

Study of supramolecular structure of petroleum asphaltenes

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Abstract

The article is devoted to the topical problem of studying the supramolecular structure of petroleum asphaltenes. They are the prospective materials for molecular electronics and nanotechnology. At present, the properties of asphaltenes at the supramolecular level are studied by various experimental methods and methods of mathematical modeling.

As objects of a research the asphaltenes concentrated in residual fractions of vacuum distillation of the West Siberian oil with a temperature of boiling more than 500 °C were used. Asphaltenes of samples allocated with dissolution of fractions in toluene with the subsequent sedimentation by surplus of *n*-heptane by Golde's technique. Results of ASM-researches show existence of steady units from nanoclusters of oil asphaltenes in the form of structures of an ellipsoidal form about 4.5 nm high and with a lateral size up to 100 nm.

The research of supramolecular structure of nanoclusters of oil asphaltenes in the GAUSSIAN software package is executed. Calculation was carried out by method of molecular mechanics of MM with full optimization of geometry. The structure of molecular fragments of a nanoparticle of asphaltenes is defined according to data of ¹H, ¹³C NMR and IR of spectroscopy and the chemical analysis earlier. These data will be agreed with results of works on identification of molecules of asphaltenes by the ASM method of high resolution. Follows from calculations that the nanoclusters having an appearance of quasicrystal reniform structures with number of molecular fragments from 2 to 10 are steadiest, at the same time the distance between the planes of molecular fragments of a nanocluster is in the range from 3.53 up to 3.67 Å, and diameter of particles 11-40 Å. Data on height of nanoclusters will well be agreed with results of ASM-researches for small structures. Calculations of supramolecular structure of oil asphaltenes by method of molecular mechanics show considerable energy of intermolecular interaction of structural molecular fragments of 60-118 kJ/mol that testifies to a possibility of self-assembly of ordered structures from these nanoparticles visualized by means of ASM. The received results are confirmed by data of the X-ray diffraction analysis and electric measurements on energy of activation of hopping conductivity (129.58 kJ/mol) and also the carried-out earlier thermodynamic calculations. As appears from calculations, the increased stability of quasicrystal structure which arises, most likely, as a result of transfer of a charge between fragments as molecules have the low potential of ionization and high affinity to an electron is characteristic of nanoclusters.

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