

# Activity Coefficients at Infinite Dilution Measurements for Organic Solutes and Water in the Ionic Liquid 1-Ethyl-3-methylimidazolium Trifluoroacetate

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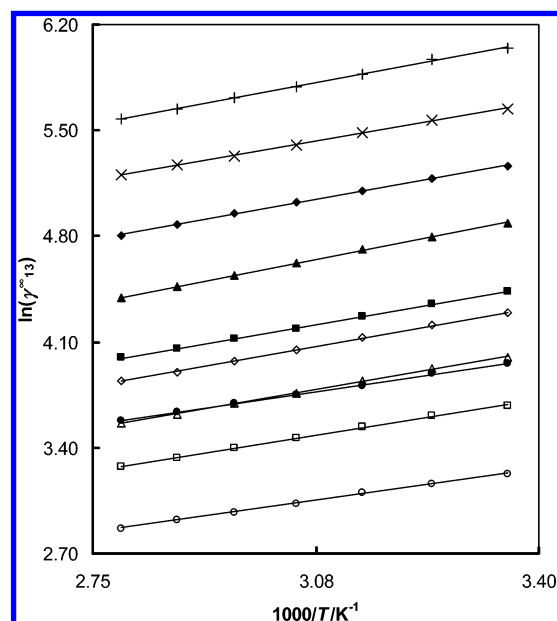
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The activity coefficients at infinite dilution,  $\gamma_{13}^{\infty}$  for 29 solutes, alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols and water in the ionic liquid 1-ethyl-3-methylimidazolium trifluoroacetate ([EMIM][TFA]), were determined by gas–liquid chromatography at temperatures from 298.15–368.15 K. The partial molar excess enthalpies at infinite dilution  $\Delta H_1^{E,\infty}$  values were calculated from the experimental  $\gamma_{13}^{\infty}$  values obtained over the temperature range. The selectivities for the hexane/benzene and cyclohexane/benzene separation were calculated from  $\gamma_{13}^{\infty}$  and compared to the literature values for other ionic liquids, NMP and sulfolane.

## Introduction

This work is a continuation of our investigations on the determination of activity coefficients at infinite dilution for many solutes in ionic liquids using gas–liquid chromatography. Our previous work includes measurements of  $\gamma_{13}^{\infty}$  for organic solutes in the ionic liquids (ILs): 1-hexyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)-imide,<sup>1</sup> 1-butyl-3-methyl-imidazolium 2-(2-methoxyethoxy)-ethyl sulfate,<sup>2</sup> and 1-butyl-3-methyl-imidazolium octyl sulfate.<sup>3</sup> In recent years ILs have become very popular as they have very important properties, such as wide liquid range, stability at high temperature, no flammability, and negligible vapor pressure, and can be used as replacements for conventional volatile, flammable, and toxic organic solvents. Activity coefficients at infinite dilution provide useful information about the possibility of use of an IL in separation processes. The selectivities and capacities at infinite dilution can be directly calculated from  $\gamma_{13}^{\infty}$  values for different separation problems. To expand our knowledge about nature of ILs, a systematic study on physicochemical properties is needed. Experimental  $\gamma_{13}^{\infty}$  data are also needed to expand thermodynamic models such as UNIFAC.<sup>4</sup>

Use of ionic liquids as solvents for liquid extraction processes is one of their promising applications. In our previous study, the new IL [ethyl(2-hydroxyethyl)dimethylammonium bis-((trifluoromethyl)sulfonyl)imide ( $C_2NTf_2$ )] for the aromatic/aliphatic separation by the liquid–liquid equilibria (LLE) study on {hexane + benzene +  $C_2NTf_2$ }, or {hexane + *p*-xylene +  $C_2NTf_2$ }, or {hexane, or octane + *m*-xylene +  $C_2NTf_2$ } systems at 298.15 K was tested.<sup>5</sup> In that paper the selectivity of benzene, or *p*-xylene, or *m*-xylene/hexane phase separation was examined.<sup>5</sup> The selectivities for systems (hexane + benzene +  $C_2NTf_2$ ) and (octane + *m*-xylene +  $C_2NTf_2$ ) were higher than  $S = 20$ . Better selectivity was observed in the system octane + *m*-xylene +  $C_2NTf_2$  ( $S = 31$ – $22$ ) than in the system hexane + *m*-xylene +  $C_2NTf_2$  ( $S = 11$ – $2$ ).<sup>5</sup>



