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## LETTER TO THE EDITOR

# The concentration dependence of the Ni<sup>2+</sup> hydration geometry in aqueous solution

D H Powell†§ and G W Neilson‡

† Institut Laue–Langevin, BP 156X, 38042 Grenoble Cédex, France

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

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**Abstract.** Results are presented of neutron diffraction experiments on a series of solutions of NiCl<sub>2</sub> in D<sub>2</sub>O. Contrary to results from a previous investigation, no change in the Ni<sup>2+</sup> hydration geometry is found in the concentration range 0.1 molal to 2.0 molal. A simple model is introduced in an attempt to deduce information on the distribution of orientations of the hydrated water molecules.

Neutron diffraction with isotopic substitution has proved a powerful probe to examine the structure of aqueous electrolyte solutions (Enderby and Neilson 1981). Solutions of NiCl<sub>2</sub> are highly suited to such experiments, since both nickel and chlorine have isotopes with a large separation of neutron scattering lengths. Much work has thus focused on these solutions, and both ion–solvent and ion–ion correlation functions have been obtained (Powell *et al* 1989, Neilson and Enderby 1983).

One result of the early neutron scattering work on solutions of NiCl<sub>2</sub> in D<sub>2</sub>O was that the mean of the tilt angle,  $\varphi$  (figure 1), was calculated to be around 40° in a 4.41 molal solution and decreased to zero as the concentration was lowered to 0.42 molal (Neilson and Enderby 1978). This result has caused some controversy, and is apparently inconsistent with NMR data (Friedman 1985, Struis *et al* 1987). Given that the original observation is only just outside the quoted errors, it was felt worthwhile to make a systematic concentration study utilising the recently increased experimental accuracy brought about by improvements in neutron instrumentation and sample preparation.

The mean tilt angle,  $\bar{\varphi}$ , has been calculated from the mean distances  $\bar{r}_{\text{NiO}}$ ,  $\bar{r}_{\text{NiH}}$  obtained from neutron diffraction experiments. The meaning of this angle is rather unclear given the observation (Neilson and Enderby 1983) that water molecules in the hydration shell undergo significant ‘wagging’ motions. Bopp *et al* (1979) compare two simulations of NaCl in water, using the ST2 and central force models for water. For the Na<sup>+</sup> hydration shell, these authors found that the probability density,  $P(\cos \varphi)$ , of the tilt angle is centred around  $\cos \varphi = +1$  (i.e. a ‘dipole’ type configuration) for the central force model and around  $\cos \varphi \approx 0.6$  (i.e. a ‘lone-pair’ type configuration) for the ST2

§ Current address: Institut de Chimie Minerale et Analytique, Place du Château 3, 1005 Lausanne, Switzerland.

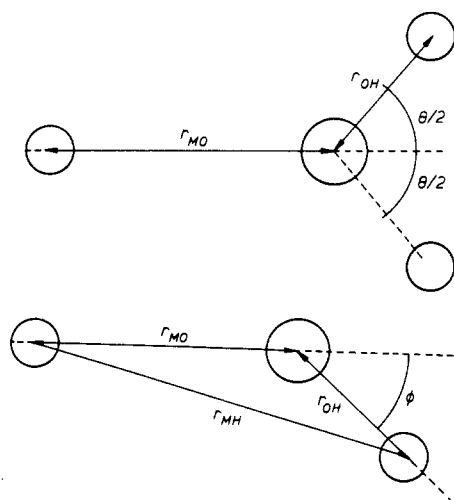


Figure 1. An instantaneous  $\text{Ni}^{2+} \dots \text{H}_2\text{O}$  conformation in two projections.

model. Szasz *et al* (1982) consider the orientational information available from a hypothetical first-order difference experiment using simulated data for  $\text{MgCl}_2$  in water. They conclude that there is no direct way to calculate  $P(\cos \varphi)$  from the diffraction data. To overcome this difficulty, a simple model is presented below which allows one to assess the compatibility of the experimental data with various possible values of  $P(\cos \varphi)$ .

