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# Peculiarities of Intramolecular Motions in Ionic Liquids

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## 1. Introduction

Room temperature ionic liquids (RTILs) have been studied intensely during last two decades, because they can often be used as green and efficient solvents for many chemical reactions in organic chemistry, for electrochemical applications, and for industrial catalytic and extraction processes (Mamantov & Popov, 1994; Wasserscheid & Welton, 2002, 2008; Rogers & Seddon, 2003; Dyson & Geldbach, 2005; Anastas et al., 2010). RTILs have been investigated with various physical-chemical methods because they can easily interact with different surfaces and chemical environments, that is sure important for practice. For better practical applications, characterization of the transport and solvating properties, of the molecular mobility in RTILs as in a new class of reaction media. Recent studies with the use of different spectroscopic methods form now a new research area, although to date there are rather few reports on fundamental investigations of such systems.

Among various unique properties distinguish ionic liquids from common molecular solvents, such as: high viscosity, a broad liquid temperature range, high thermal stability, negligible vapor pressure, a wide electrochemical window, recyclability, and high solvation ability, the mechanism of molecular motions in RTILs media is of great importance. There are two, from the first view independent, types of reorientation movements: mobility of the whole particle (any molecule or ion, including both ionic parts of RTIL itself and dissolved molecules) and the intramolecular reorganization. Also, historically, all movements are usually divided on rotational and translational with different physical formalism for describing them. Relatively recently it was experimentally shown by Wasserman & Kovarski, 1986; Kovarski, 1997 that there is a certain quantitative correlation between rotational,  $D_{rot}$ , and translational,  $D_{tr}$ , diffusion coefficients. Easy to see, that knowledge of such dynamic characteristics for various ionic liquids is very valuable for applications, i.e., in catalysis, organic synthesis, absorption and separation, for electro-chemical processes in RTILs.

Traditional physical and physico-chemical methods present information about various macroscopic (bulk) parameters such as viscosity,  $\eta$ , dielectric constants  $\epsilon$ , dipole moments  $\mu$ , refractive indices  $n_D$ , and some others at different temperatures. Several experimental methods are used for recording molecular dynamic properties in liquid solutions: nuclear magnetic resonance spectroscopy (NMR), fluorescence, ionic conductivity, electron paramagnetic resonance (EPR) spectroscopy, and some others. However, such processes as salvation, chemical interaction between reagents, electron and energy transfer, etc., take

place on a microscopic (molecular) level with non-directed interaction forces (dipole/dipole, ion/dipole forces) and directed interactions (hydrogen bonding, electron pair acceptor-donor interactions) between solute and solvent molecules (Israelachvili, 1991; Reichardt, 2005; Akdogan et al., 2010).

All these processes are much more complex in ionic liquids than in molecular solvents since they consist of cations and anions, which both have their own distinct space interactions. Besides the electrostatic interactions, the RTIL ions can act as hydrogen-bond donors (or acceptors) and also can have hydrophobic interactions, i.e. interact by associating hydrophobic hydrocarbon moieties to avoid an unfavorable polar environment (Israelachvili, 1991). Molecular modeling and computer simulations have been used to describe structures and interactions in some ionic liquids (Pádua et al., 2007). The structural features of several RTILs were described as selforganized phases with some segregation of the charged zones from the non-polar side chain zones, which depend on the length of side chains. Longer side chains form larger non-polar domains, which “diluted” the electrostatic interactions between the charged groups (zones), similar to micellar arrangements of surfactants in water (Tokuda et al., 2005). Evidently, the existence of two kinds of domains in ionic liquids determines different solvation of various solutes by RTILs according to their polarity, charges and also the hydrophobic aliphatic chains.

The 1-alkyl-3-methylimidazolium ionic liquids can be depicted in general as it is shown in Fig. 1, where  $A^-$  is an anion, and  $C_n^+$  means a cation alkyl group  $C_nH_{2n+1}$ . All RTILs of this line have common abbreviations: Mmim $^+A^-$ , or simply MmimA ( $n = 1$ , M is methyl), EmimA ( $n = 2$ , E is ethyl), PmimA ( $n = 3$ , P is propyl), BmimA ( $n = 4$ , B is butyl), HmimA ( $n = 6$ , H is hexyl), OmimA ( $n = 8$ , O is octyl), DmimA ( $n = 10$ , D is decyl), etc.

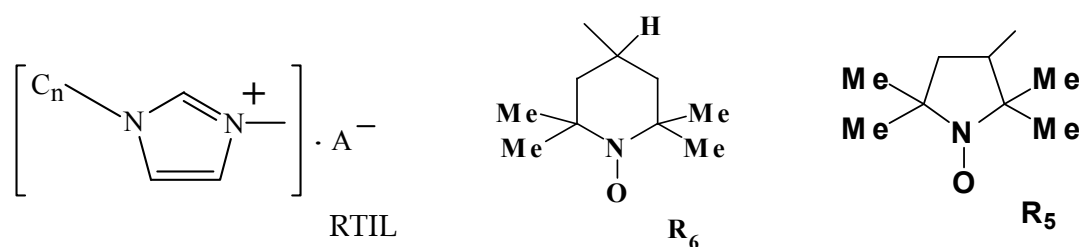


Fig. 1. The imidazoline ionic liquid structure and a paramagnetic fragments  $-R_6$  and  $-R_5$

One of the most powerful methods for investigation the structure, spatial organization and physical-chemical properties of complex and supramolecular systems on the microscopic, molecular level is EPR spectroscopy in its spin label/probe technique variant (Berliner, 1976; Buchachenko & Wasserman, 1976; Likhtenstein, 1976). Usually, nitroxide radicals of different structure were used for studying of structural peculiarities of ionic liquids and the mobility of spin probes in them. We will discuss shortly the most important results obtained by different authors below.

Seems, the first paper on the EPR study of RTIL Emim $^+I^-$ , was published by Noël et al., 1992. EPR spectra of 2,2,6,6-tetramethylpiperidin-1-yl (R<sub>6</sub>H, see Fig. 1) and of 4-amino-2,2,6,6-tetramethylpiperidin-1-yl (R<sub>6</sub>NH<sub>2</sub>) were obtained at several temperatures, and the rotational correlation time values,  $\tau_c$ , were plotted vs. Stokes coordinates  $T/\eta$ , where T is the absolute temperature, and  $\eta$  is a macroscopic viscosity. In the molecular solution, mineral oil, the rotational correlation time of R<sub>6</sub>NH<sub>2</sub> was ca. 30 times longer than for R<sub>6</sub>H.

This was explained as the result of a specific interaction of the RTIL ions with the  $\text{NH}_2$  moiety of  $\text{R}_6\text{NH}_2$  contrary to  $\text{R}_6\text{H}$ .

Polarity of several ionic liquids was examined by  $^{14}\text{N}$  hyperfine coupling constant of nitroxide radical measured by EPR method. Polarity parameters measured from EPR data agreed well with those by solvatochromic dyes, and it was judged that EPR spectroscopy is another valuable technique for the determination polarity of ionic liquids (Kawai et al., 2004).

