

Ionic hydration by neutron scattering

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Abstract - The method of differences applied to neutron diffraction data obtained from isotopically different aqueous solutions is described. It is shown that the method allows a detailed description of ionic hydration to be given. Several examples of the technique are discussed.

INTRODUCTION

This is a review of how the method of neutron diffraction can, when combined with isotopic substitutions, yield direct information about the structure and formula of aquoions in solution.

If we perform any sort of scattering experiments (figure 1) on liquids the quantity that contains structural information is the variation of the differential scattering cross section with scattering angle. We shall denote this quantity as $I(\theta)$ which in fact is a weighted average of all the *partial structure factors* (see below) relevant to the liquid structure. For binary liquids (e.g. molten KCl) there are three partial structure factors. For KCl in D_2O (heavy water being generally preferred as the solvent in neutron studies) there are ten partial structure factors, which we will denote by $S_{\alpha\beta}$ with $\alpha, \beta = K, Cl, O$ or D .

In Fig. 2 I show the weighting of each of these terms for a 1 mol/kg solution of KCl in D_2O and it is evident that the scattering will be dominated by the water terms. Effects due to ionic hydration, which are reflected in $S_{KO}, S_{KD}, S_{ClO},$ and S_{ClD} , will be all but lost in $I(\theta)$; similarly, the important ion-ion terms, $S_{KK}, S_{KCl}, S_{ClCl}$, are not in practice observable in the total diffraction pattern.

There is another disadvantage in working with total diffraction patterns. Strictly speaking, there is no elastic scattering from any liquid, and corrections have to be applied to the observed scattered intensity if $I(\theta)$ is to be determined in a form useful for further analysis. For neutrons, these corrections are nowadays referred to as the "Placzek corrections" and are especially severe for liquids containing H or D. The combination of these difficulties, and different but comparable ones so far as X-rays are concerned, have made the interpretation of total diffraction patterns from aqueous solutions difficult and often ambiguous. In particular, the detailed nature of ionic hydration has been almost impossible to establish without recourse to extensive modelling.

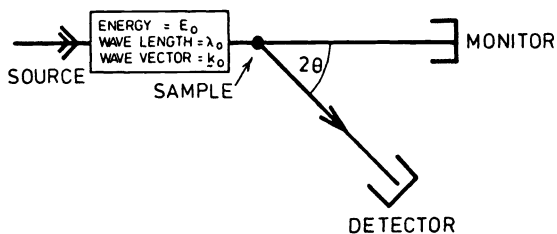
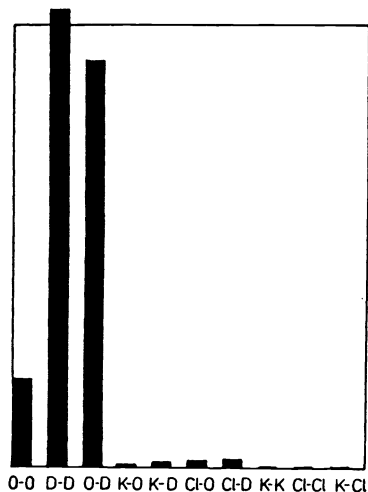


Fig. 1. Conventional arrangement for diffraction studies. The wave vector of the scattered wave is k_1 .

Fig. 2. The weighting of the various contributions to a total neutron pattern for a 1 mol/kg solution of KCl in heavy water.



FORMALISM

If neutrons are incident on a liquid containing several nuclear species, a measure of the amplitude of the scattered waves is given by

$$\sum_{\alpha} b_{\alpha} \sum_{i(\alpha)} \exp(-ik_{\nu} r_{i1}(\alpha)) \quad (1)$$

where b_{α} is the neutron coherent scattering length, and $r_{i1}(\alpha)$ denotes the position of the i th nucleus of α type. The differential scattering cross section for elastic scattering is given by

$$I(k) = \sum_{\alpha} \sum_{\beta} b_{\alpha} b_{\beta}^* \sum_{i(\alpha)} \sum_{j(\beta)} \exp ik_{\nu} (r_{\nu j}(\beta) - r_{\nu i}(\alpha)) \quad (2)$$

To do diffraction experiments, an intense source of neutrons is required. This is normally a high flux nuclear reactor, although pulsed sources based on nuclear spallation will play a major role in the future. The quantity $k = k_0 - k_1$ is the scattering vector whose modulus, k , for elastic scattering (i.e. $|k_0| = |k_1|$), is given by

$$k = 4\pi \sin \theta / \lambda_0 \quad (3)$$

where θ is half the scattering angle.

