

Physical properties and phase equilibria of the system isopropyl acetate + isopropanol + 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide

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ABSTRACT

Densities, refractive indices and dynamic viscosities of binary and ternary mixtures composed of isopropyl acetate, isopropanol, 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ($[C_8\text{mim}][\text{NTf}_2]$) have been determined at 298.15 K and atmospheric pressure. The excess molar volumes and dynamic viscosity changes of mixing have been calculated and correlated using the Redlich–Kister polynomial equation. Isobaric vapour–liquid equilibrium (VLE) data have been determined experimentally for these binary and ternary systems at 101.32 kPa. The equilibrium data have been adequately correlated by means of Wilson, NRTL, and UNIQUAC equations for the liquid phase activity coefficient.

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1. Introduction

Ionic liquids offer alternatives to conventional molecular solvents in many industrial processes. These solvents are often fluid at room temperature, and commonly consist of organic cationic species and inorganic species; they have no measurable vapour pressure and hence can emit no Volatile Organic Compounds [1].

An important use of ionic liquids in the industry is its use as replacement of volatile organic solvents in the separation of azeotropic mixtures, which offers several advantages such as avoiding possible solvent losses to the atmosphere, less complex processes and a simpler regeneration of the solvent [2].

Separation of isopropyl acetate and isopropanol by common distillation is not possible because they form a minimum boiling point azeotrope [3,4], but a modified distillation using $[C_8\text{mim}][\text{NTf}_2]$ as entrainer could be used for this aim. That is the reason for which we have afforded a thermodynamic study on binary and ternary mixtures of isopropyl acetate, isopropanol and $[C_8\text{mim}][\text{NTf}_2]$.

In this work, densities, refractive indices and dynamic viscosity for the mixtures of isopropyl acetate, isopropanol and

1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ($[C_8\text{mim}][\text{NTf}_2]$) at 298.15 K and atmospheric pressure were determined. Using these experimental properties, excess molar volumes, and dynamic viscosity changes of mixing were calculated and correlated by means of Redlich–Kister polynomial [5]. Also isobaric vapour–liquid equilibrium (VLE) at 101.32 kPa of the binary and ternary systems were determined and correlated by means of the Wilson [6], NRTL [7] and UNIQUAC [8] equations.

2. Experimental

2.1. Materials

The ionic liquid used in this work, 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide, $[C_8\text{mim}][\text{NTf}_2]$, was synthesized in our laboratory following the published procedure [9]. To reduce the water content to negligible values (lower than 36 ppm determined using 756 Karl–Fisher Coulometer), high vacuum and moderate temperature (353.15 K) were applied to the IL several days, always immediately prior to their use. The chloride concentration was 15 ppm measured by means of the capillary electrophoresis. The ionic liquid was analyzed by ^1H and ^{13}C NMR (Supplementary Material) to confirm the absence of any major impurities. Estimated purity is >99.5 mass%.

Isopropanol and isopropyl acetate were supplied by Sigma–Aldrich and had nominal purities >99.5 and 99.6 mass%,

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Component	CASRN ^a	$10^{-6}\omega$ (H ₂ O)	ρ (g cm ⁻³)	n_D		η (mPas)		T_b (K)	
				This work	Literature	This work	Literature	This work	Literature
Isopropyl acetate	108-21-4	98.225	0.86621	0.8702 [10], 0.86625 [15]	1.37480	1.3750 [10]	0.481	361.45	361.751 [10], 361.54 [13], 361.54 [14]
Isopropanol	67-63-0	174.93	0.78088	0.78126 [10], 0.781152 [16]	1.37502	1.3752 [10]	2.073	355.37	355.392 [10]
[C ₈ mim][NTf ₂]	178631-04-4	35.93	1.32076	[9], 1.321 [11], 1.321 [12]	1.43298	1.43331 [9]	92.51	—	—

^a CASRN, Chemical Abstract Service Registry Number.

respectively. Gas chromatography (GC) analysis did not detect any appreciable peak of impurities. Information about the pure components, experimental densities, refractive indices, and viscosities, at 298.15 K and boiling temperatures at 101.32 kPa is shown in Table 1 together with published values for these parameters [9–16].

2.2. Measurements

All weighing was carried out on a Mettler Toledo AT261 balance with an uncertainty of $\pm 10^{-4}$ g. Water contents were measured using a Karl–Fisher titrator in a Metrohm 737 KF coulometer. Densities of the pure liquids and mixtures were measured in an Anton Paar DMA 5000 densimeter with viscosity correction and with self-control of temperature to ± 0.01 K using Peltier effect. The uncertainty in the density measured is $\pm 10^{-5}$ g cm⁻³. Refractive indices were measured in an ATAGO RX-5000 refractometer with Hero Therm thermostat to maintain the temperature at 298.15 ± 0.02 K. The uncertainty in the refractive index measurement is $\pm 4 \times 10^{-5}$.

The kinematic viscosity was determined by Ubbelohde microviscometer. Three viscometers (capillaries type I, II and III) were used in the experiments according to the different viscosity values of the mixtures. The capillaries are calibrated and credited by the company and then checked by ourselves measuring the viscosity of different pure liquids. Flow time measurements are performed by Lauda Processor Viscosity System PVS1 with a resolution of 0.01 s. The temperature of the viscometer was kept constant using a Lauda clear view thermostat D 20 KP with a through-flow cooler DLK 10, being the uncertainty of measurements ± 0.005 K. Viscosity measurements were repeated at least three times for each sample and were found to be repeatable to within 0.03 s for times less than 100 s and ± 0.5 s for bigger times. Kinematic viscosity of solution ν is given by

$$\nu = K(t - y) \quad (1)$$

where ν is the kinematic viscosity, t is the flow time, K , is the capillary constant provided by manufacturer and y is the kinetic energy correction used if necessary. Dynamic viscosities are calculated from kinematic viscosities and densities. The uncertainty for the dynamic viscosity determination is estimated to be $\pm 0.5\%$.

Vapour–liquid equilibria (VLE) data are determined in a Labodes 602 Distillation apparatus that recycles both liquid and vapour phases (Fischer Labor und Verfahrenstechnik, Germany). This still is equipped with a Fischer digital manometer that measure to within ± 0.01 kPa and an ASL F250 Mk II Precision Thermometer, operating with a wired PT100 PRT, that provides the temperature of the system with an overall accuracy of ± 0.02 K. Distillation is carried out at 101.32 kPa under inert argon atmosphere. The compositions of the phases in equilibrium were determined using the densities and refractive indices measurements as analysis method. The precision of this method to obtain the composition was determined using test samples prepared by weighing: the maximum deviation between the measured and true composition was ± 0.002 mole fraction.

