

LOW-FIELD DNP STUDIES OF SOLVENT MOLECULES AT THE CARBON CHAR/LIQUID INTERFACE

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Introduction

The first observation of solid-liquid electron spin density transfer by the contact Overhauser mechanism [1] seen in a system consisting of hardwood chars suspended in water is reported. Proton Dynamic Nuclear Polarization (DNP) enhancement was investigated in aqueous suspensions of several types of chars, where both positive and negative Overhauser effects were detected in different samples. The positive DNP effect is strong evidence for the presence of an electron-nuclear scalar interaction at solid-liquid interface.

To date, only a few studies have been published of solid-liquid energy transfer between sublevels in magnetic spin systems consisting of species with different gyromagnetic ratios [2-3]. All of these have described the dominant "solid-state" DNP effect due to pure dipole-dipole (through space) intermolecular interactions, such as those observed between free radical labels immobilized on a silica gel surface and solvent protons [2].

Contact DNP in solutions of paramagnetic ions is seldom observed for protons because of the very small contact hyperfine coupling that usually exists between unpaired electrons in a solute molecule and hydrogen atoms in solvent molecules. Until now, contact DNP for water protons was only observed in aqueous solutions of Mn²⁺ and Wurster's blue perchlorate [4,5].

The scalar coupling seen in aqueous hardwood char's suspensions demonstrates for the first time that there is electron delocalization from paramagnetic centers on the surface to water protons in the solvent, since the contact interaction demands that there be non-zero value for the electronic wave function at the nucleus. The positive DNP effect was accompanied by a significant difference between spin-lattice and spin-spin relaxation times of water protons.

The proton DNP enhancement observed in aqueous char suspensions was strongly temperature dependent. In contrast to ordinary free radical solutions, the increase of scalar polarization with temperature was observed. It suggests the possibility of exchange processes at the solid-liquid interface. For several hardwood chars the sign of the water proton DNP enhancement changed from negative to positive, indicating a change in the relative contributions from scalar and dipole-dipole nuclear-electron coupling.

Experimental

Method

In the coupled nuclear-electron system, the time dependence of NMR polarization enhancement $\langle I_z \rangle$ can be described by the equation:

$$d\langle I_z \rangle / dt = -[\langle I_z \rangle - I_0] - \xi f (\langle S_z \rangle - S_0) / T_{1n}, \quad (1)$$

where we used designations introduced by Abragam [6].

For many systems, it can be assumed that on the long time scale of nuclear relaxation, the electronic relaxation happens instantaneously. This assumption gives us the initial conditions for the integration of Eq.(1) in pulsed DNP conditions. For a two-pulse Hahn NMR sequence following after EPR saturating pulse, the master equation describing the relative enhancement A of the nuclear spin echo signal V derived from a polarized sample can be obtained from (1):

$$A = [V \exp(2\tau_1 / T_{2n}) - V_0] / V_0 = A_{\max} Z [1 - \exp(-\tau_p / T_{1n})] \exp(-\tau_d / T_{1n}), \quad (2)$$

where V_0 is the amplitude of non-polarized echo, τ_p is the duration of the EPR saturation pulse, $\tau_d = t - \tau_p$, and $A_{\max} = -\xi f |\gamma_s / \gamma_I|$; Z is the EPR saturation parameter.

¹H pulsed DNP relaxation technique at low magnetic field has been applied [7]. A spiral delay line (helix) was used to enhance the EPR saturating field. The duty cycle of the EPR saturating pulses can be chosen to avoid microwave heating of the sample. Experiments were carried out under the following conditions: $\nu_1 = \omega_I / 2\pi = 0.5\text{MHz}$, $B_0 = 117.5\text{G}$; the electron resonance frequency $\nu_s = 328.9\text{MHz}$.

Samples

Samples of chars were obtained from various kinds of woods (e.g. hardwoods, softwoods) by charring under H₂ and CH₄ flow. The samples were heated at the rate of 10° C per hour according to a pre-selected heat treatment profile, with a maximum temperature ranging from 420-720°C. Prior to measuring, chars were finely ground to a particle size of about 10 μm. The samples were suspended in water, and then bubbled with pure helium for 15 min. The EPR spectra of chars in water consisted of a single Lorentzian line with a peak-to-peak line width of about 0.5 G, and a typical free radical g-factor, close to the free electron value of 2.0023. Experimental details of char synthesis are described in [8].