A combined electrochemical and EPR spectroscopic study has been applied to investigate the translational and rotational diffusion of probe molecule  $\text{R}_6\text{H}$  in five RTILs (Evans et al., 2005). It was revealed that two types of motion, rotation and translational diffusion, were followed an Arrhenius dependence on the temperature. In the isotropic RTILs, the activation energies calculated from Arrhenius plots for the translational diffusion coefficient  $D_{\text{tr}}$ , obtained by electrochemical measurements, correlation time  $\tau_c$  and solvent viscosity  $\eta$  were essentially equivalent in a given ionic liquid. In two ionic liquids containing the tris(*n*-hexyl)tetradecylphosphonium cation, however, the rotational activation energies,  $E_{\text{rot}}$ , were determined to be 5–10 kJ/mol lower than those estimated from simple hydrodynamic model and translational diffusion. The authors explained this due to the adoption of a more ordered bilayer structure in these systems consisting of alternating ionic and lipophilic regions: the discrepancy in the activation energies reflected the more significant proportion of time, which spin probes spend rotating in the non-polar areas (Evans, et al., 2005).

The rotational and translational movements of several different spin probes ( $\text{R}_6\text{H}$ ,  $\text{R}_6\text{OH}$ ,  $\text{R}_6\{\text{N}(\text{CH}_3)_3\}^+\text{I}^-$ ) in various RTILs ( $[\text{C}_n\text{H}_{2n+1}]\text{mim}^+\text{A}^-$  at  $n = 2, 4-10$  and  $\text{A}^- = \text{BF}_4^-, \text{PF}_6^-$ ) at 293 K were carried out in (Stoesser et al., 2006; Strehmel et al., 2006). Analysis of EPR spectra showed that the mentioned spin probes as well as  $^{15}\text{N}$ - $\text{R}_6\text{H}$  and completely deuterated  $^{15}\text{N}$ - $\text{R}_6\text{O-D}_{17}$  allowed obtain qualitative information about microviscosity and micropolarity of ionic liquids. Rotational correlation times  $\tau_c$  and hyperfine coupling constant  $a$  of the probes were obtained by computer simulation of the EPR spectra. The idea of “microviscosity effects” allowed the authors explain the spin probe behavior in RTILs. Investigation of spin exchange of  $\text{R}_6\text{H}$ ,  $\text{R}_6\text{OH}$ , and  $\text{R}_6\{\text{N}(\text{CH}_3)_3\}^+\text{I}^-$  dissolved in ionic liquids showed a tendency of probes aggregation in the case of the nonpolar  $\text{R}_6\text{H}$ . It was surprising that authors did not calculate the spin exchange rate constants  $k_e$  at least in some cases: this could put the work to the quantitative level. Two different kinds of species (isolated and aggregated ones) were observed in the case of polar spin probes  $\text{R}_6\text{OH}$  and  $\text{R}_6\{\text{N}(\text{CH}_3)_3\}^+\text{I}^-$ . EPR tomography investigations of lateral diffusion of spin probes in RTILs corresponded to the results obtained in rotational diffusion experiments (Stoesser et al., 2006).

Dynamic line broadening effects caused by electron-self exchange reactions within the methylviologene redox couple  $\text{MV}^{++} \leftrightarrow \text{MV}^{\bullet+}$  have been studied by EPR spectroscopy in ionic liquids  $\text{BmimBF}_4$ ,  $\text{BmimPF}_6$ , and  $\text{Emim}^+[\text{SO}_4(\text{C}_2\text{H}_5)]^-$  (Grampp et al., 2006). In this case, methylviologene radicals,  $\text{MV}^{\bullet+}$ , acted as specific spin probes with well-resolved EPR spectra. The temperature dependences of the EPR coupling constants were similar to those measured in usual organic solvents, and allowed estimate the activation energy values in the range of 27.4 kJ/mol in  $\text{Emim}^+[\text{SO}_4(\text{C}_2\text{H}_5)]^-$  to 42.1 kJ/mol in  $\text{BmimPF}_6$ , respectively. Such large values of thermodynamic constants,  $E_a$ , are also reported in (Chumakova et al., 2010).

Structural and dynamic microheterogeneity of  $\text{OmimBF}_4$  were observed by EPR spectroscopy using  $\text{R}_6\text{OH}$  spin probe at low ( $c_1 = 4.6 \cdot 10^{-3}$  M) and high ( $c_2 = 5.3 \cdot 10^{-2}$  M) concentrations (Pergushov et al., 2009). In the experiments with increasing temperature over

77 K, the authors observed that practically all spin probes (within the accuracy of EPR spectra recording) were concentrated in the areas with very high concentration ( $c_3 \approx 1.0$  M) in a narrow temperature range at  $210 \pm 10$  K. The mechanism of this effect was discussed in the paper but was not proved by independent other experimental methods. It is interesting that microstructuring of this RTIL occurs at temperatures which are at 10–50 K higher than  $T_g$  - the glass transition temperature of OmimBF<sub>4</sub>.

Results of the EPR study of rotational diffusion ( $\tau_c$ ) in viscous ionic liquids: BmimBF<sub>4</sub> and BmimPF<sub>6</sub> with proxyl radical (R<sub>5</sub>COOH) in a molecular and anionic forms were analysed in (Miyake et al., 2009). The experimental average  $\tau_c$  values and activation energies for rotational diffusion disagreed with those calculated from fractional Stokes-Einstein-Debye equations.

The effects of halides, carbon dioxide and water on the physical properties of Emim<sup>+</sup>[(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>N]<sup>−</sup> have been extensively studied by Barrosse-Antle et al., 2009. The system was studied using cyclic voltammetry, chronoamperometry, and EPR spectroscopy. Diffusion coefficients in the pure and CO<sub>2</sub>-saturated ionic liquid revealed a decrease in activation energy  $E_{a_t}$  of translational diffusion from 29.0 to 14.7 kJ/mol, suggesting a reduction in the viscosity of the RTIL with addition of CO<sub>2</sub>. EPR spectroscopy was used to calculate  $\tau_c$  coefficients of a spin probe R<sub>6</sub>H. Arrhenius plots of  $\tau_c$  in the pure and CO<sub>2</sub>-saturated RTIL resulted in a similar drop in  $E_{a_{rot}}$  from 28.7 to 18.2 kJ/mol. It was concluded that the voltammetric response of the electroactive species in RTILs is not independent of other solutes.

The influence of the alkyl chain length in 1-alkyl-mim [(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>N]<sup>−</sup>, alkyls are: C<sub>n</sub>H<sub>2n+1</sub>, n = 1, 2, 3, 4, 6, 8, 10, on the rotation of piperidine-1-yloxy (R<sub>6</sub>−) derivatives substituted in the fourth position has been reported in (Strehmel et al., 2010). The substitution was done with either hydrogen bonding OH- group (R<sub>6</sub>OH) or with ionic fragments, such as the cationic (R<sub>6</sub>[N(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>I<sup>−</sup>, R<sub>6</sub>[N(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>−</sup>) or the anionic sulfate group (R<sub>6</sub>SO<sub>4</sub>-K<sup>+</sup>). Structural variation of the ionic liquids resulted in differences of their viscosity influenced the rotation  $\tau_c$  values of the spin probes. The average rotational correlation times  $\tau_c^{aver}$  of the spin probes dissolved in RTILs depended strongly on the substituent in 4<sup>th</sup> position in the piperidine ring.  $\tau_c$  values depended linearly on the ionic liquid viscosity in the case of the R<sub>6</sub>OH probe forming hydrogen bonding with the RTILs, while in contrast to this, a deviation from the Stokes-Einstein behavior was found in the case of rotation of the charged spin probes in the ionic liquid with an alkyl chain longer hexyl, i.e., with  $n \geq 6$ . This effect was explained by phase separation on a molecular level between the charged part of the RTIL and the long alkyl chains bound to the imidazolium ion. The anionic spin probes strongly interacted with the imidazolium ion (Strehmel et al., 2010).

