Published in final edited form as:

J Phys Chem B. 2015 February 19; 119(7): 3185–3193. doi:10.1021/jp512487y.

Study of Nanostructural Organization of Ionic Liquids by Electron Paramagnetic Resonance Spectroscopy

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Abstract

The X-band electron paramagnetic resonance spectroscopy (EPR) of a stable, spherical nitroxide spin probe, perdeuterated 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl (pDTO) has been used to study the nanostructural organization of a series of 1-alkyl-3-methylimidazolium tetrafluoroborate ionic liquids (ILs) with alkyl chain lengths from two to eight carbons. By employing nonlinear least-squares fitting of the EPR spectra, we have obtained values of the rotational correlation time and hyperfine coupling splitting of pDTO to high precision. The rotational correlation time of pDTO in ILs and squalane, a viscous alkane, can be fit very well to a power law functionality with a singular temperature, which often describes a number of physical quantities measured in supercooled liquids. The viscosity of the ILs and squalane, taken from the literature, can also be fit to the same power law expression, which means that the rotational correlation times and the ionic liquid viscosities have similar functional dependence on temperature. The apparent activation energy of both the rotational correlation time of pDTO and the viscous flow of ILs and squalane increases with decreasing temperature; in other words, they exhibit strong non-Arrhenius behavior. The rotational correlation time of pDTO as a function of η/T , where η is the shear viscosity and T is the temperature, is well described by the Stokes-Einstein-Debye (SED) law, while the hydrodynamic probe radii are solvent dependent and are smaller than the geometric radius of the probe. The temperature dependence of hyperfine coupling splitting is the same in all four ionic liquids. The value of the hyperfine coupling splitting starts decreasing with increasing alkyl chain length in the ionic liquids in which the number of carbons in the alkyl chain is greater than four. This decrease together with the decrease in the hydrodynamic radius of the probe indicates a possible existence of nonpolar nanodomains.

Graphical Abstract

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Notes

The authors declare no competing financial interest.

Supporting Information

Figures of an experimental EPR spectrum and its fit, and the absorption and dispersion components of the EPR lines, A_{abs} vs T for DTBN, pDTEMPO, pDTEMPOL and pDTO in water. Tables of fitted parameters of eq 5, A - and g -tensor principal values. Ionic liquids viscosity data. This material is available free of charge via the Internet at <http://pubs.acs.org>

Keywords

ionic liquids; EPR spectral fitting; Stokes-Einstein-Debye equation; supercooled liquids; nanodomains

Introduction

Ionic liquids (ILs) are substances usually made of poorly coordinated large ions whose melting temperatures are below 373 K. Because of the possibility of combining a large variety of anions and cations, one can design an enormous number of ILs, such that they are quite often called “designers solvents.”¹ Compared to common organic solvents, ILs have interesting and peculiar physicochemical properties, such as negligible vapor pressure, good electric conductivity, high viscosity, variable hydrophobicity and hydrophilicity,^{2–4} high thermal stability and negligible flammability.⁵ For those reasons, ILs can be used in a broad range of applications, such as organic synthesis,⁶ catalysis,^{7–8} adsorption, electrochemistry, analytical chemistry,⁹ ionic exchange, and synthesis of new nano-sized sensor systems.^{10–11}

Electron Paramagnetic Resonance (EPR) spectroscopy has been utilized in the studies of ILs since their discovery.^{5, 12–13} Specifically, the EPR nitroxide spin probe method has shown its usefulness in studying a wide range of the physicochemical properties of ILs. The hyperfine coupling spacing of a nitroxide spin probe is a good measure of the polarity of a solvent,¹⁴ and as such, it has been applied to study the polarity of a variety of ILs.^{15–18} Using the EPR spin probe method, Pergushov et al. have detected structural and dynamic heterogeneity in a 1-octyl-3-methylimidazolium tetrafluoroborate solution.¹⁹ In 1992, Noel et al.²⁰ studied the solvation of two nitroxide spin probes, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPAMINE), in ionic liquids. They have concluded that the solvation properties of ILs are similar to those of polar organic solvents such as dimethylformamide and dimethyl sulfoxide.²⁰ Recently, a new comprehensive study has been published on the solvation of three TEMPO based probes with different 4-position substituents: 4-R-2,2,6,6-tetramethylpiperidine-1-oxyl, where R is $\text{N}(\text{CH}_3)_3^+$ (CAT-1), COO^- (TEMPO-4-carboxylate) and OH^- (TEMPOL) in n-alkyl-imidazolium based ILs with different alkyl chain lengths and two different anions, BF_4^- and PF_6^- .²¹ The study's results support the view that ILs consist of polar and nonpolar domains, where the polar domains are made of anions and cations, while the alkyl chains form the nonpolar domains.

