CALIFORNIA STATE UNIVERSITY, NORTHRIDGE

NANOSTRUCTURAL ORGANIZATION OF IONIC LIQUIDS
INVESTIGATED BY 16 DSE NITROXIDE SPIN PROBE

A thesis submitted in partial fulfillment of the requirements
For the degree of Master of Science in Physics

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ABSTRACT

NONSTRUCTURAL ORGANIZATION OF IONIC LIQUIDS INVESTIGATED BY 16 DSE NITROXIDE SPIN PROBE

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Master of Science in Physics

16 - Doxyl-stearic acid methyl ester (16-DSE) nitroxide spin probe was used as a model of a long chain alkane to study the rotational diffusion of long chain alkanes in a series of 1-alkyl-3-methylimidazolium tetrafluoroborate room temperature ionic liquids (RTILs) with alkyl chain lengths from two to eight carbons. By applying nonlinear least-squares spectral fitting data analysis, we have obtained very precise values of the rotational correlation time and hyperfine coupling spacing of 16-DSE. Also, a power law function with a singular temperature, which is often used to fit physical quantities measured in supercooled liquids, was used to fit the rotational correlation time of 16-DSE in RTILs. Since the power law function fits the rotational correlation time data almost perfectly, it means $\eta/T$ s that the rotational correlation time of 16-DSE in RTILs exhibits a strong non-Arrhenius behavior similarly to the viscosity of RTILs. The rotational correlation time is a linear function of, where $\eta$ is the shear viscosity and $T$ is the temperature. The rotation of 16-DSE is faster than the one predicted by the Stokes-Einstein-Debye equation (SED), and the hydrodynamic radius of 16-DSE is solvent dependent. Using the rotational correlation time of a small, spherical nitroxide spin probe, perdeuterated 2,2,6,6-tetramethyl-4-oxopiperidine-1-
oxyl (pDTO), we were able to estimate the rotational correlation time of the alkyl chain of 16-DSE. The similarity of the rotational correlation times and the degree of anisotropy of the rotational motion in RTILs with alkyl chain lengths of six and eight carbons suggest the possible existence of large nonpolar nano-domains. The hyperfine coupling spacing of 16-DSE has the same temperature dependence in all four ionic liquids, and decreases with increasing alkyl chain length. When compared to the values of the hyperfine coupling spacing of 16-DSE in alcohols, those values indicate that the relative permittivity of RTILs are comparable to those of alcohols.
INTRODUCTION

A new class of solvents referred to as room temperature ionic liquids (RTILs) \(^1\) have recently attracted a high attention both in academia and industry due to their interesting and distinctive physicochemical properties. Ionic liquids are entirely made up of ions. Since they are usually composed of bulky and asymmetric cations with anions, which are poorly coordinated, their melting points are often below 373 K. The low melting points make RTILs a viable alternative to volatile organic solvents.\(^2\) RTILs have no measurable vapor pressure, low melting point, tunable viscosity, adjustable hydrophobicity and hydrophilicity, good conductivity, variable polarity and good thermal stability. These promising and useful features, offer a bright future for using these liquids as effective solvents.\(^2\)\(^-\)\(^3\) For example, having a negligible vapor pressure is considered as one of the most intriguing property of ionic liquids because it lowers the solvent’s flammability and the chances of atmospheric contamination, so they are sometimes called green solvents.\(^1\) Because the cation and anion components of the ionic liquids may be varied, the solvent properties could be optimizing for a wide range of applications. For that reason, RTILs have become the solvents of choice in many applications, such as nano-sized sensors, electrochemistry, organic synthesis, catalysis, ionic exchange and adsorption \(^1\) and are known as “designer solvents”.

Oil sands (tar sands and bituminous sands) contain a mixture of sand, clay, water and bitumen, a highly viscous and dense form of petroleum. Petroleum is mostly composed of a large variety of hydrocarbons, one of which are alkanes. As we know, petroleum can be refined into gasoline, diesel fuel, kerosene and jet fuel. Gasoline contains the alkanes from pentane to octane, while diesel fuel, kerosene and jet fuel contain the ones from nonane to hexadecane. Tar
sands represent two-thirds of the world’s oil reserves. Significant quantities of oil sands are found in Canada and Eastern Utah. A common process in recovering the bitumen from the Canadian oil sands is applying the process of warm water. The water is utilized to create a slurry consistency of the oil sand, which aids the process of extracting the oil from the sand. As a result, an oil containing froth consisting is formed, so that, the froth is easily extracted from the surface. However, the amount of bitumen recovered from the froth will be minimal due to the existence of mineral fines content. For example, problems can occur in processing the low-grade oil sands because of the high percentage of clay fines. Utah tar sands have a high viscosity bitumen compared to the Canadian oil sands, which has made it even harder to recover the bitumen using a hot water process. Recently, it has been shown that certain ILs can be used to extract bitumen from Canadian oil sands. The process involves mixing an oil sand sample with an ILs and a non-polar hydrocarbon solvent at room temperature. Once a multiphase system made up of a sand-clay slurry, an ILs layer and an organic non-polar solvent layer with the bitumen is formed, it is easy to separate the components and extract the oil.

Electron Paramagnetic Resonance (EPR) spectroscopy was discovered in Kazan State University by soviet physicist Yevgeny Zavoisky in 1944. This spectroscopic technique can be used in a wide range of areas such as biology, physics and chemistry. EPR comes in handy as a good spectroscopic technique for studying paramagnets, which consist of atoms and molecules with unpaired electrons, called free radicals. The occurrence of free radicals in nature is very low, because they can easily react with surrounding atoms and molecules. Fortunately, there are some stable versatile probes containing a free radical center, such as nitroxide spin probes. Nitroxide spin probes can be used as external probes in a variety of systems. Because those probes are usually
small molecules and can be used in small amounts, they minimally perturb their surroundings. For that reason, they are regarded as sensitive “reporters” of their environment.

