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Experimental $p-\rho-T$ Data for 1-Butyl-3-methylimidazolium Tetrafluoroborate at Temperatures from (240 to 353) K and at Pressures up to 60 MPa

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Supporting Information

ABSTRACT: New experimental data on the density of 1-butyl-3-methylimidazolium tetrafluoroborate are reported, obtained with a constant-volume apparatus described here in detail. The measurements were conducted along eight isochores at temperatures from (354 to 240) K and at nominal pressures of 1 MPa and from (10 to 60) MPa with a 10 MPa step. The combined uncertainty at the 95 % confidence level of a density measurement is estimated to be less than 1 $kg \cdot m^{-3}$, i.e., 0.1 %. A Tait-type equation was developed describing the $\rho(T, p)$ dependence. The equation is fitted to the data of the present work and to critically assessed data of other authors compiled from the literature. Values of the coefficient of isothermal compressibility and of isobaric thermal expansion for 1-butyl-3-methylimidazolium tetrafluoroborate were calculated from the correlation equation and compared with experimental data from the literature. An unusual decreasing dependence of the isobaric thermal expansion coefficient on temperature, observed by other authors, was confirmed.

INTRODUCTION

The 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMIM][BF_4]$) with the solid−liquid equilibrium temperature of 202 K is one of the most widely studied ionic liquids. Nevertheless, experimental data on the pressure dependence of its density for temperatures below 273 K are absent in the open literature. Measurements of the $[BMIM][BF_4]$ density have hitherto been conducted most often in the temperature range above room temperature where they are feasible by using a common apparatus. To make possible measurements of the pressure dependence of the density at subroom and subzero temperatures, we have constructed a new apparatus based on the constant-volume principle.

In the literature, there are available a total of 413 experimental data points on density of $[BMIM][BF_4]$ at atmospheric pressure at temperatures from (273 to 415) K from 55 authors.[1−32,34,36−57] A total of 632 data points on pressure dependence of the $[BMIM][BF_4]$ density for temperatures from (273 to 472) K and up to 300 MPa in pressure have been published by Rebelo et al.,[12] Azevedo et al.,[14] Tomida et al.,[21] Gardas et al.,[24] Harris et al.,[25] Jacquemin et al.,[27] Tekin et al.,[33] Abdulagatov et al.,[35] Machida et al.,[40] Han et al.,[44] Rilo et al.,[53] and Sanmamed et al.[55] Table 1 gives an overview of the literature sources for experimental density data for $[BMIM][BF_4]$. The experimental density values by different authors are scattered over a band of a relative half-width of about 1.5 % of the $[BMIM][BF_4]$ density value (see Figure S3 in the Supporting Information).

The aim of the present study was to obtain new experimental data for 1-butyl-3-methylimidazolium tetrafluoroborate density in a subambient temperature region and especially below 273 K where it has not yet been studied in this respect at all. The second objective of the present paper is to provide a detailed description of the used new constant-volume apparatus and the corresponding measurement and data evaluation procedures. Third, a description of the $[BMIM][BF_4]$ pressure−density−temperature relation is presented developed based on the new data and on critically assessed experimental data by different authors available in the literature.

EXPERIMENTAL SECTION

Description of the Apparatus. A new apparatus to measure the density of liquids has been designed and constructed based on the constant-volume principle. It consists in closing of a known mass, m, of the investigated liquid in a measuring vessel with an accurately calibrated volume, V. Then the dependence of the sample pressure on temperature is measured along the quasi-isochore generated by the temperature and pressure dependence of the measuring vessel volume. After that, a certain known mass of the sample is added into the vessel or taken out, and the measurement continues along the new isochore selected in this way.

The reported apparatus makes possible density measurements at temperatures from (183 to 363) K and up to 60 MPa in pressure. Figure 1 shows a schematic diagram of the constant-volume apparatus used in the present measurements. The measuring pressure vessel PV (piezometer), 193 cm^3 in volume, is cylindrical, thick-walled with an outer and inner diameter of 126 mm and 48 mm, respectively, and made of the stainless steel AISI 321. The thickness of the piezometer upper flange and bottom is 20 mm. The vessel is placed in a thermostat TH and connected

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Table 1. Literature Sources for Experimental Density Data for the 1-Butyl-3-methylimidazolium Tetrafluoroborate with the Sample Water Content Given as Water Mass Fraction, *w*, in Percent[a]

		temp. range	press. range			
author(s)	year	T/K	p/MPa	100 w	methods	no. of data
Suarez et al.[1]	1998	279.0 to 333.5	0.1	n/a	dil	6
Huddleston et al.[2]	2001	298.15	0.1	0.4530	pyc	1
Branco et al.[3]	2002	298.15	0.1	n/a	pyc	1
Seddon et al.[4]	2002	293.15 to 363.15	0.1	0.0307	pyc	8
Nishida et al.[5]	2003	298.15	0.1	0.0050	vtd	1
Wang et al.[6]	2003	298.15	0.1	0.1600	vtd	1
Xu et al.[7]	2003	293.15 to 393.15	0.1	n/a	pyc	7
Aki et al.[8]	2004	298.2 to 333.2	0.1	0.1200	pyc	3
Fredlake et al.[9]	2004	295.45 to 343.85	0.1	0.1900	pyc	5
Kim et al.[10]	2004	298.2 to 323.2	0.1	n/a	pyc	6
Ohlin et al.[11]	2004	295	0.1	n/a	pyc	1
Rebelo et al.[12]	2004	278.15 to 333.15	0.1 to 60	0.0075	vtd	26
Tokuda et al.[13]	2004	288.15 to 313.15	0.1	0.0040	vtd	6
Azevedo et al.[14]	2005	298.34 to 332.73	0.1 to 60	0.0075	vtd	67
Lopes et al.[15]	2005	298.15 to 333.15	0.1	0.0070	vtd	4
Van Valkenburg et al.[16]	2005	333.15	0.1	0.0800	vtd	1
Yang et al.[17]	2005	278.15 to 343.15	0.1	n/a	pyc	28
Deetlefs et al.[18]	2006	298.15	0.1	0.0295	vtd	1
Jacquemin et al.[19]	2006	292.89 to 391.28	0.1	0.0070	vtd	9
Liu et al.[20]	2006	298.15	0.1	n/a	pyc	1
Tomida et al.[21]	2006	293.15 to 353.15	0.1 to 20	0.0336	piez	20
Zafarani-Moattar and Shekaari[22]	2006	298.15 to 318.15	0.1	n/a	vtd	5
Zhou et al.[23]	2006	303.15 to 353.15	0.1	0.0200	pyc	8
Gardas et al.[24]	2007	293.15 to 393.15	0.1 to 10	0.0485	vtd	77
Harris et al.[25]	2007	273.15 to 363.15	0.1 to 300	0.0068	vtd	86
Huo et al.[26]	2007	293.15 to 343.15	0.1	0.0920	vtd	8
Jacquemin et al.[27]	2007	292.94 to 414.92	0.1 to 40	0.0070	vtd	46
Malham et al.[28]	2007	298.15	0.1	0.0720	vtd	1
Navia et al.[29]	2007	298.15 to 308.15	0.1	n/a	vtd	27
Inglesias-Otero et al.[30]	2007	293.15 to 323.15	0.1	n/a	vtd	14
Sanmamed et al.[31]	2007	293.15 to 323.15	0.1	0.2614	vtd	31
Shekaari and Zafarani-Moattar[32]	2007	298.15	0.1	n/a	vtd	1
Tekin et al.[33]	2007	298.15 to 398.15	0.3 to 40	n/a	vtd	45
Zhang et al.[34]	2007	298.15	0.1	n/a	vtd	1
Abdulagatov et al.[35]	2008	298.15 to 398.15	0.2 to 40	n/a	vtd	45
Hernández-Fernández et al.[36]	2008	298.15	0.1	n/a	pyc	1
Jacquemin et al.[37]	2008	293.15 to 343.15	0.1	0.0070	vtd	22
Jin et al.[38]	2008	298.15	0.1	0.0061	pyc	1
Kumar[39]	2008	283.15 to 343.15	0.1	0.0200	vtd	13
Machida et al.[40]	2008	313.1 to 472.2	0.1 to 200	0.0250	pyc, dil	181
Tian et al.[41]	2008	298.15	0.1	0.0010	vtd	1
Gao et al.[42]	2009	298.15 to 313.15	0.1	0.0010	vtd	4
García-Miaja et al.[43]	2009	293.15 to 318.15	0.1	0.0013	vtd	6
Han et al.[44]	2009	293.20 to 393.20	0.1 to 2	n/a	vtd	8
Klomfar et al.[45]	2009	283.01 to 350.81	0.1	0.0050	hbd	15
	2009	281.45 to 352.74	0.1	0.1446	hbd	15
Rilo et al.[46]	2009	298.15	0.1	0.1040	vtd	1
Singh et al.[47]	2009	298.15 to 318.15	0.1	0.0200	vtd	3
Soriano et al.[48]	2009	298.2 to 353.2	0.1	n/a	vtd	17
Stoppa et al.[49]	2009	298.15	0.1	n/a	vtd	1

