



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.

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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 $\theta = 104.5^\circ$ 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

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

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

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

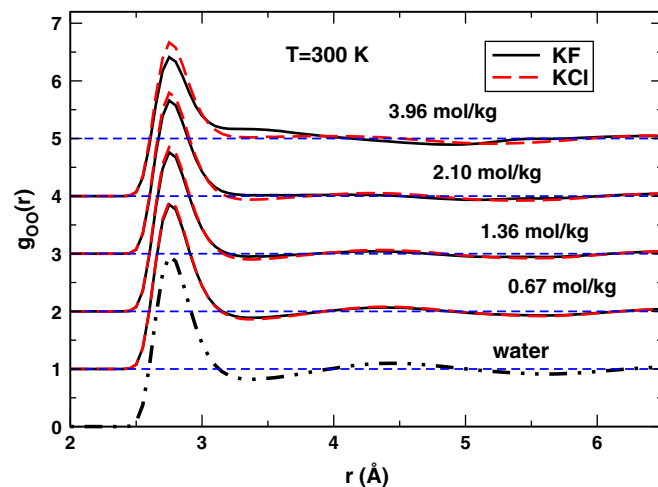


Fig. 1. Comparison of the $g_{OO}(r)$ of water in $KF(aq)$ (solid line) and in $KCl(aq)$ (dashed line) solutions at increasing concentrations compared with pure TIP4P water at $T = 300$ K.

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.

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.

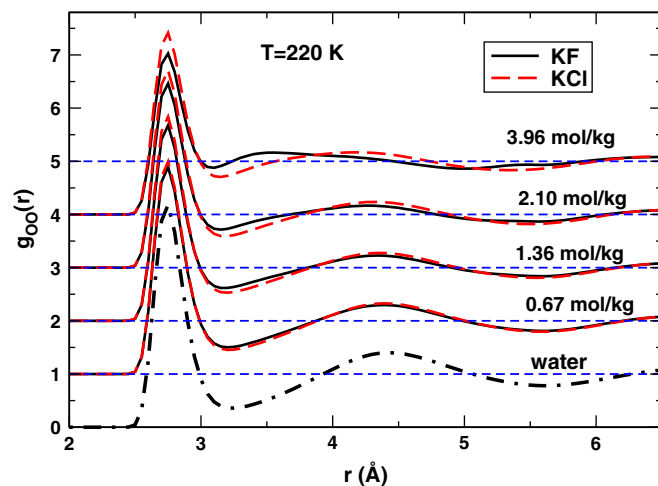


Fig. 2. Same as Fig. 1 at $T = 220$ K.

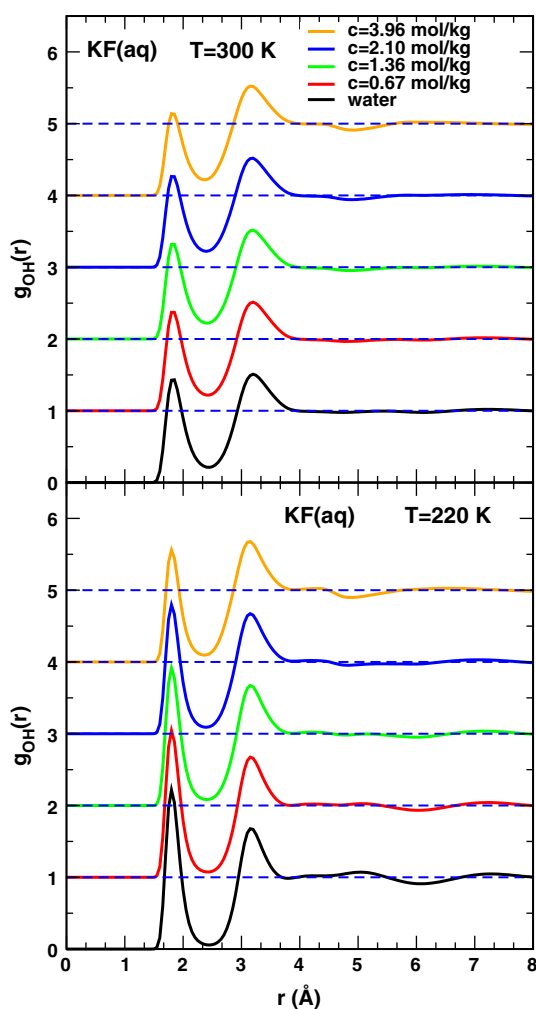


Fig. 3. Oxygen–hydrogen RDF of water in $KF(aq)$ solution at increasing concentration compared with pure TIP4P water at $T = 300$ K (top) and $T220$ K (bottom).

