Neutron Diffraction, Isotopic Substitution and the Structure of Aqueous Solutions [and Discussion]

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Neutron diffraction, isotopic substitution and the structure of aqueous solutions

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The structural properties of liquids that contain more than one atomic species are difficult to unravel. The essential reason for this is that conventional diffraction experiments measure a rather coarse average of all the $\frac{1}{2}\nu(\nu+1)$ partial structure factors that characterize a liquid containing ν species.

This paper describes the way that neutron diffraction experiments carried out on samples that are identical in all respects, except that the isotope of one or more of the species has been changed, can overcome this problem. It is shown that the systematic use of isotopes, by virtue of the dependence of the neutron scattering amplitude on isotope, enables partial structure factors to be extracted directly from diffraction data. A detailed account of the method applied to a range of aqueous solutions of electrolytes under various experimental conditions is given.

In particular, *first-order difference* experiments yield information on ion–water conformations. Data are now available for the cations Ni^{2+}, Ca^{2+} and Li^{+} and these results will be discussed in detail. The data for Ni^{2+} are of particular interest because they show that the substantial angle of tilt between the plane of the water molecule and the Ni–O axis gradually disappears as the concentration is reduced.

The only anion studied so far is Cl^{-} but the experiments have been carried out for a wide range of counter ions. We have shown that for such different electrolytes as $CaCl_2$, NaCl and LiCl, the nature of the hydration around the Cl^{-} ion is essentially the same.

Finally, the method of *second-order difference* yields directly ion–ion correlations. The experiments described include Cl–Cl structure factors in NaCl and $NiCl_2$ solutions, and the Ni–Ni structure factor in $NiCl_2$ solutions. Comparisons made with theoretical predictions based on the primitive model of electrolytes show that in certain cases, the molecular nature of the water is a crucial factor in determining ion–ion correlations. In other cases, the primitive model contains most of the essential physics.

1. Introduction

In the extensive literature devoted to the structural problem of aqueous electrolyte solutions, two distinct themes have emerged. The first of these is to do with the coordination, orientation and conformation of the water–ion subsystem. This aspect of the solution problem, usually referred to as hydration, has been the subject of an enormous amount of experimental effort. It is however, fair comment that until recently important questions like, for example, the detailed dependence on concentration of the conformation of the ion–water system or the sensitivity of hydration to the nature of the counter-ion were largely unanswered. The theoretical methods available to discuss hydration are extensive and range from the techniques of coordination chemistry through quantum mechanical cluster calculations and finally to computer simulations based on a model water potential. What is badly needed is a sharp experimental test of these theories; we believe that the method of neutron diffraction on isotopically enriched samples described below meets that need.

The second general theme concerns the correlations between ions. Here we can discern two important sub-themes. In the 'primitive' view of electrolytes, the molecular nature of the water is neglected and the problem becomes the classic one in liquid state physics: given a known (and relatively simple) interaction, what structure will result? At the other extreme, essentially chemical notions like complexing, ion-pairing and stable species are used. The validity of both approaches can be tested in terms of *ion–ion* correlation functions and once again these are accessible through the isotopic substitution method. In this paper I shall review what has been achieved so far and what the future prospects are for this subject.

2. THE METHOD

We have shown that the neutron '*first order*' difference method (Soper *et al.* 1977; Neilson & Enderby 1978; Enderby & Neilson 1980) allows one to gain direct information about the detailed arrangement of the water molecules around the ions in aqueous solutions. Let us consider a salt MX_n (M = metal; X = halide) dissolved in heavy water, D_2O, and let c represent the atomic fraction of M. The quantity that is central to the method is the algebraic difference in the absolute differential scattering cross section as a function of the scattering vector k from two samples that are identical in all respects except that the isotopic state of M (or X) has been changed; this quantity, denoted $\Delta_M(k)$ or $\Delta_X(k)$ is the sum of four partial structure factors $S_{\alpha\beta}(k)$ weighted in such a way that only those relating to ion–water correlations are significant. Explicitly:

$$\Delta_M(k) = A_1(S_{MO}(k)-1)+B_1(S_{MD}(k)-1)+C_1(S_{MX}(k)-1)+D_1(S_{MM}(k)-1) \tag{1}$$

and

$$\Delta_X(k) = A_2(S_{XO}(k)-1)+B_2(S_{XD}(k)-1)+C_2(S_{MX}(k)-1)+D_2(S_{XX}(k)-1), \tag{2}$$

where

$$A_1 = \tfrac{2}{3}c(1-c-nc)f_O(f_M-f'_M); \quad A_2 = \tfrac{2}{3}nc(1-c-nc)f_O(f_X-f'_X);$$

$$B_1 = \tfrac{4}{3}c(1-c-nc)f_D(f_M-f'_M); \quad B_2 = \tfrac{4}{3}nc(1-c-nc)f_D(f_X-f'_X);$$

$$C_1 = 2nc^2f_X(f_M-f'_M); \quad C_2 = 2nc^2f_M(f_X-f'_X); \quad \text{and}$$

$$D_1 = c^2(f_M^2-(f'_M)^2); \quad D_2 = n^2c^2(f_X^2-(f'_X)^2).$$

Here f_O and f_D are the neutron coherent scattering amplitudes for oxygen and deuterium and f_M, f'_M, f_X and f'_X are the scattering amplitudes for the isotopic states used in producing the salt MX_n.

The properties of $\Delta(k)$ have been discussed in detail elsewhere (Soper *et al.* 1977) and need not be enlarged on here. The crucial property, apart from the fact that $A, B > C, D$, is that the high k Placzek distortions in the differential scattering cross section from aqueous solutions are essentially eliminated so that a weighted distribution function $G(r)$ can be determined from

$$G(r) = \frac{1}{2\pi^2\rho r}\int \Delta(k)\, k \sin(kr)\, dk, \tag{3}$$

where ρ is the total number density, by standard numerical quadrature. In terms of the partial radial distribution functions, $g_{\alpha\beta}(r)$, it follows at once that

$$G_M(r) = A_1(g_{MO}-1)+B_1(g_{MD}-1)+C_1(g_{MX}-1)+D_1(g_{MM}-1) \tag{4}$$

and

$$G_X(r) = A_2(g_{XO}-1)+B_2(g_{XD}-1)+C_2(g_{MX}-1)+D_2(g_{XX}-1). \tag{5}$$

Since A and B are much greater than C and D the method yields a high resolution measurement of an appropriate combination of g_{MO} and g_{MD} or g_{XO} and g_{XD}.

