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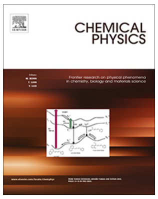

Ether bond effects in quaternary ammonium and phosphonium ionic liquid-propanol solutions

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The liquid-liquid equilibria (LLE) of quaternary ammonium and phosphonium ionic liquid (IL)-propanol solutions were examined. The ILs contained cations with or without ether bonds; the anion in all the ILs was bis(trifluoromethanesulfonyl)imide (TFSI$^-$). The cations without ether groups are tributylmethyl ammonium (N4441$^+$), triethylpentyl phosphonium (P2225$^+$), triethyloctyl phosphonium (P2228$^+$), and tributylmethyl phosphonium (P4441$^+$). The cations containing ether groups are *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium, (N122(2O1)$^+$), triethyl(methoxymethyl) phosphonium (*P*222(1O1)$^+$), and triethyl(2-methoxyethyl) phosphonium, (*P*222(2O1)$^+$). Propanol isomer effect was observed to affect the LLEs, reflecting the geometrical factors and hydrophobicities of 1-propanol and 2-propanol. According to Raman spectroscopy, the TFSI$^-$ anion conformers in the mixtures were altered in the presence of ether bonds in the cations. The universal quasichemical (UNIQUAC) interaction parameters are consistent with significant factors affecting IL-propanol solutions, such as the type of cation (ammonium or phosphonium), ether bonds, TFSI$^-$ conformers, and propanol isomer effects.

1. Introduction

Ionic liquids (ILs) are attracting attention as novel and promising potential solvents [1–6]. ILs consist entirely of cations and anions. By exploiting the outstanding properties of ILs, such as their chemical and thermal stabilities and vapor pressures close to zero, sustainable green chemistry technology has been developed that is beneficial to the environment and thus to society. Recently, IL-assembled energy devices have been greatly improved for industrial applications [7–12]. Among ILs, quaternary ammonium and phosphonium ILs are considered to have potential as stable electrolytes in electrochemical devices. Compared with ammonium ILs, phosphonium ILs have lower viscosities [13]. Furthermore, ILs with greatly lowered viscosities have been designed and synthesized by substituting ether bonds [14,15]. The phosphonium cations commonly used in ILs are triethylpentyl phosphonium (P2225$^+$), triethyloctylphosphonium (P2228$^+$), triethyl (methoxymethyl) phosphonium (P222(1O1)$^+$), and triethyl(2-methoxyethyl) phosphonium (P222(2O1)$^+$). Hydrophobic ILs commonly contain bis(trifluoromethanesulfonyl)imide (TFSI$^-$) anion. Due not only to their low viscosities but also their excellent electrochemical properties, ether bond-substituted phosphonium ILs are regarded as fascinating electrolytes. Also, the fundamental data regarding ether bond-substituted phosphonium ILs support that ether-modified cations are suitable electrolytes for supercapacitor [16]. A higher energy density of the capacitor is induced by the molecular orientational order near the surface of the electrode. The electronegative portion of the ether bond of the cation is related to the performance of the capacitor. 2D NMR experiments indicate different cation-anion interactions when the cation is unmodified P2228$^+$ or ether bond-substituted (2-ethoxyethoxy) ethyltriethyl phosphonium (P222(2O2O2)$^+$) [17]. Importantly, ether bond-mediated interactions differ from those of unmodified quaternary phosphonium cations.

Pure ILs are designed to possess inherent functionality on the basis of their cation and anion combinations. Additives to ILs provide the possibility of new applications. Moreover, dilutions using cheap additives such as water, alcohol, and acetone are useful to reduce costs, as ILs are expensive. For example, CO$_2$ capture at room temperature and ambient pressure was increased by dilution of trimethylbutylammonium with 2-propanol ([N4111][TFSI]) [18]. In contrast, by adding 2-propanol to an imidazolium IL, [C$_2$mim][TFSI], its electric double layer capacitance was increased compared to that of 1-propanol-based mixtures [19]. The 1-alkyl-3-methylimidazolium cation is expressed as C$_n$mim$^+$, where *n*

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indicates the alkyl chain length. In both cases, higher performance was obtained in the propanol-rich region, which coincides with a specific concentration, x_{UCST}, in LLEs. Thermodynamically, the upper critical solution temperature (T_{UCST}) is important to express the phase separations of IL-based mixtures. Therefore, we examined phase stabilities of the mixed systems by determining their LLEs [20–22]. In [C$_n$mim][TFSI], the alkyl chain length effect of T_{UCST} was examined, combined with the alcohol isomer effect [20,21]. The crossover n (n_c) from ionic liquid-like to liquid crystal-like behavior was found to be around $n = 6$ [20,21]. Recently, cage energy landscape was introduced to explain ionic nature and organic nature of the ILs [23]. The local minimum of the free energy landscape [24] is quite important to evaluate the phase stability. The n_c value was determined by the disappearance of crossing of the clouding temperature curves, density, and conformations of TFSI$^-$ anion. In contrast, the hydroxyl group effects of cations such as choline were clarified in LLEs, compared with trimethypropylammonium (N3111$^+$) cation [22]. The alcohol isomer effect was clearly observed in the LLEs. In addition to the LLEs, the conformation stabilities of TFSI$^-$ anion were clarified by Raman spectroscopy with regard to phase stability. The two stable conformers of TFSI$^-$ anion are assigned as C_1 (*cis*) and C_2 (*trans*) [25–28]. Using a quaternary ammonium cation containing ether bonds, *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium, [N122(2O1)][TFSI], the ratio of C_2/C_1 of the TFSI$^-$ anion revealed good packing efficiency under high pressure [29].

