ASPHALTENS OF OIL AND OF HIDROCARBONS DISTILLATES AS NANOSCALE SEMICONDUCTORS

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ABSTRACT

The asphaltenes are composed mainly of polyaromatic carbon with NSO-compounds combined with traces vanadium and nickel, which are in porphyrin structures. The asphaltenes include   paramagnetic centers. The concentration of free radical is 10^{19}-10^{20} spin /g (EPR). The experiment and calculation results indicate that the molecular complexes of the asphalt pitch substances on the nanomolecular level associates in the structural units' formation with the charge transfer properties involved. The spectra and quantum calculations indicate that the most probable centers for the electron transfer are the structures containing the aromatic rings, heteroaromatic rings and the corresponding free radicals. [1] The calculations showed that the asphaltenes structural units, containing from 6 to 13 aromatic rings have the forbidden gap size from 4.92-6.49 eV - for the molecular fragments and from 2.84 to 3.20 eV - for the free radical form. This indicates possible belonging of the asphaltenes to the amorphous compensatory organic broadband semiconductors. The experiments for estimation band gap of the molecules asphaltenes confirmed by of computing ab-initio methods. The Asphaltenes have nanomolecular structures, that can be   used as a semiconductors for nanoelectronics.

INTRODUCTION

The asphaltenes are complex substances that are found in grude oil, bitumen and high-boiling hydrocarbons distillates. The asphaltenes are composed mainly of polyaromatic carbon with heterocyclic compounds combined with traces vanadium and nickel, which are in porphyrin structures. The asphaltenes include   paramagnetic centers. The concentration of free radical is 10^{19}-10^{20} spin /g (EPR). Average molecular mass ascertain in diapason 500- 2500 u (mass spectrum) . The molecules of asphaltenes may contain 5- 10-member bensene and naphteno rings in their structure. The oil dispersion systems which include oils itself and high-boiling oil fractions are the asphalt pitch substances (APS) colloidal solutions, represented by the resins and asphaltenes. According to F.G. Unger [1] ideas, the oil resins and asphaltenes represent paramagnetic metastable substances, where the paramagnetic asphaltene fragments are the micelles formation centers in dispersed hydrocarbon environments. Around the micelles core the solvate layers are grouped in the

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order of the dispersed system intermolecular interaction potentials decrease. The electron structure of asphaltenes have not been researched enough.

The aim of this work is to study the electronic structure of the heteroatomic nanoparticles of the asphaltenes molecules using the electron spectroscopy and computational chemistry. The aim of this work is to study the electronic structure of the heteroatomic fragments of the nanoparticles of asphaltene moleculas using the electron phenomenological spectroscopy and computational chemistry methods

METHODS OF RESEARCH AND ANALYSIS

Unlike conventional method, the phenomenological spectroscopy(EPS) studies a substances as a single whole without separating the spectrum of the substance into characteristic frequencies and wavelengths of individual functional groups or components of the systems.[2,3] The electronic phenomenological spectroscopy is based on the regularities of the relations bet ween absorptivity coefficients and physicochemical properties of the substance the values of physicochemical properties of a substance are proportional to its ultraviolet and/or visible absorption [2].

Let us consider the method, which was proved in our previous works [1]. The ionization potential (PI) and electron affinity (EA) are estimated according to empirical dependences which links these characteristics with integral index of absorption θ (1).
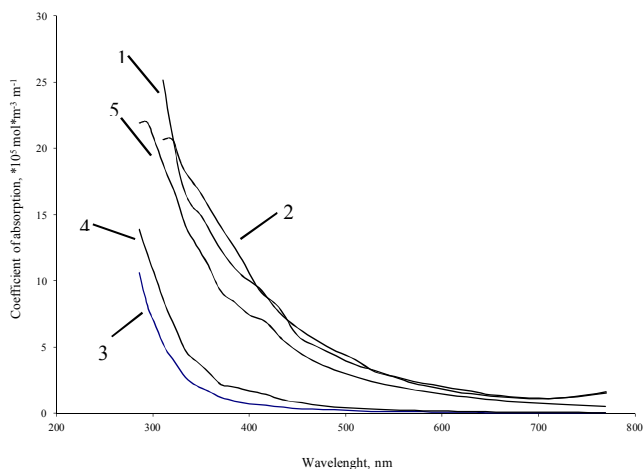

Figure 1. Absorption spectrum of asphaltene toluene solutions in UV and VIS area: 1 – asphaltenes of Surgut oilfield, 2 - asphaltenes of Ust-Balyksk oilfield, 3 - asphaltenes of Petelinsk oilfield, 4 - asphaltenes of Arlan oilfield, 5 - asphaltenes of Radaevsk oilfield

The test subjects are asphaltenes, separated from crude oils, oil fractions and solid deposits, including paraffins. The solid deposits were processed by benzene, filtered out from the impurities and paraffins. Then the asphaltenes were isolated from the samples properly by sedimentation with the n-heptane excess by Marcusson method.

