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Thermophysical and Thermodynamic Properties of 1-Butyl-3-methylimidazolium Tetrafluoroborate and 1-Butyl-3-methylimidazolium Hexafluorophosphate over an Extended Pressure Range

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The current study focuses on 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF₄], and 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF₆]. The objective is to study the influence of pressure as well as that of the anion on several properties of this type of ionic liquid. The speed of sound and densities in pure ionic liquids (ILs) as a function of temperature and pressure have been determined. Several other thermodynamic properties such as compressibilities, expansivities, and heat capacities have been obtained. To the best of our knowledge, this research comprises both the first speed of sound data and the first evaluation of heat capacities at high pressures for ILs. Speed of sound measurements have been carried out in broad ranges of temperature (283 < *T*/K < 323) and pressure (0.1 < *p*/MPa < 150), sometimes inside the metastable liquid region using a nonintrusive microcell. The *T*–*P* melting line of [bmim][PF₆] has also been determined by an acoustic method. Density measurements have been performed for broad ranges of temperature (298 < *T*/K < 333) and pressure (0.1 < *p*/MPa < 60) using a vibrating tube densimeter. The pressure dependence of the heat capacities, which is generally mild, is found to be highly dependent on the curvature of the temperature dependence of the density.

Introduction

Despite the fact that hexafluorophosphate, [PF₆][−], and tetrafluoroborate, [BF₄][−], based ILs can undergo hydrolysis producing HF in contact with water¹ (mainly at high temperatures²), they are historically the most important and most commonly investigated. We have thus chosen these anions coupled with the much studied cation 1-butyl 3-methylimidazolium for our initial speed of sound studies.

Despite the increasing attention that room-temperature ionic liquids (RTILs) have recently received with respect to their thermophysical and thermodynamic properties, overall information is still scarce. Examples of very recent reviews and systematic studies can be found, for instance, in references 3–6 and references therein.

The speed of sound, *u*, is a property that can be experimentally determined with great precision over a broad range of temperature and pressure. Because *u* can be related to the first pressure partial derivative of density, accurate speed of sound data can be used to enhance the development of equations of state. Furthermore, it is a very useful source of information for computing values of other thermodynamic properties that are difficult to obtain at extreme experimental conditions, such as calorimetric data at high pressures. One possible method for deriving a wealth of thermodynamic properties consists of the measurement of the whole (*p*, *ρ*, *T*) and (*p*, *u*, *T*) surfaces to obtain by differentiation the derived properties of the

investigated compound. This method has proven useful, for instance, in the calculation of derived properties of protonated and deuterated acetone.^{7,8} However, commonly accepted as a more reliable method for deriving thermodynamic properties from speed of sound data is that which allows, by integration, the calculation of (*p*, *ρ*, *T*) and (*p*, *C_p*, *T*) surfaces from merely one isobar of both density and isobaric heat capacity.^{9–12} This method allows one to calculate other thermophysical properties such as isentropic (*κ_S*) and isothermal (*κ_T*) compressibilities, isobaric thermal expansivities (*α_p*), isobaric (*C_p*) and isochoric (*C_v*) heat capacities, and thermal pressure coefficients (*γ_v*) over the entire range of pressure of the speed of sound measurements. Whenever available, these values are compared with literature data obtained via other methods.

Experimental Section

Acoustic Cell and Densimeter. Measurements of the speed of sound were performed in the temperature range of 283 < *T*/K < 323 and pressure range of 0.1 < *P*/MPa < 150. The speed of propagation of sound waves in liquids was determined using a nonintrusive method at an operational frequency of 0.5 MHz. We used the same experimental setup as previously described in great detail elsewhere.⁷ Pressure was measured using an Omega pressure transducer, which was calibrated against a high-accuracy Heise gauge. The pressure precision and accuracy are better than ±0.05%. The acoustic cell was placed in a Hart Scientific calibration bath (stability ±0.001 K), and temperature was measured by a four-wire platinum resistance thermometer (PRT) coupled to a Keithley digital multimeter (model DMM 199). The PRT was previously

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calibrated, thus allowing temperature measurements on the ITS-90 scale with an estimated uncertainty of better than ± 0.01 K. Typically, the uncertainty and repeatability of the speed of sound measurements are $\pm 0.2\%$ and $\pm 0.05\%$, respectively. Likewise, densities were measured using an Anton Paar DMA 512P densimeter⁷ in the temperature range of 298 K to 333 K and the pressure range of 0.1 MPa to 60 MPa. The density overall uncertainty is estimated to be better than 0.02%. It should be noted that this value might increase slightly if one considers possible viscosity corrections.¹³ These corrections rely on both the existence of viscosity data⁵ and properly evaluated equations for the correlation between viscosity and signal damping. As for the first, to date there are no viscosity data for these ILs at pressures different from atmospheric. In the case of the latter, different corrections have been proposed¹³ that basically depend on the instrument model and viscosity range. These issues are still under debate. In light of the above-mentioned caveats, we have not performed any viscosity corrections. Therefore, all of the results of the subsequent derived properties and their discussion are based on raw density data. Nonetheless, at atmospheric pressure, one should expect a downward density shift in the low-temperature range between 0.05% and 0.06% and 0.03% and 0.04% for [bmim][PF₆] and [bmim][BF₄], respectively, decreasing to about 0.02% for both ILs in the high-temperature range.

Chemicals. [bmim][PF₆] was synthesized and purified at the QUILL Centre, Belfast, according to procedures found elsewhere.^{14,15} It was washed several times with water to decrease the chloride content. It was determined that no precipitation (of AgCl) occurred by the addition of AgNO₃ to the wash water. [bmim][BF₄] was purchased from Solvent Innovation (stated purity > 98%). The Cl⁻ content, measured with a Cl⁻-specific electrode using the standard addition method, was 20 ppm and 100 ppm for [bmim][PF₆] and [bmim][BF₄], respectively. To reduce the water content and volatile compounds to negligible values, vacuum (0.1 Pa) and moderate temperature (60 °C) were applied to the [bmim][PF₆] and [bmim][BF₄] samples for several days always immediately prior to their use. The samples were analyzed by Karl Fisher titration and showed a mass % of water lower than 75 ppm ("Crison" Karl Fischer titration) and (70 \pm 10) ppm (coulometric "Aquapal" Karl Fischer) for both [bmim][PF₆] and [bmim][BF₄].

Results and Discussion

[bmim][PF₆]. Speed of sound measurements have been carried out in a broad range of temperature (283 < T/K < 323) and pressure (0.1 < p/MPa < 150), sometimes inside the metastable, supercooled liquid region. Figure 1 and Table 1 report the speed of sound behavior as pressure and temperature change for [bmim][PF₆]. 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.

Original data have been fitted to a Pade 3 \times 3 equation of the form

$$(u/\text{m}\cdot\text{s}^{-1}) = \frac{\sum_{i=0}^2 \sum_{j=0}^2 a_{ij} (T/K)^i (p/\text{MPa})^j}{\sum_{k=0}^2 \sum_{l=0}^2 b_{kl} (T/K)^k (p/\text{MPa})^l} \quad (1)$$

The values of the coefficients were calculated by means of a least-squares analysis of the experimental results

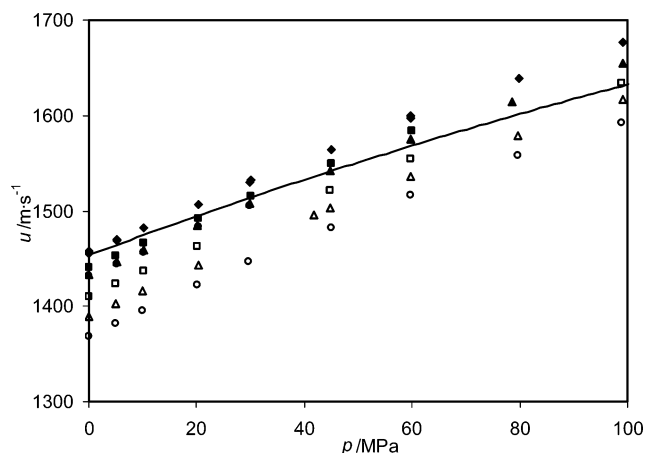


Figure 1. Isotherms of the experimental speed of sound of [bmim][PF₆]. The line represents the border between the stable and metastable, supercooled liquid. (See the text.) ♦, 283.16 K; ■, 291.15 K; ▲, 293.16 K; □, 303.16 K; △, 313.16 K; ○, 323.15 K.

Table 1. Experimental Speed of Sound, u , Data for [bmim][PF₆] as a Function of Temperature, T , and Pressure, p

p/MPa	$u/\text{m}\cdot\text{s}^{-1}$	p/MPa	$u/\text{m}\cdot\text{s}^{-1}$	p/MPa	$u/\text{m}\cdot\text{s}^{-1}$
$T = 283.16$ K					
0.100	1455.52	0.100	1432.85		
0.100	1457.60	5.157	1446.45		
5.088	1468.58	10.195	1459.01		
5.131	1470.64	20.215	1484.18		
10.263	1481.79	29.959	1507.92		
20.249	1506.72	44.757	1542.20		
29.954	1529.87	59.732	1574.70		
29.995	1532.46	78.627	1613.77		
44.961	1564.25	99.149	1654.46		
59.682	1596.68				
59.829	1599.61				
79.904	1638.64				
99.077	1677.06				
124.179	1724.36				
150.925	1772.61				
$T = 291.15$ K					
0.100	1440.19				
5.069	1453.26				
10.166	1466.63				
20.400	1492.36				
30.019	1515.72				
44.920	1549.95				
59.912	1583.22				
$T = 293.16$ K					
0.100	1432.85				
5.157	1446.45				
10.195	1459.01				
20.215	1484.18				
29.959	1507.92				
44.757	1542.20				
59.732	1574.70				
78.627	1613.77				
99.149	1654.46				
$T = 294.16$ K					
0.100	1431.59				
5.125	1444.54				
10.105	1457.17				
20.357	1483.23				
29.785	1506.04				
$T = 303.16$ K					
0.100	1410.27				
5.078	1423.48				
10.204	1437.13				
20.225	1462.82				
44.714	1521.26				
59.773	1554.58				
$T = 313.16$ K					
0.100	1389.49				
5.010	1402.83				
10.043	1416.43				
20.319	1443.30				
41.702	1495.14				
44.866	1502.87				
59.754	1536.27				
79.721	1578.64				
99.097	1617.38				
125.283	1662.16				
$T = 323.25$ K					
0.100	1367.98				
5.061	1381.82				
9.942	1395.37				
20.234	1422.72				
29.721	1446.75				
44.935	1482.19				
59.711	1515.95				
79.553	1557.89				
98.901	1592.52				

Table 2. Coefficients of Equation 1 for T/K , p/MPa , and $u/\text{m}\cdot\text{s}^{-1}$ within the Interval (283 < T/K < 323, 0.1 < p/MPa < 100)

a_{ij}	j		
	0	1	2
0	-2.98041×10^4	6.35774×10^1	-1.53934×10^{-1}
1	-5.78316	8.03545×10^{-1}	9.68016×10^{-3}
2	4.03798×10^{-1}	-3.61889×10^{-3}	-3.23951×10^{-5}
b_{kl}	L		
	0	1	2
0	1.00000	-1.66204×10^{-1}	2.51840×10^{-5}
1	-1.56369×10^{-1}	2.30593×10^{-3}	3.04219×10^{-6}
2	5.47760×10^{-4}	-6.07700×10^{-6}	-1.11069×10^{-8}

(using the algorithm of Marquardt–Levenberg) and are given in Table 2. The standard deviation between the experimental and fitted values is found to be 0.07%. This fitting equation was screened for 40 isotherms within the experimental temperature range (283 < T/K < 323), thus in steps of 1 K, and for steps of 0.1 MPa within the

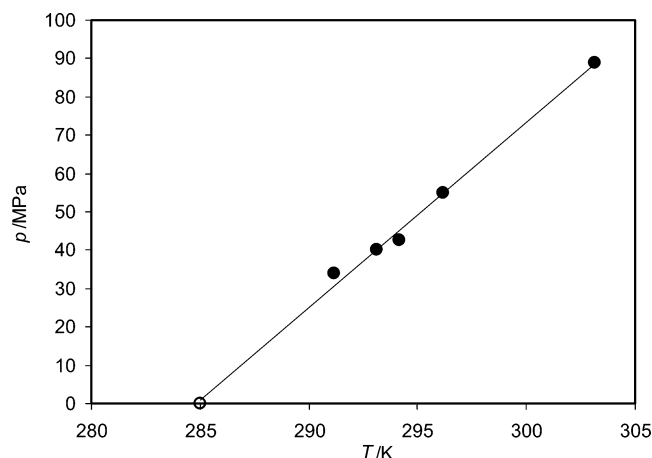


Figure 2. Melting line of [bmim][PF₆]. ●, Acoustic determinations. ○, Visual determination.

