Home   Search   Collections   Journals   About   Contact us   My IOPscience

The solvation of ions

The solvation of ions

J E Enderby

H H Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, UK

Abstract. A review of the application of neutron scattering to the study of ionic solvation is presented. Particular emphasis is placed on the use of isotopic substitution and incoherent quasi-elastic scattering.

1. Introduction

This paper is concerned with the impact that neutron diffraction and quasi-elastic neutron spectroscopy has had on the study of aqueous solutions of strong electrolytes. Consider a liquid formed by dissolving an electrolyte MX_n in H_2O so that the solution contains $M^{n(+)}$ cations, X^- anions and water molecules. In order to describe this system structurally, ten pair correlations are required $(g_{MO}(r), g_{MH}(r) \ldots g_{XX}(r))$ and to generalize the description to include the dynamical aspects of the liquid, ten distinct Van Hove correlation functions $(G_{MO}(r, t), G_{MH}(r, t), \ldots, G_{XX}(r, t))$ and four self-correlation functions $(G_H(r, t), G_O(r, t), G_M(r, t), G_X(r, t))$ have to be invoked. It is this plethora of correlation functions that makes a fundamental description of aqueous solutions so difficult. Diffraction experiments tend to yield a gross average over several correlation functions. However, because of two key properties of neutron scattering, it is possible to isolate individual correlation functions or combinations of them that are of chemical or physical interest. The two properties are (a) the isotope effect whereby the scattering amplitude b depends on the number of neutrons in the nucleus for a given Z and (b) the large incoherent scattering cross-section associated with the protons in (light) water. Both of these features have been exploited by Peter Egelstaff to whom this contribution is dedicated. In order to limit the scope, I shall focus particularly on cationic hydration, although much of what is written applies to anions as well.

2. The method of differences

Soper *et al* (1977) first showed that the neutron 'first-order' difference method yields direct information about the detailed arrangement of the water molecules around the ions in aqueous solutions. It does this by eliminating from $F(k)$, the normalized intensity of scattered neutrons, those contributions *other* than those directly related to cationic 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, has been changed.
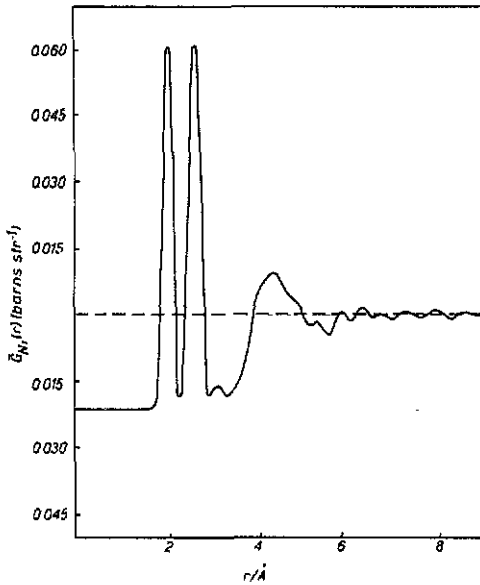
Figure 1. $\bar{G}_{Ni}(r)$ for a 1.46 molal $NiCl_2$ solution in heavy water (Neilson and Enderby 1978).

In terms of the correlation functions $g_{\alpha\beta}(r)$, Soper *et al* showed that the difference in scattered intensity yields the quantity $\bar{G}_M(r)$ where

$$\bar{G}_M(r) = A(g_{MO}(r) - 1) + B(g_{MD}(r) - 1) + C(g_{MX}(r) - 1) + D(g_{MM}(r) - 1).$$

Since A and B are much greater than C and D the method yields a high-resolution measurement of the combination of $g_{MO}(r)$ and $g_{MD}(r)$ thus defining the nature of ionic hydration. The coefficients A, B, C and D are determined by the concentration and the change in scattering length introduced by isotopic substitution.

An example of $\bar{G}_M(r)$ is shown in figure 1, and refers to a 1.46 molal $NiCl_2$ solution in heavy water. The appearance of two distinct peaks corresponding to $\bar{r}_{MO}$ and $\bar{r}_{MD}$ is typical for well-hydrated ions (i.e. those for which the lifetime τ_b of attachment of a water molecule to the ion exceeds $\approx 5 \times 10^{-10}$ s). For the more labile aquaions, the penetration of $g_{MO}(r)$ by $g_{MH}(r)$ often means that the two-peak structure characteristic of Ni^{2+} is not seen. In Ag^+, for example, the two peaks are just resolved, whereas for K^+, only one broad peak centred on ≈ 3 Å is observed.

3. The importance of H/D substitutions

Although knowledge of $\bar{G}_M(r)$ represents a significant advance on what was available prior to 1977, for some applications it is highly desirable to separate $\bar{G}_M(r)$ further into $g_{MO}(r)$ and $g_{MH}(r)$. This can be done by making additional measurements on solutions in both heavy and light water. The technique is difficult because of the large incoherent scattering cross section of protons, but Powell *et al* (1989) have successfully obtained reliable first-order differences for ions dissolved in light water. The comparison of $g_{NiH}(r)$ obtained by this technique with $g_{MgH}(r)$ obtained by computer simulation is shown in
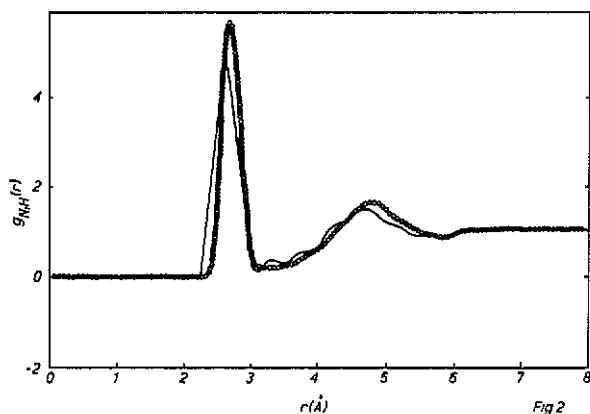
Figure 2. The pair correlation function $g_{NiH}(r)$ (solid line) for a 2 molal $NiCl_2$ solution in water (Powell *et al* 1989) compared with $g_{NiH}(r)$ (dotted line) obtained from MD computer simulation (Dietz *et al* 1982).

