DIFFRACTION STUDIES OF ION–WATER INTERACTIONS*

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Abstract – Much of our information on ion-water interaction has been
inferred from macroscopic thermodynamic and transport properties of ionic
solutions. It has now become clear that it is both necessary and feasible
to probe these interactions directly at the molecular level. Defining ion-
water interactions as the positional and orientational correlations between
ion-water pairs in solution, we have a measurable quantity (the diffraction
pattern) from which these correlations can be determined.

Ionic solutions were among the first liquids to which x-ray diffraction was
applied, and a large number of studies have been reported over the years.
However, the interpretation of a single diffraction pattern is always dif-
ficult, often ambiguous, and never unique. This ambiguity of interpretation
is greatly reduced if a solution is studied with several types of radiation
(x-ray, neutron, electron), and a few such studies have been reported. The
only currently feasible way of uniquely determining the correlations between
water molecules and monatomic ions in solution is to vary the scattering
factor of the ion; a simple difference measurement then yields the ion-
water correlations. This has been done using the isotopic substitution
method in neutron diffraction. It can also be done using synchrotron x-
radiation and anomalous dispersion techniques.

Diffraction studies of ion-water interactions have yielded detailed and
unambiguous information for only a few concentrated solutions. This situ-
ation may be expected to change dramatically during the next decade.

INTRODUCTION

Enormous effort has been invested in experimental determinations of the properties of water
and aqueous solutions, in attempts to interpret these properties in terms of molecular inter-
actions, and in the development of models with which known properties can be correlated and
unknown properties predicted. Despite the effort, our factual knowledge is meager and our
understanding rudimentary.

Neither the existing theories of the liquid state, nor the available methods of statistical
mechanics have yet provided a useful and tractable description of liquids composed of
molecules between which there are strong non-central, saturable, forces such as exist in
water. Only for relatively simple systems, such as dilute solutions of spherical ions in
water, have these difficulties been overcome. In these cases the "primitive model," which
considers only the interaction of charged hard spheres in a dielectric continuum, has pro-
vided a useful and tractable description of thermodynamic properties. With increasing ion
concentrations the primitive model breaks down because the ion-water interactions can no
longer be neglected. The theoretical and experimental effort has therefore shifted to the
prediction and measurement of ion-water interactions.

Because of their spherical symmetry, alkali and halide ions are especially suitable for
theoretical investigations. Their interaction with water molecules have been studied in
extensive ab initio calculations for small ion-water clusters (Ref. 1). Their behavior in
the Ben-Naim-Stillinger model of liquid water (Ref. 2) has been studied using the molecular
dynamics computer simulation technique (Ref. 3). These investigations have provided a
large body of results which can be compared with results derived from experiments.
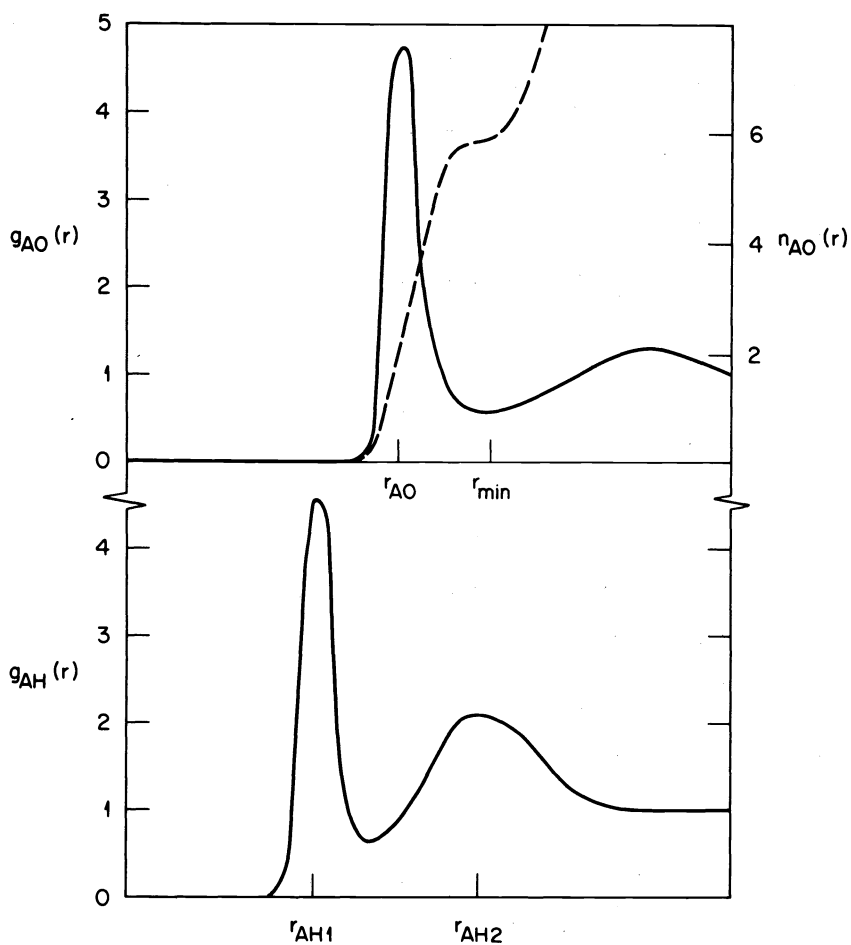
Fig. 1. Hypothetical distribution functions for oxygen atoms, $g_{AO}(r)$, and hydrogen atoms, $g_{AH}(r)$, around an anion A. The broken line gives the number of nearest oxygen atoms around an origin ion as a function of the distance (Eq. 2 of the text).