The '*second order*' difference method (Howe *et al.* 1974; Enderby & Neilson 1980) allows one to gain direct information about ion–ion correlations. Let us again consider a salt MX_n dissolved in $\mathrm{D_2O}$ and let $\varDelta_{\mathrm{M}_1}(k)$ and $\varDelta_{\mathrm{M}_2}(k)$ represent the two first-order differences for three solutions with M in the isotopic state M, 'M and "M. Similarly let $\varDelta_{\mathrm{X}_1}(k)$ and $\varDelta_{\mathrm{X}_2}(k)$ be the corresponding quantities for isotopic substitutions of the anion X. It follows from equations (1) and (2) that

$$S_{\mathrm{MM}}(k) = \frac{\varDelta_{\mathrm{M}_1}(k)}{A^{(2)}_{\mathrm{M}}} - \frac{\varDelta_{\mathrm{M}_2}(k)}{B^{(2)}_{\mathrm{M}}} + 1; \tag{6}$$

$$S_{\mathrm{XX}}(k) = \frac{\varDelta_{\mathrm{X}_1}(k)}{A^{(2)}_{\mathrm{X}}} - \frac{\varDelta_{\mathrm{X}_2}(k)}{B^{(2)}_{\mathrm{X}}} + 1; \tag{7}$$

with coefficients $A_{\mathrm{M}} \ldots B_{\mathrm{X}}$ given by

$$A^{(2)}_{\mathrm{M}} = c^2(f_{\mathrm{M}} - f'_{\mathrm{M}})\,(f'_{\mathrm{M}} - f''_{\mathrm{M}}); \quad B^{(2)}_{\mathrm{M}} = c^2(f_{\mathrm{M}} - f''_{\mathrm{M}})\,(f'_{\mathrm{M}} - f''_{\mathrm{M}});$$

$$A^{(2)}_{\mathrm{X}} = n^2c^2(f_{\mathrm{X}} - f'_{\mathrm{X}})\,(f'_{\mathrm{X}} - f''_{\mathrm{X}}); \quad B^{(2)}_{\mathrm{X}} = n^2c^2(f_{\mathrm{X}} - f''_{\mathrm{X}})\,(f'_{\mathrm{X}} - f''_{\mathrm{X}}).$$

To obtain the cross term S_{MX}, we must use four samples whose isotopic state can be represented by

$$\mathrm{MX}_{n'},\ {}'\mathrm{MX}_{n'},\ \mathrm{M'X}_{n'},\ {}'\mathrm{M'X}_{n}.$$

Let $\varDelta^{\mathrm{X}}_{\mathrm{M}}$ represent the algebraic difference in intensity between the scattering from the first and the second samples, and $\varDelta'^{\mathrm{X}}_{\mathrm{M}}$ the difference between the third and the fourth sample. Straightforward manipulation yields

$$S_{\mathrm{MX}}(k) = \frac{\varDelta^{\mathrm{X}}_{\mathrm{M}} - \varDelta'^{\mathrm{X}}_{\mathrm{M}}}{2nc^2(f_{\mathrm{M}} - f'_{\mathrm{M}})\,(f_{\mathrm{X}} - f'_{\mathrm{X}})} + 1. \tag{8}$$

In real space, the three ion–ion radial distribution functions can be obtained through

$$g_{\alpha\beta}(r) = \frac{1}{2\pi^2\rho r}\int [S_{\alpha\beta}(k) - 1]\, k \sin(kr)\, \mathrm{d}k, \tag{9}$$

by analogy with (3) with α, β = M or X.

3. Experimental results

3.1. *The hydration of cations*

In the research programme carried out so far, three cations have been investigated. Salts of $\mathrm{NiCl_2}$ (isotopically changing the Ni), $\mathrm{CaCl_2}$ (isotopically changing the Ca) and LiCl (isotopically changing the Li) were dissolved in $\mathrm{D_2O}$ and the concentrations and coefficients A_1, B_1, C_1, and D_1 are given in table 1. The statement made in §2 that C_1 and D_1 are small compared with A_1 and B_1 is evidently true. We now consider each of these cations in turn.

3.1.1. $\mathrm{Ni^{2+}}$

Our evidence on $\mathrm{Ni^{2+}}$ hydration derives from the detailed study of $\mathrm{NiCl_2}$ solutions made over a wide range of concentrations by Neilson & Enderby (1978). An example of $\varDelta_{\mathrm{Ni}}(k)$ and of $G_{\mathrm{Ni}}(r)$ is shown in figures 1 and 2. It is particularly significant that at $r \approx 3.0$ Å†, $G_{\mathrm{Ni}}(r)$

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† 1 Å = 10^{-10} m = 10^{-1} nm.

close to the sum $-(A_1+B_1+C_1+D_1)$ implying (equation (4)) that g_{NiO} and g_{NiD} are both small at this value of r; this reflects the stability of the first hydration shell. The two peaks located at 2.07 and 2.67 Å can be identified with Ni–O and Ni–D correlations respectively, on the grounds that the ratio of the areas beneath them, when weighted by r^2, is almost exactly $A_1:B_1$. An integral over $4\pi r^2 G_{\mathrm{Ni}}(r)$ for $1.8 < r < 3.0$ Å yields the number of water molecules in the first coordination shell, the so-called *hydration number*. We are therefore able for the first time to investigate the concentration dependence of the conformation of Ni–D_2O provided we know the geometry of the water molecule.

