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# In Situ Electron Spin Resonance Study of Molecular Dynamics of Asphaltenes at Elevated Temperature and Pressure

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**ABSTRACT:** A comparison of the behavior of asphaltene molecules extracted from crude oil and dissolved in aromatic solvent as a model system with the behavior of vanadium-containing molecules in real crude oils via electron spin resonance *in situ* technique showed that the changes of rotational mobility of asphaltene molecules can be related to the changes of the local viscosity and environment of the asphaltenes as well as the characteristic sizes of vanadyl-containing fragments because of aggregation/disaggregation processes in crude oils. The information about the mobility of asphaltene molecules in different local environments at different temperatures and pressures is an important step in understanding both the aggregation of the asphaltenes and crude oil fouling processes in addition to the conditions required for the deposits to be formed.

## INTRODUCTION

The energy efficiency in the oil industry depends largely upon the prevention or reduction of deposits and fouling of crude oil in pipelines and heat exchangers. It is generally accepted that asphaltenes are the main component of the deposits formed and play a key role in fouling processes.<sup>1,2</sup> Indeed, asphaltenes have a tendency to self-associate to form aggregates that can flocculate and precipitate under certain operating conditions.<sup>3</sup> However, despite the huge number of studies devoted to the investigation of asphaltene mean molar mass, shape, and structure at both molecular and aggregate levels and their physicochemical properties, a mechanism of asphaltene aggregation in real oils still remains unresolved in the literature.<sup>4</sup>

One reason for these uncertainties is the complex molecular structure of asphaltenes that are defined as the heaviest fractions of crude oil insoluble in normal alkanes (*n*-pentane, *n*-heptane, etc.).<sup>5</sup> Besides alkyl-substituted aromatic structures and aliphatic chains, asphaltenes can incorporate functional groups containing heteroatoms, including sulfides and nitrogen-containing saturated structures<sup>6</sup> and some carbonyl, ether, or ester groups.<sup>7</sup> These complex structures of asphaltenes are known to deactivate and shorten the operational lifetime of hydrotreating catalysts used for heavy oil processing because of the deposition and coke formation onto the active catalytic sites.<sup>8–10</sup> This provided motivation for finding new ways for the conversion of asphaltenes into valuable chemicals.<sup>11,12</sup>

Another essential factor that affects the processes of asphaltene precipitation is related to asphaltene local environment in crude oil. The composition of the surrounding fluid along with pressure and temperature play an important role in the asphaltene stability.<sup>13,14</sup> For example, an addition of paraffin solvent changes the solubility of asphaltenes in the bulk oil

because paraffin solvent properties affect interactions among asphaltenes and resins.<sup>1</sup> The high temperatures and pressures can also change the local environment of asphaltene molecules, resulting in either an increase or decrease of asphaltene solubility in crude oil.<sup>14,15</sup> Thus, the prediction and control of oil stability and asphaltene solubility under certain conditions requires fundamental studies of the intermolecular interactions between asphaltenes and their local environment and *in situ* investigation of local rheological properties of crude oil and molecular dynamics of asphaltenes in different surroundings.

Advanced characterization techniques have been used to study the structure and properties of asphaltenes at many diverse levels,<sup>3</sup> including Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS),<sup>16</sup> small-angle X-ray and neutron scattering,<sup>17,18</sup> nuclear magnetic resonance imaging,<sup>19–21</sup> X-ray absorption near edge structures (XANES),<sup>22</sup> magneto-optical spectroscopy,<sup>23</sup> attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy,<sup>24</sup> high-Q ultrasonic spectroscopy,<sup>25</sup> and many others. Nevertheless, quite often, researchers face experimental limitations that convolute the phase behavior of heavy oils and hamper phase behavior measurement, interpretation, and prediction. An *in situ* regime is needed to elucidate and separate the factors that have influence on the stability of asphaltenes in crude oils and determine the mechanism of deposit formation and fouling by advanced techniques.<sup>26</sup> These measurements should provide us with experimental data on molecular dynamics of asphaltenes, local intrinsic viscosity, diffusion, and sedimentation velocity to determine the macroscopic phase

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behavior of heavy oils and to predict the precipitation of some constituents from crude oil under particular conditions.

