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Isobaric vapour–liquid equilibria and physical properties for isopropyl acetate + isopropanol + 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide mixtures

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ARTICLE INFO

Article history: Received 6 August 2010 Received in revised form 30 September 2010 Accepted 1 October 2010 Available online 8 October 2010

Keywords: Physical properties Vapour-liquid equilibrium Isopropyl acetate Isopropanol 1-Butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide

ABSTRACT

Experimental densities, refractive indices and dynamic viscosities of binary and ternary mixtures of isopropyl acetate, isopropanol and 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ([C₄mim][NTf₂]) have been determined at 298.15 K and atmospheric pressure. The excess molar volumes as well as molar refraction and viscosity changes of mixing have been calculated and adequately fitted to the Redlich–Kister equation. The adjustable parameters and the standard deviations between experimental and calculated values are reported.

Vapour–liquid equilibrium (VLE) data have been obtained for these binary and ternary systems at 101.32 kPa and were adequately correlated by means of NRTL and UNIQUAC equations for the liquid phase activity coefficient.

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1. Introduction

During the last years, ionic liquids (ILs) have gained large interest in science and industry fields. They have no detectable vapour pressure and most of them possess a large liquid range being thermally and chemically stable. Therefore, they seem to be ideal systems for different challenging purposes such as many separation operations [1–3]. Also, the large number of different combinations of anions and cations offers the possibility to prepare ILs which properties can be tailored to suit the special requirements of their application [4].

The aim of our research is to study the use of ILs 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 [5,6]. In that context, we have previously studied the use of 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C₈mim][NTf₂] as an azeotrope breaker of isopropanol + isopropyl acetate system in an extractive distillation [7] and in this paper we extend to study 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide [C₄mim][NTf₂] IL.

Densities, refractive indices and dynamic viscosities for the mixtures of isopropyl acetate, isopropanol and 1-butyl-3methyl-imidazolium bis(trifluoromethylsulfonyl)imide have been measured at 298.15 K and atmospheric pressure. The excess molar volumes, molar refraction changes of mixing and viscosity changes of mixing were calculated from the measured properties and correlated with the composition data using Redlich–Kister polynomial [8]. Furthermore, isobaric vapour–liquid equilibrium (VLE) at 101.32 kPa of the involved binary and ternary systems were determined and correlated by means of the NRTL [9] and UNI-QUAC [10] equations. In the surveyed literature, VLE data for isopropanol+[C_4 mim][NTf₂] binary system have only been found for isothermal conditions at 353.15 K [11,12]. No comparable data were found for the other involved binary or ternary systems containing isopropyl acetate and ionic liquid [C_4 mim][NTf₂].

2. Experimental

The ionic liquid used in this work, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_4mim][NTf_2]$, was synthesized in our laboratory by reaction of 1-methylimidazole (Aldrich, >99 mass %, GC) with an excess of 1-bromobutane (Merck, >98 mass %) to produce the $[C_4mim][Br]$. This bromide was mixed



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| Table 1 |
|---|
| Physical properties at $T = 298.15$ K and boiling point at atmospheric pressure of the pure components. |

| | | | $ ho/(\mathrm{gcm^{-3}})$ | | n _D | | $\eta/(mPas)$ | | T/K | |
|---|--------------------|--------------------------|---------------------------|--------------------------------------|----------------|------------|---------------|-------------------------|-----------|------------------------------|
| Component | CASRN ^a | $10^{-6} \omega (H_2 O)$ | This work | Literature | This work | Literature | This work | Literature | This work | Literature |
| Isopropyl acetate | 108-21-4 | 98.225 | 0.86621 | 0.8702[14] 0.86625[15] | 1.37480 | 1.3750[14] | 0.481 | 0.52[14] | 361.45 | 361.751[14] 361.54[16,17] |
| Isopropanol | 67-63-0 | 174.93 | 0.78088 | 0.78126[14] 0.781152[18] | 1.37502 | 1.3752[14] | 2.073 | 2.0436[14] 2.061[18] | 355.37 | 355.392[14] |
| [C ₄ mim][NTf ₂] | 174899-83-3 | 46.33 | 1.436579 | 1.43[19] 1.437[20] 1.4366 [21] | 1.42692 | 1.427[19] | 50.680 | 49.9[20] | - | - |

^a CASRN, Chemical Abstract Service Registry Number.

with lithium bis(trifluoromethanesulfonyl) imide salt, Li[NTf₂] (Solvionic, >99 mass %) in deionized water to obtain [C₄min][NTf₂] by ion metathesis reaction. After washing, the purification of [C₄min][NTf₂] was completed by heating it under high vacuum for 48 h (1 mbar, 353.15 K). More details about the experimental procedure can be found in earlier publications [13]. The water mass fraction was determined by means of a Karl Fisher titration method carried out in a Metrohm 737 KF and resulted in 46.3 ppm. No bromide concentration was detected by means of capillary electrophoresis. The ionic liquid was analyzed by ¹H NMR and ¹³C NMR spectroscopy to confirm the absence of any major impurities.

Isopropanol and isopropyl acetate were supplied by Sigma–Aldrich and had nominal purities >99.5 and 99.6 mass %, respectively. No appreciable peaks of impurities were detected by gas chromatography analysis. Information about the pure components, water mass fractions, experimental densities, refractive indices, and viscosities, at 298.15 K and boiling temperatures at 101.32 kPa are shown in Table 1 and compared with those found in the literature [14–21].

2.1. Physical properties

The mixtures were prepared by filling glass vials with the liquids using syringe and weighing at once on a Mettler Toledo AT261 balance, which measured to within ± 0.0001 g, for calculating the composition by mass difference. Vials were closed with screw caps to ensure a secure seal. The sample was taken from the vial with a syringe through a PTFE-faced silicone septum and is immediately put into the apparatus.

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 $\pm 3 \times 10^{-5} \, g \, cm^{-3}$.

Refractive indices were measured in an ATAGO RX-5000 refractometer with a Hero Therm thermostat to maintain the temperature within 298.15 \pm 0.02 K. The uncertainty in the refractive index measurement is $\pm 4 \times 10^{-5}$.

