

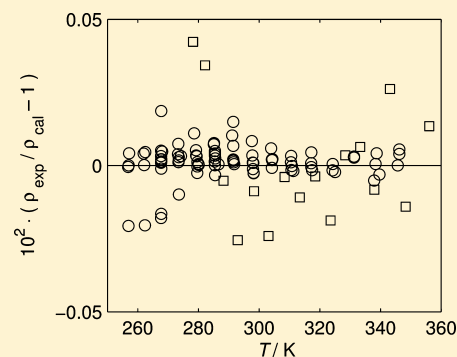
# $P$ – $\rho$ – $T$ Measurements for 1-Ethyl and 1-Butyl-3-methylimidazolium Dicyanamides from Their Melting Temperature to 353 K and up to 60 MPa in Pressure

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**S** Supporting Information

**ABSTRACT:** New experimental data on the density of two 1-alkyl-3-methylimidazolium based dicyanamides ( $[\text{C}_n\text{-MIM}][\text{N}(\text{CN})_2]$ ,  $n = 2$  and 4) are reported, obtained with a constant volume apparatus, which makes possible density measurements at subzero temperatures. The measurements were conducted at temperatures from 350 K down to the melting temperature of the substance and at nominal pressures of 1 MPa and from (10 to 60) MPa with a 10 MPa step. The combined uncertainty at the 0.95 confidence level of the resultant density data is estimated to be less than  $1 \text{ kg}\cdot\text{m}^{-3}$ , that is, 0.1 % relative to the density value. A group contribution model of the  $p$ – $\rho$ – $T$  relation based on a large amount of data by different authors for 1- $\text{C}_n$ -3-methylimidazolium-based ionic liquids with  $n = 2, 4,$  and 6 and with the  $[\text{BF}_4]$ ,  $[\text{CF}_3\text{SO}_3]$ , and  $[\text{N}(\text{CN})_2]$  anions describes the dependence of density, isobaric expansivity, and isothermal compressibility on temperature, pressure, the length of the alkyl side chain of the cation, and the anion. This makes it possible to obtain the most reliable values of the density and to assess which sets of data can be considered as more certain than others.



## INTRODUCTION

Ionic liquids are presently the subject of considerable research interest due to their enormous potential for applications and suitable environmental properties. An extensive research on thermophysical properties of ionic liquids is not inspired solely by concrete applications but equally by the effort to establish a comprehensive base of fundamental knowledge of these properties. Among them, the  $p$ – $\rho$ – $T$  relation of a fluid is a key thermophysical property essential for the development of a thermodynamic property model of the substance. It is also a property which affects nearly all applications of the fluid. Comprehensive property data are also requisite for the development of correlations and predictive schemes. In this respect, the 1-alkyl-3-methylimidazolium-based dicyanamides ( $[\text{C}_n\text{-MIM}][\text{N}(\text{CN})_2]$ ) occupy an important position among the imidazolium-based ionic liquids as they show relatively low density and viscosity and relatively high surface tension. The temperature and pressure dependence of the density of 1-alkyl-3-methylimidazolium dicyanamides have not been studied experimentally very extensively up to now. Density measurements of  $[\text{EMIM}][\text{N}(\text{CN})_2]$  and  $[\text{BMIM}][\text{N}(\text{CN})_2]$  with melting points at (255 and 223) K, respectively, have hitherto been conducted only in the temperature range above room temperature where they are feasible by using a common apparatus. But from the point of view of fundamental knowledge all temperature ranges are equally important. Results of any subsequent analysis of the accumulated experimental data, such as the construction of a predictive scheme, the development of a thermodynamic property formulation, or the theoretical

modeling of the data, are more conclusive when the range of temperatures and pressures of the data on which the analysis is based is broader.

A description of the temperature dependence of the density of the two 1-alkyl-3-methylimidazolium dicyanamides of interest at the pressure 0.1 MPa and a survey of works<sup>1–10</sup> devoted to this topic is given in the paper by Klomfar et al.<sup>11</sup> The pressure dependence of the density of  $[\text{BMIM}][\text{N}(\text{CN})_2]$  has been studied only by de Castro et al.<sup>10</sup> in the temperature region from (293 to 363) K up to 60 MPa. No data are available for the density–pressure dependence of  $[\text{EMIM}][\text{N}(\text{CN})_2]$  in open literature.

The first aim of the present study was to obtain new experimental data for the density of 1- $\text{C}_n$ -3-methylimidazolium dicyanamides with  $n = 2$  and 4 in the temperature region from 353 K down to their melting temperatures, (255 and 223) K, respectively. In the subzero temperature region  $[\text{EMIM}][\text{N}(\text{CN})_2]$  and  $[\text{BMIM}][\text{N}(\text{CN})_2]$  have not yet been studied in this respect at all.

Under the situation when the results of the density measurements for ionic liquids reported by different authors often exhibit remarkable differences and by far do not agree within their stated uncertainties, some additional information is necessary to assess which of the data sets are to be considered more certain than others. To this purpose, a group contribution model is developed

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based on the fact that the dependence of the ionic liquid molar volume on the alkyl side chain length of the cation is linear and the same for the imidazolium based ionic liquids with various anions. The model is based on the same assumptions used by Rebelo et al.,<sup>12</sup> Esperanca et al.,<sup>13</sup> and Jacquemin et al.<sup>14</sup> to develop a group contribution model for the density–temperature relation at 0.1 MPa for different sets of ionic liquids. Gardas and Coutinho<sup>15</sup> extended the group contribution model to describe the temperature and pressure dependence of the density. They assumed for this purpose that the isobaric expansivity and isothermal compressibility have values common for all ionic liquids included into the model.

