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Do ions affect the structure of water? The case of potassium halides

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ABSTRACT

We study the structural properties of aqueous solutions of potassium chloride and fluoride at ambient conditions and upon supercooling with the use of molecular dynamics. We perform the calculations at increasing concentration in a range from 0.67 mol/kg up to 3.96 mol/kg. We investigate the modifications of the hydration shells and the changes in the water structure induced by the presence of the ions. The oxygen–oxygen structure is strongly dependent on the ionic concentration while the hydrogen bonding is well preserved. The results show that increasing the ion concentration is analogous to increase pressure on pure water. The KF salt has a stronger effect on water due to the fluoride anion. F^- appears also more effective as substitutional of the oxygen in the water network with possible relevant consequences on the tendency of water to transform to the high density phase.

1. Introduction

The effects of dissolved ions on the structure of water are the subject of a never ending debate for a long time [1–3]. The ionic aqueous solutions are the subject of several experimental [4–12] and computer simulation studies [13–28]. In spite of the great effort there are still a number of unsolved questions. The main issues concern how the short range order, the hydrogen bond network and the phase diagram of water are changed by the interaction with ions [27–30]. The basic systems are typically solutions of simple salts, alkali halides, where the hydration shells of water around the ions can be studied more in details [31–34].

A subject of discussion concerns the use of the concept of structure breaker or maker ions according to the idea of the Hofmeister series [35,36,13]. This classification scheme has been questioned [37,6–8,24] and there are evidences from experiments [7] and computer simulations [24,38] indicating that the effect of the ions is similar to the application of pressure on pure water. This analogy between the effects of ions and pressure has been addressed for a long time [21] but it is still a matter of discussion [22].

Besides the traditional problems a new interest in the field has grown in recent years. Computer simulation studies found that the anomalous behaviour of water upon supercooling is preserved in solutions with salts at low and moderate concentration [39–41] with a shift of the hypothesized second critical point of water in a region accessible to experiments [25,26,42]. The phase diagrams of the aqueous solutions in the supercooled region show that the addition of salt perturbs the low density liquid (LDL) structure of water and stabilizes the high density liquid (HDL) phase.

In previous work we already addressed the problem of the structure of water in solutions [24]. In particular we compared more in details the effects of two salts with the same anion Cl^- in combination either with Na^+, classified as structure maker or K^+ considered a structure breaker cation. The results show that the structure of water in solution is mainly affected by the ion concentration but it is weakly dependent on the type of salt. Moreover upon increasing concentration water structure shows the tendency to get the features of the HDL phase.

Here we want to test further the effects of the ions in this framework. For this reason we study and compare the results for $KCl(aq)$ and $KF(aq)$. The aqueous solutions of these potassium halides seem to be of particular interest. Their structural properties have been studied at increasing concentration with neutron scattering combined with the EPSR technique [6]. K^+ ions are regarded to have little effect on water structure [6,13] so that it is possible to catch more directly the effects of the anions. In particular it is interesting to understand the effect on water of a relatively small anion, F^-, with a greater charge density and for this reason classified as structure maker.

In the next section we give the details of the simulation. In Section 3 we report the structural properties of water in solution with *KCl* and *KF*. The hydration of ions is discussed in Section 4. The conclusions are given in Section 5.

2. Details of simulations

We performed Molecular Dynamics (MD) simulations of TIP4P water in solution with *KF* and *KCl* salts. TIP4P is a rigid site model [43] where a water molecule is represented with four sites. Two

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positive charged sites mimic hydrogen atoms (H). They are connected to the neutral oxygen (O) site, whose negative charge is shifted by 0.15 Å in the molecular plane and attributed to the fourth site (X). The geometry consists in two OH bonds of length 0.9572 Å with an angle $\theta = 104.5°$ between them. The OX line forms an angle $\theta/2$ with the OH bonds. Each H site has an effective charge of 0.52e, and these charges are neutralized by the negative X charge. The oxygens of the water molecules interact with a Lennard–Jones (LJ) potential. The TIP4P model can reproduce well both structural and thermodynamic properties of water [25,44]. Also the ion–ion and the ion–water interactions are represented by a combination of Coulombic and LJ potentials. The potential can be written in general as

$$u_{\alpha\beta}(r)=\frac{q_\alpha q_\beta}{r_{\alpha\beta}}+4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{12}-\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{6}\right]. \tag{1}$$

The ion–ion parameters are taken from Jensen and Jorgensen (JJ) [45], while the ion–water parameters are derived by using geometric mixing rules. The JJ parameters can reproduce very well the structural characteristics and the free energies of hydration of the ions. All the parameters of Eq. (1) are reported in Table 1.

In the simulations we use a total number of water molecules and ions fixed at $N_w + N_{ions} = 512$ with an equal number of anions and cations. For each concentration c we have $N_w = 500$ for $c = 0.67$ mol/kg, $N_w = 488$ for $c = 1.36$ mol/kg, $N_w = 476$ for $c = 2.10$ mol/kg, $N_w = 448$ for $c = 3.96$ mol/kg.

We applied periodic boundary conditions. The interaction potentials were truncated at $r_{cut} = 10$ Å taking into account the long range electrostatic effects with the Particle Mesh Ewald (PME) method.

