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# Determination of Activity Coefficients at Infinite Dilution of 35 Solutes in the Ionic Liquid, 1-Butyl-3-methylimidazolium Tosylate, Using Gas−Liquid Chromatography

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The activity coefficients at infinite dilution, $\gamma_{13}^{\infty}$, for hydrocarbon solutes, alcohols, water, thiophene, ethers, and ketones in the ionic liquid 1-butyl-3-methylimidazolium tosylate (*p*-toluenesulfonate), [BMIM][TOS], have been determined by gas−liquid chromatography at temperatures $T$ = (338.15, 348.15, 358.15, and 368.15) K. The selectivity values have been calculated at $T$ = 338.15 K, and the results indicate that the ionic liquid [BMIM][TOS] should be considered as a solvent for separation of aromatic sulfur compounds from alkanes. The partial molar excess enthalpy values at infinite dilution $\Delta H_1^{E\infty}$, determined in this work, together with the values $\gamma_{13}^{\infty}$ have been discussed in terms of intermolecular interactions and compared to results of related systems obtained earlier by us and from the literature.

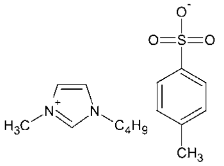
## Introduction

This work is a continuation of our investigations into the activity coefficients at infinite dilution $\gamma_{13}^{\infty}$ values of tosylate-based ionic liquids (ILs).[1,2] Aliphatic hydrocarbons are weakly soluble in tosylate-based ionic liquids, whereas aromatic compounds are very soluble.[3−9] The results of solubility in the binary systems are a good indication that the ILs may show good separation of aromatics from aliphatics. It was shown by us using phase equilibria study of binary systems that aliphatic hydrocarbons have a low solubility and benzene and *n*-alkylbenzenes a high solubility in the ILs: tetra-*n*-butylphosphonium tosylate, [$B_4$P][TOS],[4] or tri-*iso*-butyl(methyl)phosphonium tosylate, [$B_3$MP][TOS],[5] or 1-butyl-3-methylimidazolium tosylate, [BMIM][TOS],[6] or *N*-butyl-4-methylpyridinium tosylate, [BM$^4$Py][TOS],[7] or *N*-butyl-3-methylpyridinium tosylate, [BM$^3$Py][TOS].[8] Recently, our group determinated the solid−liquid equilibria (SLE) of thiophene with ionic liquids involving tosylate-based ILs: [BM$^4$Py][TOS], or [BM$^3$Py][TOS], or *N*-hexyl-3-methylpyridinium tosylate [HM$^3$Py][TOS], or 1,4-dimethylpyridinium tosylate [M$^{1,4}$Py][TOS], or 2,4,6-collidine tosylate [M$^{2,4,6}$Py][TOS] at ambient pressure.[9] The results showed that aromatic sulfur compounds (e.g., thiophene) are very soluble in these ILs and that some of these ILs can be used for the extraction of sulfur compounds from alkanes.

The [BMIM][TOS] (Table 1) reveals simple eutectic mixtures with complete miscibility in the liquid phase in the binary systems containing water or an alcohol.[6] In the case of mixtures {[BMIM][TOS] + *n*-hexane, or benzene, or alkylbenzene, or thiophene}, the eutectic systems with mutual immiscibility in the liquid phase with an upper critical solution temperature (UCST) were detected.[6] The basic thermal properties of the pure [BMIM][TOS], that is, melting and glass-transition temperatures, the enthalpy of fusion, as well as the densities have been presented by us earlier.[6]

The careful examination of the activity coefficients at infinite dilution of tosylate-based ILs has shown that the selectivities, $S_{12}^{\infty}$ ($S_{ij}^{\infty} = \gamma_{i3}^{\infty}/\gamma_{j3}^{\infty}$), and capacities, $k_2^{\infty}$ ($k_j^{\infty} = 1/\gamma_{j3}^{\infty}$), at infinite dilution for different ionic liquids based on imidazolium, or pyridinium, or phosphonium cations with the tosylate anion are promising for the separation of aromatics or thiophene from aliphatics. However, the pyridinium cation in the [BM$^4$Py][TOS][7] shows much lower selectivities for separating aromatics from aliphatics than does [EMIM][TOS] (values extrapolated to the infinite dilution)[10] or lower in comparison with many other ionic liquids discussed in a recently published review.[11]

