Experimental Investigation of C$_{60}$/NMP/Toluene Solutions by UV–Vis Spectroscopy and Small-Angle Neutron Scattering

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Abstract—The transformation of the C$_{60}$ fullerene cluster state into C$_{60}$/N-methylpyrrolidone (NMP) solution after the addition of a nonpolar solvent (toluene, electric permittivity $\varepsilon = 2.4$) is studied. The results of ultraviolet–visible spectroscopy and small-angle neutron scattering measurements are used for comparison of the C$_{60}$/NMP/toluene system with C$_{60}$/NMP mixtures with a high-polar solvent (water, $\varepsilon = 80$). As to the observed reorganization of the cluster state, the C$_{60}$/NMP/toluene system is similar to the C$_{60}$/NMP/water system. This effect is explained by the formation of charge-transfer complexes in the initial C$_{60}$/NMP solution. These complexes are thought to be soluble in both binary mixtures. The connection between the cluster-reorganization effect and solvatochromism is discussed.

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INTRODUCTION

In recent years the relationship between cluster formation and solvatochromism in fullerene solutions has been intensively discussed [1]. A clear understanding of the processes responsible for the optical properties of these systems is necessary for their efficient use in topical applications such as optical shutters or photodynamic therapy in biomedicine [2, 3].

For solutions of the C$_{60}$ fullerene, the origin of the solvatochromic effects (change in the shape of the spectrum with time or under a slight change in the composition of the solvent) is considered to be first of all due to the formation of clusters of fullerene molecules [4, 5], and also the formation of charge-transfer complexes (CTC) between the fullerene molecules and the solvent molecules [6, 7]. In mixtures, where one of the components poorly dissolves C$_{60}$, and the other readily dissolves it, aggregation, which is reversible (depending on the ratio of the component fractions) and, consequently, leads to reversible changes in the absorption spectrum, is often considered to be the origin of the solvatochromic effect [4, 5]. When solvatochromic effects are due to CTC formation, changes in the spectrum are often irreversible, and the processes, which occur in the system, depend on the chemical and physical properties of the solvent, composition of the mixture and aggregation state of fullerene in a complex manner. The formation of such complexes with fullerene is characteristic for solvents, which have electronegative elements in their composition such as nitrogen and oxygen [8].

This work is devoted to studying the processes of cluster formation in a solution of C$_{60}$/N-methyl-2-pyrrolidone/toluene and its relationship with the solvatochromic effects. N-methyl-2-pyrrolidone (NMP) is a polar solvent (electric permittivity $\varepsilon = 32$) with two electronegative atoms (nitrogen and oxygen) in the composition of its molecule that forms complexes with C$_{60}$ fullerene molecules with charge transfer according to the donor–acceptor mechanism [6]. It was shown earlier that the absorption spectrum of such a system is smoothed out within a month after preparation (the temporal solvatochromic effect) [9, 10]. The characteristic spectrum is reversible only for the freshly prepared C$_{60}$/NMP solution, when a pronounced solvatochromic effect is observed upon the addition of water ($\varepsilon = 80$) or pure solvent NMP [11, 12]. The smoothing out of the spectrum is renewed with time for the pure solution and for the mixture and does not change upon dilution. The temporal solvatochromic effect correlates with the growth of clusters in the system, the size of which reach 500 nm within a month after preparation and which are partly destroyed upon the addition of water to the system [9].

The purpose of this work was to study the relationship between cluster formation and the solvatochromic effect in the C$_{60}$/NMP solution when it is diluted with toluene ($\varepsilon = 2.4$). Unlike previous studies with water (high-polarity solvent), here a low-polarity sol-
vent is added to the initial solution, which, just as well as water, mixes with NMP in any proportion. The essential difference is that toluene, in contrast to water, dissolves C₆₀ well. The change in the initial cluster state was recorded by small-angle neutron scattering (SANS).

