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Physico-chemical Properties of Binary and Ternary Mixtures of Ethyl Acetate + Ethanol + 1-Butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide at 298.15 K and Atmospheric Pressure

Alfonsina E. Andreatta · Alberto Arce · Eva Rodil · Ana Soto

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Abstract Densities, viscosities and refractive indices have been measured at 298.15 K and atmospheric pressure for binary and ternary mixtures of ethanol, ethyl acetate and 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl) imide [C_4mim][NTF_2]. From these experimental properties, the corresponding excess properties have been calculated and adequately fitted with the Redlich-Kister polynomial equation. The adjustable parameters and standard deviations between experimental and calculated values are reported. Interest of this mixture is due to the possibility of using [C_4mim][NTF_2] as an entrainer in the extractive distillation of ethanol + ethyl acetate. These results are compared with previously determined experimental data for mixtures of ethyl acetate and/or ethanol with the ionic liquid 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide, [C_8mim][NTF_2].

Keywords Density · Refractive index · Dynamic viscosity · Ionic liquid

1 Introduction

Room temperature ionic liquids (ILs) are emerging as replacements for traditionally used volatile organic solvents. They are composed of organic cations and organic or inorganic anions. They are called "designer solvents" because desired properties can be obtained by combination of their ions [1]. To design processes involving ionic liquids as solvents, it

A.E. Andreatta · A. Arce (✉) · E. Rodil · A. Soto
Chemical Engineering Department, University of Santiago de Compostela,
15782 Santiago de Compostela, Spain
e-mail: alberto.arce@usc.es

Present address:
A.E. Andreatta
PLAPIQUI, Universidad Nacional del Sur – CONICET, Camino La Carrindanga Km 7, Casilla 717,
8000 Bahía Blanca, Argentina

is necessary to know the physico-chemical properties of the pure salts and their related mixtures.

In recent years, ionic liquids of the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, [$C_n$mim][NTF_2] series have become popular due to their combined relatively low viscosity [2, 3] and high thermal stability [4]. Experimental measurements of their physico-chemical properties are scarce and clearly needed.

In this context, physico-chemical properties such as densities, refractive indices and dynamic viscosities have been measured at 298.15 K and atmospheric pressure for ternary mixtures of ethyl acetate + ethanol + 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide [C_4mim][NTF_2], and for their corresponding binary mixtures containing [C_4mim][NTF_2]. Interest in this mixture is based on the possibility of using [C_4mim][NTF_2] IL as an entrainer for the extractive distillation of ethanol + ethyl acetate [6]. No available information was found in the literature about the volumetric and viscosity properties of these binary and ternary mixtures. A comparison was made of the physico-chemical and excess properties of mixtures of ethyl acetate and/or ethanol with the IL studied in this work and the corresponding system with 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide [C_8mim][NTF_2] [5], in order to analyze the effect of the alkyl chain.

2 Experimental Section

2.1 Chemicals

The chemicals purchased for the experiments were ethyl acetate (99.8%, Sigma-Aldrich) and ethanol (99.9%, Merck). Gas chromatographic (GC) analysis did not detect any appreciable peaks due to impurities. No further purification of these products was carried out. The ionic liquid 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide, [C_4mim][NTF_2], was synthesized in our laboratory by reaction of 1-methylimidazole (Aldrich, > 99% by GC) with an excess of 1-bromobutane (Merck, > 98%) to produce the [C_4mim][Br]. This bromide salt was mixed with the lithium bis(trifluoromethanesulfonyl)-imide salt, Li[NTF_2] (Solvionic, >99%), in deionized water to obtain [C_4min][NTF_2] by an ion metathesis reaction. After washing, the purification of [C_4min][NTF_2] 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 [7]. The water mass fraction was determined by means of a Karl Fischer titration carried out in a Metrohm 737 KF, which yielded the mass fraction $\omega = 46.3 \times 10^{-6}$. No bromide was detected by means of capillary electrophoresis. The ionic liquid was analyzed by ^{1}H NMR and ^{13}C NMR spectroscopy to confirm the absence of any major impurities.

Table 1 gives a comparison between experimental and literature [8–12] data of the density, refractive index and dynamic viscosity, in addition to reporting the water content of the pure components.

