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**On Accurate Measurements of Diffusion Coefficients by PGSE NMR  
Methods (Version 2)  
-Room-Temperature Ionic Liquids-**

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Diffusion coefficients of molecules, ions and particles in materials can be measured by pulsed-gradient spin-echo NMR (PGSE-NMR) methods and we have two articles in the Internet as following.

“Introduction to measure diffusion phenomena by PFG-NMR” (in Japanese) 2006/05/05  
[http://www.jeol.co.jp/technical/ai/nm/pfg-nmr\\_02.pdf](http://www.jeol.co.jp/technical/ai/nm/pfg-nmr_02.pdf)

“Applications of PGSE-NMR methods to homogeneous liquids -organic solution electrolytes-”  
(in Japanese) 2008/2/11  
<http://www.jeol.co.jp/technical/ai/nm/application-note/nm071008/nm071008.pdf>

In this article, we will show the accurate measurements of the diffusion coefficients ( $D$ ) by using room-temperature ionic liquids (RTIL, IL) as examples. To obtain reliable values, it is important to prepare sample conditions and set the proper measuring parameters. We have indicated the basic principles of the measuring methods in the Introduction above and will not repeat again here. Every analytical method has inevitable limitations in accuracies of values measured. To understand the accuracy of  $D$  values measured by the PGSE-NMR methods, we will describe the measuring conditions and the reliability of the experimental values for the  $D$ 's of three ILs having different viscosities. Proper estimation of the error range is important to evaluate translational diffusion phenomena of ILs if valid conclusions on their properties are to be drawn. In the present version, the data of  $D$  values of an IL measured by the steady-state field gradient NMR method were added on the data of the PGSE-NMR method. The agreement is excellent and the validity of the  $D$  values is clearly shown.

ILs have attracted much attention due to their unique properties and possible usages such as electrolytes and solvents. Careful and accurate measurements are important to obtain

meaningful  $D$  values for enabling the physical properties of the ILs to be characterized. In this article the precise experimental conditions and criteria for obtaining the accurate diffusion data of ILs are presented, since inattention to these issues results in improper  $D$  values, which may lead to questionable conclusions such as intrinsic internal gradients of ILs.

Generally, the  $D$ 's of viscous ILs are small compared with solutions prepared from organic and aqueous solvents and thus require larger pulsed field gradient (PFG) to obtain sufficient PGSE attenuation so that accurate  $D$  data can be obtained. PGSE studies of mixed organic compounds, including displaying the data as diffusion-ordered spectroscopy (DOSY) plot are now popular and many sophisticated PGSE sequences have been proposed where the required strength of the PFG is at most 1 T/m. The measurements of  $D$ 's of ILs require much higher PFGs up to 10 T/m depending on temperature, and generally special PFG probes are used. The two most commonly used pulse sequences to measure the  $D$ 's of ILs are shown in Fig. 1. Basically two equivalent PFGs are applied to the sample, where the first PFG marks the initial position of each nuclei and the second PFG detects the position after a time interval,  $\Delta$ . First, a modified Hahn spin-echo (SE) ( $90^\circ$ - $\tau$ - $180^\circ$ - $\tau$ -Acq) was proposed to incorporate two PFGs and for nuclei having shorter  $T_2$ , the stimulated echo (STE) ( $90^\circ$ - $\tau_1$ - $90^\circ$ - $\tau_2$ - $90^\circ$ - $\tau_1$ -Acq) was introduced. PGSE data obtained using either pulse sequence can be analysed by the Stejskal and Tanner equation as described below.

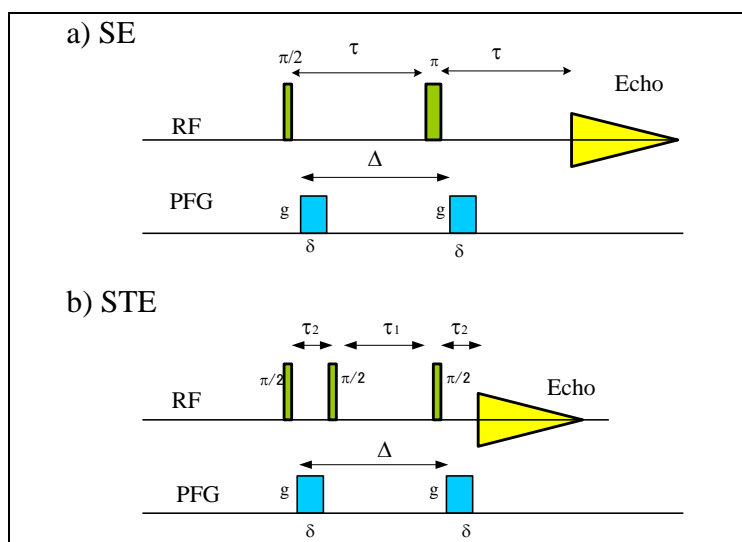


Figure 1. (a) SE and (b) STE-based PGSE sequences used to measure the self-diffusion coefficients ( $D$ 's).

The basic assumptions in the setup of NMR diffusion measurements to be analysed by the Stejskal and Tanner equation are: (1) all the species must be in a homogeneous external

magnetic field to prevent signal attenuation from background magnetic field gradients. The magnitude of the background field gradient can be estimated by the line width of signals with inherently long  $T_2$  values. (2) The sample must be placed in the constant region of the PFG, and (3) the RF field must be homogeneous to produce accurate  $90^\circ$  and  $180^\circ$  pulses over the whole sample. In particular, condition (2) may be hard to achieve for viscous ILs since the requisite large PFGs with constant profile can only be generated over very limited volume due to technical limitations. If the sample conditions were not proper, the measurements may include artifacts.