The b-factor for neutrons is isotropic and isotope-dependent, and bears no simple relation to the atomic weight. However, it is the isotope dependence which is the significant property for this review, because it allows the b appearing in equation 2 to be changed without upsetting the basic physics and chemistry of the liquid. This is the method of *isotopic substitution* on which we rely heavily in order to provide precise and direct structural information about ionic solutions. An example of the change in b with isotope is afforded by the chloride ion. Chlorine-35 has a scattering length of 11.70 fm whereas the scattering length for chlorine-37 is only 2.90 fm.

In order to demonstrate the connection between $I(k)$ and the real space structure, let us introduce the *partial radial distribution function*, or *pair correlation function* $g_{\alpha\beta}(r)$, which measures the probability of finding a β -type particle at a distance r from an α -type particle placed at the origin. To be more precise, let us place an α -type particle at the origin and ask what is the average number of β -type particles that occupy a spherical shell of radii r and $r+dr$ at the same instant. That number is given by

$$dn_r = 4\pi\rho_{\beta} g_{\alpha\beta}(r) r^2 dr \quad (4)$$

where $\rho_{\beta} = N_{\beta}/V$ (5)

and N_{β} is the number of β species contained in the sample of volume V . Equation (4) defines $g_{\alpha\beta}(r)$, which like its counterpart for a pure liquid, tends to unity at large r . We now define the *partial structure factor* $S_{\alpha\beta}(k)$ introduced earlier by

$$S_{\alpha\beta}(k) = 1 + \frac{4\pi N}{Vk} \int dr (g_{\alpha\beta}(r) - 1) r \sin kr \quad (6)$$

or

$$g_{\alpha\beta}(r) = 1 + \frac{V}{2\pi Nr} \int dk (S_{\alpha\beta}(k) - 1) k \sin kr \quad (7)$$

where $N = \sum_{\alpha=1}^i N_{\alpha}$. We also define the atomic fraction of the α -species c_{α} by $c_{\alpha} = N_{\alpha}/N$.

These definitions allow us to express $I(k)$ as

$$I(k) = N \left[\sum_{\alpha} c_{\alpha}^2 b_{\alpha}^2 + F(k) \right] \quad (8)$$

where

$$F(k) = \sum_{\alpha} \sum_{\beta} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} (S_{\alpha\beta}(k) - 1). \quad (9)$$

THE METHOD OF DIFFERENCES

We have shown that the neutron 'first order' difference method (ref. 1, 2 and 3) allows one to gain direct information about the detailed arrangement of the water molecules around the ions in aqueous solutions. It does this by effectively eliminating from $F(k)$ all terms *other* than those directly related to ionic hydration. The quantity that is central to the method is the algebraic difference of $F(k)$ from two samples that are identical in all respects except that the isotopic state of the cation, M , (or the anion X) has been changed; this

quantity, denoted $\Delta_M(k)$ or $\Delta_X(k)$ is the sum of four partial structure factors $S_{\alpha\beta}(k)$ weighted in such a way that only those relating to ion-water correlations are significant. Explicitly:

$$\begin{aligned} \Delta_M(k) &= A_M(S_{MO}(k)-1) + B_M(S_{MD}(k)-1) + C_M(S_{MX}(k)-1) + D_M(S_{MM}(k)-1), \\ \Delta_X(k) &= A_X(S_{XO}(k)-1) + B_X(S_{XD}(k)-1) + C_X(S_{MX}(k)-1) + D_X(S_{XX}(k)-1), \end{aligned} \tag{10}$$

