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Hydration of ions in aqueous RbCl solutions

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Abstract

Structural studies have been carried out on aqueous rubidium chloride solutions at three concentrations. Particle configurations consistent with neutron and x-ray diffraction data were obtained by reverse Monte Carlo modelling. By applying several coordination constraints, the generally accepted concept concerning the hydration of chloride ions could be tested in detail. The structural models generated may be made consistent with Cl^- ions surrounded by six neighbouring water molecules, of which only three can connect to the ion via straight $\text{Cl} \dots \text{H}-\text{O}$ (hydrogen bond) angles.

1. Introduction

The microscopic structure of water can change for many reasons, among which an important one is the presence of solutes [1]. In this study we wish to consider effects brought about by *ionic* solutes.

Aqueous salt solutions have been of great scientific interest for a long time [2, 3]. Despite this there are still uncertainties about the details of their microscopic structure. The microscopic structure of water, that is, the network of hydrogen bonds, is perturbed by the presence of ions. The changes may be qualitatively different in cases of different ions. Too small (like Li^+ [4]) or too big (like Rb^+ [5]) ions may not fit well and distort the web of H-bonded water molecules; on the other hand, special ones like H^+ may even strengthen the network [2, 6].

Ionic diameters and charges, i.e. electrostatic interactions, determine the number and orientation of dipolar water molecules around ions. There have been a number of attempts to describe these interactions by model potentials and using molecular dynamics (MD) computer simulations (see, e.g., [7–9]). The validity of the model (in most cases, pair) potentials may be assessed by comparing total structure factors directly obtained by diffraction experiments to those calculated from MD simulation (see, e.g., [9]). The comparison is most frequently made at the (partial) radial distribution function level [8]; it is fair to say that agreement between experiment and simulation at the structure factor level is qualitative at its best [9]. This is

Table 1. Hydration numbers of the Cl^- ion as given in the literature. r is the distance of the first minimum of the corresponding prdf in Å, within which the n neighbours are calculated. ND/XD, neutron/x-ray diffraction measurement; NDIS, neutron diffraction with isotopic substitution; MD, molecular dynamics simulations.

References	Method	$r(\text{Cl-O})$	$n(\text{Cl-O})$	$r(\text{Cl-H})$	$n(\text{Cl-H})$
[2]	ND,XD	—	6	—	—
[3]	NDIS	3.2 ^a	ca 5.8	2.26 ^a	—
[10]	ND	—	<6	—	—
[7]	MD	3.2 ^a	6.3	—	—
[16]	RMC	4	7.4	—	4.14
[15]	ND	3.25 ^a	—	2.24 ^a	4.4
[8]	MD	3.8	7.3	2.9	6.4
[12]	NDIS	3.78	6.2–7.1	2.88	5.6–6.4

^a Only the peak position was given.

the reason why details of the microscopic structure, such as atomic distances and coordination numbers, are best calculated from experimental diffraction data (see, e.g., [2, 3, 10, 11]).

Trends of structural changes can be observed as a function of ionic concentration. In some cases these trends may even be visible directly in the form of the diffraction signal [2, 5, 12, 13]; however, it is the partial radial distribution functions (prdfs, $g_{ab}(r)$) that are most important for identifying structural changes.

In the case of four component systems such as salt solutions, it is practically impossible to obtain all ten partial radial distribution functions from diffraction experiments. Instead, structural modelling is available for establishing if a particular idea/theory/model is consistent with the (certainly less than ten; in many cases, only at most three) measured structure factors. In this work we attempt to establish such a link for the important case of the chloride anion, using the rubidium cation as counterion.

Apart from being one of the simplest anions, the chloride ion has the largest biological importance of anions in living cells. It has a life important role in biochemical communication; it is the counterion of H, Na, K, Ca or Mg cations, during the ion-pump transport between the two sides of the cell membrane [14].