In the present paper, three representative ILs of which the cations are 1-ethyl-3-methyl-imidazolium ( $[EMIm]^+$ ), 1-methyl-1-propylpyrrolidinium ( $[P_{13}]^+$ ), and triethyl-n-pentyl-phosphonium ( $[TEPP]^+$ ) and the anion bis(trifluoromethylsulfonyl)amide ( $[TFSA]^-$ ) is common. The values of the viscosity measured at  $30^\circ\text{C}$  are shown in Table 1. The  $^{31}\text{P}$  diffusion coefficients of  $[TEPP]$  were also measured in addition to  $^1\text{H}$  data. The chemical structures are shown below.

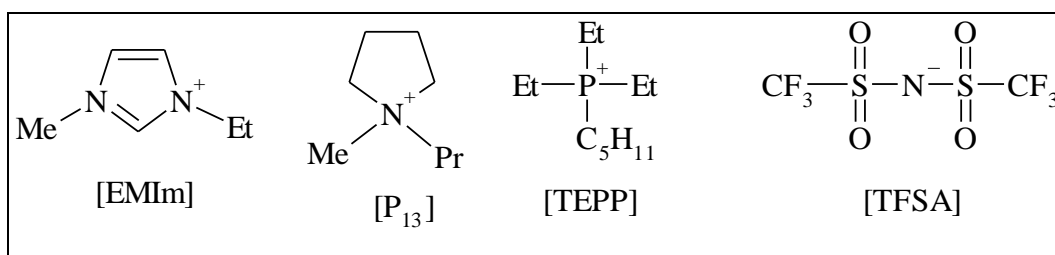


Table 1. The viscosity( $\eta$ ) of the ILs and the  $T_1$  and  $T_2$  of the signals measured at  $30^\circ\text{C}$  under 6.4 T SCM.

	$[EMIm][TFSA]$	$[P_{13}][TFSA]$	$[TEPP][TFSA]$
$\eta$ (m PAS)	27.7	49.8	68.2
$^{19}\text{F}$ $T_1$ (s)	1.23	0.90	0.85
$^{19}\text{F}$ $T_2$ (s)	0.39	0.25	0.19
$^1\text{H}$ $T_1$ (s)	1.60-1.88 (ring H) 0.73 (CH <sub>2</sub> ) 0.80 (N-CH <sub>3</sub> ) 1.23 (CH <sub>3</sub> (Et))	0.51, 0.58 (pyrCH <sub>2</sub> ) 0.46 (N-CH <sub>3</sub> ) 0.38, 0.43 (CH <sub>2</sub> 's) 0.61 (CH <sub>3</sub> (Et))	0.39 (CH <sub>2</sub> (Et)) 0.41-0.59 (CH <sub>2</sub> 's) 0.67 (CH <sub>3</sub> (Et)) 0.88 (t-CH <sub>3</sub> )
$^1\text{H}$ $T_2$ (s)	0.15 (N-CH <sub>3</sub> )	0.12 (N-CH <sub>3</sub> ) 0.015 (pyrCH <sub>2</sub> )	-
$^{31}\text{P}$ $T_1$ (s)			1.85
$^{31}\text{P}$ $T_2$ (s)			0.030

## Sample preparation

For NMR diffusion measurements, the samples were placed into 5-mm NMR microtubes (BMS-005J, Shigemi, Tokyo) to a height of 5 mm. The magnetic susceptibility of the sample tube is closely matched to solution samples thereby affording good magnetic homogeneity over the whole sample volume. The length of the sample was intentionally made short so that it lay within the constant region of the applied PFG. The line width of H<sub>2</sub>O in the same sample conditions was adjusted to be better than 5 Hz. Generally, the line widths of ILs are broader and depend on temperature and do not always become sharper at higher temperature.

## NMR Measurements

All NMR spectra were measured on a Tecmag Apollo with a 6.4 T wide bore magnet using a multinuclear JEOL PFG probe and controlled by a JEOL console. The applied magnetic gradient is constant for samples up to 10 mm in length and the maximum gradient strength is about 20 T/m. The gradient strength was calibrated by using H<sub>2</sub>O and D<sub>2</sub>O (<sup>2</sup>H NMR at the frequency 41.5 MHz). The <sup>1</sup>H, <sup>19</sup>F and <sup>31</sup>P NMR spectra were measured at 270.2, 254.2 and 109.4 MHz, respectively. All measurements were performed without sample spinning to prevent disturbance from sample motion. T<sub>1</sub> and T<sub>2</sub> measurements were performed by the inversion recovery (180°-τ-90°-Acq) and the Hahn echo (90°-τ-180°-τ-Acq) pulse sequences, respectively and the T<sub>1</sub> and T<sub>2</sub> values at 30°C are given in Table 1.

## Fitting of Echo Signals

The diffusion measurements were performed using the SE and STE pulse sequences shown in Fig. 1. In the case of free diffusion, the echo attenuation,  $E$ , is related to the experimental variables and the diffusion coefficient  $D$  is obtained by the Stejskal-Tanner equation,

$$E = \frac{S}{S_0} = \exp(-\gamma^2 g^2 \delta^2 D (\Delta - \frac{\delta}{3})), \quad (1)$$

where  $\gamma$  is the gyromagnetic ratio of nucleus under study,  $S$  is the amplitude of echo signal and  $S_0$  is the amplitude where  $g = 0$ ,  $g$  is the strength of the gradient pulse of duration  $\delta$ , and  $\Delta$  is the interval between the leading edges of the gradient pulses. For a freely diffusing system it is possible to measure the diffusion coefficients by varying  $\delta$ ,  $g$ , or  $\Delta$ . In the present case, the measurements were performed by holding  $g$  constant and varying  $\delta$  under software control on our spectrometer. Since the effective PFG amplitude is  $\delta \times g$ , the result is the same measured by the conditions of fixing  $\delta$  and varying  $g$ .  $\Delta$  defines the timescale of diffusion measurement and

in a homogeneous liquid system, the measured  $D$  is independent of  $\Delta$ . It must be noted that long  $\Delta$  brings the reduction of the signal-to-noise ratio of the echo signals and also is easily affected by artifactual convection effects especially in high temperature. The diffusion coefficients and the fitting errors were determined by regressing Eq. 1 onto the resulting PGSE attenuation data using non-linear least squares regression using Origin (OriginLab, MA). The data are presented below in a linearized form to enable easy comparison.

