

Hydration of Metal and $(\text{CH}_3)_4\text{N}^+$ Ions in Solutions of Mixed Salts

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Dedicated to Professor Alfred Klemm in honour of his 100th birthday

Molecular dynamic simulations of aqueous solutions containing Me_4NCl and an inorganic salt, NaCl , MgCl_2 or CaCl_2 , have been performed at room temperature. Flexible models have been employed for the Me_4N^+ -ions and the water molecules. The hydration of the ions has been discussed on the basis of the radial and angular distribution functions. The geometrical arrangement of the water molecules in the coordination shell has been deduced from the distributions of the angles between two vectors connecting the ion and an oxygen and of the angles between three oxygens. The addition of Me_4N^+ does not influence noticeably the size and structure of the cationic hydration shells, but it affects remarkably their persistence, causing a fast exchange of the water molecules between the shell and the bulk solvent.

Key words: Hydration of Ions; Aqueous Solutions of Hydrophobes; MD Simulation.

1. Introduction

Hydrophobic hydration and hydrophobic association play a key role in chemistry and biology. Despite a lot of experiments and computer simulations, the nature of these effects is not yet fully understood. There are, however, no doubts that the water H-bonded network and a tendency to maintain these H-bonds are crucial [1]. Intuitive models of hydrophobic hydration, based on thermodynamic findings [2], see water molecules forming a clathrate around apolar solutes and assume an enhancement of the water structure in the vicinity of hydrophobes. It is known that the mobility of water molecules in solutions of hydrophobes is reduced. This has often been taken as evidence for the enhancement of the water structure. Computer simulations [3] have shown a tangential orientation of the water molecules around apolar solutes, which is consistent with the clathrate-like structures deduced from thermodynamic finding. Recent nuclear magnetic resonance (NMR), dielectric relaxation, and femto-second infrared (IR) experiments have also confirmed that hydrophobes affect the dynamics of the water molecules [4–6], but neither computer simulations nor diffraction experiments [7, 8] have demonstrated an enhancement of the water structure.

Alkali and alkali earth ions play an important role in many biological processes, which occur in systems containing hydrophobic groups. There are several clues that the biological activity of the metal ions depends on their hydration [9]. Thus, the question appears whether the presence of apolar groups affects the hydration of metal ions. Though the interactions of apolar solutes with water are weaker than those of metal ions, self-diffusion experiments [10–12] have shown that in solutions of inorganic salts and apolar compounds the hydrodynamic radii of Na^+ and Ca^{2+} ions are reduced, whereas that of $(\text{CH}_3)_4\text{N}^+$ remains unaffected. This suggests a partial dehydration of the metal ions.

Aqueous solutions of tetraalkylammonium salts are frequently employed as model systems to investigate hydrophobic phenomena. Though their ‘hydrophobic’ behaviour increases with the increasing length of the alkyl chain, the aqueous solution of $(\text{CH}_3)_4\text{NCl}$ can also serve as the model system since $(\text{CH}_3)_4\text{N}^+$ is ‘more apolar’ than ‘ionic’ [13].

In order to investigate a possible interrelation between the hydration of the biologically important (Na^+ , Mg^{2+} , Ca^{2+}) ions and the ‘apolar’ $(\text{CH}_3)_4\text{N}^+$ ion, we have carried out molecular dynamics (MD) simulations of NaCl , MgCl_2 , and CaCl_2 dissolved in aqueous solutions of $(\text{CH}_3)_4\text{NCl}$.

2. Details of the Simulation

The MD simulations were carried out at an average temperature of 299 K in the microcanonical (NVE) ensemble. The concentrations of both salts were 0.55 M. This means that in all simulations the periodic cube contained 400 water molecules, four molecules of $(\text{CH}_3)_4\text{NCl}$, and four molecules of the inorganic salt. The lengths of the boxes were calculated from the experimental densities of the aqueous solutions of the mixed salts at 298 K.

The water molecule was treated as a flexible three-site body with partial charges located on the oxygen ($q_{\text{O}} = -0.66 e_0$) and the hydrogens ($q_{\text{H}} = 0.33 e_0$). The interactions between the water molecules were described by the potential derived by Bopp, Jancso, and Heinzinger, called BJH potential [14]. This effective potential is the sum of two parts representing the intra- and intermolecular interactions; it permits internal vibrations of the molecule.

