

# Measurement of High-Pressure Densities and Atmospheric Viscosities of Ionic Liquids: 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide and 1-Hexyl-3-methylimidazolium Chloride

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**(5)** Supporting Information

**ABSTRACT:** Atmospheric densities and viscosities of ionic liquids, 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ( $[C_6C_1Im][Tf_2N]$ ) and 1hexyl-3-methylimidazolium chloride ( $[C_6C_1Im][Cl]$ ), were measured with a Stabinger viscometer at temperatures from (293 to 373) K. High-pressure densities ( $p \le 200$  MPa) for  $[C_6C_1Im][Tf_2N]$  and  $[C_6C_1Im][Cl]$  were measured with a bellows type apparatus at temperatures from (312 to 452) K. Samples were analyzed for the water and 1-methylimidazole content before and after the measurements. For  $[C_6C_1Im]$  $[Tf_2N]$ , combined expanded uncertainties were estimated to be (1.0 and 1.8) kg·m<sup>-3</sup> for atmospheric and high-pressure



density, respectively, and 0.85 % for viscosity. For  $[C_6C_1Im][Cl]$ , combined expanded uncertainties were estimated to be (1.1 and 2.5) kg·m<sup>-3</sup> for atmospheric and high-pressure density, respectively, and 1.59 % for viscosity. The measured densities and viscosities of  $[C_6C_1Im][Tf_2N]$  in this work agreed with some of the available literature values within their experimental uncertainties. The effect of colored impurities and the source of sample on densities and viscosities of  $[C_6C_1Im][Cl]$  were determined to be less than the experimental uncertainties. The  $[C_6C_1Im][Tf_2N]$  did not decompose over the full temperature range during the measurements, while  $[C_6C_1Im][Cl]$  decomposed at temperatures greater than 392 K.

## INTRODUCTION

Research on ionic liquids is spread over many fields<sup>1</sup> with each field requiring many types of physical properties.<sup>2</sup> Density and viscosity are two of the most essential physical properties that are relevant to fluid dynamics and transport phenomena. The reliability of physical property measurements depends on the ionic liquid purity, its handling, and its stability.<sup>3,4</sup>

Impurities in the sample can be classified into three groups: (i) residual starting materials and side reaction products, (ii) water contamination either before or after the experimental measurements, and (iii) decomposition products that form during the measurement.

Residual starting materials include 1-methylimidazole for imidazolium-based ionic liquids and halides for nonhalide ionic liquids, respectively. The presence of 1-methylimidazole in an imidazolium-based ionic liquid causes the viscosity to decrease.<sup>5</sup> The presence of chloride impurity in an ionic liquid causes the density to decrease and the viscosity to increase.<sup>5</sup> Distillation can be applied to remove the 1-methylimidazole content from ionic liquids.<sup>6</sup> For determining the residual 1-methylimidazole in an ionic liquid, UV–vis analysis is preferable to <sup>1</sup>H NMR analysis due to limits of detection.<sup>7</sup> Impurities that impart color to an ionic liquid are considered as side reaction products, because most ionic liquids are clear colorless liquids.<sup>8</sup> However, the color of an ionic liquid does not seem to strongly affect many of its physical properties, although this point has not been studied in detail.<sup>7</sup> Absorbents, such as activated charcoal, alumina or silica, are used to remove colored impurities from ionic liquids.<sup>9,10</sup> The color of an ionic liquid can be evaluated by UV–vis analysis<sup>9,11</sup> and by fluorescence analysis.<sup>11</sup>

During the sample preparation and measurement, an ionic liquid can absorb water from the air or residual water present on the surfaces of the apparatus. Most of ionic liquids exhibit a decrease in the density with an addition of water;<sup>12–15</sup> however, there are some cases for which the slight amount of water in an ionic liquid causes an increase in the density as has been reported for 1-hexyl-3-methylimidazolium chloride<sup>16,17</sup> and 1-ethyl-3-methylimidazolium acetate.<sup>18</sup> The residual water content generally causes a decrease in the density of a dried ionic liquid, and the density reduction becomes larger with

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increasing temperatures.<sup>12,14,15</sup> Karl Fischer titration is commonly used for the determination of water content in ionic liquids.<sup>13</sup>

Decomposition products from imidazolium-based ionic liquids contain 1-methylimidazole.<sup>19</sup> Determination of 1-methylimidazole in the ionic liquid can be made by HPLC-UV method,<sup>7,20</sup> GC-FID method,<sup>7</sup> colorimeter,<sup>21</sup> and potentio-metric titration.<sup>19</sup>

In this work, the densities of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ( $[C_6C_1Im][Tf_2N]$ ) and 1hexyl-3-methylimidazolium chloride ( $[C_6C_1Im][Cl]$ ) were measured at pressures up to 200 MPa from (312 to 452) K. and the viscosities of these ionic liquids were measured at atmospheric pressure from (293 to 373) K. The ionic liquid  $[C_6C_1Im]$  [Tf<sub>2</sub>N] was chosen to verify the procedures of measurement because many data are available in the literature,  $^{13,22-29}$  and IUPAC has proposed this ionic liquid as a reference substance.<sup>30,31</sup> The ionic liquid [C<sub>6</sub>C<sub>1</sub>Im][Cl] can dissolve cellulose,<sup>32</sup> and so it has some technological importance for processing of biomass and lignocellulose materials. For  $[C_6C_1Im][Tf_2N]$ , although densities and viscosities at atmospheric pressure are available, density data at high pressures are limited in the range of temperature and pressure ( $T \le 423$  K,  $p \le 140$  MPa).<sup>22,24,29</sup> For [C<sub>6</sub>C<sub>1</sub>Im][Cl], literature values of density and viscosity at atmospheric pressure do not agree within their uncertainties,<sup>16,17,33-36</sup> and density data at high pressures have not been reported. Samples in the literature generally specify the water content only before the measurement with the exception of the work of David et al. (Table S1, Supporting Information).<sup>16,17,33-37</sup> The analysis of water content in the measured [C6C1Im][Cl] is needed because ionic liquids with a chloride readily absorb moisture.<sup>38,39</sup> The effect of colored impurities and the source of ionic liquid (synthesis and commercial) on densities and viscosities of  $[C_6C_1Im][Cl]$  were investigated in this work. Long-term thermal stabilities for  $[C_6C_1Im][Tf_2N]$  and  $[C_6C_1Im][Cl]$  are unavailable so far,<sup>40</sup> and although this is not addressed in this work, analyses were made to assess the stability of the ionic liquids over the period of measurement. To examine the decomposition and the water uptake of the ionic liquid during the measurements, concentrations of 1-methylimidazole and water in the ionic liquid were analyzed both before and after the experimental measurements.

#### EXPERIMENTAL METHODS

Materials. The 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ( $[C_6C_1Im][Tf_2N]$ , 99 %, Merck) used in the study was supplied by a commercial source. The reported halide content in  $[C_6C_1Im][Tf_2N]$  by the manufacturer was less than 100 w = 0.001. The ionic liquid was dried under a reduced pressure at 333 K over 10 h before each measurement. Four types of 1-hexyl-3-methylimidazolium chloride ( $[C_6C_1Im][Cl]$ ) were used for purposes of comparison between their properties: (i) commercial  $[C_6C_1Im][Cl]$  (> 97 %, Fluka) without decolorization treatment, (ii) synthesized  $[C_6C_1Im][Cl]$  without decolorization treatment, (iii) synthesized [C<sub>6</sub>C<sub>1</sub>Im][Cl] with single-pass decolorization treatment, and (iv) synthesized  $[C_6C_1Im][Cl]$  with triple-pass decolorization treatment as described in detail in the Supporting Information (Table S2 and Figures S1 and S2). The  $[C_6C_1Im][Cl]$  was synthesized from 1-methylimidazole (99) %, Aldrich) and 1-chlorohexane (99 %, Aldrich) in acetonitrile (99.9 %, Sigma-Aldrich). Before the synthesis, 1-methylimidazole was distilled under potassium hydroxide (Wako), 1chlorohexane was dried with molecular sieves 4A (Wako), and acetonitrile was dried with molecular sieves 3A (Wako). All  $[C_6C_1Im][Cl]$  samples were dried under a reduced pressure at 343 K over 1 d before each measurement.

