

PREPARATION AND CHARACTERIZATION OF A NEW CLUSTERED $\{C_{70}\}_n$ FULLERENE MATERIAL

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A new clustered fullerene material $\{C_{70}\}_n$ has been prepared and studied using UV/vis spectroscopy, dynamic light scattering and liquid-liquid extraction. The material was prepared from aqueous fullerene dispersions of C_{70} by ultracentrifugation. The dispersions were obtained via an ordinary solvent-exchange procedure. Liquid-liquid extraction of $\{C_{70}\}_n$ from water to the organic phase without any extra reagents was observed for the first time. $\{C_{70}\}_n$ fullerene solid material was made and characterized with transmission electron microscopy and differential scanning calorimetry.

Keywords: fullerenes, solid material, extraction properties, DSC.

1. Introduction

Currently, technologies exist for the production of new fullerene materials [1]. Unique properties of fullerenes find a number of applications in various branches of science and technology. Of much importance are their use for the immobilization and transport of medicines [2-4]. At both cellular and macro levels, their aqueous solutions (aqueous fullerene dispersions, AFDs) are powerful antioxidants that adsorb free radicals and prevent aging and various pathologies like cancer, cardiovascular diseases etc. [2, 5, 6]. Fullerene clusters of certain sizes may create an antiviral cell barrier as well [7, 8]. Preparation of hydrophilic fullerene-based nanomaterials is on demand. Such materials may be prepared from C_{70} and higher fullerenes rather than from C_{60} only. An approach to this is to make AFDs from the corresponding fullerene followed by the treatment of the resulting colloidal solution. However, the methods of characterization and analytical control over the properties of such novel AFD-based materials are not well-developed yet. Thus, the preparation and physicochemical studies of the materials based on C_{60} , C_{70} or higher fullerenes seems rather appropriate.

Thus, the aim of this study is to (i) improve the general procedure for preparing aqueous fullerene dispersions; (ii) to work out an approach for preparing a solid powdered material from fullerene C_{70} ; and (iii) to carry out the physicochemical characterization of the prepared clustered material.

2. Materials and Methods

Commercially available fullerene C_{70} 99%+ (LLC “Neo Tech Production”, Russia) was used throughout. Chemically pure benzene and toluene (“Reachim”, Russia) and water (18.2 M Ω ×cm) from a Milli-Q purification system (Millipore, France) were used. The investigations of dynamic light scattering (DLS) were made using a Malvern “Zetasizer nano ZS” instrument. Spectrophotometric measurements were made using a Varian Cary 50 spectrophotometer. Ultrasonic treatment was performed with a piezoceramic emitter without

a concentrator immersed in the solution. The resonance frequency was 35 kHz, power up to 0.3 kW, volume 1–1.5 L. A DSC-30 TA Mettler Toledo differential scanning calorimeter was used to capture heating traces from 243 up to 313 K with a scanning rate of 5 K/min. High-resolution transmission electron microscopy (HRTEM) imaging was carried out using a JEM 2100F transmission electron microscope with accelerating voltage 200 kV.

AFD C_{70} was produced as reported elsewhere [9] with increased power of the sonication system, thus when increasing the quantity of fullerenes, the sonication duration is two weeks. The absorption spectra of AFD C_{70} completely matched the spectra described in [10, 11]. Aqueous solutions of fullerenes (Fig. 1) were prepared by the following procedure. A weighed portion of fullerene (0.5–0.6 g) was placed into a 200-mL volumetric flask, dissolved in 100 mL of toluene and sonicated for 2 h at 353 K; next, the solution was diluted to mark with toluene. Next, the prepared toluene solution was placed into a conic flask and 1 L of Milli-Q water was added, and the solution was sonicated for 14 days (12 h per day) at the maximum power setting of 0.3 kW at 353 K until complete evaporation of toluene (checked with LC/MS). Next, the solution was heated up for 30 min, and boiled for 15 min and filtered through a Shott filter followed by a $0.45\text{-}\mu\text{m}$ microporous membrane filter. The concentration of fullerene (130 ± 1 ppm, $n = 3$, $P = 0.95$) was measured by performing the total organic carbon analysis (TOC). The TOC analyzer was calibrated with a series of potassium hydrogen phthalate (KHP) samples with the 1-200 ppm range for carbon. The least square fit of TOC versus peak area gave c , ppm = $(10.2 \pm 0.1)S_{area}$, a.u., $P = 0.95$, $n = 7$, $r = 0.99863$.

2.1. General procedure for preparing $\{C_{70}\}_n$ fullerene material

Solid powered $\{C_{70}\}_n$ materials were produced as follows. AFDs of C_{70} were concentrated by ultracentrifugation. The solution was centrifuged for 25 min at 30000 rpm (298 K). Next, mother liquor was decanted by injection syringe and concentrated quantity of AFD was heated up to fully evaporation at 378 K. The resulting absorption spectrum of AFD C_{70} is shown in Fig. 1.