The solvation of nitroxide radicals in ionic liquids studied by high-field EPR spectroscopy was investigated in (Akdogan et al., 2010). Better to understand of RTILs solvating spin probes of different chemical structure, a pulsed high-field EPR spectroscopy at W-band ( $\approx 94$  GHz) and continuous wave EPR at X-band ( $\approx 9.4$  GHz) were used. Three spin probes with various substitutes at the 4-position of the nitroxide ring: R<sub>6</sub>OH, R<sub>6</sub>[N(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>I<sup>−</sup>, and R<sub>6</sub>COO-Na<sup>+</sup> were dissolved in imidazolium RTILs: EmimBF<sub>4</sub>, BmimBF<sub>4</sub>, BmimPF<sub>6</sub>, HmimBF<sub>4</sub>, as well as in molecular solvents (methanol, water-glycerol). The rotational motion of the charged spin probes in RTILs was about fivefold slower than that of R<sub>6</sub>OH. The anion variation from BF<sub>4</sub><sup>−</sup> to PF<sub>6</sub><sup>−</sup> in RTILs decreased the rotational mobility measured by  $\tau_c$ . The use of high-field EPR gave very important, especially for the EPR spectra



simulation, spin-Hamiltonian parameters of the Zeeman,  $\hat{g}$ , and hyperfine,  $\hat{A}$ , tensors of several radicals dissolved in ionic liquids. Possible environment of spin probes was proposed. The  $R_6\text{COO}^-$  probe was sensitive to the length of alkyl group, i.e., this probe should be close to the nonpolar region of RTILs. These results showed that spin probes used could report about their localization in different RTIL domains with different dielectric properties. These results are in good agreement with a nanophase separation model discussed in literature.

Unfortunately, all measurements in two last perfect works were done at room temperature, and the energetic parameters could not be determined. Also, the authors did not try to simulate EPR spectra, therefore, they could operate only with average rotational correlation time constants  $\tau_c^{\text{aver}}$ , while it was recently proved that  $\tau_c$  values differ noticeably for the rotation around x-, y- and z-axes in the case of imidazolium ionic liquids (Chumakova et al., 2010). Indeed,  $\tau_c^{\text{aver}} = (\tau_c^x \cdot \tau_c^y \cdot \tau_c^z)^{1/3}$  or  $\tau_c^{\text{aver}} = [\tau_c^{\parallel} \cdot (\tau_c^{\perp})^2]^{1/3}$ , where  $\tau_c^x$ ,  $\tau_c^y$ ,  $\tau_c^z$  correspond to the appropriate axes, and  $\tau_c^{\parallel}$  and  $\tau_c^{\perp}$  are  $\tau_c$  values in the case of the axial rotation; the same relations are correct for the rotational diffusion coefficients  $D_{\text{rot}}^{\text{aver}}$  (Schneider & Freed, 1989; Akdogan et al., 2010). Therefore, the results obtained in (Strehmel et al., 2010; Akdogan et al., 2010) are qualitative but not quantitative.

We would like to stress that in all these publications the authors investigated peculiarities of the rotational and translational diffusion of spin-probe molecules in various room temperature ionic liquids, compared them with molecular dynamics in common organic solvents. Correlations with Stokes-Debye-Einstein or Stokes-Einstein laws were found. Areas in RTILs (polar, non-polar), in which spin probes (hydrophilic, charged, hydrophobic) are localized were determined. Just recently, attention of the scientists was attracted to another type of molecular motions in the ionic liquids (Tran et al., 2007a, 2009). Such processes as well as solvent effects on them can be examined in detail by EPR spectroscopy with the use of stable nitroxide biradicals (Parmon et al., 1977a, 1980).

Solvent effects on intramolecular electron spin exchange in biradicals have been investigated in various solvents, including  $\text{Bmim}^+\text{PF}_6^-$ , by electron spin resonance (ESR) spectroscopy at room temperature (Tran et al., 2007a). Using biradicals contained different radical fragments and bridges of various length and composition, it was demonstrated that interactions among solvent molecules and biradicals took place at the radical fragment and also at the functional group in the connecting bridge. The experimentally measured parameters: the exchange integral  $|J|$  and characteristic time of an intramolecular movements,  $\tau_{\text{eff}}$  have been compared with solvent viscosity and polarity parameters (macroscopic level) and longitudinal solvent relaxation time (microscopic level). The strong evidence of hydrogen bonding between solvent and different sites of the biradicals was found, in some cases even surpassing the other effects.

Intramolecular electron spin exchange has been studied in detail in  $\text{Bmim}^+\text{PF}_6^-$  for four nitroxide biradicals,  $(\text{CH}_2)_5[\text{CONHR}_6]_2$ ,  $R_6-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-R_6$ ,  $(\text{H}_5\text{C}_6)\text{O}=\text{P}(\text{OR}_6)_2$ , and  $\text{O}=\text{S}(\text{OR}_6)_2$ , as a function of temperature and the nature of the connecting bridge between two  $>\text{NO}^\bullet$  centers (Tran et al., 2009). Temperature variations of the isotropic nitrogen hyperfine splitting (hfs) constant  $a$ , and exchange integral values  $|J/a|$  were measured from EPR spectra. Thermodynamic parameters of the conformational rearrangements were obtained for rigid and flexible biradicals dissolved in  $\text{Bmim}^+\text{PF}_6^-$ , and were compared with that in toluene solutions. The analysis of spin exchange in biradicals dissolved in  $\text{BmimPF}_6$  showed, and the data were explained as a result of the specific intramolecular conformational

transitions in a biradical molecule. It was revealed that some biradical molecules, which are rather rigid in common molecular solvents, became flexible under the influence of the ionic liquid. Such strange behaviour of these “semi-rigid” molecules needed special investigation and explanation.

Therefore, the main goal of this work is the investigation and analysis of regularities and peculiarities of the intramolecular movements in nitroxide biradicals dissolved in various RTILs, their correlation with macroscopic parameters, first of all, viscosity, and determining their energetic characteristics. To aid in this effort, we have explored the temperature dependence of the dynamic changes in probe molecules of different structure in several RTIL solvents using traditional CW X-band EPR technique. Theoretical aspects, experimental details, obtained results and conclusions will be reported in the following sections.