For all plausible values of the bond length and angle, the data show unambiguously that for concentrations in excess of 1 molal the angle of tilt, θ, between the Ni–O axis and the plane of the water molecule is substantial (figure 2 and table 2). As the concentration of $NiCl_2$ is

TABLE 1. SCATTERING LENGTH AND SAMPLE PARAMETERS (CATION HYDRATION)

electrolyte solution	isotopes	abundance (%)	scattering lengths 10^{-12} cm	c	molality	A/mb†	B/mb	C/mb	D/mb
$NiCl_2.D_2O$	^{N}Ni ^{62}Ni	— 94.9	1.03 −0.79	0.0270	4.41	17.4	40.0	5.05	0.32
				0.0192	3.05	12.6	29.0	2.52	0.15
				0.0093	1.46	06.4	14.6	0.61	0.04
				0.0056	0.85	03.85	08.85	0.22	0.013
				0.0028	0.42	01.94	04.46	0.054	0.00338
				0.00057	0.086	00.40	00.92	0.0023	0.00015
$CaCl_2.D_2O$	^{N}Ca ^{44}Ca	— 95.4	0.466 0.18	0.0275	4.49	03.0	06.8	0.09	0.02
$LiCl.D_2O$	^{6}Li ^{7}Li	82.2 99.9	0.180 0.233	0.0277	3.57	03.47	07.92	0.85	−0.011

† 1 millibarn (mb) = 10^{-31} m^2.

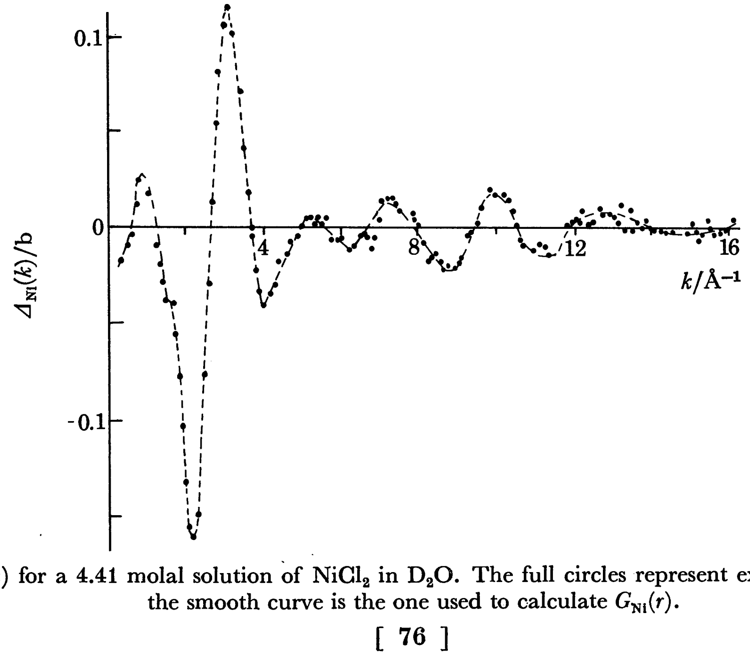

FIGURE 1. $\Delta_{\mathrm{Ni}}(k)$ for a 4.41 molal solution of $NiCl_2$ in D_2O. The full circles represent experimental points and the smooth curve is the one used to calculate $G_{\mathrm{Ni}}(r)$.

reduced, the Ni–O distance remains fixed, and although the errors in the measured value of the Ni–D distance become appreciable, the results strongly suggest that this distance increases. This provides clear structural evidence for the distortion of the hydration spheres as the packing fraction of the hydrated ions is increased; these observations, when combined with energy calculations, will allow a realistic estimate to be made of the repulsive part of the interionic potential. There are, so far as we are aware, no theoretical studies of the Ni–H_2O system from any of the standpoints discussed in §1. A neutron diffraction study of the crystal hydrate yields values for Ni–O, Ni–H and θ of 2.05 Å, 2.59 Å and 47°, respectively (Kleinberg 1969). These results emphasize the close similarity between concentrated solutions and their crystal hydrates (Friedman & Lewis 1976). The new feature of the solution data, i.e. the concentration

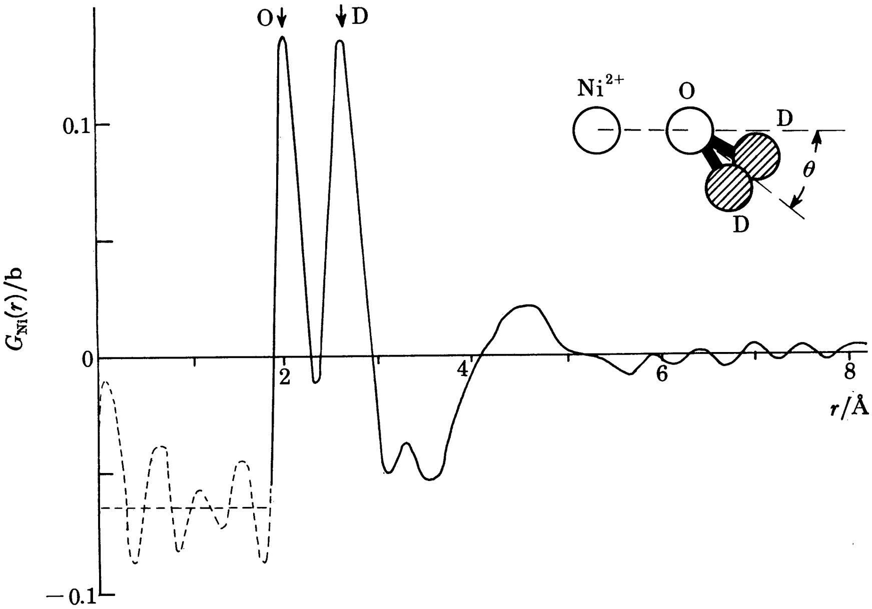

FIGURE 2. $G_{Ni}(r)$ for a 4.41 molal solution of $NiCl_2$ in D_2O.

