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Temperature Dependence of Interactions Between Stable Piperidine-1-yloxyl Derivatives and a Semicrystalline Ionic Liquid**

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The stable 2,2,6,6-tetramethylpiperidine-1-yloxyl and its derivatives with hydrogen-bond-forming (-OH, -OSO₃H), anionic (-OSO₃⁻ bearing K⁺ or [K(18-crown-6)]⁺ as counter ion), or cationic (-N⁺(CH₃)₃ bearing I⁻, BF₄⁻, PF₆⁻ or N⁻(SO₂CF₃)₂ as counter ion) substituents are investigated in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide over a wide temperature range. The temperature dependence of the viscosity of the ionic liquid is well described by the Vogel–Fulcher–Tammann equation. Interestingly, the temperature dependence of the rotational correlation time of the spin probes substituted with either a hydrogen-bond-forming group or an ionic substituent can be described using the Stokes–Einstein equation. In contrast, the temperature dependence of the rotational correlation time of the spin probe without an additional substituent at the 4-position to the nitroxyl group does not follow this trend. The activation energy for the mobility of the unsubstituted spin probe, determined from an Arrhenius plot of the spin-probe mobility in the ionic liquid above the melting temperature, is comparable with the activation energy for the viscous flow of the ionic liquid, but is higher for spin probes bearing an additional substituent at the 4-position. Quantum chemical calculations of the spin probes using the 6-31G+d method give information about the rotational volume of the spin probes and the spin density at the nitrogen atom of the radical structure as a function of the substituent at the spin probes in the presence and absence of a counter ion. The results of these calculations help in understanding the effect of the additional substituent on the experimentally determined isotropic hyperfine coupling constant.

1. Introduction

lonic liquids have gained importance in various fields of application, such as batteries, fuel cells, solar cells, stationary phases in gas chromatography, reaction media for electrodeposition of metals, and solvents for chemical reactions in organic and polymer chemistry.^[1–6,7a–n] Examples of chemical reactions are polymerizations occurring via a radical mechanism.^[7] Free radical polymerization and even controlled radical polymerizations, such as atom-transfer radical polymerization, reversible addition–fragmentation chain-transfer polymerization, and nitroxide-mediated polymerization, have been investigated in ionic liquids.^[7a–n] The control mechanism is realized in nitroxidemediated polymerization by using, for example, 2,2,6,6-tetramethylpiperidine-1-yloxyl derivatives.^[7o–s]

The mobility of the radicals in the ionic liquids is important for the molecular weight of the polymers obtained. The broad variability of the chemical structure of ionic liquids composed of various cations and anions results in a broad variability of their properties. This allows tailoring of an ionic liquid to fulfill desired special applications. The use of ionic liquids as solvents for chemical reactions requires ionic liquids with a broad liquid range and a moderate viscosity to guarantee optimal reactant mixing and diffusion of both reactants and reaction products.

The properties of ionic liquids, such as viscosity and self-diffusion of the individual ions of the ionic liquid, depend strongly on temperature.^[8,9] Furthermore, the mobility of solutes in an ionic liquid is temperature dependent as well.^[8b,10] The structure and properties of the ionic liquid and the interactions between the solute and the individual ions of the ionic liquid are dominating factors of influence on the mobility of a solute in an ionic liquid. 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (IL; Scheme 1 a) has received increased attention among the ionic liquids because of its low melting point, low viscosity, and high conductivity.^[11] Therefore, this ionic liquid may become important for applications in electrochemistry and additionally as a solvent in chemical reactions.

Furthermore, stable radicals comprise models for reactive radical species formed during chemical reactions. These stable radicals have also been used as spin probes to discover the viscosity- and polarity-related parameters of ionic liquids that in-

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Scheme 1. a) 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (IL). b) Substituted piperidine-1-yloxyl derivatives used for investigation of IL.

dicate interactions between the spin probes and the ionic liquids on a molecular level. Various spin probes of different structure have been investigated in ionic liquids.^[12] Recently, 2,2,6,6-tetramethylpiperidine-1-yloxyl derivatives with various substituents at the 4-position with respect to the nitroxyl group were successfully used to investigate imidazolium tetra-fluoroborates and imidazolium hexafluorophosphates.^[8b, 12f,g,j-I] Temperature-dependent measurements on the glass-forming 1-butyl-3-methylimidazolium tetrafluoroborate show that both the additional substituent at the spin probe and the temperature used for the experiments are important factors of influence on the spin-probe rotation. This is expressed by the average rotational correlation time (τ_{rot}) and the hyperfine coupling constant related to nitrogen [A_{iso} ^{[14}N)].^[8b, 13]

