**Excess Thermodynamic and Volumetric Properties of Binary Mixtures containing Ionic Liquid [Bmim][NTf₂]and Dimethyl Carbonate from T = (298.15to 323.15) K**

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**Abstract** - The density (\( \rho \)), ultrasonic velocity (\( u \)) and refractive index (\( n \)) of the binary mixtures of 1-Butyl 3-Methylimidazolium bis (Trifluoromethylsulfonyl)Imide ([Bmim][NTf₂]) and dimethyl carbonate (DMC)and those of pure liquids were measured using Anton Paar vibrating tube density and sound velocity meter (DSA 5000 M) and Dr. Kernchen Abbemat (Anton Paar, Austria) refractometer over the whole composition range as a function of temperature between 298.15 and 323.15 K in steps of 5K at atmospheric pressure. From the experimental data, the excess values of molar volumes (\( V_m^E \)), partial molar volume (\( V_m^P \)), partial molar volume at infinite dilution (\( V_m^{E0} \)), isentropic compressibility (\( k_S^E \)), acoustic impedance (\( Z^E \)), free length (\( L_f^E \)), speeds of sound (\( u^E \)), and deviations in refractive index (\( \Delta n_D \)) were calculated and fitted to a Redlich–Kister type equation. The negative values of \( V_m^{E0}, k_S^E, L_f^E \) and positive values of \( Z^E, u^E, \Delta n_D \) indicate the existence of strong interactions between the components.

**Keywords**: Bmim imide, dimethyl carbonate, Density, ultrasonic velocity, Refractive index, excess/deviation parameters, Redlich–Kister type equation.

**INTRODUCTION**

Since Ionic liquids (ILs) have large variety of new applications, a major focus of study is being carried out both at laboratory and industrial scale. The interesting properties such as negligible volatility or non-flammability make them suitable for the replacement of conventional liquids.

The measurement of physical properties is one of the most important research areas involving ILs for the use of them from laboratory level to industrial applications.

Basing on how they attain the charge, Ionic liquids are divided into three types:

1. protic; 
2. aprotic; and 
3. zwitter ionic.

Protic ILs are formed by proton-transfer reaction as acid and base as they donate and accept hydrogen bonds making hydrogen bonded network like water [1]. Aprotic ILs consist of imidazolium and pyrrolidium based cations and form inter molecular hydrogen bonds but not as protic ILs.

Polarity is an important parameter to describe nature of a solvent. Ionic liquids are considered to be highly polar but weak as coordinating solvent [2]. Their polarity is between that of the water and chlorinated organic solvents.

Solvent feature of ionic liquid comes from H-bond donation from cation, H-bond accepting functionality of the anion, and π-π bonding. ILs are immiscible to non polar organic solvents and can be used in two phase system.

They have applicable electrochemical window. For some ILs it is in the range of ~6V [3]. However choice of electrode has some effect on the electrochemical window. Ionic liquids like ammonium, piperidinium, morpholinium with 4 coordinated nitrogen have larger electrochemical window compared to others [3].

In the present work BMIM imide ionic liquid was mixed with well known green solvent dimethyl carbonate in different proportions and the density, sound velocity and refractive index were measured for each mixture at six temperatures in steps of 5K from 298.15K to 323.15K.

[Bmim] [NTf₂] has many applications such as extracting solvent for the removal of many organic compounds through liquid–liquid extraction [4, 5], in chromatography [6] and enzyme catalysis in ionic liquids [7], etc.

Dimethyl carbonate (DMC) can be used as an anti-knocking agent and can possibly (partially) replace MTBE or ethanol as a fuel additive [8]. In addition, DMC can potentially replace dimethyl sulfate and methyl halides in methylation reactions [9]. DMC is relatively non toxic, especially in comparison to the mentioned chemicals [10]. It is of great importance to understand the mixing behavior of ILs in dimethyl carbonate and to provide accurate physicochemical data. The thermo acoustic, volumetric and refractive index data of [Bmim][NTf₂] with dimethyl carbonate were not reported earlier.

