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On the scaling behavior of electric conductivity in [C₄mim][NTf₂]

Z. Wojnarowska* a,b, G. Jarosz a,b, A. Grzybowski a,b, J. Pionteck c, J. Jacquemin d, M. Paluch a,b

In this letter we examine, for the first time, the molar conductivity behavior of the deeply supercooled room temperature ionic liquid [C₄mim][NTf₂] in the temperature, pressure and volume thermodynamic space in terms of density scaling regime \( (TV)^{−1} \) combined with the equation of state (EOS). The exponent \( γ_σ \) determined from the Avramov model analysis is compared with the coefficient obtained from the viscosity studies carried out at moderate temperatures. Therefore, the experimental results presented herein provide the answer to long-standing question regarding the validity of thermodynamic scaling of ionic liquids over a wide temperature range, \( i.e. \) from the normal liquid state to the glass transition point. Finally, we investigate the relation between the dynamic and thermodynamic properties of [C₄mim][NTf₂] represented by scaling exponent \( γ \) and Grüneisen constant \( γ_G \), respectively.

Introduction

Over the last decade, ionic liquids (ILs) have received a considerable amount of scientific attention as a novel class of solvents or additives due to their unique physical properties and their wide range of potential applications.\(^1\) An appropriate combination of cations and anions makes them attractive as potential pharmaceutical ingredients,\(^2\) green solvents as well as, promising electrolytes for fuel cells and batteries.\(^3\) The use of ionic liquids in electrochemical devices is driven by their unique physical properties, such as low melting points, low vapor pressure, non-flammability, thermal and chemical stability, or broad electrochemical window.\(^4\) However, one of the most desired feature of these media is their high electric conductivity (\( σ \)). Therefore, in the last years many efforts have been dedicated to understanding the conductivity mechanism in ion-containing systems and consequently to predict the \( σ \) behavior under various thermodynamic conditions.\(^5\)

As is well known, a temperature decrease below the melting point of a given material leads to two different solid forms: crystalline state with a regular arrangement of atoms and disordered glass state. Since typically ILs do not manifest a tendency to the crystallization on cooling, most of them can be easily transformed to the amorphous state.\(^6\) During this process, the mobility of the ions enormously slows down, resulting in a dramatic decrease (up to 10 orders of magnitude) in their electrical conductivity over a relatively narrow temperature range, \( i.e. \), between \( T_m \) and \( T_g \). Although the rapid cooling is probably the simplest method for controlling the molecular dynamics of ILs, it does not mean that this is the only route. An alternative method for is the compression of liquid under isothermal conditions.\(^7\) Such experiments, which are much less exploited mainly due to the technical difficulties, are crucial in order to formulate a universal description of the transport properties for ionic conductors.

According to recent reports, the electrical conductivity (or any other dynamic property of ILs such as viscosity, conductivity relaxation or diffusion coefficient) measured at different temperatures and pressures, can be analyzed together in terms of the thermodynamic (or density) scaling concept.\(^8\) According to this idea, both isobaric and isothermal data can be expressed as a single universal curve if they are plotted against \( (TV)^{−1} \).\(^9\) It is frequently implied that the parameter \( γ \), which is regarded as a characteristic material constant, is straightforwardly related to the one third of the exponent appearing in the repulsive part of the soft Lennard-Jones (LJ) potential. It has been confirmed several times that the density scaling concept is satisfied for various ionic conductors.\(^10\) However, in each of these studies it was tested using the data measured only over a narrow temperature range around \( T_m \). Thus, the question about the validity of density scaling for ILs over a wide temperature range, \( i.e. \) from the deeply supercooled liquid (where \( η=10^{12} \text{ Pa·s} \) ) to normal liquid state (where \( η=10^{2} \text{ Pa·s} \) ) is still open.

