



Measurements of activity coefficients at infinite dilution for organic solutes and water in the ionic liquid 1-butyl-1-methylpyrrolidinium tricyanomethanide



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ABSTRACT

The activity coefficients at infinite dilution, γ_{13}^{∞} , for 62 solutes, including alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, water, thiophene, ethers, ketones, acetonitrile, pyridine and 1-nitropropane in the ionic liquid 1-butyl-1-methylpyrrolidinium tricyanomethanide, [BMPYR][TCM] were determined by gas–liquid chromatography at six temperatures over the range of (318.15 to 368.15) K. The partial molar excess Gibbs free energy, ΔG_1^E , enthalpy ΔH_1^E , and entropy term $T_{ref}\Delta S_1^E$ at infinite dilution were calculated from the experimental γ_{13}^{∞} values obtained over the temperature range. The densities of [BMPYR][TCM] were measured within temperature range from 318.15 K to 368.15 K. The gas–liquid partition coefficients, K_1 were calculated for all solutes. The values of selectivity for few separation problems as hexane/benzene, cyclohexane/benzene, heptane/thiophene were calculated from γ_{13}^{∞} and compared to literature values for *N*-methyl-2-pyrrolidinone (NMP), sulfolane, and other ionic liquids based on [BMPYR]⁺ cation. In comparison with the former measured ILs, [BMPYR][TCM] present quite high selectivity for the separation of aromatic hydrocarbons and aliphatics hydrocarbons, an average capacity for benzene. The data presented here shows that [BMPYR][TCM] ionic liquid can be used as an alternative solvent for the separation of thiophene from the aliphatic hydrocarbons.

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1. Introduction

Ionic liquids (ILs) are widely proposed as new solvents in the several applications in new technologies under development [1–5]. In recent years the new methods are proposed for using ILs in extraction, extractive distillation and separation [6–8]. The desulfurization process of fuels is based on the extraction of the sulfur compounds, which are more soluble in the IL than aliphatic hydrocarbons [7]. More popular at the new bibliography is however, the combining method of oxidation and extraction [9]. ILs must be thermally and chemically stable and must offer the high selectivity of extraction. This is the important information for engineering design of extraction process. The selectivity is possible to calculated from the measurements of activity coefficients at infinite dilution, γ_{13}^{∞} . In this work, we present the new ionic liquid, 1-butyl-1-methylpyrrolidinium tricyanomethanide, [BMPYR][TCM], which was proposed by us for the separation of sulfur compounds and alkanes. The possible extraction of aromatic hydrocarbons from

aliphatic hydrocarbons and especially of thiophene from heptane is expected with high selectivities. The anion [TCM][−] {C(CN)₃[−]} was used already for the extraction of thiophene and dibenzothio-
phene with a very good result of the extraction (about 95 wt%) for the simultaneous separation from alkanes with pyridinium-based and imidazolium-based ILs [7].

Three pyrrolidinium-based ionic liquids have been studied by us recently: 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate, [BMPYR][FAP], 1-butyl-1-methylpyrrolidinium tetracyanoborate, [BMPYR][TCB] and 1-butyl-1-methylpyrrolidinium tricyanomethanide, [BMPYR][TCM] in ternary liquid–liquid equilibrium (LLE). The [TCM][−] anion in comparison with [TCB][−] and [FAP][−] anions showed much higher selectivity and slightly lower distribution ratio for extraction of thiophene from aliphatic hydrocarbons [10].

The values of activity coefficients at infinite dilution of a solute in the IL provide the basic information on the intermolecular interaction between solute and the IL. The lowest values are usually observed for alkynes, polar substances as alcohols, ketones or ethers which is a result of hydrogen bonding, the Π – Π , n – Π , or other strong interactions [11–13]. An interesting review on the all measured γ_{13}^{∞} up to 2010 was presented recently by Marciniak [14].

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In this work, continuing our studies on the selectivity of the separation of aromatic and aliphatic hydrocarbons, or extraction of sulfur compounds from alkanes the examination on γ_{13}^{∞} of selected 62 organic compounds and water in the ionic liquid [BMPYR][TCM] was provided. The main focus of these measurements was put on data of aliphatic and aromatic hydrocarbons as well as thiophene and pyridine. The discussion on the separation of many different mixtures including aromatic/aliphatic hydrocarbons, or desulphurization, or denitrogenation of fuels will be provided. The comparisons with previously-published [BMPYR]-based ILs is presented. The thermodynamic properties at infinite dilution at chosen temperature $T = 328.15$ K were analysed to describe the intermolecular interactions and to identify the potential of [BMPYR][TCM] to be used as a new solvent in the discussed separation processes. The density of the IL as a function of temperature is determined for the calculation of the gas–liquid partition coefficients K_L .

2. Experimental

2.1. Chemicals and materials

The sample of 1-butyl-1-methylpyrrolidinium tricyanomethanide, [BMPYR][TCM], was purchased from Iolitec (≥ 0.98 mass fraction purity); $M = 234.23$ g · mol⁻¹, CAS No. 878027-72-6. The sample was dried for several days at $T = 300$ K under reduced pressure to remove volatile impurities and trace water. After this procedure, the impurity of Iolitec sample was not recalculated in mole fraction concentrations due to the fact that the GLC technique separates any impurities on the column. Most of the solutes were purchased from Sigma Aldrich or Fluka. The sources and mass fraction purities of materials used are listed in table 1S in the Supplementary Material. The structure of [BMPYR][TCM] is shown in table 1.

