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## A neutron diffraction study of NiCl<sub>2</sub> in D<sub>2</sub>O and H<sub>2</sub>O. A direct determination of $g_{\text{NiH}}(r)$

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**Abstract.** The technique of neutron diffraction and isotopic substitution has been applied to solutions of 2 mol kg<sup>-1</sup> nickel chloride in light and heavy water. The results were used to obtain  $g_{\text{NiH}}(r)$  directly. Good agreement is found between the experimental  $g_{\text{NiH}}(r)$  with that derived from a computer simulation study in which Mg<sup>2+</sup> (usually regarded as isomorphically equivalent to Ni<sup>2+</sup>) was the cation. A neutron diffraction study, again using the isotopic difference method, was also made of 2 mol kg NiCl<sub>2</sub> in a 'null' mixture of H<sub>2</sub>O and D<sub>2</sub>O. Results show that the Ni<sup>2+</sup> cation is preferentially deuterated, a result in disagreement with recent theoretical calculations by Newton and Friedman.

### 1. Introduction

Solutions of nickel chloride are reference systems for the study of the structural properties of electrolyte solutions by neutron diffraction. The results of such studies can be used to obtain an understanding of the local ionic structure and to test computer simulations at the partial-structure-factor level. However, hitherto, experiments have been carried out using heavy water (D<sub>2</sub>O).

The work described in this paper is concerned with three aspects of aqueous electrolyte solutions. The first is technical and concerns the applicability of the neutron isotopic difference method to ionic solutions that contain light water. It will be recalled (Enderby *et al* 1987) that in previous experiments heavy water was used as the solvent in order to overcome effects from incoherent scattering produced when neutrons are scattered by protons. In § 4 the feasibility of using H<sub>2</sub>O as solvent is demonstrated for a 2 mol kg<sup>-1</sup> aqueous solution of nickel chloride.

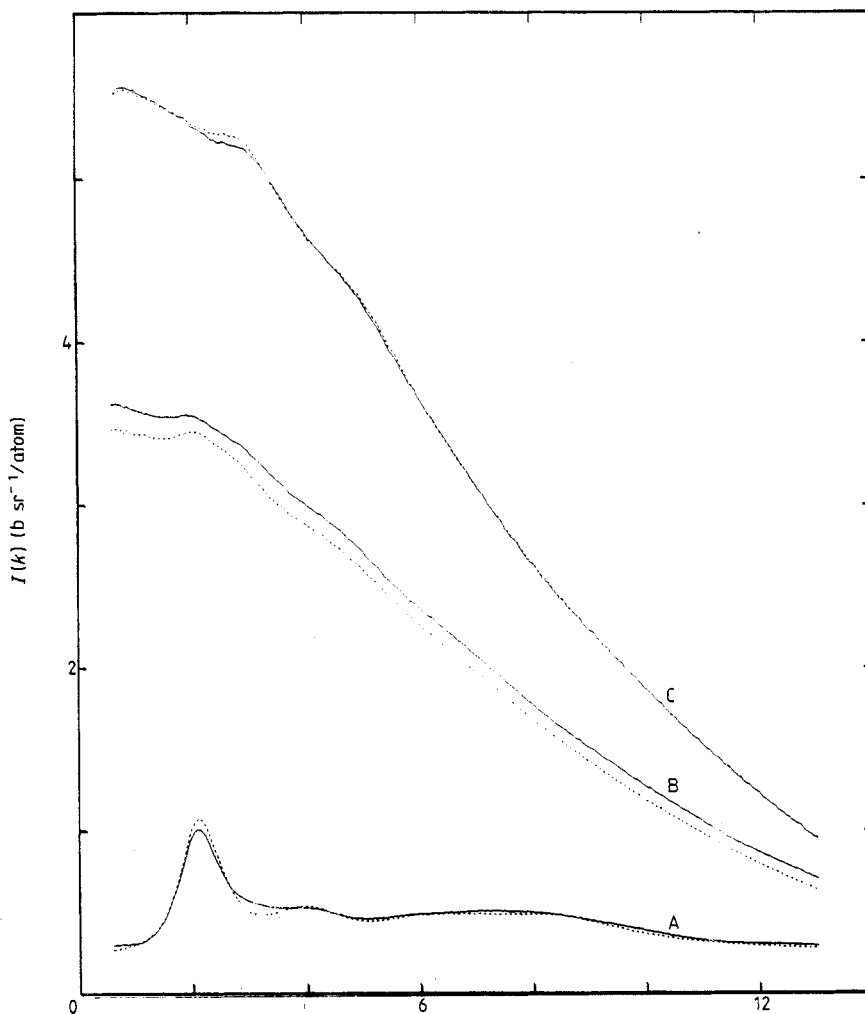
The second aspect concerns the determination of the ion–water structure, where it is demonstrated that by a combination of results from 2 mol kg<sup>-1</sup> NiCl<sub>2</sub> in light and heavy water, the radial distribution function  $g_{\text{NiH}}(r)$  can be obtained. Consequently a direct comparison can be made with computer simulation studies of Dietz *et al* (1982), and information obtained about angular correlations in the second hydration shell of Ni<sup>2+</sup>.

The third aspect of this study concerns the degree to which H<sub>2</sub>O and D<sub>2</sub>O molecules are equivalent. According to Newton and Friedman (1985) a degree of 'fractionation' should be observable for divalent and trivalent cations by the isotope substitution method of neutron diffraction. Their arguments are based on thermodynamic, spectroscopic and

solid state structural data, and they predict that a small divalent cation, such as  $\text{Mg}^{2+}$  or  $\text{Ni}^{2+}$  should, in an  $\text{H}_2\text{O}/\text{D}_2\text{O}$  mixture, be preferentially hydrated. A quantitative estimate of the accuracy of their theory can be obtained in principle by the use of  $\text{H}_2\text{O}/\text{D}_2\text{O}$  mixtures.

