Diffraction studies of aqueous electrolyte solutions

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Abstract - The structural properties of several aqua ions in
solution have been determined by neutron and X-ray diffraction.
Neutron diffraction combined with isotopic substitution
provides direct information about ionic hydration and ion-ion
correlations.   In particular, systematic studies of
different series of ions shows characteristic behaviour which
depends on ionic size, charge and electronic configuration.

The relatively new method of X-ray diffraction combined with
isomorphic substitution   has been applied to Ni^{2+}/Mg^{2+}
and Na^+/Ag^+ isomorphic pairs. The results show that the
second order difference technique provides a formally exact
determination of cation-cation correlations within the
isomorphic approximation. The results are consistent with
those obtained from the neutron diffraction isotopic
difference methods, and pave the way for a more comprehensive
investigation of ionic structure in solution as a function of
concentration, counterion and pressure and temperature.

1. INTRODUCTION

Neutron and X-ray diffraction methods provide a means by which the
structure of an aqueous electrolyte solution can be elucidated (1). This
structure is defined in terms of the pair radial distribution functions $g_{\alpha\beta}(r)$
of which there are ten in a system of the general form MX_nH_2O: three
which pertain to the solvent $- g_{HH}, g_{HO}, g_{OO}$, three which are relevant to
the solute g_{MM}, g_{MX}, g_{XX}, and four which refer to correlations between the
solute and the solvent $- g_{MO}, g_{MH}, g_{XO}, g_{XH}$. As will be shown below, each of
these functions contributes in varying degrees to a neutron or X-ray
scattering pattern (see Fig.1).

It is the object of the experimentalist to determine each of the functions
$g_{\alpha\beta}$ as precisely as possible in order to have a basic knowledge of the
structure of the solution. However, because of the complexity of an
electrolyte solution it is not possible to obtain all this information.
Nevertheless, over the past decade, difference methods of neutron and
X-ray diffraction have been developed, and we now possess a much more
detailed description of the ionic structure of electrolyte solutions (2).

The method of isotopic substitution combined with neutron diffraction
allows direct determination of both ion-water structure (the first order
difference method), (3) and ion-ion structure (the second order difference
method), (4) of the solution. The equivalent method for X-ray diffraction
based on isomorphic substitution has been introduced to facilitate the
determination of quantitative information for ion-ion correlations from a
second order difference between diffraction patterns of solutions shown to
be isomorphic at the first order difference level (5).

The usefulness of determining the pairwise structure of a solution is underlined by
its relevance to (i), the systematic categorisation of the relative strengths of ions
and (ii) the provision of a means of testing, at the microscopic level, the results of
theoretical calculations and computer simulations (6).

2. DIFFRACTION METHODS

As is well established (7), a beam of particles (neutrons or X-rays) of wavelength, λ incident on a target, will produce a diffraction pattern, $I(\theta)$ at a scattering angle, θ. After the appropriate data analyses, $I(\theta)$ can be reduced to the structure factor, $F(k)$, where $k = 4\pi\sin(\theta/2)/\lambda$ is the amplitude of the scattering vector. $F(k)$ contains the basic structural information of the liquid : viz

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

where c_α is the concentration of species α whose scattering is characterised by b_α For neutron scattering b_α is termed the coherent scattering and is independent of k (8). For X-ray scattering b_α is the atomic form factor and exhibits a strong k dependence (9). The double summation is over all independent scattering species. To distinguish between the X-ray and neutron structure factors we use $F(k)$ for the former.

The partial structure factor $S_{\alpha\beta}(k)$ is related to the Fourier transformation of the radial pair distribution function :

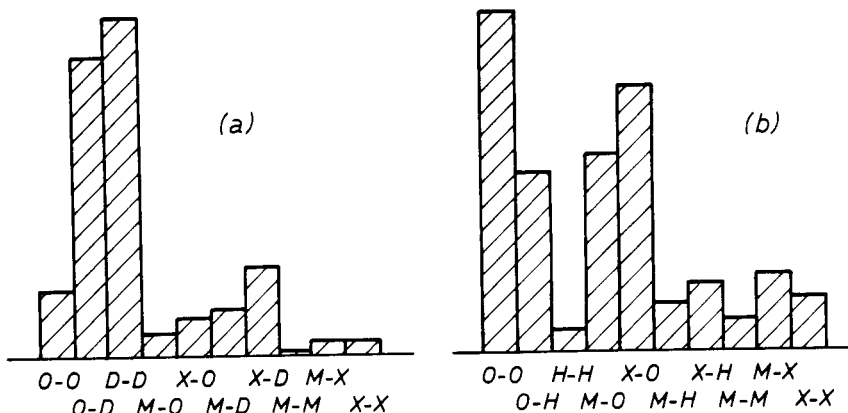$$g_{\alpha\beta}(r) - 1 = 1/(2\pi^2\rho r) \int [S_{\alpha\beta}(k) - 1] k \sin kr \, dr \tag{2}$$

