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X-ray and neutron scattering studies of the hydration structure of alkali ions in concentrated aqueous solutions

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Abstract

The presence of ions in water provides a rich and varied environment in which many natural processes occur with important consequences in biology, geology and chemistry. This article will focus on the structural properties of ions in water and it will be shown how the 'difference' methods of neutron diffraction with isotopic substitution (NDIS) and anomalous X-ray diffraction (AXD) can be used to obtain direct information regarding the radial pair distribution functions of many cations and anions in solution. This information can subsequently be used to calculate coordination numbers and to determine ion–water conformation in great detail. As well as enabling comparisons to be made amongst ions in particular groups in the periodic table, such information can also be contrasted with results provided by molecular dynamics (MD) simulation techniques. To illustrate the power of these 'difference' methods, reference will be made to the alkali group of ions, all of which have been successfully investigated by the above methods, with the exception of the radioactive element francium. Additional comments will be made on how NDIS measurements are currently being combined with MD simulations to determine the structure around complex ions and molecules, many of which are common in biological systems.

Keywords: Aqueous solution; Ionic hydration; Neutron scattering; X-ray scattering; Isotopic substitution

1. Introduction

As testimony to the importance of ions in the natural world, one only has to consider the range of topics covered in the symposium for which the work described in this paper is reproduced. Although many methods are available to study the properties of ions in solution, we would argue that from an experimental viewpoint the most fruitful of these are associated with neutron and X-ray scattering methods [1]. In the following paper, we restate the salient points of the methods we have developed, and explain why we believe these provide the best understanding we have currently on the structure of ionic hydration.

The methods themselves exploit the basic properties of the atoms and nuclei which make up the system: neutrons scatter isotropically from the nuclei via the strong interaction, whereas X-rays are scattered anisotropically by the atomic electrons via the electromagnetic interaction. These properties ensure that in neutron diffraction (ND) experiments the data obtained can be directly related via Fourier transformation to the pairwise structure of a solution. Moreover, by selective use of isotopes, the structure around particular ionic species can be obtained at the highest possible resolution by the difference methods of neutron diffraction and isotopic substitution (NDIS) [2]. By contrast, X-ray diffraction (XRD) experiments provide structural information which is indirectly related to the structure via a convolution of the partial structure factors and the atomic form factors of the atoms of the solution (see next section). It is possible, by a judicious choice of isomorphic species [3] or by exploitation of the anomalous scattering properties of heavy ions [4], to significantly improve the resolution of ionic structure and gain information which is almost equivalent to that obtained from NDIS.

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Although X-ray and neutron scattering can be regarded as the most suitable experimental probes of interatomic structure in liquids, many other experimental methods have been employed to determine albeit indirectly, the properties of ions in solution. Indeed, much of the current language used to define and contrast ions within and amongst groups of the periodic table originates from macroscopic measurements of enthalpy and entropy of hydration, together with results for viscosity, mobility, etc., of solutions [5,6]. Additionally spectroscopic methods such as NMR, EXAFS, IR absorption spectroscopy, Brillouin light scattering, etc., have been crucial in obtaining information on structural and dynamical information [7,8]. However, it must be underlined that such methods require many assumptions when analysing and interpreting the experimental data.

It is also clear that much progress in this area has been due to the significant role played by computer simulation [9,10]. Molecular modelling of a system of ions and water molecules in a given statistical mechanical ensemble provides exact information for a particular interaction potential. The validity of this approach can be justified by how well the results fit experimental data.

In this article, we present results derived from X-ray and neutron diffraction experiments using the methods described in the following section. In order to illustrate the power of these methods, reference is made to the alkali series of ions.

2. Diffraction methods

In a diffraction experiment in an aqueous solution of a salt (MX_n) in water (H_2O), there are 10 structure factors $S_{ij}(q)$ each of which contributes to a varying degree to the scattering pattern [2]. The coherent cross section of the scattering can be written as

$$\begin{aligned}F(q) &= \sum_i \sum_j f_i f_j c_i c_j (S_{ij}(q)-1)\\ &= c_H^2 f_H^2 (S_{HH}(q)-1) + 2c_H c_0 f_H f_0 (S_{H0}(q)-1)\\ &\quad + c_0^2 f_0^2 (S_{00}(q)-1) + 2c_H c_M f_H f_M (S_{HM}(q)-1)\\ &\quad + 2c_0 c_M f_0 f_M (S_{0M}(q)-1) + 2c_H c_X f_H f_X (S_{HX}(q)-1)\\ &\quad + 2c_0 c_X f_0 f_X (S_{0X}(q)-1) + c_M^2 f_M^2 (S_{MM}(q)-1)\\ &\quad + 2c_M c_X f_M f_X (S_{MX}(q)-1) + c_X^2 f_X^2 (S_{XX}(q)-1) \qquad (1)\end{aligned}$$

where c_i is the atomic concentration of species 'i' whose q-independent neutron coherent scattering length (generally labelled b) or q-dependent X-ray atomic form factor is $f_i(q)$. $S_{ij}(q)$ is the partial structure factor of species 'i' and 'j' and is related to the partial pair radial distribution function $g_{ij}(r)$ via the equation

$$g_{ij}(r)-1 = \frac{1}{2\pi\rho r}\int_0^\infty (S_{ij}(q)-1)q\sin qr dq \qquad (2)$$

where ρ is the atomic number density of the solution and at molal concentrations has a value of typically about 0.1 Å^{-3}.

