

Studies of motions and interactions of molecules in ionic liquid electrolytes by nuclear magnetic resonance.

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For a couple of decades, the interest for ionic liquids has been rising, due to their unique conductivity, viscosity or diffusion properties. In particular, their stability at high voltage makes them interesting candidates for lithium battery electrolytes. However, the difficulty in characterising weak molecular interactions and fast motions between ions means that the liquid « structures » are not fully understood.

Our goal is to use the ^7Li - ^1H Heteronuclear Overhauser Effect to probe the cation-cation interactions in a LiFSI solution in Pyr13FSI (N-methyl-N-propyl pyroliidinium fluorosulfonylimide). ^7Li - ^1H HOE transfers can be measured in 1D experiment, with a normalisation of the magnetisation with respect to a quantitative ^1H spectrum. HOE transfers are weak, with recovered ^1H magnetisation equal to 10-5. For a correct determination of the cross-relaxation rate, longitudinal relaxation times and diffusion effects must be taken into account when, first, the mixing time stops being negligible compared to the T_1 's, and second, when PFG's are used for the selection of coherence pathways.

Using an expression of the spectral density for intermolecular dipole-dipole interaction derived for self-diffusing hard spheres¹, we show that the HOE can be interpreted as a measure of the distance of closest approach between spins in weakly interacting ion pairs, and measure the effect of increasing lithium concentration in ILs solutions.

1. Kruk, D. *et al.* Determining diffusion coefficients of ionic liquids by means of field cycling nuclear magnetic resonance relaxometry. *J. Chem. Phys.* **140**, 244509 (2014).