The neutron diffraction experiments were performed on the D20 diffractometer of the ILL, Grenoble, with an incident wavelength of 0.94 Å. For each concentration studied, neutron diffraction patterns were measured for two solutions of  $\text{NiCl}_2$  in  $\text{D}_2\text{O}$  which were identical except for the isotopic composition of the nickel. The experimental intensities were corrected and placed on an absolute scale as described previously (Soper *et al* 1977). From the difference of the two corrected intensities one obtains the first-order difference function

$$\Delta_{\text{Ni}}(k) = A(S_{\text{NiO}}(k) - 1) + B(S_{\text{NiD}}(k) - 1) + C(S_{\text{NiCl}}(k) - 1) + D(S_{\text{NiNi}}(k) - 1) \quad (1)$$

where

$$\begin{aligned} A &= 2c_{\text{Ni}}c_{\text{O}}b_{\text{O}}(b_{\text{Ni}} - b'_{\text{Ni}}) & B &= 2c_{\text{Ni}}c_{\text{D}}b_{\text{D}}(b_{\text{Ni}} - b'_{\text{Ni}}) \\ C &= 2c_{\text{Ni}}c_{\text{Cl}}b_{\text{Cl}}(b_{\text{Ni}} - b'_{\text{Ni}}) & D &= c_{\text{Ni}}^2[b_{\text{Ni}}^2 - (b'_{\text{Ni}})^2] \end{aligned}$$

where  $c_{\alpha}$  and  $b_{\alpha}$  are the atomic fraction and coherent neutron scattering lengths of species  $\alpha$ , and  $b_{\text{Ni}}$  and  $b'_{\text{Ni}}$  are the mean coherent scattering lengths of nickel for the two isotopic compositions employed. The partial structure factors,  $S_{\alpha\beta}(k)$ , are related to the partial pair radial distribution functions,  $g_{\alpha\beta}(r)$ , via the Fourier transform

$$S_{\alpha\beta}(k) = 1 + \frac{4\pi}{k} \rho_0 \int_0^{\infty} (g_{\alpha\beta}(r) - 1) r \sin kr \, dr \quad (2)$$

where  $\rho_0$  is the number density of the solution. The Fourier transform of  $\Delta_{\text{Ni}}(k)$  is thus given by

$$\begin{aligned} G_{\text{Ni}}(r) &= \frac{1}{2\pi^2 \rho_0 r} \int_0^{\infty} dk k \sin kr \Delta_{\text{Ni}}(k) \\ &= A(g_{\text{NiO}}(r) - 1) + B(g_{\text{NiD}}(r) - 1) + C(g_{\text{NiCl}}(r) - 1) + D(g_{\text{NiNi}}(r) - 1). \end{aligned} \quad (3)$$

**Table 1.** The compositions of the samples and the scattering and absorption cross-sections used in the correction procedures (the atomic number density of the solutions was  $0.100 \pm 0.002 \text{ \AA}^{-3}$ ).

Solution	$c_{\text{Ni}}$	$c_{\text{Cl}}$	$c_{\text{O}}$	$c_{\text{D}}$	$c_{\text{H}}^\dagger$	$\sigma_s^\ddagger$ (b/atom)	$\sigma_a^\S$ (b/atom)
2.0 molal <sup>nat</sup> NiCl <sub>2</sub> in D <sub>2</sub> O	0.0128	0.0256	0.3205	0.6395	0.0015	4.66	0.92
2.0 molal <sup>62</sup> NiCl <sub>2</sub> in D <sub>2</sub> O	0.0128	0.0256	0.3205	0.6386	0.0024	4.58	1.04
0.5 molal <sup>58</sup> NiCl <sub>2</sub> in D <sub>2</sub> O	0.0033	0.0066	0.3300	0.6584	0.0016	4.30	0.24
0.5 molal <sup>62</sup> NiCl <sub>2</sub> in D <sub>2</sub> O	0.0033	0.0066	0.3300	0.6574	0.0026	4.28	0.27
0.1 molal <sup>58</sup> NiCl <sub>2</sub> in D <sub>2</sub> O	0.00066	0.00133	0.3327	0.6599	0.0055	4.30	0.05
0.1 molal <sup>62</sup> NiCl <sub>2</sub>	0.00066	0.00133	0.3327	0.6591	0.0063	4.31	0.06

