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Neutron diffraction studies of electrolytes in null water: a direct determination of the first hydration zone of ions

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Abstract

A method of neutron diffraction is described which enables the first hydration zone of small cations to be investigated at atomic resolution. It is shown that the cation structures of aqueous electrolyte solutions dissolved in a 'null' mixture of water (H_2O) and heavy water (D_2O), can be calculated directly from the neutron scattering patterns. The hitherto unresolved structure around Na^+ is used to illustrate the power of this method, the accuracy of which is discussed formally with reference to standard nickel chloride solutions. Possible applications to a variety of other systems and at different thermodynamic states are proposed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the following paper we present a new method to determine the primary ionic hydration of cations calculated from neutron diffraction experiments on aqueous electrolyte solutions. Although studies of hydration structure based on the difference methods of neutron diffraction and isotopic substitution (NDIS) have been carried out for about 30 years [1], there remain many ions whose primary hydration shells are not well characterized. For example, it may be surprising to realize that the number of water molecules around a Na^+ cation has yet to be determined. Moreover, the hydration structures of many other ions, such as Mn^{2+}, Co^{3+}, Be^{2+}, etc, which do not have isotopes suitable for exploitation by means of NDIS [1] have still to be experimentally resolved. There are also many whose structures are only known under ambient conditions, but their hydration structures change radically with changes in thermodynamic state (e.g. Cu^{2+}, Ni^{2+}, Co^{3+}, etc). As we show below, our new procedures represent one way to fill this information gap.

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The method described in this paper is introduced to discover whether neutron diffraction could still be used to obtain information on the hydration shells around ions. The method itself derives from that of NDIS, and exploits the fact that a ‘null’ water mixture can be prepared to render correlations between hydrogen and other atoms effectively non-existent in the diffraction patterns. It then becomes possible to obtain direct information on the nearest-neighbour hydration structure of small metal cations, M, in terms of the first correlation of the pair distribution function $g_{\mathrm{MO}}(r)$. Additionally, provided that the primary oxygen–oxygen correlation is well defined and can be subtracted from the total oxygen atom $G(r)$ (see equation (6)), it is also possible to determine the first correlation of the pair distribution function of the anion, X, and the oxygen atoms $g_{\mathrm{XO}}(r)$. However, as we shall see below, the error associated with the calculation of coordination number is significantly larger than in the case of that determined by NDIS.

To follow the details of this technique, we note that the normalized structure factor $F(Q)$ for aqueous solutions of a salt ($\mathrm{MX_n}$) in water $\mathrm{H_2O}$ can be written as:

$$F(Q) = \sum_{\alpha}\sum_{\beta} c_\alpha c_\beta \bar{b}_\alpha \bar{b}_\beta (S_{\alpha\beta}(Q) - 1) \tag{1}$$

where c_α is the atomic concentration of species α and $\bar{b}_\alpha$ is its corresponding mean coherent neutron scattering length. $S_{\alpha\beta}(Q)$ is the partial structure factor for atoms α and β and is related via Fourier transformation to the corresponding radial pair distribution function $g_{\alpha\beta}(r)$:

$$g_{\alpha\beta}(r) - 1 = \frac{1}{2\pi^2 \rho r}\int_0^{\alpha} (S_{\alpha\beta}(Q) - 1) Q \sin(Qr)\, \mathrm{d}Q \tag{2}$$

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

Equation (1) can be written explicitly as

$$\begin{aligned} F(Q) = {} & c_{\mathrm{O}}^2\bar{b}_{\mathrm{O}}^2(S_{\mathrm{OO}}(Q) - 1) + c_{\mathrm{H'}}^2\bar{b}_{\mathrm{H'}}^2(S_{\mathrm{H'H'}}(Q) - 1) + 2c_{\mathrm{H'}}c_{\mathrm{O}}\bar{b}_{\mathrm{H'}}\bar{b}_{\mathrm{O}}(S_{\mathrm{H'O}}(Q) - 1) \\ & + 2c_{\mathrm{O}}\bar{b}_{\mathrm{O}}\bar{c}_{\mathrm{M}}\bar{b}_{\mathrm{M}}(S_{\mathrm{OM}}(Q) - 1) + 2c_{\mathrm{H'}}\bar{b}_{\mathrm{H'}}c_{\mathrm{M}}\bar{b}_{\mathrm{M}}(S_{\mathrm{H'M}}(Q) - 1) \\ & + 2c_{\mathrm{O}}\bar{b}_{\mathrm{O}}\bar{c}_{\mathrm{X}}\bar{b}_{\mathrm{X}}(S_{\mathrm{OX}}(Q) - 1) + 2c_{\mathrm{H'}}\bar{b}_{\mathrm{H'}}c_{\mathrm{X}}\bar{b}_{\mathrm{X}}(S_{\mathrm{H'X}}(Q) - 1) \\ & + c_{\mathrm{M}}^2\bar{b}_{\mathrm{M}}^2(S_{\mathrm{MM}}(Q) - 1) + c_{\mathrm{X}}^2\bar{b}_{\mathrm{X}}^2(S_{\mathrm{XX}}(Q) - 1) + 2c_{\mathrm{M}}c_{\mathrm{X}}\bar{b}_{\mathrm{M}}\bar{b}_{\mathrm{X}}(S_{\mathrm{MX}}(Q) - 1). \end{aligned} \tag{3}$$