### [EMIm][TFSA]

$^1\text{H}$  spectra of [EMIm] observed by various modes are shown in Fig. 2. The spectrum observed after a single pulse together with its spectral assignment is shown in Fig. 2(a).

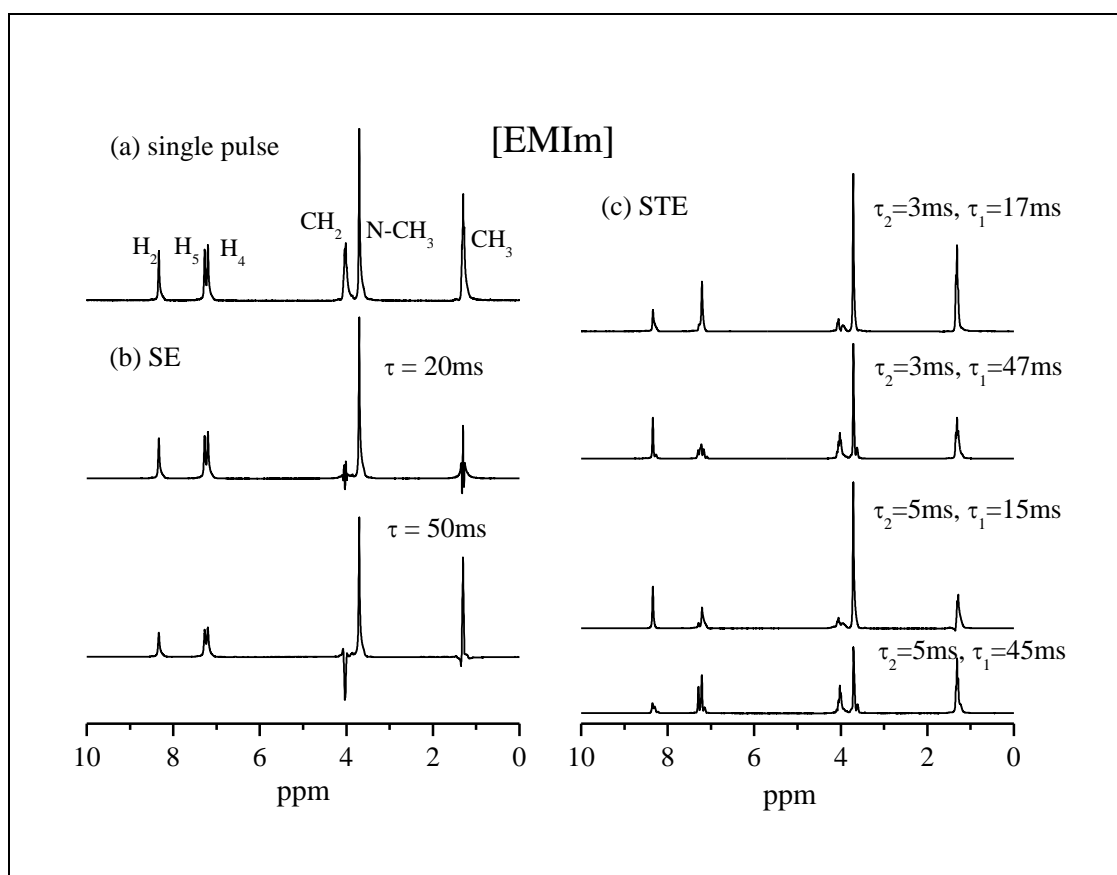


Figure 2.  $^1\text{H}$  spectra of [EMIm] measured with (a) single pulse, (b) Hahn (SE) and (c) stimulated echo (STE) sequences with RF pulse different intervals. The STE echo signals were measured with small and short PFGs.

The spin-spin coupling  $J$  influences the phases of the resonances in the observed echo signals depending on the  $J$ -values. For example, echo signals for resonances with  $J = 7$  Hz are distorted significantly around  $\tau = 23$  ( $= 1/(2\pi J)$ ),  $45$  ( $= 2/(2\pi J)$ ),  $68$  ( $= 3/(2\pi J)$ ) ms etc. In Table 1, the  $^1\text{H}$   $T_1$  values are given for the all signals and the  $^1\text{H}$   $T_2$  value was obtained only for the N-CH<sub>3</sub> signal. The  $J$ -coupling modulations produce deleterious effects in PGSE experiments such that depending on the choice of  $\tau$ , there can be large loss in signal-to-noise and distortion of the line-shape. Nevertheless, providing that there is sufficient signal-to-noise, the correct diffusion coefficient will be obtained. Thus, the effects of  $J$ -evolution on the [EMIm] echo signals obtained with the SE sequence are shown in Fig. 2(b) for the cases of  $\Delta = 20$  and  $50$  ms. Although the ethyl signals are significantly influenced by the  $J$ -evolution, the N-CH<sub>3</sub> and imidazolium ring proton signals with negligible spin-spin coupling are almost unchanged and in all cases the evolution effects are insensitive to the presence or absence of the PFGs. The signals obtained with the STE sequence for different delay combinations under short and small PFGs are shown in Fig 2(c). Without PFGs, the  $J$ -coupled signals were significantly distorted. Clearly, the  $D$  measurements of individual peaks are limited due to choices of the RF pulse intervals. In addition to suitable values of the intervals between the RF pulses with respect to the relaxation times to retain sufficient signal intensity and minimize distortion due to  $J$ -evolution, to obtain a  $D$  value, three parameters must be set, i.e.,  $\Delta$ ,  $\delta$ , and  $g$  as shown in Fig. 1. For freely diffusing species the values of these three parameters are somewhat arbitrary, provided that the sufficient signal attenuation can be achieved to enable an accurate diffusion measurement. The effective PFG strength is determined by  $\delta \times g$ .

