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

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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][NTf₂])} 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 ΔG^{*E} were calculated and the results were fitted to a Redlich-Kister polynomial equation. Also, enthalpic and entropic parts of the ΔG^{*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.

Keywords: density; viscosity; excess molar Gibbs free energy; aniline; *N*, *N*-dimethylaniline; ionic liquids

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]⁻) or bistriflamide ([NTf₂]⁻) 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][NTf₂])}. 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 ΔG^{*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.

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 ρ and viscosities η 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 Figures 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.

Table 1 – Sample Description

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

Table 2 - Densities ρ and Viscosities η of the Pure Components at Temperature T and at Atmospheric Pressure (0.1 MPa)^a

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

^aStandard uncertainties u are: $u(T) = 0.01$ K; $u(p) = 0.005$ MPa; $u(\rho) = 1$ kg·m⁻³, and relative standard uncertainty $u_r(\eta) = 2.2$ %, with a level of confidence of 68%. ^bAlonso *et al.* [29]; ^cTsierkezos *et al.* [30]; ^dKatz *et al.* [31]; ^eKharat and Nikam [32]; ^fZubinand Naved [33]; ^gArce *et al.* [34]; ^hVraneš *et al.* [35]; ⁱDominguez *et al.* [36].

2.2 Apparatus and procedures

Experimental measurements of density ρ were performed by an Anton Paar DMA 5000 digital vibrating U-tube densimeter. Viscosities η 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 1×10^{-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⁻³ and $\pm 3 \times 10^{-3}$ mPas, respectively. However, average standard uncertainty of the measured densities was estimated to be 1 kg·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 $3 \cdot 10^{-3}$ mPas for less viscous fluids and 1.2 mPas 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 equation (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.

