

ORGANIZATION OF FULLERENE CLUSTERS IN THE SYSTEM C_{60} /N-METYL-2-PYRROLIDONE

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Abstract

Fullerene clusters in the solution of C_{60} in N-methyl-2-pyrrolidone (NMP) were investigated using UV-Vis spectroscopy, small-angle neutron scattering and mass-spectroscopy. Changes with time and on addition of water to the solution were analyzed. Contribution of the Mie scattering into absorption spectrum was estimated and compared with the experimental data.

Introduction

The solutions of fullerene C_{60} in nitrogen-containing solvents (pyridine, N-methyl-2-pyrrolidone (NMP), benzonitrile and acetonitrile) are of current interest due to the cluster formation in them [1-3]. The presence of clusters, aggregates with highly packed structure, was confirmed previously by electron microscopy [1-3], dynamic light scattering [1, 2], sedimentation analysis [4] and small-angle neutron scattering (SANS) [4, 5, 6]. The present work is a continuation of systematic investigations of cluster formation in the system C_{60} /NMP. NMP is a comparatively good solvent for C_{60} (solubility is 0.89 mg/ml [7]) and is miscible with water. It can be used for fullerene transfer into aqueous media, which is important for employing biological activity of fullerenes in medical applications [8, 9]. The purpose of this study was to analyze the temporal solvatochromic effect of the C_{60} /NMP system using UV-Vis spectroscopy, SANS and mass-spectroscopy. Estimation of the Mie scattering contribution into a UV-Vis spectrum was performed. The effect of water addition into the system under study was also analyzed.

Experimental section

Fullerene (Fullerenovye Tekhnologii, purity > 99.5%) was dissolved in NMP (Merck, purity > 99.5%) to obtain the C_{60} /NMP system. Then the solution was stirred for four days at room temperature. The solution was stored for one month after preparation in a dark place at room tempera-

ture. The solution concentration $c = 0.72$ mg/ml was determined from the absorbance value at a wavelength of 342 nm, which was measured at Hitachi U-2000 spectrophotometer. Ternary solutions C_{60} /NMP/ H_2O were obtained by addition of distilled water (Millipore) to the C_{60} /NMP solution.

Absorption spectra were obtained using Shimadzu UV-2401PC (wavelength range of 200 800 nm) and Hitachi U-2000 (wavelength range of 200 1000 nm) UV/Vis spectrophotometers. 1 mm path length quartz cells were used.

SANS experiments were performed on the Yellow Submarine small-angle diffractometer at the research steady-state reactor of the Budapest Neutron Centre (BNC), Hungary. Sample-to-detector distances of 1.3 m and 5.6 m and the mean neutron wavelength of 0.45 nm were used. The observable SANS signal as a function of the modulus of momentum transfer, q , was registered in the interval $q = 0.1 - 1 \text{ nm}^{-1}$. Samples were placed in 1 mm thick quartz cells (Hellma). Scattering curves were corrected for the background, buffer (NMP and NMP/ H_2O solutions) and an empty cell and calibrated against a 1-mm water sample in a standard way [10].

Laser desorption/ionization time-of-flight mass spectrometry (LDI TOF MS) was used for ion production. Measurements were conducted using the Bruker Daltonics Autoflex II instrument. Solutions of fullerene were deposited onto the surface of a standard steel target. The method provided record of mass spectra in the range 0 5000 Da. Data for 10 different points of the target were accumulated to smooth variations of sample distribution on the target.

Results and Discussions

A change of UV-Vis spectrum with time (temporal solvatochromic effect) was observed within one month after preparation of the C_{60} /NMP system (Fig. 1). This change reflects the fullerene cluster formation. Dynamic light scattering (DLS) measurements for this solution revealed clusters with a characteristic size of 500 nm [5]. The growth of scattering particles in the solution leads to an increase in the Mie scattering contribution into the absorption spectrum. The Mie scattering contribution can be estimated according to the following formalism.

