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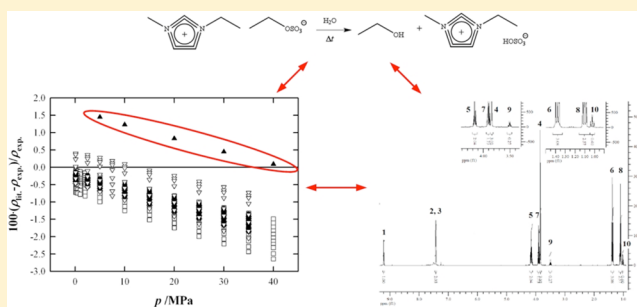
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Comments and Additional Work on “High-Pressure Volumetric Properties of Imidazolium-Based Ionic Liquids: Effect of the Anion”

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ABSTRACT: This work follows a publication of our group in *J. Chem. Eng. Data* 2007, 52, 2204–2211 presenting high temperature and pressure density data for five imidazolium-based ionic liquids. At this period, very few ionic liquid density data were available in the literature, especially at high pressure, and the uncertainty of published results was calculated with respect to the literature data available for three of the five ionic liquids studied. Since 2007, the ionic liquid density databank has largely increased. In this work, a comparison of our published data in *J. Chem. Eng. Data* 2007, 52, 2204–2211, with more than 1800 high pressure data coming from the literature up to December 2011 is presented to assess the uncertainty of our published values. The claimed uncertainty is close to 0.31 % for all IL density data sets except in the case of the $[C_1C_2Im][EtSO_4]$, where the uncertainty is up to 1.1 %. Reported data in *J. Chem. Eng. Data* 2007, 52, 2204–2211, for this particular ionic liquid cannot be used as a reference. For this ionic liquid, new density measurements of the same sample batch have been remeasured by using the same experimental technique, and new experimental data presented herein are clearly higher than our previous published results. A 1H NMR analysis of the sample has confirmed hydrolysis of the ethylsulfate anion to ethanol and hydrogenate anion which explains the differences observed between our density data and the literature.



■ INTRODUCTION

Ionic liquids are high performance fluids that constitute a class of promising compounds for the development of innovative technologies in a wide range of engineering and material science applications both in processes (synthesis, catalysis, separations, electrochemistry) and in devices (optical, lubricants, batteries, photovoltaic cells).¹ Their density is crucial information for the engineering design of industrial scale processes. Particularly accurate density data are necessary for the introduction in chemical engineering or thermodynamic models.² The knowledge of the volumetric properties of ionic liquids also contributes to the description and understanding of this medium at a molecular level, in terms of structure/structuration and interactions. Finally, density gives information on their purity as this property is very sensible to the presence of impurities. For example, it is well-documented by ourselves^{3–5} and other authors^{6–10} that the presence of water and/or halogenated compounds dramatically changes the physical properties of ionic liquids.

To provide accurate reference data, our group measured and published in 2007 (*J. Chem. Eng. Data* 2007, 52, 2204–2211) the densities of five imidazolium-based ionic liquids (1-butyl-3-methylimidazolium tetrafluoroborate, $[C_1C_4Im][BF_4]$; 1-butyl-3-methylimidazolium hexafluorophosphate, $[C_1C_4Im][PF_6]$; 1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide,

$[C_1C_4Im][Tf_2N]$; 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, $[C_1C_2Im][Tf_2N]$; 1-ethyl-3-methylimidazolium ethylsulfate, $[C_1C_2Im][EtSO_4]$) as a function of temperature from (293 to 415) K and over an extended pressure range from (0.1 to 40) MPa using a vibrating-tube densimeter.¹¹ For most of these ionic liquids, no density data were available in 2007 for comparison. As of December 2011, new high-pressure density data are now available in the literature, and based on an up-dated density databank,^{12–31} new comparisons are now possible to ensure the quality of the data we published in 2007.