2.2. Water content

The water content was analysed by the Karl-Fisher titration technique before preparing the column. The sample of 3 cm³ of the IL was dissolved in methanol (Merck) and titrated with steps of 0.0025 cm³. The results obtained have shown the water content to be less than $370 \cdot 10^{-6}$. The error on the water content was $\pm 2\%$ for the 3 cm³ IL injected.

2.3. Apparatus and experimental procedure

The methodology of the present investigation was described by us in many previous papers [10–12]. The PerkinElmer Clarus 500 gas chromatograph equipped with a thermal conductivity detector (TCD) was used. The data were collected and processed using TotalChrom Workstation software. Glass columns of length 1 m and 4 mm internal diameter were used. The column preparation and the packing method used in this work have been described in detail in our previous work [11,12]. Chromosorb W/AW-DCMS 100/120 mesh was used as the solid support and was supplied by Sigma-Aldrich. The [BMPYR][TCM] was dissolved in methanol and

dispersed in Chromosorb. After coating, the solvent was evaporated using a rotary evaporator. The masses of the stationary phase and of the solid support were weighed with a precision ± 0.0001 g, achieving an uncertainty in the IL loading on the column on the order of $2 \cdot 10^{-4}$ mmol. The solvent column packing were 45.10 (9.5712 mmol) and 49.93 (11.412 mmol) mass per cent of [BMPYR][TCM]. The large column packing is used to prevent the residual adsorption of solute onto the column packing, what is important especially for alkanes. The inlet pressure, P_i , was measured by a pressure gauge installed on the gas chromatograph with an uncertainty of ± 0.1 kPa and the outlet pressure, P_o , was measured using an Agilent Precision Gas Flow Meter having an uncertainty of ± 0.07 kPa. The flow rate of carrier gas was determined using the same Agilent Precision Gas Flow Meter which was placed at the outlet after the detector and had an uncertainty of ± 0.1 cm³ · min⁻¹. 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 duly corrected for water vapour pressure. Solute injections ranged from (0.01 to 0.3) · 10⁻³ cm³ and can be considered to be at infinite dilution on the column. The temperature of the column was maintained constant to within ± 0.02 K. Each experiment was repeated two to three times to establish repeatability. Retention times were generally reproducible to within (10⁻³ to 10⁻²) min depending upon the temperature and the individual solute. At each temperature, values of the dead time, t_G , equivalent to the retention time of a completely non-retained component were also measured. For the TCD detector air was used as a non-retainable 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 vapour pressure.

2.4. Density measurements

The density of the [BMPYR][TCM] was measured using an Anton Paar GmbH 4500 vibrating-tube densimeter (Graz, Austria). The temperature was controlled with two integrated Pt 100 platinum thermometers provided good precision of (± 0.01 K). The densimeter includes an automatic correction for the viscosity of the sample. The apparatus is precise to within $1 \cdot 10^{-5}$ g · cm⁻³, and the overall uncertainty of the measurements was estimated to be better than $5 \cdot 10^{-5}$ g · cm⁻³. The calibration of the densimeter was performed at atmospheric pressure using doubly distilled and degassed water, specially-purified benzene (CHEMIPAN, Poland 0.999), and dried air.

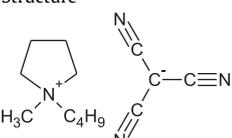
3. Theoretical basis

The gas–liquid chromatography (GLC), is easy and widely used method. The γ_{13}^{∞} for solute (1) partitioning between a carrier gas (2) and a non-volatile liquid solvent (3), here the IL are calculated from the solute retention according to the equations developed by Everett [15] and Cruickshank *et al.* [16]:

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

In this expression, n_3 is the number of moles of solvent on the column packing, R is the gas constant, T is the column temperature, V_N denotes the net retention volume of the solute, P_1^* is the saturated vapour 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} (the carrier gas is helium) is the mixed second virial coefficient of the solute and carrier gas, and V_1^{∞} is the partial molar volume of the solute at infinite dilution in the

TABLE 1
Investigated ionic liquid: structure, name and abbreviation of name.

Structure	Name, abbreviation
	1-butyl-1-methylpyrrolidinium tricyanomethanide, [BMPYR][TCM]

solvent. The parameters required in the calculations of the γ_{13}^{∞} were developed using equations and constants taken from the literature [17]. The values of B_{12} were calculated using the Tsonopolous [18] equation. The parameters for the Tsonopolous equation are described in [18]. The pressure correction term, J_2^3 , is given by Grant [19]

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

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

$$V_N = \left(J_2^3\right)^{-1} U_o(t_R - t_G), \quad (3)$$

TABLE 2

Average experimental activity coefficients at infinite dilution, γ_{13}^{∞} , for various solutes in [BMPYR][TCM] at different temperatures.^a