In 1988, Oudard et al. ⁶⁻⁷ published two articles in which they used EPR spectroscopy to study the physicochemical properties of RTILs. Since then, the EPR nitrooxide spin probes technique has been used to study a wide range of the physicochemical properties of RTILs including polarity, ⁸⁻⁹ solvation, ¹⁰ rotational diffusion, ¹¹⁻¹³ and microheterogeneity. ¹¹, ¹⁴ Rotational and translational diffusion of 1-oxyl-2,2,6,6-tetramethyl-4-oxypiperidine (TEMPOL) nitroxide spin probe in the room temperature ionic liquid (RTIL) 1-octyl-3-methylimidazolium tetrafluoroborate ([C₈mim][BF₄]) has been published. ¹⁵ Evans et al. have studied the translational and rotational diffusion of the stable spin probe TEMPO (2,2,6,6-tetramethyl-4-oxypiperidine) in a series of RTILs. ¹¹ After comparing their EPR diffusion data to the diffusion data obtained by an electrochemical method, they found that the two of those RTILs have the rotational activation energies about 5 to 10 kJ mol⁻¹ lower than their viscous and translational activation energies. They suggested that these discrepancies might be caused by more order structures consisting of alternating polar and nonpolar regions in these RTILs. ¹¹

Also, Mladenova et al. ¹⁶ have studied four nitrooxide spin probes in four RTILs using EPR spectroscopy. They found that the rotational diffusion in the temperature range 280 to 380 K, was well described by the Stokes-Einstein-Debye equation (SED) equation. Specifically, they found that the rotational correlation time extracted from the C line width parameter was linear with η/T, where η is the shear viscosity and T is the temperature. Mladenova et al. also found that the activation energy of the probes’ rotational motion in each RTILs reasonably agreed with those of
RTILs viscous flow. In contrast, Miyake et al. have observed that the rotational correlation time of proxyl spin probes in $[C_2\text{mim}][\text{BF}_4]$ and $[C_4\text{mim}][\text{PF}_6]$ followed a fractional SED law in the same way as the rotation of TEMPO in supercooled liquids.

Because the value of the hyperfine coupling spacing of a nitroxide spin probe is very sensitive to the polarity of a solvent, it has been used to study the polarity of a number of RTILs. Recently, Merunka et al. have measured the rotational correlation time and hyperfine coupling spacing of the perdeuterated 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl (pDTO or pD-TEMPONE) in a series of 1-alkyl-3-methylimidazolium tetrafluoroborate RTILs with the alkyl chain length from two to eight carbons. The rotational correlation time of pDTO in RTILs, as well as their viscosity, were well described by a power law functionality with a singular temperature, which often describes a number of physical quantities measured in supercooled liquids. The authors also found that the apparent activation energy of both the rotational correlation time of pDTO and the viscous flow of RTILs exhibited strong non-Arrhenius behavior. The rotational diffusion of pDTO was a linear function of $\eta/T$, in other words, it obeyed the SED equation. As the number of carbons in the alkyl chain increased the value of the hyperfine splitting decreased due to the decrease in polarity of the solvent. From the uneven spacing of the rotational correlation time as a function of $\eta/T$ and the hyperfine coupling spacing as a function of $T$, as well as the equal values of the exponent in the power law equation for the RTILs whose alkyl chains have four or more carbons, Merunka et al. concluded that the structure of these RTILs was different from that of $[C_2\text{mim}][\text{BF}_4]$. In other words, the size of non-polar domains increases with increasing alkyl chain length. In addition, the temperature dependence of the rotational correlation
time of pDTO and the viscosity of RTILs, and a strong non-Arrhenius behavior indicate RTILs may have regions of distinct and interchanging dynamics.

This thesis aims to examine the rotational correlation time and hyperfine coupling spacing’s of Doxyl-stearic acid methyl ester (16-DSE) in a series of 1-alkyl-3-methylimidazolium tetrafluoroborate RTILs with the alkyl chain length from two to eight carbons. 16-DSE is a spin probe, which consists of a doxyl free radical at the 16-carbon of an 18-carbon alkyl chain, and as such, it is a good model of hexadecane which is a an alkane hydrocarbon with chemical formula $C_{16}H_{34}$. In the end of this study we expect to learn the following; how long alkanes solvate in RTILs, and how their solvation properties are affected by the nanostructural organization of RTILs.
THEORY

Electron Paramagnetic Resonance (EPR), also known as Electron Spin Resonance (ESR) spectroscopy is mainly focused on the interactions of unpaired electrons with their immediate surroundings and the measurements of the energy difference between the atomic or molecular states. Once the energy differences are known, one can obtain the knowledge of the identity, structure and dynamics of the atoms and molecules in the studied sample. 22 X-band EPR spectroscopy is a commonly used spectroscopic technique to study paramagnetic systems in the frequency range of 9-10 GHz.

The unpaired electron possess a magnetic moment, $\mu$, which is caused by its intrinsic properties of charge and spin. Most of the time, in EPR spectroscopy one deals with the spin magnetic moment $\mu_S$, because the angular magnetic moment of the electron’s orbits is quenched. When the spin magnetic moment is placed in an external magnetic field $B_0$, it will have two quantum states. In its state of lowest energy, the spin magnetic moment aligns with the external magnetic field. Since the electron has a spin of $\frac{1}{2}$, this parallel state is labeled by $M_S = -\frac{1}{2}$, where $M_S$ is the projection of $\mu_S$ on the direction of the magnetic field. Its second quantum state, when $\mu_S$ is aligned against the magnetic field, is a state of highest energy designated as $M_S = \frac{1}{2}$. If the direction of the z axis is along, the energy of $\mu_S$ in the magnetic field $B_0$, the magnetic energy of $\mu_S$

$$E = -\mu_z B_0 = \pm \frac{1}{2} g_e \beta_e B_0$$ (1)
where $\mu_z = - g_e \beta_e M_S$, $g_e$ is the electron g-factor and $\beta_e$ is the Bohr magneton. The g-factor for the free electron is 2.002319304386(20), and it is also approximately equal to 2 for most samples, but can vary depending on the electron configuration and surroundings of the radical. Since, the Zeeman effect is the splitting of a spectral line or lines into two or more spectral lines when the source is placed in a magnetic field, these energy levels are referred as the electronic Zeeman energies.

