

Asphaltenes as new objects for nanoelectronics

M Yu Dolomatov^{1,2}, A M Petrov¹, R Z Bakhtizin¹, M M Dolomatova¹, I R Khairudinov², S A Shutkova¹, E A Kovaleva¹, N Kh Paymurzina¹

¹Department of physical electronics and nanophysics, Bashkir State University, 32, Validy Str., Ufa 450076, Russia

²Department of Technology of oil and gas, Ufa State Petroleum Technical University, 1, Kosmonavtov Str., Ufa 450062, Russia

E-mail: dolomatov@gmail.com

Abstract. Abstract. Modern carbon nanomaterials (carbon nanotubes, graphenes, fullerenes, polycyclic molecules) are products of rather complicated technologies. Therefore development of new not expensive materials on the basis of natural substances, in particular high-molecular compounds of oil – asphaltenes, is actual for nanoelectronics. Asphaltenes are complex materials that are found in crude oil, bitumen and high-boiling hydrocarbons distillates. Usually asphaltenes are composed mainly of polyaromatic carbon with a small amount of vanadium and nickel, which are in porphyrin structures. Molecules of asphaltenes may contain 5-10-member benzene and naphthenic rings in their structure and also have paramagnetic centers. A variety of techniques: electronic phenomenological spectroscopy (EPS), atomic force microscopy (AFM) and quantum chemistry calculations were used to define the structure of oil asphaltenes. It was supposed that asphaltene fraction is a strong donor (ionization potential 4.10-6.70 eV) and an acceptor (electron affinity 1.80-2.50 eV). The structures of asphaltenes fragments were calculated by RHF-6-31G** methods. AFM images of asphaltenes obtained from crude oil showed the presence of structure fragments ranged from 3 to 10 nm, disposed to strong intermolecular interactions. We used doped compounds for formation of wide band gap amorphous semiconductors from a concentrates of asphaltens. Changes of conductivity in dispersed petroleum systems (DPS) were studied during a pyrolysis at 500 K. The numerous experiments defined of conductivity testify about phase transitions dielectric – semiconductor in DPS for range of 360 – 400 K. The main conclusion is paramagnetic phase of asphaltenes is organic amorphous wide band gap semiconductor. Besides this substance can be consider as an organic spin glasses.

1. Introduction

Modern carbon nanomaterials are expensive products of difficult technology (carbon nanotubes, graphenes, fullerenes, polycyclic molecules). Therefore, search of new cheap materials based on natural substances, in particular high-molecular compounds of petroleum – asphaltenes, is actual for nanoelectronics. Asphaltenes are complex substances that are found in crude oil, bitumen and high-boiling hydrocarbons distillates [1]. Asphaltenes are composed mainly of polyaromatic carbon with vanadium and nickel traces, which are in porphyrin structures. Molecules of asphaltenes may contain 5-10-member benzene and naphthenic rings in their structure. Asphaltenes have paramagnetic centers. We had the research task to define electron, molecular and supramolecular structure of various asphaltenes.

2. Objects and methods

Experimental methods of electronic phenomenological spectroscopy (EPS) [2], atomic force microscopy (AFM) and quantum chemistry were used to definite the structure of petroleum asphaltenes. The EPS is based on the regularities of the relations between the absorption coefficients and electronic properties of the substance. Effective Ionization potential (EIP) and effective electron affinity (EEA) of



asphaltenes have been estimated according to empirical dependences linking these characteristics with integral force of oscillator (1) and (2) in UV and/or VIS spectrum regions under consideration:

$$E = \alpha_1 + \alpha_2 \theta \quad (1)$$

$$\theta = \int_{\varepsilon_1}^{\varepsilon_2} \int_{\lambda_1}^{\lambda_2} f(\varepsilon_\lambda) d\varepsilon d\lambda \quad (2)$$

where E is effective ionization potential or effective electron affinity, eV; α_1 , α_2 are empirically determined coefficients, eV and eV·mole⁻¹·nm⁻¹ respectively; ε_λ is molar absorption coefficient; λ_1 , λ_2 are borders of wavelengths in the spectrum in UV and (or) visible regions.

The structures of asphaltenes model fragments were calculated by RHF-6-31G** methods [3].

Electrical measurements were performed as follows: samples were placed in a cylindrical thermostatic cell consisting of a hollow bronze shell and fluoroplastic cover with mounted aluminum electrode. The shell's bottom utilized as the second electrode. The oil-to-oil thermostat, boiling point of the transformer oil - 220 °C., provided uniform heating of measuring cell. Yokogawa UT750 controller with thermocouple and digital display maintained the required heating rate and accuracy. Laboratory setup for the electrical properties measurements was assembled on NI ELVIS II (National Instruments) hardware-software complex. The temperature dependence of electric conductivity for the samples was obtained in the temperature range of 25 – 165 °C with 20 °C increment. The specimens were kept at the required temperature during 30 minutes before measurements start to avoid adverse inertial effects.

