

# The Structure of Aqueous Electrolyte Solutions: Comparison of Computer Simulation and Experiment

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*Dedicated to Karl Heinzinger on the occasion of his 60th birthday.*

This review compares results of neutron and X-ray diffraction experiments with computer simulation and theoretical calculation for aqueous electrolyte solutions at the atomic level in terms of the partial radial distribution functions of several ionic solutions, and includes results for the ion-water and ion-ion structure of systems containing alkali ions, alkaline earth ions, transition metal cations and a few anions.

## 1. Introduction

The past decade has seen a significant improvement in our understanding of the behavior of aqueous electrolyte solutions. The combination of high quality diffraction studies on the one hand [1] and large scale computational calculations on the other [2] has meant that a detailed knowledge of the microscopic properties of ionic solutions is within our grasp. This is particularly true at the level of the pair radial distribution functions  $g_{\alpha\beta}(r)$ , which represent the most basic structural information of a solution. In an aqueous solution of the form  $\text{MX}_n$  in water ( $\text{H}_2\text{O}$ ) ten such functions exist: three which refer to the solvent,  $g_{\text{HH}}(r)$ ,  $g_{\text{HO}}(r)$ ,  $g_{\text{OO}}(r)$ ; three which represent the solute,  $g_{\text{MM}}(r)$ ,  $g_{\text{MX}}(r)$ ,  $g_{\text{XX}}(r)$ ; and four which characterise the solute-solvent structure,  $g_{\text{MH}}(r)$ ,  $g_{\text{MO}}(r)$ ,  $g_{\text{XO}}(r)$ . Computer simulation based on pair potentials can be used to calculate all these functions [2].

Unfortunately this is not so experimentally. The best that can be achieved at present is to employ the isotopic difference methods of neutron diffraction, usually to solutions of electrolyte in heavy water [1]. (Heavy water is used in order to minimise the prohibitively large incoherent scattering and Placzek effects from hydrogen, although in recent years the use of  $\text{H}_2\text{O}$  as solvent has proved feasible or certain favourable systems [3].) At the first order difference level information is obtained on ionic hydration in terms of

a linear combination of  $g_{\text{MO}}(r)$  and  $g_{\text{MD}}(r)$  or  $g_{\text{XO}}(r)$  and  $g_{\text{XD}}(r)$ .

The second order difference method can be used to calculate  $g_{\text{MM}}(r)$ ,  $g_{\text{XX}}(r)$ , and  $g_{\text{MX}}(r)$  directly from six neutron diffraction experiments on solutions of six isotopically different  $\text{MX}_n$  salt samples [4]. In recent years it has been shown that X-ray diffraction and isomorphic substitution can also be used to obtain  $g_{\text{MM}}(r)$  directly from three experiments [5]. However the method is less widely applicable, relying on pairs of ions such as  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$  whose isomorphism must be demonstrated either by comparison with results derived from a neutron first order difference experiment or by self consistency checks of X-ray first order difference results.

In this paper, results determined experimentally will be presented and discussed in conjunction with those derived from computer simulation and theoretical calculation. In particular, the molecular dynamics (M.D.) results of Heinzinger and co-workers will be compared with those obtained from neutron and X-ray diffraction studies. Furthermore experimental determined ion-ion radial distribution functions will be compared with similar quantities obtained from theoretical work [6]. Where relevant comments will be made on the limitations of experimental results and the failure of computer simulation to correspond with experiment in particular cases.

## 2. Ion-Water Structure

It is certainly the case that the derivation of detailed structural information of a complex liquid from total

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X-ray or neutron diffraction patterns is fraught with difficulties [7]. The main reason lies in the relative contributions from all pair correlation functions to the scattering intensity, which for the case of aqueous electrolyte solutions under normal conditions is dominated by the three water correlations. However by means of the isotopic difference methods of neutron diffraction or the isomorphous difference method of X-ray diffraction the situation can be appreciably improved to the extent that ion-water and ion-ion structure can be extracted from the data, and it is at this level that experimental results can be usefully compared with those of computer simulation and theoretical calculation. Results derived from the first order method of neutron diffraction can be expressed in terms of a linear combination of all  $g_{1z}(r)$ 's which refer to the isotopically substituted ion I, and is written formally as