All ionic liquids were identified by <sup>1</sup>H and <sup>13</sup>C NMR analyses. The residual content of 1-methylimidazole in all ionic liquids was measured with HPLC-UV method, and was  $w_{\rm MIm} = (100 \ w \le 0.05)$  for all ionic liquids. The water content of ionic liquids was determined with Karl Fischer titration and found to be  $w_{\rm H_2O} = (100 \ w = (0.002 \pm 0.001))$  for  $[C_6C_1\rm{Im}][Tf_2\rm{N}]$  and  $w_{\rm H_2O} = (100 \ w = (0.011 \pm 0.004))$  for  $[C_6C_1\rm{Im}][Cl]$ , respectively. The purities of  $[C_6C_1\rm{Im}][Tf_2\rm{N}]$  and  $[C_6C_1\rm{Im}]$ . [Cl] are estimated to be above 99.9 % taking into account the amounts of 1-methylimidazole and water as impurities in the ionic liquid. Detailed descriptions of the analyses are given in the Supporting Information (Table S2).

Acetonitrile (99.9 %, Sigma-Aldrich) was used as a mobile phase in the HPLC analysis. Ethyl acetate (99 %, Wako) and activated charcoal (Darco, Sigma-Aldrich) were used for washing and decolorizing of synthesized [C<sub>6</sub>C<sub>1</sub>Im][Cl], respectively. Water that had a conductivity of less than 6  $\mu$ S· m<sup>-1</sup> was used as a solvent for the decolorization, in the HPLC analysis and in the calibration of the density measurement. Potassium dihydrogenphosphate (99 %, Wako) was used to control the pH in the HPLC analysis. Deuterated dimethyl sulfoxide, DMSO- $d_6$  (99.9 %, Aldrich), deuterated water, D<sub>2</sub>O (99.9 %, Acros) and deuterated dichloromethane,  $CD_2Cl_2$  (99.9 %, Wako) were used in the NMR analyses. In the calibration procedure for the density and viscosity measurements at atmospheric pressure, certified reference fluids JS20 (Nippon Grease), N44 (Cannon), N415 (Cannon) and JS2000 (Nippon Grease) were used. For determining the water content of the ionic liquids with Karl Fischer titration, Coulomat AG (Fluka) and Coulomat CG (Fluka) were used as an anolyte solution and as a catholyte solution, respectively.

Density and Viscosity Measurement at Atmospheric Pressure. Densities and viscosities at atmospheric pressure were measured simultaneously with a Stabinger viscometer (Anton Paar, SVM3000).<sup>41'</sup> The measured density was corrected for the viscosity effect according to the instrument operational features, and standard uncertainties of the apparatus were u(T) = 0.02 K,  $u(\rho) = 0.5$  kg·m<sup>-3</sup> and  $u_r(\eta) = 0.35$  %. The temperature was controlled to within 0.005 K, and the wait time after temperature stabilization for each measurement was 30 s. Stabilities of density and viscosity were judged by the change of density and viscosity being within 0.3  $kg{\cdot}m^{-3}$  and 0.07 %, respectively, over a period of 60 s. The calibration of the apparatus was performed with certified reference fluids described in the previous section. Measurements of the certified reference fluids and water were carried out over the range of temperatures from (293.15 to 373.15) K that corresponded to the range of densities (778.7 to 997.0) kg·m<sup>-3</sup> and viscosities (5.85 to 1780) mPa·s.

Measurements in duplicate of the ionic liquid with the Stabinger viscometer were performed from (293.15 to 373.15) K for  $[C_6C_1Im][Tf_2N]$  and from (303.15 to 373.15) K for  $[C_6C_1Im][Cl]$ , respectively. Due to the calibration range of the Stabinger viscometer, viscosities of  $[C_6C_1Im][Cl]$  at the lower temperatures (303.15 and 313.15) K are not reported. Prior to sample loading, nitrogen gas was flowed into the instrument at 333.15 K for 30 min to dry the measurement cell. When the

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sample was loaded, the first 2 mL of sample was used for wetting the surfaces in the viscometer. Subsequently, 1 mL of sample was added and the measurement was started from the lowest temperature to the highest temperature of 373.15 K. After the measurement at 373.15 K was made, 1 mL of sample was added and the measurement was started from 373.15 K to the lowest temperature of the measurement. This cycle was repeated twice, that is, the four runs were made for each measurement. The water content in the sample after each set of runs was determined by Karl Fischer titration. When the second cycle was finished, the measured sample was analyzed with NMR and HPLC to characterize the sample and to quantify the content of 1-methylimidazole. For verifying the apparatus, measurements of the certified reference fluids were performed from (293.15 to 373.15) K after cleaning and drying of the measurement cell.

The NMR spectra of measured samples did not change from that of sample before and after the measurements. The concentration of 1-methylimidazole in the measured samples was less than 100 w = 0.05, which is evidence that no decomposition occurred during the measurements. The water content of the measured samples increased to  $100 w = (0.004 \pm 0.002)$  for  $[C_6C_1\text{Im}][Tf_2\text{N}]$  and  $100 w = (0.022 \pm 0.008)$  for  $[C_6C_1\text{Im}][Cl]$ , respectively, and this can probably be attributed to the residual water in the apparatus or the absorption of water during recovery of the measured sample.

For  $[C_6C_1Im][Tf_2N]$ , the uncertainty of water content as  $u(w_{H_2O}) = (100 \ w = 0.004)$  gave  $u(\rho) = 0.06 \ \text{kg}\cdot\text{m}^{-3}$  and  $u_r(\eta) = 0.21 \ \%.^{13}$  The uncertainty of temperature in the apparatus gave  $u(\rho) = 0.02 \ \text{kg}\cdot\text{m}^{-3}$  and  $u_r(\eta) = 0.08 \ \%$ . The uncertainties of measurements were  $u(\overline{\rho}) = 0.10 \ \text{kg}\cdot\text{m}^{-3}$  and  $u_r(\overline{\eta}) = 0.08 \ \%$ . Combined expanded uncertainties with a level of confidence of 0.95 (k = 2) were estimated to be  $U_c(\rho) = 1.0 \ \text{kg}\cdot\text{m}^{-3}$  and  $U_{cr}(\eta) = 0.85 \ \%$ .

For  $[C_6C_1\text{Im}][\text{Cl}]$ , the uncertainty of water content as  $u(w_{\text{H}_2\text{O}}) = (100 \ w = 0.019)$  gave  $u(\rho) = 0.27 \ \text{kg}\cdot\text{m}^{-3}$  and  $u_r(\eta) = 0.70 \ \%$ .<sup>16</sup> The uncertainty of temperature in the apparatus gave  $u(\rho) = 0.01 \ \text{kg}\cdot\text{m}^{-3}$  and  $u_r(\eta) = 0.11 \ \%$ . The uncertainties of measurements were  $u(\overline{\rho}) = 0.03 \ \text{kg}\cdot\text{m}^{-3}$  and  $u_r(\overline{\eta}) = 0.06 \ \%$ . Combined expanded uncertainties were estimated to be  $U_c(\rho) = 1.1 \ \text{kg}\cdot\text{m}^{-3}$  and  $U_{c,r}(\eta) = 1.59 \ \%$  with a level of confidence of 0.95 (k = 2).

Density Measurement at Pressures up to 200 MPa. Densities at high pressure were measured with a bellows type apparatus.<sup>42-44</sup> Standard uncertainties of the apparatus were u(T) = 0.1 K, u(p) = 0.10 MPa at less than 90 and 0.25 MPa at above 90 MPa, and u(v) = 0.04 %. The reference condition for density was at 312 K under atmospheric pressure, and the density was measured with the Stabinger viscometer. Measurements of ionic liquids were performed over the range of (312 to 452) K and (10 to 200) MPa. The procedure for the measurements followed that of Machida et al.45 After the isobaric series of measurements at (451 to 452) K were completed, the measurement at (312 to 313) K was made again to verify the apparatus and the integrity of the sample. The measured sample was analyzed with NMR, HPLC, and Karl Fischer titration. Densities at atmospheric pressure from (331 to 452) K were extrapolated from isothermal densities at high pressure using the Tait equation (eq 1), since the Tait equation can provide good correlation of liquid densities over a wide range of conditions. The uncertainty of extrapolations that used the Tait equation for densities at atmospheric pressure was

estimated to be 0.01 % from results of calibrations with water. Therefore, the uncertainty of densities at atmospheric pressure was estimated to be equal to that value at high pressure.

