BEHAVIOR OF FULLERENE C$_{70}$ IN BINARY ORGANIC SOLVENT MIXTURES AS STUDIED USING UV-VIS SPECTRA AND DYNAMIC LIGHT SCATTERING

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In this paper, the formation of colloidal species of fullerene C$_{70}$ in organic solvents was studied. The examining of the UV-visible spectra was accompanied by particle size analysis using dynamic light scattering, DLS. Stock solutions of C$_{70}$ in non-polar toluene and *n*-hexane were diluted with polar solvents acetonitrile and methanol. The appearance of colloidal species with a size within the range of ≈50–500 nm is accompanied by alterations of the absorption spectra.

In the toluene–acetonitrile and toluene–methanol binary mixed solvents at 25 ^{o}C, the absorption spectra of C$_{70}$ (5×10^{-6} M) tend to retain the features of the spectrum in neat aromatic solvent even if the C$_{70}$ molecules are gathered into colloidal aggregates. Earlier such phenomenon was observed for C$_{60}$ in benzene–acetonitrile and toluene–methanol solvent systems. This gives support to the idea of rather stable primary solvate shells formed by aromatic molecules around the fullerene molecules. The behavior of C$_{70}$ in toluene mixtures with methanol was compared with the earlier reported results from this laboratory for the C$_{60}$ fullerene in the same solvent system.

The study of *n*-hexane–methanol mixtures was performed at elevated temperature because of limited miscibility of these solvents at 25 ^{o}C. Accordingly, the C$_{70}$–toluene–methanol system was also examined at 40 ^{o}C. A small but distinctly noticeable difference was revealed. Whereas in the case of the last-named system, the absorption spectrum typical for molecular form of C$_{70}$ is still observable when colloidal species are already present in the solution, the turning-point between molecules and colloids as determined by both UV-visible spectra and DLS coincides for the *n*-hexane–methanol binary mixed solvent. Hence, the solvation shells formed by the aliphatic solvent around C$_{70}$ are less stable as compared with those formed by toluene.

Finally, the absorption spectra of C$_{70}$ in the mixed solvents toluene–*n*-hexane were analyzed. These data give some support to the assumption of preferable solvation of the C$_{70}$ molecules by the aromatic co-solvent.

Keywords: fullerene C$_{70}$, toluene, *n*-hexane, acetonitrile, methanol, molecular solutions, organosol, UV-visible absorption spectra, dynamic light scattering, particle size.

State of the Arts

Behavior of fullerenes C$_{60}$ and C$_{70}$ in solvents of different nature was a matter of numerous studies during last decades [1–8]. In nonpolar solvents, these compounds probably exist in molecular form, especially if equilibrium methods are used for the preparation of the solutions [7–9]. Now it is of common knowledge that addition of polar solvents results in formation of (nanosized) colloidal species.

Let us consider state of the arts. As early as 1993, Sun and Bunker revealed that the absorption and emission spectra of C$_{70}$ in toluene change dramatically at adding acetonitrile and ascribed this phenomenon to fullerene aggregation [10]. This study was continued by the authors [11,12]. Next was a detailed study by Ghosh et al. [13], who used dynamic light scattering, DLS, spectrophotometry, steady state emission spectra, fluorescence polarization, and fluorescence lifetimes for C$_{70}$ in toluene–acetonitrile solvent system and in other binary mixed solvents: benzene–acetonitrile (methanol, hexane), benzonitrile–acetonitrile (hexane), and *o*-dichlorobenzene – acetonitrile.

Rudalevige et al. [14] confirmed the formation of C$_{60}$ and C$_{70}$ aggregates in mixtures of benzene or toluene with acetonitrile using static and dynamic light scattering, as well as photoluminescence.

Alargova et al. examined the behavior of C$_{60}$ and C$_{70}$ transferred to acetonitrile from different nonpolar solvents [15]. In all the above studies, fullerenes in acetonitrile form aggregates, or nanosized colloidal particles.

A more detailed consideration of the problem is presented in a review paper [8]. Note that fullerenes readily form crystal solvates with many solvents in the solid state [4,8]. Some nitrogen-containing

solvents, e.g., *N*-methylpyrrolidine-2-one, exhibit specific interactions with fullerenes [16,17], and such systems should be considered separately.

Naturally, when studying fullerenes in a mixed solvent it is important to estimate the critical composition (if any) of the transformation of molecular solution to a colloidal system. Nath et al. examined mixtures of nonpolar solvents with polar ones via spectrophotometry and revealed that in the case of C_{60} such a critical composition corresponds to the relative permittivity of $\varepsilon_r \geq 13$ [18], whereas for C_{70} this threshold corresponds to much higher polarity, $\varepsilon_r \approx 27$–31 [19].

A study in our laboratory showed that the critical composition depends on the fullerene concentration, at least for the C_{60}–toluene–methanol system [20]. On going from 4×10^{-7} M to 4×10^{-5} M C_{60}, the threshold changes from 67.5 to 55.0–57.5 vol. % CH_3OH [20]. Basing on both DLS and spectrophotometry, some other regularity concerning the above system were also discussed in this paper [20]. In another publication [21], the peculiarities of C_{60} behavior in benzene–acetonitrile systems were reported.

