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Ultrasonic and Volumetric Properties of 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate Ionic Liquid with 2-Propanol or Tetrahydrofuran at Several Temperatures

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ABSTRACT: Densities and speeds of sound of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate mixtures with 2-propanol and tetrahydrofuran (THF), as well as of the pure components, have been measured over the whole range of compositions at $T = (278.15$ to $328.15)$ K and $P = (101 \pm 2)$ kPa. From these experimental data, the excess molar volume, excess speed of sound, and excess isentropic compressibility 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

Ionic liquids (ILs) are salts made up of an organic greatly asymmetric substituted cation such as imidazolium, pyridinium, pyrrolidinium, tetraalkylphosphonium, quaternary ammonium, and so forth and an anion such as halide, hexafluorophosphate, tetrafluoroborate, trifluoromethanesulfonate, acetate, alkylsulfate, and so forth, being its main feature to have a very low melting point, mainly below 100 °C. 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,[1] ILs exhibit unique properties: they are liquid in a wide range of temperatures, have no effective vapor pressure, are outstandingly good solvents for a wide range of inorganic, organic, and polymeric materials, and have a high thermal stability.[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] Applications as catalysts for organic and organometallic synthesis,[5,6] lubricants, thermofluids, plasticizers, and electrically conductive liquids in electrochemistry have also been reported.[2]

During the past few years, investigations on thermophysical and thermodynamic properties of pure ILs and their mixtures with molecular solvents have shown great augmentation. However, it is necessary to have a sufficiently large data bank available not only for process and product design but also for the development of property correlations. Specifically, experimental data of density and speed of sound of binary mixtures are important not only to design and control chemical processes but from the theoretical point of view to predict the properties and characteristics of ILs.[7]

In the present work, we report the volumetric and acoustical properties of binary mixtures of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]) with two polar solvents, a protic one, 2-propanol, and an aprotic, tetrahydrofuran (THF), over the whole range of compositions, at temperatures from (278.15 to 328.15) K and a pressure of 0.1 MPa. Both binary mixtures have total miscibility in the operation range. 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.

Despite the importance of triflate-based ILs in industrial applications, physical properties of few binary mixtures of [emim][triflate] with solvents have been reported, and those are as follows: water,[8−10] methanol,[9] ethanol,[9,11] 1-propanol,[9] nitromethane,[12] acetone,[13] methyl acetate,[13] and ethyl acetate.[13] To our knowledge, no experimental density and speed of sound measurements have been reported in the literature for the binary mixtures studied in this work.

EXPERIMENTAL SECTION

Materials. The IL used was 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (CAS Registry No. 145022-44-2). Because of its hygroscopic character, it was desiccated at 0.2 Pa overnight prior to use. The water content of the IL, determined by Karl Fischer titration, was lower than 0.0005, expressed as mass fraction. 2-Propanol (CAS Registry No. 67-63-0) and THF (CAS Registry No. 109-99-9) were purchased from Merck. Both solvents were degassed ultrasonically and dried over molecular sieves of type 3 Å supplied by Grace, the purities of them being ascertained by gas chromatography (GC). The chemical specifications of the materials used are reported in Table 1. As shown in Table 2, densities and speeds of sound of all the chemicals gave a good agreement with the corresponding literature values at 298.15 K.[8,9,11,13−26]

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

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Table 1. Specifications of Chemical Samples

chemical name	source	mass fraction purity	purification method	final water mass fraction	analysis method
2-propanol	Merck	0.998	ultrasonic degassing, molecular sieve drying		GC[a]
THF[b]	Merck	0.998	ultrasonic degassing, molecular sieve drying		GC
[emim][triflate][c]	Solvent Innovation	>0.98	vacuum desiccation	<0.0005	KF[d]

[a] GC = gas chromatography. [b] THF = tetrahydrofuran. [c] [emim][triflate] = 1-ethyl-3-methylimidazolium trifluoromethanesulfonate. [d] KF = Karl Fischer titration.

Table 2. 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}	
chemical	exptl	lit.	exptl	lit.
[emim][triflate]	1383.58	1383.58[a,b]	1435.6	1435.6[a,b]
		1383.60[c]		
		1385.3[d]		
		1387.07[e]		
2-propanol	780.89	780.98[f]	1138.16	1139.3[j]
		780.88[g]		1139[k]
		780.80[h]		
		781.10[i]		
THF	882.02	881.95[l]	1277.37	1278.49[m]
		881.996[m]		1277.90[q]
		881.98[n]		
		882.0[o]		
		882.37[p]		
		882.5[i]		

[a] Reference 9. [b] Reference 13. [c] Reference 8. [d] Reference 11. [e] Reference 14. [f] Reference 15. [g] Reference 16. [h] Reference 17. [i] Reference 18. [j] Reference 19. [k] Reference 20. [l] Reference 21. [m] Reference 22. [n] Reference 23. [o] Reference 24. [p] Reference 25. [q] Reference 26.

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 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

$$V_m = \frac{M_m}{\rho} \quad (1)$$

where $M_m = (x_1 M^\circ_1 + x_2 M^\circ_2)$, 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

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

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

$$\kappa_S = \frac{1}{\rho \cdot u^2} = \frac{V_m}{M_m \cdot u^2} \quad (3)$$

Combined standard uncertainties were estimated to be less than $7 \cdot 10^{-9}$ m^3·mol^{-1} for molar volume and 0.05 TPa^{-1} for the isentropic compressibility.