**Table 1. Investigated Ionic Liquid: Chemical Structure, Name, and Abbreviation**

| Structure | name, abbreviation |
|---|---|
|  | 1-butyl-3-methylimidazolium tosylate,<br>[BMIM][TOS] |

Thus, this article is concerned with the investigation of activity coefficients at infinite dilution, $\gamma_{13}^{\infty}$, of alkanes, cycloalkanes, alk-1-enes, alk-1-ynes, benzene, alkylbenzenes, alcohols, water, thiophene, ethers, and ketones in the ionic liquid 1-butyl-3-methylimidazolium tosylate using gas−liquid chromatography at temperatures $T$ = (338.15, 348.15, 358.15, and 368.15) K.

## Experimental Section

***Materials.*** The solvent, ionic liquid, that is, 1-butyl-3-methylimidazolium tosylate, [BMIM][TOS], was supplied by Fluka, Germany, and was reported to have a mass fraction purity of ≥ 97 %. Immediately prior to measurements, the ionic liquid was thoroughly degassed and dried by subjecting the subcooled liquid to a very low pressure of about $5 \cdot 10^{-3}$ Pa at a temperature about 300 K for approximately 24 h. This procedure removed any volatile chemicals and water from the ionic liquid. No other attempt was made to analyze impurities in the ionic liquid. Water was twice distilled, degassed, deionized, and filtered with

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Milipore Elix3. The solutes, alkanes, cycloalkanes, alk-1-enes, alk-1-ynes, benzene, alkylbenzenes, alcohols, thiophene, ethers, and ketones, were obtained from Sigma-Aldrich Chemie GmbH, Steinheim, Germany (mass fraction purity of ≥ 97 %). Solutes were used without further purification because the GLC technique separates any impurities.

***Experimental Procedure.*** The experiments were performed using a Perkin-Elmer Clarus 500 gas chromatograph 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.[1,2] Glass columns of length (1 and 4) mm internal diameter were used. Coating the solid support material with the ionic liquid was performed by dispersing a certain portion of Chromosorb into a solution of the ionic liquid in methanol followed by evaporation of the solvent using a rotary evaporator. The masses of the stationary phase and of the solid support were weighed with a precision ± 0.0001 g. The solvent column packing varied from (0.448 to 0.5203) mass fraction of the ionic liquid, large enough to prevent any residual adsorption of solute onto the column packing, as was observed in previous works.[10,12] For each temperature, the measurements were repeated by using two 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 experiments, each column was conditioned by passing carrier gas at high flow rate (about 2 $\mathrm{cm^3 \cdot s^{-1}}$) and at the high temperature (about 360 K) over a period of about 8 h.

The outlet pressure $P_o$ was kept at atmospheric pressure. The pressure drop ($P_i - P_o$) varied between (40 and 80) kPa depending on the flow rate of the carrier gas. The pressure drop was measured by a pressure transducer implemented in the chromatograph with an uncertainty of ± 0.1 kPa. The atmospheric pressure was measured using a digital barometer with an uncertainty of ± 0.1 hPa.

The carrier gas was helium, and the flow rate of the 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 (1.1 to 2.5) $\mathrm{cm^3 \cdot s^{-1}}$. Solute injections ranged from (0.01 to 0.3) μL and were considered to be at infinite dilution on the column. Injection was provided manually with the syringe 1 μL.

Experiments were carried out at different temperatures (in steps of 5 K) in the range from $T = 338.15$ K to $T = 368.15$ K. High temperatures of these measurements were predicted by the high melting temperature of the IL, $T_{\mathrm{fus}} = 330.16$ K.[6] The temperature of the column was maintained constant to within ± 0.02 K. The temperature of the column was controlled many times in the ovens of a chromatograph with an additional electronic thermometer P 550 (Dostmann electronic GmbH). At a given temperature, each experiment was repeated 2 to 4 times to check the reproducibility. The average of these measurements was taken as the final value for one loading of the column. Retention times were generally reproducible within (0.001 to 0.01) min. At each temperature, values of the dead time $t_G$ identical to the retention time of a nonretainable component were measured. While our apparatus 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 error associated with the selectivity and capacity is less than 4 %, which means "1" for the average values of selectivity and "0.01" for the average values of capacity.