TABLE 2. HYDRATION OF Ni^{2+}

solute	molality	ion–oxygen distance/Å	ion–deuterium distance/Å	θ/deg†	hydration number
$NiCl_2$	0.086	2.07 ± 0.03	2.80 ± 0.03	0 ± 20	6.8 ± 0.8
	0.46	2.10 ± 0.02	2.80 ± 0.02	17 ± 10	6.8 ± 0.8
	0.85	2.09 ± 0.02	2.76 ± 0.02	27 ± 10	6.6 ± 0.5
	1.46	2.07 ± 0.02	2.67 ± 0.02	42 ± 8	5.8 ± 0.3
	3.05	2.07 ± 0.02	2.67 ± 0.02	42 ± 8	5.8 ± 0.2
	4.41	2.07 ± 0.02	2.67 ± 0.02	42 ± 8	5.8 ± 0.2

† θ is the angle between the plane of the water molecule and the Ni–O axis.

TABLE 3. HYDRATION OF Ca^{2+}

solute	molality	ion–oxygen distance/Å	ion–deuterium distance/Å	θ/deg†	hydration number
$CaCl_2$	4.49	2.40 ± 0.03	2.93 ± 0.05	51 ± 15	5.5 ± 0.2

† θ is the angle between the plane of the water molecule and the Ca–O axis.

dependence of θ is, as yet, unexplained. A final comment to make on the Ni^{2+} data concerns the feature in $G_{Ni}(r)$ for $3.7 \leqslant r \leqslant 5.3$ Å. This is the first *structural* evidence for the existence of a *second* hydration shell; this shell becomes better defined as the concentration of $NiCl_2$ is reduced. The experimental resolution does not allow the ion–water configuration to be elucidated in detail but integration of $4\pi r^2 G(r)$ for $3.7 < r < 5.3$ Å yields a second hydration number of 15 ± 2.

Table 4. Hydration of Li^+

solute	molality	ion–oxygen distance/Å	ion–deuterium distance/Å	θ/deg†	hydration number
LiCl	3.57	1.95 ± 0.02	2.55 ± 0.02	40 ± 10	5.5 ± 0.3

† θ is the angle between the plane of the water molecule and the Li–O axis.

3.1.2. Ca^{2+}

So far only one concentration of Ca^{2+} has been studied (Cummings *et al.* 1980) with the results shown in table 3. The ion–water conformation consistent with the data resembles that found for Ni and the measured Ca–O distance is exactly that given by molecular orbital calculations on an isolated ion–water pair (Kollman & Kuntz 1972). However, the molecular orbital calculations suggest that θ is zero for such a pair, in disagreement with these data. In the condensed phase, it is often suggested that a more favourable configuration may be one in which an oxygen lone pair points towards the Ca^{2+} ion and this model leads to a θ of *ca.* 60°, in reasonable agreement with the experimental value. It is clearly necessary to make measurements on more dilute solutions where this effect can be separated from that due to the distortion of the hydration spheres bought about by close packing; such an experiment has recently been completed (N. A. Hewish & J. E. Enderby, unpublished). The data, though not yet fully analysed, show that θ is *ca.* 40° at 1 molal. Thus the lone-pair argument, which should become increasingly valid at low c, is not supported by experiment so far as divalent cations are concerned. We therefore turn to the third cation studied, Li^+.

3.1.3. Li^+

Experiments on lithium salts (Newsome *et al.* 1980*a*) are complicated by the high absorption of ^6Li. A detailed study has shown that the ion–water distances are not dependent on the numerical procedures used to analyse data from highly absorbing samples like ^6LiCl in D_2O. There is, however, more uncertainty in the measured hydration number. The experiments on Li salts are of special interest because Li is a small, simple and monovalent ion. The results, summarized in table 4, show that θ is appreciably smaller than that expected from the lone pair configuration even at the high concentration used in the experiment. Once again, the importance of varying the concentration is evident but as it seems highly unlikely that an increase in θ would arise as c is *reduced*, we believe that the emphasis in much of the published work on the role of the lone pair electrons in deciding ion–water configurations in the condensed phase is in urgent need of revision. Our data at low concentrations for Ni^{2+} and Ca^{2+} support this conclusion. The hydration number, though subject to a large uncertainty at present, clearly favours *octahedral* rather than the *tetrahedral* coordination, a matter of long standing dispute in solution chemistry.

3.2. *The hydration of anions*

The method has been applied to Cl^- and in a wide range of solutions (table 5). Typical results for $\Delta_{Cl}(k)$ and $G_{Cl}(r)$ are shown in figures 3 and 4, where the Cl^-–D_2O conformation consistent with these data is shown. A summary of all the results is presented in table 6. When we compare the nature of the Cl^- hydration among the various solutions, several conclusions emerge. First, the general form of $G_{Cl}(r)$ is remarkably similar in all cases. This apparent lack of sensitivity of anionic hydration to the nature of the counter-ion (with the exception of Ni^{2+}) emphasizes the importance of *local* effects. The coefficients of the partial radial distribution functions are more favourable in some cases than others, and the enhanced resolution thereby obtained allow us to define closely the Cl^-–D_2O geometry. The data clearly favour the linear configuration tentatively proposed by Soper *et al.* (1977), but with a tilt angle generally less than 7°. The Cl–O distance is in good agreement with the value predicted by quantum mechanical cluster calculations (Schuster *et al.* 1975); it differs from that found in the early molecular dynamics simulation studies of Heinzinger (1976), which employed the so-called ST2 potential (Stillinger & Rahman 1974). It will be important to consider what refinements to this potential are needed if the simulation studies are to reflect more accurately the new data, and progress along these lines has been reported (Pàlinkàs *et al.* 1977). The exceptional case, Ni^{2+}, clearly deserves further study; the fact that Ni^{2+} is a transition metal ion may have special significance, and indeed a dilution experiment recently performed (G. W. Neilson, unpublished) indicates that the tilt angle disappears at low *c*. Finally, it should be noted for the

