

Multi-nuclear PFG spectroscopy on a benchtop NMR spectrometer

Molecular diffusion is the mechanism that defines molecular mobility in solutions. The study of diffusion processes is of interest in widespread fields in science where transport of mass needs to be determined. NMR is the method of choice to quickly determine self-diffusion coefficients of chemical species in solution. A commonly used NMR technique requires the combination of pulsed field gradients with a stimulated echo sequence (PGSTE). The spectroscopically resolved version of this sequence makes it possible to measure the diffusion coefficient of different molecules in a mixture by measuring the diffusion attenuation of the signal of each particular chemical group of each molecular structure. The diffusion version of the Spinsolve is a benchtop spectrometer that comes with gradient coils to make this type of experiments possible. The power of the combination of pulsed field gradients with spectroscopy has been demonstrated in the past to acquire DOSY (Diffusion Ordered Spectroscopy) type experiments. In this application note we take advantage of the multinuclear feature of the Spinsolve spectrometers to get access to a bigger variety of molecules that could be present in a mixture. The possibility to measure the signal of different nuclei is also advantageous in cases where signal overlapping in the ^1H spectrum does not allow for accurate separation of each component. To demonstrate the power of multi-nuclear diffusion measurements we have chosen an example where ^1H , ^{19}F , and ^7Li provide access to three different molecular species.

With the growing market for electric and hybrid cars, a major focus of scientists today lies on the development of more efficient rechargeable batteries. In these devices, lithium salts are used as electrolytes dissolved in room-temperature ionic liquids (RTILs), which are desirable materials because of their low vapor pressure and electrochemical stability. Here, the knowledge of the diffusional behaviour helps to tune the systems to the desired properties. Furthermore, ionic liquids are used as special media in synthesis and as extractants.

To demonstrate the possibility to determine diffusion constants for three different ions, of which each has an exclusive nucleus, different mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM- BF_4) and lithium tetrafluoroborate (LiBF_4) were analysed (Figure 1). BMIM- BF_4 is one of the most studied ionic liquids. BMIM $^+$ contains ^1H as NMR active species, BF_4^- contains ^{19}F , and the Li^+ ion can only be accessed by measuring ^7Li .

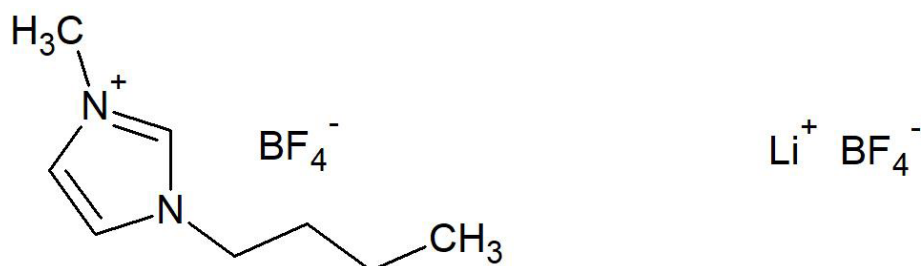


Figure 1: BMIM- BF_4 (left) and LiBF_4 (right).

Figure 2 shows the NMR spectra of the three ions. The ^1H spectrum of BMIM^+ shows the signals of all chemical groups present in this molecule and the ratios corresponding to the number of ^1H present in each group is cross checked by the integral of each peak (Fig. 2a). The fluorine spectrum of BF_4^- shows a singlet at about -148 ppm as expected from the literature (Fig. 2b). Finally, the Li^+ ion also shows a singlet at almost 0 ppm which is very easy to quantify (Fig. 2c).