Our present GC model is, in general, capable of describing the dependence of density, isobaric expansivity, and isothermal compressibility of imidazolium-based ionic liquids on temperature, pressure, the length of the alkyl side chain of the cation, and the anion. The model is based only on density data and requires no additional independent information. It is an extension of the model presented in our previous study<sup>11</sup> for the 0.1 MPa molar volume of 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  $[N(CN)_2]$ .

The group contribution model is used as a tool of performing data quality assessment through their intercomparison. The data conforming better to the model can be considered as more certain in the sense of relative certainty within the context of data by different authors. Though the predictive capability of the model is of secondary importance here, nevertheless it demonstrates the fidelity of the model to the data.

## EXPERIMENTAL SECTION

**Apparatus and Experimental Uncertainties.** The isochoric apparatus used in the present measurements is described in detail elsewhere,<sup>16</sup> together with the measuring and data evaluation procedure. There are also reported results of testing the apparatus. The special features of the apparatus to which the achieved accuracy of the density measurements is to be ascribed are described in the paper ref 17. The apparatus makes possible density measurements at temperatures from (183 to 363) K and up to 60 MPa in pressure. The used isochoric method provides values for the density relative to a density  $\rho_{ref}$  of the sample at some selected reference state  $T_{ref}, p_{ref}$  which is used to determine volumetrically the amount of the sample filled into the measuring cell.<sup>16</sup> The value of the reference density we determined in an independent experiment by using the buoyancy method as described in detail in ref 11. The expanded combined uncertainty at a 0.95 confidence level of the reference density is estimated to be  $0.0002\rho_{ref}$ . The total uncertainty in the resultant values of the density therefore consists of a contribution due to the isochoric method and due to the uncertainty in the reference density value  $\rho_{ref}$ . The overall expanded combined uncertainty at a 0.95 confidence level associated with the isochoric method and the reference density amounts to  $0.001\rho$ .<sup>16</sup> This uncertainty has been evaluated from the quadratic sum of uncertainties in the directly measured quantities that enter the working equation of the method.

The pressure measurements are recorded by two absolute pressure gauges (Paroscientific Inc., Digiquartz model 43KR and 415K) with a measuring range of (20 and 100) MPa, respectively. The manufacturer-specified standard uncertainty of the pressure measurements is 0.01 % of the full gauge range,

that is, less than (0.002 and 0.01) MPa for the range of (20 and 100) MPa, respectively.

The measuring cell temperature is measured on the ITS-90 with a precision thermometry bridge ASL F700 and a 25  $\Omega$  platinum resistance thermometer Tinsley (Type 5187 SA) calibrated with ITS-90 fixed points at National Physical Laboratory, London. The thermometer has a certified uncertainty of  $\pm 1$  mK. The total uncertainty in the temperature measurement due to the thermometer and due to the inhomogeneity of the bath temperature field is estimated to be close to  $\pm 5$  mK.

The special features of the used apparatus to which the achieved accuracy of the density measurement is to be ascribed are as follows: (i) to calibrate the volume of the measuring cell a positive displacement pump/volumeter Ruska (model 2270-803) providing resolution of 0.001 cm<sup>3</sup> is used, (ii) the volumeter is used also to determine the mass of the sample inserted into the measuring cell, (iii) the temperature control of the sample is brought to a metrological level, (iv) the necessary correction to the measured density for the effect of the noxious volume was minimized by the design and it can be accurately evaluated owing to the noxious volume thermostating, and (v) uncertainty contributions following from the accuracy level of the repeated reference state adjustment were minimized by thermostating the volumeter chamber. Complete details are given in ref 16.

**Materials.** Table 1 lists main primary characteristics of the samples studied, including their suppliers, their manufacturer

**Table 1. Basic Information on the Samples Used in the Present Study: Their Suppliers, Stated Mass Fraction Purities, Mass Fraction Water Content, and Their Respective Values of the Reference Parameters  $T_{ref}, p_{ref}$  and  $\rho_{ref}$  Used in Measurements**

	[EMIM][N(CN) <sub>2</sub> ]	[BMIM][N(CN) <sub>2</sub> ]
supplier <sup>a</sup>	Merck	Merck
minimum mass fraction purity	0.98	0.98
water mass fraction $w \cdot 10^6$	145	33
reference temperature $T_{ref}/K$	298.15	298.15
reference pressure $p_{ref}/MPa$	0.1	0.1
reference density $\rho_{ref}/kg \cdot m^{-3}$	1108.36	1059.05

<sup>a</sup>Merck KGaA, Darmstadt, Germany.

stated minimum mass fraction purities, and the initial water mass fraction in the samples as measured in our laboratory with the coulometric Karl Fischer titrator Mettler Toledo C30. The samples were used without further purification except drying by intensive stirring and evaporation under vacuum at temperature 353 K. No decomposition of the ILs was observed at the experimental conditions.

## RESULTS AND DISCUSSION

**Density.** For [EMIM][N(CN)<sub>2</sub>], the  $p$ - $\rho$ - $T$  measurements were performed along 12 isochores at temperatures from the melting temperature to approximately 346 K and in pressure up to 60 MPa at 85 individual  $p$ - $T$  set points. For [BMIM][N(CN)<sub>2</sub>], the measurements were performed along nine isochores at temperatures from (237 to 350) K at 58 individual  $p$ - $T$  set points. The resultant densities obtained from the evaluation procedure taking into account all necessary corrections<sup>16</sup> are presented in Table 2.

