Influence of the Electric Charge of Spin Probes on their Diffusion in Room Temperature Ionic Liquids

B. Y. Mladenova Kattnig1, N. A. Chumakova2,3, D. R. Kattnig1, I. A. Grigor’ev4, G. Grampp5, and A. I. Kokorin2,6

1 Living Systems Institute, University of Exeter, Stocker Road, Exeter, EX4 4QD, UK.
2 N.N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Science, Kosygin St. 4, Moscow, 119991, Russia
3 M.V. Lomonosov Moscow State University, Chemistry Department, Leninskiye Gory, 1/3, Moscow, 119991, Russia
4 N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry Siberian Branch of the Russian Academy of Sciences, Lavrentiev Ave., 9, Novosibirsk, 630090, Russia
5 Institute of Physical and Theoretical Chemistry, Graz University of Technology, Graz 8010, Austria
6 Plekhanov Russian University of Economics, Moscow 115093, Russia

ABSTRACT

The rotational and translational diffusion of negatively charged and uncharged spin probes in five imidazolium-based room-temperature ionic liquids (RTILs), 1-ethyl-3-methylimidazolium tetrafluoroborate, emimBF₄, 1-butyl-3-methylimidazolium tetrafluoroborate, bmimBF₄, 1-octyl-3-methylimidazolium tetrafluoroborate, omimBF₄, 1-octyl-3-methylimidazolium hexafluorophosphate, omimPF₆ and 1-octyl-3-methylimidazolium chloride, omimCl, has been studied by means of electron paramagnetic resonance (EPR) spectroscopy. Detailed analyses of the spin-Hamiltonian parameters and spin exchange interactions have been carried out. The temperature dependences of the line broadening induced by the electronic dipole-dipole interaction and the electron spin exchange coupling are determined. The translational mobility of spin probes is semi-quantitatively characterized and successfully explained in the framework of a hypothesis based on the assumption of polar and unpolar domains within the RTILs.

INTRODUCTION

Room temperature ionic liquids (RTILs) are salts with a melting point lower than 100°C. Due to their unique physicochemical properties, they have attracted the attention of scientists and technologists. Considered to be environmentally “green”, they find application in a wide range of areas such as catalysis, extractions, electrochemistry, specific chemical reactions, and
numerous other areas. Some of the exceptional properties of RTILs are their non-flammability, negligible vapor pressure, high thermal stability and a large electrochemical window.\textsuperscript{7,8} RTILs are considered to be designer solvents, \textit{i.e.} combining various anions and cations, at least one million different RTILs can be realized. Over 100 ionic liquids are now comparable in their respective applications with traditionally used molecular solvents (approximately 600 molecular solvents are in use in industry today).\textsuperscript{9} A notable characteristic of RTILs is their tendency to be structured at molecular level. An excellent review on this topic has been published by Hayes, Warr and Atkin.\textsuperscript{10} The structure formation of the solvent is an important factor determining the mobility of the solute and its ability to undergo chemical transformations. Thus, RTILs present a unique class of solvents and the investigation of their properties is an urgent task of modern physical chemistry.

It is well known that one of the most powerful methods for obtaining experimental results on the structure and dynamic properties of self-organized systems is the spin probe method. This technique is based on introducing a small amount of a stable paramagnetic substance into the system under investigation and the subsequent observation of the radical properties by electron paramagnetic resonance (EPR) spectroscopy.\textsuperscript{11} Most commonly used spin probes are stable nitrooxide radicals. The high anisotropy of their spin hamiltonian parameters leads to high sensitivity of their EPR spectra to the rotational and translational mobility and orientational distribution of the radicals. Different piperidine-based nitrooxide spin probes, both electro-neutral and positively or negatively charged at the 4\textsuperscript{th} position, were used for studying the physicochemical properties of RTILs.\textsuperscript{12}

The isotropic hyperfine splitting constant (hfs), $a_N$, and the rotational correlation times, $\tau_{\text{rot}}$, of nitrooxide radicals can be readily obtained from their EPR spectra. In Ref. 13, the values of $\tau_{\text{rot}}$ of spin probes in RTILs were determined by the simulation of their EPR spectra and, for rapid movements, by analysis of the ratio of the intensities of spectral lines. These parameters reveal the microviscosity and micropolarity in RTILs, which were compared with those obtained for glycerol-water mixtures and selected organic solvents.\textsuperscript{13}

Later, for the same non-charged, apolar probes dissolved in ionic liquids, an increased tendency of aggregation was observed.\textsuperscript{14} On the other hand, for the substituted, more polar probes ($R_6\text{-OH}$ and $R_6\text{-NH}_2$, with $R_6$ standing for the TEMPO-backbone) two kinds of species, isolated and aggregated ones, were detected. EPR tomographic studies of the translational diffusion in bmimBF$_4$ and dmimBF$_4$ (1-decyl-3-methylimidazolium tetrafluoroborate) at 293 K were also compared with the results of the rotational diffusion.\textsuperscript{14}
For a better understanding of solvation effects in RTILs, the FT-EPR spectra of \( \alpha \)-hydroxydiphenyl-methyl radical dissolved in several RTILs of tert-alkylammonium or alkylimidazolium salts with PF\(_6^–\), BF\(_4^–\), (CF\(_3\)SO\(_2\))\(_2\)N\(^–\), CF\(_3\)SO\(_3^–\), Cl\(^–\) and Br\(^–\) anions were measured.\(^{15}\) The hfs constant of the hydroxyl proton depended on Gutmann’s donor number of the anions, while the hfs constants of phenyl \( \alpha \)-protons were essentially the same for these RTILs. Thus, the electron donor character of the anions was suggested to be important for radical solvation in RTILs through the anion-OH hydrogen bond.

