



# Excess molar volumes and viscosity behaviour of binary mixtures of aniline/or *N,N*-dimethylaniline with imidazolium ionic liquids having triflate or bistriflamide anion



Danijela Soldatović<sup>a</sup>, Jelena Vuksanović<sup>b</sup>, Ivona Radović<sup>b</sup>, Zoran Višak<sup>c,\*</sup>, Mirjana Kijevčanin<sup>b,\*</sup>

<sup>a</sup> Public Company Nuclear Facilities of Serbia, 12-14 Mike Petrovića Alasa, Vinča, 11351 Belgrade, Serbia

<sup>b</sup> Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

<sup>c</sup> School of Engineering and Applied Sciences, Aston University, Birmingham B4 7ET, United Kingdom

## ARTICLE INFO

### Article history:

Received 12 July 2016

Received in revised form 7 February 2017

Accepted 8 February 2017

Available online 14 February 2017

### Keywords:

Density

Viscosity

Excess molar Gibbs free energy

Aniline

*N,N*-dimethylaniline

Ionic liquids

## ABSTRACT

In this study, densities and viscosities of four binary systems {aniline/*N,N*-dimethylaniline + 1-butyl-3-methylimidazolium triflate ([bmim][OTf])} and {aniline/*N,N*-dimethylaniline + 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][NTf<sub>2</sub>])} were measured at atmospheric pressure and within the temperature range  $T = (288.15 \text{ to } 333.15) \text{ K}$ . Excess molar volumes  $V^E$ , viscosity deviations  $\Delta\eta$  and excess molar Gibbs energies of activation of viscous flow  $\Delta G^{*E}$  were calculated and the results were fitted to a Redlich-Kister polynomial equation. Also, enthalpic and entropic parts of the  $\Delta G^{*E}$  function were determined, at the same composition, for three studied systems that exhibit complete miscibility, since {aniline + [bmim][OTf]} is a partially miscible system. Considering the calculated thermodynamic properties, molecular interactions in the investigated binary systems were analysed and are discussed.

© 2017 Elsevier Ltd.

## 1. Introduction

One of the most exact definitions of ionic liquids [1] defines them as ionic compounds (salts) that have glass transition or normal melting points below 100 °C. They possess two main characteristics that qualify them as promising alternatives to classical (toxic) solvents: (i) negligible vapour pressures in a wide temperature range [2,3] thus providing low atmospheric pollution and (ii) diverse solvent power – they dissolve well a number of both polar and non-polar solutes, as it was reported [4] and reviewed in literature [5,6]. Therefore, ionic liquids found their applications as separation/extraction solvents for diverse solutes: for amino acids separation and purification [7–9], carbohydrate separation [10], for extraction of proteins [11], phenols [12], azo dyes [13], or for removal of free fatty acids [14].

On the other hand, ionic liquids reveal very interesting fundamental features: (i) they have specific structure represented by polar (ionic) and non-polar (aliphatic) domains [4], which is crucial for the aforementioned diverse solvent power and (ii) they allow a variety of interactions in their mixtures: dispersion forces between

aliphatic chains present in the mixtures of imidazolium ionic liquids with alcohols [15]; strong interactions such as ionic (Coulomb forces [16] and ion-dipole interactions [17]), hydrogen bonds [15,18–20], and specific interactions with the aromatic compounds [21–23].

Thus, following the aforementioned attractiveness and importance of ionic liquids and their mixtures, we have carried out studies that include phase behaviour of ionic liquid mixtures [24–26] or their thermophysical properties [27]. In this work, as a continuation of these efforts, densities and viscosities have been measured for four binary mixtures of important toxic solvents aniline or *N,N*-dimethylaniline with two imidazolium ionic liquids based on triflate ([OTf]<sup>−</sup>) or bistriflamide ([NTf<sub>2</sub>]<sup>−</sup>) anion: {aniline/*N,N*-dimethylaniline+1-butyl-3-methylimidazolium triflate([bmim][OTf])} and {aniline/*N,N*-dimethylaniline + 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][NTf<sub>2</sub>])}. The measurements were carried out at ten temperatures ranging from 288.15 K to 333.15 K with a step of 5 K and at atmospheric pressure. From these experimental results, excess molar volumes  $V^E$ , deviations in viscosity  $\Delta\eta$  and excess molar Gibbs energies of activation of viscous flow  $\Delta G^{*E}$  were calculated and correlated by the Redlich-Kister equation [28]. Considering these calculated properties, the molecular interactions existing between the aniline and *N,N*-dimethylaniline with ILs were analysed and are discussed.

\* Corresponding authors.

E-mail addresses: [z.visak@aston.ac.uk](mailto:z.visak@aston.ac.uk) (Z. Višak), [mirjana@tmf.bg.ac.rs](mailto:mirjana@tmf.bg.ac.rs) (M. Kijevčanin).

## 2. Experimental

### 2.1. Chemicals

The list of studied chemicals, their suppliers and stated purities is presented in Table 1. All the chemicals were kept in dark bottles in an inert atmosphere and degassed by an ultrasonic bath before sample preparation. Ionic liquids were already purified of volatile solvents and dried using the usual vacuuming procedure applied in our earlier studies [24–27]. In order to check the purity of the pure components, their experimental values of densities  $\rho$  and viscosities  $\eta$  were compared with the respective literature values at several temperatures (Table 2). A more thorough comparison of the experimental values for density and viscosity with the available literature is given graphically in Figs. 1 and 2. From this detailed analysis the average relative deviations ARD ( $ARD = 100 \cdot (Y_{\text{exp}} - Y_{\text{cal}})/(n \cdot Y_{\text{exp}})$ , where  $n$  is the total number of literature data points for each property  $Y$  and each compound), were calculated. The highest ARD in density is 0.1% and in viscosity 3.22%. Thus, the agreement with literature is rather good for both studied properties and no further purification was applied.

### 2.2. Apparatus and procedures

Experimental measurements of density  $\rho$  were performed by an Anton Paar DMA 5000 digital vibrating U-tube densimeter. Viscosities  $\eta$  of the pure substances and the corresponding binary mixtures were measured using a digital Stabinger viscometer (model SVM 3000/G2). Detailed description of both apparatus can be found in our previous work [37].

All the mixtures were prepared gravimetrically using a Mettler AG 204 balance with a precision  $1 \times 10^{-7}$  kg. The uncertainty of the mole fraction calculation was less than  $\pm 1 \times 10^{-4}$ . Densities and viscosities were measured with the repeatability of  $\pm 1 \times 10^{-2}$  -

kg·m<sup>-3</sup> and  $\pm 3 \times 10^{-3}$  mPa·s, respectively. However, average standard uncertainty of the measured densities was estimated to be  $1 \text{ kg}\cdot\text{m}^{-3}$  taking into account the stated purity of chemicals as suggested in literature [38]. For the viscosity measurements of the pure components average standard uncertainty was  $3 \times 10^{-3}$  - mPa·s for less viscous fluids and 1.2 mPa·s for those of high viscosity, assessed using the following equation:

$$u(\eta) = \left[ \frac{1}{n(n-1)} \sum_{i=1}^n (\eta_{\text{exp},i} - \bar{\eta}_{\text{lit},i})^2 \right]^{1/2} \quad (1)$$

In the equation above  $\eta_{\text{exp},i}$  and  $\bar{\eta}_{\text{lit},i}$  are our measured viscosity for the pure compounds and the average experimental viscosity obtained from the reported experimental values in literature for a given isotherm and given compound, respectively;  $n$  is the number of experimental points (in this case actually the number of isotherms).

For the mixture measurements the average standard uncertainties calculated using Eq. (1) applied on our measurements of both density and viscosity were lower than the respective values for the pure components given above. The relative standard uncertainty 2.2% was accepted for the mixture properties.

## 3. Results

The experimental values of densities  $\rho$  and viscosities  $\eta$  and the calculated values of the excess molar volumes  $V^E$ , viscosity deviations  $\Delta\eta$  and excess Gibbs energies of activation of viscous flow  $\Delta C^{*E}$  of four binary mixtures in temperature range  $T = (288.15 \text{ to } 333.15) \text{ K}$  and at atmospheric pressure are reported in Table 3. However, the system aniline + [bmim][OTf] was already investigated in literature [80,81] revealing partial miscibility. Consequently, following the liquid-liquid miscibility data from reference [80] all the measurements for this system were performed

**Table 1**  
Sample description.

Component full name	Abbreviation used in the text	Source	Initial mass fraction purity
Aniline		Sigma-Aldrich	$\geq 0.995$
<i>N,N</i> -dimethylaniline		Merck	$\geq 0.99$
1-Butyl-3-methylimidazolium triflate	[bmim][OTf]	IOLITEC	0.99
1-Butyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide	[bmim][NTf <sub>2</sub> ]	IOLITEC	0.99

**Table 2**  
Densities  $\rho$  and viscosities  $\eta$  of the pure components at temperature  $T$  and at atmospheric pressure (0.1 MPa).<sup>a</sup>

Component	$T/\text{K}$	$10^{-3} \rho/\text{kg}\cdot\text{m}^{-3}$		$\eta/\text{mPa}\cdot\text{s}$	
		exp.	lit.	exp.	lit.
Aniline	293.15	1.0217	1.021747 <sup>b</sup>	4.407	4.404 <sup>c</sup>
	298.15	1.0174	1.017404 <sup>b</sup>	3.737	3.773 <sup>d</sup>
	303.15	1.0130	1.013152 <sup>b</sup>	3.197	3.190 <sup>e</sup>
<i>N,N</i> -dimethylaniline	293.15	0.9565	0.956033 <sup>f</sup>	1.415	1.373 <sup>f</sup>
	298.15	0.9523	0.951946 <sup>f</sup>	1.302	1.289 <sup>f</sup>
[bmim][OTf]	298.15	1.2991	1.29868 <sup>g</sup>	80.10	
[bmim][NTf <sub>2</sub> ]	293.15	1.4398	1.43927 <sup>h</sup>	61.47	62.08 <sup>h</sup>
	298.15	1.4350	1.43430 <sup>h</sup>	49.11	50.05 <sup>h</sup>
	303.15	1.4302	1.42940 <sup>h</sup>	39.95	41.24 <sup>h</sup>

<sup>a</sup> Standard uncertainties  $u$  are:  $u(T) = 0.01 \text{ K}$ ;  $u(p) = 0.005 \text{ MPa}$ ;  $u(\rho) = 1 \text{ kg}\cdot\text{m}^{-3}$ , and relative standard uncertainty  $u_r(\eta) = 2.2\%$ , with a level of confidence of 68%.

<sup>b</sup> Alonso et al. [29].

<sup>c</sup> Tsierkezos et al. [30].

<sup>d</sup> Katz et al. [31].

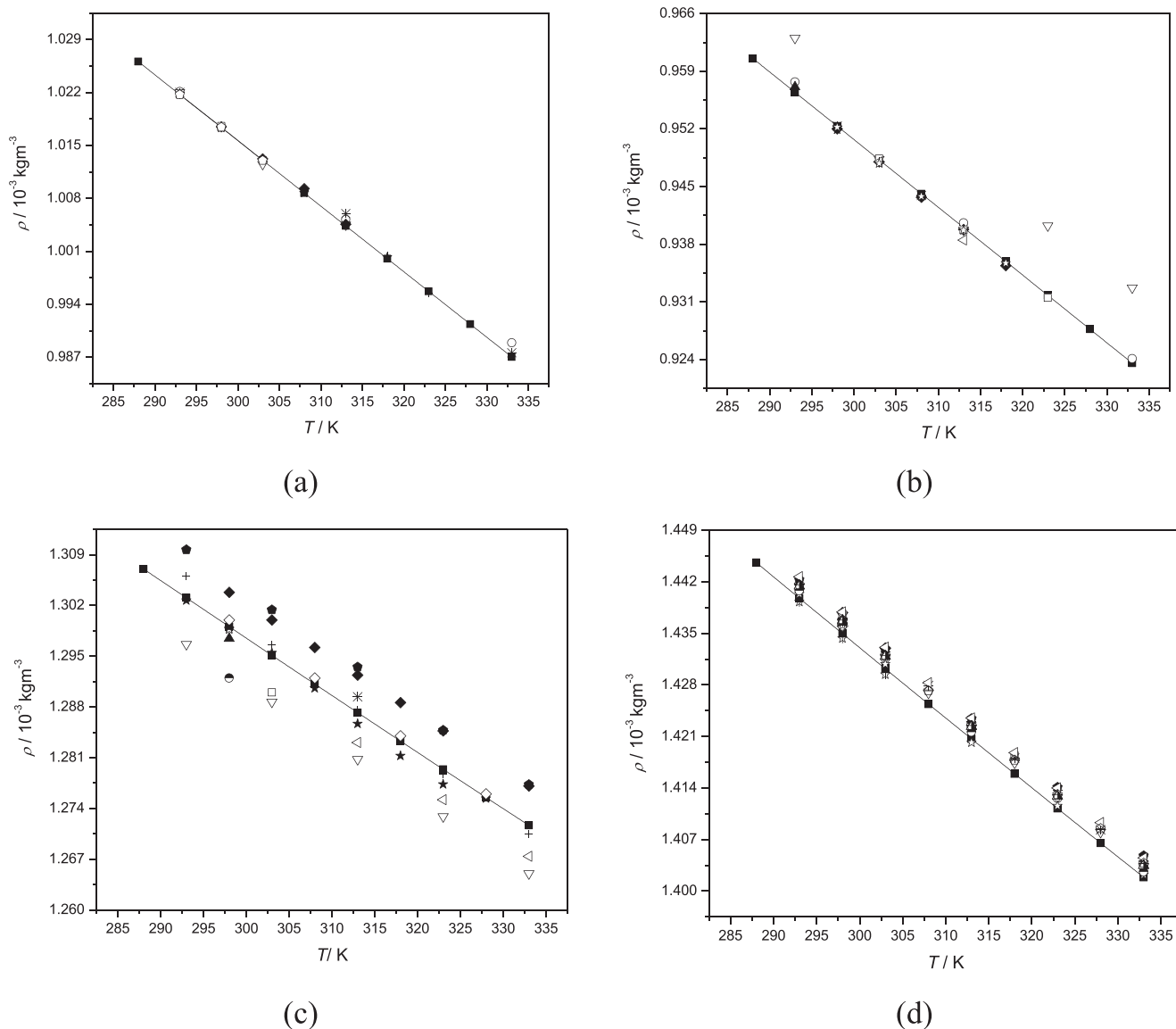
<sup>e</sup> Kharat and Nikam [32].

<sup>f</sup> Master and Malek [33].

<sup>g</sup> Arce et al. [34].

<sup>h</sup> Vraneš et al. [35].

<sup>i</sup> Dominguez et al. [36].