Table 2. Present Experimental Data on Densities  $\rho$  for [EMIM][N(CN)<sub>2</sub>] and [BMIM][N(CN)<sub>2</sub>] as a Function of Temperature  $T$  and Pressure  $p$ 

$T$	$p$	$\rho$	$T$	$p$	$\rho$
K	MPa	kg·m <sup>-3</sup>	K	MPa	kg·m <sup>-3</sup>
1-Ethyl-3-methylimidazolium Dicyanamide [EMIM][N(CN) <sub>2</sub> ]			1-Ethyl-3-methylimidazolium Dicyanamide [EMIM][N(CN) <sub>2</sub> ]		
298.157	0.1034	1108.35	256.923	29.975	1145.41
298.157	40.265	1122.54	267.706	49.662	1144.45
291.792	29.944	1123.08	267.704	9.7532	1132.18
285.434	19.560	1123.61	291.47	50.178	1130.13
274.207	0.7757	1124.56	291.467	9.7540	1116.28
279.650	9.9606	1124.10	286.615	2.0090	1116.68
304.225	49.724	1122.03	297.911	20.011	1115.75
310.573	59.616	1121.51	310.805	40.003	1114.68
285.437	19.459	1123.61	317.445	50.073	1114.13
285.391	9.8165	1120.27	324.195	60.082	1113.57
280.013	1.0168	1120.72	304.281	29.918	1115.22
291.613	19.904	1119.75	304.344	10.634	1108.27
297.976	30.141	1119.22	298.078	1.0202	1108.78
304.201	39.942	1118.71	310.522	20.049	1107.77
310.652	49.941	1118.17	337.917	60.055	1105.54
317.225	59.899	1117.62	317.186	29.905	1107.23
280.040	1.0776	1120.72	317.167	9.765	1099.76
285.452	9.8149	1120.27	311.244	1.092	1100.23
285.503	20.153	1123.73	324.282	20.103	1099.19
279.594	10.349	1124.23	338.387	40.023	1098.06
279.661	20.569	1127.70	345.693	50.073	1097.48
268.056	0.6497	1128.69	331.281	30.008	1098.63
285.507	30.235	1127.20	331.293	9.8624	1090.95
291.509	40.153	1126.69	325.017	1.1271	1091.44
297.754	50.232	1126.16	338.742	20.149	1090.36
303.935	60.074	1125.65	346.215	30.275	1089.77
273.510	10.041	1128.22	346.223	9.8731	1081.75
273.491	19.943	1131.55	339.672	1.0740	1082.20
1-Butyl-3-methylimidazolium Dicyanamide [BMIM][N(CN) <sub>2</sub> ]			1-Butyl-3-methylimidazolium Dicyanamide [BMIM][N(CN) <sub>2</sub> ]		
262.456	0.6196	1132.49	298.184	40.659	1074.02
279.413	30.010	1131.04	291.052	30.032	1074.57
285.415	40.116	1130.53	304.811	50.325	1073.50
291.453	50.059	1130.01	311.344	59.700	1072.99
297.625	60.101	1129.48	284.466	20.074	1075.10
267.704	9.8940	1132.04	277.981	10.008	1075.61
267.708	20.196	1135.44	273.279	2.7675	1075.98
273.249	29.805	1134.96	277.917	9.9551	1075.61
279.197	40.050	1134.45	277.964	30.503	1082.82
285.078	50.002	1133.94	270.553	18.709	1083.42
291.086	59.995	1133.42	284.145	40.138	1082.33
261.968	9.9502	1135.94	291.445	51.356	1081.75
257.123	1.2508	1136.35	297.265	60.158	1081.29
267.671	20.023	1135.45	259.682	1.0300	1084.28
267.705	29.968	1138.56	265.239	10.141	1083.84
273.400	39.951	1138.06	265.249	30.347	1090.66
279.220	50.024	1137.55	271.134	39.925	1090.18
285.128	60.064	1137.04	277.415	50.079	1089.67
256.974	10.611	1139.49	283.668	59.955	1089.17
262.109	19.886	1139.04	259.122	20.009	1091.16
267.697	29.879	1138.56	248.088	1.1705	1092.06
267.711	40.066	1141.75	253.328	10.197	1091.63
273.343	49.967	1141.26	253.334	29.961	1098.11
278.570	59.071	1140.80	259.172	39.931	1097.63
256.825	20.357	1142.71	265.123	50.114	1097.14
267.671	39.943	1141.75	271.066	59.859	1096.65
267.701	49.706	1144.45	247.769	20.189	1098.57
273.552	60.051	1143.95	237.204	1.3279	1099.45
262.332	39.980	1144.93			

Table 2. continued

$T$	$p$	$\rho$
K	MPa	kg·m <sup>-3</sup>
1-Butyl-3-methylimidazolium Dicyanamide [BMIM][N(CN) <sub>2</sub> ]		
242.136	9.9869	1099.05
298.179	40.270	1073.65
291.052	29.671	1074.21
291.056	11.299	1067.78
284.154	1.0388	1068.31
296.970	19.796	1067.32
325.320	60.007	1065.14
284.230	1.1483	1068.31
317.984	49.917	1065.70
310.980	40.117	1066.24
303.971	30.176	1066.78
303.972	10.315	1059.42
299.210	3.7191	1059.78
311.013	20.033	1058.89
325.555	39.796	1057.80

$T$	$p$	$\rho$
K	MPa	kg·m <sup>-3</sup>
1-Butyl-3-methylimidazolium Dicyanamide [BMIM][N(CN) <sub>2</sub> ]		
333.119	50.157	1057.22
340.796	60.149	1056.64
318.275	30.183	1058.34
318.267	9.9110	1050.46
311.367	0.6766	1050.98
326.005	19.921	1049.89
341.310	39.980	1048.75
349.322	50.089	1048.15
333.670	30.169	1049.32
333.667	9.9181	1041.19
326.531	0.8763	1041.71
341.769	20.126	1040.59
349.802	9.6292	1031.41
349.804	30.031	1040.31
342.411	0.7815	1031.94