This article examines the thermodynamic scaling concept in the vicinity of the glass transition region for the prototypical aprotic room temperature ionic liquid 1-butyl-3-methylimidazolium...
bis[(trifluoromethyl)sulfonyl]imide, [C₄mim][NTf₂]. To determine the value of scaling exponent γ, the electrical conductivity data were analyzed in the temperature-pressure-volume thermodynamic space in terms of the modified Avramov entropic model. The outcomes of such analysis have been compared with the results of the analogous study carried out for the viscosity data measured for the normal liquid state of [C₄mim][NTf₂].

Experimental

Sample characterization.
The sample tested herein is the 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide [C₄mim][NTf₂]. This sample was synthesized and purified in-house in the QUILL center within a purity, expressed in mole fraction unit, close to 99%. Prior to use, IL was treated for 15 hours at 323.15 K under vacuum (lower than 1 Pa), the sample was then considered as dried and was then stored under nitrogen atmosphere to avoid water contamination from atmosphere. After this treatment, its halide content was determined by using suppressed ion chromatography (IC), and lithium content of the sample was then determined by inductively coupled plasma analysis (ICP). These measurements revealed very low levels of bromide and lithium in the IL sample, which are close to 5·10⁻⁶ and 8·10⁻⁷ in mass fraction units, respectively. Water content of the selected IL determined by Karl Fischer titration was close to 60 ppm, i.e. 0.006 wt%.

Dielectric measurements
Ambient pressure dielectric measurements of [C₄mim][NTf₂] were performed over a wide frequency range from (10⁻¹ to 10⁶) Hz using a Nova-Control GMBH Alpha dielectric spectrometer. During the measurements, the sample was placed between two stainless steel electrodes of the capacitor. The dielectric spectra were collected over the temperature range from (179 to 233) K. The temperature was controlled by the Novo-Control Quattro system, with the use of a nitrogen gas cryostat. Temperature stability of the samples was better than 0.1 K. For the pressure dependent BDS experiment the capacitor with the studied material was placed in the high-pressure chamber and compressed using the silicone fluid. The sample was in contact only with stainless steel and Teflon. The pressure was measured by using a Nova Swiss tensometric pressure meter with a resolution of 0.1 MPa. The temperature was controlled within 0.1 K by means of Weiss fridge.

Pressure-volume-temperature (PVT) measurements
The PVT experiments were carried out by means of a fully automated GNOMIX high pressure dilatometer. The apparatus is described elsewhere. The principle of the GNOMIX-PVT apparatus is the confining fluid technique. About 1.9 g of the IL has been added into the cell and the remaining cell volume was filled with mercury acting as confining fluid., which ensures that the material is under hydrostatic pressure at all times. PVT data in the range from 10 MPa to 200 MPa in increments of 10 MPa, and from room temperature up to 150 °C in steps of 5 K have been collected in the isothermal standard mode. The values for 0.1 MPa are obtained by extrapolation of the values for 10 MPa to 30 MPa in steps of 1 MPa according to the Tait equation for each temperature using the standard PVT software. In the studied range the accuracy limit for the absolute values of the specific volume is within 0.002 cm³/g.

Results and discussion
In order to investigate the conducting properties of [C₄mim][NTf₂] at various thermodynamic conditions, broadband dielectric spectroscopy was employed. This experimental tool enables us to probe the charge transport in the IL by measuring the complex dielectric function ε*, which is equivalent to the complex electric conductivity σ*, - the most commonly applied approach to present the dielectric data of conducting materials:

\[ \sigma^*(f, T, P) = -\varepsilon_0 \varepsilon \sigma'(f, T, P) = \sigma'(f, T, P) + i \sigma''(f, T, P) \]  (1)

In the above equation ε₀ is the vacuum permittivity while the σ’ and σ” are the real and imaginary part of the complex quantity, respectively.