We note that the first three terms in this equation represent the pair structure for the water molecules, the next four terms represent the anion and cation hydration, and the last three terms are the ion structure. By considering the size of each term, we note further that, by preparing a solution in which $\bar{b}_{\mathrm{H'}} \sim 0$, we can effectively minimize or even eliminate contributions from correlations between the hydrogen atoms and other atoms to the structure function $F(Q)$. Assuming that this is feasible, and we will discuss the practicality of this procedure in the Experimental section below, we can rewrite equation (3) as

$$\begin{aligned} F(Q) = {} & c_{\mathrm{O}}^2\bar{b}_{\mathrm{O}}^2(S_{\mathrm{OO}}(Q) - 1) + 2c_{\mathrm{O}}c_{\mathrm{M}}\bar{b}_{\mathrm{O}}\bar{b}_{\mathrm{M}}(S_{\mathrm{OM}}(Q) - 1) + 2c_{\mathrm{O}}c_{\mathrm{X}}\bar{b}_{\mathrm{O}}\bar{b}_{\mathrm{X}}(S_{\mathrm{OX}}(Q) - 1) \\ & + c_{\mathrm{M}}^2\bar{b}_{\mathrm{M}}^2(S_{\mathrm{MM}}(Q) - 1) + c_{\mathrm{X}}^2\bar{b}_{\mathrm{X}}^2(S_{\mathrm{XX}}(Q) - 1) + 2c_{\mathrm{M}}c_{\mathrm{X}}\bar{b}_{\mathrm{M}}\bar{b}_{\mathrm{X}}(S_{\mathrm{MX}}(Q) - 1). \end{aligned} \tag{4}$$

We now consider the size of the constant coefficients of the various terms, and find that, at the ionic concentrations of the solutions in our study, the last three terms will contribute at most 4% to the total function $F(Q)$. If we ignore their contribution, we obtain the following good approximation to the structure factor:

$$F'(Q) = c_{\mathrm{O}}^2\bar{b}_{\mathrm{O}}^2(S_{\mathrm{OO}}(Q) - 1) + 2c_{\mathrm{O}}c_{\mathrm{M}}\bar{b}_{\mathrm{O}}\bar{b}_{\mathrm{M}}(S_{\mathrm{OM}}(Q) - 1) + 2c_{\mathrm{O}}c_{\mathrm{X}}\bar{b}_{\mathrm{O}}\bar{b}_{\mathrm{X}}(S_{\mathrm{OX}}(Q) - 1). \tag{5}$$

Of these three terms, the oxygen–oxygen structure factor dominates $F'(Q)$, with relative contributions of up to 40% from the ion–oxygen terms, depending on their concentrations. However, the point to realize is that, when these terms are considered in real space, one finds the following form for the pair distribution function of the solution:

$$G(r) \approx c_{\mathrm{O}}^2 \bar{b}_{\mathrm{O}}^2 (g_{\mathrm{OO}}(r) - 1) + 2c_{\mathrm{O}}c_{\mathrm{M}}\bar{b}_{\mathrm{O}}\bar{b}_{\mathrm{M}}(g_{\mathrm{OM}}(r) - 1) + 2c_{\mathrm{O}}c_{\mathrm{X}}\bar{b}_{\mathrm{O}}\bar{b}_{\mathrm{X}}(g_{\mathrm{OX}}(r) - 1). \tag{6}$$

