J. Chem. Eng. Data **2010,** *55,* 1377–1388

Density, Speed of Sound, and Refractive Index of 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate with Acetone, Methyl Acetate, and Ethyl Acetate at Temperatures from (278.15 to 328.15) K

Ernesto Vercher, Francisco J. Llopis, M. Vicenta González-Alfaro, and Antoni Martínez-Andreu*

Departamento de Ingeniería Química, Escuela Técnica Superior de Ingeniería, Universitat de València,
46100 Burjassot, Valencia, Spain

Densities, speeds of sound, and refractive indices of the binary mixtures of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]) with acetone, methyl acetate, and ethyl acetate were experimentally measured over the whole range of compositions at T = (278.15 to 328.15) K and a pressure of 0.1 MPa. From these experimental data, excess molar volumes, excess isentropic compressibilities, molar refractions, and deviations in refractive indices have been calculated and fitted to an extended version of the Redlich−Kister equation, which takes into account the dependence on composition and temperature simultaneously. The Prigogine−Flory−Patterson theory has been used to speculate on the cause of the volumetric variations for these mixtures.

Introduction

Room-temperature ionic liquids (ILs) are salts made up of an organic greatly asymmetric substituted cation and an inorganic weak anion. These cations, substituents, and anions can be virtually varied at will to change their chemical and physical properties.[1] Because of their structure and ionic interactions, ILs exhibit unique properties: they have very low melting points (mainly below 100 °C) and a liquidus range of 300 °C, have no effective vapor pressure, are outstandingly good solvents for a wide range of inorganic, organic, and polymeric materials, exhibit Brönsted, Lewis, and Franklin acidity as well as superacidity, and are thermally stable up to 200 °C.[2] They are often used as a “green” solvent replacing volatile organic solvents, extraction media for separation processes,[3] and entrainers for extractive distillation.[4,5] Applications as catalysts for organic and organometallic synthesis, lubricants, thermofluids, plasticizers, and electrically conductive liquids in electrochemistry have also been reported.[2]

To better understand the nature of ILs and expand their applications as well as to design any technological processes, detailed knowledge on the thermodynamic behavior of ILs is required.[6] During the last few years, investigations on thermophysical and thermodynamic properties of pure ILs and their mixtures with molecular solvents have shown great augmentation. The International Union of Pure and Applied Chemistry (IUPAC) Ionic Liquid Database[7] provides up-to-date information on thermophysical properties of 339 ILs and their mixtures, with more than 75 000 data points obtained from 422 references. However, it is necessary to accumulate a sufficiently large data bank not only for process and product design but also for the development of correlation of properties.

In the present work, we report the volumetric, acoustical, and optical properties of binary mixtures of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]) with acetone, methyl acetate, or ethyl acetate over the whole range of compositions, at temperatures from (278.15 to 328.15) K and a pressure of 0.1 MPa. The values of the excess molar volume, isentropic compressibility, excess isentropic compressibility, molar refraction, and deviations in refractive indices were then calculated from the measured density, speed of sound, and refractive index data and fitted to polynomial equations.

Despite the importance of triflate-based ILs in industrial applications, physical properties of few binary mixtures have been reported, and those are as follows: ([emim][triflate] + water),[8−10] ([emim][triflate] + methanol),[9] ([emim][triflate] + ethanol),[9,11] ([emim][triflate] + 1-propanol),[9] and ([emim][triflate] + nitromethane).[12] To our knowledge, no measurements of density, speed of sound, or refractive index have been reported in the literature for the binary mixture studied in this work.

Experimental Section

Materials. The IL used was 1-ethyl-3-methylimidazolium trifluoromethanesulfonate supplied by Solvent Innovation (Purum, minimum mass fraction 0.98). Because of its hygroscopic character, it was dried over a desiccant at a pressure of 0.2 Pa overnight prior to use. The water mass fraction in the IL determined by Karl Fisher titration was $x_w < 0.0005$. The solvents used were acetone (Merck, SupraSolv, residue on evaporating < 3 $g \cdot m^{-3}$, water mass fraction < 0.0005), methyl acetate (Fluka, puriss, p.a., minimum mass fraction 0.995), and ethyl acetate (Merck, SupraSolv, residue on evaporating < 3 $g \cdot m^{-3}$, water mass fraction < 0.0002). These solvents were degassed ultrasonically and dried over molecular sieves of type 0.3 nm supplied by Grace, and they were used without further purification, their purity being ascertained by gas chromatography (GC). Densities, speeds of sound, and refractive indices of all of the chemicals at T = 298.15 K gave a good agreement with the corresponding literature values,[8−25] as shown in Table 1.

Apparatus and Procedure. Samples of (5 to 8) g were prepared by filling glass vials with the liquids and weighing them on a Mettler AE200 analytical balance, which measured with a precision of 0.0001 g. Vials were closed with screw caps

---

* Corresponding author. E-mail: antoni.martinez@uv.es. Fax: +34 963 544 898.

10.1021/je9005618

to ensure a secure seal and to prevent evaporation. The uncertainty in mole fractions was estimated to be less than ± 0.0001.

Measurements of the density, ρ, and the speed of sound, u, of pure components and binary mixtures were carried out using a digital vibrating-tube densimeter and speed of sound analyzer (Anton Paar DSA 5000) with a proportional temperature controller that kept the samples at working temperature with an uncertainty of ± 0.001 K. This analyzer automatically corrects the influence of viscosity on the measured density. The apparatus was calibrated at $T = 298.15$ K with bidistilled water and dry air. Standard uncertainties of measurements were estimated to be less than ± 0.007 $\text{kg}\cdot\text{m}^{-3}$ for density and ± 0.05 $\text{m}\cdot\text{s}^{-1}$ for the speed of sound.

Measurements of the refractive index, n_D, of pure components and binary mixtures were carried out using an automatic refractometer (ABBEMAT-HP Dr. Kernchen) with a proportional temperature controller that kept the samples at working temperature with an uncertainty of ± 0.01 K. The apparatus was calibrated by measuring the refractive index of Millipore quality water and tetrachloroethylene. The calibration was checked every day with Millipore quality water. Standard uncertainties of measurements were estimated to be less than $\pm 2\cdot 10^{-5}$.

Results and Discussion

Molar volume, V_m, can be determined from density values using the expression

$$V_m = \frac{M_m}{\rho} \tag{1}$$

where $M_m = (x_1M°_1 + x_2M°_2)$, the molar mass of the mixture, is obtained from that of pure component i, $M°_i$, and its mole fraction x_i.

The isentropic compressibility, κ_S, defined as

$$\kappa_S = -\frac{1}{V_m}\left(\frac{\partial V_m}{\partial P}\right)_S = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_S \tag{2}$$

can be determined from density and speed of sound values by means of the Laplace equation

$$\kappa_S = \frac{1}{\rho u^2} = \frac{V_m}{M_m u^2} \tag{3}$$

The molar refraction, R, can be defined from refractive index and molar volume as

$$R = \frac{n_D^2 - 1}{n_D^2 + 2}V_m \tag{4}$$

Combined standard uncertainties were estimated to be less than $\pm 1\cdot 10^{-8}$ $\text{m}^3\cdot\text{mol}^{-1}$ for molar volume, ± 0.05 TPa^{-1} for the isentropic compressibility, and $\pm 5\cdot 10^{-8}$ $\text{m}^3\cdot\text{mol}^{-1}$ for molar refraction.

Properties of Pure Liquids. The experimental data for the density ρ, speed of sound u, and refractive index n_D of pure components together with the molar volume V_m, isentropic compressibility κ_S, and molar refraction R are given in Table 2. For all of the components, the density, the speed of sound, and the refractive index decrease when the temperature increases. In consequence, the molar volume and the isentropic compressibility of all of the components increase with the temperature, for the tested temperature range. With regard to the molar refraction, its value scarcely increases with the temperature.

As will be seen later, the isobaric thermal expansivity α_P of pure components, defined as

$$\alpha_P = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \tag{5}$$

and the isobaric molar heat capacity C_P will be needed for calculating the excess properties of component mixtures. For all of the components and from an empirical perspective, some third-order polynomials were found to satisfactorily correlate the change of density with temperature. From them and using eq 5, the isobaric thermal expansivity α_P at every temperature reported in Table 2 was obtained. In this table, the isobaric molar heat capacity C_P of pure components at the same temperatures has been also reported. For solvents, they were obtained from equations proposed in the Daubert and Danner[19] data compilation, whereas for [emim][triflate], values given by Diedrichs and Gmehling[26] have been taken.

Properties of Liquid Mixtures. The experimental data for the density, ρ, and speed of sound, u, for {[emim][triflate] (1) + acetone (2)}, {[emim][triflate] (1) + methyl acetate (2)}, and {[emim][triflate] (1) + ethyl acetate (2)} together with the isentropic compressibility, κ_S, determined from eq 3 are given in Tables 3, 4, and 5 at several temperatures. As can be seen, the density of all of the mixtures always increases with the IL mole fraction, x_1, and decreases with temperature, T. The same behavior is observed for the speed of sound of [emim][triflate] (1) + solvent (2). For the isentropic compressibility, the behavior

Table 1. Comparison of Experimental Density ρ, Speed of Sound u, and Refractive Index n_D of Pure Liquids at $T = 298.15$ K with Literature Data

	ρ		u		n_D	
	$\text{kg}\cdot\text{m}^{-3}$		$\text{m}\cdot\text{s}^{-1}$			
component	exptl	lit.	exptl	lit.	exptl	lit.
[emim][triflate]	1383.58	1383.60[a] 1385.3[d,e,f]	1435.6	1435.6[b]	1.43320	1.43338[c]
acetone	784.76	784.30[g]	1165.0	1161.0[h,i] 1163[k] 1167.9[l]	1.35597	1.3560[j] 1.35596[g]
methyl acetate	927.01	927.5[g]	1150.7	1149.53[m] 1150[n] 1151[o] 1155[p]	1.35881	1.3589[c]
ethyl acetate	894.33	894.4[g]	1140.0	1139.6[q] 1140[k,o] 1141[p,r]	1.36994	1.3704[c]

[a] Ref 8. [b] Ref 9. [c] Ref 13. [d] Ref 10. [e] Ref 11. [f] Ref 12. [g] Ref 14. [h] Ref 15. [i] Ref 16. [j] Ref 19. [k] Ref 17. [l] Ref 18. [m] Ref 20. [n] Ref 21. [o] Ref 22. [p] Ref 23. [q] Ref 24. [r] Ref 25.

