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LETTER TO THE EDITOR

The hydration of ions in aqueous solution: reverse Monte Carlo analysis of neutron diffraction data

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Abstract. The reverse Monte Carlo (RMC) technique has been used to model 2m NiCl₂ aqueous solution using as input the results of several neutron diffraction experiments where the technique of isotopic substitution has been used. It is shown that RMC provides a valuable means of analysing such data and that information about the hydration shells, for instance the orientations of water molecules within them, can be obtained.

The recently developed reverse Monte Carlo (RMC) method (McGreevy and Pusztai 1988) allows three-dimensional structures to be derived that accurately reproduce experimental diffraction data and thus give greater insight into the details of this structure than is possible with conventional methods of analysing such data. So far this method has been applied to binary liquids (McGreevy 1989, Howe 1989a), to solids showing disorder (Keen *et al* 1989), and to liquids of diatomic molecules (Howe 1989b). I report here the first attempt to apply it to an aqueous solution that differs from the above systems in that the concentration of the ions is rather small.

Over the years there have been many neutron diffraction experiments, using the technique of isotopic substitution, on a variety of different aqueous solutions. A summary of some of these and a description of the method is given by Enderby *et al* (1987). Because both nickel and chlorine possess isotopes with relatively large differences in scattering lengths, NiCl₂ is particularly suitable for study in this way and a number of experiments, at various concentrations, have been reported (Neilson and Enderby 1978, Newsome *et al* 1981, Neilson and Enderby 1982, Cummings *et al* 1980, Powell *et al* 1989, Powell 1989) in which the hydration of the nickel or the chloride ion has been investigated. This is, then, a good system on which to try the new method.

The RMC method for studying the structure of atomic or ionic liquids has been described in detail by McGreevy and Pusztai (1988). To summarise, it uses a standard Metropolis Monte Carlo algorithm (Markov chain, periodic boundary conditions etc) but with the 'sum of squares' difference between the measured total structure factors and those calculated from the RMC configuration, in place of energy calculated from an interaction potential, as the criterion for acceptance or rejection of new configurations. The total structure factors for the configuration are simply the appropriate combinations of the partial structure factors. The partial structure factors are obtained by Fourier

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Table 1. The closest distances (in Å) down to which pairs of atoms of various types were allowed to approach one another.

	Ni	Cl	O	H
Ni	4.0			
Cl	4.0	4.0		
O	1.7	2.7	2.0	
H	2.3	1.9	1.1	1.6

transformation of the pair correlation functions ($g(r)$ s) calculated for the configuration (for which reason it is essential that the configuration is not so small that truncation effects are important in this transformation). An extension of the method to molecular liquids, using a 'semi-rigid' treatment of the molecule, has been described elsewhere (Howe 1989b). It involves dividing the partial structure factors involving correlations between or within molecules (in this case $A_{\text{OH}}(Q)$ and $A_{\text{HH}}(Q)$) into intermolecular and intramolecular parts. The former are calculated from the intermolecular parts of $g(r)$ just as in the case of atomic liquids, while the latter are given the form $(\sin Qd/Qd) \exp(-\gamma^2 Q^2/2)$, where d is the interatomic distance in the molecule and γ its RMS variation. Once the total structure factors for the RMC configuration are found, the 'sum of squares' difference from the experimental data is calculated after subtraction of a constant (a high Q limit) from each data set to maximise agreement (Howe 1989a).

The calculation was started from a configuration consisting of 400 water molecules, 16 Ni^{2+} ions, and 32 Cl^- ions corresponding to a concentration of 2m in heavy water. (Concentrations have generally been given in terms of molality although this is somewhat unfortunate because the same molality corresponds to different concentrations (by mole fraction) in light and heavy water. In what follows '2m' shall mean that concentration that is 2m in heavy water.) This configuration was created by placing the ions and molecules at random positions and orientations and then moving them at random until no pairs of atoms approached one another closer than the distances given in table 1. During the calculation, this restriction on closest distances of approach was maintained. With the exception of those between pairs of ions, these distances are based on the closest distances of approach that have been found in NiCl_2 solution and in water by conventional analysis of neutron scattering data. The restriction on the ion-ion distances was more arbitrary, being simply designed to prevent ions penetrating the hydration shells of other ions. The parameters used in calculating the intramolecular parts of $A_{\text{OH}}(Q)$ and $A_{\text{HH}}(Q)$ were those obtained by Soper and Phillips (1986) for pure water.

