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Solvent Structures Around Na^+ and Cl^- Ions in Water

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The structural orientation of water in the hydration shells of Na^+ and Cl^- has been obtained from a Monte Carlo simulation of a 0.55 molal NaCl solution, using the MCY model for water. The probability of first shell coordination numbers has been calculated and is compared with data of previous studies using various model systems.

(Keywords: Monte-Carlo-simulation; Hydration; NaCl *Solution; Coordination numbers; Solution structure)*

Zur Lösungsmittel-Struktur rund um Na^+ *und* Cl^- *Ionen in Wasser*

Es wurde mittels einer Monte Carlo-Simulation einer 0.55 molalen NaCl-Lösung unter Verwendung des MCY-Modells für Wasser die Lösungsmittelorientierung von Wasser in der Hydrat-Hülle von Na^+ und Cl^--Ionen erhalten. Die wahrscheinlichsten Koordinationszahlen der ersten Hydrat-Schale werden diskutiert und mit den Daten aus früheren Untersuchungen verschiedener Modellsysteme verglichen.

Introduction

Numerous radial distribution functions and the first hydration numbers have been reported for various ions in 2.2 molal aqueous solution, using the ST 2[1] and CF (central force) model[2—6] but relatively few reports have been given using the MCY model[7,8]. Recently, we have performed such a study on concentrated NaCl solutions[9]. In this work, we intended to obtain data for the first hydration shell geometry in dilute NaCl solution and to test the MCY potential in comparison to other models, for which similar studies are published.

Method of Calculation

In our Monte Carlo computer simulation the basic box contained 200 water molecules, $2\,Na^+$ and $2\,Cl^-$ ions equivalent to a 0.55 molal NaCl solution. From the experimental density a sidelength of the periodic box of 18.22 Å was deduced. The configurational energy of the system was calculated under the assumption of pairwise additivity by means of potential functions derived from *ab initio* quantum mechanical calculations on water—water and ion—water interactions[10, 11]. Further details of the simulation are given in[9]. The cut-offs for the evolution of data for the first hydration shell only were minima in the g_{IO} radial distribution functions at 3.00 and 3.9 Å for Na^+ and Cl^-, respectively. Using this definition histograms of the number of nearest neighbours were constructed. The distribution of cosines was measured as a function of $\cos\theta$, θ being defined as the angle between the dipole moment vector of water and the vector pointing from oxygen towards the ions.

Results and Discussion

1. Hydration Numbers

Experimental hydration numbers for ions depend strongly on experimental techniques and evaluation method[12]. For the Monte Carlo results, the coordination number, i.e. the average number n of water molecules within a sphere of given radius rm_1 may be defined as:

$$n = 4\pi\rho \int_0^{rm_1} g_{IO}(r)\, r^2\, \delta r,$$

where $g_{IO}(r)$ is the calculated radial distribution functions. The limit rm_1 is set at the position of the first minimum in $g_{IO}(r)$ and ρ is the average density of water in the simulation. Direct information about the ion-oxygen pair correlation in aqueous solution may also be obtained from X-ray and neutron diffraction[13] and allows an experimental determination of n. A summary of data from theoretical and experimental studies on Na^+, Cl^- and NaCl in water is given in Table 1 a (for Na^+) and 1 b (for Cl^-). For Na^+, our results completely agree with recent theoretical studies and experimental data. Apparently, concentration does not influence coordination numbers and ion—water distances within the range of these studies. For Cl^- we find the same agreement with studies on similar dilute systems.

However, concentrated solutions seem to show somewhat different values. This difference in behaviour can be explained by the weaker

Table 1. *Coordination numbers n_{IO} and average ion-oxygen (first neighbour) distances r_{IO}: a) data for sodium ion; b) data for chloride ion*

Table 1 a

Single ion or solute	Molality or ion : water	r_{IO} (Å)	n_{IO}	Method^(Ref.)^
Na^+	1 : 125	2.29	6.0	*Impey,* MD (MCY)[8]
Na^+	1 : 215	2.35	5.96	*Beveridge,* MC (MCY)[7]
Na^+	1 : 125	2.33	6.0	*Jorgensen,* MC (TIP 4)[14]
Na^+	1 : 200	2.33	5.4	*Clementi,* MC (MCY)[18]
NaCl	2 : 200	2.4	6.0	*Clementi,* MC[19]
NaCl	16 : 200	2.3	6.6	*Heinzinger,* MD (ST 2)[1]
NaCl	16 : 200	2.3	6.1	*Heinzinger,* MD (ST 2)[4]
NaCl	16 : 200	2.3	5.9	*Heinzinger,* MD (CF)[5]
NaCl	2 and 4	2.42	4	X-ray[13a]
NaCl	5.0	2.41	6	X-ray[13b]
NaCl	4 : 200	2.3	6.1	this work, MC (MCY)

