Measurement of Infinite Dilution Activity Coefficients of Alcohols, Ketones, and Aromatic Hydrocarbons in 4-Methyl-*N*-butylpyridinium Tetrafluoroborate and 1-Butyl-3-methylimidazolium Hexafluorophosphate by Gas−Liquid Chromatography

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The infinite dilution activity coefficients of C_1 to C_5 alcohols, acetone, 2-butanone, acetylacetone, toluene, and xylene isomers in 4-methyl-*N*-butylpyridinium tetrafluoroborate ([bmpy][BF_4]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) were measured by gas−liquid chromatography (GC) from (306.6 to 334.8) K and atmospheric pressure. In these measurements with GC, [bmpy][BF_4] or [bmim][PF_6] was used as a stationary phase. The infinite dilution activity coefficients in this work were not affected by the gas flow rate. It was found that the values of 1-propanol, 1-butanol, and 1-pentanol for the infinite dilution activity coefficients in [bmim][PF_6] were larger than those for their isomers. For xylene isomers, the activity coefficients of *m*-xylene are the largest. The effects of the cation and anion species composing ionic liquid on the activity coefficients were also investigated. The activity coefficients for alcohols, ketones, and aromatic hydrocarbons in the ionic liquids were affected by the anion species more strongly than the cation species of the ionic liquid. The partial molar excess enthalpies at infinite dilution for the solutes in ionic liquids were obtained from the temperature dependence of the infinite dilution activity coefficients. Moreover, the partial molar excess entropies were also calculated from the enthalpies. The excess enthalpy and entropy contributions to the activity coefficients in ionic liquid were investigated.

Introduction

Ionic liquids have been applied widely in various fields, such as reaction solvent,[1,2] heat transfer media,[3] separation solvent,[4,5] and lubricant,[6] because of some of their unique properties, such as low vapor pressures, nonflammability, and miscibility with polar or nonpolar solvents. The physical properties of ionic liquids can be controlled by combinations of cation and anion. The separation techniques using their properties were applied for extractions of metal ions,[7,8] aromatic hydrocarbons, and alcohols[9,10] and for removal of sulfur compound from gasoline.[11,12] Meindersma et al.[9] reported the extraction of aromatic hydrocarbons from aliphatic hydrocarbon mixtures including hydrocarbons where the boiling points are very close. The extraction of 1-butanol from fermentation broth was also studied by Fadeev et al.[10] In these extraction processes, it is important for process design to understand the phase equilibria for ionic liquid mixtures as fundamental knowledge. The infinite dilution activity coefficients of solutes in ionic liquid are highly useful for partition in solvent + ionic liquid systems. For the extractions from naphtha cracker[9] and fermentation both,[10] the infinite dilution activity coefficients of aromatic hydrocarbon isomers or alcohol isomers in ionic liquid are needed to optimize the operation conditions.

The experimental data of the infinite dilution activity coefficients in ionic liquid have been reported for the numerous organic compounds, alkanes,[13–21] aromatic hydrocarbons,[14,16–21] alcohols,[15,17,18,20,22–24] ketones,[18,20,23,24] esters,[18,23,25] and aldehydes.[18] Almost all these data were obtained by the gas−liquid chromatography (GC) method. In this method, ionic liquids were used as the stationary phase because of their negligible vapor pressure. Zhou et al.[23] measured the infinite dilution activity coefficients for 1-propanol, 1-butanol, and 1-pentanol isomers in [bmim][BF_4]. Using these data, the selectivities at infinite dilution between these alcohols and hexane in [bmim][BF_4] were derived. The experimental data for xylene isomers in [bmim][BF_4] were given by Zhou and Wang.[19]

The activity coefficients of solutes in ionic liquid can be affected by the cation or anion species composing the ionic liquid. In this work, the infinite dilution activity coefficients of C_1 to C_5 alcohols, acetone, 2-butanone, acetylacetone, toluene, and xylene isomers in [bmpy][BF_4] and [bmim][PF_6] were measured by the GC method. The differences of the activity coefficients for isomers of 1-propanol, 1-butanol, 1-pentanol, and xylene were discussed. The effects of the cation or anion species on the infinite dilution activity coefficients were also investigated from the experimental data in this work and the literature.[19,23] The partial molar excess enthalpies and entropies at infinite dilution in [bmpy][BF_4] and [bmim][PF_6] were obtained from the temperature dependence of the infinite dilution activity coefficients.