**Fig. 1.** Comparison of the current experimental density values (■) vs. temperature with literature values for pure: (a) aniline – (○) Vogel et al. [39]; (▽) Sumer et al. [40]; (◆) Katz et al. [41]; (□) Kumar et al. [42]; (+) Almasi et al. [43]; (✱) Costello et al. [44]; (★) MacNeil et al. [45]; (◇) Alonso et al. [29]; (b) *N,N*-dimethylaniline – (○) Costello et al. [44]; (▲) Vogel et al. [39]; (▽) Oskoei et al. [46]; (◆) Saleh et al. [47]; (□) Pandiyan et al. [48]; (+) Katz et al. [41]; (✱) Kumar et al. [42]; (★) Radwan et al. [49]; (◁) Kondaiah et al. [50]; (☆) MacNeil et al. [45]; (◇) Master and Malek [33]; (c) [bmim][OTf] – (▲) Vercher et al. [51]; (▽) Montalbán et al. [52]; (◆) Soriano et al. [53]; (□) Tokuda et al. [54]; (+) Gardas et al. [55]; (✱) Fredlake et al. [56]; (★) Klomfar et al. [57]; (✱) Shamsipur et al. [58]; (◁) Mbondo et al. [59]; (◇) Batista et al. [60]; (●) McHale et al. [61]; (★) Arce et al. [34]; (d) [bmim][NTf<sub>2</sub>] – (○) Hiraga et al. [62]; (▲) Kanakubo et al. [63]; (▽) de Castro et al. [64]; (◆) Jacquemin et al. [65]; (□) Widowati et al. [66]; (+) Currás et al. [67]; (✱) Azevedo et al. [68]; (★) Hamidova et al. [69]; (●) Tariq et al. [70]; (◁) Jacquemin et al. [71]; (☆) Montalbán et al. [52]; (◇) Zhang et al. [72]; (●) Tariq et al. [73]; (★) Seoane et al. [74]; (▲) Harris et al. [75]; (△) Atilhan et al. [76]; (⊖) Salgado et al. [77]; (★) Vraneš et al. [35].

only in the miscible region but the results were not presented graphically but only in the table. Also, for the system {*N,N*-dimethylaniline + [bmim][OTf]}, irregularity in IL rich concentration range is observed, and in order to investigate actual mixture's behaviour, additional measurements were conducted in composition region close to 0.1 *N,N*-dimethylaniline mole fraction. The additional results confirmed this density behaviour in the IL rich region. The graphical representation is given in the Fig. S1.

The excess molar volumes  $V^E$  were calculated using the experimental densities  $\rho$  of binary mixtures and the pure components  $\rho_i$  from the equation:

$$V^E = \sum_{i=1}^N x_i M_i \left[ \left( \frac{1}{\rho} \right) - \left( \frac{1}{\rho_i} \right) \right] \quad (2)$$

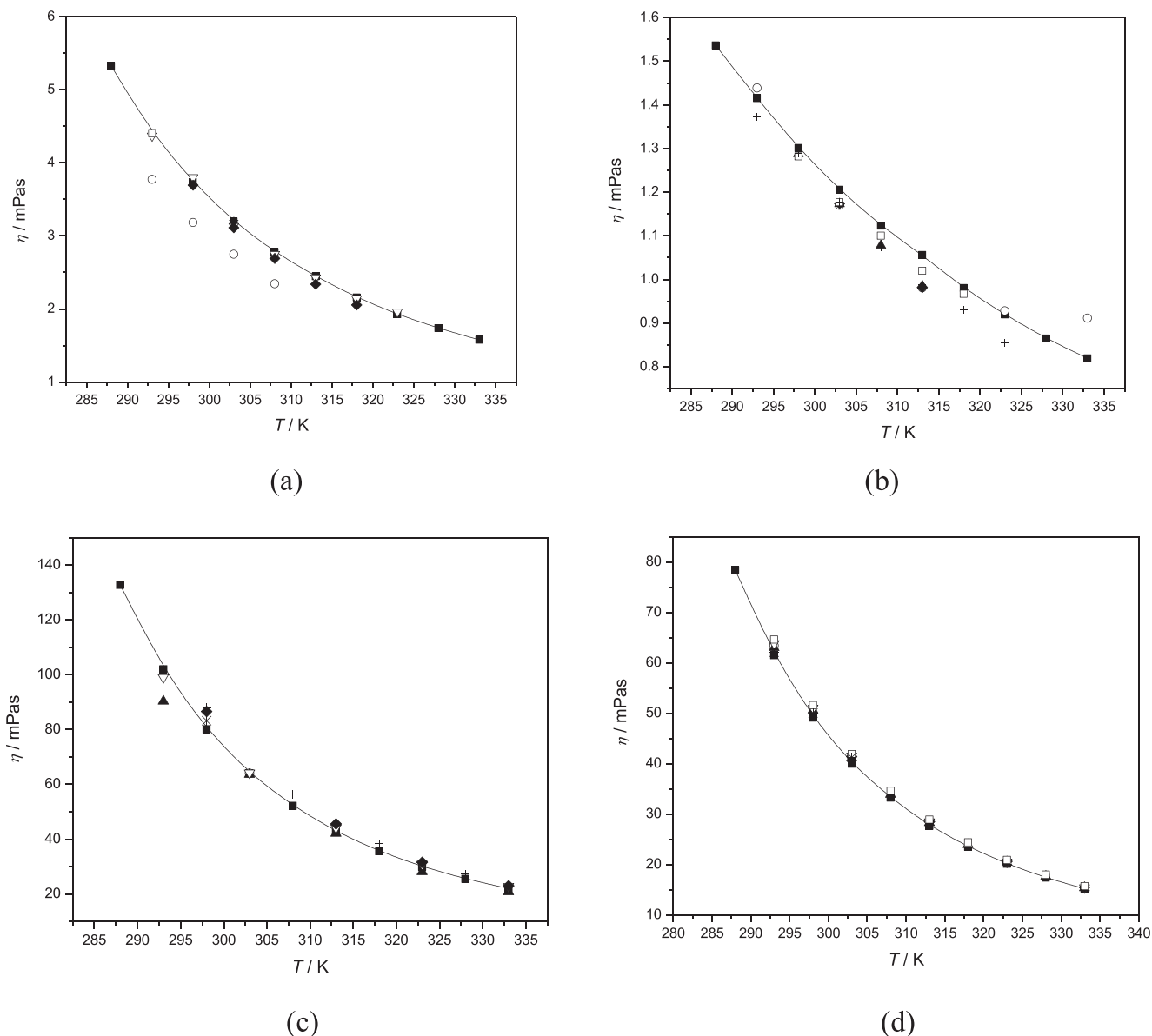
where  $N$  equals the number of components,  $x_i$  is the mole fraction of component  $i$  in mixture and  $M_i$  is the molar mass of component  $i$ .

The viscosity deviations  $\Delta\eta$  were calculated from the viscosity of the pure component  $\eta_i$  and mixture  $\eta$ , according to the equation:

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

Excess molar Gibbs energies of activation of viscous flow,  $\Delta G^{*E}$ , were calculated combining the obtained volumetric and viscosity values, following the equation:

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



**Fig. 2.** Comparison of the current experimental viscosity values (■) vs. temperature with literature values for pure: (a) aniline–(∇) Almasi et al. [43]; (◆) MacNeil et al. [45]; (□) Tsierkezos et al. [30]; (○) Katz et al. [31]; (★) Kharat and Nikam [32]; (b) *N,N*-dimethylaniline – (○) Oskoei et al. [46]; (▲) Katz et al. [41]; (◆) Kondaiah et al. [50]; (□) MacNeil et al. [45]; (+) Master and Malek [33]; (c) [bmim][OTf] – (○) Tokuda et al. [54]; (▲) Shamsipur et al. [58]; (∇) Seddon et al. [78]; (◆) Mbondo et al. [59]; (+) Batista et al. [60]; (✱) Mchale et al. [61]; (d) [bmim][NTf<sub>2</sub>] – (○) Hiraga et al. [62]; (▲) Tariq et al. [79]; (∇) Harris et al. [75]; (◆) Atilhan et al. [76]; (□) Salgado et al. [77]; (✱) Vraneš et al. [35].

In Eq. (3)  $\eta$  and  $V$  represent viscosity and molar volume of solution, respectively; the subscripts 1 and 2 indicate components of a binary mixture.

Three properties calculated by Eqs. (2)–(4) were correlated with Redlich-Kister (RK) polynomial equation [28]:

$$Y = x_1 x_2 \sum_{p=0}^k A_p (2x_1 - 1)^p \quad (5)$$

In Eq. (5)  $Y$  represents  $V^E$ ,  $\Delta\eta$  or  $\Delta G^{*E}$ ;  $A_p$  are the fitting parameters, and  $k + 1$  equals the number of parameters, which was optimized using the F-test. The fitting parameters  $A_p$  and the corresponding root-mean-square deviations (rmsd)  $\sigma$ , defined by:

$$\sigma = \left( \sum_{i=1}^m \frac{(Y_{exp}^E - Y_{cal}^E)^2}{m} \right)^{1/2} \quad (6)$$

Values are given in Table 4 for excess molar volume  $V^E$  and viscosity deviation  $\Delta\eta$ . In Eq. (6),  $m$  equals the number of experimental data points.

Excess molar volumes obtained from the experimental values and those calculated using the RK polynomial are presented in Fig. 3, as a function of amine mole fraction  $x_1$ . The systems {aniline + [C<sub>4</sub>mim][NTf<sub>2</sub>]} and {*N,N*-dimethylaniline + [C<sub>4</sub>mim][OTf]} have a S-shaped  $V^E$ -curve which changes sign from positive to negative values, while going to higher  $x_1$  mole fractions; the maximum and minimum are at  $x_1 = 0.1$  and  $x_1 = 0.6$ , respectively (Fig. 3 (a) and (b)). System {*N,N*-dimethylaniline + [bmim][NTf<sub>2</sub>]} (Fig. 3 (c)) exhibits an asymmetrical curve with negative  $V^E$  values and the minimum approximately at  $x_1 = 0.6$ . As we mentioned ahead, the system {aniline + [bmim][OTf]} was already investigated and reported in the literature revealing its partial miscibility [80,81] and, thus, its presentation is not given graphically. For all systems,

**Table 3**

Density  $\rho$ , viscosity  $\eta$ , excess molar volumes  $V^E$ , viscosity deviations  $\Delta\eta$ , excess Gibbs energy of activation of viscous flow  $\Delta G^E$  for the investigated binary systems in temperature range  $T = (288.15 \text{ to } 333.15) \text{ K}$  and at atmospheric pressure (0.1 MPa).<sup>a</sup>

$x_1$	$10^{-3} \cdot \rho / \text{kg} \cdot \text{m}^{-3}$	$10^6 \cdot V^E / \text{m}^3 \cdot \text{mol}^{-1}$	$\eta / \text{mPa} \cdot \text{s}$	$\Delta\eta / \text{mPa} \cdot \text{s}$	$\Delta G^E / \text{kJ} \cdot \text{kmol}^{-1}$
<i>Aniline (1) + [bmim][OTf] (2)</i>					
<i>T = 288.15 K</i>					
0.0000	1.3070		132.7		
0.1000	1.2952	−0.0695	110.3	−9.692	393.44
0.1995	1.2832	−0.3519	90.93	−16.38	751.88
0.8999	1.0924	−0.6254	8.953	−9.124	567.14
1.0000	1.0261		5.324		
<i>T = 293.15 K</i>					
0.0000	1.3031		102.0		
0.1000	1.2912	−0.0729	85.32	−6.913	398.31
0.1995	1.2792	−0.3643	70.62	−11.91	754.11
0.3002	1.2652	−0.6388	57.65	−15.05	1075.14
0.8999	1.0883	−0.6506	7.312	−6.863	561.48
1.0000	1.0217		4.407		
<i>T = 298.15 K</i>					
0.0000	1.2991		80.10		
0.1000	1.2872	−0.0784	67.55	−4.908	406.05
0.1995	1.2753	−0.3793	56.11	−8.757	757.36
0.3002	1.2613	−0.6612	45.90	−11.28	1069.45
0.8999	1.0842	−0.6769	6.184	−5.198	582.19
1.0000	1.0174		3.737		
<i>T = 303.15 K</i>					
0.0000	1.2951		64.02		
0.1000	1.2832	−0.0827	54.55	−3.392	421.15
0.1995	1.2713	−0.3958	45.50	−6.388	771.87
0.3002	1.2574	−0.6867	37.27	−8.492	1075.15
0.8999	1.0801	−0.7045	5.256	−4.030	592.05
1.0000	1.0130		3.197		
<i>T = 308.15 K</i>					
0.0000	1.2911		52.18		
0.1000	1.2793	−0.0898	44.41	−2.826	408.75
0.1995	1.2674	−0.4116	37.16	−5.161	756.53
0.3002	1.2534	−0.7101	30.61	−6.736	1062.33
0.8999	1.0760	−0.7317	4.538	−3.186	599.76
1.0000	1.0087		2.780		
<i>T = 313.15 K</i>					
0.0000	1.2872		42.76		
0.1000	1.2754	−0.0963	36.56	−2.161	408.89
0.1995	1.2635	−0.4274	30.70	−4.011	752.86
0.3002	1.2495	−0.7333	25.37	−5.283	1052.96
0.8999	1.0720	−0.7592	3.929	−2.551	585.84
1.0000	1.0044		2.445		
<i>T = 318.15 K</i>					
0.0000	1.2833		35.66		
0.1000	1.2714	−0.1019	30.60	−1.712	408.94
0.1995	1.2596	−0.4437	25.83	−3.150	756.81
0.3002	1.2456	−0.7584	21.47	−4.132	1062.30
0.3996	1.2292	−0.9972	17.67	−4.603	1317.61
0.8999	1.0679	−0.7876	3.503	−2.009	634.99
1.0000	1.0000		2.159		
<i>T = 323.15 K</i>					
0.0000	1.2794		30.01		
0.1000	1.2675	−0.1076	25.85	−1.349	409.98
0.1995	1.2557	−0.4598	21.90	−2.501	757.61
0.3002	1.2418	−0.7831	18.28	−3.292	1062.50
0.3996	1.2253	−1.0271	15.11	−3.671	1317.76
0.8999	1.0638	−0.8162	3.117	−1.621	650.57
1.0000	0.9957		1.927		
<i>T = 328.15 K</i>					
0.0000	1.2755		25.50		
0.1000	1.2637	−0.1132	22.17	−0.9564	424.50
0.1995	1.2518	−0.4763	18.82	−1.941	766.08
0.3002	1.2379	−0.8086	15.71	−2.655	1059.57
0.3996	1.2214	−1.0583	13.02	−2.987	1308.66
0.8999	1.0597	−0.8455	2.755	−1.361	621.56
1.0000	0.9914		1.738		
<i>T = 333.15 K</i>					
0.0000	1.2717		22.00		
0.1000	1.2598	−0.1177	19.07	−0.8863	409.04
0.1995	1.2480	−0.4918	16.23	−1.699	747.98
0.3002	1.2340	−0.8335	13.63	−2.241	1048.13

(continued on next page)

Table 3 (continued)