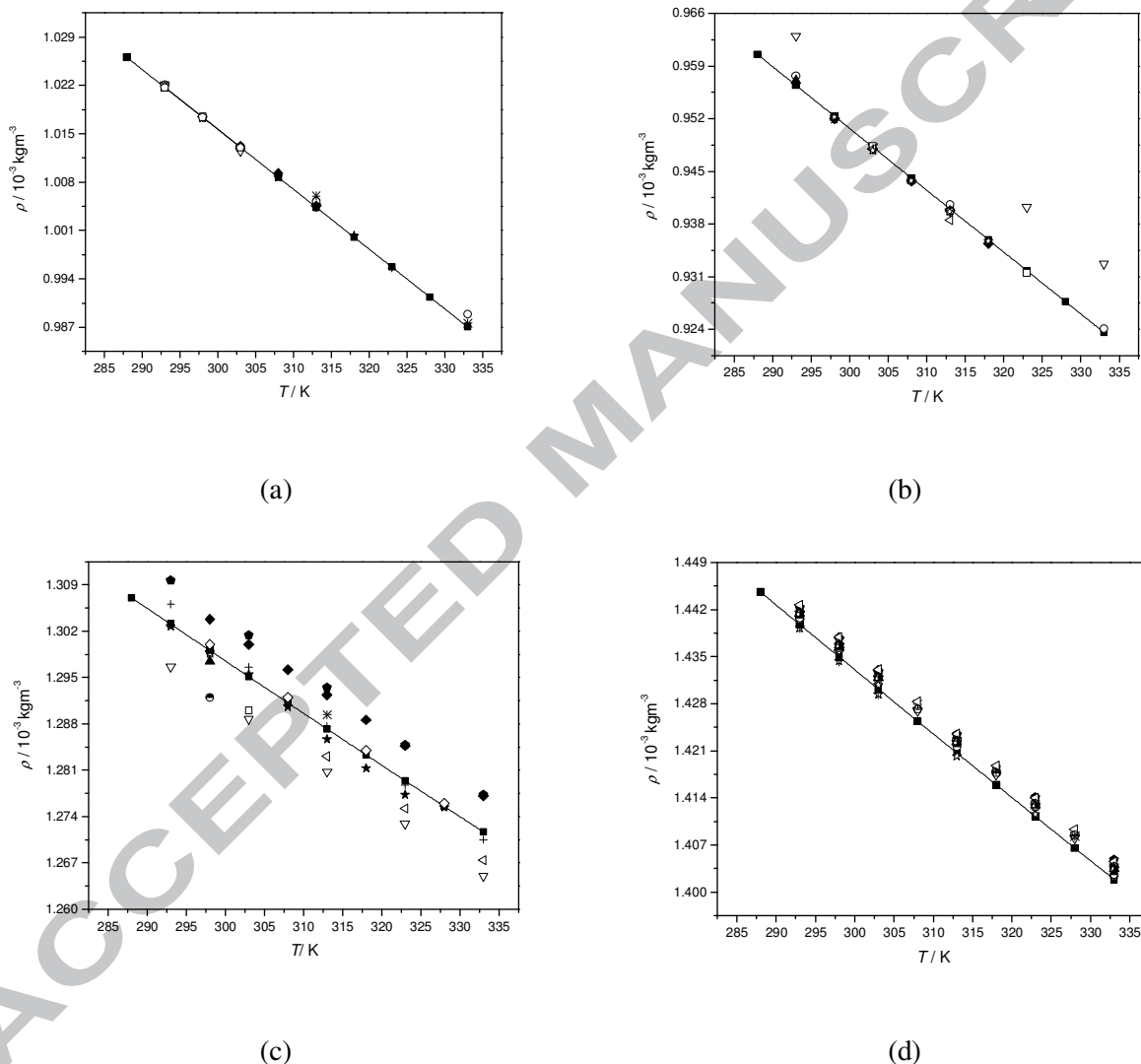
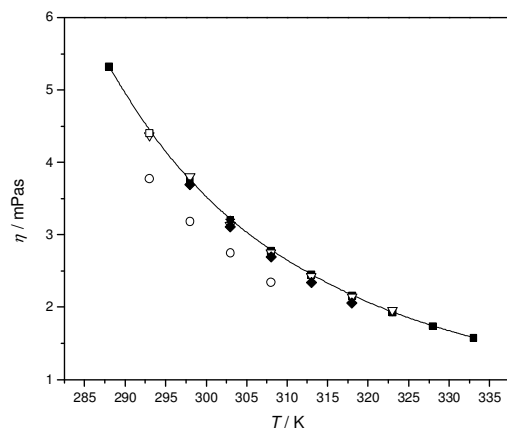
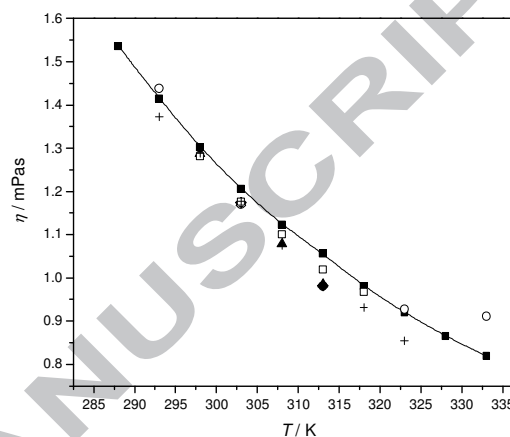


Figure 1 – Comparison of the current experimental density values (—) vs. temperature with literature values for pure: (a) aniline- (□) Vogel *et al.* [39]; (●) Sumer *et al.* [40]; (⊙) Katz *et al.* [41]; (⊗) Kumar *et al.* [42]; (⊕) Almasi *et al.* [43]; (⊖) Costello *et al.* [44]; (⊗) MacNeil *et al.* [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]; (⊗) Zubin and Naved [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.*

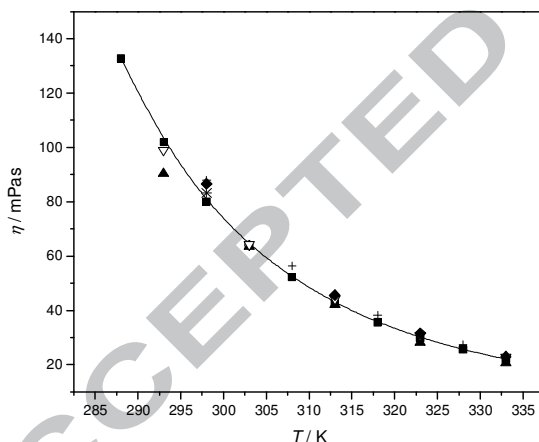
[59]; (●) Batista et al. [60]; (■) McHale et al. [61]; (□) Arce et al. [34]; (d) [bmim][NTf2] - (□) Hiraga et al. [62]; (▨) Kanakubo et al. [63]; (♣) de Castro et al. [64]; (⊙) Jacquemin et al. [65]; (⋈) Widowati et al. [66]; (⊕) Currás et al. [67]; (⊖) Azevedo et al. [68]; (⊗) Hamidova et al. [69]; (⊛) 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].