Though fullerene solutions in such solvents as *n*-hexane should be considered as true ones, i.e., molecular, some examples of oversaturated solutions with C_{60} colloidal species about 200 nm have been reported [22]. On the other hand, Ginzburg et al. [23–27] disclosed unusual properties of C_{60} and C_{70} in aromatic solvents (benzene, toluene, xylenes) using ebullioscopy, X-ray diffraction patterns, and some other methods: the fullerene molecules are surrounded by shells of hundreds aromatic solvent molecules. This allows considering such molecular solutions as a kind of periodic colloidal systems, or colloidal crystals [10].

This paper is aimed to elucidate some features of C_{70} solutions in mixed toluene- and *n*-hexane-based solvent systems and to make some conclusions concerning the state of fullerenes in polar–nonpolar binary mixed solvents.

Experimental

The C_{70} sample (NeoTechProduct., 99 %+) was used as received. After storing a weight amount of C_{70} in toluene or *n*-hexane about two weeks, the solution was filtered using the 0.22 μm pore sized PTFE filters. The solubility of C_{70} in these two solvents is (1.27; 1.67; 1.8)×10^{-3} M and 1.5×10^{-5} M, respectively [8]. In the case of toluene, the amount of C_{70} was substantially below the solubility limit, and after filtration practically no substance was left on the filter. Thus, the concentration was calculated assuming complete dissolution. In the case of *n*-hexane, a marked quantity of the fullerene was collected on the filter, and therefore in this case the concentration of the stock solution was determined using the reported value of the molar absorptivity [28]. All solutions were stored in the dark. Toluene, *n*-hexane, acetonitrile, and methanol were purified and dehydrated via standard procedures. The absorption spectra were run using the Hitachi U-2000 spectrophotometer against solvent blanks. A Zetasizer Nano ZS apparatus (Malvern Instruments) was used for analyzing the particle size distribution via DLS. Sun and Bunker [11] demonstrated the dependence of spectroscopic results in the procedure of solution preparation in the C_{70}–toluene–CH_3CN system. We used the following method. An aliquot of toluene was placed into a flask, a polar component was added and the solution was mixed. In such way the solution was almost made up to the mark. Then, a small volume of the stock solution of C_{70} was added and after mixing the measurements were done. This procedure allowed avoiding the appearance of a broad and unstable in time absorption band about 700 nm observed by Sun and Bunker [11]. In the case of the *n*-hexane–methanol system, the C_{70} solution in *n*-hexane was mixed with the required volume of methanol; both solutions were preliminary heated and all solvent parameters necessary for processing the DLS data were used for 40 °C. Normally, the colloidal particles are formed just after preparation of the solutions, contrary to the case of toluene–*N*-methylpyrrolidine-2-one system [16], and as a rule were stable within several h. The solvent composition was expressed as volume percent if not otherwise specified.

Results and Discussion

Toluene–acetonitrile system, 25 °C

As it was mentioned in the overview, this is currently the most studied system. Our results confirm the published data. In Figure 1, the absorption spectra are presented. In pure toluene, the absorption maxima are as follows: λ_{max} = 315; 334; 365; 383; and 473 nm.
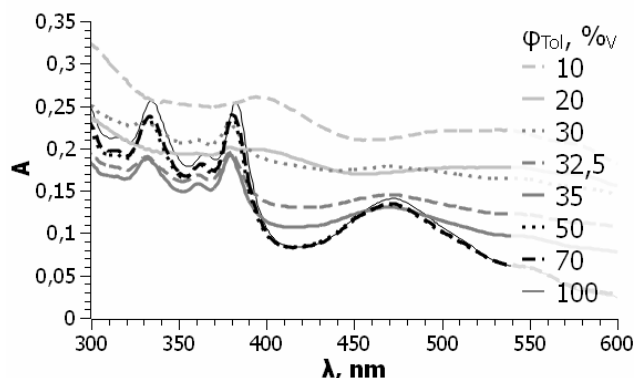
Figure 1. Selected absorption spectra of C_{70} (5×10^{-6} M) in the toluene–acetonitrile solvent system at 25 $^{\circ}$C.

A gradual decreasing in the intensity at 382 nm takes place along with the increase in the first CH_3CN fraction. Up to 50 % of toluene, positions of the maxima alter but slightly; a hypsochromic shift of ca. 1–2 nm was observed. Further rise of the acetonitrile content cause dramatic changes of the spectra, especially within the range of 500–600 nm (see the spectrum at 30 % toluene). The absorption maxima became fuzzy, the integral intensity strongly increases. Such absorption is an evidence of aggregation of fullerene molecules. Under such conditions, a contribution of light scattering cannot be ruled out. Our spectral data resemble in outline those reported by others [10,13,19].