<sup>†</sup> Measured, before and after the experiments, using IR absorption.

<sup>‡</sup> Calculated, using the measured total cross-section for D<sub>2</sub>O at the incident wavelength.

<sup>§</sup> At an incident neutron wavelength of 1.8 Å.

Information on coordination numbers may be obtained from  $G_{\text{Ni}}(r)$  using the relation

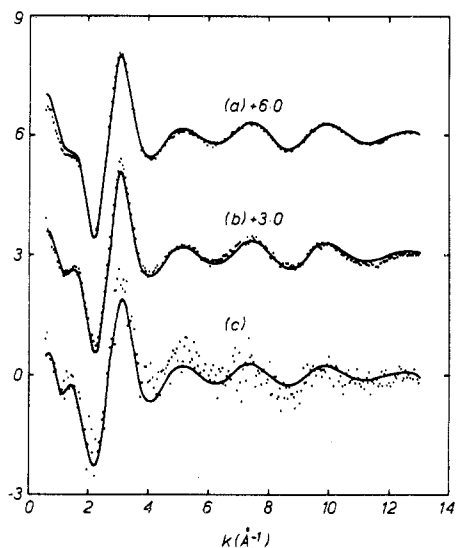
$$\bar{n}_{\text{Ni}}^\alpha = c_\alpha \rho_0 \int_{r_1}^{r_2} 4\pi r^2 g_{\text{Ni}\alpha}(r) dr \quad (4)$$

where  $\bar{n}_{\text{Ni}}^\alpha$  is the mean number of  $\alpha$  particles in a region  $r_1 \leq r \leq r_2$  around a Ni<sup>2+</sup> ion.

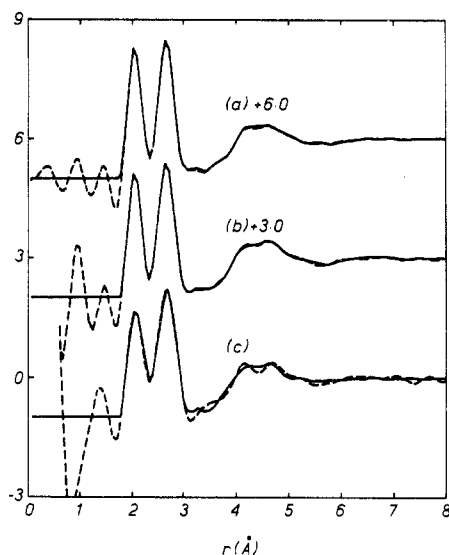
The compositions to the three pairs of solutions, and the parameters relevant to the correction procedures are given in table 1. The first-order difference functions,  $\Delta_{\text{Ni}}(k)$ , scaled to facilitate comparison between the different concentrations, are shown in figure 2. As described previously (Powell *et al* 1989), small corrections have been made for the different light water contents of the samples. The effect of these corrections on the  $r$ -space functions,  $G_{\text{Ni}}(r)$  (figure 3), is marginal. The weighting factors  $A$ ,  $B$ ,  $C$ ,  $D$  are given in table 2. For all three concentrations  $A$ ,  $B \gg C$ ,  $D$  so that the difference functions are dominated by the terms relevant to Ni<sup>2+</sup> hydration.