## 2. Dynamic aspects of the intramolecular electron spin exchange

All biradicals can be conditionally divided by their structural peculiarities of the bridge connecting radical centers, and dynamic properties at three groups: rigid, long-chain flexible, and short chain flexible molecules (Parmon et al., 1980; Kokorin, 2004). Rigid biradicals, in which nitroxide rings bound via acetylene or p-phenylene fragments, can not be useful for studying the intramolecular mobility and transformations (Kokorin, 2004; Kokorin et al., 2006). The short-chain biradicals can reflect only rotational mobility because the only mechanism of intramolecular spin exchange in them is the indirect one, i.e. via a chain of atoms and bonds connecting the radical rings (Parmon et al., 1980; Grampp et al., 2004; Tran et al., 2009). Structural features of such biradicals do not allow realize a straight collision between radical centers of the same molecule, therefore, the direct mechanism of spin exchange is impossible for them. The electron spin exchange in flexible biradicals of the third group, the long-chain biradicals, occurs via direct collisions of the radical centers and the overlapping of the electron orbitals of two unpaired electrons (Parmon et al., 1975; Tran et al., 2007b, 2009). In these conformational transitions take place both translational and rotational motions. This difference in mechanisms of spin exchange is reflected in a formal procedure of determination the dynamic characteristics and thermodynamic parameters for flexible biradicals of different length.

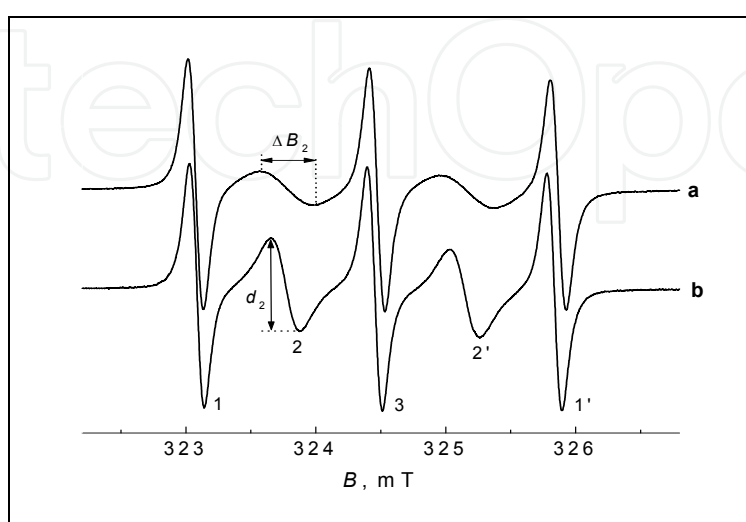


Fig. 2. EPR spectra of biradical **I** in toluene at 295 (a) and 344 K (b).

Fig. 2 shows typical changes in EPR spectra of long-chain nitroxide biradicals in a molecular solvent. For such flexible rather long-chain molecules, the dynamic properties of the chain can be described as the “cage effect”, and they are modeled well by a three-conformational model (Parmon et al., 1975; Tran et al., 2007b). If one attach two nitroxide radicals to the opposite ends of any molecule, it may be possible to characterize the intramolecular movements of the chain and the influence of temperature and solvents on them, measuring parameters of the spin-spin interaction between the unpaired electrons. In the dynamic system, temperature changes of the quintet EPR spectra of flexible biradicals are typical for the case of strong ( $|J| \gg a$ ) exchange among three conformations: an “elongated” conformation A with  $J_A = 0$  (and lifetime  $\tau_A$ ), and two conformations B and C (with total lifetime  $\tau_{BC}$ ), in which the radical fragments are nearby each other in the “cage” of the solvent molecules, but with  $J_B = 0$ , and ( $|J_C| \gg a$ ) (Parmon et al., 1975). The movement of the radical fragments inside the cage is fast, and transitions from outside to inside the cage are slow, i.e.,  $a \cdot \max(\tau_A, \tau_{BC}) > 1$  (Parmon et al., 1975, 1977a). This model allows one to obtain the thermodynamic parameters for the intramolecular transitions in the long-chain biradical. The ratio  $\tau_{BC}/\tau_A$  can be calculated from the experimental EPR spectra by comparison with the integral intensities  $I_2$  and  $I_1$  of the lines 2, 2' and 1, 1' respectively, according to (Parmon et al., 1975):

$$I_2/I_1 \approx d_2(\Delta B_2)^2/d_1(\Delta B_1)^2, \quad (1)$$

where  $d_1$  and  $d_2$  are the amplitudes and  $\Delta B_1$  and  $\Delta B_2$  the widths of lines 1 and 2 (averaged over the lines 1 and 1' or 2 and 2'). It has been obtained that (Parmon et al., 1975).

$$\tau_{BC}/\tau_A = 3(I_2/I_1)/[2 - (I_2/I_1)]. \quad (2)$$

The analysis of the lines 2 and 2' narrowing with temperature allows one to make conclusions about the motion of the radical fragments inside the cage. In the case of the fast modulation of the exchange interaction, the exchange broadening  $1/T_2$  of these lines is described by the expression (Parmon et al., 1980):

$$1/T_2 = a^2\tau_{\text{eff}}/4, \quad (3)$$

where  $\tau_{\text{eff}}$  is a complex combination of the modulation parameters and its value is close to the longest of characteristic times of the intramolecular motions. For the Lorentzian lines (Buchachenko & Wasserman, 1976):

$$a\tau_{\text{eff}} = 2\sqrt{3} |\gamma_e| (\Delta B_2 - \Delta B_1)/a \quad (4)$$

where  $a$  is taken in frequency units and  $\gamma_e$  is the magnetogyric ratio of the free electron. Supposing the Arrhenius dependence between  $\tau_{BC}/\tau_A$ ,  $\tau_{\text{eff}}$  and the temperature  $T$ , we obtain:

$$\tau_{BC}/\tau_A = \exp(\Delta S/R - \Delta H/RT), \quad (5)$$

$$\tau_{\text{eff}} = \tau_0 \exp(\varepsilon/RT), \quad (6)$$

one can calculate the values of the enthalpy  $\Delta H$  and of the entropy  $\Delta S$  of the cage, as well as the parameters  $\varepsilon$  and  $\tau_0$ , which characterize movements inside the cage. Here  $\tau_0$  is the characteristic time of the motions by which a transition between the effective conformation with  $J_B = 0$  and  $|J_C| \gg a$ , would take place at the absence of the activation energy barrier  $\varepsilon$  between them.



For the flexible short-chain biradicals, the temperature changes of the EPR spectra are analogous to those shown in Fig. 2. In this case, changes could be described in terms of the two-conformational model with fast transitions taking place between conformations (Parmon et al., 1980; Grampp et al., 2004). In this model, one conformation is with  $J_1 = 0$  (and lifetime  $\tau_1$ ), and another conformation (with lifetime  $\tau_2$ ) is with  $|J_2| \gg a$ . This model allows one to obtain the thermodynamic parameters for the intramolecular transitions. The analysis of the narrowing of the “exchange” lines (2 and 2' shown in Fig. 2) with temperature results in calculation parameters:  $a\tau_{\text{eff}}$ ,  $\tau_0$  and  $\varepsilon$  using Eqs. (4) and (6) in the case of fast modulation of the exchange interaction, and for the Lorentzian lines (Grampp et al., 2004). Parameters  $\varepsilon$  and  $\tau_0$ , again, characterize the movements inside the biradical molecule.

