

## Transport Properties in Ionic Liquids and Ionic Liquid Mixtures: The Challenges of NMR Pulsed Field Gradient Diffusion Measurements

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Pulsed field gradient NMR is a powerful method for the measurement of diffusion coefficients in liquids and solids and has begun to attract much attention in the ionic liquids field. However, aspects of the methodology as traditionally applied to solutions may not be uniformly applicable in these more viscous and chemically complex systems. In this paper we present data which shows that the Pulsed Gradient Spin Echo (PGSE) method in particular suffers from intrinsic internal gradients and can produce apparent diffusion coefficients which vary by as much as 20% for different  $^1\text{H}$  nuclei within a given molecule—an obvious anomaly. In contrast, we show that the Pulsed Gradient Stimulated Echo method does not suffer from this problem to the same extent and produces self-consistent data to a high degree of accuracy (better than 1%). This level of significance has allowed the detection, in this work, of subtle mixing effects in  $[\text{C}_3\text{mpyr}][\text{NTf}_2]$  and  $[\text{C}_4\text{-mpyr}][\text{NTf}_2]$  mixtures.

### Introduction

Ionic liquids (ILs) describe a class of materials that are salts being in the liquid state below 100 °C. This is an arbitrary distinction, but the most important distinction to make for these compounds is that they are a unique ionic electrolyte or solvent system that is accessible at practical temperatures and pressures. The broader family of ionic liquids offers a range of compounds that possess a unique combination of thermal and electrochemical stability, as well as being chemically stable toward many different types of compounds.<sup>1,2</sup> A hindrance to pure ionic liquids being used in many applications is that few, if any, ionic liquids will exhibit all the properties that are suitable to any given situation. For example, an ionic liquid may have an electrochemical window that permits certain electrochemistry at the extremes of potential, but such a low conductivity that practical current capacities are prohibitively low.<sup>3</sup> One avenue of research is to use mixtures of ionic liquids with other compounds to change the material properties. Studies of such systems have shown that even small additions of a low molecular weight solvent can have a dramatic increase in the transport properties relative to the properties of the pure ILs.<sup>4</sup> This does, however, lead to the loss of the desirable properties such as low vapor pressure that were the attraction of the ionic liquid in the first place. Therefore, *mixtures* of ionic liquids become a promising route to new systems possessing combinations of properties and are now beginning to be investigated.<sup>5–15</sup> Several research groups have used binary mixtures of ionic liquids in electrochemical applications and have shown improved performance in the device. For example, Grätzel's research group has used mixtures of iodide and tricyanomethide imidazoliums to make an electrolyte for dye-sensitized solar cells with higher conductivity and improved efficiency.<sup>14,16</sup> Similarly, Egashira et al. have used binary mixtures of various ionic liquids

to show improved conductivity, thermal and electrochemical stability, and how these characteristics affect lithium electrochemistry in these binary electrolytes.<sup>6,9,11</sup> Therefore, it appears that ionic liquid mixtures hold a promising future for improvements in electrolyte materials for device application as well as other chemical technologies, e.g., chemical separation<sup>17</sup> not discussed here.

Though property changes are identified and anecdotally predicted, the understanding of fundamental mechanisms at the molecular level is lacking. Properties such as viscosity ( $\eta$ ), ionic conductivity ( $\sigma$ ), and diffusion ( $D$ ) are all interlinked, yet the relationship between these can be complex. Therefore, each of these needs to be individually measured to gain an understanding of the implications of a change in any of the properties. Measuring the physical properties of these materials has only begun in earnest in more recent years.<sup>7,18–23</sup> In this paper we investigate the methods of measurement of, in particular,  $D$  in ionic liquids and describe some subtle mixing effects in mixtures of ILs.

Diffusion is most easily studied by using Pulsed Field Gradient Nuclear Magnetic Resonance (pfg NMR). This technique has been used to measure diffusion in several different ionic liquids previously, though different methodologies have been used.<sup>20–22,24–28</sup> The main NMR methods used to measure diffusion are Pulsed Gradient Spin Echo (PGSE) and Pulsed Gradient Stimulated Echo (PGSTE). Both have been used in the ILs field; however, during the course of our experiments, it became obvious that a more careful choice of experimental conditions was necessary to achieve accurate diffusion measurements in ILs and that this was especially important for the more viscous systems. While different approaches have been used in the past literature, the reasons for choosing a particular method are not always apparent. In this paper, we examine the effect of using the two different approaches, and the implications this has for the diffusion data obtained. In addition, the basic NMR theory presented by Stejskal and Tanner<sup>29</sup> and Tanner<sup>30</sup> is briefly

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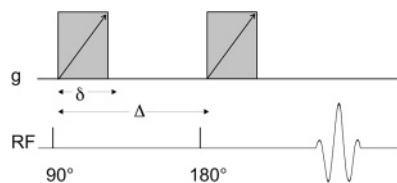


Figure 1. Pulse sequence for PGSE.

discussed to provide some understanding of why simple PGSE experiments may not be the method of choice in some IL systems.

