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$P-\rho-T$ Measurements for 1-Alkyl-3-methylimidazolium-Based Ionic Liquids with Tetrafluoroborate and a Trifluoromethanesulfonate Anion

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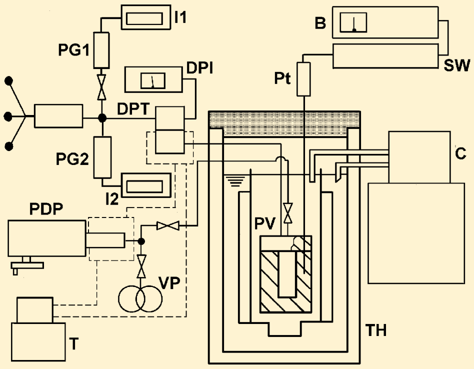
Supporting Information

ABSTRACT: The present paper reports results of density measurements for 1-C_n-3-methylimidazolium-based tetrafluoroborates and trifluoromethanesulfonates with n = 2 and 4 and with n = 2, 4, and 6, respectively. For the tetrafluoroborates, the measurements were performed at temperatures from (285 and 220) K, respectively, to approximately 357 K. For the trifluoromethanesulfonates, the measurements were conducted at temperatures from 353 K down to the melting temperature of the substance. Data at nominal pressures of 1 MPa and from (10 to 60) MPa with a 10 MPa step were obtained. An isochoric apparatus was used, making possible density measurements at temperatures below 273.15 K. The combined uncertainty at the 95 % confidence level in the resultant density data due to the measuring procedure is estimated to be 1 kg·m^{-3}, that is, about 0.1 % relative to the density value. Results of a quantitative analysis are reported of the effect of water and chloride anion impurities present in the sample on the density of the ionic liquids of interest. The sodium cation was studied experimentally as a candidate for the impurity causing an increase in ionic liquid density. At the same mass fraction, the sodium cation proves to be four times more effective than the chloride anion in changing the density of [HMIM][BF_4].



INTRODUCTION

Ionic liquids exhibit an extraordinary potential to be used in a variety of research and technological applications along with favorable environmental properties. As a result, they became currently a subject of an intense research with significant effort being focused on the measurement of their thermophysical properties. Among them the $p-\rho-T$ relation of a fluid is a fundamental property essential for the development of a thermodynamic property model for a substance. It is also a property which affects nearly all applications of the fluid. Though the melting temperature of a number of ionic liquids lies significantly below 273 K, the $p-\rho-T$ measurements are most often conducted in the above-room-temperature range where they are feasible by using a common apparatus. But from the point of view of fundamental knowledge all temperatures are equally important. Any subsequent processing of the accumulated experimental data such as their theoretical analysis, development of predictive schemes, or thermodynamic property formulations is the more conclusive with the broader range of temperatures and pressures of the data on which it is based. To make possible measurements of pressure dependence of density at subroom temperatures and especially below 273 K we have constructed a new apparatus based on the constant volume principle as described in detail in our previous study.[1]

The present study is a continuation of our previous measurements of the $p-\rho-T$ relation for 1-butyl-3-methylimidazolium tetrafluoroborate,[1] the melting temperature of which is 202 K. Compared to the [BMIM][BF_4] with 12 studies on its $p-\rho-T$ relation, only moderate attention has been paid up to now to the experimental determination of the temperature and pressure dependence of the density of 1-ethyl- and 1-hexyl-3-methylimidazolium tetrafluoroborates. Table 1 gives an overview of the literature sources[2−31] for experimental density data for the two tetrafluoroborates of interest together with the corresponding temperature and pressure region, sample water content, the measuring method used, and the number of data points. The $p-\rho-T$ relation for [EMIM][BF_4] was studied by Gardas et al.,[11] Taguchi et al.,[15] and Sanmamed et al.,[19] and for [HMIM][BF_4] by Taguchi et al.,[15] Sanmamed et al.,[19] and Safarov and Hassel.[29] For both ionic liquids these data cover the temperature range from (283 to 473) K, and the pressures range from (0.1 to 200) MPa. The $p-\rho-T$ measurements for [HMIM][BF_4] with a melting point at 198 K have hitherto been conducted only in the temperature range above room temperature.

The density values for [EMIM][BF_4] by different authors, including the 0.1 MPa data, are spread over an interval with a width of about 7 % relative to the density, or if the pycnometric measurements are excluded, of about 2 % (Figure 1). Thus, no matter what the actual value of the [EMIM][BF_4] density is, for

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Table 1. Literature Sources for Experimental Density Data for the Ionic Liquids of Interest with the Sample Water Content Given as Water Mass Fraction, w[a]

author(s)	year	temp. range T/K	press. range p/MPa	$w \cdot 10^6$	methods	no. of data
1-Ethyl-3-methylimidazolium Tetrafluoroborate [EMIM][BF_4]						
Noda et al.[2]	2001	293 to 313	0.1	1	vtd	5
Seddon et al.[3]	2002	298.15 to 363.15	0.1	525	pyc	8
Nishida et al.[4]	2003	298.15	0.1	5	pyc	1
Zhao et al.[5]	2003	293.1	0.1	n/a	pyc	1
Zhang et al.[6]	2004	293.15 to 323.15	0.1	n.a.	pyc	7
Zhou et al.[7]	2004	298.15	0.1	200	pyc	1
Van Valkenburg et al.[8]	2005	333.1	0.1	65	vtd	1
Zhou et al.[9]	2005	298.15	0.1	300	vtd	1
Vila et al.[10]	2006	298.15	0.1	n/a	vtd	1
Gardas et al.[11]	2007	293.15 to 393.15	0.1 to 30	365	vtd	96
Navia et al.[12]	2007	298.15 to 308.15	0.1	n/a	vtd	9
Shiflett and Yokozeki[13]	2007	285.0 to 305.0	0.1	207	pyc	5
Wong et al.[14]	2008	303.20 to 323.20	0.1	n/a	vtd	5
Taguchi et al.[15]	2009	293.15 to 472.40	0.1 to 200	90	vtd, dil	184
Klomfar et al.[16]	2009	293.41 to 353.07	0.1	314	hdb	13
Rilo et al.[17]	2009	298.15	0.1	220	vtd	1
Stoppa et al.[18]	2009	298.15	0.1	n/a	vtd	2
Sanmamed et al.[19]	2010	283.15 to 323.18	0.1 to 60	800	vtd	117
Currás et al.[20]	2010	293.15 to 333.23	0.1	200	vtd	5
Shamsipur et al.[21]	2010	283.15 to 363.15	0.1	n/a	vtd	9
this work	2011	285.12 to 356.40	1.0 to 60	105	piez	74
1-Hexyl-3-methylimidazolium Tetrafluoroborate [HMIM][BF_4]						
Letcher and Reddy[22]	2004	298.15	0.1	n/a	vtd	1
Wagner et al.[23]	2004	298	0.1	n/a	pyc	1
Wagner et al.[24]	2004	298	0.1	n/a	pyc	1
Letcher and Reddy[25]	2005	298.15	0.1	n/a	vtd	1
Sanmamed et al.[26]	2007	288.15 to 323.15	0.1	1709	vtd	36
Navia et al.[12]	2007	298.15 to 308.15	0.1	n/a	vtd	18
Muhammad et al.[27]	2008	298.15 to 358.15	0.1	324	vtd	7
García-Miaja et al.[28]	2009	293.15 to 318.15	0.1	13	vtd	6
Taguchi et al.[15]	2009	293.15 to 472.50	0.1 to 200	23	vtd, dil	184
Klomfar et al.[16]	2009	283.61 to 352.77	0.1	157	hdb	15
Rilo et al.[17]	2009	298.15	0.1	273	vtd	1
Stoppa et al.[18]	2009	298.15	0.1	n/a	vtd	1
Safarov and Hassel[29]	2010	283.15 to 373.13	0.1 to 100	n/a	vtd	91
Sanmamed et al.[19]	2010	283.15 to 323.18	0.1 to 60	600	vtd	117
Klomfar et al.[30]	2010	268.65 to 356.07	0.1	51	hbd	18
Zhu et al.[31]	2011	298.15	0.1	n/a	vtd	1
this work	2011	219.19 to 357.12	0.1 to 60	51	piez	67
1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate [EMIM][TFA]						
Rodríguez and Brennecke[32]	2006	278.15 to 348.15	0.1	980	vtd	8
Vercher et al.[33]	2007	278.15 to 338.15	0.1	500	vtd	7
García-Miaja et al.[34]	2008	293.15 to 318.15	0.1	130	vtd	6
Gardas et al.[35]	2008	293.15 to 393.15	0.1 to 35	21	vtd	91
Wong et al.[14]	2008	303.20 to 323.20	0.1	n/a	vtd	5
Klomfar et al.[30]	2010	268.45 to 355.90	0.1	105	hbd	18
this work	2011	264.14 to 347.77	0.1 to 60	93	piez	61
1-Butyl-3-methylimidazolium Trifluoromethanesulfonate [BMIM][TFA]						
Fredlake et al.[36]	2004	295.75 to 342.95	0.1	2800	pyc	5
Tokuda et al.[37]	2006	288.10 to 313.10	0.1	40	vtd	6
Gardas et al.[38]	2007	293.15 to 393.15	0.1 to 10	18	vtd	77
García-Miaja et al.[34]	2008	293.15 to 318.15	0.1	130	vtd	6
Ge et al.[39]	2008	303.15 to 343.15	0.1	n/a	pyc	7
Tariq et al.[40]	2009	293.15 to 333.15	0.1	70	vtd	4
Soriano et al.[41]	2009	298.20 to 353.20	0.1	n/a	vtd	17
Shamsipur et al.[21]	2010	283.15 to 363.15	0.1	n/a	vtd	9
Klomfar et al.[30]	2010	292.93 to 355.84	0.1	28	hbd	26
this work	2011	290.50 to 350.15	1 to 60	32	piez	61