where $\rho = N/V$ is the total number density of the solution and is typically $0.1 \, \text{\AA}^{-3}$

The coordination number of atom A in a shell of thickness Δr at r around a central atom B is given by:

$$n_B^A = c_A \rho 4\pi r^2 g_{AB}(r) \Delta r \tag{3}$$

2.1 DIFFERENCE METHODS

Fig.1 shows the relative contributions of the various structural correlations to the neutron and X-ray $F(k)$'s for a concentrated aqueous electrolyte solution. It is obvious from this figure that the possibility of obtaining any information from a neutron diffraction experiment about anything other than the solvent structure is unlikely. It is also unlikely that much information is forthcoming from an X-ray diffraction measurement on the same system other than that pertaining to S_{OO}, S_{XO}, S_{MO}. Moreover, because the X-ray form factors are k-dependent, it is often not possible to obtain individual $g_{\alpha\beta}(r)$'s directly because of resolution broadening.


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   (a)                                    (b)

O-O  D-D  X-O  X-D  M-X          O-O  H-H  X-O  X-H  M-X
   O-D  M-O  M-D  M-M  X-X          O-H  M-O  M-H  M-M  X-X
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Figs. 1-(a) Relative weighting of the ten pair correlation functions in the neutron diffraction pattern (Equ(1)) of a 4 molar $NiCl_2$ heavy water solution.

-(b) Relative weighting of the ten pair correlation functions in the X-ray diffraction $F(k)$ (Equ.1) of a 4 molar $NiCl_2$ water solution.

In order to progress therefore, one must devise a superior method if we wish to determine ion-water and ion-ion structure. And it is for this reason that the difference methods of diffraction have been developed (Fig.2).
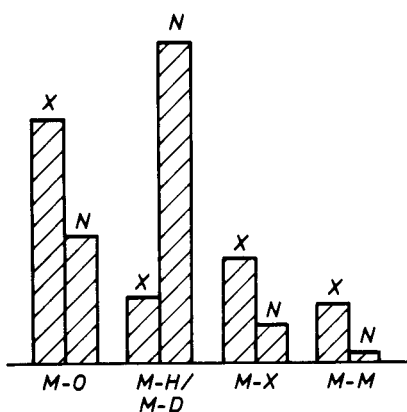
Fig.2. Relative weighting of the 4 pair correlation functions in the X-ray (X) and neutron (N) difference functions (Equ.4) for 4 molar $NiCl_2$ in water (X-ray coefficients are for k = 0).

First order differences: ion–water structure

The first order difference method of neutron diffraction was introduced during the 1970's (3), and since then, many new and useful results have been obtained for the ion-water structure in a variety of solutions (10).

It is a straightforward matter to show (3) from Equ.(2) that if the F(k)'s are obtained for two solutions of the same concentration of electrolyte in heavy water, and whose cation (or anion) differs only in its isotopic state defined by b (i.e. b' and b") then

$$\Delta_M(k) = F_1(k) - F_2(k) = A(S_{MO}(k)-1) + B(S_{MD}(k)-1)$$

$$+ C(S_{MX}(k)-1) + D(S_{MM}(k)-1) \tag{4}$$

$$A = 2c_M c_O b_O \Delta b_M , \quad B = 2c_M c_D b_D \Delta b_M , \quad C = 2c_M c_X b_X \Delta b_M$$

$$D = c_M^2 \Delta b_M^2 , \quad \Delta b_M = b_M' - b_M'' , \quad \Delta b_M^2 = b_M'^2 - b_M''^2$$

Fourier transformation of $\Delta(k)$ gives –

$$G(r) = Ag_{MO} + Bg_{MD} + Cg_{MX} + Dg_{MM} + E \tag{5}$$

where $\quad E = -(A + B + C + D)$

Generally A,B >> C,D and Equ.5 primarily gives information of the ion-water coordination.