To correlate experimental data on the density pressure dependence for ILs up to high pressures, most often the Tait-type eq 1 is used.

$$\rho(T, p) = \frac{\rho(T, p_{\text{ref}})}{1 - a_2 \ln \left[ \frac{B(T) + p / p_{\text{ref}}}{B(T) + 1} \right]} \quad (1)$$

where

$$\rho(T, p_{\text{ref}}) / \text{kg} \cdot \text{m}^{-3} = \frac{a_0}{1 + a_1 \tau} \quad (2)$$

and

$$B(T) = a_3 + a_4 \tau \quad (3)$$

with  $\tau = T / (100 \text{ K})$ . The pressures  $p$  and  $p_{\text{ref}}$  can be given in arbitrary but equal pressure units. The coefficients in eqs 1, 2, and 3 are dimensionless. In the case of ionic liquids with small thermal expansion coefficients, the rational eq 4 can be used equally well for not too high pressures up to 60 MPa

$$\rho(T, p) / \text{kg} \cdot \text{m}^{-3} = \frac{a_0}{1 + a_1 \tau + a_2 \tau \pi + a_3 \pi^2} \quad (4)$$

where  $\pi = p / (1 \text{ MPa})$  is a dimensionless pressure variable. The eqs 1 and 4 were fitted to the experimental [EMIM][N(CN)<sub>2</sub>] and [BMIM][N(CN)<sub>2</sub>] density data from this work and to the 0.1 MPa density data by Klomfar et al.<sup>11</sup> Table 3 gives the resultant coefficients  $a_i$  of eqs 1, 2, 3, and 4 for the investigated

Table 3. Coefficients  $a_i$  of the Correlation eqs 1 and 4 of the Present Experimental Density Data for [EMIM][N(CN)<sub>2</sub>] and [BMIM][N(CN)<sub>2</sub>]

	[EMIM][N(CN) <sub>2</sub> ]		[BMIM][N(CN) <sub>2</sub> ]	
	eq 1	eq 4	eq 1	eq 4
$a_0$	1346.0	1345.38	1288.7	1288.39
$a_1$	0.0719	0.07173	0.07273	0.072648
$a_2$	0.1094	$-1.359 \cdot 10^{-4}$	0.1054	$-1.504 \cdot 10^{-4}$
$a_3$	6451.6	$5.746 \cdot 10^{-7}$	5551.2	$6.960 \cdot 10^{-7}$
$a_4$	-1055.7		-896.6	
rmsd/kg·m <sup>-3</sup>	0.10	0.15	0.10	0.09

ionic liquids together with the corresponding root-mean-square deviations, rmsd's. The coefficients  $a_i$  are given to a number of significant figures that is consistent with the uncertainty of the coefficients. In Figures 1 and 2, deviations are depicted of the

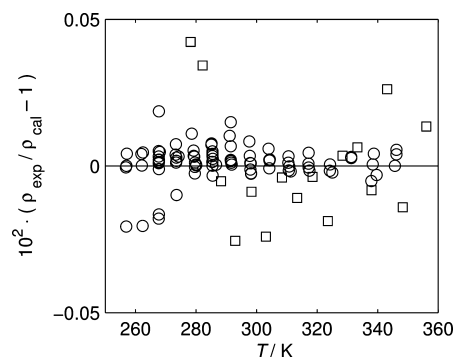


Figure 1. [EMIM][N(CN)<sub>2</sub>]: Relative deviations  $10^2(\rho_{\text{exp}}/\rho_{\text{calc}} - 1)$  of the experimental density data,  $\rho_{\text{exp}}$ , from the values  $\rho_{\text{calc}}$  calculated from the present correlation eq 4 as a function of temperature  $T$ . □, Klomfar et al.;<sup>11</sup> ○, this work.

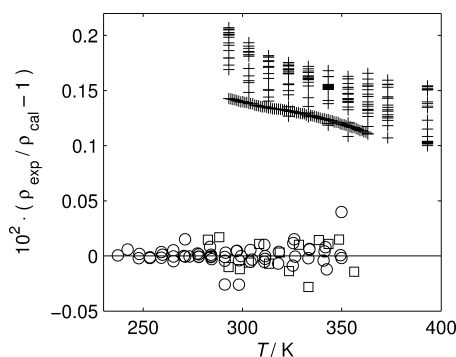


Figure 2. [BMIM][N(CN)<sub>2</sub>]: Relative deviations  $10^2(\rho_{\text{exp}}/\rho_{\text{calc}} - 1)$  of the experimental density data,  $\rho_{\text{exp}}$ , from the values  $\rho_{\text{calc}}$  calculated from the correlation eq 4 as a function of temperature  $T$ . +, de Castro et al.;<sup>10</sup> □, Klomfar et al.;<sup>11</sup> ○, this work.

experimental data from their respective representative eq 4. Most of the experimental densities lie within the interval



of  $\pm 0.0002\rho$  from the correlation. Equation 4 makes it possible to express the molar volume  $V_m$  of the ionic liquid using a function linear in coefficients  $a_r$ . This makes possible to develop a group contribution model for the molar volume of the ionic liquids as described in the next subsection.

The values of the isobaric thermal expansion coefficient  $\alpha_p$  ( $K^{-1}$ ) (eq 5) evaluated from the correlation eq 1 and 4 differ from each other by  $\pm 3\%$  of  $\alpha_p$  both for [EMIM][N(CN)<sub>2</sub>] and [BMIM][N(CN)<sub>2</sub>]. Similarly, the differences in the values of the isothermal compressibility  $\kappa_T$  ( $MPa^{-1}$ ) (eq 6) calculated from eqs 1 and 4 lie in the interval from  $(-1$  to  $5)\%$  of  $\kappa_T$ .

$$\alpha_p = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_p \quad (5)$$

$$\kappa_T = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial p} \right)_T \quad (6)$$

The above-mentioned differences in the coefficients  $\alpha_p$  and  $\kappa_T$  give a certain idea of the accuracy with which these coefficients can be evaluated by differentiating the density correlation equations of various functional forms.