Table 1. continued

author(s)	year	temp. range T/K	press. range p/MPa	$w\cdot 10^6$	methods	no. of data
1-Hexyl-3-methylimidazolium Trifluoromethanesulfonate [HMIM][TFA]						
Klomfar et al.[30]	2010	293.95 to 355.39	0.1	98	hdb	13
this work	2011	303.14 to 351.77	0.1 to 60	113	piez	48

^{a}vtd, vibrating tube densitometer; pyc, pycnometer; piez, piezometer; dil; dilatometer; hbd, hydrostatic-balance densitometer.

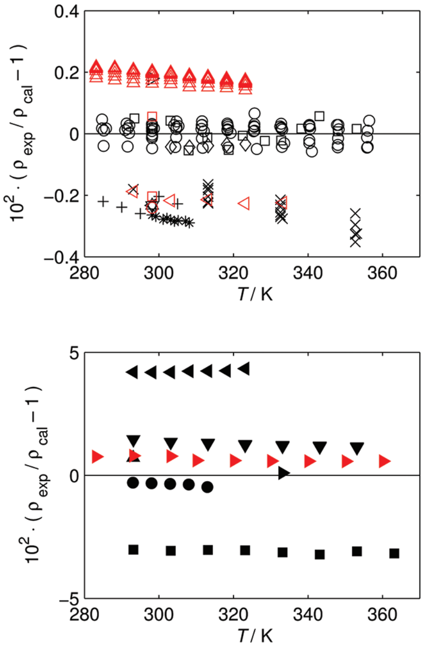

Figure 1. [EMIM][BF$_4$]: deviations of experimental density data, ρ_{exp}, of different authors from the values, ρ_{cal}, calculated from the eq 3 as a function of temperature T. ●, Noda et al.;[2] □, Seddon et al.;[3] △, Nishida et al.;[4] ▲, Zhao et al.;[5] ◀, Zhang et al.;[6] ◁, Zhou et al.;[7] ▶, Van Valkenburg et al.;[8] ▷, Zhou et al.;[9] ▽, Vila et al.;[10] ▼, Gardas et al.;[11] *, Navia et al.;[12] +, Shiflett and Yokozeki;[13] ◀, Wong et al.;[14] ×, Taguchi et al.;[15] □, Klomfar et al.;[16] red ○, Rilo et al.;[17] red □, Stoppa et al.;[18] red △, Sanmamed et al.;[19] red ◁, Curras et al.;[20] red ▶, Shamsipur et al.;[21] ○, this work.

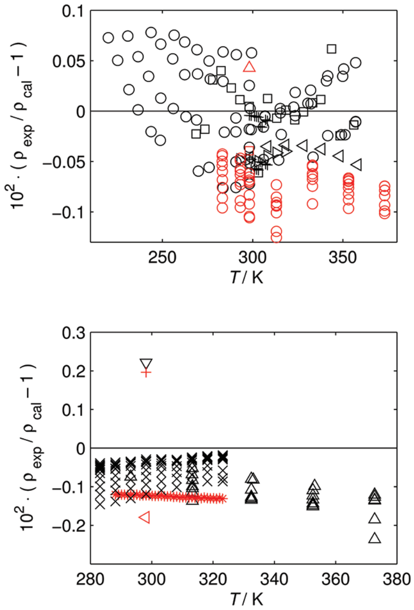

Figure 2. [HMIM][BF$_4$]: deviations of experimental density data, ρ_{exp}, of different authors from the values, ρ_{cal}, calculated from the eq 3 as a function of temperature T. ▽, Letcher and Reddy;[22] red ◁, Wagner et al.;[24] red +, Letcher and Reddy;[25] red *, Sanmamed et al.;[26] +, Navia et al.;[12] ◁, Muhammad et al.;[27] ▷, García-Miaja et al.;[28] △, Taguchi et al.;[15] □, Klomfar et al.;[30] red □, Rilo et al.;[17] red △, Stoppa et al.;[18] red ○, Safarov and Hassel;[29] ×, Sanmamed et al.;[19] red ▽, Zhu et al.;[31] ○, this work.

most of the existing $p-\rho-T$ data points the density lie beyond the limit of 0.1 % from it. Therefore the present knowledge of the [EMIM][BF$_4$] density is only a rough, and further measurements are highly desirable. In the case of [HMIM][BF$_4$] the situation is a little better. The interval over which the density values by different authors are spread has a width of about 0.4 % (Figure 2).

The literature sources for the pressure dependence of the density of the 1-alkyl-3-methylimidazolium-based trifluoromethanesulfonates are quite scarce. Table 1 gives an overview of the literature sources,[14,21,30,32−41] for the experimental density data for the three trifluoromethanesulfonates, most of which are the 0.1 MPa data. The pressure dependence of the density of [EMIM][TFA] and [BMIM][TFA] was studied only by Gardas et al.[35,38] in the temperature region from (293 to 393) K up to (30 and 10) MPa, respectively. No data are available for the density-pressure dependence of [HMIM][TFA] in the open literature. A description of the temperature dependence of the density of the 1-alkyl-3-methylimidazolium tetrafluoroborates and triflates of interest at 0.1 MPa and a survey of the works of other authors devoted to this topic is given in the papers by Klomfar et al.[16,30]

The primary aim of the present study was to obtain new experimental data for the density of 1-ethyl- and 1-hexyl-3-methylimidazolium tetrafluoroborate and of 1-C$_n$-3-methylimidazolium trifluoromethanesulfonates with n = 2, 4, and 6 in the temperature region from about 353 K down to their melting temperature. The melting temperatures of the ionic liquids of interest are given in Tables 2 and 3. In the case of the 1-hexyl-3-methylimidazolium tetrafluoroborate, with melting temperature of 198 K the actual measurement ended at 220 K because on the quasi-isochore starting at this temperature, solidification took place at pressure of 50 MPa. Also the melting temperature of [EMIM][TFA] (T_m = 264 K) lies in the subzero temperature region (at temperatures below 273.15 K) in which, in respect to the density, it has not yet been studied at all. We did not conduct the measurements on subcooled liquid in the present study, though the ionic liquids when fully dried, can remain as liquids for long periods of time (i.e., month) at a temperatures well below their melting points.

