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Determination of the Activity of 1-Methyl-3-octylimidazolium Bis(trifluoromethanesulfonyl)amide in Binary Ionic Liquids from the Solubility in Water[†]

Yuko Hirohata, Naoya Nishi, and Takashi Kakiuchi*

Department of Energy and Hydrocarbon Chemistry, Kyoto University, Kyoto 615-8510, Japan

For the binary ionic liquid (IL)−water (W) two-phase systems formed by the ILs 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)amide ($[C_8mim^+][C_1C_1N^-]$) and tetrahexylammonium bis(trifluoromethanesulfonyl)amide, which have a common anion, the activities of $[C_8mim^+][C_1C_1N^-]$ in the water-saturated binary IL phase have been determined from the solubility of C_8mim^+ in the W phase at different mole fractions of the IL ($x^{IL}_{C_8mimC_1C_1N}$) at five different temperatures between (278 and 328) K. The variation of the activity coefficients of $[C_8mim^+][C_1C_1N^-]$ in the IL phase with $x^{IL}_{C_8mimC_1C_1N}$ is by and large in harmony with the regular solution model. However, small but systematic deviations from the model have been discerned and are likely to result from the phase transition of the binary ILs at $x^{IL}_{C_8mimC_1C_1N} \approx 0.3$, which causes changes in the microheterogeneity in the assemblies of the IL-constituent ions. The standard Gibbs energy for transfer of $[C_8mim^+][C_1C_1N^-]$ from the water-saturated IL to W ($\Delta_{tr}G^{\ominus,IL\rightarrow W}_{m,C_8mimC_1C_1N}$), which was evaluated from the temperature dependence of the solubility, is 30−34 $kJ\cdot mol^{-1}$ over the temperature range studied. The standard enthalpy for transfer of $[C_8mim^+][C_1C_1N^-]$ from IL to W is positive and increases linearly from 4 $kJ\cdot mol^{-1}$ at 283 K to 24 $kJ\cdot mol^{-1}$ at 318 K.

1. Introduction

One of the strong advantages of ionic liquids (ILs) as fluid and conducting materials is that their physical properties can be tuned by choosing the proper cations and anions.[1,2] This tunability can be further expanded by introducing binary or ternary IL mixtures, for which the number of available ILs is innumerable. Binary ILs have been applied to solar cells,[3−14] gas chromatography,[15] organic reactions,[16] inorganic reactions,[17−20] and enzymatic reactions.[21,22]

When an IL consists of hydrophobic cations and anions, the IL is immiscible with water (W) and forms an IL−W two-phase system. Such an IL−W two-phase system is one of the most promising systems for liquid−liquid extraction and electroanalytical applications of ILs.[23,24]

However, the number of reports on the thermodynamic properties of binary ILs is limited to a few.[25−29] In the present study, the activities of the salt that constitutes the binary IL phase saturated with water were determined from the solubility of the salt in W in a binary IL−W two-phase system. The IL phase is a pseudobinary phase because it is saturated with water. The binary IL−W two-phase system we used consists of a common anionic species, bis(trifluoromethanesulfonyl)amide ($C_1C_1N^-$), and two cationic species, 1-methyl-3-octylimidazolium (C_8mim^+) and tetrahexylammonium (THA^+). The activity of $[C_8mim^+][C_1C_1N^-]$ in the IL phase was determined from the solubility of C_8mim^+ in W at different mole fractions of $[C_8mim^+][C_1C_1N^-]$ in the IL at five different temperatures between (278 and 328) K.

2. Experimental Section

2.1. Materials. 1-Methylimidazole (> 98 %) and 1-chlorooctane (> 99 %) were obtained from Wako Pure Chemical Industries, Ltd., and Tokyo Chemical Industry Co., Ltd. (TCI), respectively. Tetrahexylammonium bromide (THABr, > 98 %) and an aqueous solution (0.7 mass fraction) of the acid form of bis(trifluoromethanesulfonyl)amide (HC_1C_1N, > 99 %) were obtained from TCI and Central Glass Co., Ltd., respectively. Other chemicals were of reagent grade. All of these reagents were used without further purification. Water was distilled and deionized using a Milli-Q water system (Millipore).

1-Methyl-3-octylimidazolium chloride ($[C_8mim^+][Cl^-]$) was synthesized according to the method of Gordon et al.[30] by mixing 1-methylimidazole and 1-chlorooctane at 70 °C for 47 h. The crude $[C_8mim^+][Cl^-]$, a yellowish and viscous liquid, was washed with ethyl acetate under reflux four times, after which volatile trace impurities were removed with a vacuum pump. The product was identified using ^1H NMR analysis.

