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The structure of Cl^- solutions in ethylene glycol studied by neutron diffraction

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Abstract. The method of isotopic substitution in neutron diffraction is applied to study the coordination environment of Cl^- in a 0.999(3) molal solution of NaCl in fully deuterated ethylene glycol (EG). It is shown that the EG molecules act as monodentate ligands to give a $Cl(EG)_4^-$ complex that comprises $Cl^- \ldots D$–O hydrogen bonds which are approximately linear and of length 2.14(3) Å. The results are compared with those obtained for the Cl^- coordination complex in aqueous and methanolic solution. It is found that there is a reduction from $\simeq 6$ to $\simeq 4$ in the number of ligands binding to Cl^- on changing the solvent from water to EG and that, for all three solvents, the $Cl^- \ldots D$–O hydrogen bond is typically linear. The effect of a small hydrogen imbalance between the solutions used for isotopic substitution experiments is briefly considered.

1. Introduction

The purpose of this paper is to present first results on the coordination environment of the chloride ion in fully deuterated ethylene glycol ($ODCD_2CD_2OD$ or EG) solution as measured by using the method of isotopic substitution in neutron diffraction. The present study was motivated by the overall need to know the structure of coordination complexes in order to understand kinetic processes, such as the mechanism by which ligand exchange occurs, and transport phenomena, such as the mobility of ions in different solvent media. The method of isotopic substitution in neutron diffraction, as applied to Cl^- solutions, is helpful in this respect since there are chlorine isotopes that have a large coherent neutron scattering length contrast. This allows for all of the partial pair distribution functions (PDFs) that describe the structure of the solution to be eliminated, *except* for those that involve the Cl^- ion (Soper *et al* 1977, Enderby *et al* 1987).

The Cl^- ion is itself of particular interest since it is a typical counter-ion in electrolyte solution and there is a considerable body of knowledge on its coordination environment, at the PDF level, from studies using neutron diffraction (e.g. Cummings *et al* 1980, Neilson and Enderby 1983, Copestake *et al* 1985, Powell *et al* 1988, Powell 1989), computer simulation (e.g. Impey *et al* 1983, 1987, Spohr *et al* 1988, Sprik *et al* 1990, Dang *et al* 1991, Guàrdia *et al* 1991, Marx *et al* 1991) and extended RISM theory (Hirata and Levy 1987). Furthermore, unlike the ClO_4^- and NO_3^- counter-ions, for which the isotopic substitution method can also be applied, the Cl^- ion has, at least in aqueous solution, a relatively well defined primary solvation shell (Neilson and Enderby 1982, Neilson *et al* 1985, Heinje *et al* 1987, Bergström *et al* 1991). This can only help in facilitating a detailed comparison between the Cl^- conformations in water and in EG. NaCl was chosen since it is regarded as a 'strong electrolyte' in the respect that its solutions in EG are, at least at low concentrations, fully dissociated (Santos and Spiro 1972). In the present work the solution concentration is 0.999(3) molal (mol kg^{-1}) giving an NaCl:EG ratio of 1:14.7.

Part of the interest in the higher alcohols EG and glycerol stems from certain similarities between these solvents and water. For example, all three liquids are hydrogen bonded and they have large relative permittivities which make them good solvents for ionic salts. It is also of interest that the partial molar volumes of alkali metal halides dissolved in EG are quite close to those in water (Zana and Yeager 1982). Furthermore, the ratio of the alkali metal to halide species ionic mobilities is approximately the same in all three solvents (Santos and Spiro 1972, Blanco *et al* 1989), although the absolute values do of course scale roughly with the solvent viscosity. It is natural to ask whether these observations can be correlated with similarities in the structure of the Cl^-–solvent-molecule complexes.

Additional motivation for the present study has been provided by our recent work on the structure of Ni^{2+} solutions in EG where it was found that $Ni(EG)_3^{2+}$ tris-chelate complexes are formed and that there is a spatially well defined hydrogen bond of length $\simeq 1.8(1)$ Å between EG ligands in the first and second solvation shell of the cation (Lond *et al* 1991). The existence of two separate hydroxyl groups within the EG molecule enables it to act as a bidentate oxygen donor ligand. The structural consequence of the hydroxyl group pair for the Cl^-–EG-molecule interaction is, however, unknown. Furthermore, there have been recent attempts at modelling the structure of the higher alcohols by using molecular dynamics methods (Root and Stillinger 1989). Detailed experimental information at the PDF level on solutions of salts in the higher alcohols is important if these computations are to be developed and extended to ionic solutions.

In the first part of this paper, the essential theory behind the isotopic substitution method in neutron diffraction, as applied to ionic solutions, is outlined. Next, the experimental method and results are given. Attention is paid to the nature of inelasticity corrections as there was a small imbalance between the hydrogen content of the two solutions that were used for the diffraction experiments. The results are discussed in terms of the nature of the Cl^-–EG-molecule complex and a detailed comparison is made with neutron diffraction results for the Cl^-–water complex in a solution of NaCl in D_2O (Barnes *et al* 1987) for which the Cl^-:solvent-molecule ratio is nearly the same. A comparison is also made with the Cl^-–methanol-molecule conformations as calculated by molecular dynamics methods.

2. Theory

The isotopic substitution method in neutron diffraction, as applied to the problem of ionic solutions, has been described in detail elsewhere (Enderby *et al* 1987). To summarize, diffraction experiments are conducted on two fully deuterated EG solutions which are identical in every respect except for the isotopic composition of the Cl^- ion. Deuterated solvents are preferred owing to the large incoherent cross section of hydrogenated materials. Each measured intensity is then corrected for background scattering, placed on an absolute scale by comparison with a vanadium standard, and corrected for multiple and container scattering as well as for attenuation of the beam by the sample and container materials (Salmon and Benmore 1992). The quantity thus derived is, for each solution, a total structure factor $F_0(k)$ given by

$$F_0(k) = F(k) + \sum_{\alpha=1}^{\mu} c_\alpha \frac{\sigma_\alpha^s}{4\pi} + \epsilon(k) \tag{1}$$

where k is the scattering vector, c_α and σ_α^s are, respectively, the atomic fraction and total bound (coherent and incoherent) scattering cross section of species α, and μ (= 5) is the total number of chemical species in the solution. The most prominent contribution to the correction term $\epsilon(k)$ arises because of a departure from the static approximation in the case of neutron scattering from liquids and is a particular problem when light nuclei are present (Powles 1973, Squires 1978). $F(k)$ is a linear sum of the partial structure factors, $S_{\alpha\beta}(k)$, whose Fourier transforms yield the partial PDFS $g_{\alpha\beta}(r)$:

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

with

$$g_{\alpha\beta}(r) = 1 + \frac{1}{2\pi^2 n_0 r} \int_0^\infty (S_{\alpha\beta}(k) - 1) k \sin(kr)\,\mathrm{d}k \tag{3}$$

where b_α is the coherent neutron scattering length of species α and n_0 is the total atomic number density of the solution. $g_{\alpha\beta}(r)$ gives a measure of the probability of finding an atom of species β at a distance r from an atom of type α located at the origin of coordinates. It is defined in such a way that the mean number of particles of type β contained in the volume defined by two concentric spheres of radii r_1 and r_2, centred on a particle of type α, is given by

$$\bar{n}_\beta^\alpha = 4\pi n_0 c_\beta \int_{r_1}^{r_2} r^2 g_{\alpha\beta}(r)\,\mathrm{d}r. \tag{4}$$

Equation (4) was used to calculate coordination numbers in the present work.

In the solution studied here, $F(k)$ comprises 15 $S_{\alpha\beta}(k)$ functions. However, if the coherent scattering length of the anion is changed by substituting enriched chlorine isotope (^{37}Cl, $b_{'\mathrm{Cl}}$) in place of chlorine having the natural isotopic abundance ($^{\mathrm{N}}$Cl, b_{Cl}), subtraction of the two corresponding $F_0(k)$ functions (equation (1)) gives

$$\Delta_{\mathrm{Cl}}^0(k) \equiv \mathcal{A}\,{}^{\mathrm{N}}F_0(k) - \mathcal{B}\,{}^{37}F_0(k) = \Delta_{\mathrm{Cl}}(k) + \mathcal{D} + \epsilon'(k) \tag{5}$$

where $\mathcal{D} = c_{\mathrm{Cl}}(\sigma_{\mathrm{Cl}}^s - \sigma_{'\mathrm{Cl}}^s)/4\pi$ and pertains to the self-scattering from the nuclei, and $\mathcal{A}$, $\mathcal{B}$ are constants which are identical to unity if the $F_0(k)$ functions have been properly corrected. The first-order difference function $\Delta_{\mathrm{Cl}}(k)$ is given by

$$\begin{aligned} \Delta_{\mathrm{Cl}}(k) = {} & A(S_{\mathrm{ClO}}(k) - 1) + B(S_{\mathrm{ClD}}(k) - 1) + C(S_{\mathrm{ClC}}(k) - 1) \\ & + D(S_{\mathrm{ClNa}}(k) - 1) + E(S_{\mathrm{ClCl}}(k) - 1) \end{aligned} \tag{6}$$

where $\Delta b = b_{\mathrm{Cl}} - b_{\prime\mathrm{Cl}}$, $A = 2c_{\mathrm{Cl}}c_{\mathrm{O}}b_{\mathrm{O}}\,\Delta b$, $B = 2c_{\mathrm{Cl}}c_{\mathrm{D}}b_{\mathrm{D}}\,\Delta b$, $C = 2c_{\mathrm{Cl}}c_{\mathrm{C}}b_{\mathrm{C}}\,\Delta b$, $D = 2c_{\mathrm{Cl}}c_{\mathrm{Na}}b_{\mathrm{Na}}\,\Delta b$ and $E = c_{\mathrm{Cl}}^2(b_{\mathrm{Cl}}^2 - b_{\prime\mathrm{Cl}}^2)$ and the real-space picture is obtained from

$$\Delta G_{\mathrm{Cl}}(r) = \frac{1}{2\pi^2 n_0 r}\int_0^\infty \Delta_{\mathrm{Cl}}(k) k \sin(kr)\,\mathrm{d}k = A(g_{\mathrm{ClO}}(r) - 1) + B(g_{\mathrm{ClD}}(r) - 1) + C(g_{\mathrm{ClC}}(r) - 1) + D(g_{\mathrm{ClNa}}(r) - 1) + E(g_{\mathrm{ClCl}}(r) - 1). \qquad (7)$$

An important property of the difference function $\Delta_{\mathrm{Cl}}^0(k)$ is that, providing the solutions are identical in every respect (except for their chlorine isotope compositions), the $\epsilon(k)$ term in equation (1) will be, to first order, identical for both solutions (Soper *et al* 1977), so that it cancels to give a negligible $\epsilon'(k)$ term in equation (5). The validity of this statement can be checked on several accounts. Firstly, since $S_{\alpha\beta}(k) \to 1$ in the limit as $k \to \infty$, $\Delta_{\mathrm{Cl}}^0(k)$ should oscillate about the calculated self-scattering $\mathcal{D}$-value (Cossy *et al* 1989). Secondly, since $g_{\mathrm{Cl}\beta}(r) = 0$ at r-values below the distance of closest approach to Cl (that is, r_{min}), $\Delta G_{\mathrm{Cl}}(r)$ should equal the calculated limit $\Delta G_{\mathrm{Cl}}(0) = -(A + B + C + D + E)$ at low r. In practice $\Delta G_{\mathrm{Cl}}(r)$ will oscillate about this calculated value owing to statistical noise on the k-space data, truncation of the data at a finite k-value and systematic errors (such as a finite $\epsilon'(k)$ term giving rise to a residual slope). However, provided that these effects are small, setting $\Delta G_{\mathrm{Cl}}(r)$ equal to the $\Delta G_{\mathrm{Cl}}(0)$ limit for $r \leqslant r_{\mathrm{min}}$ and Fourier backtransforming will yield a function $\tilde{\Delta}_{\mathrm{Cl}}(k)$ that is in close agreement at all k-values with $\Delta_{\mathrm{Cl}}(k)$. Large discrepancies between $\Delta_{\mathrm{Cl}}(k)$ and $\tilde{\Delta}_{\mathrm{Cl}}(k)$ are a warning sign. For example, when $\epsilon'(k) = 0$ a large discrepancy at low-k often signifies that $\Delta G_{\mathrm{Cl}}(r)$ oscillates about an incorrect low-r value and therefore indicates an inadequacy in the correction procedure (Salmon and Benmore 1992). Thirdly, $\Delta_{\mathrm{Cl}}(k)$ should satisfy the sum-rule relation (Enderby *et al* 1966)

$$\int_0^\infty \Delta_{\mathrm{Cl}}(k)\,k^2\,\mathrm{d}k = 2\pi^2 n_0\,\Delta G_{\mathrm{Cl}}(0). \qquad (8)$$

There exist, therefore, at least three validity criteria that the first-order difference functions must satisfy.