Basing on our preliminary experiments, [Bmim][NTf₂] was found to be miscible with dimethyl Carbonate at all proportions. Hence, it is proposed to measure the densities (\( \rho \)), speeds of sound (\( u \)), refractive...
indices \((n_D)\) of the binary mixtures of \([\text{Bmim}][\text{NTf}_2]\) with dimethyl carbonate in the temperature range from 298.15 to 323.15K and over the whole composition range and to estimate their excess/deviation properties for their potential application in industrial processes. On the basis of the measured values the properties such as excess values of molar volumes \((\bar{V}_m^E))\), partial molar volumes, partial molar volumes at infinite dilution \((\bar{V}_m^E,\infty))\), isentropic compressibility \((k_s^E))\), acoustic impedance \((Z^E))\), free length \((L_f^E))\), speeds of sound \((u^E))\), and deviations in refractive index \(\Delta n_D\) for binary mixtures were fitted using Redlich–Kister type polynomial equation.

### 2 EXPERIMENTAL

**Chemicals:**
The ionic liquid, (BMIM imide) or \([\text{Bmim}][\text{NTf}_2]\), with purity 0.99 in mass fraction was used in this work. It was purchased from Iolitec, GmBH (Germany), while the dimethyl carbonate was supplied by Sigma Aldrich. The IL \([\text{Bmim}][\text{NTf}_2]\) was used without any further purification and dimethyl carbonate was further purified by distillation. The measured density, speed of sound and refractive index of the pure liquids at atmospheric pressure are compared with literature values to verify the purity of liquids under investigation and are presented in table 1. Ever since the concept of hindered internal rotation about single bonds was established, it has been expected that esters of simple carboxylic acids might exist in a conformational equilibrium in their fluid states. Such equilibrium is expected, on theoretical grounds, to involve the two planar conformations for DMC (shown in fig. 1d).

![Fig1a: Ball and stick model of Bmim NTf₂](image1.png)

![Fig 1b: 1-Butyl 3-Methylimidazolium cation](image2.png)

![Fig1c: molecular structure of dimethyl carbonate](image3.png)

![Fig 1d: molecular conformations of dimethyl carbonate](image4.png)

**Table 1: Experimental and literature values of density, velocity and refractive index at temperatures 298.15K to 323.15K**

<table>
<thead>
<tr>
<th>T/K</th>
<th>([\text{Bmim}][\text{NTf}_2])</th>
<th>(\rho \text{ kgm}^{-3})</th>
<th>(\text{Lit.})</th>
<th>(u \text{ ms}^{-1})</th>
<th>(\text{Lit.})</th>
<th>(n_D)</th>
<th>(\text{Lit.})</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>T/K</th>
<th>(\text{Dimethyl carbonate})</th>
<th>(\rho \text{ kgm}^{-3})</th>
<th>(\text{Lit.})</th>
<th>(u \text{ ms}^{-1})</th>
<th>(\text{Lit.})</th>
<th>(n_D)</th>
<th>(\text{Lit.})</th>
</tr>
</thead>
<tbody>
<tr>
<td>318.15</td>
<td>1036.79</td>
<td>1035.60[15]</td>
<td>1113.09</td>
<td>-</td>
<td>1.3570</td>
<td>1.3622[17]</td>
<td></td>
</tr>
<tr>
<td>323.15</td>
<td>1030.04</td>
<td>1028.40[15]</td>
<td>1092.16</td>
<td>-</td>
<td>1.3547</td>
<td>1.3590[17]</td>
<td></td>
</tr>
</tbody>
</table>
3. THEORY:
The experimentally measured values of $\rho$, $u$ and $n_0$ were used to calculate the values of thermodynamic and acoustical parameters such as molar volume ($V_m$), intermolecular free length ($L_f$), isentropic compressibility ($k_s$). The derived excess/deviation parameter values are shown in Table 2.