Table 1 b

Single ion or solute	Molality or ion : water	r_{IO} (Å)	n_{IO}	Method^(Ref.)^
Cl^-	1 : 125	3.29	7.2	*Impey,* MD (MCY)[8]
Cl^-	1 : 215	3.25	8.36	*Beveridge,* MC (MCY)[7]
Cl^-	1 : 125	3.21	7.4	*Jorgensen,* MC (TIP 4)[14]
Cl^-	1 : 200	3.4	4	*Clementi,* MC (MCY)[18]
NaCl	2 : 200	3.4	5.1	*Clementi,* MC (MCY)[19]
NaCl	16 : 200	2.7	6.7	*Heinzinger,* MD (ST 2)[1]
NaCl	16 : 200	3.30	7.9	*Heinzinger,* MD (ST 2)[4]
NaCl	16 : 200	3.30	8.4	*Heinzinger,* MD (CF)[5]
NaCl	2 and 4	3.14	6	X-ray[13a]
NaCl	5	3.16	6	X-ray[13b]
NaCl	5.32	3.20	5.5	neutron diffraction[13c]
NaCl	4 : 200	3.3	7.1	this work, MC (MCY)

binding of H_2O to Cl^-, compared to Na^+, and, therefore, easier deformation of the Cl^- solvation shell.

The distribution of coordination numbers for ions obtained from our simulation is shown in Fig. 1. The favourite coordination number for Na^+ is found in the range 4–7. The most probable number of nearest neighbours is 6, corresponding to octahedral coordination. Our results can be compared with a system containing one single Na^+ ion using MCY[7] as well as TIPS 4[8] potential for water (cf. Fig. 1).

The Monte Carlo (MC) calculations with only a single ion in the basic cell show a very high probability for the coordination number 6. Our distribution is somewhat broader within the range 4–7.

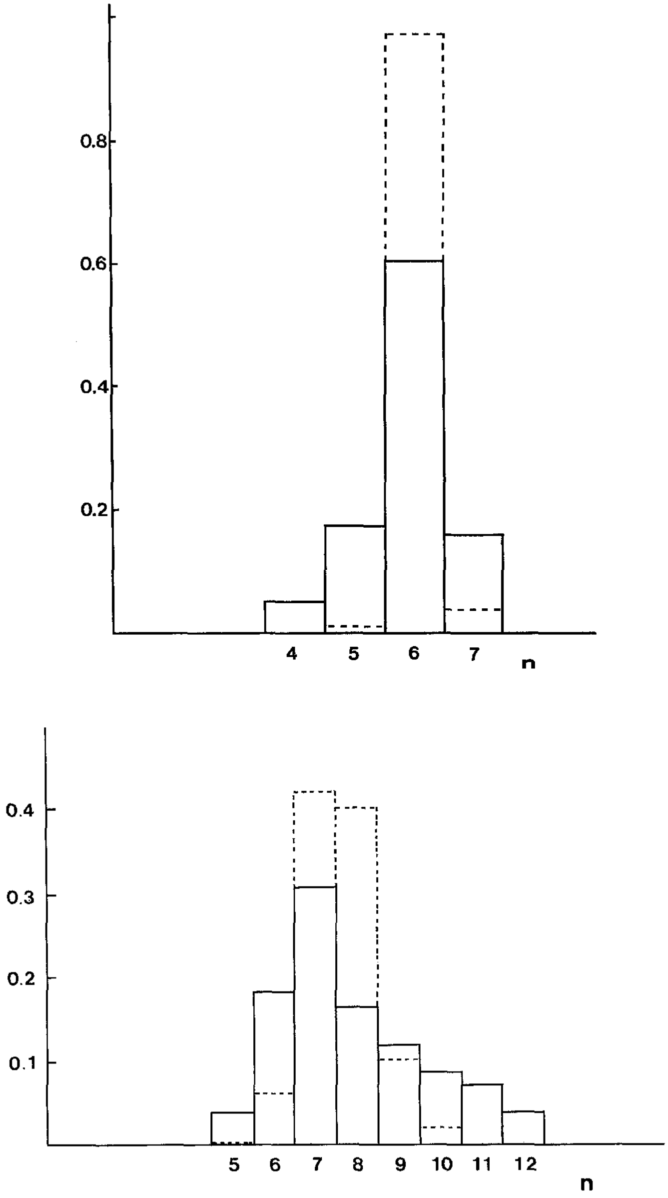

Fig. 1. Distribution of the coordination numbers of ions; MCY model (full) and TIPS4 (dashed): *a* Na^+; *b* Cl^-

