On the structure of aqueous hydrogen chloride solutions

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Abstract
Neutron and x-ray diffraction data taken on aqueous HCl/DCl solutions at different concentrations (Triolo and Narten 1975 *J. Chem. Phys.* **63** 3624) have been analysed by means of the reverse Monte Carlo modelling technique. Partial radial distribution functions, numbers of neighbours and cosine distributions of bond angles have been calculated from the resulting particle configurations. Based on these results, the original interpretation of experimental data must be altered; Cl–H/D correlations, for instance, seem to have a more important role than had been thought previously.

1. Introduction

Aqueous salt solutions have an important role in life; for instance, they are essential substrates of metabolic reactions. Also, their technical/industrial role can hardly be overestimated; corrosion, for example, is one of the most studied phenomena. As a consequence, aqueous electrolytes are frequently the chosen subjects of experimental and theoretical studies [1, 2]. Hydrogen chloride (here, both HCl and DCl) is a very common and important electrolyte (acid) solution from both industrial and biological points of view.

Ions in aqueous solutions may be responsible for structure 'breaking' or 'making', depending on their influence on the hydrogen bonding network of pure water. Acidic protons resulting from the dissociation of HCl/DCl molecules are assumed to fit well into the H-bond network made of water molecules (and therefore, they are generally considered as 'structure makers'), whereas the role of the chloride ions is less clear in this respect. Furthermore, the number of water molecules to which acidic protons are attached permanently (i.e., in other words, the existence of the entity H_3O^+) is still an open question [3, 4].

The structure (and more specifically, the hydration structure) is evidently concentration dependent. At low concentration the probability that an ion (including special ones, like the proton or the hydroxile ion) has a 'full' hydration shell is much higher than at higher concentrations (close to saturation). At very high concentrations the hydration shells are likely to be distorted.

Determination of the microscopic (hydration) structure of aqueous solutions poses several major difficulties: for instance, being (at least) four-component systems (H/D, O, cation, anion), there are (at least) ten partial pair correlation functions (ppcfs), $g_{ij}(r)$, that characterize their structure at the two-particle level. Deriving all of these ppcfs via the traditional, matrix inversion based, method would require results ('total structure factors', tsfs) from (at least) ten independent diffraction experiments, which is clearly a requirement that cannot be (and has never been) fulfilled in practice. Furthermore, even in highly concentrated solutions, the molar fraction of the ions is relatively low (a maximum value of greater than about 0.1 is quite rare), so that ppcfs containing ionic contributions will have low weighting factors in the total structure factors. That is, ion–water and, particularly, ion–ion correlations are usually not well represented by diffraction results; instead, detecting changes in terms of the water structure as a function of the salt concentration is expected to be more reliable.

The most basic set of diffraction experiments for a multicomponent system contains one neutron and one x-ray diffraction measurement (possibly carried out on the same sample). In principle, further data sets may be obtained by, for instance, making use of the technique of isotopic substitution in neutron diffraction. The possibility of H/D substitution for electrolyte solutions might seem appropriate; however, difficulties with handling the large incoherent inelastic scattering from ^{1}H may introduce considerable uncertainties (for a discussion of these difficulties, see e.g. [5]).

Considering the importance of this class of materials, it would be highly desirable if the amount (and accuracy) of information that can be obtained on the microscopic structure of aqueous electrolyte solutions on the basis of the two simplest diffraction experiments could be established. Interestingly, there are not many studies where the x-ray and neutron diffraction results, as a function of the ion concentration, are reported/exploited together. From the (small) set of such studies, the case of hydrochloric acid was chosen for the present study, for its essential role in chemical research and industry. Also note that aqueous hydrogen chloride solutions may be considered as the simplest case where hydrated protons play an important role.

For a four-component system, two measured total structure factors are far too few for any 'direct' analysis. For this reason, we aim here at building large structural models, containing thousands of particles; these models would be consistent with measured diffraction data. Reverse Monte Carlo (RMC) modelling [6] lends itself as a suitable tool for such an approach. In short, the RMC algorithm moves atoms/ions around randomly and calculates partial $g_{ij}(r)$s directly from particle coordinates after each (most frequently, single-atom) move. Fourier transformation of the ppcfs leads to partial structure factors (psfs) and the total (calculated) structure factor(s) of the system will be the weighted sum(s) of these psfs. Acceptance of particle moves is based on the comparison between calculated and experimental tsfs. After a certain (usually large) number of accepted moves, the calculated total structure factor(s) will approach the experimental one(s) to within experimental error levels.

