ORIGINAL CONTRIBUTION

Interfacial tension and wetting behavior of air/oil/ionic liquid systems

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Abstract We measured the interfacial tension and the density of air/*n*-hexane, *n*-decane, 1-perfluorohexane/1-hexyl-3-methyl-imidazolium hexafluorophosphate systems as a function of temperature. From the air/ionic liquid surface tension values, it was suggested that Coulombic interaction between imidazolium cations and counter anions are not so much different between the surface and bulk. The density values indicated that the decrease of surface tension by saturating organics was closely correlated to the mutual solubility between ionic liquid and organics. Interfacial tension at the oil/ionic liquid interfaces suggested that ionic liquid molecules were more ordered at the oil/ionic liquid interfaces compared to the air/ionic liquid interfaces, but the decrease of the entropy due to the interfacial orientation of ionic liquid was compensated by the increase of the entropy due to the contact of different chemical species. The initial spreading coefficients and the Hamaker constants indicated that all the oil phases spread at the air/ionic liquid interfaces spontaneously, and form the complete wetting films.

Keywords Ionic liquid · Interfacial tension · Density · Interfacial structure

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Introduction

In general, melting points of inorganic electrolytes are exceedingly higher than a room temperature due to the strong Coulomb interaction between cation and anion, e.g., 801 °C for NaCl and 755 °C for NaBr. On the contrary, melting points of organic electrolytes are usually lower compared to inorganic electrolytes, and the liquid state is sometimes realized even at a room temperature by choosing suitable combination of cationic and anionic species. Such electrolytes with a low melting point are referred to "room temperature ionic liquid" (RTIL). Ethylammonium nitrate is the first RTIL synthesized by Walden in 1914 [1]. After finding that synthesized dialkylimidazolium ionic liquid is stable even in the atmospheric environment [2, 3], RTILs have attracted a lot of attention as novel alternative solvents of the common organic solvents [4–6], materials for electrochemical cells [7, 8], triborogical materials [9, 10], and so on, because of their relatively wide electrochemical windows, negligibly low vapor pressure, etc.

Although widespread physical and chemical properties of RTILs are essential not only for fully understanding why RTILs are liquid even at low temperatures but also for proper choice of RTILs for a specific application, and actually such data have been accumulating extensively [11–15], it seems to be insufficient and often inadequate especially about surface properties. The most important aspect with respect to RTILs is of *course* that they are in the liquid state around room temperatures. Besides this, RTILs have basically amphiphilic chemical structure. Thus, RTILs are similar to liquid polyethylene glycol surfactants in these two respects and therefore a wide variety of colloid and interface science is expected by using RTILs. Interfacial tension is one of the important physicochemical characters in the colloid and interface science and it plays important roles

in several applications such as emulsification, extraction, multiphasic homogeneous catalytic reactions, and so on.

In this study, we examined interfacial properties of air/ RTIL (A/IL-0) and air/alkane-saturated RTIL (A/IL), air/ RTIL-saturated oil (A/O), and RTIL-saturated alkane/alkane-saturated RTIL (O/IL) systems and then the wetting state of air/alkane/RTIL systems. Hereafter, the abbreviations of IL-0, IL, and O will be employed in the symbols for specifying pure RTIL, those saturated with oil, and oil saturated with RTIL, respectively. The RTIL employed is 1-hexyl-3-methyl-imidazolium hexafluorophosphate (HMIM PF6) and the alkanes are *n*-hexane (C6), *n*-decane (C10), and *n*-perfluorohexane (FC6).

Experimental

n-Hexane, *n*-decane, and *n*-perfluorohexane were purchased from Aldrich Chemical Co. *n*-Hexane and *n*-decane were distilled under atmospheric and reduced pressures, respectively. *n*-Perfluorohexane was distilled after extracting water-soluble impurities by water. Their purities were confirmed by interfacial tension against water and observing no time dependence of the interfacial tension. Water was distilled three times; the second and third stages were done from dilute alkaline permanganate solution. 1-Hexyl-3-methylimidazolium hexafluorophosphate was supplied by the Nippon Synthetic Chemical Industry Co. and was used without further purification. Its water content was confirmed to be 210 ppm by Karl Fisher method.

