

Interatomic structure of aqueous ionic solutions

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Abstract

A knowledge of the structural properties of aqueous solution helps provide valuable insight into the rich variety of chemical and physical behaviour which such systems exhibit. Besides helping to characterise the interatomic coordination, such information can also be used to test the validity of theoretical model calculations.

INTRODUCTION AND BACKGROUND

In a paper delivered at the 19th Conference in this series on Solution Chemistry [1], it was demonstrated how X-ray and neutron diffraction methods could be used to determine the pairwise structure of aqueous electrolyte solutions. In particular, it was shown that for an aqueous electrolyte solution of the form of a salt MX_n in water (H_2O) these methods give information on the ten pair radial distribution functions $g_{\alpha\beta}(r)$. These ten $g_{\alpha\beta}(r)$'s can be conveniently grouped into three sets which refer to (i) the structure of the solvent - $g_{\text{HH}}(r)$, $g_{\text{OH}}(r)$ and $g_{\text{OO}}(r)$, (ii) the structure of the solute - $g_{\text{MM}}(r)$, $g_{\text{MX}}(r)$ and $g_{\text{XX}}(r)$, and (iii) the solute-solvent structure - $g_{\text{MO}}(r)$, $g_{\text{MH}}(r)$, $g_{\text{XO}}(r)$ and $g_{\text{XH}}(r)$. The difference methods of neutron diffraction and isotopic substitution (NDIS), and X-ray diffraction and isomorphic substitution (XDIS) enables one to probe these three aspects of a solution with varying degrees of quantitative accuracy. It will be recalled that prior to our previous article [1] which was published in 1988, our primary interest was in the characterisation of the aqua ion structure as defined by $G_i(r)$ which to a good approximation is given by a linear sum of $g_{\text{IO}}(r)$ and $g_{\text{IH}}(r)$. (NDIS difference methods were initially applied to salts dissolved in heavy water (D_2O); this served to minimise systematic and statistical errors which arise when water (H_2O) is employed. Because of improvements in instrument design and computer codes, and an increase in neutron fluxes the NDIS methods can be used nowadays on samples which contain H_2O .) A systematic study was made and information obtained from the first order difference NDIS method for about twelve aqua ion species. It was also shown that results from NDIS experiments performed at the second order difference level could be used to determine ion-ion correlations in particularly favourable systems. This work was augmented by XDIS studies on a few specific systems which were susceptible to the isomorphic difference method. The combined picture which emerged was that both X-ray and neutron diffraction could be used to provide quantitative information of interionic structure in aqueous solutions. Application of NDIS methods was limited only by neutron fluxes and samples characterisation and successful work had been carried out on two systems.

During the past five years there have been significant improvements in neutron scattering methodology and computational techniques which have enabled several new initiatives to be undertaken. A wider body of

knowledge has become available and inroads have been made into all three structural aspects of the solution, as well as into systems under extremes of pressure and temperature. A brief overview of how the subject has developed during this period is given below. More detailed accounts of the work referred to can be found in the references.

AQUA ION STRUCTURE

The NDIS first order difference method continues to provide the primary means by which the aqua ion coordination in solution can be determined quantitatively [2]. Results are now available for a wide variety of cations including those belonging to the alkali and alkaline earth series, the first transition metal group, the rare earths, and one or two others such as Ag^+ , ND_4^+ and Zn^{2+} [3]. The hydration structure of Cl^- [4] and the complex NO_3^- anion [5] have also been the subject of recent investigations.

There are characteristic differences in aqua cation structure both within and between the various groups [6]. For example, it would appear that the hydration structure of the singly charged alkalis becomes progressively less well structured in moving from Li^+ to Na^+ to K^+ . The results suggest that a correlation exists between the ionic charge density and the degree of definition of the hydration shell of the ion. A similar behaviour is observed in the case of the doubly charged alkaline earth cations, Mg^{2+} [7], Ca^{2+} [8], Sr^{2+} [9], with the additional observation that the coordination number of Ca^{2+} is concentration dependent [8].

