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New Method Based on the UNIFAC-VISCO Model for the
Estimation of Dynamic Viscosity of (Ionic Liquid + Molecular Solvent)
Binary Mixtures

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ABSTRACT

The modified UNIFAC-VISCO model was applied to evaluate the viscosity of (ionic liquid + molecular solvent) mixtures as the function of the composition and temperature at atmospheric pressure. The values of interaction parameters between ionic groups, $\alpha_{\text{ion/ion}}$ were collected from our previous paper (Zhao et al. J. Chem. Eng. Data 61 (2016) 3908-3921), while the parameters between the common organic groups, $\alpha_{\text{organic/organic}}$ were taken from Chevalier et al. (Chem. Eng. Sci. 49 (1994) 1799–1806). Another 376 unknown interaction parameters ($\alpha_{\text{organic/organic}}$ and $\alpha_{\text{ion/organic}}$) were calculated by regression of 3365 experimental binary viscosity data for 119 different binary systems as a function of temperature and component composition. Then, this model was assessed through the evaluation of 781 viscosity data points for 24 different binary systems not originally included in the correlation set. The relative absolute average deviation (RAAD%) of the correlation and evaluation for the viscosity of the investigated binary mixtures is close to 5.0% and 7.7%, respectively, which proves that the UNIFAC-VISCO based method proposed in this work is reliable for the estimation of the viscosity of ionic liquid-based binary mixtures.

Keywords: UNIFAC-VISCO; Ionic Liquids; Molecular Solvents; Viscosity; Group Contribution Model
1. INTRODUCTION

In recent years, ionic liquids (ILs) have attracted the attention of scientific communities due to their unique properties, such as chemical and thermal stability, high ionic conductivity, low vapor pressure, and easy tuning of their physicochemical properties by altering the cation, anion, or substituent [1]. Among the various properties, viscosity property is of considerable importance in the design of heat transfer equipment, liquid-liquid extractors, process piping, and other units [2]. For industrial applications, IL-cosolvent mixtures are promising alternatives to traditional organic liquids, since pure IL mixing with the organic liquid can confer a suitable viscosity to the mixture [1]. Consequently, many modeling efforts have been reported in the literature [1–13] regarding the viscosity of IL-cosolvent mixtures, used as electrolyte solutions.

In this regard, literature models can be categorized as (i) simple correlation equations, such as the Seddon [3], Grunberg-Nissan [9], and McAllister models [10]; (ii) Eyring’s theory based methods, like the Eyring-UNIQUAC [11], Eyring-NRTL [12], Eyring-MTSM [8], Eyring-Flory-Huggins [7], and Eyring-Wilson models [13]; and (iii) predictive methods, for example, UNIFAC-VISCO [6] and ASOG-VISCO models [6].

Wang et al. [2] compared the Eyring-UNIQUAC model and the Eyring-NRTL model (α fixed at 0.25) in the case of 35 binary mixtures containing ILs with a total of 1014 data points. The authors highlighted that a better evaluation of the viscosity could be achieved by using the Eyring-UNIQUAC (RAAD% of 2.6%) than by using Eyring-NRTL
Bajić et al. [6] used the Seddon, Grunberg-Nissan, McAlister, Eyring-UNIQUAC and Eyring-NRTL models to correlate the viscosity of 11 (IL + solvent) binary systems covering a wide temperature range. Within, McAlister and the three-parameter Eyring-NRTL models showed the best results with average percentage deviations ($PD_{max}$) below 1% in all cases. It should be noted that the reference in the denominator of the percentage deviation ($PD_{max}$) calculation is the maximum of experimental values. The Seddon model gives the highest deviation above 1% in all cases when compared with other correlative models, except for three cases; (2-butanone + [C₄mim][BF₄]), (H₂O + [C₃mmim][BF₄]), and (methyl methacrylate + [C₄mim][PF₆]). Fang et al. [7] proposed a method based on the Eyring’s absolute reaction rate theory, which was coupled with the Flory-Huggins equation, to estimate the viscosity of 527 binary mixtures including 63 (IL + solvent) mixtures. The RAAD% of the proposed method assessed using 2554 data points of the 63 ionic liquid containing systems is close to 3.73% which shows a better viscosity predictive capability than the Grunberg-Nissan equation (7.42%), for example. Furthermore, Ciocirlan et al. [1] tested 6 methods (i.e. G-N, McAllister, Eyring-Flory-Huggins, Eyring-UNIQUAC, Eyring-NRTL, and Eyring-Wilson) in terms of four binary systems ([C₂mim][BF₄] + dimethyl sulfoxide / ethylene glycol / acetonitrile / 1,4-dioxane) at (293.15, 298.15, 303.15, 313.15, 323.15, 333.15, 343.15, and 353.15) K. The McAllister model gives the best viscosity evaluation below 1.34% quantified by RAAD% at each temperature for three systems ([C₂mim][BF₄] + dimethyl sulfoxide / acetonitrile / 1,4-
dioxane). For the other system, [C$_2$mim][BF$_4$] + ethylene glycol, the best result was reported using the Eyring-Flory-Huggins based method with a RAAD% of 1.54%, while the McAllister method also showed a good result with RAAD% of 1.60%. The poorest result estimated for these four systems is with the G-N model, ranging from 1.93% up to 6.01% calculated by RAAD% at the eight temperatures. For the series of Eyring-based models, Eyring-Wilson gives the poorest results with a RAAD% of 2.1% and 2.9% in two systems containing dimethyl sulfoxide, and acetonitrile, respectively. Eyring-Flory-Huggins shows the poorest estimation with a 1.5% RAAD% in the system with ethylene glycol and also a poor result with 1.1% of RAAD% in the 1,4-dioxane containing system. Generally, the other two Eyring-based models (i.e. UNIQUAC and NRTL) show a better evaluation, the RAAD% are lower than 1.9% at each temperature point for all the four investigated systems. Atashrouz et al. [8] reported an Eyring’s theory method coupled with a modified two-suffix-margules model (Eyring-MTSM). To validate the capability of the Eyring-MTSM model, the authors also made a clear comparison with the Eyring-NRTL model using 5512 experimental data points for 122 IL-based mixtures. Based on this work, these authors demonstrated the higher accuracy of the Eyring-MTSM method, with a RAAD% close to 2% compared to 2.8% observed using the Eyring-NRTL model.

