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## The hydration structure of $\text{Br}^-$ from anomalous x-ray diffraction

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**Abstract.** The method of anomalous x-ray diffraction (AXD) was applied to an aqueous solution of 6 molal RbBr in water. Data were gathered at two wavelengths below the absorption edge of  $\text{Br}^-$ . Corrections were made for attenuation, inelastic scattering and background and container scattering. The corrected data were renormalized and put on an absolute scale of electron units. Fourier transformation of these results provided information on the  $\text{Br}^-$  hydration. It is found that the Br–O nearest neighbour distance is 3.4 Å and the first coordination shell contains between 6 and 7.5 water molecules. There is no evidence to suggest any longer range hydration structure.

### 1. Introduction

The properties of aqueous electrolyte solutions are strongly influenced by ion type and concentration, and a knowledge of the structure around ions provides essential information needed to understand the origin of their rich and varied behaviour. In the 1970s, the method of neutron diffraction and isotopic substitution (NDIS) was developed and used to determine the hydration properties of a number of ions as a function of concentration, counterion type and recently pressure and temperature [1, 2]. The NDIS method yields quantitative structural information on the total radial distribution function of an ion  $I$ ,  $G_I(r)$ , in terms of a linear combination of its pair distribution functions  $g_{I\alpha}(r)$ . At relatively low ionic concentrations (less than 2 molal),  $G_I(r)$  is dominated by the hydration structure and is used to make definitive statements about the coordination and conformation of an ion in solution. Results can also be used as a critical test of computer simulation and theoretical studies of model systems [3].

Despite the success of the NDIS method, the pairwise functions  $g_{XO}(r)$  and  $g_{XH}(r)$  of many ions are not known. For example, although the hydration structure of alkali ions such as  $\text{Li}^+$  and  $\text{K}^+$  is well established [4, 5], that for  $\text{Na}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  remains to be determined. (A method based on isomorphic x-ray diffraction and NDIS has been used with some success for  $\text{Na}^+$ ; however, the accuracy of the information is appreciably less than that obtained from an NDIS type experiment [6]). The situation is even more critical for the halogen ions where only the chloride hydration structure is fully determined [7].

Although it is unlikely that other methods will provide structural information at the same level of accuracy as the NDIS method, it is likely that x-ray methods which employ synchrotron radiation can be used to provide some details of ion–water and ion–ion structure. Indeed, the EXAFS spectroscopic technique has been widely applied to ions with atomic number  $Z > 25$  to determine nearest neighbour distances and coordination numbers, although the accuracy of

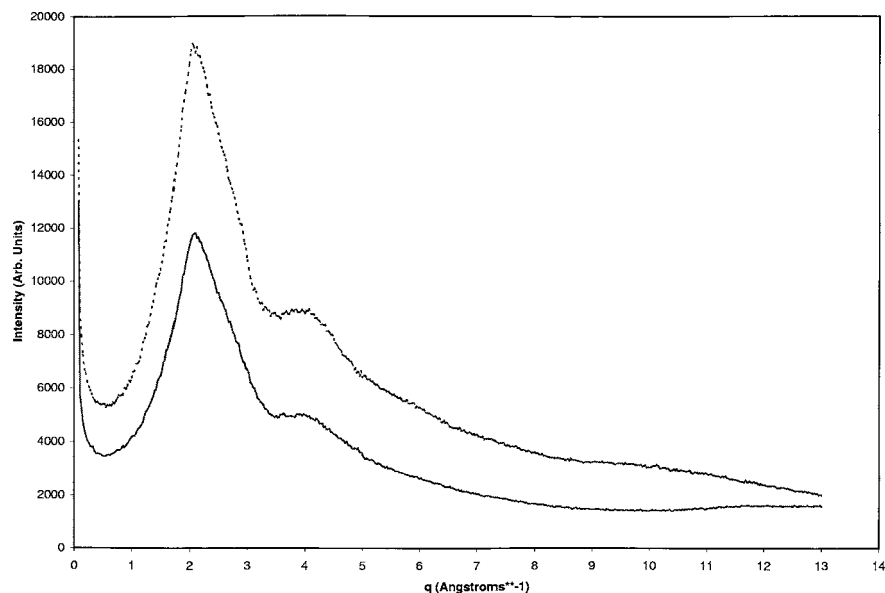
these is uncertain [8]. Additionally, anomalous x-ray diffraction (AXD) is being developed at various facilities and applied to both crystalline and liquid materials [9, 10].

