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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 electroneutral surface, the C_{60} molecule (as a solid particle)

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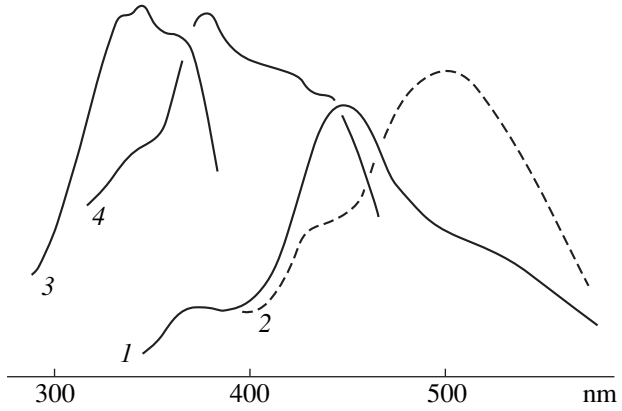

Fig. 1. Typical spectra of C_{60}: (*1*, *2*) luminescence (curve *2* illustrates a time variation of the emission spectrum); (*3*, *4*) luminescence excitation at (*3*) 410 and (*4*) 497 nm.

loses its metallic properties. In this case, an excited C_{60} particle with electron-acceptor properties must contain a bound electron-hole pair. Indeed, the luminescence spectra of C_{60} absorbed in a microporous glass or adsorbed on the surface of polymer molecules exhibit bands peaked at 365, 368, and 410, 433 nm shifted from the 361 and 407 nm bands in accordance with the frequencies of the characteristic vibrational states of C_{60} (Fig. 1).

The thermal stability of fullerenes, together with high electronegativity and polarizability of C_{60} [15, 19], allows this molecule to be considered as an adatom of large radius possessing the properties of elements of the VII group. For example, C_{60} is, like iodine, soluble in nonpolar solvents and has the values of ionization energy and E_a close to those of At [10].

Thus, C_{60} may exhibit, depending on the environment, both the individual molecular properties and the properties of metallic or semiconducting particles, or even halogen atoms. This accounts for the ability of C_{60} to form compounds with various types of chemical bonds, for the large energies of C_{60} adsorption on electron-donor surfaces, and for the effective solid-state interaction of C_{60} with ionic and/or molecular compounds [20].

A 10% decrease in the intermolecular distance in C_{60} crystals as compared to the interlayer spacing in graphite (3.35–3.36 Å) suggests that the π–π exchange interaction in this system is possible as well. A high mobility of C_{60} molecules near the position of equilibrium in the crystal lattice [13] allows us to assume that, when the carbon cell shifts from the equilibrium position, one of the neighboring molecules may act as a donor, and the other, as an acceptor of electron density. A shift of the π-states of the donor molecule to a low-energy level of the acceptor molecule corresponds to E_aC_{60} = 2.65 eV [13]. This model, in which the donor and acceptor are equivalent, can be applied to any pair of molecules. Therefore, the interaction between low-energy states and π-states of the acceptor molecule must be a fundamental energy characteristic of a C_{60} crystal. For the calculated mean energy of 3.435 eV, an equidistant value with respect to E_aC_{60} is 1.865 eV corresponding to the bandgap of C_{60} fullerite [9, 13]. This implies that the $2C_{60}$ dimer is an element of self-similarity in the fullerite structure, which may pass as a whole into solution to perform as the self-similarity element in the corresponding fractal aggregates [13].

In a non-associated C_{60} molecule, the electron shell thickness can be considered as corresponding to the thermodynamic equilibrium between the orbital and covalent radii of carbon atoms (1.39 Å). In this case, the ratio of the volume occupied by a carbon atom to the volume of a C_{60} molecule is $\cong$0.78. The same value is obtained for the density ratio of C_{60} fullerite (ρ = 1.697 g/cm^3) and graphite ($\cong$2.25 g/cm^3) calculated taking into account a difference in C–C bond lengths [5, 13]. For an equivalent surface filling of the entire C_{60} volume, the density (ρ) of fullerite increases to reach the ρ value for graphite. Therefore, the volume of the interlayer space in graphite is equivalent to the intermolecular volume in fullerite. A special feature of the C_{60} structure is the presence of pentahedra uniformly distributed over the carbon cell surface, whereby each carbon atom is shared by two hexagons and one pentagon. This implies that the pentahedra are formed as a result of self-organization in the excited C_{60} molecules.

A collective character of the self-organization of carbon molecules into an aromatic structure is indicated by coinciding energies of formation of the C_{60} molecules and π–σ-plasmons [13, 14]. It was also pointed out [13, 14] that the synthesis of fullerenes from C-clusters is an effective process provided that an energy released upon the contact of clusters amounts to a few eV, which is just the energy characteristic of the electron affinity of linear carbon molecules [21]. Therefore, the excited amorphized graphite-like clusters and chain molecules in a C_{sh} structure may form aromatic fullerene-like molecules. This is confirmed by a pyrolytic synthesis of fullerenes from chain hydrocarbons under conditions of weak interaction with environment in an oxygen-free atmosphere.

