Group Contribution Method for Evaluation of Volumetric Properties of Ionic Liquids Using Experimental Data Recommended by Mathematical Gnostics

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ABSTRACT: The volumetric properties of 81 different ionic liquids (ILs) have been modeled as a function of temperature and pressure using an extended version of the group contribution method previously reported by our group (Jacquemin et al. J. Chem. Eng. Data 2008, 53, 716–726). Prior to correlating collected data from the literature using this model, the mathematical gnostics was used to critically analyze experimental density data sets as a function of temperature (from 217–473 K) and pressure (from 0.1–207 MPa) to be then able to recommend one data set for each IL. In addition, recommended density data sets were then fitted as a function of temperature and pressure using a series of mathematical equations reported in the literature. These fitting equations were then assessed through the comparison of the calculated mechanical coefficients with the limited directly measured experimental data reported in the literature. Among these recommended data sets, 5399 density data points for 54 different ILs were then used as the training data set to determine the temperature and pressure dependences on the effective molar volume of 31 different cations and 24 different anions. Then 2522 density data points for 27 other ILs were used as a test data set to determine the accuracy of this method. In light of this analysis, excellent agreement was observed between calculated and recommended literature data within the whole temperature and pressure ranges investigated herein as stated by the overall relative average absolute deviation (RAAD) for each volumetric property, which was lower than 0.31% and 3.5% in the case of the density and isobaric thermal expansion coefficient of pure ILs, respectively. Finally, this model was further assessed with other methods reported in the literature in the case of the evaluation of the density of binary mixtures of two ILs as a function of temperature at atmospheric pressure. This analysis demonstrates that the proposed method shows a good ability to evaluate the density even in the case of mixture of ILs with a RAAD lower than 0.25%.

1. INTRODUCTION

Ionic liquids (ILs) have been widely discussed in the literature, due to their potential uses as green solvents. Many ILs have some unique characteristics such as high ionic conductivity, polarity, thermal and chemical stability, nonflammability, and non-volatility. Such unique properties allow ILs to be good replacements for traditional organic solvents. ILs are often viewed as “designer solvents” as their properties can be tuned by a suitable combination of the ions including some specific functionalities added into their structures. A large number of research groups have focused on their application from the laboratory scale to the industry. Despite the increased popularity of ILs, the experimental data for properties of a wide range of ILs, in particular for their thermodynamic properties, such as density and viscosity, are still lacking and scarce, much less the accurate values at high pressure. The reason for the limited density data has been explained previously. Therefore, models able to evaluate the density need to be developed for a wide range of ILs as a function of both temperature and pressure. Different methods have been reported into the literature to evaluate the density and molar volume of ILs. These methods are mainly based on (i) the group contribution model.

Supporting Information
The volume parameters were used to calculate the density of 59 ILs, with a temperature and reference pressure. These estimated volume of groups and fragments in ILs were estimated at ambient elements: cation core, anion core, and substituents attached to the molar volume (\( V_m \)), which allowed the evaluation of IL density over a wide temperature range (273.15–393.15 K) and pressure range (0.1–100 MPa).

Ye and Shreese\( ^{18} \) proposed the use of a group contribution method for the density evaluation of ILs. The volume parameters of groups and fragments in ILs were estimated at ambient temperature and reference pressure. These estimated volume parameters were used to calculate the density of 59 ILs, with a mean absolute deviation of 0.007 g cm\(^{-3} \). Then Gardas and Coutinho\( ^{17} \) made an extension of the method reported by Ye and Shreese,\( ^{34} \) which allowed the evaluation of IL density over a wide temperature range (273.15–393.15 K) and pressure range (0.1–100 MPa).

Rebelo and co-workers\( ^{18} \) defined the molar volume (\( V_m \)) of an IL as a sum of the effective molar volumes of the constituent cation and anion (\( V_{cation} \) and \( V_{anion} \)). This concept was also applied to calculate the molar volume of unknown ILs by Slattery et al.\( ^{14} \). Rebelo and co-workers\( ^{18} \) observed an “ideal” volumetric behavior for a series of 1-C\(_2\)-3-methylimidazolium based ILs that the molar volume (\( V_m \)) is linearly dependent on the number of CH\(_2\) groups in the alkyl chain. On the basis of the assumption of the “ideal” volumetric behavior, Jacquemin et al.\( ^{10,11} \) proposed a group contribution method to calculate the effective molar volume of ions and further fitted the effective molar volumes of ions using a Tait-type equation. The correlated volumetric parameters of ions were used to evaluate 5080 density values over a broad temperature range (273–423 K) and pressure range (0.1–207 MPa) within 0.36%.

Some other group contribution methods\( ^{17,18,29} \) considered the functional group contributions; however, differences existed in the definition of functional groups. Lazuz\( \acute{\text{e}} \)s et al.\( ^{17} \) divided each IL into three parts: cation core, substituents attached to the cation core, and the whole anion. Qiao et al.\( ^{18} \) defined each IL as a combination of cation center, substituents attached to the cation center, and functional groups constituting the anion. Paduszynski et al.\( ^{29} \) reported that each IL was composed of three basic elements: cation core, anion core, and substituents attached to the cores.

Qiao et al.\( ^{18} \) selected 51 groups to establish the GCM. The density of an IL was a sum of the contributions of all included groups. The temperature and pressure dependences of contributions for each group were estimated respectively by correlation of 7381 data points for 123 ILs. However, only 188 data points of three ILs were used to test the quality of this model. This still needs further investigation to prove its applicability. Lazuz\( \acute{\text{e}} \)s et al.\( ^{17} \) expressed the reference molar volume of IL (298.15 K and 0.1 MPa) as a summation of the contributions of all involved groups. Thus, the reference density (298.15 K and 0.1 MPa) was calculated as the molecular weight divided by the reference molar volume. Then Lazuz\( \acute{\text{e}} \)s et al.\( ^{17} \) used a linear equation to describe the temperature and pressure dependence of density. The developed linear model estimated 3530 data points for 310 ILs within 0.73%. Paduszynski et al.\( ^{29} \) estimated the contributions of 177 functional groups at reference temperature (298.15 K) and pressure (0.1 MPa). The molar volume of an IL (298.15 K and 0.1 MPa) was calculated based on the contributions of all functional groups occurring in the IL, and thus, the density (298.15 K and 0.1 MPa) was calculated as well. Then the density as a function of temperature at 0.1 MPa was calculated using a linear equation, and the density at high pressure was estimated using a Tait-type equation. This work estimated 16830 densities for 1028 ILs with the RAAD% of being 0.51%.