$$G_I(r) = \sum_z A_z \{g_{1z}(r) - 1\}, \quad (1)$$

where  $G_I(r)$  is the total distribution of the ion and  $A_z$  are constants which depend on the concentration of the solution and the mean coherent neutron scattering lengths of the atoms of the solution. The sum extends over all species in the solution. At ordinary concentrations ( $< 3$  molal),  $G_I(r)$  is dominated by the ion-water terms, i.e.  $A_O$  and  $A_H$  (or  $A_D$ ) are much greater than  $A_M$  and  $A_X$ , and therefore contains information of the ion water structure. It is also possible to derive a coordination number from  $G_I(r)$  by integration over a particular range. For example the number of oxygen

atoms around ion I,  $n_I^O$ , is obtained by identifying a part of  $G_I(r)$  with  $g_{1O}(r)$  and carrying out integration over the range where it can be readily identified. When  $G_I(r)$  is that for a cation and it contains well resolved peaks and integration is carried out over the region of the first coordination region, then  $n_I^O$  is equated to the ion's hydration number. For anions, the hydration number is identified with a similar integration, but this time  $n_I^D$  is calculated.

The first order difference derived from an X-ray diffraction experiment can also be used to determine a hydration number in a way similar to that described above [5]. However in this case a sophisticated fitting procedure is required because the  $A_z$ 's of (1) are now composed of convolutions over the atomic form factors.

#### (i) Alkali Ions and $ND_4^+$

Aqueous solutions of alkali salts are among the most extensively studied liquid systems [8]. Being singly charged with a relatively simple 'closed shell' chemistry the alkali ions are extremely suitable for model calculations based primarily on particle size [9]. Comparison of the ion water structures of  $Li^+$ ,  $Na^+$ ,  $K^+$  derived from the difference methods of X-ray and neutron diffraction shows a trend away from a well-resolved nearest neighbour hydration shell for  $Li^+$  (Fig. 1) towards a broad featureless hydration shell for the larger  $K^+$  ion (Figure 2). Furthermore for even larger  $ND_4^+$  cation (often considered as a pseudo alkali ion) the trend continues (Fig. 3) [10, 11].

Of particular interest is the change across the series in coordination number, which strictly can only be properly defined for  $Li^+$  and  $Na^+$ , both of which have a well defined cut-off to their hydration shells. The values calculated from the experimental results for  $Li^+$  for  $n_{Li}^O$  range from 3.3 at 9.95 molal to 5.5 at 3.57 molal [12]. The result derived from an X-ray diffraction first order isomorphous difference for  $Na^+$  is calculated to be  $5 \pm 1$  in an aqueous sodium nitrate solution [13]. A puzzle in the case of  $Li^+$  coordination remains at high concentration, in that although it may retain six nearest neighbours some contact with the anions must arise. The results of computer simulation for highly concentrated solutions of  $LiCl$  do not show this [14]. The discrepancy could be a consequence of strong orientational effects of  $Cl^-$  in solution which is not usually included in the ion-water potentials used for  $Cl^-$ . For further discussion see Section (iv).

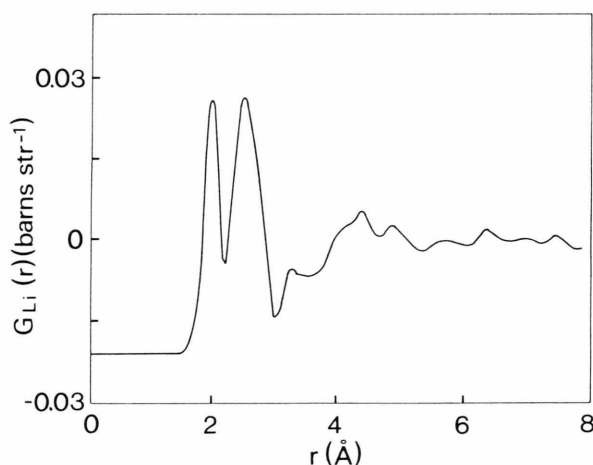


Fig. 1. The total lithium ion radial distribution function,  $G_{Li}(r)$ , for 3.57 molal  $LiCl$  in heavy water [1].