Experimental

Materials. The ionic liquid 4-methyl-*N*-butylpyridinium tetrafluoroborate ([bmpy][BF_4]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) were supplied from Merck Ltd. Chromosorb W/AW-DMCS (mesh 100/120) was obtained from GL Science Inc., Japan, and used as a support material for the ionic liquid in a gas chromatograph (GC) column.

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Table 1. Mass of Ionic Liquids (2) and Chromosorb (4) in the GC Column and Mass Fraction w_2

ionic liquid	m_2/g	m_4/g	100 w_2
[bmpy][BF$_4$]	1.029	3.800	0.213
[bmim][PF$_6$]	0.169	1.519	0.100

Reagent-grade chemicals, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 3-methyl-1-butanol, acetone, 2-butanone, acetylacetone, toluene, *o*-xylene, *m*-xylene, and *p*-xylene, were supplied from Wako Pure Chemical Industries Co., Ltd. The purities of methanol and ethanol were more than 99.8 % and 99.5 % by GC analysis, respectively. For 1-pentanol, 2-pentanol, 3-pentanol, and 3-methyl-1-butanol, the purities were more than 98.0 %. The purities of the other chemicals were more than 99.0 %.

Preparation of the GC Column. Chromosorb was dispersed in the ionic liquid and dichloromethane mixture. The solution was stirred for two hours at 333 K. Then, dichloromethane was removed by vacuum evaporation. The chromosorb coated with ionic liquid was introduced into a stainless steel column, 3 mm inside diameter and 0.5 m length, by using a vibrator to provide uniform packing. The amounts of ionic liquids and chromosorb are listed in Table 1.

Apparatus and Procedure. The GC method was used for the measurements of infinite dilution activity coefficients in ionic liquid. A detailed description of the apparatus and operating procedure were given in the previous work.[13] The measurements were performed by GC with a thermal conductivity detector (Shimadzu GC-14B). Helium was used as carrier gas. A soap bubble flow meter was used for the determination of the carrier gas flow rate U. In the measurements, a solute with air was injected into the GC column. The standard time was determined from the detected time for air assuming that air was a nonretentive compound. The retention time for the solute was obtained from the differences between the standard time and the detected time for solute.

The standardized retention volume V_N is given by the following equation[26]

$$V_{\mathrm{N}} = JU(t_{\mathrm{R}} - t_{\mathrm{G}})\frac{T_{\mathrm{col}}}{T_{\mathrm{f}}}\left[1 - \frac{p_{\mathrm{w}}^{\mathrm{o}}}{p_{\mathrm{out}}}\right] \qquad (1)$$

where T_{col} and T_{f} are the temperatures at the column and the carrier gas flow meter, respectively. t_{R} and t_{G} denote the retention times of solute and air. p°_{w} and p_{out} are the saturation pressure of water at T_{f} and the pressure at the column outlet in GC, equal to the atmospheric pressure. The factor of J is to correct the influence of the pressure drop through the GC column and is obtained by[26]

$$J = \frac{3}{2}\frac{(p_{\mathrm{in}}/p_{\mathrm{out}})^2 - 1}{(p_{\mathrm{in}}/p_{\mathrm{out}})^3 - 1} \qquad (2)$$

where p_{in} is the pressure at the column inlet in the GC column. The infinite dilution activity coefficient is derived from the standardized retention volume as follows[27]

