

Neutron Diffraction Methods Applied to Aqueous Solutions¹

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Results of neutron diffraction studies are presented and discussed for a variety of aqueous electrolyte solutions. Attention is focused on the ion-water and ion-ion structures, which are directly determined from the first- and second-order isotopic difference methods, respectively. A systematic survey is given of the coordinating properties of several ionic species including some of the alkalis, the transition metals, and numerous others. Such information is useful in providing (i) a clearer picture of the relative hydrating strengths of ions and (ii) a quantitative experimental test of results from theoretical calculations and computer simulations of models. Although most work has been carried out under ambient conditions, we make reference to a few investigations at elevated pressure and draw attention to the particular strengths of neutron-diffraction techniques when working at both high pressure *and* high temperature.

KEY WORDS: distribution function; ionic hydration; isotopic substitution; neutron diffraction.

1. INTRODUCTION

The difference methods of neutron diffraction with isotopic substitution offer a unique probe of the microstructural properties of liquid and amorphous systems. During the past decade these methods have been successfully applied to molten salts [1], molecular liquids [2], and aqueous solutions [3]. Information has been obtained in terms of the pair radial distribution functions $g_{\alpha\beta}(r)$ which have been used to identify the local-coordination of a given atom or ion.

¹ Invited paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

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For an aqueous solution of the general form $\text{MX}_n \cdot \text{D}_2\text{O}$ there are 10 $g_{\alpha\beta}(r)$'s: 3 associated with the solvent, g_{OO} , g_{OD} , and g_{DD} ; 3 that refer to the solute, g_{MM} , g_{MX} , and g_{XX} ; and 4 that characterize the solute-solvent structure, g_{MO} , g_{MD} , g_{XO} , and g_{XD} . (Note that in a neutron diffraction experiment heavy water is used instead of water because of the latter's destructively strong incoherent scattering.)

The first-order isotopic difference method of neutron diffraction [4] enables one to determine direct information on the ion-water structure. The difference function, $\bar{G}_I(r)$, which is obtained from neutron diffraction studies of two chemically identical solutions that differ only in the isotopic states (b_I and b'_I) of the cation (or anion), I, can be formally written as [4]

$$\bar{G}_I = Ag_{\text{IO}}(r) + Bg_{\text{ID}}(r) + Cg_{\text{II}}(r) + Dg_{\text{II}}(r) + E \quad (1)$$

where $A = 2c_{\text{O}}c_I b_{\text{O}} \Delta b_I$, $B = 2c_{\text{D}}c_I b_{\text{D}} \Delta b_I$, $C = 2c_I c_I b_I \Delta b_I$, $D = c_I^2(b_I^2 - b_I'^2)$, $E = -(A + B + C + D)$, and $\Delta b_I = (b_I - b'_I)$. b_α (in units of 10^{-15} m) is the neutron coherent scattering length [5] of isotope α , whose atomic fraction is c_α .

The second-order difference method is applied to neutron diffraction studies of three or four chemically identical solutions that differ only in the isotopic state of the ions. From measurements on three solutions containing significantly different amounts of isotopes of ion I, one can determine unambiguously $g_{\text{II}}(r)$. In addition, a double substitution of ions I and J can be used to obtain diffraction data for four chemically identical solutions from which one can calculate $g_{\text{IJ}}(r)$.

$\bar{G}_I(r)$ [Eq. (1)] and the individual $g_{\text{II}}(r)$ and $g_{\text{IJ}}(r)$'s can be used to build a model of the ionic structure from identification of ion-ion and ion-water distances and coordination numbers, the latter being defined by the number n_I^β of particles β around an ion I in the range $r_1 \leq r \leq r_2$, i.e.,

$$n_I^\beta = \rho c_\beta \int_{r_1}^{r_2} 4\pi r^2 g_{\text{I}\beta}(r) dr \quad (2)$$

where ρ is the number density of the solution and is typically 0.1 \AA^{-3} .

