The Structural and Dynamic Properties of some Transition Metal Aqua Cations: Results from Neutron Scattering

G. W. Neilson, S. Ansell, and J. Wilson
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL,
United Kingdom

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Dedicated to Professor Hitoshi Ohtaki on the occasion of his 60th birthday

The following paper comprises a survey of the role neutron scattering methods have played to help understand the origins of the diverse properties of electrolyte solutions which contain transition metal cations. It is seen how neutron diffraction and isotopic substitution is able to resolve the local structure around contrasting ions, such as Cr^{3+}, Ni^{2+}, Fe^{3+}, Fe^{2+}, Cu^{2+}, without recourse to sophisticated modelling procedures. Quasielastic neutron scattering (QNS) provides insight into the dynamics of the protons in solution. The results enable one to distinguish between cations whose water molecules are coordinated on time scales larger than 5×10^{-9} s, shorter than 10^{-10} s, or intermediate between those two limits. QNS also provides information on the existence of a second relatively short-lived hydration shell distinct from the bulk water.

Introduction

Aqueous solutions which contain transition metal (TM) cations occupy an important position in many branches of science. The contrasting coordination of $[Fe^{2+}]_{aq}$ and $[Fe^{3+}]_{aq}$ is of significance in explaining the fundamental aspects of electrochemical reactions [1]. Additionally, cations such as Cu^{2+}, Mn^{2+}, Ni^{2+} and the closely related cation Zn^{2+}, play important roles in the activity of large biomolecules in solutions [2].

In the following paper, which is dedicated to Dr. H. Ohtaki, a leading scientist in the field of solution chemistry, we review the contribution neutron scattering methods have made to the elucidation of the interatomic structure and dynamics of aqueous electrolytes which contain TM cations. Foremost amongst these are the first and second order difference techniques of neutron diffraction and isotopic substitution, NDIS, which enable one to determine structural information on all three aspects of an aqueous salt solution ($MX_n \cdot H_2O$), i.e. that associated with the solvent, the solute, and the interactions between the solute and solvent [3]. This is achieved by a determination of the radial pair distribution functions $g_{IJ}(r)$, which are the first in a hierarchy of functions used to represent the equilibrium structure of a liquid. For an aqueous electrolyte solution, $g_{HH}(r)$, $g_{HO}(r)$, $g_{OO}(r)$ describe the structure of the water molecules in solution, $g_{MM}(r)$, $g_{MX}(r)$, $g_{XX}(r)$ that of the salt and $g_{MO}(r)$, $g_{MH}(r)$, $g_{XO}(r)$ and $g_{XX}(r)$ represent the ion-water structure. The first order difference method is based on a single substitution of one ionic species (e.g. $^{62}NiCl_2$ for $^{NAT}NiCl_2$) and enables one to determine, by direct Fourier transformation of the experimental data, the coordination of all other atomic species to the substituted ion. This first order difference function is written as

$$G_I(r) = A\,g_{IO}(r) + B\,g_{IH}(r) + C\,g_{IJ}(r) + D\,g_{II}(r) + E\,,$$

where

$$A = 2\,c_O c_I b_O(b_I - (b_I)'), \quad B = 2\,c_H c_I b_H(b_I - (b_I)'),$$
$$C = 2\,c_J c_I b_J(b_I - (b_I')), \quad D = c_I^2\,((b_I)^2 - (b_I')^2),$$
$$E = -\,(A + B + C + D)\,.$$

c_α is the atomic concentration of species α whose mean coherent neutron scattering length is b_α, and b_I and b_I' are the isotopic states of the subsituted ion. The second order difference method involves more than one substitution. For example, determination of $g_{\alpha\alpha}(r)$ is obtained from diffraction results of 3 isotopically distinct solutions in the species α, and $g_{\alpha\beta}(r)$ from diffraction results of 4 isotopically distinct solutions in both α and β.

Results for $G_I(r)$ give information on the hydration structure of the aqua ion I, in terms of closest approach of water molecules, hydration number $\bar{n}_I^O$, ion-water conformation, and extent of the ion-water cor-

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Reprint requests to Dr. G. W. Neilson.

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relation [3]. A rough guide to the stability of the aqua ion complex can be gauged from the shape of peaks in $G_I(r)$ (see e.g. Fig. 3), where $G_{Ni}(r)$ clearly suggests that the $[Ni^{2+}]_{aq}$ constitutes a relatively long-lived entity, a result confirmed by nuclear magnetic relaxation (NMR) and quasielastic neutron scattering (QNS) measurements.

