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1996 J. Phys.: Condens. Matter 8 9275

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## Structural studies of ionic solutions under critical conditions

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Received 15 July 1996, in final form 6 August 1996

**Abstract.** The methods of neutron diffraction and isotopic substitution (NDIS) provide a direct means to probe the structure of a complex fluid mixture. The method is easily extended to studies under non-ambient conditions for which large sample containers can be used to withstand temperatures of up to 500°C and pressures of 2000 bar. Within the past few years NDIS experiments have been performed on aqueous solutions of several salts at temperatures up to and beyond their critical states. The results show that both the aqua ion and hydrogen bond structure change appreciably with increases in temperature.

### 1. Introduction

During the past five years, the difference methods of neutron diffraction and isotopic substitution (NDIS) have been extended to include studies of water and aqueous electrolyte solutions up to and beyond their critical points [1, 2]. Recall that the critical point for water (H<sub>2</sub>O) is given by  $T_c = 647.07$  K,  $p_c = 220.46$  MPa and  $\rho_c = 322.78$  kg cm<sup>-3</sup> [3]. It is only slightly different from that of heavy water (D<sub>2</sub>O) [4]. However, the critical point of aqueous electrolytes is shifted significantly to higher temperatures with the addition of ions [5].

The main focus of the NDIS experiments has been to monitor changes in ionic complexation and water structure in order to gain insight into the origins of the increased chemical reactivity of supercritical aqueous solutions, which are used in the breakdown of toxic wastes [6]. A second aspect of this work has been to use the results to examine the validity of results derived from computer simulations [7], in which the use of models enables calculations of chemical properties under regimes as yet inaccessible to diffraction experiments.

It will be recalled that the structure of a liquid can be conveniently represented by a hierarchy of distribution functions. Neutron diffraction enables one to determine, by direct Fourier transformation, the pairwise, time-average structure. For an aqueous electrolyte solution (MX<sub>n</sub>, H<sub>2</sub>O) this is represented by the following ten-pair radial distribution functions;  $g_{MM}(r)$ ,  $g_{MX}(r)$  and  $g_{XX}(r)$  for the solute;  $g_{HH}(r)$ ,  $g_{OH}(r)$  and  $g_{OO}(r)$  for the solvent; and  $g_{MO}(r)$ ,  $g_{MH}(r)$ ,  $g_{XO}(r)$  and  $g_{XH}(r)$  for the ionic hydration. The difference methods of isotopic substitution allow these functions to be calculated either in terms of a linear combination or individually [8]. For example, the ionic hydration can be obtained from

$$G_I(r) = Ag_{IO}(r) + Bg_{IH}(r) + Cg_{IJ}(r) + Dg_{II}(r) - E$$

where

$$A = 2c_O c_I b_O (b_I - b'_I) \quad B = 2c_H c_I b_H (b_I - b'_I) \quad C = 2c_I c_J b_J (b_I - b'_I)$$

$$D = c_I^2 [(b_I)^2 - (b'_I)^2] \quad E = -(A + B + C + D).$$

$c_a$  is the atomic concentration of species  $\alpha$ , whose neutron coherent scattering length is  $b_a$ .  $b_I$  and  $b'_I$  represent the two different scattering lengths for the isotopes of the ion I. Analysis of  $G_I(r)$  is used to determine the hydration number  $\bar{n}_I$  and the conformation of the ion with its surrounding water molecules. Except for extremely high ionic concentrations ( $c_I > 0.1$  at.%),  $A, B \gg C, D$  and  $G_I(r)$  is completely dominated by the ion water structure.

The second-order difference method involves two or more substitutions of particular species and allows the determination of the individual correlations. However, it is as yet not possible to determine  $g_{OO}(r)$  to a high degree of precision, because the  $b$  values for the isotopes of oxygen are almost the same. In that which follows, we summarize the results obtained to date on how the interatomic structure of water molecules and ionic hydration changes with temperature and pressure.

