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ORIGINAL ARTICLE

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Dynamic nuclear polarization in suspensions of liquid asphalts in weak magnetic field*

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Abstract Nuclear Magnetic Resonance (NMR) and the Overhauser Effect (OE) type Dynamic Nuclear Polarization (DNP) were used to study MC-30 liquid asphalt in a weak magnetic field of 1.437 mT. Intermolecular spin-spin interactions occur between diffusing nuclear spins in the suspending fluid medium and unpaired electron spin in the liquid asphalt. Benzene, toluene, quinoline, pyridine, chlorobenzene, tetralin, nitrobenzene, ethylbenzene, and thiophene were used as the suspending fluid medium. The EPR spectrum of the liquid asphalt MC-30 is a single line of Gaussian shape in weak field. Some solvents can strip the natural resins from the asphaltene surface so that effectively closer contact can occur. The solvents which have highly polarizable and chemically active regions, and have chlorine or nitrogen atoms, can form stereospecific transient complexations.

Key words Nuclear magnetic resonance · Overhauser effect · Dynamic nuclear polarization · Liquid asphalts · Intermolecular spin-spin interactions

1 Introduction

Dynamic nuclear polarization in paramagnetic solutions and suspensions is critically dependent upon the motion of the molecules, which have nuclear and electron spins. The DNP technique is based here upon the intermolecular spin-spin interactions. The nuclear spins are the proton spins of the $^1H_1$ nuclei of the solvent molecules. The electron spins belong to the unpaired electrons delocated on the asphaltene micelles in asphalts. DNP is a double resonance phenomenon such that the NMR signal of the suspending fluid medium protons is enhanced when the electron spin resonance (ESR) of the unpaired electrons present in the medium is stimulated. The enhancement factor of the NMR signal depends upon the duration and intensity of magnetic interactions between both the spins. Such interactions can be modulated with the rotational or/and translational motions of both molecules and micelles in the sample. The unpaired electron is delocalized on the incomplete carbon bonds of the condensed aromatic* structure of the asphaltene micelles in colloidal asphalt suspensions (Gutowsky et al. 1958).

Poindexter (1972) Yalçıner (1981a,b) (1987) (1996) (1997) and Gülsün (1980) (1981) have investigated the DNP of the suspensions of some asphalts and asphaltenes. The aim of this work is to investigate the DNP parameters of liquid asphalt MC-30 extracted from crude petroleum of Libyan origin and to show the usefulness of the DNP method for characterizing asphalt behavior in a variety of solvents in the weak magnetic field of 1.437 mT.

The theory of the Overhauser Effect (OE), in weak magnetic fields, has been given elsewhere (Poindexter 1972; Yalçıner 1981a; Gülsün 1981). Figure 1 shows the energy levels of such a two-spin system. For this system transition probabilities via relaxation can be written as:

$$\begin{array}{llll} & m_s & m_I & m_s \quad m_I \\ w_0: & | + & - \rangle \Leftrightarrow | - & + \rangle \text{flip-flop} \\ & & & \text{(with the frequency } \omega_s + \omega_I), \\ w_2: & | + & + \rangle \Leftrightarrow | - & - \rangle \text{flip-flip} \\ & & & \text{(with the frequency } \omega_s - \omega_I), \\ w_1: & | \pm & - \rangle \Leftrightarrow | \pm & + \rangle m_s = \text{constant} \\ & & & \text{(with the frequency } \omega_I), \end{array}$$

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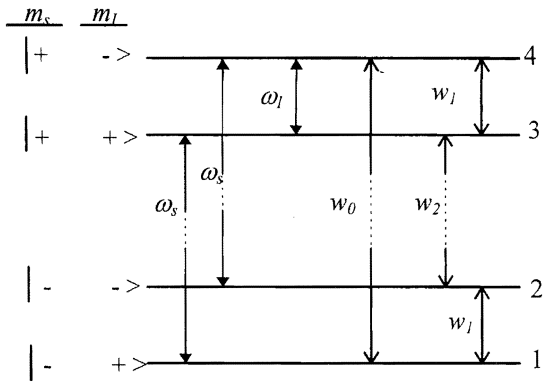


Fig. 1 The energy levels of intermolecular nuclear-electron two-spin system

where $w_1 = w_1' + w_1''$. $2w_1'$ is the transition probability due to nuclear-electron spin coupling and $2w_1''$ is the transition probability due to other mechanisms.