In this study, we investigated the phase stabilities of quaternary ammonium and phosphonium ILs by adding propanol. By determining the LLEs and using Raman spectroscopy, it was clarified that the mixtures are governed by the type of cation (ammonium or phosphonium), propanol isomer effects, ether bonds, and the conformation stability of TFSI$^-$ anion in the solutions. The universal quasichemical (UNIQUAC) interaction parameters support the experimental results.

2. Materials and methods

The ILs used in this study were composed of hydrophobic quaternary ammonium or phosphonium cations and TFSI$^-$ anion. The cations without ether bonds are tributylmethyl ammonium (N4441$^+$), P2225$^+$, P2228$^+$, and tributylmethyl phosphonium (P4441$^+$) (Kanto Chemical Co.) (Fig. 1). The ether bond-substituted cations are N122(2O1)$^+$, P222(1O1)$^+$, and P222(2O1)$^+$ (Kanto Chemical Co.). 1-propanol (99.5%) and 2-propanol (99.5%) (Kanto Chemical Co.) were selected as propanol additives.

To determine the LLEs, 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 was visually observed. By visual cloud-point determinations, the accuracies of the clouding temperatures were found to be within 1.0 °C. A liquid N_2 pot was used for further cooling. The temperature was monitored with a Pt100 temperature sensor (Netsushin Co.). The cooling rate was 1.5 °C/min.

The Raman spectra were measured with a backscattering geometry using a micro-Raman spectrometer system (NRS-5100, JASCO). Radiation of 532 nm from a Nd:YAG laser was used as the excitation source with a power of 6 mW. The Raman spectra were measured at room temperature.

We performed density functional theory (DFT) calculations to investigate the interactions between the cations and anion. The conformations of the TFSI$^-$ anion were optimized in the simulation box. All DFT calculations were performed using the B3LYP and 6–31++G** basis set [30,31] of the PC-GAMESS package [32].

3. Results and discussion

3.1. LLEs of quaternary ammonium and phosphonium IL – propanol solutions

Fig. 2(a) to (c) reveal the LLEs of the [N122(2O1)][TFSI], [N4441][TFSI], and [P4441][TFSI] mixtures upon cooling, respectively. Pure [N122(2O1)][TFSI], which contains ether bonds, did not crystallize at the minimum temperature (Fig. 2(a)) [33]. In the 1-propanol- and 2-propanol-based mixtures, the clouding temperature curves almost coincide with each other over the entire concentration region. The coincidence of the curves corresponds to the small difference in T_{UCST}, ΔT_{UCST} (Table 1). Here ΔT_{UCST} is defined as $\Delta T_{UCST} = T_2 - T_1$, where T_1 and T_2 are the T_{UCST} values of the 1-propanol- and 2-propanol-based mixtures, respectively. Another characteristic feature of the [N122(2O1)][TFSI] mixtures is that the two curves cross near 70 mol%. In case of [C$_n$mim][TFSI]-propanol [20] and [C$_n$mim][TFSI]-butanol [21], the existence of a crossing point in the clouding temperature curves at $n < 6$ implies that the ILs can be classified as ionic nature, based on the cage energy landscape [23]. Here, n reveals the alkyl chain length of the C$_n$mim$^+$ cation, and n_c is defined as crossover n from ionic liquid-like (ionic nature) to liquid crystal-like (organic nature) phases [20,21]. We stress that ionic or organic nature is distinguishable in the LLEs. To interpret the ether bond effects in the quaternary ILs, appearance or disappearance of the crossing point in the LLEs is regarded as a good indicator of molecular interactions such as ionic nature or organic nature. Compared with the LLE of the ether bond-substituted [N122(2O1)][TFSI] (Fig. 2(a)), an entirely different LLE was observed in the [N4441][TFSI]-propanol system (Fig. 2(b)). Focusing on the phase separation, the crossing point in the LLE disappeared, reflecting organic nature [23]. Also, a large ΔT_{UCST} was found for the [N4441][TFSI]-propanol system (Table 1). From the viewpoint of solidification, pure [N4441][TFSI] crystallized at −3.5 °C. Here, crystallization is indicated by open squares in the figure. Upon addition of propanol, the crystallization temperature decreased. Particularly in the 2-propanol-based mixtures, the temperature noticeably decreased with increasing concentration. Moreover, the propanol concentration region of the crystal phase in the 2-propanol-based mixture was narrower than that in the 1-propanol-based mixture. The branch-shaped 2-propanol disturbs the crystal nucleation of [N4441][TFSI]. This tendency was also observed in the phase separation process; the T_{UCST} of the 2-propanol-based mixture is higher than that of the 1-propanol-based mixture. In the propanol-rich region, 2-propanol is readily excluded from [N4441][TFSI]. Here, it should be noted that the propanol isomer effect is not only derived from the geometrical factor but also from hydrophobicity [21,22]. To distinguish the solubility effects of ammonium and phosphonium, the LLE of the [P4441][TFSI]-propanol system was determined. The molecular structure of [P4441][TFSI] is exactly the same as that of [N4441][TFSI] except for the central nitrogen (Fig. 1). Because the TFSI$^-$ anion is common to the ammonium and phosphonium systems, we can compare the cation effects directly. The crystallization temperature of pure [P4441][TFSI] was found to be −29 °C (Fig. 2(c)). In the [P4441][TFSI]-propanol system, the crystallization temperature did not depend on the type of propanol isomer. The molecular interactions between phosphonium cation and propanol additives may be relatively weak. Thus, the geometrical and hydrophobic differences between 1-propanol and 2-propanol did not contribute to the mixtures in phosphonium-based systems.

Fig. 3(a) and (b) indicate the alkyl chain length dependence of the LLEs of phosphonium IL-propanol solutions. Pure [P2225][TFSI] crystallized at approximately −25 °C; the crystallization tempera-