The second aim was to obtain a reliable uncertainty estimate using a quantitative model of the effect of impurities based on appropriate experimental data. The density data for ionic liquids by different authors available in the literature often show scattering, which is much larger than that commonly observed for traditional organic solvents. It is quite usual that the density data obtained for a ionic liquid by different authors do not agree to each other within the limits of their stated uncertainties. The origin of these discrepancies is not yet fully understood. The uncertainty estimates presented in experimental studies often relate only to the measuring method and its concrete realization

Table 2. Basic Information on the BF_4 Samples Used in the Present Study: Their Suppliers, Stated Mass Fraction Purities, Mass Fraction Water Content, and Their Respective Values of the Reference Parameters T_{ref}, p_{ref}, and ρ_{ref}, Used in Measurements

	[EMIM][BF_4]	[HMIM] [BF_4]
supplier	Solvent Innovation[a]	Solvionic[b]
minimum mass fraction purity	0.998	0.99
water content (mass fraction)	$105 \cdot 10^{-6}$	$51 \cdot 10^{-6}$
maximum halide content (mass fraction)	$175 \cdot 10^{-6}$	$100 \cdot 10^{-6}$
melting point T_m/K	284	198
reference temperature T_{ref}/K	298.15	298.15
reference pressure p_{ref}/MPa	0.1	0.1
reference density ρ_{ref}/kg·m^{-3}	1283.02	1145.61

[a] Solvent-Innovation GmbH, Cologne, Germany. [b] Solvionic SA, Toulouse, France.

Table 3. Basic Information on the TFA Samples Used in the Present Study: Their Suppliers, Stated Mass Fraction Purities, Mass Fraction Water Content, and Their Respective Values of the Reference Parameters T_{ref}, p_{ref}, and ρ_{ref}, Used in Measurements

	[EMIM] [TFA]	[BMIM] [TFA]	[HMIM] [TFA]
supplier	IoLiTec[a]	Solvionic[b]	IoLiTec[a]
minimum mass fraction purity	0.99	0.99	0.99
water content (mass fraction)	$93 \cdot 10^{-6}$	$32 \cdot 10^{-6}$	$113 \cdot 10^{-6}$
maximum halide content (mass fraction)	$100 \cdot 10^{-6}$	$25 \cdot 10^{-6}$	$100 \cdot 10^{-6}$
melting point T_m/K	264	286	302
reference temperature T_{ref}/K	298.15	298.15	303.15
reference pressure p_{ref}/MPa	0.1	0.1	0.1
reference density ρ_{ref}/kg·m^{-3}	1385.78	1298.59	1235.40

[a] Ionic Liquids Technologies GmbH, Heilbronn, Germany. [b] Solvionic SA, Toulouse, France.

and do not account for a possible effect of impurities present in the used sample. Jacquemin et al.[42] give an estimation showing that under usual conditions the uncertainty coming from the effect of impurities is about 0.4 % and that it is dominant in relation to the contribution of the method. Based on the fact, that the effect of water content can be effectively reduced by drying the sample, Troncoso et al.[43] conclude that the chloride anion content is the dominant cause of differences between the density values obtained by different authors. Seddon et al.[44] published three values of density of [BMIM][BF_4]−[BMIM]-[Cl] mixtures, which provide empirical evidence on the effect of chloride anion impurities on the density of [BMIM][BF_4].

■ EXPERIMENTAL SECTION

General Remarks. For details on the isochoric apparatus and the measuring and data evaluation procedure used in the present measurements we refer the reader to our earlier study.[1] Here we only recall the details relevant to the accuracy of the resultant $p-\rho-T$ data. The present apparatus has been designed utilizing experience gained with a previous isochoric apparatus[47−49] designed and operated in the Laboratory of the Thermophysical Properties of Fluids of IT. The apparatus makes possible density measurements at temperatures from (183 to 363) K and in pressures up to 60 MPa. The used isochoric method gives values for the density relative to a density ρ_{ref} of the sample at some selected reference state T_{ref}, p_{ref}, which is used to determine volumetrically the amount of the sample filled into the measuring cell.[1] Thus, the total uncertainty in the resultant values of the density includes a contribution due to the isochoric method and due to the uncertainty in the reference density value ρ_{ref}. The overall expanded combined uncertainty at a 0.95 confidence level associated with the isochoric method and the reference density amounts to 0.001ρ.[1] This uncertainty has been evaluated from the quadratic sum of uncertainties in the directly measured quantities that enter the working equation of the method. In each particular measurement, the impurities present in the sample act as an additional source of uncertainty in the reference density determination. The effect of impurities is analyzed later in the Results section. The present isochoric apparatus has several special features which are critical to achieving high accuracy of the $p-\rho-T$ measurements. We highlight these features briefly in the following subsection.

Apparatus and Procedure. In principle, the isochoric method consists in closing of a known mass, m, of the investigated liquid in a measuring vessel with an accurately calibrated volume, V, so that the density of the sample is $\rho = m/V$. Then the temperature is incremented along the isochore, and the corresponding sample pressures are measured. In practice, the expansion of the cell volume with increasing temperature and pressure has to be allowed for in the density evaluation. For this purpose, the actual volume $V(T,p)$ of the piezometer at a temperature T and pressure p is expressed as $V = V_{ref}\nu(p,T)$, where V_{ref} is the total volume of the cell calibrated at some selected reference temperature and pressure T_{ref}, p_{ref}, and the function $\nu(p,T)$ describes the temperature and pressure expansion of the cell from the reference state.

In the construction of the piezometer for a constant volume apparatus working at subzero temperatures, it is impossible to avoid a volume connected with the sample cell but being at a different temperature. This volume is referred to as a noxious or a spurious volume. The value V_{nox} of the noxious volume and the mass m_{nox} of the sample contained in it must be allowed for in the sample density evaluation. Thus, for a real constant volume apparatus the density is evaluated from the equation

$$\rho = \frac{m_{tot} - m_{nox}}{(V_{ref} - V_{nox})\nu(p, T)} \tag{1}$$

where m_{tot} is the total mass of the sample filled in the piezometer system including the noxious volume. The evaluation of the correction for the noxious volume ranks together with the determination of the piezometer actual volume among the most important potential sources of uncertainties of the isochoric method. In the following, we describe the special features of the present apparatus resulting in a substantial reduction of the uncertainties in the quantities m_{tot}, m_{nox}, V_{ref}, V_{nox}, and $\nu(p,T)$ entering the working equation.

(i) To calibrate the volume $V_{ref} = 193$ cm^3 of the measuring cell a positive displacement pump/volumeter Ruska (model 2270-803) providing resolution of 0.001 cm^3 was used. The volume V_{ref} was determined by filling the piezometer with a calibration medium at a reference condition. As a suitable calibration medium the ionic liquid [EMIM][BF_4] was used as it has a sufficiently low pressure of saturated vapor at the reference temperature of 298.15 K.

(ii) The volumeter was used also to determine the mass m_{tot} of the sample inserted into the measuring cell system. The mass of the sample was determined as $m_{\mathrm{tot}} = V_{\mathrm{fill}}\rho_{\mathrm{ref}}$, where V_{fill} is the volume of the sample filled into the measuring cell at reference conditions.

(iii) The noxious volume V_{nox} was extremely minimized by a proper apparatus design so that the uncertainty arising from applying the correction $(\Delta\rho)_{\mathrm{nox}}$ for the noxious volume given by the relation $(\Delta\rho)_{\mathrm{nox}}/\rho = (V_{\mathrm{nox}}/V_{\mathrm{ref}})(1 - \rho_{\mathrm{nox}}/\rho)$ is marginal[1] ($V_{\mathrm{nox}} = 0.78\ \mathrm{cm}^3$, $V_{\mathrm{ref}} = 193\ \mathrm{cm}^3$). The standard uncertainty $u(\Delta\rho_{\mathrm{nox}})$ associated with the correction to the noxious volume is equal to $10^{-5}\ \rho$.

(iv) The noxious volume is thermostatted to the reference temperature, so that the correction to the mass of the sample m_{tot} for the mass $m_{\mathrm{nox}} = V_{\mathrm{nox}}\rho_{\mathrm{nox}}$ contained in the noxious volume can be accurately evaluated.

