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Heterogeneous Nature of Relaxation Dynamics of Room-Temperature Ionic Liquids $(EMIm)_2[Co(NCS)_4]$ and $(BMIm)_2[Co(NCS)_4]$

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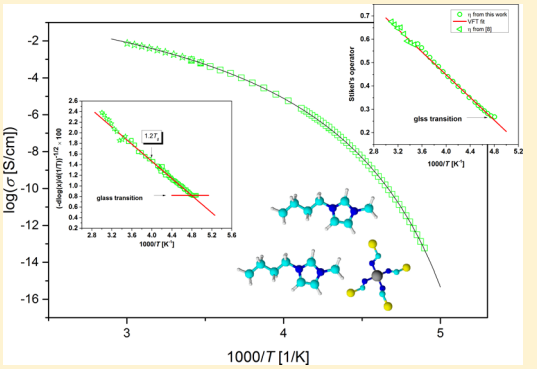
Supporting Information

ABSTRACT: Dynamic crossover above T_g has been recognized as a characteristic feature of molecular dynamics of liquids approaching glass transition. Experimentally, it is manifested as a change in Vogel−Fulcher−Tammann dependence or a breakdown of the Stokes−Einstein and related relations. In this paper, we report the exception from this rather general pattern of behavior. By means of dielectric, ultrasonic, rheological, and calorimetric methods, dynamics of two good ionic conductors $(BMIm)_2[Co(NCS)_4]$ and $(EMIm)_2[Co(NCS)_4]$ of less common stoichiometry (2:1) was studied in a very broad temperature range. However, none of the mentioned dynamic changes was observed in the entire studied temperature range. On the contrary, the single VFT and the same fractional Walden coefficient were found for conductivity and viscosity changes over 12 decades. Moreover, ultrasonic studies revealed that the data at temperatures which cover the normal liquid region cannot be fitted by a single exponential decay, and the Cole−Cole function should be used instead.



INTRODUCTION

Ionic liquids (ILs) have triggered great interest in both science and industry. Their special attraction lies in their unique properties like a huge range of fluidity, chemical and thermal stability, high conductivity ($>10^{-4}$ S·cm^{-1}), or a large electrochemical window together with fast ion mobility, all of which make them especially promising candidates for electrochemical applications.[1] Furthermore, many of them are nonvolatile and nonflammable, although nowadays it is obvious that these properties are not general.[2] In addition, their impact on the natural environment is not as neutral as it was thought earlier, although they are still regarded as "green" chemicals. Another branch of industry interested in special properties of ILs is pharmacy.[3,4]

Among different classes of ILs, metal-containing ones attract particular attention of researchers due to properties that cannot be associated with typical ILs.[5] Unfortunately, the most popular ILs with halogenometalate complexes as anions turn out to be unstable.[5] A new class of substances are liquids with thio- and isotiocyanatometalates of transition metals in anions.[6] In the previous papers,[7,8] few basic properties of newly synthesized paramagnetic 1-alkyl-3-methylimidazolium ionic liquids $(EMIm)_2[Co(NCS)_4]$ and $(BMIm)_2[Co(NCS)_4]$ were reported. These substances appeared to have many features interesting for engineers.[7,8] However, their chemical structure, less common stoichiometry (2:1) due to divalent anion, and complex nature of the anion makes them also very interesting from the point of view of basic science. Recently, molecular dynamics of supercooled and glassy ILs have been extensively studied. An in-depth knowledge of molecular dynamics' behavior near T_g of ionic liquids is also necessary to formulate a complete theory of a liquid-glass transition. Thus, we decided to expand the scope of our interests beyond the common physicochemical characteristics of these materials. In this paper, we focused on the molecular dynamics of both mentioned ILs in normal and supercooled liquid as well as in a glassy state.

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Combining ultrasonic, dielectric, rheological, and calorimetric methods, we were able to trace evolution of dynamical properties of studied samples over 12 decades, down to the glass transition temperature. As a result, we observed several interesting phenomena like non-Newtonian behavior, lack of the dynamical crossover in the range of $1.2-1.5T_g$, and slight decoupling between conductivity and structural relaxation times. Because $(EMIm)_2[Co(NCS)_4]$ and $(BMIm)_2[Co(NCS)_4]$ behave differently than commonly noted for ionic liquids, it provides a better understanding of the mechanisms governing molecular dynamics of such type of substances over a very wide temperature range, including the supercooled state.