Although the usual practice in RMC is to calculate the partial structure factors of this configuration and combine these in the relevant proportions to be compared with the total structure factors obtained in the experiment, in this case the large Placzek effects for the total structure factors make this less appropriate. Instead just one total structure factor was used for this comparison—after it had been corrected for Placzek effects (Powles 1981). Comparison was also made with the functions $S_{\text{NiO}}(Q)$ and $S_{\text{NiH}}(Q)$ obtained from nickel differences for 2m NiCl_2 in heavy and light water (Powell *et al* 1989), the chloride difference function obtained for 2m NiCl_2 solution in light water (Powell 1989), and a chloride difference for NaCl in heavy water (Barnes *et al* 1987). The difference function for NaCl was used because a similar one was not available for NiCl_2 and it has been shown that the hydration of the chloride ion is insensitive to the

Table 2. The coefficients of the various partial structure factors in the difference functions used in the RMC calculation.

Partial structure factor	NiCl ₂ in D ₂ O	S _{NiO}	S _{NiH}	NiCl ₂ in D ₂ O difference	NaCl in H ₂ O difference
A _{NiNi} (Q)	0.000 174	0.008			
A _{NiCl} (Q)	0.000 649	0.123		0.000 399	0.000 23
A _{NiO} (Q)	0.004 91	1.000			
A _{NiH} (Q)	0.011 28		1.000		
A _{ClCl} (Q)	0.000 606			0.000 570	0.000 42
A _{ClO} (Q)	0.009 16			0.006 238	0.005 06
A _{ClH} (Q)	0.021 06			-0.008 043	0.011 65
A _{OO} (Q)	0.034 61				
A _{OH} (Q)	0.159 18				
A _{HH} (Q)	0.183 02				

type of cation. The contributions of the various Faber–Ziman partial structure factors to these functions are listed in table 2.

As the calculation proceeds, the difference between the RMC and the experimental structure factors tends to decrease (although after any individual move it may increase), at first rapidly and then more slowly, until it reaches a point after which continued execution produces no further improvement. The calculation is then deemed to have converged. The results at convergence are shown in figure 1. The agreement of the RMC results with all the difference functions is rather good, especially since they were calculated using so few ions. The agreement with the total structure factor is rather poorer. This suggests that although we have a good representation of the ion–water correlations, the water–water correlations are less well represented. This may simply be due to the size of the RMC configuration: we know from experience that too small a configuration often cannot produce satisfactory agreement with the data and in this case the large size of hydrated ion complexes ($\approx 6\text{--}7 \text{ \AA}$) compared with the box length ($\approx 23 \text{ \AA}$) may accentuate the problem.

Another problem with the water–water correlations is that the scattering lengths of oxygen and deuterium are such that there is a large degree of cancellation of the partial structure factors in the total structure factor obtained by neutron diffraction from heavy water, as is apparent from the pair correlation function, $g(r)$, obtained from it which is nearly featureless. As a result, the total structure factor of heavy water, and of solutions in heavy water, does not contain much information on the relative orientations of the water molecules. RMC on pure water (Howe 1988) using the data of Soper and Phillips (1986) has shown that as a consequence the total structure factor of heavy water can be reproduced well by a structure quite unlike that believed to be the structure of water, and that it is necessary to include data from light water, or at least a mixture of light and heavy water, to remedy this. The difficulty with this is that Placzek effects for light water are even worse than they are for heavy water and the corrections do not seem entirely satisfactory.