2. EXPERIMENTAL

Two conditions are essential in order to carry out difference experiments successfully [6]. First, the samples themselves must be well characterized, and second, the diffraction experiments must give data which have the highest possible degree of statistical accuracy.

To meet the first condition, the samples are prepared under glove-box conditions, and checks are made of water (H_2O) content by infrared spec-

troscopy and isotopic content by mass spectrometry. As a result, the heavy water/water ratio is known to $\sim 0.05\%$, and the isotopic abundance of the substituted ionic species is known to 0.02% . We have also recently introduced the use of liquid chromatography to assist in the identification of relative concentrations where acidic solutions are made. Density is checked to $\sim 0.1\%$. And because of recent work on Fe^{3+} solutions, pH is now routinely monitored.

The second condition is met by carrying out experiments on diffractometers sited on high-flux nuclear reactors such as the D4B and D20 at I.L.L., Grenoble, and the 7C2 at C.E.N., Saclay, France, and on pulsed sources such as the L.A.D. at ISIS, Rutherford-Appleton Laboratory, U.K.

The actual experiments are carried out in evacuated chambers so as to minimize air scattering which becomes particularly noticeable at small angles. One major advantage of neutron techniques over X-ray techniques is that because of the relatively low absorption of thermal neutrons by matter, sample containers can be fabricated from materials made of iron, steel, titanium, and aluminium. This is particularly useful when carrying out experiments on water and aqueous solutions under nonambient conditions [7]. Furthermore, it is often possible to make a "null" alloy container from elements such as titanium and zirconium which will not contribute to the structural part of the diffraction pattern. No such technique is available for X-ray or electron diffraction methods.

The data reduction procedures are now well established [6] and exploit recent developments in computational methods. In recent years maximum entropy techniques have been introduced in order to improve the quality of raw data and subsequent data handling procedures [8].

3. RESULTS AND DISCUSSION

The *total* neutron diffraction pattern of an aqueous electrolyte solution is dominated by correlations between the water molecules of a solution. In particular, it can provide information regarding the near-neighbor D-D and D-O coordination. However, it is not particularly useful when attempting to determine ion-water and ion-ion structure and certainly much less so than the complementary method of X-ray diffraction [9]. In order to determine such information, one is forced to adopt the first- and second-order isotopic difference methods of neutron diffraction [6].

3.1. Ionic Hydration

The first-order isotopic difference method of neutron diffraction is particularly suited to the determination of an ion-solvent structure in

Table I. 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	Ref. No.
Li ⁺	LiCl	27.77	1.95 ± 0.02	2.31 ± 0.02	75 ± 5	2.3 ± 0.2	12
		9.95	1.95 ± 0.02	2.50 ± 0.02	52 ± 5	3.0 ± 0.5	13
		3.57	1.95 ± 0.02	2.55 ± 0.02	40 ± 5	5.5 ± 0.3	11
K ⁺	KCl	4.0	2.60 ± 0.1	3.0-3.2	—	4.2 ± 0.4	14
		3.6	2.50 ± 0.03	2.92 ± 0.04	45 ± 4	3.7 ± 0.3	15
Ag ⁺	AgNO ₃	4.0	2.41 ± 0.02	2.97 ± 0.04	—	4.1 ± 0.3	16
		5.0	2.8-3.2	3.4-3.8	—	10.0-12.0	17
ND ₄ ⁺	ND ₄ NO ₃	12.0	2.8-3.2	3.4-3.8	—	7.0 ± 0.5	18
		4.49	2.41 ± 0.03	3.04 ± 0.03	34 ± 9	6.4 ± 0.3	19
Ca ²⁺	CaCl ₂	2.80	2.39 ± 0.02	3.02 ± 0.03	34 ± 9	7.2 ± 0.2	4
		1.0	2.46 ± 0.03	3.07 ± 0.03	38 ± 9	10.0 ± 0.6	20
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	20
Ni ²⁺	NiCl ₂	1.46	2.07 ± 0.02	2.67 ± 0.02	42 ± 8	5.8 ± 0.3	4
		0.85	2.09 ± 0.02	2.76 ± 0.02	27 ± 10	6.6 ± 0.5	20
Ni ²⁺	Ni(ClO ₄) ₂	0.42	2.10 ± 0.02	2.80 ± 0.02	17 ± 10	6.8 ± 0.8	21
		0.086	2.07 ± 0.03	2.80 ± 0.04	0 ± 20	6.8 ± 0.8	22
Cu ²⁺	CuCl ₂	3.80	2.07 ± 0.02	2.67 ± 0.02	42 ± 8	5.8 ± 0.2	22
		4.32	1.96 ± 0.03	2.58 ± 0.03	38 ± 6	3.6 ± 0.3	23
Cu ²⁺	Cu(ClO ₄) ₂	2.00	1.96 ± 0.04	2.58 ± 0.03	38 ± 6	4.1 ± 0.3	24
		1.00	1.96 ± 0.03	2.58 ± 0.03	38 ± 6	3.8 ± 0.2	24
Nd ³⁺	NdCl ₃	2.85	2.48 ± 0.02	3.13 ± 0.02	24 ± 4	8.5 ± 0.2	24
		2.38	2.37 ± 0.03	3.04 ± 0.03	17 ± 3	7.4 ± 0.5	25