Electron spin resonance (ESR) spectroscopy is a powerful tool for the investigation of paramagnetic species and dynamics of their local environment in various media,<sup>27</sup> including systems at elevated temperature and pressure.<sup>28</sup> A quantitative analysis of the resonance adsorption line shape and the averaging of hyperfine or spin–orbital anisotropic interactions can provide *in situ* data on the size and rotation dynamics of the paramagnetic molecules and their clusters,<sup>29</sup> information about the interactions between the radicals,<sup>30</sup> and phenomena of local concentration changes, including sub- and supercritical fluids.<sup>31,32</sup>

Despite the unique opportunities, ESR spectroscopy is generally used to characterize asphaltenes and their stability as well as oil species for the presence of vanadyl paramagnetic centers and so-called free radicals.<sup>33–35</sup>  $\text{VO}^{2+}$  centers are known to be a part of vanadium and nickel organometallic compounds that exist mainly as petroporphyrine structures or other porphyrin-like coordination spheres around the metal in crude oils and their heavy fractions.<sup>3</sup> Five-coordinated square pyramidal vanadyl complexes are paramagnetic and exhibit quite an informative ESR spectrum. The  $\text{VO}^{2+}$  ion has one unpaired electron, whose ground-state configuration ( $d^1$ ) is non-degenerate. Large energy splitting between ground and excited states is connected with a strong axial component of the crystalline field arising because of the short V–O bond that allow us to observe intense narrow ESR lines at room and higher temperatures.<sup>36,37</sup> Thus, the detailed analysis of vanadyl  $\text{VO}^{2+}$  resonance parameters ( $g$  value and hyperfine coupling constant) can give us information about the  $\text{VO}^{2+}$  ligand nature.<sup>38</sup>

ESR spectra of vanadyl complexes present in different solutions at various temperatures resulted in the spectra with different averaging of the anisotropies originated from hyperfine interaction of one unpaired electron with the  $^{51}\text{V}$  nucleus spin moment of  $7/2$  and anisotropic  $g$  factor.<sup>39</sup> For the characteristic rotational correlation time  $\tau_c$  smaller than  $\cong 2 \times 10^{-10}$  s, eight components are observed in the  $\text{VO}^{2+}$  ESR spectra. The splitting between these lines is defined by an isotropic hyperfine interaction constant. At correlation times from  $\cong 2 \times 10^{-10}$  to  $\cong 10^{-12}$  s, an asymmetry observed in the hyperfine structure (HFS) of the  $\text{VO}^{2+}$  ion spectrum (that manifests itself in the lines of the different intensity) is explained by incomplete averaging of the anisotropies of the  $g$  factor and the hyperfine interaction (HFI).<sup>39</sup> At  $\tau_c \gg 2 \times 10^{-8}$  s, the well-known anisotropic vanadyl spectrum is observed.<sup>37,40</sup> It was shown earlier for some simple molecules that, at the intermediate regime ( $2 \times 10^{-10} < \tau_c < 2 \times 10^{-8}$  s), a rigorous analysis of motional line shape can correctly elucidate the effects of the molecular dynamics of the complexes that include the paramagnetic  $\text{VO}^{2+}$  fragment.<sup>41</sup>

This paper reports the first investigation of the temperature-dependent rotational mobility of the asphaltene molecules in crude heavy oil samples based on the analysis of the anisotropic interactions registered in the ESR spectra. The detailed analysis of the ESR spectra of the  $\text{V}^{4+}$ -containing asphaltenes observed within a wide temperature range at elevated pressure and under an *in situ* regime allow us to separate the contributions of asphaltene molecules of different sizes that move with different characteristic rotational time.

A comparison of the behavior of asphaltene molecules extracted from crude oil and dissolved in aromatic solvents as a

model system with the behavior of vanadium-containing molecules in real crude oils showed that the changes of rotational mobility of asphaltene molecules can be related to the changes of the local viscosity and environment of the asphaltenes as well as the characteristic sizes of vanadyl-containing fragments because of aggregation/disaggregation processes in crude oils. Similar experiments were performed for the oil/heptane mixtures. The information about the mobility of asphaltene molecules in different local environments at different temperatures and pressures is an important step in understanding both the aggregation of the asphaltenes and crude oil fouling processes in addition to the conditions required for the deposits to be formed.

