The Effect of Glassing Matrix Deuteration on ^{13}C Dynamic Nuclear Polarization at 5 T

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Introduction

Hyperpolarization via fast-dissolution dynamic nuclear polarization (DNP) is employed to provide a several-thousand-fold enhancement of the NMR and MRI signals in the liquid-state. The high degree of spin alignment from the electrons is transferred to the nuclear spins via microwaves under a magnetic field and low temperature. The sample is typically consisted of an isotopically-enriched biomolecule dissolved in a glassing matrix and doped with trace amounts of free radicals. It has been reported previously that at 3.35 T and T~1 K, deuteration of the glassing matrix is beneficial for ^{13}C samples doped with large ESR linewidth free radical 4-oxo-TEMPO—^{13}C polarization levels improved as much as 2.5-times compared to the same samples with non-deuterated glassing solvents.[1] The main goal of this study is to investigate if this sample preparation method is still beneficial at a higher field at 5 T and 1.2 K where ESR spectral and relaxation properties of free radical electron changes.[2]

Experimental Methods

200 µL aliquots of 3 M [1-^{13}C] sodium acetate samples doped with 40 mM 4-oxo-TEMPO in 1:1 v/v (*i*) glycerol:H_2O or (*ii*) glycerol:D_2O were prepared. Similar ^{13}C samples were prepared and doped with 15 mM trityl OX063. Each sample was inserted in the homebuilt 5 T hyperpolarizer at NHMFL-UF with T~1.2 K base temperature and equipped with a 140 GHz microwave source. The samples were irradiated at the positive polarization peak for TEMPO (140.71 GHz). The ^{13}C polarization buildup curve for each sample was monitored using a Bruker 500 MHz NMR console connected to the NMR probe placed in a continuous-flow cryostat. The ^{13}C polarization buildup curves were measured by applying a shallow flip-angle rf pulse every 200 s.

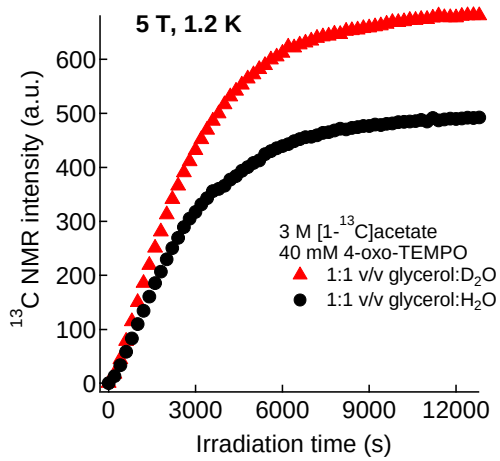

Fig. 1 Representative ^{13}C polarization buildup curves of TEMPO-doped ^{13}C acetate samples with non-deuterated and partially deuterated glassing solvents taken at 5 T and 1.2 K.

Results and Discussion

Fig. 1 shows representative ^{13}C polarization buildup curves of TEMPO-doped [1-^{13}C] acetate samples at 5 T and 1.2 K. Evident in this graph is the improved of DNP-enhanced ^{13}C polarization signal when the water solvent was replaced by deuterated water. The maximum 13C DNP signal improved by about 25% with partial deuteration of the glassing matrix. It is expected that full deuteration of the glassing solvent would further improve the DNP signal. This phenomenon can be explained thermodynamically in terms of heat load in thermal mixing DNP process. Replacement of protons (γ=42.58 MHz/T) by deuterons (γ=6.54 MHz/T) means that the heat load of the nuclear Zeeman system is reduced, thus it is easier for the electron dipolar reservoir to 'cool' the nuclei at a lower spin temperature.[1]

Conclusions

Similar to the behavior of ^{13}C DNP at 3.35 T, deuteration of the glassing matrix on ^{13}C samples doped with large ESR linewidth free radical 4-oxo-TEMPO is still beneficial at 5 T. This implies that the spin temperature or thermal mixing model is still dominant at 5 T despite changes in the ESR spectral and relaxation properties of the free radical. The effect of this sample preparation method on ^{13}C samples doped with narrow ESR linewidth free radical trityl OX063 is also investigated at 5 T.

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References

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[2] Lumata, L., *et al.*, Phys Chem Chem Phys, **15**, 9800-9807 (2013).