



Phase behavior in quaternary ammonium ionic liquid-propanol solutions: Hydrophobicity, molecular conformations, and isomer effects



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ABSTRACT

In ionic liquids (ILs), the effects of a quaternary ammonium cation containing a hydroxyl group were investigated and compared with the effect of a standard quaternary ammonium cation. The cation possessing a hydroxyl group is choline, Chol⁺, and the anion is bis(trifluoromethylsulfonyl)imide, TFSI⁻. Crystal polymorphism of pure [Chol][TFSI] was observed upon both cooling and heating by simultaneous X-ray diffraction and differential scanning calorimetry measurements. In contrast, [N3111][TFSI] (N3111⁺: *N*-trimethyl-*N*-propylammonium), a standard IL, demonstrated simple crystallization upon cooling. By adding 1-propanol or 2-propanol, the phase behaviors of the [Chol][TFSI]-based and [N3111][TFSI]-based mixtures were clearly distinguished. By Raman spectroscopy, the TFSI⁻ anion conformers in the liquid state were shown to vary according to the propanol concentration, propanol isomer, and type of cation. The anomalous behaviors of pure [Chol][TFSI] and its mixtures are derived from hydrogen bonding of the hydroxyl group of Chol⁺ cation coupled with the hydrophobicity and packing efficiency of propanol.

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1. Introduction

In biochemical engineering, choline-based ionic liquids (ILs) are playing important roles in new types of solutions. The outstanding features of choline cation, Chol⁺, have been clarified by recent research [1–6]. Particularly, in choline dihydrogen phosphate ([Chol][dhp]), a protein was preserved in its native holding for a long time [6]. [Chol][dhp] aqueous solution has been found to be very useful for biochemical engineering. Also, it was found that [Chol][dhp] can stabilize DNA triplex formation [7]. Molecular dynamics (MD) simulations have been used to estimate the positions of choline ions in the DNA triplex. Furthermore, [Chol][dhp] can reduce mismatches of DNA with a target [8]. A DNA sensing system has been developed using [Chol][dhp]. Other applications of the choline-based ILs have been proposed [9]. Fascinating ideas, such as blood preservation, have been suggested in the literature. In addition to its application in biochemical engineering, choline can be used in green chemistry as an environmentally friendly solvent and has demonstrated outstanding effects [10,11]. In fundamental science, the inherent features of choline were examined by MD [12–14] and quantum chemical calculations [15]. The MD simulations suggest dynamic heterogeneity, driven by strong

hydrogen bonding [14]. Hydrogen bonding at high temperature was demonstrated during the diffusion process; this was characterized as non-Gaussian diffusion. In contrast, the local structure was visualized by quantum chemical calculations [15]. Six- and seven-membered ring-like structures were optimized in the simulation box. Interesting findings regarding geometrical factors have been derived from hydrogen bonding and charge transfer studies.

In non-choline-based ILs, protein structures as a function of water concentration were examined by small-angle X-ray scattering (SAXS) [16–20]. For example, a lysozyme demonstrates structural variety in a 1-butyl-3-methylimidazolium nitrate ([C₄mim][NO₃])–water system [16]. A partial globular state occurs at a specific water concentration. This partial refolding is explained by the nanometer-sized confined water, which is called a “water pocket.” Direct evidence of water pockets was provided by complementary use of SAXS and small-angle neutron scattering (SANS) [21]. From the SANS peak, the average size of the water pocket was estimated to be 2 nm. When half of the lysozyme is captured in the 2 nm-sized water pocket, the immersed part of the lysozyme achieves a partial refolded state. More importantly, crystallization in [C₄mim][NO₃] x mol% D₂O is suppressed at x = 70–90 mol% even upon slow cooling [22]. The water concentration region of the amorphous state coincides with that of the water pocket at room temperature. The mixture in the water-rich region can be utilized for cryopreservation for biochemical engineering.

