X-ray and neutron diffraction studies on concentrated aqueous solutions of sodium nitrate and silver nitrate

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Abstract. Neutron diffraction experiments have been conducted on 3.1M (molar) solutions of $^{107}AgNO_3$ and $^{109}AgNO_3$ in heavy water, and the first-order difference method of isotopic substitution has been used to obtain the local structure around $Ag^+_{[aq]}$. The results of this work have been used in conjunction with those from an x-ray diffraction study of 3.1M (molar) $AgNO_3$ and $NaNO_3$, to establish the degree of structural isomorphism between $Na^+_{[aq]}$ and $Ag^+_{[aq]}$. It has been shown that $Na^+_{[aq]}$ and $Ag^+_{[aq]}$ are sufficiently isomorphic to enable useful pictures to be obtained for both Na^+ hydration and $Ag^+–Ag^+$ co-ordination. Comparison with previous results for the other alkali metal ions shows that, in terms of the strength of hydration, Na^+ is intermediate between Li^+ and K^+.

1. Introduction

The object of this paper is to present the results from a series of neutron and x-ray diffraction experiments, which were chosen to provide information about Na^+ co-ordination in aqueous solution.

It will be recalled that Na^+ is the second ion in the alkali metal series, and that aqueous solutions of alkali salts are important in many branches of science. Of particular interest to biologists is the contrasting behaviour of $Na^+_{[aq]}$ and $K^+_{[aq]}$, which gives rise to the concept of the ionic pump across a cell membrane (Williams 1971). To understand this and other types of aqueous alkali metal ion behaviour it is necessary to possess a detailed picture of their local ionic structure.

In recent years we have been able to determine quantitatively the structure around Li^+ and K^+ in aqueous solution (Newsome *et al* 1980, Neilson and Skipper 1985). This was achieved by the difference method of neutron diffraction, which is based on isotopic substitution (Soper *et al* 1977, Enderby and Neilson 1980), and provides direct structural information in terms of the radial pair distribution functions, $g_{M\beta}(r)$, specific to the substituted ionic species, M. The results for Li^+ and K^+ show that Li^+ has a well defined hydration shell, whereas K^+ does not.

The equivalent problem for Na^+ is this: since it has an ionic radius ($r_i = 0.98$ Å) which is intermediate between those of Li^+ ($r_i = 0.60$ Å) and K^+ ($r_i = 1.33$ Å), is its co-ordination more akin to that of Li^+ or K^+? Unfortunately it is not a simple matter to answer this question. Sodium is not susceptible to the difference method of isotopic

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substitution (it is mono-isotopic) and it is not a strong scatterer of x-rays (the ion has only 10 electrons). Some other means must therefore be found to help resolve its structure in solution.

Because of the importance of $Na^+_{[aq]}$, we have examined the feasibility of applying the difference method of x-ray diffraction based on isomorphic substitution (Skipper *et al* 1986). This was done by investigating the degree to which $Ag^+_{[aq]}$ is isomorphic with $Na^+_{[aq]}$. At first sight this may appear to be a surprising choice of substitution, given that Ag^+ has a highly delocalised electronic structure and many of its salts are insoluble in water. However, there are many solvation properties which are similar for the two ions. For example, Shannon and Prewitt (1969) find that in a four fold co-ordination geometry their effectiive ionic radii are almost the same; $r_{Ag^+} = 1.02$ Å and $r_{Na^+} = 0.99$ Å. Furthermore, results obtained from nuclear magnetic resonance (NMR) by Hertz (1973) show that the B coefficients of the spin–lattice relaxation are identical. Finally, thermodynamic measurements of ion association in nitrate solutions give pK values in the same range (Davies 1962). With these observations as encouragement, we undertook the following sets of diffraction experiments.

The method of isomorphic substitution first requires that a neutron diffraction difference experiment be carried out on one of the samples, using the formally correct method of isotopic substitution. In this case a 3.16M (molar) silver nitrate solution was used, in which replacement of ^{107}Ag by ^{109}Ag enabled the difference functions $\Delta_M(k)$ and $G_M(r)$ to be obtained. Although the results of this work are interesting in their own right, being part of our ongoing study of the Ag^+ ion in solution, for the present case we only discuss them briefly, and then move on to consider their relevance to the x-ray studies.

X-ray diffraction experiments were carried out on three 3.16M (molar) aqueous solutions; $AgNO_3$ (I), $NaNO_3$ (II) and a 50:50 mixture of $NaNO_3$ and $AgNO_3$ (III). The method of isomorphic substitution was then applied to Na^+ and Ag^+. The first-order difference function, $\tilde{G}_{MO}(r)$, was checked against the formally correct neutron result for Ag^+, $G_M(r)$, thus allowing us to estimate the degree of isomorphism between Na^+ and Ag^+. A further test of this isomorphism was made by carrying out a self-consistency check between the two independent x-ray difference functions, obtained from solutions [I − II] and [III − II].

2. Theoretical background

The quantity which can be extracted from a single diffraction experiment, in which x-rays or neutrons of wavelength λ are scattered through an angle 2θ by an aqueous solution (MX_n in D_2O), is the structure factor

$$F(k) = \sum_\alpha \sum_\beta c_\alpha c_\beta f_\alpha(k) f_\beta(k) [S_{\alpha\beta}(k) - 1] \tag{1}$$

where $k = 4\pi(\sin\theta)/\lambda$, c_α is the atomic fraction of species α and $f_\alpha(k)$ the scattering factor of species α for the radiation in question. $S_{\alpha\beta}(k)$ is the partial structure factor for atoms α and β, and is directly related to the partial radial distribution function, $g_{\alpha\beta}(r)$, by Fourier transformation

$$g_{\alpha\beta} = 1 + (1/2\pi^2\rho r) \int_0^\infty [S_{\alpha\beta}(k) - 1] \sin(kr) k \, dk \tag{2}$$

where ρ is the number density of the sample, and is typically 0.1 Å^{-3}. In the present case

ten differently weighted partial structure factors contribute to the total structure factor.