$$\ln \gamma_1^{\infty} = \ln\left(\frac{n_2 R T_{\mathrm{col}}}{V_{\mathrm{N}} p_1^{\mathrm{o}}}\right) - \frac{B_{11} - V_1^{\mathrm{o}}}{R T_{\mathrm{col}}} p_1^{\mathrm{o}} + \frac{2B_{13} - V_1^{\infty}}{R T_{\mathrm{col}}} J p_{\mathrm{out}} \qquad (3)$$

where n_2 is the amount of substance for ionic liquid (subscript 2) used as the stationary phase in the GC column; R is the gas constant; and p°_1 is the vapor pressure of the solute (subscript 1). B_{11} and B_{13} denote the second virial coefficients of pure solute and that between the solute and carrier gas (subscript 3). V_1° and V_1^{∞} are the liquid volume of pure solute and the partial molar volume of solute in ionic liquid at infinite dilution. The vapor pressures of solutes are available from the literatures.[28–30] The liquid volumes of the pure solutes V_1° were estimated using the critical properties as given in the literature.[28] The partial molar volumes V_1^{∞} were assumed to be equal to V_1°. The second virial coefficients B_{11} and B_{13} were obtained from the method proposed by Tsonopoulos.[31] The experimental repeatability was the following, column pressure ± 0.2 kPa, atmospheric pressure ± 0.4 kPa, temperature ± 0.08 K, retention time ± 0.7 s, and carrier gas flow rate $\pm\ (0.01 \cdot 10^{-7})\ \mathrm{m}^3 \cdot \mathrm{s}^{-1}$. Also, the combined standard uncertainties of the infinite dilution activity coefficients in this work were 0.17 in maximum.

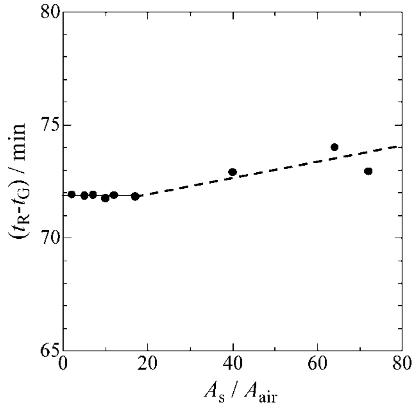

Figure 1. Effect of injected amount of solute on retention time for methanol in [bmpy][BF$_4$] at 306.6 K. A_{s}, peak area of solute; A_{air}, peak area of air; t_{R}, retention time of solute; t_{G}, retention time of air.

Results and Discussion

Infinite Dilution Activity Coefficient. Before measurement of the infinite dilution activity coefficients, the dependence of the injected amounts into the GC column for solutes on the retention time was checked. Figure 1 shows the dependence of the injected amounts on the retention time for methanol in [bmpy][BF$_4$] at 306.6 K. The retention time increase with the peak area ratio of methanol to air is described by the broken line in Figure 1, and the retention times were almost constant in the range of the peak area ratio of methanol to air smaller than 15, explained by the solid line in Figure 1. These regions of the peak area ratio of solute to air were used for all solutes of the measurements of the infinite dilution activity coefficients.

In the GC method, it is often important to give the dependence of the carrier gas flow rate on the infinite dilution activity coefficients. The measurements for all solutes were carried out in the various flow rates of carrier gas. For example, the results of the infinite dilution activity coefficients of methanol, ethanol, acetone, and 2-butanone in [bmpy][BF$_4$] at 306.6 K are shown in Figure 2, where it is seen that the activity coefficients are independent of the carrier gas flow rates investigated in this work. For the other solutes, it was confirmed that the carrier gas flow rate did not affect the infinite dilution activity coefficients.

