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Article

High-Pressure ESR Spectroscopy: On the Rotational Motion of Spin Probes in Pressurized Ionic Liquids

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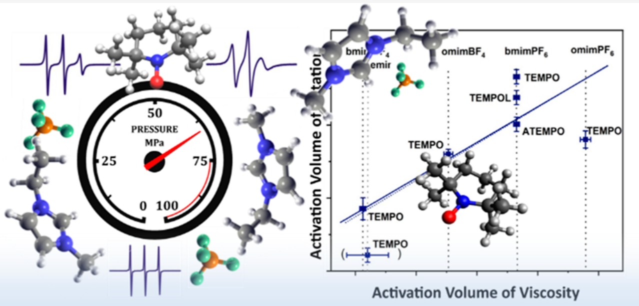
ABSTRACT: We report high-pressure (up to 50 MPa) ESR-spectroscopic investigations on the rotational correlation times of the nitroxide radicals 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPOL), and 4-amino-2,2,6,6-tetramethylpiperidine 1-oxyl (ATEMPO) in the ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate (emimBF$_4$), 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF$_6$), 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF$_4$), 1-methyl-3-octylimidazolium tetrafluoroborate (omimBF$_4$), and 1-methyl-3-octylimidazolium hexafluorophosphate (omimPF$_6$). The activation volumes (38.5−56.6 Å^3) determined from pressure dependent rotational diffusion coefficients agree well with the pressure dependent viscosities of the ionic liquids. Experimentally, the fractional exponent of the generalized Stokes−Einstein−Debye relation is found to be close to one.



■ INTRODUCTION

Room temperature ionic liquids (RTILs) exhibit a larger number of unusual physical properties, making them attractive as solvent media for academic and industrial applications.[1−13] Beside their well-known physical properties such as an extremely low vapor pressure, wide electrochemical windows, and high thermal stability, recently astonishing nanostructured effects have been reported, like the formation of nano- to mesoscaled polar and unpolar domains. Peric et al. reported in a detailed study about the nanostructured organization of RTILs using perdeuterated TEMPONE radical as a spin probe.[14] Only two papers deal with time-resolved (TR) ESR-spectroscopy. Kawai et al. and recently Fedin et al. report on the spin dynamics of triplet and doublet states in RTILs.[15,16]

High-field ESR-spectroscopic studies support the assumption that polar domains are formed by anions and cations whereas the unpolar domains are formed by the alkyl chains of the RTILs. Using charged and uncharged nitroxide radicals, several authors reported different correlation times based on different anions in the RTILs.[17−19]

Interactions between imidazolium-based ionic liquids and some nitroxyl radicals carrying different substituents, such as hydrogen bonding −OH or ionic $-N(CH_3)^{3+}$ and $-OSO^{3-}$ substituents have been systematically investigated by Zhang et all.[20] Their studies based on density functional theory calculations predict significant reduction of the mobility of ionic radicals in ionic liquids compared to systems containing neutral radicals.

The study of diffusion influenced reactions is of great interest not only because of the generally high viscosity of the RTILs but also from the viewpoint of solute−solvent cage and microenvironmental effects.[21−23]

The rotational mobility of organic radicals in conventional solvents and in room temperature ionic liquids sensed by ESR-spectroscopy has been subject of several articles published by Feed, Strehmel, Evans, and Kawai.[24−33] The first study on rotational motion in RTILs was published by Allendoerfer et al. in 1992.[34]

Rotational motion of spin probes in imidazolium-based ionic liquids has been reported by Sengupta and Miyake as well.[35−37]

Studies on pressure-dependent ESR-line width and rotational correlation times of vandyl acetylacetonate in variety of nonhydrogen-bonded solvents have been reported by Hwang at al.[38] Recently Hubbel et al. reintroduced the application of high-pressure ESR spectroscopy to biochemical reactions in water. They report on protein-folding, conformational equilibria of spin-labeled proteins.[39−41]

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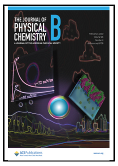

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For the study of the 3-carboxypropyl radical, disagreeing rates of rotational diffusion and the corresponding activation energies with those calculated from the Stokes–Einstein–Debye (SED) relation have been found. Often a fractional dependence on $(\eta/T)^x$ is suggested with $x < 1$ where η and T denote the dynamic viscosity and the temperature, respectively. Such corrections could indicate a slippage of the solute in the solvent cage. The microviscosity model introduced by Gierer and Wertz is mainly used for such deviations.[42]

