Araştırma Makalesi / Research Article

Year-Dependent Change of DNP Parameters in p-Difluorobenzene Suspension with Asphaltene

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Abstract

Petroleum asphaltenes are the heaviest, most aromatic and most complex component of crude oil and asphaltenes are paramagnetic. Overhauser Dynamic nuclear polarization (ODNP) were performed to study samples of asphaltene/p-Difluorobenzene at 1.53 mT. p-difluorobenzen solvent with asfalten in three different concentrations waiting five years with oxygen removed have been stuied. Dynamic nuclear polarization parameters were determined by performing ODNP experiments again. The results of our studies and the calculated parameters, especially the coupling parameter, indicates that there were dipolar interactions between nuclei and free electron spins. These dipolar interactions indicate that, at the end of five years the the asphaltene micelles in suspension agglomerated and that make the molecule movements slower. The obtained dynamic nuclear polarization parameters were compared with their values in the literature and it was observed that the parameters decreased slightly with time.

Keywords: DNP, Overhauser Effect, Asphaltene, Sample Age.

Asfaltenli p-Diflorobenzen Süspansiyonunda DNP Parametrelerinin Yıla Bağlı Değişimi

Öz

Petrol asfaltenleri ham petrolün en ağır, en aromatik ve en kompleks bileşenidir ve asfaltenler paramanyetiktir. Overhauser Dinamik nükleer polarizasyon (ODNP), 1.53 mT'da asfalten/p-Diflorobenzen örneklerini incelemek için gerçekleştirildi. Oksijenden uzaklaştırılarak beş yıl bekletilen asfaltenli p-difluorobenzen çözgen üç farklı konsantrasyonda çalışıldı. ODNP deneyleri tekrar yapılarak, Dinamik nükleer polarizasyon parametreleri belirlendi. Çalışmalarımızın sonuçları ve hesaplanan parametreler, özellikle çiftlenme parametresi, çekirdek ve serbest elektron spinleri arasında dipolar etkileşmeler olduğunu göstermektedir. Bu dipolar etkileşmeler, beş yılın sonunda süspansiyondaki asfalten misellerinin topaklandığını ve molekül hareketlerini yavaşlattığını göstermektedir. Elde edilen dinamik nükleer polarizasyon parametreleri literatürdeki değerleri ile karşılaştırılmış ve parametrelerin zamanla bir miktar azaldığı görülmüştür.

Anahtar kelimeler: DNP, Overhauser Etkisi, Asfalten, Örnek Yaşı.

1. Introduction

Asphaltenes are important components of crude oils and bitumens, and they have an amorphous structure. There is no exact chemical formula and molecular weight for asphaltene [1-3]. Nowadays, It enables analytical studies, including magnetic resonance studies of crude oil, which is a center of interest for science and industry [4].

Electron spin resonance experiments performed by many researchers show that asphaltenes are paramagnetic [4-6]. Free radical occurs due to incomplete carbon bonds in the dense aromatic structure of asphaltene particles. That is, free electrons occur due to incomplete carbon bonds. DNP in asphalt suspensions, first performed by Poindexter [7] in a weak constant magnetic field.

Dynamic nuclear polarization (DNP) has recently received great attention for its ability to increase signal densities by several times of magnitude in nuclear magnetic resonance (NMR) experiments. DNP, a technique well known in paramagnetic solutions and suspensions, depends on the movement of molecules containing nuclei and free electron spins. This technique, is becoming more and more popular as it magnifies nuclear spin polarization. That is a useful technique in determining asphaltene molecular dynamics and structure of asphaltene. In the case of Overhause DNP, It is a pair of magnetic resonance technique in which nuclear magnetic resonance is observed at the moment when the electron resonance of a paramagnetic substance with which a substance interacts simultaneously is observed. In solution-state, nuclear polarization increas by the methods of Overhauser DNP based on the effect of transfer the polarization from electronic spins to a system of nuclear spins. In our study, the nuclear spins are proton spins, which are the nuclei of the hydrogen atom in the solvent molecule. The Electron spins belong to the intense aromatic structure of asphaltene micelles, unpaired electron delocalized at incomplete carbon bonds. Asphaltenes, which are a mixture of complex molecules, are often a colloidal system with paramagnetic parts in itself [8].