4. Hydration of cations and anions

The potassium–water and the anion–water RDF are reported in Figs. 4 and 5 for ambient conditions and $c = 0.67$ mol/kg. The effects

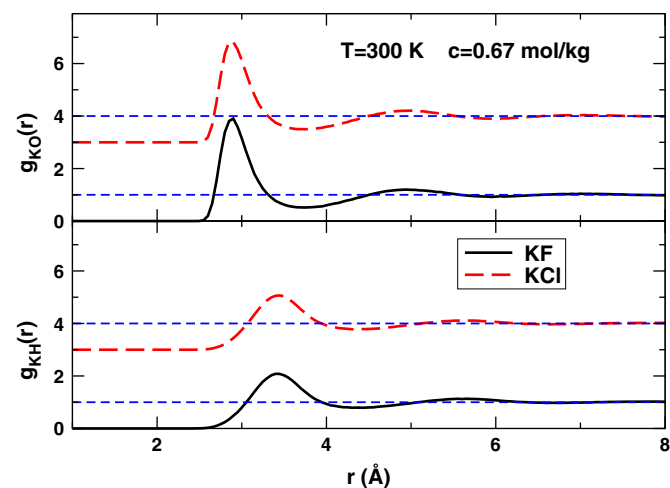


Fig. 4. Potassium–oxygen RDF (top) and potassium–hydrogen RDF (bottom) in $KF(aq)$ (solid line) and in $KCl(aq)$ (dashed line) for $T = 300$ K and concentration 0.67 mol/kg.

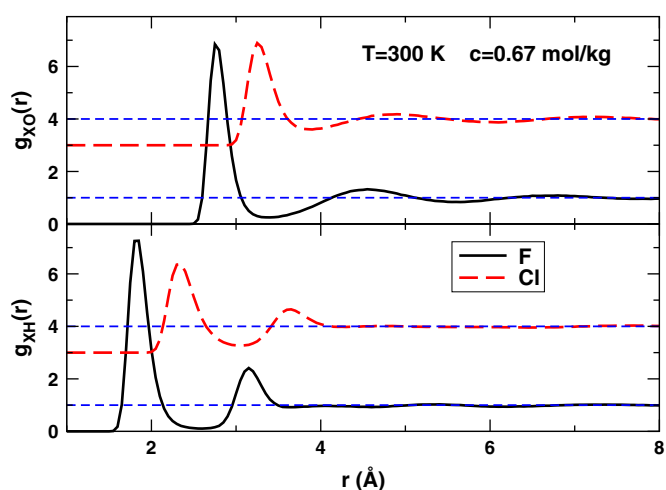


Fig. 5. Anion–oxygen RDF (top) and anion–hydrogen RDF (bottom) in $KF(aq)$ (solid line) and in $KCl(aq)$ (dashed line) for $T = 300$ K and concentration 0.67 mol/kg.

of concentration and temperature are not relevant and for this reason we show the results only for these thermodynamic conditions.

As seen in Fig. 4 the $g_{KO}(r)$ is similar in $KCl(aq)$ and $KF(aq)$. There is evidence of a local strong correlation of oxygens around the potassium ions with a first peak located at 2.9 Å, a second shell is present at around 4.9 Å. Also the $g_{KH}(r)$ is similar in both the solutions. The first peak is at 3.4 Å and the second around 5.4 Å. By comparing with the $O-H$ distance in the water structure the hydrogen shells are shifted to higher distances. These shifts of the hydrogens with respect to oxygens are in agreement with the analysis of the experimental data [6].

In Fig. 5 the anion–water $g_{XO}(r)$ and $g_{XH}(r)$ RDF show that oxygens and hydrogens form well defined first shells around the anions. In both the solutions the hydrogens are closer to the anions and they have also a second well defined and separated shell. The correlation of the hydrogens appears stronger around fluoride due to its higher charge density. For both fluoride and chloride there is evidence of a good short range order with a distance between the $O-X$ and the $H-X$ first peaks of 0.9 Å circa.

