

# Activity Coefficients at Infinite Dilution of Organic Solutes in 1-Ethyl-3-methylimidazolium Tetrafluoroborate Using Gas–Liquid Chromatography

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The activity coefficients at infinite dilution,  $\gamma_i^\infty$ , for 25 organic solutes, alkanes, alkenes, alkyl benzenes, acetonitrile, acetone, 1,4-dioxane, tetrahydrofuran, ethyl acetate, and chloromethanes, in the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF<sub>4</sub>]) have been measured by the gas–liquid chromatographic method at temperatures from (303.15 to 363.15) K. The partial molar excess enthalpies at infinite dilution,  $H_i^{E,\infty}$ , of the solutes in the ionic liquid were also derived from the temperature dependence of the  $\gamma_i^\infty$  values.

## Introduction

This work continues our studies on the determination of activity coefficients at infinite dilution,  $\gamma_i^\infty$ , of various solutes (*i*) by the gas–liquid chromatographic method (GLC) for hydrophilic ionic liquids (ILs).<sup>1–7</sup> Heintz et al.<sup>8–16</sup> and Letcher et al.<sup>17–25</sup> measured  $\gamma_i^\infty$  of various solutes in a number of ILs. 1-Ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF<sub>4</sub>]) was synthesized in 1992, which is the first of the new ILs with air and moisture stability.<sup>26</sup> In this work, the activity coefficients at infinite dilution,  $\gamma_i^\infty$ , for 25 polar and nonpolar solutes in [EMIM][BF<sub>4</sub>] at temperature from (303.15 to 363.15) K have been measured. The partial molar excess enthalpies at infinite dilution,  $H_i^{E,\infty}$ , of the solutes in the ionic liquid were also derived from the temperature dependence of the  $\gamma_i^\infty$  values.

## Experimental section

**Materials.** The organic solutes including alkanes, alkenes, alkyl benzenes, acetonitrile, acetone, 1,4-dioxane, tetrahydrofuran, ethyl acetate, and chloromethanes were purchased from Beijing Chemical Reagents Company. Their mass fraction purities were above 99 %. All chemicals were used without further purification. The ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF<sub>4</sub>]) was prepared via the traditional two steps. First, 1-ethyl-3-methylimidazolium bromide was synthesized with equimolar amounts of 1-methylimidazole and ethyl bromide. Second, [EMIM][BF<sub>4</sub>] was prepared by anion metathesis in water using NaBF<sub>4</sub>. NaBr precipitate was removed by filtration, and the remaining water was removed by rotary evaporation. The crude product was dissolved in dichloromethane, and the solution was washed with a small amount of cooled deionized water five times until the aqueous solution did not form any precipitate with AgNO<sub>3</sub> solution. The solvent dichloromethane was removed by rotary evaporation, and the [EMIM][BF<sub>4</sub>] was dried under high vacuum at 343 K for 8 h to remove volatile impurities. Water mass fractions analyzed by Karl Fischer analysis were less than 10<sup>–3</sup>. The

**Table 1. Relative Uncertainties in the Measured and Derived Quantities**

parameters	relative uncertainty
$t_r - t_G$	± 2.8 %
$U_0$	± 0.5 %
$P_i$	± 0.6 %
$P_0$	± 0.02 %
$J$	± 1 %
$P_i^0$	± 0.01 % to ± 0.30 %
$n_3$	± 0.6 %
$\gamma_i^\infty$	± 5 %

chemical shifts for <sup>1</sup>H NMR spectra (parts per million, D<sub>2</sub>O) appear as follows: δ 8.646 [s, 1H, H(2)], 7.437 [s, 1H, H(4)], 7.370 [s, 1H, H(5)], 4.202 [m, 2H, NCH<sub>2</sub>], 3.838 [s, 3H, NCH<sub>3</sub>], and 1.464 [t, 3H, CH<sub>3</sub>]. Impurity peaks were not observed in the <sup>1</sup>H NMR. Before use, the IL was subjected to vacuum evaporation at (323 to 333) K over 24 h to remove possible traces of solvents and moisture.