Strehelmel et al. have published several interesting articles on spin probes studies of the imidazolium RTILs. In Ref. 16, the group showed that the localization of R\(_6\)-NH\(_2\) strongly depended on the structure of RTILs.\(^{16}\) In imidazolium RTILs with shorter alkyl chains, the micropolarity was close to DMSO, while much lower values were found for RTILs with longer alkyl chains. The influence of the alkyl chain length in imidazolium-based RTILs was also studied via the rotational tumbling of R\(_6\)-OH, R\(_6\)-N(CH\(_3\))\(_3\)\(^+\)\(I^–\), R\(_6\)-N(CH\(_3\))\(_3\)(CF\(_3\)SO\(_2\))\(_2\)N\(^–\), and R\(_6\)-SO\(_4^–\) anions in Refs. 15 and 17. The rotational correlation times of the spin probes dissolved in ionic liquids are also dependent on the structure of the nitroxides. For example, \( \tau _{rot} \) exhibited a linear dependence on the RTIL viscosity in the case of the R\(_6\)-OH probe, which is forming only hydrogen bonds with the probed RTILs. However, deviations from the Debye-Stokes-Einstein law were found in the case of the charged spin probes in RTILs with a longer alkyl chain.\(^{17}\) This effect was explained by suggesting a “phase separation” on the molecular level between charged parts of the ionic liquid and the longer alkyl chains of the imidazolium cation.

The temperature dependence of \( \tau _{rot} \) of the spin probes R\(_6\)-H, R\(_6\)-OH, R\(_6\)-NH\(_2\), and K\(_2\)(SO\(_3\))\(_2\)NO\(^–\) (Fremy’s salt, FS) in emimC\(_2\)H\(_5\)SO\(_4\), bmimPF\(_6\), emimBF\(_4\), and bmimBF\(_4\) was studied by Grampp et al.\(^{18}\) It was shown that in the range of 280–380 K the rotational motion was well described by the extended Debye-Stokes-Einstein law.

The analysis of the temperature behavior of rotational correlation times for PADS, TEMPO, CProxy\(_1\), CProxy\(_1\)H, and cholestane radicals in different RTILs showed that mostly \( \tau _{rot} \) were within the range calculated on the basis of Stokes-Einstein-Debye hydrodynamic theory with stick and slip boundary conditions or described by Gierer-Wirtz theory. There are a few exceptions revealed in the case of small probes in some RTILs containing BF\(_4^–\) and PF\(_6^–\) anions.\(^{19}\)

A dual probe, pyrene chromophore covalently linked to R\(_6\)-radical via an ester bridge, was investigated by UV-Vis, fluorescence and EPR spectroscopy.\(^{16}\) Molecular solvents of different polarity and RTILs with either imidazolium or pyrrolidinium cations and various anions((CF\(_3\)SO\(_2\))\(_2\)N\(^–\), BF\(_4^–\), P(C\(_2\)F\(_5\))\(_3\)F\(_3^–\), or N(CN)\(_2^–\)) were studied. The probe did not show
solvatochromism and was much less mobile than the R₆-H spin probe. This was explained by the bulk of the pyrenyl group bound to the nitroxide radical.¹⁶ For a better understanding of how RTILs solvate compounds of different chemical nature, the pulsed high-field EPR spectroscopy, W-band, was used in parallel with cw X-band EPR spectroscopy. Three R₆-based spin probes with different functional groups: R₆-N(CH₃)₃⁺, R₆-COO⁻, and R₆-OH were dissolved in imidazolium RTILs with different alkyl chain lengths and anions were studied.²⁰ Molecular solvents methanol and water–glycerol were used as well. It has been shown that the rotational mobility of the charged probes in RTILs was about fivefold slower than that of the R₆-OH. The anion variation from BF₄⁻ to PF₆⁻ in RTILs most strongly slowed down the rotation, as measured by the τᵣₒᵣ value of R₆-N(CH₃)₃⁺ while a τᵣᵣ of R₆-COO⁻ was least affected. Changes of the spin-hamiltonian parameters gₓₓ and Azz, measured by W-band EPR for R₆-N(CH₃)₃⁺ in RTILs and CH₃OH, were very small compared to that of R₆-COO⁻, indicating that cation probes are located in the polar areas of RTILs comparable to methanol. The gₓₓ value of R₆-COO⁻ was sensitive to the length of the alkyl groups of the used RTILs.