Table 3. *T*–*p* Melting-Line Data of [bmim][PF₆]

<i>T</i> /K	<i>p</i> /MPa
285.00	0.1
291.15	34.0
293.15	40.2
294.16	42.5
296.15	55.0
303.15	88.9

experimental interval of pressure ($0.1 < p/\text{MPa} < 100$) for a total of 41 000 data points. No poles for this rational function were found. Also, neither the temperature nor the pressure derivatives of $u(p, T)$ as described by eq 1 present any anomalies. Therefore, eq 1 can be safely used for interpolations. It is already well known that ILs are relatively easy to metastabilize, meaning that, on cooling, they may remain liquid below their equilibrium melting line (supercooling). A liquid is said to be supercooled when it is found as such either at temperatures lower than those of the melting line or at pressures above it (for positively sloped melting lines). In the case of [bmim][PF₆], we have witnessed solidification several times in our isothermal runs intended to determine the speed of sound as a function of pressure. Because a crystalline phase cannot be superheated,¹⁶ whenever solidification occurred we decided to lower the pressure slowly until the liquid state was again restored. Thus, we were able to detect several points of the melting line of [bmim][PF₆], since the difference between the speed of sound in this IL between the two states (solid versus liquid) is significant ($u_{\text{sol}} - u_{\text{liq}} \approx 1000 \text{ ms}^{-1}$). Figure 2 and Table 3 present the solid/liquid phase transition line. Within the experimental uncertainty ($\pm 0.1 \text{ K}$, $\pm 10 \text{ bar}$), the *p*–*T* melting line shows linear behavior between coordinates (285.0 K, 0.1 MPa) and (303.15 K, 89.6 MPa), evolving with a slope of $dp/dT = 4.87 \text{ MPa} \cdot \text{K}^{-1}$. The first coordinate corresponds to our visual determination of melting at atmospheric pressure obtained in a sealed glass vessel by multiple cycles of slow temperature change. It agrees reasonably well with two values (283.15 K¹⁷ and 283.51 K¹⁸) reported, but not with the one (276.43 K¹⁹) for water-free [bmim][PF₆]. It disagrees with that reported (277.15 K¹⁷) for water-equilibrated [bmim][PF₆]. The Clayperon equation can now be used to calculate the volume change on melting provided that one knows the corresponding enthalpy change. We note that literature values do not agree. Although Magee et al.¹⁸ report a value of 19.6 kJ mol^{-1} , Domanska and Marciniak¹⁹ determined a value of 9.21 kJ mol^{-1} . In our calculations, we have chosen the first value because their melting temperature agrees

Table 4. Coefficients of Second-Order Polynomial Fits, $Y = A + B(T/K) + C(T/K)^2$, to Atmospheric Isobars of $Y = \rho$ or $Y = C_p$

	$\rho/\text{kg} \cdot \text{m}^{-3}$	$C_p/\text{J} \cdot \text{K}^{-1} \cdot \text{kg}^{-1}$
A	1620.7039	−1641.9284
B	−0.87955633	17.750623
C	8.4814007×10^{-5}	$-2.4889525 \times 10^{-2}$

reasonably well with ours. Solidification in [bmim][PF₆] is accompanied by a contraction of about 7% ($\Delta V_S = -14.1 \text{ cm}^3 \cdot \text{mol}^{-1}$). This value is highly dependent on the standardization of the enthalpy of fusion.

The use of the speed of sound data to derive other thermodynamic properties requires a knowledge of one isobar of both density and heat capacity. There are already two sets of data available from different groups.^{4,18,20} The choice of the isobars for the thermodynamic properties calculations was based on the comparison of both density and isobaric heat capacity data. The values presented by Magee et al.¹⁸ seem more precise and are greater than those of Gu et al.²⁰ and Fredlake et al.⁴ for both quantities (which may possibly be an indication of higher sample purity because it is quite uncommon to find typical impurities that are responsible for the increase in these properties). However, despite the fact that, in turn, these densities¹⁸ are slightly lower than those presented by us^{3,21} (for about 0.1%) and by Tokuda et al.⁵ (for about 0.35%), that is the best set of combined data of densities and heat capacities along one isobar.

The atmospheric isobars of both density and heat capacity¹⁸ were fitted with a second-order polynomial equation up to 330 K. The coefficients of the fittings are shown in Table 4. The method used to derive other thermodynamic properties is based on well-established thermodynamic relations. The speed of sound, u , is directly related to the pressure derivative of the density, ρ , through eq 2, in which the subscript *S* denotes the condition of constant entropy.

$$\left(\frac{\partial \rho}{\partial p}\right)_S = \frac{1}{u^2} \quad (2)$$

This derivative is related to the isothermal pressure derivative and the isobaric temperature derivative of the density through eq 3, where C_p is the specific heat capacity at constant pressure.

$$\left(\frac{\partial \rho}{\partial p}\right)_S = \left(\frac{\partial \rho}{\partial p}\right)_T - \frac{T}{\rho^2 C_p} \left(\frac{\partial \rho}{\partial T}\right)_p^2 \quad (3)$$

Rearranging the last equation and combining it with eq 2 creates eq 4, which also incorporates the definition of the thermal expansion coefficient, α_p :

$$\left(\frac{\partial \rho}{\partial p}\right)_T = \frac{1}{u^2} + \frac{T}{C_p} \alpha_p^2 \quad (4)$$

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T}\right)_p \quad (5)$$

It can also be shown that the isothermal pressure partial derivative of the isobaric heat capacity can be calculated with eq 6:

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -\frac{T}{\rho} \left[\alpha_p^2 + \left(\frac{\partial \alpha_p}{\partial T}\right)_p \right] \quad (6)$$

Thus, given an isobar of the density and of C_p , it is possible to integrate eqs 4 and 6 over pressure,²² thus obtaining the (*p*, ρ , *T*) and (*p*, C_p , *T*) surfaces within the

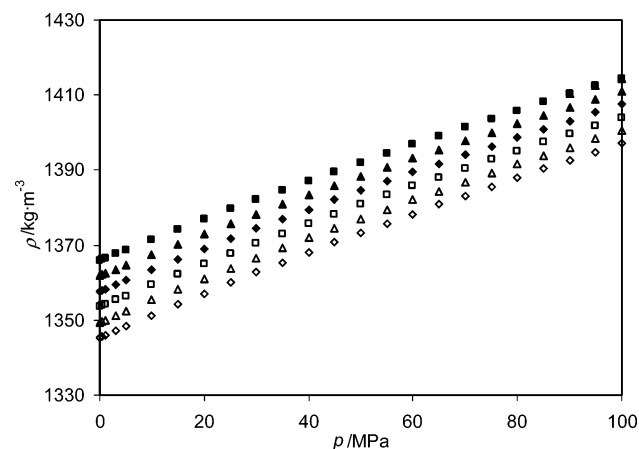


Figure 3. Isotherms for the density of [bmim][PF₆]. ■, 298.15 K; ▲, 303.15 K; ◆, 308.15 K; □, 313.15 K; △, 318.15 K; ◇, 323.15 K.

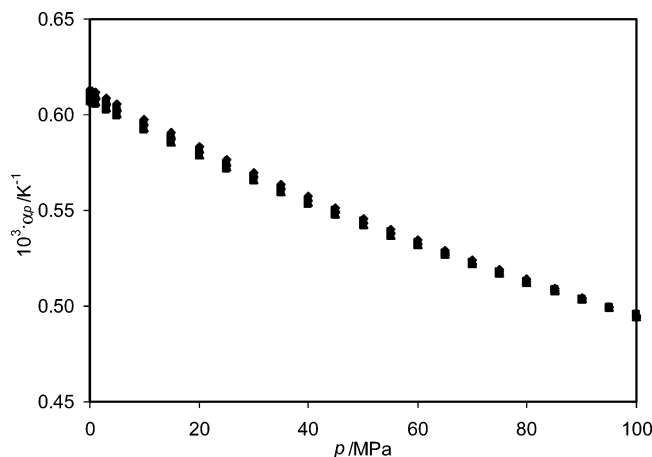


Figure 4. Isotherms for the isobaric expansivity of [bmim][PF₆]. ■, 298.15 K; ▲, 303.15 K; ◆, 308.15 K; □, 313.15 K; △, 318.15 K; ◇, 323.15 K.

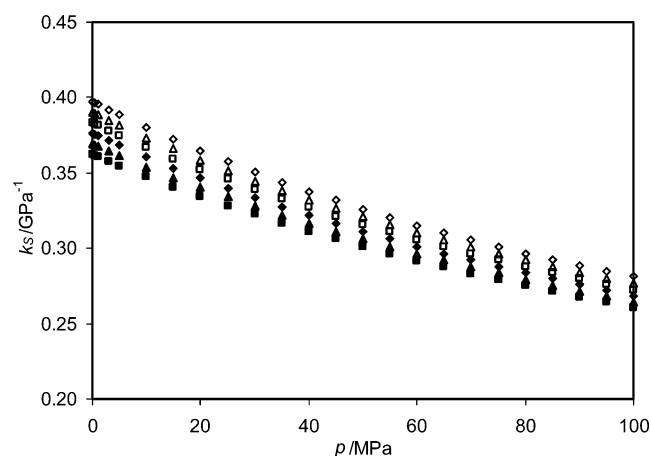


Figure 5. Isotherms for the isentropic compressibility of [bmim][PF₆]. ■, 298.15 K; ▲, 303.15 K; ◆, 308.15 K; □, 313.15 K; △, 318.15 K; ◇, 323.15 K.

range of pressure and temperature of the experimental speed of sound data. The numerical integration procedure also allows one to calculate other properties, such as the isentropic compressibility, κ_S , isothermal compressibility, κ_T , isobaric thermal expansivity, α_p , isochoric heat capacity C_v , and thermal pressure coefficient, γ_v . The estimated overall uncertainties (including sample impurities) are as follows: isentropic compressibility, κ_S (1%); isothermal compressibility, κ_T (2%); isobaric thermal expansivity, α_p

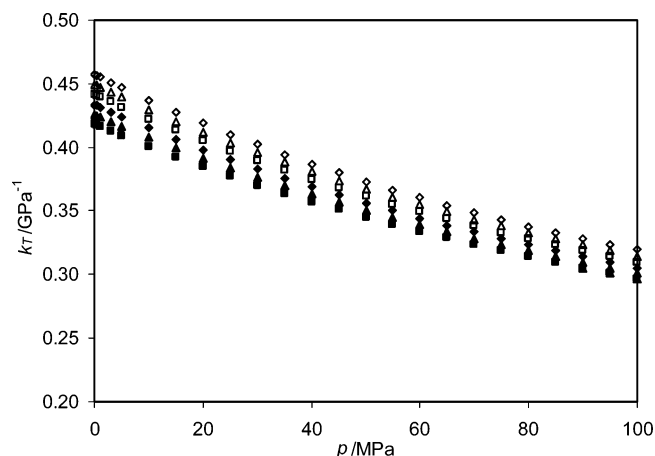


Figure 6. Isotherms for the isothermal compressibility of [bmim][PF₆]. ■, 298.15 K; ▲, 303.15 K; ◆, 308.15 K; □, 313.15 K; △, 318.15 K; ◇, 323.15 K.

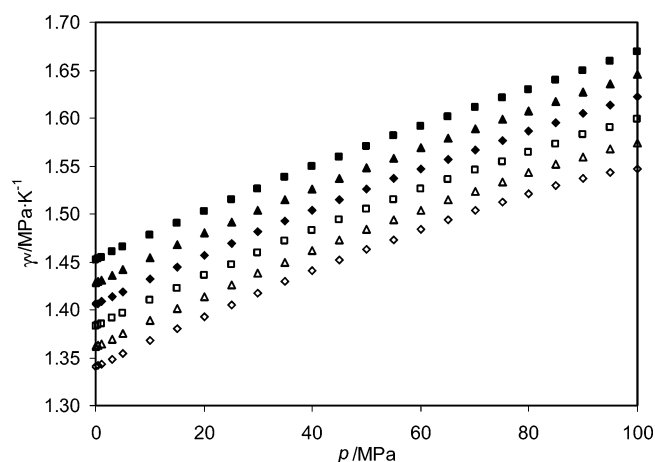


Figure 7. Isotherms for the thermal pressure coefficient of [bmim][PF₆]. ■, 298.15 K; ▲, 303.15 K; ◆, 308.15 K; □, 313.15 K; △, 318.15 K; ◇, 323.15 K.

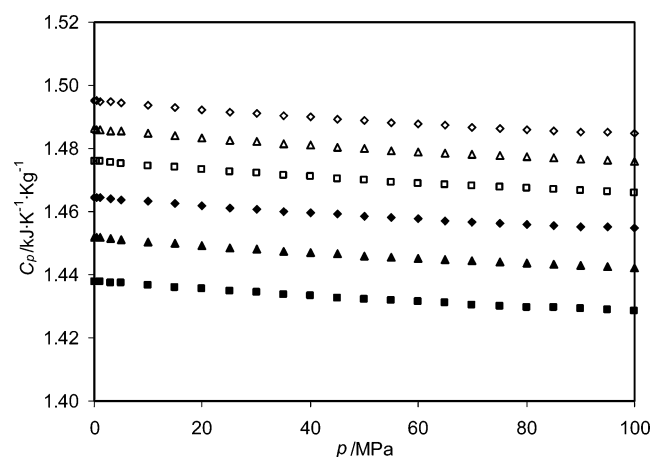


Figure 8. Isotherms for the isobaric heat capacity of [bmim][PF₆]. ■, 298.15 K; ▲, 303.15 K; ◆, 308.15 K; □, 313.15 K; △, 318.15 K; ◇, 323.15 K.

