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Interaction of Molecules in Solutions of C_{60} in Polar Solvents

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Abstract

The features of fullerene C_{60} in N-methyl-2-pyrrolidone (NMP) solutions and NMP/water solvents were studied using optical absorption spectroscopy, dynamic light scattering (DLS) and atomic force microscopy (AFM). When 30% distilled water was added to the C_{60}/NMP solution, a bathochromic shift (by ~9 nm) and a hyperchromic effect for the characteristic absorption maximum (~331 nm) for the solution, as well as a relatively weak and broad new absorption region around 440 nm, were found. These optical changes are explained by the partial destruction of C_{60}-C_{60} and C_{60}-NMP complexes when water is added to the solution, and the formation of new C_{60}-water complexes or mixed solvate shells of C_{60}-NMP and C_{60}-water during their reorganization. It was determined that at a constant concentration of C_{60} in solutions, the maximum hydrodynamic diameter of the synthesized fullerene nanoaggregates in a C_{60}/NMP solution is ~23 nm, and in a C_{60}/NMP/water solution is ~33 nm.

Keywords: C_{60} Fullerene; C_{60}/NMP; C_{60}/NMP/Water; Optical Absorption Spectrum; Nanoaggregate; Hydrodynamic Diameter

Abbreviations: DLS: Dynamic Light Scattering; AFM: Atomic Force Microscopy.

Introduction

The interaction processes of the light fullerenes (C_{60}, C_{70}) with molecules of various organic and inorganic solvents are actively being studied [1,2]. One of the functions of fullerenes is the formation of donor-acceptor complexes when dissolved in one- and two-component solvents [3]. Additionally, fullerene molecules are known to exhibit control over unusual behavior associated with self-organization [4-6].

An effective direct method for observing physical processes occurring in solutions of fullerenes in experiments is to freeze the solution using an "automated vitrobot" at a very high speed (approximately 10^3 °C/sec) and study it using an transmission electron microscope [7]. Additionally, indirect experimental methods, such as X-ray diffraction analysis (XRD), mass spectrometry, optical spectroscopy, dynamic and static light scattering methods and others are considered effective for determining the physical and chemical properties of fullerenes in various solvents [8-11]. By employing these research methods in a comprehensive manner, it becomes possible to identify different approaches for synthesizing complex structural nanomaterials with novel physicochemical properties based on fullerene molecules.

Currently, due to their unique properties, fullerene-containing nanomaterials are used in nano- and microelectronics devices, solar energy applications including panels and photovoltaic elements, green energy technologies, hydrogen gas storage, sensors, therapeutic purposes in medicine, drug delivery systems in pharmacology, biotechnologies, biochip preparation [12-16]. The potential use of fullerene molecules in modern medicine is mainly attributed to their ability to penetrate lipid membranes, act as effective photosensitizers in singlet oxygen formation, and deactivate free radicals [16,17]. Methods for synthesizing quasispherical materials with monomolecular and porous (fractal) structures based on C_{60} and C_{70} fullerenes in one-component solvents were defined in [18,19]. Synthesis of one-dimensional nanomaterials from the C_{60} molecule in a two-component solvent system was described by the authors of [20,21]. It's worth noting that the interactions between fullerene and solvent molecules, as well as the physical processes involved when transferring C_{60} fullerene to biologically compatible solutions (such as aqueous and alcoholic solutions), are not yet fully understood and require further research.

Hence, the aim of this study is to investigate C_{60}/N-methyl-2-pyrrolidone and C_{60}/N-methyl-2-pyrrolidone/water solutions using optical spectroscopy, atomic force microscopy, and dynamic light scattering (DLS).