Interestingly, one notes that the first correlation in $g_{\mathrm{OO}}(r)$ will appear at around 2.8 Å, which is well beyond that for the first hydration peak in many $g_{\mathrm{OM}}(r)$s. Moreover, if one can also assume that a single experiment on a null water sample can be used to obtain $g_{\mathrm{OO}}(r)$ directly from Fourier transformation of $S_{\mathrm{OO}}(Q)$, one can then subtract this function from equation (5) and obtain

$$\Delta F'(Q) = 2c_{\mathrm{O}}c_{\mathrm{M}}\bar{b}_{\mathrm{O}}\bar{b}_{\mathrm{M}}(S_{\mathrm{OM}}(Q) - 1) + 2c_{\mathrm{O}}c_{\mathrm{X}}\bar{b}_{\mathrm{O}}\bar{b}_{\mathrm{X}}(S_{\mathrm{OX}}(Q) - 1) \tag{7}$$

which, on Fourier transformation, gives

$$\Delta G(r) = 2c_{\mathrm{O}}c_{\mathrm{M}}\bar{b}_{\mathrm{O}}\bar{b}_{\mathrm{M}}(g_{\mathrm{OM}}(r) - 1) + 2c_{\mathrm{O}}c_{\mathrm{X}}\bar{b}_{\mathrm{O}}\bar{b}_{\mathrm{X}}(g_{\mathrm{OX}}(r) - 1). \tag{8}$$

Thus, provided that we can obtain $\Delta G(r)$, we will be able to extract information on the primary hydration of both the anion and cation, realizing that the extraction of longer-range correlations may well overlap significantly. Before we proceed, a word of caution is appropriate regarding the extraction of information on the ion–oxygen correlations. For the case of the cation–oxygen correlations, it is unlikely that contamination from a residual contribution due to non-cancellation of the oxygen atom–oxygen atom nearest-neighbour peak, expected in the range $2.6 < r(\text{Å}) < 3.5$, will adversely affect results for Ni^{2+}, Li^{+}, and Na^{+} with nearest-neighbour ion–oxygen peaks expected at 2.06, 1.96, and 2.35 Å, respectively. However, it is possible that the extraction of detailed information may be seriously compromised. Nevertheless, as we show below, even for the case of Cl^{-} with its first correlation to an oxygen atom in the same region as the first O–O correlation of water, the result is consistent with that obtained from the formally exact NDIS method . . ..

It might well be asked, ‘why has this procedure not been used before?’ The use of null water samples for the study of pure water has indeed been used previously, as has the use of water mixtures of H_2O and D_2O in aqueous solutions, [2, 3]. However, in those cases, the aims of the studies were to identify aspects of the *water* structure. Additionally, the applications of the difference methods of NDIS were limited to ions with isotopes whose neutron scattering lengths were sufficiently different, [4]. Of additional relevance is the significant improvement in neutron diffractometer performance in recent years and the concurrent increase in computational power, facilitating greater accuracy in the data corrections (see appendix). For example, the upgrade in reactor instruments such as D20 and D4 at the Institut Laue Langevin (ILL), Grenoble, France, has meant that scattering data can be obtained for aqueous mixtures with a reliability of better than 0.1%, and sometimes to order of 0.01% [5]. It is therefore now opportune to introduce this method and to assess critically its limitations and accuracy.

To achieve this, we begin by discussing results with reference to the ionic structure of nickel chloride solutions, which have been the subject of detailed study over the past 30 years and are sufficiently robust to test the accuracy of the method, [2, 4]. Internal checks are also used, as well as the fact that the water structure itself is well known [6].

We then illustrate the power of the procedure with a study of the Na^{+} ion primary hydration in aqueous solutions of sodium chloride. This alkali ion, being mono-isotopic, cannot be studied directly by NDIS, or by x-ray or neutron diffraction, as its correlations to water molecules are only weakly present in the scattering patterns, [7]. Moreover, the recently developed methods of anomalous x-ray diffraction (AXD) [8] cannot be applied, as the energy resonances of the ion cannot yield a large enough Q-range to resolve the hydration structure.

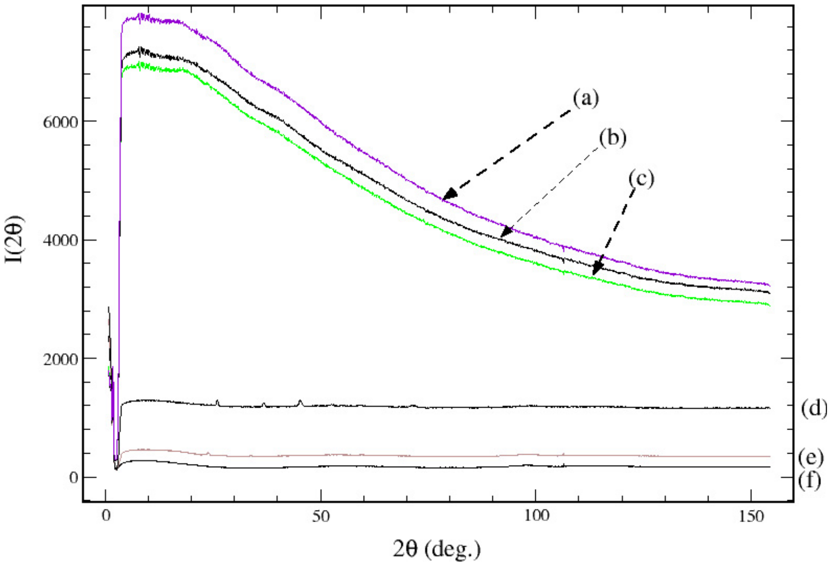

Figure 1. Normalized intensity data, $I(Q)$, for samples: (a) null water; (b) 3 molal $NiCl_2$ null water solution; (c) 4 molal NaCl null water solution; (d) vanadium rod (3 mm diameter); (e) empty Ti/Zr container; (f) background.