In the present work, RMC modelling yielded sets of particle coordinates ('configurations') which were consistent with one neutron and one x-ray total structure factor of aqueous HCl/DCl solutions at several concentrations. In order to provide a description of the microscopic structure, partial pair correlation functions, numbers of first neighbours and cosine distributions have been calculated from the particle configurations.

2. Experimental data

Experimental data have been taken from Triolo *et al* [3]. Of the five concentrations reported, three were selected for this study, mainly because 'corresponding' x-ray and neutron measurements were carried out on samples that had quite different HCl and DCl concentrations

Table 1. Some details of the simulations. Ion pairs/D_2O means the ratio of DCl and water molecules used in the simulation.

	DCl·30D$_2$O	DCl·9D$_2$O	DCl·3D$_2$O	Water
Number density (Å^{-3})	0.0969	0.0957	0.0878	0.099
Ion pairs/D$_2$O	300/4680	500/4500	1000/3000	0/4000
Mole fractions	0.0314	0.100	0.245	—
Molarity	1.85	6.16	18.5	—
Box length (Å)	26.53	26.65	25.02	19.64
Maximum atomic displacement/ move (Å)	0.1	0.1	0.1	0.1

Table 2. Neutron weights for the various concentrations of DCl solutions.

	D$^+$–D$^+$	D$^+$–Cl	D$^+$–O	D$^+$–D	Cl–Cl	Cl–O	Cl–D	O–O	O–D	D–D
DCl·3D$_2$O	0.0037	0.0105	0.0192	0.0441	0.0075	0.0275	0.0633	0.0250	0.1151	0.1323
DCl·9D$_2$O	0.0005	0.0015	0.0083	0.0190	0.0011	0.0119	0.0273	0.0324	0.1491	0.1713
DCl·30D$_2$O	0.0000	0.0001	0.0027	0.0061	0.0001	0.0038	0.0087	0.0358	0.1648	0.1895
pure D$_2$O	—	—	—	—	—	—	—	0.0919	0.4225	0.4857

Table 3. Cutoff distances that act effectively as hard sphere constraints for the different particle pairs.

Data modelled	Neutron + x-ray			Neutron + x-ray		Neutron		Neutron + x-ray		
	D$^+$–D$^+$	D$^+$–Cl	D$^+$–O	D$^+$–D	Cl–Cl	Cl–O	Cl–D	O–O	O–D	D–D
Cutoffs (Å)	3.0	2.0	1.6	2.0	2.5	2.5	1.6	2.5	0.9	1.4

(see table 1 of [3]). For instance, the highest molar fraction of HCl in H$_2$O (which was a sample for x-ray diffraction) was 0.2, whereas the 'corresponding' neutron data were taken at a molar fraction of 0.245 (DCl in D$_2$O). For this reason, only RMC modelling of the neutron data alone could be carried out at this very high concentration. Concentrations and densities of the data sets modelled here can be found in table 1. Weighting factors for the neutron total structure factors are given in table 2. As is obvious, water–water correlations dominate the neutron diffraction results, even at the highest concentration. For the x-ray weights we used the Q-dependent values calculated on the basis of atomic form factors from the literature [7]; for the hydrogen atom/ion, the value of zero has been adapted, in accordance with reference [3]. Figure 1 shows the Q-dependence of the x-ray weights for medium HCl concentration (molar fraction of the electrolyte: 0.1). Figure 1 demonstrates that even the *relative* weights are Q-dependent; that is, the weighting factors for the ppcfs are different at different Q-values. This is why if traditional methods (involving direct Fourier transformation of the tsf) are applied then some sort of approximation is necessary for obtaining r-space information. For most aqueous solutions, including the one referred to in figure 1, O–O correlations contribute the most to the x-ray scattering pattern; only at extremely high electrolyte concentrations can the ion–water pairs match (or at least, approach) the importance of the water O–O ppcf.