Herein, we discuss the temperature-dependent mobility of 2,2,6,6-tetramethylpiperidine-1-yloxyl derivatives with distinct substituents at the 4-position in **IL**, which is an example of a semicrystalline ionic liquid. The structural variation at the 4-position of the nitroxyl radical covers hydrogen, hydroxy, sulfuric acid, cationic, and anionic substituents to provide additional information about the interactions between such stable radicals and the ionic liquid. In addition, the formation of hydrogen-bonding or ionic interactions between the spin probe and the ionic liquid include additional interactions. This can be explored in these experiments. Moreover, quantum chemical calculations provide information about the rotational volume of the spin probes and the spin density distribution.

2. Results and Discussion

2.1. Thermal Properties of the Ionic Liquid

The liquid range of ionic liquids is very important for their application as solvents in chemical reactions.^[7e] The liquid state of the ionic liquid **IL** (Scheme 1a) is limited by its melting point and the temperature, where mass loss is lower than



0.5 wt% as determined by thermogravimetric analysis. The broad liquid range of this ionic liquid covers the temperature

region from 272 to 570 K. Furthermore, IL exhibits a semicrystalline morphology (Figure 1). The heating scan in the differen-

Figure 1. DSC curve of **IL** obtained at a heating rate of 5 K min⁻¹ (T_g : 186 K; $T_{recryst}$: 232 K; T_m : 272 K).

tial scanning calorimetry (DSC) curve shows glass transition (T_q) at 186 K, recrystallization ($T_{\rm recryst}$) at 232 K, and melting ($T_{\rm m}$) of the crystal structures formed at 272 K. No crystallization occurs during cooling, neither with a cooling rate of 5 Kmin⁻¹ nor of 1 Kmin⁻¹. This metastable system can be supercooled from a melt to form a glassy state. Perturbation of the supercooled liquid state by heating results in transformation of the supercooled liquid state into a more stable state bearing a lower free energy by recrystallization from the supercooled liquid state, thus resulting in crystal structures. The temperature regime strongly influences crystal formation.^[14] This is the main difference from the glass-forming 1-butyl-3-methylimidazolium tetrafluoroborate, which was discussed in a previous paper.^[8b] Although semicrystallinity is mainly discussed in the field of polymers, this effect may also play an increasing role in the field of ionic liquids.^[15] The semicrystallinity makes it interesting to explore the spin-probe mobility in different phases/temperatures of this ionic liquid.

Furthermore, the viscosity of the ionic liquid strongly depends on the temperature used for the measurement. The Vogel–Fulcher–Tammann equation [Eq. (1)]:

$$\ln(\eta) = -1.608 + \frac{694.8}{T - 167} \tag{1}$$

where η is in mPas, well describes this behavior over a temperature (*T*) range between 278 and 373 K (Figure 2). The parameters of Equation (1) obtained in the fit depicted in Figure 2 result in $R^2 = 0.9989$.

2.2. Selection of Spin Probes

Piperidine-1-yloxyl derivatives bearing different polar substituents at the 4-position with respect to the nitroxyl radical structure were selected for mobility investigations (Scheme 1 b). The interactions of the substituted piperidine-1-yloxyl derivatives (**2**–**4**) with the ionic liquid are discussed and compared with those of the unsubstituted piperidine-1-yloxyl (**1**). ESR spectra exhibit the influence of the ionic liquid on the mobility



Figure 2. Vogel–Fulcher–Tammann plot of the temperature dependence of the viscosity (η) of **IL** using Equation (1).

of the piperidine-1-yloxyl derivatives. A significant line broadening begins upon dissolving the piperidine-1-yloxyl derivatives in ionic liquids compared to organic solvents, for example, dimethyl sulfoxide (DMSO).^[8b, 12j-I] Figure 3 depicts the ESR spectra of 1, 2, 3a, 3c, and 4d. The structural differences of the spin probes result in differences in the interactions between the individual spin probes and the ionic liquids. The ESR spectrum of 1 displays the interactions between the radical structure and the ionic liquid (Figure 3a). The ESR spectra of all the other spin probes show a line broadening relative to the spectrum of 1. This line broadening is attributed to the additional interactions with the substituent at the 4-position of the spin probe and the ionic liquid. A slight line broadening occurs in the case of 2 substituted by a hydroxyl group (Figure 3 b). Additional hydrogen bonding between the hydroxyl group and the anion of the ionic liquid may cause the slightly hin-