The interfacial tension of the A/IL-0 ($\gamma^{A/IL-0}$), A/IL ($\gamma^{A/IL}$), O/IL ($\gamma^{O/IL}$), and A/O ($\gamma^{A/O}$) were measured as a function of temperature T from 288.15 to 308.15 K under atmospheric pressure by the pendant drop method based on the drop shape analysis [16]. The experimental error was about ±0.05 mN m^{-1}. For the saturated RTIL and oil systems, the mixture of oil and ionic liquid was sufficiently stirred by using magnetic rotor at given temperatures for at least 6 h to establish the mutual solubility equilibrium, and was permitted to stand for several hours to completely separate into two transparent phases.

The densities of the RTIL, oil-saturated RTIL, and RTIL-saturated oil were measured by use of Anton Paar DMA 60/ 602 vibrating-tube digital density meter at temperatures from 288.15 to 308.15 K under atmospheric pressure. Temperature was controlled within 0.01 K by circulating temperature-regulated water around the vibrating-tube cell.

Results and discussion

The surface tension $\gamma^{A/IL-0}$ (open circles) decreases gradually and almost linearly with increasing T as shown

in Fig. 1. $\gamma^{A/IL-0}$ is ca. 39 mN m^{-1} and considerably higher than that of hydrocarbon chain of HMIM cation (*n*-hexane, 18 mN m^{-1}) at 298.15 K, but rather similar to that of cation ring of HMIM (imidazole, 44 mN m^{-1}) [17]. Thus the top layer of the RTIL surface may not be fully covered by hydrocarbon chains, but the imidazolium rings may be in contact with air to some extent. Considering that usual inorganic molten salts have the surface tension values around 200 mN m^{-1} and water has 72 mN m^{-1} at 298.15 K, contribution of polar interaction to the surface tension of HMIM PF6 against the air is expected to be smaller than water. The contribution from van der Waals interaction to the surface tension γ^{VDW} is estimated from the Lifshitz theory by using the equation

$$\gamma^{VDW} \approx \frac{A_{air/liquid}}{24\pi(0.165nm)^2} \tag{1}$$

and

$$A_{air/liquid} \approx \frac{3}{4}kT\left(\frac{\varepsilon_{air} - \varepsilon_{liquid}}{\varepsilon_{air} + \varepsilon_{liquid}}\right)^2 + \frac{3h\nu_e}{16\sqrt{2}}$$
$$\times \frac{(n_{air} - n_{liquid})^2}{(n_{air} + n_{liquid})^{3/2}}, \tag{2}$$

where ε_i and n_i are the dielectric constant and the refractive index of the component i (i=air, liquid) and ν_e is the main absorption frequency in the UV and typically around 3×10^{15} s^{-1}. It is well-known that the surface tension estimated from Eq. 1 agrees well with the experimental one for almost all apolar solvents [18].

For the air/water surface, the van der Waals contribution is estimated to be about 18 mN m^{-1} by substituting n=1.33 and ε=80.1 for water and n=1 and ε=1 for air, and the residual 54 mN m^{-1} comes from the contribution of the hydrogen bonding between water molecules. The refractive index of HMIM PF6 is about 1.42 as given in [19] and the dielectric constant is presumed to be about 10 from [20]. Then the estimated van der Waals contribution of the air/ HMIM PF6 surface is about 25 mN m^{-1} and higher than that of water as expected from its amphiphile chemical structure having hydrocarbon chain. However, the polar contribution of about 14 mN m^{-1} is smaller than that of water of about 54 mN m^{-1}. This may suggest that ion pair formation takes place significantly and thus RTIL molecules are in the state as if they were nonionic chemicals in the surface layer.

