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The structure of Cl^- in aqueous solution: an experimental determination of $g_{\text{ClH}}(r)$ and $g_{\text{ClO}}(r)$

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Abstract. The first and second isotopic difference methods of neutron diffraction have been applied to solutions of 2 molal NiCl_2 in H_2O and 1.8 molal NiCl_2 in D_2O . The results were used to obtain the radial pair distribution functions $g_{\text{ClH}}(r)$ and $g_{\text{ClO}}(r)$. Analysis of these functions shows that Cl^- is coordinated to 6.4(3) water molecules at near-neighbour Cl–H(1), Cl–O and Cl–H(2) distances of 2.28(3) Å, 3.1(1) Å and 3.7(1) Å respectively. The data transcend those obtained in previous studies, which were carried out only at the level of the first difference, and so provide a sharper test of theoretical results obtained from computer simulation or integral equations.

1. Introduction

The Cl^- ion is a useful probe of anion properties in solution and is an important ion in its own right (Sharpe 1990, Hummer and Soumpasis 1992). Its coordination in solution can be determined experimentally by x-ray and neutron diffraction (Neilson and Enderby 1983, Magini *et al* 1988) and theoretically by means of computer simulation methods (Zhu and Robinson 1992) or by integral equation techniques (Friedman *et al* 1991). In previous studies it has been established that Cl^- has a characteristic local coordination which is remarkably insensitive to ionic concentration, counterion and moderate changes in temperature and pressure (Cummings *et al* 1980). The shape of the total Cl^- radial distribution function $G_{\text{Cl}}(r)$ obtained at the first difference level by neutron diffraction is characterized by two well defined peaks centred around 2.2 Å and 3.2 Å. The first of these reflects Cl–H(1) interactions, whilst the second is an unresolved pair Cl–O and Cl–H(2). The most widely accepted geometry of the Cl– H_2O interaction consistent with both experimental and theoretical studies is shown in figure 1. For relatively low concentrations (< 2 molal) the coordination number saturates at approximately six. The explanation of this apparently well defined geometry coexisting with dynamical behaviour in which water molecules are coordinated to Cl^- on a timescale of less than 10^{-11} s (Hertz 1973), is that the effective intermolecular potential of the Cl^- – H_2O pair is directional in character and favours the near-linear hydrogen bond implied in figure 1.

The aim of the present paper is to present and discuss new results for Cl^- hydration which have been obtained from isotopic difference methods of neutron diffraction on solutions of nickel chloride in *both* light and heavy water. By working at the second difference level, the individual pair distribution functions $g_{\text{ClH}}(r)$ and $g_{\text{ClO}}(r)$ (the latter being subject to a small correction) can be determined directly. In this way it is possible to resolve structure in $G_{\text{Cl}}(r)$, notably around the second peak, and hence discuss the Cl^- – H_2O

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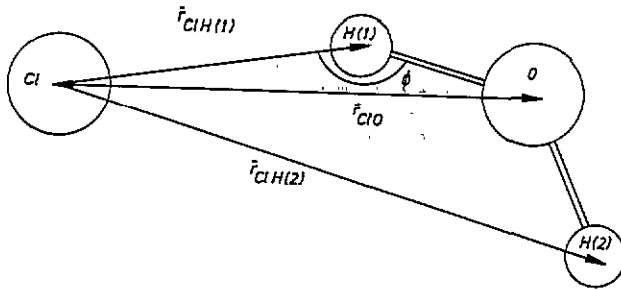


Figure 1. The configuration of the Cl^- - H_2O pair.

conformation in greater detail than before. The results provide a critical test of theoretical calculations, the most recent of which now include polarization corrections.