Experimental investigations may be divided into two classes: (1) measurements of bulk thermodynamic and transport properties which are predominantly determined by ion-water interactions, and (2) measurements which probe these interactions at the molecular level.

Properties falling into class (1) are variation of thermodynamic functions ($\Delta G, \Delta H, \Delta S$), partial molal coefficients (volume, heat capacity, etc.) and intrinsic solute coefficients (diffusion, friction, conductivity, etc.). A traditional approach has been to compare these solvation data with the predictions of models in which the ion is treated as a macroscopic body and the solvent as a medium characterized by macroscopic properties. Deviations of solvation coefficients from these simple model predictions are then attributed to the formation of solvation complexes.

Measurements falling into class (2) are spectroscopy and diffraction. Both of these methods yield results that can be related to probability functions of the locations and velocities of water molecules around an ion in solution. These correlation functions are related by liquid state theory to the intermolecular forces on the one hand, and by statistical mechanics to measurable thermodynamic and transport properties on the other.

CORRELATION FUNCTIONS

A simple example of a time-correlation function is the velocity autocorrelation function

$$<\underset{\sim}{\chi}(0) \cdot \underset{\sim}{\chi}(t)> \tag{1}$$

which is the ensemble average of the scalar product of the velocity $\underset{\sim}{\chi}$ of a given particle at time zero and its velocity at time t. The function (1) is related to a time constant characteristic of the system which can be derived from NMR measurements, and the time integral over (1) is proportional to the diffusion constant.

Among the spatial correlation functions, the atom pair distribution function $g_{\alpha\beta}(r)$ has proved to be most useful. It is defined so that $N_\beta \rho g_{\alpha\beta}(r) d\underset{\sim}{r}$ is the average number of β atoms in a volume element $d\underset{\sim}{r}$ a radial distance r away from an α atom at the origin. Hence, the function $g_{\alpha\beta}(r)$ is a measure of the local particle density in the vicinity of any origin particle in a fluid of bulk particle density ρ and N_β is the number of β atoms per particle. We will discuss ion-water interactions in terms of these atom pair distribution functions which are accessible from diffraction experiments. Such a description is, of course, not complete because it neglects the important dynamic aspects of ion-water interactions. However, a complete description in terms of space-time correlation functions is premature as well as outside the scope of this review.

Ion-water correlations
The spatial correlations between a monatomic ion (I) and its surrounding water molecules can be described by two atom pair distribution functions, namely $g_{IO}(r)$ and $g_{IH}(r)$. The functions $g_{IO}(r)$ and $g_{IH}(r)$ measure the probability density for finding an oxygen atom and a hydrogen atom, respectively, at $\underset{\sim}{r}$ when an ion is at the origin. Hence, the function $g_{IO}(r)$ describes the positional and $g_{IH}(r)$ the orientational correlations between an ion and its surrounding water molecules.

To illustrate this, we show in Fig. 1 two hypothetical distribution functions for oxygen atoms, $g_{AO}(r)$, and hydrogen atoms, $g_{AH}(r)$, around an anion A. The distribution functions must assume zero value near the origin because two atoms cannot occupy the same position at the same time, and they oscillate with rapidly decreasing amplitude around the value $g(r) = 1$ which is descriptive of uniform distributions. The function $g_{AO}(r)$ has a pronounced maximum at r_{AO}, the most probable near neighbor distance, followed by a minimum at r_{min} (Fig. 1). The number of nearest neighbor oxygen atoms around an origin ion is given by the integral

