

Behavior of C₇₀ Fullerene in a Binary Mixture of Xylene and Tetrahydrofuran

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Abstract: The self-organization properties of C₇₀ fullerene molecules in a xylene/tetrahydrofuran binary mixture were studied for the first time by optical absorption, refractometry, and dynamic light scattering. A correlation has been established between the change in the refractive index of the C₇₀/xylene/tetrahydrofuran solution and the degree of self-organization of C₇₀ molecules in the medium at various concentrations and storage periods of the solution. It is shown that the features of the optical absorption spectrum of C₇₀/xylene/tetrahydrofuran at a fixed low concentration of fullerene are sensitive to its storage time. It was determined that the beginning time of the formation of C₇₀ nanoclusters and their final size depend on the degree of concentration of fullerene and the time spent keeping the solution. The observed nature of the C₇₀ fullerene solution in a binary mixture may help to elucidate its mechanism of self-organization in the future.

Keywords: C₇₀ fullerene; xylene/tetrahydrofuran; self-organization; refractive index; DLS; UV-Vis absorption; nanocluster



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1. Introduction

Currently, the attention of scientists around the world is focused on studying the characteristics of nanoparticles of various natures, the synthesis of nanostructured functional materials that are based on them, as well as the possibility of using them as promising materials for applications [1–4]. It is known that due to the high degree of distribution of atoms on the surface of nanomaterials and their quantum limitations, they have unusual, unique properties that differ from the properties of their bulk materials [5].

The study of allotropic forms of carbon, one of the most dynamically developing areas of modern science, is also associated with the study of fullerenes [6]. All carbon atoms in fullerene molecules are attractively distributed on their quasi-spheroidal surfaces, which causes unusual features of their behavior in solutions [7–9]. Among the currently most studied families of fullerene molecules is the C₇₀ molecule, whose structure corresponds to a cellular ring structure resembling a rugby ball. Due to its unique physical and chemical properties, C₇₀ fullerene has a wide range of applications as the main building block in nanotechnologies, electromagnetic devices, solar panels, sensors, pharmaceuticals, tribological materials, coatings, etc. [10–14].

Currently, depending on the solubility of C₇₀ fullerene in one-component solvents, fullerene solutions can be divided into solutions in low-polar solvents (with a good solubility) and solutions in polar solvents (weakly soluble or almost insoluble) [15]. In experiments, the formation of C₇₀-based complexes in high-concentration solutions in “good” (low polar) solvents sometimes occurs easily [16–18], but plainly colloidal solutions are often formed, depending on the preparation method of the solution [19,20]. The spontaneity of the self-aggregation of C₇₀ molecules in “good” solvents indicates a strong dispersion

interaction of fullerene. The study of the behavior of C_{70} fullerene in one-component polar solvents [21–25], and in particular the transfer of fullerene into water, opens the way for the use of fullerene for biological and medical purposes.

To date, many scientific papers have been published on the study of the characteristics of C_{70} fullerene in various two-component organic solvents [26–29]. In this case, C_{70} fullerene solutions are mainly considered as dispersed systems, since the C_{70} molecule tends to self-organize in binary solutions. Mixing fullerene in “good” solvents with polar solvents easily leads to the formation of true colloidal systems [30,31]. There is evidence that the nature of self-organization of C_{70} fullerene is affected not only by the content of the solvent used, but also by the concentration of the fullerene itself [32,33].

Understanding the self-organization of C_{70} molecules in solutions is necessary for the synthesis of nanostructured materials that are based on them using well-controlled properties. The determination of the start time and duration of clustering of C_{70} molecules in solutions has also not been fully studied. These issues are a very complex experimental problem and require systematic study, since the phenomena controlling self-organization take place at subnanometer sizes. In particular, the study of physical processes occurring at low concentrations of C_{70} fullerene in two-component solvents is of interest from both fundamental and practical points of view.