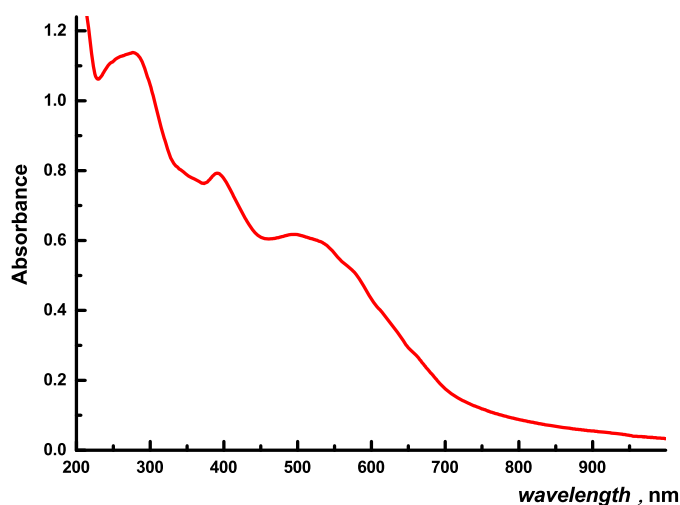


FIG. 1. Absorption spectrum of prepared aqueous dispersions of fullerenes C_{70}

2.2. Liquid-liquid extraction AFD C to toluene

Toluene without any extra reagents was added to AFD C₇₀ at a volume ratio of 1 to 1. Next, we performed the ultrasonic treatment at the maximum power setting of 0.3 kW and 378 K for 2 h in a closed test tube to prevent toluene evaporation. Then, we centrifuged the suspension at 4000 rpm for 15 min. Finally, the absorbance spectra of aqueous and organic phases were registered and compared to a toluene solution of pristine C₇₀ fullerenes and original AFD C₇₀ (see Figs. 2 and 3).

2.3. Differential scanning calorimetry (DSC) traces

The samples studied were mechanical mixtures ($\sim 1 : 3$ by weight) of the solid $\{C_{70}\}_n$ and the solvent (water or benzene), respectively. A sample of the tested substance was placed into a standard aluminum container and sealed. Calorimetric measurements were carried out at a heating rate of 5 K/min. A Ni-Au thermocouple was used as a detector of the heat flux. The temperature of the sample was measured by a platinum resistance thermometer. Pre-calibration was performed on the basis of data for the enthalpies of melting for indium, lead, and zinc. The calibration of the heat flux was carried out based on data for the enthalpy of melting of an indium standard sample. The enthalpy of melting of the samples studied was calculated from the squares of the corresponding peaks in the DSC trace. The temperature was measured with an accuracy of ± 0.2 K.

2.4. DLS analysis and HRTEM

DLS particle size distributions and ζ -potentials in AFD were measured with a 100 averages of 15 s scans to gain a histogram with the accuracy *ca.* 5%. The TEM specimens were prepared by dispersing the particle suspensions in ethyl alcohol onto TEM carbon-copper grids and by exsiccation in vacuum at 10^{-2} mm Hg.

3. Results and Discussion

3.1. Liquid-liquid extraction

For the first time, we observed the extraction of fullerenes from aqueous solutions to toluene with considerable distribution constant. This extraction distinguishes these experiments from previous reports for AFD C₆₀, where direct extraction was not observed, and AFD C₆₀ has been transferred to the organic phase only after addition of an inorganic salt [12]. We compared the absorption spectra of C₇₀ extracted into toluene from AFD C₇₀ and that of pristine C₇₀ dissolved in toluene (Fig. 2) and those for the aqueous phase of AFD C₇₀ before and after a sonication treatment during the extraction (Fig. 3). The shapes of spectra in Fig. 2 fully match, and we did not observe any red or blue shifts between the pristine toluene solutions and that from the extraction procedure using $dA/d\lambda$ and $d^2A/d\lambda^2$ derivative spectrophotometry in the UV/vis range.

Next, we calculated the recovery of the fullerene from AFD using the absorption spectra of AFD before and after the extraction (Fig. 3), which averaged *ca.* $97 \pm 2\%$, ($n = 3$, $P = 0.95$). Based on these results, one may assume that the C₇₀ recovered from AFD is a monomer, not subjected to any chemical modification and C₇₀ clusters in AFD are weakly bonded associates of C₇₀ monomers covered by a hydrophilic shell.