where

$$\begin{aligned} A_M &= \frac{2}{3}c(1-c-nc)b_O(b_M-b'_M); & A_X &= \frac{2}{3}nc(1-c-nc)b_O(b_X-b'_X); \\ B_M &= \frac{4}{3}c(1-c-nc)b_D(b_M-b'_M); & B_X &= \frac{4}{3}nc(1-c-nc)b_D(b_X-b'_X); \\ C_M &= 2nc^2b_X(b_M-b'_M); & C_X &= 2nc^2b_M(b_X-b'_X); \\ D_M &= c^2(b_M-b'_M)^2; & D_X &= n^2c^2(b_X-b'_X)^2; \end{aligned}$$

and b_O and b_D are the neutron coherent amplitudes for oxygen and deuterium and b_M, b'_M, b_X and b'_X are the mean scattering amplitudes for the isotopic states used in producing the salt MX_n .

The properties of $\Delta(k)$ have been discussed in detail elsewhere (Refs. 1, 2) and need not be enlarged on here. The crucial property, apart from the fact that $A, B > C, D$, is that the Placzek distortions in $F(k)$ are essentially eliminated so that a difference function $\bar{G}(r)$ can be determined directly from

$$\bar{G}(r) = \frac{V}{2\pi^2 Nr} \int \Delta(k)k \sin(kr)dk. \tag{11}$$

In terms of the correlation functions, $g_{\alpha\beta}(r)$, it follows at once that

$$\bar{G}_M(r) = A_M(g_{MO}-1) + B_M(g_{MD}-1) + C_M(g_{MX}-1) + D_M(g_{MM}-1) \tag{12}$$

and
$$\bar{G}_X(r) = A_X(g_{XO}-1) + B_X(g_{XD}-1) + C_X(g_{MX}-1) + D_X(g_{XX}-1). \tag{13}$$

Since A and B are much greater than C and D the method yields a high resolution measurement of an appropriate combination of g_{MO} and g_{MD} or g_{XO} and g_{XD} . These quantities define the nature of ionic hydration and form the basis of further discussion. A convenient notation is to represent the dependence of $F(k)$ on isotope by the notation $F_p^q(k)$ where p is the isotopic state of the cation and q is the isotopic state of the anion.

AN EXAMPLE : 4.35 mol/kg $NiCl_2$ in D_2O .

To illustrate the method, we shall consider the recent work of Neilson and Enderby (Ref. 3) on a concentrated nickel chloride solution. The nickel ($Ni \rightarrow {}^{62}Ni$) and chloride substitution give rise to the values of $A_M \dots D_X$ shown in Table 1 and it is clear that the conditions $A, B > C, D$ is satisfied.

TABLE 1.

first order difference	A/mb [†]	B/mb	C/mb	D/mb
$\Delta_{Ni}(k) = \frac{N_F}{N} - \frac{62}{N}F$	17.4	40.0	5.05	0.32
$\Delta_{Cl}(k) = \frac{N}{35}F - \frac{N}{37}F$	14.9	34.4	2.30	3.50

[†] 1 millibarn (mb) = $10^{-31} m^2$.

TABLE 2. The hydration of Ni^{2+} in $NiCl_2$ solution (4.35 molal)

Ni^{2+} -oxygen distance/Å	Ni-O		Ni-D		θ/deg^{\dagger}	coordination number
	half-width at half-maximum/Å	Ni^{2+} -deuterium distance/Å	half-width at half-maximum/Å			
2.07±0.02	0.13±0.01	2.67±0.02	0.19±0.01	40±10	5.8±0.2	

[†] θ is the angle shown in Fig. 4 and is calculated on the assumption that the angle DOD is 105° and r_{OD} is 0.98Å.

