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Volumetric and Ultrasonic Studies of 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate Ionic Liquid with Methanol, Ethanol, 1-Propanol, and Water at Several Temperatures

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The speed of sound and density of mixtures of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim]-[triflate]) with methanol, ethanol, 1-propanol, and water, as well as of the pure components have been experimentally measured over the whole range of compositions at $T = (278.15 \text{ to } 338.15)$ K and atmospheric pressure. From these experimental data, the excess molar volume, excess isentropic compressibility, and excess speed of sound 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 also been used to explain the behavior of these systems.

Introduction

Room-temperature ionic liquids (ILs) are salts with very low melting points (mainly below 100 °C). Typically, ionic liquids comprise an organic greatly asymmetric substituted cation (imidazolium, pyridinium, pyrrolidinium, quaternary ammonium, tetraalkylphosphonium, etc.) and an inorganic weak anion (hexafluorophosphate, tetrafluoroborate, trifluoromethanesulfonate, halide, nitrate, acetate, alkylsulfate, etc.). 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 a liquidus range of 300 °C; are outstandingly good solvents for a wide range of inorganic, organic, and polymeric materials; exhibit Brönsted, Lewis, and Franklin acidity as well as superacidity; have no effective vapor pressure; and are thermally stable up to 200 °C.[2] They are often used as a “green” solvent replacing volatile organic solvents, catalysts for organic and organometallic synthesis,[3−5] extraction media for separation processes,[6] and entrainers for extractive distillation.[7−10] Applications as lubricants, thermofluids, plasticizers, and electrically conductive liquids in electrochemistry have also been reported.[2]

Despite their interest and importance, the physicochemical properties of ionic liquids have not been systematically studied, and the detailed knowledge on the thermodynamic behavior of the mixtures of ionic liquids with molecular solvents, which is important for the design of any technological processes, is very limited. Specifically, experimental data of density and speed of sound of a binary mixture are important not only to design and control chemical processes but also from the theoretical point of view to predict the properties and characteristics of ILs.[6]

As far as we know, very few publications[11−18] about the density and excess volume of IL + solvent systems have been published prior to the year 2006. From then, the number of works[19−33] has been doubled, thus showing the interest of the scientific community toward this topic. In practically all the reported cases, the IL is made of a 1-alkyl-3-methylimidazolium[11,13−33] cation and a tetrafluoroborate,[11−15,17,19,21,22] hexafluorophosphate,[16,18,21,26,29,31,33] or alkylsulfate[20,25,27,28,31,33] anion. The solvents more used in the mixture with the IL are water,[11,14,15,20,22,27,28,32] *n*-alcohols,[12,17−21,23−25,27,30,31] 2-cetones,[13,16,26,33] acetonitrile,[13,18,21] and esters.[16,26,33]

In the present work, we report the volumetric and acoustical properties of the 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]) + methanol, + ethanol, + 1-propanol, and + water systems over the whole range of compositions at temperatures from (278.15 to 338.15) K. The values of the excess molar volume, excess isentropic compressibility, and excess speed of sound were then calculated from the measured density and speed of sound data and fitted to polynomial equations. This IL has been previously used by us as an entrainer for the extractive distillation of acetone + methanol[9] and methyl acetate + methanol[10] azeotropic systems.

To our knowledge, no experimental density or speed of sound measurements have been reported in the literature for the [emim][triflate] + *n*-alcohol systems. However, Rodríguez and Brennecke[28] have reported densities and excess molar volumes for the [emim][triflate] + water system, at $T = (278.15 \text{ to } 348.15)$ K.

Experimental Section

Materials. The ionic liquid used was 1-ethyl-3-methylimidazolium trifluoromethanesulfonate supplied by Solvent Innovation (Purum, minimum mass fraction 98 %). Because of its hygroscopic character, it was desiccated at 0.2 Pa overnight prior to use. The water mass fraction in the IL determined by Karl Fisher titration was $x_w < 0.05$ %. Its density at 298.15 K agrees well with that reported in the literature[28] as showed in Table 1. The solvents used were dried methanol (Riedel-de Haën, Analytical Reagent, minimum mass fraction 99.8 %), absolute ethanol (Merck, GR grade, minimum mass fraction 99.9 %), 1-propanol (Merck, GR grade, minimum mass fraction 99.5 %), and water (Merck, HPLC grade, residue on evaporating <

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

	ρ/kg·m^{-3}		u/m·s^{-1}	
component	exptl	lit.	exptl	lit.
[emim][triflate]	1383.58	1383.60^{a}	1435.6	–
methanol	786.49	786.49^{b}	1102.3	1102.53^{b}
ethanol	785.10	785.07^{b}	1142.9	1143.22^{b}
1-propanol	799.56	799.51^{c}	1205.4	1205.69^{d}
water	997.06	997.043^{e}	1497.1	1497.00^{f}

[a] Ref 28. [b] Ref 34. [c] Ref 35. [d] Ref 36. [e] Ref 37. [f] Ref 38.

5 g·m^{-3}). These alcohols were degassed ultrasonically and dried over molecular sieves of type 3 Å supplied by Grace, and they were used without further purification. The purities of the solvents were ascertained by GC, their densities and speeds of sound at 298.15 K giving a reasonable agreement with the corresponding literature values,[34−38] 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 to ensure a secure seal and to prevent evaporation. The uncertainty in mole fractions was estimated to be less than 0.0001 for all the samples except the IL + water mixtures with an IL mole fraction higher than 0.80, in which the uncertainty can become as high as 0.0002.

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 accuracy of 0.001 K. This analyzer automatically corrects the influence of viscosity on the measured density. The apparatus was calibrated at 298.15 K with bidistilled water and dry air. Standard uncertainties of measurements were estimated to be less than 0.007 kg·m^{-3} for density and 0.05 m·s^{-1} for speed of sound.

Results and Discussion

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

$$V_{\mathrm{m}} = \frac{M_{\mathrm{m}}}{\rho} \tag{1}$$

where $M_m = (x_1M_1^\circ + x_2M_2^\circ)$, 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

$$\kappa_{\mathrm{S}} = -\frac{1}{V_{\mathrm{m}}}\left(\frac{\partial V_{\mathrm{m}}}{\partial P}\right)_{\mathrm{S}} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_{\mathrm{S}} \tag{2}$$

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

$$\kappa_{\mathrm{S}} = \frac{1}{\rho \cdot u^2} = \frac{M_{\mathrm{m}}}{V_{\mathrm{m}} \cdot u^2} \tag{3}$$

The combined standard uncertainty for molar volume was estimated to be less than 0.005 cm^3·mol^{-1}, although for mixtures with an IL mole fraction higher than 0.80 the combined uncertainty can become as high as (0.010, 0.012, 0.018, and 0.030) cm^3·mol^{-1} when the solvent is 1-propanol, ethanol, methanol, and water, respectively. This higher uncertainty for the IL-concentrated mixtures can be due to the uncertainty in mole fraction of the mixture when the molar mass of components is very different. For the isentropic compressibility, the combined standard uncertainty was estimated to be less than 0.05 TPa^{-1}.

Volumetric Properties of Pure Liquids. The experimental data for the density ρ and speed of sound u of methanol at T = (278.15 to 318.15) K, ethanol at T = (278.15 to 328.15) K, and 1-propanol, water, and [emim][triflate] at T = (278.15 to

Table 2. Density ρ, Molar Volume V_m, Speed of Sound u, Isentropic Compressibility κ_S, Isobaric Molar Heat Capacity C_P, and Isobaric Thermal Expansivity α_P of Pure Methanol, Ethanol, 1-Propanol, Water, and [emim][triflate] at Several Temperatures

T/K	ρ/kg·m^{-3}	V_m/cm^3·mol^{-1}	u/m·s^{-1}	κ_S/TPa^{-1}	C_P/J·mol^{-1}·K^{-1}	α_P/kK^{-1}	T/K	ρ/kg·m^{-3}	V_m/cm^3·mol^{-1}	u/m·s^{-1}	κ_S/TPa^{-1}	C_P/J·mol^{-1}·K^{-1}	α_P/kK^{-1}
Methanol													
278.15	805.25	39.791	1169.50	907.97	77.61^{a}	1.162	308.15	777.02	41.237	1069.78	1124.55	83.24^{a}	1.224
288.15	795.89	40.259	1135.49	974.50	79.30^{a}	1.178	318.15	767.45	41.751	1037.71	1210.04	85.49^{a}	1.256
298.15	786.49	40.741	1102.29	1046.45	81.17^{a}	1.199							
Ethanol													
278.15	802.14	57.433	1212.52	847.96	105.32^{a}	1.055	308.15	776.44	59.333	1109.16	1046.89	116.38^{a}	1.124
288.15	793.65	58.047	1177.69	908.46	108.66^{a}	1.072	318.15	767.63	60.014	1075.80	1125.60	120.79^{a}	1.160
298.15	785.10	58.679	1142.88	975.15	112.34^{a}	1.095	328.15	758.62	60.727	1042.79	1212.22	125.59^{a}	1.202
1-Propanol													
278.15	815.45	73.697	1275.27	754.05	134.47^{a}	0.967	318.15	783.19	76.732	1137.83	986.23	156.04^{a}	1.068
288.15	807.54	74.418	1239.86	805.54	139.27^{a}	0.983	328.15	774.72	77.572	1104.40	1058.29	162.41^{a}	1.110
298.15	799.56	75.161	1205.37	860.81	144.47^{a}	1.005	338.15	765.98	78.456	1070.97	1138.23	169.18^{a}	1.159
308.15	791.46	75.931	1171.41	920.78	150.05^{a}	1.033							
Water													
278.15	999.99	18.016	1426.58	491.37	75.93^{a}	0.0160^{c}	318.15	990.22	18.194	1536.76	427.62	75.24^{a}	0.4225^{c}
288.15	999.12	18.032	1466.49	465.40	75.60^{a}	0.1509^{c}	328.15	985.70	18.277	1547.57	423.60	75.27^{a}	0.4910^{c}
298.15	997.06	18.069	1497.11	447.48	75.38^{a}	0.2572^{c}	338.15	980.56	18.373	1553.13	422.78	75.36^{a}	0.5539^{c}
308.15	994.05	18.124	1520.16	435.33	75.27^{a}	0.3457^{c}							
[emim][triflate]													
278.15	1400.51	185.818	1482.23	325.00	364.14^{b}	0.6078	318.15	1366.86	190.393	1391.29	377.96	385.55^{b}	0.6075
288.15	1392.02	186.951	1458.35	337.78	370.05^{b}	0.6082	328.15	1358.59	191.552	1369.65	392.37	390.09^{b}	0.6065
298.15	1383.58	188.092	1435.56	350.71	375.57^{b}	0.6084	338.15	1350.38	192.716	1348.51	407.23	394.36^{b}	0.6051
308.15	1375.19	189.239	1413.16	364.13	380.72^{b}	0.6081							

[a] From ref 39. [b] From ref 40. [c] From ref 41.