The GLC technique was tested for the system hexane in hexadecane at $T = 298.15$ K, and the results compared very favorably with the literature values.[13]

## Theoretical Basis

The equation developed by Everett[14] and Cruickshank et al.[15] was used in this work to calculate the $\gamma_{13}^{\infty}$ of solutes in the ionic liquid

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

In this work, subscript 1 refers to a solute; 2 refers to the carrier gas; and 3 refers to the solvent, [BMIM][TOS]. $n_3$ is the number of moles of solvent on the column packing; $R$ is a gas constant; $T$ is the column temperature; $V_N$ denotes the net retention volume of the solute; $P_1^*$ is the saturated vapor pressure of the solute at temperature $T$; $B_{11}$ is the second virial coefficient of pure solute; $V_1^*$ is the molar volume of the solute; $P_o$ is the outlet pressure; $P_o J_2^3$ is the mean column pressure; $B_{12}$ (where 2 refers to helium) is the mixed second virial coefficient of the solute and the carrier gas; and $V_1^{\infty}$ is the partial molar volume of the solute at infinite dilution in the solvent. The $V_1^{\infty}$ was taken as the same as $V_1^*$ for every solute.

The values of $B_{11}$ and $B_{12}$ were calculated using the McGlashan and Potter equation[16]

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

where $n$ refers to the number of carbon atoms. Using the Hudson and McCoubrey combining rules,[17] $V_{12}^c$ and $T_{12}^c$ were calculated from the critical properties of the pure components.[18]

The pressure correction term $J_2^3$ is given by[19]

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

The net retention volume of the solute, $V_N$, is given by[20]

$$V_N = J_2^3 U_o (t_R - t_G) \tag{4}$$

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 the equation and constants taken from the literature.[21−23] 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.[24,25]

## Results and Discussion

Table 2 lists the average $\gamma_{13}^{\infty}$ values for the varying amounts of solvent on the column packing in the temperature range from (338.15 to 368.15) K and partial molar excess enthalpies at infinite dilution, $\Delta H_1^{E,\infty}$, determined from the Gibbs−Helmholtz equation

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

The results were determined for different columns, each operated by two different researchers. Figures 1 to 5 show the

**Table 2. Average Experimental Activity Coefficients at Infinite Dilution, $\gamma_{13}^{\infty}$, for the Solutes in Ionic Liquid [BMIM][TOS] at Different Temperatures and the Partial Molar Excess Enthalpies at Infinite Dilution, $\Delta H_1^{E,\infty}$**

| | $T$/K | | | | $(\Delta H_1^{E,\infty})$ |
|---|---|---|---|---|---|
| | 338.15 | 348.15 | 358.15 | 368.15 | $(J \cdot mol^{-1})$ |
| *n*-hexane | 36.3 | 31.5 | 29.2 | 27.6 | 1848 |
| *n*-heptane | 48.1 | 42.2 | 39.2 | 36.6 | 1836 |
| *n*-octane | 63.9 | 57.7 | 53.0 | 49.6 | 1728 |
| *n*-nonane | 86.1 | 77.5 | 71.3 | 66.5 | 1748 |
| *n*-decane | 118.7 | 106.5 | 98.3 | 90.8 | 1800 |
| cyclopentane | 11.3 | 9.92 | 9.34 | 8.99 | 1525 |
| cyclohexane | 16.3 | 14.6 | 13.4 | 12.5 | 1808 |
| cycloheptane | 17.7 | 16.3 | 15.4 | 14.5 | 1355 |
| cyclooctane | 21.3 | 19.7 | 18.6 | 17.6 | 1300 |
| pent-1-ene | 13.7 | 12.6 | 11.9 | 11.2 | 1350 |
| hex-1-ene | 18.0 | 16.6 | 15.7 | 14.9 | 1275 |
| hept-1-ene | 24.2 | 22.5 | 21.5 | 20.4 | 1133 |
| oct-1-ene | 33.1 | 31.0 | 29.5 | 28.2 | 1091 |
| hex-1-yne | 3.69 | 3.78 | 3.86 | 3.94 | −444 |
| hept-1-yne | 5.13 | 5.23 | 5.34 | 5.43 | −387 |
| oct-1-yne | 7.12 | 7.28 | 7.39 | 7.45 | −310 |
| benzene | 1.96 | 1.93 | 1.93 | 1.93 | 100 |
| toluene | 3.03 | 3.01 | 2.99 | 2.97 | 148 |
| ethylbenzene | 4.45 | 4.40 | 4.36 | 4.32 | 207 |
| *o*-xylene | 4.07 | 4.01 | 3.96 | 3.93 | 233 |
| *m*-xylene | 4.76 | 4.67 | 4.63 | 4.58 | 249 |
| *p*-xylene | 4.73 | 4.64 | 4.61 | 4.56 | 245 |
| methanol | 0.217 | 0.219 | 0.221 | 0.223 | −184 |
| ethanol | 0.359 | 0.357 | 0.358 | 0.358 | 12 |
| propan-1-ol | 0.437 | 0.434 | 0.437 | 0.437 | −10 |
| water | 0.191 | 0.196 | 0.201 | 0.207 | −544 |
| thiophene | 1.11 | 1.13 | 1.14 | 1.16 | −282 |
| THF | 1.88 | 1.87 | 1.86 | 1.85 | 118 |
| MTBE | 8.28 | 7.84 | 7.58 | 7.37 | 784 |
| diethyl ether | 6.57 | 6.36 | 6.16 | 5.93 | 685 |
| dipropyl ether | 15.5 | 15.2 | 14.2 | 13.6 | 923 |
| dibutyl ether | 29.2 | 27.7 | 26.3 | 25.2 | 1002 |
| acetone | 1.48 | 1.46 | 1.45 | 1.42 | 272 |
| pentan-2-one | 2.68 | 2.64 | 2.61 | 2.58 | 252 |
| pentan-3-one | 2.68 | 2.65 | 2.63 | 2.60 | 191 |