The rather smaller differences between the RMC results and the experimental data for the difference functions may be due entirely to the small number of ions in the configuration although it is possible that there may also be small errors in the experimental data. One possibility in particular is that of Placzek effects in the interference

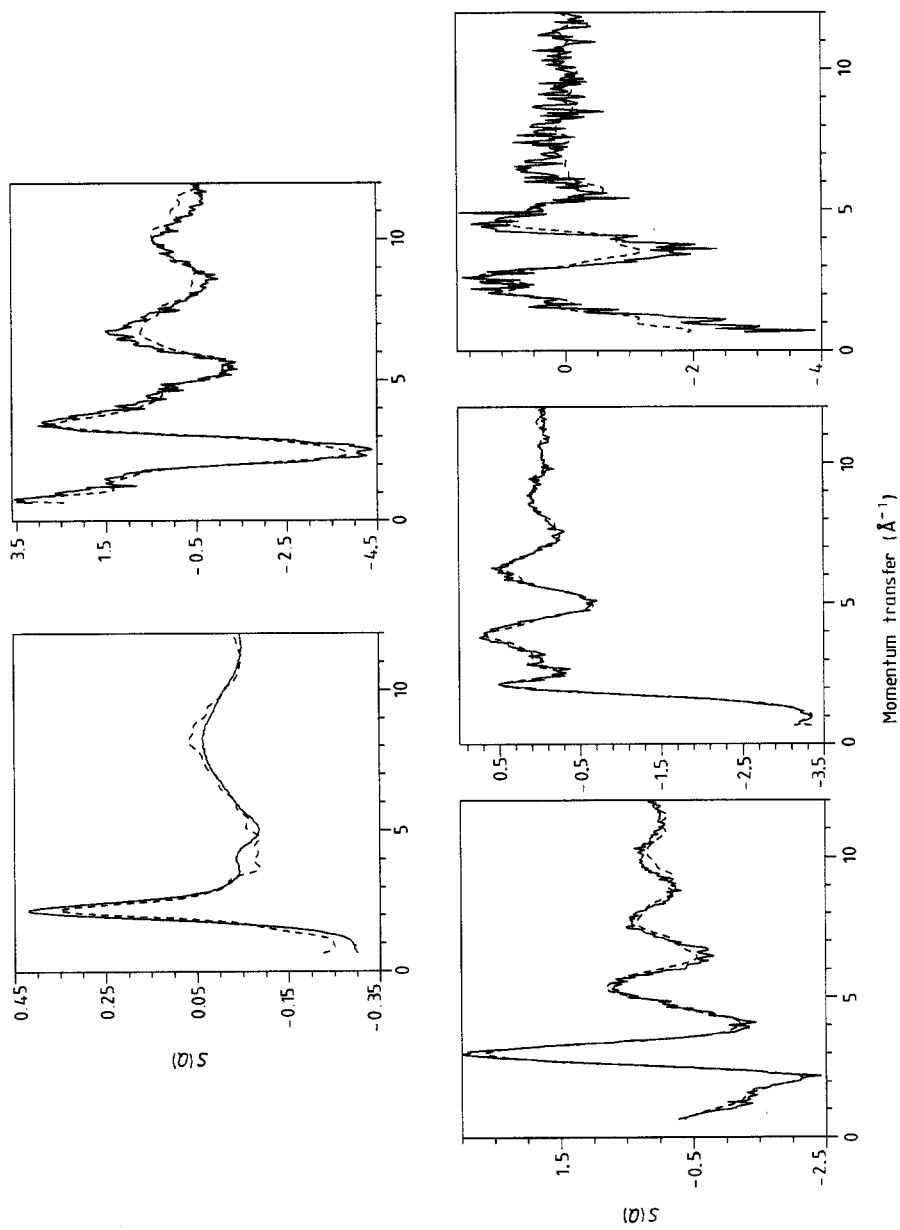


Figure 1. The RMC results (broken traces) compared with the experimental data (full traces) for a total structure factor for NiCl_2 in heavy water (top left), the function S_{NiCl_2} (top right), the function S_{NaCl} (bottom left), the difference function ($\times 100$) for NaCl in heavy water (bottom centre) and the difference function ($\times 100$) for NiCl_2 in light water (bottom right).