3. Experimental method

The solutions were made from Na$^{\mathrm{N}}$Cl (Aldrich Gold Label) and from Na^{37}Cl (4.33% ^{35}Cl, 95.67% ^{37}Cl, Isotec Incorporated, USA) as supplied by the manufacturers and without further purification, except for drying on a vacuum line at 154 °C for $\simeq$ 20 hours. The solutions were prepared by weight in a high-purity argon-filled glovebox by using fully deuterated EG (99% enrichment, Cambridge Isotope Laboratories, USA). The concentrations were checked by first passing an aliquot of the electrolyte through an ion-exchange column (BDH, Amberlite IR120H resin). The eluted acid solution was then boiled vigorously to drive off dissolved CO_2 (Vogel 1978) and, after cooling, was titrated against NaOH solution under nitrogen with a pH meter. The sample densities were measured by using a Paar DMA602 apparatus incorporating a Hetofrig water bath in order to maintain the measuring cell at constant temperature.

Further details of the sample preparation are given by Lond (1991) and the solution parameters are presented in table 1. The coherent neutron scattering length of the anion in the ^{N}Cl and ^{37}Cl samples was, respectively, 9.5792(8) fm and 3.45(6) fm, and the enumerated values of the coefficients A–E in equations (6) and (7) are (in mb) 0.941(9), 3.20(3), 1.08(1), 0.0199(2) and 0.0359(2) respectively. The scattering length values were taken from Sears (1984).

Table 1. Experimental details of the solutions.

Solute	Molality (mol kg^{-1})	Designation of scattering pattern	Density at 23 °C (g cm^{-3})
Na^{N}Cl	0.997(2)	$^{N}F_0(k)$	1.255(2)
Na^{37}Cl	1.000(2)	$^{37}F_0(k)$	1.257(2)

Solute	n_0 (atom Å^{-3})	Total scattering cross section (b)[a]	Total absorption cross section at 0.7042 Å (b)[b]
Na^{N}Cl	0.1064	3.923(6)	0.0905(8)
Na^{37}Cl	0.1066	3.831(6)	0.00873(4)

[a] Calculated by using the free-atom cross sections (Sears 1984).

[b] Absorption cross sections taken from Sears (1984).

The diffraction experiments were made by using the D4B instrument at the Institut Laue–Langevin, Grenoble. The incident wavelength was 0.7042 Å, and the scattered neutrons were detected with two 64-channel multidetectors, which were calibrated by using the scattering from a vanadium bar. Diffraction patterns were taken for (1) the solutions in their container; (2) the empty solution container; (3) the instrumental background with the sample absent; (4) a cadmium bar of comparable dimensions to that of the sample in order to estimate the background correction at low scattering angles (Bertagnolli *et al* 1976); (5) a vanadium standard rod of radius 0.4 cm. The solution container was a hollow cylinder of inside radius 0.400 cm and wall thickness 0.025 cm and was fabricated from a titanium–zirconium alloy having a nominal coherent scattering length of zero and an attenuation coefficient of 0.334 cm^{-1} at a wavelength of 0.7 Å. The cylinder axis was oriented perpendicular to the incident beam and the sample temperature was about 23 °C. Free-atom cross sections were used in the data analysis since this choice has proved successful in previous work on EG (Lond *et al* 1991) and methanolic (Powell and Neilson 1990) solutions at the 0.7 Å neutron wavelength.

4. Results

The observed total structure factors for the solutions, $^{N}F_0(k)$ and $^{37}F_0(k)$, are shown in figure 1. Of interest is the absence of a so-called first sharp diffraction peak or pre-peak at low k-values ($\simeq 0.5$ Å^{-1}) but the presence of such a feature in a 0.956 molal solution of $Ni(CF_3SO_3)_2$ in EG (Lond *et al* 1991). This indicates an absence of significant intermediate-range ordering within the NaCl solution.

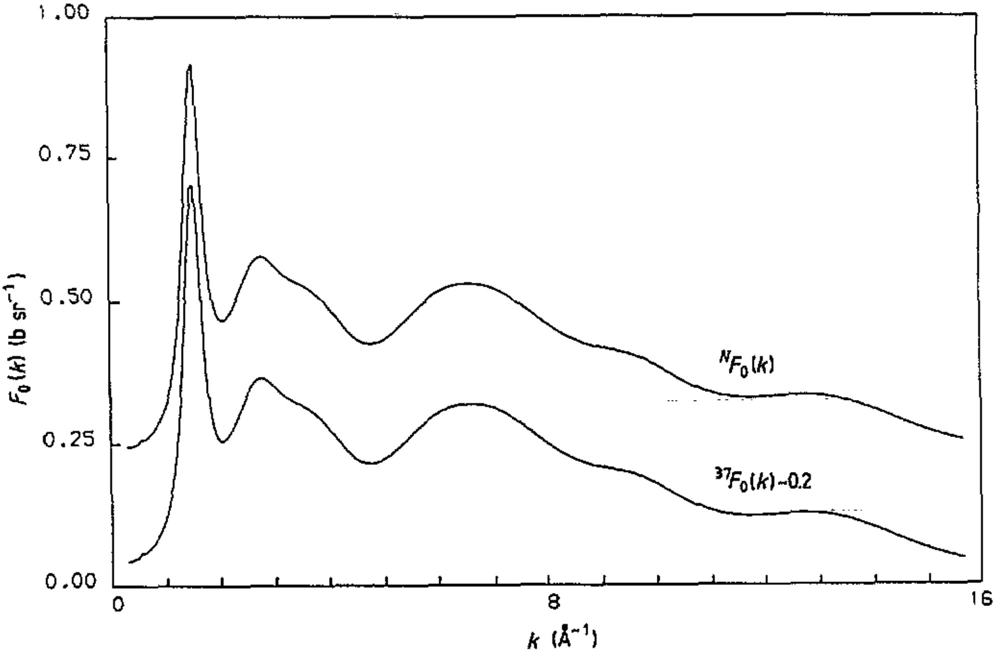

Figure 1. The measured $F_0(k)$ functions for a 0.999(3) molal solution of NaCl in fully deuterated EG.

