A Low Field Fluorine-Electron Double Resonance Study for GALV and BDPA in Some Aliphatic and Aromatic Solvents

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Z. Naturforsch. **64a,** 477 – 484 (2009); received August 25, 2008 / revised December 18, 2008

Dynamic nuclear polarization experiments were performed to study the solutions of the stable free radicals Galvinoxyl and α,γ-Bisdiphenylene-β-phenyl allyl complex with benzene (1 : 1) in some highly fluorinated aliphatic and aromatic solvents. The measurements were performed at four different temperatures to test the dipolar and the scalar part of the coupling between the fluorine nucleus (^{19}F) and the unpaired electron. It was found that in the samples with Galvinoxyl the dipolar interactions are more effective for the aromatic solvents, while the scalar interactions are more effective for the aliphatics. An alteration from negative to positive region for the nuclear-electron coupling parameter informing on scalar or dipole-dipole interaction was observed only for 2,2,3,4,4,4-Hexafluoro-1-butanol solvent with increasing temperature. The nuclear-electron coupling parameter varies between -0.003 and 0.228 in all aliphatic solvents and between 0.180 and 0.318 in aromatic solvents. Overhauser enhancement was not observed in the samples prepared with Hexadecafluoroheptane, Heptafluorobutyric acid, and Nonafluoropentanoic acid for both free radicals in all temperatures. These solvents may have scavenging effects on the radicals due to their behaviour.

Key words: Dynamic Nuclear Polarization; Fluorine-Electron Double Resonance; Oximetry; Free Radical; Free Radical Scavenger.

1. Introduction

Dynamic nuclear polarization (DNP) is a well-known double resonance technique that permits the enhancement of polarization of nuclei in samples containing paramagnetic species. In the Overhauser effect (OE) type DNP for free radical solutions. If electron paramagnetic resonance (EPR) of the paramagnetic solute is saturated, important changes in the intensity of the nuclear magnetic resonance (NMR) signal of the solvent occur [1, 2]. Positive or negative DNP enhancements can be observed depending on whether the scalar or the dipolar coupling is dominant.

The studies at low magnetic fields are important in order to obtain comparable interaction parameters for various systems. DNP is sensitive to variations of the ratio of the dipolar and the scalar coupling. The dipolar interactions depend on the geometrical structures of the colliding molecules, while the scalar interactions depend on the chemical environment of both receptor nucleus and unpaired electron. Therefore, DNP of fluorine has attracted much attention, since it exhibits mixed scalar and dipolar interactions for all systems [3].

In low magnetic fields, the nuclear-electron coupling parameter ρ varies from $+0.5$ (pure dipolar) to -1.0 (pure scalar), and ρ is measured between these limits in the literature [3 – 9]. The intensities and the spectral densities of the intermolecular scalar interactions could arise from the direct contact between the solvent nuclei and the unpaired electrons of the free radical, or from a temporary overlapping of delocalized molecular orbitals during the diffusion process. Dipolar interactions are modulated by translational diffusion of both solvent and free radical molecules.

Magnetic double resonance techniques have been applied to study intermolecular interactions and molecular motions in solutions by DNP. ^{19}F nuclei in a number of fluorinated aliphatic and aromatic solvents were used as a probe to detect dipolar and scalar interactions with electron spins of dissolved free radical molecules. The contact interactions, in particular, mirror the dependence of intermolecular couplings upon the chemical structure.

DNP with fluorinated solutions is current both in fundamental studies [10] and applications [11 – 13]. The main reason for the low field studies is the necessity for lower frequencies in order to prevent power deposition and sample heating in samples [14]. Perfluorocarbon (PFC) emulsions have been used extensively in EPR oximetry supported by OE [15]. The aim of this work is to give new information on DNP parameters of some highly aromatic and aliphatic fluorinated solutions depending upon temperature at low field.

2. Theory

The main theory of DNP in solutions of free radicals has been given in the literature [1, 16 – 19]. Figure 1 shows the energy level diagram of a nucleus with a spin 1/2 and an electron two-spin system. m_S and m_I are the magnetic quantum numbers for electron and nucleus, respectively.