**Apparatus and Procedure.** The GLC apparatus, column preparation, packing method, experimental process, and the method of checking the stability of the experimental conditions have been described in our previous work.<sup>1–3</sup> In this work, dry nitrogen was used as the carrier gas, and dichloromethane was used as solvent to coat the ionic liquid onto the solid support. The volume of the samples injected into the GC probes was from (0.1 to 2) μL. The experiments were carried out over a temperature range from (303.15 to 363.15) K.

The  $\gamma_i^\infty$  values were obtained by the equation proposed by Cruickshank et al.<sup>27</sup> and Everett.<sup>28</sup> The way of deducing  $\gamma_i^\infty$  from the experiments was given in our previous work.<sup>1–3</sup> The data needed for the equations have been obtained in the following way. Molar volumes of solutes,  $V_i^0$ , were estimated using their experimental densities,<sup>29</sup> and partial molar volumes of solute at infinite dilution,  $V_i^\infty$ , have been assumed to be equal to  $V_i^0$ . Values of the vapor pressure of the pure liquid solute *i*,  $P_i^0$ , for all solutes were calculated from the Antoine equation, with Antoine coefficients given by Boublik et al.<sup>30</sup>  $B_{11}$  is the second virial coefficient of the solute (1), and  $B_{12}$  is the cross second virial coefficient of the solute (1) with the carrier gas (2).  $B_{11}$  and  $B_{12}$  have been estimated according to the equations suitable for polar liquids by Tsonopolous's method.<sup>31</sup> Critical

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**Table 2. Experimental Activity Coefficients at Infinite Dilution,  $\gamma_i^\infty$ , for Various Solutes in the Ionic Liquid 1-Ethyl-3-methylimidazolium Tetrafluoroborate at Temperatures of (303.15 to 363.15) K**

solutes ( <i>i</i> )	<i>T</i> /K = 303.15	<i>T</i> /K = 313.15	<i>T</i> /K = 323.15	<i>T</i> /K = 333.15	<i>T</i> /K = 343.15	<i>T</i> /K = 353.15	<i>T</i> /K = 363.15
Alkanes							
pentane	68.78	62.52	57.64	53.85	49.03	45.66	42.12
hexane	101.4	95.27	90.60	85.28	77.40	74.47	69.46
heptane	153.5	138.1	124.1	111.3	104.2	96.00	90.39
octane	216.5	200.7	186.9	172.8	157.8	148.7	139.8
nonane	319.1	293.9	271.9	254.2	248.2	234.8	223.8
decane	1112.5	984.3	861.4	751.4	642.8	544.7	455.8
cyclohexane	70.55	60.88	49.73	39.65	31.17	27.46	21.90
methylcyclohexane	92.97	79.67	67.65	58.92	51.36	43.32	32.26
2,2,4-trimethylpentane	158.31	142.56	123.82	112.29	101.48	85.84	75.30
Alkenes							
cyclohexene	21.81	19.65	16.64	14.39	12.75	10.51	9.13
styrene	3.375	3.443	3.489	3.558	3.620	3.654	3.734
Alkyl Benzenes							
benzene	2.127	2.107	2.087	2.052	2.018	1.986	1.963
toluene	3.678	3.659	3.615	3.560	3.516	3.482	3.399
ethylbenzene	6.49	6.30	6.11	5.89	5.58	5.44	5.31
<i>o</i> -xylene	4.73	4.69	4.64	4.58	4.50	4.41	4.34
<i>m</i> -xylene	5.88	5.71	5.57	5.32	5.17	4.98	4.83
<i>p</i> -xylene	5.41	5.30	5.14	5.03	4.96	4.88	4.76
Solvents							
acetonitrile	0.892	0.875	0.853	0.832	0.814	0.792	0.769
acetone	1.232	1.257	1.266	1.293	1.313	1.330	1.334
1,4-dioxane	1.346	1.397	1.423	1.436	1.467	1.485	1.511
tetrahydrofuran	1.872	1.852	1.834	1.817	1.796	1.766	1.735
ethyl acetate	2.938	2.920	2.892	2.867	2.835	2.795	2.755
Chloromethanes							
dichloromethane	1.123	1.161	1.206	1.255	1.319	1.360	1.385
trichloromethane	1.361	1.375	1.390	1.409	1.426	1.460	1.495
tetrachloromethane	4.31	4.41	4.56	4.66	4.80	4.89	4.98