## ■ EXPERIMENTAL SECTION

Experiments were performed with heavy oil<sup>17</sup> containing 6.7% asphaltenes and 4.1% sulfur (Table 1). The asphaltenes were extracted

**Table 1. Oil Group Composition (Mass %)**

Hydrocarbons	
saturated	21.0
aromatic	37.1
total	58.1
Resin	
benzene	19.4
alcobenzene	15.6
total	35.1
Asphaltene Components	
asphaltenes	6.6
asphaltenic acids	0.1
total	6.7

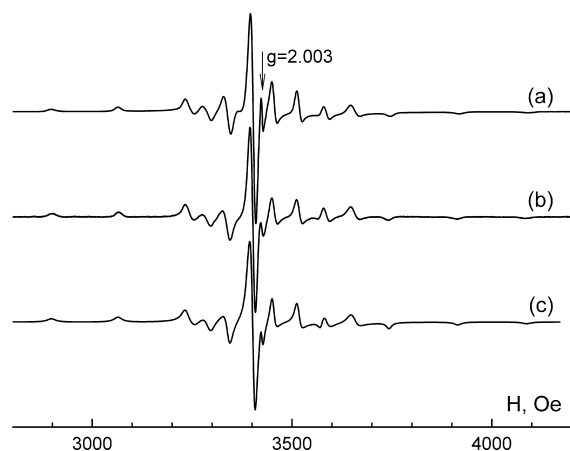
from this oil following a modified ASTM method D6560-00<sup>5</sup> by substituting heptane and toluene as solvents for hexane and benzene, respectively, to facilitate distillation. All solvents used were reagent-grade or higher.

The samples for the high-temperature ESR experiments were prepared in the following way. The required amount of crude oil or asphaltenes in benzene was introduced into the thick wall quartz capillary at room temperature. The outer and inner diameters of the capillaries were 2.8 and 1.2 mm, respectively. After the deoxygenation procedure by repeated freeze–pump–thaw cycles, the capillary with the frozen solution was flame-sealed under vacuum conditions to obtain a 50 mm length sample. Tests have shown that the sealed capillaries with the substances inside can withstand a pressure of 10 MPa, which is sufficient to convert the benzene into the supercritical state [ $T_c = 562$  K (289 °C), and  $P_c = 4.9$  MPa].

The ESR spectra were recorded with a Bruker X-band EleXsys 500 spectrometer equipped with a high-temperature ER4114HT cavity. A regular high-temperature system used for the measurement of spectra at high temperatures did not provide a sufficient uniform heating of the samples along the whole length. To increase the homogeneity of the temperature in the whole capillary, an additional resistive heating of the upper capillary part was applied as described earlier.<sup>32</sup> This allowed for the temperature gradient to decrease to  $\sim 2$  °C/cm at  $T \sim 400$  °C. The temperature was controlled with two thermocouples located in the upper and lower parts of the sample. The regular rate of the monotonous temperature increase during heating of the sealed capillary was  $\sim 2$  °C/min.

## ■ RESULTS AND DISCUSSION

Figure 1 shows the ESR spectrum of asphaltenes extracted from the heavy oil (Figure 1a) recorded at room temperature. This ESR absorption is specific for the paramagnetic systems containing  $\text{VO}^{2+}$  fragments with one unpaired electron spin,



**Figure 1.** (a) ESR spectra of solid asphaltene as extracted from the oil, (b) asphaltene dispersed in benzene with 1:3 volume ratio, respectively, and (c) calculated ESR spectrum using the parameters listed in Table 2. The spectra are registered at  $T = 20\text{ }^{\circ}\text{C}$ .