Many experimental [2, 3, 10, 12, 15] and simulation [7, 8, 16] studies have been carried out that concerned the hydration structure of the chloride ion. Some key results can be found in table 1. Most chloride salts dissolve well in water, hence solvated ions have acceptable contributions to the measured neutron or x-ray diffraction data (see table 2). Results have been interpreted in various ways [2, 3, 10, 16]; the most widely accepted view is a sixfold coordination of the anion, with a straight O–H...Cl H-bond angle (in other words, the H...Cl...O angle, where the H and O atoms belong to the same water molecule, is close to zero). [3] concludes, on the basis of a set of neutron diffraction studies, that the anion most probably has a rather quickly changing hydration sphere with about six water molecules around it, but the exact structure is not well defined. Later, however, the sixfold coordination of the Cl^- ion was stressed more strongly [10, 16]. One may comment here that these conclusions have been drawn on the basis of difference NDIS (neutron diffraction with isotopic substitution) experiments, yielding not the pure Cl–O/Cl–H prdfs but a ‘composite’ Cl–X prdf. That is, elucidation of the hydration structure is ambiguous.

The rubidium ion has been studied less well compared to the chloride anion or other alkali cations. Studying the structure of materials containing rubidium can be hard due to the fluorescence occurring in laboratory x-ray experiments; this problem, however, can be avoided by using synchrotron x-ray and neutron diffraction data. At higher concentrations, Rb

Table 2. Cut-off distances and weighting factors. The first row shows the applied hard sphere distances. ‘ND weights’ are partial contributions to the neutron diffraction, whereas ‘XD weights’ are contributions to the x-ray diffraction data (this latter, at $Q = 0 \text{ \AA}^{-1}$) for three concentrations.

	Rb–Rb	Rb–Cl	Rb–O	Rb–H	Cl–Cl	Cl–O	Cl–H	O–O	O–H	H–H
r (Å)	3	3	2	3	3	2.7	1.8	2.5	1.5	1.8
ND weights										
1 mol%	0	0	2.7×10^{-3}	6.2×10^{-3}	0	4.0×10^{-3}	6.9×10^{-3}	9.0×10^{-2}	0.4145	0.4764
5 mol%	3.0×10^{-4}	9.0×10^{-4}	1.07×10^{-2}	2.46×10^{-2}	6.0×10^{-4}	1.4×10^{-2}	3.34×10^{-3}	8.41×10^{-3}	0.3865	0.4449
10 mol%	1.4×10^{-3}	3.8×10^{-3}	2.07×10^{-2}	4.77×10^{-2}	2.6×10^{-3}	2.8×10^{-2}	6.44×10^{-2}	7.64×10^{-2}	0.3513	0.4037
XD weights										
1 mol%	1.2×10^{-3}	1.1×10^{-3}	5.39×10^{-2}	1.33×10^{-2}	3.0×10^{-4}	2.4×10^{-2}	6.1×10^{-3}	0.5782	0.2857	3.50×10^{-2}
5 mol%	2.29×10^{-2}	2.10×10^{-2}	0.1891	4.67×10^{-2}	4.8×10^{-3}	8.6×10^{-2}	2.14×10^{-2}	0.3903	0.1928	2.38×10^{-2}
10 mol%	6.61×10^{-2}	6.07×10^{-2}	0.2576	6.36×10^{-2}	1.40×10^{-2}	0.118	2.92×10^{-2}	0.2509	0.1240	1.53×10^{-2}

Table 3. Modelling details for the three RbCl aqueous solutions.

	1 mol%	5 mol%	10 mol%
Ion pair/D ₂ O	33/3311	169/3220	345/3103
Molar ratio of ion pairs	0.0099	0.0498	0.100
Density (Å ⁻³)	0.098	0.093	0.087
Density (g/cm ³)	1.15	1.32	1.5
Half box-length (Å)	23.34	23.73	24.31

has a reasonably high weighting factor (well above 10%) in the x-ray diffraction experiment (see table 2). Few experiments have been carried out previously on the hydration structure of rubidium ions [9, 17, 18] and no special models were proposed concerning the hydration of this cation. The coordination number is generally estimated around (or somewhat above) six. One may expect that simply due to its size, the Rb ion will behave as a structure breaker, i.e. as an ion which would distort the hydrogen bonded network of water molecules, by breaking some of the H-bonds [9].

In the present work we wished to combine experimental data (total structure factors) and proposed hydration models of the anion [3, 8, 10] in the same particle configuration, so that the simple picture of the hydration could be tested directly against results of diffraction experiments. For this purpose, the reverse Monte Carlo method [19] is suitable. For the formulation of the proposed hydration model (in terms of particle coordinates), two average coordination constraints used separately and in tandem (see below) have been applied on the chloride hydration structure.