The excess/deviation parameters for the above parameters including deviations in refractive index $\Delta n$ were also calculated by using the following equations:

$$V_m = \frac{M}{\rho}$$  \hspace{1cm} (1)

Where $M_{\text{eff}}$ is the effective molecular weight ($= x_1M_1 + x_2M_2$), where $M_1$ and $M_2$ are the molar masses and $x_1$ and $x_2$ are the mole fractions of IL and dimethyl carbonate, respectively, and $\rho$ is the density of the medium.

The speed of sound ($u$) and the density of the medium ($\rho$) using Newton–Laplace equation give the intermolecular free length as:

$$L_f = \frac{k}{\sqrt{\rho \rho}}$$  \hspace{1cm} (2)

Where, $K$ is a temperature dependent constant equal to (93.875 + 0.375T) x 10$^{-6}$.

The excess molar volumes are given by:

$$V_m = \sum_{i=1}^{N} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i}\right)$$  \hspace{1cm} (3)

Where $\rho$ is the density of the mixture and $M_i$, $x_i$ and $\rho_i$ are the molar mass, mole fraction, and density of the $i$th component in the mixture, respectively.

The isentropic compressibility, $k_s$, is computed directly from the measured values of speed of sound and density using the Newton–Laplace equation:

$$k_s = -\frac{1}{V_m} \left(\frac{\partial V_m}{\partial \rho}\right) = \left(\frac{1}{\rho u^2}\right) = \left(\frac{V_m}{M u^2}\right)$$  \hspace{1cm} (4)

Excess isentropic compressibility is given by:

$$k_s^E = k_s - \sum_{i=1}^{2} x_i k_{ Si}$$  \hspace{1cm} (5)

Where, $k_s$ is the isentropic compressibility

The excess intermolecular free length is given by:

$$L_f^E = L_f - [x_1 L_{f1} + x_2 L_{f2}]$$  \hspace{1cm} (6)

The excess speeds of sound, $u^E$ are estimated in binary mixtures using the following expression proposed by Douheret et al. [18]:

$$u^E = u - [x_1 u_1 + x_2 u_2]$$  \hspace{1cm} (7)

Table 2: The excess parameters of binary mixtures of BMIM imide and dimethyl carbonate.

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$\Delta U$</th>
<th>$\Delta k_s^{10^{10}}$</th>
<th>$2\times 10^{10}$</th>
<th>$L_f^E$</th>
<th>$\Delta n$</th>
<th>$\Delta k_s^{10^{10}}$</th>
<th>$V_m^E$</th>
<th>$\Delta V_m^{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
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<td>0.0000</td>
</tr>
<tr>
<td>0.1010</td>
<td>12.8047</td>
<td>-0.5778</td>
<td>0.1030</td>
<td>-0.0236</td>
<td>0.0142</td>
<td>0.0461</td>
<td>0.0461</td>
<td></td>
</tr>
<tr>
<td>0.1945</td>
<td>20.4161</td>
<td>-0.8056</td>
<td>0.1319</td>
<td>-0.0334</td>
<td>0.0198</td>
<td>0.0512</td>
<td>0.0512</td>
<td></td>
</tr>
<tr>
<td>0.2994</td>
<td>22.7964</td>
<td>-0.8617</td>
<td>0.1712</td>
<td>-0.0362</td>
<td>0.0215</td>
<td>0.0429</td>
<td>0.0429</td>
<td></td>
</tr>
<tr>
<td>0.3999</td>
<td>20.7558</td>
<td>-0.6168</td>
<td>0.1331</td>
<td>-0.0262</td>
<td>0.0166</td>
<td>0.0222</td>
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<td></td>
</tr>
<tr>
<td>0.4976</td>
<td>30.3474</td>
<td>-0.9790</td>
<td>0.1559</td>
<td>-0.0394</td>
<td>0.0205</td>
<td>0.0505</td>
<td>0.0505</td>
<td></td>
</tr>
</tbody>
</table>

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Table 3: coefficients ($A_i$) of Redlich–Kister polynomial for excess parameters

