

## Rotational and Translational Mobility of Nitroxide Spin Probes in Ionic Liquids and Molecular Solvents

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**Abstract** Rotational and translational movements of 1-oxyl-2,2,6,6-tetramethyl-4-oxypiperidine (TEMPOL) spin probe in the room temperature ionic liquid (RTIL) 1-octyl-3-methylimidazolium tetrafluoroborate (omimBF<sub>4</sub>) and in two molecular solvents, 1-propanol and isopropyl benzene (cumene), have been studied by X-band electron paramagnetic resonance (EPR) spectroscopy. Rotational correlation times  $\tau_c$  of spin probes and the intermolecular spin exchange rate constants  $k_c$  were measured from EPR spectra at different temperatures and TEMPOL concentrations, and compared with the published data. The  $\tau_c$  values were calculated both by known equations and from the EPR spectra simulation. Rotation movements of TEMPOL in omimBF<sub>4</sub> cannot be described by the model of the isotropic Brownian diffusion, which is valid for conventional solvents. The correct modeling of EPR spectra in RTIL can be achieved with the assumption of different rotational mobility of the spin probe around different molecular axes. The rotational,  $D_{\text{rot}}$ , and translational,  $D_{\text{tr}}$ , diffusion coefficients were calculated from  $\tau_c$  and  $k_c$  values. The Debye–Stokes–Einstein law is valid in all three solvents while the dependence of  $D_{\text{tr}}$  on  $T/\eta$  is not linear in Stokes–Einstein coordinates. The effective activation energy  $E_{\text{rot}}^a$  of the rotational movements in omimBF<sub>4</sub> is noticeably higher than the corresponding values for conventional solvents, while the effective activation energies  $E_{\text{tr}}^a$  of the translational movements are comparable in all solvents studied.

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## 1 Introduction

The structure, properties and dynamics of room temperature ionic liquids (RTIL) are under investigation for the past two decades because these special solvents are now widely used in catalysis, electrochemistry, organic synthesis, etc. [1, 2]. For prognostication efficiency and kinetic rates of chemical reactions, the understanding of regularities and peculiarities of the diffusion processes of reagent molecules in RTIL is needed. One of the most informative methods of investigating both translational and rotational molecular movements is the electron paramagnetic resonance (EPR) technique in a variant of spin probe method [3–5]. Stable nitroxide radicals are usually used as spin probes because they have rather simple EPR spectra. Their line widths depend mostly on the rotational and translational diffusion as well. This leads to averaging the anisotropic (Zeeman, hyperfine, and dipole–dipole) interactions. In addition, these line widths depend on the intermolecular spin exchange. Therefore, the EPR spectra of the radical probe provide important information about structural organization and dynamics of its local environment.

Studies of rotational and translational movements of several different spin probes in various RTIL at 293 K were carried out in Refs. [6–8]. The temperature dependences of the radical rotation and translation in several RTIL have been described in Ref. [9], in which rotation of the probes was examined with EPR spectroscopy, and their translational diffusion was characterized by electrochemical experiments. Interesting continuation of these studies should be the quantitative investigation of the rotational and translational diffusion of nitroxide probes in RTIL in a wide temperature interval with the use of the same EPR technique. For correct evaluation of the results obtained, one has to compare the appropriate results in RTIL with those obtained for the same radicals at the same conditions in some usual organic solvents.

In the present work, we have measured the diffusion coefficients and values of the activation energy for rotational and translational movements of TEMPOL (1-oxyl-2,2,6,6-tetramethyl-4-oxypiperidine) in the ionic liquid omimBF<sub>4</sub> (1-octyl-3-methylimidazolium tetrafluoroborate), as well as in nonpolar isopropyl benzene (cumene) and polar 1-propanol solvents.

## 2 Experimental

Commercial 1-octyl-3-methylimidazolium tetrafluoroborate (purity >98.5%) was purchased from Fluka, Germany, and used as received, preserved under Ar. Cumene was purified of aqueous and peroxide admixtures by distillation over metallic sodium. 1-propanol contained ~4% of water estimated by <sup>1</sup>H nuclear magnetic resonance.

Dissolved oxygen was removed from TEMPOL solutions in cumene and 1-propanol by the fivefold cycle “freezing of the sample at 77 K—pumping out up to  $\approx 10^{-3}$  Torr—heating to room temperature”. Before preparation of TEMPOL solutions in omimBF<sub>4</sub>, the solvent aliquot ( $\approx 0.5$  ml) was kept under slow blowing of the chemically pure Ar for 30 min for removing the dissolved O<sub>2</sub> and residual

