Research paper

Surface tension anomalies in room temperature ionic liquids-acetone solutions

Hiroshi Abe [a],*, Keisuke Murata [a], Shota Kiyokawa [a], Yukihiro Yoshimura [b]

[a] Department of Materials Science and Engineering, National Defense Academy, Yokosuka 239-8686, Japan
[b] Department of Applied Chemistry, National Defense Academy, Yokosuka 239-8686, Japan

A B S T R A C T

Surface tension anomalies were observed in room temperature ionic liquid (RTIL)-acetone solutions. The RTILs are 1-alkyl-3-methylimidazorium iodide with $[C_nmim][I]$ in a $[C_nmim][I]$-x mol% acetone. The maximum value of the surface tension appeared at 40 mol% acetone, although density decreased monotonically with an increase in acetone concentration. A small alkyl chain length effect of the C_nmim^+ cations was observed in the surface tension. By the Gibbs adsorption isotherm, it was found that I^- anion-mediated surface structure became dominant above 40 mol%. In the different $[C_nmim][TFSI]$-acetone mixtures, normal decay of the surface tension was observed on the acetone concentration scale, where $TFSI^-$ is bis(trifluoromethanesulfonyl)imide.

1. Introduction

Room temperature ionic liquids (RTILs) are widely utilized in various fields owing to their outstanding properties, such as nearly zero vapor pressure [1–3]. The RTILs simply consist of cation and anion. Nanostructures of RTILs have been investigated [4–7]. One is polar and non-polar nanodomains as intrinsic nanostructures of RTILs. The other is self-organized or artificially synthesized nanostructures. In layered nanostructures, molecular arrays of RTILs are significant information for energy harvesting devices such as lithium-ion batteries, dye sensitized solar cells, and the electric double layer capacitors [8–12].

Surface tension of RTILs and their binary systems were investigated at the air-liquid interface [13–20]. Alkyl chain length effect of the surface tension was clearly observed in 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, $[C_nmim]$[TFSI], where n is the alkyl chain length of C_nmim^+ cation [15]. Density of the $[C_nmim]$[TFSI] monotonically decreased with an increase in n [21]. In contrast, surface tension in the $[C_nmim]$[TFSI] system had the minimum value at $n = 6$ [15]. Since low dimensional molecular arrays contribute directly to the surface tension, surface structures of $[C_nmim]$[TFSI] could be different from the bulk liquid structures above $n = 6$. Surface structure of $[C_2mim]$[NO_3] was visualized in the snapshot of the simulation box in

molecular dynamic (MD) simulation [22]. Surface density and molecular orientational orders on the surface are quite different from the bulk structure. Surface density of $[C_4mim][BF_4]$ and $[C_4mim][PF_6]$ was obtained experimentally by X-ray reflectivity [23]. The density of the surface was 18% higher than that of the bulk.

Molecular interactions of acetone in the RTILs were calculated by quantum-chemical COSMO-RS method [24]. Acetone was characterized as a hydrogen bond acceptor. The hydrogen bonding of acetone was represented by an anisotropic surface charge density. An acetone additive in the simulation box was found to stabilize $[C_2mim][PF_6]$. Acetone solubility into the RTILs was examined by the changing anions [25]. From vapor-liquid equilibria (VLE), the dilution activity coefficients as a thermodynamic property were estimated using the nonrandom two-liquid activity coefficient model. Phase behaviors of the RTIL-acetone binary systems were clarified by VLE [26] and lower critical solution temperature (LCST) type [27]. The LCST property was utilized in the separation technique.

In this study, we investigated surface tension of RTIL-acetone binary systems. The binary systems were $[C_nmim][I]$-x mol% acetone and $[C_nmim]$[TFSI]-x mol% acetone. The $[C_nmim][I]$-acetone system has a maximum value of surface tension at 40 mol% acetone, whereas the $[C_nmim]$[TFSI]-acetone system exhibits a monotonic decrease of surface tension with an increasing acetone concentration. The surface anomaly was induced by the surface iodide-acetone molecular interactions.

