Density, Speed of Sound, and Derived Thermodynamic Properties of Ionic Liquids over an Extended Pressure Range. 4. [C_3mim][NTf_2] and [C_5mim][NTf_2]

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The current study focuses on 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [C_3mim][NTf_2], and 1-pentyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [C_5mim][NTf_2]. The objective is to study the influence of pressure as well as that of the cation's alkyl chain length on several properties of this type of ionic liquids. Speed of propagation of ultrasound waves and densities in pure ionic liquids as a function of temperature and pressure have been determined. Other thermodynamic properties such as compressibilities and expansivities have been obtained. Speed of sound measurements have been carried out in broad ranges of temperature ($298 < T/K < 338$) and pressure ($0.1 < p/MPa < 200$). A novel high-pressure ultrasonic cell was designed and built to allow for precise speed of sound measurements in liquids. The uncertainty of the speed of sound measurements is 0.05 %. A detailed description of the cell is presented. Density measurements have been performed over a broad range of temperature ($298 < T/K < 333$) and pressure ($0.1 < p/MPa < 60$) using a vibrating-tube densimeter. The density overall uncertainty is 0.02 %.

Introduction

The increasing attention given to ionic liquids (ILs) as possible replacement solvents for volatile organic compounds is driving their research toward the development of a sustainable green chemistry, guiding efforts in this field in the direction of new, harmless substances.[1,2] The thermophysical characterization of ILs is by no means extensive[3−8] (the scenario is even narrower if mixtures and solutions are considered[9−13]).

We have thus chosen to embark on the study of the thermodynamic and acoustic properties of a possibly cleaner alternative, namely, the ionic liquid series containing the popular cation 1-C_n-3-methylimidazolium combined with the anion bis(trifluoromethylsulfonyl)amide, $[N\{SO_2(CF_3)\}_2]^-$. Due to their combined low viscosity, broad temperature range of liquid stability, and absence of halogen atoms in potentially chemically reactive forms, the [$C_n$mim][NTf_2] is one of the most promising class of ILs that can become important in diverse applications.

Speed of sound measurements, u, have proved to be powerful sources of valuable information of thermodynamic properties for pure liquids and mixtures.[14,15] If the pulse-echo technique is considered, there are generally two main methods of measuring speed of sound data, namely, through intrusive[16−19] or non-intrusive methods.[20−23] The design of the cell used in this work is very similar to that described by Pires and Guedes,[16] joining together its good accuracy with a total, small cell volume of 30 cm^3.

The speed of sound, u, is a property that can be experimentally determined with great precision over a broad range of temperature and pressure. Together with experimental density data, it allows the calculation of isentropic and isothermal compressibilities, κ_S and κ_T, respectively; isobaric thermal expansivities, α_p; and thermal pressure coefficients, γ_v, over the entire range of pressure and temperature of the speed of sound measurements. If one isobar of C_p is available, speed of sound data permit, by integration, the calculation of the whole (p, C_p, T) surface.[21,24−27]

Experimental Section

Acoustic Cell and Densimeter. A new high-pressure acoustic cell was built in order to measure the speed of propagation of ultrasonic waves in ionic liquids. The cell shape was based on one previously built[16,17] with the total volume of the system reduced to one that would be workable for IL. Figure 1 shows both a diagram and a photograph of the speed of sound cell.

The echoes of the ultrasonic wave were generated and detected by a piezoelectric transducer (D), which is used as both emitter and receptor. It was a ceramic disk (ref PIC255 from PI Ceramics) made of lead, zirconate, and titanate (PZT). The disk was 10 mm diameter and 0.5 mm thick and had a fundamental vibration frequency of 4 MHz.

The spacers (B) made of pure copper (+99.99 %) were 3.5 mm diameter and 12.5 mm or 22.5 mm long. The pure copper allows one to control more precisely the expansion or contraction that occurs by changing pressure and temperature. The reflector's shape was designed to improve the quality of the final output. The electrical contact to the piezoelectric transducer was made on one side directly to one of the reflectors and on the other to a copper ring insulated by a Teflon ring from the main cell.

The acoustic cell was placed inside a new pressure vessel designed to handle with safety a pressure of 200 MPa. The top

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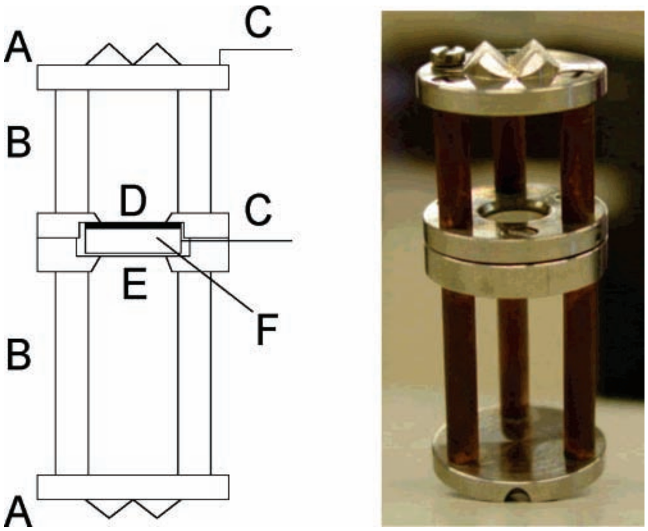

Figure 1. Schematic representation of the new cell used for speed of sound measurements: A, reflector; B, copper spacers; C, wire conductors; D, PZT; E, Teflon ring; F, copper ring.

opening was closed by the extrusion of a Teflon O-ring. The seal also has an HF_4 connector in order to attach the wire feedthrough, from Conax Buffalo Technologies (model PL-(AM2/S316B)-26-A2-G), that would allow the passage of the two electrical wires to the outside of the cell. The pressure vessel was placed in a thermostatic bath designed to work between (−30 and 100) °C. The temperature controller was from Hart Scientific (model 2100) allowing for long-term temperature stability better than ± 5 mK. The probe used with the controller was also from Hart Scientific (model 2620). Temperature was measured with a Hart Scientific (model 5613) platinum RTD with a nominal resistance of 100 Ω. The RTD was used in conjunction with a Yokogawa (model 7561) multimeter with 6.5 digits and an uncertainty of 0.1 mΩ. All together, the temperature measurement uncertainty was estimated to be better than 0.01 K.