Figure 3. ESR spectra of the spin probes a) 1, b) 2, c) 3 a, d) 3 c, and e) 4 d in the ionic liquid at 283 K.

dered rotation of this spin probe. The line broadening is greater in the case of 3a substituted by a sulfuric acid group (Figure 3 c), which comprises a relatively strong acid. Therefore, additional hydrogen bonding is possible with the anion of the ionic liquid. Additional ionic interactions exist between the sulfate group and the imidazolium ion. These two kinds of interactions may cause the stronger line broadening of 3a compared to 2. The anionic spin probes 3b and 3c show a stronger line broadening than 3a because they possess an ionic substituent building up additional ionic interactions with the imidazolium ion (Figure 3 d). The anionic spin probes 3b and 3c differ in the size of the counter ion, which is either potassium or potassium complexed with 18-crown-6, respectively. Furthermore, complexation of the potassium ion by crown ether results in an improved solubility of 3c in the ionic liquid compared to **3b**.^[12] This gives a huge benefit in using such compounds in a wide variety of applications where dissolution in the target matrix may cause a problem.

The ionic spin probes **3b** and **3c** as well as **4a–d** display the strongest line broadening in the ESR spectra (see Figure 3d and e for examples), which shows the strong interaction with the surrounding IL. The line broadening in the ESR spectra of 3b, 3c, and 4a-d is attributed to additional interactions between the ionic substituent at the spin probe and either the cation or anion of the ionic liquid. The anionic spin probes 3b and 3c bear the potassium ion as counter ion, which is complexed with crown ether in the case of 3 c. The spin probes 3 b and 3c exhibit different molar volumes as long as one considers them as ion pairs that should interact differently with the surrounding IL. An increase in the molar volume should result in a broadening of the ESR lines. In the case of ion exchange with the surrounding IL, one obtains spin probes with a counter ion originating from the IL. Under such circumstances the ESR spectra must be similar for 3b and 3c. From this finding one can conclude that counter-ion exchange occurs with the imidazolium ion of the ionic liquid. Otherwise, one would expect broader lines in the case of 3c in comparison with 3b attributable to the larger volume of the potassium crown ether complex relative to potassium. The cationic spin probes 4a-d differ in their anion structure. The size of the anions increases in the order: $I^- < BF_4^- < PF_6^- < NTf_2^-$. This may cause differences in the anion exchange with the bis(trifluoromethylsulfonyl)imide (NTf_2^{-}) anion of the ionic liquid.

2.3. Molecular Considerations of the Spin Probes

The spin probes selected differ regarding their size and functionality, in particular considering the substitution at the 4-position of the nitroxyl radical. Density functional theory (DFT) calculations provide a deeper insight into the molecular structure depending on the substitution pattern and counter ion as well as electron distribution at the radical nitrogen atom. The latter responsibly tunes the hyperfine coupling constant related to nitrogen, A_N . The higher the electron density at the radical nitrogen, the larger the hyperfine coupling constant.^[13]

Table 1 summarizes the results obtained based on the $6\mathchar`-31\mbox{G}+d$ method. Compared to the results obtained in a pre-

Table 1. Summary of calculation results obtained by applying density functional theory using the $6\mathchar`-d$ method.

Spin Probe ^[a]	$V_{\rm rot}^{\rm calc} [Å^3]^{\rm [b]}$	$ ho^{[c]}$	q [N] ^[d]	A _N [G] ^[e]		
1	208	0.4592	0.2830	13.76		
2	285	0.4597	0.2275	13.57		
3-without	329	0.4832	0.1849	13.80		
3a	325	0.4557	0.1773	13.52		
3 b	359	0.4460	0.1823	13.58		
3c	627	0.4651	0.2962	13.70		
3-BMIm	513	0.4681	0.1856	13.65		
4-without	326	0.4695	0.1986	13.29		
4b	482	0.4457	0.2059	13.40		
4d	325	0.4452	0.2699	13.66		
[a] Structure of the spin probe according to Scheme 1. [b] This was converted from the molar volume obtained in the calculation. [c] Spin density at the NO group. [d] Partial charge of the nitrogen at the NO group.						