(v) The uncertainty contributions following from the accuracy level of the repeated reference state adjustment in the volumeter chamber during the filling cycle was minimized by thermostatting the volumeter chamber to the reference temperature (for details see our previous paper[1]).

(vi) The temperature control of the sample is brought to a metrological level as it is described in the subsection "Temperature Measurement and Control".

(vii) The function $\nu(p,T)$ describing the temperature and pressure expansion of the cell from the reference state has the form given in eq 2.

$$\nu = 1 + 3\alpha(T - T_{\mathrm{ref}}) + \beta(p - p_{\mathrm{ref}}) \tag{2}$$

The coefficient α (K^{-1}) in eq 2 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 and β 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. To evaluate the coefficient β a model of the pressure vessel as a finite thick-walled cylinder[45] was used. The standard uncertainty associated with the function $\nu(p,T)$ following from uncertainties of the coefficients α and β is estimated to be 0.0003ρ.[1] As described in the following subsection, we have verified experimentally that for the thick-walled pressure vessel used in our apparatus, eq 2 linear in pressure provides values of the temperature and pressure expansion function $\nu(p,T)$ fairly close to its actual values.

Validation of the Apparatus and Procedure. The apparatus and the measuring and data evaluation procedures have been tested by measurements on methanol at temperatures from (211 to 351) K and in pressures up to 50 MPa. Relative deviations of the obtained methanol densities from the internationally agreed upon formulation for the thermodynamic properties of methanol by de Reuck and Craven[46] lie within an interval of ± 0.05 % which is in accordance with the uncertainty estimate.[1] To express the comparison in terms of the corrections to the raw density $\rho_{\mathrm{raw}} = m_{\mathrm{tot}}/V_{\mathrm{ref}}$ we define the overall correction $\Delta\rho$ applied to the raw density as $\Delta\rho = \rho - \rho_{\mathrm{raw}}$, where ρ is the resultant value of the density. Figure 3 provides a comparison of the overall correction $(\Delta\rho)_{\mathrm{our}} = \rho_{\mathrm{our}} - \rho_{\mathrm{raw}}$, as applied to the raw methanol density in the present evaluation procedure, with the correction $(\Delta\rho)_{\mathrm{deReuck}} = \rho_{\mathrm{deReuck}} - \rho_{\mathrm{raw}}$ following from the density value ρ_{deReuck} given by the equation of state by de Reuck and Craven.[46] The correction reaches a value of about 4 $\mathrm{kg \cdot m^{-3}}$ at a maximum, while the difference between the calculated value of the correction used in data evaluation and the value following from the calibration measurement is about 2 orders of magnitude less (0.04 $\mathrm{kg \cdot m^{-3}}$ at maximum, i.e., 0.0005ρ).

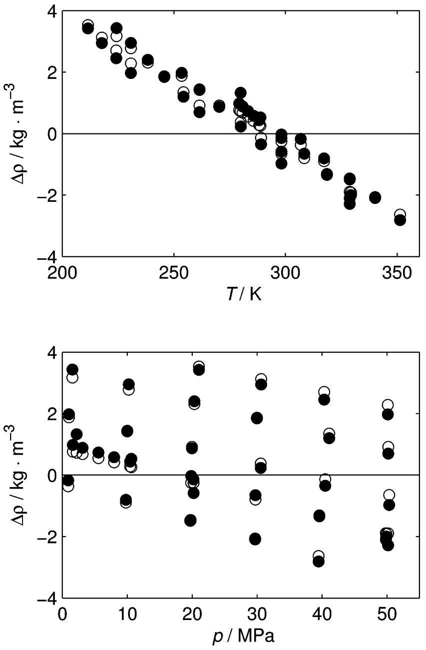

Figure 3. Comparison of the overall correction $(\Delta\rho)_{\mathrm{our}} = \rho_{\mathrm{our}} - \rho_{\mathrm{raw}}$ applied to the raw methanol density in the present evaluation procedure with the correction $(\Delta\rho)_{\mathrm{deReuck}} = \rho_{\mathrm{deReuck}} - \rho_{\mathrm{raw}}$ following from the density value ρ_{deReuck} given by the equation of state by de Reuck and Craven.[46] ●, $(\Delta\rho)_{\mathrm{our}}$; ○, $(\Delta\rho)_{\mathrm{deReuck}}$.

The treatment of the noxious and the piezometer volume in the present apparatus was also used and validated in the previous version of the apparatus constructed and operated in our laboratory.[47−49] The values for methanol and HFC-134a density obtained with this apparatus[47,48] agree with the internationally agreed upon formulations of the thermodynamic properties for these substances[46,50] to better than 0.1 %. Similarly, the density values for HFC-227ea, obtained with this apparatus,[49] agree with the values calculated from the National Institute of Standards and Technology (NIST) Standard Reference Database 23—REFPROP[51] to within ± 0.1 %.

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 in the piezometer. The long-term temperature stability varies within (± 0.001 to ± 0.003) K 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 manufacturer's 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 the inhomogeneity of the bath temperature field. 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 0.005 K. Therefore, the total uncertainty in the temperature measurement is estimated to be close to ± 0.005 K.

Pressure Measurement. A low-temperature differential pressure null transducer and indicator placed outside the bath separates the sample from 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) with a measuring range of (20 to 100) MPa, respectively. The manufacturer-specified repeatability and standard uncertainty of the pressure measurements are both 0.01 % of the full gauge range, that is, less than (0.002 to 0.01) MPa for the range of (20 to 100) MPa, respectively. Even if the actual pressure in the piezometer is measured with the declared accuracy, an error in the pressure value to which the obtained density is related may arise, when the sample is not fully equilibrated, and it may even become the dominant one.

Materials. Tables 2 and 3 list the main primary characteristics of the samples studied, including their suppliers, their manufacturer stated minimum mass fraction purities, the initial water mass fraction in the samples as measured in our laboratory with the coulometric Karl Fischer titrator Mettler Toledo C30, and the upper-bound to the chloride ion mass fraction as stated by the manufacturer. The samples were used without further purification except for drying by intensive stirring and evaporation under vacuum at a temperature of 353 K. No decomposition of the ILs was observed at the experimental conditions.

■ RESULTS AND DISCUSSION

Density. The measurements of density for [EMIM][BF_4] and [HMIM][BF_4] were performed at about 70 individual p-T points at temperatures from (285 and 220) K, respectively, to approximately 357 K and in pressure up to 60 MPa. For each of the three trifluoromethanesulfonates of interest, the density measurements were performed at temperatures from about its melting temperature to approximately 353 K and in pressure up to 60 MPa at about 60 individual $p-T$ points. The reference values of the density (Table 2 and 3) used in the measurements and data evaluation were calculated from the correlations of the 0.1 MPa density data published by Klomfar et al.[16,30] A brief note concerning the results of the 0.1 MPa density measurements on two different samples of [HMIM][BF_4] reported in our two papers[16,30] is given in the Supporting Information. The resultant density values obtained from the evaluation procedure taking into account all necessary corrections[1] are presented in Tables S1 to S5 in the Supporting Information together with the temperature and pressure values to which the densities are related.

To correlate the obtained density data, the procedure *nlinfit* from the Matlab Statistic Toolbox was employed. It uses the Levenberg−Marquardt modification to the Gauss−Newton method algorithm. The Tait-type eq 3 was used for this purpose.

$$\rho(T, p) = \frac{\rho(T, p_{\text{ref}})}{1 - a_5 \ln\left[\dfrac{B(T) + p/p_{\text{ref}}}{B(T) + 1}\right]} \tag{3}$$

where

$$\rho(T, p_{\text{ref}}) = \frac{a_1}{1 + a_2\tau} \tag{4}$$

and

$$B(T) = a_3 + a_4\tau \tag{5}$$

with $\tau = T/(100\ \text{K})$. The pressures p and p_{ref} can be given in arbitrary but equal pressure units. With exception of the coefficient a_1, the dimension of which is kg·m^{-3}, all other coefficients in eqs 3, 4, and 5 are dimensionless. The equations were fitted to the density data from this work and to the 0.1 MPa density data by Klomfar et al.[16,30] The number of terms in eqs 4 and 5 is just necessary and sufficient for the achievement of the obtained statistical accuracy of the correlation function. In this sense, the number of terms is optimal and unambiguously determined.

