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NON-ARRHENIUS BEHAVIOUR OF NMR SELF-DIFFUSION OF THE NEAT ROOM TEMPERATURE IONIC LIQUID 1-BUTYL-3-METHYL IMIDAZOLIUM TETRAFLUOROBORATE [BMIM][BF_4]

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Room temperature ionic liquid (RTIL) 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) was investigated using ^{1}H, ^{19}F, ^{11}B and ^{10}B DOSY NMR spectroscopy in a temperature range of 288–338 K. The dynamics of the [BF_4] anion and [bmim] cation have been found to be similar, indicating that both constituents behave as a rigid unit in the studied temperature range. The diffusion coefficients varied from $6.9 \cdot 10^{-11}$ m^2 s^{-1} at the highest temperature to $6.1 \cdot 10^{-12}$ m^2 s^{-1} at the lowest temperature. The dynamics of the diffusion coefficient was found not obeying the Arrhenius law and therefore was analyzed using the Vogel–Fulcher–Tammann (VFT) equation for the diffusivity. The glass transition temperature was found to be in a range of 172–181 K, which coincides with the values obtained using other techniques and found in the literature; the parameter *B* which is related to activation energy was found equal to 828–1115 K.

Keywords: NMR, ionic liquids, diffusion, DOSY

1. Introduction

Room temperature ionic liquids (RTILs) are a class of salts that remain liquid at room temperature. Numerous combinations of organic cations and organic or inorganic anions allow one to finely tune the properties of RTILs, and therefore, they are often called 'designer solvents'. A negligible vapour pressure, a high thermal stability, solvation properties, a tunable viscosity, polarity and hydrophilicity, and an electrochemical window make RTILs a unique medium for chemistry, materials science or engineering [1–3]. Among others, the most promising technological applications of RTILs are their use as electrolytes for novel battery systems or as heat carrier material for solar energy harvesting [4, 5]. Moreover, recent advancements in bio-active RTILs, in which both the cation and anion are biologically relevant molecular motifs, show promise for medical applications, such as drug administering systems, due to their lower toxicity [6–8]. All these technological and medical applications make the toxicity of RTILs an increasingly important research topic [9].

Imidazolium-based RTILs and, in particular, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) are among the most studied examples. The imidazolium scaffold provides the thermal stability of RTILs and the favourable solubility in most solvents, while the tetrafluoroborate anion contributes to a low viscosity and ionic conductivity [10]. These features have led to a widespread use of [bmim][BF_4] and similar RTILs as a solvent for organic reactions, an electrolyte component in batteries and supercapacitors, and as media for separation processes [11–15]. These applications require a detailed understanding of the physical properties of [bmim][BF_4], namely viscosity, conductivity, and an electrochemical window, which are highly sensitive to RTIL purity and the amount of water in the system [16–18].

High-resolution and solid-state NMR spectroscopy, in combination with theoretical simulations and complementary experimental techniques, is a powerful method for studying ionic liquids [19]. Among NMR-based methods, diffusion ordered spectroscopy (DOSY) is a valuable technique that allows one to investigate ion dynamics, self-organization and the formation of co-existing phases in RTIL systems [8, 20–22].

Due to the importance of RTILs for technological applications and the capabilities offered by NMR, the aim of the present work is to investigate the temperature dependence of diffusion of one neat RTIL, namely 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), using ^{1}H, ^{19}F, ^{11}B and ^{10}B diffusion ordered spectroscopy (DOSY NMR). This RTIL was chosen (i) as a stable model compound for the fundamental investigation of cation and anion dynamics and (ii) as an excellent RTIL probe due to the presence of NMR active nuclei in both ions.

2. Experiment

All NMR experiments were carried out at 11.8 T on a *Bruker* Avance III 500 NMR spectrometer operating at 500.25, 470.70, 160.5, 154.0, 53.75 and 125,79 MHz for ^{1}H, ^{19}F, ^{11}B, ^{10}B and ^{13}C, respectively, using 5 mm BBO (BroadBand Observe) probe. The sample temperature was varied in the 288–338 K range within an accuracy of 0.1 K and a DMSO-d_6 capillary insert was used for the lock signal. For 1D ^{1}H, ^{19}F, ^{11}B and ^{10}B measurements, a standard pulse sequence employing the $\pi/2$ excitation was used while the ^{13}C measurement was performed with the ^{1}H decoupling. ^{1}H, ^{19}F, ^{11}B, ^{10}B and ^{13}C $\pi/2$ pulses were set to 17.5, 16, 9, 23 and 10 μs, respectively. For multinuclear (^{1}H, ^{19}F, ^{11}B, ^{10}B) DOSY experiments, a stimulated spin echo-based pulse sequence was used (stebpgp1s). For these measurements, the gradient pulse length was set to 1.2–9.1 ms, the diffusion time was set to 0.5–2.5 s, and 8 scans for 16 increments were collected where gradient strength was varied from 2 to 95%. The diffusion coefficients were determined from the peak intensities (I) by varying the gradient strength (g), and the data were processed using the well-known equation

$$I = I_0 e^{-D\gamma^2 g^2 \delta^2 (\Delta - \delta/3)}, \quad (1)$$

where I_0 is the peak intensity without a gradient, D is the diffusion coefficient, γ is the gyromagnetic ratio of the observed nucleus, δ is the duration of the gradient pulse, and Δ is the diffusion time.