Besides the group contribution methods, another approach is the correlation between the density and other physical properties of ILs. Bandrè\( \acute{\text{e}} \)s et al.\( ^{33} \) calculated the molar volume of IL from its refractive index by means of the Lorentz–Lorenz relation and estimated the density based on its surface tension using the parachor parameter model. Similarly, Deetlefs et al.\( ^{21} \) also reported density evaluations using the parachor and molar refraction.

Recently, equations of state (EoS) have been developed by some researchers to evaluate the density of an IL. Ji and Adidharma\( ^{25} \) described the density of imidazolium-based ILs, over a temperature range (293.15–415 K) and a pressure range up to 650 bar, using heterosegmented statistical associating fluid theory (hetero-SAFT) with the average relative deviations better than 0.9%. However, only imidazolium-based ILs were examined using this theory, which thus limited the applicability of this theory to various ILs. Alavianmehr et al.\( ^{36} \) reconstructed an ion contribution EoS based on the electrolyte perturbation theory to model the volumetric properties of ILs with an average absolute deviation of about 0.64%. In that work, each IL was divided into two charged hard-spheres representing the cation and anion. Some density data were required for the optimization of the hard-sphere diameter and the nonbonded interaction energy. Similarly, Wang et al.\( ^{26} \) developed an alternative EoS based on the electrolyte perturbation theory to predict the density of imidazolium-based ILs. The difference from the method developed by Alavianmehr et al.\( ^{36} \) was that each IL was divided into several groups representing cation, anion, and alkyl substituents. Shen et al.\( ^{23} \) made an extension of the Valderrama and Robles group contribution model\( ^{11} \) for the critical properties to predict the density of ILs using the Patel-Teja equation of state (PT-EoS). During this work, 918 data points at ambient temperature and atmospheric pressure were correlated with a global relative average absolute deviation of being 4.4%. This method may lead to large errors for the density evaluation up to high pressures.

Lazuz\( \acute{\text{e}} \)s et al.\( ^{20} \) proposed a method combining a simple group contribution model and the artificial neural network (ANN). Therein, 2410 density data of 250 ILs were used to train the ANN method, and 773 experimental data points for 72 other ILs were compared with the evaluated ones with an accuracy lower than 0.5%. Valderrama et al.\( ^{3} \) and Kovačević et al.\( ^{38} \) also proposed methods based on the ANN for the IL density evaluation, with an acceptable accuracy for engineering calculations.

Moreover, the available PVT data would allow the development of the quantitative structure–property relationship (QSPR) for the IL density. Lazuz\( \acute{\text{e}} \)s et al.\( ^{19} \) reported a QSPR method containing 11 descriptors to correlate 2465 experimental data and evaluated 555 data points with an accuracy of 2%. Ten QSPRs were applied by Trohalaki et al.\( ^{32} \) to evaluate the density of bromide-based ILs. Each QSPR used by Trohalaki et al.\( ^{32} \) only had a single descriptor, which provided an accurate density estimation for the 13 bromide salts.

Palomar et al.\( ^{35} \) performed for the first time COSMO-RS (Conductor like Screening MOdel for Real Solvents) calculation to predict the density and molar volume of ILs, but only at a single temperature (298 K) and pressure (0.1 MPa). Furthermore, Preiss et al.\( ^{36} \) predicted the ionic and molecular volumes of ILs by COSMO calculation and then correlated to the temperature-dependent density.
Herein, we present an extension of the previously developed group contribution model to evaluate the volumetric properties of ILs as a function of temperature and high pressure. This model is based on the “ideal-volume” model assuming that the molar volume of the IL is a sum of the effective molar volume of cation and anion. This model has been performed by our group to evaluate the density of over 5080 experimental data points within 0.3% as a function of temperature range (273–423 K) and pressure up to 207 MPa. Among these recommended data, 5399 data points of 54 ILs were used for correlation to properties of ILs as a function of temperature and high pressure.

However, discrepancies in the experimental data for the same IL affect the quality of the correlation and thus the development of any model. Therefore, in the present work, mathematical gnostics was used to analyze the experimental data and recommend a data set for each IL. There were 7921 data points for 81 ILs recommended over a wide temperature range (256–473 K) and pressure up to 200 MPa. Among these recommended data, 5399 data points of 54 ILs were used for correlation to obtain the volumetric parameters. Then 2522 data points of other 27 ILs were compared with the evaluated data. In addition, a comparison was conducted to highlight the predictive capacity of this approach with other GCMs available in the literature in the case of the evaluation of density of IL binary mixtures. Finally, the mechanical coefficients of the pure ILs were derived from the Tait fitting equations and compared with the limited directly measured experimental values having been reported in the literature to date.

2. DATA ANALYSIS

First, we collected the experimental density data of ILs as a function of temperature from (217–473) K and pressure from (0.1–207) MPa from the literature. The paper focuses on the estimation of ILs density at high pressure; hence, only the ILs of which the density data at high pressure have been reported in the literature, were collected. A database was established containing over 16092 experimental densities of 81 ILs. The database is provided in the Supporting Information. An overview of all the experimental data is presented in Table S1 of the Supporting Information, which summarizes the references reporting the measurement densities for each IL, number of data points, temperature range, and pressure range.