EXPERIMENTAL SECTION

Ionic liquids investigated ($(EMIm)_2[Co(NCS)_4]$ **(I)** and $(BMIm)_2[Co(NCS)_4]$) **(II)** were synthesized and purified as described in ref 7. All samples were kept under argon, and prior to use, they were additionally degassed by a vacuum pump over 24 h to remove possible traces of solvents and moisture. The water concentration (93.863 ppm for **(I)** and 132.72 ppm **(II)**) was checked by Karl Fischer titration.

The ambient pressure, isothermal, frequency dependent dielectric measurements were carried out using a Novo-Control GMBH Alpha Analyzer in a frequency range from 10^{-2} to 10^7 Hz. The sample was placed in a parallel flat stainless steel capacitor. Temperature was controlled by a Novo-Control Quattro system, with a nitrogen gas cryostat. Temperature stability of the sample was better than 0.1 K.

Calorimetric measurements were carried out by Mettler-Toledo DSC apparatus equipped with a liquid nitrogen cooling accessory and a HSS8 ceramic sensor (heat flux sensor with 120 thermocouples) with implemented stochastic temperature-modulated differential scanning calorimetry (TMDSC) method (TOPEM). Temperature and enthalpy calibrations were performed by using indium and zinc standards.

Ultrasound absorption measurements were performed with the use of the homemade apparatus (described in detail in ref 9) working on the standard pulse technique (first traveling pulse and the variable path length). The measurements were performed for some chosen discrete frequencies from range 10 to 300 MHz by means of three pairs of ultrasonic heads at the temperatures (293.15 and 298.15) K and at atmospheric pressure. Temperature (±0.05 K) was maintained with the thermostat unit. To avoid contact with air, the measuring cell was filled with argon during the measurements.

RESULTS AND DISCUSSION

Generally speaking, the ionic liquids $(EMIm)_2[Co(NCS)_4]$ **(I)** and $(BMIm)_2[Co(NCS)_4]$ **(II)** are relatively easy to supercool. However, the first one shows some tendency for crystallization, which is in agreement with other imidazole-based ILs.[5] In this case, a cold crystallization was observed at T_c = 264 K with melting point at T_m = 292 K when heated with a rate of 5 K/min. The crystallization process does not occur at higher heating rates.

Dielectric spectra were measured in a temperature range from below T_g (208 K for **(I)** and 209 for **(II)**) up to 293.15 K for $(BMIm)_2[Co(NCS)_4]$ and 233.15 K for $(EMIm)_2[Co(NCS)_4]$. Usually the dielectric data of conducting materials are analyzed in either conductivity or electrical modulus representation. Both representations trace the same phenomena and are interrelated with each other. The results in both representations are shown in Figure 1a,b and Figure 1c,d for **(I)** and **(II)**, respectively. In an imaginary part of modulus spectra

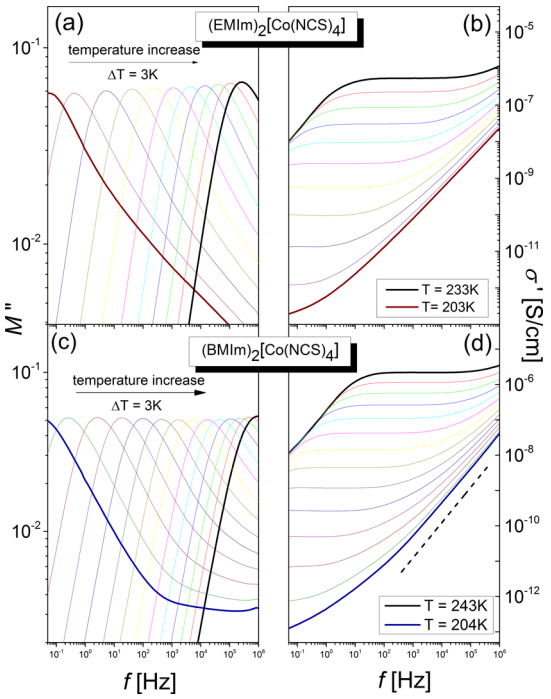

Figure 1. Representative spectra of imaginary part of modulus and real part of conductivity for $(EMIm)_2[Co(NCS)_4]$ (a,b) and $(BMIm)_2[Co(NCS)_4]$ (c,d). Dashed line in panel (d) shows the slope equal to 1. The horizontal arrow indicates the direction of the experiment.

