Variations of water's local-structure induced by solvation of NaCl*

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The researches on the structure of water and its changes induced by solutes are of enduring interests. The changes of the local structure of liquid water induced by NaCl solute under ambient conditions are studied and presented quantitatively with some order parameters and visualized with 2-body and 3-body correlation functions. The results show that, after the NaCl are solvated, the translational order t of water is decreased for the suppression of the second hydration shells around H_2O molecules; the tetrahedral order $\langle q \rangle$ of water is also decreased and its favorite distribution peak moves from 0.76 to 0.5. In addition, the orientational freedom k and the diffusion coefficient D of water molecules are reduced because of new formed hydrogen-bonding structures between water and solvated ions.

Keywords: water structure, local order, solute perturbation, molecular simulation
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1. Introduction

Although the single water molecule seems very simple, liquid water represents a large number of specific properties and is the most important solvent for life on earth.[1] Because of the tetrahedral shape and polarity of the water molecule, which gives rise to a directional hydrogen-bond (H-bond) and forming 3 dimensional H-bond network, there exists specific local orders in water.[2] When any solute is solvated, the interactions between water and solute molecules will change the original water structure. These changes are important for the distinct physical and chemical characters of water as solvent. Thus a clear view of the local structure and the understanding of how it is perturbed by different kinds of solutes is of crucial importance for a wide range of disciplines[3,4] including solution physics and chemistry, electrochemistry, mineralogy, geochemistry and biology.[5]

There are many kinds of solutes: organic or inorganic, charged or uncharged, hydrophilic or hydrophobic. In particular, monovalent ions can be easily dissolved in water and take on many important physiology functions. Thus the perturbation of water structure due to monovalent ions is a basic topic and has attracted much attention.[6,7] Early literature often deals with this issue in terms of *electrostriction* as the reduction of the solvent volume caused by the polarizing effects of ions.[8,9] Recently with classical molecular simulations[10−12] and new experimental methods such as x-ray scattering,[13,14] neutron diffraction,[7,15,16] as well as IR or Raman spectroscopy,[17] the local structure making or breaking effects of different ionic solutes on the surrounding water network of H-bonds are reported widely. However, instead of many qualitative descriptions of these effects, there is a lack of quantitative descriptions of the local structural changes of water.

Quantifying the local order in liquid water and other amorphous materials is a challenging issue that has received considerable attention. There are some reports characterizing and discussing local orders of water as a noncrystalline substance under different thermodynamical states.[2,18−20] These methods are essentially based on the identification of appropriate metrics for both positional and angular order through some integrated measure of the overall amount of order emerging from microscopic correlations. As far as we know, the details of the changes of water's local structure induced by solutes are not presented in this way.

In this paper we study the changes of the local

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structure of water at 298 K and 1.013×10^5 Pa induced by NaCl, which is a kind of typical monovalent salt, with molecular modeling techniques. The structural order of water is quantitatively described with translation order t, tetrahedral order q and some dynamical properties such as orientational rotational freedom k and self-diffusion coefficient D. In addition, the changes of 3-d spacial distribution of water around one H_2O molecule and the 3-body distributions of oxygen and hydrogen atoms around Na–Cl ion pairs, which present new local structures in NaCl solvent are also given and analysed.

After the description of the models and simulation details, we present the results and discussions in Section 3. Conclusions is given at the end.

2. Models and simulation details

Although some sophisticated potential functions of water are still being developed,[21,22] in this work the most widely used SPC/E model (Table 1)[23] is adopted because its description is, overall, very satisfactory under ambient conditions when compared with experiments.[21] The SPC/E water comprises 3 point-charges and a spherical Lennard–Jones core. The intermolecular energy consists of two parts:

$$E_{\rm p} = E_{\rm lj} + E_{\rm c}, \tag{1}$$

where

$$E_{\rm lj} = \sum_{m,n} 4\varepsilon_{mn}\left[\left(\frac{\sigma_{mn}}{r_{mn}}\right)^{12} - \left(\frac{\sigma_{mn}}{r_{mn}}\right)^{6}\right] \tag{2}$$