As a turning-point, the toluene content of 32.5 to 35 % should be considered. At 32.5 %, the λ_{max} values of C_{70} somewhat differ from those in pure toluene: 315; 333; 361; 380; and 470 nm, but some features of molecular spectrum, e.g., the band with λ_{max} around 380 nm, are still observed. In Figure 2 (left), the dependences of the absorbance at 470 nm and 600 nm on the solvent composition are depicted. Abrupt changes occur within the range of 30–36 % toluene. The A_{600} symbol means the absorption at 600 nm. H_{470} denotes the additional intensity of absorption after subtracting the "basic line". The latter is drawn from absorption at 540 nm to 425 nm in pure toluene.

In Figure 2 (right), the dependence of particle size is presented. It can be firmly stated that the aggregation of the C_{70} molecules occurs at toluene content around 40 %. This corresponds to a decrease in the fluorescence quantum yield and integral absorption intensity [11]. Hence, the absorption spectrum retains the main features that are typical for the molecular fullerene, while the particle size is over 200 nm. As a plausible reason, we may assume that the fullerene molecules hold their initial aromatic solvation shell even when colloidal species are formed. At higher content of acetonitrile, the C_7H_8 molecules are probably replaced by CH_3CN. As an alternative explanation, the presence of single molecules solvated with toluene may be assumed. Than their absence in the DLS picture should be explained by overlapping their signal by strong scattering of colloidal species. Sun and Bunker, however, consider such assumption as improbable basing on the fluorescence and fluorescence excitation spectra [11].
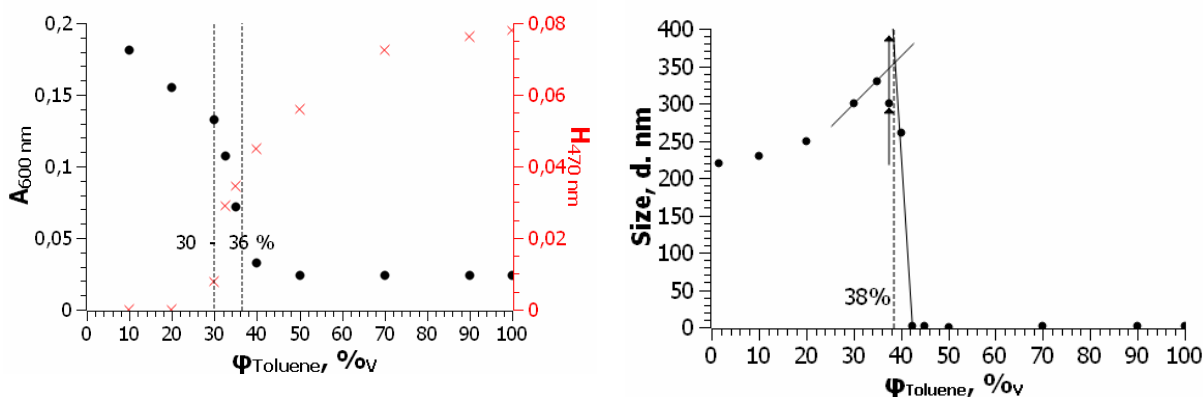

Figure 2. Alterations of the electronic absorption spectra of C_{70} (left; optical path length 1.00 cm) and the particle size distribution (by intensity, right) in toluene–acetonitrile solvent system, fullerene concentration 5×10^{-6} M; 25 $^{\circ}$C. The size at 37.5 % toluene increases over time.

Particle size distribution is typified in Figure 3. The results for 30 % toluene agree with those published by Ghosh et al. for 6×10^{-6} M C_{70}; see Fig. 4C in ref. [13]. Note, that in acetonitrile-reach mixed solvents, the size of colloidal species is substantially smaller as compared with those just after the turning-point (Figure 2, right and Figure 3), like in the C_{60}–toluene–methanol system [20].
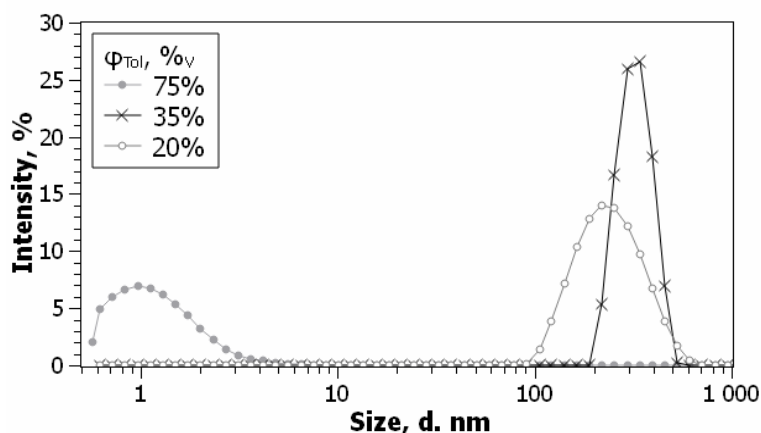

Figure 3. Examples of particle size distribution (by intensity) C_{70} (5×10^{-6} M) in the toluene–acetonitrile solvent system at 25 °C.