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

x_1	ρ / kg·m^{-3}	V_m^E / cm^3·mol^{-1}	u / m·s^{-1}	u^E / m·s^{-1}	κ_S / TPa^{-1}	κ_S^E / TPa^{-1}	x_1	ρ / kg·m^{-3}	V_m^E / cm^3·mol^{-1}	u / m·s^{-1}	u^E / m·s^{-1}	κ_S / TPa^{-1}	κ_S^E / TPa^{-1}
						T = 278.15 K							
0.0505	930.38	−0.336	1216.34	52.35	726.49	−72.50	0.6012	1330.42	−0.378	1432.72	63.87	366.18	−36.16
0.1005	1018.16	−0.473	1253.28	78.68	625.30	−92.81	0.6994	1353.20	−0.298	1447.85	47.31	352.53	−25.01
0.1502	1084.09	−0.548	1284.95	93.21	558.68	−96.63	0.7965	1371.53	−0.216	1460.58	31.32	341.78	−15.64
0.1999	1135.25	−0.574	1312.52	100.89	511.32	−93.73	0.8443	1379.25	−0.161	1466.36	23.84	337.19	−11.58
0.3005	1210.76	−0.573	1356.49	102.43	448.86	−79.94	0.8984	1387.51	−0.131	1472.01	15.08	332.62	−7.18
0.4007	1262.73	−0.514	1388.69	93.46	410.66	−63.88	0.9489	1394.45	−0.092	1477.51	7.74	328.50	−3.64
0.4926	1298.36	−0.467	1411.35	80.86	386.67	−50.26							
						T = 288.15 K							
0.0505	921.13	−0.367	1185.98	55.43	771.84	−84.12	0.6012	1321.68	−0.406	1409.11	68.97	381.05	−41.57
0.1005	1008.98	−0.516	1225.28	83.79	660.16	−107.68	0.6994	1344.52	−0.318	1424.43	51.44	366.56	−28.86
0.1502	1074.98	−0.598	1258.61	99.70	587.24	−112.09	0.7965	1362.92	−0.228	1437.19	34.31	355.22	−18.13
0.1999	1126.21	−0.626	1287.07	107.96	536.02	−108.45	0.8443	1370.67	−0.170	1442.97	26.24	350.39	−13.48
0.3005	1201.81	−0.622	1332.02	109.74	468.97	−92.13	0.8984	1378.95	−0.137	1448.67	16.87	345.55	−8.47
0.4007	1253.87	−0.557	1364.73	100.38	428.21	−73.52	0.9489	1385.93	−0.096	1453.96	8.70	341.31	−4.30
0.4926	1289.56	−0.504	1387.66	87.11	402.71	−57.81							
						T = 298.15 K							
0.0505	911.87	−0.401	1156.48	58.62	819.96	−97.55	0.6012	1313.03	−0.439	1386.04	73.93	396.44	−47.44
0.1005	999.81	−0.564	1197.97	88.90	696.93	−124.56	0.6994	1335.93	−0.343	1401.54	55.34	381.07	−32.96
0.1502	1065.90	−0.653	1232.80	106.06	617.30	−129.43	0.7965	1354.37	−0.246	1414.37	37.01	369.09	−20.71
0.1999	1117.20	−0.683	1262.10	114.89	561.93	−124.87	0.8443	1362.15	−0.183	1420.23	28.38	363.96	−15.42
0.3005	1192.91	−0.677	1307.97	116.88	490.00	−105.63	0.8984	1370.46	−0.146	1425.92	18.28	358.87	−9.69
0.4007	1245.07	−0.607	1341.25	107.18	446.47	−84.15	0.9489	1377.46	−0.100	1431.14	9.36	354.45	−4.88
0.4926	1280.83	−0.547	1364.43	93.18	419.38	−66.07							
						T = 308.15 K							
0.0505	902.59	−0.439	1127.52	61.78	871.49	−112.84	0.6012	1304.44	−0.479	1363.41	79.15	412.40	−54.12
0.1005	990.64	−0.617	1171.25	94.11	735.85	−143.87	0.6994	1327.40	−0.373	1379.13	59.53	396.09	−37.66
0.1502	1056.83	−0.713	1207.40	112.42	649.07	−149.07	0.7965	1345.89	−0.266	1391.99	39.91	383.46	−23.65
0.1999	1108.22	−0.746	1237.54	121.88	589.19	−143.48	0.8443	1353.69	−0.199	1398.03	30.80	377.96	−17.69
0.3005	1184.06	−0.739	1284.33	124.17	512.00	−120.92	0.8984	1362.03	−0.157	1403.71	19.92	372.61	−11.15
0.4007	1236.32	−0.662	1318.17	114.18	465.51	−96.18	0.9489	1369.05	−0.106	1408.80	10.15	368.03	−5.58
0.4926	1272.16	−0.595	1341.66	99.55	436.69	−75.47							
						T = 318.15 K							
0.0505	893.26	−0.482	1099.19	65.21	926.56	−130.90	0.6012	1295.91	−0.524	1341.24	84.71	428.96	−61.75
0.1005	981.42	−0.674	1144.83	99.33	777.43	−165.96	0.6994	1318.93	−0.408	1357.34	64.14	411.53	−43.10
0.1502	1047.74	−0.778	1182.47	119.01	682.60	−171.71	0.7965	1337.48	−0.290	1370.14	43.06	398.28	−27.04
0.1999	1099.25	−0.817	1213.45	129.15	617.82	−164.88	0.8443	1345.30	−0.217	1376.24	33.29	392.46	−20.23
0.3005	1175.24	−0.807	1261.19	131.85	534.95	−138.49	.8984	53.66	−0.169	1381.97	21.64	386.81	−12.79
0.4007	1227.62	−0.725	1295.51	121.52	485.35	−109.93	0.9489	1360.70	−0.112	1386.98	11.00	382.03	−6.37
0.4926	1263.55	−0.651	1319.40	106.33	454.63	−86.25							

338.15) K, together with the molar volume V_m and the isentropic compressibility κ_S, are given in Table 2. For all the components, the density decreases and the molar volume increases as temperature increases. With regard to the speed of sound, its value decreases for [emim][triflate] and the alcohols and increases for water when the temperature increases. In consequence, the isentropic compressibility of [emim][triflate] and the alcohols increases with the temperature, whereas that of water decreases as the temperature increases into the tested temperature range.

In Table 2, we have also reported the isobaric molar heat capacity C_P values of pure components at the same temperatures obtained from empirical equations. For the alcohols and water, we have used those proposed in the Daubert and Danner data compilation,[39] and for [emim][triflate], we used that proposed by Diedrichs and Gmehling.[40]

As will be seen later, the isobaric thermal expansivity α_P of pure components is needed for calculating the excess properties of component mixtures. The isobaric thermal expansivity α_P is defined as

$$\alpha_P = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \qquad (4)$$

For water, we have taken isobaric thermal expansivity values reported by Kell,[41] and they are shown in Table 2. For [emim][triflate] and the alcohols and from an empirical perspective, third-order polynomials were found to satisfactorily correlate the change of density with temperature for each component. From them and using eq 4, we obtained the isobaric thermal expansivity of these components at each temperature reported in Table 2. As far as alcohols and [emim][triflate] are concerned, our isobaric thermal expansivity values at 298.15 K and those reported in the literature[28,42,43] agree within 0.1%.

Apart from that, the variation of isobaric thermal expansivity for [emim][triflate] has the same behavior as that reported by Rebelo et al.[14] and Rodríguez and Brennecke,[28] who stated that isobaric thermal expansivity of ILs remains constant or decreases slowly with temperature. The uncertainty associated with this magnitude hinders us in being more precise.

Volumetric Properties of Liquid Mixtures. The experimental data for the density, ρ, and speed of sound, u, for the [emim]-[triflate] (1) + methanol (2), + ethanol (2), + 1-propanol (2), and + water (2) binary mixtures together with the isentropic compressibility, κ_S, determined by means of the Laplace equation (eq 3) are given in Tables 3 to 6 at several temperatures. As can be seen, the density of all the mixtures always

Table 4. Density ρ, Excess Molar Volume V_m^E, Speed of Sound u, Excess Speed of Sound u^E, Isentropic Compressibility κ_S, and Excess Isentropic Compressibility κ_S^E for the Binary System [emim][triflate] (1) + Ethanol (2) at T = (278.15 to 328.15) K

	ρ	V_m^E	u	u^E	κ_S	κ_S^E		ρ	V_m^E	u	u^E	κ_S	κ_S^E
x_1	kg·m^{-3}	cm^3·mol^{-1}	m·s^{-1}	m·s^{-1}	TPa^{-1}	TPa^{-1}	x_1	kg·m^{-3}	cm^3·mol^{-1}	m·s^{-1}	m·s^{-1}	TPa^{-1}	TPa^{-1}
							T = 278.15 K						
0.0499	802.14	−0.263	1212.52	29.57	847.96	−39.86	0.5932	1264.18	−0.367	1394.83	63.43	406.58	−37.99
0.1000	892.80	−0.378	1232.96	47.60	736.79	−57.02	0.6928	1299.43	−0.300	1416.18	49.87	383.72	−27.50
0.1503	965.56	−0.439	1252.69	60.44	659.99	−65.20	0.8020	1331.10	−0.201	1435.87	32.80	364.38	−16.69
0.1999	1025.77	−0.474	1273.50	69.91	601.11	−68.69	0.8517	1359.80	−0.158	1454.20	24.82	347.76	−12.22
0.3009	1075.78	−0.502	1294.55	79.65	554.68	−66.57	0.9017	1371.25	−0.127	1461.89	16.39	341.24	−7.86
0.4001	1156.45	−0.463	1333.90	79.84	485.99	−58.42	0.9492	1382.03	−0.077	1468.98	8.83	335.31	−4.13
0.5015	1216.18	−0.416	1366.81	73.29	440.13	−47.90							
							T = 288.15 K						
0.0499	793.65	−0.288	1177.69	31.78	908.46	−46.89	0.5932	1255.54	−0.400	1370.61	68.83	423.98	−43.95
0.1000	884.25	−0.415	1201.13	51.46	783.87	−67.19	0.6928	1290.81	−0.325	1392.43	54.31	399.57	−31.84
0.1503	956.95	−0.482	1223.08	65.53	698.56	−76.76	0.8020	1322.51	−0.216	1412.31	35.96	379.09	−19.39
0.1999	1017.12	−0.521	1245.56	75.89	633.72	−80.72	0.8517	1351.24	−0.169	1430.73	27.19	361.54	−14.17
0.3009	1067.12	−0.550	1267.89	86.17	582.94	−77.60	0.9017	1362.70	−0.135	1438.29	18.16	354.74	−9.20
0.4001	1147.78	−0.508	1308.55	86.24	508.82	−67.75	0.9492	1373.50	−0.081	1445.46	9.79	348.46	−4.83
0.5015	1207.52	−0.455	1342.17	79.17	459.72	−55.36							
							T = 298.15 K						
0.0499	785.10	−0.316	1142.88	34.80	975.15	−56.23	0.5932	1246.96	−0.439	1346.92	74.44	442.04	−50.72
0.1000	875.66	−0.456	1170.11	56.05	834.09	−79.84	0.6928	1282.26	−0.355	1369.18	58.84	416.01	−36.68
0.1503	948.32	−0.531	1194.17	71.24	739.46	−90.74	0.8020	1313.99	−0.236	1389.28	39.06	394.30	−22.33
0.1999	1008.47	−0.573	1218.21	82.33	668.18	−94.93	0.8517	1342.74	−0.184	1407.84	29.56	375.75	−16.31
0.3009	1058.46	−0.606	1241.66	93.20	612.80	−90.54	0.9017	1354.22	−0.146	1415.44	19.80	368.58	−10.60
0.4001	1139.14	−0.560	1283.72	93.04	532.70	−78.55	0.9492	1365.03	−0.087	1422.67	10.58	361.95	−5.50
0.5015	1198.91	−0.501	1317.99	85.41	480.16	−63.94							
							T = 308.15 K						
0.0499	776.44	−0.348	1109.16	37.19	1046.89	−66.01	0.5932	1238.43	−0.486	1323.63	80.22	460.89	−58.36
0.1000	867.01	−0.503	1139.42	60.24	888.40	−93.79	0.6928	1273.76	−0.392	1346.39	63.58	433.08	−42.18
0.1503	939.65	−0.587	1165.70	76.71	783.18	−106.37	0.8020	1305.52	−0.261	1366.72	42.35	410.07	−25.67
0.1999	999.81	−0.634	1191.36	88.37	704.69	−110.62	0.8517	1334.31	−0.203	1385.42	32.12	390.46	−18.77
0.3009	1049.81	−0.669	1215.68	100.08	644.54	−104.99	0.9017	1345.80	−0.159	1393.07	21.66	382.89	−12.25
0.4001	1130.53	−0.621	1259.25	99.78	557.82	−90.61	0.9492	1356.63	−0.094	1400.42	11.55	375.86	−6.34
0.5015	1190.34	−0.555	1294.16	91.72	501.59	−73.57							
							T = 318.15 K						
0.0499	767.63	−0.384	1075.80	39.73	1125.60	−77.60	0.5932	1229.94	−0.540	1300.74	86.31	480.54	−67.12
0.1000	858.25	−0.558	1109.14	64.53	947.14	−110.03	0.6928	1265.32	−0.436	1323.94	68.67	450.88	−48.51
0.1503	930.92	−0.652	1137.53	82.24	830.16	−124.41	0.8020	1297.12	−0.290	1344.61	45.90	426.41	−29.52
0.1999	991.10	−0.704	1164.71	94.47	743.78	−128.66	0.8517	1325.93	−0.225	1363.47	34.84	405.68	−21.56
0.3009	1041.14	−0.743	1189.87	107.22	678.41	−121.66	0.9017	1337.44	−0.173	1371.13	23.68	397.71	−14.15
0.4001	1121.93	−0.691	1235.07	106.89	584.32	−104.55	0.9492	1348.27	−0.101	1378.68	12.58	390.21	−7.28
0.5015	1181.81	−0.619	1270.70	98.43	524.04	−84.69							
							T = 328.15 K						
0.0499	758.62	−0.428	1042.79	42.34	1212.22	−91.26	0.5932	1221.51	−0.605	1278.31	92.86	500.99	−77.28
0.1000	849.37	−0.622	1079.19	68.99	1010.90	−129.14	0.6928	1256.93	−0.484	1301.77	74.44	469.48	−56.03
0.1503	922.10	−0.728	1109.70	87.98	880.67	−145.54	0.8020	1288.75	−0.325	1323.04	50.08	443.29	−34.19
0.1999	982.34	−0.787	1138.38	100.82	785.53	−149.71	0.8517	1317.62	−0.252	1342.09	38.22	421.35	−25.05
0.3009	1032.44	−0.830	1164.35	114.74	714.45	−141.09	0.9017	1329.14	−0.191	1349.85	26.27	412.91	−16.59
0.4001	1113.33	−0.774	1211.21	114.54	612.26	−120.87	0.9492	1339.98	−0.112	1357.58	13.99	404.92	−8.55
0.5015	1173.30	−0.693	1247.65	105.78	547.53	−97.76							

increases with the IL mole fraction, x_1, and always decreases with temperature, T. It is worth noting that [emim][triflate] has a density higher than water and the alcohols at each temperature. The same behavior is observed for the speed of sound of the [emim][triflate] (1) + alcohol (2) binary systems. For the isentropic compressibility of the [emim][triflate] (1) + alcohol (2) binary systems, the behavior is also very regular but logically contrary to the last ones: it decreases with x_1 and increases with T.