is the Lennard–Jones interaction, and

$$E_{\rm c} = \sum_{m,n} \frac{q_m q_n}{4\pi\varepsilon_0 r_{mn}} \tag{3}$$

is the electrostatic interaction. In these equations, r_{mn} is the distance between two atom sites, ε_{mn} and σ_{mn} determine the energy and distance scales of Lennard–Jones interaction, q is the atomic partial charge and ε_0 is the vacuum permittivity. The charges determine the molecular polarity. The Lennard–Jones core provides short-range inter-molecule repulsion and describes the molecular size.[23,24] The H-bond and local orientational structure of water are controlled by the collaboration of these two kinds of interactions.

The ions of NaCl are considered as charged Lennard–Jones particles. Both interactions between two ions and between ion and water molecule are also described by Eq. (1). The Lennard–Jones parameters of Na^+ and Cl^- ions proposed by Smith and Dang are adopted (Table 1).[25] Lorentz–Berthelot mixing rule is used to derive interaction parameters between different atom species.[26]

Table 1. Atomic parameters of electrostatic and Lennard–Jones potential adopted in this work.

atom species		Q/e	σ/Å	ε/(kJ·mol^{-1})
SPC/E[23]	O	–0.8476	3.166	0.6507
	H	0.4238	0.0	0.0
ions[25]	Na^+	1.0	2.350	0.544
	Cl^-	–1.0	4.400	0.419

The simulation cells with cubic periodic boundary conditions contain 1800 H_2O molecules for pure water, and 100 pairs of Na^+ and Cl^- ions are added for NaCl solution. The molarity of NaCl is 3.1 M (1 M=1 mol/dm^3) (molal), which is lower than the experimental saturated concentration of 5.4 M.[27] At the initial point, water molecules are located with random orientation on FCC lattice and the ions are distributed randomly in water. The simulations are based on NPT ensemble condition realized by Nosé–Hoover scheme.[28] Firstly, the systems are equilibrated at 350 K for 100 ps. Then they are cooled down to 298 K during 100 ps. After that, 10 ns evolution at 1.013×10^5 Pa pressure and 298 K temperature, with a relaxation time of 500 fs for pressure and 100 fs for temperature, are carried out for analysis. The integrating time step is 1 fs. The cutoff of long-rang interactions is 9 Å (1 Å=0.1 nm), and Ewald sum method[26] is adopted to treat electrostatic interactions. The Ewald screening parameter is taken as $\alpha = 3/R_{\rm cut}$, while the reciprocal space cutoff is determined by $\pi^2 k_{\rm max}^2/\alpha^2 = 9$. The intramolecular constraints of water molecules are conserved by SHAKE procedure.[29] Our simulation program is derived from M.DynaMix package.[30]

3. Results and discussion

3.1. Radial distribution function and translational order of water

Figure 1 gives the radial distribution functions (RDFs) of water [$g(r)_{\rm OO}$, $g(r)_{\rm OH}$ and $g(r)_{\rm HH}$] in both pure water and NaCl solvent. In comparison, all the first peaks of these RDFs are decreased after the solvation of the ions. This means that the first coordinate shells around water molecules are partially substituted

by ion solutes and the H-bond strength between water molecules is reduced.

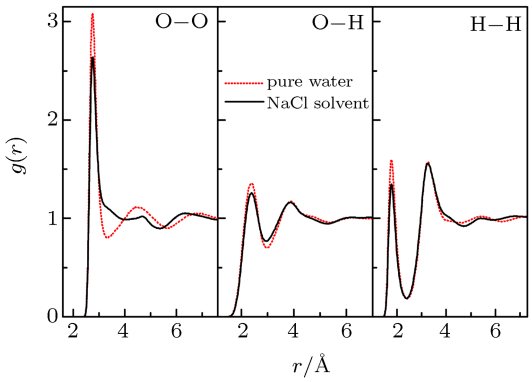


Fig. 1. (colour online) The RDFs between atoms of water molecules in pure water (red dot line) and NaCl solutions (black solid line).