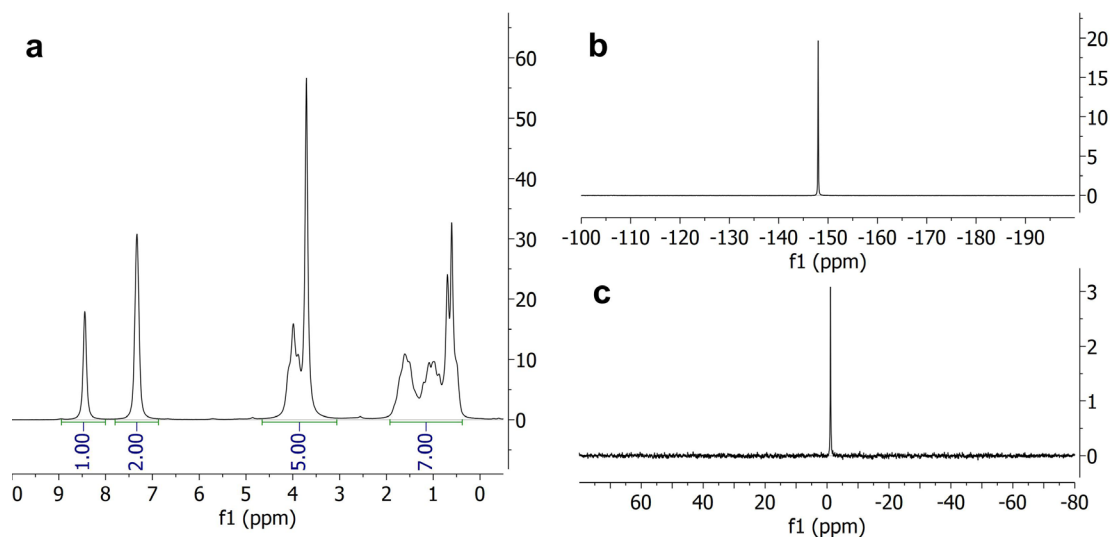


Figure 2: Proton (a), fluorine (b) and lithium (c) spectra of $\text{BMIM-BF}_4 + \text{LiBF}_4$. The proton and fluorine spectra were recorded on neat BMIM-BF_4 in single scan experiments in less than 10 s each. The lithium spectrum was recorded on 16.7 mg/mL LiBF_4 in BMIM-BF_4 with four scans in 20 s.

Experimental information

The Spinsolve® 60 Lithium Diffusion benchtop NMR spectrometer used for these studies generates a magnetic field of 1.47 T aided by a modern Halbach permanent magnet. At this magnetic field strength samples containing protons (^1H), fluorine (^{19}F), and lithium (^7Li) nuclei can be measured at frequencies of 62.49 MHz, 58.80 MHz and 24.28 MHz, respectively. The homogeneity of the magnetic field, measured as the width at half height of the signal peak of a reference water sample (5/95 v/v $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixture) is 0.32 Hz (5 ppb) and a linewidth of 13 Hz (213 ppb) is measured at 0.55% of the peak height. The system is equipped with a gradient coil that generates a maximum field gradient of 210 mT/m. The recovery time of the gradient coil is less than 2 ms (time required by the magnetic field to get stable after a field gradient pulse). The schematic of the stimulated echo sequence including pulsed field gradients (PGSTE) used to determine the self-diffusion coefficients is shown in Figure 3.

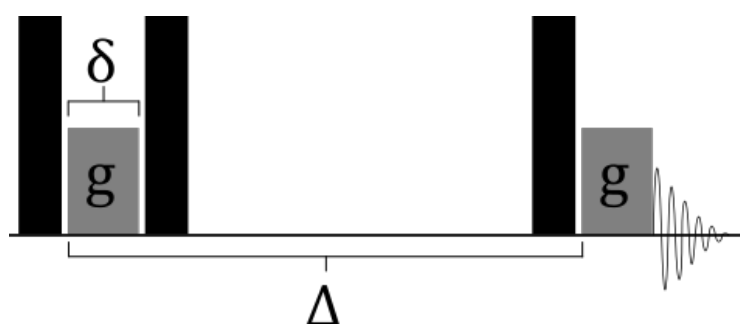


Figure 3: Pulse sequence of the PGSTE experiment. Grey rectangles are gradients with strength g and duration δ . Black rectangles are 90° pulses. Δ is the delay between the gradients.