$x_1$	$10^{-3} \cdot \rho / \text{kg} \cdot \text{m}^{-3}$	$10^6 \cdot V^E / \text{m}^3 \cdot \text{mol}^{-1}$	$\eta / \text{mPa} \cdot \text{s}$	$\Delta \eta / \text{mPa} \cdot \text{s}$	$\Delta G^E / \text{kJ} \cdot \text{kmol}^{-1}$
0.3996	1.2176	-1.0890	11.38	-2.457	1309.04
0.8999	1.0556	-0.8753	2.474	-1.147	615.70
1.0000	0.9870		1.577		
<i>Aniline (1) + [bmim][NTf<sub>2</sub>] (2)</i>					
<i>T = 288.15 K</i>					
0.0000	1.4446		78.37		
0.1000	1.4293	0.2327	66.29	-4.768	353.45
0.2000	1.4143	-0.0060	55.87	-7.884	680.78
0.3029	1.3968	-0.3754	46.48	-9.759	980.72
0.4013	1.3764	-0.6623	38.49	-10.56	1219.23
0.5024	1.3500	-0.8208	31.09	-10.58	1396.12
0.6002	1.3175	-0.8504	24.56	-9.966	1472.62
0.7000	1.2746	-0.7753	18.38	-8.861	1400.77
0.8002	1.2182	-0.6754	13.46	-6.460	1237.97
0.9000	1.1404	-0.4470	8.743	-3.885	731.97
1.0000	1.0261		5.324		
<i>T = 293.15 K</i>					
0.0000	1.4398		61.47		
0.1000	1.4244	0.2457	52.16	-3.606	353.78
0.2000	1.4095	-0.0022	44.10	-5.958	681.18
0.3029	1.3921	-0.3853	36.82	-7.363	981.50
0.4013	1.3717	-0.6817	30.60	-7.969	1219.77
0.5024	1.3454	-0.8445	24.83	-7.975	1397.00
0.6002	1.3129	-0.8757	19.71	-7.507	1474.42
0.7000	1.2701	-0.8015	14.86	-6.665	1406.48
0.8002	1.2138	-0.7045	10.93	-4.876	1238.59
0.9000	1.1361	-0.4698	7.190	-2.923	741.05
1.0000	1.0217		4.407		
<i>T = 298.15 K</i>					
0.0000	1.4350		49.11		
0.1000	1.4196	0.2569	42.13	-2.442	372.25
0.2000	1.4046	-0.0001	35.90	-4.135	709.47
0.3029	1.3873	-0.3964	30.13	-5.238	1011.95
0.4013	1.3670	-0.7018	25.12	-5.778	1247.89
0.5024	1.3407	-0.8689	20.42	-5.888	1418.46
0.6002	1.3083	-0.9021	16.28	-5.595	1492.17
0.7000	1.2655	-0.8279	12.40	-4.952	1433.03
0.8002	1.2094	-0.7348	9.223	-3.579	1275.35
0.9000	1.1317	-0.4922	6.100	-2.174	768.69
1.0000	1.0174		3.737		
<i>T = 303.15 K</i>					
0.0000	1.4302		39.95		
0.1000	1.4147	0.2785	34.28	-2.003	365.85
0.2000	1.3998	0.0091	29.28	-3.321	702.36
0.3029	1.3826	-0.4079	24.70	-4.120	1009.52
0.4013	1.3624	-0.7244	20.73	-4.477	1252.56
0.5024	1.3361	-0.8964	16.98	-4.507	1432.22
0.6002	1.3037	-0.9302	13.64	-4.251	1514.42
0.7000	1.2610	-0.8566	10.47	-3.755	1461.53
0.8002	1.2050	-0.7662	7.802	-2.739	1292.65
0.9000	1.1274	-0.5160	5.198	-1.674	783.71
1.0000	1.0130		3.197		
<i>T = 308.15 K</i>					
0.0000	1.4254		33.22		
0.1000	1.4098	0.2954	28.63	-1.550	371.84
0.2000	1.3950	0.0155	24.55	-2.585	711.92
0.3029	1.3779	-0.4187	20.77	-3.228	1020.12
0.4013	1.3577	-0.7475	17.48	-3.523	1263.38
0.5024	1.3315	-0.9247	14.38	-3.548	1444.49
0.6002	1.2991	-0.9584	11.58	-3.373	1522.34
0.7000	1.2565	-0.8848	8.919	-2.995	1466.59
0.8002	1.2006	-0.7975	6.706	-2.156	1306.44
0.9000	1.1230	-0.5395	4.497	-1.327	794.50
1.0000	1.0087		2.780		
<i>T = 313.15 K</i>					
0.0000	1.4206		27.68		
0.1000	1.4050	0.3127	23.94	-1.219	373.01
0.2000	1.3902	0.0202	20.59	-2.040	712.75
0.3029	1.3732	-0.4310	17.48	-2.555	1019.24
0.4013	1.3531	-0.7709	14.76	-2.797	1260.15
0.5024	1.3269	-0.9509	12.17	-2.828	1437.47
0.6002	1.2946	-0.9877	9.843	-2.691	1513.80
0.7000	1.2520	-0.9141	7.607	-2.408	1451.60
0.8002	1.1962	-0.8302	5.770	-1.717	1297.15
0.9000	1.1187	-0.5634	3.898	-1.071	782.06
1.0000	1.0044		2.445		

Table 3 (continued)

$x_1$	$10^{-3} \cdot \rho / \text{kg} \cdot \text{m}^{-3}$	$10^6 \cdot V^E / \text{m}^3 \cdot \text{mol}^{-1}$	$\eta / \text{mPa} \cdot \text{s}$	$\Delta \eta / \text{mPa} \cdot \text{s}$	$\Delta G^E / \text{kJ} \cdot \text{kmol}^{-1}$
$T = 318.15 \text{ K}$					
0.0000	1.4159		23.53		
0.1000	1.4002	0.3248	20.44	-0.9529	380.88
0.2000	1.3855	0.0211	17.66	-1.597	726.79
0.3029	1.3685	-0.4456	15.05	-2.006	1038.46
0.4013	1.3485	-0.7963	12.76	-2.198	1283.48
0.5024	1.3224	-0.9808	10.57	-2.222	1465.42
0.6002	1.2901	-1.0181	8.586	-2.119	1544.55
0.7000	1.2476	-0.9450	6.677	-1.895	1487.62
0.8002	1.1918	-0.8632	5.093	-1.337	1335.76
0.9000	1.1144	-0.5884	3.461	-0.8350	818.79
1.0000	1.0000		2.159		
$T = 323.15 \text{ K}$					
0.0000	1.4112		20.13		
0.1000	1.3955	0.3304	17.56	-0.7507	386.43
0.2000	1.3808	0.0166	15.22	-1.269	735.11
0.3029	1.3639	-0.4628	13.02	-1.603	1047.91
0.4013	1.3439	-0.8215	11.06	-1.767	1292.66
0.5024	1.3178	-1.0099	9.193	-1.794	1473.32
0.6002	1.2856	-1.0488	7.501	-1.706	1555.32
0.7000	1.2431	-0.9756	5.864	-1.525	1500.38
0.8002	1.1874	-0.8968	4.498	-1.067	1349.49
0.9000	1.1101	-0.6132	3.076	-0.6716	830.25
1.0000	0.9957		1.927		
$T = 328.15 \text{ K}$					
0.0000	1.4065		17.39		
0.1000	1.3908	0.3305	15.22	-0.6004	390.34
0.2000	1.3762	0.0068	13.24	-1.019	741.28
0.3029	1.3593	-0.4822	11.36	-1.293	1055.20
0.4013	1.3394	-0.8475	9.679	-1.429	1300.26
0.5024	1.3133	-1.0386	8.076	-1.450	1482.30
0.6002	1.2811	-1.0804	6.609	-1.386	1561.81
0.7000	1.2387	-1.0071	5.194	-1.239	1508.61
0.8002	1.1831	-0.9312	4.002	-0.8625	1356.08
0.9000	1.1058	-0.6387	2.755	-0.5483	834.57
1.0000	0.9914		1.738		
$T = 333.15 \text{ K}$					
0.0000	1.4019		15.20		
0.1000	1.3862	0.3190	13.34	-0.5013	391.78
0.2000	1.3716	-0.0108	11.63	-0.8460	745.13
0.3029	1.3547	-0.5024	10.01	-1.069	1061.55
0.4013	1.3348	-0.8710	8.557	-1.178	1308.80
0.5024	1.3088	-1.0648	7.159	-1.198	1490.69
0.6002	1.2766	-1.1123	5.882	-1.143	1572.32
0.7000	1.2342	-1.0390	4.639	-1.025	1517.94
0.8002	1.1787	-0.9659	3.587	-0.7118	1362.52
0.9000	1.1015	-0.6645	2.477	-0.4625	831.75
1.0000	0.9870		1.577		
<i>N,N</i> -dimethylaniline (1) + [bmim][OTf] (2)					
$T = 288.15 \text{ K}$					
0.0000	1.3070		132.7		
0.1000	1.2788	1.2347	97.56	-22.05	373.97
0.2000	1.2598	0.5850	72.76	-33.73	756.89
0.2998	1.2408	-0.3372	54.03	-39.37	1118.06
0.3970	1.2183	-0.9589	39.34	-41.30	1401.05
0.5045	1.1880	-1.2908	26.08	-40.47	1566.28
0.5996	1.1565	-1.3910	16.87	-37.20	1535.61
0.6997	1.1185	-1.3677	10.05	-30.89	1354.71
0.7994	1.0744	-1.1586	6.003	-21.85	1170.53
0.8945	1.0248	-0.6999	3.271	-12.11	1189.36
1.0000	0.9606		1.536		
$T = 293.15 \text{ K}$					
0.0000	1.3031		102.0		
0.1000	1.2747	1.2430	75.74	-16.20	371.40
0.2000	1.2558	0.5846	57.09	-24.79	752.93
0.2998	1.2368	-0.3480	42.84	-29.00	1111.74
0.3970	1.2143	-0.9772	31.52	-30.54	1392.45
0.5045	1.1839	-1.3122	21.17	-30.09	1555.54
0.5996	1.1525	-1.4119	13.93	-27.75	1535.08
0.6997	1.1144	-1.3862	8.502	-23.12	1375.87
0.7994	1.0703	-1.1738	5.207	-16.38	1215.10
0.8945	1.0207	-0.7095	2.905	-9.121	1251.75
1.0000	0.9565		1.415		

(continued on next page)

Table 3 (continued)

$x_1$	$10^{-3} \cdot \rho / \text{kg} \cdot \text{m}^{-3}$	$10^6 \cdot V^E / \text{m}^3 \cdot \text{mol}^{-1}$	$\eta / \text{mPa} \cdot \text{s}$	$\Delta \eta / \text{mPa} \cdot \text{s}$	$\Delta G^E / \text{kJ} \cdot \text{kmol}^{-1}$
$T = 298.15 \text{ K}$					
0.0000	1.2991		80.10		
0.1000	1.2706	1.2677	59.89	-12.33	345.14
0.2000	1.2518	0.5928	45.66	-18.68	711.40
0.2998	1.2327	-0.3594	34.75	-21.73	1061.57
0.3970	1.2102	-0.9981	25.94	-22.88	1334.03
0.5045	1.1799	-1.3351	17.76	-22.58	1494.97
0.5996	1.1484	-1.4346	11.92	-20.93	1475.33
0.6997	1.1104	-1.4084	7.419	-17.55	1312.15
0.7994	1.0662	-1.1919	4.615	-12.49	1137.95
0.8945	1.0166	-0.7197	2.627	-6.988	1158.39
1.0000	0.9523		1.302		
$T = 303.15 \text{ K}$					
0.0000	1.2951		64.02		
0.0200	1.2879				
0.0501	1.2811				
0.1000	1.2666	1.2844	48.11	-9.634	326.30
0.1402	1.2598				
0.1800	1.2535				
0.2000	1.2477	0.5943	37.00	-14.46	683.13
0.2998	1.2287	-0.3742	28.44	-16.76	1026.62
0.3970	1.2063	-1.0214	21.69	-17.40	1321.35
0.5045	1.1759	-1.3608	14.77	-17.56	1431.55
0.5996	1.1444	-1.4596	10.23	-16.13	1455.06
0.6997	1.1063	-1.4316	6.471	-13.60	1293.11
0.7994	1.0621	-1.2110	4.102	-9.705	1126.87
0.8945	1.0124	-0.7307	2.374	-5.459	1140.52
1.0000	0.9482		1.206		
$T = 308.15 \text{ K}$					
0.0000	1.2911		52.18		
0.1000	1.2625	1.3041	39.48	-7.590	315.46
0.2000	1.2437	0.5973	30.69	-11.28	670.96
0.2998	1.2248	-0.3901	23.90	-12.97	1019.38
0.3970	1.2023	-1.0467	18.27	-13.64	1291.65
0.5045	1.1719	-1.3884	12.85	-13.57	1449.64
0.5996	1.1403	-1.4864	8.866	-12.70	1430.13
0.6997	1.1022	-1.4566	5.713	-10.74	1279.27
0.7994	1.0580	-1.2315	3.681	-7.684	1117.75
0.8945	1.0083	-0.7427	2.164	-4.346	1122.56
1.0000	0.9441		1.123		
$T = 313.15 \text{ K}$					
0.0000	1.2872		42.76		
0.1000	1.2585	1.3186	32.19	-6.397	271.51
0.2000	1.2397	1.3186	25.20	-9.214	615.60
0.2998	1.2208	-0.4045	19.91	-10.35	970.94
0.3970	1.1983	-1.0714	15.46	-10.74	1253.86
0.5045	1.1679	-1.4158	11.04	-10.68	1414.87
0.5996	1.1363	-1.5144	7.692	-10.06	1386.59
0.6997	1.0982	-1.4823	5.032	-8.547	1236.61
0.7994	1.0539	-1.2518	3.302	-6.119	1084.92
0.8945	1.0042	-0.7543	1.988	-3.467	1100.63
1.0000	0.9400		1.056		
$T = 318.15 \text{ K}$					
0.0000	1.2833		35.66		
0.1000	1.2545	1.3396	27.14	-5.056	276.02
0.2000	1.2357	0.6011	21.46	-7.271	622.74
0.2998	1.2169	-0.4217	17.10	-8.166	978.24
0.3970	1.1944	-1.0988	13.40	-8.499	1260.67
0.5045	1.1639	-1.4459	9.681	-8.485	1425.37
0.5996	1.1323	-1.5435	6.840	-8.028	1407.21
0.6997	1.0942	-1.5097	4.540	-6.856	1264.87
0.7994	1.0499	-1.2746	3.011	-4.927	1110.59
0.8945	1.0001	-0.7674	1.828	-2.812	1096.77
1.0000	0.9359		0.9805		
$T = 323.15 \text{ K}$					
0.0000	1.2794		30.01		
0.1000	1.2504	1.3681	22.96	-4.136	266.25
0.2000	1.2318	0.6070	18.30	-5.888	610.47
0.2998	1.2129	-0.4390	14.72	-6.569	966.23
0.3970	1.1905	-1.1270	11.63	-6.825	1248.76
0.5045	1.1600	-1.4765	8.500	-6.832	1413.99
0.5996	1.1283	-1.5732	6.076	-6.490	1399.12
0.6997	1.0901	-1.5382	4.088	-5.566	1261.94
0.7994	1.0458	-1.2983	2.747	-4.008	1110.92
0.8945	0.9960	-0.7797	1.692	-2.296	1091.35
1.0000	0.9318		0.9197		



Table 3 (continued)