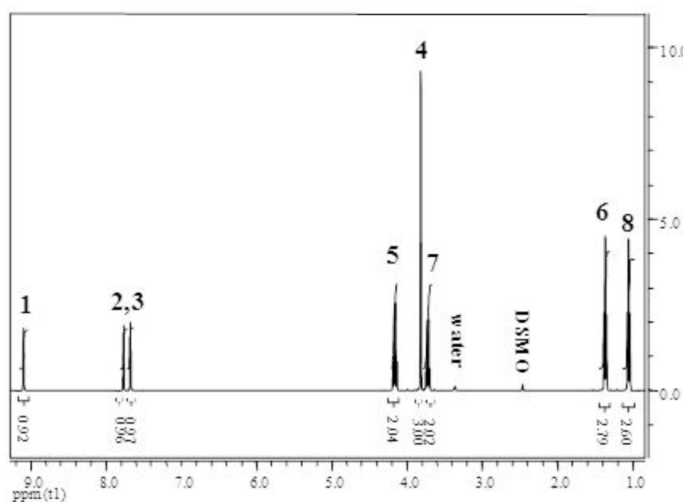
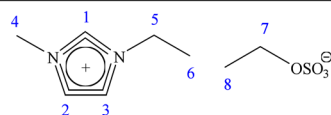
It is the objective of the present work to present a critical overview of our previously published density data in *J. Chem. Eng. Data* 2007, 52, 2204–2211 with more than 1800 density data available in the literature over temperature and pressure ranges from (293 to 423) K and (0.1 to 40) MPa.^{11–31} In the case of $[C_1C_2Im][EtSO_4]$, for which large deviations between our published data and the literature are observed, new experimental measurements of the density and 1H NMR analysis are also presented.

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a) ^1H -NMR spectroscopy (400 MHz, DMSO-d_6) measured by the Wasserscheid's group in 2005



b) ^1H -NMR spectroscopy (400 MHz, CDCl_3) measured by our group in 2011

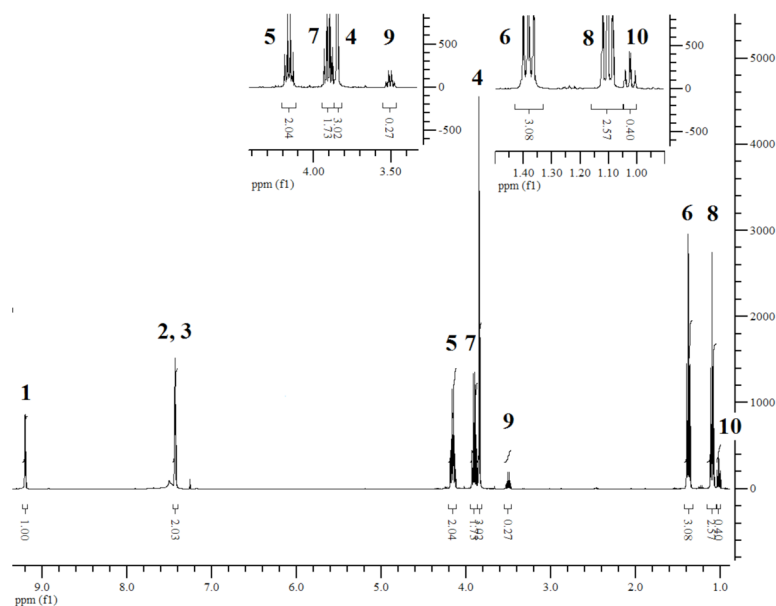
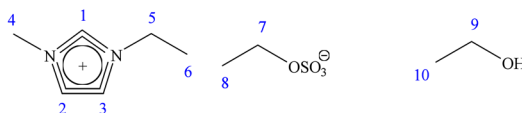


Figure 1. ^1H NMR results for the $[\text{C}_1\text{C}_2\text{Im}][\text{EtSO}_4]$ decomposition over time: (a) as received in 2005; (b) same sample batch in 2011.

EXPERIMENTAL SECTION

Materials. The 1-ethyl-3-methylimidazolium ethylsulfate, $[\text{C}_1\text{C}_2\text{Im}][\text{EtSO}_4]$ (CAS Registry No. 342573-75-5), is the same sample as the one used in 2007. Since 2007, this sample was kept

under nitrogen atmosphere in a Schlenk tube. It was supplied in 2005 by the group of Prof. Wasserscheid (University of Erlangen-Nürnberg, Germany) with a minimum stated purity of 0.99 in mole fraction as shown on the ^1H NMR spectra presented in Figure 1a.