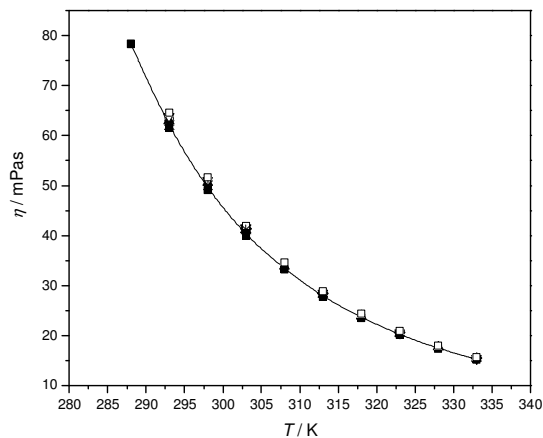
(a)



(b)



(c)



(d)

Figure 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]; (⊕) Zubinand Naved [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][NTf2] - (□) Hiraga et al. [62]; (▨) Tariq et al. [79]; (♣) Harris et al. [75]; (⊙) Atilhan et al. [76]; (⋈) Salgado et al. [77]; (●) Vraneš et al. [35].

3. Results

The experimental values of densities ρ and viscosities η and the calculated values of the excess molar volumes V^E , viscosity deviations $\Delta\eta$ and excess molar Gibbs energies of activation of viscous flow ΔG^{*E} of four binary mixtures in temperature range $T = (288.15$ to $333.15)$ 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 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 Figure S1.

Table 3 - Density ρ , Viscosity η , Excess Molar Volumes V^E , Viscosity Deviations $\Delta\eta$, excess Gibbs energy of activation of viscous flow ΔG^{*E} for the investigated binary systems in Temperature Range $T = (288.15$ to $333.15)$ K and at Atmospheric Pressure (0.1 MPa)^a

x_1	$10^{-3} \cdot \rho /$ $\text{kg} \cdot \text{m}^{-3}$	$10^6 \cdot V^E /$ $\text{m}^3 \cdot \text{mol}^{-1}$	$\eta /$ $\text{mPa} \cdot \text{s}$	$\Delta\eta /$ $\text{mPa} \cdot \text{s}$	$\Delta G^{*E} /$ $\text{kJ} \cdot \text{kmol}^{-1}$
Aniline (1) + [bmim][OTf] (2)					
$T = 288.15$ K					
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		
$T = 293.15$ K					
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		
$T = 298.15$ K					
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		
			$T = 303.15 \text{ K}$		
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		
			$T = 308.15 \text{ K}$		
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		
			$T = 313.15 \text{ K}$		
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		
			$T = 318.15 \text{ K}$		
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		
			$T = 323.15 \text{ K}$		
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		
			$T = 328.15 \text{ K}$		
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		
			$T = 333.15 \text{ K}$		
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
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		

Anilin (1) + [bmim][NTf₂] (2)

$T = 288.15 \text{ K}$

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		
$T = 293.15 \text{ K}$					
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		
$T = 298.15 \text{ K}$					
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		
$T = 303.15 \text{ K}$					
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		
$T = 308.15 \text{ K}$					
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		
$T = 313.15 \text{ K}$					
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		
$T = 318.15 \text{ K}$					
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)					
<i>T</i> = 288.15 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		
<i>T</i> = 293.15 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		
<i>T</i> = 298.15 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		
<i>T</i> = 303.15 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		

$T = 328.15 \text{ K}$

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		
N, N -dimethylaniline (1) + [bmim][NTf ₂] (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		
			$T = 308.15 \text{ K}$		
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		

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

The excess molar volumes V^E were calculated using the experimental densities ρ of binary mixtures and the pure components ρ_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 η_i and mixture η , 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, ΔG^{*E} , were calculated combining the obtained volumetric and viscosity values, following the equation:

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

In equation (3) η 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 equations (2)-(4) were correlated with Redlich-Kister (RK) polynomial equation [28]:

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

In equation (5) Y represents V^E , $\Delta\eta$ or ΔG^{*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) σ , 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 equation (6), m equals the number of experimental data points.