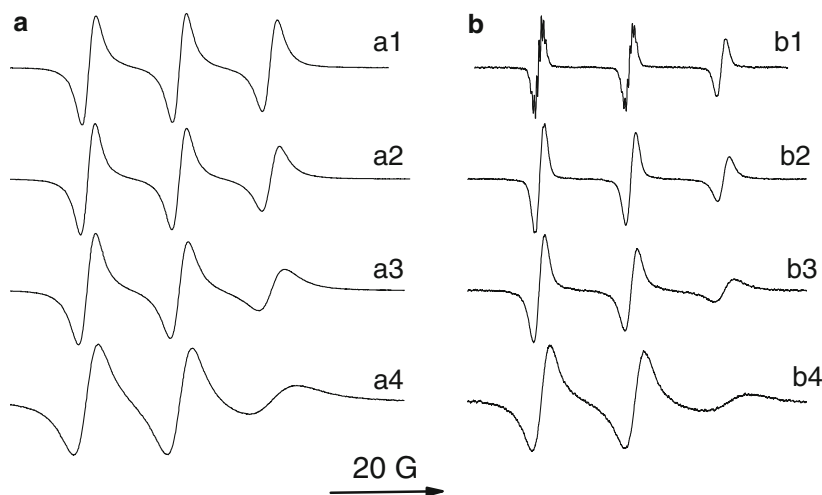
traces of H<sub>2</sub>O, and after dissolving the appropriate mass of TEMPOL, pumped out at 60°C under pressure of about 10<sup>-3</sup> Torr during 2–3 h.

The EPR samples in glassy tubes had the internal diameter of 1.5 mm (with working volume of the solution of about 0.04 ml) in the case of cumene and 1-propanol, and glassy capillaries (internal diameter of ≈0.8 mm and working volume of ≈0.007 ml) when omimBF<sub>4</sub> was used as a solvent.

A Varian E-3 X-band EPR spectrometer equipped with a Varian E-4557-9 temperature control unit (with accuracy of ±1°C) was used to record the spectra in 5–7 min after the end of temperature stabilization. The concentration of dissolved TEMPOL was checked by double integration of the corresponding EPR spectra as described in Ref. [10] and comparison with a crystal of CuCl<sub>2</sub>·2H<sub>2</sub>O with the known amount of paramagnetic centers; the accuracy of determination was not worse than ±15%.

### 3 Results and Discussion

EPR spectra of TEMPOL solutions in omimBF<sub>4</sub>, cumene and 1-propanol were recorded at different concentrations in the temperature range of 220–380 K. Figure 1 presents typical TEMPOL spectra in omimBF<sub>4</sub>. One can see that with the temperature increase, a noticeable decrease in the line widths takes place as a result of enhancing the mobility of the spin probe and averaging the anisotropy of Zeeman and hyperfine structure (hfs) interaction tensors. It should be stressed that EPR spectra lines of the samples with higher radical concentration are much broader than those of less concentrated solutions due to the dipole–dipole coupling between radicals and the Heisenberg spin exchange. Similar results were also obtained in 1-propanol and cumene solutions.



**Fig. 1** EPR spectra of 40.0 mM (a) and 0.1 mM (b) TEMPOL in omimBF<sub>4</sub> at: 350 (a1, b1), 320 (a2, b2), 300 (a3, b3), and 280 K (a4, b4)

### 3.1 The Rotational Mobility of Spin Probes

In the case when EPR spectra of nitroxide radicals consist of three well-resolved lines, and in the absence of both dipole–dipole and exchange interactions, the rotational correlation times  $\tau_c$  of nitroxide spin probes can be determined from a well-known equation [11]:

$$\tau_c = K\Delta H_{+1} \left( (I_{+1}/I_{-1})^{0.5} - 1 \right) \times 10^{-10}. \quad (1)$$

Here  $\Delta H_{+1}$  is a peak-to-peak width of the low-field component of a triplet spectrum;  $I_{+1}$  and  $I_{-1}$  are amplitudes of the low-field and high-field lines, respectively;  $K$  is a coefficient which is determined by the anisotropy of magnetic parameters of the radical in the investigated matrix [5, 12]. The main values of the  $g$ -tensor, hfs tensor and  $K$  for TEMPOL in omimBF<sub>4</sub>, cumene, and 1-propanol are listed in Table 1. These parameters were obtained by computer modeling of experimental EPR spectra recorded at 77 K.

The correlation time value  $\tau_c$  is connected with the rotational diffusion coefficient  $D_{\text{rot}}$  of the radical:

$$D_{\text{rot}} = 1/(6\tau_c). \quad (2)$$

The values of  $D_{\text{rot}}$  (measured in reciprocal seconds) calculated using Eqs. (1) and (2) from EPR spectra shown in Fig. 1 are given in Table 2 as  $D_{\text{rot}}^{\text{form}}$ .

