Measurements of Activity Coefficients at Infinite Dilution for Organic Solutes and Water in the Ionic Liquid 1-Butyl-1-methylpiperidinium Thiocyanate

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The activity coefficients at infinite dilution (γ_{13}^{∞}) for 33 solutes: alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, ethers, ketones, and water in the ionic liquid, 1-butyl-1-methylpiperidinium thiocyanate ([BMPIP][SCN]), were determined by gas−liquid chromatography over the temperature range (318.15 to 358.15) 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 heptane/benzene, cyclohexane/benzene, and heptane/thiophene separation problems were calculated from the γ_{13}^{∞} and compared to the literature values for other ionic liquids with thiocyanate-based anion or with a butyl-methyl-substituted cation.

Introduction

Ionic liquids (ILs) have unique properties that make them suitable substitutes for use in technological processes for volatile organic compounds. Recently, the interest of new ILs is increasing to the pyrrolidinium-based ILs[1–3] and piperidinium-based ILs.[4–10] The specific properties of piperidinium-based ILs are: a broad temperature range of the liquid phase, extremely low vapor pressure, a structure similarity to pyrrolidinium-based ILs, high solubility in water, low toxicity, and a density lower than those of pyrrolidinium-based ILs. All of these physicochemical properties make the piperidinium-based ILs potentially useful in many industrial processes. The 1-ethylpiperidinium tetrafluoroborate was used in the electrochemical processes.[5] A high thermal stability, possible application in lithium-ion batteries and other electrochemical devices, high ionic conductivity, and low toxicity were presented for 1-alkyl-1-methylpiperidinium-based and 1-alkyl-1-methylpyrrolidinium-based ILs with different anions.[7] The mutual solubility of 1-propyl-1-methylpiperidinium bis{(trifluoromethyl)sulfonyl}imide, [PMPIP][NTf$_2$], with water was measured and calculated with a conductor-like screening model for real solvent (COSMO-RS) or a quantitative structure−property relationship (QSPR) model.[8,9] Densities and isothermal compressibilities of different ILs including the piperidinium-based ILs and pyrrolidinium-based ILs were measured and discussed for different anions and cations.[10] Unfortunately, it was shown that the viscosity for the thiocyanate anion, [SCN]$^-$, is slightly higher than that for the [NTf$_2$]$^-$ anion and that the viscosity for the 1-propyl-1-methylpiperidinium cation is higher than for imidazolium-, pyrrolidinium-, and ammonium-based cations.[11]

The phase equilibrium (liquid + liquid), LLE, of the 1-propyl-1-methylpiperidinium bis{(trifluoromethyl)sulfonyl}imide, [PMPIP][NTf$_2$], with water was presented earlier as immiscible in the liquid phase system with an upper critical solution temperature, UCST.[8]

After years of measurements of phase equilibria and of activity coefficients at infinite dilution, γ_{13}^{∞}, we can conclude that the piperidinium-based ILs could be, by the similarity to pyrrolidinium-based ILs, very promising.[1,12–16]

Recently, the activity coefficients of many organic solvents and water were measured in [PMPIP][NTf$_2$].[17] The selectivities obtained for the separation of the aromatic hydrocarbons from the aliphatic hydrocarbons were on the average level, but the selectivity for the heptane/thiophene separation problem was quite high, $S_{12}^{\infty} = 29.9$ at $T = 323.15$ K.

The choice of anion in this work is a result of our systematic measurements of γ_{13}^{∞} and phase equilibria for the thiocyanate-based ILs.[18–23] In separation processes, the selectivity and capacity can be directly calculated from activity coefficients at infinite dilution (γ_{13}^{∞}) for different separation problems.[24] Two thiocyanate-based ILs, 1-ethyl-3-methylimidazolium thiocyanate, [EMIM][SCN], and 1-butyl-3-methylimidazolium thiocyanate, [BMIM][SCN], were investigated by us as separation media for aliphatic and aromatic hydrocarbons and for thiophene and aliphatic hydrocarbons with very high selectivities and average capacities.[18,19] The highest selectivity values ever published indicated that these two ILs are the best for solvent extraction processes for different separation problems.

It is generally known that an increase of the alkyl chain length increases the capacity and decreases the selectivity for different ILs (imidazolium, pyridinium, pyrrolidinium, and ammonium).

The aim of this work was to measure activity coefficients at infinite dilution of the piperidinium-based IL: 1-butyl-1-methylpiperidinium thiocyanate [BMPIP][SCN] in alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, ethers, ketones, and water using a gas−liquid chromatography (GLC) method. The investigation includes the effect of the alkyl chain length of the solutes and the influence of temperature.