TABLE 5. SCATTERING LENGTH AND SAMPLE PARAMETERS (ANION HYDRATION)

electrolyte solution	isotope	abundance (%)	scattering lengths 10^{-12} cm	*c*	molality	*A*/mb	*B*/mb	*C*/mb	*D*/mb
LiCl	^{35}Cl	99.35	1.17	0.0588	9.95	16.6	38.3	−1.34	4.38
	^{37}Cl	90.4	0.35						
	^{35}Cl	99.35	1.17	0.0227	3.57	06.95	16.0	−0.2	0.6
	^{37}Cl	90.41	0.35						
NaCl	^{35}Cl	99.35	1.17	0.0331	5.32	09.9	22.7	0.65	1.37
	^{37}Cl	90.4	0.35						
RbCl	^{35}Cl	99.35	1.17	0.0192	2.99	05.8	13.3	0.52	0.46
	^{37}Cl	90.4	0.35						
$CaCl_2$	^{35}Cl	99.35	1.17	0.0275	4.49	16.0	36.8	1.16	3.77
	^{37}Cl	90.4	0.35						
$NiCl_2$	^{35}Cl	99.35	1.17	0.0270	4.35	15.7	36.3	2.40	3.60
	^{37}Cl	90.4	0.35						

TABLE 6. HYDRATION OF ANIONS OBTAINED BY NEUTRON DIFFRACTION

solute	molality	Cl–D(1)/Å	Cl–O/Å	Cl–D(2)/Å (range)	ψ/deg (range)	coordination number
LiCl	3.57	2.25 ± 0.02	3.34 ± 0.05	—	0	5.9 ± 0.2
LiCl	9.95	2.22 ± 0.02	3.29 ± 0.04	3.50–3.68	0	5.3 ± 0.2
NaCl	5.32	2.26 ± 0.03	3.20 ± 0.05	—	0–20	5.5 ± 0.4
RbCl	4.36	2.26 ± 0.03	3.20 ± 0.05	—	0–20	5.8 ± 0.3
$CaCl_2$	4.49	2.25 ± 0.02	3.25 ± 0.04	3.55–3.65	0–7	5.8 ± 0.2
$NiCl_2$	4.35	2.29 ± 0.02	3.20 ± 0.04	3.40–3.50	22–32	5.7 ± 0.2

case of $CaCl_2$ that 5.8 ± 0.2 water molecules surround each Cl^- ion and 5.5 ± 0.2 water molecules surround each Ca^{2+} ion. Thus about 17 water molecules are instantaneously coordinated to each molecule of $CaCl_2$, which implies, for a 4.49 molal solution (*ca.* 11 water molecules per $CaCl_2$ molecule), substantial sharing of the water molecules between the cations and anions. The structural implications of this, particularly for the Ca–Cl radial distribution function, will form the basis of a future study. Water sharing is clearly significant for $NiCl_2$ solutions also, the only other case where both ions have been studied in the same solution.

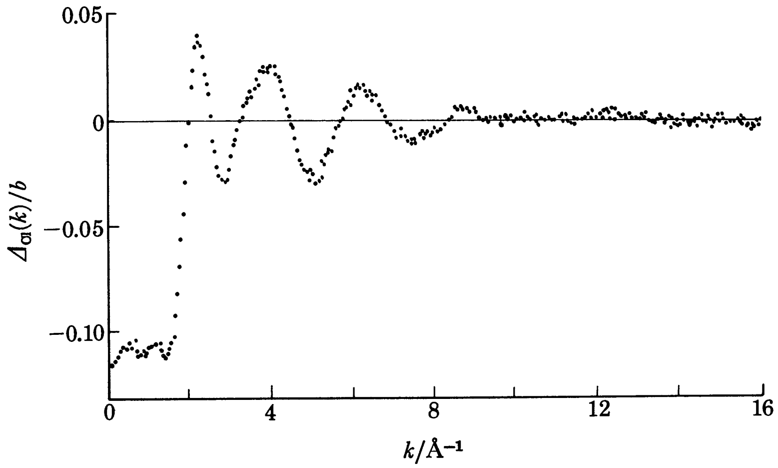

FIGURE 3. $\Delta_{Cl}(k)$ for a 9.95 molal solution of LiCl in D_2O. (J. R. Newsome, personal communication.)

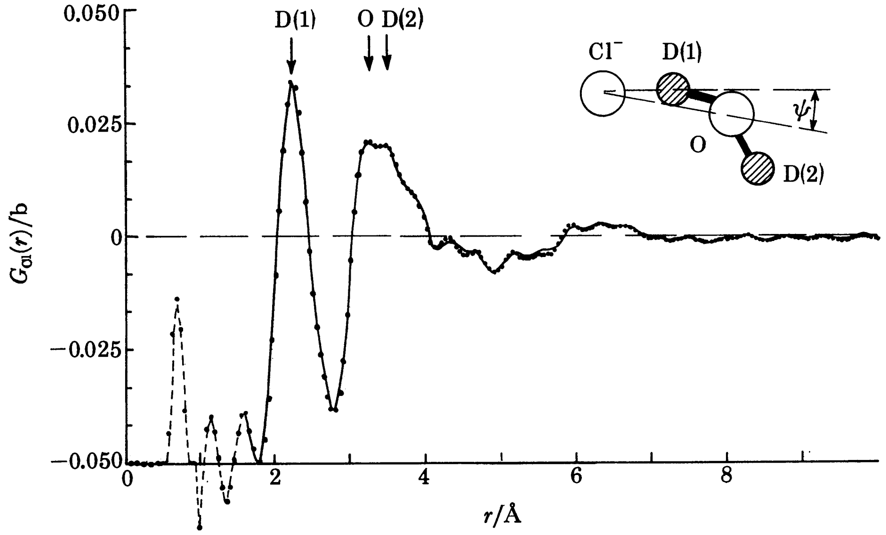

FIGURE 4. $G_{Cl}(r)$ for a 9.95 molal solution of LiCl in D_2O. (J. R. Newsome, personal communication.)