**Table 3. Comparison of Activity Coefficients at Infinite Dilution,  $\gamma_i^\infty$ , with the Values in the Literature**

solutes ( <i>i</i> )	$\gamma_i^\infty$					
	<i>T</i> /K = 303.15		<i>T</i> /K = 323.15		<i>T</i> /K = 343.15	
	this work	lit. <sup>33</sup>	this work	lit. <sup>33</sup>	this work	lit. <sup>33</sup>
hexane	101.4	124.88	90.60	113.21	77.40	64.75
heptane	153.5	201.52	124.1	172.56	104.2	138.52
cyclohexane	70.55	53.72	49.73	46.17	31.17	38.89
2,2,4-trimethylpentane	158.31	221.60	123.82	167.85	101.48	162.38
benzene	2.127	2.42	2.087	2.51	2.018	2.47
toluene					3.516	4.03
ethylbenzene			6.11	7.05	5.58	6.87
acetone			1.266	1.11	1.313	1.14
ethyl acetate			2.892	3.08	2.835	3.32
trichloromethane			1.390	0.73	1.426	0.84

parameters needed for the calculations were available from the literature.<sup>31</sup> The cross critical properties  $P_{cij}$ ,  $T_{cij}$ ,  $V_{cij}$ , and  $Z_{cij}$  and acentric factor  $\omega_{ij}$  were calculated using equations given in the literature.<sup>31,32</sup> From a propagation of error analysis, the  $\gamma_i^\infty$  values in this work are estimated to have an uncertainty within  $\pm 5\%$ . The uncertainties in the measured and derived quantities are listed in Table 1.

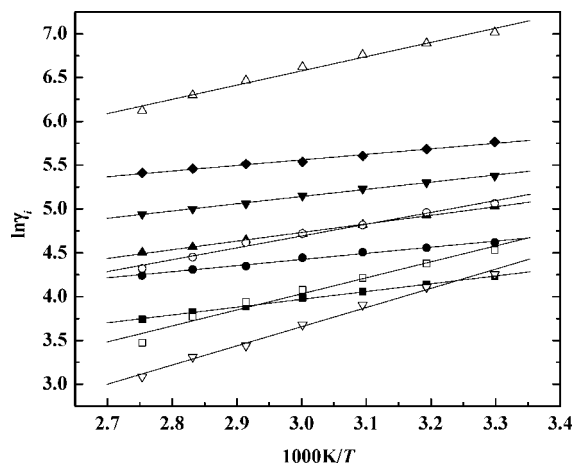
## Results and Discussion

Experimental results of  $\gamma_i^\infty$  for 25 solutes in [EMIM][BF<sub>4</sub>] at different temperatures are presented in Table 2. The  $\gamma_i^\infty$  values for the linear *n*-alkanes increase with increasing chain length. The branching of the alkane skeleton reduces the values of  $\gamma_i^\infty$  in comparison with the corresponding linear alkanes. Introduction of the double bond in the six-membered ring (cyclohexene) causes a reduction of  $\gamma_i^\infty$ . For the aromatic compounds, the values of  $\gamma_i^\infty$  are distinctly lower in comparison with those of the alkanes and alkenes, and the values of  $\gamma_i^\infty$  increase with increasing size of the alkyl group.