The rotational diffusion coefficients can be also determined by computer modeling EPR spectra. Recently, an example of such modeling for nitroxide spin

**Table 1** Spin Hamiltonian parameters of TEMPOL in different solvents

Solvent	$g_{xx}^a$	$g_{yy}^a$	$g_{zz}^a$	$A_{xx}^b$ (G)	$A_{yy}^b$ (G)	$A_{zz}^c$ (G)	$K$
Cumene	2.0092	2.0058	2.0020	7.5	4.6	35.6	$5.3 \times 10^{-10}$
1-Propanol	2.0092	2.0059	2.0019	6.7	5.8	35.3	$5.0 \times 10^{-10}$
omimBF <sub>4</sub>	2.0091	2.0063	2.0020	6.3	6.1	36.0	$4.8 \times 10^{-10}$

<sup>a</sup> Accuracy,  $\pm 0.0002$ ; <sup>b</sup> accuracy,  $\pm 0.5$  G; <sup>c</sup> accuracy,  $\pm 0.2$  G

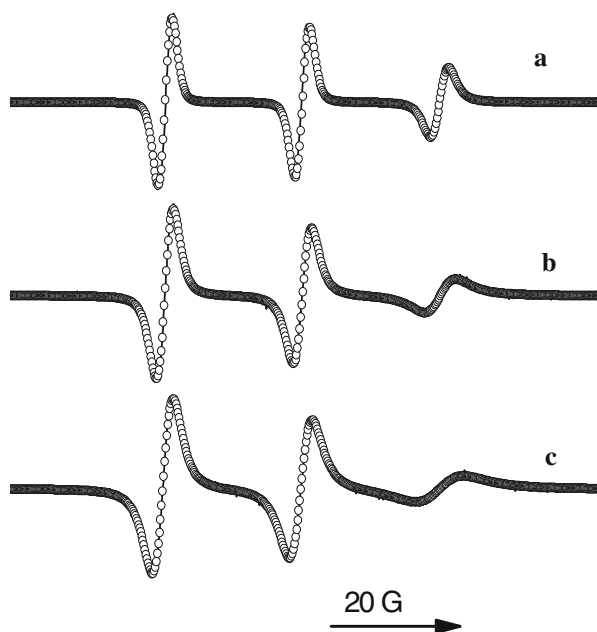
**Table 2** Rotational diffusion coefficients  $D_{\text{rot}}$  for TEMPOL in omimBF<sub>4</sub>

$T$ (K)	$D_{\text{rot}}^x \times 10^{-8}$ (s <sup>-1</sup> )	$D_{\text{rot}}^y = D_{\text{rot}}^z \times 10^{-8}$ (s <sup>-1</sup> )	$D_{\text{rot}}^{\text{aver}} \times 10^{-8}$ (s <sup>-1</sup> )	$D_{\text{rot}}^{\text{form}} \times 10^{-8}$ (s <sup>-1</sup> )
280	2.0	0.38	0.66	0.72
290	3.2	0.58	1.02	1.05
295	3.9	0.72	1.27	1.28
300	5.2	0.94	1.66	1.54
310	9.0	1.57	2.81	2.46
320	13.3	2.64	4.53	3.71

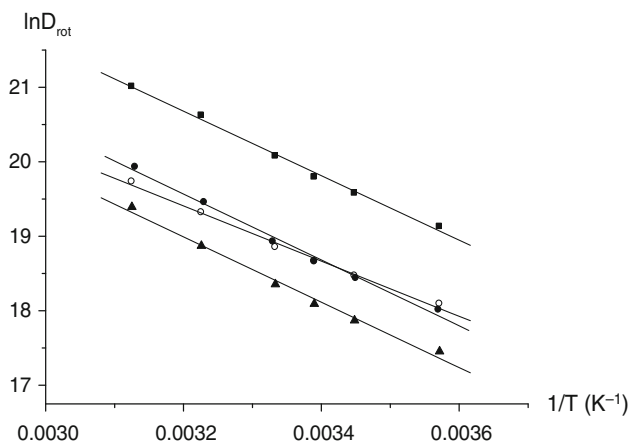
$D_{\text{rot}}^x$ ,  $D_{\text{rot}}^y$  and  $D_{\text{rot}}^z$  are rotations around the X, Y and Z axes, respectively.  $D_{\text{rot}}^{\text{form}}$  is calculated using Eqs. (1) and (2).  $D_{\text{rot}}^{\text{aver}} = (D_{\text{rot}}^x D_{\text{rot}}^y D_{\text{rot}}^z)^{1/3}$  [13, 14]

probes dissolved in RTIL at 298 K was presented in Ref. [7]. In our case, the EPR spectra simulation of TEMPOL in omimBF<sub>4</sub> was carried out using the nonlinear least-square method, and for calculations of the theoretical spectra, the program described in Ref. [13] was used. The movement of spin probes, which averaged their magnetic parameters, was assumed as Brownian rotational diffusion and the rotation around different molecular axes could realize with different rates. It was found that the best agreement between the model and the experimental spectra is achieved in the case when the tensor of the rotational diffusion coefficient is axial: the rotation of TEMPOL radicals around the *X*-axis of the *g*-tensor (the N–O bond of nitroxide radicals) is little faster than in the *Y*–*Z* plane. Figure 2 illustrates our computer simulations for several TEMPOL spectra in omimBF<sub>4</sub>. The appropriate diffusion coefficients are listed in Table 2. One can see that diffusion coefficients, which were calculated at averaging of the values obtained by EPR spectra modeling, are very close to those estimated using Eqs. (1) and (2).