Solute	T/K					
	318.15	328.15	338.15	348.15	358.15	368.15
Pentane	16.7	16.0	15.3	14.5	13.9	13.4
Hexane	23.4	22.3	21.1	20.1	19.2	18.3
3-Methylpentane	21.0	20.1	19.1	18.1	17.3	16.6
2,2-Dimethylbutane	21.1	20.3	19.2	18.4	17.8	17.0
Heptane	33.7	31.8	29.9	27.9	26.3	24.9
Octane	48.1	45.3	41.6	39.1	36.9	34.5
2,2,4-Trimethylpentane	39.1	36.9	35.0	32.8	31.1	29.4
Nonane	68.8	63.9	58.2	54.3	50.8	47.1
Decane	99.2	91.3	82.4	76.4	70.9	65.2
Cyclopentane	7.53	7.29	7.00	6.71	6.48	6.27
Cyclohexane	11.1	10.6	10.0	9.49	9.10	8.74
Methylcyclohexane	15.9	15.3	14.4	13.6	13.0	12.4
Cycloheptane	13.5	12.9	12.2	11.5	10.9	10.4
Cyclooctane	17.2	16.3	15.3	14.3	13.6	12.9
Pente-1-ene	7.51	7.40	7.29	7.14	7.00	6.92
Hex-1-ene	10.6	10.3	10.0	9.68	9.42	9.15
Cyclohexene	5.16	5.10	4.99	4.86	4.77	4.68
Hept-1-ene	15.0	14.7	14.2	13.7	13.3	12.9
Oct-1-ene	21.8	21.0	20.1	19.2	18.5	17.8
Dec-1-ene	43.2	41.4	39.4	37.4	35.6	33.8
Pen-1-yne	2.10	2.17	2.23	2.27	2.30	2.35
Hex-1-yne	2.87	2.97	3.03	3.07	3.11	3.16
Hept-1-yne	4.03	4.15	4.21	4.24	4.28	4.32
Oct-1-yne	5.73	5.85	5.89	5.90	5.91	5.93
Benzene	1.02	1.04	1.07	1.09	1.11	1.13
Toluene	1.43	1.47	1.51	1.55	1.57	1.60
Ethylbenzene	2.11	2.15	2.19	2.23	2.25	2.29
<i>o</i> -Xylene	1.76	1.81	1.85	1.90	1.93	1.97
<i>m</i> -Xylene	2.06	2.12	2.17	2.21	2.25	2.30
<i>p</i> -Xylene	2.01	2.06	2.12	2.16	2.21	2.25
Styrene	1.12	1.16	1.20	1.24	1.27	1.31
α -Methylstyrene		1.67	1.76	1.84	1.90	1.97
Methanol	0.699	0.670	0.646	0.625	0.607	0.590
Ethanol	0.967	0.918	0.876	0.836	0.801	0.770
Propan-1-ol	1.14	1.08	1.03	0.983	0.945	0.913
Propan-2-ol	1.20	1.13	1.08	1.02	0.984	0.950
Butan-1-ol	1.43	1.34	1.27	1.22	1.16	1.11
Butan-2-ol	1.34	1.27	1.21	1.16	1.12	1.09
2-Methyl-propan-1-ol	1.42	1.32	1.24	1.17	1.12	1.07
<i>tert</i> -Butanol	1.30	1.23	1.18	1.14	1.11	1.09
Water	0.973	0.922	0.884	0.833	0.801	0.770
Thiophene	0.709	0.730	0.752	0.773	0.794	0.821
Tetrahydrofuran	0.848	0.868	0.890	0.911	0.934	0.952
1,4-Dioxane	0.642	0.669	0.697	0.721	0.745	0.768
<i>tert</i> -Butyl methyl ether	3.45	3.52	3.56	3.58	3.62	3.69
Methyl <i>tert</i> -pentyl ether	4.83	4.89	4.90	4.88	4.89	4.91
Ethyl <i>tert</i> -butyl ether	8.44	8.39	8.31	8.16	8.09	8.02
Diethyl ether	3.34	3.37	3.38	3.37	3.39	3.40
Di- <i>n</i> -propyl ether	8.43	8.33	8.16	7.97	7.82	7.73
Di- <i>iso</i> -propyl ether	8.99	9.02	8.91	8.79	8.63	8.57
Di- <i>n</i> -butyl ether	17.3	16.7	16.1	15.5	14.9	14.4
Acetone	0.624	0.639	0.650	0.662	0.675	0.687
Pentan-2-one	1.03	1.05	1.08	1.10	1.12	1.14
Pentan-3-one	1.00	1.03	1.06	1.08	1.11	1.13
Methyl acetate	1.00	1.02	1.04	1.06	1.08	1.09
Ethyl acetate	1.41	1.43	1.46	1.47	1.50	1.53
Methyl propanoate	1.24	1.27	1.30	1.32	1.35	1.38
Methyl butanoate	1.69	1.72	1.76	1.79	1.82	1.85
Butanal	0.907	0.930	0.949	0.968	0.986	1.01
Acetonitrile	0.558	0.563	0.566	0.569	0.572	0.576
Pyridine	0.567	0.580	0.592	0.603	0.617	0.627
1-Nitropropane		0.742	0.752	0.762	0.772	0.782

^a Standard uncertainties are $u(\gamma_{13}^{\infty}) < 3\%$, $u(T) = 0.02$ K.

where t_R and t_G are the retention times for the solute and an unreturned gas, respectively, and U_o is the column outlet flow rate, corrected for the vapour pressure of water by

$$U_o = U \left(1 - \frac{P_w}{P_o} \right) \frac{T}{T_f}, \quad (4)$$

where T_f is the temperature at the column outlet, P_w is the vapour pressure of water at T_f , and U is the flow rate measured with the flow meter.