To prepare $[C_8mim^+][C_1C_1N^-]$, equimolar amounts of $[C_8mim^+][Cl^-]$ and an aqueous solution of HC_1C_1N were mixed in methanol. Methanol was then removed with an evaporator, and HCl was extracted in W from the remaining liquid (a mixture of $[C_8mim^+][C_1C_1N^-]$ and HCl) using a dichloromethane−water two-phase system. The washing was repeated more than 10 times, until Cl^- was not detected when a few drops of a $AgNO_3$ solution were added to the supernatant solution. The $[C_8mim^+][C_1C_1N^-]$ obtained was dried under vacuum.

To prepare $[THA^+][C_1C_1N^-]$, equimolar amounts of THABr and HC_1C_1N as an aqueous solution were mixed in methanol. The washing procedure was the same as that described above for $[C_8mim^+][C_1C_1N^-]$. The purified $[THA^+][C_1C_1N^-]$ was a colorless liquid with high viscosity.

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* Corresponding author. Tel: +81-75-383-2489. Fax: +81-75-383-2490. E-mail: kakiuchi@scl.kyoto-u.ac.jp.

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2.2. Preparation of Binary ILs. Before binary ILs were prepared, [C_8mim^+][$C_1C_1N^-$] and [THA^+][$C_1C_1N^-$] were dried under vacuum. The mass fraction of the water content in the ILs was typically lower than 0.0001. Binary ILs were prepared by mixing [C_8mim^+][$C_1C_1N^-$] and [THA^+][$C_1C_1N^-$] gravimetrically at different mole fractions of [C_8mim^+][$C_1C_1N^-$], $x^{IL}_{C_8mimC_1C_1N}$, namely, 1.0, 0.95, 0.90, 0.85, 0.70, 0.50, 0.30, 0.20, 0.15, 0.10, and 0.05. Water was added to each binary IL to form an IL−W two-phase system in a 50 mL vial. After the mixtures were stirred overnight with a stirrer at ambient temperature, the vials were put into a temperature-controlled bath (± 0.1 °C). The concentration of C_8mim^+ was measured at least 1 day after the bath temperature was set at a specific value.

2.3. Mutual Solubility Measurements. The solubility of [C_8mim^+][$C_1C_1N^-$] in the W-rich phase was determined using UV spectroscopy (UV-1600PC, Shimadzu) at (278, 288, 298, 308, and 328) K ± 0.1 K at atmospheric pressure, making use of the absorption maximum at 211 nm due to the imidazolium ring of C_8mim^+.[31] The cell for UV measurements was 10 mm × 2 mm × 45 mm (2 mm light path). When the temperature for the partitioning experiments was 298 K or higher, the temperature for the UV spectroscopy measurements was kept at the partition equilibration temperature by circulating water into the cell holder to avoid the formation of small droplets of [C_8mim^+][$C_1C_1N^-$] in W during the UV measurement. When the equilibration temperature was below 298 K, the UV measurements were performed at ambient temperature. Triplicate measurements were made for each sample.

The molar extinction coefficient of C_8mim^+ in W was determined using aqueous solutions with [C_8mim^+][Cl^-] concentrations of (2.44, 1.22, and 0.30) $mmol \cdot dm^{-3}$ at 298, 308, and 328 K. The mass fraction of the water content of [C_8mim^+][Cl^-] employed was 0.0036, as determined with a Karl Fischer (KF) coulometer. The absorbance was found to be independent of temperature, and the molar extinction coefficient, ε, was determined to be $4.20 \cdot 10^2\ m^2 \cdot mol^{-1}$. Anthony et al.[31] reported $4.19 \cdot 10^2$ and $4.17 \cdot 10^2\ m^2 \cdot mol^{-1}$ for [C_8mim^+][PF_6^-] and [C_8mim^+][BF_4^-], respectively, which are close to our result. The solubility of water in the IL-rich phase was determined by the KF method.

3. Theory

3.1. Distribution Equilibrium of Ions Constituting a Binary IL between IL and W. Suppose that a binary IL consisting of two cationic species, C_1^+ and C_2^+, and an anionic species, A^-, is in contact with water. The ionic species are partitioned between the IL and W phases. The condition of the partition equilibrium is

$$\tilde{\mu}_i^{IL} = \tilde{\mu}_i^{W} \tag{3.1}$$

for all three species, C_1^+, C_2^+, and A^-, where $\tilde{\mu}_i^{\alpha}$ is the electrochemical potential of ion i (i = C_1^+, C_2^+, or A^-) in phase α (α = IL or W).

