Journal of Molecular Liquids 304 (2020) 112754

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Thermodynamic study of binary mixtures of toluene with ionic liquids, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, 1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide and 1-butylpyridinium bis(trifluoromethylsulfonyl)imide

Dorota Warmińska [a],*, Iwona Cichowska-Kopczyńska [b]

[a] *Department of Physical Chemistry, Chemical Faculty, Gdańsk University of Technology, 80-233 Gdańsk, Poland*
[b] *Department of Process Engineering and Chemical Technology, Chemical Faculty, Gdańsk University of Technology, 80-233 Gdańsk, Poland*

ARTICLE INFO

Article history:
Received 14 October 2019
Received in revised form 18 February 2020
Accepted 19 February 2020
Available online 22 February 2020

Keywords:
Density
Viscosity
Refractive index
Toluene
Ionic liquid

ABSTRACT

Densities, refractive indices and viscosities at 293.15, 298.15, 303.15, 308.15 and 313.15 K of binary mixtures of toluene with 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, 1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide and 1-butylpyridinium bis(trifluoromethylsulfonyl)imide have been measured over the miscible region at $p = 0.1$ MPa. From the experimental data, values of excess molar volume, excess thermal expansion, deviation in refractive index, deviation in viscosity and excess Gibbs energy of activation for viscous flow have been calculated. These properties have been fitted to the Redlich-Kister-type polynomial equation in order to analyse non-ideal behaviour of the studied mixtures. Moreover, partial and apparent molar volumes of toluene and ionic liquid in their binary systems have been calculated. Finally, the effects of temperature and cation of ionic liquid on the physicochemical properties were analysed and discussed in terms of intermolecular interactions occurring in the studied systems.

1. Introduction

For decades, emission of volatile organic compounds (VOCs) has been a matter of concern for scientists. Organics are common ingredients of many products and due to their omnipresence and negative impact on human and environment, they should be considered as a threat. They originate from petroleum refining industry where separation of aromatics from aliphatic hydrocarbon mixtures is of particular importance because the boiling points of these compounds are rather close [1]. Several methods have been found to separate VOCs and many solvents have been examined in this regard, for example ethylene glycols [2], sulfolane [3]. Use of such solvents is not environmentally friendly as it consumes a lot of energy and produces additional waste streams. In the last two decades, a lot of attention was given to ionic liquids (ILs) and still they have a constant interest of scientists. Unique properties, such as chemical and thermal stability, extremely low vapour pressure, non-flammability and ability to dissolve wide range of both organic and inorganic compounds make them excellent substitute for traditional volatile solvents. The most often ILs are composed of a large cation and a smaller anion that determine their properties which can be easily adjusted by proper selection of ions, introduction of functional groups or customizing alkyl chain length. Practically unlimited number of combinations enables use of ionic liquids in many chemical processes. However, in order to take advantage of these solvents, it is a key issue to determine their physicochemical properties.

Ionic liquids are widely considered as extraction solvents for organic compounds [4–7] and as liquid phase in liquid membrane processes [5,8–10], specifically imidazolium and pyridinium based. 1-ethyl-3-methylimidazolium dicyanamide was examined in toluene extraction from cyclohexane and heptane with separation selectivity with regard to heptane reaching 124 [11]. Corderi et al. investigated the use of 1-ethyl-3-methylimidazolium methylsulfate in the same system and obtained maximum selectivity of 139 [12] which indicates that not only the cation but also the anion takes part in separation, though Garcia et al. reported maximum value of 88 [13]. Mixed systems ILs have also been used for toluene extraction from its mixture with aliphatic compounds with promising effectiveness, Larriba et al. used imidazolium ILs mixture [14], pyridinium ILs mixture [15] as well as imidazolium and pyridinium ILs system [16]. Several ionic liquids, mainly imidazolium and pyridinium, have been tested for extraction of toluene from mixtures with heptane, octane, decane, cyclohexane and the conclusion is that the selection of the solvent is a crucial issue in obtaining satisfying selectivity and solute distribution ratio [17,18]. Therefore, to

---

* Corresponding author.
E-mail address: dorwarmi@pg.edu.pl (D. Warmińska).

https://doi.org/10.1016/j.molliq.2020.112754

design a process utilizing ionic liquids, the knowledge on both phase behaviour and physical properties for the pure compounds and its mixtures is of a great importance.

To our best knowledge, the excess properties for binary systems containing 1-butylpyridinium bis(trifluoromethylsulfonyl)imide and molecular solvent have not been studied so far. For systems containing 1-alkyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, volumetric studies only for 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl)imide were performed [19–21]. Requejo et al. measured some densities for the system $[C_{41}Pyrr][NTf_2]$ + toluene at 283.15 K [21].

Herein, densities, viscosities and refractive indices of the binary mixtures of $[C_{41}Pyrr][NTf_2]$, $[C_{61}Pyrr][NTf_2]$ and $[C_4Py][NTf_2]$ with toluene were measured at atmospheric pressure and temperatures from 293.15 K to 313.15 K. As the studied systems exhibit miscibility gap, measurements concerned the solutions the ionic liquid-rich phase only. On basis of experimental values of physicochemical properties, values of excess molar volume, excess thermal expansion, deviation in refractive index, deviation in viscosity and excess Gibbs energy of activation for viscous flow were estimated and correlated by the Redlich-Kister-type polynomial equation. The effects of temperature and cation of ionic liquid on the physicochemical properties were also discussed.

2. Experimental

2.1. Materials

The ionic liquids used in this study, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, 1-hexyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl)imide and 1-butylpyrydinium bis (trifluoromethylsulfonyl)imide were purchased from Io-li-tec (Ionic Liquids Technologies GmbH, Heilbronn, Germany) and toluene was supplied by POCh (Avantor Performance Materials Poland S.A.). The chemicals were used as received from the supplier. Moreover, to reduce their water content, ionic liquids were dried prior the experiments by treating them under vacuum for around 48 h at 363 K. Table 1 presents the corresponding information. The average water content in the reagents was measured by the Karl Fischer titration method (831 KF Coulometer apparatus from Metrohm). Fig. 1 shows the ions structures of ionic liquids studied.

Table 2 presents the thermophysical properties of pure compounds at work temperatures and at atmospheric pressure (p = 0.1 MPa) together with comparison with literature data. As is seen, the experimental values of density, viscosity and refractive index obtained for toluene were in good agreement with the values found in the literature. For ionic liquids, there was an appreciable difference for the data among the various authors, mainly because of the different water content. Moreover, it should be noted, that for ILs the literature data are limited and differ remarkably from each other. To our best knowledge, the values of refractive index for 1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide have been measured only at 298.15 K so far.

The miscibility of toluene in the ionic liquids was determined using a procedure based on the cloud point method. Briefly, a specific amount of ionic liquid toluene was placed in a glass gastight bottle and stirring was applied. Toluene was added dropwise from a microliter syringe until a change in the turbidity of the sample was observed. The resulting binary mixture was weighted again, and its composition was calculated.

The binary mixtures for density, viscosity and refractive index measurements were prepared by mass and were kept in special gastight stopper glass bottles to avoid toluene evaporation and absorption of moisture. The weighting was done using an analytical balance RADWAG AS 60/220/C/2 with the precision of 0.01 mg. The uncertainty in the mole fraction was estimated to be less than $\pm 1 \cdot 10^{-4}$.

2.2. Measurements

The densities of the binary mixtures were measured at different temperatures with a digital vibration-tube analyzer (Anton Paar DMA 5000, Austria) with proportional temperature control that kept the samples at working temperature with an accuracy of 0.01 K. Prior to each series of measurements, the apparatus was calibrated using double distilled and degassed water, and with dry air at atmospheric pressure (0.1 MPa). The standard uncertainty of density measurement was better than $0.35\ kg \cdot m^{-3}$.

The viscosity measurements were carried out using LVDV-III Programmable Rheometer (Searle cone-plate viscometer; Brookfield Engineering Laboratory, USA), controlled by a computer. The temperature of the samples was controlled within ±0.01 K using a thermostatic water bath (PolyScience 9106, USA). CP-40 cone (angle 0.8°, radius 2.4 cm) and 0.5 ml ionic liquid were used. Dynamic viscosity was determined based on the ratio of shear stress (N/m^2) and shear rate (1/s) at 5 points. The obtained flow curves were used to calculate the dynamic viscosity. The displays of the viscometer were verified with certified viscosity standard N100 and S3 provided by Cannon at 298.15 ± 0.01 K. The standard uncertainty of viscosity measurement was better than 1%.

The refractive indices were measured using an Abbe refractometer (RL-3, Poland) equipped with a thermostat for controlling the cell temperature with an accuracy of ±0.1 K. The standard uncertainty of refractive index measurement on the n_D scale was 0.0002. At least three independent measurements were taken for each sample at each temperature to assure effectiveness of the measurement.

3. Results

For systems based on ionic liquids with 4 carbon atoms in the cation, the solubility expressed with mole fraction of toluene in IL did not exceed 0.76, for ionic liquid with hexyl chain the solubility was 0.81. Moreover, the solubility was constant within the range ± 0.003 over the temperature range of 293–318 K. Such behaviour is confirmed with data reported by Gonzalez et al. [42]. Authors determined solubility of benzene, toluene, ethylbenzene, o-xylene, m-xylene and p-xylene in 1-ethyl-3-methylpirydinium ionic liquids with ethylsulfate, bis (trifluoromethylsulfonyl)imide anions and 1-propyl-3-

Table 1
Specification of the pure compounds used in this work.

Chemical name	Source	CAS number	Purity/mass fraction[a]	Water content $/10^6 w(H_2O)$[b]
Toluene	POCh	108-88-3	0.99	223
1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide $[C_{41}Pyrr][NTf_2]$	Io-li-tec	223437-11-4	0.99	345
1-Hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide $[C_{61}Pyrr][NTf_2]$	Io-li-tec	380497-19-8	0.99	543
1-Butylpyrydinium bis(trifluoromethylsulfonyl)imide $[C_4Py]][NTf_2]$	Io-li-tec	187863-42-9	0.99	621

[a] As stated by the supplier.
[b] Karl Fischer titration.