## Experimental Section

**Materials.** The ionic liquids *N*-methyl-*N*-propylpyrrolidinium dicyanamide ([C<sub>3</sub>mpyr][dca]), *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([C<sub>3</sub>mpyr][NTf<sub>2</sub>]), *N*-methyl-*N*-butylpyrrolidinium bis(trifluoromethylsulfonyl)amides ([C<sub>4</sub>mpyr][NTf<sub>2</sub>]), and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([C<sub>2</sub>mim][NTf<sub>2</sub>]) were synthesized as described previously,<sup>31–33</sup> while trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)amide ([P<sub>6,6,6,14</sub>][NTf<sub>2</sub>]) was used as received (Cytec). All ionic liquids were dried at 70 °C under vacuum for 48 h, and stored in a N<sub>2</sub> drybox. Water content of the samples was measured by using Karl Fischer analysis, and found to be the following: [C<sub>3</sub>mpyr][dca] = 334 ppm, [C<sub>4</sub>mpyr][NTf<sub>2</sub>] = 55.8 ppm, and [C<sub>3</sub>mpyr][NTf<sub>2</sub>] < 5 ppm (water content was below detection limit).

The bromide content of the ionic liquids was analyzed by using ion selective electrodes, calibrated with tetrabutylammonium bromide as a standard. Bromide contents were found to be <20 ppm for all ionic liquids.

**Ionic Conductivity (EIS).** Ionic conductivity was measured by using a glass cell, in which a glass plunger was inserted, having two platinum wires as electrodes. Samples were loaded in a N<sub>2</sub> atmosphere, and this atmosphere was maintained by an O-ring seal between the vial and the electrode. The cell was calibrated by using a 0.01 M KCl aqueous solution at 25 °C. A Solartron SI1260 Impedance/gain phase analyzer and Solartron 1296 dielectric interface with Solartron Impedance Measurement software (v.3.3.1) was used to measure impedances.

**Viscosity.** Viscosity was measured with an Anton Paar Viscometer, using Visiolab software. A 1.8 mm internal diameter glass tube was used with a 1.5 mm diameter stainless steel ball. Samples were loaded into the tube in a N<sub>2</sub> atmosphere, and sealed with a glass stopper and a glass cap.

**NMR Method.** <sup>1</sup>H NMR experiments were carried out on a Bruker Avance 300 spectrometer fitted with a water-cooled Bruker Diff30 diffusion probe at an observation frequency of 300.14 MHz. Samples were referenced against TMS (0 ppm). Samples were loaded in a N<sub>2</sub> atmosphere in Schott NMR tubes with an outer diameter of 5 mm and a length of 178 mm. At this stage, attention was not paid to the sample height in the tube, so sample heights varied from 20 to 50 mm. Sample tubes were capped with a plastic lid, then the top was wrapped in a Teflon film.

**Pulsed Field Gradient Spin Echo (PGSE) Pulse Method.** The PGSE pulse sequence is shown in Figure 1. When using the PGSE pulse sequence, the pulse duration (δ) was typically kept to 1 ms with a diffusion time (Δ) of 20 ms. Gradient strengths were used in the range of 500–1500 G·cm<sup>−1</sup>.

**Pulsed Field Gradient Stimulated Echo (PGSTE) Pulse Method.** PGSTE pulse sequence is described in greater detail later. When using the PGSTE pulse sequence, δ was 1–2 ms