The samples of Sh-1 and GC exhibit, in addition to similar X-ray-amorphous structures and coinciding features in the 400–1600 cm^{-1} (see Fig. 2, curves *1* and *2*) range of the IR absorption spectra, close values of the strength characteristics, thermal expansion coefficients, heat capacity, and electric conductivity [5]. On the other hand, the thermal conductivity values differ 6–7 times. The low thermal conductivity of Sh-1 as compared to that of GC, with close values of most macrophysical characteristics, implies that the interphase boundaries may contain a considerable amount of heat-scattering centers. A middle (arithmetic mean) value

between the densities of graphite and C_{60} fullerite at 290 K is 0.02 g/cm^3 greater than the density of GC. This difference is related to a fully amorphized phase present in the GC structure [5], the density of which may be comparable with that of soot (ρ = 2.1–2.18 g/cm^3). Thus, the GC structure can be considered as a superposition of graphite-like packets (GLPs) with ultimate geometries of bent hexagonal layers.

The ratio of limiting values of the interplanar spacing in GLPs (3.65 and 3.41 Å for C_{sh} with globular and sheet morphology, respectively [3]) coincides with the density ratio of the corresponding types of Sh-1 (1.83–1.96 g/cm^3), which indicates that these packets are the main structural units of C_{sh}. A 2–7% increase in the interlayer spacing in GLP with respect to that in crystalline graphite corresponds to a decrease in the density down to ρ = 2.1–2.2 g/cm^3. This estimate does not take into account a possible change in the density within 2–4% due to a difference in interatomic distances between the C_{sh} and graphite structures, since the bending and small dimensions of GLPs necessarily imply the presence of carbon vacancies. For a C_{sh} structure porosity of 10–12% [5], the average density of GLPs correspond to the ρ value of Sh-1. A middle value between the densities of GLPs and C_{60} fullerite (1.9–1.95 g/cm^3) falls in the range of ρ values of Sh-1. For an average C-globule size of about 10 nm, the free volume of C-globules coincides with that of C_{60} molecules provided that the globules form a four-layer packet, which accounts for the fullerene-like structure of C_{sh} [3, 4, 22]. A smaller number of features in the IR spectrum of Sh-1 in comparison with the spectrum of GC (see Fig. 2, curves *1* and *2*) is indicative of a higher degree of order in the shungite carbon structure.

The density of C_{60} was estimated as ρ = 2.03 g/cm^3 [19]. Determined within the framework of the fullerene-like model, the interglobular porosity must fall within 30–35%, while the total porosity must be about 40%. A discrepancy between this estimate and the value (10–12%) presented above is eliminated if we assume that (i) a soot-like phase and/or C_n carbon phase is present in the inter- and intraglobular space and (ii) the GLPs are for the most part intercalated [8]. The latter assumption, like the hypothesis of a fullerene-like C_{sh} structure, is based upon the coincidence of the main spectral features observed in the 400–1500 cm^{-5} range for Sh-1 and C_{60} dimers in a KCl matrix [20] (Fig. 2, curves *2* and *3*). The IR spectrum of Sh-1 displays a Raman band of graphite at 1575–1580 cm^{-1}; the fact that this band is allowed in the IR spectrum is also related to the intercalation of monovalent electron-donor carbon atoms [23].

Considering GLPs as the walls of globules cannot explain the fact that the number of layers in the GLPs is odd before and even after the heat treatment of Sh samples [3]. A fractal character of the C_{sh} structure implies a mixed type of the interaction between GLPs and the absence of any pronounced GLP orientation. An evidence for the glassy structure of C_{sh} is provided by the coincidence of the Sh-1 density with that (ρ = 1.9 g/cm^3) of the melt of a mixture comprising chain and aromatic C-clusters [24]. In this context, the globular structure can be considered as resulting from an ordered mass rearrangement within a closed volume, beginning with nucleation of the graphite-like networks in the field of uniformly distributed catalytically active centers. A decrease in the number of crystallization centers corresponds to an increase in the size of GLPs and, hence, of the C-globules.

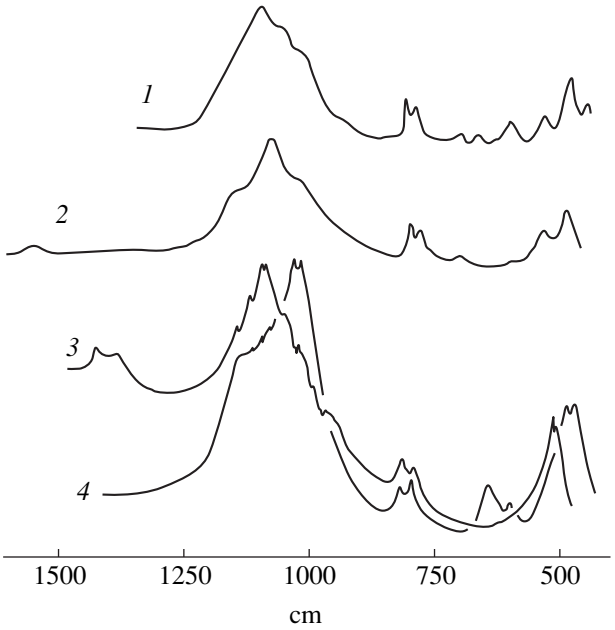

Fig. 2. IR absorption spectra: (*1*) glassy carbon; (*2*) shungite (Sh-1); (*3*) C_{60} in KCl matrix; (*4*) solid amorphized C_{60}-methylpyrrolidone phase.

