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A neutron diffraction study on the structure of Cl^- solutions in hydrogen-bonded molecular solvents

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Abstract. The method of isotopic substitution in time-of-flight neutron diffraction is applied to measure the coordination environment of Cl^- in a 0.999(2) molal solution of NaCl in fully deuterated glycerol. It is shown that the glycerol molecules act as monodentate ligands to give a $\text{Cl}(\text{glycerol})_3^-$ complex that comprises $\text{Cl}^- \cdots \text{D}-\text{O}$ hydrogen bonds, which are approximately linear and of length 2.17(3) Å. The results are compared with those obtained for the solvation of Cl^- in solutions of its salts in water, methanol and ethylene glycol (EG). A reduction from approximately six (water) to four (methanol and EG) to three (glycerol) is found for the Cl^- solvation number as the solvent is changed and, for all four solvents, the $\text{Cl}^- \cdots \text{D}-\text{O}$ hydrogen bond is typically linear.

1. Introduction

The object of this paper is to present first results on the coordination environment of the chloride ion in fully deuterated glycerol or glycerine ($\text{DOCD}_2\text{CD}(\text{OD})\text{CD}_2\text{OD}$) and hence to observe how the Cl^- complex alters as the molecular solvent is changed from water to ethylene glycol (EG) to glycerol. The Cl^- ion is a typical counter-ion in electrolyte solution and there is a considerable body of knowledge on its coordination environment in water at the partial pair distribution function level from studies using neutron diffraction (e.g. Powell *et al* 1993), computer simulation (e.g. Zhu and Robinson 1992), extended reference interaction site model (RISM) theory (e.g. Hummer and Soumpasis 1992) and other integral equation techniques (Friedman *et al* 1991). Information on the coordination complex of Cl^- in EG has also been made available by a recent neutron diffraction study (Salmon and Lond 1992). NaCl was chosen as the salt since it is regarded as a 'strong electrolyte' in the respect that its solutions in both EG and glycerol are, at least at low concentrations, fully dissociated (Santos and Spiro 1972, Blanco *et al* 1989).

Motivation for studying the higher alcohols EG and glycerol stems, in part, from certain similarities between these solvents and water. For example, all three liquids are hydrogen bonded and they have large relative permittivities (table 1), which makes them good solvents for ionic salts. Also the ratio of the halide to alkali metal species ionic molar conductivities (i.e. the ratio of their ionic mobilities) is similar in all three protic solvents, although the absolute values scale roughly with the solvent viscosity (table 1). It is natural to ask whether these observations can be correlated with similarities in the structure of the Cl^- complex. There has also been a recent attempt at modelling the structure of liquid glycerol using the molecular dynamics (MD) method (Root and Stillinger 1989), which is a first step to simulating the structure of electrolytes in the higher alcohols.

In section 2 the essential theory behind the isotopic substitution method in neutron diffraction, as applied to ionic solutions, is outlined. The experimental method and results

Table 1. The viscosity, η , and relative permittivity, ϵ_r , of pure solvents water, EG and glycerol at 25 °C (Blanco *et al* 1989). The ionic molar conductivities at infinite dilution, λ^0 , for Na⁺ and Cl⁻ in these solvents at 25 °C are also given.

| Solvent | η (10 ⁻⁴ Pa s) | ϵ_r | λ^0 (Na ⁺) (mS m ² mol ⁻¹) | λ^0 (Cl ⁻) (mS m ² mol ⁻¹) | λ^0 (Cl ⁻)/ λ^0 (Na ⁺) |
|----------|-----------------------------------|--------------|--|--|--|
| Water | 8.90 | 78.3 | 5.020 ^a | 7.639 ^a | 1.522 |
| EG | 168.4 | 40.7 | 0.3107 ^b | 0.5073 ^b | 1.633 |
| Glycerol | 9100 | 42.7 | 0.0125 ^c | 0.0174 ^c | 1.392 |

^a Kay and Evans (1966).

^b Santos and Spiro (1972).

^c Blanco *et al* (1989).

are then given in, respectively, sections 3 and 4, with special attention being paid to the nature of the corrections as there was a small imbalance between the hydrogen content of the two solutions used for the diffraction experiments. The results are finally compared in section 5 with those obtained for the Cl⁻ complex in solutions of its salts in water, methanol and EG.