**Density Data Analysis.** In our previous study,<sup>11</sup> we have developed a group contribution model for the 0.1 MPa molar volume of eight ionic liquids with 1-C<sub>n</sub>-3-methylimidazolium cations with  $n = 2, 4,$  and  $6$  and with the anions [BF<sub>4</sub>], [CF<sub>3</sub>SO<sub>3</sub>], and [N(CN)<sub>2</sub>]. The GC model is based on a large amount of experimental data by different authors and makes it possible, through assessing their conformity with the model, to identify the data, which are more certain than others. In the present study we have extended the GC model to include the dependence of the density on the pressure. Only statistically significant terms were included in the model equation, found using a stepwise regression procedure. For the molar volume  $V_{ij}$  of a ionic liquid consisting of the  $i$ -th cation and the  $j$ -th anion one thus obtains

$$\begin{aligned} V_{ij}/(\text{cm}^3 \cdot \text{mol}^{-1}) = & a_j^\pm + b_j^\pm \tau + c_j^\pm \pi + d_j^\pm \tau \pi + e_j^\pm \pi^2 \\ & + (a^+ + b^+ \tau + c^+ \pi + d^+ \tau \pi \\ & + e^+ \pi^2) n_i \end{aligned} \quad (7)$$

The variables  $\tau$  and  $\pi$  defined as  $\tau = (T - 298.15)/(100 \text{ K})$  and  $\pi = (p - 0.1)/(1 \text{ MPa})$  are suitably transformed temperature and pressure variables of the model. Owing to this choice of variables, the pressure-independent terms of eq 7 describe the temperature dependence of the molar volume at the pressure of 0.1 MPa and therefore should be identical to the equally denoted terms in the GC model for the 0.1 MPa densities presented in ref 11, eq 5. The variable  $n_i$  equals to the number of pairs of CH<sub>2</sub> groups in the  $i$ th cation alkyl side chain. The convention for  $n$  we introduce in agreement with other authors<sup>12–14</sup> to obtain results directly comparable with theirs. In accordance with the notation introduced in ref 11 the terms  $a_j^\pm$  and  $b_j^\pm \tau$  represent the common contribution of the methylimidazolium cation [MIM]<sup>+</sup> and of the  $j$ th anion to the molar volume of the ionic liquid at a temperature of 298.15 K and a pressure of 0.1 MPa, while the newly introduced terms  $c_j^\pm \pi$ ,  $d_j^\pm \tau \pi$ , and  $e_j^\pm \pi^2$  describe the pressure dependence of this contribution. Similarly, the term proportional to  $n_i$  represents the contribution of the alkyl side chain of the cation containing  $n_i$  pairs of CH<sub>2</sub> 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 given by eq 7 on both 0.1 MPa density data and on selected  $p$ - $\rho$ - $T$  data for the eight ionic liquids with 1-C<sub>n</sub>-3-methylimidazolium cations with  $n = 2, 4,$  and  $6$  and with [BF<sub>4</sub>], [CF<sub>3</sub>SO<sub>3</sub>], and [N(CN)<sub>2</sub>] anions. Only those sets of data for the  $p$ - $\rho$ - $T$  relation are usable for fitting the pressure dependence of the GC model, the low-pressure limit of which is at least nearly consistent within their experimental uncertainties to the GC model of the 0.1 MPa density from our previous study.<sup>11</sup> If this requirement was not met, the derivatives of the resultant equation would be distorted, and reasonable agreement with the experimental data on the isobaric thermal expansivity and isothermal compressibility could not be obtained. Thus, the present GC model is based on the following data: (i) 861 data points for the dependence of the density on the temperature at 0.1 MPa from 53 studies by different authors for the eight ionic liquids of interest including our data<sup>11,18,19</sup> and (ii) a total number of 807 data points for the  $p$ - $\rho$ - $T$  relation for the eight ionic liquids of interest with  $p > 0.1$  MPa including 497 data points from our previous measurements<sup>16,17</sup> and from the present study. The temperature ranges of the data are given in Table 4.

The used 0.1 MPa data are identical to those used to develop the group contribution model of 0.1 MPa density dependence on temperature presented in our previous study.<sup>11</sup> The list of citations of the sources of the used 0.1 MPa density data is available in the Supporting Information to the present paper. Table 4 lists all of the literature sources of the  $p$ - $\rho$ - $T$  data sets that were used in the model fitting. Only those lying within the limit of  $\pm 0.003\rho$  from the resultant GC model were selected to this purpose. From the whole data set only data points with  $T < 353 \text{ K}$  and with  $p < 60 \text{ MPa}$  were used. The data were analyzed using the group contribution model of eq 7. While for separate correlations of the  $p$ - $\rho$ - $T$  data for the eight ionic liquids considered here, 40 parameters are needed, the resultant model eq 7 contains only 16 adjusted nonzero parameters. Table 4 gives the average absolute relative deviations, AARD, from the GC model of the used individual  $p$ - $\rho$ - $T$  data sets for the eight ionic liquids of interest, the values of the molar masses used in the present study to convert densities of the ionic liquids to their molar volumes, and the temperature and pressure ranges of the data sets. The model parameters were determined by minimization of the objective function  $S$  given by eq 8

$$S = \sum_{i,j,k} [V_{ij}^{\text{calc}}(T_k, p_k) - V_{ij}^{\text{exp}}(T_k, p_k)]^2 \quad (8)$$