## 2. Experimental

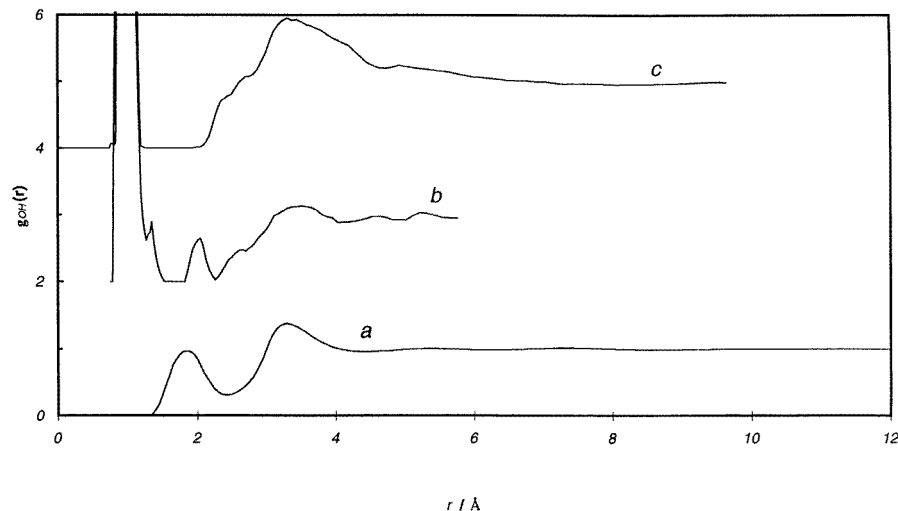
As has been stressed elsewhere [9], the inherent power of neutron scattering methods is due to the fact that the uncharged neutrons can penetrate condensed matter relatively easily and interact predominantly via the strong force with the nuclei of the system. As a result, it is a straightforward matter to perform experiments on solids and liquids under extreme conditions. Moreover, the fact that isotopes of some elements have a negative scattering length means that alloys can be made which show no coherent neutron scattering. The most common of these alloys is titanium zirconium ( $\text{Ti}_{0.68}\text{Zr}_{0.32}$ ) which has the strength of an intermediate steel and is therefore suitable for the construction of pressure 'cells'. An additional advantage of this material is that it is resistant to corrosion.

In the case of a diffractometer sited on a reactor, the pressure containers are usually cylindrical in shape, whereas for pulsed-source instruments a planar geometry is preferred. Both types of container have been used successfully in experiments on water and aqueous solutions at temperatures up to about 500 °C and pressures up to 2000 bar [9]. This is despite the fact that the volume of the samples is less than one tenth of the volume overall.

## 3. Results

### 3.1. Water structure in electrolytes

It is well known that the atomic structure of pure water changes significantly with the application of pressure and temperature [1,10]. Moreover, when ions are present in significant amounts, the hydrogen bonding is appreciably altered [11]. In an effort to understand the contrasting behaviour of the Hofmeister series of ions, Leberman and Soper [12] proposed an interesting correlation between ion type and pressure in the way different ions perturb water structure. Of additional significance is the role of temperature in its effect on hydrogen bonding. Results for a 1 M aqueous solution of sodium chloride demonstrated that an increase in temperature is far more effective in altering the structure than is the presence of ions (figure 1), so it is likely that only relatively high ionic concentrations will affect the water structure significantly [13]. It will clearly be of interest to discover whether



**Figure 1.** The oxygen atom–hydrogen atom pair distribution function,  $g_{OH}(r)$ : (a) water under ambient conditions; (b) 1 M sodium chloride aqueous solution at 300 °C and 120 bar ( $g_{OH}(r)$  displaced by +2 units); and (c) 1 M sodium chloride aqueous solution at 460 °C and 800 bar ( $g_{OH}(r)$  displaced by +4 units).

such kinetic effects can be incorporated within the present framework of computer models in the simulation of the H-bond structure of solutions.

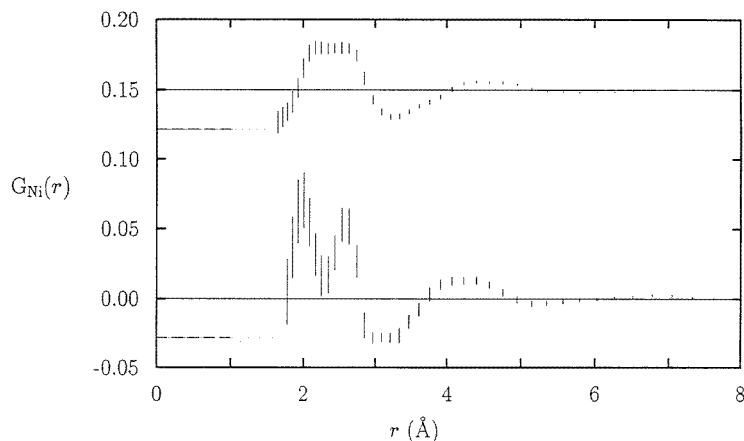
### 3.2. Aqua ion structure

Because nickel and chlorine have isotopes with large differences in  $b$  values, much NDIS work has been targeted at solutions which contain  $\text{Ni}^{2+}$  and  $\text{Cl}^-$  ions [14, 15]. Previous work on concentrated solutions of nickel chloride showed that the  $\text{Ni}^{2+}$  hydration remains intact over a range of temperature  $25^\circ\text{C} \leq T \leq 150^\circ\text{C}$  and at pressures up to 1.5 kbar. Results for  $\text{Cl}^-$  in lithium chloride and nickel chloride show that the  $\text{Cl}^-$  hydration is also relatively insensitive to pressures up to 1 kbar.

