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The solvation structure of Ni²⁺ in methanol

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Received 2 February 1990, in final form 10 April 1990

Abstract. A neutron diffraction study has been carried out on 1 mol kg⁻¹ solutions of nickel chloride in deuterated methanol. Isotopic substitution was applied to the nickel ions and the hydroxyl hydrogen of the methanol. The Ni²⁺ first-order difference radial distribution functions show that the Ni²⁺ . . . methanol conformation is characterised by the mean distances $r_{\text{NiO}} = 2.07(2)$ Å, $r_{\text{NiH(l)}} = 2.62(2)$ Å and $r_{\text{NiC}} = 3.16(2)$ Å (H(l) refers to the hydroxyl hydrogen/deuterium atom).

The pair radial distribution function, $g_{\text{NiH(l)}}(r)$ was calculated, and combined with the first-order difference results to demonstrate that Ni²⁺ is coordinated to 3.7(3) methanol molecules and at least 0.8(3) Cl⁻ ions.

1. Introduction

The macroscopic properties of electrolyte solutions depend strongly on the nature of the solvent (Burgess, 1978). However, it is not clear what determines these properties although, according to Burgess (1978) the dielectric constant ϵ , and the existence of hydrogen bonding are important. To a certain extent, primitive model calculations, where the solution is treated as hard ions in a dielectric continuum, can be used to understand the microscopic origins of solution properties. More sophisticated calculations, however, show that solvent molecular structure and short range solute solvent interactions are also important (Hirata and Levy 1987).

The neutron first-order difference technique has previously been applied to a variety of aqueous electrolyte solutions, and generally gives definitive information on ionic hydration structure (Enderby and Neilson, 1979). It is of interest to see if the method yields useful information on ionic solvation in other solvents. The technique was therefore applied with nickel isotope substitution to solutions of NiCl₂ in methanol.

Nickel chloride was chosen as the electrolyte since, because of the availability of suitable nickel and chlorine isotopes, it has been widely studied in aqueous solution by neutron diffraction (Neilson and Enderby 1983). Methanol was chosen as the solvent because (i) NiCl₂ solutions in methanol can be made sufficiently concentrated for the neutron experiments and (ii) the comparison with aqueous solution is interesting given that water and methanol are both hydrogen bonded liquids, but have significantly

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different dielectric constant ($\epsilon = 32.7$ for methanol compared with $\epsilon = 78.3$ for water, Covington and Dickinson, 1973).

A recent development of neutron diffraction studies of aqueous solutions by Powell *et al* (1989) is the combination of the first order difference with H to D substitution in the water in order to isolate ion-hydrogen correlation functions. The first order difference experiments were, therefore, performed with both CD_3OD and CD_3OH solvent, in order to determine the Ni^{2+} -hydroxyl hydrogen correlation functions, and to facilitate interpretation of the data.

2. Theory

The theory of the neutron first-order difference method, as applied to aqueous solutions, has been adequately described elsewhere (Soper *et al* 1977). Only those relations necessary to understand this article will be introduced here.

From a single neutron diffraction experiment on a multicomponent liquid one obtains, after correction and normalisation, a scattering cross section $I(k)$ ($k = 4\pi/\lambda \sin \theta$ where 2θ is the scattering angle and λ the incident wavelength). In the absence of inelasticity effects this may be written

$$I(k) = F(k) + \sum_{\alpha} c_{\alpha} b_{\alpha}^2 \quad (1)$$

where c_{α} and b_{α}^2 are the atomic fraction and mean square scattering length respectively of species α . The total structure factor, $F(k)$, is a linear combination of partial structure factors

$$F(k) = \sum_{\alpha} \sum_{\beta} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} (S_{\alpha\beta}(k) - 1) \quad (2)$$

where b_{α} is the mean coherent scattering length of species α . The partial structure factor, $S_{\alpha\beta}(k)$, is related to the partial pair radial distribution function by the Fourier transform

$$g_{\alpha\beta}(r) = 1 + \frac{1}{2\pi^2 \rho_n} \int_0^{\alpha} k^2 (S_{\alpha\beta}(k) - 1) \frac{\sin(kr)}{(kr)} dk \quad (3)$$

where ρ_n is the atomic number density of the liquid. The Fourier transform of $F(k)$, denoted $G(r)$, is thus a linear combination of partial pair radial distribution functions

$$G(r) = \sum_{\alpha} \sum_{\beta} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} (g_{\alpha\beta}(r) - 1). \quad (4)$$