The effective potentials for the inorganic ions were derived from ab initio calculations by fitting the potential energies between the ions and water molecule, assuming the BJH model. Details of the potential parameters have been presented previously [15–17]. These potentials describe the structures of the coordination shells of the inorganic ions in aqueous solutions correctly.

The $(\text{CH}_3)_4\text{N}^+$ ion was considered as a flexible five-site body with partial charges located on nitrogen ($q_{\text{N}} = -0.56 e_0$) and on the methyl groups, treated as pseudo-atoms ($q_{\text{Me}} = +0.39 e_0$) [18]. A spectroscopic-type potential was employed to keep the charged sites together. This potential was expressed in terms of two internal coordinates: the stretch of the N–Me bond and the bending of the Me–N–Me angle. The intermolecular part of the potential was the sum of Coulomb and Lennard–Jones terms. The Lennard–Jones parameters were presented previously [18]. All interactions of the inorganic ions with Me_4N^+ were also expressed as sums of Coulomb and Lennard–Jones terms and the potential parameters were calculated according to the standard combining rules. The Lennard–Jones parameters for the inorganic ions were taken from Koneshan et al. [19].

In all simulations, the initial configurations were obtained by a random placement of the particles in the cubic box. Ewald summation was applied for the Coulomb interactions and the shifted force potential

method was used for all non-Coulomb ones [20]. The simulation time step was 0.25 fs. After about 10 ps of equilibration, the simulations were extended up to 100 ps. Coordinates and velocities of all sites were collected in 1 fs intervals. In all simulations the stability of the potential energy was better than 0.1%. For all simulated solutions the temperature, averaged over the whole simulation runs, was 299 ± 4 K.

3. Results and Discussion

In all simulated solutions, an ion association does not occur and the hydration shells of Cl^- are independent of the cations. Also in the presence of Me_4NCl , ionic association does not occur. Therefore the radial distribution functions between Cl^- and the water sites are identical in all simulated solutions. The g_{ClO} and g_{ClH} functions exhibit peaks at 0.330 and 0.242 nm. The position of the g_{ClO} peak agrees with the average distance between the anion and the oxygen atoms deduced from X-ray diffraction, 0.326 nm [21]. These first peaks are not clearly separated from the bulk. This is evident for the high flexibility of the anionic hydration shell and for an easy exchange of the water molecules between this shell and the bulk. The short distance between the anion and the hydrogens suggests almost linear hydrogen bonds between the anion and the water molecules. Indeed, the most probable value for the angle between the vector connecting Cl^- with the water-oxygen and the intramolecular OH bond is about 10° . Integration of the first peaks of the g_{ClO} and g_{ClH} functions indicates that the coordination shell of Cl^- consists of about 8 water molecules. The same coordination number has been reported for aqueous solutions of NaCl, MgCl_2 , and CaCl_2 [22].

3.1. Structure of the Hydration Shells of the Metal Ions

The radial distribution functions for the metal cations and water-oxygen in solutions of Me_4NCl are presented in Figure 1 and compared with the analogous functions in aqueous solutions. The influence of the Me_4NCl on the distribution of the oxygens around the sodium and magnesium cations is seen to be almost negligible. The first peaks of the radial distribution functions between the Na^+ and Mg^{2+} ions and oxygen appear at 0.23 and 0.202 nm, respectively. The same distances, which agree very well with the experimental

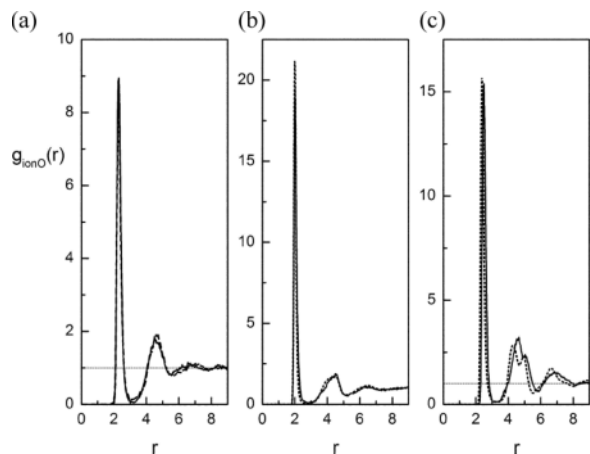


Fig. 1. Cation-oxygen radial distribution functions in aqueous (dashed) and Me_4NCl solutions of NaCl (a), MgCl_2 (b), and CaCl_2 (c).

data (0.24 [23] and 0.20 nm [24], respectively), have been obtained in simulations of aqueous solutions of NaCl [17] and MgCl_2 [25]. One should, however, notice that these first peaks are slightly lower than those in aqueous solutions. Integration of the first peaks of the ion–oxygen radial distribution function up to its first minimum yields the number of the water molecules in the first coordination shell. In aqueous solutions, the Na^+ and Mg^{2+} ions are six-coordinated [17, 22]. The addition of Me_4NCl does not affect the size of the Na^+ shell and this cation remains six-coordinated, but the first coordination shell of Mg^{2+} is slightly larger and consists of 7 water molecules.