3. Results and data treatment

3.1. Physical properties

Experimental values obtained for densities, ρ , dynamic viscosities η , and refractive indices n_D of mixtures with isopropanol, isopropyl acetate and [C₈mim][NTf₂] at 298.15 K at atmospheric pressure are listed in Tables 2 and 3. These tables also include the calculated values of excess molar volumes V^E and viscosity changes of mixing $\Delta\eta$, calculated by means of the following expressions;

Table 2

Densities, ρ ; excess molar volumes, V^E ; refractive indices, n_D ; dynamic viscosities, η ; viscosity changes of mixing, $\Delta\eta$ for binary systems at 298.15 K and atmospheric pressure.

x_1	ρ (g cm ⁻³)	n_D	η (mPa s)	V^E (cm ³ mol ⁻¹)	$\Delta\eta$ (mPa s)
Isopropyl acetate (1)+isopropanol (2)					
0.1199	0.79354	1.37417	1.278	0.213	-0.605
0.2041	0.80203	1.37374	1.021	0.311	-0.727
0.2940	0.81058	1.37344	0.812	0.388	-0.794
0.3802	0.81832	1.37330	0.722	0.442	-0.746
0.4855	0.82739	1.37331	0.635	0.460	-0.665
0.5877	0.83568	1.37339	0.563	0.452	-0.575
0.7138	0.84552	1.37369	0.538	0.376	-0.399
0.7681	0.84964	1.37383	0.515	0.322	-0.336
0.8777	0.85756	1.37419	0.500	0.203	-0.176
Isopropyl acetate (1)+[C ₈ mim][NTf ₂] (2)					
0.0415	1.31443	1.43222	81.81	-0.051	-6.878
0.0984	1.30577	1.43130	70.33	-0.222	-13.12
0.1644	1.29472	1.43009	58.16	-0.403	-19.22
0.2055	1.28714	1.42923	51.89	-0.491	-21.70
0.3010	1.26767	1.42702	38.25	-0.732	-26.56
0.3956	1.24468	1.42458	26.57	-0.912	-29.54
0.4996	1.21435	1.42091	17.09	-1.125	-29.44
0.5837	1.18433	1.41742	11.42	-1.243	-27.37
0.7048	1.12929	1.41083	5.785	-1.356	-21.86
0.8036	1.06865	1.40324	2.993	-1.277	-15.56
0.8991	0.98894	1.39275	1.389	-0.978	-8.374
Isopropanol (1)+[C ₈ mim][NTf ₂] (2)					
0.0331	1.31664	1.43251	85.24	0.009	-4.280
0.0660	1.31240	1.43205	78.10	0.042	-8.445
0.1050	1.30722	1.43149	71.48	0.045	-11.53
0.1823	1.29584	1.43031	60.13	0.046	-15.88
0.2732	1.28029	1.42862	47.98	0.038	-19.83
0.3284	1.26948	1.42746	39.87	0.010	-22.94
0.4097	1.25088	1.42551	33.13	-0.002	-22.33
0.5055	1.22413	1.42269	24.79	-0.056	-22.00
0.5848	1.19642	1.41988	19.09	-0.115	-20.53
0.6747	1.15599	1.41568	13.79	-0.174	-17.70
0.7832	1.08754	1.40856	8.606	-0.268	-13.07
0.8966	0.97252	1.39645	4.615	-0.278	-6.806

Excess molar volumes, V^E :

$$V^E = V_M - \sum_i x_i V_i \quad (2)$$

where V_i represents the molar volume of pure component i and V_M refers to the molar volume of the mixture calculated as

$$V_M = \sum_i \frac{x_i M_i}{\rho} \quad (3)$$

here x_i and M_i are the mole fraction of component i in the mixture and its molar mass.

The viscosity changes of mixing, $\Delta\eta$:

$$\Delta\eta = \eta_M - \sum_i x_i \eta_i \quad (4)$$

where η_M is the dynamic viscosity of the mixture and η_i , the viscosity for the component i .

Fig. 1 shows the excess molar volumes and viscosity changes of mixing for the three binary systems: isopropyl acetate (1)+isopropanol (2), Fig. 1(a); isopropyl acetate (1)+[C₈mim][NTf₂] (2), Fig. 1(b); isopropanol (1)+[C₈mim][NTf₂] (2), Fig. 1(c). For the ternary system, Fig. 2 shows the isolines corresponding to: (a) density, (b) refractive index and (c) dynamic viscosity and Fig. 3 shows (a) the isolines of excess molar volumes and (b) the isolines of the viscosity changes of mixing. No comparable data were found in the survey literature for the binary and ternary systems.

3.1.1. Correlation of physical properties

The calculated data for V^E and $\Delta\eta$ were correlated with the composition data, x_i , by Redlich-Kister polynomial [5], which for binary

mixtures is

$$Q_{ij} = x_i x_j \sum_k A_k (x_i - x_j)^k \quad (5)$$

where Q_{ij} is V^E or $\Delta\eta$, x_i is the mole fraction of component i , A_k is the polynomial coefficient, and k is the number of the polynomial coefficient. For ternary systems the corresponding equation is

$$Q_{123} = Q_{12} + Q_{23} + Q_{13} + x_1 x_2 x_3 \left(\begin{array}{l} A + B(x_1 - x_2) + C(x_2 - x_3) + D(x_1 - x_3) + \\ E(x_1 - x_2)^2 + F(x_2 - x_3)^2 + G(x_1 - x_3)^2 + \dots \end{array} \right) \quad (6)$$

where Q_{123} represents V^E or $\Delta\eta$ for the ternary mixture isopropyl acetate (1)+isopropanol (2)+[C₈mim][NTf₂] (3) and Q_{ij} is the Redlich-Kister polynomial for the same property fitted to the binary systems data.

Eqs. (5) and (6) were fitted to the appropriate parameter-composition data for the binary and ternary systems by least-squares regression, applying Fisher's *F*-test [17] to establish the number of coefficients. These coefficients and their mean standard deviations are listed in Table 4 for the binary systems and Table 5 for the ternary system. The mean standard deviation was calculated by the usual equation

$$\sigma = \left[\frac{1}{n-1} (Q_{\text{exp}} - Q_{\text{calc}})^2 \right]^{1/2} \quad (7)$$

where n is the number of points.

Table 3

Physical and excess properties for isopropyl acetate (1)+isopropanol (2)+[C₈mim][NTf₂] (3) ternary system at 298.15 K and atmospheric pressure.