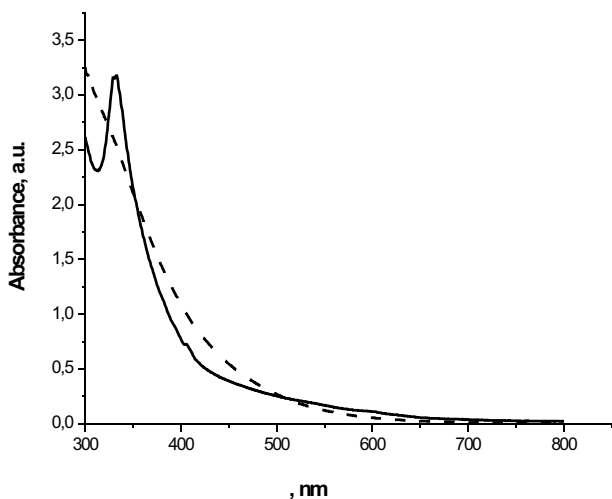


Figure 1. Change in the UV-Vis spectrum of the C₆₀/NMP solution (concentration 1 mM) with time: solid line corresponds to fresh C₆₀/NMP and dashed line is the solution one month later after preparation.

The Beer-Lambert law, which expresses relation between the transmission of light and the path length, has the form:

$$I = I_0 \exp(-kL) \tag{1}$$

where I_0 is the intensity of the incident light and I is the intensity after passing through a sample, L is the cell path length and k is the extinction coefficient: $k = \epsilon N$, where ϵ is the molar extinction coefficient and N is the particle concentration. Therefore the Beer-Lambert law can be written as:

$$A = \lg \frac{I_0}{I} = \frac{2.303}{L} kL \tag{2}$$

where A is the absorbance. On the other hand, the extinction coefficient is related to the scattering coefficient, as follows:

$$k = \frac{3}{4} k_s N, \tag{3}$$

where k is the scattering coefficient. The expression for the scattering coefficient can be derived from the theory of electromagnetic radiation propagation in an optically inhomogeneous medium [11]:

$$k = \frac{2\pi}{\lambda} r^2 |F(z)|^2 \tag{4}$$

where $F(z) = \frac{3}{4} \left[\frac{m^2 - 1}{m^2 + 2} \right] m \frac{n}{n_0}$, is the refractive indexes' ratio of the particles and medium, in our case $m = 1.05$,

$$F(z) = \frac{2}{z^2} \left[\frac{z^4}{4} - 5z^2 + (4z^2 - 16)(\text{Ciz} - \ln z - C) - 2z \sin z - 14(\cos z - 1) \right] \tag{5}$$

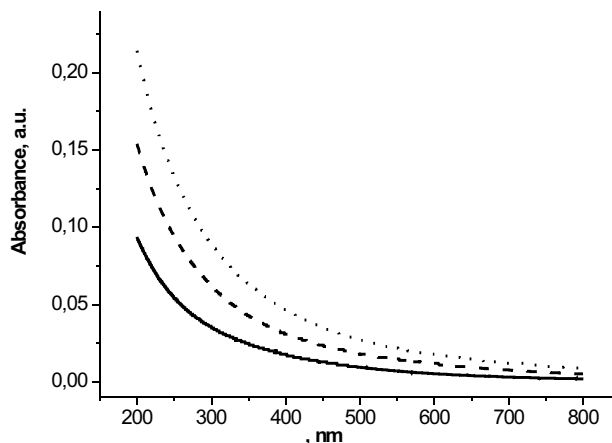


Figure 2. Computer calculation of the Mie scattering: The solid line corresponds to the particle radius $r = 100$ nm, the dashed line — $r = 150$ nm and the dotted line — $r = 200$ nm.

$$\text{Ciz} = \int_0^\pi \frac{\cos t}{t} dt, \quad C = 0.577 \text{ is the Euler constant and } z = \frac{2\pi r}{\lambda}$$

Equation (4) relates the scattering coefficient to the size of spherical particles and is valid up to $z = 5$, where z is the dimensionless size parameter given by the expression:

$$z = \frac{2\pi r}{\lambda} \tag{6}$$

where r is the particle radius and λ is the light wavelength. The condition $z < 0.3$ corresponds to the case of the Rayleigh scattering.