It can be seen that $g(r)_{\mathrm{OO}}$ is most sensitive to the presence of ions. There is not only evident decrease in its first peak but also violent changes in its second shell. In pure water, the second shell of $g(r)_{\mathrm{OO}}$ locates at about 1.7 times the distance of the first shell and is regarded as a typical signature of tetrahedral liquid.[20] After the ions are solvated, the peak of $g(r)_{\mathrm{OO}}$ is suppressed to be more flat and its value is near 1.0 — the average density of water. This phenomenon indicates that the local structure of water as solvent is less tetrahedral than pure water. The tetrahedral order will be quantitatively discussed in Section 3.2.

Out of the first shell, there is no evident variation in $g(r)_{\mathrm{OH}}$ and $g(r)_{\mathrm{HH}}$. This is consistent with the experimental results reported in Ref. [7], where authors which compare the structure changes of water induced by ionic solutes to the effects of increasing pressure of water and conclude that the ions changes the relative position of the oxygen sites but has no evident affection on the topology of H-bond network in water.

The radial correlation shown in RDFs is associated with a translational order (t), which measures the tendency of pairs of atom species to be separated by preferential distances.[2,19,20] The translational order can be defined as:

$$t = r_{\mathrm{m}}^{-1} \int_0^{r_{\mathrm{m}}} |g(r) - 1| \mathrm{d}r. \tag{4}$$

It vanishes for an ideal gas, and is large for a crystal. The translational orders between different atom pairs of water are shown in Table 2. In the calculations, the integrations are all carried out to $r_{\mathrm{m}} = 8.0$ Å where the RDFs becomes close unity.

Table 2. Translational order t, tetrahedral order $\langle q \rangle$, orientational freedom k and diffusion coefficient D of water molecules. $\langle q \rangle$, t and k are dimensionless. The unit of D is 10^{-9} m^2/s.

	t_{OO}	t_{OH}	t_{HH}	$\langle q \rangle$	k	D
pure water	0.40	0.27	0.24	0.64	3.29	2.45
NaCl solution	0.36	0.26	0.23	0.52	1.93	1.54

In pure water, $(t_{\mathrm{OO}} = 0.40) > (t_{\mathrm{OH}} = 0.27) > (t_{\mathrm{HH}} = 0.24)$. This tells us that oxygen atoms are most translationally ordered. The probability for O–O pair to be separated with the same distance is bigger than O–H and H–H pairs. As hydrogen atom is much lighter than oxygen atom, the thermodynamical movement of hydrogen is more violent than that of oxygen and the orientational centre of water molecule locates around its oxygen site. In this way, the translational arrangement involving hydrogen atom are more flexible. So, t_{OH} and t_{HH} are smaller than t_{OO}, and t_{HH} is smallest.

After the ions are solvated, t_{OO} decreases from 0.40 to 0.36, while t_{OH} and t_{HH} are only reduced by 0.01. The evident decrease of t_{OO} tells us that the density modulations around water molecules over 3 coordination shells (8 Å) are changed and become more orderless. However the changes of the hydrogen bond network cannot be evidently detected from the changes of t_{OH}.

3.2. Tetrahedral order and spacial distribution of water

Because of the directional H-bonding, the nearest four neighbours of one water molecule are tend to be arranged tetrahedrally. The local tetrahedral order at each water site i can be defined by a sum over the angles subtended by its four nearest adjacent oxygens:[2,31,32]

$$q_i = 1 - \sum_{j<k}^{6} 3/8[\cos\theta_{jik} + 1/3]^2. \tag{5}$$

Its ensemble average, $\langle q \rangle$, can be taken as the measure of the tetrahedral order of bulk water. $\langle q \rangle$ is 0 for an ideal gas and 0.33 for a Lennard–Jones liquid.[2] For a perfect tetrahedral ice, both q_i and $\langle q \rangle$ equal 1.0. In fluid state, H_2O molecules keep drifting and their orientation is unstable. Thus transient q_i changes dynamically ($-3 \leq q_i \leq 1$), and $\langle q \rangle$ of water is reported varying between 0.38 and 1.0 under different thermodynamic conditions.[3,33]

Figure 2 shows the distribution curves of q in pure water and NaCl solution studied in this work.