3. Simulation details

Reverse Monte Carlo simulations have been carried out at three different concentrations, using one x-ray and on neutron diffraction data set [3]; pure liquid water served as reference data (from the same series of measurements [3]). Tables 1 and 3 provide some details of the
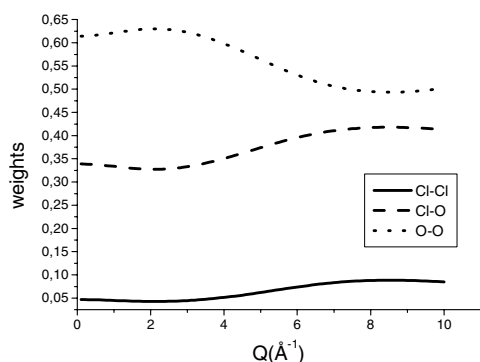
Figure 1. X-ray weights for the DCl·9H$_2$O solution.

calculations. Initial configurations were prepared by placing the ions and the oxygen atoms randomly in the simulation boxes. After some Monte Carlo (MC)-like hard sphere moves water hydrogens were added to the oxygens. Water molecules were kept together by 'fixed neighbours constraints' (fncs) [5, 8]. Intramolecular O–H/D (bonded) and H/D–H/D (non-bonded) distances within water molecules were allowed to vary within 0.9–1.1 and 1.4–1.7 Å, respectively. First each system was run as a molecular hard sphere simulation, for making sure that the (intramolecular) O–H/D bond orientations are random when modelling data are started.

For maximizing the number of hydrogen bonds between water molecules, we used a coordination constraint which aimed at forcing two (non-bonded, 'intermolecular') hydrogen atoms to be within 1.7–2.0 Å from each water oxygen. 'Structure-breaking/making' effects can then be detected by comparing the maximum achievable level of H-bonding in the solutions to that in pure water. ('Unconstrained' calculations, meaning no coordination constraints in addition to the intramolecular ones, were also run for each system, for comparison and for establishing the maximum level of consistency with experimental data.)

4. Results and discussion

Figure 2 compares experimental and (RMC) model $S(Q)$s. As is evident, building structural models that are consistent with available experimental data was relatively easy; note that these models were also consistent with fncs that kept flexible water molecules together. (Remember that at the highest concentration only the neutron data were fitted; see section 2.)

Some of the partial $g_{ij}(r)$ functions obtained from the simulations are shown in figure 3. As can be seen from table 2, the ppcfs shown have at least moderate contributions to the total structure factors; other ppcfs (with sometimes negligible weights) are neither shown nor discussed here, mostly due to their high level of uncertainties. The H/D–H/D partials—although they do have reasonable weights in the neutron data—do not show any peculiar features, apart from a weak indication of possible slight changes of the intermolecular structure with increasing concentration, and therefore their further discussion is omitted here.