Figure 3 shows the Arrhenius plots of  $D_{\text{rot}}$  for TEMPOL solutions in omimBF<sub>4</sub>. The  $D_{\text{rot}}$  values were determined both by EPR spectra modeling and by calculation using Eqs. (1) and (2). The effective activation energies of TEMPOL rotation are equal to  $30.8 \pm 1.3$  kJ/mol for the  $D_{\text{rot}}$  parameter calculated from equations and to  $36.8 \pm 1.6$  kJ/mol for  $D_{\text{rot}}$  determined from the spectra simulation. In our case, when the rotation of paramagnetic probes is not isotropic, calculations by Eqs. (1) and (2) do not lead to serious errors in the determination of  $D_{\text{rot}}$  parameters, but to estimate the activation energy of the rotational diffusion, one has to perform the numerical modeling of EPR spectra.



**Fig. 2** Experimental (*solid line*) and simulated (*open circles*) EPR spectra of 0.1 mM TEMPOL in omimBF<sub>4</sub> at 320 (a), 300 (b) and 290 K (c)

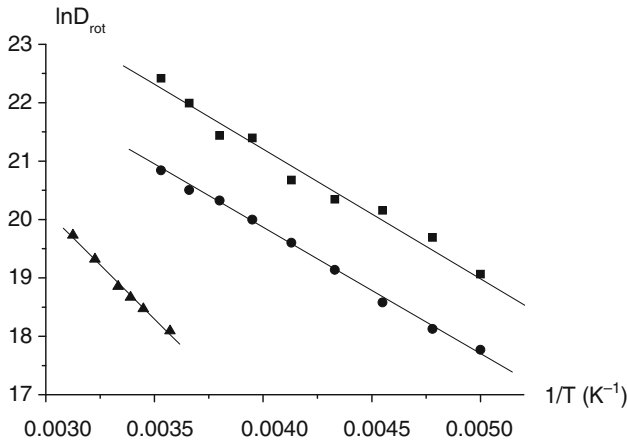


**Fig. 3**  $D_{\text{rot}}$  as a function of temperature for TEMPOL in omimBF<sub>4</sub> calculated using Eqs. (1) and (2) (open circles) and from simulated EPR spectra for the rotation around the X-axis (solid squares), around the Y- or Z-axis at  $D_y = D_z$  (solid triangles), and for the averaged rotation:  $D_{\text{aver}} = (D_x D_y D_z)^{1/3}$  (solid circles)

The  $D_{\text{rot}}$  values obtained in this work for TEMPOL radicals dissolved in omimBF<sub>4</sub> are in close agreement with the published results on the rotational mobility of spin probes in RTIL. Thus, the  $D_{\text{rot}}$  coefficients calculated from the data of Ref. [7] for TEMPOL solutions in 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF<sub>4</sub>), and in 1-decyl-3-methylimidazolium tetrafluoroborate (dmimBF<sub>4</sub>) at 293 K are equal to  $1.3 \times 10^8$  and  $3.3 \times 10^7$  s<sup>-1</sup>, respectively. The  $D_{\text{rot}}$  coefficients reported for TEMPO (2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl) solutions in 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide (emim[Tf<sub>2</sub>N]) in a temperature range of 280–320 K were measured in the interval between  $5.4 \times 10^7$  and  $4.0 \times 10^8$  s<sup>-1</sup>, and the rotational activation energy of TEMPO in emim[Tf<sub>2</sub>N], estimated from the Arrhenius plot of  $\tau_c$  values, was equal to  $27.8 \pm 0.3$  kJ/mol [9].

The EPR spectra simulation of TEMPOL in cumene and 1-propanol showed that the rotation of paramagnetic probes in these media at temperatures higher than 200 K is described well by the model of isotropic Brownian movements; therefore, the coefficients of the rotational diffusion were calculated using Eqs. (1) and (2). Figure 4 shows the temperature dependence of  $D_{\text{rot}}$  for TEMPOL solutions in omimBF<sub>4</sub>, cumene and 1-propanol. The activation energy values and pre-exponential coefficients of rotation calculated from these plots are listed in Table 3. It follows from these results that the  $E_{\text{rot}}^{\text{a}}$  values, characterizing the rotational diffusion, for TEMPOL probes dissolved in nonpolar (cumene) and polar (1-propanol) solvents practically coincide in the error limits, while the  $E_{\text{rot}}^{\text{a}}$  value measured for TEMPOL in omimBF<sub>4</sub> is noticeably larger. In our opinion, the  $E_{\text{rot}}^{\text{a}}$  value obtained for omimBF<sub>4</sub> reflects the higher energy of the intermolecular interaction between spin probes and RTIL ions than that in conventional solvents.

