



# 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

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## 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.

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## 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

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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-butylpyridinium 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.

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

| Chemical name  | Source    | CAS number  | Purity/mass fraction <sup>a</sup> | Water content /10 <sup>6</sup> w(H <sub>2</sub> O) <sup>b</sup> |
|--|-----------|-------------|-----------------------------------|---|
| Toluene  | POCh      | 108-88-3    | 0.99                              | 223   |
| 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide<br>$[C_{41}Pyrr][NTf_2]$ | Io-li-tec | 223437-11-4 | 0.99                              | 345   |
| 1-Hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide<br>$[C_{61}Pyrr][NTf_2]$ | Io-li-tec | 380497-19-8 | 0.99                              | 543   |
| 1-Butylpyridinium bis(trifluoromethylsulfonyl)imide<br>$[C_4Py][NTf_2]$                  | Io-li-tec | 187863-42-9 | 0.99                              | 621   |

<sup>a</sup> As stated by the supplier.

<sup>b</sup> Karl Fischer titration.

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  $0.35 \text{ kg} \cdot \text{m}^{-3}$ .

The viscosity measurements were carried out using LV DV-III Programmable Rheometer (Searle cone-plate viscometer; Brookfield Engineering Laboratory, USA), controlled by a computer. The temperature of the samples was controlled within  $\pm 0.01$  K using a thermostatic water bath (PolyScience 9106, USA). CP-40 cone (angle  $0.8^\circ$ , radius 2.4 cm) and 0.5 ml ionic liquid were used. Dynamic viscosity was determined based on the ratio of shear stress ( $\text{N/m}^2$ ) 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  $298.15 \pm 0.01$  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  $\pm 0.1$  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  $\pm 0.003$  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-methylpyridinium ionic liquids with ethylsulfate, bis(trifluoromethylsulfonyl)imide anions and 1-propyl-3-

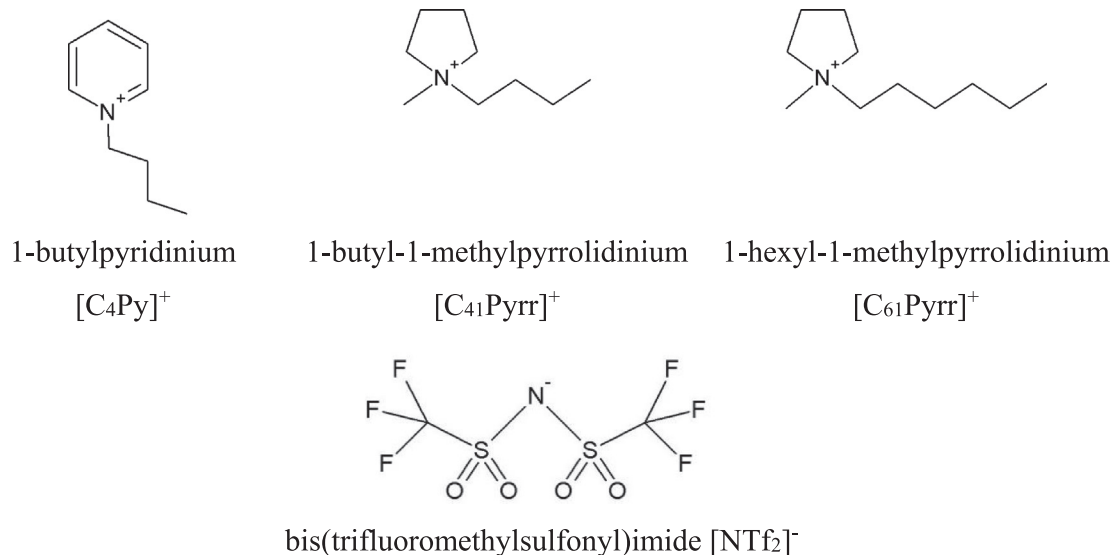


Fig. 1. Chemical structures of ions comprising ionic liquids used in this study.

methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [42]. Requejo et al. measured mutual solubility of the same hydrocarbons in 1-butyl-1-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-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide and 1-butylpyridinium bis(trifluoromethylsulfonyl)imide over the miscible region in the temperature range of  $T = 293.15\text{--}318.15$  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:  $[\text{C}_{41}\text{Pyrr}][\text{NTf}_2] > [\text{C}_{61}\text{Pyrr}][\text{NTf}_2] < [\text{C}_4\text{Py}][\text{NTf}_2]$  for density,  $[\text{C}_{41}\text{Pyrr}][\text{NTf}_2] < [\text{C}_{61}\text{Pyrr}][\text{NTf}_2] < [\text{C}_4\text{Py}][\text{NTf}_2]$  for refractive index and  $[\text{C}_{41}\text{Pyrr}][\text{NTf}_2] < [\text{C}_{61}\text{Pyrr}][\text{NTf}_2] > [\text{C}_4\text{Py}][\text{NTf}_2]$  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:

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

where  $\rho$  is the density of a mixture and  $x_i$ ,  $M_i$ , and  $\rho_i$  are the mole fraction, the molar mass and the density of a component  $i$ , respectively.

From refractive indices, the deviations in refractive index,  $\Delta n_D$ , were calculated using the following equation:

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

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

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

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

The excess Gibbs energy of activation for viscous flow,  $\Delta G^E$ , was calculated using the equation:

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

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  $\eta_1$ ,  $\eta_2$ ,  $V_1$  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]:

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

**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<sup>a</sup>.

| T/K                                       | $\rho/(\text{kg}\cdot\text{m}^{-3})$ |   | $\eta/(\text{mPa}\cdot\text{s})$ |   | $n_D$  |                            |
|---|--------------------------------------|---|----------------------------------|---|--------|----------------------------|
|   | 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 <sub>41</sub> Pyrr][NTf <sub>2</sub> ] |                                      |   |                                  |   |        |                            |
| 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 <sub>61</sub> Pyrr][NTf <sub>2</sub> ] |                                      |   |                                  |   |        |                            |
| 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 <sub>4</sub> Py][NTf <sub>2</sub> ]    |                                      |   |                                  |   |        |                            |
| 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 |                            |

<sup>a</sup> 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,  $u(\rho) = 0.35$  kg·m<sup>-3</sup>,  $u(n_D) = 0.0002$  and  $u_r(\eta) = 1\%$ .

**Table 3**

Densities  $\rho$ , excess molar volumes  $V^E$ , refractive indices  $n_D$ , refractive index deviations  $\Delta n_D$ , viscosities  $\eta$ , viscosity deviations  $\Delta\eta$  and excess Gibbs free energy of activation of viscous flow  $\Delta G^E$  of toluene (1) + [C<sub>41</sub>Pyrr][NTf<sub>2</sub>]/[C<sub>61</sub>Pyrr][NTf<sub>2</sub>]/[C<sub>4</sub>Py][NTf<sub>2</sub>] systems at  $T = 293.15$ – $313.15$  K and at atmospheric pressure (0.1 MPa)<sup>a</sup>.

| $x_1$   | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $V^E/10^{-6}\text{m}^3\cdot\text{mol}^{-1}$ | $n_D$  | $\Delta n_D$ | $\eta/\text{mPa}\cdot\text{s}$ | $\Delta\eta/\text{mPa}\cdot\text{s}$ | $\Delta G^E/\text{J}\cdot\text{mol}^{-1}$ |
|---|------------------------------------|---|--------|--------------|--------------------------------|--------------------------------------|---|
| Toluene (1) + [C <sub>41</sub> Pyrr][NTf <sub>2</sub> ] (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 <sub>61</sub> Pyrr][NTf <sub>2</sub> ] (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)

| $x_1$  | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $V^E/10^{-6}\text{ m}^3\cdot\text{mol}^{-1}$ | $n_D$  | $\Delta n_D$ | $\eta/\text{mPa}\cdot\text{s}$ | $\Delta\eta/\text{mPa}\cdot\text{s}$ | $\Delta G^E/\text{J}\cdot\text{mol}^{-1}$ |
|--|------------------------------------|--|--------|--------------|--------------------------------|--------------------------------------|---|
| 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 <sub>4</sub> Py][NTf <sub>2</sub> ] (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)

| $x_1$  | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $V^E/10^{-6}\text{m}^3\cdot\text{mol}^{-1}$ | $n_D$  | $\Delta n_D$ | $\eta/\text{mPa}\cdot\text{s}$ | $\Delta\eta/\text{mPa}\cdot\text{s}$ | $\Delta G^E/\text{J}\cdot\text{mol}^{-1}$ |
|--------|------------------------------------|---|--------|--------------|--------------------------------|--------------------------------------|---|
| 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                                       |

<sup>a</sup>  $x_1$  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<sup>-3</sup>;  $u(n_D) = 0.0002$ ;  $u_r(\eta) = 1\%$  and  $u(V^E) = 0.08 \cdot 10^{-6}$  m<sup>3</sup>·mol<sup>-1</sup>.