## 2. Experimental details

The application of the neutron first-order-difference method to studies of aqueous solutions has been described in detail elsewhere (Soper *et al* 1977), so only a summary specific to the present study need be given.



**Figure 1.** The total corrected scattering cross sections,  $I(k)$  for: (A)  $2.0 \text{ mol kg}^{-1}$   $\text{NiCl}_2$  in  $\text{D}_2\text{O}$ ; (B)  $2.0 \text{ mol kg}^{-1}$   $\text{NiCl}_2$  in  $\text{H}_2\text{O}$ ; (C)  $2.0 \text{ mol kg}^{-1}$   $\text{NiCl}$  in a null mixture. The full and dotted curves indicate solutions containing  $^{61}\text{Ni}$  and  $^{62}\text{Ni}$  respectively.

Neutron diffraction experiments were performed on pairs of solutions of NiCl<sub>2</sub> in water, which were identical in concentration and the isotopic composition of water, but differed in the isotopic composition of nickel. The neutron diffractometer, D20 at the ILL, Grenoble, was used for all the experiments. The incident wavelength of the beam was 0.938 Å. The solutions were held in a cylindrical container of 2.5 mm internal diameter and 0.74 mm wall thickness, made from an alloy of titanium and zirconium that has nominally a zero coherent scattering cross section. The data for each solution (see figure 1) were corrected for instrumental background, container scattering, self-attenuation (Paalman and Pings 1962) and multiple scattering (Blech and Averbach 1965) and were put on an absolute scale by reference to a vanadium standard (North *et al* 1968)—see also the Appendix. The sample compositions, and the scattering parameters used in these corrections procedures are given in table 1.

**Table 1.** Sample properties relevant to the correction procedures (values of scattering parameters obtained from Sears (1984).

Solution	Atomic fraction of solution components					Mean scattering cross section <sup>a</sup> (b/atom)	Mean absorption cross section <sup>b</sup> (b/atom)
	c <sub>Ni</sub>	c <sub>Cl</sub>	c <sub>O</sub>	c <sub>D</sub>	c <sub>H</sub>		
2.0 mol kg <sup>-1</sup> <sup>nat</sup> NiCl <sub>2</sub> in D <sub>2</sub> O	0.0128	0.0256	0.32050	0.6395	0.0015 <sup>c</sup>	4.66	0.48
2.0 mol kg <sup>-1</sup> <sup>62</sup> NiCl <sub>2</sub> in D <sub>2</sub> O	0.0128	0.0256	0.3205	0.6386	0.0024 <sup>c</sup>	4.58	0.54
2.0 mol kg <sup>-1</sup> <sup>nat</sup> NiCl <sub>2</sub> in H <sub>2</sub> O	0.0116	0.0232	0.3218	—	0.6435	23.68	0.54
2.0 mol kg <sup>-1</sup> <sup>62</sup> NiCl <sub>2</sub> in H <sub>2</sub> O	0.0116	0.0232	0.3218	—	0.6435	23.58	0.60
2.0 mol kg <sup>-1</sup> <sup>nat</sup> NiCl <sub>2</sub> in null mixture	0.0120	0.0240	0.3213	0.2204	0.4222 <sup>d</sup>	17.11	0.52
2.0 mol kg <sup>-1</sup> <sup>62</sup> NiCl <sub>2</sub> in null mixture	0.0120	0.0240	0.3213	0.2198	0.4228 <sup>d</sup>	17.03	0.58

<sup>a</sup> Calculated using total cross sections for D<sub>2</sub>O and H<sub>2</sub>O of 12.31 and 71.69 b respectively at the incident neutron wavelength (Hughes and Harvey 1985).

<sup>b</sup> At the incident neutron wavelength.

<sup>c</sup> Measured before and after the experiment by infrared absorption.

<sup>d</sup> Measured before and after the experiment by proton NMR.

The intensity for each solution can, within the static approximation (Squires 1978), be written as

$$I(k) = \sum_{\alpha} c_{\alpha} b_{\alpha}^2 + F(k) \quad (1)$$

where

$$F(k) = \sum_{\alpha} \sum_{\beta} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} (S_{\alpha\beta}(k) - 1) \dots \quad (2)$$

and  $c_{\alpha}$ ,  $b_{\alpha}^2$  and  $b_{\alpha}$  are the atomic fraction, mean square scattering length and mean coherent scattering length, respectively, of species  $\alpha$  (Ni, Cl, O, H, D). The magnitude of the scattering vector is denoted by  $k$ . The partial structure factor  $S_{\alpha\beta}(k)$  is given by

$$S_{\alpha\beta}(k) = 1 + \frac{4\pi\rho_0}{k} \int dr (g_{\alpha\beta}(r) - 1) r \sin kr \quad (3)$$

where  $\rho_0$  is the atomic number density of the solution (taken as  $0.100 \text{ \AA}^{-3}$  for all the solutions considered here).

In practice, the static approximation implicit in equation (1), does not hold for hydrogenous liquids and this leads to distortions in  $I(k)$  which appear as a characteristic droop. The corrections to eliminate such distortions are commonly referred to as the 'Placzek corrections'.

If an algebraic difference between the data for a pair of solutions differing only in nickel isotopic composition is taken, the difference function  $\Delta_{\text{Ni}}(k)$  is obtained. Specifically

$$\Delta_{\text{Ni}}(k) = A(S_{\text{NiO}}(k) - 1) + B(S_{\text{NiD}}(k) - 1) + C(S_{\text{NiH}}(k) - 1) \\ + D(S_{\text{NiCl}}(k) - 1) + E(S_{\text{NiHI}}(k) - 1) \quad (4)$$

where

$$A = 2c_{\text{Ni}}c_{\text{O}}b_{\text{O}}(b_{\text{Ni}} - b'_{\text{Ni}}) \\ B = 2c_{\text{Ni}}c_{\text{D}}b_{\text{D}}(b_{\text{Ni}} - b'_{\text{Ni}}) \\ C = 2c_{\text{Ni}}c_{\text{H}}b_{\text{H}}(b_{\text{Ni}} - b'_{\text{Ni}}) \\ D = 2c_{\text{Ni}}c_{\text{Cl}}b_{\text{Cl}}(b_{\text{Ni}} - b'_{\text{Ni}}) \\ E = (c_{\text{Ni}})^2[(b_{\text{Ni}})^2 - (b'_{\text{Ni}})^2]$$

and  $b_{\text{Ni}}$  and  $b'_{\text{Ni}}$  are the mean coherent scattering lengths of nickel in the two solutions.

