Physical Properties of Binary and Ternary Mixtures of Ethyl Acetate, Ethanol, and 1-Octyl-3-methyl-imidazolium Bis(trifluoromethylsulfonyl)imide at 298.15 K

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Densities, viscosities, and refractive indices for binary and ternary mixtures of ethanol, ethyl acetate, and 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide have been determined at 298.15 K and atmospheric pressure. Excess molar volumes, and viscosity and molar refraction changes of mixing have been calculated from the measured physical properties. These changes of mixing have been adequately fitted to the Redlich−Kister polynomial equation. The adjustable parameters and the standard deviations between experimental and calculated values are reported.

Introduction

Ionic liquids (ILs) have gained increasing attention during recent years because of their extraordinary properties.[1] Moreover, the large number of cation and anion combinations allows the modification of their thermodynamic properties. Therefore, ILs can be adjusted or tuned[2] to provide a desired density, viscosity, melting point, hydrophobicity, miscibility, and so on to suit the requirements of a particular process. This creates new opportunities for separation or reaction processes. ILs are the basis of an emerging technology[3] that could significantly benefit the chemical industry by providing more environmentally friendly and efficient synthesis and processing systems.

Numerous physical and chemical properties are required for the synthesis, characterization, and applications of ILs. To design any process involving ILs on an industrial scale, it is necessary to know a range of physical properties including viscosity and density among others. Physical properties are necessary for hydraulic calculations, fluid transport through pipes and pore surfaces, mass and energy transfer calculations, and so on.

In this work, we investigated the ethanol + ethyl acetate + 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ternary system. The interest of the system is based on the possibility of using the ILs as entrainers in the extractive distillation of the mixture ethanol + ethyl acetate.[4] The IL has been selected according to its miscibility with these components, its low melting point (below room temperature), and its easy synthesis. Experimental data of densities, ρ, refractive indices, n_D, and dynamic viscosities, η, of the binary and ternary mixtures of ethanol, ethyl acetate, and 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide were determined over the entire composition range at 298.15 K and atmospheric pressure. Moreover, the excess molar volumes, V^E, viscosity, $\Delta\eta$, and molar refraction, ΔR, changes of mixing were calculated and correlated with composition using the Redlich−Kister polynomial equations. No comparable data for this ternary system were found in the surveyed literature.

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Experimental Section

Materials. Ethyl acetate (ω > 99.8 %) was supplied by Aldrich, and ethanol (ω > 99.9 %) was supplied by Merck. No further purification of these products was carried out. The IL, 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide, [C_8mim][NTf_2], was synthesized in our laboratory by reaction of 1-methylimidazole (Aldrich, > 99 %, GC) with an excess of 1-chlorooctane (99 %, Aldrich) to produce [C_8mim][Cl]. This chloride was mixed with Li[NTf_2] salt in deionized water, and thus we obtained the [C_8min][NTf_2] by ion metathesis. More details of the experimental procedure can be found in earlier publications.[5] After being washed, the purification of [C_8min][NTf_2] was completed by being heated under high vacuum for 48 h (1 mbar, 353.15 K). The water mass fraction was determined by means of a Karl Fisher titration method carried out in a Metrohm 737 KF and resulted in $\omega = 36 \cdot 10^{-6}$. The chloride concentration was $14.2 \cdot 10^{-6}$, measured by means of capillary electrophoresis. The IL was analyzed by ^{1}H NMR and ^{13}C NMR spectroscopy (Supporting Information) to confirm the absence of any major impurities.

Table 1 shows a comparison between experimental and literature[6−9] data of density, refractive index, and dynamic viscosity in addition to the water content of pure components.

Experimental Apparatus and Procedure. All weighing was carried out in a Mettler Toledo AT 261 balance with an uncertainty of $\pm 10^{-4}$ g. The uncertainty in the mole fractions of the prepared mixtures was estimated to be $\pm$ 0.0002. Densities were measured in an Anton Paar DMA 5000 densimeter. This instrument automatically corrects the viscosity influence on density over the whole viscosity range. The viscosity correction for this densimeter is adequately checked.[10] The uncertainty in the measurement is $\pm 3 \cdot 10^{-5}$ g·cm^{-3}. Refractive indices were measured in an ATAGO RX-5000 refractometer with a Hero Therm thermostat to maintain the temperature. The uncertainty in the refractive index measurement is $\pm 4 \cdot 10^{-5}$.

The kinematic viscosity was determined by micro Ubbelohde viscometer technique. Three micro Ubbelohde viscometers (capillaries I, II, and III) were used in the experiments according to the different viscosity values of the mixtures. The capillaries are calibrated and credited by the company and verified by ourselves by measuring the viscosity of different pure liquids.