The first of the well-separated peaks in  $G_{\text{Ni}}(r)$  may be associated with  $g_{\text{NiO}}(r)$ , the second with  $g_{\text{NiD}}(r)$ . The mean interatomic distances and coordination numbers obtained from  $G_{\text{Ni}}(r)$  are given in table 3. It can be seen that there is no shift in either the NiO or the NiD peak, and hence no change in the mean tilt angle,  $\bar{\varphi}$ . The apparent broadening of the peaks for the 0.1 molal solution is probably a result of the increased noise on  $\Delta_{\text{Ni}}(k)$ .

The structural parameters describing Ni<sup>2+</sup> hydration obtained by Neilson and Enderby (1978) are shown in table 4. There is a clear discrepancy with the data presented here. The first-order difference function,  $\Delta_{\text{Ni}}(k)$ , for a 0.42 molal solution of NiCl<sub>2</sub> in D<sub>2</sub>O, from which Neilson and Enderby (1978) obtained their results, is compared in figure 4 with the above data for a 0.5 molal solution. The technological improvements between the two measurements are reflected in the increased statistical accuracy of the new data. The noise and early truncation of the original measurement may disguise significant systematic errors, leading to the erroneous results obtained.



**Figure 2.** Scaled first-order difference functions  $\Delta_{\text{Ni}}(k)/-G_{\text{Ni}}(0)$  for (a) 2 molal, (b) 0.5 molal and (c) 0.1 molal  $\text{NiCl}_2$  in heavy water. The full circles represent data points and the curves through them are spline fits 'back transformed' after setting  $G_{\text{Ni}}(r) = G_{\text{Ni}}(0)$  for  $r < 1.8 \text{ \AA}$ .



**Figure 3.** Scaled radial distribution functions  $G_{\text{Ni}}(r)/-G_{\text{Ni}}(0)$  for (a) 2 molal, (b) 0.5 molal and (c) 0.1 molal  $\text{NiCl}_2$  in heavy water. The broken curves are the Fourier transforms of the data points in figure 2, and the solid curves give, after Fourier transformation, the solid curves in figure 2.

**Table 2.** Weighting factors for the different contributions to the measured difference functions.

Solution	A (mb)	B (mb)	C (mb)	D (mb)
2.0 molal $\text{NiCl}_2$ in $\text{D}_2\text{O}$	8.499	19.431	1.121	0.081
0.5 molal $\text{NiCl}_2$ in $\text{D}_2\text{O}$	2.633	6.002	0.087	0.013
0.1 molal $\text{NiCl}_2$ in $\text{D}_2\text{O}$	0.569	1.270	0.007	0.001

The instantaneous  $\text{Ni}^{2+}$ -water conformation is parametrised as shown in figure 1. The water molecule is considered to be rigid, and the conformation symmetrical as shown in the figure. It is readily shown that

$$\cos \varphi = [T_{\text{NiH}}^2 - (r_{\text{OH}}^2 + r_{\text{NiO}}^2)]/2r_{\text{NiO}}r_{\text{OH}} \cos(\theta/2). \quad (5)$$

The probabilities of the distances  $r_{\text{NiO}}$  and  $r_{\text{NiH}}$  occurring are related to the radial distribution function (using equation (4)) via

$$P(r_{\text{Ni}\alpha} = r) \propto d\bar{n}_{\text{Ni}\alpha}^r/dr \propto r^2 g_{\text{Ni}\alpha}^{(r)}. \quad (6)$$

The only *direct* method of calculating the probability density  $P(\cos \varphi)$  from the radial