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Table 1. Investigated IL: Chemical Structure, Name, and Abbreviation

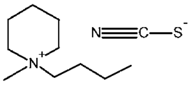
Structure	Name, abbreviation	M / g·mol^{-1}
	1-Butyl-1-Methylpiperidinium Thiocyanate, [BMPIP][SCN]	214.38

Table 2. Column Specification and Chromatograph Condition

	column 1	
	[BMPIP][SCN]	column 2
loading /%	44.93	35.26
mass coated/g	4.4616	3.8347
column length/m	1	
column i.d. /mm	4	
column temperature/K	318.15−368.15	
injector temperature/K	423.15	
detector temperature/K	423.15	
carrier gas	helium	
flow/cm^3·min^{-1}	15−100	

Experimental Section

Materials and Methods. The IL was as follows: [BMPIP]-[SCN] (IoLiTec Ionic Liquids Technology GmbH, Germany Merck, Germany, 0.98 in mass fraction; synthesized on request). The structure of the IL is shown in Table 1. All high purity solvents were supplied from Sigma-Aldrich and were used without any further purification because the GLC technique separated any impurities on the colums.

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 have been described previously.[25,26] Glass columns of lengths (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 IL was performed by dispersing a certain portion of Chromosorb in a solution of the IL in methanol followed by evaporation of the solvent using a rotating evaporator. The masses of the stationary phase and of the solid support were weighed with a precision of ± 0.0001 g. The solvent column packing varied from (35.26 to 44.93) mass percent of the IL, large enough to prevent any residual adsorption of solute onto the column packing. For each temperature the measurements were repeated by using two different columns with different mass percent packing (see Table 2). The results of the measurements for two different columns at two temperatures are shown as an example in Table 1S in the Supporting Information (SI). Care was taken to ensure that the methanol had completely evaporated from the IL-coated solid before making up the column. Before the experiment each column was conditioned by blowing carrier gas at a high flow rate (about 2.0 cm^3·s^{-1}) at the high temperature (about 373 K) through about 8 h.

The outlet pressure P_o was kept at atmospheric pressure. The pressure drop ($P_i - P_o$) was varied between (55 and 80) kPa depending on the flow rate of the carrier gas. The pressure drop was measured by a gas chromatograph with an uncertainty of ± 0.1 kPa. The atmospheric pressure was measured using a digital barometer with an uncertainty of ± 0.01 kPa.

The carrier gas was helium. The flow rate of carrier gas was (15 to 100) cm^3·min^{-1} and determined using a calibrated soap bubble flowmeter which was placed at the outlet after the detector. There was one flow rate for one solute, and the picture of this is shown in Table 2S in the SI. 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. Solute injections ranged from (0.01 to 0.3) μL and were considered to be at infinite dilution on the column.

Experiments were carried out at different temperatures (in steps of 10 K) between (318.15 and 358.15) K. The temperature of the column was maintained constant to within ± 0.02 K. At a given temperature, each experiment was repeated 2 to 4 times to check the reproducibility. Retention times were generally reproducible within (0.001 to 0.01) min depending on the temperature and the individual solute. At each temperature, values of the dead time t_G identical to the retention time of a nonretainable component were measured. While our GC was equipped with a TCD detector, air was used as a nonretainable component. The estimated overall error in γ_{13}^{∞} 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.[27]

Theoretical Basis

The equation developed by Everett[28] and Cruickshank et al.[29] was used in this work to calculate the γ_{13}^{∞} of solutes in the IL:

$$\ln \gamma_{13}^{\infty} = \ln\left(\frac{n_3RT}{V_N P_1^*}\right) - \frac{P_1^*(B_{11} - V_1^*)}{RT} + \frac{P_o J_2^{\,3}(2B_{12} - V_1^{\infty})}{RT} \tag{1}$$

The V_N denotes the net retention volume of the solute, P_o the outlet pressure, $P_oJ_2^{\,3}$ 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[30] equation for alkanes and Tsonopolous[31] equation for the rest of solvents. Using the Hudson and McCoubrey combining rules,[32,33] critical parameters for mixtures were calculated from the critical properties of the pure component.

The pressure correction term J_2^3 is given by

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

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

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

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.[34–36] Critical data used to calculate B_{11} and B_{12} were obtained from literature.[37,38] The fundamental values of critical parameters and B_{11} and B_{12} were presented in our previous work in the SI.[39]

Table 3. Average Experimental Activity Coefficients at Infinite Dilution γ_{13}^{∞} for the Solutes in the IL [BMPIP][SCN] at Different Temperatures and Excess Molar Enthalpies at Infinite Dilution, $\Delta H_1^{E,\infty}$

