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EPR study of spectra transformations of the intrinsic vanadyl-porphyrin complexes in heavy crude oils with temperature to probe the asphaltenes' aggregation

M.R. Gafurov [a,*], M.A. Volodin [a,b], A.A. Rodionov [a], A.T. Sorokina [a], M.Yu. Dolomatov [c,d], A.V. Petrov [e], A.V. Vakhin [a], G.V. Mamin [a], S.B. Orlinskii [a]

[a] *Kazan Federal University, Kremlevskaya, 18, Kazan, 420008, Russia*
[b] *Sakhalin Energy Investment Company, Ltd., Dzerzhinskogo, 35, Yuzhno-Sakhalinsk, 693020, Russia*
[c] *Bashkir State University, Validy, 32, Ufa, 450076, Russia*
[d] *Ufa State Petroleum Technical University, Kosmonavtov, 1, Ufa, 450000, Russia*
[e] *Institute of Petroleum Refining and Petrochemistry, Iniciativnaya, 12, Ufa, 450065, Russia*

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ABSTRACT

Temperature dependencies of electron paramagnetic resonance spectra of intrinsic paramagnetic vanadyl complexes and dynamical viscosity for two heavy crude oils and asphalt samples are measured. Transitions between the different motional conditions (from the rigid to the fast motion regimes) are observed. The rotational correlation times (in the model of the isotropic diffusion) are extracted. It is shown that the characteristic temperatures for the motional regime transitions are mainly defined by the asphaltenes' content. From our analysis it follows that the thermal treatment leads to the destruction of the asphaltene complexes onto the 4–5 small pieces. The results indicate that paramagnetic vanadyl complexes are the sensitive intrinsic probes to study qualitatively and quantitatively structural transformations of aspahltenes of heavy crude oils in-situ.

1. Introduction

Asphaltene constituents of petroleum (defined as the heaviest fractions of crude oil insoluble in normal alkanes) impact all aspects of crude oil production and utilization (Trukhan et al., 2017; Speight, 2015; Ganeeva et al., 2011). The content of the high-molecular asphaltene components could reach the values of 45 wt % in native oils and up to 73 wt % in natural asphalts and bitumen. Undesirable asphaltene precipitation is a serious concern to the petroleum industry because asphaltenes can block catalyst active sites, plug up well bores and stop oil production, in addition to blocking pipelines (Ganeeva et al., 2011; Gawel et al., 2005; Yen and Chilingarian, 2000). As it is stressed anew in the recent review by Martyanov et al. (2017), a fundamental condition for the development of effective processes for heavy oil production and processing is the understanding of the key factors that determine the aggregative behaviour and stability of oil disperse systems (ODS), behaviour and chemical transformations of their components under various external conditions including elevated temperature.

Asphaltenes are known to form nanosized colloidal particles “nanocrystallites”, “nanocolloids”, or “nanoaggregates”. It is shown that asphaltenes aggregation begins already at their concentrations as high as 10 mg/L in some “good” organic solvents, as described by Evdokimov et al. (2016), Mullins et al. (2014) and by Shkalikov et al. (2010). The littlest aggregates contain 5–8 small asphaltene molecules. For example, in the well-known Yen-Mullins model (Mullins et al., 2014) the asphaltenes are defined as a central moderately-sized polycyclic aromatic hydrocarbon ring system linked with alkane chains on the exterior, with nanoaggregates up to six molecules and clusters of eight nanoaggregates on average (Lima et al., 2017).

However, after decades of intensive studies, the association and aggregation of asphaltenes are still not well characterized and are subjects of ongoing debate (Lima et al., 2017; Trukhan et al., 2017; Evdokimov et al., 2016; Ganeeva et al., 2011). Additionally, structural and molecular variability of asphaltenes do not allow to use an exact copy of one model which satisfactory describes a properties of one sort of ODS to other ODS. Therefore, the complex analytical study of each kind of ODS is in need both for the fundamental research and practical applications.