Results on the water structure in terms of $g_{HH}(r)$, $g_{OH}(r)$, and $g_{OO}(r)$ are as yet unavailable for transition metal salt solutions. There is no doubt that a determination of these functions is feasible, as they have been determined in aqueous solutions of lithium chloride [4], where it is found that the water structure only becomes appreciably affected by the presence of ions at concentrations $\gg 1$ molal. It will be interesting to see how the water structure, especially the H-bond network, changes when 2:1 or 2:2 electrolytes are present in solution.

The solute structure can be used to determine the degree of ion association, and the extent to which primitive model calculations can usefully be applied to an aqueous electrolyte solution [5]. We present in the next section results for the cases of nickel chloride and copper chloride solutions at high concentrations.

The method of quasielastic scattering (QNS) provides a means to probe the dynamics of the water molecules in solution [6, 7]. In particular, because neutrons are scattered strongly and incoherently by protons, it is possible to distinguish between 3 regimes. The time scale associated with an NQS experiment is typically in the range $5 \times 10^{-9} \leq t \leq 10^{-10}$, and analysis of data in terms of either a single Lorentzian or two Lorentzians allows one to determine whether the protons are best described by one or two diffusion coefficients. In the former case the water molecules are said to be in fast exchange, i.e. $\tau \ll 10^{-10}$ s, and indistinguishable from bulk water. If two Lorentzians are required to analyse the data, then, depending on the parameters, the water molecules can be identified as being in intermediate exchange, i.e. $10^{-10} \leq \tau(s) \leq 5 \times 10^{-9}$ or in slow exchange, i.e. $\tau \gg 5 \times 10^{-9}$ s. The transition metal cations discussed below are seen to have hydration shells whose water molecules are in slow or intermediate exchange. Moreover, the QNS results for long lived aqua cations such as $[Ni^{2+}]_{aq}$ can give information on the dynamic nature of the second hydration shell [7].

Results from NDIS and QNS can be usefully compared with those derived from other methods. In recent years several reviews, and one in particular [8], have appeared which list the coordination properties of ions in terms of aqua ion structure and dynamics. It is important to note that not all probes are equivalent, even though the same properties are reported. Whereas diffraction, especially NDIS, offers a direct probe of ionic structure, spectroscopic and thermodynamic measurements are indirect and require assumptions that may lead to conflicting results. This is the main reason that large discrepancies appear in the literature for hydration numbers, particularly for the more labile ions [10].

The method most closely related to neutron diffraction is that of X-ray diffraction, the results of which when analysed with a suitable model can be used to gain information on cation-oxygen correlations and coordination numbers [9]. When X-ray diffraction is combined with isomorphic substitution (XDIS), it is often possible to obtain $g_{MO}(r)$ to a good approximation. It is particularly useful at the second order difference level in the determination of $g_{MM}(r)$ [10]. However, the method depends on the availability of suitable isomorphs and is limited by the chemistry of ionic species. An alternative and more widely applicable technique is that based on extended X-ray absorption fine structure (EXAFS) spectroscopy [11]. The advantage of this method is that the data are specific for a given ion, e.g. Cu^{2+}, and a single sample is required. Moreover, information can be obtained at relatively low concentration. However, the method is based on interactions between electrons of the ion and X-rays and a degree of model fitting is required.

Infra-red, ultra-violet and optical spectroscopies are also used to obtain information on ionic solvation, especially in cases such as Zn^{2+} and Cu^{2+} where complexation is found. However, the results are not quantitative in the same sense as those derived from diffraction method. Thermodynamic properties are often used to deduce ionic properties such as hydration numbers. It is clear that such information is at best a qualitative guide to the relative strength of the coordination properties of ions.

From the dynamic viewpoint, nuclear magnetic relaxation (NMR) offers a wide ranging technique for the determination of residence times over several decades for water molecules [12]. Together with tracer diffusion and chemical kinetics one can build up a picture of the aqua ion dynamics and the half-life of a particular cation water-complex [13].

The use of computer simulation has served to help understand all aspects of solution structure and dy-

Table 1. Hydration shell properties of transition metal cations[a].