This paper presents experimental studies of C_{70} /xylene/tetrahydrofuran solutions at low fullerene concentrations by optical absorption, refractometry, and dynamic light scattering (DLS). The stabilization times of the cluster formation in fullerene solution are also discussed.

2. Materials and Methods

Fullerene C_{70} with a high purity (99.5%) as well as *o*-xylene (C_8H_{10} , hereafter referred to as xylene) and tetrahydrofuran (C_4H_8O , hereafter referred to as THF) organic solvents used in the present study were acquired from Sigma-Aldrich, Saint Louis, MO, (USA). All chemicals were used as received. THF is a good soluble in xylene, and their dielectric constant is ~ 7.52 and ~ 2.57 , respectively.

To prepare C_{70} fullerene solutions of various concentrations, a weighed portion of a preliminarily prepared C_{70} fullerene crystal was added to a flask with precisely measured amounts of aromatic and non-aromatic solvents (xylene and THF at a volume ratio of 0.9:0.1, respectively). Then, the resulting mixture was dissolved in a hermetically sealed glass flask at room temperature for 4–5 h with mechanical stirring using a programmable laboratory magnetic stirrer “MS-11 H” (WIGO, Pruszkow, Poland) with a frequency of 2.5 Hz. The solutions were filtered through a dense filter with a pore size of $\sim 0.22 \mu\text{m}$. In the C_{70} /xylene/THF system, the concentrations of C_{70} fullerene used in our experiments are below the solubility limit [22], and after filtration, almost no substance remains on the filter. The concentration of the fullerene C_{70} obtained in this way in the initial solution was further considered to be the initial concentration.

The exact values of the refractive indices (n) of C_{70} /xylene/THF systems with two different concentrations ($\sim 1.19 \times 10^{-5}$ and $\sim 2.37 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) were measured using a digital refractometer PAL-BX/RI (ATAGO, Fukui, Japan) at the wavelength of the D_1 -line of the sodium atom ($\sim 589.3 \text{ nm}$). The measurement accuracy of the refractive index of the solution was ± 0.0003 . The values reported in this work are the average of at least three independent replicated data.

Optical absorption spectra of C_{70} solutions were recorded on a Shimadzu UV-2700 UV-Vis recording spectrophotometer (Shimadzu, Osaka, Japan) with a spectral resolution of $\sim 0.1 \text{ nm}$ in the spectral range of ~ 185 – 900 nm .

The nature of the distribution of the dispersed phase of C_{70} fullerene over the average hydrodynamic diameter in solutions was studied by dynamic light scattering (DLS) on a Zetasizer Nano ZEN3600 system (Malvern Instruments Ltd., Malvern, Worcestershire, UK) equipped with a He-Ne laser (4 mW at 632.8 nm). The position of the detection system of the device is placed at a scattering angle of 175° .

Zetasizer Nano ZEN3600 is a highly sensitive analyzer of effective hydrodynamic diameters (from ~0.3 nm to ~10 μm) of fullerene clusters in solutions. The DLS method makes it possible to determine the value of the diffusion coefficient of nanoclusters in a fullerene solution by analyzing the correlation function of scattered light intensity fluctuations over time. The hydrodynamic diameter (d_h) of the synthesized fullerene nanoclusters, in turn, depends on the diffusion coefficient (D_h) of nanoclusters, according to the well-known Stokes–Einstein formula [34]:

$$d_h = \frac{kT}{3\pi D_h \eta} \quad (1)$$

where k is the Boltzmann constant, T is the absolute temperature, and η is the dynamic viscosity.

All measurements on C_{70} solution samples were performed at room temperature ($T \approx 24 \pm 1$ °C). Storage of freshly prepared C_{70} solutions for different times was carried out in the dark.