3.2. DLS and HRTEM experiments

The size of AFD C₇₀ was found to be *ca.* 105, 140, and 160 nm respectively for number, volume and intensity size distributions (Fig. 4). Moreover, we carried out the

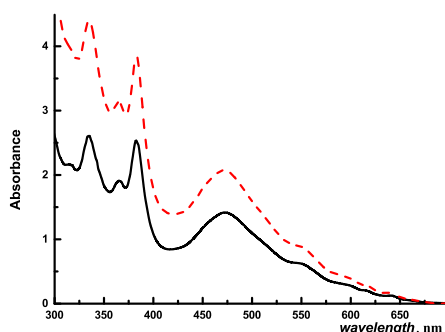


FIG. 2. Absorption spectra of fullerenes C_{70} extracted from AFD (black solid line) and pristine fullerenes C_{70} dissolved in toluene (red dash line)

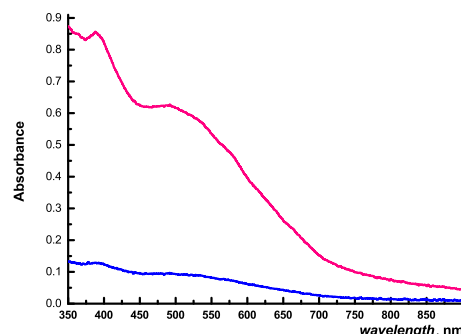


FIG. 3. Absorption spectra of AFD C_{70} before and after sonication treatment for 2 hours

measurements of ζ -potential for AFD C_{70} , which was estimated to be -40.8 ± 0.9 mV, and a rather low polydispersity index (PDI) of 0.08 was calculated for a AFD concentration of $14.6 \mu\text{M}$.

HRTEM data of the fullerene nanoparticles shows that the material is in fact clustered and shows spherical particles. HRTEM data for the target solid material (see Fig. 5) correlates well with above-discussed DLS data. Thus, we suggest that AFDs are not clumped together into large particles during the evaporation of the residual water. The particle size within the solid clustered material was found to be *ca.* 134 nm. The average number of C_{70} molecules in the cluster in terms of the spherical model was estimated at *ca.* 5×10^5 . The density of the cluster was assumed to be 1.7 g/cm^3 as in the C_{70} crystal.

3.3. DSC experiments

Finally, we recorded thermal effects related to the melting of water or, in another case, of benzene in the samples studied (see 2.3). In both cases, two peaks were observed (Figs. 6 and 7) that we believe corresponded to the melting of water (benzene) in the bulk solvent and in the pores within the clustered $\{C_{70}\}_n$ fullerene material. We assume that $\{C_{70}\}_n$ is a powder consisting of nanoclusters similar to nanodiamond powders [13]. Such powders show reproducible porous structures that disperse the solvent. Nanoparticles have solvent-filled pores in the secondary structure, and the extra peak in the DSC trace from the low temperature side corresponds to the solvent melting in the pores. For comparison, DSC experiments were carried out for pristine fullerene C_{70} mixed with water or benzene. Pristine C_{70} does not form nanoclusters and the corresponding secondary structure. As expected, in both cases the single peak of melting of the bulk solvent was observed only (Figs. 8 and 9). The differences between two peaks of melting in Figs. 6 and 7, ΔT_m , are 1.0 ± 0.4 K and 3.9 ± 0.4 K for water and benzene, respectively. For a similar $\{C_{60}\}_m$ material with water ΔT_m was previously reported as equal to 2 K [1].

The Gibbs-Kelvin equation was used to calculate the diameters of the nanophase in pores. We obtained diameters of *ca.* 40 ± 5 nm and *ca.* 30 ± 5 nm for water and benzene, respectively. These values are in agreement, which suggests that two solvents occupy the

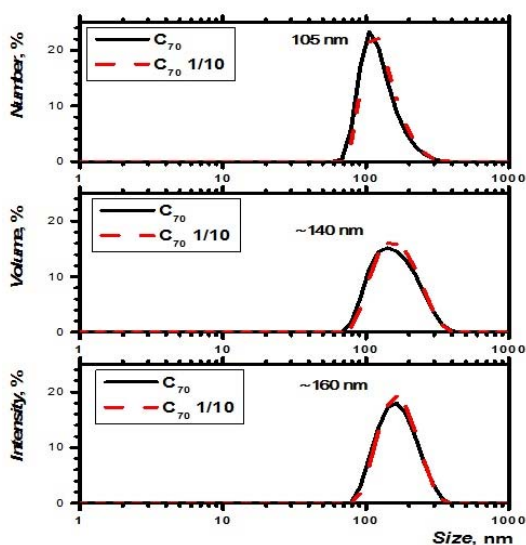


FIG. 4. Number, volume, and intensity size distributions for the AFD C_{70} (black solid line) and dispersion diluted by a factor of 10 (red dashed line)

