

Reorientational dynamics of water in aqueous ionic solutions at supercritical conditions: A computer simulation study

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Abstract

We present results of a computer simulation study on the reorientational dynamics of water molecules in aqueous ionic solutions at supercritical conditions. We carried out molecular dynamics simulations along the isotherm $T=650$ K and densities ranging from $\rho=0.7$ g cm⁻³ down to $\rho=0.05$ g cm⁻³. We adopted the SPC/E water model. The ionic species included Na⁺ and Cl⁻ ions. Our attention has been focused on the reorientational dynamics of the solvation shell molecules. Reorientational correlation times are reported and compared with those corresponding to pure water at the same thermodynamic conditions. We find that the influence of the ions goes beyond the first solvation shell and significantly affects the motion of the molecules lying in the second solvation shell. This differs with earlier studies of aqueous ionic solutions at room temperature.

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1. Introduction

Liquid water is a peculiar substance since it has extraordinary microscopic properties uncommon to the majority of liquids. There is general agreement that the main responsibility for those properties has to be charged to the presence in water of a special type of molecular bond called “hydrogen-bond” (HB) [1,2]. Hence, hydrogen-bond distributions and the rates of HB breaking and reformation drive microscopic water dynamics in the sub-picosecond time scale. When turning to supercritical conditions we can force water to change some of its properties, because the density can be experimentally controlled by pressure and temperature changes, varying the microscopic ambient in between liquid-like and gas-like environments. In such landscape, big variations of the static dielectric constant happen. It is reduced from ~ 80 at ambient conditions to only ~ 6 in a typical supercritical regime. The behavior of water is then closer to a non-polar solvent, instead of its polar solvent characteristics at room temperature. This

fact produces the well-known ability of supercritical water to dissolve non-polar organic reactives and also explains the existence of separated contact ion pairs in a low-density ambient, turning to dissociated ions when density is increased.

Ionic aqueous solutions are ubiquitous in nature and play a central role in environmental and industrial processes like microbiology [3], oxidation of chemical and biochemical wastes [4], metal corrosion [5] or electrode processes [6], to mention a few examples. The presence of ionic species can produce important perturbations of both the structure and dynamics of water through changes in the behavior of the HB network. Further, the mechanisms of aqueous ion solvation are arguably called to play a key role in the understanding of proton and charge transfer reactions. From the experimental side, electric field [7], calorimetric [8] conductivity [9], infrared and Raman spectroscopic measurements [10–12], extended X-ray absorption fine structure spectroscopy [13,14], neutron diffraction with isotopic substitution [15–17] and, more recently, nonlinear femtosecond spectroscopy [18] are able to reveal indirect information on dynamics of aqueous ionic solvation. On the theoretical side, integral equation calculations and numerical studies based on computer simulations report

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valuable information on structural and dynamical properties of ionic aqueous solutions at ambient [19–21], high-temperature [22–26] and supercritical states [27–35]. As the “third way”, computer simulation has emerged as a powerful tool for investigating the microscopic properties of liquids and liquid solutions. Computer simulations can provide experimentally inaccessible information which may be very useful for a deep understanding of these systems at the molecular level. This information is also very helpful for interpreting experimental data such as those resulting from spectroscopic experiments. The wide use of the Monte Carlo and molecular dynamics (MD) techniques has allowed the investigation of hydrogen-bond dynamics through the calculation of HB lifetimes in bulk water at different thermodynamic conditions [36–40] and, more recently, in aqueous electrolyte solutions at room temperature [20,41]. However, the studies related to HB and reorientational dynamics in supercritical ionic aqueous solutions are scarce in the literature.

In this contribution we report the results of an MD study on the reorientational dynamics of water molecules in aqueous ionic solutions at supercritical conditions. The outline of this paper is as follows. Computational details of the MD simulations are given in Section 2. The structure and residence times of water molecules around the ionic species are determined in Section 3. The orientations of solvation shell molecules are analyzed in Section 4. Section 5 is devoted to the reorientational dynamic properties and conclusions are given in Section 6.

