

High-frequency EPR study of the nanoaggregated oil asphaltenes[†]

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A series of twelve asphaltene samples extracted from the heavy oils and the oxidized bitumen has been studied with the high-frequency W-band (94 GHz) continuous wave and pulsed electron paramagnetic resonance (EPR) spectroscopy. Transverse and longitudinal relaxation of the free radical and the vanadyl-porphyrin was studied for each sample. Significant contribution of the spectral diffusion to the transverse magnetization decay ascribed to the free radical and the vanadyl-ion spin-dipole interaction is revealed. This indicates that the distance between the free radical and the vanadyl complex is of few nanometers, which in turn means that the vanadyl-porphyrins participate actively in building of the asphaltene aggregates via the intermolecular interactions. Thus, the capabilities of the high-frequency and pulse EPR spectroscopy to derive a new and unique information on asphaltenes which had not been obtained before from the traditional X-band (10 GHz) EPR studies of these complex systems are demonstrated.

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1. Introduction

Heavy oils and natural bitumen comprise a significant amount of asphaltenes - the high-molecular compounds with a strong tendency towards aggregation. Presence of asphaltenes complicates the processes of the oil recovery, transportation and refining [1]. Asphaltenes are apparently the most complex fraction of oil. The basic criterion for assignment of the substances to the family called "asphaltenes" is their similarity in solubility in definite solvents, namely, insolubility in *n*-alkanes and solubility in the toluene. Elemental composition of asphaltenes includes mostly the carbon (80 – 86%), hydrogen (6 – 8%), oxygen (0.5 – 2%), nitrogen (0.5 – 2%), sulfur (2 – 9%) and metals (Ni and V) [2]. Nickel and vanadium are present mainly in the porphyrin complexes [3, 4].

Asphaltenes are the main structurizing agents in the oil disperse systems. for a long time due to the insufficient knowledge of the mechanisms and conditions of asphaltene self-association it was impossible to find out whether the measured quantities characterize asphaltene monomers or their complex molecular aggregates. Currently, the two basic models of the asphaltene molecules are generally accepted which are the "continent" and "archipelago"-type structures. Continent-type molecules include a large aromatic nuclei with with poor alkyl steric hindrance, possess a rigid structure, tend towards the aggregation with stacking structure formation due to the $\pi - \pi$ bonding and have up to 6% of crystal-like phase [5,6]. Archipelago-type molecules possess relatively small aromatic nuclei with more alkanes. Aggregates of the latter are of a small size,

[†]This is footnote of the title

totally amorphous and well dissolved in aromatic solvents [1,7]. Whether the vanadyl-porphyrin complex is a constituent of the asphaltene molecules or the composite aggregates are formed due to the intermolecular interaction is still an open question.

The complicated nature of asphaltens is intensely studied by a variety of methods and techniques [8]. Since 1950s the electron paramagnetic/spin resonance (EPR / ESR) spectroscopy is among them [3, 4, 9–11] though its application is mainly restricted to the conventional X-band (~ 10 GHz) EPR in the continuous wave (*cw*) mode. EPR-spectroscopy allows to obtain the information on either the stable free radical (FR) localized within the polyaromatic condensed nuclei of the asphaltene molecules, or the vanadyl-porphirine complexes [3]. Therefore a systematic investigation of the asphaltene sample series including the initial asphaltenes and the concentrates of its different molecular types should provide with the new data on the asphaltene and vanadyl-porphirine molecule states in oils and bitumen.

Commercial availability and relative affordability of the high-frequency (frequencies higher than 35 GHz) EPR spectrometers with the possibility to exploit different pulsed techniques open the new horizons in scientific research and routine EPR application due to the advantages such as the increased spectral and temporal resolution, enhanced sensitivity. The main scope of this paper is to demonstrate the capabilities of the modern high-frequency (W-band, 94 GHz) EPR spectroscopy for investigations of asphaltenes.

2. Materials and methods

The list of the investigated samples is presented in Table 1. Asphaltene samples have been extracted from the Carbon oils and oxidized bitumen utilizing a standard approach [12]. Using the fractional precipitation of asphaltenes from the toluene solution [13] the initial extracted asphaltenes A_{init} were separated into two fractions: fraction A1 - the one that precipitates from the solution on adding of 65% of the precipitant (petroleum-ether), and A2 - the fraction precipitating on adding of the maximal (90 %) amount of the precipitant.

