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Temperature Dependence of the Surface Tension and Density at 0.1 MPa for 1-Ethyl- and 1-Butyl-3-methylimidazolium Dicyanamide

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Supporting Information

ABSTRACT: Experimental air−liquid interfacial tension data and density data are presented for two ionic liquids with the 1-C_n-3-methylimidazolium cation, $n = 2$ and 4, and the dicyanamide anion. The measurements were performed at atmospheric pressure in the temperature range from (278 to 356) K using the Krüss K100MK2 tensiometer. The accuracy of the surface tension measurements was confirmed by employing the Wilhelmy plate and the du Noüy ring methods in parallel. The combined expanded uncertainty at 0.95 confidence level associated with the Wilhelmy plate method is estimated to be 0.1 $\mathrm{mN \cdot m^{-1}}$. The density data were obtained using a buoyancy method with an estimated expanded uncertainty at 0.95 confidence level of $3 \cdot 10^{-4}\rho$. An analysis of the experimental density data, using a group contribution model, performed for eight ionic liquids with the 1-C_n-3-methylimidazolium cation ($n = 2, 4, 6$) and tetrafluoroborate and trifluoromethanesulfonate and the dicyanamide anion indicates that the uncertainty arising from impurities present in the sample is dominant. The upper-bound estimate for the overall expanded uncertainty ($k = 2$) in the density measurements including the uncertainty stemming from impurities in the sample is equal to $\pm 0.002\rho$. The model is capable of providing predictions for pure imidazolium-based ionic liquids with $[BF_4]$, $[CF_3SO_3]$, and $[N(CN)_2]$ anions.

INTRODUCTION

In recent years, ionic liquids attract continuous interest of both academic and industrial researchers as promising substances for the development of environmentally friendly chemical products and processes. For the proper design of any industrial process using ionic liquids, it is necessary to know their thermophysical properties such as the density, heat capacity, and viscosity. Comprehensive property data are also requisite for the development of correlations and predictive schemes. As a result, an extensive experimental research on thermophysical properties of ionic liquids is being conducted. Nevertheless, for many ionic liquids, data on different thermophysical properties are still available only from a few literature sources or even are nonexistent at all.[1] Moreover, the results reported by different authors or obtained by different methods often exhibit remarkable differences and by far do not agree within their stated uncertainties, whether due to the concrete realization of the method employed or owing to impurities contained in the samples used. The information given by the authors of the data on how the data have been obtained is often not sufficient to explain post facto how these differences have arisen. Only a large body of experimental data obtained by different authors using different methods and samples from different sources provides a base to assess critically the reliability of each individual data set. The reliability of the resultant data can be established with the aid of correlation model capable of providing accuracy near to that of the experimental data. Therefore, further experimental studies are required to accumulate a database sufficiently large so that reliable property values can be derived based on it.

The main aim of the present study was to perform measurements of the surface tension and density at atmospheric pressure in the temperature range from (278 to 356) K for 1-ethyl- and 1-butyl-3-methylimidazolium dicyanamide. The study is a continuation of our previous similar studies for 1-alkyl-3-methylimidazolium-based ionic liquids with tetrafluoroborate and trifluoromethanesulfonate anions.[2−6] Tables 1 and 2 give an overview of the literature sources for experimental surface tension[7−11] and for density data[8,10−18] for the two ionic liquids of interest, together with the corresponding temperature region, sample water content, the measuring method used, and the number of data points. The 11 available studies provide a total of 16 data points for the surface tension and 149 data points for a 0.1 MPa density of the two ionic liquids of interest.

The second objective of the study was to establish reliable density values for the investigated ionic liquids with the aid of an intercomparison of all of the available 0.1 MPa density data for ionic liquids with a 1-alkyl-3-methylimidazolium cation and with tetrafluoroborate, trifluoromethanesulfonate, and dicyanamide anions. On this basis, the upper-bound estimation of the real uncertainty of the performed density measurements is evaluated. To analyze the mutual consistency of the data sets by different authors and to identify the data that may be considered as outliers with remarkable differences from others, we developed a group contribution model to predict the density at the atmospheric pressure for the ionic liquids of interest as a function of the temperature. The model is based on the same assumptions as that proposed by Rebelo et al.[19] for ionic liquids with the 1-alkyl-3-methylimidazolium cation and with $[BF_4]$, $[PF_6]$, $[NTf_2]$, $[NO_3]$, and [Cl] anions. Esperanca et al.[20] extended the model to phosphonium-based ionic liquids with [Cl], $[CH_3CO_2]$, and

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Table 1. Literature Sources for Experimental Surface Tension Data for the Ionic Liquids of Interest with the Sample Water Content Given as Water Mass Fraction, *w*

author(s)	year	temp. range T/K	methods	no. of data	$w \cdot 10^6$
1-Ethyl-3-methylimidazolium Dicyanamide [EMIM][N(CN)$_2$]					
Martino et al.[7]	2006	298.15	capillary rise	1	n/a
Froba et al.[8]	2008	293.15	pendant drop	1	1886
Fletcher et al.[9]	2010	293	du Noüy ring	1	100
this work	2011	278.18 to 348.54	Wilhelmy plate	15	120
	2011	278.16 to 356.46	du Noüy ring	16	120
1-Butyl-3-methylimidazolium Dicyanamide [BMIM][N(CN)$_2$]					
Sanchez et al.[10]	2009	293.15 to 344.15	du Noüy ring	12	68
Carrera et al.[11]	2010	293.15	pendant drop	1	150
this work	2011	282.53 to 356.49	Wilhelmy plate	15	46
	2011	282.54 to 356.47	du Noüy ring	15	46