Table 1. Relative Absolute Average Deviations RAAD between the Published Densities of Our Work¹¹ and of the Literature^{12–31} Reported Temperature and Pressure Ranges Correspond to the T and p Intervals Where Each Comparison Was Realized

IL	Nb data	T/K	p/MPa	100-RAAD	reference
[C ₁ C ₄ Im][BF ₄]	14	[298–323]	[0.1–30]	0.12	12
	26	[293–333]	[0.1–40]	0.44	13
	67	[293–333]	[0.1–40]	0.46	14
	20	[293–353]	[0.1–20]	0.57	15
	45	[298–398]	[0.1–40]	0.98	16
	61	[293–353]	[0.1–40]	0.10	17
	77	[293–393]	[0.1–10]	0.12	18
	62	[293–348]	[0.1–40]	0.40	19
	45	[298–398]	[0.1–40]	0.98	20
	37	[313–423]	[0.1–40]	0.36	21
	28	[313–423]	[0.1–2]	0.37	22
subtotal	599	[293–423]	[0.1–40]	0.37	12–23
[C ₁ C ₂ Im][Tf ₂ N]	96	[293–393]	[0.1–30]	0.18	24
	42	[293–373]	[0.1–40]	0.25	25
subtotal	138	[293–373]	[0.1–40]	0.20	24, 25
[C ₁ C ₄ Im][Tf ₂ N]	203	[293–423]	[0.1–40]	0.03	26

IL	Nb data	T/K	p/MPa	100-RAAD	reference
[C ₁ C ₄ Im][PF ₆]	161	[293–333]	[0.1–40]	0.06	27
	364	[293–423]	[0.1–40]	0.04	26, 27
[C ₁ C ₄ Im][PF ₆]	156	[293–333]	[0.1–40]	0.78	14
	20	[293–353]	[0.1–20]	0.08	15
	45	[298–398]	[0.1–40]	0.18	16
	37	[313–423]	[0.1–40]	0.52	21
	22	[298–343]	[0.1–40]	0.55	28
subtotal	280	[293–423]	[0.1–40]	0.58	14–16, 21, 28
[C ₁ C ₂ Im][EtSO ₄]	1381	[293–423]	[0.1–40]	0.31	12–28
	203	[293–423]	[0.1–40]	1.41	27
[C ₁ C ₂ Im][EtSO ₄]	63	[293–333]	[0.1–35]	0.89	29
	108	[293–343]	[0.1–35]	0.83	30
	80	[293–393]	[0.1–35]	0.63	31
	454	[293–423]	[0.1–40]	1.06	27, 29–31
total for the five ILs	1835	[293–423]	[0.1–40]	0.50	12–31

The ionic liquid sample was recently reconditioned under vacuum before use according to the same procedure as in 2007.¹¹ After treating the ionic liquid for 15 h at room temperature under vacuum (lower than 1 Pa), the sample is considered as dried and is conditioned under nitrogen atmosphere. After this treatment and before all of the density measurements, the sample is analyzed for water content using coulometric Karl Fischer titration (Mettler Toledo DL31). The water content is typically (190 ± 10) ppm. To avoid any contact with atmosphere, a Schlenk-type tube and a syringe equipped with a luer lock valve are used to load the samples into the densimeter.

Density Measurement. The experimental apparatus used to measure the densities is the U-shape vibrating-tube densimeter (Anton Paar, model DMA 512) operating in a static mode previously used in 2007. A new calibration procedure using *n*-heptane, bromobenzene, and 2,4-dichlorotoluene is now used according to the method proposed by Schilling et al.³² The temperature is maintained constant to 0.01 K by means of a recirculating bath equipped with a PID temperature controller (Julabo FP40-HP). For measuring temperature a 100 Ω platinum resistance thermometer (uncertainty 0.02 K, accuracy 0.04 K) is used. The pressure is measured using a manometer (Druck, model PTX 610, (0 to 70) MPa, uncertainty 0.5 % full scale). The uncertainty of the density measurements reported herein is $10^{-4} \text{ g}\cdot\text{cm}^{-3}$.¹¹

NMR Spectroscopy. ¹H NMR spectra are recorded on a Bruker Avance 400 MHz instrument (Bruker Biospin, Wissembourg, France) at 298 K. The solvent used is deuterated chloroform, and the sample is placed in a sealed capillary tube. The detection limit for NMR when using a deuterated solvent capillary tube is ± 2 %.³³