Figure 5 presents the dependence of the rotational diffusion coefficients for TEMPOL solutions in omimBF<sub>4</sub>, cumene and 1-propanol on the parameter  $T/\eta$ , where  $T$  is the absolute temperature in kelvin, and  $\eta$  is the dynamic viscosity of the



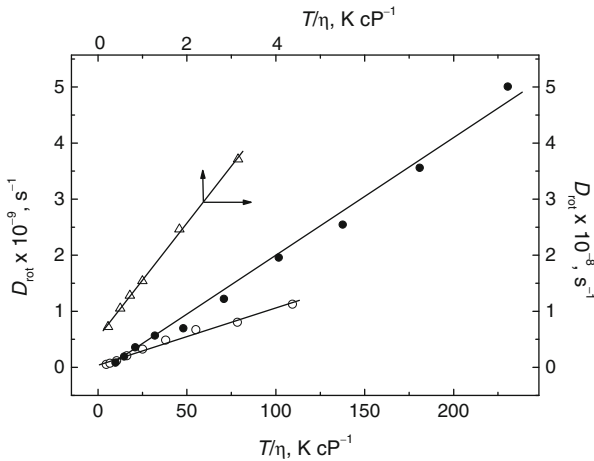
**Fig. 4**  $D_{\text{rot}}$  as a function of temperature for TEMPOL dissolved in omimBF<sub>4</sub> (solid triangles), 1-propanol (solid circles) and cumene (solid squares)

**Table 3** Parameters of rotational,  $E_{\text{rot}}^{\text{a}}$ ,  $D_{\text{rot}}^0$ , and translational,  $E_{\text{tr}}^{\text{a}}$ ,  $D_{\text{tr}}^0$  diffusion of TEMPOL dissolved in different solvents

Solvent	$E_{\text{rot}}^{\text{a}}$ (kJ/mol)	$D_{\text{rot}}^0$ (s <sup>-1</sup> )	$E_{\text{tr}}^{\text{a}}$ (kJ/mol)	$D_{\text{tr}}^0$ (cm <sup>2</sup> /s)
Cumene	18.4 ± 0.9	1.2 × 10 <sup>13</sup>	13.4 ± 0.6	4.5 × 10 <sup>-4</sup>
<i>n</i> -Propanol	18.0 ± 0.6	2.4 × 10 <sup>12</sup>	20.5 ± 1.4	3.6 × 10 <sup>-3</sup>
omimBF <sub>4</sub>	30.8 ± 1.3	3.8 × 10 <sup>13</sup>	19.0 ± 1.2	1.3 × 10 <sup>-4</sup>

solvent, i.e., in the axes of the Debye–Stokes–Einstein law. The values of  $\eta$  for 1-propanol and cumene were taken from Ref. [15], and for omimBF<sub>4</sub> from Ref. [16]. One can see that in the investigated temperature interval, all plots are linear for usual solvents and RTIL as well.  $D_{\text{rot}}$  values were determined in different intervals of the  $T/\eta$  parameter for omimBF<sub>4</sub> and the rest of solvents but, nevertheless, it is possible to conclude that the rotation movements of TEMPOL in omimBF<sub>4</sub> are a bit faster than in 1-propanol and cumene. For example, in omimBF<sub>4</sub>, at  $T/\eta = 3.2$  K/cP, the value of  $D_{\text{rot}} = 3.7 \times 10^8$  s<sup>-1</sup>; in 1-propanol at  $T/\eta = 4.6$  K/cP,  $D_{\text{rot}} = 5.2 \times 10^7$  s<sup>-1</sup>; and in cumene at  $T/\eta = 9.8$  K/cP,  $D_{\text{rot}} = 8.3 \times 10^7$  s<sup>-1</sup>.

From the slopes of the plots presented in Fig. 5, the radii of the rotated probes were calculated. They are 3.8 Å in 1-propanol, 2.9 Å in cumene, and 1.8 Å in omimBF<sub>4</sub>. These values can be compared with the hydrodynamic radius of the TEMPOL molecule, which was determined in polysaccharides: it was 2.5 Å [17]. The effect of the solvent nature on the value of the magnitude of the effective hydrodynamic radius calculated by the Debye–Stokes–Einstein equation is well known. For example, it was reported in Ref. [18] that such a radius calculated for TEMPO in cumene is close to 5.5 Å, while in vaseline oil this value was only 0.57 Å. It looks like the hydrodynamic radius estimated with the use of the Debye–Stokes–Einstein equation is an effective parameter, which does not characterize the real size of the probe molecule.



**Fig. 5**  $D_{\text{rot}}$  as a function of  $T/\eta$  parameter (Debye–Stokes–Einstein coordinates) for TEMPOL dissolved in omimBF<sub>4</sub> (open triangles), 1-propanol (open circles) and cumene (solid circles)

### 3.2 The Translational Mobility of Spin Probes

The translational diffusion rate constant can be measured from the concentration broadening of EPR lines of spin probes [19]. In our experiments this broadening was measured at every temperature as a peak-to-peak difference between the EPR line widths  $\Delta H_c$  at two different concentrations  $c$  of TEMPOL. It should be mentioned that for low concentrations of TEMPOL recorded at high temperatures (Fig. 1, spectrum *b1*), the hyperfine splitting of 12 protons of four methyl groups of the nitroxide ring are developed, and in such a case, we measured  $\Delta H_c$  from the line envelope for all three components of the TEMPOL spectrum.

We have observed a linear dependence between  $\Delta H_c$  of TEMPOL EPR lines and concentration of the probe in omimBF<sub>4</sub> at constant temperature. This fact of linearity of  $\Delta H_c$  on  $c$  in omimBF<sub>4</sub> indicates that in omimBF<sub>4</sub> matrix such processes as dimerization of probe molecules or heterogeneous spatial distribution of spin probes did not take place, and the line broadening at any certain temperature and at relatively high TEMPOL concentration should be caused by spin exchange and dipole–dipole interaction.