Table 1. Continued

		temp. range	press. range			
author(s)	year	T/K	p/MPa	100 w	methods	no. of data
Tariq et al.[50]	2009	293.15 to 333.15	0.1	0.0070	vtd	4
Qi and Wang[51]	2009	288.15 to 303.15	0.1	0.0010	vtd	4
Carrera et al.[52]	2010	293.15	0.1	0.0150	pyc	2
Rilo et al.[53]	2010	298.15 to 323.15	0.1 to 30	0.1000	vtd	14
Sánchez et al.[54]	2010	283.15 to 363.15	0.1	0.0100	vtd	9
Sanmamed et al.[55]	2010	283.15 to 323.15	0.1 to 60	0.0060	vtd	117
Yan et al.[56]	2010	298.15 to 313.15	0.1	0.0010	vtd	4
Li et al.[57]	2010	298.15 to 313.15	0.1	0.0010	vtd	4
this work	2010	239.75 to 354.16	0.1 to 60	0.0036	piez	61

[a] vtd, vibrating tube densitometer; pyc, pycnometer; piez, piezometer; dil, dilatometer; hbd, hydrostatic-balance densitometer.

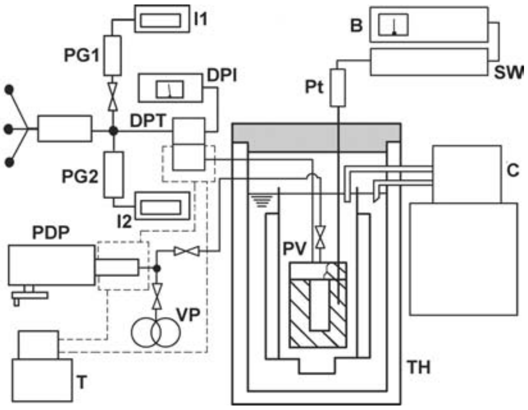

Figure 1. Schematic diagram of the constant-volume apparatus. B, thermometer bridge ASL F700; C, cryostat Lauda Ultra-Kryomat RUK 90; DPI, differential pressure null indicator Ruska 2416-711; DPT, differential pressure null transducer Ruska 2413-703; I1, Paroscientific Digiquartz Inteligent Display 730; I2, Paroscientific Digiquartz Inteligent Display 735; PDP, positive displacement pump/volumeter Ruska 2279-803; PG1, Paroscientific Digiquartz pressure gauge 43KR; PG2, Paroscientific Digiquartz pressure gauge 415K; Pt, platinum resistance thermometer Tinsley 5187 SA; PV, pressure vessel; VP, high vacuum apparatus Lavat AV63; T, thermostat Lauda UB 40; TH, thermostat; SW, switchbox interface ASL SB158 and multichannel switchbox ASL SB148; — — —, T = 298.15 K.

through valves to a vacuum and filling system and through the low-temperature differential pressure null transducer and indicator DPT Ruska (models 2413-703 and 2416-711) to a pressure measuring system. The measuring vessel is filled with the sample by a positive displacement pump/volumeter Ruska (PDP, model 2270-803) with a total discharge volume of 250 cm^3. The discharge volume is read on a scale and dial with resolution of (1 and 0.01) cm^3, respectively; the vernier enables determination of 0.001 cm^3. The volumeter is connected with valves to the measuring vessel and to a high vacuum apparatus Lavat AV 63 (VP).

Pressure Measurement. The low-temperature differential pressure null transducer and indicator DPT (Figure 1) placed outside the bath separates the sample from the oil-filled pressure transmission system connected to a piston-type injector for the pressure adjustment. The uncertainty of the null indication is certified not to exceed ± 0.005 % or ± 70 Pa, whichever is greater. The pressure measurements are recorded by two Paroscientific absolute pressure gauges (Paroscientific Inc., Digiquartz model 43KR and 415K), PG1 and PG2 (Figure 1), with a measuring range of (20 and 100) MPa, respectively. The manufacturer-specified repeatability and standard uncertainty of the pressure measurements are both 0.01 % of the full gauge range, i.e, less than (0.002 and 0.01) MPa for the range of (20 and 100) MPa, respectively.

Temperature Measurement and Control. A vacuum-isolated double-walled thermostat/cryostat is supplied with the heat exchange medium from the cryostat Lauda Ultra-Kryomat RUK 90 working as an external source of cold down to 183 K. After the bath has reached the set temperature, it takes typically 2 h to attain the steady state condition. The long-term temperature stability varies within (± 1 to ± 3) mK depending on the sample and the set-point temperature. The thick-walled pressure vessel provides an effective smoothing of the bath temperature oscillations. The measuring cell temperature is measured on ITS-90 with a precision thermometry bridge ASL F700 and a 25 Ω platinum resistance thermometer Tinsley (Type 5187 SA) calibrated with ITS-90 fixed points at National Physical Laboratory, London. The manufacturers' stated uncertainty of the thermometer is ± 0.001 K. The thermometer is inserted into a hole drilled into the cell wall.

The uncertainty in the temperature measurement is due to the thermometer and due to inhomogeneity of the bath temperature field. The thermometer has a certified uncertainty of ± 1 mK. The temperature field homogeneity was assessed using a system of calibrated Pt100 resistance thermometers placed into the bath surrounding the piezometer. The temperature difference across the pressure vessel was found not to exceed 5 mK. Therefore, the total uncertainty in the temperature measurement is estimated to be close to ± 5 mK.

Material. The sample of the [BMIM][BF$_4$] used in the reported measurements with the specified minimum mass fraction purity of 0.999 was obtained from Solvent Innovation GmbH. The sample was used without further purification except drying by intensive stirring and evaporation under vacuum at the temperature of 353 K. The water mass fraction in the sample filled into the volumeter as measured in our laboratory with a coulometric Karl Fischer titrator Mettler Toledo C30 was thus $w(H_2O) = 36 \cdot 10^{-6}$.

