PρT Measurements of Imidazolium-Based Ionic Liquids

Ramesh L. Gardas,[‡] Mara G. Freire,[‡] Pedro J. Carvalho,[‡] Isabel M. Marrucho,[‡] Isabel M. A. Fonseca,[§] Abel G. M. Ferreira,*,[§] and João A. P. Coutinho[‡]

CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal, and Departamento de Engenharia Química, Faculdade de Ciências a Tecnologia, Universidade de Coimbra, Polo II, Pinhal de Marrocos, 3030-290 Coimbra, Portugal

Experimental density measurements are reported, and the derived thermodynamic properties, such as the isothermal compressibility, the isobaric expansivity, and the thermal pressure coefficient are presented as Supporting Information for several imidazolium-based ionic liquids (ILs), namely, 1-ethyl-3-methyl-imidazolium bis-(trifluoromethylsulfonyl)imide $[C_2mim][NTf_2]$, 1-heptyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide $[C_7mim][NTf_2]$, 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide $[C_8mim][NTf_2]$, 1-ethyl-3-methyl-imidazolium tetrafluoroborate $[C_2mim][BF_4]$, and 1-butyl-3-methyl-imidazolium tricyanomethane $[C_4mim][C(CN)_3]$ in the pressure ($0.10 < p/MPa < 30.00$) and temperature ($293.15 < T/K < 393.15$) domains. These ILs were chosen to provide an understanding of the influence of the cation alkyl chain length and the anion influence on the properties under study. Experimental densities are correlated with the Tait equation with an average absolute deviation (AAD) less than 0.04 %. Experimental densities are in good agreement with the densities obtained by some recent predictive methods proposed in the literature.

Introduction

Ionic liquids (ILs) are a special class of molten salts having an appreciable liquid range. A commonly accepted practical definition for an ionic liquid is a salt with a melting temperature below the boiling point of water.[1] Most salts identified in the literature as ionic liquids are liquid at room temperature and often at substantially lower temperatures. Apart from these unusually low melting temperatures, ILs are characterized by a negligible vapor pressure,[2,3] a broad liquid range,[4] and a very rich and complex behavior as solvents[5–8] that can be modified by changing the nature of the cation or anion.

For the successful and large-scale use of ILs, an intensive and systematic investigation of their physicochemical properties is necessary. These properties are of interest from the point of view of both fundamental and applied research. On the other hand, a detailed knowledge of the thermophysical properties of ILs is important in relating microscopic and macroscopic behavior.[9–12] Studies on physical and chemical properties of ionic liquids, property measurement methodology, high-quality data on reference systems, standards for reporting thermodynamic data, and the creation of a comprehensive database have been promoted by NIST, IUPAC, and DDB (the Dortmund Data Bank).[13–15] During the past few years, investigations of thermophysical and thermodynamic properties have increased remarkably, but they are by no means exhaustive.[16–31]

Ionic liquids usually consist of a large, asymmetric organic cation coupled with a generally smaller, weakly coordinating anion. Because a large number of cationic and anionic structure combinations are possible, their physicochemical properties can be easily tuned by changing the structure of the component ions. Thus, a goal of the present study is to present reliable data for the density of five ILs and their temperature and pressure

dependence. As it is impossible to measure all the possible combinations of anions and cations, it is necessary to make accurate measurements on selected systems to provide results that may be used to develop correlations and to test predictive methods.

The most commonly used cations are those of the 1-alkyl-3-methyl-imidazolium family, $[C_nmim]$. On the other hand, the bis(trifluoromethylsulfonyl)imide anion, $[NTf_2]$, has gained in recent years some importance among the commonly used anions due to its stability to moisture, air, and high-temperature conditions. The ILs based on the $[BF_4]$ anion are historically important and commonly investigated, despite the fact that tetrafluoroborate can undergo hydrolysis producing HF in contact with water,[32,33] mainly at high temperatures.[34]

This paper is a continuation of previous work[35] on high-pressure densities and derived thermodynamic properties of imidazolium-based ILs. In this work, the experimental measurements of the pressure ($0.10 < p/MPa < 30.00$) and temperature ($293.15 < T/K < 393.15$) dependence of the density and derived thermodynamic properties, such as the isothermal compressibility, the isobaric expansivity, and the thermal pressure coefficient of several imidazolium-based ILs, are presented as Supporting Information.

The objective of this work is to contribute for the databank of thermodynamic properties of pure ILs and to investigate the relationship between ionic structures and their density, to establish principles for the molecular design of ILs. For that purpose, the $[C_2mim]$ cation was studied in combination with two anions, $[NTf_2]$ and $[BF_4]$, to conclude about the anion effect. On other hand, the $[NTf_2]$ anion was combined with three different cations, $[C_2mim]$, $[C_7mim]$, and $[C_8mim]$, to study the effect of alkyl chain length on the imidazolium ring on the density and derived properties. This completes the characterization of the $[C_nmim][NTf_2]$ series, with *n* ranging from 2 to 8, being carried by us[35,36] and Rebelo and co-workers.[24,26] To the best of our knowledge, this is also the first description of the

* To whom correspondence should be addressed. E-mail: abel@eq.uc.pt.
‡ Universidade de Aveiro.
§ Universidade de Coimbra.

densities and derived properties of a tricyanomethane-based ionic liquid.

The liquid densities were correlated with the Tait equation,[37] and other thermodynamic properties such as the isothermal compressibility, the isobaric expansivity, and the thermal pressure coefficient were calculated and reported as Supporting Information. The results show that the Tait equation correlates well the pure ILs studied with an average absolute deviation (AAD) less than 0.04 %.

The results of our study indicate that the density of the imidazolium-based ILs can be manipulated by judicious selection of the cation and anion. A regular increase in the molar volume with the addition of −CH₂ groups to the cation alkyl chain length was observed. The molar volume is also proportional to the anion effective size, and a simple ideal-volume model is shown to provide a good description of the imidazolium molar volumes at ambient conditions. Predictive density results obtained from the Ye and Shreeve[38] and Valderrama and Robles[39] methods are also in good agreement with the experimental results.

Experimental Section

Materials. Experimental densities were measured for five imidazolium-based ILs, namely, [C₂mim][NTf₂], [C₇mim]-[NTf₂], [C₈mim][NTf₂], [C₂mim][Bf₄], and [C₄mim][C(CN)₃], having molecular weights of (391.32, 461.45, 475.48, 197.97, and 229.28) g·mol⁻¹, respectively. The [C₂mim][NTf₂], [C₇-mim][NTf₂], and [C₈mim][NTf₂] were synthesized based on a metathesis anion exchange reaction of [Cₙmim][Br] (n = 2, 7, and 8) with [Li][Tf₂N] in water, according to the reported literature.[40] The reagents [Cₙmim][Br] (n = 2, 7, and 8) and [Li][Tf₂N] were acquired at IoLiTec with purities of > 99 % and > 98 %, respectively. After the IL syntheses, their purities were checked by ¹H, ¹³C, and ¹⁹F NMR spectroscopy.

The bromide content was quantified by ionic chromatography (Chromatography system Metrohm: Separation Column: Metrosep A Supp 4; Eluent: 2.00 mM NaHCO₃, 2.40 mM Na₂CO₃, 950 mL of H₂O, 50 mL of acetonitrile; flow rate: 0.5 mL·min⁻¹) and was less than (100·10⁻⁶) mole fraction in all samples. The [C₂mim][BF₄] and [C₄mim][C(CN)₃] were acquired at Merck with a mass fraction purity ≥ 99 % and a mole fraction of chloride ion ≤ (100·10⁻⁶).

To reduce the water content and volatile compounds to negligible values, a vacuum (0.1 Pa) at moderate temperature (353 K) for at least 48 h was applied to all the IL samples prior to their use. After this proceeding, the water content in the ILs was determined, with a Metrohm 831 Karl−Fischer coulometer indicating very low levels of water mass fraction content, as (42, 48, 21, 365, and 474)·10⁻⁶ for [C₂mim][NTf₂], [C₇mim]-[NTf₂], [C₈mim][NTf₂], [C₂mim][BF₄], and [C₄mim][C(CN)₃], respectively. The anolyte used for the coulometric Karl−Fischer titration was Hydranal-Coulomat AG from Riedel-de Haën.