$\Delta_{\mathrm{Cl}}(k)$ is illustrated in figure 2(*a*). It was obtained from $\Delta^0_{\mathrm{Cl}}(k)$ by subtracting a constant of 9 mb which is comparable with the calculated value $\mathcal{D} = 8$ mb. However, there is a residual slope on $\Delta_{\mathrm{Cl}}(k)$, implying that $\epsilon'(k)$ cannot be neglected in the present analysis, and the corresponding $\Delta G_{\mathrm{Cl}}(r)$ function is noisy. Notwithstanding, there are discernible physical features in $\Delta G_{\mathrm{Cl}}(r)$ and it is readily shown, by forming $\tilde{\Delta}_{\mathrm{Cl}}(k)$ with $r_{\mathrm{min}} = 1.84$ Å, that the major effect of the slope is pronounced oscillations at the lowest r-values: the comparison of $\Delta_{\mathrm{Cl}}(k)$ and $\tilde{\Delta}_{\mathrm{Cl}}(k)$ in figure 2(*a*) shows that the slope has been essentially eliminated by suppressing the features in $\Delta G_{\mathrm{Cl}}(r)$ for $r \leqslant r_{\mathrm{min}}$. It therefore remains to discuss the probable errors resulting in the $\epsilon'(k)$ slope and the possible scenarios for their correction. The problem of residual slopes is not uncommon in ionic solution work (e.g. Neilson and Skipper 1985, Salmon *et al* 1988, Powell *et al* 1989, van der Maarel *et al* 1989, Powell and Neilson 1990, Cartailler *et al* 1991) and a variety of empirical corrections have been applied. The relative merits of the varying approaches are nevertheless still unclear, and the effect of different $\epsilon'(k)$ approximations will therefore be considered.

4.1. The $\epsilon'(k)$ correction

The existence of a slope on $\Delta_{\mathrm{Cl}}(k)$ shows an error in one or other of the measured $F_0(k)$ functions. The source of this error could not, however, be traced to the solutions having imbalanced concentrations since these were measured to be the same within experimental error (table 1). Moreover, the magnitude of these errors is at least comparable with that in our previous work on $\mathrm{Ni(CF_3SO_3)_2}$ in EG where $\epsilon'(k) \simeq 0$ (Lond *et al* 1991). The possibility was also discounted of the $\epsilon(k)$ terms in the observed $F_0(k)$ (equation (1)) being significantly different as a consequence of a strong coupling between the inelastic scattering of neutrons within a solution

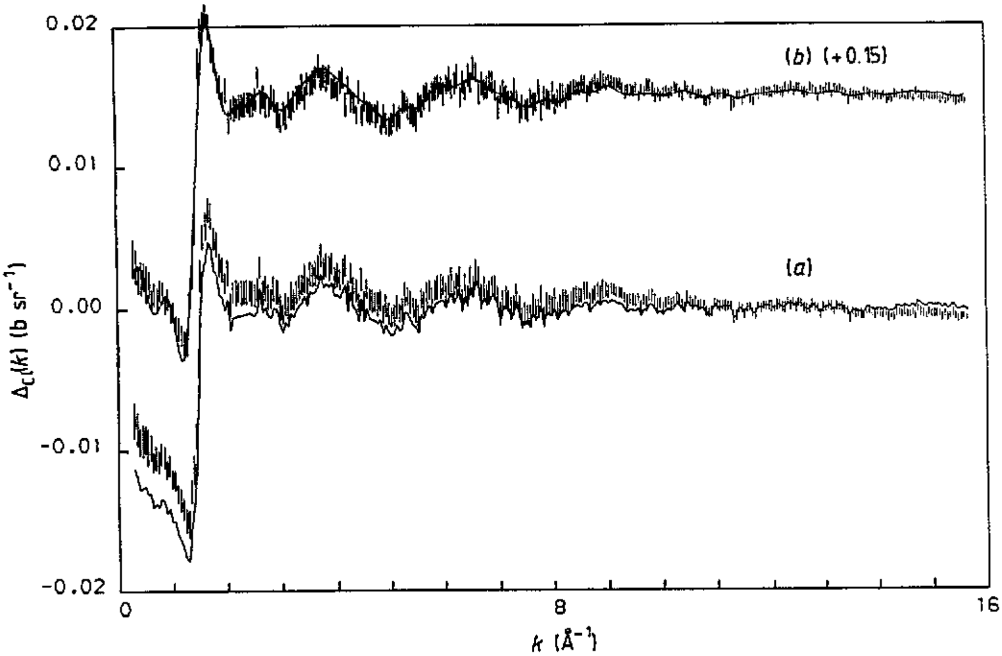

Figure 2. $\Delta_{\mathrm{Cl}}(k)$ obtained by combining the $F_0(k)$ of figure 1 using equation (5) with (*a*) $\mathcal{A} = \mathcal{B} = 1$, $\mathcal{D} = 9$ mb, $\epsilon'(k) = 0$ or (*b*) $\mathcal{A} = 1.005$, $\mathcal{B} = 1$, $\mathcal{D} = 10$ mb, $\epsilon'(k)$ derived from $\mathrm{TbH}_{1.6}$ (see the text). The bars give the statistical errors on the data and full curves give $\tilde{\Delta}_{\mathrm{Cl}}(k)$, the Fourier backtransform of $\Delta G_{\mathrm{Cl}}(r)$ after the unphysical oscillations at $r \leqslant r_{\mathrm{min}}$ have been set to the calculated $\Delta G_{\mathrm{Cl}}(0)$ limit.

and the chlorine species ($^{\mathrm{N}}$Cl and ^{37}Cl) having markedly different energy-dependent absorption cross sections (see, e.g. van der Maarel *et al* 1989, Cartailler *et al* 1991). Although the chlorine isotopes do have different absorption cross sections at a neutron wavelength of 0.7 Å (table 1), there are no nearby absorption resonances, and previous aqueous solution work, using chlorine isotopes at the same neutron wavelength, did not incur problems of this type (Powell *et al* 1988).

