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Dynamics of the Ionic Liquid 1-Butyl-3-Methylimidazolium Bis(Trifluoromethylsulphonyl)imide studied by Nuclear Magnetic Resonance Dispersion and Diffusion

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Abstract

The dynamics of the imidazolium based room temperature ionic liquid Bmim Tf2N was investigated by means of nuclear magnetic resonance relaxation dispersion (NMRD) and nuclear magnetic resonance pulsed field gradient (NMR-PFG) diffusion experiments on the bulk liquid in a wide range of temperatures. Relaxation and diffusion properties were determined for anions and cations individually, giving evidence of heterogeneities in the dynamics of the ionic liquid. The relevant NMR relaxation mechanisms are the inter- and intramolecular dipolar interaction between the molecular ions reflecting the molecular translational and rotational diffusion. Rotational and translational correlation times could be obtained and showed different dependences on temperature. The experimental diffusion values follow the Vogel-Fulcher-Tammann (VFT) relation above a transition temperature T_c ~1.26 T_g, below which a deviation was observed. Differential scanning calorimetry experiments show a transition at the same temperature.

1. Introduction

Low temperature melting organic salts commonly referred to as ionic liquids (ILs) possess physical properties distinctly different from common molecular liquids. They have received considerable interest due to some of their particular properties like negligible vapour pressure, thermal and chemical stability and relatively high ionic conductivity. They possess a broad range of applications, for instance, as reaction media or ionic conductors in solid-state batteries and fuel cells [1].

In order to gain an insight into the physico-chemical properties of ionic liquids and to expand their range of applicability, there is much interest in the study of their molecular motions that finally control transport (and, hence, conductivity) properties in these materials [2,3]. The microscopic properties of some selected ILs have been investigated recently [4–7]. A common theoretical description is not fully available though, in part because of the asymmetric charge distribution in the molecular ions that determines the electrostatic interaction potential and Coulomb forces. ILs are in their majority glass-forming systems [3,8]. A fundamental question is how the structure and molecular dynamics of this kind of solvents will be affected when they are supercooled. Close to the glass transition temperature, they exhibit a non-exponential structural relaxation due to the collective nature of their dynamics. Their characteristic relaxation times often have non-Arrhenius temperature dependence [9,10]. This departure from the Arrhenius behaviour is found for most of the glass forming systems in properties like diffusivity and viscosity [11–13]. Studies based on nuclear magnetic resonance (NMR) and other techniques suggest that the observed non-exponential behaviour is related to a superposition of relaxation processes, i.e. during supercooling, distinct relaxing domains are gradually grown, each characterized by an individual relaxation rate [13–16]. Information about the characteristic fluctuation times and length-scales of these domains have been obtained by different techniques such as optical and dielectric spectroscopy [11], multidimensional NMR spectroscopy [15], and high field NMR relaxometry [5,17]. However, few investigations were carried out on ILs in supercooled states. A recent study on Bmim Tf2N showed a dynamic crossover at low temperatures in the structural relaxation process, however, such a crossover was not obvious is the ionic diffusion process [8]. This remains puzzling since the dynamic crossover is expected to appear in all dynamic properties of glass-forming systems.

In order to further investigate the dynamics of the imidazolium derived ionic liquid Bmim Tf2N, nuclear magnetic resonance relaxation dispersion (NMRD) [18] and PFG-NMR [19] techniques were combined over a wide range of temperatures. This IL possesses the advantage of having two different NMR-active nuclei, ^{1}H and ^{19}F on cations and anions, respectively, that allows the separate identification of the dynamic properties of the ions from relaxation and self-diffusion. Furthermore, the

NMR relaxometry studies have been used for the indirect determination of translational (self-) diffusion coefficients. Conventional pulsed field gradient (PFG) NMR diffusion measurements were performed on the same system in order to directly compare the results. In addition, differential scanning calorimetry (DSC) [20] has been used to measure the thermal properties of the IL.

