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

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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 $\sim 1.8$ 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 sp²-hybridized carbon atoms [2].

Fullerenes Cₙ (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 Cₙ (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 C₆₀ 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 (C₆₀) from freshly prepared carbon black after the synthesis process. In addition, C₆₀ fullerene exhibits unique optical properties that have high potential for wide photo-optical applications [22]. Fullerene C₆₀ 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 C₆₀ fullerene molecules in weakly polar solvents, for example, in xylene.

In this work, we demonstrate new experiment measurements of refractive index of solutions of C₆₀ in xylene that will be useful to determine crucial concentration at which cluster formation is stable. We also study of optical absorption characteristics of C₆₀ solutions over time to determine the structural stability of the colloidal system.

II. Materials and methodology

In the experiments, we used fullerene C₆₀ 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 C₆₀-xylene were mechanically stirred in a laboratory magnetic stirrer "Vortex Dlab MX-S" for 0.5 h at a temperature of ~22±1°C.

The refractive indices of C₆₀ 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 D₂-line. For the refractive index measurements, C₆₀ solutions in xylene were prepared in a concentration range of C₆₀~0.4–3.0 mg/ml.

The geometrical sizes of the synthesized mC₆₀ nanoclusters (where m is the number of fullerene C₆₀ molecules in nanocluster) were measured by dynamic light scattering (DLS) on a Zetasizer Nano ZS instrument (Malvern Instruments, Oxford, UK).

Electronic absorption spectra of C₆₀ 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 C₆₀ molecules and the change in the refractive indices of the C₆₀ fullerene solution. The dependence of the experimental refractive indices of fresh prepared solution of fullerene C₆₀ in xylene on the concentration of the solute is shown in Figure 1. The change in the value of the refractive index of the solvent with an increase in the concentration of the solute should be dependent on the degrees of intermolecular interactions C₆₀~C₆₀ and C₆₀~xylene. It can be seen that in the concentration range of fullerene C₆₀ 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 C₆₀~C₆₀ and C₆₀~xylene intermolecular interactions occur in the solution. As a result, a xylene molecule forms a layer around C₆₀ molecules in solution, and ultimately small mC₆₀ nanoclusters are synthesized on their basis. However, it can be seen from Fig. 1 that starting with a concentration of C₆₀ in a solution of ~1.8 mg/ml, the angle of the dependence line decreases markedly. This indirectly shows that in the concentration of C₆₀ in solution from ~1.8 mg/ml to ~3.0 mg/ml intermolecular interactions...
$C_{60}$-$C_{60}$ 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.

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.

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...
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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References

C₆₀ фуллеренини эритмасида ўз-ўзидан йигилиш жараёнлари баркарорлигини ўрганиш

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Рефрактометрия усули ёрдамида C₆₀ фуллеренинг қисиқлдаги эритмасининг нур синдириш кўрсаткичи кийматларининг ўзгариши динамикаси ўрганилди. C₆₀ концентрацияси ~1.8 мг/мл бўлганда, нур синдириш кўрсаткичининг C₆₀ концентрациясига чиқили боғлиқли қўйилиши кўрсатилди. Бу четлаши C₆₀-C₆₀ ўртасидаги кўп миқдордаги молекул ўзаро таъсирлар ва эритматда катта ўлчамдаги нанокластерларнинг ҳосил бўлиши билан боғлиқ. Ёрдамийнинг динамиқ сочилёни (UEDS) методи ёрдамида эритматларда синтезланган C₆₀ нанокластерлари ўлчами эртган модданинг дастлабки концентрациясиға боғлиқли ҳўрнатилди. C₆₀ нинг юқориқон концентрациясига каттароқ диаметрдаги нанокластерлар синтези олиб келади. Қисиқлдаги C₆₀ фуллерени молекулаларининг вакт бўйича ўз-ўзидан ташкилланган жараёнлар оптик спектроскопия ёрдамида ўрганилди. Эритматда синтез қилинган фуллерен нанокластерларининг баркарорлиги ҳусусияти мухокама қилини. Олинган натижалар нанотехнологияда ўз-ўзидан йигилиш жараёнларининг тушуниш ва яниг наноматериалларни ишлаб чиқишда муҳим аҳамиятга эга.

Калит сўзлар: C₆₀ фуллерен, қисиқлдаги эритма, оптик спектрлар, рефрактометр, наноструктура, кластер ҳосил бўлиши, баркарорлик.