In this paper, we present a detailed AXD study of  $\text{Br}^-$  hydration structure in a concentrated solution of RbBr. Although AXD results for  $\text{Br}^-$  hydration have already been published [11], we feel that the results presented here are more representative of the  $\text{Br}^-$  coordination, the data having been collected in a high energy resolution diffractometer and critically analysed [12].

## 2. Experimental method

### 2.1. Sample

Anomalous x-ray diffraction experiments were carried out on an aqueous solution of 6 molal rubidium bromide at ambient conditions on the ID1 instrument at the ESRF (Grenoble). The sample was prepared from Analar grade RbBr salt which was dissolved directly in deionized water. During the experiment, the sample was contained in a 0.5 mm silica tube; to avoid overheating due to the high x-ray flux ( $10^{13} \text{ s}^{-1}$  in the 1 mm beam) the sample was peristaltically pumped during each experimental run. Data were collected (figure 1) at two energies ( $-5 \text{ eV}$ ,  $-200 \text{ eV}$ ) below the bromide edge ( $13.474 \text{ keV}$ ); this ensures that corrections for fluorescence were unnecessary. Data were also gathered for background and empty container. Each run consisted of several scans over a  $Q$ -range of  $0.2 \leq Q \text{ (}\text{\AA}^{-1}\text{)} \leq 12$  corresponding to  $1^\circ \leq 2\theta \leq 143^\circ$ .



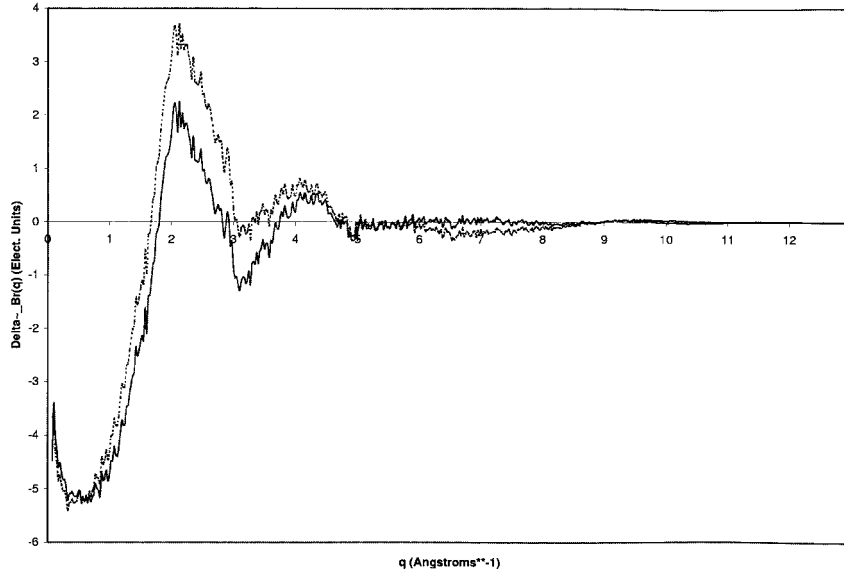
**Figure 1.** Measured scattering intensities from a 6 molal RbBr solution at two energies below the Br K edge (full line at 5 eV and dashed line at 200 eV).

### 2.2. Data analysis

Measured raw data were normalized to the same flux of incident photons, which was monitored for each measurement at each angle throughout the experiment.

Corrections for inelastic effects due predominantly to Compton scattering and to a much lesser extent resonant Raman scattering were not needed because of the use of an InSb(111)

analyser crystal. This crystal rejected inelastically scattered photons with an accuracy of a few eV. Additional inelastic effects arising from the wide slit geometry were accounted for by working with the difference between the data sets. This procedure was adopted since it is clear that the same inelastic behaviour is anticipated at the two incident energies, which are separated by approximately 200 eV.