2. Experimental details

Neutron diffraction experiments were performed on four samples of isotopically enriched chlorine in nominally 2 molal NiCl_2 aqueous solutions. Data were taken on the D20 diffractometer of the ILL (Grenoble, France), operated at a neutron wavelength of 0.940 Å. The solutions were contained in thin $\text{Ti}_{0.356}\text{Zr}_{0.644}$ 'null' alloy cylinders. The internal diameter chosen for H_2O solutions (5 mm) optimized the effective coherent scattering in the presence of substantial incoherent scattering (Powell 1989, Powell *et al* 1989). For D_2O solution, standard 8 mm cylinders were used. The compositions of the samples, and the cross sections used in the data analysis correction procedures, are given in table 1. The data for each solution were corrected for instrumental background, container scattering, self-attenuation (Paalman and Pings 1962) and multiple scattering (Blech and Averbach 1965) and were put on an absolute scale by reference to a vanadium standard (North *et al* 1968). The multiple scattering was assumed to be isotropic, and was treated as a constant to be subtracted from the data, after correction for attenuation. It should be noted that, for the solutions in H_2O , the calculated multiple scattering was 42% of the total scattering. However, the scattering cross sections for the two samples differ by only 0.4 b (table 1), so that the calculated multiple-scattering correction to the first difference function is 7 millibarn $\text{sr}^{-1}/\text{atom}$ i.e., of the same order as the statistical errors. The simple isotropic correction described above was, therefore, adequate (see also Powell *et al* 1989).

Table 1. The compositions of the samples and the scattering and absorption cross sections (σ_s and σ_a) used in the correction procedures. The atomic number density of the solutions is $0.100 \pm 0.002 \text{ \AA}^{-3}$ and c_α is the atomic fraction of the α species.

Solution	c_{Ni}	c_{Cl}	c_{O}	c_{D}	c_{H}^a	σ_s^b	σ_a^c
1.8 m $\text{Ni}^{35}\text{Cl}_2$ in D_2O	0.0116	0.0232	0.3218	0.6413	0.0023	4.71	0.99
1.8 m $\text{Ni}^{37}\text{Cl}_2$ in D_2O	0.116	0.0232	0.3218	0.6412	0.0024	4.31	0.14
2.0 m $\text{Ni}^{35}\text{Cl}_2$ in H_2O	0.0116	0.0232	0.3218	0.001	0.6436	23.77	1.21
2.0 m $\text{Ni}^{37}\text{Cl}_2$ in H_2O	0.0116	0.0232	0.3218	0.001	0.6436	23.37	0.36

^a Measured using IR absorption for the D_2O samples.

^b Calculated using measured total cross sections for D_2O and H_2O at the incident wavelength (Hughes and Harvey 1985) in barns (b). $1 \text{ b} = 10^{-28} \text{ m}^2$.

^c At an incident neutron wavelength of 1.8 Å.

Solutions of the type described here are characterized by a set of fifteen radial distribution functions $g_{\alpha\beta}(r)$, ($\alpha, \beta \in \text{Ni, Cl, O, H, D}$) and the corresponding structure

factors $S_{\alpha\beta}(k)$, which are related through

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

with n equal to the total number density. By means of the substitution $^{35}\text{Cl} \rightarrow ^{37}\text{Cl}$, first-order difference functions can be obtained (Soper *et al* 1977). These relate to $S_{\alpha\beta}(k)$ and $g_{\alpha\beta}(r)$ through the well known equations

$$\Delta_{\text{Cl}}(k) = A[S_{\text{ClO}}(k) - 1] + B[S_{\text{ClD}}(k) - 1] + C[S_{\text{ClH}}(k) - 1] + D[S_{\text{ClNi}}(k) - 1] + E[S_{\text{ClCl}}(k) - 1] \quad (2)$$

$$G_{\text{Cl}}(k) = A[g_{\text{ClO}}(r) - 1] + B[g_{\text{ClD}}(r) - 1] + C[g_{\text{ClH}}(r) - 1] + D[g_{\text{ClNi}}(r) - 1] + E[g_{\text{ClCl}}(r) - 1] \quad (3)$$

where

$$A = 2c_{\text{Cl}}c_{\text{O}}b_{\text{O}}(b_{\text{Cl}} - b'_{\text{Cl}}) \quad B = 2c_{\text{Cl}}c_{\text{D}}b_{\text{D}}(b_{\text{Cl}} - b'_{\text{Cl}}) \quad C = 2c_{\text{Cl}}c_{\text{H}}b_{\text{H}}(b_{\text{Cl}} - b'_{\text{Cl}})$$

$$D = 2c_{\text{Cl}}c_{\text{Ni}}b_{\text{Ni}}(b_{\text{Cl}} - b'_{\text{Cl}}) \quad E = c_{\text{Cl}}^2[(b_{\text{Cl}})^2 - (b'_{\text{Cl}})^2]$$

and c_{α} , b_{α} , b'_{α} are respectively the atomic fractions and scattering lengths of the α species.