For a solution of NiCl_2 there are five atomic species, hence fifteen $g_{\alpha\beta}(r)$. The total radial distribution function, $G(r)$, is thus difficult to interpret in terms of individual pair correlations. In addition, for solutions containing H or D, inelasticity effects cause significant distortion of $I(k)$. This is most evident in a fall-off of the self-scattering terms (the final term in (1)) with k , and makes it difficult to extract $F(k)$ from $I(k)$.

In the first-order difference method, $I(k)$ is measured for two solutions identical except for the isotopic composition of one of the atomic species. Subtraction of the two $I(k)$ values, after correction for the difference in self-scattering terms, yields the much

simpler first-order difference function. For the case of NiCl₂ in methanol, this function is denoted $\Delta_{\text{Ni}}(k)$ and is given by

$$\Delta_{\text{Ni}}(k) = A_{\text{O}}(S_{\text{NiO}}(k) - 1) + A_{\text{D}}(S_{\text{NiD}}(k) - 1) + A_{\text{H}}(S_{\text{NiH}}(k) - 1) \\ + A_{\text{C}}(S_{\text{NiC}}(k) - 1) + A_{\text{Cl}}(S_{\text{NiCl}}(k) - 1) + A_{\text{Ni}}(S_{\text{NiNi}}(k) - 1) \quad (5)$$

where

$$A_{(\alpha \neq \text{Ni})} = 2c_{\text{Ni}}c_{\alpha}b_{\beta}(b_{\text{Ni}} - b'_{\text{Ni}}) \\ A_{\text{Ni}} = c_{\text{Ni}}^2[(b_{\text{Ni}})^2 - (b'_{\text{Ni}})^2]$$

b_{Ni} and b'_{Ni} denote the mean coherent scattering length of nickel in the two solutions. Only those correlation functions relating to nickel remain in the difference function. It has been shown (Soper *et al* 1977) that inelasticity corrections to $\Delta_{\text{Ni}}(k)$ are negligible. The Fourier transform of $\Delta_{\text{Ni}}(k)$ is given by

$$G_{\text{Ni}}(r) = A_{\text{O}}(g_{\text{NiO}}(r) - 1) + A_{\text{D}}(g_{\text{NiD}}(r) - 1) + A_{\text{H}}(g_{\text{NiH}}(r) - 1) \\ + A_{\text{C}}(g_{\text{NiC}}(r) - 1) + A_{\text{Cl}}(g_{\text{NiCl}}(r) - 1) + A_{\text{Ni}}(g_{\text{NiNi}}(r) - 1). \quad (6)$$

It is useful to define a running coordinate number

$$\bar{n}_{\text{Ni}}^{\beta}(r) = 4\pi\rho_{\text{n}}c_{\beta} \int_0^{\infty} g_{\text{Ni}\beta}(r)r^2 dr \quad (7)$$

which is the mean number of β atoms in a sphere of radius r about a Ni²⁺ ion. If the integral is over the range of a well defined first peak in $g_{\text{Ni}\beta}(r)$ then $\bar{n}_{\text{Ni}}^{\beta}$ is the primary coordination number of β about Ni²⁺. Frequently, a peak in $G_{\text{Ni}}(r)$ may be associated with an individual $g_{\text{Ni}\beta}(r)$, and in this case, one can calculate a coordination number from $G_{\text{Ni}}(r)$ using

$$\text{eff} \bar{n}_{\text{Ni}}^{\beta} = \frac{4\pi\rho_{\text{n}}c_{\beta}}{A_{\beta}} \int_{r_1}^{r_2} r^2(G_{\text{Ni}}(r) - G_{\text{Ni}}(0)) dr \quad (8)$$