An expression for the equation of motion of the nuclear polarization can be written as [20]

$$\frac{dP_z}{dt} = -(w_o + 2w_I + w_2)\left[(P_z - P_o) - \frac{w_2 - w_o}{w_o + 2w_I + w_2}(\Pi_z - \Pi_o)\right]. \quad (1)$$

P_z and Π_z represent the dynamic polarization of nuclear spins and unpaired electron spins, respectively. P_o and Π_o represent the polarizations at the thermal equilibrium.

In the steady state, i. e. $dP_z/dt = 0$, the Overhauser enhancement factor is defined as

$$A = \frac{P_z - P_o}{P_o} = \rho f s \left|\frac{\gamma_S}{\gamma_I}\right|, \quad (2)$$

where γ_S and γ_I are electronic and nuclear gyromagnetic ratios, respectively, $\gamma_S < 0$, $\gamma_I > 0$, and $\left|\frac{\gamma_S}{\gamma_I}\right| = 700$ for ^{19}F. f is the leakage factor for the nuclear relaxation $(0 \le f \le 1)$, s is the saturation factor which is equal to 1 for the complete EPR saturation $(0 \le s \le 1)$, and ρ is the nuclear-electron coupling parameter, which is a measure of the nature and the random time dependence of the nuclear-electron interaction and given as

$$\rho = -\frac{A_\infty}{700 \cdot f}. \quad (3)$$

If the saturation condition is fulfilled, the reciprocal of the enhancement factor extrapolated for the infinite EPR power is given as

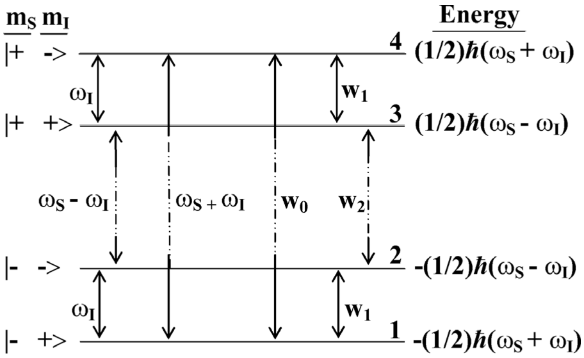

Fig. 1. Energy level diagram of a nucleus with a spin 1/2 and electron two-spin system. m_S and m_I are the magnetic quantum numbers for electron and nucleus, respectively. w_i and ω_i $(i = 0, 1, 2)$ are the transition probabilities and the transition frequencies, respectively. It is $\omega_S/\omega_I = 700$ for ^{19}F nucleus.

$$\left(\frac{P_z - P_o}{P_o}\right)^{-1}_{s \to 1} \to A_\infty^{-1}. \quad (4)$$

In the white spectral region, i. e. in the extreme narrowing case $(\omega_S \tau_t \ll 1)$, the parameter K that characterizes the relative importance of scalar and translational dipolar interactions is given by [5]

$$K = \frac{2}{15}\frac{J_{Sc}(0)}{J_I^D(0)}, \quad (5)$$

where $J_{Sc}(0)$ and $J_I^D(0)$ are the spectrum intensity functions in the white spectral region. Further [3, 21] K can be written as

$$K = \frac{0.966 - 1.953\rho}{1 + \rho}. \quad (6)$$

3. Experimental

3.1. The Free Radicals and Solvents

The stable free radicals Galvinoxyl (GALV) and α,γ-Bisdiphenylene-β-phenyl allyl complex with benzene (1 : 1) (BDPA) and the solvents were taken from Aldrich Chem. Co. (USA) and Fluka (Switzerland), respectively. The solvents are 1-Iodotridecafluorohexane (ITFH), 2,2,3,4,4,4-Hexafluoro-1-butanol (HF1B), N-Methyl-bis-trifluoroacetamide (MBFA), Hexafluoroacetylacetone (HFAA), Hexadecafluoroheptane (HDFH), Heptafluorobutyric acid (HFBA), Nonafluoropentanoic acid (NFPA), Octafluorotoluene

(OFT) and Hexafluorobenzene (HFB). The purities of the solvents are between 90% and 99%.