The experimental data of the infinite dilution activity coefficients in ionic liquid were determined from the averages of those in the several carrier gas flow rates. Tables 2 and 3 show the temperature dependences of the infinite dilution activity coefficients of alcohols, ketones, and aromatic hydrocarbons in [bmpy][BF$_4$] and [bmim][PF$_6$]. The comparisons between the data for methanol, ethanol, and acetone in [bmpy][BF$_4$] in this

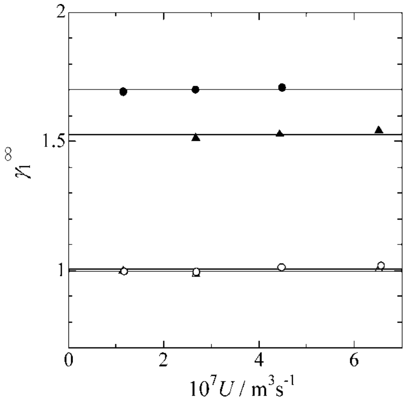

Figure 2. Dependence of carrier gas flow rate on infinite dilution activity coefficients for methanol, ethanol, acetone, and 2-butanone in [bmpy][BF$_4$] at 306.6 K. ○, methanol; ●, ethanol; △, acetone; ▲, 2-butanone. −, average value of infinite dilution activity coefficient in various gas flow rates.

Table 2. Infinite Dilution Activity Coefficients γ_1^∞ for Alcohols and Ketones in [bmpy][BF$_4$][a]

	γ_1^∞		
solute	T/K = 306.6	T/K = 315.9	T/K = 325.3
this work			
methanol	1.01 ± 0.01	0.980 ± 0.002	0.907 ± 0.005
ethanol	1.70 ± 0.005	1.62 ± 0.003	1.49 ± 0.008
acetone	0.995 ± 0.007	1.01 ± 0.006	1.03 ± 0.008
2-butanone	1.53 ± 0.01	1.57 ± 0.02	1.59 ± 0.02
literature[24,b]			
methanol	1.14	1.05	0.975
ethanol	1.85	1.71	1.57
acetone	0.905	0.910	0.914

[a] The experimental repeatability σ was obtained from the following equation. $\sigma = 1/N \sum_{i=1}^{N} |\gamma_1^\infty - \gamma_1^{\infty,(i)}|$; N, number of data points. [b] The values from the literature[24] were obtained by the interpolations of the infinite dilution activity coefficient data at (313 to 343) K.

Table 3. Infinite Dilution Activity Coefficients γ_1^∞ for Alcohols, Ketones, and Aromatic Hydrocarbons in [bmim][PF$_6$][a]

	γ_1^∞		
solute	T/K = 315.9	T/K = 325.3	T/K = 334.8
methanol	2.16 ± 0.005	1.95 ± 0.02	1.81 ± 0.02
ethanol	3.02 ± 0.008	2.69 ± 0.03	2.47 ± 0.04
1-propanol	4.01 ± 0.02	3.46 ± 0.02	3.18 ± 0.03
2-propanol	3.65 ± 0.04	3.16 ± 0.03	2.85 ± 0.03
1-butanol	5.59 ± 0.01	4.77 ± 0.05	4.24 ± 0.05
2-butanol	4.29 ± 0.01	3.78 ± 0.04	3.37 ± 0.06
2-methyl-1-propanol	5.03 ± 0.02	4.38 ± 0.04	3.84 ± 0.07
1-pentanol	9.71 ± 0.09	8.01 ± 0.08	6.47 ± 0.15
2-pentanol	5.66 ± 0.07	4.99 ± 0.08	4.38 ± 0.07
3-pentanol	4.70 ± 0.01	4.14 ± 0.04	3.78 ± 0.05
3-methyl-1-butanol	7.71 ± 0.05	6.34 ± 0.12	5.20 ± 0.10
acetone	0.707 ± 0.005	0.709 ± 0.002	0.699 ± 0.01
2-butanone	0.987 ± 0.005	0.990 ± 0.005	0.983 ± 0.01
acetylacetone	1.15 ± 0.01	1.07 ± 0.01	1.03 ± 0.01
toluene	1.71 ± 0.02	1.59 ± 0.02	1.71 ± 0.01
o-xylene	2.37 ± 0.02	2.21 ± 0.01	2.20 ± 0.02
m-xylene	2.38 ± 0.02	2.43 ± 0.04	2.36 ± 0.02
p-xylene	2.27 ± 0.01	2.24 ± 0.02	2.28 ± 0.05

[a] The experimental repeatability σ was obtained from the following equation. $\sigma = 1/N \sum_{i=1}^{N} |\gamma_1^\infty - \gamma_1^{\infty,(i)}|$; N, number of data points.