To test effects of changing  $g$  and  $\delta$  on the on accuracy of determined  $D$  values, PGSE measurements were performed using the SE sequence on the NCH<sub>3</sub> signal of [EMIm] at  $30$  °C. For a fixed  $g$ , measurements were performed with 20 different  $\delta$  values. The longest  $\delta$  values set as 1, 2, 3 and 4 ms and PGSE attenuation data were plotted for  $\Delta = 20$  and  $50$  ms in Fig. 3(a) and (b), respectively. All plots look single exponential as expected from Eq. 1. The estimated error for each plot ( $\sim \pm 0.02 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ ) from the Origin software is an underestimate of the true error contained in the experimental  $D$  value, because the calculated  $D$  values scatter in larger extents under the different measuring parameters. When  $\Delta=20$  ms, the  $D$  was evaluated to be  $6.3 \pm 0.15 \times 10^{-11} \text{ m}^2\text{s}^{-1}$  and for  $\Delta=50$  ms it was found to be  $6.2 \pm 0.05 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ . The slightly lower  $D$  value at  $\Delta = 50$  ms is reasonable because of the general trend of  $\Delta$ -dependent  $D$  values in the low temperature region as shown in Figs. 4 and 8. The larger deviation observed at  $\Delta = 20$  ms may be related to the shape of the PFG or hardware limitation. The  $D$  values of the measurable peaks of [EMIm] were consistent within experimental errors for both the SE and STE-base PGSE pulse sequences.

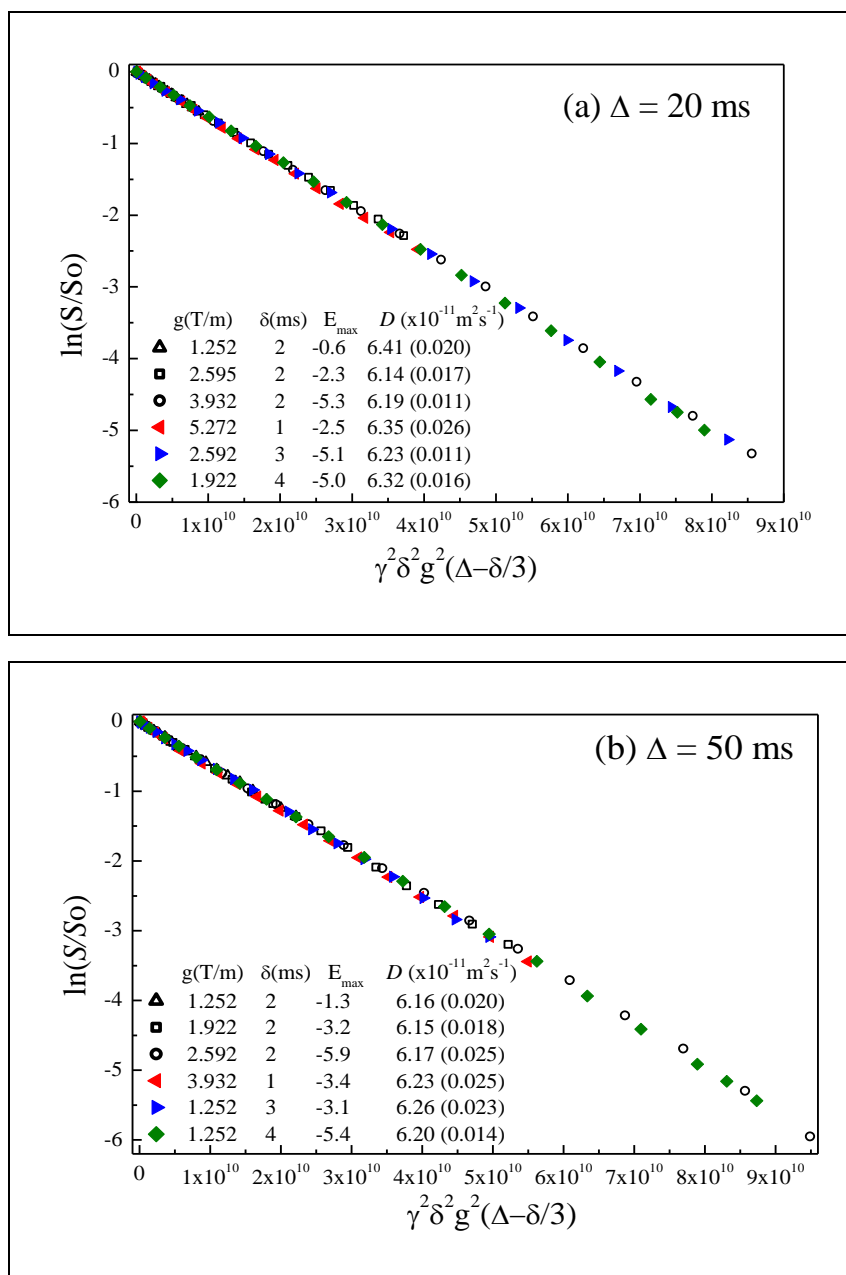


Figure 3. PGSE attenuation plots for the single N-CH<sub>3</sub> signal of [EMIm] at 30 °C obtained by varying  $\delta$  at different  $g$  values for (a)  $\Delta = 20$  ms and (b)  $\Delta = 50$  ms. Twenty different  $\delta$  values were used in each measurement. The diffusion coefficients with accompanying error for each data set are given in the inset, where the maximum attenuation ( $\ln(S/S_0)$ ) is included.