Measuring Procedure. The measuring procedure consists of a stepwise change of the temperature of the measuring cell filled with a sample and recording the equilibrium pressure. The measurement of the mass of the sample filled into the cell is converted by the volumeter to a measurement of the sample volume at some selected reference state. The volumeter cylinder, provided for this purpose with a double-wall thermostatted jacket, is filled with the sample and brought to a thermodynamic equilibrium in a selected reference state defined by its temperature $T_{\mathrm{ref}} = 298.15$ K and pressure $p_{\mathrm{ref}} = 0.1$ MPa. The initial position, V_{fill1}, of the volumeter plunger is read on the volumeter scale. Then the filling valve of the measuring cell is opened, and the cell having been beforehand brought to some required temperature is filled to a demanded pressure. After closing the filling valve, the reference state of the sample remaining in the volumeter is restored accurately. Then the final position, V_{fill2}, of the plunger is read. Thus, the mass of the sample filled in the piezometer is given by the relation

$$m_{\mathrm{ref}} = \rho_{\mathrm{ref}}(V_{\mathrm{fill2}} - V_{\mathrm{fill1}}) \qquad (1)$$

where ρ_{ref} is the density of the investigated liquid in the reference state, the value $\rho_{\mathrm{ref}} = 1201.33\ \mathrm{kg\cdot m^{-3}}$ of which has been determined in an independent experiment.[45]

The gross volume V_{ref} of the piezometer system including the differential pressure null transducer at reference conditions, T_{ref} and p_{ref}, was determined by filling the measuring cell system using the volumeter, both brought to reference conditions. The volume V_{ref} is then given by the volumeter readings $V_{1\mathrm{cal}}$ and $V_{2\mathrm{cal}}$ as

$$V_{\mathrm{ref}} = V_{2\mathrm{cal}} - V_{1\mathrm{cal}} \qquad (2)$$

A suitable calibrating medium was used for this purpose. The value of $V_{\mathrm{ref}} = 193.203\ \mathrm{cm^3}$ with an estimated standard uncertainty of $\pm$ 0.0023 $\mathrm{cm^3}$ was obtained as a mean of results of repeated measurements.

Data Evaluation. The density ρ of the sample is evaluated from the net volume, V, of the piezometer and the net mass, m, of the sample contained in it as $\rho = m/V$. The values of these two quantities are to be evaluated from the primary data. In the construction of the piezometer for a constant-volume apparatus working at subzero temperatures, it is impossible to avoid volumes connected with the sample cell but being at a different temperature. A correction to the final density has to be introduced for this volume which is referred to as a noxious volume. The evaluation of the correction for the noxious volume ranks together with determination of the piezometer actual volume among the most important sources of possible uncertainties of the method. The treatment of the noxious and the piezometer volume in the present apparatus is described in the following two subsections.

Piezometer Volume. The net volume $V(T, p)$ of the piezometer is evaluated using eq 3 from the gross volume V_{ref} obtained in the calibration measurement by making allowance for the noxious volume V_{nox}, the volume V_{ci} of the part of the connecting capillary being inside the thermostat, the temperature dilatation of the cell material, and the pressure expansion of the cell

$$V = (V_{\mathrm{ref}} - V_{\mathrm{nox}} - V_{\mathrm{ci}})[1 + 3\alpha(T - T_{\mathrm{ref}}) + \beta(p - p_{\mathrm{ref}})] \qquad (3)$$

The noxious volume, $V_{\mathrm{nox}} = V_{\mathrm{dpt}} + V_{\mathrm{co}}$, consists of the volume of the chamber of the differential pressure null transducer ($V_{\mathrm{dpt}} = 0.6\ \mathrm{cm^3}$) and of a small part V_{co} (0.177 $\mathrm{cm^3}$, 5.65 cm in length, 0.2 cm in diameter) of the transducer connecting capillary which is outside the piezometer thermostat/cryostat. The remaining part of the connecting capillary V_{ci} (1.197 $\mathrm{cm^3}$, 38.105 cm in length) is inside the thermostat. The transducer is imbedded in an aluminum block which is together with the outer part of the connection capillary thermostatted to the reference temperature T_{ref} so that the amount of the sample contained can be calculated with reasonable accuracy.

The coefficient α/K^{-1} in eq 3 is the temperature dilatation coefficient of the measuring cell material, and β/MPa^{-1} is the temperature-dependent coefficient of the cell volume expansion with pressure. The values of the coefficients α (eq 4) and β (eq 5) are calculated from the values of the thermal and elastic coefficients taken from the material property data sheet of the stainless steel AISI 321 from which the pressure vessel is made.

$$\alpha/\mathrm{K}^{-1} = 1.50\cdot 10^{-5}[1 + 3.13\cdot 10^{-4}\ \mathrm{K}^{-1}(T - T_{\mathrm{ref}})] \qquad (4)$$

$$\beta/\mathrm{MPa}^{-1} = 1.51\cdot 10^{-5}[1 + 2.75\cdot 10^{-4}\ \mathrm{K}^{-1}(T - T_{\mathrm{ref}})] \qquad (5)$$

To evaluate the coefficient β, a model of the pressure vessel as a finite thick-walled cylinder[58] was used, giving

$$\beta = \frac{2\,(1+\mu)\left(\frac{R}{r}\right)^2 + 3\,(1 - 2\mu)}{\left[\left(\frac{R}{r}\right)^2 - 1\right]E} \qquad (6)$$

with $\mu = E/(2G - 1)$, where G (MPa) and E (MPa) are the shear and Young's modulus, respectively, and R/cm and r/cm are the outer and inner diameter of the cylinder, respectively. The values of the slightly temperature-dependent coefficient β lies near $1.50\cdot 10^{-5}\ \mathrm{MPa}^{-1}$. It is quite enough to know β with a relative uncertainty of 10 % to reduce the order of magnitude of the uncertainty introduced by the calculation of the sample cell pressure expansion to the level of 0.01 %. The used thick-walled pressure vessel with such a small linear pressure expansion coefficient ensures that the possible nonlinear pressure effect is negligible within the region of not too high pressures up to 60 MPa. The correction $(\Delta\rho)_\beta$ to the density for the pressure expansion of the pressure vessel takes its maximum value $(\Delta\rho)_\beta/\rho = 0.0009$ at the upper limit $p = 60$ MPa of pressures. For the pressure expansion coefficient β known with the standard relative uncertainty of 10 %, the correction $(\Delta\rho)_\beta$ to density is determined with standard uncertainty better than 0.0001ρ.

In the present measurements, the correction $(\Delta\rho)_\alpha$ to the density for the temperature dilatation of the pressure vessel material takes its maximum relative value $(\Delta\rho)_\alpha/\rho = 0.0027$ at the upper limit $T = 353$ K of the temperature interval. For the temperature dilatation coefficient α known with the standard relative uncertainty of 10 %, the correction to density is determined with standard uncertainty better than 0.0003ρ.

Mass of the Sample. The net mass m of the sample contained in the cell is obtained from the total mass m_{ref} filled into the system by subtracting the mass m_{nox} of the sample contained in the pressure null transducer system, in general, at temperature different from that of the cell.

$$m = m_{\mathrm{ref}} - m_{\mathrm{nox}} \qquad (7)$$

The mass m_{nox} contained in the transducer system is calculated as a sum of the parts contained in its subvolumes under different temperatures

$$m_{\mathrm{nox}} = V_{\mathrm{nox}}\rho(T_{\mathrm{nox}}, p) + V_{\mathrm{ci}}\rho(T, p) \qquad (8)$$

where $V_{\mathrm{nox}} = V_{\mathrm{dpt}} + V_{\mathrm{co}}$. V_{dpt}, V_{co}, and V_{ci} are the volumes of the differential pressure null transducer chamber and of the parts of the connecting capillary outside and inside the thermostat, respectively. The volumes V_{co} and V_{ci} were calculated from the length and from the inner diameter of the capillary. The temperature of the part V_{ci} of the connecting capillary situated inside the thermostat is equated to the temperature T of the sample in the piezometer. The effect of possible temperature gradients is considered as negligible. The part V_{co} of the connecting capillary outside the thermostat is thermostatted together with the body of the transducer to the reference temperature, and therefore their temperature is equated to T_{ref}. The correction for the sample mass contained in the differential pressure null transducer system can be applied only iteratively as, for the calculation of the mass m_{nox}, the measured density—pressure—temperature relation is required.