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, time-of-flight neutron diffraction experiments are conducted on two fully deuterated glycerol 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. The measured intensity at each scattering angle, 2θ , 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 (Soper *et al* 1989). The quantity thus derived for each solution is the observed total structure factor $F_0(k, \theta)$ given by

$$F_0(k, \theta) = F(k) + \sum_{\alpha=1}^{\mu} c_{\alpha} \frac{\sigma_{\alpha}^s}{4\pi} [1 + \epsilon_{\alpha}(k, \theta)] \quad (1)$$

where k is the elastic 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. $\epsilon_{\alpha}(k, \theta)$ is a term that, provided the data have been properly corrected, arises from inelasticity effects owing to a departure from the static approximation in the case of neutron scattering from liquids (Powles 1973, 1978, Egelstaff 1987, Howe *et al* 1989). This problem is most pronounced when light nuclei are present but is reduced in the present case by performing the experiments with the SANDALS instrument (Soper 1989) at the ISIS pulsed neutron source. $F(k)$ is a linear sum of the partial structure factors, $S_{\alpha\beta}(k)$, whose Fourier transforms yield the partial pair distribution functions $g_{\alpha\beta}(r)$:

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

with

$$g_{\alpha\beta}(r) = 1 + \frac{1}{2\pi^2 n_0 r} \int_0^\infty [S_{\alpha\beta}(k) - 1] k \sin(kr) dk \quad (3)$$

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

$$\bar{n}_\alpha^\beta = 4\pi n_0 c_\beta \int_{r_1}^{r_2} r^2 g_{\alpha\beta}(r) dr \quad (4)$$

which is the expression used to calculate coordination numbers in the present work.

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

$$\Delta_{\text{Cl}}^0(k, \theta) = H^{\text{N}} F_0(k, \theta) - I^{37} F_0(k, \theta) = \Delta_{\text{Cl}}(k) + J + \varepsilon'(k, \theta). \quad (5)$$

In equation (5), H and I are empirical constants, which are introduced to allow for any multiplicative error on an observed total structure factor. If the data have been properly corrected $H = I = 1$; else they are chosen such that the left hand side of equation (1) is rewritten as either $H^{\text{N}} F_0(k, \theta)$ or $I^{37} F_0(k, \theta)$. $J = c_{\text{Cl}}(\sigma_{\text{Cl}}^{\text{S}} - \sigma_{\text{Cl}}^{\text{N}})/4\pi$ and pertains to the self-scattering from the nuclei and $\varepsilon'(k, \theta)$ is a residual inelasticity correction. The first-order difference function $\Delta_{\text{Cl}}(k)$ is given by

$$\Delta_{\text{Cl}}(k) = A[S_{\text{ClO}}(k) - 1] + B[S_{\text{ClD}}(k) - 1] + C[S_{\text{ClC}}(k) - 1] + D[S_{\text{ClNa}}(k) - 1] \\ + E[S_{\text{ClCl}}(k) - 1] \quad (6)$$

where $\Delta b = b_{\text{Cl}} - b_{\text{Cl}}$, $A = 2c_{\text{Cl}}c_{\text{O}}b_{\text{O}}\Delta b$, $B = 2c_{\text{Cl}}c_{\text{D}}b_{\text{D}}\Delta b$, $C = 2c_{\text{Cl}}c_{\text{C}}b_{\text{C}}\Delta b$, $D = 2c_{\text{Cl}}c_{\text{Na}}b_{\text{Na}}\Delta b$, $E = c_{\text{Cl}}^2[b_{\text{Cl}}^2 - b_{\text{Cl}}^2]$ and the real space picture is obtained by Fourier transformation, namely

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

An important property of each $\Delta_{\text{Cl}}^0(k, \theta)$ function is that, provided the solutions are identical in every respect (except for their Cl isotope compositions), the $\varepsilon_\alpha(k, \theta)$ terms in equation (1) will be, to first order, identical for both solutions so that they cancel to give a negligible $\varepsilon'(k, \theta)$ term in equation (5). The validity of this statement can be tested on several accounts (e.g. Salmon and Benmore 1992). Firstly, since $S_{\alpha\beta}(k) \rightarrow 1$ in the limit as $k \rightarrow \infty$, $\Delta_{\text{Cl}}^0(k, \theta)$ should at a particular 2θ value oscillate about the calculated self-scattering value, J . Secondly, since $g_{\text{Cl}\beta}(r) = 0$ at r -values below the distance of closest approach to Cl^- (that is, r_{min}), $\Delta G_{\text{Cl}}(r)$ should be equal to the calculated limit

