

Intermolecular Magnetic Spin-Spin Interaction in Asphaltene Suspensions at 1.53 mT

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In this study, Overhauser effect (OE) type of dynamic nuclear polarization (DNP) experiments were performed to study suspensions of MC800 asphaltene in bromopentafluorobenzene, chloropentafluorobenzene and hexafluorobenzene aromatic solvents. The experiments were performed at a low field of 1.53 mT in a double-resonance nuclear magnetic resonance (NMR) spectrometer. In this technique the nuclei of diffusing solvent molecules and the unpaired electron existing on the asphaltene micelles interact magnetically. The DNP parameters were determined. Additionally, the interactions between ^{19}F nuclei of the solvent and the electrons delocalized on the asphaltene are interpreted. The highest enhancement factor value (5.90) was obtained for the hexafluorobenzene solvent medium, because between these, hexafluorobenzene has the highest fluorine atom number. The solvent molecules attach to the colloidal asphaltene particles for a very short time forming complexes and making scalar interaction. Morphologies of asphaltene surfaces depending on the solvent effects were observed by using scanning electron microscopy (SEM).

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1. Introduction

Treatment of petroleum, residua, heavy oil, or bitumen with a low-boiling liquid hydrocarbon results in materials known as asphaltenes. Asphaltenes are dark brown to black friable solids and their solubility varies in a large degree from benzene derivatives to n-alkanes. Asphaltenes consist of condensed polynuclear aromatic ring systems bearing alkyl side chains with hetero elements (i.e. nitrogen, oxygen, and sulphur) [1].

Dynamic nuclear polarization (DNP) is a well-known double resonance technique of magnetic resonance. In this technique, the nuclear magnetic resonance (NMR) is observed during simultaneous irradiation of the electron spin resonance (ESR). In the Overhauser effect (OE) type of DNP for free radical solutions, if the ESR of the paramagnetic solute is saturated, important changes in the intensity of the NMR signal of the solvent occur [2].

Gutowsky et al. [3] have found the g -value (i.e., Landé factor) to be 2.0030 ± 0.0005 in their crude petroleum ESR investigations. The unpaired electrons were responsible for the paramagnetism and they were delocalized on the incomplete carbon bonds of the condensed aromatic structure of the asphaltene particles. The theory of the OE, in low magnetic fields, is available in the literature [4, 5].

The aim of this work is to analyze the microscopic morphology of asphaltene; to study in a low magnetic field of 1.53 mT at room temperature the DNP parameters in colloidal suspensions consisting of fluorocarbons and asphaltene extracted from MC-800 liquid asphalt, which

is obtained from Iranian heavy crude oil; and to show the utility of the DNP method for characterizing asphaltene behavior in a variety of solvents.

The theory of DNP via the OE in solutions of free radicals has been provided in the literature [6, 7]. As the ESR power is increased, saturation factor, s , goes to 1, thus the NMR signal enhancement $(P_z/P_0) - 1$ increases and converges to a finite value. $[(P_z/P_0) - 1]^{-1}$ is inversely proportional to ESR power. For the infinite ESR power, one obtains enhancement factor A_∞ as

$$\left(\frac{P_z - P_0}{P_0}\right)_{s \rightarrow 1}^{-1} \rightarrow \left(-\rho f \left|\frac{\gamma_S}{\gamma_I}\right|\right)^{-1} = A_\infty^{-1}, \quad (1)$$

where P_0 and P_z are the equilibrium values of nuclear spin polarization and the dynamic polarization respectively. γ_S and γ_I are the electronic and nuclear gyromagnetic ratios, respectively, $\gamma_S < 0$, $\gamma_I > 0$ and $|\gamma_S|/|\gamma_I| = +700$ for ^{19}F . f is the leakage factor for the nuclear relaxation, ρ is the nuclear-electron coupling parameter given as

$$\rho = -A_\infty/700 \times f. \quad (2)$$

In the white spectral region, i.e., for extreme narrowing ($\omega_S \tau_t \ll 1$), the parameter K , which characterizes the relative importance of the scalar and translational dipolar interactions, is given by [8]