In contrast to these findings, Evans et al. have reported on the activation energy of rotational diffusion of TEMPO, which correlates well with the activation energies of the viscous flow of the RTILs as predicted by the classical SED-relation.[25]

Strehmel at al. reported on the influence of the alkyl chain length of the RTILs on the rotation of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPOL) radical. A linear correlation of the rotational correlation times with the viscosity is also reported by these authors. For charged spin probes, deviations from the SED-behavior are found.[26]

We recently studied the temperature dependence of several spin probes in RTILs and found good correlation with the SED-equation, albeit too small hydrodynamic radii, even if deviations from the spherical shape of the spin probes and microviscosity corrections are taken into account.[21,23,43−45]

All these studies reported in the literature focused on viscosity and/or temperature dependent measurements. To get insights into the free-volume effect, the formation and coalescence of specific domains in RTILs, additional pressure dependent investigations appear worthwhile. Here, we report for the first time on pressure dependent measurements of rotational correlation times undertaken with the aim of revealing detailed information on the corresponding activation volumes, $\Delta V^{\ddagger}$.

■ METHODS

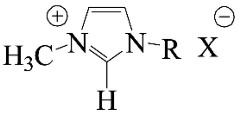
CW-ESR spectra were recorded using a JEOL PE-3X spectrometer equipped with an improved microwave bridging system and an AEG magnet. A cylindrical TEM_{011}-cavity was used. The spectrometer operated at a microwave frequency of around 9.5 GHz and employed a 100 kHz field modulation. A home build flow-through sample cell system, allowing measurements at elevated pressures of up to 100 MPa is described elsewhere.[46,47]

The ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate ($emimBF_4$, > 98%), 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$, > 99%), and 1-butyl-3-methylimidazolium tetrafluoroborate ($bmimBF_4$,>99%) were purchased from Ionic Liquids Technologies (IoLiTec, Germany). 1-methyl-3-octylimidazolium tetrafluoroborate ($omimBF_4$, > 98%) and 1-methyl-3-octylimidazolium hexafluorophosphate ($omimPF_6$, > 98%) were obtained from Solchemar, Portugal. Structures of the studied RTILs are shown in Scheme 1

On account of the fact that small traces of water can change significantly the rotational correlation times of the spin labels, all RTILs were dried for at least 24 h under high vacuum (<5 × 10^{-5} Torr) and at elevated temperatures (327–337 K). The dried ionic liquids were stored in Schlenk tubes under an argon atmosphere. The tubes were furthermore placed in an desiccator over P_4O_{10} and kept in dark.

Used spin labels (see Figure 1) 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, > 99%) and 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (ATEMPO, > 97%) were obtained from Sigma-Aldrich. Before use, TEMPO was purified by sublimation. 4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl, (TEMPOL, ≥ 97%,) was purchased from Fluka and used as received.

Scheme 1. Ionic Liquids Used



$R= -C_2H_5, -C_4H_9, -C_8H_{17}$

$X^- = PF_6^-, BF_4^-$

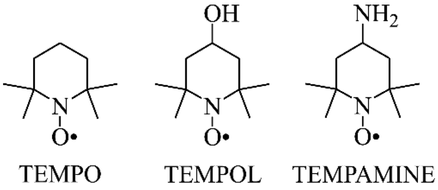


Figure 1. Used spin labels

The volume of the RTILs was determined gravimetrically from the density of the corresponding solvent. In order to avoid line broadening effects, due to spin–spin interactions, the radical concentrations were kept low at 3 × 10^{-4} M to 5 × 10^{-4} M. Standard Schlenk techniques were employed to transfer the sample solutions under argon atmosphere into the ESR-spectrometer. All samples were measured at 295 ± 1 K. Prior each measurement at least 15 min were allowed for thermostatting. The pressure was increased from 0.1 to 50 MPa following reduction to 0.1 MPa in steps of 2.5 MPa. No hysteresis was found for all measurements. EPR spectra were simulated using EasySpin toolbox for Matlab.[47,48] The *g*- and *A*-tensors were determined from measurements of the corresponding sample at 80 K using a Bruker E580-FF/CW spectrometer by courtesy of the Ruđer Bošković Institute (Zagreb, Croatia), equipped with a liquid helium/nitrogen cryostat (Oxford Instruments).[43,44] The spin-Hamiltonian parameters of the investigated sin probes in the studied ILs used for the simulation of the experimental EPR spectra are listed in Table 1.