2. Experimental method

The following solutions were prepared under ambient conditions by dissolution of the anhydrous analar grade salts in a null water mixture: (a) null water which is an isotopic mixture of $(H_2O)_{0.637}$ and $(H_2O)_{0.363}$; (b) 3 molal $NiCl_2$ in null water; (c) 1.5 molal $NiCl_2$ in null water; (d) 4 molal NaCl in null water; and (e) 2 molal NaCl in null water.

Each sample was allowed to equilibrate for 1 h in a sealed vial prior to being transferred to the Ti/Zr null scattering container. Neutron diffraction data were then collected on the D20 diffractometer at the ILL, Grenoble, France.

The calculation of the $F'(Q)$s and $\Delta F'(Q)$s followed a standard procedure which involved subtraction of the background and container with correction for absorption, multiple and incoherent scattering [1], together with an additional correction associated the self-scattering from H_2O molecules (see appendix). The diffraction patterns, (figure 1) were normalized with reference to a standard vanadium rod to yield $F(Q)$s in units of barns str^{-1}. The correct amount of the $F(Q)$ for null water ($S_{OO}(r)$) was then subtracted to yield $F'(Q)$s (figure 2). This subtraction performs two important functions: it effectively removes the inelastic scattering effects from the diffraction pattern (figure 2), and it allows the changes in the structure due to the ions to be observed more clearly. The data were then Fourier filtered of all frequency components that corresponded to r-space features of less than 1.5 Å to give $\Delta F'(Q)$s (figure 3). The corresponding $\Delta G(r)$s were calculated by direct Fourier transformation of the results in figure 3 and included a maximum entropy procedure to ensure self-consistency between Q-space and real-space information. Further details of the analysis are presented in the appendix.

3. Results and discussion

The results shown in figure 4 demonstrate that the experimental procedures can be used to provide difference data for ionic structure on a level comparable to that obtained by NDIS.

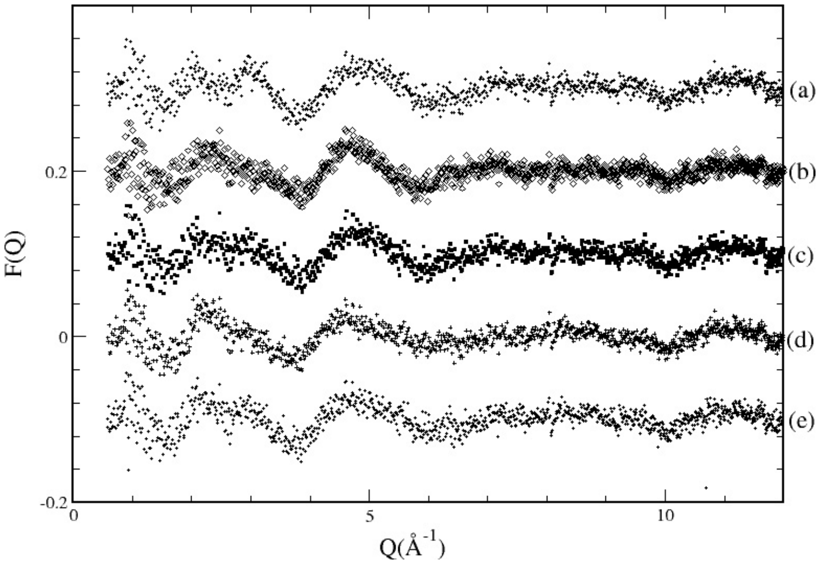

Figure 2. Structure factors $F(Q)$ (equation (4)) for (a) null water, (b) 3 molal $NiCl_2$ null water solution, (c) 1.5 molal $NiCl_2$ null water solution, (d) 4 molal NaCl null water solution, (e) 2 molal NaCl null water solution.