Generally, correlative models often yield lower deviations, but require enough experimental data for the determination of parameters in the correlation equations. However, a significant advantage of the predictive models is that a given property, such
as viscosity could be evaluated for unknown mixtures by using a set of interaction parameters regressed using well-defined training datasets. Two predictive methods, based on the UNIFAC-VISCO and ASOG-VISCO models, respectively were applied for modeling the viscosity of IL-based mixtures [6]. Bajić et al. [6] calculated the interaction parameters ($\alpha_{mn}$) between the group ([C2mim][C2SO4], [-mim][BF4], [-mim][PF6], and [C4mim][NO3]) and the organic functional groups by correlating experimental data of 11 binary mixtures. However, the determination of the groups in the ionic liquid components is not clear and uniform, sometimes on the basis of the whole IL (such as [C2mim][C2SO4] and [C4mim][NO3]) and sometimes on the basis of the core structure of the IL ([-mim][BF4] and [-mim][PF6]). In fact more work is requested to assess properly the quality of the proposed method using novel and original viscosity datasets.

In this work, we aim to develop the UNIFAC-VISCO model for correlation, and then evaluation of the viscosity of (IL + molecular solvent) binary mixtures. The method used for molecules’ cleavage is different from the division method reported by Bajić et al. [6]. Each cation or anion, constituting the IL, is defined as an individual group, which is coincident with the method of ionic groups determination for the viscosity estimation of pure ILs and binary ILs mixtures reported in our previous work [14,15].

As a result, 119 binary systems with a total of 3365 experimental data points were regressed altogether to obtain the interaction parameters between functional groups ($\alpha_{ion/organic}$ and $\alpha_{organic/organic}$). Then other 24 binary mixtures, not involved in
the training set, were compared from the pure evaluated values to test the validity of the interaction parameters and thus the model developed in the current study.
2. DEVELOPMENT OF THE PROPOSED MODEL

2.1 Database. In this work, 4146 experimental viscosity data at 0.1 MPa for 143 binary mixtures were collected from the NIST database, as a function of the composition over a broad temperature range (from 273.15 K to 363.15 K). As discrepancies between the literature datasets for a given system could be observed, the experimental viscosities for each binary system, used to establish the UNIFAC-VISCO model, were taken only from one reference. The UNIFAC-VISCO model calculates the binary viscosities on the basis of the pure components’ properties. The references that also report the pure components’ densities and viscosities were preferred, thus identical measurement uncertainties for the properties of pure ILs and mixtures containing ILs increase the accuracy of the optimized binary interaction parameters. If the values of the pure component’s properties are not provided in the selected reference, the molar volume and viscosity of pure ILs were calculated by using the methods previously proposed by our group [14–17]. In the database, 3365 data points of 119 binary mixtures from literature [18-86], as a function of temperature and component composition, were used for optimization of interaction parameters and 781 data points of another 24 binary mixtures were used to validate the performance of the proposed model. Table 1 shows the list of the selected binary systems along with their corresponding temperature range and composition.
Table 1. List of the selected (ionic liquid + molecular solvent) binary mixtures