	T/K					$\Delta H_1^{E,\infty}$
	318.15	328.15	338.15	348.15	358.15	kJ·mol^{-1}
hexane	124[a]	104	89.2	78.4	68.5	13.9
heptane	170	142	127	111	102	12.1
octane	236	206	185	161	150	10.9
nonane	333	293	267	233	214	10.5
decane	487	433	390	342	310	10.8
cyclopentane	27.7[b]	24.4	22.2	20.1	19.1	8.9
cyclohexane	39.9	36.0	32.6	29.6	27.7	8.8
cycloheptane	44.3	41.5	37.4	34.7	32.8	7.4
cyclooctane	60.0	54.1	49.2	44.8	42.2	8.5
hex-1-ene	40.9	36.7	34.5	32.1	30.2	7.0
hept-1-ene	60.4	55.7	51.9	48.1	45.9	6.6
oct-1-ene	89.6	83.0	77.0	71.3	67.2	6.9
hex-1-yne	6.06	6.10	6.16	6.19	6.22	−0.60
hept-1-yne	9.17	9.20	9.21	9.25	9.31	−0.33
oct-1-yne	13.6	13.6	13.6	13.7	13.7	−0.21
benzene	1.90[c]	1.93	1.95	1.98	2.00	−1.1
toluene	3.14	3.17	3.19	3.21	3.23	−0.66
ethylbenzene	5.19	5.18	5.17	5.16	5.15	0.17
o-xylene	4.15	4.18	4.21	4.24	4.26	−0.60
m-xylene	5.23	5.24	5.25	5.26	5.27	−0.17
p-xylene	5.00	5.04	5.06	5.09	5.12	−0.53
methanol	0.360	0.361	0.361	0.361	0.362	−0.13
ethanol	0.639	0.627	0.616	0.606	0.599	1.6
water		0.331	0.335	0.340	0.345	−1.4
thiophene	1.10	1.13	1.17	1.20	1.23	−2.5
THF	2.28	2.31	2.34	2.36	2.39	−1.1
MTBE	13.1	12.7	12.3	12.0	11.7	2.6
diethyl ether	11.9	11.5	11.0	10.7	10.4	3.3
dipropyl ether	35.1	32.8	30.9	29.2	27.9	5.4
dibutyl ether	79.2	73.4	68.1	63.5	60.5	6.5
acetone	1.48	1.49	1.49	1.49	1.50	−0.23
pentan-2-one	3.05	3.06	3.06	3.07	3.07	−0.17
pentan-3-one	3.07	3.07	3.09	3.10	3.10	−0.30

[a] The error is 124 ± 3.7. [b] The error is 27.7 ± 0.8. [c] The error is 1.90 ± 0.06.

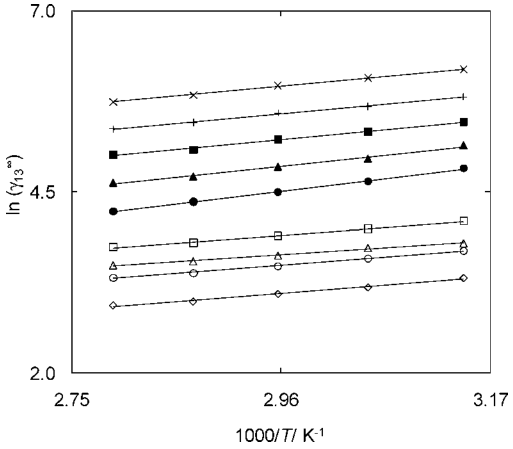


Figure 1. Plot of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ of [BMPIP][SCN] with solutes: ●, hexane; ▲, heptane; ■, octane; +, nonane; ×, decane; ◇, cyclopentane; ○, cyclohexane; △, cycloheptane; □, cyclooctane.

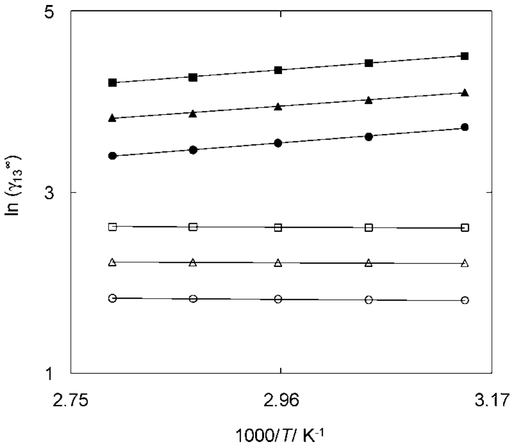


Figure 2. Plot of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for [BMPIP][SCN] with solutes: ●, hex-1-ene; ▲, hept-1-ene; ■, oct-1-ene; ○, hex-1-yne; △, hept-1-yne; □, oct-1-yne.

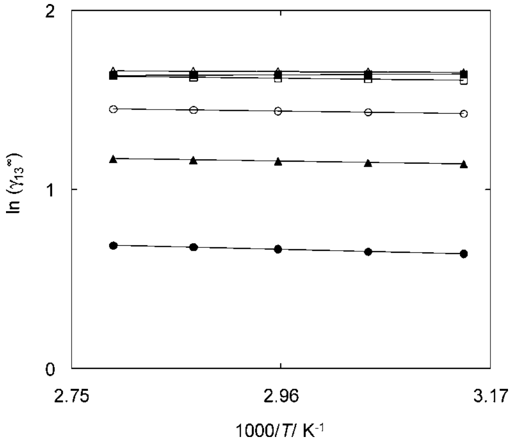


Figure 3. Plot of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for [BMPIP][SCN] with solutes: ●, benzene; ▲, toluene; ■, ethylbenzene; ○, *o*-xylene; △, *m*-xylene; □, *p*-xylene.