Table 2. Literature Sources for Experimental Density Data for the Ionic Liquids of Interest with the Sample Water Content Given as Water Mass Fraction, *w*

author(s)	year	temp. range T/K	methods[a]	no. of data	$w \cdot 10^6$
1-Ethyl-3-methylimidazolium Dicyanamide [EMIM][N(CN)$_2$]					
Froba et al.[8]	2008	273.15 to 363.15	vtd	19	1886
Wong et al.[12]	2008	303.2 to 323.2	vtd	5	n/a
Schreiner et al.[13]	2010	298.15 to 333.15	vtd	5	30
this work	2011	278.22 to 356.09	hbd	16	120
1-Butyl-3-methylimidazolium Dicyanamide [BMIM][N(CN)$_2$]					
Fredlake et al.[14]	2004	297.15 to 355.85	pyc	6	5150
Stoppa et al.[15]	2009	298.15	vtd	1	50
Sanchez et al.[10]	2009	293.15 to 363.15	vtd	8	680
Carvalho et al.[16]	2010	278.15 to 363.15	vtd	18	28
Zech et al.[17]	2010	278.15 to 338.15	vtd	7	80
Carrera et al.[11]	2010	293.15	pyc	1	150
Castro et al.[18]	2010	293.15 to 363.15	vtd	79	110
this work	2011	282.57 to 356.24	hbd	15	46

[a] vtd: vibrating tube densitometer, pyc: pycnometer, htd: hydrostatic-balance densitometer.

[NTf$_2$] anions. Jacquemin et al.[21] developed a model of the same type based on a collection of 16 ionic liquids with six different cations with an alkyl side chain and with [BF$_4$], [PF$_6$], [NTf$_2$], [OTf], [EtSO$_4$], [FAP], and [SCN] anions. Our model is based on 861 data points from our measurements and from the literature for the density of the 1-alkyl-3-methylimidazolium-based ionic liquid with [BF$_4$], [CF$_3$SO$_3$], and [N(CN)$_2$] anions.

EXPERIMENTAL SECTION

Materials. Table 3 gives the suppliers of the samples used in the present measurements, minimum mass fraction purities of the samples as specified by suppliers, and the water content expressed by the water mass fraction as measured in our laboratory with the coulometric Karl Fischer titrator Mettler Toledo C30 just before the measurements. The samples were used without further purification except drying.

Surface Tension and Density Measurements. In the present study, both the surface tension and the density measurements were performed using the Krüss K100MK2 tensiometer. For the surface tension measurements the Wilhelmy plate method and the du Noüy ring method were used in parallel while the density was measured by the buoyancy method. The essential details of the apparatus and the experimental procedures have been described elsewhere.[2] Here, we only recall the details relevant to the resultant data accuracy. The sample vessel of the apparatus is placed in a vessel thermostatted externally by a Julabo MB-5 thermostat, which gives a bath temperature stability of ± 0.02 K. At temperatures below 298 K, in addition, external immersion cooler Lauda ETK30 is employed. In this way, the sample temperature stability of the order of magnitude of 0.01 K is achieved. The sample temperature is measured with a platinum resistance thermometer immersed into the sample with a manufacturer's stated standard uncertainty of 0.02 K.

The Wilhelmy plate surface tension measurement procedure was tested by measuring the surface tension of water and methanol. The results obtained for methanol were published in a separate paper.[22] The deionized water supplied by Carl Roth GmbH & Co. KG under the registered mark Rotipuran p.a. (puriss grade) and the dried methanol supplied by Merck KGaA under the registered mark SeccoSolv were employed for the testing. The maximal mass fraction of H_2O contained in the methanol sample as specified by supplier was $5 \cdot 10^{-5}$. The expanded combined uncertainty at 0.95 confidence level $u_c(\gamma)$ associated with the method is estimated to be 0.1 $\text{mN} \cdot \text{m}^{-1}$ for the resultant surface tension values γ.

For the purpose of the buoyancy density measurements, the apparatus was calibrated[5] using toluene as a calibration standard. The buoyancy density measurement procedure was tested by measuring the density of water (Rotipuran p.a., Merck). A set of 725 density values measured at temperatures from (283 to 343) K show a single measurement standard deviation of $15 \cdot 10^{-5}\rho$ from the IAPWS-95 formulation[23] of the thermodynamic properties of water. The average absolute deviation of the data set from the IAPWS-95 formulation[23] equals $12 \cdot 10^{-5}\rho$, while the mean arithmetic deviation is $2 \cdot 10^{-5}\rho$. The experimental uncertainty of the buoyancy density measurements may somewhat differ for individual ionic liquids owing to their different viscosity, thermal conductivity, and isobaric heat capacity, which affects the action of natural convection. The uncertainty associated with possible impurities contained in the sample is discussed in the Results and Discussion section. The repeatability of the present surface tension, density, and temperature measurements expressed in terms of the experimental standard deviation of the values obtained within one experimental run is typically 0.05 $\text{mN} \cdot \text{m}^{-1}$, 0.05 K, and 0.2 $\text{kg} \cdot \text{m}^{-3}$, respectively.

The measurements were performed in 4 h periods, one period a day. After each 4 h measurement period, the samples were dried by intensive stirring and evaporation under vacuum at a temperature of 353 K for 4 h and then kept under vacuum overnight. The mass fraction water content of $(30 \text{ to } 100) \cdot 10^{-6}$ was usually achieved. The water content of the samples was measured in our laboratory with the coulometric Karl Fischer titrator Mettler Toledo C30.

The measurements were taken at the only one temperature during each 4 h measurement period. No change in the surface tension or density value that could be attributed to the increased mass fraction of the gases or moisture absorbed from air by the sample was observed during particular one-day measurements.

Table 3. Suppliers of the Ionic Liquid Samples Used in the Present Study, Their Stated Mass Fraction Purities, and Water Mass Fraction, *w*

ionic liquid	supplier	mass fraction purity	$w \cdot 10^6$
$[EMIM][N(CN)_2]$	Merck[a]	0.98	120
$[BMIM][N(CN)_2]$	Merck[a]	0.98	46

[a] Merck KGaA, Darmstadt, Germany.