(4%); isobaric heat capacity, C_p (5%); isochoric heat capacity, C_v (8%); and thermal pressure coefficient, γ_v (6%). It should be noted that in the case of heat capacities the major contribution to the uncertainty lies in that of the original calorimetric data. The integration was carried out from atmospheric pressure up to 100 MPa. The results obtained for several thermodynamic properties are presented in Figures 3 to 9 and Tables 5 to 11.

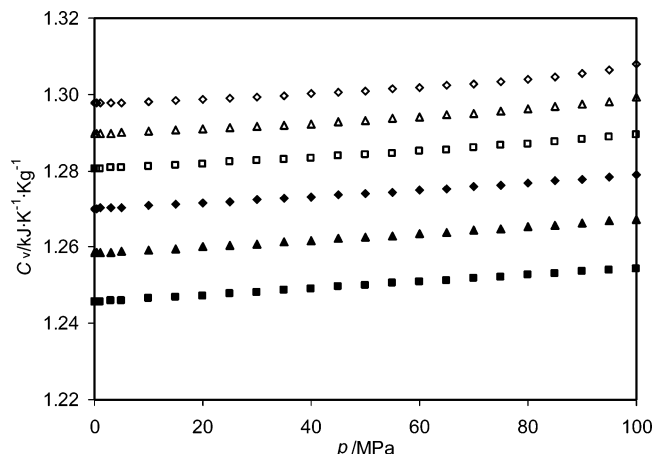


Figure 9. Isotherms for the isochoric heat capacity of [bmim]-[PF₆]. ■, 298.15 K; ▲, 303.15 K; ◆, 308.15 K; □, 313.15 K; △, 318.15 K; ◇, 323.15 K.

The isothermal compressibility results can be compared with those of Gu et al.²⁰ showing deviations that go from

−1% at atmospheric pressure to +12% at 100 MPa and 298.2 K and from −9% to +13% at 323.2 K.

As for the heat capacities, results for both the isobaric and isochoric heat capacities reveal, in practice, pressure independence.

Although expansivities decrease markedly with pressure, according to Figure 4 and Table 8 they present a tendency to increase very mildly with increasing temperature at constant pressure. This trend agrees with that reported by Tokuda et al.⁵ at atmospheric pressure. Nonetheless, within the typical experimental uncertainty of α_p calculations (4%) the expansivities of [bmim][PF₆] can, in practice, be considered almost temperature-independent. This behavior contradicts that which has been reported in other works^{18,20} in which α_p of [bmim][PF₆] decreases as temperature rises. This contradiction underlies numerical difficulties in the data evaluation associated with very subtle effects and was previously noticed in different communications^{3,6,23}. The point is that 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

Table 5. Calculated Values of Density, ρ , for [bmim][PF₆]

p/MPa	T/K						p/MPa	T/K					
	298.15	303.15	308.15	313.15	318.15	323.15		298.15	303.15	308.15	313.15	318.15	323.15
	$\rho/\text{kg}\cdot\text{m}^{-3}$							$\rho/\text{kg}\cdot\text{m}^{-3}$					
0.1	1366.0 ₀	1361.8 ₆	1357.7 ₂	1353.5 ₉	1349.4 ₆	1345.3 ₃	45	1389.6 ₄	1385.8 ₄	1382.0 ₄	1378.2 ₅	1374.4 ₆	1370.6 ₈
0.5	1366.2 ₃	1362.0 ₉	1357.9 ₆	1353.8 ₃	1349.7 ₀	1345.5 ₈	50	1392.0 ₆	1388.2 ₉	1384.5 ₃	1380.7 ₇	1377.0 ₁	1373.2 ₆
1	1366.5 ₂	1362.3 ₈	1358.2 ₅	1354.1 ₂	1350.0 ₀	1345.8 ₈	55	1394.4 ₅	1390.7 ₁	1386.9 ₇	1383.2 ₅	1379.5 ₂	1375.8 ₁
3	1367.6 ₅	1363.5 ₃	1359.4 ₂	1355.3 ₁	1351.2 ₁	1347.1 ₁	60	1396.8 ₀	1393.0 ₉	1389.3 ₈	1385.6 ₉	1381.9 ₉	1378.3 ₁
5	1368.7 ₇	1364.6 ₇	1360.5 ₈	1356.4 ₉	1352.4 ₀	1348.3 ₂	65	1399.1 ₁	1395.4 ₃	1391.7 ₆	1388.0 ₉	1384.4 ₃	1380.7 ₇
10	1371.5 ₅	1367.4 ₉	1363.4 ₃	1359.3 ₉	1355.3 ₄	1351.3 ₀	70	1401.4 ₀	1397.7 ₄	1394.1 ₀	1390.4 ₆	1386.8 ₃	1383.2 ₀
15	1374.2 ₇	1370.2 ₅	1366.2 ₄	1362.2 ₃	1358.2 ₂	1354.2 ₂	75	1403.6 ₅	1400.0 ₃	1396.4 ₁	1392.8 ₀	1389.1 ₉	1385.5 ₉
20	1376.9 ₄	1372.9 ₆	1368.9 ₉	1365.0 ₂	1361.0 ₅	1357.0 ₉	80	1405.8 ₇	1402.2 ₈	1398.6 ₉	1395.1 ₀	1391.5 ₂	1387.9 ₅
25	1379.5 ₇	1375.6 ₃	1371.6 ₉	1367.7 ₆	1363.8 ₃	1359.9 ₁	85	1408.0 ₇	1404.5 ₀	1400.9 ₃	1397.3 ₈	1393.8 ₃	1390.2 ₈
30	1382.1 ₅	1378.2 ₄	1374.3 ₄	1370.4 ₅	1366.5 ₆	1362.6 ₇	90	1410.2 ₃	1406.6 ₉	1403.1 ₅	1399.6 ₂	1396.1 ₀	1392.5 ₈
35	1384.6 ₉	1380.8 ₂	1376.9 ₅	1373.0 ₉	1369.2 ₄	1365.3 ₉	95	1412.3 ₇	1408.8 ₅	1405.3 ₄	1401.8 ₃	1398.3 ₄	1394.8 ₅
40	1387.1 ₈	1383.3 ₅	1379.5 ₂	1375.6 ₉	1371.8 ₇	1368.0 ₆	100	1414.4 ₉	1410.9 ₉	1407.5 ₀	1404.0 ₂	1400.5 ₅	1397.1 ₀

Table 6. Calculated Values of κ_T for [bmim][PF₆]

p/MPa	T/K						p/MPa	T/K					
	298.15	303.15	308.15	313.15	318.15	323.15		298.15	303.15	308.15	313.15	318.15	323.15
	κ_T/GPa^{-1}							κ_T/GPa^{-1}					
0.1	0.417 ₉	0.425 ₆	0.433 ₅	0.441 ₄	0.449 ₃	0.457 ₃	45	0.351 ₀	0.356 ₇	0.362 ₄	0.368 ₁	0.374 ₀	0.379 ₈
0.5	0.417 ₁	0.424 ₉	0.432 ₇	0.440 ₆	0.448 ₅	0.456 ₄	50	0.345 ₁	0.350 ₆	0.356 ₁	0.361 ₇	0.367 ₃	0.373 ₀
1	0.416 ₂	0.423 ₉	0.431 ₇	0.439 ₆	0.447 ₄	0.455 ₄	55	0.339 ₅	0.344 ₈	0.350 ₁	0.355 ₅	0.361 ₀	0.366 ₅
3	0.412 ₆	0.420 ₂	0.427 ₉	0.435 ₆	0.443 ₄	0.451 ₂	60	0.334 ₀	0.339 ₁	0.344 ₃	0.349 ₆	0.354 ₉	0.360 ₃
5	0.409 ₁	0.416 ₆	0.424 ₁	0.431 ₇	0.439 ₄	0.447 ₁	65	0.328 ₈	0.333 ₈	0.338 ₈	0.343 ₉	0.349 ₁	0.354 ₃
10	0.400 ₆	0.407 ₈	0.415 ₁	0.422 ₄	0.429 ₇	0.437 ₂	70	0.323 ₇	0.328 ₆	0.333 ₅	0.338 ₄	0.343 ₅	0.348 ₆
15	0.392 ₅	0.399 ₄	0.406 ₄	0.413 ₅	0.420 ₆	0.427 ₇	75	0.318 ₉	0.323 ₆	0.328 ₄	0.333 ₂	0.338 ₁	0.343 ₁
20	0.384 ₈	0.391 ₅	0.398 ₂	0.405 ₀	0.411 ₉	0.418 ₈	80	0.314 ₂	0.318 ₈	0.323 ₄	0.328 ₁	0.332 ₉	0.337 ₈
25	0.377 ₄	0.383 ₉	0.390 ₄	0.397 ₀	0.403 ₆	0.410 ₂	85	0.309 ₇	0.314 ₁	0.318 ₆	0.323 ₂	0.327 ₉	0.332 ₈
30	0.370 ₃	0.376 ₆	0.382 ₉	0.389 ₃	0.395 ₇	0.402 ₁	90	0.305 ₄	0.309 ₇	0.314 ₀	0.318 ₅	0.323 ₂	0.328 ₀
35	0.363 ₆	0.369 ₇	0.375 ₈	0.381 ₉	0.388 ₁	0.394 ₃	95	0.301 ₁	0.305 ₃	0.309 ₅	0.313 ₉	0.318 ₆	0.323 ₅
40	0.357 ₂	0.363 ₀	0.368 ₉	0.374 ₉	0.380 ₉	0.386 ₉	100	0.297 ₁	0.301 ₀	0.305 ₁	0.309 ₅	0.314 ₂	0.319 ₅

Table 7. Calculated Values of κ_S for [bmim][PF₆]

p/MPa	T/K						p/MPa	T/K					
	298.15	303.15	308.15	313.15	318.15	323.15		298.15	303.15	308.15	313.15	318.15	323.15
	κ_S/GPa^{-1}							κ_S/GPa^{-1}					
0.1	0.362 ₀	0.368 ₉	0.375 ₉	0.382 ₉	0.389 ₉	0.396 ₉	45	0.306 ₁	0.311 ₂	0.316 ₃	0.321 ₄	0.326 ₅	0.331 ₇
0.5	0.361 ₃	0.368 ₃	0.375 ₃	0.382 ₃	0.389 ₂	0.396 ₂	50	0.301 ₂	0.306 ₁	0.311 ₁	0.316 ₀	0.321 ₀	0.326 ₀
1	0.360 ₆	0.367 ₅	0.374 ₅	0.381 ₄	0.388 ₄	0.395 ₃	55	0.296 ₄	0.301 ₂	0.306 ₀	0.310 ₈	0.315 ₇	0.320 ₅
3	0.357 ₆	0.364 ₄	0.371 ₃	0.378 ₁	0.384 ₉	0.391 ₈	60	0.291 ₉	0.296 ₅	0.301 ₂	0.305 ₉	0.310 ₆	0.315 ₃
5	0.354 ₆	0.361 ₄	0.368 ₁	0.374 ₈	0.381 ₆	0.388 ₃	65	0.287 ₅	0.292 ₀	0.296 ₅	0.301 ₁	0.305 ₇	0.310 ₃
10	0.347 ₅	0.354 ₀	0.360 ₅	0.367 ₀	0.373 ₅	0.379 ₉	70	0.283 ₃	0.287 ₇	0.292 ₁	0.296 ₅	0.301 ₀	0.305 ₅
15	0.340 ₈	0.347 ₀	0.353 ₃	0.359 ₅	0.365 ₈	0.372 ₀	75	0.279 ₂	0.283 ₅	0.287 ₈	0.292 ₁	0.296 ₄	0.300 ₉
20	0.334 ₃	0.340 ₃	0.346 ₄	0.352 ₄	0.358 ₄	0.364 ₅	80	0.275 ₃	0.279 ₄	0.283 ₆	0.287 ₈	0.292 ₁	0.296 ₅
25	0.328 ₂	0.334 ₀	0.339 ₈	0.345 ₆	0.351 ₅	0.357 ₃	85	0.271 ₅	0.275 ₅	0.279 ₆	0.283 ₇	0.287 ₉	0.292 ₂
30	0.322 ₃	0.327 ₉	0.333 ₅	0.339 ₂	0.344 ₈	0.350 ₄	90	0.267 ₉	0.271 ₈	0.275 ₇	0.279 ₈	0.283 ₉	0.288 ₃
35	0.316 ₇	0.322 ₁	0.327 ₅	0.333 ₀	0.338 ₄	0.343 ₉	95	0.264 ₃	0.268 ₁	0.272 ₀	0.275 ₉	0.280 ₁	0.284 ₆
40	0.311 ₃	0.316 ₅	0.321 ₈	0.327 ₁	0.332 ₄	0.337 ₆	100	0.260 ₈	0.264 ₅	0.268 ₂	0.272 ₂	0.276 ₆	0.281 ₅