Results and Discussion

The average γ_{13}^{∞} values are listed in Table 3. The values of γ_{13}^{∞} for homological series of solutes increase with an increase of the solute alkyl chain length. This is typical dependence, observed for all ILs. The smallest interaction with solutes and the highest values of γ_{13}^{∞} were observed for alkanes (for example for heptane $\gamma_{13}^{\infty} = 170$ at $T = 318.15$ K), cycloalkanes, and alkenes. Much lower values for the same carbon number were obtained for alkynes. The dibutyl ether has a surprising high value ($\gamma_{13}^{\infty} = 79.3$ at $T = 318.15$ K). The cyclic structure of cycloalkanes reduces the value of γ_{13}^{∞} in comparison to the corresponding linear alkane. The γ_{13}^{∞} is in the same range of order for hex-1-ene and for cyclohexane, but for longer chain alkenes these values are much higher for the cyclohydrocarbons with the same carbon number. Alkynes and aromatic hydrocarbons have smaller values of γ_{13}^{∞} than alkanes, cycloalkanes, and alkenes. For benzene and thiophene the values are 1.90 and 1.10, respectively ($T = 318.15$ K), which is lower than for ethers and ketones. The smallest values of γ_{13}^{∞}, indicating the strongest interactions between solvent and solute, was observed for water. For alcohols the values of γ_{13}^{∞} are slightly higher than those for water. These polar compounds usually interact very strongly with a polar IL. In this case, the major influence on values of γ_{13}^{∞} has very strong interactions between −OH group in alcohols with the anion of the IL.

Figures 1 to 5 show the natural logarithm of the activity coefficients in the IL as a function of the inverse absolute temperature for all investigated solutes in [BMPIP][SCN]. The temperature dependence of γ_{13}^{∞} is different for the different solutes. 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, alcohols (except ethanol), water, tetrahydrofuran (THF), and ketones.

Table 3 lists the partial molar excess enthalpies at infinite dilution $\Delta H_1^{E,\infty}$ determined from the Gibbs−Helmholtz equation over the temperature range (318.15 to 358.15) K:

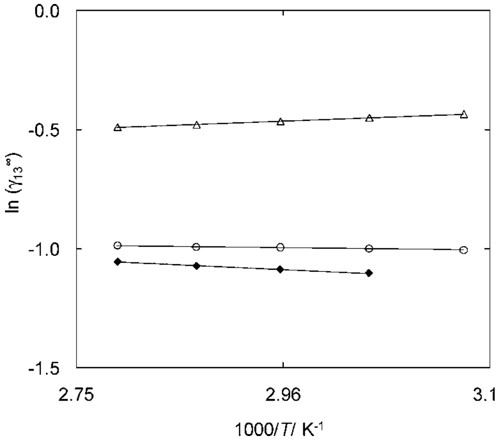


Figure 4. Plot of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for [BMPIP][SCN] with solutes: ○, methanol; △, ethanol; ♦, water.

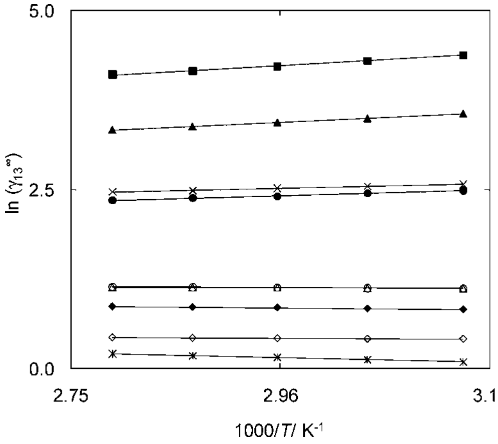


Figure 5. Plot of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for [BMPIP][SCN] with solutes: ●, diethyl ether; ▲, dipropyl ether, ■, dibutyl ether; ♦, THF; ×, methyl *tert*-butyl ether (MTBE); ○, pentan-2-one; △, pentan-3-one; ◇, propan-2-one; ∗, thiophene.

$$\frac{\partial \ln \gamma_i^{\infty}}{\partial(1/T)} = \frac{\Delta H_1^{\mathrm{E},\infty}}{R} \tag{4}$$

The $\Delta H_1^{\mathrm{E},\infty}$ values are negative for alkynes, aromatic hydrocarbons including thiophene (with exception of ethylbenzene), methanol, water, THF, and ketones. The negative values of the partial molar excess enthalpies at infinite dilution mean that the interactions between solute and solvent are higher than for similar molecules. For alkynes it is caused by interaction between the triple bond and polar anions of the IL. For THF and ketones, the $\Delta H_1^{\mathrm{E},\infty}$ values are negative for many different ILs.

A very important factor in the design of extraction processes is the knowledge about selectivity S_{12}^{∞} and capacity k_2^{∞} of entrainers, which can be calculated directly from experimental γ_{13}^{∞} values:

$$S_{12}^{\infty} = \gamma_{13}^{\infty}/\gamma_{23}^{\infty} \tag{5}$$

$$k_2^{\infty} = 1/\gamma_{23}^{\infty} \tag{6}$$

where "3" is an IL.