$\Delta G_{\text{Cl}}(0) = -(A + B + C + D + E)$ at low r . In practice $\Delta G_{\text{Cl}}(r)$ 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 $\varepsilon'(k, \theta)$ term giving rise to a residual slope on $\Delta_{\text{Cl}}^0(k, \theta)$). However, provided these effects are small, setting $\Delta G_{\text{Cl}}(r)$ equal to the $\Delta G_{\text{Cl}}(0)$ limit for $r \leq r_{\text{min}}$ and Fourier back-transforming will yield a function $\tilde{\Delta}_{\text{Cl}}(k)$ that is in close agreement at all k -values with $\Delta_{\text{Cl}}(k)$. Thirdly, the sum-rule relation

$$\int_0^{\infty} \Delta_{\text{Cl}}(k) k^2 dk = 2\pi^2 n_0 \Delta G_{\text{Cl}}(0) \quad (8)$$

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

3. Experimental method

The 0.999(2) molal (mol kg^{-1}) solutions were made from $\text{Na}^{\text{N}}\text{Cl}$ (99.999%, Aldrich Gold Label) and Na^{37}Cl (4.33% ^{35}Cl , 95.67% ^{37}Cl , Isotec Incorporated) which were dried on a vacuum line under 0.1 Torr pressure at 160 °C for ~ 24 h. The solutions were prepared by mass in a high-purity Ar-filled glove box by using fully deuterated glycerol (Cambridge Isotope Laboratories). The H content of this glycerol was found to be 1.80(7)% by means of proton magnetic resonance experiments in which a solution of 2-methyl-2-propanol in D_2O was used as a reference sample. The density of the solutions was found, by using a Paar DMA602 apparatus, to be 1.403(3) g cm^{-3} at 20 °C, which gives $n_0 = 0.1133(2) \text{ \AA}^{-3}$. The coherent neutron scattering length of the anion in the $^{\text{N}}\text{Cl}$ 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) 1.057(10), 3.15(3), 1.21(1), 0.0220(2) and 0.0395(2) respectively. The scattering length values were taken from Sears (1992).

The diffraction experiments were performed using the SANDALS instrument at ISIS (Soper 1989). Data were collected in six groups of detectors, at mean 2θ values of 11.8°, 13.1°, 14.6°, 16.2°, 18.1° and 21.1°, which had a constant resolution $\Delta k/k = 0.03$. Diffraction patterns were taken for (i) the solutions in their container at ~ 20 °C; (ii) the empty solution container; (iii) the instrumental background with the sample absent and (iv) a V standard plate of thickness 3.412(7) mm. The solution container was a hollow slab of 1 mm wall thickness and 4 mm spacing and was fabricated from a Ti–Zr alloy having a nominal coherent scattering length of zero. Owing to the high solution viscosity at room temperature the container was filled by gently warming both it and the solution in a high-purity Ar-filled glove box. The data analysis was made using the ATLAS suite of programs (Soper *et al* 1989). The wavelength-dependent total cross section of the solutions was found by using the tabulated (Sears 1992) absorption and free-atom cross sections for Na and Cl and the measured cross section for glycerol. The latter quantity was determined by a transmission experiment using the LAD instrument at ISIS. Measured values were used for the wavelength-dependent total cross section of both Ti–Zr and V.

4. Results

The $F_0(k, \theta)$ for the six detector groups showed a significant 2θ dependence, which could not be attributed solely to different inelasticity correction terms. However, it is of interest

that these functions did not exhibit a so-called first sharp diffraction peak (FSDP) or pre-peak at low k ($\sim 0.5 \text{ \AA}^{-1}$ —see figure 1), unlike solutions of $\text{Ni}(\text{CF}_3\text{SO}_3)_2$ in glycerol (Okan and Salmon 1994) and in EG (Lond *et al* 1991), which indicates the absence of significant intermediate-range ordering. Also there is no high- k droop, which is a feature of the total structure factor for deuterated liquids as measured using reactor-based instruments (e.g. Salmon and Lond 1992).