* Corresponding author.
  E-mail address: ab@nda.ac.jp (H. Abe).

2. Materials and methods

The hydrophilic and hydrophobic RTILs used in this study were [C$_n$mim][I] (n = 3, 4, and 6) (Kanto Chemical Co.) and [C$_n$mim][TFSI] (n = 3, 4, and 6) (Kanto Chemical Co. and IoLiTec GmbH), respectively. Acetone (99.5%) (Kanto Chemical Co.) was used as an additive.

Surface tension was measured using capillary rise method (Dyne Gauge, DG-1, Surfgauge Instruments Co.). Measurement range was 0–80 mN/m and its resolution was 1 mN/m. Liquid density of the mixtures was measured using a density/specific gravity meter (DA-645, Kyoto Electronics Manufacturing Co.) across a temperature range of 0–90 °C. Accuracy of the density and temperature measurements was estimated to be $\pm 5 \times 10^{-5}$ g/cm^3 and ± 0.03 °C, respectively.

3. Results and discussion

Densities of [C$_n$mim][I]-acetone mixtures at 24 °C are shown in Fig. 1. In pure [C$_n$mim][I] (n = 3, 4, and 6), densities decreased proportional to the alkyl chain length (n) [28]. In the mixtures, monotonic decreases in the densities were obtained. The dependence of the densities on additive concentration is consistent with previous studies [29–31]. Here in [C$_6$mim][I]-acetone, decreasing rate of density in the acetone-poor region is different from other [C$_3$mim][I]- and [C$_4$mim][I]-acetone systems. Previously, density of C$_6$mim$^+$ cation-based mixed system showed the crossover-like behavior. For instance, in the [C$_n$mim][TFSI]-butanol system, the densities were reflected by a crossover point from ionic liquid-like behavior to liquid crystal-like [31]. The crossover point of n_c was found to be 6. Recently, Shi and Wang proposed the idea of an ionic nature and organic nature of RTILs by introducing the cage energy landscape [32]. We confirm that, at $n = n_c$, a competition between the ionic nature and the organic nature occurred in the [C$_n$mim][TFSI]-butanol system. Thus, in [C$_n$mim][I]-acetone mixtures, different concentration dependence of densities occurs at n = 6. Due to the n_c, the negative slope of the density with increased acetone concentration was smaller for this system than for [C$_3$mim][I]- and [C$_4$mim][I]-based densities (Fig. 1).

Fig. 2 shows a plot of surface tensions of [C$_n$mim][I]-acetone versus acetone concentration at 24 °C. In contrast to additive concentration dependence of the density and the surface tension in the previous studies [13–20], the surface tension in [C$_n$mim][I]-acetone had the maximum value at 40 mol% acetone. Here, we

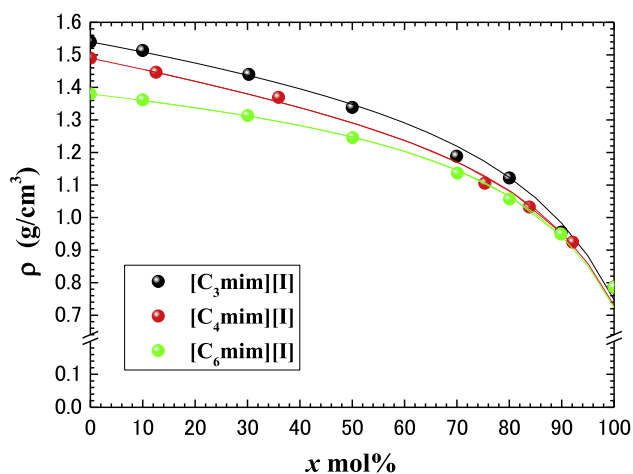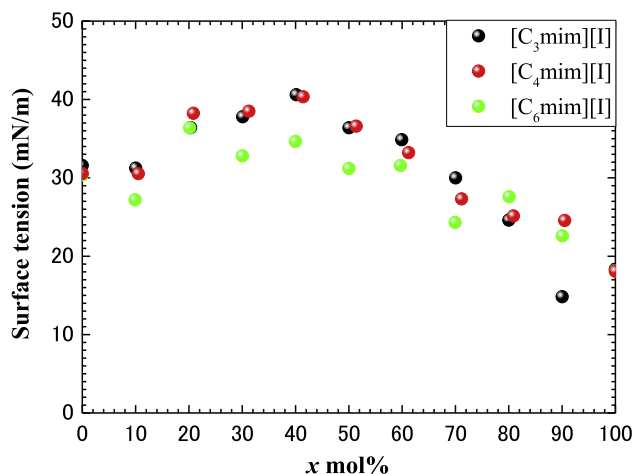**Fig. 2.** Surface tensions of [C$_n$mim][I]-acetone mixtures as a function of acetone concentration. The maximum value of the surface tensions appeared at 40 mol% acetone.