The  $\Delta$ -dependence of  $D$  for species in structurally heterogeneous systems like polymers and porous materials is referred to as anomalous diffusion and been reviewed by Metzler and Klafter (R. Metzler and J. Klafter, *J. Physics Reports*, **2000**, 339, 1). ILs cannot be assumed to

have such structures resulting in motional restrictions. Experimentally, the  $\Delta$ -dependence  $D$ 's have been observed in the lower temperature region especially in viscous ILs, and the phenomena may be related to ionic interactions (K. Hayamizu, S. Tsuzuki and S. Seki, *J. Phys. Chem. A* **2008**, *112*, 12027). Since [EMIm][TFSA] is a representative IL, the  $\Delta$ -dependent  $D$ 's were measured as shown in Fig. 4 (a) and (b) for [EMIm] and [TFSA] in the temperature range -20 to 30 °C, respectively. Only a small increase in the  $D$  values was observed with decreasing  $\Delta$  in both [EMIm] and [TFSA] and the effect increased as the temperature decreased in the present sample.

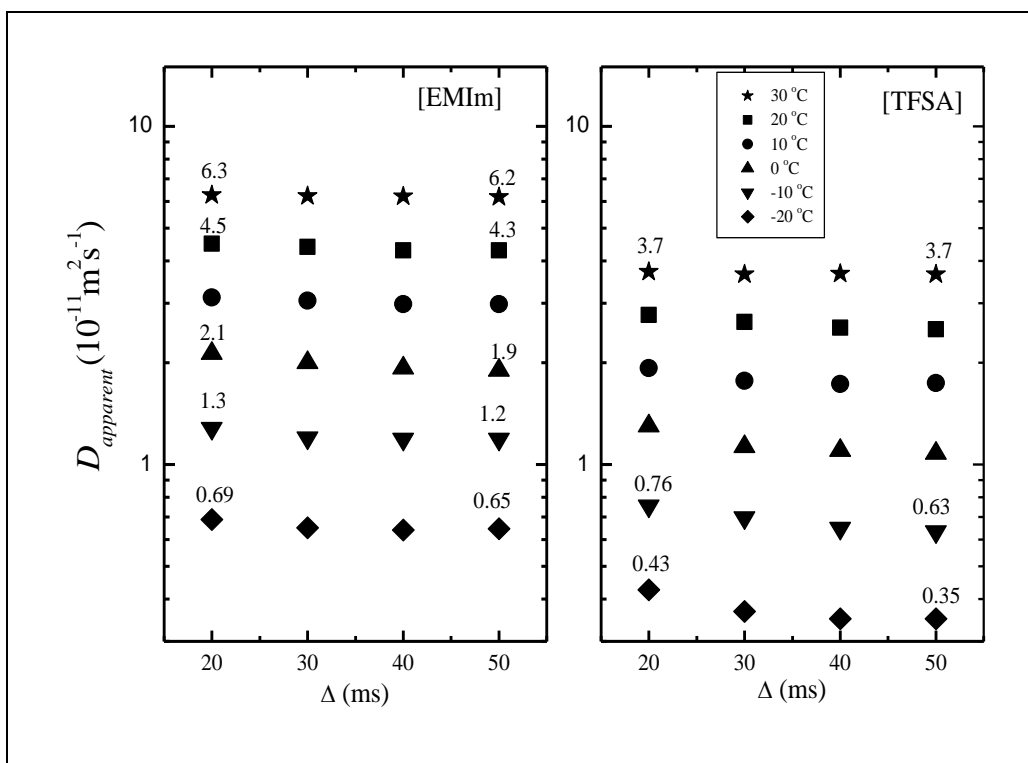


Figure 4. The  $\Delta$  dependent  $D$ 's (i.e.,  $D_{apparent}$ ) of [EMIm][TFSA] measured in the temperature range from -20 to 30 °C.

The temperature dependent  $D$  values of [EMIm][TFSA] were measured in five different samples using various PFG probes, and the data are plotted in Fig. 5 including previously published data. Recently, the purity of ILs has been recognized to influence physical properties, and consequently greater efforts have been made to obtain pure ILs. The addition of H<sub>2</sub>O to [BMIm][TFSA] was reported to increase the ion diffusion. In the present variable temperature measurements, to exclude convection effects in the high temperature range,  $D$  values were obtained at least two different  $\Delta$ 's, since the convection effects are  $\Delta$ -dependent and the apparent  $D$  value becomes larger with longer  $\Delta$  (K. Hayamizu and W. S. Price, *J. Magn. Reson.*



2004, 167, 328). In the low temperature range where the  $\Delta$ -dependent  $D$ 's were observed, the  $D$  value at the long  $\Delta$  was adopted, where the  $D$  values do not vary with  $\Delta$ . Our data were obtained from the early stage of ILs research from different [EMIm][TFSA] including the synthesized independently (A, B and C) and commercial available samples (D and E) and the purity of the sample (E) was high where no extra peak was observed. Although variation is observed in the low temperature region, the general agreement in the data of  $D$ 's for [EMIm] and [TFSA] at each temperature is excellent within the experimental errors. Recently, data were kindly offered from Prof. K. R. Harris of The University of New South Wales, in Canberra Australia and added in Fig. 5. The measurements were made quite independently using a laboratory-built probe for steady-gradient spin-echo NMR at 20 MHz. The agreement is surprisingly excellent and indicates that the  $D$ 's are physical constants independent from the measuring methods and measuring frequencies (magnetic field).