It can be shown (Soper *et al* 1977) that the contributions of Placzek corrections to the difference function are negligible to first order (see the Appendix); residual corrections to the experimental difference function may be made by reference to the sum rule

$$\int_0^{\infty} dk k^2 (S_{\alpha\beta}(k) - 1) = -2\pi^2 \rho_0 \quad (5)$$

and hence

$$\int_0^{\infty} dk k^2 \Delta_{\text{Ni}}(k) = -2\pi^2 \rho_0 (A + B + C + D + E). \quad (6)$$

It is usually sufficient to add or subtract a small constant from the measured  $\Delta_{\text{Ni}}(k)$  to ensure that it is consistent with equation (6).

The real-space difference function is obtained by Fourier transformation:

$$G_{\text{Ni}}(r) = \frac{1}{2\pi^2 \rho_0 r} \int_0^{\infty} dk \Delta_{\text{Ni}}(k) k \sin(kr) \quad (7)$$

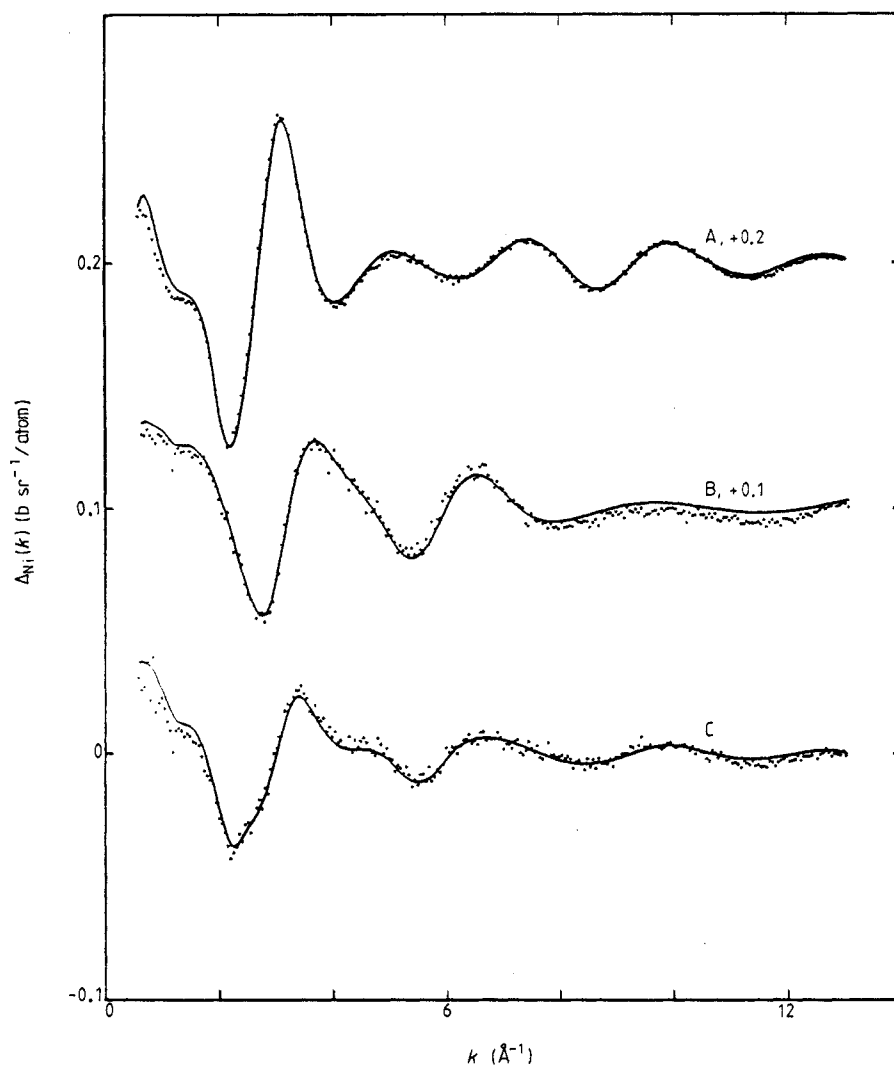
giving

$$G_{\text{Ni}}(r) = A(g_{\text{NiO}}(r) - 1) + B(g_{\text{NiD}}(r) - 1) + C(g_{\text{NiH}}(r) - 1) \\ + D(g_{\text{NiCl}}(r) - 1) + E(g_{\text{NiHI}}(r) - 1). \quad (8)$$

The weighting factors  $A$ ,  $B$ ,  $C$ ,  $D$ ,  $E$  for the differences discussed here are given in table 2. It can be seen that  $D$  and  $E$  are small compared with  $A$ ,  $B$ ,  $C$ , so the first-order difference is dominated by those terms involving nickel hydration.

**Table 2.** Weighting factors of the different contributions to the measured difference functions.

Solution	A (mb)	B (mb)	C (mb)	D (mb)	E (mb)
2.0 mol $\text{kg}^{-1}$ $\text{NiCl}_2$ in $\text{D}_2\text{O}$	8.499	19.431	—	1.121	0.081
2.0 mol $\text{kg}^{-1}$ $\text{NiCl}_2$ in $\text{H}_2\text{O}$	7.811	—	-10.067	0.927	0.061
2.0 mol $\text{kg}^{-1}$ $\text{NiCl}_2$ in null mixture	8.080	6.363	-6.846	0.996	0.067

**Figure 2.** The first-order-difference functions,  $\Delta_{\text{Ni}}(k)$ , for: (A) 2.0 mol  $\text{kg}^{-1}$   $\text{NiCl}_2$  in  $\text{D}_2\text{O}$ ; (B) 2.0 mol  $\text{kg}^{-1}$   $\text{NiCl}_2$  in  $\text{H}_2\text{O}$ ; (C) 2.0 mol  $\text{kg}^{-1}$   $\text{NiCl}_2$  in a null mixture. The full circles represent data points, while the full curves are spline fits consistent with  $G_{\text{Ni}}(r) = G_{\text{Ni}}(0)$  below  $r = 1.8 \text{ \AA}$ .

