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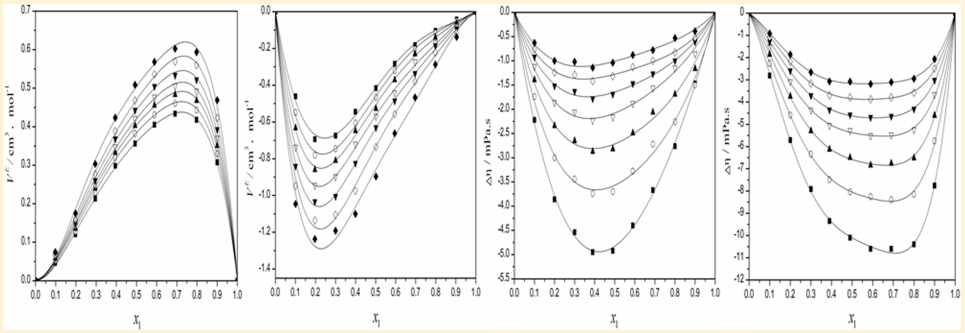
Densities and Viscosities of the Binary Mixtures of 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide with *N*-Methyl-2-pyrrolidone or Ethanol at T = (293.15 to 323.15) K

Hongwei Yao,[†,‡] Shuheng Zhang,[†,‡] Jieli Wang,[†,§] Qing Zhou,[†] Haifeng Dong,[†] and Xiangping Zhang*[,†]

[†]Beijing Key Laboratory of Ionic Liquids Clean Process, State Key Laboratory of Multiphase Complex System, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

[‡]College of Chemistry and Chemical Engineering, Graduate University of Chinese Academy of Sciences, Beijing 100049, P. R. China

[§]College of Chemical Engineering and Technology, Beijing University of Chemical Technology, Beijing 100029, China



ABSTRACT: The densities and viscosities of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][NTf$_2$]) + *N*-methyl-2-pyrrolidone (NMP) and [EMIM][NTf$_2$] + ethanol mixtures were investigated over the mole fraction range from (0.1 to 0.9) and at temperatures from (293.15 to 323.15) K at intervals of 5 K. The densities can be well-represented by the quadratic equation, and the viscosities can be represented in the form of the Vogel equation. The excess molar volumes (V^E) and viscosity deviations ($\Delta\eta$) were calculated, and the results were fitted to the Redlich−Kister equation using a multiparametric nonlinear regression method. The estimated parameters of the Redlich−Kister equation and standard deviation were also presented. The results showed that the densities and viscosities were dependent strongly on NMP or ethanol content. Comparatively, the viscosity deviation $\Delta\eta$ was more sensitive to temperature than the excess molar volume V^E.

1. INTRODUCTION

Ionic liquids (ILs) have attracted considerable attention because of their unique physical and chemical properties, including nonvolatility, thermal stability, and reusability. Particularly, ILs have controlled miscibility,[1,2] which results in many possible combinations of cations and anions[3,4] and allows a large variety of interactions and applications.[5] Due to an increasing importance of ILs in many fields of technology, a large number of publications dealing with the thermophysical properties of these low-temperature molten salts can be found in the literature.[6] Recently lots of research[7,8] show that the contents mixed with ILs will affect the physicochemical and thermophysical properties of ILs evidently. To study the molecular interactions between the various components of the mixtures and also to understand engineering applications concerning heat transfer, mass transfer, and fluid flow, it is important to study the experimental data of densities and viscosities of binary mixtures of ILs systematically.

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide ([EMIM][NTf$_2$]), as an IL with low viscosity, has been reported several times in literature.[9,10] The experimental density values of [EMIM][NTf$_2$] (at p = 0.101 MPa) were reported by Safarov et al.[11] Its viscosities were reported by Van-Oanh et al.,[12] and its osmotic coefficients and vapor pressures were reported by Calvar et al.[13] In these articles, density and viscosity data of the mixtures of [EMIM][NTf$_2$] with organic solvents have not yet been mentioned.

In this work, the densities and viscosities of mixtures consisting of [EMIM][NTf$_2$] + *N*-methyl-2-pyrrolidone (NMP) and [EMIM][NTf$_2$] + ethanol as a function of composition from (293.15 to 323.15) K were studied. The excess molar volume V^E and the viscosity deviation $\Delta\eta$ of these binary systems were obtained and fitted to the Redlich−Kister equation. The influences of NMP or ethanol content and temperature on the physical properties were analyzed.