3.3. *Ion–ion correlations*

The first application of the second order difference method was made by Howe *et al.* (1974) to a 4.41 molal† solution of $NiCl_2$ in D_2O. The isotopic state of the Ni was changed so that data only for one of three partial structure factors, $S_{NiNi}(k)$, were obtained. $S_{NiNi}(k)$ was

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† Not 5.51 molal as incorrectly stated in the original article.

characterized by (*a*) a well defined peak at a k of *ca.* 1 Å^{-1} and (*b*) considerable distortion beyond k of *ca.* 2 Å^{-1}, which was ascribed by the authors to the incomplete cancellation of the Plazek corrections. Neilson & Enderby (1980) repeated and extended the measurements to include Cl substitutions and eliminated the Plazek distortions by careful sample preparations in which the light water content of the samples was properly balanced. The results are shown in figures 5 and 6; the existence of the peak at 1 Å^{-1} is confirmed for the Ni–Ni case and is clearly demonstrated for the Cl–Cl case. However, these experiments are at the very limit of the existing technique and the results are not yet of sufficient accuracy to derive a fully self-consistent $g_{\mathrm{NiNi}}(r)$ or $g_{\mathrm{ClCl}}(r)$. We shall therefore restrict our discussion to k-space, although it is hoped in future to improve the basic technique and thereby allow data of higher quality to be obtained.

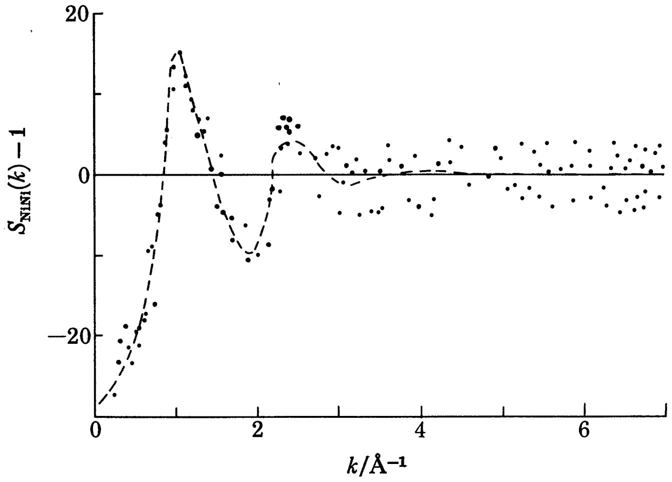

FIGURE 5. The partial structure factor, $S_{\mathrm{NiNi}}(k)$ for a 4.41 molal solution of $NiCl_2$ in D_2O.

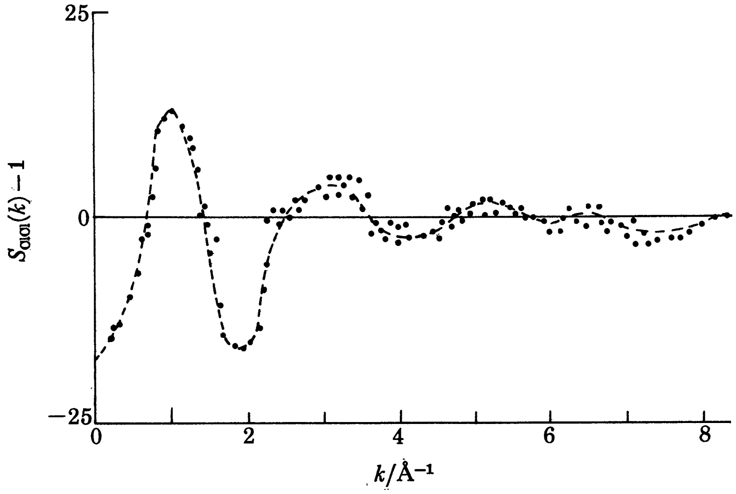

FIGURE 6. The partial structure factor, $S_{\mathrm{ClCl}}(k)$ for a 4.41 molal solution of $NiCl_2$ in D_2O.

In their original article, Howe *et al.* (1974) argued that the data implied that the ions were arranged in a more ordered way than would be expected from primitive models. Experimental support for this view came from a variety of sources (March & Tosi 1974; Fontana 1976; Cubiotti *et al.* 1977), and was further strengthened by the observation that the position k_0 of the prepeak in $F(k)$ the *total* diffraction pattern, characteristic of $NiCl_2$ solutions, scaled to the one-third power of the molarity (Neilson *et al.* 1975). This approach was challenged by Quirke & Soper (1977) who showed that by representing the Ni^{2+} and Cl^- ions (appropriately 'dressed' by six water molecules) as hard spheres, substantial values of $S_{\mathrm{NiNi}}(k)$ at the first maximum could be obtained. It is now clear, however, that hard-sphere structure factors are

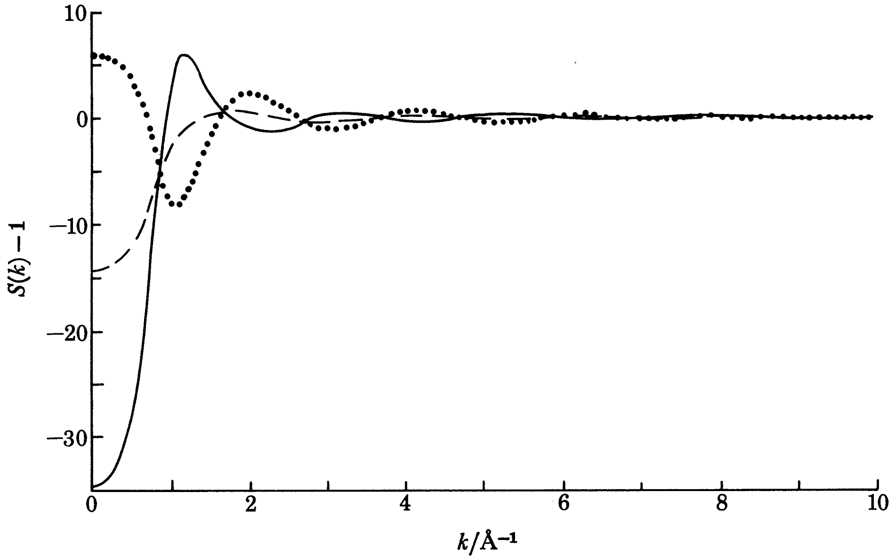

FIGURE 7. Partial structure factors derived for a primitive model of a molal solution of $NiCl_2$. The diameter was chosen as 3.0 Å and the dielectric constant taken as 60. Full curve, $S_{\mathrm{NiNi}}(k)$; broken curve, $S_{\mathrm{ClCl}}(k)$; dotted curve, $S_{\mathrm{NiCl}}(k)$ (M. Telo da Gama & R. E. Evans, private communication).