The signal amplitude $S(t)$ that is recorded in this experiment as a function of the gradient pulse amplitude and duration is given by following equation:

$$S(t) = S(0) \exp \left[-D\gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right) \right]$$

Here, $S(0)$ is the signal amplitude without gradients, γ is the gyromagnetic ratio of the observed nucleus and D is the self-diffusion coefficient. Repeating the experiment with different values of g and plotting $\ln(S(t))$ against $\gamma^2 g^2 \delta^2 (\Delta - \delta/3)$ results in a straight line with slope $-D$.

For this study, 5 samples were prepared with different LiBF_4 concentrations. The samples were prepared by adding 16.7 mg, 50.0 mg, 83.3 mg, and 116.6 mg to 1 mL of BMIM-BF_4 and homogenized by rigorous shaking. Once the salt was completely dissolved, 0.5 mL of the solution were transferred into a standard 5 mm NMR tube. A fifth tube was filled with 0.5 mL neat BMIM-BF_4 . All measurements were conducted with the Spinsolve® software as shown in Fig. 4.

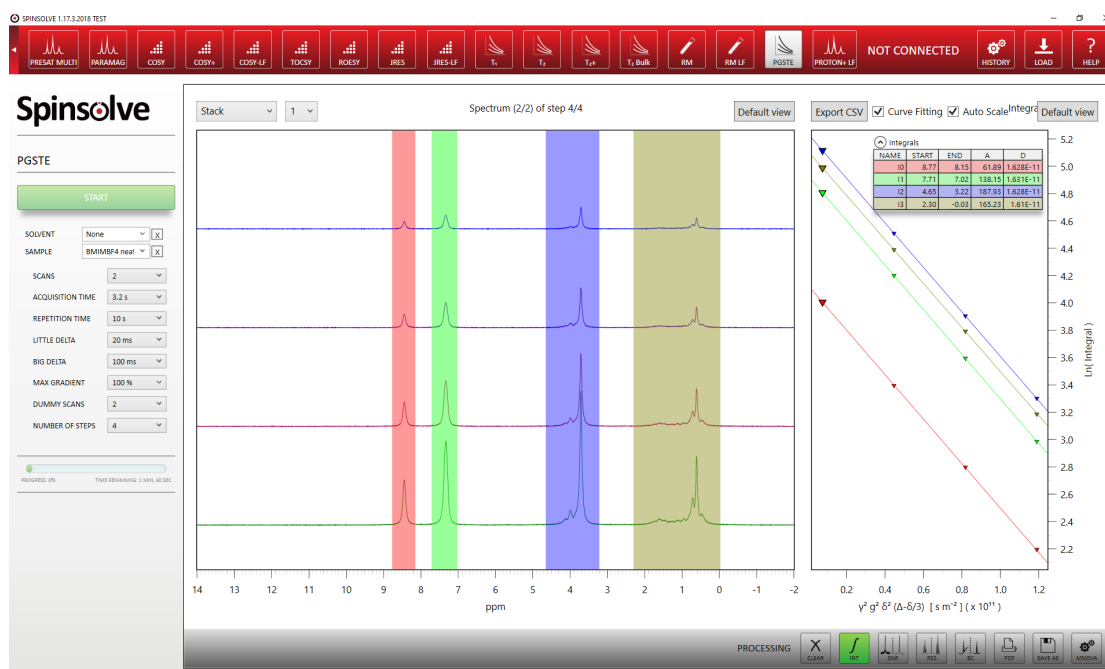


Figure 4: User interface in the Spinsolve® software for diffusion measurements.

The software interface allows one to set the experimental parameters by simply modifying the entries on the panel shown on the left. The list exposes standard NMR parameters like number of scans, number of dummy scans, acquisition time, and repetition time, but also includes the parameters related to the diffusion experiment, like maximum gradient strength, number of steps, duration of the gradient pulses δ , and separation between gradient pulses Δ . The maximum gradient strength divided by the number of steps gives the gradient intervals for the single measurements. For example, with a maximum gradient strength of 100% and number of steps of four, the four experiments will be recorded with gradient strengths of 25%, 50%, 75% and 100%, respectively. In the middle panel of the screen the data is displayed. There, integral regions can be defined, basic processing parameters toggled, and different views of the spectra can be selected. For example, a single spectrum, superimposed spectra, or stacked spectra can be selected. On the right-hand side the integrals are plotted, and the analysis is done fully automatically by the Spinsolve® software.

