Journal of Molecular Liquids 263 (2018) 109–117

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

A link between viscosity and cation-anion contact pairs: Adventure on the concept of structure-making/breaking for concentrated salt solutions

Hong Peng *, Anh V. Nguyen

School of Chemical Engineering, The University of Queensland, Brisbane, Queensland 4072, Australia

ARTICLE INFO

Article history:
Received 8 January 2018
Received in revised form 29 April 2018
Accepted 30 April 2018
Available online 02 May 2018

Keywords:
Viscosity
TIP4P/2005
Cation anion interaction
Structure-making
Hydration shell
Molecular dynamics

ABSTRACT

We investigated structure properties of structure-making salts (LiCl, NaCl, and NaBr) and structure-breaking salts (KCl and KBr) solutions of 0.5 M to 4 M using TIP4P/2005 water model and OPLS ionic force fields. The viscosity results show a good trend with experimental values for all salts. For the water structure, the O—O number decreased with increasing salt concentrations but is independent of the salt types. There is an extra shoulder (Cl-O/LiCl) or no obvious low-point at the first minimum point of anion oxygen RDF patterns (Cl-O/NaCl and Br-O/NaBr) while two structure-breaking salts show a normal minimum point (Cl-O/KCl and Br-O/KBr). Additionally, we observed that the ratio (R_{12}) of primary and second shell cation-anion numbers showed a similar trend as the viscosity behaves with increasing salt concentration. For structure-making salts, values of R_{12} increased with increasing salt concentrations while R_{12} values of structure-breaking salts slightly decreased with concentration. These observations may indicate that the change in viscosity is due to the disturbance of cation-anion contact hydration pairs, not the free water hydrogen network.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Effect of salts on water structure has been investigated for many years in broad research fields, from biochemistry (e.g., protein precipitations) [1–4] to froth flotation (e.g., film stability) [5–7]. When salts dissolve in water, the ions are hydrated by water molecules to form hydration shell. This would cause the re-structure of water molecules around hydration shells which disturbed the original hydrogen bond network in the pure liquid water. In his classical treatise [1], Gurney first proposed the structure-making and structure-breaking ions, based on their effect on water structure and also link this notion with a change in solution viscosity. Based on the change in solution viscosity, the salts have been classified as structure-making (increasing viscosity) and structure-breaking (decreasing viscosity). Since then, the effect of ions on water structures remains a long-time debate, even many works on experimental tests [8–13] and molecular simulation works [14–17] have been done. In his work, Samoilov explained that bulk viscosity correlated with the exchange rate of water molecules in the first hydration shell of ions [18]. The change in the activation energy of the exchange water nearby is positive for high ionic charge density (structure-making ions) while it is negative for lower ionic charge density (structure-breaking ions). Later on, in seminal works by Collins [2,4], he explained further the change in the absolute heat of hydration could be used for characterizing salt ions from the thermodynamic state. However, the link between the salt-water structure at the microscopic level and the macroscopic properties of salt solutions is not fully understood.

Molecular simulation has been used to investigate the pure water and salt solutions, from one single ion to concentrated brine solutions [15,19–22]. In early days, the water models used in the most investigations are exclusively expandable SPC/E model or its polarizable models (PROL) [15,21,23–25]. Using SPC/E water model, Moucka et al. investigated the effect of different NaCl ion models on the prediction of basic properties for a wide range of concentrations [26]. They showed that most of the tested ion force fields could not predict the basic structure properties for the large range concentrations. In a very recent investigation [27], a comparison of classical interatomic water and ion models was conducted on LiCl concentrations up to 4 M. They also found the water models had a significant effect on properties of salt solutions. It is necessary to optimize the force fields of both water and ion models used in the simulation. Aragones et al. initially used TIP4P-Ew water model in combining with JC ion models to study the structure of LiCl salt solutions up to 10 M [28]. The results indicated they needed to modify the Lorentz-Berthelot (LB) mixing rules to get the best fit of RDFs in simulation compared with experimental data. However, by combining TIP4P water model and OPLS ion models, Singh et al. also studied the various properties of LiCl solutions in the range of 0.1 M to 19 M by molecular simulation [29]. Without optimizing LB mixing rules, they also obtained a good agreement between simulation data and experimental results. Recently, we have explored the interfacial properties of concentrated KCl solutions using common OPLS ion models with two common

* Corresponding author.
E-mail address: h.peng2@uq.edu.au (H. Peng).

https://doi.org/10.1016/j.molliq.2018.04.145
0167-7322/© 2018 Elsevier B.V. All rights reserved.

Table 1
Potential parameters of ions.

Ion	Name	σ (nm)	ε (KJ/mol)	Charge
Li^+	OPLS-406	0.213	0.0765	1
Na^+	OPLS-407	0.333	0.0116	1
K^+	OPLS-408	0.493	0.0014	1
Cl^-	OPLS-401	0.442	0.493	−1
Br^-	OPLS-402	0.462	0.376	−1

Table 2
Mole fraction of water-ion concentrations.