2. Computational details

We carried out MD simulations on a system containing one ion, either Na^+ or Cl^- and 255 water molecules with periodic boundary conditions. In each case, the temperature of the system was fixed at $T=650$ K and the size of the cubic box was chosen to give a solvent density interval ranging from $\rho=0.7$ and 0.05 g cm^{-3} . The SPC/E model was adopted for water–water interactions [42]. This is a three-site water model which has been widely used for pure water as well as for aqueous ionic solutions. Ion–water forces were modeled by means of a sum of pairwise additive Coulombic and 6–12 Lennard-Jones site–site potentials. The Lorentz-Berthelot mixing rules, i.e. $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ were assumed. We adopted the set of ion Lennard-Jones parameters derived by Dang [43]. All the potential parameters are collected in Table 1.

In order to carry out the simulations, we employed the integration algorithm of Berendsen et al. [44] with a time step of 0.002 ps and a thermal bath coupling parameter of 0.2 ps.

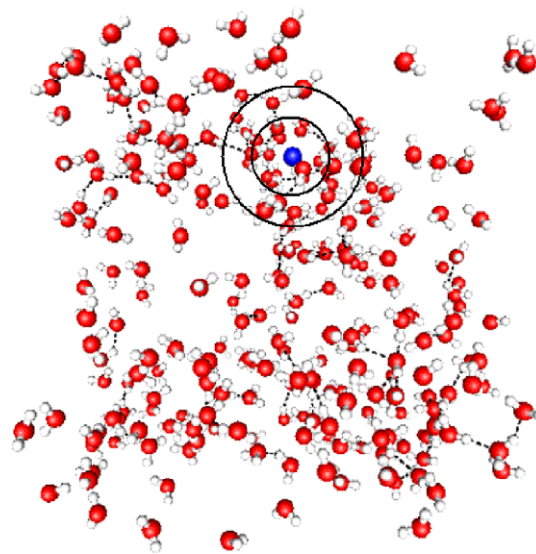


Fig. 1. Snapshot of an MD configuration of one Na^+ ion (in blue) in SPC/E water at $T=650$ K and $\rho=0.3$ g cm^{-3} . The circles correspond to the 1st and 2nd solvation shells (see the text). The dashed lines indicate H-bonded molecules. Oxygens (red), hydrogens (white).

Short-ranged forces were truncated at half the box length and the Ewald summation method with conducting boundary conditions [45] was applied to account for long-ranged Coulomb interactions. Each run consisted of an initial equilibration period of 50 ps and a production period of 500 ps to collect statistically meaningful properties. A snapshot of a typical MD configuration is depicted in Fig. 1. The circles correspond to the 1st and 2nd solvation shells. The radii of the shells were determined from the minima of the ion–oxygen radial distribution functions (see next section). The dashed lines indicate H-bonded molecules. A detailed analysis of the H-bond dynamics will be reported elsewhere [46].

3. Ion–water structure and residence times

The ion–oxygen radial distribution functions $g_{\text{IO}}(r)$ obtained for both Na^+ and Cl^- at different solvent densities are shown in Fig. 2. The position of the first and second minima of these functions allowed us to determine the radii R_{shell} of the first and second solvation shells, respectively. First minima are well resolved for Na^+ whereas they are rather unclear for Cl^- . In all cases, the second minima are ambiguous. We observe that both first and second solvation shells are located at nearly the same positions for all densities in the case of Na^+ . Conversely, for Cl^- the position of the first minimum in the $g_{\text{IO}}(r)$ tends to move to larger values as density decreases. These two features were also observed by Rasaiah et al. [31] at 683 K and densities ranging from 1 to 0.2 g cm^{-3} . The assumed R_{shell} values and the mean number of molecules within a given shell n_{shell} are listed in Table 2. The number of water molecules is reduced as density decreases in both shells, as expected. In the first shell, the changes are only up to 1 molecule, considering the two extremal densities. The largest variations are found in the

Table 1
Interaction potential parameters

Ion/atom	ϵ (kcal/mol)	σ (Å)	q (e)	Ref.
Na^+	0.100	2.584	+1.0	[43]
Cl^-	0.100	4.401	−1.0	[43]
Oxygen	0.155	3.166	−0.8476	[42]
Hydrogen			+0.4236	[42]

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