Table 8. Calculated Values of α_p for [bmim][PF₆]

p/MPa	T/K						p/MPa	T/K					
	298.15	303.15	308.15	313.15	318.15	323.15		298.15	303.15	308.15	313.15	318.15	323.15
	$10^3\alpha_p/\text{K}^{-1}$							$10^3\alpha_p/\text{K}^{-1}$					
0.1	0.606 ₉	0.608 ₁	0.609 ₃	0.610 ₆	0.611 ₈	0.613 ₀	45	0.547 ₅	0.548 ₃	0.549 ₁	0.549 ₉	0.550 ₇	0.551 ₅
0.5	0.606 ₃	0.607 ₅	0.608 ₇	0.609 ₉	0.611 ₂	0.612 ₄	50	0.542 ₀	0.542 ₇	0.543 ₅	0.544 ₂	0.544 ₉	0.545 ₇
1	0.605 ₅	0.606 ₇	0.607 ₉	0.609 ₁	0.610 ₄	0.611 ₆	55	0.536 ₆	0.537 ₃	0.538 ₀	0.538 ₇	0.539 ₃	0.540 ₀
3	0.602 ₄	0.603 ₆	0.604 ₈	0.606 ₀	0.607 ₂	0.608 ₄	60	0.531 ₅	0.532 ₁	0.532 ₇	0.533 ₃	0.533 ₉	0.534 ₅
5	0.599 ₄	0.600 ₆	0.601 ₈	0.602 ₉	0.604 ₁	0.605 ₃	65	0.526 ₄	0.527 ₀	0.527 ₅	0.528 ₁	0.528 ₆	0.529 ₂
10	0.592 ₁	0.593 ₂	0.594 ₃	0.595 ₅	0.596 ₆	0.597 ₈	70	0.521 ₆	0.522 ₀	0.522 ₅	0.523 ₀	0.523 ₅	0.524 ₀
15	0.585 ₀	0.586 ₁	0.587 ₂	0.588 ₃	0.589 ₄	0.590 ₄	75	0.516 ₈	0.517 ₂	0.517 ₇	0.518 ₁	0.518 ₅	0.518 ₉
20	0.578 ₂	0.579 ₂	0.580 ₃	0.581 ₃	0.582 ₃	0.583 ₄	80	0.512 ₃	0.512 ₆	0.512 ₉	0.513 ₃	0.513 ₆	0.513 ₉
25	0.571 ₆	0.572 ₆	0.573 ₆	0.574 ₆	0.575 ₆	0.576 ₆	85	0.507 ₈	0.508 ₁	0.508 ₃	0.508 ₆	0.508 ₈	0.509 ₀
30	0.565 ₃	0.566 ₂	0.567 ₂	0.568 ₁	0.569 ₁	0.570 ₀	90	0.503 ₆	0.503 ₇	0.503 ₈	0.503 ₉	0.504 ₁	0.504 ₂
35	0.559 ₂	0.560 ₁	0.561 ₀	0.561 ₀	0.562 ₇	0.563 ₆	95	0.499 ₅	0.499 ₅	0.499 ₄	0.499 ₄	0.499 ₃	0.499 ₃
40	0.553 ₃	0.554 ₁	0.554 ₉	0.555 ₈	0.556 ₆	0.557 ₄	100	0.495 ₇	0.495 ₄	0.495 ₁	0.494 ₈	0.494 ₅	0.494 ₃

Table 9. Calculated Values of γ_v for [bmim][PF₆]

p/MPa	T/K						p/MPa	T/K					
	298.15	303.15	308.15	313.15	318.15	323.15		298.15	303.15	308.15	313.15	318.15	323.15
	$\gamma_v/\text{MPa}\cdot\text{K}^{-1}$							$\gamma_v/\text{MPa}\cdot\text{K}^{-1}$					
0.1	1.45 ₂	1.42 ₉	1.40 ₆	1.38 ₃	1.36 ₂	1.34 ₁	45	1.56 ₀	1.53 ₇	1.51 ₅	1.49 ₄	1.47 ₃	1.45 ₂
0.5	1.45 ₃	1.43 ₀	1.40 ₇	1.38 ₄	1.36 ₃	1.34 ₂	50	1.57 ₀	1.54 ₈	1.52 ₆	1.50 ₅	1.48 ₃	1.46 ₃
1	1.45 ₅	1.43 ₁	1.40 ₈	1.38 ₆	1.36 ₄	1.34 ₃	55	1.58 ₁	1.55 ₉	1.53 ₇	1.51 ₅	1.49 ₄	1.47 ₃
3	1.46 ₀	1.43 ₆	1.41 ₃	1.39 ₁	1.37 ₀	1.34 ₉	60	1.59 ₁	1.56 ₉	1.54 ₇	1.52 ₅	1.50 ₄	1.48 ₄
5	1.46 ₅	1.44 ₂	1.41 ₉	1.39 ₇	1.37 ₅	1.35 ₄	65	1.60 ₁	1.57 ₉	1.55 ₇	1.53 ₅	1.51 ₄	1.49 ₃
10	1.47 ₈	1.45 ₅	1.43 ₂	1.41 ₀	1.38 ₈	1.36 ₇	70	1.61 ₁	1.58 ₉	1.56 ₇	1.54 ₅	1.52 ₄	1.50 ₃
15	1.49 ₁	1.46 ₇	1.44 ₅	1.42 ₃	1.40 ₁	1.38 ₀	75	1.62 ₁	1.59 ₈	1.57 ₇	1.55 ₅	1.53 ₄	1.51 ₂
20	1.50 ₃	1.48 ₀	1.45 ₇	1.43 ₅	1.41 ₄	1.39 ₃	80	1.63 ₀	1.60 ₈	1.58 ₆	1.56 ₄	1.54 ₃	1.52 ₁
25	1.51 ₅	1.49 ₂	1.46 ₉	1.44 ₈	1.42 ₆	1.40 ₅	85	1.64 ₀	1.61 ₇	1.59 ₅	1.57 ₃	1.55 ₁	1.53 ₀
30	1.52 ₆	1.50 ₄	1.48 ₁	1.45 ₉	1.43 ₈	1.41 ₈	90	1.64 ₉	1.62 ₇	1.60 ₅	1.58 ₂	1.56 ₀	1.53 ₇
35	1.53 ₈	1.51 ₅	1.49 ₃	1.47 ₁	1.45 ₀	1.42 ₉	95	1.65 ₉	1.63 ₆	1.61 ₃	1.59 ₁	1.56 ₈	1.54 ₄
40	1.54 ₉	1.52 ₆	1.50 ₄	1.48 ₃	1.46 ₁	1.44 ₁	100	1.66 ₉	1.64 ₆	1.62 ₃	1.59 ₉	1.57 ₄	1.54 ₇

Table 10. Calculated Values of C_p for [bmim][PF₆]

p/MPa	T/K						p/MPa	T/K					
	298.15	303.15	308.15	313.15	318.15	323.15		298.15	303.15	308.15	313.15	318.15	323.15
	$C_p/\text{kJ}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$							$C_p/\text{kJ}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$					
0.1	1.43 ₈	1.45 ₂	1.46 ₅	1.47 ₆	1.48 ₆	1.49 ₅	45	1.43 ₃	1.44 ₇	1.45 ₉	1.47 ₀	1.48 ₀	1.48 ₉
0.5	1.43 ₈	1.45 ₂	1.46 ₄	1.47 ₆	1.48 ₆	1.49 ₅	50	1.43 ₂	1.44 ₆	1.45 ₉	1.47 ₀	1.48 ₀	1.48 ₉
1	1.43 ₈	1.45 ₂	1.46 ₄	1.47 ₆	1.48 ₆	1.49 ₅	55	1.43 ₂	1.44 ₆	1.45 ₈	1.46 ₉	1.47 ₉	1.48 ₈
3	1.43 ₈	1.45 ₁	1.46 ₄	1.47 ₆	1.48 ₆	1.49 ₅	60	1.43 ₁	1.44 ₅	1.45 ₈	1.46 ₉	1.47 ₉	1.48 ₈
5	1.43 ₇	1.45 ₁	1.46 ₄	1.47 ₅	1.48 ₅	1.49 ₄	65	1.43 ₁	1.44 ₅	1.45 ₇	1.46 ₈	1.47 ₉	1.48 ₇
10	1.43 ₇	1.45 ₁	1.46 ₃	1.47 ₅	1.48 ₅	1.49 ₄	70	1.43 ₁	1.44 ₄	1.45 ₇	1.46 ₈	1.47 ₈	1.48 ₇
15	1.43 ₆	1.45 ₀	1.46 ₃	1.47 ₄	1.48 ₄	1.49 ₃	75	1.43 ₀	1.44 ₄	1.45 ₆	1.46 ₈	1.47 ₈	1.48 ₆
20	1.43 ₅	1.44 ₉	1.46 ₂	1.47 ₃	1.48 ₃	1.49 ₂	80	1.43 ₀	1.44 ₄	1.45 ₆	1.46 ₇	1.47 ₇	1.48 ₆
25	1.43 ₅	1.44 ₉	1.46 ₁	1.47 ₃	1.48 ₃	1.49 ₂	85	1.42 ₉	1.44 ₃	1.45 ₆	1.46 ₇	1.47 ₇	1.48 ₆
30	1.43 ₄	1.44 ₈	1.46 ₁	1.47 ₂	1.48 ₂	1.49 ₁	90	1.42 ₉	1.44 ₃	1.45 ₅	1.46 ₇	1.47 ₇	1.48 ₅
35	1.43 ₄	1.44 ₈	1.46 ₀	1.47 ₁	1.48 ₂	1.49 ₀	95	1.42 ₉	1.44 ₃	1.45 ₅	1.46 ₆	1.47 ₆	1.48 ₅
40	1.43 ₃	1.44 ₇	1.46 ₀	1.47 ₁	1.48 ₁	1.49 ₀	100	1.42 ₉	1.44 ₂	1.45 ₅	1.46 ₆	1.47 ₆	1.48 ₅

Table 11. Calculated Values of C_v for [bmim][PF₆]

p/MPa	T/K						p/MPa	T/K					
	298.15	303.15	308.15	313.15	318.15	323.15		298.15	303.15	308.15	313.15	318.15	323.15
	$C_v/\text{kJ}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$							$C_v/\text{kJ}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$					
0.1	1.24 ₆	1.25 ₈	1.27 ₀	1.28 ₁	1.29 ₀	1.29 ₈	45	1.24 ₉	1.26 ₂	1.27 ₄	1.28 ₄	1.29 ₃	1.30 ₁
0.5	1.24 ₆	1.25 ₈	1.27 ₀	1.28 ₁	1.29 ₀	1.29 ₈	50	1.25 ₀	1.26 ₃	1.27 ₄	1.28 ₄	1.29 ₃	1.30 ₁
1	1.24 ₆	1.25 ₉	1.27 ₀	1.28 ₁	1.29 ₀	1.29 ₈	55	1.25 ₀	1.26 ₃	1.27 ₄	1.28 ₅	1.29 ₄	1.30 ₁
3	1.24 ₆	1.25 ₉	1.27 ₀	1.28 ₁	1.29 ₀	1.29 ₈	60	1.25 ₁	1.26 ₃	1.27 ₅	1.28 ₅	1.29 ₄	1.30 ₂
5	1.24 ₆	1.25 ₉	1.27 ₀	1.28 ₁	1.29 ₀	1.29 ₈	65	1.25 ₁	1.26 ₄	1.27 ₅	1.28 ₆	1.29 ₅	1.30 ₂
10	1.24 ₆	1.25 ₉	1.27 ₁	1.28 ₁	1.29 ₀	1.29 ₈	70	1.25 ₂	1.26 ₄	1.27 ₆	1.28 ₆	1.29 ₅	1.30 ₃
15	1.24 ₇	1.26 ₀	1.27 ₁	1.28 ₂	1.29 ₁	1.29 ₈	75	1.25 ₂	1.26 ₅	1.27 ₆	1.28 ₇	1.29 ₆	1.30 ₃
20	1.24 ₇	1.26 ₀	1.27 ₂	1.28 ₂	1.29 ₁	1.29 ₉	80	1.25 ₃	1.26 ₅	1.27 ₇	1.28 ₇	1.29 ₆	1.30 ₄
25	1.24 ₈	1.26 ₀	1.27 ₂	1.28 ₂	1.29 ₁	1.29 ₉	85	1.25 ₃	1.26 ₆	1.27 ₇	1.28 ₈	1.29 ₇	1.30 ₅
30	1.24 ₈	1.26 ₁	1.27 ₂	1.28 ₃	1.29 ₂	1.29 ₉	90	1.25 ₄	1.26 ₆	1.27 ₈	1.28 ₈	1.29 ₇	1.30 ₅
35	1.24 ₉	1.26 ₁	1.27 ₃	1.28 ₃	1.29 ₂	1.30 ₀	95	1.25 ₄	1.26 ₇	1.27 ₈	1.28 ₉	1.29 ₈	1.30 ₆
40	1.24 ₉	1.26 ₂	1.27 ₃	1.28 ₃	1.29 ₂	1.30 ₀	100	1.25 ₄	1.26 ₇	1.27 ₉	1.29 ₀	1.29 ₉	1.30 ₈

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 $\ln \rho = f(T)$. If this function proves to be linear,

then $\ln V = f(T)$ is as well, and α_p is constant (temperature-independent). Moreover, the choice of a logarithmic function avoids the

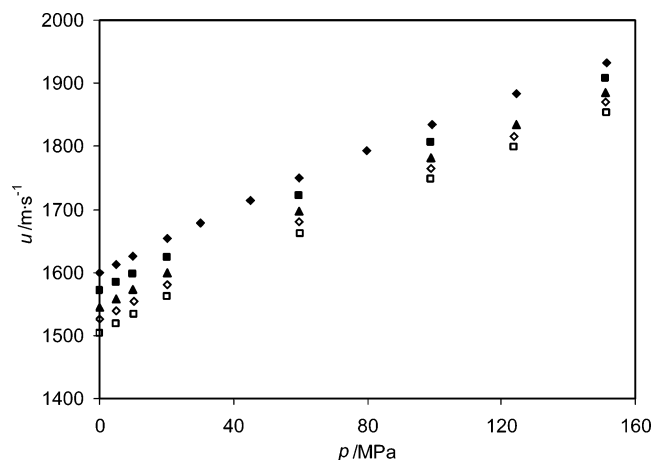


Figure 10. Isotherms for the experimental speed of sound in [bmim][BF₄]. ♦, 283.15 K; ■, 293.15 K; ▲, 303.15 K; ◇, 313.15 K; □, 323.15 K.