ODNP technique was used to examine asphaltene/p-Difluorobenzene samples at 1.53 mT. In this method, intermolecular spin spin interactions occur between the nuclear spins in the diffused solvent molecules and the unpaired electron spins in the asphaltene [9]. The goal of this study is to examine the DNP parameters by doing a similar study (with the DNP technique) for the asphaltene / p-difluorobenzene sample prepared previously, and to examine the year-dependent change on DNP parameters in asphaltene suspensions by comparing with the results five years ago.

Experimental application of ODNP and its theory can be provided in literature [5, 10, 11]. Including the observed nuclear polarizations, P_z, the thermal equilibrium values, P_0; the Overhauser DNP enhancement factor is given by [12-14].

$$E = \frac{P_Z}{P_0} = 1 - \rho f s \left| \frac{\gamma_e}{\gamma_n} \right| \tag{1}$$

where, γ_e and γ_n, are the gyromagnetic ratios of the electron and nuclear spins, respectively. The leakage factor f, the saturation factor s when the ESR is at full saturation, it becomes equal to 1. The nuclear-electron coupling parameter ρ, in the white spectrum approach, is +0.5 for pure dipolar interaction and -1 for pure scalar coupling. The ρ values obtained vary between the limit values of +0.5 and -1.

When being complete EPR saturation ($s=1$), the inverse of E factor is extrapolated for the infinite ESR power is derived as

$$\left(\frac{P_Z - P_0}{P_0} \right)^{-1}_{s \to 1} = - \left(\rho f \left| \frac{\gamma_e}{\gamma_n} \right| \right)^{-1} = E_\infty^{-1} \ . \tag{2}$$

For infinite electron spin concentration, f goes to one, from there the ultimate enhancement factor (U_∞) is reached.

$$(E_\infty^{-1})_{f \to 1, \ c \to \infty} \to \left(-\rho \left| \frac{\gamma_e}{\gamma_n} \right| \right)^{-1} = U_\infty^{-1} \tag{3}$$

ρ parameter is calculated (for ^{1}H; $|\gamma_e/\gamma_n| = 658$) with

$$\rho = -U_\infty/658 \ . \tag{4}$$

The importance on dependent scalar coupling is K parameter. Since ρ is an experimentally obtainable parameter, the parameter K can be easily calculated.

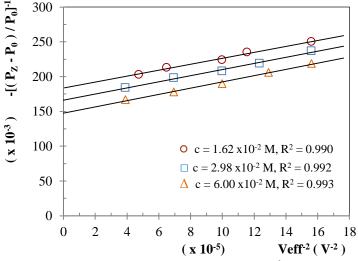$$K = \frac{1 - 2\rho}{1 + \rho} \tag{5}$$

2. Material and Methods

MC-800 liquid petroleum asphalt was taken from the Tupraṣ Refinery in Kirikkale, Turkey. This asphaltane obtained from asphalt and it has a paramagnetic feature. p-difluorobenzene was purchased from Aldrich Chemical Co. (USA). Basic constants and NMR sensitivity of p-difluorobenzene, molecular weight; 114.09 g/mol, boiling point; 88-89 ^{o}C, melting point; -13 ^{o}C, density; 1.170 g/cm^{3}, and calculated NMR sensitivity; 1.24x10^{22} spin/cm^{3}, respectively.

The suspensions had been prepared before in 2015 in three different asphaltene concentrations. These concentrations are 1.8 kg/m^{3}, 3.3 kg/m^{3} and 6.2 kg/m^{3}, respectively. The presence of oxygen affects the enhancement factor. Degassing treatment should be performed in order to minimize the interactions with air molecules, to take the EPR line to easy saturation and to ensure the long life of the sample. Degassing process was performed in Leybold-Heraeus vacuum system at 10 Pa pressure value. The prepared samples were kept for 5 years in a closed environment with a temperature range of 4-8 ^{o}C.

