

Low-temperature thermal decomposition of heavy petroleum distillates: interconnection between the electrical properties and concentration of paramagnetic centres

M Dolomatov^{1,2}, M Gafurov³, A Rodionov³, G Mamin³, L. Miquel González³,
A Vakhin³, A Petrov^{2,4,*}, R Bakhtizin¹, I Khairudinov^{2,4}, and S Orlinskii³

¹ Bashkir State University, 32 Validy Str., Ufa, Russia

² Ufa State Petroleum Technological University, 1 Kosmonavtov Str., Ufa, Russia

³ Kazan Federal University, 18 Kremlevskaya Str., Kazan, Russia

⁴ Institute of Petroleum Refining and Petrochemistry, 12 Inicativnaya Str., Ufa, Russia

E-mail: petrovchemistry@gmail.com

Abstract. Changes of paramagnetic centers (PC) concentration in petroleum dispersed systems (PDS) are studied in the process of low-temperature thermolysis. Complex investigation of physicochemical, rheological and electrophysical properties of high-boiling oil fractions is performed. Based on the analysis of the experimental results it can be concluded that the PDS under investigation can be regarded as amorphous broadband organic semiconductors for which PC plays a role of dopant. It shows the perspectives of the asphaltenes usage as a basis for the photovoltaic devices.

1. Introduction

Petroleum fluid can be considered as a petroleum disperse system (PDS) - a hybrid of a solution and a colloidal dispersion (of crystallizing waxes, self-associating asphaltenes, etc.) [1]. Understanding of complex behavior of PDS under the thermal treatment is expected to be a challenge. Nevertheless, as it was stressed by Evdokimov et al., relatively simple experiments on only one of the PDS components can shed light on details of phase transformations in such systems [2], [3].

As one of the constituents of PDS, a paramagnetic phase can be the subject of interest: one gram of PDS contains 10^{16} - 10^{21} paramagnetic centers (PC, [4]-[6]). The majority of PC is concentrated in the high-molecular PDS components such as asphaltenes, resins and polycyclic aromatic hydrocarbons (PAH). The content of the high-molecular PDS components could reach the values of 45 wt % in native oils and up to 73 wt % in natural asphalts and bitumen [4]. Assuming that asphaltenes and resins have molecular weight of about 1000 amu [4], they could contain up to one unpaired electron per molecule. Obviously, such high concentration of PC should (or could) affect not only the paramagnetic properties of substance but (at least partially) also the electrical qualities of PDS.

Electrical properties of asphaltenes and bitumen are the matter of intensive research for decades that are briefly reviewed in [7], [8]. It was shown that the temperature dependence of the electrical conductivity in some PDS resembles those for the organic broadband semiconductors [7], [9]-[11]. But there is still no detailed description of the process(es) that would adequately describe the thermal generation-recombination of PC in PDS and influence of PC on the electrical properties of PDS [12].



Among numerous additional motivations to investigate the processes of generation-recombination of PC in PDS, the most significant are related to understanding the mechanisms of photodegradation – the PC linewidth and radicals number decreases with sunlight irradiation time of some tenth of hours [13], as well as by the discrepancies in the PC concentrations derived from the conventional and pulsed EPR measurements [14].

2. Materials and Methods

Samples of asphalt and its group components (asphaltenes and maltenes) were investigated. Asphalt (Asphalt produced by Propane Deasphalting, APD) was obtained by means of second stage propane deasphaltization of the Western Siberian oil tar. The APD was fractionated in two steps. Firstly, asphaltenes and resins were precipitated by adding an excess (1:40) of cold isooctane (Sigma-Aldrich) followed by flushing in Soxhlet's apparatus with hot isooctane. The remaining residue was fractionated into asphaltenes and maltenes by passing the alcohol-benzene mixture (5:1) through a column. Endpoint maltenes fraction was isolated by evaporation of the solvent from the extract. The separation scheme is shown in Figure 1.