2. Material and Methods

The ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl) imide (Bmim Tf2N) was investigated. It was purchased from Sigma Aldrich, Germany and used without further purification. The samples were placed in a vacuum oven for at least 24 h at 383 K to remove any water or dissolved gasses. The density is 1.45 g/cm^3 [21]. The melting (T_m) and glass transition (T_g) temperatures are 270.4 and 186 K, respectively [22].

The primary NMR-active nucleus in the cation Bmim is ^{1}H, present in the alkyl groups as well as in the imidazolium ring. On the other hand, the anion Tf2N has two trifluoromethyl groups at both ends of the molecule with the NMR-active nucleus ^{19}F.

The measurements of ^{1}H and ^{19}F NMR longitudinal relaxation time T_1 were performed at different magnetic field strengths, covering a proton Larmor frequency range from a few kHz up to 20 MHz with the help of a fast field-cycling [18] NMR relaxometer (Stelar s.r.l., Mede, Italy). This device has been equipped with auxiliary coils for the compensation of the earth magnetic field and stray fields from other magnets. Within the experimental errors, all relaxation curves could be described by monoexponential functions for well over one decade of the signal amplitude. The NMR diffusion measurements were carried out on a 7 Tesla NMR spectrometer (Avance III, Bruker, Rheinstetten, Germany) equipped with a Diff-30 diffusion probe with a maximum gradient of 12 T/m. The NMR pulsed field gradient (PFG) stimulated echo pulse sequence was used for this purpose. In both systems, the temperature was controlled with an accuracy of 0.2 K using, at low temperatures, a precooled stream of dry air or evaporated N_2 gas. A script written in Python 2.7 was used to fit the T_1 relaxation dispersion data. In order to verify the purity of the used substances, NMR spectra were obtained on a different high-resolution Bruker NMR spectrometer operating at the ^{1}H-Larmor frequency of 300 MHz. No traceable peaks for water or other impurities were observed.

The DSC measurement was carried out on a Perkin-Elmer 7 Series Thermal Analysis System. An oven-dried sample of 44.2 mg of Bmim Tf2N was placed in a closed aluminium pan. An empty pan was used as the reference. Evaporated liquid nitrogen served as the cooling agent, and a mixture of dry nitrogen and argon gasses (ratio 2:1) was used as the base purge gas for cooling. Dry nitrogen gas was constantly purged through the sample. A cooling/heating rate of 5 K/min was used as following: the sample was cooled from 298 K down to 173 K. The temperature of the sample was then kept at 173 K for 15 min and heated back to 298 K.

3. Results and Discussion

A series of NMR spin-lattice relaxation times T_1 were measured as a function of the ^{1}H and ^{19}F Larmor frequencies by means of the field cycling technique. The experiments were done covering a broad range of temperatures: from 353 K down to 163 K for the case of the ^{1}H-T_1 measurements, and from 293 K to 176 K for the case of the ^{19}F-T_1. As expressed in the introduction, it is possible to experimentally discriminate the spin-lattice relaxation of each ion due to the fact that the cations contain ^{1}H nuclei and the anions ^{19}F nuclei. The dispersion curves, $T_1(\omega)$, are shown in figure 1 as a function of the external magnetic field expressed in frequency units. At room temperature the curves show weak dependence on the Larmor frequency and both ions exhibit similar frequency dependence.