natural logarithm of the activity coefficients of solutes in the ionic liquid as a function of the inverse absolute temperature for all systems investigated.

In each group of compounds, alkanes, cycloalkanes, alk-1-enes, alk-1-ynes, aromatic hydrocarbons, alcohols, ethers, and ketones, $\gamma_{13}^{\infty}$ increases with an increase of solute alkyl chain. This is also a typical behavior for other measured ionic liquids based on the alkyl-imidazolium cation. For alkanes, cycloalkanes, alk-1-enes, aromatic hydrocarbons, ethers, and ketones, values of $\gamma_{13}^{\infty}$ decrease with increasing temperature. For the rest of the investigated solutes, alkyn-1-es, alcohols, water, and thiophene, this dependency is reversed (see Figures 2, 4, and 5). For ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [BMIM][$CF_3SO_3$], the same behavior was found.[26] For the alcohols, the low values can be attributed to the interactions between the lone pair of electrons on the oxygen atom of the alcohol with the positively charged cation of the ionic liquid.

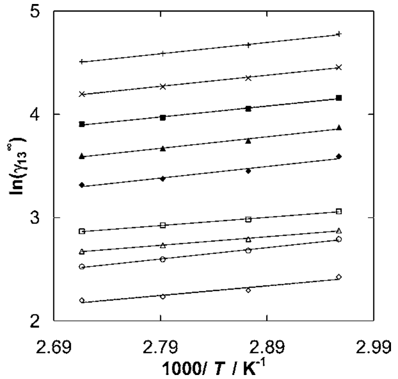

**Figure 1.** Plot of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ of [BMIM][TOS] for the solutes: ●, *n*-hexane; ▲, *n*-heptane; ■, *n*-octane; ×, *n*-nonane; +, *n*-decane; ◇, cyclopentane; ○, cyclohexane; Δ, cycloheptane; □, cyclooctane.

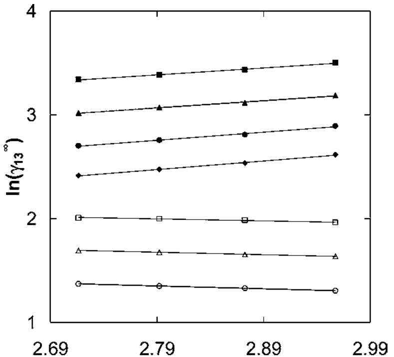

**Figure 2.** Plot of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for [BMIM][TOS] for the solutes: ◆, pent-1-ene; ●, hex-1-ene; ▲, hept-1-ene; ■, oct-1-ene; ○, hex-1-yne; Δ, hept-1-yne; □, oct-1-yne.