In the previous studies on C_{60} in this laboratory, similar regularities were observed. In a benzene–acetonitrile mixed solvent, the absorption band with λ_{max} = 335 nm at 50 % benzene is close to that in pure benzene (only the intensity drops by ca. 20 %), while the colloidal species with the size of 100-200 nm are registered via DLS; the data refer to C_{60} concentration of 4×10^{-5} M [29]. The data obtained for C_{60} in the toluene–methanol system are of the same type [20]. In 50 % toluene solution, the band maximum, 336 nm, is the same as in toluene, whereas the intensity is ca. 18 % lower than in the entire aromatic solvent, though large colloidal species are already present in the solution (fullerene concentration 6.8×10^{-6} M; 25 °C). Even at 30 % toluene, a band with the same λ_{max} is observed, though of much lower intensity [20].

Nath et al. established the threshold content of the polar solvent where the aggregation begins by examining the absorption spectra of C_{60} within the range of 450–650 nm [18, 19]. As it was already stated in the pioneering work by Sun and Bunker for C_{70} in toluene–acetonitrile mixed solvent [10] and confirmed by us for C_{60} in toluene–methanol system [20], such threshold depends to some extent on the fullerene concentration. Though Sun and Bunker preferred to use for the aggregates under discussion the term "cluster" and expected the C_{70} solution at 70 % acetonitrile quite different from a conventional colloidal solution [10], both results reported by Ghosh [13] and our data (Figure 2, right) indicate the presence of colloidal species at the corresponding concentrations of the fullerene.[*] The lower the fullerene concentration is, the higher content of a polar solvent is necessary to reach the aggregation. This is quite understandable because of poor solubility of fullerenes in polar solvent.

More interesting is another observation made by Sun and Bunker: under conditions of extreme dilution, down to 8×10^{-8} M, the absorption spectrum in 70 % CH_3CN is close to the spectrum in neat toluene. In this connection, Sun and Bunker stated "The result indicates that the formation of the new species involves more than one C_{70} molecule" [10]. As these authors have not used the DLS method, we made the corresponding measurements. Even at somewhat higher C_{70} concentration of 1.2×10^{-7} M, only species of about 1 nm (like shown in Figure 3) were found in 70 % acetonitrile.

Concluding, at least the first stages of the fullerene aggregation occur in the systems under study with retaining some part of the primary aromatic shell as follows from matching the UV-vis and DLS data. Also, the lower the toluene content is, the smaller is the size of the colloidal species. In extreemely diluted C_{70}, the aggregates are undetectable via the DLS method even in 70 % of acetonitrile.

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[*] *The coagulation of such aggregates by electrolytes [29] additionally confirms their typically colloidal nature.*

Toluene–methanol system, 25 °C

Now let us compare the above data with those previously reported for C_{60} in the same solvent system [20]. In the last-named study, a DLS investigation of C_{60} within the whole range of toluene–methanol binary mixed solvent was performed at three concentrations of the fullerene, 4×10^{-7}, 4×10^{-6}, and 4×10^{-5} M. In brief, the conclusions are as follows:

(i) At 4×10^{-7} M C_{60} the aggregates appear at 67.5 vol % methanol, whereas in 4×10^{-5} M solution, it already occur at 55.0–57.5 vol % of alcohol. Similar tendency was observed for C_{70} in the toluene–acetonitrile system by Sun and Bunker [11].

(ii) Normally, the higher the fullerene concentration is, the larger are the aggregates at the same composition of the mixed solvent. For C_{70} in toluene–acetonitrile system, similar tendency was reported by Ghosh et al., see ref. [13], Fig. 4B,C.

(iii) The dependence of the size of the aggregates on the methanol content is in line with the Volmer's rule [30]: the less soluble is the compound in the given solvent, the smaller particles are formed. For example, at 4×10^{-7} M C_{60} in 99; 95; and 70 vol. % methanol, the particle size is around 200; 260-320; and 470–500 nm, respectively. The polydispersity index, PDI, increases in the same direction. As an alternative (or additional) explanation, the participation of toluene in the aggregates may be proposed. Because fullerenes readily form solvates containing hundreds of toluene molecules [27], they may aggregate not as "bare" C_{60} molecules, but rather as solvates, at least at high toluene content in the mixed solvent.

(iv) The results obtained at C_{60} concentration of 4×10^{-6} M are closer rather to those for 4×10^{-7} M C_{60}, than for 4×10^{-5} M.

Note, that at 6.8×10^{-6} M C_{60} a band at 336 nm, typical for the monomeric species, was observed not only at 70 %, but even at 80 % of methanol, where the 300 nm-sized colloidal species predominate.