2. Reverse Monte Carlo calculations

RbCl solutions were studied at concentrations of 1, 5 and 10 molar per cent (mol%). Experimental data (neutron and x-ray weighted total structure factors) were taken from a recent comprehensive diffraction study on aqueous Rb and Cs halides; details of the experiments and the complete set of data will be published separately [13]. Neutron diffraction measurements have been conducted by using the SLAD liquids and amorphous diffractometer (NFL Studsvik, Sweden) [20]. X-ray diffraction experiments have been performed at the SPring-8 synchrotron facility (Japan), using the high energy x-ray beamline BL04B2 [21].

RMC++ [22], the C++ realization of the standard reverse Monte Carlo algorithm, has been applied in all simulations reported in this contribution. The RMC method is described elsewhere in detail (see, e.g., [19, 22]), so only the parts relevant for the present study are mentioned here.

Random configurations have been created as described in [4, 6]. Some details of the simulations are shown in table 3. For the water intramolecular structure, fixed neighbour constraints (fncs) [22] have been applied, effective on the intramolecular O–H and H–H pairs; intermolecular cut-off distances (see table 2) have been handled separately from fncs. In addition, an intermolecular coordination constraint on the O . . . H pairs was also installed in the same way as described in [4, 6], in order to maximize the number of perfectly H-bonded water molecules in the system (this constraint will be referred to later as ‘w’). The ‘w’ constraint has been applied in all calculations reported here.

When an acceptable fit was reached, the calculations were focused on the proposed model of chloride ion hydration, according to which—on average—six water molecules surround the Cl⁻ anions. To this end, two average coordination constraints have been introduced. First a

Table 4. Goodness-of-fit, χ^2 , values and coordination numbers, n , for the three aqueous RbCl solutions, as calculated up to $r1(2)$, the first (second) minimum of the corresponding $g(r)$ (r is given in Å). Second column: maximum ratio of perfectly H-bonded water molecules (within the water network), in%. The letters ‘w, o, h’ in the first column indicate the set of coordination constraints applied during the calculation in question; for instance, ‘w, o, h, 10 m%’ means that for the 10 mol% solution, H-bonding (‘w’), Cl–O (‘o’) and Cl–H (‘h’) constraints were all applied (for a more detailed definition of constraints, see section 2).

Constraint (m%)	χ^2	‘w’	$r(\text{Cl-O})$	$n(\text{Cl-O})$	$r1(\text{Cl-H})$	$n1(\text{Cl-H})$	$r2(\text{Cl-H})$	$n2(\text{Cl-H})$
w, 1	118.25	28	3.7	5.7	2.5	2.1	3.7	12.8
w, 5	55.63	25	"	6.0	"	2.4	"	12.0
w, 10	23.90	22	"	5.8	"	2.4	"	11.0
w, o, 1	118.07	25	3.7	6.0	2.7	3.1	4.0	15.0
w, o, 5	55.81	23	"	6.0	"	3.2	"	15.8
w, o, 10	24.09	16	"	6.0	"	3.1	"	14.7
w, h, 1	117.37	29	3.7	6.6	2.55	3.1	2.95/3.7	6.2/12.8
w, h, 5	55.31	25	"	6.8	"	3.1	"	6.1/12.1
w, h, 10	23.79	20	"	6.3	"	3.2	"	6.1/11.3
w, o, h, 1	116.62	25	3.7	6.0	2.55	3.6	2.9/4.0	5.5/16.4
w, o, h, 5	55.49	23	"	6.0	"	3.2	"	5.3/15.8
w, o, h, 10	23.74	18	"	6.0	"	3.2	"	5.2/14.4

constraint for having six water oxygens within a distance of 3.7 Å from the anion has been introduced (this constraint will be referred to as ‘o’). When this condition could be satisfied, a second constraint was introduced which required six hydrogens within 2.9 Å (this constraint will be referred to as ‘h’). Finally, to complete the picture, the ‘h’ constraint has been applied on its own. Note that in this type of constraint not the exact but the average coordination number is prescribed; that is, in principle, it should be easier to fulfil these (the ‘o’ and ‘h’ constraints) than the ‘w’ constraint.

The constraints just introduced may be viewed as tools for scrutinizing the local environment around the aqueous ions to assess what structures are supported by the data. The ‘o’ constraint is aimed at fixing the number of water molecules around the chloride anion, without requiring any specific orientation of the molecules. The ‘h’ constraint on its own would fix the number of H atoms around the anion, but it cannot ensure that the six H atoms belong to six water molecules. The combination of ‘o’ and ‘h’ constraints is the most sophisticated requirement applied in the present study: fulfilling both would mean the realization of the idealized picture of the first hydration shell [3, 10, 16] in which six water molecules are H-bonded to the chloride ion. In the next section, the feasibility of these models is investigated.