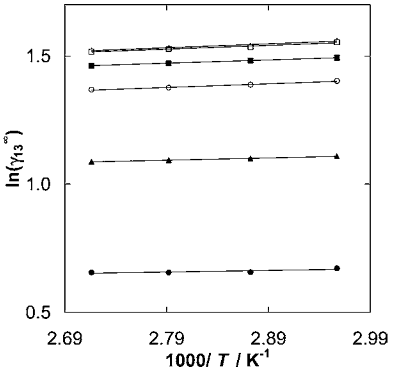

**Figure 3.** Plot of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for [BMIM][TOS] for the solutes: ●, benzene; ▲, toluene; ■, ethylbenzene; ○, *o*-xylene; Δ, *m*-xylene; □, *p*-xylene.

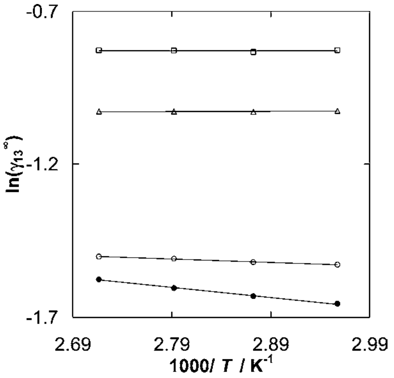

**Figure 4.** Plot of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for [BMIM][TOS] for the solutes: ○, methanol; Δ, ethanol; □, propan-1-ol; ●, water.

The $\Delta H_1^{E,\infty}$ values are negative for alk-1-ynes, methanol, propan-1-ol water, and thiophene, as is shown in Figures 2, 4, and 5 for the temperature dependencies. Such properties were shown by other ILs such as for example [BMIM][$CF_3SO_3$].[26] The negative values of the partial molar excess enthalpies at infinite dilution mean that the interactions of solute−solvent pairs are higher than for solute−solute pairs. This behavior is caused by interaction between polar cations or/and anions of the IL and triple bond in alk-1-ynes, polar hydroxyl groups in

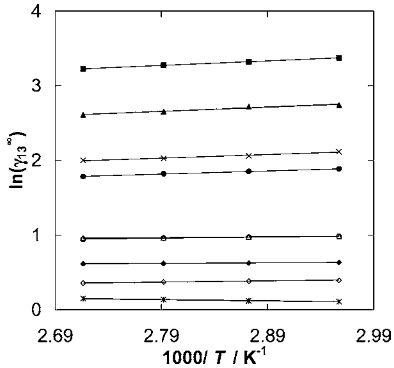

**Figure 5.** Plot of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for [BMIM][TOS] for the solutes: ●, diethyl ether; ▲, dipropyl ether; ■, dibutyl ether; ◆, THF; ×, MTBE; ○, pentan-2-one; Δ, pentan-3-one; ◇, acetone; ∗, tiophene.

alcohols and water, and polarizable $\pi$-electrons in aromatic thiophene. Thus, the large negative values obtained for the alk-1-yne molecules (from $-310$ J·mol$^{-1}$ to $-444$ J·mol$^{-1}$) indicate a strong interaction between the alk-1-yne and the IL. The $\Delta H_1^{E\infty}$ values for alcohols methanol and propan-1-ol are negative ($-184$ J·mol$^{-1}$ for methanol) and can be thought of as being due to the breakdown of the alcohol self-association on mixing. The lowest value was observed for water, $\Delta H_1^{E,\infty} = -544$ J·mol$^{-1}$.

The influence of the cation on $\gamma_{13}^{\infty}$ values can be discussed on comparison of two tosylate-based ILs investigated in this work, [BMIM][TOS] and [BMPy][TOS].[1] Higher $\gamma_{13}^{\infty}$ values were found for [BMIM][TOS] than for [BMPy][TOS] with alkanes. This means that with these groups of compounds weaker interactions occur with the [BMIM]$^+$ cation than the [BMPy]$^+$ cation. Opposite behavior was found for the rest of the solutes, alk-1-ynes, aromatic hydrocarbons, and alcohols, but the differences are not significant. For benzene, the $\gamma_{13}^{\infty}$ values are two times lower for the [BMIM]$^+$ cation than for the [BMPy]$^+$ cation. This simple comparison gives the conclusion that the IL investigated herein may be better in the separation process of aromatic hydrocarbons from aliphatic hydrocarbons.