Table 4. 1-Ethyl-3-Methylimidazolium Dicyanamide, $[EMIM][N(CN)_2]$: Mean Values of the Experimental Readings of Temperature, T, and Surface Tension, γ, with Their Expanded Uncertainties at the 0.95 Confidence Level, $2u(T)$, and $2u(\gamma)$, Evaluated from the Standard Deviation of the Mean by Applying Coverage Factor $k = 2$, and the Number of the Averaged Data Readings

$T \pm 2u(T)$ K	$\gamma \pm 2u(\gamma)$ $mN \cdot m^{-1}$	no. of data
	Wilhelmy Plate Method	
278.18 ± 0.006	61.74 ± 0.030	30
282.17 ± 0.002	61.23 ± 0.006	254
288.32 ± 0.002	60.67 ± 0.008	97
292.96 ± 0.001	60.47 ± 0.006	158
298.31 ± 0.001	60.00 ± 0.014	130
303.06 ± 0.001	59.62 ± 0.008	195
308.37 ± 0.002	59.40 ± 0.002	113
313.30 ± 0.002	58.84 ± 0.005	75
318.40 ± 0.002	58.54 ± 0.006	329
323.52 ± 0.003	58.18 ± 0.008	151
328.38 ± 0.002	57.96 ± 0.003	119
333.33 ± 0.005	57.50 ± 0.006	79
338.11 ± 0.008	56.98 ± 0.011	49
343.19 ± 0.008	56.71 ± 0.007	285
348.45 ± 0.007	56.36 ± 0.010	138
	du Noüy Ring Method	
278.16 ± 0.004	61.96 ± 0.015	10
282.21 ± 0.017	61.63 ± 0.017	10
288.28 ± 0.005	61.07 ± 0.025	10
292.96 ± 0.007	61.27 ± 0.013	10
298.30 ± 0.008	60.62 ± 0.012	10
303.07 ± 0.006	60.56 ± 0.019	10
308.32 ± 0.021	60.13 ± 0.019	10
313.38 ± 0.021	59.89 ± 0.022	10
318.38 ± 0.019	58.88 ± 0.029	10
323.62 ± 0.040	58.93 ± 0.015	10
328.35 ± 0.040	58.26 ± 0.038	10
333.33 ± 0.027	57.82 ± 0.043	10
338.21 ± 0.044	57.31 ± 0.038	10
343.25 ± 0.038	56.85 ± 0.045	10
348.34 ± 0.012	57.03 ± 0.022	10
356.46 ± 0.019	55.62 ± 0.089	10

Table 5. 1-Butyl-3-Methylimidazolium Dicyanamide, $[BMIM][N(CN)_2]$: Mean Values of the Experimental Readings of Temperature, T, and Surface Tension, γ, with Their Expanded Uncertainties at the 0.95 Confidence Level, $2u(T)$, and $2u(\gamma)$, Evaluated from Standard Deviation of the Mean by Applying Coverage Factor $k = 2$, and the Number of the Averaged Data Readings

$T \pm 2u(T)$ K	$\gamma \pm 2u(\gamma)$ $mN \cdot m^{-1}$	no. of data
	Wilhelmy Plate Method	
282.53 ± 0.002	46.71 ± 0.015	81
288.31 ± 0.002	46.37 ± 0.018	44
292.97 ± 0.001	46.14 ± 0.007	257
298.67 ± 0.002	45.81 ± 0.007	284
303.21 ± 0.001	45.42 ± 0.008	207
308.40 ± 0.002	45.33 ± 0.005	245
313.40 ± 0.002	45.01 ± 0.009	130
318.59 ± 0.002	44.81 ± 0.006	104
323.24 ± 0.002	44.47 ± 0.022	55
328.43 ± 0.002	44.21 ± 0.008	196
333.09 ± 0.002	43.98 ± 0.018	47
338.46 ± 0.003	43.65 ± 0.016	65
343.34 ± 0.003	43.48 ± 0.008	60
348.72 ± 0.004	43.16 ± 0.006	141
356.49 ± 0.013	42.72 ± 0.013	68
	du Noüy Ring Method	
282.54 ± 0.025	46.51 ± 0.115	10
288.36 ± 0.010	46.40 ± 0.073	10
292.97 ± 0.009	46.24 ± 0.096	10
298.69 ± 0.009	45.88 ± 0.078	10
303.20 ± 0.007	45.87 ± 0.060	10
308.43 ± 0.013	45.56 ± 0.053	10
313.45 ± 0.020	44.99 ± 0.108	10
318.82 ± 0.017	45.11 ± 0.045	10
323.30 ± 0.017	44.50 ± 0.058	10
328.55 ± 0.024	44.12 ± 0.049	10
333.18 ± 0.012	43.99 ± 0.041	10
338.48 ± 0.022	43.53 ± 0.093	10
343.65 ± 0.018	43.22 ± 0.153	10
348.78 ± 0.038	43.48 ± 0.091	10
356.47 ± 0.015	42.66 ± 0.101	10

These results are consistent with those obtained in our previous studies.[22,24] At low water molar fractions, in general, below a certain value of about $x = 2.5 \cdot 10^{-4}$ ($w \approx 1000 \cdot 10^{-6}$) the surface tension of ionic liquids depends on the water content much less than for higher water concentrations in the sample.