Going back to the solutions of C_{70} examined in the present study, we can argue that the picture is quite similar. Even at 35 % of toluene, the spectrum is similar to that in pure toluene except intensity increase at wavelength over 400 nm (Figure 4).
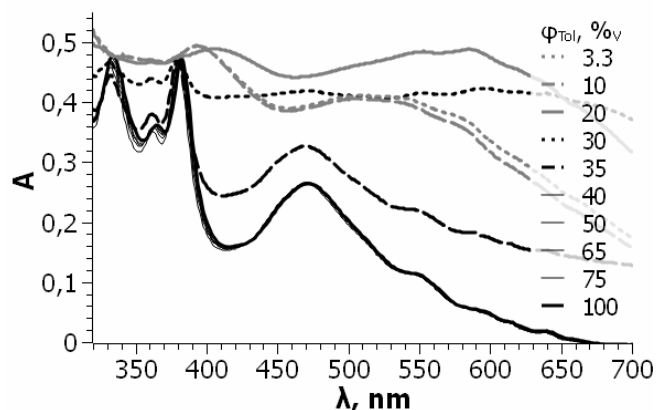

Figure 4. Selected absorption spectra of C_{70} (5×10^{-6} M) in the toluene–methanol solvent system at 25 °C, normalized at absorption at 382 nm.

At the same time, at such composition of the solvent colloidal species already appear (Figure 5, fullerene concentration 5×10^{-6} M). As in the previous case, the size of the colloidal particles rises (here: up to 480 nm) and then decreases along with decrease in the content of toluene.

The peculiarity of this system consists in the appearance of small amounts of 100–200 nm-sized particles even at 40, 50, 60 % toluene, however, only in the distribution by intensity. They are absent in other types of distributions, but they are observed repeatedly and their percentage in the above mixed solvents is 15, 11, and 3%, respectively. In the C_{60}–toluene–methanol system, small amounts of such particles were observed even at 5 % of methanol [20].

Further increase in the methanol fraction results in formation of colloidal species, which are observable also in distributions by volume and particle number.
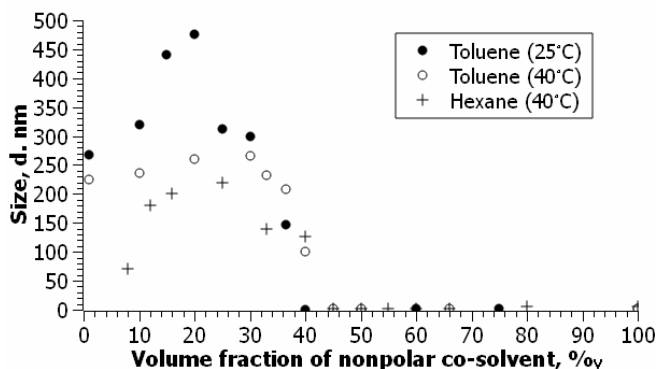
Figure 5. Alterations of the particle size distribution (by intensity) in toluene–methanol and *n*-hexane–methanol solvent systems; 25 ⁰C.

Toluene–methanol system, 40 °C

The reason for studying this system at an enhanced temperature was further comparing with the *n*-hexane–methanol system, which tends to stratify below 40 ⁰C [31]. The spectra are presented in Figure 6, particle sizes are given above in Figure 5.
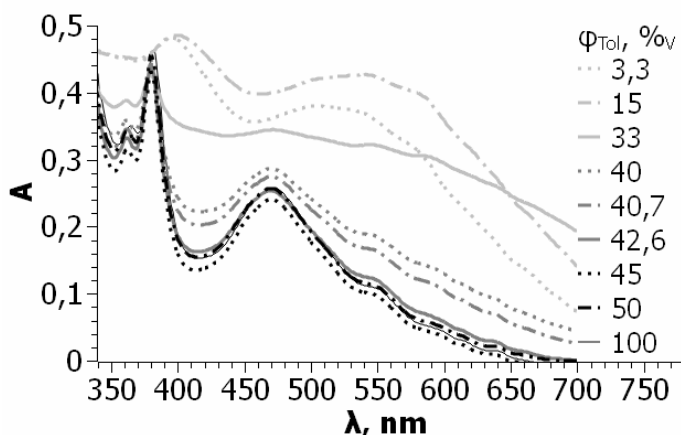

Figure 6. Selected absorption spectra of C_{70} (5×10^{-6} M) in the toluene–methanol solvent system at 40 ⁰C, normalized at absorption at 382 nm.
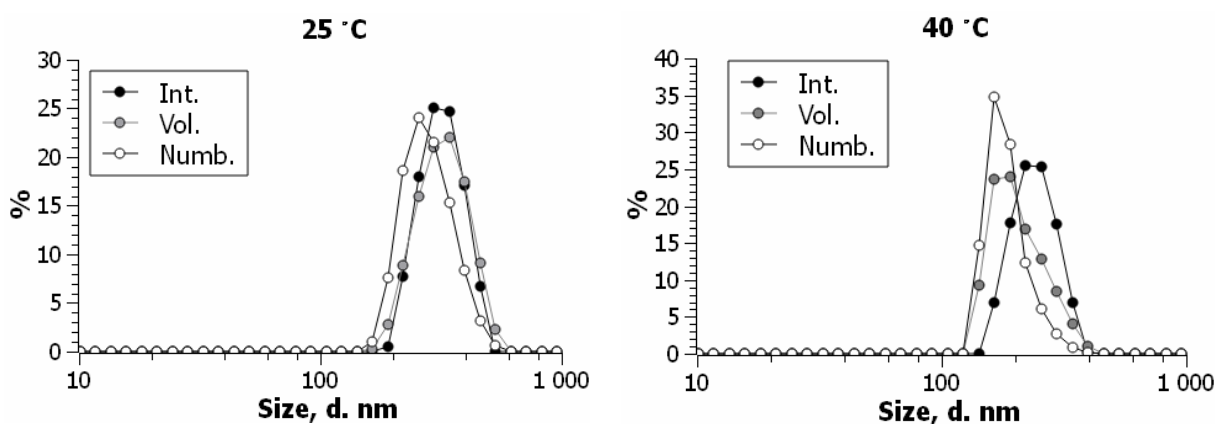