The rotational diffusion of nitroxide spin probes in ILs has been studied quite often^{17–18, 20–27} because of the fact that nitroxides are very “sensitive reporters” of their environment²⁸ and therefore can provide valuable information on ILs. Using a combined electrochemical and EPR spectroscopic approach, Evans et al.²² have studied the rotational and translational diffusion of the stable free radical TEMPO in five room temperature ILs. In three of the ILs studied they found that the activation energies of translation, rotation and viscosity are similar. In the remaining two ILs containing the tris(*n*-hexyl)tetradecylphosphonium cation, the rotational activation energies were about 5 – 10 kJmol^{–1} lower than the viscous flow and translational activation energies. The authors suggested that these two ILs might have more ordered structures consisting of alternating ionic and hydrocarbon regions.²² Strehmel et al.¹⁷ have investigated the rotational diffusion of TEMPO, TEMPOL and CAT-1 in a series of imidazolium based ILs bearing either [BF₄] or [PF₆] at 293 K. Since the authors did not observe Stokes Einstein behavior, they applied the Gierer and Wirtz theory²⁹ to find the influence of microviscosity on the dynamics of the spin probes. Their analysis indicated that the activation for the jump into the available free volume was negligible, which means that the activation of the viscous flow dominates in the investigated ILs.¹⁷ Recently, Mladenova et al.²⁶ have investigated the rotational correlation time of TEMPO, TEMPOL, TEMPAMINE and Fremy’s salt in 1-ethyl-3-methylimidazolium ethylsulfate, [C₂mim][ES], [C₂mim][BF₄], [C₄mim][BF₄], and [C₄mim][PF₆] in the temperature range from 280 to 380 K. The rotational correlation time of all the spin probes obeyed the extended Stokes-Einstein-Debye (SED) law, that is, it was a linear function of $\eta(T)/T$ and the hydrodynamic probe radii were smaller than the geometric radii of the probes. The activation energy for the probe’s rotational tumbling in each solvent were reasonably close to those of the ILs viscous flow.²⁶ On the other side, Miyake et al.²³ have observed that the rotational correlation time of proxyl radicals in [C₄mim][BF₄] and [C₄mim][PF₆] obeys a fractional SED law, which they compared with the rotation of TEMPO in supercooled liquids.

The nanostructural organization of *n*-alkyl-imidazolium ILs has been studied by molecular dynamics (MD) simulations.^{30–31} Those studies indicate that the nanostructure of *n*-alkyl-imidazolium ILs depends on the length of the alkyl chain. For ILs with short alkyl chains, less than C₄, cation headgroups and anions are homogeneously distributed³⁰ due to their electrostatic interactions. Since the alkyl chain collective aggregation energy is smaller than the electrostatic energy, the IL molecules are distributed mainly homogeneously. When the alkyl chain length becomes equal or longer to C₄, the alkyl chains start to aggregate, forming nonpolar domains, which permeate the tridimensional network of cation headgroups and anions.³¹

The present study intends to examine the rotational correlation time and hyperfine coupling spacings of perdeuterated 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl (pDTO) in a series of 1-alkyl-3-methylimidazolium tetrafluoroborate ILs with the alkyl chain length from two to eight carbons. By carrying out a careful EPR spectral data analysis, we attempt firstly to gain experimental evidence of long alkyl chain aggregation and secondly to find out how the rotational dynamics of a solute in ILs compare to that in supercooled liquids.

Materials and Methods

Materials

4-Oxo-2,2,6,6-tetramethylpiperidine- d_{16} -1-oxyl, perdeuterated-Tempone (pDTO - CDN Isotopes) and squalane (Acros Organics) were used as received. 1-Ethyl-3-methylimidazolium tetrafluoroborate ([C₂mim][BF₄]), 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄mim][BF₄]) and 1-hexyl-3-methylimidazolium tetrafluoroborate ([C₆mim][BF₄]) were purchased from TCI America and were used as received. 1-Methyl-3-octylimidazolium tetrafluoroborate (IoLiTec Ionic Liquids Technologies) ([C₈mim][BF₄]) was used as received. The concentration of pDTO in all samples was 0.2 mM. The samples were drawn into 50- μ L capillaries (radius $\approx$ 450 μ m), which were then sealed at both ends by an open flame. cw-EPR spectra were recorded with an X-band Bruker ESP 300E spectrometer equipped with a Bruker variable temperature unit. The sample temperature was measured with a thermocouple using an Omega temperature indicator and was maintained stable within ± 0.2 °C. To ensure uniform temperature of the sample, the temperature equilibration time at each temperature was taken for at least five minutes. Five first-harmonic EPR spectra were recorded at each temperature by setting the microwave power to 5 mW, sweep time to 84 s, time constant to 20.5 ms, modulation frequency to 100 kHz and modulation amplitude to 0.2 G. The spectra were then transferred to a personal computer and were analyzed using our home-written computer program Lowfit as detailed in previous publications.^{32–34}