RESULTS AND DISCUSSION

Comparison with Literature Data. The first part of this work consisted in the collection of new high-pressure density data from the literature,^{12–31} and comparison with our original data published in *J. Chem. Eng. Data* in 2007.¹¹ These comparisons are presented in Table 1 along with the percent relative absolute average deviation (100-RAAD) between density values published for the five ILs by our group previously,¹¹ and those available in the literature,^{12–31} for temperature ranging from (293 to 423) K and pressures up to 40 MPa. In each case, the

reported percent RAAD was calculated from the prior evaluation of each individual relative deviation (RD) reported in these temperature and pressure ranges between data from the literature with those from our original publication in *J. Chem. Eng. Data* in 2007.¹¹

$$100 \cdot \text{RAAD} = \frac{100}{N} \sum \left| \frac{\rho_{\text{lit}} - \rho_{\text{exp}}}{\rho_{\text{exp}}} \right| = \frac{100}{N} \sum |\text{RD}| \quad (1)$$

with N the total number of data used; ρ_{lit} the high-pressure density values from the literature;^{12–31} and ρ_{exp} the corresponding value obtained from our experimental work.¹¹ The RAAD can be regarded as a measure of the accuracy of our published data.

As shown in Figure 2 and reported in Table 1, in the case of [C₁C₄Im][BF₄], a percent RAAD value of 0.37 % is obtained by

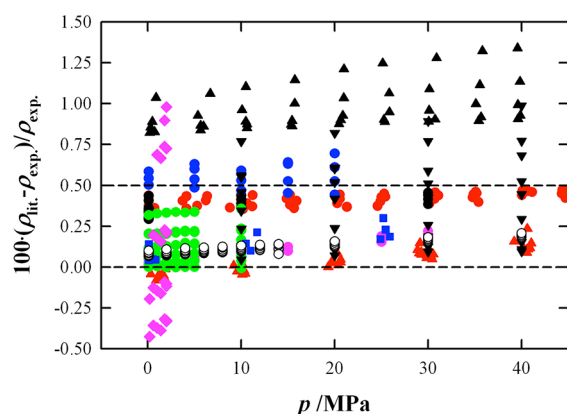


Figure 2. Percentage deviations $100(\rho_{\text{lit}} - \rho_{\text{exp}})/\rho_{\text{exp}}$ of the literature high-pressure density from our published data,¹¹ for [C₁C₄Im][BF₄]: pink ●, Rilo et al.;¹² black ●, Rebelo et al.;¹³ red ●, de Azevedo et al.;¹⁴ blue ●, Tomida et al.;¹⁵ black ▲, Safarov et al.;^{16,20} red ▲, Klomfar et al.;¹⁷ green ●, Gardas et al.;¹⁸ blue ■, Harris et al.;¹⁹ black ▼, Machida et al.;²¹ pink ◆, Han et al.;²² ○, Sanmamed et al.²³ for temperatures ranging from (293 to 423) K and pressures up to 40 MPa.

comparing of original density data with 599 high-pressure density data published in the literature with the same IL.^{12–23} This result is

in agreement with the uncertainty claimed in our original publication. Except when compared with the data of Han et al.,²² our experimental densities are systematically lower than those presented in the literature which is consistent with a higher water content in our samples, as already explained in the original paper. Our density data are in excellent agreement over the whole temperature and pressure ranges with those published by Rilo et al.,¹² Klomfar et al.,¹⁷ Gardas et al.,¹⁸ and Sanmamed et al.²³ with a maximum percent RAAD of (0.12, 0.10, 0.12, and 0.13) %, respectively. Our data are coherent with the set of data proposed by Rebelo et al.,¹³ de Azevedo et al.,¹⁴ Tomida et al.,¹⁵ Harris et al.,¹⁹ Machida et al.,²¹ and Han et al.²² within an accuracy close to 0.50 % as claimed in our previous paper. Larger deviations (up to 0.98 %) are obtained with data published by Safarov et al.^{16,20} For $[\text{C}_1\text{C}_4\text{Im}][\text{PF}_6]$ ¹⁶ and $[\text{C}_1\text{C}_2\text{Im}][\text{NTf}_2]$,²⁵ excellent agreement is observed with Safarov et al. data over the whole temperature and pressure ranges with uncertainties of (0.18 and 0.25) %, respectively, which indicate the coherence of the data published by both groups. The large deviations observed for $[\text{C}_1\text{C}_4\text{Im}][\text{BF}_4]$ can be due to the purity of the samples, especially because this IL is not a water-stable compound.³⁴ However, the claimed uncertainty by our group in the case of the $[\text{C}_1\text{C}_4\text{Im}][\text{BF}_4]$ is 0.37 %, taking into account all high-pressure density data published in the literature, as shown in Table 1 and in Figure 2. This uncertainty is in agreement with that reported by Klomfar et al. regarding calculated deviations between different literature data sets in the case of the density of $[\text{C}_1\text{C}_4\text{Im}][\text{BF}_4]$ (see especially their Supporting Information).¹⁷