The interaction of the spin magnetic moment in an external field with an electromagnetic field of the appropriate frequency $\nu$, such that the energy $h\nu$ is equal to the energy difference between the two quantum states, induces transitions between the two electronic Zeeman energy levels

$$\Delta E = h\nu = g_e \beta_e B$$  \hspace{1cm} (2)

where $B$ represents the magnetic field that satisfies the resonance condition and it is called the “field for resonance.” In order to fulfill the resonance equation, one can either vary or sweep $\nu$ and the frequencies at which absorption occurs give the energy differences of the states. This approach is usually used in conventional spectroscopy. Since the energy difference between two states can be controlled by varying the magnetic field, equation 2, in EPR spectroscopy, the frequency of the electromagnetic field is held constant, while the magnetic field is swept. An EPR spectral line occurs when the energy of the radiation matches the energy difference between the two states, equation 2.

The unpaired electron, which produces the EPR spectrum, is usually part of a molecule or
Figure 1: (a) Energy levels and allowed EPR transitions for an \( S = \frac{1}{2}, I = 1 \) atom (nitrogen) for which \( A > 0 \). (b) First-harmonic EPR spectrum.

an atom. The nuclei in the atoms surrounding the unpaired electron often can have nuclear magnetic moments, which can interact with the spin magnetic moment of the electron; this interaction is called the hyperfine interaction. The hyperfine interaction gives a lot of information about the sample under study, such as the number and identity of atoms around the unpaired electron. It can also give us the distances of those atoms from the electron.\(^{22-23}\)

The nitrooxide spin probe has an unpaired electron and a nitrogen atom in its vicinity, Schemes 1 and 2. The nucleus of the nitrogen atom has a spin \( I = 1 \), which means that in an external magnetic field there are three allowed projections of the nuclear magnetic moment on the \( z \) direction, which is along the magnetic field. These projections are labeled by the values \( M_I = -1, M_I = 0 \) and \( M_I = 1 \), Figure 1a. The \( S = \frac{1}{2}, I = 1 \) quantum system in an external field has six energy levels. According to the selection rules \( \Delta M_S = \pm 1 \) and \( \Delta M_I = 0 \), only three transitions (resonances)
are allowed, Figure 1a. Figure 1b shows a typical first-derivative EPR spectrum in an increasing magnetic field. The resonance condition now includes the hyperfine coupling constant $A$, which measure the magnetic energy interaction between the unpaired electron and nucleus. The value of $A$ can be easily extracted from the first-derivative EPR spectrum, Figure 1b.

![Figure 2: X-band Bruker ESP 300E Spectrometer.](image)

An overview of the operation of an EPR spectrometer is provided as follows.  As shown in figure 2, the EPR spectrometer consists of three main parts: a source, which produces electromagnetic radiation, a sample, which is subjected to the radiation and a detector, which measures the amount of radiation that passes through the sample. The sample is located in a microwave cavity, which is a metal box that amplifies weak signals from the sample. The other crucial components of the EPR spectrometer are the microwave bridge and the EPR magnet. The
microwave bridge, which is a box, consists of a klystron, which is the electromagnetic radiation source and a detector, which is a Schottky Barrier diode. The klystron generates microwave radiation that travels through a waveguide to a variable attenuator where the intensity of the microwaves is reduced. In the next step, the microwaves arrive at a circulator where they are directed toward the microwave cavity containing the sample. The circulator is a device that redirects the microwaves at its ports. If there are no spectroscopic transitions the incident microwave radiation is completely stored in the microwave cavity, which is a microwave analog of RCL resonant circuit consisting of a resistor (R), an inductor (L) and a capacitor (C). When the sample absorbs microwave energy due to spectroscopic transitions, some of the incident radiation is reflected. The circulator directs this reflected radiation only to the detector and not back to the microwave source. Since the reflected power is caused by the spectroscopic transitions in the sample, the detector converts the reflected microwaves in an EPR spectrum.
MATERIALS AND METHODS

The nitroxide spin probe used in this work was 16-Doxy1-stearic acid methyl ester (16-DSE, also called 2-Ethyl-2-(15-methoxy-15-oxopentadecyl)-4,4-dimethyl-3-oxazolidinylloxy, free radical). 16-DSE was purchased from Sigma-Aldrich and was used as received. The structure formula of 16-DSE is shown in Scheme 1, while Figure 3 shows its three dimensional structure. Due to its unpaired electron that is located on the N-O bond, Scheme 1, 16-DSE is a good spin probe to explore solvents with hydrocarbon domains. One can also notice in Scheme 1 and Figure 3 that the nitroxide moiety is close to the end of 18 carbon alkyl chain. Based on this, the motion of the alkyl chain end will influence the motion of the probe, and because of this effect, we will be able to measure the rotational motion the alkyl chain end.