The kinematic viscosity was determined by micro Ubbelohde viscometer technique. Two micro Ubbelohde viscometers (capillaries I and II) were used in the experiments according to the different viscosity values of the mixtures. The capillaries are calibrated and credited by the company and verified by ourselves measuring the viscosity of different pure liquids. Results were found in good agreement with published values. 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 in ± 0.005 K using a Lauda clear view thermostat D 20 KP with a through-flow cooler DLK 10. Viscosity measurements were repeated at least three times for each sample and were found to be repeatable to within 0.03 s for times minor than 100 s and ± 0.5 s for bigger times. Kinematic viscosity of solution v is given by

$$\upsilon = \eta / \rho = K(t - y) \tag{1}$$

Table 2

Density, ρ , refractive index, n_D , dynamic viscosity, η , excess molar volume, V^{ε} , molar refraction change of mixing, ΔR , and viscosity change of mixing, $\Delta \eta$, for Isopropyl acetate + [C₄mim][NTf₂] and Isopropanol+[C₄mim][NTf₂] at 298.15 K.

| X_1 | $ ho/(\mathrm{gcm^{-3}})$ | n _D | $\eta/(mPas)$ | $V^{\rm E}/({\rm cm^3~mol^{-1}})$ | ΔR | $\Delta \eta /(mPas)$ | | | |
|---|---------------------------|----------------|------------------------|-----------------------------------|------------|-----------------------|--|--|--|
| Isopropyl acetate $(1) + [C_4 mim][NTf_2](2)$ | | | | | | | | | |
| 0.0514 | 1.42508 | 1.42609 | 44.31 | -0.142 | 0.009 | -3.789 | | | |
| 0.1096 | 1.41117 | 1.42501 | 38.56 | -0.310 | 0.007 | -6.617 | | | |
| 0.1554 | 1.39942 | 1.42412 | 33.87 | -0.433 | 0.010 | -9.012 | | | |
| 0.1972 | 1.38810 | 1.42326 | 30.34 | -0.555 | 0.011 | -10.45 | | | |
| 0.2961 | 1.35820 | 1.42092 | 22.58 | -0.790 | 0.014 | -13.24 | | | |
| 0.4241 | 1.31234 | 1.41733 | 14.46 | -1.082 | 0.020 | -14.93 | | | |
| 0.5168 | 1.27249 | 1.41420 | 10.07 | -1.261 | 0.028 | -14.67 | | | |
| 0.5998 | 1.23054 | 1.41070 | 6.918 | -1.378 | 0.023 | -13.65 | | | |
| 0.7017 | 1.16862 | 1.40538 | 4.356 | -1.445 | 0.017 | -11.10 | | | |
| 0.7981 | 1.09544 | 1.39882 | 2.363 | -1.341 | 0.019 | -8.252 | | | |
| 0.8918 | 1.00535 | 1.39016 | 1.410 | -1.009 | 0.019 | -4.501 | | | |
| | | Is | sopropanol (1)+[C4mim] | [NTf ₂](2) | | | | | |
| 0.0515 | 1.42723 | 1.42621 | 45.44 | 0.019 | 0.010 | -2.738 | | | |
| 0.0962 | 1.41852 | 1.42549 | 41.20 | 0.032 | 0.010 | -4.805 | | | |
| 0.1921 | 1.39779 | 1.42385 | 33.45 | 0.022 | 0.011 | -7.890 | | | |
| 0.3213 | 1.36398 | 1.42124 | 24.50 | -0.025 | 0.014 | -10.56 | | | |
| 0.3896 | 1.34250 | 1.41962 | 20.46 | -0.054 | 0.018 | -11.29 | | | |
| 0.4869 | 1.30605 | 1.41685 | 15.84 | -0.096 | 0.022 | -11.17 | | | |
| 0.5173 | 1.29291 | 1.41578 | 14.67 | -0.109 | 0.016 | -10.87 | | | |
| 0.6074 | 1.24791 | 1.41240 | 11.22 | -0.164 | 0.020 | -9.934 | | | |
| 0.6943 | 1.19286 | 1.40818 | 8.545 | -0.220 | 0.016 | -8.389 | | | |
| 0.7996 | 1.10282 | 1.40129 | 5.859 | -0.260 | 0.015 | -5.955 | | | |
| 0.8995 | 0.97852 | 1.39152 | 3.898 | -0.244 | 0.008 | -3.062 | | | |
| | | | | | | | | | |

Table 3

Density, ρ , refractive index, n_D , dynamic viscosity, η , excess molar volume, V^E , molar refraction change of mixing, ΔR , and viscosity change of mixing, $\Delta \eta$, for the Isopropyl acetate (1)+Isopropanol (2)+[C₄mim][NTf₂] (3) ternary system at 298.15 K.