Their ensemble averages $\langle q \rangle$ are listed in Table 2. The q distribution of Lennard–Jones liquid[2] is also given for comparison. It can be seen that there exists an evident bimodal character in the q distribution curves of water, different from the single-peak shape of Lennard–Jones liquid. The right one sites at $q = 0.76$ (high-q peak) and the left one sites at $q = 0.5$ (low-q peak). In pure water, high-q peak is predominant and $\langle q \rangle$ is 0.64. This means that the ice-like tetrahedral local arrangements are kept well in pure water, although the molecules are moving dynamically. In NaCl solution, the high-q peak is reduced, while the low-q peak is increased and becomes the main peak. Accordingly $\langle q \rangle$ is decreased to 0.52. These changes show that the local tetrahedral structure in pure water is broken down after the solvation of NaCl.

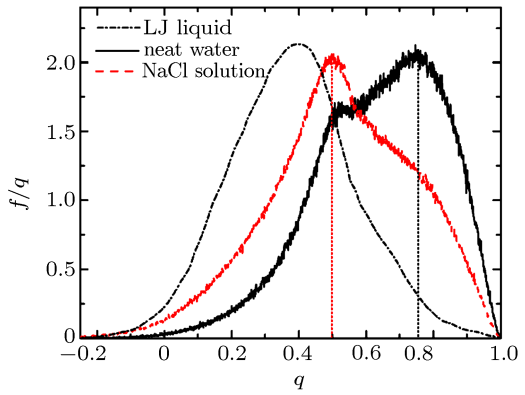


Fig. 2. (colour online) The distribution of tetrahedral order, q_i, in pure water (black solid line) and NaCl solvent (red dashed line). The area under each curve is normalized to unity. The distribution of Lennard–Jones liquid (black dash-dot line)[2] is given for comparison.

The changes of tetrahedral order in water can be presented vividly with spatial density functions [SDF, $g(r, \Omega)$] of water around one water molecule, which gives the rendering of relative positions and probability of neighbouring water molecules around the central one. In Fig. 3, the average density of water is set as 1.0. The isosurfaces of relative density of water $\rho_r = 5.0$, 3.0 and 1.5 are presented.

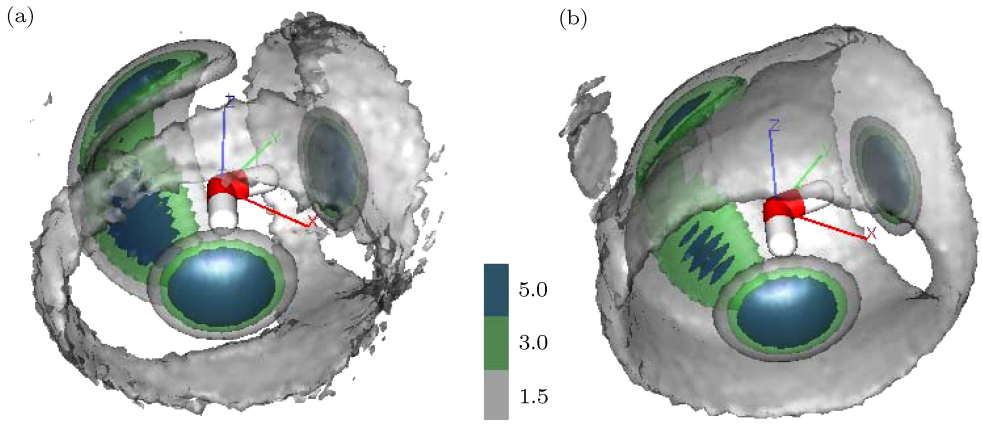


Fig. 3. (colour online) The spatial density functions, $g(r, \Omega)$, of water around H_2O molecule in pure water(a) and ion solvent(b). The scale of the isosurface is the relative density of water.