2.2 Experimental Setup and Procedure

Weighings were carried out in a Mettler Toledo AT 261 balance with an uncertainty of $\pm 1 \times 10^{-4}$ g, and the uncertainties of the compositions of the prepared mixtures were estimated to be ± 0.0002 mole fractions. Densities were measured in an Anton Paar DMA 5000 densimeter. This instrument automatically corrects for the influence of viscosity on density

Table 1 Physical properties of the pure components at $T = 298.15$ K

Component	CASRN[a]	ω (H_2O)/10^{-6}	ρ/(g·cm^{-3})		n_D		η/(mPa·s)	
			This work	Literature	This work	Literature	This work	Literature
Ethyl acetate	141-78-6	167	0.89440	0.89455 [8]	1.36983	1.36978 [8]	0.426	0.426 [8]
Ethanol	64-17-5	347	0.78514	0.78493 [8]	1.35928	1.35941 [8]	1.054	1.0826 [8]
[C_4mim][NTF_2]	174899-83-3	46	1.43658	1.43 [9]	1.42692	1.427 [9]	50.7	52[b] [9]
				1.436 [10]				44 [10]
				1.437 [11]				49.9 [11]
				1.4366 [12]				

[a]CASRN, Chemical Abstract Service registry number

[b]At 293 K

over the whole viscosity range. The viscosity correction for this type of densimeter has been adequately checked [13]. The uncertainties in the temperature and density measurements are ±0.01 K and $\pm 3 \times 10^{-5}$ g·cm^{-3}, respectively. Refractive indices were measured with an ATAGO RX-5000 refractometer with a Hero Therm thermostat to maintain the temperature within ±0.02 K. The uncertainties in the refractive index measurements are $\pm 4 \times 10^{-5}$.

The kinematic viscosities were determined with micro Ubbelohde viscometers. Two micro Ubbelohde viscometers (capillaries I and II) were used in the experiments according to the different viscosity values of the mixtures. The capillaries were calibrated and certified by the manufacturer, and were verified by us by measuring the viscosity of different pure liquids. Flow-time measurements were performed with the Lauda Processor Viscosity System PVS1 with a resolution of 0.01 s. The temperature of the viscometer was kept constant within ±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 less than 100 s and ±0.5 s for higher times. The kinematic viscosity of a solution, υ, is given by

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

where υ is the kinematic viscosity, t is the flow time, K is the capillary constant reported by the manufacturer, and y is the kinetic energy correction that is used if necessary. Dynamic viscosities were calculated from the kinematic viscosities and densities. The uncertainty for the dynamic viscosity determinations is estimated to be ±0.5%.

3 Experimental Results and Discussion

Densities, ρ, refractive indices, n_D, dynamic viscosities, η, excess molar volumes, V^E and molar refraction changes of mixing, ΔR, at 298.15 K and atmospheric pressure are reported in Table 2 for the binary systems ethyl acetate + [C$_4$min][NTF$_2$] and ethanol + [C$_4$min][NTF$_2$], and in Table 3 for the ternary system ethyl acetate + ethanol + [C$_4$min][NTF$_2$]. The physico-chemical properties of the ethyl acetate + ethanol binary system have been published previously [5].

The excess molar volumes V^E, and the viscosity $\Delta\eta$ and molar refraction ΔR changes of mixing were calculated from the experimental values using the following expressions:

$$V^E = V_M - \sum_i x_i V_i \tag{2}$$

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

$$\Delta R = R_M - \sum_i x_i R_i \tag{4}$$

where V_M is the molar volume of the mixture, R_M is the molar refraction of the mixture obtained from the Lorentz–Lorenz equation:

$$R_M = \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right) V_M \tag{5}$$

and x_i, V_i, η_i, and R_i are the mole fraction, the molar volume, the viscosity, and the molar refraction, respectively, for component i. Uncertainties in the values of V^E and ΔR were

Table 2 Densities ρ, refractive indices n_D, dynamic viscosities η, excess molar volume V^E, molar refraction changes of mixing ΔR, and viscosity changes of mixing $\Delta\eta$ at 298.15 K for binary systems

x	$\rho/(g\cdot cm^{-3})$	n_D	$\eta/(mPa\cdot s)$	$V^E/(cm^3\cdot mol^{-1})$	$\Delta R/(cm^3\cdot mol^{-1})$	$\Delta\eta/(mPa\cdot s)$
			x Ethyl acetate + $(1-x)$ [C_4mim][NTF_2]			
0.0522	1.42735	1.42614	44.4	−0.132	0.008	−3.63
0.0920	1.41978	1.42546	40.0	−0.217	0.011	−6.02
0.1818	1.40111	1.42377	30.6	−0.430	0.013	−11.0
0.2303	1.38988	1.42274	26.5	−0.538	0.013	−12.6
0.2982	1.37254	1.42116	21.1	−0.674	0.018	−14.6
0.4204	1.33575	1.41775	13.67	−0.915	0.019	−15.9
0.4752	1.31612	1.41591	10.91	−0.978	0.026	−15.9
0.5937	1.26566	1.41114	6.54	−1.139	0.031	−14.3
0.6953	1.21004	1.40569	3.93	−1.212	0.029	−11.8
0.7954	1.13855	1.39835	2.21	−1.167	0.022	−8.50
0.8933	1.04377	1.38804	1.105	−0.871	0.020	−4.68
			x Ethanol + $(1-x)$ [C_4mim][NTF_2]			
0.0793	1.42561	1.42581	42.6	−0.022	0.004	−4.20
0.1174	1.41977	1.42521	38.5	−0.028	0.006	−6.38
0.1393	1.41618	1.42486	36.8	−0.023	0.011	−6.93
0.2058	1.40462	1.42366	31.4	−0.049	0.009	−9.11
0.2578	1.39448	1.42265	27.3	−0.067	0.013	−10.6
0.3450	1.37484	1.42066	21.6	−0.097	0.015	−12.0
0.3840	1.36489	1.41969	19.4	−0.127	0.017	−12.3
0.4122	1.35716	1.41891	17.91	−0.152	0.016	−12.3
0.5622	1.30478	1.41362	11.15	−0.230	0.014	−11.6
0.6880	1.23928	1.40712	7.11	−0.291	0.020	−9.43
0.7967	1.15332	1.39852	4.36	−0.343	0.019	−6.78
0.8984	1.02390	1.38526	2.46	−0.335	0.010	−3.63

