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The structure of ions in solution

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Abstract. Recent experiments aimed at enhancing the understanding of aqueous ionic solutions are summarized, and some possibilities for future studies are outlined.

The past two decades have seen significant progress in our understanding of aqueous ionic solutions [1]. This has been especially the case at the atomic level, where the difference methods of neutron and x-ray scattering [2] on the one hand, and computer simulation techniques [3] on the other, have enabled structural properties to be determined and compared in terms of the pair radial distribution functions.

A body of knowledge derived from experiment now exists concerning aquaion structure for several groups of ions under various conditions of concentration, pH, temperature and pressure. For the cases of the alkali [4] and alkaline earth [5] series of cations there is a clear correlation between the aquaion structure and the ionic charge density. By contrast, the transition metal cations appear to possess their own singular coordination which depends strongly on electronic state: Ni^{2+} and Cr^{3+} for example exhibit stable hydration structures characterized by well-defined ion–oxygen and ion–hydrogen distances [6, 7], whereas Fe^{3+} has a coordination which depends on counterion and pH [8], and Cu^{2+} has a structure reflecting the dynamical Jahn–Teller effect in solution [9]. The lanthanide series of rare earth cations also exhibit well-defined hydration shells, and results for Dy^{3+} and Sm^{3+} confirm predictions based on NMR studies of a change over in coordination number from eight for the heavy lanthanides to nine for the lighter ones [10].

Within the past few years, a series of experiments have been carried out on the following systems

(i) Neutron diffraction experiments were carried out on aqueous solutions of isotopically enriched NiCl_2 in $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures [11]. The difference methods of isotopic substitution were employed to investigate isotope effects in solution. In particular, the local coordination around Ni^{2+} was determined in water, heavy water and a ‘null’ mixture ($\text{H}_2\text{O}_{0.641}/\text{D}_2\text{O}_{0.359}$) of these two solvents. The results showed that contrary to theoretical calculations of Newton and Friedman [12] Ni^{2+} is preferentially deuterated. Investigations of isotopic fractionation will continue and experiments are in progress for solutions containing Cr^{3+} for which a much larger effect is predicted [12].

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(ii) In collaboration with Professor E U Franck (University of Karlsruhe) an apparatus was built for high quality neutron diffraction studies on water and electrolyte solutions at temperatures and pressures in the ranges $25 < T (^{\circ}\text{C}) < 400$, $1 < p$ (bar) < 2000 . Experiments were successfully undertaken on heavy water and a concentrated aqueous solution of NiCl_2 in heavy water [13]. The diffraction data were analysed by standard procedures and the results for heavy water showed that its structure is sensitive to changes in p and T . Although individual correlations are not easily discernible from the total patterns, it is evident that near the critical point long range order occurs. Results for 3 molal NiCl_2 in heavy water show that the $\text{Ni}^{2+}(\text{aq})$ structure is remarkably stable over the range $25 < T (^{\circ}\text{C}) < 150$, $1 < p$ (bar) < 1500 .

(iii) In an attempt to develop an alternative method to the second order difference method of neutron diffraction, x-ray diffraction experiments were carried out on pairs of solutions which had similar structural properties. Comparison of the neutron and x-ray results at the first-order difference level was used to establish isomorphism between cation pairs. Consequently, a second-order difference was calculated from the x-ray diffraction data and the cation-cation partial structure factor $S_{++}(k)$ was calculated. Successful experiments have been carried out on aqueous solutions of the isomorphic pairs $\text{Ni}^{2+}/\text{Mg}^{2+}$ [14] and Na^+/Ag^+ [15]. It is anticipated that this work will continue, and another possible pair ($\text{CrO}_4^{2-}/\text{SO}_4^{2-}$) will, if isomorphism is demonstrated, enable us to make the first determination of $S_{--}(k)$ for a complex anion.

(iv) A study of nickel chloride in methanol (both CD_3OD and CD_3OH) was undertaken and the results obtained at the first- and second-order difference level showed that the Ni^{2+} first coordination shell contains 3.7(3) methanol molecules and 0.8(3) Cl^- ions [16].

(v) A detailed study was also made of Cl^- coordination in aqueous solutions of ZnCl_2 . The results showed that at concentrations greater than 2 molal, direct contacts occur between Cl^- and Zn^{2+} [17]. In collaboration with Dr Bellissent-Funel (CE N Saclay), a complementary investigation based on the first-order difference method was made using Zn isotopes [18], and the results confirmed the conclusion drawn from the study of Cl^- hydration. By comparison, for aqueous solutions of 2 molal zinc triflate there is no evidence for direct contacts between cation and anion. It is proposed that this work will continue, and include a study of Zn^{2+} coordination as a function of counterion, concentration and temperature.

(vi) In collaboration with Dr J C van der Maarel (University of Leiden), a study was undertaken of the coordination of Li^+ in aqueous solutions of lithium hydroxide and polyacrylic acid [19]. The results clearly demonstrate that the small Li^+ counterions remain 'dressed' with their hydration shell and are solvent separated from the polymer chain, a result consistent with that inferred from NMR studies.

(vii) The general nature of the formalism of the isotopic difference method has enabled a study to be made of Ni^{2+} coordination in a heavy water solution adenosine triphosphate (ATP) [20]. The results of a first-order difference study provide the first structural evidence that Ni^{2+} makes direct contact with the triphosphate group of the ATP molecule.

In the short term it is proposed to carry out a few new experiments that are designed to explore aspects of structure in more complex systems. Indeed a study is already well under way of the hydrophobic hydration in solutions of argon under pressure in heavy water at ambient temperature, the point of interest being the degree to which the experimentally determined argon atom coordination agrees with that calculated from

computer simulation [21]. Another study being organized concerns an investigation of possible conformational changes around anions and cations which might take place when an aqueous solution is subjected to supercritical temperatures and pressures [22].

In the longer term, the difference methods of x-ray and neutron diffraction could, because of their universal formalism, be applied to an even wider variety of complex systems under various conditions, where the answer to a specific structural question is sought. Possible candidates for study might include

(i) the structure of polyelectrolyte solutions in the region of the sol-gel transition, where a knowledge of the counter-cation radial distribution function would provide useful information regarding the transition from a uniform structure to one where cross-linkage occurs;

(ii) electrolyte structure in the region of an electrode, perhaps under actual running conditions;

(iii) use of isomorphic replacement techniques for x-ray diffraction on a wider basis, perhaps developing chemical or physical methods to tune the isomorphism of particularly suitable species.

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