[e] Fermi Hyperfine coupling constant.

vious study,^[8b] we chose a less expensive calculation method because some of the spin probes are too large for stronger basis sets. Thus, the results obtained allow a better comparison of the entire data set but keeping in mind that more accuracy is not possible for the larger probes; that is, **3c** and any anionic probe **3** bearing as counter ion the cation of the ionic liquid, which is 1-butyl-3-methylimidazolium (BMIm). Therefore, the latter is called **3-BMIm**. Such a probe molecule can be formed in an ion-exchange process by dissolution of the ionic spin probes **3b** or **3c** in the ionic liquid. Ion exchange can also occur with the anions of the ionic liquid. Spin probe **4d** comprises the anion of the ionic liquid.

The results obtained for the charged spin probes with no counter ion (3 and 4) show the same trend as previously published with a larger basis set.^[8b] That is, the charge of the substituent in the 4-position influences the spin density at the nitrogen atom, which finally has an impact on the charge on this atom, and the Fermi hyperfine splitting constant. Thus, a substituent with a negative charge results in a higher spin density on the nitrogen atom, while a substituent with positive charge directs the spin density in the opposite direction; that is, the nitrogen exhibits less spin density compared to 1 that has only hydrogen at the 4-position. The fact that substitution in the 4-position to the nitroxyl radical changes both the spin density and the charge of the nitrogen of the NO group can be discussed as a certain result of hyperconjugation, because there are four σ bonds between the radical nitrogen and the charged substituent. Under these circumstances, incorporation of different counter ions must also have an impact on the spin density of the NO group because the counter ion compensates a part of the charge of the substituent in the 4-position. Therefore, less charge is available for interaction between the substituent at the 4-position and the NO group.

Our calculations even prove that this assumption holds for all charged ions bearing either a positively or negatively charged group at the 4-position. Consideration of the data obtained for the radicals exhibiting an -OSO₃⁻ group show a decrease of the spin density of the nitrogen at the NO group if a counter ion is introduced. Thus, most of the charge of the sulfonyl group interacts with the counter ion. Data obtained for 3 c and 3-BMIm are more or less comparable with 1 that has only hydrogen atoms at the 4-position of the nitroxyl radical. A similar trend was also observed for the cationic probes 4. The fact that spin and charge density change upon switching the nature of the counter ion must also influence the dynamics of the spin probe if the NO group interacts with the surrounding ionic liquid. Furthermore, the mentioned ion exchange can also interfere with the behavior of the spin probe because another rotational volume has to be considered. Thus, the probes 3-BMIm and 4d exhibit ion pairs as a result of an exchanged cation and anion by the surrounding matrix, respectively. This must be experimentally observable in the viscositydependent experiments providing information about the rotational volume as long as the probe exhibits Stokes-Einstein behavior. Because 3b and 3c have different rotational volumes, there should be a difference in the rotational volume observed in the experiment as long as both spin probes exist as ion pairs. Ion exchange with the ions of the surrounding matrix changes the situation.

2.4. Dynamic Behavior of the Spin Probes

The rotational correlation time τ_{rot} is a quantitative measure for the spin-probe mobility embedded in the ionic liquid. This is calculated from the average rate constant for rotational diffusion (RBAR) using Equation (2):

$$\tau_{\rm rot} = 10^{-\rm RBAR} \tag{2}$$

The latter is determined from the spectra by using the method of Budil et al.,^[16] and shows a different pattern of linewidth depending on both spin-probe structure and mobility in the ionic liquid. The higher the mobility of the nitroxyl radical in the matrix, the smaller the linewidth of the ESR lines becomes.

Table 2 summarizes the rotational correlation times for the spin probes for measurements at room temperature. The lowest value and therefore highest mobility exists in the case

Table 2. Summary of data describing the dynamics of different spin probes in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. These are the average rotational correlation time τ_{rotr} the activation energy E_{ar} the rotational volume V_{rotr} and the ratio between experimental determined rotational volume and calculated volume obtained from density functional theory calculations V_{rot}/V_{rot} calc.

Spin Probe	$ au_{ m rot}{}^{[a]}$ [ns]	$E_{\rm a}$ [kJ mol ⁻¹]	$V_{\rm rot}^{[b]}$ [Å ³]	V _{rot} V ^{calc}
1	0.9	14	No Stokes-Einstei	n behavior
2	2.0	36	75	0.26
3a	5.9	16	145	0.45
3 b	6.7	25	156	0.43
3c	6.5	26	153	0.24
4a	8.8	24	147	-
4b	7.8	26	128	0.39
4c	7.8	22	177	-
4d	7.7	19	131	0.27
[a] Taken at tion (3).	room tempe	rature. [b] Calcu	lated from the slop	pe of Equa-