Pressure transducers were chosen in order to have good precision over the entire measuring range. The pressure transducers are from Omega (models PX03D1-3KA5T and PX03D1-30KA5T) with maximum pressure range of 20.68 MPa and 206.8 MPa respectively. Both transducers are connected to a digital panel meter also from Omega (model DP41E). Both sets of transducers and meter were calibrated against a primary standard, a Ruska Instrument Corporation (model 2450) dead weight gauge from Instituto Superior Técnico, Lisboa, Portugal. The repeatability of the pressure transducers is 0.05 % of the full scale.

For pressure measurements, an auxiliary fluid (water) different from the ionic liquid was used. This is because one generally believes that water should be less aggressive to the transducers than ILs. It is necessary, as already proven with success,[25−28] to implement a long 1/16-in. buffer line in which the contact between water and the IL was made.

The function generator was from Wavetek (model 90) and was used to synthesize a burst of five sinusoidal cycles with a frequency of 4 MHz, amplitude of 15 V peak to peak, and an electric impedance of the signal of 50 Ω. A second signal, or trigger, was sent to the oscilloscope to synchronize it. The oscilloscope used in this work was of 100 MHz bandwidth from Yokogawa (model DL 1200A).

Calibration of the Speed of Sound Apparatus. The calibration of the new speed of sound cell was done by measuring one speed of sound datum point and using the copper expansion/contraction to evaluate the distance difference between both acoustical paths.[29,30] The experimental datum point measurement for calibration of the cell was performed at 298 K and 10 MPa with benzene. The calibration was then tested in the whole (p, T) range with different fluids (namely, benzene,[31] toluene,[32] methanol,[33] and acetone[28]) by comparison with literature data. Equations 1 and 2 relate the length of the acoustical pathway, L, with temperature and pressure:

Table 1. Coefficients for Equations 3 and 4 Used To Determine the Length Difference of the Acoustical Pathways

a/K^{-1}	$1.11 \cdot 10^{-5}$	e/K^{-5}	$-6.49 \cdot 10^{-17}$
b/K^{-2}	$3.24 \cdot 10^{-8}$	f/K^{-6}	$1.70 \cdot 10^{-20}$
c/K^{-3}	$-7.40 \cdot 10^{-11}$	K/MPa	$1.14 \cdot 10^{6}$
d/K^{-4}	$9.97 \cdot 10^{-14}$	$L(T_{ref}, p_{ref})$	11.632 mm

$$L(T) = L(T_{ref})[X(T) - X(T_{ref}) + 1] \tag{1}$$

$$L(p) = L(p_{ref})\left(1 - \frac{p - p_{ref}}{K}\right)^{1/3} \tag{2}$$

where K is a constant and $X(T)$ is defined by eq 3:

$$X(T) = aT + \frac{b}{2}T^2 + \frac{c}{3}T^3 + \frac{d}{4}T^4 + \frac{e}{5}T^5 + \frac{f}{6}T^6 \tag{3}$$

Equations 1 and 2 can be combined to obtain eq 4 used to calculate the difference distance between the two ultrasonic pathways:

$$L(p, T) = L(p_{ref}, T_{ref})[X(T) - X(T_{ref}) + 1]\left(1 - \frac{p - p_{ref}}{K}\right)^{1/3} \tag{4}$$

The coefficients used in these equations are shown in Table 1.

The accuracy of the speed of sound measurements was estimated based on repetitive measurements of several liquids in the whole (p, T) range, and a value of 0.15 m·s^{-1}, equivalent to approximately 0.012 %, was obtained. The uncertainty in these measurements depends on the data used in the calibration. It was estimated an uncertainty of 0.05 % based on the standard deviations obtained for the different fluids. Likewise, densities were measured using an Anton Paar DMA 512P densimeter[28] in the temperature range of (298 to 333) K and the pressure range of (0.1 to 60) MPa. The overall uncertainty in density is estimated to be about 0.02 %, judging by the residuals of the overall fit in comparison with literature data for the calibrating liquids. It should be noted that this figure may increase slightly if one considers possible viscosity corrections.[34,35] This type of corrections, irrespective of their origin, relies on both the existence of pressure-dependent viscosity data and properly evaluated equations for the correlation between viscosity and signal damping. These issues are still under debate, and in light of the above-mentioned caveats plus the inexistence of viscosity data for the currently studied ionic liquids, we have not performed any viscosity corrections. Therefore, all the results of the subsequent derived properties and their discussions are based on raw density data. It should be noted, however, that the bistriflamide anion combined with dialkylimidazolium cations provide us with low-viscosity ILs.[5] For instance, at atmospheric pressure, a slight downward shift (due to the viscosity correction) in the value of density of about 0.02 % for [C_2mim][NTf_2] at 298 K—which decreases to 0.01 % at 333 K—is estimated (similar figures for [C_4mim][NTf_2]).

