Intermolecular Effects of Fluorocarbons on MC800 Asphaltene and their Characterization

H.E. Kirimli*, H. Ovalioglu and C. Akay

Uludag University, Faculty of Arts and Sciences, Department of Physics, 16059, Bursa, Turkey

Nuclear magnetic resonance and dynamic nuclear polarization experiments were performed to study suspensions of asphaltene in the fluorocarbons at a low magnetic field of 1.53 mT, at room temperature. The asphaltene was extracted from MC800 liquid asphalt, which was of Heavy Iran origin. The elemental composition and the surface morphology of the asphaltene were determined by scanning electron microscopy and energy dispersive X-ray analysis. Intermolecular spin-spin interactions occur between nuclear spins of hydrogen in the solvent medium and the free electron spins in the asphaltene micelles. The electron paramagnetic resonance spectrum of the asphaltene was obtained and the saturation experiments were applied to the samples prepared in vacuum. The main ^{1}H DNP parameters were listed. Chemical composition and molecular structure of the asphaltene were analyzed. Scanning electron microscope images have shown that asphaltenes are constituted of agglomerated particles and smooth surfaces. Energy dispersive X-ray analysis has shown that the most abundant element is carbon.

1. Introduction

Asphaltenes, which are a part of petroleum, are regarded to be polar species, have larger aromatic structures and are containing alkyl chains, heteroatoms (such as O, S and N) and some metals [1]. Asphaltenes have unpaired electrons, which are observed using the electron spin resonance (ESR) experiments in crude petroleum [2].

Dynamic nuclear polarization (DNP) utilizes the liquid state interaction between nuclei and unpaired electron spins to generate an increased nuclear polarization upon the saturation of ESR transitions of the radicals. The maximum DNP enhancement of the NMR signal is given by the electron-to-nuclear gyromagnetic ratios γ_e/γ_n. This ratio for proton spin is 660. In this study, the nuclear spins are the proton spins, which are the ^{1}H nuclei of the solvent medium and the electron spins belong to the free electrons on the asphaltene micelles. The unpaired electrons were delocalized on the incomplete carbon bonds of the condensed aromatic structure of the asphaltene particles [3]. By DNP method we have revealed dipolar interaction between hydrogen atoms of the solvent and unpaired electrons of colloidal asphaltene. Electron spin saturation and DNP enhancements have been obtained and DNP parameters determined in low magnetic field. Chemical composition and morphology of MC800 asphaltene were investigated using scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis.

2. Materials and equipment

The equipment and technical details of the double resonance spectrometer used in this work have been extensively described in prior publications [4–6]. Further

information on the theory and applications of DNP for liquid samples is available in literature [6–9]. DNP experiments were performed at 1.53 mT with a resonance frequency of 61.2 kHz for the ^{1}H nuclei and 42.6 MHz for the electrons. The asphaltene was extracted from liquid asphalt MC800. The asphalt was taken from the Tupraş Refinery in Kirikkale, Turkey. The suspensions were prepared in three different asphaltene concentrations. The solvents were purchased from Aldrich Chemical Co. (USA) (Table I). The samples in Pyrex tubes were degassed and sealed.

TABLE I

Basic constants and NMR sensitivity of selected solvents. (1) Fluorobenzene (C_6H_5F), (2) o-Difluorobenzene ($C_6H_4F_2$), (3) m-Difluorobenzene ($C_6H_4F_2$), (4) p-Difluorobenzene ($C_6H_4F_2$).

Solvent	Molecular weight [g mol^{-1}]	Boiling point [°C]	Melting point [°C]	Density [g cm^{-3}]	NMR sensitivity (×10^{22} spin/cm^3)
(1)	96.10	85	−42	1.024	0.64
(2)	114.09	92	−34	1.158	1.22
(3)	114.09	83	−59	1.163	1.23
(4)	114.09	88–89	−13	1.170	1.24

The surface morphology and chemical composition analysis of the asphaltene were examined using a LEO 1430-VP SEM (LEO Electron Microscopy Ltd., Cambridge, UK) operated at 20 kV, with energy dispersive X-ray analysis capabilities. EDX analysis was used to identify the elemental composition of localized areas on sample particle surfaces.