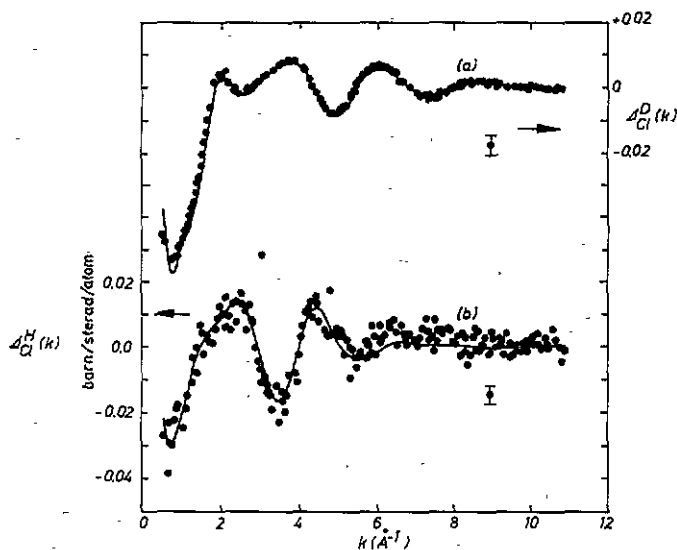
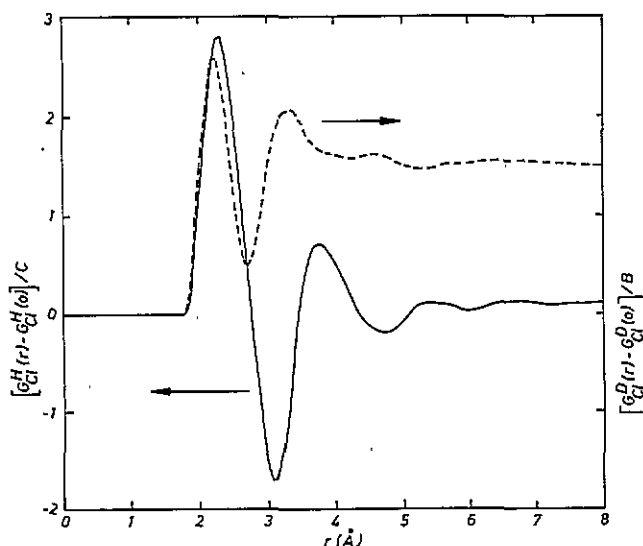


Figure 2. The first-order difference functions for 1.8 molal NiCl_2 in D_2O , denoted $\Delta_{\text{Cl}}^{\text{D}}(k)$ (curve a) and 2.0 molal NiCl_2 in H_2O , denoted $\Delta_{\text{Cl}}^{\text{H}}(k)$ (curve b). The filled circles represent data points while the curves are spline fits formed after setting $G_{\text{Cl}}(r) = G_{\text{Cl}}(0)$ for $r \leq 1.8 \text{ \AA}$.

The $\Delta_{\text{Cl}}(k)$ for the H_2O and D_2O samples are shown in figure 2. The weighting factors A – E are shown in table 2. As is the case for most isotopic substitution experiments at the first-difference level, A , B and C are large compared with D and E , so the difference functions are dominated by those terms relevant to the hydration of Cl^- . In figure 3 the first-difference functions in real space normalized by subtracting the theoretical $G_{\text{Cl}}(0)$ and dividing by B (for the D_2O sample) or C (for the H_2O sample) are compared. The results confirm the validity of the correction procedures, the small differences on the trailing edge of the first peak arising from the penetration of $g_{\text{ClH}}(r)$ by $g_{\text{ClO}}(r)$. Furthermore, the normalized $G_{\text{Cl}}^{\text{D}}(r)$ shown in figure 3 for NiCl_2 in D_2O agrees within experimental error with earlier studies for a variety of solutions at concentrations such that the direct metal–chloride interactions are absent (Powell *et al* 1988).

Table 2. The weighting factors for the different contributions to the measured first-difference functions.