| γ. | Ya | $o/(g cm^{-3})$ | np | n/(mPas) | $V^{E}/(cm^{3}mol^{-1})$ | ΔR | $\Delta n /(mPas)$ |
|--------|-----------|------------------|---------|----------------------|--------------------------|-------|--------------------|
| ×1 | <u>^2</u> | p/(gem) | пр | <i>I</i> //(III a 3) | v /(cm mor) | | |
| 0.8775 | 0.1101 | 0.87774 | 1.37652 | 0.715 | 0.013 | 0.009 | -0.565 |
| 0.7871 | 0.1914 | 0.88663 | 1.37785 | 0.899 | 0.013 | 0.015 | -0.970 |
| 0.6915 | 0.2772 | 0.89649 | 1.37934 | 0.839 | -0.009 | 0.018 | -1.652 |
| 0.5981 | 0.3612 | 0.90650 | 1.38088 | 0.962 | -0.034 | 0.022 | -2.138 |
| 0.4951 | 0.4537 | 0.91806 | 1.38268 | 1.145 | -0.080 | 0.024 | -2.626 |
| 0.4080 | 0.5320 | 0.92831 | 1.38421 | 1.231 | -0.134 | 0.020 | -3.108 |
| 0.3137 | 0.6167 | 0.93954 | 1.38585 | 1.629 | -0.164 | 0.018 | -3.325 |
| 0.1911 | 0.7270 | 0.95471 | 1.38803 | 2.216 | -0.199 | 0.014 | -3.537 |
| 0.0964 | 0.8121 | 0.96679 | 1.38980 | 2.893 | -0.213 | 0.015 | -3.477 |
| 0.0433 | 0.8597 | 0.97380 | 1.39083 | 3.342 | -0.226 | 0.014 | -3.373 |
| 0.8884 | 0.0893 | 0.89371 | 1.37822 | 0.674 | -0.133 | 0.007 | -1.070 |
| 0.7933 | 0.1654 | 0.91687 | 1.38106 | 0.754 | -0.218 | 0.014 | -2.065 |
| 0.6833 | 0.2534 | 0.94358 | 1.38427 | 0.967 | -0.312 | 0.019 | -3.096 |
| 0.6059 | 0.3153 | 0.96210 | 1.38646 | 1.151 | -0.350 | 0.025 | -3.787 |
| 0.5141 | 0.3888 | 0.98406 | 1.38889 | 1.439 | -0.398 | 0.020 | -4.537 |
| 0.4148 | 0.4682 | 1.00719 | 1.39144 | 1.954 | -0.385 | 0.025 | -5.145 |
| 0.3209 | 0.5434 | 1.02907 | 1.39378 | 2.329 | -0.380 | 0.024 | -5.832 |
| 0.1943 | 0.6447 | 1.05833 | 1.39680 | 3.457 | -0.361 | 0.018 | -6.135 |
| 0.1396 | 0.6885 | 1.07081 | 1.39806 | 3.826 | -0.339 | 0.016 | -6.386 |
| 0.0963 | 0.7231 | 1.08063 | 1.39914 | 4.391 | -0.319 | 0.020 | -6.310 |
| 0.0502 | 0.7599 | 1.09104 | 1.40009 | 5.042 | -0.294 | 0.013 | -6.179 |
| 0.8918 | 0.0754 | 0.90954 | 1.38005 | 0.674 | -0.284 | 0.011 | -1.5/3 |
| 0.7939 | 0.1436 | 0.94657 | 1.38418 | 0.900 | -0.441 | 0.013 | -2.946 |
| 0.6949 | 0.2126 | 0.98244 | 1.38809 | 1.205 | -0.571 | 0.014 | -4.257 |
| 0.5934 | 0.2833 | 1.01698 | 1.39176 | 1.648 | -0.592 | 0.027 | -5.4/1 |
| 0.5025 | 0.3407 | 1.04070 | 1.39471 | 2.065 | -0.601 | 0.025 | -0.539 |
| 0.4134 | 0.4088 | 1.0/453 | 1.39744 | 2.698 | -0.558 | 0.031 | -7.360 |
| 0.3076 | 0.4825 | 1.10043 | 1.40035 | 3.331 | -0.520 | 0.019 | -8.234 |
| 0.2246 | 0.5403 | 1.13030 | 1.40257 | 4.334 | -0.460 | 0.018 | -8.605 |
| 0.1079 | 0.5799 | 1.14011 | 1.40599 | 5.510 | -0.393 | 0.018 | -0.730 |
| 0.1285 | 0.6586 | 1.15081 | 1.40501 | 7 245 | 0.298 | 0.023 | -8.788 |
| 0.0343 | 0.0530 | 0.92309 | 1 38149 | 0.736 | -0.238 | 0.009 | -1 964 |
| 0.7857 | 0.1290 | 0.92584 | 1 38722 | 1 1 3 9 | -0.627 | 0.005 | -3.831 |
| 0.6807 | 0.1230 | 1 02259 | 1 39204 | 1.133 | -0.742 | 0.013 | -5 498 |
| 0.5925 | 0.2453 | 1.05889 | 1 39559 | 2 052 | -0.768 | 0.023 | -6967 |
| 0.4940 | 0.3045 | 1.09649 | 1 39911 | 2.841 | -0.734 | 0.025 | -8 240 |
| 0.4323 | 0.3417 | 1 11882 | 1 40115 | 3 425 | -0.704 | 0.023 | -8 950 |
| 0.3234 | 0.4072 | 1.15563 | 1.40440 | 4.692 | -0.587 | 0.023 | -9.963 |
| 0.2338 | 0.4611 | 1.18405 | 1.40690 | 6.034 | -0.484 | 0.024 | -10.50 |
| 0.1724 | 0.4980 | 1.20251 | 1.40845 | 7.198 | -0.398 | 0.021 | -10.62 |
| 0.0965 | 0.5437 | 1.22463 | 1.41038 | 8.856 | -0.315 | 0.018 | -10.55 |
| 0.0419 | 0.5765 | 1.23985 | 1.41175 | 10.18 | -0.244 | 0.022 | -10.37 |
| 0.8913 | 0.0545 | 0.93960 | 1.38315 | 0.830 | -0.534 | 0.001 | -2.463 |
| 0.7957 | 0.1023 | 0.99619 | 1.38918 | 1.226 | -0.780 | 0.009 | -4.539 |
| 0.6948 | 0.1529 | 1.04930 | 1.39448 | 1.818 | -0.885 | 0.018 | -6.556 |
| 0.5975 | 0.2016 | 1.09540 | 1.39886 | 2.583 | -0.925 | 0.019 | -8.306 |
| 0.5095 | 0.2456 | 1.13306 | 1.40232 | 3.516 | -0.874 | 0.026 | -9.650 |
| 0.3953 | 0.3028 | 1.17718 | 1.40608 | 5.072 | -0.737 | 0.023 | -11.05 |
| 0.2951 | 0.3530 | 1.21231 | 1.40908 | 6.813 | -0.598 | 0.024 | -11.89 |
| 0.2028 | 0.3992 | 1.24218 | 1.41161 | 8.954 | -0.463 | 0.023 | -12.14 |
| 0.1459 | 0.4277 | 1.25933 | 1.41306 | 10.39 | -0.355 | 0.028 | -12.18 |
| 0.1010 | 0.4502 | 1.27239 | 1.41409 | 11.81 | -0.280 | 0.022 | -11.92 |
| 0.0466 | 0.4775 | 1.28780 | 1.41537 | 13.56 | -0.209 | 0.017 | -11.58 |
| 0.8835 | 0.0466 | 0.95978 | 1.38531 | 0.941 | -0.682 | 0.002 | -3.125 |
| 0.7822 | 0.0871 | 1.02797 | 1.39238 | 1.510 | -0.962 | 0.011 | -5.670 |
| 0.6774 | 0.1290 | 1.08854 | 1.39817 | 2.393 | -1.055 | 0.016 | -8.010 |
| 0.5990 | 0.1604 | 1.12863 | 1.40183 | 3.242 | -1.056 | 0.018 | -9.574 |
| 0.4903 | 0.2039 | 1.17782 | 1.40615 | 4.813 | -0.968 | 0.021 | -11.34 |
| 0.4548 | 0.2181 | 1.19258 | 1.40735 | 5.423 | -0.931 | 0.015 | -11.83 |
| 0.2931 | 0.2827 | 1.25230 | 1.41235 | 9.071 | -0.628 | 0.026 | -13.15 |
| 0.2003 | 0.3199 | 1.28237 | 1.414/9 | 11.01 | -0.470 | 0.018 | -13.20 |
| 0.145/ | 0.341/ | 1.29905 | 1.41014 | 13.8U | -0.371 | 0.018 | -12.90 |
| 0.0903 | 0.0007 | 1,21200 | 1,41/24 | 15.30 | -0.277 | 0.018 | -12.00 |
| 0.0327 | 0.5/89 | 1.52310 | 1.41823 | 17.01 | -0.109 | 0.021 | -12.01 |
| 0.0333 | 0.0510 | 1 04207 | 1 30308 | 1.001 | -0.756 | 0.009 | -5.250 |
| 0.6980 | 0.0021 | 1 10436 | 1 20062 | 2 628 | -1.055 | 0.025 | -0.132 |
| 0.5992 | 0.1104 | 1 15879 | 1 40443 | 3 975 | _1.134 | 0.020 | _10.82 |
| 0 5095 | 0 1461 | 1 20166 | 1 40824 | 5 659 | -1.055 | 0.030 | -12 34 |
| 0.3971 | 0 1796 | 1,24850 | 1 41203 | 8 372 | -0.898 | 0.018 | -13.64 |
| 0.2976 | 0.2093 | 1.28446 | 1.41502 | 11.55 | -0.693 | 0.027 | -14 02 |
| 0.1968 | 0.2393 | 1.31706 | 1.41756 | 15.45 | -0.502 | 0.015 | -13.72 |
| 0.1520 | 0.2527 | 1.33021 | 1.41859 | 17.49 | -0.385 | 0.016 | -13.28 |