(Note. Heavy water solutions are used in neutron diffraction experiments because of its lower incoherent scattering than ordinary water.)

Second order differences: ion–ion coordination

The second order difference method of neutron diffraction was first applied to a concentrated solution of $NiCl_2$ in heavy water (4). The $NiCl_2$. D_2O system is particularly well suited to these types of experiments because of the large number of widely varying b values of Ni and Cl(8). The method requires F(k)'s for <u>three</u> isotope substitutions of the cation (or anion), and the analysis yields the <u>ionic</u> p.s.f. $S_{II}(k)$ –

$$S_{II}(k) = \frac{1}{c_I^2 (b_I'-b_I'')(b_J'-b_J'')} \left[\frac{F(k)-F(k)}{b_I'-b_I''} - \frac{F(k)-F_4(k)}{b_I''-b_I'''} \right] \tag{6}$$

The cation-anion p.s.f. can be obtained from the F(k)'s of <u>four</u> isotopically distinct cation and anion samples –

$$S_{IJ}(k) = \frac{1}{2c_Ic_J(b_I'-b_I'')(b_J'-b_J'')} \left[(F_{1I}-F_{2I}) - (F_{1J}-F_{2J}) \right] \tag{7}$$

The corresponding pair distribution functions $g_{II}(r)$ and $g_{IJ}(r)$ can be obtained from Equs.6 and 7 using Equ.2.

Despite the early success of the study of a 4.35 molal solution of $NiCl_2$ in heavy water the $g_{II}(r)$ has only been obtained in one other solution - 14.9 molal LiCl in heavy water [11]. The reasons for this are (i) the requirement of long counting times to get data of high statistical accuracy and (ii) the need for economically priced isotopes whose b values are significantly different. It is often the case that no suitable isotopes are available, as, for example, with sodium.

In order to overcome these problems we developed the method of X-ray diffraction with isomorphic substitution. This method is not new and indeed, Bol and co-workers carried out some very significant studies of solutions using this technique [12]. However, in their studies, isomorphism was never justified, and their interest was limited to ionic hydration. The method as discussed below aims to show how information of the ion-ion structure can be obtained, and in doing so is justified by reference to neutron diffraction results of ionic hydration, and self consistency checks of X-ray results pertaining to the first order difference structure.

To see this we return to the analysis appropriate to the first order difference method, and this time we apply the formalism to X-ray diffraction studies of equimolar solutions of isomorphically distinct atomic species.

At this stage it is worth discussing how isomorphic pairs are initially identified. This is done on the basis of (i) solid state coordination in a particular valence state [13],   (ii) information regarding solution kinetics [14], and (iii) neutron scattering properties that require that one of the species is susceptible to the neutron diffraction first order difference method. A secondary condition is that the isomorphs should be sufficiently well separated in atomic numbers so that reliable differences between X-ray diffraction patterns can be obtained. Suitable pairs to date include Ni^{2+}/Mg^{2+}, and Na^{+}/Ag^{+}, albeit the isomorphism of the latter pair is only approximate. Other pairs, whose isomorphism is yet to be demonstrated, may include Tl^{+}/Rb^{+} and Cr^{3+}/Al^{3+} [15].

The isomorphic difference method is also valid for neutron diffraction [16]. Indeed, it could be exploited with great effect for elements which do not differ greatly in their position in the periodic table, e.g. the rare earths. However, as we are principally interested in obtaining ion-ion correlations, X-ray diffraction methods are stressed because of the brighter beams available and the non-requirement of expensive isotopically enriched samples.

We now develop the formalism appropriate to the X-ray diffraction isomorphic difference methods [17]. It is essentially the same as that for the neutron diffraction methods, but with the important difference that the b's are k-dependent [9]. To distinguish them from the neutron b's we use the form b^X.