The equation of motion of the nuclear polarization can be written as (Kramer et al. 1965):

$$\frac{dP_z}{dt} = -(w_0 + 2w_1 + w_2) \times \left[(P_z - P_0) - \frac{w_2 - w_0}{w_0 + 2w_1 + w_2} (\Pi_z - \Pi_0) \right] \quad (1)$$

2 Results

The double resonance weak field NMR spectrometer has a static magnetic field H_o of about 1.437 mT. The resonance frequency is 61.166 kHz for protons, and 40.247 MHz for electrons. The latter can vary between 20–70 MHz during data collection for EPR spectra.

The liquid asphalt MC-30 is extracted from crude Libyan petroleum. The solvents used in this work are given in Table 1 with the molecular weights (MW), the freezing points (fp), and the viscosities (η).

The samples were prepared in three different asphalt concentrations all in 7 cc of solvent. After weighting the asphalt it was dissolved in solvent and degassed under vacuum at about 10^3 Pa and sealed.

For the determination of the A_∞ values, the reverse of the enhancement factor (i.e., the ratio $[(P_z - P_o)/P_o]^{-1}$), should be obtained as a function of the reciprocal value of the ESR power, which is proportional to the H_{1e}^{-2} or V_{eff}^{-2}, where V_{eff} is the high frequency voltage on the ESR coil. In the case of the full ESR saturation, Π_z is zero and the saturation factor s will go to 1. In order to obtain full saturation, the ESR power should go to infinity or V_{eff}^{-2} to zero. The A_∞^{-1} values correspond to the intersection points of the $V_{\text{eff}}^{-2} = 0$ line and the extrapolated best fit lines, Fig. 2.

Table 1. Basic constants of selected solvents

Solvent	MW	fp (°C)	η (10^{-3} kg m^{-1} s^{-1})
(1) Tetralin	132.21	− 36.0	2.10
(2) Toluene	92.14	− 95.0	0.59
(3) Benzene	78.12	5.5	0.65
(4) Ethylbenzene	106.17	− 95.0	0.69
(5) Quinoline	129.16	− 15.0	3.60
(6) Thiophene	84.14	− 38.0	0.65
(7) Chlorobenzene	112.56	− 45.6	0.80
(8) Pyridine	79.10	− 42.0	0.97
(9) Nitrobenzene	123.11	7.0	2.00

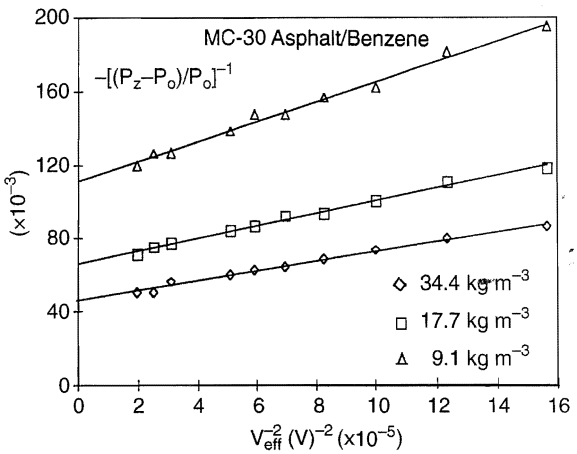


Fig. 2 An example of the evaluation of A_∞

As the EPR spectrum is the single line and has only one Gaussian peak (Fig. 3). The samples are saturated only at 42.5 MHz, which is near to the maximum of the spectrum.

As the A_∞^{-1} values are proportional to the reciprocal of the asphalt concentration c^{-1}, the ultimate enhancement factor U_∞ could be easily found. (Fig. 4.) The U_∞^{-1} values correspond to the intersection points of the $c^{-1} = 0$ line and the extrapolated best fit lines.

All measurements were performed at 23 ± 2°C.

The DNP parameters are listed in Table 2. The second column gives the asphalt concentration c, and the third column gives A_∞ values of the individual experimental result for each sample. The fourth column gives U_∞ values for each suspending fluid medium. The nuclear-electron coupling parameter ρ is a measure of the interaction of nuclear spins with the unpaired electron spins. The distribution factor f, the saturation factor s, the parameter K, the T_{10}^{-1} values and the total nuclear spin-lattice relaxation rate T_1^{-1} are also given. The low-frequency relaxation rate normalized by asphalt concentration c, $2w_1'/c$ values are also given. $(w_2 - w_0)/c$ values are tabulated at the last column.

The parameter K is the relative importance of scalar and translational dipolar interaction and is given as $K = 2J^{Sc}(0)/15J_1^D(0)$.