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of 1 bearing no substituent in the 4-position. Thus, this probe interacts with the ionic liquid only via the radical structure (NO group). Additional interactions via an additional substituent placed at the 4-position are missing in the case of 1. All other spin probes exhibit higher $\tau_{\rm rot}$ values and therefore lower mobility in IL compared to 1. This is caused by interactions between the additional substituent at the 4-position to the nitroxyl radical with the ionic liquid. Thus, this substituent significantly interferes with the rotation of the spin probe. Stronger interactions are observed if the substituent bears an ionic moiety (3 and 4), while incorporation of a hydroxyl group (2) only slightly decreases the spin-probe mobility. The spin probe 3a contains with the sulfuric acid group a strong acidic substituent, which causes an average rotational correlation time between the $\tau_{\rm rot}$ values of the neutral probe **2** and the anionic probes 3b and 3c.

Furthermore, the form of the ESR spectra and the linewidth of the three lines strongly depend on temperature. The spinprobe mobility is almost frozen at low temperatures (Figures 4a,b and Figures 5a,b) showing nearly no changes of



Figure 4. ESR spectra of the spin probe 3 c in the ionic liquid at a) 170, b) 260, c) 280, and d) 380 K.

spectral shape, and therefore $\tau_{\rm rot}$ is large exhibiting nearly no changes at the glass transition of the semicrystalline ionic liquid. Surprisingly, the spin-probe mobility strongly changes above the melting point of the ionic liquid upon heating at 280 K (Figure 4c and Figure 5c). A further increase of temperature results in an additional increase of the spin-probe mobility, which results in smaller lines of the ESR spectra (Figure 4d and Figure 5d).



Figure 5. ESR spectra of the spin probe 4d in the ionic liquid at a) 170, b) 260, c) 280, and d) 380 K.

Typical Arrhenius diagrams for the τ_{rot} values calculated from the shape of the ESR spectra are shown in Figure 6a and b for the spin probes **3b** and **4d**, respectively. These probes deviate from the expected linear behavior at specific temperatures. Above the melting point, the curves exhibit the expected linear behavior in the Arrhenius diagram for both spin probes. On the other hand, nearly no mobility changes are observed when the sample temperature passes the glass transition tem-



Figure 6. Arrhenius plots of the rotational correlation time τ_{rot} obtained at different temperatures for a) probe **3b** and b) probe **4d** in the ionic liquid.

perature (T_{q}) of the ionic liquid. Because there are only slight increases of the rotational mobility above $T_{\rm g}$ in the case of the spin probe 3b, the probe can only monitor a small decrease of $\tau_{\rm rotv}$ which possibly ranges within the experimental fluctuation of our experimental setup. Comparable results were recently discussed for the spin-probe mobility in the glass-forming ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate.[8b] After recrystallization is finished mobility starts in the case of the spin probe **3b**, although the mobility of **4d** stays frozen up to the melting point. However, the straight line in the Arrhenius plot describing the mobility of 3b in the melt is not valid for the mobility of this spin probe in the temperature region between recrystallization and melting of the crystal structures formed. Furthermore, these plots show that the mobility of the cationic spin probe 4d, which undergoes strong ionic interactions with the anion of the ionic liquid, is more hindered in the ionic liquid in comparison with the anionic spin probe 3b, which interacts with the cation of the ionic liquid.

Table 2 summarizes the parameters obtained from the Arrhenius plot above the melting point. The calculated activation energy E_a only slightly differs for the charged spin probes **3b**, 3c, and 4. E_a has the lowest value for 1, which only interacts via the radical structure (NO) with the ionic liquid. Surprisingly, the highest activation energy was obtained in the case of 2 that has the capability to form additional hydrogen bonds with the ionic liquid. In contrast, the activation energy is significantly smaller for 3a compared to 2, although additional hydrogen bonding to the anion of the ionic liquid is possible in the case of 3a as long as this probe does not dissociate into the corresponding ions. Nevertheless, 3a possesses a higher acidity than 2, and perhaps it must be considered as a probe molecule that dissociates into its respective ions in the ionic liquid. Therefore, 3a can be discussed as a spin probe exhibiting partially the property of an anion. The partial ionic property of 3a becomes clearer by comparing the rotational correlation time of **3a** with those of **3b** and **3c** (Table 2). The τ_{rot} value of 3a is closer to those of 3b and 3c, which indicates additional interactions between the anionic substituent of the spin probe and the cation of the ionic liquid. Thus, a structure based on ion exchange between the probes 3a-c and the ionic liquid favors the description of our dynamics observed in the ESR experiments; this is 3-BMIm. Furthermore, the anionic spin probes **3b** and **3c** show similar τ_{rot} values. This is a further hint that cation exchange occurs between the counter ions of the spin probes with the imidazolium ion of the ionic liquid. If no counter-ion exchange occurs, differences should be found in the τ_{rot} values of **3b** and **3c** because these cations differ in their size, which should result in differences in the rotational mobility as well. However, this is not the case.