Table 4 shows influence of structure of ILs based on [BM-substituted]$^+$ cation or [SCN]$^-$ anion on S_{12}^{∞} and k_2^{∞} for heptane/benzene, cyclohexane/benzene, and heptane/thiophene separation problems at $T = 323.15$ K. The IL investigated in this work, [BMPIP][SCN], reveals the third high value of selectivity after [EMIM][SCN] and [BMIM][SCN].[18,19] The selectivity is 81.1 for heptane/benzene, 19.9 for cyclohexane/benzene, and 138.5 for heptane/thiophene. Unfortunately, the capacities were higher for the ILs with the [NTf$_2$]$^-$ anion. Many ILs based on butyl-methyl substituents exhibit lower selectivities than [EMIM]-[SCN], [BMIM][SCN], and [PMPIP][SCN].[40–50] For ILs based on the [SCN]$^-$ anion, the selectivities are usually much higher than for other ILs, for example, [BMPy][BF$_4$].[47]

Conclusions

Activity coefficients at infinite dilution for various solutes in the IL 1-butyl-1-methylpiperidinium thiocyanate were measured, and the high selectivities at infinite dilution for three tested separation problems, heptane/benzene, cyclohexane/benzene, and heptane/thiophene, were found in comparison to similar ILs with different anions. However, the selectivities were lower than those for the imidazolium-based thiocyanate ILs.

Supporting Information Available:

Table 1S: the experimental activity coefficients at infinite dilution γ_{13}^{∞} for the solutes in ionic liquid [BMPIP][SCN] at different

Table 4. Selectivities, S_{12}^{∞}, and Capacities, k_{12}^{∞}, at Infinite Dilution for Several ILs Based on the 1-Alkyl-1-methylpyrrolidinium Cation or Thiocyanate Anion, NMP, and Sulfolane for Different Separation Problems at $T = 323.15$ K

	S_{12}^{∞}			k_2^{∞}	k_2^{∞}	
solvent	heptane/benzene	cyclohexane/benzene	heptane/thiophene	benzene	thiophene	ref
[BMPIP][SCN]	**81.1**	**19.9**	**138.5**	**0.52**	**0.89**	**this work**
[PMPIP][NTf$_2$]	26.2	11.5	29.9	1.07	1.22	17
[EMIM][SCN]	109	25.7	-	0.29	-	18
[BMIM][SCN]	90.7	20.4	156	0.46	0.79	19
[HMIM][SCN]	35.0	11.7	53.0	0.50	0.76	20
[BMPy][SCN]	66.4	16.1	112	0.59	0.99	40
[BMPYR][SCN]	73.0	18.4	123	0.53	0.93	40
[BMIM][BF$_4$]	47.0	15.6	-	0.41		41
[BMIM][CF$_3$SO$_3$]	28.7	10.6	39.3	0.63	0.86	42
[BMIM][C$_2$H$_5$SO$_4$]	59.8	16.5	-	0.36		43
[BMIM][MDEGSO$_4$]	37.3	12.5	-	0.50		44
[BMIM][NTf$_2$]	20.2	8.6	-	1.11		43
[BMIM][OcSO$_4$]	6.1	3.5	-	0.69		45
[BMIM][PF$_6$]	31.6	10.9	42.0	0.51	0.68	46
[BMPy][BF$_4$]	49.8	16.3	-	0.61		47
[BMPy][NTf$_2$]	23.5	10.4	26.6	1.38	1.56	48
[BMPy][TOS]	13.8	5.1	-	0.25		49
[BMPYR][CF$_3$SO$_3$]	38.6	13.9	53.1	0.68	0.94	12
[BMPYR][NTf$_2$]	20.8	9.0	-	1.14		50

temperatures for two columns; table 2S: the flow rates for different solutes. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Domańska, U. Physico-chemical Properties and Phase Behaviour of Pyrrolidinium-based Ionic Liquids. *Int. J. Mol. Sci.* **2010**, *11*, 1825–1841.

(2) Lombardo, M.; Easwar, S.; Pasi, F.; Trombini, C.; Dhavale, D. D. Protonated Arginine and Lysine as Catalysts for the Direct Asymmetric Aldol Reaction in Ionic Liquids. *Tetrahedron* **2008**, *68*, 9203–9207.

(3) Pont, L.; Marcilla, R.; De Meatza, I.; Grande, H.; Mecerreyes, D. Pyrrolidinium-based Polymeric Ionic Liquids as Mechanically and Electrochemically Stable Polymer Electrolytes. *J. Power Sources* **2009**, *188*, 558–563.

(4) Azaceta, E.; Tena-Zaera, R.; Marcilla, R.; Fantini, S.; Echeberria, J.; Pomposo, J. A. Electrochemical Deposition of ZnO in a Room Temperature Ionic Liquid: 1-Butyl-1-methylpyrrolidinium Bis(trifluoromethanesulfonyl)imide. *Electrochem. Commun.* **2009**, *11*, 2184–2186.