The sample could be supercooled upon lowering the temperature far below its melting point. Over this range of temperature, the IL exhibits a considerable change in its molecular dynamics, reflected by the steeper dispersion of the measured NMR spin-lattice relaxation times as a function of the external magnetic field. In order to visualize the temperature dependence, the data are represented as a function of the reciprocal temperature for a number of selected Larmor frequencies in figure 2. A broad minimum in T_1 is seen for lower frequencies and the shape of the curves are generally asymmetric [23]. No indication of a discontinuity is observed which would be a signature of a liquid-solid phase transition process. However, differences in the temperature dependence of the spin-lattice relaxation are observed for each ionic species. Above T_g, a minimum in the T_1 values for both ions is found for all the Larmor frequencies shown in figures 2a and 2b. For lower temperatures, clear minima are only observed in the relaxation times of the anions (figure 2b). This fact emerges as a signature of two different dynamic processes in the anionic molecules for the supercooled ionic liquid. The existence of a corresponding second minimum for cations at even lower temperatures ($T < 163$ K) can, however, not be excluded.

In liquids, the predominant contribution for spin ½ (^{1}H and ^{19}F) NMR spin-lattice relaxation is provided by dipole-dipole interactions through space. The dipolar couplings are modulated by random molecular tumbling. They include interactions between the nuclear spins in a single molecule (intra), i.e. reorientations and rotations, and between nuclear spins located on different molecules (inter) that are approaching each other and alter the intermolecular (spin) distances. Thus, the angular-frequency dependent NMR spin-lattice relaxation time, $T_1(\omega)$, for ^{1}H spins is given by the summation of rotational and translational spin-lattice relaxation rates

$$\frac{1}{T_{1,\,\text{total}}^{\text{H}}(\omega_{\text{HH}})} = \frac{1}{T_{1,\,\text{Rot}}^{\text{H}}(\omega_{\text{H}})} + \frac{1}{T_{1,\,\text{Trans}}^{\text{H}}(\omega_{\text{H}})}\,. \tag{1}$$

ω_H is the Larmor frequency of ^{1}H, which is defined as $\omega_{\text{H}} = \gamma_{\text{H}} B_0$, where γ_{H} is the gyromagnetic ratio of ^{1}H and B_0 is the magnetic flux density.

The frequency dependence of the T_1 relaxation time for homonuclear intramolecular dipolar interaction is well described by the Bloembergen, Purcell, and Pound theory [23–25] and is written as

$$T_{1,\,\text{Rot}}^{\text{H}}(\omega_{\text{H}})^{-1} = k_{Rot}^{\text{H}}[I_{Rot}(\omega_{\text{H}}) + 4 I_{Rot}(2\omega_{\text{H}})]\,, \tag{2}$$

where $I_{Rot}(\omega)$ is the spectral density function defined as the Fourier-transform of the orientational autocorrelation function $G(\tau)$ of the fluctuating dipolar coupling [23] and k_{Rot}^{H} is the homonuclear intramolecular dipolar coupling constant of ^{1}H spins

$$k_{Rot}^{H} = \left(\frac{\mu_0}{4\pi}\right)^2 (5r^6)^{-1} \gamma_H^4 \hbar^2\, \text{I}(\text{I}+1) \tag{3}$$

μ_0 is the vacuum permeability, I is the spin number (= ½ for ^{1}H and ^{19}F), $\hbar$ is the reduced Planck constant, and r is the internuclear distance. For a rigid molecule, intramolecular contributions arise exclusively from molecular rotations. Assuming a single correlation time, the rotational contribution to the spectral densities can be modelled by the Lorentz function [23],

$$I_{Rot}^{\mathrm{H}}(\omega_{\mathrm{H}}) = \frac{\tau_R^{\mathrm{H}}}{1+(\omega\tau_R^{\mathrm{H}})^2} \qquad (4)$$

where τ_R^{H} is the rotational correlation time for ^{1}H which, in this case, represents the average time for a molecular axis to change its direction by one radian [25]. Equations (1) to (4) can be similarly written for ^{19}F by substituting the H superscripts by F.

In the limit of $\omega\tau_R \ll 1$, the spectral density becomes frequency independent and T_1 turns to be constant at varying magnetic field strength. At the opposite limit T_1 follows a ω^2 dependence. T_1 assumes a well-pronounced minimum at a temperature where $\omega\tau_R \sim 1$, and a symmetric behaviour when plotted as a function of T^{-1}. None of these conditions is met for the sample under study, which indicated that the simple form of eq. (2) is insufficient to explain the molecular dynamics, and that both contributions in eq. (1) need to be considered.