Table 12. Experimental Speed of Sound, u , Data for [bmim][BF₄] as a Function of Temperature, T , and Pressure, p

p/MPa	$u/\text{m}\cdot\text{s}^{-1}$	p/MPa	$u/\text{m}\cdot\text{s}^{-1}$	p/MPa	$u/\text{m}\cdot\text{s}^{-1}$
$T = 283.15 \text{ K}$					
0.100	1599.51	59.673	1721.05	20.070	1580.96
4.956	1612.54	98.994	1806.08	59.719	1679.35
9.954	1626.20	151.068	1907.30	99.014	1765.79
20.130	1653.13			123.975	1816.59
30.003	1678.26	$T = 303.15 \text{ K}$		151.204	1869.96
44.948	1714.66	0.100	1544.88	$T = 323.15 \text{ K}$	
59.705	1749.05	5.080	1558.60	0.100	1503.36
79.788	1793.04	10.091	1572.45	4.999	1517.83
99.235	1833.62	20.063	1599.53	10.202	1533.40
124.380	1882.86	59.767	1697.00	20.046	1561.37
151.416	1932.20	99.007	1782.61	59.977	1662.08
		124.609	1834.02	99.014	1748.81
$T = 293.15 \text{ K}$					
0.100	1570.23	$T = 313.15 \text{ K}$		123.945	1798.92
5.094	1583.99	0.100	1525.22	151.374	1853.24
10.075	1597.70	5.091	1539.35		

Table 13. Coefficients of Equation 1 for T/K , p/MPa , and $u/\text{m}\cdot\text{s}^{-1}$ within the Interval ($283 < T/\text{K} < 323$, $0.1 < p/\text{MPa} < 100$)

a_{ij}	j		
i	0	1	2
0	1.11539×10^3	1.16241×10^1	-1.85200×10^{-2}
1	-1.03226×10^1	-8.64584×10^{-2}	1.23988×10^{-4}
2	2.10054×10^{-2}	1.55385×10^{-4}	-2.03876×10^{-7}

b_{kl}	L		
k	0	1	2
0	1.00000	5.81502×10^{-3}	-1.49739×10^{-5}
1	-8.43584×10^{-3}	-4.13259×10^{-5}	9.95819×10^{-8}
2	1.63578×10^{-5}	7.19818×10^{-8}	-1.63623×10^{-10}

[bmim][BF₄]. Speed of sound measurements have been carried out at broad ranges of temperature ($283 < T/\text{K} < 323$) and pressure ($0.1 < p/\text{MPa} < 160$). Figure 10 and Table 12 show the speed of sound behavior with pressure and temperature for [bmim][BF₄]. Equation 1 was used to fit the experimental data, and all of the tests proved the nonexistence of poles in the (p, u, T) surface considered. The values of the fitting coefficients are provided in Table 13. The standard deviation between the experimental and fitted values is found to be 0.04%.

Density measurements have been carried out at broad ranges of temperature ($298 < T/\text{K} < 333$) and pressure (0.1

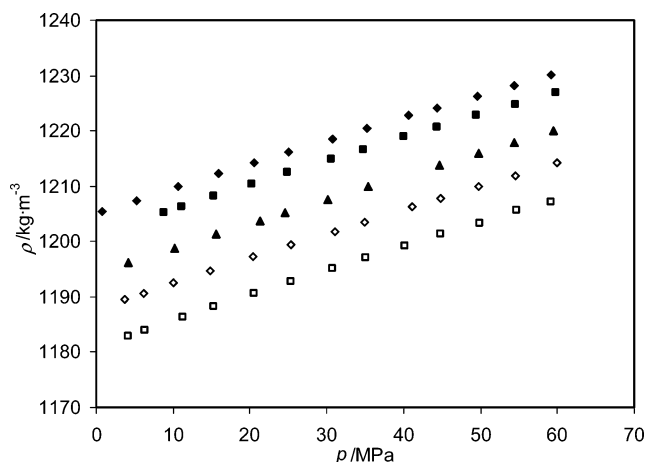


Figure 11. Isotherms for the experimental density of [bmim][BF₄]. ♦, 298.34 K; ■, 303.23 K; ▲, 313.01 K; ◇, 322.85 K; □, 332.73 K.

Table 14. Experimental Density, ρ , Data for [bmim][BF₄] as a Function of Temperature, T , and Pressure, p

p/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	p/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	p/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$
$T = 298.34 \text{ K}$					
0.1	1205.03	44.31	1220.61	25.40	1199.38
0.70	1205.32	49.50	1222.73	31.09	1201.87
5.28	1207.44	54.49	1224.75	34.85	1203.51
10.60	1209.87	59.82	1226.85	41.13	1206.23
15.92	1212.24			44.88	1207.85
20.54	1214.26	$T = 313.01 \text{ K}$		49.83	1209.95
25.00	1216.18	0.1	1194.59	54.52	1211.91
30.71	1218.62	4.13	1196.19	59.92	1214.20
35.19	1220.47	10.18	1198.82	$T = 332.73 \text{ K}$	
40.66	1222.73	15.65	1201.26	0.1	1181.05
44.37	1224.21	21.30	1203.75	4.13	1182.92
49.66	1226.32	24.58	1205.19	6.35	1183.98
54.34	1228.16	30.11	1207.62	11.21	1186.30
59.23	1230.05	35.39	1209.88	15.22	1188.15
		44.70	1213.84	20.54	1190.55
		49.72	1215.92	25.28	1192.70
$T = 303.23 \text{ K}$					
0.1	1201.29	54.43	1217.91	30.76	1195.16
8.78	1205.30	59.45	1219.95	35.08	1197.05
11.17	1206.40	$T = 322.85 \text{ K}$		40.11	1199.23
15.23	1208.22	0.1	1187.85	44.86	1201.24
20.27	1210.43	3.73	1189.50	49.84	1203.35
24.89	1212.44	6.22	1190.68	54.76	1205.70
30.67	1214.92	10.02	1192.47	59.13	1207.20
34.77	1216.66	14.87	1194.68		
40.02	1218.85	20.45	1197.20		

Table 15. Coefficients of Second-Order Polynomial Fits, $Y = A + B(T/\text{K}) + C(T/\text{K})^2$, to Atmospheric Isobars of $Y = \rho$ or $Y = C_p$

	$\rho/\text{kg}\cdot\text{m}^{-3}$	$C_p/\text{J}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$
A	1476.2773	2056.7965
B	-1.1035102	-5.2008507
C	6.5020339×10^{-4}	1.2456247×10^{-2}

$< p/\text{MPa} < 60$). The experimental data are presented both in Figure 11 and Table 14.

The derived thermodynamic properties were calculated by the integration method using isobaric density data of this current work and heat capacities taken from literature data²³ at 0.1 MPa. The atmospheric isobars of both density and heat capacity were fitted with a second-order polynomial equation. The coefficients of the fittings are reported in Table 15. The integration was carried out from atmospheric pressure up to 150 MPa. The results obtained for several thermodynamic properties are presented in Figures 12 to 17 and Tables 16 to 21.

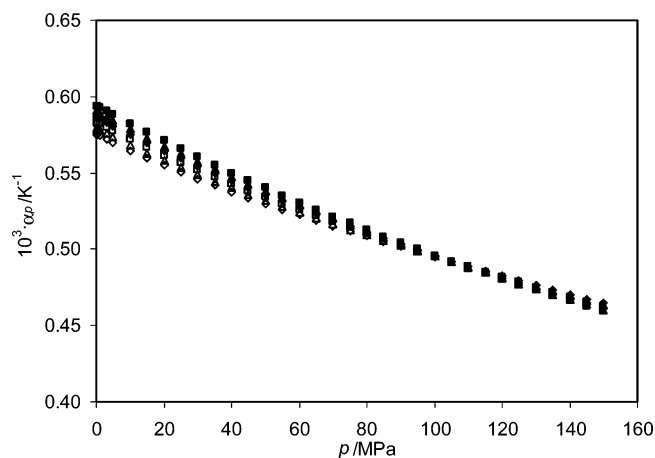


Figure 12. Isotherms for the isobaric expansivity of [bmim][BF₄]. ■, 298.15 K; ▲, 303.15 K; ◆, 308.15 K; □, 313.15 K; △, 318.15 K; ◇, 323.15 K.

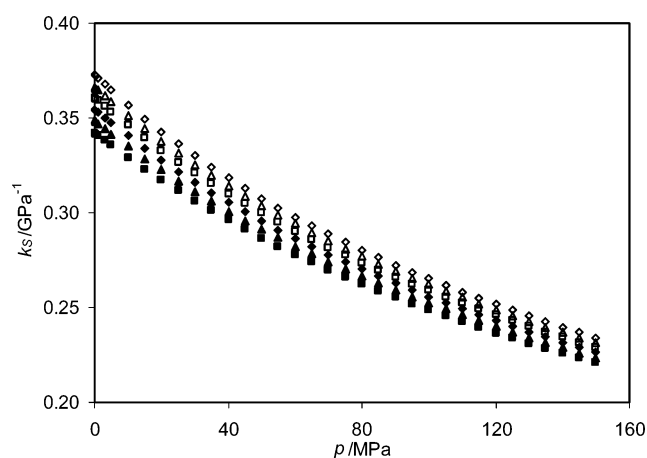


Figure 13. Isotherms for the isentropic compressibility of [bmim][BF₄]. ■, 298.15 K; ▲, 303.15 K; ◆, 308.15 K; □, 313.15 K; △, 318.15 K; ◇, 323.15 K.

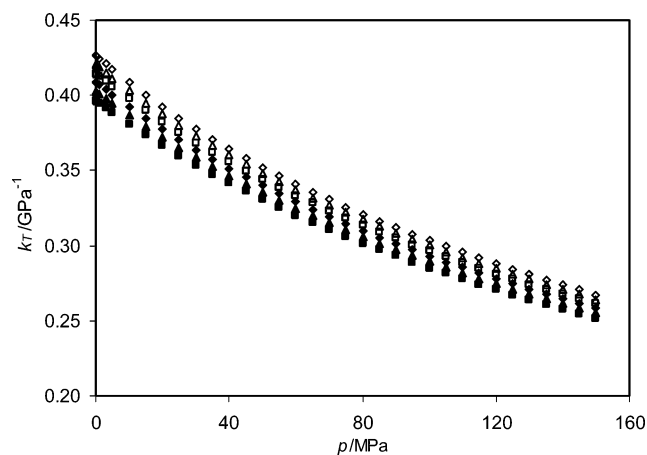


Figure 14. Isotherms for the isothermal compressibility of [bmim][BF₄]. ■, 298.15 K; ▲, 303.15 K; ◆, 308.15 K; □, 313.15 K; △, 318.15 K; ◇, 323.15 K.

The comparison between the density data taken from the integration procedure and the experimental ones shows good agreement with a maximum deviation smaller than 0.1%, even at pressures as high as 60 MPa. This deviation is small and can be ascribed to the uncertainty of the speed of sound measurements because this quantity is responsible for about 85% of the calculated $d\rho/dp$ in the integration process.

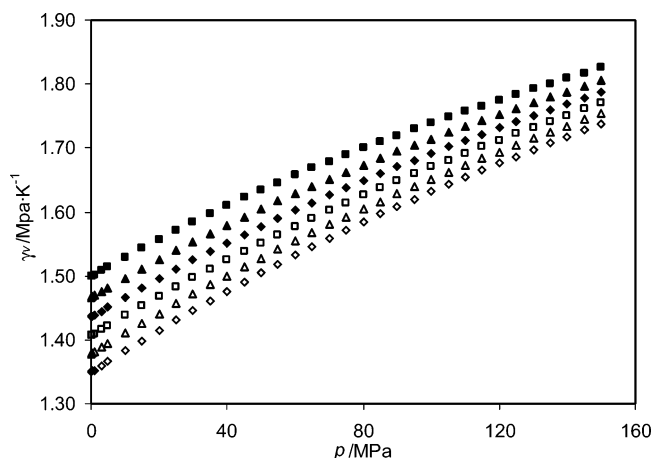


Figure 15. Isotherms for the thermal pressure coefficient of [bmim][BF₄]. ■, 298.15 K; ▲, 303.15 K; ◆, 308.15 K; □, 313.15 K; △, 318.15 K; ◇, 323.15 K.