Binary mixtures of the hydrophilic RTIL bmimBF₄ and water were studied using W-band EPR spectroscopy in by Kattnig et al.²¹ FS, R₆-H, R₆-OH, R₆-NH₂ and R₆-COO⁻ were used as spin probes. The g- and hfs- tensors were measured at low temperatures. Interactions of the >N–O⁺ moiety of apolar R₆-H and ionic FS with nano-domains, depending on the probe structure, were revealed. Changing the water content caused only small variations of parameters, suggesting that the probes are shielded from aqueous subdomains.²¹

A systematic study of micro-heterogeneous mixtures of the bmimBF₄ and water using cw EPR was continued in Ref 22.²² A mesoscopic picture of the micro-heterogeneous mixtures was revealed using cryo-TEM. Six spin probes differed in polarity, charge and Lewis basicity, FS, (CH₃)₂Im⁺SO₄⁻, where Im denotes the imidazolium-ring radical, were used to map the dependence of the micro-polarity and rotation mobility of the probes on the ionic liquid concentration. The critical aggregation concentration has been determined and the local water concentration (LWC) estimated from the Mukerjee hydrophilicity index. A simple geometrical model of the RTIL aggregates was used to describe the micro-heterogeneous system. It became apparent that spin probes are not statically located within the aggregates on the EPR timescale. For example, the dianionic FS binds to the surface of the RTIL aggregates, sampling predominantly the aqueous phase.

In Ref. 23, both pulse- and cw-EPR were applied for investigating binary mixtures of bmimBF₄ and water at temperatures below the glass transition point. It has been found that the
local properties of the IL-rich domains were closely in neat IL and in IL-water mixtures. The coexistence of two types of IL environments was in particular observed when one of them had progressively suppressed the molecular mobility upon temperature increase within ~($T_g$-60K) and $T_g$. This anomaly reflects the structural rearrangement of ionic liquids on the nanometer scale which was previously observed for series of RTILs in Ref. 24.

In all works above the authors have measured only hfs constants and $\tau_{rot}$ values and did not consider their translational diffusion. Such approach, new for ionic liquids, has been suggested in Refs 25 and 26. Rotational and translational movements of the R6-OH spin probe in the ionic liquid, omimBF$_4$, and in molecular solvents 1-propanol and iso-propyl benzene (cumene), were studied by X-band EPR spectroscopy. $\tau_{rot}$ values of R6-OH were obtained from direct-simulations of the EPR spectra considering the anisotropic rotational mobility of the spin probe around different molecular axes. The translational diffusion coefficients, $D_{tr}$, were calculated from the intermolecular spin exchange rate constants, $k_e$, which were determined by analysis of the concentration broadening of the spectral lines. It was found that the Debye–Stokes–Einstein law is valid in all three solvents while the dependence of $D_{tr}$ is non-linear in the Stokes–Einstein coordinate $T/\eta$. The effective activation energy of the rotational movements, $E_{rot}$, in omimBF$_4$ is noticeably higher than in the molecular solvents, while the effective $E_{tr}$ values of the translational mobility were comparable in all solvents studied. Similar results were obtained from the R6-OH probe dissolved in five imidazolium-based RTILs and glycerol. In highly viscous RTILs, the rotational mobility of the probe differed for different molecular axes. The dependence of the $D_{tr}$ coefficients on the Stokes parameter $T/\eta$ was nonlinear, i.e., deviations from the Stokes-Einstein law were observed.

Recently a new method of determining electron spin exchange rate from the analysis of the EPR spectrum shape was proposed by Salikhov et al. It has been convincingly shown that the contribution of the magnetic dipole-dipole interaction to the spin coherence transfer, which was previously neglected, can significantly affect the shape of the EPR spectrum. According to this approach, the best way to measure the spin exchange rate constant is the analysis of the dispersion contribution to the EPR lines, but not the measurement of the lines broadening. We have to note that until now this new method was applied only for investigation of the nitrooxide radical’s behavior in unstructured media (squalane and water-glycerol mixtures) at relatively high concentrations of spin probes (5-25 mM).

The goal of this work is an experimental study of translational mobility of two nitroxides – both negatively charged and uncharged – in series of imidazolium-based ionic liquids. The
radicals have structures which are similar to those of the cations of the studied RTILs, thus the probes will disturb the matrix structure as little as possible. Based on the above literature data, it is to be expected that negatively charged and uncharged probes would be predominantly localized in the polar and apolar areas of ionic liquids, respectively. Comparing the mobility of the radicals should thus provide a better understanding of the molecular organization of ionic liquids.

**EXPERIMENTAL SECTION**

In this work the following imidazolium-based RTILs, with general structure given in Fig.1, have been used:

\[
\begin{align*}
X &= BF_4^-, PF_6^-, Cl^- \\
R &= Ethyl-, Butyl-, Octyl-
\end{align*}
\]

**Figure 1.** Structure of the studied RTILs

1-ethyl-3-methylimidazolium tetrafluoroborate, emimBF₄, >98%, IoLiTec Ionic Liquids Technologies GmbH, Germany, 
1-butyl-3-methylimidazolium tetrafluoroborate, bmimBF₄, >99%, IoLiTec, 
1-octyl-3-methylimidazolium tetrafluoroborate, omimBF₄, >98%, Solchemar, Portugal 
1-octyl-3-methylimidazolium hexafluorophosphate, omimPF₆, >98%, Solchemar and 
1-octyl-3-methylimidazolium chloride, omimCl, >97%, Fluka. 