While the activity coefficients at infinite dilution are determined as a function of temperature, $\ln \gamma_{13}^\infty$ can be split to its respective limiting enthalpic and entropic components

TABLE 3

Limiting partial molar excess enthalpies $\Delta H_1^{E,\infty}$, excess Gibbs free energies $\Delta G_1^{E,\infty}$, and entropies $T_{ref} \Delta S_1^{E,\infty}$ for organic solutes and water in [BMPYR][TCM] at the reference temperature $T_{ref} = 338.15 \text{ K}$.^a

Solute	$\Delta H_1^{E,\infty}/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta G_1^{E,\infty}/\text{kJ} \cdot \text{mol}^{-1}$	$T_{ref} \Delta S_1^{E,\infty}/\text{kJ} \cdot \text{mol}^{-1}$
Pentane	4.4	7.56	-3.18
Hexane	4.8	8.47	-3.66
3-Methylpentane	4.7	8.19	-3.51
2,2-Dimethylbutane	4.3	8.21	-3.94
Heptane	6.0	9.44	-3.47
Octane	6.5	10.4	-3.88
2,2,4-Trimethylpentane	5.6	9.84	-4.28
Nonane	7.4	11.3	-3.95
Decane	8.2	12.3	-4.16
Cyclopentane	3.7	5.42	-1.76
Cyclohexane	4.7	6.44	-1.70
Methylcyclohexane	5.0	7.44	-2.46
Cycloheptane	5.1	6.98	-1.85
Cyclooctane	5.8	7.62	-1.83
Pente-1-ene	1.7	5.46	-3.80
Hex-1-ene	2.9	6.36	-3.44
Cyclohexene	2.0	4.45	-2.46
Hept-1-ene	3.0	7.33	-4.33
Oct-1-ene	4.0	8.31	-4.31
Dec-1-ene	4.8	10.2	-5.36
Pen-1-yne	-2.1	2.11	-4.21
Hex-1-yne	-1.7	2.97	-4.72
Hept-1-yne	-1.3	3.88	-5.15
Oct-1-yne	-0.5	4.82	-5.36
Benzene	-2.0	0.11	-2.14
Toluene	-2.2	1.05	-3.23
Ethylbenzene	-1.6	2.09	-3.69
<i>o</i> -Xylene	-2.1	1.62	-3.73
<i>m</i> -Xylene	-2.0	2.05	-4.10
<i>p</i> -Xylene	-2.2	1.97	-4.13
Styrene	-3.0	0.40	-3.40
α -Methylstyrene	-4.1	1.40	-5.52
Methanol	3.3	-1.09	4.37
Ethanol	4.4	-0.23	4.67
Propan-1-ol	4.3	0.21	4.05
Propan-2-ol	4.6	0.33	4.29
Butan-1-ol	4.8	0.80	4.00
Butan-2-ol	4.0	0.65	3.35
2-Methyl-propan-1-ol	5.5	0.76	4.69
<i>tert</i> -Butanol	3.3	0.56	2.76
Water	4.6	-0.22	4.82
Thiophene	-2.8	-0.86	-1.97
Tetrahydrofuran	-2.3	-0.39	-1.91
1,4-Dioxane	-3.5	-1.10	-2.39
<i>tert</i> -Butyl methyl ether	-1.2	3.43	-4.63
Methyl <i>tert</i> -pentyl ether	-0.2	4.33	-4.55
Ethyl <i>tert</i> -butyl ether	1.1	5.80	-4.75
Diethyl ether	-0.3	3.31	-3.62
Di- <i>n</i> -propyl ether	1.8	5.78	-3.99
Di- <i>iso</i> -propyl ether	1.1	6.00	-4.95
Di- <i>n</i> -butyl ether	3.6	7.68	-4.07
Acetone	-1.9	-1.22	-0.64
Pentan-2-one	-2.0	0.13	-2.14
Pentan-3-one	-2.5	0.08	-2.60
Methyl acetate	-1.7	0.05	-1.75
Ethyl acetate	-1.5	0.98	-2.49
Methyl propanoate	-2.0	0.65	-2.64
Methyl butanoate	-1.8	1.48	-3.26
Butanal	-2.0	-0.20	-1.83
Acetonitrile	-0.6	-1.57	0.97
Pyridine	-1.9	-1.49	-0.45
1-Nitropropane	-1.3	-0.81	-0.51

^a Standard uncertainties are $u(\Delta H_1^{E,\infty}) = \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$; $u(\Delta G_1^{E,\infty}) = \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$; $u(T_{ref} \Delta S_1^{E,\infty}) = \pm 0.05 \text{ kJ} \cdot \text{mol}^{-1}$.

$$\ln \gamma_{13}^{\infty} = \frac{\Delta H_1^{E,\infty}}{RT} - \frac{\Delta S_1^{E,\infty}}{R} \quad (5)$$

Assuming that the temperature dependence follows a linear van't Hoff relation

$$\ln \gamma_{13}^{\infty} = a/T + b, \quad (6)$$

the partial molar excess enthalpy, $\Delta H_1^{E,\infty} = Ra$, and $\Delta S_1^{E,\infty}$ at infinite dilution can be obtained from the slope and intercept.

