High-frequency EPR study of crude oils

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Abstract. Four different samples of crude oil were studied by means of high-frequency W-band (94 GHz) electron paramagnetic resonance (EPR) spectroscopy with the aim to develop new methods of crude oil quality control. High spectral resolution of W-band allowed to avoid an overlap of spectra contributors. The ratio K between the integral intensity of the low-field EPR component of the vanadyl complexes to that of free radical line was chosen as an attribute of each sample. Using the K-parameters and EPR spectra simulations the crude oil leaking between adjacent horizons is shown. Pulsed EPR experiments allowed detecting free radicals signals only. It is demonstrated that the extracted transverse relaxation time could be used as an additional parameter which characterizes the origin of the crude oil and nature of the oil paramagnetic centers.

1. Introduction

Due to the great heterogeneity of properties and composition of crude oils from different oilfields, a task to develop the methods of monitoring the characteristics of crude oils is still of a great importance. Electron paramagnetic resonance (EPR) is known as one of the informative tools for oil research but the vast majority of EPR applications were and are restricted to the conventional X-band (9 GHz) measurements. The main scope of the present work is to demonstrate some capabilities of the modern high-frequency (W-band, 94 GHz) EPR spectroscopy for investigation of crude oils.

2. Materials and Methods

A list of the investigated samples is presented in table 1. Samples 1 and 2 are from the same oilfield and well but extracted from different depths. Sample 4 has been investigated to prove the suggestion about the oil leaking from Vereian horizon to Bashkirian horizon.

| Sample No. | Oilfield    | Well No. | Horizon            |
|------------|-------------|----------|--------------------|
| 1          | Akanskoe    | 2023     | Bashkirian (bottom) |
| 2          | Akanskoe    | 2023     | Bashkirian (top)   |
| 3          | Yamashinskoe| 7220     | Tournai            |
| 4          | Akanskoe    | 27       | Vereian            |

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All samples 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 $B_0$ [1, 2].

3. Results
In figure. 1 the CW EPR spectrum of sample 3 is presented which is a typical one for the whole series of samples studied. EPR spectra of oil are due to the hyperfine structure of vanadyl complex VO$^{2+}$ ($^{51}$V$^{4+}$, $3d^1$, $S = 1/2$, $I = 7/2$, $g_\parallel = 1.9640 \pm 0.0005$, $g_\perp = 1.9840 \pm 0.0005$) and from the single line of carbon free radicals (FR), which is in agreement with results of [3, 4, 5].

Atoms in the vanadyl-porphyrins are arranged practically in a plane defining thus the g-factor and hyperfine A tensor have an axial symmetry [4, 5, 6]. The EPR spectrum of the vanadyl-ions consists of the 16 lines representing the $2 \times 8$ hyperfine patterns for the parallel and the perpendicular complex orientations.

An important consequence of the microwave frequency increase revealed in the observed CW EPR 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.

![Figure 1](image)

**Figure 1.** The CW EPR spectrum of sample 3. Other four lines of vanadyl in parallel orientation are outside of scale.

For comparison of CW EPR spectra from different oil samples we have considered the ratio $K$ of vanadyl line integral intensity to FR line integral intensity. The difference in the spectra intensity is clearly visible in figure. 2 and figure. 3 (shaded area of figure. 1). table 2 contains calculated values of K-parameter for all studied oil samples. EasySpin subroutine module was used for EPR spectra simulations [7].

Samples 1 and 2 extracted from the different depth of the same well have different values of K parameter that could indicate the destruction of vanadyl-porphyrins in the oxidation processes. Indeed, the rate of the oxidation processes depends on the occurrence depth and, as a rule, increases towards to the earth surface [8]. As followed from the signal intensities, the concentration of paramagnetic species in sample 2 is significantly higher than that in sample 1. The presumable oil leaking from Vereian horizon to the top of Bashkirian horizon can be confirmed by the same lineshapes and values of K-parameter for samples 2 and 4.
Figure 2. The CW EPR spectra of FR and low-field vanadyl component for all samples.

Figure 3. The CW EPR spectra of FR and low-field vanadyl component for samples 1, 2, 4.

Table 2. K-parameter values.

| Sample No. | 1   | 2   | 3   | 4   |
|------------|-----|-----|-----|-----|
| K-parameter| 39.2| 16.3| 8.6 | 20.2|

For getting the detailed information about the FR, electronic spin-echo (ESE) detected EPR spectra of FR were measured [9, 10]. ESE-detected EPR spectrum for oil sample 2 is shown in figure. 4.

Figure 4. ESE-detected EPR spectrum of sample 2 ($g_{||} = 2.0028 \pm 0.0005$, $g_{\perp} = 2.0040 \pm 0.0005$).

Figure 5. ESE decay for sample 3.

In ESE-detected spectra an inhomogeneous single line caused by presence of FR only is registered. Due to their short relaxation times [3] signals from vanadyl-ions were not obtained. The ESE-signal for sample 1 had not been observed probably due to low concentration of
paramagnetic species.

Transverse relaxation was studied tracking the primary ESE amplitude while varying $\tau$ [9, 10]. The observed transverse magnetization decay for sample 3 is shown in figure. 5. Values of transverse relaxation times for all samples are represented in table 3.

Table 3. Transverse relaxation times of FR.

| Sample No. | 1   | 2    | 3    | 4    |
|------------|-----|------|------|------|
| $T_2$, ns  | -   | 185 ± 3 | 154 ± 2 | 197 ± 5 |

The possibility to detect FR ESE in liquid samples of crude oil and its inhomogeneous broadening indicates that FR is located within the large molecular clusters of asphaltenes. Otherwise transverse relaxation would be significantly shorter and unreachable for measuring by our equipment at RT due to the averaging caused by high mobility of paramagnetic species. Slight difference in the values of transverse relaxation time (table 3) between different samples can be explained by differences in sample viscosities.

4. Conclusion

Application of the high-frequency (W-band) EPR allows to resolve spectrally the free radicals and the vanadyl-ions components of the EPR spectra of crude oil. It gives an opportunity to gain a deeper insight to the origin of the paramagnetic centers important both for the industrial applications and fundamental research.

The ratio of integral intensities of vanadyl line to FR line (K-parameter) and transverse relaxation time of FR allow to distinguish oil types and could serve as fingerprints of the hydrocarbon origin.

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