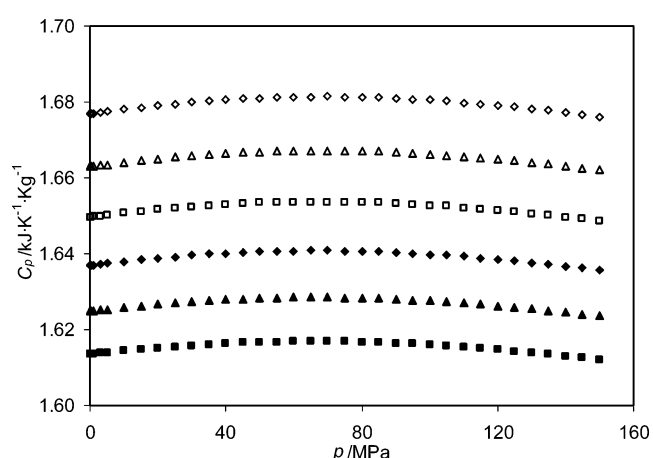


Figure 16. Isotherms for the isobaric heat capacity of [bmim][BF₄]. ■, 298.15 K; ▲, 303.15 K; ◆, 308.15 K; □, 313.15 K; △, 318.15 K; ◇, 323.15 K.

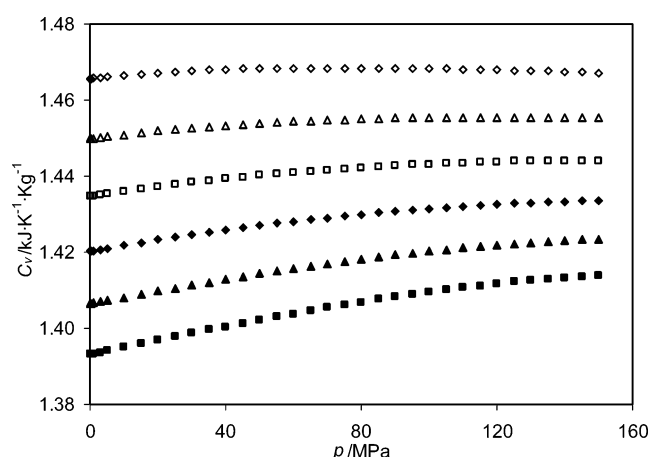


Figure 17. Isotherms for the isochoric heat capacity of [bmim][BF₄]. ■, 298.15 K; ▲, 303.15 K; ◆, 308.15 K; □, 313.15 K; △, 318.15 K; ◇, 323.15 K.

At atmospheric pressure, literature data show that whereas Huddleston et al.¹⁷ report $1.12 \text{ g}\cdot\text{cm}^{-3}$ and $1.17 \text{ g}\cdot\text{cm}^{-3}$ (their ref 36), values found in the articles of Wang et al.,²⁴ Seddon et al.,²⁵ Fredlake et al.,⁴ and Tokuda et al.⁵ are quoted as $1.21105 \text{ g}\cdot\text{cm}^{-3}$, $1.2048 \text{ g}\cdot\text{cm}^{-3}$, $1.2037 \text{ g}\cdot\text{cm}^{-3}$, and $1.2035 \text{ g}\cdot\text{cm}^{-3}$, respectively. (In the latter two cases, a least-squares fit to their data was applied to make comparisons at the same nominal temperature of 298.15 K.)

Table 16. Calculated Values of κ_T for [bmim][BF₄]

p/MPa	T/K						p/MPa	T/K					
	298.15	303.15	308.15	313.15	318.15	323.15		298.15	303.15	308.15	313.15	318.15	323.15
	κ_T/GPa^{-1}							κ_T/GPa^{-1}					
0.1	0.396 ₃	0.402 ₆	0.408 ₆	0.414 ₄	0.420 ₂	0.426 ₄	70	0.310 ₆	0.315 ₀	0.319 ₂	0.323 ₂	0.327 ₀	0.330 ₆
0.5	0.395 ₆	0.401 ₉	0.407 ₉	0.413 ₇	0.419 ₅	0.425 ₆	75	0.306 ₀	0.310 ₄	0.314 ₅	0.318 ₄	0.322 ₁	0.325 ₇
1	0.394 ₈	0.401 ₁	0.407 ₁	0.412 ₈	0.418 ₅	0.424 ₆	80	0.301 ₆	0.305 ₉	0.309 ₉	0.313 ₈	0.317 ₄	0.321 ₀
3	0.391 ₆	0.397 ₈	0.403 ₇	0.409 ₃	0.415 ₀	0.420 ₉	85	0.297 ₃	0.301 ₅	0.305 ₅	0.309 ₃	0.312 ₉	0.316 ₄
5	0.388 ₅	0.394 ₅	0.400 ₃	0.405 ₉	0.411 ₄	0.417 ₂	90	0.293 ₂	0.297 ₃	0.301 ₂	0.304 ₉	0.308 ₅	0.312 ₀
10	0.380 ₉	0.386 ₇	0.392 ₃	0.397 ₇	0.403 ₀	0.408 ₅	95	0.289 ₁	0.293 ₂	0.297 ₁	0.300 ₇	0.304 ₂	0.307 ₇
15	0.373 ₆	0.379 ₃	0.384 ₇	0.389 ₉	0.394 ₉	0.400 ₁	100	0.285 ₂	0.289 ₂	0.293 ₀	0.296 ₆	0.300 ₁	0.303 ₅
20	0.366 ₇	0.372 ₂	0.377 ₄	0.382 ₄	0.387 ₃	0.392 ₃	105	0.281 ₄	0.285 ₄	0.289 ₁	0.292 ₇	0.296 ₁	0.299 ₄
25	0.360 ₀	0.365 ₄	0.370 ₅	0.375 ₃	0.380 ₀	0.384 ₈	110	0.277 ₈	0.281 ₆	0.285 ₃	0.288 ₈	0.292 ₂	0.295 ₅
30	0.353 ₆	0.358 ₉	0.363 ₈	0.368 ₆	0.373 ₁	0.377 ₆	115	0.274 ₂	0.278 ₀	0.281 ₆	0.285 ₀	0.288 ₄	0.291 ₇
35	0.347 ₅	0.352 ₆	0.357 ₅	0.362 ₁	0.366 ₅	0.370 ₈	120	0.270 ₇	0.274 ₄	0.278 ₀	0.281 ₄	0.284 ₆	0.287 ₉
40	0.341 ₆	0.346 ₆	0.351 ₄	0.355 ₈	0.360 ₁	0.364 ₄	125	0.267 ₃	0.271 ₀	0.274 ₅	0.277 ₈	0.281 ₀	0.284 ₃
45	0.336 ₀	0.340 ₉	0.345 ₅	0.349 ₉	0.354 ₁	0.358 ₁	130	0.264 ₀	0.267 ₆	0.271 ₀	0.274 ₃	0.277 ₅	0.280 ₇
50	0.330 ₅	0.335 ₃	0.339 ₈	0.344 ₁	0.348 ₂	0.352 ₂	135	0.260 ₈	0.264 ₄	0.267 ₇	0.270 ₉	0.274 ₁	0.277 ₃
55	0.325 ₃	0.330 ₀	0.334 ₄	0.338 ₆	0.342 ₆	0.346 ₅	140	0.257 ₇	0.261 ₂	0.264 ₅	0.267 ₆	0.270 ₇	0.273 ₉
60	0.320 ₂	0.324 ₈	0.329 ₂	0.333 ₃	0.337 ₂	0.341 ₀	145	0.254 ₇	0.258 ₁	0.261 ₃	0.264 ₄	0.267 ₄	0.270 ₅
65	0.315 ₃	0.319 ₈	0.324 ₁	0.328 ₁	0.332 ₀	0.335 ₇	150	0.251 ₇	0.255 ₀	0.258 ₂	0.261 ₂	0.264 ₂	0.267 ₃

Table 17. Calculated Values of κ_S for [bmim][BF₄]

p/MPa	T/K						p/MPa	T/K					
	298.15	303.15	308.15	313.15	318.15	323.15		298.15	303.15	308.15	313.15	318.15	323.15
	κ_S/GPa^{-1}							κ_S/GPa^{-1}					
0.1	0.342 ₂	0.348 ₅	0.354 ₅	0.360 ₄	0.366 ₃	0.372 ₆	70	0.270 ₀	0.274 ₁	0.278 ₀	0.281 ₇	0.285 ₃	0.288 ₈
0.5	0.341 ₆	0.347 ₉	0.353 ₉	0.359 ₈	0.365 ₇	0.372 ₀	75	0.266 ₁	0.270 ₂	0.274 ₀	0.277 ₆	0.281 ₁	0.284 ₅
1	0.340 ₉	0.347 ₂	0.353 ₂	0.359 ₀	0.364 ₉	0.371 ₁	80	0.262 ₅	0.266 ₄	0.270 ₁	0.273 ₇	0.277 ₁	0.280 ₄
3	0.338 ₂	0.344 ₄	0.350 ₃	0.356 ₀	0.361 ₈	0.367 ₉	85	0.258 ₉	0.262 ₇	0.266 ₄	0.269 ₈	0.273 ₁	0.276 ₄
5	0.335 ₆	0.341 ₆	0.347 ₄	0.353 ₁	0.358 ₇	0.364 ₇	90	0.255 ₄	0.259 ₂	0.262 ₇	0.266 ₁	0.269 ₄	0.272 ₅
10	0.329 ₁	0.335 ₀	0.340 ₆	0.346 ₀	0.351 ₄	0.357 ₀	95	0.252 ₁	0.255 ₇	0.259 ₂	0.262 ₅	0.265 ₇	0.268 ₈
15	0.323 ₀	0.328 ₆	0.334 ₀	0.339 ₂	0.344 ₄	0.349 ₇	100	0.248 ₈	0.252 ₄	0.255 ₈	0.259 ₀	0.262 ₁	0.265 ₂
20	0.317 ₁	0.322 ₆	0.327 ₈	0.332 ₈	0.337 ₇	0.342 ₈	105	0.245 ₆	0.249 ₁	0.252 ₅	0.255 ₆	0.258 ₇	0.261 ₇
25	0.311 ₅	0.316 ₈	0.321 ₈	0.326 ₇	0.331 ₄	0.336 ₂	110	0.242 ₆	0.246 ₀	0.249 ₂	0.252 ₃	0.255 ₃	0.258 ₃
30	0.306 ₁	0.311 ₂	0.316 ₁	0.320 ₈	0.325 ₄	0.329 ₉	115	0.239 ₆	0.242 ₉	0.246 ₁	0.249 ₁	0.252 ₀	0.254 ₉
35	0.301 ₀	0.305 ₉	0.310 ₇	0.315 ₂	0.319 ₆	0.324 ₀	120	0.236 ₇	0.240 ₀	0.243 ₀	0.246 ₀	0.248 ₈	0.251 ₇
40	0.296 ₀	0.300 ₈	0.305 ₄	0.309 ₈	0.314 ₁	0.318 ₃	125	0.233 ₉	0.237 ₁	0.240 ₁	0.243 ₀	0.245 ₇	0.248 ₆
45	0.291 ₂	0.296 ₀	0.300 ₄	0.304 ₇	0.308 ₈	0.312 ₈	130	0.231 ₁	0.234 ₂	0.237 ₂	0.240 ₀	0.242 ₇	0.245 ₅
50	0.286 ₇	0.291 ₃	0.295 ₆	0.299 ₇	0.303 ₇	0.307 ₆	135	0.228 ₄	0.231 ₅	0.234 ₃	0.237 ₁	0.239 ₈	0.242 ₅
55	0.282 ₃	0.286 ₇	0.291 ₀	0.295 ₀	0.298 ₈	0.302 ₆	140	0.225 ₈	0.228 ₈	0.231 ₆	0.234 ₃	0.236 ₉	0.239 ₆
60	0.278 ₀	0.282 ₄	0.286 ₅	0.290 ₄	0.294 ₂	0.297 ₈	145	0.223 ₃	0.226 ₂	0.228 ₉	0.231 ₅	0.234 ₁	0.236 ₈
65	0.273 ₉	0.278 ₂	0.282 ₂	0.286 ₀	0.289 ₇	0.293 ₂	150	0.220 ₈	0.223 ₆	0.226 ₃	0.228 ₈	0.231 ₃	0.234 ₀