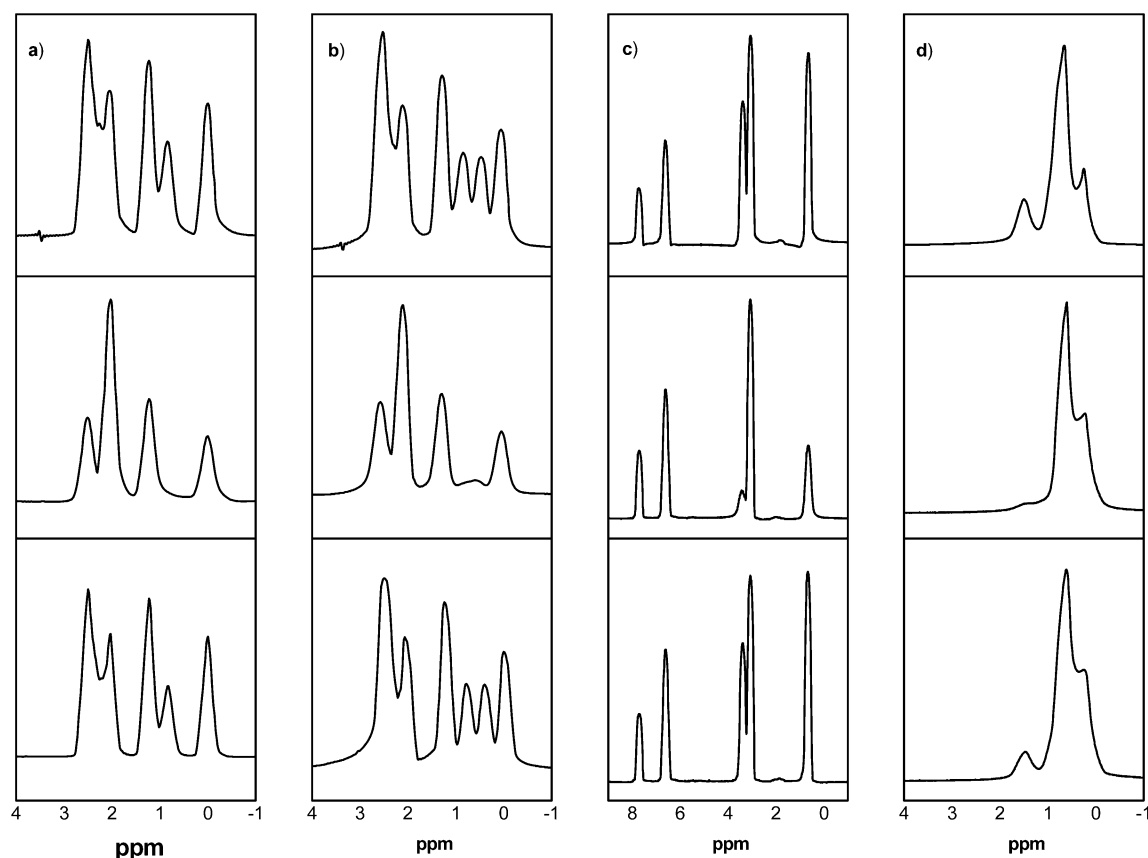


Figure 2. NMR spectra (top to bottom: single pulse, PGSE, PGSTE) for (a) [C<sub>3</sub>mpyr][NTf<sub>2</sub>], (b) [C<sub>4</sub>mpyr][NTf<sub>2</sub>], (c) [C<sub>2</sub>mim][NTf<sub>2</sub>], and (d) [P<sub>6,6,6,14</sub>][NTf<sub>2</sub>].

**TABLE 1:  $^1\text{H}$  Self-Diffusion Measurements ( $\times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ) at 20 °C with PGSE as a Function of Peak in Its Spectrum (peaks labeled as they appear in Figure 2, left to right)**

	[C <sub>3</sub> mpyr][NTf <sub>2</sub> ]	[C <sub>4</sub> mpyr][NTf <sub>2</sub> ]	[C <sub>3</sub> mpyr][dca]	[C <sub>2</sub> mim][NTf <sub>2</sub> ]	[P <sub>6,6,14</sub> ][NTf <sub>2</sub> ]
peak 1	1.84 ± 0.01	1.33 ± 0.01	3.80 ± 0.02	4.60 ± 0.05	0.247 ± 0.005
peak 2	1.73 ± 0.01	1.30 ± 0.01	3.64 ± 0.05	4.50 ± 0.05	0.223 ± 0.005
peak 3	1.71 ± 0.01	1.29 ± 0.01	3.69 ± 0.03	4.75 ± 0.05	
peak 4	1.67 ± 0.01	1.14 ± 0.05	3.54 ± 0.04	4.50 ± 0.05	
peak 5		1.27 ± 0.01	3.66 ± 0.03	4.50 ± 0.05	
peak 6					

**TABLE 2:  $^1\text{H}$  Self-Diffusion Measurements ( $\times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ) at 20 °C with PGSTE as a Function of Peak in Its Spectrum (peaks labeled as they appear in Figure 2, left to right)**

	[C <sub>3</sub> mpyr][NTf <sub>2</sub> ]	[C <sub>4</sub> mpyr][NTf <sub>2</sub> ]	[C <sub>3</sub> mpyr][dca]	[C <sub>2</sub> mim][NTf <sub>2</sub> ]	[P <sub>6,6,14</sub> ][NTf <sub>2</sub> ]
peak 1	1.83 ± 0.01	1.40 ± 0.01	3.77 ± 0.04	4.65 ± 0.05	0.234 ± 0.005
peak 2	1.80 ± 0.01	1.38 ± 0.01	3.72 ± 0.04	4.69 ± 0.05	0.233 ± 0.005
peak 3	1.82 ± 0.01	1.40 ± 0.01	3.77 ± 0.04	4.59 ± 0.05	0.226 ± 0.005
peak 4	1.80 ± 0.01	1.38 ± 0.01	3.69 ± 0.04	4.57 ± 0.05	
peak 5	1.82 ± 0.01	1.38 ± 0.01	3.75 ± 0.04	4.74 ± 0.05	
peak 6		1.38 ± 0.01			

long and a diffusion time of 80 ms was used. Gradient strengths were used in the range of 500–1500  $\text{G}\cdot\text{cm}^{-1}$ . To ensure the absence of spurious echoes or ringing in the spectra, the PGSTE pulse was also used with a spoiler gradient. This did not appear to significantly change the diffusion data for the systems investigated here.