whose interaction with the  $^{51}\text{V}$  nucleus spin moment of  $7/2$  results in a hyperfine structure. The anisotropic spectrum obtained is characteristic for the immobilized or slowly rotated paramagnetic molecules with frequency  $\nu \ll A_{\text{HFI}}$ , where  $A_{\text{HFI}}$  is the hyperfine interaction constant that allows us to observe anisotropy of the  $g$  and the HFI tensor.<sup>42</sup> The anisotropic HFS spectrum is the sum of parallel and perpendicular features for each of eight HFS components corresponding to the different projections of nuclear spin  $^{51}\text{V}$ . In addition, an easily saturated symmetrical singlet with the  $g$  factor of  $2.003 \pm 0.001$  close to the  $g$  factor of a free electron is also observed in the spectrum. This single line is traditionally associated with the absorption of carbon  $\pi$  systems in asphaltene.<sup>43</sup>

The computer simulation allowed for achieving a good agreement between the calculated  $\text{VO}^{2+}$  ESR spectrum and experimental resonance absorption of asphaltene. The  $g$  and HFI tensors identified (Table 2) are close to the values that are

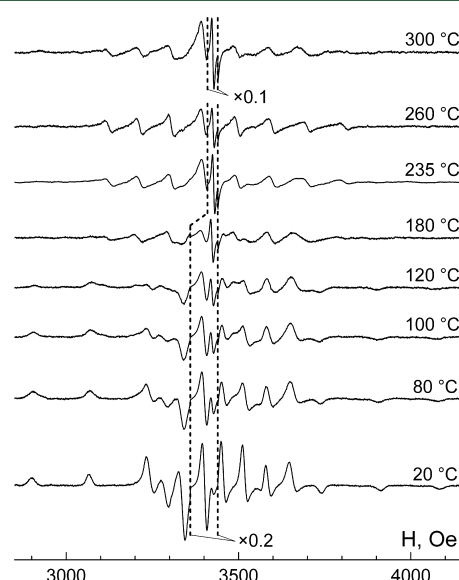
**Table 2.** Parameters of the Calculated  $\text{VO}^{2+}$  ESR Spectrum (Figure 1c) That Describes the Experimental ESR Absorption Spectrum of the Asphaltene (Figure 1a) in the Best Way

$g_{\parallel}$	$1.963 \pm 0.002$
$g_{\perp 1}$	$1.984 \pm 0.002$
$g_{\perp 2}$	$1.982 \pm 0.002$
$A_{\parallel}$	$166 \pm 2\text{ Oe}$
$A_{\perp 1}$	$58 \pm 2\text{ Oe}$
$A_{\perp 2}$	$54 \pm 2\text{ Oe}$

characteristic for the vanadyl porphyrin complexes.<sup>37</sup> The best fit was achieved with slightly non-axial  $g$  and HFI tensors. These features can refer to the different environments of  $\text{VO}^{2+}$  paramagnetic ions in asphaltene,<sup>38</sup> leading to a dispersion of  $g$  and HFI tensor components and, consequently, a broadening of the effective line width that corroborates the previous results.<sup>44</sup>

The ESR spectrum of asphaltene dissolved in benzene at  $T = 20\text{ }^{\circ}\text{C}$  is depicted in Figure 1b. The spectrum is very similar to the ESR spectrum of extracted asphaltene (Figure 1a), except hardly noticeable broadening of the HFS lines (Figure 1), and can be described with the same  $g$  and HFI tensors (Table 2).

The temperature increase of the asphaltene solution leads to the gradual broadening of the anisotropic HFS lines and the appearance of the eight-component isotropic spectrum (Figure 2). This is the manifestation of the effective averaging of the



**Figure 2.** ESR spectra of asphaltene dispersed in benzene with the volume ratio  $V_{\text{asphaltene}}/V_{\text{benzene}} \sim 1:3$ , registered at different temperatures *in situ* (the temperatures are shown near the spectra for convenience). The specimen was sealed inside the capillary with the outer and inner diameters of 2.8 and 1.2 mm, respectively. The ratio of solution volume (at normal conditions) to full volume is  $(V_{\text{asphaltene}} + V_{\text{benzene}})/V_{\text{full}} = 0.38$ . The average density of the benzene inside the capillary was equal to the critical value with the accuracy of 10%. The microwave frequency is  $\nu = 9.60\text{ GHz}$ .

anisotropic interactions because of the sufficiently fast rotation of the paramagnetic molecules. The residual asymmetry observed in the hyperfine structure of the  $\text{VO}^{2+}$  ion isotropic spectrum at  $T = 235\text{ }^{\circ}\text{C}$  that manifests itself in the different width and peak–peak intensity of the eight lines (Figure 2) is explained by the incomplete averaging of the anisotropies of the  $g$  factor and the HFI.<sup>45</sup> In this case, the line width depends upon the nuclear spin number  $m$  that can be well-defined by the equation  $\Delta H = A + Bm + Cm^2$  according to ref 42.