Although the general forms of $F_x(k)$ and $F_n(k)$ are the same, they have different shapes because of the different scattering processes involved. X-rays are scattered anisotropically by the electron densities of individual atoms, whereas neutrons are scattered isotropically by the nuclei of the system. Bearing in mind the concentration factors, $c_\alpha f_\alpha(k)$, $F_x(k)$ is dominated by correlations between oxygen atoms themselves and oxygen atoms and heavy species. $F_n(k)$, on the other hand, is dominated by the water correlations. If one works in terms of the total structure factor and its Fourier transform it is therefore easier to obtain ionic structural information, albeit limited, from x-ray diffraction. However, by using difference techniques the resolution of neutron and x-ray diffraction data can be greatly improved. For neutrons the method is based on isotopic substitution of the ions, and is formally exact. For x-rays the method involves isomorphic substitution of the ions, which is only approximately valid in solution.

2.1. Neutron diffraction difference method

The first order difference function for neutron diffraction, $\Delta_M(k)$, can be obtained directly from a difference between the structure factors of two solutions which differ only in the isotopic content of the cation or anion. $\Delta_M(k)$ contains only the four terms involving the substituted species. Taking the case of the cation (M)

$$\Delta_M(k) = F_n^I(k) - F_n^{II}(k)$$

$$\Delta_M(k) = AS_{MO}(k) + BS_{MD}(k) + CS_{MX}(k) + DS_{MM}(k) - E \tag{3}$$

where $A = 2c_O c_M b_O \Delta b_M$, $B = 2c_D c_M b_D \Delta b_M$, $C = 2c_X c_M b_X \Delta b_M$, $D = c_M^2 \Delta^2 b_M$ and $E = A + B + C + D$. b_α is the neutron scattering length of species α, which is independent of k, and $\Delta b_M = b_M - b_{M'}$ and $\Delta^2 b_M = b_M^2 - b_{M'}^2$. Heavy water is used as the solvent because deuterium has a much smaller incoherent neutron scattering cross section than hydrogen. Fourier transformation of $\Delta_M(k)$ gives the real space distribution, $G_M(r)$, which only contains the four terms involving the substituted species

$$G_M(r) = (1/2\pi^2 \rho r) \int_0^\infty \Delta_M(k) \sin(kr) k \, dk$$

$$G_M(r) = Ag_{MO}(r) + Bg_{MD}(r) + Cg_{MX}(r) + Dg_{MM}(r) - E. \tag{4}$$

The co-ordination number of atom α around M in the range r_1 and r_2 is then given by

$$\bar{n}_M^O = (4\pi\rho c_\alpha/A) \int_{r_1}^{r_2} (g_{MO}(r) + E) r^2 \, dr. \tag{5}$$

2.2. X-ray diffraction difference method

It is not possible to obtain a formally exact difference function from x-ray diffraction experiments because the x-ray form factors, $f_\alpha(k)$, depend on k and atomic number, z_α. There is, therefore, no means of substitution equivalent to the isotope method. However, by comparing the scattering due to two species which have very similar structure in solution, and making reference to neutron results, it is possible to improve the resolution of x-ray data. This is the basis of the isomorphic substitution method, which is now discussed.

The difference function, $\tilde{\Delta}_M(k)$, between the x-ray structure factors for the two

proposed isomorphic solutions, MX_n and $M'X_n$ in H_2O, can be constructed in the same way as the neutron difference function (equation (3)). This is then divided by the coefficient of the cation–oxygen correlation to give

$$\tilde{\Delta}_{MO}(k) = \tilde{\Delta}_M(k)/A(k)$$

$$\tilde{\Delta}_{MO}(k) = [\tilde{S}_{MO}(k) - 1] + B(k)/A(k)[\tilde{S}_{MH}(k) - 1]$$
$$+ C(k)/A(k)[\tilde{S}_{MX}(k) - 1] + D(k)/A(k)[\tilde{S}_{MM}(k) - 1] \tag{6}$$

where $S_{\alpha\beta}(k)$ has been replaced by

$$\tilde{S}_{\alpha\beta}(k) = S_{\alpha\beta}(k) - [S_{\alpha'\beta}(k) - S_{\alpha\beta}(k)]\{f_{\alpha'}(k)/[f_\alpha(k) - f_{\alpha'}(k)]\}$$

because M and M' may not be perfect isomorphs. $A(k)$, $B(k)$, $C(k)$ and $D(k)$ are the k-dependent analogues of A, B, C and D in equation (4). The reason we divide by $A(k)$ is to deconvolute the cation–oxygen correlations so that

$$\tilde{G}_{MO}(r) = (1/2\pi^2\rho r) \int_0^\infty \Delta_{MO}(k) \sin(kr)k \, dk$$

$$\tilde{G}_{MO}(r) = \tilde{g}_{MO}(r) - \{1 + [B(0) + C(0) + D(0)]/A(0)\} + \int [H_{B,A}|(r - r')|\tilde{g}_{MH}(r')$$
$$+ H_{C,A}|(r - r')|\tilde{g}_{MX}(r') + H_{D,A}|(r - r')|\tilde{g}_{MM}(r')] \, dr' \tag{7}$$

where

$$H_{X,Y}(r) = (2/\pi) \int_0^\infty [X(k)/Y(k)] \cos(kr) \, dk$$

$$\tilde{g}_{\alpha\beta}(r) = g_{\alpha\beta}(r) - \int [g_{\alpha'\beta}(r') - g_{\alpha\beta}(r')]H_{f',f-f'}|(r - r')| \, dr'.$$

The measured co-ordination number of oxygen atoms around the cation in the range r_1 to r_2 is then

$$\bar{n}_M^O = 4\pi\rho c_O \int_{r_1}^{r_2} \tilde{G}_{MO}(r)r^2 \, dr. \tag{8}$$

The degree of isomorphism can be checked by referring to the neutron result (equation (4)), which is an exact representation of the cation co-ordination. If the nearest-neighbour cation–oxygen correlation is the same in both cases (to a good approximation) then isomorphism is established. Another useful demonstration of isomorphism can be made if the two independent difference functions, $\tilde{G}_{MO}(r)$, obtained from solutions [I − II] and [III − II] are compared. If the pair are not isomorphs the different weightings of the cations in the two $\tilde{G}_{MO}(r)$ will result in a discrepancy between the measured nearest-neighbour cation–oxygen correlations.