### 3. Experimental details

Five ionic liquids: OmimPF<sub>6</sub>, OmimBF<sub>4</sub>, BmimBF<sub>4</sub>, BmimPF<sub>6</sub>, and EmimBF<sub>4</sub> (purity  $\geq 98.5\%$  for all of them), were purchased from Fluka for our investigation. The problem of RTILs purity is very important, therefore, in order to remove remaining water, before using, all RTILs were dried at high vacuum ( $< 5 \cdot 10^{-5}$  Torr) at elevated temperatures (50-60°C) during at least 24 h. This set of RTILs should allowed us compare the intramolecular mobility in flexible biradicals in solutions with different viscosity, and also to study influence of the alkyl length, i.e., of the cation nature, as well as of the anion nature. The volume of the RTIL was estimated by measuring the exact mass of the solvent and literature data for the corresponding densities at room temperature. The sample solutions were transferred under argon atmosphere into capillaries of 0.8 mm inner diameter and, after freeze were sealed off in vacuum. This procedure was used to remove molecular oxygen and to prevent the influence of spin exchange between the triplet form,  $^3\text{O}_2$ , and nitroxide radicals.

Three biradicals,  $(\text{CH}_2)_5[\text{CONHR}_6]_2$  (**I**),  $\text{O}=\text{S}(\text{OR}_6)_2$  (**II**), and  $(\text{H}_5\text{C}_6)\text{O}=\text{P}(\text{OR}_6)_2$  (**III**), where  $\text{R}_6$  is shown in Fig. 1, were used in this work. Biradical concentrations were kept sufficiently low ( $\leq 2 \times 10^{-4}$  M) to eliminate intermolecular exchange broadening (Molin, et al., 1980). EPR spectra were recorded on a Bruker ELEXSYS 560 series spectrometer equipped with an ER 4131VT temperature control system (accuracy  $\pm 0.5$  K) and a field-frequency controlled unit. The sample temperature was varied in the region from 290 to 390 K. In addition, EPR spectra of each sample were recorded at 120 K before and after measuring each temperature series. At least for 10 minutes were allowed for the sample to reach thermal equilibrium with the heat bath before the measurements have been initiated. For each experimental spectrum, the hfs constant  $a$  as well as the line positions, widths and intensities were measured. The modulation amplitude never exceeded 0.2 G to avoid overmodulation of EPR lines.

Parameters of the intramolecular motions at different temperatures  $T$  were compared with the appropriate viscosity value,  $\eta$ . Fig. 1 presents the dependence of  $\eta$  as a function of temperature in Arrhenius co-ordinates for biradical **I** dissolved in OmimBF<sub>4</sub>, OmimPF<sub>6</sub> (Harris et al., 2006), BmimBF<sub>4</sub> (Harris et al., 2007), BmimPF<sub>6</sub> (Harris et al., 2005), and EmimBF<sub>4</sub> (Noda et al., 2001). It is seen from Fig. 1 that the Arrhenius plots are not linear in a wide temperature range, but they are practically linear at temperatures  $320 < T < 390$  K, at which we have studied the exchange behaviour and mobility in biradicals; linearity of  $\ln \eta$  vs.  $T^{-1}$  is typical for usual molecular solvents (Grampp et al., 2004).

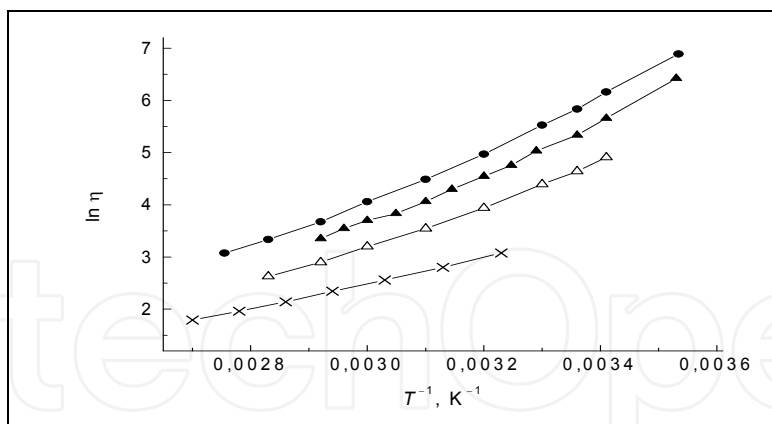


Fig. 3. Viscosity of RTILs  $\eta$  as a function of temperature: EmimBF<sub>4</sub> (×), BmimBF<sub>4</sub> (Δ), OmimBF<sub>4</sub> (●), BmimPF<sub>6</sub> (▲)

#### 4. Motions in long flexible molecules

Flexible rather long-chain biradicals with 10 or more bonds in a chain binding two nitroxide radical rings allow modeling both translational and rotational intramolecular motions. Biradical **I** is soluble in various polar and non-polar solvents, therefore, it was chosen for temperatures are given in Fig. 4. Similar spectra have been recorded in many classical solvents earlier (Tran et al., 2007b), as it is seen in Fig. 2, and the temperature behaviours of the spectra is similar in all the solvents, but an interval of these changes sufficiently depends on the solvent nature. EPR spectra presented in Fig. 4 are analogous to that recorded in viscous solvents such as cyclohexanol and 1-octanol (Tran et al., 2007b).

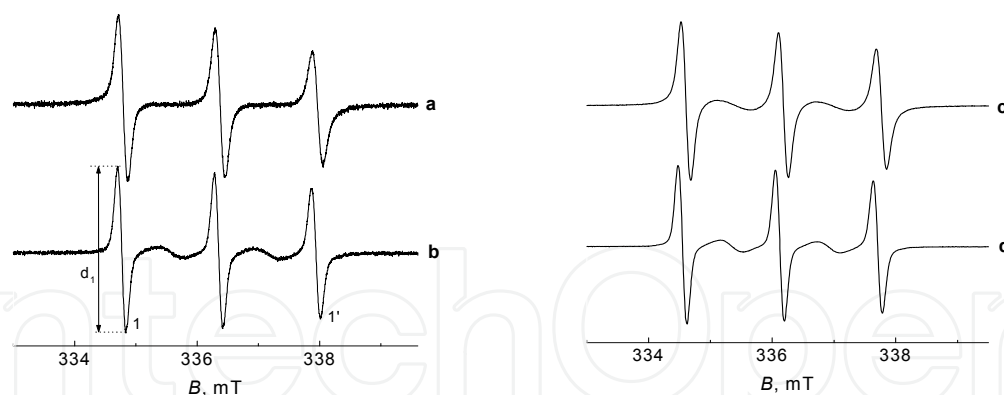


Fig. 4. EPR spectra of biradical **I** in OmimBF<sub>4</sub> at 370 (a), 410 (b), and in BmimPF<sub>6</sub> at 410 (c), 430°K (d).

The hyperfine splitting constant  $a$ , as a function of temperature, for biradicals **I–III**, dissolved in different ionic liquids, is given in Fig 5. One can see that changes of  $a$  with temperature for all biradicals in RTILs are smaller to those in various molecular solvents in the case of piperidine-1-oxyl ring radicals and biradicals (Kokorin, 2004; Kokorin et al., 2006; Tran et al., 2009). It means that the electrostatic interaction between cations and anions of the ionic liquids and paramagnetic  $>\text{N}-\text{O}^\bullet$  groups do not reveal any specific peculiarities in comparison with molecular organic solvents.