denoted that aqueous H$_2$SO$_4$ as other simple molecular system provides the maximum value of the surface tensions [33]. To our knowledge, this is first observation of the surface anomaly of the binary [C$_n$mim][I]-acetone system. Furthermore, in the [C$_6$mim][I]-acetone mixture, the local maximum value of the surface tension is relatively lower than [C$_3$mim][I]- and [C$_4$mim][I]-based systems. In Fig. 2, data deviations are not ignored. Intrinsically, surface tensions of [C$_6$mim][I]-acetone had deviations of ~10 mN/m in spite of several measurements of the same samples. The reason is that C$_6$mim$^+$ cation ($n = n_c$) is destabilized by the competition between the ionic nature and the organic nature as mentioned earlier. In case of [C$_3$mim][I]- and [C$_4$mim][I]-based mixtures, the surface tension deviations became less than 5 mN/m. The relative large deviations imply that the surface states could be unstable in the [C$_n$mim][I]-acetone system. A comparison between other systems was done to interpret the n dependence of surface tension. The effect on the alkyl chain length of the surface tension was clearly observed in other system of pure [C$_n$mim][TFSI] (n = 1–10) (Fig. S1) [17,34]. Even in pure [C$_n$mim][TFSI], surface tensions are influenced by the alkyl chain length. For the n-plot of the surface tension of pure [C$_n$mim][TFSI], the minimum value is at n = 6 (20 °C).

In order to clarify the anomalous local maximum of surface tension in the [C$_n$mim][I]-acetone, we measured densities and surface tensions of the normal [C$_n$mim][TFSI]-acetone systems. Acetone additive was selected to enable a direct comparison. According to previous studies of mixed system [13–20], surface tension decreases monotonically with increasing additive concentrations. Similar to the normal binary systems, there was no local maximum of the surface tension in other [C$_n$mim][TFSI]-acetone systems (Fig. 3). In the [C$_n$mim][TFSI]-acetone system, the deviation of the surface tensions were suppressed within 2 mN/m. Moreover, a small alkyl chain length effect is observed in the [C$_n$mim][TFSI]-acetone mixtures. Surface tension curves (n = 3, 4, and 6) in Fig. 3 coincide with each other, particularly above 50 mol%. Considering the small deviations of the surface tensions and less alkyl chain length effect, the TFSI$^-$ anion could contribute to stabilization of the surface states in the [C$_n$mim][TFSI]-acetone system. Also, densities of the [C$_n$mim][TFSI]-acetone show a monotonic decrease depending on the acetone concentration and the alkyl chain length (Fig. S2). In the [C$_n$mim][TFSI]-acetone, differences between the surface and bulk properties are represented only in the alkyl chain length effect. The small effect of n on surface tension in TFSI$^-$-based mixtures remains unclear.

Fig. 1. Acetone concentration dependence of densities of [C$_n$mim][I]-acetone mixtures at 24 °C.