Prior to use trace impurities of water were removed from the RTILs by drying them *in vacuo* \(p < 5 \times 10^{-5} \text{ mbar}\) at elevated temperatures (313–337 K) for at least 24h. This is an essential procedure since the remnants of water can significantly influence the rotational motion of the studied spin probes.\(^{18}\) Subsequently all RTILs were stored in Schlenk tubes under argon atmosphere and kept in a desiccator over \(\text{P}_4\text{O}_{10}\) and in the dark. The molecular solvents Toluene, > 99.8%, ChimMed Co., Ltd and Methanol, ≥ 99.9%, Sigma-Aldrich, have been dried over molecular sieves (4 Å and 3 Å respectively).
The spin probes Im-CONH$_2$ and Im-COONa, presented in Figure 2, have been synthesized in accordance with procedures described in Ref. 31 and provided to AIK by Prof. L. B. Volodarsky.$^{32}$

**Fig. 2** Structures of the used imidazoline spin probes, a) Im-CONH$_2$ and b) Im-COONa

All samples were prepared gravimetrically, i.e. calculating the volumes and molar concentrations using the literature densities of the RTILs. The samples were transferred into capillaries under argon atmosphere and sealed off under vacuum following repeated freeze–pump–thaw cycles. EPR spectra were recorded at radical concentrations of approximately 5·10$^{-4}$ M and 5·10$^{-2}$ M.

**EPR measurements**

EPR spectra were recorded on a CW X-band Bruker ELEXSYS E500 spectrometer equipped with a digital temperature control unit, ER4131VT, and field-frequency lock. The sample temperature was varied in the range from 280 to 390 K ± 0.1 K in steps of 10 K with 10 min time for thermostatting prior to each measurement. The modulation amplitude (0.05 G) and the microwave power (0.25 mW) were kept constant during all measurements.

**RESULTS AND DISCUSSION**

**Spin-Hamiltonian Parameters of Im-CONH$_2$ and Im-COONa in Ionic Liquids**

Spin-Hamiltonian parameters of the studied nitroxides in RTILs were determined by simulation of the EPR spectra recorded at 90 K and at microwave frequency of 95 GHz (W-band) and are summarized in Table 1.$^{21}$ Under these conditions the molecular motion is practically frozen, and the shape of the spectrum is defined by the magnetic parameters of the radicals.
Table 1. Spin-Hamiltonian parameters of the nitroxides in ionic liquids.

<table>
<thead>
<tr>
<th></th>
<th>$g_{xx}$</th>
<th>$g_{yy}$</th>
<th>$g_{zz}$</th>
<th>$A_{xx}$ / MHz</th>
<th>$A_{yy}$ / MHz</th>
<th>$A_{zz}$ / MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>ImCONa emimBF$_4$</td>
<td>2.00942</td>
<td>2.00649</td>
<td>2.00258</td>
<td>9.5</td>
<td>10.7</td>
<td>93.7</td>
</tr>
<tr>
<td>bmimBF$_4$</td>
<td>2.00932</td>
<td>2.00647</td>
<td>2.00259</td>
<td>10.0</td>
<td>11.1</td>
<td>94.3</td>
</tr>
<tr>
<td>omimBF$_4$</td>
<td>2.00940</td>
<td>2.00649</td>
<td>2.00260</td>
<td>11.4</td>
<td>11.0</td>
<td>93.6</td>
</tr>
<tr>
<td>omimPF$_6$</td>
<td>2.00943</td>
<td>2.00647</td>
<td>2.00259</td>
<td>8.2</td>
<td>12.2</td>
<td>93.5</td>
</tr>
<tr>
<td>omimCl</td>
<td>2.00947</td>
<td>2.00648</td>
<td>2.00260</td>
<td>8.1</td>
<td>11.9</td>
<td>92.3</td>
</tr>
<tr>
<td>MeOH</td>
<td>2.00935</td>
<td>2.00647</td>
<td>2.00262</td>
<td>17.5</td>
<td>11.7</td>
<td>94.0</td>
</tr>
<tr>
<td>H$_2$O/glycerol</td>
<td>2.00900</td>
<td>2.00641</td>
<td>2.00262</td>
<td>11</td>
<td>12.2</td>
<td>97.4</td>
</tr>
<tr>
<td>ImCONH$_2$ emimBF$_4$</td>
<td>2.00942</td>
<td>2.00649</td>
<td>2.00258</td>
<td>9.5</td>
<td>10.7</td>
<td>93.8</td>
</tr>
<tr>
<td>bmimBF$_4$</td>
<td>2.00942</td>
<td>2.00648</td>
<td>2.00261</td>
<td>10.1</td>
<td>11.4</td>
<td>93.2</td>
</tr>
<tr>
<td>omimBF$_4$</td>
<td>2.00947</td>
<td>2.00651</td>
<td>2.00262</td>
<td>9.3</td>
<td>11.2</td>
<td>92.9</td>
</tr>
<tr>
<td>omimPF$_6$</td>
<td>2.00947</td>
<td>2.00651</td>
<td>2.00263</td>
<td>10.2</td>
<td>11.3</td>
<td>92.9</td>
</tr>
<tr>
<td>omimCl</td>
<td>2.00958</td>
<td>2.00651</td>
<td>2.00261</td>
<td>9.5</td>
<td>11.6</td>
<td>91.9</td>
</tr>
<tr>
<td>MeOH</td>
<td>2.00935</td>
<td>2.00643</td>
<td>2.00264</td>
<td>12.7</td>
<td>13.5</td>
<td>94.0</td>
</tr>
<tr>
<td>H$_2$O/glycerol</td>
<td>2.00899</td>
<td>2.00640</td>
<td>2.00261</td>
<td>12.4</td>
<td>12.6</td>
<td>96.9</td>
</tr>
<tr>
<td>toluene</td>
<td>2.00952(5)</td>
<td>2.00650(4)</td>
<td>2.00262</td>
<td>11.7</td>
<td>11.9</td>
<td>92.3</td>
</tr>
</tbody>
</table>