Volumetric Properties of Pure Liquids. The experimental data for the density ρ and speed of sound u of [emim][triflate] and 2-propanol at T = (278.15 to 328.15) K, and THF at T = (278.15 to 318.15) K, together with the molar volume V_m and the isentropic compressibility κ_S are given in Table 3. For all of the components, the density decreases and the molar volume increases with increasing temperature. With regard to the speed of sound, its value decreases with increasing temperature. In consequence, the isentropic compressibility of [emim][triflate] and the solvents increase with increasing temperature.

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

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

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 4, the isobaric thermal expansivity α_P at every temperature reported in Table 3 was obtained. Their combined standard uncertainty was estimated to be less than 0.002 kK^{-1}. As far as solvents and [emim][triflate] are concerned, our isobaric thermal expansivity values at 298.15 K and those reported in the literature[8,26,27] agree within 0.1 %. In Table 3, the isobaric molar heat capacity C_P values of pure components at the same temperatures have been also reported. For 2-propanol and THF, they were obtained from correlations proposed in the Daubert and Danner data compilation,[28] whereas for [emim][triflate], values given by Diedrichs and Gmehling[29] have been taken.

Volumetric Properties of Liquid Mixtures. The experimental data for the density, ρ, and speed of sound, u, for the [emim][triflate] (1) + 2-propanol (2) and [emim][triflate] (1) + THF (2) binary mixtures, together with the isentropic compressibility, κ_S, determined from eq 3, are given at several temperatures in Tables 4 and 5, respectively. As it can be seen, the density of all of the mixtures increases with the IL mole fraction, x_1, and decreases with increasing temperature, T. The same behavior is observed for the speed of sound of the mixtures. For the isentropic compressibility, the behavior is also very regular but logically contrary to the last ones: it decreases with x_1 and increases with T.

Table 3. 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 2-Propanol, THF, and [emim][triflate] at Several Temperatures[a]

T	ρ	V_m	u	κ_S	C_P	α_P
K	kg·m^{-3}	cm^3·mol^{-1}	m·s^{-1}	TPa^{-1}	J·mol^{-1}·K^{-1}	kK^{-1}
			2-Propanol			
278.15	797.34	75.370	1208.50	858.74	141.90[b]	1.006
288.15	789.22	76.146	1173.07	920.77	148.98[b]	1.041
298.15	780.89	76.959	1138.16	988.56	156.52[b]	1.084
308.15	772.28	77.817	1103.25	1063.85	164.43[b]	1.137
318.15	763.32	78.730	1068.09	1148.36	172.64[b]	1.198
328.15	753.95	79.708	1032.57	1243.99	181.05[b]	1.269
			THF			
278.15	903.71	79.783	1374.98	585.30	119.10[b]	1.189
288.15	892.92	80.747	1325.78	637.16	121.47[b]	1.214
298.15	882.02	81.744	1277.37	694.85	123.98[b]	1.242
308.15	871.00	82.778	1229.61	759.36	126.62[b]	1.273
318.15	859.84	83.853	1182.37	831.91	129.38[b]	1.308
			[emim][triflate][c]			
278.15	1400.51	185.818	1482.23	325.00	364.14	0.6078
288.15	1392.02	186.951	1458.35	337.78	370.05	0.6082
298.15	1383.58	188.092	1435.56	350.71	375.57	0.6084
308.15	1375.19	189.239	1413.16	364.13	380.72	0.6081
318.15	1366.86	190.393	1391.29	377.96	385.55	0.6075
328.15	1358.59	191.552	1369.65	392.37	390.09	0.6065

[a] Standard uncertainties u are $u(T) = 0.001$ K, $u(\rho) = 7\cdot10^{-3}$ kg·m^{-3}, $u(u) = 0.05$ m·s^{-1}, and the combined expanded uncertainty U_c is $U_c(V_m) = 7\cdot10^{-9}$ m^3·mol^{-1}, $U_c(\kappa_S) = 0.05$ TPa^{-1}, and $U_c(\alpha_P) = 0.002$ kK^{-1}. [b] From ref 28. [c] From ref 9.

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 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. 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, Douhéret et al.[30] stated it must be calculated using the expression of Benson and Kiyohara[31]

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

where ϕ_i $(= x_iV^\circ_i/V_m^{id})$ is the volume fraction of component i, and $\kappa^\circ_{S,i}$, $\alpha^\circ_{P,i}$, and $C^\circ_{P,i}$ 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[30]

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

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

Furthermore, Douhéret et al.[30] 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.

In Tables 4 and 5, excess molar volumes, excess speeds of sound, and excess isentropic compressibilities for the two 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 1.4 times that of the corresponding properties.