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

The standard deviation of fit,  $\sigma$ , was calculated as

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

where  $N$  is the number of experimental data.

Parameters  $A_i$  of Eq. (5) and the corresponding  $\sigma$  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,  $\Delta n_D$ , viscosity deviations,  $\Delta\eta$ , and excess Gibbs free energies of activation of viscous flow,  $\Delta G^E$ , 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<sub>41</sub>Pyrr][NTf<sub>2</sub>] + toluene) mixtures present practically the same values of excess molar volumes than those obtained for the system of ([C<sub>61</sub>Pyrr][NTf<sub>2</sub>] + 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<sub>41</sub>Pyrr][NTf<sub>2</sub>], [C<sub>61</sub>Pyrr][NTf<sub>2</sub>], [C<sub>4</sub>Py][NTf<sub>2</sub>] are 303.03, 337.37 and 287.53 cm<sup>3</sup>·mol<sup>-1</sup>, respectively, which are much greater than the molar volume of toluene (106.87 cm<sup>3</sup>·mol<sup>-1</sup>) 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<sub>4</sub>Py][NTf<sub>2</sub>] + toluene) system is larger than that for ([C<sub>41</sub>Pyrr][NTf<sub>2</sub>] + toluene) and ([C<sub>61</sub>Pyrr][NTf<sub>2</sub>] + 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  $\pi$ - $\pi$  interactions between 1-butylpyridinium 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<sub>41</sub>Pyrr][NTf<sub>2</sub>] + toluene) system together with literature results for the systems ([C<sub>41</sub>Pyrr][NTf<sub>2</sub>] + methanol), ([C<sub>41</sub>Pyrr][NTf<sub>2</sub>] + ethanol), ([C<sub>41</sub>Pyrr][NTf<sub>2</sub>] + 1-propanol) at 298.15 K and for ([C<sub>41</sub>Pyrr][NTf<sub>2</sub>] + toluene) at 283.15 K [19,21,46]. It should be added that, the excess molar volumes for the system ([C<sub>41</sub>Pyrr][NTf<sub>2</sub>] + 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<sup>-3</sup> at 283.15 K.

As can be seen the excess molar volumes for the ([C<sub>41</sub>Pyrr][NTf<sub>2</sub>] + toluene) system are considerably more negative than those obtained for the systems ([C<sub>41</sub>Pyrr][NTf<sub>2</sub>] + 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<sub>41</sub>Pyrr][NTf<sub>2</sub>] + 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,  $\alpha_p$ , for all compositions of binary systems, was calculated from the equation:

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

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

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

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

where  $\alpha_{p,i}$  and  $\Phi_i$  are the thermal expansion coefficients and the volume fractions for pure components  $i$ , respectively. The values of  $\alpha_p$  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  $([\text{C}_4\text{Py}][\text{NTf}_2] + \text{toluene})$  system confirm conclusions from excess molar volumes which suggest the strongest molecular interactions in this system. Moreover, the excess thermal expansion observed for