A most peculiar observation can be made concerning the (water–)H/D–O $g(r)$s: a very high concentration of hydrogen chloride seems to enhance the hydrogen bond network of the water molecules. Note that for the highest concentration, results for the unconstrained run are shown; that is, the unexpectedly strong first intermolecular peak cannot be attributed to any external effects but it must be considered as an inherent feature of the data. At lower concentrations, even the 'network-enhancing' coordination constraint (see section 3) could
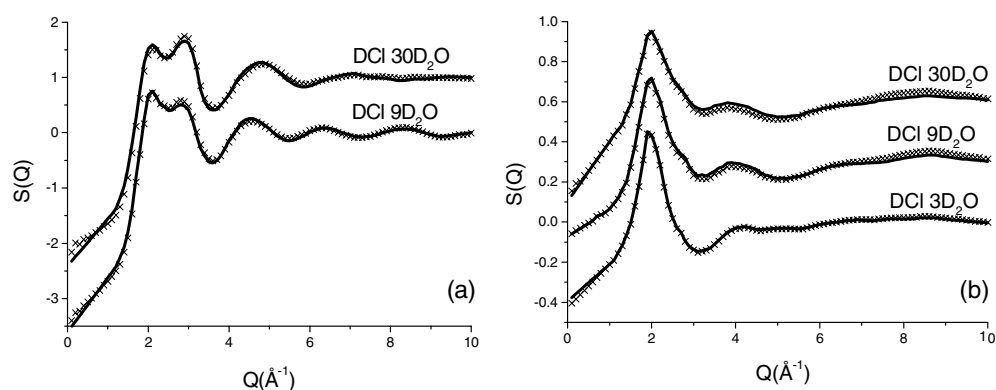
Figure 2. Experimental (solid) and fitted (crosses) x-ray (a) and neutron (b) diffraction data.
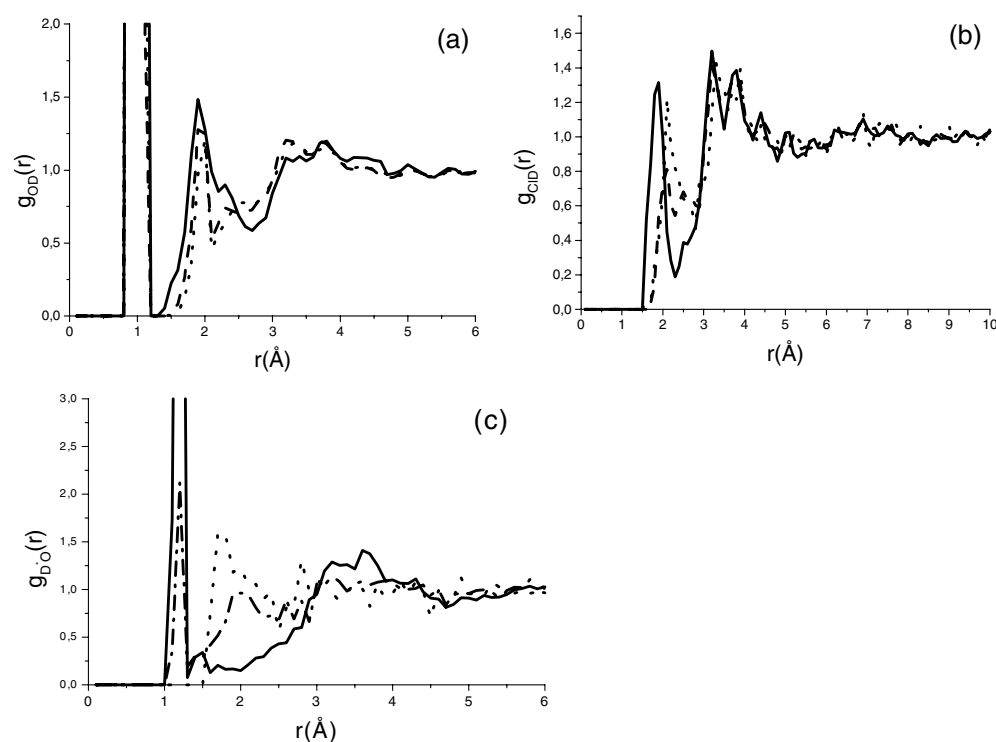

Figure 3. Partial $g_{ij}(r)$ functions calculated from the simulation for each concentration: (a) O–H/D; (b) Cl–H/D; (c) H^+/D^+–O. Solid curve: DCl·3H$_2$O; dash–dotted curve: DCl·9H$_2$O; dotted curve: DCl·30H$_2$O. Note that for the O–H/D and the Cl–H/D ppcfs at the highest concentration, the results of unconstrained RMC calculations are shown.

not achieve a similarly high level of H-bonding between the water molecules. Based on this finding it can be confirmed that H^+-ions at high concentration act as a 'structure-makers' so much that the effect of the chloride ions (which are thought more like 'structure-breakers') is compensated for. This seems rather surprising if we consider that the number of water molecules per ion decreases to 1.5 at this concentration. It has to be noted that, in [3], no similar effect was observed (although their analyses were not sensitive to this ppcf).
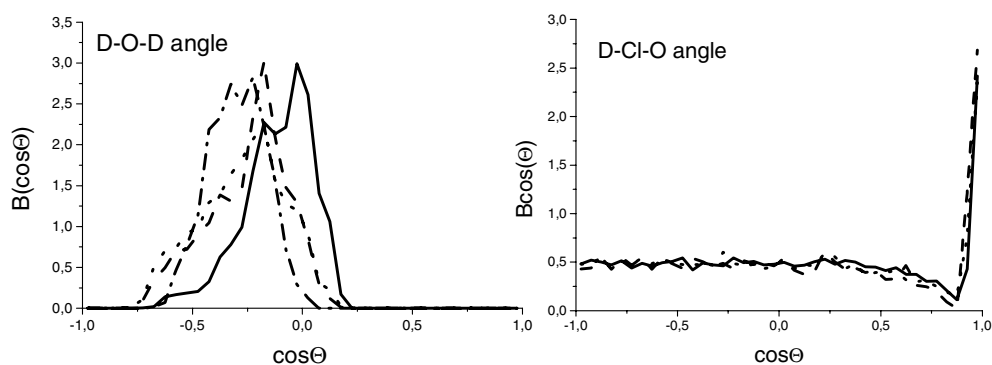
Figure 4. Cosine distributions of 'bond angles' at different concentrations. DCl·3H$_2$O (solid), DCl·9H$_2$O (dashed) and DCl·30H$_2$O (dotted), pure water (dashed–dotted).