3.2. Preparation of the Samples

The samples were prepared at 3 mM concentration. The samples in pyrex tubes of 18 mm diameter were degassed by using at least five freeze-pump-thaw cycles with liquid nitrogen at about 10^{-3} Pa in Leybold-Heraeus vacuum system and sealed. Degassing procedure is necessary, otherwise oxygen in the sample does not permit easy stimulation of the EPR line.

3.3. Spectrometer

The experiments were performed at a low field double resonance NMR spectrometer, which operates at 1.53 mT. The spectrometer, which uses the continuous-wave technique has the resonance frequency of 61.2 kHz for ^{19}F nuclei and 43 MHz for electrons. The signals are detected by the amplitude modulation technique, using Q-meter detection and then they are amplified in a low frequency, narrow-band amplifier, which is connected to a phase sensitive detector and then to a recorder. The external magnetic field is swept by a digital sweep generator [22]. The spectrometer has also an automatic temperature control system using liquid nitrogen vapour or heated air flow. The spectrometer is described in the previous papers [21, 22].

In the low field DNP investigations, the observations are based on the pure and the double resonance NMR signal intensities (P_o and P_z). The usual amplitude modulation technique gives the signals as the derivatives of the central bands, first and second side bands. The P_o and P_z values are taken as the peak-to-peak values of the derivatives of the central bands.

The saturation experiments for each sample were performed in the liquid phase with an accuracy of ±2 °C. For each sample, at four different temperatures, P_o was measured four times and P_z values were obtained from at least seven different EPR powers in order to saturate electronic spin polarization.

3.4. Determination of the DNP Parameters

The saturation factor is given by

$$s = \frac{\Pi_o - \Pi_z}{\Pi_o} \qquad (7)$$

where Π_o is the electronic spin polarization in the thermal equilibrium and Π_z is the dynamic polarization. For infinite EPR power, Π_z will be equal to zero and s to one, the enhancement factor A will take the A_∞ value according to (2).

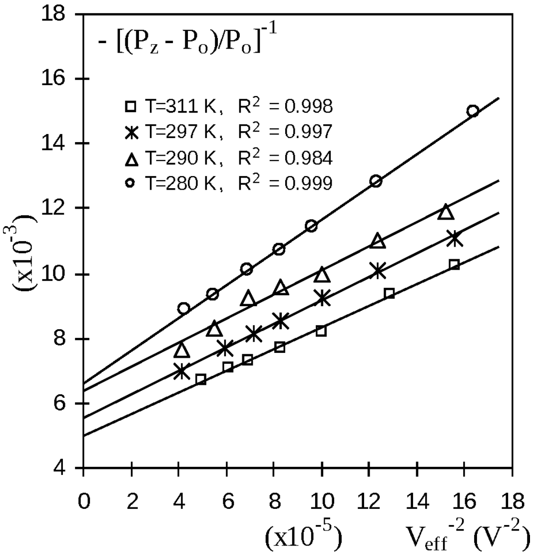

Fig. 2. The variation of $-[(P_z - P_o)/P_o]^{-1}$ versus V_{eff}^{-2} for GALV/HFB sample at four different temperatures. The A_∞^{-1} values correspond to the intersection points of the $V_{\text{eff}}^{-2} = 0$ line and the extrapolated best fit lines. The R^2 values show the degree of agreement between the linear fit function and the experimental points.

