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

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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 $(TV^\gamma)^{-1}$ 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.^{1,2,3} An appropriate combination of cations and anions makes them attractive as potential pharmaceutical ingredients^{4,5,6,7}, or green solvents⁸ as well as, promising electrolytes for fuel cells and batteries.⁹ 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.^{10,11} However, one 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.^{12,13}

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.¹⁴ 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.^{15,16} 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.¹⁷ According to this idea, both isobaric and isothermal data can be expressed as a single universal curve if they are plotted against $(TV^\gamma)^{-1}$.¹⁸ 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.^{19,20,21,22} 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 $\eta \approx 10^{12}$ Pa·s) to normal liquid state (where $\eta \approx 10^{-2}$ 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.²³ 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 $5 \cdot 10^{-6}$ and $8 \cdot 10^{-7}$ 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 10^6) Hz using a Novo-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 dilatometer²⁴. The apparatus is described elsewhere^{25,26}. 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 software²⁶. In the studied range the accuracy limit for the absolute values of the specific volume is within $0.002 \text{ cm}^3/\text{g}$.

Since the PVT apparatus measures only the changes in the specific volume, it is necessary to correct the measured values by adding the specific volume at known, typically ambient conditions, which is $0.6955 \text{ cm}^3/\text{g}$ (0.1 MPa and 25 °C).²⁷

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.²⁸

$$\sigma^*(f, T, P) = i2\pi f \epsilon_0 \epsilon^*(f, T, P) = \sigma'(f, T, P) + i\sigma''(f, T, P) \quad (1)$$

In the above equation ϵ_0 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} Hz to 10^6 Hz, under isobaric ($P = 0.1 \text{ MPa}$) and isothermal ($T = 233 \text{ K}$) conditions as shown in Figs. 1a and 1b, respectively. In this figure, plotted high-pressure data represent only one of the three data sets (*e.g.* isothermal condition) measured herein. The two other isotherms were recorded at (213 and 223) K. As illustrated in Fig. 1, the $\sigma'(f)$ curves are characterized by: (i), a frequency-independent region known as the dc conductivity (σ_{dc}); (ii), a low-frequency deviation from the plateau attributed to the polarization effect, typical for ion-conducting materials, and; (iii), the power law behavior observed at higher frequencies. These three regions can be easily distinguished if the spectra are shifted on both the conductivity and frequency scales to superimpose each other. The result of such procedure is presented herein in the form of the so-called “master curve” as shown in the Fig. 1 inset. Interestingly, by superimposing a number of $\sigma'(f)$ 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.

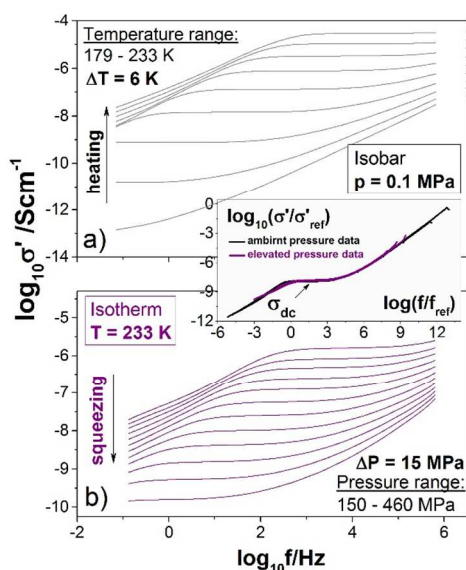


Figure 1. Dielectric relaxation spectra of [C₄mim][NTf₂] presented in the conductivity representation in the form of frequency dependent data measured at various temperature (a) and pressure (b) conditions. The inset panel presents the superimposed dielectric spectra taken at ambient and elevated pressure.

From further inspection of $\sigma'(f)$ data, it becomes obvious that 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 σ_{dc} were determined. These data were then recalculated to represent the molar conductivity Λ_{mol} of the selected IL as the function of temperature and pressure as shown in Figs. 2a and 2b, respectively.