We have measured the EPR spectra of pDTO in [C₈mim][BF₄] at 20 °C, $\tau_R = 0.988 \pm 0.011$ ns, as a function of microwave power in order to check the extent of power saturation broadening. In the range from 1 to 6.3 mW, we found the Lorentzian EPR pp line widths to be the same within the range of experimental error, having values of 1.115 ± 0.015 , 1.250 ± 0.019 and 2.89 ± 0.30 G, respectively. The sample saturated at 63 mW. Therefore, we believe that pDTO did not substantially saturate in the experiments, since almost all data have τ_R shorter than 1 ns. If we use the formula from Weil et al.³⁵, page 513, and assume that the microwave magnetic field is 0.251 G ($B_{1max} \approx k P_{max}$; $k \approx 1$), we get that T_1 is approximately 0.5 μ s; if we assume $k = 0.5$, we obtain $T_1 = 2$ μ s. If we calculate the Lorentzian EPR line width as a function of microwave power using these values, we observe good agreement with experimental data. Also, we verified the literature values and found that T_1 for different nitroxides having $\tau_R \approx 1$ ns is approximately 5 μ s.^{36–37} Obviously our estimate of T_1 is only as good as our estimate of B_1 , but we believe that it is within an order of magnitude of the correct value. Therefore, it looks like the values of T_1 in our cases are certainly less than $1/f_{mod} = 10$ μ s.

EPR Spectroscopy

The EPR spectrum of a nitroxide spin probe contains information on the structure and dynamics of the probe. The first-derivative field-swept EPR spectrum can be represented by

$$Y(B) = \sum_{M_I} (V_{pp}(M_I)S_{M_I}(B) + V_{disp}(M_I)D_{M_I}(B)) \quad (1)$$

where 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, and the sum in eq 1 is over the nuclear quantum number $M_I = +1, 0$, and -1 , which correspond to the low-, central, and high-field EPR lines, respectively. Since we expect the EPR lines to be slightly inhomogeneously broadened due to unresolved deuterium hyperfine interaction, $S_{M_I}(B)$ is Gaussian-Lorentzian sum approximation to Voigt EPR absorption and $D_{M_I}(B)$ is modeled as a Lorentzian only.^{38–39} The Gaussian dispersion shape is described by an integral form,⁴⁰ which requires a longer computational time. In the case of pDTO in [C₈mim][BF₄], the Gaussian line width is 0.20 ± 0.02 G and except for a few EPR spectra at low temperatures, most spectra do not have noticeable dispersion. For those reasons and the fact that there was no difference in the output line width parameters when replacing the Voigt dispersion by the Lorentzian dispersion,⁴¹ we decided to use the Lorentzian dispersion shape in the Lowfit analysis. The sum function contains a mixing parameter, which is used to extract the Lorentzian and Gaussian contributions to the line widths. V_{pp} is the peak-to-peak amplitude of the absorption and V_{disp} is the maximum heights of $D_{M_I}(B)$, where $D_{M_I}(B)$ consists of instrumental and sample dispersion. The instrumental dispersion is the same for all three lines. The sample dispersion can be induced by Heisenberg spin exchange (HSE) and dipole-dipole (DD) interactions^{32, 42–43} and is opposite for the low- and high-field lines. The HSE and DD induced dispersion can be used for separating the effects of HSE and DD interactions on EPR spectra of nitroxide spin probes in solution.⁴³ Even in the absence of HSE and DD, which is when the concentration of the spin probe is extremely low, the spectral fitting of the EPR lines still reveals the existence of dispersion in the EPR line shape. This dispersion contribution previously presented in Figure 12 of ref⁴³ and Figures S2–S4 in the Supporting Information could be explained by the Freed et al. approach⁴⁴ which is based on the stochastic Liouville equation and involves a relaxation matrix with all contributions: secular, pseudo-secular and non-secular. Mladenova et al.²⁶ also suggested that the dispersion signal is of pseudo-secular origin; in other words, from the off-diagonal contributions to the relaxation superoperator. For this reason, the height of the dispersion signal is directly proportional to the rotational correlation time; the longer the rotational correlation time, the greater the dispersion component in the EPR lines.