Table II. Chloride and Perchlorate Ion Hydration at Room Temperature as Determined by Neutron Diffraction

Ion	Solute	Molality	Cl ⁻ -D(1) (Å)	Cl ⁻ -O (Å)	Cl ⁻ -D(2) (Å)	ψ (deg)	Coordination number	Ref. No.	
Cl ⁻	LiCl	14.9	2.24 ± 0.02	3.25 ± 0.03	3.50-3.60	0	4.4 ± 0.3	26	
		9.95	2.22 ± 0.02	3.29 ± 0.04	3.50-3.68	0	5.3 ± 0.2	27	
	NaCl	3.57	2.25 ± 0.02	3.34 ± 0.04	3.50-3.70	0	5.9 ± 0.2	27	
		5.32	2.26 ± 0.03	3.20 ± 0.05	—	0-20	5.5 ± 0.4		
		3.62	2.27 ± 0.02	3.32 ± 0.03	—	0-10	5.6 ± 0.2	28	
		4.36	2.26 ± 0.03	3.20 ± 0.05	—	0-20	5.8 ± 0.3	27	
	RbCl	4.49	2.25 ± 0.02	3.25 ± 0.04	3.55-3.65	0-7	5.8 ± 0.2	27	
		4.35	2.29 ± 0.02	3.20 ± 0.04	3.40-3.50	5-11	5.7 ± 0.2	27	
	CaCl ₂	3.00	2.23 ± 0.03	3.25 ± 0.05	3.40-3.50	0-8	5.5 ± 0.4	22	
		4.32	2.27 ± 0.03	3.25 ± 0.05	—	0-3	3.3 ± 0.4		
	NiCl ₂	45.1	2.25 ± 0.05	—	—	—	1.0 ± 0.9	29	
		(100°C)	—	—	—	—	—	—	
	ClO ₄ ⁻	NdCl ₃	19.4	2.25 ± 0.03	3.40 ± 0.2	3.7-3.9	0-7	1.9 ± 0.4	28
			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			
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			
NaClO ₄	0.25	2.27 ± 0.03	—	—	—	5.6 ± 0.2	30		
	2.85	2.29 ± 0.02	3.45 ± 0.04	—	0	3.9 ± 0.2			
		3.25	2.9 ± 0.2	3.7 ± 0.3	—	4.5	31		

electrolyte solutions. Results have been obtained for several ionic systems as a function of ionic concentration, ion size, valence, and counterion type (Tables I and II). A systematic study is now under way of the hydrating properties of several groups of elements including alkalis, alkaline earths, transition metals, and several types of anions.