The electronic absorbance spectrums were registered on the double-beam spectrometer in the range of 280 ... 760 nm in the dilute toluene solutions at the asphaltenes concentrations of 1.10 gram-mol / m^3.   The spectra in the visible and ultraviolet range have no clear absorption fields (*Figure 2*).

Ab initio RHF/3-21G** method (Restricted Hartree-Fock method) with the minimal basis of Gaussian functions and full geometry optimization [4] was used to calculate the molecules..

RESULTS AND DISCUSSION

Further calculation of IP and EA average values were based on the corre-lations [2,3] between the electronic states energies and oscillators integral strengths (OIS):

$$E = \alpha_1 + \alpha_2\theta$$

$$\Theta = \int_{\varepsilon_1}^{\varepsilon_2} \int_{\lambda_1}^{\lambda_2} \varepsilon_\lambda d\lambda \tag{1}$$

where: E— effective IP or EA, *eV*; α_1, α_2 — empirical coefficients, de-pending on the orbital type, permanent in this series, respectively *eV*, *eV·gram-mol·m^{-3}* (for IP— $\alpha_1 = 9.495$, $\alpha_2 = -2.38$, for EA — $\alpha_1 = 0.11$, $\alpha_2 = 0.98$); θ — OIS logarithmic function, *m^3·10^{-10}·gram-mol^{-1}*.

OIS logarithmic function was calculated on the area under the absorption curve by the trapezoid method:

$$\theta = \int_{\lambda_0}^{\lambda_n} \lg k_\lambda d\lambda \approx \frac{\lambda_n - \lambda_0}{n}\left[\frac{\lg k_0 + \lg k_n}{2} + \lg k_1 + \lg k_2 + \ldots + \lg k_{n-1}\right] + \frac{\lambda_n - \lambda_1}{n}\lg M \tag{2}$$
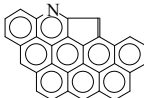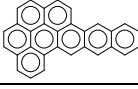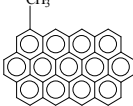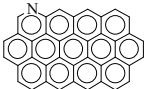
where: ε_λ — molar absorption coefficient at specific wavelengths in the near ultraviolet and visible spectrum area, *m^3·gram-mol^{-1}·m^{-1}*; *n* — number of the spectrum sampling points in the radiation absorption area.; λ_0 , λ_k — the spectrum boundaries, *nm*; *M* - molecular weight, *gram/mol*.

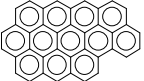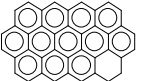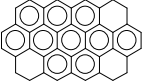It was revealed, during the study of different asphaltenes and hydrocarbon systems origin data, that asphaltene fraction is a strong electron donor and ac-ceptor at the same time (IP=4.37-5.8 eV, EA=1.65-2.66 eV). This means, that the processes in asphaltenes solutions and concentrates, including those related to ARPD (asphalt, resin and paraffin deposits), may be described by the for-mation of molecular charge-transfer complexes.

Table 1 – Donor-acceptor properties of asphaltenes and resins by the electronic spectroscopy data

Asphaltenes	PI, eV	EA, 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 – IP and EA values, computed on the base of the model fragments of resins and asphaltenes molecular and stable free-radical forms

Model structure	Molecular form (M)			Free-radical form (R) without hydrogen (H)		
	IP, eV	EA, eV	Forbidden gap,eV	IP, eV	EA, eV	Forbidden gap, eV
1	2	3	4	5	6	7
	7.05	1.47	5.58	5.43	1.89	3,54
	6.67	1.22	5.46	5.15	2.04	3.10
	6.44	1.36	5.08	4.99	1.96	3.02
	7.11	0.92	6.20	5.47	2.23	3.24
	6.39	1.44	4.95	4.95	1.91	3.04
	6.55	1.52	5.03	5.06	1.86	3.20

1	2	3	4	5	6	7
	6.57	1.32	5.25	5.08	1.98	3.10
	6.65	1.30	5.35	5.14	1.99	3.14
	6.80	0.62	5.16	5.24	2.41	2.84

Our studies assume that the asphaltenes in the liquid phase decompose into free radicals, according to the equations [1]:

$$M_n = \overset{\bullet}{R} + \overset{\bullet}{R}_{n-1} \quad , \qquad (3)$$

where M_n - the asphaltenes molecular form, $\overset{\bullet}{R}_n$ and $\overset{\bullet}{R}_{n-1}$ - the asphaltenes free radical forms. The oil resins and asphaltenes model fragments were selected to feature the elementary structural units in the associates decay scheme (3). In order to simulate the resins the polycyclic aromatic structures with the molecular masses of 276-379 amu (compounds 1-4) were used. Structures with molecular masses of 398-512 amu and the number of aromatic rings from 6 to 13 reflect the asphaltenes (compounds 5-9).