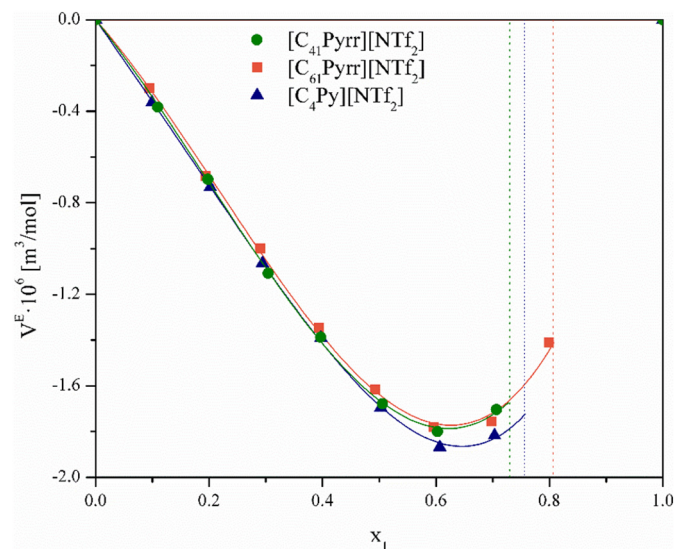


Fig. 2. Excess molar volumes,  $V^E$ , for toluene (1) + ionic liquid (2) at  $p = 0.1 \text{ MPa}$  as a function of mole fraction,  $x_1$  at  $T = 298.15 \text{ K}$ : ●,  $[\text{C}_{41}\text{Pyrr}][\text{NTf}_2]$ ; ■,  $[\text{C}_{61}\text{Pyrr}][\text{NTf}_2]$ ; ▲,  $[\text{C}_4\text{Py}][\text{NTf}_2]$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

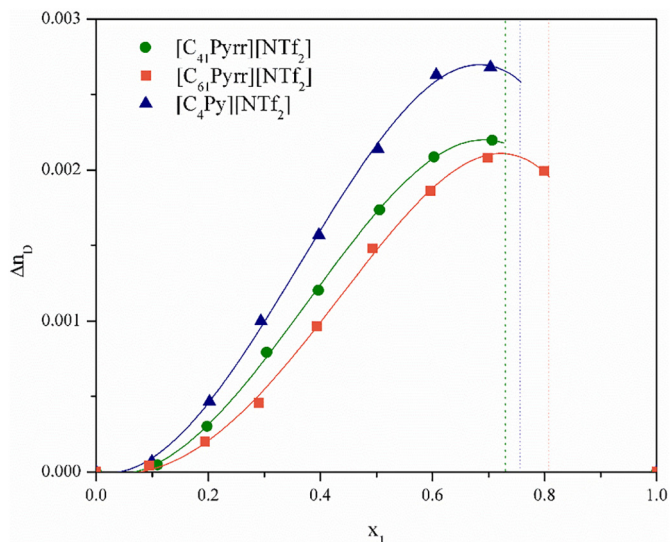


Fig. 3. Deviations in refractive index,  $\Delta n_b$ , for toluene (1) + ionic liquid (2) at  $p = 0.1 \text{ MPa}$  as a function of mole fraction,  $x_1$  at  $T = 298.15 \text{ K}$ : ●,  $[\text{C}_{41}\text{Pyrr}][\text{NTf}_2]$ ; ■,  $[\text{C}_{61}\text{Pyrr}][\text{NTf}_2]$ ; ▲,  $[\text{C}_4\text{Py}][\text{NTf}_2]$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

$([\text{C}_{41}\text{Pyrr}][\text{NTf}_2] + \text{toluene})$  system differs considerably from that observed for  $([\text{C}_{61}\text{Pyrr}][\text{NTf}_2] + \text{toluene})$ . 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.

#### 4.3. Partial and apparent molar volumes

The partial molar volumes of toluene and the studied ionic liquids in their binary mixtures,  $\bar{V}_1$  and  $\bar{V}_2$ , were calculated from the Eqs. (9) and (10), knowing the molar volumes of the pure components,  $V_1^0$  and  $V_2^0$ :

