Uzbek Journal of Physics
DOI: https//doi.org/10.52304/.v25i2.423

Features of C_{60} fullerene in the toluene-hexane solvent system

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Received 05.04.2023, revised 19.04.2023

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Методами рефрактометрии, УФ-видимой спектроскопии, динамического рассеяния света (ДРС) и электронной микроскопии изучены закономерности самоагрегации молекул C_{60} в растворе C_{60}/толуол/гексан. Экспериментально показано, что при незначительном увеличении как концентрации фуллерена C_{60}, так и объемной доли толуола в растворе C_{60}/толуол/гексан наблюдается изменение показателя преломления и поведения оптического спектра среды. Увеличение содержания толуола в растворе проявляется как положительный сольватохромный эффект, так и гиперхромный эффект в интенсивной полосе поглощения при ~328.8 нм. В то же время методом ДРС установлено, что с увеличением мольной доли толуола в системе C_{60}/толуол/гексан размер синтезированных внутри раствора нанокластеров уменьшается. После испарения гексана и толуола из капель раствора фуллерена, перенесенных на нагретую подложку (до ~30°C), на поверхности подложки формируются нитевидные кристаллические наноструктуры на основе фуллерена C_{60}.

Ключевые слова: фуллерен C_{60}, смесь растворителей толуол/гексан, самоагрегация, показатель преломления, ДРС, нанокластер, нановискеры.

The behaviors of self-aggregation of C_{60} molecules in solution of C_{60}/toluene/hexane were studied by the methods of refractometry, ultraviolet-visible spectroscopy, dynamic light scattering (DLS) and electron microscopy. It has been experimentally shown that with a slight increase in both the concentration of C_{60} fullerene and the volume fraction of toluene in a C_{60}/toluene/hexane solution, a change in the refractive index of the medium and in the behavior of the optical spectrum is observed. An increase in the content of toluene in the solution manifests both a positive solvatochromic effect and a hyperchromic effect in the intense absorption band at ~328.8 nm. At the same time, it was established by DLS that with an increase in the mole fraction of toluene in the C_{60}/toluene/hexane system, the size of nanoclusters synthesized inside the solution decreases. After evaporation of hexane/toluene from fullerene solution droplets transferred to a heated substrate (up to ~30°C), filamentary crystalline nanostructures based on C_{60} fullerene are formed on the substrate surface.

Keywords: fullerene C_{60}, toluene/hexane solvent mixtures, self-aggregation, refractive index, DLS, nanocluster, nanowhiskers.

I. Introduction

Among various nanoscale materials, carbon containing nanomaterials have unique optical, electrical, thermal, and mechanical properties [1-2]. Presently, solutions of carbon containing nano-particles, in particular fullerenes C_n (n = 60, 70, …), have increasingly attracting the attention of physicists and chemists as natural models of self-organizing systems [3-4]. Experimental works [5-12] show the possibility of controlling self-organizing systems by controlling the type and amount of used solvents, the concentration of the

solute and external conditions (ambient temperature, method of preparing a solution, etc.). The properties of the synthesized nanoclusters (for example, the refractive index, optical absorption, electrokinetic potential, thermal conductivity, etc.) become dependent on their geometric dimensions and differ markedly from the properties of their constituent isolated fullerene molecules with a diameter ~0.7 nm [13-17]. A better understanding of the processes of interaction and aggregation occurring between the molecule of fullerenes and solvents is important for the development of new nanomaterials based on fullerenes. Currently, fullerene-containing nanomaterials are in the focus of attention for use in electronics [18-20], such as diodes, transistors, solar cells, electronic batteries, in the field of medicine [21-22] as an antioxidant, proactive agent for cells, in tribology [23], in surface coatings [24], in the creation of new molecular networks [25], as well as in sensor technologies [26]. At the same time, many important questions about intermolecular (interparticle) interactions inside and out of solution, leading to self-organization of fullerene molecules in binary solutions, remain debatable.

The aim of this work is to experimentally study the UV-Vis absorption spectra and refractive index of solutions of fullerene C_{60} (purity of >99.8%, Sigma Aldrich, USA) in binary mixtures of solvents "toluene+hexane" at various concentrations of the components and to determine the size and morphological characteristics of nanostructures of C_{60} by dynamic light scattering (DLS) and electron microscopy methods.

II. Materials and methodology

To prepare C_{60} solutions of specified concentration, preweighed C_{60} fullerene powder was added to a vial containing accurately measured hexane, toluene, and/or hexane/toluene mixtures. The resulting mixture was dissolved in a hermetically sealed glass flask at room temperature for 5 h with mechanical stirring using a 2.5 Hz programmable laboratory magnetic stirrer "MS-11 H" (WIGO, Poland).