<table>
<thead>
<tr>
<th>No.</th>
<th>Ionic Component (1)</th>
<th>Organic Component (2)</th>
<th>Temperature Range (K)</th>
<th>Range of $x_1$ (mol%)</th>
<th>No. of Data Points</th>
<th>Measurement Uncertainty</th>
<th>RAAD (%)</th>
<th>Ref. ($\mu$)</th>
<th>Ref. ($\rho_{ij}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[C$<em>{2}$mim][C$</em>{2}$SO$_{4}$]</td>
<td>1-propanol</td>
<td>298.15 to 328.15</td>
<td>0.0273 to 0.8381</td>
<td>27</td>
<td>±0.006 (mPa • s)</td>
<td>3.62</td>
<td>[18]</td>
<td>[18]</td>
</tr>
<tr>
<td>2</td>
<td>[C$<em>{2}$mim][C$</em>{2}$SO$_{4}$]</td>
<td>methanol</td>
<td>298.15 to 328.15</td>
<td>0.0083 to 0.8654</td>
<td>33</td>
<td>±0.006 (mPa • s)</td>
<td>6.35</td>
<td>[18]</td>
<td>[18]</td>
</tr>
<tr>
<td>3</td>
<td>[C$<em>{2}$mim][C$</em>{2}$SO$_{4}$]</td>
<td>ethanol</td>
<td>298.15 to 328.15</td>
<td>0.0137 to 0.9377</td>
<td>30</td>
<td>±0.006 (mPa • s)</td>
<td>4.34</td>
<td>[19]</td>
<td>[19]</td>
</tr>
<tr>
<td>4</td>
<td>[C$<em>{2}$mim][BF$</em>{4}$]</td>
<td>methanol</td>
<td>278.15 to 318.15</td>
<td>0.0499 to 0.9476</td>
<td>65</td>
<td>2%</td>
<td>2.73</td>
<td>[20]</td>
<td>[20]</td>
</tr>
<tr>
<td>5</td>
<td>[C$<em>{2}$mim][BF$</em>{4}$]</td>
<td>ethanol</td>
<td>288.15 to 318.15</td>
<td>0.5447 to 0.9054</td>
<td>24</td>
<td>0.3%</td>
<td>3.57</td>
<td>[21]</td>
<td>[20]</td>
</tr>
<tr>
<td>6</td>
<td>[C$<em>{2}$mim][C$</em>{2}$SO$_{4}$]</td>
<td>water</td>
<td>298.15 to 328.15</td>
<td>0.0494 to 0.9285</td>
<td>24</td>
<td>±0.006 (mPa • s)</td>
<td>2.54</td>
<td>[19]</td>
<td>[19]</td>
</tr>
<tr>
<td>7</td>
<td>[C$<em>{2}$mim][BF$</em>{4}$]</td>
<td>dimethyl sulfoxide</td>
<td>303.15 to 333.15</td>
<td>0.0998 to 0.8999</td>
<td>36</td>
<td>&lt;0.6%</td>
<td>2.04</td>
<td>[22]</td>
<td>[22]</td>
</tr>
<tr>
<td>8</td>
<td>[C$<em>{2}$mim][BF$</em>{4}$]</td>
<td>N,N-dimethylformamide</td>
<td>303.15 to 333.15</td>
<td>0.1001 to 0.8984</td>
<td>36</td>
<td>&lt;0.6%</td>
<td>0.97</td>
<td>[22]</td>
<td>[22]</td>
</tr>
<tr>
<td>9</td>
<td>[C$<em>{2}$mim][BF$</em>{4}$]</td>
<td>dimethylacetamide</td>
<td>303.15 to 333.15</td>
<td>0.1006 to 0.9004</td>
<td>36</td>
<td>&lt;0.6%</td>
<td>1.47</td>
<td>[22]</td>
<td>[22]</td>
</tr>
<tr>
<td>10</td>
<td>[C$<em>{2}$mim][BF$</em>{4}$]</td>
<td>water</td>
<td>303.15 to 353.15</td>
<td>0.1001 to 0.8998</td>
<td>72</td>
<td>±0.01 (mPa • s)</td>
<td>7.41</td>
<td>[23]</td>
<td>[23]</td>
</tr>
<tr>
<td>11</td>
<td>[C$<em>{4}$mim][BF$</em>{4}$]</td>
<td>methanol</td>
<td>303.15 to 333.15</td>
<td>0.0999 to 0.8997</td>
<td>36</td>
<td>±0.35%</td>
<td>3.50</td>
<td>[24]</td>
<td>[24]</td>
</tr>
<tr>
<td>12</td>
<td>[C$<em>{4}$mim][BF$</em>{4}$]</td>
<td>dimethyl sulfoxide</td>
<td>293.15 to 353.15</td>
<td>0.0722 to 0.9155</td>
<td>63</td>
<td>±0.1%</td>
<td>3.11</td>
<td>[25]</td>
<td>[25]</td>
</tr>
<tr>
<td>13</td>
<td>[C$<em>{4}$mim][BF$</em>{4}$]</td>
<td>2-butanone</td>
<td>298.15</td>
<td>0.0498 to 0.8995</td>
<td>13</td>
<td>±0.3%</td>
<td>2.36</td>
<td>[26]</td>
<td>[26]</td>
</tr>
<tr>
<td>14</td>
<td>[C$<em>{4}$mim][BF$</em>{4}$]</td>
<td>dimethylacetamide</td>
<td>303.15 to 333.15</td>
<td>0.1001 to 0.8994</td>
<td>36</td>
<td>±0.35%</td>
<td>2.56</td>
<td>[24]</td>
<td>[24]</td>
</tr>
<tr>
<td>15</td>
<td>[C$<em>{4}$mim][BF$</em>{4}$]</td>
<td>N,N-dimethylformamide</td>
<td>298.15</td>
<td>0.053 to 0.8976</td>
<td>13</td>
<td>±0.3%</td>
<td>2.46</td>
<td>[26]</td>
<td>[26]</td>
</tr>
<tr>
<td>16</td>
<td>[C$<em>{4}$mim][BF$</em>{4}$]</td>
<td>acetonitrile</td>
<td>298.15</td>
<td>0.0487 to 0.9018</td>
<td>13</td>
<td>±0.3%</td>
<td>4.73</td>
<td>[26]</td>
<td>[26]</td>
</tr>
<tr>
<td>17</td>
<td>[C$<em>{4}$mim][BF$</em>{4}$]</td>
<td>ethyl formate</td>
<td>298.15</td>
<td>0.05 to 0.8996</td>
<td>13</td>
<td>±0.3%</td>
<td>4.56</td>
<td>[27]</td>
<td>[27]</td>
</tr>
<tr>
<td>18</td>
<td>[C$<em>{4}$mim][BF$</em>{4}$]</td>
<td>triethanolamine</td>
<td>303.15 to 343.15</td>
<td>0.1301 to 0.7054</td>
<td>25</td>
<td>&lt;0.1%</td>
<td>11.61</td>
<td>[28]</td>
<td>[28]</td>
</tr>
<tr>
<td>No.</td>
<td>Ionic Liquid</td>
<td>Compound</td>
<td>Temperature Range</td>
<td>P (mPa•s) Range</td>
<td>n</td>
<td>σ (mPa•s)</td>
<td>1/t</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>--------------</td>
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<td></td>
</tr>
<tr>
<td>19</td>
<td>[C₄mim][BF₄]</td>
<td>methyl acetate</td>
<td>298.15</td>
<td>0.0501 to 0.8999</td>
<td>13</td>
<td>±0.3%</td>
<td>4.58</td>
<td>[27]</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>[C₄mim][BF₄]</td>
<td>pyridine</td>
<td>298.15</td>
<td>0.193 to 0.8941</td>
<td>8</td>
<td>±1%</td>
<td>0.28</td>
<td>[29]</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>[C₄mim][BF₄]</td>
<td>chloroform</td>
<td>298.15</td>
<td>0.1509 to 0.8921</td>
<td>9</td>
<td>±1%</td>
<td>1.52</td>
<td>[29]</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>[C₄mim][BF₄]</td>
<td>dichloromethane</td>
<td>298.15</td>
<td>0.1605 to 0.9</td>
<td>9</td>
<td>±1%</td>
<td>3.02</td>
<td>[29]</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>[C₄mim][BF₄]</td>
<td>N-methyl-2-pyrrolidone</td>
<td>298.15 to 318.15</td>
<td>0.3049 to 0.7945</td>
<td>15</td>
<td>±0.3%</td>
<td>1.59</td>
<td>[30]</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>[C₄mim][NTf₂]</td>
<td>ethanol</td>
<td>278.15 to 338.15</td>
<td>0.051 to 0.907</td>
<td>40</td>
<td>±0.1%</td>
<td>1.96</td>
<td>[31]</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>[C₄mim][NTf₂]</td>
<td>N-methyl-2-pyrrolidone</td>
<td>293.15 to 323.15</td>
<td>0.0978 to 0.9002</td>
<td>63</td>
<td>±0.1%</td>
<td>3.24</td>
<td>[32]</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>[C₂mim][NTf₂]</td>
<td>benzene</td>
<td>298.15 to 328.15</td>
<td>0.508 to 0.865</td>
<td>16</td>
<td>±0.35%</td>
<td>1.67</td>
<td>[33]</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>[C₄mim][NTf₂]</td>
<td>thiophene</td>
<td>298.15 to 328.15</td>
<td>0.23 to 0.911</td>
<td>20</td>
<td>±0.35%</td>
<td>4.17</td>
<td>[33]</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>[C₄mim][NTf₂]</td>
<td>γ-butyrolactone</td>
<td>293.15 to 323.15</td>
<td>0.1005 to 0.8995</td>
<td>63</td>
<td>±1%</td>
<td>3.06</td>
<td>[34]</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>[C₄mim][NTf₂]</td>
<td>2,2,2-trifluoroethanol</td>
<td>278.15 to 333.15</td>
<td>0.1252 to 0.9123</td>
<td>72</td>
<td>±2%</td>
<td>4.59</td>
<td>[35]</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>[C₆mim][NTf₂]</td>
<td>isopropyl acetate</td>
<td>298.15</td>
<td>0.1082 to 0.9486</td>
<td>11</td>
<td>±0.5%</td>
<td>4.65</td>
<td>[36]</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>[C₆mim][NTf₂]</td>
<td>methyl diethanolamine</td>
<td>303.15 to 323.15</td>
<td>0.101 to 0.9011</td>
<td>45</td>
<td>±1%</td>
<td>6.97</td>
<td>[37]</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>[C₆mim][NTf₂]</td>
<td>1-propanol</td>
<td>278.15 to 338.15</td>
<td>0.048 to 0.8999</td>
<td>40</td>
<td>±0.3%</td>
<td>3.70</td>
<td>[38]</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>[C₆mim][NTf₂]</td>
<td>chloroform</td>
<td>288.2 to 318.2</td>
<td>0.074 to 0.906</td>
<td>40</td>
<td>±2~3%</td>
<td>4.18</td>
<td>[39]</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>[C₆mim][NTf₂]</td>
<td>1-octene</td>
<td>283.15 to 348.15</td>
<td>0.72 to 0.95</td>
<td>16</td>
<td>±1%</td>
<td>3.07</td>
<td>[40]</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>[C₆mim][BF₄]</td>
<td>ethanol</td>
<td>288.15 to 318.15</td>
<td>0.098 to 0.9</td>
<td>36</td>
<td>±0.3%</td>
<td>5.30</td>
<td>[21]</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>[C₆mim][BF₄]</td>
<td>2-methyl-2-propanol</td>
<td>298.15</td>
<td>0.1017 to 0.9</td>
<td>9</td>
<td>±0.01 (mPa•s)</td>
<td>7.98</td>
<td>[43]</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>[C₆mim][BF₄]</td>
<td>3-amino-1-propanol</td>
<td>303.15 to 308.15</td>
<td>0.0536 to 0.9204</td>
<td>18</td>
<td>±0.01 (mPa•s)</td>
<td>4.86</td>
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<td>32</td>
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<td>0.0988 to 0.8475</td>
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<td>298.15</td>
<td>0.0492 to 0.8931</td>
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<td>[C&lt;sub&gt;4&lt;/sub&gt;py][NTf&lt;sub&gt;2&lt;/sub&gt;]</td>
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| 44  | [C<sub>4</sub>py][BF<sub>4</sub>] | dichloromethane | 298.15 | 0.08071 to 0.94508 | 8 | ±1% | 7.72 | [47] | ±
| 45  | [C<sub>4</sub>py][BF<sub>4</sub>] | water  | 298.15 | 0.024 to 0.82817 | 9 | ±1% | 4.43 | [47] | ±
| 46  | [C<sub>4</sub>py][BF<sub>4</sub>] | methanol | 298.15 | 0.05255 to 0.91576 | 9 | ±1% | 3.87 | [47] | ±