Solution	A (mb)	B (mb)	C (mb)	D (mb)	E (mb)
1.8 m NiCl ₂ in D ₂ O	6.238	14.264	0.00	0.399	0.570
2.0 m NiCl ₂ in H ₂ O	6.238	0.00	-8.043	0.399	0.570

**Figure 3.** Normalized r -space difference function (see text), 1.8 molal NiCl₂ in D₂O (broken curve) and 2.0 molal NiCl₂ in H₂O (full curve).

As was established by Powell *et al* (1989) in their work on Ni²⁺, it is now possible to proceed to a second difference assuming, at the level of accuracy relevant to this work, that H and D are isomorphic (i.e. that $S_{\text{ClD}}(k) = S_{\text{ClH}}(k)$). Thus, in an obvious notation,

$$S_{\text{ClH}}(k) = 1 + [\Delta_{\text{Cl}}^{\text{D}}(k) - \Delta_{\text{Cl}}^{\text{H}}(k)] / (B - C) \quad (4)$$

so that $S_{\text{ClH}}(k)$ and $g_{\text{ClH}}(r)$ can be obtained directly (figures 4(a) and 5(a) from the data in figure 2. Inserting (4) in (2) and simplifying, we find that

$$\begin{aligned} S_{\text{ClO}}(k) &= 1 \left[C \Delta_{\text{Cl}}^{\text{D}}(k) - B \Delta_{\text{Cl}}^{\text{H}}(k) \right] / A(C - B) - (D/A) [S_{\text{ClNi}}(k) - 1] - (E/A) [S_{\text{ClCl}}(k) - 1] \\ &= S_{\text{ClO}}^*(k) - (D/A) [S_{\text{ClNi}}(k) - 1] - (E/A) [S_{\text{ClCl}}(k) - 1]. \end{aligned}$$

Since D/A and E/A are numerically small (0.064 and 0.091 respectively) the two correction terms will be neglected in the subsequent analysis required to transform the $S_{\text{ClO}}^*(k)$ shown in figure 4(b) into the $g_{\text{ClO}}(r)$ shown in figure 5(b). This step is justified by the detailed study of Neilson and Enderby (1983) who showed that the maximum values of $g_{\text{ClNi}}(r)$ and $g_{\text{NiNi}}(r)$ occurred at 4.6 and 4.7 Å, well removed from the position of the peak in $g_{\text{ClO}}(r)$.

3. Discussion

If we consider the individual $g_{\text{ClH}}(r)$ and $g_{\text{ClO}}(r)$ and the structural parameters shown in figure 5 and table 3, several firm conclusions can be drawn. First, the new results decisively confirm the widely accepted geometry described in figure 1. The 'linear' configuration is fully justified and the 'dipolar' model (which still appears in text-books from time to time) can, in agreement with all recent calculations, be finally rejected.

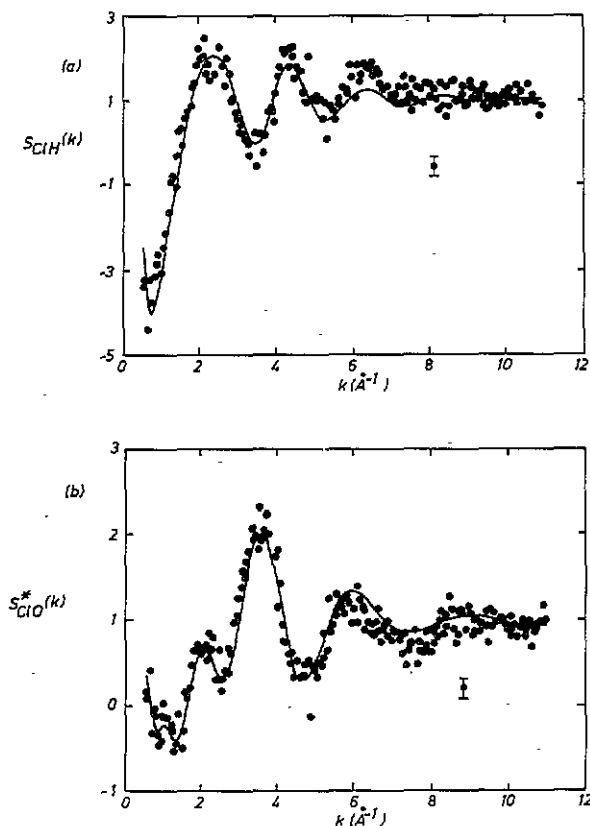


Figure 4. The partial structure for factors (a) $S_{\text{ClH}}(k)$ and (b) $S_{\text{ClO}}^*(k) = S_{\text{ClO}}(k) + 0.064 [S_{\text{ClNi}}(k) - 1] + 0.09 [S_{\text{ClCl}}(k) - 1]$.