The relative value $(\Delta\rho)_{nox}/\rho$ of the density correction $(\Delta\rho)_{nox}$ for the noxious volume can be expressed in the form

$$\frac{(\Delta\rho)_{nox}}{\rho} = \frac{V_{nox}}{V_{ref}}\left(1 - \frac{\rho_{nox}}{\rho}\right) \tag{9}$$

The part of the connecting capillary inside the sample cell thermostat does not contribute to the density correction to the noxious volume. For $V_{nox} = 0.78\ \text{cm}^3$, $V = 193\ \text{cm}^3$, and the maximum relative difference between sample density in the piezometer and in the noxious volume $|\rho - \rho(T_{ref}, p)|/\rho = 0.04$, the maximum relative value of the correction to the density for the noxious volume is $(\Delta\rho)_{nox}/\rho = 1.6\cdot10^{-4}$, while the uncertainty of the correction is negligible. Thus, the maximum value $(\Delta\rho)_{tot}$ of the total correction applied is

$$(\Delta\rho)_{tot} = (\Delta\rho)_{\alpha} + (\Delta\rho)_{\beta} + (\Delta\rho)_{nox} = 0.0038\rho \tag{10}$$

i.e., 0.38 % relative to the measured density ρ. The standard uncertainty of the total correction to density is thus estimated to be better than 0.0004ρ.

Uncertainties. As discussed in the previous sections, the experimental fluid density data are evaluated using eqs 1 to 8. Thus, the uncertainty $u(\rho)$ of a single fluid density ρ measurement is a function of the 17 input variables entering the density evaluation procedure

$$u(\rho) = U[V_{ref},\rho_{ref},V_{fill1},V_{fill2},T_{ref1},T_{ref2},p_{ref1},p_{ref2},\alpha,\beta,T,p,T_{nox},\rho_{nox},V_{nox},V_{ci},\rho_{ci}] \tag{11}$$

The state parameters T_{ref1}, p_{ref1} and T_{ref2}, p_{ref2} of the sample in the volumeter cylinder before filling and after filling are here included among the input parameters for the purpose of the uncertainty analysis. The actual values of the temperature and pressure of the sample in the volumeter cylinder can slightly differ from the nominal target values T_{ref}, p_{ref}. Assuming that all the values of the input variables X_i are independent, the variance of ρ is

$$u(\rho) = \sum_{i=1}^{17}\left(\frac{\partial\rho}{\partial X_i}u(X_i)\right)^2 \tag{12}$$

where X_i ($i = 1$ to 17) represents the 17 input variables in eq 11, and the combined standard uncertainty is the square root of the variance.[59] Table 2 gives besides the value of each individual input quantity X_i an estimation of its standard uncertainty $u(X_i)$ and the square root of the contribution of the quantity to the variance $\partial\rho/\partial X_i u(X_i)$, both expressed in percent relative to the quantity value and to the density value, respectively. In Table 2, the quantities are arranged according to their contribution to the variance. The values of the parameters T_{ref1}, p_{ref1}, T_{ref2}, p_{ref2}, and T_{nox} of the reference state restored during the piezometer filling procedure and in the noxious volume can slightly differ from the nominal values T_{ref} and p_{ref}, and therefore they also might be sources of uncertainty. Uncertainties that stem from the volumeter readings V_{1cal} and V_{2cal} and from the restorations of the reference state in the cell volume calibration are contained in the uncertainty of the cell gross volume V_{ref}. The density $\rho(T_{ref}, p)$ used for evaluation of the sample mass m_{nox} contained in the differential pressure null transducer system is denoted ρ_{nox} in Table 2, and the ultimate value of its standard uncertainty is estimated to be 0.1 %. The variables T, p, p_{ref2}, V_{ci}, and T_{ci} with quite negligible effect on the resultant uncertainty are not included in the table. Only uncertainties of the first three quantities in Table 2 contribute relevantly to the density uncertainty. Thus the estimated 95 % confidence level uncertainty of a single measurement takes the values from ± 0.01 % in the reference state to ± 0.06 % at the end points of the range of the experimental temperatures.

Table 2. Input Variables X_i of the Density Evaluation Procedure and Their Uncertainties $u(X_i)$ and Square Roots $(\partial\rho/\partial X_i)u_{Xi}$ of Their Respective Contributions to the Variance $u(\rho)^2$, Expressed in Percent Relative to X_i and ρ, Respectively

X_i	range of X_i	$10^2\cdot u_{Xi}/X_i$	$10^2\cdot(1/\rho)(\partial\rho/\partial X_i)u_{Xi}$
α	$1.5\cdot10^{-5}\ \text{K}^{-1}$	10	from 0.0 to 0.027
β	$1.5\cdot10^{-5}\ \text{MPa}^{-1}$	10	from 0.0 to 0.010
ρ_{ref}	$1201\ \text{kg}\cdot\text{m}^{-3}$	0.01	0.01
V_{nox}	$0.78\ \text{cm}^3$	10	0.0020
V_{ref}	$193\ \text{cm}^3$	0.0023	0.0012
T_{ref1}	298 K	0.005	0.0008
T_{ref2}	298 K	0.005	0.0008
V_{fill1}	(193 to 200) cm^3	0.0005	0.0005
V_{fill2}	(193 to 200) cm^3	0.0005	0.0005
ρ_{nox}	$1201\ \text{kg}\cdot\text{m}^3$	0.1	0.0004
P_{ref1}	0.1 MPa	10	0.0004
T_{nox}	298 K	0.3	0.0002

The very small values of the uncertainty estimates stem from the following facts: (i) the accuracy of the method is based especially on a high accuracy of the volumeter measurements (with resolution of 1 mm^3), which secure small uncertainty of the determination both of the piezometer volume and of the sample mass relative to the reference density; (ii) the temperature control is brought to a metrological level; (iii) some of the variables (V_{nox}, ρ_{nox}, T_{nox}, p, T) enter only into the calculations of the correction, which is small in itself, and therefore, their contributions to the combined uncertainty are yet much smaller; and (iv) small uncertainty contributions of the variables T_{ref1}, T_{ref2}, p_{ref1}, and p_{ref2} follow from the level of accuracy of the reference state adjustment and in the case of p_{ref1} and p_{ref2} also from the smallness of the derivative $\partial\rho/\partial p$.

The repeatability of the density measurements at given temperature and pressure can be expressed in terms of the experimental standard deviation of the gross density values m_{ref}/V_{ref} obtained in repeated measurements. From the repeatability of the determination of the gross mass m_{ref} and the gross volume V_{ref} from the volumeter plunger position readings (eqs 1 and 2), it follows that the value of the density measurement repeatability is $1.7\cdot10^{-5}\rho_{ref}$.

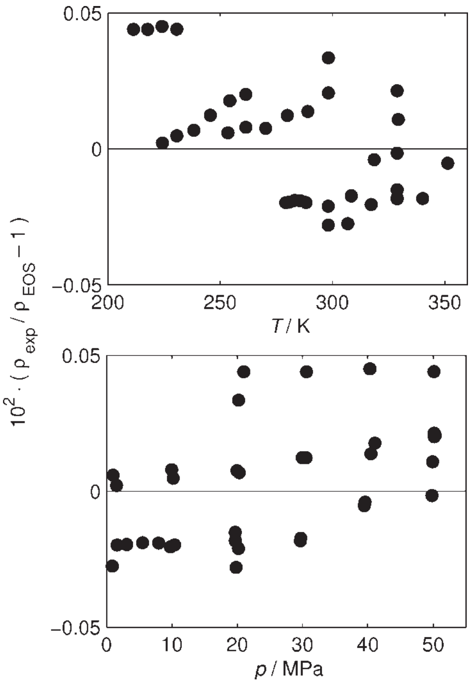

Figure 2. Deviations of the experimental density data of methanol, ρ_{exp}, from the values ρ_{EOS} calculated from the correlation by de Reuck and Craven[60] as a function of temperature and pressure. ●, this work.