$$n_{AO} = \rho_w \int_0^{r_{min}} 4\pi r^2 g(r) dr \tag{2}$$

with ρ_w the bulk number density of water molecules. The coordination number n_{AO} is well defined only if $g_{AO}(r_{min}) = 0$, indicating a tightly bound, static layer of water molecules in the first coordination sphere of anion. In general, $g_{AO}(r_{min}) > 0$ indicating a loosely bound, dynamic layer of water molecules and no clear distinction between the first and second coordination spheres. In a similar manner, the functions $g_{AH}(r)$ yield information on the location and the number of hydrogen atoms from the water molecules in the first coordination sphere around an ion. The hypothetical curves shown in Fig. 1 (bottom) would indicate

that one hydrogen atom is located at r_{AH1} between the anion and the oxygen atom and the other at r_{AH2}, pointing away from the ion.

The structural information contained in the ion-water distribution functions $g_{IO}(r)$ and $g_{IH}(r)$ can thus be used to construct geometrical models for position and orientation of nearest neighbor water molecules around an ion in a practically unique way. Another important use of these distribution functions is to test ion-water potential functions in computer experiments using the Monte Carlo or molecular dynamics method. With both the force law and the distribution functions known, molecular theories of ion-water interactions can be tested.

DIFFRACTION EXPERIMENTS

We now turn to the experimental determination of ion-water correlations from diffraction experiments. Our discussion will be in general terms, illustrated by typical examples. Precise and comprehensive information is given in the various references.

The atom pair correlation functions $h_{\alpha\beta}(r) \equiv g_{\alpha\beta}(r) - 1$ are related to the experimentally accessible partial structure functions $\hat{h}_{\alpha\beta}(k)$ by a Fourier integral, namely

$$h_{\alpha\beta}(r) = (2\pi^2 r)^{-1} \int_0^\infty k\hat{h}_{\alpha\beta}(k) \sin(kr) dk \; , \tag{3}$$

with $\hbar k$ the magnitude of the momentum transfer in a scattering experiment. For elastic scattering the momentum transfer coordinate k is simply related to the scattering angle 2θ and the wavelength λ of the radiation according to

$$k = (4\pi/\lambda)\sin\theta \; . \tag{4}$$

In conventional x-ray and neutron diffraction experiments a detector is used to count the scattered radiation at a preset angle θ. The measured intensity $I(\theta)$ is related to the coherent cross section σ_c per unit solid angle Ω by the general expression (Ref. 4)

$$I(\theta) = \alpha(\theta)[\partial\Omega_c/\partial\Omega + \sigma(\theta)] \; . \tag{5}$$

The calibration parameters $\alpha(\theta)$ and $\sigma(\theta)$ depend on the scattering geometry; major contributions to $\alpha(\theta)$ are absorption and polarization and the parameter $\sigma(\theta)$ is due largely to incoherent and multiple scattering. For a properly designed diffraction experiment the calibration parameters can be either measured or computed with good accuracy.

The coherent scattering cross section is related to the static coherent scattering function S(k), defined below, by the expression

$$\partial\sigma_c/\partial\Omega = S(k) + D(k) \tag{6}$$

with the momentum transfer coordinate k defined in Eq. 4. The term D(k) describes deviations from the "static approximation," (Ref. 5) which assumes that the scattering particles are rigidly bound, so that all exchange of energy between radiation and sample can be neglected. In a liquid the particles may be considered as "bound" only if their mass M is very large compared to the mass m of the scattered photons or neutrons, and if the energy E_0 of the incident radiation is much larger than the energy transfer in scattering processes. If these conditions are not met, the departure D(k) from the static approximation must be considered, and lead to corrections of order m/M to the cross sections obtained from the scattering experiment. For x-rays ($\lambda \sim 1$ Å, $E_0 \sim 10^4$ eV) the dynamic corrections are negligible. For neutrons ($\lambda \sim 1$ Å, $E_0 \sim 10^{-1}$ eV) the incident energy is comparable to the energy transfer in molecular librations, and the dynamic corrections are significant. They can be calculated with good accuracy for heavy nuclides (Ref. 6). For aqueous systems the presence of hydrogen atoms (H or D) gives rise to correction terms which cannot, at present, be calculated and this has been a major obstacle to the application of neutron diffraction to aqueous solutions.

