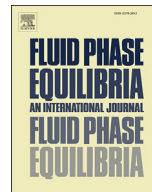




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Effect of water concentration on the microstructures of choline chloride/urea (1:2) /water mixture

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ABSTRACT

Molecular dynamics was utilized to investigate the properties of ChCl/urea (1:2)/water mixtures from pure ChCl/urea to infinitely dilute solution. To further study the mechanism at molecular scale, the local microstructure variation in the mixtures with the increase of water content was analyzed in detail. Simulation results showed that neither choline cations nor chloride anions are saturated by the coordinated water molecules, even when the water molar fraction reaches 0.9. The hydration number proportions for different ions indicated that the hydration strength of chloride anion is stronger than that of choline cation, which may play greater effects on the properties of mixtures. This result is further confirmed by the analysis of interaction energy between cation (anion) and water molecules. Moreover, the ion pairing between choline cations and chloride anions is a dominant factor to affect the solution properties at lower water content, whereas the hydration turns to be the dominant factor with increasing water content. The competition between ion pairing and ionic hydration could be the intrinsic mechanism resulting in non-ideal properties.

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1. Introduction

In recent years, ionic liquids (ILs) have attracted increasing attentions both in academic and industrial communities due to their desirable properties, such as negligible vapour pressure, exceptional thermal and electrochemical stabilities, and excellent solvation capacity for both organic and inorganic compounds, etc. [1–4] However, the defects of high viscosity and expensive price of pure ILs restrict its large-scale application in industry [5]. Adding water into pure ILs is the most common and facile way to overcome these drawbacks of pure ILs, which is considered as one of the most promising methods to achieve breakthroughs in the industrial applications [6].

Experimental studies [7–9] have demonstrated that adding water can greatly change the properties of the mixture. Choline dihydrogen phosphate ([Ch][DHP]) is a typical example. [Ch][DHP] with 20 wt% water is shown to be an excellent solvent for cytochrome c and other proteins, while proteins are usually insoluble in pure ILs [10,11]. In addition to the solubility for other components,

the thermodynamic properties of aqueous ILs also exhibit a high degree of non-ideal behaviour, such as viscosity [12], excess molar volume (V^E) [13] and mixed enthalpy [14]. These non-ideal phenomena suggested that aqueous ILs are a type of unique mixture and its microstructures are extremely complex, so that existing theories and models of mixed solvents and those of aqueous solutions usually fail to be applied directly. Aqueous ILs have stronger electrostatic interaction compared with that of conventional mixed organic solvents, whereas they have more complex molecular structures compared with those of aqueous electrolyte solutions. Therefore, investigation of the microstructure of aqueous ILs can facilitate to abstract the physical models and elucidate underlying mechanism at molecular scale. It is also indispensable to further build predictive models based on molecular parameters.

Deep eutectic solvents (DESs) were firstly reported in 2001 by Abbott et al. [15] and considered as a new type of ILs [16]. DESs have been widely used in electrochemistry and catalysis, organic synthesis, dissolution and separation, material chemistry because they can be easily synthesized and environmentally friendly [17]. Choline chloride/urea (ChCl/urea) is one of the most widely used DESs due to its lower price compare with conventional ILs and a promising future for large-scale industrial applications. In our

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previous experimental studies [13], we found that when the mole fraction of water increases to about 15%, the viscosity of {ChCl/urea (1:2) + water} decreases rapidly by 80% compared to pure ChCl/urea (1:2). Our experimental studies also showed that the V^E of the system first decreases and then increases with increasing of water content from 0 to 100%. These non-ideal properties aroused our interest to further investigate its underlying mechanism.

Many studies [18,19] have been conducted on the micro-mechanism of IL/water mixtures. Wang et al. [20,21] performed atomistic simulations to investigate the microstructure of aqueous solutions of trihexyltetradecylphosphonium bis(oxalato)borate ([P6,6,6,14][BOB]) IL and found that the competition of the hydrogen bond (H-bond) interaction, the electrostatic interaction between the charged ions, and the dispersion interaction between the hydrophobic alkyl chains of [P6,6,6,14] cations results in the change of macroscopic properties. Bhattacharjee et al. [22] believed that the optimum combination of the H-bonds between the mixture components and the high occupation degree of IL interstitials with water molecules causes the minima of V^E .