The isosurfaces of $\rho_r = 5.0$ and 3.0 show the most favoured tetrahedral coordinating positions around one H_2O molecule. In comparison with in NaCl solution, the $\rho_r = 5.0$ isosurface occupies large area in pure water. This is particularly noticeable for the nearest neighbours against the central oxygen site. Because the solvated NaCl makes water to be less tetrahedral, the possibility for direct H-bond between water molecules are decreased consequently. Thus the area of high water density ($\rho_r = 5.0$), corresponding to the first hydration shell, around each water molecule becomes smaller in NaCl solvent than in pure water.

The distribution of $\rho_r = 1.5$ is mainly determined by the shape of the second hydration shell of water. In pure water, the profile of $\rho_r = 1.5$ is like two thin rings around each hydrogen atom and perpendicular to the O–H bond respectively. After ions are solvated, they become thicker and broader. The unoccupied area between them in pure water is filled up with water of $\rho_r = 1.5$ also. These changes account for the formation of the flat and compacted second peak in $g(r)_{OO}$ as shown in Fig.1 and show that the tetrahedral lo-

cal structure of pure water is melted after NaCl are solvated.

The pictures of SDFs derived from our molecular simulations are consistent with the results traced from neutron diffraction experiments in Ref. [7].

3.3. Spacial correlations between water and ions

The RDFs between ion pairs [$g(r)_{\mathrm{NaCl}}$, $g(r)_{\mathrm{NaNa}}$, $g(r)_{\mathrm{ClCl}}$] and between ion and water [$g(r)_{\mathrm{NaO}}$, $g(r)_{\mathrm{NaH}}$, $g(r)_{\mathrm{ClO}}$, $g(r)_{\mathrm{ClH}}$] are shown in Fig. 4. The attraction between Na^+ and Cl^- accommodates two main peaks in $g(r)_{\mathrm{NaCl}}$. As has been pointed out,[34–36] the first and second peaks in $g(r)_{\mathrm{NaCl}}$ are relevant to the relative stability and probability of directly contacted ion pair (CIP) and solvent separated ion pair (SSIP), respectively. The repulsion between like ions causes the first peaks of $g(r)_{\mathrm{NaNa}}$ and $g(r)_{\mathrm{ClCl}}$ to locate far beyond that of $g(r)_{\mathrm{NaCl}}$. Because of the large distance, the correlations between like ions are weak and the fluctuation in $g(r)_{\mathrm{NaNa}}$ and $g(r)_{\mathrm{ClCl}}$ are smaller than that in $g(r)_{\mathrm{NaCl}}$.

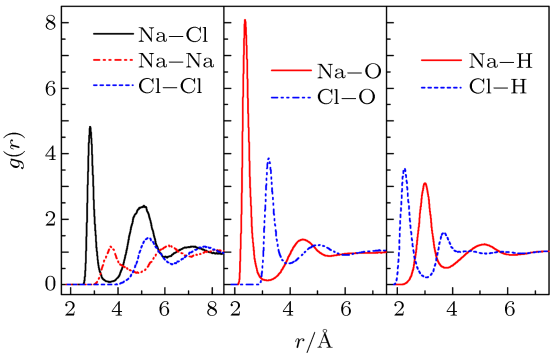


Fig. 4. (colour online) The RDFs between two ions (a), ion-Oxygen (b) and ion-Hydrogen (c). They show the correlations between ions and between ion and water molecules.

As there exist two distinct peaks in the RDFs between ion and water, there are two hydration shells around each ion. To study the microstructure of water around ions in detail, the average distributions of water around Na^+–Cl^- CIP and SSIP are calculated. The distribution function is defined as

$$g(r_3|r_{12}) = g_3(r_1, r_2, r_3)/g_2(r_{12}), \tag{6}$$

where $g_3(r_1, r_2, r_3)$ is the 3-D distribution function of three kinds of particles (i.e. Na^+, Cl^- and O or H atom) and $g_2(r_{12})$ is the RDF between Na^+ and Cl^-.[36] In this work, r_{12} is 2.82 Å for CIP and 5.20 Å for SSIP. They are the positions of the first and second peaks of $g(r)_{\mathrm{NaCl}}$.