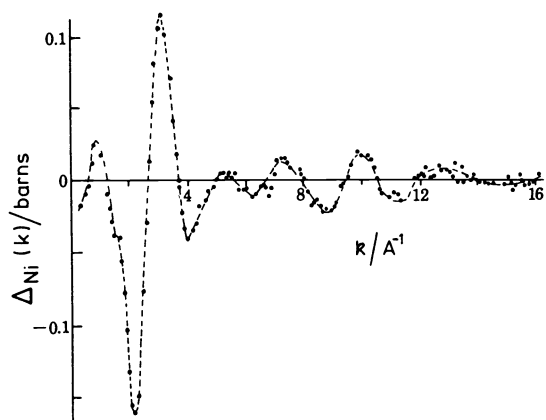


Fig. 3. $\Delta_{Ni}(k)$ for a 4.41 mol/kg solution of $NiCl_2$ in D_2O .

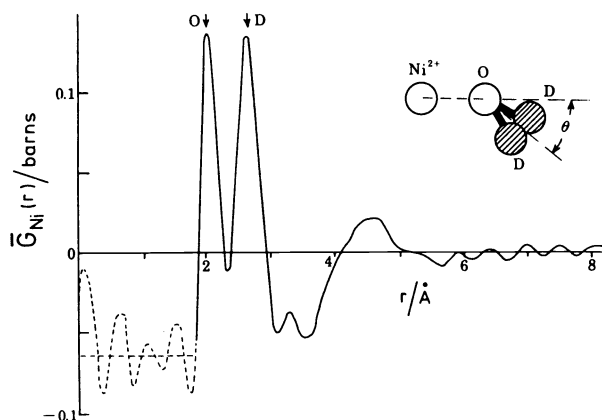


Fig. 4. $\bar{G}_{Ni}(r)$ for a 4.41 mol/kg solution of $NiCl_2$ in D_2O .

The first order difference $\Delta_{Ni}(k)$ derived from $N^N F(k)$ and ${}^{62}N F(k)$, where the letter N refers to samples of natural isotopic composition, is shown in Fig. 3 and the corresponding $\bar{G}_{Ni}(r)$ is given in Fig. 4. Table 2 contains a summary of distances, the tilt angle and the peak widths. In solution the inner hydration complex of Ni^{2+} is $Ni(H_2O)_6^{2+}$, a result known for many years (Ref. 4). The lifetime of this inner sphere is very long (ca. 30 μs) a fact reflected in $\bar{G}_{Ni}(r)$ by its low value around 3Å; on the other hand, n.m.r. studies suggest that the symmetry of the complex is less than cubic, which implies a significant angle of tilt, θ . It is therefore satisfying that the form of $\bar{G}_{Ni}(r)$ 'decisively supports the generally accepted stoichiometry for the complex' (quoted from Ref. 5). It was precisely because so much was known about $Ni^{2+}(aq)$ and the favourable neutron properties of its nucleus that this cation was chosen for a detailed study.

In Figs. 5 and 6 we show $\Delta_{Cl}(k)$ and $\bar{G}_{Cl}(r)$ derived from ${}^{35}N F(k)$ and ${}^{37}N F(k)$: the principal geometrical characteristics are given in table 3.

TABLE 3. The coordination of Cl^- in 4.35 molal solution of $NiCl_2$

$Cl^- - D(1)/\text{Å}$	$Cl^- - O/\text{Å}$	$Cl^- - DD(2)/\text{Å}$ (range)	ψ^\dagger/deg	coordination number
2.29 ± 0.02	3.20 ± 0.04	3.40-3.50	7 ± 3	5.7 ± 0.2

$\dagger\psi$ is the angle shown in Fig. 6 and is calculated on the assumption that the angle DOD is 105° and r_{OD} is 0.98Å.

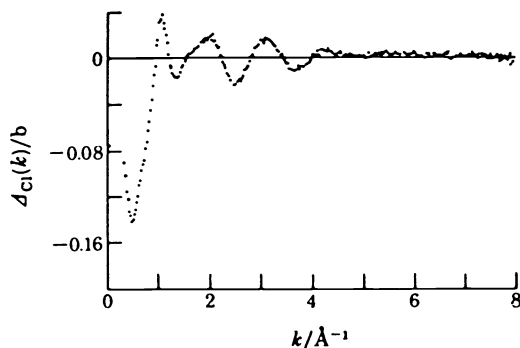


Fig. 5. $\Delta_{Cl}(k)$ for a 4.35 mol/kg solution of $NiCl_2$ in D_2O .