All of the excess properties, Q^E, for each system were correlated with the IL mole fraction, x_1, by means of an extended version[32] of the Redlich−Kister[33] equation, using the

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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) + 2-Propanol (2) at T = (278.15 to 328.15) K[a]

x_1	ρ / kg·m^{-3}	$10^6\,V_m^E$ / m^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			
0.0499	868.82	−0.210	1220.56	19.75	772.60	−27.70
0.0996	929.80	−0.287	1233.28	32.91	707.11	−41.80
0.1500	984.20	−0.356	1249.73	44.83	650.56	−52.03
0.2001	1032.07	−0.415	1267.87	54.94	602.76	−58.66
0.2994	1111.77	−0.447	1305.62	69.85	527.66	−63.78
0.4004	1177.58	−0.460	1341.69	76.73	471.74	−61.02
0.4997	1231.42	−0.481	1373.59	76.33	430.41	−53.92
0.5999	1276.64	−0.435	1401.74	69.62	398.65	−44.12
0.7019	1315.15	−0.295	1426.30	57.06	373.77	−32.59
0.7987	1347.13	−0.215	1446.99	41.53	354.53	−21.76
0.8519	1362.88	−0.159	1457.95	32.27	345.19	−16.14
0.8989	1375.94	−0.113	1465.93	22.20	338.20	−10.71
0.9462	1388.37	−0.073	1474.32	12.31	331.37	−5.74
			T = 288.15 K			
0.0499	860.62	−0.235	1188.24	22.19	822.97	−34.08
0.0996	921.53	−0.326	1203.22	37.11	749.55	−51.45
0.1500	975.84	−0.400	1221.39	50.31	686.93	−63.53
0.2001	1023.66	−0.464	1240.64	61.16	634.68	−70.85
0.2994	1103.29	−0.499	1279.65	76.61	553.51	−75.61
0.4004	1169.07	−0.510	1316.53	83.50	493.51	−71.49
0.4997	1222.91	−0.528	1348.79	82.54	449.49	−62.56
0.5999	1268.13	−0.475	1377.28	75.07	415.71	−50.87
0.7019	1306.65	−0.326	1402.57	61.91	389.04	−37.67
0.7987	1338.64	−0.236	1423.39	45.04	368.71	−25.06
0.8519	1354.39	−0.175	1434.08	34.61	359.01	−18.36
0.8989	1367.46	−0.123	1442.48	24.11	351.45	−12.30
0.9462	1379.89	−0.078	1450.78	13.21	344.31	−6.51
			T = 298.15 K			
0.0499	852.27	−0.266	1156.36	24.65	877.48	−41.60
0.0996	913.15	−0.374	1173.57	41.37	795.14	−62.82
0.1500	967.41	−0.457	1193.34	55.82	725.88	−76.91
0.2001	1015.19	−0.526	1213.71	67.47	668.68	−85.03
0.2994	1094.81	−0.566	1254.20	83.76	580.67	−89.52
0.4004	1160.58	−0.576	1291.85	90.67	516.30	−83.74
0.4997	1214.45	−0.591	1324.67	89.37	469.25	−72.77
0.5999	1259.68	−0.530	1353.63	81.25	433.25	−58.92
0.7019	1298.20	−0.368	1379.39	67.17	404.84	−43.57
0.7987	1330.20	−0.266	1400.52	49.04	383.27	−28.98
0.8519	1345.96	−0.198	1411.15	37.56	373.10	−21.14
0.8989	1359.02	−0.139	1419.76	26.33	365.04	−14.22
0.9462	1371.46	−0.087	1428.10	14.46	357.52	−7.52
			T = 308.15 K			
0.0499	843.73	−0.306	1124.50	27.22	937.30	−50.70
0.0996	904.62	−0.434	1143.92	45.79	844.78	−76.42
0.1500	958.87	−0.528	1165.29	61.55	768.02	−92.85
0.2001	1006.67	−0.606	1186.83	74.08	705.24	−101.92
0.2994	1086.30	−0.651	1228.84	91.33	609.62	−106.01
0.4004	1152.12	−0.661	1267.47	98.50	540.29	−98.34
0.4997	1206.03	−0.670	1300.96	96.95	489.91	−84.97
0.5999	1251.27	−0.599	1330.44	88.18	451.50	−68.52
0.7019	1289.82	−0.422	1356.68	73.07	421.23	−50.60
0.7987	1321.82	−0.305	1378.12	53.50	398.34	−33.61
0.8519	1337.58	−0.226	1388.70	40.87	387.67	−24.41
0.8989	1350.65	−0.159	1397.55	28.82	379.07	−16.48
0.9462	1363.08	−0.098	1405.97	15.86	371.13	−8.72
			T = 318.15 K			
0.0499	834.95	−0.358	1092.45	29.93	1003.54	−61.86
0.0996	895.92	−0.512	1114.14	50.49	899.19	−93.05
0.1500	950.21	−0.620	1137.15	67.65	813.85	−112.23
0.2001	998.06	−0.708	1159.92	81.20	744.71	−122.41
0.2994	1077.77	−0.760	1203.59	99.61	640.50	−125.99
0.4004	1143.67	−0.769	1243.34	107.23	565.61	−116.05
0.4997	1197.63	−0.771	1277.61	105.54	511.54	−99.78
0.5999	1242.91	−0.685	1307.66	96.10	470.51	−80.19
0.7019	1281.48	−0.489	1334.42	79.88	438.23	−59.13
0.7987	1313.50	−0.352	1356.18	58.70	413.94	−39.25
0.8519	1329.26	−0.262	1366.71	44.78	402.75	−28.40
0.8989	1342.33	−0.183	1375.86	31.82	393.54	−19.27
0.9462	1354.76	−0.110	1384.26	17.52	385.21	−10.17
			T = 328.15 K			
0.0499	825.89	−0.423	1060.09	32.78	1077.44	−75.57
0.0996	887.02	−0.611	1084.32	55.67	958.85	−113.81
0.1500	941.42	−0.740	1108.97	74.30	863.73	−136.16
0.2001	989.35	−0.838	1132.97	88.91	787.43	−147.50
0.2994	1069.21	−0.900	1178.52	108.79	673.38	−150.48
0.4004	1135.22	−0.906	1219.46	116.96	592.36	−137.66
0.4997	1189.27	−0.897	1254.61	115.23	534.20	−117.83
0.5999	1234.58	−0.791	1285.19	105.01	490.40	−94.31
0.7019	1273.20	−0.574	1312.60	87.67	455.87	−69.50
0.7987	1305.24	−0.412	1334.84	64.81	429.98	−46.16
0.8519	1320.99	−0.305	1345.20	49.31	418.34	−33.23
0.8989	1334.07	−0.213	1354.57	35.18	408.53	−22.59
0.9462	1346.50	−0.127	1363.14	19.51	399.68	−11.97