Table 4 - Parameters A_p of equation (4) and the corresponding RMSD σ for binary mixtures aniline + [bmim][OTf], aniline + [bmim][NTf₂], *N,N*-dimethylaniline + [bmim][OTf] and *N,N*-dimethylaniline + [bmim][NTf₂] at temperature T and at atmospheric pressure (0.1 MPa)

	T/K	A_0	A_1	A_2	A_3	A_4	σ
Aniline (1) + [bmim][OTf] (2)							
$10^6 \cdot V^E / \text{m}^3 \cdot \text{mol}^{-1}$	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
$\Delta\eta / \text{mPa} \cdot \text{s}$	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
$\Delta G^{*E}/\text{kJ}\cdot\text{kmol}^{-1}$	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

Anilin (1) + [bmim][NTf₂] (2)

$10^6\cdot V^E/\text{m}^3\cdot\text{mol}^{-1}$	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
$\Delta\eta/\text{mPa}\cdot\text{s}$	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
$\Delta G^{*E}/\text{kJ}\cdot\text{kmol}^{-1}$	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

N,N-dimethylaniline (1) + [bmim][OTf] (2)

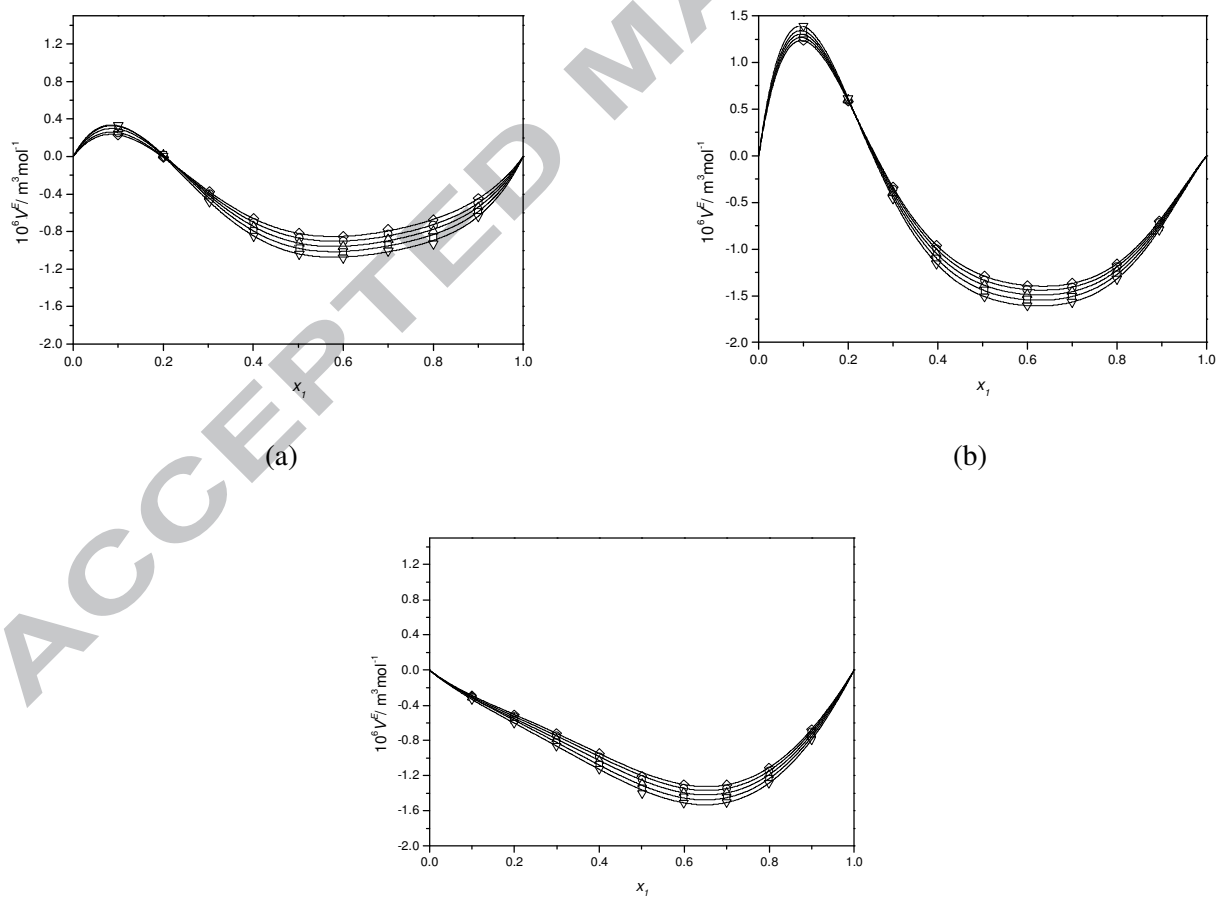
$10^6\cdot V^E/\text{m}^3\cdot\text{mol}^{-1}$	288.15	-5.1289	-3.7663	4.5686	-14.7340	13.1024	0.0002
	293.15	-5.2131	-3.7880	4.6294	-14.8872	13.2061	0.0004
	298.15	-5.3073	-3.7884	4.6846	-15.2668	13.5444	0.0002
	303.15	-5.4098	-3.7939	4.7082	-15.5494	13.8445	0.0002
	308.15	-5.5214	-3.7914	4.7595	-15.8950	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
$\Delta\eta/\text{mPa}\cdot\text{s}$	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
$\Delta G^{*E}/\text{kJ}\cdot\text{kmol}^{-1}$	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