As seen from Figure 1, the presence of Me_4NCl does not influence the second shell of Mg^{2+} and the g_{MgO} function, similar to the one in aqueous solution of MgCl_2 , exhibits a second broad and asymmetric peak, centred around 0.45 nm. Its position coincides with the distance 0.41 nm extracted from X-ray scattering [26]. The first and second maxima of g_{MgO} are well separated, thus the number of water molecules in the second shell can be determined unambiguously. In aqueous solution, the second coordination shell of Mg^{2+} contains 16 water molecules, in solution with the apolar Me_4N^+ ions this second shell is slightly bigger and contains 18 water molecules.

Addition of Me_4NCl affects the position and shape of the first peak of the g_{CaO} function. In aqueous solution, the average distance from Ca^{2+} to the nearest oxygens, computed from MD simulation,

0.237 nm [27] coincides with the experimental result, about 0.24 nm [28]. In the solution with Me_4NCl , the first peak is lower and is upshifted to 0.25 nm. The g_{CaO} function also exhibits a second peak, centred at 0.46 nm. It is worthwhile noticing that in aqueous solutions this second maximum is split into two peaks of similar heights, centred around at 0.43 and 0.49 nm. As seen from Figure 1c, in the solution of Me_4NCl this splitting vanishes. An addition of methanol produces a similar effect [27].

When Me_4NCl is added, both shells of Ca^{2+} increase in population. The first shell consists of 11 molecules whereas the second one contains more than 30. In aqueous solution, these shells consist of 10 and 27 water molecules [15, 27]. The slight increase of the larger coordination number seems to be in contrast with a decrease of the hydrodynamic radius of Ca^{2+} , and in consequence a decrease of the ‘dynamic’ hydration number of this cation [12]. This ‘dynamic’ hydration number, however, concerns only the molecules the motions of which are correlated with the ion. Their residence time in the ionic shell must be longer than a characteristic time for the ion translations. We shall come back to this point below.

The internal structure of a coordination shell can be characterized by the following angles:

- (i) the angle φ , i. e. the angle between the dipole moment and the vector pointing from the ion centre to the oxygen;
- (ii) the angle θ , i. e. the angle between two vectors pointing from the ion centre to the nearest oxygens and
- (iii) the angle ψ , i. e. the angle between three oxygen atoms of molecules in the hydration shells.

The distributions of φ (not shown here) with a persistent dominant peak at $\cos(\varphi) = -1$ show that the addition of Me_4NCl does not affect the orientation of the water molecules in the first shells of the inorganic cations, and the antidipole orientation is always favoured. However, the dipole moments of a few water molecules in the Ca^{2+} shell are tilted by about 50° from the antidipole orientation, as it can be deduced from a shoulder at $\cos(\varphi) = -0.65$. Similar distortion of the antidipole orientation has been observed previously [15, 27] in aqueous solution.

The distributions of the angle between pairs of vectors pointing from the cation to the neighbouring oxygen atoms, presented in Figure 2, describe the symme-

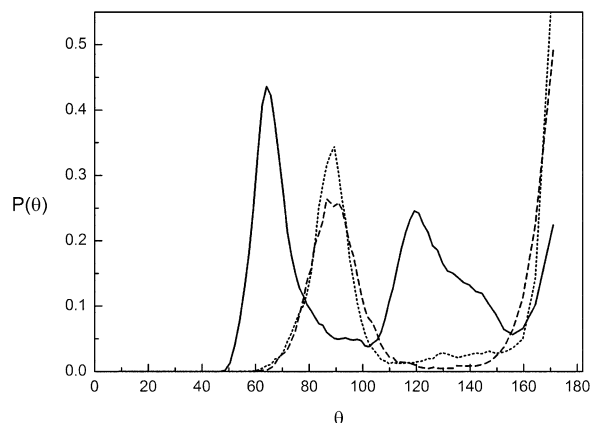


Fig. 2. Distribution of the angle θ between two vectors connecting the cation with the nearest oxygen atoms in the shells of Na^+ (dashed), Mg^{2+} (dotted), and Ca^{2+} (solid).

try of the first coordination shell. Two peaks centred at 90° and 180° prove that the addition of Me_4NCl does not affect the structure of the shells of Na^+ and Mg^{2+} and that the water molecules form octahedra around these cations. The distribution of the angles between triplets of oxygen atoms, with two peaks centred at 60° and 90° , shown in Figure 3, confirms the lack of influence of the Me_4N^+ on the octahedral symmetry of the Na^+ and Mg^{2+} shells.