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Alongside the addition of water to hydrophilic ILs, alcohols are regarded as potential additives for hydrophobic ILs. To reduce material cost, it is necessary to dilute hydrophobic ILs using alcohol. In fact, CO₂ separation techniques [23] and electric double layer capacitors [24] have been much improved by adding alcohol. The hydrophobic ILs contain bis(trifluoromethylsulfonyl)imide (TFSI⁻) anion. The characteristic feature of TFSI⁻ anion is two stable conformers; one is C₁ (*cis*), and the other is C₂ (*trans*) (Fig. 1) [25–27]. Combined with density functional theory (DFT) calculations, it was clarified that the conformers of TFSI⁻ anion reveal liquid stability or instability [28,29]. Phase diagrams of [C_nmim][TFSI] (2 ≤ n ≤ 10), -propanol [28] and -butanol [29] systems indicate phase stabilities depending on alkyl-side chain length (n) and alcohol isomers. Here C_nmim⁺ is the 1-alkyl-3-methylimidazolium cation. At approximately n = 6, a crossover from ionic-like behavior to liquid crystal-like behavior occurs changing the conformation of the TFSI⁻ anion. The conformations of TFSI⁻ anion have been investigated not only in imidazolium ILs but also in quaternary ammonium ILs. The conformation stability of [N3111][TFSI] (N3111⁺: N-trimethyl-N-propylammonium) was compared with DFT calculations [30]. Furthermore, low temperature phase behaviors of [N3111][TFSI] were examined by differential scanning calorimetry (DSC) and infrared spectroscopy [31]. Accompanied by crystallization of [N3111][TFSI], the conformational ratio of C₁ and C₂ changed drastically at low temperature. Moreover, in IL-propanol mixtures, the C₁ and C₂ conformers of TFSI⁻ anion also provide insight into CO₂ capture [23]. [N4111][TFSI] (N-trimethyl-N-butylammonium) becomes unstable upon the addition of 2-propanol. High CO₂ capture in the [N4111][TFSI]-2-propanol system implies that, when CO₂ is absorbed, the unstable IL-2-propanol system is promoted to a stable liquid phase. Recently, the nanostructures of protic ionic liquid (pIL)-alcohol systems have been reported [32,33]. To understand the macroscopic properties of these systems, the local liquid structures and molecular conformations of the mixed systems are very significant.

In this study, we investigated the crystallizations of pure [Chol][TFSI] and pure [N3111][TFSI] by simultaneous X-ray diffraction and DSC measurements. In addition to the pure systems, the phase behaviors of [Chol][TFSI]-propanol were compared with those of [N3111][TFSI]-propanol. Both in the pure and mixed systems, on the molecular level, the hydroxyl group of the quaternary ammonium cation govern the mixing state.

2. Experiments and simulations

The ILs used in this study are hydrophobic [Chol][TFSI] (IoLiTec GmbH) and [N3111][TFSI] (Kanto Chemical Co.) (Fig. 1). 1-propanol (99.5%) and 2-propanol (99.5%) (Kanto Chemical Co.) were selected as propanol additives. The intrinsic molecular properties are listed in Table 1.

Simultaneous X-ray diffraction and DSC measurements were carried out using SmartLab (Rigaku Co.). The wavelength of the incident X-ray (Cu K α radiation) was 0.1542 nm. The cooling and heating rates were 5 °C/min. Dry N₂ gas was flowed in the DSC cell. The temperature range was 50 °C to –100 °C. Crystal structure analysis was conducted using FOX [34] and Conograph [35]. Conograph was used to determine the crystal lattice parameters. Then, global optimization of FOX was used to identify the crystal structure.

To determine the phase diagrams, the mixtures were cooled from 30 °C to –60 °C using an ethanol bath (Yamato Scientific Co., BE200); at this point, clouding and crystallization of the mixtures were visually observed. By visual cloud-point determinations, the accuracy of the clouding temperatures was found to be within 1.0 °C. Several thermal cycles using the same sample and measurements using different samples at the same concentration were used to determine the experimental errors of the clouding temperatures. A liquid N₂ pot was used for further cooling [28,29]. The temperature was monitored with Pt100 (Netsushin Co.). The cooling rate was 1.5 °C/min.

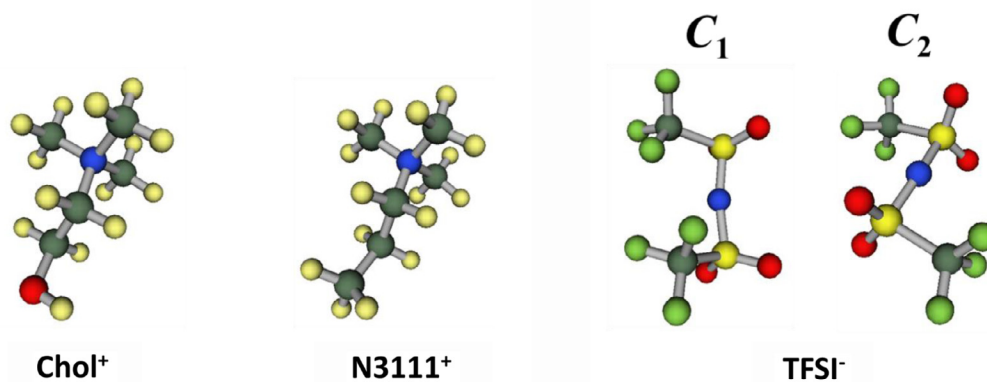


Fig. 1. Molecular structures of Chol⁺, N3111⁺, and TFSI⁻. TFSI⁻ anion has two stable conformers, C₁ and C₂.

Table 1
Molecular properties of the cations, anion, and propanol additives.

Cations		Anion	Additives		
Chol ⁺	N3111 ⁺	Two conformers	Two isomers		
–OH	–CH ₃	C ₁ (<i>cis</i>)	1-Propanol	2-Propanol	
		C ₂ (<i>trans</i>)			
← Polarity →		← Packing →		← Hydrophobicity →	

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