For the [emim][triflate] (1) + water (2) binary system at 278.15 K, the speed of sound increases suddenly when x_1 increases. It starts from $u_2^\circ = 1426.6$ m·s^{-1} at $x_1 = 0$, reaches a maximum value $u \approx 1575$ m·s^{-1} at $x_1 \approx 0.10$, and then slowly decreases until $u_1^\circ = 1482.23$ m·s^{-1} at $x_1 = 1$. When the temperature increases, u_2° ($x_1 = 0$) increases and u_1° ($x_1 = 1$) decreases, the maximum dropping at smaller and smaller x_1 values. At $T = 338.15$ K, the maximum has practically disappeared, and the dependence of u on x_1 is always decreasing. The behavior of the speed of sound of the [emim][triflate] + water systems can be seen in Figure 1, in which we have not plotted the experimental points for clarity, and only four of the seven temperatures have been drawn.

The variation of the isentropic compressibility of the [emim][triflate] (1) + water (2) binary system is also as irregular as the speed of sound. It decreases suddenly when x_1 increases until reaching a minimum from which it slowly increases. This effect is more marked at 278.15 K because $\kappa_{S,2}^\circ$ ($x_1 = 0$) presents its largest value and $\kappa_{S,1}^\circ$ ($x_2 = 0$) presents its smaller one, whereas at 338.15 K, it is smoother, as seen in Figure 1 as well.

Excess Volumetric Properties of Liquid Mixtures. In a general form, if we designate V_m, u, or κ_S as Q, the excess property Q^E is defined as the difference between the actual value of Q and that corresponding for an ideal-mixture

Table 5. Density ρ, Excess Molar Volume V_m^E, Speed of Sound u, Excess Speed of Sound u^E, Isentropic Compressibility κ_S, and Excess Isentropic Compressibility κ_S^E for the Binary System [emim][triflate] (1) + 1-Propanol (2) at T = (278.15 to 338.15) K

x_1	ρ / $kg \cdot m^{-3}$	V_m^E / $cm^3 \cdot mol^{-1}$	u / $m \cdot s^{-1}$	u^E / $m \cdot s^{-1}$	κ_S / TPa^{-1}	κ_S^E / TPa^{-1}	x_1	ρ / $kg \cdot m^{-3}$	V_m^E / $cm^3 \cdot mol^{-1}$	u / $m \cdot s^{-1}$	u^E / $m \cdot s^{-1}$	κ_S / TPa^{-1}	κ_S^E / TPa^{-1}
T = 278.15 K													
0.0501	885.81	−0.149	1279.79	14.42	689.26	−17.12	0.6007	1280.35	−0.207	1412.25	45.31	391.60	−27.01
0.1001	946.17	−0.228	1286.31	23.45	638.76	−25.73	0.7000	1316.97	−0.166	1432.27	36.88	370.15	−20.25
0.1504	998.62	−0.237	1296.00	30.72	596.20	−30.94	0.7996	1348.61	−0.122	1450.34	26.12	352.51	−13.32
0.2004	1044.76	−0.255	1308.30	37.22	559.20	−34.80	0.8503	1363.09	−0.095	1459.01	20.07	344.64	−9.88
0.3002	1122.37	−0.279	1335.85	46.63	499.29	−38.17	0.8905	1373.86	−0.070	1465.75	15.13	338.79	−7.25
0.3993	1184.64	−0.278	1363.10	50.70	454.32	−36.93	0.9510	1389.10	−0.040	1475.06	6.96	330.86	−3.22
0.5010	1237.17	−0.245	1389.17	50.02	418.85	−32.73							
T = 288.15 K													
0.0501	877.77	−0.166	1247.29	16.46	732.30	−21.29	0.6007	1271.85	−0.235	1387.95	49.96	408.15	−31.78
0.1001	938.00	−0.254	1255.93	26.94	675.87	−32.05	0.7000	1308.46	−0.187	1408.42	40.87	385.28	−23.87
0.1504	990.36	−0.267	1267.29	35.31	628.71	−38.50	0.7996	1340.11	−0.137	1426.71	29.11	366.60	−15.75
0.2004	1036.43	−0.289	1280.69	42.40	588.27	−42.85	0.8503	1354.58	−0.106	1435.49	22.51	358.26	−11.74
0.3002	1113.94	−0.315	1309.80	52.44	523.27	−46.22	0.8905	1365.36	−0.078	1441.91	16.72	352.27	−8.47
0.3993	1176.17	−0.313	1337.94	56.49	474.96	−44.16	0.9510	1380.60	−0.043	1451.22	7.70	343.93	−3.76
0.5010	1228.67	−0.276	1364.56	55.40	437.10	−38.78							
T = 298.15 K													
0.0501	869.67	−0.186	1215.57	18.46	778.19	−26.04	0.6007	1263.40	−0.269	1364.32	54.62	425.23	−37.08
0.1001	929.80	−0.283	1226.27	30.39	715.22	−39.28	0.7000	1300.00	−0.214	1385.16	44.72	400.92	−27.79
0.1504	982.09	−0.302	1239.17	39.78	663.11	−47.04	0.7996	1331.65	−0.155	1403.79	31.99	381.07	−18.35
0.2004	1028.09	−0.328	1253.67	47.50	618.87	−51.95	0.8503	1346.12	−0.120	1412.66	24.77	372.25	−13.68
0.3002	1105.54	−0.357	1284.29	58.18	548.40	−55.25	0.8905	1356.91	−0.088	1418.96	18.27	366.02	−9.80
0.3993	1167.74	−0.356	1313.39	62.30	496.44	−52.29	0.9510	1372.15	−0.048	1428.32	8.38	357.23	−4.32
0.5010	1220.23	−0.315	1340.54	60.74	456.04	−45.52							
T = 308.15 K													
0.0501	861.50	−0.210	1184.31	20.48	827.59	−31.60	0.6007	1255.01	−0.311	1341.14	59.66	443.00	−43.26
0.1001	921.55	−0.319	1197.09	33.96	757.23	−47.81	0.7000	1291.61	−0.247	1362.34	48.90	417.15	−32.35
0.1504	973.78	−0.345	1211.40	44.30	699.78	−56.94	0.7996	1323.26	−0.179	1381.34	35.17	396.05	−21.41
0.2004	1019.75	−0.375	1227.00	52.71	651.36	−62.51	0.8503	1337.74	−0.138	1390.29	27.27	386.74	−15.96
0.3002	1097.15	−0.409	1259.12	64.10	574.91	−65.71	0.8905	1348.52	−0.102	1396.49	20.04	380.25	−11.38
0.3993	1159.35	−0.408	1289.20	68.36	518.97	−61.70	0.9510	1363.76	−0.055	1405.94	9.25	370.96	−5.04
0.5010	1211.84	−0.364	1316.90	66.39	475.83	−53.32							
T = 318.15 K													
0.0501	853.22	−0.239	1153.43	22.59	880.96	−38.21	0.6007	1246.67	−0.363	1318.36	65.03	461.51	−50.42
0.1001	913.23	−0.363	1168.11	37.50	802.52	−57.66	0.7000	1283.29	−0.290	1339.97	53.40	434.00	−37.65
0.1504	965.42	−0.397	1183.85	48.87	739.08	−68.44	0.7996	1314.94	−0.209	1359.35	38.59	411.56	−24.95
0.2004	1011.37	−0.433	1200.55	58.01	686.01	−74.75	0.8503	1329.41	−0.161	1368.23	29.81	401.81	−18.49
0.3002	1088.78	−0.473	1234.23	70.22	602.93	−77.85	0.8905	1340.19	−0.118	1374.46	21.92	394.97	−13.18
0.3993	1150.97	−0.472	1265.31	74.69	542.68	−72.60	0.9510	1355.43	−0.062	1384.01	10.13	385.16	−5.83
0.5010	1203.49	−0.424	1293.63	72.38	496.52	−62.37							
T = 328.15 K													
0.0501	844.80	−0.274	1122.65	24.72	939.20	−46.02	0.6007	1238.39	−0.428	1295.93	71.00	480.82	−58.93
0.1001	904.80	−0.417	1139.17	41.08	851.67	−69.23	0.7000	1275.01	−0.340	1317.93	58.43	451.55	−43.94
0.1504	956.99	−0.462	1156.49	53.69	781.28	−82.14	0.7996	1306.67	−0.245	1337.64	42.40	427.72	−29.12
0.2004	1002.94	−0.505	1174.29	63.62	723.06	−89.29	0.8503	1321.14	−0.188	1346.57	32.78	417.44	−21.56
0.3002	1080.39	−0.552	1209.53	76.74	632.68	−92.20	0.8905	1331.92	−0.138	1352.89	24.23	410.20	−15.42
0.3993	1142.62	−0.550	1241.71	81.54	567.62	−85.52	0.9510	1347.16	−0.072	1362.50	11.30	399.86	−6.87
0.5010	1195.18	−0.498	1270.71	78.97	518.17	−73.14							
T = 338.15 K													
0.0501	836.19	−0.319	1092.05	27.11	1002.79	−55.71	0.6007	1230.15	−0.504	1273.89	77.58	500.93	−69.03
0.1001	896.24	−0.484	1110.24	44.79	905.19	−83.03	0.7000	1266.78	−0.401	1296.24	63.94	469.82	−51.34
0.1504	948.48	−0.543	1129.26	58.81	826.77	−98.59	0.7996	1298.46	−0.288	1316.46	46.71	444.38	−34.11
0.2004	994.46	−0.593	1148.19	69.59	762.75	−106.69	0.8503	1312.91	−0.218	1325.31	36.03	433.64	−25.14
0.3002	1072.00	−0.650	1185.00	83.68	664.31	−109.24	0.8905	1323.72	−0.163	1331.71	26.72	425.98	−18.03
0.3993	1134.29	−0.646	1218.28	88.86	593.99	−100.76	0.9510	1338.96	−0.083	1341.44	12.57	415.04	−8.07
0.5010	1186.91	−0.588	1248.07	86.12	540.88	−85.87							

at the same thermodynamic state, Q^{id}

$$Q^E = Q - Q^{id} \tag{5}$$

Defining and calculating the properties of liquid ideal-mixtures is not always something straightforward. Whereas for ideal-mixture molar volume the definition is direct

$$V_m^{id} = x_1 \cdot V_1^{\circ} + x_2 \cdot V_2^{\circ} \tag{6}$$

where x_i is the mole fraction of component i and V_i° is the molar volume of pure component i at the mixture temperature and pressure, for the isentropic compressibility, on the other hand, that is not true. In a rigorous paper, Douhéret et al.[44] examined the different approaches used to calculate liquid ideal-mixture quantities and identified some common errors. They have stated that the thermodynamic ideal-mixing rule for the isentropic compressibility can be obtained correctly using the expression derived by Benson and Kiyohara[45]

$$\kappa_S{}^{id} = \phi_1 \kappa_{S,1}^{\circ} + \phi_2 \kappa_{S,2}^{\circ} + T\left[\frac{\phi_1 V_1^{\circ}(\alpha_{P,1}^{\circ})^2}{C_{P,1}^{\circ}} + \frac{\phi_2 V_2^{\circ}(\alpha_{P,2}^{\circ})^2}{C_{P,2}^{\circ}} - \frac{V_m^{id}(\alpha_P^{id})^2}{C_{P,m}^{id}}\right] \tag{7}$$