The highest τ_{rot} value is obtained for **4a** in the ionic liquid, which is also slightly higher than the τ_{rot} value of the spin probes **4b–d**. These τ_{rot} values are similar, thus indicating the similarity of the anion exchange of the spin probes **4b** and **4c** with the bis(trifluoromethylsulfonyl)imide anion of the ionic liquid. The spin probe **4d** possesses the same anion as the ionic liquid. Similarities in the τ_{rot} values between **4b–d** indi-

cate similar surroundings of these spin probes, although the higher $\tau_{\rm rot}$ value of **4a** may be a hint for an incomplete anion exchange of the l⁻ by the bis(trifluoromethylsulfonyl)imide under the experimental conditions chosen.

The anionic spin probes **3b** and **3c** exhibit similar activation energies. This is again a hint for a similar behavior of both probes in the ionic liquid. Because these probes exhibit a different rotational volume, the fact that both of them exhibit similar dynamics even supports the hypothesis of ion exchange with the surrounding ionic liquid. Similar activation energies are also obtained for the cationic spin probes 4a and 4b. The spin probe 4c shows a slightly lower activation energy than 4a and 4b. Furthermore, the lowest activation energy in the row of the cationic spin probes was obtained for 4d, which has the same counter ion as the ionic liquid. Comparison of the activation energy determined by the mobility of the spin probes (Table 2) and the value for the activation energy of the viscous flow (E_n) published in the literature (14 kJmol⁻¹) shows that only spin probe **1** exhibits a comparable agreement.^[17] The activation energy for the spin-probe mobility is higher in all examples bearing either a hydrogen-bondforming substituent or an ionic substituent at the 4-position, which indicates that additional interactions exist requiring additional activation energy. Thus, the activation energy measured by the spin probes is a sum of the activation energy related to the viscous flow and an additional intrinsic activation energy that does not depend on viscosity.

2.6. Stokes-Einstein Behavior

Interestingly, the temperature dependence of τ_{rot} shows Stokes–Einstein behavior [Eq. (3)] for the probes **2–4**:

$$\tau = \frac{V_{\rm m} \cdot \pi}{k_{\rm B}} \cdot \frac{\eta}{\overline{T}} \tag{3}$$

We observed in a previous study that Stokes–Einstein behavior did not occur in 1-butyl-3-methylimidazolium tetrafluorobora-te.^[8b] Microviscosity theory described the data obtained in the imidazolium tetrafluoroborate.

The spin probes **2–4** can additionally interact with the ionic liquid via the substituent placed at the 4-position. In these examples, τ_{rot} is proportional to the macroscopic viscosity of the **IL** discussed in this work. The slope results in the rotational volume of the probe. Each probe possesses a different molar volume if one considers these probes as pairs with the counter ion (Table 1). However, no differences in the slope of Equation (3) were observed for the probes **3b** and **3c** (Figure 7).

Both spin probes possess the largest differences regarding their rotational volume if one includes the counter ion. The fact that both probes exhibit a similar slope indicates that the rotational volume must be the same for both probes, which again supports the idea of ion exchange between the spin probe and the corresponding ions of the surrounding ionic liquid. In the case of no ion exchange between the spin probe and the ionic liquid, one would expect similar data by dividing the rotational volume of the probe by the value calculated



Figure 7. Stokes–Einstein plot [Eq. (3)] of rotational correlation time (τ_{rot}) versus macroscopic viscosity (η) for the spin probes **3 b** (\bullet) and **3 c** (\bullet) in **IL**.

from the DFT calculations (V_{rot}/V_{rot}^{calc} , Table 1). However, we observed the opposite behavior (compare last column of Table 2), which means that this assumption cannot hold. All charged probes 3a-c and 4a-d exhibit a similar rotational volume of about 148 Å³ on average. This data set is only describable if a probe structure with similar rotational volume responsibly describes the rotational dynamics, which is only the case for probes with no counter ion (3-without and 4-without). An ion pair based on an ion exchange, which can be either 3-BMIm or 4d, must result in a different slope of Equation (3) and therefore in a distinct rotational volume. No counter ion means for our understanding that, within the experiment, only a structure appears with a volume that is comparable to those of 3-without and 4-without. It is also clear to us that to each ion belongs a counter ion. There would be several interpretations possible to explain this phenomenon, which we would not like to continue based on our available data.