■ RESULTS AND DISCUSSION

Surface Tension. For each IL sample, a total of about 2000 individual Wilhelmy plate and about 160 du Noüy ring readings were taken at 15 temperature points between (278 and 356) K. In most cases, at each temperature, three runs were performed with the Wilhelmy plate. Each withdrawal of the Wilhelmy plate gives from 6 to 7 evaluated individual readings of the surface tension force as a rule. One du Noüy ring run was taken as a rule containing 10 readings of the surface tension force. In comparison with the surface tension measurements on

Table 6. Coefficients γ_0 and T_0 of eq 1, Their 0.95 Confidence Interval Half-Width, $u(\gamma_0)$, and $u(T_0)$, and the Root-Mean-Square Deviation, rmsd, of the Experimental Data from eq 1

	$\gamma_0 \pm u(\gamma_0)$	$T_0 \pm u(T_0)$	rmsd
ionic liquid	$\mathrm{mN \cdot m^{-1}}$	K	$\mathrm{mN \cdot m^{-1}}$
[EMIM][N(CN)$_2$]	82.26 ± 0.77	1105.0 ± 26.0	0.09
[BMIM][N(CN)$_2$]	61.72 ± 0.43	1158.0 ± 21.0	0.05

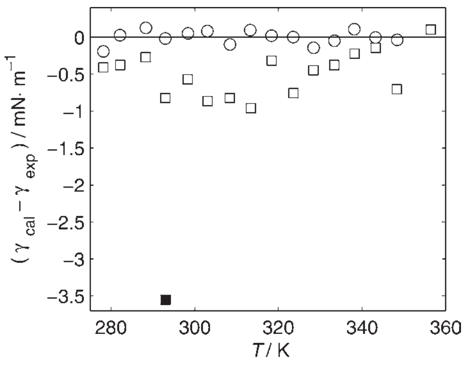

Figure 1. [EMIM][N(CN)$_2$]: deviations of experimental surface tension data, γ_{exp}, of different authors from the values, γ_{cal}, calculated from eq 1 as a function of temperature T. ■, Fletcher et al.;[9] ○, this work (Wilhelmy plate method); □, this work (du Noüy ring method). Data from two literature sources[7,8] are not shown due to high deviation.

1-alkyl-3-methylimidazolium-based ionic liquids with [PF$_6$], [NTf$_2$], [CF$_3$SO$_3$], and [BF$_4$] anions performed previously in our laboratory,[2−4] it was much more difficult to obtain for dicyanamides at different temperatures surface tension values reasonably consistent to each other, obeying a linear temperature dependence. The sample had to be stirred before each measurement run to homogenize possible surface-active impurities accumulated in the surface layer. The values obtained without stirring show a scatter of several percent of the measured surface tension value. Tables 4 and 5 give averages of the values of the temperature and surface tension obtained at the individual set point temperatures together with the type A expanded uncertainty at the 0.95 confidence level calculated from the standard deviation of the mean by applying the coverage factor k = 2. The last column of the table gives the number of the averaged individual data readings. The experimental Wilhelmy plate surface tension data were correlated using eq 1.

$$\gamma(T) = \gamma_0\left(1 - \frac{T}{T_0}\right) \qquad (1)$$

Table 6 gives the coefficients of the correlation of the Wilhelmy data points for the samples studied together with the estimates of the uncertainty at 0.95 confidence level for the equation parameters and the root-mean-square deviation (rmsd) of the experimental surface tension values from those calculated from eq 1. In Figures 1 and 2, deviations from eq 1 are plotted of the present experimental data and of the data reported by other authors. The obtained linear dependence of the measured surface tension with temperature as well as the repeatability of the results over the 14 days measurements indicates the preservation of the sample integrity.

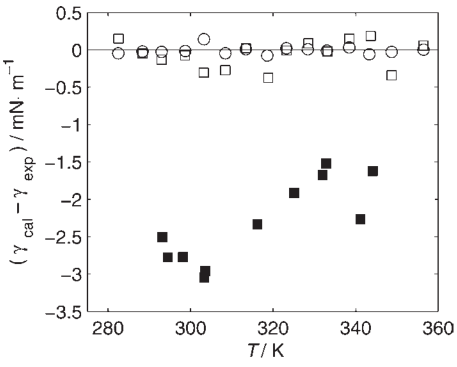

Figure 2. [BMIM][N(CN)$_2$]: deviations of experimental surface tension data, γ_{exp}, of different authors from the values, γ_{cal}, calculated from eq 1 as a function of temperature T. ■, Sanchez et al.;[10] ○, this work (Wilhelmy plate method); □, this work (du Noüy ring method). One literature source[11] is not shown due to high deviations.

The difficulty of the surface tension measurements for 1-alkyl-3-methylimidazolium dicyanamides seems to be documented by the extreme magnitude of the differences between data from different authors, which are of the order of percent relatively to the measured surface tension γ up to 0.29γ. Only the surface tension−temperature relation obtained for [BMIM][N(CN)$_2$] by Sanchez et al.[10] agrees with the present results within ± 3 $\mathrm{mN \cdot m^{-1}}$ (Figure 2). The surface tension values obtained by Carrera et al.[11] are by 0.17γ less than ours, while the values by Sanchez et al. are up to 0.06γ greater. For [EMIM][N(CN)$_2$] surface tension, only three data points are available in the literature obtained by Martino et al.[7] Froba et al.,[8] and Fletcher et al.,[9] with deviations from the correlation eq 1 of 0.06γ, −0.27γ, and −0.29γ, respectively.