The scattering function S(k) may be written as the sum of three terms, namely

$$S(k) = S_s(k) + S_m(k) + S_d(k) \; . \tag{7}$$

The "self" term, $S_s(k)$, is due to the interference of two quanta of radiation scattered from the same atom and depends only on the atomic scattering factors. The molecular scattering function, $S_m(k)$, contains only contributions from atom pairs within a molecule (water, poly-atomic ions). The terms $S_s(k)$ and $S_m(k)$ can be calculated from the atomic scattering factors and the intramolecular distances. The distinct scattering function, $S_d(k)$, contains the contributions from atoms in different molecules. The function $S_d(k)$ is a weighted sum of the partial structure functions $\hat{h}_{\alpha\beta}(k)$ defined in Eq. (3), namely

$$S_d(k) = \rho_o \sum_{\alpha=1}^{m} \sum_{\beta=1}^{m} f_\alpha f_\beta \hat{h}_{\alpha\beta}(k) , \tag{8}$$

where a stoichimetric unit containing m atoms is chosen as representative of the liquid which contains n such units and $\rho_o = n/V$ is the bulk number density. The type of radiation used in the scattering experiment enters Eq. (8) through the scattering factors f_α.

Scattering factors

Neutrons are scattered by atomic nuclei, and the neutron scattering factor f^N depends on the isotopic state of the nucleus but not (in the static approximation) on the variable k. There is no large systematic variation of the neutron scattering factors with the atomic number Z, and hence neutrons are an excellent probe for the location of light atoms such as hydrogen.

X-ray scattering arises from electron-photon interactions. Therefore the atomic x-ray scattering factors are proportional to the atomic number Z and depend strongly on the variable k, falling off to very low values at large k. The fall-off in $f^X(k)$, and therefore the low scattered intensity at large values of k, is more than off-set by the much larger intensity of the available x-ray sources. Neutron sources are weak when compared to standard x-ray tubes, and the flux from the best nuclear reactors is only $\sim10^{-7}$ of that in a 1 eV energy band from synchrotron x-rays. The Z-dependence of the x-ray scattering factors makes it impossible in practice to locate hydrogen atoms in aqueous solutions. Water molecules are "seen" by x-rays as spherically symmetric and can be characterized by a single x-ray scattering factor (Ref. 7).

Atomic scattering factors are in general complex, and dispersion occurs in the vicinity of an absorption edge. Unlike neutrons, x-rays have strong resonances with every atom at energies of the electron binding energies. Synchrotron sources emit intense photon fluxes from the visual into the hard x-ray region. This provides for the selection of a particular energy (wavelength) to enhance or decrease the x-ray scattering factor of any element.

DISCUSSION OF RESULTS

Ionic solutions were among the first liquids to which x-ray diffraction was applied, and a large number of studies have been reported over the years. Neutron diffraction has only recently been applied to aqueous solutions (Ref. 8), and electron diffraction studies have not yet been reported. The results published over the past ~30 years have recently been comprehensively reviewed (Ref. 9), and only typical examples will be discussed here.

Single experiments

The interpretation of a single diffraction pattern is always difficult, often ambiguous, and never unique. A common method of analysis is to construct a distinct structure function, namely

$$H_d(k) \equiv M(k) S_d(k) \tag{9}$$

with $S_d(k)$ defined in Eqs. 7 and 8. The factor M(k) is chosen to change the scale to that characteristic of one stoichiometric unit of solution, and a common choice is

$$M(k) = \left[\sum_{\alpha=1}^{m} f_\alpha(k) \right]^{-2} , \tag{9a}$$

with summation over the m atoms in a stoichiometric unit. Fourier inversion of the distinct structure function yields a radial distribution function, namely

$$G_d(r) \equiv 1 + (2\pi^2\rho r)^{-1} \int_0^\infty k H_d(k) \sin(kr) dk , \tag{10}$$

which, from Eqs. 8 and 9, is seen to be a weighted sum of atom pair correlation functions modified by products of atomic scattering factors. This function is mainly of use in identifying the peak locations of the dominant atom pair correlations.