3. Results and discussion

Figure 1 shows the experimental neutron and x-ray total structure factors, $F_N(Q)$ and $F_X(Q)$, respectively, together with their RMC fits. The quality of the fits to diffraction data was the same during all simulations, regardless of the constraints applied. There were very small variations in terms of the value of the χ^2 (see table 4), but these cannot be detected visually.

Even at the highest concentrations the structure factors (particularly the neutron weighted ones) are dominated by the intra- and intermolecular structure of water. The corresponding (O–O, O–H and H–H) partial radial distribution functions are shown in figure 2. On the $g_{\text{oo}}(r)$ function a small peak around 3.3 Å grows out of the shoulder on the high r side of the first maximum as concentration increases. Similar findings have been reported previously

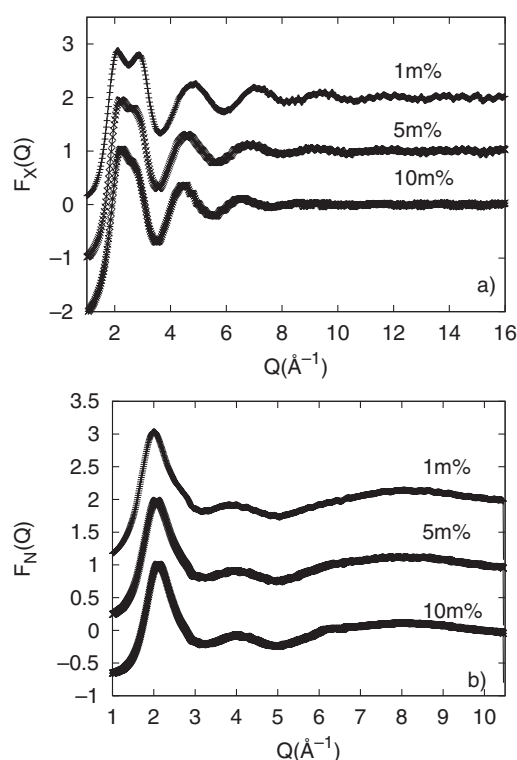


Figure 1. Experimental total structure factors, determined by x-ray (a) and neutron (b) diffraction, for aqueous RbCl solutions at three concentrations (symbols); the same functions obtained by RMC modelling are also shown (solid line).

(see, e.g., [4]). It seems that in pure water the main maximum is actually a composition of two contributions, which tend to separate as the concentration of water decreases. (This point will be investigated further over a wide range of aqueous ionic solutions in a subsequent publication.)

The H–H and O–H partials are influenced to a large extent by the ‘w’ constraint applied, so that they will not be discussed much further here. It may, however, be noted that the maximum number of perfectly hydrogen bonded water molecules decreases as the salt concentration grows (see table 4). This indicates the expected distortion of the H-bond network of the water molecules; the distortion seems to be less severe than for LiCl solutions [4] (the concentration ranges for the two—RbCl and LiCl—salts are not the same, which prevents a more quantitative comparison). The same distortion effect can be seen in figure 3 where angle distribution functions corresponding to the water (sub-)structure are displayed. Clearly, the trend that increasing salt concentration decreases the number of straight O...H–O (hydrogen) bond angles is not influenced by the various constraints imposed on the hydration shell of the anions. The O...O...O angle distribution does not seem to be influenced by the ionic concentration, which indicates that it is only the re-orientation of the O–H bonds that is responsible for the concentration driven alterations of the O...H–O angles.

X-ray data are sensitive to the hydration sphere of the rubidium ion, in the form of the Rb–O partial rdf, particularly at the higher concentration values, since the weighting factor of this prdf is quite large (the Rb–O prdf actually has the largest weight in the x-ray diffraction pattern

