The study of supramolecular structure of asphaltenes by atomic force microscopy

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Abstract. The article is devoted to the actual problem of studying the supramolecular structure of oil asphaltenes. They are the prospective structural materials for molecular electronics and nanotechnology. At present, the properties of asphaltenes at the supramolecular level are studied by various physical and physicochemical methods as well as by methods of mathematical modelling. The aim of the work is research of asphaltenes supramolecular structure by atomic force microscopy (AFM), comparison of experimental data with the calculations of computer simulation, and high resolution visualization of asphaltene crystallites. The topography of asphaltenes monomolecular layer is observed by AFM. Separate objects of disc-shaped form – crystallites obtained as a result of the association of individual molecules of asphaltenes are clearly visible. In addition, some structural parameters are calculated.

1. Introduction
Recently, much attention has been paid to the works, in which organic substances are used as materials for electronics. This is due to the unique properties of elements of organic electronics, which exhibit semiconductor and even metal properties, and the size of these elements can be comparable to the size of an organic molecule [1-3].

Asphaltenes are the prospective structural materials for molecular electronics. It is known that asphaltenes in oil dispersed systems are in the form of supramolecular structures ranging in size from 1 to 1000 nm, which allows us to consider asphaltenes as a promising object of nanotechnology. At present, the properties of asphaltenes at the supramolecular level are studied by various physical, physicochemical methods and methods of mathematical modelling [4-7].

Asphaltene is the high molecular weight component of crude oil, consisting of 90-95% of hydrocarbon. Besides carbon, hydrogen, oxygen, and nitrogen, the asphaltene molecule also includes sulphur [8]. Asphaltenes have an increased tendency to association and formation of liquid crystal or supramolecular structures. In 1961, T. Yen proposed the so-called burst model of the asphaltenes structure of "plate to plate" type [9]. At present, two models of asphaltenes aggregation – the "continental" type and the "archipelago" type structure are generally recognized [10,11]. The structure of the "archipelago" is unlikely for asphaltenes extracted from the residue of thermal cracking, because chemical bonds binding polycyclic fragments of the molecule are destroyed in the process of cracking. Considering the tendency of polycyclic molecules to associate, an important question is to determine the degree of molecules association in solution. Asphaltenes were also studied by mass spectrometry and field ionization [12], mass spectrometry with photoionization [13], and laser desorption mass
spectrometry [14]. By means of physical methods, concentrations, at which the asphaltenes structure changes in the solution, were determined [15].

It was found by Schneider et al. [16] using the method of fluorescent correlation spectroscopy, that solutions of oil asphaltenes in toluene at concentrations up to $10^{-4}$ wt. (0.1 g/l) manifested themselves as true solutions. Mullins et al. [17], as well as Freed et al. [18] found that with an increase in the concentration of more than $10^{-4}$ wt. stable nanoaggregates of 8 - 10 molecules were formed. With a mass fraction of more than $5 \times 10^{-3}$ wt. (5 g/l), further formation of clusters of nanoaggregates took place. At concentrations above $5 \times 10^{-3}$ wt. (50 g/l) a gel-like grid was formed. Thereby, the degree of molecular association increases depending on the concentration of the solution, which is important to consider during microscopic studies.

The aim of the work is study of asphaltenes supramolecular structure by atomic force microscopy (AFM), comparison of experimental data with the calculations of computer simulation, and high resolution visualization of asphaltene crystallites.

2. Materials and methods

The asphaltenes isolated from thermal cracking residues by Soxhlet extractor were used as the research object. Average molar mass number of asphaltenes according to the optical spectroscopy is 1200 a.m.u. The solution concentration for film preparing is 0.1 g/l. Under these conditions, we should expect a weak molecules association in solution.

Mica was chosen as the substrate because of its atomically smooth surface. We have used AFM Ntegra-Prima (NT-MDT, Zelenograd, Russia) for the high resolution imaging of surface topography and calculation of structure parameters of asphaltene molecules. The scanning of the samples was carried out by the HA_NC cantilevers (TipsNano, Russia) with the curvature radius of 10 nm, tip's cone angle of 30°, and force constant of 12 N/m. Under the ambient conditions and with the correct concentration of the solution, a single molecule of asphaltene can be visualized.