The electrochemical potential of ion i in phase α may be written as

$$\tilde{\mu}_i^{\alpha} = \mu_i^{\ominus,\alpha} + RT \ln a_i^{\alpha} + z_i F \phi^{\alpha} \tag{3.2}$$

where $\mu_i^{\ominus,\alpha}$, a_i^{α}, z_i, and ϕ^{α} are the standard chemical potential of i, the activity of i, the charge on i in the signed unit of electronic charge, and the inner potential in α, respectively. We take the standard state of μ_i^{IL} as the IL when the mole fraction of C_1A is unity and the concentration scale of C_1^+ in the IL as the mole fraction. The standard state for μ_i^{W} is referred to infinite dilution with the molar concentration scale for all of the ions. In eq 3.2, R, T, and F, are the gas constant, the absolute temperature, and the Faraday constant, respectively.

3.2. Solubility Product of a Single-Component IL in W. In the case of a single-component IL, C_1A, composed of monovalent cation C_1^+ and monovalent anion A^-, eqs 3.1 and 3.2 give the following equilibrium conditions for the partition of C_1A between the IL and W:[32]

$$\mu_{C_1^+}^{\ominus,IL} + F\phi^{IL} = \mu_{C_1^+}^{\ominus,W} + RT \ln a_{C_1^+}^{W} + F\phi^{W} \tag{3.3}$$

$$\mu_{A^-}^{\ominus,IL} - F\phi^{IL} = \mu_{A^-}^{\ominus,W} + RT \ln a_{A^-}^{W} - F\phi^{W} \tag{3.4}$$

By adding these equations, we obtain

$$\Delta_{tr} G_{m,C_1A}^{\ominus,IL \to W} = -RT \ln K_{SP,C_1A}^{W} \tag{3.5}$$

in which $K^W_{SP,\,C_1A}$ is the solubility product of C_1A in W, that is,

$$K_{SP,C_1A}^{W} = a_{C_1^+}^{W} a_{A^-}^{W} \tag{3.6}$$

and $\Delta_{tr} G_{m,C_1A}^{\ominus,IL \to W}$ is the molar Gibbs energy for transfer of C_1A from IL to W. The latter quantity is the sum of the molar Gibbs energies for the transfers of C_1^+ and A^- from IL to W:

$$\Delta_{tr} G_{m,C_1A}^{\ominus,IL \to W} = \Delta_{tr} G_{m,C_1^+}^{\ominus,IL \to W} + \Delta_{tr} G_{m,A^-}^{\ominus,IL \to W} \tag{3.7}$$

where

$$\Delta_{tr} G_{m,i}^{\ominus,IL \to W} = \mu_i^{\ominus,W} - \mu_i^{\ominus,IL} \tag{3.8}$$

The standard enthalpy for transfer of C_1A from IL to W, $\Delta_{tr} H_{m,C_1A}^{\ominus,IL \to W}$, can be determined from the temperature dependence of the solubility product using the Gibbs−Helmholtz equation:

$$\Delta_{tr} H_{m,C_1A}^{\ominus,IL \to W} = \left[\frac{\partial}{\partial (1/T)} \left(\frac{\Delta_{tr} G_{m,C_1A}^{\ominus,IL \to W}}{T} \right) \right]_P \tag{3.9}$$

3.3. Determination of the Activity of [C_8mim^+][$C_1C_1N^-$] in the Binary IL Phase. The partition equilibrium of a binary IL and W can be treated in a way similar to that briefly described above for a single-component IL and W.[32] If the solubility product of C_1A in W when the mole fraction of C_1A in the IL is $x^{IL}_{C_1A}$ is defined as

$$K_{SP,C_1A}^{W,x^{IL}_{C_1A}} = a^{W}_{C_1^+(x^{IL}_{C_1A})} a^{W}_{A^-(x^{IL}_{C_1A})} \tag{3.10}$$

where $a^{W}_{i(x^{IL}_{C_1A})}$ ($i = C_1^+$ or A^-) is the activity of i in W at $x^{IL}_{C_1A}$, we have

$$a^{IL}_{C_1^+(x^{IL}_{C_1A})} a^{IL}_{A^-(x^{IL}_{C_1A})} = \frac{K_{SP,C_1A}^{W,x^{IL}_{C_1A}}}{K_{SP,C_1A}^{W}} \tag{3.11}$$

The solubility or the solubility product of C_1A in W is thus a measure of the activity of C_1A in the binary IL.