$x_1$	$10^{-3} \cdot \rho / \text{kg} \cdot \text{m}^{-3}$	$10^6 \cdot V^E / \text{m}^3 \cdot \text{mol}^{-1}$	$\eta / \text{mPa} \cdot \text{s}$	$\Delta \eta / \text{mPa} \cdot \text{s}$	$\Delta G^E / \text{kJ} \cdot \text{kmol}^{-1}$
$T = 328.15 \text{ K}$					
0.0000	1.2755		25.50		
0.1000	1.2464	1.3908	19.60	-3.433	255.31
0.2000	1.2278	0.6106	15.74	-4.831	597.38
0.2998	1.2090	-0.4568	12.77	-5.343	954.65
0.3970	1.1866	-1.1558	10.19	-5.533	1238.96
0.5045	1.1560	-1.5089	7.522	-5.548	1406.02
0.5996	1.1244	-1.6056	5.435	-5.292	1394.28
0.6997	1.0861	-1.5686	3.702	-4.560	1260.48
0.7994	1.0418	-1.3227	2.517	-3.289	1112.62
0.8945	0.9919	-0.7926	1.569	-1.895	1080.34
1.0000	0.9277		0.8649		
$T = 333.15 \text{ K}$					
0.0000	1.2717		22.00		
0.1000	1.2424	1.4204	16.91	-2.977	232.33
0.2000	1.2238	0.6169	13.64	-4.123	566.87
0.2998	1.2051	-0.4754	11.16	-4.494	925.85
0.3970	1.1827	-1.1864	8.982	-4.610	1214.73
0.5045	1.1521	-1.5420	6.706	-4.609	1386.63
0.5996	1.1204	-1.6379	4.896	-4.405	1378.65
0.6997	1.0821	-1.5993	3.365	-3.815	1242.59
0.7994	1.0377	-1.3481	2.311	-2.757	1094.46
0.8945	0.9878	-0.8064	1.463	-1.591	1046.80
1.0000	0.9235		0.8192		
<i>N,N</i> -dimethylaniline (1) + [bmim][NTf <sub>2</sub> ] (2)					
$T = 288.15 \text{ K}$					
0.0000	1.4446		78.37		
0.1000	1.4237	-0.2891	65.15	-5.538	557.22
0.2000	1.3997	-0.5053	52.22	-10.78	1019.03
0.2993	1.3726	-0.7182	40.50	-14.87	1384.71
0.4001	1.3411	-0.9475	30.39	-17.23	1674.77
0.5005	1.3048	-1.2035	21.72	-18.20	1829.72
0.5993	1.2619	-1.2987	15.08	-17.24	1887.68
0.7000	1.2093	-1.3047	9.887	-14.70	1808.45
0.7996	1.1450	-1.1091	6.069	-10.86	1543.05
0.8997	1.0640	-0.6753	3.332	-5.911	992.99
1.0000	0.9606		1.536		
$T = 293.15 \text{ K}$					
0.0000	1.4398		61.47		
0.1000	1.4189	-0.2991	51.31	-4.154	547.90
0.2000	1.3949	-0.5177	41.41	-8.043	1005.64
0.2993	1.3679	-0.7326	32.39	-11.11	1369.41
0.4001	1.3364	-0.9649	24.57	-12.87	1661.94
0.5005	1.3001	-1.2221	17.79	-13.62	1822.02
0.5993	1.2573	-1.3203	12.54	-12.94	1889.12
0.7000	1.2048	-1.3264	8.365	-11.07	1821.97
0.7996	1.1406	-1.1276	5.249	-8.200	1577.00
0.8997	1.0597	-0.6848	2.957	-4.481	1051.90
1.0000	0.9565		1.415		
$T = 298.15 \text{ K}$					
0.0000	1.4350		49.11		
0.1000	1.4141	-0.3017	41.27	-3.054	528.65
0.2000	1.3902	-0.5269	33.64	-5.909	972.55
0.2993	1.3631	-0.7476	26.64	-8.160	1328.33
0.4001	1.3317	-0.9843	20.44	-9.535	1608.49
0.5005	1.2955	-1.2428	15.06	-10.12	1768.26
0.5993	1.2527	-1.3423	10.77	-9.691	1826.60
0.7000	1.2003	-1.3471	7.288	-8.355	1749.12
0.7996	1.1362	-1.1474	4.642	-6.239	1491.88
0.8997	1.0554	-0.7003	2.673	-3.423	967.00
1.0000	0.9523		1.302		
$T = 303.15 \text{ K}$					
0.0000	1.4302		39.95		
0.1000	1.4094	-0.3056	34.05	-2.029	539.73
0.2000	1.3855	-0.5378	27.97	-4.235	977.88
0.2993	1.3585	-0.7649	22.26	-6.099	1319.20
0.4001	1.3271	-1.0050	17.16	-7.286	1582.96
0.5005	1.2909	-1.2656	12.73	-7.829	1730.62
0.5993	1.2482	-1.3673	9.207	-7.525	1786.13
0.7000	1.1958	-1.3700	6.338	-6.492	1716.32
0.7996	1.1318	-1.1680	4.120	-4.851	1473.62
0.8997	1.0512	-0.7152	2.418	-2.674	954.69
1.0000	0.9482		1.206		

(continued on next page)

Table 3 (continued)

$x_1$	$10^{-3} \cdot \rho / \text{kg} \cdot \text{m}^{-3}$	$10^6 \cdot V^E / \text{m}^3 \cdot \text{mol}^{-1}$	$\eta / \text{mPa} \cdot \text{s}$	$\Delta\eta / \text{mPa} \cdot \text{s}$	$\Delta G^E / \text{kJ} \cdot \text{kmol}^{-1}$
$T = 308.15 \text{ K}$					
0.0000	1.4254		33.22		
0.1000	1.4046	-0.3129	28.31	-1.701	519.16
0.2000	1.3808	-0.5508	23.37	-3.430	948.20
0.2993	1.3538	-0.7821	18.75	-4.862	1287.20
0.4001	1.3224	-1.0260	14.66	-5.725	1559.92
0.5005	1.2863	-1.2894	10.96	-6.195	1702.38
0.5993	1.2437	-1.3926	8.018	-5.968	1758.74
0.7000	1.1913	-1.3971	5.585	-5.169	1688.69
0.7996	1.1274	-1.1896	3.684	-3.872	1450.58
0.8997	1.0469	-0.7278	2.205	-2.138	945.27
1.0000	0.9441		1.123		
$T = 313.15 \text{ K}$					
0.0000	1.4206		27.68		
0.1000	1.3999	-0.3157	23.60	-1.416	497.42
0.2000	1.3761	-0.5612	19.61	-2.749	917.88
0.2993	1.3492	-0.8014	15.88	-3.830	1255.82
0.4001	1.3178	-1.0499	12.50	-4.527	1519.77
0.5005	1.2818	-1.3149	9.438	-4.916	1657.05
0.5993	1.2391	-1.4198	7.005	-4.720	1721.27
0.7000	1.1869	-1.4219	4.931	-4.113	1645.85
0.7996	1.1231	-1.2123	3.299	-3.092	1409.96
0.8997	1.0427	-0.7434	2.028	-1.699	933.33
1.0000	0.9400		1.056		
$T = 318.15 \text{ K}$					
0.0000	1.4159		23.53		
0.1000	1.3951	-0.3141	20.23	-1.054	502.74
0.2000	1.3714	-0.5699	16.90	-2.121	922.46
0.2993	1.3445	-0.8216	13.77	-3.017	1256.82
0.4001	1.3133	-1.0744	10.93	-3.585	1522.95
0.5005	1.2772	-1.3421	8.335	-3.911	1666.47
0.5993	1.2346	-1.4484	6.213	-3.805	1720.22
0.7000	1.1824	-1.4512	4.422	-3.325	1649.37
0.7996	1.1187	-1.2362	3.005	-2.495	1427.60
0.8997	1.0384	-0.7592	1.858	-1.385	936.04
1.0000	0.9359		0.9805		
$T = 323.15 \text{ K}$					
0.0000	1.4112		20.13		
0.1000	1.3905	-0.3270	17.37	-0.842	496.18
0.2000	1.3668	-0.5882	14.60	-1.694	912.20
0.2993	1.3399	-0.8422	11.97	-2.415	1244.95
0.4001	1.3087	-1.1008	9.561	-2.885	1508.12
0.5005	1.2727	-1.3697	7.359	-3.158	1652.75
0.5993	1.2302	-1.4779	5.535	-3.084	1707.16
0.7000	1.1780	-1.4768	3.980	-2.705	1637.56
0.7996	1.1144	-1.2600	2.739	-2.031	1421.77
0.8997	1.0342	-0.7756	1.716	-1.131	933.81
1.0000	0.9318		0.9197		
$T = 328.15 \text{ K}$					
0.0000	1.4065		17.39		
0.1000	1.3858	-0.3336	15.09	-0.6463	496.20
0.2000	1.3621	-0.6029	12.74	-1.347	907.35
0.2993	1.3354	-0.8638	10.49	-1.953	1234.43
0.4001	1.3042	-1.1286	8.443	-2.334	1498.49
0.5005	1.2682	-1.3985	6.548	-2.571	1642.49
0.5993	1.2257	-1.5090	4.976	-2.510	1702.90
0.7000	1.1736	-1.5061	3.621	-2.201	1641.43
0.7996	1.1100	-1.2852	2.504	-1.672	1412.61
0.8997	1.0299	-0.7924	1.591	-0.9307	933.12
1.0000	0.9277		0.8649		
$T = 333.15 \text{ K}$					
0.0000	1.4019		15.20		
0.1000	1.3812	-0.3417	13.19	-0.5719	481.38
0.2000	1.3575	-0.6184	11.19	-1.132	890.89
0.2993	1.3308	-0.8857	9.288	-1.610	1221.22
0.4001	1.2996	-1.1551	7.516	-1.932	1481.48
0.5005	1.2637	-1.4246	5.864	-2.140	1622.21
0.5993	1.2213	-1.5403	4.494	-2.089	1684.99
0.7000	1.1692	-1.5362	3.288	-1.846	1615.48
0.7996	1.1057	-1.3107	2.299	-1.403	1390.64
0.8997	1.0257	-0.8084	1.485	-0.7771	927.32
1.0000	0.9235		0.8192		

<sup>a</sup> Standard uncertainties  $u$  are:  $u(x_1) = \pm 1 \times 10^{-4}$ ;  $u(T) = 0.01 \text{ K}$ ;  $u(p) = 0.005 \text{ MPa}$ ;  $u(\rho) = 1 \text{ kg} \cdot \text{m}^{-3}$ , and relative standard uncertainty  $u_r(\eta) = 2.2\%$  with 68% level of confidence.

**Table 4**Parameters  $A_p$  of Eq. (4) and the corresponding RMSD  $\sigma$  for binary mixtures aniline + [bmim][OTf], aniline + [bmim][NTf<sub>2</sub>], *N,N*-dimethylaniline + [bmim][OTf] and *N,N*-dimethylaniline + [bmim][NTf<sub>2</sub>] at temperature  $T$  and at atmospheric pressure (0.1 MPa).

	$T/K$	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$\sigma$	
			<i>Aniline (1) + [bmim][OTf] (2)</i>					
$10^6 \cdot V^E/m^3 \cdot mol^{-1}$	288.15	-4.0543	-3.4438	-2.6990	-0.6542	4.6855	0.0005	
	293.15	-4.1633	-3.4986	-2.8005	-0.8045	4.7230	0.0005	
	298.15	-4.2808	-3.5462	-2.9184	-0.9557	4.7625	0.0005	
	303.15	-4.4043	-3.5726	-3.0747	-1.1669	4.8750	0.0005	
	308.15	-4.5336	-3.6343	-3.1610	-1.2889	4.8614	0.0005	
	313.15	-4.6590	-3.6946	-3.2791	-1.4234	4.8898	0.0005	
	318.15	-4.7919	-3.7471	-3.3987	-1.5881	4.9410	0.0005	
	323.15	-4.9248	-3.8054	-3.51978	-1.7451	4.9897	0.0005	
	328.15	-5.0638	-3.8680	-3.6398	-1.9050	5.0421	0.0005	
	333.15	-5.2014	-3.9355	-3.7667	-2.0743	5.1126	0.0005	
	$\Delta\eta/mPa \cdot s$	288.15	-88.543	14.086	-24.932	-15.783		0.8035
		293.15	-66.365	8.9851	-15.764	-13.350		0.3716
		298.15	-50.036	7.7725	-9.5124	-15.245		0.3694
		303.15	-38.555	5.4886	-4.1468	-15.452		0.2621
308.15		-30.136	4.5578	-5.0643	-10.985		0.1900	
313.15		-23.823	3.3912	-3.6154	-9.4493		0.1439	
318.15		-18.617	2.4783	-3.1857	-7.0552		0.1188	
323.15		-14.844	2.0073	-2.5636	-6.0688		0.0699	
328.15		-11.985	2.3661	-1.3797	-8.0764		0.0381	
333.15		-9.6898	2.5164	-2.4921	-6.7383		0.0268	
$\Delta G^E/kJ \cdot kmol^{-1}$		288.15	5727.55	1236.62	-654.88			8.4515
		293.15	5652.81	1159.85	-541.79			8.0588
		298.15	5612.91	1248.98	-231.22			7.6932
		303.15	5579.37	1208.75	42.53			7.3238
	308.15	5580.75	1347.40	0.68			7.1086	
	313.15	5691.73	1347.54	-418.21			17.4500	
	318.15	5799.96	1674.20	-97.70			14.1225	
	323.15	5791.75	1738.61	63.51			13.3994	
	328.15	5728.05	1499.85	-35.05			18.6463	
	333.15	5750.16	1572.30	-281.40			20.6359	
				<i>Aniline (1) + [bmim][NTf<sub>2</sub>] (2)</i>				
	$10^6 \cdot V^E/m^3 \cdot mol^{-1}$	288.15	-3.2746	-1.8072	3.2284	-4.5865		0.0131
		293.15	-3.3693	-1.8543	3.2853	-4.9093		0.0136
		298.15	-3.4665	-1.9029	3.3294	-5.2108		0.0149
303.15		-3.5767	-1.9149	3.5199	-5.6376		0.0160	
308.15		-3.6894	-1.9690	3.6484	-5.9795		0.0182	
313.15		-3.7942	-1.9678	3.7537	-6.4290		0.0215	
318.15		-3.9137	-2.0095	3.8299	-6.7654		0.0232	
323.15		-4.0301	-2.0518	3.8468	-7.0265		0.0253	
328.15		-4.1447	-2.0859	3.7974	-7.2624		0.0267	
333.15		-4.2490	-2.1559	3.6364	-7.3083		0.0276	
$\Delta\eta/mPa \cdot s$		288.15	-42.408	6.1419	-8.8439			0.2101
		293.15	-31.967	4.7498	-6.7242			0.1476
		298.15	-23.557	1.8537	-3.2639			0.1442
		303.15	-18.034	2.3201	-3.6879			0.0987
	308.15	-14.255	1.5303	-2.7278			0.0984	
	313.15	-11.345	1.0783	-2.0967			0.0873	
	318.15	-8.9272	0.8051	-1.5880			0.0784	
	323.15	-7.1915	0.6233	-1.0178			0.0628	
	328.15	-5.8313	0.4264	-0.7793			0.0556	
	333.15	-4.8032	0.3561	-0.7522			0.0494	
	$\Delta G^E/kJ \cdot kmol^{-1}$	288.15	5559.71	2715.49	920.35			19.3814
		293.15	5562.91	2739.18	964.18			17.0730
		298.15	5649.67	2752.65	1259.23			20.0153
		303.15	5707.56	2907.29	1224.87			17.1330
308.15		5744.36	2910.44	1305.61			19.6058	
313.15		5718.76	2838.92	1269.74			21.2901	
318.15		5823.93	2969.81	1458.38			22.1407	
323.15		5860.02	2997.13	1552.07			22.4089	
328.15		5891.19	2999.15	1577.16			22.4089	
333.15		5932.26	3005.31	1530.51			22.3447	
				<i>N,N-dimethylaniline (1) + [bmim][OTf] (2)</i>				
$10^6 \cdot V^E/m^3 \cdot mol^{-1}$		288.15	-5.1289	-3.7663	4.5686	-14.7340	13.1024	0.0002
		293.15	-5.2131	-3.7880	4.6294	-14.8872	13.2061	0.0004
		298.15	-5.3073	-3.7884	4.6846	-15.2668	13.5444	0.0002
	303.15	-5.4098	-3.7939	4.7082	-15.5494	13.8445	0.0002	
	308.15	-5.5214	-3.7914	4.7595	-15.8950	14.1445	0.0005	
	313.15	-5.6334	-3.8209	4.8265	-16.1247	14.3614	0.0006	
	318.15	-5.7526	-3.8242	4.8483	-16.4815	14.7357	0.0005	
	323.15	-5.8741	-3.8188	4.8314	-16.9237	15.2925	0.0004	
	328.15	-6.0044	-3.8389	4.8712	-17.2720	15.6872	0.0005	
	333.15	-6.1374	-3.8355	4.8835	-17.7386	16.2187	0.0006	

(continued on next page)

Table 4 (continued)