N,N-dimethylaniline (1) + [bmim][NTf₂] (2)

$10^6\cdot V^E/\text{m}^3\cdot\text{mol}^{-1}$	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
$\Delta G^{*E}/\text{kJ}\cdot\text{kmol}^{-1}$	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

Excess molar volumes obtained from the experimental values and those calculated using the RK polynomial are presented in Figure 3, as a function of amine mole fraction x_1 . The systems {aniline + [C₄mim][NTf₂]} and {*N,N*-dimethylaniline + [C₄mim][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 (Figure3(a) and (b)). System {*N,N*-dimethylaniline + [bmim][NTf₂]} (Figure3(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 [82,83] and, thus, its presentation is not given graphically. For all systems, absolute V^E values in the minima regions increase with increasing temperature from 288.15 K to 333.15 K.



(c)

Figure 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][NTf₂](2); (b) *N,N*-dimethylaniline(1) + [bmim][OTf] (2); (c) *N,N*-dimethylaniline(1) + [bmim][NTf₂](2) at following temperatures: (◇) 288.15 K, (○) 298.15 K, (△) 308.15 K, (□) 318.15 K, (▽) 328 K, (—) RK equation.

Viscosity deviations are plotted vs. x_1 mole fractions along with the values calculated from the RK polynomial (Figure 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.