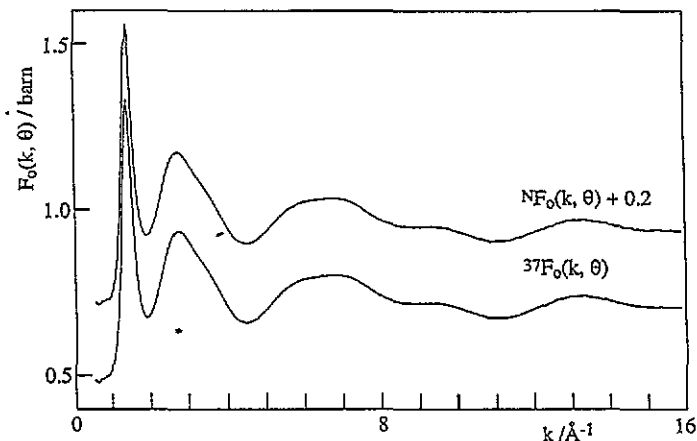


Figure 1. The measured functions ${}^N F_0(k, \theta)$ and ${}^{37} F_0(k, \theta)$ at $2\theta = 21.1^\circ$ for a 0.999 molal solution of NaCl in fully deuterated glycerol.

$\Delta_{\text{Cl}}(k)$ was formed for each detector group using equation (5) with $H = I = 1$. It was found that the corresponding $\Delta G_{\text{Cl}}(r)$ did not oscillate around the correct low- r limit. The problem was traced to an incorrect normalization of the ${}^N F_0(k, \theta)$ functions, which most likely arose from a small bubble in the highly viscous solution, and was solved by setting $H = 1.015$ (a variation of H by ± 0.005 had no significant effect on the results) with $I = 1$. However, as shown in figure 2(a), there remained a disagreement between $\Delta_{\text{Cl}}(k)$ and $\tilde{\Delta}_{\text{Cl}}(k)$ for each detector group, which shows that $\varepsilon'(k, \theta) \neq 0$. The disagreement occurred at low k and was largest for the $2\theta = 21.1^\circ$ detector group, which suggests that it is most likely caused by a small hydrogen imbalance between the two solutions. This suggestion is confirmed (see figure 2(b)) by the similar shape of the $F_0(k, \theta)$ functions for H_2O as measured using SANDALS (Soper 1994) and the difference $[\Delta_{\text{Cl}}(k) - \tilde{\Delta}_{\text{Cl}}(k)]$ for each detector group.

The effect of a small hydrogen imbalance will, owing to the large incoherent cross section of the proton, have its most significant effect on the terms involving σ_a^s and $\varepsilon_\alpha(k, \theta)$ in equation (1) whilst leaving the $F(k)$ term essentially unchanged. The excess atomic fraction of hydrogen in the ${}^N\text{Cl}$ sample was estimated by noting the factor by which the $F_0(k, \theta)$ for H (as obtained from the $F_0(k, \theta)$ for H_2O) had to be multiplied in order to be placed on the same scale as the function $[\Delta_{\text{Cl}}(k) - \tilde{\Delta}_{\text{Cl}}(k)]$ for each detector group. It was also estimated by noting the magnitude by which the J value required in equation (5) was larger than the calculated value $J = 8.5$ mb. The H imbalance was found to be small, amounting to between 1 and 4% of the total D and H content of the solution.

The correction terms were estimated by setting $\varepsilon'(k, \theta) = [\Delta_{\text{Cl}}(k) - \tilde{\Delta}_{\text{Cl}}(k)]$ for each detector group. It was found that the revised $\Delta_{\text{Cl}}(k)$ functions for each group agreed within experimental error and they were therefore summed to give the final $\Delta_{\text{Cl}}(k)$ function of