The representative dielectric spectra of the [C₄mim][NTf₂] collected in the frequency interval ranging from 10⁻¹ to 10⁶ Hz, under isobaric (P = 0.1 MPa) and isothermal (T = 233 K) conditions as shown in Figs. 1a and 1b, respectively. In this figure, plotted high-pressure data represent only one of the three data sets for example the so-called “master curve” as shown in the Fig. 1 inset. Interestingly, by superimposing a number of σ’(f) spectra, measured at different temperature and pressure conditions, almost perfect scaling plot is then obtained. The only noticeable difference in the master curve profiles refers to the plateau region, which takes a slightly broader frequency range in the case of ambient pressure data. Unfortunately, due to the lack of literature data available to date, we are not able to assess whether it is a universal behavior or it is only an exception to the general scaling rule.
pressure range of (10–200) MPa. The experimental points used herein are both isobaric cooling and isothermal compression of [C4mim][NTf2] liquid brings about a dramatic decrease in the dc conductivity value. To analyze the data more quantitatively the temperature and pressure dependences on $\sigma_{dc}$ were determined. These data were then recalculated to represent the molar conductivity $\Lambda_{\infty}$ of the selected IL as the function of temperature and pressure as shown in Figs. 2a and 2b, respectively.

As illustrated in Figs.2a and 2b, the ambient pressure data, as well as, those presented as different pressures using isothermal curves reveal a non-Arrhenius behavior. This implies that in the selected IL both the activation energy and activation volume are not constant with respect to investigated temperatures and pressures but they increase with cooling/squeezing. This result seems to be a general rule when considering the supercooled liquid state of aprotic ionic liquids. On the contrary, the Arrhenius dependence of $\log_{10} \Lambda_{\infty}(P)$ was found for some protic ionic conductors in the vicinity of liquid to glass transition. In the past, a wide variety of models have been proposed for describing the non-Arrhenius temperature/pressure dependence on dynamic properties of supercooled liquids like structural relaxation time, viscosity or conductivity relaxation. However, beyond any doubt, the most frequently used equation is the empirical Vogel–Fulcher–Tammann (VFT) law and its pressure counterpart:

$$
T = T_0 \exp \left( \frac{B}{P - P_0} \right)
$$

where $T$ is the temperature, $T_0$ is the temperature at which the viscosity is $10^6$ Pa s, $B$ is the pressure dependence on the activation energy and $P_0$ is the pressure at which the viscosity is $10^6$ Pa s.

### Table 1. The molar conductivity of [C4mim][NTf2] recorded at isobaric (0.1 MPa) and isothermal (213.15, 223.15, 233.15 K) conditions.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>Isobar 0.1 MPa</th>
<th>Isotherm 213.15 K</th>
<th>Isobar 0.1 MPa</th>
<th>Isotherm 223.15 K</th>
<th>Isobar 0.1 MPa</th>
<th>Isotherm 233.15 K</th>
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<tr>
<td></td>
<td>$P$ [MPa]</td>
<td>$\Lambda_{\infty}$ [S·cm$^{-1}$·mol$^{-1}$]</td>
<td>$P$ [MPa]</td>
<td>$\Lambda_{\infty}$ [S·cm$^{-1}$·mol$^{-1}$]</td>
<td>$P$ [MPa]</td>
<td>$\Lambda_{\infty}$ [S·cm$^{-1}$·mol$^{-1}$]</td>
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* Standard uncertainty is $\log_{10} \Lambda_{\infty} = 0.01$ S·cm$^{-1}$·mol$^{-1}$.

### Table 2. The electric conductivity of [C4mim][NTf2] recorded at isobaric (0.1 MPa) and isothermal (213.15, 223.15, 233.15 K) conditions.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>Isobar 0.1 MPa</th>
<th>Isotherm 213.15 K</th>
<th>Isobar 0.1 MPa</th>
<th>Isotherm 223.15 K</th>
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<td>$P$ [MPa]</td>
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* Standard uncertainty is $\log_{10} \sigma_{dc} = 0.01$ S·cm$^{-1}$.

### Figure 1. Dielectric relaxation spectra of [C4mim][NTf2] presented in the conductivity representation in the form of frequency dependent data measured at various temperature (a) and pressure (b) conditions. The inset panel presents the superimposed dielectric spectra taken at ambient and elevated pressure.