Results and discussion

Correlation of experimental and theoretical results has been achieved in this work through consideration of proton-electron spin dipole-dipole interaction and of chemical exchange of solvent molecules. A model of molecular migration at the solid-liquid interface was constructed to account for the experimental DNP observations. According to the model, expression (2) can be represented in the form:

$$A = -|\gamma_s/\gamma_l| f Z (1 - \delta) / 2(1 + \delta), \quad (3)$$

where we introduced a designation:

$$\delta = M(\tau_c/\tau_l)/(1 + \omega_s^2\tau_c^2) = (1 - 2\xi)/(1 + 2\xi) \quad (4)$$

and parameter M can be defined as the relative intensity of the scalar and d-d interactions.

Assuming an Arrhenius temperature dependence for the correlation times in (4), the value of the activation enthalpy of the chemical exchange process (water desorption) at the solid-liquid interface is found to be $E_h = 13.5$ kcal/mole. A value of activation energy $E_t = 2.1$ kcal/mole for translational diffusion and for electronic relaxation $E_s = 2.0$ kcal/mole also were obtained by the fitting program. Calculations also give the value of the exchange correlation time $\tau_c(300^\circ\text{K}) = 1.6 \times 10^{-6}$ s. Utilizing the difference between the experimental proton T_{1n} and T_{2n} relaxation times and DNP results, it is possible to estimate the contact hyperfine coupling constant at the solid-liquid interface $a = 5.3 \times 10^{-3}$ MHz. The values of the enthalpy of activation of chemical exchange E_h , as well as the hyperfine scalar constant a strongly suggest the presence of weak chemisorption bonds at the solid/liquid interface that are capable of facilitating the electronic delocalization whose effect is observed in these DNP experiments.

The temperature dependence of the DNP effect seen in aqueous char suspensions is the result of a delicate balance between dipole-dipole and scalar interactions as well as the competition between corresponding correlation times at the solid/liquid interface. The translational diffusion of water molecules is responsible for d-d relaxation, which dominates at low temperatures. The scalar interaction is modulated mainly by electron spin relaxation and an isotropic proton-electron spin chemical exchange process on the surface. The scalar relaxation of Type II [6] is responsible for solid-liquid interactions in chars suspensions at room temperature. As the temperature increases, the effect of exchange interactions in char suspensions becomes predominant because $E_h > E_t$, and the positive dynamic polarization increases. The increase in the relative contribution of the contact interaction to proton relaxation mainly is a result of the decrease in the life time τ_h ($E_h > E_s$) of the water protons in the short-lived hydrated complex at the hardwood chars interface as the temperature increases.

The possible influence of a gradual transition from the pure Overhauser effect to the pure "solid-state" effect on the value of DNP enhancement can not be in principle excluded

in such systems.

In any case at the paramagnetic surface of hardwood char, the water protons are subjected to a strong scalar coupling with the unpaired electron, but at low temperatures the exchange process is far too slow to modulate the scalar coupling fast enough to stimulate the relaxation transitions required to produce a positive DNP enhancement. Since the main rate constant for the build-up of the Overhauser effect is the nuclear spin-lattice relaxation time T_{1n} , positive polarization will occur only if the lifetime τ_h of the solvent water protons at the hardwood char interface is comparable to T_{1n} on the surface. The value of τ_h obtained here exceeds the value for electron relaxation τ_s on the surface of chars under study, and electron-nuclear cross-relaxation process thus can occur during the proton-electron contact. 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.

It should be noted, that the basic condition for EPR hyperfine structure observation in such systems

$$a \tau_c > 1$$

is not satisfied in the case of aqueous chars suspensions. As a result there no superhyperfine structure in the EPR spectrum has ever been observed in such systems. The proton chemical shifts for molecules adsorbed on paramagnetic catalytic surfaces also have in general been obscured by broad resonance lines.

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