## Results and Discussion

Figures 2 shows the NMR spectra obtained for four ionic liquids with a range of viscosities under three different pulse conditions: single  $\pi/3$  pulse followed by acquisition, pulsed gradient spin echo, and pulsed gradient stimulated spin echo. The pulse sequences are given in the methodology section above; the spectra are from the third spectrum in the experiment (this avoids any problems with anomalous phasing errors). A dramatic difference is clearly evident between the simple single pulse experiment (labeled 1D) and the PGSE spectra. The peak intensities are significantly altered, and some peaks even disappear completely, in particular for the more viscous [P<sub>6,6,14</sub>][NTf<sub>2</sub>] and [C<sub>3</sub>mpyr][NTf<sub>2</sub>] samples. In the case of the [C<sub>2</sub>mim][NTf<sub>2</sub>] there seems to be only a slight effect on some peaks from the pulse sequence used; this may be due to the fact that this ionic liquid has a relatively low viscosity (21cP).

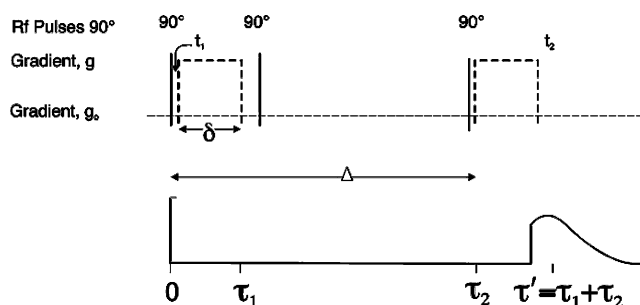
These differences in the spectra are primarily a result of different  $T_2$  relaxations for the different proton signals leading to loss of magnetization during the echo experiment, even in the absence of any gradient being applied. Thus for the more viscous phosphonium-based IL, the peak intensities are significantly diminished and indeed it was difficult to measure accurate diffusion coefficients with PGSE sequences in this case.

In some cases, when the PGSTE sequence was used (without the spoiler gradient), multiple echoes were observed which led to a messy spectrum and again diffusion coefficients were difficult to extract without significant errors. The optimum 2D diffusion spectra were usually obtained when using PGSTE sequences with a spoiler gradient that removed the multiple echoes. Tables 1 and 2 present the diffusion coefficients for the individual ionic liquids at 20 °C with both PGSE and PGSTE sequences. When the system is relatively fluid, as was the case with the [C<sub>2</sub>mim][NTf<sub>2</sub>] ionic liquid, the PGSE and PGSTE sequences gave the same diffusion data. However, in the more viscous systems this is not the case. Data acquired with PGSE in viscous systems differed depending on which peak was analyzed. These numbers were generally also significantly lower than those determined with PGSTE. Also, diffusion numbers determined with PGSTE were consistent within error for each

peak in the spectrum. It is difficult to see why these differences occur since, according to the simple equations used to extract  $D$  from pfg-NMR, the magnetization decay should be independent of relaxation phenomena in any one experiment.  $T_2$  will only be important when comparing experiments where  $T_2$  is different. Nonetheless, it is very clear that if accurate and reliable diffusion coefficients are to be determined in ionic liquids, it seems preferable to ensure that the spectrum obtained following the echo experiment is close to that expected from the 1D spectrum.

When mixtures of ILs were investigated, the choice of experiment became even more paramount. Figure 4 shows the spectra obtained with single-pulse PGSE and PGSTE in mixtures of [C<sub>3</sub>mpyr][NTf<sub>2</sub>] and [C<sub>4</sub>mpyr][NTf<sub>2</sub>] at various ratios. When the PGSE sequence was used the [C<sub>4</sub>mpyr][NTf<sub>2</sub>] could not be separately identified given that the peaks at 0.45 and 0.85 ppm were not visible. However, the PGSTE sequence allowed the separate observation of the two species in the  $^1\text{H}$  spectra. The peak at 0.45 ppm increases with increasing concentration of [C<sub>4</sub>mpyr][NTf<sub>2</sub>] and is associated purely with the [C<sub>4</sub>mpyr]<sup>+</sup> cation. Hence the diffusion coefficient determined from that peak represents the diffusion of only the [C<sub>4</sub>mpyr]<sup>+</sup> in the mixture. The remaining peaks are present in both components of the IL mixture and hence the diffusion coefficients measured are an average over the two cation species. Given the [C<sub>4</sub>mpyr]<sup>+</sup> will most likely have a larger hydrodynamic radius this species will move more slowly in the mixture, as was indeed observed in the data shown in Figure 5. All the magnetization decay curves had excellent fits to eq 1 despite the two different species associated with each.

To understand the discrepancy in the results presented above stemming from the method used, a brief discussion of the NMR methodology and equations used to determine  $D$  from pfg-NMR is given below.