**Figure 1.** Plot of  $\ln(\gamma_{13}^{\infty})$  vs  $1/T$  for the solutes (●) *n*-pentane, (■) *n*-hexane, (▲) *n*-heptane, (◆) *n*-octane, (×) *n*-nonane, (+) *n*-decane, (○) cyclopentane, (□) cyclohexane, (△) cycloheptane, and (◇) cyclooctane.

The nonvolatility of IL in combination with their remarkable separation efficiency and selectivity enable new processes for the separation of azeotropic mixtures which, in comparison to conventional separation processes, might offer a potential for cost savings. Until now, it cannot be predicted which IL is the best one for certain applications. Some ILs such as 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide, [EMIM]-[NTf<sub>2</sub>], or 1-ethyl-3-methyl-imidazolium ethyl sulfate, [EMIM]-[EtSO<sub>4</sub>], or [MBPy][BF<sub>4</sub>] are excellent entrainers for the separation of aliphatic from aromatic hydrocarbons by extractive distillation or extraction.<sup>6–9</sup> Generally, the separation of the aromatic hydrocarbons/aliphatic hydrocarbons decreases with increasing length of the alkyl chain on the imidazolium, or ammonium cation, or anion of the IL.

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**TABLE 1: The Experimental Activity Coefficients at Infinite Dilution  $\gamma_{13}^{\infty}$  for the Solutes in Ionic Liquid [EMIM][TFA] at Different Temperatures and Excess Molar Enthalpies at Infinite Dilution  $\Delta H_1^{E,\infty}$  for Investigated Ionic Liquid**

solute	T/K								$\Delta H_1^{E,\infty}/\text{J}\cdot\text{mol}^{-1}$
	298.15	308.15	318.15	328.15	338.15	348.15	358.15	368.15	
<i>n</i> -pentane	52.3	48.9	45.3	42.5	40.1	37.9	35.8		5596
<i>n</i> -hexane	84.2	77.8	71.2	66.1	61.6	57.8	54.4		6531
<i>n</i> -heptane	132.8	121.2	111.0	101.9	93.9	87.0	80.8		7373
<i>n</i> -octane	193.0	178.4	163.9	151.8	140.8	130.8	122.2		6805
<i>n</i> -nonane	282.0	261.5	240.4	222.7	207.0	194.1	183.0		6486
<i>n</i> -decane	422.2	391.1	355.7	327.2	302.7	281.1	264.0		7084
cyclopentane	25.2	23.7	22.2	20.7	19.6	18.5	17.6		5360
cyclohexane	39.6	37.0	34.5	32.0	29.9	28.0	26.4		6045
cycloheptane	54.7	50.6	46.7	43.1	40.1	37.4	35.2		6612
cyclooctane	73.0	67.4	62.1	57.1	53.2	49.4	46.4		6770
pent-1-ene	23.8	22.7	21.7	20.7	19.9	19.0	18.4		3820
hex-1-ene	34.1	32.4	31.2	29.7	28.5	27.5	26.5		3721
hept-1-ene	54.9	51.6	49.3	46.9	44.4	42.3	40.6		4473
oct-1-ene	84.7	80.0	75.8	71.8	68.3	64.9	61.9		4641
pent-1-yne	3.844	3.916	3.998	4.064	4.130	4.202	4.265		-1539
hex-1-yne	5.958	6.081	6.160	6.270	6.353	6.432	6.511		-1301
hept-1-yne	7.769	8.159	8.499	8.842	9.187	9.477	9.836		-3448
oct-1-yne			15.43	15.40	15.38	15.35	15.33		147
benzene	2.747	2.753	2.759	2.767	2.773	2.781	2.790	2.796	-233
toluene	4.337	4.373	4.403	4.433	4.462	4.485	4.502	4.520	-543
ethylbenzene			7.380	7.365	7.347	7.334	7.320	7.308	192
<i>o</i> -xylene			6.330	6.326	6.321	6.317	6.313	6.310	63
<i>m</i> -xylene			7.455	7.449	7.445	7.439	7.435	7.431	63
<i>p</i> -xylene			7.133	7.146	7.161	7.173	7.183	7.195	-169
methanol				0.219	0.223	0.227	0.230	0.233	-1573
ethanol				0.373	0.381	0.387	0.394	0.402	-1862
propan-1-ol					0.494	0.505	0.517	0.531	-2474
butan-1-ol					0.627	0.648	0.671	0.697	-3634
water						0.143	0.152	0.159	-5607