Although there have been only a few structural studies on ionic liquid surfaces, it is very informative to mention them. Watson et al. [21] examined the composition of cationic and anionic species at the 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF6) surface by the direct recoil spectroscopy measurement. They concluded

Fig. 1 Interfacial tension versus temperature: (**a**) air-RTIL-FC6 system; (**b**) air-C10-RTIL system; (**c**) air-C6-RTIL system; *open circle*, A/IL-0; *filled triangle*, A/IL; *filled circle*, O/IL; *open square*, A/O

that there are equal amounts of cationic and anionic species at the surface and the average orientation of the cation ring is normal to the surface. The former finding implies the ion pair formation even at the surface and may support our view that the Coulombic contribution to the surface tension is rather small although RTIL is an electrolyte. Deutsch et al. [22] examined the surface structure of BMIM PF6 surface by the X-ray reflectivity measurement and suggested that the electron density at the surface is ~18% higher than that of the bulk. Iimori et al. [23] suggested that the average orientation of hydrocarbon chain is normal to the surface by the sum-frequency generation measurement. Thus, the structure at molecular level is still controvertible.

It is seen in Fig. 1 that the $\gamma^{A/IL-0}$ (open circles) are lowered to $\gamma^{A/IL}$ (filled triangles) by dissolving oils to the order of FC6>C10>C6. This lowering is mainly attributable to two factors, i.e., the solubility of oil into RTIL because the oils have much lower surface tension compared to $\gamma^{A/IL-0}$ and the surface activity of the dissolved oil at the A/IL surface. To examine this point, the densities ρ^{IL} of the oil-saturated RTIL phases employed in the calculation of surface tension are available and shown as a function of T in Fig. 2. The $\rho^{IL}-\rho^{IL-0}$ is about $-2\sim-3\times10^{-4}$, $3\sim5\times10^{-3}$, and $1.3\sim1.7\times10^{-2}$ g cm^{-3} for FC6, C10, and C6, respectively; the solubility of FC6 molecules is very much smaller and that of hydrocarbons is larger for the shorter chain. Assuming the ideal mixing of RTIL and oils from the viewpoint of volume, the mole fraction of oils in the RTIL phases was calculated from the density values of ρ^{IL-0} and ρ^{O-0} as about $\sim7\times10^{-4}$, $4\sim6\times10^{-3}$, and $1.4\sim1.6\times10^{-2}$ for
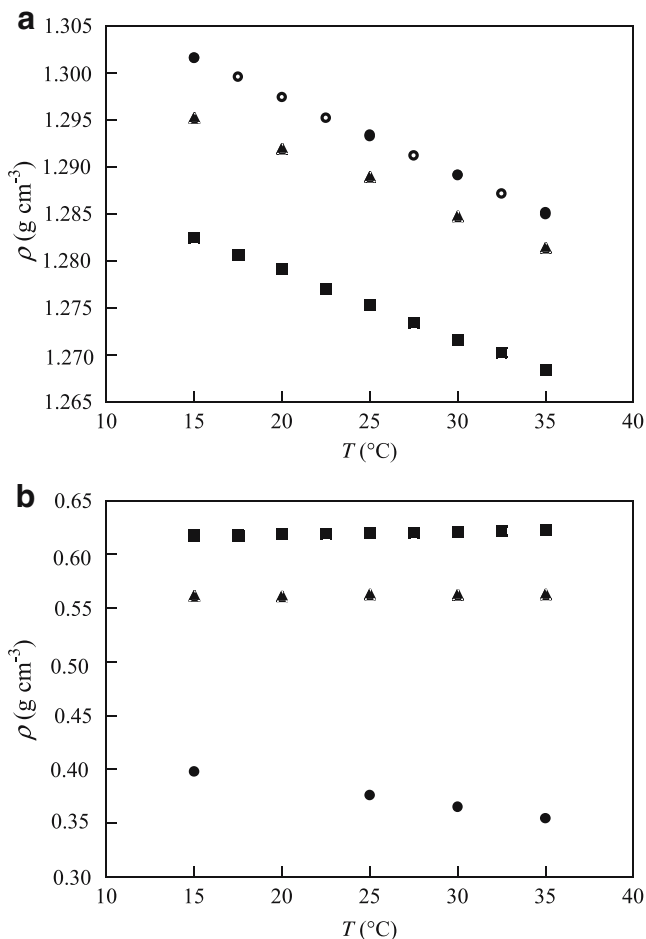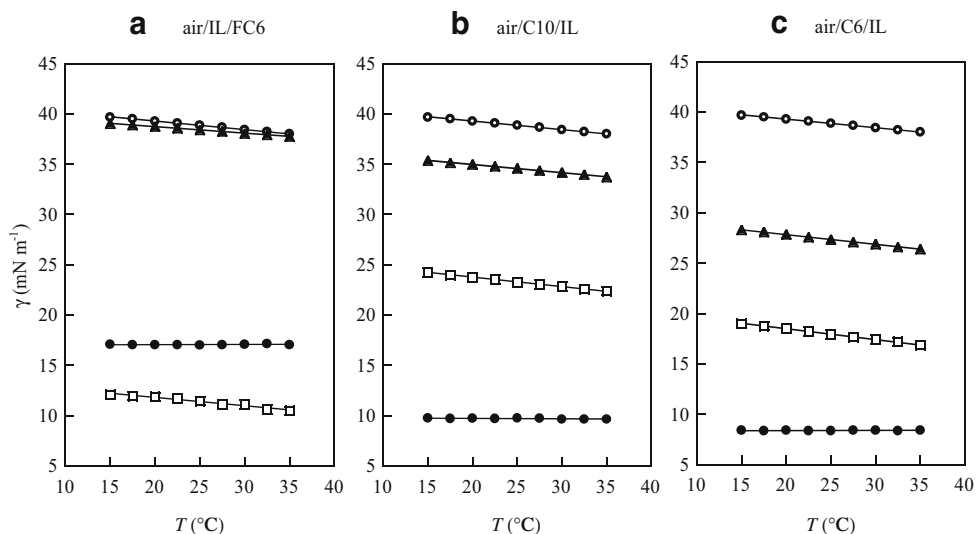