The scattering coefficient mentioned above and concentration expressed as a number of particles per unit volume were used to calculate the Mie scattering contribution to the UV-Vis spectrum according to the equations (1-6).

The calculation of the Mie scattering was performed for spherical particles of several sizes (Fig. 2). The power-law and normal size distributions of particles were taken into account to reveal a possible polydispersity effect. No significant effect was found. One can see (Fig. 3) that the Mie scattering has insignificant contribution to the UV-Vis spectrum at the wavelength range of 200 - 700 nm. Therefore we can conclude that changes in the UV-Vis spectrum are due to absorption, which relates to electronic state of fullerene molecules. Fullerene forms donor-acceptor complexes with the molecules of the solvent. The character of interaction between fullerene molecules and NMP changes with time [3]. These facts are likely to be responsible for the changes of the UV-Vis spectrum with time.

Dilution of the fresh C₆₀/NMP system with water leads to solvatochromic effect (Fig. 4). The results of the SANS experiments for the C₆₀/NMP and C₆₀/NMP/H₂O systems are presented in Fig. 5. One can see that the SANS signal from the C₆₀/NMP system with a smooth UV-Vis spectrum is very weak. The reason for this fact is that clusters are very large in this case (more than 100 nm in size), so the scattering is concentrated in the range of the smallest values of momentum transfer modulus, which are inaccessible to conventional small-angle spectrometers. Addition of

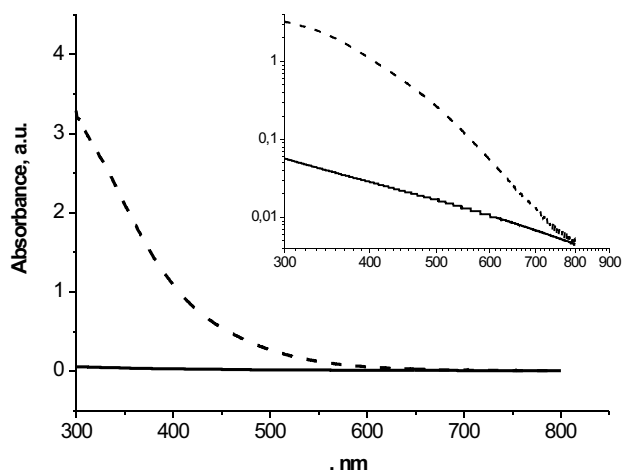


Figure 3. Comparison of the experimental UV-Vis data with the computer calculation of the Mie scattering. The dashed line corresponds to the experimental curve of the C_{60} /NMP solution and the solid line is the computer calculation of the Mie scattering for the particle radius $r = 140$ nm. The inset presents the spectra in the logarithmic scale.

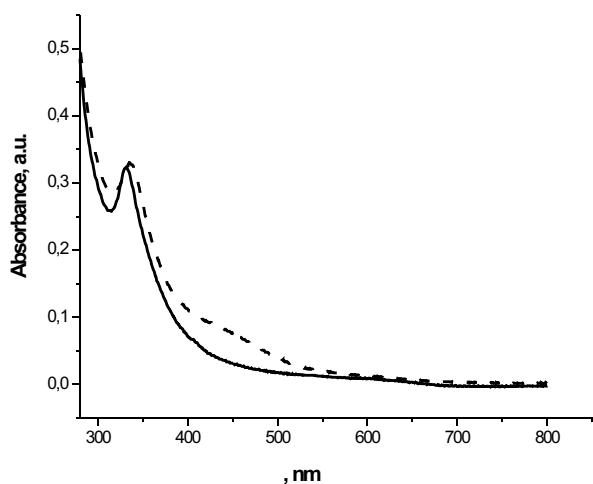


Figure 4. Change in the UV-Vis spectrum as a result of water addition to the C_{60} /NMP system. The solid line corresponds to the C_{60} /NMP solution and the dashed line is C_{60} /NMP/ H_2O . The C_{60} concentration in both solutions is $0,007$ mg/ml.

sufficient amount of water (50 vol. %) to the system leads to a relatively sharp increase in the scattering signal. This increase is related to the formation of clusters of smaller sizes (from 10 to 100 nm) since the volume fraction of fullerene in the solution is less than 0.1 vol. % and interparticle interaction is negligible.