The addition of the apolar Me_4N^+ ion improves the symmetry of the Ca^{2+} shell. In aqueous solution, the angular distribution exhibits two peaks, centred at 65° and around 135° , and only the former peak might be expected for tetrahedral or hexahedral

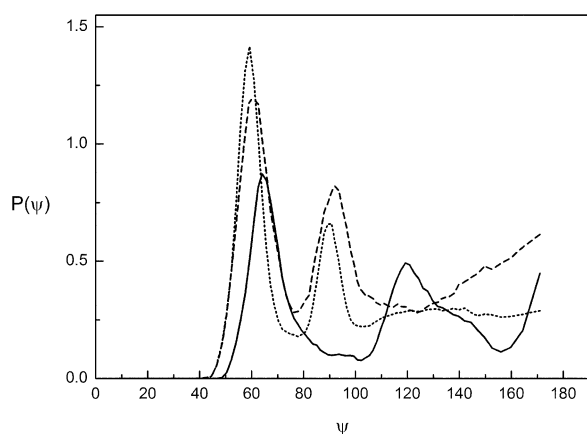


Fig. 3. Distribution of the angle ψ between three oxygens in the shells of Na^+ (dashed), Mg^{2+} (dotted), and Ca^{2+} (solid).

symmetries [15, 27]. In Me_4NCl solutions, as seen from Figure 2, the most probable angles are smaller, about 60° and 120° . These most probable angles are close to values, which might be expected for tetrahedral or hexahedral symmetry. Even though the structure of the Ca^{2+} shell seems to be closer to tetrahedral or hexahedral symmetry, the shoulder observed at about 135° suggests that some of the water molecules do not fit into a polyhedron around Ca^{2+} . The improvement of the symmetry of the Ca^{2+} shell is also confirmed by the O–O–O angles (see Fig. 3). This angular distribution exhibits two broad peaks around 64° and 120° , which fit better the tetrahedral or hexahedral symmetry than the angles about 55° and 107° found in aqueous solution [25].

3.2. Structure of the Me_4N^+ Shell

Despite strong interactions between water and metal cation, the addition of the inorganic salts does not affect the hydration shell of the Me_4N^+ ion at the concentration studied. In solutions of metal chlorides the g_{NO} and g_{MeO} functions are almost identical to the ones in aqueous solution. As an example the g_{NO} and g_{MeO} functions, determined in the CaCl_2 solutions, are presented in Figure 3 and compared with those in pure Me_4NCl solution. Broad peaks of the g_{NO} and g_{MeO} functions are observed around 0.45 and 0.36 nm, respectively. Their positions coincide with the distances of 0.47 and 0.37 nm extracted from neutron diffraction experiments [29]. It is worthwhile noticing that the result 0.36 nm from the methyl group to oxygen is typical for the distance between the carbon atom of an apolar group and water [30].

Integration of the g_{NO} functions up to their first minima indicates that the addition of NaCl and MgCl_2 affects neither the size nor the structure of the Me_4N^+ shell, which consist, like in aqueous solution, of 27–28 tangentially oriented water molecules. Though the presence of CaCl_2 does not influence the tangential orientation of the water molecules in the Me_4N^+ shell, it reduces the hydration number to about 20 molecules.

3.3. Residence Time of the Water Molecules in the Ion Shells

An important feature of ions in solutions is the persistence of the water molecules in the hydration shells.

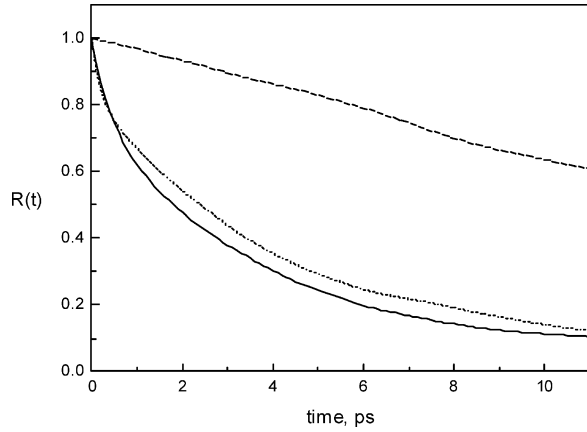


Fig. 4. Residence correlation functions for the water molecules in the shells of Na^+ (dashed), Cl^- (dotted), and Me_4N^+ (solid).