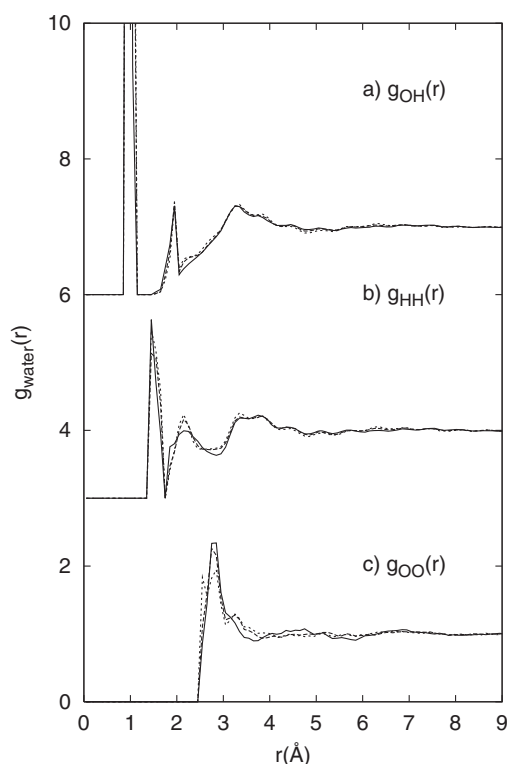


Figure 2. (a) $g_{\text{OH}}(r)$, (b) $g_{\text{HH}}(r)$ and (c) $g_{\text{OO}}(r)$ partial radial distribution functions at three concentrations in aqueous RbCl solutions (solid line, 1 mol%; dashed line, 5 mol%; dotted line, 10 mol%).

at the highest concentration, cf table 2). Figure 4 shows the $g_{\text{RbO}}(r)$ prdfs and Rb...O–H angle distributions within the hydration shell (as calculated up to 3.1 Å). Similarly to RbBr solutions [9], a rather broad distribution of these angles has been found, with a maximum roughly at the tetrahedral angle (109.5°).

The size of the hydration shell changes with increasing concentration. At higher concentrations the first shell becomes more distinct, as the clear minimum of the Rb–O prdf around 3 Å signifies (figure 4). This seems to be in contrast with findings of [4] that concern the hydration shell of the Li^+ cation. Note, however, that the concentration range considered in the present study is very different from that of [4], where the molar fraction of LiCl varied between 0.0581 and 0.25. (The small, gradually emerging second maximum at 3.3 Å may not be a real feature of the solution, as it coincides exactly with the position of the emerging second maximum of the O–O prdf; this issue can only be clarified on the basis of a more comprehensive study of Rb salt solutions.)

With increasing ionic concentration the average number of water molecules in the cation hydration shell decreased from between 7 and 8 to between 5 and 6 as calculated up to 3.9 Å (or from about 5 to 2.5, if calculated up to 3.1 Å, the position of the emerging deep minimum of the Rb–O prdf). This is consistent with values reported previously for the rubidium hydration shell [17, 18, 23]. It may be noted that in RbBr solutions, the hydration shell appeared to be less well defined, with slightly less water molecules located in the shell [9].

Now we turn to our main subject, the description of the Cl^- anion hydration. As mentioned in section 1, there seems to be a consensus in the literature about the hydration shell of chloride

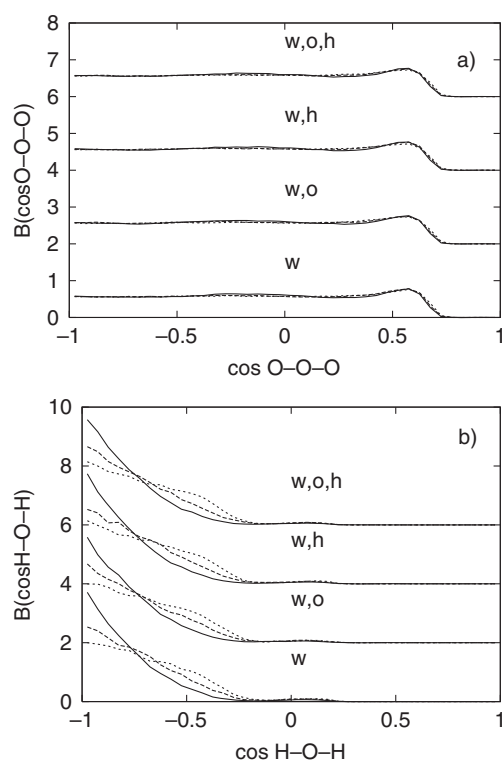


Figure 3. Cosine distribution functions characteristic to the water substructure. (a) $O \dots O \dots O$ (b) $O-H \dots O$ angles. Solid line, 1 mol%; dashed line, 5 mol%; dotted line, 10 mol%.

ions (see, e.g., [3, 10]); there are six water molecules around them and one of their H atoms points towards the anion. In what follows, this very detailed picture is scrutinized, based on the diffraction data considered here.