Table 6. Density ρ, Excess Molar Volume V_m^E, Speed of Sound u, Excess Speed of Sound u^E, Isentropic Compressibility κ_S, and Excess Isentropic Compressibility κ_S^E for the Binary System [emim][triflate] (1) + Water (2) at T = (278.15 to 338.15) K

x_1	ρ / $\mathrm{kg{\cdot}m^{-3}}$	V_m^E / $\mathrm{cm^3{\cdot}mol^{-1}}$	u / $\mathrm{m{\cdot}s^{-1}}$	u^E / $\mathrm{m{\cdot}s^{-1}}$	κ_S / $\mathrm{TPa^{-1}}$	κ_S^E / $\mathrm{TPa^{-1}}$	x_1	ρ / $\mathrm{kg{\cdot}m^{-3}}$	V_m^E / $\mathrm{cm^3{\cdot}mol^{-1}}$	u / $\mathrm{m{\cdot}s^{-1}}$	u^E / $\mathrm{m{\cdot}s^{-1}}$	κ_S / $\mathrm{TPa^{-1}}$	κ_S^E / $\mathrm{TPa^{-1}}$
T = 278.15 K													
0.0178	1065.40	−0.048	1510.49	99.62	411.39	−61.23	0.4976	1364.71	0.006	1510.68	59.52	321.08	−26.86
0.0502	1146.23	−0.116	1562.95	163.00	357.14	−89.96	0.5495	1370.64	0.030	1505.27	49.50	321.99	−22.17
0.1004	1218.92	−0.133	1575.03	175.06	330.71	−89.48	0.6039	1375.99	0.049	1500.77	40.63	322.67	−18.07
0.1501	1262.90	−0.149	1569.54	163.39	321.43	−80.42	0.6476	1379.90	0.049	1497.41	34.06	323.20	−15.09
0.2002	1292.15	−0.138	1559.57	145.74	318.18	−70.01	0.6996	1383.92	0.057	1493.96	27.11	323.75	−11.93
0.2507	1312.86	−0.106	1548.97	127.43	317.46	−60.14	0.7510	1387.36	0.071	1491.05	21.02	324.21	−9.18
0.2980	1327.87	−0.093	1539.76	111.43	317.64	−52.00	0.8496	1392.97	0.090	1486.62	11.20	324.83	−4.76
0.3498	1340.33	−0.055	1530.48	95.34	318.52	−43.99	0.8942	1395.40	0.070	1484.81	7.21	325.06	−3.04
0.4000	1350.21	−0.035	1522.78	81.67	319.39	−37.38	0.9498	1398.09	0.048	1482.92	2.80	325.26	−1.14
0.4498	1358.15	−0.007	1516.22	69.74	320.28	−31.66							
T = 288.15 K													
0.0178	1062.57	−0.028	1528.98	84.01	402.57	−48.77	0.4976	1356.19	0.073	1488.54	49.16	332.78	−22.86
0.0502	1140.95	−0.066	1563.67	137.61	358.46	−73.59	0.5495	1362.12	0.091	1483.02	40.88	333.80	−18.91
0.1004	1211.96	−0.061	1564.93	147.69	336.92	−74.60	0.6039	1367.47	0.103	1478.28	33.51	334.63	−15.40
0.1501	1255.19	−0.067	1554.13	137.17	329.85	−67.57	0.6476	1371.38	0.098	1474.81	28.10	335.25	−12.88
0.2002	1284.06	−0.052	1541.34	121.84	327.81	−59.08	0.6996	1375.40	0.099	1471.28	22.42	335.88	−10.23
0.2507	1304.57	−0.021	1529.19	106.19	327.80	−50.88	0.7510	1378.85	0.105	1468.21	17.41	336.44	−7.87
0.2980	1319.46	−0.009	1519.17	92.71	328.39	−44.12	0.8496	1384.47	0.112	1463.58	9.45	337.20	−4.16
0.3498	1331.85	0.026	1509.22	79.07	329.64	−37.33	0.8942	1386.90	0.084	1461.71	6.23	337.47	−2.73
0.4000	1341.71	0.041	1501.12	67.60	330.76	−31.75	0.9498	1389.61	0.055	1459.69	2.65	337.74	−1.13
0.4498	1349.63	0.064	1494.29	57.66	331.83	−26.92							
T = 298.15 K													
0.0178	1058.88	−0.011	1541.84	71.81	397.26	−40.00	0.4976	1347.68	0.131	1466.70	41.16	344.93	−19.74
0.0502	1135.19	−0.024	1561.14	117.44	361.45	−61.58	0.5495	1353.62	0.144	1461.07	34.19	346.07	−16.32
0.1004	1204.72	0.001	1552.87	125.88	344.23	−63.40	0.6039	1358.98	0.150	1456.21	28.00	347.01	−13.29
0.1501	1247.30	0.004	1537.62	116.45	339.10	−57.82	0.6476	1362.90	0.139	1452.67	23.45	347.70	−11.11
0.2002	1275.85	0.023	1522.51	103.08	338.13	−50.72	0.6996	1366.93	0.134	1449.06	18.71	348.40	−8.82
0.2507	1296.20	0.055	1509.12	89.64	338.75	−43.79	0.7510	1370.38	0.134	1445.90	14.51	349.04	−6.78
0.2980	1311.01	0.066	1498.42	78.14	339.72	−38.05	0.8496	1376.01	0.131	1441.05	7.84	349.96	−3.56
0.3498	1323.37	0.097	1488.01	66.48	341.28	−32.20	0.8942	1378.45	0.097	1439.22	5.27	350.23	−2.38
0.4000	1333.21	0.109	1479.63	56.75	342.61	−27.41	0.9498	1381.16	0.061	1437.12	2.30	350.57	−1.00
0.4498	1341.13	0.127	1472.59	48.34	343.85	−23.24							
T = 308.15 K													
0.0178	1054.44	0.003	1549.85	61.99	394.82	−33.52	0.4976	1339.19	0.184	1445.00	34.99	357.62	−17.30
0.0502	1128.98	0.013	1555.73	101.01	365.97	−52.39	0.5495	1345.14	0.192	1439.33	29.07	358.85	−14.31
0.1004	1197.22	0.056	1539.08	108.08	352.62	−54.63	0.6039	1350.52	0.192	1434.39	23.81	359.88	−11.66
0.1501	1239.24	0.068	1520.07	99.68	349.23	−50.11	0.6476	1354.45	0.177	1430.80	19.94	360.64	−9.76
0.2002	1267.53	0.091	1503.06	88.01	349.21	−44.10	0.6996	1358.50	0.166	1427.15	15.94	361.41	−7.76
0.2507	1287.75	0.125	1488.67	76.41	350.41	−38.15	0.7510	1361.96	0.161	1423.95	12.39	362.11	−5.98
0.2980	1302.52	0.134	1477.44	66.56	351.72	−33.22	0.8496	1367.61	0.147	1418.93	6.71	363.17	−3.13
0.3498	1314.85	0.163	1466.72	56.57	353.53	−28.14	0.8942	1370.05	0.109	1417.16	4.65	363.43	−2.16
0.4000	1324.69	0.171	1458.13	48.25	355.05	−23.97	0.9498	1372.76	0.067	1415.00	2.14	363.82	−0.97
0.4498	1332.62	0.185	1450.96	41.09	356.44	−20.34							
T = 318.15 K													
0.0178	1049.35	0.016	1553.49	53.79	394.88	−28.51	0.4976	1330.70	0.235	1423.37	29.85	370.92	−15.19
0.0502	1122.35	0.046	1547.70	87.23	371.96	−45.04	0.5495	1336.69	0.237	1417.70	24.81	372.22	−12.57
0.1004	1189.47	0.108	1523.69	93.04	362.12	−47.39	0.6039	1342.09	0.232	1412.73	20.31	373.34	−10.24
0.1501	1231.02	0.129	1501.54	85.57	360.30	−43.68	0.6476	1346.04	0.212	1409.15	17.02	374.13	−8.58
0.2002	1259.09	0.156	1482.97	75.37	361.14	−38.52	0.6996	1350.10	0.196	1405.49	13.62	374.95	−6.83
0.2507	1279.22	0.191	1467.81	65.35	362.84	−33.37	0.7510	1353.58	0.186	1402.28	10.60	375.70	−5.26
0.2980	1293.96	0.199	1456.11	56.80	364.49	−29.07	0.8496	1359.26	0.161	1397.05	5.60	376.94	−2.67
0.3498	1306.30	0.226	1445.27	48.30	366.49	−24.66	0.8942	1361.70	0.120	1395.46	4.08	377.12	−1.95
0.4000	1316.15	0.230	1436.58	41.18	368.16	−21.02	0.9498	1364.42	0.073	1393.27	1.95	377.56	−0.91
0.4498	1324.11	0.241	1429.34	35.05	369.66	−17.84							
T = 328.15 K													
0.0178	1043.69	0.029	1553.11	46.84	397.22	−24.51	0.4976	1322.22	0.284	1401.73	25.59	384.92	−13.37
0.0502	1115.22	0.080	1537.13	75.43	379.50	−38.93	0.5495	1328.25	0.280	1396.18	21.36	386.22	−11.11
0.1004	1181.47	0.157	1506.73	80.10	372.83	−41.22	0.6039	1333.68	0.271	1391.20	17.49	387.41	−9.05
0.1501	1222.62	0.187	1482.00	73.50	372.40	−38.15	0.6476	1337.66	0.246	1387.65	14.68	388.24	−7.60
0.2002	1250.52	0.219	1462.19	64.58	374.02	−33.68	0.6996	1341.75	0.225	1384.04	11.81	389.07	−6.09
0.2507	1270.60	0.255	1446.49	55.97	376.15	−29.21	0.7510	1345.25	0.210	1380.83	9.22	389.87	−4.70
0.2980	1285.34	0.262	1434.60	48.69	378.02	−25.51	0.8496	1350.97	0.175	1375.47	4.80	391.25	−2.33
0.3498	1297.70	0.287	1423.60	41.33	380.23	−21.62	0.8942	1353.41	0.130	1374.04	3.72	391.36	−1.83
0.4000	1307.60	0.288	1414.91	35.26	382.00	−18.46	0.9498	1356.14	0.078	1371.85	1.90	391.82	−0.92
0.4498	1315.58	0.294	1407.67	30.02	383.60	−15.68							
T = 338.15 K													
0.0178	1037.50	0.042	1548.94	40.72	401.74	−21.16	0.4976	1313.75	0.332	1380.03	21.66	399.68	−11.55
0.0502	1107.94	0.109	1524.17	65.01	388.52	−33.70	0.5495	1319.83	0.323	1374.73	18.23	400.91	−9.69
0.1004	1173.24	0.206	1488.23	68.53	384.83	−35.64	0.6039	1325.30	0.309	1369.70	14.82	402.19	−7.82
0.1501	1214.07	0.244	1461.46	62.72	385.64	−33.07	0.6476	1329.31	0.279	1366.21	12.43	403.03	−6.56
0.2002	1241.85	0.281	1440.72	54.93	387.95	−29.17	0.6996	1333.43	0.253	1362.68	10.02	403.87	−5.27
0.2507	1261.90	0.319	1424.67	47.55	390.43	−25.30	0.7510	1336.96	0.233	1359.53	7.83	404.67	−4.06
0.2980	1276.67	0.325	1412.93	41.60	392.36	−22.25	0.8496	1342.74	0.187	1354.21	4.01	406.10	−1.96
0.3498	1289.07	0.348	1401.67	35.04	394.85	−18.69	0.8942	1345.17	0.141	1352.86	3.22	406.18	−1.61
0.4000	1299.02	0.345	1393.04	29.87	396.70	−15.96	0.9498	1347.92	0.083	1350.68	1.67	406.66	−0.82
0.4498	1307.06	0.348	1385.89	25.42	398.33	−13.55							

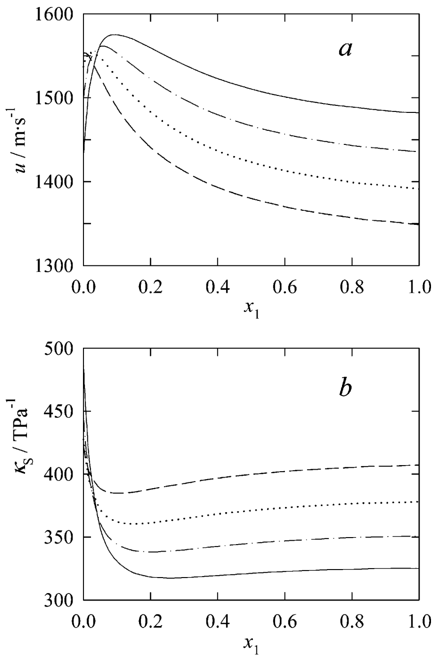

Figure 1. (a) Speed of sound u and (b) isentropic compressibility κ_S for the [emim][triflate] (1) + water (2) binary system, as a function of mole fraction x_1 of the IL at different temperatures: solid lines, 278.15 K; dashed-dotted lines, 298.15 K; dotted lines, 318.15 K; dashed lines, 338.15 K.

ϕ_i ($=x_iV_i^\circ/V_m^{id}$) is the volume fraction of component i, whereas $\kappa_{s,i}^\circ$, $\alpha_{P,i}^\circ$, and $C_{P,i}^\circ$ 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[44]

$$\alpha_P^{id} = \phi_1 \cdot \alpha_{P,1}^\circ + \phi_2 \cdot \alpha_{P,2}^\circ \tag{8}$$

$$C_{P,m}^{id} = x_1 \cdot C_{P,1}^\circ + x_2 \cdot C_{P,2}^\circ \tag{9}$$

Furthermore, Douhéret et al.[44] also stated that speed of sound in an ideal-mixture may be calculated using the equation

$$u^{id} = (\rho^{id}\kappa_S^{id})^{-1/2} = \left(\frac{V_m^{id}}{\kappa_S^{id}M_m}\right)^{1/2} \tag{10}$$

where M_m is the molar mass of the liquid mixture. The combined standard uncertainty for the ideal properties was estimated to be the same as that for the actual properties: less than 0.005 $cm^3 \cdot mol^{-1}$ for ideal molar volume excepting the highest IL-concentrated mixtures, 0.05 $m \cdot s^{-1}$ for ideal speed of sound, and 0.05 TPa^{-1} for ideal isentropic compressibility.