Secondly, the value of \bar{r}_{ClH} of $2.28 \pm 0.03 \text{ \AA}$ derived directly from $g_{\text{ClH}}(r)$ is in excellent agreement with previous studies based on $G_{\text{Cl}}(r)$. The first maximum in $g_{\text{ClO}}(r)$ occurs at $3.1 \pm 0.1 \text{ \AA}$. In earlier studies the position of the broad second peak in $G_{\text{Cl}}(r)$ was sometimes (incorrectly) ascribed to \bar{r}_{ClO} alone, with the result that the apparent chloride-oxygen distance quoted was too long by $\sim 0.05 \text{ \AA}$. This work essentially resolves the difference noted by Magini *et al* (1988) between the \bar{r}_{ClO} distances obtained by total x-ray diffraction and by the first-difference method, particularly when it is remembered that the former approach requires some degree of modelling.

A third point to note is that the full width at half maximum (FWHM) of $g_{\text{ClH}}(r)$ and $g_{\text{ClO}}(r)$ is 0.39 and 0.35 \AA respectively. In terms of the probability density $P(\cos \phi)$ of the angle ϕ defined in figure 1, the near equality of the two FWHMs cannot be taken as direct evidence that $P(\cos \phi)$ is sharply peaked around 180° (the linear bond configuration). Since $r_{\text{ClO}} = (r_{\text{ClH}}^2 + r_{\text{OH}}^2 - 2r_{\text{ClH}}r_{\text{OH}} \cos \phi)^{1/2}$, the envelope for fluctuations in r_{ClO} induced by vibrational displacements of r_{ClH} will accommodate fluctuations arising from $\cos \phi$ changing from -1 (linear) to -0.30 (dipole). In fact, as was first pointed out explicitly by Szasz *et al* (1982) and discussed further by Powell and Neilson (1990), there is no reliable inversion scheme to derive $P(\cos \phi)$ from $g_{\alpha\beta}(r)$ alone, and modelling methods such as molecular dynamics (MD) or reverse Monte Carlo (MC) methods (see, for example, McGreevy 1990) have to be employed.

In aqueous solutions the coordination number \bar{n}_α^β has usually been obtained by integrating the relevant $g_{\alpha\beta}(r)r^2$ up to its first minimum (see, for example, Neilson and Enderby 1983). This procedure gave coordination numbers for water molecules around Cl^- , again in the concentration range where direct metal-chloride interactions are not significant,