As an example we show in Fig. 2 radial distribution functions for a concentrated hydrochloric acid solution (Ref. 8b). The function $G_d^X(r)$, derived from x-ray diffraction, shows peaks at 2.5 Å due to $H_3O^+\cdots OH_2$ interactions and at 3.1 Å due to $Cl^-\cdots O$ interactions. The peak at 3.6 Å may be ascribed to $Cl^-\cdots Cl^-$ interactions, but this assignment as well as interpretation of the features beyond ~4 Å is quite uncertain. The function $G_d^N(r)$, derived from neutron diffraction, shows peaks at 1.6 Å and 2.1 Å which may be ascribed to $O\cdots D$ and $D\cdots D$ interactions from neighboring D_2O molecules and D_3O^+ ions. The broad features in $G_d^N(r)$ beyond ~3 Å cannot be interpreted at all because they must be the envelope of many $O\cdots D$ and $D\cdots D$ interactions.
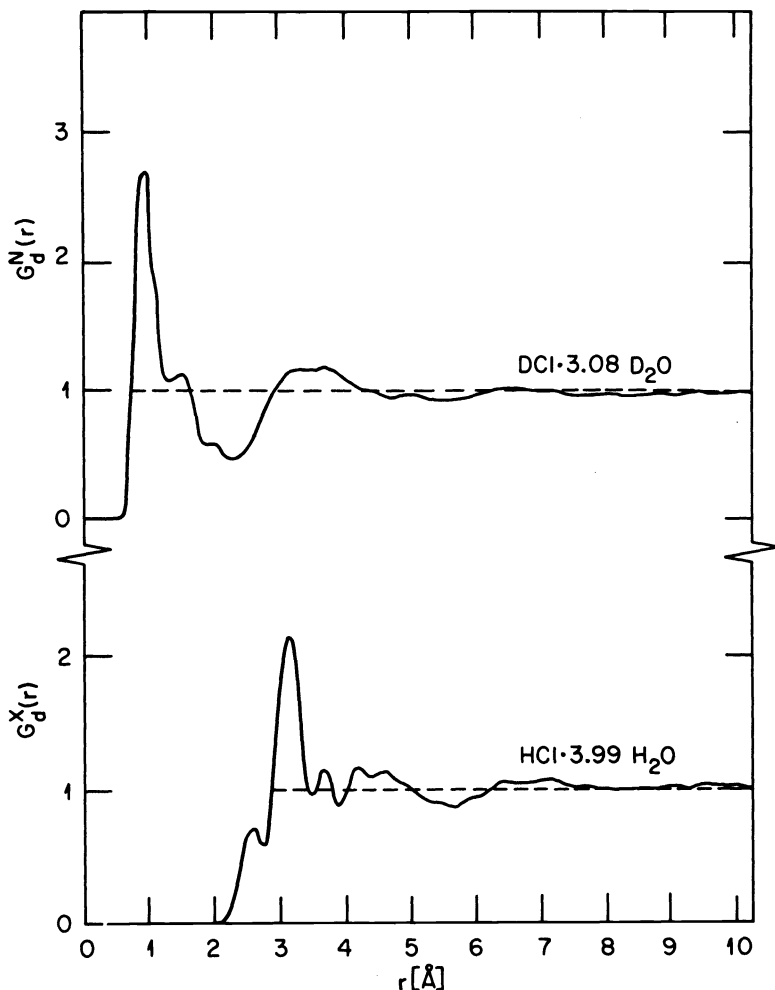

Fig. 2. Distinct radial distribution functions for two concentrated hydrochloric acid solutions. $G_d^X(r)$ and $G_d^N(r)$ are derived from x-ray and neutron diffraction experiments, respectively.

In a more quantitative interpretation of results from a single diffraction experiment the ion-water interactions have often been successfully described in terms of only nearest neighbor interactions. The most frequent distances and coordination numbers are then obtained from a least-squares fit of the structure function computed for the model against the diffraction data. Most of our knowledge about ion-water interactions stems from such an analysis of results from a single diffraction experiment.

Almost all diffraction studies of aqueous solutions have been carried out at molar concentrations M > 1 because, at lower concentrations, the ion-water interactions are very

difficult to "see" with conventional diffraction techniques. There are, however, at least two exceptions:

The first concerns x-ray diffraction from solutions with ions having an atomic number Z (and hence a scattering factor) much larger than that of water. As an example we show in Fig. 3 radial distribution functions for a uranyl chloride solution containing about 1000 water molecules per ion (0.1 mol % U) (Ref. 10). At these low concentrations deviations in the mutual arrangement of water molecules from that found in the pure solvent cannot be detected. Hence, the weighted structure function of pure water can be subtracted from that of the solution. The Fourier transform of the difference curve (Fig. 3, bottom) shows only the peaks characteristic of ion-water and ion-ion interactions.
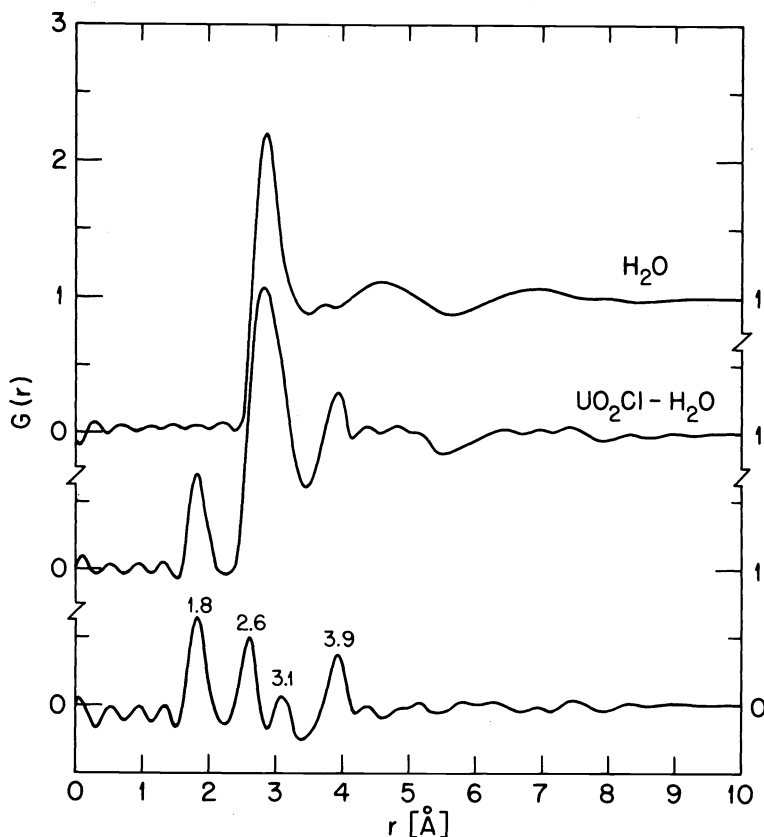