Figure 7. The particle size distribution by intensity, volume, and number for C_{70} (5×10^{-6} M) in the toluene–methanol binary solvent, 10 vol. % of toluene at 25 ⁰C.

The morphology of the absorption curve retains in outline down to 42.6 % toluene, despite some intensity decrease in the short wavelength portion. Along with further decrease in the content of toluene, a flattering of the spectral curve and substantial rise of the integral absorption takes place. The

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peak about 380 nm is observable even at 30 % toluene. This band undergoes a slight hypsochromic 3-4 nm shift as compared with the band in entire toluene.

In the DLS patterns, the turning-point corresponds to 40 % toluene (Figure 5). Again, as at 25 $^{\circ}$C, at 45 and 50 % toluene, 25–75 nm-sized particles were observed only in the distribution by intensity (35 and 20 %, respectively). The particles size in the undoubtedly colloidal region is maximal at 30 % toluene, and then decreases (Figure 5). Normally, at the elevated temperature the colloidal species are smaller than at 25 $^{\circ}$C, whereas other regularities typical for fullerenes in toluene(or benzene)–polar solvent mixed solvents are fulfilled.

In Figure 7, the particle size distributions of C_{70} at 25 and 40 $^{\circ}$C are exemplified for toluene content of 10 %. In these conditions we are talking about typical organosols.

n-Hexane–methanol system, 40 °C

The absorption spectra are presented in Figure 8, and the alterations of size are already given in Figure 5.
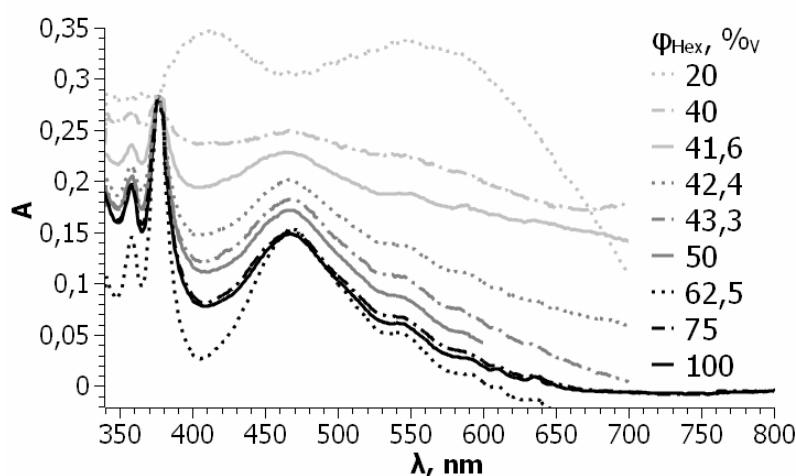

Figure 8. Absorption spectra of C_{70} in the *n*-hexane–methanol solvent system at 40 $^{\circ}$C, normalized at absorption at 377 nm.

In this system, the *n*-hexane was introduced in form of a portion of the stock fullerene solution. Therefore, the concentration of C_{70} in the working solutions was inconstant. For example, at *n*-hexane content of 100; 66.7; 50; 25; 15; and 10 %, the C_{70} concentrations in the working solutions were (10.0; 6.67; 5.0; 2.5; 1.5; and 1.0) $\times 10^{-6}$ M.

In Figure 5 it is clearly seen that the turning-point is at 40 % *n*-hexane. At 55–45 % *n*-hexane some 50–100 nm-sized particles are observed only by intensity, but rather distinct (30–60%) and repeatable. At the content of the hydrocarbon < 40%, big particles are fixed in all types of distribution. Here, a decrease in size at high concentrations of methanol is also evident, as in the toluene-containing systems (Figure 5). However, it should be taken into account that the fullerene concentration is very low in this range.

The character of the electronic absorption spectra at 42.4–41.6 % of C_6H_{14} retains the features of that in entire *n*-hexane, though some alterations in the long wavelength portion are evident (Figure 8). At 40 % *n*-hexane, the spectrum changes cardinally.

Hence, whereas in the case of the last-named system, the absorption spectrum typical for molecular form of C_{70} is still observable when colloidal species are already present in the solution, the turning-point between molecules and colloids as determined by both UV-visible spectra and DLS coincides for the *n*-hexane–methanol binary mixed solvent. Hence, the solvation shells formed by the aliphatic solvent around C_{70} are less stable as compared with those formed by toluene.