In the case of rotational frequencies much greater than magnetic anisotropies,⁴⁵ the peak-to-peak Lorentzian line width, ΔB_m^L can be expressed as:

$$\Delta B_m^L = A + Bm + Cm^2 \quad (2)$$

where m is the m th component of the nitrogen nuclear spin. A is the Lorentzian line width of the central line, $m_I = 0$, and it is determined by motional modulation of the anisotropic Zeeman and hyperfine interactions, as well as the spin rotational interaction. B and C are related to the rotational motion of the probe according to⁴⁶

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

$$C = 1.81 \times 10^6 [(\Delta A)^2 + 3(\delta A)^2] \tau_C \left(1 - \frac{3}{8} \frac{1}{1 + \omega_N^2 \tau_C^2} - \frac{1}{8} \frac{1}{1 + \omega_e^2 \tau_C^2} \right) \quad (4)$$

where $\Delta A = A_{zz} - \frac{1}{2}(A_{xx} + A_{yy})$, $\delta A = \frac{1}{2}(A_{xx} - A_{yy})$, and A_{xx} , A_{yy} and A_{zz} are the principal values of the hyperfine tensor. Similar expressions hold for the g -tensor. $\omega_N = (8.8 \times 10^6) A_N$, where A_N is the isotropic hyperfine splitting and ω_e is the EPR spectrometer frequency.

Results and Discussion

Rotational Correlation Time

The rotational correlation times of pD₂O, τ_R , as a function of temperature in the four ionic liquids and squalane, are shown in Figure 1. The solid lines through the data are fits to the power law^{47–49}

$$\tau_R = \tau_{R0} \left(\frac{T}{T_0} - 1 \right)^{-\gamma} \quad (5)$$

where τ_{R0} and γ are constants and T_0 is a thermodynamic singular temperature. Speedy and Angell⁴⁷ showed that eq 5 with $T_0 = 228$ K fits very well a variety of thermodynamic properties of liquid water in the temperature range -38 to 150 °C, that is, in the supercooled and normal range. We have recently measured the rotational correlation time of four small nitroxide spin probes in supercooled and normal water and have been able to fit them well to eq 5; all the correlation coefficients were 0.999.⁵⁰ As it can be seen in Figure 1, τ_R of pD₂O in the ILs and squalane is described reasonably well by eq 5 with the same value of T_0 ; the parameters of the fits and correlation coefficients are presented in Table 1. It can be noted that the longer the hydrocarbon chain of the IL is, the longer the rotational correlation time is, as has been previously observed.²⁴

The literature data for the viscosity of [C₂mim][BF₄] (Supporting Information Table S4), [C₄mim][BF₄] (Supporting Information Table S5), [C₆mim][BF₄] (Supporting Information Table S6), [C₈mim][BF₄] (Supporting Information Table S7) and squalane^{51–55} are presented in Figure 2. The solid lines are again fits to eq 5 assuming $T_0 = 228$ K; the parameters of the fits and correlation coefficients are presented in Table 2. When we fit all three parameters in eq 5, the correlation coefficients are the same (see Supporting Information – Tables S1 and S2), while the parameters are slightly more spread then in the case when $T_0 = 228$ K; the average of the values from Tables S1 and S2 is 227.4 K.

The mode coupling theory (MCT) was proposed to describe structural dynamics of supercooled liquids whose transport properties exhibit non-Arrhenius behavior.^{56–57} In MCT, the viscosity and diffusion as a function of temperature are well represented by eq 5, which can describe the increase of the time scale over 2–4 orders of magnitude. According to the spatially heterogeneous dynamics scenario for diffusion in supercooled liquids, the average local molecular motion displacements are different in different parts of the system and change with time, such that there are always clusters of molecules that are more mobile and clusters of molecules that are less mobile than the average molecule of the system.⁴⁸

The appearance and disappearance of these clusters in the system are governed by cooperative interactions. Ideally, if one could neglect activated processes in the system, then the effect of the cooperative interactions would be to freeze the system at T_0 since this cannot realistically be achieved, eq 5 is a good fit formula for transport properties only at $T > T_0$.⁵⁷ In other words, following Sciortino et al.,^{58–59} T_0 can be attributed to a “kinetic glass transition” where structural dynamics are arrested. Obviously, τ_R and η are described well by eq 5, but it is quite unexpected to observe the same T_0 . Qvist et al.,⁶⁰ cautioned from interpreting the parameters of eq 5 within the framework of mode coupling theory due to the fact they did not observe the same T_0 for the translational and rotational diffusion of water molecules in supercooled water. On the other side, we observe the same T_0 for τ_R and η for each solvent, which partially satisfy the universality of the mode coupling theory.^{57, 60} Unfortunately, at the moment, we do not understand why T_0 , the spatially heterogeneous dynamics, appears to be similar in the variety of the solvents we studied; this point needs more research. For that reason, we regard this approach as an empirical approach, which allows us to describe well the temperature change of the rotational correlation time and viscosity in ILs. Comparing the values of γ in Tables 1 and 2, one can notice that they are very close to each other for each solvent. This implies that the temperature functional dependence of τ_R and η is very similar.