The cation–cation partial structure factor, $\tilde{S}_{MM}(k)$, can be constructed from a second-order difference

$$\tilde{S}_{MM}(k) = 1 + \tilde{\Delta}_M^1/A'(k) - \tilde{\Delta}_M^2/B'(k) \tag{9}$$

where

$$\tilde{\Delta}_M^1 = F_M^I(k) - F_M^{II}(k) \qquad \tilde{\Delta}_M^2 = F_M^I(k) - F_M^{III}(k)$$
$$A'(k) = c_M^2[f_M(k) - f_{M'}(k)][f_{M'}(k) - f_{M''}(k)]$$

Table 1. The properties of the solutions used in the neutron diffraction experiments.

Solution	Isotopic content	Sample density (g cm^{-3})	%H$_2$O
3.16M ^{107}AgNO$_3$ in D$_2$O	0.988 ^{107}Ag 0.012 ^{109}Ag	1.55	0.3
3.16M ^{109}AgNO$_3$ in D$_2$O	0.006 ^{107}Ag 0.994 ^{109}Ag	1.55	0.3

$$B'(k) = c_M^2[f_M(k) - f_{M''}(k)][f_{M'}(k) - f_{M''}(k)].$$

The cation–cation partial distribution function, $\bar{g}_{MM}(r)$, can then be obtained by applying equation (2). In the case of true isomorphism this will be an exact result for the cation–cation pair correlation function. This analysis assumed that the various $f_\alpha(k)$ are known.

3. Experimental methods

The neutron diffraction experiments were carried out on the D4B diffractometer at the ILL, Grenoble. Heavy water equimolar solutions of ^{107}AgNO$_3$ and ^{109}AgNO$_3$ (table 1) were prepared under glove box conditions in our chemical laboratory at Bristol. After checks of the light heavy water ratios by IR spectrometry, the samples were transported in sealed containers to the ILL. Neutron diffraction data for the two samples were obtained and corrected for absorption, multiple scattering and incoherent scattering, and normalised by reference to a vanadium standard, to give a structure factor, $F_n(k)$ in units of b sr^{-1} nucleus. The difference function, $\Delta_M(k)$ was obtained from a direct difference between the two structure factors (equation (3)). Fourier transformation of $\Delta_M(k)$ gave the real space distribution function $G_M(r)$ (equation (4)), with $A = 2.7$ mb, $B = 5.2$ mb, $C = 0.2$ mb, $D = 0.1$ mb and $E = 8.2$ mb. These coefficients show that $G_N(r)$ is dominated by Ag–O and Ag–D correlations, and consequently provides information of the Ag$^+$ hydration.

X-ray diffraction data were obtained for three equimolar aqueous solutions of NaNO$_3$, AgNO$_3$ and a 50:50 mixture of AgNO$_3$ and NaNO$_3$, on a θ–θ diffractometer manufactured by Rigaku Corporation, Japan. The data were corrected for background, multiple scattering, absorption, polarisation, Compton scattering and incoherent scattering using the procedures described by Skipper (1987). They were normalised to electron ^{2}Å^{-3} by the method of Habenschuss and Spedding (1979), and the total structure factor, $F_x(k)$ (equation (1)), of each solution was determined.

Fourier transformation of $F_x(k)/[\Sigma c_\alpha^2 f_\alpha(k)^2]$ gives a total distribution function, $G_X(r)$, which represents the average structure of the solution. Apart from the obvious intra-molecular O–H peak of the water molecules, at about 1 Å, $G_X(r)$ is too ambiguous to be interpreted directly. In the case of Ag$^+$, and presumably Na$^+$, there is no strong cation–oxygen correlation, as demonstrated by the neutron diffraction study of Sandstrom *et al* (1985). It is therefore not possible to obtain a reliable measure of the Na$^+$–O correlation. To proceed further we followed the procedure outlined in § 2.2, and determined first- and second-order difference functions for the three solutions (table 1). The results of this analysis are presented and discussed in § 4.