X-ray diffraction data are obtained for two equimolar solutions whose cations (or anions) are isomorphs. The F(k)'s of the solutions are calculated and their difference is taken :

$$\tilde{\Delta}_{M/M'} = F^X_1(k) - F^X_2(k) = A^X(S_{MO}-1) + B^X(S_{MH}-1) + C^X(S_{MX}-1) + D^X(S_{MM}-1) \quad (8)$$

where $A^X = 2c_M c_O b^X_O \Delta b^X_{M/M'}$, $B^X = 2c_H c_M b^X_H \Delta b^X_{M/M'}$, $C^X = 2c_X c_M b^X_X \Delta b^X_{M/M'}$

and $D^X = c^2_M \left[b^X_M{}^2 - b^X_M{}^2 \right]$, $\Delta b_{M/M'} = b^X_M - b^X_{M'}$

The coefficients A, B, C, D, are functions of k, and Fourier transformation of $\Delta_{M/M'}(k)$ will not, in general, give a clear picture of the ion water structure. However, Equ.8 can be used to establish the degree to which M and M' are isomorphic. This is done by comparing the Fourier transform of $\Delta_{M/M'}(k)/A^X$ and the 'true' $g_{MO}(r)$ as obtained in Equ.2. If the first peak in $g_{MO}(r)$ is well defined, such as in the case of a strongly hydrating cation, the comparison is readily made. Isomorphism is claimed if the $g_{MO}(r)$ obtained from X-rays is the same as that obtained from neutrons over the region of the first hydration zone. It is not possible to check the isomorphism beyond this region because of the inherently poor structural resolution beyond the first shell. However, since the main aim of the X-ray difference method is to obtain ion-ion structure and this structure is determined by longer range coulomb effects [17], it is sufficient to have established isomorphism in the first coordination shell around the ion.

Having demonstrated that M and M' are isomorphic, a third X-ray diffraction experiment is carried out on a 50/50 equimolar mixture of $MX_n.H_2O$ and $M'X_n.H_2O$. The F(k) of this solution is determined and combined with the other two F(k)'s of the individual solutions to give, within the isomorphic approximation, a formally exact equation for the p.s.f. $S_{MM}(k)$, viz

$$S_{MM}(k) = \frac{1}{c_M^2 (b_{M'}^x - b_{M/M'}^x)} \left[\frac{F_1^x - F^x}{b_M^x - b_{M'}^x} - \frac{F_1^x - F_3^x}{b_M^x - b_{M/M'}^x} \right] \tag{9}$$

where $b_{M/M'}^x$ is the appropriate atomic form factor for the mixture, i.e.

$$b_{M/M'}^x \qquad \qquad b_{M/M'}^x = \frac{b_M^x + b_M^x}{2}$$

The results of the third solution may also be used to provide additional confirmation of the isomorphism between M and M'. This is done by comparing Fourier transforms of two first order differences, $(F_1^x - F_2^x)/A^x$ and $(F_1^x - F_3^x)/(A^x)$ say. If these are self consistent in terms of the nearest neighbour ion-oxygen correlation, then M and M' are isomorphic.

In summary, the main advantage of the isomorphic method as applied to X-ray diffraction is that a systematic series of experiments over a wide range of p,T, ionic concentration, and counterion type can be undertaken economically in a relatively short period of time.

3. RESULTS AND DISCUSSION

3.1 IONIC HYDRATION

Tables 1 and 2 list the ion-D_2O coordination properties for all ions so far studied by the neutron diffraction first order difference technique. There is a rich variety of behaviour for these ions and in many cases the trends observed confirm model structures proposed on the basis of spectroscopic and thermodynamic studies (19). The results also provide theorists with a useful test of both model potential calculations (20) and computer simulation procedures (21).

TABLE 1. Cation hydration at room temperature as determined by neutron diffraction