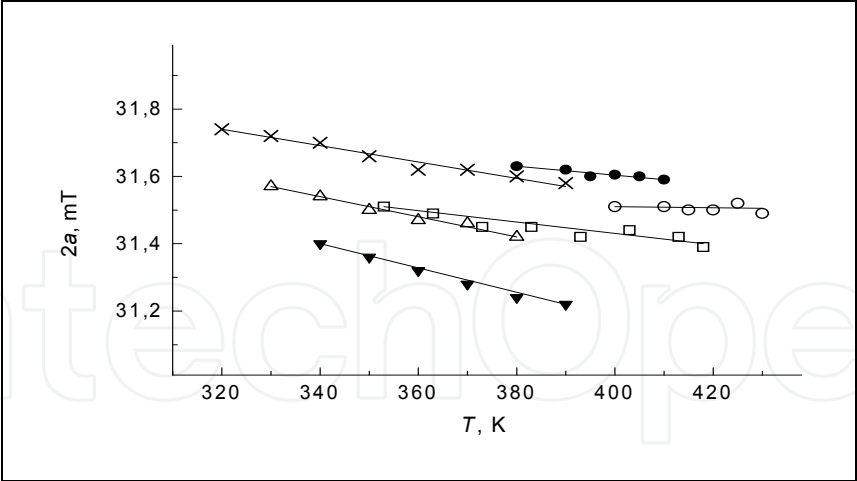


Fig. 5. Hyperfine splitting constant  $a$  as a function of temperature for biradicals **I** in OmimBF<sub>4</sub> (•), BmimPF<sub>6</sub> (o), **II** in OmimPF<sub>6</sub> (▼), BmimBF<sub>4</sub> (Δ), EmimBF<sub>4</sub> (x), and **III** in BmimPF<sub>6</sub> (□).

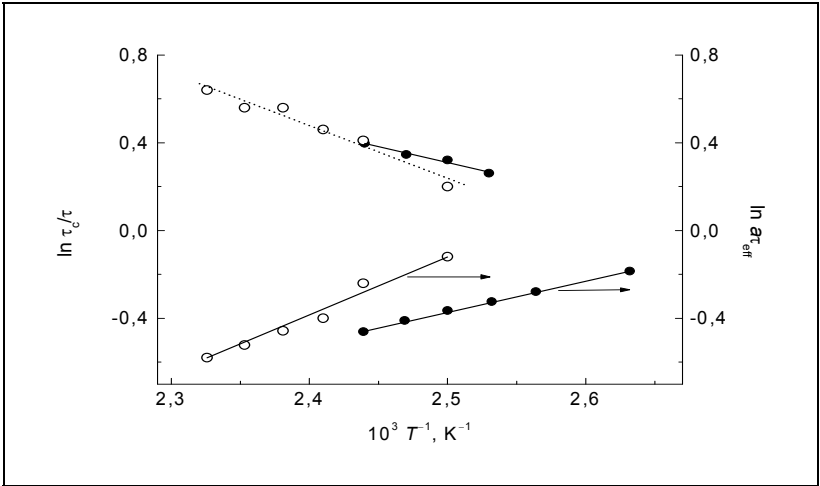


Fig. 6.  $\tau_c/\tau$  and  $a\tau_{\text{eff}}$  as a function of temperature for biradical **I** in OmimBF<sub>4</sub> (•) and BmimPF<sub>6</sub> (o).

Linear temperature dependences of the ratio  $\tau_{\text{BC}}/\tau_{\text{A}}$  and  $a\tau_{\text{eff}}$  on temperature in Arrhenius coordinates (Eqs. 5 and 6) for **I** dissolved in BmimPF<sub>6</sub> and OmimBF<sub>4</sub> are shown in Fig. 6, and thermodynamic parameters  $\Delta H$ ,  $\Delta S$ ,  $\varepsilon$  and  $\tau_0$ , calculated by these equations are given in Table 1. The parameter  $\tau_{\text{BC}}/\tau_{\text{A}}$  increases with temperature, while  $a\tau_{\text{eff}}$  decreases. Temperature changes of  $\tau_{\text{BC}}/\tau_{\text{A}}$  in BmimPF<sub>6</sub> and OmimBF<sub>4</sub> are reasonably larger than in toluene, which themselves are slight since for the long-chain biradicals, the entrance into the cage is mainly connected with steric, i.e. entropic, rather than energetic factors (Parmon et al., 1975; Grampp et al., 2004). One can see that the values of the enthalpy and entropy of the solvent cage formed around the biradical **I** are noticeably larger in the case of RTILs compared with those obtained in toluene (Parmon et al., 1975; Tran et al., 2007b) , but also differ for BmimPF<sub>6</sub> and OmimBF<sub>4</sub>. This means that structural rearrangements in ionic liquids, necessary for the conformational changes of **I**, need additional energy for their realization. Only further experiments with variation RTILs and new long-chain biradicals will allow real understanding of the role of RTILs cations and anions in this effect.

Solvent	Temperature range, K	$\Delta H$ , kJ/mol	$\Delta S$ , J/mol ·K	$\varepsilon$ , kJ/mol	$-\log \tau_0 \pm 0.3$
BmimPF <sub>6</sub>	400-430	20.0 ± 2	52 ± 5.4	22.0 ± 0.8	11.4
OmimBF <sub>4</sub>	380-410	11.9 ± 1.2	32.4 ± 3.1	11.7 ± 0.2	10.2
Toluene <sup>a</sup>	295-344	3.6 ± 0.3	16.7 ± 1.8	10.6 ± 0.3	10.8
Cyclohexanol <sup>a</sup>	354-385	-	-	28.6 ± 0.5	12.4
1-octanol <sup>a</sup>	324-384	-	-	23.0 ± 0.3	11.9
Water <sup>a</sup>	293-364	-	-	18.9 ± 0.4	12.0

<sup>a</sup> Tran et al., 2007b

Table 1. Thermodynamic parameters  $\varepsilon$ ,  $\tau_0$ ,  $\Delta H$ , and  $\Delta S$  for biradical **I** in different solvents

The  $\varepsilon$  value, which characterizes movements inside the cage, is twice larger in BmimPF<sub>6</sub> compared to toluene but similar to the value in aqueous solutions and in viscous alcohols such as 1-octanol or cyclohexanol (Table 1). It is surprising that  $\varepsilon$  in OmimBF<sub>4</sub> is also twice less compared to BmimPF<sub>6</sub>, and very close to a toluene value. Clarifying of these effects will become possible after collecting new results obtained for the same spin probe dissolved in different ionic liquids. Values of  $\log \tau_0$  are still similar to each other as it has been predicted by the theory (Parmon et al., 1973, 1980) and confirmed experimentally for many solvents (Grampp et al., 2004; Tran et al., 2007b).