Table 3 (Continued)

| <i>x</i> ₁ | <i>x</i> ₂ | $ ho/(\mathrm{gcm^{-3}})$ | n _D | $\eta/(mPas)$ | $V^{\rm E}/({ m cm^3~mol^{-1}})$ | ΔR | $\Delta \eta /(mPas)$ |
|-----------------------|-----------------------|---------------------------|----------------|---------------|----------------------------------|------------|-----------------------|
| 0.0983 | 0.2687 | 1.34549 | 1.41993 | 20.13 | -0.294 | 0.024 | -12.55 |
| 0.0523 | 0.2824 | 1.35767 | 1.42081 | 22.82 | -0.175 | 0.016 | -11.51 |
| 0.8854 | 0.0230 | 0.98614 | 1.38804 | 1.137 | -0.851 | 0.008 | -3.979 |
| 0.7964 | 0.0409 | 1.06031 | 1.39548 | 1.868 | -1.154 | 0.015 | -6.850 |
| 0.7009 | 0.0600 | 1.12594 | 1.40165 | 3.059 | -1.224 | 0.032 | -9.519 |
| 0.6042 | 0.0794 | 1.18181 | 1.40644 | 4.728 | -1.190 | 0.025 | -11.76 |
| 0.5045 | 0.0994 | 1.23100 | 1.41067 | 7.096 | -1.113 | 0.026 | -13.43 |
| 0.3993 | 0.1205 | 1.27511 | 1.41420 | 10.36 | -0.941 | 0.016 | -14.42 |
| 0.3116 | 0.1381 | 1.30704 | 1.41680 | 13.89 | -0.751 | 0.021 | -14.44 |
| 0.2175 | 0.1570 | 1.33766 | 1.41924 | 18.34 | -0.564 | 0.017 | -13.79 |
| 0.1723 | 0.1661 | 1.35088 | 1.42035 | 21.03 | -0.427 | 0.031 | -12.93 |
| 0.1274 | 0.1751 | 1.36368 | 1.42123 | 23.56 | -0.351 | 0.009 | -12.22 |
| 0.0877 | 0.1830 | 1.37418 | 1.42203 | 26.39 | -0.234 | 0.009 | -10.99 |
| 0.8974 | 0.0104 | 0.98724 | 1.38818 | 1.122 | -0.890 | 0.008 | -4.003 |
| 0.7869 | 0.0216 | 1.08642 | 1.39790 | 2.231 | -1.250 | 0.016 | -7.900 |
| 0.6937 | 0.0310 | 1.15308 | 1.40395 | 3.722 | -1.355 | 0.014 | -10.63 |
| 0.6076 | 0.0397 | 1.20414 | 1.40836 | 5.603 | -1.308 | 0.017 | -12.64 |
| 0.5101 | 0.0496 | 1.25322 | 1.41242 | 8.549 | -1.204 | 0.010 | -14.12 |
| 0.4075 | 0.0600 | 1.29647 | 1.41596 | 12.51 | -0.977 | 0.020 | -14.80 |
| 0.3071 | 0.0701 | 1.33314 | 1.41894 | 17.67 | -0.812 | 0.016 | -14.19 |
| 0.2250 | 0.0784 | 1.35916 | 1.42094 | 22.53 | -0.606 | 0.011 | -13.04 |
| 0.1617 | 0.0848 | 1.37737 | 1.42238 | 27.25 | -0.447 | 0.013 | -11.19 |
| 0.1135 | 0.0897 | 1.39039 | 1.42336 | 30.71 | -0.345 | 0.004 | -9.909 |
| 0.0700 | 0.0941 | 1.40145 | 1.42421 | 34.77 | -0.242 | 0.000 | -7.824 |

where υ is the kinematic viscosity, η is the dynamic viscosity, ρ is the solution density, 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 $\pm 0.5\%$.

2.2. Vapour-liquid equilibria (VLE)

The vapour–liquid equilibria were carried out in a Labodest 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.

Liquid equilibrium compositions in the binary systems were determined by densimetry. Liquid and vapour equilibrium compositions in the ternary systems were determined by densimetry and refractometry. The precision of this analysis method was determined using test samples prepared by weighing. The maximum deviation found between the measured and real composition was ± 0.004 mole fraction for binary systems and for ternary system in the case of mixtures with IL composition lower than 0.2. For the mixtures of the three components with higher IL composition this method led to high deviations, as a result of the parallelism between the density and refractive index isolines. For this reason, for this part of ternary system gas chromatography was selected as analysis technique.

Isopropanol and isopropyl acetate compositions were determined by GC using an internal standard method. Ionic liquid composition was calculated by difference. The chromatographic analysis was carried out in an HP 6890 Series gas chromatograph, equipped with a thermal conductivity detector



Fig. 1. Excess molar volumes (○) and dynamic viscosity changes of mixing (♦) for binaries systems at 298.15 K and atmospheric pressure: (a) isopropanol + [C₄mim][NTf₂] and (b) isopropyl acetate + [C₄mim][NTf₂]. The continued lines are Redlich-Kister correlations.



Fig. 2. Isolines for isopropyl acetate (1)+isopropanol (2)+[C₄mim][NTf₂] (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).

(TCD), a capillary column HP-FFAP polyethylene glycol TPA ($25 \text{ m} \times 200 \text{ }\mu\text{m} \times 0.3 \text{ }\mu\text{m}$), and an empty precolumn to protect the column and collect the ionic liquid that could not be retained by the liner. The detector and injector temperature was 523.15 K. The oven was maintained at constant temperature of 383.15 K. Column flow was fixed at 0.9 ml/min. The carrier gas was helium. With this analysis method, maximum deviation found between the measured and real compositions was ± 0.003 mole fraction.