4. Results and discussion

4.1. Ag$^+$ hydration by neutron diffraction

The neutron diffraction results are shown in figure 1. $G_M(r)$ (figure 1(b)), is similar to that obtained in the earlier investigation of Ag$^+$ in aqueous perchlorate solutions
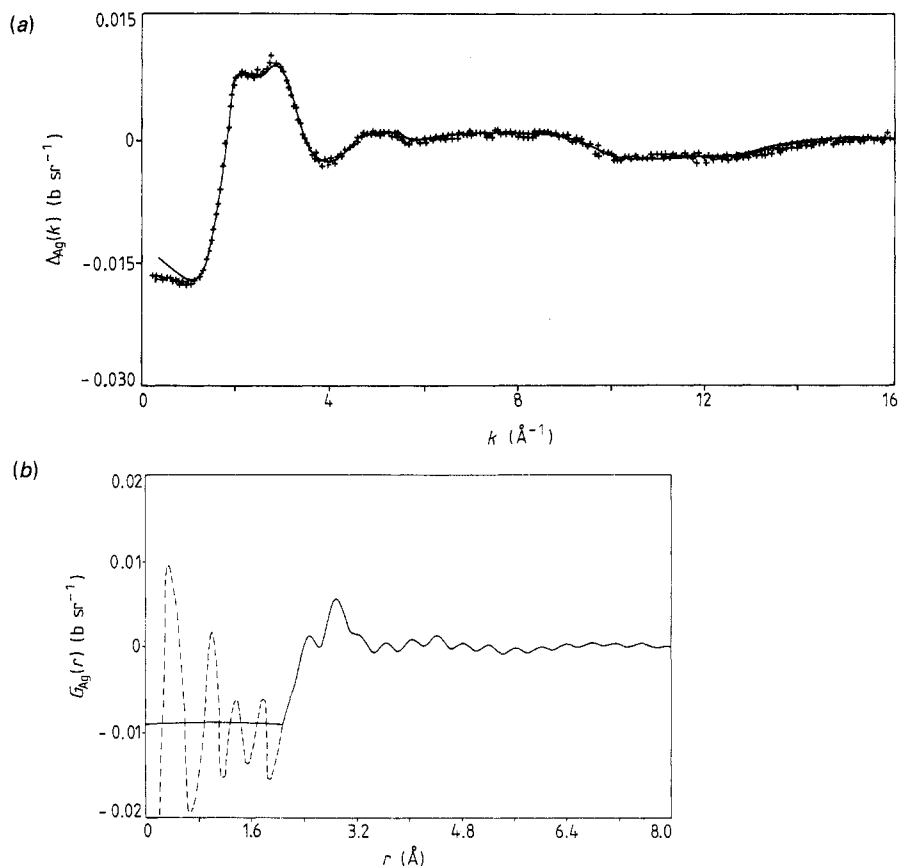
Figure 1. (*a*) The neutron first-order difference function, $\Delta_{Ag}(k)$, for Ag^+ in a 3.1 molal solution of $AgNO_3$ in heavy water. The full curve is the result of back Fourier transformation of the $G_{Ag}(r)$ in figure 1(*b*), after the removal of oscillations below $r = 2.05$ Å and extrapolation to $G_{Ag}(0) = -0.0082$. (*b*) The neutron first-order difference radial distribution function, $G_{Ag}(r)$, for Ag^+ in a 3.1 molal solution of $AgNO_3$ in heavy water.

(Sandstrom *et al* 1985). Because of the superior statistics in the present case (the data were gathered over a period twice that of the perchlorate study) there is less noise on the resulting $\Delta_M(k)$ (figure 1(*a*)). It is a straightforward matter to show that for a 3.16M solution of $AgNO_3$ the difference function of equation (4) is given by

$$G_{Ag}(r) = 0.0027g_{AgO}(r) + 0.0052g_{AgD}(r) + 0.0002g_{AgX}(r)$$
$$+ 0.0001g_{AgAg}(r) - 0.082. \tag{4'}$$

Interpretation follows that of the earlier study, and we are led to the conclusion that the Ag–O and Ag–D nearest-neighbour distances are 2.40 ± 0.02 Å and 2.90 ± 0.05 Å, respectively. Integration over the range $r_1 = 2.1$ Å to $r_2 = 3.35$ Å (equation (5)) gives a co-ordination number of 3.7 ± 0.5. We conclude that to a good approximation the co-ordination of the Ag^+ ion is independent of anion.

4.2. Isomorphism between $Ag^+_{[aq]}$ and $Na^+_{[aq]}$, and Na^+ hydration

The values of the effective ionic radii and the results of previous diffraction experiments suggest that the substitution of Ag^+ for Na^+ can be used to determine the structure
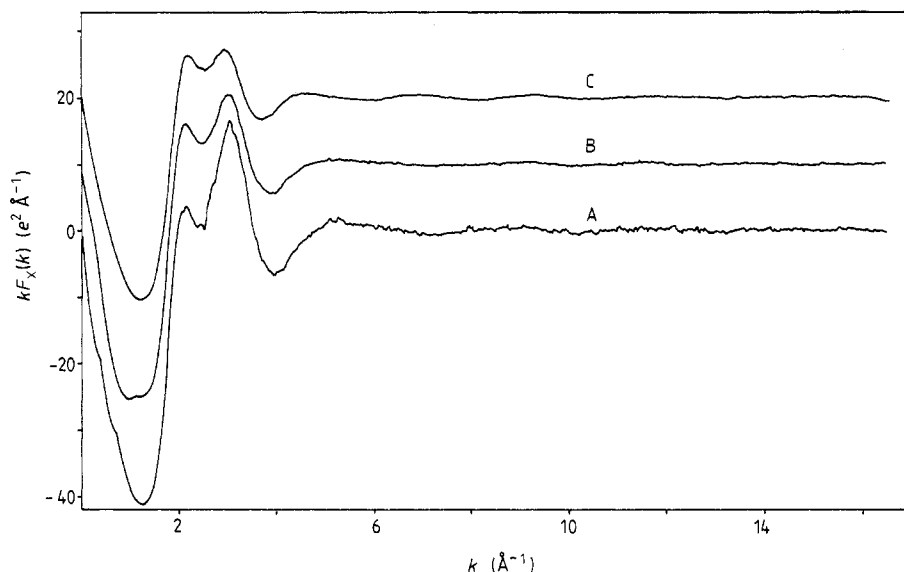
Figure 2. The x-ray structure factors, $kF_x(k)$ for 3.16M: curve A, AgNO₃; curve B, a 50:50 mixture of AgNO₃ and NaNO₃ (displaced by $10\,e^2\,\text{Å}^{-1}$); curve C, NaNO₃ (displaced by $20\,e^2\,\text{Å}^{-1}$).

around Na⁺ in water (Shannon and Prewitt 1969, Huheey 1975, Yamaguchi *et al* 1984, Caminiti *et al* 1980). However, because the Pauling radii and hydration energies of the ions are different ($0.98\,\text{Å}$ and $-407\,\text{kJ mol}^{-1}$ for Na⁺; $1.26\,\text{Å}$ and $474\,\text{kJ mol}^{-1}$ for Ag⁺) the chemistries of the two ions are, in general, dissimilar.