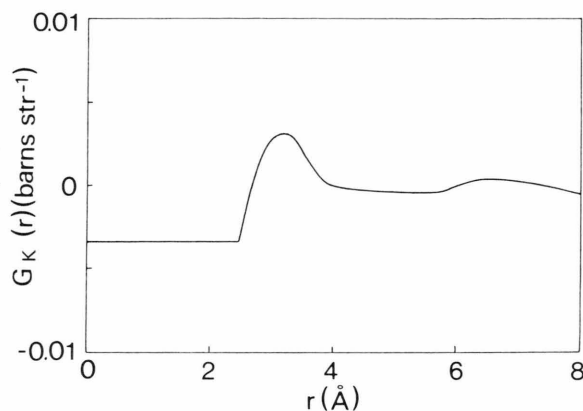


Fig. 2. The potassium ion radial distribution function,  $G_K(r)$ , for 4 molal KCl in heavy water [1].

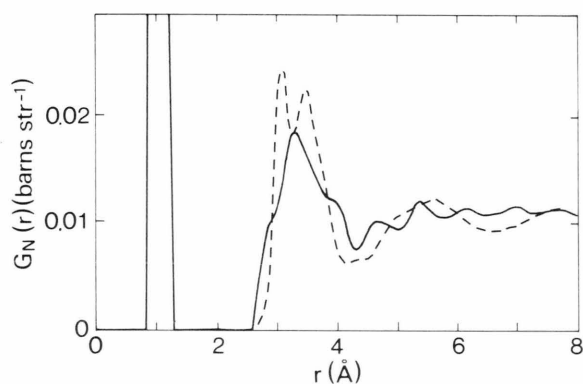


Fig. 3. The total radial distribution function,  $G_{ND_4}(r)$ , for 5 molal  $ND_4Cl$  in heavy water [10]. The full curve is the experimental result and the dashed curve is  $G_{ND_4}(r)$  as calculated from the  $NH_4-O$  and  $NH_4-H$  distributions obtained in the simulation study of Szasz and Heinzinger [1].

(ii) *Alkaline Earth Ions:  $Be^{2+}$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$*

This series represents the next level of complexity in terms of ionic species in water. As with the alkali ions, a fairly straightforward approach has been adopted in modelling the hydration properties of these ions [2]. The experimental results show a general trend towards a 'washing out' of the nearest neighbour hydration shell as the ion size is increased [1]; the  $Mg^{2+}$  ion, which is isomorphic with  $Ni^{2+}$  in aqueous solution [3, 5] has a well-defined octahedral coordination, that of  $Ca^{2+}$  is fairly well-defined (Fig. 4) but with a coordination number which increases from about 6 at 5 molal to about 10 at 1 molal [15], and the result for  $Sr^{2+}$  is poorly resolved (Fig. 5) with no evidence of correlations beyond the first hydration shell [16].

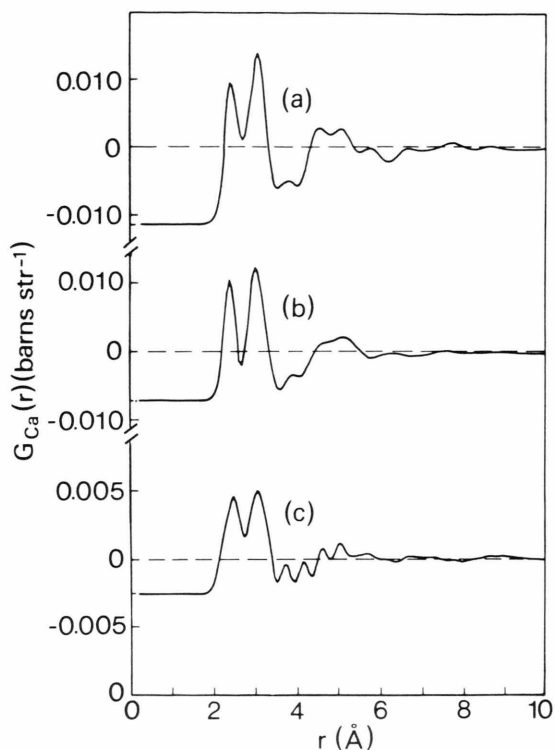


Fig. 4. The total calcium ion radial distribution function,  $G_{Ca}(r)$ , for 3 solutions of  $CaCl_2$  in heavy water (a) 4.5 molal, (b) 2.8 molal, (c) 1 molal [15].