Fig. 2 (**a**) Density of pure RTIL and oil-saturated RTIL: *open circle*, pure RTIL; *filled circle*, FC6-saturated RTIL; *filled triangle*, C10-saturated RTIL; *filled square*, C6-saturated RTIL; (**b**) density difference between oil-saturated RTIL and RTIL-saturated oil: *filled circle*, $\rho^{FC6}-\rho^{IL}$; *filled triangle*, $\rho^{IL}-\rho^{C10}$; *filled square*, $\rho^{IL}-\rho^{C6}$

Table 1 Interaction parameters at 298.15 K

	Hexane	Decane	Perfluorohexane
Φ (oil/IL)	0.92	0.87	0.79
Φ (oil/water)	0.55	0.53	0.47

Table 2 Interfacial tension and interfacial excess entropy at 298.15 K

	Hexane		Decane		Perflourohexane	
	$-(\partial\gamma/\partial T)$	γ at 298.15 K	$-(\partial\gamma/\partial T)$	γ at 298.15 K	$-(\partial\gamma/\partial T)$	γ at 298.15 K
O/IL	0	8.36	0	9.76	0	17.04
A/O	0.106	17.91	0.093	23.29	0.083	11.46
A/O-0	0.102	17.89	0.092	23.37	0.094	11.44
A/IL	0.096	27.33	0.081	34.60	0.064	38.41
O/IL-0	0.084	38.90	0.084	38.90	0.084	38.90

FC6, C10, and C6, respectively. Thus, the decrease of $\gamma^{A/IL}$ from $\gamma^{A/IL-0}$ is in parallel relation to the decrease in the solubility of the organics into the RTIL phase.

It should be mentioned with respect to the surface activity of the oils that, as $\gamma^{A/IL}$ is much higher than the corresponding $\gamma^{A/O-0}$ of the respective oils given in Table 1, it may be said that the mole fraction of oils at the air/RTIL surface is not so large. $\rho^O - \rho^{O-0}$ is the order of 10^{-4} g cm^{-3} and $\gamma^{A/O}$ is almost the same as $\gamma^{A/O-0}$ within the experimental error for the C10 and C6 system. For the FC6 system, $\rho^O - \rho^{O-0}$ is the order of 1.5×10^{-2} g cm^{-3}, the mole fraction of RTIL in the FC6 is about $2.5 \sim 4.2 \times 10^{-2}$, but $\gamma^{A/O}$ has almost the same value as $\gamma^{A/O-0}$.