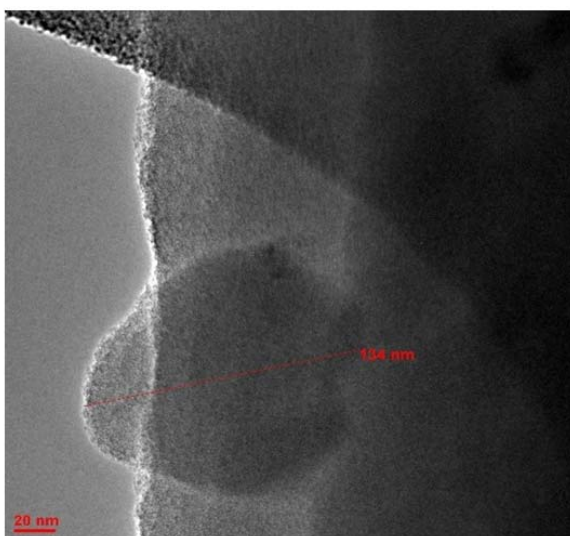


FIG. 5. TEM image of an AFD sample prepared by ultracentrifugation technique

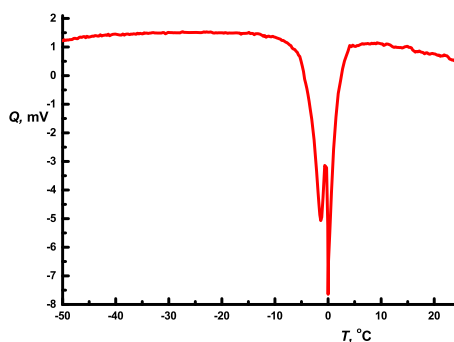


FIG. 6. Typical DSC trace of $\{C_{70}\}_n$ material with two endothermic effects for melting of water

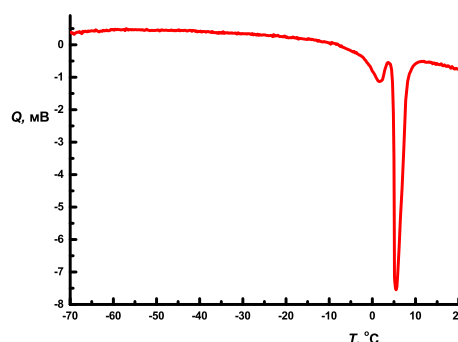


FIG. 7. Typical DSC trace of $\{C_{70}\}_n$ material with two endothermic effects for melting of benzene

same voids within the secondary structure formed by C_{70} aggregates. It is worth noting that solvents with different properties — water and benzene — interact with $\{C_{70}\}_n$ material in the same manner. Both solvents are dispersed onto the $\{C_{70}\}_n$ secondary structure. It is also noteworthy that benzene neither dissolves nor distracts C_{70} aggregates formed in an AFD.

4. Conclusions

The study clearly demonstrated evidence for the formation of a new C_{70} based material with unique properties. The material was produced in the form of aqueous fullerene

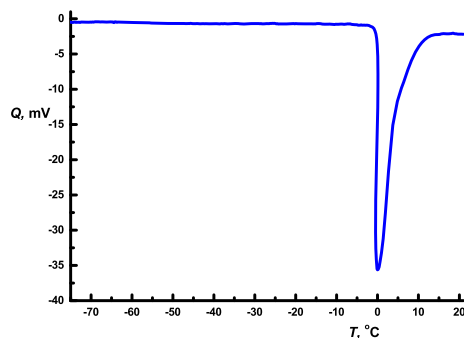


FIG. 8. Typical DSC trace of pristine C_{70} with water. A single endothermic effect observed corresponded to the melting of bulk water

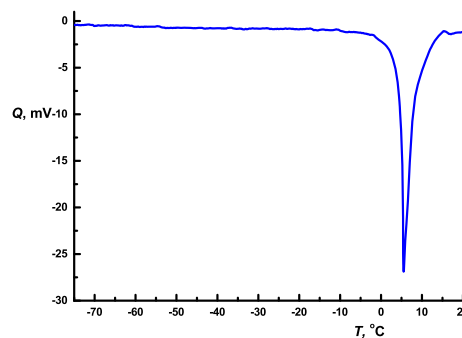


FIG. 9. Typical DSC trace of pristine C_{70} with benzene. A single endothermic effect observed corresponded to the melting of bulk water

dispersions and as a dry powder. In the first case, it was characterized using UV-vis spectra, dynamic light scattering and liquid-liquid extraction while in the second by means of differential scanning calorimetry and transmission electron microscopy. We observed liquid-liquid extraction of C_{70} from aqueous fullerene dispersions to monomeric solution in toluene with admissible recovery characteristics. The data obtained allows one to put forward a qualitative schematic structure for the C_{70} clusters in aqueous fullerene dispersions and in the powder. The developed procedure may be used to prepare clustered materials and aqueous fullerene dispersions for other members of the fullerene family.

Acknowledgments

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