Only the viscosity-dependent behavior of the spin probe **1** cannot describe the change of τ_{rot} according to Equation (3). These data rather follow the trend of Equation (4):

$$\frac{\eta}{T\tau_{\rm rot}} = \frac{k_{\rm B}}{6\pi V_{\rm rot} f'} + \frac{k_{\rm B}}{6\pi V_{\rm rot} f'} \cdot \frac{\xi_{\rm Stokes}^0}{\xi_2^0} \cdot \eta^{\rm x} \tag{4}$$

This expression is based on the microviscosity theory by Spernol, Gierer, and Wirtz, which was previously applied to the spin probes dissolved in 1-butyl-3-methylimidazolium tetrafluoroborate.^[8b] The results obtained show a straight line indicating that Equation (4) is applicable to describe the viscosity dependence between τ_{rot} and η . The exponent x discloses the influence of the activation energy for diffusion into the free volume (E_2) on the dynamics; that is, $x = 1 - E_2 / E_n$. We obtained x = 0.79 meaning that 79% of spin-probe molecules describe diffusion according to the macroscopic viscous flow, while 21% of spin-probe molecules undergo diffusion by jumping into the free volume of the matrix. Because all other probes follow the Stokes-Einstein behavior, further discussion with 1 is not possible. This result is surprising, and comparison with the results obtained during investigation of 1-butyl-3-methylimidazolium tetrafluoroborate^[8b] demonstrates how the anion of the ionic liquid strongly affects the diffusion behavior of dissolved probes in an ionic liquid. While the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate mainly causes a diffusion behavior according to the Spernol–Gierer–Wirtz model,^[8b] the diffusion of the dissolved spin-probe molecule switches to Stokes–Einstein diffusion just by changing to the bis(trifluoro-methylsulfonyl)imide anion.

2.7. Probing of Micropolarity

The hyperfine coupling constant is a measure for the micropolarity of a surrounding matrix.^[13] Because the radical electron is localized at either the oxygen or nitrogen atom, our experiment can see only the nitrogen, and therefore the interaction between the radical electron and this atom. The larger the hyperfine coupling constant related to nitrogen A_{N} , the larger the electron density of the unpaired electron at the nitrogen atom.^[13]

The isotropic hyperfine coupling constants $[A_{iso}(^{14}N)]$ obtained for the spin probes are summarized in Table 3. Data show similar $A_{iso}(^{14}N)$ values for the neutral probes **1** and **2** as

Table 3. Summary of hyperfine coupling constants $A_{iso}(^{14}N)$ obtained from the ESR spectra of the spin probes 1–4 dissolved in 1-butyl-3-meth-ylimidazolium bis(trifluoromethylsulfonyl)imide at room temperature.									
Spin Probe	1	2							
$A_{iso}(^{14}N)$ [G]	16.11	16.01							
Spin Probe	3 a	3 b	3 c						
A _{iso} (¹⁴ N) [G]	16.11	16.14	16.11						
Spin Probe	4 a	4 b	4 c	4 d					
A _{iso} (¹⁴ N) [G]	15.84	15.84	15.84	15.87					

well as for the probes with a sulfate group in the 4-position no matter whether a smaller (**3 b**) or larger cation (**3 c**) functions as counter ion. These results even support our findings disclosed in the viscosity-dependent measurements that a cation of almost similar size must be available in the case of **3 a**-**c**. The micropolarity obtained is generally comparable with that of DMSO.^[8b, 12]-I]

Furthermore, the isotropic hyperfine coupling constants are nearly independent of the temperature in the case of the spin probes 1, 2, and 4 in the temperature region between 280 and 380 °C. In contrast, the spin probe 3a substituted with the sulfuric acid group and the anionic spin probes 3b and 3c show a decrease in the $A_{iso}(^{14}N)$ value between 280 and 300 $^{\circ}C$, although these values are nearly independent of the temperature at higher temperatures. Similar values for the hyperfine coupling constants in the case of both the anionic spin probes 3b and 3c (Figure 8b) on the one hand and the cationic spin probes 4a-d (Figure 8c) on the other hand support the hypothesis of counter ion exchange between the counter ion of the spin probe and the ionic liquid ion. The data obtained clearly show that there is almost no difference in the hyperfine splitting constants of the anionic spin probes and the cationic spin probes, although one could expect this from the theoretical predictions (Table 1). Furthermore, the isotropic hyperfine coupling constant for the cationic spin probes 4a-d are lower than the $A_{iso}(^{14}N)$ values for the anionic spin probes **3b** and **3c** (Table 3). This is attributed to the lower spin density at the ni-