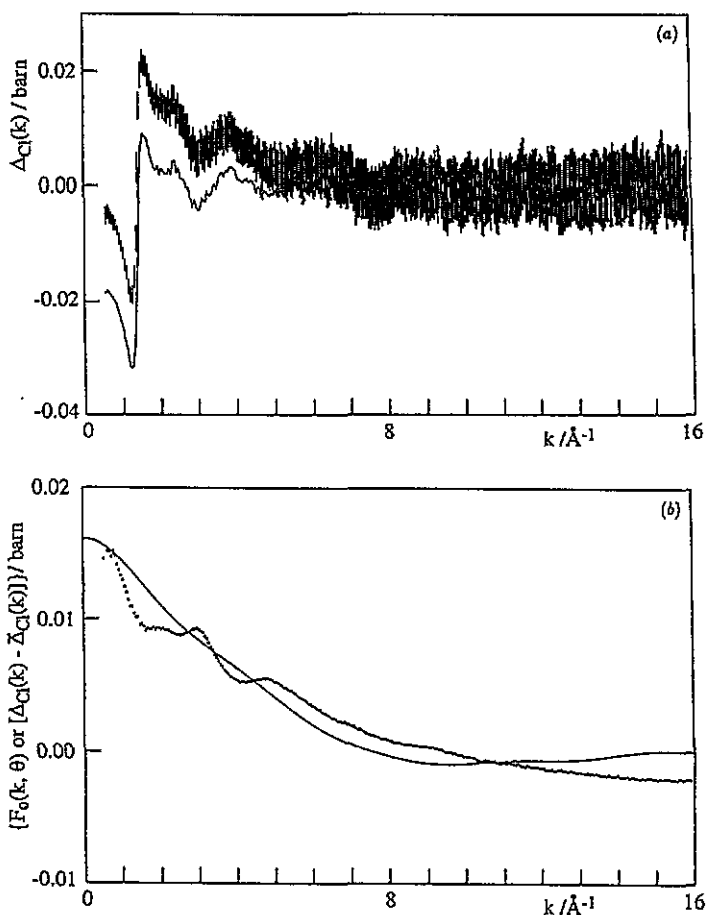


Figure 2. (a) $\Delta_{C1}(k)$ at $2\theta = 21.1^\circ$ obtained by combining the $F_0(k, \theta)$ of figure 1 using equation (5) with $H = 1.015$, $I = 1$, $e'(k, \theta) = 0$ and $J = 44$ mb. The bars give the statistical errors on the data and the full curve gives $\bar{\Delta}_{C1}(k)$, the Fourier backtransform of the corresponding $\Delta G_{C1}(r)$ after the unphysical oscillations at $r \leq r_{\min}$ have been set to the calculated $\Delta G_{C1}(0)$ limit. (b) A comparison between $[\Delta_{C1}(k) - \bar{\Delta}_{C1}(k)]$ at $2\theta = 21.1^\circ$ (full curve) and a scaled version of $F_0(k, \theta)$ for H_2O at the same scattering angle (dotted curve).

figure 3(a), which satisfies the sum rule relation (equation (8)). As shown in the figure 3, the final $\Delta_{C1}(k)$ is qualitatively similar to that observed for both a 0.999 molal solution of NaCl in EG (Salmon and Lond 1992) and a 3.62 molal solution of NaCl in D_2O (Barnes *et al* 1987).

5. Discussion

$\Delta G_{C1}(r)$ was obtained both by direct Fourier transformation (FT) and by the minimum noise (MIN) reconstruction method of Soper (Soper 1990, Soper *et al* 1993). The object of the latter method is to avoid some of the problems associated with direct FT and to provide a smooth r -space function compatible with the measured $\Delta_{C1}(k)$. The first peak in $\Delta G_{C1}(r)$ occurs at 2.17(3) Å (MIN solution) or 2.20(3) Å (FT solution). It is the most prominent feature and is assigned to $g_{CID}(r)$ because the D atoms of the glycerol hydroxyl groups are