In our previous theoretical studies, we found that both ionic hydration and ion pairing have significant effects on the properties of aqueous solutions. For weak hydration ions (e.g. K^+ , Cl^-), we defined a “hydration factor” to obtain a more accurate hydration number of ion [23]. For strong hydration ions (e.g. Mg^{2+} , Li^+), we found that dehydration and coordination in the second hydration shell are important in separation of ions with similar nature [24]. Ion pairs and hydrated ions always coexist in many high concentration solutions. The formation of ion pairs in solutions can change the microstructure of the surrounding water molecules [25,26]. The existence and competition of ion pairing and hydration have a significant effect on the properties of aqueous solutions. The consideration of ion pairing and ionic hydration is important in micro-mechanism [27], and it can also help us verifying and proposing predictive models of aqueous solutions [28]. However, related discussion of ion pairing and ionic hydration on aqueous ILs is less compared with H-bonds analysis.

To study the microscopic mechanism and then further obtain the local composition of ChCl/urea/water mixtures with varied water content, in this work, molecular dynamics (MD) simulations were performed to obtain a deeper insight into the microstructure of ChCl/urea/water mixtures at different water concentrations. The focus was to understand how the ionic hydration and ion pairing change with water content in the mixtures, providing knowledge for the aqueous IL applications and the development of a theoretical model.

2. Simulation models and methods

In this work, 11 ChCl/urea/water mixtures, in which the molar ratio of ChCl to urea was 1:2 (ChCl: urea), and the water molar fraction ranged from 0 to 100%, were investigated. This particular mole ratio of ChCl to urea was chosen because the mixture of ChCl and urea with this ratio is much more stable with a freezing point of

12 °C [6], making it suitable for many applications [29,30]. Fig. 1 shows several snapshots of the ChCl/urea/water mixtures.

In simulation, the boxes contain 500 urea molecules and 250 ChCl molecules, and the number of water molecules was adjusted from 0 to 2250 to achieve the particular assigned concentration from pure ChCl/urea to the mixture with 0.9 molar fraction of water. A system containing 1 ChCl/urea (1:2) and 1000 water molecules was also simulated to obtain the saturated hydration number of anion and cation, which can be approximately considered as an infinite dilution solution.

The extended simple point charge (SPC/E) [31] model was used for water molecules, and the CHARMM27 all atom force field generated by SwissParam [32] was used to describe the ChCl and urea molecules. Although scaling partial charges of atoms is a common method to match experimental results, we used the partial charge directly generated by SwissParam, because Shah et al. [33] used this set of force field parameter and charges to investigate the thermo-physical properties of ChCl/urea/water mixtures, and the reliability of these parameters has been verified by comparing with the experimental results and they could be enough helpful for us to understand the qualitative mechanism. The 12-6 Lennard–Jones (LJ) potential combining a coulombic potential was used to describe the intermolecular interactions (Eq. (1)).

$$U(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \quad (1)$$

The Lorentz-Berthelot mixing rules were chosen to calculate the LJ parameters of the cross interactions. The force field parameters are summarized Table 1. The periodic boundary condition was applied to all the three dimensions. The Particle Mesh Ewald (PME) method [34] was used to calculate the long-range electrostatic interaction with a cut-off for a real space of 1.0 nm. The short-range van der Waals cut-off was set to be 1.0 nm. All the cases, after energy minimization, were first equilibrated in 2 ns NVT ensemble and 2 ns NPT ensemble, respectively, and every production run was performed for 8 ns in the NPT ensemble with 2 fs time step and saved every 0.2 ps. The temperature in the system was controlled by V-rescale thermostat, and the temperature in simulation was

Table 1
Force field parameters used in the simulation.

Site	$\epsilon/\text{kJ}\cdot\text{mol}^{-1}$	σ/nm	q/e
CN	0.230	0.388	0.503
N	0.837	0.330	0.145
CO	0.230	0.388	0.28
HC	0.0092	0.235	0.0
OH	0.636	0.315	-0.68
HO	0.192	0.04	0.4
Cl^-	0.628	0.404	-1.0
OW	0.636	0.315	-0.834
HW	0.000	0.000	0.417

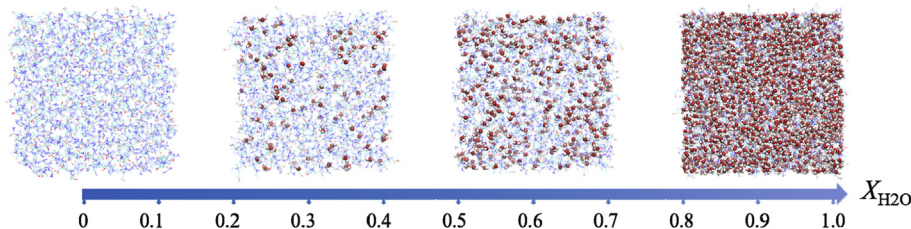


Fig. 1. Snapshots of ChCl/urea/water with 0, 0.3, 0.6, 0.9 molar fraction of water, respectively.

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