3. Results and discussion

3.1. Physical properties

The experimental densities, ρ , dynamic viscosities η , and refractive indices n_D obtained at 298.15 K and atmospheric pressure for the isopropanol+[C₄mim][NTf₂] and isopropyl acetate+[C₄mim][NTf₂] binary systems and isopropanol+isopropyl acetate+[C₄mim][NTf₂] ternary system are listed in Tables 2 and 3, respectively. If we compare these results with the previously obtained data [7] for isopropanol and isopropyl acetate with an other imidazolium ionic liquid with longer alkyl chain length and the same anion, [C₈min][NTF₂], we can observe that when increasing the alkyl chain length the density of the pure ionic liquid and their mixtures decreases and the dynamic viscosity increases. The corresponding physical properties of isopropanol + isopropyl acetate have been showed in this previous work [7].

Tables 2 and 3 also include the values of excess molar volumes, V^{E} , and viscosity, $\Delta \eta$, and molar refraction changes of mixing, ΔR , calculated by means of the following expressions;

$$V^{\rm E} = V_{\rm M} - \sum_{i} x_i V_i \tag{2}$$

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

$$\Delta R = R_{\rm M} - \sum_{i} x_i R_i \tag{4}$$

where $V_{\rm M}$ is the molar volume of the mixture, η is the dynamic viscosity of the mixture, $R_{\rm M}$ is the molar refraction of the mixture obtained from the Lorentz–Lorenz equation, and V_i , η_i , and R_i are the molar volume, the viscosity, and the molar refraction for the component *i*, respectively.

Fig. 1 shows the excess molar volumes and viscosity changes of mixing for binary systems. As it can be seen, the excess molar volumes for the isopropanol + $[C_4min][NTf_2]$ binary system show an s-shaped dependence on composition with small positive values in the isopropanol poor region and negative values with a minimum around $-0.26 \text{ cm}^3 \times \text{mol}^{-1}$ at the other extreme. It is the same



Fig. 3. Isolines for isopropyl acetate (1)+isopropanol (2)+[C₄mim][NTf₂] (3) at 298.15 K and atmospheric pressure: (a) Excess molar volume (cm³ mol⁻¹) and (b) Viscosity changes of mixing $\Delta \eta$ (mPa s).

qualitative behaviour found in the case of $[C_8min][NTf_2]$ where minimum was found at $-0.28 \text{ cm}^3 \times \text{mol}^{-1}$. On the other hand, the isopropyl acetate + $[C_4min][NTf_2]$ binary system shows negative values in all range, with a minimum around $-1.45 \text{ cm}^3 \times \text{mol}^{-1}$ at around 0.7 mole fraction of the ester [7]. In the case of this system with $[C_8min][NTf_2]$ a minimum around $-1.36 \text{ cm}^3 \times \text{mol}^{-1}$ was found for approximately the same composition. The viscosity changes of mixing for these binary mixtures are negative with large values due to the differences between the viscosity of the compounds, around -11 mPa s for isopropanol + $[C_4min][NTf_2]$ and around -15 mPa s for isopropyl acetate + $[C_4min][NTf_2]$. Higher deviations of ideality were found for mixtures of $[C_8min][NTf_2]$ with minima of -22.9 mPa s and -29.5 mPa s, respectively.

For the isopropyl acetate + isopropanol + $[C_4min][NTf_2]$ ternary system, Fig. 2 shows (a) density, (b) refractive index and (c) dynamic viscosity isolines and Fig. 3 shows (a) excess molar volumes and (b) viscosity changes of mixing isolines. Comparing behaviour of this system and system of ionic liquid with longer alkyl chain length [7], in both cases excess molar volume are negative over the entire range of composition and reaches a minimum which correspond to the isopropyl acetate + IL binary system. The viscosity changes of mixing for both ternary systems have also negative values with a minimum corresponding to the binary mixture of isopropyl acetate + IL.

The molar refraction changes of mixing, ΔR , are positive for all the systems over the entire range, but the values of this property are very low which makes its use difficult.

3.1.1. Correlation of physical properties

The calculated data of $V^{\rm E}$, $\Delta \eta$ and ΔR were correlated with the composition data by Redlich–Kister polynomial [8], which for binary mixtures is

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

where Q_{ij} is V^{E} , ΔR 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

$$Q_{123} = Q_{12} + Q_{23} + Q_{13} + x_1 x_2 x_3 (A + B(x_1 - x_2) + C(x_2 - x_3))$$

+ $D(x_1 - x_3) + E(x_1 - x_2)^2 + F(x_2 - x_3)^2 + G(x_1 - x_3)^2 + \dots)$
(6)

Table 4

Coefficients and standard deviations σ obtained using the Redlich–Kister polynomial to correlate V^{E} , ΔR , and $\Delta \eta$ for binary systems.

| Property | A ₀ | <i>A</i> ₁ | A ₂ | A ₃ | σ |
|--|----------------|-------------------------------|--------------------------|----------------|-------|
| | | Isopropyl acetate (1) + Isopr | ropanol (2) | | |
| $V^{\rm E}/({\rm cm}^3 {\rm mol}^{-1})$ | 1.8457 | -0.0662 | 0.1197 | _ | 0.004 |
| ΔR | 0.0843 | -0.0036 | 0.0081 | _ | 0.001 |
| $\Delta \eta /(\text{mPas})$ | -2.6061 | 2.3034 | -1.7346 | _ | 0.018 |
| | | Isopropyl acetate (1)+[C4mi | m][NTf ₂](2) | | |
| $V^{\rm E}/({\rm cm}^3{\rm mol}^{-1})$ | -4.8976 | -3.5046 | -2.9692 | -1.7514 | 0.007 |
| ΔR | 0.0936 | 0.0340 | - | _ | 0.003 |
| $\Delta \eta /(\text{mPas})$ | -58.929 | 12.927 | - | _ | 0.133 |
| | | Isopropanol (1)+[C4mim] | [NTf ₂](2) | | |
| $V^{\rm E}/({\rm cm}^3 {\rm mol}^{-1})$ | -0.3996 | -0.9977 | -1.1183 | -1.3369 | 0.005 |
| ΔR | 0.0786 | - | - | _ | 0.003 |
| $\Delta \eta /(m Pa s)$ | -44.273 | 12.105 | - | - | 0.066 |

Table 5

Coefficients and standard deviations σ obtained using the Redlich–Kister polynomial, to correlate V^{E} , ΔR , and $\Delta \eta$ for the isopropyl acetate (1) + isopropanol (2) + [C₄mim][NTf₂] (3) ternary system.

| Property | Α | В | С | D | Е | F | G | σ |
|--|---------|---------|---------|---------|--------|---------|---------|-------|
| $V^{\rm E}/({\rm cm}^3 {\rm mol}^{-1})$ | -7.4176 | 0.8662 | -9.2581 | -10.967 | 5.7737 | -17.503 | -15.794 | 0.019 |
| ΔR | -0.1666 | -0.2046 | 0.0101 | 0.0955 | - | - | - | 0.004 |
| $\Delta \eta /(m Pa s)$ | 4.3236 | 9.7297 | 8.0291 | 1.2681 | - | - | - | 0.084 |

where Q_{123} represents V^{E} , ΔR or $\Delta \eta$ for the ternary mixture isopropyl acetate (1)+isopropanol (2)+[C_4mim][NTf_2] (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 [22] to establish the number of coefficients. These coefficients and their mean standard deviations are listed in Tables 4 and 5 for the binary and ternary systems respectively. The mean standard deviation was calculated by the usual equation

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

where *n* is the number of data points.

