

Supporting Information

Influence of Zn²⁺ and Water on the Transport Properties of a Pyrrolidinium Dicyanamide Ionic Liquid

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Experimental

Variable temperature T₁ relaxation data was fitted to the Bloembergen Purcell Pound (BPP) Equation for heteronuclear coupling and then combined with the Arrhenius Equation (Equation S1), to give the fit parameters shown in Table S1. As *C* was left as a floating parameter, average internuclear distances between the ¹³C and ¹H nuclei were calculated using Equation S2.

$$\tau_c = \tau_0 e^{\frac{-E_a}{RT}}$$

Equation S1

Where τ_c is the correlation time (traditionally the time taken for the coupling nuclei to undergo rotation through one radian with respect to one another) (s), τ_0 is a pre-exponential factor, E_a is the Arrhenius activation energy (kJ.mol⁻¹), T is the temperature (K) and R is the gas constant (J.K⁻¹.mol⁻¹).

$$C = \frac{2}{15} \left(\frac{\mu_0 \gamma_C \gamma_H \hbar}{4\pi r_{CH}^3} \right)^2$$

Equation S2

Where μ_0 is the permeability of a vacuum, γ_C and γ_H are the gyromagnetic ratios of ¹³C and ¹H respectively (rad . s⁻¹ . T⁻¹), $\hbar$ is the reduced Planck's constant and r is the distance between the ¹³C and ¹H nuclei (m).

Results & Discussion

Table S1: Fitted parameters of the BPP Equation for fits shown in Figure 8, and a calculation of the internuclear radius (r) from the C parameter using Equation 4

$\chi_{\text{Zn}^{2+}}$	C ($\times 10^8$)	E_a / $\text{kJ}\cdot\text{mol}^{-1}$	τ_0 / s	R^2	r / $\text{\AA}$
0	$10.9 \pm$	27 ± 1	$7.6 \times 10^{-16} \pm$	0.9988	1.38
	13.7		2.0×10^{-16}		
5	9.1 ± 1.1	18 ± 1	$6.5 \times 10^{-14} \pm$	0.9982	1.28
			1.2×10^{-14}		
9	6.7 ± 1.6	20 ± 7	$1.2 \times 10^{-13} \pm$	0.9824	1.32
			2.4×10^{-13}		
20	6.9 ± 1.7	30 ± 2	$7.0 \times 10^{-15} \pm$	0.9593	1.39
			4.7×10^{-15}		
29	7.5 ± 0.1	25 ± 2	$8.3 \times 10^{-14} \pm$	0.9742	1.36
			5.5×10^{-14}		

The parameters outlined in Table 6 appear to show no recognizable trend in either the activation energy (E_a) or the pre-exponential factor (τ_0), which does not seem unreasonable considering the complex nature of ionic liquid systems, the assumptions inherent in the BPP equation and the difficulties in measuring accurate correlation time measurements in electrolytes of this nature. However, when the floating C parameter is resolved to find the internuclear distance between the coupling spins, a length in the range of 1.3 Å is obtained. This value may indicate any of several physical explanations:- That the cation is in close proximity to the dca anion, that the dca carbon may indeed be predominantly coupling to the cyano nitrogen, or that the BPP equation is not capable of providing this information accurately in this electrolyte system when applied in this manner.

As mentioned above, the BPP Equation contains many inherent assumptions about the nature of the nuclei under study, which may explain the observed results. Chiefly, it is applied to *intramolecular* coupling – coupling between two nuclei directly bonded to one another – which is relatively strong when compared to the *intermolecular* through space ^{13}C - ^1H coupling we are assuming between the anion and cation in our system. Caution should be taken especially when a lack of certainty in the spin-lattice relaxation

mechanism exists. It is a particular challenge to consider IL systems containing no spin $\frac{1}{2}$ nuclei on the molecule of interest and it represents a challenge for researchers conducting analyses of this nature in non-protonated and non-halogenated systems like dca.

A second consequence of the two coupling spins being directly bonded to one another is that there is *rotational motion* between the two spins. In systems previously analysed, τ_c is the time taken for the spins to undergo rotation of one radian, and temperature dependant deviation from this has been used to infer more complex reorientation of a molecule.

As the [C₄mpyr][dca] system is assumed to lack directly bonded coupling nuclei, the through space ^{13}C - ^1H coupling has several options unavailable in a bonded system. As well as traditional rotational motion, the system may also undertake *translational motion* as the internuclear distance changes and *reorientational motion* as the molecules change positions with respect to one another. All of these factors will be contained within the value of τ_c and are not able to be separated using this analysis.

In summary, it has been determined that a *quantitative* analysis of both the mobility and chemical environment of the ^{13}C nucleus is not possible in this particular IL system when the spin-lattice relaxation contributions of ^{13}C - ^{14}N are ignored and the heteronuclear BPP Equation is applied to the variable temperature T_1 relaxation data. Despite this, our findings suggest that it is possible to extract *qualitative* conclusions about the mobility of this IL system, as the value of the T_1 minimum was found to shift to higher temperatures with the addition of Zn^{2+} . In contrast, the T_1 value at the minima followed no observable trend, suggesting that this particular method is inappropriate for inferring information about the chemical environment of the ^{13}C nucleus.