Results and discussion

For ^1H and ^{19}F four different gradient strengths are sufficient to determine the self-diffusion coefficients, whereas for ^7Li 16 different strengths were used. Nevertheless, to demonstrate the excellent quality of the data, in Figure 5 the spectra of the 50 mg/mL sample, measured with 16 steps, are shown.

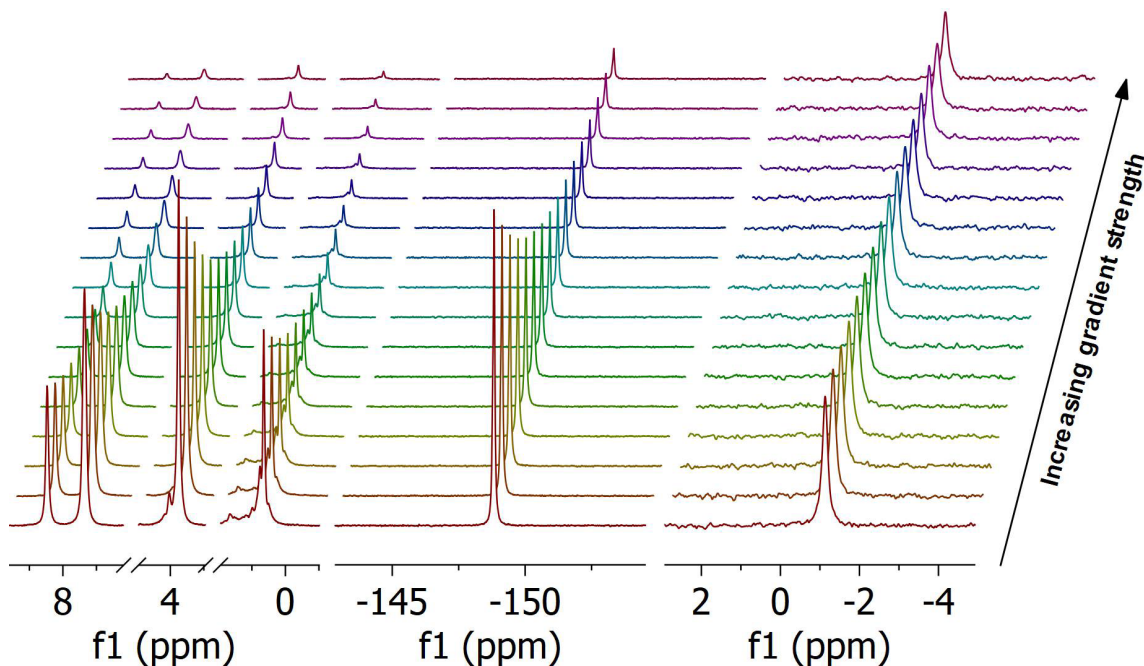


Figure 5: PGSTE experiments of 50 mg/mL LiBF_4 in BMIM-BF_4 . From left to right: proton, fluorine and lithium.

In order to compare the diffusional behaviour of the five different samples, the logarithms of the normalized integrals are plotted against $\gamma^2 g^2 \delta^2 (\Delta - \delta/3)$. In this way, the integral of the signal at the lowest gradient strength is set to one. Linear fits of the data give the self-diffusion coefficients of the different samples.