Although the value of τ_R in squalane is about an order of magnitude faster than the value of τ_R in $[\text{C}_2\text{mim}][\text{BF}_4]$, the viscosities of the two solvents are comparable. The high viscosity of squalane is caused by its long branched structure, while the high viscosity in the case of $[\text{C}_2\text{mim}][\text{BF}_4]$, with a short alkyl chain, is due to the electrostatic interactions between the cationic and anionic parts of the molecule. pDTO is a neutral molecule, which is soluble in both polar solvents, such as water, and nonpolar solvents, such as alkanes.⁶¹ The N-O[•] moiety of pDTO can be involved in hydrogen bonding.⁶² In squalane, pDTO can rotate quite freely. On the other hand, the N-O[•] moiety of pDTO in $[\text{C}_2\text{mim}][\text{BF}_4]$ is hydrogen bonded to the acidic imidazolium protons,²¹ which is the main reason for the slowing down of pDTO rotation, Figure 1. The remaining part of the nitroxide very likely interacts with the other side of the alkyl tail of the organic cation.²¹ Since the viscosities of squalane and $[\text{C}_2\text{mim}][\text{BF}_4]$ are very similar, Figure 2, the longer rotational correlation time in $[\text{C}_2\text{mim}][\text{BF}_4]$, Figure 1, can be regarded as a measure of the hydrogen bonding between N-O[•] and the acidic imidazolium protons. The increases in τ_R in the remaining ILs, Figure 1, can be related to the increases in their viscosities, Figure 2.

Although ILs do not have long-range order, they very likely have nanodomains.^{21, 30–31} One can hypothesize that pDTO in ILs experiences regions of different and interchanging dynamics. As Katting et al.,⁶³ we also observe unimodal EPR spectra, which means that the spin probe transfer rate between the domains is very fast on the EPR time scale, such that the EPR parameters can be treated as the average values of the domain parameter values.

EasySpin is a versatile EPR simulation and fitting software.^{64–65} In order to confirm the results of our data analysis using our EPR line fitting program Lowfit,⁴² we have fitted a number of EPR spectra in ILs using EasySpin. Lowfit gives very precise values of EPR line field positions, line heights and Lorentzian and Gaussian line widths. The magnetic field positions are used to find the hyperfine coupling spacing A_{abs} , while the Lorentzian line

widths are used to calculate the rotational correlation time τ_R . EasySpin uses a full quantum mechanical numerical simulation, which can be combined with EPR spectral fitting, to extract the underlying structural and dynamic parameters, such as A - and g -principal values, τ_R , etc.^{64–65} The EasySpin function `chili` used in this study is based on the theory developed and implemented by Freed's group.^{44, 66} EasySpin fitting requires more care when choosing initial guesses and more time than Lowfit fitting, due to the larger number of parameters and complex quantum mechanical calculations. For that reason we have fitted just a limited representative number of experimental spectra.

Figure 3 shows the comparison of the rotational correlation time of pDTO in ILs obtained by fitting using the EasySpin function `chili` and Lowfit. EasySpin simulations assumed the isotropic rotational diffusion of pDTO. The A - and g -principal values in different ILs that are needed for calculating τ_R values are averages of all values obtained from the EasySpin fits and are presented in Table S3 in the Supplemental Information. As it can be seen in Figure 3, the agreement between the two fitting methods is very good.

The dependence of τ_R on η/T is usually given by

$$\tau_R = \frac{4\pi r^3}{3} \frac{\eta}{kT} \quad (6)$$

where, ideally, r should be the van der Waals radius of the probe, r_{vdW} . In most experiments, r is different from r_{vdW} and it is called the hydrodynamic radius. The ratio of r to r_{vdW} can go from zero, for the perfectly slip boundary condition, to unity for the stick boundary condition, which corresponds to hydrodynamic behavior. The value of the hydrodynamic radius can tell us about the interactions of the probe with its immediate surroundings.^{67–68} The rotational correlation time of pDTO in ILs and squalane as a function of η/T is shown in Figure 4. The solid lines are linear fits to the data, whose correlation coefficients are 0.9999 ([C₂mim][BF₄]), 0.999 ([C₄mim][BF₄]), 0.994 ([C₆mim][BF₄]), 0.9985 ([C₈mim][BF₄]) and 0.9999 (squalane). Obviously, τ_R obeys the SED equation. The hydrodynamic radii calculated from the slopes of the lines in Figure 4 are all smaller than the van der Waals radius of pDTO, which is 3.48 Å.⁶⁹ The hydrodynamic radius of pDTO is 1.8 Å in [C₂mim][BF₄], 1.4 Å in [C₄mim][BF₄], 1.35 Å in [C₆mim][BF₄], 1.3 Å in [C₈mim][BF₄] and 0.74 Å in squalane. The hydrodynamic radius of pDTO in [C₂mim][BF₄] is much larger than those in the remaining three ILs and squalane. Since the only difference between the solvents in the IL series is C₂H₄, one would expect that the radii should be equally spaced. The bigger discrepancy between the first and second solvent could be explained by assuming that the microscopic structure of [C₂mim][BF₄] is different than those of the remaining three ILs.