There are two interactions which are caused by concentration broadening of EPR lines of spin probes: the magnetic dipole–dipole interaction and the spin exchange interaction. When temperature increases, the translational diffusion of paramagnetic molecules increases, and as a result, the effect of intermolecular Heisenberg exchange on  $\Delta H_c$  increases, while of the dipolar interaction decreases. Evidently, at the certain interval of viscosity and temperature, the effect of both processes can be comparable. A procedure how to determine magnitudes of both these interactions was suggested in Ref. [20]. The following formula describes such a case:

$$\delta H_c = [A \times \exp(-E_{\text{tr}}^a/kT) + B \times \exp(E_{\text{tr}}^a/kT)]c. \quad (3)$$



Here  $\delta H_c$  is the line broadening,  $E_{tr}^a$  is the activation energy of translational movements, and  $c$  is the difference in concentrations of two radical solutions. The first summand term in Eq. (3) describes the effect of the exchange broadening, and the second term describes the effect of the dipole–dipole coupling.

Figure 6 presents temperature dependences of the line broadening  $\delta H_c$  divided into the difference of concentrations  $c$  in two TEMPOL solutions in omimBF<sub>4</sub>, 1-propanol and cumene, and also the result of application of Eq. (3) to the experimental data. The experimental dependence of the concentration broadening of EPR lines on temperature was described in accordance with Eq. (3) by the least-square method, with a simultaneous variation of three parameters:  $A$  (contribution of the exchange interaction to the line broadening),  $B$  (contribution of the dipole–dipole interaction), and the activation energy of translational movements  $E_{tr}^a$ . Contributions of dipole–dipole and spin exchange interactions to the line broadening determined by such a procedure are also shown in Fig. 6. This allowed us to calculate the exchange rate constant and the translational diffusion coefficient. It is seen that for omimBF<sub>4</sub> and 1-propanol, viscosity and temperature values in our experiments were in the interval, where both these interactions have comparable contributions to the broadening of EPR lines. In the case of cumene, in the experimental temperature interval, contributions of the dipolar coupling to  $\delta H_c$  are practically negligible comparing with those of spin exchange. Recently, a theoretical analysis of the contributions of the Heisenberg exchange and dipole–dipole interactions in diluted solutions of nitroxide spin probes to the shape of their EPR spectra was published [23]. It was shown that these contributions interfere rather often, and the approaches to obtain the molecular-kinetic and exchange integral parameters by analyzing the EPR spectra dependence on the radical concentration and the solvent viscosity were discussed.

The contribution of spin exchange to the broadening of EPR lines  $\delta H_{exch}$  is connected with the spin exchange rate constant,  $k_e$ , by the following equation [19]:

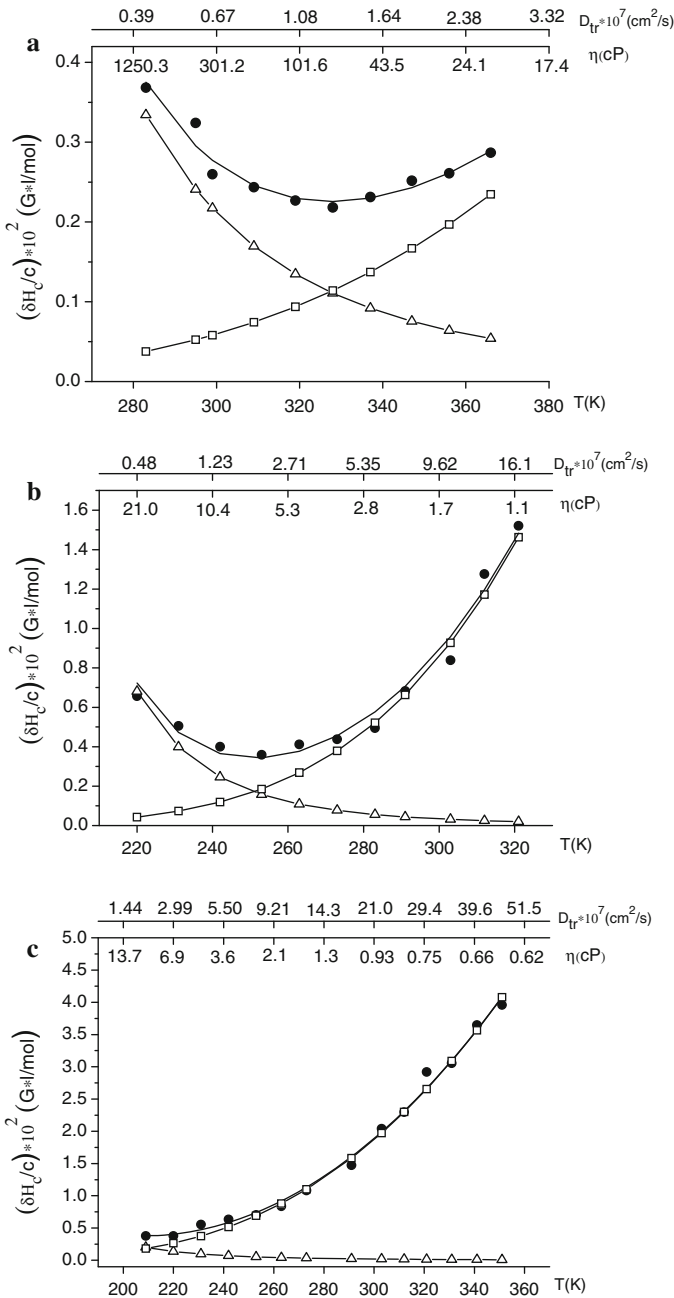
$$k_e = [1.52 \times 10^7 (g/2)(2/3)(\delta H)_{exch}] / c. \quad (4)$$