The coordination number of α atoms around β is defined for the range $r_1 \leq r(\text{Å}) \leq r_2$ as

$$\bar{n}_\beta^\alpha = 4\pi c_\alpha \rho \int_{r_1}^{r_2} g_{\alpha\beta}(r) r^2 \mathrm{d}r \qquad (3)$$

A hydration number for an ion I in solution can therefore be calculated from either

$$\bar{n}_I^O = 4\pi\rho c_O \int_{r_1}^{r_2} g_{IO}(r) r^2 \mathrm{d}r \qquad (4a)$$

or

$$\bar{n}_I^H = 4\pi\rho c_H \int_{r_1}^{r_2} g_{IH}(r) r^2 \mathrm{d}r \qquad (4b)$$

depending on which of the ion–water correlations of the $g_{\alpha\beta}(r)$ values can be more easily identified.

Before discussing the composition of $F(q)$, we note that it is calculated from the following equation:

$$F(q) = \alpha(q)[I(q) + \beta(q)] \qquad (5)$$

where $I(q)$ is the intensity of neutrons or X-rays measured in a detector situated at an angle 2θ to the direction of the incident beam whose wavelength is λ and $q = 4\pi\sin(\theta)/\lambda$. $\alpha(q)$ and $\beta(q)$ are correction factors (Table 1) which can be calculated in a straightforward way [11]. Significantly, for neutron scattering the correction terms are easier to determine for heavy water solutions than for light water solutions because incoherent scattering and inelastic scattering is much less for the deuteron than for the proton. And prior to the advent of fast computing techniques much of the early studies of ionic hydration were carried out in heavy water. However, it is now possible to use light water and indeed null water solutions to study details of the individual ion–oxygen and ion–hydrogen correlations, [12,13]. Refinement of the calculations of $F(q)$ and differences between $F(q)$ values can also be made; these involve the use of 'sum rules' which arise from the fact that $S_{\alpha\beta}(q) \to 1$ as $q \to \infty$, and $g_{\alpha\beta}(r) = 0$ for $r < r_{\min}$ where $r_{\min}$ is some minimum distance within which there is zero probability of finding another particle β around the original particle α. An additional correction which involves the self scattering H_2O can also be used for mixtures of H_2O and D_2O such as in null water to improve the accuracy of the information obtained for coordination numbers.

One can see from Eq. (1) that the first three terms in $F(q)$ represent the water structure, the following four are the ionic hydration structure and the last three describe correlations between the ions themselves. In order to see how each of these groups of terms contribute to the scattering it is helpful to consider a particular solution, and as an example we have

Table 1
Physical origins of corrections terms $\alpha(q)$ and $\beta(q)$ in the calculation of $F(q)$

	$\alpha(q)$	$\beta(q)$
Neutrons	Sample geometry Apparatus geometry Absorption in sample and container	Multiple scattering Incoherent scattering Inelastic (Placzek) scattering
X-rays	Sample geometry Apparatus geometry Absorption in sample and container Polarization	Compton scattering Multiple scattering

Table 2
Contributions to $F(q)$ (Eq. (1)) for a 3 m aqueous solution of sodium chloride

	X-rays (%)	Neutrons (%)
Water	73	92
Ion hydration	25	7
Ion–ion	2	1

selected a 3 molal (m) aqueous solution of sodium chloride. As Table 2 shows, the X-ray and neutron scattering patterns are dominated mainly by the water structure itself, with contributions to the ionic hydration of less than 10% to the latter and less than 25% to the former. By breaking down these three contributions further, one can appreciate how individual pair correlations contribute. It is of additional interest to note that because of the differing scattering properties of X-rays and neutrons that the individual partial structure factors of water will contribute differently to a scattering pattern. As Fig. 1a shows, in the case of water – for X-rays, the dominant term in the scattering is that due to O–O correlations (~64%) with contributions of ~32% for O–H and ~4% for H–H%. By contrast a neutron scattering pattern is dominated by H–H correlations and O–H correlations with the O–O contribution ~8%. Thus if one wishes to study the water structure it is likely that X-ray diffraction will give the most useful information on $g_{OO}(r)$. However, as Soper, Ricci and colleagues have shown, NDIS studies based on isotopic substitution of the hydrogen atoms of the water molecules can also be used to determine $g_{OO}(r)$ to a good approximation [14,15]. By similar means, useful studies of perturbations to the water network due to the presence of ions in solutions have also been carried out [16]. It is also possible to study the details of the water molecule itself with X-rays as the O–H intramolecular correlation in $g_{OH}(r)$ can be readily determined [17].