Materials and Methods

C_{60} fullerene powder with purity >99.8% (Sigma Aldrich, USA), N-methyl-2-pyrrolidone (C_5H_9NO) with purity >99.5% and double distilled water were used in the experiments. The maximum solubility of C_{60} fullerene in N-methyl-2-pyrrolidone (NMP) is ~0.89 mg/ml, but it is practically insoluble in water. Polar NMP with dielectric constant $\varepsilon = 32$ is completely miscible with water with $\varepsilon=80$ in an arbitrary volume. The mixture of C_{60} powder and NMP was intensively mixed using a magnetic rotator "MS-11H" (WIGO, Poland), and a C_{60}/NMP solution with a concentration of ~0.017 mg/ml was prepared. In another case, distilled water was gradually added to the C_{60}/NMP solution and mixed using a magnetic rotator, and a C_{60}NMP/water solution with a concentration of ~0.017 mg/ml was prepared. In this case, the volume fractions of NMP and water in the solution are 70:30, respectively. All experiments were performed at room temperature ($T \approx 24 \pm 1$°C).

Electronic absorption spectra of the studied solutions were obtained using a Shimadzu UV-2700 spectrophotometer (Shimadzu, Japan) in the wavelength range of ~300÷800 nm.

Morphological properties of C_{60} fullerene nanoaggregates synthesized in solution were studied using an atomic force microscope (AFM) brand "Solver Next" (NT-MDT, Russia).

Hydrodynamic sizes of C_{60} fullerene nanoaggregates were measured by dynamic light scattering (DLS) on a Zetasizer Nano ZEN3600 (Malvern Instruments Ltd.). The device is equipped with a He-Ne laser (with a wavelength of ~633 nm and a power of ~5 mW), the laser beam is directed at the object at an angle of 173°.

Experimental Results and their Discussion

First, the properties of the optical absorption spectra of C_{60}/NMP and C_{60}/NMP/water solutions were studied (Figure 1). The initial concentration of C_{60} fullerene in the studied solutions is approximately 0.017 mg/ml. In the optical absorption spectrum of C_{60} fullerene in NMP solvent, it is characterized by the presence of maximum absorption at a wavelength of ~331 nm (Figure 1). If the C_{60}/NMP solution is kept at a constant concentration for a certain period of time, NMP molecules form complexes with C_{60} fullerene molecules through the donor-acceptor mechanism, resulting in shifts, flattening, and changes in intensity of the ~331 nm absorption peak (hypo- or hyperchromic effects) [22]. A clear solvatochromatic effect was observed in the optical absorption spectrum of the resulting C_{60}/NMP/water solution (Figure 1) when 30% distilled water was added to the C_{60}/NMP solution. The optical absorption spectrum of the C_{60}/NMP/water solution shows a main absorption maximum at ~340 nm and a relatively weak broad absorption region around ~440 nm. Upon adding water to the C_{60}/NMP solution, the C_{60}-C_{60} and C_{60}-NMP complexes are partially broken and rearranged. In this case, the formation of new C_{60}-water complexes or C_{60}-NMP and C_{60}-water mixed solvate shells occurs, which does not happen when fullerene is added directly to water. The maximum at ~340 nm in the optical absorption spectrum of the C_{60}/NMP/water solution corresponds to C_{60}-NMP and C_{60}-water mixed complexes, while the broad optical absorption at ~440 nm can be explained by the formation of new C_{60}-water complexes.

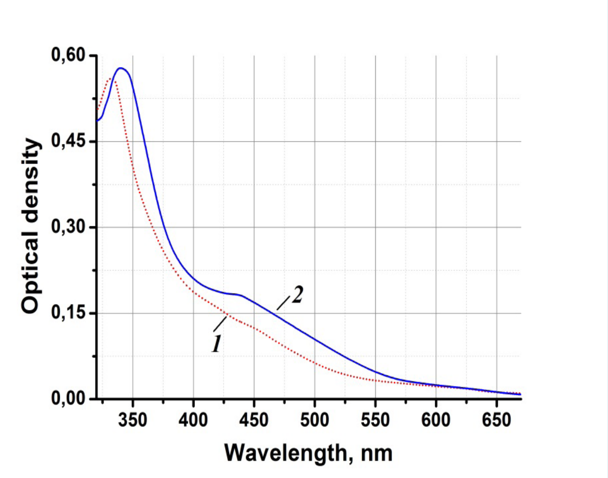

Figure 1: Optical absorption spectra of C_{60}/NMP (curve 1) and C_{60}/NMP/water (curve 2) solutions. The initial concentration of C_{60} fullerene in solutions is ~0.017 mg/ml.