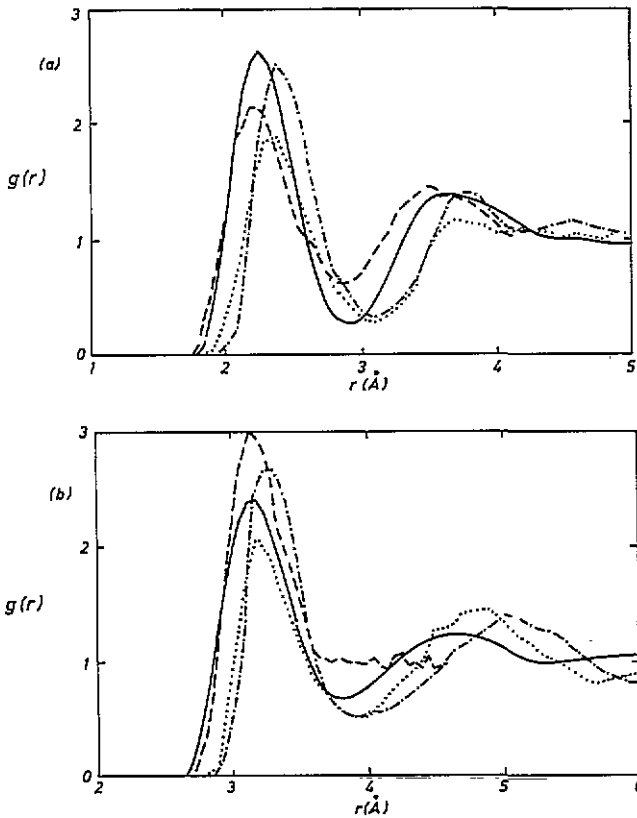


Figure 5. The radial distribution functions (a) $g_{ClH}(r)$ and (b) $g_{ClO}(r)$ (full curves) derived from experiment compared with the simulation results of Dietz *et al* (1982) (broken curves), Bounds (1985) (dotted curves) and Impey *et al* (1983) (chain curves).

Table 3. Coordination properties of chloride in water.

$\bar{r}_{ClH(1)}$ (Å)	\bar{n}_{Cl}^H ^a	\bar{r}_{ClO} (Å)	\bar{n}_{Cl}^O ^a	$\bar{r}_{ClH(2)}$ (Å)
2.28 ± 0.03	6.4 ± 0.3	3.1 ± 0.1	7.0 ± 0.4	3.7 ± 0.1

^a The average coordination numbers of β centres around an α centre is defined as $\bar{n}_\alpha^\beta = 4\pi\rho_\beta \int_0^{r_s} g_{\alpha\beta}(r)r^2 dr$ where ρ_β is the number density of the β species and r_s is the value of r at the first minimum in $g_{\alpha\beta}(r)$. Because of penetration effects by water molecules outside the first coordination shell, \bar{n}_{Cl}^H rather than \bar{n}_{Cl}^O is the primary coordination number.

of between 5.5 and 6.2 (Cummings *et al* 1980, Enderby *et al* 1987, Powell *et al* 1988). These numbers were, however, derived from $G_{Cl}(r)$ and overlapping peaks make the cut-off value of r used in the calculation somewhat arbitrary. In the present study, such arbitrariness is removed and the value obtained for \bar{n}_{Cl}^H of 6.4 ± 0.3 is, we believe, the most reliable so far obtained.

Finally, we consider the comparison of the experimental distribution functions with those derived from computer simulation (MD or MC). Following the pioneering study of Heinzinger and coworkers in the late 1970s (Heinzinger and Vogel 1976) many studies of the chloride ion in solution were undertaken during the period 1978–1985. The results of these studies were, in the main, compared with experiment at the first-difference (i.e. $G_{Cl}(r)$) level and, apart from a tendency to overestimate the coordination number by $\sim 30\%$, the measure of agreement secured was deemed to be satisfactory. Now that we are in a position to make a detailed comparison at the $g_{\alpha\beta}(r)$ level it is evident (figure 5) that even the best of the earlier simulations do not capture some essential features in the experimental data, a fact disguised by cancellation of discrepancies in the formation of the linear combination

of $g_{\text{ClH}}(r)$ and $g_{\text{ClO}}(r)$ to obtain $G_{\text{Cl}}(r)$. It should be noted that the experimental and theoretical results often refer to different concentration and counterion regimes. However, given the observed insensitivity of chloride coordination to these variables, the comparison is a valid one.