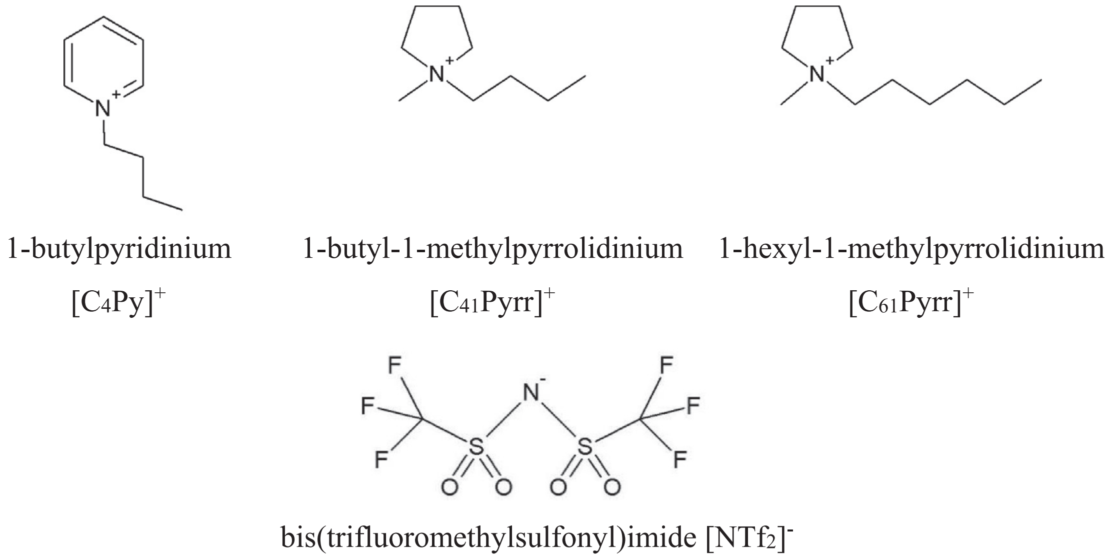

Fig. 1. Chemical structures of ions comprising ionic liquids used in this study.

mthylpuriridinium bis(trifluoromethylsulfonyl)imide [42]. Requejo et al. measured mutual solubility of the same hydrocarbons in 1-butyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate, 1-butyl-1-methylpyrrolidinium dicyanamide, butyltrimethylammonium bis (trifluoromethylsulfonyl)imide and tributylmethylammonium bis (trifluoromethylsulfonyl)imide and found that the impact of temperature is very small [21].

Experimental data for densities, refractive indices and viscosities as well as the calculated values of excess molar volumes, deviations in refractive index, viscosity deviations and excess Gibbs free energies of activation of viscous flow for the binary systems of toluene with 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, 1-hexyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide and 1-butylpyridinium bis(trifluoromethylsulfonyl)imide over the miscible region in the temperature range of $T = 293.15–318.15$ K and at 0.1 MPa are presented in Table 3.

For the all systems studied, the density, refractive index and viscosity decrease with the increase of temperature. Moreover, the density and refractive index present a linear dependence with temperature, whereas the viscosity decreases with temperature increase exponentially.

At all investigated temperatures, the density and viscosity decrease, while the refractive index increases with increasing mole fraction of toluene. These polynomial dependences follow the same trend as the properties for the pure ILs: $[C_{41}Pyrr][NTf_2] > [C_{61}Pyrr][NTf_2] < [C_4Py]][NTf_2]$ for density, $[C_{41}Pyrr][NTf_2] < [C_{61}Pyrr][NTf_2] < [C_4Py]][NTf_2]$ for refractive index and $[C_{41}Pyrr][NTf_2] < [C_{61}Pyrr][NTf_2] > [C_4Py]][NTf_2]$ for viscosity. From these results, it is possible to conclude that the density decreases with the increase in alkyl chain length of the cation of the IL and when pyridinium cation of the ionic liquid is replaced by 1-methylpyrrolidinium cation. The refractive index increases with the increase in alkyl chain length of the cation of the IL and decreases with the changing cation of the ionic liquid from pyridinium to 1-methylpyrrolidinium. Moreover, the effect of increase in alkyl chain length of the cation of the IL on density and refractive index is distinctly weaker than the effect of the replacing of pyridinium cation by 1-methylpyrrolidinium cation. The dependences of the viscosity on mole fraction of toluene as well as the viscosities of pure ionic liquids are mainly the result of differences in molar mass of ILs.

Using measured densities, the values of excess molar volume, V^E, were calculated according to the following equation:

$$V^E = \sum_{i=1}^{n} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i}\right) \tag{1}$$

where ρ is the density of a mixture and x_i, M_i, and ρ_i are the mole fraction, the molar mass and the density of a component i, respectively.

From refractive indices, the deviations in refractive index, Δn_D, were calculated using the following equation:

$$\Delta n_D = n_D - \sum_{i=1}^{n} \Phi_i n_{Di} \tag{2}$$

where n_D and n_{Di} are the refractive index of a mixture and a pure component i, respectively and Φ_i denotes the volume fraction of a pure component i.

Based on the viscosities of the mixtures, η, and pure component i, η_i, the viscosity deviations $\Delta\eta$ were obtained according to the equation:

$$\Delta\eta = \eta - \sum_{i=1}^{n} x_i \eta_i \tag{3}$$

The excess Gibbs energy of activation for viscous flow, ΔG^E, was calculated using the equation:

$$\Delta G^E = RT\left[\ln(\eta V) - \left(x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2)\right)\right] \tag{4}$$

where R is the gas constant, T is the absolute temperature and V is the molar volume of the mixture defined as: $V = (x_1 M_1 + x_2 M_2)/\rho$. The symbols η_1, η_2, V_1 and V_2 represent viscosity of toluene, viscosity of ionic liquid, molar volume of toluene and molar volume of ionic liquid, respectively.

Excess molar volumes, deviations in refractive index, viscosity deviations and excess Gibbs free energies of activation of viscous flow were correlated with composition according to Redlich-Kister polynomial equation [43]:

$$Y^E = x_1(1 - x_1)\sum_{i=0}^{j} A_i (2x_1 - 1)^i \tag{5}$$

Table 2
Thermophysical properties of the pure compounds at $p = 0.1$ MPa and at work temperatures and comparison of densities, dynamic viscosities and refractive indices with literature data[a].

T/K	$\rho/(\mathrm{kg \cdot m^{-3}})$		$\eta/(\mathrm{mPa \cdot s})$		n_D	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
Toluene						
293.15	866.86	866.84 [22], 866.877 [23]	0.598	0.5936 [22],	1.4962	1.49631 [22], 1.49666 [24]
298.15	862.20	862.18 [22], 862.221 [23]	0.569	0.5698 [22],	1.4933	1.49338 [22], 1.49386 [24]
303.15	857.54	857.51 [22], 875.554 [23], 875.55 [25]	0.539	0.5410 [22], 0.522 [25]	1.4908	1.49042 [22], 1.4901[25]
308.15	852.85	852.83 [22],852.873 [23], 852.72 [25]	0.509	0.5140 [22], 0.493 [25]	1.4878	1.48751 [22], 1.48821 [24]
313.15	848.16	848.16 [22], 848.02 [25]	0.485	0.4854 [22], 0.467 [25]	1.4851	1.48461 [22], 1.4849 [25]
$[C_{41}Pyrr][NTf_2]$						
293.15	1398.44	1399.00 [20], 1387.01[26], 1398.92 [19]	90.174	86.05 [26], 90 [27], 97.664 [19]	1.4236	1.42442 [28], 1.4241 [29]
298.15	1394.02	1394.57 [20], 1382.02 [26], 1394.3 [30], 1394.59 [31], 1394.49 [19]	70.124	76.73 [20], 68.16 [26], 74 [27], 77.69 [19]	1.4223	1.42302 [28]
303.15	1389.60	1390.02 [20], 1378.02 [26], 1390.09 [19]	56.189	61.67 [20], 54.05 [26], 57 [27], 65 [32], 60 [33], 62.87 [19]	1.4211	1.42160 [28], 1.4191 [29]
308.15	1385.20	1385.48 [20], 1374.03 [26], 1385.66 [19]	45.798	50.49 [20], 44.38 [26], 40 [32], 51.17 [19]	1.4198	1.42014 [28]
313.15	1380.81	1380.09 [20], 1370.03 [26], 1381.29 [19]	37.990	41.73 [20], 35.76 [26], 39 [27], 42.31[19]	1.4182	1.41874 [28], 1.4160 [29]
$[C_{61}Pyrr][NTf_2]$						
293.15	1339.51	1336.4 [34]	136.230	113 [35]	1.4267	
298.15	1335.24	1332.0 [34] 1336.0 [30], 1335.3 [36]	103.120	96 [37]	1.4258	1.425 [37]
303.15	1331.00	1327.7 [34]	79.590	77 [37]	1.4243	
308.15	1326.78	1323.4 [34]	63.070	62 [37]	1.4230	
313.15	1322.56	1319.1 [34]	51.010	51 [37], 52.7 [35]	1.4216	
$[C_4Py]][NTf_2]$						
293.15	1452.78	1458 [27]	68.867	73 [27], 77.715 [38]	1.4435	
298.15	1448.07	1450 [27] 1454.7 [39]	52.842	59 [27], 58.3 [40]	1.4420	
303.15	1443.37	1444.0 [41], 1448 [27], 1450.6 [39]	41.940	49.4 [41], 48 [27], 46.7 [40]	1.4407	1.4415 [41]
308.15	1438.70	1434.7 [41], 1442 [27], 1446.2 [39]	33.754	40.087 [38]	1.4393	1.4386 [41]
313.15	1434.05	1438 [27], 1441.7 [39]	27.629	33.8 [41], 32[27], 31.4 [40]	1.4377	

[a] Standard uncertainties u are $u(T) = 0.01$ K for densities and viscosities and $u(T) = 0.1$ K for refractive index, $u(p) = 0.001$ MPa, $u(\rho) = 0.35\ \mathrm{kg \cdot m^{-3}}$, $u(n_D) = 0.0002$ and $u_r(\eta) = 1\%$.

Table 3
Densities ρ, excess molar volumes V^E, refractive indices n_D, refractive index deviations Δn_D, viscosities η, viscosity deviations $\Delta\eta$ and excess Gibbs free energy of activation of viscous flow ΔG^E of toluene (1) + [C_{41}Pyrr][NTf_2]/[C_{61}Pyrr][NTf_2]/[C_4Py]][NTf_2] systems at T = 293.15–313.15 K and at atmospheric pressure (0.1 MPa)[a].