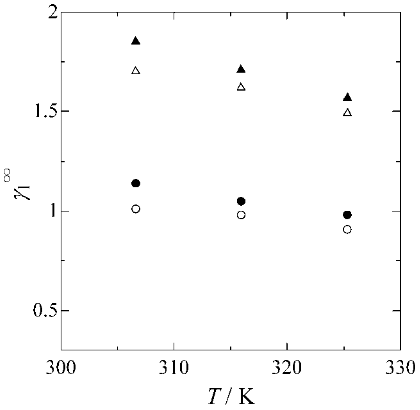

Figure 3. Temperature dependence of infinite dilution activity coefficients for alcohols in [bmpy][BF$_4$]. ○, methanol in this work; ●, methanol in the literature;[24] △, ethanol in this work; ▲, ethanol in the literature.[24]

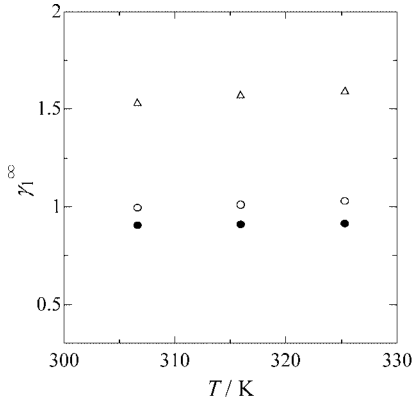

Figure 4. Temperature dependence of infinite dilution activity coefficients for ketones in [bmpy][BF$_4$]. ○, acetone in this work; ●, acetone in the literature;[24] △, 2-butanone in this work.

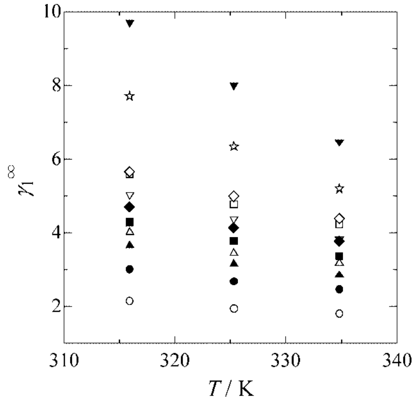

Figure 5. Temperature dependence of infinite dilution activity coefficients for alcohols in [bmim][PF$_6$]. ○, methanol; ●, ethanol; △, 1-propanol; ▲, 2-propanol; □, 1-butanol; ■, 2-butanol; ▽, 2-methyl-1-propanol; ▼, 1-pentanol; ◇, 2-pentanol; ◆, 3-pentanol; ☆, 3-methyl-1-butanol.

work and those from the literature[24] are also presented in Table 2 and Figures 3 and 4. The activity coefficients for methanol, ethanol, and acetone in [bmpy][BF$_4$] in this work are slightly larger than those from the literature.[24] The differences of the infinite dilution activity coefficients are about 0.1. As shown in Figure 3, the infinite dilution activity coefficients of methanol and ethanol in [bmpy][BF$_4$] decrease with increasing temperature, while for acetone and 2-butanone, the activity coefficients increase slightly with increasing temperature as shown in Figure 4. Figure 5 presents the results for methanol, ethanol, and isomers of 1-propanol, 1-butanol, and 1-pentanol in [bmim][PF$_6$]. The infinite dilution activity coefficients decrease with an increase in temperature. The values also increase with an increase in the carbon chain length of alcohol. The infinite dilution activity coefficients for methanol and ethanol in [bmim][PF$_6$] are larger than those in [bmpy][BF$_4$] as described from the comparisons in Figures 3 and 5. For isomers of propanol, butanol, and pentanol, 1-alcohols show the largest