Scheme 1: 16 - Doxyl-stearic acid methyl ester (16-DSE)

1-Ethyl-3-methyl-imidazolium tetrafluoroborate [C\textsubscript{2}min][BF\textsubscript{4}] (Figure 4), 1-butyl-3-methylimidazolium tetrafluoroborate [C\textsubscript{4}min] [BF\textsubscript{4}] (Figure 5), and 1-hexyl-3-methylimidazolium tetrafluoroborate [C\textsubscript{6}min] [BF\textsubscript{4}] (Figure 5) were purchased from TCI America and were used as received. 1-Methyl-3-octylimidazolium tetrafluoroborate [C\textsubscript{8}min] [BF\textsubscript{4}] (Figure 6) was purchased from IoLiTec Ionic Liquids Technologies and was used as received. One can observer that each
RTILs molecule consists of a cation and an anion. The bulky and asymmetric cation, consisting of a charged imidazolium molecule (part with two nitrogen atoms colored dark blue) in Figures (4 - 6) is of variable (scalable) size, while the small inorganic tetrafluoroborate anion (part with a fluorine atom colored dark green) remains the same size in all four RTILs.

**Figure 3:** 16 - Doxyl-stearic acid methyl ester (oxygen (red); nitrogen (dark blue); carbon (gray) and hydrogen (light blue)
Figure 4: 1-Ethyl-3-methylimidazolium tetrafluoroborate ([C$_2$min] [BF$_4$]). fluorine (yellow green); boron(green); nitrogen (dark blue); carbon (grey) and hydrogen (light blue).

Figure 5: 1-Butyl-3-methylimidazolium tetrafluoroborate ([C$_4$min] [BF$_4$]); fluorine (yellow green); boron (green); nitrogen (dark blue); carbon (grey) and hydrogen (light blue).
Figure 6: 1-Hexyl-3-methylimidazolium tetrafluoroborate ([C₆min][BF₄]); fluorine (yellow green); boron (green); nitrogen (dark blue); carbon (grey) and hydrogen (light blue).

Figure 7: 1-Octyl-3-methylimidazolium tetrafluoroborate ([C₈min][BF₄]); fluorine (yellow green); boron (green); nitrogen (dark blue); carbon (grey) and hydrogen (light blue).
The present work aims to measure the similarity between the rotational motion of 16-DSE and the rotational motion of the small spin probe perdeuterated 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl (pDTO or pD-TEMPONE) in a series of ionic liquids. Therefore, the structure formula of pDTO is illustrated in Scheme 2. The rotational correlation time of pDTO from reference will be used to extract the rotational correlation time of the carbon alkyl chain end in 16-DSE.

![Scheme 2](image)

**Scheme 2**: Perdeuterated 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl (pDTO or pD-TEMPONE).

In this experiment, four samples of ionic liquids containing a concentration of 0.2 mM of 16-DSE, accurate to about 2%, were drawn into 50 μl capillaries (radius of ~ 450 μm) which were then sealed at both ends by an open flame. The low concentration of 16-DSE ensures that there is no EPR line broadening and dispersion in the EPR spectrum due to Heisenberg spin exchange and dipole-dipole interactions, which can distort the values of the rotational correlation time and hyperfine coupling constant of 16-DSE. Each sample tube was inserted in a quartz tube (bought from Wilmad Glass company), which was then placed into the EPR cavity of a Bruker ESP 300E spectrometer, Figure 2, equipped with a Bruker variable temperature unit (Model B-VT-3000). In order to make sure that the sample temperature was stable within ± 0.5 K, the temperature equilibration time at each temperature was about 5 minutes. The sample temperature was
monitored with a thermocouple manufactured by Bailey Instruments, which was connected to an Omega temperature indicator. The tip of the thermocouple was placed just above the active portion of the microwave cavity. Five first-harmonic EPR spectra were recorded in the temperature range from 293 to 393 K with intervals of 5 K. The EPR spectra were measured employing a sweep time of 60 s; time constant, 40 ms; microwave power, 5 mW; and sweep width, 50 G. The modulation frequency was 100 kHZ, while the modulation amplitude was set at 1.0 G, comparable to the minimum observed total line widths. The EPR spectrometer was controlled and run by EWWIN 2012 EPR software (Scientific Software Services), while the acquired EPR spectra were analyzed with the homemade computer program Lowfit.

In our experiment, the EPR spectra of the 16-DSE nitroxide spin probe consist of three well-resolved hyperfine EPR lines due to the coupling of the unpaired electron spin with nitrogen nucleus spin (see Figures 1 and 2). The widths and heights of the EPR lines are in most cases affected by the fluctuations of the anisotropic terms in the magnetic Hamiltonian caused by the molecular motion. The EPR lines are narrow and tall for rapid motion, but as motion slows down, they become broader and shorter. The amplitude of the frequency fluctuations is characterized by the mean square value of the anisotropic magnetic interactions, while the coherence of the fluctuations is given by the rotational correlation time $\tau_R$ of the random motion.\(^5\) The rotational correlation time can be viewed as a measure of the length of time over which the probe remains in a given orientation. The data analysis of EPR line shape and line widths can be performed in terms of a rotational correlation time $\tau$.\(^5, 24\) The peak-to-peak Lorentzian line width, $\Delta B_m^L$ can be expressed as

$$\Delta B_m^L = A + B_m + C_m^2$$

(3)
where \( m \) is the \( m \)th component of the nitrogen nuclear spin. \(^{35} A \) is the Lorentzian line width of the central line, \( m_1 = 0 \), thus it is derived from the motional modulation of the anisotropic Zeeman and the hyperfine interaction. \( B \) and \( C \) are associated with rotational motion of the probe and are given by

\[
B = 0.103\omega_e \left[ \Delta g \Delta A + 3(\delta g)(\delta A) \right] \tau_B \left( 1 + \frac{3}{4} \frac{1}{1 + \omega_e^2 \tau_B^2} \right)
\]

(4)

\[
C = (1.81 \times 10^6) \left[ (\Delta A)^2 + 3(\delta A)^2 \right] \tau_c \left( 1 - \frac{3}{8} \frac{1}{1 + \omega_N \tau_C^2} - \frac{1}{8} \frac{1}{1 + \omega_e^2 \tau_C^2} \right)
\]

(5)

where \( \Delta A = A_{zz} - \left( \frac{1}{2} \right)(A_{xx} + A_{yy}) \), \( \delta A = \left( \frac{1}{2} \right)(A_{xx} - A_{yy}) \) and \( A_{xx}, A_{yy} \) and \( A_{zz} \) are the principal values of the hyperfine tensor. \( \Delta g \) and \( \delta g \) are given in the similar way. \( \omega_N = (8.8 \times 10^6) A_N \), where \( A_N \) is the isotropic hyperfine splitting and \( \omega_e \) is the EPR spectrometer frequency.

