W-band EPR of vanadyl complexes aggregates on the surface of Al₂O₃

G. Mamin*, M. Gafurov, A. Galukhin, I. Gracheva, F. Murzakhanov, A. Rodionov, and S. Orlinskii
Kazan Federal University, 18 Kremlevskaya Str., Kazan, Russia
E-mail: george.mamin@kpfu.ru

Abstract. Structural characterization of metallocorphyrins, asphaltenes and their aggregates in complex systems such as native hydrocarbons is in the focus of scientific and industrial interests since many years. We present W-band (95 GHz) electron paramagnetic resonance (EPR) study in the magnetic field of about 3.4 T and temperature of 100 K for Karmalinskoe oil, asphaltenes and asphaltenes deposited on the surface of Al₂O₃. Features of the obtained spectra are described. Shift to the higher frequencies allows to separate spectrally the contributions from paramagnetic complexes of different origin and define the EPR parameters more accurately comparing to the conventional X-band (9 GHz). Changes of the EPR parameters are tracked. We suggest that the proposed approach can be used for the investigation of structure of vanadyl complexes aggregates in crude oil and their fractions.

1. Introduction
Paramagnetic properties and electron paramagnetic resonance (EPR) spectra in complex hydrocarbon systems (like oil rocks, crude oil, bitumen, their fractions, etc. which we will denote in the text as PDS – petroleum disperse system) are mainly defined by the presence of complexes of d-metals (first of all V, Ni, Fe) and stable “free” radicals (FR). It is usually assumed that FR are mainly concentrated in the heaviest PDS fraction - asphaltenes and arise due to the delocalized π-electrons of the aromatic rings and stable organic radicals of the side chains. One has to note that the exact location and structure of FR in PDS are still undefined and the researchers are conventionally referred to the paramagnetic centers detected in coals [1, 2]. Therefore, it would not be considered in details in this work.

Another important type of paramagnetic centers in PDS which is detected in asphaltenes and resins fractions are vanadyl based porphyrins. Metalloporphyrins in heavy oils were first discovered in 1930s by Treibs [3, 4], who postulated the biological origin of these compounds. Vanadyl (VO²⁺) porphyrin is one of the most abundant forms of metalloporphyrin, and is of particular significance as a biomarker in the context of oil formation research [5]. PDS porphyrins exist in homologous manifolds of several structural classes and manifest great structural diversity [6, 7]. The molecule can contain different types of substitutions, including alkyl, cycloalkane, and aromatic groups and possesses near planar anisotropic structure [8-10].

The possibility of using the paramagnetic VO²⁺ complexes as a probe for studying complex disordered systems such as PDS is determined by their resolved anisotropic structure in the electron paramagnetic resonance (EPR) spectra [9-11] which can be also further spectrally separated from FR EPR by shifting to high frequencies/ high magnetic fields [12, 13]. Nevertheless, there were no many papers on this issue in the near past [14, 15]. Commercial availability of the pulsed high field EPR spectrometers open new ways for the PDS analysis, investigation of the asphaltenes’ structure,
processes of their treatment, etc. using intrinsic paramagnetic centers as sensitive probes [9, 10, 12, 16-18].

One of the advantages of EPR is that species can be investigated without any additional treatment, in native environment. In paper [10] we have demonstrated that W-band EPR and ENDOR of VO$_{2+}$ containing complexes are very similar for two very different crude oils. From other side, in paper [11] we have shown that the temperature dependencies of X-band (9 GHz) VO$_{2+}$ EPR spectra at T > 400 K are different for the same oil samples. It can serve as a sign that VO$_{2+}$ complexes are the part of stable asphaltene structure/structures which are universal at least for some types of PDS and VO$_{2+}$ is a sensitive native paramagnetic centre to probe the PDS structure.

In the past [19, 20] the deposition of monolayers or double layers of model (“pure”) VO$_{2+}$ complexes like V$_2$O$_5$, for example, was widely used to investigate and influence the active sites of different catalytic supports, including alumina (Al$_2$O$_3$) one. In this research we use the inverse approach - an attempt to unravel some features of the VO$_{2+}$ complexes aggregates in PDS by using asphaltenes deposition on the surface of Al$_2$O$_3$. Our own experience of characterization of Al$_2$O$_3$ bulk and surfaces with EPR/ENDOR along with the corresponding literature reviews are gathered in ref. [21-23].

The effect of surrounding matrices, temperature, catalytic treatments, etc. on model VO complexes and those in maltenes, resins, asphaltenes in EPR is conventionally accounted through the small deviations of components of g-factors between each other and from the value of g-factor of free electron (see detailed explanation in Section 3) [19, 20, 24]. Obviously, for the high frequency experiments such shift and differences should be more pronounced. But as it was already mentioned, no experimental evidence for that was provided.