Toluene–n-hexane system, 25 °C

Finally, the absorption spectra of C_{70} in toluene–*n*-hexane system were studied. Normalized UV-visible spectra are presented in Figure 9. In this special case, the procedure was as follows. Two

volumes of solvents were mixed, e.g. 75 vol.% *n*-hexane means that 7.5 mL of this solvent (containing C_{70}) were mixed with 2.5 mL of toluene, etc.
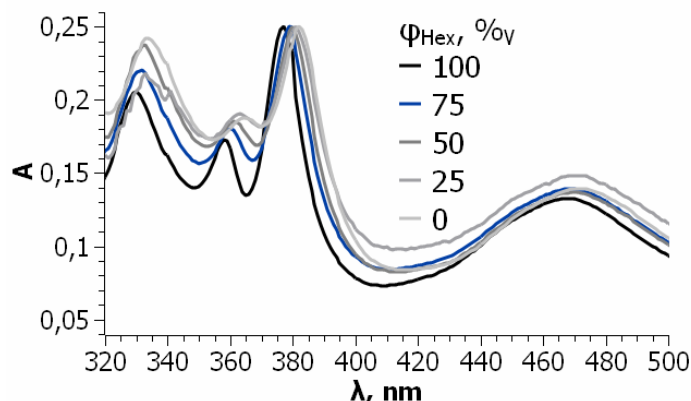

Figure 9. Selected normalized absorption spectra of C_{70} in the toluene–*n*-hexane solvent system; fullerene concentrations: (10.0; 7.5; 5.0; 2.5; and 57,5)$\times 10^{-6}$ M, respectively.

Though both co-solvents belong to nonpolar ones, these spectral data allow to shed some light upon the solvation character. The gradual bathochromic shift on going from *n*-hexane to toluene and the absence of an isosbestic point allows expecting that the replacement of aliphatic molecules by aromatic ones occurs little by little. The shifts are relatively small. Indeed, Ghosh et al. mentioned that the color of C_{70} in benzene–*n*-hexane solutions does not display color change [13].

In the system of interest, the shifts from 376.5 to 382.0 and from 358.1 to 364.5 nm equal to 5.5 and 6.4 nm, respectively (Table 1). But even this modest solvatochromic effect discloses a tendency to preferred solvation of C_{70} molecules by toluene. Indeed, the average values of λ_{max} are 379.3 and 361.3 nm, respectively. In both vol % and molar fraction scales, these values correspond to somewhat lower content of toluene. The same conclusion can be made using wave numbers instead of wavelengths. Thus, despite the proximity of the absorption peaks in both solvent, an evidence of better solvation by toluene molecules is obtained.

Table 1. Positions of two characteristic absorption maxima in the C_{70} UV-spectra in the toluene–*n*-hexane system, 25 °C

Toluene, volume %	Toluene, molar fraction	Absorption maxima, nm	
100	1.00	382.0	364.5
75	0.787	381.0	363.3
50	0.552	380.0	362.0
37	0.420	379.5	361.5
25	0.291	379.2	362.8
17	0.201	379.0	361.0
10	0.120	378.0	359.4
5	0.061	377.0	358.6
0	0	376.5	358.1

Conclusions

1. Formation of colloidal species of C_{70} in toluene–acetonitrile, toluene–methanol, and *n*-hexane–methanol binary solvent mixtures is detected by both UV-visible spectroscopy and dynamic light scattering methods. In all the examined systems, some turning-point from molecular solution to organosol can be fixed by both methods.
2. Whereas for the *n*-hexane–methanol system at 40 °C the turning point as estimated by UV-visible spectra and DLS measurements agree, in the toluene–acetonitrile (at 25 °C) and in toluene–methanol systems (at 25 and 40 °C) the absorption spectra retain some distinct features of molecular absorption even when colloidal aggregates are firmly detected in the solution. This agrees with our previous data for C_{60} in benzene–acetonitrile and toluene–methanol

solvent systems. It may be explained by high affinity of aromatic molecules to the fullerenes: some C_{70} (and C_{60}) molecules form aggregates keeping their aromatic solvation shells.

3. UV spectra of C_{70} in the toluene–n-hexane binary mixtures confirm a better expressed affinity of toluene to the all-carbon molecule. Better solvation of C_{70} with the aromatic toluene as compared with the aliphatic n-hexane is in line with the solubility of the fullerene in these two solvents, 1.6×10^{-3} and 1.5×10^{-5} M, respectively.

4. Organosols of C_{70} obey some rules, like previously observed for C_{60} in similar systems. High content of the polar solvent, high temperature, and low fullerene concentration favor formation of smaller colloidal particles.

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Н.А. Марфунин, Н.О. Мчедлов-Петросян. Поведение фуллерена C$_{70}$ в бинарных смесях органических растворителей, исследованное при помощи электронной спектроскопии и динамического рассеяния света.