Ion	Solute	Molality	Ion-oxygen distance(Å)	Ion-deuterium distance (Å)	θ (deg)	Hydration number	Reference
Li$^+$	LiCl	27.77	1.95 ± 0.02	2.31 ± 0.02	75 ± 5	2.3 ± 0.2	
		9.95	1.95 ± 0.02	2.50 ± 0.02	52 ± 5	3.0 ± 0.5	(22)
		3.57	1.95 ± 0.02	2.55 ± 0.02	40 ± 5	5.5 ± 0.3	
K$^+$	KCl	4.0	2.60 ± 0.1	3.0 - 3.2	-	4.2 ± 0.4	(23)
Ag$^+$	AgNO$_3$	3.6	2.50 ± 0.03	2.92 ± 0.04		3.7 ± 0.3	(24)
	AgClO$_4$	4.0	2.41 ± 0.02	2.97 ± 0.04	45° ± 4°	4.1 ± 0.3	(4)
ND$_4^+$	ND$_4$Cl	5.0	2.8 - 3.2	3.4 - 3.8	-	10.0 - 12.0	(25)
	ND$_4$NO$_3$	12.0	2.8 - 3.2	3.4 - 3.8		7.0 ± 0.5	(26)
Ca^{2+}	CaCl$_2$	4.49	2.41 ± 0.03	3.04 ± 0.03	34 ± 9	6.4 ± 0.3	(27)
		2.80	2.39 ± 0.02	3.02 ± 0.03	34 ± 9	7.2 ± 0.2	
		1.0	2.46 ± 0.03	3.07 ± 0.03	38 ± 9	10.0 ± 0.6	
Ni^{2+}	NiCl$_2$	4.41	2.07 ± 0.02	2.67 ± 0.02	42 ± 8	5.8 ± 0.2	(4)
		3.05	2.07 ± 0.02	2.67 ± 0.02	42 ± 8	5.8 ± 0.2	
		1.46	2.07 ± 0.02	2.67 ± 0.02	42 ± 8	5.8 ± 0.3	(28)
		0.85	2.09 ± 0.02	2.76 ± 0.02	27 ± 10	6.6 ± 0.5	
		0.42	2.10 ± 0.02	2.80 ± 0.02	17 ± 10	6.8 ± 0.8	
		0.086	2.07 ± 0.03	2.80 ± 0.04	0 ± 20°	6.8 ± 0.8	
Ni^{2+}	Ni(ClO$_4$)$_2$	3.80	2.07 ± 0.02	2.67 ± 0.02	42 ± 8	5.8 ± 0.2	(29)
Cu^{2+}	CuCl$_2$	4.32	1.96 ± 0.03	2.58 ± 0.03	38 ± 6	3.6 ± 0.3	(30)
	Cu(ClO$_4$)$_2$	2.00	1.96 ± 0.04	2.58 ± 0.03	38 ± 6	4.1 ± 0.3	
	Cu(NO$_3$)$_2$	1.00	1.96 ± 0.03	2.58 ± 0.03	38 ± 6	3.8 ± 0.2	
Nd^{3+}	NdCl$_3$	2.85	2.48 ± 0.02	3.13 ± 0.02	24 ± 4	8.5 ± 0.2	(31)
Dy^{3+}	DyCl$_3$	2.38	2.37 ± 0.03	3.04 ± 0.03	17 ± 3	7.4 ± 0.5	(32)

TABLE 2. Chloride and perchlorate ion hydration at room temperature as determined by neutron diffraction.

Ion	Solute	Molality	Cl⁻-D(1) (A)	Cl⁻-O (A)	Cl⁻-D(2) (A)	γ(deg)	Hydration number	Reference
Cl⁻	LiCl	14.9	2.24 ± 0.02	3.25 ± 0.03	3.50 - 3.60	0	4.4 ± 0.3	(33)(34)
		9.95	2.22 ± 0.02	3.29 ± 0.04	3.50 - 3.68	0	5.3 ± 0.2	
		3.57	2.25 ± 0.02	3.34 ± 0.04	3.50 - 3.70	0	5.9 ± 0.2	
	NaCl	5.32	2.26 ± 0.03	3.20 ± 0.05	-	0-20	5.5 ± 0.4	(34)
		3.62	2.27 ± 0.02	3.32 ± 0.03	-	0-10	5.6 ± 0.2	(38)
	RbCl	4.36	2.26 ± 0.03	3.20 ± 0.05	-	0-20	5.8 ± 0.3	(33)
	CaCl₂	4.49	2.25 ± 0.02	3.25 ± 0.04	3.55 - 3.65	0-7	5.8 ± 0.2	(33)
	NiCl₂	4.35	2.29 ± 0.02	3.20 ± 0.04	3.40 - 3.50	5-11	5.7 ± 0.2	
	NiCl₂	3.00	2.23 ± 0.03	3.25 ± 0.05	3.40 - 3.50	0-8	5.5 ± 0.4	
	CuCl₂	4.32	2.27 ± 0.03	3.25 ± 0.05	-	0-3	3.3 ± 0.4	(30)
	ZnCl₂	45.1 (100°C)	2.25 ± 0.05				1.0 ± 0.9	(35)
		19.4	2.25 ± 0.03	3.40 ± 0.2	3.7 - 3.9	0-7	1.9 ± 0.4	
		4.9	2.25 ± 0.03	3.40 ± 0.15	3.7 - 3.9	0-3	3.7 ± 0.5	
		4.00	2.27 ± 0.03	-	-	-	4.4 ± 0.2	(34)
		1.95	2.27 ± 0.03	-	-	-	4.5 ± 0.2	
		1.00	2.27 ± 0.03	-	-	-	4.5 ± 0.2	
		0.48	2.27 ± 0.03	-	-	-	5.1 ± 0.2	
		0.25	2.27 ± 0.03	-	-	-	5.6 ± 0.2	
	NdCl₃	2.85	2.29 ± 0.02	3.45 ± 0.04	-	0	3.9 ± 0.2	(36)
ClO₄⁻	NaClO₄	3.25	2.9 ± 0.2	3.7 ± 0.3			4.5	(37)