Chemicals. [C_3mim][NTf_2] and [C_5mim][NTf_2] were synthesized and purified at the QUILL Centre, Belfast, according

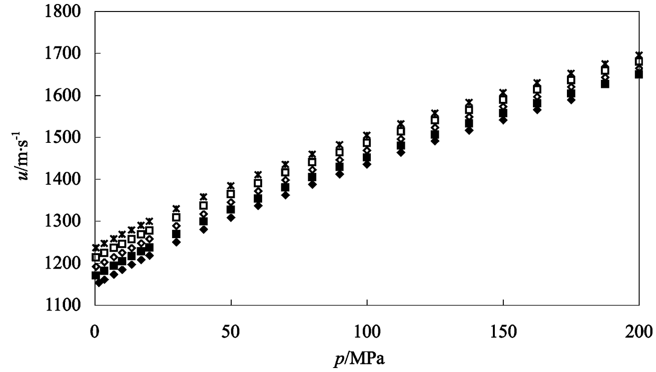

Figure 2. Isotherms of the experimental speed of sound of [C_3mim][NTf_2]: $*$, 298.15 K; □, 308.15 K; ◇, 318.15 K; ■, 328.15 K; ◆, 338.15 K.

Table 2. Experimental Speed of Sound, *u*, Data for [C_3mim][NTf_2] as a Function of Temperature, *T*, and Pressure, *p*

	u/m·s^{-1}				
p/MPa	T/K = 298.15	T/K = 308.15	T/K = 318.15	T/K = 328.15	T/K = 338.15
0.50	1236.40	1214.02	1192.26	1170.93	
1.42					1153.52
3.50	1246.48	1224.39	1202.88	1181.79	1161.22
7.00	1258.18	1236.21	1214.97	1194.19	1173.83
10.00	1268.01	1246.21	1225.22	1204.67	1184.36
13.50	1279.22	1257.57	1236.83	1216.44	1196.58
17.00	1290.02	1268.63	1248.18	1228.01	1208.31
20.00	1299.22	1278.04	1257.69	1237.74	1218.25
30.00	1329.19	1308.64	1288.68	1269.23	1250.40
40.00	1357.52	1337.09	1317.81	1299.09	1280.66
50.00	1384.47	1364.73	1345.72	1327.29	1309.19
60.00	1410.30	1391.01	1372.24	1354.21	1336.67
70.00	1435.09	1416.15	1397.82	1380.11	1362.89
80.00	1459.03	1440.33	1422.30	1405.14	1388.10
90.00	1482.12	1463.69	1446.35	1429.10	1412.30
100.00	1504.51	1486.41	1468.93	1452.23	1435.77
112.50	1531.68	1513.63	1496.47	1480.06	1463.88
125.00	1557.56	1539.91	1523.20	1506.92	1491.10
137.51	1582.75	1565.16	1548.43	1532.75	1517.04
150.00	1605.96	1589.56	1572.88	1557.03	1541.44
162.50	1629.62	1613.29	1596.63	1581.20	1565.97
175.00	1652.47	1636.28	1619.97	1604.64	1589.49
187.50	1674.50	1658.62	1642.70	1627.34	
200.00	1695.88	1680.42	1664.60	1649.56	

to procedures found elsewhere.[36] They were washed several times with water to decrease the chloride content. It was checked that no precipitation (of AgCl) would occur by addition of $AgNO_3$ to the wash water. In order to reduce the water content and volatile compounds to negligible values, vacuum (0.1 Pa) and moderate temperature (70 °C) were applied to both samples for several days always immediately prior to their use. Both samples were analyzed by Coulometric Karl Fischer (Metrohm) titration and showed the ratio of the mass of water to that of ionic liquid to be less than 150 ppm. Benzene (Allied Signal), toluene (Aldrich), methanol (Pronalab), and acetone (Merck) were supplied with stated purities higher than 99.7 %, 99.8 %, 99.8 %, and 99.9 %, repectively.

Results and Discussion

[C_3mim][NTf_2]. Sound-speed measurements have been carried out in broad ranges of temperature (298 < T/K < 338) and pressure (0.1 < p/MPa < 200). Figure 2 and Table 2 report the speed of sound behavior of [C_3mim][NTf_2] as a function of pressure and temperature. For the sake of economy, data are presented at nominal temperatures that, typically, differ from the actual ones by no more than 0.01 K.

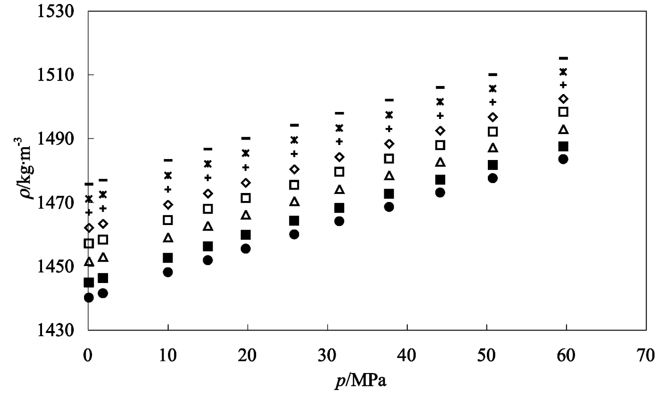

Figure 3. Isotherms of the experimental density of [C_3mim][NTf_2]: —, 298.15 K; $*$, 303.15 K; +, 308.15 K; ◇, 313.15 K; □, 318.15 K; △, 323.15 K; ■, 329.15 K; ●, 333.15 K.