10.1021/je800899w CCC: $40.75 © 2009 American Chemical Society
Published on Web 02/11/2009

Table 1. Physical Properties of the Pure Components at $T = 298.15$ K

component	CASRN[a]	$10^{-6}\omega$ (H_2O)	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[6]	1.36983	1.36978[6]	0.4256	0.426[6]
ethanol	64-17-5	347	0.78514	0.78493[6]	1.35928	1.35941[6]	1.054	1.0826[6]
[C_8mim][NTf_2]	178631-04-4	36	1.32059	1.32076,[7] 1.32,[8] 1.321,[9]	1.43298	1.43331[7]	92.51	90.0,[8] 95.0,[9]

[a] CASRN: Chemical Abstract Service registry number.

Table 2. Physical and Excess Properties for the Binary Systems at 298.15 K and Atmospheric Pressure

x	ρ / g·cm^{-3}	n_D	η / mPa·s	V^E / cm^3·mol^{-1}	ΔR	$\Delta\eta$ / mPa·s
			x Ethyl Acetate + (1 − x) Ethanol			
0.0941	0.80065	1.36064	0.855	0.056	0.005	−0.140
0.1919	0.81509	1.36193	0.692	0.097	0.009	−0.241
0.2836	0.82727	1.36309	0.619	0.127	0.013	−0.257
0.4044	0.84169	1.36447	0.541	0.147	0.015	−0.259
0.5014	0.85205	1.36548	0.505	0.158	0.017	−0.234
0.6085	0.86253	1.36649	0.467	0.154	0.016	−0.204
0.6949	0.87030	1.36724	0.444	0.145	0.014	−0.173
0.7929	0.87851	1.36811	0.436	0.122	0.013	−0.120
0.8957	0.88660	1.36895	0.424	0.076	0.007	−0.067
			x Ethyl Acetate + (1 − x) [C_8mim][NTf_2]			
0.0493	1.31493	1.43216	78.89	−0.077	−0.005	−9.081
0.1112	1.30734	1.43115	65.93	−0.215	−0.003	−16.35
0.1546	1.30155	1.43042	58.25	−0.312	0.005	−20.02
0.2125	1.29310	1.42930	48.82	−0.425	0.011	−24.13
0.3102	1.27660	1.42726	34.78	−0.589	0.045	−29.17
0.4040	1.25753	1.42453	24.15	−0.730	0.030	−31.16
0.4779	1.23988	1.42219	17.54	−0.879	0.035	−30.96
0.5967	1.20386	1.41721	9.795	−1.027	0.035	−27.77
0.7035	1.16022	1.41123	5.384	−1.120	0.044	−22.35
0.8233	1.08962	1.40097	2.284	−1.049	0.034	−14.41
0.9016	1.02264	1.39100	1.233	−0.815	0.037	−8.254
			x Ethanol + (1 − x) [C_8mim][NTf_2]			
0.0959	1.31129	1.43164	71.28	0.051	0.004	−12.46
0.1162	1.30917	1.43133	67.63	0.047	0.001	−14.25
0.1935	1.30029	1.43016	55.53	0.036	0.013	−19.28
0.2269	1.29602	1.42965	51.54	0.029	0.026	−20.21
0.3304	1.28078	1.42766	39.23	−0.009	0.039	−23.06
0.4164	1.26519	1.42549	29.89	−0.070	0.028	−24.54
0.5412	1.23517	1.42143	19.92	−0.148	0.024	−23.09
0.6012	1.21621	1.41886	15.86	−0.181	0.022	−21.67
0.7033	1.17346	1.41319	10.25	−0.264	0.023	−17.93
0.8067	1.10685	1.40447	5.830	−0.316	0.034	−12.90
0.8967	1.01050	1.39142	3.079	−0.315	0.025	−7.426

Results were found to be in good agreement with published values. Flow time measurements are performed by the Lauda processor viscosity system PVS1 with a resolution of 0.01 s. The temperature of the viscometer was kept constant using a Lauda clear view thermostat D 20 KP with a through-flow cooler DLK 10. 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 longer times. The kinematic viscosity of solution v is given by

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

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

Temperatures of the densimeter, refractometer, and viscometer were measured with uncertainties of (± 0.01, ± 0.02, and ± 0.005) K, respectively.

Results

The densities, ρ, refractive indices, n_D, dynamic viscosities, η, excess molar volumes, V^E, viscosity, $\Delta\eta$, and molar refraction, ΔR, changes of mixing at 298.15 K and atmospheric pressure are reported in Tables 2 and 3 for the ethyl acetate + ethanol + [C_8min][NTf_2] ternary system and its binary systems: ethyl acetate + ethanol, ethyl acetate + [C_8min][NTf_2], and ethanol + [C_8min][NTf_2]. The excess molar volumes, V^E, viscosity, and molar refraction changes of mixing were calculated from experimental values using the following expressions

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

$$\Delta\eta = \eta - \sum_i x_i \eta_i \quad (3)$$

$$\Delta R = R_M - \sum_i x_i R_i \quad (4)$$

where V_M is the molar volume of the mixture, η is the dynamic viscosity, R_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, viscosity, and molar refraction, respectively, of the component i.