Using the dynamic light scattering (DLS) method, the hydrodynamic sizes of particles in the studied solutions of C_{60} fullerene were determined. DLS measures Brownian motion in a C_{70} solution and relates it to the size of nanoaggregates. For this, the device (Zetasizer Nano ZEN3600) illuminates a fullerene solution with an He-Ne laser and analyzes fluctuations in the intensity of the scattered light. Next, the diffusion coefficient of dispersed particles in the solution is determined by analyzing the correlation function of fluctuations in the intensity of scattered light. Then, from the diffusion coefficient, the hydrodynamic size of C_{70} nanoaggregates is calculated using the well-known Stokes-Einstein equation. Output from a typical DLS experiment give us a graph of the distribution of hydrodynamic diameters of light-scattering nanoaggregates by intensity. Figure 2 illustrates the distribution of hydrodynamic diameters (by intensity) of nanoaggregates synthesized in C_{60}/NMP and C_{60}/NMP/water solutions of the fixed C_{60} concentration. It is evident that in the C_{60}/NMP solution (Figure 2), the diameters of the main fraction of light-scattering fullerene nanoaggregates are distributed in the range of ~11.8÷36.5 nm, with the maximum distribution of C_{60} nanoaggregates being around 23 nm. Considering that the total dielectric constant of the C_{60}/NMP/water solution is higher than that of the C_{60}/NMP solution, it is clear that intermolecular interactions are relatively strong in the C_{60}/NMP/water solution.

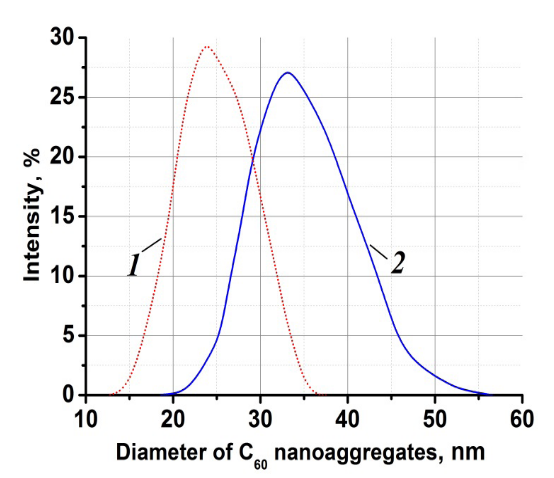

Figure 2: Distribution of hydrodynamic diameter of aggregates synthesized in C_{60}/NMP (curve 1) and C_{60}/NMP/water (curve 2) solutions by intensity. The initial concentration of C_{60} fullerene in solutions is ~0.017 mg/ml.

The maximum value of the hydrodynamic diameter of C_{60} nanoaggregates synthesized in the C_{60}/NMP/water solution shifts to ~33 nm. In turn, the hydrodynamic sizes of C_{60} nanoaggregates in the C_{60}/NMP/water solution are distributed in the range of ~18.6÷56.5 nm (Figure 2). Therefore, the addition of 30% distilled water to the C_{60}/NMP solution results in the redistribution of intermolecular interactions and the reorganization of C_{60} nanoparticles. This indicates a specific interaction of water with the C_{60} fullerene molecules initially dissolved in the NMP solvent. After the rearrangement of C_{60} nanoparticles in the C_{60}/NMP/water solution, it is evident that the geometrical dimensions of C_{60} nanoaggregates increase compared to those in the C_{60}/NMP solution.

Figure 3 shows the atomic force microscopy (AFM) image of aggregates synthesized in the C_{60}/NMP/water solution. It can be observed that the C_{60} aggregates synthesized in the solution exhibit a quasi-spherical shape, with their geometrical dimensions varying in diameter within the range of $d_n \approx 20 \div 60$ nm. These nanoaggregates are composed of $n = \left(\frac{d_n}{d_0}\right)^3 \approx 24389 \div 636056$ monomer C_{60} molecules, which has a diameter $d_0 \approx 0.7$ nm.