4. Results and Discussion

4.1. Mutual Solubility. The solubility of C_8mim^+ in the W-rich phase is listed in Table 1 and plotted in Figure 1. The error bars in Figure 1 indicate 95 % confidence intervals. The solubility of C_8mim^+ increases with $x^{IL}_{C_8mimC_1C_1N}$ and also with T. The solubility of water in the IL-rich phase also increases with $x^{IL}_{C_8mimC_1C_1N}$ (Table 2 and Figure 2), reflecting the fact that C_8mim^+ is more hydrophilic than THA^+. It is notable, however, that the water content does not appreciably change when $x^{IL}_{C_8mimC_1C_1N} < 0.2$ and increases rapidly with $x^{IL}_{C_8mimC_1C_1N}$ when $x^{IL}_{C_8mimC_1C_1N} > 0.2$ (Figure 2). This suggests that the solubility of

Table 1. Composition ($x^{\mathrm{IL}}_{\mathrm{C_8mimC_1C_1N}}$) and Temperature ($T$) Dependences of the Solubility of $\mathrm{C_8mim^+}$ in the W-Rich Phase ($c^{\mathrm{W}}_{\mathrm{C_8mim^+}}$)

	$c^{\mathrm{W}}_{\mathrm{C_8mim^+}}$/mmol·dm^{-3}				
$x^{\mathrm{IL}}_{\mathrm{C_8mimC_1C_1N}}$	$T/K = 278$	$T/K = 288$	$T/K = 298$	$T/K = 308$	$T/K = 328$
1.00	1.40	1.46	1.55	1.76	2.33
0.95	1.37	1.42	1.51	1.71	2.29
0.90	1.32	1.37	1.47	1.66	2.23
0.85	1.27	1.33	1.43	1.61	2.17
0.70	1.16	1.21	1.30	1.47	1.99
0.50	0.976	1.02	1.09	1.25	1.69
0.30	0.739	0.780	0.851	0.970	1.34
0.20	0.600	0.631	0.690	0.784	1.09
0.15	0.516	0.544	0.599	0.681	0.943
0.10	0.418	0.441	0.484	0.552	0.764
0.05	0.294	0.312	0.341	0.389	0.538

water in the binary IL remains limited when $x^{\mathrm{IL}}_{\mathrm{C_8mimC_1C_1N}}$ is small and $\mathrm{C_8mim^+}$ is dispersed in the $\mathrm{THA^+}$-rich IL phase.

Freire et al.[33] reported that the mole fraction of water in the $[\mathrm{C_8mim^+}][\mathrm{C_1C_1N^-}]$ phase at 298.15 K was 0.1868 (i.e., a value of 0.0086 for the mass fraction), which is close to our results.

4.2. Determination of the Standard Gibbs Energy and Enthalpy of the Transfer of $[\mathrm{C_8mim^+}][\mathrm{C_1C_1N^-}]$ from IL to W. The solubility of $\mathrm{C_8mim^+}$ in the W-rich phase at $x^{\mathrm{IL}}_{\mathrm{C_8mimC_1C_1N}} = 1.0$ is shown in Figure 3 as a function of temperature between (278 and 328) K. The solubility of $\mathrm{C_8mim^+}$ can be equated with the solubility of $[\mathrm{C_8mim^+}][\mathrm{C_1C_1N^-}]$ in W, because no other electrolytes are contained in W. We evaluated $\Delta_{\mathrm{tr}}G^{\ominus,\mathrm{IL}\rightarrow\mathrm{W}}_{\mathrm{m,C_8mimC_1C_1N}}$ from eq 3.5 using the Debye-Hückel limiting law for the activity coefficients of $\mathrm{C_8mim^+}$ and $\mathrm{C_1C_1N^-}$. The temperature dependence of $\Delta_{\mathrm{tr}}G^{\ominus,\mathrm{IL}\rightarrow\mathrm{W}}_{\mathrm{m,C_8mimC_1C_1N}}$ is shown in Figure 4. The values of $\Delta_{\mathrm{tr}}G^{\ominus,\mathrm{IL}\rightarrow\mathrm{W}}_{\mathrm{m,C_8mimC_1C_1N}}$ are positive, ranging from (30 to 34) kJ·mol^{-1} over the measured temperature range, and increase with temperature. The positive value of $\Delta_{\mathrm{tr}}G^{\ominus,\mathrm{IL}\rightarrow\mathrm{W}}_{\mathrm{m,C_8mimC_1C_1N}}$ corresponds to the poor solubility of $[\mathrm{C_8mim^+}][\mathrm{C_1C_1N^-}]$. Freire et al.[33] evaluated $\Delta_{\mathrm{tr}}G^{\ominus,\mathrm{IL}\rightarrow\mathrm{W}}_{\mathrm{m,C_8mimC_1C_1N}}$ at 298.15 K from the solubility using the relationship $\Delta_{\mathrm{tr}}G^{\ominus,\mathrm{IL}\rightarrow\mathrm{W}}_{\mathrm{m,C_8mimC_1C_1N}} = -RT \ln c^{\mathrm{W}}_{\mathrm{C_8mim^+}}$. Their reported value of $\Delta_{\mathrm{tr}}G^{\ominus,\mathrm{IL}\rightarrow\mathrm{W}}_{\mathrm{m,C_8mimC_1C_1N}}$ was 25.537 ± 0.002 kJ·mol^{-1}, which is considerably smaller than our result (32.3 kJ·mol^{-1} at 298 K). The value of $\Delta_{\mathrm{tr}}G^{\ominus,\mathrm{IL}\rightarrow\mathrm{W}}_{\mathrm{m,C_8mimC_1C_1N}}$ recalculated using eq 3.5 with the solubility reported by them is 31.4 kJ·mol^{-1}, which is in good agreement with our result.