Errors: $g$: ±0.00003, $A_{xx}$: ±1 MHz, $A_{yy}$: ±0.3 MHz, $A_{zz}$: ±0.1 MHz if not stated otherwise

It is well known that spin-Hamiltonian parameters of the nitroxides are sensitive to the polarity of the media. This sensitivity is predominantly attributed to the formation of hydrogen bonds between the nitroxide group and the functional groups of the matrix molecules. In the case of structured matrix, such as ionic liquids, these parameters reflect polarity of the local environment of the radicals. The most sensitive parameters are $g_{xx}$ and $A_{zz}$. Figure 3 summarizes the values of these parameters for Im-CONH$_2$ and Im-COO Na in RTILs under investigation as well as in some polar and apolar low molecular solvents.

Figure 3. The $g_{xx}$ and $A_{zz}$ values of nitroxides measured in ionic liquids. Figure 3a is an enlarged part of Figure 3b.
The values $g_{xx}$ and $A_{zz}$ in water, methanol, ethanol and toluene convincingly show sensitivity of these parameters to polarity of the environment. When analyzing the magnetic parameters of these radicals in the ionic liquids, it is important to note that in all RTILs, except emimBF$_4$, the charged radical is localized in more polar environment when compared with the uncharged one. This observation is interpreted to reflect the micro-structuring of the imidazole-based RTILs with hydrocarbon substitutes including more than three carbon atoms, which is widely discussed in literature.$^{10,34}$ Due to the Coulomb interaction, the charged radical is localized predominantly in the areas formed by the charged heads of the cations and the anions of the ionic liquids (polar domains), while uncharged radicals are localized in the areas formed by saturated substitutes (apolar domains).

We would like to point out that the values of the magnetic parameters of our nitroxides, both charged and uncharged, in omimCl show less polar local environment compared to other RTILs. In fact, the parameters of the radicals in omimCl are close to those of uncharged radicals in toluene. Nevertheless, omimCl appears as a strongly structured medium due to significant difference of the magnetic parameters for charged and uncharged radicals. The structural formation of this RTIL was in fact experimentally confirmed by the X-ray diffraction method$^{35}$, small– and wide-angle X-ray scattering$^{36}$ and time dependent fluorescence depolarization.$^{37}$ It is possible that the structure of polar domains formed by omimCl differs from the structures of the polar domains of other RTILs. Based on the results of the theoretical works$^{38–40}$ devoted to study the H-bonding between anions and polar ‘heads’ of cations in emimCl, emimBF$_4$, emimPF$_6$, and bmimPF$_6$, it can be concluded that polar domains of imidazolium-based RTILs form hydrogen-bond networks. At the same time, it is known that the viscosities of RTILs depend strongly on van-der-Waals interactions and H-bonding.$^{41}$ The viscosity of omimCl is more than an order of magnitude higher than the viscosities of other RTILs used, perhaps due to much stronger H-bonding between the comparably small Cl$^-\,$ anions and imidazolium cations. In such a case, the integration of the charged spin probes into the structure of polar domains is difficult due to the energetic reasons. Due to the high mobility of microstructures of RTILs, relative to the EPR timescale,$^{42}$ the average time of contact of the charged fragments of omimCl with the charged spin probe is much longer than with the uncharged ones. Thus, the obtained data are interpreted to demonstrate different localization of charged and uncharged radicals in imidazolium-based RTILs.
**Translational Diffusion of Nitroxide Radicals in Ionic Liquids.**

The characteristics of the translational diffusion of Im-CONH$_2$ and Im-COONa in RTILs were determined by analyzing the temperature dependences of the concentration broadening of the spectral lines as has been done in Refs. 25 and 26. As an example, Fig. 4 shows the EPR spectra of radicals Im-CONH$_2$ and Im-COONa in bmimBF$_4$, recorded at 360 K for different radical concentrations. One can see that spectra of the more concentrated solutions are considerably broadened in comparison with the spectra of the less concentrated samples.

![EPR spectra](image)

**Figure 4.** EPR spectra of (a) Im-CONH$_2$ at concentrations of $2.7 \cdot 10^{-4} M$ (solid lines) and $4.9 \cdot 10^{-2} \text{ mol/l}$ (dash lines) and (b) Im-COONa at concentrations of $5.4 \cdot 10^{-4} M$ (solid lines) and $4.9 \cdot 10^{-2} \text{ mol/l}$ (dash lines) in bmimBF$_4$ at 360 K.