Experimental Procedure. Experimental densities were measured using an Anton Paar DMA 60 digital vibrating tube densimeter, with a DMA 512P measuring cell in the temperature range (293.15 to 393.15) K and pressure range (0.10 to 30.00) MPa. Figure 1 shows the installation of the DMA 512P cell and the peripheral equipment used. The temperature in the vibrating tube cell was measured with a platinum resistance probe which has a temperature uncertainty of ± 0.01 K coupled with a GW Instek Dual Display Digital Multimeter (GDM-845). A Julabo P-5 thermostatic bath with silicone oil as circulating fluid was used in the thermostat circuit of the measuring cell which was held constant to ± 0.01 K. The diameter of the tube
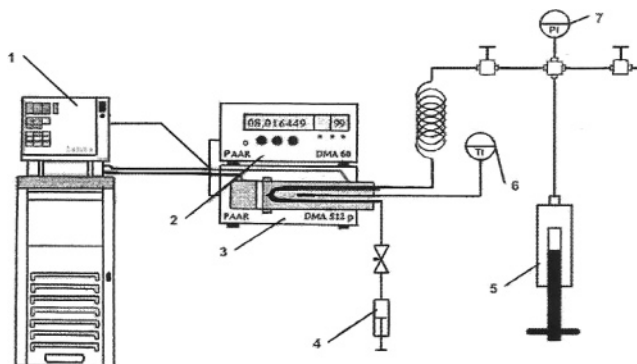

Figure 1. Experimental setup for the measurement of ionic liquid densities at high pressures: 1, Julabo FP-50 thermostatic bath; 2, DMA 60 (Anton Paar) device for measuring the period of oscillation; 3, measuring cell DMA 512P (Anton Paar); 4, syringe for sample introduction; 5, pressure generator model HIP 50-6-15; 6, PT probe; 7, pressure transducer WIKA, S-10.

Table 1. Experimental Density, ρ, Data for [C₂mim][NTf₂], [C₇mim][NTf₂], and [C₈mim][NTf₂] as a Function of Temperature and Pressure

p	ρ/kg·m⁻³ at T/K							
MPa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	393.15
				[C₂mim][NTf₂]				
0.10	1526.0	1514.9	1503.8	1493.0	1482.4	1472.0	1461.9	1424.0
1.00	1526.7	1515.6	1504.5	1493.7	1483.1	1472.7	1462.7	1424.9
2.00	1527.4	1516.3	1505.3	1494.5	1483.9	1473.5	1463.5	1425.9
3.00	1528.1	1517.0	1506.0	1495.3	1484.7	1474.4	1464.4	1426.8
4.00	1528.8	1517.7	1506.8	1496.0	1485.5	1475.2	1465.2	1427.8
5.00	1529.5	1518.5	1507.5	1496.8	1486.3	1476.0	1466.1	1428.8
7.50	1531.3	1520.3	1509.4	1498.8	1488.3	1478.1	1468.2	1431.2
10.00	1533.0	1522.1	1511.3	1500.7	1490.4	1480.2	1470.4	1433.6
15.00	1536.5	1525.7	1515.0	1504.6	1494.4	1484.3	1474.6	1438.5
20.00	1540.0	1529.3	1518.7	1508.5	1498.4	1488.4	1478.9	1443.3
25.00	1543.5	1532.9	1522.5	1512.4	1502.4	1492.5	1483.2	1448.1
30.00	1547.1	1536.6	1526.2	1516.3	1506.5	1496.7	1487.5	1453.0
				[C₇mim][NTf₂]				
0.10	1352.8	1342.5	1332.5	1322.8	1313.9	1304.2	1295.3	1261.8
1.00	1353.4	1343.2	1333.2	1323.5	1314.6	1304.9	1296.0	1262.6
2.00	1354.1	1343.9	1333.9	1324.3	1315.4	1305.8	1296.9	1263.6
3.00	1354.8	1344.6	1334.7	1325.0	1316.2	1306.6	1297.7	1264.6
4.00	1355.5	1345.3	1335.4	1325.8	1317.0	1307.4	1298.6	1265.5
5.00	1356.2	1346.1	1336.2	1326.6	1317.8	1308.2	1299.4	1266.5
7.50	1358.0	1347.9	1338.1	1328.5	1319.8	1310.2	1301.6	1268.9
10.00	1359.7	1349.7	1339.9	1330.4	1321.8	1312.2	1303.7	1271.3
15.00	1363.3	1353.3	1343.7	1334.3	1325.8	1316.3	1308.0	1276.2
20.00	1366.8	1357.0	1347.5	1338.2	1329.8	1320.3	1312.2	1281.0
25.00	1370.3	1360.6	1351.2	1342.0	1333.8	1324.4	1316.5	1285.8
30.00	1373.8	1364.3	1355.0	1345.9	1337.8	1328.4	1320.8	1290.7
				[C₈mim][NTf₂]				
0.10	1328.1	1315.7	1305.6	1296.2	1286.8	1278.0	1269.3	1236.4
1.00	1328.7	1316.3	1306.3	1296.9	1287.5	1278.7	1270.1	1237.3
2.00	1329.4	1317.1	1307.0	1297.6	1288.3	1279.6	1270.9	1238.3
3.00	1330.1	1317.8	1307.8	1298.4	1289.1	1280.4	1271.8	1239.3
4.00	1330.7	1318.5	1308.5	1299.2	1289.9	1281.2	1272.7	1240.2
5.00	1331.4	1319.2	1309.2	1299.9	1290.7	1282.1	1273.5	1241.2
7.50	1333.1	1321.0	1311.1	1301.8	1292.7	1284.2	1275.6	1243.7
10.00	1334.8	1322.8	1312.9	1303.7	1294.7	1286.2	1277.8	1246.2
15.00	1338.3	1326.3	1316.6	1307.5	1298.7	1290.4	1282.1	1251.1
20.00	1341.7	1329.9	1320.3	1311.3	1302.7	1294.6	1286.3	1256.1
25.00	1345.1	1333.5	1324.0	1315.2	1306.7	1298.8	1290.6	1261.1
30.00	1348.5	1337.1	1327.7	1319.0	1310.7	1303.0	1294.9	1266.0

is 1/16 in., and the buffer is more than 1 m in length which guarantees the inexistence of diffusion of the hydraulic liquid in the liquid contained in the cell of the densimeter.

The required pressure was generated and controlled with a pressure generator (model 50-6-15, Mftd. from High-Pressure Equipment Co.), using acetone as the hydraulic fluid. Pressures were measured with a pressure transducer (Wika Transmitter
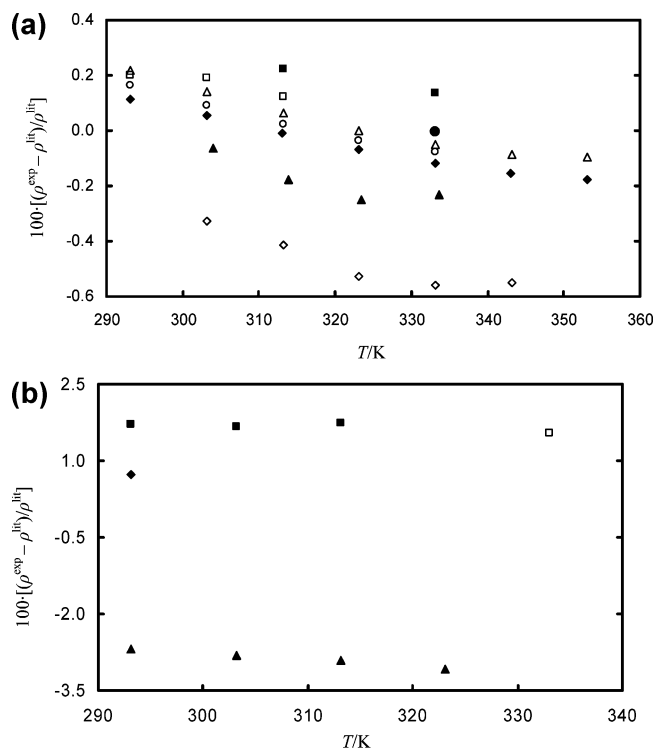
(a)

(b)