Higher $\gamma_{13}^{\infty}$ values with alkanes were found also for [BMIM][TOS] than for [BMIM][$CF_3SO_3$],[26] and they were slightly higher at the same temperature for benzene and alkylbenzenes for [BMIM][TOS] than for [BMIM][$CF_3SO_3$].[26] This means that with these groups of compounds weaker interactions with alkanes occur with the [TOS]$^-$ anion than with the [$CF_3SO_3$]$^-$ anion. It suggests also similar selectivity for the aromatics/aliphatics separation process. For ionic liquids based on the [$CF_3SO_3$]$^-$ anion, alkanes, alk-1-ynes, benzene, alkylbenzenes, ksylenes, and MTBE have much lower values of $\gamma_{13}^{\infty}$ than for ILs based on the [TOS]$^-$ anion. This suggests that the ionic liquid investigated here has lower interaction with these solutes.

Table 3 lists selectivities $S_{ij}^{\infty}$ and capacities $k_j^{\infty}$ at infinite dilution for ionic liquids based on the 1-butyl-3-methylimidazolium cation and on the tosylate anion, as well as for *N*-methyl-2-pirrolidinone, NMP,[34] and sulfolane[35] for different separation problems at $T = 338.15$ K.

It is not surprising that the investigated ionic liquid, [BMIM][TOS], shows higher selectivity in the separation of aliphatic from aromatic hydrocarbons as many other ionic liquids than commonly used entrainers such as NMP or sulfolane. However, the selectivity is slightly higher for [BMIM][$CF_3SO_3$][26] in comparison with [BMIM][TOS].

Table 3 shows that by changing the anion (for the same cation, [BMIM]$^+$) it is possible to increase the selectivity in *n*-heptane/benzene (aromatics/aliphatics separation problem) almost three times for 1-butyl-3-methylimidazolium thiocyanate IL, [BMIM][SCN],[27] or more than two times for 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][$BF_4$],[28] or almost two times for 1-butyl-3-methylimidazolium ethylsulfate, [BMIM][$EtSO_4$].[29] Two other ILs presented in Table 3 have slightly higher selectivity, 1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)-ethylsulfate, [BMIM][$MDEGSO_4$],[30] and 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][$PF_6$].[31]

The best capacity for the aromatics/aliphatics separation, between the discussed imidazolium-based ILs, is shown for [BMIM][$CF_3SO_3$][26] ($k_2^{\infty} = 0.62$). It should be emphasized that changing the anion from [TOS]$^-$ to bis(trifluoromethylsulfonyl)imide, [$NTf_2$]$^-$,[32] increases the capacity more than two times (for slightly lower selectivity for [BMIM][$NTf_2$]).

Changing the cation from [BMIM]$^+$ to [BMPy]$^+$ (for the same anion [TOS]$^-$) decreases the selectivity two times.[1] An interesting and high value of selectivity was obtained for 1-ethyl-3-methylimidazolium tosylate, [EMIM][TOS], which was superior in terms of other values, but it was the value obtained from the linear extrapolation to the saturated column.[10]

For the separation of cyclohydrocarbons from aromatic hydrocarbons by different ILs, the selectivities keep the same order as discussed earlier, but the values of selectivities are much lower.

Table 3 summarizes also the selectivities and capacities for chosen hydrocarbon/thiophene separation problems. The results for

**Table 3. Selectivities $S_{12}^{\infty}$ and Capacities $k_{12}^{\infty}$ at Infinite Dilution for Several Ionic Liquids Based on 1-Butyl-1-methylimidazolium Cation, or Tosylate Anion, NMP, and Sulfolane for Different Separation Problems at $T = 338.15$ K**

| | $S_{12}^{\infty}$ | | | $k_{12}^{\infty}$ |
|---|---|---|---|---|
| solvent | *n*-heptane/benzene | cyclohexane/benzene | *n*-heptane/thiophene | benzene |
| [BMIM][TOS][a] | 24.6 | 8.3 | 43.3 | 0.51 |
| [BMIM][$CF_3SO_3$][b] | 25.4 | 9.4 | 34.9 | 0.62 |
| [BMIM][SCN][c] | 74.2 | 16.9 | 126.3 | 0.45 |
| [BMIM][$BF_4$][d] | 65.6 | 14.6 | 96.3 | 0.46 |
| [BMIM][$EtSO_4$][e] | 47.9 | 14.1 | | 0.35 |
| [BMIM][$MDEGSO_4$][f] | 30.6 | 10.7 | | 0.50 |
| [BMIM][$PF_6$][g] | 27.6 | 8.8 | 36.8 | 0.45 |
| [BMIM][$NTf_2$][h] | 19.9 | 8.6 | | 1.20 |
| [BMIM][$OcSO_4$][i] | 6.3 | 3.6 | | 0.68 |
| [BMPy][TOS][j] | 12.8 | 4.4 | | 0.25 |
| [EMIM][TOS][k,l] | 98.2 | 14.8 | 181.8 | 0.38 |
| NMP[m] | | 5.7 | | 0.67 |
| sulfolane[n] | 19.6 | 6.4 | | 0.43 |