### Figure 2 Panels (a) and (b) present the molar conductivity data of [C4mim][NTf2] measured at various isobaric and isothermal conditions, respectively. Panel (c) presents the isobaric dependences of volume in the pressure range of (10–200) MPa. The experimental points used herein are reported in Table 1, Table 2 and Table 4.
\[ \Lambda_{\text{mol}} = \Lambda_{\text{mol}0} \exp \left( \frac{DT_0}{T - T_0} \right) \]  
\[ \Lambda_{\text{mol}} = \Lambda_{\text{mol}0} \exp \left( \frac{DP_0}{P - P_0} \right) \]  

Similar to the temperature VFT equation (Eq. 2), its pressure equivalent (Eq. 3) includes three parameters: \( \Lambda_{\text{mol}0}, D, \) and \( P_0. \) However, only two of them: \( D_{\text{v}} \) and \( P_0 \) have to be extracted from the numerical fitting analysis. Since the pre-exponential coefficient refers to the dc conductivity value at ambient pressure, which can be easily determined directly from the measurements. Representative fits of Eqs. 2 and 3 to the experimental data are denoted as solid lines in Figs. 2a and 2b using parameters reported in Table 3.

Table 3. Parameters obtained from fitting of VFT, pVFT, EOS and Avramov equations, to the experimental data of [C<sub>4</sub> mim][NTf<sub>2</sub>] ionic liquid

<table>
<thead>
<tr>
<th>Function of State</th>
<th>Parameter</th>
<th>[C&lt;sub&gt;4&lt;/sub&gt; mim][NTf&lt;sub&gt;2&lt;/sub&gt;]</th>
</tr>
</thead>
<tbody>
<tr>
<td>VFT (Eq.2)</td>
<td>(-\log p_{\text{vT}})</td>
<td>3.17±0.03</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>6.23±0.06</td>
</tr>
<tr>
<td></td>
<td>T&lt;sub&gt;ref&lt;/sub&gt;/K</td>
<td>143.9±0.2</td>
</tr>
<tr>
<td>pVFT (Eq.3)</td>
<td>T/K</td>
<td>213 ± 23</td>
</tr>
<tr>
<td></td>
<td>(-\log p_{\text{T}})</td>
<td>3.40±0.01</td>
</tr>
<tr>
<td></td>
<td>p&lt;sub&gt;0&lt;/sub&gt;/MPa</td>
<td>3.21±0.10</td>
</tr>
<tr>
<td></td>
<td>(\rho)/g/cm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>1149±41</td>
</tr>
<tr>
<td>Equation of State (Eq.5)</td>
<td>A&lt;sub&gt;0&lt;/sub&gt;/cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.6439±9.6×10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>A&lt;sub&gt;d&lt;/sub&gt;/cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>4.23±0.10</td>
</tr>
<tr>
<td></td>
<td>A&lt;sub&gt;2&lt;/sub&gt;/cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>1.03±0.03</td>
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<tr>
<td></td>
<td>B&lt;sub&gt;3&lt;/sub&gt;/MPa</td>
<td>33.59±5</td>
</tr>
<tr>
<td></td>
<td>b/K&lt;sup&gt;2&lt;/sup&gt;</td>
<td>4.190±10</td>
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<tr>
<td>Avramov model (Eq.6)</td>
<td>(-\log p_{\text{vT}})</td>
<td>12.2±0.02</td>
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<tr>
<td></td>
<td>A</td>
<td>70.49±0.79</td>
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<tr>
<td></td>
<td>(\phi)</td>
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</tr>
<tr>
<td></td>
<td>(\psi)</td>
<td>3.05±0.01</td>
</tr>
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</table>

Since we are fundamentally interested in the electrical conductivity behavior across the temperature, pressure and volume thermodynamic space, it is essential to perform additional dilatometric measurements. Due to the general technical difficulties involved in estimating the volume of the sample at extremely low temperature, it is a standard practice to perform the PVT experiments at moderate temperatures above the room conditions: i.e. in the normal liquid state of the [C<sub>4</sub> mim][NTf<sub>2</sub>].