Figure 5 shows the contour map of Oxygen and Hydrogen around CIP and SSIP. Two stable hydration shells around both Na^+ and Cl^- and the prefer orientation of water molecules in the centre hydration shell are presented clearly: negatively charged Oxygen around Na^+ and positively charged Hydrogen around Cl^-.

The favorite hydration sites around the ions can be identified according to the intensity of the contour in Fig. 5. For each ion in CIP, there are 3 favorite hydration sites. It can be deduced that there exists a hydration crown capping on and a hydration belt circling around the ion, because the counter intensity is rotationally invariant around the axis connecting Na^+ and Cl^-.

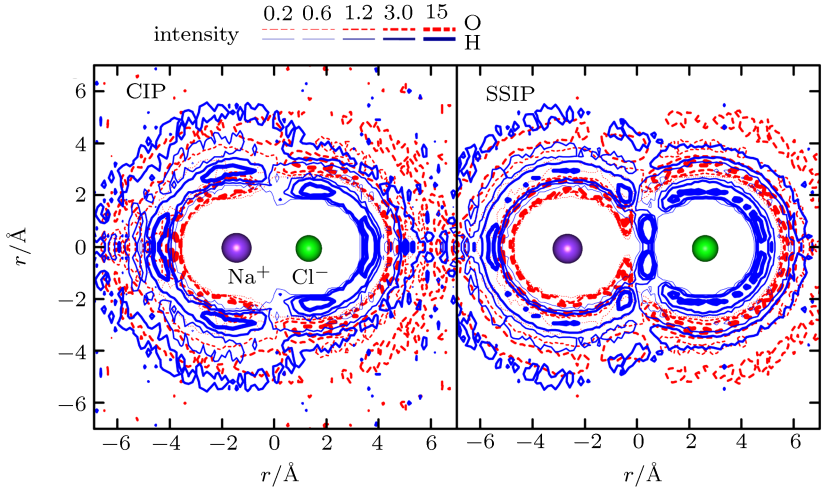


Fig. 5. (colour online) The 3-body distribution function of water [oxygen (red dash line), hydrogen (blue solid line)] around CIP (left) and SSIP (right).

For SSIP, the favorite hydration sites locate between the ion pair, forming a water bridge connecting Na^+ and Cl^-. It can be interpreted that the SSIP is formed by constraining the orientation of water molecules between the cation and anion. For the bridging water molecule, one O–H bond is directly involved in the formation of SSIP, the other O–H bond should form H-bond with neighbouring water molecules for stablility. So the bridging water molecule is deviated away from the line through Na^+ and Cl^- and there exist two bridging hydration sites for each ion in Fig. 5.

The hydrogen shells around individual ion or ion pair show the new formed local structures of water in NaCl solvent. The selective hydration sites around the ions are determined by the direction and strength of H-bond and the balance between the formation of new hydration structures around ions and the maintenance of the original hydration network in pure water.[33]

Because the translational orders has a sequence of $t_{OO} > t_{OH} > t_{HH}$ and the tetrahedral order are determined by oxygen atoms, the local structure of water is mainly controlled by the arrangement of oxygen sites. Table 3 gives the effective radius, R_x, of the first and second oxygen shells around Na^+ and Cl^-. Smaller R_x means strong interactions between ions and oxygen site. It can be seen that, for all three cases: single ion, CIP and SSIP, both the first and the second oxygen shells around Na^+ are more compacted than that around Cl^-. Thus, cations account more for the local structure changes of water than anions do. In this way, for calculating some thermodynamic properties of some electrolyte solution, the effective hydration diametre (RH) for cation, and the Pauling diametre (RP) for anion, were adopted as shown in reference.[37,38]

Table 3. The effective radius (R_x/Å) of the first and second Oxygen shells around Na^+ and Cl^- extracted from RDFs (single ion, R_{SI}) and 3-d distributions of oxygens around both CIP (R_{CIP}) and SSIP (R_{SSIP}). R_x is defined as the distance between the position of maximum intensity of RDF or 3-d distributions shells and the ion.