x_1	x_2	ρ (g cm ⁻³)	n_D	η (mPas)	V^E (cm ³ mol ⁻¹)	$\Delta\eta$ (mPas)
0.8920	0.0974	0.87565	1.37675	0.487	-0.001	-1.127
0.8113	0.1702	0.88278	1.37831	0.556	0.008	-1.905
0.7114	0.2602	0.89203	1.38033	0.688	-0.013	-2.820
0.6184	0.3441	0.90099	1.38225	0.818	-0.051	-3.665
0.4880	0.4617	0.91374	1.38497	1.106	-0.085	-4.745
0.3937	0.5466	0.92338	1.38712	1.371	-0.131	-5.469
0.2909	0.6393	0.93412	1.38927	1.819	-0.176	-6.099
0.1941	0.7266	0.94436	1.39140	2.391	-0.205	-6.541
0.1537	0.7631	0.94881	1.39228	2.730	-0.228	-6.627
0.1093	0.8031	0.95368	1.39326	3.122	-0.245	-6.700
0.0627	0.8451	0.95889	1.39442	3.513	-0.267	-6.799
0.8967	0.0827	0.89079	1.37898	0.633	-0.124	-1.876
0.7934	0.1654	0.91448	1.38314	0.814	-0.212	-3.720
0.7073	0.2344	0.93382	1.38608	1.018	-0.289	-5.207
0.6146	0.3085	0.95403	1.38932	1.264	-0.352	-6.780
0.5279	0.3779	0.97232	1.39225	1.644	-0.383	-8.100
0.4280	0.4580	0.99271	1.39541	2.110	-0.390	-9.595
0.3183	0.5458	1.01447	1.39861	3.000	-0.391	-10.86
0.2383	0.6099	1.02989	1.40081	3.654	-0.380	-11.77
0.1933	0.6459	1.03826	1.40216	4.370	-0.351	-11.94
0.1533	0.6779	1.04566	1.40312	4.867	-0.332	-12.23
0.0887	0.7296	1.05764	1.40489	5.982	-0.324	-12.38
0.9007	0.0696	0.90413	1.38090	0.690	-0.258	-2.635
0.8020	0.1388	0.93858	1.38621	0.952	-0.408	-5.201
0.7031	0.2081	0.97059	1.39096	1.356	-0.520	-7.626
0.5850	0.2909	1.00569	1.39603	1.962	-0.580	-10.40
0.5079	0.3450	1.02702	1.39914	2.557	-0.595	-12.01
0.3948	0.4243	1.05601	1.40303	3.554	-0.547	-14.26
0.2920	0.4963	1.08038	1.40644	5.075	-0.467	-15.68
0.1975	0.5625	1.10155	1.40898	6.747	-0.400	-16.71
0.1489	0.5966	1.11207	1.41044	7.896	-0.377	-16.95
0.0986	0.6319	1.12239	1.41180	9.160	-0.314	-17.13
0.0472	0.6679	1.13275	1.41305	10.82	-0.269	-16.95
0.8904	0.0661	0.92236	1.38355	0.805	-0.408	-3.786
0.8009	0.1201	0.96238	1.38943	1.144	-0.586	-6.802
0.7424	0.1553	0.98632	1.39290	1.494	-0.674	-8.643
0.5906	0.2469	1.04117	1.40073	2.591	-0.749	-13.24
0.4949	0.3046	1.07120	1.40440	3.800	-0.713	-15.62
0.3999	0.3619	1.09822	1.40786	5.096	-0.645	-17.88
0.2991	0.4227	1.12435	1.41117	7.236	-0.550	-19.52
0.2127	0.4748	1.14477	1.41370	9.469	-0.437	-20.53
0.1552	0.5095	1.15765	1.41523	11.37	-0.375	-20.78
0.1056	0.5394	1.16821	1.41657	13.20	-0.311	-20.81
0.0547	0.5701	1.17868	1.41784	15.39	-0.254	-20.53
0.8956	0.0523	0.93376	1.38522	0.879	-0.521	-4.484
0.7937	0.1033	0.98835	1.39295	1.465	-0.762	-8.663
0.6930	0.1537	1.03427	1.39925	2.300	-0.893	-12.53
0.5907	0.2049	1.07425	1.40441	3.576	-0.920	-16.04
0.4922	0.2542	1.10765	1.40860	5.200	-0.867	-19.03
0.3975	0.3016	1.13558	1.41207	7.289	-0.721	-21.36
0.3016	0.3496	1.16095	1.41525	10.12	-0.571	-23.01
0.2135	0.3937	1.18223	1.41787	13.41	-0.465	-23.85
0.1272	0.4369	1.20118	1.42004	17.57	-0.348	-23.72
0.0416	0.4798	1.21827	1.42202	22.44	-0.200	-22.85
0.8866	0.0458	0.95221	1.38786	1.031	-0.647	-5.752
0.8043	0.0789	1.00230	1.39477	1.635	-0.868	-9.717
0.7088	0.1175	1.05109	1.40129	2.662	-0.983	-14.00
0.5918	0.1647	1.10041	1.40754	4.353	-0.982	-18.81
0.4923	0.2048	1.13535	1.41184	6.820	-0.886	-21.86
0.3766	0.2514	1.17005	1.41601	10.45	-0.737	-24.66
0.2959	0.2840	1.19119	1.41854	13.89	-0.617	-25.71
0.2005	0.3225	1.21350	1.42109	18.83	-0.454	-26.07
0.1568	0.3401	1.22294	1.42223	21.70	-0.391	-25.62
0.1067	0.3603	1.23299	1.42351	24.97	-0.278	-25.14
0.0608	0.3788	1.24189	1.42448	28.73	-0.206	-23.93
0.9017	0.0298	0.95377	1.38790	1.031	-0.696	-5.799
0.8013	0.0603	1.02236	1.39743	1.891	-0.996	-11.42
0.6943	0.0928	1.08014	1.40488	3.497	-1.130	-16.72
0.6020	0.1208	1.12028	1.40989	5.264	-1.073	-20.91
0.4865	0.1559	1.16189	1.41487	9.044	-0.946	-24.60
0.3902	0.1851	1.19095	1.41830	13.07	-0.808	-26.79
0.2858	0.2169	1.21773	1.42143	19.03	-0.587	-27.57
0.1847	0.2475	1.24044	1.42417	26.96	-0.418	-26.17
0.1461	0.2592	1.24821	1.42509	30.55	-0.329	-25.07
0.0868	0.2772	1.25961	1.42643	35.08	-0.222	-24.37

Table 3 (Continued)

x_1	x_2	ρ (g cm $^{-3}$)	n_D	η (mPa s)	V^E (cm 3 mol $^{-1}$)	$\Delta\eta$ (mPa s)
0.0295	0.2947	1.26974	1.42751	41.79	-0.090	-21.36
0.8976	0.0205	0.96887	1.38997	1.171	-0.817	-6.879
0.7983	0.0404	1.04203	1.40001	2.266	-1.127	-13.13
0.7099	0.0581	1.09284	1.40641	3.917	-1.222	-18.01
0.5995	0.0801	1.14298	1.41258	6.834	-1.150	-23.25
0.4943	0.1012	1.18124	1.41712	11.24	-1.001	-26.63
0.3958	0.1209	1.21101	1.42064	16.65	-0.849	-28.49
0.3030	0.1395	1.23483	1.42336	23.51	-0.671	-28.50
0.2083	0.1584	1.25582	1.42590	31.98	-0.469	-27.03
0.1601	0.1681	1.26550	1.42689	37.38	-0.378	-25.20
0.1054	0.1790	1.27569	1.42804	43.57	-0.266	-23.05
0.0445	0.1912	1.28611	1.42920	52.26	-0.117	-18.86
0.8963	0.0100	0.98137	1.39172	1.308	-0.901	-7.810
0.7159	0.0275	1.10775	1.40841	4.633	-1.280	-19.50
0.5873	0.0400	1.16673	1.41529	9.168	-1.158	-25.68
0.4849	0.0499	1.20328	1.41957	14.71	-1.034	-28.66
0.3910	0.0590	1.23069	1.42280	21.48	-0.847	-29.71
0.2921	0.0686	1.25499	1.42559	31.38	-0.632	-28.04
0.1953	0.0780	1.27535	1.42781	42.31	-0.433	-25.17
0.1425	0.0831	1.28504	1.42892	50.13	-0.272	-21.75
0.1090	0.0863	1.29097	1.42962	54.46	-0.204	-20.21
0.0552	0.0915	1.29986	1.43060	62.40	-0.085	-16.75

Table 4Coefficients and standard deviations σ obtained using the Redlich–Kister polynomial, Eq. (5), to correlate V^E and $\Delta\eta$ for binary systems.