In Tables 3 to 6, excess molar volumes, excess speeds of sound, and excess isentropic compressibilities for the four binary systems are also reported. Given that the excess 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 properties will be $2^{1/2}$ times that of the corresponding properties. So, they will be less than 0.007 $cm^3 \cdot mol^{-1}$ for excess molar volume, excepting the highest IL-concentrated mixtures, 0.07 $m \cdot s^{-1}$ for excess speed of sound, and 0.07 TPa^{-1} for excess isentropic compressibility. Taking into account that the mean values for κ_S^E and u^E are about -75 TPa^{-1} and 75 $m \cdot s^{-1}$, respectively, the relative error in these quantities is not more than 0.1 %. On the contrary, values of excess molar volumes are very small ($-0.82 < V_m^E/cm^3 \cdot mol^{-1} < 0.35$) because the mixtures behave like quasi-ideal ones, and in this way, the combined uncertainty can even become higher than the V_m^E values. This may happen with the water mixtures, in which the standard uncertainty is greater, whereas the V_m^E values are very close to zero when they pass from negative to positive values. This behavior of V_m^E, which is very common in many systems that approach an ideal-liquid mixture, has been barely commented on in the literature.

All the excess properties, Q^E, for each system were correlated with the IL mole fraction, x_1, by means of an extended version[17] of the Redlich−Kister[46] equation

$$Q^E = x_1(1-x_1)\frac{\sum_{i=0}^{m} A_i(2x_1-1)^i}{1+\sum_{j=1}^{n} B_j(2x_1-1)^j} \tag{11}$$

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.

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

$$A_i = A_{i_0} + A_{i_1}(T - 273.15) + A_{i_2}(T - 273.15)^2 \tag{12}$$

$$B_j = B_{j_0} + B_{j_1}(T - 273.15) + B_{j_2}(T - 273.15)^2 \tag{13}$$

Table 7. Coefficients of the Fitting Equation (eq 14) for Excess Molar Volumes ($V_m^E/cm^3 \cdot mol^{-1}$) and the Standard Deviations (σ) of the [emim][triflate] (1) + Methanol (2), + Ethanol (2), + 1-Propanol (2), and + Water (2) Mixtures

	$10^1 Z_{l,0}$	$10^3 Z_{l,1}$	$10^6 Z_{l,2}$	$\sigma/cm^3 \cdot mol^{-1}$		$10^1 Z_{l,0}$	$10^3 Z_{l,1}$	$10^6 Z_{l,2}$	$\sigma/cm^3 \cdot mol^{-1}$
	[emim][triflate] (1) + Methanol (2)					[emim][triflate] (1) + 1-Propanol (2)			
$Z = A, l = 0$	−17.326	−13.281	−118.12	0.0125	$Z = A, l = 0$	−9.4079	−6.7855	−223.81	0.0100
$Z = A, l = 1$	0.8273	9.2810	−100.57		$Z = A, l = 1$	4.5975	4.8417	3.6753	
$Z = A, l = 2$	−3.7878	10.954	−76.870		$Z = A, l = 2$	0.5503	−7.9158	304.91	
$Z = A, l = 3$	−	−	−		$Z = A, l = 3$	−	−	−	
$Z = B, l = 1$	6.9112	0.1993	−0.2820		$Z = B, l = 1$	1.0752	1.7016	−14.008	
$Z = B, l = 2$	−0.7665	−0.6888	0.9505		$Z = B, l = 2$	−4.4145	−0.1541	−44.389	
	[emim][triflate] (1) + Ethanol (2)					[emim][triflate] (1) + Water (2)			
$Z = A, l = 0$	−15.949	−11.699	−180.21	0.0145	$Z = A, l = 0$	−0.8172	26.134	−73.269	0.0066
$Z = A, l = 1$	14.677	−8.2251	360.74		$Z = A, l = 1$	8.7977	−26.813	84.384	
$Z = A, l = 2$	−9.3064	4.1555	356.33		$Z = A, l = 2$	−8.1025	28.322	−83.667	
$Z = A, l = 3$	−	−	−		$Z = A, l = 3$	10.259	−7.7534	−62.716	
$Z = B, l = 1$	−0.5776	4.9217	−112.88		$Z = B, l = 1$	−	−	−	
$Z = B, l = 2$	−3.1221	0.2557	−160.16		$Z = B, l = 2$	−	−	−	

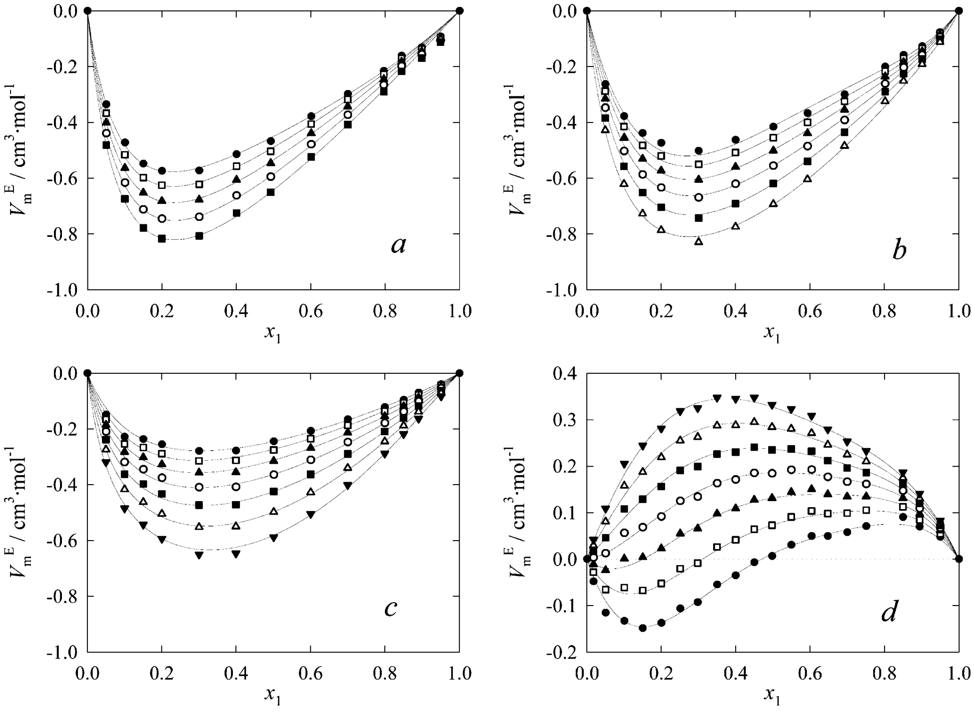

Figure 2. Excess molar volume V_m^E for the [emim][triflate] (1) + solvent (2) binary systems at different temperatures: ●, 278.15 K; □, 288.15 K; ▲, 298.15 K; ○, 308.15 K; ■, 318.15 K; △, 328.15 K; ▼, 338.15 K. The solid lines represent the corresponding correlation by an extended version of the Redlich−Kister equation (eq 14). Solvent: (a) methanol; (b) ethanol; (c) 1-propanol; (d) water.

Table 8. Coefficients of the Fitting Equation (eq 14) for Excess Isentropic Compressibility (κ_S^E/TPa^{-1}) and the Standard Deviations (σ) of the [emim][triflate] (1) + Methanol (2), + Ethanol (2), + 1-Propanol (2), and + Water (2) Mixtures

	$10^1\ Z_{l,0}$	$10^2\ Z_{l,1}$	$10^4\ Z_{l,2}$	σ/TPa^{-1}		$10^1\ Z_{l,0}$	$10^2\ Z_{l,1}$	$10^4\ Z_{l,2}$	σ/TPa^{-1}
	[emim][triflate] (1) + Methanol (2)					[emim][triflate] (1) + 1-Propanol (2)			
$Z = A, l = 0$	−1848.5	−231.82	−239.34	0.307	$Z = A, l = 0$	−1235.6	−163.71	−264.55	1.121
$Z = A, l = 1$	1283.8	80.186	154.56		$Z = A, l = 1$	1005.7	178.67	303.01	
$Z = A, l = 2$	−474.09	−148.87	96.110		$Z = A, l = 2$	−461.03	−11.136	−11.191	
$Z = A, l = 3$	−	−	−		$Z = A, l = 3$	−	−	−	
$Z = B, l = 1$	7.4685	0.5003	−0.4507		$Z = B, l = 1$	0.0729	−0.1012	−0.0969	
$Z = B, l = 2$	−1.1310	0.5339	−0.5831		$Z = B, l = 2$	−1.4976	−0.4975	−0.2464	
	[emim][triflate] (1) + Ethanol (2)					[emim][triflate] (1) + Water (2)			
$Z = A, l = 0$	−1803.8	−237.95	−269.83	0.461	$Z = A, l = 0$	−1123.6	157.25	−86.974	1.062
$Z = A, l = 1$	932.18	89.333	187.82		$Z = A, l = 1$	958.98	−196.43	149.47	
$Z = A, l = 2$	−153.46	−12.340	−81.775		$Z = A, l = 2$	−668.17	165.38	−145.43	
$Z = A, l = 3$	−	−	−		$Z = A, l = 3$	−	−	−	
$Z = B, l = 1$	5.8796	0.2365	−0.2396		$Z = B, l = 1$	10.079	0.5303	−0.4549	
$Z = B, l = 2$	−1.2851	0.0989	−0.1699		$Z = B, l = 2$	0.4567	0.5202	−0.4037	

Table 9. Coefficients of the Fitting Equation (eq 14) for Excess Speed of Sound (u^E/m·s^{-1}) and the Standard Deviations (σ) of the [emim][triflate] (1) + Methanol (2), + Ethanol (2), + 1-Propanol (2), and + Water (2) Mixtures

	$Z_{l,0}$	$10^1\ Z_{l,1}$	$10^3\ Z_{l,2}$	σ/m·s^{-1}		$Z_{l,0}$	$10^1\ Z_{l,1}$	$10^3\ Z_{l,2}$	σ/m·s^{-1}
	[emim][triflate] (1) + Methanol (2)					[emim][triflate] (1) + 1-Propanol (2)			
$Z = A, l = 0$	302.05	22.530	4.1535	1.959	$Z = A, l = 0$	190.93	18.440	7.7753	0.759
$Z = A, l = 1$	−273.72	−19.507	4.3853		$Z = A, l = 1$	−48.444	−12.808	5.1485	
$Z = A, l = 2$	292.74	21.094	−4.2296		$Z = A, l = 2$	−4.8715	10.652	−2.0978	
$Z = A, l = 3$	−243.33	−6.7737	−10.520		$Z = A, l = 3$	−10.277	−0.7346	−5.1463	
$Z = B, l = 1$	−	−	−		$Z = B, l = 1$	−	−	−	
$Z = B, l = 2$	−	−	−		$Z = B, l = 2$	−	−	−	
	[emim][triflate] (1) + Ethanol (2)					[emim][triflate] (1) + Water (2)			
$Z = A, l = 0$	281.87	22.453	5.8681	1.055	$Z = A, l = 0$	254.83	−43.090	26.870	1.244
$Z = A, l = 1$	−168.28	−12.626	0.7818		$Z = A, l = 1$	−104.24	20.324	−20.912	
$Z = A, l = 2$	85.118	10.492	1.7531		$Z = A, l = 2$	31.937	1.8521	−0.8707	
$Z = A, l = 3$	−46.631	−9.1041	5.0601		$Z = A, l = 3$	−	−	−	
$Z = B, l = 1$	−	−	−		$Z = B, l = 1$	1.3074	0.0450	−0.1123	
$Z = B, l = 2$	−	−	−		$Z = B, l = 2$	0.3462	0.0460	−0.1120	

In this way, the number of coefficients is reduced because the total number of parameters for each binary system will be ($3 \times k$) but not ($t \times k$), where t is the number of different temperatures tested for each system. So, from eqs 11 to 13, we will use the following expression to simultaneously correlate the excess properties with the temperature T and

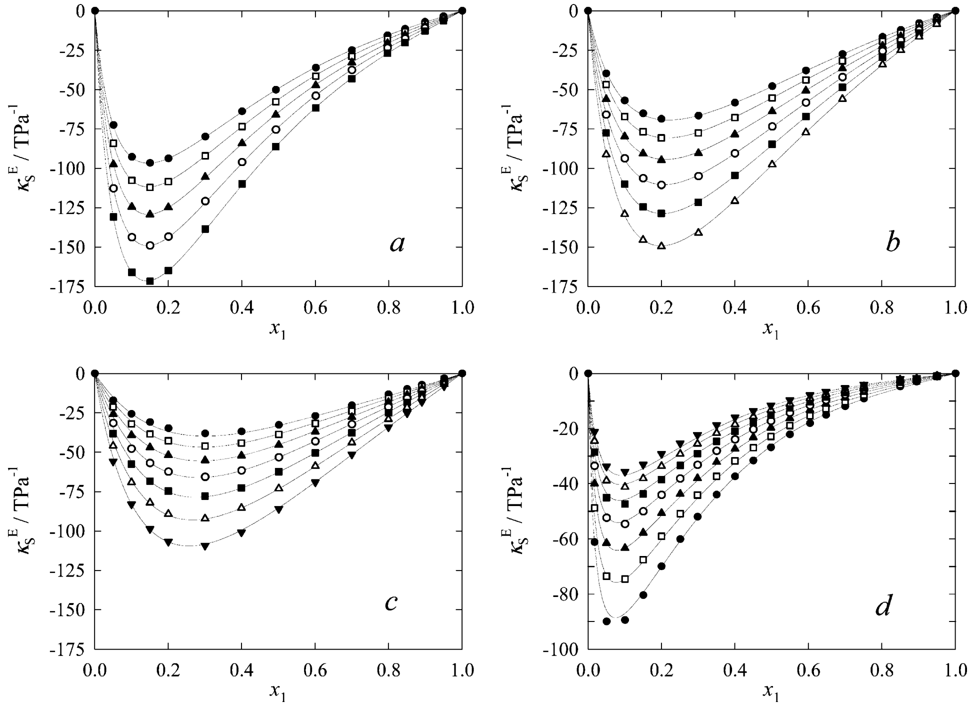

Figure 3. Excess isentropic compressibility κ_S^E for the [emim][triflate] (1) + solvent (2) binary systems at different temperatures: ●, 278.15 K; □, 288.15 K; ▲, 298.15 K; ○, 308.15 K; ■, 318.15 K; △, 328.15 K; ▼, 338.15 K. The solid lines represent the corresponding correlation by an extended version of the Redlich−Kister equation (eq 14). Solvent: (a) methanol; (b) ethanol; (c) 1-propanol; (d) water.