**Figure 3.** Pulse sequence for PGSTE.

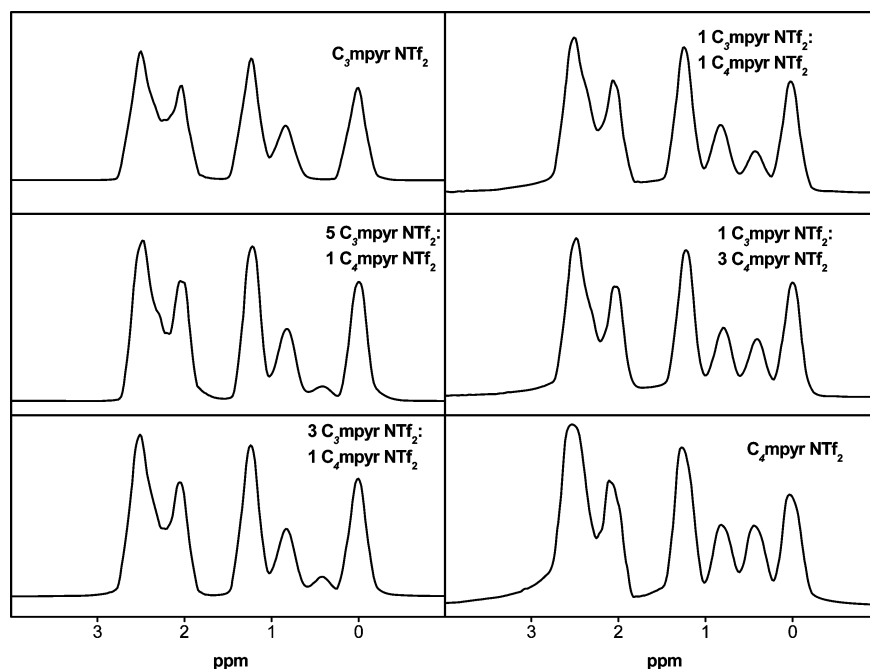


Figure 4. PGSTE spectra for [C<sub>3</sub>mpyr][NTf<sub>2</sub>] and [C<sub>4</sub>mpyr][NTf<sub>2</sub>] for different concentrations.

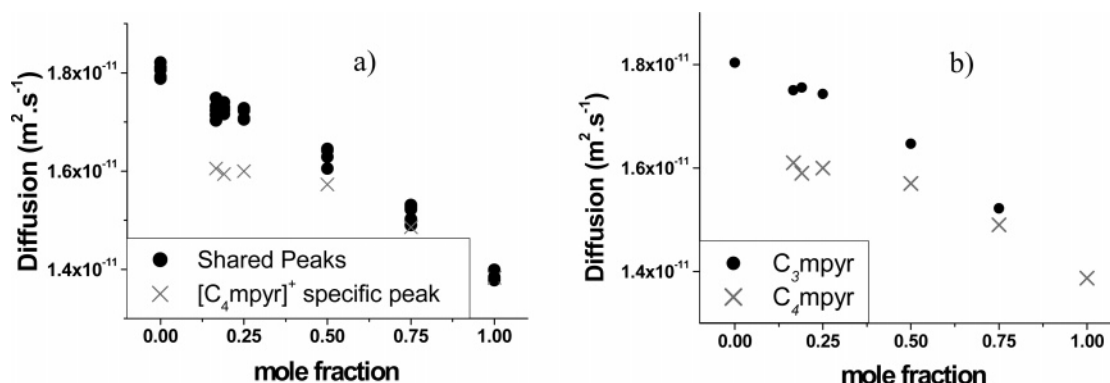


Figure 5. <sup>1</sup>H diffusion coefficients per mole fraction of [C<sub>4</sub>mpyr][NTf<sub>2</sub>] in [C<sub>3</sub>mpyr][NTf<sub>2</sub>] for (a) raw diffusion numbers of each peak and (b) weighted diffusion coefficients.

**NMR Methodology. PGSE Sequence.** Figure 1 shows the pulse sequence typically used in the PGSE method for determining diffusion. The variables are the gradient  $g$ , the gradient pulse width  $\delta$ , or the diffusion time  $\Delta$ . These can be manipulated to obtain the optimum magnetization decay from which the diffusion coefficient can be extracted with use of the standard equation.<sup>29</sup> Given the high viscosity (and hence small  $D$ ) for many ionic liquids of interest, strong gradients are definitely beneficial. Typically 18 T/m are now available and can yield diffusion coefficients (accurately) down to  $\sim 10^{-15} \text{ m}^2 \text{ s}^{-1}$ . The problem that we face in using the PGSE sequence with ILs is that the high viscosity usually leads to low spin–spin relaxation times ( $T_2$ ) and thus the length of diffusion time  $\Delta$  available for the measurement is limited. At the same time, ion exchange between clusters/domains in ILs means that a sufficiently long  $\Delta$  is needed to measure the average  $D$  for a given species.<sup>20,34</sup>