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Table 1. Comparison of Measured Densities ρ and Viscosities η of the [EMIM][NTf_2], NMP, and Ethanol with Literature Values

	ρ/g·cm^{-3}		η/mPa·s	
T/K	exp.	lit.	exp.	lit.
		[EMIM][NTf_2]		
293.15	1.523284	1.52337[11]	40.24	40.1[7]
		1.52353[16]		38.6[16]
298.15	1.518251	1.51834[11]	33.36	
		1.51845[16]		
303.15	1.513232	1.51341[16]	28.10	28.7[7]
				27.1[16]
308.15	1.508204	1.50839[16]	23.93	
313.15	1.503162	1.50333[11]	20.66	21.1[7]
		1.50338[16]		19.4[16]
318.15	1.498194	1.49839[16]	17.98	
323.15	1.493330	1.49341[16]	15.80	15.7[7]
				14.9[16]
		NMP		
293.15	1.032313	1.0304[17]	1.811	
298.15	1.027962	1.0259[17]	1.667	1.656[18]
		1.02872[18]		
		1.02832[19]		
		1.0286[20]		
		1.02759[21]		
303.15	1.023521	1.0217[17]	1.543	
308.15	1.019060	1.0159[17]	1.437	
313.15	1.014607	1.0120[17]	1.343	1.322[18]
318.15	1.010141	1.0082[17]	1.258	
323.15	1.005677	1.0030[17]	1.184	1.175[18]
		Ethanol		
293.15	0.789831	0.7900[22]	1.189	1.2097[22]
		0.7893[23]		1.1802[23]
298.15	0.785535	0.7857[22]	1.095	1.0990[22]
		0.78500[24]		1.105[24]
303.15	0.781220	0.7809[22]	1.003	0.9971[22]
		0.7807[23]		1.0191[23]
308.15	0.776875	0.7780[22]	0.9140	0.9083[22]
		0.77631[24]		0.921[24]
313.15	0.772480	0.7733[22]	0.8450	0.8280[22]
		0.7725[23]		0.8424[23]
318.15	0.768042	0.76744[24]	0.7650	0.771[24]
323.15	0.762564	0.7636[23]	0.7040	0.7081[23]

2. EXPERIMENTAL SECTION

Materials. NMP (>99 % pure), ethanol (>99.8 % pure), Li[NTf_2], and ethyl bromide were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., China. 1-Methylimidazole (99 %) was supplied by Johnson Matthey Company, and these regents were used without further purification.

Synthesis of IL. [EMIM][NTf_2] was prepared according to the following method. First, 1-ethyl-3-methylimidazolium bromide was synthesized by dropping ethyl bromide (1.3 mol) into 1-methylimidazole (1 mol) at 283 K and mixing for 6 h under 303 K. Then ethyl acetate was added into the mixture and was removed by a separating funnel, and this step was repeated five times. The remaining ethyl acetate was removed by rotary evaporation, and the solution was dried under high vacuum at 323 K for at least 24 h to get 1-ethyl-3-methylimidazolium bromide ([EMIM]Br) at very high purity (99 %). Second, [EMIM][NTf_2] was prepared by metathesis reactions from the corresponding bromide. [Li][NTf_2] (1 mol) was dissolved in H_2O (50 mL) and was added into [EMIM][Br] (1 mol). The mixture was stirred for at least 24 h at room temperature, and crude [EMIM][NTf_2] was synthesized. Then the crude [EMIM][NTf_2] was extracted in dichloromethane (50 mL) and cooled below 278 K. The dichloromethane solution was washed with cooled ultrapure water (30 mL) five times until the aqueous solution did not form any precipitate with 0.1 mol·L^{-1} $AgNO_3$ solution. The solvent dichloromethane was removed by rotary evaporation, and the [EMIM][NTf_2] was dried under high vacuum at (323 to 333) K for at least 6 h.

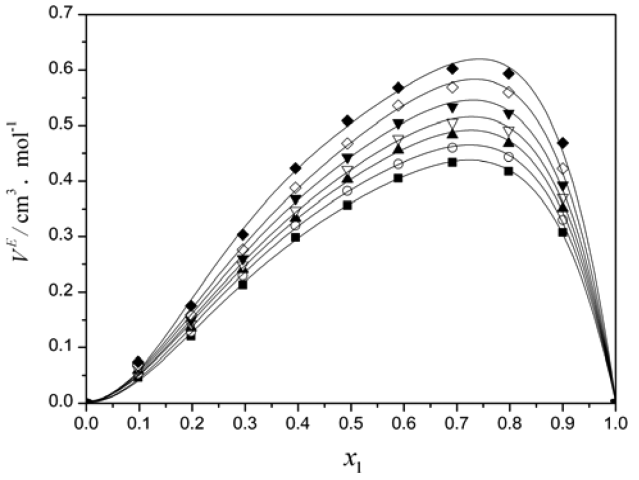

Figure 1. Excess molar volumes of the [EMIM][NTf_2] (1) + NMP (2) system at various temperatures: ■, 293.15 K; ○, 298.15 K; ▲, 303.15 K; ▽, 308.15 K; ▼, 313.15 K; ◇, 318.15 K and ◆, 323.15 K.