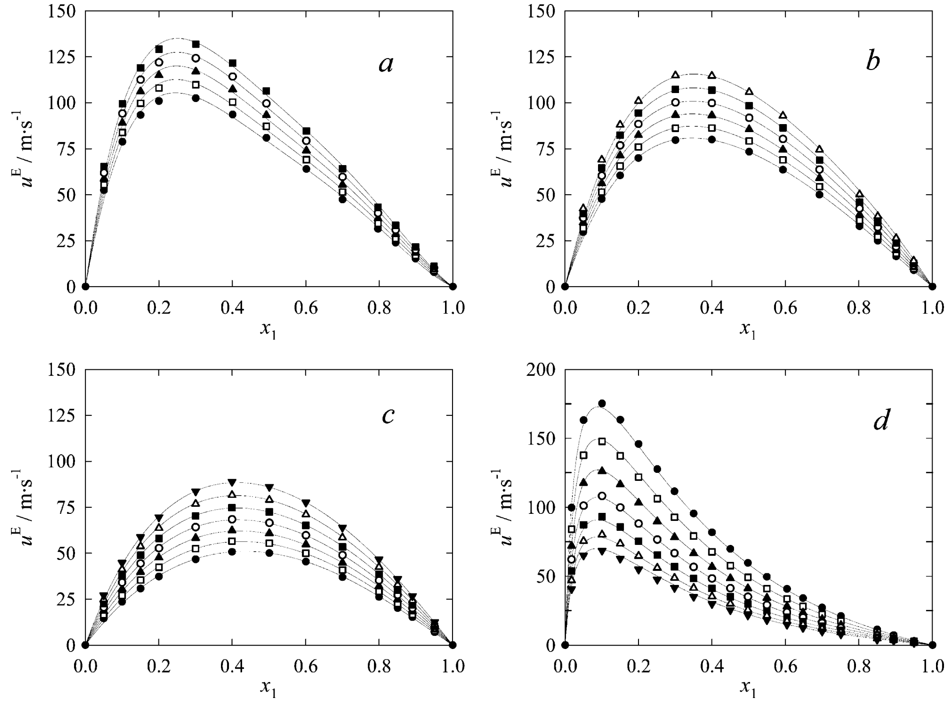

Figure 4. Excess speed of sound u^E for the [emim][triflate] (1) + solvent (2) binary systems at different temperatures: ●, 278.15 K; □, 288.15 K; ▲, 298.15 K; ○, 308.15 K; ■, 318.15 K; △, 328.15 K; ▼, 338.15 K. The solid lines represent the corresponding correlation by an extended version of the Redlich−Kister equation (eq 14). Solvent: (a) methanol; (b) ethanol; (c) 1-propanol; (d) water.

the IL mole fraction x_1

$$Q^E = x_1(1-x_1)\frac{\sum_{i=0}^{m}[A_{i_0} + A_{i_1}(T - 273.15) + A_{i_2}(T - 273.15)^2](2x_1 - 1)^i}{1 + \sum_{j=1}^{n}[B_{j_0} + B_{j_1}(T - 273.15) + B_{j_2}(T - 273.15)^2](2x_1 - 1)^j} \tag{14}$$

The fitting parameters were estimated by the least-squares method, and the values obtained are given in Tables 7 to 9, together with the standard deviations calculated by applying the expression

$$\sigma = \left[\frac{\sum_{i=1}^{p}(Q^E_{\mathrm{exptl},i} - Q^E_{\mathrm{calcd},i})^2}{p - 3(m + n + 1)}\right]^{1/2} \tag{15}$$

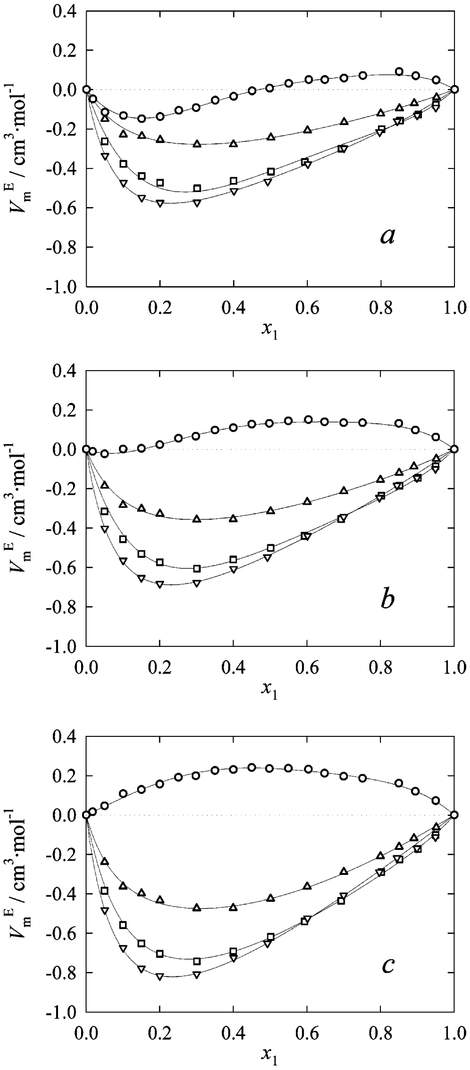

Figure 5. Excess molar volume V_m^E for the [emim][triflate] (1) + solvent (2) binary systems at different temperatures. Solvent: ▽, methanol; □, ethanol; △, 1-propanol; ○, water. (a) $T = 278.15$ K; (b) $T = 298.15$ K; (c) $T = 318.15$ K. The solid lines represent the corresponding correlation by an extended version of the Redlich−Kister equation (eq 14).

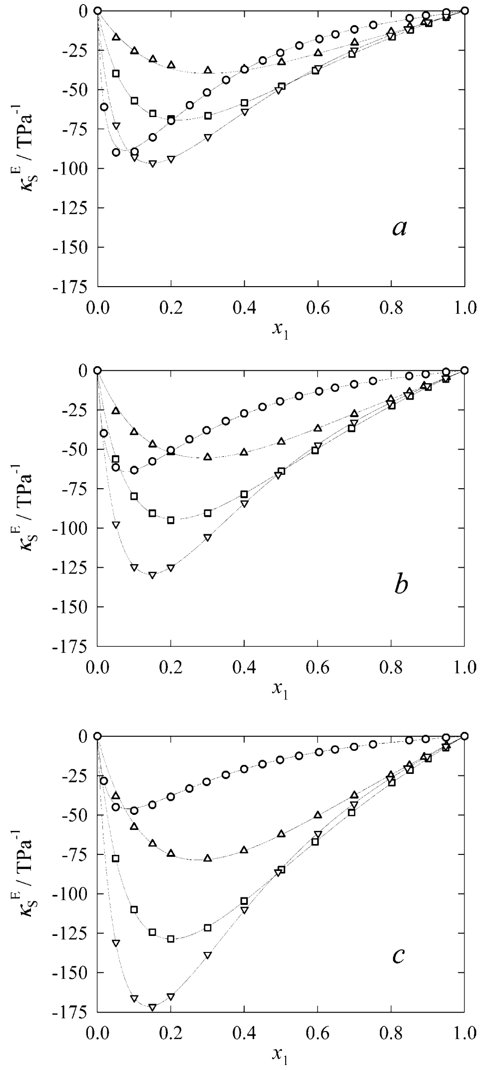

Figure 6. Excess isentropic compressibility κ_S^E for the [emim][triflate] (1) + solvent (2) binary systems at different temperatures. Solvent: ▽, methanol; □, ethanol; △, 1-propanol; ○, water. (a) $T = 278.15$ K; (b) $T = 298.15$ K; (c) $T = 318.15$ K. The solid lines represent the corresponding correlation by an extended version of the Redlich−Kister equation (eq 14).

in which p is the number of experimental data points. The choice of m and n values for the degrees of polynomics in eq 14 was made using the Akaike's Information Criterion (AIC).[47] Figures 2 to 4 show, respectively, the experimental values of V_m^E, κ_S^E, and u^E vs the IL mole fraction at all the temperatures tested together with the curves obtained from eq 14 using the fitting parameters, for each binary system. Perhaps some behaviors can be better understood in Figures 5 to 7, in which we have drawn the experimental values of V_m^E, κ_S^E, and u^E vs the IL mole fraction, x_1, for all binary systems at once, at $T = (278.15, 298.15, \text{and } 318.15)$ K. To describe and explain the behavior of the excess properties, we will distinguish between IL + alcohol systems and the IL + water system because their behavior is very different.

[emim][triflate] + Alcohol Systems. The behavior of the three systems (IL + methanol, IL + ethanol, and IL + 1-propanol) is regular and very similar. V_m^E and κ_S^E are always negative, and u^E is always positive in the whole range of compositions and temperatures. The excess molar volume V_m^E decreases; that is, it becomes more negative when the temperature increases as seen in Figure 2. The fitting curves are asymmetric, and they present a minimum at low values of the IL mole fraction, which becomes less negative and moves to greater values of x_1 when the alcohol chain augments, as seen in Figure 5. In this figure, it can also be seen that, for $x_1 > 0.6$, the V_m^E experimental points of IL + methanol and IL + ethanol systems mingle, and it even seems as though they cross. The V_m^E curve of the IL + 1-propanol system keeps its independence. The same dependence of IL + n-alcohol systems on temperature and chain length was reported by Heintz et al.[17] and Arce et al.[19] for [omim][BF$_4$], by Domanska et al.[20] for [mmim][MeSO$_4$], [bmim][MeSO$_4$], and [bmim][OcSO$_4$], by González et al.[24] for [omim][Cl], and by Lachwa et al.[30] for [hmim][Tf$_2$N]. We want to make perfectly clear that V_m^E is not always negative for all the systems cited: it can be negative or positive, but it always increases when the temperature decreases or the alcohol chain augments.

The V_m^E behavior of [emim][triflate] + alcohol 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, including those of polar components. Arce et al.,[19] Domanska et al.,[20] and Zafarani-Moattar and Shekaari[21] have applied the PFP theory to correlate the excess molar volumes of IL +

solvent systems, including aqueous systems. The PFP theory considers the V_m^E of binary mixtures to be the sum of three contributions:[48] (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 alcohol molecules. In the present study, the following form of the PFP theory has been used to estimate V_m^E values:

$$\frac{V_m^E}{x_1V_1{*} + x_2V_2{*}} = \frac{V_m^E(\text{int})}{x_1V_1{*} + x_2V_2{*}} + \frac{V_m^E(\text{fv})}{x_1V_1{*} + x_2V_2{*}} + \frac{V_m^E(\text{ip})}{x_1V_1{*} + x_2V_2{*}} = \frac{(\tilde{V}^{1/3} - 1)\tilde{V}^{2/3}\Psi_2\theta_1\chi_{21}}{((4/3)\tilde{V}^{-1/3} - 1)P_2{*}} - \frac{(\tilde{V}_1 - \tilde{V}_2)^2((14/9)\tilde{V}^{-1/3} - 1)\Psi_1\Psi_2}{((4/3)\tilde{V}^{-1/3} - 1)\tilde{V}} + \frac{(\tilde{V}_1 - \tilde{V}_2)(P_1{*} - P_2{*})\Psi_1\Psi_2}{P_2{*}\Psi_1 + P_1{*}\Psi_2} \qquad (16)$$

where $\tilde{V}_i$ and $\tilde{V}$ are the reduced volume of pure components and mixtures, respectively; $V_i{*}$ is the characteristic volume; and $P_i{*}$ is the characteristic pressure of pure components. In eq 16, Ψ_i is the molecular contact energy fraction. All these quantities can be deduced from the molar volumes V_i°, isobaric heat capacities $C_{P,i}^\circ$, isobaric thermal expansivity $\alpha_{P,i}^\circ$, and isentropic compressibility $\kappa_{S,i}^\circ$ values of pure components reported in Table 2, using Flory's formalisms given elsewhere,[21,48] and they are listed in Table 10.