Property	A_0	A_1	A_2	A_3	σ
Isopropyl acetate (1)+isopropanol (2)					
V^E (cm 3 mol $^{-1}$)	1.8457	-0.0662	0.1197	-	0.004
$\Delta\eta$ (mPa s)	-2.6061	2.3034	-1.7346	-	0.018
Isopropyl acetate (1)+[C ₈ mim][NTf ₂] (2)					
V^E (cm 3 mol $^{-1}$)	-4.4480	-3.2158	-3.1870	-2.9797	0.014
$\Delta\eta$ (mPa s)	-116.63	30.384	-3.7730	-	0.397
Isopropanol (1)+[C ₈ mim][NTf ₂] (2)					
V^E (cm 3 mol $^{-1}$)	-0.1857	-1.1223	-1.5989	-1.6033	0.008
$\Delta\eta$ (mPa s)	-88.095	27.168	-16.091	-	0.497

Table 5Coefficients and standard deviations σ obtained using the Redlich–Kister polynomial, Eq. (6), to correlate V^E and $\Delta\eta$ for the isopropyl acetate (1)+isopropanol (2)+[C₈mim][NTf₂] (3) ternary system.

Property	A	B	C	D	E	F	G	σ
V^E (cm 3 mol $^{-1}$)	-8.8528	2.1439	-10.180	-10.611	4.4763	-10.271	-17.960	0.024
$\Delta\eta$ (mPa s)	10.277	-0.8894	-6.5898	-5.4135	-26.800	35.028	108.21	0.346

Table 6

Experimental vapour–liquid equilibrium data of the binary system isopropyl acetate (1)+isopropanol (2) at 101.32 kPa.

T (K)	x_1	y_1	T (K)	x_1	y_1
355.26	0.0105	0.0155	354.83	0.6371	0.5560
355.12	0.0236	0.0333	355.25	0.6808	0.5889
354.84	0.0528	0.0713	355.55	0.7140	0.6183
354.67	0.0813	0.0947	355.92	0.7430	0.6446
354.52	0.0907	0.1159	356.32	0.7714	0.6703
354.21	0.1358	0.1652	356.67	0.7952	0.6959
354.05	0.1661	0.1947	357.04	0.8176	0.7203
353.93	0.1913	0.2187	357.40	0.8384	0.7428
353.83	0.2177	0.2417	357.86	0.8602	0.7708
353.75	0.2457	0.2663	358.46	0.8879	0.8082
353.67	0.2992	0.3075	358.72	0.8977	0.8270
353.65	0.3290	0.3299	358.97	0.9115	0.8409
353.66	0.3571	0.3509	359.33	0.9246	0.8642
353.72	0.4080	0.3873	359.39	0.9278	0.8662
353.80	0.4482	0.4154	359.62	0.9366	0.8824
353.92	0.4858	0.4443	359.72	0.9408	0.8880
354.08	0.5199	0.4656	360.16	0.9575	0.9157
354.30	0.5629	0.4961	360.64	0.9739	0.9464
354.45	0.5893	0.5159	361.12	0.9906	0.9776

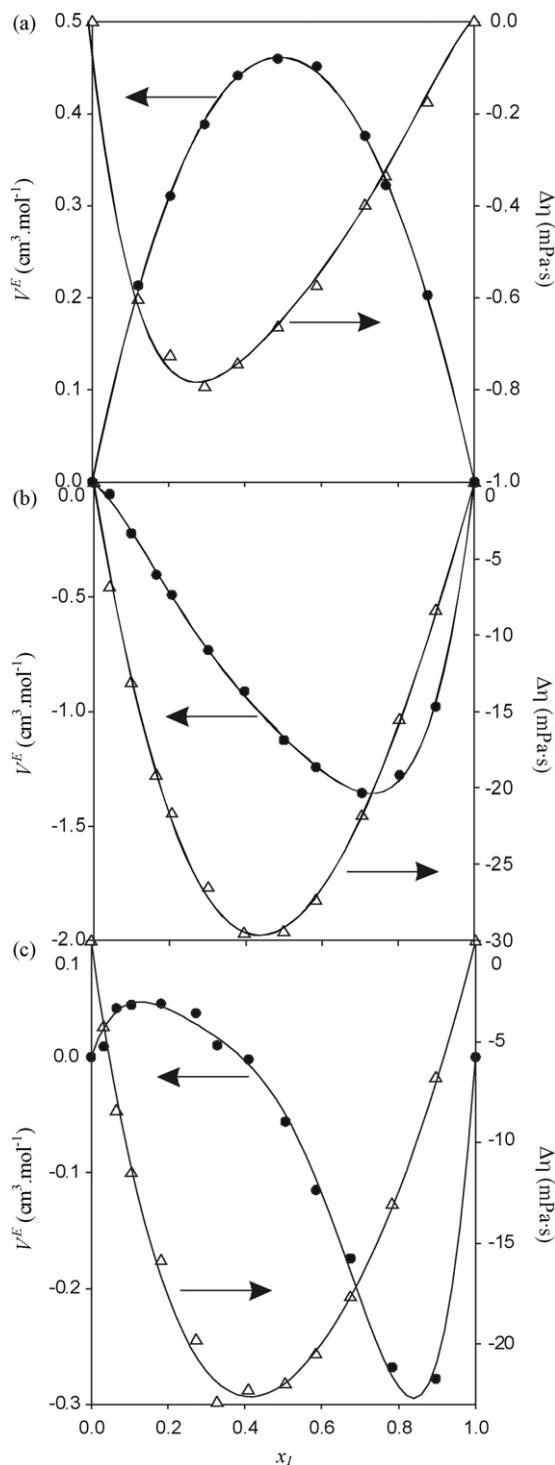


Fig. 1. Excess molar volumes (●) and viscosity change of mixing (Δ) at 298.15 K at atmospheric pressure for the binary systems: isopropyl acetate (1)+isopropanol (2) (a); isopropyl acetate (1)+[C₈mim][NTf₂] (2) (b); isopropanol (1)+[C₈mim][NTf₂] (2) (c); the solid line represent the theoretical fit of this data to Eq. (5).

3.2. Vapour–liquid equilibrium

The boiling temperature, T , the mole fractions of isopropyl acetate in the liquid, x_i , and vapour, y_i , phases for the VLE at 101.32 kPa of the isopropyl acetate (1)+isopropanol (2) binary system were reported in Table 6. Fig. 4(a) shows the VLE experimental data for the binary system and also shows data previously published by other authors [3,4] to establish a comparison. As it can be

Table 7

Experimental vapour–liquid equilibrium data for the binary systems: isopropyl acetate (1)+[C₈mim][NTf₂] (2) and isopropanol (1)+[C₈mim][NTf₂] (2) at 101.32 kPa.