Of wide interest is the hydration of transition metal cations which are present in many systems of biological significance. The Ni^{2+} cation represents a useful probe of cation structure because of its favourable neutron scattering properties. Consequently it has been used in several 'test' experiments: these include studies of (i) preferential hydration, such as is anticipated for strong cations in equimolar mixtures of water and heavy water [10]; (ii) counterion effects which could occur in aqueous solutions of large macro ions and small counterions [11]; (iii) temperature and pressure effects on hydration structure [12,13]; (iv) the effect of glassification on hydration structure [14]; (v) changes in coordination due to a change in dielectric constant [15]. The hydration structure has also been determined for several other TM cations - Cr^{3+} [16], Fe^{2+} [17], Fe^{3+} [18] and Cu^{2+} [19,20]. The results for Cr^{3+} are much as expected for such a stable cation and show a well defined first hydration shell, with strong evidence for a second shell. The two cations of iron, Fe^{2+} and Fe^{3+} , have appreciably different near neighbour Fe-O and Fe-D distances of 2.12(2) Å and 2.75(5) Å, and 2.01(2) Å and 2.68(3) Å respectively. They both, however, possess a 6-fold nearest neighbour coordination and second hydration shell. Results for the cupric ion show clear evidence of a Jahn-Teller distortion with a first hydration shell of 4+2 water molecules [20].

NDIS studies were also undertaken on several rare earth cations, Nd^{3+} , Dy^{3+} and Yb^{3+} [21-23]. As anticipated these strong trivalent ions have well-defined hydration shells. Interestingly, the coordination number changes from 9 for the lighter RE ions (La^{3+} , Nd^{3+}) to 8 for the heavier ones (Yb^{3+} , Lu^{3+}).

The Cl^- anion has been the subject of extensive NDIS studies, the main reason being that its hydration properties offer a sensitive test of model computation. The indications to date are that although theory can give a good representation of Cl^- hydration, there are appreciable discrepancies in quantitative detail, especially as regards coordination number. Even when polarisable water molecules are included in the simulation, differences

between experiment and theory are evident [4,24]. The only other anion which has been studied in detail is the complex nitrate anion NO_3^- . The NDIS method applied to nitrogen atoms shows that the planar nitrate ion has a characteristically weak hydration shell which is consistent with its geometric shape [5,25]. An XDIS experiment on equimolar solutions of sodium nitrate, sodium bromate and sodium chlorate suggests that NO_3^- and BrO_3^- are isomorphous in aqueous solution [26]. The corresponding anion hydration is relatively weak.

A more comprehensive discussion of the aqua ion coordination of all the above species and many more can be found in the various references and also the recent review article by Neilson and Tromp [3].

SOLUTE STRUCTURE

As mentioned in the Introduction, the coordination of ions is accessible from second order differences based on NDIS and XDIS experiments, albeit the latter method provides less accurate information. Within the past few years results from NDIS studies have become available for a few systems including concentrated solutions of nickel nitrate ($g_{\text{NiNi}}(r)$, $g_{\text{NiN}}(r)$) and lithium chloride ($G_{\text{LiLi}}(r)$, $g_{\text{LiCl}}(r)$ and $g_{\text{ClCl}}(r)$). Both sets of results confirm and extend those undertaken previously [5,27]. For nickel salt solutions there is a systematic increase in the nearest neighbour cut-off distance in $g_{\text{NiNi}}(r)$ when progressively larger counter anions are present [5,28]. For the concentrated lithium chloride solution (14 molal) it is observed that although the ion-ion structure is similar to that of the molten salt, the presence of water tends to smear out the 3 $g(r)$'s [5,29].

Within this general area, NDIS experiments have also been undertaken on 'fragile' glasses of 14m LiCl in heavy water and 4m $\text{Ni}(\text{NO}_3)_2$ in heavy water. Although the results have yet to be analysed fully, a preliminary analysis suggests a pronounced increase in the ionic structure in both systems. This is most clearly seen in the NO_3^- hydration, although it is also evident in the enhanced structure of the ion-ion $g(r)$'s in lithium chloride.

A similar NDIS study is being planned on the classical glass forming system $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{ND}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$, which system exhibits a smooth glass transition at $T_G \sim 215$ K. It will be interesting to examine whether structural changes are scale with temperature and density or show a discontinuous change.

