

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

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The activity coefficients at infinite dilution,  $\gamma_{13}^{\infty}$  for 32 solutes: alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, tetrahydrofuran, *tert*-butyl methyl ether, and water in the ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM][CF<sub>3</sub>SO<sub>3</sub>] were determined by gas–liquid chromatography at the temperatures from 298.15 to 368.15 K. The partial molar excess enthalpies at infinite dilution values  $\Delta H_1^{E,\infty}$  were calculated from the experimental  $\gamma_{13}^{\infty}$  values obtained over the temperature range. The selectivities for the hexane/benzene, cyclohexane/benzene, *n*-hexane/thiophene, *n*-decane/thiophene, cyclohexane/thiophene, toluene/thiophene, and oct-1-ene/thiophene separation problems were calculated from the  $\gamma_{13}^{\infty}$ . Obtained values were compared to the literature values for the other ionic liquids, NMP, and sulfolane.

## Introduction

In recent years ionic liquids (ILs) have become the subject of an increasing number of investigations. Due to their unique properties such as wide liquid range, stability at high temperatures, no flammability and negligible vapor pressure, ionic liquids can be used in separation processes, successfully replace the conventional volatile, flammable and toxic organic solvents. Since the ILs have a negligible vapor pressure, the gas–liquid chromatography (GLC) is a suitable method for measuring the activity coefficients at infinite dilution  $\gamma_{13}^{\infty}$ . Activity coefficients at infinite dilution provide useful information about possibility of using of the IL in separation processes. The selectivities and capacities at infinite dilution can be directly calculated from  $\gamma_{13}^{\infty}$  values for different separation problems. Among the separations of mixtures of industrial importance, an improved separation process for the systems involving aromatic and aliphatic hydrocarbons and liquid–liquid extraction of sulfur (thiophene) from hydrocarbons is of considerable interest.<sup>1–13</sup>

Our previous work includes measurements of  $\gamma_{13}^{\infty}$  for organic solutes in the ionic liquids connected with the separation problem of aromatics from aliphatics included between other ILs: 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide,<sup>1</sup> 1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)-ethyl sulfate,<sup>2</sup> 1-butyl-3-methylimidazolium octyl sulfate,<sup>3</sup> 1-ethyl-3-methylimidazolium thiocyanate [EMIM][SCN]<sup>4</sup> and 1-ethyl-3-methylimidazolium trifluoroacetate [EMIM][TFA].<sup>5</sup> Different types of cations and anions can be combined, and their respective structures tailored, to modify the properties of the resulting IL according to the interest in each specific application. Ionic liquids which have been shown to have potentially excellent entrainer properties for the separation of aliphatic from aromatic hydrocarbons by extractive distillation or extraction are, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf<sub>2</sub>N]), or 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO<sub>4</sub>]), or 4-methyl-*N*-butylpyridinium tetrafluoroborate ([BMPy][BF<sub>4</sub>]).<sup>6–9</sup> Generally, the selectivity for the separation of aromatic hydrocarbons/aliphatic hydrocarbons

decreases with increasing length of the alkyl chain on the imidazolium, or ammonium cation, or anion of the IL.

Other related ILs which have been studied to determine their potential for separating hexane/benzene mixtures, have been reported by our group and also by other workers include the following:  $S_{ij}^{\infty} = 12.4$  (at 298.15 K) for [HMIM][Tf<sub>2</sub>N];<sup>1</sup>  $S_{ij}^{\infty} = 23.0$  (at 313.7 K) for 1-ethyl-2,3-dimethylimidazolium bis{(trifluoromethyl)sulfonyl}imide ([EMMIM][Tf<sub>2</sub>N]);<sup>10</sup>  $S_{ij}^{\infty} = 21.53$  (at 313.9 K) for [EMIM][Tf<sub>2</sub>N],<sup>10</sup> and  $S_{ij}^{\infty} = 36.8$  (at 313 K) for [MBPy][BF<sub>4</sub>].<sup>11</sup> The best selectivity values for hexane/benzene separation (at 298.15 K) were obtained for [EMIM][SCN],  $S_{ij}^{\infty} = 95.4$ ,<sup>4</sup> [EMIM][EtSO<sub>4</sub>],  $S_{ij}^{\infty} = 41.4$ ,<sup>7</sup> or for 1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)ethylsulfate, [BMIM][MDEGSO<sub>4</sub>],  $S_{ij}^{\infty} = 39.7$ <sup>2</sup> and for [EMIM][Tf<sub>2</sub>N],  $S_{ij}^{\infty} = 37.5$ .<sup>12</sup> These values were all determined from activity coefficients at infinite dilution measurements.