The studied room temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate[bmim][BF_4] was obtained from *Sigma-Aldrich* (98.5% purity) and was dried under vacuum for 24 h prior to NMR measurements.

3. Results and discussion

Firstly, for the studied neat [bmim][BF_4] (Fig. 1(a)) 1D ^{1}H, ^{19}F, ^{11}B, ^{10}B and ^{13}C NMR spectra were recorded (Fig. 1 (b–f)). For the ^{1}H and ^{13}C NMR spectra, the spectral assignments were performed (Fig. 1(b, c)) and are in agreement with the previously reported data [23–25].

The ^{19}F NMR spectrum (Fig. 1(d)) of the BF_4^- anion consists of two spectral lines, which is the consequence of the secondary ^{10}B/^{11}B isotope effect of approximately 25 Hz. The ^{19}F resonance assigned to $^{11}BF_4^-$ appears as a partially resolved quartet due to scalar coupling with ^{11}B (I = 3/2); spectral fitting yields $J(^{19}F–^{11}B)$ = 1.3 Hz. The ^{19}F NMR line assigned to $^{10}BF_4^-$ is observed as a singlet. The ratio of the integrals of ^{19}F spectral lines (1:4) assigned to $^{11}BF_4^-$ and $^{10}BF_4^-$ moieties is consistent with natural abundances of both boron isotopes (^{10}B 19.9% and ^{11}B 80.1%). In addition to these main lines, two very weak signals (1/1000 of the intensity of the main lines) at –148.56 and –146.62 ppm were observed and were assigned to $BF_3(OH)^-$ impurity [25].

The obtained ^{11}B NMR resonance is observed as a pentet due to scalar coupling with four fluorine nuclei $J(^{11}B–^{19}F)$ = 1.3 Hz. In the ^{10}B NMR spectrum, a singlet is observed and is assigned to the $^{10}BF_4^-$ ion. No signals corresponding to $BF_3(OH)^-$ were detected in the ^{11}B and ^{10}B NMR spectra as they are masked by noise due to their low intensity. Summing up, using ^{1}H, ^{19}F, ^{11}B, ^{10}B and ^{13}C NMR, the full spectral assignment for the cation [bmim] and anion [BF_4] was performed.

To investigate the dynamics of anion and cation in the neat [bmim][BF_4] separately, ^{19}F, ^{11}B, ^{10}B and ^{1}H DOSY measurements have been performed (Fig. 2). Such and similar RTILs are convenient for DOSY investigation because both cation and