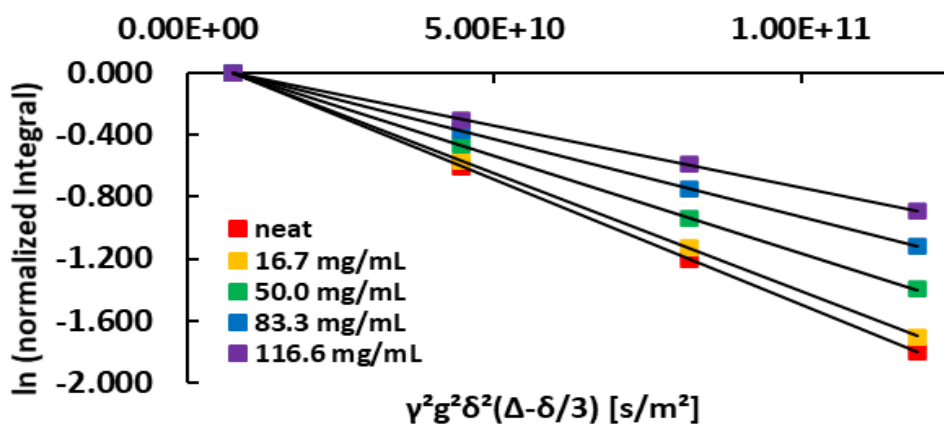


Figure 6: ^1H data of the PGSTE measurements.

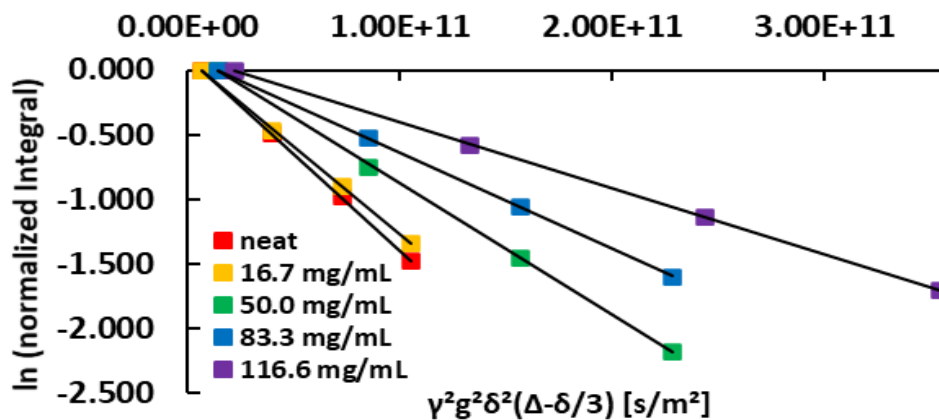


Figure 7: ^{19}F data of the PGSTE measurements.

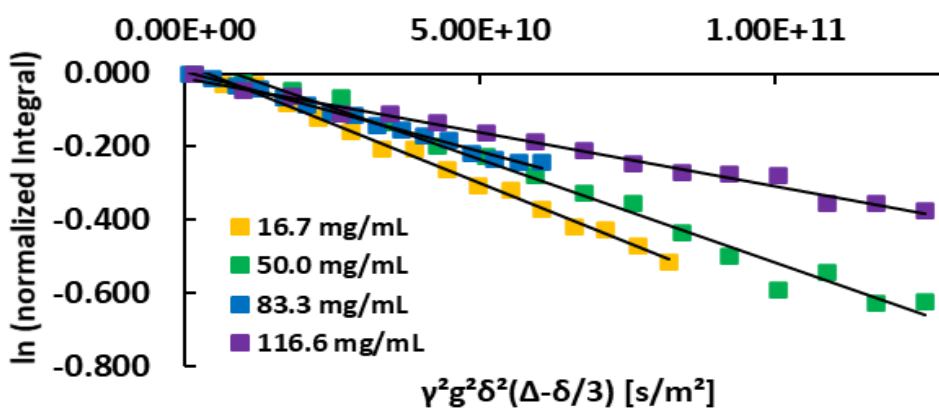


Figure 8: ^7Li data of the PGSTE measurements.