The ability of the ILs as 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [OcMIM][Tf<sub>2</sub>N], or 1-octyl-3-methylimidazolium tetrafluoroborate, [OcMIM][BF<sub>4</sub>] to act as solvents in the liquid–liquid extraction of thiophene from aliphatic hydrocarbons (*n*-hexane, *n*-heptane, *n*-hexadecane),<sup>13</sup> or cyclohexane,<sup>14</sup> or methylcyclohexane<sup>15</sup> has been recently developed. According to the new regulations refineries have to reduce sulfur level for liquid fuels. The S-limit will be reduced in Europe to 10 ppm by 2009. Deep desulfurization process will be required by most refiners to achieve legislative requirements in Europe and the USA. New technologies could use different methods to reduce the amount of sulfur including liquid–liquid extraction with application of ILs. The great interest of using ILs to solve this problem is shown by many laboratories.<sup>13–20</sup> Sulfur with aromatic compounds is more difficult to remove from liquid fuel-oils. As model substances the thiophene and thiophene-derivatives have been used.<sup>13–15</sup>

The objective of this work is determination of activity coefficients at infinite dilution for different solutes in ionic liquid using gas–liquid chromatography and to analyze the viability of using the [BMIM][CF<sub>3</sub>SO<sub>3</sub>] as solvent in the separation of aliphatic/aromatic hydrocarbons, and in the separation of thiophene from mixtures with hydrocarbons.

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This paper presents  $\gamma_{13}^\infty$  for 32 solutes (alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, tetrahydrofuran (THF), *tert*-butyl methyl ether (MTBE) and water in the ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM][CF<sub>3</sub>SO<sub>3</sub>] in the temperature range from 298.15 to 368.15 K.

## Experimental Procedures and Results

**Materials or Chemicals.** The ionic liquid [BMIM][CF<sub>3</sub>SO<sub>3</sub>] had a purity of >0.999 mass fraction and was supplied by MERCK. 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 90 °C for approximately 5 h. This procedure removed any volatile chemicals and water from the ionic liquid. The solutes, purchased from Aldrich and Fluka, had a purity above 0.99 mass fraction and 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 PerkinElmer Clarus 500 gas chromatograph equipped with a thermal conductivity detector (TCD). The data were collected and processed using a TotalChrom Workstation software.

The column preparation and the packing method used in this work, has been described previously.<sup>21,22</sup> Glass columns of length 1 and 4 mm internal diameter 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  $\pm 0.0001$  g. The solvent column packing varied from 45.1 to 55.2 mass percent of the ionic liquid, large enough to prevent any residual absorption of solute onto the column packing, as was observed in recently published works.<sup>23,24</sup> 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  $2.5 \text{ cm}^3 \cdot \text{s}^{-1}$ ) at the high temperature (about 100 °C) through about 8 h.

