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Dedicated to the 115th anniversary of B.A. Arbuzov's birth

Study of Organic Self-Assembled Nanosystems by Means of High-Frequency ESR/ENDOR: The Case of Oil Asphaltenes

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Abstract—An approach to investigate self-assembly of oil disperse systems based on high-field electron nuclear double resonance has been suggested. As exemplified by asphaltenes, the oil components most prone to self-assembly, the formation of planar rather than multilayer structures has been directly evidenced experimentally. The suggested method can be applied to elucidate the self-assembly mechanism in wide range of organic objects.

Keywords: complex self-assembled nanosystem, oil disperse system, asphaltene, vanadium porphyrin complexes, electron nuclear double resonance

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Many of materials and phenomena in physics, chemistry, soil science, biology, and social sciences can be described by models of self-assembled systems. The study of complex self-assembled systems started in mid-twentieth century has led to the appearance of the self-assembly theory [1–4]. It implies the formation of higher-level system via self-assembly of many identical lower-level elements. The number of the constituting elements in the complex nanosized systems is limited and they are usually different. Hence, the application of conventional methods developed in the study of complex self-assembled systems is often inefficient in the analysis of complex nanosystems. The available experimental and theoretical approaches should be modified accordingly.

We have earlier demonstrated the prospects of application of high-frequency (high-field) electron spin resonance (ESR) and electron nuclear double resonance (ENDOR) methods to investigation of self-assembled nanoparticles as exemplified by the cases of ZnO nanoparticles [5, 6], nanosized hydroxyapatite [7, 8], paramagnetic anthraquinone complexes on γ-Al_2O_3 surface [9, 10], and nanodiamonds [11, 12]. Here we present and discuss the experimental study of the bonding responsible for the self-assembly of asphaltenes by means of ESR/ENDOR.

Asphaltenes are major structuring components of oil disperse systems. An asphaltene molecule is a fused system containing on the average 6–10 aromatic and 2–3 naphthene cycles surrounded by 0.55–0.65 nm hydrocarbon chains and containing also hetero-atoms (S, N, O) and metals (V, Ni, Fe, Ca, etc.). The size of asphaltene molecule is of 1–2 nm, average molecular mass being about 750 [13]. The composition and structure of asphaltene molecules make them prone to multiple intermolecular interactions: hydro-gen bonds, acid-base, dipole-dipole, π-complex, exchange, and others, with the formation of ordered hierarchical aggregates. Therefore, asphaltene molecules in oil systems can exist in the form of molecules, nano-aggregates, clusters, or floccules, depending on the concentration [14–16]. In view of polydispersity of the