2. Materials and Methods

Crude oil was extracted from the oil core of the Karmalinskoe oilfield (Volga-Ural basin, Republic of Tatarstan, Russia). Compositional analysis of the oil sample (SARA analysis) was conducted according to the common technique [25] which includes asphaltenes precipitation from heptane and further chromatographic separation of the non-asphaltic oil components through column filled with alumina. SARA (saturated, aromatic, resins) analysis data of the studied crude oil are presented in Table 1. Organic solvents, such as, toluene, heptane, dichloromethane, methanol (purity of all solvents was no less than 99.5%) were purchased from Component-Reaktiv and used without additional purification. Aluminum oxide (particle size 0.05-0.15 mm, neutral) were purchased from Sigma-Aldrich.

| SARA analysis, % | Saturated | Aromatic | Resins | Asphaltenes |
|----------------|-----------|----------|--------|-------------|
| 19.4           | 45.8      | 29.0     | 8.4    |

To prepare sample with the adsorbed asphaltenes (As), 1.000 g of Al$_2$O$_3$ was added to dichloromethane solutions containing 2×10$^{-3}$ g×ml$^{-1}$ of As in a round bottom flasks. Obtained mixtures were shacked for 30 min, and then Al$_2$O$_3$ with adsorbed asphaltenes was filtered off and dried in vacuum evaporator under reduced pressure (20 mbar, 40 °C). The resulting sample we will denote as Q30A. The calculations show that the deposited As amount corresponds to mono or double layer on the aluina surface.

W-band EPR spectra at T = 100 K were registered with Bruker EleSys 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. The ability to detect ESE gives an opportunity to use more advanced pulsed techniques in the near future. X-band concentration measurements are done by using Bruker
ESP-300 with double cavity ER4105DR by comparing the integrated intensities of the spectra of a test sample and a reference sample (powder of DPPH and Mn\(^{2+}\) in MgO). Spectra simulation are done in Easyspin package for MatLab [26].

3. Results and Discussion.
Initial Al\(_2\)O\(_3\) samples are EPR silent within the sensitivity limit of our instruments. Comparison of the W-band ESE spectra for crude oil, As powder and deposited Q30A sample are shown in Figure 1. The EPR spectra contain two contributions: the first one is related to VO\(^{2+}\) complex (V\(^{4+}\)+O\(^{-2}\)→VO\(^{2+}\)) whereas the second (single line) can be attributed to “free” radical(s). As it was already mentioned, shift to the W-band allows In this work we are concentrating on the tracing of EPR of VO\(^{2+}\) complex in the W-band. EPR spectrum of VO\(^{2+}\) at X-band is described in details in [11].

![Figure 1. The W-band ESE spectra at T = 100 K of initial oil sample (the lower curve), As sample (in the middle) and Q30A (top line). Arrow indicates the line due to FR. Other parts of spectra are due to VO\(^{2+}\) paramagnetic complexes.](image)

EPR spectra of Oil and As are very similar. It allows suggesting that As structure remains the same as in the initial oil sample after the extraction process. Alteration of EPR pattern for the deposited Q30A sample is glaringly obvious but it is hard to describe numerically. To follow the changes for the deposited sample, we have to characterize the EPR spectra in details (see Figure 2).

The largest interaction in the high-field experiments is the Zeeman one between the magnetic moment of the unpaired electronic spin \(S\) and \(B_0\). The VO\(^{2+}\) paramagnetic complex is characterized by \(S = \frac{1}{2}\) and, therefore, by two projections of \(m_s = \pm 1/2\) onto the direction of \(B_0\). The electron Zeeman interaction is described by the parameter called \(g\)-factor with the typical values close to value 2.00. Another interaction (common applicable to hydrocarbon systems) is the spin-nuclear one. As a nucleus could also have a magnetic moment, the interaction of the unpaired electron with the nucleus splits the electron energy levels, generating a structure called hyperfine structure in the EPR spectrum – each energy level splits into a closely spaced group of \((2I+1)\) sublevels (here \(I\) is the nuclear spin quantum number), described by the hyperfine parameter \(A\). For \(^{51}\)V nuclear spin \(I = 7/2\).
Figure 2. The energy levels and the corresponding absorption EPR spectrum for VO$^{2+}$ complex calculated for the microwave frequency $\nu = 94$ GHz, $g_\parallel = 1.963$, $g_\perp = 1.985$, $A_\parallel = 470$ MHz, $A_\perp = 150$ MHz. Particular contributions from every EPR transition are color marked. Calculations are done in EasySpin package for Matlab [26].