Cation	Counterion	Concentration (molality)	Ion-water distances (Å) $\bar{r}_{MO}$	Ion-water distances (Å) $\bar{r}_{MH}$	Cation-anion distance (Å) $\bar{r}_{MX}$	Coordination numbers $\bar{n}_{MO}$ [b]	Coordination numbers $\bar{n}_{MX}$	Ref.
Cr^{3+}	ClO_4^-	2.2	1.98(2)	2.60(3)	–	6.0(5)	–	[20]
Fe^{2+}	Cl^-	1	2.12(2)	2.75(5)	–	6.0(3)	–	
Fe^{3+}	NO_3^-	1.5	2.01(2)	2.68(3)	–	6.0	–	
	ClO_4^-	2.0	2.02(2)	2.65(3)	–	6.3(3)	–	
Ni^{2+}	Cl^-	2	2.06(2)	2.67(2)	–	5.9(1)	–	
	Cl^-	0.1	2.06(2)	2.69(2)	–	5.4(5)	–	
	ClO_4^-	3.8	2.07(2)	2.67(2)	–	5.8(2)	–	
	NO_3^-	3.4	2.05(2)	2.64(2)	–	5.7(3)	–	
	SO_4^{2-}	2.0	2.06(2)	2.65(2)	–	6.6(2)	–	
Cu^{2+}	Cl^-	4.3	1.96(2)	2.54(3)	–	3.4(2)	–	
	Cl^-	4.0	1.96(2)	2.54	–	3.3(3)	3.0(3)	
	ClO_4^-	2	1.96	–	–	4.1(3) [c]	–	
	NO_3^-	1	–	–	–	4.0(2) [c]	–	
Zn^{2+}	Cl^-	4	2.09(2)	2.74 [d]	2.28 [d]	4.1(3) [d]	1.4 [d]	
	$(CF_3SO_3)^-$	2	2.09(2)	2.69(3)	–	5.3(3)	–	

[a] Errors in parenthesis. – [b] Equivalent to hydration number. – [c] Jahn-Teller effect giving 4+2 coordination. – [d] Based on gaussian fit to composite peak.

namics. Heinzinger and co-workers have pioneered the application of molecular dynamics methods in the determination of $g_{\alpha\beta}(r)$'s, power spectra, and diffusion coefficients. The simulations are (though not always) carried out on a periodic box of particles, cations, anions and water molecules interacting via pairwise forces. Even with a relatively small number of particles, it is interesting to observe that the results are often in excellent agreement with experiment [14]. As regards the solute structure, Haymet and colleagues [15] have carried out a systematic study of the cation and anion coordination in 1-1, 2-1, 2-2 and 3-1 electrolytes, where the solution is represented as soft spheres in a dielectric continuum. There is a clear change in the $g(r)$'s as a function of concentration and of charge density. It will be interesting to see at what level of detail theoretical and experimental results diverge.

Results

1. Aqua Ion Structure and Dynamics

The d-character of the electronic ground state of the TM cations, and to a lesser extent that of Zn^{2+}, indicate that a six-fold coordination might be anticipated in aqueous solution. Moreover, because residence times of water molecules in the first hydration shells range from $\sim 10^{-10}$ s for Cu^{2+} or Zn^{2+} to $>10^6$ s for Cr^{3+}, one might anticipate relatively strongly correlated aqua cation structures to occur.

Although TM cations are evident in a large number of oxidation states [2], only a few of them are sufficiently long-lived in solution to be studied by neutron scattering methods. For example, cations such as Ti^{3+}, Ti^{4+}, V^{2+} and V^{3+} are stable only in special conditions of pH and in an oxygen free environment. Consequently their hydration structures have yet to be examined by diffraction methods. A further problem arises in the case of cations of cobalt and manganese. Both species are monoisotopic, and therefore aqua ion structures of Co^{2+} and Mn^{2+} are not accessible from NDIS. We have carried out a neutron diffraction study based on *isomorphic* substitution of Ni^{2+} and Mn^{2+}. However, the information is less satisfactory and results are subject to greater error.

This review is therefore only concerned with those TM cations which can be prepared by straightforward laboratory procedures which are suitable for isotope labelling [16]. The cations which have been studied by NDIS are listed in Table 1, which gives details of the nearest neighbour coordination and includes cation-oxygen, cation-hydrogen (deuterium) distances and coordination numbers. For completeness we include the coordination properties of Zn^{2+}.