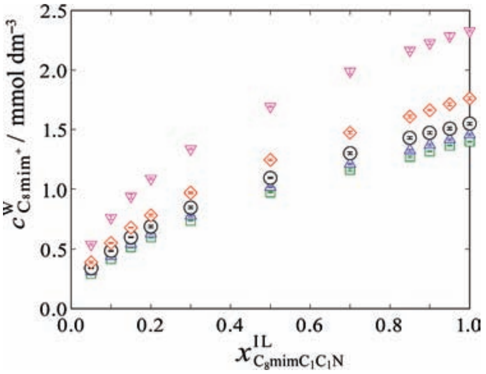

Figure 1. Composition and temperature dependences of the solubility of $\mathrm{C_8mim^+}$ in the W-rich phase. The binary IL is composed of $[\mathrm{C_8mim^+}][\mathrm{C_1C_1N^-}]$ and $[\mathrm{THA^+}][\mathrm{C_1C_1N^-}]$: ▽, 328 K; ◇, 308 K; ○, 298 K; △, 288 K; □, 278 K.

Table 2. Solubility of W in the IL-Rich Phase, Given as the Mass Fraction ($w^{\mathrm{IL}}_{\mathrm{W}}$), for Different Compositions of ($[\mathrm{C_8mim^+}] + [\mathrm{THA^+}]$)$[\mathrm{C_1C_1N^-}]$ ($x^{\mathrm{IL}}_{\mathrm{C_8mimC_1C_1N}}$) at 25 °C

$x^{\mathrm{IL}}_{\mathrm{C_8mimC_1C_1N}}$	1.00	0.95	0.90	0.85	0.70	0.50	0.30	0.20	0.15	0.10	0.05	0.0
$100\ w^{\mathrm{IL}}_{\mathrm{W}}$	0.96	0.89	0.82	0.76	0.62	0.48	0.39	0.35	0.33	0.32	0.30	0.32

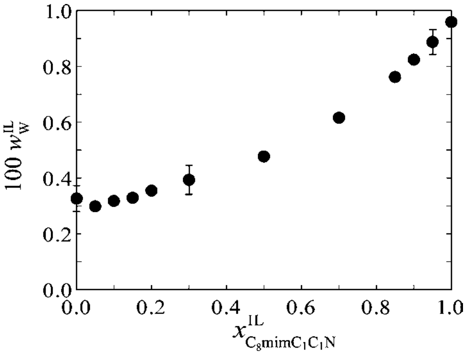

Figure 2. Composition dependence of the solubility of W in the IL-rich phase at 298 K. The binary IL is composed of $[\mathrm{C_8mim^+}][\mathrm{C_1C_1N^-}]$ and $[\mathrm{THA^+}][\mathrm{C_1C_1N^-}]$.

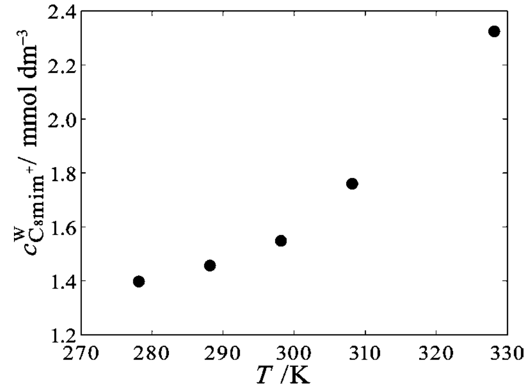

Figure 3. Temperature dependence of the solubility of $\mathrm{C_8mim^+}$ in the $[\mathrm{C_8mim^+}][\mathrm{C_1C_1N^-}]$−W two-phase system.