Figure 2c shows the \( V_{\text{sp}}(T) \) data of [C<sub>4</sub> mim][NTf<sub>2</sub>] plotted for six representative pressure conditions collected in Table 4. As expected under constant pressure conditions, the value of the IL specific volume systematically decreases with cooling. To parameterize the obtained experimental points we have then applied the following equation of state (EOS) \(^1\):  
\[ \left( \frac{V}{V_0} \right)^{\gamma_{\text{EOS}}} = 1 + \frac{\gamma_{\text{EOS}}}{B_{\gamma}(P_0)} (P - P_0) \]  
where \( V_0 = V(P_0) \) and \( B_\gamma(P_0) \) denotes the isothermal bulk modulus at the reference state defined by \( P_0 \). \(^3\) In general, Eq.4 can be also rewritten as:  
\[ V(T, P) = \left[ 1 + \frac{\gamma_{\text{EOS}}}{B_{\gamma}(P_0)} (P - P_0) \right]^{-\frac{1}{\gamma_{\text{EOS}}}} \]  
where  \( V_0 = A_0 + A_1(T - T_0) + A_2(T - T_0)^2 \) and \( T_0 \) is the glass transition temperature at ambient pressure, \( T_0 = T_0(P_0) \), determined herein from standard calorimetric measurement (\( T_0 = 182 \) K).

The fitting parameters obtained from simultaneous analysis of all \( V_{\text{sp}}(T) \) isobars at fixed \( T_0 \) and \( P_0 \) are then reported in the Table 3.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
\( V_{\text{sp}} \) /cm<sup>3</sup> & Pressure /MPa \\
\hline
291.65 & 0.1 \\
295.69 & 0.1 \\
300.58 & 0.1 \\
305.32 & 0.1 \\
310.17 & 0.1 \\
314.78 & 0.1 \\
319.61 & 0.1 \\
324.59 & 0.1 \\
329.26 & 0.1 \\
334.07 & 0.1 \\
339.7 & 0.1 \\
344.57 & 0.1 \\
349.32 & 0.1 \\
354.36 & 0.1 \\
359.37 & 0.1 \\
364.33 & 0.1 \\
369.28 & 0.1 \\
374.32 & 0.1 \\
379.04 & 0.1 \\
384.33 & 0.1 \\
389.41 & 0.1 \\
394.21 & 0.1 \\
399.32 & 0.1 \\
404.31 & 0.1 \\
409.32 & 0.1 \\
414.35 & 0.1 \\
419.42 & 0.1 \\
424.37 & 0.1 \\
\hline
\end{tabular}
\caption{The volumetric data of [C<sub>4</sub> mim][NTf<sub>2</sub>] recorded under isothermal conditions.}
\end{table}

Combining the high-pressure dielectric results with PVT data we are now able to express the electrical conductivity of [C<sub>4</sub> mim][NTf<sub>2</sub>] measured at various temperature and pressure conditions as a function of the specific volume. The result of such conversion is presented in the form of two-dimensional surface in Fig. 3. Having the \( \Lambda_{\text{mol}} \) data in \( T-V' \) representation, we can now verify the validity of thermodynamic scaling relation for the investigated IL by plotting \( \log(\rho_{\text{vT}}/\rho_{\text{T}}) \) vs. \( (T'V') > 1 \). However, to perform such test, first it is necessary to find the scaling exponent. According to the literature reports, the parameter \( \gamma \) can be determined by many different ways.\(^4\)\(^1\) However, one of the most noteworthy and convenient method is based on the entropic model originally formulated by Avramov for describing the \( \eta(T,P) \) dependences,\(^4\)\(^2\), and then extended to the \( T-V \) plane by Casalini et al.\(^2\) Herein, to parameterize the conductivity data of [C<sub>4</sub> mim][NTf<sub>2</sub>] and consequently to determine the value of the \( \gamma \) exponent the modified Avramov equation in the following form was applied:

\[ \log \Lambda_{\text{mol}} = \phi \left( \frac{2C_{\gamma}}{ZR} \right) \]  