The selectivities calculated from experimental activity coefficients at infinite dilution made by different authors for hexane/benzene mixtures are for example as follows:  $S_{ij}^{\infty} = 2.76$  (at 323.15 K) for 1-hexadecyl-3-methyl-imidazolium tetrafluoroborate, [C<sub>16</sub>MIM][BF<sub>4</sub>];<sup>10</sup>  $S_{ij}^{\infty} = 12.4$  (at 298.15 K) for [HMIM]-[NTf<sub>2</sub>];<sup>1</sup>  $S_{ij}^{\infty} = 5.1$  (at 298.15 K) for [OcMIM][NTf<sub>2</sub>];<sup>3</sup>  $S_{ij}^{\infty} = 23.0$  (at 313.7 K) for 1-ethyl-2,3-dimethyl-imidazolium bis-[(trifluoromethyl)sulfonyl]imide [EMMIM][NTf<sub>2</sub>];<sup>11</sup>  $S_{ij}^{\infty} = 21.53$  (at 313.9 K) for [EMIM][NTf<sub>2</sub>];<sup>11</sup> and  $S_{ij}^{\infty} = 36.8$  (at 313 K) for [MBPy][BF<sub>4</sub>] [27].<sup>12</sup> More experimental selectivity data were presented for the heptane/benzene system at 313.15 K for [OcMIM][Cl], [EMIM][NTf<sub>2</sub>], and [BMIM][PF<sub>6</sub>], and the values are  $S_{ij}^{\infty} = 11.3$ , 24.8, and 34.8 (at 313.15 K), respectively.<sup>13</sup>

From the activity coefficients at infinite dilution measurements the best values for hexane/benzene separation at 298.15 K were obtained for [EMIM][EtSO<sub>4</sub>],  $S_{ij}^{\infty} = 41.4$ ,<sup>9</sup> or for [EMIM][NTf<sub>2</sub>],  $S_{ij}^{\infty} = 24.49$  or for 1-butyl-3-methyl-imidazolium 2-(2-methoxyethoxy)ethylsulfate, [BMIM][MDEGSO<sub>4</sub>],  $S_{ij}^{\infty} = 39.7$ ,<sup>2</sup> and for [EMIM][NTf<sub>2</sub>],  $S_{ij}^{\infty} = 37.5$ .<sup>14</sup>

This paper presents  $\gamma_{13}^{\infty}$  for 29 solutes (alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols, and water) in ionic liquid 1-ethyl-3-methylimidazolium trifluoroacetate ([EMIM][TFA]) in the temperature range from 298.15 to 368.15 K.

## Experimental Procedures and Results

**Materials or Chemicals.** The IL investigated here, 1-ethyl-3-methylimidazolium trifluoroacetate, was obtained from Merck. The sample's purity was >98 mass %. The ionic liquid was further purified by subjecting the liquid to a very low pressure of about  $5 \times 10^{-3}$  Pa at temperature about 70 °C for approximately 5 h. This procedure removed any volatile chemicals and water from the ionic liquid. The solutes (alkanes,