[a] Standard uncertainties u are $u(T)$ = 0.001 K, $u(\rho) = 7\cdot10^{-3}$ kg·m^{-3}, $u(u)$ = 0.05 m·s^{-1}, and the combined expanded uncertainty U_c is $U_c(x_1)$ = 0.0001, $U_c(V_m^E) = 1\cdot10^{-8}$ m^3·mol^{-1}, $u(u^E)$ = 0.07 m·s^{-1}, $U_c(\kappa_S)$ = 0.05 TPa^{-1}, and $U_c(\kappa_S^E)$ = 0.07 TPa^{-1}.

Padé (m, n) approximant,

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

which is the best approximation of a function by a rational function of a given order.[34]

By taking into account the influence of temperature on the excess properties, all of the coefficients A_i and B_j for each system

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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) + THF (2) at T = (278.15 to 318.15) K[a]

x_1	ρ / kg·m^{-3}	$10^6\,V_m^E$ / m^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			
0.0510	964.39	−0.482	1362.74	8.56	558.37	−10.30
0.1000	1013.94	−0.725				
0.1503	1059.68	−0.998				
0.2001	1098.67	−1.110	1373.32	38.28	482.60	−33.75
0.3001	1166.19	−1.362	1387.73	47.22	445.27	−37.82
0.3992	1217.18	−1.171	1403.51	50.28	417.08	−35.92
0.4995	1261.10	−1.055	1414.68	44.14	396.22	−29.32
0.5990	1297.75	−0.900	1432.49	42.05	375.51	−25.58
0.7014	1330.00	−0.725	1446.62	33.93	359.29	−19.25
0.7965	1356.21	−0.583	1459.00	24.68	346.39	−13.30
0.8490	1369.15	−0.480	1465.42	18.88	340.11	−9.93
0.8990	1380.34	−0.342	1470.47	12.20	335.04	−6.29
0.9511	1391.34	−0.201	1476.02	5.41	329.90	−2.80
			T = 288.15 K			
0.0510	953.89	−0.522	1316.86	10.02	604.54	−13.05
0.1000	1003.61	−0.783	1318.70	21.96	572.98	−24.70
0.1503	1049.68	−1.084	1325.42	33.29	542.30	−34.77
0.2001	1088.88	−1.209	1334.75	43.01	515.49	−41.50
0.3001	1155.19	−1.326	1353.77	54.30	472.34	−46.41
0.3992	1207.94	−1.278	1372.73	58.39	439.32	−44.92
0.4995	1252.06	−1.153	1388.05	54.18	414.54	−38.26
0.5990	1288.87	−0.984	1405.85	49.79	392.57	−32.25
0.7014	1321.24	−0.790	1421.38	40.60	374.63	−24.39
0.7965	1347.55	−0.630	1434.58	29.75	360.58	−16.87
0.8490	1360.54	−0.517	1441.44	23.00	353.75	−12.67
0.8990	1371.78	−0.368	1446.39	14.86	348.45	−8.01
0.9511	1382.83	−0.216	1452.26	6.93	342.88	−3.71
			T = 298.15 K			
0.0510	943.29	−0.565	1271.73	11.52	655.49	−16.40
0.1000	993.23	−0.849	1275.54	24.03	618.82	−29.95
0.1503	1039.61	−1.178	1285.50	37.33	582.08	−42.87
0.2001	1079.04	−1.316	1297.41	48.49	550.57	−51.27
0.3001	1145.24	−1.401	1320.76	61.96	500.56	−57.37
0.3992	1198.76	−1.399	1342.75	66.97	462.68	−55.69
0.4995	1243.08	−1.265	1361.38	63.87	434.05	−48.31
0.5990	1280.05	−1.080	1379.93	57.91	410.26	−40.07
0.7014	1312.54	−0.864	1396.76	47.45	390.52	−30.28
0.7965	1338.96	−0.684	1410.85	34.93	375.21	−20.92
0.8490	1352.00	−0.560	1418.10	27.07	367.80	−15.70
0.8990	1363.27	−0.397	1423.08	17.48	362.21	−9.90
0.9511	1374.36	−0.231	1429.25	8.26	356.19	−4.61
			T = 308.15 K			
0.0510	932.59	−0.611	1227.05	12.96	712.17	−20.36
0.1000	982.77	−0.920	1233.29	26.61	668.99	−36.77
0.1503	1029.50	−1.280	1246.47	41.97	625.19	−53.11
0.2001	1069.18	−1.435	1260.66	54.35	588.51	−63.21
0.3001	1135.87	−1.543	1288.66	70.48	530.14	−71.21
0.3992	1189.62	−1.535	1313.33	76.20	487.35	−68.70
0.4995	1234.16	−1.389	1335.45	74.46	454.33	−60.50
0.5990	1271.30	−1.188	1354.51	66.70	428.73	−49.44
0.7014	1303.92	−0.950	1372.64	54.94	407.04	−37.33
0.7965	1330.44	−0.747	1387.63	40.66	390.35	−25.78
0.8490	1343.53	−0.609	1395.25	31.59	382.34	−19.33
0.8990	1354.82	−0.428	1400.35	20.55	376.40	−12.23
0.9511	1365.93	−0.247	1406.81	9.91	369.91	−5.77
			T = 318.15 K			
0.0510	921.76	−0.661	1182.83	14.46	775.42	−25.24
0.1000	972.18	−0.995	1191.37	29.22	724.70	−45.00
0.1503	1019.22	−1.384	1207.17	46.13	673.28	−64.80
0.2001	1059.30	−1.568	1224.53	60.73	629.57	−77.96
0.3001	1126.45	−1.695	1257.06	79.55	561.79	−87.97
0.3992	1180.52	−1.688	1284.53	86.19	513.38	−84.49
0.4995	1225.28	−1.529	1309.67	85.40	475.82	−74.84
0.5990	1262.63	−1.313	1329.87	76.49	447.82	−60.85
0.7014	1295.36	−1.046	1349.02	63.08	424.20	−45.74
0.7965	1321.98	−0.818	1365.07	47.07	405.94	−31.64
0.8490	1335.11	−0.662	1372.87	36.51	397.40	−23.61
0.8990	1346.41	−0.462	1378.13	23.94	391.06	−14.99
0.9511	1357.57	−0.264	1384.92	11.75	384.05	−7.16

