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Multifrequency (9 and 95 GHz) EPR study of stable radicals in asphaltene fractions of oils and bitumen

M. Gafurov¹, G. Mamin^{1,*}, Yu. Ganeeva^{1,2}, T. Yusupova^{1,2}, M. Volodin^{1,3},
I. Gracheva¹ and S.Orlinskii¹

¹ Kazan Federal University, 18 Kremlevskaya Str., Kazan, Russia

² Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, 420088 Kazan, Russia

³ Sakhalin Energy Investment Company, Ltd., Dzerzhinskogo, 35, 693020 Yuzhno-Sakhalinsk, Russia

* E-mail: george.mamin@kpfu.ru

Abstract. Structural characterization of asphaltenes in complex systems such as native hydrocarbons is in the focus of scientific and industrial interests since many years. Various analytical tools and approaches are used for that. We present the results of our study of asphaltene fractions A1 and A2 with the predominantly “island” type and “archipelago” type asphaltene molecules by conventional and pulsed electron paramagnetic resonance (EPR) at X-band (9 GHz) and W-band (95 GHz) with aim to expand the abilities of EPR technique for asphaltene characterization. Shift to the higher frequencies allows to separate spectrally the contributions from paramagnetic complexes of different origin, define the EPR parameters more accurately comparing to the conventional X-band EPR. Application of pulsed techniques allows (at least partially) to separate the radicals in time domain. Features of the obtained spectra are described. Electronic relaxation times are found to be different for stable “free” radical for A1 and A2 fractions. We suggest that the obtained results can be used for investigation of various petroleum systems.

1. Introduction

Asphaltene is known as the *cholesterol of petroleum* because of its ability to precipitate, deposit, and as a result, interrupt the continuous production of oil from underground reservoirs. Despite decades of research, asphaltene composition and molecular structure as well as their impact on the mechanisms of asphaltene stabilization are not completely understood. Chemical analyses of asphaltenes indicate that they contain fused ring structures, naphthenic rings, and some aliphatic chains with hydrogen and carbon; small quantities of heteroatoms, such as nitrogen, sulfur, and oxygen; and trace metals, such as vanadium and nickel [1]-[11].

Today it seems to be (due to the application of advanced analytical techniques like time-resolved fluorescence depolarization (TRFD), high-field mass spectrometry (MS), atomic electron microscopy (AEM)) that the consensus is that asphaltenes are monomeric and their molecular weights are in the range of between about 250 and 1200 g/mol is achieved [12], [13] though also not completely [14]. Disagreement remains on the molecular structure. There are two schools of thought as to the nature of aromatic core organization within asphaltene compounds. The classic island architecture, also referred as “like your hand” model, depicts asphaltenes consisting of one aromatic core with peripheral alkyl



side chains. On the contrary, the archipelago model suggests that asphaltenes contain more than one aromatic core linked by alkyl bridges. The relative abundances of single- and multicore compounds in asphaltenes are still being debated despite decades of investigation [1]-[13]. There are still challenges of how to determine the accurate molecular structure, constituent and structure-behaviour relationships of asphaltene.

Commercial availability of the pulsed high field electron paramagnetic resonance (EPR) spectrometers open new ways for the analysis of petroleum dispersed systems (PDS), investigation of the asphaltenes' structure, processes of their treatment, etc. using intrinsic paramagnetic centers as sensitive probes [15]-[17]. Paramagnetic properties and EPR spectra in PDS (such as oil rocks, crude oil, bitumen, kerogens, their fractions, etc) are mainly defined by the presence of complexes of d-metals (first of all V) and stable "free" radicals (FR). FR are mainly concentrated in asphaltenes and arise due to the delocalized π -electrons of the aromatic rings and stable organic radicals of the side chains. It can be suggested that relaxation and spectroscopic parameters of FR derived at various microwave (MW) frequencies can give additional information about the asphaltene structure but such type of investigation is rare [16], [18], [19] and does not cover even a part of all possible cases due to the complexity of PDS and the limited amount of PDS species studied so far. The aim of this paper is to expand on these objectives the abilities of the pulsed EPR at the W-band range ($\nu_{MW} \approx 95$ GHz) for asphaltene structure characterization.