**Figure 2.** Corrected and normalized difference,  $\tilde{\Delta}_{Br}(q)$  (defined in equation (2)). The full line corresponds to the calculated function and the dashed line corresponds to the best fitting one showing no structure at small  $r$  (obtained by calculating back Fourier transforms of a modified function in real space).

The difference data were then corrected for absorption and scattering of the beam in the sample and container [13]. This correction was initially carried out on the individual intensities, which although in principle more accurate gave problems because of the sample dependent background. Instead, by applying the correction to the difference we overcame the need to subtract the background directly from the measured intensities. A small inaccuracy of less than 5% in the attenuation factors was calculated. A calculation of multiple scattering revealed that this accounts for less than 1% of the total scattering from our samples. Moreover, since this will be of similar magnitude at the two energies, this correction was ignored.

After all the corrections have been applied we can write the difference between the two corrected intensities as:

$$\begin{aligned} (I(q, E) - I(q, E')) = CN \left( \sum_{\alpha} (c_{\alpha} f_{\alpha} f_{\alpha}^{*} - c_{\alpha} f'_{\alpha} f'_{\alpha}^{*}) \right. \\ \left. + \sum_{\alpha} \sum_{\beta} c_{\alpha} c_{\beta} (f_{\alpha} f_{\beta}^{*} - f'_{\alpha} f'_{\beta}^{*}) (S_{\alpha\beta}(q) - 1) + D \right) \end{aligned} \quad (1)$$

where  $N$  represents the total number of particles,  $c_{\alpha}$  is the atomic fraction,  $f_{\alpha}(q, E)$  is the total atomic form factor for the atomic species  $\alpha$ ,  $f'_{\alpha}(q, E')$  is the total atomic form factor at the second energy  $E'$ ,  $S_{\alpha\beta}(q)$  is the partial structure factor which carries all the information about the correlation between atoms  $\alpha$  and  $\beta$  and each sum extends over the four atomic species,  $C$  and  $D$  are parameters which ensure normalization of the data.

This equation is made up of two contributions. The first term is called the ‘self-term’ and is due to the correlation of each atom with itself. The second term is the ‘distinct-term’, due to the correlation of every atom with all the others; this is the one that carries the information about the structure and is approximately one order of magnitude smaller than the self-term.

The self-term was calculated from tabulated values of the  $f_\alpha(q)$ ,  $f_\alpha(q, E)$ . This functional form exhibits a monotonic decline with increasing  $q$  and was fitted to the difference function. This procedure enabled us to calculate  $NC$  and  $D$ , and hence normalize our data to an absolute scale of electron units. The distinct term was extracted from equation (1) by subtracting the self-term (figure 2):

$$\begin{aligned} \tilde{\Delta}_{Br}(q) = & c_{Br}^2 \operatorname{Re}(f_{Br} f_{Br}^* - f'_{Br} f_{Br}^{*'}) (S_{BrBr} - 1) + 2c_{Br} c_{Rb} \operatorname{Re}(f_{Rb} f_{Br}^* - f'_{Rb} f_{Br}^{*'}) \\ & \times (S_{RbBr} - 1) + 2c_{Br} [c_O \operatorname{Re}(f_O f_{Br}^* - f'_O f_{Br}^{*'}) (S_{OBr} - 1) \\ & + c_H \operatorname{Re}(f_H f_{Br}^* - f'_H f_{Br}^{*'}) (S_{HBr} - 1)] \end{aligned} \quad (2)$$

where, in contrast to the NDIS experiments, it should be emphasized that the atomic form factors depend on  $q$ .

$\tilde{\Delta}_{Br}(q)$  was Fourier transformed to give the x-ray modified total  $\text{Br}^-$  pair distribution function  $\tilde{G}_{Br}(r)$ , which according to equation (2) is a sum of the pair correlation functions,  $g_{YBr}(r)$ , convoluted with the  $q$  dependent form factors. The effect of these form factors is to broaden and diminish in height the real pair correlation functions.

