through the ion–dipole interaction. The r values for well structured solvents such as water and formamide are larger than for the other solvents having similar A_N values. Larger N values are found for aprotic solvents having two methyl groups which may be oriented towards Br^-. The almost linear correlation of A_N with h throughout the series of solvents studied implies that the solvent effect upon the ^{31}P NMR chemical shift for PEt_3O is a similar function of N, r and σ to that in equation (6). We believe that the EXAFS method provides additional empirical solvation parameters such as r, N and σ which are intimately related with the solvation structures.

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