Table 2. Density ρ, Molar Volume V_m, Speed of Sound u, Isentropic Compressibility κ_S, Refractive Index n_D, Molar Refraction R, Isobaric Molar Heat Capacity C_P, and Isobaric Thermal Expansivity α_P of Pure Acetone, Methyl Acetate, Ethyl Acetate, and [emim][triflate] at Several Temperatures

T / K	ρ / $kg \cdot m^{-3}$	$10^6\ V_m$ / $m^3 \cdot mol^{-1}$	u / $m \cdot s^{-1}$	κ_S / TPa^{-1}	n_D	$10^6\ R$ / $m^3 \cdot mol^{-1}$	C_P / $J \cdot mol^{-1} \cdot K^{-1}$	α_P / kK^{-1}
Acetone								
278.15	807.41	71.934	1256.48	784.51			123.14[a]	1.388
288.15	796.14	72.952	1210.66	856.97	1.36146	16.16	124.64[a]	1.422
298.15	784.76	74.010	1164.95	938.96	1.35597	16.17	126.31[a]	1.461
308.15	773.21	75.116	1118.48	1033.83	1.35054	16.19	128.16[a]	1.505
318.15	761.47	76.274	1073.74	1139.07	1.34491	16.20	130.19[a]	1.556
Methyl Acetate								
278.15	953.04	77.729	1243.46	678.62			136.61[a]	1.347
288.15	940.12	78.798	1196.84	742.59	1.36414	17.57	139.32[a]	1.384
298.15	927.01	79.912	1150.69	814.71	1.35881	17.58	142.03[a]	1.425
308.15	913.68	81.077	1104.73	896.79	1.35367	17.61	144.74[a]	1.470
318.15	900.13	82.298	1059.25	990.14	1.34823	17.63	147.45[a]	1.520
Ethyl Acetate								
278.15	918.50	95.924	1231.02	718.44			166.33[a]	1.300
288.15	906.48	97.195	1185.18	785.36	1.37519	22.26	168.41[a]	1.333
298.15	894.33	98.516	1140.02	860.35	1.36994	22.28	170.80[a]	1.368
308.15	882.02	99.891	1095.30	945.05	1.36460	22.30	173.47[a]	1.406
318.15	869.52	101.327	1050.99	1041.17	1.35919	22.32	176.44[a]	1.447
328.15	856.85	102.825	1007.38	1150.03	1.35368	22.33	179.71[a]	1.491
[emim][triflate]								
278.15	1400.51[b]	185.818	1482.23[b]	325.00			364.14[c]	0.6078
288.15	1392.02[b]	186.951	1458.35[b]	337.78	1.43599	48.88	370.05[c]	0.6082
298.15	1383.58[b]	188.092	1435.56[b]	350.71	1.43320	48.90	375.57[c]	0.6084
308.15	1375.19[b]	189.239	1413.16[b]	364.13	1.43040	48.92	380.72[c]	0.6081
318.15	1366.86[b]	190.393	1391.29[b]	377.96	1.42767	48.95	385.55[c]	0.6075
328.15	1358.59[b]	191.552	1369.65[b]	392.37	1.42494	48.97	390.09[c]	0.6065

[a] From ref 19. [b] From ref 9. [c] From ref 26.

is also very regular and logically contrary to the last ones: it decreases with x_1 and increases with T.

The experimental data for the refractive index, n_D, for the same binary mixtures together with the molar refraction, R, determined from eq 4 are given in Tables 6, 7, and 8 at several temperatures. It can be seen that the refractive index of all of the mixtures always increases with IL mole fraction, x_1, and decreases with temperature, T. For the molar refraction of the binary systems, their values almost linearly increase with the IL mole fraction, x_1, and scarcely increase with the temperature.

Excess and Derived Quantities of Liquid Mixtures. For any thermodynamic quantity, as V_m or κ_S, its excess property can be defined as the difference between its actual value and that corresponding for an ideal mixture at the same thermodynamic state,

$$\begin{aligned} V_m^E &= V_m - V_m^{id} \\ \kappa_S^E &= \kappa_S - \kappa_S^{id} \end{aligned} \tag{6}$$

Similarly, for nonthermodynamic quantities, such as the refractive index and molar refraction, deviations from an ideal mixture, which are equivalent to an excess function for an equilibrium quantity, can be obviously defined as

$$\Delta n_D = n_D - n_D^{id} \tag{7}$$

$$\Delta R = R - R^{id} \tag{8}$$

Defining and calculating the properties of liquid ideal mixtures is not always anything straightforward. For ideal-mixture molar volume, the definition is direct:

$$V_m^{id} = x_1 V_1^o + x_2 V_2^o \tag{9}$$

where x_i is the mole fraction of component i and V_i^o is the molar volume of pure component i at the mixture temperature and pressure. For the isentropic compressibility Douhéret et al.[27] stated that it must be calculated using the expression:

$$\kappa_S^{id} = \phi_1 \kappa_{S,1}^o + \phi_2 \kappa_{S,2}^o + T\left[\frac{\phi_1 V_1^o (\alpha_{P,1}^o)^2}{C_{P,1}^o} + \frac{\phi_2 V_2^o (\alpha_{P,2}^o)^2}{C_{P,2}^o} - \frac{V_m^{id} (\alpha_P^{id})^2}{C_{P,m}^{id}}\right] \tag{10}$$

where ϕ_i $(= x_i V_i^o / V_m^{id})$ is the volume fraction of component i, whereas $\kappa_{S,i}^o$, $\alpha_{P,i}^o$, and $C_{P,i}^o$ are the isentropic compressibility, the isobaric thermal expansivity, and the isobaric molar heat capacity, respectively, of pure component i at the mixture temperature and pressure. α_P^{id} and $C_{P,m}^{id}$ are the isobaric thermal expansivity and the isobaric molar heat capacity, respectively, of the ideal mixture defined as[27]

$$\alpha_P^{id} = \phi_1 \alpha_{P,1}^o + \phi_2 \alpha_{P,2}^o \tag{11}$$

$$C_{P,m}^{id} = x_1 C_{P,1}^o + x_2 C_{P,2}^o \tag{12}$$

For the molar refraction in an ideal mixture, Iglesias-Otero et al.[28] and Brocos et al.[29] propose

$$R^{id} = x_1 R_1^o + x_2 R_2^o \tag{13}$$

and Iglesias-Otero et al.[28] recommend calculating the refractive index in an ideal mixture through

$$n_D^{id} = \left[\frac{(n_{D,1}^o)^2 (n_{D,2}^o)^2 + 2\phi_1 (n_{D,1}^o)^2 + 2\phi_2 (n_{D,2}^o)^2}{2 + \phi_1 (n_{D,2}^o)^2 + \phi_2 (n_{D,1}^o)^2}\right]^{1/2} \tag{14}$$

where $n_{D,i}^o$ is the refractive index of pure component i at the mixture temperature and pressure. The combined standard

Table 3. Density ρ, Excess Molar Volume V_m^E, Speed of Sound u, Isentropic Compressibility κ_S, and Excess Isentropic Compressibility κ_S^E for the Binary System [emim][triflate] (1) + Acetone (2) at T = (278.15 to 318.15) K

	ρ	10^6 V_m^E	u	κ_S	κ_S^E
x_1	$kg \cdot m^{-3}$	$m^3 \cdot mol^{-1}$	$m \cdot s^{-1}$	TPa^{-1}	TPa^{-1}
		T = 278.15 K			
0.0500	887.53	−0.798	1280.29	687.39	−56.28
0.0999	953.96	−1.252	1299.73	620.53	−84.48
0.1501	1010.97	−1.560	1313.45	573.37	−95.29
0.2004	1060.17	−1.761	1327.80	535.01	−99.79
0.2988	1138.02	−1.845	1356.40	477.61	−97.80
0.4007	1201.10	−1.771	1382.40	435.67	−86.93
0.5006	1250.85	−1.604	1404.46	405.30	−72.58
0.6007	1291.81	−1.376	1423.53	382.01	−56.98
0.7014	1326.90	−1.178	1441.02	362.93	−41.85
0.7998	1354.50	−0.768	1455.58	348.46	−26.86
0.8435	1365.96	−0.637	1462.54	342.25	−21.06
0.9006	1379.40	−0.405	1469.38	335.77	−12.79
0.9501	1390.54	−0.239	1475.94	330.12	−6.37
		T = 288.15 K			
0.0500	876.86	−0.888	1233.34	749.73	−61.68
0.0999	943.44	−1.367	1253.54	674.54	−93.59
0.1501	1000.75	−1.702	1273.09	616.53	−110.76
0.2004	1050.21	−1.920	1291.77	570.63	−118.54
0.2988	1128.31	−2.001	1324.65	505.09	−117.05
0.4007	1191.78	−1.930	1353.03	458.34	−104.04
0.5006	1241.69	−1.740	1376.74	424.90	−86.79
0.6007	1282.81	−1.489	1397.25	399.29	−68.23
0.7014	1318.05	−1.266	1415.85	378.47	−50.16
0.7998	1345.77	−0.826	1430.90	362.92	−32.19
0.8435	1357.29	−0.684	1437.83	356.38	−25.06
0.9006	1370.81	−0.436	1445.72	349.02	−15.61
0.9501	1382.00	−0.255	1452.12	343.15	−7.72
		T = 298.15 K			
0.0500	866.08	−0.981	1191.09	813.87	−74.14
0.0999	932.87	−1.493	1214.29	727.00	−112.41
0.1501	990.52	−1.860	1236.64	660.16	−133.27
0.2004	1040.29	−2.099	1257.51	607.89	−142.52
0.2988	1118.66	−2.177	1293.53	534.26	−140.31
0.4007	1182.49	−2.104	1324.31	482.20	−124.57
0.5006	1232.59	−1.892	1349.65	445.39	−103.75
0.6007	1273.89	−1.616	1371.60	417.27	−81.58
0.7014	1309.28	−1.366	1391.32	394.56	−59.95
0.7998	1337.12	−0.894	1407.02	377.77	−38.47
0.8435	1348.69	−0.737	1414.27	370.70	−29.92
0.9006	1362.28	−0.472	1422.54	362.75	−18.67
0.9501	1373.52	−0.274	1429.13	356.47	−9.23
		T = 308.15 K			
0.0500	855.21	−1.088	1149.88	884.35	−92.18
0.0999	922.28	−1.639	1175.97	784.05	−137.65
0.1501	980.27	−2.039	1200.76	707.52	−162.17
0.2004	1030.37	−2.302	1223.69	648.13	−172.79
0.2988	1109.04	−2.378	1262.93	565.32	−169.40
0.4007	1173.23	−2.299	1296.07	507.41	−150.04
0.5006	1223.54	−2.064	1323.05	466.90	−124.72
0.6007	1265.02	−1.760	1346.52	435.99	−98.10
0.7014	1300.58	−1.479	1367.32	411.27	−72.02
0.7998	1328.53	−0.970	1383.70	393.14	−46.26
0.8435	1340.15	−0.799	1391.21	385.53	−35.94
0.9006	1353.81	−0.512	1399.93	376.90	−22.51
0.9501	1365.09	−0.295	1406.65	370.22	−11.12
		T = 318.15 K			
0.0500	844.23	−1.209	1109.28	962.62	−112.26
0.0999	911.64	−1.806	1138.21	846.71	−166.52
0.1501	969.97	−2.238	1165.39	759.10	−195.45
0.2004	1020.44	−2.527	1190.42	691.53	−207.87
0.2988	1099.45	−2.602	1232.82	598.45	−203.18
0.4007	1164.02	−2.517	1268.44	533.95	−179.76
0.5006	1214.55	−2.255	1297.12	489.36	−149.27
0.6007	1256.22	−1.921	1322.00	455.48	−117.39
0.7014	1291.94	−1.607	1343.78	428.65	−86.06
0.7998	1320.01	−1.057	1360.99	408.99	−55.40
0.8435	1331.68	−0.868	1368.69	400.86	−42.96
0.9006	1345.41	−0.559	1377.68	391.60	−26.89
0.9501	1356.74	−0.320	1384.72	384.40	−13.35