Earlier, we have reported the linear dependence of the line broadening with increasing the spin probes concentration in RTILs at a constant temperature. Reiterating the observations and discussion from this study, the line broadening of EPR spectra is caused by two main reasons: the electronic dipole-dipole interaction of radicals and electron spin exchange (Heisenberg exchange). At low temperatures, when the translational mobility of the spin probe is hindered, the main contribution to the broadening is the dipole-dipole interaction. At high temperatures, the rapid translational movements of radicals average the dipole-dipole interaction and at the same time lead to an increase of the spin exchange coupling. Evidently, this implies the existence of a temperature range for which contributions of the dipole-dipole and spin exchange interactions to the line broadening are comparable in magnitude.
The problem of differentiating contributions of dipole-dipole and spin exchange interactions to the shape and a line width of EPR spectra is difficult and has been deemed not analytically solvable in the past.\textsuperscript{43} Recently, important progress has been realized through works of Salikhov and co-workers, which has been summarized in several review articles and a recent book.\textsuperscript{27–30} The developed procedure is based on the analysis of the dispersion contribution into the spectrum. In fact, this contribution is usually relatively small and does not exceed 10-12% of the intensity of the main lines.

Specifically, in the limit of slow, equivalent spin exchange, the contribution of the spin exchange and dipole-dipole interaction to the additional homogeneous broadening of the $k^{th}$ resonance is given by

$$\Delta \Omega_k = \frac{1}{T_{2d}} + \varphi_k \frac{1}{T_{2d}'} + k_{ex}(1 - \varphi_k) c,$$

where $T_{2d}$ and $T_{2d}'$ are the electron dipole-dipole induced spin decoherence and spin coherence transfer times, respectively, $\varphi_k$ denotes the degeneracy of the $k^{th}$ hyperfine line ($\varphi_k = 1/3$ for $^{14}$N nitroxides) and $c$ the concentration of spin-probes.\textsuperscript{27} The spin exchange rate constant can be written in the form

$$k_{ex} = 4\pi Dr_{ex},$$

where $D$ is the diffusion coefficient of mutual, translational diffusion and $r_{ex}$ is an effective radius that depends on the interaction between spin-probes, the spatial dependence of the exchange coupling constant and the collision dynamics. For free, continuous diffusion and assuming a strong exchange interaction that decays exponentially with spin-probe distance, $r_{ex}$ is approximately given by

$$r_{ex} \approx \frac{1}{2} \left\{ R + \frac{1}{\kappa} \left( \ln \left( \frac{|J_0|}{D\kappa} \right) + 2\Gamma \right) \right\}. $$

Here, $R$ is the distance of closest approach of the spin probes, i.e. the collision radius, $J_0$ the exchange interaction at the contact distance and $1/\kappa$ its characteristic decay length, and Gamma the Euler–Mascheroni constant.\textsuperscript{44–46}
Eq. (1) is based on a second-order perturbation description of paramagnetic relaxation (Redfield theory) assuming continuous diffusion and the absence of three-radical effects. In this limit, both relaxation rates are proportional to $c / D$, i.e. $T_{1d}^{-1}, T_{2d}^{-1} \propto c / D$. Note furthermore that eq. (1) gives the true linewidth $\Delta \Omega_k$, which is not in general related to the observed peak-to-peak linewidth in EPR spectra by a constant factor of $3^{1/2} |\gamma_e|/2$, as frequently but erroneously assumed. This complication is the result of the spin exchange-dependent admixture of a dispersion contribution, as highlighted in Salikhov's new paradigm of spin exchange. Only for the central line of the spectra of $^{14}$N-nitroxide spin probes the dispersion contribution is approximately zero (see eq. (114) in Ref. 27).

The brief summary of concentration-dependent line broadening given above, motivates the differentiation of dipolar and exchange-related contributions based on the temperature dependence of the concentration broadening, in the form first proposed by Nayeem at al. Assuming that the temperature dependence of the diffusion coefficient is that of an activated process with effective activation energy $E_{tr}$, i.e. $D(T) = D_\infty \exp(-E_{tr} / k_B T)$ and neglecting the $D$ (and thus $T$) dependence of $r_{ex}$, the broadening of the central spectral line may be described as

$$
\Delta B_{pp} (m_j = 0) = \left[ A' \exp \left( -\frac{E_{tr}}{k_B T} \right) + B' \exp \left( \frac{E_{tr}}{k_B T} \right) \right] \Delta c .
$$

(4)

Here, $\Delta B_{pp}$ is the concentration broadening of the spectral line, expressed via its peak-to-peak linewidth and $\Delta c$ is the difference of concentrations of the probe. The parameters of $A'$ and $B'$ characterise the contributions of spin exchange and dipole-dipole and spin exchange interactions between the radicals, respectively. This approach was originally proposed for the determination of the translational mobility of spin probes in liquid crystals, but was not widely adapted due to the small temperature range of the mesophase existence limiting the reliability of data fitting. More recently, the idea was however applied for spin probes in RTILs, for which a large accessible temperature range often spanning 100 – 150 K allows the accurate analysis of the individual contributions to the spectral line broadening based on eq. (4).25,26