Both the discussed imidazolium-based ionic liquids show a linear variation of the surface tension with temperature. Therefore, the values of the surface entropy equal to the negative temperature derivative of the surface tension, $s^{\gamma}(T) = -\mathrm{d}\gamma/\mathrm{d}T$, are constant with temperature. The surface tension of [EMIM][N(CN)$_2$] reach the highest value among ionic liquids with [BF$_4$], [CF$_3$SO$_3$], [NTf$_2$], and [PF$_6$] anions.[4] With exception of the two anions, [NTf$_2$] and [CF$_3$SO$_3$], the surface entropy values follow for the [EMIM] cation the same order of anions as the surface tension values itself, which is identical to their order according to decreasing effective volume of the cation. The two dicyanamides of interest make an exception to the rule that for 1-alkyl-3-methylimidazolium based ionic liquids the surface entropy increases with the cation alkyl said-chain length.[4]

Density. The present study provides 31 new experimental data points on the density−temperature relation at a pressure of 0.1 MPa for the two imidazolium-based ionic liquids with dicyanamide anion. These experimental density values are means calculated from a total of about 1450 and 2300 individual buoyancy readings on [EMIM][N(CN)$_2$] and [BMIM][N(CN)$_2$], respectively, which have been altogether taken in the present study at 16 temperature points between (278 and 356) K. Table 7 gives averages of all of the values of temperature and density obtained at the individual nominal temperature points together with the estimate of their type A expanded uncertainty at the 0.95 confidence level calculated in the same way as in the case of the surface tension. The last column of the table gives the number of the averaged individual data readings. The data were fitted to a rational equation:

$$\rho(T) = \frac{\rho_0}{1 + a\tau} \qquad (2)$$

Table 7. Mean Values of the Experimental Readings of Temperature, T, and Density, ρ, with their Expanded Uncertainties at a 0.95 Confidence Level, $2u$, Evaluated from the Standard Deviation of the Mean by Applying Coverage Factor $k = 2$, and the Number of the Averaged Data Readings

$T \pm 2u$ K	$\rho \pm 2u$ $\mathrm{kg \cdot m^{-3}}$	no. of data
1-Ethyl-3-methylimidazolium Dicyanamide $[\mathrm{EMIM}][\mathrm{N(CN)_2}]$		
278.22 ± 0.001	1122.06 ± 0.009	60
282.14 ± 0.008	1119.35 ± 0.014	94
288.24 ± 0.006	1114.86 ± 0.009	122
292.97 ± 0.006	1111.51 ± 0.011	94
298.33 ± 0.002	1108.17 ± 0.021	157
303.07 ± 0.002	1104.91 ± 0.021	107
308.40 ± 0.002	1101.67 ± 0.011	80
313.41 ± 0.002	1098.36 ± 0.007	67
318.47 ± 0.001	1095.19 ± 0.012	80
323.54 ± 0.002	1091.80 ± 0.011	60
328.39 ± 0.002	1088.97 ± 0.009	80
333.31 ± 0.002	1085.89 ± 0.020	80
337.99 ± 0.004	1082.80 ± 0.033	80
343.12 ± 0.006	1079.98 ± 0.007	148
348.32 ± 0.006	1076.33 ± 0.021	80
356.09 ± 0.008	1071.84 ± 0.022	60
1-Butyl-3-methylimidazolium Dicyanamide $[\mathrm{BMIM}][\mathrm{N(CN)_2}]$		
282.57 ± 0.003	1069.14 ± 0.022	139
288.35 ± 0.006	1065.46 ± 0.021	130
292.96 ± 0.008	1062.23 ± 0.060	41
298.68 ± 0.003	1058.58 ± 0.024	157
303.20 ± 0.003	1055.80 ± 0.025	192
308.39 ± 0.003	1052.72 ± 0.019	211
313.34 ± 0.002	1049.45 ± 0.027	134
318.75 ± 0.002	1046.21 ± 0.018	233
323.43 ± 0.002	1043.15 ± 0.020	136
328.43 ± 0.003	1040.34 ± 0.010	216
333.23 ± 0.004	1037.03 ± 0.020	238
338.44 ± 0.006	1034.31 ± 0.011	107
343.31 ± 0.007	1031.35 ± 0.012	121
348.66 ± 0.008	1028.19 ± 0.016	70
356.24 ± 0.010	1023.40 ± 0.014	208

where $\tau = T/100$. Table 8 gives coefficients ρ_0 and a of eq 2 used to correlate the experimental data together with the estimates of their uncertainty at 0.95 confidence level and the rmsd of the experimental density values from those calculated from eq 2. The standard deviation of the density from the fitting function eq 2 of 0.23 $\mathrm{kg \cdot m^{-3}}$ for $[\mathrm{EMIM}][\mathrm{N(CN)_2}]$ and 0.14 $\mathrm{kg \cdot m^{-3}}$ for $[\mathrm{BMIM}][\mathrm{N(CN)_2}]$ are consistent with the result of calibration measurements on water (rmsd = 0.15 $\mathrm{kg \cdot m^{-3}}$). Figures 3 and 4 show deviations of the experimental data points from eq 2.

The density values obtained for $[\mathrm{EMIM}][\mathrm{N(CN)_2}]$ by Wong et al.[12] are by about 0.8 $\mathrm{kg \cdot m^{-3}}$ (i.e., by about 0.0007ρ) greater than our present density values for $[\mathrm{EMIM}][\mathrm{N(CN)_2}]$, which are approximately by about 8 $\mathrm{kg \cdot m^{-3}}$ (i.e., 0.007ρ) greater than the values obtained by Schreiner et al.[13] (Figure 3). Our results for $[\mathrm{BMIM}][\mathrm{N(CN)_2}]$ agree within $\pm 0.001\rho$ with the vibrating-tube densimeter results by Zech et al.[17] and Sanchez et al.[10] (Figure 4). The temperature dependence of the $[\mathrm{BMIM}][\mathrm{N(CN)_2}]$ density obtained by other authors differs from that obtained by us by up to 0.004ρ (6 $\mathrm{kg \cdot m^{-3}}$).[16]