T (K)	x_1	T (K)	x_1	T (K)	x_1
Isopropyl acetate (1)+[C ₈ mim][NTf ₂] (2)					
361.54	0.9973	365.93	0.8130	377.88	0.6125
361.69	0.9861	366.18	0.8063	379.45	0.5897
361.99	0.965	367.10	0.7833	383.65	0.5448
362.28	0.9404	368.13	0.7639	388.15	0.4919
362.74	0.9143	369.43	0.7388	396.63	0.4261
363.25	0.8899	370.14	0.7249	402.20	0.3896
363.82	0.8701	371.43	0.7039	410.75	0.3358
364.03	0.8645	372.73	0.6847	420.99	0.2844
364.68	0.8459	374.35	0.6572		
365.25	0.8277	375.97	0.6337		
Isopropanol (1)+[C ₈ mim][NTf ₂] (2)					
355.46	0.9949	359.68	0.7809	369.95	0.5558
355.59	0.9847	360.23	0.7637	372.24	0.5214
355.76	0.9707	360.75	0.7448	375.06	0.4867
356.15	0.9458	361.80	0.7123	375.86	0.4789
356.59	0.9154	362.97	0.6855	380.66	0.4337
357.20	0.8812	363.94	0.6675	388.11	0.3739
357.66	0.8596	365.43	0.6364	391.60	0.3532
358.45	0.8309	366.56	0.6083	401.60	0.3174
358.98	0.8042	367.54	0.5968		

seen, the VLE data determined in this work are in small discrepancy with those from Mato and Cepeda [3] and Belova et al. [4].

Table 7 summarized the vapour–liquid equilibrium data for the binary systems: isopropyl acetate (1)+[C₈mim][NTf₂] (2) and isopropanol (1)+[C₈mim][NTf₂] (2). The equilibrium temperatures for these binary systems at 101.32 kPa are summarized in temperature composition diagram shown in Fig. 4(b). Since IL is essentially non-volatile, the vapour in equilibrium with the boiling liquid phase is exclusively constituted by isopropyl acetate or isopropanol, respectively. No equilibrium temperatures could be determined in the range of very high concentration of IL, due to [C₈mim][NTf₂] decomposition problems. Tokuda et al. [18] determined the decomposition temperature to be 698.15 K, higher temperatures lead to the back alkylation of the anion.

The calculated experimental compositions for the liquid and vapour phases in equilibrium as well as the equilibrium temperatures for the ternary system isopropyl acetate + isopropanol + [C₈mim][NTf₂] are listed in Table 8. Fig. 5 shows the composition triangular diagram, where each arrow has its origin at the point corresponding to the composition of the liquid phase and its final end at the point corresponding to the composition of the vapour phase in equilibrium. The calculated liquid isotherms are depicted in Fig. 6, indicating the different compositions of ternary liquid mixtures which would boil at the same temperature.

3.2.1. Correlation of VLE

The correlation of the experimental (P , T , x , y) results is performed with a computer program that runs a non-linear regression method based on the maximum likelihood principle. Due to the lack of thermodynamic parameters for the IL, the vapour phase was considered ideal in the binary and ternary systems with IL. For the binary systems isopropyl acetate+[C₈mim][NTf₂] and isopropanol+[C₈mim][NTf₂] this approximation is adequate, since the IL is basically non-volatile and isopropyl acetate and isopropanol are, respectively, the only component in the vapour phase. For the ternary system, this assumption might mean high deviations between the model and experimental data. Saturation pressures were calculated from Antoine's equation:

$$\log(P_i^s/\text{kPa}) = A - \frac{B}{(T/\text{K}) + C} \quad (8)$$

Table 8Boiling temperatures (T) and liquid and vapour mole fraction (x_1, y_1) for isopropyl acetate (1)+isopropanol (2)+[C₈mim][NTf₂] (3) at 101.3 kPa.

T (K)	x_1	x_2	y_1	y_2
355.88	0.1429	0.7600	0.1680	0.8320
355.89	0.1032	0.8099	0.1204	0.8796
355.93	0.3332	0.5513	0.3627	0.6373
355.97	0.3082	0.5733	0.3343	0.6657
355.98	0.1580	0.7353	0.1862	0.8138
356.02	0.2498	0.6305	0.2920	0.7080
356.04	0.0784	0.8336	0.0994	0.9006
356.10	0.2046	0.6751	0.2311	0.7689
356.10	0.2277	0.6503	0.2615	0.7385
356.13	0.0356	0.8923	0.0453	0.9547
356.14	0.1834	0.7003	0.2062	0.7938
356.16	0.0430	0.8745	0.0634	0.9366
356.87	0.4200	0.4423	0.4356	0.5644
357.62	0.4668	0.3846	0.4914	0.5086
357.98	0.3227	0.4972	0.3444	0.6556
358.07	0.2645	0.5512	0.3103	0.6897
358.62	0.0461	0.7585	0.0815	0.9185
358.71	0.1856	0.6112	0.2288	0.7712
358.93	0.1514	0.6371	0.1782	0.8218
359.15	0.1053	0.6801	0.1306	0.8694
359.66	0.3290	0.4525	0.3828	0.6172
360.33	0.0129	0.7436	0.0504	0.9496
360.73	0.5622	0.2510	0.5931	0.4069
360.84	0.4134	0.3658	0.5142	0.4858
361.01	0.5149	0.2714	0.5699	0.4301
361.11	0.3846	0.3784	0.4667	0.5333
361.90	0.1079	0.6075	0.1661	0.8339
362.19	0.0389	0.6672	0.0628	0.9372
362.69	0.1188	0.5745	0.0832	0.9168
362.82	0.6069	0.1892	0.7461	0.2539
364.45	0.6755	0.1221	0.8616	0.1384
364.70	0.1466	0.5213	0.2523	0.7477
364.86	0.1181	0.5483	0.2444	0.7556
364.97	0.4717	0.2502	0.6291	0.3709
365.06	0.7395	0.0724	0.9451	0.0549
365.17	0.1816	0.4842	0.2941	0.7059
365.34	0.6453	0.1305	0.8463	0.1537
365.50	0.0710	0.5800	0.1749	0.8251
365.57	0.6932	0.0859	0.9048	0.0952
366.24	0.0065	0.6245	0.0915	0.9085
366.67	0.7802	0.0102	0.9861	0.0139
367.59	0.1776	0.4531	0.2993	0.7007
367.97	0.1152	0.4850	0.1624	0.8376
369.06	0.4423	0.2248	0.6653	0.3347
369.07	0.3909	0.2652	0.6143	0.3857
369.20	0.0235	0.5563	0.0944	0.9056
369.65	0.4091	0.2412	0.6325	0.3675
370.13	0.2176	0.3836	0.3517	0.6483
370.14	0.4475	0.2112	0.6944	0.3056
371.32	0.4617	0.1905	0.7342	0.2658
371.49	0.0573	0.5056	0.1978	0.8022
371.83	0.6678	0.0256	0.9778	0.0222
373.56	0.2201	0.3524	0.4254	0.5746
375.76	0.0932	0.4235	0.2489	0.7511
376.40	0.4773	0.1295	0.8325	0.1675
377.13	0.3161	0.2328	0.5805	0.4195
377.32	0.0003	0.4672	0.0804	0.9196
378.91	0.2360	0.3013	0.5345	0.4655
379.69	0.1059	0.3763	0.2575	0.7425
381.56	0.5183	0.0423	0.9589	0.0411
381.96	0.4824	0.0752	0.9627	0.0373
382.24	0.1650	0.2959	0.3388	0.6612
382.50	0.0010	0.4195	0.1105	0.8895
383.45	0.3372	0.1872	0.7801	0.2199
383.46	0.1319	0.3215	0.2648	0.7352
386.38	0.1408	0.2889	0.3524	0.6476
387.32	0.1712	0.2435	0.3710	0.6290
387.80	0.0483	0.3502	0.1161	0.8839
387.98	0.0010	0.3853	0.1406	0.8594
393.63	0.2349	0.1413	0.4711	0.5289
395.98	0.0488	0.3100	0.2790	0.7210
396.59	0.0787	0.3056	0.3634	0.6366
402.30	0.3682	0.0210	0.9999	0.0001
406.18	0.0011	0.3116	0.2268	0.7732
406.84	0.1685	0.1434	0.6520	0.3480
408.17	0.2627	0.0801	0.9701	0.0299