The outlet pressure  $P_o$  was kept at atmospheric pressure. The pressure drop ( $P_i - P_o$ ) was varied between 25 and 80 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 0.8 to  $2.1 \text{ cm}^3 \cdot \text{s}^{-1}$ . Solute injections ranged from 0.01 to  $0.3 \mu\text{L}$  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 2–4 times to check the reproducibility. Retention times were generally reproducible within 0.001–0.01 min. Absolute values of reten-

tion times varied between 1.6 s to 100 min depending on the individual solute and temperature. 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>25</sup>

**Theoretical Basis.** The equation developed by Everett<sup>26</sup> and Cruickshank et al.<sup>27</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>28</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. Using the Hudson and McCoubrey combining rules,<sup>29,30</sup>  $V_{12}^*$  and  $T_{12}^*$  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

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

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 equation and constants taken from the literature.<sup>31–33</sup> Critical data used to calculate  $B_{11}$  and  $B_{12}$ , and ionization energies used in the calculation of  $T_{12}^*$ , were obtained from literature.<sup>34,35</sup>

## Results and Discussion

Table 1 lists the average  $\gamma_{13}^\infty$  values for the 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:

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

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

**TABLE 1: Average Experimental Activity Coefficients at Infinite Dilution  $\gamma_{13}^\infty$  for the Solutes in Ionic Liquid [BMIM][CF<sub>3</sub>SO<sub>3</sub>] 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	35.0	31.0	27.8	25.1	22.9	20.9	19.1		8889
<i>n</i> -hexane	41.6	38.1	34.7	32.1	29.8	27.7	26.0		7033
<i>n</i> -heptane	55.9	51.2	47.4	43.8	40.9	38.2	35.7	33.9	6559
<i>n</i> -octane	78.3	71.8	65.9	61.0	57.2	53.1	49.9	47.0	6662
<i>n</i> -nonane	113	102	93.2	86.1	79.9	74.0	69.2	64.7	7200
<i>n</i> -decane	163	148	135	124	114	105	97.8	91.0	7644
cyclopentane	14.9	13.7	12.6	11.8	11.0	10.3	9.68		6441
cyclohexane	20.6	18.9	17.5	16.2	15.2	14.2	13.3	12.5	6458
cycloheptane	24.8	23.0	21.3	19.9	18.6	17.6	16.6	15.7	5957
cyclooctane	32.4	29.8	27.5	25.6	23.9	22.3	21.0	19.9	6346
pent-1-ene	13.7	12.9	12.0	11.4	10.7	10.2	9.73		5128
hex-1-ene	17.6	16.7	15.9	15.2	14.5	14.0	13.4	12.9	4073
hept-1-ene	24.7	23.5	22.4	21.4	20.5	19.7	19.0	18.3	3893
oct-1-ene	35.5	33.5	31.9	30.2	28.9	27.6	26.5	25.6	4282
pent-1-yne	2.65	2.71	2.75	2.80	2.84	2.89	2.93		−1484
hex-1-yne	3.68	3.75	3.83	3.89	3.96	4.02	4.06	4.13	−1484
hept-1-yne	5.36	5.44	5.53	5.58	5.66	5.72	5.78	5.85	−1124
oct-1-yne	7.83	7.88	7.93	7.97	8.02	8.06	8.10	8.13	−500
benzene	1.55	1.57	1.58	1.59	1.61	1.62	1.63	1.64	−721
toluene	2.31	2.33	2.35	2.37	2.40	2.42	2.43	2.45	−812
ethylbenzene	3.71	3.71	3.71	3.70	3.70	3.70	3.70	3.69	68
<i>o</i> -xylene		3.06	3.08	3.11	3.13	3.15	3.16	3.18	−619
<i>m</i> -xylene		3.63	3.65	3.67	3.69	3.71	3.72	3.74	−474
<i>p</i> -xylene		3.50	3.52	3.55	3.57	3.60	3.62	3.64	−655
methanol	0.737	0.701	0.669	0.641	0.617	0.593	0.571	0.551	3764
ethanol	1.07	1.01	0.958	0.911	0.871	0.832	0.798	0.768	4338
propan-1-ol		1.27	1.20	1.14	1.09	1.04	1.00	0.959	4371
butan-1-ol		1.66	1.57	1.49	1.42	1.35	1.29	1.23	4710
water				0.809	0.776	0.747	0.721	0.696	3773
THF	1.21	1.22	1.23	1.24	1.25	1.25	1.26	1.27	−704
thiophene	1.14	1.15	1.15	1.16	1.17	1.18	1.18	1.19	−543
MTBE	4.21	4.19	4.17	4.15	4.14	4.12	4.10		390