For the determination of the A_∞ value, the reciprocal of the enhancement factor (i. e. $A^{-1} = [(P_z - P_o)/P_o]^{-1}$) should be obtained as a function of reciprocal value of the EPR power, which is proportional to H_{1e}^{-2} or V_{eff}^{-2}, where V$_{\text{eff}}$ is the high frequency voltage on the EPR coil. A^{-1} is equal to A_{end}^{-1} for the maximum obtainable EPR power. In the case of full EPR saturation, the EPR power should go to infinity or V_{eff}^{-2} to zero. The variation of $-[(P_z - P_o)/P_o]^{-1}$ versus V_{eff}^{-2} for GALV/HFB sample at four different temperatures is given in Figure 2. The A_∞^{-1} values correspond to the intersection points of the $V_{\text{eff}}^{-2} = 0$ line and the extrapolated best-fit line. The R^2 values in Figure 2 show the degree of agreement between the linear fit function and the experimental points.

The leakage factor f was taken as 0.90 ± 0.05 for all samples by using the literature information on fluorinated GALV and BDPA solutions [3, 8]. ρ and K values were calculated from (3) and (6), respectively.

4. Results and Discussion

4.1. EPR Spectrum

It is important to obtain the EPR spectrum of free radicals to measure the DNP parameters in a given magnetic field, because each peak in the spectrum should be separately saturated at or near the maximum. Figure 3 shows the EPR spectrum of the GALV free radical in HFB solvent medium which is obtained at 23 °C. During this experiment, the ratio of υ_s (in MHz) to V_{eff} (in V) was 6.5, because (i) the inhomogeneous line broadening is larger than the line width of a single EPR-line and, (ii) the local field distribution has a Lorentzian form. Therefore $H_{1\text{e}}$, the amplitude of the magnetic field produced by the EPR-coil with the frequency υ_s, must not be too large, otherwise the broadening due to saturation invalidates the condition (i). The spectrum has the inhomogeneous line broadening, and it can be said that it has a single Gaussian lineshape, which is formed by the superposition of several Lorentzians, and has a maximum at about 45.8 MHz. We have obtained a fit function for the EPR spectrum of the GALV free radical in HFB solvent medium, in a low magnetic field of 1.53 mT, at room temperature. The above and the other samples were saturated at 45.0 MHz near to the peak frequency.

4.2. DNP Parameters

The experimental DNP parameters A_∞, s, ρ, and K are tabulated in Table 1. A_∞ values vary between -143.7 and 2.0 for the aliphatic solvents, and -200.4 and -113.3 for the aromatic solvents. The saturation factor s was calculated as the ratio of the enhancement factor A_{end} over A_∞. A_{end} corresponds to the available maximum EPR power. Actual saturations between 0.51 and 0.83 were achieved. Enhancements were not observed, especially for acidic solutions, of both radicals at four different temperatures. The nuclear-electron coupling factor ρ is positive for the aliphatic solvents except for HF1B (between -0.003 and 0.228), and positive for the aromatic solvents (between 0.180 and 0.318).

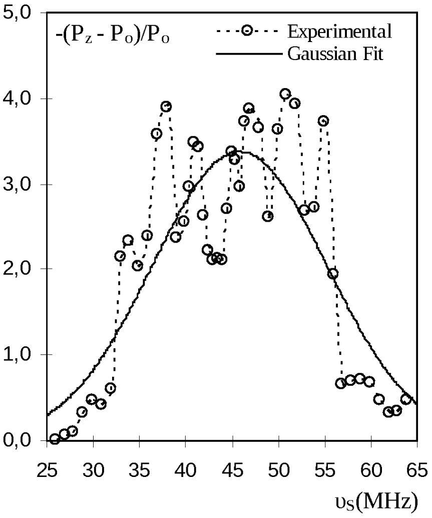

Fig. 3. EPR spectrum of the BDPA/HFB sample at 296 K. The fitted curve is a single Gaussian with 45.8 MHz peak frequency and 9.4 MHz standard deviation.