Although total neutron diffraction studies of ionic hydration in aqueous electrolytes have been carried out, they are usually less informative than total X-ray diffraction. This is due to the similarity in the strength of neutron scattering which is directly related to the scattering lengths b (=f) of the atomic nuclei of the ions (Eq. (1)). Therefore, models are required to assist in the interpretation of data.

It is also clear from Table 2 that any attempt to obtain structural information on ionic hydration and the ion–ion correlations from a single measurement of $F(q)$ will require sophisticated modelling procedures. Indeed this remains the case and procedures are used which are based on results from single hydrated salt crystals. The ability to resolve ion structure does however improve for X-rays when studying structure in salts of heavy ions especially at higher concentrations. However, even here, significant contributions from the oxygen atoms of the water molecules prevent the extraction of details of the ionic structure and modelling is still required.

Fig. 1b shows the relative contributions which correlations between the cations and anions and all other species make to the X-ray and neutron scattering patterns of a 3 m aqueous solution of sodium chloride. From this, one observes that there are significant contributions from the ion hydrogen and the ion oxygen correlations for the case of neutron scattering, whereas the X-ray pattern will be dominated by the ion–oxygen terms with much smaller contributions from ion hydrogen and ion–ion terms. Of course, the extraction of ionic structure from X-ray data becomes easier for solutions containing ions with large numbers of electrons such as Cs^+, I^-, etc.

When all this information is taken together, one concludes that it will not be possible from a single X-ray or neutron diffraction pattern to gain definitive and detailed information directly about the ion hydration in a solution. Thus, if one wishes to obtain information on ion structure from a scattering experiment other methods need to be used.

3. Isotopic substitution

In the 1970s, the difference methods of neutron diffraction and isotopic substitution (NDIS) were introduced to overcome the need to use sophisticated model procedures alluded to above. By selective use of isotopes, it was shown that a first order difference between neutron diffraction patterns of two isotopically distinct salts in water could be used to calculate the total radial distribution fraction $G_I(r)$ of an ion, I [2,18] where

$$G_I(r) = Ag_{I0}(r) + Bg_{IH}(r) + Cg_{IJ}(r) + Dg_{II}(r) - E \qquad (6)$$

where $E=A+B+C+D$, and J is the counter ion.

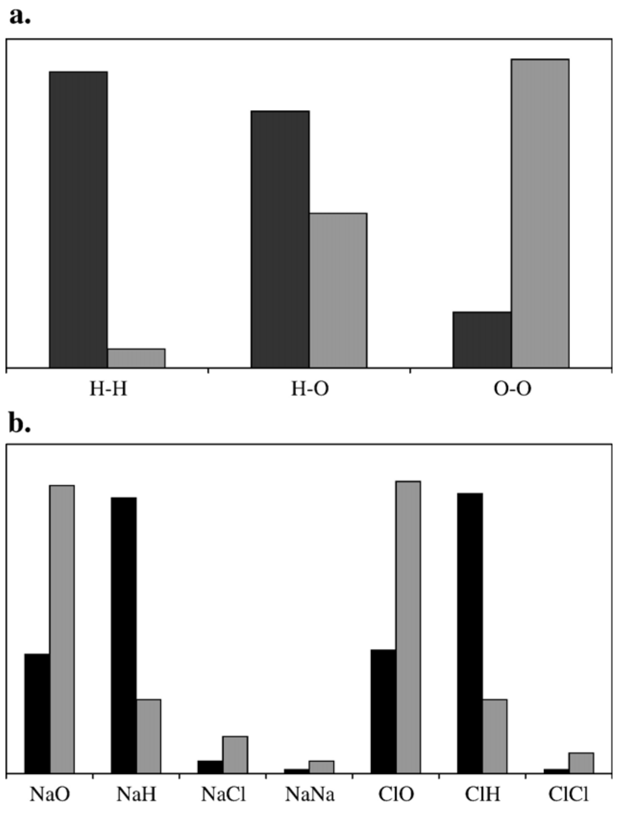

Fig. 1. (a) Relative contributions of water molecule pair correlations to total X-ray (grey) and total neutron (black) scattering patterns for 3 m NaCl. (b) Relative contributions of ion–H_2O and ion–ion pair correlations to X-ray (grey) and neutron (black) scattering patterns in 3 m NaCl.

The first sets of experiments were carried out in heavy water in order to overcome problems due to the high spin incoherent scattering and inelastic (Placzek) scattering of hydrogen nuclei. In recent years, with the new generation of detectors and faster computational facilities the situation is less of a problem and now salt solutions in both H_2O and D_2O are studied with almost equal accuracy.

The scattering lengths of hydrogen and deuterium are −3.74 fm and +6.67 fm respectively. It is thus possible to make up a null mixture of H_2O and D_2O such that all correlations to the hydrogen atoms of the system do not contribute to the coherent scattering pattern. As a result the Fourier transformation of the structure factor $F_{\mathrm{null}}(q)$ for the solution can be written as

$$G(r) = Ag_{00}(r) + Bg_{0M}(r) + Cg_{0X}(r) + Dg_{MM}(r) + Eg_{MX}(r) + Fg_{XX}(r) - H \quad (7)$$

where $H=A+B+C+D+E+F$.