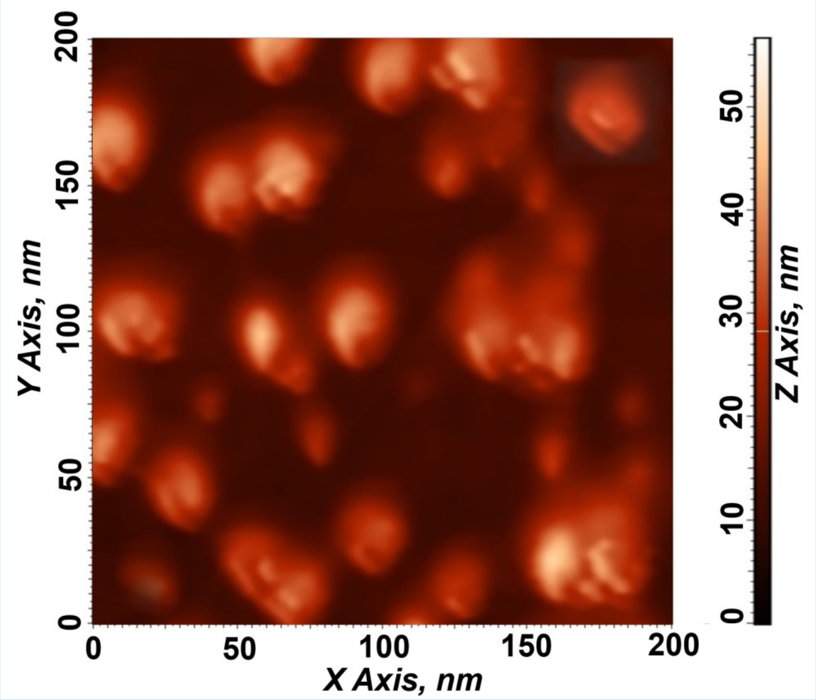

Figure 3: Three-dimensional AFM-image of nanoaggregates synthesized in a C_{60}/NMP/water solution. The concentration of C_{60} fullerene in the solution is ~0.017 mg/ml.

Thus, on the basis of research using optical absorption spectroscopy, dynamic light scattering and atomic force microscopy methods of C_{60} fullerene solutions in one- and two-component polar solvents (NMP and NMP/water), new properties of formation of nanoaggregates were determined. The obtained scientific results are important for effective use in the field of nanotechnology, especially in nano- and microelectronics and modern medicine.

Conclusion

In the optical absorption spectroscopy method, a maximum at a wavelength of ~331 nm was identified in the absorption spectrum of a low-concentration C_{60}/NMP solution. A clear solvatochromatic effect was observed in the optical absorption spectrum of the C_{60}/NMP/water solution containing 30% by volume of distilled water, characterized by a "red shift" of the main absorption peak by approximately 9 nm and an increase in absorption. Additionally, a relatively weak broad absorption band ~440 nm appeared in the C_{60}/NMP/water solution. The "red shift" of the main absorption peak corresponds to the formation of C_{60}-NMP and C_{60}-water mixed complexes, while the broad optical absorption at ~440 nm indicates the formation of new C_{60}-water complexes.

The diameters of the fullerene nanoaggregates synthesized in the C_{60}/NMP solution, as determined by the DLS method, range ~11.8÷36.5 nm, with the maximum distribution centered ~23 nm. In the C_{60}/NMP/water solution (with a water volume fraction of 30%), the maximum hydrodynamic diameter of C_{60} nanoaggregates was ~33 nm, with their diameters distributed in the range of ~18.6÷56.5 nm. The addition of distilled water to the C_{60}/NMP solution resulted in the redistribution of intermolecular interactions and reorganization of C_{60} nanoparticles, leading to an increase in their geometric dimensions compared to those in the C_{60}/NMP solution.

The geometrical dimensions of the C_{60} aggregates synthesized in the C_{60}/NMP/water solution, as determined by the AFM method, range ~20÷60 nm. Additionally, it was demonstrated that C_{60} nanoaggregates predominantly assemble in a quasi-spherical form.

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