Relative to those of an Na⁺ ion, the outer electrons of an Ag⁺ ion are weakly bound and extend to larger distances from the nucleus. For this reason many compounds of Ag⁺ have a marked covalent character, and are insoluble in water (Cotton and Wilkinson 1972). This is not the case for AgNO₃, for which the concentration of a saturated aqueous solution is about 14M. It is probable, however, that even in this system the ion–solvent interactions result in considerable overlap of the respective electron densities. It is this degree of chemical bonding between Ag⁺ and H₂O which reduces the effective radius of the ion and makes structural isomorphism with Na⁺ possible in these systems.

A practical disadvantage of the substitution of Ag⁺ for Na⁺ is that the results are less sensitive to the structure around the species of most interest: Na⁺. However, as mentioned earlier, isotopic substitution is not possible for this ion and conventional methods of x-ray diffraction are not able to resolve fully the structure around Na⁺ ions (Caminiti *et al* 1980).

Solutions of 3.1 molar AgNO₃ (I), NaNO₃ (II) and a 50:50 mix of I and II (III) were prepared, and the data analysed to give the $F_x(k)$ (figure 2). Two first-order difference functions, $\tilde{\Delta}_M(k)$, and their Fourier transforms, $\tilde{G}_{MO}(r)$, were obtained from the combinations $[F_X^I(k) - F_X^{II}(k)]$ and $[F_X^{III}(k) - F_X^{II}(k)]$ (figures 3 and 4). Comparison between the two $\tilde{G}_{MO}(r)$ shows that although the peak position is the same ($2.40 \pm 0.05\,\text{Å}$), increasing the relative weighting of Na⁺ reduces the measured nearest-neighbour cation–oxygen correlation, $\tilde{g}_{MO}(r)$. $g_{AgO}(r)$ is therefore not identical to $g_{NaO}(r)$. This is confirmed by comparing the x-ray result with the neutron distribution function, $G_{Ag}(r)$, of § 4.1 (figure 5). It is possible that the difference between $g_{AgO}(r)$ and $g_{NaO}(r)$ is a result of some inner-sphere complexing around Ag⁺ (Yamaguchi *et al*

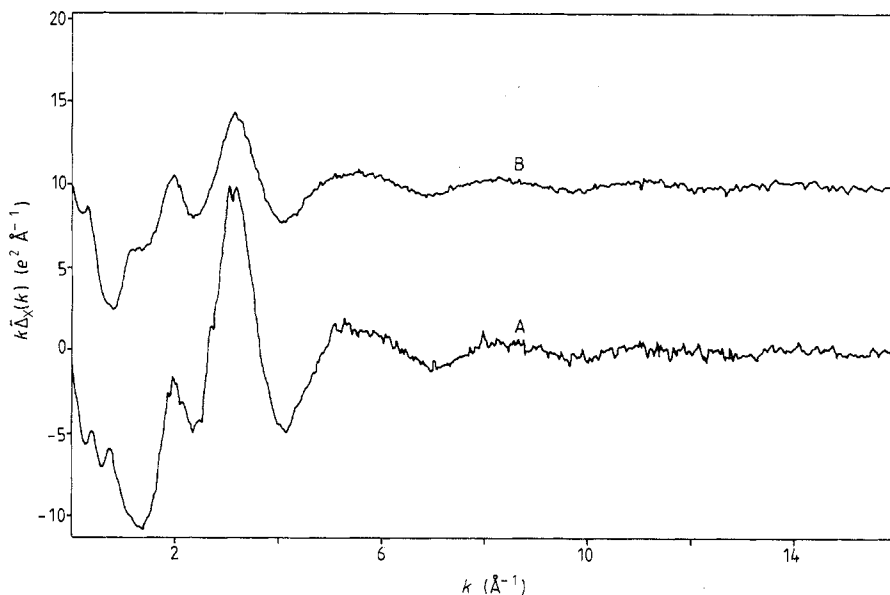**Figure 3.** The x-ray first-order difference functions, $k\tilde{\Delta}_M(k)$, for 3.13M solutions of AgNO$_3$/NaNO$_3$ (table 1). Curve A is for solutions [I − II] and curve B for solutions [III − II] (displaced by 10 e^2 Å^{-1}).
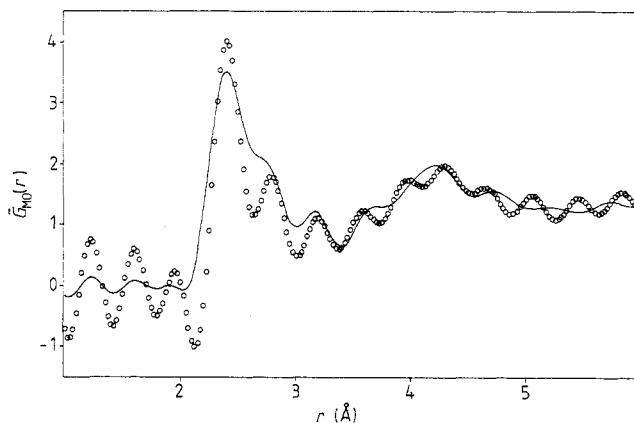

Figure 4. The x-ray first-order difference radial distribution functions, $\tilde{G}_{MO}(r)$, for 3.13M solutions of AgNO$_3$/NaNO$_3$. The full curve is for solutions [I − II] and the open circles are for solutions [III − II] (table 1).

1984). However, it is difficult to demonstrate this effect using x-ray diffraction techniques, since it is not possible to distinguish between the oxygen atoms of water and those of nitrate ions. Bearing these observations in mind we proceed with caution in the interpretation of $\tilde{G}_{MO}(r)$.