Figure 1 shows the excess volumes and viscosity changes of mixing for the three binary systems: (a) ethyl acetate + ethanol, (b) ethyl acetate + [C_8min][NTf_2], and (c) and ethanol+ [C_8min][NTf_2]. For the ethyl acetate + ethanol binary system,

Table 3. Physical and Excess Properties for the Ethyl Acetate (1) + Ethanol (2) + [C_8mim][NTf_2] (3) Ternary System at 298.15 K and Atmospheric Pressure

x_1	x_2	ρ / g·cm^{-3}	n_D	η / mPa·s	V^E / cm^3·mol^{-1}	ΔR	$\Delta\eta$ / mPa·s
0.8849	0.1035	0.90663	1.37241	0.498	−0.081	0.013	−1.062
0.8735	0.1138	0.90787	1.37266	0.503	−0.090	0.013	−1.170
0.7954	0.1840	0.91647	1.37435	0.555	−0.156	0.014	−1.887
0.6802	0.2876	0.92911	1.37686	0.679	−0.223	0.020	−2.898
0.5940	0.3650	0.93865	1.37889	0.773	−0.261	0.033	−3.654
0.5043	0.4457	0.94876	1.38068	0.928	−0.300	0.028	−4.383
0.4189	0.5225	0.95846	1.38257	1.076	−0.327	0.034	−5.076
0.3104	0.6200	0.97093	1.38481	1.371	−0.351	0.032	−5.850
0.2274	0.6947	0.98048	1.38642	1.610	−0.353	0.028	−6.429
0.1905	0.7278	0.98468	1.38705	1.824	−0.345	0.023	−6.578
0.1248	0.7869	0.99241	1.38831	2.113	−0.345	0.018	−6.937
0.0800	0.8272	0.99776	1.38928	2.461	−0.347	0.019	−7.031
0.8748	0.0997	0.92911	1.37615	0.588	−0.250	0.015	−2.252
0.7846	0.1715	0.95243	1.38022	0.733	−0.362	0.024	−3.846
0.6915	0.2456	0.97543	1.38412	0.936	−0.453	0.030	−5.438
0.5910	0.3256	0.99895	1.38800	1.199	−0.511	0.035	−7.113
0.4913	0.4050	1.02098	1.39149	1.570	−0.528	0.038	−8.663
0.3835	0.4908	1.04363	1.39496	2.037	−0.520	0.036	−10.28
0.2797	0.5734	1.06426	1.39804	2.726	−0.483	0.034	−11.59
0.1952	0.6406	1.08046	1.40051	3.493	−0.453	0.035	−12.45
0.1462	0.6797	1.08956	1.40165	4.020	−0.428	0.022	−12.87
0.1078	0.7103	1.09663	1.40272	4.540	−0.415	0.022	−13.09
0.0502	0.7561	1.10682	1.40418	5.392	−0.373	0.019	−13.35
0.8768	0.0857	0.94728	1.37908	0.685	−0.355	0.019	−3.252
0.7742	0.1570	0.98577	1.38552	0.930	−0.528	0.033	−5.931
0.6981	0.2099	1.01159	1.38960	1.261	−0.608	0.035	−7.767
0.5954	0.2813	1.04336	1.39451	1.663	−0.662	0.037	−10.29
0.4921	0.3531	1.07192	1.39884	2.392	−0.644	0.044	−12.51
0.3889	0.4249	1.09793	1.40273	3.145	−0.606	0.049	−14.70
0.2817	0.4994	1.12262	1.40640	4.576	−0.554	0.054	−16.32
0.1993	0.5567	1.14002	1.40852	5.829	−0.485	0.027	−17.41
0.1489	0.5917	1.15003	1.40998	6.763	−0.429	0.031	−17.92
0.0995	0.6261	1.15956	1.41124	7.881	−0.382	0.024	−18.21