Table 4. Density ρ, Excess Molar Volume V_m^E, Speed of Sound u, Isentropic Compressibility κ_S, and Excess Isentropic Compressibility κ_S^E for the Binary System [emim][triflate] (1) + Methyl Acetate (2) at T = (278.15 to 318.15) K

	ρ	10^6 V_m^E	u	κ_S	κ_S^E
x_1	$kg \cdot m^{-3}$	$m^3 \cdot mol^{-1}$	$m \cdot s^{-1}$	TPa^{-1}	TPa^{-1}
		T = 278.15 K			
0.0502	1010.10	−0.564	1259.82	623.76	−26.33
0.1006	1058.30	−0.911	1278.42	578.16	−44.30
0.1501	1099.41	−1.160	1298.13	539.76	−56.79
0.2001	1135.42	−1.309	1316.62	508.07	−63.69
0.3003	1196.62	−1.564	1350.22	458.39	−67.94
0.3999	1243.17	−1.480	1376.91	424.29	−62.16
0.4997	1281.71	−1.366	1399.99	398.07	−53.14
0.6000	1313.96	−1.195	1420.40	377.22	−42.61
0.7000	1341.07	−0.983	1438.45	360.38	−31.70
0.7986	1363.97	−0.741	1454.41	346.60	−21.02
0.8509	1374.90	−0.609	1462.25	340.16	−15.49
0.9008	1384.25	−0.435	1469.14	334.70	−10.17
0.9504	1393.09	−0.276	1475.58	329.68	−5.00
		T = 288.15 K			
0.0502	997.80	−0.618	1215.54	678.30	−31.78
0.1006	1046.52	−0.999	1236.54	624.94	−53.63
0.1501	1088.09	−1.272	1258.51	580.26	−68.75
0.2001	1124.48	−1.436	1279.24	543.43	−77.27
0.3003	1186.31	−1.708	1316.59	486.30	−82.48
0.3999	1233.30	−1.618	1346.03	447.53	−75.60
0.4997	1272.18	−1.491	1371.15	418.10	−64.65
0.6000	1304.71	−1.300	1393.26	394.84	−51.93
0.7000	1332.05	−1.064	1412.70	376.17	−38.73
0.7986	1355.14	−0.798	1429.70	361.02	−25.78
0.8509	1366.17	−0.652	1437.99	353.98	−19.06
0.9008	1375.61	−0.464	1445.25	348.03	−12.61
0.9504	1384.52	−0.292	1452.03	342.57	−6.35
		T = 298.15 K			
0.0502	985.37	−0.679	1171.72	739.19	−38.47
0.1006	1034.65	−1.099	1195.08	676.72	−64.99
0.1501	1076.72	−1.401	1219.38	624.63	−83.34
0.2001	1113.53	−1.583	1242.35	581.85	−93.77
0.3003	1176.03	−1.872	1283.49	516.18	−100.03
0.3999	1223.49	−1.777	1315.76	472.12	−91.78
0.4997	1262.72	−1.634	1343.04	439.05	−78.51
0.6000	1295.53	−1.422	1366.82	413.17	−63.04
0.7000	1323.10	−1.159	1387.55	392.56	−47.00
0.7986	1346.39	−0.865	1405.58	375.94	−31.27
0.8509	1357.51	−0.703	1414.36	368.25	−23.12
0.9008	1367.03	−0.500	1421.99	361.77	−15.31
0.9504	1376.02	−0.311	1429.12	355.83	−7.73
		T = 308.15 K			
0.0502	972.78	−0.748	1128.17	807.67	−46.87
0.1006	1022.69	−1.213	1153.82	734.48	−79.03
0.1501	1065.29	−1.546	1180.48	673.62	−101.32
0.2001	1102.55	−1.748	1205.89	623.72	−114.23
0.3003	1165.76	−2.059	1250.81	548.29	−121.58
0.3999	1213.71	−1.957	1285.92	498.26	−111.56
0.4997	1253.32	−1.798	1315.45	461.10	−95.46
0.6000	1286.43	−1.561	1340.93	432.32	−76.65
0.7000	1314.23	−1.269	1362.93	409.62	−57.10
0.7986	1337.70	−0.942	1381.97	391.42	−37.97
0.8509	1348.91	−0.762	1391.20	383.04	−28.07
0.9008	1358.51	−0.540	1399.24	375.97	−18.62
0.9504	1367.58	−0.333	1406.71	369.52	−9.45
		T = 318.15 K			
0.0502	960.03	−0.826	1084.82	885.12	−56.85
0.1006	1010.60	−1.342	1112.82	799.04	−96.08
0.1501	1053.78	−1.711	1141.89	727.78	−123.25
0.2001	1091.53	−1.937	1169.66	669.65	−139.03
0.3003	1155.50	−2.270	1218.67	582.72	−147.90
0.3999	1203.97	−2.161	1256.66	525.96	−135.66
0.4997	1243.97	−1.983	1288.45	484.23	−116.06
0.6000	1277.38	−1.719	1315.63	452.28	−93.14
0.7000	1305.42	−1.393	1338.90	427.32	−69.33
0.7986	1329.08	−1.029	1358.89	407.46	−46.05
0.8509	1340.38	−0.828	1368.58	398.32	−34.03
0.9008	1350.04	−0.585	1377.02	390.64	−22.60
0.9504	1359.19	−0.357	1384.81	383.65	−11.50

Table 5. Density ρ, Excess Molar Volume V_m^E, Speed of Sound u, Isentropic Compressibility κ_S, and Excess Isentropic Compressibility κ_S^E for the Binary System [emim][triflate] (1) + Ethyl Acetate (2) at T = (278.15 to 328.15) K

x_1	ρ / $\text{kg}\cdot\text{m}^{-3}$	$10^6\ V_m^E$ / $\text{m}^3\cdot\text{mol}^{-1}$	u / $\text{m}\cdot\text{s}^{-1}$	κ_S / TPa^{-1}	κ_S^E / TPa^{-1}
		T = 278.15 K			
0.0501	967.32	−0.430	1237.99	674.52	−16.22
0.1003	1011.38	−0.757	1249.02	633.79	−29.84
0.1502	1051.15	−1.014	1263.82	595.61	−41.90
0.2004	1087.57	−1.210	1280.48	560.79	−51.34
0.3002	1150.92	−1.457	1313.91	503.30	−61.25
0.4002	1203.84	−1.486	1343.69	460.08	−60.69
0.5002	1248.95	−1.404	1371.16	425.87	−54.80
0.6009	1288.17	−1.248	1397.01	397.77	−45.97
0.6999	1321.89	−1.050	1420.48	374.92	−35.53
0.8006	1351.91	−0.783	1442.81	355.33	−24.03
0.8492	1365.02	−0.628	1453.00	347.00	−18.29
0.9008	1378.11	−0.455	1463.25	338.90	−12.05
0.9501	1389.89	−0.274	1472.57	331.79	−6.00
		T = 288.15 K			
0.0501	955.66	−0.474	1193.70	734.36	−19.83
0.1003	999.99	−0.828	1206.14	687.40	−36.21
0.1502	1040.09	−1.112	1222.85	642.96	−51.11
0.2004	1076.84	−1.330	1241.49	602.51	−62.80
0.3002	1140.70	−1.598	1278.80	536.07	−75.24
0.4002	1194.03	−1.631	1311.70	486.76	−74.74
0.5002	1239.47	−1.539	1341.58	448.26	−67.55
0.6009	1278.96	−1.365	1369.40	416.95	−56.70
0.6999	1312.90	−1.143	1394.01	391.96	−43.65
0.8006	1343.10	−0.847	1417.93	370.32	−29.72
0.8492	1356.29	−0.678	1428.61	361.26	−22.68
0.9008	1369.47	−0.488	1439.30	352.49	−15.03
0.9501	1381.32	−0.291	1448.98	344.81	−7.63
		T = 298.15 K			
0.0501	943.87	−0.522	1150.05	801.04	−24.14
0.1003	988.52	−0.908	1163.86	746.82	−43.79
0.1502	1028.97	−1.221	1182.45	695.08	−62.08
0.2004	1066.05	−1.463	1203.03	648.14	−76.41
0.3002	1130.49	−1.759	1244.23	571.39	−91.82
0.4002	1184.26	−1.795	1280.36	515.10	−91.42
0.5002	1230.04	−1.693	1312.73	471.77	−82.64
0.6009	1269.80	−1.498	1342.40	437.02	−69.25
0.6999	1303.96	−1.249	1369.01	409.19	−53.59
0.8006	1334.35	−0.921	1393.71	385.82	−36.25
0.8492	1347.63	−0.736	1404.85	375.99	−27.64
0.9008	1360.89	−0.527	1415.98	366.49	−18.33
0.9501	1372.81	−0.312	1426.03	358.20	−9.33
		T = 308.15 K			
0.0501	931.96	−0.575	1106.81	875.91	−29.35
0.1003	976.94	−0.997	1121.78	813.42	−52.69
0.1502	1017.77	−1.344	1142.24	753.07	−75.11
0.2004	1055.22	−1.612	1165.07	698.16	−93.01
0.3002	1120.28	−1.938	1210.15	609.53	−111.88
0.4002	1174.52	−1.980	1249.48	545.36	−111.46
0.5002	1220.67	−1.866	1284.38	496.61	−100.76
0.6009	1260.71	−1.649	1315.95	458.04	−84.31
0.6999	1295.11	−1.371	1344.17	427.35	−65.24
0.8006	1325.68	−1.006	1370.00	401.90	−44.07
0.8492	1339.04	−0.803	1381.61	391.23	−33.60
0.9008	1352.38	−0.572	1393.17	380.97	−22.29
0.9501	1364.37	−0.336	1403.60	372.03	−11.40
		T = 318.15 K			
0.0501	919.88	−0.634	1063.87	960.49	−35.56
0.1003	965.24	−1.096	1080.13	888.00	−63.61
0.1502	1006.48	−1.482	1102.30	817.70	−90.82
0.2004	1044.34	−1.780	1127.28	753.52	−112.89
0.3002	1110.07	−2.142	1176.46	650.87	−136.11
0.4002	1164.82	−2.189	1219.01	577.73	−135.57
0.5002	1211.35	−2.063	1256.57	522.83	−122.55
0.6009	1251.69	−1.820	1290.12	480.00	−102.42
0.6999	1286.31	−1.508	1319.80	446.31	−79.11
0.8006	1317.07	−1.102	1346.78	418.60	−53.36
0.8492	1330.51	−0.877	1358.82	407.06	−40.63
0.9008	1343.92	−0.623	1370.79	395.99	−26.94
0.9501	1355.98	−0.364	1381.58	386.36	−13.78
		T = 328.15 K			
0.0501	907.62	−0.695	1021.30	1056.30	−42.49
0.1003	953.35	−1.200	1039.16	971.37	−76.94
0.1502	995.07	−1.631	1062.70	889.87	−109.44
0.2004	1033.39	−1.967	1090.05	814.41	−136.98
0.3002	1099.87	−2.370	1143.32	695.54	−165.34
0.4002	1155.15	−2.423	1189.30	612.04	−164.76
0.5002	1202.08	−2.283	1229.43	550.38	−148.78
0.6009	1242.72	−2.010	1264.92	502.92	−124.18
0.6999	1277.58	−1.661	1296.01	466.01	−95.76
0.8006	1308.52	−1.208	1324.07	435.91	−64.51
0.8492	1322.04	−0.959	1336.55	423.43	−49.11
0.9008	1335.52	−0.678	1348.92	411.51	−32.58
0.9501	1347.65	−0.393	1360.07	401.14	−16.74