The NMR spectra of measured samples did not change from that of the sample before and after the measurements. The concentration of 1-methylimidazole in the dmeasured samples was less than 100 w = 0.05 for  $[C_6C_1\text{Im}][\text{Tf}_2\text{N}]$  and 100  $w = (0.62 \pm 0.03)$  for  $[C_6C_1\text{Im}][\text{Cl}]$ , respectively. This indicates that, although  $[C_6C_1\text{Im}][\text{Tf}_2\text{N}]$  did not decompose, some decomposition of  $[C_6C_1\text{Im}][\text{Cl}]$  did occur during the measurements. The water content of the measured samples increased to 100  $w = (0.005 \pm 0.002)$  for  $[C_6C_1\text{Im}][\text{Tf}_2\text{N}]$  and 100  $w = (0.107 \pm 0.013)$  for  $[C_6C_1\text{Im}][\text{Cl}]$ , respectively.

For  $[C_6C_1\text{Im}][\text{Tf}_2\text{N}]$ , the uncertainty of water content as  $u(w_{\text{H}_2\text{O}}) = (100 \ w = 0.003)$  gave  $u(\rho) = 0.05 \ \text{kg}\cdot\text{m}^{-3}$ .<sup>13</sup> The uncertainties of loading mass, volume, temperature, and pressure in apparatus gave  $u(\rho) = (0.11, 0.60, 0.09, \text{ and } 0.28)$  kg·m<sup>-3</sup>, respectively. The uncertainty of density at atmospheric pressure was  $u(\rho^0) = 0.51 \ \text{kg}\cdot\text{m}^{-3}$ , which is the combined uncertainty of the measured density with the Stabinger viscometer. The uncertainty of measurements calculated from the difference between first and second runs was  $u(\overline{\rho}) = 0.21 \ \text{kg}\cdot\text{m}^{-3}$ . The combined uncertainties with a level of confidence of 0.95 (k = 2) was estimated to be  $U_c(\rho) = 1.8 \ \text{kg}\cdot\text{m}^{-3}$ .

For  $[C_6C_1Im][Cl]$ , the uncertainty of water content as  $u(w_{H2O}) = (100 \ w = 0.096)$  gave  $u(\rho) = 0.72 \ \text{kg}\cdot\text{m}^{-3}$ .<sup>16</sup> The uncertainties of mass of the loaded sample, volume, temperature and pressure in apparatus gave  $u(\rho) = (0.11, 0.50, 0.06 \text{ and } 0.14) \ \text{kg}\cdot\text{m}^{-3}$ , respectively. The uncertainty of density at atmospheric pressure was  $u(\rho^0) = 0.57 \ \text{kg}\cdot\text{m}^{-3}$ , which is the combined uncertainty of the measured density with the Stabinger viscometer. The uncertainty of measurements calculated from the difference between first and second runs was  $u(\bar{\rho}) = 0.72 \ \text{kg}\cdot\text{m}^{-3}$ , and this includes the influence of decomposition of the measured sample to the density. The combined expanded uncertaintY with a level of confidence of 0.95 (k = 2) was estimated to be  $U_c(\rho) = 2.5 \ \text{kg}\cdot\text{m}^{-3}$ .

## CORRELATION METHODS

To correlate the measured densities at high pressure in this work, the Tait equation was used in the following form:  $^{46}$ 

$$\rho/\text{kg}\cdot\text{m}^{-3} = \frac{\rho^0/\text{kg}\cdot\text{m}^{-3}}{1 - C\ln\left[\frac{B + (p/\text{MPa})}{B + 0.1}\right]}$$
(1)

where *B* in eq 1 has units of Pa and is expressed as a function of the absolute temperature as follows:

$$B = b_0 \exp[b_1(T/K)]$$
<sup>(2)</sup>

Parameters in eqs 1 and 2 (*C*,  $b_0$ /Pa, and  $b_1/K^{-1}$ ) for each ionic liquid were obtained by fitting the density data using Levenberg–Marquardt algorithm with analytical derivatives.<sup>47</sup> In eq 1,  $\rho^0$  represents the density at atmospheric pressure and was described as

$$\frac{1}{\rho^0/\text{kg·m}^{-3}} = a_0 + a_1(T/\text{K}) + a_2(T/\text{K})^2$$
(3)

The determination of parameters in eq 3  $(a_0/\text{m}^3\text{kg}^{-1}, a_1/\text{m}^3\text{kg}^{-1}\text{K}^{-1})$  for each ionic liquid was obtained by fitting the density data at atmospheric pressure

using singular value decomposition.<sup>47</sup> For the correlation of measured viscosities, the following equation was used:

$$\ln\left(\frac{\eta/\mathrm{mPa}\cdot\mathrm{s}}{\eta^0}\right) = d_0 + \frac{d_1}{d_2 + (T/\mathrm{K})} \tag{4}$$

where  $\eta^0 = 1$  mPa·s and  $d_0$ ,  $d_1/K$ , and  $d_2/K$  are adjustable parameters that are determined by fitting the viscosity data of each ionic liquid using Levenberg–Marquardt algorithm with analytical derivatives.<sup>47</sup> Adjustable parameters in eqs 1–4 were determined by minimizing the following objective function (O.F.)

O. F. = 
$$\frac{1}{n} \sum_{i=1}^{n} \left( \frac{X_{\text{cal},i} - X_{\exp,i}}{U_{c}(X_{\exp,i})} \right)^{2}$$
 (5)

where X refers to the density or viscosity,  $U_c(X)$  is the combined expanded uncertainty of X measurement, *n* is the number of measurements, and the subscripts of "cal" and "exp" refer to calculated and experimental measured values, respectively. For evaluation of the correlation, values of bias and average relative deviation (ARD) were used as follows:

bias = 
$$100 \cdot \frac{1}{n} \sum_{i=1}^{n} \left( \frac{X_{\text{cal},i}}{X_{\exp,i}} - 1 \right)$$
 (6)

ARD = 
$$100 \cdot \frac{1}{n} \sum_{i=1}^{n} \left| \frac{X_{\text{cal},i}}{X_{\text{exp},i}} - 1 \right|$$
 (7)

Derivatives of the Tait equation were used to estimate the isobaric thermal expansivities and the isothermal compressibilities of each ionic liquid (Supporting Information).

#### RESULTS AND DISCUSSION

Measured Densities and Viscosities of  $[C_6C_1Im][Tf_2N]$ at Atmospheric Pressure as Shown in Table 1. Table 2 shows atmospheric densities extrapolated from high-pressure data to atmospheric pressure using the Tait equation (eq 1) at

Table 1. Measured Densities  $\rho$  and Viscosities  $\eta$  at Atmospheric Pressure over the Temperature *T* Range (293.13 to 373.15) K for 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide ( $[C_6C_1Im][Tf_2N]$ ) and 1-Hexyl-3-methylimidazolium Chloride ( $[C_6C_1Im][Cl]$ )<sup>*a*</sup>

	$[C_6C_1Im]$	][TF <sub>2</sub> N]	$[C_6C_1Im][Cl]$		
T/K	$ ho/{\rm kg}{\cdot}{\rm m}^{-3}$	$\eta/\mathrm{mPa}\cdot\mathrm{s}$	$ ho/{\rm kg}{\cdot}{\rm m}^{-3}$	$\eta/\mathrm{mPa}\cdot\mathrm{s}$	
293.15	1376.3	90.06			
303.15	1367.1	56.25	1035.1	В	
313.15	1358.0	37.44	1029.5	В	
323.15	1348.9	26.25	1023.9	1806	
333.15	1339.9	19.21	1018.4	810.3	
343.15	1331.0	14.55	1012.8	404.3	
353.15	1322.2	11.36	1007.4	220.6	
363.15	1313.3	9.091	1002.1	129.7	
373.15	1304.7	7.434	997.1	81.34	