From the results of the quantitative analysis of the effect of the water content on the [BMIM][BF$_4$] density,[45] it follows that the water mass fraction of $36 \cdot 10^{-6}$ of the present sample reduces its density by 0.0014 % compared to pure [BMIM]-[BF$_4$].

Validation of the Apparatus. The new apparatus and the measuring and data evaluation procedures have been tested by measurements on methanol. A sample with minimum mass fraction purity of 0.999 and with water mass fraction of $3 \cdot 10^{-5}$ supplied by Merck KGaA, Darmstadt, Germany, was used for this purpose. Measurements at 36 temperature−pressure points on 5 isochores at temperatures from (211 to 351) K and up to 50 MPa have been performed. Relative deviations of the obtained methanol densities from the internationally agreed upon formulation for the thermodynamic properties of methanol by de Reuck and Craven[60] are depicted in Figure 2. The deviations lie within a band of ± 0.05 % which is in accordance with the uncertainty estimate.

RESULTS AND DISCUSSION

Density. A total of 61 individual measurements were carried out along eight quasi-isochores at temperatures between (240 and 354) K at pressures from (1 to 60) MPa. The resultant densities obtained from the evaluation procedure taking into account all necessary corrections are presented in Table 3.

Using the present data and critically assessed data from the literature, a representative eq 13 of the Tait type has been developed for the [BMIM][BF$_4$] density

$$\rho(T, p) = \frac{\rho(T, p_{\mathrm{ref}})}{1 - b_3 \ln\left[\dfrac{B(T) + p/p_{\mathrm{ref}}}{B(T) + 1}\right]} \qquad (13)$$

Table 3. Present Experimental Data on Densities ρ for [BMIM][BF$_4$] as a Function of Temperature T and Pressure p

T/K	p/MPa	ρ/kg·m^{-3}
298.118	0.1059	1201.65
298.131	10.109	1204.56
292.092	1.9404	1204.98
305.026	19.306	1204.07
313.037	29.821	1203.50
321.613	40.890	1202.88
327.983	48.935	1202.42
337.094	59.633	1201.76
298.124	9.5508	1204.57
292.092	1.4458	1204.99
313.058	29.280	1203.51
313.045	10.270	1194.38
305.528	0.8986	1194.90
320.513	19.693	1193.85
328.178	29.263	1193.30
336.350	39.210	1192.70
344.315	48.811	1192.12
353.675	59.697	1191.42
328.175	28.863	1193.30
328.176	10.050	1184.05
320.097	0.3286	1184.62
336.681	20.276	1183.44
344.203	29.113	1182.90
354.156	40.617	1182.17
328.224	10.050	1184.05
328.181	29.052	1193.14
313.034	9.7903	1194.22
313.038	30.149	1203.70
298.138	10.428	1204.76
298.138	29.887	1213.94
291.460	20.613	1214.42
278.132	1.6600	1215.35
305.667	40.148	1213.41
321.398	60.815	1212.26
313.606	50.546	1212.83
284.095	10.163	1214.93
284.057	30.274	1223.71
291.266	40.686	1223.19
298.580	50.942	1222.67
305.535	60.508	1222.17
276.946	19.845	1224.21
264.468	1.1974	1225.08
270.250	9.9638	1224.68
270.252	30.434	1233.04
276.968	40.555	1232.57
283.484	50.231	1232.10
290.086	59.872	1231.63
263.701	20.360	1233.50
251.624	1.4315	1234.33
257.247	10.286	1233.95
257.259	30.540	1242.41
263.492	40.569	1241.97
269.793	50.298	1241.52

Table 3. Continued

T/K	p/MPa	ρ/kg·m^{-3}
275.567	59.083	1241.11
251.148	20.631	1242.83
239.754	1.8754	1243.62
244.146	9.1872	1243.32
244.152	30.106	1251.69
250.803	41.033	1251.23
256.789	51.047	1250.80
262.282	59.764	1250.41

where

$$\rho(T, p_{\text{ref}}) = \frac{a_0}{1 + \sum_{i=1}^{3} a_i \tau^i} \tag{14}$$

$$B(T) = \sum_{i=0}^{2} b_i \tau^i \tag{15}$$

with $\tau = T/(100\ \text{K})$. With exception of the coefficient a_0, the dimension of which is kg·m^{-3}, all other coefficients a_i and b_i in eqs 13 to 15 are dimensionless. The equation was fitted to selected data sets meeting the requirement that at their low-pressure limit the accepted pressure-dependent data should be at least nearly consistent to the accepted 0.1 MPa data within their experimental uncertainties. If this requirement was not met, the derivatives of the resultant equation would be distorted, and good agreement with the experimental data on isobaric thermal expansivity could not be obtained. Thus, the pressure dependence data from this work and the data of Machida et al.[40] have been combined in the fitting with the 0.1 MPa data of Zafarani-Moattar and Shekaari,[22] Harris et al.,[25] Inglesias-Otero et al.,[30] Navia et al.,[29] Shekaari and Zafarani-Moattar,[32] and Klomfar et al.[45] While most authors obtained their data on the [BMIM][BF$_4$] density using a vibrating tube densimeter, Machida acquired his data by a variable-volume method using a metal bellows.

Within the present study, 57 literature sources of experimental data have been collected containing a total of 1045 data points on the (p, ρ, T) relation of [BMIM][BF$_4$]. Thirteen of the 57 cited literature sources provide only one data point. Most of the data points lie within the temperature interval from (293 to 353) K. Figure S4 in the Supporting Information provides an overall idea on the distribution of all the data points on the [BMIM][BF$_4$] density available from the literature in the $p-T$ plane. Temperatures below 273 K down to 240 K are covered only by the data set of the present study. At pressures above 0.1 MPa, only 180 data points of Machida et al.[40] prove to be well consistent with the above-mentioned 0.1 MPa data sets evaluated as the most reliable.[45]

Table 4 gives the resultant coefficients a_i and b_i of the eqs 13 to 15 for the 1-butyl-3-methylimidazolium tetrafluoroborate. Figure 3 shows deviations of the experimental (p, ρ, T) data used in fitting, from the resultant representative eq 13. Most of the deviations lie within the band of ± 1.0 kg·m^{-3}. The procedure *nlinfit* from the Matlab Statistic Toolbox used to fit the density data estimates the 95 % confidence level uncertainty of the density values calculated from the obtained eq 13 to be less than 0.02 % of the measured density value.

Table 4. Coefficients a_i and b_i of Equations 13 to 15 with Their 95 % Confidence Interval Half-Widths, $2u(a_i)$ and $2u(b_i)$

i	$a_i \pm 2u(a_i)$	$b_i \pm 2u(b_i)$
0	1503.2 ± 18.0	5567.0 ± 25
1	$(1.0742 \pm 0.10)\cdot 10^{-1}$	-1263.6 ± 13
2	$(-1.1784 \pm 0.33)\cdot 10^{-2}$	85.55 ± 1.6
3	$(1.3610 \pm 0.32)\cdot 10^{-3}$	$(9.55 \pm 0.18)\cdot 10^{-2}$

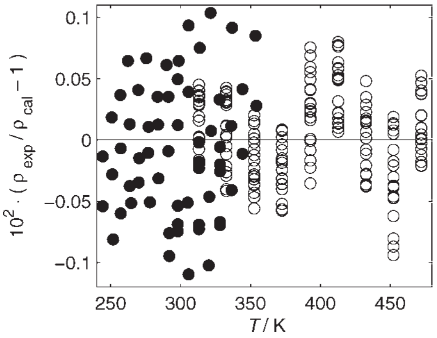

Figure 3. Deviations of the experimental density data, ρ_{exp}, used for the present correlation from the values ρ_{cal} calculated from the correlation eq 13 as a function of temperature. ○, Machida et al.;[40] ●, this work.