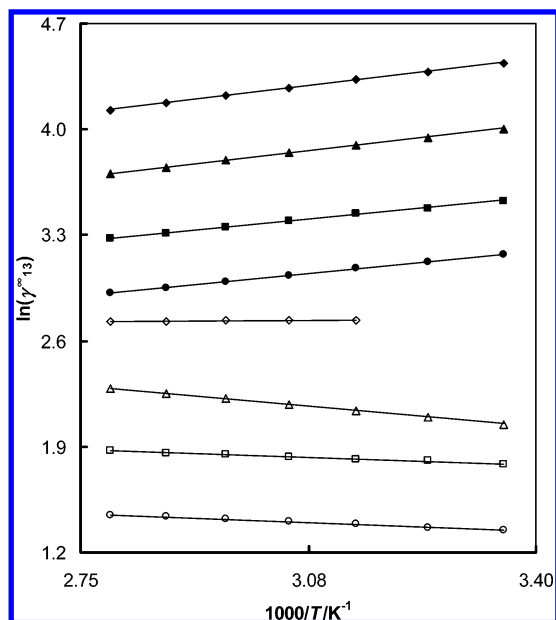
alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, and alcohols), purchased from Aldrich and Fluka, were used without further purification because the GLC technique separated any impurities on the column.

**Apparatus and Experimental Procedure.** The experiments were performed using a Perkin-Elmer Clarus 500 gas chro-

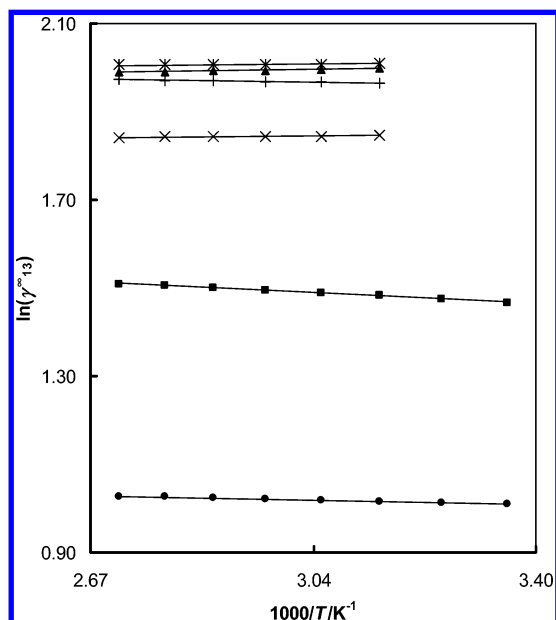
**TABLE 2: Selectivities  $S_{12}^{\infty}$  and Capacities  $k_2^{\infty}$  at Infinite Dilution for Ionic Liquids Based on 1-Alkyl-3-methyl-imidazolium Cation, NMP, and Sulfolane for Different Separation Problems at  $T = 298.15$  K**

solvent	$S_{12}^{\infty}$			$k_2^{\infty}$
	<i>n</i> -hexane (1)/ benzene (2)	cyclohexane (1)/ benzene (2)	benzene (2)	
[MMIM][CH <sub>3</sub> OC <sub>2</sub> H <sub>4</sub> SO <sub>4</sub> ] <sup>a</sup>	40.9 <sup>m</sup>	26.1 <sup>m</sup>		0.22 <sup>m</sup>
[MMIM][NTf <sub>2</sub> ] <sup>b</sup>	30.8 <sup>m</sup>	17.5 <sup>m</sup>		0.75 <sup>m</sup>
[MMIM][CH <sub>3</sub> SO <sub>4</sub> ] <sup>a</sup>	15.8 <sup>m</sup>	19.6 <sup>m</sup>		0.13 <sup>m</sup>
[EMIM][TFA] <sup>n</sup>	30.7	14.4		0.36
[EMIM][C <sub>2</sub> H <sub>5</sub> SO <sub>4</sub> ] <sup>b</sup>	40.8 <sup>m</sup>	21.7 <sup>m</sup>		0.37 <sup>m</sup>
[EMIM][NTf <sub>2</sub> ] <sup>b</sup>	24.5 <sup>m</sup>	13.8 <sup>m</sup>		0.84 <sup>m</sup>
[BMIM][MDEGSO <sub>4</sub> ] <sup>c</sup>	39.7	16.9		0.49
[BMIM][NTf <sub>2</sub> ] <sup>b</sup>	16.7 <sup>m</sup>	10.2 <sup>m</sup>		1.14 <sup>m</sup>
[BMIM][OcSO <sub>4</sub> ] <sup>d</sup>	5.1	3.5		0.70
[HMIM][BF <sub>4</sub> ] <sup>e</sup>	23.0	13.4		1.04
[HMIM][PF <sub>6</sub> ] <sup>f</sup>	21.8	12.3		0.97
[HMIM][NTf <sub>2</sub> ] <sup>g</sup>	12.4	8.2		1.48
[OMIM][MDEGSO <sub>4</sub> ] <sup>h</sup>	9.2			0.72
[OMIM][Cl] <sup>i</sup>	8.6	5.3		0.50
[OMIM][NTf <sub>2</sub> ] <sup>j</sup>	8.6 <sup>m</sup>	5.9 <sup>m</sup>		1.59 <sup>m</sup>
NMP <sup>k</sup>	13.0 <sup>m</sup>	8.0 <sup>m</sup>		0.96 <sup>m</sup>
NMP + 3% (w/w) water <sup>k</sup>	16.3 <sup>m</sup>	9.8 <sup>m</sup>		0.75 <sup>m</sup>
NMP + 6% (w/w) water <sup>k</sup>	19.0 <sup>m</sup>	10.9 <sup>m</sup>		0.52 <sup>m</sup>
sulfolane <sup>l</sup>	20.5 <sup>m</sup>	12.5 <sup>m</sup>		0.42 <sup>m</sup>