<sup>a</sup>Standard uncertainty is u(T) = 0.02 K, and combined expanded uncertainties with a 0.95 level of confidence (k = 2) are  $U_c(\rho) = (1.0$ and 1.1) kg·m<sup>-3</sup> for  $[C_6C_1\text{Im}][\text{Tf}_2\text{N}]$  and  $[C_6C_1\text{Im}][\text{Cl}]$ , respectively, and  $U_{c,r}(\eta) = (0.85$  and 1.59) % For  $[C_6C_1\text{Im}][\text{Tf}_2\text{N}]$  and  $[C_6C_1\text{Im}][\text{Cl}]$ , Respectively. <sup>B</sup>Value out of Calibration Range for the Stabinger Viscometer. each temperature. Densities measured with the Stabinger viscometer and those extrapolated from high-pressure data agreed within our reported uncertainties. Determined parameters were  $a_0 = 0.60583 \text{ m}^3\text{kg}^{-1}$ ,  $a_1 = 3.4273 \cdot 10^{-4} \text{ m}^3\text{kg}^{-1}\text{K}^{-1}$  and  $a_2 = 2.368 \cdot 10^{-7} \text{ m}^3\text{kg}^{-1}\text{K}^{-2}$  for eq 3, and  $d_0 = -1.967$ ,  $d_1 = 824.2/\text{K}$ , and  $d_2 = -165.707/\text{K}$  for eq 4, respectively. The values of bias and ARD were (+0.01 and 0.02) % for density and (< 0.01 and 0.02) % for viscosity, respectively.

Figures 1 and 2 show relative deviation plots of atmospheric densities and viscosities of  $[C_6C_1Im][Tf_2N]$  for values reported in this work compared with the literature. In Figure 1, densities at temperatures below 373 K agreed with literature values of Ahosseini et al. except at 348 K,<sup>25</sup> IUPAC group,<sup>30</sup> Safarov et al.<sup>29</sup> and Seoane et al.<sup>28</sup> within the combined expanded uncertainty for this work [(0.07 to 0.08) %]. The uncertainties of density reported by Ahosseini et al.  $(0.15 \%)^{25}$  and Tariq et al.  $(0.4 \%)^{26}$  are consistent with the uncertainty of this work. For densities at temperatures greater than 373 K, data of this work agreed with values of Tariq et al.<sup>26</sup> within the uncertainty of this work [(0.13 to 0.15) %], but were larger than values of Safarov et al.<sup>29</sup> The difference in densities between this work and Safarov et al.<sup>29</sup> tends to become greater at temperatures higher than 373 K. The deviation of values reported by Safarov et al.  $(0.06 \%)^{29}$  and values in this work can be attributed to following points. Safarov et al. estimated the uncertainty only from the viscosity effects on the density measurement,<sup>29</sup> which causes an underestimation of the uncertainty. Further, the higher residual water content in the ionic liquid of Safarov et al.  $(100 \ w \le 0.03)^{29}$  than that of this work  $[100 \ w = (0.002 -$ 0.005)] causes a decrease in the density of the dried ionic liquid at high temperatures.

In Figure 2, viscosities of this work agreed with literature values of IUPAC group<sup>30</sup> and Tariq et al.<sup>27</sup> within the combined expanded uncertainty for this work (0.85 %) and the literature (2 %). Viscosities reported by Ahosseini and Scurto except at 298 K<sup>23</sup> and Seoane et al.<sup>28</sup> were smaller than values of this work. Ahosseini and Scurto measured samples that contained 100 w = 0.013 water content after measurement and less than 100 w = 0.001 bromide content using an oscillatingpiston viscometer.<sup>23</sup> The trends of data reported in this work were similar to those reported by Ahosseini and Scurto,<sup>23</sup> so that the difference in the values between these works is probably due to the method for viscosity measurement. Seoane et al. measured samples that contained 100 w = 0.007 water content before measurement and less than 100 w = 0.01 halide content using an Ubbelohde type viscometer.<sup>28</sup> The smaller values of Seoane et al.<sup>28</sup> than those of this work can be attributed to the absorption of water in the sample during the measurement, because it is difficult to prevent the water absorption with this type of viscometer.

Density Measurements of  $[C_6C_1Im][Tf_2N]$  at High Pressures as Shown in Table 2. Densities were represented by eqs 1–3 with values of bias and ARD as (<0.01 and 0.01) % with parameters  $b_0 = 566.5/Pa$ ,  $b_1 = -4.224 \times 10^{-3}/K^{-1}$ , and C = 0.08645. Figure 3 shows a relative deviation plot of the densities for  $[C_6C_1Im][Tf_2N]$  between this work and the literature. Densities agreed with literature values of Esperança et al.<sup>24</sup> and Kandil et al.<sup>22</sup> within the combined expanded uncertainty for this work [(0.12 to 0.15) %] and the literature (0.11 % for Esperança et al.<sup>24</sup> and 0.3 % for Kandil et al.<sup>22</sup>). Densities reported by Safarov et al.<sup>29</sup> at temperatures below 373 K agreed with values of this work within the uncertainty of this work and the literature [(0.05 to 0.06) %], but those at Table 2. Measured Densities  $\rho$  at High Pressures p up to 200 MPa for 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide ([C<sub>6</sub>C<sub>1</sub>Im][Tf<sub>2</sub>N]) over the Temperature T Range (312.6 to 452.3) K<sup>a</sup>

	T/K							
p/MPa	312.6	332.4	352.3	372.5	392.7	412.7	432.6	452.3
				$ ho/{\rm kg}{\cdot}{\rm m}^{-3}$				
0.1	1358.5 <sup>b</sup>	1340.0 <sup>c</sup>	1322.2 <sup>c</sup>	1304.4 <sup>c</sup>	1286.8 <sup>c</sup>	1269.8 <sup>c</sup>	1252.4 <sup>c</sup>	1235.6 <sup>c</sup>
10.0	1365.7	1348.1	1330.9	1313.7	1296.8	1280.4	1263.7	1247.6
20.0	1373.0	1355.9	1339.3	1322.6	1306.3	1290.4	1274.3	1258.8
30.0	1380.1	1363.3	1347.3	1330.9	1315.1	1299.8	1284.2	1269.2
40.0	1386.7	1370.4	1354.5	1338.6	1323.4	1308.4	1293.3	1278.8
50.0	1392.8	1377.0	1361.5	1346.0	1331.1	1316.5	1301.7	1287.6
60.0	1399.0	1383.2	1368.2	1353.0	1338.5	1324.3	1309.7	1295.9
70.0	1404.6	1389.3	1374.6	1359.6	1345.4	1331.5	1317.3	1303.9
80.0	1410.2	1395.1	1380.6	1366.0	1352.1	1338.5	1324.5	1311.3
90.0	1415.5	1400.5	1386.5	1372.1	1358.3	1345.0	1331.2	1318.3
100.0	1420.7	1406.3	1392.0	1378.0	1364.5	1351.3	1337.8	1325.1
110.0	1425.8	1411.5	1397.5	1383.7	1370.3	1357.5	1344.1	1331.8
120.0	1430.8	1416.5	1402.7	1389.1	1376.0	1363.2	1350.3	1338.0
130.0	1435.5	1421.3	1408.0	1394.3	1381.5	1368.9	1356.1	1344.1
140.0	1440.1	1426.1	1412.8	1399.4	1386.8	1374.3	1361.9	1349.9
150.0	1444.5	1430.9	1417.6	1404.4	1391.9	1379.8	1367.3	1355.5
160.0	1448.9	1435.4	1422.1	1409.3	1397.0	1384.9	1372.4	1360.8
170.0	1453.0	1439.7	1426.8	1414.0	1401.8	1389.9	1377.5	1366.2
180.0	1457.6	1444.0	1431.4	1418.5	1406.5	1394.7	1382.5	1371.3
190.0	1461.6	1448.4	1435.5	1423.1	1411.1	1399.4	1387.4	1376.4
200.0	1465.9	1452.6	1439.9	1427.4	1415.7	1404.0	1392.2	1381.2

<sup>a</sup>Standard uncertainties are u(T) = 0.1 K, u(p) = 0.1 MPa for  $0.1 and 0.25 MPa for <math>p \ge 90$  MPa, and the combined expanded uncertainty is  $U_c(\rho) = 1.8$  kg·m<sup>-3</sup> with a level of confidence of 0.95 (k = 2). <sup>b</sup>Measured value with Stabinger viscometer. <sup>c</sup>Extrapolated value from high-pressure data to atmospheric pressure using the Tait equation (eq 1) at each temperature.