A residence time of the water molecules in the ionic shells was calculated from the time correlation function $R(t)$, proposed previously by Impey et al. [31]. This time correlation function is defined as follows:

$$R(t) = \frac{\sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \kappa_{ij}(t + \Delta t)}{N_\alpha N_\beta}. \quad (1)$$

N_α is the number of ions, and N_β denotes the number of water molecules in the sphere of the radius defined by the first minimum of g_{ionO} . $\kappa_{ij}(t)$ is the step function: $\kappa_{ij}(t) = 1$ if the j molecule is in the ion shell and $\kappa_{ij}(t) = 0$ otherwise. $R(t)$ has been computed for at least 500 consecutive configurations with a time interval $\Delta t = 0.2$ ps [27].

Examples of $R(t)$ obtained for the ions in the $\text{NaCl} + \text{Me}_4\text{NCl}$ solution are displayed in Figure 4. It is seen that $R(t)$ decrease monotonously. They can be fitted by a double exponential decay:

$$R(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right). \quad (2)$$

Assuming that τ_1 is the shorter of the two times, the second term describes the persistence of the molecules in the ion shells, whereas the first one concerns the escape of a molecule located close to the border of the ionic shell. A_1 and A_2 are the fractions of the molecules involved into both processes.

The influence of the Me_4N^+ ions on the lifetime of the hydration shells of the inorganic ions is dramatic. In aqueous solutions, the first coordination shells of the

Na^+ , and particularly those of Ca^{2+} and Mg^{2+} ions, are very stable. About 90% of the water molecules stay in the Na^+ shells for about 170 ps [32]. The persistence times of the first coordination shells of the alkali earth cations are much longer, and more than 95% of the water molecules do not leave the shells of Ca^{2+} and Mg^{2+} during the whole simulation time of 150 ps [22, 27]. Such feature agrees with the very long lifetime of the first coordination shells of Ca^{2+} (about 700 ps) and Mg^{2+} (about 420 ps) reported by Koneshan et al. [19]. The addition of Me_4NCl destabilizes the first shells of the metal cations. Less than 90% of the water molecules stay in the Na^+ shell during about 20 ps. The persistence of the Ca^{2+} and Mg^{2+} shells is much longer, but remarkably shorter than in aqueous solutions. Only about 80% of the water molecules stay in the Ca^{2+} shell during 80 ps. The most stable one is the first shell of Mg^{2+} since we find about 90% of the molecules to reside there for more than 120 ps. The shorter persistence of the coordination shells agrees with a decrease of the hydrodynamic radii of Na^+ and Ca^{2+} , postulated from the self-diffusion experiments [12].

Even though the Cl^- shell is not very stable in aqueous solution, the addition of Me_4NCl destabilizes also this shell. In aqueous solution about 76% of the water molecules stay in the Cl^- shell for at least 20 ps [32]. When Me_4NCl is added, the Cl^- shell becomes very flexible, only about 60% of the water molecules reside longer than 6 ps. The exchange of the water molecules between the Me_4N^+ shell and the bulk water is rather fast. In aqueous solution the persistence of this shell does not exceed 5 ps, yet the addition of metal chlorides does not affect the residence time.

4. Conclusions

The results presented here indicate that the influence of the ‘apolar’ Me_4N^+ ion on the hydration of the metal ions is stronger than the influence of the strongly hydrated metal cations on the Me_4N^+ shells. The addition of Me_4NCl affects only very little the coordination numbers and the structures of the hydration shells of Na^+ , Mg^{2+} , and Ca^{2+} ions. The presence of the ‘apolar’ cation affects, however, remarkably the exchange of water molecules between the cation shells and the bulk solvent. This may be a phenomenon, which influences the biological activity of the metal ions.

Despite strong interactions of the metal ions with water, the addition of NaCl, MgCl_2 , and CaCl_2 does not affect noticeably the hydration shells of the Me_4N^+ ions. Only in CaCl_2 solution, the number of water molecules in the Me_4N^+ shell is slightly reduced.

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