Table 4 gives the resultant coefficients a_i of eqs 3, 4, and 5 for the investigated ionic liquids and the root-mean-square deviation, rmsd, of the experimental data from the corresponding representative eq 3. In Figures 1, 2, and 4 to 6 deviations are depicted of the experimental data from their respective representative eq 3. Most of the experimental data points on the density of [EMIM][BF_4] and [HMIM][BF_4] used for fitting lie within a band of ± 0.0006ρ and ± 0.0008ρ, respectively, around the correlation. The correlation function for the present density data for [EMIM][BF_4] agree with the results of Wong et al.,[14] Stoppa et al.,[18] and Safarov and Hassel[29] to better than 0.1 % and with most of other authors within ± 0.2 %. Relative differences from eq 3 of the density data for [HMIM][BF_4] by most authors range from (−0.15 to 0.05) %; the data of Navia et al.[12] and Muhammad et al.[27] agree with the correlation within to ± 0.05 %.

Table 4. Coefficients a_i of Equations 3 to 5[a]

i	[EMIM] [BF_4]	[HMIM] [BF_4]	[EMIM] [TFA]	[BMIM] [TFA]	[HMIM] [TFA]
a_1/kg·m^{-3}	1551.1	1400.3	1693.8	1613.7	1523.5
a_2	0.07009	0.07448	0.07455	0.08154	0.07692
a_3	7600	5000	5581.0	3925.0	3043.0
a_4	−1060	−680	−952.0	−689.0	−499.0
a_5	0.15	0.128	0.110	0.085	0.079
rmsd/kg·m^{-3}	0.45	0.38	0.37	0.33	0.20

[a] p_{ref} = 0.1 MPa for all ILs in the present study.

All of the present experimental density data points for the three triflates lie within the interval of relative deviations of ± 0.06 % of the measured density value around their respective correlation eq 3. The correlation function for [EMIM][TFA] density agrees within 0.3 % with the 0.1 MPa data by Rodriguez and Brennecke,[32] Vercher et al.,[33] and Garcia-Miaja et al.[34] (Figure 4), all being close to each other also in the temperature derivative. The only one data set on the pressure dependence of the density of [EMIM][TFA] by Gardas et al.[38] (up to 30 MPa)

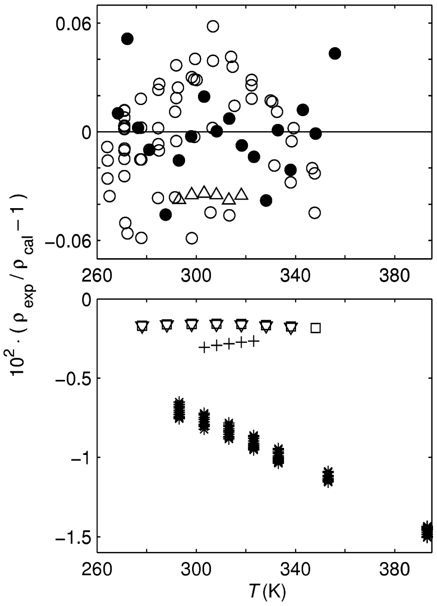

Figure 4. [EMIM][TFA]: deviations of experimental density data, ρ_{exp}, of different authors from the values, ρ_{cal}, calculated from eq 3 as a function of temperature T. □, Rodríguez and Brennecke;[32] ▽, Vercher et al.;[33] △, García-Miaja et al.;[34] *, Gardas et al.;[35] +, Wong et al.;[14] ●, Klomfar et al.;[30] ○, this work.

clearly differs from the results of other authors both in density value and in its temperature derivative.

The respective correlation eq 3 of the present pressure-dependent density data for [BMIM][TFA] agree within 0.05 % with the 0.1 MPa data by Garcia-Miaja et al.[34] and Tokuda et al.[37] (Figure 5) and within 0.2 % with the only one data set on the pressure dependence of the density of [BMIM][TFA] available in literature by Gardas et al.[38] (up to 10 MPa). Only the deviations of the present density data for [HMIM][TFA] from the respective correlation eq 3 are depicted in Figure 6 as no density data for [HMIM][TFA] are available in the literature.

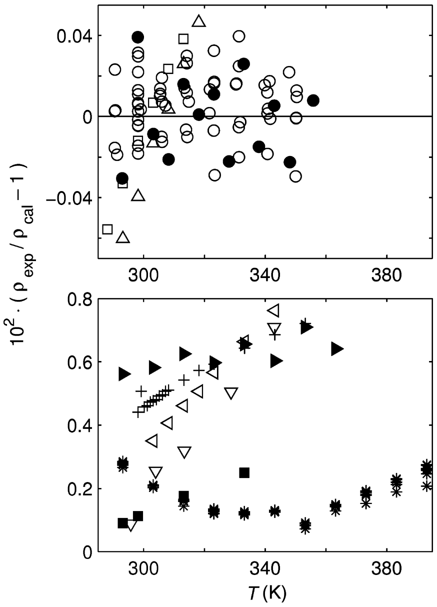

Figure 5. [BMIM][TFA]: deviations of experimental density data, ρ_{exp}, of different authors from the values, ρ_{cal}, calculated from eq 3 as a function of temperature T. ▽, Fredlake et al.;[36] □, Tokuda et al.;[37] *, Gardas et al.;[35] △, García-Miaja et al.;[34] ◁, Ge et al.;[39] ■, Tariq et al.;[40] +, Soriano et al.;[41] ▶, Shamsipur et al.;[21] ●, Klomfar et al.;[30] ○, this work.

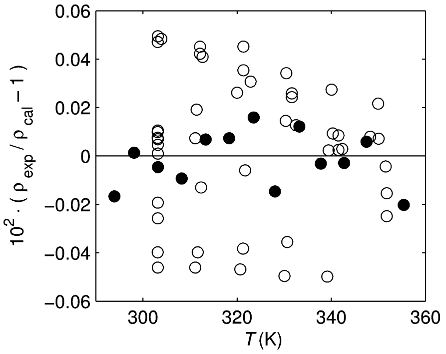

Figure 6. [HMIM][TFA]: deviations of experimental density data, ρ_{exp}, of different authors from the values, ρ_{cal}, calculated from eq 3 as a function of temperature T. ●, Klomfar et al.;[30] ○, this work.

Quantitative Analysis of the Effect of Impurities. The reference value ρ_{ref} of the density, used in the present $p-\rho-T$ data evaluation, was determined in an independent experiment using the buoyancy method.[16,30] The expanded uncertainty at 0.95 confidence level associated with a single buoyancy measurement consists of the uncertainty of the buoyancy method, estimated to $4 \cdot 10^{-4}\,\rho$, and of an additional uncertainty associated with the effect of impurities possibly present in the used sample. In experimental studies, speculations frequently appear attempting to attribute at least in part the observed differences between the density data by different authors to impurities present in the used samples. The water and the chloride anions are commonly regarded[42,44] as the most important sources of uncertainties.

In the following, the effect of the above-mentioned impurities on the density of imidazolium-based ionic liquids with the tetrafluoroborate anion is evaluated. The density of a sample containing impurities we denote as ρ_{mix} and for a single impurity define by eq 6

$$\rho_{mix} = \frac{xM_{imp} + (1-x)M_{IL}}{xV_{imp} + (1-x)V_{IL} + V^{E}} \tag{6}$$

The subscripts IL and imp indicate the molar mass M and the molar volume V for the ionic liquid and for the impurity, respectively, and V^{E} is the excess volume of the mixture. The chloride impurity with the mole fraction of x in a methylimidazolium-based tetrafluoroborate with a given cation [C_nMIM] is to be treated[44] as an admixture of the imidazolium-based chloride with the same cation [C_nMIM] and of the same mole fraction x in the mixture. For mixtures of ionic liquids, the ideal-mixing approximation[60] can be safely used by assuming $V^{E} = 0$, while experimental data on the excess volume for a water–ionic liquid mixture should be taken from the literature.