Table 8 (Continued)

T (K)	x_1	x_2	y_1	y_2
410.29	0.1135	0.1705	0.5133	0.4867
412.25	0.1008	0.1941	0.4588	0.5412
416.34	0.0579	0.2008	0.3609	0.6391
421.62	0.1419	0.1023	0.4712	0.5288
430.23	0.1489	0.0863	0.7686	0.2314
433.01	0.0004	0.2382	0.5757	0.4243
435.00	0.0643	0.1756	0.8110	0.1890
447.13	0.0613	0.1300	0.7121	0.2879

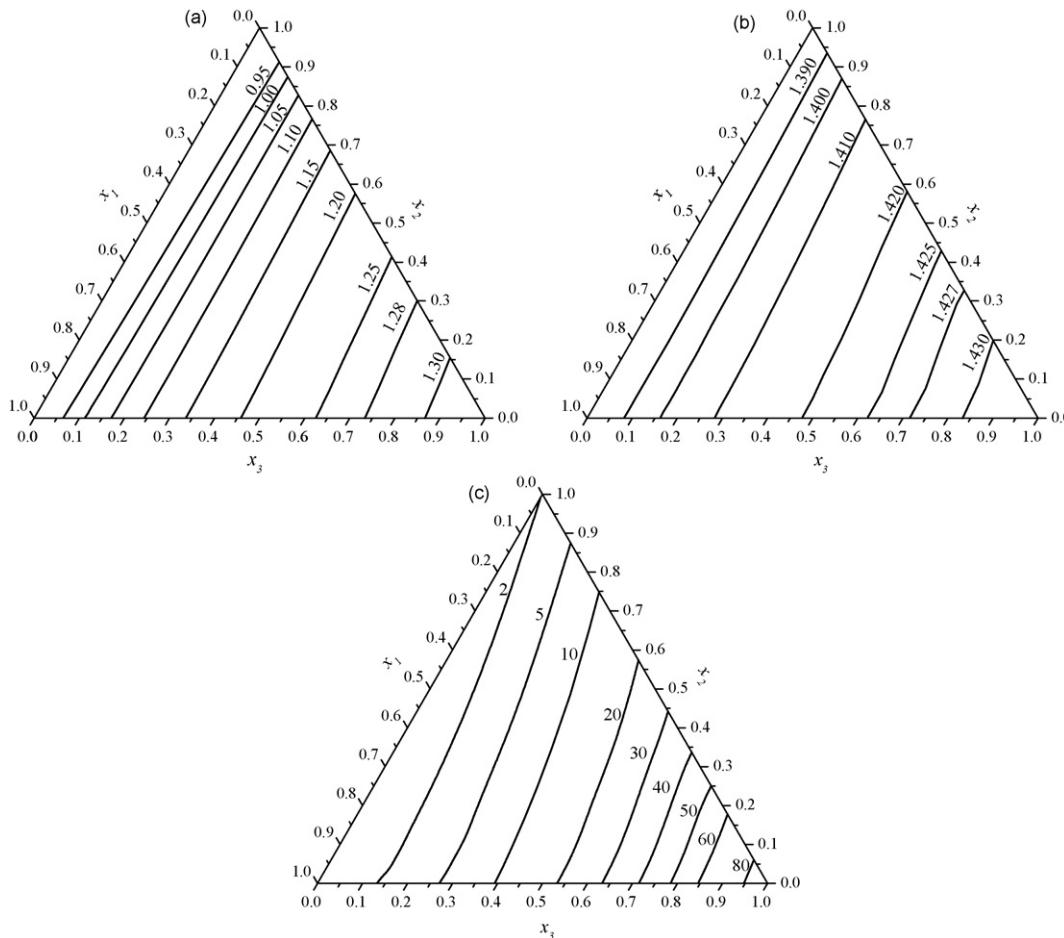


Fig. 2. Isolines for isopropyl acetate (1) + isopropanol (2) + $[C_8\text{mim}][\text{NTf}_2]$ (3) at 298.15 K and atmospheric pressure: (a) density, ρ (g cm^{-3}), (b) refractive index, n_D and (c) dynamic viscosity, η (mPa s).

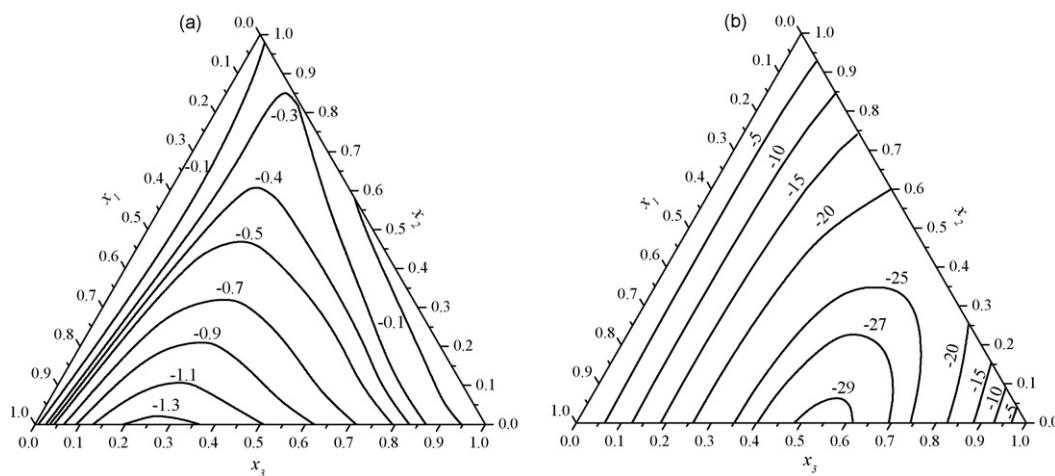


Fig. 3. Isolines for isopropyl acetate (1) + isopropanol (2) + $[C_8\text{mim}][\text{NTf}_2]$ (3) at 298.15 K and atmospheric pressure: (a) excess molar volume ($\text{cm}^3 \text{mol}^{-1}$) and (b) viscosity changes of mixing $\Delta\eta$ (mPa s).