This results most probably from the influence of the larger number of ions in the system studied. In the case of Cl^- the distribution fluctuates over a relatively wide range of 5 to 12 water molecules. This confirms the assumption of a weaker ion—water interaction and a more flexible first hydration shell. It should also be noted that the first minimum in the Cl-oxygen radial distribution function is less pronounced than that of the corresponding Na-oxygen function, suggesting easier diffusion of water molecules to and from the first hydration shell of Cl^-. These data can be compared with calculations of *Jorgenson*[14] and *Beveridge*[7]. Their investigations also lead to coordination numbers of about 7–8, in agreement with present results. However, in our study, these coordination numbers have a lower relative probability and the whole range of distribution is wider again. The average hydration number of Cl^- ion in our stimulation was found to be about 7, which is larger than the value obtained experimentally by X-ray[13a, 13b] and neutron diffraction methods[13c]. We consider this difference to be at least partly due to the higher concentration used in the experimental work.

2. *Angular Distribution of Water Molecules*

From the relative position of the main peak in the ion-oxygen and ion-hydrogen radial distribution functions, the orientation of water molecules in the hydration sphere can be deduced. Such data have been shown, however, to be only of limited significance[15—17].

In order to provide more reliable information about the orientation of the water molecules, the distribution of cosine θ has to be evaluated directly. θ is defined as the angle between the dipole moment vector of water and the vector pointing from the oxygen atom towards the ion. In the case of Na^+, the angular distribution of the water dipoles has its maximum at $\cos\theta = -1$ (cf. Fig. 2). This result indicates that the water molecules are preferentially in a ion-dipole oriented position (C_2V symmetry). The comparison of structural orientation of water molecules in the first hydration shell of Na^+ with other water models (CF and ST 2) is also shown as insert in Fig. 2. Molecular dynamics studies using the ST 2 potential model for water show a preference of the "lone pair" orientation for Na^+ whereas calculations with the central force (CF) model indicate a preference of ion-dipole orientation. The disagreement of the ST 2 results seems to be due to the fact, that the lone pair direction is emphasized in this model through the pronounced negative point charges representing such "lone pairs".

However, a pronounced shoulder in our distribution curve indicates, that $\cos\theta = -0.82$ ($\theta = 145°$) leads to a somewhat favourable configuration, corresponding to a "lone pair" orientation, which however does not reach the stability or the "best" configuration with $\theta = 180°$.

The distribution of $\cos\theta$ for Cl^-/H_2O is also shown in Fig. 2. The mean value of $\cos\theta$ is about 0.67, corresponding to an angle of 48°, the maximum is located at $\theta = 44°$. The average orientation of water molecules around a Cl^- ion can therefore be characterized by nearly linear hydrogen bonds. All other computer simulations as well as experimental data[5,7,13c,20] are in full agreement with these data. It should be noted that the distribution curve for Cl^- shows a remarkable tailing at negative values of $\cos\theta$. This indicates that there is a rapid decrease in the orientation of the water molecules at even slightly larger water—ion distances, where coulombic forces (and hence ion-dipole orientation) become increasingly dominant over overlap-determined orientation.

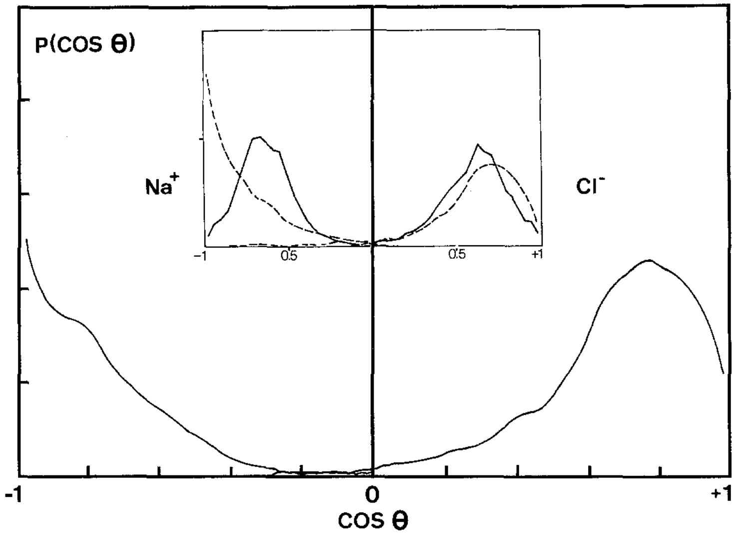

Fig. 2. Cosine distribution of the angle between the vector pointing from the oxygen atom towards the center of the ion and the dipole moment vector of the water molecules in the first hydration shell of Na^+ and Cl^-, for 0.55 molal NaCl solution. Distributions are normalized. The insert shows the distribution of $\cos\theta$ in the first hydration shell of ions for a 2.2 molal NaCl solution, using ST 2 (full) and CF (dashed) water model, according to Ref.[5]

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