For small mole fractions x or mass fractions w of an impurity present in the sample of a ionic liquid (say for $x < 0.01$), it is practical to express the impurity effect $\Delta\rho = \rho_{mix} - \rho$ relative to the density ρ of a pure ionic liquid as $\Delta\rho/\rho = A_x x$ or $\Delta\rho/\rho = A_w w$ where

$$A_x = \frac{1}{\rho}\left(\frac{\partial \rho_{mix}}{\partial x}\right)_{x=0} \tag{7}$$

For A_w it holds

$$A_w = \left(\frac{\partial x}{\partial w}\right)_{x=0} A_x \tag{8}$$

where at $x = 0$, $(\partial x/\partial w) = M_{IL}/M_{H_2O}$ for the water impurity and $(\partial x/\partial w) = M_{IL}/M_{Cl}$ for the chloride impurity. For A_x it follows from eq 6

$$A_x = \frac{M_{imp} - M_{IL}}{M_{IL}} - \frac{V_{imp} - V_{IL}}{V_{IL}} - \frac{1}{V_{IL}}\left(\frac{\partial V^E}{\partial x}\right)_{x=0} \tag{9}$$

or in an alternative form

$$A_x = \frac{M_{imp}}{M_{IL}}\left[1 - \frac{\rho_{IL}}{\rho_{imp}} - \frac{\rho_{IL}}{M_{imp}}\left(\frac{\partial V^E}{\partial x}\right)_{x=0}\right] \tag{10}$$

So the total impurity effect A_x consists of the excess volume contribution A_x^E given by the term containing V^E and of the ideal-mixing contribution A_x^{id} given by the other terms of eq 9 or 10.

To evaluate the impurity effect using eq 9 or 10 the liquid density or liquid molar volume of the impurity at temperatures of interest has to be known. But no density data are available for subcooled [EMIM][Cl] that has its melting point at 361 K. To express the temperature dependence of the 0.1 MPa densities of the [EMIM][Cl]−[EMIM][BF_4] mixtures far below the melting point of [EMIM][Cl] we use a group contribution (GC) model based on experimental data on densities for [EMIM][BF_4], [BMIM][BF_4], [HMIM][BF_4], [HMIM][Cl], and [OMIM][Cl] available in the literature. Thus, the contribution of the [EMIM]$^+$ cation and [Cl]$^-$ anion to the volume of the mixture will be obtained from densities of other ionic liquids. For this purpose, we assume that in the temperature range of interest the molar volume V_m of a system containing one 1-C_{2n}-3-methylimidazolium cation and the [BF_4]$^-$ and [Cl]$^-$ anions can be described by eq 11 as a sum of contributions V_n^+ and V_j^- (j = 1,2) of the molar volumes of the cation with alkyl side chain of n pairs of CH_2 groups and two anions [Cl]$^-$ and [BF_4]$^-$, respectively

$$V_m = V_n^+ + xV_1^- + (1 - x)V_2^- \tag{11}$$

Here x is the mole fraction of the chloride anions in the mixture. Each of the contributions V_n^+, V_j^- (j = 1,2) is assumed to depend linearly on the temperature. Further, we assume that the value of the contribution V_n^+ of the cation consists of the contribution $a_{MIM} + b_{MIM}\tau$ from the methylimidazolium group of the cation and of the contribution $(a^+ + b^+\tau)n$ of the number n of pairs of CH_2 groups in the cation alkyl side chain. The variable τ defined as $\tau = (T - 298.15)/100$ is a suitably transformed temperature variable of the model. The contribution of the j-th anion (j = 1,2) has the form $V_j^- = a_j^- + b_j^-\tau$.

Based on the above-mentioned assumptions, the molar volume V_m of the considered ionic liquid system is expressed by eq 12.

$$V_m/(\text{cm}^3\cdot\text{mol}^{-1}) = (a_{MIM} + b_{MIM}\tau) + (a^+ + b^+\tau)n + x(a_1^- + b_1^-\tau) + (1 - x)(a_2^- + b_2^-\tau) \tag{12}$$

The values of the parameters a_{MIM}, b_{MIM}, a^+, and b^+ are common to all 1-alkyl-3-methylimidazolium cations while the parameters a_j^- and b_j^- have a specific value for each anion.

For a pure ionic liquid with n pairs of the CH_2 groups in the alkyl chain and with the j-th anion the model eq 12 reduces to an equation with $x = 0$. In such a case, the contributions a_{MIM} and a_j^- and similarly the contributions b_{MIM} and b_j^- cannot be discriminated by using only density data, which for ionic liquid with the j-th anion determine only sums $a_j^\pm = a_{MIM} + a_j^-$ and $b_j^\pm = b_{MIM} + b_j^-$. Thus, for the molar volume V_{nj} of a ionic liquid eq 13 is valid.

$$V_{nj}/(\text{cm}^3\cdot\text{mol}^{-1}) = a_j^\pm + b_j^\pm\tau + (a^+ + b^+\tau)n \tag{13}$$

The coefficient $a_j^\pm$ represents the common contribution of the methylimidazolium cation [MIM]$^+$ and of the j-th anion to the molar volume of the ionic liquid, while the term $b_j^\pm\tau$ describes the temperature dependence of this contribution. Similarly, the term $(a^+ + b^+\tau)n$ represents the contribution of the alkyl side chain of the cation containing n pairs of CH_2 groups. Owing to the choice of the origin of the temperature variable at 298.15 K, the value of the parameter a^+ is equal to the variation of the molar volume V_{nj} per the addition of two carbon atoms into the alkyl side chain of the cation at this temperature.

The parameters of the GC model represented by eq 13 were determined by least-squares fitting of the model to the data sets by different authors, which was in the study[56] identified as the most certain. These data include 217 experimental data points from 14 different studies[4,7,10,12−16,30,52−57] on the density of three tetrafluoroborates with the [C_nMIM] cation with n = 2, 4, and 6. In addition 0.1 MPa density data for two chlorides with n = 6 and 8 available[58,59] from the literature were included into the database used for fitting. The resultant correlation is characterized by the value of the average absolute relative deviation, AARD, of 0.0005. Figure 7 shows deviations of the 0.1 MPa density data as obtained by authors of the present study[16,30] for the 1-C_n-3-methylimidazolium tetrafluoroborates (n = 2, 4, 6) from the GC model. Based on the GC model the upper bound to the overall uncertainty of the density measurements at the 0.95 level including a potential effect of impurities can be reasonably estimated to 0.002ρ. The deviations of the densities by other authors to which the model was fitted lie mostly within the deviation interval ± 0.004ρ and are not displayed here. Figure 8 shows deviations from the present GC model of the 0.1 MPa density data for the

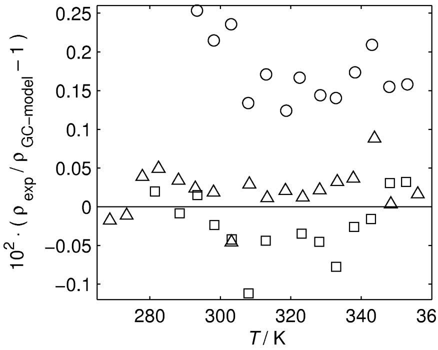

Figure 7. Deviations of experimental 0.1 MPa data on the density, ρ_{exp}, by Klomfar et al.[16,30] from the values of $\rho_{GC\text{-model}}$, calculated from eq 13 as a function of temperature, T. ○, [EMIM][BF_4]; □, [BMIM][BF_4], △, [HMIM][BF_4].