When the values of \( \tau \) range from 0.05 to 1 ns, Equations 4 and 5 take the simple linear form

\[
\tau_B = \frac{1}{0.103\omega_e \left[ \Delta g \Delta A + 3(\delta g)(\delta A) \right]} B = k_B B
\]

(6)

\[
\tau_C = \frac{8/5}{(1.81 \times 10^6) \left[ \Delta g \Delta A + 3(\delta g)(\delta A) \right]} C = k_C C
\]

(7)

The values of the principal components of \( A \) tensor for 16-DSE are \( A_{xx} = 5.5 \) G, \( A_{yy} = 5.5 \) G and \( A_{zz} = 33 \) G, while the values of the principal components of \( g \) tensor are are \( g_{xx} = 2.0094 \), \( g_{yy} = 2.0060 \) and \( g_{zz} = 2.0023 \). Using these values and assuming the magnetic field to be 3330G, we get \( k_B = -1.11 \) and \( k_C = 1.169 \).
The first-derivative experimental EPR spectrum of a nitroxide spin probe described in terms of measurable quantities is best represented by the following simple analytical form.

\[ Y(B) = \sum_{M_I} \left( V_{pp}(B) S_{M_I}(B) + V_{disp}(M_I) D_{M_I}(B) \right) \]  

Equation 8 is used in the homemade non-linear EPR spectral line fitting program Lowfit, which is used to analyze the EPR data. \( V_{pp} \) is the peak-to-peak amplitude of the absorption EPR lines, \( V_{disp} \) is the maximum height of the dispersion EPR lines, while \( B \) is the swept magnetic field. \( S_{M_I}(B) \) and \( D_{M_I}(B) \) are the absorption and dispersion parts of the EPR lines, respectively. The sum is over the nitrogen nuclear quantum number \( M_I = +1, 0, -1 \), which correspond to the low-, central- and high-field EPR lines. In particular, \( S_{M_I}(B) \) is a Gaussian-Lorentzian sum function, which approximates the Voigt EPR line shape extremely well, while \( D_{M_I}(B) \) is represented as a Lorentzian only. The Voigt EPR line shape is caused by inhomogeneous broadening due to unresolved deuterium hyperfine interaction. For that reason, the EPR Voigt line widths extracted from the EPR spectrum cannot be used in Equation 6 to calculate \( \tau_R \). Instead, we have to use the mixing parameter contained in the sum function to extract the Lorentzian and Gaussian contributions to the line widths. Once we have extracted the Lorentzian line widths we can calculate the rotational correlation time \( \tau_R \) according to the procedure outlined in Equations 6 to 10. Since Lowfit give very precise values of EPR line field positions, we can calculate the hyperfine coupling spacing \( A_{abs} \), which is half the distance between the resonance fields of the outer lines of the EPR absorption component.
RESULTS AND DISCUSSIONS

Figure 8 (a) shows an experimental spectrum of 0.2 mM of 16-DSE nitroxide spin probe in [C₆mim][BF₄] at 75 °C. In fact, the nonlinear least squares fit is superimposed on the spectrum to show the goodness of the fit. The goodness of the fit can also be seen in the residual (d), which is almost a straight line. The weak lines in the residual, Figure 8 (d), are due to the natural abundance of ¹³C in the probe, and are not included in the fitting function. The fit is the sum of the absorption (b) and dispersion (c) spectral components.

![Figure 8](image_url)

**Figure 8.** (a) EPR experimental spectrum (blue line) and its fit (red line) of 0.2 mM 16-DSE in [C₆mim][BF₄] at 75 °C. The nonlinear least squares fit is indistinguishable from the spectrum. The absorption (b) and dispersion (c) components of the fit. The dispersion contribution to the spectrum is negligible, which implies that there is no Heisenberg spin exchange. (d) The difference between the experimental spectrum and the fit. ΔBₚₚ is the peak to peak observed line width. 2Aₐₚ is the distance between the resonance fields of the outer lines of the absorption component.
All the fitting parameters necessary for the data analysis, such as the absorption hyperfine coupling constant, \( A_{\text{abs}} \), and the Lorentzian line widths, \( \Delta B_{\text{pp}}^L (m) \), are extracted from the absorption EPR spectrum, Figure 8 (b). Note that \( A_{\text{abs}} \), is defined to be one-half of the difference in the resonance fields of the high- and low-field absorption lines. The value of \( A_{\text{abs}} \) is sensitive to the nature of molecules in the probe’s surroundings, and as such, it is a good measure of the polarity of a solvent. The fact that the dispersion contribution in the EPR spectrum is negligible means that there are no Heisenberg spin exchange collisions and dipole-dipole interactions, which, when present, can produce EPR line broadening and can distort the value of the rotational correlation time.