In Table 2 we report the coordination numbers of water around cations and anions. With an ion X in the origin the coordination number of an atom α of water is defined as

$$N_{X\alpha} = 4\pi\rho_{\alpha} \int_0^{r_1} dr r^2 g_{X\alpha}(r) \quad (2)$$

where r_1 is the position of the first minimum after the peak of the first shell. The coordination numbers in the case of $KCl(aq)$ decrease with concentration, while they remain almost unchanged in $KF(aq)$.

The results show that the hydration of the different ions is similar in the two solutions. The RDF however show different features and it is interesting to analyse more in details the ion–water RDF and compare them with the $O-O$ and the $O-H$ RDF. In Figs. 6 and 7 we report the comparison of the $g_{XO}(r)$ with the g_{OO} for $T = 300$ K and the

Table 2
Coordination numbers of the first shell of water around ions.

	mol/kg	N_{KO}	N_{ClO}	N_{ClH}
$KCl(aq)$	0.67	6.8	6.9	6.8
	3.96	6.0	6.6	6.2
	mol/kg	N_{KO}	N_{FO}	N_{FH}
$KF(aq)$	0.67	7.0	6.6	6.6
	3.96	7.3	6.6	6.6

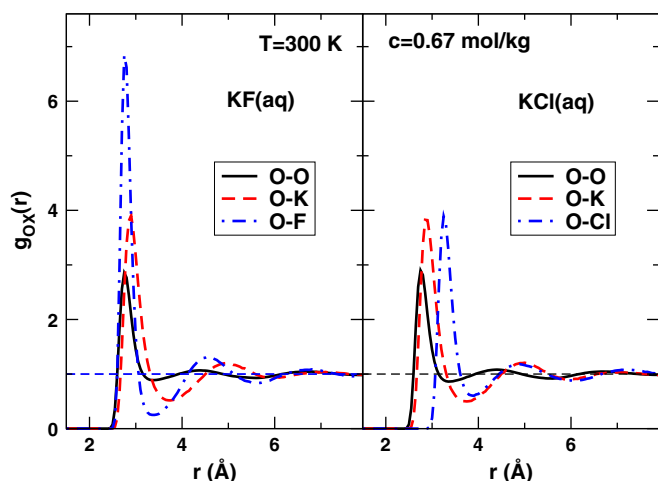


Fig. 6. Comparison of the $g_{OO}(r)$, $g_{OK}(r)$ with $g_{OF}(r)$ (left panel) and g_{OCl} (right panel) for $T = 300$ K and concentration 0.67 mol/kg.

concentrations $c = 0.67$ mol/kg and $c = 3.96$ mol/kg respectively. The $g_{KO}(r)$, as already seen in Fig. 4, does not show differences between the two salt solutions. In both the solutions the RDF of ions with oxygens are weakly dependent on the concentration. While the ions are able to keep rigid the first oxygen shell, changes with concentration are found in the second peak of the $g_{OO}(r)$. This is evident in particular in $KF(aq)$ at the highest concentration for which the second shell of the $g_{OO}(r)$ is strongly distorted.

Concerning the $g_{FO}(r)$, it is interesting to note that the $F-O$ correlation appears rather different from the $Cl-O$ correlation. The first shell of O around F is very sharp and located at the same position as the first shell around an oxygen in the origin. The $g_{FO}(r)$ moreover is in phase with the $g_{OO}(r)$ while the g_{ClO} is out of phase with the $g_{OO}(r)$ and instead, starting with the second shell, it is in phase with the $g_{FO}(r)$. These structural differences are related to the effective repulsion of the LJ potential. From Table 1 it is evident that the volume excluded effects would be very similar in the $F-O$ and in the $O-O$ correlation. In Fig. 8 we show the $g_{HX}(r)$ at $T = 300$ K and the highest concentration (the results are very similar for the lowest one). Fluoride ion appear to be able to keep the short range order of water in similar way as Cl^- . This is evident in Fig. 8 where the g_{HF} shows in both cases a very high first peak. From this point of view it is not clear the interpretation of fluoride as structure maker able