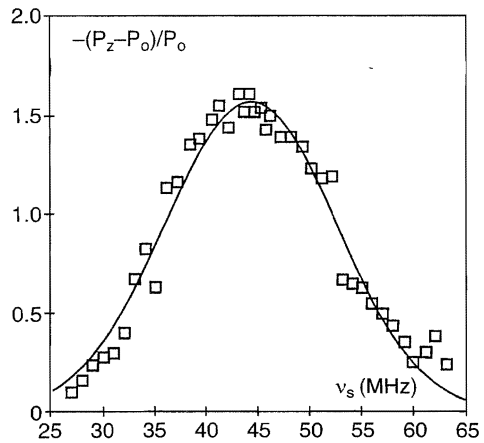


Fig. 3 The EPR spectrum of asphalt/ethylbenzene (17.6 kg m^{-3})

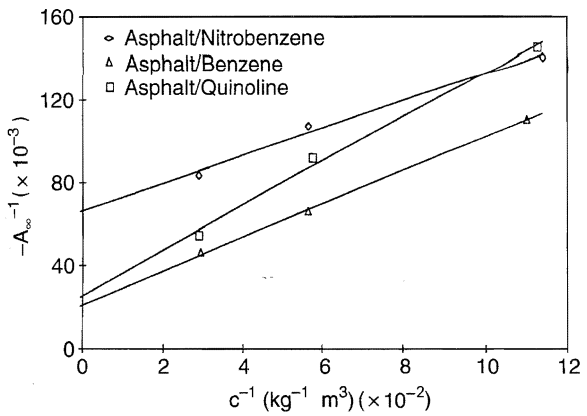


Fig. 4 Examples of the evaluation of ultimate enhancement U_∞

3 Discussion and conclusions

The EPR spectrum of asphalt/ethylbenzene at a concentration 17.6 kg m^{-3} is given in Fig. 3. This spectrum is obtained under the following conditions: (i) The inhomogeneous line broadening was larger then the linewidth of a single EPR line. (ii) The local field distribution has Lorentzian form. On the other hand, H_{1e} must not be too large. Otherwise the broadening due to the saturation invalidates condition (i). The EPR spectrum is found to be independent of the kind of suspending fluid medium. The obtained spectrum is a best fit Gaussian to

Table 2 DNP parameters of the asphalt suspensions

Suspending fluid *medium*	c (kg m^{-3})	A_∞	U_∞	ρ	f	s	K	T_{10}^{-1} (s^{-1})	T_1^{-1} (s^{-1})	$2w_1'/c$ (10^{-3} s^{-1} kg^{-1} m^3)	$(w_2-w_0)/c$ (10^{-3} s^{-1} kg^{-1} m^3)
	8.6	− 2.5			0.015	0.880			0.355		
(1) Tetralin ($C_{10}H_{12}$)	17.0	− 4.9	− 161.3	0.245	0.030	0.959	0.410	0.350	0.361	0.6	0.15
	34.5	− 9.3			0.058	0.892			0.372		
	8.6	− 6.7			0.131	0.910			0.071		
(2) Toluene	17.8	− 12.3	− 51.3	0.078	0.240	0.862	0.783	0.062	0.082	1.0	0.08
($C_5H_5CH_3$)	34.5	− 19.0			0.370	0.979			0.098		
	9.1	− 9.0			0.194	0.922			0.056		
(3) Benzene	17.7	− 15.1	− 46.3	0.070	0.326	0.934	0.804	0.045	0.067	1.2	0.08
(C_6H_6)	34.4	− 21.6			0.467	0.917			0.084		
	9.0	− 5.7			0.124	0.930			0.120		
(4) Ethylbenzene	17.6	− 9.7	− 46.1	0.070	0.210	0.928	0.804	0.105	0.133	1.7	0.12
($C_6H_5C_2H_5$)	34.1	− 16.4			0.356	0.878			0.163		
	8.9	− 6.8			0.181	0.941			0.366		
(5) Quinoline	17.4	− 10.8	− 37.6	0.057	0.287	0.935	0.838	0.300	0.421	7.5	0.43
(C_9H_7N)	34.8	− 18.2			0.484	0.923			0.581		
	8.7	− 8.7			0.240	0.943			0.050		
(6) Thiophene	17.2	− 13.1	− 36.2	0.055	0.362	0.901	0.843	0.038	0.060	1.4	0.08
(C_4H_4S)	34.9	− 21.3			0.588	0.939			0.092		
	8.7	− 10.4			0.340	0.913			0.083		
(7) Chlorobenzene	17.4	− 15.0	− 31.6	0.048	0.475	0.960	0.863	0.055	0.105	3.3	0.16
(C_6H_5Cl)	35.2	− 21.8			0.712	0.931			0.191		
	8.6	− 6.5			0.207	0.908			0.092		
(8) Pyridine	17.4	− 10.7	− 31.4	0.048	0.341	0.897	0.863	0.073	0.111	2.2	0.11
(C_5H_5N)	34.9	− 16.3			0.519	0.877			0.152		
	8.8	− 7.1			0.473	0.831			0.241		
(9) Nitrobenzene	17.7	− 9.3	− 15.0	0.023	0.620	0.882	0.932	0.127	0.334	13.1	0.30
($C_6H_5NO_2$)	34.9	− 12.0			0.800	0.925			0.635		