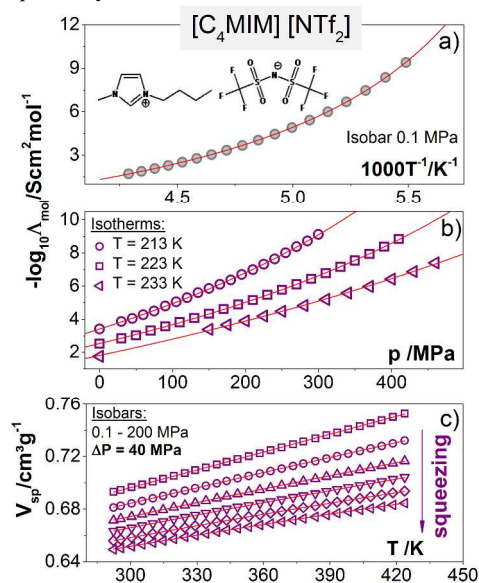


Figure 2 Panels (a) and (b) present the molar conductivity data of [C₄mim][NTf₂] measured at various isobaric and isothermal conditions, respectively. Panel (c) presents the isobaric dependences of volume in the pressure range of (10–200) MPa. The experimental points used herein are reported in Table 1, Table 2 and Table 4.

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

T [K]	$-\log_{10}\Lambda_{mol}/\text{Scm}^2\text{mol}^{-1}$ *						
	Isobar 0.1 MPa	P [MPa]	Isotherm 213.15 K	P [MPa]	Isotherm 223.15	P [MPa]	Isotherm 233.15 K
233.15	1.70	0.1	3.39	0.1	2.52	0.1	1.75
230.15	1.88	30	3.85	30	2.83	150	3.37
227.15	2.07	45	4.03	50	3.02	175	3.65
224.15	2.28	60	4.25	70	3.30	200	3.89
221.15	2.52	75	4.48	90	3.55	225	4.18
218.15	2.76	90	4.78	110	3.81	250	4.47
215.15	3.03	105	5.04	130	4.06	280	4.82
212.15	3.33	120	5.29	150	4.33	310	5.18
209.15	3.66	135	5.59	170	4.61	340	5.57
206.15	4.03	150	5.83	190	4.87	370	5.97
203.15	4.43	165	6.09	210	5.14	400	6.40
200.15	4.89	180	6.36	230	5.46	430	6.86
197.15	5.41	195	6.68	250	5.77	460	7.39
194.15	5.98	210	6.98	270	6.09		
191.15	6.67	225	7.31	290	6.42		
188.15	7.46	240	7.63	310	6.77		
185.15	8.35	255	7.99	330	7.15		
182.15	9.39	270	8.36	350	7.53		
		285	8.71	370	7.93		
		300	9.12	390	8.36		
				410	8.82		

* Standard uncertainty is $\log_{10}\Lambda_{mol} = 0.01 \text{ Scm}^2\text{mol}^{-1}$

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

T [K]	$-\log_{10}\sigma_{dc}/\text{Scm}^{-1}$ *						
	Isobar 0.1 MPa	P [MPa]	Isotherm 213.15 K	P [MPa]	Isotherm 223.15	P [MPa]	Isotherm 233.15 K
233.15	4.15	0.1	5.83	0.1	4.96	0.1	4.19
230.15	4.32	30	6.29	30	5.26	150	5.79
227.15	4.51	45	6.46	50	5.46	175	6.07
224.15	4.73	60	6.69	70	5.74	200	6.31
221.15	4.96	75	6.91	90	5.99	225	6.60
218.15	5.20	90	7.21	110	6.24	250	6.89
215.15	5.47	105	7.47	130	6.49	280	7.23
212.15	5.77	120	7.72	150	6.75	310	7.59
209.15	6.10	135	8.02	170	7.03	340	7.98
206.15	6.46	150	8.26	190	7.29	370	8.37
203.15	6.87	165	8.51	210	7.56	400	8.81
200.15	7.32	180	8.78	230	7.88	430	9.27
197.15	7.84	195	9.10	250	8.18	460	9.79
194.15	8.42	210	9.40	270	8.50		
191.15	9.10	225	9.72	290	8.84		
188.15	9.89	240	10.04	310	9.18		
185.15	10.78	255	10.40	330	9.56		
182.15	11.82	270	10.77	350	9.94		
		285	11.12	370	10.34		
		300	11.52	390	10.77		
				410	11.23		

* Standard uncertainty is $\log_{10}\sigma_{dc} = 0.01/\text{Scm}^{-1}$

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.¹⁶ This result seems to be a general rule when considering the supercooled liquid state of aprotic ionic liquids.⁴⁹ On the contrary, the Arrhenius dependence of $\log_{10}\Lambda_{mol}(P)$ was found for some protic ionic conductors in the vicinity of liquid to glass transition.^{29,30,31,32} 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–Tamman (VFT) law and its pressure counterpart^{33,34,35,36}:

$$\Lambda_{mol} = \Lambda_{mol0} \exp\left(\frac{DT_0}{T - T_0}\right) \quad (2)$$

$$\Lambda_{mol} = \Lambda_{mol0} \exp\left(\frac{D_P P_0}{P_0 - P}\right) \quad (3)$$