3.2. Vapour-liquid equilibrium

The vapour–liquid equilibrium data at 101.32 kPa for isopropyl acetate + $[C_4mim][NTf_2]$ and isopropanol + $[C_4mim][NTf_2]$ binary systems are summarized in Table 6. The equilibrium temperatures for these binary systems at 101.32 kPa are summarized in temperature diagram shown in Fig. 4. Since IL is essentially non-volatile, the vapour phase is entirely isopropyl acetate or isopropanol, respectively. No equilibrium temperatures could be determined in the range of very high concentration of IL, due to $[C_4mim][NTf_2]$ decomposition problems. Tokuda et al. [23] determined the decomposition temperature to be 700.15 K, higher temperatures lead to the back alkylation of the anion. The VLE data of the binary system isopropyl acetate + isopropanol have been published previously [7]. In addition, as comparison, Fig. 4 shows the vapour–liquid equilibrium for isopropanol and isopropyl acetate with $[C_8mim][NTf_2]$.

Table 7 lists the boiling temperature and the mole fractions of and isopropyl acetate and isopropanol in the liquid and vapour phases of the isopropyl acetate+isopropanol+[C_4 mim][NTf₂] ternary system (*T*, x_i and y_i , respectively). 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 number of points has been reduced for the sake of clarity). The calculated liquid isotherms are depicted in Fig. 6, indicating the different compo-

Table 6

Experimental vapour-liquid equilibrium data for the binary systems: isopropyl acetate $(1)+[C_4mim][NTf_2]$ (2) and isopropanol $(1)+[C_4mim][NTf_2]$ (2) at 101.32 kPa.

| $Isopropylacetate(1)+[C_4mim][NTf_2](2)$ | | $Isopropanol(1)+[C_4mim][NTf_2](2)$ | | |
|--|-----------------------|-------------------------------------|-----------------------|--|
| T/K | <i>x</i> ₁ | T/K | <i>x</i> ₁ | |
| 361.76 | 0.9794 | 355.66 | 0.9842 | |
| 362.09 | 0.9463 | 355.85 | 0.9678 | |
| 362.59 | 0.9031 | 356.05 | 0.9479 | |
| 363.00 | 0.8760 | 356.44 | 0.9116 | |
| 363.67 | 0.8477 | 356.95 | 0.8768 | |
| 364.39 | 0.8201 | 357.6 | 0.8260 | |
| 365.16 | 0.7901 | 358.24 | 0.7934 | |
| 366.41 | 0.7545 | 358.80 | 0.7693 | |
| 367.38 | 0.7313 | 359.49 | 0.7414 | |
| 368.18 | 0.7125 | 360.44 | 0.7050 | |
| 369.35 | 0.6817 | 361.30 | 0.6791 | |
| 370.88 | 0.6508 | 362.81 | 0.6329 | |
| 372.41 | 0.6186 | 363.66 | 0.6112 | |
| 373.21 | 0.5945 | 364.94 | 0.5855 | |
| 375.12 | 0.5735 | 366.10 | 0.5618 | |
| 376.78 | 0.5488 | 368.10 | 0.5239 | |
| 378.17 | 0.5315 | 370.31 | 0.4896 | |
| 380.78 | 0.5007 | 372.69 | 0.4528 | |
| 382.97 | 0.4734 | 374.62 | 0.4303 | |
| 385.58 | 0.4353 | 377.01 | 0.4070 | |
| 391.35 | 0.3753 | 381.69 | 0.3611 | |
| 396.45 | 0.3324 | 385.77 | 0.3214 | |
| 401.97 | 0.2933 | 390.49 | 0.2944 | |
| 407.18 | 0.2552 | 396.00 | 0.2638 | |
| 415.08 | 0.2245 | 401.66 | 0.2331 | |
| | | 408.85 | 0.2008 | |
| | | 415.91 | 0.1925 | |

sitions of ternary liquid mixtures which would boil at the same temperature.

In comparison with the vapour–liquid equilibrium for mixtures with $[C_8 \text{mim}][\text{NT}f_2][7]$, as it was expected, the increase of the alkyl chain ionic liquid increased the equilibrium temperatures of the mixture.

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



Fig. 4. Experimental VLE data at 101.32 kPa of: (a) (\blacktriangle) isopropanol + [C_4 mim][NTf₂]; (\bigtriangleup) isopropanol + [C_8 mim][NTf₂]; (b) (\bigcirc) isopropyl acetate + [C_4 mim][NTf₂]; (\blacklozenge) isopropyl aceta

Table 7

Boiling temperatures (*T*) and liquid and vapour mole fraction (x_1, y_1) for isopropyl acetate (1)+isopropanol (2)+[C₄mim][NTf₂] (3) at 101.3 kPa.