The excellent quality of the data is demonstrated by the highly linear behaviour of the curves shown in Figure 6, Figure 7 and Figure 8. The values of the maximum gradient strength, δ and Δ were optimized for the different samples in order to achieve a signal attenuation that covers a good dynamic range. Linear fitting of these data points gives the self-diffusion coefficients for the three different nuclei and thus the three different ions in the different samples. The results as well as the coefficients of determination are shown in Table 1.

Table 1: Diffusion coefficients and coefficients of determination of the PGSTE measurements.

Conc. LiBF_4 [mg/mL]	D (^1H) [m^2/s]	D (^{19}F) [m^2/s]	D (^7Li) [m^2/s]
	R^2	R^2	R^2
0 (neat BMIM-BF_4)	1.62E-11	1.49E-11	–
	0.99998	0.99999	–
16.7	1.52E-11	1.37E-11	6.42E-12
	0.99998	0.99975	0.99457
50.0	1.25E-11	1.03E-11	5.57E-12
	0.99999	0.99989	0.98408
83.3	9.99E-12	7.45E-12	4.37E-12
	0.99999	0.99999	0.99274
116.6	7.99E-12	5.15E-12	2.96E-12
	0.99989	0.99995	0.98798

The coefficients of determination for the proton and fluorine measurements are all better than 0.99, which is an indicator of the good quality of the measurements. Due to the lower gyromagnetic ratio ^7Li is less sensitive than ^1H and ^{19}F and therefore the signal-to-noise ratio for ^7Li . Nevertheless, the coefficients of determination for lithium are all well above 0.98.

As expected, the diffusion coefficients decrease with increasing lithium salt concentrations due to an increase in the viscosity of the samples. Plotting the different self-diffusion coefficients as a function of the concentration of lithium salt, a linear dependence of the diffusion coefficient is revealed, within the investigated concentration range (Fig. 9). The coefficients of the linear fit for each ion are listed in Table 2.

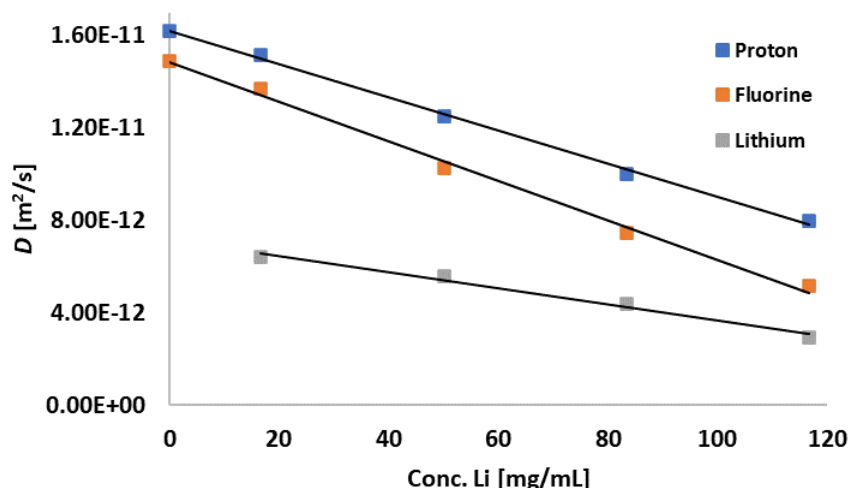


Figure 9: Lithium concentration dependence of D.

Table 2: Fitting equations describing the dependence of the diffusion coefficient on the lithium concentration.

	Proton	Fluorine	Lithium
Equation	$y = -1.20\text{E-}13x + 1.62\text{E-}11$	$y = -8.58\text{E-}14x + 1.49\text{E-}11$	$y = -3.47\text{E-}14x + 7.15\text{E-}12$
R ²	0.9976	0.9955	0.9883

Conclusion

We demonstrated in this application note the power of a Spinsolve® benchtop NMR spectrometer to determine self-diffusion coefficients of three different nuclei that belong to three different species dissolved in the sample. This feature has made possible to study the molecular mobility of different mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate and lithium tetrafluoroborate. This approach is not limited to this system of ions and can easily be transferred to different ionic liquids and lithium salts and also to different nuclei.

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