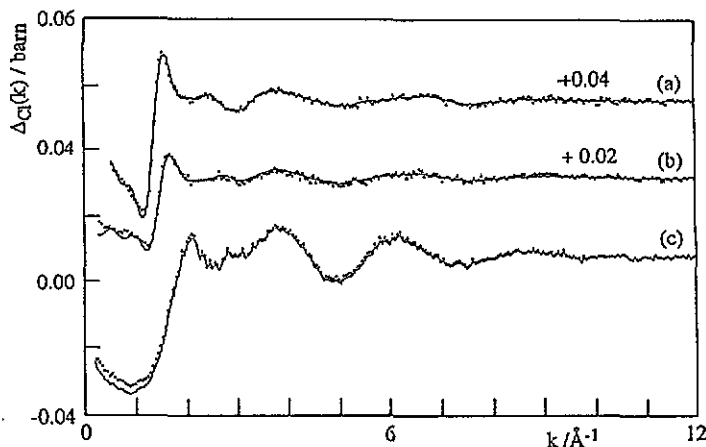


Figure 3. (a) The final $\Delta_{\text{Cl}}(k)$ function for a 0.999 molal solution of NaCl in glycerol as obtained by combining the data for the six detector groups using equation (5) with $H = 1.015$, $I = 1$ and $\varepsilon'(k, \theta) = [\Delta_{\text{Cl}}(k) - \bar{\Delta}_{\text{Cl}}(k)]$ for each detector group. The mean J value for the six detector groups was 44 mb. The filled circles give the data points and the full curve gives the MIN solution. (b) $\Delta_{\text{Cl}}(k)$ for a 0.999 molal solution of NaCl in EG (filled circles and full curve as in (a)). (c) $\Delta_{\text{Cl}}(k)$ for a 3.62 molal solution of NaCl in D_2O . The filled circles give the data points and the full curve gives $\bar{\Delta}_{\text{Cl}}(k)$, the Fourier backtransform of the corresponding $\Delta G_{\text{Cl}}(r)$ after the unphysical oscillations at $r \leq r_{\text{min}}$ have been set to the calculated $\Delta G_{\text{Cl}}(0)$ limit.

expected to be adjacent to Cl^- on chemical grounds. The r -space representation of the data is therefore plotted in figure 4(a) as the function

$$\begin{aligned} [\Delta G_{\text{Cl}}(r) - \Delta G_{\text{Cl}}(0)]/B = & g_{\text{ClD}}(r) + (A/B)g_{\text{ClO}}(r) + (C/B)g_{\text{ClC}}(r) \\ & + (D/B)g_{\text{ClNa}}(r) + (E/B)g_{\text{ClCl}}(r). \end{aligned} \quad (9)$$

Integration of the first peak over the range $1.84 \leq r \text{ (\AA)} \leq 2.64$ using equation (4) gives $\bar{n}_{\text{Cl}}^{\text{D}} = 3.0(2)$ for both the MIN and FT solutions. This coordination number should be robust because, even in the event of inner sphere complexing of Cl^- by Na^+ , $g_{\text{NaCl}}(r)$ is given a relatively small weighting (the D/B ratio is 7.0×10^{-3}) and it is not expected to overlap substantially with the first peak in $\Delta G_{\text{Cl}}(r)$. For example, a comparison with the measured structure of molten NaCl (Biggin and Enderby 1982) places the majority of the first peak in $g_{\text{NaCl}}(r)$ beyond the region of the first peak in $\Delta G_{\text{Cl}}(r)$. Furthermore, in an MD simulation on the structure of a 1.791 molal aqueous NaCl solution (Zhu and Robinson 1992) the first peak in $g_{\text{NaCl}}(r)$ is at 2.6 Å, which places it at the minimum after the first peak where $\Delta G_{\text{Cl}}(r) \simeq \Delta G_{\text{Cl}}(0)$, and a similar result is found from extended RISM calculations on NaCl in H_2O (Hummer and Soumpasis 1992). Also, the first minimum in the mean force potential for the Na^+-Cl^- ion pair in aqueous solution was calculated to be 2.9 Å from a constrained MD simulation (Guàrdia *et al* 1991) while an extended RISM calculation for the same potential in methanolic solution found the first minimum to be about the contact separation of 2.8 Å (Hirata and Levy 1987).