Table 8. Coefficients ρ_0 and a of eq 2, Their 0.95 Confidence Interval Half-Widths, $2u(\rho_0)$ and $2u(a)$, and Root-Mean-Square Deviation, rmsd, of the Experimental Data from eq 2

ionic liquid	$\rho_0 \pm 2u(\rho_0)$ $\mathrm{kg \cdot m^{-3}}$	$a \pm 2u(a)$	rmsd $\mathrm{kg \cdot m^{-3}}$
$[\mathrm{EMIM}][\mathrm{N(CN)_2}]$	1346.0 ± 2.5	$(7.190 \pm 0.070) \cdot 10^{-2}$	± 0.21
$[\mathrm{BMIM}][\mathrm{N(CN)_2}]$	1288.7 ± 1.9	$(7.273 \pm 0.056) \cdot 10^{-2}$	± 0.14

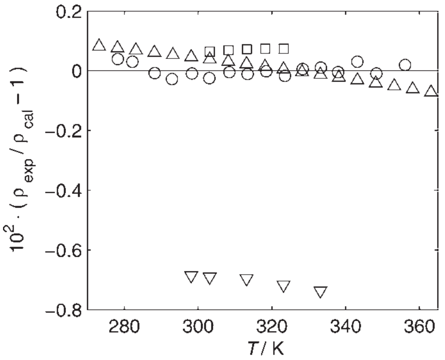

Figure 3. $[\mathrm{EMIM}][\mathrm{N(CN)_2}]$: deviations of experimental density data, ρ_{exp}, of different authors from the values, ρ_{cal}, calculated from eq 2 as a function of temperature T. △, Froba et al.;[8] □, Wong et al.;[12] ▽, Schreiner et al.;[13] ○, this work.

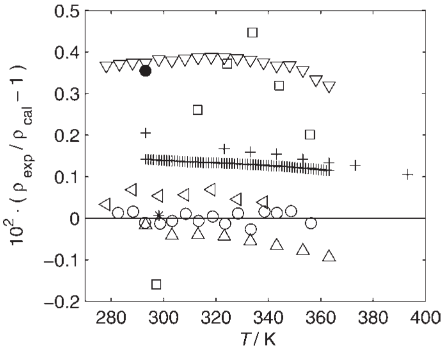

Figure 4. $[\mathrm{BMIM}][\mathrm{N(CN)_2}]$: deviations of experimental density data, ρ_{exp}, of different authors from the values, ρ_{cal}, calculated from eq 2 as a function of temperature T. △, Sanchez et al.;[10] ●, Carrera et al.;[11] □, Fredlake et al.;[14] ∗, Stoppa et al.;[15] ▽, Carvalho et al.;[16] left-pointing triangle, Zech et al.;[17] +, Castro et al.;[18] ○, this work.

Density Data Analysis. To assess the reliability of the 0.1 MPa density data by different authors from their intercomparison, we developed a model based on the group contribution method. We assume that in the temperature range of interest the molar volume V_m of a general system containing N^+ different 1-alkyl-3-methylimidazolium cations and N^- different anions can be described by eq 3 as a sum of contributions

V_i^+ ($i = 1, ..., N^+$) and V_j^- ($j = 1, ..., N^-$) of the individual anions and cations, respectively.

$$V_m = \sum_{i=1}^{N^+} x_i^+ V_i^+ + \sum_{j=1}^{N^-} x_j^- V_j^- \tag{3}$$

Here x_i^+ and x_j^- are the molar fractions of the singly charged cations and anions, respectively, which must obey the electroneutrality condition $\Sigma x_i^+ = \Sigma x_i^- = 1/2$. Each of the contributions V_i^+ and V_j^- is assumed to depend linearly on the temperature. Further, we assume that the value of the contribution V_i^+ of the i-th cation consists of the contribution $a_{\mathrm{MIM}} + b_{\mathrm{MIM}}\tau$ from the methylimidazolium group of the cation and of the contribution $(a^+ + b^+\tau)n_i$ of the number n_i of pairs of CH_2 groups in the i-th cation alkyl side chain. The convention for n we introduce in agreement with other authors[19−21] to obtain results directly comparable with theirs. 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 has the form $V_j^- = a_j^- + b_j^-\tau$. In general, terms involving higher powers of temperature can be introduced into the model if they are statistically significant. But it is not the case of the present data, which cover a relatively narrow temperature interval.

On the basis of these assumptions, the molar volume V_m of a general ionic liquid system is expressed by eq 4

$$V_m/(\mathrm{cm^3 \cdot mol^{-1}}) = \frac{1}{2}(a_{\mathrm{MIM}} + b_{\mathrm{MIM}}\tau) + (a^+ + b^+\tau)\sum_{i=1}^{N^+} x_i^+ n_i + \sum_{j=1}^{N^-} x_j^-(a_j^- + b_j^-\tau) \tag{4}$$

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. Thus, the number of parameters of the model eq 4 is equal to $2N^- + 4$.

For pure ionic liquids the model eq 4 reduces to a set of equations for the individual ionic liquids with $x_i^+ = x_j^- = 1/2$ for all i and j. 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 $a_j^\pm = (a_{\mathrm{MIM}} + a_j^-)/2$ and $b_j^\pm = (b_{\mathrm{MIM}} + b_j^-)/2$. For the molar volume V_{ij} of a ionic liquid consisting of the i-th cation and the j-th anion one thus obtains

$$V_{ij}/(\mathrm{cm^3 \cdot mol^{-1}}) = a_j^\pm + b_j^\pm\tau + (a^+ + b^+\tau)n_i \tag{5}$$

The coefficient $a_j^\pm$ represents the common contribution of the methylimidazolium cation $[\mathrm{MIM}]^+$ 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 $(a^+ + b^+\tau)n_i$ represents the contribution of the alkyl side chain of the cation containing n_i 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^+ equals to the variation of the molar volume V_{ij} per addition of two carbon atoms into the alkyl side chain of the cation at this temperature.