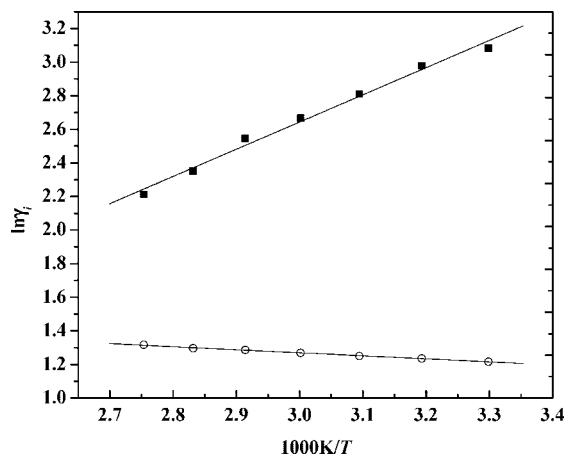
**Table 4. Coefficients *a* and *b* of Equation 1,  $\gamma_i^\infty$  at 298.15 K Calculated Using Equation 1, Values of  $H_i^{E,\infty}$  Derived from Equation 1, Standard Deviation  $\sigma$** 

solute ( <i>i</i> )	<i>a</i>	<i>b</i> /K	$\gamma_i^\infty$ 298.15K	$H_i^{E,\infty}$ /kJ·mol <sup>-1</sup>	$\sigma$
Alkanes					
pentane	1.3015	889.17	72.51	7.39	0.0088
hexane	2.3208	701.02	106.9	5.83	0.0158
heptane	1.7812	983.58	160.8	8.18	0.0125
octane	2.6843	819.21	228.6	6.81	0.0090
nonane	3.6562	634.63	325.3	5.28	0.0152
decane	1.6989	1625.70	1276	13.52	0.0416
cyclohexane	-2.9046	2187.17	84.03	18.18	0.0411
methylcyclohexane	-1.4466	611.90	1.83	5.09	0.0658
2,2,4-trimethylpentane	0.6437	1349.23	175.7	11.22	0.0323
Alkenes					
cyclohexene	-2.2131	1618.94	24.95	13.46	0.0352
styrene	1.8112	-180.55	3.34	-1.50	0.0029
Alkyl Benzenes					
benzene	0.2536	153.73	2.16	1.04	0.0036
toluene	0.8411	142.03	3.73	1.18	0.0060
ethyl benzene	0.6065	385.59	6.68	3.21	0.0089
<i>o</i> -xylene	1.0376	158.82	4.81	1.32	0.0070
<i>m</i> -xylene	0.5614	369.75	6.06	3.07	0.0078
<i>p</i> -xylene	0.9272	230.75	5.48	1.92	0.0039
Solvents					
acetonitrile	-0.9972	269.70	0.91	2.24	0.0059
acetone	0.7169	-153.78	1.22	-1.28	0.0044
1,4-dioxane	0.9575	-197.51	1.34	-1.64	0.0063
tetrahydrofuran	0.1879	134.58	1.90	1.12	0.0055
ethylacetate	0.6965	117.25	2.97	0.97	0.0048
Chloromethanes					
dichloromethane	1.4568	-408.16	1.09	-3.39	0.0077
trichloromethane	0.7119	-122.92	1.35	-1.02	0.0014
tetrachloromethane	2.3630	-274.01	4.24	-2.28	0.0033

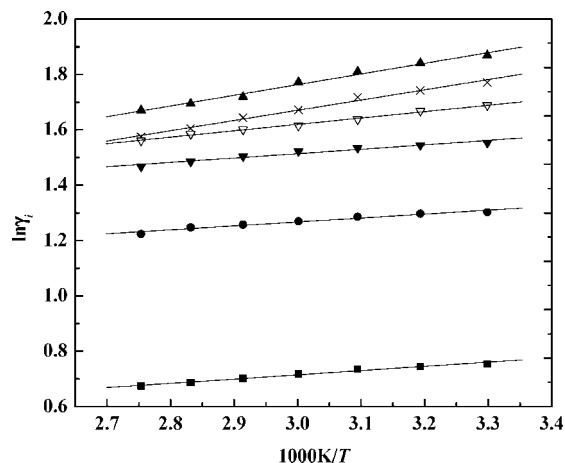
The  $\gamma_i^\infty$  values of polar solutes were in the order of ethylacetate > tetrahydrofuran > 1,4-dioxane > acetone > acetonitrile. The  $\gamma_i^\infty$  values of dichloromethane and trichloromethane are similar and clearly lower than that for tetrachlo-