The calculation of coordination numbers requires that the scale obtained after normalization of the intensities is correct. The normalization was checked by comparing the value at small  $r$  obtained from the experimental data with that expected from the theoretical weighting factors for each  $g_{YBr}(r)$ ; that is:

$$\begin{aligned} \tilde{G}_{Br}(0) - 1 = & -2c_{Br} c_{Rb} \operatorname{Re}(f_{Rb} f_{Br}^* - f'_{Rb} f_{Br}^{*'}) - c_{Br}^2 \operatorname{Re}(f_{Br} f_{Br}^* - f'_{Br} f_{Br}^{*'}) \\ & - 2c_{Br} c_O \operatorname{Re}(f_O f_{Br}^* - f'_O f_{Br}^{*'}) - 2c_{Br} c_H \operatorname{Re}(f_H f_{Br}^* - f'_H f_{Br}^{*'}) \end{aligned} \quad (3)$$

where the form factors are evaluated at  $q = 0$ .

The expected value for the normalization when obtained as described before is  $-1.44$  electron units at  $r = 0$  and the value obtained from the experimental data was  $-1.47$ .

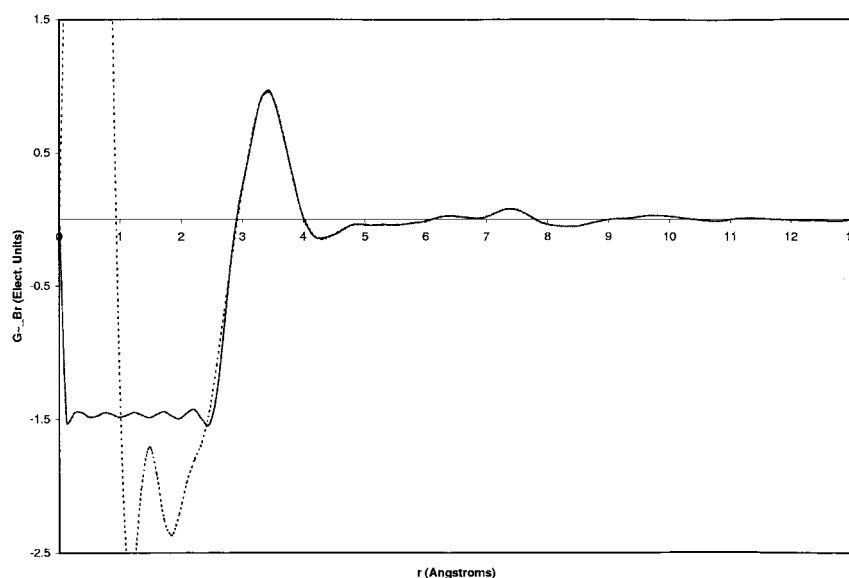
Because  $\tilde{G}_{Br}(r)$  is the result of a F.T. of partial structure factors multiplied by  $q$  dependent atomic form factors, care must be taken in the evaluation of coordination numbers. We have approached this difficulty in two ways. The more general method is to fit Gaussians to  $\tilde{G}_{Br}(r)$  and try to account for the different expected contributions from each pair distribution function. A more specific method works well for the case in which there is no overlap of the different  $g(r)$  in real space. It is then possible to calculate the Fourier transform of  $\tilde{\Delta}_{Br}(q)$  divided by the weighting factor of certain contribution. This will allow a more accurate value of the coordination number of that contribution to be obtained.

The system studied in this case was a solution of RbBr in water and overlap between the pair contribution functions associated with O and H will occur in the hydration peak. Hydrogen in the water molecule is responsible for one-quarter of the total scattering (it contributes with two electrons) and it cannot be disregarded; as a consequence the coordination number of water was calculated instead of that for Br–O (see next paragraph).