Fig. 3. Correlation functions for pure water (top) and $UO_2Cl_2-N(CH_3)_4OH$ solution in water (center). Also shown is the difference (bottom). The peaks at 1.8 Å, 2.6 Å, 3.1 Å, and 3.9 Å can be ascribed to U···O distance in the UO_2^{2+} ion, to the U···O distances in the complex, to Cl$^-$···O distance, and to U···U interactions in the polynuclear complex, respectively. More details can be found in Ref. 10.

The second, more general, method for probing the environment of an ion in dilute solution is extended absorption fine structure analysis (EXAFS). Here the x-ray absorption coefficient is measured as a function of energy. The fine structure on the high energy side of an absorption edge contains information on the distribution of nearest neighbors around the absorbing ion. The phenomenon is caused by interference of a photoelectron ejected by the absorbing ion with electrons scattered back by the surrounding atoms. The EXAFS method is a very sensitive probe and ion-water interactions have been studied in 0.1 M solutions (Ref. 11).

Difference experiments
The only currently feasible way of uniquely determining the correlations between water molecules and monatomic ions in solution is to vary the scattering factor of the ion. This

has been done using the isotopic substitution method in neutron diffraction (Ref. 9).   It can also be done using synchrotron x-radiation and anomalous dispersion techniques.

Using neutron diffraction, one measures the diffraction patterns from two ionic solutions which are identical in all respects except the isotopic state of one of the ions.   The algebraic difference, Δ, between the two scattering cross sections (6) may then be written as

$$\Delta = \Delta S(k) + \Delta D(k). \tag{11}$$

As mentioned before, our inability to calculate the dynamic corrections, $D(k)$, for neutron scattering from aqueous solutions has been a major obstacle.   The first major advantage of difference experiments is the disappearance of this obstacle.   This is so because the dominant contributions to $D(k)$ are from water molecules and they cancel out.   The remaining corrections $\Delta D(k)$ in (11) are small and can be computed with good accuracy.   Hence, the construction of the function $\Delta S_d(k)$ from (7) is straightforward.   The distinct structure function can now be written as

$$\Delta S_d^N(k) = A\hat{h}_{IO}(k) + B\hat{h}_{ID}(k) + C\hat{h}_{II}(k) \ , \tag{12}$$

with $\hat{h}_{\alpha\beta}(k)$ the partial structure functions for ion-oxygen, ion-deuterium, and ion-ion interactions.   The constants A, B, and C depend on the difference Δf_I between the scattering factors of the isotopes of ion I, the scattering factors of O and D, and on the stoichiometry of the solution.   We note that contributions from atom pairs in different water molecules are absent in (12); the cancellation of terms from water-water interactions, which dominate a single diffraction pattern, is the second major advantage of difference experiments.   The factors A and B in (12) are linear, while C is quadratic in the ion concentration.   This means that, for a wide range of concentrations, the constants A and B are much larger than C and hence $\Delta S_d(k)$ is, for practical purposes, determined by the terms from ion-water interactions.