Similar conclusions are obtained by comparing our published data for $[\text{C}_1\text{C}_2\text{Im}][\text{NTf}_2]$, $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$, and $[\text{C}_1\text{C}_4\text{Im}][\text{PF}_6]$, with available high-pressure density data in the literature, where 138,^{24,25} 364,^{26,27} and 280^{14–16,21,28} literature data points are used for the comparisons with percent RAAD of (0.20, 0.04, and 0.58) %, respectively. Except in the case of $[\text{C}_1\text{C}_2\text{Im}][\text{EtSO}_4]$, our published density data have an uncertainty close to 0.31 %, over the whole temperature and pressure ranges investigated.

In the case of $[\text{C}_1\text{C}_2\text{Im}][\text{EtSO}_4]$, as shown in Figure 3, our published values are systematically higher than those now

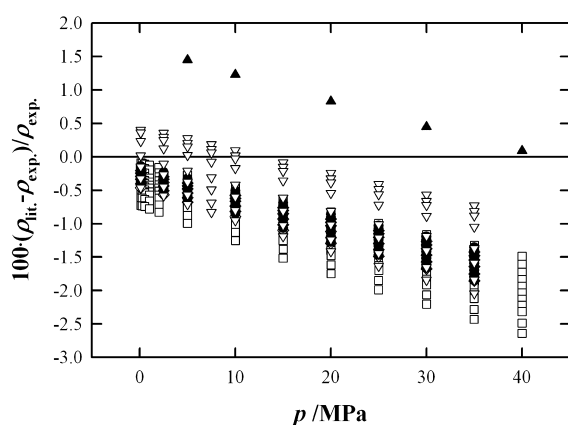


Figure 3. Percentage deviations $100(\rho_{\text{lit}} - \rho_{\text{exp}})/\rho_{\text{exp}}$ of the literature high-pressure density from our published data,¹¹ for $[\text{C}_1\text{C}_2\text{Im}][\text{EtSO}_4]$: \square , Castro et al.;²⁷ \diamond , Hofman et al.;²⁹ \bullet , Matkowska et al.;³⁰ ∇ , Tome et al.;³¹ \blacktriangle , this work by using the same sample batch for temperatures ranging from (293 to 423) K and pressures up to 40 MPa.

available in literature.^{27,29–31} Deviations up to (1.41, 0.89, 0.83, and 0.63) % are observed from high-pressure values reported by Castro et al.,²⁷ Hofman et al.,²⁹ Matkowska et al.,³⁰ and Tome

et al.,³¹ respectively. Such deviations cannot be explained only by the uncertainty of the apparatus, since a deviation of 1.41 % corresponds to an error up to $0.02 \text{ g}\cdot\text{cm}^{-3}$ in the measured density. Additionally, two other articles based on the measurement of high-pressure density of $[\text{C}_1\text{C}_2\text{Im}][\text{EtSO}_4]$ have been accepted since December 2011, for which similar conclusions were made.^{35,36} To verify that no experimental error had been done during the measurements done in 2007, new density measurements have been performed using the same technique and sample batch. The results are presented in Table 2 along with

Table 2. New Experimental Densities, ρ , of the $[\text{C}_1\text{C}_2\text{Im}][\text{EtSO}_4]$ between (5 and 40) MPa at 302.88 K and Their Comparisons with Calculated Values by Using Tait Equation Parameters Previously Published with the Same Sample Batch¹¹

p/MPa	this work	calculated from ref 11	100-RAAD
	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	
5	1.2589	1.2410	1.45
10	1.2608	1.2454	1.23
20	1.2645	1.2541	0.83
30	1.2681	1.2625	0.45
40	1.2717	1.2705	0.09

densities calculated with the Tait equation proposed to fit our data of 2007. The new set of density data is higher (0.81 %) than the previous one, and as can be observed in Figure 3, present larger deviations with literature.^{27,29–31}