	$Na^+_{Fir.}$	$Na^+_{Sec.}$	$Cl^-_{Fir.}$	$Cl^-_{Sec.}$
R_{SI}	2.38	4.46	3.24	4.96
R_{CIP}	2.90	4.70	3.14	4.95
R_{SSIP}	2.36	4.72	3.21	4.83

3.4. Orientational freedom and self-diffusion constant of water molecules

The orientational freedom of H_2O molecule is an important dynamical order which is associated with the H-bond flexibility and strength. As proposed by Kirkwood,[26,39] it can be quantitatively described with a factor k defined as:

$$k = \frac{\langle M^2 \rangle - \langle |M| \rangle^2}{N\mu^2}, \tag{7}$$

where μ denotes the dipole moment of single water molecule, N is the number of water molecules per unit volume and $M = \sum_{i=1}^{N} u_i^2$ is the instantaneous collective dipole of the sample unit. As shown in Table 2, k is changed from 3.29 in pure water to 1.93 with NaCl added. The electrostatic interactions introduced by charged ions slow down the orientational movement of water molecules. In this way, the dipole fluctuation of water is reduced as solvent.

As a complement to the orientational freedom, the translational movement of water molecules is described with self-diffusion constant(D) which might be derived from mean square displacement:[26]

$$D = \lim_{t\to\infty} \langle [R(t) - R(0)]^2 \rangle / 6t. \tag{8}$$

Similar with the changes of orientational freedom, the translational movement of water molecules are also slowed down from 2.45×10^{-9} $m^2 \cdot s^{-1}$ in pure water to 1.54×10^{-9} $m^2 \cdot s^{-1}$ in NaCl solution.

The decrease of k and D implies that the hydration shells around the ions are more stable than the H-bond network in pure water. The strong columbic attraction and repulsion introduced by the ions inhibit the thermodynamic movement and local orientation of water molecules through making new hydration shell structures around the ions.

4. Conclusion

The information on the local structure of liquid water and its changes induced by solutes are important for our understanding of the complex interactions between water and solutes and revealing the distinctiveness of water as the most crucial bio-solvent. Here we present the changes of the local structure of water induced by NaCl through some order parameters quantitatively and different kind of distribution functions such as RDF, 3-D spacial distributions and three-body correlations.

The translational order of water is reduced by the ion solutes because of the breakdown of the second hydration shells around water molecules. The biggest change occurs in t_{OO}, which decreases from 0.40 to 0.36. It indicates that the position of oxygen is more sensitive than that of hydrogen to the presence of the NaCl solute.

As the result of the structure breaking effects of ions, which changes the relative orientation of neighbouring H_2O and breaks the H-bond network in pure water, the main peak of the distribution curve of tetrahedral parameter q in water moves from high-q site to low-q site, and $\langle q \rangle$ is decreased from 0.64 to 0.52. These phenomena are presented clearly in the changes of the spacial distribution of hydration shells around H_2O molecules.

The 3-body distributions of the oxygen and hydrogen atoms around Na–Cl ion pairs of CIP and SSIP give the picture of new hydration shell structures in NaCl solvent and present the structure making effects of ions. As a result of the formation of these new hydration structures around the ions, both the orientational and translational freedom of water molecules are reduced.

This paper presents a quantitative (order parameters)-qualitative (distribution maps) unified method based on molecular simulation to describe the changes of water's local structure induced by electrolyte. There are many factors, such as the species and concentrations of solutes, temperature and pressure conditions etc., which affect the local structure of water as a solvent. Our study on these effects and the underlying physical mechanisms using both molecular simulation and density functional theory are in progress.

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