The O/IL interfacial tension $\gamma^{O/IL}$ (filled circles) is plotted against T in Fig. 1. The $\gamma^{O/IL}$ values are considerably small compared with $\gamma^{A/IL}$ but in the same order of C6 <C10<FC6 as $\gamma^{A/IL}$. According to the theoretical consid-
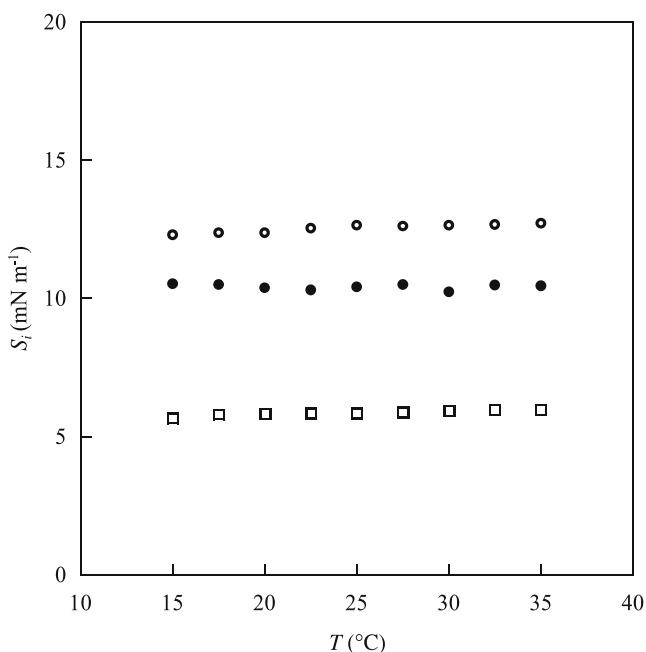

Fig. 3 Initial spreading coefficient versus temperature: *open circle*, C6; *filled circle*, C10.; *open square*, FC6

eration of the interfacial tension based on the combining relation of the interaction by van Oss [24], interfacial tension $\gamma^{\alpha/\beta}$ is expressed in terms of surface tension $\gamma^{air/\alpha}$ and $\gamma^{air/\beta}$ as

$$\gamma^{\alpha/\beta} = \gamma^{air/\alpha} + \gamma^{air/\beta} - 2\Phi\sqrt{\gamma^{air/\alpha}\gamma^{air/\beta}}, \quad (3)$$

where Φ is the interaction parameter that is closely correlated to the contribution from polar interaction to the interfacial tension; Φ is smaller than, equal to, and larger than unity for apolar/polar, apolar/apolar, and polar/polar interfaces, respectively. The Φ values at 298.15 K are summarized in Table 1. It should be noted that, although the Φ values are smaller than unity, they are higher than that of the corresponding oil/water interfaces as shown in Table 1, e.g., Φ(C6)=0.55, Φ(C10)=0.53, Φ(FC6)=0.47, respectively.

Therefore, it is said that the polar contribution to the interfacial tension of oil/HMIM PF6 systems is much smaller than that of the corresponding oil/water interfaces. This finding is in accord with the suggestion from the surface tension $\gamma^{A/IL-0}$ and the direct recoil spectroscopy measurement that ion pairs are formed even at the surface. Spectroscopic or optical methods are expected to provide structure information as for the A/IL interface, which are much more difficult for the O/IL interfaces, and there is no one as far as we aware.