[a] Standard uncertainties u are $u(T)$ = 0.001 K, $u(\rho) = 7\cdot10^{-3}$ kg·m^{-3}, $u(u)$ = 0.05 m·s^{-1}, and the combined expanded uncertainty U_c is $U_c(x_1)$ = 0.0001, $U_c(V_m^E) = 1\cdot10^{-8}$ m^3·mol^{-1}, $u(u^E)$ = 0.07 m·s^{-1}, $U_c(\kappa_S)$ = 0.05 TPa^{-1}, and $U_c(\kappa_S^E)$ = 0.07 TPa^{-1}.

have been expressed as a second-order polynomial on T:

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

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

In this way, the number of coefficients is reduced because the total number of parameters for each binary system will not be $(t \times k)$ but $(3 \times k)$, where $k = m + n + 1$ is the total number of adjustable coefficients in each polynomial term, and t is the number of different temperatures tested for each system. Therefore, using eqs 11 to 13, we will simultaneously correlate the excess properties with the temperature T and the IL mole fraction x_1. The fitting parameters were estimated by the least-squares method, and the values obtained are given in Tables 6 to 8, together with the standard deviations calculated by applying the expression:

$$\sigma = \left[\frac{\sum_{i=1}^{p}\left(Q^E_{\mathrm{exptl},i} - Q^E_{\mathrm{calcd},i}\right)^2}{p - 3\cdot(m + n + 1)}\right]^{1/2} \quad (14)$$

in which p is the number of experimental data points. The choice of m and n values for the degrees of polynomials in eq 11 was made using the Akaike's Information Criterion (AIC).[35]

Figures 1 to 3 show, respectively, the experimental values of V_m^E, κ_S^E, and u^E versus the IL mole fraction x_1 at all of the temperatures tested, besides the curves obtained using the fitting

Table 6. Coefficients of the Fitting Equation for Excess Molar Volumes (V_m^E/cm^3·mol^{-1}) and the Standard Deviations (σ) of the [emim][triflate] (1) + 2-Propanol (2) and [emim][triflate] (1) + THF (2) Mixtures

	$Z_{l,0}$	$10^3\ Z_{l,1}$	$10^6\ Z_{l,2}$	$10^6\ \sigma$ / m^3·mol^{-1}
[emim][triflate] (1) + 2-Propanol (2)				
$Z = A, l = 0$	−1.8283	−9.6130	−387.038	0.0140
$Z = A, l = 1$	−0.9667	−1.9725	−128.695	
$Z = A, l = 2$	0.4847	−0.8253	87.230	
$Z = A, l = 3$	0.7858	7.2209	−86.201	
$Z = B, l = 1$	0.8026	−1.0560	25.095	
[emim][triflate] (1) + THF (2)				
$Z = A, l = 0$	−4.0289	−30.4724	−326.061	0.0296
$Z = A, l = 1$	2.7597	19.9861	140.521	
$Z = A, l = 2$	−2.9696	−20.0852	88.642	
$Z = A, l = 3$				
$Z = B, l = 1$				