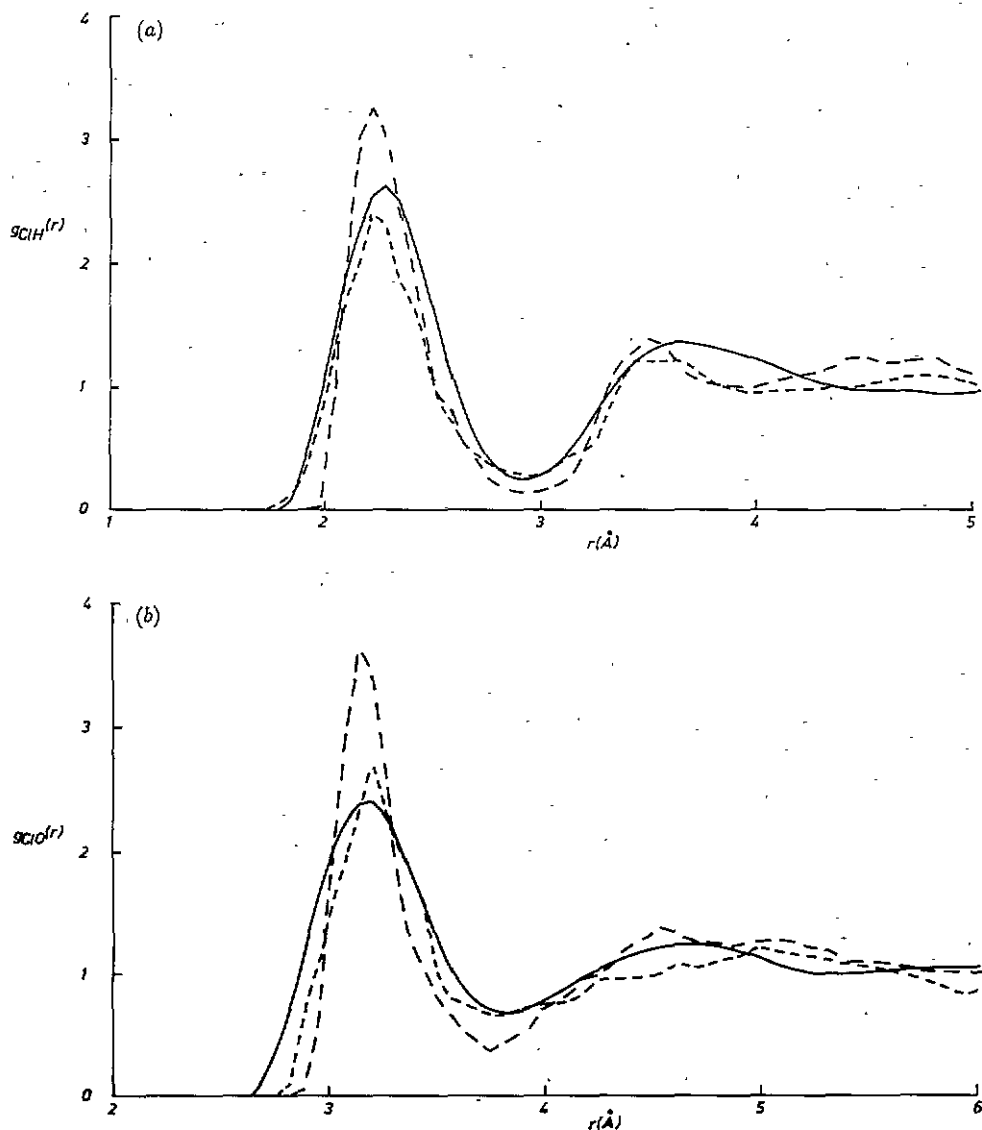


Figure 6. The radial distribution function (a) $g_{\text{ClH}}(r)$ and (b) $g_{\text{ClO}}(r)$ (full curves) derived from experiments, compared with the simulation results of Sprik *et al* (short-dashed curves) and Dang *et al* (long-dashed curved).

In the recent study, Sprik *et al* (1990) have argued that many of the earlier difficulties arise from the failure to account properly for the polarizability of the water and/or the chloride ion. The results of Sprik *et al* simulation, which used a polarizable water model, are in much better agreement with experiment than those from earlier studies, particularly with respect to the chloride–oxygen and chloride–hydrogen distances and coordination numbers

(figure 6). There is, however, a tendency for the radial distribution function to be too sharp as compared with the experimental functions. This may be due, as pointed out by Sprik *et al*, to an inadequate representation of the repulsive part of the chloride–water potential (represented by A/r^{12}) or to the neglect of the polarizability of the chloride ion. Dang *et al* (1991) have shown that the neglect of multiple-body interactions can also affect the form of the radial distribution functions. Their results, with a polarizable water model and including multiple-body effects, are also shown in figure 6. While the width of the peaks is in better agreement with experiment than those of Sprik *et al* (1990), the agreement of the peak positions is less good. The challenge to describe satisfactorily the chloride–water coordination still remains (Hummer and Soumpasis 1992), but the experimental partial radial distribution functions presented here indicate where improvements are required and will provide a crucial test of new models.

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