**Figure 1.** Relative deviation plot for densities measured at atmospheric pressure for  $1 - h \exp[1-3 - m \operatorname{ethylimidazolium} bis-(trifluoromethylsulfonyl) imide ([C<sub>6</sub>C<sub>1</sub>Im][Tf<sub>2</sub>N]). Calculated values were obtained from eq 3 in which parameters were obtained by fitting data of this work; <math>\bigcirc$ , Measured values with the Stabinger viscometer in this work;  $\bigcirc$ , calculated values from measurements with the dilatometer in this work using eq 1;  $\Box$ , Ahosseini et al.;<sup>25</sup> dotted down triangle, calculated values from IUPAC proposed equation;<sup>30</sup> ×, Safarov et al.;<sup>29</sup> +, Seoane et al.;<sup>28</sup>  $\triangle$ , Tariq et al.<sup>26</sup> Dashed and dashdotted lines are the uncertainties of data reported in this work for measured values [(0.07 to 0.08) %] and calculated values with eq 1 [(0.13 to 0.15) %], respectively.

temperatures above 373 K were smaller than values of this work. The difference in densities between this work and Safarov et al.<sup>29</sup> tends to become large at high pressures and at temperatures above 373 K (Figure S3, Supporting Information), which can be attributed to the higher residual water content of the ionic liquid used in Safarov et al.<sup>29</sup> than that of



**Figure 2.** Relative deviation plot for viscosities measured at atmospheric pressure for 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ( $[C_6C_1Im][Tf_2N]$ ). Calculated values were obtained from eq 4 in which parameters were obtained by fitting data of this work;  $\bigcirc$ , this work;  $\square$ , Ahosseini and Scurto;<sup>23</sup> dotted down triangle, calculated values from IUPAC proposed equation;<sup>30</sup> +, Seoane et al.;<sup>28</sup>  $\triangle$ , Tariq et al.<sup>27</sup> Dashed lines are the uncertainty of data reported in this work (0.85 %).

this work.<sup>12,14,15</sup> The high pressure density data of Safarov et al.<sup>29</sup> are inconsistent with data reported in this work.

Using the Tait equation (eq 1) with the fitting parameters determined from the density data reported in this work, isobaric thermal expansivities,  $\alpha_p$ , and isothermal compressibilities,  $\beta_T$ , for  $[C_6C_1Im][Tf_2N]$  were calculated (Tables S3 and S4, Supporting Information). For  $\alpha_p$  of  $[C_6C_1Im][Tf_2N]$ , two trends were noted for the variation of  $\alpha_p$  with temperature at a given pressure (Table S3, Supporting Information). At pressures less than 30 MPa, for a given pressure, the calculated



**Figure 3.** Relative deviation plot for densities measured at high pressures for  $1 - h \exp[1-3 - m \operatorname{eth} y] \operatorname{imid} azolium bis-(trifluoromethylsulfonyl) imide ([C<sub>6</sub>C<sub>1</sub>Im][Tf<sub>2</sub>N]). Calculated values were obtained from eqs 1 to 3 in which parameters were obtained by fitting data of this work; <math>\odot$ , this work;  $\Box$ , Esperança et al.;<sup>24</sup> dotted diamond, Kandil et al.;<sup>22</sup> ×, Safarov et al.<sup>29</sup> Dashed lines are the uncertainty of data reported in this work [(0.12 to 0.15) %].

 $\alpha_{\rm p}$  showed a slight maximum as temperature was increased. At pressures of 30 MPa and higher generally, the calculated  $\alpha_{\rm p}$  of  $[C_6C_1Im][Tf_2N]$  always decreased with increasing temperature at a given pressure. Safarov et al. reported an the increase in isobaric thermal expansivities with temperatures at all pressures,<sup>29</sup> which is inconsistent with values estimated in the literature<sup>48</sup> and in this work. Navia et al. showed experimentally that an increasing temperature cause a decrease in the isobaric thermal expansivities.<sup>48</sup> Trends of the isobaric thermal expansivities with temperature were similar to results reported by Navia et al.,<sup>48</sup> but were in conflict with values reported by Safarov et al.<sup>29</sup> (Figure S4, Supporting Information). For isothermal compressibilities, calculated values of this work decreased with increasing pressures at all temperatures and were in agreement with the available literature<sup>24,29</sup> (Table S4 and Figure S5, Supporting Information).

Measured Densities and Viscosities of [C<sub>6</sub>C<sub>1</sub>Im][CI] at Atmospheric Pressure as Shown in Table 1. Combined uncertainties of density and viscosity for each source of  $[C_6C_1Im]$  [Cl] were compared (Tables S5 and S6, Supporting Information). Both the source of the sample and the colored impurities had an indistinguishable effect on densities and viscosities within the uncertainties of the measurement in this work. Table 3 shows atmospheric densities extrapolated from high-pressure data to atmospheric pressure using the Tait equation (eq 1) at each temperature. Densities measured with the Stabinger viscometer and those extrapolated from highpressure data agreed to within our reported uncertainties. Determined parameters were  $a_0 = 0.8257 \text{ m}^3 \text{ kg}^{-1}$ ,  $a_1 = 4.1113 \cdot$  $10^{-4} \text{ m}^3\text{kg}^{-1}\text{K}^{-1}$ , and  $a_2 = 1.768 \cdot 10^{-7} \text{ m}^3\text{kg}^{-1}\text{K}^{-2}$  for eq 3 and  $d_0$ = -3.19947,  $d_1 = 1309.517$ /K, and  $d_2 = -200.794$ /K for eq 4, respectively. The values of bias and ARD were (+0.01 and 0.02) % for eq 3 and (-0.03 and 0.02) % for eq 4, respectively.

Figures 4 and 5 show relative deviation plots of atmospheric densities and viscosities for  $[C_6C_1Im][Cl]$  between this work and the literature. In Figure 4, densities in this work agreed with literature values of Gómez et al.<sup>16</sup> and Ning et al.<sup>36</sup> to within 0.2 %, with those of He et al.<sup>35</sup> to within 0.3 %, and with those of Sastry et al.<sup>17</sup> to within 0.6 %. These deviations can probably be explained by the absorption of water by the ionic liquid during the measurements made by those researchers.

Table 3. Measured Densities  $\rho$  at High Pressures p up to 200 MPa for 1-Hexyl-3-methylimidazolium chloride ([C<sub>6</sub>C<sub>1</sub>Im][Cl]) over the Temperature T Range (311.5 to 451.2) K<sup>a</sup>

				T,	/K			
p/MPa	311.5	331.2	351.2	371.5	391.6	411.6	431.4	451.2
				$ ho/kg \cdot m^{-3}$				
0.1	1030.4 <sup>b</sup>	1019.1 <sup>c</sup>	1007.8 <sup>c</sup>	997.1 <sup>c</sup>	986.5 <sup>c</sup>	976.2 <sup>c</sup>	965.7 <sup>c</sup>	955.0 <sup>c</sup>
10.0	1034.2	1023.3	1012.3	1001.8	991.4	981.3	971.1	960.7
20.0	1038.2	1027.4	1016.7	1006.3	996.2	986.3	976.3	966.2
30.0	1041.9	1031.3	1020.9	1010.7	1000.8	991.0	981.3	971.4
40.0	1045.5	1035.1	1024.9	1014.9	1005.2	995.5	986.0	976.4
50.0	1049.0	1038.8	1028.7	1018.8	1009.3	999.8	990.6	981.1
60.0	1052.4	1042.3	1032.4	1022.7	1013.3	1004.0	994.9	985.6
70.0	1055.7	1045.7	1036.0	1026.4	1017.2	1008.0	999.0	989.9
80.0	1058.9	1049.1	1039.4	1030.0	1020.9	1011.9	1003.1	994.1
90.0	1061.9	1052.3	1042.8	1033.4	1024.6	1015.6	1006.9	998.3
100.0	1065.1	1055.4	1046.0	1036.9	1028.0	1019.2	1010.6	1002.1
110.0	1067.9	1058.5	1049.3	1040.2	1031.4	1022.7	1014.2	1005.8
120.0	1070.9	1061.5	1052.3	1043.3	1034.7	1026.1	1017.7	1009.4
130.0	1073.6	1064.4	1055.3	1046.4	1037.9	1029.4	1021.2	1012.9
140.0	1076.5	1067.2	1058.2	1049.4	1041.0	1032.7	1024.4	1016.4
150.0	1079.1	1070.1	1061.1	1052.4	1044.1	1035.9	1027.7	1019.6
160.0	1081.7	1072.8	1063.9	1055.3	1047.1	1038.9	1030.9	1022.9
170.0	1084.5	1075.5	1066.7	1058.0	1050.0	1041.9	1033.9	1025.9
180.0	1087.1	1078.1	1069.4	1060.9	1052.8	1044.8	1037.0	1029.1
190.0	1089.6	1080.7	1072.0	1063.5	1055.6	1047.7	1039.9	1032.1
200.0	1092.0	1083.4	1074.6	1066.2	1058.4	1050.5	1042.8	1035.1