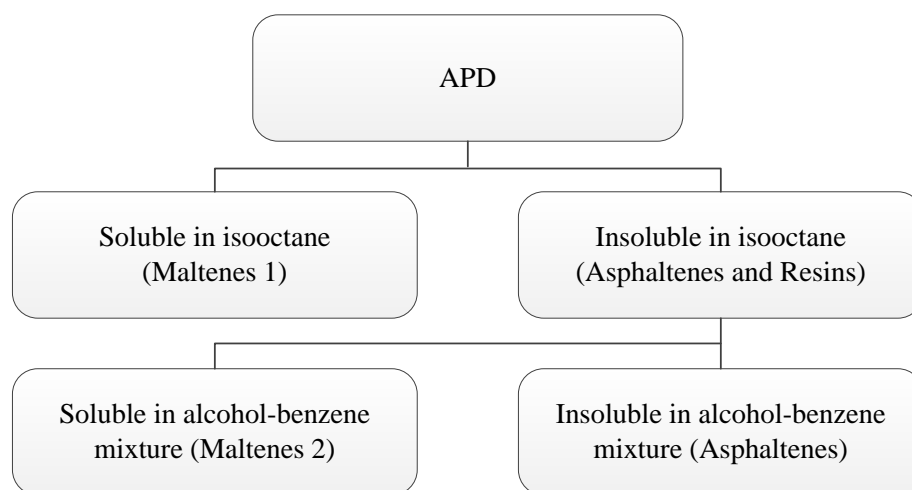


Figure 1. APD separation scheme.

The APD group composition was determined from SARA (Saturated and Aromatic hydrocarbons, Resins and Asphaltenes) analysis using a Gradient-M chromatograph (Ufa, Russia). 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. Elemental analysis was done by X-ray fluorescence measurements (Spectroscan Max GV, S.-Petersburg, Russia). The molecular weight was estimated by naphthalene cryoscopy.

Fourier-transform infrared (FTIR) spectra of asphaltenes and resins were detected using a Shimadzu IRAffinity-1S spectrophotometer in (400-4000) cm^{-1} range with the resolution of 1 cm^{-1} . Samples for IR analysis were prepared as follows. A small amount of the substance was triturated in an agate mortar, poured with hot toluene and thoroughly mixed. The resulting suspension was put on the plate and placed under the IR lamp to vaporize the toluene and dry the film.

Effective electron affinity (EEA) and the effective ionization potential (EIP) were determined from the analysis of the ultraviolet and visible absorption spectra on SF 2000 (Russia) spectrophotometer in the range of (190-780) nm with 1 nm step via the procedure described in [15].

Electrical measurements were performed as follows. Samples are placed into the cylindrical thermostatic cell consisting of a hollow bronze shell and fluoroplastic cover with the mounted aluminum electrode. The shell's bottom is utilized as the second electrode. Homogeneous heating of

the measuring cell was provided by the oil-to-oil thermostat, boiling point of the transformer oil is 220 °C. Yokogawa UT750 controller with thermocouple and digital display maintained the required heating rate and accuracy. The electric conductivity was measured in the temperature range of 25 – 165 °C with 20 °C increment. The species were kept at the required temperature during 30 minutes before the measurements' start to avoid adverse inertial effects. The measurements were done only for APD and maltenes due to the considerable complexity of accurate electrical measurements for solid asphaltenes.

EPR spectra of the samples were obtained using 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 – 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 samples (Cu-DETC solution and DPPH powder) with a known concentration of PC. Samples heating was occurred 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 (20 – 500) °C was obtained with (15 – 20) °C increment, heating rate 2 °C/min and temperature setting accuracy of not less than ± 2 °C ([16], [17]) Modulation amplitude 0.1 mT was chosen to investigate narrow EPR lines of free radicals. Microwave power level was equal to 1 mW in order to avoid saturation effects.

3. Results and Discussion.

Investigated APD contains saturated fraction of 8.5% by weight, aromatics – 58.6 wt %, resins – 30.4 wt % and asphaltenes – 17.8 wt %. Some physical and chemical properties for the investigated species are presented in Table 1.

Table 1. Physical properties of the investigated PDS species at 20 °C.

	APD	Asphaltenes	Maltenes
Density at 20 °C (kg/m ³)	1044	1084	978
Average molecular weight, amu	878	1250	669
Elemental composition, wt %			
C	87.0	81.0	84.2
H	10.4	7.7	10.8
S	1.6	4.8	2.2
N	0.30	1.6	0.5
O	0.60	4.9	2.3
Concentration of paramagnetic centers at RT, 10 ¹⁸ spin/g			
FR	1.5±0.3	9.0±1.2	4.1±0.5
VP	5.2±0.8	12.8±3.0	5.6±0.1
Electronic characteristics, eV			
EIP	6.18	5.47	6.41
EEA	2.12	1.78	2.04

Table 2 shows the values for the APD viscosity with temperature. Different models for the explanation of the temperature dependencies of η in PDS can be found in literature [18]. Our data can be adequately described by exponent based on the Arrhenius equation

