

Measurements of Activity Coefficients at Infinite Dilution in Solvent Mixtures with Thiocyanate-Based Ionic Liquids Using GLC Technique

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The activity coefficients at infinite dilution, γ_{13}^∞ for 34 solutes—alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, water, thiophene, ethers, and ketones—in the ionic liquid 1-butyl-4-methylpyridinium thiocyanate, [BMPy][SCN], and in 1-butyl-1-methylpyrrolidinium thiocyanate, [BMPYR][SCN], were determined by gas–liquid chromatography at the temperature range 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 γ_{13}^∞ values obtained over the temperature range. The selectivities for the *n*-heptane/benzene, cyclohexane/benzene, and *n*-heptane/thiophene separation problems were calculated from the γ_{13}^∞ . Obtained values were compared to the literature values for the other ionic liquids, NMP, and sulfolane.

Introduction

The knowledge of activity coefficients at infinite dilution, γ_{13}^∞ , is of particular importance for the reliable design of thermal separation processes and for the synthesis and design of new technologies. In recent years, ionic liquids (ILs) have become a new medium for separation processes. Furthermore, reliable γ_{13}^∞ values are required to select selective solvents (ionic liquids as entrainers) for separation processes such as extractive distillation, extraction, and separation of the azeotropic mixtures. Since ILs have a negligible vapor pressure, gas–liquid chromatography (GLC) is a suitable method for measuring the activity coefficients at infinite dilution. Selectivities, S_{ij}^∞ ($S_{ij}^\infty = \gamma_{i3}^\infty/\gamma_{j3}^\infty$), and capacities, k_2^∞ ($k_2^\infty = 1/\gamma_{j3}^\infty$), at infinite dilution can be directly calculated from γ_{13}^∞ values for the synthesis, simulation, and optimization of separation processes. An entrainer should show a high selectivity at infinite dilution, a low viscosity, a high flash point, a low melting point, and a boiling point higher than those of the separated components. Furthermore, it should be nontoxic, nonflammable, noncorrosive, and recyclable. Among the separations of mixtures of industrial importance, an improved separation process for systems involving aromatic and aliphatic hydrocarbons and liquid–liquid extraction of sulfur (thiophene) from aliphatic hydrocarbons is of considerable interest.^{1–10}

This paper is a continuation of our wide ranging investigation into ILs containing the thiocyanate anion.^{1,11–16} Three thiocyanate-based ILs (1-ethyl-3-methylimidazolium thiocyanate, [EMIM][SCN]; 1-butyl-3-methylimidazolium thiocyanate, [BMIM][SCN]; and 1-hexyl-3-methylimidazolium thiocyanate, [HMIM][SCN]) were investigated by us as a separation medium for aromatic and aliphatic hydrocarbons or for alkanes and thiophene with very high selectivities and capacities. The phase equilibria of these ILs were determined with hydrocarbons, alcohols, water, and thiophene.^{11–14} Determination of activity coefficients at infinite dilution of organic solutes and water in these ILs by gas–liquid chromatography (GLC) has been reported to show the highest selectivity values ever published for ionic liquids.^{1,15,16}

The phase equilibria in binary systems of aromatic hydrocarbons and thiophene in the imidazolium-based ILs with thiocyanate anion reveals the lower critical solution temperature, LCST, and the immiscibility in binary mixture shifted to a very low mole fraction of the IL.^{11,12,14} The other characteristic point is that the solubility of aliphatic hydrocarbons in imidazolium-based ILs with thiocyanate anion is very low in comparison with those in the other ILs.^{11,12}

Differences in solubilities in binary systems are usually the first indications for possible use in separation processes. Different types of cations and anions can be combined, and their respective structures can be tailored to modify the properties of the resulting IL according to the interest in each specific application. ILs that have been shown to have potentially excellent entrainer properties for the separation of aliphatic hydrocarbons from aromatic hydrocarbons by extractive distillation or extraction are 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N]), 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO₄]), and 4-methyl-*N*-butylpyridinium tetrafluoroborate ([BMPy][BF₄]).^{2–4}

The desulfurization of diesel fuel, which was described by us earlier,¹⁴ is one of the most important and popular technological problems. According to new regulations, refineries have to reduce sulfur levels for liquid fuels in the U.S. and in Europe. The S limit had to be reduced in Europe to 10 ppm by 2009. Deep desulfurization processes will be required by most refiners to achieve legislative requirements in Europe and the U.S.