In order to model the intermolecular contribution in eq. (1), the structure of the ionic liquid under study must be taken into account. Cations and anions in Bmim Tf2N ionic liquid contain ^{1}H and ^{19}F, respectively. These ions are distributed in the liquid in a way to neutralise the total charge. Tumbling of the ions cause fluctuations in the interionic distances about its mean value. Therefore it is important to consider both types of intermolecular interactions in the liquid, the homonuclear (co-ions) and heteronuclear (counter-ions) interactions.

The experiments to measure ^{1}H-T_1 relaxation times are carried out in the condition that the RF pulses are on-resonance with the ^{1}H-spins while off-resonance for ^{19}F-spins. Hence the ^{19}F-spin populations are not altered from their thermal equilibrium by the RF pulses and only the ^{1}H-spins evolve through the experiment. In such a condition, ^{1}H-spins can have intermolecular dipolar interactions with like-spins (HH) and unlike-spins (HF). The dominating contribution to the intermolecular relaxation is the translational motion which can be written for ^{1}H-T_1 as the sum of translational relaxation rates of homo- (HH) and hetero- (HF) nuclear [23,25],

$$\frac{1}{T^{H}_{1,\,\mathrm{Trans}}(\omega_H)} = \frac{1}{T^{HH}_{1,\,\mathrm{Trans}}(\omega_H)} + \frac{1}{T^{HF}_{1,\,\mathrm{Trans}}(\omega_H)}, \tag{5}$$

and the homonuclear and heteronuclear translational relaxation rates are given respectively as [19,23]

$$T^{\mathrm{HH}}_{1,\,\mathrm{Trans}}(\omega_H)^{-1} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{3}{10}\gamma_H^4\hbar^2[I_{Trans}(\omega_H) + 4I_{Trans}(2\omega_H)], \tag{6}$$

$$T^{HF}_{1,\,\mathrm{Trans}}(\omega_H)^{-1} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{1}{10}\gamma_H^2\gamma_F^2\hbar^2[I_{\mathrm{Trans}}(\omega_H - \omega_F) + 3I_{\mathrm{Trans}}(\omega_H) + 6I_{\mathrm{Trans}}(\omega_H + \omega_F)], \tag{7}$$

where I_{Trans} accounts for the translational spectral density function (eq. 8), ω_{H} and ω_{F} are the Larmor frequencies of ^{1}H and ^{19}F, respectively. The normal (or Fickian) intermolecular translational diffusion can be assumed in order to calculate the corresponding correlation function. Applying the basic relaxation theory following reference [23] for the longitudinal relaxation time, the following spectral density is found,

$$I_{Trans}(\omega) = \frac{2N_H}{\zeta^3}\int_0^\infty [J_{3/2}(u)]^2 \frac{u\tau_T}{u^4 + \omega^2\tau_T^2}\,du, \tag{8}$$

where u is a dimensionless integration variable and the product of the minimum distance of approach, ζ, between molecules and the reciprocal of the internuclear distance vector, r, in its Fourier space. N_H is the number density of ^{1}H spins. The characteristic translational correlation time $\tau_T = \zeta^2/2D$, is defined as the average time necessary to make a single random molecular jump of the order of the molecular size. D is the effective translational diffusion constant of the ions of IL.

The correlation times corresponding to the equations (6) and (7) are τ_T^{HH} and τ_T^{HF}, respectively. Exchanging the ‘H’ and ‘F’ notations in equations (5) to (8) will equivalently give the corresponding translational relaxation rates for ^{19}F from which τ_T^{FF} and τ_T^{FH} times will be obtained.

