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Diffusion Coefficients from 13C PGSE NMR Measurements—Fluorine-Free Ionic Liquids with the DCTA− Anion

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**S** *Supporting Information*

ABSTRACT: Pulsed-field gradient spin−echo (PGSE) NMR is a widely used method for the determination of molecular and ionic self-diffusion coefficients. The analysis has thus far been limited largely to ^{1}H, ^{7}Li, ^{19}F, and ^{31}P nuclei. This limitation handicaps the analysis of materials without these nuclei or for which these nuclei are insufficient for complete characterization. This is demonstrated with a class of ionic liquids (or ILs) based on the nonfluorinated anion 4,5-dicarbonitrile-1,2,3-triazole (DCTA−). It is demonstrated here that ^{13}C-PGSE NMR can be used to both verify the diffusion coefficients obtained from other nuclei, as well as characterize materials that lack commonly scrutinized nuclei — all without the need for specialized NMR methods.

SECTION: Kinetics, Spectroscopy
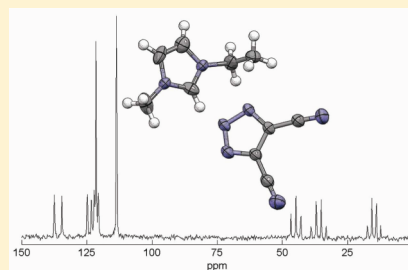
Nuclear magnetic resonance (NMR) spectroscopy, especially the pulsed-field gradient spin−echo (PGSE) technique, has been used extensively to measure diffusion coefficients of molecules and ions,[1−4] including the ions in ionic liquids (ILs), salts that melt at low temperature.[5−11] For the ILs reported here, however, the anion, 4,5-dicarbonitrile-1,2,3-triazole (DCTA−)[12−18] (Figure 1), is devoid of both fluorine and hydrogen, which typically serve as convenient probes. Attempts to follow ^{15}N-enriched DCTA− have proven unsuccessful due to the poor NMR properties (low γ, long relaxation time) of this nuclei. ^{13}C nuclei were therefore utilized instead (at natural abundance, Figure 2) as the probe — an approach that has never been attempted before with conventional PGSE-NMR (although there are a few reports of the use of the ^{13}C nuclei for specialized NMR diffusion measurement techniques[19−21]). Reported here are the results for the diffusion coefficient measurements of the IL anions and cations from ^{13}C- and ^{1}H-NMR, as well as the thermal phase behavior and transport properties of the ILs.

Potential and practical applications of ILs are growing exponentially due to their favorable properties such as high thermal stability, low to negligible vapor pressure, tunable polarity as solvents, high conductivity, and so forth.[22−24] The basic principles for designing ILs are to combine charge delocalization and low surface energy for both the cation and anion with shape factors, such as low symmetry and five-
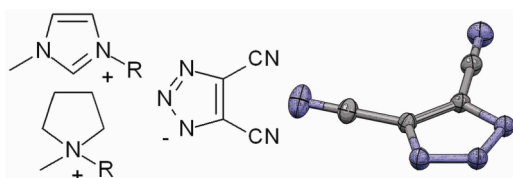
Figure 1. IL cation and anion structures studied in this work:,1-alkyl-3-methylimidazolium (IM_{10R}^+), N-alkyl-N-methylpyrrolidinium (PY_{1R}^+), and 4,5-dicarbonitrile-1,2,3-triazole (DCTA−), where R is an alkyl group (i.e., 2, ethyl; 3, propyl; 4, butyl).

membered rings, which make close packing in a crystal more improbable, thus reducing the melting point (T_m) of the salt. The classical example is the 1-butyl-3-methylimidazolium (IM_{104}^+) cation (Figure 1), which readily forms low melting salts with a wide variety of anions.[11] The most widely used anion is bis(trifluoromethanesulfonyl)imide or $N(SO_2CF_3)_2^−$ (TFSI−), which, though very bulky, possesses extensive charge delocalization and conformational flexibility due to the facile rotation around the S−N−S bonds.[25−27] The use of nonfluorinated anions such as DCTA−, instead of TFSI−, is of
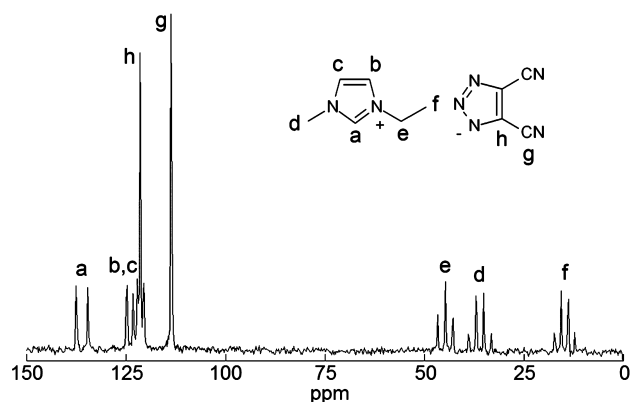
Figure 2. ^{13}C NMR spectrum of $IM_{102}DCTA$ at 25 °C.