Figure 2. Relative deviations between the experimental density data of this work and those reported in the literature as a function of temperature. (a) [C$_2$mim][NTf$_2$] at 0.10 MPa: ▲, Fredakle at al.;[19] □, Noda et al.;[44] ◆, Krummen et al.;[49] ●, Lopes et al.;[50] ○, Hong et al.;[51] △, Jacquemin et al.[52] [C$_8$mim][NTf$_2$] at 0.10 MPa: ◇, Kato and Gmehling;[53] ■, Aki et al.[54] (b) [C$_2$mim][BF$_4$] at 0.10 MPa: ■, Noda et al.;[44] □, Van Valkenburg et al.;[48] ◆, Zhao et al.;[55] ▲, Zhang et al.[56]

Table 2. Experimental Density, ρ, Data for [C$_2$mim][BF$_4$] and [C$_4$mim][C(CN)$_3$] as a Function of Temperature and Pressure

p	ρ/kg·m^{-3} at T/K							
MPa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	393.15
	[C$_2$mim][BF$_4$]							
0.10	1305.5	1296.5	1288.4	1280.1	1272.3	1264.8	1257.3	1229.7
1.00	1305.9	1296.9	1288.8	1280.6	1272.8	1265.3	1257.8	1230.2
2.00	1306.3	1297.3	1289.2	1281.0	1273.3	1265.8	1258.3	1230.7
3.00	1306.7	1297.8	1289.7	1281.5	1273.7	1266.2	1258.8	1231.3
4.00	1307.1	1298.2	1290.1	1282.0	1274.2	1266.7	1259.3	1231.9
5.00	1307.6	1298.6	1290.6	1282.4	1274.7	1267.2	1259.8	1232.4
7.50	1308.6	1299.7	1291.7	1283.6	1275.9	1268.4	1261.0	1233.8
10.00	1309.7	1300.8	1292.9	1284.8	1277.1	1269.7	1262.3	1235.3
15.00	1311.8	1303.0	1295.1	1287.1	1279.4	1272.1	1264.7	1238.1
20.00	1313.9	1305.2	1297.4	1289.5	1281.8	1274.5	1267.2	1240.9
25.00	1316.0	1307.4	1299.6	1291.8	1284.2	1277.0	1269.7	1243.7
30.00	1318.1	1309.6	1301.9	1294.2	1286.6	1279.4	1272.2	1246.5
	[C$_4$mim][C(CN)$_3$]							
0.10	1051.8	1043.8	1036.3	1029.4	1022.5	1016.3	1009.9	986.7
1.00	1052.1	1044.2	1036.8	1029.8	1022.9	1016.7	1010.3	987.3
2.00	1052.6	1044.6	1037.2	1030.3	1023.4	1017.2	1010.8	987.8
3.00	1053.0	1045.0	1037.7	1030.8	1023.9	1017.7	1011.3	988.4
4.00	1053.4	1045.5	1038.1	1031.2	1024.3	1018.2	1011.8	989.0
5.00	1053.8	1045.9	1038.5	1031.7	1024.8	1018.6	1012.3	989.5
7.50	1054.8	1046.9	1039.7	1032.8	1026.0	1019.9	1013.5	990.9
10.00	1055.9	1048.0	1040.8	1033.9	1027.2	1021.1	1014.7	992.3
15.00	1058.0	1050.1	1043.0	1036.3	1029.6	1023.5	1017.2	995.0
20.00	1060.1	1052.3	1045.2	1038.6	1031.9	1025.9	1019.6	997.8
25.00	1062.2	1054.4	1047.5	1040.9	1034.3	1028.3	1022.1	1000.6
30.00	1064.3	1056.5	1049.7	1043.2	1036.7	1030.8	1024.5	1003.4

S-10, Mftd. from WIKA Alexander Wiegand GmbH & Co.) with a maximum uncertainty of ± 0.025 MPa.

The calibration of the vibrating tube densimeter was described in a previous work.[35] The equation proposed by Niesen[41] which has a solid theoretical basis as discussed by Holcom and

Table 3. Coefficients of Equation 2, along with Standard Deviation of the Fit, σ

ionic liquid	a_1 kg·m^{-3}	a_2 kg·m^{-3}·K^{-1}	a_3 kg·m^{-3}·K^{-2}	σ kg·m^{-3}
[C$_2$mim][NTf$_2$]	1965.889	−1.8568	1.2170·10^{-3}	0.08
[C$_7$mim][NTf$_2$]	1754.516	−1.7145	1.1728·10^{-3}	0.21
[C$_8$mim][NTf$_2$]	1787.101	−2.0648	1.6905·10^{-3}	0.73
[C$_2$mim][BF$_4$]	1656.185	−1.5259	1.1222·10^{-3}	0.16
[C$_4$mim][C(CN)$_3$]	1384.321	−1.4994	1.2421·10^{-3}	0.22

Table 4. Coefficients of Equations 1 and 3, along with Standard Deviation of the Fit, σ, and Average Absolute Deviation, AAD, of Equation 1

ionic liquid	C	b_1 MPa	b_2 MPa·K	σ kg·m^{-3}	AAD %
[C$_2$mim][NTf$_2$]	0.4799	−292.041	3.9216·10^5	0.07	0.004
[C$_7$mim][NTf$_2$]	0.4628	−242.854	3.3356·10^5	0.20	0.011
[C$_8$mim][NTf$_2$]	0.5221	−408.642	4.1698·10^5	0.59	0.038
[C$_2$mim][BF$_4$]	0.6895	−275.008	7.0674·10^5	0.12	0.007
[C$_4$mim][C(CN)$_3$]	0.6459	−257.718	5.5484·10^5	0.17	0.014

Outcalt[42] was fitted to the density data of the reference liquids used for that purpose. The standard deviation of the fitting is less than ± 1 kg·m^{-3}, and the average absolute deviation, AAD, from the reference density data used in the calibration is 0.002 %.

The influence of the viscosity on the densities was evaluated. To check the effect of viscosity on the density, a viscosity correction for compounds with viscosities < 100 mPa·s was applied with the equation proposed for the density uncertainty of an Anton Paar DMA 512 densimeter.[43] For compounds with viscosities higher than 400 mPa·s, the correction factor becomes constant[44] and equal to 0.5 kg·m^{-3}, and between (100 and 400) mPa·s, the viscosity correction follows an intermediate behavior. Considering, for example, the available viscosity data for [C$_2$-mim][NTf$_2$][45,46] and [C$_2$mim][BF$_4$][46−50] at atmospheric pressure and temperature in the range (293.15 to 343.15) K, where the viscosity of both ILs is inferior to 100 mPa·s, allowed us to calculate an average density uncertainty less than 0.3 kg·m^{-3}. For other ILs and/or other higher pressures where the viscosity increases, the correction value was assumed as 0.5 kg·m^{-3}, being inferior to the uncertainty in the overall density data, which is 1 kg·m^{-3}, and for that reason, viscosity corrections were neglected in the present work.

Results and Discussion

Density Measurements. Density measurements were carried out at temperatures ranging from (293.15 to 393.15) K and pressures from (0.10 to 30.00) MPa. The experimental data obtained are reported in Tables 1 and 2 for all the ILs studied.