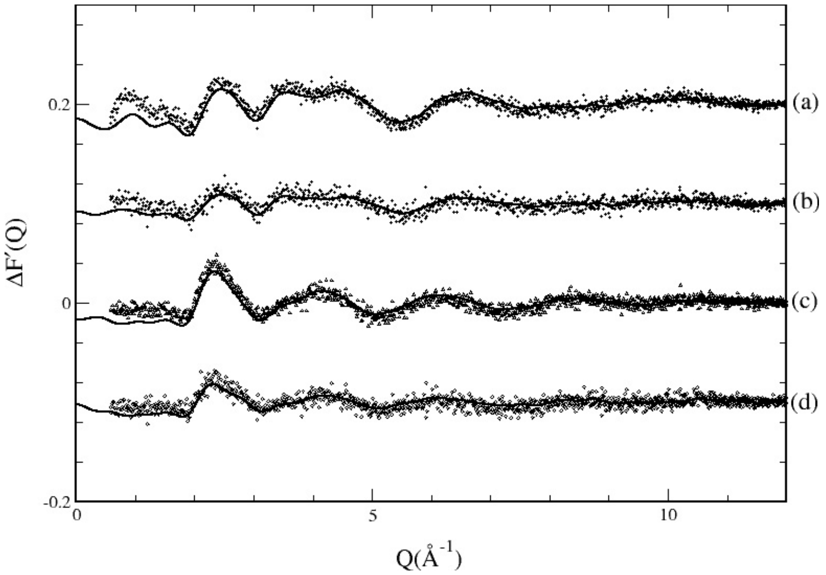

Figure 3. Structure factors $\Delta F'(Q)$ (equation (7)) for (a) 3 molal $NiCl_2$ null water solution, (b) 1.5 molal $NiCl_2$ null water solution, (c) 4 molal NaCl null water solution, (c) 2 molal NaCl null water solution. The solid lines through the experimental data are the back transformations of the edited real-space results in figure 4. It is also interesting to note that, in the region of interest, the structural information is unaffected by the transformation.

Using the data sets for the 3 molal and 1.5 molal $NiCl_2$ solutions as references, for both solutions we calculate a peak position for Ni–O of 2.06(4) Å and a coordination number, n_{Ni}, of 5.8(5). Similarly, for the Cl–O nearest-neighbour correlation at 3.1 Å, we obtain a

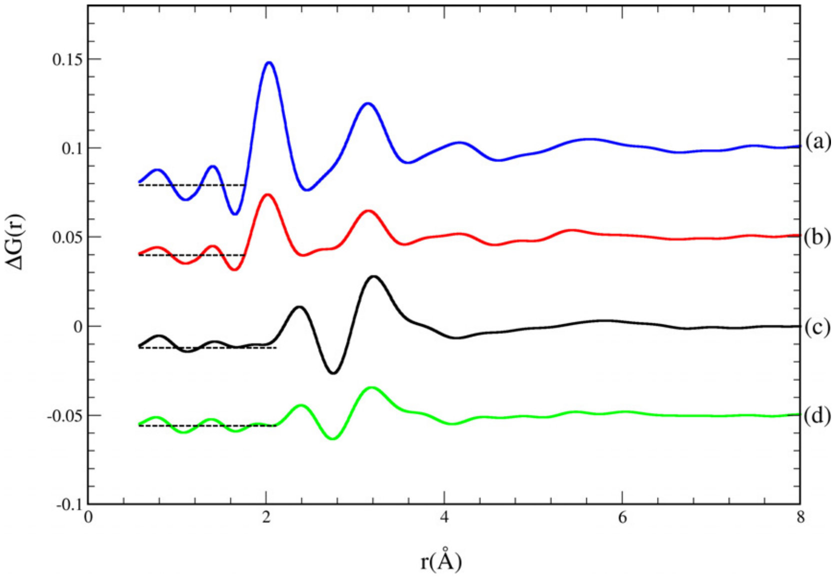

Figure 4. Distribution functions $\Delta G(r)$ (equation (8)): (a) 3 molal $NiCl_2$ null water solution, where $\Delta G(r) = 0.0065g_{\mathrm{NiO}}(r)+0.0120g_{\mathrm{ClO}}(r)+0.0011g_{\mathrm{NiCl}}(r)+0.0011g_{\mathrm{ClCl}}(r)-0.0206$ and shifted by 0.10; (b) 1.5 molal $NiCl_2$ null water solution, 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. Note that the back transformation results shown as lines in figure 3 are obtained after editing the $G(r)$ between $0 \leqslant r(\text{Å}) \leqslant 1.8$ to correspond to that of the theoretical value of $\Delta G(0)$.

coordination number, n_{Cl}, of 7.4(0.8). The difference in accuracy of the two coordination numbers is taken into account by the possibility of some remnant of the O–O nearest-neighbour correlation, which has not been completely taken into account in proceeding from equation (5) to (7). These results are in very good agreement with what has been previously found in NDIS experiments in heavy-water solutions of $NiCl_2$ with values of the separation of Ni–O = 2.07 Å and $n_{\mathrm{Ni}} = 5.8$ [4], and that of Cl–O = 3.1(1) Å and $n_{\mathrm{Cl}} = 6.4(3)$ [2]. It is also worth noting the evidence for a second shell of water molecules, presumably around Ni^{2+} centred around 4.2 Å.