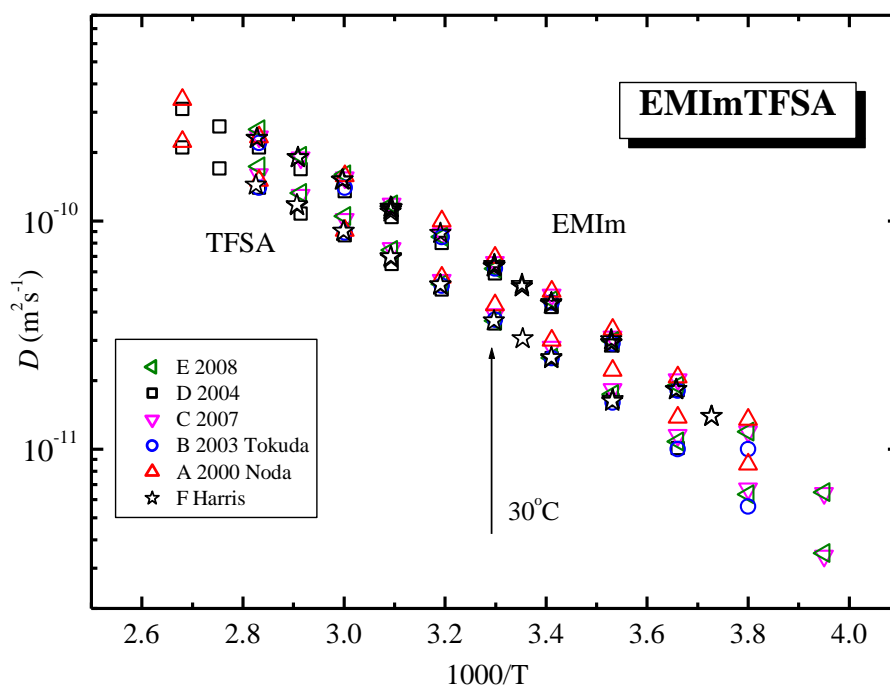


Figure 5. The temperature dependent  $D$ 's of [EMIm][TFSA] measured for the five different samples observed using various probes by our group. **A**: measured in 2000, the first measurement of  $D$  values for ILs at  $\nu_H = 200$  MHz (A. Noda, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B* **2001**, 105, 4603). **B**: measured in 2003 as a series of measurements of ILs,  $\nu_H = 400$  MHz (H. Tokuda, K. Hayamizu, K. Ishii, M.A.B.H. Susan and M. Watanabe, *J. Phys. Chem. B* **2004**, 108, 16593). **C**: measured in 2004 related to other ILs,  $\nu_H = 200$  MHz (K. Hayamizu, Y. Aihara, H. Nakagawa, T. Nukuda and W. S. Price, *J. Phys. Chem. B* **2004**, 108, 19527). **D**:

measured in 2007,  $\nu_{\text{H}} = 270$  MHz and **E**: recent sample (S. Tsuzuki, K. Hayamizu and S. Seki, *J. Phys. Chem. B* **2010**, *114*, 16329 and K. Hayamizu, S. Tsuzuki, S. Seki and Y. Umebayashi, *J. Chem. Phys.* **2011**, *135*, 84505). The samples A, B, C were synthesized independently, and the samples D and E were from commercial sources. **F**: measured by Prof. K. R. Harris by steady-gradient spin-echo NMR at 20 MHz, and presented by M. Kanakubo, K. R. Harris, S. Tsuduki, T. Umechy, T. Makino and A. Suzuki at 32<sup>nd</sup> International Conference on Solution Chemistry (2011).

### [P<sub>13</sub>][TFSA]

The spectral pattern and corresponding assignment of [P<sub>13</sub>] is shown in Fig. 6(a). Except for NCH<sub>3</sub>, the signals have *J*-couplings. The T<sub>1</sub> and T<sub>2</sub> data are summarized in Table 1. The effects of *J*-evolution in the SE and STE sequences are shown in Fig. 6(b) and (c), respectively.

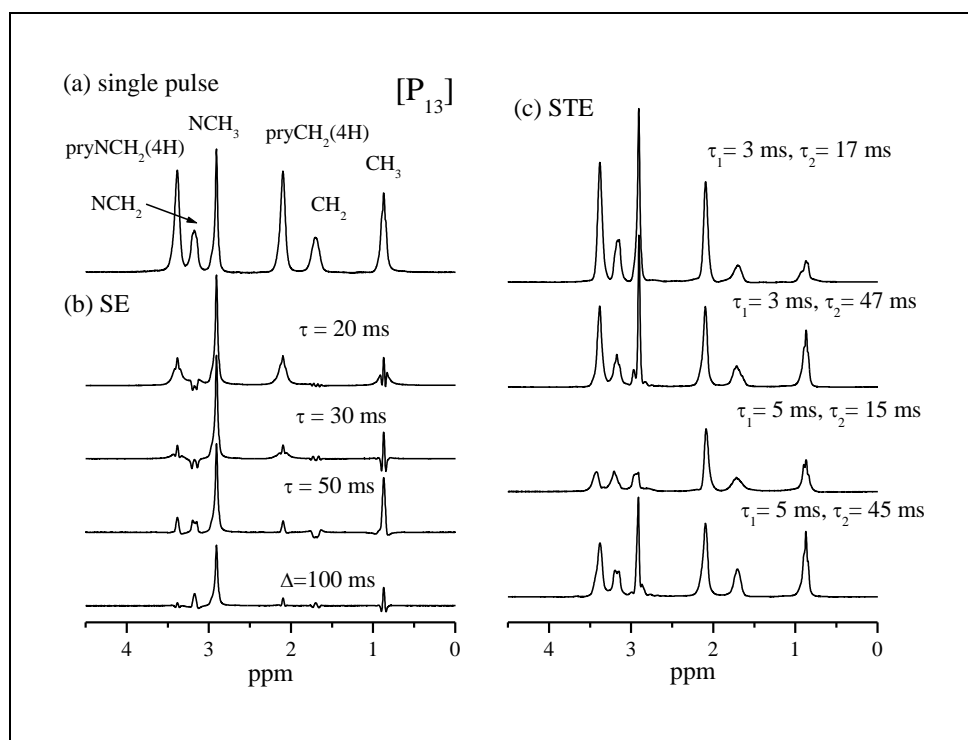


Figure 6. The <sup>1</sup>H spectra of [P<sub>13</sub>] measured by (a) single pulse, (b) Hahn and (c) stimulated echoes with different RF pulse intervals. The STE echo signals were measured with small and short PFGs.

