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Solid−Liquid Electron Density Transfer in Aqueous Char Suspensions by ^{1}H-Pulsed Dynamic Nuclear Polarization at Low Magnetic Field

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There are only a few reports of solid−liquid energy transfer between sublevels in magnetic spin systems consisting of species with different gyromagnetic ratios.[1−6] Most of these describe the dominant “solid-state” dynamic nuclear polarization (DNP) effect due to pure dipole−dipole (through-space) intermolecular interactions, such as those observed between free radical labels immobilized on a surface and solvent protons.[1−3] The only instance of solid−liquid electron density transfer thus far reported involved a ^{13}C DNP scalar contact mechanism between CCl_4 and nitroxide radicals immobilized on silica gel.[4] The importance of a scalar contact Overhauser mechanism by proton spin diffusion and the “three-spin” effect were suggested in a solid multicomponent polymeric mixture.[5,6]

The scalar mechanism for *liquid−liquid* DNP transfer in solutions of stable free radicals[3,9] mainly has been seen in nuclei with large hyperfine constant value, such as ^{31}P, ^{13}C, and ^{19}F. Contact DNP for protons (^{1}H) is seldom observed because of the very small contact hyperfine coupling that usually exists between unpaired electrons in a paramagnetic molecule and hydrogen atoms in solvent molecules.[9] For water protons, the contact *liquid−liquid* DNP was seen only in aqueous solutions of Mn^{2+} and Wurster’s blue perchlorate.[10,11]

Much of the chemical utility of DNP stems from its sensitivity to the contact scalar interaction, because scalar coupling is proportional to the unpaired electron density at the nucleus, which is a characteristic of different kinds of chemical bonding.[3−9] A particularly important class of hyperfine interactions involves water molecules, which are of obvious interest in biology, chemistry, technology, etc.

In contrast to traditional NMR and EPR spectroscopies, where high magnetic fields provide important chemical information, relaxation phenomena including DNP often have more complicated field dependences.[8] Low magnetic fields are of special interest in liquid (chemical) DNP applications because then the corresponding cross-relaxation spectral density functions are greatest. Thus, the DNP enhancement in liquids increases with decreasing external magnetic field strength, so DNP often is especially effective in low fields.[3,8,9]

In recent years, magnetic resonance techniques have been used extensively to study paramagnetic centers in carbonaceous solids and the process of carbonization.[12−14] The unpaired electrons responsible for the paramagnetism of chars are generally thought to represent stable free organic radicals created during the heat-treatment carbonization. Despite significant progress in these studies, the structure of char paramagnetic centers, the process of free radical formation during carbonization, and the nature of hyperfine interactions on the surface of chars are not fully understood.

Here, we report the first observation of solid−liquid electron spin density transfer by the contact Overhauser mechanism for several types of newly synthesized chars in aqueous suspensions, using a pulsed DNP technique at low magnetic field. Experimental details are described elsewhere.[15,16]

The time dependence of NMR polarization $\langle I_z \rangle$ in a coupled nuclear-electron system is written[17]

$$d\langle I_z\rangle/dt = -[(\langle I_z\rangle - I_o) + \xi f(\langle S_z\rangle - S_o)]/T_{1n} \qquad (1)$$

where ξ is the nuclear-electron coupling parameter. I_o and S_o represent the equilibrium nuclear and electronic magnetization, respectively. The leakage factor for nuclear spins is given by $f = 1 - T_{1n}/T_{1n}(o)$, T_{1n} and $T_{1n}(o)$ being the nuclear spin−lattice relaxation times in a char suspension and pure solvent.