**TABLE 2: Selectivities  $S_{12}^\infty$  and Capacities  $k_2^\infty$  at Infinite Dilution for Ionic Liquids Based on 1-Butyl-3-methylimidazolium 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))	
[BMIM][MDEGSO <sub>4</sub> ] <sup>a</sup>	39.7	16.9	0.49
[BMIM][BF <sub>4</sub> ] <sup>b</sup>	37.3 <sup>h</sup>	19.7 <sup>h</sup>	0.58 <sup>h</sup>
[BMIM][PF <sub>6</sub> ] <sup>c</sup>	–	16.7 <sup>h</sup>	0.63 <sup>h</sup>
[BMIM][CF <sub>3</sub> SO <sub>3</sub> ] <sup>i</sup>	26.8	13.3	0.64
[BMIM][Tf <sub>2</sub> N] <sup>d</sup>	16.7 <sup>h</sup>	10.2 <sup>h</sup>	1.14 <sup>h</sup>
[BMIM][OCSO <sub>4</sub> ] <sup>e</sup>	5.1	3.5	0.70
NMP <sup>f</sup>	13.0 <sup>h</sup>	8.0 <sup>h</sup>	0.96 <sup>h</sup>
NMP + 3% (w/w) water <sup>f</sup>	16.3 <sup>h</sup>	9.8 <sup>h</sup>	0.75 <sup>h</sup>
NMP + 6% (w/w) water <sup>f</sup>	19.0 <sup>h</sup>	10.9 <sup>h</sup>	0.52 <sup>h</sup>
sulfolane <sup>g</sup>	20.5 <sup>h</sup>	12.5 <sup>h</sup>	0.42 <sup>h</sup>

<sup>a</sup> Reference 2. <sup>b</sup> Reference 36. <sup>c</sup> Reference 37. <sup>d</sup> Reference 7. <sup>e</sup> Reference 3. <sup>f</sup> Reference 40. <sup>g</sup> Reference 41. <sup>h</sup> Calculated from extrapolated values. <sup>i</sup> This work.

$\gamma_{13}^\infty$  for series of solutes increase with an increase of the solute alkyl chain and decrease of temperature. Only for alkenes, alkynes, aromatic hydrocarbons, THF and thiophene the function of temperature is opposite. This behavior is typical for other ILs. High values of  $\gamma_{13}^\infty$  signify very small interactions between solute and solvent. The highest values of  $\gamma_{13}^\infty$  can be observed for alkanes, alkenes, and cycloalkanes. It is typical for ionic liquids based on imidazolium cation. The values of  $\gamma_{13}^\infty$  for alkenes are lower than for alkanes for the same carbon number. This is caused by interaction of double bonding in alkenes with polar ionic liquid. Cyclic structure of cycloalkanes reduces the