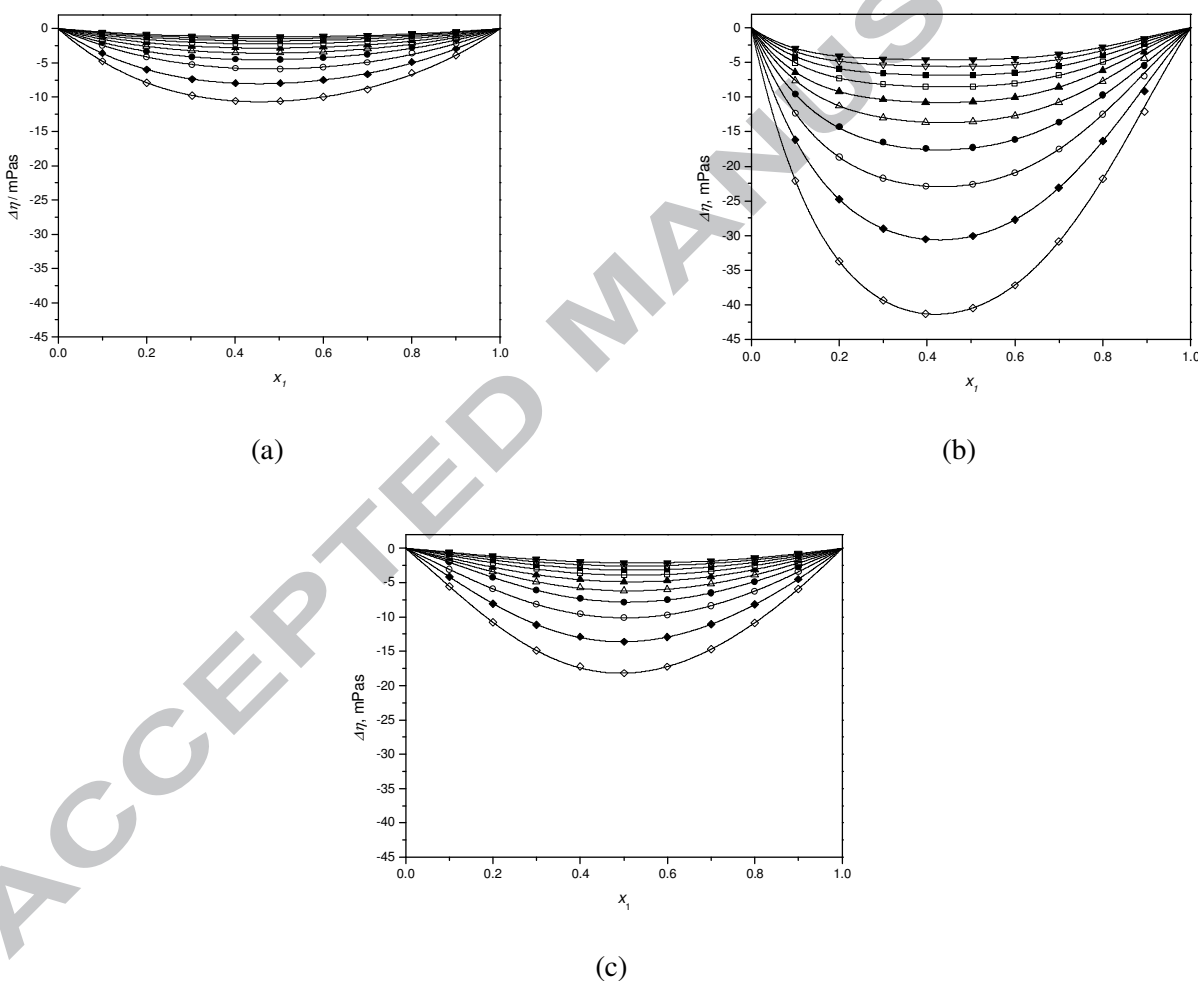


Figure 4 - Experimental values of viscosity deviation $\Delta\eta$ as a function of aniline / *N,N*-dimethylaniline mole fraction x_1 for the systems: (a) aniline (1) + [bmim][NTf₂](2); (b) *N,N*-dimethylaniline(1) + [bmim][OTf] (2); (c) *N,N*-dimethylaniline(1) + [bmim][NTf₂](2) at following temperatures: (◇) 288.15

K, (◆) 293.15 K, (○) 298.15 K, (●) 303.15 K, (Δ) 308.15 K, (▲) 313.15 K, (□) 318.15 K, (■) 323.15 K, (▽) 328 K, (▼) 333 K, (—) RK equation.