3. Results and discussion

It was supposed, during the origin data study of different asphaltenes and hydrocarbon systems (table 1), that asphaltene fraction is a strong electron donor and acceptor at the same time (IP=4.10 - 6.70 eV, EA=1.80 - 2.50 eV). This means, that the processes in asphaltenes solutions and concentrates, including those related to ARPD (asphalt, resin and paraffin deposits), may be described by the formation of molecular charge-transfer complexes.

Table 1. Electronic structure data of the semiconductors on the base of resins and asphaltenes

Asphaltenes	EIP, eV	EEA, eV	Forbidden gap, eV	Imref, eV
Asphaltenes of Radaevsk oilfield	5.70	1.85	3.85	1.93
Asphaltenes of Surgut oilfield	5.20-5.70	2.10-2.50	3.10-3.20	1.55-1.60
Asphaltenes of straight-run stocks	4.37-5.27	2.44-2.50	1.93-2.77	0.96-1.38
Asphaltenes of tar	4.70-4.90	2.10-2.15	2.60-2.75	1.30-1.38
Asphaltenes of Kushkul oilfield	5.20	1.90	3.30	1.65

The earlier made assumption, that paramagnetic phase of oil asphaltenes belongs to amorphous, compensated, wideband semiconductors is confirmed. AFM study of asphaltenes obtained from crude oil showed the presence of structure fragments ranged from 3 nm to 10 nm, disposed to strong intermolecular interactions. We used different doped compounds for formation of wide gap amorphous semiconductors from a concentrates of asphaltens. Thus, paramagnetic phase of asphaltenes can be used as available semiconductors for nanoelectronics.

The calculations results are confirmed by the EPS spectroscopic data (table 2).

Table 2. Computed and experimental ranges of IP and EA

Data	IP, eV	EA, eV
By UV and VIS spectrums	4.37-5.70	1.85-2.50
Computed molecular fragments (RHF/3-21G** method)	6.36-7.56	0.54-1.65
IP and EA estimation of free-radical fragments	4.92-5.79	1.78-2.45

According to the experimental estimates, IP values are in the range from 4.37 to 5.70 eV, EA - in the range from 1.85 to 2.50 eV. Thus, the best agreement with the experiment is observed for the free radical fragments. Quantum-chemical calculations of molecular and radical fragments with total geometry optimization by molecular mechanics and methods 6-31G** display that the structure of naphtheno-aromatic fragments of asphaltenes is nonplanar and has a “bowl” form (figure 1). The computing of condensed model asphaltene structures shows, that in extreme case of total aromatization of all rings condensed asphaltene fragment have the “plate” structure (figure 1).

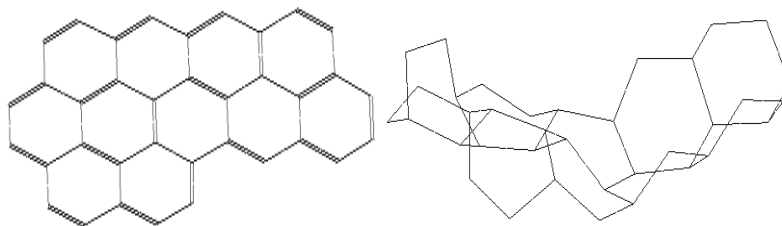


Fig. 1. Condensed models of the asphaltene structure fragments in the cases of total aromatization of the rings and double bonds full absence ("bowl")

There is electrons charge carrier in the asphaltenes [4, 5]. The asphaltenes conductivity were determine of the jump mechanism, as another polycyclic hydrocarbons [4, 5]. The asphaltenes are bulk porous materials, therefore their conductivity depend on external pressure. The asphaltene conductivity less then 10^{-12} S by atmospheric pressure and temperature 298 K. The conductivity increase at rank of the pressure 0 - 10 MPa from 10^{-12} S to $2 \cdot 10^{-11}$ S. The conductivity has increased from 10^{-12} S to $2 \cdot 10^{-9}$ S by the temperature variance in the interval from 293 to 453 K. the 'Maximum of conductivity was registered for samples oil asphaltenes. For all asphaltenes were observed linear volt-ampere characteristic into interval 0-500V. The conductivity of a DPS substantial increase in comparison with pure asphaltenes. With the increasing reheat temperature from 293 to 453 K, the conductivity values increase from 10^{-12} S to 10^{-5} S for DPS.

This unexpectedly a largeness conductivity value can be explain of the free radicals appearance, that are particulars with an unpaired electron.