x_1	ρ/kg·m^{-3}	$V^E/10^{-6}$ m^3·mol^{-1}	n_D	Δn_D	η/mPa·s	$\Delta\eta$/mPa·s	ΔG^E/J·mol^{-1}
Toluene (1) + [C_{41}Pyrr][NTf_2] (2)							
293.15 K							
0.0000	1398.40	0.000	1.4238	0.00000	90.174	0.000	0.0
0.1093	1378.24	−0.374	1.4268	0.00000	66.941	−13.444	705.6
0.1978	1359.46	−0.678	1.4298	0.00022	51.519	−20.936	1216.7
0.3041	1333.49	−1.080	1.4341	0.00065	36.608	−26.324	1748.9
0.3965	1306.44	−1.351	1.4385	0.00110	25.999	−28.656	2086.9
0.5054	1268.01	−1.635	1.4446	0.00165	17.039	−27.859	2417.5
0.6027	1225.11	−1.756	1.4510	0.00201	11.019	−25.171	2547.6
0.7066	1166.37	−1.659	1.4591	0.00209	6.259	−20.618	2417.6
1.0000	866.86	0.000	1.4962	0.00000	0.598	0.000	0.0
298.15 K							
0.0000	1393.96	0.000	1.4223	0.00000	70.124	0.000	0.0
0.1093	1373.77	−0.382	1.4253	0.00005	52.334	−10.189	676.0
0.1978	1354.99	−0.697	1.4283	0.00030	41.499	−14.866	1225.5
0.3041	1329.00	−1.108	1.4326	0.00079	29.964	−19.007	1753.0
0.3965	1301.94	−1.388	1.4369	0.00120	21.883	−20.660	2119.8
0.5054	1263.48	−1.679	1.4429	0.00174	14.957	−20.011	2505.6
0.6027	1220.53	−1.800	1.4492	0.00209	10.080	−18.125	2691.7
0.7066	1161.76	−1.704	1.4572	0.00220	5.731	−15.242	2510.3
1.0000	862.20	0.000	1.4935	0.00000	0.569	0.000	0.0
303.15 K							
0.0000	1389.54	0.000	1.4211	0.00000	56.189	0.000	0.0
0.1093	1369.34	−0.394	1.4241	0.00010	42.866	−7.241	695.9
0.1978	1350.55	−0.719	1.4270	0.00030	34.069	−11.111	1222.5
0.3041	1324.53	−1.138	1.4312	0.00076	25.033	−14.231	1757.5
0.3965	1297.45	−1.425	1.4355	0.00124	18.657	−15.465	2142.1
0.5054	1258.97	−1.725	1.4414	0.00178	13.057	−15.004	2547.4
0.6027	1215.98	−1.848	1.4477	0.00224	9.110	−13.540	2782.8
0.7066	1157.15	−1.749	1.4556	0.00240	5.279	−11.585	2602.2
1.0000	857.54	0.000	1.4909	0.00000	0.539	0.000	0.0
308.15 K							
0.0000	1385.14	0.000	1.4198	0.00000	45.798	0.000	0.0
0.1093	1364.91	−0.403	1.4228	0.00017	34.885	−5.964	661.7
0.1978	1346.11	−0.738	1.4257	0.00044	28.405	−8.434	1225.0
0.3041	1320.08	−1.170	1.4297	0.00078	21.581	−10.444	1813.8
0.3965	1292.97	−1.464	1.4339	0.00126	16.477	−11.363	2231.4
0.5054	1254.47	−1.773	1.4397	0.00182	11.862	−11.045	2674.5
0.6027	1211.43	−1.898	1.4459	0.00233	8.399	−10.105	2914.3
0.7066	1152.56	−1.799	1.4537	0.00259	5.050	−8.745	2785.7
1.0000	852.85	0.000	1.4878	0.00000	0.509	0.000	0.0
313.15 K							
0.0000	1380.74	0.000	1.4182	0.00000	37.990	0.000	0.0
0.1093	1360.51	−0.419	1.4213	0.00031	29.432	−4.460	676.5
0.1978	1341.70	−0.764	1.4242	0.00062	24.079	−6.492	1229.0
0.3041	1315.62	−1.201	1.4282	0.00103	18.546	−8.039	1824.2
0.3965	1288.51	−1.507	1.4323	0.00146	14.352	−8.766	2249.9
0.5054	1249.98	−1.824	1.4381	0.00211	10.631	−8.403	2734.7
0.6027	1206.89	−1.951	1.4442	0.00262	7.575	−7.813	2959.6
0.7066	1147.96	−1.849	1.4517	0.00270	4.731	−6.757	2890.6
1.0000	848.16	0.000	1.4850	0.00000	0.485	0.000	0.0
Toluene (1) + [C_{61}Pyrr][NTf_2] (2)							
293.15 K							
0.0000	1339.51	0.000	1.4267	0.00000	136.230	0.000	0.0
0.0942	1325.69	−0.292	1.4290	0.00009	103.136	−20.311	668.5
0.1943	1309.00	−0.661	1.4319	0.00028	77.261	−32.616	1380.7
0.2900	1290.13	−0.972	1.4353	0.00066	55.631	−41.273	1919.8
0.3938	1265.71	−1.303	1.4397	0.00116	37.271	−45.551	2378.4
0.4930	1237.07	−1.563	1.4447	0.00166	24.385	−44.980	2693.8
0.5961	1199.60	−1.735	1.4509	0.00209	14.737	−40.640	2842.0
0.6986	1150.89	−1.712	1.4583	0.00222	8.363	−33.118	2794.9
0.7993	1085.91	−1.375	1.4674	0.00197	4.124	−23.698	2343.8
1.0000	866.85	0.000	1.4962	0.00000	0.598	0.000	0.0
298.15 K							
0.0000	1335.24	0.000	1.4258	0.00000	102.836	0.000	0.0
0.0942	1321.40	−0.300	1.4280	0.00004	79.268	−13.930	670.3
0.1943	1304.72	−0.684	1.4308	0.00020	61.244	−22.721	1372.8
0.2900	1285.81	−1.000	1.4340	0.00046	44.908	−28.275	1951.9
0.3938	1261.41	−1.348	1.4383	0.00096	30.918	−31.648	2426.2
0.4930	1232.75	−1.616	1.4432	0.00148	20.680	−31.739	2744.6
0.5961	1195.17	−1.780	1.4492	0.00186	12.892	−28.980	2913.4
0.6986	1146.39	−1.756	1.4565	0.00208	7.612	−23.782	2905.2
0.7993	1081.33	−1.410	1.4655	0.00199	3.838	−17.258	2443.9

(continued on next page)

Table 3 (*continued*)

x_1	ρ/kg·m^{-3}	$V^E/10^{-6}$ m^3·mol^{-1}	n_D	Δn_D	η/mPa·s	$\Delta\eta$/mPa·s	ΔG^E/J·mol^{-1}
1.0000	862.19	0.000	1.4934	0.00000	0.569	0.000	0.0
303.15 K							
0.0000	1331.00	0.000	1.4243	0.00000	79.593	0.000	0.0
0.0942	1317.15	−0.310	1.4266	0.00018	62.317	−9.826	672.2
0.1943	1300.44	−0.702	1.4295	0.00048	48.003	−16.230	1368.8
0.2900	1281.49	−1.023	1.4327	0.00078	36.698	−19.973	1972.1
0.3938	1257.08	−1.383	1.4370	0.00135	25.955	−22.509	2468.6
0.4930	1228.38	−1.657	1.4418	0.00184	17.853	−22.767	2812.0
0.5961	1190.74	−1.823	1.4477	0.00221	11.169	−21.298	2939.4
0.6986	1141.90	−1.798	1.4549	0.00245	6.931	−17.437	3004.2
0.7993	1076.76	−1.446	1.4637	0.00233	3.477	−12.930	2471.2
1.0000	857.53	0.000	1.4907	0.00000	0.539	0.000	0.0
308.15 K							
0.0000	1326.78	0.000	1.4230	0.00000	63.066	0.000	0.0
0.0942	1312.90	−0.317	1.4251	0.00002	50.163	−7.007	680.9
0.1943	1296.16	−0.717	1.4279	0.00028	39.598	−11.314	1406.2
0.2900	1277.20	−1.050	1.4301	0.00055	30.333	−14.594	1981.0
0.3938	1252.75	−1.418	1.4351	0.00100	22.169	−16.264	2522.6
0.4930	1224.02	−1.700	1.4398	0.00149	15.658	−16.568	2894.6
0.5961	1186.32	−1.869	1.4458	0.00209	10.644	−15.131	3190.1
0.6986	1137.42	−1.845	1.4529	0.00240	6.490	−12.876	3164.4
0.7993	1072.19	−1.485	1.4616	0.00238	3.150	−9.916	2493.0
1.0000	852.84	0.000	1.4878	0.00000	0.509	0.000	0.0
313.15 K							
0.0000	1322.56	0.000	1.4216	0.00000	51.009	0.000	0.0
0.0942	1308.66	−0.326	1.4238	0.00016	40.964	−5.284	676.2
0.1943	1291.91	−0.7400	1.4266	0.00046	32.725	−8.467	1401.2
0.2900	1272.91	−1.078	1.4297	0.00078	25.671	−10.688	2006.1
0.3938	1248.44	−1.457	1.4337	0.00120	19.296	−11.818	2584.9
0.4930	1219.66	−1.744	1.4383	0.00167	14.049	−12.052	2999.2
0.5961	1181.91	−1.917	1.4442	0.00227	9.543	−11.348	3253.5
0.6986	1132.94	−1.893	1.4511	0.00251	5.883	−9.832	3212.0
0.7993	1067.63	−1.526	1.4596	0.00247	2.944	−7.682	2566.9
1.0000	848.15	0.000	1.4851	0.00000	0.495	0.000	0.0
Toluene (1) + [C_4Py]][NTf_2] (2)							
293.15 K							
0.0000	1452.78	0.000	1.4435	0.00000	68.867	0.000	0.0
0.0994	1431.63	−0.318	1.4457	0.00013	54.239	−7.841	648.2
0.2022	1406.42	−0.707	1.4485	0.00047	41.673	−13.391	1264.7
0.2939	1380.51	−1.030	1.4516	0.00105	31.515	−17.286	1696.2
0.3972	1346.15	−1.349	1.4555	0.00165	22.631	−19.117	2126.9
0.5025	1304.10	−1.650	1.4601	0.00224	15.100	−19.464	2382.0
0.6068	1252.39	−1.820	1.4653	0.00262	10.003	−17.442	2586.2
0.7033	1191.79	−1.762	1.4708	0.00264	6.110	−14.742	2481.5
1.0000	866.86	0.000	1.4962	0.00000	0.598	0.000	0.0
298.15 K							
0.0000	1448.07	0.000	1.4420	0.00000	52.942	0.000	0.0
0.0994	1426.89	−0.361	1.4441	0.00007	42.915	−4.730	682.2
0.2022	1401.73	−0.732	1.4469	0.00047	33.543	−8.731	1296.6
0.2939	1375.82	−1.065	1.4499	0.00100	25.903	−11.575	1738.3
0.3972	1341.45	−1.391	1.4537	0.00157	19.003	−13.075	2174.1
0.5025	1299.38	−1.696	1.4582	0.00214	13.642	−12.934	2558.8
0.6068	1247.65	−1.868	1.4634	0.00263	9.088	−12.038	2725.0
0.7033	1187.09	−1.817	1.4688	0.00268	5.534	−10.542	2559.6
1.0000	862.20	0.000	1.4935	0.00000	0.569	0.000	0.0
303.15 K							
0.0000	1443.37	0.000	1.4407	0.00000	41.940	0.000	0.0
0.0994	1422.15	−0.365	1.4429	0.00022	34.606	−3.217	688.8
0.2022	1397.05	−0.758	1.4457	0.00067	27.596	−5.974	1317.5
0.2939	1371.14	−1.100	1.4485	0.00106	21.683	−8.088	1768.8
0.3972	1336.77	−1.435	1.4521	0.00151	16.230	−9.264	2215.9
0.5025	1294.69	−1.747	1.4565	0.00208	11.992	−9.145	2632.4
0.6068	1242.94	−1.922	1.4615	0.00248	8.213	−8.607	2824.1
0.7033	1182.30	−1.860	1.4669	0.00266	5.194	7.628	2708.0
1.0000	857.54	0.000	1.4909	0.00000	0.539	0.000	0.0
308.15 K							
0.0000	1438.70	0.000	1.4393	0.00000	33.754	0.000	0.0
0.0994	1417.43	−0.367	1.4415	0.00028	28.436	−2.012	712.0
0.2022	1392.38	−0.783	1.4442	0.00071	22.887	−4.145	1332.3
0.2939	1366.47	−1.134	1.4470	0.00118	18.360	−5.623	1806.1
0.3972	1332.11	−1.482	1.4505	0.00162	14.213	−6.335	2304.1
0.5025	1290.01	−1.800	1.4548	0.00222	10.539	−6.510	2692.9
0.6068	1238.22	−1.975	1.4597	0.00267	7.484	−6.099	2937.7
0.7033	1177.56	−1.913	1.4650	0.00293	4.960	−5.412	2899.9
1.0000	852.85	0.000	1.4878	0.00000	0.509	0.000	0.0
313.15 K							