estimated to be less than 0.005 $cm^3\cdot mol^{-1}$. The uncertainty in the $\Delta\eta$ values was estimated to be less than 0.1 mPa·s.

Figure 1 shows the excess molar volumes and viscosity changes from mixing for the ethanol + [C_4min][NTF_2] and ethyl acetate + [C_4min][NTF_2] binary systems. As it can be seen, the excess molar volumes for the ethanol + [C_4min][NTF_2] binary system are negative over the whole composition range with a minimum value of -0.38 $cm^3\cdot mol^{-1}$. The ethyl acetate + [C_4min][NTF_2] binary system also shows negative values over the whole range, with a minimum value around -1.2 $cm^3\cdot mol^{-1}$. No comparable data were found in the surveyed literature for these binary systems. The viscosity changes from mixing of these binary liquids are negative with large values, due to the differences between the viscosity of the compounds of around -12.5 mPa·s for ethanol + [C_4min][NTF_2] and around -16 mPa·s for ethyl acetate + [C_4min][NTF_2] systems.

If we compare these results with previously obtained data [5] for binary mixtures of ethanol or ethyl acetate with a different imidazolium ionic liquid having a longer alkyl chain length and the same anion, [C_8min][NTF_2], then we can observe that increasing the alkyl

Table 3 Densities ρ, refractive indices n_D, dynamic viscosities η, excess molar volumes V^E, molar refraction changes of mixing ΔR, and viscosity changes of mixing $\Delta\eta$ at 298.15 K for the ternary ethyl acetate (1) + ethanol (2) + $[C_4mim][NTF_2]$ (3) mixtures

x_1	x_2	ρ/(g·cm^{-3})	n_D	η/(mPa·s)	V^E/(cm^3·mol^{-1})	ΔR/(cm^3·mol^{-1})	$\Delta\eta$/(mPa·s)
0.8229	0.1591	0.91487	1.37267	0.523	−0.139	0.010	−0.908
0.7708	0.2059	0.92100	1.37350	0.557	−0.166	0.014	−1.17
0.6745	0.2924	0.93274	1.37505	0.658	−0.226	0.018	−1.61
0.5842	0.3736	0.94410	1.37648	0.736	−0.281	0.018	−2.05
0.4786	0.4684	0.95759	1.37821	0.869	−0.318	0.024	−2.52
0.3908	0.5473	0.96915	1.37947	1.023	−0.344	0.019	−2.86
0.2861	0.6413	0.98322	1.38111	1.252	−0.354	0.022	−3.23
0.1894	0.7282	0.99650	1.38245	1.533	−0.347	0.017	−3.49
0.1579	0.7565	1.00093	1.38289	1.636	−0.344	0.016	−3.57
0.1037	0.8052	1.00869	1.38368	1.848	−0.340	0.013	−3.66
0.0584	0.8459	1.01531	1.38431	2.09	−0.338	0.009	−3.68
0.8998	0.0800	0.92341	1.37366	0.526	−0.203	0.008	−0.967
0.7923	0.1658	0.95365	1.37747	0.681	−0.366	0.014	−1.96
0.6933	0.2448	0.98058	1.38069	0.829	−0.456	0.020	−2.86
0.5989	0.3201	1.00565	1.38357	1.006	−0.512	0.024	−3.69
0.5020	0.3974	1.03076	1.38629	1.235	−0.540	0.024	−4.49
0.3986	0.4799	1.05680	1.38911	1.585	−0.534	0.029	−5.25
0.2957	0.5621	1.08203	1.39164	2.03	−0.496	0.029	−5.89
0.2115	0.6293	1.10241	1.39369	2.49	−0.467	0.028	−6.33
0.1551	0.6743	1.11582	1.39494	2.84	−0.440	0.024	−6.59
0.1181	0.7038	1.12442	1.39573	3.11	−0.409	0.023	−6.71
0.0632	0.7476	1.13728	1.39692	3.67	−0.379	0.018	−6.73
0.8644	0.0953	0.95418	1.37746	0.656	−0.383	0.011	−1.85
0.7989	0.1414	0.98104	1.38067	0.789	−0.510	0.013	−2.73
0.6967	0.2132	1.02031	1.38523	1.026	−0.626	0.021	−4.06
0.6021	0.2797	1.05423	1.38902	1.324	−0.671	0.030	−5.22
0.4946	0.3553	1.09040	1.39273	1.727	−0.685	0.025	−6.46
0.3973	0.4237	1.12109	1.39589	2.32	−0.660	0.028	−7.36
0.2658	0.5162	1.15940	1.39955	3.24	−0.544	0.028	−8.46
0.1954	0.5657	1.17895	1.40142	3.92	−0.490	0.026	−8.87
0.1495	0.5980	1.19121	1.40254	4.39	−0.441	0.024	−9.11
0.0992	0.6333	1.20462	1.40379	5.10	−0.417	0.018	−9.16
0.0564	0.6634	1.21551	1.40487	5.74	−0.371	0.021	−9.19
0.9051	0.0571	0.95250	1.37724	0.658	−0.411	0.005	−1.71
0.8020	0.1191	1.00798	1.38384	0.890	−0.644	0.016	−3.58
0.6956	0.1830	1.05877	1.38954	1.289	−0.766	0.024	−5.35
0.6152	0.2314	1.09329	1.39325	1.684	−0.785	0.031	−6.60
0.5057	0.2972	1.13624	1.39767	2.33	−0.781	0.033	−8.19
0.3878	0.3681	1.17747	1.40168	3.28	−0.695	0.032	−9.65
0.2880	0.4281	1.20914	1.40464	4.46	−0.600	0.026	−10.5
0.1963	0.4832	1.23588	1.40716	5.71	−0.487	0.027	−11.1