The hydration structure is characterized by the $g_{ClH}(r)$ and $g_{ClO}(r)$ prdfs, shown in figure 5 for the present calculations on RbCl solutions. The average number of water molecules around the Cl^- ions obtained using the various constraints are collected in table 4.

At higher concentrations, the $Cl-O$ prdf has a considerable weight, about 10%, in the x-ray diffraction data (see table 2). The curves are dominated by the main maximum at around/slightly above 3 Å, the remaining parts being rather featureless. The separation of the first coordination sphere (which is the hydration shell) can hardly be made at all: the lowest value of $g_{ClO}(r)$ is much higher than zero at the position of the minimum (in fact, it is almost one; a value of zero would signify a perfect separation). The position of the first minimum, i.e. the boundary of the hydration shell, cannot be determined unequivocally (as the minimum is rather shallow): it is somewhere between 3.5 and 4 Å. This situation, i.e. the vagueness of the hydration shell, does not change even when the 'o' and 'h' constraints are applied. This finding may be taken as an indication that the larger halide anions—of which chloride has the highest charge density and thus polarizing power—do not coordinate water molecules nearly as strongly as the alkaline counterions.

A remark concerning the effects of the 'o' constraint on the $Cl-O$ prdf may be appropriate here: the number of water molecules that are within this diffuse hydration shell depends very strongly on where actually the boundary of the shell is set; that is, the $Cl-O$ coordination number is not really an appropriate tool for characterizing the hydration of chloride anions.

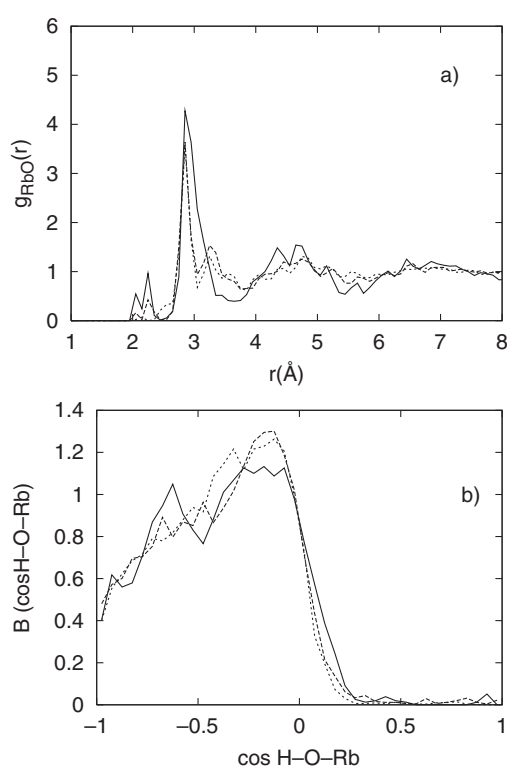


Figure 4. Cation hydration. (a) $g_{\text{RbO}}(r)$ partial radial distribution function; (b) cosine distribution of the H–O...Rb angles. Solid line, 1 mol%; dashed line, 5 mol%; dotted line, 10 mol%.

The first two clear maxima—at ca 2.2 and 3.4 Å—of the $g_{\text{ClH}}(r)$ function of the ‘w’ constrained model (figure 5) reflect the (average) orientation of a water molecule in the hydration shell. The first peak belongs to the first shell of hydrogen atoms of the closest water molecules. The second peak refers to the other hydrogens of these water molecules, a little more than 1 Å further away from the ion. These values agree well with those found in the literature [3, 8, 10].

In between these two clear maxima, however, there seems to be another, very small maximum, at around 2.7 Å, whose intensity varies depending on the exact combination of constraint applied. In the calculations without the ‘h’ constraint, this peak smears out as concentration grows. With the ‘h’ constraint on, this extra peak grows to match the intensity of the first (‘real’) maximum (found just above 2 Å). The most important point is that even with the ‘h’ constraint, the maximum (average) number of H atoms within 2.9 Å is less than 5.5—note that this is the upper limit the diffraction data allow, at the expense of distorting $g_{\text{ClH}}(r)$ strongly. Without the ‘h’ constraint, calculating up to the position of the minimum (at about 2.55 Å), this number is only around three (see table 4 for more details). Calculating the number of neighbouring H atoms up to the same value for the ‘h’ and ‘o, h’ constrained cases provides only very slightly higher coordination numbers, suggesting that the ‘h’ constraint cannot influence the near neighbourhood of chloride anions (i.e. cannot bring more than three H atoms as close as 2.2 Å, the position of the first maximum). In other words, the ‘h’ constraint does not rotate water molecules so that one of their hydrogens would point towards the anion—perhaps because the result would not be consistent with available diffraction data.