Table 3 (*continued*)

x_1	ρ/kg·m^{-3}	V^E/10^{-6} m^3·mol^{-1}	n_D	Δn_D	η/mPa·s	$\Delta\eta$/mPa·s	ΔG^E/J·mol^{-1}
0.0000	1434.05	0.000	1.4377	0.00000	27.629	0.000	0.0
0.0994	1412.73	−0.370	1.4399	0.00032	23.666	−1.264	726.9
0.2022	1387.73	−0.808	1.4426	0.00080	19.283	−2.858	1348.2
0.2939	1361.83	−1.172	1.4453	0.00123	15.835	−3.816	1853.9
0.3972	1327.46	−1.529	1.4489	0.00184	12.297	−4.449	2348.1
0.5025	1285.33	−1.852	1.4531	0.00243	9.226	−4.764	2710.7
0.6068	1233.53	−2.032	1.4581	0.00309	6.621	−4.538	2945.7
0.7033	1172.83	−1.966	1.4632	0.00327	4.293	−4.245	2812.0
1.0000	848.16	0.000	1.4850	0.00000	0.485	0.000	0.0

[a] x_1 is the mole fraction of toluene. Standard uncertainties u for each variables are $u(T) = 0.01$ K for densities and viscosities and $u(T) = 0.1$ K for refractive index; $u(p) = 0.001$ MPa; $u(x_1) = 0.0001$; $u(\rho) = 0.35$ kg·m^{-3}; $u(n_D) = 0.0002$; $u_r(\eta) = 1\%$ and $u(V^E) = 0.08 \cdot 10^{-6}$ m^3·mol^{-1}.

where Y^E represents V^E, Δn_D, $\Delta\eta$ or ΔG^E of a mixture, A_i values are the adjustable parameters and $j + 1$ is their number.

The standard deviation of fit, σ, was calculated as

$$\sigma = \left[\frac{\sum_i \left(Y^E_{calc} - Y^E_{exp}\right)^2_i}{N-j-1}\right]^{1/2} \qquad (6)$$

where N is the number of experimental data.

Parameters A_i of Eq. (5) and the corresponding σ for the systems studied at $T = 293.15$–313.15 K and at atmospheric pressure 0.1 MPa are presented in Table S1 (Supplementary material).

It is established that for the optimum form of the model equation, the standard deviation of fit should be close to experimental uncertainty. As can be seen in Table S1 for the studied properties that requirement is met almost for all parameters, except for deviations in refractive index and the excess thermal expansions. It could be explained by an overestimation of experimental uncertainty values or underestimation of uncertainty of the model.

The plots of excess molar volumes V^E, deviations in refractive index, Δn_D, viscosity deviations, $\Delta\eta$, and excess Gibbs free energies of activation of viscous flow, ΔG^E, against mole fraction of toluene, x_1, for the studied mixtures at 298.15 K are presented in Figs. 2–5. Solid lines represent the corresponding correlation of Redlich-Kister and dotted lines correspond to the limit of miscibility. It can be seen from figures, that the Redlich-Kister polynomial dependence correlates successfully the data, providing a good description of the solution behaviour of the all binary systems investigated. Moreover, the all studied systems present asymmetrical curves of excess molar volumes, which are quite common in mixtures containing two components with a large molar volume difference, as is indeed the case.

4. Discussion

4.1. Excess molar volumes

It is evident, that toluene-containing systems show the negative values of excess molar volumes over the entire range of the composition and they are very similar to each other. However, the considerably largest negative V^E values are observed for the system containing 1-butylpyridinium bis(trifluoromethylsulfonyl)imide. The ([C_{41}Pyrr][NTf_2] + toluene) mixtures present practically the same values of excess molar volumes than those obtained for the system of ([C_{61}Pyrr][NTf_2] + toluene). It can be therefore concluded that the alkyl chain length of the cation of ionic liquid does not seem to have an important effect on the V^E values. This conclusion is consistent with the results obtained by Gonzalez et al. [44].

Excess molar volume depends mainly on two factors: intermolecular forces between the components of mixture and on packing due to differences in the size and shape of the molecules. As the studied systems exhibit a miscibility gap in the liquid phase, the high positive deviations from ideality must appear. Thus, the interactions between toluene and IL have to be weaker than those between like molecules. Therefore, negative values of excess molar volumes observed in the all studied systems indicate that after mixing ionic liquid with toluene effective packing occurs. The molar volumes for [C_{41}Pyrr][NTf_2], [C_{61}Pyrr][NTf_2], [C_4Py][NTf_2] are 303.03, 337.37 and 287.53 cm^3·mol^{-1}, respectively, which are much greater than the molar volume of toluene (106.87 cm^3·mol^{-1}) at $T = 298.15$ K. The large difference between the molar volumes of components suggests that after mixing the relatively small toluene molecules may fit into the interstices of the ionic liquid. Therefore, the filling effect of aromatic hydrocarbon in the interstices of ionic liquids, that is in fact weakening of the repulsive interactions between IL and toluene molecules leads to the negative values of the excess molar volumes. A similar phenomenon was observed by Goddu et al. for the systems of *N*-methylaniline with 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide or 1-butyl-3-methylimidazolium hexafluorophosphate [45].

Furthermore, the more negative values of V^E in the system containing 1-butylpyridinium bis(trifluoromethylsulfonyl)imide compared to those in the other two systems with ionic liquids based on 1-methylpyrrolidinium cation indicate that the strength of molecular interaction in the ([C_4Py]][NTf_2] + toluene) system is larger than that for ([C_{41}Pyrr][NTf_2] + toluene) and ([C_{61}Pyrr][NTf_2] + toluene). This phenomenon could be explained by the smallest molar volume and the smaller steric hindrance of the pyridinium cation in comparison to 1-methylpyrrolidinium one, and the π–π interactions between 1-butylpyrydinium bis(trifluoromethylsulfonyl)imide and toluene, which cannot occur in the systems containing non-aromatic ionic liquids.

Since volumetric measurements for binary systems with 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide have only been studied so far among others ILs investigated in the present study, Fig. 6 presents our data of excess molar volumes for the ([C_{41}Pyrr][NTf_2] + toluene) system together with literature results for the systems ([C_{41}Pyrr][NTf_2] + methanol), ([C_{41}Pyrr][NTf_2] + ethanol), ([C_{41}Pyrr][NTf_2] + 1-propanol) at 298.15 K and for ([C_{41}Pyrr][NTf_2] + toluene) at 283.15 K [19,21,46]. It should be added that, the excess molar volumes for the system ([C_{41}Pyrr][NTf_2] + toluene) were calculated using the data obtained by Requejo et al. [21]. In calculations, we have used the density for toluene from Ref. [44] equal to 876.10 kg·m^{-3} at 283.15 K.

As can been seen the excess molar volumes for the ([C_{41}Pyrr][NTf_2] + toluene) system are considerably more negative than those obtained for the systems ([C_{41}Pyrr][NTf_2] + alcohol). Obviously, it is the result of strong self-association of alcohols in comparison to toluene not only through dipole-dipole interactions but also through hydrogen bonding which does not occur between aromatic hydrocarbon molecules. Moreover, as the excess molar volumes are only slightly dependent on temperature, it can be concluded that the literature data for the system for ([C_{41}Pyrr][NTf_2] + toluene) are in the accordance to our results.

Table 3 shows the excess molar volumes for the all systems studied at all temperature investigated. As is seen, an increase in temperature (293.15–313.15 K) results in a decrease of the excess molar volumes over the entire range of concentration of toluene. It can be explained by the fact that the increasing temperature generally weakens the intermolecular interactions and strengthens the packing efficiency, thereby decreasing the V^E values.

4.2. Coefficient of thermal expansion

The coefficient of thermal expansion, α_p, for all compositions of binary systems, was calculated from the equation:

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P = -\left(\frac{\partial ln\rho}{\partial T}\right)_P \qquad (7)$$

and it was found to be independent on temperature as the dependence of lnρ on T was linear. The linearity of the function $ln\rho = \mathrm{f}(T)$ was taken into account because of its high value of the determination coefficient higher than 0.9999 and small standard deviation smaller than 0.05 $\cdot\ 10^{-4}\ \mathrm{K}^{-1}$ obtained for each system.

Then, the excess thermal expansion, $\Delta\alpha_p$, was calculated using the equation:

$$\Delta\alpha_p = \alpha_p - \sum_{i=1}^{n} \Phi_i \alpha_{p,i} \qquad (8)$$

where $\alpha_{p,i}$ and Φ_i are the thermal expansion coefficients and the volume fractions for pure components i, respectively. The values of α_p and $\Delta\alpha_p$ at 298.15 K are given in Table S2 in Supporting material and the dependence of the excess thermal expansion on toluene mole fraction, x_1, is plotted in Fig. 7. It can be seen that the values of excess thermal expansion are negative in the whole composition range for the all systems studied. As positive $\Delta\alpha_p$ are typical for the systems containing molecules capable to self-associate, the obtained results indicate that interactions between toluene and ionic liquids molecules and the packing efficiency of toluene accommodation in the interstitial regions of ILs networks dominate over effect of self-association of ionic liquid [47]. The most negative values of excess thermal expansion obtained for the ([C$_4$Py][NTf$_2$] + toluene) system confirm conclusions from excess molar volumes which suggest the strongest molecular interactions in this system. Moreover, the excess thermal expansion observed for ([C$_{41}$Pyrr][NTf$_2$] + toluene) system differs considerably from that observed for ([C$_{61}$Pyrr][NTf$_2$] + toluene). It clearly suggests that interactions increase with the shortening of the alkyl chain length in the cation of ionic liquid occurring in the system and this effect dominates over the effect connected with the packing efficiency.