Table 3. Coefficients of Equation 5 for *T*/K, *p*/MPa, and *u*/m·s^{-1} within the Interval (298 < *T*/K < 338; 0.5 < *p*/MPa < 200) for [C_3mim][NTf_2]

a	2097.79060	f	$1.741622 \cdot 10^{-3}$
b	4.99937876	g	$-5.324645 \cdot 10^{-6}$
c	$-9.0145612 \cdot 10^{-3}$	h	$1.758677 \cdot 10^{-9}$
d	-4.584871112	i	$-5.521286 \cdot 10^{-4}$
e	$3.382448 \cdot 10^{-3}$		

Original data have been fitted to eq 5 of the form:

$$(u/\text{m}\cdot\text{s}^{-1}) = \frac{a + b(p/\text{MPa}) + c(p/\text{MPa})^2 + d(T/\text{K}) + e(T/\text{K})^2}{1 + f(p/\text{MPa}) + g(p/\text{MPa})^2 + h(p/\text{MPa})^3 + i(T/\text{K})} \quad (5)$$

The fitting coefficients are presented in Table 3. The standard deviation between the experimental and fitted values is found to be 0.015 %.

Density measurements have been carried out at a broad range of temperatures (298 < T/K < 333) and pressures (0.1 < p/MPa < 60). The experimental data are presented both in Figure 3 and in Table 4. The experimental data are in reasonable agreement, better than 0.1 %, with the literature ones[37] at atmospheric pressure and 25 °C. As far as the authors are aware of, no other experimental data are available for comparison of the properties of [C_3mim][NTf_2].

The measured properties can be combined through eq 6 to derive the isentropic compressibility of fluid under investigation as presented in the Supporting Information in Figure S1 and Table S1:

$$\kappa_S = \frac{1}{\rho u^2} \quad (6)$$

The absence of heat capacity data compelled the direct use of the derivatives of density in order to obtain the derived thermodynamic properties of this substance (namely, α_p, κ_T, and γ_v). The fitting of isobaric density data was performed through the Tait equation as presented in eq 7. This equation is known to represent well the density behavior of liquids over pressure at constant temperature:

$$\frac{1}{\rho} = \frac{1}{C} + A \ln\left(\frac{B + p/\text{MPa}}{B + 0.1}\right) \quad (7)$$

The parameters for each isotherm are shown in Table 5. The isothermal compressibility is calculated using the isothermal

Table 4. Experimental Density, ρ, Data for $[C_3mim][NTf_2]$ as a Function of Temperature, T, and Pressure, p

p/MPa	ρ/kg·m^{-3}						
	T/K = 298.15	T/K = 299.15	T/K = 300.15	T/K = 301.15	T/K = 302.15	T/K = 303.15	T/K = 308.15
0.10	1475.70	1474.62	1473.66	1472.79	1471.92	1471.14	1466.83
1.83	1476.98	1475.87	1474.94	1474.07	1473.15	1472.39	1468.10
10.02	1483.13	1482.12	1481.10	1480.19	1479.27	1478.49	1474.12
14.98	1486.69	1485.68	1484.68	1483.74	1482.84	1482.00	1477.65
19.75	1490.06	1489.01	1488.07	1487.10	1486.21	1485.41	1480.89
25.86	1494.22	1493.18	1492.27	1491.35	1490.42	1489.57	1485.18
31.48	1497.95	1496.89	1496.03	1495.08	1494.19	1493.32	1489.00
37.77	1502.01	1500.95	1500.11	1499.16	1498.29	1497.43	1493.05
44.17	1506.01	1504.95	1504.13	1503.18	1502.37	1501.50	1497.15
50.75	1509.97	1509.07	1508.14	1507.27	1506.46	1505.60	1501.36
59.59	1515.10	1514.22	1513.35	1512.51	1511.74	1510.93	1506.81

p/MPa	ρ/kg·m^{-3}							
	T/K = 313.15	T/K = 318.15	T/K = 323.15	T/K = 325.15	T/K = 327.15	T/K = 329.15	T/K = 331.15	T/K = 333.15
0.10	1462.07	1457.05	1451.66	1449.44	1447.19	1444.85	1442.53	1440.12
1.83	1463.28	1458.31	1452.94	1450.74	1448.52	1446.17	1443.83	1441.48
10.02	1469.31	1464.41	1459.11	1456.98	1454.88	1452.55	1450.37	1448.04
14.98	1472.86	1467.91	1462.75	1460.64	1458.57	1456.27	1454.12	1451.88
19.75	1476.15	1471.30	1466.15	1464.08	1461.98	1459.81	1457.75	1455.51
25.86	1480.43	1475.51	1470.44	1468.44	1466.38	1464.24	1462.22	1460.01
31.48	1484.36	1479.58	1474.24	1472.46	1470.37	1468.26	1466.27	1464.11
37.77	1488.40	1483.63	1478.57	1476.81	1474.75	1472.67	1470.70	1468.58
44.17	1492.56	1487.95	1482.86	1481.18	1479.18	1477.09	1475.13	1473.05
50.75	1496.83	1492.22	1487.24	1485.62	1483.65	1481.63	1479.63	1477.56
59.59	1502.49	1498.46	1493.03	1491.56	1489.60	1487.58	1485.58	1483.54

Table 5. Coefficients of the Tait Equation (eq 7) for the Density of $[C_3mim][NTf_2]$ at Each Isotherm ($0.1 < p$/MPa < 60)