Typical $G(r)$'s are shown in Figs.3 and 4 for the ion water structure of a strong cation, Ni^{2+}, (28) and an anion Cl^-(33). As can be seen in the insets both these ions possess a well-defined local conformation. Cations such as Li^+ and Ca^{2+} and to a lesser extent Cu^{2+} have a similarly well-defined conformation to Ni^{2+}. However, such is not the case in general, especially for K^+(23) or for complex ions such as ND_4^+(25), NO_3^-(36), ClO_4^-(37).

Almost all the results in Tables 1 and 2 have been discussed in detail elsewhere (10), and rather than discuss them further here, I shall instead refer to some recent studies which are about to be published or are in the process of analysis.

Of particular interest recently has been an investigation of Cu^{2+} where we have demonstrated the dependence of the Cu^{2+} hydration on both counterion and concentration. Furthermore, we have shown that in order to explain the results of a 4.3 molal $CuCl_2$ heavy water solution, there must be direct contacts between Cu^{2+} and Cl^- (30).

The behaviour of Fe^{2+} and Fe^{3+} in solution science has been of long historical interest (39). During the past two years we have been investigating the coordination of Fe^{3+} and found it to be strongly dependent on counterion type and pH (40). In highly acidic aqueous perchlorate solution at pH ~ 0 there is evidence of a six fold coordination and a degree of hydrolysis. In aqueous nitrate solutions at similar concentrations and pH, hydrolysis is also observed. However, there is only a five fold Fe^{3+} - O coordination (40).

The properties of 'hard' ions such as Ni^{2+} and Li^+ in more complex solutions is the subject of current investigation. We have recently shown that in a solution of Ni-adenosine triphosphate in heavy water that the Ni^{2+} ion binds directly to the triphosphate group (41), confirming indirect spectroscopic studies. A study is also underway on the properties of Li^+ coordination in solutions of LiOD/polyacrylic acid/heavy water, where the interest is in the degree to which Li^+ coordinates to the polyelectrolyte.