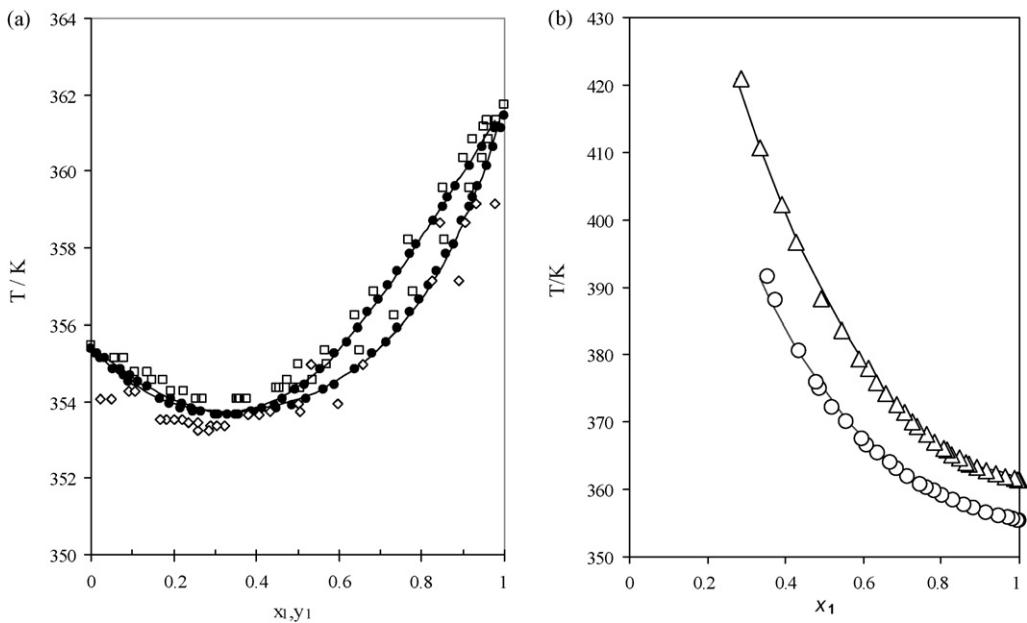


Fig. 4. Experimental VLE data at 101.32 kPa of the binary systems: (a) isopropyl acetate (1) + isopropanol(2), this work (●), Ref. [3] (□), Ref. [4] (◊); (b) (Δ) isopropyl acetate (1) + [C₈mim][NTf₂] (2), and (○) isopropanol (1) + [C₈mim][NTf₂] (2); the solid line represent the data correlated using NRTL ($\alpha = 0.2$) model (—).

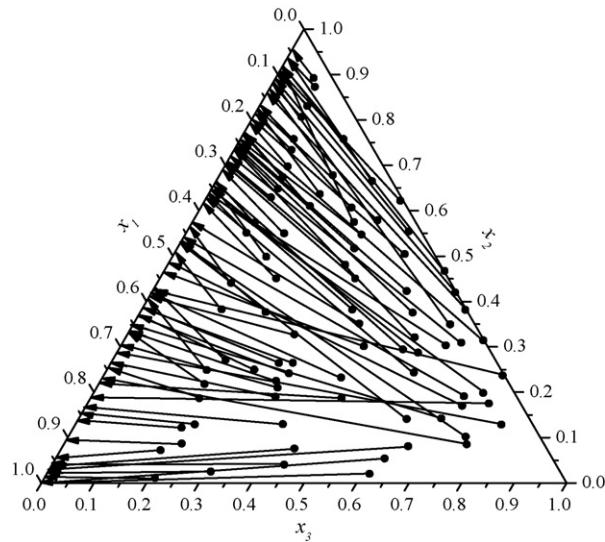


Fig. 5. Experimental VLE data for the ternary system isopropyl acetate (1) + isopropanol (2) + [C₈mim][NTf₂] (3) at 101.32 kPa.

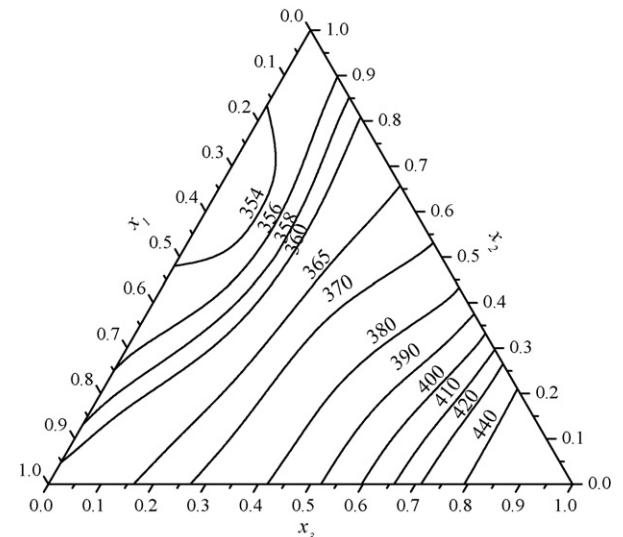


Fig. 6. Temperature (K) isolines for isopropyl acetate (1) + isopropanol (2) + [C₈mim][NTf₂] (3) at 101.32 kPa.

Table 9
Antoine coefficients A, B and C for Eq. (8).

Compound	A	B	C
Isopropyl acetate [13]	6.46612	1436.530	-39.485
Isopropanol [19]	6.86100	1357.427	-75.814

using values for the coefficients A, B, and C reported on Table 9 as taken from literature [13,19], and arbitrarily setting them to fictional values in order to lead to a negligible vapour pressure for [C₈mim][NTf₂].

The models used to calculate the liquid phase activity coefficients are Wilson's equation, UNIQUAC equation and the NRTL equation, setting the non-randomness parameter, α , to different values and selecting the value giving the best correlation. The UNIQUAC structural parameters q and r were calculated by group contribution methods [20,21]. The binary interaction parameters and root mean standard deviation in temperature, pressure and liquid and vapour compositions are listed for each activity coefficient model in Tables 10 and 11 for all the binary systems and ternary system, respectively.

Table 10

Correlation of VLE data of the indicated binary systems: model parameters (Wilson, NRTL and UNIQUAC) and root mean deviations (σ) in equilibrium temperature (T), liquid and vapour phase compositions (x, y) and pressure (P).