A significant factor influencing the asphaltene aggregation and

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* Corresponding author.
E-mail address: Marat.Gafurov@kpfu.ru (M.R. Gafurov).

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precipitation is their local environment, which determines the nature of intermolecular interactions of asphaltenes with other ODS components. It is evident that prediction of crude oil stability and solubility of asphaltenes under specified conditions requires the fundamental knowledge of the character of intermolecular interactions between asphaltenes and other heavy oil components present in the local environment. This knowledge can be gained only by means of in situ studies of local rheological properties of crude oils and molecular dynamics of asphaltenes under various conditions (Martyanov et al., 2017, Trukhan et al., 2017).

As it was already mentioned, because studying asphaltene properties in the actual (native) ODS and its fractions is difficult (especially for the optical studies), the vast majority of experimental and theoretical work has been conducted on systems wherein asphaltene obtained from the ODS was then dissolved in simple solvents. Electron paramagnetic resonance (EPR) techniques do not require the diluted samples and can sense the intrinsic paramagnetic centres (PC) also in the unfractioned species, i.e., in the native environment (see Yen and Chilingarian, 2000; Khasanova et al., 2017; Gafurov et al., 2018 for reviews on this topic). Following the changes of the EPR spectroscopic parameters of PC (for example with temperature) one can gain additional information about ODS.

Metalloporphiryns in heavy oils were first discovered by Treibs (1936) who postulated the biological origin of these compounds from chlorophyll, bacteriochlorophylls, hemes, and other tetrapyrrolic biochemical (Gourier et al., 2010). Vanadyl containing porhyrins, including paramagnetic species with VO^{2+}as a core, are the important part of many ODS and the object of EPR investigations (Reynolds, 1985; Yakubov et al., 2017; Biktagirov et al., 2017; Gracheva et al., 2016; Ramachandran et al., 2015; Gourier et al., 2010; Gilinskaya, 2008).

Since recently a role of VO^{2+} in the asphaltene and asphaltene-resin aggregation has begun to be extensively discussed (Dechaine and Gray, 2010). From the relaxation times measurements for "free" organic radical (FR) and VO^{2+} by Mamin et al. (2016), the existence of the dipole-dipole coupling manifested in the acceleration of the transverse relaxation times of FR was found for different asphaltenes. Consequently, it was proposed that VO^{2+} complexes can participate in construction of the asphaltene aggregates via the intermolecular interactions. The first evidence that the magneto-optical activity in asphaltenes can also be due to the vanadyls in asphaltenes was presented recently by Edelman et al. (2016). Trukhan et al. (2017) found that the precise simulation of the vanadyls' EPR spectra is an effective tool for the quantitative determination of the asphaltene sizes in different oil fractions in situ and allows one to find their size distribution in crude oils. Cui et al. (2017a, 2017b) show that small changes of components of g-factor of vanadyls in asphaltenes, maltenes and resins can be used to track the mobility of VO^{2+} complexes under the different treatment.

In this work we inspect the changes of the conventional EPR spectrum of the intrinsic paramagnetic vanadyl complexes during the thermal treatment of heavy crude oil and asphalt samples with the aim to gain information about the ODS structure and dynamics as well as to show the abilities of the conventional EPR approaches for the in-situ analysis.

2. Materials and methods

2.1. Materials

There is no unique ODS classification (Briggs et al.,. 1988; Yen and Chilingarian, 2000; Souza et al., 2012). According to Briggs et al. (1988), heavy oils are defined as having the room temperature viscosity η_0 from 100 to 10 000 mPa s and density higher than 930 kg/m^3. Heavy crude oils from Ashalchinskoe and Mordovo-Karmalskoe oilfields and of asphalt obtained by means of second stage propane deasphalting of the Western Siberian oil tar and were studied. They were investigated by SARA (Saturated and Aromatic hydrocarbons, Resins and Asphaltenes) analysis and stored sealed in dark place at room temperature. No special procedures for the oxygen removing were conducted. Some physical properties of the samples are listed in Table 1. Analysis of the organic solutions of the samples # 1 and #2 with nuclear magnetic resonance (NMR) were presented by Rakhmatullin et al. (2017). Additional information for sample # 3 and its fractions one can find in the paper of Dolomatiov et al. (2016).