Concentration (M)	0	0.5	1	2	4
N_{water}	891	875	859	825	761
N_{ion}	0	8	16	33	65

water models: SPC/E and TIP4P/2005 [30]. The results indicated that TIP4P/2005 water model in combining with OPLS ion models has much better performance on the prediction of interfacial properties with increasing salt concentrations compared with experimental data. Especially, the simulated viscosity values show a very good increasing trend with experimental values.

In this study, we expand our research to investigate ion-water structure and thermodynamic viscosity data for five different salts as a function of the salt concentration from 0.5 M to 4 M. We apply the TIP4P/2005 water and OPLS ion models in the simulations. We aim to explore the linkage between ion-water/ion-ion interaction and bulk shear viscosity to reveal the concept of structure-breaking/making at the atomic level.

2. Methods

2.1. Interaction energy models

The isotropic site-site potential was used in this simulation. The pair potential $U(r_{ij})$ consists a sum of interactions between site "i" and site "j" separated by distance r_{ij}. These interactions are spherically symmetrical and depend on the distance between these sites. The equation for this potential is described as [31]

$$U(r_{ij}) = 4\sum_{i=1}^{NLJ}\sum_{j=1}^{NLJ}\varepsilon_{ij}\left\{\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right\} + \sum_{i=1}^{NCL}\sum_{j=1}^{NCL}\frac{q_i q_j}{r_{ij}} \quad (1)$$

where the first and second terms on the left-hand side represent the 12–6 Lennard–Jones (LJ) dispersion and repulsion interactions. The third term describes the Coulomb law of electrostatic interaction (CL). q_i and q_j are the charges of sites. ε_{ij} and σ_{ij} are the combined LJ well-depth and collision diameter of the two sites calculated based on the Lorentz-Berthelot mixing rules [32]. NLJ and NCL are the numbers of LJ and CL interaction sites in the system.

For the water interaction models, the TIP4P/2005 [30,33] was employed in the simulations. It consists of one LJ central site located on oxygen nucleus and three-coulomb sites. Two positive charges are located on two hydrogens while the negative charge is placed in the designed 'M' site along the bisector of the H—O—H angle. The distance of OH bond is 0.9572 Å and the angle of H—O—H is 104.52°. The OPLS model for ions described by Jorgensen [34,35] is used as they are the default in the OPLS force field distributed with the GROMACS package. The standard Lorentz-Berthelot combination rules for the OPLS model were used to obtain the LJ parameters between atoms of different species in both sets of potential parameters as shown in Table 1.

2.2. Simulation procedure

The simulations were performed at the canonical NVT ensemble (at constant temperature and volume) using GROMACS package [36]. The temperature is fixed at 300 K by using v-rescale. Both LJ and electrostatic interactions were truncated at 1.2 nm. Long-range electrostatic interactions are corrected with Ewald summation method using Particle Mesh Ewald for the reciprocal part [37]. The simulation box size was fixed at around 3.0 nm which would be adjusted according to system density. Each simulation was for a constant number of ions and water according to the varying concentrations as shown in Table 2. The leap-frog method with a time step of 1 fs was used to integrate the particle motion. A total simulation time was 3 ns including 0.5 ns for equilibrium period and 2.5 ns for sampling stage which was used to calculate the properties [30,38].

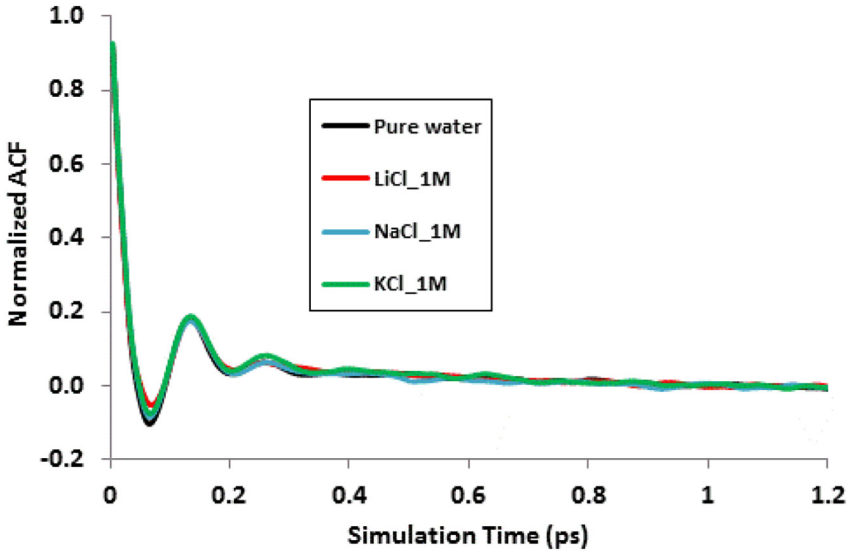

Fig. 1. Normalized autocorrelation functions at 300 K for pure water and 1 M salt solution.

Download English Version:

https://daneshyari.com/en/article/7842128

Download Persian Version:

https://daneshyari.com/article/7842128

Daneshyari.com