MATERIALS AND METHODS

C₆₀ fullerene (“Fullerene technologies”, purity >99.5%), toluene (“Merck”, purity >99.5%) and N-methyl-2-pyrrolidone (“Merck”, purity >99.5%) were used for preparation of the samples. During the preparation of the C₆₀/NMP system, the fullerene was dissolved in NMP and it was mixed with a magnetic mixer at room temperature for 6 h. To obtain the three-component C₆₀/NMP/toluene system, toluene was added to the C₆₀/NMP system (storage time of 4 weeks). The solutions were prepared with a toluene content from 20 to 80% of the total volume of the system.

The experiments were performed using the Yellow Submarine small-angle scattering setup at the stationary neutron reactor, Budapest Neutron Center (Budapest, Hungary). The differential scattering cross section per sample volume unit (the scattering) averaged over the radial angle ϕ was measured and analyzed as a function of the module of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$, where $\lambda$ is the neutron wavelength and $\theta$ is the scattering angle. A quasi-monochromatic neutron beam ($\lambda = 0.41$ nm, monochromaticity $\Delta\lambda/\lambda = 15\%$) was used. A position–sensitive detector with a size of 64 × 64 cm was placed after the sample at a distance of 2 m. The measured $q$-range was 0.1–1 nm⁻¹. A 1 mm H₂O standard was used for calibration and reduction of the scattering curves to absolute values [13].

Quartz cuvettes (Hellma Analytics) with a thickness of 1 mm were used in the SANS measurements. Solvents and corresponding mixtures without C₆₀ were used as baseline samples. All measurements were carried out for standard (nondeuterated) components.

RESULTS AND DISCUSSION

The absorption spectra of the fullerene in the weakly polar solvents (toluene or benzene), in which C₆₀ is readily soluble, are characterized by a peak at approximately 330 nm (Fig. 1). Depending on the properties of the solvent, the CTCs formed between C₆₀ and the solvent molecules lead to a shift of the peak at 330 nm and change in its intensity (hypo- or hyperchromic effects), which is individual for each solvent [14]. It was shown earlier [9, 11] that the absorption spectrum of the C₆₀/NMP solution is smoothed out with time (temporal solvatochromism) leading to the complete disappearance of the peak at 330 nm. The addition of a third component (water or toluene) to the C₆₀/NMP system with the smoothed out spectrum does not lead to the re-appearance of the peak characteristic for molecular solutions of the fullerene (Fig. 1), unlike experiments with a fresh solution [15]. However, the hyperchromic effect is observed which indicates the appearance of new CTCs with molecules of the added solvent.

The SANS data for the C₆₀/NMP/toluene system are given in Fig. 2 in comparison with the C₆₀/NMP/water system. Neutron scattering in the case of the initial C₆₀/NMP solution is at the background level within a month after its preparation. This indicates the presence of aggregates in the system with a size of greater than 100 nm. Scattering from such formations is within the range of very small scattering angles, inaccessible to standard configurations of the SANS experiment, and repeats the results obtained earlier [10]. The addition of toluene, analogous to the addition of water, leads to an increase in the scattering intensity due to the appearance of new fullerene clusters in the solution with a size of 10–100 nm, corresponding to the $q$-range, in which the measurements were performed. It was shown earlier that such a change in the scattering in the case of the C₆₀/NMP/water system is related to partial dissolution of the initial clusters due to the formation of specific CTCs with time, which are soluble in the NMP/water mixture. In this case, the dissolution of clusters is apparently caused by the initial solubility of the fullerene in toluene and the NMP/toluene mixture. The solubility of C₆₀ in toluene (C₆₀ ~ 2.8 mg/mL) greatly exceeds the solubility of C₆₀ in NMP (0.89 mg/mL). Interestingly, the same as in the case of the addition of water, the destruction of clusters upon the addition of toluene has a critical character. The reorganization of the C₆₀ clusters occurs when the