Density data for some of the studied ILs are already available in the open literature but only at atmospheric pressure,[19,46,50,51−58] and the relative deviations between the experimental data obtained in this work are presented in Figures 2(a) and 2(b). To the best of our knowledge, no literature data on densities were previously available for [C$_7$mim][NTf$_2$] and [C$_4$mim]-[C(CN)$_3$]. Experimental data for [C$_2$mim][NTf$_2$] and [C$_8$mim]-[NTf$_2$] are in good agreement with available literature values. The relative deviations are ranging from (−0.6 to 0.2) %, and for [C$_2$mim][BF$_4$], the deviations from our data and the literature are ranging from (−3.1 to 1.7) %. As for [C$_2$mim][NTf$_2$], it is worth noting the excellent agreement with all available literature data at atmospheric pressure[19,46,51−54] (within 0.2 %). [C$_8$mim]-[NTf$_2$] density values are lower (within 0.6 %) than Kato et al.[55] and slightly higher (within 0.2 %) than Aki et al.[56] For the density comparison of [C$_8$mim][NTf$_2$], density data are calcu-
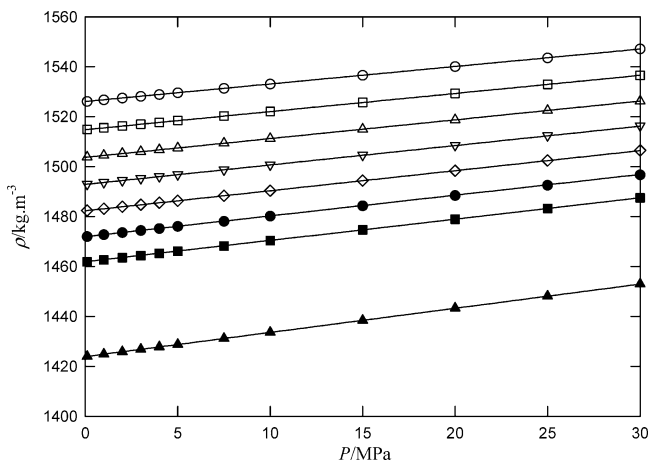
Figure 3. Isotherms of the density, ρ, for [C$_2$mim][NTf$_2$]. The symbols refer to the experimental data: $\bigcirc$, 293.15 K; $\square$, 303.15 K; $\triangle$, 313.15 K; $\triangledown$, 323.15 K; $\diamondsuit$, 333.15 K; $\bullet$, 343.15 K; $\blacksquare$, 353.15 K; $\blacktriangle$ 393.15 K.
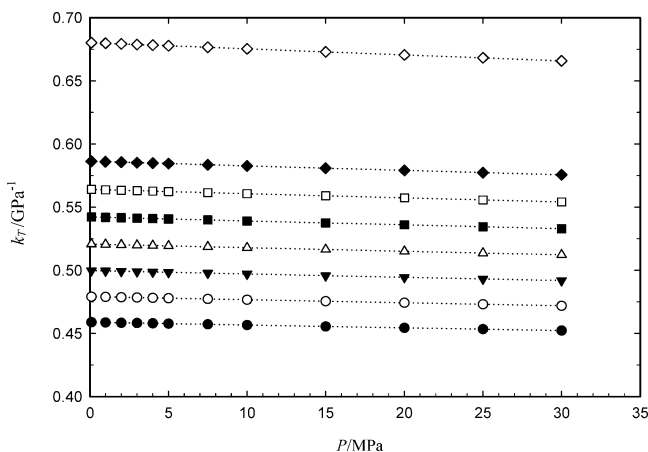
Figure 4. Isotherms for the isothermal compressibility of [C$_2$mim][NTf$_2$]: $\bullet$, 293.15 K; $\bigcirc$, 303.15 K; $\blacktriangledown$, 313.15 K; $\triangle$, 323.15 K; $\blacksquare$, 333.15 K; $\square$, 343.15 K; $\blacklozenge$, 353.15 K; $\diamondsuit$, 393.15 K.
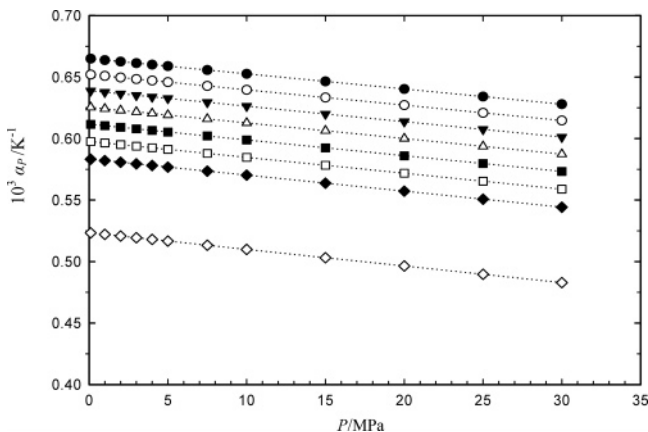
Figure 5. Isotherms for the isobaric expansivity of [C$_2$mim][BF$_4$]: $\bullet$, 293.15 K; $\bigcirc$, 303.15 K; $\blacktriangledown$, 313.15 K; $\triangle$, 323.15 K; $\blacksquare$, 333.15 K; $\square$, 343.15 K; $\blacklozenge$, 353.15 K; $\diamondsuit$, 393.15 K.

lated from molar volume for Aki et al.[56] Experimental density data of [C$_2$mim][BF$_4$] show considerably higher negative deviations (ranging from -2.7 % to -3.1 %) than the values of Zhang et al.[58] and also show positive deviations (1.7 %) from Noda et al.[46] These deviations can be due essentially to the salt's purity, including water and halides content, and also to the experimental technique adopted.

From the experimental densities for a given anion, it is observed that as the alkyl chain length in the imidazolium cation increases the density of the corresponding IL decreases. The average change of (17.4 ± 0.5) cm$^3 \cdot$mol^{-1} by the addition of $-$CH$_2$ groups observed in the measured data is in good agreement with that reported by Azevedo et al.[23,24] and Esperança et al.[25,26] and is anion-size independent.

Derived Thermodynamic Properties. The experimental density values can be used to calculate some thermodynamic properties, such as the isothermal compressibility, κ_T, the isobaric thermal expansion coefficient, α_p, and the thermal pressure coefficient, γ_v.

The following form of the Tait equation[37]

$$\rho = \frac{\rho(T, P = 0.1 \text{ MPa})}{\left\{1 - C \ln\dfrac{(B + P)}{(B + 0.1)}\right\}} \tag{1}$$

where

$$\rho(T, P = 0.1 \text{ MPa}) = a_1 + a_2 T + a_3 T^2 \tag{2}$$

was fitted to the density data. In eq 2, a_1, a_2, and a_3 were found by fitting to the experimental $\rho(T, P = 0.1 \text{ MPa})$ and are given in Table 3.

Coefficient B is defined as

$$B = b_1 + \frac{b_2}{T} \tag{3}$$

The coefficients C, b_1, and b_2 were obtained by fitting the Tait equation to experimental data, and their values along with standard deviation σ of fit are given in Table 4.

$$\sigma = \left[\sum_{i=1}^{N_p} (\rho_{calcd} - \rho_{exptl})_i^2 / (N_p - k)\right]^{1/2} \tag{4}$$

where N_p represents the number of points ($N_p = 96$) and k is the number of adjusted parameters ($k = 3$). The average absolute deviation (AAD) was defined as

$$\text{AAD} = \frac{1}{N_p} \sum_{i=1}^{N_p} 100 |(\rho_{calcd} - \rho_{exptl})/\rho_{exptl}|_i \tag{5}$$

and is listed in Table 4. Figure 3 shows good agreement between the experimental density data and isotherms obtained with the Tait equation.

The Tait equation is an integrated form of an empirical equation representative of the isothermal compressibility behavior vs pressure. The effect of pressure in density is best described by the isothermal compressibility, κ_T, that is calculated using the isothermal pressure derivative of density according to the following

$$\kappa_T = -\frac{1}{V_m}\left(\frac{\partial V_m}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T = \left(\frac{\partial \ln \rho}{\partial P}\right)_T \tag{6}$$

where ρ is the density and P is the pressure at constant temperature, T. The isothermal compressibilities can be calculated using eqs 1 and 6

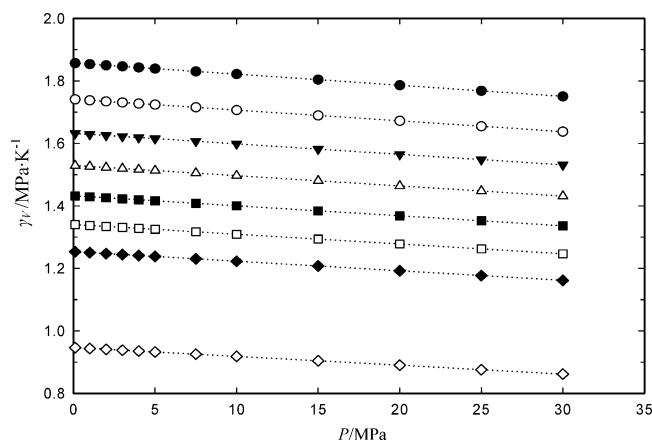$$\kappa_T = \left(\frac{C}{B + P}\right)\left(\frac{\rho}{\rho(T, P = 0.1 \text{ MPa})}\right) \tag{7}$$

Figure 6. Isotherms for the thermal pressure coefficient of [C$_4$mim]-[C(CN)$_3$]: ●, 293.15 K; ○, 303.15 K; ▼, 313.15 K; △, 323.15 K; ■, 333.15 K; □, 343.15 K; ◆, 353.15 K; ◇, 393.15 K.