**Table 3.** Ni<sup>2+</sup> hydration parameters obtained from the first-order difference data.

Solution	$\bar{r}_{\text{NiO}}$ (Å)	$\bar{r}_{\text{NiD}}$ (Å)	$\bar{n}_{\text{Ni}}^{\text{O}}$	$\bar{n}_{\text{Ni}}^{\text{D}}$
2.0 molal NiCl <sub>2</sub> in D <sub>2</sub> O	2.06(2)†	2.67(2)†	5.9(1)	11.7(2)†
0.5 molal NiCl <sub>2</sub> in D <sub>2</sub> O	2.06(2)	2.68(2)	5.6(2)	11.5(4)
0.1 molal NiCl <sub>2</sub> in D <sub>2</sub> O	2.07(2)	2.69(2)	5.4(2)	12.0(4)

† Errors in NiO and NiD distances were computed from the addition of statistical noise to a hypothetical  $\Delta_{\text{Ni}}(k)$  (Powell 1989).

**Table 4.** Ni<sup>2+</sup> hydration parameters obtained by Neilson and Enderby (1978) for solutions of NiCl<sub>2</sub> in D<sub>2</sub>O.

Concentration of NiCl <sub>2</sub> solution (molal)	$\bar{r}_{\text{NiO}}$ (Å)	$\bar{r}_{\text{NiD}}$ (Å)	$\bar{\varphi}$ (deg)†	$\bar{n}_{\text{Ni}}^{\text{D}_2\text{O}}$
4.41	2.07(2)	2.67(2)	42(8)	5.8(2)
3.05	2.07(2)	2.67(2)	42(8)	5.8(2)
1.46	2.07(2)	2.67(2)	42(8)	5.8(2)
0.85	2.09(2)	2.76(2)	27(10)	6.6(5)
0.42	2.10(2)	2.80(2)	17(10)	6.8(8)
0.086	2.07(2)	2.80(2)	0(20)	6.8(8)

† Assuming  $r_{\text{OD}} = 1.0$  Å and  $\varphi_{\text{OD}} = 105.5^\circ$ .

distribution functions is by making the assumption that  $r_{\text{NiO}}$  and  $r_{\text{NiH}}$  are independent. In this case

$$P(\cos \varphi) = \int_0^\alpha P(r_{\text{NiO}} = r)P(r_{\text{NiH}} = r : \cos \varphi, r_{\text{MO}} = r) dr \quad (7)$$

where  $P(a : b, c)$  is the probability of  $a$ , consistent with  $b$  and  $c$ . Such a calculation was shown to be unrealistic by Szasz *et al* (1982), since it gave a  $P(\cos \varphi)$  inconsistent with that obtained directly from their simulation.

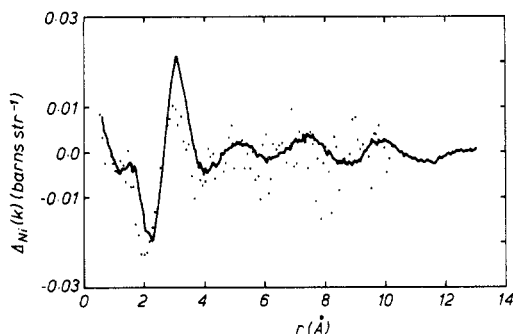
An alternative indirect method can be formulated on the assumption that  $r_{\text{NiO}}$  and  $\varphi$  are independent. For this situation one can write

$$P(r_{\text{NiH}} = r) = \int_0^\infty P(r_{\text{NiO}} = r')P(\cos \varphi : r, r') dr'. \quad (8)$$

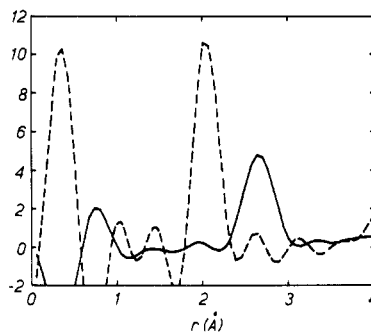
Using relations (5) and (6) one obtains

$$r^2 g_{\text{NiH}}(r) = \int r'^2 g_{\text{NiO}}(r') P\left(\cos \varphi = \frac{r^2 - r'^2 - r_{\text{OH}}^2}{2rr_{\text{OH}} \cos(\theta/2)}\right) dr' \quad (9)$$

where the integral is over the range of the first peak in  $g_{\text{NiO}}(r)$ . From this and a model



**Figure 4.**  $\Delta_{\text{Ni}}(k)$  for a 0.5 molal solution of  $\text{NiCl}_2$  in heavy water (full curve) compared with (points)  $\Delta_{\text{Ni}}(k)$  for the 0.42 molal solution in heavy water obtained by Neilson and Enderby (1978).