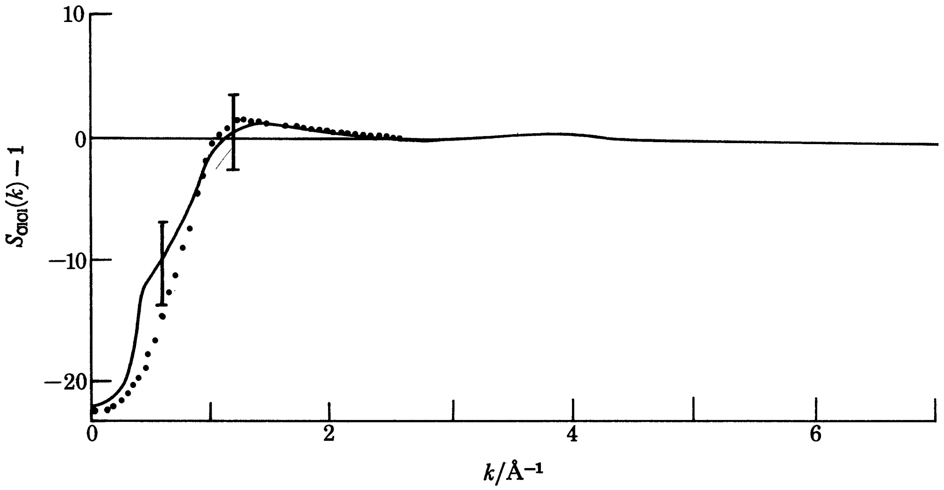

FIGURE 8. The partial structure factor $S_{\mathrm{ClCl}}(k)$ for a 5.32 molal solution of NaCl in D_2O. Full curve, experiment; dotted curve, theory (mean spherical approximation).

vastly changed once Coulomb interactions are included (see especially Enderby & Neilson 1980). An analytic and instructive approach to the evaluation of ion–ion structure factors within the primitive model is the so-called mean spherical approximation (Waisman & Lebowitz 1972) whose properties have been recently explored in this laboratory by Telo da Gama & Evans (private communication).

The *k*-space results derived from the work of Telo da Gama & Evans for a 4 molal solution of $NiCl_2$ in D_2O with an effective ionic diameter chosen to be 3.0 Å are shown in figure 7. Clearly this approach fails to predict the marked peaks found in our experiments for the *like* distribution functions. The newer and more reliable data therefore support the original conclusions of Howe *et al.* (1974) and March & Tosi (1974), that primitive models either with or without Coulomb interactions are inconsistent with the experimental facts so far as $NiCl_2$ is concerned. A series of investigations has been recently completed for Cl^- ions in a range of 1–1 systems is in progress (Newsome *et al.* 1980*b*). In the only case so far analysed in detail (a 5.32 molal solution of NaCl), the experimental data agree in their general form with those predicted by Telo da Gama & Evans (see figure 8). It is our view that the molecular nature of the water is a crucial factor in sustaining long-range effects in certain aqueous solutions and an extension of the approach developed by Outhwaite (1976) and others is a necessary step towards a more reliastic theory. In other cases, the primitive model appears to contain all the essential physics. The distinction arises, we believe, from *intermediate*-range chemical effects, i.e. those that cannot be incorporated in the primitive model by adjusting the ion size. In order to identify these ions, for which intermediate-range chemical effects are important, a more systematic investigation is needed and we turn finally to consider what experiments could form part of a future research programme.

TABLE 7

valence	ion	possible isotopes	scattering lengths known	feasibility	
				hydration	ion–ion correlations
1	Li^+	^{6}Li ^{7}Li	yes	2	3
1	$(ND_4)^+$	^{14}N ^{15}N	yes	2	4
1	Ag^+	^{107}Ag ^{109}Ag	yes	2	4
1, 2	Cu^+, Cu^{2+}	^{63}Cu ^{65}Cu	yes	1	3
2	Mg^{2+}	^{24}Mg ^{25}Mg	yes	2	4
2	Ca^{2+}	^{40}Ca ^{44}Ca	yes	1	2
2	Ni^{2+}	^{58}Ni ^{60}Ni ^{62}Ni	yes	1	2
2	Ba^{2+}	^{138}Ba ^{137}Ba	no	?	?
2	Sr^{2+}	^{86}Sr ^{88}Sr	no	?	?
2	Zn^{2+}	^{64}Zn ^{68}Zn	yes	4	5
2	Sn^{2+}	^{102}Sn ^{122}Sn	yes	4	5
2	Hg^{2+}	^{200}Hg ^{202}Hg	no	?	?
2, 3	Fe^{2+}, Fe^{3+}	^{56}Fe ^{57}Fe	yes	1	2
2, 3	Cr^{2+}, Cr^{3+}	^{52}Cr ^{53}Cr	yes	1	2
−1	Cl^-	^{35}Cl ^{37}Cl	yes	1	2
−1	I^-	^{127}I ^{129}I†	no	?	?
−1	$(NO_2)^-$, $(NO_3)^-$	^{14}N ^{15}N	yes	1	3
−1	$(CN)^-$, $(SCN)^-$	^{14}N ^{15}N	yes	1	2
−1	$(ClO_3)^-$, $(ClO_4)^-$	^{35}Cl ^{37}Cl	yes	1	2
−2	$(SO_3)^-$, $(SO_4)^-$	^{32}S ^{33}S	yes	3	4
−2	$(CO_3)^-$	^{12}C ^{13}C	yes	4	5

† Slightly radioactive.