<table>
<thead>
<tr>
<th>$V_{e}(\times 10^{-4} m^{3} mol^{-1})$</th>
<th>$RKC/Tem$</th>
<th>$A_0$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$A_4$</th>
<th>$\sigma$</th>
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<td>$298.15$</td>
<td>-0.0036</td>
<td>-0.0026</td>
<td>-0.0028</td>
<td>-0.0009</td>
<td>0.0001</td>
<td>0.00000077</td>
<td></td>
</tr>
<tr>
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<td>-0.0028</td>
<td>-0.0026</td>
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<td>0.00000098</td>
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<tr>
<td>$323.15$</td>
<td>-0.004</td>
<td>-0.0029</td>
<td>-0.0003</td>
<td>-0.001</td>
<td>0.00000095</td>
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<td></td>
</tr>
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<td>$343.15$</td>
<td>-0.0042</td>
<td>-0.0003</td>
<td>-0.0003</td>
<td>-0.0012</td>
<td>0.0000006</td>
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<td></td>
</tr>
<tr>
<td>$380.15$</td>
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<td>-0.0032</td>
<td>-0.0002</td>
<td>-0.0012</td>
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<td></td>
</tr>
<tr>
<td>$420.15$</td>
<td>-0.0047</td>
<td>-0.0034</td>
<td>-0.0032</td>
<td>-0.0012</td>
<td>0.0000010</td>
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<tr>
<td>$500.15$</td>
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<td>-0.0029</td>
<td>-0.0003</td>
<td>-0.0012</td>
<td>0.00000095</td>
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</tr>
<tr>
<td>$651$</td>
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<td>-1.7337</td>
<td>-1.5024</td>
<td>-0.2247</td>
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<td></td>
</tr>
<tr>
<td>$303.15$</td>
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<td>-1.8744</td>
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<td>0.001210</td>
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</tr>
<tr>
<td>$323.15$</td>
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<td>-2.0486</td>
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<tr>
<td>$343.15$</td>
<td>-3.7848</td>
<td>-2.8912</td>
<td>-2.2401</td>
<td>-1.4415</td>
<td>-0.4386</td>
<td>0.001510</td>
<td></td>
</tr>
<tr>
<td>$380.15$</td>
<td>-4.1353</td>
<td>-3.1648</td>
<td>-2.4716</td>
<td>-1.5496</td>
<td>-0.5074</td>
<td>0.002490</td>
<td></td>
</tr>
<tr>
<td>$420.15$</td>
<td>-4.5136</td>
<td>-3.4515</td>
<td>-2.6897</td>
<td>-1.7165</td>
<td>-0.5302</td>
<td>0.002250</td>
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</tr>
<tr>
<td>$500.15$</td>
<td>-5.0015</td>
<td>-3.7951</td>
<td>-2.9289</td>
<td>-1.8877</td>
<td>-0.5533</td>
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</tr>
<tr>
<td>$651$</td>
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<td>-3.9801</td>
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<td>-0.9804</td>
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<tr>
<td>$303.15$</td>
<td>-0.6872</td>
<td>0.40144</td>
<td>0.26571</td>
<td>0.09555</td>
<td>-0.0212</td>
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<tr>
<td>$323.15$</td>
<td>0.6267</td>
<td>0.40664</td>
<td>0.26852</td>
<td>0.09212</td>
<td>-0.02618</td>
<td>0.00027</td>
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</tr>
<tr>
<td>$343.15$</td>
<td>0.63825</td>
<td>0.41091</td>
<td>0.27134</td>
<td>0.08990</td>
<td>-0.03028</td>
<td>0.00029</td>
<td></td>
</tr>
<tr>
<td>$380.15$</td>
<td>0.64721</td>
<td>0.41599</td>
<td>0.27637</td>
<td>0.08149</td>
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<tr>
<td>$420.15$</td>
<td>0.65590</td>
<td>0.41967</td>
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<td>0.00039</td>
<td></td>
</tr>
<tr>
<td>$500.15$</td>
<td>-0.1218</td>
<td>-0.0923</td>
<td>-0.0708</td>
<td>-0.0362</td>
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<td>$303.15$</td>
<td>-0.1327</td>
<td>-0.0997</td>
<td>-0.0758</td>
<td>-0.0400</td>
<td>-0.00043</td>
<td>0.000076</td>
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</tr>
<tr>
<td>$323.15$</td>
<td>-0.1440</td>
<td>-0.1079</td>
<td>-0.0833</td>
<td>-0.0432</td>
<td>-0.00022</td>
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<tr>
<td>$343.15$</td>
<td>-0.1562</td>
<td>-0.1167</td>
<td>-0.0910</td>
<td>-0.0463</td>
<td>-0.0013</td>
<td>0.000097</td>
<td></td>
</tr>
<tr>
<td>$380.15$</td>
<td>-0.1690</td>
<td>-0.1263</td>
<td>-0.0969</td>
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</tr>
<tr>
<td>$420.15$</td>
<td>-0.1832</td>
<td>-0.1366</td>
<td>-0.1036</td>
<td>-0.0525</td>
<td>-0.0043</td>
<td>0.000126</td>
<td></td>
</tr>
</tbody>
</table>
Where, \( x \) values have been taken from 0 to 4. The corresponding leastsquares method. In the present investigation the \( \nu \) parameters of the function and are determined using the dimethyl carbonate, respectively and the A following expression:

\[
Δn_D = n_D - [x_1n_{D1} + x_2n_{D2}]
\]

The excess/deviation properties have been fitted to a Redlich–Kister type polynomial equation given by:

\[
Y^E = x_1x_2\sum_{i=0}^{j} A_i(x_2 - x_1)^i
\]

Where, \( x_1 \) and \( x_2 \) are the mole fraction of ionic liquid and dimethyl carbonate, respectively and the \( A_i \) are adjustable parameters of the function and are determined using the leastsquares method. In the present investigation the ‘i’ values have been taken from 0 to 4. The corresponding standard deviations \( \sigma (Y^E) \) have been calculated using the following expression:

\[
\sigma(Y^E) = \left( \frac{\sum(Y_{exp} - Y_{cal})^2}{m-n} \right)^{1/2}
\]

where ‘m’ is the total number of experimental points and \( n \) is the number of coefficients in eq.(22). The calculated values of the coefficients \( A_i \) along with the standard deviations, \( \sigma (Y^E) \) are given in Table 4.

4. RESULTS AND DISCUSSION

In the present study, excess molar volume (\( V^E_m \)), excess partial molar excess volume (\( \overline{\nu}_m^E \)), partial molar excess volume at infinite dilution (\( \overline{\nu}_m^{E,\infty} \)), excess isentropic compressibility (\( \kappa^E_s \)), excess free length (\( L^E_f \)), excess acoustic impedance (\( Z^E \)), excess ultrasonic velocity (\( u^E \)), and deviations in refractive index (\( Δn_D \)) were calculated. The strength of interactions present between the component molecules of the binary mixture under study is indicated by the variations observed in these excess/deviation parameters. Further these variations are effected by the composition, molecular size, shape and temperature.

Excess molar volumes \( V^E_m \) for binary mixture of [Bmim][NTf₂] and dimethyl carbonate as a function of composition from 298.15 to 328.15 K are shown in Fig. 1. The contraction in the volume of the mixture can be attributed to the formation of hydrogen bonds between the ionic liquid [Bmim][NTf₂] and dimethyl carbonate.

The values of \( V^E_m \) become more negative with increase in temperature. This is due to the fitting of smaller dimethyl carbonate molecules into the voids created by larger IL molecules leading to decrease in volume of the mixture to a greater extent, which results in more negative \( V^E_m \) values with increase in temperature.