The molecular surface fraction of the ionic liquid, θ_1, can be calculated[21,48] from the molecular surface/volume ratio, S_i, of the components. The S values for methanol, ethanol, 1-propanol, and water 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.[49] In the literature, there are no structure parameters r and q for ILs, and the Bondi method of molecular group contribution[50] can only be applied to nonelectrolyte systems. However, Banerjee et al.[51] have obtained, via the polarizable continuum model, the structure parameters for three homologous series of ILs, [C$_n$mim][Cl], [C$_n$mim][BF$_4$], and [C$_n$mim][PF$_6$], with n varying from 1 to 8, and for [C$_4$mim][triflate]. From these data, we have checked that although r and q values are different inside each series and therefore are different inside the van der Waals volumes and areas as well, the S ratio remains constant in each series. Because of this, we have taken for our IL, [emim][triflate], the same value as Banerjee et al.[51] reported for [C$_4$mim][triflate]: 10.43 nm^{-1}. In Table 10, we have also listed the S values for all the pure components.

The interactional parameter χ_{21} can be evaluated if values of the excess molar enthalpies are known. Because these values are not available for our binary systems, it is a common practice to use χ_{21} as the only adjustable parameter to fit the experimental V_m^E values to eq 16. The interactional parameter χ_{21} thus obtained by the least-squares method over the whole composition range for each system and temperature represents the intermolecular interaction between components of mixtures. The values for this parameter at different temperatures were listed in Table 11, 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) + alcohol (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 these systems present minimum values at this composition. A perusal of Table 11 reveals that, for the [emim][triflate] + alcohol systems, the interactional contribution is positive and increases with the temperature, probably due to the strong self-association between alcohol molecules which prevents the alcohol−IL strong interactions, whereas free volume and internal pressure contribute negatively to the V_m^E(PFP) values which both decrease when temperature increases, the thermal effect being more pronounced for the free volume contribution. It is also clear from Table 11 that the contribution due to internal pressure, V_m^E(ip), seems to play a dominant role in deciding the sign and magnitude of the excess molar volume because it is larger than the other two contributions for all the systems studied at all working temperatures.

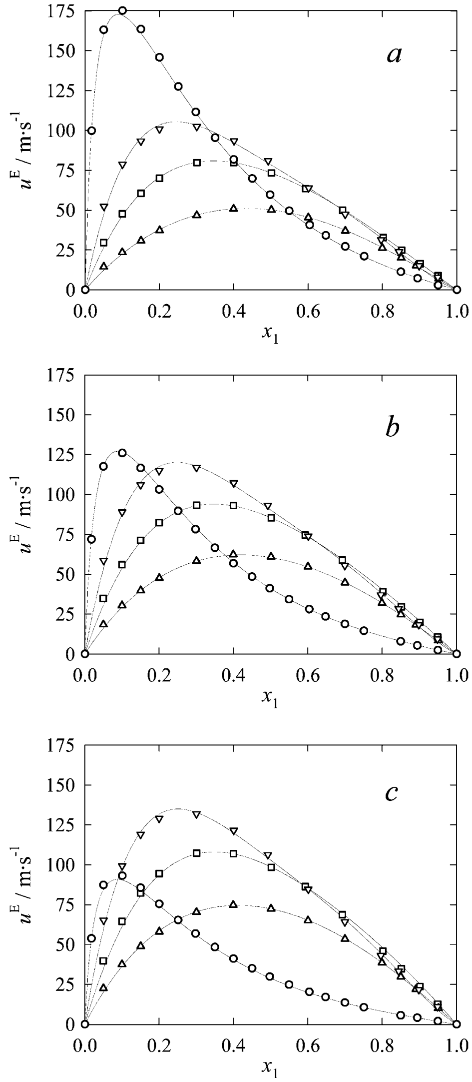

Figure 7. Excess speed of sound u^E for the [emim][triflate] (1) + solvent (2) binary systems at different temperatures. Solvent: ▽, methanol; □, ethanol; △, 1-propanol; ○, water. (a) T = 278.15 K; (b) T = 298.15 K; (c) T = 318.15 K. The solid lines represent the corresponding correlation by an extended version of the Redlich−Kister equation (eq 14).

Even though the PFP theory leads to a one-parameter model, the agreement between experimental and calculated values using

Table 10. Characteristic Parameters for Pure Methanol, Ethanol, 1-Propanol, Water, and [emim][triflate] at Several Temperatures, Used in PFP Theory Calculations

T / K	$\tilde{V}$	V^* / cm^3·mol^{-1}	P^* / MPa	S / nm^{-1}	T / K	$\tilde{V}$	V^* / cm^3·mol^{-1}	P^* / MPa	S / nm^{-1}
				Methanol					
278.15	1.265	31.463	469.73	16.49[a]	308.15	1.300	31.727	470.95	16.49[a]
288.15	1.275	31.566	468.90	16.49[a]	318.15	1.313	31.787	473.63	16.49[a]
298.15	1.287	31.654	469.31	16.49[a]					
				Ethanol					
278.15	1.245	46.148	447.12	15.43[a]	308.15	1.280	46.356	455.66	15.43[a]
288.15	1.255	46.249	448.38	15.43[a]	318.15	1.294	46.363	461.99	15.43[a]
298.15	1.267	46.318	450.97	15.43[a]	328.15	1.310	46.342	469.93	15.43[a]
				1-Propanol					
278.15	1.227	60.045	452.00	14.89[a]	318.15	1.276	60.151	474.75	14.89[a]
288.15	1.237	60.142	454.43	14.89[a]	328.15	1.291	60.066	485.43	14.89[a]
298.15	1.249	60.192	459.13	14.89[a]	338.15	1.309	59.943	497.78	14.89[a]
308.15	1.261	60.194	465.92	14.89[a]					
				Water					
278.15	1.004	17.937	9.14	25.08[a]	318.15	1.123	16.198	384.20	25.08[a]
288.15	1.042	17.301	101.13	25.08[a]	328.15	1.145	15.959	477.31	25.08[a]
298.15	1.073	16.841	195.22	25.08[a]	338.15	1.166	15.755	568.51	25.08[a]
308.15	1.099	16.485	289.89	25.08[a]					
				[emim][triflate]					
278.15	1.152	161.34	594.10	10.43[b]	318.15	1.171	162.61	607.81	10.43[b]
288.15	1.157	161.63	598.73	10.43[b]	328.15	1.175	162.98	608.75	10.43[b]
298.15	1.162	161.94	602.77	10.43[b]	338.15	1.180	163.37	608.78	10.43[b]
308.15	1.166	162.26	605.75	10.43[b]					

[a] Estimated from ref 49. [b] Calculated from data of ref 51.

Table 11. Values of 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 / K	χ_{21}	V_m^E(int) / cm^3·mol^{-1}	V_m^E(fv) / cm^3·mol^{-1}	V_m^E(ip) / cm^3·mol^{-1}	V_m^E(PFP) / cm^3·mol^{-1}	V_m^E(exptl) / cm^3·mol^{-1}
			[emim][triflate] (1) + Methanol (2)			
278.15	11.824	0.067	−0.267	−0.383	−0.584	−0.573
288.15	13.569	0.080	−0.294	−0.419	−0.633	−0.622
298.15	15.104	0.093	−0.328	−0.454	−0.689	−0.677
308.15	16.319	0.105	−0.370	−0.487	−0.752	−0.739
318.15	17.332	0.116	−0.423	−0.517	−0.823	−0.807
			[emim][triflate] (1) + Ethanol (2)			
278.15	29.380	0.220	−0.236	−0.494	−0.510	−0.502
288.15	30.698	0.240	−0.265	−0.534	−0.558	−0.550
298.15	32.131	0.263	−0.303	−0.574	−0.614	−0.606
308.15	33.098	0.283	−0.353	−0.609	−0.679	−0.669
318.15	33.756	0.302	−0.418	−0.639	−0.755	−0.743
328.15	33.818	0.318	−0.501	−0.661	−0.844	−0.830
			[emim][triflate] (1) + 1-Propanol (2)			
278.15	41.222	0.359	−0.189	−0.458	−0.288	−0.279
288.15	42.228	0.384	−0.215	−0.494	−0.325	−0.315
298.15	43.088	0.410	−0.251	−0.527	−0.368	−0.357
308.15	43.482	0.433	−0.299	−0.556	−0.422	−0.409
318.15	43.325	0.452	−0.363	−0.577	−0.487	−0.473
328.15	42.342	0.465	−0.446	−0.587	−0.568	−0.552
338.15	40.465	0.468	−0.552	−0.581	−0.666	−0.650
			[emim][triflate] (1) + Water (2)			
278.15	−635.41	−2.012	−0.008	1.818	−0.202	−0.093
288.15	−364.90	−1.080	−0.048	1.108	−0.020	−0.009
298.15	−181.28	−0.516	−0.050	0.656	0.090	0.066
308.15	−52.035	−0.145	−0.038	0.362	0.179	0.134
318.15	34.437	0.096	−0.023	0.174	0.246	0.199
328.15	89.554	0.250	−0.011	0.062	0.301	0.262
338.15	123.51	0.349	−0.002	0.008	0.354	0.325

the PFP theory is good, as seen in Figure 8, 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) + alcohol (2) systems. In this figure, the effect of the aliphatic chain length of the alcohol on the different contributions can also be seen. When the chain length augments, V_m^E(int) and V_m^E(fv) augment, whereas V_m^E(ip) oscillates, those factors being responsible for the V_m^E increase.

The behavior of the excess isentropic compressibility κ_S^E for the IL + alcohol systems is very similar to the V_m^E one as reported in Figure 3. It is also negative in the whole range of

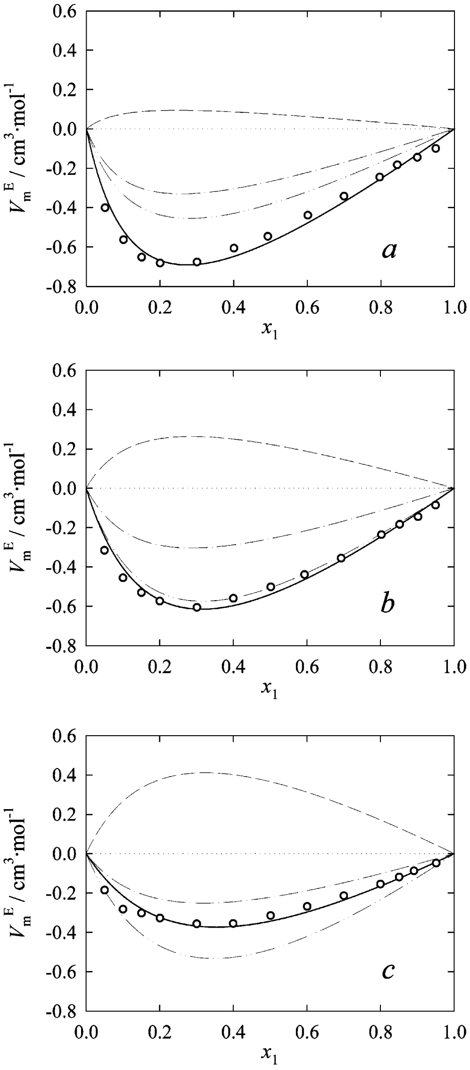

Figure 8. Excess molar volume V_m^E for the [emim][triflate] (1) + alcohol (2) binary systems at $T = 298.15$ K calculated with the Prigogine−Flory−Patterson theory: dashed line, interactional contribution; dotted-dashed line, free volume contribution; dotted-dotted-dashed line, internal pressure contribution; solid line, total excess molar volume predicted by PFP theory; ○, experimental value. Alcohol: (a) methanol; (b) ethanol; (c) 1-propanol.

temperatures and compositions, and it becomes more negative when temperature increases. The fitting curves are more asymmetric than those for V_m^E and present a minimum at lower values of the IL mole fraction, which becomes less negative and moves to greater values of x_1 when the alcohol chain augments, as better seen in Figure 6. In this figure, it can also be seen that, for $x_1 > 0.5$, the κ_S^E curves of IL + methanol and IL + ethanol systems mingle, whereas for $x_1 > 0.8$, all of the three κ_S^E curves meet.

Last, the behavior of the excess speed of sound u^E for the IL + alcohol systems is opposite to the V_m^E and κ_S^E ones as seen in Figure 4. It is always positive in the whole range of temperatures and compositions, and it becomes more positive when temperature increases. The fitting curves are slightly asymmetric and present a maximum that becomes less pronounced and moves to greater values of x_1 when the alcohol chain augments, as can be seen in Figure 7. In this figure, it is also seen that, for $x_1 > 0.6$, the u^E curves of IL + methanol and IL + ethanol systems mingle, and for $x_1 > 0.85$, all of the three u^E curves meet.