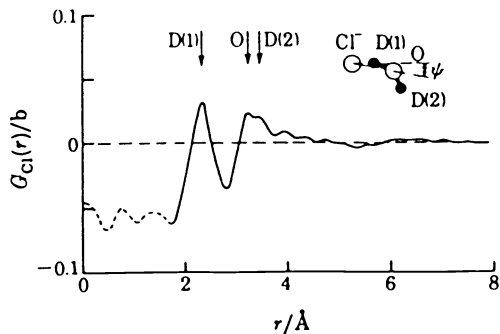


Fig. 6. $\bar{G}_{Cl}(r)$ for a 4.35 mol/kg solution of $NiCl_2$ in D_2O .

The new and surprising characteristics of the chloride-water coordination is its geometrical stability because it is known from both n.m.r. (Ref. 6) and quasi-elastic neutron studies (Ref. 7) that the Cl^- - D_2O lifetime is very short (ca. 5×10^{-12} s); the paradox can be resolved in terms of the specific nature of the Cl^- - D_2O interaction which, in turn, has important consequences for the ion-ion correlation functions (Ref. 3).

OTHER SYSTEMS

The method has been applied to the following ions: Li^+ ($^6\text{Li} \rightarrow ^7\text{Li}$), K^+ ($^{39}\text{K} \rightarrow ^{41}\text{K}$), Ca^{2+} ($^{40}\text{Ca} \rightarrow ^{44}\text{Ca}$), Cu^{2+} ($^{63}\text{Cu} \rightarrow ^{65}\text{Cu}$), Ni^{2+} ($\text{Ni} \rightarrow ^{62}\text{Ni}$), Nd^{3+} ($^{144}\text{Nd} \rightarrow ^{146}\text{Nd}$), Dy^{3+} ($^{162}\text{Dy} \rightarrow ^{164}\text{Dy}$) and to the chloride ion ($^{35}\text{Cl} \rightarrow ^{37}\text{Cl}$) with a variety of counter ions (Refs 8-17). In each case, new results, new insights and new challenges to theory have been made. Some further applications and results of the method will now be summarised.

Chloride hydration

Experiments by Cummings *et al.* (Ref. 15) and by Biggin and Enderby (Ref. 17) have shown that for a wide variety of cations, the geometric arrangement of water around chloride ions is independent of concentration (Table 4).

TABLE 4. Cl^- -water coordination (Refs 15,16,17,18)

Solute	Molality	Cl^- -D(1)/Å	Cl^- -O/Å	Cl^- -D(2)/Å (Range) (Å)	ψ (Range) (deg)	Coordination number
LiCl	3.57	2.25±0.02	3.34±0.04	-	0	5.9±0.2
LiCl	9.95	2.22±0.02	3.29±0.04	3.50-3.68	0	5.3±0.2
LiCl	14.90	2.24±0.03	3.25±0.02	3.56-3.59	0	4.4±0.3
NaCl	5.32	2.26±0.03	3.20±0.05	-	0.10	5.5±0.4
RbCl	4.36	2.26±0.03	3.20±0.05	-	0-10	5.8±0.3
ZnCl ₂	4.90	2.26±0.03	3.35±0.09	-	0-5	3.6±0.4
CaCl ₂	4.49	2.25±0.04	3.25±0.04	3.55-3.65	0-6	5.8±0.2
NiCl ₂	4.35	2.29±0.02	3.20±0.04	3.40-3.50	6-11	5.7±0.2
NiCl ₂	3.00	2.23±0.03	3.25±0.05	-	0-6	5.5±0.4
BaCl ₂	1.10	2.24±0.04	3.26±0.05	-	0-6	6.2±0.4
NdCl ₃	2.85	2.29±0.02	(3.45±0.04) [†]	-	-	3.9±0.2

[†] and refers to an average Cl^- -O/D(2) distance.