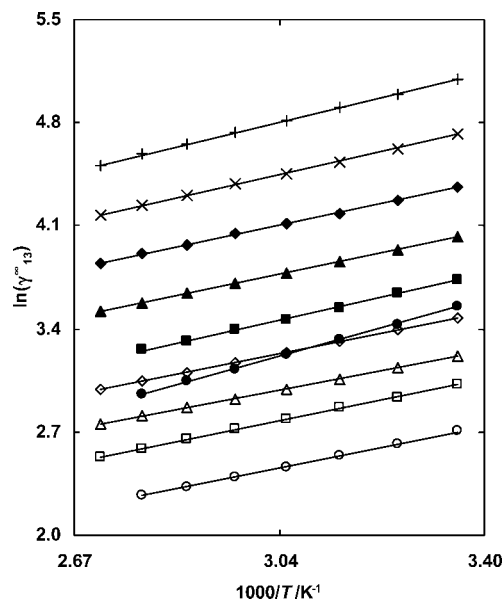
value of  $\gamma_{13}^\infty$  in comparison to the corresponding linear alkane. Alkynes and aromatic hydrocarbons have smaller values of  $\gamma_{13}^\infty$  than alkanes, alkenes and cycloalkanes. The smallest values of  $\gamma_{13}^\infty$  indicate the stronger interactions between solvent and solute. Triple bond in alkynes and six  $\pi$ -delocalized electrons in aromatics can strong interact with the polar cation and anion of ionic liquid. The smallest values of  $\gamma_{13}^\infty$  have been observed for alcohols, THF, thiophene and water. These polar compounds interact very strongly with polar ionic liquid. In this case, the major influence on values of  $\gamma_{13}^\infty$  has very strong interactions between –OH group in alcohols and water and anion of the IL and interactions between polar –O– and –S– group in THF and thiophene, respectively, and cation of the IL. The results also show that water interacts with [BMIM][CF<sub>3</sub>SO<sub>3</sub>] similar to alcohols. The isolated –O– group in MTBE can not interact strongly with IL, that is why the value of  $\gamma_{13}^\infty$  is not as small as value for the other compounds with similar characteristic group.

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

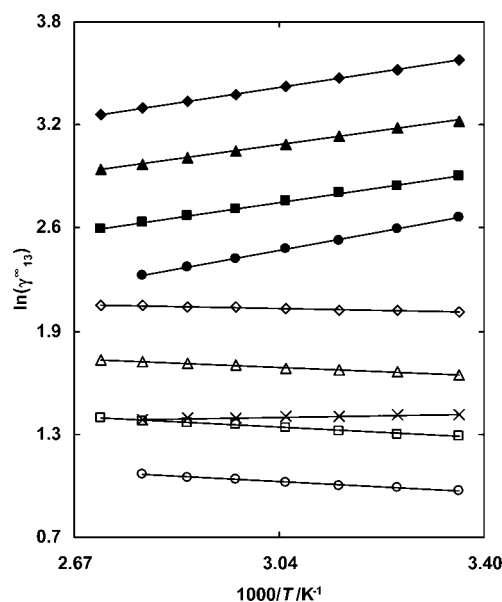
$$S_{ij}^\infty = \gamma_{i3}^\infty / \gamma_{j3}^\infty \quad (6)$$

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

For *n*-hexane/benzene separation problem selectivity  $S_{12}^\infty$  takes following order: [MDEGSO<sub>4</sub>]<sup>–</sup> > [BF<sub>4</sub>]<sup>–</sup> > [PF<sub>6</sub>]<sup>–</sup> > [CF<sub>3</sub>SO<sub>3</sub>]<sup>–</sup> > [Tf<sub>2</sub>N]<sup>–</sup> > [OCSO<sub>4</sub>]<sup>–</sup> for ILs based on the same [BMIM]<sup>+</sup> cation, but the capacity takes a different order, as follows: [Tf<sub>2</sub>N]<sup>–</sup> > [OCSO<sub>4</sub>]<sup>–</sup> > [CF<sub>3</sub>SO<sub>3</sub>]<sup>–</sup> > [PF<sub>6</sub>]<sup>–</sup> > [BF<sub>4</sub>]<sup>–</sup> > [MDEGSO<sub>4</sub>]<sup>–</sup>. As a conclusion, we can underline the point that the [CF<sub>3</sub>SO<sub>3</sub>]<sup>–</sup> anion (this work) reveals the average value