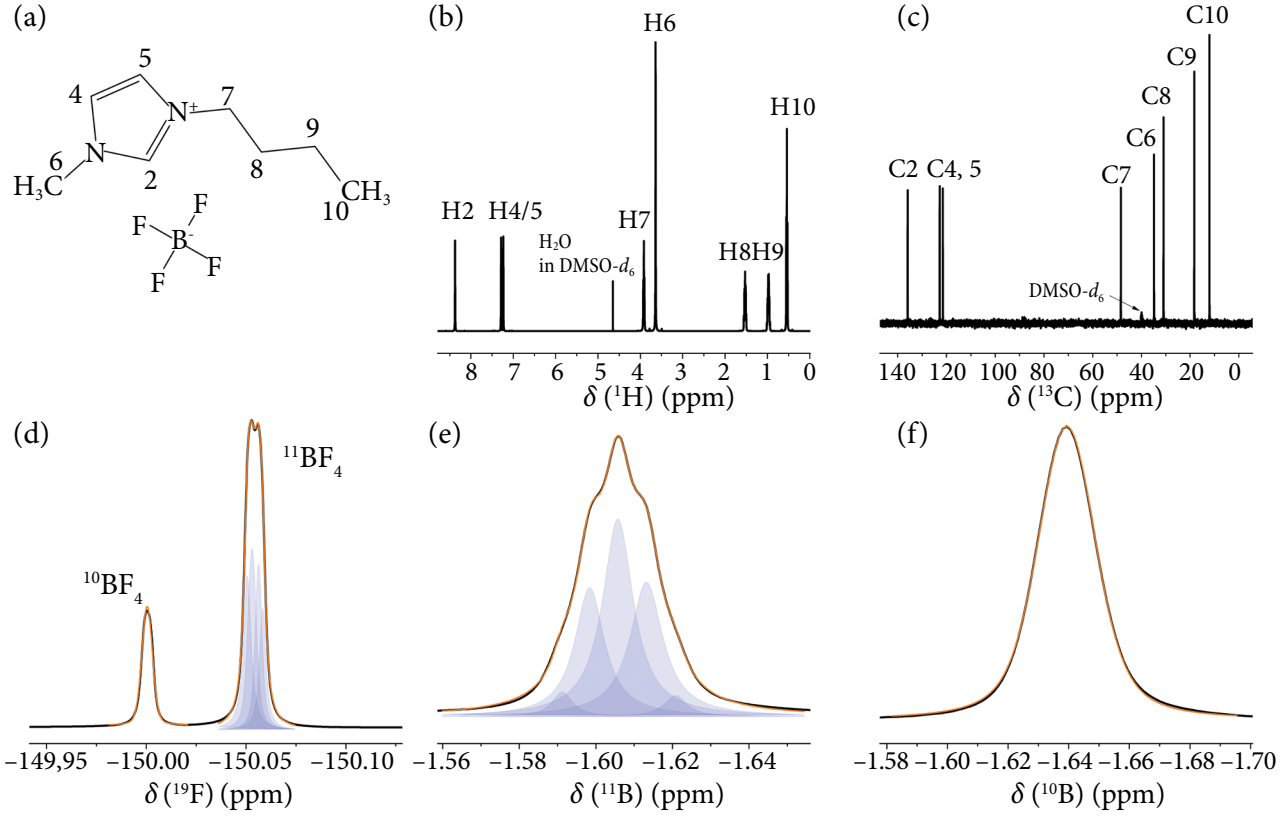

Fig. 1. (a) Chemical structure of 1-butyl-3-methyl imidazolium tetrafluoroborate [bmim][BF_4], (b) ^{1}H, (c) ^{13}C, (d) ^{19}F, (e) ^{11}B, (f) ^{10}B NMR spectra obtained for the neat [bmim][BF_4], spectral assignment and fitting shown in the figure.

anion possess NMR-active isotopes with sufficient sensitivity, e.g. ^{1}H and ^{19}F. In addition, we have also performed ^{11}B and ^{10}B DOSY experiments, which are seldom used but allow probing of isotope effects that could influence the self-diffusion process.

The measured diffusion coefficients D vary from $6.9 \cdot 10^{-11}$ m^2 s^{-1} at the highest temperature to $6.1 \cdot 10^{-12}$ m^2 s^{-1} at the lowest temperature (Fig. 2). The absolute values of diffusion coefficients D obtained for all studied nuclei, i.e. for the cation (^{1}H data) and (^{19}F, ^{11}B, ^{10}B data) anion, seem to be the same at the studied temperature range. Only the ^{1}H diffusion data at the lowest temperature range, i.e. $1000/T$ = 3.4–3.5, slightly differ, suggesting that the cation diffusion dynamic is faster than that of the anion. It has been previously shown that at lower temperatures, ion dynamics in RTILs become restricted, causing the discrepancy between the diffusion coefficients of the cation and anion [26]. Therefore, such behaviour might also be present in this system, but to confirm this, a more detailed study at lower temperatures is required.

As seen in Fig. 2, the obtained dynamics of the diffusion data does not obey the Arrhenius-type behaviour, therefore, it was analyzed using the Vogel–Fulcher–Tammann (VFT) equation for the diffusivity,

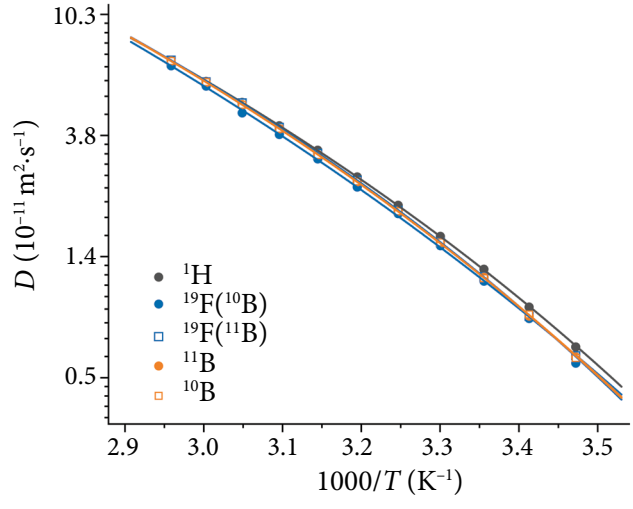

Fig. 2. Temperature dependence of ^{1}H, ^{19}F, ^{11}B and ^{10}B self-diffusion coefficients obtained using Eq. (1) for the neat [bmim][BF_4]. Fitting using the VFT model (2) is shown in solid lines.