For many cations (important exceptions being Zn^{2+} and Nd^{3+}) the Cl^- hydration number remains close to six even though the number of water molecules falls to six per chloride ion. Since the hydration requirements of the cations also have to be satisfied, this result implies extensive water sharing. For dilute solutions, the hydration number of the chloride ion remains saturated at six. Once the number of water molecules per chloride ion falls below six, the hydration number of chloride drops rapidly as the work by Copestake *et al.* (Ref. 16) demonstrates. This implies that at these high concentrations direct interactions between Cl^- and Li^+ exist and have been seen *directly* in $\bar{G}_{\text{Cl}}(r)$ by Ichikawa *et al.* (Ref. 19) and *indirectly* by Copestake *et al.* (Ref. 16).

Nickel hydration

The existence of a substantial tilt angle θ has been referred to already. In a series of experiments, the results of which are shown in Table 5, Neilson and Enderby (Ref. 12) showed that the Ni^{2+} -D distance *increases* as the molality is reduced, implying that θ approaches the dipolar value of zero. This observation still remains puzzling because solution chemists have long argued that a water lone pair orbital should point towards Ni^{2+} so that the other.

TABLE 5. Hydration of Ni^{2+} in solution (Ref. 12)

solute	Molality	Ni^{2+} -oxygen distance/Å	Ni^{2+} -deuterium distance/Å	θ /deg	Coordination number
NiCl_2	0.086	2.07±0.03	2.80±0.03	0±20	6.8±0.8
	0.46	2.10±0.02	2.80±0.02	17±10	6.8±0.8
	0.85	2.09±0.02	2.76±0.02	27±10	6.6±0.5
	1.46	2.07±0.02	2.67±0.02	40±10	5.8±0.3
	3.05	2.07±0.02	2.67±0.02	40±10	5.8±0.2
	4.41	2.07±0.02	2.67±0.02	40±10	5.8±0.2

one is able to accept a hydrogen bond. This would imply that in the limit of infinite dilution θ should tend to $\sim 55^\circ$ and not, as observed in practice tend to dipolar orientation.

Calcium hydration

Although Ca^{2+} is, like Ni^{2+} , doubly charged, this ion displays, in nature, a remarkable ability to adjust its local coordination. In solution this characteristic is also evident in that the coordination number increases from ~ 6 to ~ 10 as the concentration is reduced from 4.5 mol/kg to 1.0 mol/kg (Ref. 10). Whether or not this increase is a characteristic of all weakly hydrating ions remains to be seen. Experiments on K^+ and Li^+ (at molalities less than 3) are being planned to test this.

Dysprosium and neodymium hydration

Narten and co-workers (Refs 13 and 14) have studied these trivalent ions by the first order difference method. The form of $\bar{G}_{\text{Dy}}(r)$ and $\bar{G}_{\text{Nd}}(r)$ closely resembles that for Ni^{2+} shown in Fig. 3, which indicates the strongly hydrating character of these cations. On the other hand, the tilt angle θ is substantially less, being $24 \pm 4^\circ$ for Nd^{3+} and $17 \pm 3^\circ$ for Dy^{3+} compared with $40 \pm 10^\circ$ for Ni^{2+} at a similar ionic strength. This again demonstrates that the lone-pair argument needs to take into account the subtleties introduced by the packing of the hydration spheres and the electronic structure of the cations.

SUMMARY

The method of differences is capable of providing unique and detailed information about the nature of ionic hydration in aqueous solution. There is, of course, no need for the method to be restricted to *aqueous* solutions and active consideration is being given to the possibility of working with *non-aqueous* solvents such as methanol or DMSO. The effects of temperature, pressure and concentration needs to be studied in more detail if a full understanding of ionic hydration in a variety of thermodynamic states is to be achieved. Nevertheless, the future looks to be promising as we are at last able to capitalize on the experimental advances made in recent years.

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