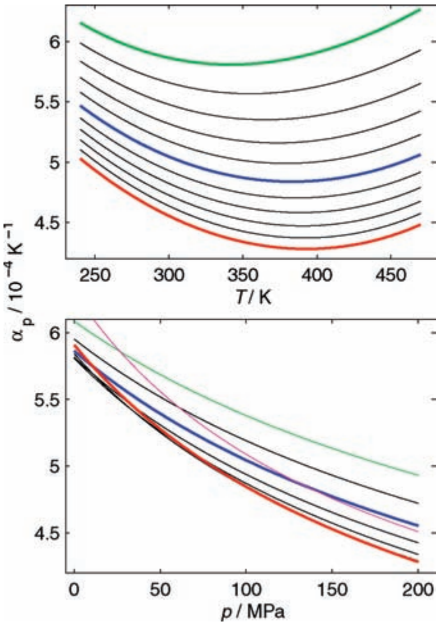

Figure 4. Isobaric thermal volume expansion coefficients α_p calculated from the correlation eq 13 as a function of temperature, T, and of pressure, p. Green line, p = 0.1 MPa and T = 250 K; blue line, p = 100 MPa and T = 300 K; red line, p = 200 MPa and T = 400 K; magenta line, T = 475 K.

Figure S1 in the Supporting Information depicts deviations of experimental data on the [BMIM][BF$_4$] density at the pressure of 0.1 MPa, obtained by different authors, from the density values calculated from eq 13 as a function of temperature. Figure S2 of the Supporting Information shows deviations of experimental data on the pressure dependence of the [BMIM][BF$_4$] density,

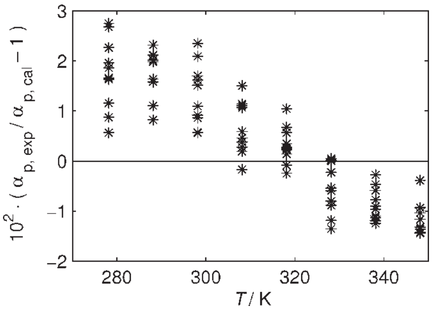

Figure 5. Deviations of the experimental data on the isobaric thermal volume expansion coefficients α_p by *, Navia et al.[61] from the values of α_p calculated from the present correlation eq 13 as a function of temperature, T.

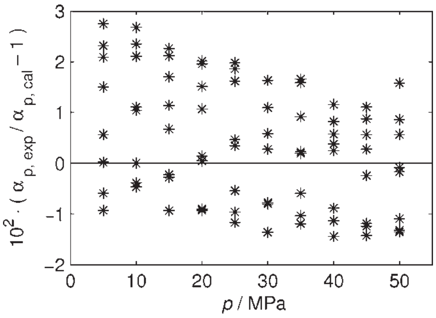

Figure 6. Deviations of the experimental data on the isobaric thermal volume expansion coefficients α_p by *, Navia et al.[61] from the values of α_p calculated from the present correlation eq 13 as a function of pressure, p.

obtained by different authors, from the density values calculated from eq 13 as a function of temperature and of pressure. An overall idea on the distribution of these deviations is provided by Figure S3 (Supporting Information).

Isobaric Thermal Expansivity and Isothermal Compressibility. The correlation eq 13 makes it possible to evaluate coefficients of isobaric thermal expansion α_p/K^{-1} and isothermal compressibility $\kappa_T/\mathrm{Pa}^{-1}$

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{16}$$

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \tag{17}$$

The calculated values of isobaric thermal volume expansion coefficients α_p are shown in Figure 4 as a function of temperature and of pressure. Figures 5 and 6 give a comparison of the calculated α_p values with experimental values of Navia et al.[61] determined directly by means of the calorimetric method. The obtained relative deviations are within ± 3 %, which is a good result for values calculated from differentiation of a fitting function. Average relative deviations of values of α_p calculated by different authors for [BMIM][BF_4] from the values directly measured by Navia et al.[61] range from (2 to 9) %. The present results confirm at subzero temperatures the commonly observed[14,24,61,62] anomalous temperature dependence of the isobaric thermal volume expansion coefficient of ionic liquids, which at the low-temperature side (Figure 4) decreases as T is raised while its slope approaches zero. At higher temperatures, after reaching a minimum, α_p increases with temperature as reported by Machida et al.[40]

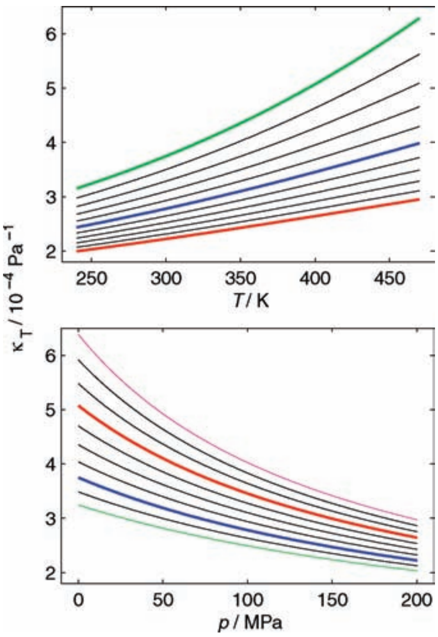

Figure 7. Isothermal compressibility κ_T calculated from the correlation eq 13 as a function of temperature, T, and of pressure, p. Green line, p = 0.1 MPa and T = 250 K; blue line, p = 100 MPa and T = 300 K; red line, p = 200 MPa and T = 400 K; magenta line, T = 475 K.

The calculated values of isothermal compressibility κ_T are presented in Figure 7 as a function of temperature and of pressure.

CONCLUSION

Experimental data on the density of 1-butyl-3-methylimidazolium tetrafluoroborate are reported in the subroom temperature range down to 240 K and up to 60 MPa in pressure where they are still lacking. The experimental data points on the 1-butyl-3-methylimidazolium tetrafluoroborate (p, ρ, T) relation obtained in the present work at temperatures from (240 to 353) K proved to be consistent with the data of other authors evaluated as the most reliable ones. An empirical equation describing the (p, ρ, T) relation of the 1-butyl-3-methylimidazolium tetrafluoroborate has been developed based upon a body of critically assessed experimental data compiled from the literature.

The comparisons of the available data on the 1-butyl-3-methylimidazolium tetrafluoroborate density have shown that the amount of the available experimental data is far less valuable to establish a description of that property than it might appear at first glance. Some of the available sets of the data are only of limited value because they show large scatter or systematic deviations when compared to other data.

The density measuring methods that do not require flowing of the fluid sample during the course of the measurement seem to be more resistant to the effects of high values of viscosity and of its strong dependence not only on temperature but also on pressure. They provide an opportunity to achieve better accuracy though at the price of poorer reproducibility and less productivity of measurements. The large scatter of the density data obtained by different authors using the vibrating tube method indicates that this method is prone to uncertainties in the case of measurements on ionic liquids. The method is capable of reaching very high accuracy in conditions for which it was originally developed, in density measurement of not too viscous liquids at atmospheric pressure. However, the application of the correction for the viscosity of the sample is complicated by the necessity to use a set of viscosity normals including the viscosity temperature dependence. The viscosity of [BMIM][BF_4] reaches values of the order of magnitude of almost 10^3 mPa·s, and moreover it also substantially depends on pressure.

Common ionic liquids with markedly low temperature of solid−liquid equilibrium come into question for further density measurements at subambient and subzero temperature ranks, for example, 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIM][BF_4]), 1-butyl-3-methylimidazolium dicyanamide ([BMIM][$(CN)_2N$]), and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM][CF_3SO_3]) with the melting point of 192 K, 223 K, and 255 K, respectively.

■ ASSOCIATED CONTENT

Supporting Information. Relative deviations of the experimental density values obtained by different authors including the present work for the 1-butyl-3-methylimidazolium tetrafluoroborate from the present correlation eq 13 as a function of temperature and pressure. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Suarez, P. A. Z; Einloft, S.; Dullius, J. E. L.; Souza, de R. F.; Dupont, J. Synthesis and physical-chemical properties of ionic liquids based on 1-*n*-butyl-3-methylimidazolium cation. *J. Chim. Phys. Phys.-Chim. Biol.* **1998**, *95*, 1626–1639.