For the ILs of which its experimental density data were reported by several papers, mathematical gnostics was used to give an analysis and recommend one data set used to establish the group contribution model. For the ILs of which its experimental densities, especially at high pressures, were reported by only one reference, recommended data could thus not be obtained by mathematical gnostics, and the given set was then considered as the recommendation data set. Mathematical gnostics is a novel axiomatic approach to uncertainty. It stems from the theory of measurement and adopting analogies from the fundamental laws of nature such as special theory of relativity and thermodynamics it provides a solid basis for defining the theoretical model of uncertainty of individual data without the need of using a prior knowledge of a distribution function of experimental errors. Properties of a finite data sample are then obtained by aggregating the properties of all individual data. The data sample may be arbitrarily small because unlike in statistics, the extrapolation step from an infinite data set to a finite data sample is not used. The distribution function, which is able to describe both unimodal and multimodal data, is estimated during data analysis. The data sample is homogeneous if and only if a unimodal global distribution function exists. The location of the maximum of the distribution function, having the meaning of the most probable value, is used as the estimated value of the quantity and the intervals obtained by marginal analysis define its tolerance. All gnostic estimates are naturally robust and are derived directly from the theory; they do not depend on any significance level selected subjectively by a data analyst. Owing to these properties, mathematical gnostics is an ideal tool for critical evaluation of data.

Herein, we give an example of data analysis of [C8mim][BF4]. The data analysis of other ILs is available in the Supporting Information. Table 1 shows the references, number of data points, temperature range, and pressure range for density data of [C8mim][BF4].

The Tait equations (eqs 1 and 2) were used to fit density data from each reference at 0.1 MPa and at high pressure, respectively:

\[
\rho_{IL}(T, p_{ref}) = \frac{1}{1 + C \ln\left(\frac{B(T) + p}{B(T) + p_{ref}}\right)}
\]

where \(p_{ref} = 0.1\) MPa. \(B(T)\) is a second-order polynomial expressed as

<table>
<thead>
<tr>
<th>ref</th>
<th>(a_0) g cm(^{-3})</th>
<th>(a_1) g cm(^{-3}) K(^{-1})</th>
<th>(a_2) g cm(^{-3}) K(^{-2})</th>
<th>RAAD %</th>
<th>(b_0) MPa</th>
<th>(b_1) MPa K(^{-1})</th>
<th>(b_2) MPa K(^{-2})</th>
<th>(C)</th>
<th>RAAD %</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>1.3330</td>
<td>–8.53 × 10(^{-1})</td>
<td>2.88 × 10(^{-1})</td>
<td>0.001</td>
<td>99.48</td>
<td>4.9956</td>
<td>0.0811</td>
<td>3.7832</td>
<td>0.102</td>
</tr>
<tr>
<td>44</td>
<td>1.2341</td>
<td>–5.16 × 10(^{-1})</td>
<td>–5.42 × 10(^{-1})</td>
<td>0.028</td>
<td>100.00</td>
<td>4.9914</td>
<td>0.1030</td>
<td>3.7836</td>
<td>0.599</td>
</tr>
<tr>
<td>45</td>
<td>1.4660</td>
<td>–1.62 × 10(^{-3})</td>
<td>1.38 × 10(^{-3})</td>
<td>0.007</td>
<td>99.53</td>
<td>4.9936</td>
<td>0.0509</td>
<td>3.7816</td>
<td>0.056</td>
</tr>
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<td>46</td>
<td>1.3433</td>
<td>–9.15 × 10(^{-4})</td>
<td>3.75 × 10(^{-3})</td>
<td>0.007</td>
<td>98.91</td>
<td>4.9965</td>
<td>0.0594</td>
<td>3.7805</td>
<td>0.101</td>
</tr>
</tbody>
</table>

Where \(\Delta T = T_p - T_{ref}\) and \(\Delta P = P_p - P_{ref}\).
The Tait parameters of [C₈mim][BF₄] are presented in Table 2 together with the relative average absolute deviations (RAAD) associated with the fits. The calculation process is completed using the least-square method in MATLAB software. The MATLAB script is available in the Supporting Information (Filename: Tait_Parameters). The Tait parameters for all the other ILs are provided in the spreadsheet of the Supporting Information.

As density property depends on the pressure and temperature, the analysis of density data by mathematical gnostics should be under identical conditions (i.e., the same temperature and pressure). Herein, we calculated the density values at temperatures of 273.15, 303.15, 333.15, and 363.15 K and pressures of 0.1, 20, 40, and 60 MPa from Tait correlations for each reference, respectively. Then mathematical gnostics was used to analyze data samples at each identical condition. The calculated densities values of [C₈mim][BF₄] at these temperatures and pressures are provided in the spreadsheet. On the basis of each data sample, the location of the maximum (Zₗ) was estimated, along with the lower bound (LB) and the upper bound (UB) of the data support, the lower bound (Zₗ) and the upper bound (Zₜₗ) of the typical data, and the lower bound (Zₜₗ) and the upper bound (Zₜₚ) of the tolerance interval, which can be found in the spreadsheet as well. For example, the calculated values of [C₈mim][BF₄] from Tait correlations based on the density data of each reference at 303.15 K and 40 MPa are listed in Table 3. The maximum of the global distribution function of this data sample was estimated by mathematical gnostics, along with tolerance intervals, presented in Table 4.

Table 3. Correlated Density Values of [C₈mim][BF₄] Using Tait Correlations from Different References at 303.15 K and 40 MPa

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P (MPa)</th>
<th>Sammamed et al.43</th>
<th>Gu et al.44</th>
<th>Gardas et al.45</th>
<th>Tomida et al.46</th>
</tr>
</thead>
<tbody>
<tr>
<td>303.15</td>
<td>40</td>
<td>1.1195</td>
<td>1.1035</td>
<td>1.1276</td>
<td>1.1241</td>
</tr>
</tbody>
</table>

Zₗ, locating at the maximum of the global distribution function is the most probable value. A value within the tolerance interval (Zₜₗ and Zₜₚ) is said to be “in tolerance”. A value within the interval of typical data (Zₗ and Zₜₗ) and outside the tolerance interval is said to be “typical”. A value within the data support (LB and UB) and outside the interval of typical data is said to be “possible” and is less precise measurement. A value outside the bounds of the data support is said to be improbable. At 303.15 K and 40 MPa, the calculated value from the Tait correlation based on the experimental data reported by Tomida et al.46 is very close to Zₗ and is the most precise. The values based on Sanmamed et al.43 also show a good accuracy. The values based on Gu et al.44 and Gardas et al.45 are less precise measurements.