From the hydrodynamic radii of pDTO in ILs, we can easily find the ratio r to r_{vdW} , which is 0.51 in [C₂mim][BF₄], 0.4 in [C₄mim][BF₄], 0.386 in [C₆mim][BF₄] and 0.37 in [C₈mim][BF₄]. These values compared well to the values measured for TEMPOL in ILs,²⁷ which are 0.44 [C₂mim][BF₄], 0.38 in [C₄mim][BF₄] and 0.35 in [C₈mim][BF₄], and are calculated using $r/r_{vdW} = \sqrt[3]{c_{rot}}$, where c_{rot} is the rotational coupling constant and whose values for TEMPOL are taken from Table 4 of ref²⁷. Additionally, the hydrodynamic radii of TEMPOL in [C₂mim][BF₄] and [C₄mim][BF₄] measured in ref²⁶ were 1.6 and 1.3 Å,

which are close to the ones we measured for pDTO in the same ILs, that is 1.8 and 1.4 Å, respectively. Therefore, we can concur with Mladenova et al.²⁷ that the rotational dynamics are close to the slip boundary condition.

Apparent activation energy

From Figures 1 and 2 one can observe that the rotational correlation time and the viscosity increase more rapidly with decreasing temperature than what would be expected from the Arrhenius behavior. In the case of an Arrhenius process, the activation energy E_A can be found from the slope of the line in an $\ln(\tau_R)$ versus $1/T$ graph,⁷⁰ that is

$$E_A = R \frac{d \ln(\tau_R)}{d(\frac{1}{T})} = -RT^2 \frac{d \ln(\tau_R)}{dT} \quad (7)$$

where R is the gas constant and E_A is constant. Similarly, in the case of a non-Arrhenius process, one can define the apparent activation energy for τ_R , E_{app}^τ , using the same expression.⁶⁰ Substituting eq 5 into eq 7 one obtains

$$E_{app}^\tau(T) = \frac{\gamma RT^2}{T - T_0} \quad (8)$$

Assuming that the activation energy is a function of temperature, then substituting

$\tau_R = \tau_0 \exp(\frac{E_A(T)}{RT})$ into eq 7 gives

$$E_{app}^\tau(T) = E_A(T) - T \frac{dE_A(T)}{dT} \quad (9)$$

where the second term can be regarded as a contribution to $E_{app}^\tau(T)$ due to thermally induced structural changes.⁶⁰

Figures 5 and 6 show the apparent activation energies for τ_R and η , respectively. In all cases the apparent activation energy increases with decreasing temperature, and becomes about 2/3 greater at the lower end of the measured range. The apparent activation energy for the rotation of pDTO in squalane and in [C₂mim][BF₄] is about the same, Figure 5, while the value of $E_{app}^\eta(T)$ is greater in squalane than in [C₂mim][BF₄], Figure 6. As expected, the values of both $E_{app}^\tau(T)$ and $E_{app}^\eta(T)$ increase with increasing number of carbons in the side chain, Figures 5 and 6. According to eq 8, when the exponent γ is the same, the apparent activation energy is the same too. Comparing the values of γ for τ_R and η in Tables 1 and 2 and looking at Figure 5 and 6, one can notice that the values of $E_{app}^\tau(T)$ and $E_{app}^\eta(T)$ for squalane and [C₂mim][BF₄] do not follow each other. On the other hand, in the case of [C₄mim][BF₄], [C₆mim][BF₄] and [C₈mim][BF₄], the apparent activation energies for τ_R and η are very close.

In many of the liquids in which spatially heterogeneous dynamics are present, the mobile molecule clusters grow in size with a decrease in T ,⁴⁸ such that the transport properties are

very likely dominated by cooperative interaction effects of the densely packed system.⁵⁷ As is well known, when thermally activated processes dominate the sample, one presents measured data as Arrhenius plots, which show that the activation energy is temperature independent.^{57, 71} Therefore, the shape of the data in Figures 5 and 6 indicate that in ILs and squalane at lower temperatures, the cooperative interactions among the molecules, not thermally activated processes, determine the temperature dependence of τ_R and η . Consequently, since the cooperative interactions increase with a decrease in T , the activation energies of τ_R and η increase, as well.⁵⁷

The apparent activation energy for water rotation in bulk D₂O and H₂O, Figure 4 of ref ⁷², in the temperature range 240 to 315 K, otherwise known as the supercooled and normal regions, have the same temperature dependence as $E_{app}^{\tau}(T)$ in Figure 5 and $E_{app}^{\eta}(T)$ in Figure 6. This anomalous (non-Arrhenius) slowing down of water rotation below 273 K is due to the disruption of molecular cooperative rotation caused by more ordered and more open tetrahedral structure of water in the supercooled region.⁷² Similarly, as mentioned above, it is very likely that ionic liquid molecules, when cooled down, form bigger clusters, and thus disrupt their own cooperative molecular motion, as well as the rotation of the probe. Also, supercooled liquids are usually characterized by a strong non-Arrhenius increase in viscosity with a decrease in temperature.⁷³ Therefore, we can concur with the conclusion of Miyake et al.²³ that the rotation of TEMPO based spin probes in ILs is similar to their rotation in supercooled liquids.