0.0424	0.6658	1.17020	1.41273	9.352	−0.337	0.021	−18.36
0.8932	0.0638	0.95585	1.38071	0.743	−0.428	0.036	−3.675
0.7892	0.1261	1.00541	1.38845	1.085	−0.635	0.032	−7.227
0.6998	0.1795	1.04198	1.39430	1.610	−0.737	0.047	−10.04
0.6078	0.2345	1.07466	1.39903	2.286	−0.758	0.040	−12.81
0.5162	0.2893	1.10346	1.40329	3.107	−0.748	0.043	−15.41
0.4132	0.3509	1.13182	1.40722	4.382	−0.676	0.035	−17.99
0.3042	0.4160	1.15833	1.41110	6.305	−0.581	0.045	−20.15
0.2069	0.4742	1.17936	1.41388	8.621	−0.475	0.031	−21.47
0.1578	0.5036	1.18933	1.41526	10.05	−0.439	0.026	−21.88
0.0987	0.5389	1.20038	1.41676	11.96	−0.350	0.025	−22.17
0.0576	0.5635	1.20775	1.41770	13.66	−0.294	0.018	−22.01
0.8999	0.0505	0.96521	1.38193	0.800	−0.482	0.023	−4.223
0.8028	0.0995	1.02001	1.39061	1.212	−0.713	0.031	−8.276
0.7065	0.1480	1.06452	1.39739	1.953	−0.808	0.037	−11.96
0.5911	0.2063	1.10845	1.40394	2.980	−0.813	0.048	−16.23
0.4990	0.2528	1.13790	1.40803	4.430	−0.763	0.039	−19.02
0.3979	0.3037	1.16575	1.41194	6.374	−0.675	0.038	−21.72
0.3119	0.3471	1.18642	1.41486	8.577	−0.566	0.043	−23.47
0.2071	0.4000	1.20888	1.41787	12.06	−0.461	0.029	−24.80
0.1685	0.4195	1.21641	1.41886	13.74	−0.413	0.023	−24.90
0.1118	0.4481	1.22676	1.42028	16.28	−0.328	0.023	−24.96
0.0645	0.4719	1.23502	1.42156	18.90	−0.273	0.036	−24.51
0.8901	0.0443	0.98547	1.38518	0.931	−0.598	0.028	−5.564
0.7900	0.0846	1.04730	1.39468	1.547	−0.829	0.029	−10.47
0.7002	0.1208	1.09139	1.40130	2.524	−0.906	0.036	−14.46
0.5947	0.1634	1.13322	1.40733	3.856	−0.887	0.037	−18.95
0.4877	0.2065	1.16773	1.41238	6.229	−0.801	0.055	−22.49
0.3874	0.2469	1.19476	1.41595	9.092	−0.692	0.037	−25.17
0.2689	0.2947	1.22172	1.41984	13.86	−0.559	0.050	−26.94
0.1848	0.3286	1.23808	1.42183	18.21	−0.429	0.023	−27.23
0.1753	0.3324	1.23985	1.42207	18.85	−0.420	0.022	−27.12
0.1317	0.3499	1.24764	1.42315	21.47	−0.373	0.020	−26.91
0.0370	0.3881	1.26257	1.42512	28.31	−0.162	0.021	−25.30
0.8981	0.0294	0.99407	1.38673	0.992	−0.648	0.043	−6.137
0.8137	0.0536	1.05407	1.39582	1.727	−0.871	0.042	−10.95
0.7173	0.0814	1.10678	1.40358	2.906	−0.944	0.046	−16.11
0.5899	0.1181	1.15950	1.41099	5.526	−0.915	0.037	−21.86
0.4936	0.1458	1.19054	1.41530	8.229	−0.827	0.034	−25.49
0.3880	0.1762	1.21845	1.41909	12.79	−0.693	0.025	−27.88
0.2964	0.2026	1.23884	1.42194	17.52	−0.569	0.028	−29.16