From the beginning, imidazolium ILs were considered as extractive solvents: 1-butyl-3-methylimidazolium chloride mixture with aluminum trichlorate, [BMIM]Cl/AlCl₃ (0.35/0.65);¹⁷ 1-butyl-3-methylimidazolium octylsulfate, [BMIM][OcSO₄];⁹ 1-ethyl-3-methylimidazolium ethylsulfate, [EMIM][EtSO₄];¹⁸ and 1-hexyl-3,5-dimethylpyridinium bis(trifluoromethylsulfonyl)imide, [NMMPy][NTf₂].⁷ It was also confirmed by Holbrey et al.¹⁹ that thiocyanate anion [SCN][−] has high extraction efficiency. The selectivity of alkane/thiophene separation increases with an increase of alkane chain and decreases with an increase of temperature. The highest value of selectivity (517.3) was observed for decane/thiophene at *T* = 298.15 K with [BMIM][SCN].¹⁵

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The intermediate selectivity (36.5 for *n*-hexane/thiophene) was obtained by us earlier for 1-butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM][CF₃SO₃]²⁰ and for triethylsulfonium bis(trifluoromethylsulfonyl)imide [Et₃S][NTf₂]²¹ (30.9 for *n*-hexane/thiophene) at *T* = 298.15 K from the activity coefficients measurements. Interestingly, most of the calculated results relate to the activity coefficient at infinite dilution measurements.^{1,15,16,20,21}

The best selectivity values for *n*-hexane/benzene separation (at 298.15 K) were obtained for [EMIM][SCN] (95.4)¹ [EMIM][EtSO₄] (41.4),³ and [EMIM][NTf₂] (37.5).²² These values were all determined from activity coefficients at infinite dilution measurements.

It was evidenced by us using phase equilibria studies of binary systems that aliphatic hydrocarbons have a very low solubility in *N*-butyl-4-methylpyridinium tosylate (*p*-toluenesulfonate), [BM⁴Py][TOS], and *N*-butyl-3-methylpyridinium tosylate (*p*-toluenesulfonate), [BM³Py][TOS], and that benzene and *n*-alkylbenzenes are readily soluble in these ILs.^{23,24} These results showed that pyridinium-based ILs are good potential entrainers in the separation of aliphatics from aromatics. However, the tosylate anion increases the melting temperature of these compounds.

It should be emphasized that the activity coefficients at infinite dilution of tosylate-based ILs have shown that the selectivities (S_{12}^{∞}) and capacities (k_2^{∞}) at infinite dilution for different ionic liquids based on pyridinium cations are not very optimistic for the separation of aromatics from aliphatics. For the cation [BM⁴Py]⁺ and tosylate anion, the S_{12}^{∞} for separating aromatics and aliphatics and the k_2^{∞} values were worse than for [NTf₂][−] and [BF₄][−].^{25,26} The other pyridinium-based ILs, for which data is available (pyridiniummethoxyethylsulfate, [Py][C₂H₅OC₂H₄SO₄],²⁷ and *N*-ethylpyridinium bis(trifluoromethylsulfonyl)imide, [EPy][NTf₂]²⁷) show higher selectivities than does [BM⁴Py][TOS].²⁸

Pyridinium-based ionic liquids with four different anions were investigated for the desulfurization of oils.¹⁰ It was observed that dimethylpyridinium ILs (*N*-butyl-2,4-dimethylpyridinium, or *N*-butyl-2,5-dimethylpyridinium bis(trifluoromethylsulfonyl)imide) have shown much greater extraction potential than other pyridinium-based ionic liquids.¹⁹ The desulfurization of fuel was also investigated using simple pyridinium-based ionic liquids such as *N*-alkylpyridinium tetrafluoroborate [aPy][BF₄] (where a = C₄, C₆, and C₈). They were found to be effective for the selective removal of aromatic heterocyclic sulfur compounds from diesel fuel at room temperature.¹⁰

For the sake of comparison, the pyrrolidinium-based ILs will be shortly analyzed. The phase equilibria data (vapor–liquid equilibria, VLE) for the 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [BMPYR][NTf₂] with alkanes and alkenes showed the possible use of this IL in the separation of aliphatic hydrocarbons from alkenes.^{29,30} After years of measurements of phase equilibria and activity coefficients at infinite dilution, we can conclude that the pyrrolidinium-based ionic liquids are very promising.^{19,29–34} In the process of desulfurization of oils using ionic liquids (extraction of dibenzothiophene from dodecane using ILs), pyrrolidinium-based ILs have shown the same selectivities as popular imidazolium-based ionic liquids but worse than those of pyridinium-based ILs.¹⁹ Recently, [BMPYR][NTf₂] was described as a suitable solvent for extraction of aromatic hydrocarbons (benzene, toluene, and ethylbenzene) from aliphatic hydrocarbons (heptane).³¹