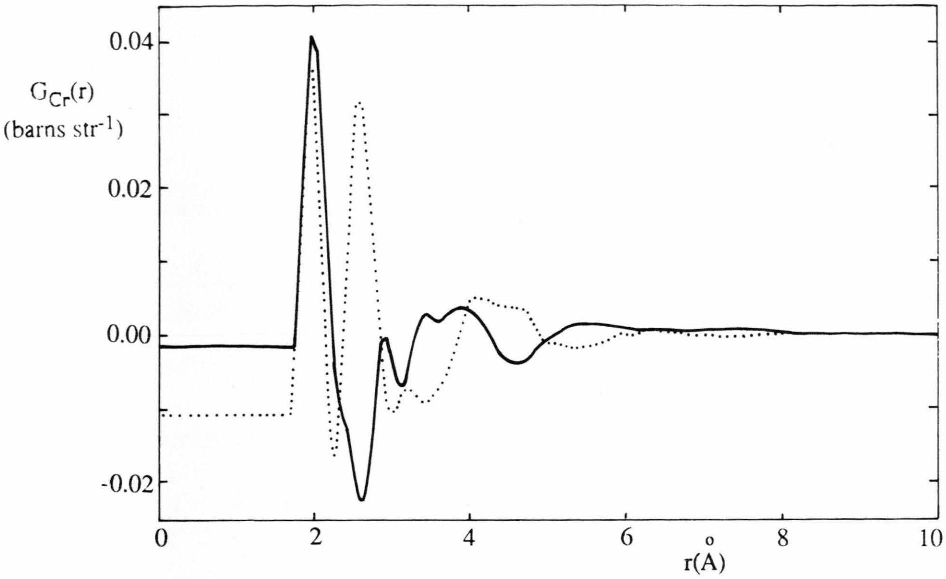

Fig. 1. The total Cr^{3+} radial distribution function $G_{Cr}(r)$ in 2 M chromium perchlorate in heavy water (broken curve), and 2.224 M chromium perchlorate in water (full curve).

Cr^{3+}

The Cr^{3+} ion of chromium possesses the most stable hydration structure of all the transition metal ions. The first NDIS determination of the local coordination of Cr^{3+} in water [17] confirmed the existence of a well-defined hydration shell of six strongly correlated near neighbour water molecules (Figure 1). There is also clear evidence of orientational correlations in a second hydration sphere which contains relatively broad peaks centred at 4 Å and 4.5 Å. QNS studies of the dynamics of $[Cr^{3+}]_{aq}$ confirm the longevity of the six-fold aqua complex [18], and show that even although the second shell of water molecules are orientationally correlated to the Cr^{3+} cation, the binding time between protons and Cr^{3+} is $< 5 \times 10^{-9}$ s.

A secondary aspect to the NDIS result for Cr^{3+} concerns the degree to which H_2O and D_2O molecules are equivalently coordinated in aqueous solution. According to a calculation of Newton and Friedman [19], Cr^{3+} should be 15% preferentially hydrogenated in a 1:1 mixture of H_2O and D_2O. The observation does not substantiate this calculation. However, it could be that this effect will occur at elevated temperatures as the calculation depends critically on compensating enthalpic and entropic effects.

It will be of interest to investigate the form of $G_{Cr}(r)$ as a function of p and T, in order to determine the thermodynamic conditions under which the aqua ion structure breaks down.

Fe^{2+} and Fe^{3+}

Although these ions have significantly different solvation properties it seems sensible to discuss them together given that the redox reaction which couples them is one of the most fundamental in chemical kinetics. Both have been investigated by NDIS [20, 21], and the ferric cation Fe^{3+} has been studied by QNS [22]. NMR studies put both aqua cations in the slow exchange regime of QNS. Water molecules coordinate to Fe^{2+} on a time scale $\sim 3 \times 10^{-7}$ s, whereas those associated with Fe^{3+} have a residence time several decades longer [8]. As might be expected, the NDIS results show that $G_{Fe}(r)$ in both cases is well defined (Fig. 2), with Fe^{3+} possessing significantly sharper nearest neighbour correlations with the surrounding water molecues. It is interesting to note that the NMR results refer to the O atoms, and it would be useful to know whether the protons of the water molecules have significantly different times from