| 47  | [C<sub>8</sub>mim][NTf<sub>2</sub>] | 2-propanol | 298.15 | 0.1034 to 0.9669 | 12 | ±0.5% | 1.76 | [48] | ±
| 48  | [C<sub>8</sub>mim][NTf<sub>2</sub>] | isopropyl acetate | 298.15 | 0.1009 to 0.9585 | 11 | ±0.5% | 1.20 | [48] | ±
| 49  | [C<sub>8</sub>mim][NTf<sub>2</sub>] | methanol | 298.15 | 0.098 to 0.9346 | 10 | ±0.5% | 3.09 | [49] | ±
| 50  | [C<sub>8</sub>mim][BF<sub>4</sub>] | 1-propanol | 298.15 | 0.0473 to 0.9118 | 13 | ± | 7.26 | [50] | ±
| 51  | [C<sub>8</sub>mim][BF<sub>4</sub>] | 2-butane | 298.15 | 0.0482 to 0.899 | 13 | ±0.01 (mPa•s) | 1.64 | [51] | ±
| 52  | [C<sub>8</sub>mim][BF<sub>4</sub>] | 2-butane | 298.15 | 0.0495 to 0.9049 | 13 | ±0.01 (mPa•s) | 1.79 | [50] | ±
| 53  | [C<sub>8</sub>mim][BF<sub>4</sub>] | ethyl acetate | 298.15 | 0.047 to 0.8908 | 13 | ±0.01 (mPa•s) | 3.88 | [51] | ±
| 54  | [C<sub>8</sub>mim][PF<sub>6</sub>] | 2-butane | 298.15 | 0.0513 to 0.9005 | 13 | ±0.2% | 5.81 | [52] | ±
| 55  | [C<sub>8</sub>mim][PF<sub>6</sub>] | acetonitrile | 298.15 | 0.1082 to 0.901 | 10 | ±1% | 1.87 | [29] | ±
| 56  | [C<sub>8</sub>mim][PF<sub>6</sub>] | dichloromethane | 298.15 | 0.1322 to 0.9247 | 10 | ±1% | 1.99 | [29] | ±
| 57  | [C<sub>8</sub>mim][PF<sub>6</sub>] | chloroform | 298.15 | 0.2674 to 0.9143 | 8 | ±1% | 2.84 | [29] | ±
| 58  | [C<sub>8</sub>mim][PF<sub>6</sub>] | cyclopentanone | 298.15 | 0.0482 to 0.9064 | 13 | ±0.2% | 1.19 | [52] | ±
| 59  | [C<sub>8</sub>mim][PF<sub>6</sub>] | N,N-dimethylethanolamine | 288.15 to 323.15 | 0.0872 to 0.8779 | 72 | ±0.1% | 5.01 | [53] | ±
| 60  | [C<sub>8</sub>mim][PF<sub>6</sub>] | N,N-dimethyformamide | 303.15 to 323.15 | 0.0276 to 0.0988 | 9 | ±0.35% | 2.08 | [54] | ±
| 61  | [C<sub>8</sub>mim][PF<sub>6</sub>] | dimethyl sulfoxide | 298.15 | 0.05 to 0.893 | 13 | ±0.5% | 2.28 | [55] | ±
| 62  | [C<sub>8</sub>mim][PF<sub>6</sub>] | water | 298.15 | 0.7854 to 0.9482 | 5 | ±1% | 2.13 | [29] | ±
| 63  | [C<sub>8</sub>mim][PF<sub>6</sub>] | methanol | 298.15 | 0.0503 to 0.8889 | 13 | ±0.5% | 6.42 | [55] | ±
| 64  | [C<sub>8</sub>mim][PF<sub>6</sub>] | methyl methacrylate | 283.15 to 353.15 | 0.0993 to 0.9014 | 117 | ±2.612% | 4.72 | [56] | ±
| 65  | [C<sub>8</sub>mim][PF<sub>6</sub>] | monoethanolamine | 288.15 to 323.15 | 0.0972 to 0.8815 | 72 | ±0.1% | 2.43 | [53] | ±
| 66  | [C<sub>4</sub>mim][PF<sub>6</sub>] | tetrahydrofuran | 298.15 | 0.0502 to 0.9595 | 13 | ±0.5% | 2.73 | [55] | ±
<table>
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<tr>
<th>No.</th>
<th>Cation</th>
<th>Anion</th>
<th>Temperature Range</th>
<th>Solubility Range</th>
<th>Solvent</th>
<th>% Solvent</th>
<th>Viscosity</th>
<th>Notes</th>
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<td>[C₄mim][PF₆]</td>
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<td>273.15 to 323.15</td>
<td>0.0504 to 0.8871</td>
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<td>7.00</td>
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<td>Relative Error</td>
<td>Density (g cm⁻³)</td>
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<td>5.69</td>
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<td>13</td>
<td>±1%</td>
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<td>111</td>
<td>[C₄mim][BF₄]</td>
<td>methyl acetate</td>
<td>298.15</td>
<td>0.0485 to 0.8827</td>
<td>13</td>
<td>±0.01 (mPa·s)</td>
<td>5.24</td>
<td>[51]</td>
</tr>
<tr>
<td>112</td>
<td>[C₄mim][PF₆]</td>
<td>ethanol</td>
<td>288.15 to 308.15</td>
<td>0.52 to 0.8</td>
<td>10</td>
<td>±3%</td>
<td>10.08</td>
<td>[80]</td>
</tr>
<tr>
<td>113</td>
<td>[C₄mim][DCA]</td>
<td>water</td>
<td>298.15 to 343.15</td>
<td>0.047 to 0.8701</td>
<td>40</td>
<td>0.65%</td>
<td>4.92</td>
<td>[59]</td>
</tr>
<tr>
<td>114</td>
<td>[C₄mpyrro][DCA]</td>
<td>γ-butyrolactone</td>
<td>273.15 to 323.15</td>
<td>0.0987 to 0.9013</td>
<td>42</td>
<td>1%</td>
<td>1.59</td>
<td>[81]</td>
</tr>
<tr>
<td>Test Set</td>
<td>Component 1</td>
<td>Component 2</td>
<td>Temperature Range</td>
<td>Viscosity Range</td>
<td>Uncertainty</td>
<td>Force Constant</td>
<td>Comments</td>
<td></td>
</tr>
<tr>
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<td>-------------</td>
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<td></td>
</tr>
<tr>
<td>1</td>
<td>[C₄mim][C₂SO₄]</td>
<td>2-propanol</td>
<td>298.15 to 328.15</td>
<td>0.0294 to 0.8772</td>
<td>±0.006 (mPa s⁻¹)</td>
<td>6.44</td>
<td>±2%</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>[C₂mim][NTf₂]</td>
<td>1-propanol</td>
<td>278.15 to 338.15</td>
<td>0.0519 to 0.9025</td>
<td>±1%</td>
<td>11.28</td>
<td>±0%</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>[C₄mim][BF₄]</td>
<td>acetone</td>
<td>298.15</td>
<td>0.0508 to 0.8949</td>
<td>±0.3%</td>
<td>11.19</td>
<td>±0%</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>[C₄mim][NTf₂]</td>
<td>1-butanol</td>
<td>298.15</td>
<td>0.1382 to 0.8952</td>
<td>1.5%</td>
<td>23.11</td>
<td>±0%</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>[C₄mim][NTf₂]</td>
<td>1-propanol</td>
<td>278.15 to 338.15</td>
<td>0.0508 to 0.9030</td>
<td>±0.5%</td>
<td>8.58</td>
<td>±0%</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>[C₄mim][NTf₂]</td>
<td>ethyl acetate</td>
<td>298.15</td>
<td>0.1067 to 0.9478</td>
<td>±0.5%</td>
<td>21.42</td>
<td>±0%</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>[C₆mim][NTf₂]</td>
<td>ethanol</td>
<td>278.15 to 338.15</td>
<td>0.047 to 0.903</td>
<td>±0.1%</td>
<td>5.91</td>
<td>±0%</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>[C₆mim][BF₄]</td>
<td>2-methyl-1-propanol</td>
<td>303.15 to 308.15</td>
<td>0.1004 to 0.8327</td>
<td>±0.3%</td>
<td>7.82</td>
<td>±0%</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>[C₆mim][BF₄]</td>
<td>1-propanol</td>
<td>293.15 to 333.15</td>
<td>0.1006 to 0.8894</td>
<td>±0.5%</td>
<td>9.80</td>
<td>±0%</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>[C₆mim][BF₄]</td>
<td>2-propanol</td>
<td>293.15 to 333.15</td>
<td>0.08354 to 0.85073</td>
<td>±0.5%</td>
<td>14.55</td>
<td>±0%</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>[C₆mim][NTf₂]</td>
<td>ethyl acetate</td>
<td>298.15</td>
<td>0.0984 to 0.9507</td>
<td>±0.5%</td>
<td>4.04</td>
<td>±0%</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>[C₆mim][BF₄]</td>
<td>2-propanol</td>
<td>298.15</td>
<td>0.0459 to 0.8697</td>
<td>±0.5%</td>
<td>7.11</td>
<td>±0%</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>[C₆mim][PF₆]</td>
<td>acetone</td>
<td>298.15</td>
<td>0.0519 to 0.8853</td>
<td>±0.2%</td>
<td>7.55</td>
<td>±0%</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>[C₆mim][PF₆]</td>
<td>3-pentanone</td>
<td>298.15</td>
<td>0.052 to 0.8912</td>
<td>±0.2%</td>
<td>7.93</td>
<td>±0%</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>[C₆mim][PF₆]</td>
<td>ethyl acetate</td>
<td>298.15</td>
<td>0.0496 to 0.9063</td>
<td>±0.2%</td>
<td>15.84</td>
<td>±0%</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>[C₆mim][SCN]</td>
<td>1-heptanol</td>
<td>298.15 to 348.15</td>
<td>0.0806 to 0.9793</td>
<td>±1%</td>
<td>4.71</td>
<td>±0%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ionic liquid</td>
<td>alcohol</td>
<td>T (K)</td>
<td>ρ (g/cm³)</td>
<td>T (K)</td>
<td>ρ (g/cm³)</td>
<td>T (K)</td>
<td>ρ (g/cm³)</td>
</tr>
<tr>
<td>---</td>
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<td>-----------</td>
<td>--------</td>
<td>-----------</td>
<td>--------</td>
<td>-----------</td>
</tr>
<tr>
<td>17</td>
<td>[C₄mim][SCN]</td>
<td>1-pentanol</td>
<td>298.15 to 348.15</td>
<td>0.0865 to 0.9807</td>
<td>66</td>
<td>&lt;0.05%</td>
<td>5.73</td>
<td>[66]</td>
</tr>
<tr>
<td>18</td>
<td>[C₄mim][SCN]</td>
<td>1-butanol</td>
<td>298.15 to 348.15</td>
<td>0.0262 to 0.9089</td>
<td>60</td>
<td>&lt;0.05%</td>
<td>5.39</td>
<td>[66]</td>
</tr>
<tr>
<td>19</td>
<td>[C₄mim][SCN]</td>
<td>1-propanol</td>
<td>298.15 to 348.15</td>
<td>0.0267 to 0.9342</td>
<td>60</td>
<td>&lt;1%</td>
<td>6.38</td>
<td>[65]</td>
</tr>
<tr>
<td>20</td>
<td>[C₄mim][SCN]</td>
<td>1-octanol</td>
<td>298.15 to 348.15</td>
<td>0.0874 to 0.9619</td>
<td>54</td>
<td>&lt;1%</td>
<td>4.62</td>
<td>[67]</td>
</tr>
<tr>
<td>21</td>
<td>[C₄mim][SCN]</td>
<td>1-nonanol</td>
<td>298.15 to 348.15</td>
<td>0.1203 to 0.9651</td>
<td>48</td>
<td>&lt;1%</td>
<td>3.81</td>
<td>[67]</td>
</tr>
<tr>
<td>22</td>
<td>[N₁₁₁₄][NTf₂]</td>
<td>1,2-propanediol</td>
<td>323.15 to 353.15</td>
<td>0.1157 to 0.868</td>
<td>49</td>
<td>±0.1%</td>
<td>6.00</td>
<td>[73]</td>
</tr>
<tr>
<td>23</td>
<td>[C₈mim][BF₄]</td>
<td>propyl acetate</td>
<td>298.15</td>
<td>0.0471 to 0.8994</td>
<td>13</td>
<td>±0.01 (mPa • s)</td>
<td>8.56</td>
<td>[51]</td>
</tr>
<tr>
<td>24</td>
<td>[C₈mim]Cl</td>
<td>1-propanol</td>
<td>298.15 to 328.15</td>
<td>0.0271 to 0.8929</td>
<td>33</td>
<td>&lt;1 (mPa • s)</td>
<td>12.99</td>
<td>[75]</td>
</tr>
</tbody>
</table>