The Cl–H/D $g(r)$ (figure 2(b)) has a distinct first maximum, particularly at the highest concentration. The downward shift, in terms of the position of the first maximum, with increasing electrolyte concentration is consistent with the concept of a more and more 'packed' hydration shell as concentration increases. At the highest concentration, exactly one water hydrogen can be found in the first coordination shell (up to about 2.3 Å). In more dilute solutions, chloride ions tend to be coordinated to more than one water molecule, although the definition of the hydration shell appears to be less sharp. (Reference [3] did not have access to this partial.)

Proton–water $g(r)$ s, characterizing the hydration of the proton, are shown in figure 3(c). As was mentioned before, the concentration of H$_3$O$^+$-ions is still an open question: most previous studies [3, 4] took it for granted that each proton is coordinated with at least one water molecule at a distance which is comparable to the O–H bonding distance in water molecules. It was our aim to check the validity of this assumption. For this reason, a further coordination constraint was introduced which required that each proton has one oxygen atom as a neighbour between 0.9 and 1.2 Å. For the highest concentration, a maximum of 59% of the protons could be forced to have one such neighbour, whereas for the medium concentration, the maximum ratio was much smaller, <20%. Note that these values are the results of strongly constraining the arrangements of particles; without constraints, not even these ratios could be achieved. It seems that such a proximity between protons and water molecules can be reached only when packing considerations become important—at very high proton concentrations. At lower concentration, the second maximum appears around 2 Å, which is more like the H-bonding distance. Up to the second minimum, at around 2.5 Å, the average number of O-neighbours is about one; most protons have this one neighbour at the 'H-bonding' distance.

Cosine distributions of H/D–O–H/D bond angles, calculated up to 1.2 Å, are shown in figure 4. These distributions, which are characteristic of the intramolecular structure of water, indicate that the shape of the water molecules changes as a result of the presence of ions in the solution. Although the trend is quite clear, it is not possible to judge if the distributions shown in figure 4 are correct quantitatively. One might speculate about the idea of different types of water molecules in electrolyte solutions; this concept was suggested on the basis of vibrational (IR) spectroscopic studies of aqueous LiCl solutions [9] where it was assumed that the spectra from water are a linear combination of 'pure' and 'salt solvated' water spectra. Possibly, the clear splitting of the H/D–O–H/D cosine distributions, particularly at the highest concentration, can be considered as an indication of a similar effect in hydrochloric acid.

Figure 4 shows the distribution of the cosines of H/D...Cl...O angles, as calculated up to the appropriate minima of the corresponding $g_{ij}(r)$s. Apart from a flat 'background' over most of the angles, a very distinct peak shows up at the value of $0°$. This feature is the signature of a nearly straight O–H/D...Cl hydrogen-bond. This finding is qualitatively consistent with the suggestion for the orientation of water molecules around Cl^- ions in alkali chloride solutions [10].

5. Conclusions

Reverse Monte Carlo simulations were carried out for aqueous hydrogen chloride solutions at several electrolyte concentrations. Total structure factors calculated from the particle configurations were in perfect agreement with experimental neutron and x-ray total structure factors; that is, our structural models are consistent with available diffraction data. Partial pair correlation functions were calculated from the final configurations of the RMC calculations.

Based on the (water–)H/D–O partial it may be suggested that at very high electrolyte concentrations the H/DCl acts as a 'structure maker'. Concerning the hydration shell of the chloride ions, a straight O–H/D...Cl hydrogen bond angle was found at each concentration. The change of the H/D–O–H/D cosine distribution function with concentration is consistent with a change in terms of molecular structure of water: the bond angle becomes smaller with increasing the number of ions. Concerning the coordination of protons, it is demonstrated that the concentration of H/D_3O^+ species must be much less than had been assumed previously.

In summary, it can be established that RMC analyses of the basic diffraction data set, containing one x-ray and one neutron total structure factor, for aqueous hydrogen chloride yielded considerably more detailed and more reliable information on the hydration structure than traditional evaluation.

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