![Fig. 2: Plots of excess molar volume (\( V^E_m \)) against mole fraction (\( x_1 \)) for binary mixtures of [Bmim][NTf₂] and Dimethyl carbonate at temperature T and atmospheric pressure.](image-url)
The strength of interaction follows the order: (323.15>318.15>313.15>308.15>303.15>298.15) K. The properties of partial molar volumes reflect the existing molecular interactions in the system. The contribution of a component of a mixture to the overall volume of the solution is interpreted in terms of Partial molar volume. Therefore, the partial molar volume is a function of composition of the mixture. The partial molar volumes \( \bar{V}_{m} \) of component 1[Bmim][NTf₂] and \( \bar{V}_{m,2} \) of component 2 (dimethyl carbonate) in the mixtures over the entire range of composition have been calculated by using the following equations:

\[
\bar{V}_{m,1} = \bar{V}_{m} + V^*_1 + x_1 \left( \frac{\partial V^*_m}{\partial x_1} \right)_{T,p}
\]  

(11)

\[
\bar{V}_{m,2} = \bar{V}_{m} + V^*_2 - x_1 \left( \frac{\partial V^*_m}{\partial x_1} \right)_{T,p}
\]  

(12)

Where \( V^*_1 \) and \( V^*_2 \) are the molar volumes of pure components of [Bmim][NTf₂] and dimethyl carbonate respectively. Differentiating the Redlich–Kister equation for \( V^*_m \), we get the derivatives \( \left( \frac{\partial V^*_m}{\partial x_1} \right)_{T,p} \) mentioned in the equations (11) and (12) are obtained by, which leads to the following equations for \( \bar{V}_{m,1} \) and \( \bar{V}_{m,2} \):

\[
\bar{V}_{m,1} = V^*_1 + x_1^2 \sum_{i=0}^{4} A_i (x_2 - x_1)^i - 2x_1x_2 \sum_{i=1}^{4} A_i(i)(x_2 - x_1)^{i-1}
\]  

(13)

Table 5: Partial molar volumes (\( V_{m,1} \) and \( V_{m,2} \) against mole fraction \( x_1 \)) for [Bmim][NTf₂] and dimethyl carbonate mixtures at temperature T and atmospheric pressure:

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( 298.15K )</th>
<th>( 303.15K )</th>
<th>( 308.15K )</th>
<th>( 313.15K )</th>
<th>( 318.15K )</th>
<th>( 323.15K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x )</td>
<td>( V_{m,1} )</td>
<td>( V_{m,2} )</td>
<td>( V_{m,1} )</td>
<td>( V_{m,2} )</td>
<td>( V_{m,1} )</td>
<td>( V_{m,2} )</td>
</tr>
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Using the above equations, \( \bar{E}_{m,1} \) and \( \bar{E}_{m,2} \) have been evaluated using:

\[
\bar{E}_{m,1} = \bar{V}_{m,1} - V^*_1
\]

(15)

\[
\bar{E}_{m,2} = \bar{V}_{m,2} - V^*_2
\]

(16)

The values of \( \bar{V}_{m,1} \) and \( \bar{V}_{m,2} \) are presented in Table 5 for all the systems. From this table, we observe that the values of \( \bar{V}_{m,1} \) and \( \bar{V}_{m,2} \) for both the components in the mixtures are lower than their individual molar volumes in the pure state, which represents the contraction of volume on mixing [Bmim][NTf₂] with dimethyl carbonate at all the temperatures under study.

The variation of excess partial molar volumes of \( \bar{E}_{m,1} \) [Bmim][NTf₂] and \( \bar{E}_{m,2} \) (dimethyl carbonate) are represented in Figures 3 and 4 respectively, in the temperature range from 298.15 to 323.15K. Inspection of these figures not only reveals the existence of strong forces between the unlike molecules but also supports the deductions drawn from excess molar volume. The partial molar volumes and excess partial molar volumes of [Bmim][NTf₂] at infinite dilution, (\( \bar{V}_{m,1} \)) and (\( \bar{V}_{m,2} \)), are given by:

\[
\bar{V}_{m,1} = A_0 + A_1 + A_2 + A_3 + \ldots = \bar{V}_{m,1} - V^*_1
\]

(17)
The data of $\bar{V}_{m,1}^E$ and $(\bar{V}_{m,1}^E)_\infty$ are presented in Table 6 at 298.15K to 323.15K in steps of 5 K. From this table, the values of $(\bar{V}_{m,1}^E)_\infty$ are found to be negative and become more negative with increasing temperature. Hence we can conclude that with increasing temperature, strong interactions increase among the unlike molecules of the mixtures. This supports the existing strong molecular interactions that were observed with the variation of $\bar{V}_m^E$.