(M''), the dominant feature is the asymmetric peak of the σ-relaxation. The inverse of the frequency of M'' peak maximum designates the relaxation time ($\tau_\sigma = (1/2)\pi f_{max}$).

Values of the dc-conductivity at a given temperature can be determined from the plateau region in the middle part of the conductivity spectrum. The temperature dependence of the dc-conductivity, presented in Figure 2, is very similar for both samples, although as expected, values of conductivity of $(EMIm)_2[Co(NCS)_4]$ are a bit higher due to the fact that shorter side chain makes these cations more mobile. For $(BMIm)_2[Co(NCS)_4]$, we were able to carry out dielectric measurements in a wider temperature range due to the lack of tendency to crystallization. Analysis of conductivity data obtained for sample **(II)** reveals unexpected behavior with decreasing temperature. In many fragile liquids (liquids with strongly non-Arrhenius temperature variations of relaxation time), the temperature dependence of relaxation times reveals several characteristic changes: At high temperatures, it follows an Arrhenius law; then at some T_A, it changes to a VFT dependence; and at some T_B between T_A and T_g, it usually crosses over to another VFT. This T_B usually appears in the range of $\sim 1.2-1.5T_g$.[10] The last change of the temperature dependence of relaxation times is observed at T_g where temperature dependence crosses over to an Arrhenius type. Among different views on the origin of the dynamic crossover at T_B, the most common ascribes it a temperature below which cooperativity becomes a crucial factor and where dynamical heterogeneity of the system starts to play a key role in the molecular dynamics.[11,12] The change of VFT dependence at T_B was observed for small molecular liquids like OTP,[13] diisobutyl

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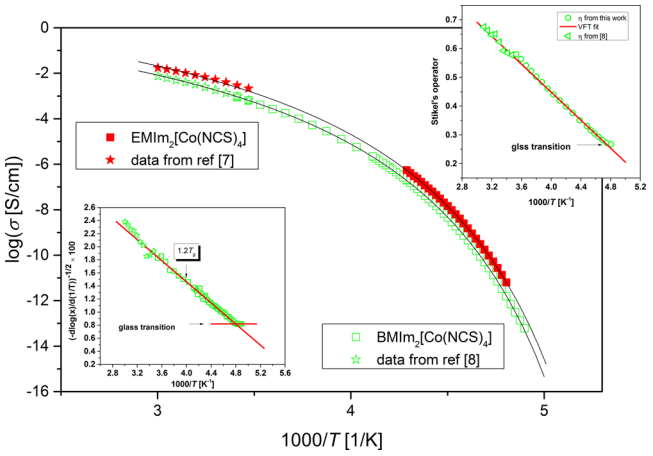

Figure 2. Activation plot of the conductivity above glass transition temperature of $(EMIm)_2[Co(NCS)_4]$ (solid squares) and $(BMIm)_2[Co(NCS)_4]$ (open squares). (ψ) and (ξ) data from refs 7 and 8, respectively. Solid lines are fits by means of eq 1 (parameters are given in Table 1 of Supporting Information). Left lower inset: Stickel's analysis for conductivity data of $(BMIm)_2[Co(NCS)_4]$. Right upper inset: Stickel's analysis for viscosity data of $(BMIm)_2[Co(NCS)_4]$.

phthalate,[14] polymers like polyisoprene,[15] and ionic liquids like (OMIm) (NTf_2).[16]

Parameter commonly used to characterize quantitatively the departure of the temperature dependence from the Arrhenius behavior at T_g (and the same the fragility of the system) is the so-called steepness index or fragility m defined as $m = (\mathrm{d}\log x/\mathrm{d}(T_g/T))|_{T=Tg}$, where x denotes one of the transport properties like viscosity and conductivity, or structural relaxation times. Fragility was originally derived for viscosity however flexibility in choosing the quantity for which the fragility is defined exists as long as they are correlated with changes of structure. In the case of our samples, fragility determined from the temperature dependence of the viscosity (at T_g taken as T for which $\eta = 10^{10}$ Pa·s) is $m = 93.4$ for sample **(I)** and $m = 87.5$ for sample **(II)**. It means that both samples are very fragile, and for such systems, T_B was sometimes observed even at such high temperatures as $1.5T_g$.