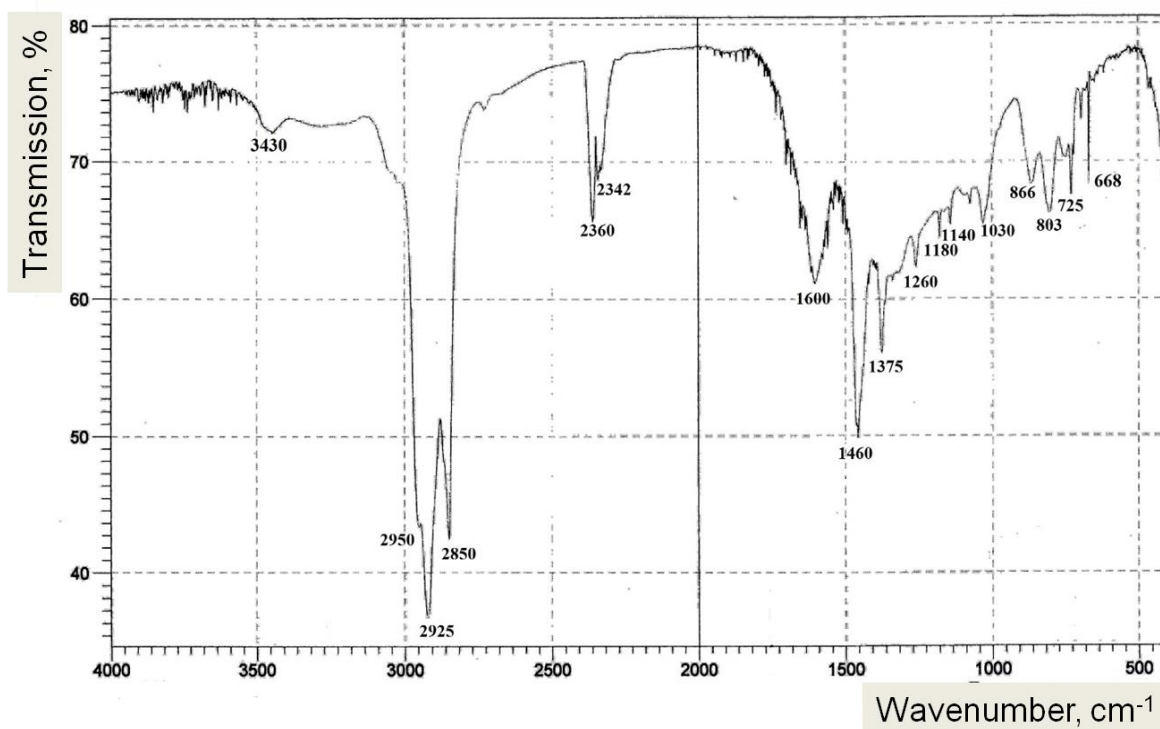
$$\eta = \eta_0 e^{\frac{E_a}{RT}} \quad (1)$$

where $\eta_0 = (3.0 \pm 1.2) \cdot 10^{-12}$ Pa·s, R is the ideal gas constant and $E_a = (86.1 \pm 0.9)$ kJ/mol is an activation energy for PDS viscous flow [19].

Table 2. Temperature dependence of the dynamic viscosity of APD

Temperature, °C	Dynamic viscosity (η), Pa·s
60	158.8
70	60.1
80	26.4
90	12.8
100	8.3
120	6.7
140	5.8
160	5.1

FTIR spectrum of asphaltenes extracted from APD is shown in Figure 2. Typical for the asphaltenes peaks are observed in the vicinity of $\approx 1600\text{ cm}^{-1}$ (stretching vibrations of the C = C bonds in the aromatic rings), ≈ 2850 , ≈ 2920 , ≈ 1460 and $\approx 1375\text{ cm}^{-1}$ (corresponding to the CH methyl and methylene groups stretching and deformation vibrations). The absorption bands at ≈ 803 , ≈ 866 , $\approx 694\text{ cm}^{-1}$ correspond to the strong substituted aromatics; the presence of alkyl substituents is proved by the peaks at ≈ 720 and $\approx 745\text{ cm}^{-1}$. The absorption bands at ≈ 694 , ≈ 1142 and $\approx 1180\text{ cm}^{-1}$ presumably correspond to OH groups in the tertiary and phenolic position as shown in ref. [20], [21]. Broad absorption band at $\approx 3432\text{ cm}^{-1}$ corresponds to the intra- and intermolecular hydrogen bonds, while at $\approx 1030\text{ cm}^{-1}$ (most likely) to the sulfoxide group. The intensive peak at $\approx 2360\text{ cm}^{-1}$ can be erroneously interpreted as due to the thiol functional group but it more likely corresponds to atmospheric CO_2 impurities, as the adjacent peak at $\approx 2342\text{ cm}^{-1}$ confirms ([20], [21]).