The gas–liquid partition coefficient $K_L = (c_1^l/c_1^g)$ for a solute partitioning between a carrier gas and the [BMPYR][TCM] was calculated from the solute retention according to the following equation [20]

$$\ln(K_L) = \ln\left(\frac{V_N \rho_3}{m_3}\right) - \frac{P_0 J_2^3 (2B_{12} - V_1^{\infty})}{RT}, \quad (7)$$

in which ρ_3 is the density of the IL and m_3 is the mass of the IL and V_1^{∞} is the partial molar volume of the solute at infinite dilution in the solvent.

4. Results and discussion

The average values obtained for γ_{13}^{∞} of the organic solutes and water in [BMPYR][TCM] determined at six temperatures (318.15, 318.15, 328.15, 338.15, 348.15 and 368.15) K are listed in table 2. The values of γ_{13}^{∞} were calculated using equation 1. The repeatability of γ_{13}^{∞} values from two columns were within $\pm 1.5\%$ for the majority of the solutes. The virial coefficients values B_{11} and B_{12} and critical parameters for most of the solutes needed for the calculation of γ_{13}^{∞} were presented in our previous publication [21].

Because of the lower interaction, the values of γ_{13}^{∞} increase with an increase of the alkyl chain length in a series of alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons (increasing radicals), alcohols, ethers, and ketones. The highest γ_{13}^{∞} value, which present the weaker interaction between the solute and solvent is observed for the decane (99.2) at $T = 318.15$ K. The value obtained in this work is much lower than that observed for other ILs [22,23]. The lower values are observed as usual for polar solutes as for methanol (0.699), 1,4-dioxane (0.642), acetone (0.624), pyridine (0.567) and acetonitrile (0.558) at $T = 318.15$ K. The γ_{13}^{∞} value for thiophene at $T = 318.15$ K has lower value (0.709) in comparison with other ILs [22–25]. This low value of γ_{13}^{∞} for thiophene is the first information about the possible high extraction of thiophene from aliphatic hydrocarbons. It may be expected as a high value. The values of γ_{13}^{∞} for aromatic hydrocarbons as benzene (1.02) and toluene (1.43) at $T = 318.15$ K are in the same range as for other ILs [22–25]. The very low value of γ_{13}^{∞} for pyridine (0.567) at $T = 318.15$ K also suggest the high selectivity of the extraction of nitrogen-compounds from alkanes.

The temperature dependences of γ_{13}^{∞} for different solutes are shown in figures 1S to 7S in the Supplementary Material. The diagrams present the plot of the natural logarithm of the γ_{13}^{∞} as a function of the inverse absolute temperature for all investigated solutes. As usual with an increase in temperature, a decrease in γ_{13}^{∞} is observed for most of the solutes including the alkanes, cycloalkanes, alkenes, alcohols, water, and few ethers. The inverse dependence on temperature is observed for alkynes, aromatic hydrocarbons, styrene, α -methylstyrene, thiophene, 1,4-dioxane, most of ethers, acetone, esters, pyridine and 1-nitropropane.

The thermodynamic functions at infinite dilution, calculated from the γ_{13}^{∞} values are listed in table 3. The partial excess molar enthalpies at infinite dilution, $\Delta H_1^{E,\infty}$, the partial excess molar Gibbs free energies at infinite dilution, $\Delta G_1^{E,\infty}$, and the partial excess molar entropies at infinite dilution, $T_{ref} \Delta S_1^{E,\infty}$, of all the solutes in [BMPYR][TCM] studied at a reference temperature $T = 338.15$ K is giving us more information about the interaction

between the solute and the IL. The standard uncertainties of the thermodynamic functions estimated, are from (0.5 to 0.8) kJ · mol⁻¹ for the majority of the solutes. The partial excess molar enthalpies at infinite dilution, $\Delta H_1^{E,\infty}$, determined from the Gibbs–Helmholtz equation exhibit negative values for alkynes, aromatic hydrocarbons, styrene, α -methylstyrene, thiophene, some ethers, ketones, esters, pyridine and 1-nitropropane. The negative values of $\Delta H_1^{E,\infty}$ manifests the stronger energetic solute–solvent interactions. The $\Delta G_1^{E,\infty}$ was calculated from the temperature dependence of γ_{13}^{∞} (see equations (5) and (6)). The $\Delta G_1^{E,\infty}$ is positive for most of the solutes excluding alcohols, water, thiophene, THF, 1,4-dioxane, acetone, butanal, acetonitrile, pyridine and 1-nitropropane. The largest positive values of $\Delta G_1^{E,\infty}$ are exhibited by aliphatic hydrocarbons (decane, 12.3 kJ · mol⁻¹). The large values for aliphatic hydrocarbons indicate again that the aliphatic hydrocarbon–IL interaction is not strong and much weaker than for polar solutes. The partial excess molar entropies at infinite dilution, $T_{ref} \Delta S_1^{E,\infty}$, are small and negative for all solutes studied except for alcohols and water, as it was observed for [EMIM][MeSO₃] [23]. It suggests that for these two ILs, [BMPYR][TCM] and [EMIM][MeSO₃] the mixing is close to ideal solutions.

The densities, measured over the temperature range from (318.15 to 368.15) K and the correlation parameters are listed in table 4. The gas–liquid partition coefficients, K_L in [BMPYR][TCM] are shown in table 5. For all solutes, K_L decreases with an increase of temperature and increases with an increase of the alkane chain length in hydrocarbons, alcohols, ethers, and also for aromatic compounds (alkane chains as substituents). The highest value is observed for styrene $K_L = 4056$ at $T = 318.15$ K. High value is also observed for pyridine (2637). The lowest value is observed for pentane (5.28).