Experimental measurement of the exact significant index of refraction (n) of the system C_{60}/toluene/hexane with different concentrations of solvents was carried out on the long-wave D_1-line of sodium atoms (~589.3 nm) on a high-sensitivity (<0.0001) digital refractometer PAL-BX/RI (ATAGO, Japan).

In experiments, the absorption measurements of C_{60} solutions were carried out on a UV-2700 UV-Vis spectrometer with a spectral resolution of ~0.1 nm (Shimadzu, Japan). Optical absorption spectra of C_{60}/toluene/hexane were taken immediately after their preparation.

Using the DLS method on a NanoSight LM10 (Malvern Instruments Ltd.), the distribution character of the dispersed phase of fullerene C_{60} over the average hydrodynamic diameter (D_h) in solutions was studied.

To study the dimensional and structural features of synthesized nanostructures of fullerene C_{60}, we used a scanning electron microscope (SEM) JSM-IT200 (Joel, Japan).

III. Results and discussion

A change in the refractive index (RI) of fullerene solutions with a change in the concentration of components gives an idea of the sensitivity of clusters of different sizes to light, which helps to select nano-sized fullerene clusters for a particular sensor system. The measured experimental values of the refractive indices of C_{60}/toluene/hexane solutions at two fixed concentrations of C_{60} fullerene (~12 and ~16 mg/dm^3) show that with an increase in the concentration of fullerene C_{60} in the solution of C_{60}/hexane/toluene, the values of RI of the solution increase. The RI values of a C_{60}/toluene solution at a C_{60} concentration of ~12 and ~16 mg/dm^3 are 1.4910 and 1.4916, respectively. At the same time, the RI values of the C_{60}/hexane solution increase from 1.3677 to 1.3689 with an increase in the C_{60} concentration from ~12 mg/dm^3 to ~16 mg/dm^3. This behavior is due to the fact that with an increase in the concentration of C_{60} in the studied solutions, the processes of self-organization of individual C_{60}-C_{60} molecules are enhanced. The latter causes more interactions between photons of light and therefore leads to an increase in the refractive index of solutions.

Figure 1 shows the UV-Vis electronic absorption spectra of freshly prepared solutions of fullerene C_{60} in a hexane (solid line) and in a two mixed solvent of hexane/toluene (a dotted line and a dash-dotted line) at fixed low concentration of C_{60} ~16 mg/dm^3. Obviously, the following characteristic absorption bands of C_{60} in hexane were observed: orbitally-allowed bands with maxima at λ_1≈328.8 nm, λ_2≈404.4 nm, a weak shoulder at λ_3≈406.7 nm and orbitally forbidden bands with maxima at λ_4≈535 nm, λ_5≈568 nm, λ_6≈590 nm, λ_7≈598 nm, a weak shoulder at λ_8≈620 nm (see solid line). With increasing the mole fraction of toluene in solution, the amplitudes of the optical

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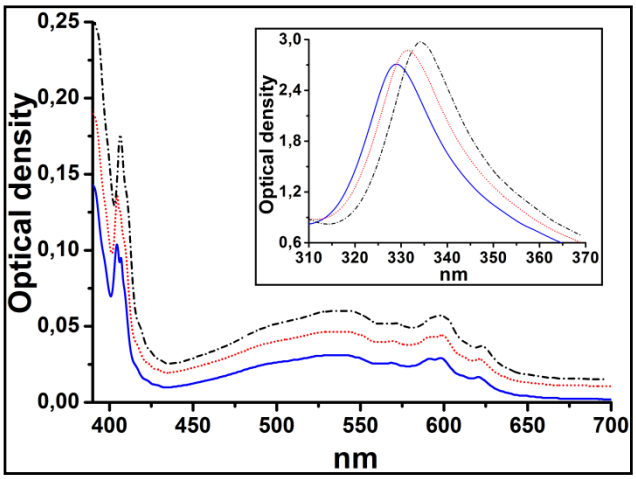


Figure 1. UV-Vis electronic absorption spectra of fullerene C_{60} solutions in hexane/toluene mixtures as a function of toluene mole fractions (M): 0.00 (a solid line), ~0.35 (a dotted line) and ~0.63 (a dash-dotted line). The inset shows the ~328.8 nm band in more detail in the solutions with the above mole fractions of toluene. The fixed concentration of C_{60} fullerene in solutions was ~16 mg/dm^3.

absorption bands in short- and long-wave parts of the spectrum increase, which indicates the presence of intermolecular interactions between the molecules of the C_{60}–C_{60} and C_{60}–solvent. In addition, with an increase in the molar fraction of toluene in the mixture, significant changes are observed in the behavior of the optical spectra with respect to the spectrum of C_{60} in hexane (see Fig. 1). In particular, at the molar fraction of toluene (~0.63 M) in solution, a bathochromic shift (positive solvatochromic effect) is observed in the bands λ_1≈328.8 nm (shifted by ~5.2 nm), λ_2≈404.4 nm (shifted by ~2.0 nm) and λ_8≈620 nm (shifted by ~3 nm). These changes indicate a significantly different charge distribution of the π-electrons of C_{60} in the excited electronic state compared to that in the ground state of the molecules after the replacement of the solvent.