Table 1. Properties of the ILs (20°C)

	T_m [°C]	η [mPa s]	ρ [g cm^{-3}]	σ [mS cm^{-1}]
$IM_{102}DCTA$	46			6.3
$IM_{104}DCTA$	−5 (22)	91	1.11	2.9
$PY_{13}DCTA$	36			3.8
$PY_{14}DCTA$	0	101	1.07	2.8

Table 2. Cation and Anion Self-Diffusion Coefficients for the ILs

		D_{cation} [×10^{-11} m^2 s^{-1}]	D_{anion} [×10^{-11} m^2 s^{-1}]
		25 °C	
$IM_{102}DCTA$	^{13}C	2.76 (±0.15)	2.50 (±0.15)
	^{1}H	3.07 (±0.05)	
$IM_{104}DCTA$	^{13}C	1.81 (±0.15)	1.80 (±0.15)
	^{1}H	1.87 (±0.05)	
$PY_{13}DCTA$	^{13}C	1.17 (±0.15)	1.48 (±0.15)
	^{1}H	1.36 (±0.05)	
$PY_{14}DCTA$	^{13}C	1.41 (±0.15)	1.68 (±0.15)
	^{1}H	1.61 (±0.05)	
		60 °C	
$IM_{102}DCTA$	^{13}C	12.80 (±0.20)	12.32 (±0.25)
	^{1}H	13.66 (±0.10)	
$IM_{104}DCTA$	^{13}C	7.22 (±0.20)	7.42 (±0.20)
	^{1}H	8.53 (±0.10)	
$PY_{13}DCTA$	^{13}C	7.80 (±0.50)	8.60 (±0.50)
	^{1}H	7.20 (±0.20)	
$PY_{14}DCTA$	^{13}C	6.39 (±0.20)	7.71 (±0.20)
	^{1}H	7.31 (±0.10)	

interest as this anion is essentially sustainable and fundamentally interesting, being mainly an azacarbon, where the conjugated nature, needed to stabilize the charge, leads to a flat shape (Figure 1) whose geometry departs markedly in size and shape from that of TFSI$^-$ and related anions.

This Letter reports the thermal and physicochemical properties of four ILs based on the heterocyclic DCTA$^-$ anion. Two classes of cations were chosen for this work, 1-alkyl-3-methylimidazolium (IM_{10R}^+) and N-alkyl-N-methylpyrrolidinium (PY_{1R}^+). The cation and anion structures are shown in Figure 1. The charge delocalization of DCTA$^-$ is easy to infer from bond flipping, but DCTA$^-$ also adds the stability of being a Hückel rule representative with extra stability based on there being the $4n + 2$ electrons, here 6 or 10 depending on whether or not the "π" systems of the two CN groups are included.
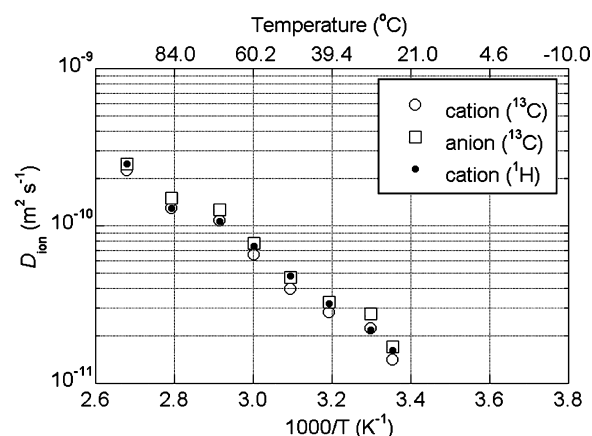

Figure 3. Cation (PY_{14}^+) and anion (DCTA$^-$) self-diffusion coefficients determined from ^{13}C and ^{1}H nuclei for $PY_{14}DCTA$.