■ RESULTS AND DISCUSSION

In this study we focus on fast tumbling spin probes (see Figure. 1). Typical ESR-spectra recorded at atmospheric and elevated pressure, together with their computer simulations, are shown on Figure. 2.

At constant temperature, pressure dependent rate constants k_r result in the corresponding experimental activation volumes $\Delta V\ddagger_{obs}$.

$$k_B T\left(\frac{\partial(\ln k_r)}{\partial p}\right)_T = -\Delta V^{\ddagger}_{obs} \tag{1}$$

The Stokes–Einstein–Debye (SED) law is routinely used in the literature, to relate rotational diffusion coefficients to solvent viscosities, eq 2.

$$\tau_r = \frac{1}{6D_r} = \frac{4\pi r^3}{3k_B}\frac{\eta(T)}{T} = \frac{1}{k_r} \tag{2}$$

Table 1. Spin-Hamiltonian Parameters of the Investigated Sin Probes in the Studied ILs

solvent	substance	g_{xx}	g_{yy}	g_{zz}	A_{xx}/MHz	A_{yx}/MHz	A_{zz}/MHz
emimBF$_4$	TEMPO	2.0111	2.0089	2.0044	44.8	27.5	−5.9
bmimBF$_4$	TEMPO	2.0087	2.0065	2.002	44.8	27.5	−5.9
bmimPF$_6$	TEMPO	2.0087	2.0065	2.002	44.8	27.5	−5.9
bmimPF$_6$	TEMPOL	2.0109	2.0089	2.0043	43.8	27.6	−7.0
bmimPF$_6$	ATEMPO	2.0111	2.009	2.0045	44.9	27.3	−7.8
omimBF$_4$	TEMPO	2.0087	2.0065	2.002	44.0	27.5	−5.9
omimPF$_6$	TEMPO	2.0087	2.0065	2.002	44.4	27.5	−5.9

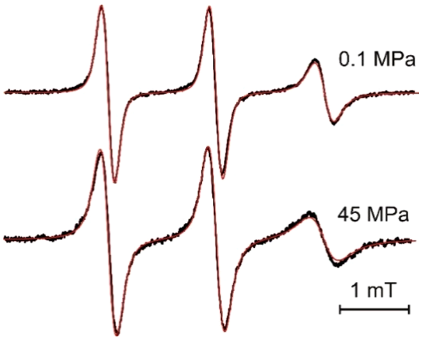


Figure 2. Pressure-dependent EPR spectra of TEMPOL in bmimPF$_6$ at 295 K (experimental black and simulated red line). The rotational rate constants extracted from the simulations are $k_r = 2.75 \times 10^7$ s^{-1} and 5.74×10^7 s^{-1} from bottom to the top, respectively.

In this expression, τ_r is the rotational correlation time, D_r the rotational diffusion coefficient, and η the dynamic viscosity of the solvent. r is an effective hydrodynamic radius that is expected to correspond or exceed the van der Waals radius of the spin probe. Often the experimental r deviates from the van der Waals one and is then denoted as hydrodynamic radius. k_B and T denote the Boltzmann constant and the absolute temperature. Deviations from SED-relation are normally expressed by a fractional SED-expression with exponent x:

$$\tau_r = \frac{1}{6D_r} \sim \left[\frac{\eta(T)}{T}\right]^x \tag{3}$$

The viscosities of the studied ionic liquids at room temperature and atmospheric pressure are listed in Table 2.

Table 2. Viscosities of the Studied Ionic Liquids at 295 K and P = 0.1 MPa

solvent	η/(mPa s)
emimBF$_4$[35]	43
bmimBF$_4$[36]	122
bmimPF$_6$[37]	327
omimBF$_4$[38]	417
omimPF$_6$[38]	919

Viscosities at elevated pressures are obtained from published data[2,11−13] and were fitted to an Arrhenius type equation, eq 4.

$$\eta(p) = \eta_0 \exp\left[\frac{V_\eta(p - p_0)}{k_B T}\right] \tag{4}$$

The fitted parameters ε_0 and V_η/k_BT are given in Table 3. The corresponding volumes V_η, given in Table 3 have been extracted from plots like that given in Figure 3.

Table 3. Coefficients of Best Fits Using eq 4[a]

Solvent	η_0	V_η/k_BT
emimBF$_4$[2]	43.34	0.010
bmimBF$_4$[12]	112.23	0.001
bmimPF$_6$[11]	284.36	0.013
omimBF$_4$[13]	353.12	0.012
omimPF$_6$[13]	733.14	0.014

[a] See refs 2, 11−13, 49, and 50.