Similar to the temperature VFT equation (Eq. 2), its pressure equivalent (Eq. 3) includes three parameters: Λ_{mol0} , D , and P_0 . However, only two of them: D_P 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. Respective 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 [C₄mim][NTf₂] ionic liquid

Function	Parameter	[C ₄ mim][NTf ₂]		
VFT (Eq.2)	$-\log\Lambda_{mol}$	-3.17±0.03		
	D	6.23±0.06		
	T_{VFT}/K	149.9±0.2		
pVFT (Eq.3)	T/K	213	223	233
	$-\log\Lambda_{mol}$	3.40±0.01	2.52±0.01	1.80±0.04
	D_P	37.2±1.7	32.3±0.9	45.8±5.6
	P_0/MPa	1149±41	1318±26	2116±57
Equation of State (Eq.5)	$A_0/cm^3 g^{-1}$	0.6439 ± 9.6×10 ⁻⁵		
	$A_1/$	(4.23 ± 0.01)×10 ⁻⁴		
	A_2	(1.04 ± 0.03)×10 ⁻⁷		
	$B_{T0}(P_0)/MP$	3359 ± 5		
	b/K^{-1}	(4.190 ± 0.008)×10 ⁻³		
	γ_{EOS}	12.26 ± 0.02		
Avramov model (Eq.6)	$-\log\Lambda_{mol}$	0.62 ± 0.08		
	A	70.49 ± 0.79		
	ϕ	5.52 ± 0.09		
	γ	3.05 ± 0.01		

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 [C₄mim][NTf₂].

Figure 2c shows the $V_{sp}(T)$ data of [C₄mim][NTf₂] 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)³⁷:

$$\left(\frac{V_0}{V}\right)^{\gamma_{EOS}} = 1 + \frac{\gamma_{EOS}}{B_T(P_0)}(P - P_0) \quad (4)$$

where $V_0=V(P_0)$ and $B_T(P_0)$ denotes the isothermal bulk modulus at the reference state defined by P_0 .³⁸ In general, Eq.4 can be also rewritten as:

$$V(T, P) = \frac{V_0}{\left[1 + \frac{\gamma_{EOS}}{B_{T0}(P_0)}(P - P_0) \cdot \exp[b(T - T_0)]\right]^{1/\gamma_{EOS}}} \quad (5)$$

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, $T_0=T_g(P_0)$, determined herein from standard calorimetric measurement ($T_0 = 182$ K).

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

Table 4. The volumetric data of [C₄mim][NTf₂] recorded under isothermal conditions.

T / K	$V_{sp} / cm^3 \cdot g^{-1}$						
	Pressure / MPa						
	0.1	10	40	80	120	160	200
292.45	0.6932	0.6812	0.6714	0.6632	0.6559	0.6492	0.6932
295.69	0.6944	0.6824	0.6726	0.6642	0.6569	0.6501	0.6944
300.58	0.6966	0.6843	0.6743	0.6658	0.6584	0.6516	0.6966
305.32	0.6987	0.6862	0.6760	0.6675	0.6599	0.6530	0.6987
310.17	0.7009	0.6882	0.6778	0.6690	0.6614	0.6544	0.7009
314.78	0.7030	0.6900	0.6795	0.6706	0.6630	0.6559	0.7030
319.61	0.7052	0.6919	0.6812	0.6722	0.6643	0.6572	0.7052
324.59	0.7074	0.6939	0.6830	0.6738	0.6658	0.6587	0.7074
329.26	0.7095	0.6957	0.6847	0.6754	0.6673	0.6600	0.7095
334.07	0.7116	0.6976	0.6863	0.6769	0.6687	0.6613	0.7116
339	0.7139	0.6996	0.6881	0.6785	0.6701	0.6626	0.7139
343.47	0.7159	0.7014	0.6897	0.6801	0.6717	0.6641	0.7159
348.32	0.7180	0.7033	0.6914	0.6816	0.6730	0.6653	0.7180
353.36	0.7203	0.7051	0.6930	0.6829	0.6742	0.6664	0.7203
358.37	0.7225	0.7070	0.6946	0.6844	0.6756	0.6677	0.7225
363.23	0.7247	0.7088	0.6962	0.6858	0.6769	0.6689	0.7247
368.29	0.7269	0.7107	0.6979	0.6874	0.6783	0.6702	0.7269
373.35	0.7292	0.7127	0.6996	0.6889	0.6798	0.6716	0.7292
378.04	0.7314	0.7145	0.7012	0.6904	0.6811	0.6728	0.7314
383.43	0.7338	0.7164	0.7029	0.6919	0.6825	0.6740	0.7338
388.41	0.7360	0.7183	0.7047	0.6934	0.6839	0.6754	0.7360
393.24	0.7383	0.7202	0.7063	0.6950	0.6853	0.6767	0.7383
398.32	0.7407	0.7221	0.7080	0.6965	0.6867	0.6779	0.7407
403.51	0.7430	0.7241	0.7097	0.6980	0.6881	0.6793	0.7430
408.32	0.7453	0.7260	0.7113	0.6995	0.6895	0.6805	0.7453
413.35	0.7476	0.7280	0.7130	0.7010	0.6908	0.6818	0.7476
418.42	0.7501	0.7300	0.7149	0.7026	0.6923	0.6831	0.7501
423.7	0.7526	0.7320	0.7166	0.7041	0.6937	0.6845	0.7526