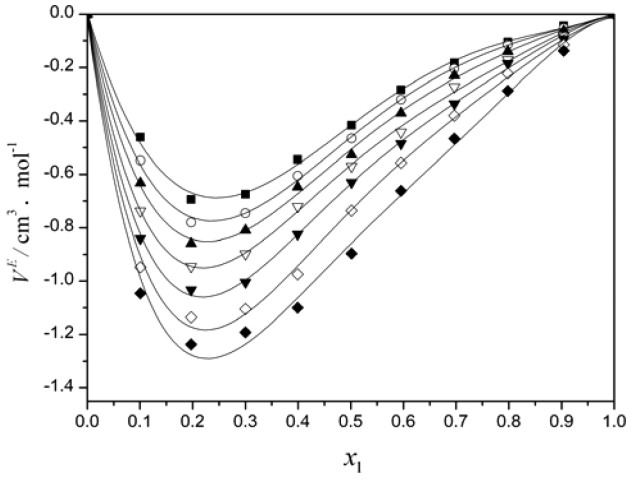

Figure 2. Excess molar volumes of the [EMIM][NTf_2] (1) + ethanol (3) system at various temperatures: ■, 293.15 K; ○, 298.15 K; ▲, 303.15 K; ▽, 308.15 K; ▼, 313.15 K; ◇, 318.15 K and ◆, 323.15 K.

Characterizations of IL. [EMIM][NTf_2] was identified by ^{1}H NMR, spectra IR, elemental analysis, and water content analysis. The ^{1}H NMR spectra were recorded on an ARX600 NMR spectrometer (Bruker) at 600 MHz with dimethyl sulfoxide (DMSO) as solvent and tetramethylsilane (TMS) as an internal standard. IR studies were conducted with a Nicolet 380 FTIR spectrometer (Thermo Nicolet). Elemental analysis was conducted with a Vario EL elemental analyzer (Elementar). Water content analysis was determined by moisture analysis instrument (787 KF Titrino).

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Table 2. Experimental Densities ρ, Viscosities η, Excess Molar Volume V^E, and Viscosity Deviation $\Delta\eta$ for Binary Mixtures of [EMIM][NTf$_2$] (1) + NMP (2) and [EMIM][NTf$_2$] (1) + Ethanol (3) from T = (293.15 to 323.15) K as a Function of Molar Fraction x_1