Table 3. Continued

x_1	x_2	ρ / g·cm^{-3}	n_D	η / mPa·s	V^E / cm^3·mol^{-1}	ΔR	$\Delta\eta$ / mPa·s
0.2087	0.2279	1.25550	1.42415	23.50	−0.403	0.023	−28.95
0.1575	0.2426	1.26441	1.42541	27.51	−0.340	0.025	−28.31
0.1042	0.2580	1.27292	1.42652	32.57	−0.253	0.017	−26.75
0.0538	0.2725	1.28042	1.42758	37.90	−0.170	0.021	−24.74
0.8952	0.0203	1.00754	1.38867	1.126	−0.715	0.037	−7.092
0.7968	0.0394	1.07980	1.39946	2.230	−0.956	0.031	−13.31
0.6913	0.0598	1.13610	1.40764	4.029	−1.024	0.031	−19.35
0.5970	0.0781	1.17423	1.41310	6.502	−0.952	0.042	−23.89
0.4956	0.0978	1.20682	1.41760	10.28	−0.842	0.039	−27.65
0.4014	0.1160	1.23148	1.42096	15.35	−0.721	0.033	−29.59
0.3052	0.1347	1.25239	1.42365	21.83	−0.560	0.012	−30.26
0.2045	0.1542	1.27074	1.42629	30.54	−0.365	0.033	−29.03
0.1600	0.1628	1.27808	1.42715	35.37	−0.308	0.009	−27.51
0.0967	0.1751	1.28749	1.42850	42.55	−0.178	0.021	−25.04
0.0507	0.1840	1.29387	1.42930	47.86	−0.095	0.010	−23.15
0.9031	0.0093	1.01113	1.38906	1.138	−0.745	0.026	−7.356
0.7979	0.0194	1.09370	1.40184	2.769	−1.004	0.060	−14.49
0.7077	0.0281	1.14388	1.40879	4.389	−1.028	0.041	−20.38
0.5961	0.0388	1.19009	1.41523	8.007	−0.951	0.037	−26.06
0.5102	0.0471	1.21765	1.41901	12.10	−0.850	0.033	−29.12
0.4059	0.0571	1.24463	1.42271	18.76	−0.687	0.032	−31.15
0.2967	0.0676	1.26733	1.42574	28.46	−0.493	0.023	−30.55
0.2012	0.0768	1.28374	1.42795	39.19	−0.298	0.022	−27.77
0.1527	0.0815	1.29110	1.42893	45.00	−0.198	0.019	−25.99
0.0984	0.0867	1.29872	1.43013	52.99	−0.087	0.046	−22.53
0.0545	0.0909	1.30443	1.43071	60.11	0.001	0.014	−19.07

Table 4. Polynomial Coefficients and Standard Deviations, σ, Obtained for Fits of Equation *5* to the V^E, $\Delta\eta$, and ΔR Composition Data for the Binary Systems

property	A_0	A_1	A_2	A_3	σ
{x Ethyl Acetate + (1 − x) Ethanol}					
V^E/(cm^3·mol^{-1})	0.6489	0.0913			0.005
ΔR	0.0666				0.001
$\Delta\eta$/(mPa·s)	−1.0142	0.6009			0.013
{x Ethyl Acetate + (1 − x) [C$_8$mim][NTf$_2$]}					
V^E/(cm^3·mol^{-1})	−3.5608	−2.8750	−3.0927	−2.2077	0.011
ΔR	0.1567	0.1388	0.0130		0.008
$\Delta\eta$/(mPa·s)	−121.87	30.129	−6.9516	30.054	0.331
{x Ethanol + (1 − x) [C$_8$mim][NTf$_2$]}					
V^E/(cm^3·mol^{-1})	−0.4330	−1.2497	−1.3793	−1.8064	0.009
ΔR	0.1119	−0.1248	0.0987	0.4952	0.003
$\Delta\eta$/(mPa·s)	−94.048	30.794	−27.029		0.401

Figure 1a also shows data previously published[10−12] by other authors to establish a comparison. As it can be seen, the excess molar volumes determined in this work are in good agreement with those of Pires et al.[11] and González et al.[12] However, there is a discrepancy with the data measured by Nikam et al.,[13] which are not in concordance with most published values. In the case of $\Delta\eta$, our experimental data are in agreement with the previously published results.[12,13] No comparable data were found in the surveyed literature for the other binary systems.

For the ethyl acetate + ethanol + [C$_8$min][NTf$_2$] ternary system, Figures 2, 3, and 4 show density, refractive index, and dynamic viscosity isolines, respectively. Figure 5 shows excess molar volume isolines, and Figure 6 shows the viscosity changes of mixing isolines.

Correlation

The calculated data of V^E, $\Delta\eta$, and ΔR were correlated with the composition data by the Redlich−Kister polynomial,[14] which for binary mixtures is

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

where Q_{ij} is V^E, $\Delta\eta$, 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

$$Q_{123} = Q_{12} + Q_{23} + Q_{13} + x_1 x_2 x_3 (A + B(x_1 - x_2) + C(x_2 - x_3) + D(x_1 - x_3) + E(x_1 - x_2)^2 + F(x_2 - x_3)^2 + G(x_1 - x_3)^2 + ...) \quad (6)$$

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

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

Conclusions

Density, refractive index, and dynamic viscosity data were determined for the ethyl acetate + ethanol + [C$_8$mim][NTf$_2$] ternary system and also for its binary systems at 298.15 K and atmospheric pressure. The excess molar volumes, V^E, viscosity,

Table 5. Polynomial Coefficients and Standard Deviations, σ, Obtained for Fits of Equation *6* to the V^E, $\Delta\eta$, and ΔR Composition Data for the Ternary System

property	A	B	C	D	E	F	G	σ
V^E/(cm^3·mol^{-1})	−6.7198	3.3935	−9.2515	−9.9298	5.5346	−5.1804	−19.491	0.029
ΔR	−0.0126	0.2847	1.0119	0.3943	−1.3647	0.2558	1.3191	0.007
$\Delta\eta$/(mPa·s)	27.504	17.625	7.9383	2.8134				0.29