Temporal Equation (1) is combined with equations (2) to (8) and used for fitting the experimental data. Global fittings of the dispersion curves were performed using a script written in Python. Three fitting parameters correspond to each nuclear and temperature (τ_T^{HH}, τ_T^{HF} and τ_R^{H} for ^{1}H and τ_T^{FF}, τ_T^{FH} and τ_R^{F} for ^{19}F) giving six correlation times as fitting parameters for both ions at every temperature. Because of the interconnected fitting parameters for cations and anion, $\tau_T^{HF} = \tau_T^{FH}$, the actual fitting correlation times reduce to five being one shared between two nuclei. The other parameters in equations (3), (6), (7), and (8) are considered as constants. Therefore it is essential to do a simultaneous fit to the ^{1}H- and ^{19}F-T_1 datasets for each temperature. The presented model suitably describes the $T_1(\omega)$ dispersion curves in the range from room temperature until 223 K. Below this temperature, deviations in the experimental data and the proposed model become noticeable.

Figure 3 depicts a sample fitting to a selected temperature showing separate contributions to the ^{1}H- and ^{19}F-T_1. Though the heteronuclear translational contribution has less impact on the ^{1}H relaxation curve, its influence on the ^{19}F-T_1 is inevitable. This is in agreement with a recent investigation [5] on imidazolium based ILs with small anions containing ^{19}F where the heteronuclear translational interactions for ^{1}H were ignored. In the current study no contribution was ignore based on the fact that the inter-ionic translations are mutually related to both ions. The bottom line of the data analysis used in the current study is the simultaneous fit to the ^{1}H and ^{19}F relaxation curves in order to best fit the interconnected fitting parameters, τ_T^{HF} and τ_T^{FH}.

The rotational correlation time τ_R for both the cation and the anion molecules are shown in figure 4a. NMR relaxometry observes an average of all the intramolecular dipolar interactions caused by the internal motions. They follow an Arrhenius temperature dependence in the range from room temperature to 238 K whereas below this temperature, τ_R of both ions deviate and apparently become less sensitive to the temperature variation. The Arrhenius regime, above 238 K, could be fitted with the equation $\tau_R = \tau_0 e^{E_R/RT}$, where R is the universal gas constant. The activation energies obtained (see figure 4) are in qualitative agreement with values found in the literature [17,26] for a similar ionic liquid (Emim Tf2N), which discuss NMR relaxation measurements at high magnetic fields, where the extreme narrowing regime was still valid. However, in these references only the intramolecular interactions are taken into account for the relaxation process.

In the same temperature range where τ_R shows Arrhenius behaviour, all three types of translational correlation times in figure 4b follow a Vogel-Fulcher-Tammann (VFT) temperature dependence $\tau_T = \tau_T^0 e^{\kappa T_0/T-T_0}$. In this equation, T_0 is usually denoted as the ideal glass-transition temperature, i.e. the theoretical low temperature limit to the liquid state. For molecular and ionic liquids, it is around 30 K to 60 K below the calorimetric glass transition temperature T_g [13]. The constant κ is the fragility parameter [27]. Liquids are called *strong* if Arrhenius behaviour is obeyed while they are called *fragile* in the other case [13]. The fitting parameters and results are shown in figure 4b.

In order to validate the theoretical NMR relaxation model, independent measurements of the translational diffusion coefficient were carried out (see experimental section above) in the relevant temperature range from 298 K until 223 K. The translational correlation times obtained from relaxation are used to calculate the effective translational correlation times as following

$$(\tau_{T,eff}^{H})^{-1} = (\tau_T^{HH})^{-1} + (\tau_T^{HF})^{-1} \qquad (9)$$

Using the relation $\tau_T = \frac{\zeta^2}{2D}$, and assuming the same ζ values used for fitting the relaxation data, diffusion coefficients can be determined. These results are plotted and compared with PFG-NMR in figure 5. An excellent agreement is found between the diffusion coefficients obtained *directly* from the PFG-NMR technique and *indirectly* from the relaxation data for the whole temperature range that could be covered by both methods. Following the same procedure and using the equation (9) for ^{19}F, the diffusion coefficients for the anions were computed from ^{19}F-T_1 relaxation data. Previously measured self-diffusion values [22] at temperatures higher than 263 K are also included in figure 5.