The powders of the A_{init} , A1 and A2 fractions with the typical particle size of about 10 μm were studied at room temperature both in the continuous wave (*cw*) and pulsed modes of the commercial Bruker Elexsys-680 spectrometer. The measurements were performed in the microwave W-band (94 GHz). In the *cw* mode the spectra were obtained utilizing a standard approach with a double modulation of an applied magnetic field B_0 [14,15]. EPR spectra in the pulsed mode were detected via primary electron spin-echo (ESE) amplitude after the two-pulse $\pi/2 - \tau - \pi$ echo sequence while scanning a magnetic field B_0 (field-swept ESE); pulse durations and a time delay between the first and the second pulses were fixed to $\pi/2 = 30$ ns and $\tau = 240$ ns [16, 17].

Transverse relaxation was studied tracking the primary ESE amplitude while varying τ . Longitudinal relaxation time constants were extracted from an inversion-recovery studies [16,17].

Simulations of the EPR spectra were performed with the Easyspin subroutine module [18].

Table 1. Studied samples.

Sample no.	Raw material	Source	Fractions
1	Technical bitumen	Oil refinery of Tatarstan Republic	A_{init} , A1, A2
2	Technical bitumen	Oil refinery of Tatarstan Republic	
3	Oil from the Carbon deposits	Akan oilfield (well 2023)	
4	Oil from the Carbon deposits	Akan oilfield (well 2262)	

3. Results

In Fig. 1a the *cw* EPR spectrum of the A_{init} fraction of sample 1 is presented which is a typical one for the whole series of samples studied. As in the case of the X-band measurements, the W-band EPR spectra of the oil asphaltenes originate mainly from the vanadyl complex VO^{2+} ($^{51}V^{4+}$, $3d^1$, $S = 1/2$, $I = 7/2$) and from the carbon free radicals (FR) [3, 4]. Atoms in the vanadyl-porphyrins are arranged practically in a plane defining thus the *g*-factor and hyperfine *A* tensor axial symmetry [3, 4, 19]. The powder EPR spectrum of the vanadyl-ions consists of the 16 "lines" representing the 2×8 hyperfine patterns for the parallel and the perpendicular complex orientations.

An important consequence of the microwave frequency increase revealed in the observed *cw*-spectra in comparison to those measured in the X-band is an almost total spectral resolution between the signals of the vanadyl-ions and the FRs: even a small difference in the *g*-factor values is enough to avoid the overlap of the two main contributors to the spectra. This, in turn, allows to perform the accurate studies of the spectroscopic and relaxation properties of these centers separately.

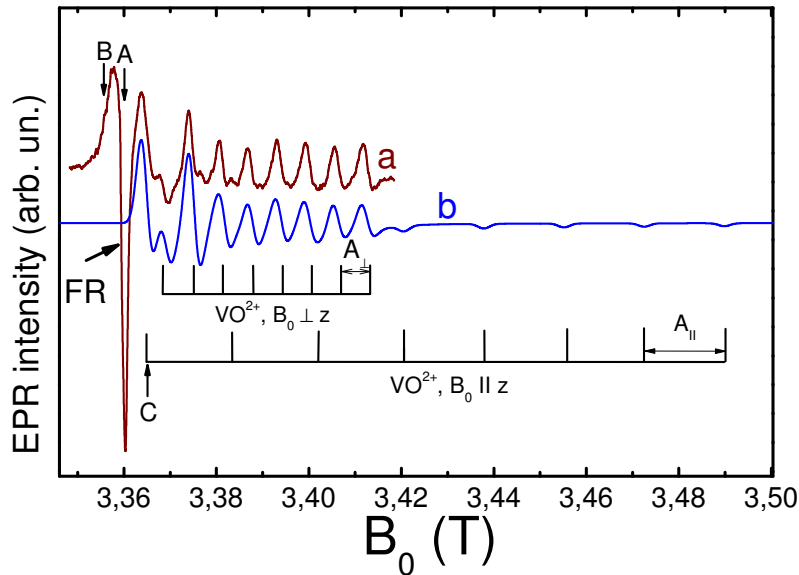


Figure 1. The *cw*-EPR spectrum of sample 1, fraction A_{init} (a) and the simulated powder spectrum of the vanadyl-ion (b).

