Structure and electrophysical properties of materials based on nanoparticles of oil asphaltenes

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This paper is a generalization of the authors' works in the field of asphaltene physics fulfilled in recent years. Specific features of the "insulator-semiconductor" phase transition in high-boiling hydrocarbon fractions are discussed. It is shown that the active resistance of the samples decreases with heating to $(65-85)^0$ C. At the same time, the concentration of paramagnetic centers increases, which is confirmed by the EPR. The growth of electrical conductivity in high-boiling hydrocarbon fractions containing asphaltenes is caused by the temperature generation of charge carriers – free radicals (spins) formed as a result of the rupture of weak carbon-carbon bonds in molecules weakened by conjugation with aromatic rings. The energy of rupture of such bonds is rather low and can be as low as 40 kJ/mol. All these facts confirm the hypothesis of the authors that in the samples a phase transition occurs from the "insulator" state to the "semiconductor" state. The dielectric-semiconductor phase transition is also due to the generation of stable free radicals, since they are strong electron acceptors and reduce the width of the forbidden band of the material. Quantum-chemical calculations confirm this hypothesis. In addition, quantum-chemical calculations of the supramolecular, molecular, and electronic structure of asphaltene nanoparticles have been carried out. An experimental study of asphaltene crystallites by the AFM method was carried out. Theoretical calculations are reasonably confirmed by the AFM data.

Keywords: nanoparticles, oil asphaltenes, carbon-carbon bonds.

Introduction

Organic semiconductor materials are increasingly widely used in electronics, photonics and other applications, but the majority of organic semiconductors are characterized by high production costs, as they are created by multi-stage organic synthesis. Therefore, the search for cheaper natural organic materials for electronics is an actual practical and scientific task. Petroleum asphaltenes and colloidal systems based on them are promising substances to be used as organic semiconductors. Asphaltenes are polycyclic substances found in crude oils and high-boiling distillates. Asphaltenes mainly contain polyaromatic carbon with N, S, O-compounds in combination with a small amount of vanadium and nickel contained in porphyrin structures. The average molecular weight of these substances is in the range of 400 to 2500 units. Molecules of asphaltenes can contain 5-10 benzene and naphthenic rings in their structure [1-3].

The purpose of this work is to generalize the data on electronic and chemical structure of petroleum asphaltenes obtained over recent years. Special attention is paid to the estimation of parameters of supramolecular structure of crystallites of nanoparticles of oil asphaltenes by the method of molecular mechanics.

Asphaltenes as semiconductors.

It is known that asphaltenes are paramagnetics [4], and the concentration of free radicals in them is $10^{19} - 10^{20}$ spin/g. It was shown in [4, 5] that an increase in the temperature in such systems leads to an increase in the concentration of paramagnetic centers (PMCs) due to homolytic disruption of carbon-carbon bonds(1), weakened by conjugation with aromatic fragments of ASB molecules forming a paramagnetic phase.

$$R_1 - H_2 - CH_2 - R_2 \leftrightarrow R_1 - CH_2^o + CH_2^o - R_2, \tag{1}$$

where R_1 and R_2 are polycyclic aromatic fragments or benzene nuclei, are free stable radicals. The energy of rupture of such bonds is rather low and can reach 40 kJ/mol [4]. According to F.G. Unger the dispersed phase of such disperse systems consists of paramagnetic high-molecular asphalt-resinous substances (ASB), distributed in a diamagnetic hydrocarbon dispersion medium [4]. Conductivity of asphaltene-containing materials based on asphaltites [6] and asphalt-resinous monomers as well as deasphalting of asphalt was studied in [7]. With increasing temperature in systems containing asphaltenes, the concentration of paramagnetic centers and electrical conductivity increase. It was established in [8-11] that the paramagnetic phase of asphaltenes, in which stable free radicals are present, belongs to the broadband amorphous organic semiconductors with a band gap of (2.5-3) eV and diamagnetic phase refers to dielectrics. In these studies, a phase transition was observed from the "insulator" state to the "semiconductor" state. This phase transition is accompanied by a sharp jump in electrical conductivity.

In [7, 10] the temperature dependence of the electrical conductivity of asphalts in the temperature range (5-110) °C (Table 1) was studied, and the temperature hysteresis of electrical conductivity was established [11]. The temperature dependence of the electrical conductivity of high-boiling carbohydrate fractions forms a bend in the temperature range (65-85) °C, the tangent of the angle of dielectric losses sharply increases above (65-85) °C. The active resistance of samples decreases with heating to (65-85) °C, and then sharply increases. In this case, the complex and reactive resistances continue to decrease with further heating.