The spin exchange rate constant is also connected with the coefficient of the translational diffusion  $D_{tr}$  as [19]:

$$k_e = 16f\pi r D_{tr}, \quad (5)$$

where  $f$  is the steric factor (for TEMPOL,  $f = 0.8$  [20]) and  $r$  is a radius of the paramagnetic particle. Since the effective hydrodynamic radii measured by us earlier for TEMPOL in solvents studied differ pretty much from the literature data, evidently, they characterize not only the spin probe size but also the process of interaction between a probe and solvent molecules during the rotational diffusion. Therefore, describing translational movements, we have used the published data on the real molecular size of TEMPOL close to 3.7 Å [21, 22].

Using Eqs. (4) and (5), we have calculated coefficients of the translational diffusion,  $D_{tr}$ , of TEMPOL radicals in omimBF<sub>4</sub>, 1-propanol and cumene solutions for all temperatures. The values obtained are shown in Fig. 6, in the upper abscissa axis. Our results are in close agreement with the results obtained from electrochemical experiments on the translational diffusion of TEMPO in emim[Tf<sub>2</sub>N]:  $D_{tr} = (0.2 \times 3.8) \times 10^{-7}$  cm<sup>2</sup>/s in the temperature range of 350–295 K [9]; and



**Fig. 6**  $\delta H/c$  as a function of temperature for TEMPOL in omimBF<sub>4</sub> (a), 1-propanol (b) and cumene (c): experimental broadening (solid circles); contribution of Heisenberg exchange (open squares); contribution of dipole–dipole interaction (open triangles).  $D_{tr}$  coefficients and  $\eta$  values are shown at the top axes

of ferrocene in tri-methyl-*n*-hexylammonium bis{(trifluoromethyl)sulfonyl}amide (TMHA[ $\text{Tf}_2\text{N}$ ]):  $D_{\text{tr}} = (0.9 \times 7.3) \times 10^{-7} \text{ cm}^2/\text{s}$  at temperatures between 298 and 373 K [24].

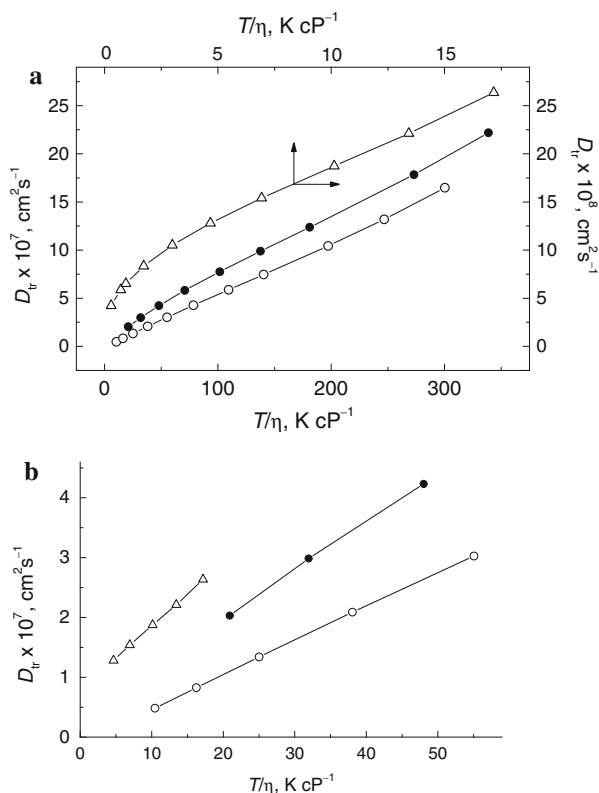
The analysis of the experimental data allowed Kovarski [11] to conclude that at  $D_{\text{tr}} < 5 \times 10^{-8} \text{ cm}^2/\text{s}$ ,  $\delta H_c$  values are mainly caused by dipole–dipole interaction, and at  $D_{\text{tr}} > 5 \times 10^{-6} \text{ cm}^2/\text{s}$ , the main contribution is connected with spin exchange. Our results are in close agreement with the published data.