**Figure 1.** Plot of  $\ln \gamma_i^\infty$  vs  $1/T$  for the solutes together with a linear correlation of the data: ■, pentane; ●, hexane; ▲, heptane; ▼, octane; ◆, nonane; Δ, decane; ▽, cyclohexane; □, methylcyclohexane; ○, 2,2,4-trimethylpentane; —, linear fit.



**Figure 2.** Plot of  $\ln \gamma_i^\infty$  vs  $1/T$  for the solutes together with a linear correlation of the data: ■, cyclohexane; ○, styrene; —, linear fit.



**Figure 3.** Plot of  $\ln \gamma_i^\infty$  vs  $1/T$  for the solutes together with a linear correlation of the data: ■, benzene; ●, toluene; ▼, *o*-xylene; ▽, *p*-xylene; ×, *m*-xylene; ▲, ethyl benzene; —, linear fit.

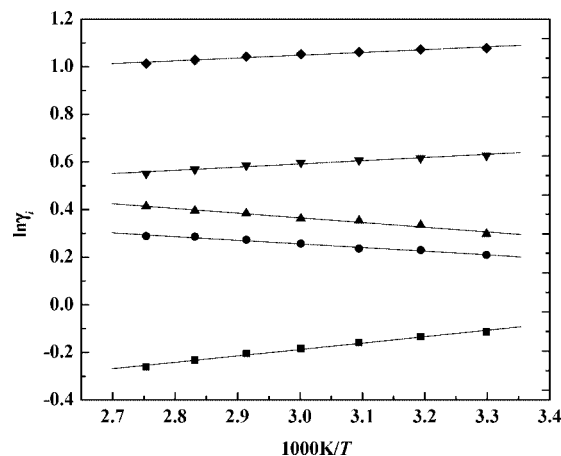
romethane. This behavior indicates that more polar solutes have better solubilities in the ionic liquid because of the preferred attractive interaction of polar molecules with the charged ions of the IL, and they were prone to strongly retain in the IL stationary phase.

Bottni et al.<sup>33</sup> have measured  $\gamma_i^\infty$  for some solutes in [EMIM][BF<sub>4</sub>] at  $T = (303, 323, \text{ and } 343) \text{ K}$  using inverse gas

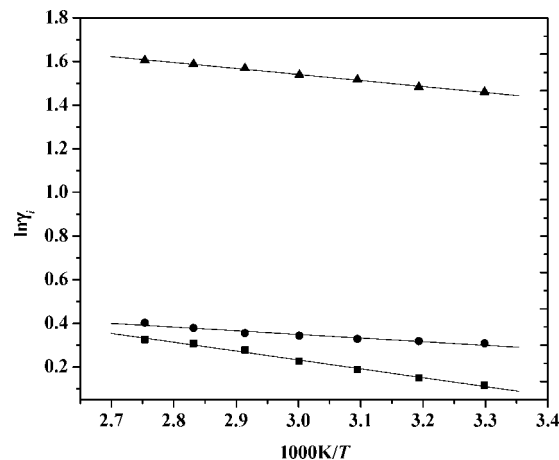
**Table 5.** Selectivity,  $S_{ij}^\infty$ , at Infinite Dilution for Different Ionic Liquids at 298.15 K

ionic liquids	hexane ( <i>i</i> )/benzene ( <i>j</i> )	cyclohexane ( <i>i</i> )/benzene ( <i>j</i> )
[EMIM][N(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> ] <sup>a</sup>	23.1	13.2
[EMIM][N(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> ] <sup>b</sup>	24.5 <sup>d</sup>	13.8 <sup>d</sup>
[EMIM][EtSO <sub>4</sub> ] <sup>b</sup>	40.8 <sup>d</sup>	21.7 <sup>d</sup>
[EMIM][TFA] <sup>c</sup>	30.7	14.4
[EMIM][BF <sub>4</sub> ] (this work)	49.5	38.9

<sup>a</sup> Ref 10. <sup>b</sup> Ref 36. <sup>c</sup> Ref 37. <sup>d</sup> The values of  $\gamma_i^\infty$  from the dilutor technique.