For illustration purposes, the isothermal compressibilities of [C$_2$mim][NTf$_2$] are shown in Figure 4. The ILs become more compressible with increasing temperature and less compressible with increasing pressure. The calculated values of κ_T are presented in the Supporting Information, as Table ST1. In the studied range of temperatures, (293.15 to 393.15) K, and pressures, (0.1 to 30.0) MPa, the isothermal compressibilities range in GPa^{-1} is, 0.452 to 0.680, 0.508 to 0.764, 0.508 to 0.801, 0.321 to 0.453, and 0.393 to 0.560, respectively, for [C$_2$mim]-[NTf$_2$], [C$_7$mim][NTf$_2$], [C$_8$mim][NTf$_2$], [C$_2$mim][BF$_4$], and [C$_4$-mim][C(CN)$_3$]. Unfortunately, there is no literature data available for the isothermal compressibilities comparisons of studied ILs. From the law of propagation of uncertainties, we have found, by the analysis of all studied ILs, that the minimum uncertainty in κ_T was $\pm\ 2\cdot10^{-3}$ GPa^{-1} (at 293.15 K and 30 MPa) and that the maximum was $\pm\ 0.5$ GPa^{-1} (at 393.15 K and 1 MPa).

The IL isothermal compressibilities are similar to those of water and high-temperature molten salts and are less compressible than organic solvents due to the strong Coulombic interactions between the ions.[59,60]

The isobaric expansivity, α_P, is defined as

$$\alpha_P = \frac{1}{V_\mathrm{m}}\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P = -\left(\frac{\partial \ln \rho}{\partial T}\right)_P \qquad (8)$$

and the following expression is derived from the Tait equation, eq 1

$$\alpha_P = -\left\{\frac{[\mathrm{d}\rho(T,P=0.1)/\mathrm{d}T]}{\rho(T,P=0.1)}\right\} + C\left\{\frac{\frac{\mathrm{d}B}{\mathrm{d}T}(P-0.1)}{\left[1 - C\ln\left(\frac{B+P}{B+0.1}\right)\right](B+0.1)(B+P)}\right\} \qquad (9)$$

where $\mathrm{d}B/\mathrm{d}T = -b_2/T^2$. The values of α_P are presented in the Supporting Information, as Table ST2, for all investigated ILs.

α_p decreases with temperature as shown in Figure 5 for [C$_2$-mim][BF$_4$]; nevertheless, the ILs studied do not notably expand with temperature. However, there are some ILs that present more significant decreases in α_p with temperature,[15] but in fact, ILs seem to not expand markedly with temperature and have α_p values lower than most organic liquids and similar to that of water. From eq 9, the isobaric expansivity, for the studied range
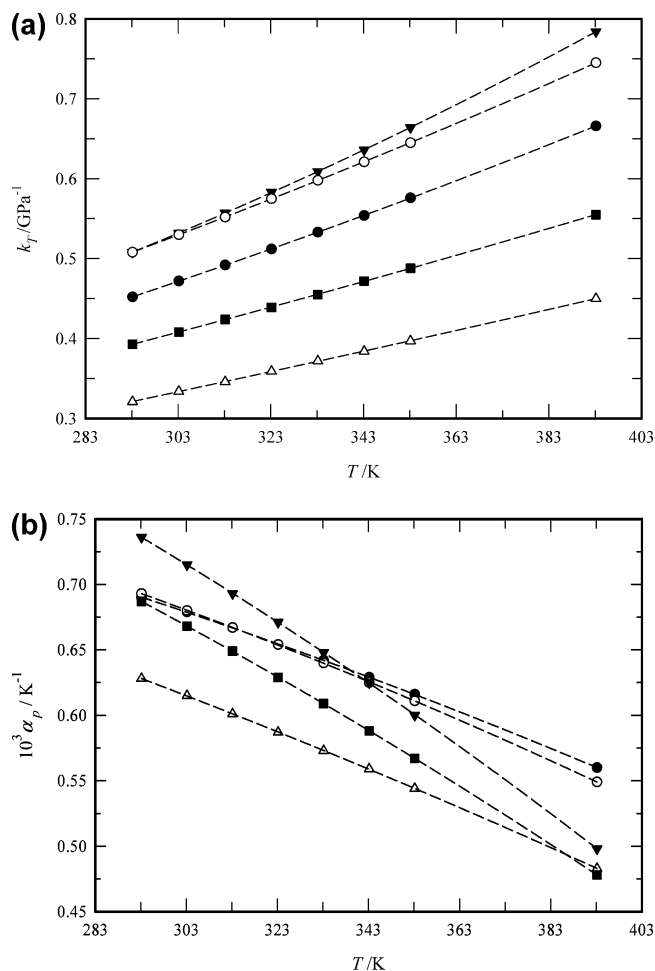

Figure 7. (a) Isothermal compressibility at 30.00 MPa as a function of temperature. (b) Isobaric expansivity at 30.00 MPa as a function of temperature: ●, [C$_2$mim][NTf$_2$]; ○, [C$_7$mim][NTf$_2$]; ▼, [C$_8$mim][NTf$_2$]; △, [C$_2$mim][BF$_4$]; and ■, [C$_4$mim][C(CN)$_3$].
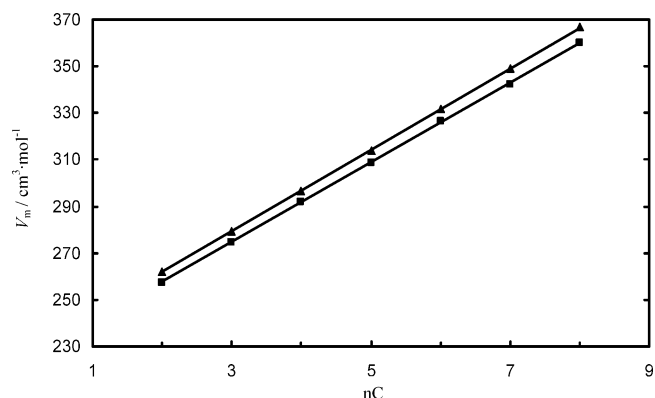

Figure 8. Orthobaric molar volume as a function of the number of carbons, nC, on the series of [C$_n$mim][NTf$_2$]: ■, 298.15 K; ▲, 323.15 K.

of temperatures (293.15 to 393.15) K and pressures (0.1 to 30.0) MPa, is {(0.560 to 0.749)$\cdot10^{-3}$, (0.549 to 0.759)$\cdot10^{-3}$, (0.498 to 0.809)$\cdot10^{-3}$, (0.483 to 0.665)$\cdot10^{-3}$, and (0.478 to 0.733)$\cdot10^{-3}$} K^{-1}, respectively, for [C$_2$mim][NTf$_2$], [C$_7$mim][NTf$_2$], [C$_8$mim]-[NTf$_2$], [C$_2$mim][BF$_4$], and [C$_4$mim][C(CN)$_3$]. A similar procedure is that used for κ_T which allows us to determine the uncertainties in α_P. The minimum value was $\pm\ 1\cdot10^{-5}$ K^{-1} (at 293.15 K and 0.1 MPa), and the maximum was $\pm\ 7\cdot10^{-4}$ K^{-1} (at 393.15 K and 30 MPa).

Table 5. Effective Molar Volume of Anions (V^*_a) and Cations (V^*_c) and Estimated Molar Volumes (V_m) at 298.15 K

	V^*_a		V^*_c	estimated V_m	exptl[b] V_m	deviation of V_m
anion	cm³·mol⁻¹	cation	cm³·mol⁻¹	cm³·mol⁻¹	cm³·mol⁻¹	%
[NTf₂]	158.7	[C₂mim]	99.2	257.9	257.4	0.2
[NTf₂]	158.7	[C₇mim]	183.8[a]	---	342.4	---
[NTf₂]	158.7	[C₈mim]	202.34	361.0	359.7	0.3
[BF₄]	53.4	[C₂mim]	99.2	152.6	152.2	0.3
[C(CN)₃]	85.3[a]	[C₄mim]	133.58	---	218.8	---

[a] Calculated in this work. [b] Obtained from eq 2.