*The molar volume of ionic liquid is calculated using the volumetric parameters provided in Table S1 of the Supporting Information. * Measurement uncertainties: 0.034 mPa • s (μ at 1-10 mPa • s), 0.214 mPa • s (μ at 11-50 mPa • s), 0.958 mPa • s (μ > 50 mPa • s).
2.2 Functional Groups. In our previous studies, the UNIFAC-VISCO model was developed to estimate the viscosity of pure ILs where each ion was regarded as an individual functional group [14,15]. In the present study, a similar approach was used to define the IL-viscosity contribution for investigated mixtures. In terms of the organic component in the mixture, the original cleavage reported by Chevalier et al. [87] was also used in the current study. The cleavages are identical for the branched and linear hydrocarbons with the same number of carbon atoms, which limits the number of organic functional groups [87]. Although isomers of organic components are not characterized by using this definition, ILs with different alkyl chain shapes (branched and linear) could be evaluated thanks to the 3D structure of ions contributing to the volume and surface area values (R and Q) [14].

Chevalier et al. [88] reported that methanol could not be split into the groups CH₃ and OH like other alcohols, due to a peculiarity. Several molecular solvents also show a similar characteristic and are defined as the single groups, such as water, chloroform, dichloromethane, pyridine, and thiophene. Table 2 shows the list of organic components and their corresponding functional groups used during this work.
2.3 Proposed Model. The UNIFAC-VISCO model is a group contribution model developed by Chevalier et al. [87,88] to predict the viscosity of the liquid mixtures. Briefly, the viscosity of a given mixture is calculated as follows:

\[
\ln(\mu) = \sum_{i=1}^{C} x_i \ln \left( \frac{\mu_i \cdot V_i}{V_m} \right) + \frac{\Delta E}{RT} - \frac{\Delta F}{RT} \tag{1}
\]

where, \( \mu \) is the viscosity of the mixture; subscript \( i \) represents the pure component in the mixture (i.e., the IL and the solvent); \( C \) is the total number of the pure components existing in the mixture, and equals 2 because only binary mixtures were investigated in this paper. \( x_i \) is the mole fraction of component \( i \); \( \mu_i \) is the pure-component viscosity of component \( i \); \( V_i \) is the pure-component molar volume of component \( i \); \( V_m \) is the ideal molar volume of the mixture calculated by using the following equation:

\[
V_m = \sum_{i=1}^{C} x_i V_i \tag{2}
\]

The UNIFAC-VISCO combinatorial term reported in the eq. 1 is defined by:

\[
\frac{\Delta E}{RT} = \sum_{i=1}^{C} x_i \ln \frac{\phi_i}{x_i} + 5 \sum_{i=1}^{C} x_i q_i \ln \frac{\theta_i}{\phi_i} \tag{3}
\]

where

\[
\theta_i = \frac{x_i q_i}{\sum_{j} x_j a_{ij}} \tag{4}
\]

\[
\phi_i = \frac{x_i r_i}{\sum_{j} x_j r_{ij}} \tag{5}
\]

\[
q_i = \sum_{K=1}^{N} n_{i,k} Q_k \tag{6}
\]

\[
r_i = \sum_{K=1}^{N} n_{i,k} R_k \tag{7}
\]

The volume \( R \) and surface area \( Q \) of ionic groups were obtained by using the COSMOthermX software (version C30_1601) as reported by our group previously [14,15,89]. \( R \) and \( Q \) values of organic groups are collected from values reported by
Fredenslund et al. [90,91]. $R$ and $Q$ values of all the functional groups are presented in the Table S2 of the Supporting Information.

The UNIFAC-VISCO residual term reported in the eq. 1 is defined by:

$$ \frac{g^p}{RT} = \sum_{i=1}^{C} x_i [\sum_{m=1}^{N} n_{m,i} (lny_m - lny_{m,i})] $$

(8)

where $N$ is the total number of the functional groups existing in the binary system; $n_m$ and $lny_m$ refer to the group fractions in the mixture, and $n_{m,i}$ and $lny_{m,i}$ refer to the group fractions in pure component $i$. $lny_m$ is defined as:

$$ \ln y_m = Q_m \left[ 1 - \ln \left( \sum_{i=1}^{N} \Theta_i \Psi_{i,m} \right) - \sum_{i=1}^{N} \frac{\Theta_{i} \Psi_{i,m,i}}{\sum_{j=1}^{N} \Theta_j \Psi_{j,i}} \right] $$

(9)

The $\Theta$ value is obtained by using eq 10:

$$ \Theta_m = \frac{x_m Q_m}{\sum_{i=1}^{N} x_i Q_i} , m = 1,2,3 ... N $$

(10)

The group interaction parameters $\Psi_{mn}$ are calculated as follows:

$$ \Psi_{mn} = \exp\left(-\frac{\alpha_{mn}}{298.15}\right) $$

(11)

where $\alpha_{mn}$ are the group interaction potential energy parameters between the defined functional groups $m$ and $n$.