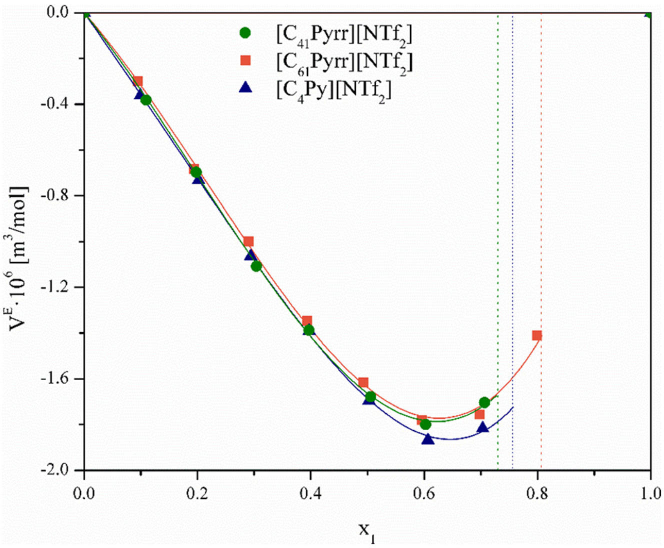

Fig. 2. Excess molar volumes, V^E, for toluene (1) + ionic liquid (2) at $p = 0.1$ MPa as a function of mole fraction, x_1 at $T = 298.15$ K: ●, [C$_{41}$Pyrr][NTf$_2$]; ■, [C$_{61}$Pyrr][NTf$_2$]; ▲, [C$_4$Py]][NTf$_2$]; solid line —, Eq. (5).

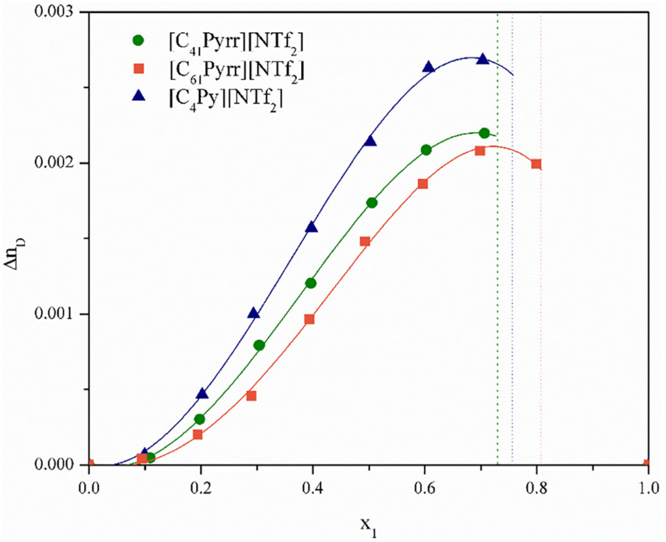

Fig. 3. Deviations in refractive index, Δn_D, for toluene (1) + ionic liquid (2) at $p = 0.1$ MPa as a function of mole fraction, x_1 at $T = 298.15$ K: ●, [C$_{41}$Pyrr][NTf$_2$]; ■, [C$_{61}$Pyrr][NTf$_2$]; ▲, [C$_4$Py]][NTf$_2$]; solid line —, Eq. (5).

4.3. Partial and apparent molar volumes

The partial molar volumes of toluene and the studied ionic liquids in their binary mixtures, $\overline{V}_1$ and $\overline{V}_2$, were calculated from the Eqs. (9) and (10), knowing the molar volumes of the pure components, V_1^o and V_2^o:

$$\overline{V}_1 = V_1^o + (x_1-1)^2\sum_{i=0}^{j} A_i(2x_1-1)^i + 2x_1(1-x_1)^2\sum_{i=0}^{j} A_i i(2x_1-1)^{i-1} \qquad (9)$$

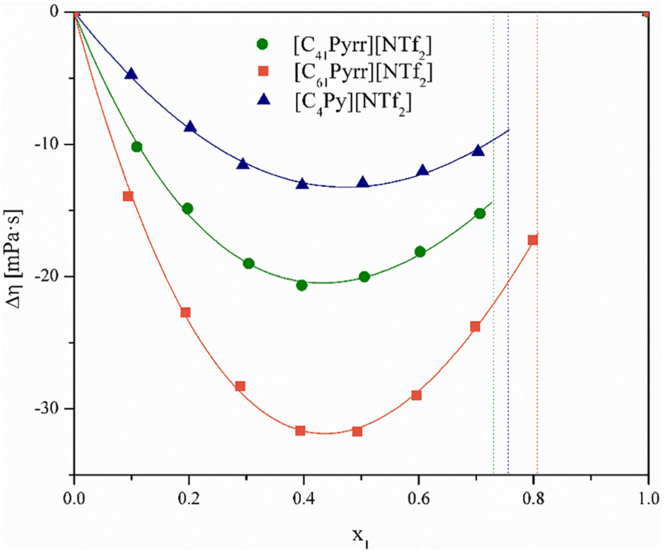

Fig. 4. Viscosity deviations, $\Delta\eta$, for toluene (1) + ionic liquid (2) at $p = 0.1$ MPa as a function of mole fraction, x_1 at $T = 298.15$ K: ●, [C$_{41}$Pyrr][NTf$_2$]; ■, [C$_{61}$Pyrr][NTf$_2$]; ▲, [C$_4$Py]][NTf$_2$]; solid line —, Eq. (5).

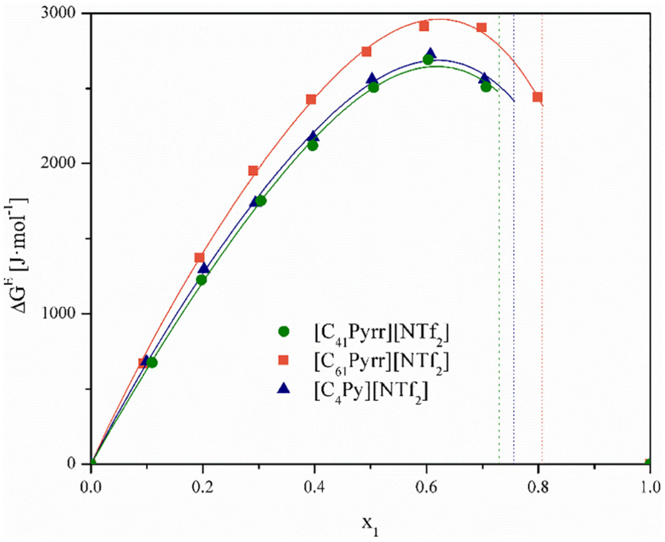

Fig. 5. Excess Gibbs free energies of activation of viscous flow, ΔG^E, for toluene (1) + ionic liquid (2) at $p = 0.1$ MPa as a function of mole fraction, x_1 at $T = 298.15$ K: ●, [C$_{41}$Pyrr][NTf$_2$]; ■, [C$_{61}$Pyrr][NTf$_2$]; ▲, [C$_4$Py]][NTf$_2$]; solid line –, Eq. (5).

$$\overline{V}_2 = V_2^o + x_1{}^2 \sum_{i=0}^{j} A_i(2x_1-1)^i - 2x_1{}^2(1-x_1)\sum_{i=0}^{j} A_i i(2x_1-1)^{i-1} \qquad (10)$$

The obtained values of the partial molar volumes and the apparent molar volumes together with the molar volumes of pure components are presented in Table S3 in Supplementary material. As can be seen, at all studied temperatures, the molar volumes of the interacting compounds in pure state were greater than their corresponding values in the mixture, indicating the reduction in volume upon adding toluene to ionic liquid. Fig. 8 shows the excess partial molar volumes of the components at 298.15 K. These properties were calculated from definition as: $\overline{V}_i^E = V_i^o - \overline{V}_i$ and their values confirm the conclusions presented above. The values of excess partial molar volumes of [C$_{41}$Pyrr][NTf$_2$] are nearly the same as these observed for [C$_{61}$Pyrr][NTf$_2$], and for [C$_4$Py][NTf$_2$] are the most negative, indicating the strongest interactions between IL and toluene in this system. Also for toluene in ([C$_4$Py]][NTf$_2$] + toluene) system the excess partial molar volumes are the most negative.

Since the partial molar properties at infinite dilution provide useful information about interactions between components of a mixture that are independent of compositions, their values for toluene were calculated.

The partial molar volumes at infinite dilution of toluene were calculated by setting $x_1 = 0$ in Eq. (9) as:

$$\overline{V}_1^\infty = V_1^o + \sum_{i=0}^{j} A_i(-1)^i \qquad (11)$$

As it has been established that the Redlich-Kister equation and its parameters do not always provide the best representation of properties of each component at infinite dilution, another approach that may be more accurate, which involves calculating the partial molar volume at infinite dilution by using their apparent molar volumes was also applied [48].

The apparent molar volumes of components of the mixtures were calculated with the equations:

$$V_{\Phi 1} = V_1^o + V^E/x_1 \qquad (12)$$

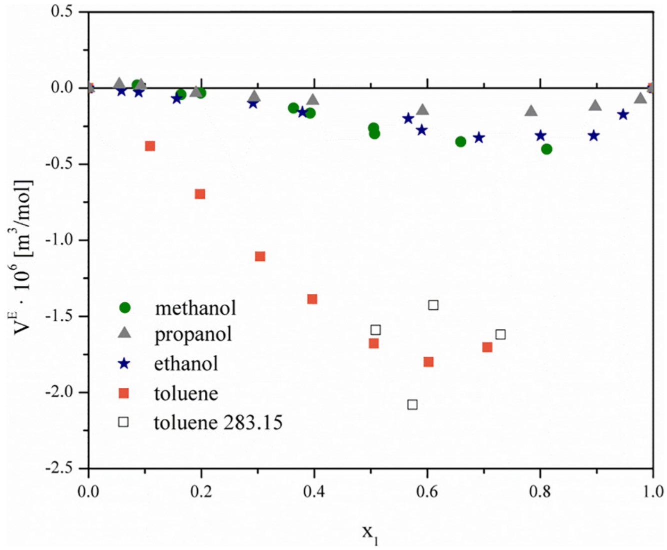

Fig. 6. Comparison of excess molar volume of binary mixture of toluene (1) + [C$_{41}$Pyrr][NTf$_2$] (2) with the data for systems [C$_{41}$Pyrr][NTf$_2$] (2) + methanol (1) or ethanol or 1-propanol (1) at $T = 298.15$ K; points: ■ toluene (1) + [C$_{41}$Pyrr][NTf$_2$] (2) this work; ● methanol (1) + [C$_{41}$Pyrr][NTf$_2$] (2) Ref. [19]; ▲ 1-propanol (1) + [C$_{41}$Pyrr][NTf$_2$] (2) Ref. [46]; ★ ethanol (1) + [C$_{41}$Pyrr][NTf$_2$] (2) Ref. [46] and □ toluene (1) + [C$_{41}$Pyrr][NTf$_2$] (2) at 283.15 K Ref. [21].

$$V_{\Phi 2} = V_2^o + V^E/(1-x_1) \qquad (13)$$

and the obtained values were identical as the once calculated from density results using the equation:

$$V_\Phi = \frac{M}{\rho} - (\rho-\rho_0)/m\rho d\rho_o \qquad (14)$$

where M denotes the molar mass of mixture. Then, the apparent molar volumes at infinite dilution were evaluated by a simple extrapolation of $V_{\Phi 1}$ to $x_1 = 0$, leading to the value of the apparent molar volume at infinite dilution of toluene. From definition, these properties are equal to the partial molar volumes at infinite dilution and they are of interest because, at the limit of infinite dilution, solute–solute interactions disappear. Table 4 presents the obtained values of the apparent and partial molar volumes at infinite dilutions of toluene in its binary systems.