A concept useful in interpreting first-order-difference data is the coordination number. The mean number of particles  $\alpha$  in a region bounded by concentric spheres of radii  $r_1$  and  $r_2$  about a  $\text{Ni}^{2+}$  ion is given by

$$\bar{n}_{\text{Ni}}^{\alpha} = 4\pi\rho_0 c_{\alpha} \int_{r_1}^{r_2} dr r^2 g_{\text{Ni}\alpha}(r). \quad (9)$$

### 3. Results

The total corrected scattering cross sections,  $I(k)$ , are shown in figure 1 and illustrate how the incoherent background and Placzek 'droop' increase on going from pure  $\text{D}_2\text{O}$  to pure  $\text{H}_2\text{O}$ . The first-order differences obtained from these data are shown in figure 2. The deviations between the full circles and the curves (see the figure caption) are a measure of systematic errors.

For the  $\text{D}_2\text{O}$  solutions a correction was made to allow for the slight imbalance of the measured light-water content of the two samples (see table 1). The correction was obtained by scaling the  $I(k)$  for  $2.0 \text{ mol kg}^{-1} \text{ NiCl}_2$  in  $\text{H}_2\text{O}$ . The corrected data are not significantly different from the uncorrected data in real space for  $r \geq 1.8 \text{ \AA}$ . For the null mixture, the difference function was corrected by the empirical procedure described in the Appendix.

The  $G_{\text{Ni}}(r)$  are shown in figure 3. The peak occurring between about 1.8 and 2.4  $\text{\AA}$  is associated with  $g_{\text{NiO}}(r)$  and that occurring between 2.4 and 3.0  $\text{\AA}$  with  $g_{\text{NiH}}(r)$  or  $g_{\text{NiD}}(r)$ . The structural parameters with errors (see the Appendix) are given in table 3.

### 4. Discussion

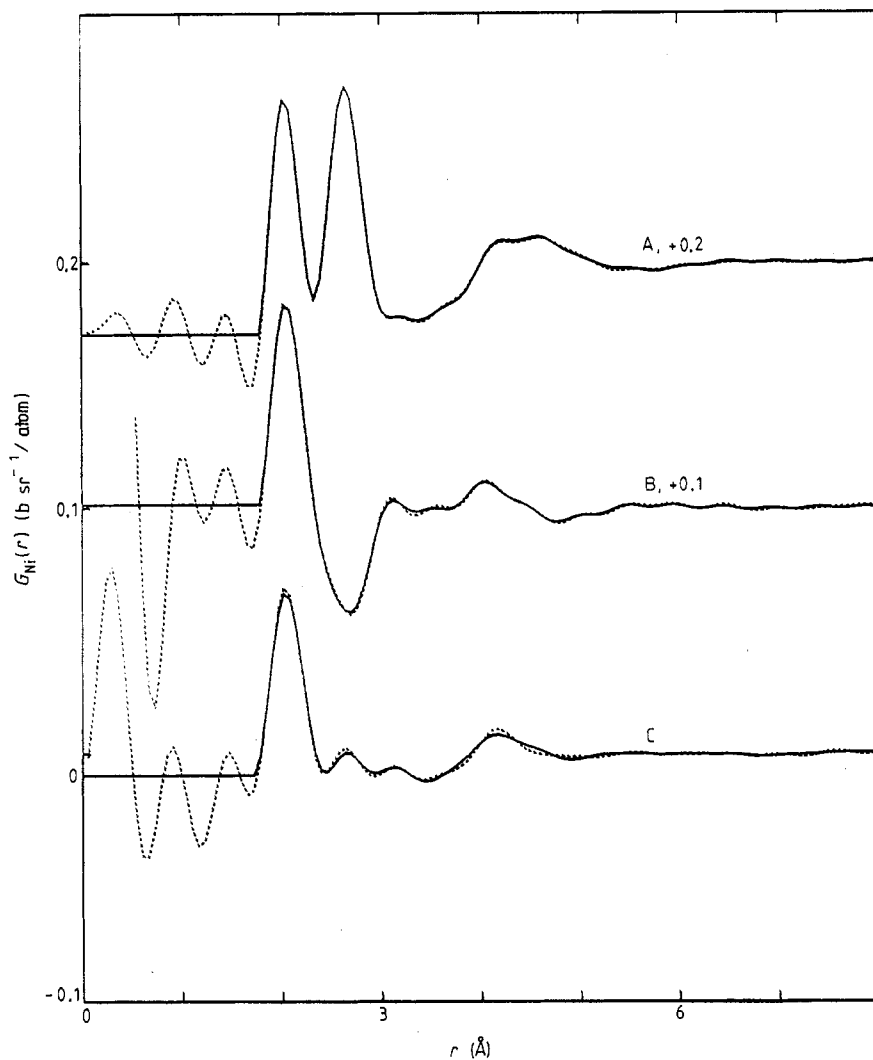
#### 4.1. Comparison of hydration in $\text{D}_2\text{O}$ and $\text{H}_2\text{O}$

The real-space structure for the solutions in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  is shown in figure 4. The  $g_{\text{NiH}}(r)$  component for the solution in  $\text{H}_2\text{O}$  makes a negative contribution to the  $G_{\text{Ni}}(r)$  (table 2). Table 3 shows that there is no evidence for any change in hydration properties between solutions in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . There is a broadening of  $g_{\text{NiH}}(r)$  with respect to  $g_{\text{NiD}}(r)$ , but this is within experimental error. The fact that  $\bar{n}_{\text{Ni}}^{\text{H}} = 2\bar{n}_{\text{Ni}}^{\text{O}}$  for both the  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  solutions confirms the absence of serious systematic errors.