	T/K	A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	σ	
$\Delta\eta/\text{mPa}\cdot\text{s}$	288.15	-162.22	41.275	-31.598	57.704		0.3107	
	293.15	-120.53	28.010	-22.178	44.484		0.2649	
	298.15	-90.500	19.011	-18.954	37.285		0.2138	
	303.15	-69.504	14.020	-17.621	28.649		0.1725	
	308.15	-54.267	8.9613	-13.746	27.486		0.1611	
	313.15	-42.742	6.2858	-14.223	27.575		0.1543	
	318.15	-33.881	4.2946	-12.072	21.325		0.1007	
	323.15	-27.292	2.9124	-10.317	19.052		0.0975	
	328.15	-22.210	1.9401	-8.6682	17.221		0.1041	
	333.15	-18.436	1.6088	-8.5216	15.025		0.0757	
	$\Delta G^{\text{E}}/\text{kJ}\cdot\text{kmol}^{-1}$	288.15	6195.49	1989.33	-570.71			26.9528
		293.15	6163.43	2210.71	-164.92			32.5902
		298.15	5924.80	2055.07	-505.48			26.8703
		303.15	5780.59	2145.93	-456.51			32.9596
		308.15	5748.48	2134.82	-565.65			31.5798
313.15		5602.05	2218.14	-943.61			37.5740	
318.15		5650.58	2323.18	-794.65			36.2771	
323.15		5609.20	2383.41	-791.50			37.4232	
328.15		5580.40	2455.21	-817.90			38.5494	
333.15		5504.67	2523.02	-1025.49			37.6908	
<i>N,N</i> -dimethylaniline (1) + [bmim][NTf <sub>2</sub> ] (2)								
$10^6\cdot V^{\text{E}}/\text{m}^3\cdot\text{mol}^{-1}$		288.15	-4.6472	-3.7438	-1.0962	1.6778		0.0410
		293.15	-4.7234	-3.8096	-1.1454	1.7862		0.0404
		298.15	-4.8037	-3.8246	-1.1765	1.6694		0.0409
		303.15	-4.8955	-3.8455	-1.1966	1.5835		0.0407
	308.15	-5.0026	-3.9030	-1.2022	1.6165		0.0380	
	313.15	-5.1046	-3.9282	-1.2012	1.5167		0.0379	
	318.15	-5.2366	-3.9573	-1.1186	1.3745		0.0330	
	323.15	-5.3282	-3.9900	-1.2302	1.3869		0.0367	
	328.15	-5.4476	-4.0259	-1.2452	1.3332		0.0356	
	333.15	-5.5678	-4.0741	-1.2668	1.3236		0.0316	
	$\Delta\eta/\text{mPa}\cdot\text{s}$	288.15	-72.785	2.4244	14.472	-7.6696		0.1984
		293.15	-54.446	1.0967	10.2844	-5.1597		0.0489
		298.15	-40.495	-0.5991	7.1285	-2.9692		0.0821
		303.15	-31.312	-1.5597	8.1687	-4.4809		0.0677
		308.15	-24.774	-1.3835	5.4580	-2.4964		0.0984
313.15		-19.477	-1.5518	3.4406	-0.5881		0.0612	
318.15		-15.642	-1.6416	3.3045	-0.9872		0.0581	
323.15		-12.624	-1.5975	2.6386	-0.5883		0.0438	
328.15		-10.280	-1.28678	2.3834	-1.0626		0.0471	
333.15		-8.4808	-1.3960	1.5564	-0.0256		0.0288	
$\Delta G^{\text{E}}/\text{kJ}\cdot\text{kmol}^{-1}$		288.15	7314.83	2671.43	1962.09			21.2393
		293.15	7285.33	2936.64	2281.26			31.9475
		298.15	7064.92	2661.06	1811.14			21.2545
		303.15	6919.69	2527.89	2079.04			20.5495
		308.15	6808.88	2567.73	1963.82			23.7784
	313.15	6641.17	2538.31	1870.71			27.2068	
	318.15	6665.53	2567.79	1922.90			26.9087	
	323.15	6608.37	2585.40	1937.03			27.6569	
	328.15	6561.93	2589.87	1985.08			24.8779	
	333.15	6488.37	2578.78	1897.92			28.7549	

absolute  $V^{\text{E}}$  values in the minima regions increase with increasing temperature from 288.15 K to 333.15 K.

Viscosity deviations are plotted vs.  $x_1$  mole fractions along with the values calculated from the RK polynomial (Fig. 4). All the systems exhibit negative  $\Delta\eta$  values. Absolute  $\Delta\eta$  values decrease with increasing temperature from 288.15 K to 333.15 K for all the investigated completely miscible binary mixtures.

Fig. 5 gives the RK curves representing the calculated values for the excess molar Gibbs energies of activation of viscous flow  $\Delta G^{\text{E}}$  for three completely miscible systems studied. Due to visibility reasons, the curves are given for five selected isotherms. As the figure shows the  $\Delta G^{\text{E}}$  values are positive for all the studied fully miscible systems.

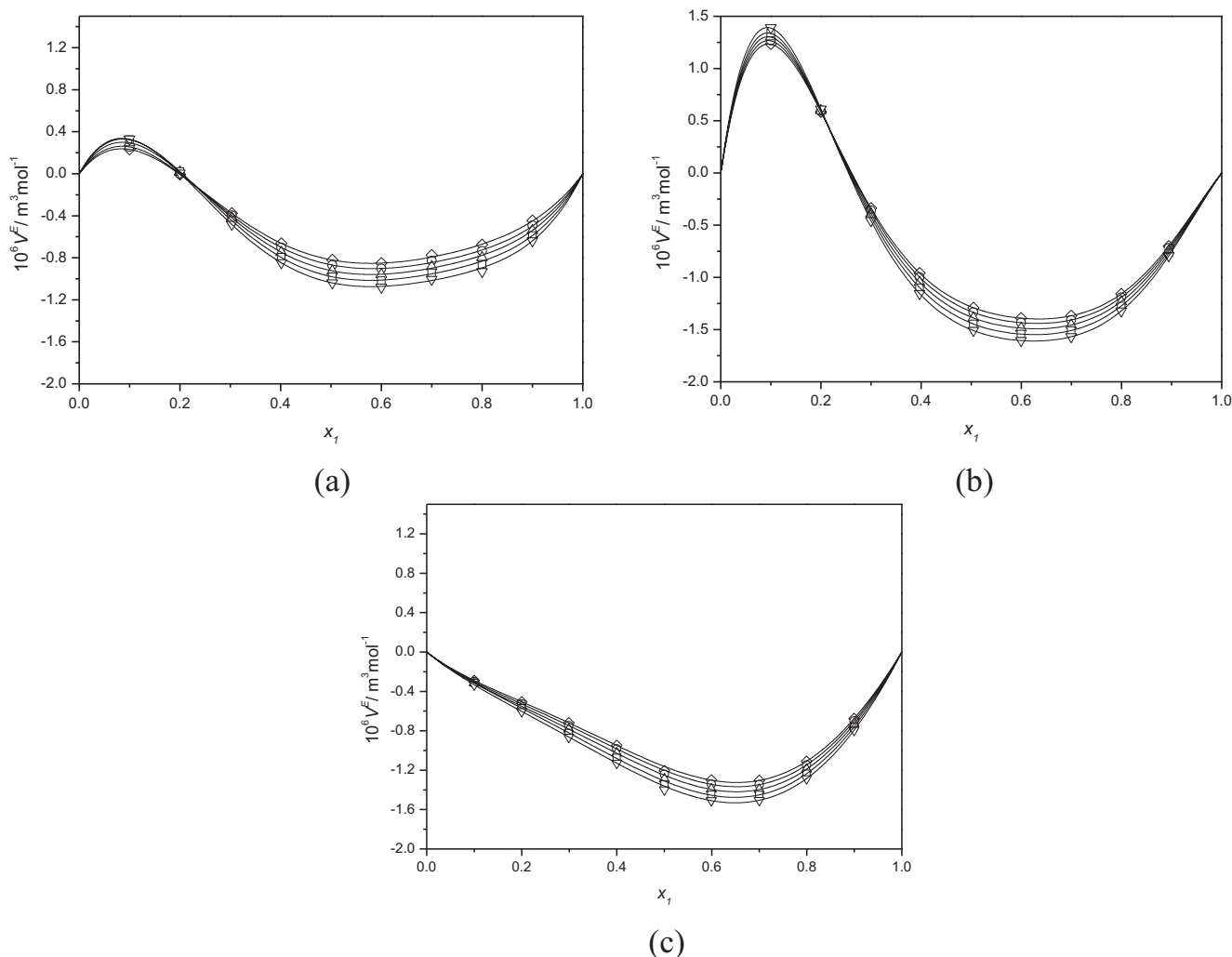
#### 4. Discussion

Mixtures studied herein consist of complex polar and hydrogen bonding compounds, thus available to form diverse interactions

between like and unlike molecules. The outcome of the interplay between these interactions is strongly linked to the deviation from the ideal behaviour of such mixtures and, thus, to the related excess thermodynamic properties or deviation functions. The latter can be explained and interpreted on the bases of the existing interactions [81–84].

##### 4.1. Analysis of the interactions between unlike and like molecules existing in the studied mixtures

Aniline and *N,N*-dimethylaniline are both polar compounds with dipole moments 1.59 D and 1.55 D, respectively [85], thus enabling dipole-dipole or ion-dipole interactions. Considering partially negatively charged nitrogen and partially positive charged hydrogen atoms from the amine group, it is evident that aniline can be both hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) (see hydrogen bond acidity  $\alpha$  (HBD ability) and hydrogen bond basicity  $\beta$  (HBA ability) parameters of aniline given



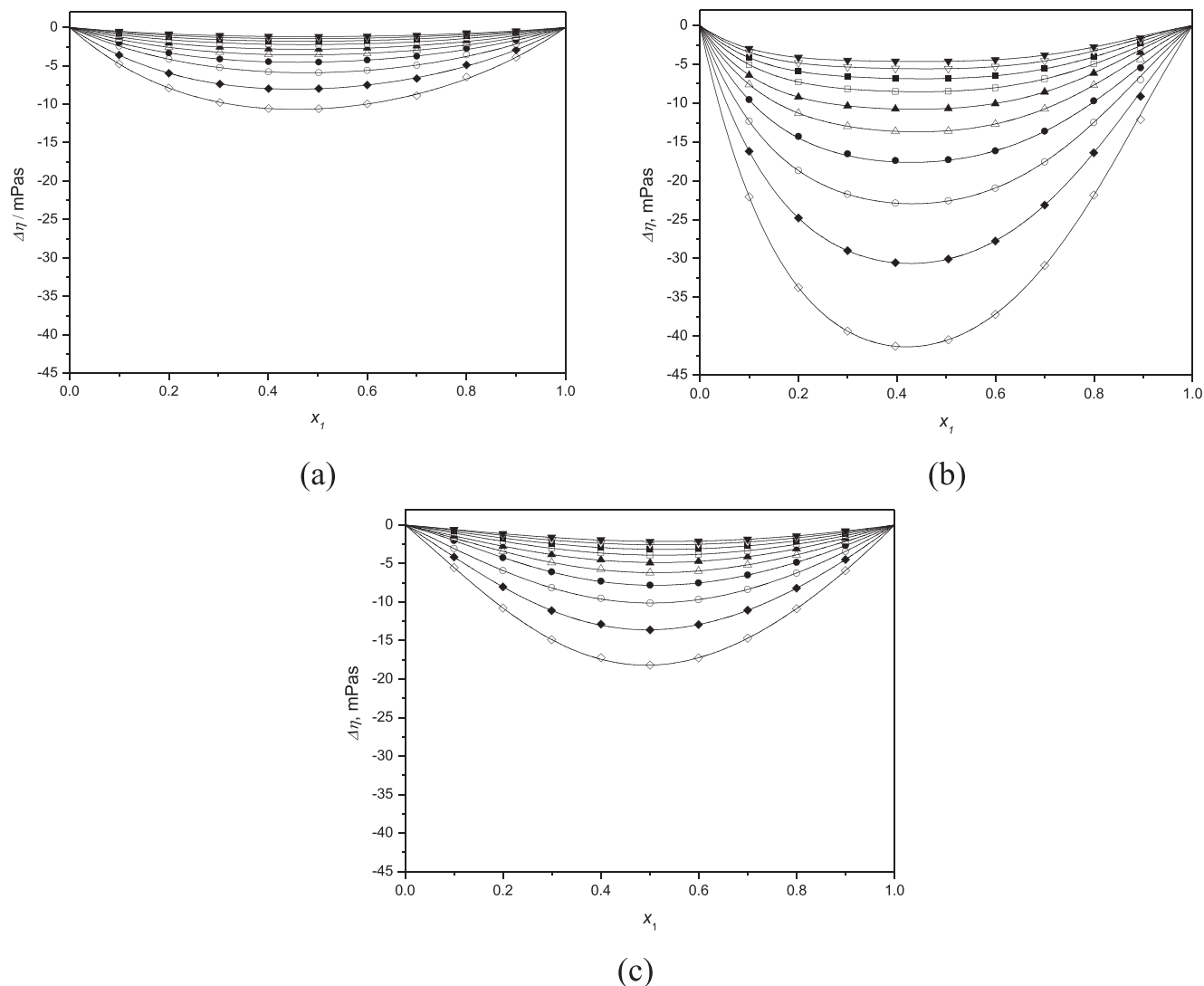
**Fig. 3.** Experimental values of excess molar volume  $V^E$  as a function of aniline/*N,N*-dimethylaniline mole fraction  $x_1$  for the systems: (a) aniline (1) + [bmim][NTf<sub>2</sub>] (2); (b) *N,N*-dimethylaniline (1) + [bmim][OTf] (2); (c) *N,N*-dimethylaniline (1) + [bmim][NTf<sub>2</sub>] (2) at following temperatures: (◇) 288.15 K, (○) 298.15 K, (△) 308.15 K, (□) 318.15 K, (▽) 328 K, (—) RK equation.

in Table 5). However, without the available hydrogen atoms, *N,N*-dimethylaniline is only a hydrogen bond acceptor ( $\alpha$  value is zero, Table 5). Thus, both aniline and *N,N*-dimethylaniline can form hydrogen bonds with aniline having more possibilities in this respect.

For the ionic liquids the situation is far more complex, considering their features listed in the introduction. Imidazolium based ILs [C<sub>4</sub>mim][OTf] and [C<sub>4</sub>mim][NTf<sub>2</sub>] both have imidazolium cation which acts as proton donor through the acidic hydrogen atom placed between two nitrogen atoms in the imidazolium ring – thus, it can build hydrogen bonds with proton acceptors [15]. This is in agreement with the hydrogen bond acidities of ionic liquids ( $\alpha$ ) listed in Table 5, in which their cations play the principle role [18,88]. Further on, both studied ionic liquids are also proton acceptors through their anions (the respective hydrogen bond basicities  $\beta$  given in Table 5 are mainly anion controlled [18,88]). Finally, as briefly stated in the introduction, the imidazolium ionic liquids form specific cation and anion interactions with the aromatic arene ring which result in the formation of cage-like structures – liquid clathrates in solutions [21–23]. The specific anion/arene ring interactions are provided between the oxygen atoms in the anion and the hydrogen in the arene ring. These interactions are stronger and more numerous in the case of [NTf<sub>2</sub>]<sup>−</sup> anion com-

pared to [OTf]<sup>−</sup>, mainly due to higher number of oxygen atoms [89]. Thus, aromatic compounds exhibit better solubility in the imidazolium ionic liquids having [NTf<sub>2</sub>]<sup>−</sup> anions [80,89,90].