(2) 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.

(3) Branco, L. C.; Rosa, J. N.; Ramos, J. J. M.; Afonso, C. A. M. Preparation and Characterization of New Room Temperature Ionic Liquids. *Chem.—Eur. J.* **2002**, *8*, 3671–3677.

(4) Seddon, K. R.; Stark, A.; Torres, M. J. Viscosity and Density of 1-Alkyl-3-methylimidazolium Ionic Liquids. *.Clean Solvents: Alternative Media for Chemical Reactions and Processing*; Abraham, M. A., Moens, L., Eds.; ACS Symposium Series 819; American Chemical Society: Washington DC, 2002; pp 34−49.

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

(6) 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.

(7) Xu, W.; Wang, L. M.; Nieman, R. A.; Angell, C. A. Ionic Liquids of chelated orthoborates as model ionic glassformers. *J. Phys. Chem. B* **2003**, *107*, 11749–11756.

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

(9) 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.

(10) Kim, K. S.; Shin, B. K.; Lee, H. Physical and Electrochemical Properties of 1-Butyl-3-methylimidazolium Bromide, 1-Butyl-3-methylimidazolium Iodide, and 1-Butyl-3-methylimidazolium Tetrafluoroborate. *Korean J. Chem. Eng.* **2004**, *21*, 1010–1014.

(11) Ohlin, C. A.; Dyson, P. J.; Laurenczy, G. Carbon monoxide solubility in ionic liquids: determination, prediction and relevance to hydroformylation. *Chem. Commun.* **2004**, *9*, 1070–1071.

(12) Rebelo, L. P. N.; Najdanovic-Visak, V.; Visak, Z. P.; Ponte, da M. N.; Szydlovski, J.; Cerderina, C. A.; Troncoso, J.; Romani, L.; Esperanca, J. M. S.; Guedes, H. J. R.; Sousa, de H. C. A detailed thermodynamic analysis of [C_4mim][BF_4] + water as a case study to model ionic liquid aqueous solutions. *Green Chem.* **2004**, *6*, 369–381.

(13) 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.

(14) Azevedo, de R. G.; Esperanca, J. M. S. S.; Najdanovic-Visak, V.; Visak, Z. P.; Guedes, H. J. R.; Ponte, da M. N.; 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.

(15) Lopes, J. N. C.; Cordeiro, T. C.; Esperança, J. M. S. S.; Guedes, H. J. R.; Hug, 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.

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

(17) Yang, J. Z.; Gui, J. S.; Lü, X. M.; Zhang, Q. G.; Li, H. W. Study on Properties of Ionic Liquid BMIBF_4. *Acta Chim. Sin.* **2005**, *63*, 577–580.

(18) Deetlefs, M.; Seddon, K. R.; Shara, M. Predicting physical properties of ionic liquids. *Phys. Chem. Chem. Phys.* **2006**, *8*, 642–649.

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

(20) Liu, W.; Zhao, T.; Zhang, Y.; Wang, H.; Yu, M. The Physical Properties of Aqueous Solutions of the Ionic Liquid [BMIM][BF_4]. *J. Solution Chem.* **2006**, *35*, 1337–1346.

(21) Tomida, D.; Kumagai, A.; Qiao, K.; Yokoyama, C. Viscosity of [bmim][PF_6] and [bmim][BF_4] at High Pressure. *Int. J. Thermophys.* **2006**, *27*, 39–47.

(22) Zafarani-Moattar, M. T.; Shekaari, H. Application of Prigogine-Flory-Patterson theory to excess molar volume and speed of sound of 1-n-butyl-3-methylimidazolium hexafluorophosphate or 1-n-butyl-3-methylimidazolium tetrafluoroborate in methanol and acetonotrile. *J. Chem. Thermodyn.* **2006**, *38*, 1377–1384.

(23) Zhou, Q.; Wang, L. S.; Chen, H. P. Densities and Viscosities of 1-Butyl-3-methylimidazolium Tetrafluoroborate + H_2O Binary Mixtures from (303.15 to 353.15) K. *J. Chem. Eng. Data* **2006**, *51*, 905–908.

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

(25) Harris, K. R.; Kanakubo, M.; Woolf, L. A. Temperature and Pressure Dependence of the Viscosity of the Ionic Liquid 1-Butyl-3-methylimidazolium Tetrafluoroborate: Viscosity and Density Relationship in Ionic Liquids. *J. Chem. Eng. Data* **2007**, *52*, 2425–2430.

(26) Huo, Y.; Xia, S.; Ma, P. Densities of Ionic Liquids, 1-Butyl-3-methylimidazolium Hexafluorophosphate and 1-Butyl-3-methylimidazolium Tetrafluoroborate, with Benzene, Acetonitrile, and 1-Propanol at T=(293.15 to 343.15) K. *J. Chem. Eng. Data* **2007**, *52*, 2077–2082.

(27) Jacquemin, J.; Husson, P.; Mayer, V.; Cibulka, I. High-pressure volumetric properties of imidazolium-based ionic liquids - Effect of the anion. *J. Chem. Eng. Data* **2007**, *52*, 2204–2211.

(28) Malham, I. B.; Letellier, P.; Mayaffre, A.; Turmine, M. Part I: Thermodynamic analysis of volumetric properties of concentrated aqueous solutions of 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-2,3-dimethylimidazolium tetrafluoroborate, and ethylammonium nitrate based on pseudo-lattice theory. *J. Chem. Thermodyn.* **2007**, *39*, 1132–1143.

(29) Navia, P.; Troncoso, J.; Romaní, L. Excess Magnitudes for Ionic Liquid Binary Mixtures with a Common Ion. *J. Chem. Eng. Data* **2007**, *52*, 1369–1374.

(30) Iglesias-Otero, M. A.; Troncoso, J.; Carballo, E.; Romani, L. Density and Refractive Index for Binary Systems of the Ionic Liquids [Bmim][BF$_4$] with Methanol, 1,3-Dichloropropane and Dimethyl Carbonate. *J. Solution Chem.* **2007**, *36*, 1219–1230.

(31) Sanmamed, Y. A.; González-Salgado, D.; Troncoso, J.; Cerdeiriña, C. A.; Romaní, L. Viscosity-induced errors in the density determination of room temperature ionic liquids using vibrating tube densitometry. *Fluid Phase Equilib.* **2007**, *252*, 96–102.

(32) Shekaari, H.; Zafarani-Moattar, M. T. Osmotic coefficients of some imidazolium based ionic liquids in water and acetonitrile at temperature 318.15 K. *Fluid Phase Equilib.* **2007**, *254*, 198–203.

(33) Tekin, A.; Safarov, J.; Shahverdiyev, A.; Hessel, E. (p, ρ, T) Properties of 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium hexafluorophosphate at T=(298.15 to 398.15) K and pressures up to p = 40 MPa. *J. Mol. Liq.* **2007**, *136*, 177–182.

(34) Zhang, Q.; Li, Z.; Zhang, J.; Zhang, S.; Zhu, L.; Yang, J.; Zhang, X.; Deng, Y. Physicochemical Properties of Nitrile-Functionalized Ionic Liquids. *J. Phys. Chem. B* **2007**, *111*, 2864–2872.

(35) Abdulagatov, I. M.; Tekin, A.; Safarov, J.; Shahverdiyev, A.; Hassel, E. Densities and Excess, Apparent, and Partial Molar Volumes of Binary Mixtures of BMIMBF4 +Ethanol as a Function of Temperature, Pressure, and Concentration. *Int. J. Thermophys.* **2008**, *29*, 505–533.