5. Motions in short molecules

Another type of nitroxide biradicals with short and rather rigid bridges between the radical fragments is represented by **II** and **III**. Their EPR spectra at 370 K in different ionic liquids are shown in Fig. 7. During many years, such biradicals were known as rigid molecules, they were investigated and described in several papers and reports (Nakajima et al., 1972; Buchachenko & Wasserman, 1976; Parmon et al., 1980; Kokorin, 2004; Kokorin et al., 1974, 2006), and it was assumed that these molecule are rigid and exist in only one conformation in all solvents used, up to glassy solutions at 77°K (Parmon et al., 1977b, 1980). Weak  $|J/a|$

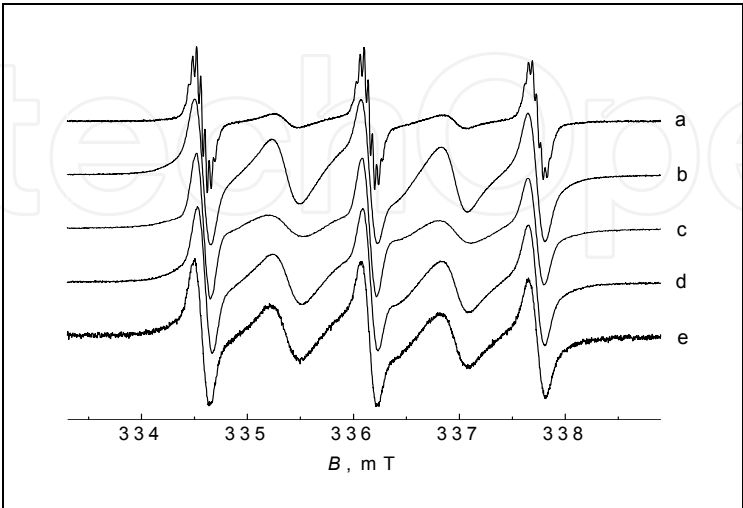


Fig. 7. EPR spectra of biradical **II** in EmimBF<sub>4</sub> (a), BmimBF<sub>4</sub> (b), OmimBF<sub>4</sub> (c), OmimPF<sub>6</sub> (d), and **III** in OmimBF<sub>4</sub> (e) at 370 K.

variations with temperature were explained as specific interactions of solvent molecules with  $>\text{N}-\text{O}^\bullet$  groups or with heteroatoms in the bridge (Kokorin et al., 2006). It should be mentioned that in the case of really rigid molecules with the indirect mechanism of spin exchange, the exchange integral value remains constant at all temperatures and varies slightly only with the solvent polarity or specific solvation (Kokorin et al., 2006).

It should be noted that in  $\text{BmimPF}_6$  at temperatures above 410–420°K, partial destruction of the biradicals takes place, with the appearance of the superimposed three-line EPR spectrum, for all the systems **I–III**. This was revealed by the noticeable increase of the main “nitroxide” lines amplitude in EPR spectra (lines 1, 3 and 1' in Fig. 2). It seems, that thermal decomposition of  $\text{BmimPF}_6$  started at 415–420°K (Huddleston et al., 2001) and the generated products react with biradical paramagnetic centers of **I–III** with formation of the appropriate radicals. The temperature at which such biradical “decay” starts depends on the ionic liquid.

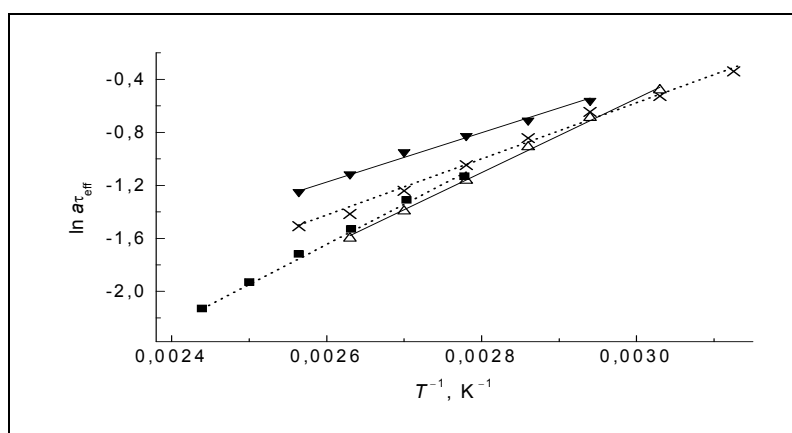


Fig. 8.  $a\tau_{\text{eff}}$  as a function of temperature for biradical **II** in  $\text{OmimPF}_6$  ( $\blacktriangledown$ ),  $\text{BmimBF}_4$  ( $\Delta$ ),  $\text{EmimBF}_4$  ( $\times$ ), and **III** in  $\text{OmimBF}_4$  ( $\blacksquare$ ).

Great difference in the behaviour of the spin exchange in all RTILs studied respectively to common molecular solvents was revealed in the case of the short-chain rather rigid biradicals **II** and **III**. Typical temperature changes in EPR spectra of these biradicals in RTILs (Fig. 7) allowed us calculate the energetic parameters  $\varepsilon$  and  $\tau_0$  of the rotational diffusion from the line width narrowing with the increase of temperature (Fig. 8) using Eq. (6). Such spectral changes can be explained by the model of two conformations with  $J_1 = 0$  and  $|J_2/a| \gg 1$ , and fast transitions between them. Conformation “2” with a large value of the exchange integral is realized at high temperatures. Experimentally measured values of  $\varepsilon$  and  $\tau_0$  are listed in Table 2.

One can see from Table 2 that elongation of the alkyl chain in the RTIL cation from ethyl to octyl at the same anion ( $\text{BF}_4^-$ ) causes the increase of the activation energy  $\varepsilon$  at 10 kJ/mol, while changing the anion,  $\text{BF}_4^-$  to  $\text{PF}_6^-$ , at the same  $\text{Bmim}^+$  seems, does not effect on the  $\varepsilon$  value. From this results, we suppose that these biradical probes are probably localized in hydrophobic areas of RTILs.

We should stress that such behaviour of **II** and **III** in room temperature ionic liquids indicates that the process of spin exchange within these biradicals has changed compared to molecular solvents (Kokorin et al., 2006, 2010): their structure became non-rigid, and intramolecular motions in **II** and **III** could be realized only at high temperatures, although the mechanism of indirect exchange was not changed in RTILs. The spectral changes due to



Biradical	Solvent	Temperature range, K	$\varepsilon$ , kJ/mol	$-\log \tau_0$	$E_\eta$ , kJ/mol
II	OmimBF <sub>4</sub>	340-390	$27.8 \pm 1.3$	$13.0 \pm 0.3$	36.6 <sup>d</sup>
	BmimBF <sub>4</sub>	330-380	$23.3 \pm 0.9$	$12.3 \pm 0.2$	32.7 <sup>g</sup>
	EmimBF <sub>4</sub>	320-390	$18.0 \pm 0.6$	$11.6 \pm 0.2$	20.1 <sup>f</sup>
	BmimPF <sub>6</sub> <sup>a</sup>	345-418	$24.0 \pm 2.2$	$12.3 \pm 0.3$	37.6 <sup>c, e</sup>
	BmimPF <sub>6</sub> <sup>b</sup>	345-420	$24.5 \pm 2.3$	$12.3 \pm 0.3$	37.6 <sup>c, e</sup>
	OmimBF <sub>4</sub> <sup>a</sup>	360-410	$20.8 \pm 2.1$	$12.1 \pm 0.2$	37.6 <sup>c, e</sup>
III	OmimBF <sub>4</sub> <sup>a</sup>	360-410	$24.0 \pm 2.2$	$12.5 \pm 0.4$	

<sup>a</sup> Kokorin et al., 2010; <sup>b</sup> Tran et al., 2009 ; <sup>c</sup> Chiappe & Pieraccini, 2004; <sup>d</sup> Harris et al., 2006; <sup>e</sup> McLean et al., 2002; <sup>f</sup> Noda et al., 2001; <sup>g</sup> Harris et al., 2007

Table 2. Thermodynamic parameters  $\varepsilon$  and  $\tau_0$  for biradicals **II** and **III** in different RTILs

modulation of the exchange integral  $|J|$  value with the temperature variations are similar to those observed for analogous short-chain and flexible biradicals:  $R_6-NHCH_2CH_2-R_6$  or  $R_6O-S-OR_6$  (Parmon et al., 1973, 1980). Seems, this is the first example when the influence of the solvent becomes so strong that rather rigid biradical molecules (**II** and **III**) became significantly more flexible. One may assume that the solvent polarity and other electrostatic parameters of the ionic liquids strongly influence the dynamic and relaxation properties of the dissolved biradicals, causing changes in the intramolecular spin exchange mechanism.