Table 7. Coefficients of the Fitting Equation for Excess Isentropic Compressibility (κ_S^E/TPa^{-1}) and the Standard Deviations (σ) of the [emim][triflate] (1) + 2-Propanol (2) and [emim][triflate] (1) + THF (2) Mixtures

	$Z_{l,0}$	$10^2\ Z_{l,1}$	$10^3\ Z_{l,2}$	σ / TPa^{-1}
[emim][triflate] (1) + 2-Propanol (2)				
$Z = A, l = 0$	−203.48	−235.61	−45.479	0.368
$Z = A, l = 1$	−42.051	173.24	2.1581	
$Z = A, l = 2$	91.202	−13.600	−4.1587	
$Z = A, l = 3$	−62.318	−29.023	2.3643	
$Z = A, l = 4$				
$Z = B, l = 1$	1.0162	−0.6445	0.0527	
[emim][triflate] (1) + THF (2)				
$Z = A, l = 0$	−108.07	−246.78	−38.077	0.546
$Z = A, l = 1$	108.16	122.61	48.964	
$Z = A, l = 2$	−117.87	83.526	−47.461	
$Z = A, l = 3$	−30.327	32.879	−26.752	
$Z = A, l = 4$	125.63	−167.34	57.554	
$Z = B, l = 1$				

parameters, for each binary system. The behavior of systems, IL + 2-propanol and IL + THF, is regular and very similar. The excess molar volume V_m^E is always negative in the whole range of compositions and temperatures, and it decreases, that is, it becomes more negative, with increasing temperature, as seen in Figure 1. The behavior of the excess isentropic compressibility κ_S^E for the IL + solvent systems is very similar to the V_m^E one as reported in Figure 2. It is also negative in the whole range of 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. Last, the behavior of the excess speed of sound u^E for the IL + solvent systems is opposite to the V_m^E and

Table 8. Coefficients of the Fitting Equation for Excess Speed of Sound (u^E/m·s^{-1}) and the Standard Deviations (σ) of the [emim][triflate] (1) + 2-Propanol (2) and [emim][triflate] (1) + THF (2) Mixtures

	$Z_{l,0}$	$Z_{l,1}$	$10^3\ Z_{l,2}$	σ / m·s^{-1}
[emim][triflate] (1) + 2-Propanol (2)				
$Z = A, l = 0$	293.57	2.0678	17.053	0.893
$Z = A, l = 1$	−66.247	−1.5522	5.9113	
$Z = A, l = 2$	−5.8971	1.4149	−2.6409	
$Z = A, l = 3$				
$Z = A, l = 4$				
[emim][triflate] (1) + THF (2)				
$Z = A, l = 0$	166.81	3.3286	10.878	0.540
$Z = A, l = 1$	−89.888	−0.23156	−6.4529	
$Z = A, l = 2$	113.15	−2.8807	27.677	
$Z = A, l = 3$	62.388	0.30332	18.621	
$Z = A, l = 4$	−194.00	3.0738	−49.039	

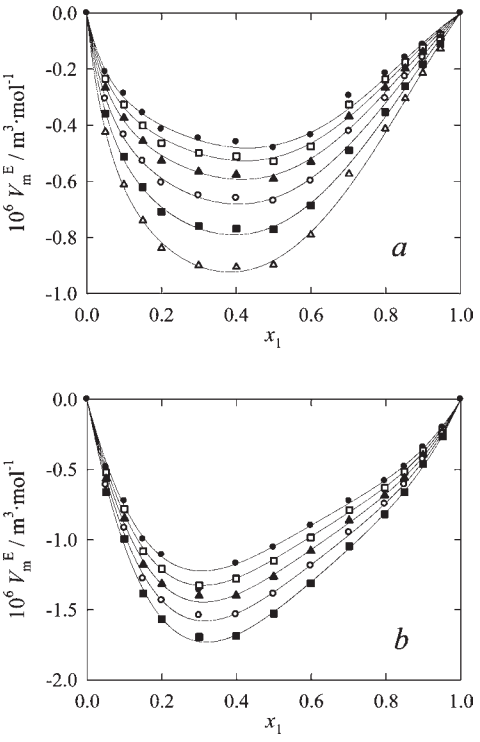

Figure 1. Excess molar volume V_m^E for the [emim][triflate] (1) + solvent (2) binary systems at different temperatures: ●, 278.15 K; □, 288.15 K; ▲, 298.15 K; ○, 308.15 K; ■, 318.15 K; △, 328.15 K. The solid lines represent the corresponding correlation by an extended version of the Redlich−Kister equation (eq 11). Solvent: (a) 2-propanol; (b) THF.

κ_S^E ones as seen in Figure 3. It is always positive in the whole range of temperatures and compositions, and it becomes more positive when temperature increases. The fitting curves are quite symmetric.

