Study of stabilization of self-assembly processes in fullerene C_{60} solution

U.K. Makhmanov[*,1,2], A.M. Kokhkharov[1], Sh.A. Esanov[1], B.A. Aslonov[1], B.A. Sindarov[1], Z. Bekmurodov[1]

[1] Institute of Ion-Plasma and Laser Technologies named after U.A. Arifov, Academy of Sciences of the Republic of Uzbekistan, 33, Durmon yuli str., 100125, Tashkent, Uzbekistan
[2] National University of Uzbekistan named after Mirzo Ulugbek, 4, University str., 100174, Tashkent, Uzbekistan

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* Corresponding author: e-mail: urol_m@mail.ru, Phone: +998 90 355 99 47

Методом рефрактометрии исследована динамика изменения показателя преломления растворов фуллерена C_{60} в ксилоле при различных концентрациях. Установлено, что отклонение от линейной зависимости показателя преломления от концентрации C_{60} происходит при концентрации C_{60}~1.8 мг/мл, что связано с наибольшим количеством молекулярных взаимодействий между C_{60}–C_{60} и образованием на их основе крупных нанокластеров в растворе. Методом динамического рассеяния света (ДРС) установлено, что конечный размер нанокластеров C_{60} в растворе зависит от начальной концентрации растворенного вещества. Более высокая начальная концентрация C_{60} приводит к синтезу крупных в диаметре нанокластеров. Методом оптической спектроскопии изучены процессы самоорганизации молекул фуллерена C_{60} в растворе ксилола во времени. Обсуждается характер устойчивости синтезированных нанокластеров фуллерена в растворе. Полученные результаты имеют особое значение для многочисленных приложений нанотехнологии для понимания процессов самосборки и разработки новых наноматериалов.

Ключевые слова: фуллерен C_{60}, раствор в ксилоле, оптические спектры, рефрактометр, наноструктура, кластерообразование, стабильность.

The dynamics of changes in the values of the refractive index of solutions of C_{60} in xylene at various concentrations has been studied by the refractometric method. It was found that the deviation from the linear form of the dependence of the refractive index on the C_{60} concentration occurs at a C_{60} concentration of ~1.8 mg/ml. The deviation is associated with the largest number of molecular interactions between C_{60}–C_{60} and the formation of large nanoclusters on their basis in solution. It was found by the dynamic light scattering (DLS) that the final size of C_{60} nanoclusters in solution depends on the initial concentration of the solute. A higher initial concentration of C_{60} leads to the synthesis of nanoclusters with a larger diameter. Using the method of optical spectroscopy, the processes of self-organization of fullerene C_{60} molecules in a xylene solution in time are studied. The character of stability of synthesized fullerene nanoclusters in solution is discussed. The results obtained are of particular importance for numerous applications of nanotechnology for understanding self-assembly processes and the development of new nanomaterials.

Keywords: fullerene C_{60}, solution in xylene, optical spectra, refractometer, nanostructure, cluster formation, stability**.**

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I. Introduction

Research on carbon-containing nanomaterials, in particular allotropic modifications of carbon, will be crucial for the future of science and technology. Allotropes of pure carbon nanostructured materials such as fullerenes, graphene, and carbon nanotubes have generated a lot of interest due to their chemical and physical properties [1]. Each carbon allotrope exhibits different properties depending on its structure and size. For example, according to carbon hybridization, fullerenes have sp^2-hybridized carbon atoms [2].

Fullerenes C_n (n=60, 70) have a quasi-spherical shape of carbon allotropy and were discovered as a result of laser evaporation of graphite with the help of Kroto's group in 1985 [3], which received the Nobel Prize in 1996 for this discovery. Fullerenes C_n (n = 60, 70) are the most studied elements of the future nano era. Fullerenes exhibit unique physical properties that have great potential for widespread use, such as solar cells [4-5], super-capacitors [6-7], diode [8], gas storage [9-10], scanning tunneling microscope tips [11], nanoelectronics [12-14], phototherapy [15-16], pharmaceutical [17] and biomedical applications [18-20].