	T/K						
x_1	293.15	298.15	303.15	308.15	313.15	318.15	323.15
			[EMIM][NTf$_2$] (1) + NMP (2)				
			ρ/g·cm^{-3}				
0.9002	1.502241	1.497092	1.491961	1.486834	1.481674	1.476540	1.471411
0.7980	1.478942	1.473784	1.468635	1.463482	1.458282	1.453092	1.448032
0.6917	1.451444	1.446291	1.441151	1.436014	1.430827	1.425651	1.420575
0.5893	1.420549	1.415415	1.410270	1.405147	1.399964	1.394812	1.389731
0.4930	1.386312	1.381192	1.376090	1.371001	1.365875	1.360772	1.355621
0.3950	1.344491	1.339439	1.334421	1.329382	1.324284	1.319235	1.314121
0.2957	1.292831	1.287871	1.282914	1.277971	1.272990	1.267997	1.262960
0.1979	1.228992	1.224194	1.219334	1.214471	1.209604	1.204731	1.199830
0.0978	1.144094	1.139450	1.134720	1.130026	1.125305	1.120611	1.115906
			η/mPa·s				
0.9002	34.93	28.70	24.29	20.83	18.12	15.79	13.95
0.7980	29.72	24.70	21.05	18.24	15.76	13.78	12.31
0.6917	24.72	20.87	17.85	15.44	13.44	11.83	10.51
0.5893	20.06	17.07	14.70	12.81	11.26	9.989	8.911
0.4930	15.84	13.60	11.82	10.37	9.174	8.180	7.344
0.3950	12.04	10.45	9.159	8.092	7.190	6.440	5.816
0.2957	8.637	7.604	6.749	6.033	5.430	4.916	4.481
0.1979	5.561	4.943	4.457	4.028	3.647	3.325	3.079
0.0978	3.344	3.026	2.754	2.519	2.314	2.130	1.980
			V^E/cm^3·mol^{-1}				
0.9002	0.3075	0.3299	0.3509	0.3700	0.3927	0.4228	0.4689
0.7980	0.4180	0.4434	0.4681	0.4920	0.5217	0.5603	0.5934
0.6917	0.4337	0.4599	0.4836	0.5055	0.5336	0.5689	0.6024
0.5893	0.4052	0.4306	0.4557	0.4765	0.5046	0.5359	0.5684
0.4930	0.3565	0.3824	0.4033	0.4210	0.4429	0.4678	0.5084
0.3950	0.2985	0.3198	0.3332	0.3474	0.3685	0.3881	0.4233
0.2957	0.2129	0.2293	0.2403	0.2481	0.2600	0.2764	0.3035
0.1979	0.1205	0.1281	0.1360	0.1425	0.1496	0.1589	0.1751
0.0978	0.0463	0.0523	0.0595	0.0613	0.0663	0.0688	0.0743
			$\Delta\eta$/cm^3·mol^{-1}				
0.9002	−1.48	−1.50	−1.16	−0.855	−0.612	−0.521	−0.391
0.7980	−2.76	−2.26	−1.69	−1.15	−1.00	−0.823	−0.538
0.6917	−3.67	−2.72	−2.06	−1.56	−1.26	−0.995	−0.784
0.5893	−4.40	−3.27	−2.49	−1.88	−1.47	−1.12	−0.886
0.4930	−4.92	−3.69	−2.82	−2.16	−1.69	−1.32	−1.05
0.3950	−4.95	−3.73	−2.87	−2.23	−1.78	−1.42	−1.14
0.2957	−4.54	−3.44	−2.65	−2.06	−1.63	−1.29	−1.03
0.1979	−3.86	−3.00	−2.34	−1.86	−1.52	−1.24	−1.00
0.0978	−2.22	−1.74	−1.39	−1.12	−0.918	−0.763	−0.633
			[EMIM][NTf$_2$] (1) + Ethanol (3)				
			ρ/g·cm^{-3}				
0.9041	1.506315	1.501313	1.496341	1.491394	1.486411	1.481541	1.476731
0.7982	1.484184	1.479171	1.474280	1.469404	1.464393	1.459600	1.454973
0.6966	1.458636	1.453693	1.448783	1.443984	1.439300	1.434533	1.429971
0.5955	1.427558	1.422721	1.417990	1.413413	1.408572	1.404000	1.399501
0.5014	1.391851	1.387125	1.382491	1.377681	1.372990	1.368707	1.364610
0.3992	1.341773	1.337181	1.332393	1.327885	1.323621	1.319804	1.316241
0.3000	1.276680	1.272192	1.267500	1.263400	1.259313	1.255227	1.252111
0.1971	1.179411	1.175213	1.170587	1.166550	1.162510	1.159513	1.156541
0.1008	1.038400	1.034141	1.029789	1.025121	1.021471	1.019104	1.015544
			η/mPa·s				
0.9041	28.74	24.52	20.90	18.05	15.74	13.84	12.28
0.7982	21.80	18.70	16.12	14.04	12.34	10.93	9.799
0.6966	17.76	15.18	13.13	11.47	10.01	8.965	8.116
0.5955	13.87	12.05	10.31	9.109	7.954	7.141	6.500

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Table 2. continued

	T/K						
x_1	293.15	298.15	303.15	308.15	313.15	318.15	323.15
				η/mPa·s			
0.5014	10.65	9.232	8.100	7.177	6.199	5.603	5.195
0.3992	7.429	6.479	5.697	5.055	4.404	3.945	3.656
0.3000	4.600	4.150	3.728	3.157	2.640	2.459	2.317
0.1971	2.780	2.350	2.160	1.900	1.645	1.412	1.307
0.1008	1.612	1.478	1.250	1.120	1.101	1.001	0.9870
				V^E/cm^3·mol^{-1}			
0.9041	−0.0436	−0.0518	−0.0629	−0.0799	−0.0939	−0.1153	−0.1382
0.7982	−0.1046	−0.1142	−0.1406	−0.1713	−0.1850	−0.2223	−0.2875
0.6966	−0.1822	−0.2042	−0.2299	−0.2731	−0.3359	−0.3801	−0.4662
0.5955	−0.2838	−0.3207	−0.3706	−0.4427	−0.4855	−0.5571	−0.6619
0.5014	−0.4165	−0.4660	−0.5266	−0.5698	−0.6308	−0.7359	−0.8966
0.3992	−0.5447	−0.6056	−0.6473	−0.7211	−0.8251	−0.9750	−1.1963
0.3000	−0.6815	−0.7468	−0.7945	−0.9009	−1.0138	−1.1271	−1.3873
0.1971	−0.7105	−0.7889	−0.8337	−0.9311	−1.0336	−1.2267	−1.4875
0.1008	−0.4613	−0.5132	−0.5602	−0.5860	−0.6952	−0.9082	−1.1033
				$\Delta\eta$/cm^3·mol^{-1}			
0.9041	−7.76	−5.75	−4.60	−3.67	−3.02	−2.49	−2.07
0.7982	−10.6	−8.15	−6.51	−5.25	−4.32	−3.58	−2.95
0.6966	−10.6	−8.39	−6.75	−5.48	−4.64	−3.79	−3.10
0.5955	−10.6	−8.26	−6.83	−5.51	−4.69	−3.87	−3.19
0.5014	−10.1	−8.04	−6.49	−5.28	−4.58	−3.79	−3.08
0.3992	−9.35	−7.50	−6.12	−5.05	−4.35	−3.69	−3.07
0.3000	−8.31	−6.63	−5.40	−4.66	−4.15	−3.47	−2.92
0.1971	−6.10	−5.10	−4.18	−3.55	−3.10	−2.75	−2.37
0.1008	−3.51	−2.87	−2.48	−2.11	−1.74	−1.50	−1.24