Figure 9: Rotational correlation time \( \tau_R \) of 16-DSE versus temperature in [C\text{6}mim][BF\text{4}] (■), [C\text{8}mim][BF\text{4}] (●), [C\text{6}mim][BF\text{4}] (■). The solid lines are fits to \( \tau_R = \tau_{R0} [T/T_0 - 1]^{-\gamma} \), and the fitting parameters are given in Table 1.
The rotational correlation time $\tau_R$ is the time that takes a spin probe to rotate through an angle of one radian and it depends on the probe's size, shape and dynamics. Figure 9 shows the mean rotational correlation time, $\tau_R = (\tau_C \tau_B)^{1/2}$, of 16-DSE free radical as a function of temperature in the four ionic liquids; $\tau_C$ and $\tau_B$ are calculated from Equations 6 and 7, respectively. The lines through the data in Figure 9 are fits to the power law

$$\tau_R = \tau_{R0} \left( \frac{T}{T_0} - 1 \right)^{-\gamma} \quad (9)$$

where $\tau_{R0}$ and $\gamma$ are constants and $T_0$ is a thermodynamic singular temperature. Speedy and Angell\textsuperscript{30} showed that equation 9 with $T_0 = 228$ K fits very well a variety of physical quantities in normal and supercooled water in the temperature range -38 to 150 °C. The same equation has been successfully used to study the rotational correlation time of pDTO in the same series of 1-alkyl-3-methylimidazolium tetrafluoroborate RTILs and squalene,\textsuperscript{20} as well as in normal and supercooled water.\textsuperscript{31} One can also observe, the longer the hydrocarbon chain in RTILs, the longer the rotational correlation time as it has been reported previously.\textsuperscript{12,20}

One can see in Figure 9 that $\tau_R$ of 16-DSE in the RTILs is described reasonably well by equation 9 with the same value of $T_0 = 228$ K; the parameters of the fits and correlation coefficients are presented in Table 1. Even when we fit all three parameters in equation 9, the correlation coefficients are the same, and values of $T_0$ are very close to 228 K, see last column in Table 1. It is interesting that when the literature data for the viscosity of $[C_2\text{mim}][BF_4]$, $[C_4\text{mim}][BF_4]$, $[C_6\text{mim}][BF_4]$ and $[C_8\text{mim}][BF_4]$ are fitted to equation 9 assuming $T_0 = 228$ K, one gets very good fits too.\textsuperscript{20}
Table 1: Power Law \( \tau_R = \tau_{R0} [T/T_0 - 1]^\gamma \) Parameters for Ionic Liquids

<table>
<thead>
<tr>
<th></th>
<th>( \tau_{R0}, \text{ns} )</th>
<th>( \gamma )</th>
<th>( R )</th>
<th>( T_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([ \text{C}_2\text{mim} ] [\text{BF}_4])</td>
<td>0.01293± 0.00009</td>
<td>3.207±0.007</td>
<td>0.999</td>
<td>224±2</td>
</tr>
<tr>
<td>([ \text{C}_4\text{mim} ] [\text{BF}_4])</td>
<td>0.0147± 0.0001</td>
<td>3.68±0.01</td>
<td>0.999</td>
<td>225±3</td>
</tr>
<tr>
<td>([ \text{C}_6\text{mim} ] [\text{BF}_4])</td>
<td>0.00876± 0.00004</td>
<td>4.559±0.006</td>
<td>0.999</td>
<td>239±2</td>
</tr>
<tr>
<td>([ \text{C}_8\text{mim} ] [\text{BF}_4])</td>
<td>0.00907± 0.00006</td>
<td>4.756±0.008</td>
<td>0.999</td>
<td>227±3</td>
</tr>
</tbody>
</table>

The values of \( \gamma \) for \( \tau_R \) of 16-DSE from Table 1 and the values \( \gamma \) for \( \tau_R \) of pDTO, Table 1 in reference\(^{20}\), and the values \( \gamma \) for the viscosity \( \eta \) of RTILs, are presented in Table 2. The values of \( \gamma \) for 16-DSE are greater than the values of \( \gamma \) for pDTO and the viscosity of RTILs for all four ionic liquids. In the case of pDTO, the temperature functional dependence of \( \tau_R \) and \( \eta \) are very similar, while in the case of 16-DSE the higher \( \gamma \) values mean that the apparent activation energy of \( \tau_R \) changes faster with temperature than the apparent activation of viscosity.\(^{20}\) A possible explanation for this effect is that the doxyl nitroxide of 16-DSE does not sense the polar and nonpolar regions of RTIL equally like pDTO and that is due to 16-DSE spin probe’s hydrocarbon tail which mostly resides closer to the nonpolar regions. Since the nonpolar regions exhibit more swelling as the length of the alkyl tail increases,\(^{22}\) the change of the apparent activation energy of \( \tau_R \) is faster than the change of the viscosity, which is a macroscopic quantity.

Table 2: Comparison of \( \gamma \) Parameters for \( \tau_R - 16 \) DSE, \( \tau_R - pDTO \) and \( \eta \) for Ionic Liquids

<table>
<thead>
<tr>
<th></th>
<th>( \gamma ) for ( \tau_R - 16 ) DSE</th>
<th>( \gamma ) for ( \tau_R - pDTO )</th>
<th>( \gamma ) for ( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([ \text{C}_2\text{mim} ] [\text{BF}_4])</td>
<td>3.207±0.007</td>
<td>2.965±0.007</td>
<td>2.57±0.02</td>
</tr>
<tr>
<td>([ \text{C}_4\text{mim} ] [\text{BF}_4])</td>
<td>3.68±0.01</td>
<td>3.564±0.009</td>
<td>3.59±0.03</td>
</tr>
<tr>
<td>([ \text{C}_6\text{mim} ] [\text{BF}_4])</td>
<td>4.559±0.006</td>
<td>4.080±0.009</td>
<td>4.16±0.003</td>
</tr>
<tr>
<td>([ \text{C}_8\text{mim} ] [\text{BF}_4])</td>
<td>4.756±0.008</td>
<td>4.33±0.01</td>
<td>4.35±0.01</td>
</tr>
</tbody>
</table>
Figure 10: Rotational correlation time $\tau_R$ of 16-DSE alkyl chain versus temperature in $[C_2\text{mim}] [\text{BF}_4]$ (●), $[C_4\text{mim}] [\text{BF}_4]$ (■), $[C_6\text{mim}] [\text{BF}_4]$ (◆), $[C_8\text{mim}] [\text{BF}_4]$ (▲).

