Distribution of vanadyl complexes and free radicals in asphaltenes fractions from electron paramagnetic resonance

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Abstract. Structural characterization of asphaltenes in complex systems is in the focus of scientific and industrial interests since many years. Asphaltenes isolated from the high-viscous Ashal’cha oil (2500 mPa·s) were studied. Five asphaltene fractions were obtained by stepwise extraction with an alcohol-benzene solvent with different alcohol contents after precipitating the asphaltenes from the oil with hot isooctane. Redistribution of paramagnetic centers between the fractions of asphaltenes is revealed by electron paramagnetic resonance (EPR) while no significant changes in EPR spectral parameters are found. The results can be used for tracking the asphaltenes formation as well as following the changes of their supramolecular structure.

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) 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 $\pi$-electrons of the aromatic rings and stable organic radicals of the side chains. Vanadyl based porphyrins in heavy oils were first discovered in 1930s by Treibs [3, 4], who postulated the biological origin of these compounds. Vanadyl (VO) 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 [8-12].

Because of its high boiling point, minimal vanadium is contained in the distillates. Additionally, the low solubility of several vanadium compounds in most solvents, specifically metalloporphyrins, facilitates their partitioning between the asphaltenes and resins [1, 2]. It is self-evident that different asphaltene fractions can also have various amount of paramagnetic centres. Dickie and Yen were the first to suggest that, having many of the same interactive
groups as asphaltenes, metalloporphyrins could also play a role in asphaltene self-assembly, adsorption, and phase separation [13]. Although the exact location and structure of FR and VO in PDS and asphaltenes are still undefined, some recent results based on the advanced EPR techniques show that VO and FR are bound in asphaltenes and their EPR parameters can serve at least as complimentary measures to follow thermal, catalytic, organizational changes in asphaltenes’ structures [14-20]. To the knowledge of authors, there are no detailed studies of the asphaltenes fractions by EPR and of redistribution of paramagnetic centres in asphaltenes fractions. It can be important for the understanding the mechanisms of asphaltenes formation and precipitation. In this paper, we present the results of conventional EPR measurements of asphaltenes fraction for Ashal’cha oil to evaluate the capabilities of conventional EPR techniques to characterize asphaltenes fractions.

2. Materials and Methods
Crude oil with the viscosity of 2500 mPa·s at room temperature was extracted from the Ashal’cha oilfield (Volga-Ural basin, Republic of Tatarstan, Russia). Compositional analysis of the oil sample (SARA analysis) was conducted according to the common technique describes in [21], for example, which includes asphaltenes precipitation from hexane and further chromatographic separation of the non-asphaltic oil components through column filled with alumina. SARA (saturated, aromatic, resins, asphaltenes) analysis data of the studied crude oil are presented in Table 1. Besides, of the presented fractions volatile organic compounds (VOC, 5.6 %) with the boiling point of less than 110 °C are found.

| SARA fractions, wt % | Saturated | Aromatic | Resins | Asphaltenes |
|----------------------|-----------|----------|--------|-------------|
| 24.9                 | 37.4      | 25.9     | 6.4    |

The oil samples (5-10 g) were treated by hot isooctane (200 ml). Then by using the mixtures of isopropanol and benzene containing 20, 40, 60, 80, 100 % of benzene in filter paper in a Soxhlet apparatus, asphaltenes fractions A1-A5, correspondingly, were obtained. Their molecular mass was determined with the Matrix-Activated Laser Desorption/Ionization (MALDI) spectrometer with time-of-flight analyzer (TOF) UltraFlex III TOF/TOF (Bruker) on the 2.5-dihydroxybenzoic acid matrix. It gives the values of 786, 1190, 1233, 1202, and 1280 a.u. for them.

Elemental analysis of crude oil asphaltene and asphaltene fractions was carried out on Perkin Elmer 2400 Series II elemental analyzer [21]. No significant difference in nitrogen (1.5-1.7 wt %) or sulfur (3.6-3.8 wt %) content with the sample number was observed. Data for carbon and hydrogen content along with the NMR analysis are published in the complimentary paper. No vanadium was detected by using the mentioned equipment.

From literature [22] it is known that the total amount of vanadium in Ashal’cha oil is estimated to be about 0.023 wt % distributed mainly in asphaltenes (0.186 wt. %) and resins (0.042 wt %). Presence of S allows to suggest that vanadyl in Ashal’cha oil has (apart of VO(N3)), VO(NS3), VO(N2S2) and VO(N3S2) as possible environments but increase in sulfur
content could be also explained by incorporation of thiophenes, i.e. various porphyrins in oil have the same VO(N$_4$) skeleton [23, 24]. Several series of porphyrins containing a core structure of N$_4$VO have been identified in fossil fuels like etioporphyrins (ETIO), deoxophylloerythroetio porphyrins (DPEP), dicyclic-deoxophylloerythroetio porphyrins (Di-DPEP), rhodo-etioporphyrins (rhodo-ETIO), rhodo-deoxophylloerythroetio porphyrins (rhodo-DPEP), and rhodo-dicyclic-deoxophylloerythroetio (rhodo-Di-DPEP). According to the studies of ref. [22], apart from etio- and phylloporphyrins, there are also rhodo- and DPEP found in asphaltenes of Ashal’cha oil and about 20-60 % of the are parts of the paramagnetic complexes.