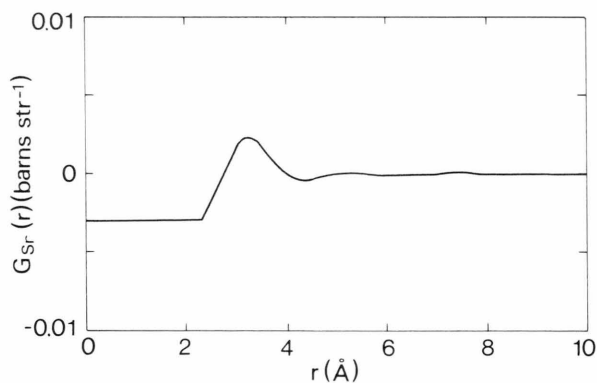


Fig. 5. The total strontium ion radial distribution function,  $G_{Sr}(r)$ , for 3 molal  $Sr(ClO_4)_2$  in heavy water [16].

The results for  $Mg^{2+}$  and  $Ca^{2+}$  are well described by computer simulation studies [17, 18]. However, for the case of  $Be^{2+}$  (an ion whose solution properties cannot be investigated by the isotope method of neutron diffraction) the results of a total X-ray diffraction study indicate a coordination number of 4 whereas the

computer simulation gives a value of 6 [19]. In assessing the merits of these results it should be pointed out that beryllium has only 4 electrons/atom and therefore the extraction of  $\text{Be}^{2+}$  – other atom correlations from X-ray results will be extremely problematical.

### (iii) Transition Metal Ions

The hydration structure of these ions shows a wide variation, a consequence presumably of differences in configuration of their electronic d-states. Several neutron diffraction studies have been carried out at the first order difference level an information is now available for  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  [1]. Results based on total X-ray diffraction experiments have also been obtained for other transition metal ions including  $\text{Cr}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  [1]. In general the transition metals have a well-defined first hydration shell with a sixfold coordination. There are, however, subtle distinctions between the content and shape of this nearest neighbour region for all the ions studied so far. For example  $\text{Ni}^{2+}$  shows a well resolved hydration shell (Fig. 6) with six water molecules uniformly arranged around the ion [3]. This configuration is remarkably insensitive to changes in counterion [20], concentration [21], pressure and temperature [22]. Similarly,  $\text{Cr}^{3+}$  possesses a very stable first coordination shell [23]. By contrast the nearest neighbour shells of  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  depend strongly on counterion, concentration and pH. The  $\text{Cu}^{2+}$  coordination [24, 25] appears to arise from the dynamic Jahn-Teller effect and in the case of copper perchlorate and copper nitrate solutions has a 4+2 configuration (Figure 7). For solutions of copper chloride the  $\text{Cu}^{2+}$  coordination shell appears to contain  $\text{Cl}^-$  ions. Similarly for solutions of iron(III) perchlorate and iron(III) nitrate the first coordination shell of  $\text{Fe}^{3+}$  shows significant distortions [26]. For the former solution, although there are six oxygen atoms as nearest neighbours, the possibility that there is a degree of ion pairing between  $\text{Fe}^{3+}$  and  $\text{ClO}_4^-$  ions cannot be ruled out even at concentrations of 1 molal. In the case of iron(III) nitrate solutions the structure is strongly dependent on preparative procedures.

From a theoretical viewpoint little has been undertaken to determine the ion-water structure for these ions. Bounds carried out a computer simulation study for  $\text{Ni}^{2+}$  based on ab initio potentials [27]. However, his results gave a coordination number of 8 which could not be justified on the basis of the experimental

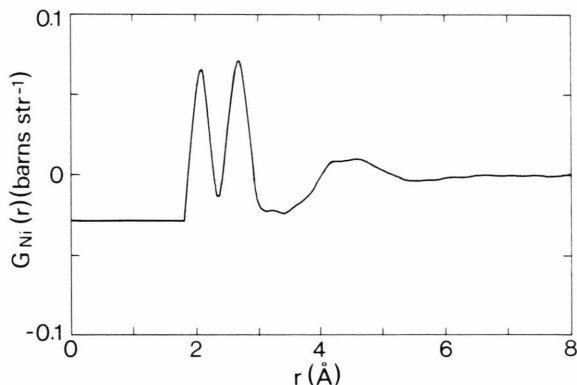


Fig. 6. The total nickel ion radial distribution function,  $G_{\text{Ni}}(r)$ , for 2 molal  $\text{NiCl}_2$  in heavy water [3].