**Figure 2.** FTIR spectrum of asphaltenes.

The existence of PC is caused by the presence of d-metals (mainly V, Ni, Fe), delocalized π -electrons of the aromatic rings and stable free radicals in PDS. EPR patterns in all the studied samples are very similar. Figure 3 presents that for APD. The EPR spectra originate from the paramagnetic vanadyl complex VO^{2+} in porphyrins ($^{51}\text{V}^{4+}$, $3d^1$, electronic spin $S = 1/2$, nuclear spin $I = 7/2$) which will be denoted as VP and from the carbon free radicals (FR) (see [4], [5], [14], [22]). VP molecule is nearly planar defining thus the g -factor and hyperfine A tensor of axial symmetry. The powder EPR spectrum of VP consists of the 16 "lines" representing the 2×8 hyperfine patterns (the projection of I is allowed to take 8 values: $\pm 7/2$; $\pm 5/2$; $\pm 3/2$; $\pm 1/2$) for the parallel and the perpendicular complex orientations. The parameters of EPR spectra at RT are $g_{\parallel} = 1.964 \pm 0.001$, $g_{\perp} = 1.984 \pm 0.001$, $A_{\parallel} = 16.8 \pm 1.2$ mT, $A_{\perp} = 5.8 \pm 0.8$ mT [23]. The wide dispersion of EPR parameters are caused by the diversity of different structural classes of petroleum porphyrins in PDS that can contain different types of substitutions and binding moieties [22].

Detailed description of VP spectrum is given in refs. [14], [22], [24]. The changes of VP EPR spectra with temperature (pronounced at $T > 200$ °C) were investigated in details in [17]. As it follows from the present experiments, the intensity of VP EPR lines in the temperature range (20-200) °C practically obeys Curie law [4]. Accurate estimation of integral intensity of VP EPR spectrum at higher temperatures is tricky due to the mentioned EPR spectra transformation and is not done in the present research.

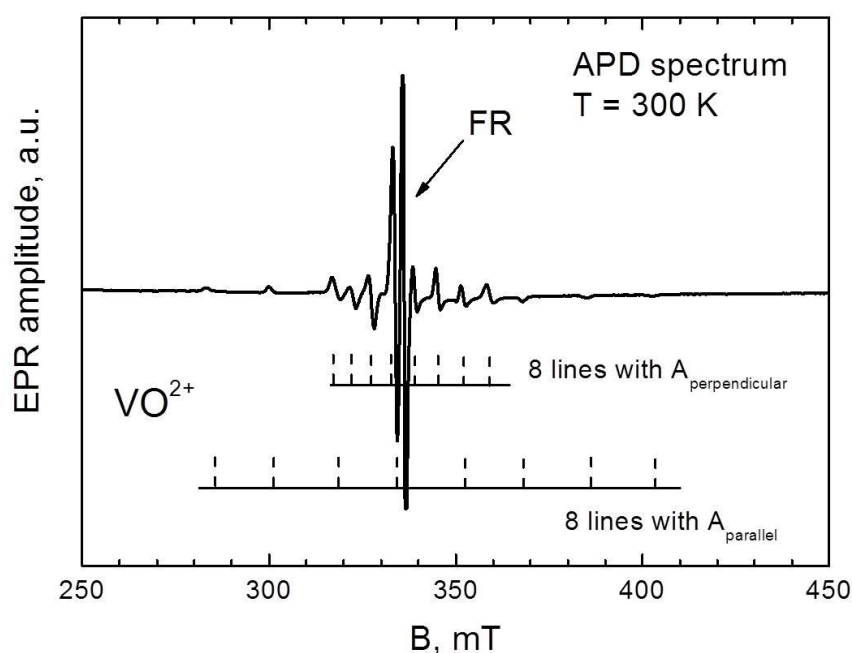


Figure 3. EPR spectrum of APD at $T = 300$ K. The lines belonging to FR and VP are marked.