where the integral is over the range of the relevant peak and

$$G_{\text{Ni}}(0) = - \sum_{\alpha} A_{\alpha} \quad (9)$$

The superscript 'eff' is used to denote 'effective coordination number' since the possibility of multiple contributions to a peak cannot always be excluded. It will be necessary later to consider the possibility of the first peak in $g_{\text{NiO}}(r)$ and that in $g_{\text{NiCl}}(r)$ contributing to a single peak in $G_{\text{Ni}}(r)$. In this case, it is readily shown that $\text{eff} \bar{n}_{\text{Ni}}^{\text{O}}$ is given by

$$\text{eff} \bar{n}_{\text{Ni}}^{\text{O}} = \bar{n}_{\text{Ni}}^{\text{O}} + (b_{\text{Cl}}/b_{\text{O}})\bar{n}_{\text{Ni}}^{\text{Cl}} \quad (10)$$

where $\bar{n}_{\text{Ni}}^{\text{Cl}}$ is the mean number of Cl⁻ ions within a range $r_1 < r < r_2$ around a Ni²⁺ ion.

3. Experimental and data analysis

Solutions of 1 mol kg⁻¹ NiCl₂ in methanol (CD₃OD and CD₃OH) were prepared by direct dissolution of the isotopically enriched salts ⁵⁸NiCl₂ and ⁶²NiCl₂, each of which had been dehydrated from aqueous solutions by refluxing with thionyl chloride. Neutron

Table 1. Atomic fractions and cross sections for solutions.

| Solution (1 mol kg ⁻¹) | Atomic fractions | | | | | | Cross sections | | |
|---|------------------|-----------------|----------------|----------------|----------------|----------------|--|--|--|
| | c _N | c _{Cl} | c _O | c _D | c _H | c _C | σ _b [†] (barns) | σ _f [‡] (barns) | σ _a [§] (barns) |
| ⁵⁸ NiCl ₂ in CD ₃ OD | 0.0059 | 0.0118 | 0.1637 | 0.6549 | — | 0.1637 | 6.95 | 3.94 | 0.43 |
| ⁶² NiCl ₂ in CD ₃ OD | 0.0059 | 0.0118 | 0.1637 | 0.6549 | — | 0.1637 | 6.86 | 3.86 | 0.48 |
| ⁵⁸ NiCl ₂ in CD ₃ OH | 0.0057 | 0.0115 | 0.1638 | 0.4914 | 0.1638 | 0.1638 | 19.07 | 6.74 | 0.47 |
| ⁶² NiCl ₂ in CD ₃ OH | 0.0057 | 0.0115 | 0.1638 | 0.4914 | 0.1638 | 0.1638 | 18.98 | 6.62 | 0.52 |

† Calculated using the bound scattering cross-section for methanol.

‡ Calculated using the free atom scattering cross-section for methanol.

§ Atomic cross section (=1.8 Å).

diffraction experiments for the NiCl₂ · CD₃OD solutions were carried out on the D4B diffractometer ($\lambda = 0.705 \text{ \AA}$) of the Institut Laue Langevin (ILL), Grenoble. The samples were contained in a titanium-zirconium Ti_{0.676}Zr_{0.324} 'null' alloy container (i.d. = 11 mm, o.d. = 12.5 mm). The neutron diffraction experiments on the NiCl₂ · CD₃OH solutions were carried out on the D20 diffractometer ($\lambda = 0.940 \text{ \AA}$) also at the ILL. Because of the presence of hydrogen, which has a large incoherent scattering cross section, these samples were contained in a smaller titanium zirconium 'null alloy' container (i.d. = 5 mm, o.d. = 6.5 mm). The relevant physical properties of the solutions and the neutron scattering cross sections used in the data analysis are given in table 1. The number density of all solutions studied was 0.091 \AA^{-3} .

A major initial problem with the analysis of data from non-aqueous solutions is that unlike the case of water (H₂O) and heavy water (D₂O) the neutrons cross sections are not known for other solvents. Instead they must be estimated from a calculation which employs the bound atom or free atom scattering cross sections (Sears 1984) of the atoms which comprise the solvent molecule. (It is possible to measure the true cross sections in a transmission experiment. However, this is not practicable on D4B or D20 at the present time.)