The behaviors of two signals of the ring CH<sub>2</sub>'s are similar because of the same *J* values. Due to the effects of *J*-evolution, accurate *D* values can only be obtained from signals having sufficient intensity. At 30°C setting  $g = 3.932$  T/m,  $\Delta = 20$  ms and changing  $\delta$  from 0.1 to 2 ms in 19

increments, the measurements were performed using both SE and STE-based PGSE sequences. The errors obtained from regressing Eq. 1 onto the data sets were always smaller than  $0.02 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ . The estimated  $D$  value from the all peaks was  $2.90 \pm 0.06 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ . At  $\Delta = 50 \text{ ms}$  a slightly precise value of  $D = 2.82 \pm 0.02 \times 10^{-11} \text{ m}^2\text{s}^{-1}$  was obtained. The apparent  $D$ 's of the anion TFSA determined from  $^{19}\text{F}$  resonance were  $2.19$  and  $2.13 \times 10^{-11} \text{ m}^2\text{s}^{-1}$  at  $\Delta = 20$  and  $50 \text{ ms}$ , respectively. The detailed data for  $[\text{P}_{13}][\text{TFSA}]$  and  $[\text{P}_{13}][\text{FSA}]$  in the neat and lithium binary samples were published. (K. Hayamizu, S. Tsuzuki, S. Seki, K. Fujii, M. Suenaga and Y. Umabayashi, *J. Chem. Phys.***133**, 194505 (2010)).

### [TEPP][TFSA]

The spectral pattern and the corresponding assignments of [TEPP] are shown in Fig. 7 (a). All  $^1\text{H}$  signals are split due to  $J$ -coupling. The  $T_1$  and  $T_2$  values of  $^{19}\text{F}$  and  $^{31}\text{P}$  resonances are given in Table 1. The  $^1\text{H}$   $T_1$  values were obtained at  $30^\circ\text{C}$  for each peak, but  $^1\text{H}$   $T_2$  value could not be obtained due to  $J$ -coupling. As shown in the SE spectra in Fig. 7(b), diffusion measurements were hampered by the effects of  $J$ -evolution. The STE echo signals with varying  $\tau_1$  and  $\tau_2$  shown in Fig. 7(c) indicate the possibility of the arbitrary choice of  $\Delta (= \tau_1 + \tau_2)$  values in the STE sequence.

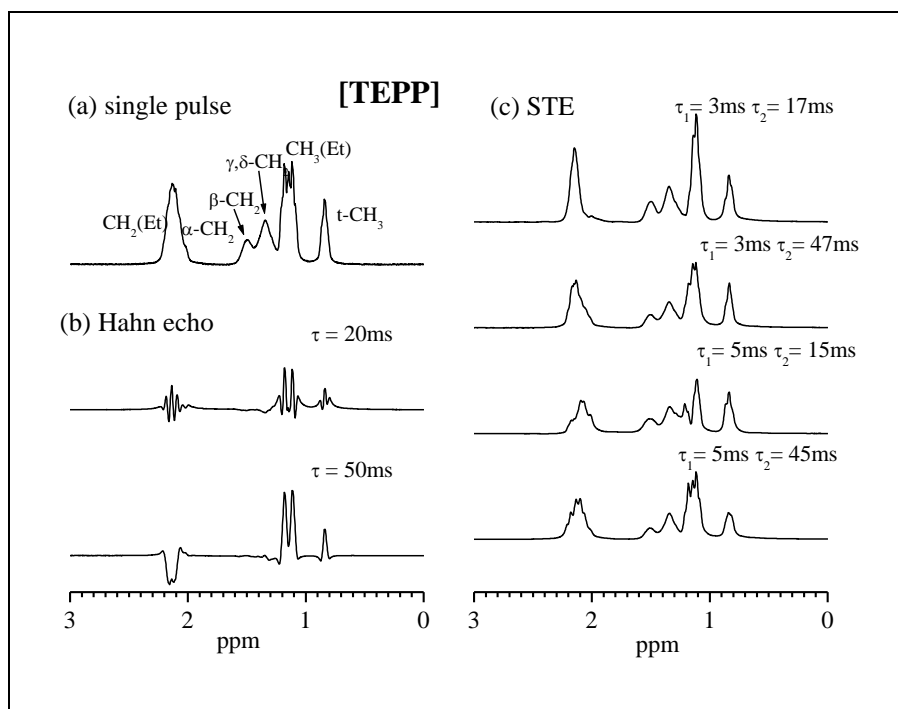


Figure 7.  $^1\text{H}$  spectra of [TEPP] measured by (a) single pulse, (b) Hahn and (c) stimulated echoes with different RF pulse intervals. The STE echo signals were measured with small and short

PFGs.