Experimental measurements by the DLS method provide additional information on the size of C_{60} clusters synthesized as a result of self-organization of molecules in the C_{60}/hexane/toluene solution. Figure 2 shows the size distribution of C_{60} clusters by light intensity in a C_{60}/hexane/toluene with toluene mole fractions ~0.35 (a dotted line) and ~0.63 (a solid line) at fixed low concentration of C_{60} ~16 mg/dm^3. Analyzing the curves, we can say that the hydrodynamic size distribution of C_{60} nanoclusters in a low concentration C_{60} solution has a so-called monomodal peak over the entire size range. It can be seen that C_{60} nanoclusters synthesized in C_{60}/hexane/toluene solutions are characterized by a hydrodynamic diameter ~0.71÷25.0 nm. Moreover, the diameter of the C_{60} nanoclusters decreases with increasing toluene content in the solution. The latter can be assumed that with an increase in the content of toluene in the system, C_{60} fullerene molecules tend to good solubility in solution.

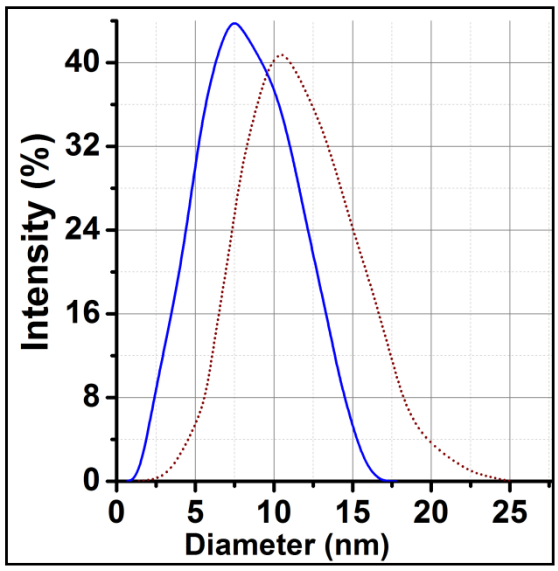


Figure 2. The size distribution of mC_{60} nanoclusters synthesized in the C_{60}/hexane/toluene system by light intensity at two different toluene mole fractions (M): ~0.35 (a dotted line) and ~0.63 (a solid line). The fixed concentration of C_{60} fullerene in solutions was ~16 mg/dm^3.

C_{60}/hexane/toluene solution with toluene mole fractions ~0.63 M (Fig. 2, a solid line) has a peak at ~7.54 nm with a distribution of fullerene nanoclusters along the hydrodynamic diameter in the size range ~0.71÷16.92 nm. At a toluene molar fraction of ~0.35 M (a dotted line), nanoclusters are synthesized in solution with a wider distribution of hydrodynamic diameter from ~2.2 nm to ~25.0 nm, and the maximum value of their diameter is ~10.44 nm. Such sharp differences in the size characteristics of the synthesized C_{60} clusters in the C_{60}/hexane/toluene medium indicate the decisive role of the solvent used in determining the nature of self-organization of C_{60} molecules.

Next, we studied the processes occurring inside evaporating drops of C_{60} fullerene solutions on the substrate surface. It is known that in recent years an ordinary "drop" rapidly evaporating due to thermal effects in a limited volume (V_0 ≈4÷12 mm^3) is considered as a simple and promising model "reactor" for

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the accelerated synthesis of various structures [8]. Under the conditions of our experiments, after evaporation of organic solvents from a drop of fullerene solution transferred onto a heated substrate, a solid phase formed on the surface of the substrate, consisting of filamentary crystal structures of C_{60} fullerene.

Figure 3 shows the SEM image of C_{60} fullerene filamentary crystal structures (nanowhiskers) synthesized in the volume of an evaporating drop of C_{60}/hexane/toluene solution located on the surface of a flat silicon substrate heated to ~30°C.