Interactions between the like-molecules in the studied solutions deserve attention as well. Thus, the shifts in vibration bands of the NH<sub>2</sub>-group to shorter wave-lengths [91] as well as the association constant and enthalpy derived from the excess Gibbs energy of mixing indicate aniline self-association. This is achieved mainly via N–H–N hydrogen bonds though dipole-dipole interactions should not be excluded either [92]. However, no self-association occurs in *N,N*-dimethylaniline. Also, in ionic liquids, cation-anion interactions exist, as a result of subtle balance between hydrogen bonds, Coulomb forces and dispersion interactions between alkyl chains [16]. Thus, spectroscopic studies [93,94] show that the overall cation-anion interactions are stronger for the [C<sub>n</sub>mim][OTf] than for the [C<sub>n</sub>mim][NTf<sub>2</sub>] ionic liquids. Another fine balance, this time between ion-solvent and cation-anion, brings ion-pairing in ionic liquids [16]. Thus, the detailed analysis of [C<sub>4</sub>mim][OTf] on the molecular level [95] reveals that anion pairing occurs through the CF<sub>3</sub> moieties of the two [OTf]<sup>−</sup> anions. So, two anions are surrounded by a cation cage that is composed of nine [C<sub>n</sub>mim]<sup>+</sup> cations, in average. Analysis of the [C<sub>n</sub>mim][NTf<sub>2</sub>] by the infra-red (IR) spectroscopy revealed both association



**Fig. 4.** Experimental values of viscosity deviation  $\Delta\eta$  as a function of aniline/*N,N*-dimethylaniline mole fraction  $x_1$  for the systems: (a) aniline (1) + [bmim][NTf<sub>2</sub>] (2); (b) *N,N*-dimethylaniline (1) + [bmim][OTf] (2); (c) *N,N*-dimethylaniline (1) + [bmim][NTf<sub>2</sub>] (2) at following temperatures: ( $\diamond$ ) 288.15 K, ( $\blacklozenge$ ) 293.15 K, ( $\circ$ ) 298.15 K, ( $\bullet$ ) 303.15 K, ( $\triangle$ ) 308.15 K, ( $\blacktriangle$ ) 313.15 K, ( $\square$ ) 318.15 K, ( $\blacksquare$ ) 323.15 K, ( $\nabla$ ) 328 K, ( $\blacktriangledown$ ) 333 K, (---) RK equation.

of imidazolium ions in ion pairs or clusters and their dissociation into free ions or smaller clusters [96]. From these two studies one can conclude that the association through ion-pairing may be stronger in the [C<sub>4</sub>mim][OTf] than in [C<sub>4</sub>mim][NTf<sub>2</sub>] due to the dissociation process present only in the latter.

Considering the interactions outlined and discussed above one can analyze the obtained excess molar volumes and deviations in viscosity behaviour for the studied systems.

#### 4.2. Analyses of the excess molar volumes

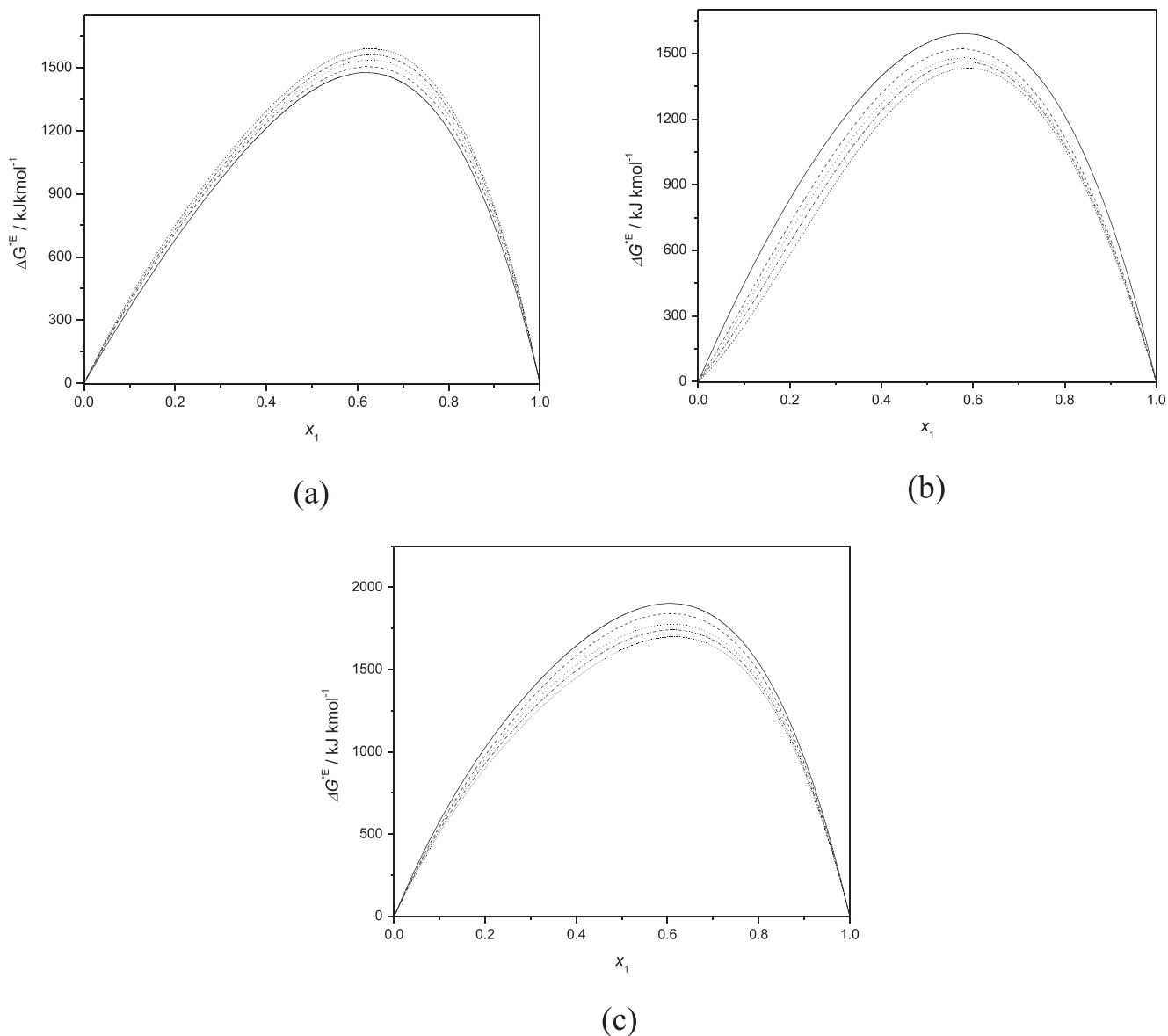
Negative  $V^E$  values (Fig. 3) are mainly the consequence of three groups of attractive interactions between unlike molecules, analysed above: (i) hydrogen bonding between ionic liquid and anilines, (ii) aforementioned specific cation-arene and anion-arene interactions which enabled cage-like structures and (iii) ion-dipole interactions between ionic liquids and polar molecules of both anilines. These interactions led to more efficient packing in the mixture compared to the pure liquids, eased by the difference in the molecular size existing in all the mixtures (see the molar volume ratios in Table 6).

However, the positive  $V^E$  values seen in Fig. 3(a) and (b) are the result of the dominance of the aforementioned interactions existing

between the like molecules in the studied systems – aniline association, cation-anion interactions and ion-pairing in ionic liquids – which prevailed over the attractive interactions between unlike molecules. Indeed, the expansion upon mixing is always observed in the mixtures rich with ionic liquids, due to the cation-anion interactions which are coupled with ion – pairing (see above). Much lower positive values of  $V^E$  in the ionic liquid rich mixtures of aniline + [bmim][NTf<sub>2</sub>] compared to the positive ones in the *N,N*-dimethylaniline+[bmim][OTf] system (see Fig. 3(a) and (b)) may be addressed to the aforementioned stronger cation-anion interactions in and more stable ion-pairing in the [bmim][OTf] ionic liquid. These distinctions along with the association of aniline (but not *N,N*-dimethylaniline) and weaker specific cation/anion interactions with the arene aromatic ring in the case of [bmim][OTf] ionic liquid (see above) were the reasons that stand behind the immiscibility exhibited in the system (aniline +[bmim][OTf]).

#### 4.3. Analysis of viscosity behaviour

Meyer et al. [97] stated that the sign of the excess molar Gibbs energy of activation of viscous flow  $\Delta G^{*E}$  are generally linked to the excess molar Gibbs energy of mixing, but its sign has the opposite physical significance to the nature of intermolecular interactions:



**Fig. 5.** RK lines of excess molar Gibbs energy of activation of viscous flow  $\Delta G^{*E}$  as a function of aniline/*N,N*-dimethylaniline mole fraction  $x_1$  for the systems: (a) aniline (1) + [bmim][NTf<sub>2</sub>] (2); (b) *N,N*-dimethylaniline (1) + [bmim][OTf] (2); (c) *N,N*-dimethylaniline (1) + [bmim][NTf<sub>2</sub>] (2) at following temperatures: (—) 288.15 K, (---) 298.15 K, (⋯) 308.15 K, (-.-.-) 318.15 K, (- - -) 333 K.

**Table 5**

Dipole moments and hydrogen bond acidity and basicity for the studied solvents and solutes.

Chemical	$\alpha$	$\beta$	$\mu/D$
Aniline	0.264 <sup>a</sup>	0.38 <sup>b</sup>	1.51 <sup>c</sup>
<i>N,N</i> -dimethylaniline	0.00 <sup>a</sup>	0.35 <sup>b</sup>	1.61 <sup>c</sup>
[bmim][OTf]	0.625 <sup>d</sup>	0.464 <sup>d</sup>	—
[bmim][NTf <sub>2</sub> ]	0.617 <sup>d</sup>	0.243 <sup>d</sup>	—

<sup>a</sup> Abraham et al. [86].

<sup>b</sup> Abraham et al. [87].

<sup>c</sup> Fischer [85].

<sup>d</sup> Crowhurst et al. [18].

positive values indicate the presence of strong, attractive interactions between unlike molecules while negative values show their absence and the domination of interactions between like molecules. Indeed, this property, as Eq. (4) shows, includes both volumetric and viscosity data thus establishing a more complete resort to the interaction analysis and discussion. However, along

with the  $\Delta G^{*E}$  function, it is also important to consider enthalpy and entropic contributions to  $\Delta G^{*E}$ , particularly in the case of the systems in which molecules differ by size, such as the present ones and those we studied recently [24]. Namely, if one obtained the value of the  $\Delta G^{*E}$  via Eq. (4) the other two related excess properties of activation of viscous flow are calculated using the equations:

$$\Delta S^{*E} = - \left[ \frac{\partial(\Delta G^{*E})}{\partial T} \right]_{p,x} \quad (7)$$

$$\Delta G^{*E} + T\Delta S^{*E} = \Delta H^{*E} \quad (8)$$

Thus, Fig. 5 presents excess molar Gibbs energies of activation of viscous flow for five of ten studied isotherms due to visibility reasons. Table 6 presents all three excess molar properties of activation of viscous flow, calculated for three studied systems which exhibited complete miscibility, at the same composition – aniline/*N,N*-dimethylaniline mole fraction equals 0.6. The positive values of  $\Delta G^{*E}$  and  $\Delta H^{*E}$  indicate strong attractive interactions in three

**Table 6**  
Excess molar properties of activation of viscous flow at 298.15 K for mixtures of the same composition ( $x_1 = 0.6$ ): Gibbs energy ( $\Delta G^{\text{E}}$ ), entropy ( $\Delta S^{\text{E}}$ ), enthalpy ( $\Delta H^{\text{E}}$ ) and entropy-related energetic term  $T\Delta S^{\text{E}}$ .

$\Delta G^{\text{E}}/\text{kJ}\cdot\text{kmol}^{-1}$	$\Delta S^{\text{E}}/\text{kJ}\cdot\text{kmol}^{-1}\cdot\text{K}^{-1}$	$T\Delta S^{\text{E}}/\text{kJ}\cdot\text{kmol}^{-1}$	$\Delta H^{\text{E}}/\text{kJ}\cdot\text{kmol}^{-1}$	$V_{\text{m}2}/V_{\text{m}1}^{\text{a}}$
1492.17	-2.3305	Aniline (1) + [C <sub>4</sub> mim][NTf <sub>2</sub> ] (2) -694.49	797.68	3.2
1475.32	3.3617	<i>N,N</i> -dimethylaniline (1) + [C <sub>4</sub> mim][OTf] (2) 1001.79	2477.11	1.7
1826.6	4.5628	<i>N,N</i> -dimethylaniline (1) + [C <sub>4</sub> mim][NTf <sub>2</sub> ] (2) 1359.71	3186.31	2.3

<sup>a</sup> Molar volume ratio at 298.15 K.

mixtures, particularly in the system *N,N*-dimethylaniline + [Bmim][NTf<sub>2</sub>] and are in the agreement with the values of the negative excess molar volumes presented in Fig. 3. Negative excess molar entropies of activation of viscous flow for the system aniline + [Bmim][NTf<sub>2</sub>] are mainly the consequence of the difference in the size of the molecules and make an important contribution to the positive value of  $\Delta G^{\text{E}}$ .

Negative deviations in viscosity presented in Fig. 4 are the result of the aforementioned ion aggregations in ionic liquids but do not reflect the overall existing interactions. Thus, if aniline or *N,N*-dimethylaniline are included in interstices of the ion aggregates there will be a fewer surfaces available for friction that may result in the reduction of viscosity [98]. Considering that *N,N*-dimethylaniline cannot self-associate it is expected more efficient packing into IL's ion aggregates comparing to aniline which can self-associate through hydrogen bonds (see above). This can explain high values of viscosity deviations for the systems with *N,N*-dimethylaniline.

## 5. Conclusions

In this paper, density  $\rho$  and viscosity  $\eta$  values for four binary mixtures {aniline + [bmim][OTf]}, {*N,N*-dimethylaniline + [bmim][OTf]}, {aniline + [bmim][NTf<sub>2</sub>]} and {*N,N*-dimethylaniline + [bmim][NTf<sub>2</sub>]}, measured at atmospheric pressure and at temperatures ranging from 288.15 K to 333.15 K with a step of 5 K, are presented. Excess molar volumes  $V^{\text{E}}$ , deviation functions of viscosity  $\Delta\eta$ , as well as excess molar Gibbs energies of activation of viscous flow  $\Delta G^{\text{E}}$ , calculated from the experimental results and correlated by the Redlich-Kister equation, are discussed on the basis of the molecular interactions between like and unlike molecules existing in the studied mixtures.

Generally highly negative excess molar volumes  $V^{\text{E}}$ , as well positive excess molar Gibbs energies  $\Delta G^{\text{E}}$  and excess molar enthalpies of activation of viscous flow  $\Delta H^{\text{E}}$  indicate the domination of strong, attractive interactions between unlike molecules – Coulomb forces, hydrogen bonding and ion-dipole interactions. These prevail over the association of aniline molecules, ion-pairing and cation-anion interactions existing with the molecules of the pure compounds. However, the difference in size of unlike molecules significantly contributes to positive  $\Delta G^{\text{E}}$  in the case of the system {aniline + [Bmim][NTf<sub>2</sub>]} and has to be taken into account.

This study clearly shows that only the simultaneous analysis of excess molar volumes, excess molar Gibbs free energies, excess molar enthalpies and excess molar entropies of activation of viscous flow can give a thorough description of molecular interactions existing in a mixture, particularly if the component molecules differ in size.

## Acknowledgements

The authors gratefully acknowledge the financial support received from the Research Fund of Ministry of Education, Science

and Technological Development, Serbia and the Faculty of Technology and Metallurgy, University of Belgrade (project No 172063).

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jct.2017.02.007>.