T/K	A(kg^{-1}·m^3)·10^5	B	C/kg·m^{-3}
298.15	−4.9726	139.52	1475.67
299.15	−5.1754	145.36	1474.60
300.15	−5.1833	144.89	1473.63
301.15	−5.5099	155.41	1472.77
302.15	−5.7743	163.27	1471.87
303.15	−5.9640	169.73	1471.11
308.15	−6.9613	200.48	1466.83
313.15	−7.9195	227.51	1462.04
318.15	−8.2270	232.92	1457.04
323.15	−8.5120	237.11	1451.68
325.15	−9.1854	252.07	1449.45
327.15	−8.9590	242.86	1447.24
329.15	−8.6925	231.77	1444.86
331.15	−7.7248	200.40	1442.52
333.15	−7.5885	193.87	1440.12

pressure derivative of density according to

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \qquad (8)$$

Unfortunately, there is no equivalent of the Tait equation for the behavior of density with temperature at constant pressure. A detailed evaluation of the raw data reveals that deviations from linearity in density-temperature (or volume-temperature) plots are so mild that the determination of the temperature coefficient of α_p is extremely dependent on the choice of the type of function to screen the data. For those situations where the statistical scatter of the raw data is large compared with an unambiguous determination of the curvature, we suggest the use of $\ln \rho = f(T)$. For $[C_3mim][NTF_2]$, the behavior of $\ln \rho$ proved to be explained by a second-order polynomial equation in temperature with the coefficients of the fitting presented in Table 6. The calculated properties, such as κ_T, α_p, and γ_V are presented as Figures S2 and S3 and Tables S2 to S4 of the Supporting Information.

$[C_5mim][NTf_2]$. Sound-speed measurements have been carried out in broad ranges of temperature ($288 < T$/K < 338) and pressure ($0.1 < p$/MPa < 150). Figure 4 and Table 7 report the

Table 6. Parameters of the Fit $\ln(\rho/\text{kg·m}^{-3}) = D + E(T/\text{K}) + F(T/\text{K})^2$ of $[C_3mim][NTf_2]$

p/MPa	D	E·10^4	F·10^6
0.10	7.0860	19.574	−4.1950
1.83	7.1003	18.698	−4.0528
10.02	7.1799	13.814	−3.2627
14.98	7.2187	11.447	−2.8779
19.75	7.2632	8.7038	−2.4333
25.86	7.2846	7.4578	−2.2239
31.48	7.2771	8.0143	−2.2990
37.77	7.3198	5.3862	−1.8666
44.17	7.3209	5.3890	−1.8496
50.75	7.3174	5.6715	−1.8759
59.59	7.2897	7.4829	−2.1332

speed of sound behavior of $[C_5mim][NTf_2]$ as a function of pressure and temperature. Again, for the sake of economy, data are presented at nominal temperatures which, typically, differ from the actual ones by no more than 0.01 K.

Original data have been fitted to eq 1 with the fitting coefficients given in Table 8. The standard deviation between the experimental and fitted values is found to be 0.015 %. Density measurements have been carried out at a broad range of temperatures ($298 < T$/K < 333) and pressures ($0.1 < p$/MPa < 60). The experimental data are presented both in Figure 5

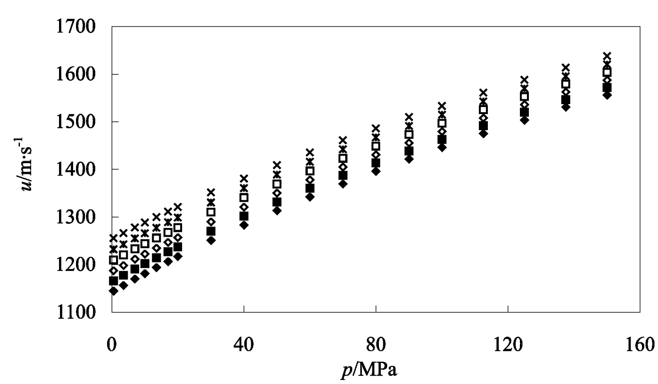

Figure 4. Isotherms of the experimental speed of sound of $[C_5mim][NTf_2]$: ×, 288.15 K; ∗, 298.15 K; □, 308.15 K; ◇, 318.15 K; ■, 328.15 K; ◆, 338.15 K.

Table 7. Experimental Speed of Sound, *u*, Data for $[C_5mim][NTf_2]$ as a Function of Temperature, *T*, and Pressure, *p*

	u/m·s^{-1}					
p/MPa	*T*/K = 288.15	*T*/K = 298.15	*T*/K = 308.15	*T*/K = 318.15	*T*/K = 328.15	*T*/K = 338.15
0.50	1255.48	1232.13	1209.44	1187.33	1165.79	1144.76
3.50	1265.99	1242.66	1220.44	1198.61	1177.44	1156.45
7.00	1278.10	1255.05	1233.11	1211.50	1190.61	1170.04
10.00	1288.26	1265.48	1243.73	1222.41	1201.76	1181.37
13.50	1299.89	1277.35	1255.85	1234.77	1214.21	1194.26
16.99	1311.16	1288.92	1267.53	1246.87	1226.60	1206.68
20.00	1320.70	1298.58	1277.47	1256.99	1236.94	1217.24
30.00	1351.71	1330.55	1310.04	1290.01	1270.51	1251.27
40.00	1380.90	1360.43	1340.39	1320.98	1301.88	1283.34
50.00	1408.96	1388.86	1369.13	1350.24	1331.71	1313.61
60.00	1435.57	1415.93	1396.71	1378.19	1360.08	1342.37
70.00	1461.25	1441.90	1423.15	1404.93	1387.20	1369.79
80.00	1486.05	1466.98	1448.60	1430.70	1413.40	1396.26
90.00	1509.92	1491.13	1472.99	1455.47	1438.39	1421.64
100.00	1533.00	1514.50	1496.64	1479.47	1462.60	1446.30
112.50	1560.88	1542.58	1525.22	1508.03	1491.61	1475.29
125.00	1587.89	1569.71	1552.60	1535.89	1519.63	1503.68
137.51	1613.55	1595.72	1579.04	1562.58	1546.57	1530.89
150.00	1637.77	1620.35	1603.65	1587.43	1571.50	1556.18

Table 8. Coefficients of Equation 5 for *T*/K, *p*/MPa, and *u*/m·s^{-1} within the Interval (288 < *T*/K < 338; 0.5 < *p*/MPa < 150) for $[C_5mim][NTf_2]$

a	2113.07193	*f*	$2.160742 \cdot 10^{-3}$
b	5.71392856	*g*	$-8.122416 \cdot 10^{-6}$
c	$-1.215653 \cdot 10^{-2}$	*h*	$5.042271 \cdot 10^{-9}$
d	−4.67077659	*i*	$-5.464547 \cdot 10^{-4}$
e	$3.480517 \cdot 10^{-3}$		

and Table 9. The experimental data are in reasonable agreement, better than 0.1 %, with the literature ones[37] at atmospheric pressure and 25 °C. As far as the authors are aware of, no other experimental data are available for comparison of the properties of $[C_5mim][NTf_2]$.