The EPR spectrum of FR is a single line with the linewidth of $\Delta H_{1/2} = (0.52-0.58)$ mT situated at g -factor 2.0028 ± 0.0005 (Figure 4). FR lineshape is neither Gaussian (G) nor Lorentzian (L) but a mix of those in ratio of about $L/G \approx 60/40$ with the same values of g -factors. It is usually assumed that FR in PDS are mainly concentrated in asphaltenes and due to the delocalized π -electrons of the aromatic rings and stable organic radicals of the side chains [4]. The variations of EPR parameters can be caused by the diversity of different types of unresolved in EPR FRs some of which are anisotropic [6]. While the FR linewidth, lineshape and line position is all investigated fractions do not vary with

temperature within the accuracy of our measurements, the intensity I of FR increases non-monotonically (Figure 5). To visualize the $I(T)$ dependencies without Curie contributions, the abscissa and ordinate axis are chosen to be $1000/T$ and $(I \cdot T)$, correspondingly. In the case of pure Curie contribution, the $(I \cdot T)$ would be parallel to the abscissa.

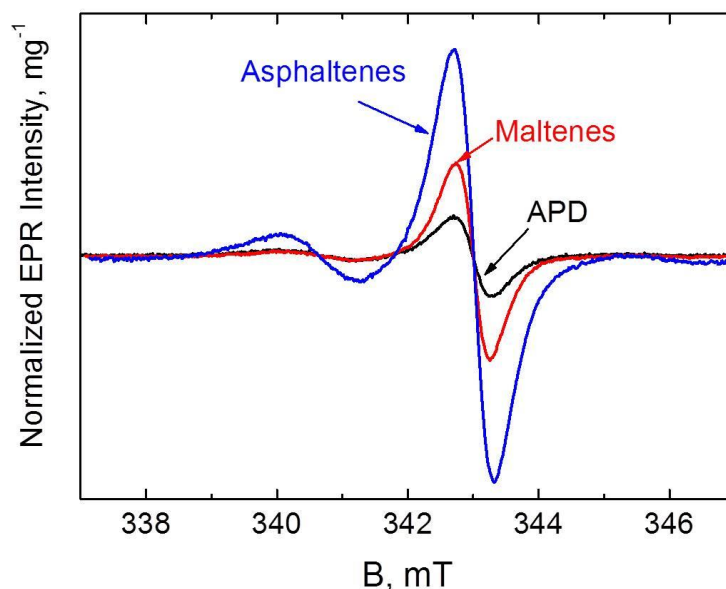


Figure 4. EPR spectra of FR in the investigated samples at $T = 300$ K normalized to the sample masses.

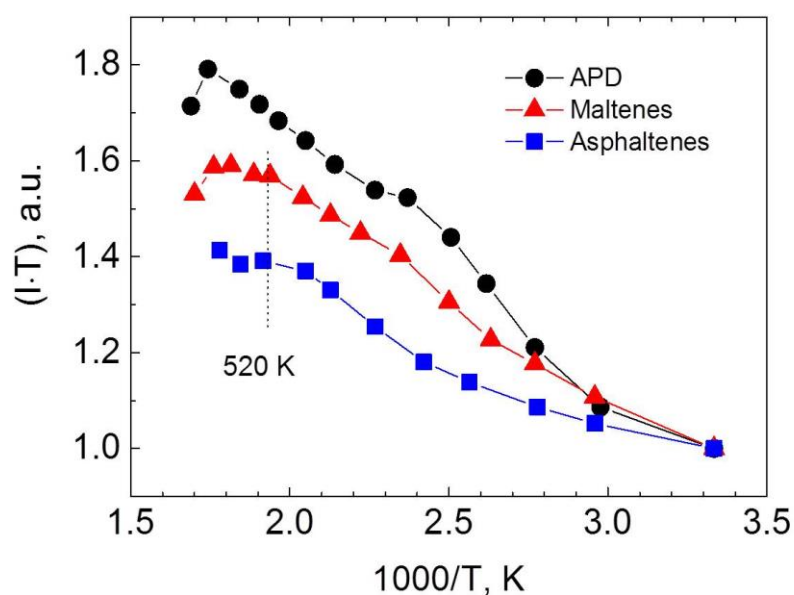


Figure 5. Dependencies of FR relative EPR intensities multiplied by the absolute temperature on the reverse absolute temperature. A dashed line corresponds to $T = 520$ K.