Charge is therefore delocalized on seven centers. This anion, with its shape and charge delocalization, can be considered as the counter equivalent of imidazolium cations.

The T_m's of the ILs are reported in Table 1 (and the Supporting Information). Both $IM_{102}DCTA$ and $PY_{13}DCTA$ are solid at room temperature, although they can remain supercooled liquids for extended periods once melted. Most of the ILs have simple phase behavior with a single low-temperature crystalline phase prior to the T_m (see Supporting Information). $IM_{102}DCTA$ gave evidence for a solid−solid phase transitions near −31 °C, albeit this was of low energy, indicating that only a minor structural change occurred during the transition. Note that a previous investigation reported that the T_m is −26 °C for $IM_{102}DCTA$ and that no T_m could be determined for $IM_{104}DCTA$ and $PY_{14}DCTA$.[15] The reported T_m for $IM_{102}DCTA$ seems to be an error in which the solid−solid phase transition was mistaken for the melt transition as the DSC heating trace is only reported to 0 °C. Depending on the thermal history for the salt, $IM_{104}DCTA$ had a T_m of either −5 or 22 °C (Supporting Information). This can be explained by the salt crystallizing into one of two different polymorphic phases, as occurs for halide salts with the IM_{104}^+ cation.[28−30]

Self-diffusion coefficient measurements were performed with a Varian Direct Digital Drive 300 NMR spectrometer ($B_0 = 7.1$ T) with a Doty dual frequency (rf coil diameters are 6 and 8 mm for X and ^{1}H, respectively) z-gradient water-cooled diffusion probe. Diffusion coefficients were measured for the ^{1}H and ^{13}C nuclei, respectively, at 300.1 and 75.5 MHz. $\pi/2$ pulses were determined to be 21 μs for ^{1}H and 18 μs for ^{13}C nuclei. Tetramethylsilane (TMS) was used as a reference for both nuclei. The sample temperature was calibrated with the standard ethylene glycol method and controlled with ±0.5 K accuracy. A PGSE sequence was used to obtain the self-diffusion coefficients for both the ^{1}H and ^{13}C nuclei, according to the very long relaxation times of these nuclei in these media (typically, values were $T_1(^{1}H) \approx 300$ ms and $T_1(^{13}C) > 5$ s). The values of the self-diffusion coefficients were extracted from the classical Stejkal and Tanner equation[1]

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

where $A(0)$ and $A(g)$ are the integrated intensities of the signals obtained, respectively, without and with gradient pulses, D is the self-diffusion coefficient, γ is the gyromagnetic ratio, g is the

gradient field strength, δ is the duration of gradient pulses, and Δ is the time between the two gradient pulses. The gradient pulse duration δ was fixed to 1.5 ms for ^{1}H and 4 ms for ^{13}C, its strength was varied from 50 to 600 G cm^{-1} in 16 steps, and Δ was fixed to 100 ms for both nuclei. ^{13}C spectra were recorded without ^{1}H decoupling, and 32 free induction decays (FIDs) were needed to get a reasonable S/N ratio; the recovery delay was 30 s, which enabled the full set of measurements necessary to determine a diffusion coefficient in 4.5 h. Spectra were recorded with 4000 data points and zero-filled to 16 000 to improve the digital resolution. An exponential filter of 7 Hz was applied to the FID. For the ^{1}H nuclei, eight FIDs were added, and a recovery delay of 15 s was used.

The self-diffusion coefficients of the ILs (Table 2) exhibit the behavior that is expected from the traditional Stokes−Einstein understanding of diffusion. Larger cation or anion size correlates with lower diffusion coefficients. For the different cations, it is possible to determine D_{cation} from both the ^{13}C and ^{1}H data independently, which provides a strong measure of confidence for the ^{13}C results. Discrepancies between the cation diffusion coefficient determined from both nuclei (Table 2 and Figure 3) are around ±10% (this may include a small systematic variation introduced by the larger gradient duration required for the ^{13}C nucleus). This work therefore clearly demonstrates the validity and utility of using standard PGSE NMR methods to obtain diffusion coefficients with the ^{13}C nucleus, a readily available probe for a diverse range of molecules and ions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Sample preparation procedure, experimental details and data (DSC, ionic conductivity and viscosity). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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