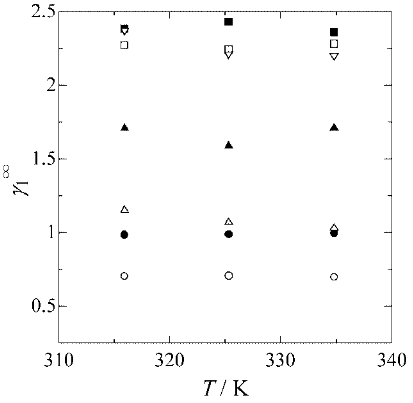

Figure 6. Temperature dependence of infinite dilution activity coefficients for ketones and aromatic hydrocarbons in [bmim][PF_6]. ○, acetone; ●, 2-butanone; △, acetylacetone; ▲, toluene; ▽, *o*-xylene; ■, *m*-xylene; □, *p*-xylene.

Table 4. Infinite Dilution Activity Coefficient Ratios in [bmpy][BF_4] (A) and [bmim][PF_6] (B) to Those in [bmim][BF_4] (C) at 315.9 K[a]

solute	$\gamma_{1,A}^\infty/\gamma_{1,C}^\infty$	$\gamma_{1,B}^\infty/\gamma_{1,C}^\infty$
methanol	1.39	3.05
ethanol	1.17	2.18
1-propanol		1.66
2-propanol		1.68
1-butanol		1.55
2-butanol		1.27
2-methyl-1-propanol		1.42
1-pentanol		1.67
3-methyl-1-butanol		1.37
acetone	0.85	0.59
toluene		0.58
o-xylene		0.57
m-xylene		0.45
p-xylene		0.44

[a] The values of infinite dilution activity coefficients in [bmim][BF_4] were obtained by interpolation of the literature data.[19,23]

values of the infinite dilution activity coefficients in [bmim][PF_6]. For butanol or pentanol isomers, the lowest values are in the case of 2-butanol or 3-pentanol. These differences arise from the polarities whose values become large due to the middle position of the hydroxy group in the carbon chain. For ketones and aromatic hydrocarbons in [bmim][PF_6], the results are shown in Figure 6. The infinite dilution activity coefficients for ketones in [bmim][PF_6] decrease slightly with temperature unlike those in [bmpy][BF_4] described above. The values for ketones increase with the number of methyl groups of the molecule. The infinite dilution activity coefficients for acetone and 2-butanone in [bmim][PF_6] are smaller than those in [bmpy][BF_4]. The activity coefficients of xylene isomers are larger than those of toluene because of the lower polarities for xylene isomers with more methyl groups. For xylene isomers, the activity coefficients of *m*-xylene are the largest among them.

The infinite dilution activity coefficients for alcohols, acetone, and aromatic hydrocarbons in [bmpy][BF_4] and [bmim][PF_6] in this work were compared with those in [bmim][BF_4] from the literature data.[19,23] These comparisons are useful to understand the effect of cation or anion species in ionic liquids on the infinite dilution activity coefficients. Table 4 lists the ratio of the infinite dilution activity coefficients in [bmpy][BF_4] and [bmim][PF_6] to those in [bmim][BF_4] at 315.9 K. The infinite dilution activity coefficients for alcohols in [bmpy][BF_4] and [bmim][PF_6] are larger than those in [bmim][BF_4], while those for ketones and aromatic hydrocarbons are smaller. For alcohols, the ratios in the case of [bmim][PF_6] are larger than those of [bmpy][BF_4]. The values for ketones in the case of [bmim][PF_6] are smaller than those of [bmpy][BF_4]. These comparisons can explain that the anion species affect the infinite dilution activity coefficients in ionic liquid more strongly than cation species. Moreover, the values of the ratio for alcohols decrease with the increase of the carbon chain length of alcohol molecules.