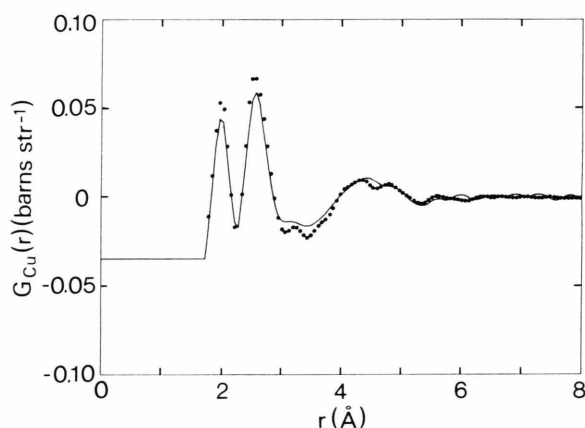


Fig. 7. The total cupric ion radial distribution function,  $G_{\text{Cu}}(r)$ , for a 1 molal solution of  $\text{Cu}(\text{NO}_3)_2$  in heavy water (full curve) and 2 molal  $\text{Cu}(\text{ClO}_4)_2$  in heavy water (dotted curve). The scaling factor for the concentration difference between the solutions ensures that the contribution to  $g_{\text{CuO}}(r)$  is the same in both [25].

results. The work of Heinzinger on  $\text{Mg}^{2+}$  gives a more encouraging result if one exploits the isomorphism of  $\text{Mg}^{2+}$  and  $\text{Ni}^{2+}$  [3] (Figure 8).

### (iv) Anions

The only monovalent anion susceptible to the difference methods of neutron diffraction is  $\text{Cl}^-$ . Other ions such as  $\text{F}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  do not have isotopes with sufficiently differing neutron scattering lengths to make these methods feasible [27].

The chloride ion has been extensively studied as a function of concentration [28], counterion [29], temperature [30], and pressure [31]. The results show

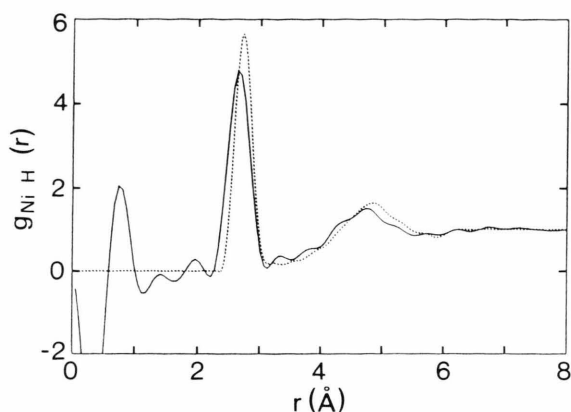


Fig. 8. Radial distribution function  $g_{\text{NiH}}(r)$  (solid line) for 2 molal  $\text{NiCl}_2$  in water [3], compared with  $g_{\text{MgH}}(r)$  (dotted curve) obtained from computer simulation [17].

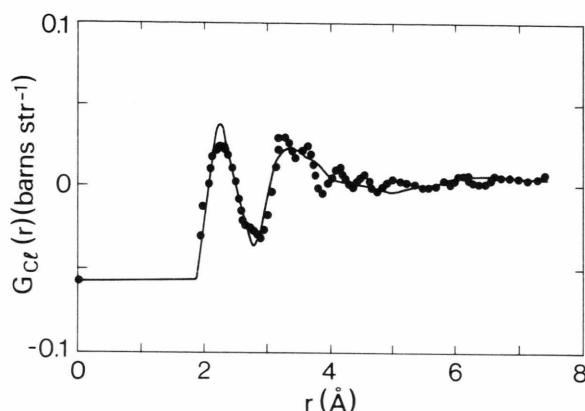


Fig. 9. The total chloride ion radial distribution function,  $G_{\text{Cl}}(r)$ , for 9.95 molal  $\text{LiCl}$  in heavy water (full curve) and 5.32 molal  $\text{NaCl}$  in heavy water (dots) scaled by the concentration factor of 1.87. A comparison of these results with computer simulation is given in Fig. 7 of [2].