| T/K | <i>x</i> ₁ | <i>x</i> ₂ | <i>y</i> ₁ | <i>y</i> ₂ |
|------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| 355.46 | 0.1428 | 0.7580 | 0.1813 | 0.8187 |
| 355.54 | 0.3229 | 0.5540 | 0.3641 | 0.6359 |
| 355.61 | 0.4361 | 0.4600 | 0.4734 | 0.5266 |
| 355.71 | 0.0110 | 0.9550 | 0.0172 | 0.9828 |
| 355.75 | 0.0484 | 0.8750 | 0.0774 | 0.9220 |
| 356.01 | 0.0120 | 0.9150 | 0.0313 | 0.9687 |
| 356.09 | 0.4934 | 0.3951 | 0.5194 | 0.4806 |
| 356.13 | 0.1125 | 0.7557 | 0.1508 | 0.8492 |
| 356.36 | 0.0801 | 0.7912 | 0.1120 | 0.8880 |
| 356.39 | 0.1660 | 0.6772 | 0.2085 | 0.7915 |
| 356.86 | 0.2301 | 0.3974 | 0.2767 | 0.7255 |
| 356.91 | 0.2684 | 0.5468 | 0.3303 | 0.6697 |
| 356.92 | 0.2184 | 0.6001 | 0.2603 | 0.7397 |
| 357.00 | 0.0277 | 0.8123 | 0.0743 | 0.9257 |
| 357.10 | 0.3275 | 0.4846 | 0.3788 | 0.6212 |
| 357.23 | 0.1520 | 0.6568 | 0.2221 | 0.7779 |
| 357.30 | 0.0874 | 0.7245 | 0.1337 | 0.8663 |
| 357.31 | 0.0686 | 0.7503 | 0.1028 | 0.8972 |
| 357.58 | 0.0959 | 0.7019 | 0.1295 | 0.8705 |
| 357.61 | 0.1166 | 0.6518 | 0.1725 | 0.8275 |
| 357.64 | 0.4294 | 0.3789 | 0.4834 | 0.5166 |
| 357.71 | 0.1152 | 0.6756 | 0.1785 | 0.8215 |
| 358.44 | 0.4935 | 0.2990 | 0.5635 | 0.4365 |
| 358.48 | 0.6929 | 0.2132 | 0.7338 | 0.2662 |
| 358.86 | 0.0421 | 0.6170 | 0.1060 | 0.8940 |
| 358.95 | 0.0368 | 0.7117 | 0.0521 | 0.9479 |
| 359.13 | 0.5337 | 0.2534 | 0.6113 | 0.3887 |
| 359.95 | 0.0999 | 0.0005 | 0.1427 | 0.8575 |
| 360.32 | 0.1951 | 0.5113 | 0.2538 | 0.7462 |
| 360.74 | 0.7928 | 0.1039 | 0.8719 | 0.1281 |
| 360.75 | 0.1638 | 0.5234 | 0.2194 | 0.7806 |
| 360.94 | 0.6532 | 0.1675 | 0.7289 | 0.2711 |
| 361.35 | 0.2604 | 0.4139 | 0.3430 | 0.6570 |
| 361.39 | 0.2195 | 0.4479 | 0.2965 | 0.7035 |
| 361.62 | 0.8514 | 0.0552 | 0.9358 | 0.0642 |
| 361.96 | 0.0345 | 0.6187 | 0.0428 | 0.9572 |
| 362.04 | 0.6381 | 0.1230 | 0.7796 | 0.2204 |
| 362.24 | 0.3017 | 0.3632 | 0.3980 | 0.6020 |
| 362.47 | 0.3849 | 0.2923 | 0.4948 | 0.5052 |
| 362.80 | 0.6657 | 0.0921 | 0.8263 | 0.1737 |
| 363.06 | 0.7037 | 0.0658 | 0.8721 | 0.1279 |
| 363.38 | 0.4205 | 0.2449 | 0.5573 | 0.4427 |
| 363.51 | 0.0518 | 0.5649 | 0.0698 | 0.9302 |
| 364.06 | 0.3156 | 0.3090 | 0.4389 | 0.5611 |
| 364.22 | 0.5521 | 0.1474 | 0.7029 | 0.2971 |
| 364.41 | 0.0741 | 0.5228 | 0.1173 | 0.8827 |
| 364.70 | 0.4912 | 0.1583 | 0.6684 | 0.3316 |
| 365 14 | 0.1005 | 0.4379 | 0.2200 | 0.7740 |
| 365.17 | 0.1433 | 0.4112 | 0.2580 | 0.7420 |
| 365.57 | 0.4531 | 0.1806 | 0.6375 | 0.3625 |
| 365.74 | 0.0927 | 0.4675 | 0.1547 | 0.8453 |
| 365.78 | 0.5919 | 0.1069 | 0.7821 | 0.2179 |
| 366.95 | 0.2062 | 0.3494 | 0.2952 | 0.7048 |
| 368.54 | 0.6516 | 0.0233 | 0.9301 | 0.0699 |
| 369.24 | 0.0245 | 0.4979 | 0.0353 | 0.9647 |
| 369.58 | 0.2222 | 0.3026 | 0.3483 | 0.6517 |
| 370.50 | 0.1128 | 0.3543 | 0.2004 | 0.7996 |
| 3/1.38 371.05 | 0.0855 | 0.3699 | 0.1587 | 0.8413 |
| 372.68 | 0.2303 | 0.3695 | 0.1213 | 0.3930 |
| 372.94 | 0.2502 | 0.2264 | 0.4446 | 0.5554 |
| 374.40 | 0.2838 | 0.1845 | 0.5001 | 0.4999 |
| 376.13 | 0.3024 | 0.1533 | 0.5541 | 0.4459 |
| 378.12 | 0.3196 | 0.1202 | 0.6253 | 0.3747 |
| 379.44 | 0.3392 | 0.0895 | 0.6995 | 0.3005 |

| Table 7 (Contin | nued) | | | |
|-----------------|-----------------------|-----------------------|-----------------------|-----------------------|
| T/K | <i>x</i> ₁ | <i>x</i> ₂ | <i>y</i> ₁ | <i>y</i> ₂ |
| 379.64 | 0.3576 | 0.0669 | 0.7551 | 0.2449 |
| 382.34 | 0.3379 | 0.0224 | 0.8735 | 0.1265 |
| 383.61 | 0.0134 | 0.3418 | 0.0273 | 0.9727 |
| 384.91 | 0.0191 | 0.3033 | 0.0525 | 0.9475 |
| 389.18 | 0.1280 | 0.2076 | 0.3141 | 0.6859 |
| 390.40 | 0.0805 | 0.2232 | 0.2188 | 0.7812 |
| 390.43 | 0.0454 | 0.2709 | 0.1123 | 0.8877 |
| 391.23 | 0.2111 | 0.0767 | 0.5265 | 0.4735 |
| 391.83 | 0.2155 | 0.0919 | 0.5661 | 0.4339 |
| 392.24 | 0.4944 | 0.0593 | 0.8342 | 0.1658 |
| 392.30 | 0.1613 | 0.1346 | 0.4329 | 0.5671 |
| 393.11 | 0.3186 | 0.0662 | 0.8905 | 0.1095 |
| 393.23 | 0.2409 | 0.0731 | 0.6665 | 0.3335 |
| 393.61 | 0.2893 | 0.0428 | 0.7791 | 0.2209 |
| 394.36 | 0.2998 | 0.0361 | 0.9282 | 0.0718 |



Fig. 5. Experimental (--) and correlated with NRTL model (- - - -) VLE data for the ternary system isopropyl acetate (1)+isopropanol (2)+[C₄mim][NTf₂](3) at 101.32 kPa.

was considered ideal in the binary and ternary systems with IL. For the binary systems isopropyl acetate $+[C_4mim][NTf_2]$ and isopropanol $+[C_4mim][NTf_2]$ this approximation is satisfactory, 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:

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

using values for the coefficients *A*, *B*, and *C* reported in Table 8 as taken from literature [16,24], and arbitrarily setting them to fictional values in order to lead to a negligible vapour pressure for $[C_4 mim][NTf_2]$.