The derived thermodynamic properties were calculated exactly with the same procedure as for $[C_3mim][NTf_2]$. The isentropic compressibility of $[C_5mim][NTf_2]$ is presented in the Supporting Information as Figure S4 and Table S5. The Tait equation parameters for each isotherm are shown in Table 10. For $[C_5mim][NTF_2]$, the behavior of ln ρ proved to be explained by a second-order polynomial equation in temperature with the coefficients of the fitting presented in Table 11. The calculated properties, such as κ_T, α_p, and γ_V are presented as Figures S5 and S6 and Tables S6 to S8 of the Supporting Information.

Figure 6 shows a comparison of the molar volumes obtained for the series of $[C_nmim][NTf_2]$ (this work and ref 26) at two temperatures indicating linear trends with slopes in close accordance with the one previously stated:[27,38] $(\partial V_m/\partial(2n)) = (34.4 \pm 0.5)$ cm^3·mol^{-1} for the variation of the molar volume per addition of two carbon atoms in the alkyl chain. In respect to the speed of sound, and assuming that the *u* value for $[C_4mim][NTf_2]$ should be the mean value between those of $[C_3mim][NTf_2]$ and $[C_5mim][NTf_2]$, the experimental value[26] of the former deviates less than 0.4 %. This difference can well be explained by the different purity of the ionic liquid samples, as well as by the compared precisions of the apparatus used in these distinct studies.

The work herein reported maps the thermodynamic and acoustical behavior of an important class of ionic liquids over

Table 9. Experimental Density, *ρ*, Data for $[C_5mim][NTf_2]$ as a Function of Temperature, *T*, and Pressure, *p*

	ρ/kg·m^{-3}						
p/MPa	*T*/K = 298.15	*T*/K = 299.15	*T*/K = 300.15	*T*/K = 301.15	*T*/K = 302.15	*T*/K = 303.15	*T*/K = 308.15
0.10	1404.45	1403.50	1402.62	1401.81	1400.89	1399.89	1395.34
1.83	1405.67	1404.78	1403.85	1403.07	1402.16	1401.18	1396.59
10.02	1411.85	1410.92	1410.01	1409.19	1408.28	1407.27	1402.73
14.98	1415.45	1414.53	1413.57	1412.71	1411.85	1410.82	1406.29
19.75	1418.80	1417.87	1416.91	1416.05	1415.20	1414.30	1409.65
25.86	1422.94	1422.01	1421.12	1420.19	1419.36	1418.46	1413.83
31.48	1426.64	1425.70	1424.81	1423.90	1423.08	1422.18	1417.59
37.77	1430.64	1429.73	1428.87	1427.94	1427.17	1426.25	1421.72
44.17	1434.54	1433.68	1432.84	1431.88	1431.17	1430.26	1425.82
50.75	1438.46	1437.64	1436.83	1435.89	1435.18	1434.31	1429.95
59.59	1443.56	1442.74	1441.99	1441.12	1440.42	1439.59	1435.35

	ρ/kg·m^{-3}							
p/MPa	*T*/K = 313.15	*T*/K = 318.15	*T*/K = 323.15	*T*/K = 325.15	*T*/K = 327.15	*T*/K = 329.15	*T*/K = 331.15	*T*/K = 333.15
0.10	1390.55	1385.75	1381.45	1379.56	1377.56	1375.46	1373.32	1371.00
1.83	1391.88	1387.09	1382.69	1380.89	1378.86	1376.78	1374.64	1372.46
10.02	1397.99	1393.29	1388.89	1387.23	1385.24	1383.20	1381.17	1379.05
4.98	1401.57	1396.90	1392.55	1390.89	1388.96	1386.93	1384.96	1382.89
19.75	1404.95	1400.31	1395.96	1394.39	1392.45	1390.47	1388.53	1386.48
25.86	1409.15	1404.59	1400.22	1398.72	1396.84	1394.89	1392.98	1390.95
31.48	1412.95	1408.43	1404.06	1402.63	1400.77	1398.85	1396.98	1395.01
37.77	1417.13	1412.65	1408.30	1406.92	1405.12	1403.20	1401.34	1399.42
44.17	1421.26	1416.86	1412.52	1411.19	1409.39	1407.56	1405.67	1403.81
50.75	1425.48	1421.15	1416.77	1415.51	1413.81	1411.94	1410.08	1408.20
59.59	1431.06	1426.81	1422.52	1421.18	1419.56	1417.73	1415.87	1414.01

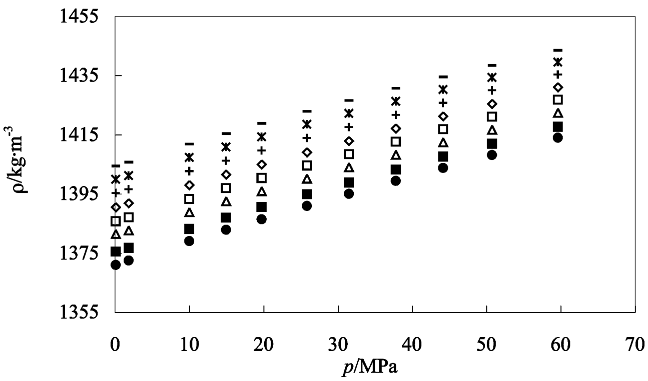

Figure 5. Isotherms of the experimental density of [C_5mim][NTf_2]: −, 298.15 K; ∗, 303.15 K; +, 308.15 K; ◇, 313.15 K; □, 318.15 K; △, 323.15 K; ■, 329.15 K; ●, 333.15 K.