The activity coefficient for various solutes (alkanes, alkenes, cycloalkanes, aromatics, alcohols, ketones, esters, ethers, and

water) were measured in pyrrolidinium-based ILs [BMPYR][NTf₂],^{29,30,33} [HMPYR][NTf₂],³⁰ [OMPYR][NTf₂],³⁰ and 1-butyl-1-methylpyrrolidinium triflate [BMPYR][CF₃SO₃].³⁴ The pyrrolidinium-based ILs were found suitable as entrainers for the separation of aliphatics from aromatics and of aromatic sulfur compounds from hydrocarbon streams.^{32–34} [BMPYR][CF₃SO₃] showed a higher selectivity in the separation of aliphatic hydrocarbons from aromatic hydrocarbons than the popular imidazolium ionic liquid [BMIM][CF₃SO₃].³⁴

As mentioned above, the phase equilibria results are important in expanding our knowledge about the nature of ILs and in assisting in the systematic study of their thermodynamic properties. Recently, the mutual solubility of the pyrrolidinium-based IL was measured in our laboratory; namely, 1-butyl-1-methylpyrrolidinium triflate [BMPYR][CF₃SO₃] with hydrocarbons (hexane, heptane, cyclohexane, benzene, toluene), showing typical low solubility of alkanes and high solubility of aromatics in this IL.³⁵

The purpose of this work is to present the potential of new ionic liquids with the thiocyanate anion and the pyridinium or pyrrolidinium cation in different separation problems from measurements of activity coefficients at infinite dilution. We believe that the selectivities calculated from these measurements are important information that allows making some predictions for future new technologies.

This paper presents γ_{13}^{∞} for 32 solutes (alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, water, thiophene, ethers, and ketones) in the ionic liquid 1-butyl-4-methylpyridinium thiocyanate, [BMPy][SCN], and in 1-butyl-1-methylpyrrolidinium thiocyanate, [BMPYR][SCN], at the temperature range from 298.15 to 368.15 K using GLC.

Experimental Procedures and Results

Materials or Chemicals. The ionic liquids [BMPy][SCN] and [BMPYR][SCN] had a purity of >0.999 mass fraction and were purchased from Liquids Technologies (Iolitec GmbH & Co. KG, Denzlingen, Germany). Both ILs are liquid at 298.15 K; [BMPy][SCN] is a dark red, dense liquid, and [BMPYR][SCN] is a dark orange, dense liquid. The ionic liquids were further purified by subjecting the liquids to a very low pressure of about 5×10^{-3} Pa at ~330 K for ~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 TotalChrom Workstation software.

The column preparation and the packing method used in this work has been described previously.^{36,37} 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 ± 0.0001 g. The solvent column packing is listed together with other column specification in Table 2. The column packing was large enough to prevent any residual absorption of solute onto the column packing, as was observed in previously published works.^{38,39} For each temper-

TABLE 1: Investigated Ionic Liquids: Chemical Structure, Name, Abbreviation

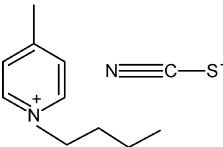
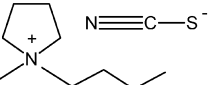
structure	name, abbreviation
	1-butyl-4-methylpyridinium thiocyanate, [BMPy][SCN]
	1-butyl-1-methylpyrrolidinium thiocyanate, [BMPYR][SCN]

TABLE 2: Column Specification and Chromatograph Conditions

	[BMPy][SCN]		[BMPYR][SCN]	
	column 1	column 2	column 1	column 2
loading/%	45.32	55.12	45.80	33.95
mass coated/g	4.6797	5.7033	4.5797	3.8399
column length/m		1		
column i.d./mm		4		
column temperature/K		298.15–368.15		
injector temperature/K		423.15		
detector temperature/K		423.15		
carrier gas		helium		
flow/cm ³ ·min ⁻¹		20–160		

ature, 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 the experiments, each column was conditioned by blowing carrier gas through the column at a high flow rate (about 2.5 cm³·s⁻¹) at the high temperature (about 100 °C) for about 8 h.

The outlet pressure P_0 was kept at atmospheric pressure. The pressure drop ($P_i - P_0$) was varied between 25 and 80 kPa, depending on the flow rate of the carrier gas. The pressure drop was measured by gas 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. 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 γ_{13}^∞ determinations were made. The flow rates were corrected for water vapor pressure and ranged from 0.8 to 2.1 cm³·s⁻¹. Solute injections ranged from 0.01 to 0.3 μ 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 ± 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 1.6 s and 90 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. Although our GC was equipped with a TCD detector, air was used as a nonretainable component. The estimated overall error in γ_{13}^∞ was $<3\%$, taking into account the possible errors in determining the column loading, the retention times, and the 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.⁴⁰

Theoretical Basis. The equation developed by Everett⁴¹ and Cruickshank et al.⁴² was used in this work to calculate the γ_{13}^∞ of solutes in the ionic liquid.