<sup>a</sup> Reference 27. <sup>b</sup> Reference 9. <sup>c</sup> Reference 2. <sup>d</sup> Reference 3. <sup>e</sup> Reference 28. <sup>f</sup> Reference 29. <sup>g</sup> Reference 1. <sup>h</sup> Reference 30. <sup>i</sup> Reference 31. <sup>j</sup> Reference 4. <sup>k</sup> NMP, *N*-methyl-2-pyrrolidinone, ref 32. <sup>l</sup> Reference 33. <sup>m</sup> Extrapolated value. <sup>n</sup> This work.



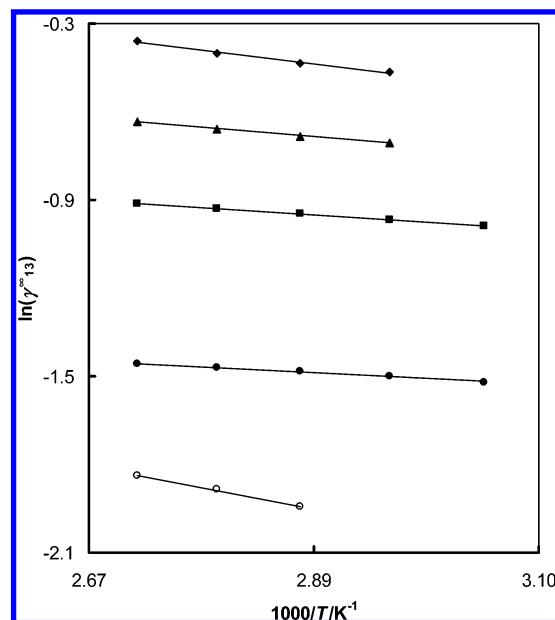
**Figure 2.** Plot of  $\ln(\gamma_{13}^{\infty})$  vs  $1/T$  for the solutes (●) pent-1-ene, (■) hex-1-ene, (▲) hept-1-ene, (◆) oct-1-ene, (○) pent-1-yne, (□) hex-1-yne, (△) hept-1-yne, and (◇) oct-1-yne.



**Figure 3.** Plot of  $\ln(\gamma_{13}^{\infty})$  vs  $1/T$  for the solutes (●) benzene, (■) toluene, (▲) ethylbenzene, (×) *o*-xylene, (\*) *m*-xylene, and (+) *p*-xylene.

matograph equipped with a thermal conductivity detector (TCD). The data were collected and processed using TotalChrom Workstation software.