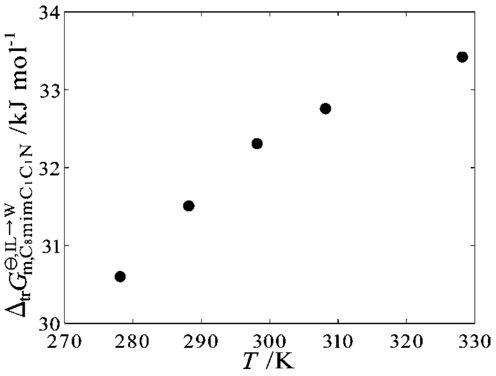

Figure 4. Temperature dependence of the standard Gibbs energy for transfer of $[\mathrm{C_8mim^+}][\mathrm{C_1C_1N^-}]$ from the $[\mathrm{C_8mim^+}][\mathrm{C_1C_1N^-}]$ phase to W.

The standard enthalpy for transfer of $[\mathrm{C_8mim^+}][\mathrm{C_1C_1N^-}]$ from IL to W, $\Delta_{\mathrm{tr}}H^{\ominus,\mathrm{IL}\rightarrow\mathrm{W}}_{\mathrm{m,C_8mimC_1C_1N}}$, was calculated from eq 3.9 and is shown as a function of T in Figure 5. $\Delta_{\mathrm{tr}}H^{\ominus,\mathrm{IL}\rightarrow\mathrm{W}}_{\mathrm{m,C_8mimC_1C_1N}}$ is positive, ranging between (4 and 24) kJ·mol^{-1} over the measured temperature range and linearly increasing with temperature. This linear dependence corresponds to the heat capacity at constant pressure of 0.53 kJ·mol^{-1} K^{-1}. The positive value of $\Delta_{\mathrm{tr}}H^{\ominus,\mathrm{IL}\rightarrow\mathrm{W}}_{\mathrm{m,C_8mimC_1C_1N}}$ indicates that the IL−IL interaction is stronger than the IL−W interaction. The standard enthalpies for transfer of imidazolium ILs have been measured calorimetrically at 298.15 K (Table 3).[34−38] It is seen that the value of $\Delta_{\mathrm{tr}}H^{\ominus,\mathrm{IL}\rightarrow\mathrm{W}}_{\mathrm{m,C_8mimC_1C_1N}}$ is comparable to those for $[\mathrm{C_2mim^+}][\mathrm{BF_4^-}]$, $[\mathrm{C_4mim^+}][\mathrm{Cl^-}]$, and $[\mathrm{C_8mim^+}][\mathrm{BF_4^-}]$, which are relatively hydrophobic ILs.

4.3. Determination of the Activity of $[\mathrm{C_8mim^+}][\mathrm{C_1C_1N^-}]$ in the IL Phase. The solubility of $[\mathrm{THA^+}][\mathrm{C_1C_1N^-}]$ in the W-rich phase at 298 K is $7\cdot10^{-6}$ mol·dm^{-3},[39] which is 2 orders

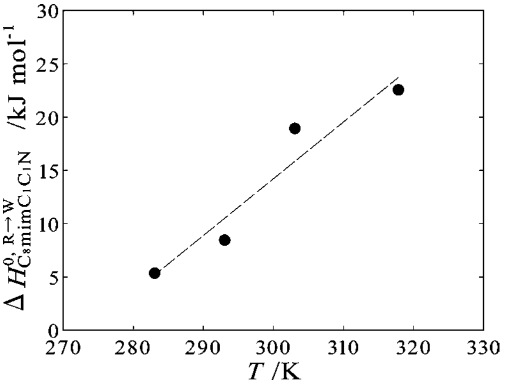

Figure 5. Temperature dependence of the standard enthalpy for transfer of [C$_8$mim$^+$][C$_1$C$_1$N$^-$] from the [C$_8$mim$^+$][C$_1$C$_1$N$^-$] phase to W.