*data are in good agreement with values reported in refs [52,39,40]

Combining the high-pressure dielectric results with *PVT* data we are now able to express the electrical conductivity of [C₄mim][NTf₂] 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 Λ_{mol} data in *T-V* representation, we can now verify the validity of thermodynamic scaling relation for the investigated IL by plotting $\log_{10}\Lambda_{mol}$ vs. $(TV^\gamma)^{-1}$. However, to perform such test, first it is necessary to find the scaling exponent. According to the literature reports, the parameter γ can be determined by many different ways.^{41,42} However, one of the most noteworthy and convenient method is based on the entropic model originally formulated by Avramov for describing the $\eta(T, P)$ dependences⁴³, and then extended to the *T-V* plane by Casalini *et al.*²³ Herein, to parameterize the conductivity data of [C₄mim][NTf₂] and consequently to determine the value of the γ exponent the modified Avramov equation in the following form was applied:

$$\log \Lambda_{mol} = \log \Lambda_{mol0} + \left(\frac{A}{TV^\gamma}\right)^\phi \quad (6)$$

where $\phi = 2C_V / ZR$ and Grüneisen parameter $\gamma = \gamma_G = (C_P / C_V - 1) / T\alpha_p$ are expressed by the set of thermodynamic quantities *i.e.* isobaric and isochoric heat capacities (C_P and C_V), the isobaric volume expansivity α_p , the gas constant R , and the degeneracy Z of the system defined 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.^{44,45} However, at the same time, a significant discrepancy between γ_G and γ values has been reported. The experimental investigations of small molecular liquids like OTP, KDE or BMPC^{46,50,47} as well as polymers⁴⁸ have demonstrated that in general the value of scaling exponent γ is much higher than γ_G 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 - V space.⁴⁹ This new relation based on the assumption that the maximal activation barrier for molecular rearrangements E_{\max} is a function of a liquid density, has in fact the same mathematical form as the modified Avramov model (Eq. 6), but there is a fundamental difference in the meaning of exponent γ .

Now it is defined as $\gamma = \gamma_{EOS} \sqrt{\phi} + \gamma_G$. 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 liquids⁵⁰ and ionic conductors.⁴⁹ Thus, it is also interesting to check its correctness for the studied IL: the [C₄mim][NTf₂]. To realize this task the Grüneisen constant was calculated in two different ways: (i) using the thermodynamic variables reported in the literature^{51,52}, *i.e.* isobaric and isochoric heat capacities estimated in the vicinity of the glass transition temperature, and the isothermal compressibility. γ_G expressed in the form of its thermodynamic definition $\gamma_G = V\alpha_p C_V^{-1} / \kappa_T$ is equal to 1.32 at $T_g = 182$ K; (ii), having already determined values of the scaling exponent γ and γ_{EOS} , giving then, $\gamma_G = 1.91$. Based on which, it can be easily seen, that we obtained a quite good agreement between Grüneisen parameter γ_G values determined by means of the two above-mentioned methods. Thus, the result obtained for [C₄mim][NTf₂] provides the next strong evidence that there is a relation between the dynamic and thermodynamic properties of supercooled liquids.

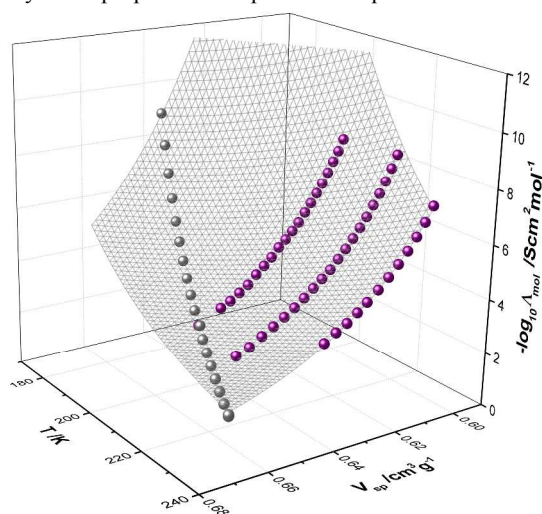


Figure 3 The molar conductivity for [C₄mim][NTf₂] as a function of temperature and volume. The three-dimensional surface was determined using the modified Avramov equation (Eq.6).