The second feature in $\Delta G_{\text{Cl}}(r)$ is broad ($2.64 \leq r \text{ (\AA)} \leq 6.75$) and has either a shoulder (MIN solution) or a peak (FT solution) at 3.07(3) Å, which is assigned to the mean Cl^- to hydroxyl O distance r_{ClO} . This assignment may be challenged because the feature is not sharply defined and there will be overlap between $g_{\text{ClO}}(r)$ and the remaining $g_{\text{Cl}\beta}(r)$ that

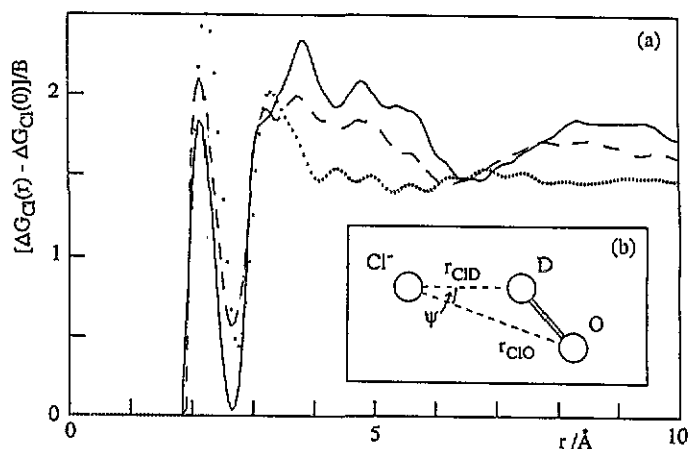


Figure 4. (a) $[\Delta G_{Cl}(r) - \Delta G_{Cl}(0)]/B$, as specified by equation (9), for a 0.999 molal solution of NaCl in glycerol (MIN, full curve), for a 0.999 molal solution of NaCl in EG (MIN, broken curve) and for a 3.62 molal solution of NaCl in D_2O (FT, dotted curve). In the case of the D_2O solution $C = 0$ in equation (9). (b) The definition of the tilt angle ψ .

occur under the broad second feature. However, the distance is in agreement with the value $r_{ClO} = 3.1(1)$ Å obtained from a recent isotopic substitution experiment in which both $g_{ClO}(r)$ and $g_{ClD}(r)$ were measured for a solution of $NiCl_2$ in water (Powell *et al* 1993). The question then arises as to the orientation of the glycerol molecule with respect to the Cl^- ion as specified, for example, by the so-called tilt angle ψ , which is defined in figure 4(b). The value of ψ (or any of the other angles in the $ClDO$ triangle) cannot be assigned uniquely (because of the finite widths of the first and second peaks in $\Delta G_{Cl}(r)$) and its probability density cannot, unfortunately, be mapped reliably from the measured $\Delta G_{Cl}(r)$ (e.g. Szász *et al* 1982, Powell and Neilson 1990, Powell *et al* 1993). Nevertheless, if the orientation is estimated by taking r_{ClD} and r_{ClO} from the $\Delta G_{Cl}(r)$ peak positions and if $r_{OD} = 0.98$ Å it is found that $4^\circ \leq \psi \leq 11^\circ$, i.e. the hydrogen bond formed between Cl^- and the hydroxyl group, $Cl^- \cdots D-O$, is approximately linear.

A 'ball-and-stick' approach was used to investigate the possibility of the glycerol molecule acting as either a bidentate or tridentate coordinating ligand with respect to the Cl^- ion. The motivation was provided by the existence of three hydroxyl groups on each solvent ligand. In the modelling procedure the glycerol molecule bond lengths were fixed at $r_{CC} = 1.52$ Å, $r_{CO} = 1.43$ Å, $r_{CD} = 1.09$ Å and $r_{OD} = 0.98$ Å (van den Enden *et al* 1983, Champeney *et al* 1986, Garawi *et al* 1987); the $\hat{C}OD$, $\hat{C}CO$ and $\hat{C}CD$ angles were taken to be tetrahedral; r_{ClD} was fixed at the measured value of 2.20 Å; and a variety of $\hat{Cl}DO$ angles were adopted assuming $\hat{D}ClD$ angles of 90° , 109° or 120° . It was found that, irrespective of the precise conformation of the glycerol molecule with respect to Cl^- , $\hat{Cl}DO$ angles in the range 120 – 180° led to a considerable distortion of the glycerol ligand as manifested by, for instance, an intramolecular angle $\hat{C}CO$ that is much larger than its tetrahedral value. The effect of reducing the $\hat{Cl}DO$ angle from 120° was to shorten the modelled r_{ClO} distance to such an extent as to place it under the first peak in $\Delta G_{Cl}(r)$, which is, however, already assigned to $g_{ClD}(r)$. A bidentate or tridentate coordinating nature for glycerol was therefore ruled out: glycerol acts as a monodentate ligand with respect to Cl^- . The broad second feature in $\Delta G_{Cl}(r)$ does not approach the value $\Delta G_{Cl}(0)$ on its high- r side (at about 6.8 Å) and is therefore consistent with there being overlap between the three glycerol molecules in the primary solvation shell of Cl^- (a number deduced from the measured \bar{n}_{Cl}^D value) and other