In order to establish whether the use of bound or free cross section is more appropriate, initial studies were made on the total scattering patterns. The diffraction data were corrected for absorption (Paalman and Pings, 1962) and multiple scattering (Blech and Averbach, 1965) using the two different sets of neutron scattering parameters given in table 1. Both sets of results were normalised to give $I(k)$ values in b sr^{-1} by reference to a vanadium standard rod (Enderby and Neilson, 1979). At this stage (see figure 1) no inelasticity (Plaszek) corrections had been introduced and consequently the reduced cross sections $I(k)$ exhibited a characteristic droop due to the presence of hydrogen and deuterium in the samples. The total structure factors $F(k)$ were extracted empirically from the $I(k)$'s as follows: for the CD₃OH solution

$$F(k) = I(k) + ak - b$$

and in the case of the CD₃OD solution

$$F(k) = I(k) + ck^2 - d$$

where a, b, c, d are empirical constants which force the results to conform to the correct limits (Enderby and Neilson, 1979). These $F(k)$ values are shown in figure 2.

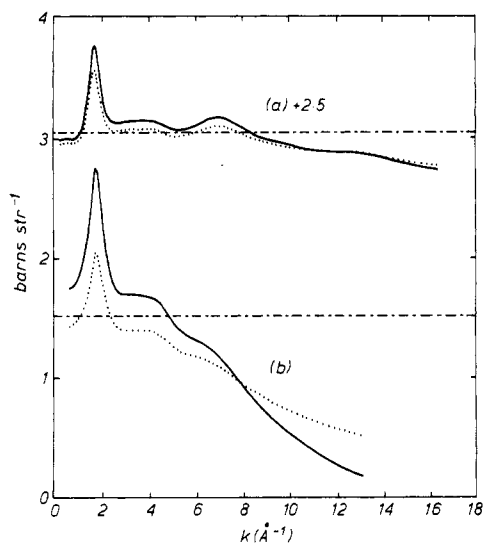


Figure 1. Total corrected scattering cross sections $I(k)$: (a) 1 mol kg^{-1} $^{58}\text{NiCl}_2$ in CD_3OD ; (b) 1 mol kg^{-1} $^{58}\text{NiCl}_2$ in CD_3OH . Bound cross sections were used in the derivation of full curves, and free cross sections were used in the derivation of dotted curves.

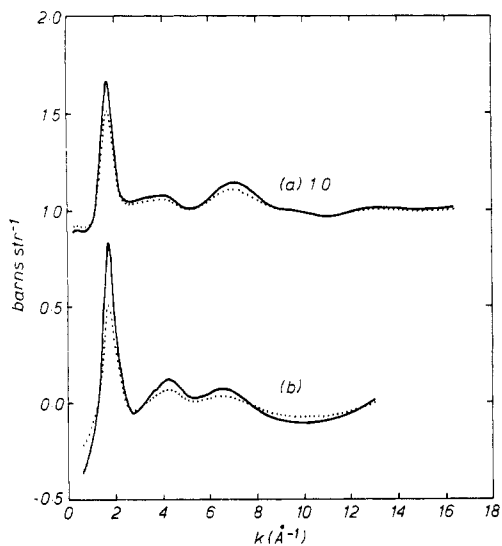


Figure 2. Structure factors $F(k)$: (a) 1 mol kg^{-1} $^{58}\text{NiCl}_2$ in CD_3OD ; (b) 1 mol kg^{-1} $^{58}\text{NiCl}_2$ in CD_3OH . See caption to figure 1 for details of full and dotted curves.

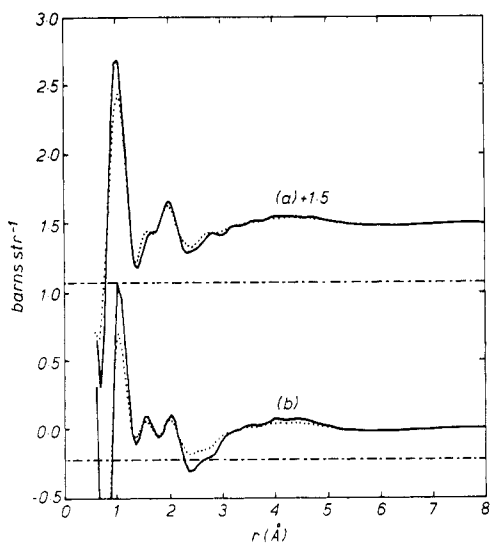


Figure 3. Total distribution functions $G(r)$ calculated from $F(k)$ values in figure 2. (a) 1 mol kg^{-1} $^{58}\text{NiCl}_2$ in CD_3OD ; (b) 1 mol kg^{-1} $^{58}\text{NiCl}_2$ in CD_3OH . See caption to figure 1 for distinction between full and dotted curves.