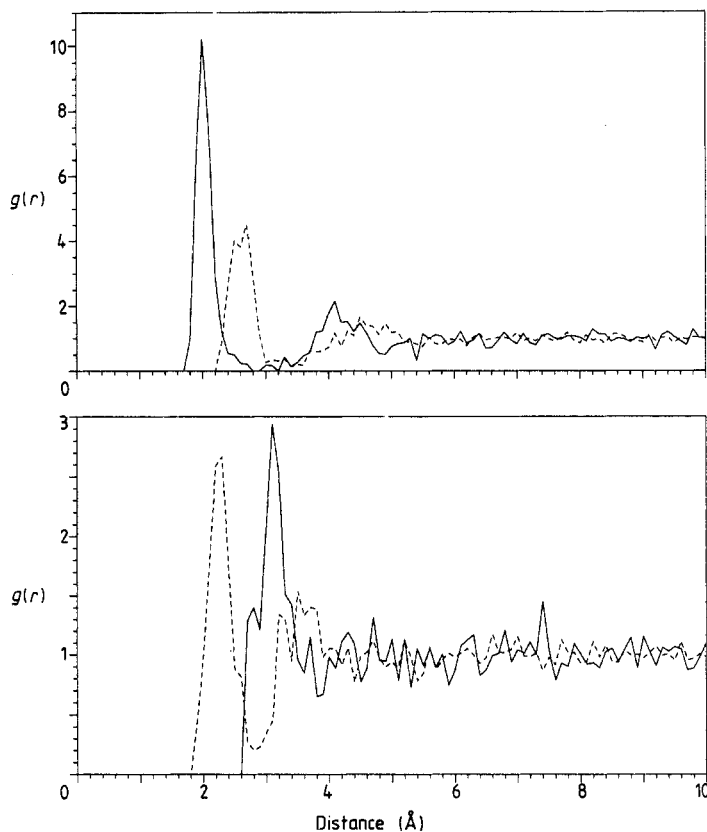


Figure 2. The partial pair correlation functions obtained from the final RMC configuration. Top: $g_{\text{NiO}}(r)$ (full trace) and $g_{\text{NiH}}(r)$ (broken trace). Bottom: $g_{\text{ClO}}(r)$ (full trace) and $g_{\text{ClH}}(r)$ (broken trace).

terms of the scattering, which are usually ignored, but which are expected to be particularly large when hydrogen or deuterium is involved.

Given that RMC is in good agreement with the experimental difference functions (and thus seems to be giving a good description of the ion–water correlations) we can look at these in more detail. The individual partial pair correlation functions $g_{\text{NiO}}(r)$, $g_{\text{NiH}}(r)$, $g_{\text{ClO}}(r)$, and $g_{\text{ClH}}(r)$ calculated from the final configuration are shown in figure 2.

It is interesting to compare these with the results of computer simulation. There have been a number of simulations of aqueous solutions (e.g. Heinzinger 1985, Heinzinger and Pálinkás 1987). Most of these have involved singly charged cations although Bounds (1985) has simulated both the Ni^{2+} and the Cl^- ions in infinitely dilute solution. Since neutron and x-ray diffraction results indicate that the structures of NiCl_2 and MgCl_2 solutions are nearly identical (Skipper *et al* 1986), it is reasonable to also make a comparison with the simulation results of Dietz *et al* (1982) for 1.1 m MgCl_2 aqueous solution. Because so few ions were used in the RMC calculation, the statistics are rather poor but nonetheless it can be seen that the partial pair correlation functions shown in figure 2 agree well with those obtained by Dietz *et al* (1982), the main difference being that the first peaks in $g_{\text{NiO}}(r)$ and $g_{\text{NiH}}(r)$ are a little lower and broader than given by

Table 3. The positions of the first minimum, and the coordination numbers calculated by integrating up to that minimum, for the partial pair correlation functions.