We apply the model in eq 5 on the density data for the eight 1-alkyl-3-methylimidazolium-based ionic liquids the 0.1 MPa density of which we have measured up to now.[5,6] While for separate correlation of the density data for the eight ionic liquids considered 16 parameters are needed, the model eq 5 require only 8 adjusted parameters. A total of 861 data points by different authors for eight ionic liquids with 1-C_n-3-methylimidazolium cations with $n = 2$, 4, and 6 and with anions $[BF_4]$, $[CF_3SO_3]$, and $[N(CN)_2]$ were analyzed using the group contribution model of eq 5. The model parameters were determined by minimization of the objective function S given by eq 6

Table 9. Coefficients $a_j^\pm$, $b_j^\pm$, a^+, and b^+ of eq 5 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	$[\mathrm{MIM}]^+ + [BF_4]$	120.80	± 0.09	6.49	± 0.36
2	$[\mathrm{MIM}]^+ + [CF_3SO_3]$	154.40	± 0.07	9.46	± 0.31
3	$[\mathrm{MIM}]^+ + [N(CN)_2]$	126.14	± 0.08	7.02	± 0.32
		a^+	$\pm 2u(a^+)$	b^+	$\pm 2u(b^+)$
	CH_2	33.69	± 0.04	2.32	± 0.15

$$S = \sum_{i,j,k}[a_j^\pm + b_j^\pm\tau_k + (a^+ + b^+\tau_k)n_i - V_{ij}^{\mathrm{exp}}(\tau_k)]^2 \tag{6}$$

The summation is taken over the ionic liquids with i-th cation and j-th anion and over the temperature points τ_k at which the molar volume V_{ij}^{exp} of the ionic liquid is given by the experiment. Table 9 gives the least-squares estimates of the model parameters together with their 0.95 confidence intervals obtained using the procedure *nlinfit* from the Matlab Statistic Toolbox. The resultant correlation is characterized by the value of the average absolute relative deviation AARD (eq 7) of 0.0026.

$$\mathrm{AARD} = \frac{1}{N}\sum_{i,j,k}|\rho_{ijk}^{\mathrm{exp}}/\rho_{ijk}^{\mathrm{calc}} - 1| \tag{7}$$

where $\rho_{ijk}^{\mathrm{exp}}$ is the experimental value of the density of the ionic liquid with the i-th cation and j-th anion at temperature τ_k and $\rho_{ijk}^{\mathrm{calc}}$ is the corresponding density value calculated from the model. The deviations of 774 data points from the model in eq 5 fall within the limits of $\pm 0.004V_m$. The 11 outlier data sets, all points of which have deviations from the common correlation greater than $0.01V_m$, contain altogether only 50 data points. Deviations of all experimental density values for the eight ionic liquids of interest available in literature from the group contribution model eq 5 are shown in Figures S1 to S8 in the Supporting Information.

The obtained values of the model parameters a^+ and $a_{[BF_4]}^\pm$ (Table 9) 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 the addition of two carbon atoms into the alkyl side chain of the cation is equal to $(33.69 \pm 0.04)\ \mathrm{cm^3 \cdot mol^{-1}}$. This value differs by 2 % from the value $(34.4 \pm 0.5)\ \mathrm{cm^3 \cdot mol^{-1}}$ obtained by Rebelo et al.,[19] 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 $a_{[BF_4]}^\pm = (a_{\mathrm{MIM}} + a_{[BF_4]}^-)/2$ of our model eq 5 with a value of $120.80\ \mathrm{cm^3 \cdot mol^{-1}}$ (Table 9) corresponds to the sum of the Esperanca et al.[20] effective molar volumes of the cation $[C_0\mathrm{MIM}]^+$ ($V_c^* = 64.82\ \mathrm{cm^3 \cdot mol^{-1}}$) and the anion $[BF_4]$

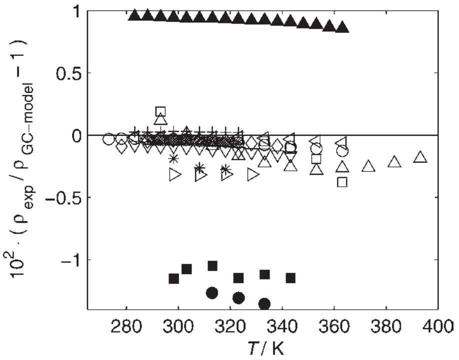

Figure 5. [OMIM][BF_4]: deviations of experimental density data, ρ_{exp}, of different authors from the values, $\rho_{GC\ model}$, calculated from eq 5 as a function of temperature T. Left-pointing triangle, Sanchez et al.;[10] ●, Blanchard et al.;[25] □, Seddon et al.;[26] ■, Gu and Brennecke;[27] ○, Harris et al.;[28] △, Gardas et al.;[29] ×, Sanmamed et al.;[30] ▲, Mokhtarani et al.;[31] ▽, Kumar;[32] *, Singh and Kumar;[33] right-pointing triangle, Restolho et al.;[34] ◇, Stoppa et al.;[35] +, Sanmamed et al.[36]

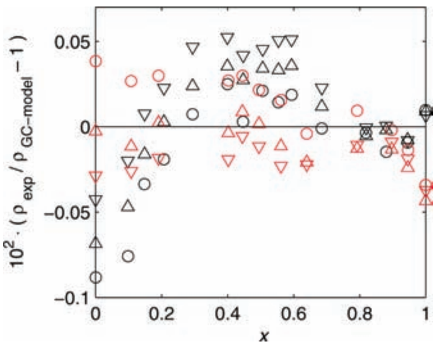

Figure 6. Deviations of the experimental data on the mixture density ρ_{exp} by Navia et al.[37] from the values of $\rho_{GC\ model}$ calculated from eq 5 as a function of the molar fraction x. x[HMIM][BF_4] + $(1 - x)$[EMIM][BF_4]: black ○, $T = 298.15$ K; black △, $T = 303.15$ K; black ▽, $T = 308.15$ K. x[HMIM][BF_4] + $(1 - x)$[BMIM][BF_4]: red ○, $T = 298.15$ K; red △, $T = 303.15$ K; red ▽, $T = 308.15$ K.