$$K = \frac{2 J_{\text{Sc}}(0)}{15 J_1^{\text{D}}(0)}, \quad (3)$$

where $J_{\text{Sc}}(0)$ and $J_1^{\text{D}}(0)$ are the scalar and translational dipolar spectral density functions, respectively. In weak fields, K is calculated from the experimental ρ value [5, 9, 10]:

$$K = \frac{1 - 2\rho}{1 + \rho}. \quad (4)$$

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2. Materials and methods

2.1. Asphaltene and solvents

The asphaltene was extracted from liquid asphalt MC-800. The asphalt was taken from the Tupras, Refinery in Kirikkale, Turkey. The suspensions were prepared in three solvents. The solvents were obtained from Aldrich Chemical Co. (USA). The properties of the selected

solvents are summarized in Table I. The prepared samples had a volume about 6.5 cm^3 and a concentration of 10.0 kg m^{-3} . The samples were degassed and sealed in Pyrex tubes. The experiments were performed in 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 42.5 MHz for electrons.

Basic parameters and NMR sensitivity of selected solvents.

No	Solvent	Formula	Purity [\geq %]	Molecular Weight [g mol^{-1}]	Boiling Point [$^{\circ}\text{C}$]	Density [g cm^{-3}]	NMR Sensitivity [$\times 10^{22} \text{ spin cm}^{-3}$]
1	Bromopentafluorobenzene	C_6BrF_5	99	246.96	137	1.98	2.42
2	Chloropentafluorobenzene	C_6ClF_5	98	202.51	117	1.57	2.33
3	Hexafluorobenzene	C_6F_6	99	186.05	81	1.61	3.13

TABLE I

2.2. Determination of the DNP parameters

In the low field DNP investigations, the observations are based on the pure and the double resonance NMR signal intensities (P_0 and P_z). The usual amplitude modulation technique gives the signals as the derivatives of the central bands and first and second side bands. The P_0 and P_z values were taken to be the peak-to-peak values of the derivatives of the central bands. All measurements were performed at $23 \pm 2^{\circ}\text{C}$. P_0 was measured four times and P_z values were obtained at five different ESR power values in order to saturate electronic spin polarization. For the determination of the A_{∞} value, the reciprocal of the enhancement factor should be obtained as a function of reciprocal value of the ESR power, which is proportional to V_{eff}^{-2} , where V_{eff} is the high frequency voltage on the ESR coil. In the case of full ESR saturation, the ESR power should go to infinity or V_{eff}^{-2} to zero. The variation of $P_0/(P_z - P_0)$ versus V_{eff}^{-2} for three samples is given in Fig. 1. The A_{∞}^{-1} values correspond to the intersection points of the $V_{\text{eff}}^{-2} = 0$ line and the extrapolated best-fit line. The leakage factor f was taken as 0.90 ± 0.05 for all samples by using the literature information [10]. ρ and K values were calculated from (2) and (4), respectively.

2.3. Scanning electron microscopy (SEM)

The surface morphology investigation of the asphaltene was performed in a LEO 1430 VP type SEM (LEO Electron Microscopy Ltd., Cambridge, UK) operated at 20 kV. Before the analysis, the asphaltene samples were ground in an agate mortar and dispersed in solvents. Asphaltene suspensions were prepared with a ratio of 3 mg asphaltene to 0.5 cm^3 of solvent. A drop of this solution was deposited on the glass substrate, and the solution was quickly drained. Then glass substrates

were inserted into the cell, placed on a metallic rotating disk, and adjusted for observation under the microscope.

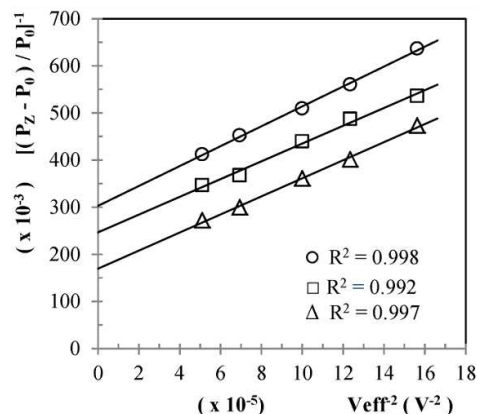


Fig. 1. The variation of $P_0/(P_z - P_0)$ versus V_{eff}^{-2} for three samples. \circ Bromopentafluorobenzene, \square Chloropentafluorobenzene, \triangle Hexafluorobenzene. The A_{∞}^{-1} values correspond to the intersection points of the $V_{\text{eff}}^{-2} = 0$ line and the extrapolated best-fit line. The R^2 values show the degree of agreement between the linear fit function and the experimental points.