For a spherical molecule, the Debye–Stokes–Einstein (DSE) law takes the form [28]

$$D = \frac{k_B T}{6\pi\eta a_0} \ , \qquad (10)$$

where a_0 is the molecular hydrodynamic radius. At temperatures above 273 K, using viscosity values and molecular volume from the literature [22,29], D values obtained from equation (6) are in agreement with the experimental data in figure 5.

The origin of the characteristic exothermic peak at around 234 K during the cooling cycle obtained from the DSC experiment (figure 6) could be related to different processes (partial freezing or possible impurities). However, the exothermic process at this temperature is compatible with the onset of a reorganization of the ionic liquid into a different dynamics seen by the NMR experiments as explained above. Therefore T_c = 234 K could be defined as a dynamical transition temperature. Below T_c, when the rotational correlation times begin to deviate from Arrhenius behaviour, the translational correlation times begin to deviate as well from the VFT relation. The experimental diffusion coefficients obtained from PFG-NMR show precisely the same deviation. The exothermic process observed in the DSC experiment matches to the T_c temperature as well. All evidences point to a transition of the molecular dynamics near the critical temperature T_c.

The limiting value of T_c, below which the presented NMR relaxation model could not be applied anymore, corresponds to the temperature where a dynamic crossover in the structural relaxation process occurs, as has been recently reported for this Ionic Liquid in references [8] and [30]. In these references no sign of a dynamic crossover is found at T_c in the ionic diffusion process, as was concluded from ionic conductivity measurements. However, in the present study the self-diffusion coefficients measured directly by PFG-NMR, as well as the one derived from NMR relaxation times measurements, show deviations from the VFT behaviour at temperatures below T_c.

Conclusions

The molecular dynamics of ionic liquids were studied by NMR relaxation dispersion in combination with NMR diffusion measurements in a broad range of temperatures. The IL used in these experiments could be supercooled to 163 K without any evidence of solidification. In the range of the magnetic field strengths where the presented measurements were carried out, NMR relaxation is sensitive to slow processes in the molecular dynamics of viscous liquids. Particularly towards low temperatures, the contribution of the fluctuations due to intermolecular translational diffusion dominates the T_1 relaxation mechanism in the IL.

It was shown that the proposed NMR relaxation model fits all the experimental T_1 data satisfactorily above the temperature T_c. The noticeably different temperature dependence of the correlation times τ_R (Arrhenius) and τ_T (VFT), evidences a decoupling of the rotational and translational dynamics in both ions even at room temperature. Moreover, evidence of a decoupling of anionic and cationic dynamics can be deduced from the temperature dependence of T_1 in figure 2 where a secondary process is just barely detectable for anions but not for cations in the accessible temperature range.

A dynamic crossover at $T_c \approx 1.26\,T_g$ was evidenced by evaluating the temperature dependence of the rotational and translational correlation times. Experimentally, deviation from the VFT in the diffusion coefficients starts being observed at the same temperature, exactly where the differential scanning calorimetry experiment shows a transition in the cooling cycle.

Several scenarios are possible in order to search for explanations on why the relaxation model fails below a certain temperature. A crossover from normal viscous dynamics to more correlated dynamics at low temperatures, possibly accompanied by a transition towards non-Fickian diffusion properties, i.e. an anomalous time dependence of the mean-squared displacement [31]; thus, the conditions for the derivation of eq. (3) become violated. Moreover, qualitative changes in the dynamics can arise as short-range order effects become more relevant due to reduced molecular mobility, resulting in a growth of the size of correlated regions $\xi(T_c) >> R^+, R^-$. These regions may be heterogeneous in the time domain as well as spatially heterogeneously distributed; in fact, the spatiotemporal nature of such fluctuations and their statistical properties have been the object of interest in amorphous materials for a considerable period of time. On the other hand, it is well known phenomenologically that a crossover at temperatures approaching the glass transition is a general characteristic of glass-forming liquids, and is expected to appear in all dynamic properties of such systems.