Figure 8. Hyperfine coupling constant A_{iso} ¹⁴N) for the spin probes a) **1** and **2**, b) **3a**, **3b**, and **3c**, and c) **4a**, **4b**, **4c** and **4d** in the ionic liquid **IL** obtained from ESR spectra taken at different temperatures.

trogen atom caused by the ammonium substituent, as was also found by quantum chemical calculations (Table 1).

3. Conclusions

Investigation of 2,2,6,6-tetramethylpiperidine-1-yloxyl derivatives dissolved in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide as a function of the temperature shows differences in the dynamic behavior depending on the substituent at the 4-position to the radical structure, which can be hydrogen-bond-forming substituents, ionic substituents, or just hydrogen. From this one can conclude that the mobility of radicals in an ionic liquid is strongly dependent on the temperature used for the experiments on the one hand, and on the nature of the substituent on the other hand, and therefore on the interactions between the spin probes and the individual ions of the ionic liquid.

Although the spin-probe volume calculated using DFT differs for the single spin probes, the rotational volume calculated from the slope of the Stokes–Einstein plot is similar for the charged spin probes. From this one can conclude that counter-ion exchange occurs between the counter ion of the spin probe and the individual ions of the ionic liquid. Furthermore, the rotational volume of the charged spin probes is about twice that of the hydroxy-substituted spin probe. From this one can conclude that the spin probes bearing ionic substituents collect more charged species in their surroundings than the hydroxy-substituted spin probe.

The higher activation energy of the spin probes bearing an additional substituent relative to the 2,2,6,6-tetramethylpiperidine-1-yloxyl without an additional substituent indicates a stronger hindrance in the mobility of the substituted spin probes. Interestingly, the activation energy for the mobility of the spin probe without additional substituent is similar to the activation energy for the viscous flow of the ionic liquid, which is known from the literature. From this one can conclude that the mobility of the unsubstituted spin probe corresponds to the viscous flow of the ionic liquid, whereas the mobility of the charged spin probes is slower than the viscous flow. This may be caused by the larger size of the 2,2,6,6-tetramethylpiperidine-1-yloxyl derivatives relative to the ions of the ionic liquid and their stronger interactions with the individual ions of the ionic liquid.

Experimental Section

1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (**IL**) was synthesized in two steps. First, 1-butyl-3-methylimidazolium chloride was made in 80% yield from 1-methylimidazole and 1-butyl chloride under stirring at 65 °C. In the second step, anion metathesis was carried out using lithium bis(trifluoromethylsulfon-yl)imide dissolved in water. After phase separation and drying in vacuo, the **IL** was obtained in 79% yield. This ionic liquid contains 300 ppm water and no halide. The spin probes **1** and **2** were purchased from Aldrich and used as obtained. Synthesis of the spin probes **3a**–**c** and **4a**–**d** is described elsewhere.^[12]–I]

DSC investigation of IL using a DSC 822^e apparatus from Mettler-Toledo with heating and cooling rates of 10 Kmin⁻¹ gave the glass transition temperature (T_{q}) at 186 K, a recrystallization at 232 K, and melting at 272 K. The glass transition was determined from the point of intersection of the tangents on the DSC curve. The viscosity was measured as function of temperature (Rheometer AR-G2, TA Instruments, equipped with a Peltier plate and 40 mm cone 1° for 0.3 mL sample volume) using a shear rate of 10 s^{-1} and a heating rate of 4 Kmin⁻¹. Furthermore, shear rate viscosity measurements were carried out using shear rates between 5 and 800 s⁻¹ at 296 and 343 K. ESR spectra of the spin probes were measured in the X band with a continuous-wave spectrometer (ELEX-SYS E500, Bruker) at 9.4 GHz. The concentration of the spin probes was about 2×10^{-3} M in the ionic liquid. Average rotational correlation times (τ_{rot}) were calculated from the average rotational diffusion rate constants, which were determined by the method of Budil et al.^[16] using the model of isotropic viscosity for the fitting procedure.

The geometric structures of the spin probes were optimized with Gaussian 03W.^[18] The methods used are explained in Table 1. A frequency calculation was carried out for each geometry obtained to check that the properties calculated belonged to a minimum.

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