Effect of the Hydrolysis Reaction of the 1-Ethyl-3-methylimidazolium Ethylsulfate over Time on Density Data. Wasserschneider et al. have reported a quick hydrolysis reaction of the 1-ethyl-3-methylimidazolium ethylsulfate, $[\text{C}_1\text{C}_2\text{Im}][\text{EtSO}_4]$ by contaminating it artificially with water at 80°C .³⁷ More recently, Ficke et al. have also demonstrated that this IL decomposes to ethanol and 1-ethyl-3-methylimidazolium hydrogensulfate, $[\text{C}_1\text{C}_2\text{Im}][\text{HSO}_4]$ over time according to the hydrolysis reaction reported in Figure 4.³⁸

The ^1H NMR spectra done in 2005 just after the synthesis of the ionic liquid confirms that no decomposition can be suspected at this period according to the detection limit of the instrument (Figure 1a). A new ^1H NMR analysis (presented in Figure 1b) was performed to check the structure and purity of the $[\text{C}_1\text{C}_2\text{Im}][\text{EtSO}_4]$ batch used during the present work. New signals corresponding to ethanol can be observed. A decomposition up to 13.5 % of the $[\text{C}_1\text{C}_2\text{Im}][\text{EtSO}_4]$ to ethanol (clearly observed in Figure 1b, as this sample was not dried prior to analysis) and $[\text{C}_1\text{C}_2\text{Im}][\text{HSO}_4]$ are observed according to the hydrolysis reaction reported in Figure 4. This result confirms the conclusion of Ficke et al. concerning the decomposition of this sample and its modification with time.³⁸ Due to the decomposition of the $[\text{C}_1\text{C}_2\text{Im}][\text{EtSO}_4]$ to $[\text{C}_1\text{C}_2\text{Im}][\text{HSO}_4]$ (and ethanol) our density data do not correspond to the density of pure $[\text{C}_1\text{C}_2\text{Im}][\text{EtSO}_4]$ but to that of a binary mixture containing (86.5 % of $[\text{C}_1\text{C}_2\text{Im}][\text{EtSO}_4]$ + 13.5 % of $[\text{C}_1\text{C}_2\text{Im}][\text{HSO}_4]$). Because of the degassing prior to the density measurements, ethanol is not present in the mixture. The presence of $[\text{C}_1\text{C}_2\text{Im}][\text{HSO}_4]$ increases the density of the sample. This conclusion is consistent with density values published in the case of the pure $[\text{C}_1\text{C}_2\text{Im}][\text{HSO}_4]$ by Costa et al.³⁹ We, therefore, recommend not using density data reported by our group on this $[\text{C}_1\text{C}_2\text{Im}][\text{EtSO}_4]$ sample (herein and previously¹¹).

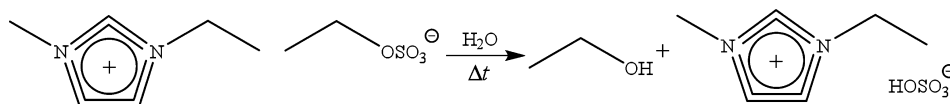


Figure 4. Hydrolysis reaction corresponding to the $[C_1C_2Im][EtSO_4]$ decomposition over time (Δt).

CONCLUSION

In this work, the consistency of our density data previously published in *J. Chem. Eng. Data* 2007, 52, 2204–2211,¹¹ was tested against more than 1800 high-pressure density data from the literature. From these comparisons, it appears that our data have an uncertainty of 0.31 %, over the whole temperature and pressure ranges investigated for all ionic liquids studied except for $[C_1C_2Im][EtSO_4]$, for which higher deviations (up to 1.0 %) are observed. New density measurements with the same apparatus and batch sample are presented here and confirm the problems with the previous results. This deviation with literature is explained by a sample decomposition to ethanol and $[C_1C_2Im][HSO_4]$. According to 1H NMR analysis, 13.5 % decomposition of $[C_1C_2Im][EtSO_4]$ was found in the sample batch used. Based on the present work, the authors recommend using reported density data in the case of $[C_1C_2Im][NTf_2]$, $[C_1C_4Im][NTf_2]$, $[C_1C_4Im][PF_6]$, and $[C_1C_4Im][BF_4]$, with an accuracy of 0.30 % over the whole temperature and pressure ranges studied,¹¹ but not the density data measured for $[C_1C_2Im][EtSO_4]$ by our group. This result clearly indicates again that ethylsulfate-based ILs are not water-stable and time-stable compounds since they hydrolyze over time in the presence of any trace of moisture coming from the atmosphere even at room temperature. This result shows also the large effect of $[C_1C_2Im][EtSO_4]$ decomposition on the density measurement.

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Notes

The authors declare no competing financial interest.

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