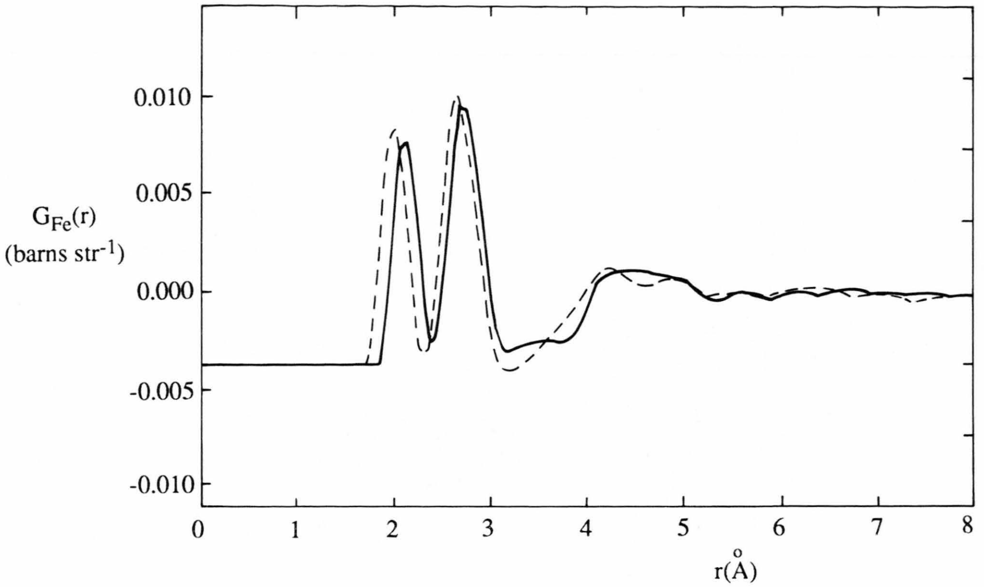

Fig. 2. The total Fe^{2+} distribution function $G_{Fe}(r)$ for 1 molal iron(II) chloride in heavy water (full curve), and the equivalent total Fe^{3+} distribution function $G_{Fe}(r)$ for 1.5 molal iron(III) nitrate in heavy water (dashed line); this latter function has been scaled for comparative purposes.

those of the O atoms and for ferric and ferrous solutions.

Clearly ferric and ferrous cations, and compounds of iron, are worthy of further investigation, particularly because of their presence in many commercially important processes, both as useful materials in chemical reactions and as unwanted products due to corrosion.

Ni^{2+}

Ni^{2+} is present in a variety of solid hydrates and in many aqueous solutions of electrolytes [2]. Moreover, nickel has several stable isotopes, each possessing widely different coherent neutron scattering lengths. The Ni^{2+} cation can be used to investigate the dependence of aqua cation structure on counterion, concentration, pressure, temperature, etc., and to test theoretical predictions of solute structure based on models of electrolyte solutions. Information from a variety of methods shows that Ni^{2+} possesses a well-defined relatively long-lived six-fold hydration shell [16, 23]. The results from NDIS (Fig. 3) highlight the details of the local $Ni^{2+}-H_2O$ conformation which is demonstrably insensitive to concentration and counterion [24]. Ni^{2+} hydration is also independent of moderate changes in pressure to 2000 bar and temperature to ~150 °C [25]. However, recent results for nickel sulphate solution at 300 °C show that the Ni^{2+} hydration is completely destroyed, and probably Ni^{2+} SO_4^{2-} pairing occurs [26]. Work is already planned to identify the range of T over which breakdown of the aqua ion takes place.

Along with Cr^{3+} (see above), Ni^{2+} has been used to probe quantum mechanical effects arising from H/D exchange in water/heavy water solutions [19]. The results are consistent with those of the Cr^{3+} study and show that Ni^{2+} has little or no preference for hydration over deuteration. Consequently, they are at variance with those of theory.

The Ni^{2+} cation has also been used to study counterion behaviour in polyelectrolyte solutions of polystyrene sulphonate in heavy water, and structural coordination in solutions of biological molecules such as nickel adenosine triphosphate in heavy water. In both cases [27, 28] we find that the Ni^{2+} cation retains a six-fold local coordination. However, about two of the sites are associated with the macromolecule itself. It is of interest to investigate further such materials with a view to understanding the origins of counterion condensation in polyelectrolytes and the role of transition metals in biochemical reactions.