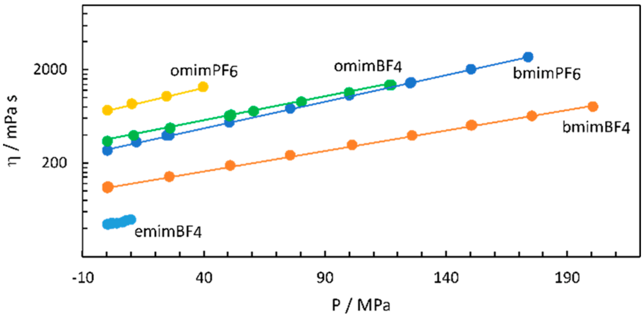


Figure 3. Pressure dependence on the viscosity of the studied room temperature ionic liquids.

From the pressure dependence of the rotational diffusion coefficients, listed in Table 4 and presented on Figure 4, the experimental activation volumes, $\Delta V^{\ddagger}_{\text{obs}}$, given in Table 5 were extracted.

Table 4. Rotational Diffusion Coefficients of Various Spin Probes in the Studied Room Temperature Ionic Liquids at Atmospheric and Elevated Pressures, T = 295 K

		$D_r \times 10^8$/s	
substance	solvent	0.1 MPa	50 MPa
TEMPO	emimBF$_4$	17.3	12.7
TEMPO	bmimBF$_4$	7.61	6.96
TEMPO	bmimPF$_6$	3.88	1.93
TEMPO	omimBF$_4$	4.91	2.83
TEMPO	omimPF$_6$	3.04	1.71
TEMPOL	bmimPF$_6$	3.09	1.53
ATEMPO	bmimPF$_6$	1.41	0.77

For all samples, the rotational diffusion coefficients agreed upon increasing and decreasing the pressure. No hysteresis was apparent.

Combining eqs 1, 2, and 3 and differentiating with respect to pressure leads to the following expression for the activation volumes:

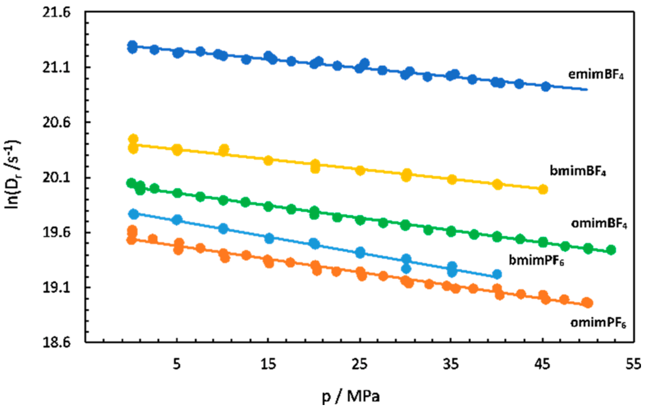


Figure 4. Rotational diffusion coefficients of TEMPO as a function of pressure at T = 295 K.

Table 5. Activation Volumes

RTIL	substance	V_η/Å^3	$\Delta V^\ddagger_{obs}$/Å^3	$\Delta\Delta V$/%
bmimBF$_4$	TEMPO	40.6 ± 0.3	38.5 ± 1.5	−5
omimBF$_4$	TEMPO	47.6 ± 0.4	46.0 ± 0.6	−3
omimPF$_6$	TEMPO	58.9 ± 0.4	48.0 ± 1.2	−19
emimBF$_4$	TEMPO	41.0 ± 1.7	32.2 ± 1.0	−22
bmimPF$_6$	TEMPO	53.2 ± 0.2	56.6 ± 1.0	6
bmimPF$_6$	TEMPOL	53.2 ± 0.2	53.8 ± 1.0	1
bmimPF$_6$	ATEMPO	53.2 ± 0.2	50.1 ± 1.0	−6

$$\Delta V^\ddagger_{obs} = -k_\mathrm{B}T\left[\frac{\ln D_r}{p}\right] = -xk_\mathrm{B}T\left[\frac{\ln \eta}{p}\right] = xV_\eta \tag{5}$$

This linear relation combines both experimental quantities $\Delta V^\ddagger_{obs}$ and V_η. The slope of such a plot is directly given by the exponent x of the fractional SED-relation, an empirical quantity normally obtained by fitting experimental and the theoretical SED-relations.