The result of global fitting the $A_{mol}(T,V)$ 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.

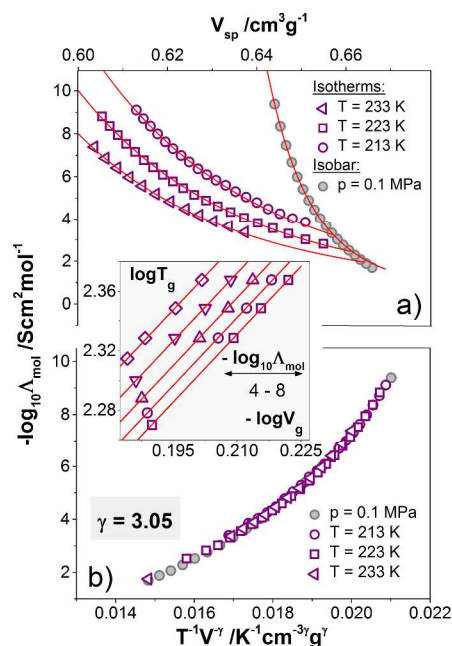


Figure 4 Panel (a) Isothermal and isobaric data for [C₄mim][NTf₂] plotted as a function of volume. Solid lines are fits to Eq. 6. Panel (b) The molar conductivity data for [C₄mim][NTf₂] plotted versus $(TV)^{-3\gamma}$ with the scaling exponent calculated herein as $\gamma = 3.05$. The inset shows the 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:⁵³

$$\log T_g = A - \gamma \log V_g \quad (7)$$

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 $\log_{10}\sigma_{dc}$ used to define the glass transition temperature T_g and volume V_g . Consequently, the value of the γ coefficient ($=3.04 \pm 0.01$), remains constant within the studied range of dynamics. In this context it should be stressed that the scaling exponent found for the [C₄mim][NTf₂] is close to the values of γ already reported for other ionic liquids such as [BMP][BOB] ($\gamma = 3.7$),⁴⁹ verapamil hydrochloride ($\gamma = 2.49$),²⁹ [C₈mim][PF₆] ($\gamma = 2.4$) or [C₄mim][PF₆] ($\gamma = 2.9$).⁵⁴ Furthermore, it is in very good agreement with the scaling coefficient determined from viscosity data measured in the normal liquid state of [C₄mim][NTf₂] ($\gamma_\eta = 2.9$).⁵⁵

Finally, the temperature, pressure and volume dependence of electrical conductivity of [C₄mim][NTf₂] can be considered in the context of thermodynamic scaling concept. As depicted from the

Fig. 4b, the experimental data rescaled vs. $(TV^{3.05})^{-1}$ collapse into a single master curve. Therefore, herein it can be stated that the scaling rule is obeyed in the case of the selected IL. Similar results were recently obtained for another aprotic ionic liquid: BMP-BOB⁴⁹ as well as for some protic ionic conductors like lidocaine hydrochloride³⁰ or verapamil hydrochloride.²⁹ Considering the validity of the density scaling theory for the studied imidazolium-based IL, the agreement between the coefficients γ_η and γ_σ should not be overlooked. Since each of these two parameters was determined from the data measured in different temperature conditions one can state that the $(TV^\gamma)^{-1}$ scaling of $[C_4mim][NTf_2]$ 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 $[C_4mim][NTf_2]$. The dielectric relaxation data presented in electric conductivity representation (σ^*) combined with PVT experimental results allow us to thoroughly examine the Λ_{mol} behavior in the temperature pressure and volume thermodynamic space. By plotting $\log_{10}\Lambda_{mol}$ as a function of $(TV^\gamma)^{-1}$ 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 $\gamma_\sigma = 3.05$ determined from the global fitting of modified Avramov model to the $\log_{10}\Lambda_{mol}(T, V)$ 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 ($\gamma_\eta = 2.9$). 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 $[C_4mim][NTf_2]$. Additionally, our investigations are the next example when the relation between the scaling exponent γ and the thermodynamically defined Grüneisen constant γ_G , recently derived by Paluch *et al.*, is satisfied also for ionic liquids.

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Notes and references

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