	Position (Å)	Coordination number
$g_{\text{NiO}}(r)$	2.8	5.19
$g_{\text{NiH}}(r)$	3.0	10.9
$f_{\text{ClO}}(r)$	3.8	7.1
$g_{\text{ClH}}(r)$	2.8	5.1

simulation. The results of Bounds (1985), however, are in poorer agreement with the RMC results, particularly in the case of $g_{\text{ClO}}(r)$.

Coordination numbers for the first peaks in the partial $g(r)$ s can be calculated by integrating $r^2g(r)$ up to the first minimum after the peak. The results are given in table 3. The peak in $g_{\text{NiO}}(r)$ is also fairly clearly defined in the $g(r)$ obtained by Fourier transformation of $S_{\text{NiO}}(Q)$ and in that case a coordination number of 5.6 is obtained. This is a little larger than the result obtained from $g_{\text{NiO}}(r)$ resulting from RMC but not very much so. Powell *et al* (1989) have obtained values between 5.5 and 6.0 by fitting Gaussians to their data. The simulations give coordination numbers of 6.0 (Dietz *et al* 1982) and 8.0 (Bounds 1985). Thus again the former simulation is in better agreement with the experiment than the latter. It is also possible to look at the hydration numbers of the individual ions: of the sixteen Ni^{2+} ions, twelve are surrounded by five water molecules, two by six, and one each by four and seven, giving a mean hydration number of 5.19, in agreement with the result obtained by integration of $r^2g_{\text{NiO}}(r)$.

The orientation of the water molecules can be described by the angle θ between the symmetry axis of the molecule and the line joining the oxygen atom and the ion. This has been calculated from molecular dynamics calculations and is one of the few things that is found to depend on the model of the water molecule used for the simulation (Heinzinger 1985). Note that the definition used here is that of Heinzinger and differs from the 'mean angle of tilt' defined for cations by Enderby *et al* (1987) by the sign of $\cos \theta$. The distribution of $\cos \theta$ for water molecules around the Ni^{2+} ion is shown in figure 3. There is a strong tendency for them to be arranged symmetrically with their lone pairs pointing towards the ion ($\cos \theta = -1$). A similar result was obtained in the simulation of Dietz *et al* (1982) although the distribution was somewhat less broad. Simulations using singly charged cations again produce a similar result when a central force model of water (Bopp *et al* 1979), similar to that used by Dietz *et al* (1982), is used but produce a rather different distribution when the ST2 (Stillinger and Rahman 1974) model is used (Heinzinger 1985). This is believed to be because the directionality of the lone-pair orbitals is exaggerated by the negative point charges of the ST2 model. The 'mean angle of tilt' is actually more of an estimate of the mean cosine. The mean value of $\cos \theta$ is found to be -0.73 corresponding to an angle of 43° —in remarkably good agreement with the 42° quoted by Enderby *et al* (1987). However it is not clear whether this angle has any real physical significance.

Finally, there is evidence of ordering in the second hydration shell in that $g_{\text{NiO}}(r)$ peaks at a shorter distance (≈ 4.1 Å) than $g_{\text{NiH}}(r)$. The same thing is observed in the computer simulation of Dietz *et al* (1982).