<sup>*a*</sup>Standard uncertainties are u(T) = 0.1 K, u(p) = 0.1 MPa for 0.1 and <math>0.25 MPa for  $p \ge 90$  MPa, and the combined expanded uncertainty of density is  $U_c(\rho) = 2.5$  kg·m<sup>-3</sup> with a 0.95 level of confidence (k = 2). <sup>*b*</sup>Measured value with Stabinger viscometer. <sup>*c*</sup>Extrapolated value from high-pressure data to atmospheric pressure with the Tait equation (eq 1) at each temperature.



**Figure 4.** Relative deviation plot for densities measured at atmospheric pressure for 1-hexyl-3-methylimidazolium chloride ( $[C_6C_1Im][Cl]$ ). Calculated values were obtained from eq 3 in which parameters were obtained by fitting data of this work;  $\odot$ , Measured values with the Stabinger viscometer in this work;  $\bullet$ , calculated values from measurements with the dilatometer in this work using eq 1;  $\Delta$ , Gómez et al.;<sup>16</sup> dotted down triangle, He et al.;<sup>35</sup> +, Ning et al.;<sup>36</sup>  $\Box$ , Sastry et al.;<sup>17</sup> ×, Seddon et al.<sup>33</sup> Dashed and dash-dotted lines are the uncertainties of data reported in this work for measured values (0.11%) and calculated values with eq 1 [(0.25 to 0.26)%], respectively.



**Figure 5.** Relative deviation plot for viscosities measured at atmospheric pressure for 1-hexyl-3-methylimidazolium chloride ( $[C_6C_1Im][Cl]$ ). Calculated values were obtained from eq 4 in which parameters were obtained by fitting data of this work;  $\odot$ , This work; dotted diamond, Fendt et al.;<sup>34</sup>  $\Delta$ , Gómez et al.;<sup>16</sup> +, Ning et al.;<sup>36</sup> × , Seddon et al.<sup>33</sup> Dashed lines are the uncertainty of data reported in this work (1.59 %).

Deviations of data reported by Seddon et al.<sup>33</sup> and values reported in this work were from (0.5 to 0.6) %. Although Seddon et al. made the measurements of samples that contained 100 w = 0.757 water content,<sup>33</sup> the reported values by Seddon et al.<sup>33</sup> were smaller than this work, and this is most likely due to the presence of 1-methylimidazole in the sample as discussed later.

In Figure 5, viscosities reported by Ning et al.<sup>36</sup> agreed with this work to within 4 %. Literature values of Fendt et al.,<sup>34</sup> Gómez et al.,<sup>16</sup> and Seddon et al.<sup>33</sup> were 5 % higher than those in this work. Gómez et al. and Seddon et al. measured samples that had a water content of 100 w = (0.048 and 0.757) before measurement using an Ubbelohde type viscometer and a cone–plate viscometer, respectively.<sup>16,33</sup> The smaller values of Gómez et al.<sup>16</sup> and Seddon et al.<sup>33</sup> than those in this work can be attributed to the high water content in the samples and the absorption of water during their measurements. A decrease in the viscosity is caused by residual content of 1-methylimidazole in the samples,<sup>5</sup> however other factors for higher values of

viscosity in this work still remain. The larger values of Ning et al.<sup>36</sup> and Fendt et al.<sup>34</sup> compared with those in this work are not easily explained by factors of water or 1-methylimidazole content in the samples.

Measured Densities of  $[C_6C_1Im][CI]$  at High Pressures as Shown in Table 3. Densities were represented by eqs 1–3 with values of bias and ARD as (<0.01 and 0.01) % with parameters  $b_0 = 662.0/Pa$ ,  $b_1 = -3.242 \cdot 10^{-3}/K^{-1}$ , and C =0.0887. Figure 6 shows measured densities of  $[C_6C_1Im][CI]$ 



**Figure 6.** Measured densities of 1-hexyl-3-methylimidazolium chloride  $([C_6C_1Im][Cl])$  plotted against the pressure at several temperatures:  $\odot$ , 312 K;  $\Box$ , 331 K;  $\triangle$ , 351 K; dotted down triangle, 372 K; dotted diamond, 392 K; dotted pentagon, 412 K;  $\triangle$ , 431 K; dotted down triangle, 451 K;  $\bigcirc$ , measured with the Stabinger viscometer in this work. Filled symbols denote extrapolated values from high-pressure data to atmospheric pressure with eq 1 at each temperature. Lines are fitted to this work with eqs 1–3.

plotted over the pressure range from (0.1 to 200) MPa at several temperatures from (312 to 451) K. As mentioned before, the HPLC analysis showed that some  $[C_6C_1Im][Cl]$ decomposed to 1-methylimidazole during the measurements. Meine et al. reported that imidazolium-based ionic liquids with a chloride easily decompose to imidazoles by heating compared with ionic liquids having a bis(trifluoromethylsulfonyl)imide anion.<sup>19</sup> After heating  $[C_6C_1Im][Cl]$  to 451 K, densities at 312 K under high pressure decreased from those before heating. This is probably due to partial decomposition of  $[C_6C_1Im][Cl]$ to 1-methylimidazole, from which it can be inferred that an increase in the 1-methylimidazole content caused the density to decrease. The average deviation of measured densities between before and after heating to (451-452) K was 0.72 kg·m<sup>-3</sup> for  $[C_6C_1Im][Cl]$  and 0.21 kg·m<sup>-3</sup> for  $[C_6C_1Im][Tf_2N]$ , respectively (Table S7, Supporting Information). However, for  $[C_6C_1Im][Tf_2N]$  heating to 392 K, the average deviation was 0.17 kg·m<sup>-3</sup> which was almost the same value as that determined for  $[C_6C_1Im][Tf_2N]$  after heating to 452 K. Thus, the measured  $[C_6C_1Im][Cl]$  at temperatures below 392 K did not seem to undergo decomposition and the uncertainty of measurements at temperatures below 392 K was less than the estimated uncertainty from all density data (2.5 kg $\cdot$ m<sup>-3</sup>). Assuming that the uncertainty of measurements was  $u(\overline{\rho}) =$  $0.17 \text{ kg} \cdot \text{m}^{-3}$ , the combined expanded uncertainties with a level of confidence of 0.95 (k = 2) was estimated to be  $U_c(\rho) = 2.0$ kg·m<sup>-3</sup>. The isobaric thermal expansivities and the isothermal

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compressibilities for  $[C_6C_1Im][CI]$  were calculated using the Tait equation (eq 1) with parameters fitted to the density data reported in this work (Tables S8 and S9, Supporting Information). The trends of calculated values were similar for both  $[C_6C_1Im][CI]$  and  $[C_6C_1Im][Tf_2N]$  ionic liquids (Figures S6 and S7, Supporting Information).