The work on alkali ions is of particular interest because of the extensive knowledge already existing about them [10]. Our own investigations have concentrated on Li^+ and K^+ ions, and we have clearly demonstrated (Figs. 1 and 2) the different coordinating strengths of these two ions [11, 13]. The results are consistent with what might be anticipated for a model based purely on electrostatic considerations. It is of interest to ask whether Na^+ , an ion of radius $r_{\text{Na}^+} = 0.96 \text{ \AA}$, intermediate between Li^+ ($r_{\text{Li}^+} = 0.60 \text{ \AA}$) and K^+ ($r_{\text{K}^+} = 1.33 \text{ \AA}$), has a coordinating geometry similar to that of Li^+ or K^+ . Unfortunately, sodium is monoisotopic and therefore not susceptible to the neutron diffraction difference methods. However, we are presently investigating the feasibility of whether isomorphic replacement and X-ray diffraction can yield the required information. Studies in which Na^+ and Ag^+ were used as isomorphs in metal nitrate solution are encouraging, despite the belief that this substitution can only be regarded as very approximate. Indeed, neutron-diffraction studies of Ag^+ hydration have been successfully carried out [14] and the results show that the Ag^+ water coordination is intermediate between that of K^+ and that of Li^+ .

Diffraction studies of the transition metal ions have yielded a wide variety of structures confirming the rich variety of thermodynamic and

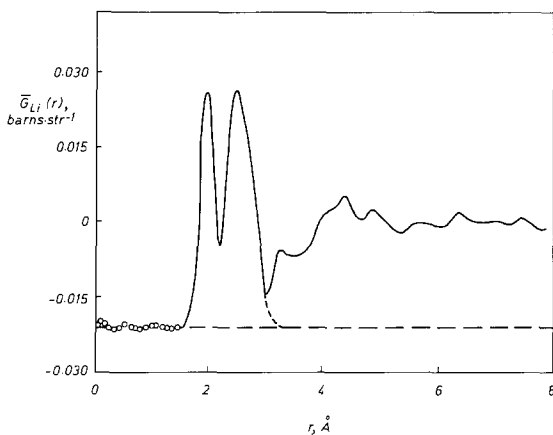


Fig. 1. The total lithium ion radial distribution function, \bar{G}_{Li} , for 3.57 molal LiCl in heavy water [13].

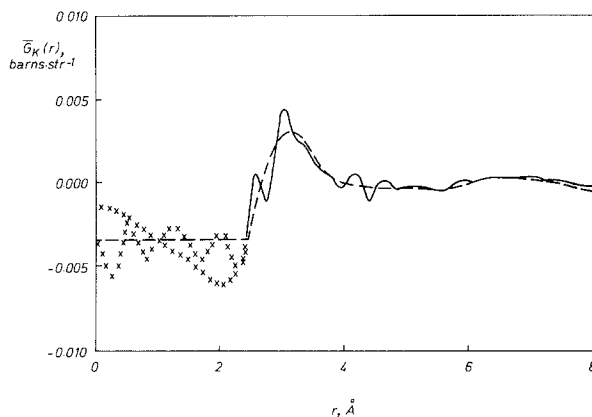


Fig. 2. The total potassium ion radial distribution function, \bar{G}_K , for 4 molal KCl in heavy water. The solid curve is the result of direct Fourier transformation of the diffraction data. The dashed curve is a result of smoothing and truncating the diffraction data (see Ref. 11 for details).

spectroscopic behavior observed in solutions which contain them [10]. Indeed, the first successful application of the isotope substitution difference method was to concentrated nickel chloride solutions, where our results confirmed earlier studies and ultimately identified the $\text{Ni}^{2+} \cdots \text{D}_2\text{O}$ molecular conformation [4, 20]. The technique has since been applied to Cu^{2+} and Fe^{3+} , where the results highlight the particular behavior of these two ions. The cupric ion shows a fair degree of versatility in solution both as a function of concentration and as a function of counterion [22]. The Fe^{3+} ion, too, has a uniquely interesting solvation structure exhibiting a well-defined local coordination [32] as might be anticipated on the grounds of kinetic measurements [10]. Results for concentrated acidic solutions of ferric nitrate and of ferric perchlorate provide the first structural evidence of hydrolysis of water molecules in the first coordination shell.