It has to be noted that for coal the lineshape of EPR spectra for FR are conventionally described by superposition of one Gaussian and up to 3 Lorentzian lines with g -factors from 2.0025 for π radicals located on aliphatic and/or aromatic hydrocarbons up to 2.0081 for sulfur containing radicals and strong temperature dependences of g -factors in the range (2.0025 - 2.0040) and linewidths $\Delta H_{1/2}$ are sometimes observed (see [25]-[27]). Obviously, the behavior of EPR parameters of samples studied in this work differs significantly from the mentioned above results. It means in its turn that the proposed for coals explanations of thermal changes of some paramagnetic properties could not be just copy-pasted for PDS systems.

Temperature dependence of EPR intensity for “free” radicals in PDS and other organic systems is conventionally explained by thermal activation of the singlet-triplet transition as it follows from [4], [5], [28]. However, our EPR data do not fully obey the model proposed there. Apparently, it is due to the FR generation and recombination. Carbon bonds weakened by conjugation with aromatic rings of asphaltenes and resins can be easily disintegrated, serving as sources of “free” radicals. The reverse process of FR recombination is also possible and should be taken into account. The complex character of the temperature dependence of PC concentration can be ascribed to the existence of different competitive processes. From one side, the viscosity decrease means the higher rate (frequency) for the PC collisions. Therefore, with temperature and viscosity lowering, the recombination rate increases. From other side, the amount of PC increases with temperature rising and the viscosity decrease. It leads to the breaking of the chemical bonds weakened by conjugation with aromatic moieties of asphaltenes. We hope to offer an appropriate kinetic model that describes the mentioned process(es) in our next publications. One of the possible models is proposed in our recent work [27].

Table 3 represents the temperature dependence of the electrical conductivity of the samples. At ambient pressure and $T = 25\text{ }^{\circ}\text{C}$ the conductivity is less than $10^{-11}\text{ }\Omega\text{m}^{-1}\cdot\text{m}^{-1}$. With the temperature increase in the range of $T = (50-180)\text{ }^{\circ}\text{C}$ a dramatic raise of conductivity up to $10^{-5}\text{ }\Omega\text{m}^{-1}\cdot\text{m}^{-1}$ is to obtain. Qualitatively, the conductivity measurements correlate with the temperature dependencies of EPR intensities (Figure 5) and with the higher concentrations of PC in maltenes in comparison to APD (Table 1) that define the earlier begin of the “dielectric-semiconductor” phase transition for maltenes and their higher conductivity at the elevated temperatures.

Table 3. The temperature dependence of the electrical conductivity of the samples

Temperature, $^{\circ}\text{C}$	Electrical conductivity, $10^{-9}\cdot\Omega\text{m}^{-1}\cdot\text{m}^{-1}$	
	APD	Maltenes
25	<0.01	<0.01
45	<0.01	<0.01
65	0.2	35
85	5	180
105	20	470
125	110	790
145	300	1400
165	750	2800

There are some evidences that the electrical conductivity in PDS is defined by the charge carriers in asphaltenes [7] and “free” radicals participate in the charge transfer [9]. It can be supposed that as for the other high polymers, the PDS conductivity can be at least partially explained by the jump mechanism (see [7], [11], [30]-[33]).

As shown in Table 1, the ionization energy of the samples is low (EIP varies in the range 5.47-6.41 eV, while EEA in the range 1.78-2.12 eV) and comparable to the ionization energy of PAH having more than four aromatic rings i.e. corresponds to the free radical containing fragments [] This

suggestion is confirmed by quantum-chemical calculations [34] and by the electrical conductivity measurements at different temperatures [30], [34]-[36]

Following the results and discussion described above, we can conclude that at least the paramagnetic phase of PDS can be regarded as an amorphous organic semiconductor. The increase of the unpaired electrons with temperature leads to the excess of holes and appearance of the *p*-type semiconductivity. Additionally, the PC as donors of electrons may narrow down the value of the dielectric/semiconductor band gap. All these results in the increase of the concentration of charge carries in the asphaltene containing substances. It means that the control of the “free” radical concentration might be used to obtain the asphaltene based semiconductors with the definite semiconducting properties. This feature could be fruitfully exploited for the construction of new asphaltenes’ based photovoltaic devices [37].

4. Conclusion

Complex investigation of physicochemical, rheological and electrophysical properties of high-boiling oil fractions is performed. The results confirm the conclusion about the stable free radicals generation in the PDS multicomponent medium with temperature. The both electrical conductivity and intensity of EPR line with temperature could be explained by radicals accumulation and recombination processes. It is suggested that at least the paramagnetic phase of PDS can be considered as an organic broadband semiconductor. It shows the perspectives of the asphaltenes’ usage as a substrate for the photovoltaic devices the properties of which can be changed through the manipulation of electron spins concentration.

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