

EPR Study of Rotational Diffusion in Viscous Ionic Liquids: Analysis by a Fractional Stokes–Einstein–Debye Law

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Rotational correlation time (τ_c) of nitroxide radical solute was determined in ionic liquids by utilizing CW EPR spectroscopy. The experimental values of τ_c determined in viscous ionic liquids disagree with the values calculated according to Stokes–Einstein–Debye (SED) equation. A fractional SED law was examined for these solute–solvent combinations.

Air- and water-stable room-temperature ionic liquids (RTILs) which are composed entirely of ions have been attracting much interest as a new series of solvents^{1,2} with physical/chemical properties such as high viscosity, low vapor pressure, and wide electrochemical window. One interesting aspect of RTILs is that the solvent properties can be controlled by choice of cation and anion components. Recently, RTILs with paramagnetic ions have been developed as paramagnetic liquids. Magnetic properties of several paramagnetic RTILs with anions of FeCl_4^- and nitroxide radicals have been investigated.^{3,4} To understand these solvent properties, diffusion motion of solvent molecules should be studied. Since the paramagnetic ionic liquids are EPR-sensitive materials, EPR linewidth analysis may give us some information on exchange processes among paramagnetic ions through translational diffusion. Rotational correlation time (τ_c) of ions is also important to understand solvent properties. Recently, the τ_c values of diluted radicals or triplet in RTILs have been measured by EPR spectroscopy.^{5–8} The results were discussed based on fractional Stokes–Einstein–Debye (SED) equation,

$$\tau_c = (4\pi r^3/3k_B) \times (\eta/T)^t \quad (1)$$

where r is hydrodynamic radius of the spherical solute and t , a fractional parameter, is typically unity. One prominent characteristic of RTIL is high viscosity, which may require a correction for conventional SED equation, namely, $t \neq 1$. In this study, we determined the τ_c values of a couple of proxyl radicals (CProxyl[−] and CProxylH)⁹ in RTILs at various temperatures and evaluated the fractional parameters accurately. To examine rotational motion of organic ion species, we synthesized a novel paramagnetic ionic liquid, BmimCProxyl.⁹ The cation part of Bmim⁺ is nonparamagnetic, and the same chemical species as all the solvent RTILs is used here (BmimPF₆ and BmimBF₄).

The synthetic procedure is briefly described below. CProxylH and Ag₂O in distilled water were stirred at 298 K for 24 h, and the resultant aqueous solution was filtered to remove dissolved Ag₂O. BmimBr was added to the remaining aqueous solution until AgBr precipitation was not observed. After filtration, the remaining solution was heated at 310 K

under vacuum to remove water, and a yellow liquid containing BmimCProxyl was produced. The crude residue was dissolved in acetonitrile to remove remaining silver compounds. After the evaporation of acetonitrile, pure BmimCProxyl liquid was obtained. The IR and ¹H NMR spectra showed the product to be composed of Bmim⁺ and CProxyl[−]. As solvents we used two RTILs,⁹ BmimBF₄ and BmimPF₆ with measured shear viscosity, η of 86 and 243 cP at 298 K, respectively. All samples were stored in a high vacuum for 3 days to remove traces of oxygen and water, and optical cells containing sample solution were sealed before measurements. Viscosity was measured by a rotational viscometer (Brookfield, a DV-II+Pro) with cones and plate geometry for a temperature range of ca. 298–310 K. RTILs were purchased from Kanto Kagaku. EPR spectra were recorded by an X-band EPR spectrometer (Bruker, ELEXIS 580E).¹⁰

For EPR measurements, we prepared samples of diluted radicals in RTILs (ca. 2 mM, $M = \text{mol dm}^{-3}$). Figure 1 shows a typical EPR spectrum which was measured for CProxylH radical. The τ_c values of radicals were determined by the analyses of a series of EPR spectra using an expression,¹¹

$$\tau_c = 6.0 \times 10^{-10} \{ (h_0/h_{-1})^{1/2} + (h_0/h_1)^{1/2} - 2 \} \Delta H_{pp}(0) \quad (2)$$

where hm_1 is the intensity of the EPR line for each nuclear spin component of N atom ($m_1 = 0, \pm 1$) and $\Delta H_{pp}(0)$ is the linewidth of the $m_1 = 0$ line as defined in Figure 1. A coefficient of $6.0 \times 10^{-10} \text{ s Gauss}^{-1}$ in eq 2 is derived using the N-atom hyperfine coupling constants of TEMPO.^{7,9} We derived the τ_c values (7×10^{-10} – $2 \times 10^{-9} \text{ s}$) as a function of temperature in the 293–313 K range, and the Arrhenius plot gave us the activation energies, which are listed in Table 1. The E_a (EPR) values determined by EPR were ca. 13–14 kJ/mol lower than calculated E_a (SED) based on SED equation with $t = 0$ and temperature-