Table 3. Standard Enthalpies for Transfer of Imidazolium ILs Measured Using a Calorimeter at 298.15 K Together with the Results of This Work

IL	$\Delta_{tr}H^{\ominus,IL\to W}_{m,C_1A}$/kJ·mol^{-1}	source
[C$_2$mim$^+$][BF$_4^-$]	13.52	ref 34
[C$_2$mim$^+$][Cl$^-$]	−8.93	ref 34
[C$_4$mim$^+$][Cl$^-$]	16.03	ref 35
[C$_4$mim$^+$][InCl$_4^-$]	−90.37	ref 35
[C$_4$mim$^+$][BF$_4^-$]	26.82 ± 0.26	ref 36
[C$_5$mim$^+$][Cl$^-$]	−17.85	ref 37
[C$_5$mim$^+$][InCl$_4^-$]	−83.06	ref 37
[C$_8$mim$^+$][BF$_4^-$]	18.97 ± 0.15	ref 38
[C$_8$mim$^+$][C$_1$C$_1$N$^-$]	13	this work

of magnitude smaller than the smallest value in this study, $3.41 \cdot 10^{-4}$ mol·dm^{-3}, which is the solubility of [C$_8$mim$^+$][C$_1$C$_1$N$^-$] at $x^{IL}_{C_8mimC_1C_1N} = 0.05$. We therefore assumed that the solubility of [THA$^+$][C$_1$C$_1$N$^-$] can be ignored (i.e., $c^{W}_{C_8mim^+} = c^{W}_{C_1C_1N^-}$, allowing us to obtain the activity of [C$_8$mim$^+$][C$_1$C$_1$N$^-$] in the IL phase from eq 3.11. The calculated activity values are shown in Figure 6 (□, 278 K; △, 288 K; ○, 298 K; ◇, 308 K; ▽, 328 K). In Figure 6, the dashed line represents the relation between the activity and the mole fraction evaluated from Raoult's law.

The activity coefficient, $\gamma^{IL}_{C_8mimC_1C_1N} = a^{IL}_{C_8mimC_1C_1N}/x^{IL}_{C_8mimC_1C_1N}$, is shown in Figure 7. The value of $\gamma^{IL}_{C_8mimC_1C_1N}$ at 298 K is slightly larger than unity and larger (smaller) than unity above (below) 298 K. The deviation of the activity coefficient from Raoult's law becomes greater as $x^{IL}_{C_8mimC_1C_1N}$ decreases, while the $\gamma^{IL}_{C_8mimC_1C_1N}$ values converge to unity as $x_{C_8mim^+} \to 1.0$; this can be explained by the regular solution model (calculated values from which are shown as dot-dashed, solid, and dotted lines in Figure 7), as described below.

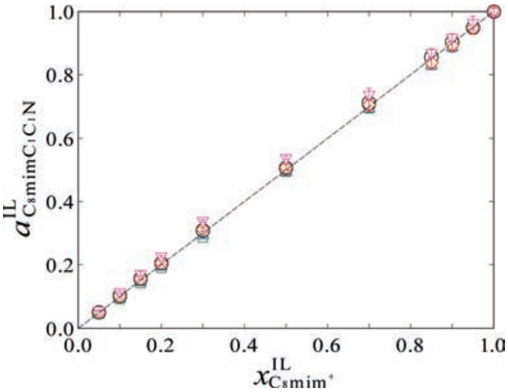

Figure 6. Activity of [C$_8$mim$^+$][C$_1$C$_1$N$^-$] in the binary IL phase: ▽, 328 K; ◇, 308 K; ○, 298 K; △, 288 K; □, 278 K. The dashed line represents the relation between activity and mole fraction evaluated from Raoult's law.

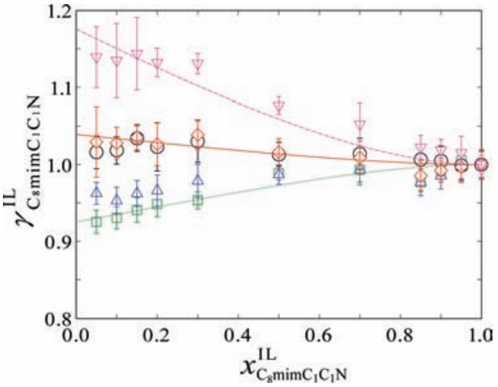

Figure 7. Activity coefficients of [C$_8$mim$^+$][C$_1$C$_1$N$^-$] in the IL phase. Lines are activity coefficients calculated using the regular solution model: ▽ and dot-dashed line, 328 K; ◇ and solid line, 308 K; ○, 298 K; △, 288 K; □ and dotted line, 278 K.