The total radial distribution functions $G(r)$ of the solution obtained by Fourier transformation of $F(k)$ are shown in figure 3. If one assumes that the peak at 1.04 \AA in $G(r)$ is a combination of the O–H1 and C–H2 intramolecular correlations (figure 4), one can calculate the value of the integral

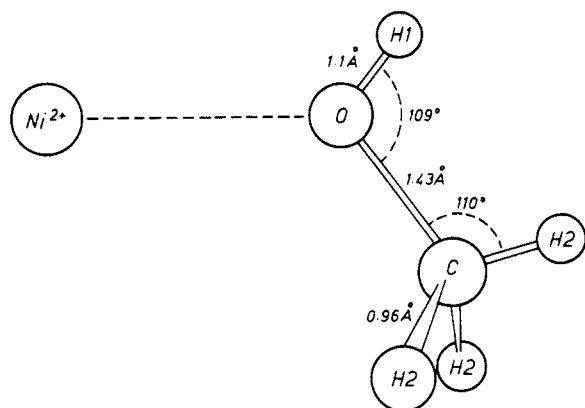


Figure 4. Sketch of the Ni^{2+} . . . methanol molecular conformation.

Table 2. Value of integral I (11) over the first peak in $G(r)$ (see text for details).

| Solution | Value of integral | | |
|---|-------------------|-------|------------|
| | Measured | | Calculated |
| 1 mol kg^{-1} $^{58}\text{NiCl}_2$ in CD_3OD | 0.49† | 0.58‡ | 0.491* |
| 1 mol kg^{-1} $^{58}\text{NiCl}_2$ in CD_3OH | 0.30† | 0.40‡ | 0.320* |

† From $I(k)$ calculated using free atom cross section.

‡ From $I(k)$ calculated using bound atom cross section.

* Calculated using $\bar{n}_\text{O}^{\text{H}(1)} = 1$ and $\bar{n}_\text{C}^{\text{H}(2)} = 3$.

$$I = \int_{\text{1st peak}} (G(r) - G(O))r^2 dr \quad (11)$$

since one expects $\bar{n}_\text{O}^{\text{H}} = 1$ and $\bar{n}_\text{C}^{\text{H}} = 3$. The value of this integral obtained from the $G(r)$ in figure 3 are compared with the calculated values in table 2. For both CD_3OH and CD_3OD solutions, the structure functions $F(k)$ and therefore $I(k)$ obtained using free-atom cross sections are most consistent with the calculated values. Consequently, these data were used to obtain the difference functions, $\Delta_{\text{Ni}}(k)$ (figure 5).

For both CD_3OD and CD_3OH solutions, there is a significant slope on the difference functions obtained by direct subtraction of the $I(k)$ for the two solutions of $^{58}\text{NiCl}_2$ and $^{62}\text{NiCl}_2$. This arises because there was water contamination of the ^{58}Ni samples (it is known that methanol absorbs water very rapidly from the atmosphere (Covington and Dickinson 1973). Infrared absorption analysis of the CD_3OH samples gives qualitative evidence of this, but not the quantitative information obtainable for D_2O solutions (Powell 1989).

The difference functions, obtained directly from the $F(k)$ values, were corrected empirically by subtracting from them a small fraction of the $I(k)$ for H_2O measured on the appropriate instrument (figure 5). Their Fourier transforms (figure 6) show there is little difference in the $G_{\text{Ni}}(r)$ values obtained by the two methods for $r > 1.8 \text{ \AA}$. The weighting factors, A_α , for the two first-order difference functions, are given in table 3. The factors which weight the terms relevant to Ni^{2+} solvation are large compared with A_{Cl} and A_{Ni} which weight the ion-ion terms.