Activation energy values  $E_{\text{tr}}^a$  of translational diffusion of TEMPOL in omimBF<sub>4</sub>, 1-propanol and cumene are given in Table 3. It should be noted that  $E_{\text{tr}}^a$  value for TEMPOL in omimBF<sub>4</sub>, in the error limits, is equal to the corresponding value for TEMPOL in 1-propanol, i.e., the energy of the translational movements of spin probes in RTIL is similar to that in a polar solvent. The  $E_{\text{tr}}^a$  value in nonpolar cumene is somewhat smaller than in omimBF<sub>4</sub> and in 1-propanol. We assume that electrostatic interactions and hydrogen bonds, which are formed between TEMPOL molecules and omimBF<sub>4</sub> or 1-propanol, produce some hindrances for free translational diffusion of spin probes.

The dependences of  $D_{\text{tr}}$  coefficients of TEMPOL in omimBF<sub>4</sub>, 1-propanol and cumene versus  $T/\eta$ , the Stokes coordinates, are shown in Fig. 7. It is seen that the Stokes–Einstein law for viscous current is not valid in the case of RTIL: in the low-temperature region, the translational movement of TEMPOL molecules becomes much slower. It is known [25–28] that many RTILs are microstructured media. Probably, the nonlinearity presented in Fig. 7a for omimBF<sub>4</sub> is caused by specific dependence of the RTIL structure on temperature.

We could compare  $D_{\text{tr}}$  coefficients of TEMPOL in omimBF<sub>4</sub> with  $D_{\text{tr}}$  values in 1-propanol and cumene in Stokes coordinates in a rather narrow temperature interval mutual for all of them (Fig. 7b). One can see that in the range of  $10 < T/\eta < 20 \text{ K/cP}$ , the difference between  $D_{\text{tr}}$  coefficients in all three solvents does not exceed 3.5 times. Values of  $D_{\text{tr}}$  measured for TEMPOL solutions in omimBF<sub>4</sub> are also very close to the published data for the molecular diffusion in viscous liquids: e.g., for TEMPOL in omimBF<sub>4</sub> at  $T/\eta = 0.93 \text{ K/cP}$ ,  $D_{\text{tr}} = 6.5 \times 10^{-8} \text{ cm}^2/\text{s}$ ; for the self-diffusion of 2-ethylhexyl benzoate at  $T/\eta = 1.22 \text{ K/cP}$ ,  $D_{\text{tr}} = 4.2 \times 10^{-8} \text{ cm}^2/\text{s}$  [29]; and in the case of diffusion of nitro-compounds in a mixture of 0.1 M LiCl with ethylene glycol at  $T/\eta = 0.99 \text{ K/cP}$ ,  $D_{\text{tr}} \sim 2 \times 10^{-8} \text{ cm}^2/\text{s}$  [30]. Thus, as it follows from our results, the translational diffusion efficiency in RTIL, in principle, does not differ much from diffusion mobility in other solvents.

At the same time, the rotational diffusion in RTIL has some peculiarities. Values of  $D_{\text{rot}}$  coefficients of TEMPOL molecules in omimBF<sub>4</sub> are approximately tenfold higher than the corresponding values in 1-propanol and cumene at the same parameters of  $T/\eta$ . Rotation movements of the spin probe in RTIL, differently to that in molecular solvents, cannot be described by the model of isotropic Brownian diffusion. Correct modeling of EPR spectra can be achieved only with the assumption of different rotational mobility of the spin probe around different molecular axes. The effective activation energy of rotational movements in RTIL is noticeably higher than the corresponding values for usual solvents. For better understanding of the mechanism of diffusion processes in RTIL, further investigation of the ionic liquids with different



**Fig. 7** **a**  $D_{tr}$  as a function of Stokes  $T/\eta$  parameter for TEMPOL dissolved in omimBF<sub>4</sub> (open triangles), 1-propanol (open circles) and cumene (solid circles); **b** at low  $T/\eta$  values

cations and anions with the use of nonpolar, polar and charged nitroxide spin probes is now in progress.

## 4 Conclusion

The spin exchange rate constants  $k_e$ , rotational correlation times  $\tau_c$ , translational  $D_{tr}$ , and rotational  $D_{rot}$  diffusion coefficients for the TEMPOL spin probe were determined through the analysis of EPR spectra at different temperatures and TEMPOL concentrations in bmimBF<sub>4</sub>, 1-propanol and cumene solutions. Rotational movements of spin probes in RTIL can be described only by the model of the anisotropic Brownian diffusion, while in molecular solvents they are well described by the isotropic model. The rotational diffusion in RTIL is a process fitted well by the Arrhenius law and by the Debye–Stokes–Einstein law. The effective activation energy of the rotation  $E_{rot}^a$  in omimBF<sub>4</sub> is noticeably higher than in the molecular solvents. The translational diffusion of probes in omimBF<sub>4</sub> is similar to that in molecular solvents: their parameters,  $k_e$  and  $D_{tr}$ , are comparable in all solvents studied;  $E_{tr}^a$  in omimBF<sub>4</sub> is similar to that in a polar solvent. It was revealed that the

Stokes–Einstein law is not valid for the translational diffusion in omimBF<sub>4</sub> at temperatures lower than 330 K.

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