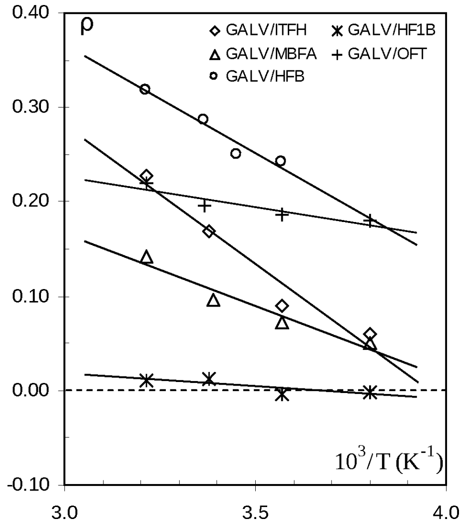

Fig. 4. The ρ nuclear-electron coupling parameters as a function of the reciprocal temperature.

The behaviour of ρ values versus the reciprocal temperature is shown in Figure 4. In ITFH, GALV has the greatest dipolar part, and its ρ values reduce, as the temperature decreases, while the GALV/HF1B has the smallest dipolar part, and its ρ values does not change effectively. Since the smallest scalar part was observed in the GALV/ITFH solution, the iodine atom may cause a stereospecific effect, hindering GALV molecule. It was found that the dipolar part is dominant for the intermolecular spin-spin interaction between unpaired electron of the GALV free radical and, both HFB and OFT, solvent ^{19}F nuclei (Fig. 4). It was observed that the dipolar part of the interaction increases for all samples with increasing temperature. We have reported previously [21] that the scalar interactions are more effective for BDPA/HFB and BDPA/OFT. As a

Table 1. The DNP parameters for the solutions of GALV and BDPA. A_∞, s, ρ, and K are the enhancement factor for infinite EPR power, the saturation factor, the nuclear-electron coupling parameter, and the relative importance of scalar and translational dipolar interaction, respectively. All samples were prepared at 3 mM.

Free Radical	Solvent	T (K)	A_∞	s	ρ	K
GALV	1-Iodotridecafluorohexane (ITFH)	311	−143.7	0.561	0.228	0.42
		296	−106.7	0.536	0.169	
		280	−56.2	0.589	0.089	
		263	−37.4	0.657	0.059	
	2,2,3,4,4,4-Hexafluoro-1-butanol (HF1B)	311	−6.9	0.783	0.011	0.93
		296	−7.7	0.756	0.012	
		280	2.0	0.730	−0.003	
		263	1.1	0.558	−0.002	
	N-Methyl-bistrifluoroacetamide (MBFA)	311	−89.5	0.712	0.142	0.60
		295	−61.0	0.664	0.097	
		280	−46.0	0.663	0.073	
		263	−31.3	0.659	0.050	
	Hexafluoroacetylacetone (HFAA)	311	0	–	0.000	No Enhancement
		298	0	–	0.000	
		280	0	–	0.000	
		263	0	–	0.000	
	Hexadecafluoroheptane (HDFH)	311	0	–	0.000	No Enhancement
		296	0	–	0.000	
		280	0	–	0.000	
		263	0	–	0.000	
	Heptafluorobutyric acid (HFBA)	311	0	–	0.000	No Enhancement
		296	0	–	0.000	
		280	0	–	0.000	
		263	0	–	0.000	
	Nonafluoropentanoic acid (NFPA)	311	0	–	0.000	No Enhancement
		295	0	–	0.000	
		280	0	–	0.000	
		263	0	–	0.000	
	Octafluorotoluene (OFT)	311	−138.5	0.760	0.220	0.44
		297	−123.2	0.725	0.196	
		280	−117.1	0.511	0.186	
		263	−113.3	0.690	0.180	
	Hexafluorobenzene (HFB)	311	−200.4	0.745	0.318	0.26
		297	−180.5	0.791	0.287	
		290	−157.2	0.826	0.250	
		280	−152.0	0.748	0.241	
BDPA	Hexadecafluoroheptane (HDFH)	311	0	–	0.000	No Enhancement
		296	0	–	0.000	
		280	0	–	0.000	
		263	0	–	0.000	
	Heptafluorobutyric acid (HFBA)	311	0	–	0.000	No Enhancement
		296	0	–	0.000	
		280	0	–	0.000	
		263	0	–	0.000	
	Nonafluoropentanoic acid (NFPA)	311	0	–	0.000	No Enhancement
		296	0	–	0.000	
		280	0	–	0.000	
		263	0	–	0.000	

result, GALV/HFB and GALV/OFT samples have positive ρ values, while BDPA/HFB and BDPA/OFT have negative ρ values (Fig. 5).