**Figure 5.** The experimentally determined pair distribution functions  $g_{\text{NiH}}(r)$  (full curve) and  $'g_{\text{NiO}}(r)' = g_{\text{NiO}}(r) + 0.123g_{\text{NiCl}}(r) + 0.008g_{\text{NiNi}}(r)$  of Powell *et al* (1989).

for the form of  $P(\cos \varphi)$ , it is possible to calculate  $g_{\text{NiH}}(r)$  from  $g_{\text{NiO}}(r)$  and compare it with the experimentally derived function. Two forms of  $P(\cos \varphi)$  are used here:

- (i) an exponential function with a maximum at  $\cos \varphi = 1$

$$P(\cos \varphi) = A \exp[(\cos \varphi - 1)/a] \quad (10)$$

- (ii) a Gaussian centred at  $\cos \varphi = b$

$$P(\cos \varphi) = A \exp[(\cos \varphi - b)^2/a^2]. \quad (11)$$

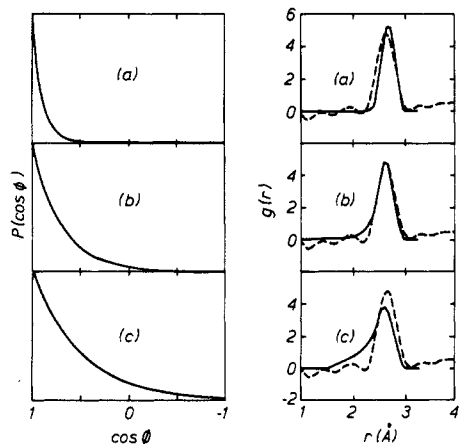
These functional forms are chosen since, with suitable parameters, they give probabilities which approximate well to those obtained from simulations.

Powell *et al* (1989) combined nickel isotope substitution with H/D substitution to obtain  $g_{\text{NiH}}(r)$  and, to a good approximation,  $g_{\text{NiO}}(r)$ , for a 2.0 molal aqueous solution of  $\text{NiCl}_2$ . These functions, shown in figure 5, are employed with the above models. The mean values  $r_{\text{OH}} = 0.98 \text{ \AA}$  and  $\theta = 105.5^\circ$  found by Neilson and Enderby (1983) for a 4.35 molal solution of  $\text{NiCl}_2$  in  $\text{D}_2\text{O}$  are used in the calculations.

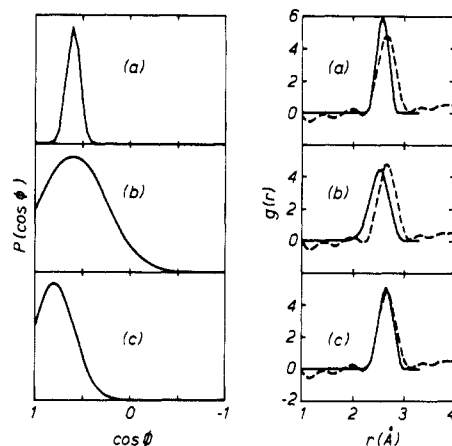
The results of applying (9) with an exponential  $P(\cos \varphi)$  (10) with a varying width parameter  $a$  are shown in figure 6. The calculations do not reproduce the exact shape of the experimentally determined  $g_{\text{NiH}}(r)$ . This is to be expected given the crudity of the model. The internal motions of the water molecule, and all but one type of angular motion in the hydration shell have been ignored. (In a simulation of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  aqueous solutions the asymmetric motions of the hydrated water are shown to contribute significantly to the width of  $g_{\text{FeH}}(r)$ .) The position of the peak maximum in the calculated pair distribution function is strongly dependent on the width parameter,  $a$ , due to the asymmetry of  $P(\cos \varphi)$ . In order to reproduce the experimentally determined position of the peak a rather broad function, compared with that obtained from a simulation of  $\text{MgCl}_2$  in water (Szasz *et al* 1982), is necessary.