## CONCLUSIONS

New high-pressure densities ( $p \leq 200$  MPa) are reported for 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ( $[C_6C_1Im][Tf_2N]$ ) and 1-hexyl-3-methylimidazolium chloride ( $[C_6C_1Im][Cl]$ ). Agreement of measured high-pressure densities and atmospheric viscosities of  $[C_6C_1Im][Tf_2N]$  were within the uncertainty of some of the available literature values. Deviation of density and viscosity values among colored and colorless  $[C_6C_1Im][Cl]$  samples, synthesized and commercial samples were below the experimental uncertainties of this work, which means that colored impurities and sources for this ionic liquid do not strongly affect density and viscosity. The thermal decomposition of  $[C_6C_1Im][Cl]$  at temperatures greater than 392 K causes a decrease in the density and an increase in the uncertainty of measured density data at high pressure.

### ASSOCIATED CONTENT

#### **S** Supporting Information

Descriptions of the preparation of all [C<sub>6</sub>C<sub>1</sub>Im][Cl] samples, analyses of ionic liquids, equations of the isobaric thermal expansivity and isothermal compressibility; figures of sample appearance and fluorescence spectra of all  $[C_6C_1Im][Cl]$ samples, deviation plot for  $[C_6C_1Im][Tf_2N]$  densities between the literature<sup>29</sup> and this work, comparisons of isobaric thermal expansivities and isothermal compressibilities for  $[C_6C_1Im]$ - $[Tf_2N]$  between the literature<sup>24,29,48</sup> and this work, isobaric thermal expansivities of  $[C_6C_1Im][Tf_2N]$  and  $[C_6C_1Im][Cl]$ plotted against temperature, isothermal compressibilities of  $[C_6C_1Im][Tf_2N]$  and  $[C_6C_1Im][Cl]$  plotted against pressure; tables of available data for density and viscosity of  $[C_6C_1Im]$ -[Cl] in the literature, sample specification for ionic liquids used in this work, densities and viscosities of all  $[C_6C_1Im][Cl]$ samples, high-pressure densities after heat treatment, and calculated values of the isobaric thermal expansivity and the isothermal compressibility. This material is available free of charge via the Internet at http://pubs.acs.org.

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## Notes

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## REFERENCES

(1) Hallett, J. P.; Welton, T. Room-Temperature Ionic Liquids: Solvents for Synthesis and Catalysis. 2. *Chem. Rev.* 2011, 111, 3508–3576.

(2) Aparicio, S.; Atilhan, M.; Karadas, F. Thermophysical Properties of Pure Ionic Liquids: Review of Present Situation. *Ind. Eng. Chem. Res.* **2010**, *49*, 9580–9595.

(3) França, J. M. P.; Nieto de Castro, C. A.; Lopes, M. M.; Nunes, V. M. B. Influence of Thermophysical Properties of Ionic Liquids in Chemical Process Design. J. Chem. Eng. Data 2009, 54, 2569–2575.

(4) Klomfar, J.; Součková, M.; Pátek, J. *P-r-T* Measurements for 1-Alkyl-3-methylimidazolium-Based Ionic Liquids with Tetrafluoroborate and a Trifluoromethanesulfonate Anion. *J. Chem. Eng. Data* **2012**, *57*, 708–720.

(5) Seddon, K. R.; Stark, A.; Torres, M. J. Influence of Chloride, Water, and Organic Solvents on the Physical Properties of Ionic Liquids. *Pure Appl. Chem.* **2000**, *72*, 2275–2287.

(6) Brown, R. L.; Stein, S. E. Boiling Point Data. In *NIST Chemistry WebBook*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2006.

(7) Stark, A.; Behrend, P.; Braun, O.; Muller, A.; Ranke, J.; Ondruschka, B.; Jastorff, B. Purity Specification Methods for Ionic Liquids. *Green Chem.* **2008**, *10*, 1152–1161.

(8) Earle, M. J.; Gordon, C. M.; Plechkova, N. V.; Seddon, K. R.; Welton, T. Decolorization of Ionic Liquids for Spectroscopy. *Anal. Chem.* **2007**, *79*, 758–764.

(9) Nockemann, P.; Binnemans, K.; Driesen, K. Purification of Imidazolium Ionic Liquids for Spectroscopic Applications. *Chem. Phys. Lett.* **2005**, *415*, 131–136.

(10) Clare, B. R.; Bayley, P. M.; Best, A. S.; Forsyth, M.; MacFarlane, D. R. Purification or Contamination? The Effect of Sorbents on Ionic Liquids. *Chem. Commun.* **2008**, 2689–2691.

(11) Burrell, A. K.; Sesto, R. E. D.; Baker, S. N.; McCleskey, T. M.; Baker, G. A. The Large Scale Synthesis of Pure Imidazolium and Pyrrolidinium Ionic Liquids. *Green Chem.* **2007**, *9*, 449–454.

(12) Rodríguez, H.; Brennecke, J. F. Temperature and Composition Dependence of the Density and Viscosity of Binary Mixtures of Water + Ionic Liquid. J. Chem. Eng. Data **2006**, *51*, 2145–2155.

(13) Widegren, J. A.; Magee, J. W. Density, Viscosity, Speed of Sound, and Electrolytic Conductivity for the Ionic Liquid 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide and Its Mixtures with Water. J. Chem. Eng. Data 2007, 52, 2331–2338.

(14) Carvalho, P. J.; Regueira, T.; Santos, L. M. N. B. F.; Fernandez, J.; Coutinho, J. A. P. Effect of Water on the Viscosities and Densities of 1-Butyl-3-methylimidazolium Dicyanamide and 1-Butyl-3-methylimidazolium Tricyanomethane at Atmospheric Pressure. *J. Chem. Eng. Data* **2009**, *55*, 645–652.

(15) Oliveira, F. S.; Freire, M. G.; Carvalho, P. J.; Coutinho, J. A. P.; Lopes, J. N. C.; Rebelo, L. P. N.; Marrucho, I. M. Structural and Positional Isomerism Influence in the Physical Properties of Pyridinium NTf2-Based Ionic Liquids: Pure and Water-Saturated Mixtures. J. Chem. Eng. Data 2010, 55, 4514–4520.

(16) Gómez, E.; González, B.; Domínguez, Á.; Tojo, E.; Tojo, J. Dynamic Viscosities of a Series of 1-Alkyl-3-methylimidazolium Chloride Ionic Liquids and Their Binary Mixtures with Water at Several Temperatures. J. Chem. Eng. Data **2006**, *51*, 696–701.

(17) Sastry, N. V.; Vaghela, N. M.; Macwan, P. M. Densities, Excess Molar and Partial Molar Volumes for Water +1-Butyl- or, 1-Hexyl- or, 1-Octyl-3-methylimidazolium Halide Room Temperature Ionic Liquids at T = (298.15 and 308.15) K. J. Mol. Liq. 2013, 180, 12–18. (18) Quijada-Maldonado, E.; Van der Boogaart, S.; Lijbers, J. H.; Meindersma, G. W.; De Haan, A. B. Experimental Densities, Dynamic Viscosities and Surface Tensions of the Ionic Liquids Series 1-Ethyl-3-methylimidazolium Acetate and Dicyanamide and Their Binary and

(19) Meine, N.; Benedito, F.; Rinaldi, R. Thermal Stability of Ionic Liquids Assessed by Potentiometric titration. *Green Chem.* **2010**, *12*, 1711–1714.

(20) Stark, A.; Ajam, M.; Green, M.; Raubenheimer, H. G.; Ranwell, A.; Ondruschka, B. Metathesis of 1-Octene in Ionic Liquids and Other Solvents: Effects of Substrate Solubility, Solvent Polarity and Impurities. *Adv. Synth. Catal.* **2006**, *348*, 1934–1941.

(21) Holbrey, J. D.; Seddon, K. R.; Wareing, R. A Simple Colorimetric Method for the Quality Control of 1-Alkyl-3methylimidazolium Ionic Liquid Precursors. *Green Chem.* **2001**, *3*, 33–36.

(22) Kandil, M. E.; Marsh, K. N.; Goodwin, A. R. H. Measurement of the Viscosity, Density, and Electrical Conductivity of 1-Hexyl-3methylimidazolium Bis(trifluorosulfonyl)imide at Temperatures between (288 and 433) K and Pressures below 50 MPa. *J. Chem. Eng. Data* 2007, *52*, 2382–2387.