W. Müller-Warmuth and K. Meise-Gresch [3] reported that the maximum enhancement ranges between -280 ($K = 0.14$) for fluorinated aliphatics and $+460$

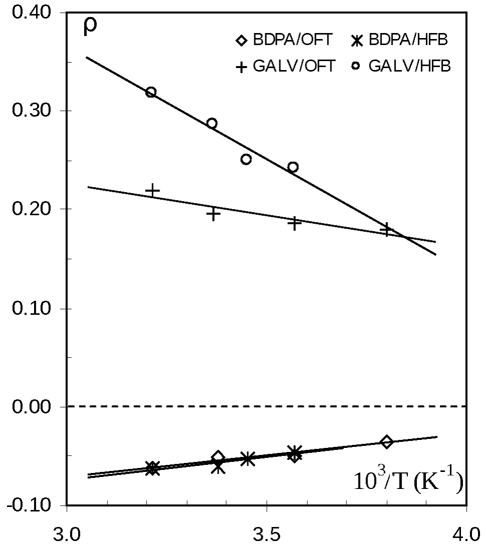

Fig. 5. The comparison of the nuclear-electron coupling parameters ρ of this work, for the solutions GALV/HFB and GALV/OFT, with BDPA/HFB and BDPA/OFT obtained before as a function of the reciprocal temperature [21].

($K = 6.8$) for fluorinated aromatics. The K parameters calculated for the maximum temperature by using (6) are between 0.42 and 0.93 for the aliphatic solvents, and 0.26 for HFB and 0.44 for OFT with GALV. These values show the effectiveness of the scalar interaction compared to the dipolar interaction in the solutions. As the K value increases, the dipolar part of the interaction decreases. As the BDPA free radical has a great mesomery, the unpaired electron can be delocalized in a π-orbital, which extends over the allyl chain and the diphenylene fragments, i. e. over the whole molecule. The plane-plane collisions between fluorinated aromatic solvent molecules and the free radical are the most effective reason for producing spin density at the solvent nuclei. On the other hand, the spin density can be also transmitted by overlapping of the unpaired orbitals of the radical with molecular orbitals of the receptor molecule during collision. Therefore, the more effective scalar interaction will be possible in the solutions of BDPA with the fluorinated aromatic solvents. However, the results obtained in this work show that the more dipolar interaction will be possible in solutions of GALV with fluorinated aromatic solvents due to the chemical structure of the GALV free radical. The sterically exposed planar π-allyl radical bis-(diphenylene) phenylallyl is capable of strong bonding interactions [23]. The allyl carbons share 30 – 50% of the unpaired spin density, with the remainder being distributed throughout the benzene rings [23]. Because of the wide exposure of electron density above and below the plane of the radical, non-stereospecific, random-bounce collisions should be effective in transmission of scalar coupling [23]. Especially high scalar coupling is observed and obtained for interactions in which randomly occurring plane-plane collisions provide good overlap between π-orbitals of the colliding molecules [23]. The unpaired spin density in GALV radical is located on the oxygen atom. In contrast to BDPA, approach of other species within bonding distance of the radical is either precluded or hindered by the flanking methyl group. Consequently, the scalar contributions to the total coupling are usually much smaller than with BDPA and arise mostly from the exchange polarization. As a consequence of the localized nature of the unpaired electron, the scalar interactions with species such as GALV are generally diminished compared to those with BDPA.

4.3. *Free Radical Scavengers*

We do not observe any Overhauser enhancement in solutions of both GALV and BDPA with HFAA, HDFH, and HFBA for all temperatures (Table 1). These acidic solvents may have scavenging effects on these radicals. They accept an electron or hydrogen radical to become stable in diamagnetic molecules. In addition, BDPA and GALV are often used as substrates to evaluate the antioxidant capacity of an antioxidant, the unpaired electron is delocalized over C and O atoms, respectively.