3. Results and Discussion

Data on the change in the refractive index (n) of C_{70} fullerene solutions provide us with important information about the interaction of solute and solvent molecules. The measured refractive index of the xylene/THF mixture (volume ratio of 0.9:0.1, respectively) is 1.4915. The change in the concentration of C_{70} fullerene in the C_{70} /xylene/THF solution from $\sim 1.19 \times 10^{-5}$ to $\sim 2.37 \times 10^{-5}$ mol·L⁻¹ led to an increase in the refractive index of the solution medium (see Table 1). With an increase in the concentration of C_{70} in the studied solutions, the intermolecular interactions of molecules are intensified, and the processes of self-organization of the fullerene molecule begin. In this case, an increase in the number of bonds between the “ C_{70} - C_{70} ” and “ C_{70} -solvent” molecules leads to a greater interaction of light photons and, consequently, to an increase in the refractive index of solutions. When the solution is stored for up to 3 days, an increase in the refractive index of the solution is observed; however, further storage of the solution (up to 9 days) leads to a decrease in the refractive index of the solution. The decrease in the refractive index of the fullerene solution with an increase in the storage period is possibly due to the enlargement of fullerene nanoclusters in time and, as a consequence, a decrease in their amount in the solution. The value of the refractive index of C_{70} /xylene/THF solution after its storage for 9 days remains virtually unchanged. The latter is connected to the stabilization of the process of self-organization of fullerene molecules in solution.

Table 1. Change in the refractive index (n) of a C_{70} /xylene/THF solution over time and depending on the concentration of C_{70} .

C_{70} /(mol·L ⁻¹)	Solution Storage Time	n
$\sim 1.19 \times 10^{-5}$	0 ^a	1.4932
	3rd day	1.4941
	6th day	1.4928
	9th day	1.4919
	12th day	1.4918
$\sim 2.37 \times 10^{-5}$	0 ^a	1.4944
	3rd day	1.4958
	6th day	1.4940
	9th day	1.4934
	12th day	1.4933

^a The freshly prepared C_{70} solution.

The optical spectrum of C_{70} /xylene/THF solution was characterized by broad absorption bands in the visible region and a relatively intense absorption in the UV region. The change in the absorption spectra in the UV-visible region of the spectrum of a freshly prepared C_{70} /xylene/THF solution with time is shown in Figure 1. In this case, the concentration of fullerene in the solution was $\sim 1.19 \times 10^{-5}$ mol·L⁻¹. The absorption spectrum of a

freshly prepared C_{70} /xylene/THF solution showed three pronounced absorption maxima at ~ 332.2 , ~ 382.7 , and ~ 470.5 nm, and two minor maxima at ~ 361.7 and ~ 535.4 nm were observed. The behavior of the optical absorption spectrum of the C_{70} /xylene/THF solution turned out to be sensitive to a certain storage time of the solution (see Figure 1). It can be seen that after keeping the initial C_{70} /xylene/THF solution for several days in a dark place, the change in the intensity of the absorption spectrum of the solution is variable. After 3 days of storage of the solution, the intensity is fully increased, and after 6 days of storage, a gradual decrease begins. In addition, there is a red shift of the maxima at ~ 332.2 nm (by ~ 1.3 nm), ~ 361.7 nm (by ~ 1.8 nm), ~ 382.7 nm (by ~ 0.4 nm) and ~ 470.5 nm (by ~ 2.1 nm). The above effects were caused by an increase in the π -conjugated system of the C_{70} cage, which indicates a decrease in the energy gap between the S_1 excited and S_0 ground states. In addition, the competition between “ C_{70} - C_{70} ” and “ C_{70} -solvent” intermolecular interactions is dominated by the binding of C_{70} molecules in time, forming fullerene associations, which subsequently combine into stable nanoclusters. The results show that after storage for 9 days and 12 days, the electronic absorption spectra of the C_{70} /xylene/THF solution were practically indistinguishable, and this allows us to conclude that the C_{70} fullerene nanoclusters formed in a mixed solution (xylene/THF) achieve stability.