Table 3 (*Continued*)

x_1	x_2	$\rho/(\mathrm{g\cdot cm^{-3}})$	n_D	$\eta/(\mathrm{mPa\cdot s})$	$V^E/(\mathrm{cm^3\cdot mol^{-1}})$	$\Delta R/(\mathrm{cm^3\cdot mol^{-1}})$	$\Delta\eta/(\mathrm{mPa\cdot s})$
0.1550	0.5080	1.24741	1.40828	6.45	−0.449	0.027	−11.2
0.1007	0.5407	1.26179	1.40964	7.42	−0.370	0.030	−11.4
0.0452	0.5740	1.27602	1.41103	8.70	−0.303	0.034	−11.2
0.8911	0.0549	0.97594	1.38007	0.714	−0.522	0.011	−2.46
0.8023	0.0997	1.03210	1.38669	1.050	−0.731	0.027	−4.36
0.7070	0.1477	1.08484	1.39240	1.521	−0.870	0.023	−6.30
0.6042	0.1995	1.13394	1.39750	2.19	−0.886	0.027	−8.23
0.5100	0.2470	1.17366	1.40148	3.05	−0.863	0.026	−9.74
0.3928	0.3062	1.21653	1.40559	4.40	−0.716	0.030	−11.4
0.2940	0.3560	1.24889	1.40868	5.97	−0.616	0.028	−12.3
0.1983	0.4042	1.27698	1.41143	7.96	−0.483	0.037	−12.7
0.1490	0.4291	1.29041	1.41250	9.07	−0.408	0.022	−12.8
0.0982	0.4547	1.30379	1.41382	10.36	−0.354	0.025	−12.9
0.0511	0.4784	1.31560	1.41483	11.87	−0.299	0.013	−12.5
0.8887	0.0450	0.99331	1.38220	0.803	−0.628	0.014	−2.99
0.7818	0.0882	1.06887	1.39076	1.308	−0.890	0.022	−5.71
0.6908	0.1250	1.12240	1.39648	1.976	−0.975	0.027	−7.79
0.6032	0.1604	1.16644	1.40099	2.80	−0.951	0.035	−9.61
0.5106	0.1978	1.20697	1.40493	3.97	−0.886	0.033	−11.2
0.3940	0.2449	1.25121	1.40914	5.82	−0.807	0.021	−12.9
0.2933	0.2857	1.28394	1.41219	8.02	−0.663	0.018	−13.8
0.1993	0.3236	1.31091	1.41472	10.53	−0.505	0.021	−14.1
0.1470	0.3448	1.32471	1.41595	12.41	−0.413	0.016	−13.8
0.0940	0.3662	1.33771	1.41715	14.33	−0.297	0.021	−13.5
0.0516	0.3833	1.34781	1.41803	16.14	−0.236	0.013	−12.9
0.9014	0.0299	0.99689	1.38256	0.806	−0.653	0.011	−3.09
0.7971	0.0615	1.08085	1.39207	1.440	−0.950	0.021	−6.13
0.6947	0.0925	1.14643	1.39898	2.35	−1.037	0.025	−8.83
0.6116	0.1177	1.19054	1.40338	3.32	−1.009	0.026	−10.8
0.5201	0.1455	1.23230	1.40750	4.81	−0.959	0.025	−12.5
0.3920	0.1843	1.28078	1.41215	7.60	−0.790	0.028	−14.2
0.2974	0.2130	1.31101	1.41499	10.46	−0.632	0.030	−14.7
0.1969	0.2434	1.33919	1.41759	14.03	−0.468	0.026	−14.7
0.1391	0.2609	1.35387	1.41892	16.65	−0.385	0.019	−14.1
0.0996	0.2729	1.36310	1.41973	18.50	−0.289	0.019	−13.6
0.0538	0.2868	1.37337	1.42067	21.0	−0.195	0.019	−12.7
0.8938	0.0216	1.01732	1.38506	0.982	−0.753	0.020	−3.71
0.8009	0.0405	1.09794	1.39395	1.644	−1.029	0.020	−6.77
0.6895	0.0632	1.17271	1.40177	2.89	−1.098	0.029	−10.0
0.6181	0.0777	1.21184	1.40572	4.09	−1.091	0.031	−11.7
0.5164	0.0984	1.25861	1.41025	6.16	−0.992	0.032	−13.7
0.3937	0.1234	1.30458	1.41456	9.59	−0.812	0.028	−15.2
0.3101	0.1404	1.33112	1.41701	13.03	−0.693	0.020	−15.1