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

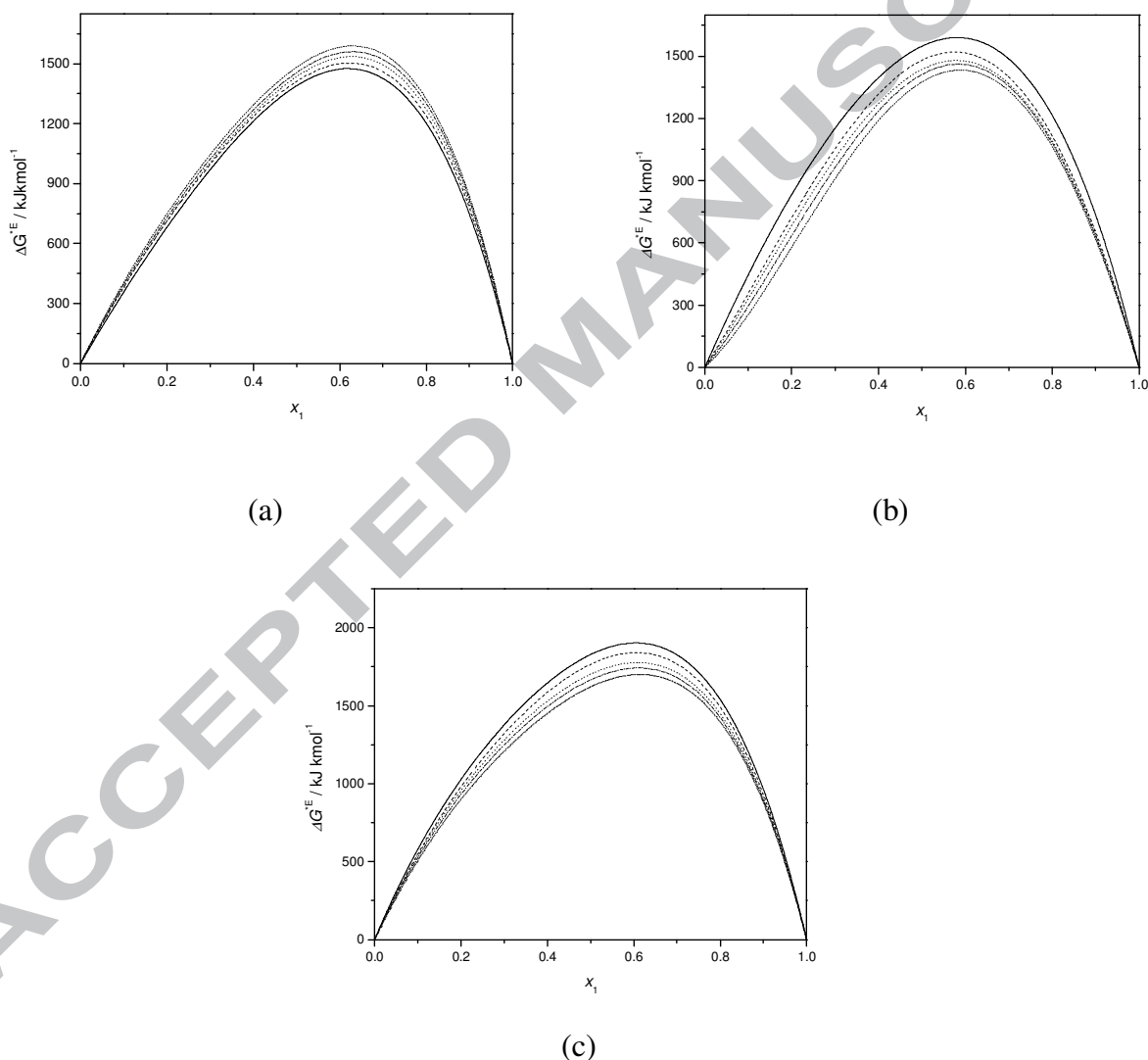


Figure 5 - RK lines of excess molar Gibbs energy of activation of viscous flow ΔG^{*E} as a function of aniline / *N,N*-dimethylaniline mole fraction x_1 for the systems: (a) aniline (1) + [bmim][NTf₂] (2); (b) *N,N*-dimethylaniline (1) + [bmim][OTf] (2); (c) *N,N*-dimethylaniline (1) + [bmim][NTf₂] (2) at following temperatures: (—) 288.15 K, (–) 298.15 K, (⋯) 308.15 K, (-.-.-) 318.15 K, (- - -) 333 K.

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 [83–86].

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 [87], 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 α (HBD ability) and hydrogen bond basicity β (HBA ability) parameters of aniline given in Table 5). However, without the available hydrogen atoms, *N,N*-dimethylaniline is only a hydrogen bond acceptor (α value is zero, Table 5). Thus, both aniline and *N,N*-dimethylaniline can form hydrogen bonds with aniline having more possibilities in this respect.

Table 5 - Dipole Moments and Hydrogen Bond Acidity and Basicity for the Studied Solvents and Solutes

Chemical	α	β	μ/D
Aniline	0.264 ^a	0.38 ^b	1.51 ^c
<i>N,N</i> -dimethylaniline	0.00 ^a	0.35 ^b	1.61 ^c
[bmim][OTf]	0.625 ^d	0.464 ^d	-
[bmim][NTf ₂]	0.617 ^d	0.243 ^d	-

^aAbraham *et al.*[88], ^bAbraham *et al.*[89], ^cFischer[87]; ^dCrowhurst *et al.*[18];

For the ionic liquids the situation is far more complex, considering their features listed in the introduction. Imidazolium based ILs [C₄mim][OTf] and [C₄mim][NTf₂] 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 (α) listed in Table 5, in which their cations play the principle role [18,90]. Further on, both studied ionic liquids are also proton acceptors through their anions (the respective hydrogen bond basicities β given in Table 5 are mainly anion controlled [18,90]). 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 $[\text{NTf}_2]^-$ anion compared to $[\text{OTf}]^-$, mainly due to higher number of oxygen atoms [91]. Thus, aromatic compounds exhibit better solubility in the imidazolium ionic liquids having $[\text{NTf}_2]^-$ anions [82,91,92].

