ASPHALTENES AS OBJECTS OF NANOELECTRONICS

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Abstract

Modern carbon nanomaterials are expensive products of difficult technology (carbon nanotubes, **graphenes**, fullerenes, polycyclic molecules). Therefore search of new cheap materials on the basis of natural substances, in particular high-molecular compounds of oil – asphaltenes, is actual for nanoelectronics,

Asphaltenes are complex substances that are found in grude 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. Experimental methods of electronic phenomenological spectroscopy (EPS), atomic force microscopy (AFM) and quantum chemistry were used to definite the structure of oil asphaltenes. EPS was proposed first by Dolomatov et al. [2]. Unlike conventional method, EPS studies substances as a single whole without separating it's spectrum into characteristic frequencies of individual functional groups and components of the radiation absorbing system. 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 θ (1) and (2) in UV and/or VIS spectrum regions under consideration:

$$E = \alpha_1 + \alpha_2 \theta, \qquad (1) \qquad\qquad \Theta = \int_{\varepsilon_1}^{\varepsilon_2} \int_{\lambda_1}^{\lambda_2} f(\varepsilon_\lambda) d\varepsilon d\lambda, \qquad (2)$$

where E is effective ionization potential or effective electron affinity, *eV*; α_1, α_2 are empirically determined coefficients, *eV* and *eV·mole·Γ^{-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.

It was revealed, during the origin data study of different asphaltenes and hydrocarbon systems (Table 1,2), that asphaltene fraction is a strong electron donor and acceptor at the same time (IP=4.37-5.70 eV, EA=1.85-2.50 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. Donor-acceptor properties of asphaltenes and resins by the EPS data

Asphaltenes	EIP, eV	EEA, eV	Forbidden gap, eV	Imref, eV
Asphaltenes and resins 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 strait-run stoks	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

Table 2. Electronic structure data of the semiconductors on the base of resins and asphaltenes (paramagnetic phase)

Semiconductors on the base of natural polycyclic hydrocarbons	Physical-chemical property				
	Effective ionization potential, eV	Effective electron affinity, eV	Imref, eV	Concentration of paramagnetic centers (carbon free radicals), 10^{18}·spin/sm^3	Molecular weight, a.m.u.
Asphaltenes of high-boiling distillates*	4,72-4,74	1,83-1,84	1,45-1,45	156-222	2394-3125
Asphaltenes, heat-treated, T=400 °C *	4,71-4,74	1,83-1,84	1,44-1,45	159-172	2733-3280
Asphaltenes of west Siberian oil deposits	4,72-4,94	1,83-1,95	1,45-1,50	44-139	980-2671
Oil asphaltenes**	4,72-4,77	1,83-1,86	1,45-1,46	203-218	1870-2295
Oil resins	4,95-5,14	1,96-2,06	1,50-1,54	19-90	464-782

* obtained by Dezortsev S.V.

** obtained after the manner of Hayrudinov I.R.

The structures of asphaltenes model fragments were calculated by RHF 3-21G**, 6-31G** methods [3]. 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.

Table 3. 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

The calculations results are confirmed by the EPS spectroscopic data (Table 3). 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 (Fig. 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 (Fig. 1).

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 μm^2. A more detailed analysis at a resolution of 500 nm (Fig. 3) 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. This means the association of molecular fragments in the complex structural units, which confirms the view Unger F.G. on the associative stacking structure of particles petroleum asphaltenes.

The main conclusion of the reseach is that paramagnetic phase of asphaltenes is organic amorphous broadband semiconductor and can find application as cheap nature material in nanoelectronics.

References

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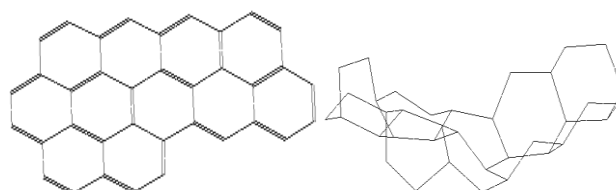
Figures

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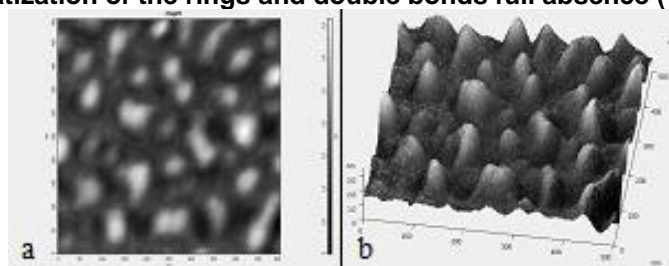

Fig. 2. Results of the supramolecular structure of asphaltenes AFM in detail: a-2D-format b-3D-format