Table 18. Calculated Values of α_p for [bmim][BF₄]

p/MPa	T/K						p/MPa	T/K					
	298.15	303.15	308.15	313.15	318.15	323.15		298.15	303.15	308.15	313.15	318.15	323.15
	$10^3\alpha_p/\text{K}^{-1}$							$10^3\alpha_p/\text{K}^{-1}$					
0.1	0.594 ₀	0.590 ₃	0.586 ₇	0.582 ₉	0.579 ₂	0.575 ₄	70	0.521 ₅	0.520 ₃	0.519 ₁	0.517 ₉	0.516 ₆	0.515 ₄
0.5	0.593 ₅	0.589 ₉	0.586 ₂	0.582 ₅	0.578 ₇	0.574 ₉	75	0.517 ₁	0.516 ₁	0.515 ₀	0.514 ₀	0.513 ₀	0.511 ₉
1	0.592 ₉	0.589 ₃	0.585 ₆	0.581 ₉	0.578 ₁	0.574 ₃	80	0.512 ₇	0.511 ₉	0.511 ₀	0.510 ₂	0.509 ₃	0.508 ₅
3	0.590 ₅	0.586 ₉	0.583 ₂	0.579 ₆	0.575 ₈	0.572 ₁	85	0.508 ₄	0.507 ₈	0.507 ₁	0.506 ₅	0.505 ₈	0.505 ₁
5	0.588 ₁	0.584 ₅	0.580 ₉	0.577 ₃	0.573 ₆	0.569 ₉	90	0.504 ₂	0.503 ₇	0.503 ₂	0.502 ₈	0.502 ₃	0.501 ₈
10	0.582 ₂	0.578 ₈	0.575 ₃	0.571 ₈	0.568 ₂	0.564 ₆	95	0.500 ₀	0.499 ₇	0.499 ₄	0.499 ₁	0.498 ₈	0.498 ₅
15	0.576 ₅	0.573 ₂	0.569 ₉	0.566 ₅	0.563 ₁	0.559 ₆	100	0.496 ₀	0.495 ₈	0.495 ₇	0.495 ₆	0.495 ₄	0.495 ₂
20	0.571 ₀	0.567 ₈	0.564 ₆	0.561 ₄	0.558 ₂	0.554 ₉	105	0.492 ₀	0.492 ₀	0.492 ₀	0.492 ₀	0.492 ₀	0.492 ₀
25	0.565 ₅	0.562 ₆	0.559 ₅	0.556 ₅	0.553 ₄	0.550 ₃	110	0.488 ₁	0.488 ₂	0.488 ₄	0.488 ₅	0.488 ₇	0.488 ₈
30	0.560 ₂	0.557 ₄	0.554 ₆	0.551 ₈	0.548 ₉	0.546 ₀	115	0.484 ₂	0.484 ₅	0.484 ₈	0.485 ₁	0.485 ₄	0.485 ₇
35	0.555 ₁	0.552 ₄	0.549 ₈	0.547 ₂	0.544 ₅	0.541 ₇	120	0.480 ₅	0.480 ₉	0.481 ₃	0.481 ₇	0.482 ₁	0.482 ₆
40	0.550 ₀	0.547 ₆	0.545 ₁	0.542 ₇	0.540 ₂	0.537 ₇	125	0.476 ₈	0.477 ₃	0.477 ₉	0.478 ₄	0.478 ₉	0.479 ₅
45	0.545 ₀	0.542 ₈	0.540 ₆	0.538 ₃	0.536 ₀	0.533 ₇	130	0.473 ₂	0.473 ₈	0.474 ₅	0.475 ₁	0.475 ₈	0.476 ₄
50	0.540 ₁	0.538 ₁	0.536 ₁	0.534 ₀	0.532 ₀	0.529 ₉	135	0.469 ₆	0.470 ₄	0.471 ₁	0.471 ₉	0.472 ₆	0.473 ₄
55	0.535 ₄	0.533 ₅	0.531 ₇	0.529 ₉	0.528 ₀	0.526 ₁	140	0.466 ₂	0.467 ₀	0.467 ₈	0.468 ₇	0.469 ₆	0.470 ₄
60	0.530 ₇	0.529 ₁	0.527 ₄	0.525 ₈	0.524 ₁	0.522 ₅	145	0.462 ₈	0.463 ₇	0.464 ₆	0.465 ₆	0.466 ₅	0.467 ₄

Table 19. Calculated Values of γ_v for [bmim][BF₄]

p/MPa	T/K						p/MPa	T/K					
	298.15	303.15	308.15	313.15	318.15	323.15		298.15	303.15	308.15	313.15	318.15	323.15
	$\gamma_v/\text{MPa}\cdot\text{K}^{-1}$							$\gamma_v/\text{MPa}\cdot\text{K}^{-1}$					
0.1	1.49 ₉	1.46 ₆	1.43 ₆	1.40 ₇	1.37 ₈	1.34 ₉	70	1.67 ₉	1.65 ₂	1.62 ₆	1.60 ₂	1.58 ₀	1.55 ₉
0.5	1.50 ₀	1.46 ₈	1.43 ₇	1.40 ₈	1.38 ₀	1.35 ₁	75	1.69 ₀	1.66 ₃	1.63 ₈	1.61 ₄	1.59 ₂	1.57 ₁
1	1.50 ₂	1.46 ₉	1.43 ₉	1.40 ₉	1.38 ₁	1.35 ₂	80	1.70 ₀	1.67 ₃	1.64 ₉	1.62 ₆	1.60 ₅	1.58 ₄
3	1.50 ₈	1.47 ₅	1.44 ₅	1.41 ₆	1.38 ₈	1.35 ₉	85	1.71 ₀	1.68 ₄	1.66 ₀	1.63 ₇	1.61 ₆	1.59 ₆
5	1.51 ₄	1.48 ₁	1.45 ₁	1.42 ₂	1.39 ₄	1.36 ₆	90	1.72 ₀	1.69 ₄	1.67 ₁	1.64 ₉	1.62 ₈	1.60 ₈
10	1.52 ₉	1.49 ₆	1.46 ₆	1.43 ₈	1.41 ₀	1.38 ₂	95	1.72 ₉	1.70 ₄	1.68 ₁	1.66 ₀	1.64 ₀	1.62 ₀
15	1.54 ₃	1.51 ₁	1.48 ₁	1.45 ₃	1.42 ₆	1.39 ₉	100	1.73 ₉	1.71 ₄	1.69 ₂	1.67 ₁	1.65 ₁	1.63 ₂
20	1.55 ₇	1.52 ₆	1.49 ₆	1.46 ₈	1.44 ₁	1.41 ₅	105	1.74 ₈	1.72 ₄	1.70 ₂	1.68 ₁	1.66 ₂	1.64 ₃
25	1.57 ₁	1.54 ₀	1.51 ₀	1.48 ₃	1.45 ₆	1.43 ₀	110	1.75 ₇	1.73 ₄	1.71 ₂	1.69 ₂	1.67 ₃	1.65 ₄
30	1.58 ₄	1.55 ₃	1.52 ₄	1.49 ₇	1.47 ₁	1.44 ₆	115	1.76 ₆	1.74 ₃	1.72 ₂	1.70 ₂	1.68 ₃	1.66 ₅
35	1.59 ₇	1.56 ₇	1.53 ₈	1.51 ₁	1.48 ₆	1.46 ₁	120	1.77 ₅	1.75 ₂	1.73 ₁	1.71 ₂	1.69 ₄	1.67 ₆
40	1.61 ₀	1.58 ₀	1.55 ₂	1.52 ₅	1.50 ₀	1.47 ₆	125	1.78 ₃	1.76 ₁	1.74 ₁	1.72 ₂	1.70 ₄	1.68 ₇
45	1.62 ₂	1.59 ₂	1.56 ₅	1.53 ₉	1.51 ₄	1.49 ₀	130	1.79 ₂	1.77 ₀	1.75 ₀	1.73 ₂	1.71 ₄	1.69 ₇
50	1.63 ₄	1.60 ₅	1.57 ₈	1.55 ₂	1.52 ₈	1.50 ₄	135	1.80 ₁	1.77 ₉	1.76 ₀	1.74 ₂	1.72 ₅	1.70 ₇
55	1.64 ₆	1.61 ₇	1.59 ₀	1.56 ₅	1.54 ₁	1.51 ₈	140	1.80 ₉	1.78 ₈	1.76 ₉	1.75 ₁	1.73 ₅	1.71 ₈
60	1.65 ₇	1.62 ₉	1.60 ₂	1.57 ₈	1.55 ₄	1.53 ₂	145	1.81 ₇	1.79 ₇	1.77 ₈	1.76 ₁	1.74 ₅	1.72 ₈
65	1.66 ₈	1.64 ₀	1.61 ₄	1.59 ₀	1.56 ₇	1.54 ₆	150	1.82 ₅	1.80 ₆	1.78 ₇	1.77 ₁	1.75 ₄	1.73 ₈

Table 20. Calculated Values of C_p for [bmim][BF₄]

p/MPa	T/K						p/MPa	T/K					
	298.15	303.15	308.15	313.15	318.15	323.15		298.15	303.15	308.15	313.15	318.15	323.15
	$C_p/\text{kJ}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$							$C_p/\text{kJ}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$					
0.1	1.61 ₃	1.62 ₅	1.63 ₇	1.65 ₀	1.66 ₃	1.67 ₇	70	1.61 ₇	1.62 ₈	1.64 ₁	1.65 ₄	1.66 ₇	1.68 ₁
0.5	1.61 ₃	1.62 ₅	1.63 ₇	1.65 ₀	1.66 ₃	1.67 ₇	75	1.61 ₇	1.62 ₈	1.64 ₁	1.65 ₄	1.66 ₇	1.68 ₁
1	1.61 ₄	1.62 ₅	1.63 ₇	1.65 ₀	1.66 ₃	1.67 ₇	80	1.61 ₇	1.62 ₈	1.64 ₁	1.65 ₄	1.66 ₇	1.68 ₁
3	1.61 ₄	1.62 ₅	1.63 ₇	1.65 ₀	1.66 ₃	1.67 ₇	85	1.61 ₇	1.62 ₈	1.64 ₀	1.65 ₃	1.66 ₇	1.68 ₁
5	1.61 ₄	1.62 ₅	1.63 ₇	1.65 ₀	1.66 ₄	1.67 ₇	90	1.61 ₆	1.62 ₈	1.64 ₀	1.65 ₃	1.66 ₇	1.68 ₁
10	1.61 ₄	1.62 ₆	1.63 ₈	1.65 ₁	1.66 ₄	1.67 ₈	95	1.61 ₆	1.62 ₈	1.64 ₀	1.65 ₃	1.66 ₇	1.68 ₁
15	1.61 ₅	1.62 ₆	1.63 ₈	1.65 ₁	1.66 ₅	1.67 ₉	100	1.61 ₆	1.62 ₈	1.64 ₀	1.65 ₃	1.66 ₆	1.68 ₀
20	1.61 ₅	1.62 ₇	1.63 ₉	1.65 ₂	1.66 ₅	1.67 ₉	105	1.61 ₆	1.62 ₇	1.64 ₀	1.65 ₂	1.66 ₆	1.68 ₀
25	1.61 ₅	1.62 ₇	1.63 ₉	1.65 ₂	1.66 ₅	1.67 ₉	110	1.61 ₅	1.62 ₇	1.63 ₉	1.65 ₂	1.66 ₆	1.68 ₀
30	1.61 ₆	1.62 ₇	1.64 ₀	1.65 ₂	1.66 ₆	1.68 ₀	115	1.61 ₅	1.62 ₇	1.63 ₉	1.65 ₂	1.66 ₅	1.67 ₉
35	1.61 ₆	1.62 ₈	1.64 ₀	1.65 ₃	1.66 ₆	1.68 ₀	120	1.61 ₅	1.62 ₆	1.63 ₉	1.65 ₁	1.66 ₅	1.67 ₉
40	1.61 ₆	1.62 ₈	1.64 ₀	1.65 ₃	1.66 ₆	1.68 ₁	125	1.61 ₄	1.62 ₆	1.63 ₈	1.65 ₁	1.66 ₄	1.67 ₉
45	1.61 ₇	1.62 ₈	1.64 ₀	1.65 ₃	1.66 ₇	1.68 ₁	130	1.61 ₄	1.62 ₅	1.63 ₈	1.65 ₁	1.66 ₄	1.67 ₈
50	1.61 ₇	1.62 ₈	1.64 ₁	1.65 ₃	1.66 ₇	1.68 ₁	135	1.61 ₃	1.62 ₅	1.63 ₇	1.65 ₀	1.66 ₄	1.67 ₈
55	1.61 ₇	1.62 ₈	1.64 ₁	1.65 ₄	1.66 ₇	1.68 ₁	140	1.61 ₃	1.62 ₅	1.63 ₇	1.65 ₀	1.66 ₃	1.67 ₇
60	1.61 ₇	1.62 ₈	1.64 ₁	1.65 ₄	1.66 ₇	1.68 ₁	145	1.61 ₂	1.62 ₄	1.63 ₆	1.64 ₉	1.66 ₃	1.67 ₇
65	1.61 ₇	1.62 ₉	1.64 ₁	1.65 ₄	1.66 ₇	1.68 ₁	150	1.61 ₂	1.62 ₄	1.63 ₆	1.64 ₉	1.66 ₂	1.67 ₆