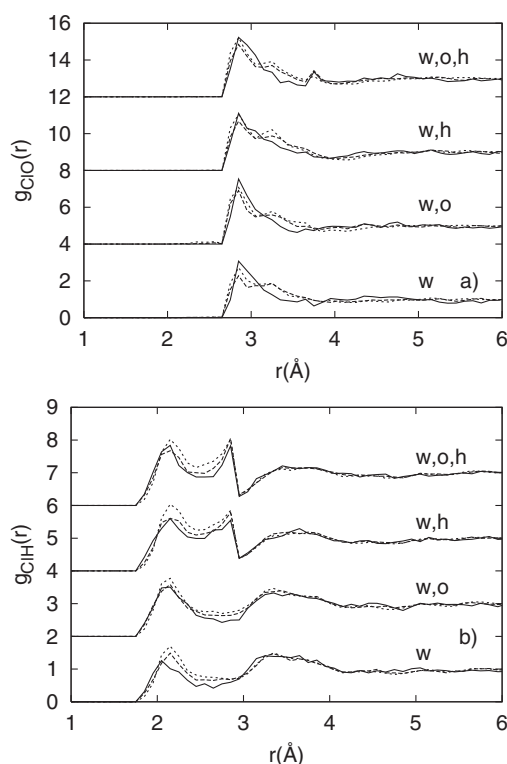


Figure 5. Anion hydration. (a) $g_{ClO}(r)$; (b) $g_{ClH}(r)$ partial radial distribution functions. The letters 'w', 'o' and 'h' refer to the actual combination of constraints (see text for details of these constraints). Solid line, 1 mol%; dashed line, 5 mol%; dotted line, 10 mol%.

The implications of the calculations with and without the 'o' and 'h' constraints can be summarized as follows: the hydration sphere of the Cl^- ion is defined only very vaguely by the Cl–O prdf. The sphere contains six (or somewhat more) water molecules (depending primarily on the choice of the radius of the coordination sphere). Out of these water molecules, only about three can reach as close as 2.2 Å to the anion; the rest cannot place their H atoms closer than about 2.7 Å. Such a distinction between 'strongly' and 'weakly' bound water molecules may well be responsible for the fact that the boundary of the hydration shell is rather diffuse. (We note that this suggestion is, by and large, consistent with findings of Copestake *et al* [15], who arrived at a $Cl \dots H$ coordination number of 4.4, as calculated up to 2.95 Å, by analysing their NDIS results.)

For finding out about the orientation of water molecules that point one of their hydrogen atoms towards the anion, $H \dots Cl \dots O$ angle distribution functions have been calculated from the particle coordinates (figure 6). The presence of straight angles is evident. That is, these water molecules that do reach as close as 2.2 Å to the anion form rather regular, straight hydrogen bond angles with the chloride ions.

4. Summary

Reverse Monte Carlo calculations have been carried out to model the structure of aqueous RbCl solutions, as a function of salt concentration. Neutron and x-ray diffraction data were combined with various constraints concerning the coordination of chloride anions.

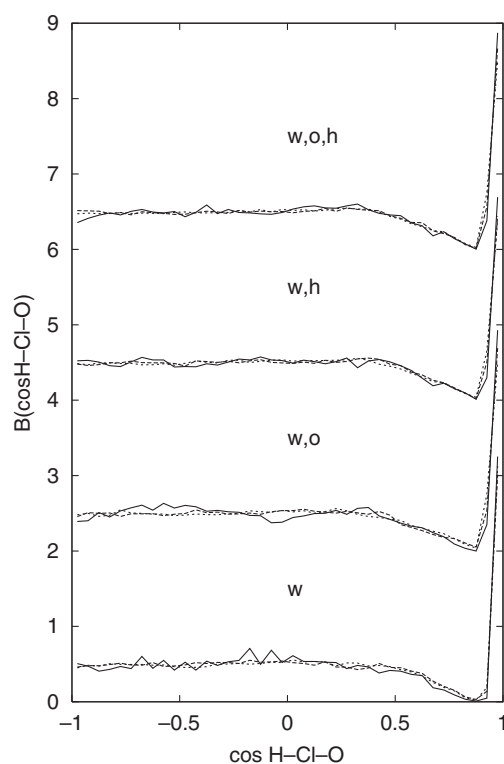


Figure 6. The H...Cl...O cosine distribution function, characteristic to the anion hydration shell. (Notations are identical to those of figure 5.)