Our studies assume that the asphaltenes in the hydrocarbons phase decompose into free radicals, according to the equations [6]:



where M_n - the molecular asphaltenes, R^\bullet and R_{n-1}^\bullet - the free radical asphaltenes.

The equilibrium (3) are shifted in right with the temperature increase. The existence of a asphaltenes free radical, as known, is confirmed by ESR data [5, 6]. The concentration of the paramagnetic centers is increased with the grown of temperature from 10^{17} to 10^{19} spin/g. The unpaired electron of free radicals are dope, and so are generated an excess of holes and semiconductors p-type. Moreover, free radicals can miniaturize of band gap, as donors of electron. As a result increases the number of charge carriers greatly within the asphaltenes compounds. Thus, the stable radicals occurrence; provides a phase transition type dielectric-semiconductor.

In an experiments was detected a negative temperature hysteresis of the conductivity. The divergence of hysteresis branches was no more than 30%. The asphaltenes permittivity compiled 5-6 units.

Thus the numerous experiments defined of conductivity testify about phase changes of type dielectric – semiconductor in DPS for areas of 400-500 K. The suggested that of conductivity dynamics is based on the processes of paramagnetic particulars doping of forbidden gap. Experimental results confirm the applicability of this hypothesis for asphaltenes, resins and high-molecular fractions with high concentration of the paramagnetic phase.

Studies of the supramolecular structure of asphaltenes by AFM [3] found that molecular structure of objects with a resolution of about 1 micron is a quasi-gel-like structure consisting of micelle-associated asphaltene molecules. The average concentration of particles in the dispersed phase is 144 particles per $1 \mu m^2$. A more detailed analysis at a resolution of 500 nm (figure 2) shows that the distance between the micelles is about 20-50 nm. The thickness of the particle diameter of 100 nm is less than 3 nm, indicating that stacking structures.

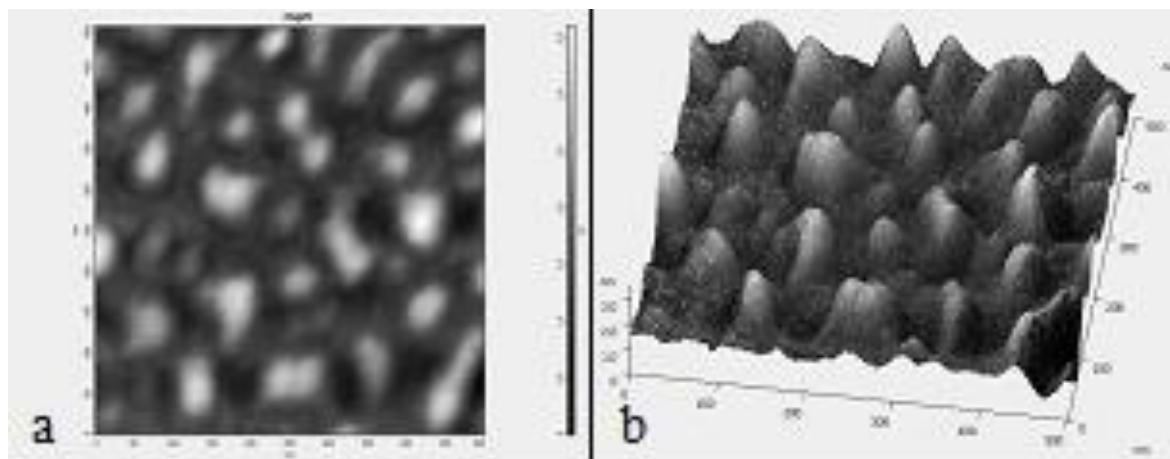


Fig. 2. Results of the supramolecular structure of asphaltenes AFM in detail: a-2D-format b-3D-format

The main of the reaseach conclusion is paramagnetic phase of asphaltenes is organic amorphous broadband semiconductor. Besides this substance can be considere in general as an organic spin glasses.

References

- [1] Dolomatov M Yu, Dezortsev S V, Shutkova S A 2012 *J. of Mat. Sci. and Eng. B* **151-157** 2
- [2] Dolomatov M Yu, Mukaeva G R, Shulyakovskaya D O 2013 *J. of Mat. Sci. and Eng. B* **183-199** 3
- [3] Dolomatov M Yu, Dezortsev S V, Bakhtizin R Z, Shutkova S A, Shulyakovskaya D O, Paymurzina N Kh 2012 *6 th International Meeting on Molecular Electronics* (France) p 160
- [4] Evdokimov I N, Losev A P 2010 *Energy&Fuels* **3959-69** 24
- [5] Yen T F, Chilingaryan G V 2000 *Asphaltenes and Asphalts 2* (Elsivier)
- [6] Unger F G, Andreeva L N 1995 *Fundamental aspects of oil chemistry. Nature of the resins and asphaltenes* (Novosibirsk: Science)