An analysis of the temperature dependences of the HFS line shape allows us to estimate the characteristic time  $\tau_{\text{rot}}$  of the reorientation of the paramagnetic molecules at a certain temperature. Indeed, the transition from an anisotropic spectrum to an isotropic spectrum occurs when the characteristic time of the molecule reorientation  $\tau_{\text{rot}}$  is about  $1/A_{\text{HFI}}$ ,<sup>42</sup> that is,  $\sim 4 \times 10^{-9}\text{ s}$  for the ESR spectra observed (Figure 1 and Table 2). It is known that  $\tau_{\text{rot}}$  at a given temperature is determined by the local viscosity  $\eta(T)$  and the characteristic radius  $R$  of the rotating particles using the Stokes–Einstein–Debye equation.

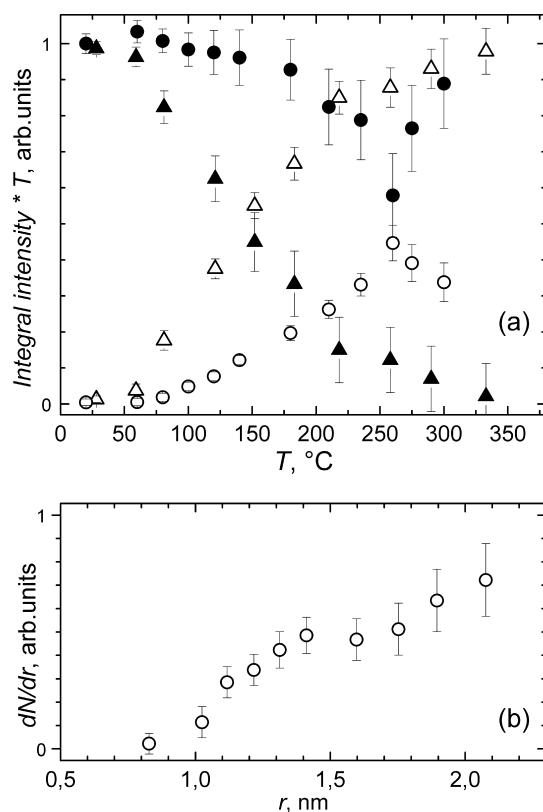
$$\tau_{\text{rot}} = (4\pi R^3/3)\eta(T)/(k_{\text{B}}T) \quad (1)$$

Thus, the analysis of the experimental ESR spectra in the temperature range, where the anisotropic spectrum transforms to the eight-component isotropic spectrum, can provide the information about the characteristic sizes of paramagnetic molecules or their aggregates containing vanadyl fragments. Indeed, the equation above gives us the average radius of the



rotating asphaltenes in the range of  $\sim 1\text{--}2$  nm using the benzene viscosity to define parameter  $\eta(T)$  that corresponds to the results obtained before.<sup>17</sup>

To estimate the size distribution of the asphaltene molecules dissolved in benzene and provide the information about the mobility of the paramagnetic molecules, the analysis of the different degrees of complexity can be used. For instance, the spectra observed (Figure 2) can be decomposed into two components: the isotropic spectrum corresponding to the fast rotating paramagnetic molecules and the anisotropic spectrum described by the anisotropic  $g$  and HFI tensors (Table 1). Figure 3 shows the temperature dependences of the integral



**Figure 3.** (a) Temperature dependence of integral intensity for isotropic (hollow symbols) and anisotropic (filled symbols) spectra components multiplied by  $T$  to compensate for the Curie–Weiss effect: (circle) asphaltene dispersed in benzene (see Figure 2) and (triangle) asphaltene in crude oil + benzene solution (Figure 4). (b) Size distribution of asphaltene molecules dispersed in benzene estimated via ESR data.

intensity for these two components multiplied by  $T$  that takes into account the changes of the magnetization of the paramagnetic system with the temperature according to the Curie–Weiss law.