2.4 Determination of The Interaction Parameters $\alpha_{mn}$. A set of interaction parameters $\alpha_{mn}$ is required for the calculation of the viscosity of binary mixtures using the UNIFAC-VISCO model. The values of interaction parameters between ionic groups ($\alpha_{ion/ion}$) were collected from our previous paper [14]. The values of interaction parameters between some organic groups ($\alpha_{organic/organic}$) were collected from Chevalier et al. [88]. The other unknown interaction parameters between organic and ionic groups ($\alpha_{ion/organic}$ and $\alpha_{organic/organic}$) were regressed by using the experimental training datasets. To obtain the values of $\alpha_{mn}$, we
performed the Marquardt [92] optimization of the following objective function:

$$OF = \frac{1}{M} \sum_{i=1}^{M} \left( \frac{\mu_{\text{exp}} - \mu_{\text{cal}}}{\mu_{\text{exp}}} \right)^2 \rightarrow \min$$  

(12)

where $M$ is the number of data points; $\mu_{\text{exp}}$ and $\mu_{\text{cal}}$ are the experimental and calculated viscosity data, respectively.

To carry out the regression, the ‘lsqnonlin’ function of the MATLAB Optimization Toolbox was used. In this work, 3365 training data were regressed altogether to obtain the global optimal values of interaction parameters.
3. RESULTS AND DISCUSSION

All the binary interaction parameters used in this work are presented in the Table S3 of the Supporting Information. The regression result was characterized by calculating the relative absolute average deviation (RAAD%, eq. 13) between the calculated ($\mu_{cal}$) and experimental viscosity ($\mu_{exp}$) data.

$$ RAAD\% = 100 \times \frac{1}{M} \sum_{i=0}^{M} \left| \frac{\mu_{exp} - \mu_{cal}}{\mu_{exp}} \right| $$

The deviation between each experimental viscosity dataset and correlated (training set; overall RAAD% close to 5.0%) for each investigated binary system used to determine the missing UNIFAC-VISCO parameters is reported in Table 1. As shown in Table 1 and in Figure 1, the quality of the developed UNIFAC-VISCO model was then assessed by comparing experimental data with those calculated for wide ranges of temperature, composition, and chemical structures leading to large values of viscosity up to 14000 mPa·s. As illustrated in Figures 1 and 2, the correlated results show, generally, a good agreement with the experimental data, except in two cases: i.e. the ([C₆mim][BF₄] + propylamine) viscosity dataset reported by Kermanpour et al. [43] and the ([C₄mim][OAc] + water) dataset published by Fendt et al. [71] for which a deviation higher than 20% is observed in both cases.

To further assess the UNIFAC-VISCO model, 781 test data points for 24 binary mixtures, not originally used during the training set, were then compared to the evaluated viscosity data by using the interaction parameters estimated by using the training set.
An arbitrary binary mixture with unknown viscosity could also be estimated thanks to the optimized values of the binary interaction parameters between the functional groups, constituting the given mixture. The evaluation result for each binary system is presented in Table 1 and is also shown in Figures 1-2. The overall RAAD% for the test set is close to 7.7% (see Table 1 and Figure 2), which demonstrates that the interaction parameters estimated during this work are accurate enough to evaluate then the viscosity data for original mixtures.

Nevertheless, as shown in Figure 2, a correlated data point for the ([C4mim][OAc] + water) binary system presents a relative deviation higher than 60%. However, only one research group reported the experimental viscosity data for the system ([C4mim][OAc] + water), to date [71]. The viscosity of the pure [C4mim][OAc] measured by Fendt et al. [71] is close to 485 mPa·s at 298.15 K; while by looking at the literature, it is obvious to highlight a clear discrepancy between experimental viscosity values reported for the [C4mim][OAc] at 298.15 K; e.g. 297 mPa·s [93], 440 mPa·s [94], 485.1 mPa·s [95], and 485 mPa·s [71]. As reported in our previous paper [14], a viscosity dataset [96] was recommended through the gnostic analysis of five viscosity datasets [71,93–96] for [C4mim][OAc] over a temperature range from (283.15 to 393.15) K. The interaction parameters between ions [C4mim]+ and [OAc]− were then calculated by regressing the recommended dataset [96], leading to an estimated viscosity value close to 424.6 mPa·s at 298.15 K for the pure component [C4mim][OAc] by using the UNIFAC-VISCO method [14]. Therefore, such a discrepancy on the pure component viscosity values definitely contributes to increasing errors during the estimation of the viscosity for the
([C₄mim][OAc] + water) binary system as shown in Figure 2.

Table 3 shows the estimation results (including correlated and evaluated data) for several main types of molecular solvents to further analyze the effect of the molecular solvent structure on the predictive capability of the UNIFAC-VISCO model. The deviation between the experimental viscosity data and those determined using the UNIFAC-VISCO model follows the order: water > amines > alcohols > esters > ketones > amides. The binary systems with water show the poorest estimation result. This trend could be attributed to the complexity of (IL + H₂O) systems, driven by strong solvent-ion interactions, like H-bonds, between water and IL, which may induce experimental (hydrolysis reaction [97], trace of water originally present in the pure IL, etc.) and computational errors. The difference between the experimental viscosity values for pure ILS used in this work for the calculation of the viscosity data of selected mixtures and those used in our previous paper [14] to determine the interaction parameters also contribute to an increase in the observed errors of the UNIFAC-VISCO model for some IL-based mixtures. In other words, the quality of the proposed method is strongly affected by the overall accuracy of data reported in the literature as expected for a such complex property like the viscosity.

Furthermore, the impact of the non-ideality of the volumetric properties of the solution on the quality of the proposed method was also exemplified by using the ([C₂mim][C₂SO₄] + 1-propanol) binary system. The experimental viscosities, densities, and excess molar volumes of this selected system are collected from González et al. [18] and provided in Table S4 of the Supporting Information, together with the
calculated binary viscosities by implementing the ideal and then the real molar volumes into the UNIFAC-VISCO model, respectively. Figure 3 shows the excess molar volumes of the system ([C2mim][C2SO4] + 1-propanol), along with the fitted curves by using the Redlich-Kister [98] equation (Eq. 14) as a function of the mole fraction of solvent.

\[ V^E = x_s(1 - x_s) \sum_{p=0}^{M} B_p(2x_s - 1)^p \]  

(14)

where \( V^E \) is the excess molar volume; \( x_s \) is the mole fraction of solvent; \( B_p \) are the Redlich-Kister fitting parameters; and \( M \) is the degree of the polynomial expansion. The fitting parameters reported by González et al. [18] are presented in Table S5 of the Supporting Information.