A close examination of Figure 2 reveals that for sample **(II)**, there is a single VFT in a form:

$$x = x_\infty \exp\left(\frac{B}{T - T_0}\right) \quad (1)$$

(where x denotes σ − conductivity or η − viscosity, x_∞ is pre-exponential factor, T_0 − temperature of an ideal glass transition and D − a material constant) can perfectly describe the temperature dependence of x in the entire temperature range above T_g. To make our experimental range of temperatures even broader, we added to Figure 2 conductivity data obtained by Geppert-Rybczyńska[7,8] in a normal liquid state at temperatures as high as 333 K, which is around $1.6T_g$.

The best way to identify precisely the existence of any specific changes in temperature dependence of the interested transport coefficient is to analyze the experimental data by means of the so-called Stickel's derivative operators.[17] These operators linearize VFT (equation1) and transform the Arrhenius relation

$$x = x_\infty \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

into a constant value according to the following equation (in the case of Arrhenius relation $T_0 = 0$):

$$[\mathrm{d}\log(x)/\mathrm{d}(1/T)]^{-1/2} = (B)^{-1/2}\cdot(1 - T_0/T) \quad (3)$$

where x is the studied property, B − a respective constant. Thus, any change in the temperature dependence of x should be visible as an intersection of straight lines. The result of such analysis for $(BMIm)_2[Co(NCS)_4]$ is presented in the inset in Figure 2. It clearly shows that the only visible crossover occurs around 209 K and is related to crossing the glass transition. On the other hand, no clear indication of existence of T_B exists up to $1.6T_g$. However, one can note a slight deviation from the line obtained for Stickel's operator applied to VFT fit at the high temperature limit of the conductivity data (see lower left inset to Figure 2). It is not possible to settle whether it is an indication of a very slight crossover in this range of temperatures or just scatter of the data. On the one hand, the deviation from the straight line obtained from VFT fit is within the upper limit of allowed deviation (basing on a 4d test). On the other hand, systematic trend of this deviation may indicate the real change in this dependence. More conclusive picture can be obtained for viscosity. Result of Stickel's analysis for viscosity data of **(II)** is shown in upper right inset of Figure 2. Again, when we add the data from ref 8, no signs of the dynamical crossover can be found at any temperature up to 323 K ∼ $1.55T_g$. It is worth mentioning that the same pattern of behavior was previously found for $(BMIm)[PF_6]$, (BMIm)-$[NTf_2]$ and $(BMIm)[TFA]$,[18] for which temperature dependence of structural relaxation times and diffusion coefficient were studied. The question arises immediately whether it can be more general behavior of ILs or at least for BMIm-based samples. In this context, it has to be noted that all the ILs studied by Griffin[18] contained BMIm cation similarly to our sample. It is interesting that one of the very few known molecular liquids for which T_B is not observed is di-*n*-butyl phthalate. It turns out that structure of di-*n*-butyl phthalate[14] slightly resembles BMIm cation. Thus, their behavior may also be similar. The influence of the cation structure on the position of the temperature at which studied crossover occurs become more visible when one takes into account the recent observation for (OMIm) (NTf_2) for which the dynamic crossover at T_B was recently found.[16] In this respect, it is also interesting to note that the lack of VFT change in a common temperature range for BMIm-based ILs is insensitive to the different stoichiometry of our ILs (2:1) caused by bivalency of the anion.

Although change in the VFT dependence is the best known sign of the studied crossover, often it is treated as a nonsufficient condition. It is a long-standing discussion on the validity of the VFT-equation fits of the data obtained at a very broad temperature range. Therefore, in parallel, other parameters are studied that can prove the existence/nonexistence of the dynamic crossover.