(5) Hirao, M.; Sugimoto, H.; Ohno, H. Preparation of Novel Room-temperature Molten Salts by Neutralization of Amines. *J. Electrochem. Soc.* **2000**, *147*, 4168–4171.

(6) Hendrson, W. A.; Young, V. G., Jr.; Pearson, W.; Passerini, S.; De Long, H. C.; Trulove, P. C. Thermal Phase Behaviour of *N*-alkyl-*N*-methylpyrrolidinium and Piperidinium Bis(trfluoromethanesulfonyl)imide Salts. *J. Phys.: Condens. Matter* **2006**, *18*, 10377–10390.

(7) Salmimen, J.; Papaiconomu, N.; Anand Kumar, R.; Lee, J.-M.; Kerr, J.; Newman, J.; Prausnitz, J. M. Physicochemical Properties and Toxicities of Hydrophobic Piperidinium and Pyrrolidinium Ionic Liquids. *Fluid Phase Equilib.* **2007**, *261*, 421–426.

(8) Freire, M. G.; Neves, C. M. S. S.; Carvalho, P. J.; Gardas, R. L.; Fernandes, A. M.; Marrucho, I. M.; Santos, L. M. N. B. F.; Coutinho, J. A. P. Mutual Solubilities of Water and Hydrophobic Ionic Liquids. *J. Phys. Chem. B* **2007**, *111*, 1382–1389.

(9) Freire, M. G.; Neves, C. M. S. S.; Ventura, S. P. M.; Pratas, M. J.; Marrucho, I. M.; Oliviera, J.; Coutinho, J. A. P.; Fernandes, A. M. Solubility of Non-aromatic Ionic Liquids in Water and Correlation Using QSPR Approach. *Fluid Phase Equilib.* **2010**, *294*, 234–240.

(10) Gardas, R. L.; Costa, H. F.; Freire, M. G.; Carvalho, P. J.; Marrucho, I. M.; Fonseca, I. M. A.; Ferreira, A. G. M.; Coutinho, J. A. P. Densities and Derived Thermodynamic Properties of Imidazolium-, Pyridinium-, Pyrrolidinium-, and Piperidinium-based Ionic Liquids. *J. Chem. Eng. Data* **2008**, *53*, 805–811.

(11) Seki, S.; Kobayashi, T.; Kobayashi, Y.; Takei, K.; Miyashiro, H.; Hayamizu, K. Effect of Cation and Anion on Physical Properties of Room-temperature Ionic Liquids. *J. Mol. Liq.* **2010**, *152*, 9–13.

(12) Domańska, U.; Redhi, G. G.; Marciniak, A. Activity Coefficients at Infinite Dilution Measurements for Organic Solutes and Water in the Ionic Liquid 1-Butyl-1-methylpyrrolidinium Trifluoromethanesulfonate Using GLC. *Fluid Phase Equilib.* **2009**, *278*, 97–102.

(13) Nebig, S.; Liebert, V.; Gmehling, J. Measurements and Prediction of Activity Coefficients at Infinite Dilution (γ^∞), Vapor-liquid Equilibria (VLE) and Excess Enthalpies (H^E) of Binary Systems with 1,1-Dialkyl-pyrrolidinium Bis(trifluoromethylsulfonyl)imide Using mod. UNIFAC(Dortmund). *Fluid Phase Equilib.* **2009**, *277*, 61–67.

(14) Holbrey, J. D.; López-Martin, I.; Rothenberg, G.; Seddon, K. R.; Sivero, G.; Zheng, X. Desulfurization of Oils Using Ionic Liquids: Selection of Cationic and Anionic Components to Enhance Extraction Efficiency. *Green Chem.* **2008**, *10*, 87–92.

(15) Pereiro, A. B.; Rodríguez, A. An Ionic Liquid Proposed as Solvent in Aromatic Hydrocarbon Separation by Liquid Extraction. *AIChE J.* **2010**, *56*, 381–386.

(16) Westerholt, A.; Liebert, V.; Gmehling, J. Influence of Ionic Liquids on the Separation Factor of Three Standard Separation Problems. *Fluid Phase Equilib.* **2009**, *280*, 56–60.

(17) Domańska, U.; Paduszyński, K. Activity Coefficients at Infinite Dilution Measurements for Organic Solutes and Water in the Ionic Liquid 1-Propyl-1-methylpiperidinium Bis{(trifluoromethyl)sulfonyl}imide Using GLC. *J. Chem. Thermodyn.* **2010**, *42*, 1361–1366.

(18) Domańska, U.; Marciniak, A. Measurements of Activity Coefficients at Infinite Dilution of Aromatic and Aliphatic Hydrocarbons, Alcohols, and Water in the New Ionic Liquid [EMIM][SCN] Using GLC. *J. Chem. Thermodyn.* **2008**, *40*, 860–866.

(19) Domańska, U.; Laskowska, M. Measurements of Activity Coefficients at Infinite Dilution of Aliphatic and Aromatic Hydrocarbons, Alcohols, Thiophene, Tetrahydrofuran, MTBE, and Water in Ionic Liquid [BMIM][SCN] Using GLC. *J. Chem. Thermodyn.* **2009**, *41*, 645–650.