[emim][triflate] + Water System. The IL + water system behaves in a very different way than that followed by the IL + alcohol systems. As seen in Figure 2, at the lowest temperature ($T = 278.15$ K), V_m^E is negative for $x_1 < 0.45$ and positive for $x_1 > 0.45$. The higher the temperature, the higher the V_m^E, and the smaller the value of x_1 where $V_m^E = 0$. For temperatures higher than 308.15 K, V_m^E stands always positive, and it continues increasing with temperature. This dependence of the IL + water system on the temperature, totally opposite to IL + alcohol behavior as shown in Figure 5, has also been reported for [bmim][BF$_4$] by Seddon et al.,[11] Rebelo et al.,[14] and Zhou et al.,[22] for [emim][BF$_4$] by Zhang et al.,[15] for [emim][EtSO$_4$] by Gómez et al.[27] and Rodríguez and Brennecke,[28] for [hmim]-[Cl] and [omim][Cl] by Gómez et al.,[32] and for [emim][triflate] and [emim][TFA] by Rodríguez and Brennecke.[28] We want to highlight that, as far as we know, there has been no mention of the different behavior of the excess molar volume of the IL + water and the IL + alcohol systems on temperature, perhaps because the dependence on temperature of the excess molar volume of binary mixtures of ILs with alcohols and water has been simultaneously studied only in one paper.[27]

We have tried to correlate the V_m^E behavior of the [emim]-[triflate] + water system using also the Prigogine−Flory−Patterson (PFP) theory, but the results were worse than those obtained for the [emim][triflate] + alcohol systems. In spite of that, the contributions and the total calculated excess molar volumes are reported in Table 11. It can be observed that the interactional contribution increases with temperature because of the increase of the interactional parameter χ_{21}, whereas the internal pressure contribution decreases due to the great augment of the characteristic pressure P^* of water, the effect of interactional contribution on the excess molar volume being predominant. The free volume contribution is negligible against the other ones.

The excess isentropic compressibility κ_S^E for the IL + water system is always negative in the whole range of temperatures and compositions as seen in Figure 3, but unlike the IL + alcohol systems, it becomes less negative when the temperature increases. The fitting curves are more asymmetric than those for the IL + alcohol systems and they present a minimum at lower values of the IL mole fraction ($x_1 \approx 0.10$), as shown in Figure 6.

According to Figure 4, the excess speed of sound u^E of the IL + water system is always positive in the whole range of temperatures and compositions, but it decreases when temperature increases. The fitting curves are very asymmetric as well, and they present a maximum at low values of the IL mole fraction ($x_1 \approx 0.10$), as seen in Figure 7. In this figure, it is also shown that, for $T = 278.15$ K, the u^E values for the IL + water system are greater than those for IL + alcohol systems; however, as temperature increases, this trend reverses, and at higher temperatures, the u^E values for water mixtures are smaller than those for alcohol mixtures.

Conclusions

Excess molar volume V_m^E, excess isentropic compressibility κ_S^E, and excess speed of sound u^E values of [emim][triflate] in methanol, ethanol, 1-propanol, and water mixtures have been calculated from the measured density and speed of sound data at $T = (278.15$ to $338.15)$ K in the whole range of concentrations. For each system, the excess 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 the systems IL + alcohol, V_m^E and κ_S^E are always negative, and they increase when temperature decreases or the aliphatic chain length increases. The behavior of u^E for these systems is the opposite: it is always positive, and it increases when temperature increases or the aliphatic chain length decreases.

For the system IL + water, the behavior of the three studied excess properties is very different. The excess molar volume at lower temperatures goes from negative values at low IL mole fraction to positive values at high IL mole fractions and increases with temperature, so from $T = 308.15$ K, it remains positive. For this aqueous system, κ_S^E is always negative, just like for the alcoholic systems, although it increases when temperature increases. The behavior of excess speed of sound u^E for this system is opposite: it is always positive, and it decreases when temperature increases.

The Prigogine−Flory−Patterson theory has a good performance in predicting excess molar volumes of mixtures of [emim][triflate] with methanol, ethanol, and 1-propanol, despite using only one fitting parameter, but it produces worse results for the [emim][triflate] + water system. In spite of that, the PFP theory is suitable for explaining the behavior of the excess molar volume for these systems.

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) Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071−2083.

(4) Wasserscheid, P.; Keim, W. Ionic Liquids−New "Solutions" for Transition Metals Catalysis. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772−3789.

(5) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. Ionic Liquid (Molten Salt) Phase Organometallic Catalysis. *Chem. Rev.* **2002**, *102*, 3667−3691.

(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) 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.

(8) Jork, C.; Seiler, M.; Beste, Y. A.; Arlt, W. Influence of Ionic Liquids on the Phase Behavior of Aqueous Azeotropic Systems. *J. Chem. Eng. Data* **2004**, *49*, 852−857.

(9) 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.

(10) Orchillés, A. V.; Miguel, P. J.; Vercher, E.; Martínez-Andreu, A. Isobaric Vapor−Liquid Equilibria for Methyl Acetate + Methanol + 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate at 100 kPa. *J. Chem. Eng. Data* **2007**, *52*, 915−920.

(11) Seddon, K. R.; Stark, A.; Torres, M. J. Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure Appl. Chem.* **2000**, *72*, 2275−2287.

(12) Heintz, A.; Klasen, D.; Lehmann, J. K. Excess Molar Volumes and Viscosities of Binary Mixtures of Methanol and the Ionic Liquid 4-Methyl-*N*-butylpyridinium Tetrafluoroborate at 25, 40, and 50 °C. *J. Solution Chem.* **2002**, *31*, 467−476.

(13) Wang, J.; Tian, Y.; Zhao, Y.; Zhuo, K. A volumetric and viscosity study for the mixtures of 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ionic liquid with acetonitrile, dichloromethane, 2-butanone and *N,N*-dimethylformamide. *Green Chem.* **2003**, *5*, 618−622.

(14) Rebelo, L. P. N.; Najdanovic-Visak, V.; Visak, Z. P.; Nunes da Ponte, M.; Szydlowski, J.; Cerdeiriña, C. A.; Troncoso, J.; Romaní, L.; Esperança, J. M. S. S.; Guedes, H. J. R.; de Sousa, H. C. A detailed thermodynamic analysis of [C$_4$mim][BF$_4$] + water as a case study to model ionic liquid aqueous solutions. *Green Chem.* **2004**, *6*, 369−381.

(15) Zhang, S.; Li, X.; Chen, H.; Wang, J.; Zhang, J.; Zhang, M. Determination of Physical Properties for the Binary System of 1-Ethyl-3-methylimidazolium Tetrafluoroborate + H$_2$O. *J. Chem. Eng. Data* **2004**, *49*, 760−764.

(16) Wang, J.; Zhu, A.; Zhao, Y.; Zhuo, K. Excess Molar Volumes and Excess Logarithm Viscosities for Binary Mixtures of the Ionic Liquid 1-Butyl-3-methylimidazolium Hexafluorophosphate with Some Organic Compounds. *J. Solution Chem.* **2005**, *34*, 585−596.

(17) 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.

(18) Zafarani-Moattar, M. T.; Shekaari, H. Volumetric and Speed of Sound of Ionic Liquid, 1-Butyl-3-methylimidazolium Hexafluorophosphate with Acetonitrile and Methanol at $T = (298.15$ to $318.15)$ K. *J. Chem. Eng. Data* **2005**, *50*, 1694−1699.

(19) Arce, A.; Rodil, E.; Soto, A. Physical and Excess Properties for Binary Mixtures of 1-Methyl-3-Octylimidazolium Tetrafluoroborate, [Omim]-[BF$_4$], Ionic Liquid with Different Alcohols. *J. Solution Chem.* **2006**, *35*, 63−78.

(20) 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.

(21) 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.

(22) Zhou, Q.; Wang, L.; Chen, H. Densities and Viscosities of 1-Butyl-3-methylimidazolium Tetrafluoroborate + H$_2$O Binary Mixtures from (303.15 to 353.15) K. *J. Chem. Eng. Data* **2006**, *51*, 905−908.

(23) Gómez, E.; Calvar, N.; Domínguez, I.; Domínguez, A. Physical properties of the ternary mixture ethanol + water + 1-hexyl-3-methylimidazolium chloride at 298.15 K. *Phys. Chem. Liq.* **2006**, *44*, 409−417.

(24) González, E. J.; Alonso, L.; Domínguez, A. Physical Properties of Binary Mixtures of the Ionic Liquid 1-Methyl-3-octylimidazolium Chloride with Methanol, Ethanol, and 1-Propanol at $T = (298.15$, 313.15, and $328.15)$ K and at $P = 0.1$ MPa. *J. Chem. Eng. Data* **2006**, *51*, 1446−1452.

(25) Arce, A.; Rodil, E.; Soto, A. Volumetric and Viscosity Study for the Mixtures of 2-Ethoxy-2-methylpropane, Ethanol, and 1-Ethyl-3-methylimidazolium Ethyl Sulfate Ionic Liquid. *J. Chem. Eng. Data* **2006**, *51*, 1453−1457.

(26) 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.

(27) Gómez, E.; González, B.; Calvar, N.; Tojo, E.; Domínguez, A. Physical Properties of Pure 1-Ethyl-3-methylimidazolium Ethylsulfate and Its Binary Mixtures with Ethanol and Water at Several Temperatures. *J. Chem. Eng. Data* **2006**, *51*, 2096−2102.

(28) 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.

(29) Zhong, Y.; Wang, H.; Diao, K. Densities and excess volumes of binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate with aromatic compound at $T = (298.15$ to $313.15)$ K. *J. Chem. Thermodyn.* **2007**, *39*, 291−296.

(30) Lachwa, J.; Morgado, P.; Esperança, J. M. S. S.; Guedes, H. J. R.; Canongia Lopes, J. N.; Rebelo, L. P. N. Fluid-Phase Behavior of {1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl) Imide, [C$_6$mim]-[NTf$_2$], + C$_2$-C$_8$ *n*-Alcohol} Mixtures: Liquid−Liquid Equilibrium and Excess Volumes. *J. Chem. Eng. Data* **2006**, *51*, 2215−2221.

(31) Pereiro, A. B.; Rodríguez, A. Study on the phase behaviour and thermodynamic properties of ionic liquids containing imidazolium cation with ethanol at several temperatures. *J. Chem. Thermodyn.* **2007**, *39*, 978−989.

(32) Gómez, E.; González, B.; Domínguez, A.; Tojo, E.; Tojo, J. Dynamic Viscosities of a Series of 1-Alkyl-3-methylimidazolium Chloride Ionic Liquids and Their Binary Mixtures with Water at Several Temperatures. *J. Chem. Eng. Data* **2006**, *51*, 696−701.

(33) 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.

(34) Zafarani-Moattar, M. T.; Sarmad, S. Volumetric and Ultrasonic Studies of the Poly(ethylene glycol) Methacrylate 360 + Alcohol Systems at 298.15 K. *J. Chem. Eng. Data* **2006**, *51*, 968−971.

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

(36) Resa, J. M.; González, C.; Goenaga, J. M. Density, Refractive Index, Speed of Sound at 298.15 K, and Vapor−Liquid Equilibria at 101.3

kPa for Binary Mixtures of Propanol + 2-Methyl-1-butanol and Propanol + 3-Methyl-1-butanol. *J. Chem. Eng. Data* **2006**, *51*, 73−78.

(37) Bettin, H.; Spieweck, F. Water density as function of temperature following introduction of the international temperature scale of 1990. *PBT-Mitt*. **1990**, *100*, 195−196.

(38) *DSA 5000 Density and Sound Velocity Analyzer. Instruction Manual*; Anton Paar GmbH: Graz, Austria, 2003.

(39) 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.

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

(41) Kell, G. S. Density, Thermal Expansivity, and Compressibility of Liquid Water from 0° to 150°C: Correlations and Tables for Atmospheric Pressure and Saturation Reviewed and Expressed on 1968 Temperature Scale. *J. Chem. Eng. Data* **1975**, *20*, 97−105.

(42) Benson, G. C.; Kiyohara, O. Thermodynamics of aqueous mixtures of nonelectrolytes. I. Excess volumes of water−*n*-alcohol mixtures at several temperatures. *J. Solution Chem*. **1980**, *9*, 791−804.

(43) Wilhoit, R. C.; Zwolinski, B. J. Physical and thermodynamic properties of aliphatic alcohols. *J. Phys. Chem. Ref. Data,* **1973**, *2* (Suppl. 1), 1−420.

(44) 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. *Chem. Phys. Chem*. **2001**, *2*, 148−161.

(45) Benson, G. C.; Kiyohara, O. Evaluation of excess isentropic compressibilities and isochoric heat capacities. *J. Chem. Thermodyn*. **1979**, *11*, 1061−1064.

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

(47) 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.

(48) 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.

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

(50) Bondi, A. van der Waals Volumes and Radii. *J. Phys. Chem*. **1964**, *68*, 441−451.

(51) Banerjee, T.; Singh, M. K.; Sahoo, R. K.; Khanna, A. Volume, surface and UNIQUAC interaction parameters for imidazolium based ionic liquids via Polarizable Continuum Model. *Fluid Phase Equilib.* **2005**, *234*, 64−76.

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