Table 4. Intervals of Data Sample for [C₈mim][BF₄] at 303.15 K and 40 MPa

<table>
<thead>
<tr>
<th>T</th>
<th>P</th>
<th>LB</th>
<th>Zₗ</th>
<th>Zₜₗ</th>
<th>Zₗₜ</th>
<th>Zₗₚ</th>
<th>Zₜₚ</th>
<th>UB</th>
</tr>
</thead>
<tbody>
<tr>
<td>303.15</td>
<td>40</td>
<td>0.9609</td>
<td>1.1070</td>
<td>1.1188</td>
<td>1.1221</td>
<td>0.1245</td>
<td>1.1273</td>
<td>1.1284</td>
</tr>
</tbody>
</table>

The residual between the density and the maximum location is also characterization of the measurement accuracy. The global deviation of residuals for one data set is described as eq 4. The data set with the smallest global deviation is recommended. In this work, the residual is not the difference between the maximum location and the experimental data, but the difference between the maximum location and the correlated densities. The calculated densities based on the Tait correlation for the density data of each reference can represent the trend of the experimental data of this reference, due to accurately fitted parameters. Figure 1 shows the deviation of data sets for [C₈mim][BF₄] from each reference. It can be observed that the data set measured by Tomida et al.46 performs better:

\[
\text{deviation} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (M - x_i)^2}
\]

where N is the number of equally likely values, and M is the maximum location.

The experimental density data of some ILs have been reported by only two references, which means only two data points at each identical condition need to be analyzed and evaluated. In this case, mathematical gnostics is not applicable, and the statistical analysis is adopted. First, the experimental data collected from each reference were correlated to obtain the Tait parameters. Second, the experimental data from both references were correlated together to obtain another set of Tait parameters. Then the calculated densities from the Tait correlations for each reference were compared with the calculated densities from the Tait correlation based on both two sets to recommend one set of two.

Golden et al.47 and Aparicio et al.48 reported 34 and 168 experimental data points of [C₈mim][C₄SO₄] as a function of pressure from (0.1 to 25) MPa and from (0.1 to 60) MPa,

![Figure 1. Global deviation of data set for [C₈mim][BF₄] from each reference: (a) Sanmamed et al.,43 (b) Gu et al.,44 (c) Gardas et al.,45 and (d) Tomida et al.46](image)
respectively. The Tait parameters used to correlate the density data from each reference and altogether are provided in the spreadsheet of the Supporting Information. Then the density values at temperatures of 273.15, 303.15, 333.15, and 363.15 K and at pressures of 0.1, 20, 40, and 60 MPa were calculated based on the Tait parameters for each reference and compared with the calculated values using the Tait parameters by correlating two sets of experimental data reported by both references, as shown in Figure 2. In Figure 2, these calculated densities based on the correlation of experimental data from Aparicio et al. as shown in Figure 2. In Figure 2, these calculated densities based on the correlation of experimental data from Aparicio et al.48 show a better agreement than those represented by Goldon et al.47 except for one case at 313.15 K and 0.1 MPa. Therefore, the data set reported by Aparicio et al.48 is recommended.

Following the described methodology, one data set for each IL was recommended. An overview of the recommended data set for each IL is presented in Table S2 of the Supporting Information, and all the recommended data are provided in the spreadsheet available in the Supporting Information. The data analysis figures for other ILs are provided in Figures S1–S32 of the Supporting Information.

3. DEVELOPMENT OF THE GROUP CONTRIBUTION METHOD

3.1. Extension of the Empirical Method Based on “Ideal” Volumetric Behavior of ILs as a Function of Pressure. Because of a large number of possible cation—anion combinations, it is not possible to measure the volumetric properties of all ILs. Moreover, the measurement of the density as a function of pressure requires the availability of appropriate experimental techniques, which require either specialized equipment or extensive calibration procedures. Thus, the development of models for the evaluation of volumetric properties of ILs as a function of temperature and pressure is essential. Herein, our group implements an extension of the “ideal-volume” model.1,5,28,37 Assuming that the IL molar volume is the addition of the cation and anion effective molar volumes, an empirical equation was proposed:

\[ V_m = V_{\text{cation}}^* + V_{\text{anion}}^* \]  

where \( V_m \) is the molar volume of the IL constituted by the cation with effective molar volume \( V_{\text{cation}}^* \) and the anion with effective molar volume \( V_{\text{anion}}^* \).

A second-degree polynomial, as shown in eq 6, was found to satisfactorily fit the variation of the ions effective molar volumes as a function of temperature:

\[ V_{\text{ion}}^*(\Delta T) = \sum_{i=0}^{2} (D_i \Delta T^i) \]  

where \( \Delta T = (T - 298.15 \text{ K}) \) and \( D_i \) are the coefficients obtained by fitting the data at 0.1 MPa:

\[ V_{\text{ion}}^*(\Delta T, p, G, H) = \frac{V_{\text{ion}}^*(\Delta T, \ p_{\text{ref}})}{1 - G \ln \left( \frac{H(\Delta T + p)}{H(\Delta T + p_{\text{ref}})} \right)} \]  

where \( V_{\text{ion}}^*(\Delta T, \ p_{\text{ref}}) \) is the reference effective molar volume calculated using eq 6; \( p_{\text{ref}} = 0.1 \text{ MPa} \). G is an adjustable parameter, and \( H(\Delta T) \) is a second-order polynomial:

\[ H(\Delta T) = \sum_{i=0}^{2} (H_i \Delta T^i) \]  

MATLAB software is used to calculate the effective molar volume of ions. The function “polyfit” was used to generate the volumetric parameters at 0.1 MPa (\( D_0, D_1, \) and \( D_2 \)). The volumetric parameters at high pressure (\( H_0, H_1, H_2, \) and \( G \)) were calculated by using the least-square method. The MATLAB script is provided in the Supporting Information (Filename: Volumetric_Parameters).