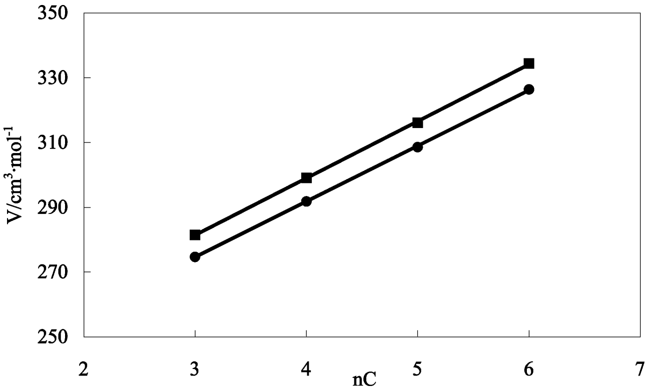

Figure 6. Orthobaric molar volume as a function of the number of carbons, nC, on the series of [$C_n$mim][NTf_2]: ●, 298.15 K; ■, 333.15 K.

Table 10. Coefficients of the Tait Equation (eq 7) for the Density of [C_5mim][NTf_2] at Each Isotherm (0.1 < *p*/MPa < 60)

T/K	*A*($kg^{-1}\cdot m^3$)$\cdot 10^5$	*B*	*C*/$kg\cdot m^{-3}$
298.15	−5.0567	127.76	1404.39
299.15	−5.2408	132.73	1403.47
300.15	−5.5324	140.70	1402.56
301.15	−5.7620	148.03	1401.79
302.15	−5.8388	149.05	1400.87
303.15	−5.9144	150.36	1399.86
308.15	−6.7625	173.04	1395.33
313.15	−7.5092	191.45	1390.58
318.15	−7.7738	194.72	1385.79
323.15	−8.0843	201.97	1381.44
325.15	−7.5258	182.69	1379.57
327.15	−7.8684	189.69	1377.56
329.15	−7.8120	186.13	1375.46
331.15	−7.3042	170.39	1373.31
333.15	−7.0226	160.44	1371.05

Table 11. Parameters of the Fit ln(ρ/kg·m^{-3}) = *D* + *E*(*T*/K) + *F*(*T*/K)^2 of [C_5mim][NTf_2]

p/MPa	*D*	*E*$\cdot 10^4$	F$\cdot 10^6$
0.10	7.2980	2.8669	−1.5317
1.83	7.3049	2.4579	−1.4621
10.02	7.3632	−1.0688	−0.88526
14.98	7.3926	−2.8386	−0.59440
19.75	7.4127	−4.0182	−0.39781
25.86	7.4350	−5.3212	−0.17803
31.48	7.4510	−6.2531	−0.016998
37.77	7.4531	−6.2921	0.0041171
44.17	7.4499	−6.0058	−0.024317
50.75	7.4349	−4.9827	−0.16883
59.59	7.3973	−2.5125	−0.53430

wide pressure and temperature ranges. These results can be merged with those previously published[26] in order to obtain the behavior of the series of 1-alkyl-3-methylimidazolium bis(trifluoromethane sulfonyl)amide with the alkyl group ranging from propyl to hexyl.

Supporting Information Available:

An additional 8 tables and 6 figures. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Rogers, R. D., Seddon, K. R., Eds. *Ionic Liquids IIIA*: *Fundamentals, Progress, Challenges, and Opportunities—Properties and Structure*; ACS Symposium Series 901; American Chemical Society: Washington, DC, 2005.

(2) Rogers, R. D., Seddon, K. R., Eds. *Ionic Liquids IIIB*: *Fundamentals, Progress, Challenges, and Opportunities—Transformations and Processes*; ACS Symposium Series 902; American Chemical Society: Washington, DC, 2005.

(3) 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.

(4) 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.

(5) 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.

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

(7) Domanska, U. Solubilities and thermophysical properties of ionic liquids. *Pure Appl. Chem.* **2005**, *77*, 543−557.

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

(9) Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D. W. Characterizing ionic liquids on the basis of multiple solvation interactions. *J. Am. Chem. Soc.* **2002**, *124*, 14247−14254.

(10) Xu, W.; Cooper, E. I.; Angell, C. A. Ionic liquids: ion mobilities, glass temperatures, and fragilities. *J. Phys. Chem. B* **2003**, *107*, 6170−6178.

(11) 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.

(12) Lachwa, J.; Szydlowski, J.; Najdanovic-Visak, V.; Rebelo, L. P. N.; Seddon, K. R.; Nunes. da Ponte, M.; Esperança, 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.

(13) Earle, M. J.; Esperança, 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.

(14) Trusler, J. P. M. *Physical Acoustics and Metrology of Fluids*; Adam Hilger: Bristol, 1991.

(15) 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.

(16) Pires, P. F.; Guedes, H. J. R. The speed of sound and isentropic compressibility of liquid difluoromethane (HFC32) from *T* = (248 to 343) K and Pressures up to 65 MPa. *J. Chem. Thermodyn.* **1999**, *31*, 55−69.

(17) Pires, P. F.; Guedes, H. J. R. The speed of sound and derived thermodynamic properties of liquid trifluoromethane (HFC23) from *T* = (258 to 303) K at Pressures up to 65 MPa. *J. Chem. Thermodyn.* **1999**, *31*, 479−490.