The column preparation and the packing method used in this work have been described previously.<sup>1-3,15,16</sup> Glass columns of length 1 m and 4 mm i.d. were used. Chromosorb W HP 80/100 mesh was used as the solid support and was supplied by SUPELCO. Coating the solid support material with the ionic liquid was performed by dispersing a certain portion of Chromosorb in a solution of the ionic liquid in methanol followed by evaporation of the solvent using a rotating evaporator. The masses of the stationary phase and of the solid support were weighed with a precision of  $\pm 0.0001$  g. The solvent column packing varied from 25 to 45 mass % of the ionic liquid, large enough to prevent any residual absorption of



**Figure 4.** Plot of  $\ln(\gamma_{13}^{\infty})$  vs  $1/T$  for the solutes (●) methanol, (■) ethanol, (▲) propan-1-ol, (◆) butan-1-ol, and (○) water.

solute onto the column packing. The average values of three columns were presented as the final result. For each temperature the measurements were repeated by using three different columns with different mass percent packing. Care was taken to ensure that the methanol had completely evaporated from the IL coated solid before making up the column. Before experiment each column was conditioned by blowing carrier gas at high flow rate (about  $3.5 \text{ cm}^3 \cdot \text{s}^{-1}$ ) at high temperature (about 373 K) through about 8 h.

The outlet pressure  $P_o$  was kept at atmospheric pressure. The pressure drop ( $P_i - P_o$ ) was varied between 20 and 60 kPa depending on flow rate of carrier gas. The pressure drop was measured by gas chromatograph with an uncertainty of  $\pm 0.1$  kPa. The atmospheric pressure was measured using a digital barometer with an uncertainty of  $\pm 0.1$  hPa.

The carrier gas was helium. The flow rate of carrier gas was determined using a calibrated soap bubble flowmeter which was placed at the outlet after the detector. The flow rate was set for a series of runs and was allowed to stabilize for at least 15 min before any  $\gamma_{13}^{\infty}$  determinations were made. The flow rates were corrected for water vapor pressure and ranged from 0.5 to  $1.7 \text{ cm}^3 \cdot \text{s}^{-1}$ . Solute injections ranged from 0.01 to  $0.2 \mu\text{L}$  and were considered to be at infinite dilution on the column.

Experiments were carried out at different temperatures (in steps of 10 K) between 298.15 and 368.15 K. The temperature of the column was maintained constant to within  $\pm 0.02$  K. At a given temperature, each experiment was repeated two to four times to check the reproducibility. Retention times were generally reproducible within 0.001–0.01 min. Absolute values of retention times varied between 2 s and 40 min depending on the individual solute. At each temperature, values of the dead time  $t_G$  identical to the retention time of a nonretainable component were measured. While our GC was equipped with a TCD detector, air was used as a nonretainable component. The estimated overall error in  $\gamma_{13}^{\infty}$  was less than 3%, taking into account the possible errors in determining the column loading, the retention times, and solute vapor pressure. The GLC technique was tested for the system hexane in hexadecane at 298.15 K and the results compared very favorably with the literature values.<sup>17</sup>

**TABLE 3: The Experimental Activity Coefficients at Infinite Dilution  $\gamma_{13}^\infty$  for Some Solutes in Ionic Liquid [EMIM][TFA] at Different Temperatures and Different Column Packing**

solute	column packing/ mass %	298.15 K	308.15 K	318.15 K	328.15 K	338.15 K	348.15 K	358.15 K
<i>n</i> -pentane	25.4	51.8	47.9	45.5	42.5	39.9	37.4	35.5
	44.8	52.8	49.9	45.0	42.6	40.4	38.4	36.2
	34.3	52.4	48.9	45.3	42.6	40.2	38.0	35.7
cyclohexane	25.4	40.5	37.7	35.1	32.5	30.3	28.4	26.8
	44.8	38.6	36.2	33.8	31.5	29.6	27.7	26.0
	34.3	39.7	37.1	34.6	32.1	30.0	27.9	26.3
hex-1-ene	25.4	33.9	32.7	31.3	29.8	28.6	27.5	26.6
	44.8	34.3	32.2	31.1	29.6	28.4	27.6	26.4
	34.3	34.2	32.3	31.2	29.7	28.6	27.6	26.6
hex-1-yne	25.4	5.99	6.12	6.16	6.29	6.39	6.46	6.56
	44.8	5.93	6.04	6.16	6.25	6.32	6.40	6.46
	34.3	5.97	6.07	6.17	6.28	6.34	6.44	6.50