The selectivity, S_{12}^{∞} and the capacity k_2^{∞} of the separation process is defined as follow [26]:

$$S_{12}^{\infty} = \gamma_{13}^{\infty} / \gamma_{23}^{\infty}, \quad (8)$$

$$k_2^{\infty} = 1 / \gamma_{23}^{\infty}. \quad (9)$$

Table 6, presents the selectivity, S_{12}^{∞} and capacity, k_2^{∞} at infinite dilution for several ILs based on the [BMPYR]⁺ cation, and different anions as well as for the typical technological solvents *N*-methyl-2-pyrrolidinone (NMP) and sulfolane. The separation problems as hexane/benzene, cyclohexane/benzene, heptane/thiophene at $T = 328.15$ K are listed in table 6 [27–34]. A closer comparison of the selectivity value of [BMPYR][TCM] obtained in this work and published earlier for [BMPYR]-based ILs [27–32] shows that the selectivity of the separation of hexane/benzene ($S_{12}^{\infty} = 21.4$) is lower than those of 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate [BMPYR][CF₃SO₃] ($S_{12}^{\infty} = 28.5$) [29] and 1-butyl-1-methylpyrrolidinium thiocyanate, [BMPYR][SCN] ($S_{12}^{\infty} = 45.0$) [30]. For the separations of aliphatics/aromatics, the selectivity of [BMPYR][TCM] is on the average level. The best is as was mentioned by us many times the 1-butyl-1-methylpyrrolidinium thiocyanate, [BMPYR][SCN] ($S_{12}^{\infty} = 45.0$) [30].

TABLE 4

Densities (ρ) at $p = 101.33$ kPa, for the ionic liquid [BMPYR][TCM] as a function of temperature.

T/K	$\rho/(g \cdot cm^{-3})$	T/K	$\rho/(g \cdot cm^{-3})$
318.15	0.99468	348.15	0.97680
328.15	0.98867	358.15	0.97094
338.15	0.98270	368.15	0.96490

$$\rho/g \cdot cm^{-3} = a/T/K + b; a = -6.01 \cdot 10^{-4}; b = 1.19.$$

Standard uncertainties are: $u(\rho) = \pm 0.00005$ g cm⁻³; $u(T) = \pm 0.02$ K; $u(p) = \pm 0.03$ kPa.

TABLE 5

Experimental gas–liquid partition coefficients, K_L , for organic solutes and water in [BMPYR][TCM] at different temperatures.^a

Solute	T/K					
	318.15	328.15	338.15	348.15	358.15	368.15
Pentane	5.28	4.21	3.44	2.88	2.43	2.07
Hexane	11.0	8.36	6.56	5.24	4.25	3.52
3-Methylpentane	10.1	7.75	6.12	4.96	4.06	3.38
2,2-Dimethylbutane	6.49	5.09	4.15	3.41	2.84	2.43
Heptane	22.4	16.2	12.1	9.38	7.34	5.87
Octane	44.8	30.8	22.4	16.5	12.3	9.60
2,2,4-Trimethylpentane	18.4	13.5	10.2	7.93	6.27	5.06
Nonane	88.8	58.6	40.9	28.8	20.9	15.7
Decane	175.0	110.0	74.0	50.0	35.0	25.4
Cyclopentane	17.7	13.6	10.8	8.76	7.19	5.98
Cyclohexane	34.8	25.8	19.9	15.7	12.5	10.1
Methylcyclohexane	47.7	34.3	25.7	19.9	15.5	12.4
Cycloheptane	110	77.30	56.3	42.2	32.1	24.9
Cyclooctane	294	196	136	97.9	71.3	53.5
Pente-1-ene	9.72	7.60	6.07	4.96	4.13	3.45
Hex-1-ene	20.6	15.3	11.7	9.23	7.36	5.99
Cyclohexene	80.4	57.5	42.7	32.6	25.2	19.9
Hept-1-ene	41.4	29.4	21.6	16.3	12.5	9.9
Oct-1-ene	82.3	55.9	39.4	28.6	21.2	16.1
Dec-1-ene	318	197	128	86.0	59.5	42.3
Pen-1-yne	47.5	34.4	25.8	19.9	15.6	12.4
Hex-1-yne	99.8	69.1	49.6	36.7	27.7	21.3
Hept-1-yne	202	133	91.6	65.2	47.4	35.2
Oct-1-yne	398	251	166	114	79.8	57.4
Benzene	380	261	185	134	99.4	75.2
Toluene	808	528	356	247	177	129
Ethylbenzene	1464	919	598	400	277	196
<i>o</i> -Xylene	2432	1490	951	625	424	295
<i>m</i> -Xylene	1691	1048	676	450	308	216
<i>p</i> -Xylene	1665	1038	668	446	304	214
Styrene	4056	2451	1538	994	666	457
α -Methylstyrene		3655	2201	1373	889	591
Methanol	373	259	185	135	100	76.2
Ethanol	514	345	238	170	124	92.0
Propan-1-ol	1088	694	459	313	219	157
Propan-2-ol	520	343	232	163	116	85.5
Butan-1-ol	2350	1437	902	589	398	277
Butan-2-ol	1050	655	428	289	200	143
2-Methyl-propan-1-ol	1535	952	612	407	278	196
<i>tert</i> -Butanol	488	318	212	147	104	76.3
Water	1217	803	541	382	272	198
Thiophene	637	431	299	214	156	116
Tetrahydrofuran	280	196	140	103	77.2	59.3
1,4-Dioxane	1376	892	595	410	289	209
<i>tert</i> -Butyl methyl ether	47.7	34.3	25.6	19.6	15.3	12.0
Methyl <i>tert</i> -pentyl ether	99.5	68.7	49.3	36.5	27.5	21.1
Ethyl <i>tert</i> -butyl ether	35.5	25.5	18.8	14.4	11.1	8.78
Diethyl ether	24.8	18.6	14.4	11.4	9.12	7.45
Di- <i>n</i> -propyl ether	66.8	46.6	33.8	25.2	19.1	14.8
Di- <i>iso</i> -propyl ether	29.1	20.8	15.5	11.8	9.26	7.31
Di- <i>n</i> -butyl ether	253	162	108	74.7	52.9	38.4
Acetone	278	196	143	107	80.9	62.6
Pentan-2-one	898	587	396	275	196	143
Pentan-3-one	905	591	397	276	196	143
Methyl acetate	179	126	91.2	67.6	51.2	39.5
Ethyl acetate	268	182	127	91.7	67.5	50.5
Methyl propanoate	329	222	154	110	80.3	60.2
Methyl butanoate	585	378	253	175	124	89.9
Butanal	365	251	179	130	97.2	73.7
Acetonitrile	754	529	381	281	211	161
Pyridine	2637	1688	1118	763	532	382
1-Nitropropane		2468	1600	1068	734	517