The integral intensity of the isotropic component of the ESR spectra is proportional to the amount of vanadyl-containing asphaltene molecules that rotate fast enough with characteristic reorientation time  $\tau_{\text{rot}}$  less than  $\sim 10/A_{\text{HFI}}$  (i.e.,  $\sim 4 \times 10^{-10}$  s). As the temperature increases up to  $T \cong 260$  °C, the integral intensity of the isotropic spectrum grows (Figure 3), indicating the increase of the amount of fast rotating molecules. We can conclude that, as the temperature rises above 230 °C, most of the asphaltene molecules start to rotate at frequencies greater than  $2 \times 10^9$  s<sup>-1</sup>. Using eq 1 and the data given in Figure 3, one

can estimate the fraction of the molecules  $N_{\text{rot}}$  whose sizes are less than the critical size  $r_c(T_c)$ , and therefore, these molecules rotate faster than  $\tau_{\text{rot}} \sim 4 \times 10^{-9}$  s, where  $r_c$  can be defined at a certain temperature  $T_c$  using the following equation:

$$r_c(T_c) = [3k_B T_c (4 \times 10^{-9} \text{ s}) / (4\pi\eta(T_c))]^{1/3} \quad (2)$$

The derivative of the  $N_{\text{rot}}$  function by  $r$  gives the size distribution of asphaltene molecules containing paramagnetic ion. According to eq 2, the range of sizes in the size distribution function obtained using the ESR data is limited by the size of the largest asphaltene molecule that starts rotating at the highest temperature studied. The size distribution estimated using ESR data in the temperature range up to 260 °C (Figure 3b) corroborates the data obtained earlier by the SAXS technique for the same asphaltene species<sup>17</sup> with a slight shift ( $\sim 0.5$  nm) of the size distribution function to the higher values. This difference seems to be connected with the higher viscosity of the asphaltene solution compared to the benzene viscosity that was used for the calculation.

It is necessary to clarify two assumptions made to obtain conclusions above. First, we suggest that, studying the species, we deal with the paramagnetic molecules having the same or at least similar ESR parameters. It means that the ligand environment of the  $V^{4+}$  ion in asphaltene molecules should have a rather close structure. Also, we assume that there is no aggregation process of asphaltenes in benzene at the temperatures analyzed ( $< 260$  °C).

The last assumption seems to be non-valid at temperatures above 260 °C. The further temperature increase results in a noticeable drop of the isotropic component intensity and a decrease of the fraction of highly mobile asphaltene molecules (Figure 3). Because the average density of the benzene inside the capillary was about the critical value with the temperature increase up to  $\sim 300$  °C, the pressure in the capillary reaches a critical value for benzene ( $\sim 5$  MPa). According to the literature data, the considerable changes of the physical–chemical properties of the solvents are observed while it goes into the supercritical state.<sup>46</sup> In particular, while the system is near the critical point, the dissolving capacity of the solvent can vary drastically, even for small density changes.<sup>47</sup> Unfortunately, in contrast to  $\text{CO}_2$  and water, there is a lack of data concerning aromatic hydrocarbon solvation properties near their critical point. We suggest that the phenomenon observed can be associated with the drop (at least 1.6 times) of the benzene local density inside the sealed capillary at temperatures above 260 °C that anyway leads to the decrease of its solvation capabilities. As a result, asphaltene molecules can agglomerate and form larger aggregates. It leads to the increase of the characteristic reorientation time  $\tau_{\text{rot}}$  according to eq 1.