(20) Domańska, U.; Krŏlikowska, M.; Arasimowicz, M. Phase Equilibria of (1-Hexyl-3-methylimidazolium Thiocyanate + Water, Alcohol or Hydrocarbon) Binary Systems. *J. Chem. Eng. Data* **2010**, *55*, 773–777.

(21) Domańska, U.; Laskowska, M.; Pobudkowska, A. Phase Equilibria Study of the Binary Systems (1-Butyl-3-methylimidazolium Thiocyanate Ionic Liquid + Organic Solvent, or Water). *J. Phys. Chem. B* **2009**, *113*, 6397–6404.

(22) Domańska, U.; Królikowski, M.; Ślesińska, K. Phase Equilibria Study of the Binary System (Ionic Liquid + Thiophene): Desulfurization Process. *J. Chem. Thermodyn.* **2009**, *41*, 1303–1311.

(23) Domańska, U.; Królikowska, M.; Królikowski, M. Thermodynamic Phase Behaviour and Physico-chemical Properties of the Binary Systems {(1-Ethyl-3-methylimidazolium Thiocyanate, or 1-Ethyl-3-methylimidazolium Tosylate + Water, or + an Alcohol}. *Fluid Phase Equilib.* **2010**, *294*, 72–83.

(24) Kato, R.; Gmehling, J. Activity Coefficients at Infinite Dilution of Various Solutes in the Ionic Liquids $[\mathrm{MMIM}]^+[\mathrm{CH_3SO_4}]^-$, $[\mathrm{MMIM}]^+[\mathrm{CH_3OC_2H_4SO_4}]^-$,$[\mathrm{MMIM}]^+[(\mathrm{CH_3})_2\mathrm{PO_4}]^-$,$[\mathrm{C_5H_5NC_2H_5}]^+[(\mathrm{CF_3}\text{-}\mathrm{SO_2})_2\mathrm{N}]^-$ and $[\mathrm{C_5H_5NH}]^+[\mathrm{C_2H_5OC_2H_4OSO_3}]^-$. *Fluid Phase Equilib.* **2004**, *226*, 37–44.

(25) Letcher, T. M.; Moollan, W. C. The Determination of Activity Coefficients of Hydrocarbons at Infinite Dilution Using a g.l.c. Technique with the Polar Solvent Tetrahydrothiophene-1,1-dioxide, c-$(\mathrm{CH_2})_4\mathrm{SO_2}$, (Sulfolane) at the Temperature 303.15 K. *J. Chem. Thermodyn.* **1995**, *27*, 867–872.

(26) Moollan, W. C. The determination of activity coefficients at infinite dilution. Ph.D. Thesis, University of Natal, Durban, 1996.

(27) Tiegs, D.; Gmehling, J.; Medina, A.; Soares, M.; Bastos, J.; Alessi, P.; Kikic, I. Activity Coefficients at Infinite Dilution. *Chemistry Data Series*, vol. IX, Part 1; Dechema: Frankfurt, 1986; p 586.

(28) Everett, D. H. Effect of Gas Imperfection on Gas-liquid Chromatography Measurements: a Refined Method for Determining Activity Coefficients and Second Virial Coefficients. *Trans. Faraday Soc.* **1965**, *61*, 1637–1639.

(29) Cruickshank, A. J. B.; Gainey, B. W.; Hicks, C. P.; Letcher, T. M.; Moody, R. W.; Young, C. L. Gas-liquid Chromatographic Determination of Cross-term Second Virial Coefficients Using Glycerol. *Trans. Faraday Soc.* **1969**, *65*, 1014–1031.

(30) McGlashan, M. L.; Potter, D. J. B. An Apparatus for the Measurement of the Second Virial Coefficients of Vapors; the Second Virial Coefficients of Some *n*-Alkanes and of Some Mixtures of *n*-Alkanes. *Proc. R. Soc. London* **1951**, *267*, 478–500.

(31) Poling, B. E.; Prausnitz, J. M. *Properties of Gases and Liquids*; McGraw-Hill Publishing: New York, 2001. http://www.myilibrary.com/Browse/open.asp?ID=91317&loc=112.

(32) Hudson, G. H.; McCoubrey, J. C. Intermolecular Forces Between Unlike Molecules. A More Complete Form of the Combining Rules. *Trans. Faraday Soc.* **1960**, *56*, 761–771.

(33) Cruickshank, A. J. B.; Windsor, M. L.; Young, C. L. Prediction of Second Virial Coefficients of Mixtures from the Principle of Corresponding States. *Trans. Faraday Soc.* **1966**, *62*, 2341–2347.

(34) Design Institute for Physical Properties, Sponsored by AIChE. *DIPPR Project 801 - Full Version*; Design Institute for Physical Property Data/AIChE: New York, 2005. http://www.knovel.com/knovel2/Toc.jsp?BookID=1187&VerticalID=0.