Table 3 (*Continued*)

x_1	x_2	$\rho/(\mathrm{g\cdot cm^{-3}})$	n_D	$\eta/(\mathrm{mPa\cdot s})$	$V^E/(\mathrm{cm^3\cdot mol^{-1}})$	$\Delta R/(\mathrm{cm^3\cdot mol^{-1}})$	$\Delta\eta/(\mathrm{mPa\cdot s})$
0.1949	0.1639	1.36246	1.41985	18.29	−0.487	0.010	−14.5
0.1475	0.1735	1.37385	1.42088	21.3	−0.383	0.009	−13.4
0.0957	0.1841	1.38555	1.42201	24.4	−0.278	0.015	−12.3
0.0430	0.1948	1.39676	1.42298	28.1	−0.184	0.005	−10.8
0.9023	0.0086	1.02310	1.38572	0.967	−0.789	0.019	−3.94
0.8040	0.0173	1.11632	1.39611	1.818	−1.079	0.035	−7.60
0.7051	0.0260	1.18725	1.40335	3.29	−1.161	0.031	−10.7
0.6029	0.0350	1.24412	1.40891	5.36	−1.098	0.029	−13.3
0.5210	0.0422	1.28137	1.41256	7.65	−1.011	0.034	−14.8
0.3936	0.0534	1.32830	1.41692	12.87	−0.789	0.030	−15.4
0.2942	0.0622	1.35831	1.41973	17.63	−0.610	0.030	−15.2
0.2189	0.0688	1.37811	1.42149	22.5	−0.485	0.016	−13.8
0.1444	0.0754	1.39536	1.42310	28.1	−0.313	0.021	−11.6
0.1168	0.0778	1.40132	1.42362	30.1	−0.255	0.017	−10.8
0.0753	0.0815	1.40977	1.42438	34.1	−0.148	0.018	−8.77

chain length decreases the density of the pure ionic liquid and their mixtures while the dynamic viscosity increases.

For excess properties, the same qualitative behavior has been found for both ILs. The binary system ethyl acetate + $[C_4min][NTF_2]$ has slightly more negative excess molar volumes than the ethyl acetate + $[C_8min][NTF_2]$ system. The same type of behavior occurs for mixtures with ethanol, raising in this case the S-shape found for ethanol + $[C_8min][NTF_2]$ mixtures (Fig. 1). Comparing the viscosity changes from mixing, both binary systems with $[C_4min][NTF_2]$ have considerably less negative values for this property than those for mixtures with $[C_8min][NTF_2]$. The same type of behavior was observed in previous studies carried out by other authors [14, 15] concerning the effect of the alkyl chain of the IL on the physico-chemistry properties of their mixtures.

For the ethyl acetate + ethanol + $[C_4min][NTF_2]$ ternary system, Figs. 2, 3 and 4 show the density, refractive index and dynamic viscosity isolines, respectively; whereas Figs. 5 and 6 show the isolines for excess molar volume and viscosity changes of mixing, respectively. The ethyl acetate + ethanol + $[C_4mim][NTF_2]$ ternary system exhibits relatively large and negative excess molar volumes over the entire range of homogeneous mixtures. They reach a minimum value of around $-1.2\ \mathrm{cm^3\cdot mol^{-1}}$, which corresponds to that of the binary ethyl acetate + $[C_4mim][NTF_2]$ system. The viscosity changes from mixing are negative with a minimum value around −16 mPa·s corresponding to the ethyl acetate + $[C_4mim][NTF_2]$ binary system. Regarding molar refraction changes from mixing for the studied systems, it is difficult to draw a real conclusion due to their small values. The qualitative behavior is exactly the same as was found for ternary mixtures with $[C_8mim][NTF_2]$.