uncertainty for the ideal properties was estimated to be the same as that for the actual properties.

Table 6. Refractive Index n_D, Molar Refraction R, and Deviation of the Refractive Index Δn_D for the Binary System [emim][triflate] (1) + Acetone (2) at T = (288.15 to 318.15) K

x_1	n_D	$10^6\ R$ / $\text{m}^3\cdot\text{mol}^{-1}$	Δn_D
	T = 288.15 K		
0.04957	1.37495	17.79	0.00494
0.10050	1.38499	19.45	0.00734
0.15027	1.39293	21.09	0.00874
0.20070	1.39936	22.74	0.00930
0.29948	1.40865	25.96	0.00887
0.39730	1.41585	29.18	0.00822
0.50181	1.42117	32.57	0.00660
0.59957	1.42541	35.78	0.00539
0.69728	1.42854	38.95	0.00385
0.77330	1.43087	41.44	0.00298
0.84521	1.43253	43.78	0.00192
0.89879	1.43368	45.53	0.00120
0.95593	1.43487	47.41	0.00052
	T = 298.15 K		
0.04957	1.36994	17.80	0.00518
0.10050	1.38033	19.46	0.00769
0.15027	1.38854	21.09	0.00915
0.20070	1.39527	22.75	0.00981
0.29948	1.40492	25.97	0.00940
0.39730	1.41237	29.19	0.00871
0.50181	1.41787	32.59	0.00699
0.59957	1.42225	35.79	0.00569
0.69728	1.42549	38.97	0.00406
0.77330	1.42786	41.46	0.00310
0.84521	1.42963	43.80	0.00202
0.89879	1.43085	45.56	0.00129
0.95593	1.43207	47.43	0.00056
	T = 308.15 K		
0.04957	1.36575	17.85	0.00618
0.10050	1.37615	19.49	0.00849
0.15027	1.38475	21.13	0.01014
0.20070	1.39155	22.78	0.01068
0.29948	1.40133	25.99	0.01006
0.39730	1.40900	29.21	0.00929
0.50181	1.41464	32.61	0.00744
0.59957	1.41908	35.80	0.00598
0.69728	1.42250	38.99	0.00433
0.77330	1.42490	41.48	0.00326
0.84521	1.42676	43.83	0.00215
0.89879	1.42803	45.58	0.00137
0.95593	1.42925	47.45	0.00057
	T = 318.15 K		
0.04957	1.36218	17.92	0.00800
0.10050	1.37308	19.57	0.01057
0.15027	1.38186	21.21	0.01217
0.20070	1.38862	22.85	0.01247
0.29948	1.39777	26.01	0.01085
0.39730	1.40574	29.24	0.01006
0.50181	1.41148	32.63	0.00802
0.59957	1.41604	35.83	0.00644
0.69728	1.41953	39.01	0.00464
0.77330	1.42199	41.50	0.00346
0.84521	1.42392	43.85	0.00229
0.89879	1.42518	45.60	0.00142
0.95593	1.42650	47.48	0.00062

Excess molar volumes and excess isentropic compressibilities for the three binary systems are reported in Tables 3 to 5, and deviations in refractive indices are reported in Tables 6 to 8. Given that the excess and derived properties are obtained as a difference between the actual and the ideal-mixture values and that both of them have the same uncertainty, the combined standard uncertainty of excess and derived properties will be 1.4 times that of the corresponding properties.

As pointed out earlier, molar refraction for all of the systems varies almost linearly with the mole fraction of IL, showing quasi-ideal behavior. Therefore, deviations in molar refraction ΔR are very small, and they are of the same order as their combined standard uncertainty or larger. For this reason, values

Table 7. Refractive Index n_D, Molar Refraction R, and Deviation of the Refractive Index Δn_D for the Binary System [emim][triflate] (1) + Methyl Acetate (2) at T = (288.15 to 318.15) K

x_1	n_D	$\frac{10^6 R}{m^3 \cdot mol^{-1}}$	Δn_D
	T = 288.15 K		
0.05083	1.37625	19.22	0.00422
0.09991	1.38561	20.80	0.00684
0.15153	1.39328	22.42	0.00821
0.19981	1.39836	23.89	0.00802
0.29968	1.40796	27.02	0.00822
0.40030	1.41462	30.14	0.00705
0.49575	1.42026	33.15	0.00642
0.59503	1.42444	36.23	0.00502
0.69617	1.42797	39.36	0.00364
0.79544	1.43089	42.44	0.00236
0.83850	1.43234	43.81	0.00215
0.89772	1.43347	45.63	0.00114
0.94660	1.43451	47.16	0.00052
	T = 298.15 K		
0.05083	1.37116	19.23	0.00425
0.09991	1.38057	20.79	0.00672
0.15153	1.38873	22.43	0.00838
0.19981	1.39419	23.90	0.00840
0.29968	1.40429	27.04	0.00877
0.40030	1.41120	30.16	0.00756
0.49575	1.41695	33.17	0.00681
0.59503	1.42123	36.24	0.00527
0.69617	1.42488	39.38	0.00382
0.79544	1.42794	42.46	0.00249
0.83850	1.42944	43.83	0.00227
0.89772	1.43061	45.65	0.00121
0.94660	1.43170	47.18	0.00056
	T = 308.15 K		
0.05083	1.36710	19.29	0.00513
0.09991	1.37793	20.90	0.00884
0.15153	1.38548	22.50	0.00972
0.19981	1.39098	23.97	0.00962
0.29968	1.40087	27.08	0.00949
0.40030	1.40804	30.20	0.00828
0.49575	1.41367	33.19	0.00717
0.59503	1.41831	36.28	0.00579
0.69617	1.42201	39.41	0.00418
0.79544	1.42510	42.49	0.00272
0.83850	1.42649	43.85	0.00231
0.89772	1.42771	45.67	0.00121
0.94660	1.42890	47.20	0.00060
	T = 318.15 K		
0.05083	1.36334	19.37	0.00659
0.09991	1.37521	21.02	0.01114
0.15153	1.38291	22.61	0.01197
0.19981	1.38871	24.08	0.01199
0.29968	1.39857	27.18	0.01149
0.40030	1.40487	30.23	0.00909
0.49575	1.41049	33.21	0.00772
0.59503	1.41533	36.31	0.00630
0.69617	1.41907	39.44	0.00451
0.79544	1.42226	42.52	0.00296
0.83850	1.42364	43.87	0.00247
0.89772	1.42488	45.69	0.00128
0.94660	1.42618	47.23	0.00069

of deviations in molar refraction have not been reported in Tables 6 to 8.

In a general form, we designate all of the excess and derived properties (V_m^E, κ_S^E, and Δn_D) as δQ. For each system δQ was correlated with the IL mole fraction, x_1, by means of an extended version[30] of the Redlich–Kister[31] equation

$$\delta Q = x_1(1 - x_1)\frac{\sum_{i=0}^{m} A_i(2x_1 - 1)^i}{1 + \sum_{j=1}^{n} B_j(2x_1 - 1)^j} \qquad (15)$$

This Padé (m, n) expression permits a great number of possible fits because the number of adjustable coefficients in each polynomial term can be different, with $k = m + n + 1$ being the total number of them.

Table 8. Refractive Index n_D, Molar Refraction R, and Deviation of the Refractive Index Δn_D for the Binary System [emim][triflate] (1) + Ethyl Acetate (2) at T = (288.15 to 328.15) K

x_1	n_D	$\frac{10^6 R}{m^3 \cdot mol^{-1}}$	Δn_D
	T = 288.15 K		
0.04887	1.38327	23.61	0.00275
0.15027	1.39622	26.34	0.00592
0.20040	1.40093	27.66	0.00634
0.29981	1.40907	30.30	0.00688
0.39902	1.41507	32.90	0.00627
0.50055	1.42038	35.60	0.00565
0.59768	1.42469	38.19	0.00493
0.69743	1.42874	40.88	0.00438
0.79615	1.43118	43.45	0.00273
0.84738	1.43242	44.79	0.00201
0.90108	1.43367	46.21	0.00132
0.94911	1.43467	47.49	0.00066
	T = 298.15 K		
0.04887	1.37802	23.61	0.00257
0.15027	1.39151	26.34	0.00594
0.20040	1.39666	27.67	0.00664
0.29981	1.40499	30.30	0.00707
0.39902	1.41144	32.92	0.00664
0.50055	1.41682	35.61	0.00584
0.59768	1.42133	38.20	0.00510
0.69743	1.42566	40.90	0.00462
0.79615	1.42823	43.47	0.00292
0.84738	1.42950	44.82	0.00213
0.90108	1.43075	46.23	0.00134
0.94911	1.43182	47.51	0.00067
	T = 308.15 K		
0.04887	1.37297	23.63	0.00268
0.15027	1.38810	26.43	0.00733
0.20040	1.39440	27.82	0.00903
0.29981	1.40234	30.40	0.00876
0.39902	1.40854	32.99	0.00779
0.50055	1.41415	35.68	0.00695
0.59768	1.41860	38.26	0.00592
0.69743	1.42254	40.92	0.00484
0.79615	1.42528	43.50	0.00310
0.84738	1.42662	44.84	0.00228
0.90108	1.42792	46.26	0.00143
0.94911	1.42903	47.53	0.00072
	T = 318.15 K		
0.04887	1.36910	23.72	0.00403
0.15027	1.38476	26.52	0.00885
0.20040	1.39170	27.93	0.01101
0.29981	1.39937	30.48	0.01016
0.39902	1.40604	33.08	0.00938
0.50055	1.41137	35.74	0.00798
0.59768	1.41549	38.29	0.00639
0.69743	1.41963	40.95	0.00526
0.79615	1.42239	43.52	0.00333
0.84738	1.42376	44.86	0.00244
0.90108	1.42471	46.24	0.00114
0.94911	1.42624	47.55	0.00076
	T = 328.15 K		
0.04887	1.36310	23.69	0.00335
0.15027	1.38129	26.61	0.01034
0.20040	1.38772	27.98	0.01181
0.29981	1.39558	30.51	0.01082
0.39902	1.40310	33.15	0.01059
0.50055	1.40906	35.84	0.00955
0.59768	1.41251	38.32	0.00702
0.69743	1.41671	40.98	0.00571
0.79615	1.41954	43.55	0.00363
0.84738	1.42094	44.89	0.00266
0.90108	1.42195	46.27	0.00131
0.94911	1.42352	47.58	0.00087