Temperature dependence of σ-relaxation times are presented in Figure 3a and b for **(I)** and **(II)**, respectively. It is commonly believed that for ILs, temperature dependence of σ and τ_σ follows that of shear viscosity η, as expected from the Walden rule for conductivity in molecular liquids. However, it was shown for several ionic materials that there is a decoupling between viscosity (structural relaxation) and conductivity

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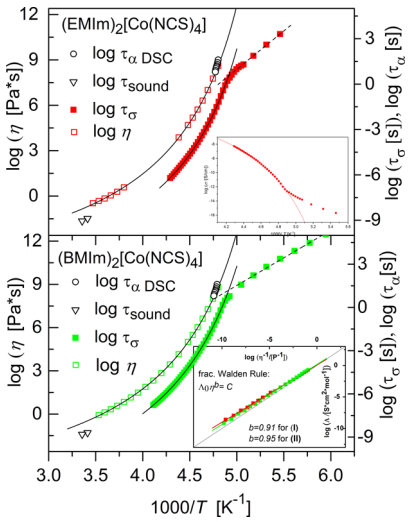

Figure 3. Relaxation map of (a) $(EMIm)_2[Co(NCS)_4]$ and (b) $(BMIm)_2[Co(NCS)_4]$. Conductivity relaxation times are compared with viscosity and structural relaxation times from TMDSC. At the highest temperature limit, relaxation times obtained from ultrasound absorption are added. Solid and dashed lines are VFT and Arrhenius fits, respectively. Crossover point on $\tau_\sigma(T)$ dependence determines T_g. Upper inset: dc-conductivity vs inverse temperature with clearly visible crossover from the VFT to Arrhenius dependence. Lower inset: Walden plot.

(conductivity relaxation). It is especially prominent for protic ionic liquids[19] due to enhanced proton conduction caused by Grotthuss mechanism.

In Figure 3, glass transition is demonstrated as a crossover from VFT (eq 1) to Arrhenius (equation2) temperature dependence of σ-relaxation times. Because the same crossover is visible on the temperature dependence of the data of dc-conductivity (see inset to Figure 3a), such a change is a physical phenomenon not an artifact resulting from application of Modulus representation. In fact, this effect has been observed for some other ionic liquids.[3,20] On the other hand, there are also examples of ionic liquids for which no decoupling between dc-conductivity and viscosity or diffusion coefficient is observed down to glass transition temperature. Among them are liquids with cations based on imidazole.[21,22] We compared these data with the viscosity and specific heat relaxation, which reflect the structural relaxation. As shown in Figure 3, inflection occurs at a temperature for which structural relaxation reaches 1000 s. Usually, these are conditions given for the glass transition. However, one has to be aware that at this temperature, conductivity relaxation times do not reach the same value. The crossover from VFT to Arrhenius-type behavior can be found around 10 s for (II) and 1 s for (I). It means that there is a decoupling between conductivity and structural relaxation. It is very interesting that such decoupling was not observed for structurally very similar IL $(BMIm)[BF_4]$.[23] It means that in this case, the anion must play an important role. The phenomenon of decoupling between studied properties is also clearly visible in the inset to Figure 3, in violation of the classical Walden rule. Instead, fractional Walden rule ($\Lambda_0\eta^b$ = const) can be used, where b is a measure of decoupling. In our case, b values equal 0.91 and 0.95 for samples (I) and (II), respectively (see the inset in Figure 3). The decoupling of diffusion and structural relaxation (viscosity) has been found in many glass forming liquids, but usually only for temperatures below T_B.[24] For our samples, almost the same values of the exponent b were obtained in the entire temperature range. This observation strengthens our view that no change in the dynamics occurs in the range of $1.2-1.5T_g$. If any crossover exists for this sample, it occurs above $1.5T_g$.