the measured values and it can be given in the following equation:

$$-\frac{(P_z - P_o)}{P_o} = 1.57 \exp\left[-(v_s - 44.2)^2/136.70\right].$$

This Gaussian is formed by the superposition of the several Lorentzians.

Twenty-seven samples were prepared and P_o and P_z signals were measured. P_o is obtained from eight measurements, four at the beginning and four at the end of the measuring process. P_z signals were taken for at least nine ESR powers which are proportional to the V_{eff}^2. An example for the evaluation of A_∞ is shown in Fig. 2 for the asphalt/benzene sample at three concentrations.

From the A_∞^{-1} values versus c^{-1} give the ultimate enhancement factor U_∞. Figure 4 shows the best fit lines for samples of asphalt with nitrobenzene, benzene, and quinoline.

The $2w_1'/c$ varies by a ratio of nearly 22:1 for the selected solvents.

The nuclear-electron coupling parameter ρ, as a function of the low-frequency relaxation component $2w_1'/c$ is shown in Fig. 5. We obtained the expression

$$\rho = 2.7 \times 10^{-3}(2w_1'/c)^{-0.512} \quad (2)$$

as the result of a power regression.

Gülsün's data (1981) for liquid asphalts MC-0 and MC-4 can be given as

$$\rho = 1.3 \times 10^{-3}\,(2w_1'/c)^{-0.637} \quad (3)$$

The nuclear-electron coupling parameter ρ, found in this work, decreases with the low-frequency relaxation component slower than the ρ values of the samples of MC-0 and MC-4.

The ρ values of the samples, nitrobenzene, pyridine, chlorobenzene, thiophene, and quinoline are smaller than that of the sample of other solvents. The smaller ρ values correspond to the bigger K parameters, that show more effective scalar interaction. This means that the closer contact occurs when the natural resins from portions of the asphaltene surface have been stripped. These five solvents probably dissolve the asphaltene with stronger stereopreference. Stereospecific transient complexation tendencies are expected, such as those provided by solvents which have highly polarizable and chemically active regions as on chlorine, nitrogen, and sulphur atoms.

The solvent molecules can attach to the colloidal asphaltene particles for an extremely short time, forming complexes and making scalar interaction with a correlation time τ_{sc}. Some solvent molecules, in the same sample, can diffuse freely in and out of the asphaltene micelles making dipolar interaction with a correlation time τ_d. The solvent molecules which are attached to the colloid obey the rotational model, and those not attached to the colloid obey the diffusion model. 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.

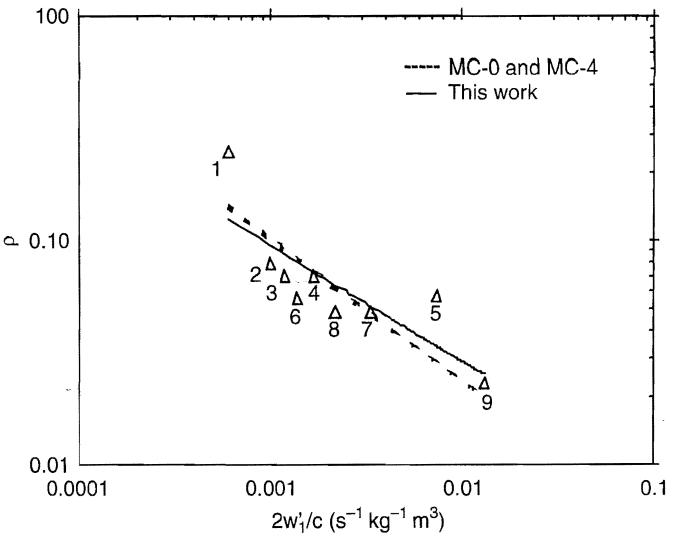


Fig. 5 The nuclear-electron coupling parameter versus the low frequency relaxation component (the numbers refer to Table 1)

The attachment of the solvent molecules can be to favored locations on the asphaltene surface, because of their diverse chemistry.