In eq 8, the anions [BF<sub>4</sub>], [CF<sub>3</sub>SO<sub>3</sub>], and [N(CN)<sub>2</sub>] are numbered with a subscript  $j$  as 1, 2, and 3, respectively. The summation is taken over the ionic liquids with  $i$ th cation and  $j$ th anion and over the temperature–pressure points  $(T_k, p_k)$  at which the molar volume  $V_{ij}^{\text{exp}}$  of the ionic liquid is given by the experiment. For the purpose of tabulation of the resultant model coefficients we use their denotation as introduced in a more concise form of the model eq 9

$$V_{ij}/(\text{cm}^3 \cdot \text{mol}^{-1}) = \sum_{\alpha=1}^5 [a_{j\alpha}^\pm + a_{\alpha}^+ n_i] \tau^k \pi^\alpha \quad (9)$$

**Table 4. Sources of the Experimental  $p$ – $\rho$ – $T$  Data for the Eight Ionic Liquids of Interest Used in Fitting the GC Model, eq 7, with Average Absolute Relative Deviations, AARD, of the Data from the Values Calculated from the Model and the Molar Masses,  $M$ , Used to Convert the Densities to the Molar Volumes**

author(s)	year	temp. range $T$ /K	press. range $p$ /MPa	AARD	no. of data used
1-Ethyl-3-methylimidazolium Tetrafluoroborate [EMIM][BF <sub>4</sub> ], $M = 197.97 \text{ g}\cdot\text{mol}^{-1}$					
Taguchi et al. <sup>20</sup>	2009	293 to 472	0.1 to 200	0.0015	22 <sup>a</sup>
Sanmamed et al. <sup>21</sup>	2010	293 to 323	0.1 to 60	0.0027	117
Klomfar et al. <sup>17</sup>	2011	285 to 356	0.1 to 60	0.0009	74
1-Butyl-3-methylimidazolium Tetrafluoroborate [BMIM][BF <sub>4</sub> ], $M = 226.02 \text{ g}\cdot\text{mol}^{-1}$					
de Azevedo et al. <sup>22</sup>	2005	298 to 333	0.1 to 60	0.0026	67
Gardas et al. <sup>23</sup>	2007	293 to 393	0.1 to 20	0.0010	77
Machida et al. <sup>24</sup>	2008	313 to 472	0.1 to 200	0.0009	25 <sup>a</sup>
Klomfar et al. <sup>16</sup>	2011	240 to 354	0.1 to 60	0.0014	61
1-Hexyl-3-methylimidazolium Tetrafluoroborate [HMIM][BF <sub>4</sub> ], $M = 254.08 \text{ g}\cdot\text{mol}^{-1}$					
Taguchi et al. <sup>20</sup>	2009	293 to 473	0.1 to 200	0.0008	22 <sup>a</sup>
Safarov and Hassel <sup>25</sup>	2010	283 to 373	0.1 to 100	0.0004	55 <sup>a</sup>
Sanmamed et al. <sup>21</sup>	2010	283 to 323	0.1 to 60	0.0006	117
Klomfar et al. <sup>17</sup>	2011	220 to 356	0.1 to 60	0.0007	67
1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate [EMIM][CF <sub>3</sub> SO <sub>3</sub> ], $M = 260.24 \text{ g}\cdot\text{mol}^{-1}$					
Klomfar et al. <sup>17</sup>	2011	264 to 348	0.1 to 60	0.0009	61
1-Butyl-3-methylimidazolium Trifluoromethanesulfonate [BMIM][CF <sub>3</sub> SO <sub>3</sub> ], $M = 288.29 \text{ g}\cdot\text{mol}^{-1}$					
Gardas et al. <sup>26</sup>	2007	293 to 393	0.1 to 10	0.0020	77
Klomfar et al. <sup>17</sup>	2011	290 to 350	0.1 to 60	0.0019	61
1-Hexyl-3-methylimidazolium Trifluoromethanesulfonate [HMIM][CF <sub>3</sub> SO <sub>3</sub> ], $M = 316.34 \text{ g}\cdot\text{mol}^{-1}$					
Klomfar et al. <sup>17</sup>	2011	303.14 to 351.77	0.1 to 60	0.0015	48
1-Ethyl-3-methylimidazolium Dicyanamide [EMIM][N(CN) <sub>2</sub> ], $M = 177.21 \text{ g}\cdot\text{mol}^{-1}$					
this work	2011	257 to 346	0.1 to 60	0.0008	85
1-Butyl-3-methylimidazolium Dicyanamide [BMIM][N(CN) <sub>2</sub> ], $M = 205.26 \text{ g}\cdot\text{mol}^{-1}$					
de Castro et al. <sup>10</sup>	2010	293 to 433	0.1 to 60	0.0003	241
this work	2011	237 to 350	0.1 to 60	0.0011	58

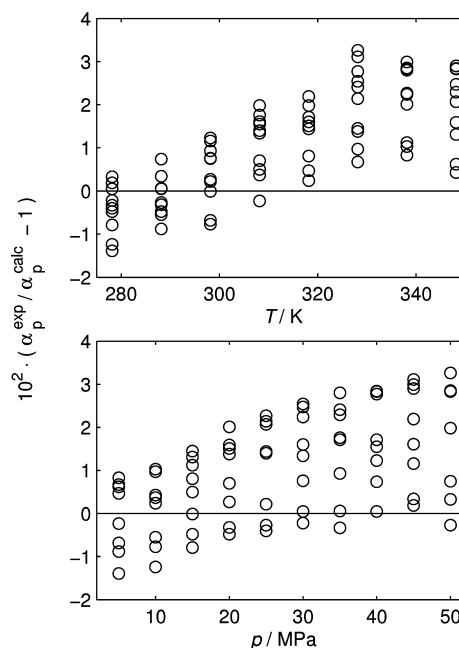
<sup>a</sup>From the whole data set only data points with  $T < 353 \text{ K}$  and with  $p < 60 \text{ MPa}$  were used in fitting the correlation.