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

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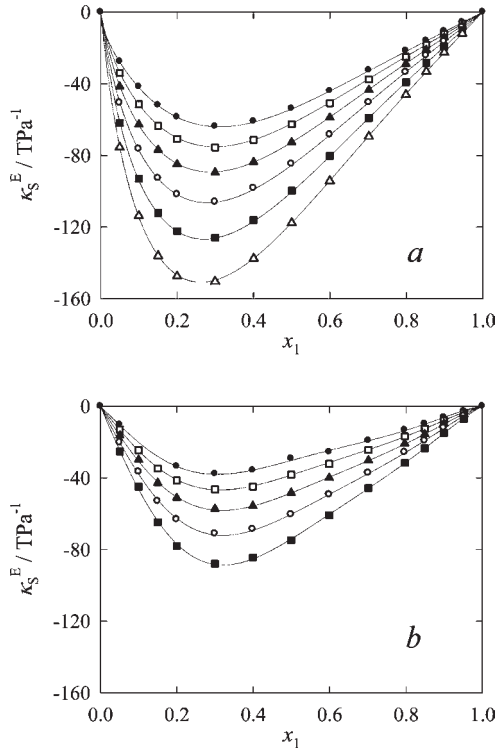

Figure 2. Excess isentropic compressibility κ_S^E for the [emim][triflate] (1) + solvent (2) binary systems at different temperatures: ●, 278.15 K; □, 288.15 K; ▲, 298.15 K; ○, 308.15 K; ■, 318.15 K; △, 328.15 K. The solid lines represent the corresponding correlation by an extended version of the Redlich−Kister equation (eq 11). Solvent: (a) 2-propanol; (b) THF.

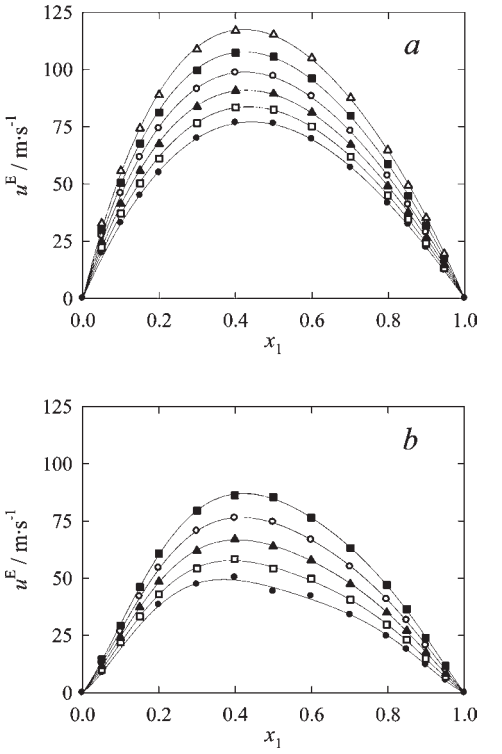

Figure 3. Excess speed of sound u^E for the [emim][triflate] (1) + solvent (2) binary systems at different temperatures: ●, 278.15 K; □, 288.15 K; ▲, 298.15 K; ○, 308.15 K; ■, 318.15 K; △, 328.15 K. The solid lines represent the corresponding correlation by an extended version of the Redlich−Kister equation (eq 11). Solvent: (a) 2-propanol; (b) THF.

thermodynamic properties for different kinds of mixtures, including those of polar components. Zafarani-Moattar and Shekaari,[36] Domanska et al.,[37] Vercher et al.,[9,13] Kumar et al.,[38−40] and Qi and Wang[41] 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:[42] (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 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:

$$\frac{V_m^E}{x_1V_1^* + x_2V_2^*} = \frac{V_m^E(\text{int})}{x_1V_1^* + x_2V_2^*} + \frac{V_m^E(\text{fv})}{x_1V_1^* + x_2V_2^*} + \frac{V_m^E(\text{ip})}{x_1V_1^* + x_2V_2^*} = \frac{(\tilde{V}^{1/3} - 1)\tilde{V}^{2/3}\Psi_2\theta_1\chi_{21}}{((4/3)\tilde{V}^{-1/3} - 1)P_2^*} - \frac{(\tilde{V}_1 - \tilde{V}_2)^2((14/9)\tilde{V}^{-1/3} - 1)\Psi_1\Psi_2}{((4/3)\tilde{V}^{-1/3} - 1)\tilde{V}} + \frac{(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)\Psi_1\Psi_2}{P_2^*\Psi_1 + P_1^*\Psi_2} \quad (15)$$

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 15, Ψ_i is the molecular contact energy fraction. All of these quantities can be deduced from the molar volumes V°_i, isobaric heat capacities $C^\circ_{P,i}$, isobaric thermal expansivity $\alpha^\circ_{P,i}$, and isentropic compressibility $\kappa^\circ_{S,i}$ values of pure components reported in Table 3, using Flory's formalisms given elsewhere,[42,36,9,13] and they are listed in Table 9.