where \( \phi = 2C_{\gamma}/ZR \) and Grüneisen parameter \( \gamma = \gamma_{\text{G}} = (C_{\gamma}/C_{\text{T}} - 1)/T(\partial p/\partial T) \) are expressed by the set of thermodynamic quantities i.e. isobaric and isochoric heat capacities \( (C_{\gamma} \) and \( C_{\text{T}}) \), the isobaric volume expansivity \( \eta_{\text{p}} \), the gas constant \( R \), and the degeneracy \( Z \) of the system as the number of escape channels for a locally moving particle.
In the past, the validity of Eq. 6 was successfully tested for a number of glass-forming liquids. However, at the same time, a significant discrepancy between \( \gamma_0 \) and \( \gamma \) values has been reported. The experimental investigations of small molecular liquids like OTP, KDE or BMPPC as well as polymers have demonstrated that in general the value of scaling exponent \( \gamma \) is much higher than \( \gamma_0 \) calculated using the thermodynamic variables. To provide the explanation of such a difference recently Paluch et al. derived the novel formula for describing the molecular dynamics of glass-forming liquids in \( T \cdot V \) space. This new relation based on the assumption that the maximal activation barrier for molecular rearrangements \( E_{\text{max}} \) is a function of a liquid density, in fact has the same mathematical form as the modified Avramov model (Eq. 6), but there is a fundamental difference in the meaning of exponent \( \gamma \).

Now it is defined as \( \gamma = \gamma_{\text{EOS}} / \phi + \gamma_G \). In this context, it should be stressed that the new definition of scaling coefficient has been found to be valid for a number of typical van der Waals liquids and ionic conductors. Thus, it is also interesting to check its correctness for the studied IL: the \([\text{C}_4\text{mim}][\text{NTf}_2]\). To realize this task the Grüneisen constant was calculated in two different ways: (i) using the thermodynamic variables reported in the literature, i.e. isobaric and isochoric heat capacities estimated in the vicinity of the glass transition temperature, and the isothermal compressibility, \( \gamma_0 \) expressed in the form of its thermodynamic definition \( \gamma_G = TVpG / \kappa_T \) is equal to 1.32 at \( T_g = 182 \) K; (ii), having already determined values of the scaling exponent \( \gamma \) and \( \gamma_{\text{EOS}} \), giving then, \( \gamma_0 = 1.91 \). Based on which, it can be easily seen, that we obtained a quite good agreement between Grüneisen parameter \( \gamma_0 \) values determined by means of the two above-mentioned methods. Thus, the result obtained for \([\text{C}_4\text{mim}][\text{NTf}_2]\) provides the next strong evidence that there is a relation between the dynamic and thermodynamic properties of supercooled liquids.

The result of global fitting the \( \Lambda_{\text{m}}(T,V) \) dependence by Eq. 6, with the set of parameters reported in the Table 3, is presented in the form of wire surface in the Fig. 3. For convenience of the further analysis, we have also plotted the fitting curves for isobaric and isothermal data as a function of the specific volume. The corresponding cross sections of the fitted surface are shown as solid lines in Fig. 4a. Now, it is clearly visible that we achieved a satisfying parameterization of the experimental points by applying the modified Avramov model. Except for the isobar at the highest measured temperature, all other experimental data are quite well represented by the fitting curves. This is reflected in the values of standard deviation collected in Table 3.

![Figure 3](Image)

**Figure 3** The molar conductivity for \([\text{C}_4\text{mim}][\text{NTf}_2]\) as a function of temperature and volume. The three-dimensional surface was determined using the modified Avramov equation (Eq.6).

![Figure 4](Image)

**Figure 4** Panel (a) Isothermal and isobaric data for \([\text{C}_4\text{mim}][\text{NTf}_2]\) plotted as a function of volume. Solid lines are fits to Eq. 6. Panel (b) The molar conductivity data for \([\text{C}_4\text{mim}][\text{NTf}_2]\) plotted versus \( T \cdot V \) with the scaling exponent calculated herein as \( \gamma = 3.05 \). The inset shows the scaling exponent determined from the linear regression of the logarithmic dependence of glass transition temperature on volume. The solid lines denote the regression lines.