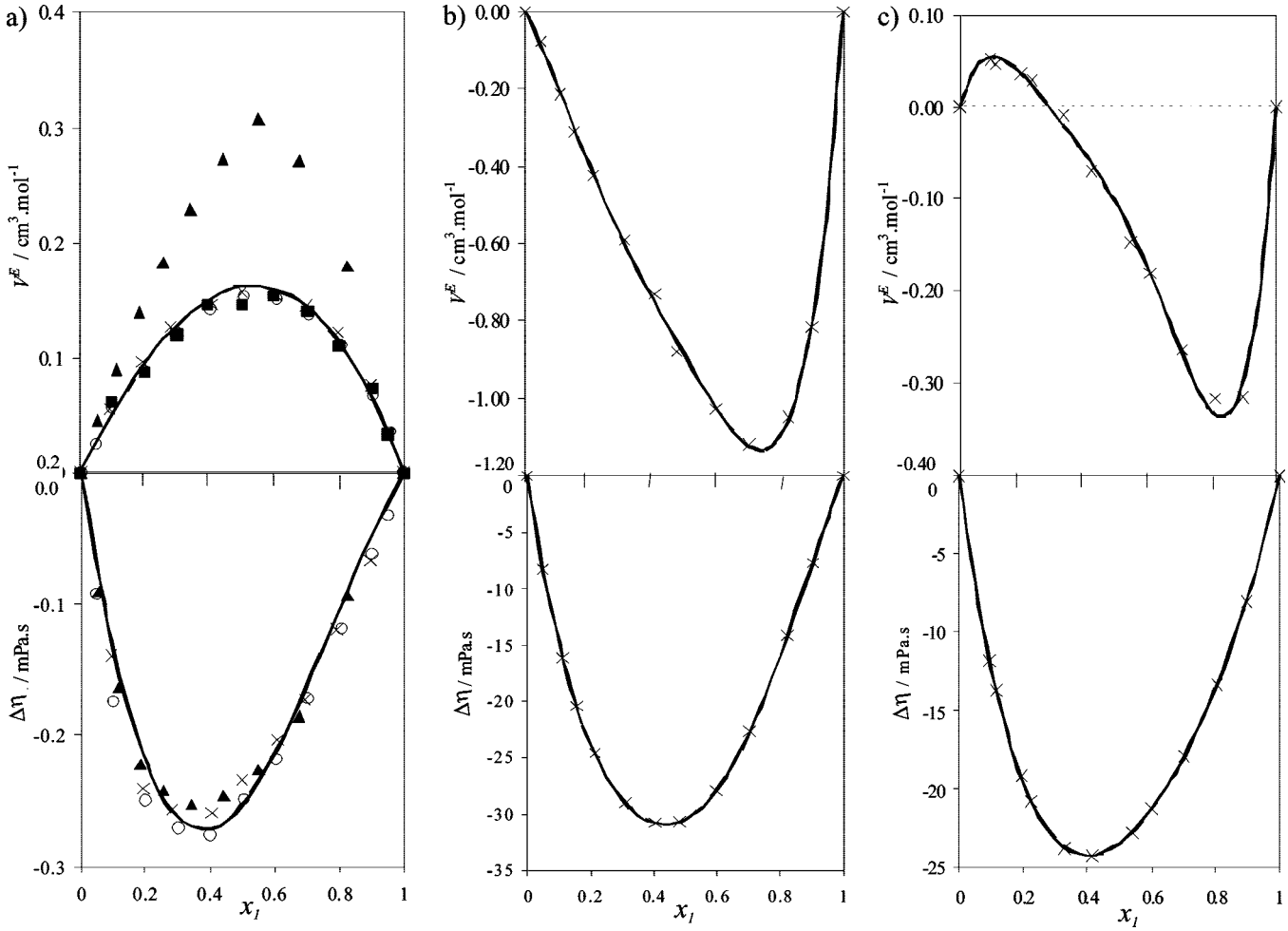

Figure 1. Excess molar volume and dynamic viscosity changes of mixing for binary systems at 298.15 K and atmospheric pressure: (a) ethyl acetate (1) + ethanol (2), (b) ethyl acetate (1) + [C_8mim][NTf_2] (2), and (c) ethanol (1) + [C_8mim][NTf_2] (2): ×, this work; ■, ref 11; ○, ref 12; ▲, ref 13; —, Redlich−Kister correlation.