The generality of the first order difference method is further underlined by the fact that work can also be undertaken on non-aqueous electrolyte solutions, and indeed a study is underway of the Ni^{2+} coordination in methanol and formanide. The aim of these studies is to determine the dependence of $g_{NiNi}(r)$ on dielectric constant.
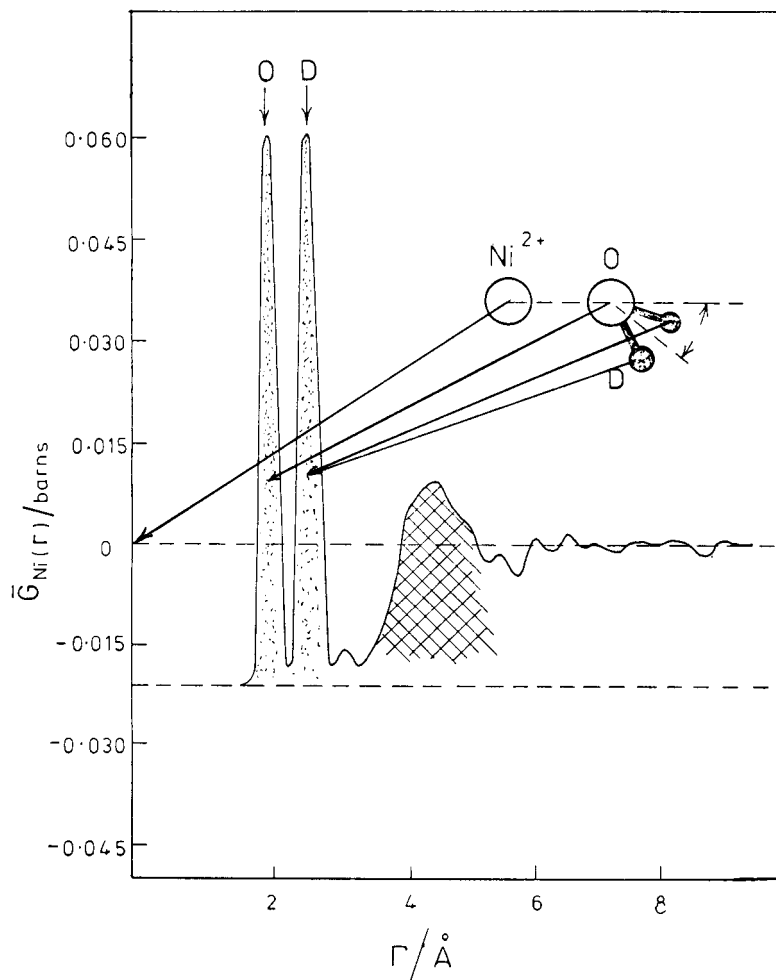
Fig.3.   The total nickel ion radial distribution function, $\bar{G}_{Ni}(r)$,
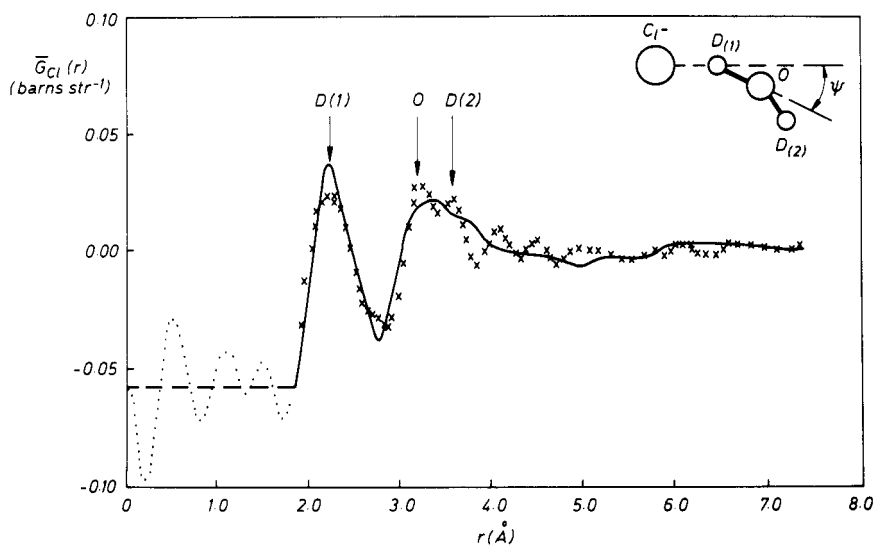for 1.46 molal solution of nickel chloride in heavy water (ref.28)

Fig.4.   The total chloride ion radial distribution function $\bar{G}_{Cl}(r)$ for (a)
9.95 molal LiCℓ in heavy water (full curve) and (b) 5.32 molal NaCℓ in
heavy water (crossed curve), scaled for concentration by 1.87.

Although the isomorphic method of X-ray diffraction is primarily aimed at the determination of ion-ion structure in solution, for the case of Na where the neutron difference method is not useable, and the nature of Na^+ hydration is of fundamental interest in biology (41), an attempt has been made to obtain an approximate understanding of Na^+- water coordination using the isomorphic pair Na^+/Ag^+. The isomorphism proposed is at best approximate. However, aqueous solutions of sodium nitrate and silver nitrate have many structural and thermodynamic properties in common (43). Furthermore, there is a high degree of self-consistency in the X-ray difference functions to support the proposed isomorphism (36). A study of 3.1 molar solutions shows that the Na^+/Ag^+ hydration is intermediate between that of Li^+ (22) and K^+ (23), and is much as expected on the basis of models inferred from spectroscopic and thermodynamic measurements.

3.2 ION–ION CORRELATIONS

As mentioned earlier, individual partial structure factors have so far only been determined in concentrated solutions of nickel chloride (4) and lithium chloride (11). It was found that the experimentally derived cation-cation distribution function was in excellent agreement with that obtained from primitive model (P.M.) calculations applied to Monte Carlo simulations (44) and hypernetted chain theory (45).

By contrast, P.M. calculations of $g_{ClCl}(r)$ deviate greatly from the experimental results for both solutions, a consequence we believe of the strong directionality of the Cl^--H_2O potential (4).

