Optimization of Polarizing Agent for Scalar Overhauser Dynamic Nuclear Polarization

Harmon, N. (FSU, Chemistry); Dubroca, T. (NHMFL); Megiel, E. (U. of Warsaw, Poland, Chemistry); van Tol, J. (NHMFL); Hill, S. (FSU, Physics and NHMFL)

Introduction

Nuclear magnetic resonance (NMR) spectroscopy of ^{13}C is a valuable tool for probing biological systems because it is both nondestructive and provides an abundance of structural and quantitative information. However, the low sensitivity of ^{13}C magnetic resonance due to its low natural abundance and gyromagnetic ratio make it difficult to quickly collect high quality spectra. Dynamic nuclear polarization (DNP) is an increasingly popular approach used to enhance NMR signals. In DNP, microwave irradiation of paramagnetic species at their respective electron resonant frequencies results in the transfer of a large electron spin polarization to surrounding nuclei. Thus far, many applications have been developed for solid state DNP including some structural analysis of membrane proteins and enzyme-inhibitor complexes. However, liquid state DNP applications are still in their infancy due to the challenge of applying the technique at high magnetic field (above 10 T). At high magnetic fields, the Overhauser DNP polarization transfer efficiency between radicals and nuclei is greatly reduced. This effect is driven by electron-nuclear interactions, namely scalar interactions and dipole-dipole interactions. Due to major improvements in instrumentation large DNP enhancements are achievable via scalar interactions. In this work we focus our efforts on improving the scalar interactions by optimizing sample preparation techniques and developing new polarizing agents.

Results

New polarizing agents were developed, and their effectiveness tested for scalar liquid Overhauser DNP at 14.1 T. The liquid DNP spectrometer which is part of the NHMFL EMR facility was used for this purpose. ^{13}C-carbon tetrachloride, a model compound, was used for comparing the NMR enhancements during DNP experiments of various polarizing agents. Special care was taken to de-oxygen the samples by storing them in an argon glovebox for several days (inducing oxygen gas diffusion out of the samples). Our group has also developed new bi-radicals, which are more effective than traditional mono-radicals in liquid DNP. For example, **Fig.1** displays the DNP enhancements of carbon tetrachloride for TEMPO and DISSPK at various concentrations. The highest enhancements are obtained for DISSPK with 20 mM, about twice as effective as for TEMPO at its optimum concentration.

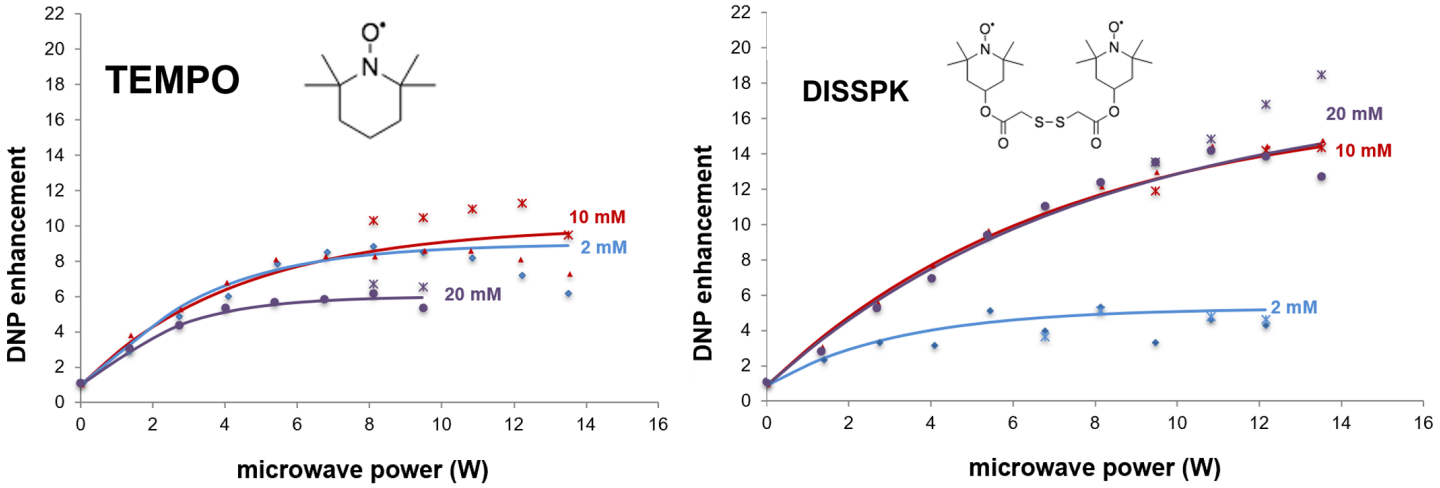

Fig.1 DNP enhancement (ratio of NMR signals of ^{13}C-carbon tetrachloride with microwave on and microwave off) as function of microwave power for various concentration of radical, as labeled, left plot, using TEMPO radical, right plot, using DISSPK radical.

Acknowledgements

The National High Magnetic Field Laboratory is supported by the National Science Foundation through NSF/DMR-1157490/1644779 and the State of Florida. Also acknowledged are the Florida State University intern program and NSF/MRI CHE-1229170.