For many systems, one can assume that, on the scale of nuclear relaxation times, electron spins relax instantly. This gives us the initial conditions to integrate eq 1. For a two-pulse Hahn NMR sequence after an EPR pumping pulse, the master equation for the relative amplitude enhancement *A* of the nuclear spin−echo signal *V* derived from a polarized sample can be obtained from eq 1

$$A = A_{\max} Z[1 - \exp(-\tau_p/T_{1n})]\exp(-\tau_d/T_{1n}) \qquad (2)$$

where $A = [V - V_o]/V_o$, V_o is the amplitude of the nonpolarized echo, τ_p is the duration of the EPR saturation pulse, $\tau_d = t - \tau_p$, $A_{\max} = - \xi f|\gamma_s/\gamma_I|$, and $|\gamma_s/\gamma_I| = 660$ for protons. The value $Z = (S_o - \langle S_z\rangle)/S_o$ in eq 2 is the saturation parameter, which depends on the EPR line shape. For a single Lorentzian EPR line, saturated in the center

$$Z = \gamma_s^{\,2}B_{1S}^{\,2}\tau_S^{\,2}/(1 + \gamma_s^{\,2}B_{1S}^{\,2}\tau_S^{\,2}) \qquad (3)$$

where $\tau_S = (T_{1S}T_{2S})^{1/2}$. In this case, the reciprocal value of the NMR enhancement, A^{-1}, depends linearly upon the square of the reciprocal of the EPR saturating field amplitude, B_{1S}^{-2}. The slope of the graph of this dependence is determined by the product of electron relaxation times $T_{1S}T_{2S}$. For an inhomogeneous EPR line, the dependence is more complicated.[18]

Parameters $A_{\max}$ and ξ in eq 2 were found experimentally by extrapolating a plot of $A^{-1}[1 - \exp(-\tau_p/T_{1n)}]\exp(-\tau_d/T_{1n})$ vs B_{1S}^{-2} to $B_{1S}^{-2} = 0$ according to eq 3. The leakage factor, *f*, was obtained

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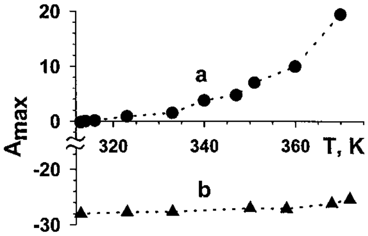

Figure 1. Temperature dependence of DNP enhancements of water protons in an aqueous suspensions of (a) hardwood char and (b) softwood char ($B_{1S} = 0.1$ G, $\tau_1 = 4$ ms, $\tau_p = 100$ ms, $\tau_d = 0$).

by measuring T_{1n} and $T_{1n}(0)$. Experimental conditions were $\nu_I = \omega_I/2\pi = 0.5$ MHz, $B_o = 117.5$ G, and $\nu_S = 328.8$ MHz.

The EPR spectra of chars in water at room temperature consisted of single, nearly Lorenzian lines, with a peak-to-peak line width of ~0.5 G, and a typical free radical *g*-factor close to the free electron value of 2.0023. Details of char synthesis are described elsewhere.[19]

In this study, proton DNP enhancement was observed in aqueous suspensions of several different types of chars. Some of the chars exhibited positive DNP enhancements; others displayed negative ones. The positive DNP observed for several hardwood chars is strong evidence of a contact interaction at the solid−liquid interface. As for Mn^{2+} in water,[10] this effect was accompanied by a significant difference between proton spin−lattice and spin−spin relaxation times ($T_{1n}/T_{2n} > 5$). In accordance with eqs 2 and 3, linear dependence of DNP enhancement A^{-1} on $B_{1s}{}^{-2}$ was observed, indicating the homogeneous nature of EPR line broadening in the chars. Best straight lines fitted to the data gave $A_{\max} = +16.4$ for hardwood and $A_{\max} = -28.6$ for softwood char suspensions.