Table 3. Parameters of the Quadratic Equation and AADs for the Density Correlation of [EMIM][NTf$_2$] (1) + NMP (2) and EMIM][NTf$_2$] (1) + Ethanol (3) from T = (293.15 to 323.15) K as a Function of Molar Fraction x_1

x_1	A_0	$10^3\,A_1$	$10^7\,A_2$	10^4 ADD
	[EMIM][NTf$_2$] (1) + NMP (2)			
1.0000	1.865	−1.315	5.105	20.00
0.9002	1.804	−1.0330	0.09048	0.05786
0.7980	1.790	−1.088	0.9095	0.2314
0.6917	1.758	−1.0610	0.5000	0.1811
0.5893	1.727	−1.0610	−1.114	0.0996
0.4930	1.675	−0.9537	−1.114	0.0996
0.3950	1.615	−0.8407	−2.776	0.1169
0.2957	1.556	−0.8068	−3.052	0.1143
0.1979	1.489	−0.7999	−2.800	0.06886
0.0978	1.412	−0.8879	−0.8524	0.1091
0.0000	1.263	−0.6912	−3.210	0.1589
	[EMIM][NTf$_2$] (1) + Ethanol (3)			
1.0000	1.865	−1.315	5.143	0.2733
0.9041	1.859	−1.398	6.657	0.2050
0.7982	1.867	−1.607	10.24	0.5197
0.6966	1.867	−1.792	13.57	0.1993
0.5955	1.790	−1.510	9.319	0.4329
0.5014	1.892	−2.423	24.47	0.9736
0.3992	2.067	−3.936	49.94	0.9239
0.3000	1.967	−3.737	47.22	1.218
0.1971	2.050	−4.960	67.95	1.479
0.1008	1.960	−5.300	73.60	3.123
0.0000	0.7537	1.048	−31.55	1.606

Table 4. Parameters of the Redlich−Kister Equation for V^E of [EMIM][NTf$_2$] (1) + NMP (2) and [EMIM][NTf$_2$] (1) + Ethanol (3)

T/K	A_0	A_1	A_2	A_3	σ
	[EMIM][NTf$_2$] (1) + NMP (2)				
293.15	1.441	1.118	0.7503	1.105	0.003383
298.15	1.537	1.159	0.8069	1.228	0.004732
303.15	1.614	1.246	0.8976	1.233	0.005844
308.15	1.682	1.313	0.9643	1.311	0.006223
313.15	1.775	1.397	1.038	1.381	0.007304
318.15	1.878	1.497	1.167	1.521	0.007130
323.15	2.015	1.435	1.298	2.022	0.01053
	[EMIM][NTf$_2$] (1) + Ethanol (3)				
293.15	−1.673	3.003	−2.124	0.02745	0.01613
298.15	−1.863	3.276	−2.338	0.1324	0.01745
303.15	−2.055	3.285	−2.444	0.4752	0.01677
308.15	−2.331	3.653	−2.647	0.1587	0.02694
313.15	−2.611	3.991	−3.140	0.5747	0.02089
318.15	−2.963	4.328	−4.247	1.988	0.01390
323.15	−3.612	5.374	−5.216	2.099	0.01241

^{1}H NMR (600 MHz, DMSO): δ 1.432 (t, 3H), 3.360 (s, 3H), 4.210 (q, 2H), 7.673 (s, 1H), 7.755 (s, 1H), 9.103 (s, 1H); IR (neat) 3160, 3121, 1352, 1194, 1139, 1057, 617, 571. Elemental analysis: C (24.48 wt %), H (2.81 wt %), N (10.71 wt %), S (16.33 wt %), O (16.41 wt %); the content of water <100 ppm.