^a Standard uncertainties are $u(K_L) < 3\%$.

It should be noted, that the capacity for benzene is for [BMPYR][TCM] close to one at $T = 328.15$ K. It is a lower value than that for other ILs, presented in table 6. The selectivity for cyclohexane/benzene ($S_{12}^{\infty} = 10.2$) is on the average level in the comparison with other ILs presented in table 6. The separation of sulfur compounds from aliphatic hydrocarbons, e.g. heptane/thiophene ($S_{12}^{\infty} = 43.56$) at $T = 328.15$ K is also lower than for four other ILs

as [BMPYR][CF₃SO₃] ($S_{12}^{\infty} = 50.5$) [29], or [BMPYR][SCN] ($S_{12}^{\infty} = 117$) [30], or 1-butyl-1-methylpyrrolidinium dicyanoamide, [BMPYR][N(CN)₂] ($S_{12}^{\infty} = 80.4$) [31], or 1-butyl-1-methylpyrrolidinium bis(oxalato)borate [BMPYR][BOB] ($S_{12}^{\infty} = 59.2$) [32]. The capacity for thiophene at $T = 328.15$ K is very high, $k_2^{\infty} = 1.37$. The very important problem is also the de-nitrogenation of fuels. The values of the selectivity for the separation of nitrogen compounds from

TABLE 6
Selectivities, S_{12}^{∞} , and capacities, k_{12}^{∞} , at infinite dilution for several ILs based on [BMPYR]⁺ cation at $T = 328.15$ K.

Ionic liquid	S_{12}^{∞}			k_{12}^{∞}	
	Hexane/benzene	Cyclohexane/benzene	Heptane/thiophene	Benzene	Thiophene
[BMPYR][TCM]	21.4	10.2	43.6	0.96	1.37
[BMPYR][FAP] ^a	16.1	11.0	21.1	1.66	1.55
[BMPYR][TCB] ^b	18.8	9.56	32.4	1.23	1.51
[BMPYR][CF ₃ SO ₃] ^c	28.5	13.2	50.5	0.67	0.93
[BMPYR][SCN] ^d	45.0	17.4	117	0.52	0.98
[BMPYR][NTf ₂] ^e	13.1	8.67		1.13	
[BMPYR][N(CN) ₂] ^f		13.9	80.4	0.69	1.13
[BMPYR][BOB] ^g		12.8	59.2	0.60	0.89
NMP ^h	9.86	6.21		0.95	
Sulfolane ⁱ	16.1	7.54		0.43	

^a Reference [27].

^b Reference [28].

^c Reference [29].

^d Reference [30].

^e Reference [26].

^f Reference [31].

^g [BOB] – bis(oxalato)borate; Reference [32].

^h Reference [33].

ⁱ Reference [34].

aliphatic hydrocarbons heptane/pyridine or heptane/1-nitropropane are ($S_{12}^{\infty} = 54.8$) and ($S_{12}^{\infty} = 42.8$) at $T = 328.15$ K. These two values are quite optimistic.

5. Conclusions

In this work, the ability of the ionic liquid 1-butyl-1-methylpyrrolidinium tricyanomethanide to act as an entrainer in the liquid–liquid extraction of aromatic hydrocarbons from aliphatic hydrocarbons, or cycloalkanes as well as extraction of sulfur compounds or nitrogen compounds from aliphatic hydrocarbons was analysed. To achieve this aim, the activity coefficients at infinite dilution were examined through the gas–liquid chromatography measurements for 62 solutes and water in [BMPYR][TCM] at six temperatures. The data were compared to published results for the ionic liquids with the same cation and different anions.

The thermodynamic functions at infinite dilution, the partial molar excess Gibbs free energies with respective enthalpic and entropic contributions and the gas–liquid partition coefficients for the same solutes were discussed.