And it can be further shown [13] that by a suitably scaled subtraction of the $g_{00}(r)$ for a pure null water sample, one can calculate the approximate function

$$\Delta G(r) \cong Jg_{M0}(r) + Kg_{X0}(r) - (J + K) \quad (8)$$

where we have assumed that at normal concentrations the contribution to the structure from ion–ion correlations can be neglected.

The success of NDIS experiments depends crucially on several factors. These include (i) high quality samples whose composition is accurately known in terms of atomic concentration and isotope content, (ii) a high flux neutron source which can provide sufficient statistical accuracy in the data, and (iii) stable instrumentation so that data are highly reproducible during the course of an experiment which takes typically ~10 h/sample. Although the NDIS methods can also be used via H/D substitution of water molecules themselves, to study how the water structure is modified by the presence of ions, we will not be concerned with this here as information derived about ion structure itself is necessarily less directly obtained.

4. Isomorphic substitution

Difference methods based on an isomorphic substitution can be applied to data from both X-ray and neutron scattering experiments. The idea of structural equivalence between certain types of ions in water was first tested by Bol and coworkers in the 1970s [3]. Since then neutron scattering experiments have been applied successfully to solutions containing the pairs Ni^{2+}/Mg^{2+} and Na^+/Ag^+ [19,20]. The advantage of using neutron scattering is that if one of the pairs is susceptible to the NDIS method then one can establish the accuracy of the information of the hydration structure of the complementary ion.

5. Anomalous scattering

In principle anomalous or resonant scattering techniques can be applied for both X-rays and neutrons. However, the only application to investigations of solution structure that we are aware of has been with X-rays [21]. Although the technique was in principle known about in the 1930s, its application to liquids has been greatly facilitated by the commissioning of diffraction instruments on a 3rd generation synchrotron source sited the ESRF facility in Grenoble, France.

The method itself exploits the fact that the scattering of X-rays by atoms is strongly modified when the X-ray energy, E (or wavelength, λ) is close to an atomic absorption edge. In that case, the total atomic form factor f, which characterises the interaction between X-rays and the electrons of the atom, is defined by:

$$f(q,E) = f_{\mathrm{o}}(q) + f'(q,E) + if''(q,E) \quad (9)$$

where $f_{\mathrm{o}}(q)$ is the normal atomic form factor, $f'(q, E)$ and $f''(q, E)$ are the dispersion corrections that account for resonant scattering processes. The energy-dependent terms are called 'anomalous' and can be obtained classically by first measuring the attenuation coefficient which is directly related to the imaginary component $f''(q, E)$ and then using a Kramers–Kronig relation to calculate $f'(q, E)$ [22]. Two possibilities can now be considered:

If the energy of the incoming X-rays is allowed to change only below the edge, it is mainly $f'(q, E)$ that changes. By fixing E to a value of about 5 eV below the absorption edge and varying q (or θ) as in a normal diffraction experiment, one obtains a first scattering pattern for a given $f'(q, E)$ for the atom or ion of interest. The value of E is then altered by a further few hundred eV below the absorption edge, and the value of $f''(q, E^N)$ is systematically changed to a larger value. A second scattering experiment on the same sample gives a slightly different pattern. The difference between the two scattering patterns is then calculated, and its Fourier transformation related to the hydration structure around the specific atom or ion. The technique is based on similar principles to NDIS, but is not limited by availability of isotopes. However, it is constrained by the q dependence of the form factors, and is only applicable to atoms or ions with atomic numbers >30, which in turn sets a limit on the q range of the diffraction data.

The actual structure function ($\tilde{G}_\alpha(r)$) is calculated from the Fourier transformation of the sum over partial structure factors $S_{\alpha\beta}(q)$ convoluted with their q-dependent X-ray atomic form factors. The effect of this convolution is to broaden peaks associated with the real structure as defined by $g_{\alpha\beta}(r)$, and thereby obscure the structural information in the true $G_\alpha(r)$. The peak positions, however, remain unchanged by the convolution process. Despite these drawbacks, we have shown that it is possible to obtain accurate information on interatomic correlations and coordination numbers [4,21]. The anomalous X-ray diffraction (AXD) method becomes exact at the second difference level such as might be used to calculate the solute structure, and provide information to test primitive model calculations of ion structures in solutions.

The second possibility is associated with the resonant absorption term $f''(q, E)$ in Eq. (9) and is the basis for extended X-ray absorption fine structure (EXAFS), which has been successfully applied to many aqueous solutions. The results obtained produce accurate values for near neighbour distances; however, determination of coordination numbers remains a matter of controversy. In contrast to diffraction methods EXAFS spectroscopy is strongly model-dependent, and although Fourier transformation procedures are used, the range of '*q*' space information is much more limited than in straightforward diffraction. However, when EXAFS results are combined with diffraction, especially NDIS they can be effective in elucidating how specific certain structural features of a particular atom or ion change with concentration, and temperature and pressure [23].