$$\ln \gamma_{13}^\infty = \ln \left(\frac{n_3 RT}{V_N P_1^*} \right) - \frac{P_1^* (B_{11} - V_1^*)}{RT} + \frac{P_0 J_2^3 (2B_{12} - V_1^\infty)}{RT} \quad (1)$$

The V_N denotes the net retention volume of the solute; P_0 , the outlet pressure; $P_0 J_2^3$, 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^∞ , 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:⁴³

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

where n refers to the number of carbon atoms. Using the Hudson and McCoubrey combining rules,^{44,45} 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

$$J_2^3 = \frac{2(P_i/P_0)^3 - 1}{3(P_i/P_0)^2 - 1} \quad (3)$$

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

$$V_N = J_2^3 U_0 (t_R - t_G) \quad (4)$$

where t_R and t_G are the retention times for the solute and an unretained gas, respectively, and U_0 is the column outlet flow rate.

The vapor pressure values were calculated using equation and constants taken from the literature.^{46–48} Critical data used to calculate B_{11} and B_{12} , and ionization energies used in the calculation of T_{12} were obtained from the literature.^{49,50}

Results and Discussion

The average experimental activity coefficients at infinite dilution, γ_{13}^∞ , for the solutes in ionic liquid [BMPy][SCN] and [BMPYR][SCN] at different temperatures 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 eq 5 are listed in Tables 3 and 4, respectively.

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

Figures 1–5 show the natural logarithm of the activity coefficients in the ionic liquid as a function of the inverse

TABLE 3: Average Experimental Activity Coefficients at Infinite Dilution, γ_{13}^{∞} , for the Solutes in Ionic Liquid [BMPy][SCN] at Different Temperatures and Partial Molar Excess Enthalpies at Infinite Dilution, $\Delta H_1^{E,\infty}$, for the Investigated Ionic Liquid

	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> -hexane	107	95.5	84.8	77.0	69.1	63.3	59.2		8482
<i>n</i> -heptane	147	130	118	108	98.5	91.3	84.0		7767
<i>n</i> -octane	216	193	175	160	145	134	123		7816
<i>n</i> -nonane	381	333	295	260	234	209	190		9850
<i>n</i> -decane	533	463	411	368	328	295	268		9630
cyclopentane	24.7	22.4	20.7	19.2	17.8	16.7	15.7		6332
cyclohexane	37.3	33.7	30.8	28.2	26.0	24.1	22.6		7112
cycloheptane	41.8	38.2	34.7	32.1	29.7	27.8	26.3		6604
cyclooctane	55.3	49.9	45.6	41.9	38.4	35.3	33.0		7294
hex-1-ene	36.8	34.1	31.8	29.9	28.0	26.5	25.2		5348
hept-1-ene	54.6	50.9	47.3	44.6	41.7	39.6	37.7		5239
oct-1-ene	90.1	83.2	76.6	71.0	66.3	62.1	58.6		6102
pent-1-yne	3.51	3.59	3.67	3.74	3.82	3.89	3.96		−1688
hex-1-yne	5.26	5.34	5.43	5.52	5.60	5.67	5.74		−1240
hept-1-yne	7.97	8.06	8.15	8.26	8.35	8.42	8.51		−927
oct-1-yne	12.0	12.1	12.1	12.2	12.2	12.2	12.3		−284
benzene	1.66	1.67	1.69	1.71	1.72	1.73	1.75	1.76	−805
toluene	2.55	2.59	2.61	2.65	2.67	2.69	2.74	2.75	−976
ethylbenzene	4.40	4.41	4.40	4.44	4.43	4.42	4.43	4.47	−155
<i>o</i> -xylene	3.27	3.28	3.31	3.35	3.40	3.43	3.48	3.51	−1002
<i>m</i> -xylene	4.11	4.12	4.14	4.23	4.25	4.28	4.33	4.38	−868
<i>p</i> -xylene	3.87	3.91	3.94	4.01	4.04	4.07	4.13	4.19	−1017
methanol	0.377	0.370	0.364	0.358	0.353	0.347	0.343	0.338	1403
ethanol	0.698	0.669	0.648	0.626	0.603	0.587	0.573	0.558	2920
water				0.305	0.308	0.310	0.312	0.315	−308
thiophene	0.963	0.984	1.00	1.02	1.03	1.05	1.07	1.08	−1516
THF	1.99	1.99	1.98	1.98	1.98	1.97	1.97		186
MTBE	10.8	10.6	10.5	10.3	10.2	10.0	9.87		1252
diethyl ether	10.3	9.97	9.68	9.41	9.12	9.03	8.80		2208
dipropyl ether	31.0	29.0	27.5	26.0	24.9	24.0	23.0		4162
dibutyl ether	71.9	66.3	62.1	58.0	54.3	51.4	49.0		5436
acetone	1.31	1.32	1.33	1.33	1.34	1.34	1.35		−363
pentan-2-one	2.78	2.76	2.75	2.75	2.73	2.72	2.73		283
pentan-3-one	2.74	2.75	2.76	2.77	2.79	2.80	2.81		−347