Table 6. Estimated Densities, ρ^{est}, by the Ye and Shreeve Method of Group Additivity, Using Volume Parameters and Their Relative Deviations, $100(\delta\rho/\rho)$, from Experimental Values for [C₂mim][NTf₂], [C₇mim][NTf₂], [C₈mim][NTf₂], [C₂mim][BF₄], and [C₄mim][C(CN)₃] at 298.15 K

ionic liquid	ρ^{est}/kg·m⁻³	$100(\delta\rho/\rho)^a$
[C₂mim][NTf₂]	1511.2	−0.6
[C₇mim][NTf₂]	1344.3	−0.2
[C₈mim][NTf₂]	1320.4	−0.1
[C₂mim][BF₄]	1289.2	−0.9
[C₄mim][C(CN)₃]	1054.7	0.7

[a] $(\delta\rho/\rho) = (\rho^{est} - \rho^{exptl})/\rho^{exptl}$, where ρ^{exptl} is obtained from eq 2.

The thermal pressure coefficient, γ_V, may be calculated according to

$$\gamma_V = \frac{\alpha_p}{\kappa_T} \tag{10}$$

The thermal pressure coefficients as a function of pressure obtained for investigated ILs, as well as the associated uncertainties, are shown in Figure 6 for [C₄mim][C(CN)₃]. The γ_V decreases with temperature and increases slightly with pressure for all the ILs studied (see Supporting Information, Table ST3). The uncertainties in γ_V were determined with the law of propagation of errors from those of α_p and κ_T. We have obtained high uncertainties of the same magnitude of the thermal pressure coefficient.

A comparison for the isothermal compressibilities and isobaric thermal expansivities as a function of temperature at a constant pressure of 30.00 MPa for the ILs studied is presented in Figure 7. From Figure 7(a), there is an indication that the ILs with higher molar volumes are generally more compressible because the κ_T increases with the alkyl chain length of the cation and with the effective anion size. On the other side, Figure 7(b) shows that the isobaric expansivity increases with the alkyl chain length of the cation and with the effective anion size.

Density Modeling

Esperança Method. Esperança et al.[26] have proposed a simple model for IL molar volume prediction, where the molar volume, V_m, of a given ionic liquid is considered as the sum of the effective molar volumes occupied by the cation, V^*_c, and the anion, V^*_a

$$V_m = V^*_c + V^*_a \tag{11}$$

Using this approach, for a given ionic liquid knowing the effective size of the anion, it is possible to determine the molar volume of the cation and vice versa. Moreover, it was verified that there is a proportional increment with the methyl groups which is irrespective of the anion identity. Thus, it was possible to use the molar volumes presented by Esperança et al.[26] for the estimation of the volume of a new anion group ([C(CN)₃]) and a new cation group ([C₇mim]). The effective molar volumes of these new groups are reported in Table 5 along with predictions of the molar volumes of the studied ionic liquids. Deviations from experimental values are ≤ 0.3 %, showing the good predictive capability of this simple model. The molar volumes for a series of ionic liquids with the same cation seem to increase with the effective anion size from [BF₄] < [NTf₂], and taking into account the results of our previous paper,[35] the same trend is shown, [C(CN)₃] < [BF₄] < [PF₆] < [NTf₂]. Due to differences in molecular weight, this effect is not directly translated into a similar dependence in the densities.

Figure 8 shows a comparison of the molar volumes obtained for the series of [C$_n$mim][NTf₂] (this work and refs 24 and 26) at two temperatures, (298.15 and 323.15) K, indicating linear trends with slopes in close accordance with the one anticipated by Esperança et al.[26] The variation of the molar volume per addition of one carbon atom in the alkyl chain, $(\partial V_m/\partial n)$, is, respectively, {(17.1 ± 0.5) and (17.5 ± 0.5)} cm³·mol⁻¹ at temperatures (298.15 and 323.15) K.

Ye and Shreeve Method. Recently, Ye and Shreeve[38] developed the method proposed by Jenkins et al.,[61] to extend its applicability to predict the density of ionic liquids. Following the procedure of Jenkins et al.,[61] they calculated volumes of a number of ions and also refined the values of a few ions. This method could be seen as a group contribution version of the Esperança method with a larger database allowing for the prediction of a much larger number of ionic liquid densities.

The density of the five investigated ILs, at 298.15 K, were calculated by directly using volume parameters of ions and

Table 7. Calculated Densities, ρ^{calcd}, with the Generalized Correlation Equation 12 and Their Relative Deviations, $100(\delta\rho/\rho)$, from Experimental Values for [C₂mim][NTf₂], [C₇mim][NTf₂], [C₈mim][NTf₂], [C₂mim][BF₄], and [C₄mim][C(CN)₃]

	[C₂mim][NTf₂]		[C₇mim][NTf₂]		[C₈mim][NTf₂]		[C₂mim][BF₄]		[C₄mim][C(CN)₃]	
	ρ^{calcd}		ρ^{calcd}		ρ^{calcd}		ρ^{calcd}		ρ^{calcd}	
T/K	kg·m⁻³	$100(\delta\rho/\rho)$	kg·m⁻³	$100(\delta\rho/\rho)$	kg·m⁻³	$100(\delta\rho/\rho)$	kg·m⁻³	$100(\delta\rho/\rho)$	kg·m⁻³	$100(\delta\rho/\rho)$
293.15	1470.0	−3.7	1417.9	4.8	1415.0	6.5	1156.5	−11.4	1131.9	7.6
303.15	1464.7	−3.3	1412.7	5.2	1409.8	7.1	1143.7	−11.8	1126.3	7.9
313.15	1459.4	−3.0	1407.4	5.6	1404.5	7.6	1130.8	−12.2	1120.7	8.1
323.15	1454.1	−2.6	1402.2	6.0	1399.2	7.9	1117.7	−12.7	1115.0	8.3
333.15	1448.8	−2.3	1396.8	6.3	1393.9	8.3	1104.3	−13.2	1109.4	8.5
343.15	1443.4	−1.9	1391.5	6.7	1388.6	8.7	1090.7	−13.8	1103.7	8.6
353.15	1438.0	−1.6	1386.2	7.0	1383.3	9.0	1077.0	−14.3	1098.0	8.7
393.15	1416.3	−0.5	1364.6	8.2	1361.7	10.1	1019.1	−17.1	1074.9	8.9

groups from Ye and Shreeve.[38] The volume of the anion $[C(CN)_3]^-$ is deduced as 123 Å^3 from $[C(NO_2)_3]^-$ (141 Å^3), NO_2 (36 Å^3), and CN(30 Å^3). Predicted density data by using volume parameters and their relative deviations from experimental data are shown in Table 6, for the investigated ILs, at 298.15 K.

Valderrama and Robles Method. Recently, Valderrama and Robles[39] used the modified Lydersen−Joback−Reid group contribution method to extend its applicability to predict the critical properties of ionic liquids. The extension of the method has been done in a simple way and also included three new groups: −B, −SO$_2$, and −P.

Using these critical properties, it is possible to predict liquid densities based on the equation of Spencer and Danner[62] that requires only the normal boiling temperature, the molecular weight, and the critical properties

$$\rho_L = \frac{MP_c}{RT_c}\left[\frac{0.3445P_c V_c^{1.0135}}{RT_c}\right]^\Omega \qquad (12)$$

$$\Omega = -\left[\frac{1 + (1 - T_R)^{2/7}}{1 + (1 - T_{bR})^{2/7}}\right] \qquad (13)$$

In these equations, ρ_L is the liquid density in grams per cubic centimeter; M is the molecular weight; R is the ideal gas constant; P_c, V_c, and T_c are critical pressure, volume, and temperature, repectively; T_R is the reduced temperature; and T_{bR} is the reduced temperature at the normal boiling point.

Using eq 12, we predicted the density values for all the investigated ILs in the temperature range (298.15 to 393.15) K and at atmospheric pressure. The normal boiling temperature and critical properties calculated by Valderrama and Robles[39] were used for the density prediction of [C$_2$mim][NTf$_2$], [C$_8$-mim][NTf$_2$], and [C$_2$mim][BF$_4$], whereas for [C$_7$mim][NTf$_2$] and [C$_4$mim][C(CN)$_3$], they are calculated using the modified Lydersen−Joback−Reid method developed by Valderrama and Robles.[39] The calculated values of T_b/K, P_c/bar, V_c /cm^3·mol^{-1}, and T_c/K for [C$_7$mim][NTf$_2$] are 920.4, 22.3, 1178.5, and 1299.6 and for [C$_4$mim][C(CN)$_3$] are 908.0, 20.4, 837.3, and 1166.7, respectively. Predicted density data from eq 12 and their relative deviations from experimental data are shown in Table 7 for all five investigated ILs.