Because of the thermal and chemical stability of \([\text{NTf}_2]^-\), the effective molar volume of the corresponding cations constituting the ILs is calculated using this algorithm (\( V_{\text{cation}} = V_m - V_{[\text{NTf}_2]}^* \)). The volumetric parameters (\( D_0, G, \) and \( H_0 \)) of \([\text{NTf}_2]^-\) have been calculated by Jaccquein et al.11 The experimental data of 19 \([\text{NTf}_2]^-\)-based ILs at high pressure have been reported. These 19 \([\text{NTf}_2]^-\)-based ILs are \([\text{C}_3\text{mim}][\text{NTf}_2], [\text{N}_{1114}][\text{NTf}_2], [\text{C}_3\text{mim}][\text{NTf}_2], [\text{C}_3\text{mpyrr}][\text{NTf}_2], [\text{C}_3\text{m}(3)\text{py}][\text{NTf}_2], [\text{C}_3\text{mim}][\text{NTf}_2], [\text{C}_3\text{mppyrr}][\text{NTf}_2], [\text{C}_3\text{mpip}][\text{NTf}_2], [\text{C}_3\text{OC}\text{mpyrr}][\text{NTf}_2], [\text{C}_3\text{mim}][\text{NTf}_2], [\text{C}_3\text{m}(2)\text{py}][\text{NTf}_2], [\text{C}_3\text{m}(3)\text{py}][\text{NTf}_2], [\text{C}_3\text{mpip}][\text{NTf}_2], [\text{C}_3\text{OC}\text{mpyrr}][\text{NTf}_2], [\text{C}_3\text{mim}][\text{NTf}_2], [\text{C}_3\text{m}(2)\text{py}][\text{NTf}_2], [\text{C}_3\text{m}(3)\text{py}][\text{NTf}_2], [\text{C}_3\text{mpip}][\text{NTf}_2], \text{and C}_3\text{eim}[\text{NTf}_2]. \) Thus, the volumetric parameters of the counterpart cations were determined. In the next step, the experimental data of ILs containing one of the 19 cations were used to calculate the molar volume of the corresponding anions. For example, the effective molar volume of \( \text{Br}^- \) was calculated using this algorithm (\( V_{[\text{Br}]} = V_m - V_{[\text{NTf}_2]}^* \)). Then the volumetric parameters of \( \text{Br}^- \) were obtained by correlating its effective molar volumes as a function of temperature and pressure. Following this methodology, the coefficients (\( D_0, G, \) and \( H_0 \)) of 51 ions were calculated.

The experimental data at high pressure of another three carboxylate-based ILs (\([\text{C}_2\text{OHC}_1\text{NH}_2][\text{C}_2\text{COO}], [\text{C}_2\text{OHC}_1\text{NH}_2][\text{C}_3\text{COO}], \) and \([\text{C}_2\text{OHC}_1\text{NH}_2][\text{C}_4\text{COO}] \)) have been collected from literature.98 These three ILs consist of the same cation and three different anions. However, the knowledge of the volumetric properties of these four ions was unknown. Herein, we proposed a method fitting the experimental data of these three ILs altogether to obtain the volumetric parameters of \([\text{C}_2\text{OHC}_1\text{NH}_2]^+, [\text{C}_2\text{COO}]^-, [\text{C}_3\text{COO}]^-, \) and \([\text{C}_4\text{COO}]^- \), simultaneously.
Table 5. Number of Data Used for the Correlation and Pure Evaluation of Volumetric Properties of ILs, along with the RAADs of Evaluated and Estimated Data for Each Ion

<table>
<thead>
<tr>
<th>ion</th>
<th>N_{Corr}</th>
<th>ILs used for correlation</th>
<th>N_{Eva}</th>
<th>ILs used for pure evaluation</th>
<th>RAAD_{Eva} (%)</th>
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4. RESULTS AND DISCUSSION

4.1. Performance of the Proposed GCM.

The volumetric parameters (\(D_a\), \(G\), and \(H_i\)) of 31 cations and 24 anions are presented in Table S3 of the Supporting Information. Then the molar volume of any cation−anion combinations can be evaluated. The experimental data of other 27 ILs, which had not been correlated, were used to compare with the pure evaluated values. The number of data used for correlation and evaluation, and the relative average absolute deviations (RAAD) from only evaluated and for all data reported herein (i.e., correlated and evaluated) for each ion were reported in Table 5.

The following expression for RAAD was applied:

\[
\text{RAAD} = \frac{1}{N} \sum_{i=1}^{N} \frac{|V_{\text{calculated}} - V_{\text{experimental}}|}{V_{\text{experimental}}}
\]

With the exception of \([\text{PF}_6]^-\) (RAAD = 3.26%), the RAAD values determined for all the other ions are less than 0.8%. Herein, we further discuss the possible reasons that result in higher deviations for \([\text{PF}_6]^-\). We used this algorithm (\(V_{\text{eff}}^[\text{PF}_6]=$$V_{\text{C}_{6}\text{mim}}^[\text{PF}_6]-V_{\text{C}_{6}\text{mim}}$$) to calculate the effective molar volume of \([\text{PF}_6]^-\), and then fitted \([\text{C}_{6}\text{mim}][\text{PF}_6]$$ experimental data to obtain the volumetric parameters of \([\text{PF}_6]^-$$ as the function of the temperature and pressure. Since the volumetric parameters of the \([\text{C}_{2}\text{mim}]+$$, \([\text{C}_{4}\text{mim}]+$$, \([\text{C}_{8}\text{mim}]+$$, and \([\text{C}_{4}\text{mmim}]+$$ have been obtained using data for other ILs, the volumetric properties of the corresponding ILs containing the \([\text{PF}_6]^-$$ are purely evaluated as a function of temperature and pressure based on the sum of the effective molar volumes of two ions. Table 6

Table 5. continued

<table>
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<tr>
<th>ion</th>
<th>(N_{\text{corr}})</th>
<th>ILs used for correlation</th>
<th>(N_{\text{eva}})</th>
<th>ILs used for pure evaluation</th>
<th>RAAD$_{\text{eva}}$ (%)</th>
<th>RAAD$_{\text{est}}$ (%)</th>
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<td>104 ([\text{C}_6\text{OHCH}_2\text{NH}_2][\text{C}_6\text{COO}]$$</td>
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<td></td>
<td>0.003</td>
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<td>42 ([\text{C}_6\text{OHCH}_2\text{NH}_2][\text{C}_4\text{COO}]$$</td>
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<td></td>
<td></td>
<td>0.004</td>
<td></td>
</tr>
<tr>
<td>([\text{C}_2\text{COO}]^-$$</td>
<td>42 ([\text{C}_6\text{OHCH}_2\text{NH}_2][\text{C}_2\text{COO}]$$</td>
<td>0</td>
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<td>0.604</td>
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Figure 3 shows the parity plot between the calculated and experimental densities and molar volumes of 81 ILs. The correlated and evaluated data are differentiated by filled circles and empty circles, respectively. Data points (5399) of 54 ILs are used for correlation with an excellent accuracy of 0.005%, and 2522 data points of other 27 ILs are used for comparison with the pure evaluated values within 0.96%. A good agreement is proved using this developed model, with a global RAAD lower than 0.31%. In Figure 3b, the data points marked by A and B are from \([\text{C}_{6}\text{mim}][\text{PF}_6]$$ and \([\text{C}_{2}\text{mim}][\text{PF}_6]$$ at high pressures and high temperatures. Area A corresponds to the data at high pressures and low temperatures. The reason has been explained beforehand.