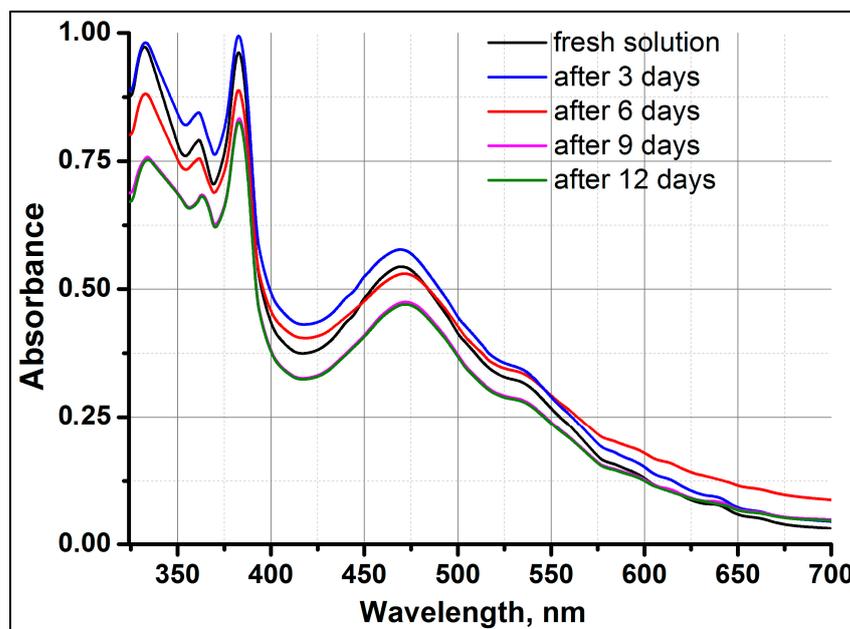


Figure 1. Change in the electron absorption spectrum of the C_{70} /xylene/THF solution with time. The initial concentration of C_{70} in the solution is $\sim 1.19 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$.

The change in absorbance of C_{70} /xylene/THF solution at a fixed characteristic wavelength (~ 470.5 nm) is reported in Figure 2a as a function of time for the initial concentration of C_{70} $\sim 2.37 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$. From this, it can be seen that the absorption changes unevenly, which is associated with an increase in the intermolecular interactions of C_{70} - C_{70} over time. If we compare the results of Figures 1 and 2a, we can say that the changes in absorption are a function of both the initial concentration of fullerene in C_{70} /xylene/THF solution and the storage time of the solution. In this case, as before (see Figure 1), the absorption amplitudes of the solution after storage for 9 days to 12 days are practically indistinguishable. The latter shows the achievement of the stability of the formed C_{70} fullerene nanoclusters in C_{70} /xylene/THF. To assess the degree of self-organization of C_{70} molecules in a C_{70} /xylene/THF solution over time, we measured the hydrodynamic diameter of C_{70} nanoclusters by the DLS method. Figure 2b shows the size distribution of formed C_{70} nanoclusters by light intensity in a C_{70} /xylene/THF with different solution storage times at a fixed concentration of C_{70} $\sim 2.37 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$: 6 days (dotted line)

and 12 days (solid line). A monomodal distribution of the hydrodynamic sizes of C_{70} nanoclusters was found. The C_{70} nanoclusters formed within 6 days are characterized by a hydrodynamic diameter in the range of $\sim 6.97 \div 19.8$ nm and have a peak at ~ 11.63 nm. With an increase in the storage time of the C_{70} /xylene/THF solution, the diameter of the C_{70} nanoclusters increases. It can be seen that within 12 days of storage of the solution, nanoclusters with a wider distribution of the hydrodynamic diameter from ~ 8.02 nm to ~ 33.15 nm are formed, and the maximum value of their diameter is ~ 18.78 nm.