**Figure 4.** Plot of  $\ln \gamma_i^\infty$  vs  $1/T$  for the solutes together with a linear correlation of the data: ■, acetonitrile; ●, acetone; ▲, 1,4-dioxane; ▼, tetrahydrofuran; ◆, ethylacetate; —, linear correlation.



**Figure 5.** Plot of  $\ln \gamma_i^\infty$  vs  $1/T$  for the solutes together with a linear correlation of the data: ■, dichloromethane; ●, trichloromethane; ▲, tetrachloromethane; —, linear correlation.

chromatography. Table 3 lists the  $\gamma_i^\infty$  values reported by these authors. For comparison, the  $\gamma_i^\infty$  values for the same solutes in this work have also been included in Table 3. The  $\gamma_i^\infty$  values except for cyclohexane at  $T = (303 \text{ and } 323) \text{ K}$ , acetone, and trichloromethane in this work are lower than that Bottini et al. reported, and there is an average discrepancy of the order of (20 to 30) % between both sets of data. The differences of the experimental method and calculation equation may result in the discrepancy in the results. Furthermore, there is the possibility of interfacial adsorption for the solutes onto the solid support, which may result in the  $\gamma_i^\infty$  values having a tendency of underestimation in particular for hydrocarbons and low polarity solutes.<sup>34</sup>

Experimental results of  $\gamma_i^\infty$  at different temperatures are correlated with temperature by the following equation

$$\ln \gamma_i^\infty = a + \frac{b}{(T/K)} \quad (1)$$

The coefficients  $a$  and  $b$ , the standard deviation  $\sigma$  of the fitted equations, and the values of  $\gamma_i^\infty$  at 298.15 K are listed in Table 4. The plots of measured  $\ln \gamma_i^\infty$  vs  $1/T$  values and the linear fit of their data are given in Figures 1 to 5, which showed a fairly good fitting quality of eq 1. According to the Gibbs–Helmholtz equation, the values for the partial molar excess enthalpy at infinite dilution,  $H_i^{E,\infty}$ , of solute  $i$  can be obtained from the slope of a straight line derived from eq 1, which were listed in Table 4. For the linear alkanes, cyclohexene, and alkyl benzenes,  $H_i^{E,\infty}$  was positive. The value of  $H_i^{E,\infty}$  for styrene, acetone, 1,4-dioxane, and chloromethanes  $H_i^{E,\infty}$  became negative. This is most probably due to the high polarizability of the oxygen and chlorine atoms and the special strength of ion-induced dipole interactions. The relative uncertainties of  $H_i^{E,\infty}$  is about  $\pm 10\%$ .

The selectivity,  $S_{ij}^\infty$ , is defined as  $S_{ij}^\infty = \gamma_{i,IL}^\infty / \gamma_{j,IL}^\infty$ <sup>35</sup> (where  $i, j$  refers to the solutes to be separated). The  $S_{ij}^\infty$  calculated from experimental  $\gamma_i^\infty$  values at 298.15 K for hexane ( $i$ )/benzene ( $j$ ) and cyclohexane ( $i$ )/benzene ( $j$ ) are presented in Table 5. The results indicated that [EMIM][BF<sub>4</sub>] can play an important role for the separation of hexane and cyclohexane from benzene. The values of  $S_{ij}^\infty$  for three isomeric xylenes at 298.15 K were 1.26 (*m*-xylene/*o*-xylene), 1.10 (*m*-xylene/*p*-xylene), and 1.14 (*p*-xylene/*o*-xylene), respectively. The results indicated that [EMIM][BF<sub>4</sub>] was not an ideal extraction solvent for separation of xylenes.

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