## References

- [1] D.R. MacFarlane, K.R. Seddon, Ionic liquids—progress on the fundamental issues, *Aust. J. Chem.* 60 (2007) 3–5, <http://dx.doi.org/10.1071/CH06478>.
- [2] Y.U. Paulechka, G.J. Kabo, A.V. Blokhin, O.A. Vydrov, J.W. Magee, M. Frenkel, Thermodynamic properties of 1-butyl-3-methylimidazolium hexafluorophosphate in the ideal gas state †, *J. Chem. Eng. Data* 48 (2003) 457–462, <http://dx.doi.org/10.1021/jje025591i>.
- [3] L.P.N. Rebelo, J.N. Canongia Lopes, J.M.S.S. Esperança, E. Filipe, On the critical temperature, normal boiling point, and vapour pressure of ionic liquids, *J. Phys. Chem. B* 109 (2005) 6040–6043, <http://dx.doi.org/10.1021/jp050430h>.
- [4] L.P.N. Rebelo, J.N.C. Lopes, J.M.S.S. Esperança, H.J.R. Guedes, J. Łachwa, V. Najdanovic-Visak, Z.P. Visak, Accounting for the unique, doubly dual nature of ionic liquids from a molecular thermodynamic and modeling standpoint, *Acc. Chem. Res.* 40 (2007) 1114–1121, <http://dx.doi.org/10.1021/ar7000556>.
- [5] Z.P. Visak, M.S. Calado, J.M. Vuksanovic, G.R. Ivanis, A.S.H. Branco, N.D. Grozdanic, M.L. Kijevcanin, S.P. Serbanovic, Solutions of ionic liquids with diverse aliphatic and aromatic solutes – Phase behaviour and potentials for applications: a review article, *Arab. J. Chem.* (2014), <http://dx.doi.org/10.1016/j.arabj.2014.10.003>.
- [6] Z.P. Visak, Some aspects of ionic liquids as diverse and versatile sustainable solvents, *J. Solution Chem.* 41 (2012) 1673–1695, <http://dx.doi.org/10.1007/s10953-012-9899-z>.
- [7] J. Wang, Y. Pei, Y. Zhao, Z. Hu, Recovery of amino acids by imidazolium based ionic liquids from aqueous media, *Green Chem.* 7 (2005) 196–202, <http://dx.doi.org/10.1039/b415842c>.
- [8] L.I.N. Tomé, V.R. Catambas, A.R.R. Teles, M.G. Freire, I.M. Marrucho, J.A.P. Coutinho, Tryptophan extraction using hydrophobic ionic liquids, *Sep. Purif. Technol.* 72 (2010) 167–173, <http://dx.doi.org/10.1016/j.seppur.2010.02.002>.
- [9] Y. Pei, Z. Li, L. Liu, J. Wang, Partitioning behaviour of amino acids in aqueous two-phase systems formed by imidazolium ionic liquid and dipotassium hydrogen phosphate, *J. Chromatogr. A* 1231 (2012) 2–7, <http://dx.doi.org/10.1016/j.chroma.2012.01.087>.
- [10] A.P. Carneiro, O. Rodríguez, E.A. Macedo, Solubility of monosaccharides in ionic liquids – experimental data and modeling, *Fluid Phase Equilib.* 314 (2012) 22–28, <http://dx.doi.org/10.1016/j.fluid.2011.10.011>.
- [11] H. Yan, J. Wu, G. Dai, A. Zhong, H. Chen, J. Yang, D. Han, Interaction mechanisms of ionic liquids [Cnmim]Br (n = 4, 6, 8, 10) with bovine serum albumin, *J. Lumin.* 132 (2012) 622–628, <http://dx.doi.org/10.1016/j.jlumin.2011.10.026>.
- [12] X. Ni, H. Xing, Q. Yang, J. Wang, B. Su, Z. Bao, Y. Yang, Q. Ren, Selective liquid-liquid extraction of natural phenolic compounds using amino acid ionic liquids: a case of  $\alpha$ -tocopherol and methyl linoleate separation, *Ind. Eng. Chem. Res.* 51 (2012) 6480–6488, <http://dx.doi.org/10.1021/ie201682h>.
- [13] H. Yan, M. Gao, J. Qiao, New ionic liquid modified polymeric microspheres for solid-phase extraction of four Sudan dyes in foodstuff samples, *J. Agric. Food Chem.* 60 (2012) 6907–6912, <http://dx.doi.org/10.1021/jf301224t>.
- [14] M.S. Manic, V. Najdanovic-Visak, M.N. da Ponte, Z.P. Visak, Extraction of free fatty acids from soybean oil using ionic liquids or poly(ethylene glycol)s, *AIChE J.* 57 (2011) 1344–1355, <http://dx.doi.org/10.1002/aic.12349>.
- [15] J.M. Crosthwaite, S.N.V.K. Aki, E.J. Maginn, J.F. Brennecke, Liquid phase behaviour of imidazolium-based ionic liquids with alcohols, *J. Phys. Chem. B* 108 (2004) 5113–5119, <http://www.scopus.com/inward/record.url?eid=2-s2.0-2342558605&partnerID=tZotx3y1>.
- [16] K. Fumino, S. Reimann, R. Ludwig, Probing molecular interaction in ionic liquids by low frequency spectroscopy: Coulomb energy, hydrogen bonding and dispersion forces, *Phys. Chem. Phys.* 16 (2014) 21903–21929, <http://dx.doi.org/10.1039/c4cp01476f>.



- [17] J. Wang, Y. Tian, Y. Zhao, K. Zhuo, A volumetric and viscosity study for the mixtures of 1-n-butyl-3-methylimidazolium tetrafluoroborate ionic liquid with acetonitrile, dichloromethane, 2-butanone and N,N-dimethylformamide, *Green Chem.* 5 (2003) 618, <http://dx.doi.org/10.1039/b303735e>.
- [18] L. Crowhurst, P.R. Mawdsley, J.M. Perez-arlandis, P.A. Salter, T. Welton, Solvent–solute interactions in ionic liquids, *Phys. Chem. Chem. Phys.* 5 (2003) 2790–2794, <http://dx.doi.org/10.1039/b303095d>.
- [19] L. Cammarata, S.G. Kazarian, P.A. Salter, T. Welton, Molecular states of water in room temperature ionic liquids, *Phys. Chem. Chem. Phys.* 3 (2001) 5192–5200, <http://dx.doi.org/10.1039/b106900d>.
- [20] U. Domańska, L.M. Casás, Solubility of phosphonium ionic liquid in alcohols, benzene, and alkylbenzenes, *J. Phys. Chem. B* 111 (2007) 4109–4115, <http://dx.doi.org/10.1021/jp070293j>.
- [21] J.D. Holbrey, W.M. Reichert, M. Nieuwenhuyzen, O. Sheppard, C. Hardacre, R.D. Rogers, Liquid clathrate formation in ionic liquid–aromatic mixtures, *Chem. Commun.* 9 (2003) 476–477.
- [22] M. Deetlefs, C. Hardacre, M. Nieuwenhuyzen, O. Sheppard, A.K. Soper, Structure of ionic liquid–benzene mixtures, *J. Phys. Chem. B* 109 (2005) 1593–1598, <http://dx.doi.org/10.1021/jp047742p>.
- [23] J. Lachwa, I. Bento, M.T. Duarte, J.N.C. Lopes, L.P.N. Rebelo, Condensed phase behaviour of ionic liquid–benzene mixtures: congruent melting of a [emim][NTf2]·C<sub>6</sub>H<sub>6</sub> inclusion crystal, *Chem. Commun. (Camb.)* (2006) 2445–2447, <http://dx.doi.org/10.1039/b602675c>.
- [24] M.S. Calado, A.S.H. Branco, J.C.F. Diogo, J.M.N.A. Fareira, Z.P. Visak, Solubility, volumetric properties and viscosity of the sustainable systems of liquid poly(ethylene glycol) 200 with imidazolium- and phosphonium-based ionic liquids: cation and anion effects, *J. Chem. Thermodyn.* 80 (2015) 79–91, <http://dx.doi.org/10.1016/j.jct.2014.08.018>.
- [25] M.S. Calado, G.R. Ivanis, J.M. Vuksanovic, M.L. Kijevcanin, S.P. Serbanovic, Z.P. Visak, “Green Meets Green” – Sustainable solutions of imidazolium and phosphonium ionic liquids with poly(ethylene glycol): solubility and phase behaviour, *Fluid Phase Equilib.* 344 (2013) 6–12, <http://dx.doi.org/10.1016/j.fluid.2013.01.019>.
- [26] N.D. Grozdanic, V. Najdanovic-Visak, M.L. Kijevcanin, S.P. Serbanovic, M. Nunes da Ponte, Z.P. Visak, Liquid–liquid phase equilibria in nicotine (aqueous) solutions, *Fluid Phase Equilib.* 310 (2011) 198–206, <http://dx.doi.org/10.1016/j.fluid.2011.08.022>.
- [27] J.M. Vuksanovic, M.S. Calado, G.R. Ivanis, M.L. Kijevcanin, S.P. Serbanovic, Z.P. Visak, Environmentally friendly solutions of liquid poly(ethylene glycol) and imidazolium based ionic liquids with bistriflamide and triflate anions: Volumetric and viscosity studies, *Fluid Phase Equilib.* 352 (2013) 100–109, <http://dx.doi.org/10.1016/j.fluid.2013.05.013>.
- [28] O. Redlich, A.T. Kister, Algebraic representation of thermodynamic properties and the classification of solutions, *Ind. Eng. Chem.* 40 (1948) 345–348, <http://dx.doi.org/10.1021/ie50458a036>.
- [29] I. Alonso, I. Mozo, I.G. De La Fuente, J.A. González, J.C. Cobos, Thermodynamics of ketone+amine mixtures 7. Volumetric and speed of sound data at (293.15, 298.15 and 303.15) K for 2-pentanone+aniline, +N-methylaniline, or +pyridine systems, *J. Mol. Liq.* 160 (2011) 180–186, <http://dx.doi.org/10.1016/j.molliq.2011.03.015>.
- [30] N.G. Tsierekzos, M.M. Palaiologou, I.E. Molinou, Densities and viscosities of 1-pentanol binary mixtures at 293.15 K, *J. Chem. Eng. Data* 45 (2000) 272–275, <http://dx.doi.org/10.1021/je9902138>.
- [31] H. Migel Katz, P.W. Lobo, S.A. Minano, Solimo, Viscosities, densities, and refractive indices of binary liquid mixtures, *Can. J. Chem.* (1971) 2605–2609.
- [32] S.J. Kharat, P.S. Nikam, Density and viscosity studies of binary mixtures of aniline+benzene and ternary mixtures of (aniline+benzene+N,N-dimethylformamide) at 298.15, 303.15, 308.15, and 313.15 K, *J. Mol. Liq.* 131–132 (2007) 81–86, <http://dx.doi.org/10.1016/j.molliq.2006.08.053>.
- [33] Z.R. Master, N.I. Malek, Molecular interaction study through experimental and theoretical volumetric, acoustic and refractive properties of binary liquid mixtures at several temperatures 1. N,N-dimethylaniline with aryl, and alkyl ethers, *J. Mol. Liq.* 196 (2014) 120–134, <http://dx.doi.org/10.1016/j.molliq.2014.03.027>.
- [34] A. Arce, H. Rodríguez, A. Soto, Purification of ethyl tert-butyl ether from its mixtures with ethanol by using an ionic liquid, *Chem. Eng. J.* 115 (2006) 219–223, <http://dx.doi.org/10.1016/j.cej.2005.10.010>.
- [35] M. Vraneš, N. Zec, A. Tot, S. Papović, S. Dožić, S. Gadžurić, Density, electrical conductivity, viscosity and excess properties of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide+propylene carbonate binary mixtures, *J. Chem. Thermodyn.* 68 (2014) 98–108, <http://dx.doi.org/10.1016/j.jct.2013.08.034>.
- [36] I. Domínguez, E.J. González, R. González, A. Domínguez, Extraction of benzene from aliphatic compounds using commercial ionic liquids as solvents: study of the liquid–liquid equilibrium at T = 298.15 K, *J. Chem. Eng. Data* 56 (2011) 3376–3383, <http://dx.doi.org/10.1021/je200334e>.
- [37] J.M. Vuksanović, E.M. Živković, I.R. Radović, B.D. Djordjević, S.P. Šerbanović, M. L. Kijevčanin, Experimental study and modelling of volumetric properties, viscosities and refractive indices of binary liquid mixtures benzene+PEG 200/PEG 400 and toluene+PEG 200/PEG 400, *Fluid Phase Equilib.* 345 (2013) 28–44, <http://dx.doi.org/10.1016/j.fluid.2013.02.010>.
- [38] R.D. Chirico, M. Frenkel, J.W. Magee, V. Diky, C.D. Muzny, A.F. Kazakov, K. Kroenlein, I. Abdulagatov, G.R. Hardin, W.E. Acree, J.F. Brenneke, P.L. Brown, P. T. Cummings, T.W. De Loos, D.G. Friend, A.R.H. Goodwin, L.D. Hansen, W.M. Haynes, N. Koga, A. Mandelis, K.N. Marsh, P.M. Mathias, C. McCabe, J.P.O. Connell, Improvement of quality in publication of experimental thermophysical property data: challenges, assessment tools, global implementation, and online support, 2013.
- [39] A.I. Vogel, Physical properties and chemical constitution Part XXII. Some primary secondary and tertiary amines, *J. Chem. Soc.* (1924) 1825–1833.
- [40] K.M. Sumer, A.R. Thompson, Refraction, dispersion, and densities for methanol solutions of benzene, toluene, aniline, and phenol, *J. Chem. Eng. Data* 12 (1967) 489–493, <http://dx.doi.org/10.1021/je60035a007>.
- [41] M. Katz, P.W. Lobo, A. Sancho Minano, H. Solimo, Viscosities, densities, and refractive indices of binary liquid mixtures MIGUEL, *Can. J. Chem.* 49 (1971) 2605–2609.
- [42] S. Kumar, A. Maken, S. Agarwal, S. Maken, Topological studies of molecular interactions of 1,4-dioxane with formamides or anilines at 308.15 K, *J. Mol. Liq.* 155 (2010) 115–120, <http://dx.doi.org/10.1016/j.molliq.2010.05.023>.
- [43] M. Almasi, P. Monjezi, Studies on thermodynamic and transport properties of binary mixtures containing alcohols and aniline, *J. Chem. Eng. Data* 61 (2016) 2510–2515, <http://dx.doi.org/10.1021/acs.jced.6b00210>.
- [44] J. Costello, S. Bowden, The temperature variation of orthobaric density difference in liquid–vapour systems. III, *Recueil* 77 (1958) 36–46.
- [45] J.H. MacNeil, R. Palepu, Viscosities and densities of binary liquid mixtures of 2-butoxyethanol with aniline and N-alkylaniline, *Thermochim. Acta* 149 (1989) 275–286, [http://dx.doi.org/10.1016/0040-6031\(89\)85289-X](http://dx.doi.org/10.1016/0040-6031(89)85289-X).
- [46] A.G. Oskoei, N. Safaei, J. Ghasemi, Densities and viscosities for binary and ternary mixtures of 1,4-dioxane + 1-hexanol + N,N-Dimethylaniline from T) (283.15 to 343.15) K, *J. Chem. Eng. Data* 53 (2008) 343–349.
- [47] M.A. Saleh, M. Alauddin, S. Begum, Excess molar volume of 1-propanol + Aniline, +N-methylaniline, +N,N-dimethylaniline, *Phys. Chem. Liq.* 39 (2001) 453–464, <http://dx.doi.org/10.1080/00319100108031676>.
- [48] V. Pandiyan, S.L. Oswal, N.I. Malek, P. Vasantharani, Thermodynamic and acoustic properties of binary mixtures of ethers. V. Diisopropyl ether or oxolane with 2- or 3-chloroanilines at 303.15, 313.15 and 323.15 K, *Thermochim. Acta* 524 (2011) 140–150, <http://dx.doi.org/10.1016/j.tca.2011.07.005>.
- [49] M.H.S. Radwan, A.A. Hanna, Binary azeotropes containing butyric acids, *J. Chem. Eng. Data* 21 (1976) 285–289, <http://dx.doi.org/10.1021/je60070a032>.
- [50] M. Kondaiah, D.S. Kumar, K. Sreekanth, D.K. Rao, Densities and viscosities of binary mixtures of propanoic acid with N,N-dimethylaniline and N,N-diethylaniline at T = (303.15, 313.15, and 323.15) K, *J. Chem. Eng. Data* 57 (2012) 352–357, <http://dx.doi.org/10.1021/je200862b>.
- [51] E. Vercher, F.J. Llopis, V. González-Alfaro, P.J. Miguel, A. Martínez-Andreu, Refractive indices and deviations in refractive indices of trifluoromethanesulfonate-based ionic liquids in water, *J. Chem. Eng. Data* 56 (2011) 4499–4504, <http://dx.doi.org/10.1021/je200479e>.
- [52] M.G. Montalbán, C.L. Bolívar, F.G. Díaz Baños, G. Villora, Effect of temperature, anion, and alkyl chain length on the density and refractive index of 1-alkyl-3-methylimidazolium-based ionic liquids, *J. Chem. Eng. Data* 60 (2015) 1986–1996, <http://dx.doi.org/10.1021/je501091q>.
- [53] A.N. Soriano, B.T. Doma, M.H. Li, Measurements of the density and refractive index for 1-n-butyl-3-methylimidazolium-based ionic liquids, *J. Chem. Thermodyn.* 41 (2009) 301–307, <http://dx.doi.org/10.1016/j.jct.2008.08.010>.
- [54] H. Tokuda, S. Tsuzuki, M.A.B.H. Susan, K. Hayamizu, M. Watanabe, How ionic are room-temperature ionic liquids? An indicator of the physicochemical properties, *J. Phys. Chem. B* 110 (2006) 19593–19600, <http://dx.doi.org/10.1021/jp064159v>.
- [55] R.L. Gardas, M.G. Freire, P.J. Carylhalo, I.M. Marrucho, I.M.A. Fonseca, A.G.M. Ferreira, J.A.P. Coutinho, High-pressure densities and derived thermodynamic properties of imidazolium-based ionic liquids, *J. Chem. Eng. Data* 52 (2007) 80–88, <http://dx.doi.org/10.1021/je60247x>.
- [56] C.P. Fredlake, J.M. Crosthwaite, D.G. Hert, S.N.V.K. Aki, J.F. Brennecke, Thermophysical properties of imidazolium-based ionic liquids, *J. Chem. Eng. Data* 49 (2004) 954–964, <http://dx.doi.org/10.1021/je034261a>.
- [57] J. Klomfar, M. Součková, J. Pátek, Temperature dependence measurements of the density at 0.1 MPa for 1-alkyl-3-methylimidazolium-based ionic liquids with the trifluoromethanesulfonate and tetrafluoroborate anion, *J. Chem. Eng. Data* 55 (2010) 4054–4057, <http://dx.doi.org/10.1021/je100185e>.
- [58] 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, <http://dx.doi.org/10.1016/j.molliq.2010.08.005>.
- [59] B.E. Mbondo Tsamba, S. Sarraute, M. Traïkia, P. Husson, Transport properties and ionic association in pure imidazolium-based ionic liquids as a function of temperature, *J. Chem. Eng. Data* 59 (2014) 1747–1754, <http://dx.doi.org/10.1021/je400841s>.
- [60] M.L.S. Batista, L.I.N. Tomé, C.M.S.S. Neves, J.R.B. Gomes, J.A.P. Coutinho, Characterization of systems of thiophene and benzene with ionic liquids, *J. Mol. Liq.* 192 (2014) 26–31, <http://dx.doi.org/10.1016/j.molliq.2013.10.014>.
- [61] G. Mchale, C. Hardacre, R. Ge, N. Doy, R.W.K. Allen, J.M. Macinnes, M.R. Bown, M.I. Newton, Density–viscosity product of small-volume ionic liquid samples using quartz crystal impedance analysis, *Ann. Chem.* 80 (2008) 5806–5811.
- [62] Y. Hiraga, A. Kato, Y. Sato, R.L. Smith, Densities at pressures up to 200 MPa and atmospheric pressure viscosities of ionic liquids 1-ethyl-3-methylimidazolium methylphosphate, 1-ethyl-3-methylimidazolium diethylphosphate, 1-butyl-3-methylimidazolium acetate, and 1-butyl-3-methylimidazolium Bis(, *J. Chem. Eng. Data* 60 (2015) 876–885, <http://dx.doi.org/10.1021/je5009679>.