Figure 4 shows the difference on the calculated viscosities induced by using the non-ideality of the system ([C2mim][C2SO4] + 1-propanol). The minimum of \( V^E \) presents at approximately \( x_s=0.6 \), as shown in Figure 3. While the largest difference between the calculated viscosities by two different molar volumes is present at nearly 0.8 mole fraction of 1-propanol. The negative excess molar volume decreases as the temperature increases. Analogous temperature dependence behavior was observed for the calculated viscosities difference in Figure 4. However, the minimum difference between the calculated viscosities is better than -0.6% for the system ([C2mim][C2SO4] + 1-propanol). The RAAD% between the experimental viscosities and the calculated viscosities assuming the system to be ideal is 3.62%, and the RAAD% between the experimental viscosities and the calculated values considering their non-ideality is 3.55%. Hence, only a global 0.07% deviation was caused by the non-ideality.
of the binary system. Therefore, it is reasonable and acceptable to assume all binary systems investigated in this work as ideal.
4. CONCLUSIONS

In this work, the experimental viscosity values of (IL + molecular solvent) binary mixtures were estimated by using the modified UNIFAC-VISCO model. During this work, 3365 experimental viscosity data for 119 different binary systems were regressed altogether to determine missing interaction parameters between ions and molecular solvent group parameters. Then, 781 experimental data of 24 binary systems, not originally included in the training set, were used to assess the performance of the established model. The overall estimation result is close to 5.5%, amongst 5% for the training result and 7.7% for the test result, which proves that the UNIFAC-VISCO-based method is able to correlate and then evaluate the viscosity of (ILs + molecular solvent) binary mixtures as the function of temperature and composition at 0.1 MPa.
ASSOCIATED CONTENT

Supporting Information

The volumetric parameters for selected cations and anions are provided in Table S1. 

$R$ and $Q$ values of the functional groups, and the interaction parameters $\alpha_{mn}$ used in this work are presented in Tables S2-S3. Experimental density, viscosity, and excess molar volume data, along with calculated viscosity values for the system ([C$_2$ mim][C$_2$ SO$_4$] + 1-propanol) are given in Table S4. Parameters fitted to the Redlich-Kister equation for the excess molar volume of ([C$_2$ mim][C$_2$ SO$_4$] and 1-propanol) are provided in Table S5.

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Notes

The authors declare no competing financial interest.
ABBREVIATIONS

UNIQUAC UNiversal QUasichemical Activity Coefficient

UNIFAC-VISCO UNIversal Functional-group Activity Coefficient-VISCOsity

NRTL Non-Random Two-Liquid

MTSM Modified Two-Suffix-Margules

ASOG-VISCO Analytical Solution Of Groups-VISCOsity

Cations:

\([\text{mim}]^+\) methylimidazolium

\([\text{C}_2\text{mim}]^+\) 1,3-dimethylimidazolium

\([\text{C}_4\text{mim}]^+\) 1-ethyl-3-methylimidazolium

\([\text{C}_3\text{mmim}]^+\) 1-propyl-2,3-dimethylimidazolium

\([\text{C}_4\text{mim}]^+\) 1-butyl-3-methylimidazolium

\([\text{C}_6\text{mim}]^+\) 1-hexyl-3-methylimidazolium

\([\text{C}_8\text{mim}]^+\) 1-octyl-3-methylimidazolium

\([\text{C}_4\text{mmim}]^+\) 1-butyl-2,3-dimethylimidazolium

\([\text{C}_4\text{py}]^+\) 1-butylpyridinium

\([\text{C}_4\text{mpyrro}]^+\) 1-butyl-1-methylpyrrolidinium

\([\text{N}_{1114}]^+\) butyl-trimethyl-ammonium

\([\text{P}_{66614}]^+\) trihexyl(tetradecyl)phosphonium

Anions:

\([\text{BF}_4]^-\) tetrafluoroborate

\([\text{NO}_3]^-\) nitrate
[NTf₂]⁻ bis(trifluoromethylsulfon酰ylimide

[C₂SO₄]⁻ methylsulfate

[C₂SO₄]⁻ ethylsulfate

[PF₆]⁻ hexafluorophosphate

[DCA]⁻ dicyanamide

[SCN]⁻ thiocyanate

[OAc]⁻ acetate

[OTf]⁻ triflate

Cl⁻ chloride

**Nomenclature**

**Roman Letters:**

\( a \)  parameter in Seddon equation

\( C \)  total number of pure components in UNIFAC-VISCO method

\( g_E^E \)  combinatorial term in UNIFAC-VISCO method

\( g_F^F \)  residual term in UNIFAC-VISCO method

\( n_{i,k} \)  total number of \( k^{th} \) group present in component \( i \)

\( M \)  number of data points

\( N \)  total number of groups

\( q_i \)  van der Waals’ surface area of component \( i \)

\( Q_k \)  group surface area parameter

\( r_i \)  van der Waals’ volume of component \( i \)

\( R_k \)  group volume parameter.
\( \mathcal{R} \) gas constant (J/mol·K)

\( T \) temperature (K)

\( V_i \) pure-component molar volume (m\(^3\)/kmol)

\( V_m \) mixture molar volume (m\(^3\)/kmol)

\( x_i \) mole fraction of the component \( i \)

\( x_s \) mole fraction of the molecular solvent

**Greek Letters:**

\( \alpha_{mn} \) group interaction parameter between groups \( m \) and \( n \)

\( \gamma_m \) residual activity coefficient

\( \rho_{\text{IL}} \) density of pure ionic liquid (g·cm\(^{-3}\))

\( \theta_i \) molecular surface area fraction of component \( i \)

\( \Theta_i \) area fraction for group \( i \)

\( \mu \) viscosity of mixture (mPa·s)

\( \mu_i \) viscosity of pure component \( i \)

\( \mu_{\text{IL}} \) viscosity of pure ionic liquid

\( \mu_{\text{exp}} \) viscosity experimentally measured

\( \mu_{\text{cal}} \) viscosity calculated by our method

\( \mu_{\text{corre}} \) viscosity correlated by the Seddon equation

\( \phi_i \) molecular volume fraction of component \( i \)

\( \Psi_{m,i} \) group interaction parameter
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