absolute temperature for all investigated solutes in [BMPy]-[SCN] and in Figures 1S to 5S of the Supporting Information in [BMPYR][SCN] ionic liquid. The temperature dependence of γ_{13}^{∞} is the same for all solutes for both ILs. The values of γ_{13}^{∞} for homological series of solutes increase with an increase of the solute alkyl chain. This property was always observed for different ILs. The influence of temperature is also typical: with an increase in temperature, the values of γ_{13}^{∞} decrease, with the exception of alkynes, aromatic hydrocarbons, tetrahydrofuran, THF (only for [BMPYR][SCN]), thiophene, water, some alcohols, and ketones.

High values of γ_{13}^{∞} signify very small interactions between solute and solvent. The highest values of γ_{13}^{∞} can be observed for alkanes, cycloalkanes, and alkenes. It is typical for any ionic liquid. The values of γ_{13}^{∞} for cycloalkanes and alkenes are lower than those for alkanes for the same carbon number. This is caused by similar structures of the cation and solvent and of interaction of double bonding in alkenes with polar ionic liquid. The cyclic structure of cycloalkanes reduces the value of γ_{13}^{∞} in comparison with the corresponding linear alkane, but the γ_{13}^{∞} is in the same range of order as for alkenes. Alkynes and aromatic hydrocarbons have smaller values of γ_{13}^{∞} than alkanes, cycloalkanes and alkenes. The smallest values of γ_{13}^{∞} indicate the stronger interactions between solvent and solute. The triple bond in alkynes and six π -delocalized electrons in aromatic hydrocarbons can strongly interact with the polar cation and an anion of the IL. The interaction between the free electron pair on the nitrogen of a cation with the aromatic ring π electrons of benzene and other aromatic hydrocarbons result in lower γ_{13}^{∞}

values of the latter. The smallest values of γ_{13}^{∞} have been observed for alcohols, water, THF, and thiophene. These polar compounds interact very strongly with a polar ionic liquid. In this case, the major influence on values of γ_{13}^{∞} has very strong interactions between the $-\text{OH}$ group in alcohols and water and an anion of the IL.

This article is concerned with the investigation of mixtures containing two different ILs. From the first results shown in Tables 3 and 4, we can observe that the [BMPYR][SCN] ionic liquid reveals much higher values of γ_{13}^{∞} for alkanes than pyridinium-based ionic liquid with similar values of γ_{13}^{∞} for aromatic hydrocarbons. It is the first information about the selectivity of these two ionic liquids in the separation process of aliphatic hydrocarbons from aromatic hydrocarbons.

Nevertheless, it seems to be convenient to show also the differences in partial molar excess enthalpies at infinite dilution $\Delta H_1^{E,\infty}$. The specific interaction between [BMPYR][SCN] ionic liquid and aromatic hydrocarbons or thiophene shows much lower values of $\Delta H_1^{E,\infty}$ than for [BMPy][SCN]. For the aromatic hydrocarbons, it is one order less (for example, $\Delta H_1^{E,\infty} = -976 \text{ J}\cdot\text{mol}^{-1}$ and $\Delta H_1^{E,\infty} = -2414 \text{ J}\cdot\text{mol}^{-1}$ for toluene and [BMPy]-[SCN] and [BMPYR][SCN], respectively), and for thiophene, it is double less (see Tables 3 and 4). In addition, one should keep in mind that we have the same anion and the same two substituents on a cation (butyl and methyl) in two investigated ionic liquids. Thus, it is mainly the influence of the aromatic six-membered ring or five-membered ring of the cation.

Table 5 shows the various selectivities, S_{12}^{∞} , and capacities, k_2^{∞} , at infinite dilution for ionic liquids based on 1-butyl-3-

TABLE 4: Average Experimental Activity Coefficients at Infinite Dilution, γ_{13}^{∞} , for the Solutes in Ionic Liquid [BMPYR][SCN] at Different Temperatures and Partial Molar Excess Enthalpies at Infinite Dilution, $\Delta H_1^{E,\infty}$, for the Investigated Ionic Liquid