6. Discussion

With the exception of francium which is present in the form of short-lived radioactive isotopes in nuclear reactors, all the other alkalis are found in salts on Earth with varying abundances. The most common are salts of sodium, followed by those of potassium and lithium. The ions Na^+ and K^+ are particularly important in biological processes, and lithium salts are useful in the treatment mental illness [24]. Being singly charged, this Group of relatively simple ions has been the subject of many experimental and theoretical studies. The need for good quality structural information is underlined by the observation that in the majority of papers which discuss molecular model computer simulation, the results are frequently discussed in terms of the pair distribution functions [9,10,25] and properties such as coordination numbers and ion–water configurations.

All of the methods discussed above have been used with varying degrees of success to obtain information on ionic hydration of these ions as a function of ionic concentration, counterion type, and temperature and pressure [26]. A summary of the results is found in Table 3.

6.1. Li^+

This ion in particular has been one of the most studied both experimentally and theoretically in terms of its hydration and general coordination properties in aqueous solution [27–30]. It is particularly well suited for study by NDIS, having two suitable isotopes (^6Li and ^7Li) with relatively large differences in their coherent neutron scattering lengths; the only substantial problem is the high absorption of ^6Li which can cause difficulties in the correction of data and the correct determination of $F(q)$ for the ^6Li salt solution. By contrast, as it only has 3 electrons, its correlations to other species in solution do not appear significantly in X-ray scattering patterns, even in relatively highly concentrated solutions. Despite this inherent limitation, total X-ray scattering studies have been made [31,32]. However, care should be taken when considering the accuracy of the information provided.

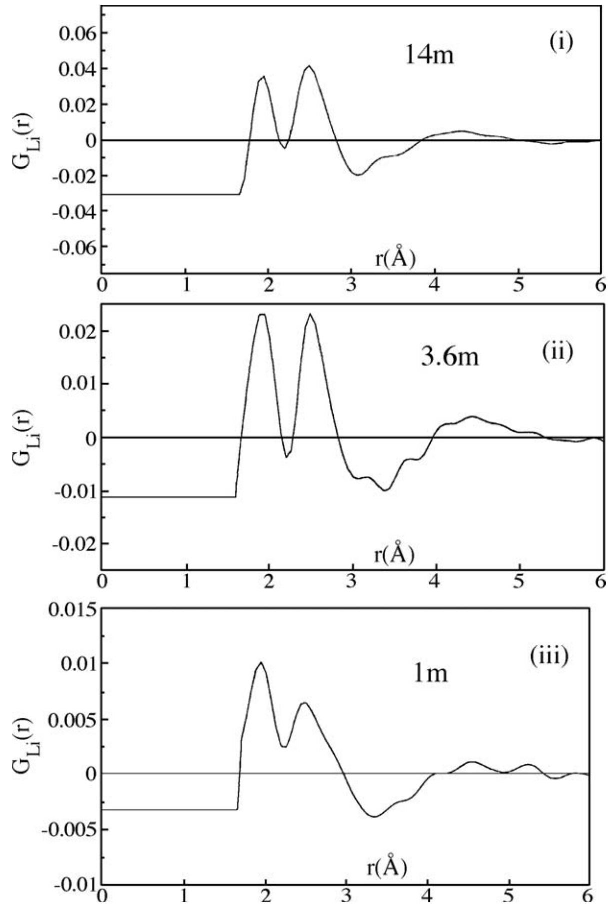

Fig. 2. The total Li^+ radial distribution functions for 3 aqueous solutions of lithium chloride in heavy water (see Howell and Neilson [34] for further details).

The NDIS first difference method has been successfully applied to Li^+ as a function of concentration in aqueous solutions of lithium chloride [33,34]. The results (Fig. 2) show

Table 3
Alkali ion coordination derived from neutron and X-ray scattering methods diffraction isotopic substitution methods

Ion	Solute (m)	r_{IO} (Å)	r_{ID} (Å)	$\bar{n}_O$	Method	Comment	Ref.
Li^+	LiCl (3.6)	1.95 (2)	2.52 (2)	5.5 (5)	NDIS	Second shell	[35]
	LiCl (1)	1.96 (2)	2.52 (2)	6.5 (10)	NDIS	Second shell	[35]
	LiOD (1.14)	1.97 (2)	2.51 (2)	4.5 (5)	NDIS	Second shell	[38]
	Li polyacrylate (1.15)	1.97 (2)	2.51 (2)	4.5 (5)	NDIS	Second shell	[38]
	LiBr (4)	1.94 (2)	2.58 (2)	4.5 (5)	NDIS	Second shell	[39]
Na^+	$NaClO_4$(4)	2.4 (2)	–	4.9 (10)	$ND_{isomorph}$		[20]
	NaCl (4, 2)	2.3 (5)	–	4.9 (10)	ND_{null}		[13]
K^+	KCl (4)	2.9–3.4		5.3 (6)	NDIS	Weak hydration	[47]
Rb^+	RbCl (4)	3.1		6.9	AXD		[21]
Cs^+	CsI(4)	3.1		7.5	AXD	Ion–ion contacts	[52]