Since the cation–oxygen peak is not well defined above 2.6 Å (figure 4), the running co-ordination number was evaluated by two methods. In the first the cation–oxygen peak was reflected from 2.1 Å about its maximum at 2.40 Å, to cover the range $r_1 =$ 2.1 Å to $r_2 = 2.7$ Å (equation (8)). In the second method the measured $\tilde{G}_{MO}(r)$ was used for the full integration between the limits $r_1 = 2.1$ Å and $r_2 = 2.8$ Å. The respective
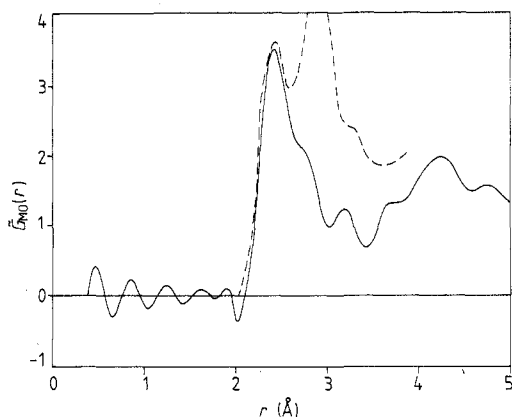
Figure 5. The x-ray (full curve) and neutron (broken curve) first-order difference distribution functions for 3.13M solutions of AgNO₃ and NaNO₃.

values obtained by these two techniques are 3.9 ± 0.5 and 4.3 ± 0.5 for solutions $[I - II]$ and 3.7 ± 0.5 and 4.0 ± 0.5 for solutions $[III - II]$. Since the peaks in question were not symmetric about 2.40 Å, the second may have been more reliable.

The values of $\bar{n}_M^O$ are weighted strongly to Ag^+ rather than Na^+, since from equations (7) and (8)

$$\bar{n}_M^O \simeq \bar{n}_M^O - (\bar{n}_{M'}^O - \bar{n}_M^O)f_{M'}(0)/[f_M(0) - f_{M'}(0)]. \tag{10}$$

The approximation involved is that $H_{f',f-f'}(r)$ is a delta function, $\delta(r)$. Although this is not the case for Ag^+ and Na^+ (figure 6(a)), $H_{f',f-f'}(r)$ has a width that is smaller than the cation–oxygen correlation in question. The convolution of $[g_{NaO}(r) - g_{AgO}(r)]$ with $H_{f',f-f'}(r)$ therefore has a shape that is very similar to $[g_{NaO}(r) - g_{AgO}(r)]$ itself. This is illustrated in figure 6(b), where the distributions, $g_{MO}(r)$, are both modelled by Gaussians with a half width of 0.25 Å. The approximation can therefore be made

$$\bar{n}_{Na}^O \simeq \bar{n}_{Ag}^O - 2\tilde{\Delta}n_M^O \tag{11}$$

where $\tilde{\Delta}n_{MO}$ is the difference between the values of $\bar{n}_M^O$ obtained from the $\tilde{G}_{MO}(r)$ of solutions $[I - II]$ and $[III - II]$, respectively. Taking $\bar{n}_{Ag}^O$ as 4.3 (present work and Sandstrom *et al* 1985) and $\tilde{\Delta}n_M^O$ as 0.3 gives $\bar{n}_{Na}^O$ as 4.9 ± 1.0.

Because hydrogen is a weak scatterer of x-rays it was not possible to isolate the M–H correlation, although there is a shoulder in the $\tilde{G}_{MO}(r)$ at $r = 2.8$ Å. There is no direct evidence for any ion pairing, as was suggested by Yamaguchi *et al* 1984.

4.3. Comparison between alkali ion co-ordination and the structure of water

The present results can be compared with those obtained for other alkali metal ions in aqueous solutions, and used to quantify the differences between structure-making (positive hydration) and structure-breaking (negative hydration) in terms of the local structure (Frank and Wen 1957). This distrinction is clearly visible in the neutron and x-ray distribution functions presented in figure 7. For reference the water–water structure, as measured by x-ray diffraction, is also shown in this diagram.

It is assumed that the shortest range correlations in $G_M(r)$ or $\tilde{G}_{MO}(r)$ are due to $g_{MO}(r)$, and that the contribution from hydrogen is small in the x-ray functions. For the case of Li^+ the results of Newsome *et al* (1981) are used. The first M–D peak in $G_M(r)$ is easily identified as being at 2.60 Å, and it does not overlap with the M–O feature at 1.95 Å. Hence, for the range 1.6 Å $< r < 2.4$ Å, $g_{MO}(r)$ is taken as $G_M(r)/A$. In the