By taking into account the influence of temperature on the excess properties, all of the coefficients A_i and B_j for each system have been expressed as a second-order polynomial on T

$$A_i = A_{i_0} + A_{i_1}(T - 273.15) + A_{i_2}(T - 273.15)^2 \tag{16}$$

$$B_j = B_{j_0} + B_{j_1}(T - 273.15) + B_{j_2}(T - 273.15)^2 \tag{17}$$

In this way, the number of coefficients is reduced because the total number of parameters for each binary system will be $(3 \cdot k)$ and not $(t \cdot k)$, where t is the number of different temperatures tested for every system. So, from eqs 15 to 17, we will use the following expression to simultaneously correlate the excess properties with the temperature T and the IL mole fraction x_1

$$\delta Q = x_1(1 - x_1) \times \frac{\sum_{i=0}^{m} [A_{i_0} + A_{i_1}(T - 273.15) + A_{i_2}(T - 273.15)^2](2x_1 - 1)^i}{1 + \sum_{j=1}^{n} [B_{j_0} + B_{j_1}(T - 273.15) + B_{j_2}(T - 273.15)^2](2x_1 - 1)^j} \tag{18}$$

The fitting parameters were estimated by the least-squares method, and the values obtained are given in Tables 9, 10, and 11, together with the standard deviations calculated by applying the expression

$$\sigma = \left[\frac{\sum_{i=1}^{p} (\delta Q_{\text{exptl},i} - \delta Q_{\text{calcd},i})^2}{p - 3(m + n + 1)}\right]^{1/2} \tag{19}$$

in which p is the number of experimental data points. The choice of m and n values for the degrees of polynomics in eq 18 was made using the Akaike's Information Criterion (AIC).[32] Figures 1, 2, and 3 show, respectively, the experimental values of V_m^E, κ_S^E, and Δn_D versus the IL mole fraction at all of the temperatures tested together with the curves obtained from eq 18 using the fitting parameters, for every binary system.

The behavior of the three systems (IL + acetone, IL + methyl acetate, and IL + ethyl acetate) is regular and very similar. V_m^E and κ_S^E are always negative, and Δn_D is always positive in the whole range of compositions and temperatures. The excess molar volume V_m^E stack decreases, that is, it becomes more negative, when the temperature increases as seen in Figure 1. The fitting curves are asymmetric, and they present a minimum at low values of the IL mole fraction, which becomes less negative in the order of acetone > methyl acetate ≥ ethyl acetate. The same V_m^E behavior for mixtures of these three solvents with [hmim][PF$_6$] was reported by Pereiro et al.[33]

Table 9. Coefficients of the Fitting Equation (eq 18) for Excess Molar Volumes (V_m^E/m$^3\cdot$mol^{-1}) and the Standard Deviations (σ) of the [emim][triflate] (1) + Acetone (2), + Methyl Acetate (2), and + Ethyl Acetate (2) Mixtures

	$Z_{l,0}$	$Z_{l,1}$	$Z_{l,2}$	$10^6\ \sigma$ / m$^3\cdot$mol^{-1}
		[emim][triflate] (1) + Acetone (2)		
$Z = A, l = 0$	$-6.234\cdot10^{-6}$	$-4.648\cdot10^{-8}$	$-3.805\cdot10^{-10}$	0.031
$Z = A, l = 1$	$-2.299\cdot10^{-7}$	$-4.387\cdot10^{-9}$	$-1.271\cdot10^{-10}$	
$Z = A, l = 2$	$-8.552\cdot10^{-7}$	$5.254\cdot10^{-9}$	$2.186\cdot10^{-11}$	
$Z = A, l = 3$				
$Z = B, l = 1$	$6.409\cdot10^{-1}$	$1.565\cdot10^{-3}$	$-1.214\cdot10^{-6}$	
$Z = B, l = 2$				
		[emim][triflate] (1) + Methyl Acetate (2)		
$Z = A, l = 0$	$-5.244\cdot10^{-6}$	$-4.116\cdot10^{-8}$	$-4.060\cdot10^{-10}$	0.030
$Z = A, l = 1$	$2.996\cdot10^{-6}$	$3.220\cdot10^{-8}$	$2.664\cdot10^{-10}$	
$Z = A, l = 2$	$-3.040\cdot10^{-6}$	$-2.024\cdot10^{-8}$	$-1.874\cdot10^{-10}$	
$Z = A, l = 3$				
$Z = B, l = 1$				
$Z = B, l = 2$				
		[emim][triflate] (1) + Ethyl Acetate (2)		
$Z = A, l = 0$	$-5.417\cdot10^{-6}$	$-4.470\cdot10^{-8}$	$-4.314\cdot10^{-10}$	0.012
$Z = A, l = 1$	$4.842\cdot10^{-6}$	$3.462\cdot10^{-8}$	$6.226\cdot10^{-10}$	
$Z = A, l = 2$	$-2.585\cdot10^{-6}$	$-1.588\cdot10^{-8}$	$-1.525\cdot10^{-10}$	
$Z = A, l = 3$				
$Z = B, l = 1$	$-4.471\cdot10^{-1}$	$1.107\cdot10^{-3}$	$-2.857\cdot10^{-5}$	
$Z = B, l = 2$				

Table 10. Coefficients of the Fitting Equation (eq 18) for Excess Isentropic Compressibility (κ_S^E/TPa^{-1}) and the Standard Deviations (σ) of the [emim][triflate] (1) + Acetone (2), + Methyl Acetate (2), and + Ethyl Acetate (2) Mixtures

	$Z_{l,0}$	$Z_{l,1}$	$Z_{l,2}$	σ / TPa^{-1}
		[emim][triflate] (1) + Acetone (2)		
$Z = A, l = 0$	$-2.665\cdot10^{2}$	$-4.382\cdot10^{0}$	$-6.708\cdot10^{-2}$	0.63
$Z = A, l = 1$	$5.428\cdot10^{-2}$	$-1.519\cdot10^{0}$	$1.186\cdot10^{-1}$	
$Z = A, l = 2$	$9.273\cdot10^{-2}$	$1.261\cdot10^{0}$	$-4.554\cdot10^{-2}$	
$Z = A, l = 3$				
$Z = B, l = 1$	$1.049\cdot10^{0}$	$-5.693\cdot10^{-4}$	$-1.311\cdot10^{-4}$	
$Z = B, l = 2$	$2.087\cdot10^{-1}$	$2.684\cdot10^{-3}$	$-1.528\cdot10^{-4}$	
		[emim][triflate] (1) + Methyl Acetate (2)		
$Z = A, l = 0$	$-1.959\cdot10^{2}$	$-3.223\cdot10^{0}$	$-6.089\cdot10^{-2}$	0.34
$Z = A, l = 1$	$2.374\cdot10^{1}$	$1.768\cdot10^{0}$	$-1.238\cdot10^{-2}$	
$Z = A, l = 2$	$-2.870\cdot10^{1}$	$-1.641\cdot10^{0}$	$4.769\cdot10^{-3}$	
$Z = A, l = 3$				
$Z = B, l = 1$	$8.288\cdot10^{-1}$	$-4.697\cdot10^{-3}$	$8.657\cdot10^{-5}$	
$Z = B, l = 2$	$2.862\cdot10^{-1}$	$-1.494\cdot10^{-3}$	$3.205\cdot10^{-5}$	
		[emim][triflate] (1) + Ethyl Acetate (2)		
$Z = A, l = 0$	$-2.016\cdot10^{2}$	$-3.395\cdot10^{0}$	$-6.746\cdot10^{-2}$	0.52
$Z = A, l = 1$	$-1.879\cdot10^{2}$	$-3.248\cdot10^{0}$	$-6.249\cdot10^{-2}$	
$Z = A, l = 2$	$-1.946\cdot10^{2}$	$-6.269\cdot10^{0}$	$1.191\cdot10^{-4}$	
$Z = A, l = 3$	$1.200\cdot10^{2}$	$2.614\cdot10^{0}$	$1.244\cdot10^{-2}$	
$Z = B, l = 1$	$1.638\cdot10^{0}$	$2.859\cdot10^{-5}$	$6.632\cdot10^{-6}$	
$Z = B, l = 2$	$1.731\cdot10^{0}$	$4.211\cdot10^{-3}$	$-9.336\cdot10^{-5}$	

Table 11. Coefficients of the Fitting Equation (eq 18) for Deviations in Refractive Index (Δn_D) and the Standard Deviations (σ) of the [emim][triflate] (1) + Acetone (2), + Methyl Acetate (2), and + Ethyl Acetate (2) Mixtures