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

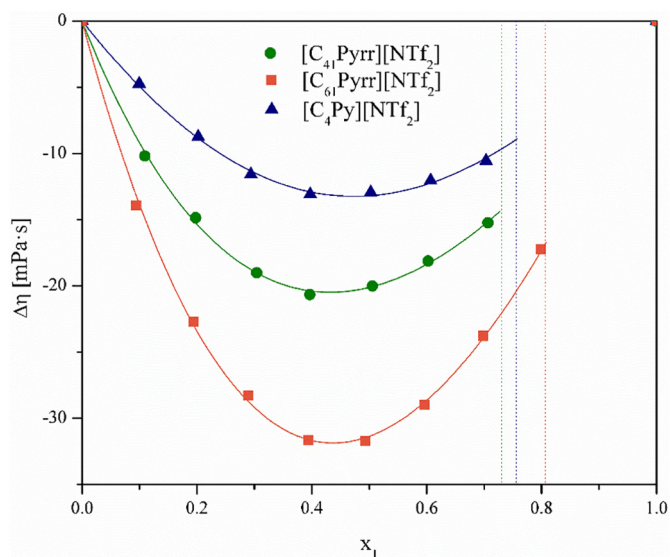
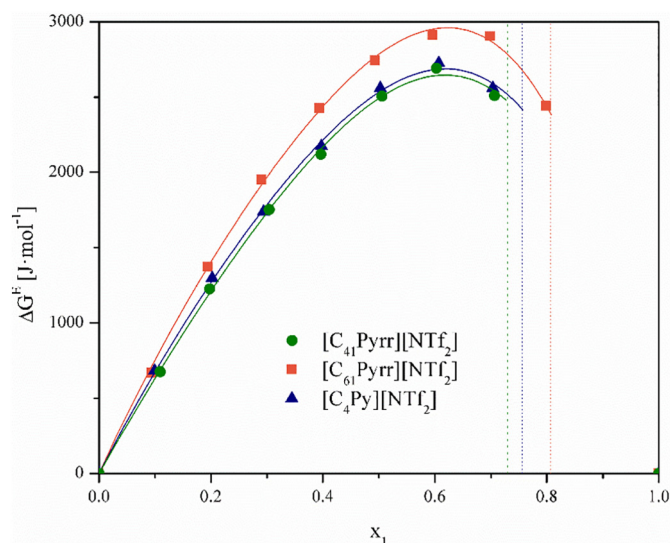


Fig. 4. Viscosity deviations,  $\Delta \eta$ , for toluene (1) + ionic liquid (2) at  $p = 0.1 \text{ MPa}$  as a function of mole fraction,  $x_1$  at  $T = 298.15 \text{ K}$ : ●,  $[\text{C}_{41}\text{Pyrr}][\text{NTf}_2]$ ; ■,  $[\text{C}_{61}\text{Pyrr}][\text{NTf}_2]$ ; ▲,  $[\text{C}_4\text{Py}][\text{NTf}_2]$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





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

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

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:  $\bar{V}_i^E = V_i^0 - \bar{V}_i$  and their values confirm the conclusions presented above. The values of excess partial molar volumes of  $[\text{C}_{41}\text{Pyrr}][\text{NTf}_2]$  are nearly the same as these observed for  $[\text{C}_{61}\text{Pyrr}][\text{NTf}_2]$ , and for  $[\text{C}_4\text{Py}][\text{NTf}_2]$  are the most negative, indicating the strongest interactions between IL and toluene in this system. Also for toluene in  $([\text{C}_4\text{Py}][\text{NTf}_2] + \text{toluene})$  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.

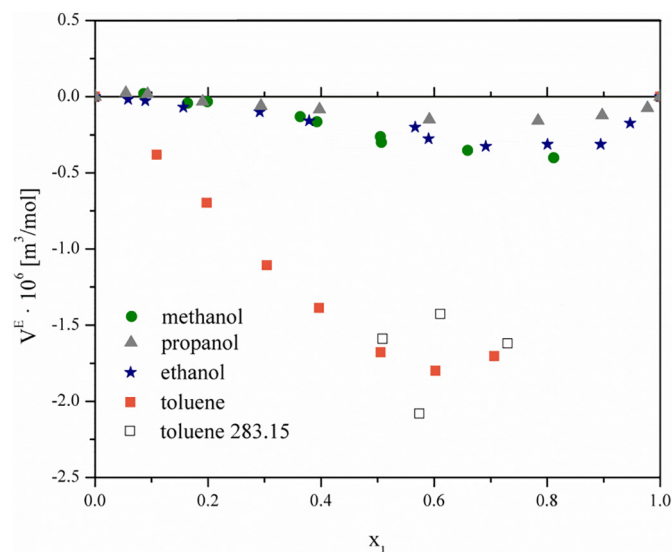
The partial molar volumes at infinite dilution of toluene were calculated by setting  $x_1 = 0$  in Eq. (9) as:

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

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:

$$V_{\Phi 1} = V_1^0 + V^E/x_1 \quad (12)$$



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

$$V_{\Phi 2} = V_2^0 + V^E/(1 - x_1) \quad (13)$$

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

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

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  $[\text{C}_4\text{Py}][\text{NTf}_2]$  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  $\Delta n_D$  is obtained in the following order:  $[\text{C}_4\text{Py}][\text{NTf}_2] > [\text{C}_{41}\text{Pyrr}][\text{NTf}_2] > [\text{C}_{61}\text{Pyrr}][\text{NTf}_2]$ . 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,  $\Delta n_D$  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

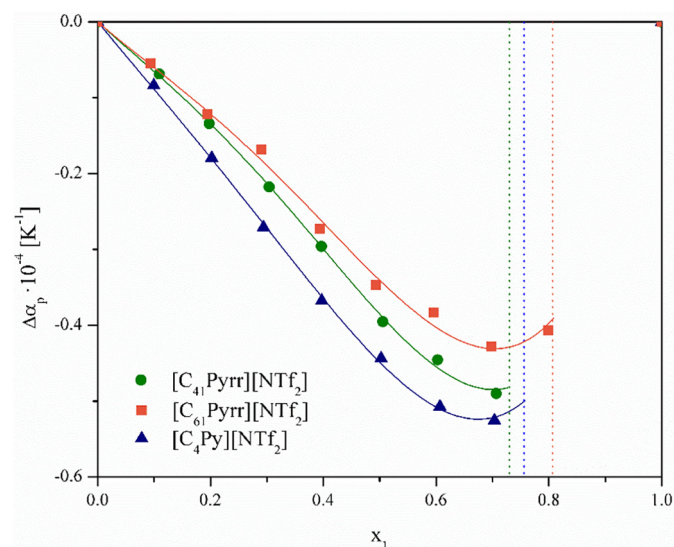


Fig. 7. Dependence of the excess thermal expansion on toluene mole fraction,  $x_1$  at 298.15 K; solid line —, Eq. (5).

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  $\Delta n_D$  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  $[C_4Py][NTf_2]$  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  $([C_4Py][NTf_2] + \text{toluene})$  and  $\Delta\eta$  for  $([C_{41}Pyrr][NTf_2] + \text{toluene})$  were higher than those found for  $([C_{61}Pyrr][NTf_2] + \text{toluene})$  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.