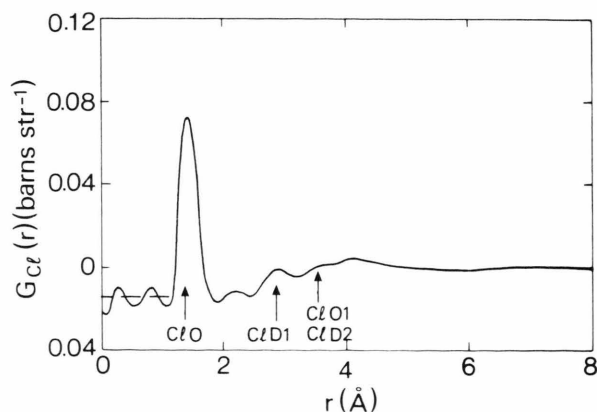


Fig. 10. The total perchlorate ion radial distribution function,  $G_{\text{Cl}}(r)$ , for 3.25 molal  $\text{NaClO}_4$  in heavy water. The intramolecular peak is readily observed at 1.43 Å.

(Fig. 9) that at concentrations where there is a sufficient number of water molecules available (i.e. <3 molal in a 1:2 electrolyte solution or <4 molal in a 1:1 solution), there are always less than six water molecules in its first coordination shell! This result is in disagreement with computer simulation [32] (usually carried out at concentrations <2 molal) which almost always gives a number >6, a consequence, perhaps, of the spherical nature (non-directionality) of the potentials used to model the  $\text{Cl}^-$  water molecule interaction.

Neutron diffraction studies have been carried out on two complex anions,  $\text{ClO}_4^-$  [33], and  $\text{NO}_3^-$  [34]. Both these ions show a relatively weak coordination to water molecules as is demonstrated by their total radial distribution functions [34], (Figure 10). Computer simulation of  $\text{ClO}_4^-$  [35], shows good agreement with experimental results derived from the neutron studies and from infra-red and Raman spectroscopy, a consequence of the relatively large size of the complex anion which can suitably be represented as a hard sphere appropriate for simulation purposes. For the case of very high concentrations of  $\text{NO}_3^-$  in solution the structure remains only weakly defined although in this case the possibility of ion pairing cannot be ignored [36].

### 3. Ion-Ion Structure

The determination of ion-ion radial distribution functions from the second order isotopic difference method of neutron diffraction is at the limit of present-day experimental capabilities, and to date only 3 solutions have been studied to this level of detail. The most complete study [4] was that on a 4.32 molal solution of  $\text{NiCl}_2$  in heavy water for which all 3  $g(r)$ 's were determined, viz.  $g_{\text{NiNi}}(r)$ ,  $g_{\text{NiCl}}(r)$ ,  $g_{\text{ClCl}}(r)$ . The result for  $g_{\text{NiNi}}(r)$  (Fig. 11) is in good agreement with a theoretical calculation of Friedman and Dudowicz [37] who used a Monte Carlo simulation of a primitive model solution. In an attempt to examine whether the other two functions could be reproduced theoretically Copestake carried out several theoretical calculation [38], based on the primitive model, and although he was unable to reproduce the experimental results found that a better fit to the experiment is obtained when the dielectric constant of the solution is taken as that for water and the hypernetted chain approximation (HWC) is used to calculate the distribution functions.



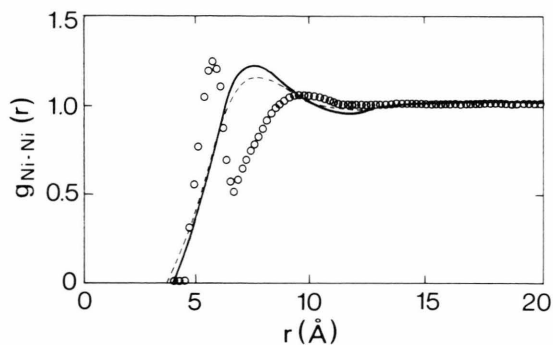


Fig. 11. The radial distribution function  $g_{\text{NiNi}}(r)$  – neutron diffraction study of 4.32 molal  $\text{NiCl}_2$  in heavy water (open circles) [4], X-ray diffraction isomorphous difference study of 3.88 Molar  $\text{NiCl}_2$  in water (full curve) [5], primitive model calculation at 4 molar of Friedman and Dudowicz (dashed curve) [37].