	$Z_{l,0}$	$Z_{l,1}$	$Z_{l,2}$	$10^3\ \sigma$
		[emim][triflate] (1) + Acetone (2)		
$Z = A, l = 0$	$2.551\cdot10^{-2}$	$7.841\cdot10^{-5}$	$1.726\cdot10^{-6}$	0.16
$Z = A, l = 1$	$-6.126\cdot10^{-3}$	$-1.103\cdot10^{-4}$	$1.768\cdot10^{-6}$	
$Z = A, l = 2$				
$Z = A, l = 3$				
$Z = B, l = 1$	$8.245\cdot10^{-1}$	$-7.607\cdot10^{-3}$	$1.823\cdot10^{-4}$	
$Z = B, l = 2$				
		[emim][triflate] (1) + Methyl Acetate (2)		
$Z = A, l = 0$	$2.436\cdot10^{-2}$	$-3.133\cdot10^{-5}$	$4.343\cdot10^{-6}$	0.31
$Z = A, l = 1$	$-7.880\cdot10^{-3}$	$2.607\cdot10^{-4}$	$-7.405\cdot10^{-6}$	
$Z = A, l = 2$				
$Z = A, l = 3$				
$Z = B, l = 1$	$8.135\cdot10^{-1}$	$-6.068\cdot10^{-3}$	$1.347\cdot10^{-4}$	
$Z = B, l = 2$				
		[emim][triflate] (1) + Ethyl Acetate (2)		
$Z = A, l = 0$	$2.122\cdot10^{-2}$	$6.490\cdot10^{-5}$	$4.182\cdot10^{-6}$	0.45
$Z = A, l = 1$	$4.308\cdot10^{-3}$	$-1.603\cdot10^{-4}$	$-3.802\cdot10^{-6}$	
$Z = A, l = 2$				
$Z = A, l = 3$				
$Z = B, l = 1$	$6.955\cdot10^{-1}$	$-1.365\cdot10^{-3}$	$-2.643\cdot10^{-5}$	
$Z = B, l = 2$				

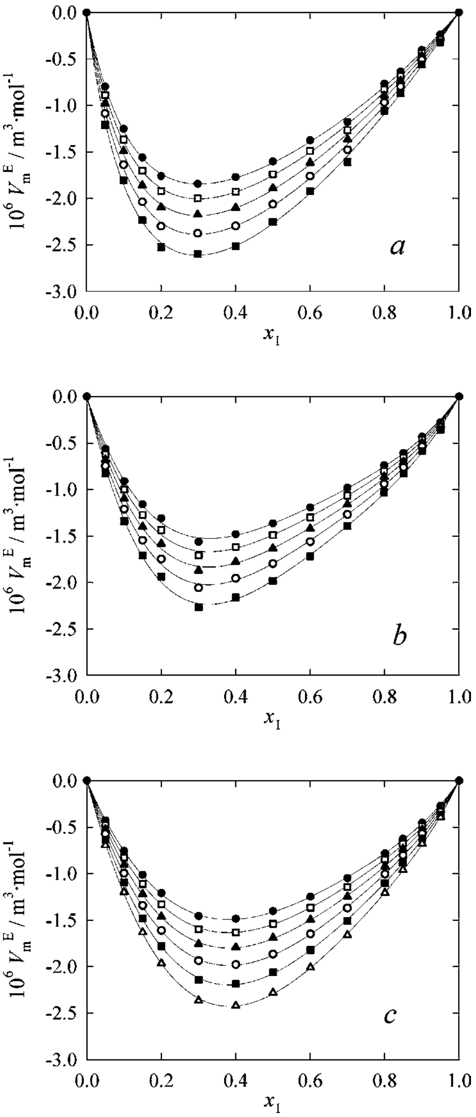

Figure 1. Excess molar volume V_m^E for the [emim][triflate] (1) + solvent (2) binary systems at different temperatures: ●, 278.15 K; □, 288.15 K; ▲, 298.15 K; ○, 308.15 K; ■, 318.15 K; △, 328.15 K. The solid lines represent the corresponding correlation by an extended version of the Redlich−Kister equation (eq 18). Solvent: (a) acetone, (b) methyl acetate, and (c) ethyl acetate.

The V_m^E behavior of [emim][triflate] + solvent systems can be predicted and correlated using the Prigogine−Flory−Patterson (PFP) theory, which has been widely used to analyze the excess thermodynamic properties for different kinds of mixtures. Zafarani-Moattar and Shekaari,[34] Domanska et al.,[35,36] Vercher et al.,[9] Kumar et al.,[37−39] and Qi and Wang[40] have applied the PFP theory to correlate the excess molar volumes of IL + solvent systems. The PFP theory considers the V_m^E of binary mixtures to be the sum of three contributions:[41] (i) the interactional contribution, which is proportional to the only interaction parameter, χ_{21}; (ii) the free volume contribution, which arises from the dependence of the reduced volume upon the reduced temperature as a result of the difference between the degree of expansion of the two components; and (iii) the internal pressure contribution, which depends both on the differences of internal pressures and on the differences of reduced volumes of the components and can be related to the structure-breaking effect of the IL on the solvent molecules. In the present study, the following form of the PFP theory has been used to estimate V_m^E values:

$$\frac{V_m^E}{x_1V_1^* + x_2V_2^*} = \frac{V_m^E(\text{int})}{x_1V_1^* + x_2V_2^*} + \frac{V_m^E(\text{fv})}{x_1V_1^* + x_2V_2^*} + \frac{V_m^E(\text{ip})}{x_1V_1^* + x_2V_2^*} = \frac{(\tilde{V}^{1/3} - 1)\tilde{V}^{2/3}\Psi_2\theta_1\chi_{21}}{((4/3)\tilde{V}^{-1/3} - 1)P_2^*} - \frac{(\tilde{V}_1 - \tilde{V}_2)^2((14/9)\tilde{V}^{-1/3} - 1)\Psi_1\Psi_2}{((4/3)\tilde{V}^{-1/3} - 1)\tilde{V}} + \frac{(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)\Psi_1\Psi_2}{P_2^*\Psi_1 + P_1^*\Psi_2} \qquad (20)$$

where $\tilde{V}_i$ and $\tilde{V}$ are the reduced volume of pure components and mixtures, respectively, V_i^* is the characteristic volume,

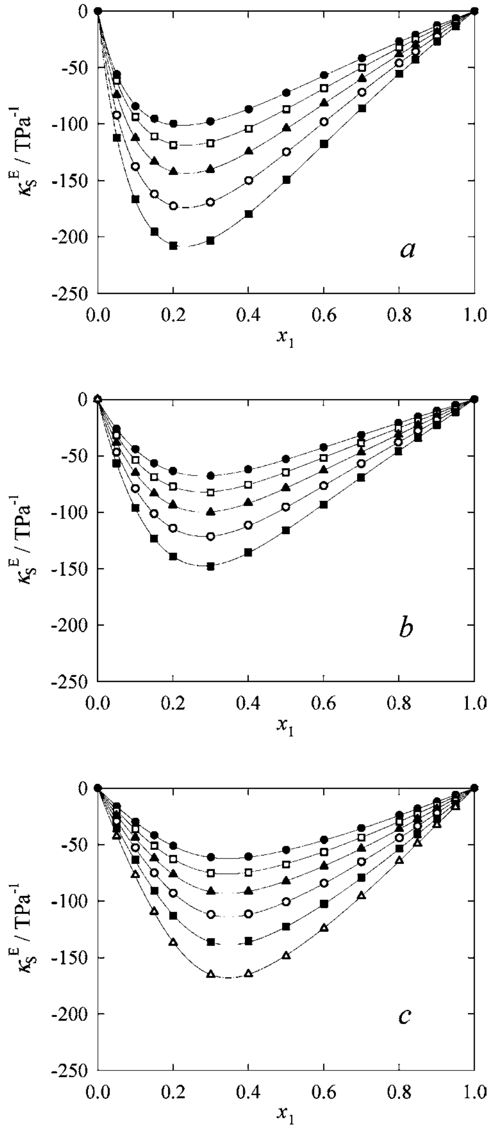

Figure 2. Excess isentropic compressibility κ_S^E for the [emim][triflate] (1) + solvent (2) binary systems at different temperatures: ●, 278.15 K; □, 288.15 K; ▲, 298.15 K; ○, 308.15 K; ■, 318.15 K; △, 328.15 K. The solid lines represent the corresponding correlation by an extended version of the Redlich−Kister equation (eq 18). Solvent: (a) acetone, (b) methyl acetate, and (c) ethyl acetate.

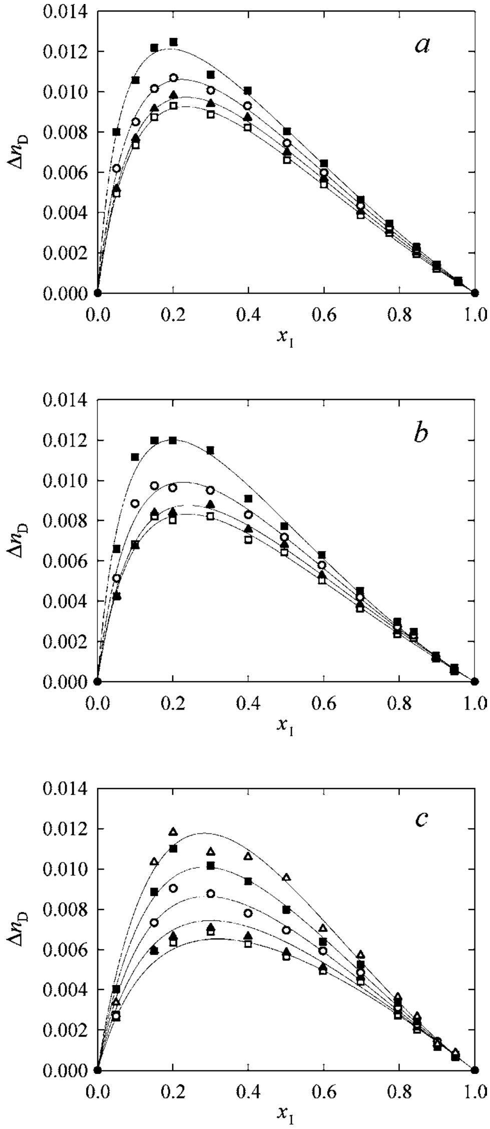

Figure 3. Deviations in refractive index Δn_D for the [emim][triflate] (1) + solvent (2) binary systems at different temperatures: □, 288.15 K; ▲, 298.15 K; ○, 308.15 K; ■, 318.15 K; △, 328.15 K. The solid lines represent the corresponding correlation by an extended version of the Redlich−Kister equation (eq 18). Solvent: (a) acetone, (b) methyl acetate, and (c) ethyl acetate.

and P_i^* is the characteristic pressure of pure components. In eq 20, Ψ_i is the molecular contact energy fraction. All of these quantities can be deduced from the molar volumes V_i^o, isobaric heat capacities $C_{P,i}^o$, isobaric thermal expansivity $\alpha_{P,i}^o$, and isentropic compressibility $\kappa_{S,i}^o$ values of pure components reported in Table 2, using Flory's formalisms given elsewhere,[9,34,41] and they are listed in Table 12.