2.2. Methods

The measurements of the dynamic viscosity η were performed using a rotary viscometer Brookfield DV2 with a thermostatic cell in the temperature range of (20–160) °C. The deviation of temperature during the measurements did not exceed ±0.5 °C and with Stabinger viscometer SVM 3000/G2 with a thermostatic cell in the temperature range of (20–100) °C with the relative error of 0.5%.

EPR spectra of the samples were obtained using an ESP-300 spectrometer (Bruker) operating at 9.4–9.9 GHz (X-band) in continuous wave mode. Spectrometer's magnetic field can be varied in the range of 20–1600 mT with an accuracy of not less than 0.01 mT, modulation frequency was fixed to 100 kHz. PC concentration was estimated at room temperature in the 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). Samples heating was done in a stream of nitrogen blown through the quartz insert in the high-temperature resonator ER 4114HT equipped with the VT thermostatic system (Oxford Instruments). For each sample the temperature dependence of the EPR spectra in the range of about (293–780) K was obtained with (8–15) °C increment, heating rate of 2 °C/min and temperature setting accuracy of not less than ± 2 °C. The chosen heating rate is slow enough to cause technical artifacts and allows to carry out the temperature experiments on a sample during a working day, Biktagirov et al. (2014) and Galukhin et al. (2016) have it recently shown. Modulation amplitude of 0.5 mT was chosen to investigate the temperature changes of vanadyl complexes. Microwave power level was equal to 25 μW in order to avoid saturation effects.

3. Results and discussion

Firstly, we present the EPR results. Fig. 1 shows the EPR spectra for sample #2 at two temperature values ($T = 297$ K and 654 K). The existence of paramagnetic centers in ODS is generally caused by the presence of *d* metals (mainly V, Ni, Fe) and stable carbon centered "free" radicals (FR). It is established that the majority of the organic FR are concentrated in the structure of a condensed polyaromatic core of asphaltene molecule while the metals locate in the polar fractions (both resin and asphaltene), with a further majority concentrated in the asphaltenes (Yen and Chilingarian, 2000). The presented spectra contain two components. The first contribution is due to the VO^{2+} complex. Because of the near planar structure of the vanadyl porphyrin complexes, the corresponding g and A tensors have an axial symmetry (Table 2). Therefore, the "powder" EPR spectrum of VO^{2+} at room and the lower temperatures consists of 16 partially overlapped components of hyperfine structure (8 lines in parallel and 8 in perpendicular orientations due to $I = 7/2$). The second (single line) can be attributed to FR. For details of the EPR spectra interpretation see Dolomatov et al., 2016; Alexandrov et al., 2014; Biktagirov et al., 2014; Yen and Chilingarian, 2000. In this work we are concentrating on the tracing of EPR of VO^{2+} complex. Temperature dependence of VO^{2+} EPR for asphalt (sample #3) is shown in Fig. 2.

From Figs. 1 and 2 it follows that the vanadyl spectra transform with temperature from the typical anisotropic "powder" spectra to the isotropic one. This transition could be characterized by two temperature values which we denote as T_{start} (EPR spectrum at $T < T_{\text{start}}$ is described by the only anisotropic "rigid" pattern) and T_{end} (at $T > T_{\text{end}}$ the EPR spectrum has only the isotropic "averaged" fast motion component). The values of T_{start} and T_{end} for the investigated samples are listed in Table 3.

As it follows from SARA analysis (Table 1), for sample #3 only the