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 2-propanol and THF were determined by dividing the van der Waals area by the van der Waals volume of the molecules obtained from the universal quasichemical (UNIQUAC) structure parameters r and q reported by Gmehling and Onken.[43] 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 15 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 10, 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 = 0.40, for both [emim][triflate] (1) + solvent (2) systems. To do the comparison, we have selected a mole fraction of x_1 = 0.40 because the V_m^E curves of all of these systems present minimum values close to this composition. A perusal of Table 10 reveals that the similar

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behavior of V_m^E of both systems observed in Figure 1 is fictitious, and it is due to the addition of the three contributions, which behave in different way each one.

For the [emim][triflate] + 2-propanol system, the interactional contribution is positive and increases with increasing 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 10 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

Table 9. Characteristic Parameters for Pure 2-Propanol, THF, and [emim][triflate] at Several Temperatures, Used in PFP Theory Calculations

T		$10^6\ V^*$	P^*	S
K	$\tilde{V}$	$m^3 \cdot mol^{-1}$	MPa	nm^{-1}
		2-Propanol		
278.15	1.235	61.029	423.31	14.87[a]
288.15	1.249	60.967	433.11	14.87[a]
298.15	1.265	60.849	445.47	14.87[a]
308.15	1.282	60.678	460.00	14.87[a]
318.15	1.302	60.463	476.36	14.87[a]
328.15	1.324	60.212	494.23	14.87[a]
		THF		
278.15	1.270	62.839	628.11	15.24[a]
288.15	1.282	62.977	625.41	15.24[a]
298.15	1.295	63.109	622.45	15.24[a]
308.15	1.309	63.235	619.09	15.24[a]
318.15	1.323	63.358	615.19	15.24[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

[a] Estimated from ref 43. [b] From ref 9.

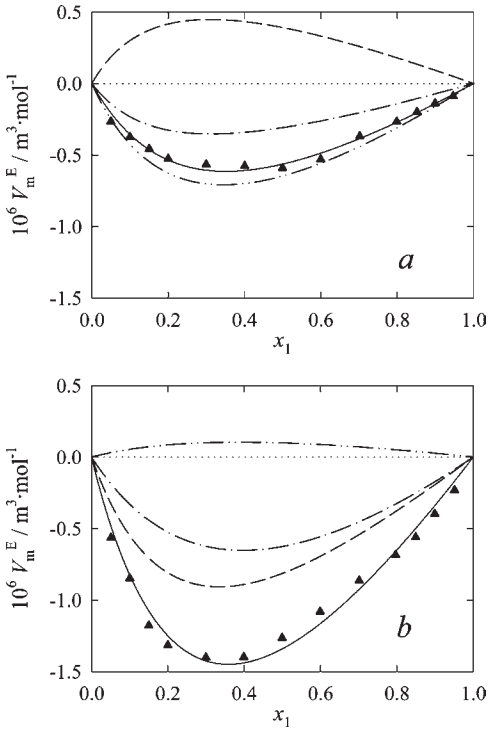

Figure 4. Excess molar volume V_m^E for the [emim][triflate] (1) + solvent (2) binary systems at T = 298.15 K calculated with the PFP theory: dashed line, interactional contribution; dotted−dashed line, free volume contribution; dotted−dotted−dashed line, internal pressure contribution; solid line, total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

Table 10. 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 = 0.40

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) + 2-Propanol (2)			
278.15	41.030	0.365	−0.220	−0.627	−0.481	−0.460
288.15	43.233	0.402	−0.271	−0.667	−0.535	−0.510
298.15	44.484	0.433	−0.341	−0.699	−0.607	−0.576
308.15	44.772	0.456	−0.434	−0.720	−0.698	−0.661
318.15	43.725	0.468	−0.558	−0.725	−0.814	−0.769
328.15	41.172	0.464	−0.719	−0.707	−0.962	−0.906
			[emim][triflate] (1) + THF (2)			
278.15	−97.70	−0.890	−0.510	0.157	−1.243	−1.171
288.15	−92.24	−0.882	−0.575	0.131	−1.327	−1.278
298.15	−88.65	−0.890	−0.652	0.103	−1.439	−1.399
308.15	−86.02	−0.908	−0.740	0.075	−1.574	−1.535
318.15	−83.12	−0.923	−0.843	0.044	−1.722	−1.688

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the other two contributions at all working temperatures. The same behavior has been observed[9] for mixtures of [emim][triflate] + methanol, ethanol, and 1-propanol.

On the other hand, for the [emim][triflate] + THF system the cross-interaction parameter χ_{21} is negative, suggesting a relative strong intermolecular specific interaction 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 10 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 and decreases when the temperature increases. The same behavior has been observed for mixtures of [emim][triflate] with other polar aprotic solvents,[13] as acetone, methyl acetate, and ethyl acetate.

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

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 2-propanol and THF mixtures have been calculated from the measured density and speed of sound data at T = (278.15 to 328.15) 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 both systems, V_m^E and κ_S^E are always negative, and they decrease with increasing temperature. The behavior of u^E for these systems is the opposite: it is always positive, and it increases with increasing temperature.

The Prigogine−Flory−Patterson theory has a good performance in predicting excess molar volumes of these mixtures, despite using only one fitting parameter. The PFP theory is suitable for explaining the great differences observed in the excess molar volume behavior of mixtures of [emim][triflate] with a protic solvent, as 2-propanol or any other alcohol, or with a polar aprotic solvent as THF, acetone, methyl acetate, or ethyl acetate.

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