Another possible source of error is an incorrect normalization of the $F_0(k)$ functions giving rise to $\mathcal{A} \neq 1$ or $\mathcal{B} \neq 1$ in equation (5). This may result, for example, if the solution container is incompletely filled since $F_0(k)$ is inversely proportional to the total number of scattering nuclei within the solution (Salmon and Benmore 1992). Indeed, if it assumed that $\mathcal{A} = 1$ and $\mathcal{B} = 1.01$, which corresponds to an incompletely filled container in the $^{37}F_0(k)$ experiment (cf Salmon *et al* 1988, Powell *et al* 1989), then a significant amount of the residual droop on $\Delta^0_{\mathrm{Cl}}(k)$ is eliminated, but not all of the validity criteria given at the end of section 2 are satisfied.

A likely cause of the finite $\epsilon'(k)$ correction is, therefore, a small hydrogen imbalance between the two solutions which results from the EG molecules having a different degree of deuteration or from light water contamination (cf Powell and Neilson 1990). Unfortunately an infra-red analysis of the solutions in the region of the O–H stretching mode did not prove this scenario conclusively owing to problems in accurately preparing standard solutions of H_2O in fully deuterated EG: the EG is expensive and only small samples could therefore be afforded. However, the ratio between the hydrogen incoherent and coherent scattering cross sections is 45:1—such that a small change in the hydrogen content of a solution will have a significant effect on the terms involving σ_α^s and $\epsilon(k)$ in equation (1), whilst leaving the $F(k)$ term essentially unchanged. Indeed the negative gradient of $\epsilon'(k)$ and the fact that $\Delta_{\mathrm{Cl}}^0(k)$ oscillates about a value of $\mathcal{D}$ that is slightly higher than calculated (9 mb compared with 8 mb), is consistent with the $^{\mathrm{N}}$Cl solution having a larger hydrogen content than the ^{37}Cl solution.

In view of these arguments and the expectation that inelasticity corrections are largest for the self-scattering terms, i.e. those *not* involving $F(k)$ (Soper *et al* 1977), $\epsilon'(k)$ will be approximated by (Squires 1978, Yarnell *et al* 1973)

$$\epsilon'(k) \propto \left(\frac{\mathrm{d}\sigma_{\mathrm{H}}}{\mathrm{d}\Omega}\right)^{\mathrm{eff}}_{\mathrm{self}} = \frac{\sigma_{\mathrm{H}}^{\mathrm{s}}}{4\pi}\int_{-\infty}^{\omega_{\max}} \eta(k_1)\frac{k_1}{k_0}S_{\mathrm{H}}^{\mathrm{s}}(k,\omega)\,\mathrm{d}\omega. \tag{9}$$

In this expression k_0 and k_1 are the wavevectors of the incident and scattered neutrons; $\eta(k_1)$ is the efficiency of the neutron detector; $S_{\mathrm{H}}^{\mathrm{s}}(k,\omega)$ is the self-dynamical structure factor for hydrogen; $\hbar\omega_{\max}$ is the energy of the incident neutron; and $\sigma_{\mathrm{H}}^{\mathrm{s}}$ is the total bound scattering cross section of hydrogen. It remains to choose a suitable form for $\epsilon'(k)$ and appropriate values for the constants in equation (5) such that all three of the validity criteria at the end of section 2 are satisfied.

As a first step simple linear and quadratic forms for equation (9), $\epsilon'(k) \propto k$ and $\epsilon'(k) \propto k^2$, were assumed (cf Neilson and Skipper 1985, Powell *et al* 1989, Powell and Neilson 1990) with $\mathcal{A} = \mathcal{B} = 1$. However, a residual slope remained on the resultant $\Delta_{\mathrm{Cl}}(k)$ function.

As a next step it was assumed that $\mathcal{A} = \mathcal{B} = 1$ and that $\epsilon'(k)$ can be taken as proportional to the effective differential cross section at an incident neutron wavelength of 0.7 Å for (i) H_2O as measured by using a black ($\eta(k_1) = \mathrm{constant}$) detector (Beyster 1968); (ii) hydrogen in crystalline $\mathrm{TbH}_{1.6}$ as measured on the D4 diffractometer (Chieux *et al* 1984); or (iii) a perfect gas comprising atoms of 1, 2 or 3 atomic mass units as calculated by Copley assuming a black detector and integrating the model scattering law at constant scattering angle (see Chieux *et al* 1984)†. Additionally it was assumed (iv) that $\epsilon'(k) = a_0 + a_2k^2 + a_4k^4$, which has often been used to correct for inelasticity effects when reactor-based experiments are made on liquids comprising light atoms (Damay *et al* 1990, Bellissent-Funel *et al* 1991). The constants a_0, a_2, a_4 are obtained by fitting the difference $\Delta_{\mathrm{Cl}}(k) - \tilde{\Delta}_{\mathrm{Cl}}(k)$ (cf figure 2(*a*)).