Turning our attention to the hydrated chloride ion we find that this is less well ordered than the hydrated nickel ion, with the first peaks in $g_{\text{ClO}}(r)$ and $g_{\text{ClH}}(r)$ being less tall and

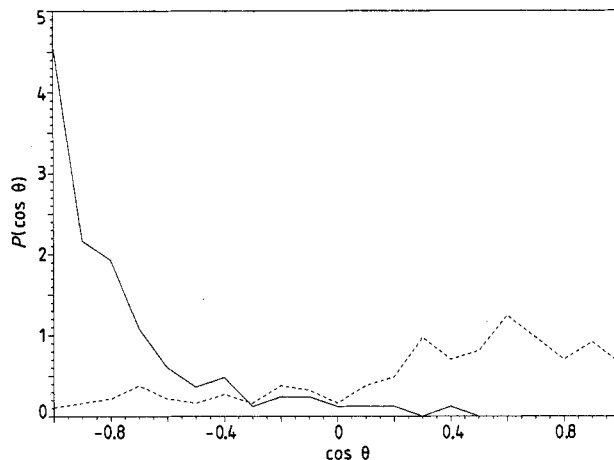


Figure 3. The distribution of $\cos \theta$ (defined in the text) for water molecules surrounding Ni^{2+} ions (full trace) and Cl^- ions (broken trace).

broader than those in $g_{\text{NiO}}(r)$ and $g_{\text{NiH}}(r)$. Following these peaks there are no minima quite so deep, especially in $g_{\text{ClO}}(r)$, meaning that there is no such a clear demarcation of the first hydration shell as there is for Ni^{2+} and that coordination numbers are less unambiguous. The distribution of hydration numbers, defined as the number of oxygen atoms within 3.8 \AA of the Cl^- ion, is two ions with three water molecules, one with five, six with six, eleven with seven, six with eight, four with nine, and two with ten, giving a mean of 7.1 in agreement with the value given in table 3. However, because of the statistical inaccuracies and the ill-defined nature of this minimum we could just as well choose 3.6 \AA as its position and get a distribution of one ion with one water molecule, one with three, three with four, two with five, twelve with six, nine with seven, three with eight, and one with nine, giving a mean of 6.1. There is thus a greater variation in hydration number of the Cl^- ion than there is with the Ni^{2+} ion although it is possible that this is a result of the relatively poor description of the water-water correlations and that improving this might have a constraining effect on the hydration number. However, computer simulation (Pálinkás *et al* 1982) shows that there is much less tendency for water molecules to occupy symmetry sites around Cl^- ions than there is around Ni^{2+} ions so this variation in hydration number could be real. The distribution of $\cos \theta$ for the nearest six water molecules within 3.8 \AA of a Cl^- ion is shown in figure 3 and is broadly of the form obtained by simulation (Dietz *et al* 1982) although it has a more significant tail for negative values. This shows that the RMC configuration has some water molecules in the hydration shell of the anion oriented so that both hydrogens are directed away from the ion, and explains why the coordination number for the first peak in $g_{\text{ClH}}(r)$ is less than that for $g_{\text{ClO}}(r)$. This is also the case, although to a lesser extent, in the simulation.

This work has shown that it is possible to use the RMC technique on systems, such as aqueous solutions, in which we are interested in species that are present only in low concentration. The results show that there is a strong tendency for the water molecules surrounding nickel ions to be oriented with their symmetry axes pointing towards the ion which suggests that the ST2 model of water is not entirely adequate for the simulation of ionic solutions. The mean value of $\cos \theta$ for Ni^{2+} hydration water molecules is in

agreement with the 'mean angle of tilt' of 42° quoted by Enderby *et al* (1987) but this should be interpreted as a measure of the width of the distribution of $\cos \theta$ and certainly not as indicating that water molecules are preferentially oriented at such an angle. There is a greater variation in the orientations and positions of water molecules surrounding chloride ions than of those surrounding nickel ions.

To proceed further with this work it is necessary to increase the size of the configuration used for the RMC calculation. This would entail using more computing power than used for this work (of the order of 100 hours of processor time on a MicroVAX II). It is also desirable to include a total diffraction pattern of a solution in light water, after a satisfactory Placzek correction, to help improve the water-water correlations, without which the three-body water-ion-water correlations describing symmetries of the hydrated ions cannot reliably be obtained. Finally, it should be noted that to get the best results from a reverse Monte Carlo analysis requires data of the highest quality.

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