The most stable and peculiar molecule of Buckminsterfullerene C_{60} is soluble in many non-polar organic solvents [21]. At the same time, non-polar solvents such as toluene, xylene, carbon disulfide, dichlorobenzene, etc., are commonly used to recover fullerene (C_{60}) from freshly prepared carbon black after the synthesis process. In addition, C_{60} fullerene exhibits unique optical properties that have high potential for wide photo-optical applications [22]. Fullerene C_{60} solutions are characterized by the formation of clusters of fullerene molecules in them [23-24], the formation of which occurs within several months after dissolution. The latter fact makes it possible to study in detail the processes occurring in the system at various stages of aggregation. However, there are few data on the temporal changes in the self-assembly processes of C_{60} fullerene molecules in weakly polar solvents, for example, in xylene.

In this work, we demonstrate new experiment measurements of refractive index of solutions of C_{60} in xylene that will be useful to determine crucial concentration at which cluster formation is stable. We also study of optical absorption characteristics of C_{60} solutions over time to determine the structural stability of the colloidal system.

II. Materials and methodology

In the experiments, we used fullerene C_{60} powder (SES Research, USA) with a purity of less than 99.8% and an organic solvent-xylene of analytical purity from Sigma Aldrich (USA).

To prepare the initial solution, the previously weighed mixtures C_{60}-xylene were mechanically stirred in a laboratory magnetic stirrer "Vortex Dlab MX-S" for 0.5 h at a temperature of ~22±1ºC.

The refractive indices of C_{60} fullerene solutions were determined using an Atago PAL-BX/RI digital refractometer (Atago, Japan) with a measurement error of <0.0001. The measurements are carried out at ~589.3 nm, the wavelength of the atomic sodium D_1-line. For the refractive index measurements, C_{60} solutions in xylene were prepared in a concentration range of C_{60}~0.4–3.0 mg/ml.

The geometrical sizes of the synthesized mC_{60} nanoclusters (where m is the number of fullerene C_{60} molecules in nanocluster) were measured by dynamic light scattering (DLS) on a Zetasizer Nano ZS instrument (Malvern Instruments, Oxford, UK).

Electronic absorption spectra of C_{60} solutions were recorded using UV-2700 UV-Vis spectrometer with a spectral resolution of ~0.1 nm and wavelength scanning from 185 to 900 nm (Shimadzu, Japan).

III. Results and discussion

First of all, we investigate the relationship between the self-assembly of the C_{60} molecules and the change in the refractive indices of the C_{60} fullerene solution. The dependence of the experimental refractive indices of fresh prepared solution of fullerene C_{60} in xylene on the concentration of the solute is shown in Figure 1. The change in the value of the refractive index of the solution with an increase in the concentration of the solute should be dependent on the degrees of intermolecular interactions C_{60}–C_{60} and C_{60}–xylene. It can be seen that in the concentration range of fullerene C_{60} in a solution of ~0.4–1.6 mg/ml, the value of the refractive index of the solution increases linearly. In our opinion, in this case, both C_{60}–C_{60} and C_{60}–xylene intermolecular interactions occur in the solution. As a result, a xylene molecule forms a layer around C_{60} molecules in solution, and ultimately small mC_{60} nanoclusters are synthesized on their basis. However, it can be seen from Fig. 1 that starting with a concentration of C_{60} in a solution of ~1.8 mg/ml, the angle of the dependence line decreases markedly. This indirectly shows that in the concentration of C_{60} in solution from ~1.8 mg/ml to ~3.0 mg/ml intermolecular interactions

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C_{60}–C_{60} are enhanced. The latter lead to the formation of rather large mC_{60} nanoclusters only on the basis of the fullerene C_{60}. The below measured results by the DLS method confirm the latter assumption.

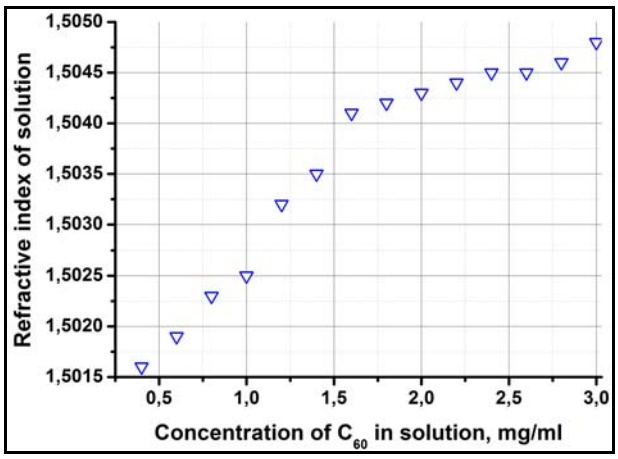


Figure 1. Dependence of the refractive index values of a fresh solution of C_{60} in xylene on the concentration of C_{60} in the solution.