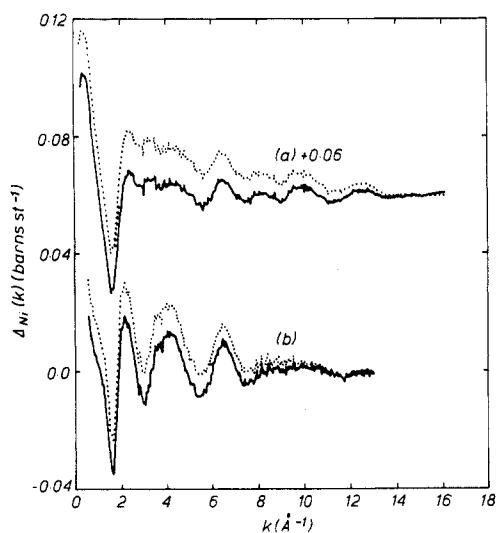


Figure 5. First order difference functions $\Delta_{\text{Ni}}(k)$; (a) $1 \text{ mol kg}^{-1} \text{NiCl}_2$ in CD_3OD and (b) $1 \text{ mol kg}^{-1} \text{NiCl}_2$ in CD_3OH . The dotted curves were obtained by direct difference of the calculated $F(k)$ values in figure 2. The full curves were obtained after application of an empirical correction, taking account of the presence of water in one of the samples (see section 2 of text).

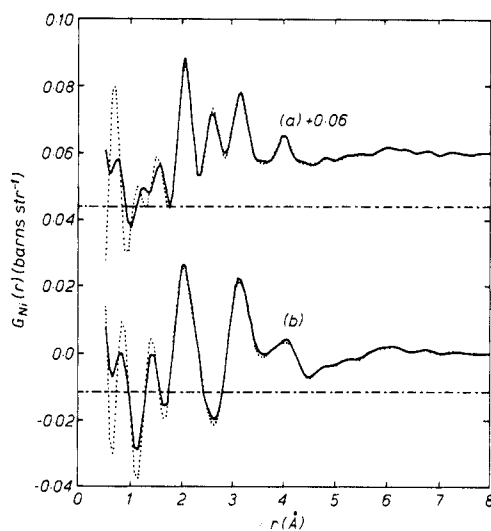


Figure 6. Total Ni^{2+} distribution functions $G_{\text{Ni}}(r)$: (a) $1 \text{ mol kg}^{-1} \text{NiCl}_2$ in CD_3OD and (b) $1 \text{ mol kg}^{-1} \text{NiCl}_2$ in CD_3OH . The dotted and full curves were obtained by Fourier transformation of the dotted and full curves in figure 5.

4. Results and discussion

4.1. Comparison of Ni^{2+} solvation in methanol and water

The $G_{\text{Ni}}(r)$ for the solutions in CD_3OD and CD_3OH are shown in figure 7 scaled so that the weighting of $g_{\text{NiO}}(r)$ is unity. The second peak is inverted in the case of the CD_3OH solutions, and can therefore be unambiguously assigned to Ni–H(1) correlations, since b_{H} is negative. One can plausibly assign the first peak to Ni–O and the third to Ni–C correlations, so that the Ni^{2+} methanol conformation is as shown in figure 4. The broad peak at around $r = 4.1 \text{ \AA}$ may reasonably be ascribed to Ni–H(2) correlations. The mean distances obtained for the first solvation shell are given in table 4 together with the value

Table 3. Weightings in millibarns of the Ni– α contributions A_α (5) to the difference functions.

| Solution | Ni–O | Ni–D | Ni–H | Ni–C | Ni–Cl | Ni–Ni |
|---|-------|--------|--------|-------|-------|-------|
| $1 \text{ mol kg}^{-1} \text{NiCl}_2$ in CD_3OD | 2.331 | 10.722 | — | 2.670 | 0.278 | 0.041 |
| $1 \text{ mol kg}^{-1} \text{NiCl}_2$ in CD_3OH | 2.265 | 7.814 | –1.460 | 2.595 | 0.262 | 0.039 |

of $\overline{n}_{\text{Ni}}^{\text{eff}}$ assuming the only contribution to the first peak is $g_{\text{NiO}}(r)$. It is difficult to separate the other peaks at the first-order difference level, so no other coordination numbers were calculated.