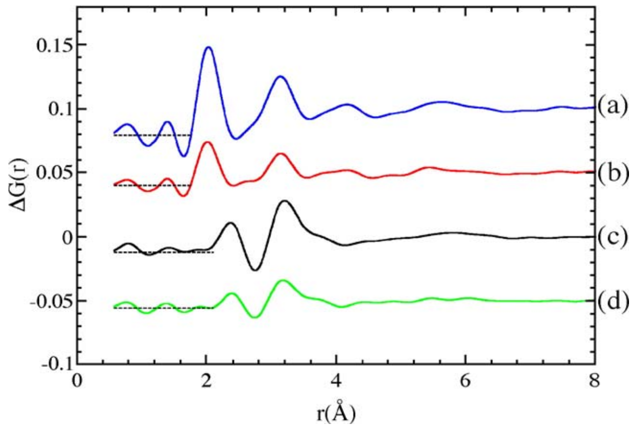

Fig. 3. Distribution functions obtained from ND experiments on nickel chloride and sodium chloride in null water, (a) 3 molal $NiCl_2$ null water solution where $\Delta G(r)=0.0065g_{\mathrm{NiO}}(r)+0.0120g_{\mathrm{ClO}}(r)+0.0011g_{\mathrm{NiCl}}(r)+0.0011g_{\mathrm{ClCl}}(r)-0.0206$ and shifted by 0.10, (b) 1.5 molal $NiCl_2$ null water solution where $\Delta G(r)=0.0033g_{\mathrm{NiO}}(r)+0.0060g_{\mathrm{ClO}}(r)+0.0003g_{\mathrm{NiCl}}(r)+0.0002g_{\mathrm{ClCl}}(r)-0.0103$ and shifted by 0.05, (c) 4 molal NaCl null water solution where $\Delta G(r)=0.0031g_{\mathrm{NaO}}(r)+0.0084g_{\mathrm{ClO}}(r)+0.0004g_{\mathrm{NaCl}}(r)+0.0005g_{\mathrm{ClCl}}(r)-0.0124$, (d) 2 molal NaCl null water solution where $\Delta G(r)=0.0016g_{\mathrm{NaO}}(r)+0.0042g_{\mathrm{ClO}}(r)+0.0002g_{\mathrm{NaCl}}(r))-0.0060$, and shifted by -0.05.

that it coordinates relatively strongly, as might be expected for such a small ion with a relatively high charge density. There is a strong dependence of coordination on concentration: as more water molecules become available as the solution is diluted one finds that the concentration number increases from around 3.3 at 14 m to around 6 at 1 m.

A study of the classical glass $LiCl{\cdot}4D_2O$ gives similar structural results to those of the liquid at the highest concentration [35]. The main features of $G_{\mathrm{Li}}(r)$ in the glass are the two peaks centred at 1.94 ± 0.03 Å and 2.53 ± 0.03 Å, which are identified with oxygen and deuterium atoms respectively. Integration under the first peak gives $n_{\mathrm{Li}}^{-\mathrm{O}}=3.0\pm0.2$ atoms.

A second coordination shell is clearly evident, centred at ≈4.3 Å. This second coordination shell has also been identified by Yamagami et al. [36] in the low temperature liquid.

These results can be compared with studies of Li^+ coordination in systems where the counterion is other than Cl^-. For example, aqueous solutions of Li-polyacrylate and lithium hydroxide [37] give values for the Li^+ hydration number of 4.5(5), with similar distances as in lithium chloride. Similarly, an NDIS study of a 4 m LiBr solution also gives a coordination number closer to 4 than those in lithium chloride at similar concentrations [38]. Because of the wide interest in this ion, many theoretical and simulation studies have been carried out [29,30,39,40]. The predominant view, which is mainly based mainly on arguments to do with the ion's solvation energy, is that at high dilution Li^+ should be coordinated to 4 water molecules. And although some simulations do give a so-called 'optimal' value of 6, they can only be made to do this by allowing for a more relaxed configuration with longer ion oxygen and ion hydrogen distances [41].

It is important to note that in a re-analysis of the original NDIS data for lithium chloride solutions, Egorov et al. [42] and Rempe et al. [43] have used the fact that the radial distribution functions are never <0, and calculated a number closer to 4 for the Li^+ coordination. There is clearly a need to confirm the accuracy of the original data and proposals are already well advanced to examine the robustness of a tetrahedral coordination for Li^+ by carrying out studies of the Li^+ ion in a number of null water ^7Li solutions as a function of concentration and counterion.

6.2. Na^+

The sodium ion is, along with Cl^-, the most abundant of all ions in the human blood. Of particular interest is how its biochemical properties compare with those of K^+ [44]. Its hydration has been investigated by the approximate method of X-ray diffraction and isomorphic substitution (XDIS) and by exploitation of the isomorphism between Na^+ and Ag^+, [20]; by combining data from NDIS on silver ($^{107}Ag/^{109}Ag$) nitrate and XD on equi-molar solutions of silver nitrate and sodium nitrate, it was possible to determine a good approximation for the Na^+ hydration shell. The generality of the assumption of isomorphism between Ag^+ and Na^- is discussed in detail in the paper by Vuilleumier and Sprik [45].