figure 2. The comparison is a reasonable one to make since Ni^{2+} and Mg^{2+} are, according to Skipper *et al* (1986), essentially isomorphic so far as their hydration characteristics are concerned. An interesting feature is the agreement between theory and experiment secured around 5 Å. This shows that orientational order in the second shell predicted by simulation is indeed observed, a level of detailed comparison only made possible by the H/D substitution technique.

4. Experimental results

A full review of the experimental data for some 20 cations was given by Neilson and Enderby (1989). Since then, interesting new data for Sr^{2+} (Neilson and Broadbent 1990), Zn^{2+} (Powell *et al* 1990) and Ni^{2+} in methanol (Powell and Neilson 1990) have been published.

5. Proton dynamics

The application of quasi-elastic neutron scattering to the solution problem exploits the high resolution available on the IN10 spectrometer at ILL Grenoble or the IRIS spectrometer at ISIS (RAL). The incoherent cross-section of the hydrogen nucleus is so large that $S(k, \omega)$ is dominated by the self-term $S_H^s(k, \omega)$, the other terms being sufficiently small that they may be neglected in the data analysis. Knowledge of $S(k, \omega)$ thus leads directly to the proton dynamics, which, provided that observation times τ_{ob} are long compared with those characteristic of vibrational and rotational motions, may be identified with that of the water molecule itself. The lower time limit for diffusive behaviour, 10^{-11} s, satisfies this constraint. In addition, the experimental conditions must obey

$$Dk^2\tau_c \ll 1$$

where τ_c is the rotational correlation time for a water molecule and D is the translational

diffusion coefficient. Typically in aqueous solutions $D \simeq 10^{-9}$ m^2 s^{-1} and $\tau_c \sim 10^{-11}$s, so k must be $\ll 1$ Å^{-1}, a severe constraint that can be satisfied in investigations involving the use of high-resolution spectrometers. For a particle obeying the diffusion equation, the self-correlation function $G_H(r, t)$ has a Gaussian form, and $S_H^S(k, \omega)$ is the Lorentzian

$$S_H^S(k, \omega) = (1/\hbar)Dk^2/[(Dk^2)^2 + \omega^2].$$

This behaviour is to be expected for ionic solutions when the τ_b is short relative to τ_{ob}. During this observation time any water molecule is able to sample the entire range of environments present in the solution, a situation is referred to as the 'fast-exchange limit'. When the opposite is the case, the so-called 'slow-exchange limit', and $\tau_b > \tau_{ob}$,

$$S_H^S(k, \omega) = (1/\hbar)\{c_1 D_1 k^2/[(D_1 k^2)^2 + \omega^2] + c_2 D_2 k^2/[(D_2 k^2)^2 + \omega^2]\}.$$

This is a functional form that applies to Ni^{2+} and Mg^{2+} in solutions of their respective chlorides (Hewish *et al* 1983). The key aspect of the Hewish *et al* analysis of the data is that one of the diffusion coefficients (D_1) is equal to that of the cation (D_{ion}), a quantity accessible from independent tracer measurements, and the relative weighting of the two Lorentzians is known from structural measurements. Thus the fitting of a curve to the data involves only D_2 as an adjustable parameter. For well-hydrated ions the values derived for D_2 cannot be equated with D_0, the diffusion coefficient of pure water, and this demonstrates that a simple two-state model ('bound' water and 'free' water) is not adequate. Salmon (1989) and his colleagues have developed these ideas further and have established the way in which the diffusive character of water molecules associated with ions and represented by D_2 varies as the radial separation increases.

References

Dietz W, Reide W O and Heinzinger K 1982 *Z. Naturf.* a **37** 1038
Hewish N A, Enderby J E and Howells W S 1983 *J. Phys. C: Solid State Phys.* **16** 1777
Neilson G W and Broadbent R D 1990 *Chem. Phys. Lett.* **167** 429
Neilson G W and Enderby J E 1978 *J. Phys. C: Solid State Phys.* **11** L625
—— 1989 *Adv. Inorg. Chem.* **34** 195
Powell D H, Gullidge P M N and Neilson G W 1990 *Mol. Phys.* **71** 1107
Powell D H and Neilson G W 1990 *J. Phys. C: Solid State Phys.* **2** 5867
Powell D H, Neilson G W and Enderby J E 1989 *J. Phys. C: Solid State Phys.* **1** 8721
Salmon P S 1989 *Physica* B **156 + 157** 129
Skipper N T, Cummings S, Neilson G W and Enderby J E 1986 *Nature* **321** 52
Soper A K, Neilson G W, Enderby J E and Howe R A 1977 *J. Phys. C: Solid State Phys.* **10** 1793