glycerol molecules. The number of additional solvent molecules cannot be unambiguously deduced on the basis of the present data owing to the presence of ion-ion correlations in $\Delta G_{\text{Cl}}(r)$. However, a maximum number of about seven is obtained for the range $2.64 \leq r$ (Å) ≤ 6.75 by neglecting the contribution of the ion-ion terms to the second feature in the $\Delta G_{\text{Cl}}(r)$ function.

Table 2. Parameters for solutions of NaCl in various fully deuterated solvents. The solution concentrations are expressed in terms of R which is the Cl⁻: solvent molecule ratio.

| Solvent | R | T (°C) | r_{ClD} (Å) | $\bar{n}_{\text{Cl}}^{\text{D}}$ | Reference |
|----------|--------|----------|----------------------|----------------------------------|----------------------------|
| Water | 1:13.8 | 21 | 2.27(2) | 5.6(2) | Barnes <i>et al</i> (1987) |
| EG | 1:14.7 | 23 | 2.14(3) ^a | 4.1(2) | Salmon and Lond (1992) |
| Glycerol | 1:10 | 20 | 2.17(3) | 3.0(2) | present work |

^a A residual hydrogen correction, $\varepsilon'(k)$, was applied to the EG data. The quoted r_{ClD} value corresponds to the $\varepsilon'(k)$ function that gave the smoothest $\Delta G_{\text{Cl}}(r)$. Other $\varepsilon'(k)$ functions gave $r_{\text{ClD}} = 2.21(3)$ Å.

In figure 4 the function $[\Delta G_{\text{Cl}}(r) - \Delta G_{\text{Cl}}(0)]/B$ for the present solution is compared with that obtained for solutions of NaCl in fully deuterated EG and in D₂O. The first peak gives $g_{\text{ClD}}(r)$ for the nearest-neighbour interaction in all of the solutions and its integration reveals a steady reduction in $\bar{n}_{\text{Cl}}^{\text{D}}$ from approximately six to three as the solvent is changed from D₂O to glycerol (table 2). On changing the solvent from water to methanol, a reduction in the solvation number of Cl⁻ from six to four has also 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 an MD study (Impey *et al* 1987). In the case of glycerol the minimum after the first peak at 2.64 Å approaches its limiting value of zero, which shows that there is a near absence of correlations involving the Cl⁻ ion. Furthermore, $g_{\text{Cl}\beta}(r)$ is proportional to the probability of finding a particle of type β at a distance r away from the Cl⁻ ion. Thus the deep minimum shows that exchange of the glycerol D atoms with Cl⁻ proceeds by a mechanism wherein their binding time is much longer than their time of transit to distances beyond the first peak in $\Delta G_{\text{Cl}}(r)$. The significantly higher viscosity of the glycerol solutions (table 1) suggests that the magnitude of this D binding time is much longer than for water ($\sim 5 \times 10^{-12}$ s, Hertz 1973) or for EG molecules. In glycerol as in water (Powell *et al* 1993), methanol (Impey *et al* 1987, Marx *et al* 1991) and EG (Salmon and Lond 1992) the solvent ligands bind to Cl⁻ by forming an essentially linear Cl⁻ ···D-O hydrogen bond.

6. Conclusion

The higher alcohols glycerol and EG act as monodentate ligands, thus enabling the remaining hydroxyl groups to make H bonds with species that lie beyond the primary solvation shell. Water also chooses to make a linear Cl⁻ ···D-O bond (as opposed to orientating such that its dipole is pointing directly at Cl⁻) so as to increase the number of potential hydrogen bonds between solvent ligands in the primary and secondary solvation shells (Sharpe 1990). As the nature of the solvent is changed there is a marked reduction in the solvation number, $\bar{n}_{\text{Cl}}^{\text{D}}$, from approximately six (water) to four (methanol and EG) to three (glycerol).

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