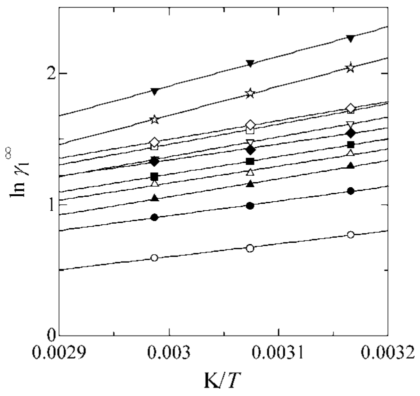

Figure 7. Relationship between ln γ_1^∞ and $1/T$ for alcohols in [bmim][PF_6]. ○, methanol; ●, ethanol; △, 1-propanol; ▲, 2-propanol; □, 1-butanol; ■, 2-butanol; ▽, 2-methyl-1-propanol; ▼, 1-pentanol; ◇, 2-pentanol; ◆, 3-pentanol; ☆, 3-methyl-1-butanol.

Partial Molar Excess Enthalpies at Infinite Dilution. The partial molar excess enthalpy at infinite dilution $H_1^{E,\infty}$ is defined by the following equation

$$H_1^{E,\infty} = H_1^{\infty} - H_1^{o,L} \tag{4}$$

where H_1^{∞} and $H_1^{o,L}$ denote the partial molar enthalpy of the solute in mixture at infinite dilution and the enthalpy of pure liquid solute, respectively. The partial molar excess enthalpy at infinite dilution $H_1^{E,\infty}$ can be also calculated from the Gibbs−Helmholtz equation as follows[32]

$$\left(\frac{\partial \ln \gamma_1^{\infty}}{\partial(1/T)}\right) = \frac{H_1^{E,\infty}}{R} \tag{5}$$

Assuming $H_1^{E,\infty}$ is a constant, the relationship between γ_1^∞ and $H_1^{E,\infty}$ can be obtained from the integration for eq 5

$$\ln \gamma_1^{\infty} = \frac{H_1^{E,\infty}}{RT} + C \tag{6}$$

where C is the integral constant. The values of $H_1^{E,\infty}$ can be calculated from the slope of the relationship between the infinite dilution activity coefficient and the temperature. Figure 7 shows the relationship between ln γ_1^∞ and $1/T$ for alcohols in [bmim][PF_6]. The slopes $H_1^{E,\infty}/R$ of these relationships were determined by the linear regressions. Table 5 lists the values of $H_1^{E,\infty}$ for alcohols, ketones, and aromatic hydrocarbons in [bmpy][BF_4] and [bmim][PF_6]. The values of $H_1^{E,\infty}$ for alcohols in [bmpy][BF_4] and alcohols, acetone, acetylacetone, toluene, *o*-, and *m*-xylenes in [bmim][PF_6] are positive. For 1-alcohols in [bmim][PF_6], $H_1^{E,\infty}$ values increase with the carbon chain length of alcohol molecules. The values of 1-butanol and 1-pentanol in [bmim][PF_6] are the largest among their isomers, and 2-butanol and 3-pentanol show the smallest values. For acetone and 2-butanone in [bmpy][BF_4] and 2-butanone, *p*-xylene in [bmim][PF_6], the values of $H_1^{E,\infty}$ are negative. The negative values of the partial excess enthalpies mean that the interactions of the solute−ionic liquid pairs are larger than those of solute−solute pairs. It is considered that the high polarity of the oxygen atom for acetone and 2-butanone increases the strength of the ion-induced interactions with the ionic liquid as

Table 5. Partial Molar Excess Enthalpies and Entropies of Alcohols, Ketones, and Aromatic Hydrocarbons at Infinite Dilution in [bmpy][BF$_4$] and [bmim][PF$_6$]

solute in [bmpy][BF$_4$]	$H_1^{E,\infty}$/(kJ·mol^{-1})	$TS_1^{E,\infty}$/(kJ·mol^{-1})*
methanol	4.75	4.80
ethanol	5.83	4.57
acetone	−1.53	−1.56
2-butanone	−1.71	−2.89

solute in [bmim][PF$_6$]	$H_1^{E,\infty}$/(kJ·mol^{-1})	$TS_1^{E,\infty}$/(kJ·mol^{-1})*
methanol	8.23	6.21
ethanol	9.36	6.46
1-propanol	10.81	7.16
2-propanol	11.52	8.12
1-butanol	12.87	8.35
2-butanol	11.23	7.41
2-methyl-1-propanol	12.56	8.32
1-pentanol	18.88	12.91
2-pentanol	11.92	7.37
3-pentanol	10.15	6.08
3-methyl-1-butanol	18.32	12.96
acetone	0.52	1.43
2-butanone	−0.51	−0.48
acetylacetone	5.14	4.77
toluene	0.05	−1.36
o-xylene	3.49	1.22
m-xylene	0.37	−1.90
p-xylene	−0.19	−2.35