Table 6. Estimation Method and Result for Each Investigated IL Containing the \([\text{PF}_6]^-$$ Anion

| IL estimation method RAAD (%) ref |
|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| \([\text{C}_{6}\text{mim}][\text{PF}_6]$$ correlation 0 Tomida et al. | 51 | | |
| \([\text{C}_{2}\text{mim}][\text{PF}_6]$$ evaluation 4.91 Taguchi et al. | 50 | | |
| \([\text{C}_{6}\text{mim}][\text{PF}_6]$$ evaluation 0.36 Tomida et al. | 51 | | |
| \([\text{C}_{4}\text{mim}][\text{PF}_6]$$ evaluation 0.37 Tomida et al. | 51 | | |
| \([\text{C}_{4}\text{mmim}][\text{PF}_6]$$ evaluation 0.17 Gardas et al. | 45 | | |

Figure 3. (a) Experimental versus calculated molar volumes and (b) calculated densities for 81 ILs where data used for (●) developing correlation and (○) evaluated data are shown.
Figure 4a and b show the distribution of relative deviations between the model calculations with the experimental molar volumes and densities, respectively. Figure 4 clearly indicates that the relative deviations of all data points are within ±10%. The relative deviations of 96.9% and 97.7% of the collected data points are located within ±2% and ±3%, for the molar volume and density properties, respectively.

In this work, we mainly focus on the evaluation of high-pressure density (volume) properties by only collecting the references reporting the high-pressure experimental data. Therefore, we compared our method with other literature models in terms of the density calculation at high pressures. Figure 5a and b summarize the calculations at high pressures for the 33 common ILs and 80 ILs, respectively. It can be seen in Figure 5 that our method developed in this work shows the lowest global RAAD% in both cases. Our method is responsible for the estimation of densities (volumes) of ILs, especially at high pressures. However, the GCMs proposed by Taherifard-Raeissi,27 and Paduszyński-Domańska29 divide the IL into smaller functional groups, which enlarge the range of applicability and increase the complexity of calculations, in turn.

4.2. Comparison with Other GCMs in the Case of Binary IL Mixtures. Comparison between different GCMs in the evaluation ability of pure ILs has been reported in the literature.10,11,16,17,29 Herein, various GCMs are compared in the case of evaluation of density of binary IL mixtures. Experimental density points (1756) for 29 binary systems were collected from the literature over a temperature range (283.15−358.15 K) at 0.1 MPa. Since the binary densities having been reported in the literature are only at atmosphere pressure, the comparison between different GCMs, made in this paper, can only contrast their performance at atmosphere pressure. Table 7 shows the overview of the experimental density for each binary system as well as the evaluation result using four GCMs. In Table 7, the first 20 binary mixtures were evaluated using four methods, and the last nine binary mixtures were evaluated using three methods due to a limited number of the effective molar volumes of ions having been reported in Gardas’ method.16 The evaluation results, for 1230 data points of 29 binary mixtures, are 0.20 (this work), 0.71 (Gardas-Coutinho16), 0.28 (Taherifard-Raeissi27), and 0.18 (Paduszyński-Domańska29), respectively. The evaluation accuracies, for 1756 data points of 29
binary mixtures, are 0.241 (this work), 0.371 (Taherifard-Raeissi27), and 0.236 (Paduszynski-Domańska29), respectively.

Generally, the method proposed by Paduszynski and Domańska29 shows the best performance, and the evaluation accuracy by our method is very close to that of Paduszynski and Domańska.29

All the experimental data of binary IL mixtures, and the calculation process using four different GCMs are provided in the spreadsheet of the Supporting Information.

### 5. MECHANICAL COEFFICIENTS

A limited number of experimental data of isobaric thermal expansion ($\alpha_p$) for ILs have been reported in the literature to date. Additionally, no directly measured data for the isothermal compressibility ($\kappa_T$) of ILs have been published to date. Table S4 in the Supporting Information summarizes the number of experimental data, temperature range, pressure range, references, and the variation with temperature and pressure for $\alpha_p$ of ILs.

<table>
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<th>binary system</th>
<th>ref</th>
<th>points</th>
<th>temp. range (K)</th>
<th>%RAAD (this work)</th>
<th>%RAAD (Gardas-Coutinho16)</th>
<th>%RAAD (Taherifard-Raeissi27)</th>
<th>%RAAD (Paduszynski-Domańska29)</th>
</tr>
</thead>
</table>
| [C₄mim][OAc]+[C₄mim]  
[N'Tf₂] | 52 | 32 | 283.15–333.15 | 0.24 | 1.4 | 0.48 | 0.67 |
| [C₄mim][N'Tf₂]+[C₄mim]  
[N'Tf₂] | 53,54 | 21 | 293.15–358.15 | 0.23 | 0.32 | 0.39 | 0.34 |
| [C₄py][BF₄]+[C₄py][N'Tf₂]  
[N'Tf₂] | 55 | 72 | 303.15–353.15 | 0.12 | 0.38 | 0.72 | 0.52 |
| [C₄py][BF₄]+[C₄m(4)py][N'Tf₂]  
[N'Tf₂] | 56 | 84 | 293.15–353.15 | 0.39 | 0.48 | 0.64 | 0.48 |
| [C₄mim][BF₄]+[C₄mim]  
[BF₄] | 57,58 | 256 | 293.15–343.15 | 0.17 | 0.6 | 0.16 | 0.08 |
| [C₄mim][BF₄]+[C₄mim]  
[BF₄] | 57 | 108 | 298.15–308.15 | 0.13 | 0.52 | 0.03 | 0.04 |
| [C₄mim][BF₄]+[C₄mim]  
[BF₄] | 57 | 126 | 298.15–308.15 | 0.17 | 0.35 | 0.09 | 0.12 |
| [C₄mim][BF₄]+[C₄mim]  
[Cl] | 59 | 42 | 303.15–333.15 | 0.51 | 2.12 | 0.06 | 0.15 |
| [C₄mim][BF₄]+[C₄mim]  
[Cl] | 59 | 42 | 303.15–333.15 | 0.26 | 2.41 | 0.14 | 0.1 |
| [C₄py][BF₄]+[C₄m(4)py][Cl] | 56 | 84 | 293.15–353.15 | 0.39 | 0.48 | 0.64 | 0.48 |