Here, we generalize the outlined approach in two regards. First, we base the analysis on the real line broadening $\Delta \Omega_k$ of all three hyperfine components. To this end, we determined the dispersion contribution from the intensity asymmetry of the individual lines and used it to derive $\Delta \Omega_k$ from the measured peak-to-peak linewidth as suggested by Salikhov in Ref 27. In this step
we utilized the exact analytic relations (as e.g. plotted in Fig. 10 of Ref 27). The average broadening associated with the three $^{14}$N hyperfine lines, $\Delta \Omega$, was subsequently subject to the analysis of its temperature dependence based on a generalization of eq. (4) which retained the $D$-dependence of $r_{ex}$ as given in eq. (3):

$$\Delta \Omega = \left[ A \left(1 + \frac{1}{2k_{r_{ex}} r_{ex}} \frac{E_{tr}}{k_{B}T} \right) \exp \left(-\frac{E_{tr}}{k_{B}T}\right) + B \exp \left(\frac{E_{tr}}{k_{B}T}\right)\right] \Delta c$$  

(5)

Here $r_{ex}$ is the exchange distance associated with the (extrapolated) diffusion coefficient $D_{\infty}$. As in a molten salt the Coulomb interaction will be effectively screened, we consider eq. (5) (which is based on eq. (3)) appropriate for both charged and uncharged spin probes in RTILs ($r_{ex}$ has been numerically calculated for charged spin probes in dielectrics in Ref. 27 and 44). In general, the actual $r_{ex}$ depends on steric and hydrodynamic factors which are not definitely known for the sparingly used radical probes Im-CNH$_2$ and Im-COONa. While it is thus difficult to estimate the exchange radii of these radicals in RTILs, it is reasonable to assume that the governing parameters are close enough for the charged and uncharged radicals used here and their dependence on the type of imidazole-based RTILs should therefore be similar. Under this assumption, we can compare qualitatively the exchange contribution of the line width $\Delta \Omega_{exchange} / \Delta c$, i.e. eq. (5) after setting $B = 0$, as a proxy of the relative translational mobility of the two spin probes in RTILs.

Figure 5 illustrates the temperature dependence of the concentration broadening of the spectral lines for the charged and uncharged radicals in bnimBF$_4$ and omimBF$_4$ as well as the results of their fitting according to eq. (5). In Figures S1 and S2 in the Supporting Information we further demonstrate that the shape of the fitted curve and the best-fitting value of $E_{tr}$ are essentially independent of the value of $r_{ex}$ in the range $r_{ex} \in [3 \, \text{Å}, \infty)$, which demonstrates the robustness of the approach (specifically, had $r_{ex}$ been estimated for probes interacting via a Coulomb potential the same conclusions would have been reached).
The extracted temperature dependences of $\Delta \Omega_{\text{exchange}} / \Delta c$ values for both spin probes in RTILs are shown in Figs. 6a and 6b. These values are proportional to the translational diffusion coefficients and $r_{\text{ex}}$ of the radicals. As an illustration, in Table 2 there are values $\Delta \Omega_{\text{exchange}} / \Delta c$ calculated for 340 K. Note that translational mobility of the uncharged radical in all RTILs is much higher than that of the charged one. The only exception presents emimBF$_4$ in which the mobility of Im-COONa slightly exceeds that of Im-CONH$_2$. We assume that this difference is caused by differences in the $r_{\text{ex}}$-values for the charged and uncharged probes.
Figure 6. Temperature dependences of the values $\Delta \Omega_{ex} / \Delta c$ for Im-COOD$_4$Na and Im-COONa in RTILs