DNP measurements were fulfill at 1.53 mT fixed magnetic field NMR spectrometer. The spectrometer is hand-made and has a resonance frequency of 61.2 kHz for protons and 43.8 MHz for electrons. The spectrometer was explained in the previous articles [15].

3. Results and Discussion

For each sample, E_{∞} values were determined by extrapolating from the optimal fit lines drawn by obtaining the inverse of the enhancement factors as a function of the inverse of the square of the high frequency voltage, which is proportional to the inverse of the ESR power. The E_{∞}^{-1} values correspond to the intersection points of the extrapolated optimal fit lines passing through the experimentally obtained points with the line $V_{eff}^{-2}=0$ (Figure1).

Figure 1. Obtaining E_{∞} for asphaltene/p-difluorobenzene sample. The R^{2} values indicate the regression of the experement points.

The ultimate enhancement factor U_{∞} was determined by extrapolating to the infinite concentration from the optimal fit lines drawn to the E_{∞} values found for that medium as a function of the inverse of the concentration. The U_{∞}^{-1} value corresponds to the point of intersection of the extrapolated optimal fit line passing through the obtained points with the line $c^{-1} = 0$ (Figure 2).
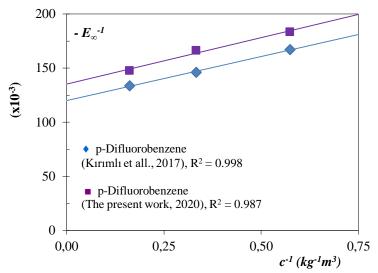
Figure 2. Obtaining U_∞ for asphaltene/p-difluorobenzene sample at three different concentrations.

After ρ value calculated from equation (4), K value can be found by equation (5). The DNP parameters obtained for the asphaltene/p-difluorobenzene sample, E_∞, E_{end}, U_∞, ρ, f, s, K are presented in Table 1. As seen in Table 1, all the E_∞ values are negative, these values vary between -6.8 and -5.4. This is due to the inversely enhancement of the signal. This situation indicates that the interaction between the nuclear spins and electron spins is dipolar. After the DNP experiments of the samples prepared in 2015 were carried out, the DNP experiments of the same samples were repeated in 2020.

Table 1. The DNP parameters (E_∞, E_{end}, U_∞, ρ, s, f, K).
(E_{end}, the enhancement factor for maximum available the EPR power)

	c (kg m^{-3})	E_∞	E_{end}	U_∞	ρ	f (E_∞/U_∞)	s (E_{end}/E_∞)	K
The present work (2020)	1.8	-5.4	5.0			0.730	0.926	
	3.3	-6.0	5.4	7.4	0.011	0.811	0.901	0.967
	6.2	-6.8	6.0			0.919	0.882	
Kırımlı et al. [8]	1.8	-6.0	-			0.718	0.833	
	3.3	-6.8	-	8.3	0.013	0.820	0.891	0.962
	6.2	-7.5	-			0.898	0.889	

4. Conclusions

The ρ value can vary from -1 in the case of pure scalar coupling to +0.5 in the case of pure dipolar coupling. The results of our studies and the calculated parameters, especially the coupling parameter, indicates that there were dipolar interactions between the nuclear spin and the electron spin. This conclusion is also supported by the parameter K.

The obtained dynamic nuclear polarization parameters were compared with their values in the literature and it was observed that the parameters decreased slightly with time. When the values obtained from this study and the ρ values obtained by Kirimli [8] are compared and the percentage change is examined, it is seen that the decrease is 10.8 %.

These dipolar interactions indicate that, at the end of five years the the asphaltene micelles in suspension agglomerated and that make the molecule movements slower. In addition, it is seen that the asphaltene micelles are aggregated to a greater extent and the interaction for this reason is reduced.

Author's Contributions

All contributions belong to the author in this paper.

Statement of Conflicts of Interest

The author has no conflict of interest regarding this article.

Statement of Research and Publication Ethics

The author declares that this study complies with Research and Publication Ethics.

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