Recently neutron diffraction studies on aqueous solutions of sodium chloride in null water, show a hydration structure slightly weaker than Li^+ with no evidence of a second shell of water molecules, Fig. 3 [13]. The Na^+–O nearest neighbour distance is 2.4 Å and a value of 4.9(5) is calculated for the hydration number of Na^+. These results are in excellent agreement with other studies and suggest that the hydration is independent of counterion type [46] and concentration (Mountain and Thirumalai [47]).

6.3. K^+

The K^+ ion is a particularly difficult ion to study by any of the techniques mentioned here. The only viable method is NDIS and experiments with this technique have been only moderately successful [48] (Fig. 4).

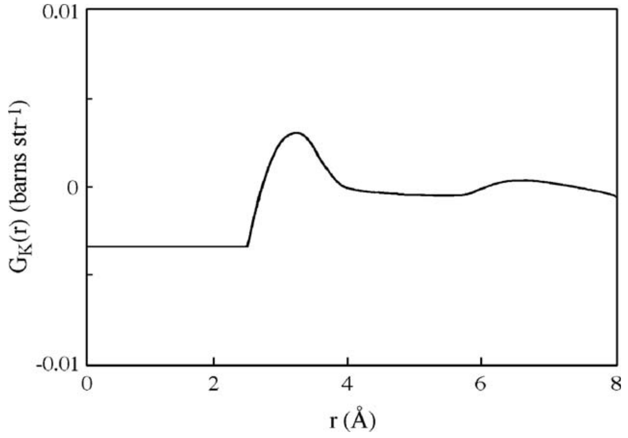

Fig. 4. The total K^+ ion radial distribution function $G_K(r)=0.0010g_{\mathrm{KO}}(r)+0.0023g_{\mathrm{KD}}(r)+0.0002g_{\mathrm{KCl}}(r)-0.0035$ in a heavy water solution of 4 molal potassium chloride.

Such an observation is similar to that inferred from the experimental work of Collins who predicts a crossover from structure breaking to structure making properties between Na^+ and K^+ [49]. Indeed one can see from the comparison of Figs. 3 and 4 that there is a clear change in the form of $G_K(r)$ and $G_{Na}(r)$ with the latter being significantly stronger.

6.4. Rb^+

The Rb^+ ion has no suitable isotopes for exploitation by NDIS. However, with an atomic number of 37 it is a strong scatterer of X-rays and recently an aqueous solution of 4 m rubidium chloride has been studied by the AXD technique [21]. The total radial distribution function, $\tilde{G}_{Rb}(r)$, of Rb^+ is relatively short-ranged (Fig. 5), with a strong peak at 3.05 Å which is identified as due to the nearest neighbour Rb^+–O correlation, and when integrated gives a hydration number of 6.9 ± 0.5. Although one cannot rule out the possibility of a second hydration shell, in the range 4–6 Å, the data in this region are fairly noisy, and it is likely that if one exists it is very weak.

Comparison of the results with those of the other alkali ions shows that, as might be expected, the ion–oxygen distance increases with the size of the bare ions and there is a slight increase in coordination number. Moreover, for an ion with a charge density of only slightly less than that of K^+, the overall structure is more similar to that of K^+ than that of Na^+ and Li^+.

There is broad agreement between the AXD results and those of an EXAFS experiment [50]. However, it appears that the nearest neighbour separation calculated from the EXAFS data is appreciably shorter than that here; this could be a real effect due to differences in concentration, or it could arise from different procedures in the data analysis. As a matter of additional interest, Beudert and coworkers report more than one distance for the mean separation of the rubidium ions and oxygen atoms [51].

6.5. Cs^+

The Cs^+ ion is the last stable ion and penultimate member of the alkali series. It has the largest ionic radius and therefore the lowest charge density. Its coordination in aqueous solution has been studied by AXD, [52]. As one might expect it has a relatively weak hydration shell (Fig. 6) and shows no evidence of any second shell or longer range structure as has been suggested in a recent MD simulation [53]. However, even in this simulation, the evidence for a second shell was strongly dependent on the choice of potential. On charge density grounds, this is not surprising given that no alkali ion other than the relatively small Li^+ shows a second shell over the range between 3 Å and 5 Å systematic increase of ion–oxygen distance which scales with alkali ion size is also observed. The result of 7.9 for Cs^+ compares reasonably with the rest of the series. Finally we note that none of the other alkali ions show such a strong tendency as Cs^+ to complex with other ions; even Rb^+ which also has a relatively large ionic radius shows no evidence of ion pairing in rubidium bromide, although it might well do so in an iodide solution.