The simulation of the powder *cw*-EPR spectrum of the vanadyl ion (Fig. 1b) was performed assuming that the respective *g* and *A* components are collinear and their values coincide with those obtained from the X-band studies ($g_{\parallel} = 1.964 \pm 0.003$, $g_{\perp} = 1.984 \pm 0.003$, $A_{\parallel} = 17 \pm 2$ mT, $A_{\perp} = 6.0 \pm 1.4$ mT) [3, 4]. Comparison of the measured spectrum to the simulated one indicates clearly that the whole EPR spectrum pattern in Fig. 1a (except of the low-field line of the FR) is described well by the hyperfine structure of the vanadyl-ion. Intensity ratio between the parallel and perpendicular spectrum "components" is typical for a powder spectrum of the axial center.

A typical ESE-detected EPR spectrum of the asphaltenes is shown in Fig. 2. In the spectra of all of the studied samples the signals of the vanadyl-ions and the FRs are observed. The detailed examination of the FR line has revealed its inhomogeneous broadening due to an averaging of the asphaltene molecules with different orientations with respect to the applied magnetic field

($g_{\parallel} = 2.0028 \pm 0.0003$, $g_{\perp} = 2.0040 \pm 0.0003$). Also, in the spectra of all the studied samples the line splitting has been detected indicating the presence of at least two types of the FRs with slightly different g -factor values (inset of Fig. 2).

Relaxation of the FRs was studied in the two spectral ranges marked with A and B in Figs. 1, 2. Relaxation measurements of the vanadyl-ions were performed on the low-field hyperfine component corresponding to the parallel orientation of the centers (marked with C in Figs. 1, 2).

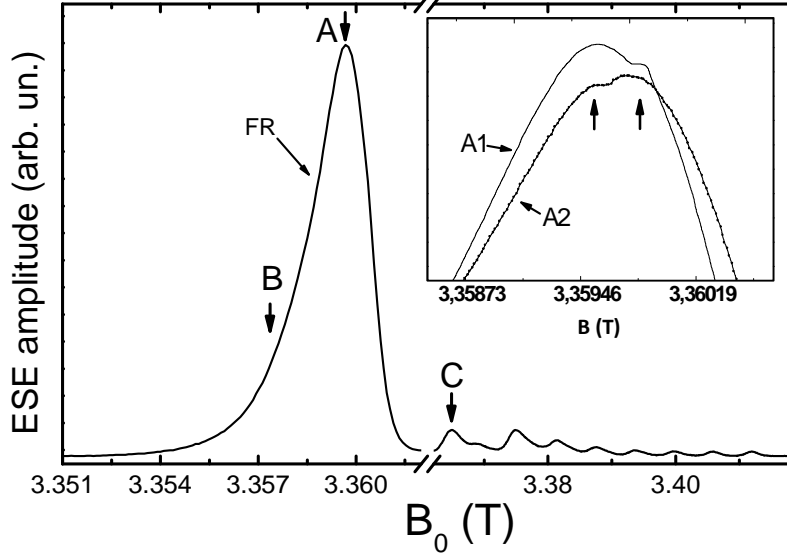


Figure 2. ESE-detected EPR spectrum of sample 1, fraction A_{init} . In the inset the spectra of fractions A1 and A2 of sample 1 in the range of the FR line maximum are shown.

We start with the relaxation properties of the FRs in asphaltenes. Measurements in the spectra ranges corresponding to the parallel and perpendicular molecule orientations (ranges A and B in Figs. 1, 2, respectively) revealed the difference in the transverse magnetization decay which will be addressed later. Transverse relaxation character deviates significantly from the simple one-exponential decay (Fig. 3). In our opinion, this difference originates from the spectral diffusion which has been considered in detail in [16,20]. Therefore the following expression has been used for a dependence of the primary ESE amplitude on the delay between the pulses in the Hahn sequence [16,20]:

$$I_{echo}(\tau) = M_{FR} \cdot \exp\left(-\frac{2\tau}{T_{2,FR}}\right) \cdot \exp(-m\tau^2), \quad (1)$$

where $T_{2,FR}$ is the transverse relaxation time of the FR, M_{FR} is a factor proportional to the concentration of the FR, m is a parameter accounting for the spectral diffusion. Expression (1) allows to describe nicely the observed relaxation curves: an example of the fit is shown in Fig. 3 with a solid line. Parameter values for the three fractions of sample 4 are presented in Table 2.