Impurity peaks were not observed in the ^{1}H NMR spectra, and the chemical shift of other peaks corresponded to the structure of the [EMIM][NTf$_2$]. The water content of the

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Table 5. Parameters of the Vogel Equation and AADs for the Viscosity Correlation of [EMIM][NTf$_2$] (1) + NMP (2) and [EMIM][NTf$_2$] (1) + Ethanol (3) from T = (293.15 to 323.15) K as a Function of Molar Fraction x_1

x_1	A_0	A_1	A_2	10^2 ADD
[EMIM][NTf$_2$] (1) + NMP (2)				
1.0000	−0.9712	559.1	−173.3	1.020
0.9002	−0.2337	358.2	−198.5	6.455
0.7980	−0.6813	442.4	−184.5	5.439
0.6917	−1.404	607.1	−161.5	0.9059
0.5893	−1.175	519.7	−168.6	0.5143
0.4930	−1.333	532.1	−163.2	0.2921
0.3950	−1.811	632.0	−146.1	0.3903
0.2957	−1.708	566.1	−146.6	0.09564
0.1979	−1.821	525.3	−144.6	0.9186
0.0978	−1.821	525.3	−144.6	0.9186
0.0000	−1.943	378.9	−143.8	0.07073
[EMIM][NTf$_2$] (1) + Ethanol (3)				
1.0000	−0.9712	559.1	−173.3	1.020
0.9041	−1.985	842.3	−135.6	3.877
0.7982	−1.558	664.9	−149.9	2.053
0.6966	−0.9650	445.4	−177.2	3.552
0.5955	−1.340	494.9	−168.6	5.721
0.5014	−1.598	522.0	−161.5	5.692
0.3992	−2.616	743.9	−132.2	3.480
0.3000	−13.76	8959	292.4	8.172
0.1971	−17.54	13005	407.7	3.199
0.1008	−0.6863	43.70	−256.0	2.870
0.0000	−51.39	150243	2621	0.3311

Table 6. Parameters of the Redlich−Kister Equation for $\Delta\eta$ of [EMIM][NTf$_2$] (1) + NMP (2) and [EMIM][NTf$_2$] (1) + Ethanol (3)

T/K	A_0	A_1	A_2	A_3	σ
[EMIM][NTf$_2$] (1) + NMP (2)					
293.15	−19.31	6.167	−2.757	−0.9268	0.04798
298.15	−14.23	5.696	−5.627	−5.595	0.06333
303.15	−10.86	4.636	−4.690	−4.107	0.05433
308.15	−8.317	4.079	−3.405	−2.580	0.05351
313.15	−6.583	2.875	−3.134	−0.8774	0.03492
318.15	−6.574	2.894	−3.156	−0.9059	0.03336
323.15	−4.052	2.153	−2.195	−0.2525	0.03514
[EMIM][NTf$_2$] (1) + Ethanol (3)					
293.15	−40.02	−9.742	−34.97	−34.08	0.1117
298.15	−31.86	−7.148	−26.20	−22.32	0.04089
303.15	−25.93	−6.088	−21.11	−15.20	0.05258
308.15	−21.25	−3.438	−17.70	−13.14	0.03779
313.15	−18.42	−1.595	−13.57	−12.29	0.05180
318.15	−15.29	0.4988	−12.00	−10.49	0.03605
323.15	−12.58	0.2466	−10.51	−9.515	0.04904

product [EMIM][NTf$_2$] was determined to be below 200 ppm. The purity of the IL was >99 %.

Density. The densities of the mixtures of [EMIM][NTf$_2$] + NMP and [EMIM][NTf$_2$] + ethanol were measured by a density meter (Anton Paar DMA 5000, Anton Paar Co., Austria). The temperature of this study was between (293.15 and 323.15) K, at 5 K intervals, the precision of which was ± 0.001 K (the temperature accuracy is controlled traceably to national standards by two integrated Pt 100 platinum thermometers), and

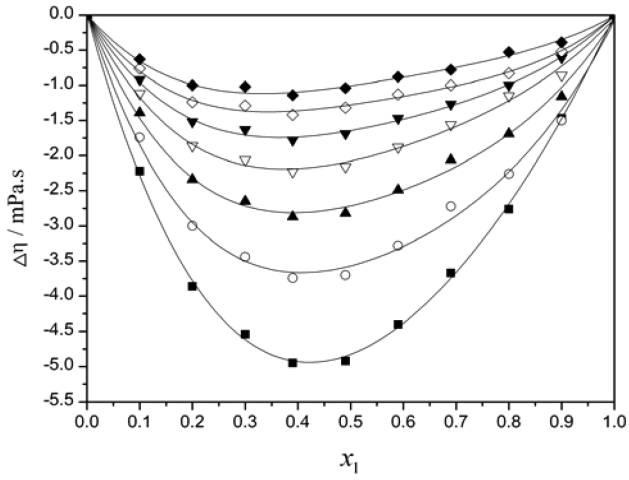

Figure 3. Viscosity deviations of the [EMIM][NTf$_2$] (1) + NMP (2) system at various temperatures: ■, 293.15 K; ○, 298.15 K; ▲, 303.15 K; ▽, 308.15 K; ▼, 313.15 K; ◇, 318.15 K and ◆, 323.15 K.