![Fig. 3: Plots of excess partial molar volume ($\bar{V}_{m,1}^E$) against mole fraction $x_1$ for [Bmim][NTf$_2$] and Dimethyl carbonate mixtures at temperature $T$ and atmospheric pressure](image1)

![Fig. 4: Plots of excess partial molar volume ($\bar{V}_{m,2}^E$) against mole fraction ($x_1$) for [Bmim][NTf$_2$] and dimethyl carbonate mixtures at temperature $T$ and atmospheric pressure](image2)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$\bar{V}_{m,1}$</th>
<th>$(\bar{V}<em>{m,1}^E)</em>\infty$</th>
<th>$\bar{V}_{m,2}$</th>
<th>$(\bar{V}<em>{m,2}^E)</em>\infty$</th>
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<tr>
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<td>291.97</td>
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<td>74.39</td>
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<td>292.89</td>
<td>-3.56</td>
<td>74.49</td>
<td>-12.39</td>
</tr>
<tr>
<td>323.15</td>
<td>293.52</td>
<td>-3.92</td>
<td>74.32</td>
<td>-13.13</td>
</tr>
</tbody>
</table>
In Fig. 4, the $k_s^E$ values for this system are found to be negative in the whole composition range at all investigated temperatures. The negative $k_s^E$ values are attributed to the strong attractive interactions between the molecules of the components [20]. In the present study, the negative $k_s^E$ values can be attributed to a closer approach of unlike molecules and a stronger interaction between components of mixtures at all temperatures. This supports the inference drawn from $\nu_m^E$.

![Fig. 4: Plots of excess isentropic compressibility ($k_s^E$) against mole fraction ($x_1$) for [Bmim][NTf2] and dimethyl carbonates mixtures at temperature T and atmospheric pressure](image.png)

In the present study, the negative $L_f^E$ were observed. The trend of $L_f^E$ values (Fig. 5) is similar to that of $k_s^E$ at all temperatures under study. The specific interactions between unlike molecules in the liquid mixture lead to negative values of $L_f^E$. The structural readjustments in the liquid mixture towards a less compressible phase of fluid and closer packing of molecules [20] also contribute to negative $L_f^E$.

Figure 6 shows that $Z^E$ is positive for the systems at all the temperatures under study. Specific acoustic impedance is a parameter that depends on the molecular packing of the mixture. The positive values of $Z^E$ indicate the presence of strong interactions between the component molecules [18].

From the figure 7 the $u^E$ values are found to be positive over the entire range of composition at all investigated temperatures. This indicates the increasing strength of interaction between component molecules of binary liquid mixtures. In general, strong interactions among the components of a mixture cause the formation of molecular aggregates and more compact structures due to which the ultrasonic velocity increases leading to positive $u^E$. On the other hand, if the structure-breaking factor predominates, it leads to expansion of the liquid mixture, and hence the ultrasonic velocity decreases resulting in negative $u^E$ [20]. The positive values of $u^E$ in the present system indicate much stronger interactions between the molecules [21].

Fig. 8 shows that the values of $\Delta n_D$ are positive over the entire range of compositions at a given temperature. The variation of refractive index deviations $\Delta n_D$ with the mole fraction of IL shows the reverse trend to $k_s^E$ [22]. This further supports the presence of strong interactions between component molecules in study.