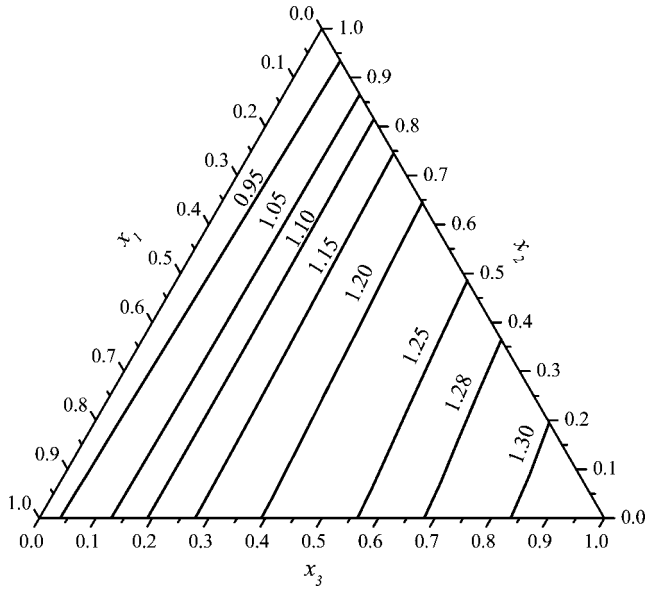

Figure 2. Density (g·cm^{-3}) isolines for {ethyl acetate (1) + ethanol (2) + [C_8mim][NTf_2] (3)} at 298.15 K and atmospheric pressure.

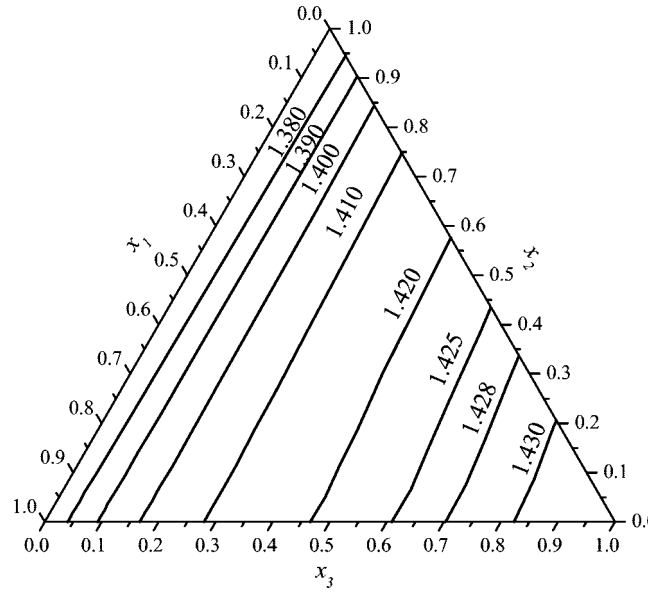

Figure 3. Refractive index isolines for {ethyl acetate (1) + ethanol (2) + [C_8mim][NTf_2](3)} at 298.15 K and atmospheric pressure.

$\Delta\eta$, and molar refraction, ΔR, changes of mixing were calculated from the physical properties.

The excess molar volumes for the ethyl acetate + [C_8mim][NTf_2] binary system are negative over the whole composition range and reach a minimum around −1.1 cm^3·mol^{-1}. Strong ion−dipole interactions between unlike molecules justify negative values of this property. The ethanol + [C_8mim][NTf_2] binary system show an S-shaped dependence

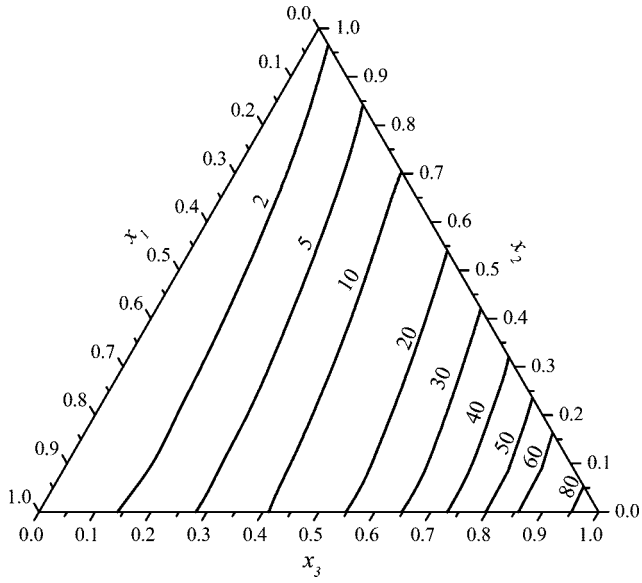

Figure 4. Dynamic viscosity (mPa·s) isolines for {ethyl acetate (1) + ethanol (2) + [C_8mim][NTf_2] (3)} at 298.15 K and atmospheric pressure.