(35) Yaws, C. L. *Chemical Properties Handbook*; McGraw-Hill: New York, 1999. http://www.knovel.com/knovel2/Toc.jsp?BookID=49&VerticalID=0.

(36) Yaws, C. L.; Narasimhan, P. K.; Gabbula, C. *Yaws' Handbook of Antoine Coefficients for Vapor Pressure* (Electronic Edition); Knovel: New York, 2005. http://www.knovel.com/knovel2/Toc.jsp?BookID=1183&VerticalID=0.

(37) Yaws, C. L. *Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds*; Knovel: New York, 2003. http://www.knovel.com/knovel2/Toc.jsp?BookID=667&VerticalID=0.

(38) Dean, J. A. *Lange's Handbook of Chemistry*; McGraw-Hill: New York, 1999. http://www.knovel.com/knovel2/Toc.jsp?BookID=47&VerticalID=0.

(39) Marciniak, A.; Wlazło, M. Activity Coefficients at Infinite Dilution Measurements for Organic Solutes and Water in the Ionic Liquid 1-Butyl-3-methyl-pyridinium Trifluoromethanesulfonate. *J. Chem. Eng. Data* **2010**, *55*, 3208–3211.

(40) Domańska, U.; Królikowska, M. Measurements of Activity Coefficients at Infinite Dilution in Solvent Mixtures with Thiocyanate-Based Ionic Liquids Using GLC Technique. *J. Phys. Chem. B* **2010**, *114*, 8460–8466.

(41) Foco, G. M.; Bottini, S. B.; Quezada, N.; de la Fuente, J. C.; Peters, C. J. Activity Coefficients at Infinite Dilution in 1-Alkyl-3-methylimidazolium Tetrafluoroborate Ionic Liquids. *J. Chem. Eng. Data* **2006**, *51*, 1088–1091.

(42) Domańska, U.; Marciniak, A. Activity Coefficients at Infinite Dilution Measurements for Organic Solutes and Water in the Ionic Liquid 1-Butyl-3-methylimidazolium Trifluoromethanesulfonate. *J. Phys. Chem. B* **2008**, *112*, 11100–11105.

(43) Krummen, M.; Wasserscheid, P.; Gmehling, J. Measurement of Activity Coefficients at Infinite Dilution in Ionic Liquids Using the Dilutor Technique. *J. Chem. Eng. Data* **2002**, *47*, 1411–1417.

(44) Letcher, T. M.; Domańska, U.; Marciniak, M.; Marciniak, A. Activity Coefficients at Infinite Dilution Measurements for Organic Solutes in the Ionic Liquid 1-Butyl-3-Methyl-imidazolium 2-(2-Methoxyethoxy) ethylsulfate Using g.l.c. at $T = (298.15, 303.15, \text{and } 308.15)$ K. *J. Chem. Thermodyn.* **2002**, *47*, 1411–1417.

(45) Letcher, T. M.; Marciniak, A.; Marciniak, M.; Domańska, U. Determination of Activity Coefficients at Infinite Dilution of Solutes in the Ionic Liquid 1-Butyl-3-methylimidazolium Octyl Sulfate Using Gas-Liquid. *J. Chem. Eng. Data* **2005**, *50*, 1294–1298.

(46) Mutelet, F.; Butet, V.; Jaubert, J.-N. Application of Inverse Gas Chromatography and Regular Solution Theory for Characterization of Ionic Liquids. *Ind. Eng. Chem. Res.* **2005**, *44*, 4120–4127.

(47) Heintz, A.; Kulikov, D. V.; Verevkin, S. P. Thermodynamic Properties of Mixtures Containing Ionic Liquids. Activity Coefficients at Infinite Dilution of Polar Solutes in 4-Methyl-*N*-butyl-pyridinium Tetrafluoroborate Using Gas-Liquid Chromatography. *J. Chem. Eng. Data* **2001**, *46*, 1526–1529.

(48) Domańska, U.; Marciniak, A. Activity Coefficients at Infinite Dilution Measurements for Organic Solutes and Water in the Ionic Liquid 4-methyl-*N*-butyl-pyridinium Bis(trifluoromethylsulfonyl)-imide. *J. Chem. Thermodyn.* **2009**, *41*, 1350–1355.

(49) Letcher, T. M.; Ramjugernath, D.; Królikowski, M.; Laskowska, M.; Naidoo, P.; Domańska, U. Activity Coefficients at Infinite Dilution Measurements for Organic Solutes in the Ionic Liquid *N*-butyl-4-methylpyridinium Tosylate Using GLC at $T = (328.15, 333.15, 338.15, \text{and } 343.15)$ K. *Fluid Phase Equilib.* **2009**, *276*, 31–36.

(50) Kato, R.; Gmehling, J. Systems With Ionic Liquids: Measurement of VLE and C1 Data and Prediction of Their Thermodynamic Behavior Using Original UNIFAC, mod. UNIFAC(Do) and COSMO-RS(Ol). *J. Chem. Thermodyn.* **2005**, *37*, 603–619.

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