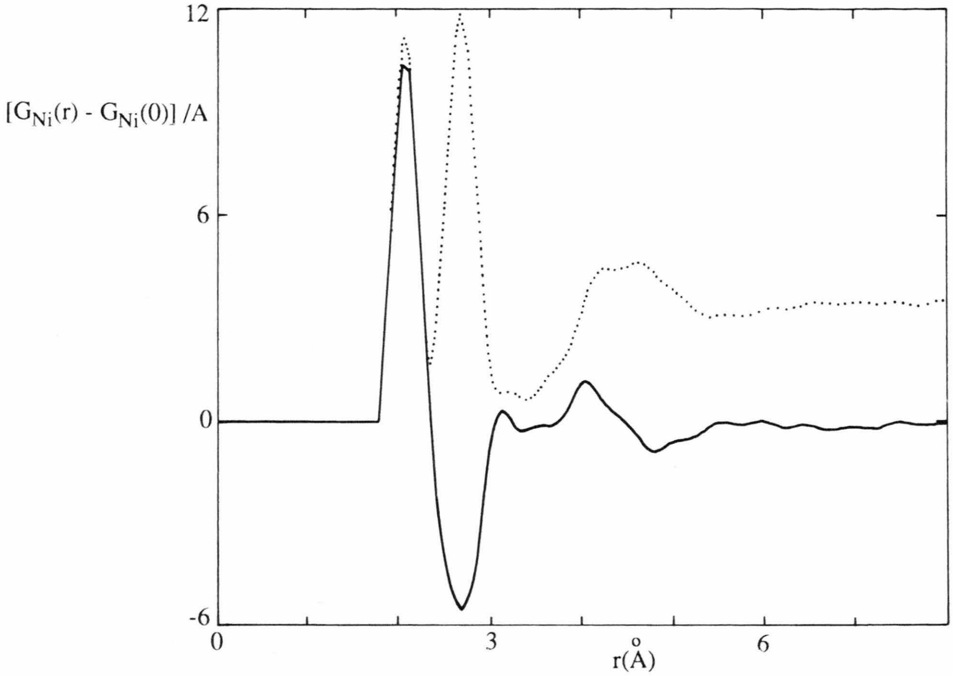

Fig. 3. The real space Ni^{2+} distribution function $(G_{Ni}(r) - G_{Ni}(0))/A$ for 2 mol kg^{-1} in heavy water (D_2O) (dotted curve), and 2 mol kg^{-1} in water (H_2O) (full curve).

For completion, we mention the contrasting study of Ni^{2+} coordination in methanol, where interest focussed on the effect of dielectric constant on coordination [29]. The results shows that in a 3 molal solution of nickel chloride the highly correlated local structure persists. However, there is a significant correlation with the Cl^- counterions. Determination of $g_{NiNi}(r)$ and $g_{NiCl}(r)$ in this system by the second order NDIS method could provide useful insights into the dependence of solute structure on dielectric constant (see next section).

Cu^{2+}

In contrast to other TM cations, the six-fold coordination of the cupric ion is distorted in both the solid and liquid states [2]. The origin of this distortion is due to the Jahn-Teller effect. Although present in all d-states ions in solids and liquids, it is sufficiently strong to be observed in only two cases – $Cr^{2+}(d^4)$ and $Cu^{2+}(d^9)$. The NDIS results (Fig. 4) on concentrated solutions of cupric salts provide clear evidence of $4+2$ configuration around Cu^{2+}. Where the counterions are NO_3^- and ClO_4^-, the local coordination is made up of 4 nearest neighbour water molecules and 2 more distant polar water molecules [30, 31]. NQS results suggest that these water molecules exchange with the bulk on a time scale of $\leq 10^{-10}$ s.

For the case of cupric chloride in solution, the NDIS results [30] show that at a concentration of 4 molal (i.e. near saturation) the 4+2 structure is severely disrupted and Cl^- displaces some of the 4 nearest neighbour water molecules (Table 1). This observation is based on an NDIS study at the second order difference level (see next section) [32]. The result also provides a structural explanation of the colour change from green to blue as the salt concentration is reduced.

Zn^{2+}

Although zinc is not a transition metal, the cation Zn^{2+} is included here as its oxidation state, d^{10}, completes the series. All structural studies of aqueous solutions containing zinc salts, including those based on NDIS [33] show that Zn^{2+} has a varied coordination depending on counterion, ion concentration and temperature [2, 3, 8]. The coordination number can vary