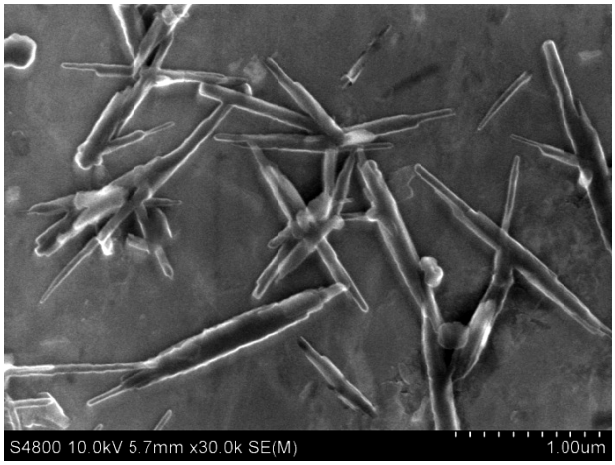


Figure 3. SEM image of C_{60} fullerene filamentary crystal structures (nanowhiskers) synthesized in the volume of an evaporating drop of C_{60}/hexane/toluene solution located on the surface of a flat silicon substrate at a temperature of T≈30 °C. The toluene molar fraction was ~0.35 M and the initial concentration of C_{60} in solution was ~18 mg/dm^3.

Under such conditions, the maximum length and width of the obtained filamentous crystalline whiskers of C_{60} reached the values of ~2.0 μm and ~200 nm, respectively (see Fig. 3). It can be noted that the proposed method for obtaining one-dimensional nanostructures based on fullerenes is simple and economical, as well as easily scaled and optimized.

III. Conclusion

Using refractometry and optical absorption methods, it was found that as the concentration of C_{60} and the volume fraction of hexane in the studied solutions of C_{60}/hexane/toluene increase, the enhancement of intermolecular interactions of molecules is accompanied by self-organization of individual fullerene molecules. An increase in the content of toluene in the C_{60}/hexane/toluene system leads to significant changes in the charge transfer between the solute and the solvent, which, in particular, exhibit both a positive solvatochromic effect and a bathochromic effect in the intense absorption band at ~328.8 nm. The DLS results show that the hydrodynamic size distribution of C_{60} nanoclusters in C_{60} solution has a monomodal peak over the entire size range. It has been established that C_{60} nanoclusters synthesized in C_{60}/hexane/toluene solutions at a fullerene concentration of ~16 mg/dm^3 are characterized by a hydrodynamic diameter of ~0.71÷25.0 nm. In particularly, at a toluene mole fraction of ~0.63 M has the hydrodynamic diameter in the size range ~0.71÷16.92 nm and ~0.34 M nanoclusters are synthesized in solution with a wider distribution of hydrodynamic diameter from ~2.2 nm to ~25.0 nm. It has been established by SEM that after the evaporation of organic solvents (hexane/toluene) from a drop of fullerene solution transferred to a heated substrate (up to ~30°C), filamentary crystal nanostructures (nanowhiskers) of C_{60} fullerene were formed on the surface of the substrate. The obtained scientific results are important for the efficient use of fullerene solutions, especially in the areas of nanotechnology requiring controlled and selective liquid disperse systems.

Acknowledgements. The present research was supported by the Fund for Basic Research of the Academy of Sciences of Uzbekistan: "Investigation of the physical regularities of the self-organization processes of organic nanoscale materials in liquid systems".

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Толуол-гексан эритувчилар тизимидаги C_{60} фуллереннинг хусусиятлари

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C_{60}/толуол/гексан эритмасида C_{60} фуллеренни молекулаларининг ўз-ўзидан агрегацияси хусусиятлари рефрактометрия, оптик спектроскопия, ёруғликнинг динамик сочилиши (ЁДС) ва электрон микроскопия методлари билан ўрганилди. C_{60}/толуол/гексан эритмасида C_{60} фуллеренни концентрацияси ва толуолнинг ҳажмий улуши бироз ортиши билан муҳитнинг синдириш кўрсаткичи ва оптик спектрларининг ўзгариши экспериментал равишда аниқланди. Эритмадаги толуол миқдорининг ортиши ~328.8 нм интенсив ютилиш соҳасида ҳам ижобий сольватохром, ҳам гиперхром эффектни намоён қилади. Шу билан бирга, ЁДС методи ёрдамида C_{60}/гексан/толуол тизимидаги толуолнинг моль улуши ортиши билан эритма ичида синтезланган нанокластерлар ўлчами камайиши аниқланди. Қиздирилган (~30°C гача) қаттиқ таглик сиртига ўтказилган фуллерен эритмаси томчиларидан гексан ва толуол буғлангандан сўнг таглик сиртида C_{60} фуллеренни асосида филаментли кристалли наноструктуралар ҳосил бўлиши ўрнатилди.

Калит сўзлар: C_{60} фуллерени, толуол/гексан эритувчилар аралашмаси, ўз-ўзидан агрегацияланиш, синдириш кўрсаткичи, ЁДС, нанокластер, нановискерлар.

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