



Probing Ion Interactions in Ionic Liquid Electrolytes by DNP NMR

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Introduction

Ionic liquids are potential replacements for the volatile and flammable liquid electrolytes currently used in energy storage devices such as lithium ion batteries. They have high intrinsic ionic conductivity, low volatility and flammability, and high electrochemical stability. However, in order to understand and improve the ion transport mechanisms occurring in these liquids, a detailed picture of the molecular interactions and particularly the solvation state of the target ion (usually Li^+ or Na^+) is needed. Indeed, ionic liquids are known to show significant structuring in the liquid phase due to the presence of strong non-covalent interactions. We recently showed that solid-state DNP NMR experiments carried out on the frozen, glassy phase can be used to extract internuclear distances and construct a 3D picture of the ion interactions that closely mimics the liquid-state phase [1]. This was demonstrated using DNP-enhanced ^{13}C - ^6Li REDOR experiments. As part of our research program at Deakin University is about developing new sodium ion battery electrolytes, the main purpose of this project was to establish whether or not ^{13}C - ^{23}Na recoupling experiments could be used to measure C-Na distances in a similar way.

Experimental

Several sodium and lithium containing pyrrolidinium-based ionic liquid samples were prepared for study with TEKPol and AMUPol radicals and different salt concentrations. ^{13}C CPMAS DNP enhancement levels were tested with these radicals, after which ^{13}C - ^{23}Na experiments (REAPDOR and RESPDOR) were carried out using the REDOR tuning box. Dephasing was observed from the ^{13}C signals with ^{23}Na recoupling pulses applied. Additionally some ^{13}C - ^6Li REDOR experiments were carried out.

Results and Discussion

^{13}C CPMAS DNP enhancement levels of around 4 were obtained from the glassy state ionic liquid electrolyte P_{13}FSI containing 1 m NaFSI and 10 mM AMUPol (Fig.1a). Dephasing of the ^{13}C signals was observed in the ^{13}C - ^{23}Na REAPDOR experiments. The signals at around 60 ppm can be seen to dephase the most (Fig. 1b), these represent the carbon sites adjacent to the nitrogen on the pyrrolidinium cation, suggesting a close association between $\text{Na}(\text{FSI})_n^-$ clusters and this positively charged region of the cation. This is consistent with our previous findings in the lithium-containing system [1]. Unfortunately, C-Na distance extraction was not possible due to poor signal-to-noise ratios at longer dephasing times.

Conclusions

This project has provided an encouraging proof of concept that C-Na distances measurements are possible to measure from glassy-state ionic liquid electrolytes by DNP NMR. While the signal-to-noise ratios of the acquired spectra were insufficient to allow reliable extraction of distances, significant dephasing was observed. Our next step will be to improve the DNP enhancement levels by optimising the concentration of the biradicals.

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References

[1] Sani, M.-A., *et al.*, Journal of Physical Chemistry Letters, **9**, 1007-1011 (2018).

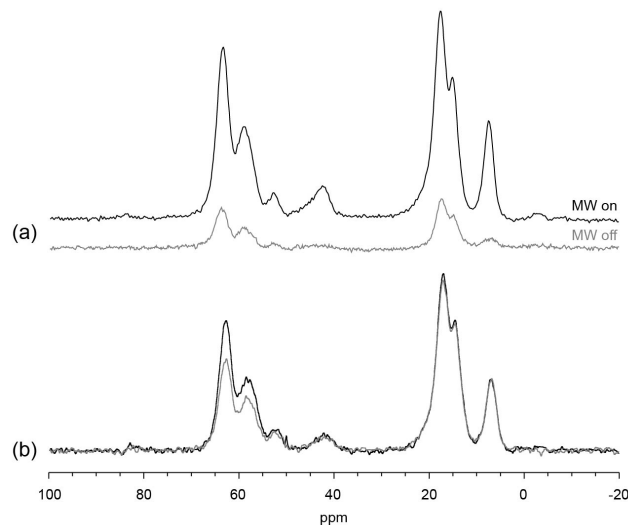


Fig.1 (a) ^{13}C CPMAS spectra obtained from P_{13}FSI -NaFSI with and without DNP enhancement, (b) ^{13}C - ^{23}Na REAPDOR experiment showing dephasing due to the applied ^{23}Na pulse (grey spectrum).