Table 5 gives the least-squares estimates of the model parameters  $a_{j\alpha}^{\pm}$  and  $a_{\alpha}^+$ , the number of significant figures of which is given in accordance with their uncertainty. The resultant correlation is characterized by the value of the average absolute relative deviation AARD (eq 10) of 0.0013.

$$\text{AARD} = \frac{1}{N} \sum_{i,j,k} |\rho_{ijk}^{\text{exp}} / \rho_{ijk}^{\text{calc}} - 1| \quad (10)$$

where  $\rho_{ijk}^{\text{exp}}$  is the experimental value of the density of the ionic liquid with the  $i$ th cation and  $j$ th anion at temperature  $T_k$  and pressure  $p_k$  and  $\rho_{ijk}^{\text{calc}}$  is the corresponding density value calculated from the model. In general, for individual ionic liquids, the model is valid in the pressure–temperature regions covered by experimental data as they are given in Table 4. However, extrapolations to temperatures corresponding to subcooled liquid states can be expected to yield reasonable values of density.

Figures 3 and 4 give a comparison of the values of the thermal expansivity  $\alpha_p$  calculated by the differentiation of the

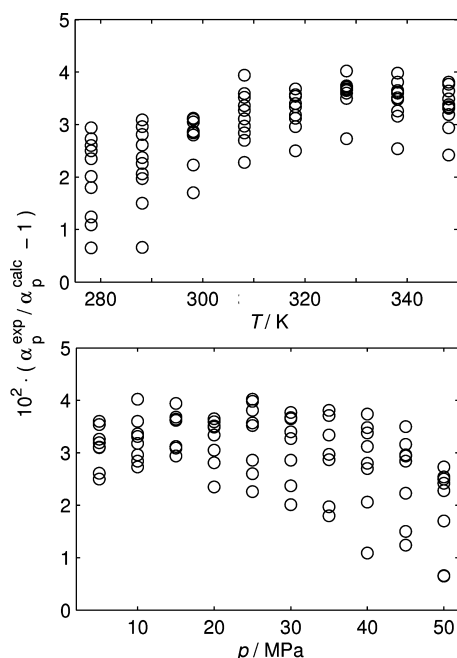


**Figure 3.** Relative deviations  $10^2(\alpha_p^{\text{exp}}/\alpha_p^{\text{calc}} - 1)$  of the experimental data on the isochoric thermal volume expansion,  $\alpha_p^{\text{exp}}$ , for [BMIM][BF<sub>4</sub>] by O, Navia et al.<sup>27</sup> from the values  $\alpha_p^{\text{calc}}$  calculated from the correlation eq 7 as a function of temperature  $T$  and pressure  $p$ .

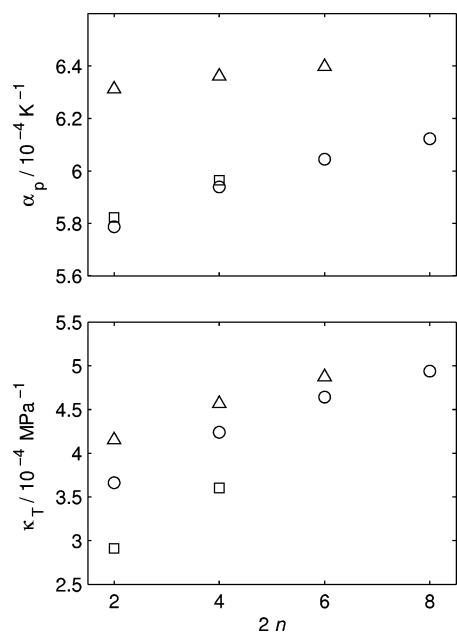
model equation with experimental values of Navia et al.<sup>27</sup> for [BMIM][BF<sub>4</sub>] and [BMIM][CF<sub>3</sub>SO<sub>3</sub>], respectively. The average absolute relative deviation of the experimental data

**Table 5. Coefficients  $a_{i,\alpha}^{\pm}$  and  $a_{\alpha}^+$  of the Group Contribution Model, Equation 9**

$\alpha$	$k_{\alpha}$	$l_{\alpha}$	$a_{i,\alpha}^{\pm}$		$a_{3,\alpha}^{\pm}$		$a_{\alpha}^+$
			[MIM][BF <sub>4</sub> ]	[MIM][CF <sub>3</sub> SO <sub>3</sub> ]	[MIM][N(CN) <sub>2</sub> ]	alkyl chain	
1	0	0	$1.20762 \cdot 10^2$	$1.54356 \cdot 10^2$	$1.26159 \cdot 10^2$	$3.371 \cdot 10^1$	
2	1	0	6.7	9.63	7.07	2.24	
3	0	1	$-3.34 \cdot 10^{-2}$	$-5.49 \cdot 10^{-2}$	$-2.33 \cdot 10^{-2}$	$-2.32 \cdot 10^{-2}$	
4	1	1	0	$-1.9 \cdot 10^{-2}$	0	$-1.04 \cdot 10^{-2}$	
5	0	2	0	0	$-1.4 \cdot 10^{-4}$	$1.02 \cdot 10^{-4}$	