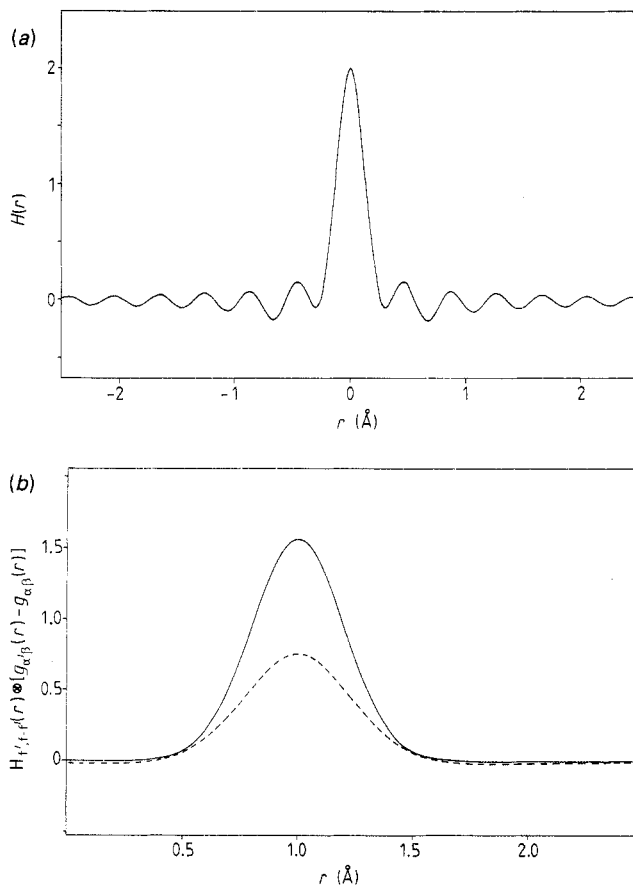**Figure 6.** (*a*) The function $H_{f',f-f'}(r)$ for Ag^+ and Na^+ in 3.13M aqueous solutions. (*b*) The convolution of $H_{f',f-f'}(r)$ with $[g_{\alpha'\beta}(r) - g_{\alpha\beta}(r)]$, where α is Ag^+ and α' is Na^+. $g_{\alpha'\beta}(r) = 5.0\,e^{-(r-r')/0.25^2}$ and $g_{\alpha\beta}(r) = 4.0\,e^{-(r-r')^2/0.25^2}$.
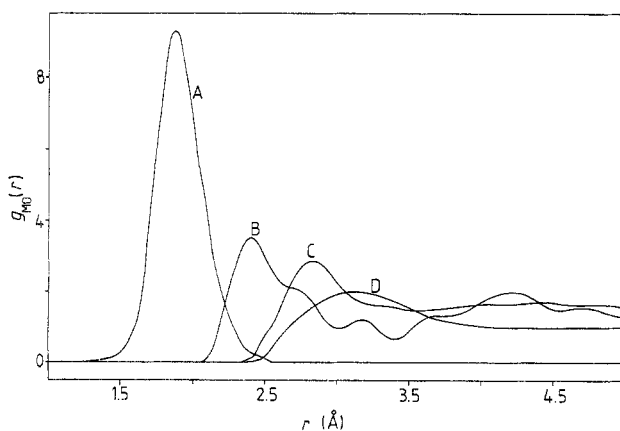

Figure 7. The $g_{MO}(r)$ for the alkali metal ions in aqueous solution. Curve A, Li^+ (neutron data of Newsome *et al* (1980)); curve B, Na^+ (present x-ray data; curve C, pure water (x-ray data of Skipper (1987)); curve D, K^+ (neutron data of Neilson and Skipper (1985)).

Table 2. The characteristics of the solutions used in the x-ray and neutron diffraction experiments.

Label	Solution	Molality	Sample density $(g\,cm^{-3})$	Linear absorption coefficient μ (cm^{-1})	Volume of unit composition V (Å^3)
I	3.13M AgNO₃ in H₂O	3.515	1.429	7.07	10.075
II	3.13M NaNO₃ in H₂O	3.499	1.165	1.37	10.033
III	3.13M AgNO₃:NaNO₃ in H₂O	3.507	1.303	5.75	10.005

neutron study of K^+ by Neilson and Skipper (1985) there is no obvious distinction between the nearest neighbour M–O and M–D correlations in the smoothed $G_M(r)$ function. For the purposes of the present work it is therefore assumed that there is no preferential orientation for the water molecules around the cation, and that $g_{MO}(r)$ is approximated by $G_M(r)/(A + B)$. The results for Na^+ were obtained directly from the x-ray difference functions described in § 4.2. Those for liquid water were obtained from the x-ray diffraction study of Skipper (1987).

These results add weight to the general views held about the relative strengths of hydration for the alkali metal ions. Li^+ and Na^+ are clearly more strongly hydrated than K^+, which is a weakly structure-breaking cation.

A large number of computer simulations have been carried out on the alkali metal ions in water. It would be expected that the most successful of these would invole a model of the solvent which allows for the polarisation of the molecules by the ions. This is the case in the Monte Carlo simulations of Clementi and Barsotti (1978) and the molecular dynamics simulations of Impey *et al* (1980). In these the water-water inter-actions are represented by the MCY model of Matsuoka *et al* (1976), in which the dipole moment of the molecules is 2.19 D. The ion–water interactions are based on the *ab initio* quantum mechanical calculations of Kistenmacher *et al* (1973), for which the dipole moment of water next to the ion ranges from 2.34 D for K^+ to 2.51 D for Li^+.

The nearest neighbour ion–water distances obtained from these calculations are in good agreement with the experimental values (table 2), but the trends in co-ordination numbers are not. This may be due to the treatment of bulk-water. It has been postulated by Rossky (1983) that the same charge distribution (and hence dipole moment) should be used for all water in an aqueous solution. Such an approach has been used by Bounds (1984), who employed a constant dipole moment, μ, of 2.19 D in all his simulations. In solutions containing Li^+ or Na^+ a larger value would be more realistic, since these ions are strongly polarising. For K^+, which is found to be weakly structure-breaking, μ would be expected to be less than 2.19 D.

4.4. Cation–cation structure in silver nitrate and sodium nitrate solutions

Although the structural isomorphism between Ag^+ and Na^+ is only approximate, a second-order difference was made and $\tilde{S}_{MM}(k)$ determined. The analysis followed that of Skipper *et al* (1986), with $S_{MM}(0)$ being taken as -49.8 (Beeby 1973). The functions $\tilde{S}_{MM}(k)$ and $\tilde{g}_{MM}(r)$ are plotted in figures 8 and 9. A residual of the M–O correlation was present in the $\tilde{g}_{MM}(r)$ obtained from the raw data, and could have been caused by an error of $\sim 2\%$ in the normalisation of the difference functions, or departures from isomorphism. The effect on $\tilde{S}_{MM}(k)$ of removing this feature, by setting $\tilde{g}_{MM}(r)$ to zero

Table 3. The structure around the alkali metal ions in concentrated aqueous solutions (r_{MO} = average nearest-neighbour cation–oxygen separation; n_{MO} = average nearest-neighbour cation–oxygen co-ordination number; c_M = ratio of cations to water molecules).