Due to high selectivity values the separation of thiophene, or pyridine from aliphatic hydrocarbons, the separation of sulfur-compounds and nitrogen-compounds seems to be feasible. Discussed in this work is the conclusion that the selectivity and capacity presented in this work offer a separation selectivity at a good level in comparison to other ionic liquids, NMP and sulfolane.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jct.2013.07.004>.

References

[1] N.V. Plechkova, K.R. Seddon, *Chem. Soc. Rev.* 37 (2008) 123–150.

- [2] J.P. Hallet, T. Welton, *Chem. Rev.* 111 (2011) 3508–3576.
 [3] J. Pernak, A. Syguda, D. Janiszewska, K. Materna, T. Praczyk, *Tetrahedron* 67 (2011) 4838–4844.
 [4] J. Pernak, J. Zabielska-Matejuk, A. Kropacz, J. Foksowicz-Flaczyk, *Holzforchung* 58 (2004) 286–291.
 [5] H.J. Huang, S. Ramaswamy, U.W. Tschirner, B.V. Ramarao, *Sep. Purif. Technol.* 62 (2008) 1–21.
 [6] Y. Beste, M. Eggersmann, H. Schoenmakers, *Chem. Ing. Tech.* 77 (2005) 1800–1808.
 [7] A.R. Hansmeir, G.W. Meindersma, A.B. de Haan, *Green Chem.* 13 (2011) 1907–1913.
 [8] A. Seeberger, A. Jess, *Green Chem.* 12 (2010) 602–608.
 [9] Ch. Yansheng, L. Changping, J. Qingzhu, L. Qingshan, Y. Peifang, L. Xiumei, U. Welz-Bierman, *Green Chem.* 13 (2011) 1224–1229.
 [10] U. Domańska, E.V. Lukoshko, M. Królikowski, *J. Chem. Thermodyn.* 61 (2013) 126–131.
 [11] U. Domańska, A. Marciniak, *J. Chem. Thermodyn.* 40 (2008) 860–866.
 [12] U. Domańska, A. Marciniak, *J. Phys. Chem. B* 111 (2007) (1988) 11984.
 [13] F. Mutelet, A.-L. Revelli, J.-N. Jaubert, L.M. Sprunger, W.E. Acree Jr, G.A. Baker, *J. Chem. Eng. Data* 55 (2010) 234–242.
 [14] A. Marciniak, *Fluid Phase Equilib.* 294 (2010) 213–233.
 [15] D.H. Everett, *Trans. Faraday Soc.* 61 (1965) 1637–1645.
 [16] A.J.B. Cruickshank, B.W. Gainey, C.P. Hicks, T.M. Letcher, R.W. Moody, C.L. Young, *Trans. Faraday Soc.* 65 (1969) 1014–1031.
 [17] Design Institute for Physical Properties, Sponsored by AIChE (2005; 2008; 2009; 2010). DIPPR Project 801 – Full Version. Design Institute for Physical Property Research/AIChE. Online version available at: <http://knovel.com/web/portal/browse/display?_EXT_KNOVEL_DISPLAY_bookid=1187&VerticalID=0>.
 [18] B.E. Poling, J.M. Prausnitz, *Properties of Gases and Liquids*, McGraw-Hill Publishing, 2001. Available from: <<http://lib.mylibrary.com?ID=91317>>.
 [19] D.W. Grant, *Gas–Liquid Chromatography*, van Nostrand Reinhold, London, UK, 1971.
 [20] U. Domańska, A. Marciniak, *J. Phys. Chem. B* 114 (2010) 16542–16547.
 [21] U. Domańska, M. Królikowska, W.E. Acree Jr, G.A. Baker, *J. Chem. Thermodyn.* 43 (2011) 1050–1057.
 [22] U. Domańska, A. Marciniak, *J. Phys. Chem. B* 114 (2008) 11100–11105.
 [23] U. Domańska, M. Królikowski, *J. Chem. Thermodyn.* 54 (2012) 20–27.
 [24] A. Marciniak, *J. Chem. Thermodyn.* 43 (2011) 1446–1452.
 [25] A. Marciniak, M. Wlazło, *J. Chem. Thermodyn.* 47 (2012) 382–388.
 [26] R. Kato, J. Gmehling, *J. Chem. Thermodyn.* 37 (2005) 603–619.
 [27] U. Domańska, E.V. Lukoshko, M. Królikowski, *Chem. Eng. J.* 183 (2012) 261–270.
 [28] U. Domańska, M. Królikowski, W.E. Acree Jr, *J. Chem. Thermodyn.* 43 (2011) 1810–1817.
 [29] U. Domańska, G.G. Redhi, A. Marciniak, *Fluid Phase Equilib.* 278 (2009) 97–102.
 [30] U. Domańska, M. Królikowska, *J. Phys. Chem. B* 114 (2010) 8460–8466.
 [31] V. Blahut, J. Dohnal, *Chem. Eng. Data* 56 (2011) 4909–4918.
 [32] A. Blahut, V. Dohnal, *J. Chem. Thermodyn.* 57 (2013) 344–354.
 [33] M. Krummen, D. Gruber, J. Gmehling, *Ind. Eng. Chem. Res.* 39 (2000) 2114–2123.
 [34] C. Mollmann, J. Gmehling, *J. Chem. Eng. Data* 42 (1997) 35–40.