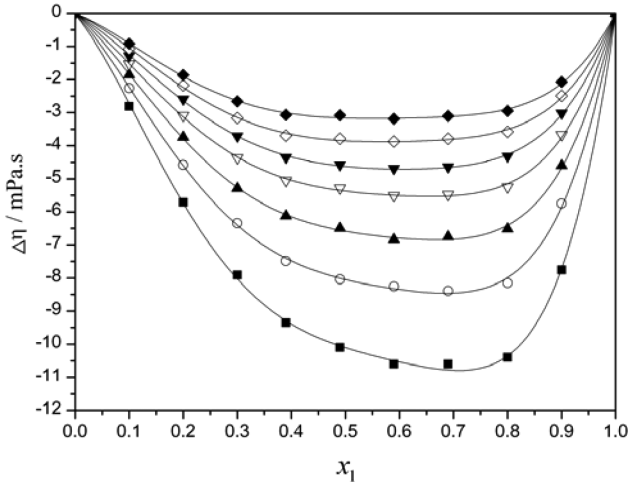

Figure 4. Viscosity deviations of the [EMIM][NTf$_2$] (1) + ethanol (3) system at various temperatures: ■, 293.15 K; ○, 298.15 K; ▲, 303.15 K; ▽, 308.15 K; ▼, 313.15 K; ◇, 318.15 K and ◆, 323.15 K.

the absolute room pressure was approximately 101 kPa at that time. The precision of measurement was ± 0.000001 g·cm^{-3}, and the accuracy of density measurements was ± 0.000005 g·cm^{-3}, which was calibrated with ultrapure water and dry air. The same data point of the same sample with one injection into the apparatus was measured three times, and the average of the data was calculated as the final density.

Viscosity. Viscosities of the mixtures of [EMIM][NTf$_2$] + NMP and [EMIM][NTf$_2$] + ethanol were measured by a viscosity meter (Anton Paar AMVn, Anton Paar Co., Austria) based on the approved and acknowledged falling ball principle according to DIN 53015 and ISO 12058. The reproducibility <2 %, repeatability <0.1 %, and calibration were carried out using ultrapure water or viscosity standard oils (no. H117, Anton Paar Co., Austria). The temperature range of this study was from (293.15 to 323.15) K, at 5 K intervals, the precision of which was ± 0.01 K (the temperature accuracy is controlled by a built-in precise Peltier thermostat), and the absolute room pressure was approximate 101 kPa at that time.

The mixtures of [EMIM][NTf$_2$] + NMP and [EMIM]-[NTf$_2$] + ethanol were prepared using a JA2003 electronic

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digital balance accurate to within ± 0.1 mg. The uncertainty in the mole fraction of the mixtures was estimated to less than ± 0.0001. The uncertainty of excess molar volumes was estimated better than ± 0.02 $cm^3 \cdot mol^{-1}$. All molar quantities are based on the International Union of Pure and Applied Chemistry (IUPAC) relative atomic mass table.

3. RESULTS AND DISCUSSION

The experimental density values for pure [EMIM][NTf_2], NMP, and ethanol in this work are in very good agreement with the values recently published literature data (Table 1), which illustrates that the measured methods are dependable. Experimentally measured densities of the mixture of [EMIM][NTf_2] (1) + NMP (2) and [EMIM][NTf_2] (1) + ethanol (3) at (293.15, 298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K throughout the whole mole fraction range are listed in Table 2. The measured data of densities could be fitted and regressed by the quadratic equations as follows:[14]

$$\rho/\mathrm{g \cdot cm^{-3}} = A_0 + A_1(T/\mathrm{K}) + A_2(T/\mathrm{K})^2 \quad (1)$$

$$\mathrm{ADD} = \frac{1}{n}\sum_{i=1}^{n} |\rho_{i,\mathrm{exptl}} - \rho_{i,\mathrm{calcd}}| \quad (2)$$

where ρ stands for the densities, A_0, A_1, and A_2 are the quadratic fitting regression parameters with the least-squares method, and ADD is the average absolute deviation between the experimental results and the calculated values by eq 2.