The neutron difference method has been applied to $NiCl_2$, NaCl, $CaCl_2$, and RbCl solutions in D_2O (Ref. 9).   We show in Fig. 4 the radial distribution function for O and D atoms around a Cl^- ion in a 5.32 molal solution of NaCl in D_2O.   The peak at 2.26 Å must be assigned to
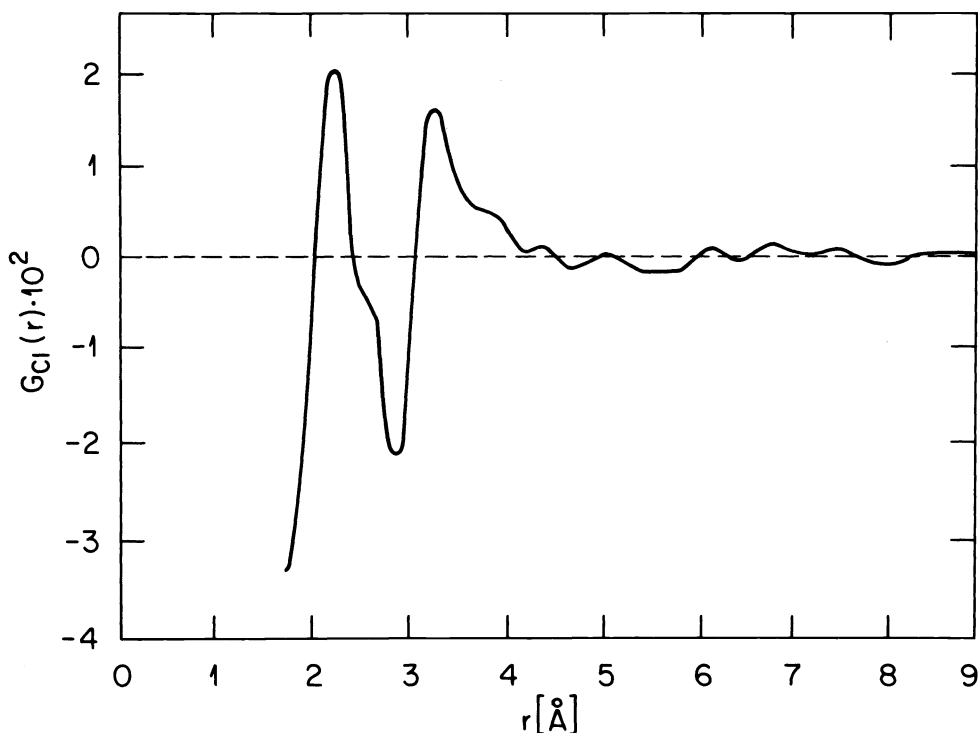

Fig. 4.   Distribution functions for oxygen and deuterium atoms around a
Cl^- ion for a 5.32 M solution of NaCl in D_2O.

Cl⁻···D interactions and the maximum at 3.20 Å arises from Cl⁻···O interactions. The
chloride-water conformation consistent with these results is shown in Fig. 5. A similar
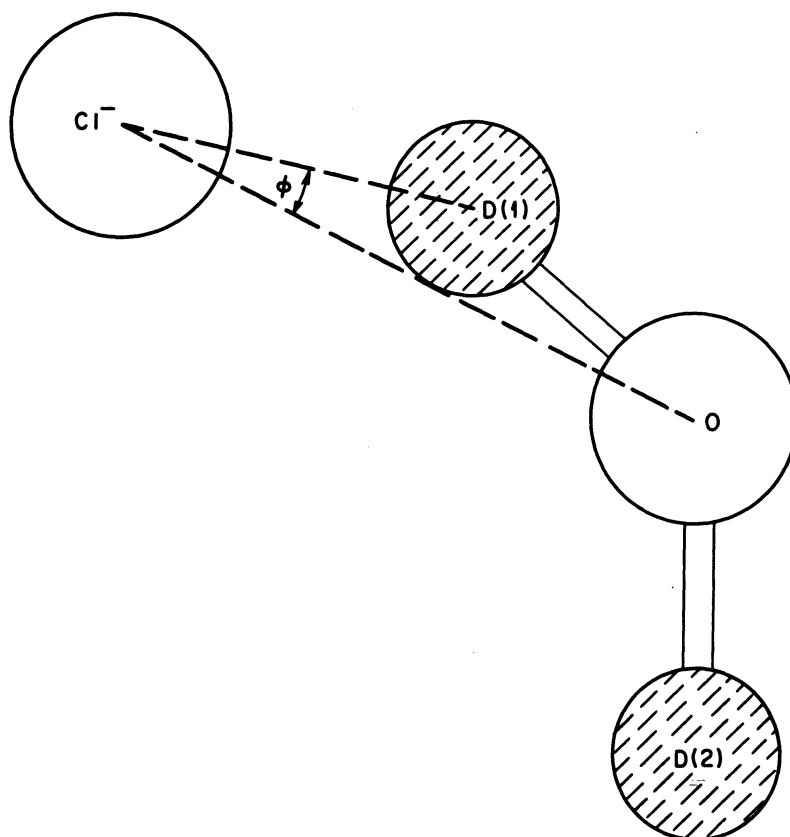conformation was found for the CaCl₂ solution.