Table 1.
Electrophysical properties of propane deasphalting asphalt [7].

Conductivity, $Om^{-1}m^{-1}$	Temperature, ^oC	Conductivity, $Om^{-1}m^{-1}$
1.00×10^{-5}	120	1.3×10^{-7}
5.10×10^{-8}	80	7.9×10^{-10}
3.06×10^{-8}	75	6.7×10^{-10}
3.45×10^{-9}	70	6.7×10^{-10}
8.80×10^{-11}	65	3.2×10^{-10}
2.50×10^{-11}	60	2.1×10^{-10}
–	50	2.9×10^{-11}
–	45	5.9×10^{-12}
–	20	1.86×10^{-13}

The dependence of the conductivity on temperature (Table 1) is obviously related to the specificity of electron-hole conduction at a low temperature.

In this case, the formation of excitons is hampered by entropy restrictions on the mobility of charge carriers. As the temperature increases, the mobility of particles with a semiconductor and quasimolecular band structures increases, which facilitates transfer of electrons. Apparently, this mechanism of electrical conductivity is universal for all types of systems containing asphaltenes, including concentrates of asphaltenes (asphalts, tar, etc.).

It is shown that the dielectric properties predominate in the molecular form (diamagnetic phase) of asphaltenes, and the free-radical form (paramagnetic phase) plays the role of an alloying addition [10]. The results of studying of asphaltenes extracted from petroleum raw materials by the methods of electronic phenomenological spectroscopy [12] show low values of the effective ionization potential of molecules (up to 4.70 eV) and high values of effective electron affinity to molecules (up to 2.10 eV), which indicates the possibility of their use as materials with a wide range of electrically conductive and donor-acceptor properties.

The above confirms the results of quantum chemical calculations of model fragments of asphaltenes [13, 14], carried out using structural chemical data, which show ionization values from 6.36 to 7.22 eV, electron affinities from 0.72 to 1.65 eV - for molecular forms; and ionization potentials from 4.94 to 5.57 eV, electron affinity - from 1.78 to 2.35 eV for free-radical forms. The width of the band gap of molecular fragments of oil asphaltenes is 5.36-6.54 eV, for free radicals it is (2.75-3.54) eV. Thus, it follows from the calculations that the diamagnetic phase of asphaltene is a dielectric and the paramagnetic phase is a wide-gap amorphous semiconductor, thereby confirming the existence of a donor-acceptor complex in asphaltene molecules, which is an additional factor in stabilizing their supermolecular structure.

This has been shown in [10, 15], and some characteristics (see Table 2) confirm this result, and together with the existence of equilibrium in process (1) and taking into account their physical properties, it is possible to consider high-boiling hydrocarbon fractions and asphaltenes as multicomponent organic spin glass (MOSS). Despite the above results, the specific features of MOSS charge transfer and electrical conductivity have not been systematized and are insufficiently studied.

Convincing evidence of the role of the paramagnetic phase in the formation of electroconductive properties of asphaltenes was obtained using the EPR method in [16].

Method of calculation

As molecular fragments of asphaltenes, structures with different ratios of aromatic and naphthenic rings were used. Molecular masses of structures are in the range from 500 to 1000 amu, the ratio C/H=(8.4-9.3). According to the chemical analysis data, the presence of nitrogen and oxygen atoms is assumed. To account for heteroatoms, structures containing pyridine rings and lateral oxygen-containing functional groups are considered [13]. The corresponding structures are presented in Table 3.

For quantum chemical calculations, the non-empirical method of Hartree-Fock quantum chemistry RHF /3-21G** and the method of molecular mechanics MM2 with full optimization of geometry were used. The band structure was

calculated taking into account the energy of formation of Frenkel excitons in asphaltene nanoparticles. It has been found that molecular fragments of petroleum asphaltenes have a concave "bowl-shaped" structure. The value of the dihedral angle α between virtual planes of aromatic and naphthenic rings is in the range (154-164) °C. Molecular fragments with a large number of naphthenic rings have an irregular, nonplanar "broken" structure with respect to the plane of benzene rings [13, 14].

Table 2.
Properties of inorganic and organic spin glasses [10,15].