The molecular surface fraction of the IL, θ_1, can be calculated from the molecular surface/volume ratio, S_i, of the components. The S values for acetone, methyl acetate, and ethyl acetate were determined by dividing the van der Waals area by the van der Waals volume of the molecules obtained from the UNIQUAC structure parameters, r and q, reported by Gmehling and Onken.[42] For the [emim][triflate] we have used the value deduced in an earlier work.[9]

The interactional parameter χ_{21} was evaluated, fitting the experimental V_m^E values to eq 20 and using the least-squares method over the whole composition range for each system and temperature. The interactional parameter χ_{21} thus obtained represents the intermolecular interaction between components of mixtures, and its value was listed at different temperatures in Table 13, as well as the three PFP contributions to excess molar volume, the PFP calculated from those, and the experimental value of the excess molar volume, at $x_1 = 0.30$, for the three [emim][triflate] (1) + solvent (2) systems. To do the comparison, we have selected a mole fraction of $x_1 = 0.30$ because the V_m^E curves of all of these systems present minimum values near this composition. A perusal of Table 13 reveals that, for the [emim][triflate] + solvent systems, the cross-interaction parameter χ_{21} is negative for all of the systems, suggesting a relative strong intermolecular specific interaction, which decreases with temperature, when mixtures are created. Free volume also contributes negatively to the V_m^E(PFP) values, decreasing when temperature increases with a thermal effect more pronounced than that of interactional contribution. It is also clear from Table 13 that the contribution due to internal pressure, V_m^E(ip), does not seem to play a dominant role in deciding the sign and magnitude of the excess molar volume because it is positive for the three systems at lower temperatures and decreases when the temperature increases, becoming negative for the acetone and ethyl acetate. This behavior is opposite to one observed in [emim][triflate] + alcohol mixtures,[9] in which the IL had a strong effect on breaking the molecular structure of alcohols. Even though the PFP theory leads to a one-parameter model, the agreement between experimental and calculated values of molar volume is good, with standard deviations in the

Table 12. Characteristic Parameters for Pure Acetone, Methyl Acetate, Ethyl Acetate, and [emim][triflate] at Several Temperatures, Used in PFP Theory Calculations

T / K	$\tilde{V}$	$10^6\ V^*$ / $\mathrm{m^3 \cdot mol^{-1}}$	P^* / MPa	S / $\mathrm{nm^{-1}}$
		Acetone		
278.15	1.305	55.112	599.33	14.96[a]
288.15	1.320	55.280	595.60	14.96[a]
298.15	1.335	55.435	591.77	14.96[a]
308.15	1.351	55.580	587.09	14.96[a]
318.15	1.369	55.715	583.35	14.96[a]
		Methyl Acetate		
278.15	1.298	59.885	653.52	15.14[a]
288.15	1.313	60.010	651.93	15.14[a]
298.15	1.329	60.136	649.43	15.14[a]
308.15	1.345	60.265	645.76	15.14[a]
318.15	1.363	60.398	641.06	15.14[a]
		Ethyl Acetate		
278.15	1.290	74.368	608.05	14.76[a]
288.15	1.304	74.541	604.14	14.76[a]
298.15	1.319	74.717	599.75	14.76[a]
308.15	1.334	74.897	594.68	14.76[a]
318.15	1.349	75.085	588.84	14.76[a]
328.15	1.366	75.282	582.40	14.76[a]
		[emim][triflate][b]		
278.15	1.152	161.34	594.10	10.43
288.15	1.157	161.63	598.73	10.43
298.15	1.162	161.94	602.77	10.43
308.15	1.166	162.26	605.75	10.43
318.15	1.171	162.61	607.81	10.43
328.15	1.175	162.98	608.75	10.43
338.15	1.180	163.37	608.78	10.43

[a] Estimated from ref 42. [b] From ref 9.

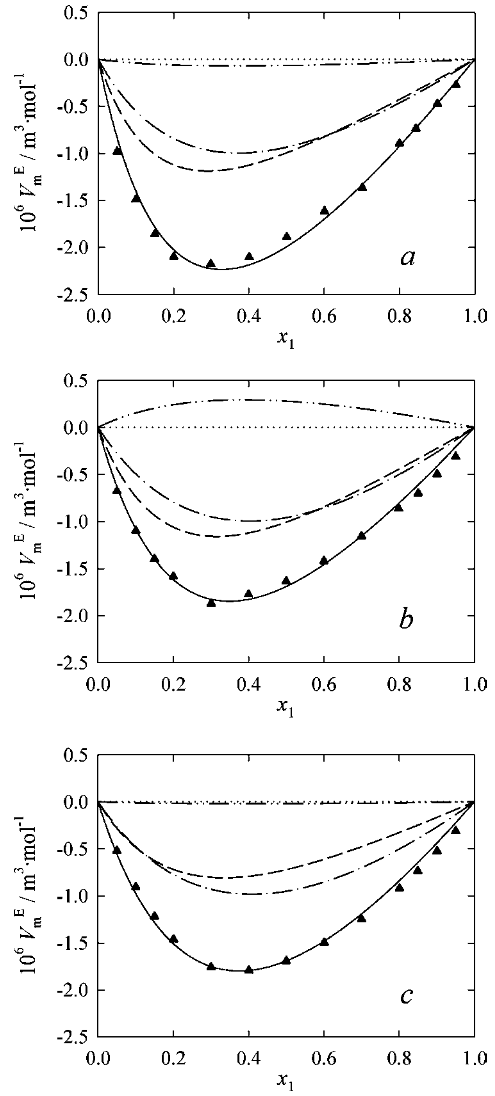

Figure 4. Excess molar volume V_m^E for the [emim][triflate] (1) + solvent (2) binary systems at T = 298.15 K calculated with the PFP theory: dashed line, interactional contribution; dotted−dashed line, free volume contribution; dotted−dotted−dashed line, internal pressure contribution; solid line, total excess molar volume predicted by PFP theory; ▲, experimental value. Solvent: (a) acetone, (b) methyl acetate, and (c) ethyl acetate.

range of (6 to 10)·10^{-8} $m^3 \cdot mol^{-1}$, as seen in Figure 4, where the three excess molar volume contributions and the total predicted value, together with the experimental values at T = 298.15 K, are shown for the [emim][triflate] (1) + solvent (2).

The behavior of the excess isentropic compressibility κ_S^E for the (IL + solvent) is very similar to that of the V_m^E one as shown in Figure 2. It is also negative in the whole range of temperatures and compositions, and it becomes more negative when temperature increases. The (mixture IL + acetone) presents the greatest absolute deviations and the (IL + ethyl acetate) system the smallest ones, but rather very close to (IL + methyl acetate).

Finally, the behavior of the deviation in the refractive index is always positive in the whole range of compositions and temperatures, and it becomes greater when temperature increases as seen in Figure 3. The fitting curves are very asymmetric, and they present a maximum at low values of the IL mole fraction. Both the magnitude and the asymmetry of the maximum are in the order of acetone > methyl acetate > ethyl acetate.

Conclusions

Excess molar volume V_m^E, excess isentropic compressibility κ_S^E, and deviations on refractive index Δn_D values of [emim][triflate] in acetone, methyl acetate, and ethyl acetate mixtures have been calculated from the measured density, speed of sound, and refractive index data at T = (278.15 to 338.15) K in the whole range of concentrations. For every system, the excess and derived properties were fitted by an extended Padé version of the Redlich−Kister equation, giving in all cases asymmetric curves. The Redlich−Kister parameters were fitted to second-order polynomials on T, to reduce their number. For all of the systems, V_m^E and κ_S^E are always negative, and they increase when temperature decreases. The behavior of Δn_D for these systems is the opposite: it is always positive, and it increases when temperature increases. For all of the systems, the effect follows the order of acetone > methyl acetate ≥ ethyl acetate.

The PFP theory has a good performance in predicting excess molar volumes of mixtures of [emim][triflate] with solvents, despite using only one fitting parameter. The analysis of relative

Table 13. Values of the PFP Interaction Parameter, χ_{21}, Interactional, V_m^E(int), Free Volume, V_m^E(fv), and Internal Pressure, V_m^E(ip), Contributions of Excess Molar Volume, and PFP Calculated, V_m^E(PFP), and Experimental, V_m^E(exptl), Excess Molar Volumes at x_1 = 0.30

T		10^6 V_m^E(int)	10^6 V_m^E(fv)	10^6 V_m^E(ip)	10^6 V_m^E(PFP)	10^6 V_m^E(exptl)
K	χ_{21}	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$
			[emim][triflate] (1) + Acetone (2)			
278.15	−120.24	−1.147	−0.764	0.029	−1.882	−1.845
288.15	−116.04	−1.168	−0.859	−0.018	−2.045	−2.001
298.15	−111.63	−1.186	−0.972	−0.069	−2.227	−2.177
308.15	−107.11	−1.205	−1.105	−0.125	−2.435	−2.378
318.15	−103.13	−1.229	−1.262	−0.176	−2.668	−2.602
			[emim][triflate] (1) + Methyl Acetate (2)			
278.15	−115.84	−1.113	−0.727	0.314	−1.527	−1.564
288.15	−111.67	−1.136	−0.830	0.300	−1.666	−1.708
298.15	−107.55	−1.158	−0.949	0.282	−1.826	−1.872
308.15	−103.37	−1.181	−1.086	0.259	−2.008	−2.059
318.15	−99.09	−1.202	−1.244	0.232	−2.214	−2.270
			[emim][triflate] (1) + Ethyl Acetate (2)			
278.15	−73.72	−0.816	−0.765	0.085	−1.497	−1.492
288.15	−69.00	−0.805	−0.866	0.035	−1.637	−1.633
298.15	−64.40	−0.792	−0.982	−0.021	−1.795	−1.798
308.15	−59.93	−0.778	−1.114	−0.082	−1.973	−1.986
318.15	−55.51	−0.760	−1.264	−0.150	−2.175	−2.195
328.15	−51.03	−0.739	−1.434	−0.224	−2.397	−2.426

contributions suggests a relative strong intermolecular specific interaction IL-solvent that decreases when temperature increases. Free volume also contributes negatively to the V_m^E(PFP) values, decreasing when temperature increases with a thermal effect more pronounced than that of interactional contribution. Likewise, the internal pressure contribution does not seem to play a dominant role in deciding the sign and magnitude of the excess molar volume.

Literature Cited

(1) Brennecke, J. F.; Maginn, E. J. Ionic Liquids: Innovative Fluids for Chemical Processing. *AIChE J.* **2001**, *47*, 2384–2389.

(2) Heintz, A. Recent developments in thermodynamics and thermophysics of non-aqueous mixtures containing ionic liquids. A review. *J. Chem. Thermodyn.* **2005**, *37*, 525–535.

(3) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. Room temperature ionic liquids as novel media for 'clean' liquid-liquid extraction. *Chem. Commun.* **1998**, 1765−1766.

(4) Seiler, M.; Jork, C.; Kavarnou, A.; Arlt, W.; Hirsch, R. Separation of Azeotropic Mixtures Using Hyperbranched Polymers or Ionic Liquids. *AIChE J.* **2004**, *50*, 2439–2454.

(5) Orchillés, A. V.; Miguel, P. J.; Vercher, E.; Martínez-Andreu, A. Ionic Liquids as Entrainers in Extractive Distillation: Isobaric Vapor-Liquid Equilibria for Acetone + Methanol + 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate. *J. Chem. Eng. Data* **2007**, *52*, 141–147.