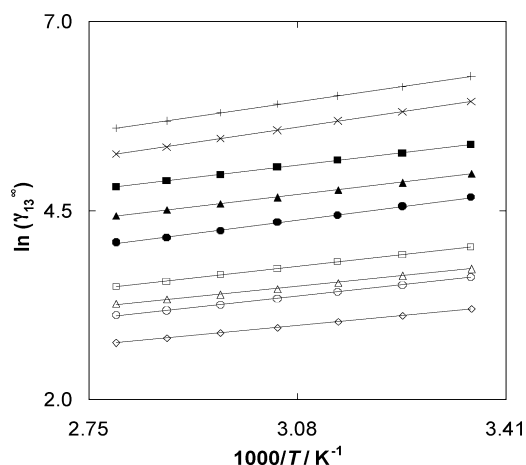
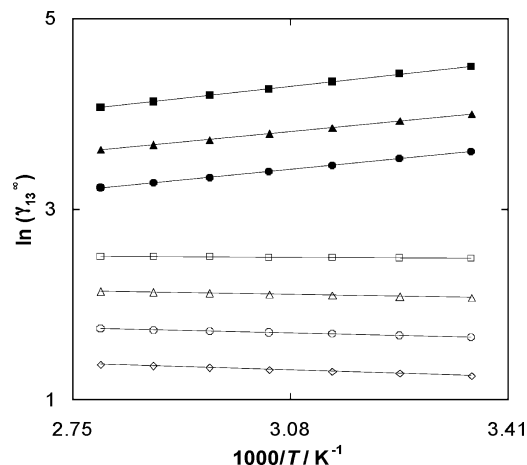
	T/K								$\Delta H_1^{E,\infty}/\text{J}\cdot\text{mol}^{-1}$
	298.15	308.15	318.15	328.15	338.15	348.15	358.15	368.15	
<i>n</i> -heptane	183	164	148	130	120	109	101		8521
<i>n</i> -octane	272	243	220	196	180	163	150		8366
<i>n</i> -nonane	408	363	325	290	266	241	218		8758
<i>n</i> -decane	615	543	486	436	395	354	322		9057
cyclopentane	28.19	25.80	23.79	21.83	20.36	19.04	17.86		6442
cyclohexane	44.05	39.84	36.45	33.16	30.92	28.73	26.97		6925
cycloheptane	51.52	46.91	43.11	39.60	37.14	34.60	32.46		6476
cyclooctane	70.41	63.42	57.85	52.71	49.08	45.36	42.26		7149
pent-1-ene	28.23	26.30	24.79	22.97	21.92	21.42	19.96		4761
hex-1-ene	40.58	38.02	35.86	33.67	32.03	30.41	29.05		4717
hept-1-ene	62.49	58.44	55.32	51.72	49.45	46.68	44.55		4759
oct-1-ene	96.61	89.81	84.41	78.45	74.47	70.12	66.68		5231
hex-1-yne	5.09	5.22	5.37	5.53	5.70	5.82	5.97		−2283
hept-1-yne	8.15	8.31	8.48	8.66	8.84	8.98	9.13		−1624
oct-1-yne	12.98	13.10	13.21	13.37	13.49	13.57	13.67		−748
benzene	1.77	1.82	1.87	1.91	1.97	2.01	2.05	2.10	−2236
toluene	2.89	2.98	3.07	3.16	3.25	3.31	3.41	3.48	−2414
ethylbenzene	5.10	5.14	5.19	5.23	5.28	5.32	5.35	5.3	−727
<i>o</i> -xylene	4.04	4.13	4.21	4.27	4.36	4.40	4.47	4.56	−1511
<i>m</i> -xylene	5.24	5.28	5.34	5.40	5.44	5.50	5.53	5.59	−853
<i>p</i> -xylene	4.97	5.02	5.09	5.16	5.21	5.25	5.31	5.36	−976
methanol	0.329	0.330	0.331	0.333	0.333	0.335	0.335	0.336	−278
ethanol	0.601	0.592	0.585	0.577	0.571	0.564	0.558	0.552	1102
water				0.263	0.269	0.273	0.277	0.281	−653
thiophene	0.993	1.04	1.07	1.11	1.15	1.19	1.23	1.26	−3120
THF	2.12	2.14	2.15	2.17	2.18	2.20	2.21	2.22	−570
MTBE	11.27	11.23	11.17	11.14	11.09	11.07	11.04		300
diethyl ether	11.04	10.83	10.60	10.33	10.15	9.95	9.75		1758
dipropyl ether	34.90	33.11	31.86	30.19	29.02	27.96	26.93		3650
dibutyl ether	84.75	78.60	74.02	69.63	65.95	62.03	58.79		5086
acetone	1.38	1.39	1.40	1.41	1.42	1.43	1.44	1.45	−703
pentan-2-one	2.96	2.97	2.99	3.00	3.02	3.04	3.05	3.06	−466
pentan-3-one	2.82	2.86	2.91	2.97	3.02	3.05	3.10	3.15	−1442

methyl-substituted cation and thiocyanate anion for different separation problems at $T = 323.15$ K. The analysis in Table 5 was made for *n*-heptane/benzene, cyclohexane/benzene, and *n*-heptane/thiophene separation problems. From a recently published, excellent review, we may observe that most of the data are in $T = 323.15$ K because sometimes ionic liquids⁵⁵ are solid at room temperature.