Taking into account that VO$^{2+}$ has a near planar symmetry, the $g$- and $A$-parameters should be regarded as anisotropic parameters having axial symmetry, i.e., $(g, A)_\parallel$ and $(g, A)_\perp$. Figure 2 presents the calculated electron-nuclear energy levels of VO$^{2+}$ paramagnetic complex, EPR transitions and the corresponding EPR absorption line with the values of $(g, A)_\parallel$ (i.e., perpendicular to VO$^{2+}$ plane, $z$ axis) and $(g, A)_\perp$ (i.e., in the VO$^{2+}$ plane or $xy$ plane) taken from [11] which will be appeared close to the obtained in the experiment (Table 2). As for the most VO$^{2+}$ related investigations, we suppose that the direction of the main axes coincide for $g$- and $A$- tensors. The powder EPR spectrum of VO$^{2+}$ represents the $2 \times 8$ hyperfine patterns (the projection of $I$ is allowed to take 8 values: of $m_I$: $\pm 7/2; \pm 5/2;$...
\( \pm 3/2; \pm 1/2 \) for the parallel and the perpendicular complex orientations. Only transitions are allowed with \( \Delta m_{S} = \pm 1 \) and \( \Delta m_{I} = 0 \).

As it can be seen from the comparison of Figures 1 and 2, experimental spectra only with some extend of accuracy can be described by the spin-Hamiltonian of the axial symmetry for the single VO\(^{2+} \) molecule. The extracted from the experimental spectra values of \( g \) - and \( A \) - components are presented in Table 2. Due to the higher frequency (the higher spectral resolution) one can define the components of \( g \)-factors with much better accuracy than in the conventional X-band. From Table 2 it follows that the transition from the bulk sample to the deposited one is accompanied by some increase of \( g_{||} \) and decrease of \( A_{\perp} \).

**Table 2.** Values of of \( g \) - and \( A \) - components for VO\(^{2+} \) paramagnetic centers at room temperature as measured in the W-band.

|        | \( g_{||} \)  | \( g_{\perp} \)  | \( B = \Delta g_{||}/\Delta g_{\perp} \) | \( A_{||} \), MHz | \( A_{\perp} \), MHz |
|--------|----------------|----------------|------------------------------------------|-------------------|-------------------|
| Oil    | 1.9610(8)      | 1.9825(5)      | 2.1                                      | 480(10)           | 155(5)            |
| As (powder) | 1.9610(8)    | 1.9825(5)      | 2.1                                      | 475(15)           | 155(5)            |
| Q30A   | 1.9630(10)     | 1.9820(5)      | 1.9                                      | 460(15)           | 155(5)            |

The first one is in the accordance with ref. [20] in which double and monolayers of V\(_2\)O\(_5\) on different surfaces were considered. Usually, for accounting of \( g \)-factor changes numerically, the B parameter has been used as a sensitive indicator of structural distortions to clarify a change in the V=O bond length which can be derived as follows:

\[
B = \frac{\Delta g_{||}}{\Delta g_{\perp}}, \quad (1)
\]

where \( \Delta g_{||} = g_{||} - g_{e} \), \( \Delta g_{\perp} = g_{\perp} - g_{e} \) and \( g_{e} \) is the free electron \( g \) value of 2.0023.

Definitely, the B parameter for the deposited sample is slightly, but larger than that in the initial asphaltene. For simple vanadyl complexes it is ascribed to a shorter V=O bond and/or a longer distance to the nitrogen ligands, i.e., the higher electron density in the axial bond and more electron delocalization to the V orbital [24]. But, in our opinion, it should be accompanied with the decrease of \( A \)-components especially in the plane of V=O bond, i.e. of \( A_{\perp} \) which was not observed; neither in the referenced paper [24] nor in our experiments. Instead that we have obtained the reduction of the out-of-plane parameter \( A_{||} \) (see Table 2). It confirms additionally that changes of the EPR parameters in PDS are mainly due to the disaggregation of the complex vanadyl aggregates rather than due to the structural changes of single VO containing molecule. We hope to address this issue in details by using the more elaborated EPR techniques like electron-nuclear double resonance (ENDOR) [27].

**4. Conclusion**

Until recently a role of metalloporphyrins in the aggregation of the PDS high-molecular weight phases was discounted or even denied. The latter experimental and theoretical studies show that vanadyls can be of crucial importance for formation of the nano-, micro- and macro aggregates [28, 29]. We hope, that the proposed approach for studying the vanadyl aggregates could help to unravel also the nature of asphaltene aggregates.
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