We performed MD simulations with the use of the Berendsen thermostat and barostat [46]. The simulations were performed at $T = 300$ K and $T = 220$ K with the pressure fixed at the atmospheric value. We used the software package GROMACS [47]. The system was equilibrated for 20 ns and the averages were calculated on 30 ns.

3. Water structure in solution

In Figs. 1–2 we report and compare the radial distribution functions (RDF) $g_{OO}(r)$ of $KF(aq)$ and $KCl(aq)$ for different salt concentrations at $T = 300$ K and $T = 220$ K respectively. They are representative of the effects of the ions on the structure of water. At $T = 300$ K the RDF are similar for low concentrations. The increase of concentration produces very different effects in the two solutions. A small shift of the second peak of the $g_{OO}(r)$ is found in $KCl(aq)$. Instead the increase of ion concentration in $KF(aq)$ induces a strong distortion of the oxygen–oxygen structure. The second peak moves from 4.4–4.5 Å to 4.1–4.2 Å. This behaviour is in agreement with the trend found in experiments [6], where the highest concentration investigated is 4.8 solutes for 100 water molecules. At the concentration of 3.96 mol/kg corresponding to 7.1:100 we find a more pronounced effect with the second shell of oxygens that almost collapses on the first shell.

Table 1
Lennard–Jones parameters of the interactions between oxygen atoms in the TIP4P water molecule, between ions and between ions and oxygen. H and X sites of water interact only by Coulomb potential.

	ϵ (kJ/mol)	σ (Å)
OO	0.649	3.154
KK	0.002	5.170
KCl	0.079	4.559
ClCl	2.971	4.020
KO	0.037	4.038
ClO	1.388	3.561
FF	2.971	3.050
KF	0.079	3.971
FO	1.388	3.102

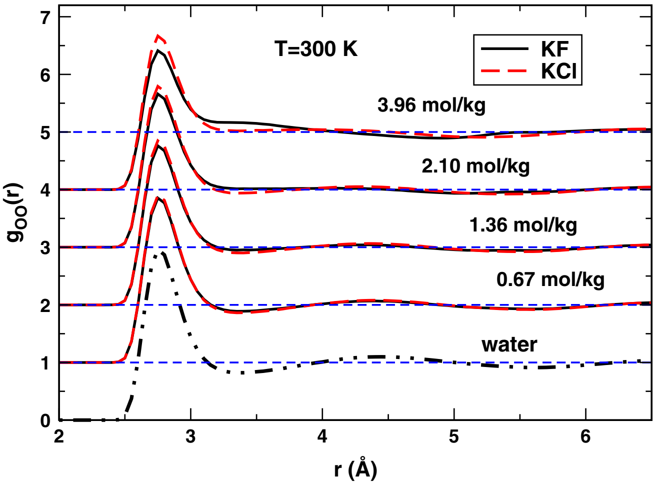

Fig. 1. Comparison of the $g_{OO}(r)$ of water in $KF(aq)$ (solid line) and in $KCl(aq)$ (dashed line) solutions at increasing concentrations compared with pure TIP4P water at $T = 300$ K.

Also at the lowest temperature of $T = 220$ K in $KF(aq)$ the second shell shifts to lower distances and for the concentration 3.96 mol/kg the second peak is located at 3.5 Å. Smaller effects are observed in $KCl(aq)$.

In spite of the perturbation of the oxygen structure it can be noted from Fig. 3, where the $g_{OH}(r)$ of $KF(aq)$ is reported, that the hydrogen bond (HB) of water is well preserved. The O–H structure does not change much with concentration and the effect of temperature is only an enhancing of the first peak. The added salt, as already found in experimental [7,8] and computer simulation [24,26] studies, distorts the arrangement of the water network but it has little effects on the O–H and H–H structures.

In our previous work [24] we found that the water structure in $NaCl(aq)$ is very similar to the structure in $KCl(aq)$, here the different behaviour in the $KF(aq)$ can be attributed to the high charge density of F^-. This effect however becomes relevant only at low temperature and high concentration.

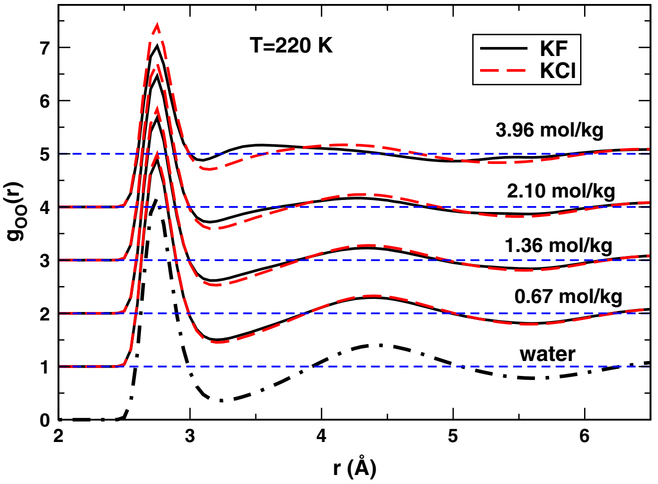

Fig. 2. Same as Fig. 1 at $T = 220$ K.