The longitudinal magnetization recovery was studied as well. No difference in the processes of the longitudinal relaxation was found for spectral ranges A and B (Fig. 1, 2) of the FR line. The relaxation constants defined under an assumption of its mono-exponential character for all the studied samples are given in Fig. 4.

Now let's switch to the relaxation properties of the vanadyl complexes in asphaltenes. In all the samples a single-exponential decay of the transverse magnetization is observed with

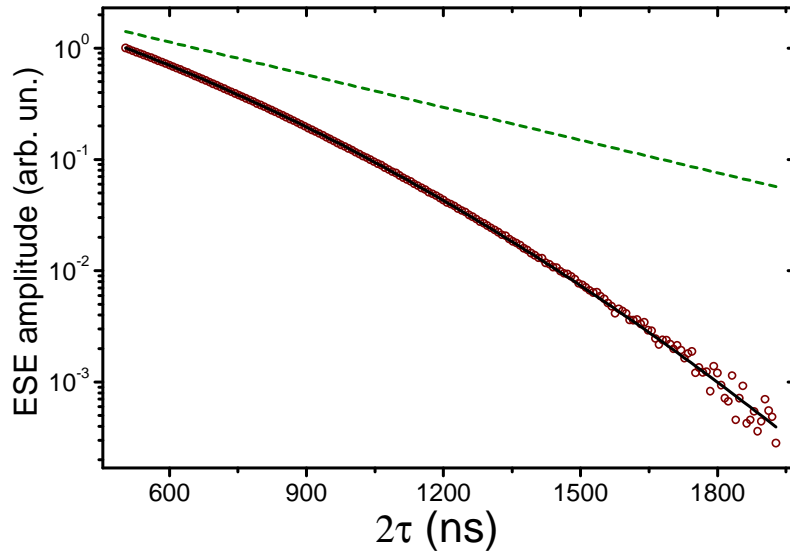


Figure 3. Dependence of the primary ESE amplitude on the delay between the two microwave pulses in the Hahn sequence of the sample 1 (fraction A_{init}). Dots indicate the experimental data, solid line is a result of the fit; exponential decay in the absence of the spectral diffusion is shown with the dashed line.

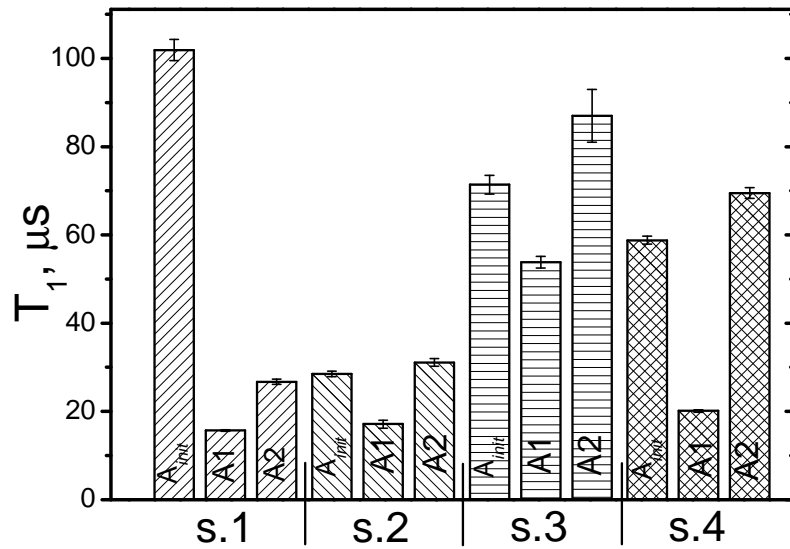


Figure 4. Longitudinal relaxation constants for the studied asphaltene samples.

the time constants within the range of 100 – 200 ns (Fig. 5). Closeness of all the measured longitudinal relaxation constants ($1.1 - 1.5 \mu\text{s}$) indicates that the vanadyl complexes possess a similar structure in the studied samples, i.e. the chemical treatment of the raw material didn't modify significantly the local surrounding of the vanadyls and their structure.