4 Correlation of Physico-chemical Properties

Calculated values of the excess molar volumes V^E, and viscosity $\Delta\eta$ and molar refraction ΔR changes from mixing, were correlated with the composition data using the Redlich-

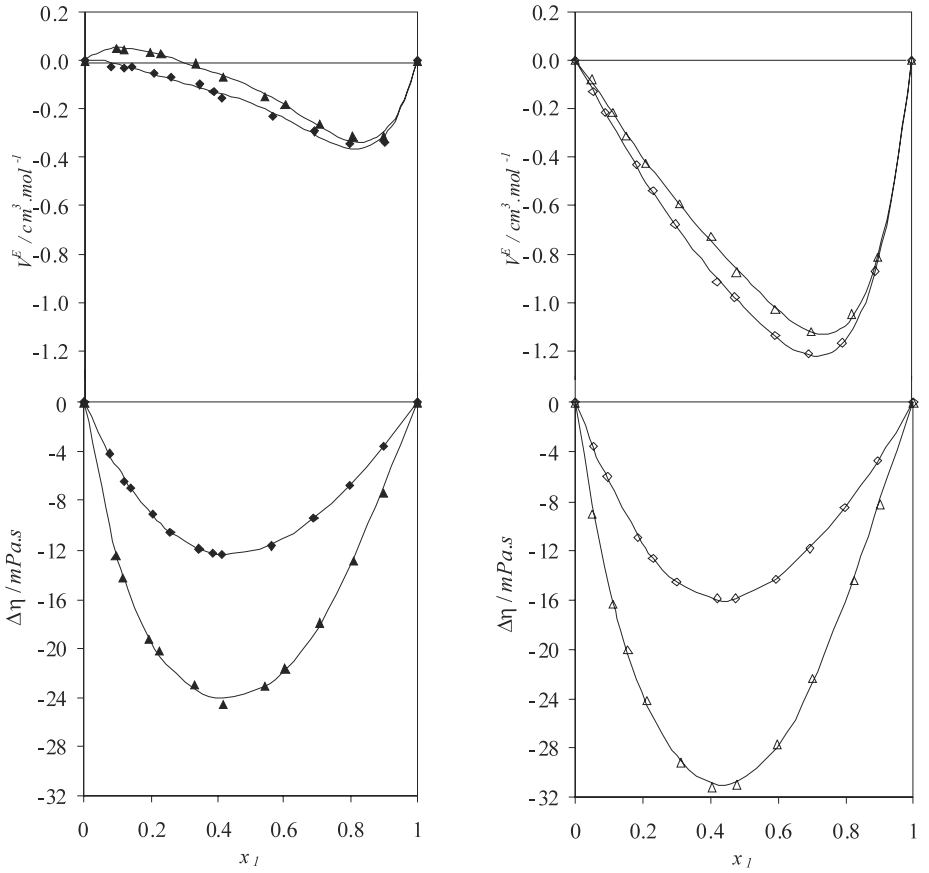

Fig. 1 Experimental excess molar volume and dynamic viscosity changes from mixing for: ◆, ethanol (1) + [C_4mim][NTF_2] (2); ▲, ethanol (1) + [C_8mim][NTF_2] (2); ◇, ethyl acetate (1) + [C_4mim][NTF_2] (2); △, ethyl acetate (1) + [C_8mim][NTF_2] (2) binary mixtures at 298.15 K and atmospheric pressure. The lines correspond to the Redlich-Kister correlations

Kister polynomial [16]. For binary mixtures the equation is

$$Q_{ij} = x_i x_j \sum_k A_k (x_i - x_j)^k \tag{6}$$

where Q_{ij} represents V^{E}, $\Delta\eta$ or ΔR; 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

$$Q_{123} = Q_{12} + Q_{23} + Q_{13} + x_1 x_2 x_3 \begin{pmatrix} A + B(x_1 - x_2) + C(x_2 - x_3) + D(x_1 - x_3) + \\ E(x_1 - x_2)^2 + F(x_2 - x_3)^2 + G(x_1 - x_3)^2 + \cdots \end{pmatrix} \tag{7}$$

where Q_{123} represents V^{E}, $\Delta\eta$ or ΔR for the ternary system and Q_{ij} is the corresponding Redlich-Kister polynomial for the same property fitted to the binary systems data.