The results for the two sodium chloride solutions are equally straightforward to interpret. The two prominent peaks centred at 2.34 and 3.20 Å appear in both solutions (figure 4) and arise, respectively, from nearest-neighbour correlations between oxygen atoms and Na^+ ions and between oxygen atoms of the water molecules and Cl^- ions. The coordination numbers for the Na–O correlation are 5.0(5) and 5.1(5) in the 4 and 2 molal solutions respectively, and those for the Cl–O correlation in the two solutions are 7.4(8) and 7.3(8) respectively. We note here that the $\Delta G(r)$s for both sodium chloride solutions are less than the zero limit over the range $2.6 < r(\text{Å}) < 3.5$, which is clearly unphysical. We believe that this feature is a consequence of a slight difference in the position of the O–O correlation in the null water and the salt solutions. The fact that it does not affect the nickel chloride solutions is interesting in itself, and can probably be explained by the fact that Ni^{2+} coordinates water much more strongly than Na^+, and that the value of the neutron scattering length of nickel is significantly greater than that for sodium.

The results are in very good agreement with those already in the literature [8, 9]. For example, the Na^+ ion has been investigated by the method of neutron diffraction and isomorphic substitution, which gives an Na^+–O nearest neighbour distance of 2.3 Å and a hydration number of 4.9(5). Interestingly, an x-ray study of a solution of sodium formate gives similar results for this ion, suggesting that its hydration structure is independent of the counter-ion [9]. Although the signal for the 2 molal solution is much weaker, the general pattern is unchanged and suggests that the ion hydration is independent of the concentration, in agreement with predictions based on computer simulations [10].

It is of interest to compare the result for Na^+ with the hydration structures of its two neighbours Li^+ and K^+ within the alkali series. The hydration for Li^+ has been studied by NDIS in aqueous (heavy water) solutions of lithium chloride [11, 12], lithium hydroxide [13], and lithium bromide [14, 15]. Although the overall hydration structure looks similar in these solutions with a clear separation between the Li–O and Li–D correlations, the actual number of water molecules in the chloride solution was calculated to be around 5.5, whereas the value in the other solutions was calculated to be closer to 4. Spectroscopic measurements and computer simulation studies based on energetic arguments [16–19] conclude that a value of 4 is more likely, and Pratt, Rempe and colleagues [20] have challenged the value of about 6 calculated from the NDIS studies of lithium chloride solutions. It is also worth noting that the coordination number for Na^+, which has an appreciably larger ionic radius than Li^+, is around 5! Experiments are therefore being planned to use the above technique to study Li^+ hydration as a function of the concentration and the counter-ion in null water solutions of the non-absorbing atom ^7Li salts and to establish whether the value of hydration number for Li^+ is closer to 4 or 6.

Comparison of the Na^+ hydration structure with that of K^+ is particularly interesting because of the role that these ions play in cellular processes [21]. It is clear from the NDIS result for K^+ [22] that the hydration structures of these two ions are appreciably different, with the K^+ ion having a much weaker coordination to water. The determination of the nearest-neighbour K–O correlation would greatly enhance our knowledge of the degree to which this is the case.

4. Conclusions

The method presented here represents a useful means to obtain structural information directly on the first hydration shell of ions which are not susceptible to the difference methods of NDIS or have insufficient numbers of electrons for AXD. The potential for the method is limited only by the amplitudes of the neutron coherent scattering lengths of the isotopes of the ions themselves and the ionic concentration of the solution.

We are currently studying the potential of the method for a number of other cations such as Be^{2+}, $Al^{3+}Mg^{2+}$, etc, i.e. all those whose isotopes have insufficient contrast for the NDIS method to be feasible.

Finally, it is important to note that the method can also be used to carry out a systematic study of the first hydration shell of cations as a function of pressure and temperature on a single sample. In comparison, a major source of difficulty for the NDIS method is in achieving the exact same state for two samples at different times in the neutron beam.

