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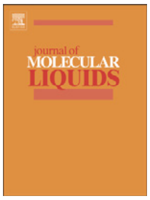

Effect of solvent composition on the structural and dynamical properties of sodium chloride solutions in water-methanol mixtures

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ABSTRACT

Molecular dynamics (MD) simulations have been performed on sodium chloride solutions in water-methanol mixtures under ambient conditions with methanol mole fractions (x_m) ranging from 0.09 to 0.87. MD simulations are performed with the flexible SPC water model and the flexible six-site model for methanol. The ions are modeled as charged Lennard–Jones spheres. The structural properties of the solutions are discussed on the basis of radial distribution functions. A chain cluster of methanol is predominant in the mixture where x_m exceeds 0.7. The number of methanol molecules are higher than water molecules in the first coordination shell of sodium and chloride ions beyond $x_m = 0.5$ and 0.48 respectively. With increasing x_m, the diffusion coefficients for water (D_{H_2O}) and for methanol (D_{CH_3OH}) initially decrease. From $x_m = 0.29$ D_{CH_3OH} increases while D_{H_2O} rises only from about 0.7. The two diffusion coefficients are equal at $x_m = 0.8$. The deduced first and second reorientational correlation times for the O—H and the dipole moment vectors for water speed up with increasing x_m. Through the τ_1/τ_2 ratio, the reorientational motion of water molecules can be entirely ascribed to a jump. O—H methanol vector reorientational occurs by a mechanism similar to that of water.

1. Introduction

The molecular structure and dynamics of Hydrogen-bonded networks are of fundamental importance across a wide range of scientific disciplines. Water molecules are associated together in an extensive three dimensional networks by Hydrogen-bonds. In addition, water is one of the most common polar solvents in synthetic chemistry. Hydrogen-bonding interactions also exist in other classes of chemical compounds leading to linear chains or cyclic associations of molecules, alcohols or carboxylic acids. For example, methanol is the most simple promising candidate among alcohol series forming hydrogen-bonded networks. In their binary mixture methanol and water are Hydrogen-bonding liquids, they are incompletely mixed at the microscopic scale.

Aqueous alcohol solutions are widely used as a solvent for chemical reaction and various analytical techniques such as solvent extraction and chromatography [1]. Alcohol-water binary mixtures have been studied extensively over the years in order to correlate the solution structure with the observed anomaly in several thermodynamic properties of these mixtures. Neutron diffraction data on a 1:9 M ratio methanol-water confirm the existence of water molecules in the shell around carbon, forming a disordered cage in which they retain the tetrahedral local coordination found in pure water [2]. Takamuku et al. [3] showed that the tetrahedral structure of water changes moderately changing into hydrogen-bonded chains of methanol molecules at mole fraction of methanol at about 0.3. In methanol-rich mixtures, short water chains and longer methanol chains build up the hydrogen-bonded clusters in the system [4,5]. Neutron diffraction with hydrogen/deuterium isotope substitution in dilute aqueous methanol solution (1:19 M ratio) showed a direct evidence of methanol association with >80% of the methanol molecules in clusters of 3 to 8 molecules [6]. Car-Parrinello molecular dynamics simulations have been performed on Li^+ and Cl^- in fully deuterated liquid methanol. It has been found that the lithium cation has a stable tetrahedral coordination whereas the chloride anion presents an average coordination number of 3.56 [7]. MD simulation for water-methanol mixture has revealed that mobility of water and methanol molecules is minimal at intermediate alcohol concentrations [8].

In the case of the orientational correlation times, earlier theoretical and experimental studies revealed that the different molecular groups in methanol have different relaxation times. For example second orientational correlation times of liquid methanol are 0.45 ps for C–D vectors [9], 3.7 , 5, 8.09 ps for the O—H vector [9–11] and 1.6 ps for dipole moment [8]. Our previous study shows that oreientational correlation times for all water vectors in aqueous NaCl solutions increase with increasing ion concentrations [12].

Water-methanol mixture has been studied for a very long time. However, to our knowledge, systematic studies of these solutions of NaCl solutions in water-methanol mixture through the entire range of methanol molar fraction are still scarce. Therefore, the objective of this work is to give more insight into their structural and dynamical

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Table 1
Values of Lennard-Jones and electrostatic interaction potentials parameters.

Intermolecular interactions			
Atom	q/e	σ (Å)	ε(kJ/mol)
O_w	−0.820	3.1656	0.650
H_w	0.410	0.000	0.000
O_m	−0.683	3.120	0.170
C_m	0.145	3.500	0.066
H_m(C)	0.040	2.500	0.030
H_m(O)	0.418	0.000	0.000
Na	1	2.35	0.544
Cl	−1	4.40	0.419

properties. The rest of the paper is organized as follows: in the first section we present the simulation methodology. In Section 2, we discuss our results in terms of radial distribution functions, self-diffusion coefficient, and orientational time correlations. Finally, our conclusions are given in Section 3.

2. Simulation details

The molecular dynamics formalism was described elsewhere [13]. Only a brief outline will be given here. The electrostatic and Lennard-Jones interaction energy between two molecules is calculated according to Eq. (1):

$$U = \sum_{i>j} \frac{q_i q_i}{4\pi\varepsilon_0 r_{ij}} + \sum_{i>j} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^2 - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^2\right] \tag{1}$$

where q_i denotes the charge on the ith atom and r_{ij} is the distance between the ith and jth atom; σ_{ij} and ε_{ij} are the corresponding constants of the Lennard-Jones potential. The values of the potential parameters q_i, σ_i, and ε_i for all particles are summarized in Table 1 [14–16]. A cubic box of 250 solvent molecules (water, methanol) and 6 ions of sodium and chloride is chosen and periodic boundary conditions with minimum image convention was used. The initial configurations are obtained by a random displacement of the particles in the box. The Lorentz-Berthelot combining rules [17] are used to describe the cross-interactions and the long-range Coulomb forces are calculated using the Ewald summation method [18]. The convergence parameter is $\alpha = \frac{5.36}{L}$ and the maximum k in the reciprocal space is such that ${k_{\max}}^2 \leq 27$. The non-Coulomb short range interactions were truncated using a spherical cut-off distance equal to the half of the cell length. The weak coupling scheme according to Berendsen et al. [19] is applied.