It was mentioned already that both the selectivity and capacity of the solvent are important for the economics of a separation process. The selectivity, S_{12}^{∞} , for *n*-heptane/benzene takes the

following order: [EMIM][SCN] (109)¹ > [BMIM][SCN] (90.7)¹⁵ > [BMPYR][SCN] (73.0, this work) > [BMPy][SCN] (66.4, this work) > [BMPy][BF₄] (49.8).⁵¹ Unfortunately, the best ionic liquid, [EMIM][SCN], has the lowest capacity, $k_2^{\infty} = 0.29$. The other ionic liquids mentioned above have capacities from 0.46 ([BMIM][SCN]) to 0.61 ([BMPy][BF₄]).

The selectivity S_{12}^{∞} for cyclohexane/benzene takes the following order: [EMIM][SCN] (25.7)¹ > [BMIM][SCN] (20.4)¹⁵ > [BMPYR][SCN] (18.4, this work) > [BMPy][BF₄] (16.3)⁵¹ > [BMPy][SCN] (16.1, this work).

**Figure 1.** Plot of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for the solutes in [BMPYR][SCN]: (▲) *n*-heptane, (■) *n*-octane, (×) *n*-nonane, (+) *n*-decane, (◇) cyclopentane, (○) cyclohexane, (Δ) cycloheptane, and (□) cyclooctane.**Figure 2.** Plot of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for the solutes in [BMPYR][SCN]: (●) hex-1-ene, (▲) hept-1-ene, (■) oct-1-ene, (○) hex-1-yne, (Δ) hept-1-yne, and (□) oct-1-yne.

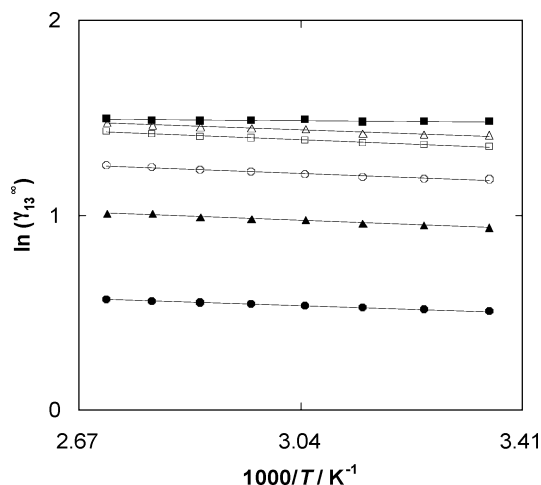


Figure 3. Plot of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for the solutes in [BMPy][SCN]: (●) benzene, (▲) toluene, (■) ethylbenzene, (○) *o*-xylene, (Δ) *m*-xylene, and (□) *p*-xylene.

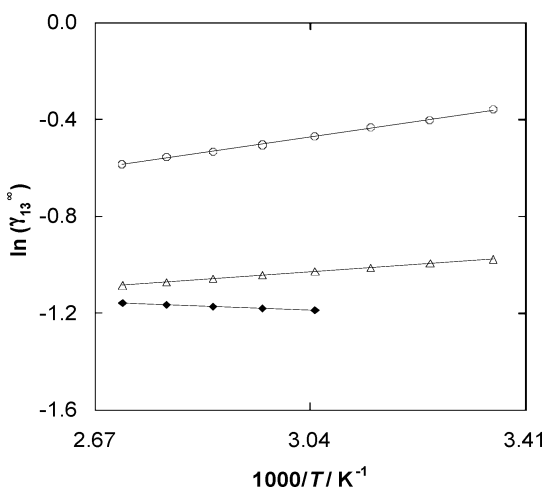


Figure 4. Plot of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for the solutes in [BMPy][SCN]: (○) methanol, (Δ) ethanol, and (◆) water.

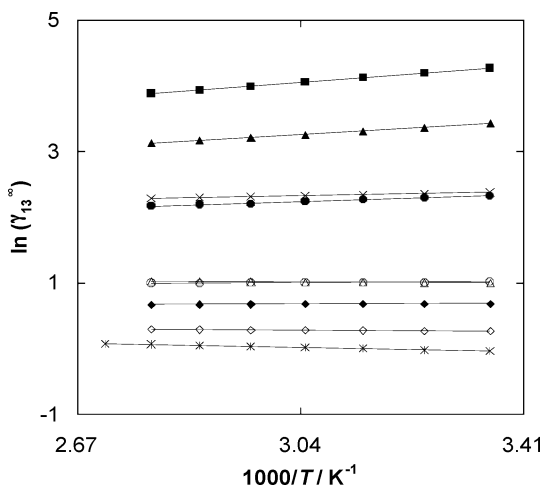


Figure 5. Plot of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for the solutes in [BMPy][SCN]: (●) diethyl ether, (▲) dipropyl ether, (■) dibutyl ether, (◆) THF, (×) MTBE, (○) pentan-2-one, (Δ) pentan-3-one, (◇) acetone, and (×) thiophene.