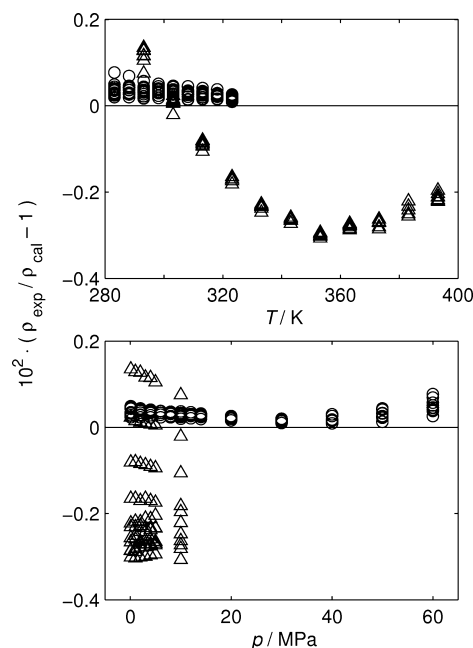


**Figure 4.** Relative deviations  $10^2(\alpha_p^{\text{exp}}/\alpha_p^{\text{calc}} - 1)$  of the experimental data on the isochoric thermal volume expansion,  $\alpha_p^{\text{exp}}$ , for [BMIM]-[CF<sub>3</sub>SO<sub>3</sub>] by O, Navia et al.<sup>27</sup> from the values  $\alpha_p^{\text{calc}}$  calculated from correlation eq 7 as a function of temperature  $T$  and pressure  $p$ .



**Figure 5.** Isochoric thermal volume expansion coefficient  $\alpha_p$  and the isothermal compressibility coefficient  $\kappa_T$  calculated from the GC model eq 7 for the nine ionic liquids of interest at the temperature of 298.15 K and the pressure of 0.1 MPa as a function of the length  $2n$  of the alkyl side chain of the cation. Anion: O, [BF<sub>4</sub>];  $\Delta$ , [CF<sub>3</sub>SO<sub>3</sub>];  $\square$ , [N(CN)<sub>2</sub>].

from the values calculated from the present GC model is 0.013 for [BMIM][BF<sub>4</sub>] and 0.03 for the data for [BMIM][CF<sub>3</sub>SO<sub>3</sub>]. For comparison we found the average absolute relative deviations from the data by Navia et al.<sup>27</sup> of the data obtained from differentiation of an equation fitted to the literature data. For [BMIM][BF<sub>4</sub>] an AARD value of 0.004 was obtained for



**Figure 6.** [OMIM][BF<sub>4</sub>]: Relative deviations  $10^2(\rho_{\text{exp}}/\rho_{\text{cal}} - 1)$  of the experimental density data,  $\rho_{\text{exp}}$ , from the values  $\rho_{\text{cal}}$  calculated from the present correlation eq 7 as a function of temperature  $T$  and pressure  $p$ . O, Sanmamed et al.;<sup>21</sup>  $\Delta$ , Gardas et al.<sup>26</sup>

the data of Sanmamed et al.,<sup>21</sup> 0.03 for de Azevedo et al.,<sup>22</sup> 0.09 for Gardas et al.,<sup>23</sup> 0.02 for Machida et al.,<sup>24</sup> 0.02 for Tekin et al.,<sup>28</sup> 0.03 for those of Tomida et al.,<sup>29</sup> and 0.03 for Jacquemin et al.<sup>30</sup> The data for [BMIM][CF<sub>3</sub>SO<sub>3</sub>] reported by Gardas et al.<sup>23</sup> give a value of 0.10 for the AARD. The comparison shows that the GC model is equally capable of yielding the values of the coefficients  $\alpha_p$  and  $\kappa_T$  as equations fitted to density data of individual ionic liquids.

To demonstrate the dependence of the thermal expansion coefficient on the length  $2n$  of the alkyl side chain of the cation, the values of the thermal expansivity coefficient  $\alpha_p$  and the isothermal compressibility  $\kappa_T$  are depicted in Figure 5, calculated from the GC model for the eight ionic liquids of interest at the temperature of 298.15 K and the pressure of 0.1 MPa as a function of the length,  $2n$ , of the alkyl side chain of the cation.

To demonstrate the capability of the model to predict densities of a ionic liquid that has not been used in the development of the model, deviations are depicted in Figure 6 of the experimental data by Sanmamed et al.<sup>21</sup> and Gardas et al.<sup>26</sup> on the pressure dependence of the density for [OMIM]-[BF<sub>4</sub>]. The average absolute relative deviation of the Sanmamed's data from the values calculated from the present GC model is 0.0003 and for the Gardas's data is 0.002.

## CONCLUSION

Experimental data on the density of two 1-alkyl-3-methylimidazolium dicyanamides with alkyl chain lengths C-2 and C-4 are reported in the temperature range from approximately 350 K down near to their melting temperature and up to 60 MPa in pressure. An isochoric apparatus was used for this purpose, which makes it possible to carry out density measurements at subzero temperatures. Up to now, the pressure dependence of the density of [BMIM][N(CN)<sub>2</sub>] have been studied only in a single work, while no data are available for the density-pressure

dependence of [EMIM][N(CN)<sub>2</sub>]. The present study yields 143 new data points to the existing data for the two ionic liquids of interest.

A predictive model based on the group contribution concept was developed using a great amount of data by different authors for eight different ionic liquids including the two dicyanamides. The model yields a reasonable basis for the assessment of the level of relative certainty in all available experimental density data sets through their intercomparison and through the determination of the conformity of the individual data sets with the used concept. The quality of the model have been confirmed by testing its fidelity to experimental data on ionic liquid density, thermal expansion, and isothermal compression coefficients, which have not been used in the model fitting stage. The density values predicted by the model thus represent the most reliable values substantiated by all data published for density of the eight ionic liquids of interest. The analysis has shown that our density data for the eight studied ionic liquids rank among the data sets that have been recognized as the more certain.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

List of citations of the sources of the 0.1 MPa density data used in the GC model fitting. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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