It is interesting to note the difference in the behaviour of  $G_{\text{Ni}}(r)$  for the solutions in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  in the region  $3.5 < r < 6 \text{ \AA}$ . The successive peak and dip in the data for the  $\text{H}_2\text{O}$  solution indicate a degree of orientation of the water molecules in the second coordination shell, with the oxygen atoms tending to point towards the cation.

#### 4.2. Determination of $g_{\text{NiH}}(r)$

Based on the assumption that  $S_{\text{NiO}}(k)$  and  $S_{\text{NiH}}(k)$  are the same in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , a combination of the two  $\Delta_{\text{Ni}}(k)$  for the solutions in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  yields the partial structure factor  $S_{\text{NiH}}(k)$  (see figure 5). The  $g_{\text{NiH}}(r)$  obtained from this function is shown in figure 6, where it is compared with  $g_{\text{MgH}}(r)$  obtained from a simulation of  $\text{MgCl}_2$  in  $\text{H}_2\text{O}$  (Dietz *et al* 1982). The two  $g(r)$  agree in their general forms. Integration between  $r_1 = 3.1 \text{ \AA}$  and  $5.3 < r_2 < 5.7 \text{ \AA}$  yields a coordination number of  $36 \pm 4$  which corresponds to  $18 \pm 2$  water molecules in the second shell.



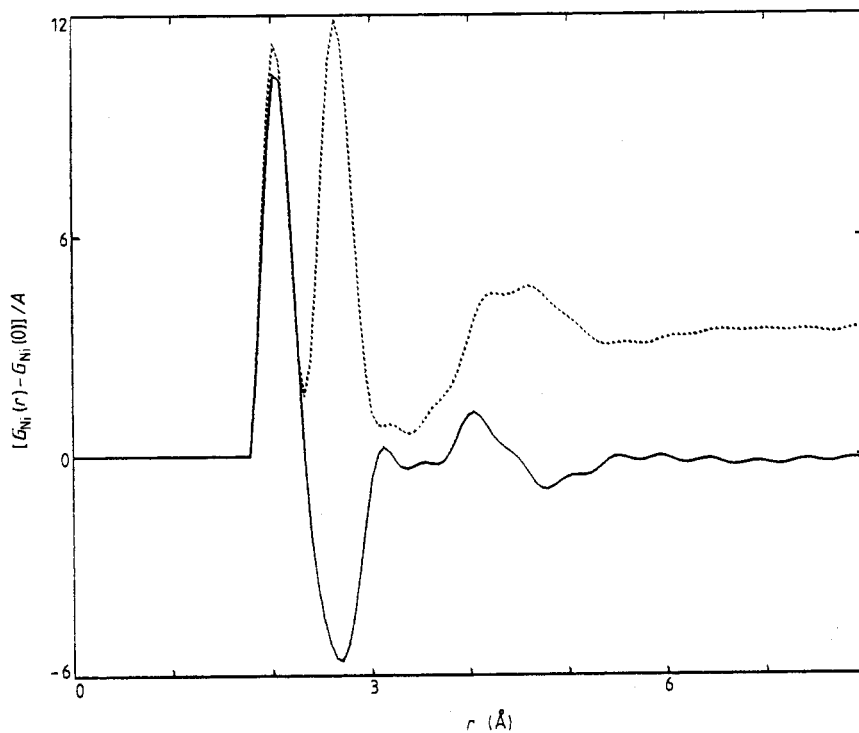
**Figure 3.** The real-space difference functions,  $G_{\text{Ni}}(r)$  for: (A) 2.0 mol kg<sup>-1</sup> NiCl<sub>2</sub> in D<sub>2</sub>O; (B) 2.0 mol kg<sup>-1</sup> NiCl<sub>2</sub> in H<sub>2</sub>O (to avoid confusion in the diagram, the unphysical oscillations below  $r = 0.6$  Å are not shown); (C) 2.0 mol kg<sup>-1</sup> NiCl<sub>2</sub> in a null mixture. The dotted curves are Fourier transforms of the experimental data points, while the full curves are transforms of splines fitted to the data, with  $G_{\text{Ni}}(r)$  set equal to  $G_{\text{Ni}}(0)$  below  $r = 1.8$  Å.

**Table 3.** Mean distances and coordination numbers obtained from the first-order-difference data. (The coordination numbers were obtained using a Gaussian fitting routine.)

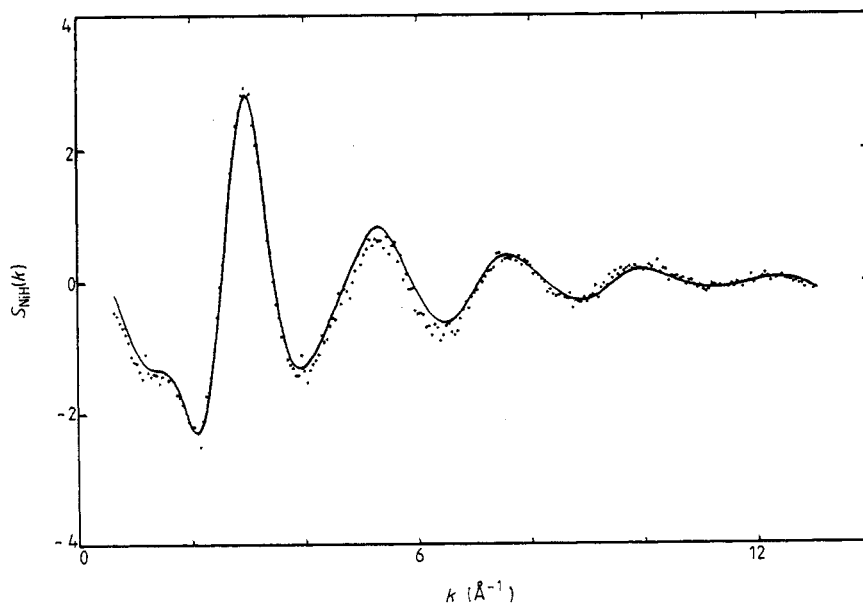
Solution	$r_{\text{NiO}}$ (Å)	$r_{\text{NiH}}$ (Å)	$n_{\text{Ni}}^{\text{O}}$	$n_{\text{Ni}}^{\text{H}\dagger}$
2.0 mol kg <sup>-1</sup> NiCl <sub>2</sub> in D <sub>2</sub> O	2.06(2)	2.67(2)	5.9(1)	11.7(2)
2.0 mol kg <sup>-1</sup> NiCl <sub>2</sub> H <sub>2</sub> O	2.07(2)	2.69(2)	6.0(2)	11.8(4)
2.0 mol kg <sup>-1</sup> NiCl <sub>2</sub> in null mixture	2.07(2)	—	5.5(5)	—