**Theoretical Basis.** The equation developed by Everett<sup>18</sup> and Cruickshank et al.<sup>19</sup> was used in this work to calculate the  $\gamma_{13}^\infty$  of solutes in the ionic liquid

$$\ln \gamma_{13}^\infty = \ln \left( \frac{n_3 RT}{V_N P_1^*} \right) - \frac{P_1^* (B_{11} - V_1^*)}{RT} + \frac{P_o J_2^3 (2B_{12} - V_1^\infty)}{RT} \quad (1)$$

The  $V_N$  denotes the net retention volume of the solute,  $P_o$  the outlet pressure,  $P_o J_2^3$  the mean column pressure,  $n_3$  the number of moles of solvent on the column packing,  $T$  the column temperature,  $P_1^*$  the saturated vapor pressure of the solute at temperature  $T$ ,  $B_{11}$  the second virial coefficient of pure solute,  $V_1^*$  the molar volume of the solute,  $V_1^\infty$  the partial molar volume of the solute at infinite dilution in the solvent, and  $B_{12}$  (where 2 refers to the carrier gas, helium) the mixed second virial coefficient of the solute and the carrier gas. The values of  $B_{11}$  and  $B_{12}$  were calculated using the McGlashan and Potter equation<sup>20</sup>

$$B/V_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n-1)(T_c/T)^{4.5} \quad (2)$$

where  $n$  refers to the number of carbon atoms. By use of the Hudson and McCoubrey combining rules,<sup>21,22</sup>  $V_{12}^c$  and  $T_{12}^c$  were calculated from the critical properties of the pure component.

The pressure correction term  $J_2^3$  is given by

$$J_2^3 = \frac{2(P_i/P_o)^3 - 1}{3(P_i/P_o)^2 - 1} \quad (3)$$

The net retention volume of the solute  $V_N$ , is given by

$$V_N = J_2^3 U_o (t_R - t_G) \quad (4)$$

**TABLE 4: Activity Coefficients at Infinite Dilution  $\gamma_{13}^\infty$  for Some Solutes in 1-Ethyl-3-methyl-imidazolium Trifluoroacetate [EMIM][TFA], 1-Ethyl-3-methyl-imidazolium Bis(trifluoromethylsulfonyl) Imide [EMIM][NTf<sub>2</sub>],<sup>9</sup> and 1-Ethyl-3-methyl-imidazolium Ethylsulfate [EMIM][EtSO<sub>4</sub>]<sup>9</sup> at  $T = 323.15$  K**

	[EMIM][TFA]	[EMIM][NTf <sub>2</sub> ]	[EMIM][EtSO <sub>4</sub> ]
<i>n</i> -hexane	68.8	24.2	81.5
cyclohexane	33.0	13.5	46.1
hex-1-ene	30.4	11.8	40.6
benzene	2.76	1.21	2.80
methanol	0.217	1.21	

where  $t_R$  and  $t_G$  are the retention times for the solute and an unretained gas, respectively, and  $U_o$  is the column outlet flow rate.

The vapor pressure values were calculated using the Antoine equation from constants obtained from the literature.<sup>23,24</sup> Critical data used to calculate  $B_{11}$  and  $B_{12}$ , and ionization energies used in the calculation of  $T_{12}^c$ , were obtained from the literature.<sup>25,26</sup>

## Results and Discussion

Table 1 lists the average  $\gamma_{13}^\infty$  values for three varying amounts of solvent on the column packing in the temperature range from 298.15 to 368.15 K and partial molar excess enthalpies at infinite dilution  $\Delta H_1^{E,\infty}$  determined from the Gibbs–Helmholtz equation

$$\frac{\partial \ln \gamma_i^\infty}{\partial (1/T)} = \frac{\Delta H_1^{E,\infty}}{R} \quad (5)$$