Figure 10 shows the 16-DSE hydrocarbon tail rotational correlation time $\tau_R$ values varied as a function of temperature. The experimental value of the rotational correlation time is determined by subtracting the rotational correlation time of 16-DSE in table 1 from pDTO. Since $\tau_R$ of 16-DSE is the sum of $\tau_R$ of the doxyl nitroxide and $\tau_R$ of the alkyl chain, it is easy to estimate $\tau_R$ of the alkyl chain, if $\tau_R$ of the doxyl nitroxide is known. Unfortunately, there are no measurements of $\tau_R$ of a neat doxyl nitroxide in RTILs, and this spin probe is not commercially available, so we are going to use $\tau_R$ of pDTO. Although, doxyl is a five membered carbon ring, while pDTO is a six membered carbon ring, one can argue that pDTO and doxyl are very similar; they are of similar size and chemical composition, so their rotational correlation times should be of the same order of magnitude. Figure 10 shows $\tau_R$ of 16-DSE alkyl chain versus temperature in $[C_2\text{mim}][\text{BF}_4]$,
[C₄mim][BF₄], [C₆mim][BF₄] and [C₈mim][BF₄]. The most interesting feature in Figure 10 is the overlapping of the τᵣ curves for [C₆mim][BF₄] and [C₈mim][BF₄].

Due to their amphiphilic character, RTILs can form polar and nonpolar domains, where nonpolar domains are made of alkyl chains, while the cations and anions make the polar domains. The molecular dynamics (MD) studies of n-alkylimidazolium RTILs indicates that their nanostructures depend on the length of the alkyl chain. When the alkyl chains are shorter than C₄, the electrostatic energy due to the interactions between anions and cations is more than the alkyl chain collective aggregation energy, so the RTILs molecules are distributed mostly homogeneously. As the alkyl chain length increases, the alkyl chains start to aggregate, forming nonpolar regions, permeating the three-dimensional network of anions and cation head groups. The rotational correlation time of the alkyl chain of 16-DSE, Figure 10, supports the aforementioned physical picture of polar and nonpolar domains for RTILs with the alkyl chain greater than C₄. In [C₆mim][BF₄] and [C₈mim][BF₄] the nonpolar domains are large enough to completely accommodate the C₁₆ alkyl chain of 16-DSE.
The rotational correlation time of 16-DSE can be related to the macroscopic shear viscosity of the solvent using the hydrodynamic SED relation

\[ \tau_R = \frac{4\pi r^3}{3k} \frac{\eta}{T} \]  

(10)

where \( T \) is the temperature, \( \eta \) shear viscosity, \( r \) is the radius of the probe and \( k \) is Boltzmann’s constant. The SED equation is usually used to describe the rotational motion of a spherical probe molecule in homogenous uniform solvent under the stick boundary conditions. \(^{33}\) The stick
boundary condition implies that at the surface of the probe the relative tangential velocity of the solvent molecules is zero. Unfortunately, the molecular probes are hardly ever spherical and the surrounding solvent are quite often non-homogeneous and non-uniform, thus the hydrodynamic theory cannot adequately predict the experimental molecular rotational correlation times. This means that the solvent molecules move relative to the surface of the probe, so it is necessary to introduce the slip boundary conditions in order to bring the hydrodynamic theory and experiment into agreement. It is common to assume that $r$ is equal to the van der Waals radius of the nitroxide spin probe, $r_{vdW}$. Very often, $r$ is different from $r_{vdW}$ and it is called the hydrodynamic radius. In other words, the hydrodynamic radius or the Stokes-Einstein radius (SED) of a solute is the radius of a hard sphere that diffuses at the same rate as the solute. The hydrodynamic radius is a measure of the influence of molecular shape on the viscosity dependence of rotation.

The hydrodynamic radii calculated from the slopes of the lines in Figure 11 using equation 10 are found to be 2.46 ± 0.06 Å in [C$_2$mim][BF$_4$], 2.31 ± 0.03 Å in [C$_4$mim][BF$_4$], 2.19 ± 0.05 Å in [C$_6$mim][BF$_4$], 2.01 ± 0.06 Å in [C$_8$mim][BF$_4$]. The solid black line in Figure 11 is the SED prediction for 16-DSE assuming $r_{vdW} = 3.5$ Å, which is radius of the doxyl nitroxide. As it can be seen in Figure 11, the doxyl nitroxide rotates much faster than predicted by Equation 10, which means that it experiences slip boundary conditions. As expected, the hydrodynamic radius decreases with increasing number of carbons in the RTILs alkyl chain. That is to say, the smaller the solvent molecule the better hydrodynamic behavior of 16-DSE is. The hydrodynamic of 16-DSE are bigger than the hydrodynamic of pDTO in the same RTILs, which are for pDTO 1.8 Å in [C$_2$mim][BF$_4$], 1.4 Å in [C$_4$mim][BF$_4$], 1.35 Å in [C$_6$mim][BF$_4$], 1.3 Å in [C$_8$mim][BF$_4$]. This difference is due to the influence of the alkyl chain on the rotation of the doxyl nitroxide.
Figure 1: $\tau_B/\tau_C$ versus temperature $T$ in [C$_2$ mim][BF$_4$] (●), [C$_4$ mim][BF$_4$] (■), [C$_6$ mim][BF$_4$] (◆), [C$_8$ mim][BF$_4$] (▲).