It was found that all of the $\epsilon'(k)$ functions, as specified by (i) to (iv), reduced the magnitude of the slope on $\Delta_{\mathrm{Cl}}^0(k)$. However, there remained a small discrepancy between $\Delta_{\mathrm{Cl}}(k)$ and $\tilde{\Delta}_{\mathrm{Cl}}(k)$ at low k which could be reduced further by assuming $\mathcal{A} = 1.005$ with $\mathcal{B} = 1$. In this way all three of the validity criteria of section 2 could be satisfied in full for most of the forms chosen for $\epsilon'(k)$. This appears reasonable since the slope correction is relatively small (it amounts to a $\lesssim 1\%$ change of $^{\mathrm{N}}F_0(k)$) and most of the $\epsilon'(k)$ functions have similar shapes as illustrated in figure 3. The corollary is that the fully corrected $\Delta_{\mathrm{Cl}}(k)$ functions are similar and all of the essential features in the corresponding $\Delta G_{\mathrm{Cl}}(r)$ are therefore the same. Indeed, for a given $\epsilon'(k)$ correction, the $\Delta G_{\mathrm{Cl}}(r)$ function obtained with $\mathcal{A} = \mathcal{B} = 1$ is almost identical (for $r \geqslant r_{\min}$) with $\Delta G_{\mathrm{Cl}}(r)$ as obtained by using $\mathcal{A} = 1.005$, $\mathcal{B} = 1$. The following discussion of the results, which is based on $\Delta_{\mathrm{Cl}}(k)$

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† Ideally the D4B diffractometer $\eta(k_1)$ function would be used in determining the $\epsilon'(k)$ correction by each of the different methods. The relevant data sets are not, however, available.

(figure 2(*b*)) and $\Delta G_{\mathrm{Cl}}(r)$ (figure 4) as derived from the $\mathrm{TbH}_{1.6}$ $\epsilon'(k)$ function, is therefore independent of the precise form of the empirical corrections applied in equation (5).

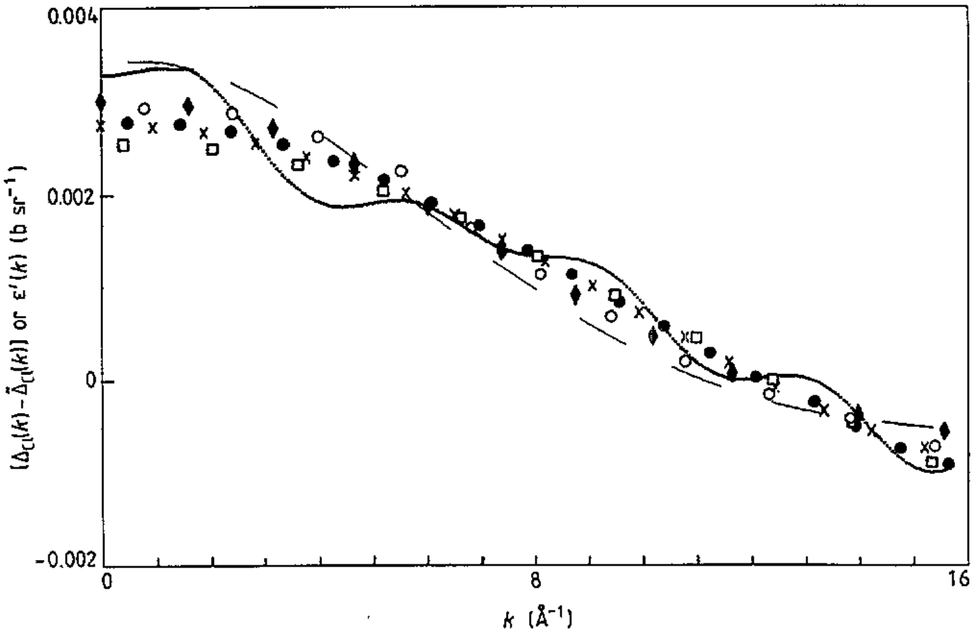

Figure 3. The function $\Delta_{\mathrm{Cl}}(k) - \tilde{\Delta}_{\mathrm{Cl}}(k)$ (dotted curve), as derived from the data of figure 1 using equation (5) with $\mathcal{A} = 1.005$, $\mathcal{B} = 1$, $\mathcal{D} = 11$ mb, $\epsilon'(k) = 0$, and its comparison with different forms for the $\epsilon'(k)$ correction. The $\epsilon'(k)$ derive (see the text) from H_2O (○); $\mathrm{TbH}_{1.6}$ (♦); perfect gas comprising particles of 1 (dashed curve), 2 (●) or 3 (□) atomic mass units; a polynomial fit to $(\Delta_{\mathrm{Cl}}(k) - \tilde{\Delta}_{\mathrm{Cl}}(k))$ (X).

5. Discussion

The first peak in $\Delta G_{\mathrm{Cl}}(r)$ at 2.14(3) Å is the most prominent feature and the deuterium atoms of the EG hydroxyl groups are expected to be adjacent to Cl^- on chemical grounds. The real-space representation of the data is therefore plotted in figure 4 as the function

$$(\Delta G_{\mathrm{Cl}}(r) - \Delta G_{\mathrm{Cl}}(0))/B = g_{\mathrm{ClD}}(r) + (A/B)g_{\mathrm{ClO}}(r) + (C/B)g_{\mathrm{ClC}}(r) + (D/B)g_{\mathrm{ClNa}}(r) + (E/B)g_{\mathrm{ClCl}}(r). \tag{10}$$

If it is assumed that there is no inner sphere complexing of Cl^- by Na^+ then integration of the first peak over the range $1.84 \leqslant r$ (Å) $\leqslant 2.64$ gives $\overline{n}_{\mathrm{D}}^{\mathrm{Cl}} = 4.1(2)$.