* $TS_1^{E,\infty}$ was calculated at 315.9 K.

explained by Heintz et al.[24] Although the partial excess enthalpies for acetone and acetylacetone in [bmim][PF$_6$] are positive, the values are much lower than those for alcohols with the same carbon number due to the high interactions with the ionic liquids.

The excess chemical potentials of the solute in ionic liquid at infinite dilution are obtained from the partial molar excess enthalpy $H_1^{E,\infty}$ and entropy $S_1^{E,\infty}$ at infinite dilution as follows

$$\mu_1^{E,\infty} = RT \ln \gamma_1^{\infty} = H_1^{E,\infty} - TS_1^{E,\infty} \tag{7}$$

Using the relationship between the activity coefficient and the chemical potential, the partial molar excess entropy $S_1^{E,\infty}$ can be calculated from the activity coefficient and the partial excess enthalpy of the solute at infinite dilution given by the following

$$TS_1^{E,\infty} = H_1^{E,\infty} - RT \ln \gamma_1^{\infty} \tag{8}$$

The partial molar excess entropies at infinite dilution of the solutes in ionic liquids at 315.9 K are also listed in Table 5. For ketones and aromatic hydrocarbons in [bmpy][BF$_4$] and [bmim][PF$_6$], the values of entropies are much lower than those for alcohols. These results arise from the fact that the randomness of solution structures for ionic liquid + ketones or aromatic hydrocarbon mixtures is highly small due to their strong interactions. The values for acetone in [bmpy][BF$_4$] are negative, while those in [bmim][PF$_6$] are positive. This means that the nonrandomness in [bmpy][BF$_4$] is larger than that in [bmim][PF$_6$]. The entropies of alcohols in [bmim][PF$_6$] increase with the carbon chain length of alcohol molecules. For methanol and ethanol in [bmpy][BF$_4$], the values of enthalpies and entropies are lower than those in [bmim][PF$_6$].

Conclusion

The gas−liquid chromatographic method was used for the measurements of the activity coefficients at infinite dilution for alcohols, ketones, and aromatic hydrocarbons in [bmpy][BF$_4$] and [bmim][PF$_6$]. The infinite dilution activity coefficients are independent of the flow rate of the carrier gas investigated in this work. For alcohols in [bmpy][BF$_4$] and alcohols, ketones, and aromatic hydrocarbons in [bmim][PF$_6$], the infinite dilution activity coefficients decrease with the temperature increase. The activity coefficients for ketones in [bmpy][BF$_4$] increase with temperature. For isomers of propanol, butanol, and pentanol in [bmim][PF$_6$], the lowest values of the activity coefficients were observed for the isomer in which the hydroxy group was at the middle of the carbon chain. The values for *m*-xylene in [bmim][PF$_6$] are larger than those for the other isomers. The effects of the cation and anion of an ionic liquid on the activity coefficients for solutes were discussed. The infinite dilution activity coefficients for solutes in ionic liquids interested in this work were affected by the anion species of the ionic liquid more strongly than the cation species. The partial molar excess enthalpies and entropies at infinite dilution for solutes in ionic liquid were obtained from the temperature dependences of the infinite dilution activity coefficient data. The entropies for the solutes are larger with larger enthalpies due to the strong interactions with ionic liquids. For alcohols, the effects of the enthalpies on the activity coefficients are larger than those of the entropies, while the effects for ketones and aromatic hydrocarbons are almost the same.

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