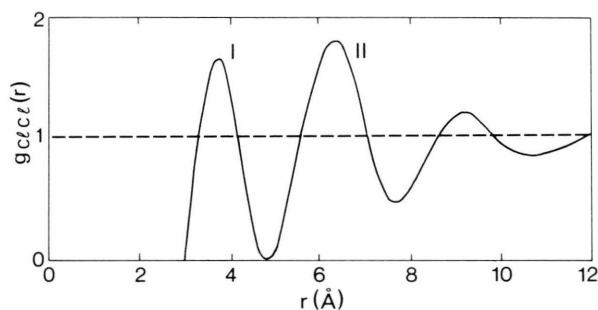


Fig. 12. The radial distribution function  $g_{\text{ClCl}}(r)$  in 14.9 molal  $\text{LiCl}$  in heavy water. The two principal peaks denoted I and II occur at 3.75 Å and 6.38 Å [39].

A second order isotopic difference study was also carried out on a 14.9 molal  $\text{LiCl}$  heavy water solution [39], and the diffraction data were used to determine  $g_{\text{ClCl}}(r)$  (Figure 2). This function was similarly highly structured as in the case of the 4.32  $\text{NiCl}_2$  solution but with the important difference that there was strong evidence of direct contacts between the  $\text{Cl}^-$  ions. From this and results for  $\text{Li}^+$  hydration at high concentration it was inferred that there is a strong likelihood of ion pairing between  $\text{Li}^+$  and  $\text{Cl}^-$ . However this suggestion can only be proven unambiguously by means of a direct determination of  $g_{\text{LiCl}}(r)$  from a second order difference experiment, which is currently planned to take place in the near future. Results of computer simulation studies are interesting in that at concentrations up to 17 molal there is no strong evidence for direct contacts between  $\text{Li}^+$  and  $\text{Cl}^-$  [14].

The third solution for which the ion-ion structure has been determined was a 4.32 molal solution of

$\text{Ni}(\text{NO}_3)_2$  in heavy water [40]. A preliminary analysis of the results for  $g_{\text{NiNi}}(r)$  shows that this function is the same within error to that originally determined for the nickel chloride solution [4], a result which suggests that there are no appreciable counterion effects at the level of the solute structure.

In recent years, X-ray diffraction in conjunction with isomorphous substitution [5] has been used to obtain cation-cation  $g(r)$ 's for several solutions including  $g_{\text{NiNi}}(r) (=g_{\text{MgMg}}(r))$  for  $\text{Ni}/\text{MgCl}_2$  and  $\text{Ni}/\text{MgBr}_2$  aqueous solutions [5], and  $g_{\text{AgAg}}(r) (=g_{\text{NaNa}}(r))$  in a concentrated  $\text{Ag}/\text{NaNO}_3$  aqueous solution [41]. More recently the determination of the first complex anion-anion  $g(r)$  has been determined by Burke [42] for an aqueous solution of  $\text{NaNO}_3/\text{BrO}_3$ , from which  $g_{\text{NO}_3\text{NO}_3}(r) (=g_{\text{BrO}_3\text{BrO}_3}(r))$  was determined.

Although this new method is limited by the number of isomorphous pairs available, and by the less exact mathematical formalism owing to the nature of the atomic form factors, the widespread availability of X-ray sources and the non-requirement of expensive isotopes makes it a potentially powerful technique for the determination of  $g_{\text{II}}(r)$ .

#### 4. Conclusions and Future Prospects

As discussed above, our knowledge of the structure of aqueous electrolyte solutions has benefitted from a combination of experimental work based on the difference methods of neutron diffraction and isotopic substitution and X-ray diffraction and isomorphous substitution on the one hand, and computer simulation and theoretical calculations of model systems on the other. The complementarity of these approaches has demonstrated that for the alkali and alkaline earth ions a fairly elementary approach based on their relative sizes can be used to understand how these ions coordinate water molecules. For other ions, where the chemical state of the ion is important, such as the transition metal ions or rare earths, a more sophisticated approach is required.

Examples of possible future work in this field might include:

- (i) a theoretical study of ionic hydration for transition metals under ambient conditions,
- (ii) a study of aqueous solutions of salts such as sodium chloride at critical temperatures and pressures,

- (iii) and investigation of ionic structure in polyelectrolyte solutions,
- (iv) a study of solution structure near a solid surface.

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