3. Results and discussion

The dynamic nuclear polarization parameters, A_{∞} , A_{end} , s , ρ and K are summarized in Table II. The saturation factor s was calculated as the ratio of the enhancement factor A_{end} to A_{∞} . A_{end} corresponds to the maximum available ESR power. In the saturation experiments, actual saturations between 62 and 74% were achieved. The enhancement factors, A_{∞} , depended

in detail on the chemical environments of both the fluorine nucleus of the solvent molecules and the unpaired electron of the asphaltene micelles. A_∞ values of 3.31, 4.06 and 5.90 were obtained in this work, as shown in Table II. This means that there are scalar (contact) interactions between the nuclear spin and the electron spin. The K parameters are 1.02, 1.02 and 1.03, showing the effectiveness of the scalar interaction. Because of the scalar interactions, the aggregation of asphaltene micelles occur.

TABLE II

The DNP parameters for the suspensions of the selected fluorocarbons with asphaltene.

Solvent Medium	A_∞	A_{end}	$s(A_{\text{end}}/A_\infty)$	ρ	K
(1) Asphaltene/ Bromopentafluorobenzene	3.31	2.43	0.735	-0.005	1.02
(2) Asphaltene/ Chloropentafluorobenzene	4.06	2.89	0.711	-0.006	1.02
(3) Asphaltene/ Hexafluorobenzene	5.90	3.68	0.624	-0.009	1.03

The chemical type of the feedstock and the technology of bitumen production have an influence on the size of the asphaltene micelles and on the extent of aggregation [11]. Gülsün and Yalçın [12] studied the asphaltenes of MC-0 and MC-4 liquid asphalts (MC-30 and MC-800 in new classification, respectively) and reported that the solvent molecules can either attach to the asphaltene colloidal particle for a very short time or diffuse freely in and out of the colloid. The closest effective distance between the interacting spins depends not only on the geometrical distance, but also on the delocalization of the unpaired electrons in the asphaltene micelles. The attachment of the solvent molecules can occur to favored locations on the asphaltene surface, because of their diverse chemistry [13]. Thus, the fluorocarbon molecular properties should be useful for a description of these systems. In complement to other techniques, DNP provides a unique probe of the asphaltene colloids on a molecular scale. Aydoğdu et al. [14] have studied Overhauser effect (OE) type of dynamic nuclear polarization experiments in suspensions of asphaltene (extracted from MC-800 liquid asphalt) in xylene isomers at a low magnetic field. Intermolecular spin-spin interactions occur between nuclear spins of hydrogen in the solvent medium and the free electron spins in the asphaltene micelles. The dipole-dipole interaction is predominant for the intermolecular spin-spin interaction in all suspensions and at all temperatures.

The scalar and dipolar interactions can be observed in solutions containing ^{19}F nuclei. The dipolar interactions are independent from the geometry of system and the chemical properties of the solution. However, the scalar interactions are extremely sensitive to the local environment and to the distribution of the bonding electrons during aggregation of the asphaltene. Short-term complexes may occur between the asphaltene micelles and

the solvent molecules. During diffusion, molecules come very close to each other or even form short-lived complexes [5]. It was reported that neither purely scalar nor purely dipolar interactions have been observed between the unpaired electrons of the asphaltene micelles and the fluorine nuclei of the solvent molecules in [5].

In this investigation, purely scalar interactions have been observed between the unpaired electrons of the asphaltene micelles and the fluorine nuclei of the solvent molecules. The results have been compared with those from literature. It is natural to expect different results from asphaltenes of different regions, in general [15]. Yet the results, obtained from the asphaltene of liquid asphalt, are in good agreement with the results of the other studies.