In this model, the odd number of layers in the packet is a consequence of the primary monolayer nucleation; however, this does not exclude the possible nucleation of two layers and an even number of layers in the packet. Thus, GLPs can be considered as the elements of self-similarity in the fractal structure of C_{sh}. Assuming the precipitation-like accumulation of C-globules, the fractal dimensionality must fall within 2.3–2.5 D [25]. The interglobular porosity of this structure must be not lower than 20%. In our opinion, it is the total porosity level of C_{sh} that is the main evidence in favor of the recrystallization mechanism. The crystallization model of C_{sh} formation is confirmed by a filament (whisker) crystal structure of some shungite carbon samples [26]. Within the framework of the vapor–liquid–crystal mechanism [27], the filament crystal growth begins in a quasiliquid phase supplied with the mobile C-clusters, which makes possible the fullerene-like structure formation [28]. The growth of filament crystals require a sufficient free volume and a small number of primary

crystallization centers. The recrystallization process may not involve some part of the C-clusters. Thus, the main difference of the GLP formation in Sh is the closed space in which the process occurs, while the free volume formation provides conditions for the secondary recrystallization of weakly bound C-clusters into the final aromatic structures.

The fact that the ρ values of GC and Sh-1 can be obtained within the framework of the same GLP model implies that a difference between the calculated and measured densities of Sh-1 (0.03–0.07%) is related to the presence of either a C-phase with ρ = 1.6–1.66 g/cm^3 characteristic of the GC samples upon a high-temperature treatment [5] or fullerenes. The use of a macrophysical value for evaluating the total density of statistically distributed C_n molecules or their small-size aggregates is possible because the inter-pore space in C_{sh} is definitely smaller than the intermolecular volume in fullerite and in the adsorbed state of C_n. The existing notions about the shungite substance formation [3], as well as the presence of organic compounds, microorganisms, and water in the shungite samples, are inconsistent with the thermal mechanism of low-density C_{sh} phase formation.

As follows from the above considerations, the concentration of C_n in Sh samples with most disordered structure is estimated at 3–5 wt % of C_{sh}. This estimate is confirmed by observation of a resolved band at 1180 cm^{-1} in the IR spectrum of Sh-1 (see Fig. 2, curve *2*), which is a characteristic band in the spectrum of C_{60}. A similar band is observed in the spectrum of a solid amorphized C_{60}–methylpyrrolidone phase (see Fig. 2, curve *4*). At the same time, the spectra of this phase and Sh-1 contain, in contrast to the spectrum of C_{60}–KCl samples [29], no characteristic bands in the region of 1420–1430 cm^{-1}, which is most probably explained by the interaction of π-states in the major part of C_n with the matrix components. The common features observed in the IR spectra of Sh-1, GC, C_{60}–KCl_x, and ultradisperse graphite particles [30] reflect the presence of like structural groups of carbon atoms forming bent hexagonal layers [31].

According to the above estimates, there are 30–40 C_n molecules per globule, which allows the associative arrangement of these molecules in the free space of C_{sh}. This hypothesis is consistent with the calorimetric effects observed in the temperature intervals near 190–200, 235–245, and 280 K. For the samples of Sh-3 dehydrated in vacuum for 24 h at 280 K, the high-temperature maximum is observed 5–7 K below, and the low-temperature maximum, 5–7 K above the corresponding peaks for Sh-1. The high-temperature maxima are usually registered during the first DSC runs in the heating modes. These features allow us to assign the observed calorimetric features to processes in the ordered molecular aggregates with various relative concentrations of C_{60} and C_{70} molecules. The low-temperature maxima are attributed to changes in the vibrational mobility of C_{60} and C_{70} molecules, and the high-temperature maxima, to changes in the structure of C_{60} fullerite with a large admixture of C_{70} [32].

The calculated estimates of the content of C_n in Sh are confirmed by data on the extraction of thermoactivated Sh-1 samples with polar solvents capable of forming compounds containing donor–acceptor bonds with C_n. The samples obtained upon the thermal removal of hydrocarbons and solvent from the extracted bitumous phase exhibited crystallization of carbonaceous particles with a cubic and/or dendrite crystal habit. The X-ray diffraction data allowed these particles to be identified with $C_{60–70}$. The spectral features of the extracted carbon particles and their solutions also corresponded to the $C_{60–70}$ structure. The estimated mass of the isolated crystalline particles varied within 1.5–2.0 wt % of the Sh-1 sample, depending on the extraction conditions. The experimental data were indicative of the possible technological efficiency of using natural fullerenes extracted from shungites in medical and ecological applications.

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