The initial task was to select the optimal concentration of asphaltenes in toluene, a working solution for subsequent preparation of samples suitable for AFM study. The working solutions with a concentration of 0.1 g/l were prepared by calculating the mass ratio of asphaltene in the toluene volume. Langmuir-Blodgett technique was used to obtain a monomolecular film of asphaltenes. After trying each of the four standard Langmuir-Blodgett techniques, we used up-draw process of the mica substrate through the film, whereby we obtained the highest quality AFM images. The deposited asphaltenes thin film was dried in the Petri dish for 60 minutes at the temperature of 24°C. The final sample was studied in the air atmosphere in AFM tapping mode.

3. Results and discussion

To demonstrate the reproducibility of the sample preparation technique, two samples prepared by one method were scanned. The topography of the monomolecular layer of asphaltenes was obtained by AFM (Figs. 1a, 2a). Individual disc-shaped objects are visible on them.

For detailed analysis, the cross-sections have been made along the lines marked in Figures 1a and 2a. Each cross-section was performed on three separate objects. According to the first cross-section profile (Fig. 1b), it can be calculated that the first object has a height of 1.5 nm and a width of 33 nm, the second one – 1.35 and 34 nm, and the third one – 1.4 and 31 nm, respectively. According to the second cross-section profile (Fig. 2b), it can be calculated that the first object has a height of 1.7 nm and a width of 36 nm, the second one – 1.3 and 36 nm, and the third one – 1.4 and 34 nm, respectively.

Thus, the results of AFM studies show disc-shaped structures constructed from asphaltene molecules associates. Analysing and comparing the sizes of objects and their location on the surface with the results of the work of other researchers [17,18], we came to the conclusion that individual disc-shaped objects are clusters of asphaltenes and their placement on the surface in a nanoaggregate state can be described by the disk-like aggregation model. When comparing our experimental results with the results of study and simulation by Ese et al. [19] and Korzhov et al. [20], it can be assumed that the investigated aggregates have a disk-shaped structure and these structures are similar to discotic liquid crystals.

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Figure 1. (a) AFM topography image of asphaltenes film (1 sample), (b) cross-section profile along the line marked at (a).

Figure 2. (a) AFM topography image of asphaltenes film (2 sample), (b) cross-section profile along the line marked at (a).

Table 1. Structural characteristics of crystallites.

| Structural characteristics                           | Sample 1   | Sample 2   |
|------------------------------------------------------|------------|------------|
| Average crystallite height, nm                       | 1.4±0.1    | 1.5±0.1    |
| Average crystallite width, nm                        | 33         | 35         |
| Interlayer distance*, nm                             | 0.35       | 0.35       |
| Average number of layers in the crystallite, pcs.    | 4          | 4          |
| Average number of molecules in a layer, pcs.         | 75         | 81         |
| Average number of molecules in the crystallite, pcs. | 300        | 324        |
| Molar mass, amu                                       | 360000     | 388800     |

* - calculated by the simulation method

According to the results of previous works on the modelling of asphaltene molecules, the height of one molecule is approximately 0.1 nm, and the length is about 1 nm [21]. Therefore, knowing the height and length of one molecule, we can calculate some parameters that are presented for clarity in Table 1. Based on the data of Table 1, it follows that the crystallite parameters of sample 1 and sample 2 have approximately the same quantitative values.
4. Conclusion

The results of the interpretation of AFM studies indicate the existence of supramolecular structures of the discotic type formed by associated molecules of asphaltenes. We have found that individual disc-shaped objects are asphaltenes crystallites and their location on the substrate surface can be described by the disk-like aggregation model. The average number of molecular structures in the crystallite is 304-324 pcs. The average number of layers in the crystallite is 4. Within each layer there are 76-81 molecules. The molar mass of the asphaltene crystallite was found. It is 364800-388800 amu. The obtained results correspond to the data of studies performed by other physical methods.

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