The XDIS method has also been employed to study solute structure in a few solutions. Results are now published for the aqueous solutions of isomorphous pairs $\text{Ni}^{2+}/\text{Mg}^{2+}$ in a variety of salt solutions [28], Na^+/Ag^+ in a 4 molar nitrate solution [30], and $\text{NO}_3^-/\text{BrO}_3^-$ in 1 molar sodium salt solutions [26]. In all cases the relevant ion-ion $g(r)$ was calculated. The result for $g_{\text{NiNi}}(r)$ ($=g_{\text{MgMg}}(r)$) in a 4 molal Ni/MgCl_2 solution is in excellent agreement with that derived from NDIS experiments on a similar system. Interestingly, $g_{\text{NaNa}}(r)$ ($=g_{\text{AgAg}}(r)$) has a more structured form than $g_{\text{NiNi}}(r)$ and is similar to $g_{\text{LiLi}}(r)$ obtained from the NDIS study referred to above [5]. The result for the nitrate/bromate pair distribution function $g_{\text{NN}}(r)$ ($=g_{\text{BrBr}}(r)$) shows well defined peaks at 5Å and 11Å and a cut-off distance which is close to the theoretical limit of direct contact between the anions.

The XDIS method also enabled a study of the hydration of Na^+ to be made and it was found that the Na^+ aqua ion structure is intermediate between that of Li^+ , where the hydration is relatively well established [3], and that of K^+ which is seen to be very weakly coordinated to water molecules [3,31].

SOLVENT STRUCTURE

Within the past two years it has become feasible to study in detail the water structure and how it is modified by the presence of ions [32]. The use of water (H_2O)/heavy water (D_2O) mixtures has allowed the calculation of $g_{\text{HH}}(r)$ and a good approximation to $g_{\text{OH}}(r)$ in aqueous electrolyte solutions of lithium chloride. For this system it is found that the hydrogen bond network remains unaffected by amounts of the salt up to 1 molal. However, when 10 molal of salt is present there are significant perturbations to the two pair distribution functions, and the number of hydrogen bonds is reduced to a value of 70% lower than in pure water.

There is no doubt that investigations of solvent structure will continue especially at extremes of temperature and pressure. Indeed, recent studies of pure water to super critical conditions shows that there are appreciable changes in all three $g_{\alpha\beta}(r)$'s [33]. Such information will provide a more critical test of the validity of theoretical model calculations which at the present time are carried out mainly under ambient conditions and give results in good agreement with experiment [34].

CONCLUSIONS AND FUTURE WORK

The broad discussion presented above demonstrates that neutron and X-ray diffraction methods continue to provide an essential means to characterise the inter atomic structure of aqueous solutions. As has been pointed out on several occasions, the NDIS methods are easily generalised to more complex systems, provided the constituents of such materials contain elements with isotopes which have a spread of neutron coherent scattering lengths. The XDIS methods too have a role to play in determining ion-ion and ion-water structure in a few favourable cases where neutron studies could prove expensive and time-consuming.

The future augurs well for NDIS methods. Their feasibility has been demonstrated in many investigations and their potential is beginning to be appreciated in other work. It is anticipated that our own work will continue on a variety of topics. In the shorter term these will include studies of (i) the structure of electrolyte solutions under critical and super critical conditions, (ii) the coordination of poly ions such as DNA, with a view to understanding the nature of counterion condensation and (iii) structural and dynamical changes which occur in the neighbourhood of the glass transition.

In the longer term it is likely that improvements in neutron facilities and sample characterisation will continue to develop and enable more far reaching studies to be undertaken. These might include the use of carbon isotopes which will enable detailed structural determinations of complex organic molecules in mixtures and solutions, and the use of radioactive isotopes such as ^{57}Co , ^{125}I which might enable NDIS methods to be applied to systems presently inaccessible to detailed investigation.

Acknowledgements

The work described above is very much a team effort, and could not have been accomplished without the able support of Drs Howell, Powell, Salmon, Skipper, Tromp and Mr Broadbent and Mr Ansell.

It is important to acknowledge the assistance of Dr John Herdman who made significant contributions to the work described. Sadly, John died in 1990 at the age of 28, well before realising his full potential as a first class research scientist.

An essential aspect of the NDIS studies has been the guidance and advice of neutron beam scientists who include Dr Chieux at ILL, Grenoble, Dr M-C Bellissent-Funel at LLB, Saclay and Dr A K Soper, ISIS, Rutherford Appleton Laboratory. Most importantly, the encouragement, insight and enthusiasm of Professor J E Enderby has been crucial to the successful outcome of the NDIS programme on aqueous solutions. Finally SERC has provided the financial support needed to carry out such a wide ranging programme of research.

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