29 binary mixtures 1756 0.241 0.371 0.236
Table 8. Relative Deviation between the Experimental Data of \( \alpha_p \) and the Calculated Values by Using Different Forms of \( B(T) \)

<table>
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<th>RAAD% ( (B(T) = \sum_{i=0}^{1} (b_i T^i) ) )</th>
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<td>([C_4\text{mim}][\text{NTf}_2] )</td>
<td>2.19</td>
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<td>([C_6\text{mim}][\text{OTf}] )</td>
<td>14.8</td>
<td>37.54</td>
</tr>
<tr>
<td>([C_2\text{mim}][\text{BF}_4] )</td>
<td>1.52</td>
<td>15.11</td>
</tr>
<tr>
<td>([C_4\text{mim}][\text{SO}_4][\text{BF}_4] )</td>
<td>3.24</td>
<td>19.95</td>
</tr>
<tr>
<td>([C_6\text{mim}][\text{BF}_4] )</td>
<td>1.33</td>
<td>13.88</td>
</tr>
<tr>
<td>([C_2\text{mim}][\text{NTf}_2] )</td>
<td>2.91</td>
<td>14.71</td>
</tr>
<tr>
<td>([C_4\text{mim}][\text{py}] )</td>
<td>1.03</td>
<td>16.85</td>
</tr>
<tr>
<td>([C_4\text{mim}][\text{BF}_4] )</td>
<td>2.48</td>
<td>23.94</td>
</tr>
<tr>
<td>([C_2\text{mim}][\text{BF}_4] )</td>
<td>3.47</td>
<td>21.2</td>
</tr>
<tr>
<td>([C_4\text{mim}][\text{NTf}_2] )</td>
<td>1.60</td>
<td>1.21</td>
</tr>
<tr>
<td>average</td>
<td>3.46</td>
<td>18.4</td>
</tr>
</tbody>
</table>

The experimental data of \( \alpha_p \) reported by Navia et al.\(^{41,42} \) are not affected by any a priori assumption because \( \alpha_p \) is directly measured, unlike the values of \( \alpha_p \) reported by other groups\(^{1,66-70} \) derived from fitting equations, which predetermine the dependence of \( \alpha_p \) against temperature. It is observed from the experimental data measured by Navia et al.\(^{41,42} \) that \( \alpha_p \) of the investigated ILs decreases with temperature due to more ionicity, which is an anomalous behavior from traditional solvents. A negative dependence of \( \alpha_p \) against pressure for the investigated ILs is similar to traditional solvents.

The densities as a function of temperature and pressure can be used to derive the mechanical coefficients, the isothermal compressibility (\( \kappa_T \)), and the isobaric thermal expansion coefficient (\( \alpha_p \)). The calculation of these mechanical coefficients provides useful information on the temperature and pressure dependence of the volumetric properties.

The isobaric thermal expansion coefficient, \( \alpha_p \), is related to the variation of the density with temperature and is defined as

\[
\alpha_p = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right) p
\]

(10)

The isothermal compressibility, \( \kappa_T \), is related to the variation of the density with pressure:

\[
\kappa_T = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial P} \right)_T
\]

(11)

The following expressions\(^{66,68} \) (eqs 12 and 13) were derived from the Tait eq (eq 2):

\[
\alpha_p = \left\{ \frac{\frac{\partial \rho(T, P = 0.1 \text{MPa})}{\partial T}}{\rho(T, P = 0.1 \text{MPa})} \right\}
\]

\[
+ C \left\{ 1 - \frac{\frac{\partial \rho(T, P = 0.1 \text{MPa})}{\partial P}}{\rho(T, P = 0.1 \text{MPa})} \right\}
\]

(12)

\[
\kappa_T = \left( \frac{C}{B + P} \right) \left( \frac{\rho}{\rho(T, P = 0.1 \text{MPa})} \right)
\]

(13)

Two different fitting equations are commonly used for derivation of \( \kappa_T \) and \( \alpha_p \) as shown in eqs 3 and 14:

\[
B(T) = \sum_{i=0}^{1} (b_i \frac{1}{T^i})
\]

(14)

The differentiation of different fitting equations could lead to different results of \( \kappa_T \) and \( \alpha_p \). Herein, two different forms of \( B(T) \) were both used to calculate the values of \( \alpha_p \) for ten ILs, of which the directly measured values of \( \alpha_p \) have been reported by Navia.\(^{41,42} \) Then the deviation from the directly measured \( \alpha_p \) was calculated, presented in Table 8. The comparison of the results calculated by two fitting equations clearly shows that the hyperbolic form of \( B(T) \) provides more accurate values of \( \alpha_p \) for each IL, except in the case of \([C_4\text{mim}][\text{NTf}_2]\). The average deviation for these ten ILs was 3.46% (calculated by the hyperbolic equation, eq 14) and 18.7% (calculated by the quadratic equation, eq 3), respectively, which proves that it is reliable to use the hyperbolic form of \( B(T) \) to calculate the values of \( \alpha_p \) for other ILs.