Generally, the cohesive forces (attraction forces) or dispersive forces between the molecules of a mixture cannot be easily assessed by any theory.
Fig. 5: Plots of excess free length ($L_{Ef}^{ex}$) against mole fraction ($x_1$) for [Bmim][NTf$_2$] and Dimethyl carbonate mixtures at temperature T and atmospheric pressure.

Fig. 6: Plots of excess acoustic impedance ($Z_{E}^{ex}$) against mole fraction ($x_1$) for [Bmim][NTf$_2$] dimethyl carbonate (2) mixtures at temperature T and atmospheric pressure.

Fig. 7: Plots of excess ultrasonic speed of sounds ($u_{E}^{ex}$) against mole fraction ($x_1$) for [Bmim][NTf$_2$] mixtures.
The electronic structure of the aromatic cations reflect the unique properties of imidazolium cations. The delocalized 3-center-4-electron configuration are contained in the electronic structure of these salts across the N1–C2–N3 moiety, a double bond between C4 and C5 at the opposite side of the ring, and a weak delocalization in the central region [23]. Almost the same charge is carried by the hydrogen atoms C2–H, C4–H, and C5–H, but carbon C2 is positively charged owing to the electron deficit in the C=N bond. On the other hand C4 and C5 are practically neutral. The properties of these ionic liquids arise from the resulting acidity of the hydrogen atoms. The hydrogen on the C2 carbon (C2–H) has been shown to bind specifically with solute molecules.

The hydrogen bonds play an important role in the stability and miscibility of the binary liquid mixtures of [Bmim][NTf₂] (1) and dimethyl carbonate (2). The nature of interaction of dimethyl carbonate molecules with the cation is different from that of anion. The characteristic groups which interact with dimethyl carbonate molecules are the C–H groups in the imidazolium ring and oxygen atoms in the anion. The complete miscibility and solvation of cations and anions in the ionic liquid is due to sufficient hydrogen bonding interactions of dimethyl carbonate with [Bmim][NTf₂]. Hence, the remarkable contraction in the volume of the mixture can be attributed to the hydrogen bonds between the ionic liquid [Bmim][NTf₂] (1) and dimethyl carbonate (2).

5 CONCLUSION

- From the experimental data, parameters such as \( V_m^E \), \( k_E^F \), \( L_f^E \), \( Z^k \), \( u^E \), \( \Delta n_D \), have been evaluated. The excess and deviation properties have been fitted to Redlich–Kister type polynomial and the corresponding standard deviations were in good agreement with the experimental value.
- The values of \( V_m^E \) become more negative with increase in temperature.
- The values of \( P_{m,3}^{E,E} \) are found to be negative and become more negative with increasing temperature. Hence, we can conclude that with increasing temperature, strong interactions increase among the unlike molecules of the mixtures. This supports the existing strong molecular interactions that were observed with the variation of \( P_{m,3}^{E,E} \).
- In the present study, the negative \( k_E^F \) values can be attributed to a closer approach of unlike molecules and a stronger interaction between components of mixtures over the entire range of composition at all temperatures under study.
- The negative \( L_f^E \) were observed. The trend of \( L_f^E \) values (Fig. 5) is similar to that of \( k_E^F \) at all temperatures under study.
- \( Z^k \) is positive for the systems at all the temperatures under study. The positive values of \( Z^k \) indicate the presence of strong interactions between the component molecules.
- Similarly the positive values of \( u^E \) indicate much stronger interactions between the molecules.
- The positive values of \( \Delta n_D \) at a given temperature over the entire composition range indicate the strong interactions between the component molecules.
- Finally it may be concluded that the observed negative values of \( V_m^E \), \( k_E^F \), \( L_f^E \), and positive values of \( Z^k \), \( u^E \), \( \Delta n_D \) clearly indicate the dominance of strong attractive forces.

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REFERENCES:


Fig. 8: Plots of deviation in refractive index (\( \Delta n_D \)) against mole fraction (\( x_1 \)) for [Bmim][NTf₂] and Dimethyl carbonate mixtures at temperature T and atmospheric pressure.