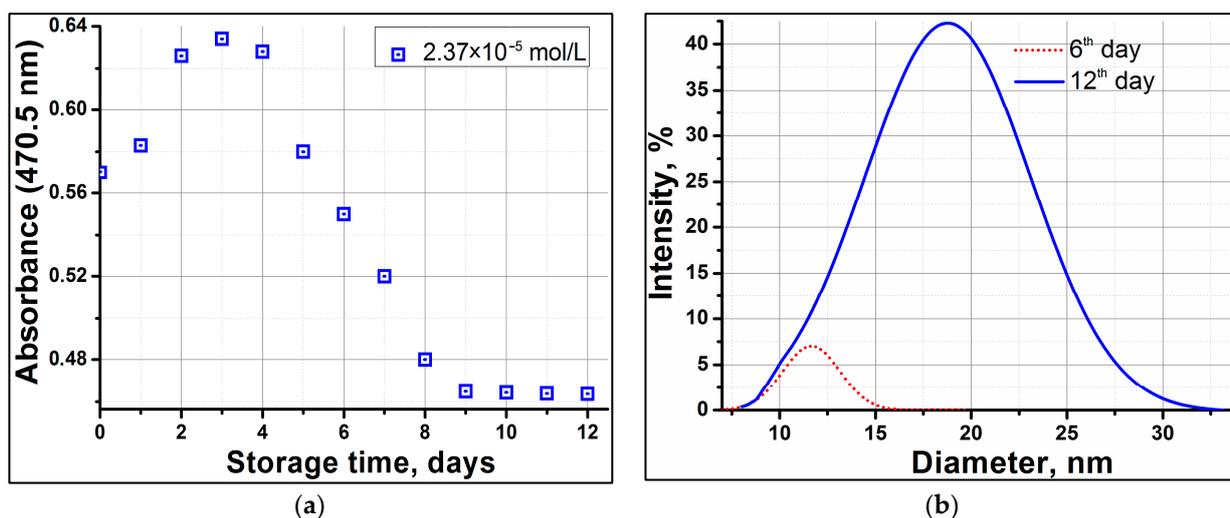


Figure 2. (a) Changes in absorbance and (b) the size distribution of C_{70} nanoclusters in a C_{70} /xylene/THF solution as a function of storage time. The initial concentration of C_{70} in the solution is $\sim 2.37 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$.

It is theoretically known that the formation of nanoclusters consisting of molecules in a solution causes partial scattering of the light falling on it and affects the UV-visible absorption spectra of the solution [35]. The results of calculations in [36] showed that Mie scattering for the particle radius $r \approx 140$ nm makes an insignificant contribution to the UV-VIS spectrum of the fullerene solution. The latter shows a mostly pure absorption in the wavelength range of $\sim 200 \div 700$ nm and refers to the electronic state of the fullerene molecules in the solution. In our case, the largest radius of formed fullerene nanoclusters was $r < 17$ nm (diameter < 34 nm, see Figure 2b), which is relatively smaller than that obtained in [36]. This allows us to conclude that the Mie scattering of light for the fullerene nanocluster with a radius of $r < 17$ nm is practically insignificant and does not affect the UV-visible spectrum of the fullerene solution.

It can be noted that in our previous work [37], the results of experiments on the self-aggregation of C_{60} fullerene molecules in a xylene/THF solvent system (with a volume fraction of 0.95:0.05, respectively) were studied. In this case, it was shown that C_{60} fractal nanoclusters with a diameter of up to ~ 135 nm having a porous structure (fractal dimension $D \approx 2.148$) are formed in C_{60} /xylene/THF, and the final geometric dimensions of nanoclusters are determined by the initial concentration of C_{60} .

The change in the intensity distribution of the average size of formed C_{70} nanoclusters in the C_{70} /xylene/THF system according to time at two fixed concentrations of fullerene C_{70} ($\sim 1.19 \times 10^{-5}$ and $\sim 2.37 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) is shown in Figure 3. It was observed that the beginning of the formation of C_{70} nanoclusters depends on the initial fullerene concentration. The formation of nanoclusters began at a C_{70} concentration of $\sim 1.19 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ from the 3rd day and at a C_{70} concentration of $\sim 2.37 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ from the 2nd day. The nanoclusters' diameter increases almost linearly up to 9 days of storage of the C_{70} /xylene/THF solution, and then the self-organization process proceeds slowly and their size remains unchanged up to 12 days. Thus, we can confirm that there is indeed a self-organization of fullerene molecules in weakly concentrated C_{70} /xylene/THF

solution, leading to the formation of small nanoclusters, and that it is a time-dependent physical process.