Fullerene monomers with molecular weight 720 Da were observed by mass-spectroscopy in the fresh C_{60} /NMP solutions (Fig. 6). A specific group of peaks with m/z equal to 696.1, 672.6, 648.8 confirms the decomposition of fullerene monomers. As shown in Figure 6, mass-spectrum consists of groups of lines which differ by 24 Da. It is due to the fact that excited fullerene clusters lose even number of carbon atoms under laser irradiation. The fullerene clus-

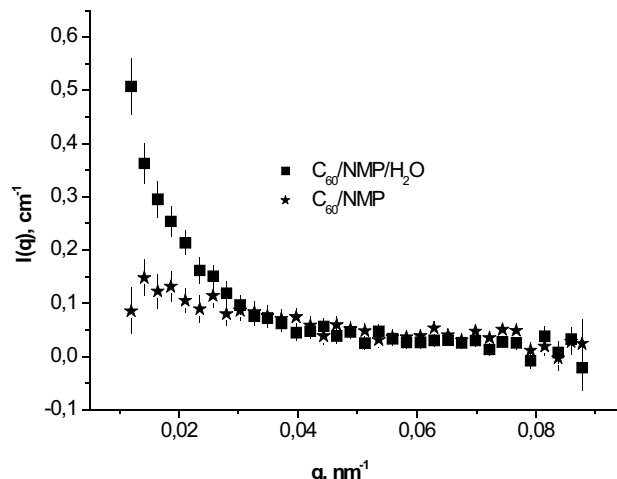


Figure 5. Comparison of SANS signals from the C_{60} /NMP and C_{60} /NMP/ H_2O systems. The C_{60} concentration in both solutions is $0,18$ mg/ml.

ters with a number of monomers from 2 to 6 are present in the fresh solution (Fig. 7). Peaks of fullerene clusters were not observed in the case of old solutions (age more than 1 month). Ions of monomer C_{60} and its typical decomposition with detached even number of carbon atoms were not observed in the spectrum either. This is indicative of the fact that fullerenes form large-scale clusters with strong bonds between the molecules and its ionization is impossible because of the great molecular weight and technical limitations of the method. Similar structural features were obtained from the SANS investigation for the C_{60} /NMP system [5] as well as for the related C_{60} /pyridine/water system [4] and aqueous colloidal solutions of C_{60} [12].

Conclusions

The temporal solvatochromic effect, which was observed in the UV-Vis spectrum, is indicative of the growth of fullerene clusters with time. From the results of small-angle neutron scattering and mass-spectroscopy we can conclude that the clusters are strongly associated aggregates and their size amounts to more than 100 nm during one month. The results of the calculations revealed that the Mie scattering contributes insignificantly to the UV-Vis spectrum, which shows mainly the pure absorption over the wavelength range of 200 - 700 nm and relates to the electronic state of fullerene molecules. Small clusters (up to fullerene molecules) are well observed by mass-spectroscopy in fresh solutions. Possibilities of mass-spectroscopy for studying kinetics of the cluster growth in the system are under discussion.