The results of dynamic light scattering for fullerene C_{60} in xylene at two different concentrations of C_{60} are shown in Fig. 2. At a concentration of C_{60}~1.05 mg/ml in xylene, the histogram shows monomodal peak in the size range of mC_{60} nanoclusters with a diameter of ~145–180 nm (see histogram *1*). In this case, the average size of fullerene nanoclusters corresponds to ~163 nm.

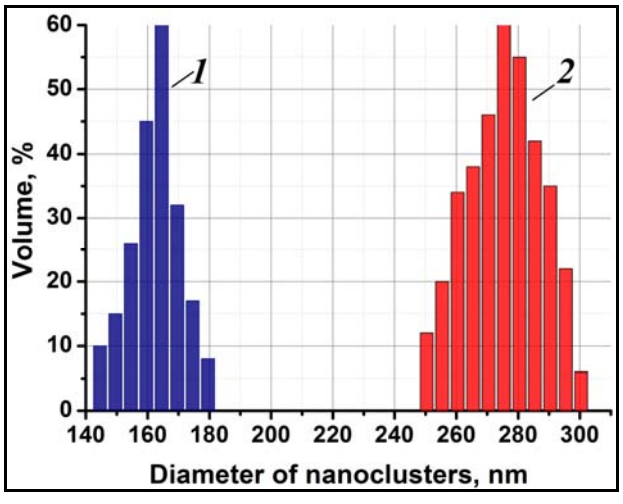


Figure 2. The size distribution of mC_{60} nanoclusters in the freshly prepared fullerene solution in xylene at two different solute concentrations: ~1.05 mg/ml (*1*) and ~1.85 mg/ml (*2*).

At a concentration of C_{60}~1.85 mg/ml in xylene, the monomodal peak becomes with a broader particle size distribution from ~250 to ~300 nm (see histogram *2*). The average size of mC_{60} nanoclusters in xylene for this concentration is ~275 nm. With an increase in the concentration of C_{60} fullerene in solution, additional self-aggregation of fullerene molecules is observed, which manifests itself in the form of a shift in the value of the hydrodynamic diameter of mC_{60} nanoclusters to a region of large sizes (see Fig. 2). In previous studies [25-26], it was shown that the synthesis of C_{60} nanoclusters occurs inside a two-component solvent xylene+tetrahydrofuran and toluene+tetrahydrofuran.

In this article also, changes in the absorbance of a C_{60} solution in xylene over time will be investigated using UV/visible spectrometry. Figure 3 shows the changes in the measured values of the optical density of a freshly prepared solution of fullerene C_{60} for different storage times. Measurements were performed at a fixed wavelength of ~336 nm. The fixed concentration of C_{60} in solution was ~1.85 mg/ml. As can be seen, inside a freshly prepared solution, the process of self-assembly of C_{60} molecules immediately begins and lasts up to 15 days, naturally, in this case, the optical density values gradually increase.

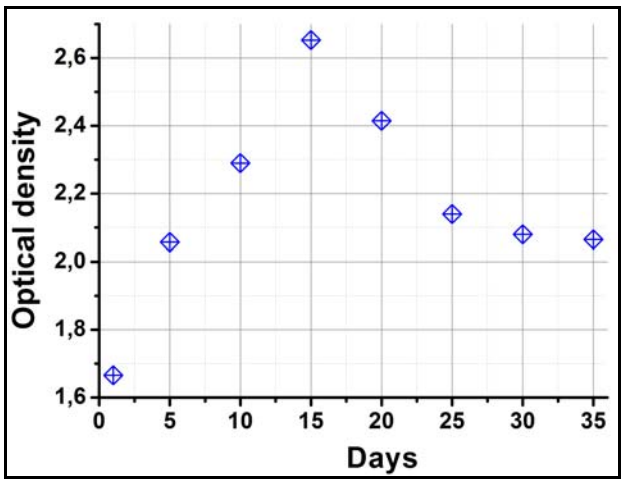


Figure 3. Change in the values of optical density of solutions of fullerene C_{60} at a fixed concentration of C_{60} ~ 1.85 mg/ml in xylene with different storage times of solutions. The measurements were carried out at a fixed wavelength of ~336 nm.