In complement to other techniques, DNP provides a unique probe of asphaltene colloids on a molecular scale.

References

Gutowsky HS, Ray BR, Rutledge RL, Unterberger RR (1958) Carbonaceous free radicals in crude petroleum. J Chem Phys 28: 744–745

Gülsün Z, Yalçıner A (1980) Dynamic nuclear polarization in colloidal asphaltene suspensions. Comm Fac Sci Univ Ankara 29 A2: 1–17

Gülsün Z (1981) Dynamic nuclear polarization in suspensions of asphalts MC-0 and MC-4. Comm Fac Sci Univ Ankara 30 A2: 19–30

Kramer KD, Müller-Warmuth W, Roth N (1965) Zur Molekülbewegung in Flüssgkeiten und Lösungen I Kern-Elektronen-Doppelresonanz: Viskosität und dielektrische Relaxation in Äther und Diäthoxyäthan. Z Naturforsch A 20: 1391–1400

Poindexter EH (1972) Dynamic nuclear polarization and molecular aggregation in asphaltene suspensions. J Colloid Interface Sci 38: 412–423

Yalçıner A, (1981a) Dynamic nuclear polarization in colloidal asphalt suspensions. J Colloid Interface Sci 79: 114–125

Yalçıner A (1981b) Dynamic nuclear polarization and EPR spectra in colloidal asphaltene suspensions. Comm Fac Sci Univ Ankara, 30, A2, 9–17

Yalçıner A, Güzelgöz MM, Çimenoğlu MA, Andiç A (1987) Dynamic nuclear polarization in colloidal Asphalt Suspensions. Z Phys Chem Neue Folge 153: 535–535

Yalçıner A, Güzelgöz MM, Çimenoğlu MA, Andiç A (1996) Dynamic nuclear polarization in suspensions of asphaltenes obtained from asphalt cements. Tr J Phys 20: 135–145

Yalçıner A, Çimenoğlu MA, Akay C, Ovalıoğlu H (1997) Intermolecular spin-spin interactions in suspensions of liquid asphalts in weak magnetic field, BPU-3, 3rd Gen Conf Balkan Phys Union, Cluj-Napoca, Romania

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References

1. Gutowsky HS, Ray BR, Rutledge RL, Unterberger RR (1958) Carbonaceous free radicals in crude petroleum. J Chem Phys 28: 744–745

2. Gülsün Z, Yalçıner A (1980) Dynamic nuclear polarization in colloidal asphaltene suspensions. Comm Fac Sci Univ Ankara 29 A2: 1–17

3. Gülsün Z (1981) Dynamic nuclear polarization in suspensions of asphalts MC-0 and MC-4. Comm Fac Sci Univ Ankara 30 A2: 19–30

4. Kramer KD, Müller-Warmuth W, Roth N (1965) Zur Molekülbewegung in Flüssgkeiten und Lösungen I Kern-Elektronen-Doppelresonanz: Viskosität und dielektrische Relaxation in Äther und Diäthoxyäthan. Z Naturforsch A 20: 1391–1400

5. Poindexter EH (1972) Dynamic nuclear polarization and molecular aggregation in asphaltene suspensions. J Colloid Interface Sci 38: 412–423

6. Yalçıner A, (1981a) Dynamic nuclear polarization in colloidal asphalt suspensions. J Colloid Interface Sci 79: 114–125

7. Yalçıner A (1981b) Dynamic nuclear polarization and EPR spectra in colloidal asphaltene suspensions. Comm Fac Sci Univ Ankara, 30, A2, 9–17

8. Yalçıner A, Güzelgöz MM, Çimenoglu MA, Andiç A (1987) Dynamic nuclear polarization in colloidal Asphalt Suspensions. Z Phys Chem Neue Folge 153: 535–535

9. Yalçıner A, Güzelgöz MM, Çimenoglu MA, Andiç A (1996) Dynamic nuclear polarization in suspensions of asphaltenes obtained from asphalt cements. Tr J Phys 20: 135–145

10. Yalçıner A, Çimenoğlu MA, Akay C, Ovalıoglu H (1997) Intermolecular spin-spin interactions in suspensions of liquid asphalts in weak magnetic field, BPU-3, 3rd Gen Conf Balkan Phys Union, Cluj-Napoca, Romania

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