The second peak at 3.15(3) Å is not sensitive to the choice of $\epsilon'(k)$ function and is therefore considered to be a real feature. It can be assigned to the mean Cl^-–hydroxyl-oxygen distance r_{ClO}, although there is overlap between $g_{\mathrm{ClO}}(r)$ and the remaining Cl^-–EG-molecule-species correlations. Indeed it is not possible to

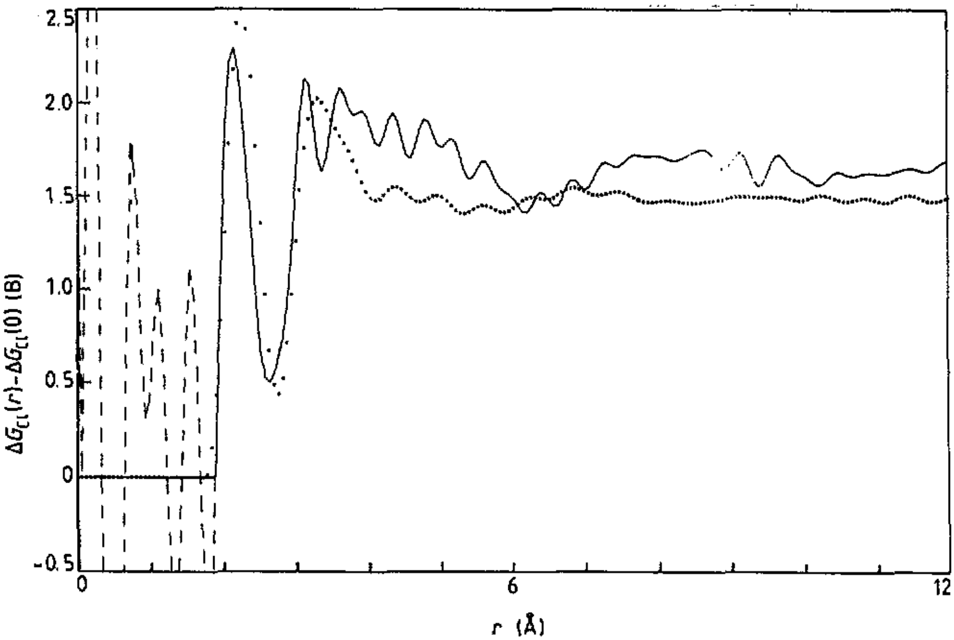

Figure 4. $(\Delta G_{Cl}(r) - \Delta G_{Cl}(0))/B$, as specified by equation (10), for a 0.999 molal solution of NaCl in EG (full curve) and for a 3.62 molal solution of NaCl in D_2O (dots). In the case of the D_2O solution $C = 0$ and the other constants are given by Barnes *et al* (1987). The EG function was obtained by Fourier transforming the data given in figure 2(*b*) and the dashed curve gives the unphysical low-*r* features that result from this procedure.

distinguish uniquely between the remaining correlations, although they are grouped into two broad features, i.e. one for $3.37 \lesssim r$ (Å) $\lesssim 6.2$ and a weaker one for $6.2 \lesssim r$ (Å) $\lesssim 10$. Beyond ~ 10 Å there is no evidence for ordering, in contrast to the coordination environment observed for Ni^{2+} in EG solution (Lond *et al* 1991).

With the present assignment, and assuming $r_{OD} = 0.99$ Å, the mean tilt angle ψ (see figure 5) is within the range 0–6°, i.e. the hydrogen bond formed between Cl^- and the hydroxyl group, $Cl^- \ldots$ D–O, is roughly linear†. A survey of the literature shows that this feature is indeed typical in aqueous and methanolic solution. For example, in aqueous solution approximately linear $Cl^- \ldots$ D–O hydrogen bonds have been found from neutron diffraction experiments aimed at measuring $\Delta G_{Cl}(r)$ (Cummings *et al* 1980, Powell *et al* 1988) and the ion–ion $g_{\alpha\beta}(r)$ (Neilson and Enderby 1983, Copestake *et al* 1985); neutron diffraction experiments in which H/D substitution was employed in order to separate the $g_{ClD}(r)$ and $g_{ClO}(r)$ contributions to $\Delta G_{Cl}(r)$ (Powell 1989); experiments in which neutron and x-ray diffraction results were combined (Narten *et al* 1973); and a host of computer simulation studies in which a variety of different intra- and inter-atomic potentials have been applied (e.g. Impey *et al* 1983, Spohr *et al* 1988, Sprik *et al* 1990, Dang *et al* 1991). In methanolic solution, molecular dynamics studies (using different model potentials)

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† There are clearly limitations in using just a single angle in order to describe the orientation of the EG molecules with respect to Cl^- (these limitations are discussed by Szász *et al* (1982) for the case of Cl^- in water). Nevertheless, the measured $\Delta G_{Cl}(r)$ shows that the hydroxyl group points almost directly at the Cl^- ion.

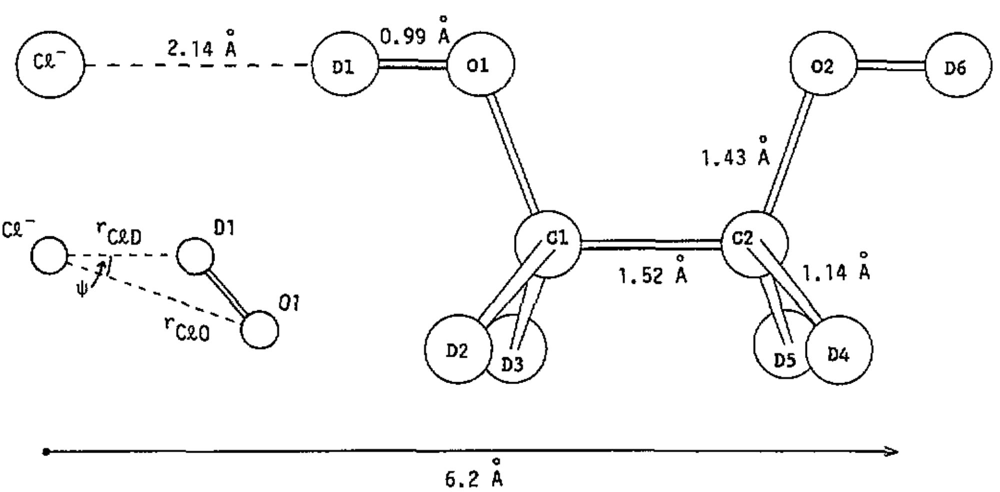

Figure 5. Sketch of a possible Cl⁻–EG-molecule conformation for a solution of NaCl in EG. The EG molecule is drawn without an intramolecular O–D…O hydrogen bond although this configuration (see Lond *et al* 1991) cannot be ruled out on the basis of the present data. The inset specifies the angle of tilt ψ.

also give linear Cl⁻ … H–O hydrogen bonds (Impey *et al* 1987, Marx *et al* 1991). The question, however, remains as to whether the EG molecules act as monodentate ligands with respect to Cl⁻, as in the case of water and methanol, or whether bidentate coordination is feasible.