Several other cations have been investigated by the first-order methods of neutron diffraction including Ca^{2+} and ND_4^+ , the results of the former showing evidence of well-defined coordination and change in coordination number (CN) with concentration [19]. Continuing interest will focus on the temperature dependence of Ca^{2+} coordination. The ND_4^+ coordination is very weak, reflecting a relatively flat ion-water potential [16]. Results from computer simulation with simple Lennard-Jones-type interactions [33] are in good agreement with results from recent experimental measurements of concentrated ammonium nitrate solutions [17]. Further

experiments on solutions containing this ion will be concerned with the degree to which direct cation-anion interactions can occur in solutions of ammonium nitrate at concentrations up to the molten salt regime.

A study of rare earth ions in solution was initiated first at Oak Ridge by Narten and co-workers [24, 25]. The interest here centers on the change in coordination number as a function of the electronic configuration of the rare earth ions (Table I). Confirmation of this trend is currently being sought by Merbach and co-workers, who are applying the first-order difference method to Sm^{3+} , Dy^{3+} , and Yb^{3+} [34].

The work described above is presently being extended to a wider variety of other systems. For example, experiments have been carried out on NiATP in heavy water, where the interest is in the extent to which Ni ions coordinate to the triphosphate group [35]. Another study is aimed at investigating the degree to which quantum effects influence the hydration of a strong cation such as Ni^{2+} [36]. Because the technique can easily be generalized to more complex systems, experiments have also been successfully carried out in urea-water systems [37] and are currently being applied to polyelectrolyte solutions.

The structure around anions has been determined for Cl^- , ClO_4^- (Table II), and NO_3^- [38]. The most extensive study by far has been that concerned with Cl^- , where the results show clearly that the Cl^- -water coordination is well defined (Fig. 3) and the number of water molecules in the first coordination shell is always less than six. These observations, taken together with the fact that hydrated water molecules of Cl^- exchange rapidly ($<10^{-11}$ s) with the bulk water, are consistent with a model in

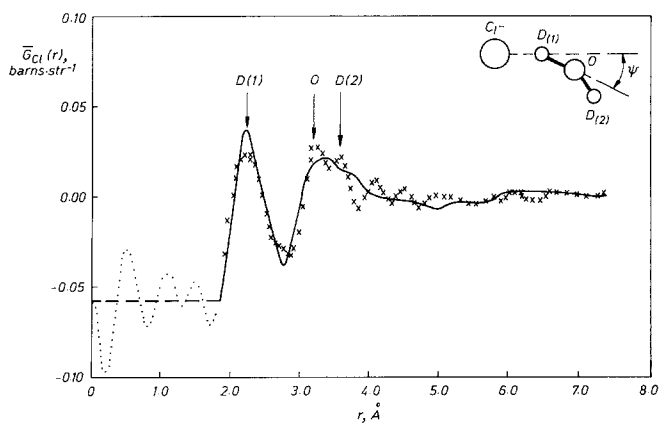


Fig. 3. The total chloride ion in radial distribution function $\bar{G}_{\text{Cl}}(r)$ for 9.95 molal LiCl in heavy water (solid curve) and 5.32 molal NaCl in heavy water (crossed curve), scaled for concentration by 1.87.

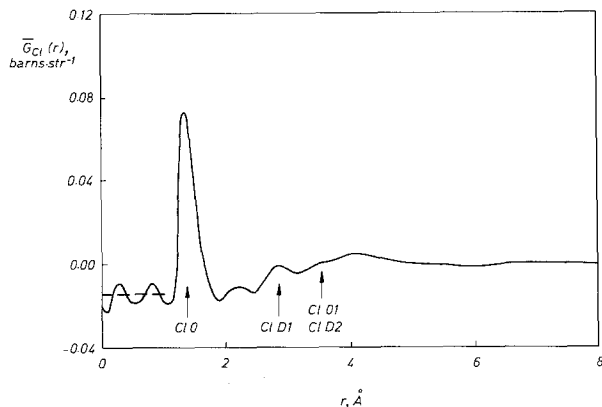


Fig. 4. The total perchlorate ion radial distribution function $\bar{G}_{Cl}(r)$ for 3.25 molal NaClO_4 in heavy water. The intramolecular peak is readily seen at 1.43 Å.