While the verification of anomalous time dependences within the experimentally accessible time range of both direct and indirect diffusion measurements is currently limited by hardware restrictions, an improved description of the results can be achieved by adapting the currently used NMR relaxation model for temperatures approaching T_g. This is most simply achieved by assuming a continuous distribution of correlation times, but a more fundamental approach has to include the rule of order formation at lower temperatures, and the interdependence of rotation and translation under conditions when discrete jumps and rotation steps need to be accounted for. As part of an ongoing study, improved models will be developed, combining relaxation and diffusion properties of IL with order parameters as obtained from multipulse NMR approaches.

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Figure captions

Figure 1. Spin-lattice relaxation time as a function of the Larmor frequency measured with the fast field cycling technique **(a)** ^{1}H-T_1 relaxation times. **(b)** ^{19}F-T_1 relaxation times. The solid lines represent the best fits of the experimental data with equations (1) to (8) using parameters $N_H = 3.12\times10^{28}$ m^{-3}, $N_F = 1.25\times10^{28}$ m^{-3}, $\zeta^{HH} = \zeta^{FF} = 2.8\times10^{-10}$ m, $\zeta^{HF} = \zeta^{FH} = 3.2\times10^{-10}$ m.

Figure 2. Spin-lattice relaxation times as a function of reciprocal temperature measured with the fast field cycling technique. Lines are guide to the eye. **(a)** ^{1}H-T_1 relaxation times. **(b)** ^{19}F-T_1 relaxation times.

Figure 3. Global fitting of T_1 relaxation dispersion data (○) for the temperature 239.3 K for **a)** cation, **b)** anion. The red, green, and blue dashed-lines show contributions of homonuclear translation, heteronuclear translational, and rotational diffusion to the T_1 relaxation times, respectively. The black solid lines display the sum of all contributions.

Figure 4. Arrhenius plots. **(a)** Rotational correlation times of ^{1}H (●) and ^{19}F (■). **(b)** Translational correlation times of ^{1}H-^{1}H (●), ^{19}F-^{19}F (■), and ^{1}H-^{19}F (=^{19}F-^{1}H) (▲). The values are obtained from fitting of T_1 relaxation dispersion curves. The data in 4a are fitted by an Arrhenius temperature dependence (see text) and similar rotational activation energies of $E_R = 29 \pm 2\ \mathrm{kJmol^{-1}}$ are obtained for both ions. The data in 4b are fitted according the VFT law (see text) considering a fixed T_0 = 170 K; $\tau_T^{0,\mathrm{HH}} = 1.42\times10^{-11}\,\mathrm{s}\ \kappa^{\mathrm{HH}} = 3.89;\ \tau_T^{0,\mathrm{FF}} = 3.09\times10^{-11}\,\mathrm{s},\ \kappa^{\mathrm{FF}} = 3.97;\ \tau_T^{0,\mathrm{FH}} = 6.24\times10^{-11}\,\mathrm{s},\ \kappa^{\mathrm{HF}} = 4.42$.

Figure 5. Temperature dependence of self-diffusion coefficients, obtained from PFG-NMR experiments (■) and from T_1 relaxation data (● and ▲), compared to the results from ref. [22] (○ and △).

Figure 6. Differential scanning calorimetry (DSC) curves during cooling-heating cycle of Bmim-Tf2N. The dashed arrows indicate the onset of the glass transition (---) and the maximum of the melting peak (---) during the heating process. The arrow at 234 K (---) indicates the onset of the transition during the cooling process.