† In this context, 'H' represents both hydrogen and deuterium.

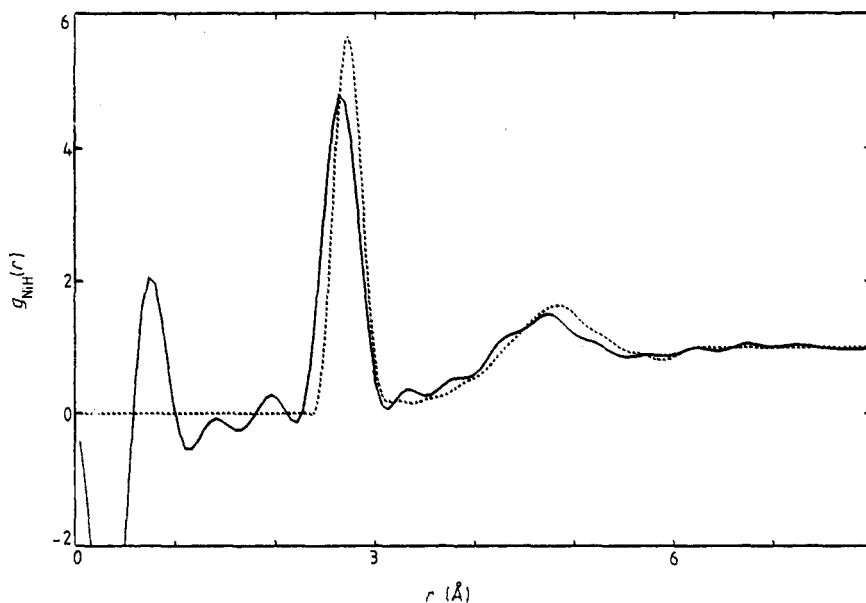




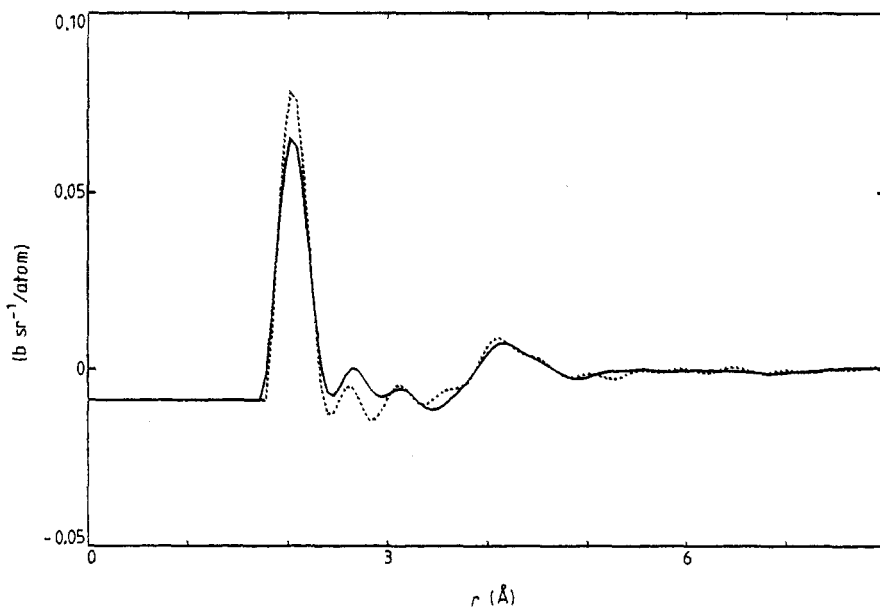
**Figure 4.** The 'normalised' real-space difference function  $(G_{\text{Ni}}(r) - G_{\text{Ni}}(0))/A$  for  $2.0 \text{ mol kg}^{-1}$   $\text{NiCl}_2$  in  $\text{D}_2\text{O}$  (dotted curve) and  $2.0 \text{ mol kg}^{-1}$   $\text{NiCl}_2$  in  $\text{H}_2\text{O}$  (full curve). To avoid confusion in the diagram, the unphysical oscillations below  $r = 1.8 \text{ \AA}$  are not shown.



**Figure 5.** The partial structure factor,  $S_{\text{NiH}}(k)$  obtained by combination of  $\Delta_{\text{Ni}}(k)$  for  $2.0 \text{ mol kg}^{-1}$   $\text{NiCl}_2$  in  $\text{D}_2\text{O}$ , and  $2.0 \text{ mol kg}^{-1}$   $\text{NiCl}_2$  in  $\text{H}_2\text{O}$ . The circles are data points, and the curve is a spline fit consistent with  $g_{\text{NiH}}(r) = 0$  below  $r = 1.8 \text{ \AA}$ .