The  $\Delta$ -dependent  $D$  values of each peak at 30 °C are shown in Fig. 8, where the  $D$  values obtained from  $^{31}\text{P}$  [TEPP] and  $^{19}\text{F}$  [TFSA] measurements are added. The  $^{31}\text{P}$  measurements were performed by changing  $\delta$  from 0.1 to 4 ms with  $g = 4.602$  T/m for  $\Delta = 50$  and 70 ms and  $g = 5.272$  T/m for  $\Delta = 20$  and 30 ms. The  $D$  values obtained from the  $^1\text{H}$  and  $^{31}\text{P}$  resonances were consistent with each other because both nuclei belong to the same species. Clear  $\Delta$  dependencies exist for both the cation [TEPP] and anion [TFSA]. The deviations of the apparent  $D$  values for the individual peaks are largest at  $\Delta = 20$  ms and it is unclear whether the variation results only from the hardware limitation or some mutual ion interaction phenomenon of the viscous IL. We adopt the  $D$  values obtained at the long  $\Delta$  for comparison with other physical data like ionic conductivity and viscosity. The  $D$ 's of [TEPP] and [TFSA] at 30°C are  $1.43 \pm 0.03$  and  $1.60 \pm 0.02 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ , respectively.

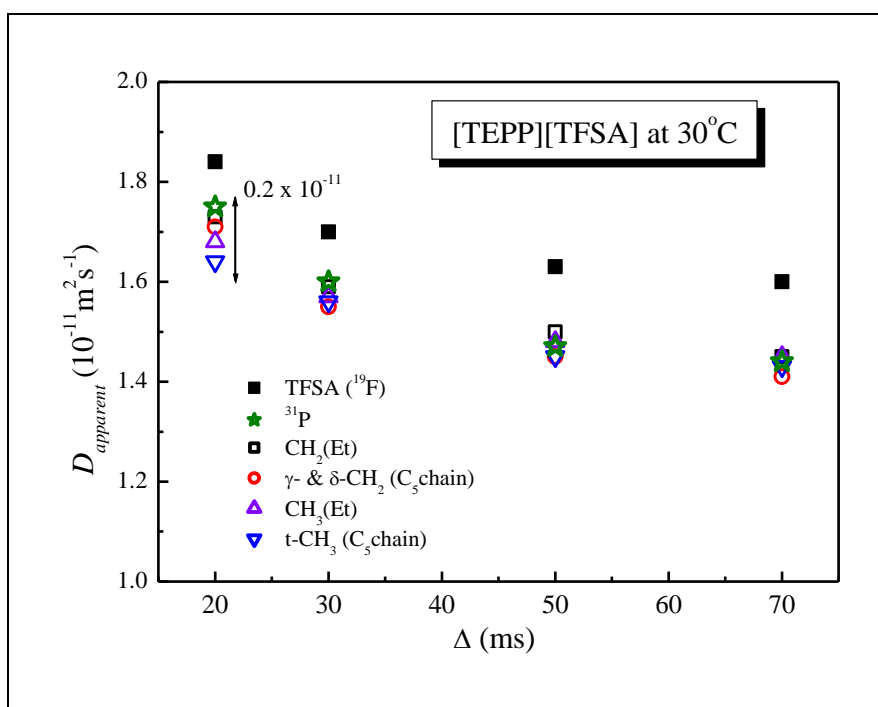


Figure 8. The  $\Delta$ -dependent apparent self-diffusion coefficients measured for each  $^1\text{H}$  and  $^{31}\text{P}$  resonance of [TEPP] and [TFSA] ( $^{19}\text{F}$  resonance).

### Concluding Remarks.

Measurements of the diffusion coefficients for viscous materials like ILs require high gradient amplitude. Care should be taken to prepare samples suitable for the particular PFG probe

available to measure accurate self-diffusion coefficients ( $D$ 's). In addition, the sample volume should be adjusted to be a suitable volume to obtain homogeneity of the external magnetic field and RF pulses, constancy of the PFG, and homogeneity of the temperature over the sample to prevent convection effects. Since each probe has unique specifications, precise and accurate calibration is important. Improper experimental settings lead to erroneous self-diffusion estimates. The errors in a measured diffusion coefficient must be estimated including factors of the experimental setups rather than the estimated errors from the data fitting alone.

After careful measurements of  $D$ 's of the three ILs, we could not find any evidence of an existing intrinsic internal gradient. The  $D$  values of the individual  $^1\text{H}$  signals within the same molecule coincide with each other including the  $^{31}\text{P}$  signal in the center of TEPP. The slightly larger variation in the diffusion data obtained at  $\Delta = 20$  ms for the viscous ILs at low temperatures may be due to interactions between individual ions. The  $\Delta$ -dependence of the diffusion coefficients of a lithium and a divalent anion of the lithium salt  $\text{Li}_2\text{B}_{12}\text{F}_{12}$  dissolved in propylene carbonate (PC) was also observed at low temperature ( K. Hayamizu, A. Matsuo and J. Arai., *J. Electrochem. Soc.* **2009**, *156*, A744) The origin of the  $\Delta$ -dependence of the ion diffusion coefficients at low temperature region cannot be explained by analogy to the anomalous diffusion in heterogeneous materials, but experimentally the  $\Delta$ -dependences of ion diffusion coefficients have been observed in viscous electrolytes and awaits further clarification.

### Acknowledgements.

The author thanks to Drs. A. Noda, H. Tokuda and S. Seki, Y. Aihara and Prof. M. Watanabe of Yokohama National University for sincere discussion on the preparation of samples, measuring conditions and the diffusion coefficient of EMImTFSA in Fig. 5. She also thanks to Prof. K. R. Harris in University of New South Wales in Canberra Australia to offer me the diffusion data measured by the steady-gradient spin-echo NMR method in Fig. 5.

### Note:

A flame-sealed sample of EMImTFSA in a 5-mm NMR microtube (BMS-005J, Shigemi) is available with NMR and diffusion data including the measuring conditions from Research Institute of Biomolecule Metrology Co., Ltd ( <http://www.ribm.co.jp/>).