2. Materials and Methods

W-band EPR spectra at $T = 300$ K were registered with Bruker ElexSys 680 EPR spectrometer by using standard electron-spin-echo (ESE) $\pi/2 - \tau - \pi$ with the $\pi/2$ pulse duration of 32 ns, time delay $\tau = 240$ ns pulse sequence. Transverse relaxation T_{2e} was studied by tracking the primary ESE amplitude with the same $\pi/2 - \pi$ pulse durations while varying τ . Longitudinal relaxation time constant T_{1e} was extracted from an inversion-recovery studies by applying the $\pi - T_{delay} - \pi/2 - \tau - \pi$ pulse sequence, where π pulse duration and τ were fixed (64 ns and 240 ns, correspondingly) while T_{delay} was varied. The value of the external magnetic field, B_0 , during the relaxation times measurements was fixed at the particular point defined from the EPR spectra. Conventional X-band measurements ($\nu_{MW} \approx 9$ GHz) are carried out on Bruker ESP-300. Spectra simulation are done in Easyspin package for MatLab [20].

The list of the studied samples is given in Table 1. Asphaltenes ($A_{init.}$) were precipitated from the raw material by the addition of $40 \text{ ml}\cdot\text{g}^{-1}$ of the petroleum ether (b.p. $40 - 70^\circ\text{C}$). Precipitated asphaltenes were washed in a Soxhlet apparatus with petroleum ether until the filtrate became colorless. Then the asphaltenes with filter were washed out with the benzene, which was then evaporated.

Table 1. List of the studied samples.

Sample	Raw Material	Source	Fractions of asphaltenes
No. 1	Oxidized bitumen	Oil refinery of Republic of Tatarstan, Russia	$A_{init.}$, A1, A2
No. 2	Crude oil taken from the Carboniferous deposits	Akan oilfield (well 2023) of Republic of Tatarstan, Russia	
No. 3	Crude oil taken from the Carboniferous deposits	Akan oilfield (well 2262) of Republic of Tatarstan, Russia	

The A1 and A2 fractions of asphaltenes were obtained as follows. One gram of A_{init} asphaltenes was first completely dissolved with 28 ml toluene. Petroleum ether (b.p. $40 - 70^\circ\text{C}$) was then added in the amount of 52 ml. The resulting solution was kept in a dark place for 24 hours and then filtered. Precipitated material was washed in a Soxhlet apparatus with toluene until the solvent became colorless, dried and weighed until there was no change in mass. Obtained fraction was called A1.

Then the petroleum ether was added to the supernatant in the amount of 228 ml and precipitated for 24 hours. Using the operations described above, the fresh precipitated material was separated, washed with toluene in a Soxhlet apparatus and dried. A2 fraction of asphaltenes was recovered by evaporating the remaining solvent.

Literature data suggest that A1 fraction possess predominantly “island” type asphaltene molecules while A2 fraction consists mainly from the “archipelago” asphaltene molecules [21].

3. Results and Discussion.

EPR spectra detected at X-band (Figure 1) and W-band (Figure 2) for the all investigated samples are very similar to each other and are defined by the presence of stable “free” radicals (FR, single line, electron spin $S = 1/2$, $g \approx 2.003$) and paramagnetic vanadyl complexes (vanadylporhyrin, VP). Due to the nearly planar skeleton structure of single VP molecule (VO^{2+} , $S = 1/2$), the VP EPR spectra could be satisfactory described by the g -tensor of axial symmetry with $g_{\parallel} \approx 1.96$, $g_{\perp} \approx 1.98$ and anisotropic hyperfine interaction with a magnetic moment $I = 7/2$ (therefore, 8 projections of I with the quantum numbers $m_I = \pm 7/2; \pm 5/2; \pm 3/2$ and $\pm 1/2$ are possible) for ^{51}V nuclei with hyperfine structure constants $A_{\parallel} \approx 480$ MHz, $A_{\perp} \approx 157$ MHz. Detailed description and investigation of VP EPR and ENDOR spectra are given in papers [15], [22]. In the present EPR for FR are investigated in more details.