Two explanations can be offered for the scalar DNP enhancement observed in hardwood char suspensions. One is the direct surface polarization of water protons by the unpaired electrons of chars due to short-lived electronic overlap. Hydrogen bonding or chemisorption, taking place during the residence time τ_h of water molecules at the surface, could provide the overlap. In this case, a molecular chemical exchange process transfers proton magnetization generated at the surface into the bulk water. Another explanation is a scalar Overhauser enhancement of the protons in char followed by spin diffusion to the protons in water through a proton exchange process. We tested this idea by measuring ^{1}H DNP of hardwood chars suspended in benzene, finding positive DNP for benzene protons. The DNP was about the same for water and benzene suspensions, suggesting that intermolecular proton exchange processes play only a small role in these systems, since proton exchange is negligible for benzene.[9,18] DNP enhancement through a "three-spin" process[6] via hydrogen in the char cannot be realized in this case, because of the nearly equal gyromagnetic ratios for protons in char and in bulk water.

A strong increase of the positive DNP enhancement with temperature was observed in aqueous suspensions of hardwood chars (Figure 1a). The negative DNP enhancement in softwood chars slightly diminishes with temperature (Figure 1b). As temperature increases, the effect of exchange interactions becomes predominant and the contact dynamic polarization increases. This is probably a result of the decrease in the lifetime τ_h of the water protons in a short-lived hydrated complex at the hardwood char−water interface.

The differences in the Overhauser enhancements of the softwood and hardwood char suspensions can be explained by the differences in the activation enthalpies (E_h) of the chemical exchange on different solid−liquid interfaces, as well as by difference in the value of the hyperfine constant *a* on different surfaces. The sign and value of DNP enhancement strongly depends on the initial materials (hardwood, softwood, etc.) and the procedure of charring. Correlation between the structure of the chars and DNP results is currently under study in our lab.

The magnitudes of the observed DNP enhancements in char suspensions are more than an order of magnitude less than the theoretical maxima for pure scalar +660 and pure dipolar −330 coupling, respectively. One possible reason is a delicate balance between dipole−dipole and scalar solid−liquid interactions. Another is the possible influence on the value of DNP enhancement of a gradual transition from the pure "liquid" DNP effect to the pure "solid effect". One expects to find this transition when the correlation time of liquid motion goes from values much shorter to values much longer than the transverse electron relaxation time T_{2S}, although more detailed criteria[20] also involve T_{1S}. The maximum value of polarization in the intermediate situation lacks the symmetry in $\Delta\omega$ of the "solid" as well as "liquid" effects ($\Delta\omega = 0$). The maximum DNP enhancement was achieved with the microwave frequency centered on the EPR line, indicating that the dynamic polarization occurs through the Overhauser mechanism, as opposed to solid-state effect.[8,18,20]

At the paramagnetic surface of hardwood chars, the protons are subjected to a strong scalar coupling with the unpaired electron, but at low temperatures the exchange process is far too slow to stimulate the relaxation transitions required to produce a positive nuclear resonance enhancement. Since the rate constant for the build-up of the Overhauser effect is the nuclear spin−lattice relaxation time T_{1n}, the positive polarization will only occur if the lifetime τ_h of the solvent hydrogen atoms at the hardwood chars interface is comparable to T_{1n} on the surface. We do not have sufficient information to know if the above conditions are fulfilled in our case, but the relaxation time of protons in water molecules adsorbed on chars will certainly be much shorter than that of protons in unperturbed diamagnetic water molecules.[21] When a water molecule jumps from the surface, the positive polarization on the hydrogen atoms will be retained, but will start to decay to the negative value expected for dipolar coupling with the relaxation time of protons in the diamagnetic molecule. If, however, the water molecule makes contact with the paramagnetic surface again before negative polarization is established, the average polarization of water protons will remain positive. The presence of pore structure may also contribute to this effect.

In summary, the Fermi contact interaction demonstrated here shows for the first time that there is electron delocalization from paramagnetic centers on the char surface to solvent water protons. The nonzero value for the electronic wave function at the nucleus suggests either weak chemisorption or hydrogen bonds or both at the solid−liquid interface.

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