Conclusions

Experimental density data for five pure ILs in the temperature range (293.15 to 393.15) K and pressure range (0.10 to 30.00) MPa are presented. Density results show that it can be explained by structural variations in the cation and anion. From the experimental data, a proportional molar volume increase with the −CH$_2$ addition to the alkyl chain length of the 1-C$_n$-3-methyl-imidazolium-based ILs and a molar volume increase with the effective anion size were observed. The liquid densities were correlated with the Tait equation[37] that has been shown to describe well all the pure ILs studied with an average absolute deviation (AAD) less than 0.04 %.

The experimental results were also used to derive some thermodynamic properties such as the isothermal compressibility, the isobaric expansivity, and the thermal pressure coefficient of the studied ILs that are difficult to obtain by direct measurements at extreme conditions of pressure and temperature.

Three recently proposed methods for the prediction of ionic liquid densities were tested against the measured densities with good results.

Supporting Information Available:

An additional three tables. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Wilkes, J. S. Short History of Ionic Liquids−from molten salts to neoteric solvents. *Green Chem.* **2002**, *4*, 73−80.

(2) Earle, M. J.; Esperançüa, J. M. S. S.; Gilea, M. A.; Canongia Lopes, J. N.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. The Distillation and Volatility of Ionic Liquids. *Nature* **2006**, *439*, 831−834.

(3) Zaitsau, Dz. H.; Kabo, G. J.; Strechan, A. A.; Paulechka, Ya. U.; Tschersich, A.; Verevkin, S. P.; Heintz, A. Experimental Vapor Pressures of 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl) imides and a Correlation Scheme for Estimation of Vaporization Enthalpies of Ionic Liquids. *J. Phys. Chem. A* **2006**, *110*, 7303−7306.

(4) Baranyai, K. J.; Deacon, G. B.; MacFarlane, D. R.; Pringle, J. M.; Scott, J. L. Thermal Degradation of Ionic Liquids at Elevated Temperatures. *Aust. J. Chem.* **2004**, *57*, 145−147.

(5) Scurto, A. M.; Aki, S. N. V. K.; Brennecke, J. CO$_2$ as a Separation Switch for Ionic Liquid/Organic Mixtures. *J. Am. Chem. Soc.* **2002**, *124*, 10276−10277.

(6) Gutowski, K. E.; Broker, G. A.; Willauer, H. D.; Huddleston, J. G.; Swatloski, R. P.; Holbrey, J. D.; Rogers, R. D. Controlling the Aqueous Miscibility of Ionic Liquids: Aqueous Biphasic Systems of Water-Miscible Ionic Liquids and Water-Structuring Salts for Recycle, Metathesis, and Separations. *J. Am. Chem. Soc.* **2003**, *125*, 6632−6633.

(7) Łachwa, J.; Szydlowski, J.; Najdanovic-Visak, V.; Rebelo, L. P. N.; Seddon, K. R.; Nunes da Ponte, M.; Esperançüa, J. M. S. S.; Guedes, H. J. R. Evidence for Lower Critical Solution Behavior in Ionic Liquid Solutions. *J. Am. Chem. Soc.* **2005**, *127*, 6542−6543.

(8) Łachwa, J.; Bento, I.; Duarte, M. T.; Canongia Lopes, J. N.; Rebelo, L. P. Condensed Phase Behaviour of Ionic Liquid-Benzene Mixtures: Congruent Melting of a [Emim][NTf$_2$]·C$_6$H$_6$ Inclusion Crystal. *Chem. Commun.* **2006**, *23*, 2445−2447.

(9) Morrow, T. I.; Maginn, E. J. Molecular Dynamics Study of the Ionic Liquid 1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate. *J. Phys. Chem. B* **2002**, *106*, 12807−12813.

(10) Shah, J. K.; Brennecke, J. F.; Maginn, E. J. Thermodynamic properties of the ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate from Monte Carlo simulations. *Green Chem.* **2002**, *4*, 112−118.

(11) Lopes, J. N. C.; Deschamps, J.; Padua, A. A. H. Modeling Ionic Liquids Using a Systematic All-Atom Force Field. *J. Phys. Chem. B* **2004**, *108*, 2038−2047.

(12) Cadena, C.; Anthony, J. L.; Shah, J. K.; Morrow, T. I.; Brennecke, J. F.; Maginn, E. J. Why Is CO$_2$ So Soluble in Imidazolium-Based Ionic Liquids? *J. Am. Chem. Soc.* **2004**, *126*, 5300−5308.

(13) IUPAC. Physical and Biophysical Chemistry Division (I), Ionic Liquids Database. http://www.iupac.org/projects/2003/2003-020-2-100.html.

(14) IUPAC Ionic Liquids Database (IL Thermo), NIST Standard Reference Database # 147. http://ilthermo.boulder.nist.gov/ILThermo/mainmenu.uix.

(15) DDB, The Dortmund Data Bank, Ionic Liquids in the Dortmund Data Bank. http://www.ddbst.de/new/frame_ionic_liquids.htm.

(16) Marsh, K. N.; Boxall, J. A.; Lichtenthaler, R. Room temperature ionic liquids and their mixtures - a review. *Fluid Phase Equilib.* **2004**, *219*, 93−98.

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

(18) Zhang, S.; Sun, N.; He, X.; Lu, X.; Zhang, X. Physical Properties of Ionic Liquids: Database and Evaluation. *J. Phys. Chem. Ref. Data* **2006**, *35*, 1475−1517.

(19) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. Thermophysical properties of imidazolium-based ionic liquids. *J. Chem. Eng. Data* **2004**, *49*, 954−964.

(20) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. Physicochemical properties and structures of room temperature ionic liquids. 1. Variation of anionic species. *J. Phys. Chem. B* **2004**, *108*, 16593−16600.

(21) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. Physicochemical properties and structures of room temperature ionic liquids. 2. Variation of alkyl chain length in imidazolium cation. *J. Phys. Chem. B* **2005**, *109*, 6103−6110.

(22) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. Physicochemical properties and structures of room temperature ionic liquids. 3. Variation of cationic structures. *J. Phys. Chem. B* **2006**, *110*, 2833−2839.

(23) Azevedo, R. G.; Esperança, J. M. S. S.; Najdanovic-Visak, V.; Visak, Z. P.; Guedes, H. J. R.; Nunes da Ponte, M.; Rebelo, L. P. N.

Thermophysical and Thermodynamic Properties of 1-Butyl-3-methylimidazolium Tetrafluoroborate and 1-Butyl-3-methylimidazolium Hexafluorophosphate over an Extended Pressure Range. *J. Chem. Eng. Data* **2005**, *50*, 997−1008.

(24) Azevedo, R. G.; Esperança, J. M. S. S.; Szydlowski, J.; Visak, Z. P.; Pires, P. F.; Guedes, H. J. R.; Rebelo, L. P. N. Thermophysical and Thermodynamic Properties of Ionic Liquids over an Extended Pressure Range: [bmim][NTf₂] and [hmim][NTf₂]. *J. Chem. Thermodyn.* **2005**, *37*, 888−899.

(25) Esperança, J. M. S. S.; Guedes, H. J. R.; Blesic, M.; Rebelo, L. P. N. Densities and Derive Thermodynamic Properties of Ionic Liquids. 3. Phosphonium-Based Ionic Liquids over an Extended Pressure Range. *J. Chem. Eng. Data* **2006**, *51*, 237−242.

(26) Esperança, J. M. S. S.; Visak, Z. P.; Plechkova, N. V.; Seddon, K. R.; Guedes, H. J. R.; Rebelo, L. P. N. Densities and Derive Thermodynamic Properties of Ionic Liquids. 3. [C₃mim][NTf₂] and [C₅mim][NTf₂]. *J. Chem. Eng. Data* **2006**, *51*, 2009−2015.