As can be seen, the values of partial and apparent molar volumes of toluene at infinite dilution are close to each other and they confirm the conclusions obtained on the basis excess partial molar volumes. The lowest values of the partial molar volumes at infinite dilution of toluene obtained for its mixture with [C$_4$Py]][NTf$_2$] irrespective temperature suggest the strongest the packing/interactions effect occurring in that system.

4.4. Deviations in refractive index

As can be seen from Fig. 3, the values of deviations in refractive index are positive over the whole composition range of binary mixtures and their dependences on mole fraction of toluene are asymmetrical. The magnitude of Δn_D is obtained in the following order: [C$_4$Py][NTf$_2$] > [C$_{41}$Pyrr][NTf$_2$] > [C$_{61}$Pyrr][NTf$_2$]. Since deviations of refractive index can be physically interpretable as the deviation of the reduced free volume, they are negatively correlated to excess molar values [49,50]. However, the extrema for both quantities occurred at nearly the same molar fraction. As stated above, Δn_D and V^E must be somehow related: if excess molar volume is negative, then there will be less free volume available than in an ideal mixture and photons will interact more strongly with the components of the solution. As a result, light will

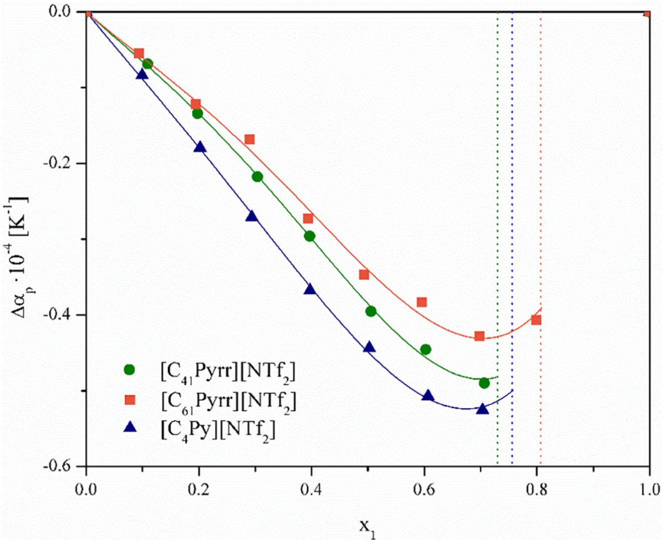

Fig. 7. Dependence of the excess thermal expansion on toluene mole fraction, x_1 at 298.15 K; solid line —, Eq. (5).

travel with a weaker velocity in the mixture and its refractive index will be higher than in an ideal solution. As a result, positive deviations of refractive index will be observed. This phenomenon occurs in the all systems investigated in the present study. Moreover, on the basis of Δn_D values, one can conclude that the temperature effect on excess molar volumes and on deviations of refractive index is similar in intensity, but opposite in sign. Thus, the behaviour of the refractive index of the binary systems toluene with [C$_{41}$Pyrr][NTf$_2$] or [C$_{61}$Pyrr][NTf$_2$] or [C$_4$Py][NTf$_2$] deviates from ideal behaviour as temperature increases.

4.5. Deviations in viscosity and excess Gibbs energy of activation for viscous flow

Table 3 shows the deviations of viscosity as function of mole fraction of toluene for each measured temperature and Fig. 4 presents $\Delta\eta$ for the all systems studied at 298.15 K. It is evident, that the viscosity deviations for the all mixtures are negative over the entire composition range and with decreasing temperature, their values become more negative. A similar phenomenon has been observed for many binary systems of ILs with molecular solvents, e.g. for the systems imidazolium based ionic liquids with acetonitrile, methanol and 1-propanol [51,52]. Moreover, as is seen from Table 3, the lowest values of deviations of viscosity were obtained the ([C$_4$Py][NTf$_2$] + toluene) and $\Delta\eta$ for ([C$_{41}$Pyrr][NTf$_2$] + toluene) were higher than those found for ([C$_{61}$Pyrr][NTf$_2$] + toluene) system. The same, viscometric measurements indicate the decreasing of deviations of viscosity with the alkyl chain length of the IL, what has been already postulated in literature [41,53].

It is known that the viscosity deviation is related to the resistance of a mixture flow [54]. Therefore, it depends on molecular interactions as well as on the size and shape of the molecules forming the solution. The positive viscosity deviations are observed in mixtures with strong specific interactions like hydrogen bonding interactions, whereas mixtures involving no relevant interactions between molecules of unequal size show negative $\Delta\eta$ values [55]. For our systems, the predominant effect is the packing effect due to important differences in volume of mixture components, that leads to negative $\Delta\eta$ values.

As can be seen from Fig. 9, showing an example of the temperature dependence of the viscosity deviations in the studied systems, the values of $\Delta\eta$ become less negative with increasing temperature. It is the result of two opposite effects associated with the increase in temperature: weakening the interaction between IL molecules and between unlike molecules and enhancing the penetration phenomenon.

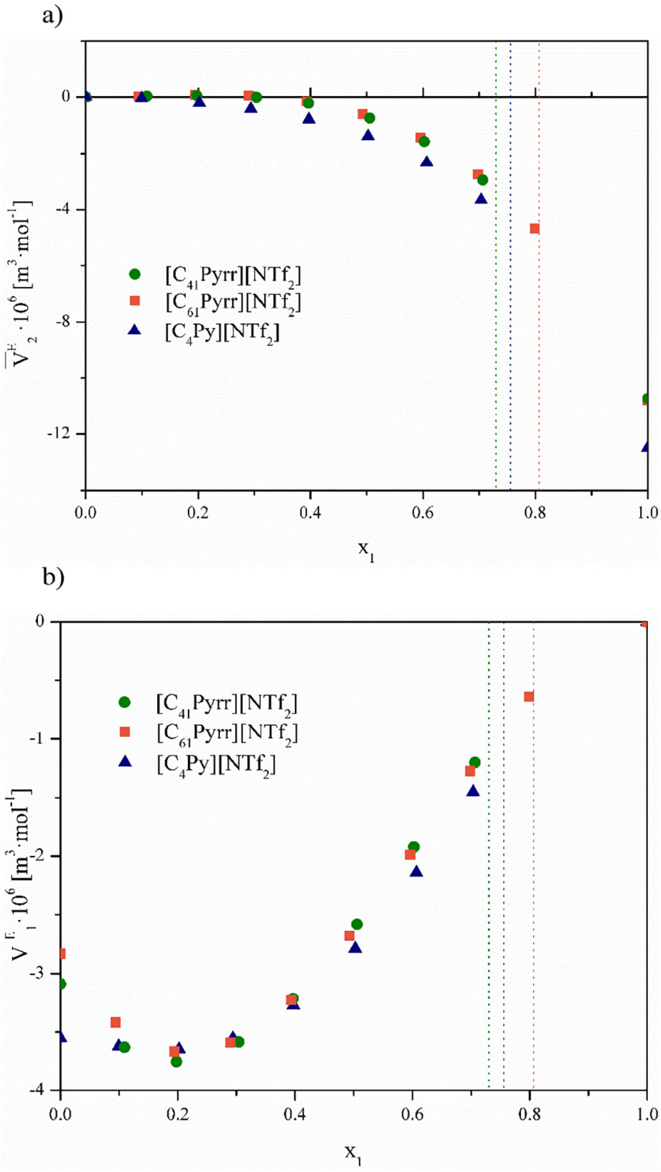

Fig. 8. Excess partial molar volumes of a) [C$_4$Py][NTf$_2$], [C$_{41}$Pyrr][NTf$_2$], [C$_{61}$Pyrr][NTf$_2$] and b) toluene at 298.15 *K* in their binary systems.

Fig. 5 presents the variation of the excess Gibbs energy of activation for viscous flow versus mole fraction of toluene for its mixtures with the ionic liquids studied.

As is seen for the all systems studied, the positive and similar values of excess Gibbs energy of activation were found. It has been found that positive values of excess Gibbs energies of activation indicate specific interactions, i.e. dipole–dipole or hydrogen bonding between unlike molecules occurring in mixture [56]. Since the interactions between toluene and IL are weak and any specific interactions in the systems studied are not expected, for the positive sign of ΔG^E must be responsible the packing effect of toluene in the interstices of ionic liquid. That effect seems to be also responsible for the negative of excess enthalpies obtained by Nebig and Gmehling for the mixtures of toluene and [C$_{41}$Pyrr][NTf$_2$]/[C$_{61}$Pyrr][NTf$_2$] [57]. The more positive values of excess enthalpies observed for system with [C$_{41}$Pyrr][NTf$_2$] in comparison to those for the respective system with [C$_{61}$Pyrr][NTf$_2$] may be a result of the higher positive contribution of breaking of associated molecules of [C$_{41}$Pyrr][NTf$_2$] or lower penetration effect. It is in agreement with our viscometric results.

Table 4
The partial and apparent molar volumes at infinite dilution of toluene in its binary mixtures at $T = 293.15–313.15$ K and at atmospheric pressure (0.1 MPa).

T/K	Toluene + [C_{41}Pyrr][NTf_2]		Toluene + [C_{61}Pyrr][NTf_2]		Toluene + [C_4Py]][NTf_2]	
	$\overline{V}^{\infty}/10^6\ m^3\cdot mol^{-1}$	$(V_{\Phi}^{\infty})/10^6\ m^3\cdot mol^{-1}$	$\overline{V}^{\infty}/10^6\ m^3\cdot mol^{-1}$	$(V_{\Phi}^{\infty})/10^6\ m^3\cdot mol^{-1}$	$\overline{V}^{\infty}/10^6\ m^3\cdot mol^{-1}$	$(V_{\Phi}^{\infty})/10^6\ m^3\cdot mol^{-1}$
293.15	103.27	103.21	103.53	103.52	103.16	103.29
298.15	103.78	103.72	104.03	104.02	103.32	103.43
303.15	104.24	104.19	104.52	104.49	103.86	104.01
308.15	104.76	104.71	105.05	105.03	104.42	104.50
313.15	105.21	104.16	105.54	105.53	104.96	105.21

5. Conclusions

Novel experimental data on the densities, dynamic viscosities and refractive indices of the pure ionic liquid [C_{61}Pyrr][NTf_2] and its binary mixtures with toluene over the miscible region at T of 293.15–323.15 K, together with the respective data for the systems of toluene with [C_{41}Pyrr][NTf_2] and [C_4Py]][NTf_2], were presented.

From the experimental values, excess molar volume, excess thermal expansion, deviation in refractive index, deviation in viscosity and excess Gibbs energy of activation for viscous flow were calculated. The parameters of the Redlich-Kister polynomial equation were adjusted to these properties with satisfactory results. Moreover, partial and apparent molar volumes of toluene and ionic liquid in their binary systems have been calculated.