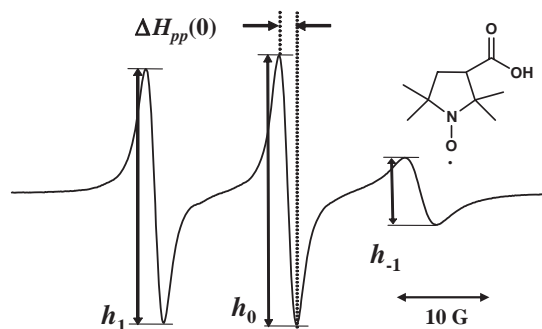
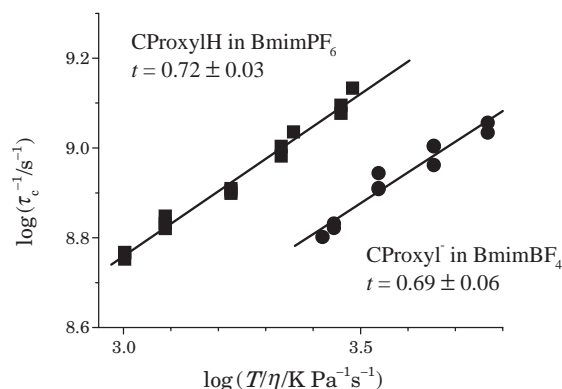


Figure 1. EPR spectrum of CProxylH (ca. 2 mM) in BmimPF₆ at 303 K.

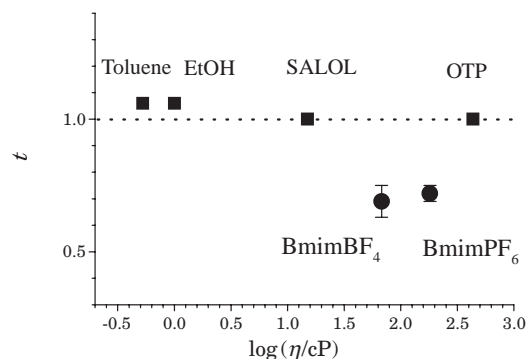
Table 1. Activation energies (kJ mol^{-1}) for rotational diffusion motion derived from the correlation times

	E_a (EPR)	E_a (SED)
CProxylH in BmimPF ₆	34.2 ± 1.2	46.9 ± 0.7
CProxyl [−] in BmimBF ₄	27.6 ± 2.3	41.3 ± 0.2

**Figure 2.** $\log(\tau_c^{-1})$ vs. $\log(T/\eta)$ plots in RTILs.

dependent η values. The result leads us to conclude that the conventional SED equation does not hold in these solvents. For the other samples (CProxyl[−] in BmimPF₆, and CProxylH in BmimBF₄), EPR lines were not well fitted by Lorentzian function, and, therefore, we refrained from analyzing them in this study. Then, we plotted the $\log(\tau_c^{-1})$ vs. $\log(T/\eta)$ relation, as shown in Figure 2 to determine parameter t referring to eq 1. The fractional parameter turns out to be ca. 0.7 in BmimBF₄ and BmimPF₆. In order to find a general trend in the t – η relation, we plotted the parameter t vs. $\log(\text{viscosity})$ as shown in Figure 3. In addition to the present data, we also plotted values for rotation of nitroxide radicals obtained from the literature^{12–14} where rotational motions were studied in organic solvents, toluene, EtOH (ethanol), OTP (*o*-terphenyl), and SALOL (phenyl salicylate). It is interesting that the t value in organic solvents remains essentially unit in a wide range of viscosity, $\eta \leq 435$ cP, which indicates that the rotational motion in organic solvents follows the SED equation regardless of the η value. On the other hand, the situation seems different in RTILs as clearly shown in Figure 3. The observation leads to a conclusion that the SED equation should be modified by introducing fractional parameter t of about 0.7. This indicates that solutes slip in these solvents during rotational motion. A similar conclusion has been reported for the rotation of TEMPO in supercooled liquids. The t values in the fractional SED equation have been determined to be 0.28 for OTP (<298 K)¹² and 0.46 for SALOL (<278 K)¹³ in which nonthermal dynamics are considered. BmimPF₆ and BmimBF₄ used in the present study are certainly different from supercooled solvents, and different rotation dynamics are expected to occur. To clarify the different rotational dynamics in RTILs and conventional organic solvent, further EPR studies are now in progress.

In summary, a paramagnetic ionic liquid, BmimCProxyl

**Figure 3.** Plot of t vs. $\log \eta$.

was synthesized, and by using BmimCProxyl and CProxylH as an EPR spectroscopy probe, the rotational motion was examined. Stokes–Einstein–Debye equation does not hold in viscous RTILs, BmimPF₆ and BmimBF₄. The solutes are thought to slip in these solvents during rotational motion.

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