Fig. 5. Model of Cl⁻-D₂O interaction consistent with the data shown in Fig. 4.
φ values range from 0° to 10° depending on the value of the O-D distance
chosen.

Difference experiments using x-ray diffraction are feasible only with synchrotron sources
which permit the "tuning" of the incident energy (wavelength) to the absorption edge of the
ion under study. Since water molecules are "seen" by x-rays as single scattering centers,
information about ion-hydrogen interactions cannot be obtained by this method. However, a
difference experiment with x-rays yields directly the function ĥ_{IO}(k) rather than the
weighted sum of the functions ĥ_{IO}(k) and ĥ_{ID}(k) accessible from neutron diffraction.
Furthermore, the enormous intensity available from synchrotron sources permits the study of
ion-water interactions at very low ionic concentrations.

The x-ray difference method is currently being applied to ionic solutions, but results
(other than EXAFS) have not yet been reported.

SUMMARY AND OUTLOOK

A solution of monatomic ions in water is described by ten different atom pair distribution
functions. The neutron diffraction pattern of such a system is dominated by D···D and
D···O interactions from water molecules, and it is extremely difficult to extract informa-
tion on ion-water interactions from a single neutron scattering experiment. The x-ray dif-
fraction pattern of an ionic solution is dominated by O···O interactions from water molecules,
and the interpretation of x-ray results is not quite as hopeless. The ambiguity of inter-
pretation is greatly reduced by studying a solution over wide concentration ranges and with
more than one type of radiation.

The only currently feasible way of uniquely determining the correlations between water
molecules and monatomic ions in solution is to vary the scattering factor of the ion; a
simple difference measurement then yields the ion-water correlations. Difference experi-
ments require a high degree of accuracy and are feasible only with high-flux neutron and

x-ray sources. This fact requires a change in attitude of the experimenter who will have to carry out the measurements in the regional, user-dedicated facilities which are becoming available in increasing numbers.

We emphasize that neutron and x-ray scattering are complementary rather than competing tools for probing ion-water interactions. Neutron difference experiments can only be done if isotopes with sufficiently different scattering factors are available, but the preparation of the labeled solutions is not always trivial. The outstanding advantage of the neutron method is its sensitivity to probe ion-hydrogen interactions. The result of a neutron difference measurement is a weighted sum of distribution functions for ion-hydrogen and ion-oxygen interactions. Such a curve can usually be uniquely interpreted in terms of distances and coordination numbers; unique separation of the two distribution functions $g_{ID}(r)$ and $g_{IO}(r)$ is, however, not possible.

X-ray difference measurements can yield uniquely the ion-oxygen distribution function, $g_{IO}(r)$, but not the ion-hydrogen distribution function, $g_{IH}(r)$. Unlike neutron diffraction, the x-ray method can probe the ion-oxygen correlations for every ion in the periodic table. However, diffraction experiments at x-ray energies below 3 keV are not practical and hence the x-ray difference method is restricted to ions having an atomic number $Z \lesssim 19$ (potassium). We note that this restriction does not apply to the EXAFS method.

For monatomic ions the feasibility of uniquely determining the ion-hydrogen and ion-oxygen distances and coordination numbers has been demonstrated. It seems also practical to uniquely determine the corresponding distribution functions by combining results from x-ray and neutron difference measurements. The situation is not so clear for polyatomic ions. The spatial arrangement of water molecules around the center of a globular ion such as ClO_4^- can be determined by x-ray and neutron difference measurements. Another interesting case concerns relatively large, hydrogen-containing species such as tetraalkylammonium ions. The orientationally averaged correlations between molecular centers dominate the diffraction pattern of such systems at relatively small values of the momentum transfer coordinate $k \gtrsim 3 \, Å^{-1}$. This region of momentum space is well suited for study with low energy ($\sim 5 \times 10^{-3}$ eV) neutrons, and the troublesome dynamic corrections can be computed with good accuracy (for these energy and momentum transfers) even for hydrogen-containing materials. Hence, the isotopic substitution method can be extended to include hydrogen and deuterium. This method of varying the H/D "contrast" between solute and solvent has been extremely successful for the determination of size and shape distributions for biological materials from small-angle neutron scattering (Ref. 12). We believe that it can be extended to study the correlations between hydrogen-containing ions and water molecules.

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