**Figure 6.** The partial pair distribution function  $g_{\text{NiH}}(r)$  for a  $2.0 \text{ mol kg}^{-1}$   $\text{NiCl}_2$  in water (full curve), compared with  $g_{\text{MgH}}(r)$  obtained from a molecular dynamics simulation (Dietz *et al* 1982) (dotted curve).



**Figure 7.** Full curve:  $G_{\text{Ni}}(r)$  for  $2.0 \text{ mol kg}^{-1}$   $\text{NiCl}_2$  in a null mixture. Dotted curve:

$$0.327G_{\text{Ni}^{\text{D}_2\text{O}}}^{\text{D}_2\text{O}}(r) + 0.680G_{\text{Ni}^{\text{H}_2\text{O}}}^{\text{H}_2\text{O}}(r) = 8.09(g_{\text{NiO}}(r) - 1) + 6.366(g_{\text{NiD}}(r) - 1)$$

$$- 6.846(g_{\text{NiH}}(r) - 1) + 0.997(g_{\text{NiCl}}(r) - 1) + 0.068(g_{\text{NiNi}}(r) - 1)$$

in units of  $10^{-3} \text{ b}$ . (The superscript on  $G_{\text{Ni}}(r)$  labels the solutions in  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$ .)

### 4.3. Isotopic fractionation of hydrated water

If  $G_{\text{Ni}}(r)$  obtained for the solution in a null mixture is compared with the appropriate combination of the  $G_{\text{Ni}}(r)$  in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  (see figure 7) a discrepancy is apparent in the region of the first peak. The neutron scattering cross sections of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  are well known (Hughes and Harvey 1985), but those for a null mixture are not. In the analysis it was assumed that the cross section for the null mixture was a weighted average of the cross sections for  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , but given the large concentration in the null mixture of HOD this approximation could lead to significant errors in the region of the first peak in  $g_{\text{NiO}}(r)$ . The uncertainty quoted in table 3 assumes a normalisation error of 10% (see the Appendix).

The difference in  $G_{\text{Ni}}(r)$  around 2.69 Å suggests that there is approximately 40% deuterium present in the hydration shell, i.e. about 5% more than in the solution as a whole. Moreover, the effect of a change of normalisation of 10% does not significantly affect this result. By contrast, the theoretical calculations of Newton and Friedman (1985) predict a preferential hydration by light-water molecules in the first coordination shell of divalent cations. However, their calculation is based on free-energy arguments which involved a high degree of enthalpy–entropy compensation. Clearly there is a need for further experimentation, and experiments are planned using  $\text{Cr}^{3+}$  for which a larger effect is predicted.

## 5. Conclusions

The above results demonstrate that the isotropic first-order-difference method can be successfully applied to aqueous electrolyte solutions of light water and of light-water/heavy-water mixtures. It is thus possible to obtain the ion–hydrogen radial distribution function and test theoretical calculation at the partial-structure-factor level. In addition, the method provides a means of studying isotopic fractionation in solutions with different amounts of water and heavy water.

## Acknowledgments

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## Appendix

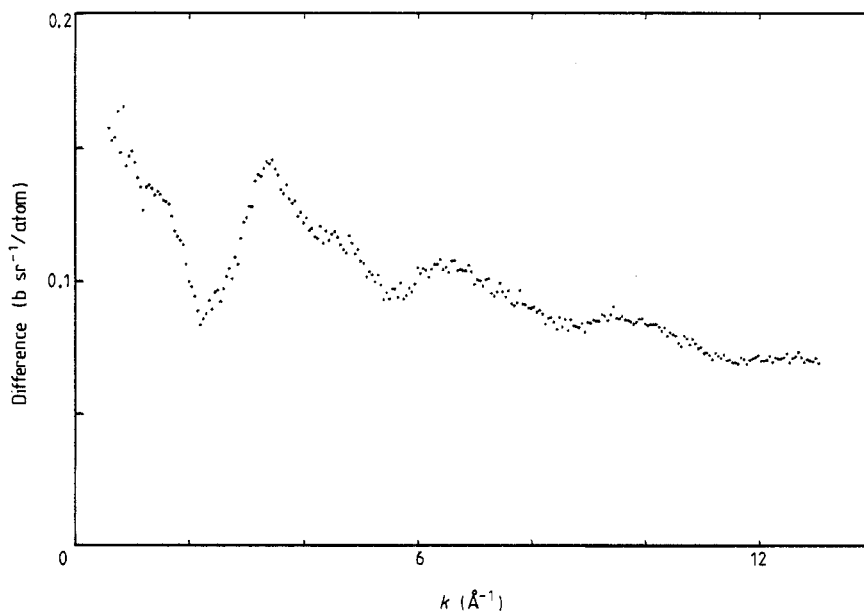
The raw data were corrected for multiple scattering and absorption (using the neutron cross sections given in table 1) and normalised by the methods referred to in the text. The multiple scattering is assumed to be isotropic, and is treated as a constant to be subtracted from the data, after correction for attenuation. Since the scattering powers of each of the pairs of isotopically enriched samples were nearly the same, the multiple

scattering essentially cancelled to better than 0.1% in the difference. The normalisation of the data was made with respect to a vanadium standard, and was independent of the multiple-scattering correction made to the samples. The normalisation was, however, crucially dependent on the attenuation corrections. (Simulations indicate that these are accurate to within 1% for an inelastic anisotropic scatterer, provided the absorption cross-section is not too large (Powell 1989). The normalisation was also dependent on attenuation and multiple-scattering corrections made to the vanadium scattering. These are known to be accurate to much better than 1% for an isotropic, elastic scatterer such as vanadium.

The run times were not optimised to give the same statistical error for each water mixture, and the errors arising from this on  $I(k)$  varied between 0.001 and 0.003  $\text{b sr}^{-1}/\text{atom}$  across the  $k$ -range for the  $\text{H}_2\text{O}$  data and the null-mixture data, and between 0.0006 and 0.0016  $\text{b sr}^{-1}/\text{atom}$  for the  $\text{D}_2\text{O}$  data. The *statistical* errors are therefore sufficiently small not to affect the Fourier transform.