- [63] M. Kanakubo, K.R. Harris, Density of 1-butyl-3-methylimidazolium bis (trifluoromethanesulfonyl)amide and 1-hexyl-3-methylimidazolium bis (trifluoromethanesulfonyl)amide over an extended pressure range up to 250 MPa, *J. Chem. Eng. Data* 60 (2015) 1408–1418, <http://dx.doi.org/10.1021/je501118w>.
- [64] C.A.N. de Castro, E. Langa, A.L. Morais, M.L.M. Lopes, M.J.V. Lourenço, F.J.V. Santos, M.S.C.S. Santos, J.N.C. Lopes, H.J.M. Veiga, M. Macatrão, J.M.S.S. Esperança, C.S. Marques, L.P.N. Rebelo, C.A.M. Afonso, Studies on the density, heat capacity, surface tension and infinite dilution diffusion with the ionic liquids [C4mim][NTf2], [C4mim][dca], [C2mim][EtOSO3] and [Aliquat][dca], *Fluid Phase Equilib.* 294 (2010) 157–179, <http://dx.doi.org/10.1016/j.fluid.2010.03.010>.
- [65] J. Jacquemin, P. Husson, V. Mayer, I. Cibulka, L. De Thermodynamique, B.P. Cnrs, High-pressure volumetric properties of imidazolium-based ionic liquids: effect of the anion, *J. Chem. Eng. Data* 52 (2007) 2204–2211, <http://dx.doi.org/10.1021/je700224j>.
- [66] E. Widowati, M.J. Lee, P-V-T properties of binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide with anisole or acetophenone at elevated pressures, *J. Chem. Thermodyn.* 63 (2013) 95–101, <http://dx.doi.org/10.1016/j.jct.2013.04.008>.
- [67] M.R. Currás, P. Husson, A.A.H. Pádua, M.F. Costa Gomes, J. García, High-pressure densities of 2,2,2-trifluoroethanol + ionic liquid mixtures useful for possible applications in absorption cycles, *Ind. Eng. Chem. Res.* 53 (2014) 10791–10802, <http://dx.doi.org/10.1021/je5008568>.
- [68] R. Gomes De Azevedo, J.M.S.S. Esperança, J. Szydłowski, Z.P. Visak, P.F. Pires, H. J.R. Guedes, L.P.N. Rebelo, Thermophysical and thermodynamic properties of ionic liquids over an extended pressure range: [bmim][NTf2] and [hmim][NTf2], *J. Chem. Thermodyn.* 37 (2005) 888–899, <http://dx.doi.org/10.1016/j.jct.2005.04.018>.
- [69] R. Hamidova, I. Kul, J. Safarov, A. Shahverdiyev, E. Hassel, Thermophysical properties of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide at high temperatures and pressures, *Braz. J. Chem. Eng.* 32 (2015) 303–316, <http://dx.doi.org/10.1590/0104-6632.20150321s00003120>.
- [70] M. Tariq, A.P. Serro, J.L. Mata, B. Saramago, J.M.S.S. Esperança, J.N.C. Lopes, L.P. N. Rebelo, High-temperature surface tension and density measurements of 1-alkyl-3-methylimidazolium bistriflamide ionic liquids, *Fluid Phase Equilib.* 294 (2010) 131–138, <http://dx.doi.org/10.1016/j.fluid.2010.02.020>.
- [71] J. Jacquemin, P. Nancarrow, D.W. Rooney, M.F. Costa Gomes, P. Husson, V. Majer, A.A.H. Pádua, C. Hardacre, Prediction of ionic liquid properties. I. Volumetric properties as a function of temperature and pressure at 0.1 MPa, *J. Chem. Eng. Data* 53 (2008) 716–726, <http://dx.doi.org/10.1021/je8002817>.
- [72] Q. Zhang, Z. Li, J. Zhang, S. Zhang, L. Zhu, J. Yang, X. Zhang, Y. Deng, Physicochemical properties of nitrile-functionalized ionic liquids, *J. Phys. Chem. B* 111 (2007) 2864–2872, <http://dx.doi.org/10.1021/jp067327s>.
- [73] M. Tariq, P.A.S. Forte, M.F.C. Gomes, J.N.C. Lopes, L.P.N. Rebelo, Densities and refractive indices of imidazolium- and phosphonium-based ionic liquids: effect of temperature, alkyl chain length, and anion, *J. Chem. Thermodyn.* 41 (2009) 790–798, <http://dx.doi.org/10.1016/j.jct.2009.01.012>.
- [74] R.G. Seoane, E.J. González, B. González, 1-Alkyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide ionic liquids as solvents in the separation of azeotropic mixtures, *J. Chem. Thermodyn.* 53 (2012) 152–157, <http://dx.doi.org/10.1016/j.jct.2012.04.026>.
- [75] K.R. Harris, M. Kanakubo, L.A. Woolf, Temperature and pressure dependence of the viscosity of the ionic liquids 1-hexyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium Bis (trifluoromethylsulfonyl)imide, *J. Chem. Eng. Data* 52 (2007) 1080–1085, <http://dx.doi.org/10.1021/je700032n>.
- [76] M. Atilhan, J. Jacquemin, D. Rooney, M. Khraisheh, S. Aparicio, Viscous behaviour of imidazolium-based ionic liquids, *Ind. Eng. Chem. Res.* 52 (2013) 16774–16785, <http://dx.doi.org/10.1021/je403065u>.
- [77] J. Salgado, T. Regueira, L. Lugo, J. Vijande, J. Fernández, J. García, Density and viscosity of three (2,2,2-trifluoroethanol+1-butyl-3-methylimidazolium) ionic liquid binary systems, *J. Chem. Thermodyn.* 70 (2014) 101–110, <http://dx.doi.org/10.1016/j.jct.2013.10.027>.
- [78] K.R. Seddon, A. Stark, M.-J. Torres, Viscosity and density of 1-alkyl-3-methylimidazolium ionic liquids, in: *Clean Solvents*, ACS Symp. Ser., 2002, pp. 34–49. <http://dx.doi.org/10.1021/bk-2002-0819.ch004>.
- [79] M. Tariq, P.J. Carvalho, J.A.P. Coutinho, I.M. Marrucho, J.N.C. Lopes, L.P.N. Rebelo, Viscosity of (C2–C14) 1-alkyl-3-methylimidazolium bis (trifluoromethylsulfonyl)amide ionic liquids in an extended temperature range, *Fluid Phase Equilib.* 301 (2011) 22–32, <http://dx.doi.org/10.1016/j.fluid.2010.10.018>.
- [80] M.S. Calado, Z. Petrovski, M.S. Manic, V. Najdanovic-Visak, E.A. Macedo, Z.P. Visak, Liquid–liquid equilibria of imidazolium ionic liquids having bistriflamide or triflate anions with aromatic non-polar and polar compounds, *Fluid Phase Equilib.* 337 (2013) 67–72, <http://dx.doi.org/10.1016/j.fluid.2012.10.007>.
- [81] S.I. Santos, E. Bogel-Lukasik, R. Bogel-Lukasik, The ionic liquid effect on solubility of aniline, a simple aromatic amine: perspective of solvents' mixture, *Fluid Phase Equilib.* 325 (2012) 105–110, <http://dx.doi.org/10.1016/j.fluid.2012.04.015>.
- [82] R. Garriga, F. Sánchez, P. Pérez, M. Gracia, Excess Gibbs energies at seven temperatures and excess enthalpies and volumes at 298.15 K of butanone with 1-propanol or 2-propanol, *Fluid Phase Equilib.* 124 (1996) 123–134.
- [83] R.B. Törres, A.Z. Francesconi, P.L.O. Volpe, Excess molar volumes of binary mixtures of acetonitrile and chloroalkanes at 298.15 K and atmospheric pressure with application of the ERAS-Model, *Fluid Phase Equilib.* 200 (2002) 1–10, [http://dx.doi.org/10.1016/S0378-3812\(01\)00817-2](http://dx.doi.org/10.1016/S0378-3812(01)00817-2).
- [84] M. Lj Kijevcanin, B.D. Djordjevic, I.R. Radovic, E.M. Živkovic, A.Ž. Tasic, S.P. Šerbanovic, Modeling of volumetric properties of organic mixtures based on molecular interactions, (n.d.).
- [85] I. Fischer, Dipole moments of some ortho-substituted anilines, *Nature* 165 (1950) 239, <http://dx.doi.org/10.1038/165239a0>.
- [86] M.H. Abraham, P.L. Grellier, D.V. Prior, P.P. Duce, J.J. Morris, P.J. Taylor, Hydrogen bonding. Part 7. A scale of solute hydrogen-bond acidity based on log K values for complexation in tetrachloromethane, *J. Chem. Soc. Perkin Trans. 2* (1989) 699–711.
- [87] M.H. Abraham, P.L. Grellier, D.V. Prior, J.J. Morris, P.J. Taylor, Hydrogen Bonding. Part 10. A Scale of Solute Hydrogen-bond Basicity using log K Values for Complexation in Tetrachloromethane, *J. Chem. Soc. Perkin Trans. 2* (1990) 521–529.
- [88] M.A. Ab Rani, A. Brant, L. Crowhurst, A. Dolan, M. Lui, N.H. Hassan, J.P. Hallett, P.A. Hunt, H. Niedermeyer, J.M. Perez-Arlandis, M. Schrems, T. Welton, R. Wilding, Understanding the polarity of ionic liquids, *Phys. Chem. Chem. Phys.* 13 (2011) 16831–16840, <http://dx.doi.org/10.1039/c1cp21262a>.
- [89] M. Blesic, J.N.C. Lopes, A.A.H. Pádua, K. Shimizu, M.F.C. Gomes, L.P.N. Rebelo, Phase equilibria in ionic liquid-aromatic compound mixtures, including benzene fluorination effects, *J. Phys. Chem. B* 113 (2009) 7631–7636, <http://dx.doi.org/10.1021/jp902178g>.
- [90] A.R. Ferreira, M.G. Freire, J.C. Ribeiro, F.M. Lopes, J.G. Crespo, J.A.P. Coutinho, An overview of the liquid–liquid equilibria of (ionic liquid + hydrocarbon) binary systems and their modeling by the conductor-like screening model for real solvents, *Ind. Eng. Chem. Res.* 50 (2011) 5279–5294, <http://dx.doi.org/10.1021/ie102471b>.
- [91] W. Gordy, Spectroscopic evidence of hydrogen bonds: Aniline and some substituted phenols, *J. Chem. Phys.* 7 (1939) 167–171.
- [92] H. Kehiaian, K. Sosnkowska-Kehiaian, Thermodynamic properties of some binary mixtures of specifically interacting non-electrolytes: Part 1. – Aniline + toluene, *Trans. Faraday Soc.* 62 (1966) 838–847.
- [93] A.M. Fernandes, M.A.A. Rocha, M.G. Freire, I.M. Marrucho, J.A.P. Coutinho, L.M. N.B.F. Santos, Evaluation of cation-anion interaction strength in ionic liquids, *J. Phys. Chem. B* 115 (2011) 4033–4041, <http://dx.doi.org/10.1021/jp201084x>.
- [94] R. Bini, O. Bortolini, C. Chiappe, D. Pieraccini, T. Siciliano, Development of cation/anion “interaction” scales for ionic liquids through ESI-MS measurements, *J. Phys. Chem. B* 111 (2007) 598–604, <http://dx.doi.org/10.1021/jp0663199>.
- [95] B. Schwenzer, S.N. Kerisit, M. Vijayakumar, Anion pairs in room temperature ionic liquids predicted by molecular dynamics simulation, verified by spectroscopic characterization, *RSC Adv.* 4 (2014) 5457–5464, <http://dx.doi.org/10.1039/c3ra46069j>.
- [96] A. Yokozeki, D.J. Kasprzak, M.B. Shiflett, Thermal effect on C-H stretching vibrations of the imidazolium ring in ionic liquids, *Phys. Chem. Chem. Phys.* 9 (2007) 5018–5026, <http://dx.doi.org/10.1039/b706497g>.
- [97] R.P.M. Mayer, R. Mayer, J. Metzger, Étude comparative entre les enthalpies libres d'activation du flot visqueux et les enthalpies libres d'excès de solution, in: *ÉTUDE Thermodyn. DES MÉLANGES Bin. Chim. Phys.*, 1971, pp. 406–412.
- [98] M.A. Chowdhury, M.A. Majid, M.A. Saleh, Volumetric and viscometric behaviour of binary systems: (1-hexanol + hydrocarbons), *J. Chem. Thermodyn.* 33 (2001) 347–360, <http://dx.doi.org/10.1006/jct.2000.0751>.