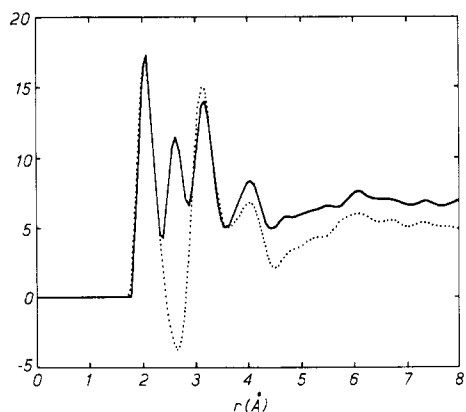


Figure 7. Comparison of the two data sets in figure 6 normalised by the coefficient A_O i.e. $(G(r) - G(0))/A_O$. Dotted curve: 1 mol kg^{-1} NiCl_2 in CD_3OH ; full curve: 1 mol kg^{-1} NiCl_2 in CD_3OD .

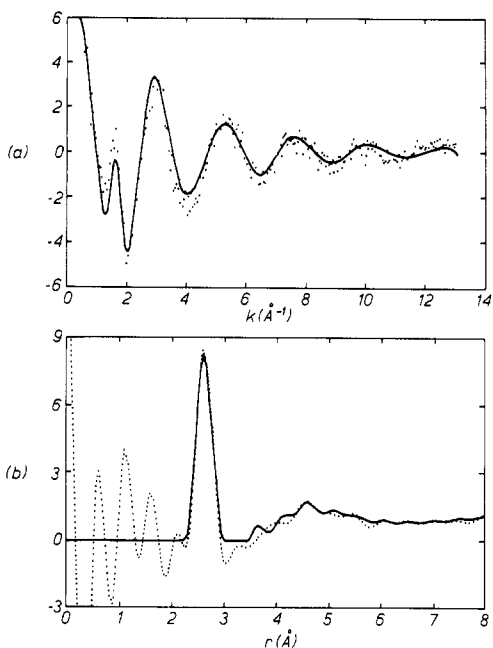


Figure 8. (a) The partial structure factor, $S_{\text{NiHl}}(k) - 1$ and (b) the pair radial distribution function $g_{\text{NiHl}}(r)$ for 1 mol kg^{-1} NiCl_2 in methanol. In (a) the dots are data points and the curve is the 'back' Fourier transform of the full curve in (b). The dotted curve in (b) is the Fourier transform of the data points.

Table 4. Structural parameters obtained from the first-order difference functions.

| Solution | \bar{r}_{NiO} | \bar{r}_{NiHl} | \bar{r}_{NiC} | $\text{eff } \bar{r}_{\text{Ni}}^{-\text{O}}$ |
|---|------------------------|-------------------------|------------------------|---|
| 1 mol kg^{-1} NiCl_2 in CD_2OD | 2.09 (2) | 2.62 (2) | 3.18 (2) | 4.7 (2) |
| 1 mol kg^{-1} NiCl_2 in CD_3OH | 2.06 (2) | 2.62 (2) | 3.14 (2) | 5.2 (2) |

There is no evidence for any difference in the Ni^{2+} coordination in the CD_3OD and CD_3OH solutions. The observed configuration is in qualitative agreement with that obtained for other ion-methanol solutions by molecular dynamics simulations which employ pairwise potentials (see e.g. Impey *et al* 1987 and Jorgensen *et al* 1982).

4.2. The radial distribution function, $g_{\text{NiH(l)}}(r)$ for NiCl_2 in $\text{CD}_3\text{OH(l)}$

The two first-order difference functions presented above differ only in the substitution of the hydroxyl deuterium for a proton. On the assumption that the structure around Ni^{2+} is unaffected by the substitution of H by D, the partial structure factor $S_{\text{NiH(l)}}(k)$ can be determined by a simple combination of the two $\Delta_{\text{Ni}}(k)$ (H(l) labels the hydroxyl proton

or deuteron). This function is shown in figure 8, together with its Fourier transform, $g_{\text{NiH(l)}}(r)$.