(27) Domanska, U. Solubilities and Thermophysical Properties of Ionic Liquids. *Pure Appl. Chem.* **2005**, *77*, 543−557.

(28) Domanska, U. Thermophysical Properties and Thermodynamic Phase behavior of Ionic Liquids. *Thermochim. Acta* **2006**, *448*, 19−30.

(29) Pereiro, A. B.; Verdia, P.; Tojo, E.; Rodriguez, A. Physical Properties of 1-Butyl-3-methylimidazolium Methyl Sulfate as a Function of Temperature. *J. Chem. Eng. Data* **2007**, *52*, 377−380.

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

(31) Greaves, T. L.; Weerawardena, A.; Fong, C.; Krodkiewska, I.; Drummond, C. J. Protic Ionic Liquids: Solvents with Tunable Phase Behavior and Physicochemical Properties. *J. Phys. Chem. B* **2006**, *110*, 22479−22487.

(32) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Griffin, S. T.; Rogers, R. D. Traditional Extractants in Nontraditional Solvents: Groups 1 and 2 Extraction by Crown Ethers in Room-Temperature Ionic Liquids. *Ind. Chem. Res.* **2000**, *39*, 3596−3604.

(33) Swatloski, R. P.; Holbrey, J. D.; Rogers, R. D. Ionic liquids are not always green: hydrolysis of 1-butyl-3-methylimidazolium hexafluorophosphate. *Green Chem.* **2003**, *5*, 361−363.

(34) Najdanovic-Visak, V.; Esperancüa, J. M. S. S.; Rebelo, L. P. N.; Nunes da Ponte, M.; Guedes, H. J. R.; Seddon, K. R.; Szydlowski, J. Phase behaviour of room temperature ionic liquid solutions: an unusually large co-solvent effect in (water + ethanol). *Phys. Chem. Chem. Phys.* **2002**, *4*, 1701−1703.

(35) Gardas, R. L.; Freire, M. G.; Carvalho, P. J.; Marrucho, I. M.; Fonseca, I. M. A.; Ferreira, A. G. M.; Coutinho, J. A. P. High-Pressure Densities and Derived Thermodynamic Properties of Imidazolium-Based Ionic Liquids. *J. Chem. Eng. Data* **2007**, *52*, 80−88.

(36) Freire, M. G.; Carvalho, P. J.; Gardas, R. L.; Santos, L. M. N. B. F.; Marrucho, I. M.; Coutinho, J. A. P. Mutual solubilities of water and ionic liquids of the [Cₙmim][Tf₂N] series. *Green Chem.,* submitted for review.

(37) Dymond, J. H.; Malhotra, R. The Tait equation: 100 years on. *Int. J. Thermophys.* **1988**, *9*, 941−951.

(38) Ye, C.; Shreeve, J. M. Rapid and Accurate Estimation of Densities of Room-Temperature Ionic Liquids and Salts. *J. Phys. Chem. A* **2007**, *111*, 1456−1461.

(39) Valderrama, J. O.; Robles, P. A. Critical Properties, Normal Boiling Temperatures, and Acentric Factors of Fifty Ionic Liquids. *Ind. Eng. Chem. Res.* **2007**, *46*, 1338−1344.

(40) Bonhôte, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 1168−1178.

(41) Niesen, V. G. (Vapor + Liquid) Equilibria and Coexisting Densities of (Carbon Dioxide + n-butane) at 311 to 395 K. *J. Chem. Thermodyn.* **1990**, *22*, 777−795.

(42) Holcomb, C. D.; Outcalt, S. L. A Theoretical-Based Calibration and Evaluation Procedure for Vibrating-Tube Densimeters. *Fluid Phase Equilib.* **1998**, *150−151*, 815−827.

(43) Fandiño, O.; Pensado, A. S.; Lugo, L.; Comuñas, M. P. J.; Fernández, J. Compressed Liquid Densities os Squalane and Pentarythritol Tetra-(2-ethylhexanoate). *J. Chem. Eng. Data* **2005**, *50*, 939−946.

(44) Fandiño, O.; Garcia, J.; Comuñas, M. P. J.; López, E. R.; Fernández, J. PρT Measurements and Equation of State (EoS) Predictions of Ester Lubricants up to 45 MPa. *Ind. Eng. Chem. Res.* **2006**, *45,* 1172−1182.

(45) Crosthwaite, J. M.; Muldoon, M. J.; Dixon, J. K.; Anderson, J. L.; Brennecke, J. F. Phase transition and decomposition temperatures, heat capacities and viscosities of pyridinium ionic liquids. *J. Chem. Thermodyn.* **2005**, *37*, 559−568.

(46) Noda, A.; Hayamizu, K.; Watanabe, M. Pulsed-Gradient Spin-Echo ¹H and ¹⁹F NMR Ionic Diffusion Coefficient, Viscosity, and Ionic Conductivity of Non-Chloroaluminate Room-Temperature Ionic Liquids. *J. Phys. Chem. B* **2001**, *105*, 4603−4610.

(47) 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 + H₂O. *J. Chem. Eng. Data* **2004**, *49*, 760−764.

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

(49) Nishida, T.; Tashiro, Y.; Yamamoto, M. Physical and electrochemical properties of 1-alkyl-3-methylimidazolium tetrafluoroborate for electrolyte. *J. Fluorine Chem.* **2003**, *120*, 135−141.

(50) Van Valkenburg, M. E.; Vaughn, R. L.; Williams, M.; Wilkes, J. S. Thermochemistry of ionic liquid heat-transfer fluids. *Thermochim. Acta* **2005**, *425*, 181−188.

(51) Krummen, M.; Wasserscheid, P.; Gmehling, J. Measurement of Activity Coefficients at Infinite Dilution in Ionic Liquids Using the Dilutor Technique. *J. Chem. Eng. Data* **2002**, *47*, 1411−1417.

(52) Lopes, J. N. C.; Cordeiro, T. C.; Esperança, J. M. S. S.; Guedes, H. J. R.; Huq, S.; Rebelo, L. P. N.; Seddon, K. R. Deviations from Ideality in Mixtures of Two Ionic Liquids Containing a Common Ion. *J. Phys. Chem. B* **2005**, *109*, 3519−3525.

(53) Hong, G.; Jacquemin, J.; Husson, P.; Costa Gomes, M. F.; Deetlefs, M.; Nieuwenhuyzen, M.; Sheppard, O.; Hardacre, C. Effect of Acetonitrile on the Solubility of Carbon Dioxide in 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide. *Ind. Eng. Chem. Res.* **2006**, *45*, 8180−8188.

(54) Jacquemin, J.; Husson, P.; Padua, A. A. H.; Majer, V. Density and viscosity of several pure and water-saturated ionic liquids. *Green Chem.* **2006**, *8*, 172−180.

(55) Kato, R.; Gmehling, J. Systems with ionic liquids: Measurement of VLE and c1 data and prediction of their thermodynamic behavior using original UNIFAC, mod. UNIFAC(Do) and COSMO-RS(Ol). *J. Chem. Thermodyn.* **2005**, *37*, 603−619.

(56) Aki, S. N. V. K.; Mellein, B. R.; Saurer, E. M.; Brennecke, J. F. High-Pressure Phase Behavior of Carbon Dioxide with Imidazolium-Based Ionic Liquids. *J. Phys. Chem. B* **2004**, *108*, 20355−20365.

(57) Zhao, H.; Malhotra, S. V.; Luo, R. G. Preparation and Characterization of three Room-Temperature Ionic Liquids. *Phys. Chem. Liq.* **2003**, *41*, 487−492.

(58) 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 + H₂O. *J. Chem. Eng. Data* **2004**, *49*, 760−764.

(59) NIST Chemistry WebBook at http://webbook.nist.gov/chemistry/.

(60) Gu, Z.; Brennecke, J. F. Volume Expansivities and Isothermal Compressibilities of Imidazolium and Pyridinium-Based Ionic Liquids. *J. Chem. Eng. Data* **2002**, *47*, 339−345.

(61) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. Relationships among Ionic Lattice Energies, Molecular (Formula Unit) Volumes, and Thermochemical Radii. *Inorg. Chem.* **1999**, *38*, 3609−3620.

(62) Spencer, C. F.; Danner, R. P. Improved Equation for Prediction of Saturated Liquid Density. *J. Chem. Eng. Data* **1972**, *17*, 236−241.