Therefore, the Tait eq (eq 2) and eq 14 were selected to calculate the values of \( \alpha_p \) and \( \kappa_T \) for the 81 ILs investigated in this work. Herein, the recommended experimental density data and the estimated density values obtained by using the GCM developed in this paper are used to correlate the Tait equation, respectively. The correlated values of \( \alpha_p \) and \( \kappa_T \) for 81 ILs from
the recommended density data and the GCM estimated density data are presented in the spreadsheet in the Supporting Information. Figure 6 shows the comparison of different results of $\alpha_i$ and $\kappa_T$ from different sources of density data. The global deviation between the $\alpha_i$ values correlated from the experimental data and the GCM estimated density data is 7.5%. For the $\kappa_T$ values, 9.8% is calculated from two different sets of density data.

6. CONCLUSIONS

The mathematical gnostics was used to analyze the experimental data and recommend one data set for each IL. The recommended data were used to establish the group contribution model (5399 data points for correlation and 2522 data points for pure prediction). It shows a good agreement with a RAAD better than 0.31%, which proves that the group contribution model proposed in this paper is able to evaluate the volumetric properties of ILs by any random cation–anion combination accurately. By comparison with literature models, our method shows the lowest global RAAD% in terms of the high-pressure density calculations. Through comparison, our method also shows an excellent performance in the density estimation of binary IL mixtures, within 0.25%. Finally, this methodology allows the determination of the mechanical coefficients within an accuracy better than 10%.

■ ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b00753.

Data analysis figures for all other ILs (PDF)
Experimental density data; Tait parameters, interval analysis, recommended data sets, calculated kappas and alpha values, and the calculation process of binary IL mixtures; summary of all experimental data collected; recommended data for each IL; volumetric parameters calculated; overview of experimental data; Matlab files (ZIP)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

Cations

\[
\begin{align*}
[C_{\text{mim}}]^+ &= \text{1-hexyl-3-methylimidazolium} \\
[C_{\text{pip}}]^+ &= \text{1-propyl-1-methylpyrrolidinium} \\
[C_{\text{py}}]^+ &= \text{1-propylpyridinium} \\
[C_{\text{pyrro}}]^+ &= \text{1-propyl-1-methylpyrrolidinium} \\
[C_{\text{pyrrol}}]^+ &= \text{1-propyl-1-methylpyrrolidinium} \\
[C_{\text{SO}_4}]^- &= \text{hexyl sulfate} \\
[C_{\text{SO}_3}]^- &= \text{hexyl sulfite} \\
[C_{\text{SO}_4}]^- &= \text{octyl sulfate} \\
[C_{\text{SO}_3}]^- &= \text{methanesulfonate} \\
[C_{\text{SCN}}]^- &= \text{thiocyanate} \\
[C_{\text{OAc}}]^- &= \text{acetate} \\
[C_{\text{COO}}]^- &= \text{propionate} \\
[C_{\text{COO}}]^- &= \text{butyrate} \\
[C_{\text{COO}}]^- &= \text{pentanoate} \\
[C_{\text{OTf}}]^- &= \text{trifluoromethanesulfonate} \\
[C_{\text{FAP}}]^- &= \text{tris(pentafluoroethyl)trifluorophosphate} \\
[C_{\text{Fluoroantimonate}}]^- &= \text{trifluoromethanesulfonate} \\
[C_{\text{Fluorophosphate}}]^- &= \text{tris(pentafluoroethyl)trifluorophosphate} \\
[C_{\text{Fluoromethylsulfonyl}}]^- &= \text{trifluoromethanesulfonate} \\
[C_{\text{Fluoromethylsulfonyl}}]^- &= \text{trifluoromethanesulfonate}
\end{align*}
\]

Anions

\[
\begin{align*}
[B(CN)_4]^− &= \text{tetracyanoborate} \\
[BF_4]^- &= \text{tetrafluoroborate} \\
[C(CN)_3]^- &= \text{tricyanomethanide} \\
[NTf_2]^- &= \text{bis(trifluoromethylsulfonyl)imide} \\
[C_{\text{SO}_4}]^- &= \text{methylsulfate} \\
[C_{\text{SO}_3}]^- &= \text{ethyl sulfite} \\
[C_{\text{SO}_4}]^- &= \text{hexyl sulfite} \\
[C_{\text{SO}_3}]^- &= \text{octyl sulfite} \\
[C_{\text{SO}_4}]^- &= \text{ethane sulfoxide} \\
[C_{\text{SCN}}]^- &= \text{thiocyanate} \\
[C_{\text{OAc}}]^- &= \text{acetate} \\
[C_{\text{COO}}]^- &= \text{propanoate} \\
[C_{\text{COO}}]^- &= \text{butyrate} \\
[C_{\text{COO}}]^- &= \text{pentanoate} \\
[C_{\text{OTf}}]^- &= \text{trifluoromethanesulfonate} \\
[C_{\text{FAP}}]^- &= \text{tris(pentafluoroethyl)trifluorophosphate} \\
[C_{\text{Fluoroantimonate}}]^- &= \text{trifluoromethanesulfonate} \\
[C_{\text{Fluorophosphate}}]^- &= \text{tris(pentafluoroethyl)trifluorophosphate} \\
[C_{\text{Fluoromethylsulfonyl}}]^- &= \text{trifluoromethanesulfonate} \\
[C_{\text{Fluoromethylsulfonyl}}]^- &= \text{trifluoromethanesulfonate}
\end{align*}
\]

Nomenclature, Roman Letters

\[
\begin{align*}
\alpha_i &= \text{Tait parameter} \\
b_i &= \text{Tait parameter} \\
C &= \text{Tait parameter} \\
D_i &= \text{volumetric parameter} \\
H_i &= \text{volumetric parameter} \\
G &= \text{volumetric parameter} \\
P_{\text{ref}} &= \text{reference pressure (0.1 MPa)} \\
p &= \text{pressure (MPa)}
\end{align*}
\]
Greek Letters

T = temperature (K)
M = maximum location
N = number of data points
V_m = molar volume of IL (cm³/mol)
V_mperimental = molar volume experimentally measured
V_mcalculated = molar volume calculated by our method
V_mcation = effective molar volume of cation (cm³/mol)
V_manion = effective molar volume of anion (cm³/mol)
x_i = correlated density (g/cm³)
Z_o = maximum location of the global distribution function
LB = lower bound of data support
UB = upper bound of data support
Z_L = lower bound of typical data
Z_U = upper bound of typical data
N_Corr = number of data points used for correlation
N_Eva = number of data points used for evaluation

REFERENCES