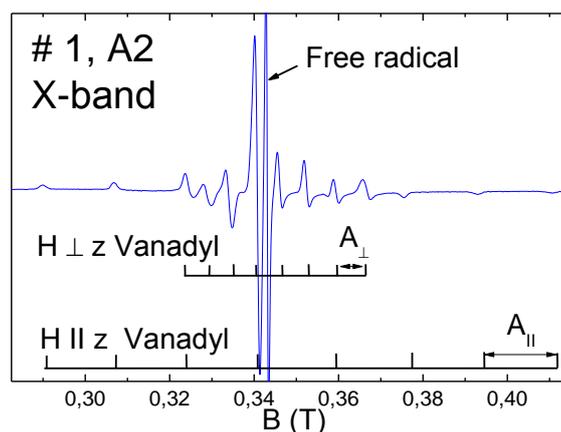


Figure 1. Conventional X-band EPR spectrum at $T = 300$ K of A2 fraction of sample #1 defined by the presence of vanadyl complexes and FR.

X-band concentration measurements allow for the estimation of the FR concentration in the range of $(3-9) \times 10^{18}$ spins per gram, while for VP, this value is in the range of $(2-5) \times 10^{18}$ spins per gram. Assuming that the molecular weight of asphaltenes is of 1000 amu, it implies one paramagnetic centre per roughly 100 asphaltene molecules.

In the case of asphaltenes deposition on various supports, we have found that the relative concentration ratio FR/VP is growing compared to the initial asphaltene [5], [6]. The results for the relative concentrations for the investigated samples are presented in Table 2. It follows that the (relative) amount of VP in A2 fraction can be significantly higher than in A1 (samples 1 and 2) or at least not less (sample 3). It gives a sign that organization of the asphaltenes molecular aggregates in thin films (i.e. deposited on surface) can differ from this in the bulk.

A usual way to fit the EPR lineshape of FR at X-band is a convolution (or sum) of Gauss and Lorentz with an isotropic g -factor and $\Gamma_G \approx \Gamma_L$ (the linewidth (Γ) for Gaussian (G) and Lorentzian (L) absorption lineshapes are connected with the full width at half maximum (FWHM) via $\Gamma_G = (2\ln 2)^{1/2} \cdot \text{FWHM}$ and $\Gamma_L = (3)^{1/2} \cdot \text{FWHM}$). In ref. [19] it was shown that in contrast to X-band, in the conventional W-band EPR the lines from FR are not symmetric and their spectral EPR linewidths became larger. Our experiments on the investigated samples in pulsed mode confirm that conclusion

(Figure 2). But from other side, as we found recently [23], for some specific oils the linewidths in X- and W-bands can be the same.

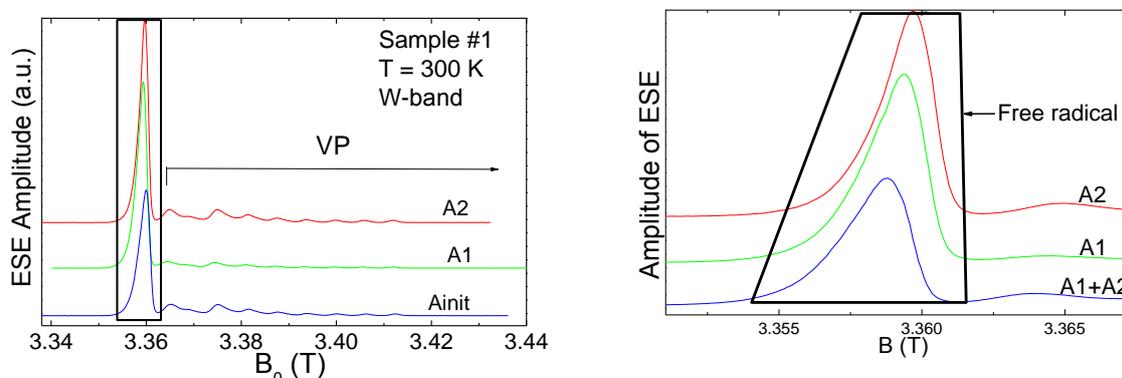


Figure 2. ESE detected EPR spectra for sample #1 in the W-band. Left panel – whole range; right panel – FR region.

Table 2. Relative concentrations [FR]/[VP] from X-band EPR measurements.

Sample	A_{init}	A1	A2
# 1	1.9(1)	3.6(2)	1.35(5)
# 2	1.15(9)	1.0(1)	0.50(5)
# 3	0.7(1)	0.7(1)	0.67(7)

There is still a problem of assigning the W-band spectrum either to one type of FR with the anisotropic EPR parameters or to a sum of contributions from several FR types. Probably, both scenario are fulfilled in complex petroleum systems. Time-domain separation can help to unravel the origin of EPR spectrum.