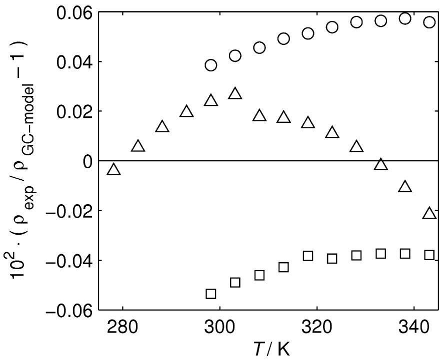

Figure 8. Deviations of experimental density data, ρ_{exp}, of different authors from the values, $\rho_{GC\text{-}model}$, calculated from eq 13 as a function of temperature, T. [HMIM][Cl]: ○, Gomez et al.;[58] [OMIM][Cl]: □, Gomez et al.;[58] △, Singh and Kumar.[59]

1-C$_n$-3-methylimidazolium chlorides (n = 6 and 8) from the literature.[58,59]

Table 5 gives the obtained values of the model parameters a^+, $a_1^\pm$, and $a_2^\pm$. They can be compared with the values of some parameters in models developed by other authors. The slope $2\partial V_m/\partial n$ at 298.15 K (given by the model parameter a^+), for the variation of the molar volume per addition of two carbon atoms into the alkyl side chain of the cation is equal to (33.58 ± 0.1) cm^3·mol^{-1}. This value differs by 2 % from the value (34.4 ± 0.5) cm^3·mol^{-1} obtained by Rebelo et al.,[60] who derived it based on densities of 1-alkyl-3-methylimidazolium ionic liquids with [BF$_4$], [PF$_6$], [NTf$_2$], [NO$_3$], and [Cl] anions. The coefficient $a_1^\pm = a_{MIM} + a_1^-$ for the [BF$_4$] anion of our model in eq 13 having a value of 121.03 cm^3·mol^{-1} (Table 5) corresponds to the sum of the Esperanca et al.[61] effective molar volumes of the cation [C$_0$MIM]$^+$ (V_c^* = 64.82 cm^3·mol^{-1}) and the anion [BF$_4$] (V_a^* = 53.4 cm^3·mol^{-1}) given in Table 4 of their paper,[61] which is equal to 118.22 cm^3·mol^{-1}. Similarly, the coefficient $a_2^\pm = a_{MIM} + a_2^-$ for the [Cl]$^-$ anion of our model eq 13 having a value of 94.32 cm^3·mol^{-1} (Table 5) corresponds to the sum of the Esperanca et al.[61] effective molar volumes of the cation [C$_0$MIM]$^+$ (V_c^* = 64.82 cm^3·mol^{-1}) and the anion [Cl]$^-$ (V_a^* = 25.9 cm^3·mol^{-1}) given in Table 4 of their paper,[61] which is equal to 90.72 cm^3·mol^{-1}. The density values calculated from the model given by eq 11 agree with the experimental data by Seddon et al.[44] on [BMIM][BF$_4$]−[BMIM][Cl] mixtures within 0.005ρ indicating thus the level of applicability of the ideal-mixing model to the mixture.

Table 5. Coefficients of eq 13 and Their 0.95 Confidence Interval Half-Widths

j	group	$a_j^\pm \pm 2u(a_j^\pm)$	$b_j^\pm \pm 2u(b_j^\pm)$
1	[MIM]$^+$ + [BF$_4$]$^-$	121.03 ± 0.05	6.41 ± 0.23
2	[MIM]$^+$ + [Cl]$^-$	94.32 ± 0.09	3.74 ± 0.41
		$a^+ \pm 2u(a^+)$	$b^+ \pm 2u(b^+)$
	CH$_2$	33.58 ± 0.02	2.39 ± 0.10

Substituting into eq 9 from the GC model given by eq 13 for the molar volume of both tetrafluoroborate and chloride ionic liquid one obtain

$$A_x = \frac{M_{Cl} - M_{BF_4}}{M_{IL}} - \frac{a_1^\pm - a_2^\pm + (b_1^\pm - b_2^\pm)\tau}{V_{IL}} \qquad (14)$$

To evaluate A_x from eq 14 for a given imidazolium tetrafluoroborate, we do not need to know the density of imidazolium chloride with the same cation. Moreover, eq 14 gives the temperature dependence of the impurity effect. If the molar volumes V_{BF_4} and V_{Cl} of the anions [BF$_4$]$^-$ and [Cl]$^-$ are known (as reported by Rebelo et al.[60] for temperature of 298.15 K) an alternative expression (eqs 15 and 16) for ρ_{mix} and A_x, respectively, can be derived

$$\rho_{mix} = \frac{M_{IL} + x(M_{Cl} - M_{BF_4})}{V_{IL} + x(V_{Cl} - V_{BF_4})} \qquad (15)$$

$$A_x = \frac{M_{Cl} - M_{BF_4}}{M_{IL}} - \frac{V_{Cl} - V_{BF_4}}{V_{IL}} \qquad (16)$$

In the literature, data on the density of IL/water mixtures both for [EMIM][BF$_4$][6,10] and for [HMIM][BF$_4$][18] are available making it possible to quantify the effect of water on the uncertainty of the measured density. Table 6 gives the values of the coefficients A_x and A_w obtained from the eqs 9, 10, 14, and 16 for the effect of the water and chloride present in the sample of [EMIM][BF$_4$] and [HMIM][BF$_4$] together with the literature source of the data used and the number of the equation used for the quantity evaluation. For the coefficient A_x, its ideal-mixing component A_x^{id} and the excess component A_x^E is given. In the last column of Table 6 the value $w_{0.001}$ of the

Table 6. Coefficients A_x^{id}, A_x^E, and A_w at a Temperature, T, Quantifying the Effect of Water, Chloride Anion, and Sodium Cation Content in the Sample and the Impurity Mass Fraction $w_{0.001}$ That Causes the Density Change by 0.001ρ

ionic liquid	impurity	source	eq	T/K	A_x^{id}	A_x^E	A_w	$w_{0.001}$
[EMIM][BF$_4$]	H$_2$O	Vila et al.[10]	7	298.15	−0.025	−0.015	−0.45	0.0023
		Zhang et al.[6]	10	293.15	−0.033	−0.001	−0.38	0.0029
				323.15	−0.033	−0.002	−0.40	0.0028
	Cl$^-$	IMM,[a] this work	14	298.15	−0.087	0	−0.48	0.0021
		IMM, Rebelo et al.[60]	16	298.15	−0.079	0	−0.44	0.0023
		IMM, this work	14	353.15	−0.083	0	−0.46	0.0022
	Na$^+$	IMM, this work, estimate	10	298.15	0.171	0	1.47	0.0007
[HMIM][BF$_4$]	H$_2$O	Stoppa et al.[18]	10	298.15	−0.015	−0.08	−0.32	0.0032
	Cl$^-$	IMM, this work	14	298.15	−0.082	0	−0.58	0.0017
		IMM, Rebelo et al.[60]	16	298.15	−0.078	0	−0.56	0.0018
		IMM, this work	14	353.15	−0.079	0	−0.57	0.0018
	Na$^+$	IMM, this work, estimate	10	298.15	0.232	0	2.56	0.0004
		IMM, this work, experiment	21	298.15	0.181	0	2.00	0.0005

[a] Ideal mixing model.

impurity mass fraction is given by which the sample density is decreased by 0.001ρ compared to the pure ionic liquid. An analysis of the same type providing similar results can be performed for the three trifluoromethanesulfonates.

Based on the quantitative assessment of the impurity effect, the following general conclusions can be made. By drying, the water mass fraction in the ionic liquid sample can usually be reduced to a value of the order of magnitude of 10^{-5} or at least 10^{-4}. Thus, the effect of the water content on the sample density is at most 0.0003ρ or less. The water effect reaches the value of 0.001ρ only for the water mass fraction w of about 0.003 or greater. In general, when the ionic liquids under discussion are well-dried, the effect of the water present in the sample on the density is marginal. Similarly, the effect of the chloride anions present in the sample reaches the value of 0.001ρ only for the chloride mass fraction w of about 0.002 or greater. But the upper-bound to the chloride ions mass fraction in the samples as stated by manufacturers most often is $w = 10^{-4}$, that is, more than an order of magnitude less. From the GC model, it also follows that the temperature dependence of both water and chloride impurity effect on the ionic liquid density is weak.