[a] This work. [b] From ref 26. [c] From ref 27. [d] From ref 28. [e] From ref 29. [f] From ref 30. [g] From ref 31. [h] From ref 32. [i] From ref 33. [j] From ref 1. [k] From ref 10. [l] At $T = 323.15$ K; values extrapolated to infinity. [m] From ref 34. [n] From ref 35.

the separation problem *n*-heptane/thiophene ($S^{\infty}_{12} = 43.3$ and capacity $k^{\infty}_{2} = 0.90$) at $T = 338.15$ K, obtained with [BMM][TOS], are better than those obtained with [BMIM][$CF_3SO_3$][26] and triethylsulfonium bis(trifluoromethylsulfonyl)imide, [$Et_3S$][$NTf_2$][36] ($S^{\infty}_{12} = 29.3$ at $T = 338.15$ K), and are very attractive. The selectivity of *n*-alkane/thiophene separation decreases with an increase of temperature. The highest literature value of selectivity $S^{\infty}_{12} = 126.6$ was observed for *n*-heptane/thiophene at $T = 338.15$ K for [BMIM][SCN].[27]

It is also worth discussing the separation of *n*-hexane (1) and hex-1-ene (2) as the representation of paraffins and olefins with [BMIM][TOS] ionic liquid. The selectivity $S^{\infty}_{12} = 2.0$ and capacity $k^{\infty}_{2} = 0.055$ at $T = 338.15$ K. A sligthly better result was obtained with 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate, [BMPYR][$CF_3SO_3$], ionic liquid.[37] The selectivity $S^{\infty}_{12} = 2.24$ and capacity $k^{\infty}_{2} = 0.057$ at $T = 338.15$ K for [BMPYR][$CF_3SO_3$][37] present a better separation mechanism than the recently published selectivity for [$Et_3S$][$NTf_2$].[36] A much higher value of selectivity can be obtained at the same temperature with [BMIM][SCN] ($S^{\infty}_{12} = 3.04$).[27]

The results from this work show the influence of the cation and anion on fundamental thermodynamic properties. An important observation found by comparing results from this work with related work from the literature is that the magnitude of $\gamma^{\infty}_{13}$ for homologous series of solutes increases as usual with an increase in the length of the alkyl chain of the hydrocarbon.

The values of $\gamma^{\infty}_{13}$, selectivity, and capacity are described at infinite dilution and are only the first approximation to the results expected in real mixtures. For the industrial separation process, where the conditions are far from those of infinite dilution, the ternary liquid−liquid equilibrium measurements are giving a better picture of ternary systems. However, for the industrial use, the multicomponent mixture has to be measured or predicted using the parameter obtained from the correlation of ternary systems.

## Conclusions

The results of the activity coefficients at infinite dilution measurements for a new ionic liquid, 1-butyl-3-methylimidazolium tosylate, [BMIM][TOS], in comparison with other ILs demonstrate a significant influence of the cation on the $\gamma^{\infty}_{13}$ and $\Delta H^{E,\infty}_{1}$ values. The data obtained were compared with those published by other authors. It was found that the investigated ionic liquid, [BMIM][TOS], shows moderate selectivity at infinite dilution for the separation of aromatic hydrocarbons from aliphatic hydrocarbons and perspective selectivity at infinite dilution for the separation of aromatic sulfur compounds from aliphatic hydrocarbons as well as for the separation of paraffins and olefins. Our results show again the influence of the cation and anion on the separation problems.

The selectivity values for [BMIM][TOS] in different separation problems were very much higher than those for other ILs and typical entrainers such as NMP[34] or sulfolane,[35] which are used in industrial separation processes of aliphatic compounds from aromatic hydrocarbons by extraction.

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.

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