As shown by Soper *et al* (1977) the Placzek corrections to a first-order-difference function for an experiment in  $\text{D}_2\text{O}$  is sufficiently small to be ignored. The arguments presented apply equally to solutions in  $\text{H}_2\text{O}$ . The residual Placzek correction to the 'self'-scattering is independent of the solvent, while the correction to the interference terms will be approximately twice as great for the  $\text{H}_2\text{O}$  solution as for the  $\text{D}_2\text{O}$  solution.

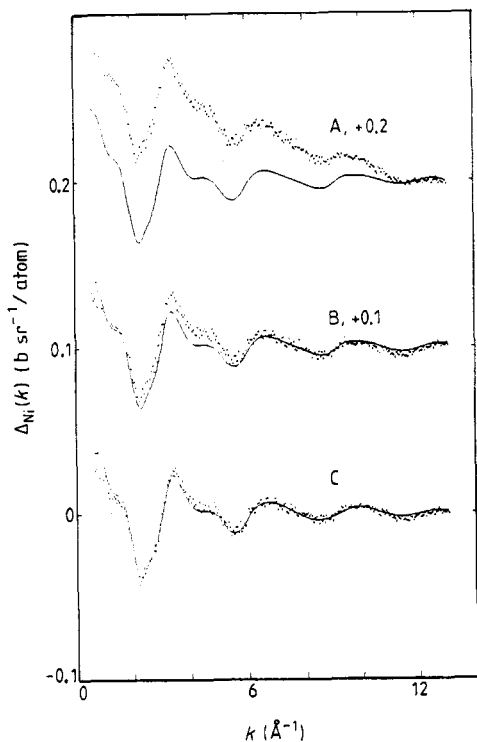
The difference function obtained for a 2.0 mol kg solution of  $\text{NiCl}_2$  in a null mixture of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  is shown in figure A1. It can be seen that there is a slope superimposed on the oscillations of the function. The magnitude and direction of this slope cannot be explained in terms of the known differences in composition between the two samples (table 1). It was, therefore, necessary to adopt some empirical correction procedures to obtain the difference function used for transformation. Three procedures were used:



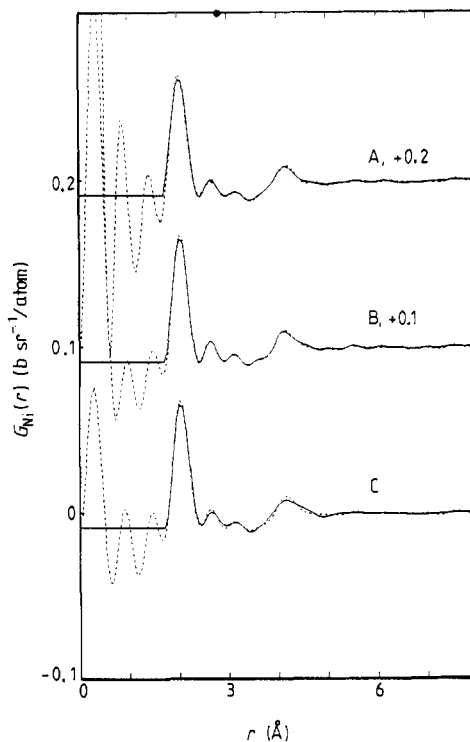
**Figure A1.** The difference obtained by direct subtraction of  $I(k)$  for  $^{nat}\text{NiCl}_2$  and  $^{62}\text{NiCl}_2$  in a null mixture.

- (i) subtract a constant from the difference function in figure A1, such that  $\Delta_{\text{Ni}}(k) \rightarrow 0$  for large  $k$ ;
- (ii) subtract a straight line of the form  $ak + b$  from figure A1, so that the corrected  $\Delta_{\text{Ni}}(k)$  is flat and satisfies the sum rule (equation (6));
- (iii) when constructing the difference function, multiply one set of data by a constant, so as to obtain a flat difference function, then subtract a constant so that the function satisfies the sum rule.

The results of these approaches are shown in figure A2, and their Fourier transformations in figure A3 from which it can be seen that at  $r$ -values above about  $1.8 \text{ \AA}$ , the  $G_{\text{Ni}}(r)$  are essentially independent of the correction procedures.



**Figure A2.** The  $\Delta_{\text{Ni}}(k)$  for  $2.0 \text{ mol kg}^{-1} \text{ NiCl}_2$  in a null mixture of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , obtained by the different methods described in the text. (A)  $\Delta_{\text{Ni}}(k) = {}^{\text{nat}}I(k) - {}^{62}I(k) - 0.072$ ; (B)  $\Delta_{\text{Ni}}(k) = {}^{\text{nat}}I(k) - {}^{62}I(k) - (0.0045k + 0.1279)$ ; (C)  $\Delta_{\text{Ni}}(k) = {}^{\text{nat}}I(k) - 1.02 {}^{62}I(k) - 0.0573$ . The superscript on  $I(k)$  indicates the isotopic composition of nickel. The full circles and the curves have the same significance as in figure 2.



**Figure A3.**  $G_{\text{Ni}}(r)$  obtained from  $\Delta_{\text{Ni}}(k)$  in figure A2, where A, B, C label the different methods as described in the text and figure A1.

The  $\Delta_{\text{Ni}}(k)$  obtained by method (iii) has been used in the main part of the paper, since this is the most self-consistent.

The extraction of  $S_{\text{NiH}}(k)$  from the first-order-difference functions is a second-order-difference procedure. However, the weighting of  $S_{\text{NiH}}(k)$  in the  $\Delta_{\text{Ni}}(k)$  is very large (50%

or more of the total function). Thus the statistical and systematic errors in  $S_{\text{NiH}}(k)$  are of the same order as those for  $\Delta_{\text{Ni}}(k)$ .

The quoted uncertainties in table 3 are based on reasonable estimates of the uncertainties in the parameters used in the correction procedures, and of the experimental errors.

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