Table 1. Fitting parameters ($R^2 > 0.99$) obtained for temperature-dependent ^{1}H, ^{19}F, ^{11}B and ^{10}B DOSY data using the Vogel–Fulcher–Tammann (VFT) equation (2).

Nucleus	^{1}H	^{19}F (^{10}B)	^{19}F (^{11}B)	^{11}B	^{10}B
D_0, $\cdot 10^{-8}$ m$^2 \cdot$ s^{-1}	1.3±0.2	3.3±2.5	1.4±0.3	1.7±0.1	1.9±0.3
B, K	846±37	1115±251	828±53	896±23	932±38
T_0, K	177±3	158±18	181±4	175±2	172±3

$$D_T = D_0 e^{(-B/T-T_0)}, \quad (2)$$

where the constants D_0 (m^2 s^{-1}) are the diffusion coefficient at very high temperature, B (K) is the empirical parameter related to the activation energy, and T_0 (K) is the theoretical glass transition temperature. Due to the high quality of the experimental data, the fitted curves coincide with the experiment perfectly ($R^2 > 0.99$). Therefore, the application of the VFT model is justified for studying [bmim][BF_4]. This model is often used to analyze the glass-forming liquids and thus is often applied for analyzing the diffusion of the short-chained imidazolium-based RTILs [27]. The fitting parameters obtained for all diffusion data (Fig. 2) are summarized in Table 1. The diffusion constants D_0 for all studied resonances are almost the same and range from $1.2 \cdot 10^{-8}$ to $1.6 \cdot 10^{-8}$ m$^2 \cdot$ s^{-1}. Only the ^{19}F resonance, which arises from the $^{19}F_4(^{10}B)$ moiety, exhibits faster diffusion dynamics, but the fitting error is significantly higher in comparison to other data. This might be due to a weaker signal in comparison to the ^{19}F signal arising from the $^{19}F_4(^{11}B)$ moiety. The parameter B is also similar across all studied resonances and is in the range 828–932 K.

The temperature T_0 was obtained in a range of 172–181 K, which coincides with the reported glass transition temperature of 176–186.5 K for this RTIL [28, 29]. Only the resonance related to $^{10}BF_4$ deviates from this trend, showing T_0 = 158±18 K. Similar tendencies described here have been previously observed and investigated for other methylimidazolium based RTILS, e.g. when the anion bis(trifluoromethane sulfonyl)imide [Rmim][$(CF_3SO_2)_2N$] was used [30].

4. Conclusions

Temperature-dependent (288–338 K) ^{1}H, ^{19}F, ^{11}B and ^{10}B diffusion data have been obtained for the neat [bmim][BF_4] RTIL. It was demonstrated that even rarely used ^{11}B and ^{10}B resonances are reliable probes for studying the dynamics of boron-containing RTILs. Our results show that the anion and cation dynamics do not follow the Arrhenius-type behaviour, and [bmim] and [BF_4] ions do not exhibit restricted dynamics. The Vogel–Fulcher–Tammann (VFT) equation for the diffusivity was found to be an appropriate theoretical model for analyzing the diffusion dynamics of this RTIL.

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NE ARENIJAUS TIPO DIFUZIJA JONINIAME SKYSTYJE 1-BUTIL-3-METILIMIDAZOLIO TETRAFLUOROBORATE [BMIM][BF_4], TIRTA DOSY BMR METODU

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Santrauka

Kambario temperatūros joninis skystis (RTIL) 1-butil-3-metilimidazolio tetrafluoroboratas ([bmim][BF_4]) buvo tirtas 288–338 K temperatūrų intervale naudojant ^{1}H, ^{19}F, ^{11}B ir ^{10}B DOSY (*Diffusion Ordered Spectroscopy*) branduolių magnetinio rezonanso (BMR) spektroskopiją. Nustatyta, kad [BF_4] anijono ir [bmim] katijono dinamika yra palyginama, todėl galima teigti, jog RTIL dinamika yra vienoda tirtame temperatūrų intervale. Difuzijos koeficientai kito nuo $6{,}9 \cdot 10^{-11}$ m^2/s esant aukščiausiai temperatūrai iki $6{,}1 \cdot 10^{-12}$ m^{-2}/s esant žemiausiai temperatūrai. Nustatyta, kad difuzijos koeficiento temperatūrinė priklausomybė neatitinka Arenijaus dėsnio, todėl ji buvo analizuota naudojant Vogelio–Fulcherio–Tammanno (VFT) lygtį difuzijos procesui aprašyti. Tirtajam RTIL stiklėjimo temperatūra nustatyta 172–181 K intervale; ši vertė sutampa su reikšmėmis, gautomis kitais metodais ir pateikiamomis literatūroje. Parametras *B*, susijęs su aktyvacijos energija, nustatytas lygus 828–1115 K.