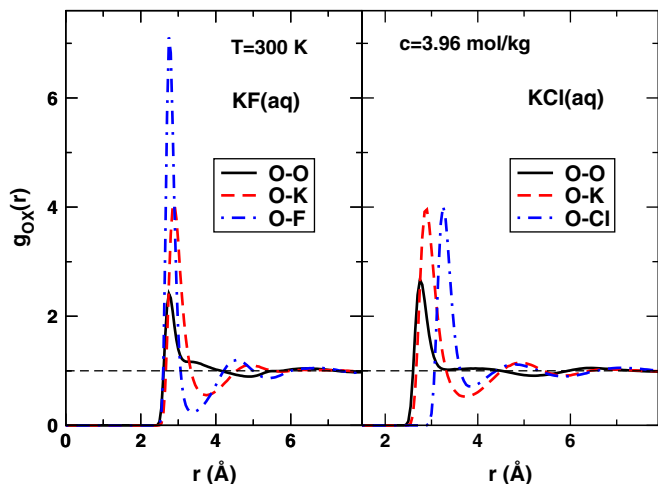


Fig. 7. Same as Fig. 6 for concentration 3.97 mol/kg.

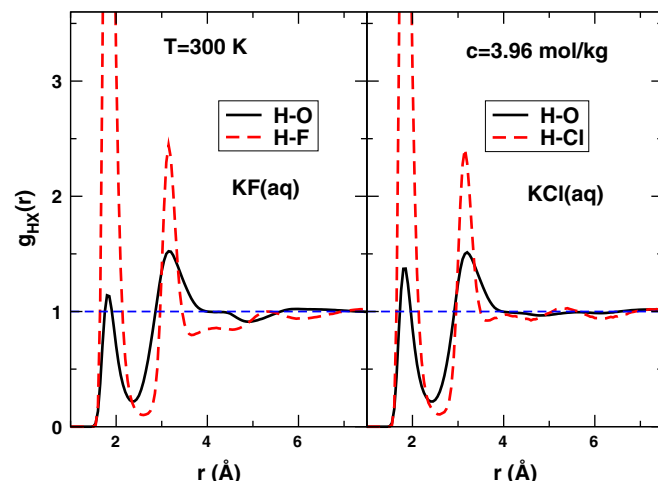


Fig. 8. At concentration 3.96 mol/kg and $T = 300$ K, on the left $g_{OH}(r)$ and $g_{FH}(r)$, on the right $g_{OH}(r)$ and $g_{CH}(r)$.

to break the surrounding HB. We note moreover that the first two shells of hydrogens around F^- are located at the same positions as they are around oxygens, while they are shifted toward higher distances in $KCl(aq)$. This makes possible that F^- ions could be more effective in substituting O in the network.

5. Conclusions

We presented the results of computer simulations of two potassium halides, KCl and KF , dissolved in water at increasing concentrations. The salts are composed with a cation that is considered to have little effect on water, and the anions F^- and Cl^- characterized by different sizes and as consequence different charge densities.

We found that both the types of salts induce a distortion of the oxygen–oxygen structure with a shift of the second shell toward low distances. This effect is more pronounced at increasing concentration and it is more evident in $KF(aq)$ than in $KCl(aq)$, particularly upon supercooling. So F^- shows to have some peculiar effect on water. On the other end the short range order of the $g_{OH}(r)$ is unaffected from the presence of ions. Our simulation indicates that the hydrogen bond network of water is perturbed by the increasing concentration of salts in similar way as found in pure water at increasing pressure. This issue is still under discussion [21,22,48] and our results are in agreement with recent experiments [7] and computer simulations [24,26].

The coordination shells of the ions around water oxygens and hydrogens are well defined and separated indicating a good short range order of the ion hydration. This is more evident for the anions. The $g_{FO}(r)$ and $g_{FH}(r)$ show more pronounced peaks. The coordination numbers of the anions around oxygens and hydrogens however are very similar. This seems to indicate that the interaction strength with water is not much different as long as the first shell is considered.

In a previous work we considered the structural properties of $NaCl(aq)$ at the single concentration $c = 0.67$ mol/kg, and for this system we knew already the phase diagram with the presence of a LDL/HDL transition [25]. For this reason it was possible to study in details how the structure of water changes when the system approaches and crosses the border of the LDL to HDL transition [26]. We found a major effect due to the substitution of oxygens with Cl^- . This favours the instability of the LDL phase that is indicated by a reduction of the distance between the first and the second peak of the $g_{OO}(r)$. The increase of ion concentration of $NaCl$ or KCl enhances this effect [24]. The substitution of oxygens with F^- appears here more effective in perturbing the second shell of oxygens. In this respect it would be

interesting to explore more in details the changes of the phase diagram of water induced by the addition of *KF* in solution.

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