EPR spectra of the samples in continuous wave (cw) mode were obtained using an ESP-300 and ElexSys 680 (Bruker) spectrometers operating at 9.4 – 9.9 GHz (X-band). FR and VO concentration was estimated at room temperature in the double cavity ER4105DR by comparing the integrated intensities of the simulated with EasySpin utility [25] the integrated intensities of the spectra of a test sample and a reference sample (powder of DPPH, Mn$^{2+}$ in MgO, and a series of Cu-DETC solutions). The value of the microwave power was chosen to be 2 $\mu$W to avoid EPR saturation effects.

3. Results and Discussion.

EPR spectra detected at X-band (Figure 1) for all fractions A$_1$-A$_5$ are very similar to each other and are defined by the presence of stable “free” radical (FR, single line, electron spin $S = 1/2$, $g \approx 2.003$, linewidth of 6.4 G) and paramagnetic vanadyl complexes. Taking into account a nearly planar skeleton structure of single VO molecule (VO$^{2+}$, $S = 1/2$), the EPR spectra could be satisfactorily described by the $g$-tensor of axial symmetry with $g_{\|} \approx 1.96$, $g_{\perp} \approx 1.98$ 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 (natural abundance of 99.75 %) with hyperfine structure constants $A_{\|} \approx 480$ MHz, $A_{\perp} \approx 157$ MHz (Table 2). In our notations the values of $(g, A)_{\|}$ correspond to the orientation perpendicular to VO$^{2+}$ plane (out of plane), along the direction $c$ and $(g, A)_{\perp}$ correspond to the orientation in the VO$^{2+}$ plane, $ab$ plane. As for the most VO$^{2+}$ related investigations, we suppose that the direction of the main axes coincide for $g$- and $A$- tensors. Comprehensive description of VO spectra, their spectra simulations and spectra changes with external treatment are given in papers [11,15,17].
**Figure 1.** Conventional X-band EPR spectra of A₃ fraction and its simulation in the self-written environment based on the EasySpin package for Matlab [25] with the parameters given in Table 2.

**Table 2.** Values of g- and A- components for VO and FR paramagnetic centers for asphaltenes.

|        | VO          | FR          |
|--------|-------------|-------------|
| g_||   1.9610(8) | 1.9825(5)   |
| g┴    | 1.9825(8)   | 1.9610(5)   |
| A_|| MHz      | 475(15)    | 155(5)     |
| A┴ MHz| g          | 2.0030(3)   | 6.4(1)     |
| ΔHpp G|            |             |

Within the accuracy of our experiments, no changes with the number of fraction in the presented spectroscopic parameters are found. It is often suggested that a difference in g-factors can or should be revealed [26]. It means that no great structural changes of single VO containing molecule or FR with fractioning in our experiments is observed. We hope to address this issue in details by using the more elaborated EPR techniques like electron-nuclear double resonance (ENDOR) [15,17].

Results for the concentration measurements in the investigated powders are presented in Table 3 and Figure 2. It follows that generally concentration of VO reduces with fraction number while the intensity of FR is growing till A₃ and then slightly drops. A very similar behaviour was reported in [15] in which precipitation of asphaltenes on alumina surface by EPR technique was investigated. It was found that the reducing of VO/FR ratio occurs with the lowering amount of the precipitated asphaltenes. It was suggested that asphaltenes with a more condensed structure and lower VO content were adsorbed on alumina. It agrees with the previously revealed trend of inverse dependence of the concentration of FR on the content of vanadyl complexes [27] and shows the potential ability (correctness) of investigation of asphaltenes’ fractioning and formation by their precipitation on various supports [15,17]. The
results became even more interesting in the light of a new wave of interest to the unraveling of features of archipelago-island asphaltene structures [28].

| Initial asphaltene | Mass from MALDI-TOF, a.u. | VO concentration, spin/g | FR concentration, spin/g | Relative concentration [VO/FR] |
|--------------------|-----------------------------|--------------------------|--------------------------|-------------------------------|
| A₁                 | 786                         | 7.5(7) 10^{18}           | 0.81(7) 10^{18}          | 9.1 [15]                     |
| A₂                 | 1190                        | 6.0(6) 10^{18}           | 1.5(1) 10^{18}           | 3.7                          |
| A₃                 | 1233                        | 6.0(6) 10^{18}           | 1.8(2) 10^{18}           | 3.45                         |
| A₄                 | 1202                        | 6.7(7) 10^{18}           | 1.8(2) 10^{18}           | 3.68                         |
| A₅                 | 1280                        | 4.0(5) 10^{18}           | 1.42(8) 10^{18}          | 2.77                         |

Figure 2. Dependence of the relative concentration VO/FR on asphaltenes mass and its linear approximation.

4. Conclusions
While no significant changes in EPR spectroscopic parameters of paramagnetic vanadyl complexes and “free” radical in Ashal’cha asphaltenes’ fractions was observed, perceptible lowering of their relative concentrations which is found to be nearly inverse proportional to the extracted atomic masses was found. The obtained feature can be used for the elucidation of the asphaltenes formation and their precipitation.

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