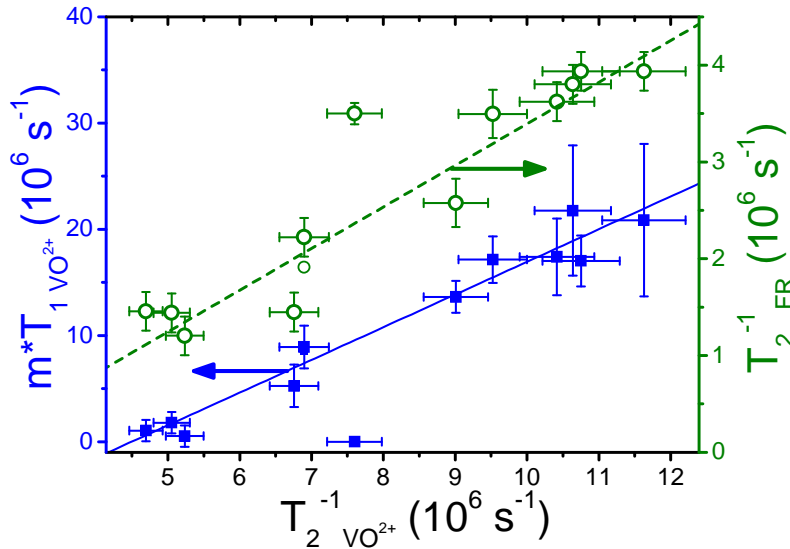


Figure 5. Results of the relaxation analysis of the whole asphaltene sample series: dependencies of the product of the vanadyl longitudinal relaxation constant to the spectral diffusion coefficient (■) and of the FR transverse relaxation rate (○) on the vanadyl transverse relaxation rate. The lines are the linear fits of the observed dependencies with the parameters presented in Eqs. (2) and (4).

4. Discussion

Let's now discuss in more detail the collected W-band pulsed-EPR data. Spectral diffusion observed in the FR transverse magnetization decay can be induced by the presence in its nearest surrounding of the vanadyl-porphyrine molecules. Vanadyl spin flips due to the electron-lattice relaxation causes the local magnetic field fluctuations at the free radical. As a consequence, the FR resonance frequencies vary in a random manner. This results in an acceleration of the transverse relaxation. During the observation of the FR transverse relaxation ($\sim 1 \mu\text{s}$) the vanadyl spins can change their orientations not more than once ($T_1 \approx 1 \mu\text{s}$) which results in a slow spectral diffusion [16] described by Eq. 1. According to [16], the spectral diffusion coefficient m is proportional to $\Delta\omega/T_{1,VO^{2+}}$, where $T_{1,VO^{2+}}$ is the longitudinal relaxation time of the vanadyl, and $\Delta\omega$ - the shift of the FR resonance frequency due to the dipole-dipole

Table 2. Parameter values obtained from the fits of the transverse relaxation decays to Eq. 1 for the fractions of sample 4, for parallel and perpendicular orientations of the asphaltene molecules with respect to the magnetic field.

Fraction	Orientation	m, ns^{-2}	$T_{2,FR}, \text{ns}$
A_{init}	parallel	$(2.8 \pm 0.1) \cdot 10^{-6}$	286 ± 3
	perpendicular	$(2.91 \pm 0.03) \cdot 10^{-6}$	
A1	parallel	$(3.2 \pm 0.1) \cdot 10^{-6}$	254 ± 6
	perpendicular	$(3.6 \pm 0.1) \cdot 10^{-6}$	
A2	parallel	$(2.44 \pm 0.02) \cdot 10^{-6}$	388 ± 4
	perpendicular	$(2.9 \pm 0.1) \cdot 10^{-6}$	

interaction with the vanadyl electron spins. The value of $\Delta\omega$ is proportional to the vanadyl-porphyrine concentration [16] and, thus, to the vanadyl transverse relaxation rate $T_{2,VO^{2+}}^{-1}$.

In Fig. 5 the experimental results for all the studied asphaltene samples are summarized. The value of m is taken for the A spectral range of the FR signal (Fig. 2) corresponding to the perpendicular orientation of the FR. As one can see from Fig. 5, the dependence of the product of vanadyl longitudinal relaxation time $T_{1,VO^{2+}}$ to the m coefficient on the vanadyl transverse relaxation rate $T_{2,VO^{2+}}^{-1}$ can rather well be fit with a line

$$m \cdot T_{1,VO^{2+}} = -(0.014 \pm 0.002) + (3.0 \pm 0.2) \cdot T_{2,VO^{2+}}^{-1}. \quad (2)$$

Such an agreement with theory [16] for all the studied samples indicates that the spectral diffusion of the FR is caused by the vanadyl-porphyrines.