As the studied systems exhibit a miscibility gap in the liquid phase, the high positive deviations from ideality must appear. Thus, the interactions between toluene and ionic liquid must be weaker than those between like molecules, i.e. mainly self-association of IL. Therefore, for the excess molar volumes, the packing effect determines the volumetric property. The π–π interactions between 1-butylpyridinium bis (trifluoromethylsulfonyl)imide and toluene and the lower steric hindrance of the pyridinium cation in comparison to 1-methylpyrrolidinium one seem to be responsible for the most negative values of excess molar volumes observed in the system of toluene with [C_4Py][NTf_2].

The excess partial molar volumes as well as the partial molar volumes at infinite dilution confirm the conclusion, that in the system of toluene with [C_4Py][NTf_2] the strongest interactions between unlike molecules can be expected.

The negative values of excess thermal expansion and viscosity deviations indicate that the packing efficiency of toluene accommodation in the interstitial regions of ILs networks dominate over effect of self-association of ionic liquid.

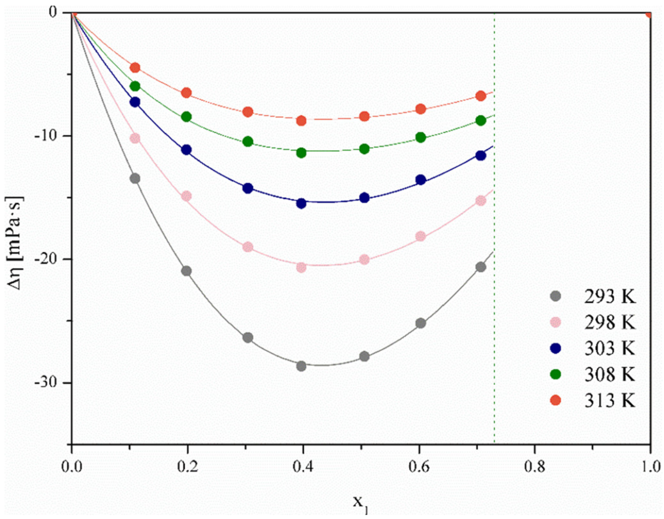

Fig. 9. The temperature dependence of the viscosity deviations of ([C_{41}Pyrr][NTf_2] + toluene) system, solid line —, Eq. (5).

The positive deviation of the excess Gibbs energy of activation for viscous flow and the order of the positive refractive deviations in the studied systems as: [C_4Py]][NTf_2] > [C_{41}Pyrr][NTf_2] > [C_{61}Pyrr][NTf_2] can also be explained by the dominance of the packing effect over self-association of ionic liquids.

The influence of elongation of the alkyl chain length of the IL is visible in the viscosity deviations as well as in the excess thermal expansions while in the excess molar volumes is practically not observed.

CRediT authorship contribution statement

Dorota Warmińska: Conceptualization, Formal analysis, Investigation, Writing - original draft, Writing - review & editing.**Iwona Cichowska-Kopczyńska:**Investigation, Formal analysis, Data curation, Writing - original draft, Writing - review & editing.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2020.112754.

References

[1] S. Corderí, N. Calvar, E. Gómez, A. Domínguez, Capacity of ionic liquids [EMim][NTf 2] and [EMpy][NTf 2] for extraction of toluene from mixtures with alkanes: comparative study of the effect of the cation, Fluid Phase Equilib. 315 (2012) 46–52, https://doi.org/10.1016/j.fluid.2011.11.016.

[2] T.A. Al-Sahhaf, E. Kapetanovic, Measurement and prediction of phase equilibria in the extraction of aromatics from naphtha reformate by tetraethylene glycol, Fluid Phase Equilib. 118 (1996) 271–285, https://doi.org/10.1016/0378-3812(95)02849-8.

[3] J. Chen, L.-P. Duan, J.-G. Mi, W.-Y. Fei, Z.-C. Li, Liquid–liquid equilibria of multi-component systems including n-hexane, n-octane, benzene, toluene, xylene and sulfolane at 298.15 K and atmospheric pressure, Fluid Phase Equilib. 173 (2000) 109–119, https://doi.org/10.1016/S0378-3812(00)00398-8.

[4] U. Domańska, M. Wlazło, Z. Dąbrowski, A. Wiśniewska, Ammonium ionic liquids in separation of water/butan-1-ol using liquid-liquid equilibrium diagrams in ternary systems, Fluid Phase Equilib. 485 (2019) 23–31, https://doi.org/10.1016/J.FLUID.2018.12.009.

[5] M.J. Salar-García, V.M. Ortiz-Martínez, F.J. Hernández-Fernández, A.P. de los Ríos, J. Quesada-Medina, Ionic liquid technology to recover volatile organic compounds (VOCs), J. Hazard. Mater. 321 (2017) 484–499, https://doi.org/10.1016/j.jhazmat.2016.09.040.

[6] E.J. González, N. Calvar, B. González, Á. Domínguez, Separation of toluene from alkanes using 1-ethyl-3-methylpyridinium ethylsulfate ionic liquid at T = 298.15 K and atmospheric pressure, J. Chem. Thermodyn. 42 (2010) 752–757, https://doi.org/10.1016/J.JCT.2010.01.008.

[7] N. Delgado-Mellado, A. Ovejero-Perez, P. Navarro, M. Larriba, M. Ayuso, J. García, F. Rodríguez, Imidazolium and pyridinium-based ionic liquids for the cyclohexane/cyclohexene separation by liquid-liquid extraction, J. Chem. Thermodyn. 131 (2019) 340–346, https://doi.org/10.1016/J.JCT.2018.11.018.

[8] I. Cichowska-Kopczynska, M. Joskowska, R. Aranowski, Wetting processes in supported ionic liquid membranes technology, Physicochem. Probl. Miner. Process. 50 (2014) https://doi.org/10.5277/ppmp140131.

[9] I. Cichowska-Kopczyńska, M. Joskowska, B. Debski, R. Aranowski, J. Hupka, Separation of toluene from gas phase using supported imidazolium ionic liquid membrane, J. Membr. Sci. 566 (2018) 367–373, https://doi.org/10.1016/J.MEMSCI.2018.08.058.

[10] Q. Gan, D. Rooney, Y. Zou, Supported ionic liquid membranes in nanopore structure for gas separation and transport studies, Desalination 199 (2006) 535–537.

[11] S. Corderí, E. Gómez, Á. Domínguez, N. Calvar, (Liquid + liquid) equilibrium of ternary and quaternary systems containing heptane, cyclohexane, toluene and the ionic liquid [EMim][N(CN)2]. Experimental data and correlation, J. Chem. Thermodyn. 94 (2016) 16–23, https://doi.org/10.1016/J.JCT.2015.10.018.

[12] S. Corderí, N. Calvar, E. Gómez, Á. Domínguez, Quaternary (liquid + liquid) equilibrium data for the extraction of toluene from alkanes using the ionic liquid [EMim]

[MSO4], J. Chem. Thermodyn. 76 (2014) 79–86, https://doi.org/10.1016/J.JCT.2014.03.008.

[13] S. García, M. Larriba, J. García, J.S. Torrecilla, F. Rodríguez, Alkylsulfate-based ionic liquids in the liquid–liquid extraction of aromatic hydrocarbons, J. Chem. Thermodyn. 45 (2012) 68–74, https://doi.org/10.1016/J.JCT.2011.09.009.

[14] M. Larriba, P. Navarro, J. García, F. Rodríguez, Liquid–liquid extraction of toluene from n-heptane by {[emim][TCM] + [emim][DCA]} binary ionic liquid mixtures, Fluid Phase Equilib. 364 (2014) 48–54, https://doi.org/10.1016/J.FLUID.2013.12.008.

[15] S. García, M. Larriba, J. García, J.S. Torrecilla, F. Rodríguez, Liquid–liquid extraction of toluene from n-heptane using binary mixtures of N-butylpyridinium tetrafluoroborate and N-butylpyridinium bis(trifluoromethylsulfonyl)imide ionic liquids, Chem. Eng. J. 180 (2012) 210–215, https://doi.org/10.1016/J.CEJ.2011.11.069.

[16] M. Larriba, P. Navarro, J. García, F. Rodríguez, Separation of toluene from n-heptane, 2,3-dimethylpentane, and cyclohexane using binary mixtures of [4empy][Tf2N] and [emim][DCA] ionic liquids as extraction solvents, Sep. Purif. Technol. 120 (2013) 392–401, https://doi.org/10.1016/J.SEPPUR.2013.10.017.

[17] S. Corderí, N. Calvar, E. Gómez, Á. Domínguez, Quaternary (liquid + liquid) equilibrium data for the extraction of toluene from alkanes using the ionic liquid [EMim][MSO4], J. Chem. Thermodyn. 76 (2014) 79–86, https://doi.org/10.1016/J.JCT.2014.03.008.

[18] M. Enayati, B. Mokhtarani, A. Sharifi, S. Anvari, M. Mirzaei, Liquid–liquid extraction of toluene from alkane with pyridinium based ionic liquid ([BPy][NO3] and [HPy][NO3]) at 298.15 K and atmospheric pressure, J. Chem. Thermodyn. 102 (2016) 316–321, https://doi.org/10.1016/J.JCT.2016.07.030.

[19] M. Geppert-Rybczyńska, J.K. Lehmann, A. Heintz, Physicochemical properties of two 1-alkyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide ionic liquids and of binary mixtures of 1-butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide with methanol or acetonitrile, J. Chem. Thermodyn. 71 (2014) 171–181, https://doi.org/10.1016/J.JCT.2013.12.009.

[20] M. Vranes, S. Dozic, V. Djeric, S. Gadzuric, Physicochemical characterization of 1-butyl-3-methylimidazolium and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, J. Chem. Eng. Data 57 (2012) 1072–1077, https://doi.org/10.1021/je2010837.

[21] P.F. Requejo, I. Díaz, E.J. González, Á. Domínguez, Mutual solubility of aromatic hydrocarbons in pyrrolidinium and ammonium-based ionic liquids and its modeling using the cubic-plus-association (CPA) equation of state, J. Chem. Eng. Data 62 (2017) 633–642, https://doi.org/10.1021/acs.jced.6b00655.

[22] J. Vuksanović, D. Soldatović, I. Radović, Z. Višak, M. Kijevčanin, Thermodynamic characterization of binary mixtures of poly(propylene glycol) 425 with toluene and o-, m- and p-xylenes, J. Chem. Thermodyn. 131 (2019) 393–403, https://doi.org/10.1016/J.JCT.2018.11.020.

[23] D. Keshapolla, S.P. Ijardar, R.L. Gardas, Temperature dependent apparent molar properties of trihexylammonium carboxylate based protic ionic liquids in toluene and dodecane, J. Mol. Liq. 272 (2018) 1058–1069, https://doi.org/10.1016/J.MOLLIQ.2018.10.114.

[24] A. Kumari, V. Aniya, N.V. Rane, P.K. Thella, B. Satyavathi, Isobaric phase equilibrium of morpholine + 1-decanol, volumetric properties and molar refractivity from 293.15 to 333.15 K of morpholine + 1-decanol and 1-octanol + toluene system with applications of Prigogine–Flory–Patterson theory, Thermochim. Acta 649 (2017) 41–53, https://doi.org/10.1016/J.TCA.2016.12.010.