Acknowledgments

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Appendix

The calculation of $F(Q)$ from the scattered intensity function $I(2\theta)$ measured in the detector is carried out as follows:

$$F(Q) = \alpha(Q)[I(Q) + \beta(Q)] \tag{A.1}$$

where $Q = 4\pi \sin(\theta)/\lambda$, and 2θ is the scattering angle and λ is the wavelength of the monochromatic beam of neutrons. $I(Q)$ is the intensity of the neutrons scattered into the initially assumed black detector at angle 2θ already corrected for background scattering and container absorption and scattering [23]. The function $\alpha(\theta)$ contains corrections for absorption within the sample and the container and also the normalization with reference to a standard vanadium rod giving scaled units of barns str^{-1}. The function $\beta(Q)$ contains corrections for multiple scattering, incoherent and inelastic (Placzek) scattering. In heavy-water solutions, these two correction terms are usually straightforward to calculate the structure factor of the solution, $F(Q)$, after Fourier transformation to a total radial pair distribution function, $G(r)$, which provides information on the pairwise structure of the liquid.

However, when a solution contains a substantial amount of light water, as for the case of 'null' water, the term $\beta(Q)$ is harder to calculate due to the large incoherent scattering and inelastic scattering of hydrogen nuclei. This correction uses an assumption for the form of the self-scattering law for H_2O molecules. In order to deal with this situation, it is convenient to rewrite equation (A.1) as

$$F(Q) = \alpha(\theta)[I(Q) + \beta'(Q)] + \gamma(Q). \tag{A.2}$$

The term $\beta'(\theta)$ contains the multiple scattering corrections, incoherent and inelastic scattering corrections for the D_2O molecules, and $\gamma(Q)$ represents the incoherent scattering and inelastic scattering from H_2O molecules in the solution.

The calculation of $\gamma(Q)$ is based on work originally published by Powles [24] and subsequently extended by Granada and co-workers [25, 26] and Zetterström *et al* [27]. The results obtained for the latter paper were aimed at the correction of data obtained from hydrogenous materials obtained on the SANDALS diffractometer at ISIS, which uses a polychromatic beam of neutrons.

In the work presented here, a revised calculation was made in order to correct data taken on either the D20 or the D4 diffractometers of the ILL. Following the procedure outline by Granada [26], three synthetic and closely similar models are introduced for the D_2O, H_2O, and HDO molecules. The models are consistent with detailed balance (A.3) and the moment expansion for $S(Q, \omega)$ (A.4). In order to refine the models so as to be consistent with the experimental data, a minimization procedure, which includes the use of Lagrange multipliers (a, b, c) and defined by equation (A.5), is used to calculate the models which best fit the data. Within the calculations, we note that the zeroth moment is unity, the first moment is $\hbar^2 Q^2/2m_n k_B T$ and includes an effective temperature T which is regarded as a free parameter, m_n is the neutron mass, k_B is Boltzmann's constant, and $\hbar$ is Planck's constant. The third moment contains two free parameters. Thus there are three parameters which are used to define the self-scattering corrections for each species of water molecule, and each parameter can be directly related to the three Lagrange multipliers.

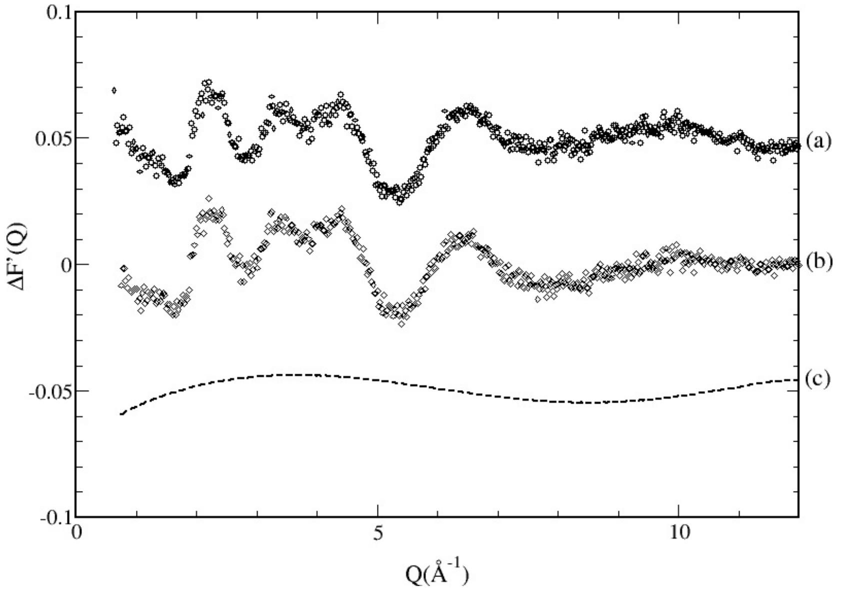

Figure A.1. Comparison of $\Delta F'(Q)$s calculated from equation (A.1) (a) and equation (A.2) (b). Also shown is the difference (c) between these curves; the Fourier transformation of this difference has little effect on the relevant structural aspects of the $G(r)$ shown in figure A.2.