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

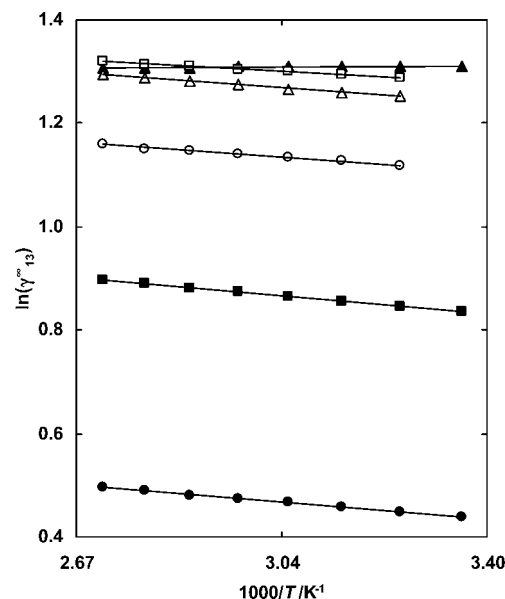


**Figure 2.** Plot of  $\ln(\gamma_{13}^{\infty})$  versus  $1/T$  for the solutes: (●) pent-1-ene, (■) hex-1-ene, (▲) hept-1-ene, (◆) oct-1-ene, (○) pent-1-yne, (□) hex-1-yne, (Δ) hept-1-yne, (◇) oct-1-yne, (×) MTBE.

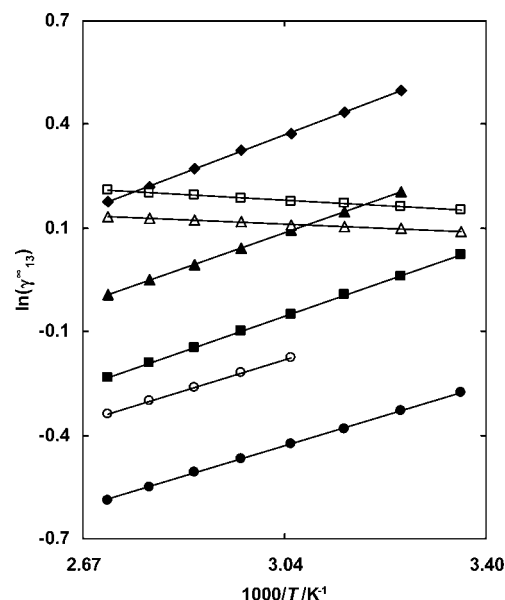
of selectivity and capacity. For the investigated IL the selectivity is higher than for NMP or sulfolane, and the capacity is also higher than that for sulfolane and NMP + 6% (w/w) water.

Table 3 shows activity coefficients at infinite dilution  $\gamma_{13}^{\infty}$  for some solutes in 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF<sub>4</sub>],<sup>36</sup> 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF<sub>6</sub>],<sup>7</sup> 1-butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM][CF<sub>3</sub>SO<sub>3</sub>], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIM][Tf<sub>2</sub>N]<sup>7</sup> and 1-butyl-3-methylimidazolium octylsulfate [BMIM][O<sub>8</sub>SO<sub>4</sub>]<sup>3</sup> at  $T = 323.15$  K. This table demonstrates a significant influence of the structure of anion on the  $\gamma_{13}^{\infty}$  values.

Table 4 compares values of  $\gamma_{13}^{\infty}$  obtained in this work with those measured by Ge et al.<sup>38,39</sup> In some cases differences are very small (for example 1% for THF, 5% for methanol), but generally differences are about 15%. Differences are probably



**Figure 3.** Plot of  $\ln(\gamma_{13}^{\infty})$  versus  $1/T$  for the solutes: (●) benzene, (■) toluene, (▲) ethylbenzene, (○) *o*-xylene, (□) *m*-xylene, (Δ) *p*-xylene.



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

caused by different values of the saturated vapor pressure  $P_1^*$  and by other thermophysical data of solutes taken to the calculations. Authors used different source of fundamental data for pure solutes than in this work. It is known problem that source of data are very often differing. The biggest difference is for *n*-decane, about 500%. There is probably calculation error in Ge et al. work,<sup>38</sup> because differences in  $\gamma_{13}^{\infty}$  between *n*-nonane and *n*-decane are very high in that work, but between *n*-octane and *n*-nonane are small. Deviations can come also from an error of Ge and co-workers in the measurements of the flow rate or/and the mass of the stationary phase. Similar errors of this team were observed with other ILs.