The models used to calculate the liquid-phase activity coefficients are NRTL, setting the non-randomness parameter α to different values and selecting the value giving the best correlation, and UNIQUAC equations. The UNIQUAC structural parameters

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

| Compound | Α | В | С |
|------------------------|---------|----------|---------|
| Isopropyl acetate [16] | 6.46612 | 1436.530 | -39.485 |
| Isopropanol [22] | 6.86100 | 1357.427 | -75.814 |

Table 9

Correlation of VLE data of the indicated binary systems: model parameters (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 | | σ (T/K) | $\sigma(x)$ | $\sigma(y)$ | σ (P/kPa |
|-------------------------|--------------------------------|---------------------------|---|-------------|-------------|----------|
| | | Isopropyl acetate (1) | +[C ₄ mim][NTf ₂](2) | | | |
| NRTL ($\alpha = 0.3$) | $\Delta g_{12} = 11795$ | $\Delta g_{21} = -4755.4$ | 0.27 | 0.0042 | 0.0005 | 0.024 |
| UNIQUAC ^a | $\Delta u_{12} = 5823.5$ | $\Delta u_{21} = -3001.6$ | 0.32 | 0.0111 | 0.0005 | 0.028 |
| | | Isopropanol (1)+[| $C_4 mim][NTf_2](2)$ | | | |
| NRTL ($\alpha = 0.1$) | $\Delta g_{12} = 24121$ | $\Delta g_{21} = -13105$ | 0.20 | 0.0068 | 0.0005 | 0.015 |
| UNIQUAC ^a | $\Delta u_{12} = 2392.7$ | $\Delta u_{21} = -1364.7$ | 0.44 | 0.0214 | 0.0006 | 0.035 |

^a Structural parameters for UNIQUAC equation; r = 4.1522, q = 3.652 for isopropyl acetate [25]; r = 2.7792, q = 2.508, q' = 0.890 for isopropanol [25]; r = 11.2, q = 7.29 for $[C_4 min][NTf_2]$ [26].

Table 10

Correlation of VLE data of the ternary system: model parameters (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 | | σ (T/K) | $\sigma(x_1)$ | $\sigma(x_2)$ | $\sigma(y_1)$ | $\sigma(y_2)$ | σ (<i>P</i> /kPa) |
|-------------------------|---|--|---------|---------------|---------------|---------------|---------------|--------------------|
| NRTL ($\alpha = 0.3$) | $\Delta g_{12} = 1753.0$ $\Delta g_{13} = 13270$ $\Delta g_{23} = 10892$ | $\Delta g_{21} = 130.55$ $\Delta g_{31} = -4797.5$ $\Delta g_{32} = -4568.2$ | 0.47 | 0.0189 | 0.0121 | 0.0057 | 0.0057 | 0.012 |
| UNIQUAC ^a | $\Delta u_{12} = 11648$ $\Delta u_{13} = -697.33$ $\Delta u_{23} = -1256.6$ | $\Delta u_{21} = -2254.1$ $\Delta u_{31} = 568.38$ $\Delta u_{32} = 2134.4$ | 0.70 | 0.0205 | 0.0165 | 0.0071 | 0.0071 | 0.087 |

^a Structural parameters for UNIQUAC equation; r = 4.1522, q = 3.652 for isopropyl acetate [25]; r = 2.7792, q = 2.508, q' = 0.890 for isopropanol [25]; r = 11.2, q = 7.29 for $[C_4 mim][NTf_2]$ [26].



Fig. 6. Temperature (K) isolines for isopropyl acetate (1)+isopropanol (2)+[C₄mim][NTf₂](3) at 101.32 kPa.

q and *r* were calculated by group contribution methods [25,26]. 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 9 and 10 for the binary and ternary systems, respectively.

Figs. 4 and 5 show the comparison of the calculated values using the NRTL equation with the experimental VLE data for the binary and ternary systems, respectively.

4. Conclusions

Densities, refractive indices and dynamic viscosities and their corresponding changes of mixing, V^{E} , $\Delta \eta$, ΔR , of binary and ternary mixtures of isopropyl acetate, isopropanol and 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ([C₄mim][NTf₂]) were evaluated at 298.15 K and atmospheric pressure. These prop-

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

In addition, experimental isobaric vapour–liquid equilibrium (VLE) data have been measured for the binary systems isopropyl acetate + $[C_4 mim][NTf_2]$ and isopropanol + $[C_4 mim][NTf_2]$ and for the ternary system isopropyl acetate + isopropanol + $[C_4 mim][NTf_2]$ at 101.32 kPa. Comparison with other data found in bibliography for the isopropanol + $[C_4 mim][NTf_2]$ binary system was not possible due to the different nature of the experiments (isothermal instead of isobaric).

The NRTL and UNIQUAC equations were used to correlate experimental VLE data of these systems obtaining results that are in agreement with the experimental data. For the binary system of isopropanol + $[C_4 mim][NTf_2]$ the NRTL equation, with α set to 0.1 gives the best results, whereas the NRTL with α = 0.3 gives smallest deviations for the isopropyl acetate + $[C_4 mim][NTf_2]$ binary system and for the isopropyl acetate + isopropanol + $[C_4 mim][NTf_2]$ ternary system. However deviations for the experimental results in the ternary system are slightly high.

Increasing of the alkyl chain length of ionic liquid from $[C_4mim][NTf_2]$ to $[C_8mim][NTf_2]$ higher deviations of ideality and boiling temperatures were found.

List of symbols

A, B, C, D, E, F, G 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
- R Molar refraction
- *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

NRTL Non-randomness parameter

- η Dynamic viscosity
- *υ* Kinematic viscosity
- ρ Density
- σ Mean standard deviation
- Δ Changes of mixing
- Δg NRTL binary interaction parameter
- Δu UNIQUAC binary interaction parameter

Subscripts

- *i i*th component
- 1, 2, 3 Components 1, 2, 3
- M Mixture

Superscripts

- k Polynomial grade
- E Excess
- S Saturation

Acknowledgments

The authors are grateful to the Universidad de Santiago de Compostela, Ministerio de Educación y Ciencia (Spain) (Proyect CTQ2009-10776), CONICET, Universidad Nacional del Sur (Argentine) and European Union (project ALFA II-400-FA) for financial support.

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