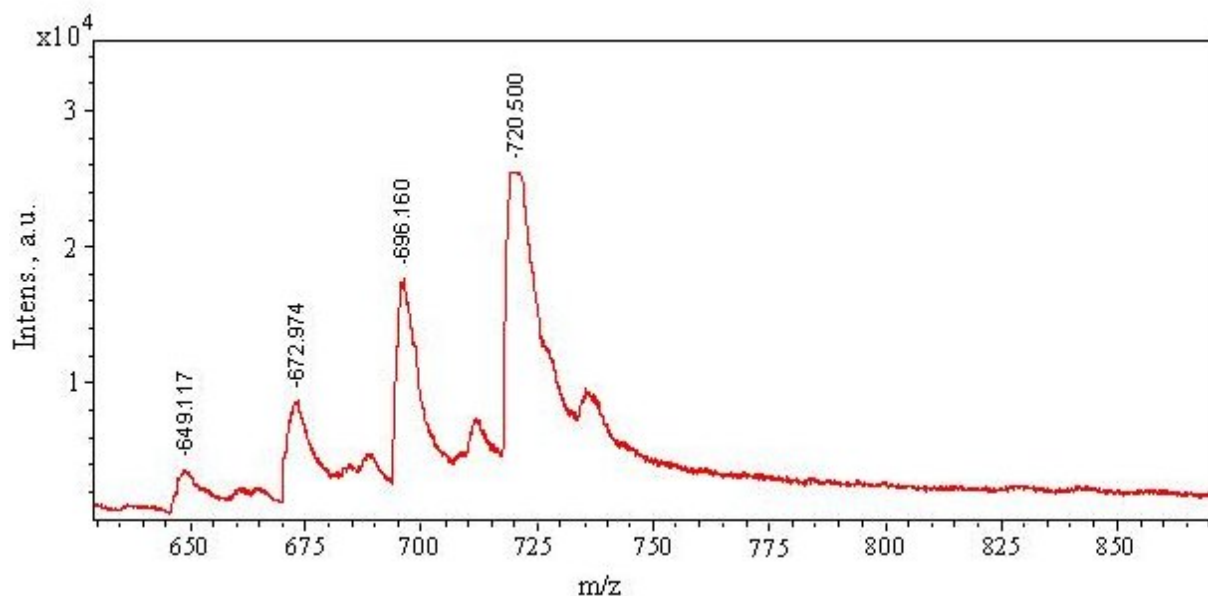


Figure 6. Mass-spectrum of fullerene monomers for a fresh solution C_{60} /NMP deposited onto the surface of the steel target.

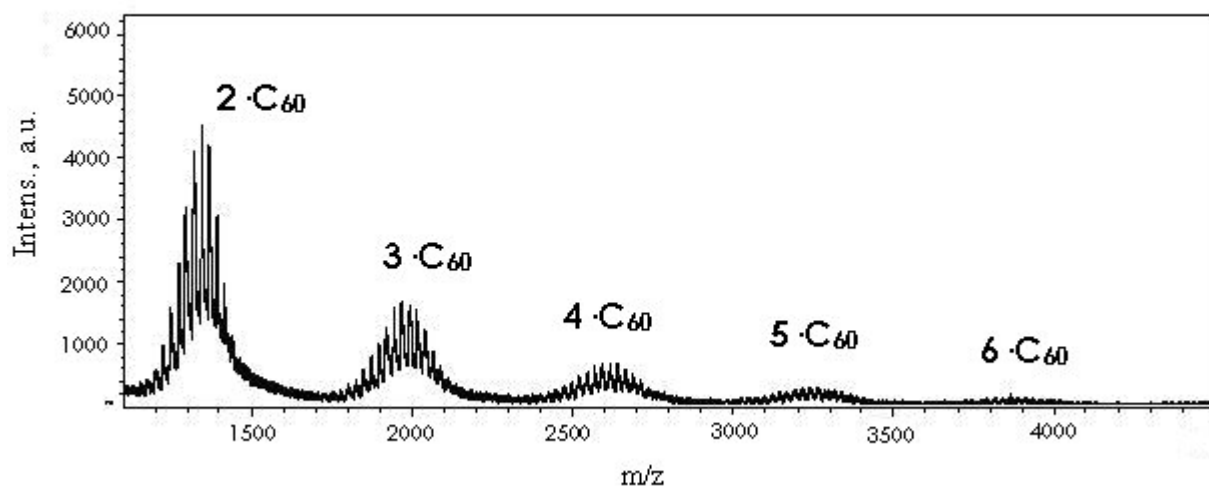


Figure 7. Mass-spectrum of fullerene clusters for fresh solutions C_{60} /NMP deposited onto the surface of the steel target. Peaks correspond to excited fullerene clusters with a number of monomers from 2 to 6.

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