The recently developed X-ray diffraction difference method of isomorphic substitution has enabled us to widen our studies of ion-ion structure. Naturally, the first study using this technique was on solutions of nickel chloride and magnesium chloride. The choice of Ni^{2+}/Mg^{2+} as an isomorphic pair was made on the basis of similar structural (13) and thermodynamic (14) properties solution. Although it is clear that Ni has a wider range of isotopes, and $g_{NiNi}(r)$ is in principle better determined by neutron diffraction methods, because of the inherently weak neutron intensity compared with a laboratory X-ray source the calculated $g_{NiNi}(r)$ from the X-ray method is of higher quality than that from neutrons (Fig.5). Moreover, because of the versatility of the X-ray methods and favourable conditioning of Equ.(9), we have been able to study $g_{NiNi}(r) = (g_{MgMg}(r))$ as a function of ionic concentration and counterion (17,46).
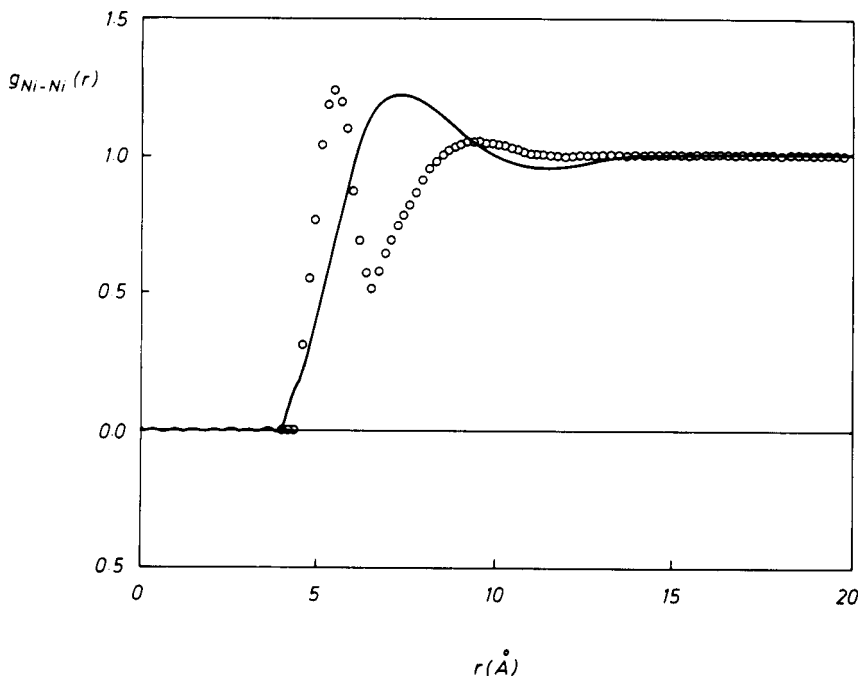

Fig.5. The cation-cation distribution function in 4.35 molal aqueous nickel chloride solution: full curve as determined from X-ray diffraction; dotted curve as determined from neutron diffraction. See text and ref.10, for explanation of difference between two results.

As mentioned above an X-ray diffraction study was made of 3.1 molar aqueous solution of sodium and silver nitrate where the isomorphic difference technique was applied to the Na^+/Ag^+ pair. The results show (17,47) that $g_{NaNa}(r) = g_{AgAg}(r)$ is a much stronger function than $g_{NiNi}(r)$ in aqueous $NiCl_2$ solution (4). This result could well be due to the counterion present, and we are presently investigating $g_{NiNi}(r)$ as a function of counterion type.

CONCLUSIONS AND FUTURE PROSPECTS

The difference methods of X-ray and neutron diffraction have been instrumental in deepening our understanding of the microscopic properties of complex liquids. They offer a means by which the relative strengths of ions can be categorised in a systematic way. Furthermore, results concerning ionic structure in terms of pair radial distribution functions and partial structure factors provide a sensitive means of checking the validity of theoretical calculations and computer simulation of specific models of the liquid.

In the past two years there have been several significant technological developments including the commissioning of a new intense pulsed neutron source at Rutherford Appleton Laboratory (U.K.) and the upgrading of the Synchrotron Radiation Source at Daresbury (U.K.). The instruments on these sources will use the latest generation of detectors and computing systems, and enable us to apply the difference methods of diffraction more widely. For example, it is anticipated that this situation will enable us to improve the quality of the results of systems described in this article, and extend our studies to a wider range of ever more complex systems under a variety of physical and chemical conditions.

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