Aside from this global change, we can notice a characteristic feature, namely, that $\gamma^{IL}_{C_8mimC_1C_1N}$ does not depend appreciably or even slightly increases with $x^{IL}_{C_8mimC_1C_1N}$ in the range $0 < x^{IL}_{C_8mimC_1C_1N} < 0.3$ over the temperature range studied. This suggests that the structure of the binary IL significantly changes at $x_{C_8mim^+} \approx 0.3$. For the binary IL *N*-tetradecylisoquinolinium (C$_{14}$Iq$^+$) + tetraheptylammonium (THpA$^+$) with the common anion bis(pentafluoroethanesulfonyl)amide, we recently reported a phase transition between two different sizes of microheterogeneous domains with an increase in the mole fraction of C$_{14}$Iq$^+$ at around 0.3.[40] In view of the similarity between the combinations in that binary IL and the one used in the present study, that is, a symmetric alkylammonium cation and a asymmetric cation with a long alkyl moiety in combination with a bis(perfluoroalkanesulfonyl)amide as the common anion, it is highly likely that a structural change similar to that found in the C$_{14}$Iq$^+$ + THpA$^+$ binary IL also takes place in the present binary system. In fact, the interfacial tension data support this hypothesis, as a plot of the interfacial tension between [C$_8$mim$^+$ + THA$^+$][C$_1$C$_1$N$^-$] and an aqueous solution as a function of $x^{IL}_{C_8mimC_1C_1N}$ exhibits a break point around $x^{IL}_{C_8mimC_1C_1N} = 0.3$.[41] From the results in Figure 7, it seems that the activity of C$_8$mim$^+$ in the THA$^+$-rich phase does not vary with $x^{IL}_{C_8mimC_1C_1N}$, whereas in the C$_8$mim$^+$-rich region it varies in accordance with the prediction of the regular solution model.

4.4. Fitting the Regular Solution Model to the Results for the Activity Coefficient of [C$_8$mim$^+$][C$_1$C$_1$N$^-$]. According to the regular solution model, γ_2, the activity coefficient of component 2 in a mixture consisting of components 1 and 2 having molar volumes V_1 and V_2 and molar amounts n_1 and n_2, respectively, is given by[42,43]

$$RT \ln \gamma_2 = k_2(1 - \Phi_2)^2 \tag{4.1}$$

where k_2 is a temperature-dependent constant and Φ_2 is the volume fraction of component 2, defined by

$$\Phi_2 = \frac{n_2V_2}{n_1V_1 + n_2V_2}$$

Values of k_2 obtained by fitting the regular solution model to the activity coefficient data are given in Table 4.

The molar volumes of [THA$^+$][C$_1$C$_1$N$^-$] and [C$_8$mim$^+$][C$_1$C$_1$N$^-$] were calculated from their densities and molecular weights. With these values, the regular solution model (eq 4.1)

Table 4. Values of k_2 Obtained by Fitting the Regular Solution Model to the Activity Coefficient Data

T/K	k_2/kJ·mol^{-1}
278	−0.18
288	−0.11
298	0.07
308	0.10
328	0.44

was fitted to the activity coefficient of [C$_8$mim$^+$][C$_1$C$_1$N$^-$] as a function of $x^{\mathrm{IL}}_{\mathrm{C_8mimC_1C_1N}}$, and the results are shown as the solid, dot-dashed, and dotted lines in Figure 7. It is seen that the regular solution model can explain the global change in the experimental activity coefficient with $x^{\mathrm{IL}}_{\mathrm{C_8mimC_1C_1N}}$, though the deviations from the regular solution model are not negligible, as described above.

5. Conclusions

The change in the activity of [C$_8$mim$^+$][C$_1$C$_1$N$^-$] with $x^{\mathrm{IL}}_{\mathrm{C_8mimC_1C_1N}}$ slightly deviates from Raoult's law. The global deviation of the activity coefficient from ideality as $x^{\mathrm{IL}}_{\mathrm{C_8mimC_1C_1N}}$ changes from 0 to 1 tends to become greater as $x^{\mathrm{IL}}_{\mathrm{C_8mimC_1C_1N}}$ decreases, which can be explained by the regular solution model as a first approximation. However, a closer look at the variation of $\gamma^{\mathrm{IL}}_{\mathrm{C_8mimC_1C_1N}}$ with $x^{\mathrm{IL}}_{\mathrm{C_8mimC_1C_1N}}$ strongly suggests that the solvation environment around C$_8$mim$^+$ considerably changes at the composition $x^{\mathrm{IL}}_{\mathrm{C_8mimC_1C_1N}} \approx 0.3$, where the phase transition presumably takes place. This may be taken as an example of the observation that changes in the structure of the microheterogeneity, which seems to be a common feature of many ILs,[44−63] can affect the thermodynamic properties of binary ILs.

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