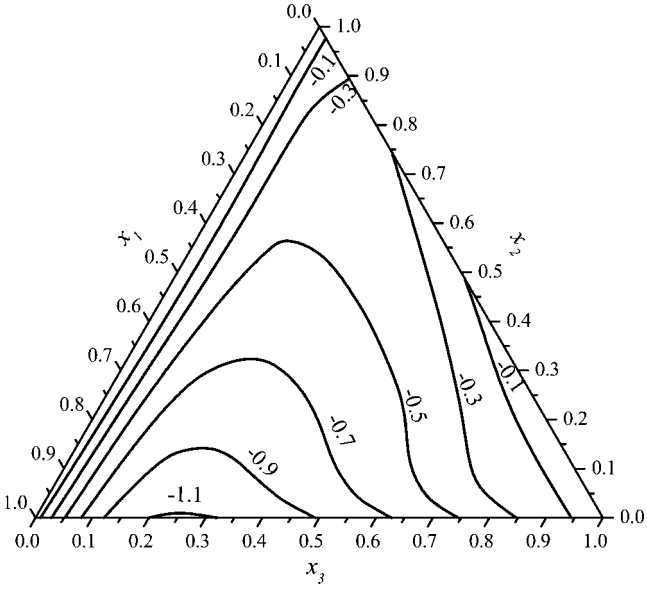

Figure 5. Excess molar volume ($cm^3 \cdot mol^{-1}$) isolines for {ethyl acetate (1) + ethanol (2) + [C_8mim][NTf_2] (3)} at 298.15 K and atmospheric pressure.

on composition with small positive values in the ethanol-poor region and negative values (around -0.3 $cm^3 \cdot mol^{-1}$) at the opposite extreme. The positive effect of the disruption of the H-bond structure at high dilution of the alcohol and the negative effect in more concentrated solutions are observed. The ethyl acetate + ethanol binary system has positive excess volumes, explained by the breaking interactions among molecules in the pure components during the mixing process, reaching a maximum around 0.16 $cm^3 \cdot mol^{-1}$.

The viscosity changes of mixing in the binary mixtures are negative with very large values in the case of mixtures with ILs because of the differences between compounds' viscosities (greater than 90 mPa·s).

The ethyl acetate + ethanol + [C_8mim][NTf_2] ternary system exhibits relatively large and negative excess molar volumes for the entire range of homogeneous mixtures. The negative excess molar volume can be attributed to a more efficient packing and

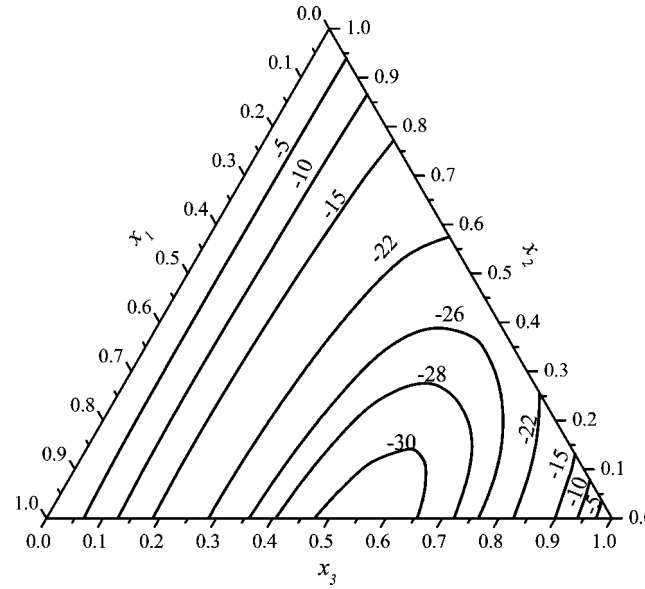

Figure 6. Viscosity change of mixing (mPa·s) isolines for {ethyl acetate (1) + ethanol (2) + [C_8mim][NTf_2] (3)} at 298.15 K and atmospheric pressure.

more attractive interactions in the mixtures than in the pure liquids. It reaches a minimum around -1.1 $cm^3 \cdot mol^{-1}$, which corresponds to the ethyl acetate + [C_8mim][NTf_2] binary system. Viscosity changes of mixing for the ternary systems are negative with a minimum around -31 mPa·s corresponding to the ethyl acetate + [C_8mim][NTf_2] binary system. Values of molar refraction changes of mixing are so small that it is difficult to establish any conclusion.

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

Supporting Information Available:

^{1}H NMR and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review November 24, 2008. Accepted January 19, 2009. We thank the Universidad de Santiago de Compostela, Ministerio de Educación y Ciencia (Spain) (project CTQ2006-07687/PPQ), CONICET, Universidad Nacional del Sur (Argentine), and European Union (project ALFA II-400-FA) for financial support.

JE800899W