The difference in the spectral diffusion coefficients m (Table 2) for the parallel and perpendicular orientations of the FR (ranges A and B in Fig. 1, 2) is due to the anisotropy of the dipole-dipole interaction. For the FR parallel orientation the amplitude of the magnetic field induced by the vanadyl spin at the FR is larger than for the perpendicular orientation, and this leads to the greater value of the spectral diffusion coefficient for the FR parallel orientation.

In all of the studied sample the influence of the FR on the vanadyl relaxation is also observed. In [16] it has been shown that the organic radicals, being the source of the spin causing the spectral diffusion, lead to the exponential decay of the primary ESE amplitude (I_{echo}):

$$I_{echo}(\tau) = M_{VO^{2+}} \cdot \exp\left(-\frac{2\tau}{T_{2,VO^{2+}}}\right) \cdot \exp(-b\tau), \quad (3)$$

where $T_{2,VO^{2+}}$ - the vanadyl transverse relaxation time, $M_{VO^{2+}}$ - the coefficient proportional to the vanadyl concentration, b - the constant, accounting for the spectral diffusion in vanadyls. Clearly, there are two additive terms defining the measured relaxation rate $T_{2,VO^{2+}}^{-1}$: the dipole-dipole interaction between the vanadyl ions, and the spectral diffusion induced by the FR spins. Constant b is proportional to the FR concentration [16] and, thus, to the FR transverse relaxation rate $T_{2,FR}^{-1}$. Experimental $T_{2,FR}^{-1}$ rate values can be fit within the experimental uncertainty with the linear dependence

$$T_{2,FR}^{-1} = -(9 \pm 4) + (0.43 \pm 0.04) \cdot T_{2,VO^{2+}}^{-1}. \quad (4)$$

This fact confirms the influence of the FR on the transverse relaxation of the vanadyl.

Spectral diffusion is observed in all the studied sample regardless of the asphaltene genesis and relative concentration of the paramagnetic centers, therefore, the vanadyl complexes in asphaltene are bonded with the FRs, *i. e.*, form the joint complex due to the intermolecular interactions and are located within the few nanometers from each other.

Comparing the longitudinal relaxation times of the FR (Fig. 4) it can be seen that for all the samples fraction A2 is characterized by the longer T_1 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 paramagnetic center surrounding in fractions A1 and A2 is different.

It is worth noting that extraction of the high-molecular (A1) and low-molecular (A2) asphaltene concentrates didn't allow to detect any significant modification in the spectroscopic and relaxation properties of either the free radicals or the vanadyl complexes. Experimental knowledge of the structural peculiarities of fractions A1 and A2 can be developed further by means of the electron-nuclear double resonance (ENDOR) spectroscopy.

5. Summary

Evidently, the transition from the traditional X-band to the high-frequency W-band EPR allows to resolve spectrally the components of the asphaltene EPR spectra originating from the free radicals and the vanadyl-ions. It gives an opportunity to gain a deeper insight to the origin of the paramagnetic centers important both for the fundamental research and industrial applications. Even besides the possibility to exploit the more elaborated EPR techniques, simply the lineshape of the FR-radical and intensity ratio between the FR and vanadyl signals, which served as the fingerprint of the hydrocarbon origin, can be determined much more accurately. Dynamical changes (dependence on pressure, temperature, treatment procedures and conditions, ageing, etc.) can be traced easily.

Relaxation characteristics can be used for these purposes as well: the relaxation times are not too short as it could be expected for the high-frequency EPR and appear in quite a comfortable range to measure them even at room temperature. The last gives an opportunity to apply different pulsed methods for the structure elucidation of the asphaltene containing materials.

Regarding the exact details presented in the paper, the interaction between the free radicals and the vanadyl-ion momenta has been revealed in all the studied samples via the spectral diffusion process in the transverse magnetization decay. It shows that the typical distance between the free radical and the vanadyl complex is of few nanometers and, thus, the vanadyl-porphyrins participate actively in building of the asphaltene particles by means of the intermolecular interactions. Application of the pulsed double resonance techniques such as an electron-nuclear (ENDOR) and electron-electron (ELDOR) is planned to study the differences in the continental and archipelago asphaltene molecular structures.

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