Model	Parameters (J mol^{-1})		$\sigma (T/\text{K})$	$\sigma (x)$	$\sigma (y)$	$\sigma (P/\text{kPa})$
Isopropyl acetate (1)+Isopropanol (2)						
Wilson	$\Delta\lambda_{12} = -122.507$	$\Delta\lambda_{21} = 2008.164$	0.06	0.0014	0.0012	0.005
NRTL ($\alpha = 0.2$)	$\Delta g_{12} = 632.2797$	$\Delta g_{21} = 1160.468$	0.06	0.0014	0.0012	0.005
UNIQUAC ^a	$\Delta u_{12} = 4593.57$	$\Delta u_{21} = -1817.94$	0.07	0.0015	0.0013	0.006
Isopropyl acetate (1)+[C ₈ mim][NTf ₂] (2)						
Wilson	$\Delta\lambda_{12} = 7070.724$	$\Delta\lambda_{21} = -8160.44$	0.27	0.0052	0.0001	5.5
NRTL ($\alpha = 0.2$)	$\Delta g_{12} = 18146.97$	$\Delta g_{21} = -9112.14$	0.17	0.0036	0.0003	0.016
UNIQUAC ^a	$\Delta u_{12} = 6036.463$	$\Delta u_{21} = -3097.46$	0.4	0.014	0.0001	0.04
Isopropanol (1)+[C ₈ mim][NTf ₂] (2)						
Wilson	$\Delta\lambda_{12} = 1176.68$	$\Delta\lambda_{21} = 16838.34$	0.34	0.0107	0.0004	0.027
NRTL ($\alpha = 0.2$)	$\Delta g_{12} = 16561.49$	$\Delta g_{21} = -8241.34$	0.19	0.0055	0.0003	0.013
UNIQUAC ^a	$\Delta u_{12} = 1897.005$	$\Delta u_{21} = -1033.01$	0.44	0.012	0.0001	0.037

^a Structural parameters for UNIQUAC equation; $r = 4.1522$, $q = 3.652$ for isopropyl acetate [20]; $r = 2.7792$, $q = 2.508$, $q' = 0.890$ for isopropanol [20]; $r = 13.8$, $q = 9.31$ for [C₈mim][NTf₂] [21].

Table 11

Correlation of VLE data of the ternary system: model parameters (Wilson, NRTL and UNIQUAC) and root mean deviations (σ) in equilibrium temperature (T), liquid and vapour phase compositions (x_i, y_i) and pressure (P).

Model	Parameters (J mol^{-1})		$\sigma (T/\text{K})$	$\sigma (x_1)$	$\sigma (x_2)$	$\sigma (y_1)$	$\sigma (y_2)$	$\sigma (P/\text{kPa})$
Wilson	$\Delta\lambda_{12} = 6439.19$ $\Delta\lambda_{13} = 3450.97$ $\Delta\lambda_{23} = 9896.98$	$\Delta\lambda_{21} = 65.059$ $\Delta\lambda_{31} = -3860.19$ $\Delta\lambda_{32} = -11589.7$	0.50	0.025	0.028	0.010	0.010	0.027
NRTL ($\alpha = 0.3$)	$\Delta g_{12} = -1913.22$ $\Delta g_{13} = 1544.57$ $\Delta g_{23} = -6305.75$	$\Delta g_{21} = 7641.56$ $\Delta g_{31} = -1178.26$ $\Delta g_{32} = 4618.34$	0.53	0.025	0.030	0.010	0.010	0.016
UNIQUAC ^a	$\Delta u_{12} = 1992.69$ $\Delta u_{13} = -1482.05$ $\Delta u_{23} = -852.77$	$\Delta u_{21} = -368.75$ $\Delta u_{31} = 1936.16$ $\Delta u_{32} = 717.76$	0.74	0.023	0.045	0.011	0.011	0.62

^a Structural parameters for UNIQUAC equation; $r = 4.1522$, $q = 3.652$ for isopropyl acetate [20]; $r = 2.7792$, $q = 2.508$, $q' = 0.890$ for isopropanol [20]; $r = 13.8$, $q = 9.31$ for [C₈mim][NTf₂] [21].

4. Conclusions

Excess molar volumes and dynamic viscosity changes of mixing were evaluated at 298.15 K and atmospheric pressure for ternary mixtures of isopropyl acetate + isopropanol + [C₈mim][NTf₂] from measurements of their density and the dynamic viscosity through them.

The excess molar volumes for isopropyl acetate + isopropanol binary system show positive values over the whole composition range reaching a maximum around $0.46 \text{ cm}^3 \text{ mol}^{-1}$. In the case of isopropyl acetate + [C₈mim][NTf₂] binary system, this property is negative over the whole composition range reaching a minimum around $-1.36 \text{ cm}^3 \text{ mol}^{-1}$. The excess molar volumes for isopropanol + [C₈mim][NTf₂] binary system show an s-shaped dependence on composition with small positive values in the isopropanol poor region and negative values (around $-0.28 \text{ cm}^3 \text{ mol}^{-1}$) at the other extreme.

The viscosity changes of mixing in the three binary mixtures are negative with very large values in the case of mixtures with ionic liquids due to the differences between compounds viscosity.

The isopropyl acetate + isopropanol + [C₈mim][NTf₂] ternary system exhibits negative excess molar volumes for the entire range of composition reaching a minimum around $-1.36 \text{ cm}^3 \text{ mol}^{-1}$, which corresponds to the isopropyl acetate + [C₈mim][NTf₂] binary system. Viscosity changes of mixing for the ternary systems are negative with a minimum around -29.5 mPa s corresponding to the isopropyl acetate + [C₈mim][NTf₂] binary system.

These properties were satisfactorily correlated by the polynomial expansion of Redlich-Kister.

Experimental VLE data are determinated for the binary systems isopropyl acetate + isopropanol, isopropyl acetate + [C₈mim][NTf₂],

isopropanol + [C₈mim][NTf₂], at the constant pressure of 101.32 kPa. At the same pressure, experimental isobaric VLE data are determined for the ternary system isopropyl acetate + isopropanol + [C₈mim][NTf₂]. The binary system isopropyl acetate + isopropanol forms a minimum boiling point azeotrope at 353.67 K with a composition near to 0.31 in molar fraction of isopropyl acetate.

The Wilson, NRTL and UNIQUAC equations used to correlate experimental VLE data of these systems turn in results that are in agreement with the experimental results. For the three binary systems the NRTL equation, with α set to 0.2, gives better results, whereas, the NRTL equation with $\alpha = 0.3$ gives smallest deviations for the ternary system. However deviations for the experimental results in the ternary system are slightly high.

List of symbols

A, B, C, D, E, F, G , etc.	coefficients (Eq. (6))
A, B, C	Antoine coefficients (Eq. (8))
n_D	refractive index
M	molecular weight
P	pressure
Q	excess or difference physical property
q	UNIQUAC area parameter
r	UNIQUAC volume parameter
T	temperature
V	molar volume
x	mole fraction in the liquid phase
y	mole fraction in the vapour phase

Greek letters

α	NRTL non-randomness parameter
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η	dynamic viscosity
ρ	density
σ	mean standard deviation
Δ	changes of mixing
Δg	NRTL binary interaction parameter
Δu	UNIQUAC binary interaction parameter
$\Delta \lambda$	Wilson binary interaction parameter

Subscripts

i	ith component
$1, 2, 3$	component 1, 2, 3
M	mixture

Superscripts

k	polynomial grade
E	excess
S	saturation

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.fluid.2009.09.015](https://doi.org/10.1016/j.fluid.2009.09.015).

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