which the Cl–water potential exhibits a highly directional sixfold symmetry reflecting the p -band nature of the Cl^- ion. The results here also show the inadequacy of computer simulation results, which always produce coordination numbers greater than 6 (39).

The water structure around ClO_4^- [31] (Fig. 4) and NO_3^- [38] ions contrasts markedly with that for Cl^- hydration. The two complex anions exhibit a relatively weak coordination, an indication of the softness of their respective ion–water potentials.

3.2. Ion–Ion Structure

Interest in ion–ion structure is stimulated by the vast theoretical literature on this subject [40]. For example, a knowledge of $g_{II}(r)$ furnishes us with a critical test of model calculations and computer simulations [3]. Of particular interest is the degree to which a primitive model—hard spheres in a dielectric continuum—can be used to reproduce experimental results.

The second-order difference method has been applied to two concentrated solutions: 4.35 m $\text{NiCl}_2 \cdot \text{D}_2\text{O}$ [41] and 14.9 m $\text{LiCl} \cdot \text{D}_2\text{O}$ [26]. In the case of the former, all three ion–ion correlation functions were determined (Fig. 5). Several conclusions were drawn which, inter alia, included the observations that (i) there is no evidence for direct contacts between Ni^{2+} and Cl^- ions; (ii) the nearest-neighbor Ni^{2+} – Ni^{2+} separation is 4.1 Å, a result in good agreement with a primitive model calculation of Friedman and Dudowicz [42]; and (iii) the form of $g_{\text{ClCl}}(r)$ is highly

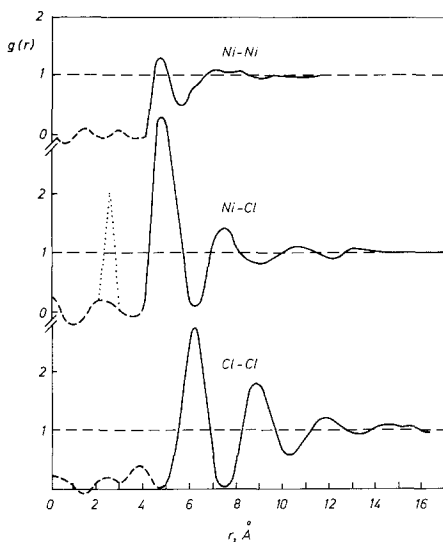


Fig. 5. The pair correlation functions $g_{\text{NiNi}}(r)$, $g_{\text{NiCl}}(r)$, and $g_{\text{ClCl}}(r)$ for 4.35 molal nickel chloride in heavy water. The dotted curve at 2.4 Å indicates the magnitude of $g_{\text{NiCl}}(r)$ if inner sphere complexing of Ni^{2+} and Cl^- ions were actually to occur.

structured, a consequence, we feel, of the highly directional nature of the Cl-water potential.

The results for the lithium chloride solution showed a $g_{\text{ClCl}}(r)$ that was highly structured. Clear evidence was found for direct contacts between Cl^- ions, which is perhaps not surprising, given that the molecule ratio of D_2O to LiCl is only 3.2 to 1. A simulation study of a 14 molal LiCl aqueous solution based on L-J potentials for ion-water interactions was unable to reproduce the experimental results [43].