### 3. Results and discussion

The function  $\tilde{G}_{Br}(r)$  (figure 3) contains a weighted sum of all four structure functions pertaining to the  $\text{Br}^-$  ion. From it we can extract information regarding the near neighbour hydration of the ion. In particular, we can ascribe the peak centred at  $3.4 \text{ \AA}$  in the range  $2.5 \text{ \AA} \leq r \leq 4.3 \text{ \AA}$  as being due to the  $\text{Br}^-$  first hydration shell. Of course, this peak will also have contributions

from  $g_{\text{BrH}}(r)$ , with a weighting factor which will be approximately one-quarter of that from the Br–O term and they cannot be disregarded. Because of the concentration of the solution we could expect contributions from  $g_{\text{BrRr}}(r)$  or possibly  $g_{\text{BrBr}}(r)$  in the range obtained for the first peak at larger distances than 3.4 Å. This hypothesis is supported by a calculation of 15 water molecules around a  $\text{Br}^-$  ion when no overlap is assumed! A more realistic estimate of the value of the coordination number is obtained by fitting gaussians to the first peak and taking its maximum as the centre of the water contribution. When this procedure is followed a more realistic value for the coordination number of between 6 and 7.5 is obtained.



**Figure 3.**  $\tilde{G}_{\text{Br}}(r)$ , defined as the  $\tilde{\Delta}_{\text{Br}}(q)$  Fourier transform. The full line corresponds to the best fitting function showing no structure at  $r$  smaller than the radius of the Br ion and the dashed line corresponds to the function calculated directly from the experimental data.

The result above represents a significant breakthrough in our knowledge of anion structure and is almost equivalent to that obtained from the NDIS method on ions such as  $\text{Cl}^-$  [7]. Comparison between  $\tilde{G}_{\text{Br}}(r)$  and  $G_{\text{Cl}}(r)$  shows that both ions have a relatively short range structure which extends no further than a first coordination shell. Moreover, it appears that the extent of the hydration shell scales with ion size, i.e. for  $r_{\text{Br}^-} = 1.96$  Å and  $r_{\text{Cl}^-} = 1.81$  Å the corresponding peak positions in their  $G(r)$  appear at 3.4 Å and 3.3 Å respectively.

Comparison of our results with those obtained from EXAFS (extended x-ray absorption fine structure) on RbBr at low concentrations [14] and another AXD experiment on  $\text{ErBr}_3$  [11] are particularly interesting. The EXAFS data covered the range  $2 \leq q(\text{Å}^{-1}) \leq 9.8$  and were fitted by a sophisticated model procedure. The result of this was to produce a relatively structured  $g(r)$  with a first peak of similar size and shape to that presented here and a coordination number of 6.9. However, there is substantial structure beyond the first shell suggesting at least two or even three subsequent hydration shells. It could be that the difference between our results and those produced from the EXAFS experiment is due to a concentration effect, suggesting that as the system dilutes the  $\text{Br}^-$ –water structure becomes enhanced. We feel that such an explanation is most unlikely as we have recently carried out an EXAFS study of RbBr aqueous solution at a number of concentrations between 0.1 and 6 molal and the raw data remain totally unaltered [15].

It is also noted that the AXD experiment on 3 molal  $\text{ErBr}_3$  in water produced an even stranger result for the  $\text{Br}^-$  coordination showing correlations in the data out to around 6 Å, and suggesting well defined correlations between  $\text{Br}^-$  ions themselves and Br–Er ions. Such correlations may well exist; however it is clear from the results shown in figure 5 of [11] that a substantial number of correlations in the  $r$ -space results can only be due to noise introduced in the Fourier transformation of ill conditioned data sets.

In order to progress further with this work it is clear that it is essential to minimize self- and counterion contributions to the total functions. This can be done by either working at lower concentrations or by using ions with widely differing atomic masses e.g. LiBr and Rb(OH).

Results from a conventional x-ray diffraction experiment on 4 M HBr confirm our results and lack of structure beyond the first hydration shell [16].

#### 4. Conclusions and future work

The results presented above show that the AXD method has the potential to provide useful and accurate information on the hydration structure for heavy ions ( $Z > 28$ ) in aqueous solution. Although less direct than the NDIS methods due to the  $q$  dependence of x-ray form factors, it is nevertheless possible to obtain quantitative details of the nearest neighbour coordination around the target ion.

The results also show that AXD can be applied to  $\text{Br}^-$  and other heavy anions, and at lower concentrations. By judicious choice of a lighter counterion it should be possible to obtain a more definitive information of the structure around a heavy ion.

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