No significant difference in T_{1e} and T_{2e} measurements were obtained along the FR EPR spectrum. The data derived at B_0 corresponding to the maximum of the ESE signal are listed in Table 3.

Table 3. Relaxation parameters for FR derived from the W-band experiments.

Sample	A_{init}	$T_{1e}, \mu s$	T_{2e}, ns
# 1	A_{init}	102(4)	247(8)
	A1	16(1)	284(8)
	A2	27(1)	365(10)
# 2	A_{init}	28.5(7)	150(7)
	A1	17(1)	131(6)
	A2	31(1)	191(8)
# 3	A_{init}	71(3)	136(7)
	A1	54(2)	126(5)
	A2	87(4)	142(6)

As it was already noted in [15], for FR (in contrast to the vanadyl complexes) T_{1e} varies significantly from sample to sample and from fraction to fraction. For all studied samples fraction A2 is characterized by the longer T_{1e} than fraction A1. Taking into account that the molecules forming the asphaltenes in both fractions are of comparable size, the difference in the relaxation rates reflects the fact that the FR surrounding is different for fractions A1 and A2. Therefore, the corresponding

ifference in the longitudinal relaxation times can be exploited for the selective investigation of the suggested asphaltene structures. Additional experimental and theoretical efforts are in need to understand the main mechanisms defining the longitudinal relaxation in asphaltenes.

The same trend is obtained for T_{2e} curves (Table 3). In ref. [15] an influence of VP on FR relaxation was investigated. Additionally, it can be supposed that the relative abundance of two asphaltenes type with the slightly different T_{2e} values can also be revealed. Indeed, as Figure 3 demonstrates, with the increase of the time delay (τ), the low-field shoulder of the EPR spectrum disappears (in A1 and A2 fractions), FR line becomes to be more symmetrical. Therefore, we suggest that “archipelago” type of asphaltenes is characterized by the longer relaxation times T_{1e} (see Table 3) and T_{2e} (of 700-800 ns for sample #1; schematically, P_1 in Figure 3) while “island” asphaltens contain FR with the slightly higher g-factor(s) and shorter relaxation times (T_{2e} of 250 ns for sample #1; schematically, P_1 in Figure 3).

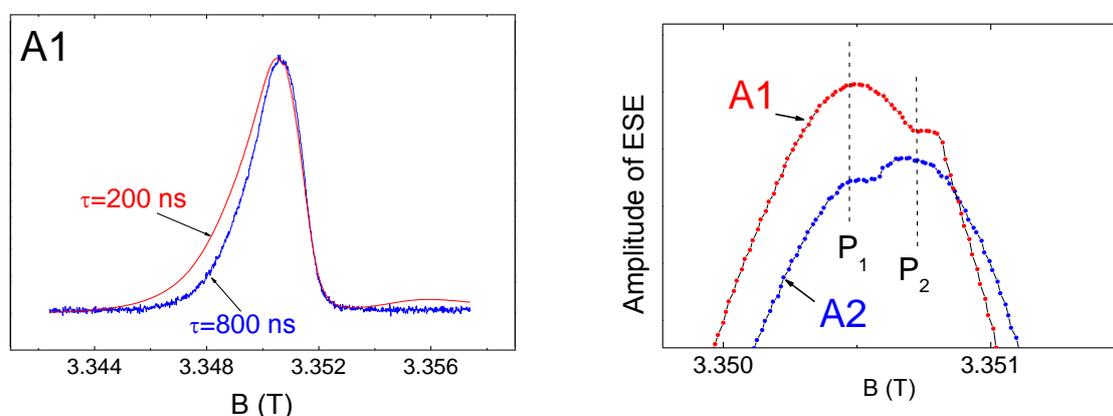


Figure 3. ESE detected EPR spectra for sample #1 in the W-band for $\tau = 200$ and 800 ns. Left panel – FR range; right panel – in the vicinity of FR ESE maximum.

4. Conclusion

In this work we show that EPR spectra of asphaltenes and relaxation characteristics of stable carbonaceous “free” radicals are sensitive to the presence of different structural asphaltenes motifs. It demonstrates further potential capabilities of EPR techniques for characterization of asphaltenes and petroleum systems with aim to elucidate asphaltenes structure.

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