The  $T_2$  effect can lead to a decay in magnetization signal, independent of diffusion effects. Providing the signal can be detected and the gradients used are sufficient to result in a diffusion-induced decay during  $\Delta$ , the  $T_2$  effect is a constant and can be neglected leading to the simplified eq 1.

$$\ln \left[ \frac{A(2\tau)}{A(0)} \right] = -\gamma^2 D \delta^2 \left( \Delta - \frac{\delta}{3} \right) g^2 \quad (1)$$

However, as the data in this paper have shown, eq 1 may nonetheless not be valid in some ionic liquid systems. To understand why, we go back to the original equations provided by Stejskal and Tanner.<sup>29</sup> Equation 2 gives the amplitude of the echo during the PGSE experiment

$$\ln \left[ \frac{A(2\tau)}{A(0)} \right] = -\gamma^2 D \left\{ \frac{2}{3} \tau^3 g_0^2 + \delta^2 \left( \Delta - \frac{\delta}{3} \right) g^2 - \delta \left[ t_1^2 + t_2^2 + \delta(t_1 + t_2) + \frac{2}{3} \delta^2 - 2\tau_1 \tau_2 \right] g \cdot g_0 \right\} \quad (2)$$

where  $g$  is the strength of the applied gradient,  $g_0$  is any other magnetic gradient the sample will experience other than the applied gradients (i.e., both from effects intrinsic to the sample (related to  $T_2$ ) and also external, e.g., other inhomogeneities),  $t_1$  and  $t_2$  are the times for the 90° and 180° pulses, respectively,  $\delta$  is the duration of the applied gradient,  $\Delta$  is the time to the  $\pi$  pulse, and  $\tau$  is half the time of the echo (i.e., echo appears at time  $t = 2\tau$ ).

As  $g_0$  approaches zero, the cross term and the  $2\tau^3 g_0^2/3$  term approach zero and the terms associated with  $g_0$  are considered negligible, leaving the expression typically used in diffusion measurements (eq 1). Strictly speaking, if  $g_0$  is zero, no echo signal will be obtainable because the dephasing stage of the



sequence occurs as a result of  $g_0$ . However,  $g_0$  is normally nonzero but  $\ll g$  and thus eq 1 is therefore still considered appropriate. In simple solutions, in a well-shimmed, highly homogeneous field this assumption is certainly valid. It should be noted that there are inherent local gradients at the molecular level due to different chemical environments, but the length scale of these is of the order of the molecular sizes and hence is usually several orders of magnitude smaller than the distances travelled by a molecule/ion during  $\Delta$ . Thus we assume that average  $g_0$  arising from these molecular level heterogeneities is insignificant relative to the applied gradient  $g$ .

Ionic liquids present a different case. These liquids are composed entirely of (usually) bulky ions with several different environments for the  $^1\text{H}$  nuclei; significant coupling will therefore be present and Brownian motion may not be sufficient to average out the dipolar interactions. Hence, even in a well-shimmed magnet, the proton line widths can approach 100 Hz. Furthermore, molecular dynamics simulations and small-angle scattering experiments suggest that some significant degree of ordering is present in ILs which may lead to domain sizes of the order of 10–100 nm.<sup>35,36</sup> This also could lead to significant intrinsic gradients; thus the terms involving  $g_0$  in eq 2 may contribute significantly to the magnetization decay and therefore affect the apparent diffusion coefficient obtained in these cases, as observed in this work. To investigate whether the effects are purely related to high viscosity, several highly viscous (greater than the ILs) saturated aqueous salt solutions were also studied in this work and  $D$  was found to be independent of the measurement technique. Further investigation of the existence of internal magnetic field gradients could be investigated through the use of additional stimulated echo pulse sequences as well as bipolar gradients, as suggested by a reviewer of this paper.<sup>37</sup>

**PGSTE Pulse Sequence.** To overcome some of the problems associated with the PGSE experiments, in particular the loss of magnetization due to  $T_2$  effects, for systems with short  $T_2$ , Tanner suggested a more complex three-pulse sequence shown in Figure 3.

The amplitude of the echo can be described by the following expression (eq 3) following some simplifying assumptions similar to those discussed above. In this experiment, the spin lattice relaxation time  $T_1$  is the limiting factor in measuring  $D$ , while  $T_2$  effects become negligible.

$$\ln \left[ \frac{A(\tau)}{A(0)} \right] = -\frac{(\tau_2 - \tau_1)}{T_2} - \frac{2\tau_1}{T_1} - \ln 2 - \gamma^2 D \tau_1^2 \left( \tau_2 - \frac{\tau_1}{3} \right) \quad (3)$$

In this case the echo shown occurs at a specific time,  $t_1 + t_2$  after the third rf pulse. The application of this pulse sequence in practice also has complications in that several echoes may be detected leading to a complex Fourier transformed spectrum (including ringing and spurious multiplets) and therefore errors in determining amplitudes of specific peaks may arise. However, this can be corrected by use of a spoiler gradient applied during the experiment that forces the dephasing of residual, spurious magnetization thereby leading to the correct magnetization response for the PGSTE sequence. In the experiments reported here, the spoiler gradient strength used was  $\sim 5\%$  of the maximum gradient and was applied for a duration of 1 ms.