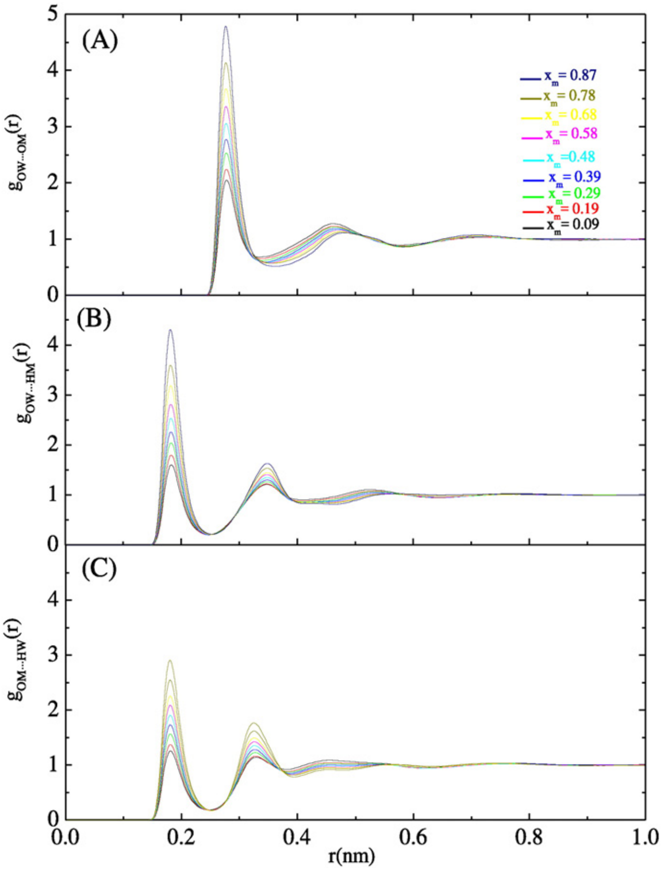

Fig. 1. (A) The oxygen water-oxygen methanol, (B) oxygen water-hydrogen methanol, (C) oxygen methanol-hydrogen water, radial distribution functions for aqueous NaCl solutions in water-methanol mixtures for different compositions.

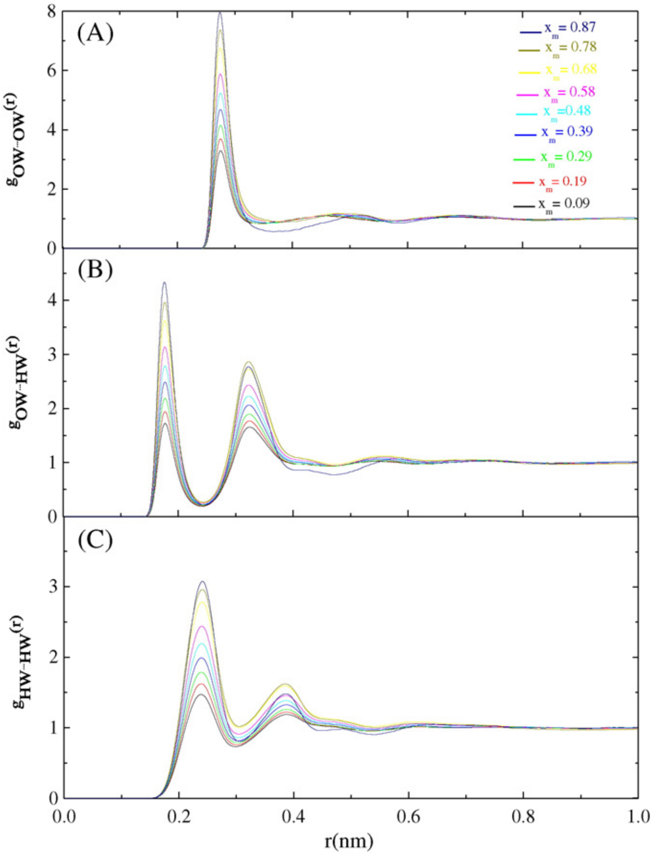

Fig. 2. (A) The oxygen water-oxygen water, (B) oxygen water-hydrogen water, (C) hydrogen water-hydrogen water, radial distribution functions for aqueous NaCl solutions in water-methanol mixtures for different compositions.

3. Results and discussion

A standard method for studying the structure of solution is to calculate the radial distribution functions $g_{ij}(r)$ [20] for the various atom-atom pairs. Another characteristic is the coordination number (n_{ij}) which defines the mean number of particles (j) in a volume defined by two concentric spheres of radii r_1 and r_2 centered on a particle i.

$$n_{ij} = 4\pi\rho_j \int_{r_1}^{r_2} g_{ij}(r) r^2 dr \tag{2}$$

The radial distribution functions (RDFs) for the $O_w \cdots O_m$, $O_w \cdots H_m$ and $O_m \cdots H_w$ pairs (O_w, O_m, H_m and H_w denote oxygen water, oxygen methanol, hydrogen methanol of hydroxyl group and hydrogen water,