Table 2 lists selectivities  $S_{12}^\infty$  and capacities  $k_2^\infty$  at infinite dilution for ionic liquids based on 1-alkyl-3-methyl-imidazolium cation for different separation problems at  $T = 298.15$  K

$$S_{ij}^\infty = \gamma_{i3}^\infty / \gamma_{j3}^\infty \quad (6)$$

$$k_j^\infty = 1 / \gamma_{j3}^\infty \quad (7)$$

Figures 1–4 show the natural logarithm of the activity coefficients in the ionic liquid as a function of the inverse absolute temperature for all investigated solutes. The values of  $\gamma_{13}^\infty$  for alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, and alcohols increase with an increase of the solute alkyl chain. This behavior is typical for all ILs tested. The values of  $\gamma_{13}^\infty$  for alkanes increase as the number of carbon atoms of alkane increases, as was observed for many ILs. However, in this work the relative influence of gas–liquid interfacial adsorption to retention of alkane on IL was not observed, as tested in recently published works.<sup>32,33</sup> Our values for the different column packing were very similar, as shown in Table 3 for a few solutes as an example. The values of  $\gamma_{13}^\infty$  for alkenes and cycloalkanes are similar for the same carbon number. For alkynes and aromatic hydrocarbons  $\gamma_{13}^\infty$  values are small, the smallest values indicate the stronger interactions between solvent and solute. Alkynes have a triple bond and aromatics have six  $\pi$ -delocalized electrons which can interact with the polar cation and anion of ionic liquid. The smaller values of  $\gamma_{13}^\infty$  involve alcohols. This is great support for the idea that the interactions between the –OH group and anion of



IL are very strong. The results also show that water interacts more strongly with the investigated IL than do alcohols.

Table 4 shows activity coefficients at infinite dilution  $\gamma_{13}^{\infty}$  for some solutes in 1-ethyl-3-methyl-imidazolium trifluoroacetate [EMIM][TFA], 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl) imide [BMIM][NTf<sub>2</sub>],<sup>9</sup> and 1-ethyl-3-methyl-imidazolium ethylsulfate [EMIM][EtSO<sub>4</sub>]<sup>9</sup> at  $T = 323.15$  K. The results demonstrate a significant influence of the anion on the  $\gamma_{13}^{\infty}$  values. For a given cation [EMIM]<sup>+</sup>, the  $\gamma_{13}^{\infty}$  values for hydrocarbons are much higher for the anion [TFA]<sup>−</sup> than those for the anion [NTf<sub>2</sub>]<sup>−</sup> and are similar to those with [EtSO<sub>4</sub>]<sup>−</sup> anion. For methanol the value of  $\gamma_{13}^{\infty}$  is much smaller for the anion [TFA]<sup>−</sup> than those for the anion [NTf<sub>2</sub>]<sup>−</sup>. This means that the activity coefficients and intermolecular interactions of different solutes in IL are very much dependent on the chemical structure of the anion.

For the same cation, the selectivity  $S_{12}^{\infty}$  for separating aromatics and aliphatics takes the order [EtSO<sub>4</sub>]<sup>−</sup> > [TFA]<sup>−</sup> > [NTf<sub>2</sub>]<sup>−</sup>, but the capacity  $k_2^{\infty}$  is largest for [NTf<sub>2</sub>]<sup>−</sup> anion and similar for [EtSO<sub>4</sub>]<sup>−</sup> and [TFA]<sup>−</sup> anions. The selectivity is higher for investigated IL than for NMP or sulfolane, but the capacity is smaller. The selectivity  $S_{12}^{\infty}$  for separating hexane/benzene for simple inorganic anions as [Br]<sup>−</sup> presented for 1-propenyl-3-methyl-imidazolium bromide or longer alkyl substituents was much lower (6.9) at 323.15 K.<sup>34</sup>

## Concluding Remarks

Activity coefficients at infinite dilution for various solutes in the ionic liquid [EMIM][TFA] were measured in the temperature range from 298.15 to 368.15 K using the GLC method. The obtained values of  $\gamma_{13}^{\infty}$  can be useful for the potential technological application of an IL as a selective solvent for separation processes. In the separation of aliphatic hydrocarbons from aromatic hydrocarbons, investigated here, the ionic liquid used shows a higher selectivity than that found by previous workers using organic solvents such as *N*-methyl-2-pyrrolidinone (NMP)<sup>35</sup> or sulfolane.<sup>36</sup> Many of ILs based on 1-alkyl-3-methyl-imidazolium cation show higher selectivity than conventional used entrainers, but in many cases the capacity for NMP and sulfolane is larger. However, the ILs have a huge advantage over conventional organic solvents, namely, the volatility of ILs is negligible and there should be little or no loss of the solvent in industrial separation processes. This is a very important point when green entrainers are required.

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