Interactions between the like-molecules in the studied solutions deserve attention as well. Thus, the shifts in vibration bands of the NH_2 -group to shorter wave-lengths [93] 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 [94]. 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 [95,96] show that the overall cation-anion interactions are stronger for the $[\text{C}_n\text{mim}][\text{OTf}]$ than for the $[\text{C}_n\text{mim}][\text{NTF}_2]$ 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 $[\text{C}_4\text{mim}][\text{OTf}]$ on the molecular level [97] reveals that anion pairing occurs through the CF_3 moieties of the two $[\text{OTf}]^-$ anions. So, two anions are surrounded by a cation cage that is composed of nine $[\text{C}_n\text{mim}]^+$ cations, in average. An analysis of the $[\text{C}_n\text{mim}][\text{NTf}_2]$ by the infra-red (IR) spectroscopy revealed both association of imidazolium ions in ion pairs or clusters and their dissociation into free ions or smaller clusters [98]. From these two studies one can conclude that the association through ion-pairing may be stronger in the $[\text{C}_4\text{mim}][\text{OTf}]$ than in $[\text{C}_4\text{mim}][\text{NTf}_2]$ 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 (Figure 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).

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 (ΔG^{*E}), entropy (ΔS^{*E}), enthalpy (ΔH^{*E}) and entropy-related energetic term $T\Delta S^{*E}$

$\Delta G^{*E} / \text{kJ}\cdot\text{kmol}^{-1}$	$\Delta S^{*E} / \text{kJ}\cdot\text{kmol}^{-1}\cdot\text{K}^{-1}$	$T\Delta S^{*E} / \text{kJ}\cdot\text{kmol}^{-1}$	$\Delta H^{*E} / \text{kJ}\cdot\text{kmol}^{-1}$	V_{m2}/V_{m1}^a
Aniline (1) + [C ₄ mim][NTf ₂] (2)				
1492.17	-2.3305	-694.49	797.68	3.2
<i>N,N</i> -dimethylaniline(1)+[C ₄ mim][OTf](2)				
1475.32	3.3617	1001.79	2477.11	1.7
<i>N,N</i> -dimethylaniline (1)+ [C ₄ mim][NTf ₂] (2)				
1826.6	4.5628	1359.71	3186.31	2.3

^aMolar volume ratio at 298.15 K

However, the positive V^E values seen in Figures 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][NTf₂] compared to the positive ones in the *N,N*-dimethylaniline+[bmim][OTf] system (see Figures 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.* [99] stated that the sign of the excess molar Gibbs energy of activation of viscous flow ΔG^{*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: 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 equation (4) shows, includes both volumetric and viscosity data thus establishing a more complete resort to the interaction analysis and discussion. However, along with the ΔG^{*E} function, it is also important to consider enthalpy and entropic contributions to ΔG^{*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 ΔG^{*E} via equation (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, Figure 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 ΔG^{*E} and ΔH^{*E} indicate strong attractive interactions in three mixtures, particularly in the system *N,N*-dimethylaniline+[Bmim][NTf₂] and are in the agreement with the values of the negative excess molar volumes presented in Figure 3. Negative excess molar

entropies of activation of viscous flow for the system aniline+[Bmim][NTf₂] are mainly the consequence of the difference in the size of the molecules and make an important contribution to the positive value of ΔG^{*E} .

Negative deviations in viscosity presented in Figure 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 [100]. 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 ρ and viscosity η values for four binary mixtures {aniline + [bmim][OTf]}, {*N, N*-dimethylaniline + [bmim][OTf]}, {aniline + [bmim][NTf₂]} and {*N, N*-dimethylaniline + [bmim][NTf₂]}, 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^E , deviation functions of viscosity $\Delta\eta$, as well as excess molar Gibbs energies of activation of viscous flow ΔG^{*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^E , as well positive excess molar Gibbs energies ΔG^{*E} and excess molar enthalpies of activation of viscous flow ΔH^{*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 ΔG^{*E} in the case of the system {aniline+[Bmim][NTf₂]} 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.

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- Measurements of densities and viscosities of aniline / *N,N*-dimethylaniline + ionic liquids mixtures.
- Detailed thermodynamic interpretation of molecular interaction is performed.
- Strong attractive interactions in three completely miscible mixtures are present, particularly in the system *N,N*-dimethylaniline + [Bmim][NTf₂].
- Aniline + [bmim][OTf] exhibits partial miscibility due to aniline association and weaker cation/anion interactions of IL with aniline ring.