The determination of ion-ion correlations by the neutron-diffraction difference method is at the limit of the present technology and relatively few systems are susceptible to this method. In the forthcoming years it will perhaps be possible to study more systems containing ions such as Li^+ , Cu^{2+} , Fe^{2+} , Fe^{3+} , Sm^{3+} , and Cl^- , but only at very high concentrations, i.e., $c \sim 0.1$ at %. An alternative means of determining $g_{\text{II}}(r)$ is being sought by using X-ray diffraction in conjunction with *isomorphic* substitution. Recent results are encouraging [44]. However, the technique is limited in applicability to suitable isomorphs, which can be established only by the first-order difference method of neutron diffraction. Further-

more, as with all X-ray structural studies, the scope is limited because of the anisotropy of the interaction between X rays and atoms [6].

3.3. Work Under Nonambient Conditions

Although most of the investigations using the difference methods of neutron diffraction have been carried out at room temperature and pressure, a few studies have also been undertaken under nonambient conditions where, in contrast to X-ray diffraction, data acquisition is much more straightforward because of the significantly smaller absorption and scattering effects from containers [45]. The advantages of neutron over X-ray methods become particularly noticeable when working at elevated pressures.

The motivation for structural studies arises from the interesting phenomena observed in a variety of aqueous electrolyte solutions at high p and T [46]. Initial investigations have concentrated on raising the temperature at room pressure or raising the pressure at ambient temperature. The former case is more straightforward and results have been obtained for solutions of 40 m ZnCl_2 , where the coordination of Cl^- was determined at 100°C (29). In recent months we have constructed a furnace suitable for work up to $200^\circ\text{C} + 1^\circ\text{C}$ at 1 bar. Preliminary results on the molten salt system ammonium nitrate have been encouraging and we plan to extend our investigations to aqueous solutions. Diffraction results have already been obtained for several aqueous electrolyte solutions at elevated pressure and room temperature. By using a "null alloy" $\text{Ti}_{0.68}\text{Zr}_{0.32}$ pressure cell (i.e., one that contributes only to the background scattering level and not to the structure), pressures of 6 kb were attained [47].

Results for heavy water showed appreciable changes in water structure, reflecting the general compression of the fluid and enhancement of the hydrogen bond network. We also found that for concentrated aqueous solutions of LiCl and NiCl_2 there is an appreciable difference in the Cl^- hydration [48].

4. CONCLUSIONS AND FUTURE PROSPECTS

A brief review has been presented of the results of neutron-diffraction experiments for a variety of concentrated aqueous electrolyte solutions. The isotopic difference methods have been used to determine structural properties in terms of ion-water correlations and ion-ion pair distribution functions. A knowledge of these properties is enabling us to characterize the relative strengths of ions in solution and examine the validity of theoretical models and solution state theories.

Neutron facilities are being improved on two fronts. First, the introduction of more sensitive detectors and larger and faster computers means that diffractometers such as the D4B at I.L.L., Grenoble, and the 7C2 at C.E.N., Saclay, France, are being commissioned, which provide higher-quality data over wider ranges of momentum transfer. Second, new sources such as the intense pulsed neutron source at ISIS, Rutherford-Appleton Laboratory, U.K., will enable us, with instruments such as the L.A.D., to extend investigations to include experiments that exploit the particular nature of a pulsed neutron beam.

These technical developments mean that new experiments can be envisaged. For example, it becomes feasible to initiate studies of solvation structure in more complex solutions such as polyelectrolytes and polar solvents. Furthermore, the particular geometry of pulsed source instruments makes them particularly suited to investigations at elevated pressure and temperature.

ACKNOWLEDGMENTS

It is a pleasure to thank my colleagues (past and present) at Bristol University, who have contributed significantly to the research program described above. In particular, the helpful advice and enthusiastic support of Professor John Enderby is gratefully acknowledged. I am also grateful to P. S. Salmon, A. C. Barnes, P. M. N. Gullidge, N. T. Skipper, J. G. Herdman, and D. H. Powell, who have carried out much of the recent experimental work. The generous financial support of the Science and Engineering Research Council is gratefully acknowledged. Finally, I would like to thank the staff of the I.L.L., Grenoble, for many happy and fruitful visits and, in particular, Dr. Pierre Chieux, who has provided expert technical and scientific advice during the course of this research.

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