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В данной работе было изучено формирование коллоидных частиц фуллерена C$_{70}$ в органических растворителях. Исследование электронных спектров поглощения сопровождалось анализом размера частиц при помощи динамического рассеяния света, ДРС. Исходные растворы C$_{70}$ в неполярных толуоле и *н*-гексане разбавляли полярными растворителями ацетонитрилом и метанолом. Появление коллоидных частиц с размерами в диапазоне ≈50–500 нм сопровождается изменением спектров поглощения. В бинарных смешанных растворителях толуол–ацетонитрил и толуол–метанол при 25 $^{\circ}$C спектры поглощения C$_{70}$ (5×10^{-6} M) проявляют тенденцию сохранять особенности спектра в чистом ароматическом растворителе, даже если молекулы C$_{70}$ присутствуют уже только в агрегатах. Ранее такое явление наблюдалось для C$_{60}$ в системах растворителей бензол–ацетонитрил и толуол–метанол. Это подтверждает предположение о наличии стабильных первичных сольватных оболочек, образованных ароматическими молекулами вокруг молекул фуллерена. Поведение C$_{70}$ в смесях толуола с метанолом сопоставлено с ранее опубликованными результатами этой лаборатории для фуллерена C$_{60}$ в той же системе растворителей.

Исследование смесей *н*-гексан–метанол проводилось при повышенной температуре из-за ограниченной смешиваемости этих растворителей при 25 $^{\circ}$C. Соответственно, система C$_{70}$–толуол–метанол была также исследована при температуре 40 °C. Было обнаружено небольшое, но отчетливо заметное различие в свойствах этих двух систем. В то время как во втором случае типичный для молекулярной формы C$_{70}$ спектр поглощения все еще наблюдается, когда коллоидные частицы уже присутствуют в растворе, точка перехода между молекулами и агрегатами совпадает для бинарного смешанного растворителя *н*-гексан–

метанол как по данным как электронной спектроскопии, так и ДРС. Следовательно, сольватные оболочки, образованные алифатическим растворителем вокруг C_{70}, менее стабильны по сравнению с оболочками, образованными толуолом.

Наконец, были проанализированы спектры светопоглощения C_{70} в смешанном растворителе толуол–*н*-гексан. Эти данные говорят в пользу предпочтительной сольватации молекул C_{70} ароматическим компонентом бинарного растворителя.

Ключевые слова: фуллерен C_{70}, толуол, *н*-гексан, ацетонитрил, метанол, молекулярные растворы, органозоли, электронные спектры поглощения, динамическое рассеяние света, размер частиц.

М.О. Марфунін, М.О. Мчедлов-Петросян. Поведінка фуллерену C_{70} у бінарних сумішах органічних розчинників, вивчена за допомогою електронної спектроскопії та динамічного розсіяння світла.

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У даній роботі було вивчене формування колоїдних частинок фуллерену C_{70} в органічних розчинниках. Вивчення електронних спектрів поглинання супроводжувалося аналізом розміру частинок за допомогою динамічного розсіяння світла, ДРС. Вихідні розчини C_{70} у неполярних толуолі та *н*-гексані розводили полярними розчинниками ацетонітрилом та метанолом. Поява колоїдних часток з розмірами у діапазоні ≈50-500 нм супроводжується зміною спектрів поглинання. У бінарних змішаних розчинниках толуол–ацетонітрил та толол–метанол при 25 °C спектри поглинання C_{70} ($5{\times}10^{-6}$ М) мають тенденцію зберігати особливості спектру у чистому ароматичному розчиннику, навіть якщо молекули C_{70} наявні лише у формі агрегатів. Раніше таке явище спостерігалось для C_{60} у системах розчинників бензол–ацетонітрил і толуол–метанол. Це підтверджує ідею щодо існування стабільних первинних сольватних оболонок, утворених ароматичними молекулами навколо молекул фуллерену. Поведінка C_{70} у сумішах толуолу з метанолом порівнювалась з раніше опублікованими результатами цієї лабораторії для фуллерену C_{60} у тій же системі розчинників.

Вивчення сумішей *н*-гексан–метанол проводилося при підвищеній температурі через обмежену змішуваність цих розчинників при 25 °C. Відповідно, система C_{70}–толуол–метанол також була досліджена при 40 °C. Було виявлено невелику, але помітну різницю. В той час як у випадку останньої системи типовий для молекулярної форми C_{70} спектр поглинання все ще спостерігається, коли колоїдні частинки вже присутні у розчині, точка переходу між молекулами та агрегатами співпадає для бінарного змішаного розчинника *н*-гексан–метанол за даними як електронної спектроскопії, так і ДРС. Таким чином, сольватні оболонки, утворені аліфатичним розчинником навколо C_{70}, є менш стабільними у порівнянні з оболонками, що утворені толуолом.

Врешті було проаналізовано спектри світлопоглинання C_{70} у змішаному розчиннику толуол–*н*-гексан. Ці дані свідчать на користь переважної сольватації молекул C_{70} ароматичним компонентом бінарного розчинника.

Ключові слова: фуллерен C_{70}, толуол, *н*-гексан, ацетонітрил, метанол, молекулярні розчини, органозолі, електронні спектри, динамічне розсіяння світла, розмір частинок.