Since the two $\Delta_{\text{Ni}}(k)$ were measured on different instruments, there is a possibility of some systematic error between them which could affect $S_{\text{NiH(l)}}(k)$ and hence $g_{\text{NiH(l)}}(r)$. However, $g_{\text{NiH(l)}}(r)$ does not change appreciably if one allows for a 10% normalisation error on either of the first-order differences. Integration over the first peak yields $\bar{n}_{\text{Ni}}^{\text{H(l)}} = 3.7 \pm 0.3$, which may be identified with the Ni^{2+} solvation number. (From the structure of the methanol molecule one expects $\bar{n}_{\text{Ni}}^{\text{H(l)}} = \bar{n}_{\text{Ni}}^{\text{O}}$.) The discrepancy between this and the value $\bar{n}_{\text{Ni}}^{\text{O}} = 5.0 \pm 0.4$ obtained from the first-order differences may be explained if there is significant cation–anion contact. Based on tabulated ionic radii for Ni^{2+} and Cl^- , one expects Ni–Cl contacts at a distance of ~ 2.4 Å. This is in the region between the Ni–O and Ni–H(l) peaks in $G_{\text{Ni}}(r)$, and so Ni–Cl correlations may well contribute to $^{\text{eff}}\bar{n}_{\text{Ni}}^{\text{O}}$. In this case (10) applies and, inserting values for b_{O} and b_{Cl} , one has

$$^{\text{eff}}\bar{n}_{\text{Ni}}^{\text{O}} = \bar{n}_{\text{Ni}}^{\text{O}} + 1.65 \bar{n}_{\text{Ni}}^{\text{Cl}}.$$

Using $^{\text{eff}}\bar{n}_{\text{Ni}}^{\text{O}} = 5.0 \pm 0.4$ and $\bar{n}_{\text{Ni}}^{\text{O}} = 3.7 \pm 0.3$, one obtains $\bar{n}_{\text{Ni}}^{\text{Cl}} = 0.8 \pm 0.3$. These data are consistent, therefore, with 3.7 ± 0.3 methanol molecules around the Ni^{2+} ion, and 0.8 ± 0.3 Cl^- ion centres within the radius $r = 2.34$ Å. Since the first peak in $g_{\text{NiCl}}(r)$ is likely to coincide only partially with that in $g_{\text{NiO}}(r)$, this should be considered as a lower bound estimate of the degree of cation–anion association.

It is interesting to note the behaviour of $g_{\text{NiH(l)}}(r)$ at higher values of r . The peak at about 4.6 Å implies significant penetration of the first solvation shell by the second coordination shell of methanol molecules. The spatial extent of the first solvation shell is much larger than for the aqueous solution, so such behaviour is not surprising. Integration from $r_1 = 3.6$ Å to 5.6 Å $< r_2 < 6.0$ Å yields 9.5 ± 1.0 methanol molecules in the second coordination shell.

The observation of direct cation–anion contacts is in marked contrast to studies of aqueous NiCl_2 solutions (Neilson and Enderby, 1983), where no such contacts are observed, even at high (4.35 mol kg^{-1}) concentration. The reduction in dielectric constant will produce stronger ion–ion interactions, but the rather open solvation structure may also make cation–anion association more likely.

5. Conclusions

The above results show that the first-order difference method of neutron diffraction can be successfully extended to non-aqueous ionic solutions. Furthermore, selective H to D substitution of a hydrogenous solvent makes possible the unique determination of ion–hydrogen correlations.

There is also evidence for direct cation–anion contacts, in contrast to results from studies of NiCl_2 aqueous solutions. Clearly it is of interest to determine $g_{\text{NiCl}}(r)$ directly. This is possible using the second-order difference method (Neilson and Enderby 1983) and, based on results presented above, it is concluded that such experiments will be feasible. In this way, a sensitive test can be made of the validity of the primitive model and its dependence on dielectric constant.

Acknowledgements

We are particularly grateful to Mr P Gullidge who prepared the samples, and Drs Pierre Chieux and Pierre Convert of the Institut Laue Langevin for their expert advice and

assistance with the diffraction experiments. The financial support of SERC is gratefully acknowledged. DHP thanks the Institut Laue Langevin for the provision of a three-year research studentship.

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