The translation mobility of the charged spin probes decreases in the order emimBF$_4$, bmimBF$_4$, omimBF$_4$ (Fig. 6b), while for the uncharged ones it is noticeably accelerated, especially from emimBF$_4$ to bmimBF$_4$. This trend contradicts the assumption of a direct proportionality of diffusional mobility and RTIL viscosity for the uncharged probe (see Table 2). The result can be interpreted on the basis of the spatial organization of these RTILs. Indeed, the molecular structuring of ionic liquids has been examined experimentally using various physical methods $^{10,35,36,48}$ and has also been replicated in models. $^{10,34,49,50}$ To date, the model of RTIL organization is as follows: highly amphiphilic ions and long hydrocarbon chains form networks that segregate charged or uncharged groups into polar or apolar domains. The charged domains are not distributed homogeneously but form a three-dimensional network, or ionic channels. These regions coexist with uncharged domains, hydrocarbon “islands” within the polar network. $^{10}$ The increase of the alkyl-chain length enables hydrocarbon domains to interconnect into sponge-like nanostructures. For the imidazolium RTILs, the butyl chain marks the transition into sponge-like structures that facilitate their comparably fast motion through the uncharged areas avoiding the charged regions. This leads to a significant increase of Im-COONa translational mobility from emimBF$_4$ to bmimBF$_4$, which we have observed experimentally.
Table 2. Macroscopic viscosities of RTILs at 295K, values $\Delta \Omega_\alpha / \Delta c$ at 340K, and effective activation energy of translational mobility of the nitroxides RCONH$_2$ and RCOONa in RTILs ($E_{tr}$)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\eta$, cP</th>
<th>$\Delta \Omega_\alpha / \Delta c$, mT·M$^{-1}$</th>
<th>$E_{tr}$, kJ·mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T=295K</td>
<td>Im-COOOna</td>
<td>Im-COONH$_2$</td>
</tr>
<tr>
<td>emimBF$_4$</td>
<td>35$^{51}$</td>
<td>1.054</td>
<td>0.648</td>
</tr>
<tr>
<td>bmimBF$_4$</td>
<td>123$^{52}$</td>
<td>0.603</td>
<td>2.302</td>
</tr>
<tr>
<td>omimBF$_4$</td>
<td>417$^{53}$</td>
<td>0.034</td>
<td>2.124</td>
</tr>
<tr>
<td>omimPF$_6$</td>
<td>923$^{53}$</td>
<td>0.043</td>
<td>1.312</td>
</tr>
<tr>
<td>omimCl</td>
<td>20868$^{54}$</td>
<td>0.234</td>
<td>1.066</td>
</tr>
<tr>
<td></td>
<td>20883$^{55}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2 presents the determined values of the effective activation energy of translational diffusion ($E_{tr}$) for Im-COONH$_2$ and Im-COOOna in all spin-probed RTILs and compares them to those previously found for the uncharged radical TEMPOL.$^{26}$ It is seen that $E_{tr}$ values for both uncharged probes dissolved in all RTILs are in the range of 14-22 kJ/mol despite of the viscosity differences of these RTILs. This fact confirms the assumption that the uncharged spin probes in RTILs move through comparable media of apolar domains formed by hydrocarbon substitutes of the cations. At the same time, there is a significant increase of $E_{tr}$ parameter for Im-COOOna in omimBF$_4$ and omimPF$_6$ (for which $E_{tr}$ is more than doubled). Assuming that the RTILs with saturated substituents including eight carbon atoms form charged “islands” within the apolar network, this finding could be interpreted in terms of charged radicals having to cross the boundaries between polar and apolar domains to encounter, which would lead to an increase of the activation energy of the translational mobility. If we accept this assumption, it is necessary to explain a rather small value of $E_{tr}$ for Im-COOOna in omimCl which differs only slightly from $E_{tr}$ of this radical dissolved in emimBF$_4$ and bmimBF$_4$. We suggest that this effect can be caused by the extremely high viscosity of omimCl, which leads to an increase in the time the radicals spend together in the ‘cage’ of the matrix, resulting in repeated spin exchange collisions. Evidently, the activation energy of the repeated collisions is much smaller than the activation energy of the macroscopic translational diffusion. Thus, in the case of very viscous media, the Heisenberg spin exchange appears to not reflect the translational diffusion of the radicals over macroscopic scales. For the same reason, the $E_{tr}$ value for Im-COONH$_2$ in omimCl ought to be less than in other RTILs under investigation, which we have confirmed experimentally. The theory of repeated collisions was discussed in detail in Refs. 56-58. Note that Chumakova et al.$^{59}$, on the basis of comparing
the translation diffusion coefficients obtained by the methodic used in the present work and also by electrochemical methods, concluded that contribution of the repeated collisions to the spin exchange interaction of TEMPOL radicals in the ionic liquid bmimBF\(_4\) is negligible. It is not unexpected though that such contribution increases significantly with increasing RTIL viscosity, as our data appear to suggest.

Thus, we can resume that the obtained results confirm the fact that translational diffusion of probing molecules in RTILs depends on the structural organization of the RTIL and not necessarily on its macroscopic viscosity. It is also evident that using charged or uncharged probes, one can obtain valuable information concerning the internal organization of such complex self-organized supramolecular systems.

**CONCLUSION**

A detailed analysis of the spin-Hamiltonian parameters and the Heisenberg spin exchange has been carried out for a series of partly microstructured imidazolium-based room temperature ionic liquids using charged and uncharged imidazole-based spin probes that resemble the RTILs’ cationic building block. The translational mobility of spin probes was semi-quantitatively characterized. Such quantitative and systematic results were obtained for the first time. EPR data concerning features of structural organization of these self-organized complex systems were compared with other results published in literature and discussed in terms of a unified concept based on domain/network formation depending on the length of hydrocarbon chains in RTILs and including the exceptional behaviour observed for the highly viscous omimCl. The received data on translational diffusion of nitroxide probes, similar by structure to RTILs, were successfully explained within the hypothesis based on formation of polar and apolar domains (networks) in room temperature ionic liquids. Interconnections among various domains are presumably determined by the length of the hydrocarbon substitutes in RTIL cations.

**AUTHOR INFORMATION**

Corresponding Author
* b.y.mladenova-kattnig2@exeter.ac.uk
SUPPORTING INFORMATION

Dependence on the linewidth broadening on temperature fitted by eq. (5) using different values of $r_\infty$.

ACKNOWLEDGEMENTS

This research received no specific grant from any funding agency. The authors would like to thank Prof. D. Hinderberger for the opportunity to use his w-band EPR spectrometer and K. Kattnig for proofreading of the manuscript.

REFERENCES