Table 21. Calculated Values of C_v for [bmim][BF₄]

p/MPa	T/K						p/MPa	T/K					
	298.15	303.15	308.15	313.15	318.15	323.15		298.15	303.15	308.15	313.15	318.15	323.15
	$C_v/\text{kJ}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$							$C_v/\text{kJ}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$					
0.1	1.39 ₃	1.40 ₆	1.42 ₀	1.43 ₅	1.45 ₀	1.46 ₆	70	1.40 ₅	1.41 ₇	1.42 ₉	1.44 ₂	1.45 ₅	1.46 ₈
0.5	1.39 ₃	1.40 ₇	1.42 ₀	1.43 ₅	1.45 ₀	1.46 ₆	75	1.40 ₆	1.41 ₈	1.42 ₉	1.44 ₂	1.45 ₅	1.46 ₈
1	1.39 ₃	1.40 ₇	1.42 ₀	1.43 ₅	1.45 ₀	1.46 ₆	80	1.40 ₇	1.41 ₈	1.43 ₀	1.44 ₂	1.45 ₅	1.46 ₈
3	1.39 ₄	1.40 ₇	1.42 ₁	1.43 ₅	1.45 ₀	1.46 ₆	85	1.40 ₈	1.41 ₉	1.43 ₀	1.44 ₂	1.45 ₅	1.46 ₈
5	1.39 ₄	1.40 ₇	1.42 ₁	1.43 ₅	1.45 ₀	1.46 ₆	90	1.40 ₈	1.41 ₉	1.43 ₁	1.44 ₃	1.45 ₅	1.46 ₈
10	1.39 ₅	1.40 ₈	1.42 ₂	1.43 ₆	1.45 ₁	1.46 ₇	95	1.40 ₉	1.42 ₀	1.43 ₁	1.44 ₃	1.45 ₅	1.46 ₈
15	1.39 ₆	1.40 ₉	1.42 ₃	1.43 ₇	1.45 ₁	1.46 ₇	100	1.41 ₀	1.42 ₀	1.43 ₁	1.44 ₃	1.45 ₅	1.46 ₈
20	1.39 ₇	1.41 ₀	1.42 ₃	1.43 ₇	1.45 ₂	1.46 ₇	105	1.41 ₀	1.42 ₁	1.43 ₂	1.44 ₃	1.45 ₅	1.46 ₈
25	1.39 ₈	1.41 ₁	1.42 ₄	1.43 ₈	1.45 ₂	1.46 ₇	110	1.41 ₁	1.42 ₁	1.43 ₂	1.44 ₃	1.45 ₅	1.46 ₈
30	1.39 ₉	1.41 ₁	1.42 ₅	1.43 ₈	1.45 ₃	1.46 ₈	115	1.41 ₁	1.42 ₂	1.43 ₂	1.44 ₄	1.45 ₆	1.46 ₈
35	1.40 ₀	1.41 ₂	1.42 ₅	1.43 ₉	1.45 ₃	1.46 ₈	120	1.41 ₂	1.42 ₂	1.43 ₃	1.44 ₄	1.45 ₆	1.46 ₈
40	1.40 ₀	1.41 ₃	1.42 ₆	1.43 ₉	1.45 ₃	1.46 ₈	125	1.41 ₂	1.42 ₂	1.43 ₃	1.44 ₄	1.45 ₆	1.46 ₈
45	1.40 ₁	1.41 ₄	1.42 ₆	1.44 ₀	1.45 ₄	1.46 ₈	130	1.41 ₃	1.42 ₃	1.43 ₃	1.44 ₄	1.45 ₆	1.46 ₈
50	1.40 ₂	1.41 ₄	1.42 ₇	1.44 ₀	1.45 ₄	1.46 ₈	135	1.41 ₃	1.42 ₃	1.43 ₃	1.44 ₄	1.45 ₅	1.46 ₈
55	1.40 ₃	1.41 ₅	1.42 ₈	1.44 ₁	1.45 ₄	1.46 ₈	140	1.41 ₃	1.42 ₃	1.43 ₃	1.44 ₄	1.45 ₅	1.46 ₇
60	1.40 ₄	1.41 ₆	1.42 ₈	1.44 ₁	1.45 ₄	1.46 ₈	145	1.41 ₄	1.42 ₃	1.43 ₃	1.44 ₄	1.45 ₅	1.46 ₇
65	1.40 ₅	1.41 ₆	1.42 ₉	1.44 ₁	1.45 ₅	1.46 ₈	150	1.41 ₄	1.42 ₄	1.43 ₄	1.44 ₄	1.45 ₅	1.46 ₇

tion of the measured densities with the integration method show average deviations of 4% and -4%, respectively. Although these values are within acceptable limits, they corroborate the strong dependence of the derivation method on the shape of the curves used to fit the experimental data and the necessity of collecting a large number of experimental points.

As for the heat capacities, the results for both the isobaric and isochoric heat capacities reveal, in practice, pressure independence.

Conclusions

This work shows the usefulness of this method in deriving precise thermodynamic properties at high pres-

tures from speed of sound measurements. It maps the physical behavior of two important ionic liquids over wide pressure and temperature ranges.

As the anion increases in size ($[\text{BF}_4]^- < [\text{PF}_6]^-$), the density increases accordingly, whereas the speed of sound shows the opposite trend. At first glance, this fact may seem counterintuitive because one tends to associate greater density with greater speed of sound. This line of thought mainly arises from comparisons (in density and speed of sound) made between the gas phase and the condensed phase. It is true that gases present smaller densities as well as speeds of propagation of sound waves than condensed phases, but this truism has little to do with density. The typical ratio between the densities of liquid to gas (far from the critical point) is on the order of thousands. However, the ratio (gas to liquid) of compressibilities is ca. 100 000. Therefore, compressibility is the factor that controls the speed of sound. It is also interesting that in these ILs (differing in the anion) if the mass density increases the molar volume also does. For instance, at atmospheric pressure and 298.15 K $V_{\text{bmimPF}_6} - V_{\text{bmimBF}_4} = 20.3 \text{ cm}^3 \cdot \text{mol}^{-1}$. This value can be attributed to the increase in the effective anion size³ from 0.089 nm³/anion of BF_4^- to 0.122 nm³/anion of PF_6^- .

Generally, one can state that speed of sound values of ILs are not too dissimilar from those typically found in conventional solvents, tending to fall in the high-value side of the range. In contrast, both compressibilities and expansivities are ca. three times smaller than values typically found in those conventional solvents. This is probably a consequence of the fact that although critical temperatures, T_c , are unknown for ILs, estimates of T_c of ILs²⁶ show that their critical temperatures are certainly much higher (if it were possible to reach the liquid–gas critical point by avoiding the thermal decomposition of the IL) than those of molecular solvents. Therefore, in the case of ILs, room-temperature conditions certainly correspond to very low reduced temperatures. It is well known that both compressibility and expansivity decrease drastically along the orthobaric line from an infinite value at the critical point to very modest values as temperature (and reduced temperature) decreases.

As for heat capacities, if comparisons are performed using molar quantities, for instance, at atmospheric pressure and 298.15 K, then $C_{p,\text{bmimPF}_6} - C_{p,\text{bmimBF}_4} = 44.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. The greater values presented by PF_6^- are mainly a consequence of the larger number of vibrational degrees of freedom of this anion compared with that of BF_4^- . In other words, as the anion's structural complexity increases, one expects improved energy storage ability.

Acknowledgment

We thank the QUILL group, Belfast, lead by Professor Kenneth Seddon for hosting some of us and helping with the synthesis and purification of [bmim][PF₆].

Literature Cited

- (1) (a) Visser, A. E.; Swatoski, 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. Eng. Chem. Res.* **2000**, *39*, 3596–3604. (b) Swatoski, 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.
- (2) Najdanovic-Visak, V.; Esperança, J. M. S. S.; Rebelo, L. P. N.; Nunes da Ponte, M.; Guedes, H. J. R.; Seddon, K. R.; Szydłowski, 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.
- (3) 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.; Szydłowski, 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., Seddon, K. R., Eds.; ACS Symposium Series 901; American Chemical Society: Washington DC, 2005; Chapter 21, 260–281.
- (4) 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.
- (5) 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.
- (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) Gomes de Azevedo, R.; Szydłowski, J.; Pires, P. F.; Esperança, J. M. S. S.; Guedes, H. J. R.; Rebelo, L. P. N. A novel nonintrusive 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*, 211–222.
- (8) Szydłowski, J.; Gomes de Azevedo, R.; Rebelo, L. P. N.; Esperança, J. M. S. S.; Guedes, H. J. R. Deuterium isotope differences in 2-propanone, $(\text{CH}_3)_2\text{CO}/(\text{CD}_3)_2\text{CO}$: a high-pressure sound-speed, density, and heat capacities study. *J. Chem. Thermodyn.* **2005**, *37*, in press (doi: 10.1016/j.jct.2004.11.001).
- (9) Trusler, J. P. M. *Physical Acoustics and Metrology of Fluids*; Adam Hilger: Bristol, U.K., 1991.
- (10) 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.
- (11) 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*, 496–502.
- (12) Daridon, J. L.; Lagrabet, 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.
- (13) (a) Private communication, Kenneth N. Marsh: 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 $T = 298 \text{ K}$ and $p = 0.1 \text{ Mpa}$ of (16 and 29) mPa·s, at Temperatures between (298 and 398) K and Pressures below 55 Mpa. *J. Chem. Eng. Data* **2005**, submitted for publication. (b) Fitzgerald, D. *Technical Assessment of the Anton Paar DMA5000 Density Meter*; H & D Fitzgerald Ltd. Publishers, 2000 (http://www.density.co.uk/review_of_5000.pdf).
- (14) Gordon, C. M.; Holbrey, J. D.; Kennedy, R.; Seddon, K. R. Ionic Liquid Crystals: Hexafluorophosphate Salts. *J. Mater. Chem.* **1998**, *8*, 2627–2636.
- (15) 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.
- (16) Debenedetti, P. G. *Metastable Liquids*; Princeton University Press: Princeton, NJ, 1996.
- (17) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. Characterization and comparison of hydrophilic and hydrophobic room-temperature ionic liquids incorporating the imidazolium cation. *Green Chem.* **2001**, *3*, 156–164.
- (18) Kabo, G. J.; Blokhin, A. V.; Paulechka, Y. U.; Kabo, A. G.; Shymanovich, M. P.; Magee, J. W. Thermodynamic Properties of 1-Butyl-3-methylimidazolium Hexafluorophosphate in the Condensed State. *J. Chem. Eng. Data* **2004**, *49*, 453–461.
- (19) Domanska, U.; Marciniak, A. Solubility of 1-Alkyl-3-methylimidazolium Hexafluorophosphate in Hydrocarbons. *J. Chem. Eng. Data* **2003**, *48*, 451–456.
- (20) 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.
- (21) Canongia Lopes, J. N.; Cordeiro, T. C.; Esperança, J. M. S. S.; Guedes, H. J. R.; Huk, 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.
- (22) Sun, T.; Biswas, S. N.; Trappeniers, N. J.; Seldam, C. A. T. Acoustic and Thermodynamic Properties of Methanol from 273 to 333 K and at Pressures to 280 MPa. *J. Chem. Eng. Data* **1988**, *33*, 395–398.

- (23) Rebelo, L. P. N.; Najdanovic-Visak, V.; Visak Z. P.; Nunes da Ponte, M.; Szydłowski, J.; Cerdeirinha, C. A.; Troncoso, J.; Romani, L.; Esperança, J. M. S. S.; Guedes, H. J. R.; de Sousa, H. C. A detailed thermodynamic analysis of [C₄mim][BF₄] + Water as a case study to model ionic liquid aqueous solutions. *Green Chem.* **2004**, *6*, 369–381.
- (24) Wang, J.; Tian, Y.; Zhao, Y.; Zhuo, K. A volumetric and viscosity study for the mixtures of 1-n-butyl-3-methylimidazolium tetrafluoroborate ionic liquid with acetonitrile, dichloromethane, 2-butanone and N, N – dimethylformamide. *Green Chem.* **2003**, *5*, 618–622.
- (25) Seddon, K. R.; Stark, A.; Torres, M.–J. Viscosity and density of 1-alkyl-3-methylimidazolium ionic liquids. In *Clean Solvents: Alternative Media for Chemical Reactions and Processing*; Abraham, M., Moens, L., Eds.; ACS Symposium Series 819; American Chemical Society: Washington, DC, 2002; pp 34–49.
- (26) Rebelo, L. P. N.; Canongia Lopes, J. N.; Esperança, J. M. S. S.; Filipe, E. On the Critical Temperature, Normal Boiling Point, and Vapor Pressure of Ionic Liquids. *J. Phys. Chem. B* **2005**, *109*, 6040–6043.

Received for review December 29, 2004. Accepted March 23, 2005. This work was financially supported by Fundação para a Ciência e Tecnologia, Portugal, under contract POCTI/EQU/35437/00. R.G.A., J.M.S.S.E., V.N.-V. and Z.P.V. are grateful to Fundação para a Ciência e Tecnologia for doctoral fellowships.

JE049534W