3. Results and discussion

3.1. EPR spectra

It is essential to obtain the EPR spectrum of free radical to measure the DNP parameters in a given magnetic

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*corresponding author; e-mail: hengin@uludag.edu.tr

field. ESR spectrum should not be affected by the solvents [4]. Figure 1 shows the EPR spectrum of the asphaltene/fluorobenzene solvent medium for three different concentrations, at room temperature. The spectrum was considered as a single Gaussian, which has been formed by the superposition of several Lorentzians. The measured values of the spectrum with the biggest concentration are best fit with a Gaussian, given by the following equation:

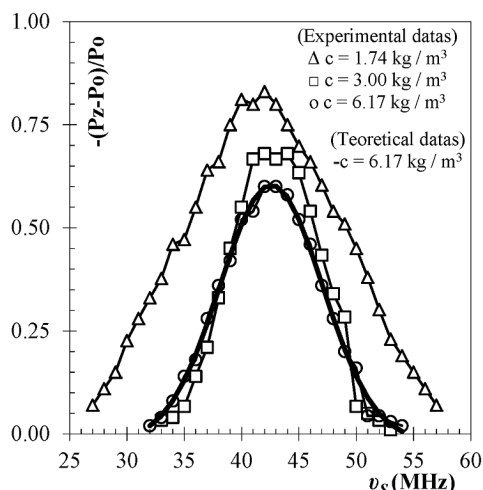$$-\frac{(P_z - P_0)}{P_0} = 0.61 \exp\left[-\frac{(v_s - 42.58)^2}{37.67}\right]. \qquad (1)$$

Fig. 1. EPR spectrum of the asphaltene/fluorobenzene solvent medium for three different concentrations. The fitted curve for 6.17 kg/m^3 radical concentration is a single Gaussian with 42.58 MHz peak frequency and 4.34 MHz standard deviation. The thick line represents the fitted curve.

3.2. DNP parameters

The NMR enhancement factor is defined as [10]

$$A = \frac{P_z - P_0}{P_0} = -\rho f s \left|\frac{\gamma_S}{\gamma_I}\right|, \qquad (2)$$

where P_0 and P_z are the NMR signal amplitudes without and with ESR saturation power, γ_S and γ_I are electronic and nuclear gyromagnetic ratios, respectively, f is the leakage factor for the nuclear relaxation, s is the saturation factor, which is equal to 1 for the complete EPR saturation, ρ is the nuclear-electron coupling parameter, which is a measure of the nuclear-electron interaction. All samples were saturated at 42.6 MHz. The variation of $-[(P_z - P_0)/P_0]^{-1}$ versus V_{eff}^{-2} for asphaltene/o-difluorobenzene sample at three different concentrations is given in Fig. 2a. A^{-1} is equal to A_{end}^{-1} for the maximum obtainable EPR power. If the saturation condition is fulfilled, the reciprocal of the enhancement factor is extrapolated for the infinite ESR power. A_∞ is the enhancement factor at complete EPR saturation and it is given as

$$A_\infty = -\rho f \left|\frac{\gamma_S}{\gamma_I}\right|. \qquad (3)$$

Since A_∞^{-1} values are proportional to the reciprocal of the radical concentration c^{-1}, the ultimate enhancement factor U_∞ can be easily found (Fig. 2b). The values of ρ can be calculated after determination of U_∞.
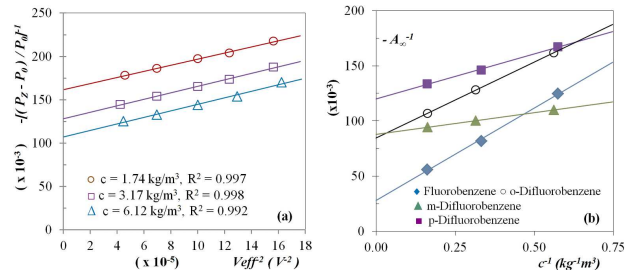
$$\rho = -\frac{U_\infty}{658}. \qquad (4)$$

Fig. 2. (a) Variation of $-[(P_z - P_0)/P_0]^{-1}$ versus V_{eff}^{-2} for asphaltene/o-difluorobenzene sample at three different concentrations. 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. (b) Examples of the determination of ultimate enhancement factors. U_∞^{-1} values correspond to the intersection points of the $c^{-1} = 0$ line and the extrapolated best-fit lines.

f value for each concentration was calculated from the ratio of A_∞/U_∞, and the s value was found as the ratio of A_{end} to A_∞. The dynamic nuclear polarization parameters, A_∞, U_∞, ρ, f and s are given in Table II. Experimental saturations are between 78 and 96%. Value of A_∞ varies between -17.8 and -3.0. It increases for all samples, as sample concentration increases. All A_∞ and U_∞ values are negative because P_z and P_0 NMR signals are opposite to each other. This situation also causes nuclear coupling parameter ρ to be positive for all solvent media. ρ value of asphaltene/fluorobenzene is 0.055, which is the biggest ρ value among all samples. This means that fluorobenzene is the most effective solvent to disperse and suspend the asphaltene among any of tested solvents. ρ values of o-difluorobenzene, m-difluorobenzene and p-difluorobenzene change according to the electronic structures and the chemical environment of ^{1}H nuclei of these three isomers.