		Molecular dynamics		Monte Carlo		Experiments	
Reference		a	b	c	d	e,f,g	
Li$^+$	r_{MO}	2.04	1.98	1.95	2.05	1.95	
	$\bar{n}_M^O$	6.0	5.3	4.0	6.0	6.0	
	c_M	1:64	1:125	1:200	1:215	1:16	
Na$^+$	r_{MO}	2.35	2.29	2.33	2.30	2.40	
	$\bar{n}_M^O$	6.2	6.0	4.3	6.0	4.9	
	c_M	1:64	1:125	1:200	1:215	1:18	
K$^+$	r_{MO}	2.86	2.76	2.69	2.92	3.1	
	$\bar{n}_M^O$	7.6	7.5	5.1	6.3	3.9	
	c_M	1:64	1:125	1:200	1:215	1:14	

a Bounds 1985.   e Newsome *et al* 1980.
b Impey *et al* 1983.   f Present work.
c Clementi and Barsotti 1978.   g Neilson and Skipper 1984.
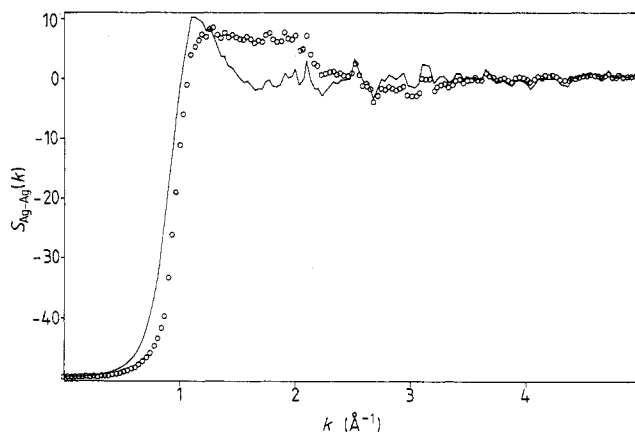d Mezei and Beveridge 1971.

Figure 8. $\tilde{S}_{Ag-Ag}(k)$ for 3.13M AgNO$_3$. Open circles, raw data: full curve, result of cutting off $\tilde{g}_{MM}(r)$ at 3.0 Å and back Fourier transformation.

below 3.0 Å and back Fourier transformation, is shown in figure 8. The presence of a systematic error in $\tilde{S}_{MM}(k)$ makes it difficult to give a realistic estimate of the errors in $\tilde{g}_{MM}(r)$.

The positions of the cut off (r_{co}) and first peak (r_p) in $\tilde{g}_{MM}(r)$ are r_{co} = 3.5 Å and r_p = 6.5 Å. These values compare with 3.8 Å and 7.0 Å respectively for 3.88M NiCl$_2$ solutions (Skipper 1987), and suggest that the hydrated Ag$^+$ is 'softer' than Ni^{2+}. This is reasonable, as Ag$^+$ is more weakly hydrated.

The function $\tilde{g}_{MM}(r)$ is the first experimental cation–cation correlation function for a 1:1 electrolyte solution, and there is no suitable theoretical function for comparison. A model with properly adjusted soft-sphere ions in a primitive solvent might be reasonable for the system, since this has been found to reproduce the essential properties of $g_{MM}(r)$ in a 4m (molal) NiCl$_2$ solution (Skipper 1987).
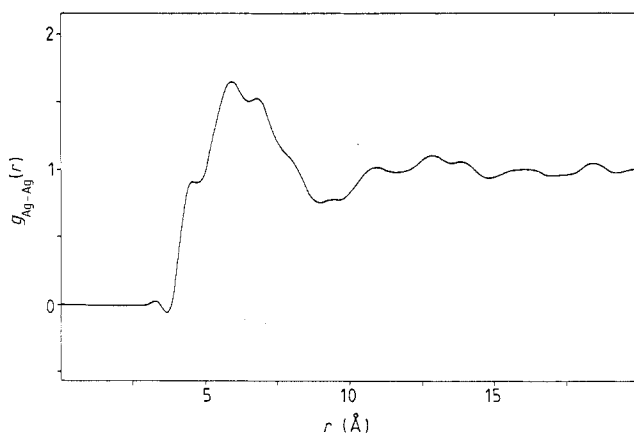
Figure 9. $\tilde{g}_{\mathrm{Ag-Ag}}(r)$ for 3.1 molar $AgNO_3$. This is the result of Fourier transformation of the full curve in figure 8.

6. Conclusions

The first-order difference method of neutron diffraction based on isotopic substitution was applied to Ag^+ in 3.16M solutions of $AgNO_3$ in heavy water. The results show that Ag^+ has a weak co-ordination shell containing about four water molecules. This is consistent with the results obtained when ClO_4^- was used as the counter-ion (Sandstrom *et al* 1985).

The difference method of x-ray diffraction based on isomorphic substitution was applied to 3.13M solutions of $AgNO_3$ and $NaNO_3$. Analysis of the data showed that although Na^+ and Ag^+ are not perfect structural isomorphs, an understanding of Na^+ hydration and Ag^+–Ag^+ correlations can be obtained. The nearest-neighbour configuration of Na^+ gave an Na^+–O distance of 2.40 ± 0.05 Å and a co-ordination number of 4.9 ± 1.0, in agreement with the earlier work of Caminiti *et al* (1980). These results were compared with those of computer simulations. The most successful models of the cation–water interactions involve a polarised water molecule, although further refinement appears to be necessary (Impey *et al* 1983, Clementi and Barsotti 1978). The second-order difference analysis gave a distribution function, $\tilde{g}_{\mathrm{MM}}(r)$, with a cut off at 3.5 Å and a first peak centred at 6.5 Å.

In future it is expected that wider use will be made of the method of isomorphic substitution, and that advantage will be taken of the improvements offered by synchrotron sources.

Acknowledgments

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