Figure 5 shows a plot according to eq 5 for TEMPO, TEMPOL, and ATEMPO in different RTILs. A slope of 1.1 ± 0.3 is found for the TEMPO probe in the investigated RTILs, and a slope of 1.0 ± 0.1 is found when all investigated substances and ILs are taken in consideration. This result indicates that in the frame of the experimental error there are no significant deviation from the SED behavior in pressurized ILs. A fractional dependence would result in $\Delta V^\ddagger_{obs} < V_\eta$ and $x < 1$. Investigations on temperature-dependent phase transitions, which may be also pressure dependent, are reported.[51−53]

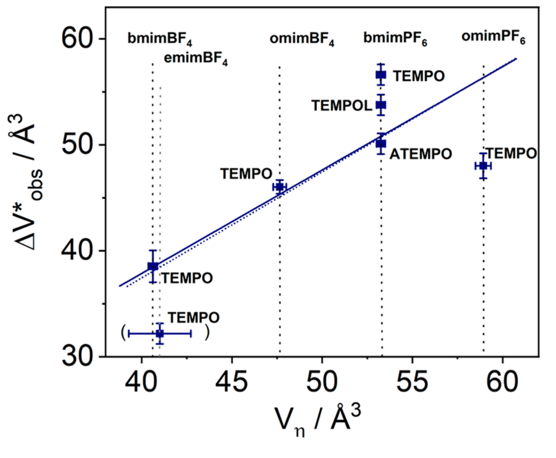


Figure 5. Plot of $\Delta V^\ddagger_{obs}$ vs V_η for the studied RTILs and spin labels. Dashed line corresponds to a slope of 1.

The quantity $\Delta\Delta V$ presented in Table 4 gives the relative deviation of $\Delta V^\ddagger_{obs}$ from V_η. For TEMPO ΔΔV does not correlate with viscosity η (see Table 4). For various probe molecules in bmimPF$_6$, ΔΔV decreases with increasing acceptor strength of the 4-substituent. For ATEMPO, a beginning decoupling of η and τ_r can be realized, which leads to a pronounced fractional SED-behavior. This is a likely consequence of the of the acceptor properties of the amino-group in the 4-position.

The agreement between experimental rotational correlation times and predictions based on the Stokes−Einstein−Debye relation appears surprising in view of the combined scientific literature so far. Many publications have documented deviations from Stokes−Einstein and Stokes−Einstein−Debye (SED) relations in pure ionic liquids and ionic liquid/solvent mixtures. Often these deviations are ascribed to strong solvent−solute interactions and/or differences in size and shape of the RTIL constituents and the molecules investigated.[54−59] On the other hand, the SED is based on continuum hydrodynamics and applies to large solutes immersed in a homogeneous environment. In fact, already Einstein pointed out that there is little reason to apply SED-like equations on the molecular scale.[60] In view of these observations, our findings of SED-behavior in pressurized room temperature ionic liquids are unforeseen, both generally and in the present RTIL context, for which RTIL constituents and spin probes are clearly of comparable size and strongly interacting.

■ CONCLUSIONS

In this study, we have shown for first time that the rotational correlation times for the spin labels TEMPO, TEMPOL, and ATEMPO in several imidazolium-based ionic liquids depend linearly on the pressure. The Stokes−Einstein−Debye relation is fulfilled, which means the correlation times τ_r are directly proportional to the viscosity η of the RTILs and no fractional correction of the SED-relation is necessitated. From experimental plots of V_{obs} versus V_η, x is found to be equal to 1. For the TEMPO radical, the quantity $\Delta\Delta V$ (%) is not related to the RTIL viscosity η. In bmimPF$_6$, $\Delta\Delta V$ decreases with increasing acceptor properties of the substituent in the 4-position. For ATEMPO, the viscosity η increases more strongly with pressure than the correlation time τ_r, indicating the beginning decoupling of η and τ_r, leading to a fractional SED-behavior.

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Author Contributions

§The manuscript was written through contributions from all authors. All authors have given approval to the final version of the manuscript. B.Y.M.K. and D.R.K. contributed equally.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

SED, Stokes–Einstein–Debye; ESR, electron spin resonance; RTIL, room temperature ionic liquid; TEMPO, 2,2,6,6-tetramethylpiperidine 1-oxyl; TEMPOL, 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl; ATEMPO, 4-amino-2,2,6,6-tetramethylpiperidine 1-oxyl

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