Table 5 summarizes the selectivities and capacities for chosen hydrocarbon/thiophene separation problems. Very optimistic results we can see for *n*-alkanes (*n*-hexane and *n*-decane), cyclohexane and oct-1-yne. The selectivity of *n*-alkane/thiophene



**TABLE 3: Activity Coefficients at Infinite Dilution  $\gamma_{13}^{\infty}$  for Some Solutes in Ionic Liquids Based on 1-Butyl-3-methylimidazolium Cation at  $T = 323.15$  K**

	[MDEGSO <sub>4</sub> ] <sup>a</sup>	[BF <sub>4</sub> ] <sup>b</sup>	[PF <sub>6</sub> ] <sup>c</sup>	[CF <sub>3</sub> SO <sub>3</sub> ] <sup>d</sup>	[NTf <sub>2</sub> ] <sup>d</sup>	[OCSO <sub>4</sub> ] <sup>e</sup>
n-hexane	59.0 <sup>h</sup>	54.2		33.4 <sup>i</sup>	12.7	7.85 <sup>i</sup>
cyclohexane	25.2 <sup>h</sup>	28.3	21.6	16.8 <sup>i</sup>	7.73	5.12 <sup>i</sup>
hex-1-ene	26.8 <sup>h</sup>			15.5 <sup>i</sup>	6.97	6.01 <sup>i</sup>
benzene	2.01 <sup>h</sup>	1.77	1.96	1.59 <sup>i</sup>	0.903	1.45 <sup>i</sup>
methanol	0.327 <sup>h</sup>	0.646 <sup>f</sup>	1.98	0.655 <sup>i</sup>	1.06 <sup>g,i</sup>	0.363 <sup>i</sup>

<sup>a</sup> Reference 2. <sup>b</sup> Reference 36. <sup>c</sup> Reference 37. <sup>d</sup> Reference 7. <sup>e</sup> Reference 3. <sup>f</sup> Reference 42. <sup>g</sup> Reference 43. <sup>h</sup> Extrapolated value. <sup>i</sup> Interpolated value.

**TABLE 4: Comparison of Values of  $\gamma_{13}^{\infty}$  Obtained in this Work with  $\gamma_{13}^{\infty}$  Measured by Ge et al.<sup>38,39</sup> at  $T = 298.15$  K**

solute	$\gamma_{13}^{\infty}$ this work	$\gamma_{13}^{\infty}$ <sup>a,c</sup>	solute	$\gamma_{13}^{\infty}$ this work	$\gamma_{13}^{\infty}$
n-pentane	35.0	27.2	ethylbenzene	3.71	4.6 <sup>a,c</sup>
n-hexane	41.6	39.2	o-xylene	3.04 <sup>c</sup>	3.6 <sup>a,c</sup>
n-heptane	55.9	58.2	m-xylene	3.61 <sup>c</sup>	4.8 <sup>a,c</sup>
n-octane	78.3	91.4	p-xylene	3.47 <sup>c</sup>	4.3 <sup>a,c</sup>
n-nonane	113	128.4	methanol	0.737	0.70 <sup>b,c</sup>
n-decane	163	978.3	ethanol	1.07	1.16 <sup>b,c</sup>
cyclohexane	20.6	23.1	propan-1-ol	1.34 <sup>c</sup>	1.52 <sup>b,c</sup>
benzene	1.55	1.8	butan-1-ol	1.77 <sup>c</sup>	2.06 <sup>b,c</sup>
toluene	2.31	2.7	THF	1.21	1.22 <sup>b,c</sup>

<sup>a</sup> Reference 38. <sup>b</sup> Reference 40. <sup>c</sup> Extrapolated value.