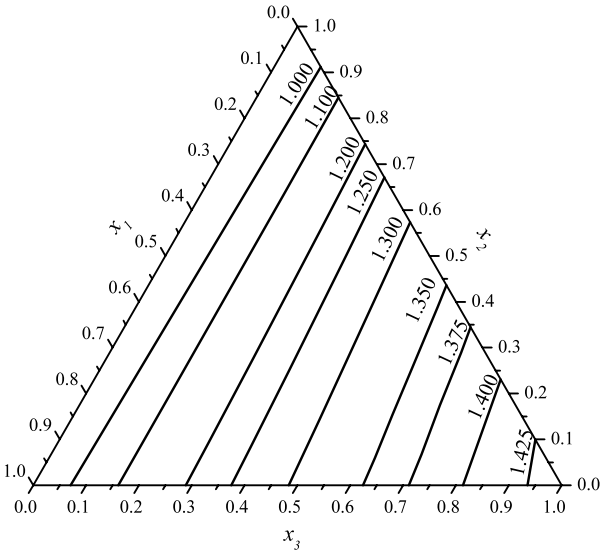

Fig. 2 Density ρ (g·cm^{-3}) isolines for ethyl acetate (1) + ethanol (2) + [C$_4$mim][NTF$_2$] (3) mixtures at 298.15 K and atmospheric pressure

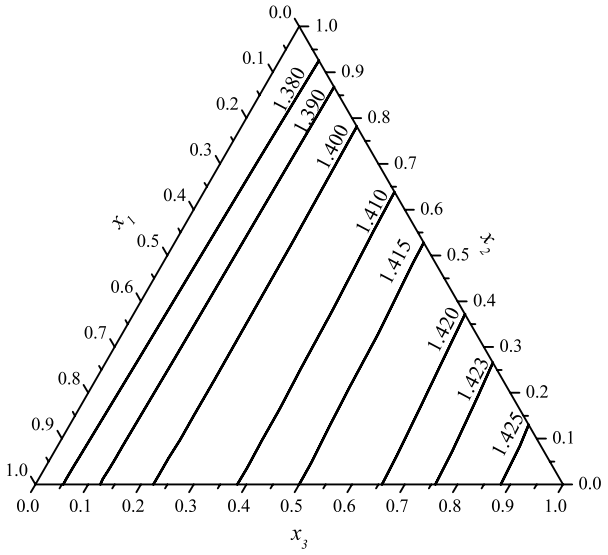

Fig. 3 Refractive index n_D isolines for ethyl acetate (1) + ethanol (2) + [C$_4$mim][NTF$_2$] (3) mixtures at 298.15 K and atmospheric pressure

Tables 4 and 5 show the Redlich-Kister coefficients for the binary and ternary systems and the standard deviations obtained in the correlations, respectively. The coefficients were obtained by fitting the coefficients of Eqs. 6 and 7 by least-squares regression. Fisher's F-test was used to define the appropriate polynomial degree.

5 Conclusions

In the present work, new experimental densities, refractive indices, and dynamic viscosities were determined for ethyl acetate + ethanol + [C$_4$mim][NTF$_2$] ternary mixtures and for

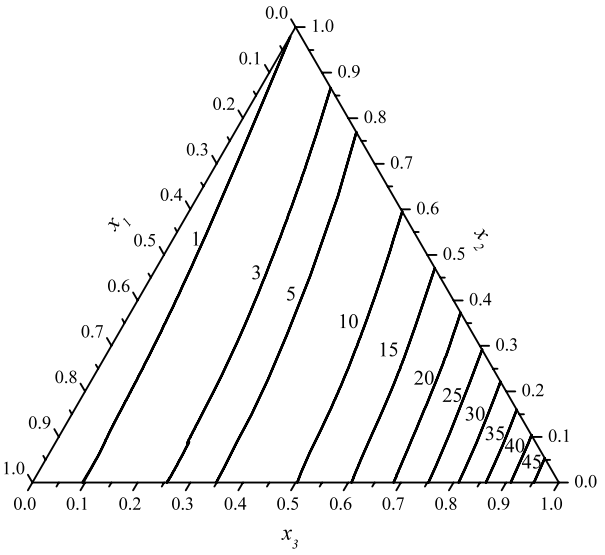

Fig. 4 Dynamic viscosity η (mPa·s) isolines for ethyl acetate (1) + ethanol (2) + $[C_4mim][NTF_2]$ (3) mixtures at 298.15 K and atmospheric pressure