It has been shown that the interfacial tension vs temperature curve gives the interfacial excess entropy per unit surface area S^H [25] as

$$-(\partial\gamma/\partial T)_p = S^H \equiv \sum_i \sum_\alpha \Gamma_i^I (s_i^I - s_i^\alpha). \quad (4)$$

Here Γ_i^I is the interfacial excess density and s_i is the partial molar entropy of component i; the superscripts I and α show that the quantities are inherent in the interfacial region and the bulk phase where the component i is dissolved, respectively. The S^H values are given in Table 2. It is seen that $S^H > 0$ for the A/IL-0, A/IL, A/O interfaces. These results suggest, from Eq. 4, that the contact of RTIL and oil with air at the surface increases the entropy

compared to when they are in the respective bulk phases. This is usual for an interface at which molecules are not highly oriented [26]. On the other hand, $S^H \approx 0$ for the O/IL interfaces. Judging from that, although the mutual solubilities of the oils and RTIL are small and the $\gamma^{O/IL}$ values are low, it is suggested that amphiphilic RTIL molecules are rather surface-active compared to the A/IL interfaces, and their hydrocarbon chains are protruded into the oil phases.

This lowers the entropies of RTIL molecules at the O/IL interfaces. Thus, $S^H \approx 0$ indicates that the entropy decrease due to the interfacial orientation of RTIL molecules is compensated by a usual entropy increase, such as S^H of the A/IL-0, A/IL, A/O interfaces, due to the contact of different chemical species at interfaces.

Now let us examine the wetting behavior of the A/IL surface by the oil phase. The wetting state is characterized by the initial spreading coefficient S_i of an oil droplet, which corresponds to the free energy change per unit area accompanied by its spreading to the oil film at the A/IL interface, defined as

$$S_i = \gamma^{A/IL-0} - \left(\gamma^{A/O} + \gamma^{A/IL}\right). \tag{5}$$

Thus, for the positive S_i, the oil droplet spreads with the decreasing free energy of the system. The initial spreading coefficients calculated from the interfacial tensions given in Fig. 1 are positive as shown in Fig. 3. As shown in [27] and our previous papers [28, 29], the Hamaker constant of the air/oil/IL system, which is indicative of the van der Waals interaction between A/O and O/IL interfaces, provides information on whether the final state is a complete wetting or a pseudo-wetting.

The Hamaker constants for the A/O/IL system $A_{A/O/IL}$ is evaluated from the Lifshitz theory[14] by using the refractive indices n and dielectric coefficients ε of the air, oil, and RTIL phases by substituting these constants into

$$A_{A/O/IL} \approx \frac{3}{4}kT\frac{(\varepsilon_A-\varepsilon_O)(\varepsilon_{IL}-\varepsilon_O)}{(\varepsilon_A-\varepsilon_O)(\varepsilon_{IL}-\varepsilon_O)} + \frac{3h\nu_e}{8\sqrt{2}}\frac{\left(n_A^2-n_O^2\right)\left(n_{IL}^2-n_O^2\right)}{\left(n_A^2+n_O^2\right)^{1/2}\left(n_{IL}^2+n_O^2\right)^{1/2}\left[\left(n_A^2+n_O^2\right)^{1/2}+\left(n_{IL}^2+n_O^2\right)^{1/2}\right]} \tag{6}$$

where the ν_e is the main absorption frequency in the UV typically around 3×10^{15} s^{-1} and we used $n_{air}=1,\varepsilon_{air}=1$, $n_{hexane}=1.37,\varepsilon_{hexane}=1.88$, $n_{decane}=1.41,\varepsilon_{decane}=1.99$ and $n_{perfluorohexane}=1.25$, and $\varepsilon_{perfluorohexane}=1.57$, respectively. The resulting Hamaker constants are 5.9×10^{-21}, 1.8×10^{-21}, 1.3×10^{-20} for hexane, decane, perfluorohexane systems and thus the van der Waals interaction between A/O and O/ IL interfaces is repulsive for all oil phases. The combination of the positive initial spreading coefficient and repulsive van der Waals interaction leads to all the oil phases spreading at the A/IL interface spontaneously, and form the complete wetting films. Taking accont of $\gamma^{A/IL}>\gamma^{A/O}$ and the positive initial spreading coefficients for the FC6

system, the oil phase that has a larger density than the RTIL phase spreads and makes a film at the RTIL/air interface, that is, the oil phase intrudes at the RTIL/air interface.

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