While PGSTE can compensate for a short  $T_2$ , there are other factors that have influenced both the quality of the spectrum and the diffusion numbers measured in this work:

**Diffusion time ( $\Delta$ ):** It has been suggested that ionic liquids have a  $\Delta$  dependent diffusion coefficient, due to intermediate chemical exchange.<sup>20</sup>

**Gradient strength:** Gradient strength maximum will be restricted by the instrument, and could inhibit the ability to measure very slow diffusion coefficients.

**Pulse time ( $\delta$ ):** Again, pulse time will be restricted by the instrument, as an extended pulse could damage the probe.

Previous measurements in heterogeneous systems such as colloids have suggested that three-pulse and four-pulse sequences yield more accurate diffusion coefficients compared with the simpler PGSE sequence.<sup>37</sup> This suggests that the more complex pulse sequences are better able to avoid  $g_0 \neq 0$  effects.

One final thing to consider in measuring variable-temperature diffusion coefficients is the effect of temperature gradients on the measured value of  $D$ . When heating a sample, most modern probes have significant temperature gradients longitudinal to the sample leading to thermal convection, and this can have a significant impact on the measured diffusion coefficient. This is most evidenced when large diffusion times,  $\Delta$ , are used. The most efficient method to alleviate these effects is to minimize the sample size to a few millimeters in height. Alternative methods using a capillary sample centered in the 5 mm NMR tube can also be employed; however, this can lead to additional gradients and inhomogeneities. This paper has focused on a comparison between PGSE and PGSTE results at room temperature where convection effects are negligible.

The remainder of this paper uses the PGSTE pulse sequence to measure diffusion of ionic liquid species in mixtures and compares this to other transport data including conductivity and viscosity in these mixtures.

**Ionic Liquid Mixtures.** Figure 4 shows the spectra obtained for varying mixtures of  $[\text{C}_3\text{mpyr}][\text{NTf}_2]$  and  $[\text{C}_4\text{mpyr}][\text{NTf}_2]$ . This system was chosen to examine the effect of mixing where the constituents have only subtle differences. In this case, the only difference is an extra methyl group on the pyrrolidinium ring. Both  $[\text{C}_3\text{mpyr}]$  and  $[\text{C}_4\text{mpyr}][\text{NTf}_2]$  have melting points below room temperature (10 and  $-18^\circ\text{C}$ , respectively) and similar room temperature viscosities (77 and 100 cP, respectively).

Since the two cations are so similar, the proton spectra are almost the same, but the peak at 0.45 ppm is unique to the  $[\text{C}_4\text{mpyr}]^+$  cation. Therefore, when analyzing the diffusion of peaks in the mixed ILs, it was assumed that this peak represented the diffusion of the  $[\text{C}_4\text{mpyr}]^+$  cation exclusively and all other peaks represent a mixture of the diffusions of the  $[\text{C}_3\text{mpyr}]^+$  and  $[\text{C}_4\text{mpyr}]^+$  cations.

The data in Figure 5a show significant deviation of the  $[\text{C}_4\text{mpyr}]^+$  peak diffusivity from all other proton diffusivities below 0.5 mol fraction  $[\text{C}_4\text{mpyr}]^+$  in  $[\text{C}_3\text{mpyr}]^+$ . Figure 5b was produced under the assumption that the diffusion numbers represented an average diffusion, but the lower diffusion peak (lower curve in Figure 5a) represented the  $[\text{C}_4\text{mpyr}]^+$  diffusion only. The diffusion numbers for Figure 5b were then determined by the fraction of  $[\text{C}_4\text{mpyr}]^+$  present. This observation can be rationalized by the fact that the  $[\text{C}_4\text{mpyr}]^+$  cation is larger and heavier than the  $[\text{C}_3\text{mpyr}]^+$  cation. Therefore, when the concentration of  $[\text{C}_4\text{mpyr}]^+$  is low enough that it has to diffuse through a  $[\text{C}_3\text{mpyr}]^+$  dominant phase, it will be sterically hindered and will therefore diffuse more slowly.

On a logarithmic plot, seen in Figure 6, it seems that the diffusion coefficient of the  $[\text{C}_3\text{mpyr}]^+$  cation is close to the ideal value expected from a weighted average of the two species (as indicated by the dotted line) whereas the  $[\text{C}_4\text{mpyr}]^+$  shows some deviation from straight line behavior. The slight excess observed

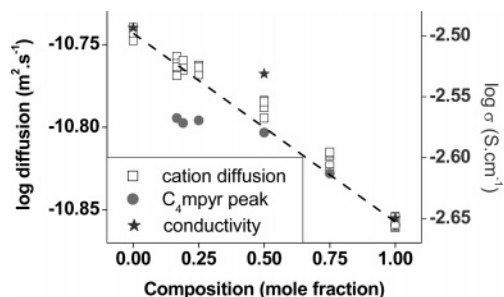


Figure 6. Conductivity and diffusion of [C<sub>4</sub>mpyr][NTf<sub>2</sub>] in [C<sub>3</sub>mpyr][NTf<sub>2</sub>].