Hyperfine Coupling Constant

Figure 7 shows the hyperfine coupling spacing, A_{abs} , of the ILs series as function of temperature extracted by Lowfit. For comparison, we also show the values of A_{iso} obtained from the EasySpin fits in Figures 8a and b. Except for a constant difference of about 30 mG, the values from the two methods agree well. We could not find a reason for the 30 mG difference. Additionally, a few points at the lower temperature have a slightly bigger difference, which is likely due to the fact that we assumed isotropic rotation in the EasySpin fitting. For a given spin probe, A_{abs} is directly proportional to the polarity of the probe's environment.¹⁴ As expected, from Figure 7 one can conclude that A_{abs} decreases as the number of carbons in the side-chain increases, except in the case of [C₂mim][BF₄] and [C₄mim][BF₄], whose A_{abs} values are quite close. In ILs we can expect the headgroups (cations) and the anions to be distributed homogeneously due to their net charge, while the side-chains tend to aggregate.³⁰ When the alkyl chains are short, the charge of the headgroups overpowers the attraction of the side chains, so the side-chains are distributed homogeneously. When the side-chains become long enough, the interactions between them are stronger and they form hydrocarbon domains. Since pDTO senses the charged and side-chain regions, and undergoes fast transfer between the regions, the observed EPR spectrum is an average of the spectra originating in those two regions. The downward shift of A_{abs} of pDTO in [C₆mim][BF₄] and [C₈mim][BF₄] is due to the length increase of the hydrocarbon side chains. In other words, Figure 7 indicates that [C₆mim][BF₄] and [C₈mim][BF₄] might have the aggregation of side-chains, while the other two ILs might not. This result supports the findings of the MD simulations of ILs of the 1-alkyl-3-methylimidazolium family with

hexafluorophosphate, that is, when the alkyl chain length becomes equal to or longer than C₄, the alkyl chains start to aggregate forming nonpolar domains.³¹

The observed increase in A_{abs} with temperature for pDTO in Figure 7 is opposite to the decrease in A_{abs} with temperature for TEMPO and TEMPOL in [C₄mim][BF₄] observed by Mladenova et al., Figure 4a of ref ²⁶, but it is the same as the increase in A_{abs} observed for TEMPAMINE [C₂mim] [ES] at higher temperatures, Figure 5 of ref ²⁶. Following a model proposed by Bullock et al.,⁷⁴ Mladenova et al.²⁶ explained in detail the temperature dependence of A_{abs} of nitroxides as a result of out-of-plane vibrations of the minimum energy configuration of the N-center. This configuration maybe either planar or pyramidal. In the pyramidal configuration, that is when the angle θ between the N-O[•] bond and the C-N-C plane is close to the value for tetrahedral symmetry (19.5°), as it is for TEMPO (19.4°) and TEMPOL (15.8°),²⁶ one expects A_{abs} to decrease with temperature as observed in ref ²⁶. The angle θ for pDTO is 0°, ⁷⁵ which is planar, so it is not surprising that A_{abs} as a function of temperature for pDTO behaves differently than the ones for TEMPO and TEMPOL. We have also observed that pDTO in water behaves differently than DTBN, TEMPO and TEMPOL (see Supporting Information – Figure S5).

Conclusions

The rotational correlation times of pDTO in all solvents studied and their viscosities can be described by eq 5, as can the rotational correlation time of pDTO in supercooled water⁵⁰ and many other thermodynamic properties of liquid water in the temperature range –38 to 150 °C.⁴⁷ The apparent activation energies $E_{app}^{\tau}(T)$ and $E_{app}^{\eta}(T)$ of both ILs and squalane increase with decreasing temperature, clearly indicating non-Arrhenius behavior of all liquids studied. The Stokes-Einstein-Debye relation describes the rotational correlation times of pDTO in the ILs and squalane.

The uneven spacings of τ_R as a function of η/T and A_{abs} as a function of T , as well as the equal values of γ for the ILs whose alkyl chains have four or more carbons, suggest that the structure of these ILs is different than that of [C₂mim][BF₄]. The temperature dependence of τ_R and η , and a strong non-Arrhenius behavior imply that ILs, just as supercooled liquids, may possess regions of distinct and interchanging dynamics.⁷³ Our experimental results support the view that ILs consist of polar and nonpolar nanodomains as shown by the MD simulations of n-alkyl-imidazolium ILs.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

D. M. and M. P. gratefully acknowledge support from NIH Grant 1 SC3 GM099635-03.

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Figure 1. Rotational correlation time τ_R of pDTO versus temperature in $[\text{C}_2\text{mim}][\text{BF}_4]$ (●), $[\text{C}_4\text{mim}][\text{BF}_4]$ (■), $[\text{C}_6\text{mim}][\text{BF}_4]$ (◆), $[\text{C}_8\text{mim}][\text{BF}_4]$ (▲) and squalane (▼). The solid lines are fits to $\tau_R = \tau_{R0} (T/(228 \text{ K}) - 1)^{-\gamma}$, and the fitting parameters are given in Table 1.