4. Future prospects

The principles behind the technique are now well established and we can look to the future. A careful study of nuclear isotopes, their level structure and their availability shows that, contrary to what is frequently supposed, a wide but exemplary series of experiments is possible. There are *at least* 14 cations and 11 anions for which appropriate isotopic substitutions can in principle be made, and these are shown in table 7. The feasibility of any given experiment depends on a combination of scattering lengths, salt concentrations and linear absorption coefficients. We are now able to state explicitly which of all the possible experiments are feasible. For simplicity, the results are expressed in table 7 on a scale of 1 to 5 (1, feasibility demonstrated, experiment well understood; 5, not possible with present technology). For practical purposes, only ions with a feasibility number in the range 1–3 need be considered at present, although an improvement in effective neutron counting rates by a factor of 10 would allow category 4 experiments to be considered. It is apparent that an extensive programme of research designed to answer many of the longstanding but specific questions in this subject is implied by Table 7. One might, for example, compare the conformation of water with respect to Fe^{2+} and Fe^{3+} ions; the nature of the hydration around *nitrate ions* is another topic that would repay investigation. A careful study of Mg^{2+} with a view to its isomorphic replacement by Ni^{2+} is yet another line of attack. So far as ion–ion correlations are concerned, important candidates for study are those for which isotopes of both cations and anions can be changed so that all three correlation functions, including the important cross-term, can be measured. Some examples are, for 1–1 systems, LiCl and ND_4NO_3; for 2–1 systems, $CaCl_2$ and $MgCl_2$; and for 3–1 systems, $FeCl_3$ and $CrCl_3$. With the development of new and powerful sources of thermal neutrons like, for example, the Rutherford Laboratory's Spallation Source, the future prospects for a major programme of research into the fundamental structure of solutions look extremely favourable.

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Discussion

E. W. J. Mitchell (*Clarendon Laboratory, Oxford, U.K.*). Lock, Missolloras, Mitchell & Stewart have repeated the measurements of the partial structure factors of molten CsCl by using the isotope substitution method, with vanadium containers rather than the silica ones used by Derrien & Dupuy. The partial $g(r)$'s have been determined and are in good agreement with the molecular dynamics simulation of Dixon & Sangster (1977) as in their fig. 2. The main features (experimental values followed by theoretical values in parentheses) are:

g_{+-}	first peak	position	3.37 Å	(3.3)
		height	4.3	(4.1)
	first minimum	position	5.4	(5.0)
g_{--}	first peak	position	4.67	(4.6)
		height	1.63	(1.7)
	subsid. peak	position	6.76	(6.6)
		height	1.09	(1.1)

The full analysis is in course of publication. We do not observe the additional features found by Derrien & Dupuy.

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J. G. Powles (*University of Kent at Canterbury, U.K.*). Professor Enderby has chosen to discuss in detail his important work on the structure of aqueous electrolytic solutions exploiting the isotope substitution method. It is perhaps worth remarking, as he is well aware, that the neutron scattering technique, and the isotope substitution method in particular, has made possible important advances in our understanding of the whole field of liquids and amorphous systems. It has been applied also with success, in particular, to molten salts (Page & Mika 1971), to molecular liquids (Bertagnolli *et al.* 1978) and to compressed gases (Soper & Egelstaff 1980), and there is no doubt that in due course we shall have very detailed and accurate information as to the structure of a great variety of fluid systems over a wide range of state conditions. This presents a serious challenge to the theory of fluids, and indeed great progress has been made in recent years in our understanding of the structure and dynamics of fluids.

It should be noted that the isotope substitution method is very demanding of instrument time wherever more than two or three different nuclei are present, even for one state point, and this further emphasizes the necessity of improved facilities especially as regards neutron flux. Nevertheless it should not be overlooked that even one structure factor for a given liquid can be extremely helpful in defining the structure of a fluid, and of course it is quite economical. In many important cases there may be only one partial structure factor anyway, e.g. fluids of homonuclear diatomic molecules, and in many cases some of the partial structure factors make only a small contribution to the total. Thus in liquid VCl_4 only S_{Cl-Cl} is significant (Gibson & Dore 1979). The important contribution of an X-ray structure factor should also not be overlooked.

Although, generally speaking, the coherent scattering length of most important isotopes are known there are still some gaps and some uncertainties (the *b* value for D was substantially changed recently!). The measurement of absolute scattering cross section is still tedious and difficult but is an important check on the analysis of data and shows the necessity of even more accurate measurement of scattering lengths.

The incoherent and the absorption cross sections are much less well known and this is important since the effect of these has to be allowed for very accurately before the coherent scattering law can be extracted, to sufficient accuracy, from the experimental data.

There is also the important problem of the recoil and detector corrections for light, and even not so light, nuclei (Powles 1979), which was neatly circumvented by Professor Enderby, but which in general presently tends to limit quite severely the accuracy of extracted coherent structure factors for many important liquids, e.g. water. This problem should also be eased by the availability of adequate fluxes of epithermal neutrons from new facilities such as the S.N.S.

It may be pointed out also that the slow neutron scattering data on liquids, and particularly on molecular liquids, have provided important information on the interatomic or intermolecular potentials (Cheung & Powles 1976), which are extremely difficult to determine by any method. This information is of course basic to our understanding of the condensed state, including crystals. The second virial coefficient method has been recently extended to neutron scattering (Powles *et al.* 1979), but here again a thorough investigation will demand the availability of much more abundant supplies of neutrons than are currently available. This seems likely to resurrect the field of neutron scattering by dilute gases, which has been rather neglected in recent years.

Finally, it may be noted that the study of the dynamics of disordered systems is developing rapidly and we may expect a major effort in this field in the next few years now that we are approaching a thorough understanding of the structural properties, which is an essential prerequisite.

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