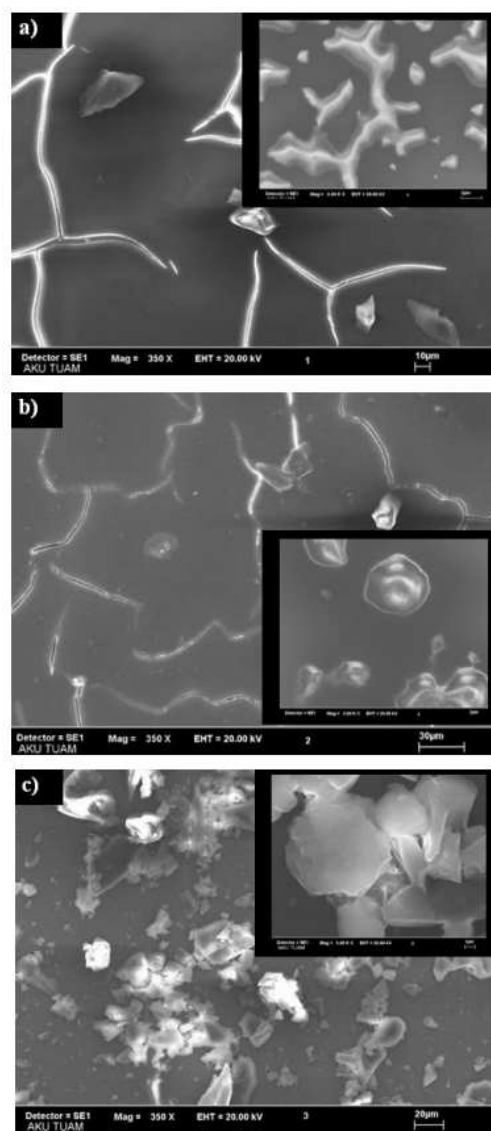


Fig. 2. SEM images of (a) asphaltene/bromopentafluorobenzene, (b) asphaltene/chloropentafluorobenzene and (c) asphaltene/hexafluorobenzene at 350 \times and 5000 \times magnifications.

Glass substrate micrographs obtained by the SEM technique are shown in Fig. 2. Superficial cracks and a smooth surface with particles of irregular shape precipitated on it, visible on asphaltene/bromopentafluorobenzene sample are shown in Fig. 2a. Sample of asphaltene/chloropentafluorobenzene shows more superficial cracks and particles of spherical shape on a smooth surface (Fig. 2b). Figure 2c shows amorphous surface with particles of irregular-shape agglomerates of the sample of asphaltene/hexafluorobenzene. There exist large and small pieces, which are most probably inorganic particles. Different solvents show variable affinities for the asphaltene surface. In Fig. 2c, in the stronger solvent, the asphaltene surface is well exposed to direct contact with the solvent molecules. However, Figs. 2a,b show less solvent effects. The difference in the morphology can be attributed to the velocity at which the asphaltene is precipitated from the dissolved state in the solvents. Different velocities cause changes in the physical appearance of the asphaltene [16]. In Fig. 2c aggregation of asphaltene is similar to that of Ref. [1]. The SEM micrographs of the asphaltene are consistent with the DNP results.

4. Conclusions

The DNP measurements were carried out on asphaltene suspensions in different solvent media in order to describe asphaltene behavior. In low magnetic fields, ρ varies from +0.5 (pure dipolar) to -1.0 (pure scalar). In our study, ρ , varies between -0.005 and -0.009. This means that the solvent molecules attach to the colloidal asphaltene particles for a very short time, forming complexes and making scalar interaction. These data suggest that the polarization of fluorine nuclei depends on their location in the solvent molecule. For the solutions such as hexafluorobenzene, its fluorine atom number is the highest and thus the enhancement is higher than in the other solvents. The highest enhancement factor value (5.90) was obtained for the hexafluorobenzene solvent medium. Even though chloropentafluorobenzene and bromopentafluorobenzene solvents have the same fluorine atom numbers, their enhancements are different. This difference is due to electronegativity. Fluorine is the most electronegative element.

The differences in morphology are due to solvent effects. Three morphological features observed in SEM are: (1) superficial cracks, (2) smooth surface with particles of different size on it and (3) agglomerate particles.

Acknowledgments

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