3.3. Chemical composition and morphology of asphaltene

Figure 3a shows the SEM images for asphaltene obtained from liquid asphaltene and Fig. 3b shows EDX spectra of asphaltene particle. In the morphology of asphaltene a smooth surface, with variable particles of irregular shapes deposited on it, were observed. In Fig. 3a focus was made on checking the amorphous white particles of different sizes. As seen in Table III, carbon element is most abundant, in accordance with Trejo [11] studies. Carbon is followed by phosphorus and sulfur. Trace metal amounts (Ni, V) are found.

TABLE II

DNP parameters for the suspensions of the selected fluoro-carbonds with asphaltene.

Solvent medium	c [kg/m^3]	A_∞	U_∞	ρ	f	s
(1)Asphaltene/ Fluorobenzene	1.7	-8.0			0.220	0.841
	3.0	-12.2	-36.3	0.055	0.337	0.876
	6.2	-17.8			0.490	0.842
(2) Asphaltene/ o-Difluorobenzene	1.8	-6.2			0.523	0.908
	3.2	-7.8	-11.8	0.018	0.660	0.887
	6.1	-9.4			0.791	0.855
(3) Asphaltene/ m-Difluorobenzene	1.8	-9.1			0.796	0.779
	3.1	-10.0	-11.4	0.017	0.872	0.843
	6.3	-10.6			0.931	0.806
(4) Asphaltene/ p-Difluorobenzene	1.8	-6.0			0.718	0.833
	3.3	-6.84	-8.3	0.013	0.820	0.891
	6.2	-7.48			0.898	0.889

TABLE III

EDX analysis of the amorphous white particle shown in Fig. 3a.

Elemental composition, [wt.%]						
C	O	Si	P	S	V	Ni
90.98	0.14	0.20	4.62	4.03	0.01	0.01

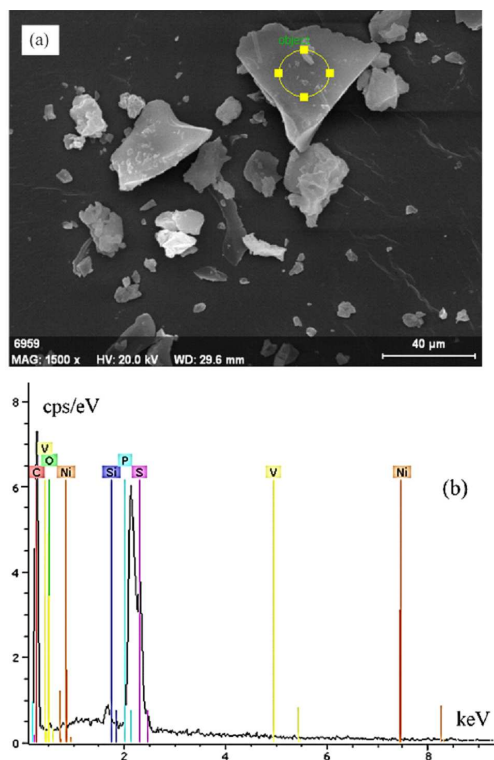

Fig. 3. (a) Microscopic structures of asphaltenes under the SEM at 1500× and (b) EDX spectra of asphaltene particle.

4. Conclusions

DNP experiments were performed to study suspensions of asphaltene in fluorocarbon solvents at 1.53 mT. We have observed a single Gaussian which was peaked around 42.6 MHz in the EPR spectra of the asphaltenes. In low magnetic fields, ρ varies from +0.5 (pure dipolar) to −1.0 (pure scalar). In our study, ρ, had varied between 0.055 and 0.013. The interactions occurring between unpaired electrons of the asphaltene micelles and the hydrogen nuclei of the solvent molecules have dipolar character. The obtained DNP parameters demonstrate that asphaltene particles have aggregated under the effect of solvent. Asphaltene particles have such elements as C, S, O and V, according to analysis of chemical composition and elemental mapping. During the analysis of the SEM images, a smooth surface, asphaltene particles with different sizes and asphaltene aggregations were observed. The most abundant element is carbon.

Acknowledgments

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