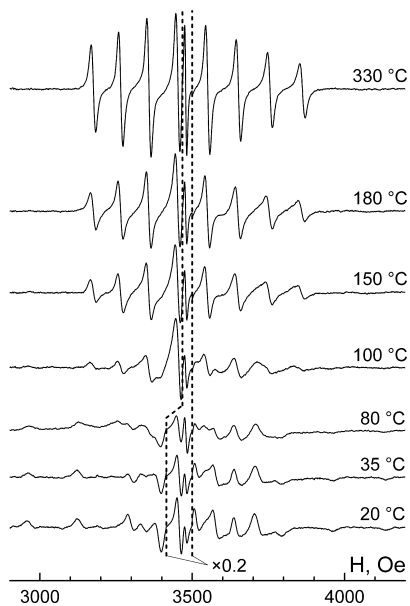
In the temperature range where the transition from the anisotropic to isotropic spectrum range occurs, the shape of the resonance absorption spectra is extremely sensitive to the  $\tau_{\text{rot}}$  value. The direct simulation of the spectrum in the transition region at a certain value  $\tau_{\text{rot}}$  allows us to obtain reliable information about the size of the rotating particle. Theoretical calculation of the spectra for asphaltene molecules of one size in the transition region shows that a relatively narrow temperature range exists, where the resonance absorption cannot be registered. This phenomenon is associated with a considerable broadening of the absorption lines in the transition regime. Indeed, while the total integral intensity of the absorption spectra remains the same, the line broadening

leads to a significant (at least 2 orders of magnitude) drop of the peak–peak intensity of the individual lines.

For a sufficiently wide size distribution of asphaltenes in the samples, it is necessary to solve the inverse problem to simulate experimental spectra. The simulation should also take into account the viscosity of the local environment of particular asphaltenes at a certain temperature. It requires time-consuming numerical calculations. At the same time, the description of intricate experimental spectra with a limited number of variable parameters makes the simulation of the EPR spectra of asphaltenes a reliable method to obtain information about the size distribution, local viscosity, and aggregation processes at different temperatures and pressures.

As an example, using the approach developed, it is very interesting to study the asphaltene mobility at elevated temperatures in crude oil *in situ*. The crude oil itself has the ESR spectrum that is very similar to those observed in extracted asphaltene species. This is related to the fact that the paramagnetic particles in the crude oil that can contribute to the ESR signal are concentrated in asphaltenes. Indeed, the oil species free of asphaltenes demonstrate no considerable ESR absorption.

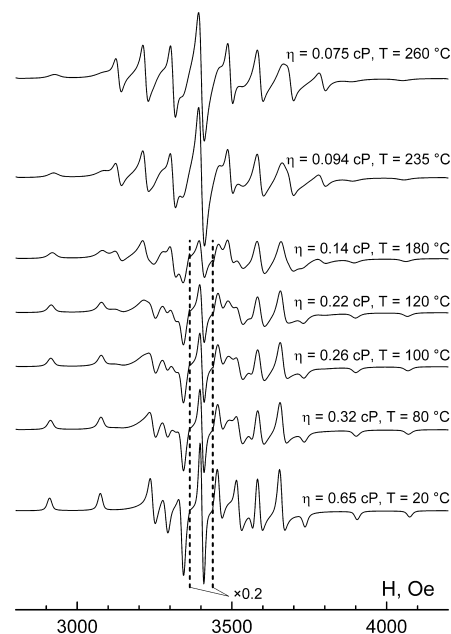
The heating of the crude oil to 150 °C almost does not affect the ESR spectra because of the high viscosity of crude oil. The dilution of oil with benzene provides the registration of the transition of the anisotropic spectrum to the isotropic spectrum and yields the information about the characteristic sizes of asphaltenes or their aggregates directly in crude oil (Figure 4). The data on the temperature dependence of the integral intensity for both isotropic and anisotropic components are included in Figure 3 itself. It can be seen that the mobility of asphaltenes increases with the temperature much faster compared to the asphaltene in benzene solution. Also, at  $T > 260$  °C, there is no reduction of the isotropic component of the



**Figure 4.** ESR spectra of asphaltene in crude oil + benzene solution with the volume ratio  $V_{\text{oil}}/V_{\text{benzene}} \sim 1:2$ , recorded at different temperatures *in situ* (the temperatures are shown near the spectra for convenience). The solution was sealed inside the capillary with the outer and inner diameters of 2.8 and 1.2 mm, respectively. The ratio of solution volume (at normal conditions) to full volume is  $(V_{\text{oil}} + V_{\text{benzene}})/V_{\text{full}} = 0.35$ . The microwave frequency is  $\nu = 9.75$  GHz.

spectrum with respect to an anisotropic component, as it was for the asphaltene/benzene system.