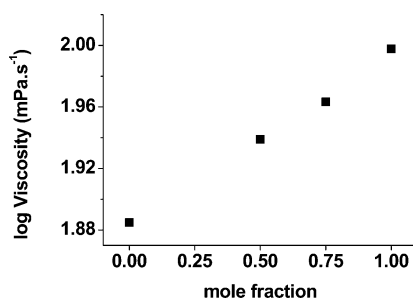


Figure 7. Log viscosity of [C<sub>3</sub>mpyr][NTf<sub>2</sub>]/[C<sub>4</sub>mpyr][NTf<sub>2</sub>] mixtures.

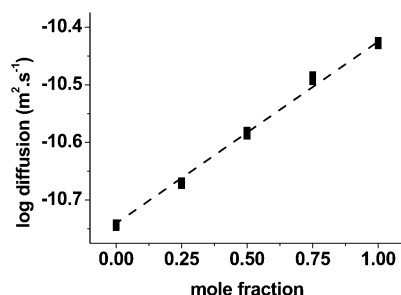


Figure 8. Log <sup>1</sup>H diffusion of [C<sub>3</sub>mpyr][dca] in [C<sub>3</sub>mpyr][NTf<sub>2</sub>].

here would be consistent with the small excess volumes previously reported in IL mixtures at intermediate concentrations.<sup>7</sup>

The ionic conductivity of the mixtures is close to a linear simple mixing behavior (on a log plot). Figure 6 also shows conductivity plotted as a function of concentration. Viscosity of the [C<sub>3</sub>mpyr]<sup>+</sup>/[C<sub>4</sub>mpyr]<sup>+</sup> mixtures shows very little deviation from simple mixing, as seen in Figure 7. This case, which is consistent with previous reports, suggests the IL structure is little affected by mixing, at least when the species being mixed are not substantially different.

Figure 8 shows the diffusion data for the cations in the [C<sub>3</sub>mpyr][NTf<sub>2</sub>] and [C<sub>3</sub>mpyr][dca] ionic liquid mixture. Similar to the [C<sub>4</sub>mpyr][NTf<sub>2</sub>] in [C<sub>3</sub>mpyr][NTf<sub>2</sub>] system, little deviation from a linear response is observed for the cation diffusion even though the two anions are distinctly different and the viscosity of the dca system is significantly lower (33 cP). This may be an indication that the cation dominates the structure and transport in such mixed systems as has been suggested from optical Kerr measurements in binary mixtures.<sup>5</sup>

## Conclusions

Using ionic liquids of different viscosities, we have shown that care must be taken when selecting a pulse sequence for measuring diffusion with pfg-NMR. The most commonly used pulse sequence, Pulsed Gradient Spin Echo (PGSE), can lead to an error in diffusion measurements of up to 20% in the

systems investigated thus far. While the origin of this error is not completely clear, it was seen that the problems encountered with PGSE were overcome by using the three-pulse Pulsed Gradient Stimulated Echo (PGSTE) pulse. With this sequence the spectra obtained were not influenced by *T*<sub>2</sub> effects, but more importantly the diffusion coefficients measured by using different peaks on the same molecule are self-consistent. Therefore, we would strongly recommend that when using pfg-NMR to measure diffusion in ionic liquid systems, care should be taken to choose a pulse sequence that will give accurate diffusion coefficients. In the systems investigated here, the PGSTE sequence consistently gave the most rigorous output and hence was used to evaluate binary mixtures.

[C<sub>3</sub>mpyr][NTf<sub>2</sub>] and [C<sub>4</sub>mpyr][NTf<sub>2</sub>] were mixed together in varying ratios to determine if any unusual mixing behavior could be seen. The diffusion of the two different cations could be distinguished, based on the assumption of an exclusive [C<sub>4</sub>mpyr]<sup>+</sup> peak in the spectrum of the mixtures. The [C<sub>4</sub>mpyr]<sup>+</sup> cation was observed to be diffusing more slowly in mixtures where the [C<sub>3</sub>mpyr]<sup>+</sup> was the majority component. This is thought to be a result of [C<sub>4</sub>mpyr]<sup>+</sup> having a larger hydrodynamic radius than [C<sub>3</sub>mpyr]<sup>+</sup>. The [C<sub>3</sub>mpyr]<sup>+</sup> cation did, however, appear to be moving slightly faster than would be expected with a simple mixing law, and this may be the cause of the slight increase in ionic conductivity observed.

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