Characteristics	Inorganic spin glasses	Organic spin glasses
Relative concentration of paramagnetic particles	from (10-3) to (10-1)	from (10-3) to (10-1)
State	Glassy	Liquid and glassy
Long-range order	No	No
Electronconductivity	Yes	Yes
Inorganic carriers of paramagnetism	Ions ofd-elements of metals	Ions ofd-elements of metals(V, Ni, Fe)
Organic carriers of paramagnetism	No	Organic stable radicals
Diamagnetic phase		Organic multi component (malts)
Dependence of magnetic susceptibility on temperature	Yes	Yes
Magnetic susceptibility	>0	> 0
g-factor	2.0020±0.0030	2.0023-2.0054

The first adiabatic ionization potentials of molecular asphaltene nanoparticles calculated for the above-described structures on the basis of the Kupmans theorem range from 6.36 to 6.99 eV. As the number of benzene rings in the molecular structures of asphaltenes containing one nitrogen atom increases from 7 to 9, the PI values increase from 6.58 to 6.99 eV. The values of the dipole moments are in the range from 0.79 to 2.48 D. To study the chemical and band structure within the framework of the Frenkel exciton model, the molecular mechanics method and the non-empirical Hartree-Fock methods were used. To study the structural characteristics of oil asphaltene crystallites, models consisting of two, three, four, five and six plates of molecular fragments of trimers of molecular particles of asphaltenes were used (Table 3). Structure of the crystalline oil asphaltenes containing 4 plates is showed on Figure 1.

As a result of investigations, the structural characteristics of the formed crystallites were determined (Table 3). It can be seen from the table that when the number of crystallite plates increases, the energy of crystallite formation increases from 490.48 to 2570.03 kJ/mol. In this case, the diameter of the particle (d) increases from 4.44 to 5.07 nm, the thickness of the crystallite (H) increases from 5.40 to 24.22 nm. The distance between individual monostructures (h) does not change and is in the range from 0.35 to 0.39 nm.

Table 3.
Structural characteristics of crystallites of petroleum asphaltenes.

Structure	Molecular mass, a.m.u.	Energy of formation, kJ/mol	Interplanar spaceh, nm	Crystallite height H, nm	Diameter d, nm	Width of the forbidden band, eV
Crystallite consisting of one plate	1416	-	-	-	-	3.18
Crystallite consisting of two plates	2832	490.477	0.35	0.54	4.44	2.97
Crystallite consisting of three plates	4248	1023.14	0.34	1.18	4.62	2.93
Crystallite consisting of four plates	5624	1549.92	0.36	1.48	4.67	2.91
Crystallite consisting of five plates	7080	2049.58	0.35-0.39	2.09	4.72	2.03
Crystallite consisting of six plates	8495	2570.03	0.35-0.36	2.42	5.07	2.01

But the P_n value decreases again, in general significantly, for the (N_m +3)-precursor while the ($Q\beta$-S_n) window still increases from (N_m +2) to (N_m +3). This phenomenon is clearly manifested in the case of the Z = 19 chain after the N=28 shell closure [6] as illustrated by Figure 1.