Figure 5 shows the simulated ESR spectra of vanadyl-containing molecules with a uniform size (radius) distribution



**Figure 5.** Theoretically calculated ESR spectra of asphaltene molecules that incorporate one  $\text{VO}^{2+}$  fragment each using the resonance parameters listed in Table 2. The spectra were simulated for the uniform size distribution of asphaltenes in the range from 0.8 to 6 nm. Characteristic rotational time values were deduced using benzene viscosity at certain temperatures with eq 2. The microwave frequency is  $\nu = 9.60$  GHz.

of the asphaltenes in the range from 0.8 to 6 nm that roughly describes the size distribution, which was previously observed experimentally by the SAXS technique for asphaltenes dissolved in benzene.<sup>17</sup> The EasySpin package was used to calculate the spectrum of individual paramagnetic molecules at different temperatures and specified values of the  $g$  factors and HFI parameters for different asphaltenes were taken into account via the line width parameters during the spectra simulation. The temperature dependence of the benzene viscosity was used for the calculation that obviously just roughly reflects the real situation in the asphaltene/benzene system. It is interesting to note that the simulated ESR spectra shown in Figure 5 describe all of the characteristic features of the experimental spectra shown in Figure 2, despite the simplicity of the model used.

The data obtained indicate the enhancing local mobility of asphaltenes in the oil compared to their mobility in benzene solution at the same temperature. In particular, the local mobility of asphaltenes observed at  $T \sim 120$  °C in the asphaltene/benzene system is reached already at  $T \sim 80$  °C in the oil/benzene system. Also, the similarity of the ESR spectra observed for these systems indicates the similarity of the size distribution of the asphaltenes in this temperature range. At the same time, it is impossible to describe the features of the ESR spectra in the oil/benzene system at higher temperatures (in particular, the increase of the fast rotating component intensity in the temperature range from 80 to 200 °C) using a fixed size distribution of asphaltenes and a monotonic temperature

dependence of the viscosity typical for the hydrocarbons, which points to the disaggregation processes of asphaltenes occurring at elevated temperatures in the oil/benzene system.

These results are in line with the data obtained earlier by Kazarian and co-workers.<sup>26,49</sup> The results suggest that the local mobility of asphaltenes depends upon all of the components, such as saturates, aromatics, resins, etc., present in the crude oil. The presence of a variety of chemical components in crude oil that are missing in the model solutions of asphaltenes can dramatically change the behavior of asphaltenes in the oil and provide their higher mobility in more viscous systems. Thus, while comparing the mobility of the asphaltenes and the stability of oil in a wide range of temperatures and pressures, one should take into account not only the amount of asphaltenes and other heavy fractions but also the other chemical components that are analyzed qualitatively.

## CONCLUSION

As a result of this work, the temperature-dependent rotational mobility of the asphaltene molecules and their aggregates in crude heavy oil samples has been investigated in comparison to the model asphaltene/benzene system using the quantitative analysis of the anisotropic interactions registered in the ESR spectra. The detailed analysis of the ESR spectra of the V<sup>4+</sup>-containing asphaltenes observed within a wide temperature range at elevated pressure and under an *in situ* regime allows us to separate the contributions of asphaltene molecules of different sizes that move with different characteristic rotational time.

Using the approach developed, the enhancing local mobility of asphaltenes in the crude oil compared to their mobility in benzene solution at the same temperature has been found. For the oil/benzene system, the gradual growth of the asphaltene mobility within the whole temperature range investigated was found (from 20 to 350 °C). For the asphaltene/benzene system, the growth of the asphaltene mobility is observed up to ~260 °C only, while at higher temperatures, the part of highly mobile asphaltenes decreases because of the asphaltene aggregation process that can be connected with the solvent transition to the supercritical state.

ESR data indicate that the features of the temperature dependence of the mobility of asphaltenes within the wide temperature range depend upon the overall chemical composition of the oil samples. The ESR *in situ* approach shows a good potential for further studies of dynamic behavior of asphaltenes on the molecular scale in crude oil and understanding processes that contribute to crude oil fouling.

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### Notes

The authors declare no competing financial interest.

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