In mathematical terms,

$$S(Q,\omega) = \exp(-\xi)S(Q,-\omega) \tag{A.3}$$

$$S_{\mathrm{n}}(Q,\omega) = \int_{-\omega_{\mathrm{n}}}^{\infty} \omega^{n} S(Q)\,\mathrm{d}\omega \tag{A.4}$$

$$1 + \ln\left[\frac{S(Q,\omega)}{S_{\mathrm{M}}(Q,\omega)}\right] + a + b\xi + c\xi^{2} = 0, \tag{A.5}$$

where $S(Q,\omega)$ the scattering law of the system of water molecules, and $\xi = \hbar\omega/k_{\mathrm{B}}T$.

In terms of the above functions, $\gamma(Q) = \int_{-\hbar\omega_{\mathrm{m}}}^{\infty} \mathrm{d}\omega\, \varepsilon(\lambda)[S_{\mathrm{M}}(Q,\omega)\exp(-(a+b\xi+c\xi^{2}))]$ where $\hbar\omega_{\mathrm{m}}$ is the energy of the monochromatic neutrons of wavelength λ, $S_{\mathrm{M}}(Q,\omega)$ is the synthetic model for the self-scattering from an $\mathrm{H_2O}$ molecule [25], and $\varepsilon(\omega)$ is the detector efficiency, which for a helium3 detector is ~0.93. Application of equation (5) to the experimental data constrain the results and facilitate a three-parameter fit to the self-scattering of the water molecules, which can then be subtracted from the scattering pattern.

A computer programme which uses this procedure was written and applied to the data obtained for the nickel chloride solution, with the results given in figures A.1 and A.2, where it can be seen that the $\Delta F'(Q)$s calculated from equations (A.1) and (A.2) are almost identical, differing only slightly in terms of a slowly varying function which has no appreciable structural effect on the corresponding $\Delta G(r)$s calculated.

The computer programme also contained procedures to carry out the Fourier transformation of data directly and without recourse to the fast Fourier transform method, and included maximum entropy constraints, which enabled a smooth extension of the data. It was noted that this latter procedure produced results which gave coordination numbers closer to that expected for Ni^{2+}, and is probably a consequence of the fact that termination errors produce ringing in the transform data with a $1/r$ decay. Thus, when one calculates a coordination number, the r^{2} factor of the integrand will, on integration, give a larger value than expected.

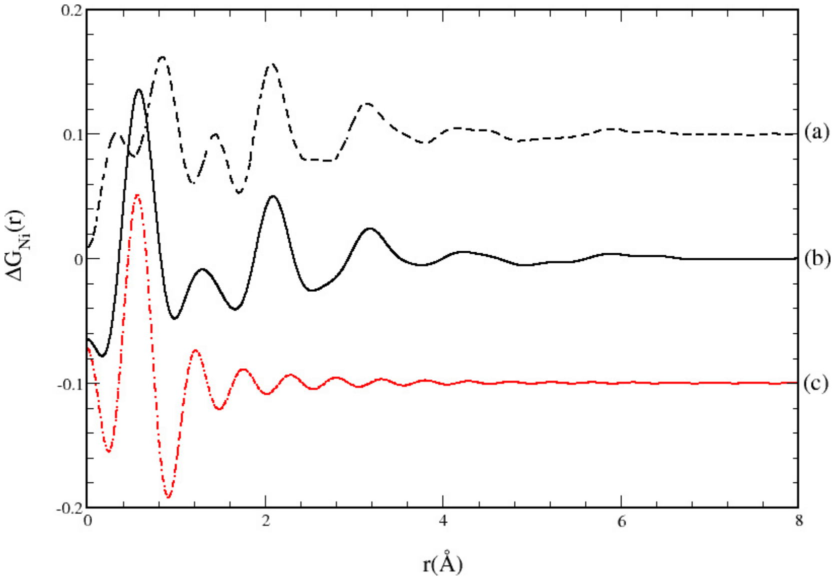

Figure A.2. The total radial distribution functions, $\Delta G(r)$, obtained from Fourier transformation of the structure factors $\Delta F'(Q)$ in figure A.1. The lowest curve shows that there are no significant structural differences in the regions of the first hydration shells of the Ni^{2+} and Cl^- ions.

Although the results shown in figure 2(A) are almost identical for the two procedures used here, we would recommend that data are treated with the procedures shown above when working with solutions containing large amounts of hydrogenous material.

A further correction based on the results of an inelastic scattering study of hydrogen [28] and applied to the H_2O molecules in the solutions was introduced to take account of higher-order coherent inelastic effects of water. As it turns out, the contribution of such a correction is featureless and accounts for less than 0.1% to $\Delta F'(Q)$, and has consequently been ignored.

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