[25] M.M. Billah, M.M.H. Rocky, I. Hossen, I. Hossain, M.N. Hossain, S. Akhtar, Densities, viscosities, and refractive indices for the binary mixtures of tri-n-butyl phosphate (TBP) with toluene and ethylbenzene between (303.15 and 323.15) K, J. Mol. Liq. 265 (2018) 611–620, https://doi.org/10.1016/J.MOLLIQ.2018.05.126.

[26] R. Zarrougui, M. Dhahbi, D. Lemordant, Effect of temperature and composition on the transport and thermodynamic properties of binary mixtures of ionic liquid N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide and propylene carbonate, J. Solut. Chem. 39 (2010) 921–942, https://doi.org/10.1007/s10953-010-9562-5.

[27] H. Tokuda, K. Ishii, M.A.B.H. Susan, S. Tsuzuki, K. Hayamizu, M. Watanabe, Physicochemical properties and structures of room-temperature ionic liquids. 3. Variation of cationic structures, J. Phys. Chem. B 110 (2006) 2833–2839, https://doi.org/10.1021/jp053396f.

[28] R.G. Seoane, S. Corderí, E. Gómez, N. Calvar, E.J. González, E.A. MacEdo, Á. Domínguez, Temperature dependence and structural influence on the thermophysical properties of eleven commercial ionic liquids, Ind. Eng. Chem. Res. 51 (2012) 2492–2504, https://doi.org/10.1021/ie2029255.

[29] M. Shamsipur, A.A.M. Beigi, M. Teymouri, S.M. Pourmortazavi, M. Irandoust, Physical and electrochemical properties of ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium trifluoromethanesulfonate and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, J. Mol. Liq. 157 (2010) 43–50, https://doi.org/10.1016/J.MOLLIQ.2010.08.005.

[30] K. Řehák, P. Morávek, M. Strejc, Determination of mutual solubilities of ionic liquids and water, Fluid Phase Equilib. 316 (2012) 17–25, https://doi.org/10.1016/J.FLUID.2011.12.008.

[31] A. Luís, K. Shimizu, J.M.M. Araújo, P.J. Carvalho, J.A. Lopes-da-Silva, J.N. Canongia Lopes, L.P.N. Rebelo, J.A.P. Coutinho, M.G. Freire, A.B. Pereiro, Influence of nanosegregation on the surface tension of fluorinated ionic liquids, Langmuir 32 (2016) 6130–6139, https://doi.org/10.1021/acs.langmuir.6b00209.

[32] J. Salminen, N. Papaiconomou, R.A. Kumar, J.-M. Lee, J. Kerr, J. Newman, J.M. Prausnitz, Physicochemical properties and toxicities of hydrophobic piperidinium and pyrrolidinium ionic liquids, Fluid Phase Equilib. 261 (2007) 421–426, https://doi.org/10.1016/J.FLUID.2007.06.031.

[33] S. Monaco, A.M. Arangio, F. Soavi, M. Mastragostino, E. Paillard, S. Passerini, An electrochemical study of oxygen reduction in pyrrolidinium-based ionic liquids for lithium/oxygen batteries, Electrochim. Acta 83 (2012) 94–104, https://doi.org/10.1016/J.ELECTACTA.2012.08.001.

[34] U. Domańska, K. Paduszyński, M. Królikowski, A. Wróblewska, Separation of 2-phenylethanol from water by liquid-liquid extraction with ionic liquids: new experimental data and modeling with modern thermodynamic tools, Ind. Eng. Chem. Res. 55 (2016) 5736–5747, https://doi.org/10.1021/acs.iecr.6b00375.

[35] G. Annat, M. Forsyth, D.R. Macfarlane, Ionic liquid mixtures — variations in physical properties and their origins in molecular structure, J. Phys. Chem. A 116 (2012) 8251–8258, https://doi.org/10.1021/jp3012602.

[36] S. Nebig, V. Liebert, J. Gmehling, Measurement and prediction of activity coefficients at infinite dilution (γ^{∞}), vapor–liquid equilibria (VLE) and excess enthalpies (HE) of binary systems with 1,1-dialkyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide using mod. UNIFAC (Dortmund), Fluid Phase Equilib. 277 (2009) 61–67, https://doi.org/10.1016/J.FLUID.2008.11.013.

[37] H. Jin, B.O. Hare, J. Dong, S. Arzhantsev, G.A. Baker, J.F. Wishart, A.J. Benesi, M. Maroncelli, Physical properties of ionic liquids consisting of the 1-butyl-3-methylimidazolium cation with various anions and the bis(trifluoromethylsulfonyl) imide anion with various cations, J. Phys. Chem. B 112 (2008) 81–92, https://doi.org/10.1021/jp076462h.

[38] F.S. Oliveira, M.G. Freire, P.J. Carvalho, J.A.P. Coutinho, J.N.C. Lopes, L.P.N. Rebelo, I.M. Marrucho, Structural and positional isomerism influence in the physical properties of pyridinium NTf2-based ionic liquids: pure and water-saturated mixtures, J. Chem. Eng. Data 55 (2010) 4514–4520, https://doi.org/10.1021/je100377k.

[39] Q. Liu, M. Yang, P. Yan, X. Liu, Z. Tan, U. Welz-Biermann, Density and surface tension of ionic liquids $[C_npy][NTf_2]$ ($n = 2, 4, 5$), J. Chem. Eng. Data 55 (2010) 4928–4930.

[40] Q. Liu, P.F. Yan, M. Yang, Z.C. Tan, C.P. Li, U. Welz-Biermann, Dynamic viscosity and conductivity of ionic liquids [Cnpy][NTf2] (n = 2, 4, 5), Wuli Huaxue Xuebao/Acta Phys. - Chim. Sin. 27 (2011) 2762–2766, https://doi.org/10.3866/PKU.WHXB20112762.

[41] M. Larriba, S. García, P. Navarro, J. García, F. Rodríguez, Physical properties of N-butylpyridinium tetrafluoroborate and N-butylpyridinium bis(trifluoromethylsulfonyl)imide binary ionic liquid mixtures, J. Chem. Eng. Data 57 (2012) 1318–1325, https://doi.org/10.1021/je300093r.

[42] E.J. González, P.F. Requejo, Á. Domínguez, E.A. Macedo, Phase equilibria of binary mixtures (ionic liquid + aromatic hydrocarbon): effect of the structure of the components on the solubility, Fluid Phase Equilib. 360 (2013) 416–422, https://doi.org/10.1016/J.FLUID.2013.09.044.

[43] O. Redlich, A.T. Kister, Algebraic representation of thermodynamic properties and the classification of solutions, Ind. Eng. Chem. 40 (1948) 345–348.

[44] E.J. González, P.F. Requejo, F.M. Maia, Á. Domínguez, E.A. Macedo, Solubility, density and excess molar volume of binary mixtures of aromatic compounds and common ionic liquids at T = 283.15 K and atmospheric pressure, Phys. Chem. Liq. 53 (2015) 419–428.

[45] B. Goddu, M.M. Tadavarthi, V.K. Tadekoru, J.N. Guntupalli, Density, speed of sound, and dynamic viscosity of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide/1-butyl-3-methylimidazolium hexafluorophosphate and N-methylaniline binary systems from T = 298.15 to 323.15 K at 0.1 MPa, J. Chem. Eng. Data 64 (2019) 2303–2319, https://doi.org/10.1021/acs.jced.8b01095.

[46] E.J. González, P.F. Requejo, Á. Domínguez, E.A. MacEdo, Physical properties of binary alcohol + ionic liquid mixtures at several temperatures and atmospheric pressure, J. Solut. Chem. 42 (2013) 746–763, https://doi.org/10.1007/s10953-013-9990-0.

[47] M. Vraneš, S. Papović, A. Tot, N. Zec, S. Gadžurić, Density, excess properties, electrical conductivity and viscosity of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide + γ-butyrolactone binary mixtures, J. Chem. Thermodyn. 76 (2014) 161–171, https://doi.org/10.1016/J.JCT.2014.03.025.

[48] Y. Li, H. Ye, P. Zeng, F. Qi, Volumetric properties of binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate with aniline, J. Solut. Chem. 39 (2010) 219–230, https://doi.org/10.1007/s10953-009-9494-0.

[49] M.A. Iglesias-Otero, J. Troncoso, E. Carballo, L. Romaní, Density and refractive index in mixtures of ionic liquids and organic solvents: correlations and predictions, J. Chem. Thermodyn. 40 (2008) 949–956, https://doi.org/10.1016/j.jct.2008.01.023.

[50] P. Brocos, Á. Piñeiro, R. Bravo, A. Amigo, Refractive indices, molar volumes and molar refractions of binary liquid mixtures: concepts and correlations, Phys. Chem. Chem. Phys. 5 (2003) 550–557, https://doi.org/10.1039/b208765k.

[51] J.Y. Wu, Y.P. Chen, C.S. Su, Density and viscosity of ionic liquid binary mixtures of 1-n-butyl-3-methylimidazolium tetrafluoroborate with acetonitrile, N,N-dimethylacetamide, methanol, and N-methyl-2-pyrrolidone, J. Solut. Chem. 44 (2015) 395–412, https://doi.org/10.1007/s10953-014-0273-1.

[52] W. Qian, Y. Xu, H. Zhu, C. Yu, Properties of pure 1-methylimidazolium acetate ionic liquid and its binary mixtures with alcohols, J. Chem. Thermodyn. 49 (2012) 87–94, https://doi.org/10.1016/J.JCT.2012.01.013.

[53] X. Li, Q. Zhou, X. Lu, S. Zhang, Densities and viscosities of binary mixtures of magnetic ionic liquids 1-alkyl-3-methylimidazolium tetrachloroferrate with ethyl acetate at temperatures (293.15 to 323.15) K, J. Mol. Liq. 243 (2017) 285–292, https://doi.org/10.1016/J.MOLLIQ.2017.08.014.

[54] F. Nabi, M.A. Malik, C.G. Jesudason, S.A. Al-Thabaiti, A review of molecular interactions in organic binary mixtures, Korean J. Chem. Eng. 31 (2014) 1505–1517, https://doi.org/10.1007/s11814-014-0173-5.

[55] T. Inoue, T. Misono, Cloud point phenomena for POE-type nonionic surfactants in imidazolium-based ionic liquids: effect of anion species of ionic liquids on the cloud point, J. Colloid Interface Sci. 337 (2009) 247–253, https://doi.org/10.1016/J.JCIS.2009.05.002.

[56] B. Garcia, R. Alcalde, J.M. Leal, J.S. Matos, Shear viscosities of the N-methylformamide- and N,N-dimethylformamide-(C1-C10) alkan-1-ol solvent systems, J. Chem. Soc. Faraday Trans. 93 (1997) 1115–1118, https://doi.org/10.1039/a607876a.

[57] S. Nebig, J. Gmehling, Prediction of phase equilibria and excess properties for systems with ionic liquids using modified UNIFAC: typical results and present status of the modified UNIFAC matrix for ionic liquids, Fluid Phase Equilib. 302 (2011) 220–225.