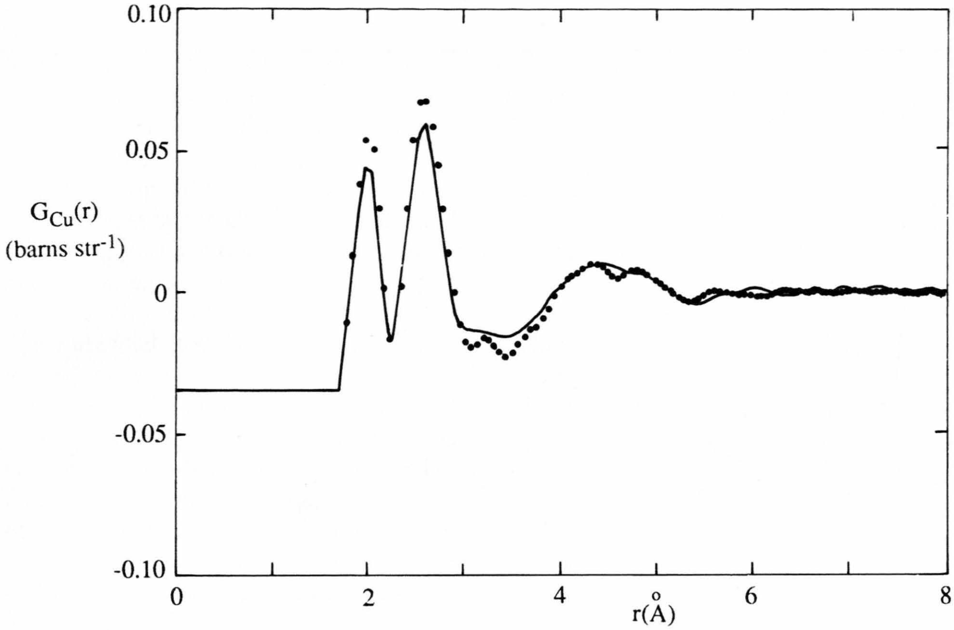

Fig. 4. The total Cu^{2+} radial distribution function $G_{Cu}(r)$ for 1 molal copper(II) nitrate in heavy water (full curve) and for a 2 molal copper nitrate heavy water solution (dotted curve). The $G_{Cu}(r)$ for the nitrate solution has been scaled for comparative purposes.

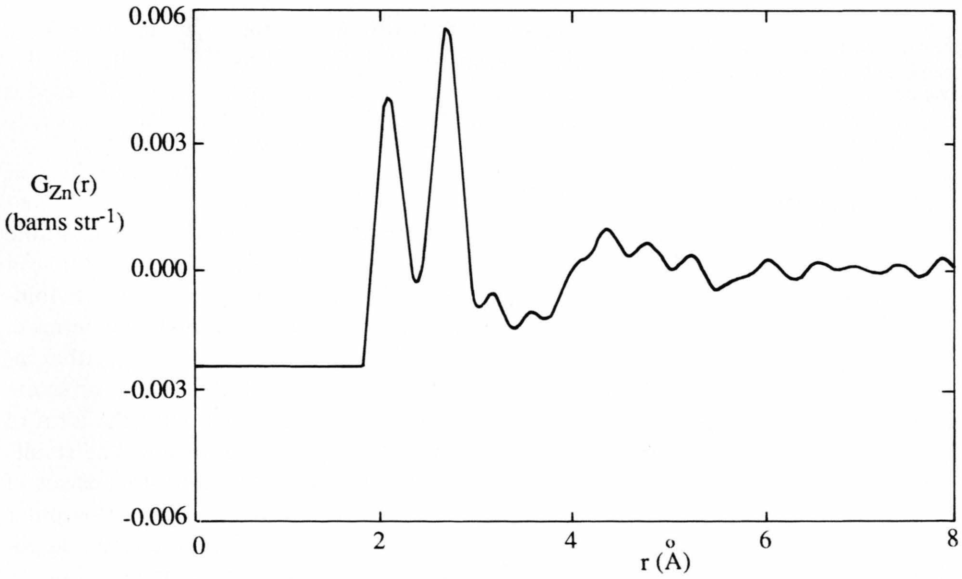

Fig. 5. The total Zn^{2+} radial distribution function $G_{Zn}(r)$ for 2 molal zinc triflate in heavy water.

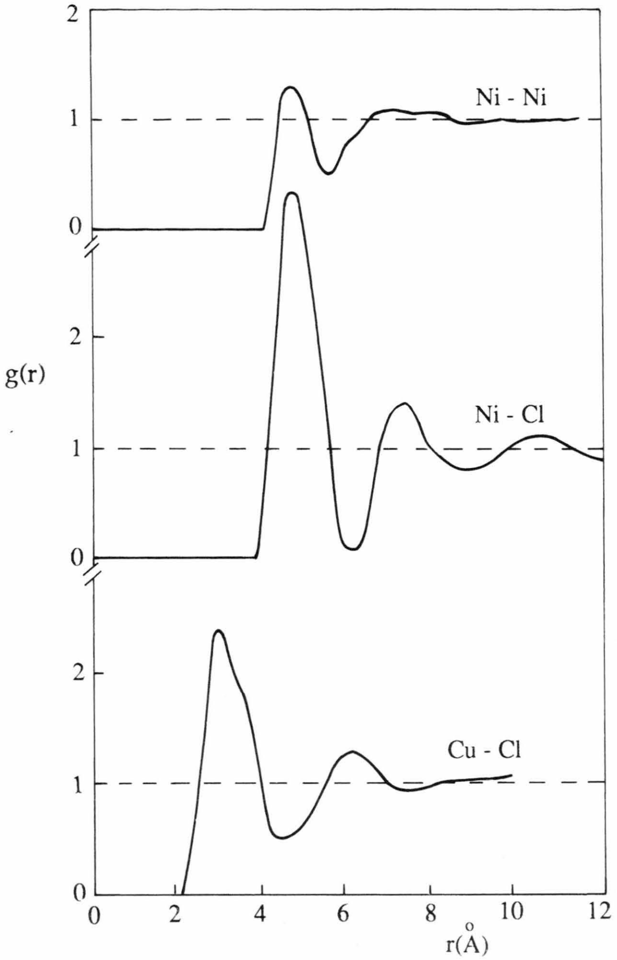

Fig. 6. The solute structure pair distribution functions $g_{\mathrm{NiNi}}(r)$ and $g_{\mathrm{NiCl}}(r)$ in 4.3 molal $NiCl_2$ in heavy water, and $g_{\mathrm{CuCl}}(r)$ in 4 molal $CuCl_2$ in heavy water.