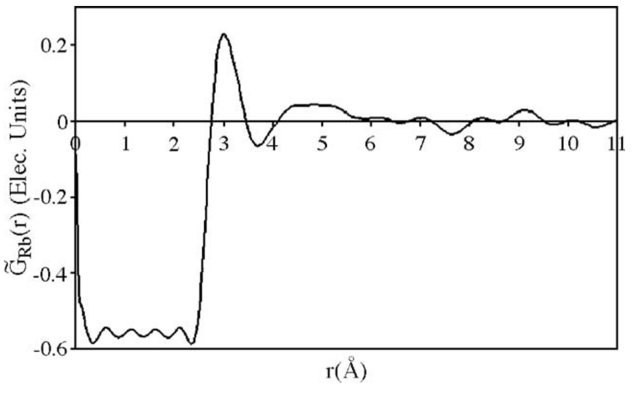

Fig. 5. $\tilde{G}_{Rb}(r)$ for Rb^+ in an aqueous solution of 4 m rubidium chloride. (see Ramos et al. [21] for more details).

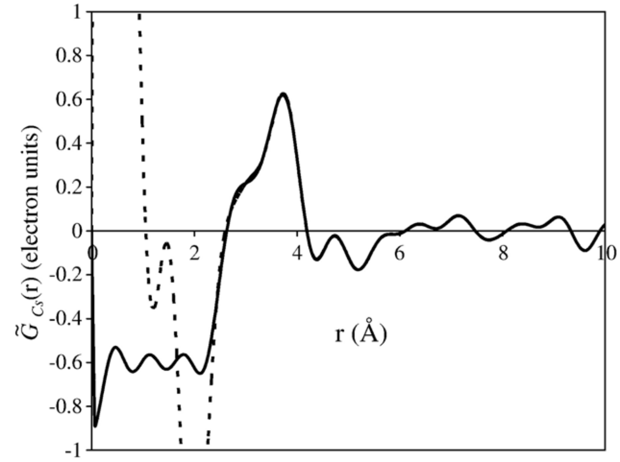

Fig. 6. $\tilde{G}_{Cs}(r)$ for Cs^+ in a 3 m CsI aqueous solution. The dotted line, prominent at low r, is the result of termination of q-space data and subsequent Fourier transformation (see Beudert et al. [51] for further details).

When taken together, it is clear from the results presented in Figs. 2–6 and in Table 3 that there is a progressive decrease in the strength of the ion coordination with increase in ion size accompanied with a small increase in coordination number. The studies also show that the extent of the perturbations to the water structure is limited primarily to the range of the first hydration shell. Only Li^+ has a significant second shell and even here only at very high concentration where counterion effects may also contribute.

7. Conclusions

The results above illustrate the contributions neutron diffraction and X-ray scattering experiments have made to understanding the hydration structure of the alkali ions in aqueous solutions. The information provided is not only useful as a systematic characterisation of ions within particular groups, but can also be used to assess the accuracy of computer simulation studies based on model potentials (see e.g., [9,10,25]). It also helps in the interpretation of results obtained from spectroscopy and thermodynamic measurements. For example, the use of terms such as kosmotrope and chaotrope or active and passive species [46,48,54], in solution, might well have their structural analogue in terms of the range and strength of hydration as by $g_{\alpha\mathrm{O}}(r)$ and $g_{\alpha\mathrm{H}}(r)$ or the $G_{\alpha}(r)$ of a hydrated species α.

There remain many details to be resolved; these include the exact nature of the Li^+ coordination and its dependence, if any, on counterion, concentration and physical state, the details of the K^+–O nearest neighbour correlation, and how it compares with that for Na^+–O, whether Cs^+ is more able to coordinate other ions and if so the role polarisability plays in concentrated aqueous solutions.

The well-established NDIS method is generally superior to all other methods for structure determination at the level of interatomic pair coordination. However, it is only suitable for atoms or ions with isotopes which show a large difference in their coherent scattering of neutrons, and even then is only useful at concentrations above about 0.5 m. The method of AXD has the potential to answer long-standing questions about the structure around species with mass number greater than about 30. However, the low X-ray scattering power of hydrogen atoms means that it is never possible to resolve the full structure of the hydration shell of an atom or ion. At present, AXD is also limited to studies of solutions at molal concentrations. In this sense, EXAFS spectroscopy has a distinct advantage and studies which incorporate AXD or NDIS as a reference, together with extensive EXAFS studies, are likely to be the best way ahead in the short term to investigate ionic structure at low concentration. It is clear from our observations that no one method will be sufficient to resolve structure at the required level of detail around all hydrated species. Instead one must rely on a full complement of diffraction and other techniques including computer simulation to answer the many and outstanding questions regarding aqueous solution properties.

As mentioned above the NDIS methods are applicable to any elements with a suitable range of isotopes with appreciably different neutron coherent scattering lengths, and there is now a large amount of information on the hydration properties of ions [1,27,30]. Moreover, in recent years, these methods have been employed to investigate biochemically significant molecules and ions such as those associated with the Hofmeister series, by exploitation of the large contrast in isotopes of nitrogen ($^{14}\mathrm{N}/^{15}\mathrm{N}$) and non-exchangeable hydrogen (H/D) [55,56]. However, in complex systems, it is necessary and profitable to use molecular dynamics simulation methods to help identify particular structures [57].

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