The selectivity S_{12}^{∞} for *n*-heptane/thiophene takes following order: [BMIM][SCN] (156)¹⁵ > [BMPYR][SCN] (123, this work) > [BMPy][SCN] (112, this work) > [BMPYR][CF₃SO₃] (53)³⁴ = [HMIM][SCN] (53).¹⁶ The capacity at infinite dilution,

TABLE 5: Selectivities S_{12}^{∞} and Capacities k_2^{∞} at Infinite Dilution for Several Ionic Liquids, NMP and Sulfolane for Different Separation Problems at $T = 323.15$ K

solvent	S_{12}^{∞}			k_{12}^{∞}
	<i>n</i> -heptane/ benzene	cyclohexane/ benzene	<i>n</i> -heptane/ thiophene	
[BMPy][SCN] ^a	66.4	16.1	112	0.59
[BMPYR][SCN] ^a	73.0	18.4	123	0.53
[Py][C ₂ H ₅ OC ₂ H ₄ SO ₄] ^b	24.4	8.2		0.26
[EPy][NTf ₂] ^b	32.8	11.8		0.74
[BMPy][BF ₄] ^c	49.8	16.3		0.61
[BMPy][NTf ₂] ^d	23.5	10.4	26.6	1.38
[BMPy][TOS] ^e	13.8	5.10		0.25
[BMPYR][CF ₃ SO ₃] ^f	38.6	13.9	53	0.68
[BMPYR][NTf ₂] ^g	20.8	9.0		1.14
[EMIM][SCN] ^h	109	25.7		0.29
[BMIM][SCN] ⁱ	90.7	20.4	156	0.46
[HMIM][SCN] ^j	35.0	11.7	53.0	0.50
NMP ^k		6.50		0.95
sulfolane ^l	22.0	8.20		0.29

^a This work. ^b Ref 27. ^c Ref 51. ^d Ref 52. ^e Ref 28. ^f Ref 34. ^g Ref 29. ^h Ref 1. ⁱ Ref 15. ^j Ref 16. ^k Ref 53. ^l Ref 54.

k_2^{∞} , is high for thiophene in both ILs (0.9). The results for aromatic compounds, because of their similarity of structure with thiophene are of little use in solvent extraction processes for separating aromatic compounds from thiophene (see γ_{13}^{∞} in Tables 3 and 4).

In conclusion, we can underline that the [SCN][−] anion (this work) reveals the highest values for the different separation problems discussed here. For the investigated ILs and all those listed in Table 5, the selectivities are higher than for *N*-methyl-2-pyrrolidinone, NMP, or sulfolane; only the capacity is lower than for NMP (with exception of [BMPYR][NTf₂]²⁹).

The selectivity of *n*-alkane/benzene and *n*-alkane/thiophene separation increases with an increase of *n*-alkane chain, and decreases with an increase of temperature.

It is noteworthy that separation of an alkane/alkene is quite high with two investigated ILs: $S_{12}^{\infty} = 2.46$ for [BMPy][SCN] and $S_{12}^{\infty} = 2.60$ for [BMPYR][SCN] for *n*-heptane/hept-1-ene at $T = 323.15$ K.

Concluding Remarks

The results of the activity coefficients at infinite dilution measurements for two new ionic liquids, 1-butyl-4-methylpyridinium thiocyanate, [BMPy][SCN], and 1-butyl-1-methylpyrrolidinium thiocyanate, [BMPYR][SCN], in comparison with another ILs demonstrate a significant influence of the cation on the γ_{13}^{∞} and ΔH_{13}^{∞} values. The data obtained were compared with those published by other authors. The selectivity values for different separation problems were very much higher than for other ILs and typical entrainers, such as NMP⁵³ or sulfolane,⁵⁴ which are used in industrial separation processes of aliphatic compounds from aromatic hydrocarbons by extraction.

The results listed in Table 5 together with other properties, such as a very low vapor pressure, paints a very optimistic picture of just how potentially important and useful [BMPy][SCN] and [BMPYR][SCN] 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.

Taking into account limiting activity coefficients improves the understanding of the nature of ILs and improves important expanding and developing G^E model parameters and group contribution methods.

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Supporting Information Available: Figures 1S–5S for the [BMPYR][SCN]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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