It should be also mentioned that the value of the scaling exponent \( \gamma = 3.05 \pm 0.01 \) obtained from the numerical fitting procedure corresponds perfectly well to the one determined in alternative, a model independent way, using the simple linear regression:

\[
\log T_g = A - \gamma \log V_g
\]

(7)

As shown in the inset of the Fig. 4, the slope of the \( \log T_g(\log V_g) \) dependences does not change irrespective of the value of \( \log V_g \) used to define the glass transition temperature \( T_g \) and volume \( V_g \). Consequently, the value of the \( \gamma \) coefficient (=3.04 ± 0.01), remains constant within the studied range of dynamics. In this context it should be stressed that the scaling exponent found for the \([\text{C}_4\text{mim}][\text{NTf}_2]\) is close to the values of \( \gamma \) already reported for other ionic liquids such as \([\text{BMP}][\text{BOB}]\) \( \gamma = 3.7 \), verapamil hydrochloride \( \gamma = 2.9 \), \([\text{C}_4\text{mim}][\text{PF}_6]\) \( \gamma = 2.4 \) or \([\text{C}_4\text{mim}][\text{PF}_6]\) \( \gamma = 2.9 \). Furthermore, it is in very good agreement with the scaling coefficient determined from viscosity data measured in the normal liquid state of \([\text{C}_4\text{mim}][\text{NTf}_2]\) \( \gamma = 2.9 \).

Finally, the temperature, pressure and volume dependence of electrical conductivity of \([\text{C}_4\text{mim}][\text{NTf}_2]\) can be considered in the context of thermodynamic scaling concept. As depicted from the
physical pressure on the dcTconductivity of the prototypical room temperature behavior in the temperature pressure and volume the rmodynamic being overlooked. Since each of these two parameters was determined based IL, the agreement between the coefficients ionic liquid [C space. By plotting log experimental results allow us to thoroughly examine  the Λ state that the (\(TV\))^1 scaling of [C\(_{\text{mim}}\)][NTf\(_2\)] works not only in the vicinity of \(T_g\) but also in the normal liquid state.

**Conclusion**

In this paper we have investigated the effect of temperature and pressure on the dc-conductivity of the prototypical room temperature ionic liquid [C\(_{\text{mim}}\)][NTf\(_2\)]. The dielectric relaxation data presented in electric conductivity representation (σ*) combined with PVT experimental results allow us to thoroughly examine the scaling of \(\Lambda_{\text{mol}}\) in the temperature pressure and volume thermodynamic space. By plotting log(\(\Lambda_{\text{mol}}\)) as a function of \((TV)^1\) we have then confirmed the validity of the density scaling concept in the supercooled liquid state of the selected IL. Interestingly, we have found that the exponent \(\gamma_\text{a} = 3.05\) determined from the global fitting of modified Avramov model to the log(\(\Lambda_{\text{mol}}\)) points, is in quite good agreement with the coefficient obtained from the analysis carried out for the viscosity data measured in the normal liquid state of studied IL (\(\gamma_\text{a} = 2.9\)). Thus, our results are the first experimental evidence that the density scaling concept is valid over a wide temperature range i.e. from the deeply supercooled liquid up to normal liquid state of [C\(_{\text{mim}}\)][NTf\(_2\)]. Additionally, our investigations are the next example when the relation between the scaling exponent \(\gamma\) and the thermodynamically defined Grüneisen constant \(\gamma_\text{a}\), recently derived by Paluch et al., is satisfied also for ionic liquids.

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**Notes and references**

24. GOMIX INC., 3809 Birchwood Drive, Boulder, CO 80304, USA.
33. Vogel, H. Phys. Z. 1921, 22, 645
34. Fulcher, G.S. J. Am. Ceram. Soc. 1925, 8, 339
42. Roland, C.M.; Casalini, R. J. Non-Cryst. Solids 2005, 251, 2581
54. Roland, C. M.; Bair, S.; Casalini, R. J. Chem. Phys. 2006, 125, 124508