from 4 to around 6 depending on environment. Because of the presence of Zn^{2+} in some enzyme catalytic reactions, it is necessary to obtain a more detailed picture of longer range aqua-ion structure.

2. *Longer Range Aqua-Ion Structure*

Although the above discussion focussed primarily on details of the first hydration shell, it is worth pointing out that strong longer range correlations suggest that second shells of water molecules are present in all cases. Indeed, in the case of Cr^{3+} the local structure persists to ~ 8 Å and indicates the presence of a third coordination shell of water molecules.

3. *Ion-Ion Structure*

The only two systems studied at this level of detail are 4.3 m nickel chloride in heavy water and 4 m cupric chloride in heavy water. In the former case all 3 solute $g_{ij}(r)$'s were determined [32], whereas in the latter only $g_{\mathrm{CuCl}}(r)$ and $g_{\mathrm{ClCl}}(r)$ were obtained [34]. Although the systems are almost at the same concentration, there are demonstrable differences in the two structure patterns. Most significant is the association of cation and anion. For the case of Cu^{2+} there is clear evidence that there are direct contacts between Cu^{2+} and Cl^-. No such interactions are observed in the case of Ni^{2+}. The reason for this presumably the strong Ni^{2+} interaction with six nearest neighbour water molecules, which also accounts for the relatively featureless form for $g_{\mathrm{NiNi}}(r)$, reflecting the fact that Ni^{2+} cations are only weakly associated with each other. It will be of primary interest to see how $g_{\mathrm{NiNi}}(r)$ changes with temperature. On the basis of observations of a 1.2 m $NiSO_4$ heavy water solution one might anticipate a dramatic change in $g_{\mathrm{NiNi}}(r)$ on heating to ~300 °C.

It appears therefore that strongly coordinated aqua cations such as Ni^{2+}, Cr^{3+} etc. will have relatively featureless $g_{++}(r)$'s. Consequently, it makes sense to model systems which contain these cations in solution as being completely "dressed" with their waters of hydration. No such models should be used for weakly coordinating cations such as Cu^{2+}, Fe^{2+}, Zn^{2+}, etc. It will therefore be of further interest to study, by NDIS, the solute structure in aqueous solutions of $CrCl_3$, a 3:1 system, and test these ideas. The results will also provide a sensitive test of recent theories of aqueous electrolytes [15].

Perspectives

It is clear that neutron scattering methods constitute a powerful means by which a quantitative picture can be obtained for all aspects of aqueous electrolyte solution structure. NDIS provides information in terms of the pair radial distribution functions $g_{\alpha\beta}(r)$, either individually when used to define the solvent or solute structure, or as a linear combination in the form of $G_1(r)$ to describe the aqua ion structure. The results can be used to characterise the contrasting effects of transition metal cations and to test both computer simulation studies of ionic hydration and the applicability of primitive model calculations of ion-ion structure. The complementary method NQS gives information on the proton dynamics in solution and enables one to determine whether the lifetime of an aqua cation complex is $>5 \times 10^{-9}$ s or $<10^{-10}$ s or somewhere in between. The method can also be used to define a mean diffusion coefficient of protons in a second hydration zone.

In the forthcoming years one can anticipate that both methods will continue to produce useful results which will help resolve many questions regarding the structure and proton dynamics of electrolyte solutions. In the short term, work is planned for several systems including NDIS experiments on Ni^{2+} counterion effects in aqueous solutions of the polyelectrolyte DNA, and a comprehensive survey of the structural changes which occur in aqueous electrolytes of $NiCl_2$ over a wide range of pressure and temperature. It is also proposed to extend NQS studies to include work on aqueous ionic fluids at elevated pressures and temperatures.

Assuming a proportional improvement in performance of neutron methods as has been witnessed in the past ten years, one can envisage many new experiments being undertaken in the longer term. Investigations might include structural studies of the interface region between a solid copper or iron surface in an aqueous medium, and real time investigations of the structural evolution of some relatively slow electrochemical reactions.

It is also worth noting that a combination of neutron and X-ray studies will offer additional information to those cation species not directly accessible to the NDIS method.

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