Sodium Cation Impurity Effect on Density. As both the presence of water and chloride in the sample causes a decrease in density, another type of impurity is necessary when increased density values are to by explained by it. The sodium and potassium cation can be considered as one of the possible candidates for such a role in ionic liquids with the tetrafluoroborate anion. Sodium and potassium tetrafluoroborates are used as a source of the tetrafluoroborate anion for the synthesis of ionic liquids, where the tetrafluoroborate plays the role of the product's anion. In the present study, we examined experimentally the effect of the sodium cation impurity on the density of [HMIM][BF$_4$]. The procedure we employed is analogical to that used by Seddon et al.[44] to determine the effect of chloride on the IL's density. A sample of ionic liquid with the sodium mole fraction x_{Na} was prepared by addition of the same mole fraction $x_{\mathrm{NaBF_4}} = x_{\mathrm{Na}}$ of sodium tetrafluoroborate (NaBF$_4$) in the sample, where

$$x_{\mathrm{Na}} = \frac{m_{\mathrm{Na}}/M_{\mathrm{Na}}}{m_{\mathrm{NaBF_4}}/M_{\mathrm{NaBF_4}} + m_{\mathrm{IL}}/M_{\mathrm{IL}}} \qquad (17)$$

and

$$x_{\mathrm{NaBF_4}} = \frac{m_{\mathrm{NaBF_4}}/M_{\mathrm{NaBF_4}}}{m_{\mathrm{NaBF_4}}/M_{\mathrm{NaBF_4}} + m_{\mathrm{IL}}/M_{\mathrm{IL}}} \qquad (18)$$

Here m (kg) is the mass of the substance specified by the subscript, and similarly M (kg·mol^{-1}) is the molar mass of the substance. It follows from eq 18 that to obtain a sample containing a sodium cation impurity with a mole fraction x_{Na}, the admixture of $m_{\mathrm{NaBF_4}}$ (g of NaBF$_4$), given by eq 19, should be added into m_{IL} (g of the ionic liquid, [HMIM][BF$_4$] in our case).

$$m_{\mathrm{NaBF_4}} = m_{\mathrm{IL}} \frac{M_{\mathrm{NaBF_4}}}{M_{\mathrm{IL}}} \frac{x_{\mathrm{Na}}}{1 - x_{\mathrm{Na}}} \qquad (19)$$

In the case of a small x_{Na}, say $x_{\mathrm{Na}} < 0.01$, eq 19 reduces to

$$m_{\mathrm{NaBF_4}} = x_{\mathrm{Na}} m_{\mathrm{IL}} M_{\mathrm{NaBF_4}}/M_{\mathrm{IL}} \qquad (20)$$

and the corresponding sodium mass fraction w_{Na} is given as $w_{\mathrm{Na}} = x_{\mathrm{Na}} M_{\mathrm{Na}}/M_{\mathrm{IL}}$. Table 7 gives results of the density measurements that we performed on three samples with w_{Na} of $0.792 \cdot 10^{-3}$, $1.562 \cdot 10^{-3}$, and $3.887 \cdot 10^{-3}$ at a temperature of 298.15 K. For small values of the mass fraction w the derivative A_w of the sample density with respect to mass fraction related to the density (eq 8) has been evaluated from the experimental values of the mixture density $\rho_{\mathrm{mix}}(w)$ and the density ρ_{IL} of pure [HMIM][BF$_4$] as

Table 7. Experimental Densities $\rho_{\mathrm{mix}}(w_{\mathrm{Na}})$ of a Sample of [HMIM][BF$_4$] Containing a Mass Fraction w_{Na} of the Sodium Cations at Temperatures near 298.15 K

	T	$\rho_{\mathrm{mix}}(w_{\mathrm{Na}})$	$\rho(w_{\mathrm{Na}} = 0)$		
$w_{\mathrm{Na}} \cdot 10^{-3}$	K	kg·m^{-3}	kg·m^{-3}	A_x	A_w[a]
0.792	298.33	1146.90	1145.72	0.117	1.30
1.562	298.23	1149.15	1145.79	0.170	1.88
3.887	298.27	1154.75	1145.77	0.181	2.00

[a] $A_w = [\rho_{\mathrm{mix}}(w_{\mathrm{Na}})/\rho(w_{\mathrm{Na}} = 0) - 1]/w_{\mathrm{Na}}$.

$$A_w = \frac{1}{\rho_{\mathrm{IL}}} \frac{\rho_{\mathrm{mix}}(w) - \rho_{\mathrm{IL}}}{w} \qquad (21)$$

The addition of the NaBF$_4$ into [HMIM][BF$_4$] causes an increase of the density. When measured by the impurity mass fraction, the sodium cation is almost four times more effective in changing the density of [HMIM][BF$_4$] than the chloride anion. Figure 9 provides a comparison of the experimentally obtained value of the impurity effect $\rho(w)/\rho_{\mathrm{IL}} - 1$ for the sodium cation with that for water and chloride. Table 6 gives the values of A_x and A_w estimated from eq 10 for the sodium anion present in [EMIM][BF$_4$] and [HMIM][BF$_4$]. The estimate consists in using the value of density of solid NaBF$_4$ (2470 kg·m^{-3}) for the liquid impurity density ρ_{imp} (see eq 10). The liquid state of NaBF$_4$ at a temperature of 298.15 K corresponds to a subcooled liquid, the density of which is not known. As a result the calculated sodium cation impurity effect is somewhat overestimated compared to the experimental values of A_x and A_w for [HMIM][BF$_4$], which are also given in Table 6.

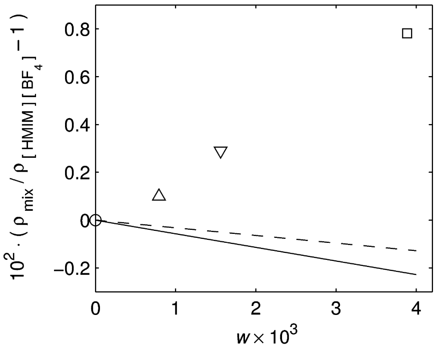

Figure 9. Effect of the impurities on the [HMIM][BF$_4$] density at a temperature of 298.15 K expressed in percent relative to the density as a function of the impurity mass fraction w. Dashed line, water; solid line, Cl$^-$ anion; Na$^+$ cation: ○, $w = 0.000$; △, $w = 0.792 \cdot 10^{-3}$; ▽, $w = 1.562 \cdot 10^{-3}$; □, $w = 3.887 \cdot 10^{-3}$.

■ CONCLUSION

The present study adds 311 new experimental data points to the existing data on the $p-\rho-T$ relation for two 1-C$_n$-3-methylimidazolium-based tetrafluoroborates and three trifluoromethanesulfonates with the alkyl side chain length $n = 2$ and 4 and $n = 2$, 4, and 6, respectively. For the tetrafluoroborates the measurements were performed at temperatures from (285 and 220) K, respectively, to approximately 357 K. For the trifluoromethanesulfonates the measurements were conducted at temperatures from 353 K down to a temperature near the melting point of the substance. For all of the ionic liquids the measurements cover the pressure range up to 60 MPa. An isochoric apparatus was used, which makes it possible to conduct density measurements at subzero temperatures. No data have hitherto been available concerning the $p-\rho-T$ relation for [HMIM][TFA] and for [HMIM][BF_4] the temperature−pressure region covered by experimental data on the density which was extended in the present study down to 220 K.

The preformed quantitative analysis of the effect of water and chloride ions shows that at the usual content of these impurities in the studied ionic liquid samples their presence in the sample causes a density decrease of the order of $10^{-4}\rho$. Thus, at usual conditions, the effect of water and chloride impurity can be considered as marginal. The sodium cation was identified as an impurity capable of causing an increase in the density of a ionic liquid sample with high efficiency.

Among common imidazolium-based ionic liquids with a markedly low temperature of solid−liquid equilibrium coming into question for further density measurements at subzero temperatures ranks for example the 1-ethyl-3-methylimidazolium dicyanamide ([EMIM][$(CN)_2N$]) and the 1-butyl-3-methylimidazolium dicyanamide ([BMIM][$(CN)_2N$]) with the melting points of (255 and 223) K, respectively.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Present experimental data on the $p-\rho-T$ relation for the five studied ionic liquids (Tables S1 to S5), and a note on the 0.1 MPa density measurements for two samples of [HMIM][BF_4] of different origins. This material is available free of charge via the Internet at http://pubs.acs.org.

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