The parameters of eq 1 and ADDs of the [EMIM][NTf_2] (1) + NMP (2) system and [EMIM][NTf_2] (1) + NMP (3) system at various temperatures were calculated and shown in Table 3. The experimental data of the two systems fitted the eq 2 very well.

The density values of the binary mixtures were used to calculate the excess molar volume, V^E, as

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \quad (3)$$

$$Y = x_1x_2\sum_{i=0}^{m} A_i(x_1 - x_2)^i \quad (4)$$

$$\sigma(Y) = \left[\sum (Y_{\mathrm{cal}} - Y_{\mathrm{exp}})^2/(n-m)\right]^{1/2} \quad (5)$$

where V^E is the excess molar volume of the mixture and M_1 and M_2 are the molar masses; x_1 and x_2 are the mole fractions of the component 1 and component 2; ρ_1 and ρ_2 are the densities of component 1 and component 2, respectively. A Redlich–Kister[15] relation was used to correlate the excess volume data (eqs 4 and 5).

Figures 1 and 2 display the dependence of V^E on the [EMIM][NTf_2] (1) + NMP (2) and the [EMIM][NTf_2] (1) + ethanol (3) mixtures at various temperatures, respectively. In Figure 1, the V^E values are positive and become more positive with increasing temperature. It shows a sharp change at around 25 mol % NMP. On the contrary, the V^E values in Figure 2 are negative and become more negative as temperature increases, with the maxima lying nearly at $x_1 \approx 0.25$. It is known that V^E is the result of several opposing effects. Interactions between like molecules lead to increased V^E values, while negative contributions to V^E arise from interactions between unlike molecules, or structural effects as changes in free volume, or interstitial accommodation. For the investigated systems, NMP is a cyclic organic molecule that interacted with [EMIM][NTf_2] as a molecule with a molecule. However ethanol is a chain-shaped molecule that can be dispersed into IL easily. The coefficients and the standard deviation (σ) are presented in Table 4.

Experimentally measured viscosities of the binary mixtures of [EMIM][NTf_2] + NMP and [EMIM][NTf_2] + ethanol are listed in Table 2. The values of pure [EMIM][NTf_2], NMP, and ethanol are also in very good agreement with the values recently published literature data (Table 1), which means the experimental values are reliable.

The measured data of viscosities could be fitted and regressed by the Vogel equations as follows:[14]

$$\eta/\mathrm{mPa \cdot s} = \exp\left[A_0 + \frac{A_1}{T/\mathrm{K} + A_2}\right] \quad (6)$$

$$\mathrm{ADD} = \frac{1}{n}\sum_{i=1}^{n} |\eta_{i,\mathrm{exptl}} - \eta_{i,\mathrm{calcd}}| \quad (2)$$

the values of A_0, A_1, A_2, and ADD of the two systems are listed in Table 5. The viscosity deviation can be calculated with eq 7:

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (7)$$

where η is the viscosity of the mixture and η_1 and η_2 are those of pure component 1 and pure component 2, respectively.

Figures 3 and 4 display the dependence of $\Delta\eta$ on the temperature of the [EMIM][NTf_2] (1) + NMP (2) system and the [EMIM][NTf_2] (1) + ethanol (3) system, respectively. It can be observed that $\Delta\eta$ values of the two systems are all negative over the measured composition range. Values of $\Delta\eta$ in Figure 3 were negative with a minimum around 40 mol % of [EMIM][NTf_2] for all temperatures. A minimum of $\Delta\eta$ is reached with the mole fraction of this IL near to 0.7 in Figure 4. It can be concluded that both the temperature and the content of solvent in IL will affect the viscosities very much.

The calculated values of $\Delta\eta$ were correlated with a Redlich–Kister[15] relation (eqs 4 and 5). The coefficients and the standard deviation (σ) are presented in Table 6.

4. CONCLUSION

New experimental data of density and viscosity for the systems of [EMIM][NTf_2] (1) + NMP (2) and [EMIM][NTf_2] (1) + ethanol (3) were measured over the whole range of compositions from (293.15 to 323.15) K. The excess molar volume V^E and viscosity deviations $\Delta\eta$ were correlated using the Redlich–Kister polynomial equation. Estimated coefficients and standard error values are also presented. The results show that the NMP or ethanol content has a stronger effect on the physical properties and excess thermodynamic properties of ILs for the binary systems. The volumetric and transport properties of the ILs can be significantly varied by adding organic solvents or changing the temperature to meet the needs of industrial requirement.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +86-10-82627080 E-mail address: xpzhang@home.ipe.ac.cn (X. P. Zhang).

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