(18) Ball, S. J.; Trusler, J. P. M. Speed of sound of *n*-hexane and n-hexadecane at temperatures between 298 and 373 K and pressures up to 100 MPa. *Int. J. Thermophys.* **2001**, *22*, 427−443.

(19) Asher, R .C. *Ultrasonic Sensors*; Institute of Physics Publishing: Bristol, 1997.

(20) McSkimin, H. J. In *Physical Acoustics—Principles and Methods*, Vol. 1, Part A; Mason, W. P., Ed.; Academic Press: New York, 1964; Chapter 4.

(21) Daridon, J. L.; Lagrabette, A.; Lagourette, B. Speed of sound, density, and compressibilities of heavy synthetic cuts from ultrasonic measurements under pressure. *J. Chem. Thermodyn.* **1998**, *30*, 607−623.

(22) Petitet, J. P.; Tufeu, R.; Le Neindre, B. Determination of the thermodynamic properties of water from measurements of the speed

of sound in the temperature range 251.15−293.15 K and the pressure range 0.1−350 MPa. *Int. J. Thermophys.* **1983**, *4*, 35−50.

(23) Kozhevnikov, V.; Arnold, D.; Grodzinskii, E.; Naurzakov, S. Phase transitions and critical phenomena in mercury fluid probed by sound. *Fluid Phase Equilib.* **1996**, *125*, 149−157.

(24) Pires, P. F.; Esperança, J. M. S. S.; Guedes, H. J. R. Ultrasonic speed of sound and derived thermodynamic properties of liquid 1,1,1,2,3,3,3-heptafluoropropane (HFC227ea) from 248 K to 333 K and pressures up to 65 MPa. *J. Chem. Eng. Data* **2000**, *45*, 496−501.

(25) Gomes de Azevedo, R.; 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.

(26) Gomes de Azevedo, R.; 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][NTf_2] and [hmim][NTf_2]. *J. Chem. Thermodyn.* **2005**, *37*, 888−899.

(27) Esperança, J. M. S. S.; Guedes, H. J. R.; Blesic, M.; Rebelo, L. P. N. Densities and derived thermodynamic properties of ionic liquids. 3. Phosphonium-based ionic liquids over an extended pressure range. *J. Chem. Eng. Data* **2006**, *51*, 237−242.

(28) Gomes de Azevedo, R.; Szydlowski, J.; Pires, P. F.; Esperança, J. M. S. S.; Guedes, H. J. R.; Rebelo, L. P. N. A novel non-intrusive microcell for sound-speed measurements in liquids. Speed of sound and thermodynamic properties of 2-propanone at pressures up to 160 MPa. *J. Chem. Thermodyn.* **2004**, *36* (3), 211−222,

(29) White, G. K.; Roberts, R. B. *High Temp.-High Pressures* **1980**, *12*, 311−317.

(30) *Metals Handbook*, 9th ed.; ASM: Strongsville, OH, 1979.

(31) Sun, T. F.; Kortbeek, P. J.; Trappeniers, N. J.; Biswas, S. N. Acoustic and thermodynamic properties of benzene and cyclohexane as a function of pressure and temperature. *Phys. Chem. Liq.* **1987**, *16*, 163−178.

(32) Muringer, M. J. P.; Trappeniers, N. J.; Biswas, S. N. The effect of pressure on the sound-velocity and density of toluene and *n*-heptane up to 2600 bar. *Phys. Chem. Liq.* **1985**, *14*, 273−296.

(33) Sun, T. F.; Biswas, S. N.; Trappeniers, N. J.; Seldam, C. A. T. Acoustic and thermodynamic properties of methanol from 273 K to 333 K and at pressures to 280 MPa. *J. Chem. Eng. Data* **1988**, *33*, 395−398.

(34) Lundstrum, R.; Goodwin, A. R. H.; Hsu, K.; Frels, M.; Caudwell, D. R.; Trusler, J. P. M.; Marsh, K. N. Measurement of the viscosity and density of two reference fluids, with nominal viscosity at $T = 298$ K and $p = 0.1$ MPa of (16 and 29) mPa·s, at temperatures between (298 and 393) K and pressures Below 55 MPa. *J. Chem. Eng. Data* **2005**, *50*, 1377−1388.

(35) Fitzgerald, D. Technical assessment of the Anton Paar DMA5000 density meter. H&D Fitzgerald Ltd Publ., 2000; http://www.density-.co.uk/ review_of_5000.pdf.

(36) Bonhôte, P.; Dias. A.-P.; Armand, M.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. Hydrophobic, highly conductive ambient-temperature molten salts. *Inorg. Chem.* **1996**, *35*, 1168−1178.

(37) Dziuba, S. V.; Bartsch, R. A. Influence of structural variations in 1-alkyl(aralkyl)-3-methylimidazolium hexafluorophosphates and bis-(trifluoromethyl-sulphonyl)imides on physical properties of the ionic liquids. *ChemPhysChem* **2002**, *3*, 161−166.

(38) Rebelo, L. P. N.; Najdanovic-Visak, V.; Gomes de Azevedo, R.; Esperança, J. M. S. S.; Nunes da Ponte, M.; Guedes, H. J. R.; Visak, Z. P.; de Sousa, H. C.; Szydlowski, J.; Canongia Lopes, J. N.; Cordeiro, T. C. Phase behavior and thermodynamic properties of ionic liquids, ionic liquid mixtures, and ionic liquid solutions. In *Ionic Liquids IIIA: Fundamentals, Progress, Challenges, and Opportunities−Properties and Structure*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 901; American Chemical Society: Washington, DC, 2005; Chapter 21, pp 270−291.

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