Further interesting details can be revealed from studies of the ultrasound absorption in normal liquid range. The ultrasound absorption coefficient α per squared frequency f (i.e. the product $\alpha \cdot f^{-2}$) for both liquids are summarized in Table 2 of Supporting Information. As evidenced from this table and Figure 4a,b, the dependence of the quotient $\alpha \cdot f^{-2}$ on frequency

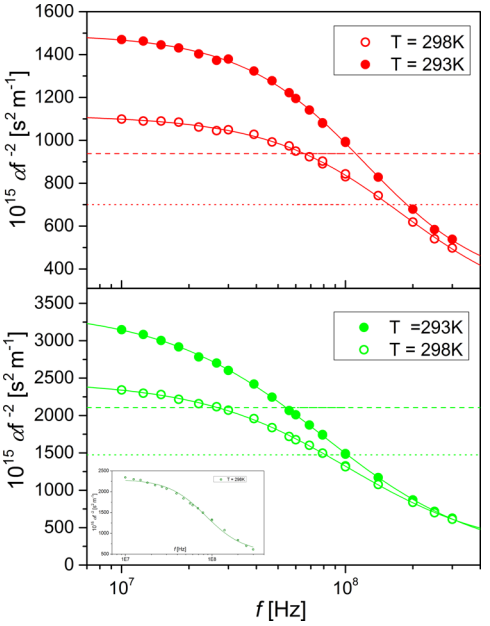

Figure 4. Ultrasound absorption coefficient per squared frequency $\alpha \cdot f^{-2}$ versus log f for (upper panel) $(EMIm)_2[Co(NCS)_4]$ and (lower panel) $(BMIm)_2[Co(NCS)_4]$ at temperatures of 293.15 K (●); and 298.15 K (○). Solid lines are fits by means of CC function. Dashed and dotted lines—classical absorption at temperatures 293.15 and 298.15 K, respectively. The inset presents the fit with use of a single Debye function to ultrasonic spectrum for $(BMIm)_2[Co(NCS)_4]$ at 298.15 K.

changes strongly with temperature. It appears also that within the investigated frequency range the quotient $\alpha \cdot f^{-2}$ is clearly dependent on frequency as high as above 10 MHz. Thus, in both cases, the dispersion characteristics $d(\alpha \cdot f^{-2})/df < 0$ is observed. Moreover, both liquids are rather highly absorbing; that is, the frequency normalized attenuation values (at T = 298.15 K and f = 100 MHz) are 837×10^{-15} and 1321×10^{-15} $s^2 \cdot m^{-1}$, respectively. At the same time, it is observed in both liquids that above some frequency, the experimental values of $\alpha \cdot f^{-2}$ are smaller than those predicted by the Navier–Stokes relation (α_{cl}). In other words, the absorption curves shown in Figure 4 indicate that $\alpha > \alpha_{cl}$ at lower frequencies and $\alpha < \alpha_{cl}$ at higher frequencies, and the curves also demonstrate that the frequency for which $\alpha = \alpha_{cl}$ decreases with increasing temperature. Most probably, this kind of behavior results from a relaxation mechanism of the viscous type. Similar behavior has been reported previously for several molecular liquids, including 1-dodecanol[25] and castor oil,[26] diols[27] as well as ionic liquids (OMIm) (NTf_2)[28] and a series of (C_nMIm) (PF_6).[29] The obtained numerical values of $\alpha_{cl} \cdot f^{-2}$ are

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summarized in Table 3 of the Supporting Information. Shear viscosity used for calculations were taken from refs 7,8.

The small ratio of the observed absorption to that calculated from the Stokes rule (i.e., classical absorption) and the negative temperature coefficients of the experimental absorption in the nondispersive region are observed for both liquids. These findings are characteristic for liquids with structural relaxation (i.e., for liquids from group III according to liquid classification in relation to absorption data).[30] Detailed inspection of Table 3 shows that for (**I**), α/α_{cl} is temperature independent. This finding indicates an equal temperature dependence of the volume viscosity, η_V, and shear viscosity. On the other hand, for (**II**), this ratio decreases with temperature. A similar scenario was observed in the case of (EMIm) and (OMIm) (NTf_2).[28] It means that changes in the alkyl chain cause the detectable differences in molecular mechanisms of the volume and shear viscosity. However, in the case of (OMIm) cation, the temperature dependence was weaker in comparison to that observed for (**II**). Immediately, the question arises as to whether it is anion dependent. Another possible scenario is that there is a maximum of difference for cations with alkyl substituent between C_2 and C_8 beyond which again the molecular mechanisms of the volume and shear viscosity become similar.