($V_a{}^* = 53.4\ \text{cm}^3 \cdot \text{mol}^{-1}$) given in Table 4 of ref 20. which equals 118.22 $\text{cm}^3 \cdot \text{mol}^{-1}$.

The predictive capability of the model is validated by comparing its predicted densities with experimental results obtained from experiments for [OMIM][BF_4][10,25−36] and two binary mixtures, x[HMIM][BF_4] + $(1 - x)$[EMIM][BF_4] and x[HMIM][BF_4] + $(1 - x)$[BMIM][BF_4].[37] Figures 5 and 6, showing deviations of the experimental data from the model, demonstrate the capability of the model to predict densities of pure ionic liquids and their mixtures that have not been used in the development of the model. The results for the mixtures give some evidence on the degree of applicability of the ideal mixing approximation to the ionic liquids.

Deviations of our experimental density values[5,6] and this work for the eight ionic liquids of interest from eq 5 are shown in Figure 7. An overwhelming majority of the data points fall within $\pm\ 0.002\rho$ (AARD = 0.13 %) of the proposed correlation, eq 5. This value can be accepted as a reasonable upper-bound estimation of the overall uncertainty in our density measurements.

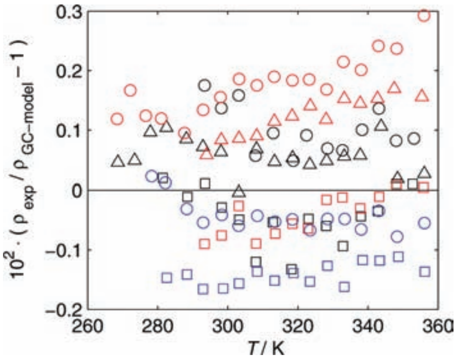

Figure 7. Deviations of the experimental density data, ρ_{exp}, obtained by the authors of the present study for the eight ionic liquids of interest[5,6] and this work from the values $\rho_{GC\ model}$ calculated from the correlation eq 5 as a function of temperature, T. Black ○, [EMIM][BF_4]; black □, [BMIM][BF_4]; black △, [HMIM][BF_4]; red ○, [EMIM][CF_3SO_3]; red □, [BMIM][CF_3SO_3]; red △, [HMIM][CF_3SO_3]; blue ○, [EMIM][$N(CN)_2$]; blue □, [BMIM][$N(CN)_2$].

Besides the experimental apparatus and measuring procedure, the other important source of uncertainty comes from impurities in the sample. As the experimental expanded uncertainty at 0.95 confidence level associated with the measuring method is $3 \cdot 10^{-4}\rho$, the remaining source of uncertainty associated with impurities is to be regarded as the dominating one. The water content and the halides content (Cl^-, Br^-) are commonly believed to be the most important sources of uncertainties. Water and halide content both cause a decrease in density. The studies on the density of IL/water mixtures available in the literature making it possible to quantify the effect of water on the uncertainty of the measured density are for the individual ionic liquids as follows: [EMIM][BF_4],[15,38,39] [BMIM][BF_4],[15,19,40,41] [HMIM][BF_4],[15] [EMIM][CF_3SO_3],[42,43] [BMIM][CF_3SO_3],[44] and [EMIM][DCA].[16]

On the basis of the above-mentioned experimental data, the following general conclusions can be made. For the samples of the ionic liquids of interest containing the water mass fraction w of the order of 10^{-4} or less, the effect of the water content on the sample density is of the order 0.0001ρ or less. The water effect reaches the value of 0.001ρ only for the water mass fraction w of the order 0.002 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.

Quantitative data on the effect of halides on the density of ionic liquids were reported by Jacquemin et al.[21] and Seddon et al.[45] A decrease of about 0.001ρ compared to IL devoid of halides is reported for small halide mass fractions up to $150 \cdot 10^{-6}$. Thus, the deviations from our group contribution model are to be ascribed, besides to the error of the model itself, to impurities other than water.

■ CONCLUSION

A total of 60 new experimental data points for the surface tension and 31 data points for the density of two ionic liquids, namely, 1-ethyl- and 1-butyl-3-methylimidazolium dicyanamide, in the temperature range from (278 to 356) K and at atmospheric pressure are presented. With the exception of three single data points from different authors, data on the surface tension for [EMIM][$N(CN)_2$] were hitherto unavailable in the literature. The 16 new data points on the density for [EMIM][$N(CN)_2$] cover a two times wider temperature interval than the 10 density data points up to now available from the literature.

To establish a basis for attempting to resolve conflicts in published values of density, a predictive model was developed based on the group contribution concept, using a great amount of data by different authors for eight different ionic liquids. The predictive model provides a reasonable basis for the assessment of the reliability of experimental density data through their intercomparison and through determination of the conformity of the individual data sets with the used concept. The effect of impurities other than water in the sample was assessed as dominant in comparison with the contribution to the uncertainty arising from the method and from the water content of the sample. The analysis shows that our density data for the eight studied ionic liquids rank among the data sets that were recognized as the more certain.

■ ASSOCIATED CONTENT

S Supporting Information. Figures 1 to 8: relative deviations of the experimental density data by different authors for ionic liquids with 1-C_n-3-methylimidazolium cations with $n = 2$, 4, and 6 and with anions $[BF_4]$, $[CF_3SO_3]$, and $[N(CN)_2]$, respectively, from the values calculated from the GC model (eq 5) as a function of temperature T. This material is available free of charge via the Internet at http://pubs.acs.org.

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