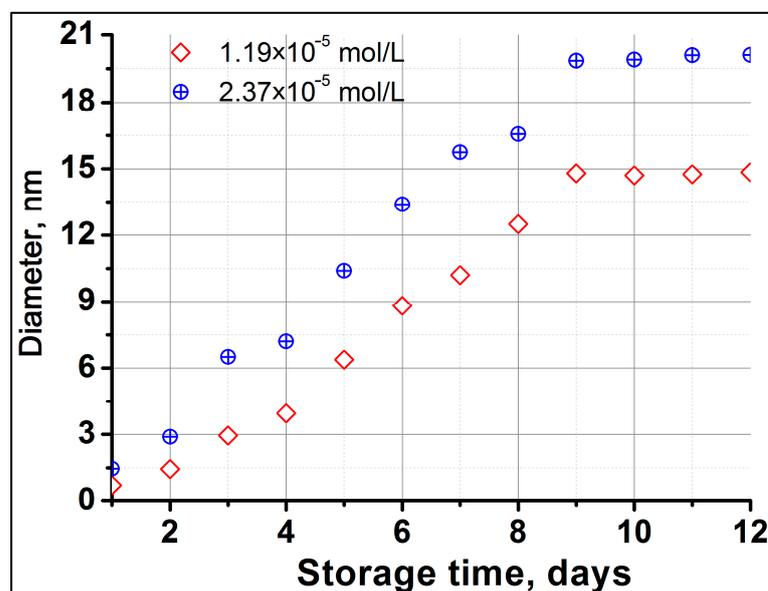


Figure 3. Change in the distribution (by intensity) of the average size of C_{70} nanoclusters in the C_{70} /xylene/THF system with time of its storage at different two fullerene concentrations.

The study of the self-assembly properties of C_{70} fullerene in binary solvents will help in the analysis of the formation of other organic nanoclusters with a similar growth and morphology. The specific parameters of C_{70} nanoclusters (stability inside and out of solution, electron-transporting, photoelectrical properties, energy storage, photovoltaic and other properties) are still not fully understood and thus represent an excellent area for future research.

4. Conclusions

We have presented the experimental results of studying the interactions and self-organization processes of C_{70} fullerene molecules in a two-component solvent system. Our experimental results, obtained using complex methods, confirm the formation of nanoclusters of C_{70} molecules in the binary (xylene/THF) solvent system. It was found that the degree of intermolecular interaction in the C_{70} /xylene/THF solution depends on the initial concentration of fullerene and the time spent keeping the solution.

It was established that with an increase in the concentration of C_{70} in a mixture of C_{70} /xylene/THF, an increase in the number of bonds between the molecules " C_{70} - C_{70} " and " C_{70} -solvent" leads to a greater interaction of light photons and, as a consequence, an increase in the refractive index of solutions. At the initial stage of storage of C_{70} /xylene/THF at a fixed concentration, an increase in the refractive index of the solution is observed, but at later periods of storage of the solution (in the period of 3–9 days), its decrease is found. The latter is associated with an increase in the size of the formed C_{70} nanoclusters over time and, as a result, a decrease in their amount in solution. The sensitivity of the behavior of the electronic absorption of a C_{70} /xylene/THF solution to a certain storage time was determined, which was manifested by a change in the intensity of the absorption spectrum and a red shift of the characteristic maxima (from ~ 0.4 nm to ~ 2.1 nm). This is caused by a decrease in the energy gap between the excited S_1 and ground S_0 states of the fullerene; ultimately, the binding of C_{70} molecules over time predominates, forming nanoclusters. In the case of weakly concentrated C_{70} /xylene/THF, the final size of the formed C_{70} nanoclusters and the velocity of the self-aggregation of fullerene molecules depend on the initial concentration of C_{70} in the solution.

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