6. Comparison with macroscopic parameters

We assume that the experimental  $\Delta H$  and  $\varepsilon$  values for **I** in different liquids including ionic liquids qualitatively should correlate, first of all, with the viscosity of the solvent, though the viscosity of BmimPF<sub>6</sub>, for example, is reported as  $\eta = 257.1$  cP at 298 K (Chiappe & Pieraccini, 2004) Indeed, the  $E_\eta$  values, which characterize temperature dependence of  $\eta$ :

$$\ln \eta(T) = \ln \eta_0 + E_\eta/RT , \tag{7}$$

are equal to 37.6, 36.6, 9.1, 15.3 and 41.7 kJ/mol for BmimPF<sub>6</sub>, OmimBF<sub>4</sub>, toluene, water and cyclohexanol, respectively. One can see that they correlate rather well with  $\varepsilon$  listed in Table 2 and for  $\varepsilon = 28.6$  kJ/mol in cyclohexanol (Tran et al., 2007b). This linear correlation between  $\ln(a\tau_{eff})$  and  $\ln \eta$  (Kokorin et al., 2010) is valid for different RTILs at rather high temperatures ( $T > 330$  K), when RTIL structure becomes homogeneous enough for spin probes, and structural heterogeneities are already lost (Triolo et al., 2007; Xiao et al., 2007). Which factors of ionic liquids influence the intramolecular spin exchange in biradicals will be clarified after further detail investigations.

One of the most important classical properties of the translational and rotational diffusion is their correlation with Stokes-Einstein and Debye-Stokes-Einstein laws correspondingly. A lot of articles have been published on this topic, and in some cases of ionic liquids and ionic-liquid mixtures their validity was not fulfilled. Therefore, we have analyzed this question in our systems. Dependences of  $\tau_c/\tau$  and  $a\tau_{eff}$  as a function of Stokes parameter  $T/\eta$  for biradicals **I-III** dissolved in OmimBF<sub>4</sub>, BmimBF<sub>4</sub>, EmimBF<sub>4</sub>, and BmimPF<sub>6</sub> are shown in Figs. 9 and 10. It is seen that linearity of all plots is good enough in all RTILs. The identical dependence for  $\tau_{BC}/\tau_A$  on  $T/\eta$  is not surprising because viscosities of OmimBF<sub>4</sub> and BmimBF<sub>4</sub> are rather close in this temperature range, and this dynamic process: movements of two radical groups for their collision, relates to translational diffusion. Rather unexpected

was validity of the Debye-Stokes-Einstein correlation for small rotational movements inside the “cage” – this process is really microscopic and its correlation with a macroscopic parameter was not obvious.

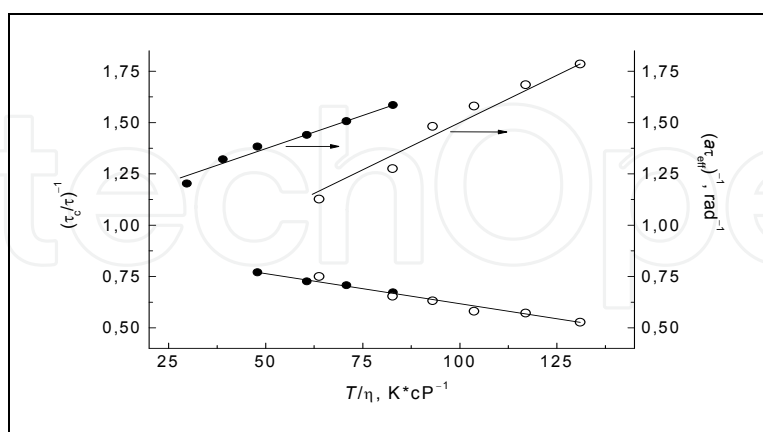


Fig. 9.  $\tau_c/\tau$  and  $a\tau_{\text{eff}}$  as a function of Stokes parameter  $T/\eta$  for biradical **I** in OmimBF<sub>4</sub> (●) and BmimPF<sub>6</sub> (○)

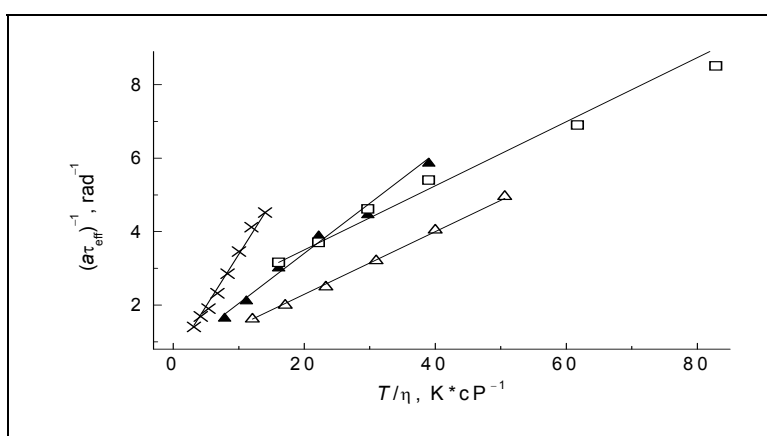


Fig. 10.  $a\tau_{\text{eff}}$  as a function of Stokes parameter  $T/\eta$  for biradical **II** in OmimBF<sub>4</sub> (▲), BmimBF<sub>4</sub> (Δ), EmimBF<sub>4</sub> (×), and **III** in BmimPF<sub>6</sub> (□)

## 7. Conclusion

The behaviour of three stable nitroxide biradicals dissolved in five imidazolium ionic liquids has been studied by EPR spectroscopy. All systems studied revealed relatively good correlation with Stokes-Einstein and Debye-Stokes-Einstein laws. Quantitative differences in thermodynamic parameters and temperature ranges of conformational changes of the biradical molecule are most likely connected to the high viscosity  $\eta$  and the high value of characteristic activation energy  $E_\eta$  of RTILs. Ionic liquids revealed new qualitative features as solvents in the case of short-chain, rather rigid nitroxide biradicals. RTILs performed specific influence on structural rearrangements and features of the intramolecular spin exchange in such biradicals dissolved in RTILs, in comparison with molecular solvents. This specificity was observed in realization of a new type of conformational transitions in such biradicals, which were explained by electrostatic interaction between polar groups of the

biradical and ions forming RTILs. Dynamics of these transitions correlates with viscosity of the ionic liquid at high temperatures and with Stokes parameter.

## 8. Acknowledgement

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