It could be established that increasing ionic concentration causes increasing distortions to the hydrogen bonded network of water molecules—that is, RbCl is a ‘structure breaker’, although to a smaller extent than, for instance, LiCl.

For the Rb cations a quite well defined coordination sphere was found, particularly at higher concentrations. The orientation of water molecules around the cations may be characterized by a broad distribution of Rb...O–H angles, peaking around the tetrahedral angle. This indicates that cations have a weak tendency to occupy a position close to one of the lone electron pairs of the O atoms.

It was also found that in the rather vaguely defined hydration shell of chloride ions, six (or somewhat more) water molecules may surround each anion. However, on average, only about three of them point straight towards the anion with one of their H atoms, whereas all other hydrogens are turned away from the ion. The six neighbouring water molecules of the hydration shell can thus be separated into about three hydrogen-bonding and three (or four) non-H-bonding water molecules.

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References

- [1] Franks F (ed) 1973 *Water, A Comprehensive Treatise* (New York: Plenum)
- [2] Narten A H, Vaslow F and Levy H A 1973 *J. Chem. Phys.* **58** 5017
- [3] Cummings S, Enderby J E, Neilson G W, Newsome J R, Howe R A, Howells W S and Soper A K 1980 *Nature* **287** 714
- [4] Harsányi I and Pusztai L 2005 *J. Chem. Phys.* **122** 124512
- [5] Harsányi I, Jóvári P, Mészáros Gy, Pusztai L and Bopp P A 2007 *J. Mol. Liq.* **131/132** 60
- [6] Harsányi I and Pusztai L 2005 *J. Phys.: Condens. Matter* **17** S59
- [7] Bopp P A, Okada I, Ohtaki H and Heinzinger K 1985 *Z. Naturf.* **40** 116
- [8] Driesner T and Cummings P T 1999 *J. Chem. Phys.* **111** 5146
- [9] Harsányi I, Pusztai L, Soetens J-C and Bopp P A 2006 *J. Mol. Liq.* **129** 80
- [10] Jal J F, Soper A K, Carmona P and Dupuy J 1991 *J. Phys.: Condens. Matter* **3** 551
- [11] Ohtaki H and Radnai T 1993 *Chem. Rev.* **93** 1157
Ohtaki H and Radnai T 1993 *Chem. Rev.* **3** 551
- [12] Soper A K and Weckström K 2006 *Biophys. Chem.* **124** 180
- [13] Pusztai L, Harsányi I, Kohara S, Wannberg A and Sheptyakov D 2006 unpublished
- [14] Kunzelmann K 2005 *J. Membr. Biol.* **205** 159
- [15] Copestake A P, Neilson G W and Enderby J E 1985 *J. Phys. C: Solid State Phys.* **18** 4211
- [16] Xu H and Kotbi M 1998 *Mol. Phys.* **94** 373
- [17] Fulton J L, Pfund D M, Wallen S L, Newville M, Stern E A and Ma Y 1996 *J. Chem. Phys.* **105** 2161
- [18] Ferlat G, San Miguel A, Jal J F, Soetens J-C, Bopp P A, Daniel I, Guillot S, Hazemann J L and Argoud R 2001 *Phys. Rev. B* **63** 134202
- [19] McGreevy R L and Pusztai L 1988 *Mol. Simul.* **1** 359
- [20] Wannberg A, Møllergård A, Zetterström P, Grönros M, Karlsson L-E and McGreevy R L 1999 *J. Neutron Res.* **8** 133
- [21] Kohara S, Suzuya K, Kashihara Y, Matsumoto N, Umesaki N and Sakai I 2001 *Nucl. Instrum. Methods A* **467/468** 1030
- [22] Evrard G and Pusztai L 2005 *J. Phys.: Condens. Matter* **17** S1
- [23] Ramos S, Barnes A C, Neilson G W and Capitan M J 2000 *Chem. Phys.* **258** 171