After 15 days of storage of the solution, the intensity of absorption is completely reduced, although the C_{60} solution remains colloidal. The results show

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that the optical density of the C_{60} solution after storage for 30 and 35 days is practically indistinguishable, which allows us to conclude that the stability of the synthesized C_{60} fullerene clusters in solution has been achieved.

The used high precision methods and the experimental results obtained can be used to analyze the character of the solvent-solute interaction in a wide range of practical applications in nanochemistry and nanophysics.

IV. Conclusion

We have investigated the stabilization of self-assembly processes of C_{60} fullerene molecules inside the fresh prepared solution by the refractometric, DLS and optical absorption spectroscopy methods. It was determined that the change in the value of the refractive index of the C_{60} solution in xylene with an increase in the concentration of the solute should depend on the enhancement of the inter-molecular interactions C_{60}–C_{60} and C_{60}–xylene. The critical concentration of C_{60} in the solution (~1.8 mg/ml), which indicates the enhancement of intermolecular interactions only C_{60}–C_{60} and the synthesis of nanoclusters only on the basis of fullerene C_{60}, was established by refractometry.

The DLS results showed that the geometric dimensions of the synthesized mC_{60} nanoclusters are determined by the initial concentration of C_{60} in the solution. An increase in the initial concentration of fullerene C_{60} in solution leads to an increase in the diameters of synthesized mC_{60} nanoclusters in solution.

Prolonged spectrometric observations of the C_{60} solution in the UV/visible range made it possible to conclude that the synthesized mC_{60} nanoclusters are highly structurally stable upon long-term storage for 30 days at room temperature in a dark place.

The experimentally obtained results on the formation of mC_{60} nanoclusters in a fresh solution and their achievement on stability in solution, apparently, open up some new possibilities for obtaining new structurally stable functional nanomaterials based on nanosized particles for micro- and opto-electronic devices, nanocomposites, photodetectors, solar cells, energy storage devices and biosensors.

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C_{60} фуллеренни эритмасида ўз-ўзидан йиғилиш жараёнлари барқарорлигини ўрганиш

У.К. Махманов[1,2], А.М. Коххаров[1], Ш.А. Эсанов[1], Б.А. Аслонов[1], Б.А. Синдаров[1], З. Бекмуродов[1]

[1] ЎзР ФА У.А. Арифов номидаги Ион-плазма ва лазер технологиялари институти, Дўрмон йўли кўчаси 33, 100125, Тошкент, Ўзбекистон
[2] Мирзо Ўлуғбек номидаги Ўзбекистон Миллий университети, Университет кўчаси 4, 100174, Тошкент, Ўзбекистон

Рефрактометрия усули ёрдамида C_{60} фуллереннинг ксилолдаги эритмасининг нур синдириш кўрсаткичи қийматларининг ўзгариш динамикаси ўрганилди. C_{60} концентрацияси ~1.8 мг/мл бўлганда, нур синдириш кўрсаткичининг C_{60} концентрациясига чизиқли боғлиқлигидан четлашиш кузатилди. Бу четлашиш C_{60}-C_{60} ўртасидаги кўп миқдордаги молекуляр ўзаро таъсирлар ва эритмада катта ўлчамдаги нанокластерларнинг ҳосил бўлиши билан боғлиқ. Ёруғликнинг динамик сочилиши (ЁДС) методи ёрдамида эритмаларда синтезланган C_{60} нанокластерлари ўлчами эриган модданинг дастлабки концентрациясига боғлиқлиги ўрнатилди. C_{60} нинг юқорироқ концентрацияси каттароқ диаметрдаги нанокластерлар синтезига олиб келади. Ксилол эритмасида C_{60} фуллерен молекулаларининг вақт бўйича ўз-ўзидан ташкилланиш жараёнлари оптик спектроскопия ёрдамида ўрганилди. Эритмада синтез қилинган фуллерен нанокластерларининг барқарор-лиги хусусияти муҳокама қилинди. Олинган натижалар нанотехнологияда ўз-ўзидан йиғилиш жараёнларини тушуниш ва янги наноматериалларни ишлаб чиқишда муҳим аҳамиятга эга.

Калит сўзлар: C_{60} фуллерен, ксилолдаги эритма, оптик спектрлар, рефрактометр, наноструктура, кластер ҳосил бўлиши, барқарорлик.

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