Figure 2. Viscosity of [C₂mim][BF₄] (●), [C₄mim][BF₄] (■), [C₆mim][BF₄] (◆), [C₈mim][BF₄] (▲) and squalane (▼) versus temperature. The solid lines are fits to $\eta = \eta_0 (T/(228 \text{ K}) - 1)^{-\gamma}$, and the fitting parameters are given in Table 2.

Figure 3.

Rotational correlation time τ_R of pDTO versus temperature obtained by fitting using (a) Lowfit in $[\text{C}_2\text{mim}][\text{BF}_4]$ (●), $[\text{C}_4\text{mim}][\text{BF}_4]$ (■), $[\text{C}_6\text{mim}][\text{BF}_4]$ (◆), and $[\text{C}_8\text{mim}][\text{BF}_4]$ (▲) and (b) EasySpin chili function in $[\text{C}_2\text{mim}][\text{BF}_4]$ (○), $[\text{C}_4\text{mim}][\text{BF}_4]$ (□), $[\text{C}_6\text{mim}][\text{BF}_4]$ (◇), and $[\text{C}_8\text{mim}][\text{BF}_4]$ (△).

Figure 4. Rotational correlation time τ_R of pDTO versus η/T in [C₂mim][BF₄] (●), [C₄mim][BF₄] (■), [C₆mim][BF₄] (◆), [C₈mim][BF₄] (▲) and squalane (▲). The solid lines are linear fits.

Figure 5. Apparent activation energy for τ_R of pDTO versus T in [C₂mim][BF₄] (●), [C₄mim][BF₄] (■), [C₆mim][BF₄] (◆), [C₈mim][BF₄] (▲) and squalane (▼).

Figure 6.

Apparent activation energy for the viscous flow of [C₂mim][BF₄] (●), [C₄mim][BF₄] (■), [C₆mim][BF₄] (◆), [C₈mim][BF₄] (▲) and squalane (▼) versus temperature.

Figure 7. Hyperfine coupling spacings A_{abs} of pDTO versus temperature in $[\text{C}_2\text{mim}][\text{BF}_4]$ (●), $[\text{C}_4\text{mim}][\text{BF}_4]$ (■), $[\text{C}_6\text{mim}][\text{BF}_4]$ (◆), $[\text{C}_8\text{mim}][\text{BF}_4]$ (▲). Individual results from five spectra are shown to indicate the reproducibility.

Figure 8. Hyperfine coupling spacings A_{abs} of pDTO versus temperature in (a) $[C_2mim][BF_4]$ (circles) and $[C_4mim][BF_4]$ (squares), and (b) $[C_6mim][BF_4]$ (circles) and $[C_8mim][BF_4]$ (squares). The full circles and squares are obtained by Lowfit, while the open circle and crossed squares are obtained by EasySpin fitting.

Table 1

Power law $\tau_R = \tau_{R0}(T/(228 \text{ K}) - 1)^{-\gamma}$ parameters for ionic liquids and squalane

	τ_{R0}/ns	γ	R
[C ₂ mim][BF ₄]	0.00532 ± 0.00004	2.965 ± 0.007	0.999
[C ₄ mim][BF ₄]	0.00432 ± 0.00004	3.564 ± 0.009	0.999
[C ₆ mim][BF ₄]	0.00390 ± 0.00003	4.080 ± 0.009	0.999
[C ₈ mim][BF ₄]	0.00430 ± 0.00003	4.33 ± 0.01	0.999
Squalane	0.000472 ± 0.00001	2.84 ± 0.01	0.998

Table 2Power law $\eta_R = \eta_0(T/(228 \text{ K}) - 1)^{-\gamma}$ parameters for ionic liquids and squalane

	η_0/mPas	γ	R
[C ₂ mim][BF ₄]	1.74 ± 0.03	2.57 ± 0.02	0.999
[C ₄ mim][BF ₄]	1.53 ± 0.06	3.59 ± 0.03	0.999
[C ₆ mim][BF ₄]	1.61 ± 0.05	4.16 ± 0.03	0.994
[C ₈ mim][BF ₄]	1.98 ± 0.02	4.35 ± 0.01	0.999
Squalane	0.77 ± 0.01	3.01 ± 0.01	0.994