The results of applying (9) with a Gaussian  $P(\cos \varphi)$  (11) are shown in figure 7. These show that in order to reproduce the position of the maximum in  $g_{\text{NiH}}(r)$ , the centre of the Gaussian must be shifted from the 'lone-pair' configuration,  $\cos \varphi = 0.6$ .

A more formal path towards a closer understanding of the conformations within the hydration shell is the comparison between the experimental results and those of computer simulation. Two possible approaches exist. The first is to start with sets of



**Figure 6.**  $P(\cos \phi)$  (exponentially decaying model) with three different values for the width parameter,  $a$ , and the pair distribution function  $g_{\text{NiH}}(r)$  calculated from (9): (a)  $a = 0.1$ ; (b)  $a = 0.3$ ; (c)  $a = 0.5$ . The broken curve is the experimental result for  $g_{\text{NiH}}(r)$ .



**Figure 7.**  $P(\cos \phi)$  (Gaussian model) (a) centred at  $\cos \phi = 0.6$ ,  $a = 0.1$ ; (b) centred at  $\cos \phi = 0.6$ ,  $a = 0.5$ ; and (c) centred at  $\cos \phi = 0.8$ ,  $a = 0.3$ ; together with the pair distribution functions  $g_{\text{NiH}}(r)$  (full curves) calculated from (9). The broken curve is the experimentally derived  $g_{\text{NiH}}(r)$ .

potentials (usually pairwise additive) which represent the interactions between the particles, and calculate, either by means of the Monte Carlo method or molecular dynamics, the relevant experimental properties. The results of Szasz *et al* (1982) for solutions of  $\text{MgCl}_2$  in water generally agree well with the neutron diffraction results for concentrated solutions of  $\text{NiCl}_2$  in water (Powell *et al* 1989). However, the separation of the two first peaks in  $G_{\text{Mg}}(r)$  (which relates to the angular distribution) is not in good agreement with that in  $G_{\text{Ni}}(r)$ .

An alternative method to this formal approach is to employ a reverse Monte Carlo procedure. McGreevy and Pusztai (1988) have used this method in order to determine possible angular correlations in liquids. The technique requires no potentials, but ensures that particles cannot coincide. It attempts to reproduce the experimental ( $k$ -space) data from three-dimensional distributions by a statistical algorithm based on a least squares minimisation scheme. Once satisfactory agreement between the experimental result and that generated from the RMC method has been achieved, it is possible to discuss angular correlations in the liquid. Howe (1989) has carried out this procedure for the data presented in this paper, and his results show agreement with  $P(\cos \phi)$  shown in figure 6(b). One major problem with the RMC method is that the information derived from it is not unique except for systems of particles which interact predominantly through pair potentials (Evans 1990).

The orientation of water molecules in the  $\text{Ni}^{2+}$  hydration shell is invariant in solutions of  $\text{NiCl}_2$  in  $\text{D}_2\text{O}$  in the concentration range 0.1 molal to 2.0 molal. The mean value of the tilt-angle,  $\phi$ , of the water molecules, which has been calculated from neutron diffraction experiments, is misleading since its meaning is dependent on the shape of the distribution  $P(\cos \phi)$ . Simple calculations show that the diffraction data are consistent with a rather broad distribution of tilt-angles, which may be centred around the planar ('dipole') configuration.



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