(23) Ahosseini, A.; Scurto, A. Viscosity of Imidazolium-Based Ionic Liquids at Elevated Pressures: Cation and Anion Effects. *Int. J. Thermophys.* **2008**, *29*, 1222–1243.

(24) Esperança, J. M. S. S.; Guedes, H. J. R.; Lopes, J. N. C.; Rebelo, L. P. N. Pressure-Density-Temperature (*p*-*r*-*T*) Surface of  $[C_6 mim]$ - $[NTf_2]$ . J. Chem. Eng. Data **2008**, 53, 867–870.

(25) Ahosseini, A.; Sensenich, B.; Weatherley, L. R.; Scurto, A. M. Phase Equilibrium, Volumetric, and Interfacial Properties of the Ionic Liquid, 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)-amide and 1-Octene. *J. Chem. Eng. Data* **2010**, *55*, 1611–1617.

(26) Tariq, M.; Serro, A. P.; Mata, J. L.; Saramago, B.; Esperançaa, J. M. S. S.; Lopes, J. N. C.; Rebelo, L. P. N. High-temperature Surface Tension and Density Measurements of 1-Alkyl-3-methylimidazolium Bistriflamide Ionic Liquids. *Fluid Phase Equilib.* **2010**, *294*, 131–138.

(27) Tariq, M.; Carvalho, P. J.; Coutinho, J. A. P.; Marrucho, I. M.; Lopes, J. N. C.; Rebelo, L. P. N. Viscosity of  $(C_2-C_{14})$  1-Alkyl-3methylimidazolium Bis(trifluoromethylsulfonyl)amide Ionic Liquids in an Extended Temperature Range. *Fluid Phase Equilib.* **2011**, 301, 22– 32.

(28) Seoane, R. G.; Corderí, S.; Gómez, E.; Calvar, N.; González, E. J.; Macedo, E. A.; Domínguez, Á. Temperature Dependence and Structural Influence on the Thermophysical Properties of Eleven Commercial Ionic Liquids. *Ind. Eng. Chem. Res.* **2012**, *51*, 2492–2504.

(29) Safarov, J.; Hamidova, R.; Zepik, S.; Schmidt, H.; Kul, I.; Shahverdiyev, A.; Hassel, E. Thermophysical Properties of 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide at High Temperatures and Pressures. J. Mol. Liq. 2013, 187, 137–156.

(30) Chirico, R. D.; Diky, V.; Magee, J. W.; Frenkel, M.; Marsh, K. N., Thermodynamic and Thermophysical Properties of the Reference ionic liquid: 1-Hexyl-3-methylimidazolium Bis[(Trifluoromethyl)Sulfonyl]amide (Including Mixtures). Part 2.Critical Evaluation and Recommended Property Values (IUPAC Technical Report). *Pure Appl. Chem.* **2009**, *81*, 791-828.

(31) Marsh, K. N.; Brennecke, J. F.; Chirico, R. D.; Frenkel, M.; Heintz, A.; Magee, J. W.; Peters, C. J.; Rebelo, L. P. N.; Seddon, K. R., Thermodynamic and Thermophysical Properties of the Reference Ionic Liquid: 1-Hexyl-3-methylimidazolium Bis[(Trifluoromethyl) Sulfonyl]amide (Including Mixtures) Part 1.Experiment al Methods and Results (IUPAC Technical Report). *Pure Appl. Chem.* 2009, *81*, 781-790.

(32) Wang, H.; Gurau, G.; Rogers, R. D. Ionic Liquid Processing of Cellulose. *Chem. Soc. Rev.* 2012, 41, 1519–1537.

(33) Seddon, K. R.; Stark, A.; Torres, M.-J. Viscosity and Density of 1-Alkyl-3-methylimidazolium Ionic Liquids. In *Clean Solvents*; American Chemical Society: Washington, DC, 2002.

(34) Fendt, S.; Padmanabhan, S.; Blanch, H. W.; Prausnitz, J. M. Viscosities of Acetate or Chloride-Based Ionic Liquids and Some of Their Mixtures with Water or Other Common Solvents. *J. Chem. Eng. Data* **2011**, *56*, 31–34.

(35) He, R.-H.; Long, B.-W.; Lu, Y.-Z.; Meng, H.; Li, C.-X. Solubility of Hydrogen Chloride in Three 1-Alkyl-3-methylimidazolium Chloride

Ionic Liquids in the Pressure Range (0 to 100) kPa and Temperature Range (298.15 to 363.15) K. J. Chem. Eng. Data **2012**, 57, 2936–2941. (36) Ning, H.; Hou, M.; Mei, Q.; Liu, Y.; Yang, D.; Han, B. The

Physicochemical Properties of Some Imidazolium-based Ionic Lliquids and Their Binary Mixtures. *Sci. China Chem.* **2012**, *55*, 1509–1518.

(37) David, O. C.; Zarca, G.; Gorri, D.; Urtiaga, A.; Ortiz, I. On the Improved Absorption of Carbon Monoxide in the Ionic Liquid 1-Hexyl-3-methylimidazolium Chlorocuprate. *Sep. Purif. Technol.* **2012**, 97, 65–72.

(38) Vitz, J.; Erdmenger, T.; Haensch, C.; Schubert, U. S. Extended Dissolution Studies of Cellulose in Imidazolium Based Ionic Liquids. *Green Chem.* **2009**, *11*, 417–424.

(39) Cao, Y.; Chen, Y.; Sun, X.; Zhang, Z.; Mu, T. Water Sorption in Ionic Liquids: Kinetics, Mechanisms and Hydrophilicity. *Phys. Chem. Chem. Phys.* **2012**, *14*, 12252–12262.

(40) Maton, C.; De Vos, N.; Stevens, C. V. Ionic Liquid Thermal Stabilities: Decomposition Mechanisms and Analysis Tools. *Chem. Soc. Rev.* **2013**, *42*, 5963–5977.

(41) Heimel, H.; Leopold, H. O.; Stabinger, H. Device for Determining the Viscosity of a Liquid. EP0926481 A2, June 30, 1999. (42) Sato, Y.; Yamasaki, Y.; Takishima, S.; Masuoka, H. Precise Measurement of the PVT of Polypropylene and Polycarbonate up to 330°C and 200 MPa. *J. Appl. Polym. Sci.* **1997**, *66*, 141–150.

(43) Machida, H.; Sato, Y.; Smith, R. L., Jr. Pressure-Volume-Temperature (PVT) Measurements of Ionic Liquids ([bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>], [bmim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>] [bmim<sup>+</sup>][OcSO<sub>4</sub><sup>-</sup>]) and Analysis with the Sanchez-Lacombe Equation of State. *Fluid Phase Equilib.* **2008**, *264*, 147–155. (44) Taguchi, R.; Machida, H.; Sato, Y.; Smith, R. L. High-Pressure Densities of 1-Alkyl-3-methylimidazolium Hexafluorophosphates and 1-Alkyl-3-methylimidazolium Tetrafluoroborates at Temperatures from (313 to 473) K and at Pressures up to 200 MPa. *J. Chem. Eng. Data* **2009**, *54*, 22–27.

(45) Machida, H.; Taguchi, R.; Sato, Y.; Smith, J. R. L. Measurement and Correlation of High Pressure Densities of Ionic Liquids, 1-Ethyl-3methylimidazolium l-Lactate ([emim][Lactate]), 2-Hydroxyethyltrimethylammonium l-Lactate ([ $(C_2H_4OH)(CH_3)_3N$ ][Lactate]), and 1-Butyl-3-methylimidazolium Chloride ([bmim][Cl]). J. Chem. Eng. Data 2011, 56, 923–928.

(46) Dymond, J. H.; Malhotra, R. The Tait Equation: 100 Years on. Int. J. Thermophys. **1988**, 9, 941–951.

(47) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. Numerical Recipes in FORTRAN: The art of scientific computing; Cambridge University Press: New York, 1992.

(48) Navia, P.; Troncoso, J.; Romaní, L. Dependence against Temperature and Pressure of the Isobaric Thermal Expansivity of Room Temperature Ionic Liquids. *J. Chem. Eng. Data* **2010**, *55*, 595– 599.