Investigations of oil asphaltenesl from the Kiengop deposit by the AFM method [11] showed that the supermolecular structure of objects with a resolution of the order of 1 micron is a quasi-ordered gel-like structure consisting of micelles-associated molecules of asphaltenes (Figure 2). The average particle concentration in the dispersed phase is 144 particles per 1 μ^2. A more detailed analysis at a resolution of up to 500 nm (Figure 3) shows that the distance between micelles is about 20-50 nm. In this case, the thickness of particles up to 100 nm in diameter does not exceed 3 nm, which indicates stacking of structures. These figures show that the theoretical calculations are reasonably confirmed by the AFM data.
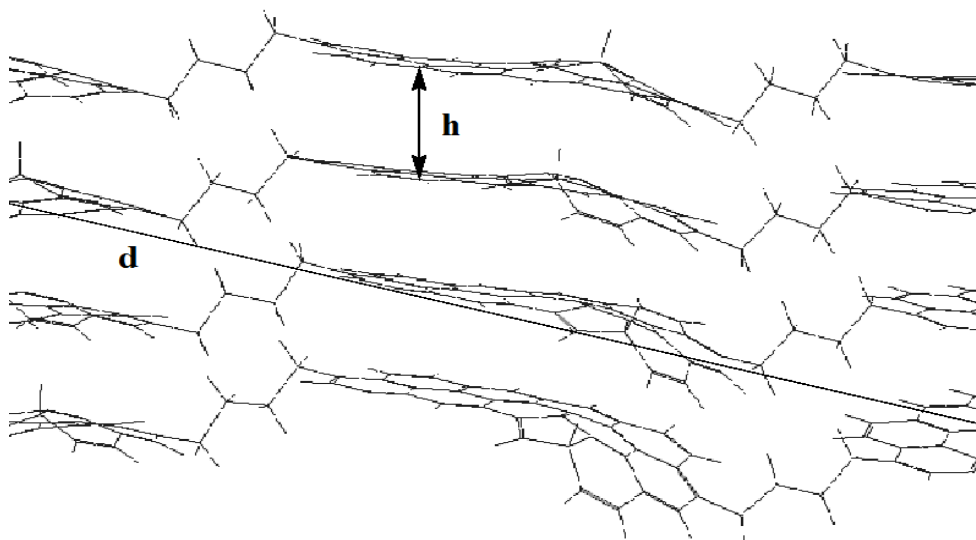
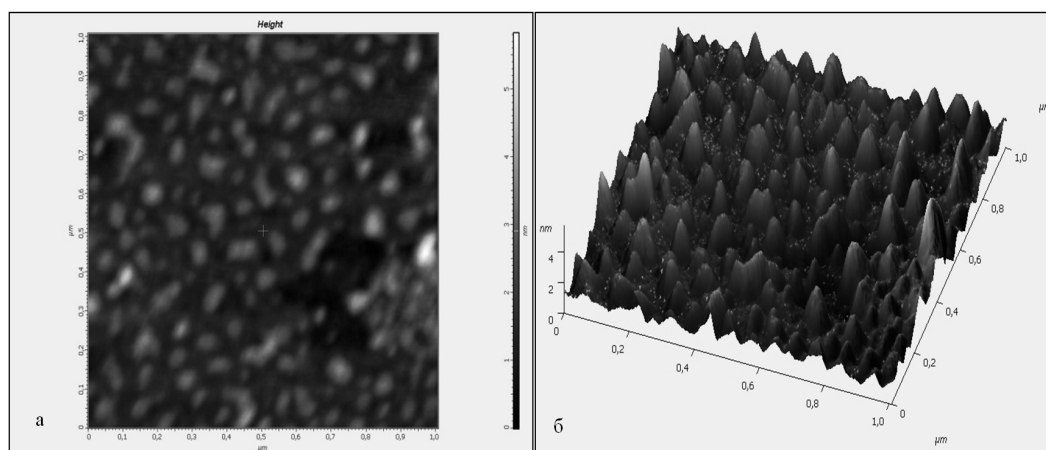Figure 1. Structure of the crystalline oil asphaltenes containing 4 plates.

Figure 2. Results of investigation of the supermolecular structure of Udmurt oil asphaltenes by the AFM method with a 1 micron precision: a-2D format, b-3D format.
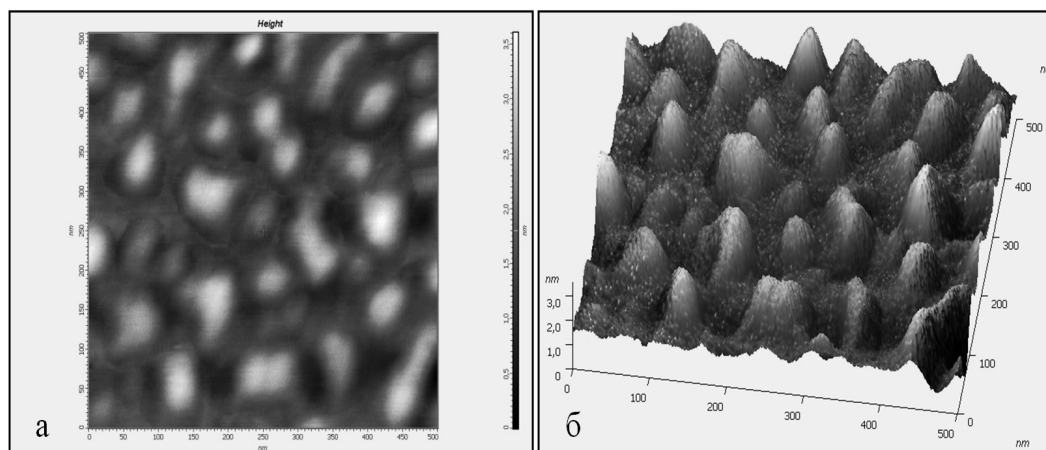

Figure 3. Results of investigation of the supermolecular structure of Udmurt oil asphaltenes by the AFM method with a 1 micron precision: a-2D format, b-3D format.

Conclusion

On the totality of the electrophysical properties: specific conductivity, width of the forbidden band, ionization potential, electron affinity, asphaltenes belong

to the class of broadband organic semiconductors. In the aggregate of magnetic and structural-morphological properties - belong to multicomponent spin glasses. Therefore, asphaltenes are unique objects of nanoelectronics.

Acknowledgments

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