The Cl⁻ complex was therefore simulated by a 'ball and stick' approach using a molecular modelling kit. In view of the measured value of $\bar{n}_{\mathrm{D}}^{\mathrm{Cl}}$ bidentate coordination complexes were modelled by assuming either square-planar or tetrahedral bonding of the hydroxyl deuterium to the Cl⁻ ion. The bond lengths for the EG molecule were fixed at the values obtained for the gas state (figure 5) and the $\mathrm{C\hat{O}D}$, $\mathrm{C\hat{C}O}$ and $\mathrm{C\hat{C}D}$ angles were taken to be tetrahedral (see Lond *et al* 1991). r_{ClD} was fixed at the measured value of 2.14 Å and a variety of $\mathrm{Cl\hat{D}O}$ angles (e.g. 90°, 109°, 120°) were adopted.

It was found that, irrespective of the precise configuration of the EG molecule with respect to Cl⁻, the $\mathrm{Cl\hat{D}O}$ angle has to remain $\ll 180°$ if there is *not* to be a considerable distortion of the EG ligand as manifested by, for instance, an intramolecular angle $\mathrm{C\hat{C}O}$ that is considerably larger than its tetrahedral value. The effect of reducing the $\mathrm{Cl\hat{D}O}$ angle from 180° is to shorten the modelled r_{ClO} distance so that it approaches the *minimum* after the first peak in $\Delta G_{\mathrm{Cl}}(r)$. A bidentate coordinating nature for EG was thereby ruled out and it was checked that the alternative, i.e. monodentate coordinating behaviour, is *not* subject to elimination on steric hindrance grounds.

A full description of the $\mathrm{Cl(EG)_4^-}$ conformations cannot be given on the basis of the present data since there is considerable overlap of the $g_{\alpha\beta}(r)$ for $3.37 \lesssim r$ (Å) $\lesssim 6.2$. However, a monodentate coordinating nature for EG is consistent (figure 5) with the first broad feature in $\Delta G_{\mathrm{Cl}}(r)$ extending out to $\simeq 6.2$ Å (figure 4). Moreover, there is sufficient area under $\Delta G_{\mathrm{Cl}}(r)$ within this range to accommodate the remaining species, which comprise the four nearest-neighbour EG ligands. Indeed a maximum of 6.4 additional EG molecules can be accommodated which, together with the observation that $\Delta G_{\mathrm{Cl}}(r) \gg \Delta G_{\mathrm{Cl}}(0)$ at the 6.2 Å minimum, suggests an overlap between the primary and secondary solvation shells of the Cl^- ion. The number of additional EG molecules is of course reduced if allowance is made for neighbouring Na^+ or Cl^- within the $3.37 \lesssim r$ (Å) $\lesssim 6.2$ range.

In figure 4 the function $(\Delta G_{\mathrm{Cl}}(r) - \Delta G_{\mathrm{Cl}}(0))/B$ for the present solution is compared with that obtained for a 3.62 molal solution of NaCl in D_2O (Barnes *et al* 1987). The first peak in *both* functions gives $g_{\mathrm{ClD}}(r)$ for the nearest-neighbour interaction. It is found that the position of $g_{\mathrm{ClD}}(r)$ is shifted to a smaller r-value for the EG solution, 2.14 Å compared with 2.27 Å, and that its integration gives rise to a smaller coordination number $\overline{n}_{\mathrm{D}}^{\mathrm{Cl}}$, i.e. 4.1(2) compared with 5.6(2). This value for $\overline{n}_{\mathrm{D}}^{\mathrm{Cl}}$ in the D_2O solution is typical of that measured for other aqueous solutions in which significant inner-sphere complexing of Cl^- by the cation is not thought to occur (Powell *et al* 1988, Salmon 1989).

In the present comparison the Cl^-:solvent-molecule ratio is approximately the same, at about 1:14 for both solutions, but the relative permittivity of water is significantly higher than that of EG (37.7 compared with 78.5 at 25 °C, Burgess 1978). Inner-sphere complexing within the EG solution cannot, therefore, be ruled out, and future neutron diffraction experiments on strong electrolytes in EG would prove helpful in determining the extent to which the observed reduction in $\overline{n}_{\mathrm{D}}^{\mathrm{Cl}}$, in going from aqueous to EG solution, is a property of the change in solvent rather than an effect caused by ionic association. However, it is noteworthy that the D/B ratio in equation (10) is relatively small (6.26×10^{-3}) and that in *molten* NaCl the first peak in $g_{\mathrm{NaCl}}(r)$ is at 2.78(2) Å while its low-r cut-off is at $\simeq 2.1$ Å (Biggin and Enderby 1982) which places the majority of this function *beyond* the region of the first peak in $\Delta G_{\mathrm{Cl}}(r)$. Furthermore, on changing the solvent from water to methanol, a reduction in the solvation number of Cl^- from six to four has been inferred from infra-red and nuclear magnetic resonance experiments (Symons 1983, Robinson and Symons 1985) and a reduction in the Cl^- solvation number, for the same change of solvent, has also been found in one of the molecular dynamics studies (Impey *et al* 1987).

6. Conclusion

The present data show that EG molecules act as monodentate ligands when coordinating to Cl^- in EG solution. This behaviour is in contrast with that observed for a solution of Ni^{2+} in EG where bidentate coordination gives rise to $\mathrm{Ni(EG)}_3^{2+}$ tris-chelate complexes (Lond *et al* 1991). The EG ligands bind to Cl^- via a hydrogen bond $\mathrm{Cl}^- \ldots \mathrm{D{-}O}$ which is approximately linear and of length 2.14(3) Å. A survey of the literature shows that linear $\mathrm{Cl}^- \ldots \mathrm{D{-}O}$ bonds are also a feature in aqueous and in methanolic solution. The reduction of the coordination number $\overline{n}_{\mathrm{D}}^{\mathrm{Cl}}$ from $\simeq 6$ to $\simeq 4$ on changing the solvent from water to EG may arise from inner-sphere complexing of the cation by the anion, but there is no strong evidence supporting the presence of this effect.

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