For rapid, isotropic motion, the values of $\tau_B$ and $\tau_C$ should be equal; that is their ratio should be equal to unity. $^{35}$ The deviation of the ratio of $\tau_B$ to $\tau_C$ from unity is a good measure of the degree of anisotropy of the rotational motion. Figure 12 shows $\tau_B/\tau_C$ versus $T$ in all the four ionic liquids. The rotation of 16-DSE in all four RTILs is anisotropic, and the degree of anisotropy changes with temperature. The degree of the anisotropy is the largest in [C$_2$ mim][BF$_4$], and decreases as the alkyl chain length increases. Also, the degree of anisotropy is the same in [C$_6$ mim][BF$_4$] and [C$_8$ mim][BF$_4$]. Again, a likely explanation for this behavior is the growth of nonpolar domains with the increasing number of carbons. In C$_2$ and C$_4$ RTILs, the polar and nonpolar domains are of similar size and are distributed more homogeneously. For that reason the NO moiety is very likely affected by both domains due to its unpaired electron. Therefore, the growth of the nonpolar domains changes the rotation of the chain end of 16-DSE. As the nonpolar
domains grow and become larger than the polar domains, 16-DSE is mostly in the nonpolar domains so the polar domains influence less its rotation. In addition, since the nitrooxide is mostly in the nonpolar domains, the rotation becomes more isotropic.

![Figure 13: Hyperfine coupling spacing $A_{abs}$ of 16-DSE versus temperature in $[C_2\text{mim}][\text{BF}_4]$ (●), $[C_4\text{mim}][\text{BF}_4]$ (▲), $[C_6\text{mim}][\text{BF}_4]$ (◆), $[C_8\text{mim}][\text{BF}_4]$ (■)]](image)

The hyperfine coupling spacing, $A_{abs}$, of the RTILs series versus temperature extracted by our homemade program Lowfit is shown in Figure 13. The relative permittivity $\varepsilon$ of an ionic liquid is inversely proportional to the size of its nonpolar domains; for example the value of $\varepsilon/\varepsilon_0$ at 278 K is 16.6 for $[C_2\text{mim}][\text{BF}_4]$, 14.4 for $[C_4\text{mim}][\text{BF}_4]$ and 11 for $[C_8\text{mim}][\text{BF}_4]$. Therefore, since the hyperfine coupling spacing is a good measure of polarity, it is not surprising that the value of $A_{abs}$ at a given temperature decreases with the increasing number of carbons in the alkyl
chain of the RTILs. It is also interesting to compare the values of $A_{\text{abs}}$ of 16-DSE measured in RTILs and alcohols$^{37}$ at 348 K, Table 3. One can observe that the values of $A_{\text{abs}}$ in alcohols and RTILs are close, though the values of $A_{\text{abs}}$ in RTILs change faster with the number of carbons in the hydrocarbon chain. This can be expected, because the size of the polar domains in alcohols are smaller due to the dynamics and structure of the alcohol molecules.

**Table 3:** Values of $A_{\text{abs}}$ of 16-DSE in RTILs and alcohols at 348 K

<table>
<thead>
<tr>
<th></th>
<th>$A_{\text{abs}}, G$</th>
<th></th>
<th>$A_{\text{abs}}, G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{[C}_2\text{mim}] [\text{BF}_4]$</td>
<td>14.8286 +/- 0.0005 Ethanol</td>
<td>14.8906 +/- 0.0004 Ethanol</td>
<td></td>
</tr>
<tr>
<td>$\text{[C}_4\text{mim}] [\text{BF}_4]$</td>
<td>14.7678 +/- 0.0006 Hexanol</td>
<td>14.7962 +/- 0.0006 Hexanol</td>
<td></td>
</tr>
<tr>
<td>$\text{[C}_6\text{mim}] [\text{BF}_4]$</td>
<td>14.7156 +/- 0.0012 Decanol</td>
<td>14.716 +/- 0.0012 Decanol</td>
<td></td>
</tr>
<tr>
<td>$\text{[C}_8\text{mim}] [\text{BF}_4]$</td>
<td>14.6631 +/- 0.0009</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CONCLUSIONS

The rotational correlation time of 16-DSE in RTILs can be described by equation 10 the same way as the rotational correlation time of pDTO. From $\tau_R$ of 16-DSE and pDTO we can estimate $\tau_R$ of the alkyl chain end of 16-DSE, which is about two and a half times longer than $\tau_R$ of pDTO. The temperature power dependence of $\tau_R$ implies that the rotational activation energy increases with decreasing temperature, in other words, it indicates non-Arrhenius behavior of all RTILs studied. The temperature dependence of $\tau_R$ and a strong non-Arrhenius behavior confirms the previous conclusion based on the temperature dependence and non-Arminius behavior of $\tau_R$ of pDTO in RTILs that RTILs may possess regions of distinct and interchanging dynamics. Also, the rotational correlation time of 16-DSE obeys the Stokes–Einstein–Debye law. From the ratio of $\tau_B$ to $\tau_C$ and the rotational correlation time of the alkyl chain end of 16-DSE one can conclude that when the number of C atoms in the alkyl chain of RTILs becomes greater than four, 16-DSE resides mostly in the nonpolar domains. This result suggests that [C$_6$ mim][BF$_4$] might be a preferred RTILs solvent for long chain hydrocarbons. The values of $A_{abs}$ in RTILs and alcohols indicate that the micro-polarities in both types of solvents, as sensed by the doxyl nitroxide, are comparable.
REFERENCES


(37) Singh, J.; Peric, M. to be published. 2016.