During the past few years, NDIS experiments at elevated temperatures and pressures have been performed on three aqueous electrolyte solutions [2, 16, 17]. Two of these studies [2, 16] were concerned with an investigation of changes in  $\text{Ni}^{2+}$  hydration with temperature. It was found that the aqua ion structure of  $\text{Ni}^{2+}$  at 300 °C is appreciably different from that at ambient: in 2 M aqueous nickel chloride at 300 °C there is a significant diminution of the  $\text{Ni}^{2+}$  hydration shell characterized by a broadening of correlation and a reduction in coordination number from 5.9(1) at ambient to 4.5(5) at 300 °C (figure 2). This result tends to confirm results of UV–visible absorption spectroscopy which were used to infer a change in the local coordination of  $\text{Ni}^{2+}$  in aqueous solutions of nickel chloride in lithium chloride [18, 19].

Of additional interest is the effective destruction of the  $\text{Ni}^{2+}$  hydration shell at 300 °C in a 1.2 M aqueous solution of nickel sulphate [2], a result which illustrates the relative ionic strength of the anions  $\text{Cl}^-$  in comparison to  $\text{SO}_4^{2-}$  in their association with  $\text{Ni}^{2+}$  cations.

Studies of  $\text{Cl}^-$  hydration have also been undertaken. In an aqueous solution of 3 M lithium ( $^7\text{Li}$ ) chloride, Yamaguchi *et al* [17] found, in an NDIS study of the chloride ion,



**Figure 2.** The total pair radial distribution function  $G_{Ni}(r)$  for  $Ni^{2+}$  in a 2 M nickel chloride heavy water solution at 100 °C and 1000 bar (lower curve); and at 300 °C and 1000 bar (upper curve displaced by 0.15 barns).

a significant reduction in the  $Cl^-$  hydration number from 5.8(2) under ambient conditions to 2.5(2) at 375 °C and 1690 bar. They also observed a lengthening of the  $Cl \cdots D_{(1)}$  bond from 2.23(2) Å to 2.33(2) Å. Results for a 2 M nickel chloride solution [16] showed broad agreement with these findings: there is a progressive drop in the hydration number of  $Cl^-$  from 6.4(3) at ambient to 4.9(5) at 300 °C and 1000 bar, and a lengthening of the  $Cl \cdots D_{(1)}$  bond from 2.28(3) Å at ambient to 2.39 Å at 300 °C. Differences in detail between these two sets of results could arise either from the contrasting counter-ion effects of  $Li^+$  and  $Ni^{2+}$  or, which is more likely, from experimental resolution; whereas the lithium chloride work was performed on the pulsed source at KEK, Japan, the nickel chloride results were obtained on the 7C2 diffractometer sited on the Orphée reactor at Saclay. Similar discrepancies have been observed in the other data sets, most notably those associated with  $Li^+$  hydration [20, 21].

#### 4. Summary

The above results show that it is now feasible to study the water structure and aqua ion structure of aqueous electrolyte solutions under supercritical conditions. It is also seen that NDIS can be used to determine changes in aqua ion structure as a function of temperature, up to near critical conditions.

In the short term, experiments are already being planned to study the dependence of the hydration of  $Li^+$  and  $Cl^-$  on temperature. Work is continuing on the dependence of water structure on temperature in the presence of ions at low concentration. It will also be of considerable interest to find out how the hydration structure changes for biologically significant cations such as  $Fe^{3+}$ ,  $Fe^{2+}$  and  $Ca^{2+}$ , for which even a modest change in temperature can cause dramatic effects.

In the longer term, it is hoped that, with increases in detector efficiencies and neutron fluxes, results will be obtained on the dependence of ion–ion structure on  $p$  and  $T$ . Such information could be correlated with studies of the dielectric constant and may also be used to assess the usefulness of primitive model calculations based on MSA or HNC theories.

## Acknowledgments

We are particularly grateful to Mr Brian Stockford, whose technical expertise contributed greatly to the success of the programme. We also thank Dr A Soper and Dr M-C Bellissent-Funel for their advice and assistance with the neutron experiments at ISIS and at Saclay. We have also greatly benefitted from discussions with Drs R H Tromp and I Howell. The financial support of the EPSRC of the UK is gratefully acknowledged, as is the award of a fellowship to PdJ under the HCM scheme of the EU.

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