(6) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem.* **2001**, *3*, 156–164.

(7) IUPAC Ionic Liquid Database (IL Thermo). NIST Standard Reference Database #147. http://ilthermo.boulder.nist.gov/ILThermo/mainmenu.uix (accessed July 1, 2009).

(8) Rodríguez, H.; Brennecke, J. F. Temperature and Composition Dependence of the Density and Viscosity of Binary Mixtures of Water + Ionic Liquid. *J. Chem. Eng. Data* **2006**, *51*, 2145−2155.

(9) Vercher, E.; Orchillés, A. V.; Miguel, P. J.; Martínez-Andreu, A. Volumetric and Ultrasonic Studies of 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate Ionic Liquid with Methanol, Ethanol, 1-Propanol, and Water at Several Temperatures. *J. Chem. Eng. Data* **2007**, *52*, 1468–1482.

(10) García-Miaja, G.; Troncoso, J.; Romaní, L. Excess enthalpy, density, and heat capacity for binary systems of alkylimidazolium-based ionic liquids + water. *J. Chem. Thermodyn.* **2009**, *41*, 161–166.

(11) García-Miaja, G.; Troncoso, J.; Romaní, L. Excess properties for binary systems ionic liquid + ethanol: Experimental results and theoretical description using the ERAS model. *Fluid Phase Equilib.* **2008**, *274*, 59–67.

(12) García-Miaja, G.; Troncoso, J.; Romaní, L. Excess molar properties for binary systems of alkylimidazolium-based ionic liquids + nitromethane. Experimental results and ERAS-model calculations. *J. Chem. Thermodyn.* **2009**, *41*, 334–341.

(13) Arce, A.; Rodríguez, H.; Soto, A. Effect of anion fluorination in 1-ethyl-3-methylimidazolium as solvent for the liquid extraction of ethanol from ethyl tert-butyl ether. *Fluid Phase Equilib.* **2006**, *242*, 164–168.

(14) *NIST/TRC Table Database (Win Table). NIST Standard Reference Database 85*; Thermodynamic Research Center, Physical and Chemical Properties Division: Boulder, CO, 2004.

(15) Casás, L. M.; Marino, G.; Iglesias, M.; Orge, B.; Tojo, J.; Mosteiro, L. Excess molar volumes, and changes of isentropic compressibilities of ternary {acetone + methanol + (2-methyl-1-propanol, or 3-methyl-1-butanol)} at $T = 298.15$ K. *J. Chem. Thermodyn.* **2001**, *33*, 1777–1789.

(16) Savaroglu, G.; Aral, E. Ultrasonic velocity and isentropic compressibilities of the ternary mixture benzene + acetone + chloroform and their corresponding binary mixtures at 298.15 K. *J. Mol. Liq.* **2003**, *105*, 79–92.

(17) Acosta, J.; Arce, A.; Rodil, E.; Soto, A. Densities, Speeds of Sound, Refractive Indices, and the Corresponding Changes of Mixing at 25 °C and Atmospheric Pressure for Systems Composed by Ethyl Acetate, Hexane, and Acetone. *J. Chem. Eng. Data* **2001**, *46*, 1176–1180.

(18) Govindarajan, S.; Kannappan, V.; Naresh, M. D.; Venkataboopathy, K.; Lokanadam, B. Ultrasonic studies on the molecular interaction of gallic acid in aqueous methanol and acetone solutions and the role of gallic acid as viscosity reducer. *J. Mol. Liq.* **2003**, *107*, 289–316.

(19) Daubert, T. E.; Danner, R. P.; Sibul, H. M.; Stebbins, C. C. *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation. DIPPR/AIChE*; Taylor & Francis: Washington, DC, 1998.

(20) Sakurai, M.; Nakamura, K.; Nitta, N.; Takenaka, N.; Mukae, K. Partial Molar Isentropic Compressions of Alkyl Acetates in Water. *J. Chem. Eng. Data* **1998**, *43*, 249–254.

(21) Sastry, N. V.; Patel, M. C. Densities, Excess Molar Volumes, Viscosities, Speeds of Sound, Excess Isentropic Compressibilities, and Relative Permittivities for Alkyl (Methyl, Ethyl, Butyl, and Isoamyl) Acetates + Glycols at Different Temperatures. *J. Chem. Eng. Data* **2003**, *48*, 1019–1027.

(22) González, B.; Domínguez, A.; Tojo, J. Dynamic Viscosities, Densities, and Speed of Sound and Derived Properties of the Binary Systems Acetic Acid with Water, Methanol, Ethanol, Ethyl Acetate and Methyl Acetate at $T = (293.15, 298.15, \text{and } 303.15)$ K at Atmospheric Pressure. *J. Chem. Eng. Data* **2004**, *49*, 1590–1596.

(23) Oswal, S. L.; Oswal, P.; Modi, P. S.; Dave, J. P.; Gardas, R. L. Acoustic, volumetric, compressibility and refractivity properties and Flory's reduction parameters of some homologous series of alkyl alkanoates from 298.15 to 333.15 K. *Thermochim. Acta* **2004**, *410*, 1–14.

(24) Resa, J. M.; Goenaga, J. M.; Lanz, J.; Iglesias, M. Vapor-Liquid Equilibrium of Binary Mixtures Containing Ethyl Acetate + 2-Methyl-1-propanol and Ethyl Acetate + 2-Methyl-1-butanol at 101.3 kPa. *J. Chem. Eng. Data* **2006**, *51*, 595–598.

(25) Pereiro, A. B.; Rodríguez, A. Thermodynamic Properties of Ionic Liquids in Organic Solvents from (293.15 to 303.15) K. *J. Chem. Eng. Data* **2007**, *52*, 600–608.

(26) Diedrichs, A.; Gmehling, J. Measurement of heat capacities of ionic liquids by differential scanning calorimetry. *Fluid Phase Equilib.* **2006**, *244*, 68–77.

(27) Douhéret, G.; Davis, M. I.; Reis, J. C. R.; Blandamer, M. J. Isentropic compressibilities-Experimental origin and the quest for their rigorous estimation in thermodynamically ideal liquid mixtures. *ChemPhysChem* **2001**, *2*, 148–161.

(28) Iglesias-Otero, M. A.; Troncoso, J.; Carballo, E.; Romaní, L. Density and refractive index in mixtures of ionic liquids and organic solvents: Correlations and predictions. *J. Chem. Thermodyn.* **2008**, *40*, 949–956.

(29) Brocos, P.; Piñeiro, A.; Bravo, R.; Amigo, A. Refractive indices, molar volumes and molar refractions of binary liquid mixtures: concepts and correlations. *Phys. Chem. Chem. Phys.* **2003**, *5*, 550–557.

(30) Heintz, A.; Klasen, D.; Lehmann, J. K.; Wertz, C. Excess Molar Volumes and Liquid-Liquid Equilibria of the Ionic Liquid 1-Methyl-3-Octyl-Imidazolium Tetrafluoroborate Mixed with Butan-1-ol and Pentan-1-ol. *J. Solution Chem.* **2005**, *34*, 1135–1144.

(31) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.

(32) Motulsky, H. J.; Christopoulos, A. *Fitting models to biological data using linear and nonlinear regression. A practical guide to curve fitting*. GraphPad Software Inc.: San Diego, CA, 2003. http://www.graphpad.com.

(33) Pereiro, A. B.; Tojo, E.; Rodríguez, A.; Canosa, J.; Tojo, J. Properties of ionic liquid HMIMPF6 with carbonates, ketones and alkyl acetates. *J. Chem. Thermodyn.* **2006**, *38*, 651–661.

(34) Zafarani-Moattar, M. T.; Shekaari, H. Application of Prigogine-Flory-Patterson theory to excess molar volume and speed of sound of 1-*n*-butyl-3-methylimidazolium hexafluorophosphate or 1-*n*-butyl-3-methylimidazolium tetrafluoroborate in methanol and acetonitrile. *J. Chem. Thermodyn.* **2006**, *38*, 1377–1384.

(35) Domanska, U.; Pobudkowska, A.; Wisniewska, A. Solubility and Excess Molar Properties of 1,3-Dimethylimidazolium Methylsulfate, or 1-Butyl-3-Methylimidazolium Methylsulfate, or 1-Butyl-3-Methylimidazolium Octylsulfate Ionic Liquids with *n*-Alkanes and Alcohols: Analysis in Terms of the PFP and FBT Models. *J. Solution Chem.* **2006**, *35*, 311–334.

(36) Domanska, U.; Laskowska, M. Phase Equilibria and Volumetric Properties of (1-Ethyl-3-Methylimidazolium Ethylsulfate + Alcohol or Water) Binary Systems. *J. Solution Chem.* **2008**, *37*, 1271–1287.

(37) Kumar, A.; Singh, T.; Gardas, R. L.; Coutinho, J. A. P. Non ideal behaviour of a room temperature ionic liquid in an aloxyethanol or poly ethers at $T = (298.15 \text{ to } 318.15)$ K. *J. Chem. Thermodyn.* **2008**, *40*, 32–39.

(38) Singh, T.; Kumar, A. Physical and excess properties of a room temperature ionic liquid (1-methyl-3-octylimidazolium tetrafluoroborate) with *n*-alkoxyethanols (C_1E_m, $m = 1$ to 3) at $T = (298.15 \text{ to } 318.15)$ K. *J. Chem. Thermodyn.* **2008**, *40*, 417–423.

(39) Singh, T.; Kumar, A.; Kaur, M.; Kaur, G.; Kumar, H. Non-ideal behaviour of imidazolium based room temperature ionic liquids in

ethylene glycol at T = (298.15 to 318.15) K. *J. Chem. Thermodyn.* **2009**, *41*, 717–723.

(40) Qi, F.; Wang, H. Application of Prigogine-Flory-Patterson theory to excess molar volume of mixtures of 1-butyl-3-methylimidazolium ionic liquids with N-methyl-2-pyrrolidinone. *J. Chem. Thermodyn.* **2009**, *41*, 265–272.

(41) Tôrres, R. B.; Francesconi, A. Z.; Volpe, P. L. O. Thermodynamics of binary liquid mixtures: application of the Prigogine-Flory-Patterson theory to excess molar volumes of acetonitrile + 1-alkanol systems. *J. Mol. Liq.* **2004**, *110*, 81–85.

(42) Gmehling, J.; Onken, U. *Vapor-Liquid Equilibrium Data Collection. DECHEMA Chemistry Data Series*; DECHEMA:, Frankfurt/Main, Germany, 1977; Vol. I, Part 1.

Received for review July 3, 2009. Accepted July 30, 2009. This research was supported by the Ministry of Education and Science of Spain and FEDER funds of the European Union, through project no. CTQ2007-60831/PPQ.

JE9005618