The empirical dependence, which connects the calculated values of the highest occupied molecular orbital energy (E_{HOMO}) and the experimental values of the ionization potentials (IP_{mol}) is:

$$IP_{mol}= A_1*E_{HOMOI}+ A_2, \qquad (4)$$

where $A_1 = 0.83$; $A_2 = 1.51$ eV.

For the calculated values of the lowest unoccupied molecular orbital energy (E_{LUMO}) and the experimental values of the affinity to the electron (EA_{mol}) the following empirical dependence is applied:

$$EA_{mol}= A_3*E_{LUMO} + A_4, \qquad (5)$$

where $A_3 = - 0.46$; $A_4 = 1.45$ eV.

The correlation coefficients equal 0.93 and 0.97 respectively. The dependences (4) and (5) were obtained for the polycyclic aromatic hydrocarbons.

It is necessary to calculate the free-radical fragments, taking into account the high concentration of the asphaltenes paramagnetic centers and the modern views onto their free-radical structure. Unfortunately, the quantum chemistry methods do not make correct IP and EA assessments for the free radicals that is

why we used the semi empirical correlation for calculating the ionization potentials (IP_{rad}) and free radicals affinities (EA_{rad}) to the electron.

$$IP_{rad} = A_5 * E_{HOMO} + A_6, \qquad (6)$$

where $A_5 = 0.72$; $A_6 = 0.36$ eV.

$$EA_{rad} = A_7 * E_{LUMO} + A_8, \qquad (7)$$

where $A_7 = -0.60$; $A_8 = 2.78$ eV.

The correlation coefficients equal 0.90 and 0.83 respectively.

The results, calibrated for the experiment, are shown in Table 2.

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$$IE_{rad} = A_5 * E_{HOMO} + A_6, \qquad (8)$$

where $A_5 = 0.72$; $A_6 = 0.36$ eV.

$$EA_{rad} = A_7 * E_{LUMO} + A_8, \qquad (9)$$

where $A_7 = -0.60$; $A_8 = 2.78$ eV.

The correlation coefficients equal 0.90 and 0.83 respectively

Table 3 – Computed and experimental ranges of IP and EA

Data	IP, eV	EA, e
By UV and VIS spectrums [5]	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 by equations (4)-(6)	4.92-5.79	1.78-2.45

The exciton formation energy can be estimated by the half of the forbidden gap value (quasi-Fermi level). The quasi-Fermi level for the resins molecular fragments values from 2.54 to 3.10 eV, for the asphaltenes molecular fragments - from 2.46 to 3.25 eV; for the free radical fragments of resins - from 1.51 to 1.77 eV, for the free radical fragments of asphaltenes - from 1.42 to 1.60 eV.

According to the calculations for the molecular fragments of the resins the IP range is about 6.44-7.25 eV, the EA range is about 0.81-1.65 eV. For the free radical fragments the IP changes from 4.99 to 5.57 eV, the EA changes from 1.78 to 2.29 eV. For the asphaltene molecular fragments the IP changes from 6.36 to 7.03 eV, the EA changes from 0.54 to 1.52 eV. For the free radi-

cal fragments the IP changes from 4.92 to 5.41 eV, the EA changes from 1.86 to 2.45 eV.

The calculations results are confirmed by the APS 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 in the free radical fragments

CONCLUSIONS

The experiment and calculation results indicate that the molecular complexes of the asphalt pitch substances on the nanomolecular level associates in the structural units' formation with the charge transfer properties involved. The spectra and quantum calculations indicate that the most probable centers for the electron transfer are the structures containing the aromatic rings, heteroaromatic rings and the corresponding free radicals. The calculations showed that the asphaltenes structural units, containing from 6 to 13 aromatic rings have the forbidden gap size from 4.92-6.49 eV - for the molecular fragments and from 2.84 to 3.20 eV - for the free radical form. This indicates possible belonging of the asphaltenes to the amorphous compensatory organic broadband semiconductors [4].

The experiments for estimation band gap of the molecules asphaltenes confirmed by of computing ab-initio methods. The Asphaltenes have nanomolecular structures, that can be used as a semiconductors for nanoelectronics.

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