(36) Hernández-Fernández, F. J.; Ríos, de los A. P.; Gómez, D.; Rubio, M.; Tomás-Alonso, F.; Víllora, G. Ternary liquid-liquid equilibria for mixtures of an ionic liquid + n-hexane an organic compound involved in the kinetic resolution of *rac*-1-phenyl ethanol (*rac*-1-phenyl ethanol, vinyl propionate, *rac*-1-phenylethyl propionate or propionic acid) at 298.2 K and atmospheric pressure. *Fluid Phase Equilib.* **2008**, *263*, 190–198.

(37) Jacquemin, J.; Ge, R.; Nancarrow, P.; Rooney, D. W.; Gomes, M. F. C.; Pádua, A. A. H.; Hardacre, C. Prediction of Ionic Liquid Properties. I. Volumetric Properties as a Function of Temperature at 0.1 MPa. *J. Chem. Eng. Data* **2008**, *53*, 716–726.

(38) Jin, H.; O'Hare, B.; Dong, J.; Arzhantsev, S.; Baker, G. A.; Wishart, J. F.; Benesi, A. J.; Maroncelli, M. Physical Properties of Ionic Liquids Consisting of the 1-Butyl-3-Methylimidazolium Cation with Various Anions and the Bis(trifluoromethylsulfonyl)imide Anion with Various Cations. *J. Phys. Chem. B* **2008**, *112*, 81–92.

(39) Kumar, A. Estimates of Internal Pressure and Molar Refraction of Imidazolium Based Ionic Liquids as a Function of Temperature. *J. Solution Chem.* **2008**, *37*, 203–214.

(40) Machida, H.; Sato, Y.; Smith, R. L., Jr. Pressure-volume-temperature (PVT) measurements of ionic liquids ([bmim$^+$][PF$_6$-], [bmim$^+$][BF$_4$-], [bmim$^+$][OcSO$_4$-]) and analysis with the Sanchez-Lacombe equation of state. *Fluid Phase Equilib.* **2008**, *264*, 147–155.

(41) Tian, Y.; Wang, X.; Wang, J. Densities and Viscosities of 1-Butyl-3-methylimidazolium Tetrafluoroborate + Molecular Solvent Binary Mixtures. *J. Chem. Eng. Data* **2008**, *53*, 2056–2059.

(42) Gao, H.; Qi, F.; Wang, H. Densities and volumetric properties of binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate with benzaldehyde at T=(298.15 to 313.15) K. *J. Chem. Thermodyn.* **2009**, *41*, 888–892.

(43) García-Miaja, G.; Troncoso, J.; Romaní, L. Excess molar properties for binary systems of alkylimidazolium-based ionic liquids plus nitromethane. Experimental results and ERAS-model calculations. *J. Chem. Thermodyn.* **2009**, *41*, 334–341.

(44) Han, C.; Xia, S.; Ma, P.; Zeng, F. Densities of Ionic Liquid [BMIM][BF4] + Ethanol, + Benzene, and + Acetonitrile at Different Temperature and Pressure. *J. Chem. Eng. Data* **2009**, *54*, 2971–2977.

(45) Klomfar, J.; Součková, M.; Pátek, J. Buoyancy density measurements for 1-alkyl-3-methylimidazolium based ionic liquids with tetrafluoroborate anion. *Fluid Phase Equilib.* **2009**, *282*, 31–37.

(46) Rilo, E.; Pico, J.; García-Garabal, S.; Varela, L. M.; Cabeza, O. Density and Surface Tension in binary mixtures of CnMIM-BF4 Ionic Liquids with water and ethanol. *Fluid Phase Equilib.* **2009**, *285*, 83–89.

(47) Singh, T.; Kumar, A.; Kaur, M.; Kaur, G.; Kumar, H. Non-ideal behaviour of imidazolium based room temperature ionic liquids in ethylene glycol at T = (298.15 to 318.15) K. *J. Chem. Thermodyn.* **2009**, *41*, 161–166.

(48) Soriano, A. N.; Doma, B. T.; Li, M. H. Measurements of the density and refractive index for 1-n-butyl-3-methylimidazolium-based ionic liquids. *J. Chem. Thermodyn.* **2009**, *41*, 301–307.

(49) Stoppa, A.; Hunger, J.; Buchner, R. Conductivities of Binary Mixtures of Ionic Liquids with Polar Solvents. *J. Chem. Eng. Data* **2009**, *54*, 472–479.

(50) Tariq, M.; Forte, P. A. S.; Gomes, M. F. C.; Lopes, J. N. C.; Rebelo, L. P. N. Densities and Refractive Indices of Imidazolium- and Phosphonium-based Ionic Liquids: Effect of Temperature, Alkyl Chain Length and Anion. *J. Chem. Thermodyn.* **2009**, *41*, 790–798.

(51) Qi, F.; Wang, H. Application of Prigogine-Flory-Patterson theory to excess molar volume of mixtures of 1-butyl-3-methylimidazolium ionic liquids with N-methyl-2-pyrrolidinone. *J. Chem. Thermodyn.* **2009**, *41*, 265–272.

(52) Carrera, G. V. S. M.; Afonso, C. A. M.; Branco, L. C. Interfacial Properties, Densities, and Contact Angles of Task Specific Ionic Liquids. *J. Chem. Eng. Data* **2010**, *55*, 609–615.

(53) Rilo, E.; Ferreira, A. G. M.; Fonseca, I. M. A.; Cabeza, O. Densities and Derived Thermodynamic Properties of Ternary Mixtures 1-Butyl-3-Methyl-Imidazolium Tetrafluoroborate + Ethanol + Water at Seven Pressures and Two Temperatures. *Fluid Phase Equilib.* **2010**, *296*, 53–59.

(54) Sánchez, L. G.; Espel, J. R.; Onink, F.; Meindersma, G. W.; Haan, de A. B. Density, Viscosity, and Surface Tension of Synthesis Grade Imidazolium, Pyridinium, and Pyrrolidinium Based Room Temperature Ionic Liquids. *J. Chem. Eng. Data* **2009**, *54*, 2803–2812.

(55) Sanmamed, Y. A.; González-Salgado, D.; Troncoso, J.; Romani, L.; Baylaucq, A.; Boned, C. Experimental methodology for precise determination of density of RTILs as a function of temperature and pressure using vibrating tube densimeters. *J. Chem. Thermodyn.* **2010**, *42*, 553–563.

(56) Yan, L.; Hong, Y.; Pingli, Z.; Feng, Q. Volumetric Properties of Binary Mixtures of the Ionic Liquid 1-Butyl-3-Methylimidazolium Tetrafluoroborate with Aniline. *J. Solution Chem.* **2010**, *39*, 219–230.

(57) Li, Y.; Ye, H.; Zeng, P.; Qi, F. Volumetric Properties of Binary Mixtures of the Ionic Liquid 1-Butyl-3-Methylimidazolium Tetrafluoroborate with Aniline. *J. Solution Chem.* **2010**, *39*, 219–230.

(58) Timoshenko, S. P.; Goodier, J. N. *Theory of Elasticity*; McGraw-Hill: New York, 1970.

(59) *Guide To The Expression Of Uncertainty In Measurement*; ISO: Geneva, Switzerland, 1993, (ISBN 92-67-10188-9).

(60) Reuck de, K. M.; Craven, R. J. B. *International Thermodynamic Tables of the Fluid State, Vol. 12: Methanol*; Blackwell Scientific Publications: Oxford, 1993.

(61) Navia, P.; Troncoso, J.; Romaní, L. Isobaric Thermal Expansivity for Ionic Liquids with a Common Cation as a Function of Temperature and Pressure. *J. Chem. Eng. Data* **2010**, *55*, 590–594.

(62) Azevedo, de R. G.; Esperanca, J. M. S. S.; Szydlowsly, J.; Visak, Z. P.; 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.

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This article was originally published ASAP on January 26, 2011. In the Supporting Information, data that should have appeared in Figure S1 was included in Figure S2 instead. The article with corrected Supporting Information was reposted on February 14, 2011.