Wei-Min Wu et al. [24] have studied the reaction with GALV free radical of some acidic solvent media and radical scavenging activity. They have found that the UV spectrum of GALV diminished gradually with time, when the antioxidants were added to the ethanol solution of GALV. Caffeic Acid Phenethyl Ester (CAPE) was one of the antioxidant that they have used.

5. Conclusions

The present study reports the experimental determination of DNP parameters of dipolar and scalar interactions, for some highly fluorinated aliphatic and aromatic solutions with GALV in a low magnetic field, at several temperatures. Results show that the measurements in the low magnetic field depend upon the competition between the dipolar and the scalar contact part of the coupling. The coupled nuclear-electron systems exhibit two types of spin-spin interactions. These interactions are the dipolar interaction, which is proportional to the inverse cube of the distance between spins of solvent nuclei and those of the unpaired electron of the free radical, and the scalar interaction, which is proportional to the unpaired electron density at the solvent nucleus. The contact interaction turns out to be more complicated. It is not only its amplitude (which is relatively measured by K, the ratio of scalar and dipolar coupling), but also the frequency spectrum, its details depend on the chemical and electronic properties of both interacting molecules. K can be obtained from low-field DNP measurements.

The ρ values of the samples HF1B and MBFA are smaller than that of the samples of the other solvents. The smaller ρ values correspond to the higher K parameters, which is indicating a more effective scalar interaction. It was found that the fluorine-electron interactions are predominantly dipolar, however involve also a scalar contribution.

The plane-plane collisions between BDPA, which has a great mesomery, and the fluorinated aromatic solvent molecules cause more predominantly scalar coupling, compared to the fluorinated aliphatic solvent molecules. Therefore, the details of the scalar (contact) interaction depend on the chemical and electronic properties of interacting molecules [21]. The scalar interactions between GALV and fluorinated aromatics and aliphatics exhibit less effectiveness comparing to the dipolar interaction.

The temperature-dependent DNP effect, seen in free radical solutions, 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 [25]. The translational diffusion of solvent molecules is responsible for the dipole-dipole relaxation, which dominates at high temperatures [25]. The scalar interaction is modulated mainly by electron spin relaxation and an isotropic fluorine-electron spin chemical exchange process on the surface.

A strong temperature dependence of the DNP enhancement was observed in free radical solutions with ITFH (Fig. 4). At the temperatures of 311 K and 296 K, the DNP enhancements are small and negative for HF1B, but as temperature decreases, DNP enhancement passes through zero and reaches positive values. Therefore, the samples with HF1B give dominant scalar interaction at low temperatures, but dominant dipolar interaction at high temperatures. The samples with GALV free radical in HFB and OFT solvent have stronger temperature dependency for DNP enhancement than the samples with BDPA free radical in HFB and OFT solvent, as seen in Figure 5.

Low field nuclear-electron double resonance experiments with HFAA, HDFH, and HFBA solutions containing organic free radicals have led to the conclusion that the solvents may cause scavenging effects on GALV and BDPA free radicals.

We believe that, in biological samples, the detailed information of chemical environment can be obtained with aromatic fluorinated solvents and free radicals which are inclined to the scalar interaction in EPR oximetry, supported by OE. Especially HFB is a good oxygen tension reporter for biological samples due to its aromatic and symmetric structure [11, 25 – 27]. In the present study, the similar experimental results were obtained for OFT. OFT has parallel behaviour with HFB containing GALV and BDPA free radical as seen in Figure 5. We believe that OFT may be a good oxygen reporter in EPR oximetry and this proposal may be tested experimentally.

Acknowledgements

This work was supported by the Research Fund of the Uludag Universtiy Project number: F-2006/61. The authors would like to thank the Uludağ University for financial support and Prof. Dr. Emin N. Özmutlu for his assistance in the preparation of the manuscript in English.

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