

Amorphous Shungite Carbon: A Natural Medium for the Formation of Fullerenes

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Abstract—A comparative analysis of data on the density, porosity, and intermolecular space of high-carbon shungites, graphite, glassy carbon, and C_{60} fullerite gave an estimate of the fullerene content in the shungite samples which agrees with the values obtained by electrochemical and polar solvent extraction methods. A low yield of fullerenes in the extracts obtained with nonpolar solvents is explained by the high polarity and large adsorption energy of fullerenes and related compounds. © 2000 MAIK “Nauka/Interperiodica”.

The methods of C_{60} and C_{70} fullerene synthesis developed by the beginning of 1990s suggested that these compounds may be present in carbon-containing rocks. Indeed, shortly after the publication of reliable data on the physicochemical properties of C_{60} and C_{70} , these fullerenes were found in high-carbon shungites [1, 2]. These shungites still remain the only natural objects known to contain aromatic carbon-containing molecules. Up to now, no investigations were undertaken to determine the concentration, molecular composition, and distribution of fullerenes and/or their derivatives in shungites (Sh) with various structures of the carbon-containing substance (C_{sh}). This information is of value for elucidating the nature of C_{sh} and identifying the component responsible for the medical and ecological properties of Sh.

Filippov *et al.* [3] pointed out that there must be a relationship between the properties of shungite carbon C_{sh} , its fullerene-like structure, and the content of C_n fullerenes. Yushkin [4] suggested that a common mechanism may be responsible for the formation of C_{sh} and C_n . These hypotheses are justified provided that the concentration of fullerenes is related to the C_{sh} structure and correlated, at least in certain types of Sh, with the content of completely amorphized carbon phase [3, 5], the latter being the most probable initial material for the C_n synthesis.

Previously [6], we have presented evidence of a commercially significant C_n content (about 1%) in Sh-3. The purpose of this work was to perform a comparative analysis of some macrophysical properties of C_{sh} , its closest structural analog—glassy carbon (GC) [7, 8], and C_{60} fullerene, with a view to estimating the limiting content of C_n and elucidating a model of metamorphism in the shungite carbon structure.

For a carbon unit cell size of 1.0 Å [9] and a covalent atomic radius of $C^0 = 0.77$ Å [10], carbon atoms in C_{60} can be considered as C^+ ions surrounded by delocalized

π -states (C^+e^-). Resonance excitation of a solvated C_{60} molecule in solution [11] must involve transitions into states with the electron affinity energy E_aC^+ evaluated [12] as $3E_aC^0 = 3.81$ eV. Taking into account the vibrational transitions in C_{60} (272, 496, and 776 cm^{-1} [11, 13]), this E_aC^+ value corresponds to the energy of the π -band maximum in the spectra of solutions. According to the quantum-chemical calculations [14], the energy position of the π -band maximum for a non-associated C_{60} molecule was evaluated as 3.43 eV, which is 65 meV below the electron work function [15]. The difference coincides, to within 3 meV, with the energy of “breathing” oscillations of the highly symmetric C_{60} molecule. Note also that 3.435 eV is the middle (arithmetic mean) value between $E_aC^0 = 1.27$ eV [10] and the ionization potential of C_{60} (5.6 eV), which confirms the above C_{60} model in the form of mutually bound C^+ ions surrounded by a cloud of π -electrons.

The non-associated C_{60} molecule admits the analogy between their delocalized π -electrons and the s - d electron states of small-size icosahedral metallic particles [9, 13]. For example, the ionization potential and the surface plasmon energy of Ag_{13} [16] virtually coincide with the corresponding values for C_{60} , while the maximum of the plasma absorption band of Ag_6 (considered as an elementary particle with metal bonds [17]) coincides with the calculated energy of the π -band maximum of the non-associated C_{60} . A difference between C_{60} and small metallic particles consists in (i) the form of the surface electron density distribution and (ii) the possibility of shape changing in the C_{60} carbon unit cell. The scattering of electromagnetic waves on these objects is determined by collective oscillations of the conduction electrons [18], while the plasma oscillations divide into π - σ - and π -states [9, 15, 19]. The π -states being localized upon adsorption on an electro-neutral surface, the C_{60} molecule (as a solid particle)