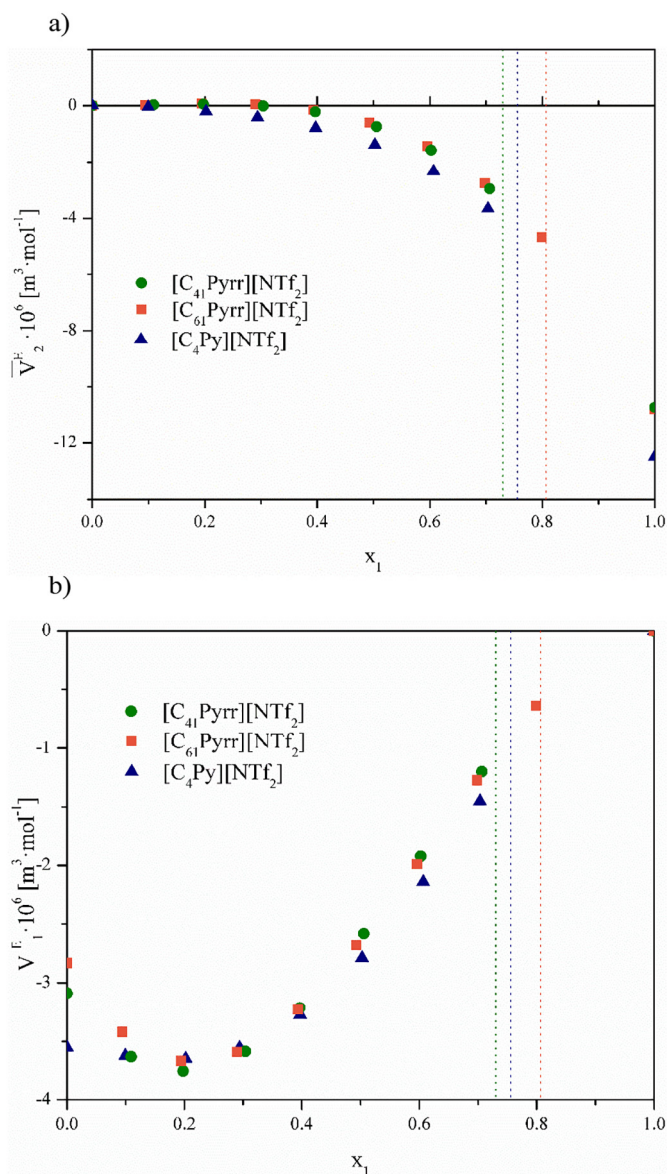


Fig. 8. Excess partial molar volumes of a)  $[C_4Py][NTf_2]$ ,  $[C_{41}Pyrr][NTf_2]$ ,  $[C_{61}Pyrr][NTf_2]$  and b) toluene at 298.15 K in their binary systems.

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  $\Delta G^E$  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  $T = 293.15\text{--}313.15$  K and at atmospheric pressure (0.1 MPa).

| T/K    | Toluene + [C <sub>41</sub> Pyrr][NTf <sub>2</sub> ]     |  | Toluene + [C <sub>61</sub> Pyrr][NTf <sub>2</sub> ]     |  | Toluene + [C <sub>4</sub> Py][NTf <sub>2</sub> ]        |  |
|--------|---|--|---|--|---|--|
|        | $\bar{V}^\infty/10^6 \text{ m}^3 \cdot \text{mol}^{-1}$ | $(V_\Phi^\infty)/10^6 \text{ m}^3 \cdot \text{mol}^{-1}$ | $\bar{V}^\infty/10^6 \text{ m}^3 \cdot \text{mol}^{-1}$ | $(V_\Phi^\infty)/10^6 \text{ m}^3 \cdot \text{mol}^{-1}$ | $\bar{V}^\infty/10^6 \text{ m}^3 \cdot \text{mol}^{-1}$ | $(V_\Phi^\infty)/10^6 \text{ m}^3 \cdot \text{mol}^{-1}$ |
| 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

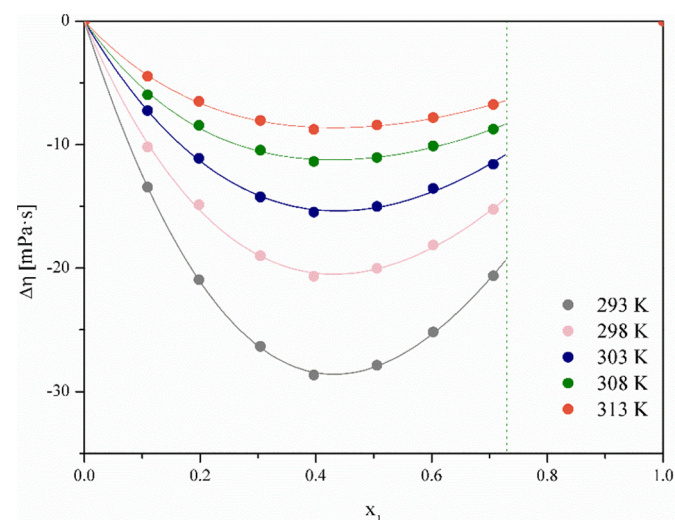
Novel experimental data on the densities, dynamic viscosities and refractive indices of the pure ionic liquid [C<sub>61</sub>Pyrr][NTf<sub>2</sub>] and its binary mixtures with toluene over the miscible region at  $T$  of 293.15–323.15 K, together with the respective data for the systems of toluene with [C<sub>41</sub>Pyrr][NTf<sub>2</sub>] and [C<sub>4</sub>Py][NTf<sub>2</sub>], 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  $\pi$ - $\pi$  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<sub>4</sub>Py][NTf<sub>2</sub>].

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<sub>4</sub>Py][NTf<sub>2</sub>] 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<sub>41</sub>Pyrr][NTf<sub>2</sub>] + 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<sub>4</sub>Py][NTf<sub>2</sub>] > [C<sub>41</sub>Pyrr][NTf<sub>2</sub>] > [C<sub>61</sub>Pyrr][NTf<sub>2</sub>] 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>.

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