**TABLE 5: Selectivities  $S_{12}^{\infty}$  and Capacity  $k_2^{\infty}$  at Infinite Dilution for Hydrocarbon/Thiophene Separation Problem Using Ionic Liquid [BMIM][CF<sub>3</sub>SO<sub>3</sub>] at  $T = 298.15, 318.15, 338.15$ , and  $358.15$  K**

separation mixture	T/K			
	298.15	318.15	338.15	358.15
n-hexane/thiophene				
$S_{12}^{\infty}$	36.5	30.2	25.5	22.0
$k_2^{\infty}$	0.88	0.87	0.85	0.85
n-decane/thiophene				
$S_{12}^{\infty}$	143.0	117.4	97.4	82.9
cyclohexane/thiophene				
$S_{12}^{\infty}$	18.1	15.2	13.0	11.3
toluene/thiophene				
$S_{12}^{\infty}$	2.0	2.0	2.0	2.0
oct-1-yne/thiophene				
$S_{12}^{\infty}$	31.1	27.7	24.7	22.4

separation increases with an increase of *n*-alkane chain, and decreases with an increase of temperature. The highest value of selectivity  $S_{12}^{\infty} = 143.0$  was observed for *n*-decane/thiophene at 298.15 K. It is possible to make some comparisons between different ILs used in this separation problem, even the other results were observed in ternary liquid–liquid equilibrium, LLE. Using [Ocmim][BF<sub>4</sub>] the highest value of selectivity of separation for *n*-hexane/thiophene at 298.15 K was 18.69,<sup>14</sup> or using [Ocmim][Tf<sub>2</sub>N] 7.55<sup>13</sup> in comparison to 36.5 (this work). The result obtained in this work for *n*-decane/thiophene (143.0) was much better than for *n*-hexadecane with using [Ocmim][Tf<sub>2</sub>N].<sup>13</sup> For cyclohexane/thiophene at 298.15 K these values were: 18.1 (this work) and 8.5 ([Ocmim][BF<sub>4</sub>]).<sup>14</sup> Unfortunately, the capacity at infinite dilution,  $k_2^{\infty}$  is small for thiophene (0.88). The results for aromatic compounds, because of similarity of the structure with thiophene are of little use in solvent extraction processes for separating aromatic compounds from thiophene (see Table 5, toluene/thiophene separation).

### Concluding Remarks

Activity coefficients at infinite dilution for various solutes in the ionic liquid 1-butyl-3-methylimidazolium trifluoromethane-

sulfonate [BMIM][CF<sub>3</sub>SO<sub>3</sub>] were measured in the temperature range from 298.15 to 368.15 K using GLC method.

The results in comparison with another ILs demonstrate a significant influence of the anion on the  $\gamma_{13}^{\infty}$  values. These values were very much higher than for entrainers such as NMP<sup>40</sup> or sulfolane,<sup>41</sup> which are used in separation processes of aliphatic compounds from aromatic hydrocarbons by extraction in industry.

The results in Table 5 together with other properties such as a very low vapor pressure, paints a very rosy picture of how just potentially important and useful IL ([BMIM][CF<sub>3</sub>SO<sub>3</sub>]) can be in the desulfurization process. The results however, must be tempered with constraints related to solubility, difficulty in regeneration and even toxicity, before making serious 'green' claims for the usefulness of ILs in industry.

These data are very important in understanding the nature of ILs and are also important in expanding and developing thermodynamic models involving mixtures containing ILs.

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**Supporting Information Available:** Tables of experimental activity coefficients at infinite dilution  $\gamma_{13}^{\infty}$  for the solutes in ionic liquid [BMIM][CF<sub>3</sub>SO<sub>3</sub>] at different temperatures and excess molar enthalpies at infinite dilution  $\Delta H_1^{\text{E},\infty}$  for investigated ionic liquid for three different columns, critical constants,  $V_c$ ,  $T_c$ , and ionization energies used in calculation of virial coefficients  $B_{11}$  and  $B_{12}$ , vapor pressures,  $P_1^*$ , molar volumes,  $V_1^*$ , and virial coefficients  $B_{11}$  and  $B_{12}$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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