From the frequency-dependent ultrasonic absorption data, relaxation times can be obtained via the following relation:

$$\alpha \cdot f^{-2} = \sum_{i=1}^{n} A_i \cdot (1 + (f/f_{i,\mathrm{rel}})^2)^{-1} + B \qquad (5)$$

where A_i and $f_{i,\mathrm{rel}}$ are the relaxation amplitudes and relaxation frequencies, respectively. B represents the sum of the classical part of absorption and contributions from processes with relaxation frequencies considerably higher than $f_{i,\mathrm{rel}}$. It appears that for the studied liquids, the frequency dependence of ultrasonic absorption data cannot be fitted with a single Debye-type relaxation processes ($n = 1$). It is in odd to what is commonly observed for ultrasonic spectra of both molecular and ionic liquids in a normal liquid regime.[27,28] Thus, in this paper, we would like to discuss fitting with a stretched function (shape parameters (α and β) should be introduced to eq 5). We found that not a Cole-Davidson but a symmetrical Cole–Cole function with the shape parameter (α_{CC}) around 0.8 provides the best fit (full results are given in a Table 4 of a Supporting Information). The relaxation times denoted as τ_{sound} (calculated as $\tau_{\mathrm{rel}} = (2\cdot\pi\cdot f_{\mathrm{rel}})^{-1}$) can be found in Figure 3. Ultrasonic results are very interesting for two reasons. First, stretching of this spectrum again proves that in the temperatures for which the spectra were taken, we are in the region which we can call a complex liquid regime. Otherwise, one single Debye relaxation should be observed. Moreover, the symmetrical shape of the spectra is puzzling. A possible explanation is that the process which can be observed by the ultrasonic method does not reveal features of the α relaxation but of the β-one. In fact, it was reported several times that in shear mechanical spectra, the amplitude of the β-process at low temperatures far exceeds the one observed for dielectric spectra.[31] Moreover, it increases much faster with temperature.[32] Thus, it is very likely that for such high frequencies as used in the ultrasonic method, it is the dominant relaxation process. In such case, our samples would be examples of scenario I according to Donth and co-workers.[33] It also explains why the relaxation times obtained from the ultrasonic experiment does not fully agree with the rest of the data (see Figure 3). If we take into account the Donth's scenario I, known the best for the PMMA, it is probable that in our case, low amplitude, slower alpha relaxation is buried beneath the lower frequency side of the clearly observed β-process. As mentioned above, there are examples for both single Debye and stretched shape of the ultrasonic spectra in the literature; it would be very interesting to determine whether these observations always correlate with the position of T_B for the studied materials, which seems to be very likely on the basis of our data.

CONCLUSIONS

Imidazole-based cations are known for their ability to form quite effective H-bonding systems. However, with the elongation of the alkyl chain, the influence of the nonpolar domains increases, and the C2 atom involved in H-bonds with sulfur atom of the anion[34,35] becomes less acidic. This probably causes higher decoupling in sample (**I**) (due to contribution from protonic conduction) and differences in ultrasound absorption. On the other hand, it is not fully understood whether sterical hindrance, various types of interactions (Coulomb interactions, H-bonds) between cations and anions or non-Newtonian nature of studied liquids are the reasons why the dynamical crossover with all accompanying phenomena is not observed in the region of $1.2-1.5T_g$. In fact, it remains an open question whether the observations (lack of change in VFT dependence at T_B, lack of the point in which Walden rule breaks down, and symmetrically stretched ultrasonic absorption spectra in the fluid regime) are related to each other and whether each of them indeed can be treated as an indicator for existence/nonexistence of a dynamical crossover. However, all our experimental data seem to indicate that the dynamical heterogeneity and cooperativity play the same role in the molecular dynamics of ionic liquids studied herein in the vicinity of T_g as it does in normal liquid state at least up to $1.5-1.6T_g$. It means that even at temperatures much higher than T_g, they behave like supercooled liquids and not like normal liquids.

More experimental data in broad temperature range are necessary to answer the question whether it is a general rule for ILs or it is only specific feature of samples based on BMIm cation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b07123.

Contains Tables 1–4 according to description given in text (PDF)

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Notes

The authors declare no competing financial interest.

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