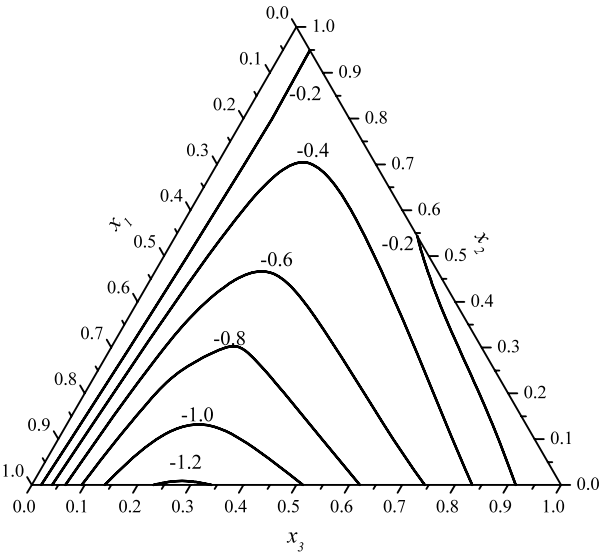

Fig. 5 Excess molar volume ($cm^3 \cdot mol^{-1}$) isolines for ethyl acetate (1) + ethanol (2) + $[C_4mim][NTF_2]$ (3) mixtures at 298.15 K and atmospheric pressure

the corresponding binary mixtures containing $[C_4mim][NTF_2]$ at 298.15 K and atmospheric pressure. The excess molar volumes V^E, and viscosity $\Delta\eta$ and molar refraction ΔR changes of mixing, were calculated for the binary and ternary systems.

These properties were compared with previously obtained data for an imidazolium ionic liquid with a longer alkyl chain length and the same anion ($[C_8mim][NTF_2]$). Increasing the alkyl chain length causes the density of the ionic liquid and their mixtures to decrease, and the excess molar volumes become slightly less negative. For the dynamic viscosity, increasing the alkyl chain length of the imidazolium ionic liquid causes the dynamic viscosity to increase dramatically, which is reflected in the higher negative values of the viscosity changes of mixing.

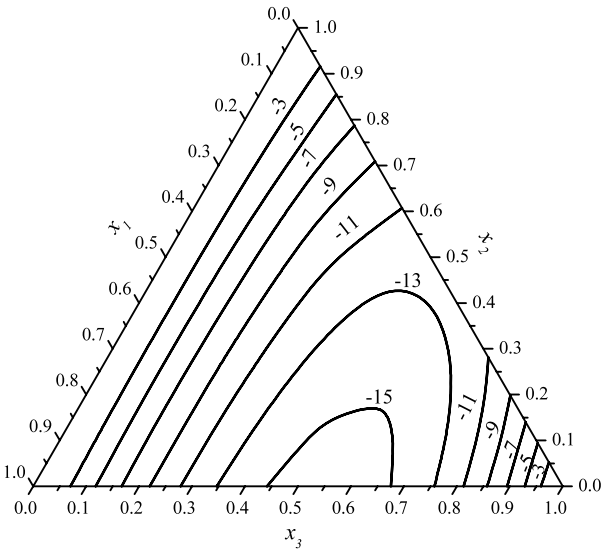

Fig. 6 Viscosity change of mixing $\Delta\eta$ (mPa·s) isolines for ethyl acetate (1) + ethanol (2) + $[C_4mim][NTF_2]$ (3) mixtures at 298.15 K and atmospheric pressure

Table 4 Coefficients and standard deviations σ obtained using the Redlich-Kister polynomial, Eq. 6, to correlate V^E, $\Delta\eta$ and ΔR for binary systems

Property	A_0	A_1	A_2	A_3	σ
		$\{x$ Ethyl acetate $+ (1-x)$ $[C_4mim][NTF_2]\}$			
$V^E/(cm^3 \cdot mol^{-1})$	−4.0707	−2.8547	−2.9027	−1.9981	0.007
$\Delta R/(cm^3 \cdot mol^{-1})$	0.1111	0.0565	–	–	0.003
$\Delta\eta$/(mPa·s)	−62.457	16.520	–	–	0.12
		$\{x$ Ethanol $+ (1-x)$ $[C_4mim][NTF_2]\}$			
$V^E/(cm^3 \cdot mol^{-1})$	−0.7022	−1.0542	−1.6765	−1.5478	0.013
$\Delta R/(cm^3 \cdot mol^{-1})$	0.0768	0.0312	–	–	0.002
$\Delta\eta$/(mPa·s)	−48.875	12.739	–	–	0.10

Table 5 Coefficients and standard deviations σ obtained using the Redlich-Kister polynomial, Eq. 7, to correlate V^E, $\Delta\eta$ and ΔR for the ethyl acetate (1) + ethanol (2) + $[C_4mim][NTF_2]$ (3) ternary system

Property	A	B	C	D	E	F	G	σ
$V^E/(cm^3 \cdot mol^{-1})$	−5.7541	0.6573	−8.7791	−10.697	6.2955	−8.6410	−17.728	0.026
$\Delta R/(cm^3 \cdot mol^{-1})$	0.0340	−0.1096	0.0152	0.1956	–	–	–	0.005
$\Delta\eta$/(mPa·s)	12.258	11.908	5.8764	1.2938	–	–	–	0.08

The Redlich-Kister equation was successfully applied to the correlation of excess properties of the studied binary and ternary systems.

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