Formation and Optical Absorption of Clusters of the *p*-tert-butylcalix[8]arene:C_{60} Complex

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Abstract. Depending on the initial concentrations of fullerene (C_{60}) and *p-tert-butyl* calix[8]arene (C[8]A) in toluene, two regimes of their interaction were distinguished. The changes in optical absorption of C_{60}:C[8]A mixed solutions observed over a period of time suggest that the following consecutive processes take place upon interaction between C_{60} and C[8]A in toluene: (1) molecular inclusion, and (2) growth and sedimentation of the insoluble C_{60}/C[8]A clusters. At increased concentrations of the components, process (2) is suppressed and stable C_{60}/C[8]A colloids can be formed. Spectral features of these colloids in different solvents clearly indicate the difference between self-aggregated C_{60} and small clusters of the complex. A specific influence of the C[8]A cage on the entrapped C_{60} molecules is also confirmed by IR spectroscopy of the complex in the solid state.

Key words: fullerene, calixarene, inclusion complex, electronic spectra.

1. Introduction

Significant progress has been made towards understanding the molecular mechanisms responsible for the stability of non-covalent complexes based on fullerene and macrocyclic compounds of complementary shapes [1–8]. The pair C_{60}-C[8]A appeared to be a very attractive model in order to investigate fundamental phenomena associated with weak non-covalent interactions.

A colour change from purple to yellow was found to accompany complexation of C_{60} and cavitands of the calixarene family [9, 10]. This change was assigned to resonant fullerene-fullerene interactions in C_{60} aggregates encapsulated by host calixarene molecules. However, this explanation does not include the interaction with calixarenes, although formation of aggregates and their stabilization in the solution is achieved exclusively due to the cavitands. The goal of this study is to identify the role of calix[8]arene in the distortion of the highly symmetrical π-electron structure of the C_{60}, leading to formation of clusters insoluble in toluene. In order to study this problem it should be important to investigate formation of the complex under limited amounts of components in a solution, varying the concentration and the molar ratio of C_{60} to C[8]A.

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2. Experimental

C[8]A was synthesized at the Institute of Organic Chemistry (Kiev) as described elsewhere [11]. The calixarene and C_{60} were dissolved in toluene separately in order to prepare 1 mg/ml stock solutions. The corresponding amounts of these stock solutions were diluted by toluene and mixed to prepare C_{60}:C[8]A mixtures with different concentrations and molar ratios of C_{60} to C[8]A. The mixtures were kept in tightly closed vials in the dark for a period from several hours to one month. A brown dense sediment formed in the mixtures was collected, dried in the dark and then used for the further experiments. Pellets for IR measurements were prepared from C_{60}/C[8]A sediment mixed with KBr powder.

Absorption spectra were measured with SPECORD M-40 and SPECORD M-80 dual-beam spectrometers in the visible and IR ranges, respectively.

3. Results and Discussion

3.1. PRECIPITATION OF THE C_{60}/C[8]A

Precipitation of the complex from C_{60}:C[8]A mixtures was monitored in order to estimate the rate of interaction between C_{60} and C[8]A. The results of visual inspection of the solutions with concentrations of C_{60} and C[8]A ranging from 10^{-4} to 10^{-3} M are given in Table I. Based on the insolubility of the C_{60}/C[8]A complex, the time required for the reaction to yield a visible precipitate is expected to be inversely proportional to the reaction rate. As dictated by the equilibrium:

$$C[8]A + C_{60} \Leftrightarrow C[8]A \cdot C_{60}, \tag{1}$$

the reaction rate should be in proportion to the product of the concentrations: $[C[8]A] \times [C_{60}]$. Indeed, no visible precipitate was observed in the C_{60}:C[8]A mixed solutions within a month, when the concentration of each component was lower than 10^{-4} M. A dark-brown precipitate was formed in one, two and six days in the mixtures with $5:1$, $4:1$ and $3:1$ molar ratios of C[8]A to C_{60}, respectively, when the concentration of C_{60} in all mixtures was equal to 10^{-4} M (Table I). For all of these solutions, only bleaching of the initial purple colour was observed while the sediment was formed. For the largest excess of C[8]A to C_{60} ($4:1$ and $5:1$ molar ratios, respectively), the remaining solutions became virtually colourless at the end of the period of one month. However, at the same production of concentrations, sedimentation was found to occur more slowly with excess of C_{60} over C[8]A (see Table I). It seems that sedimentation of the molecular inclusion complex is favorable in the presence of additional C[8]A molecules, so that an excess of C[8]A may persist in the sediment.

On the other hand, the solutions changed their colour to yellow when the concentration of the C_{60} exceeded 10^{-4} M, with the corresponding excess of C[8]A (Table I). In this case, cloudiness in the bulk of the mixture could be seen just before

Table I. Concentrations of the components in toluene solutions and time of the beginning of visible changes in the solutions

First regime							
C_{60}	10^{-4}	10^{-4}	10^{-4}	10^{-4}	10^{-4}	4×10^{-4}	5×10^{-4}
C[8]A	5×10^{-4}	4×10^{-4}	3×10^{-4}	2×10^{-4}	10^{-4}	10^{-4}	10^{-4}
Time	1 day	2 days	6 days	1 month	–	1 month	1 month
Second regime							
C_{60}	4×10^{-4}	3×10^{-4}	2×10^{-4}				
C[8]A	8×10^{-4}	9×10^{-4}	8×10^{-4}				
Time	1 day	1 day	1 day				

any sediment was formed. The cloudiness and yellowish color of the solutions remained even after continuous aging. This indicates that at least part of the complex exists in a form of C_{60}/C[8]A clusters small enough to form a stable dispersion in toluene.

It is reasonable to assume that when the concentration of the components is low, centers of nucleation are necessary, which facilitate formation of the complex under a limited amount of the substance in the solution. Successive formation of the complex will preferably occur around the aggregates formed, so that large sediments are expected to grow up finally. This is consistent with the complex formation observed as flocculation at the surface of the solution, where the probable nucleation centers are present. When the low limit of concentration is exceeded, formation of the complex occurs throughout the solution which yields change in solution colour.

3.2. ELECTRONIC ABSORPTION OF THE C_{60}/C[8]A COMPLEX

Similarly to our visual observations, two types of absorption changes could be distinguished depending on the initial concentrations of C_{60} and C[8]A. At low concentrations of the components the absorption bands of C_{60} underwent only a proportional lowering in addition to slightly increased background (Figure 1). This correlates well with the visually observed bleaching without qualitative changes in color.

The new features that were not observed in spectra of the C_{60} and C[8]A alone, appear in the solution of the C_{60}/C[8]A complex with increased concentrations of the components in toluene. All yellow solutions show an enhanced absorption in the region of 420 to 520 nm. An additional absorption near 680 nm was found after successive addition of concentrated C[8]A solution to the mixture of C_{60}/C[8]A in toluene (Figure 2, curve 2). Spectra of the C_{60}/C[8]A precipitate re-dissolved in CCl_4 (Figure 2, curve 3), showed similar features, strongly increased absorption around 450 nm and above 650 nm. At the same time, the features of C_{60} monomers,
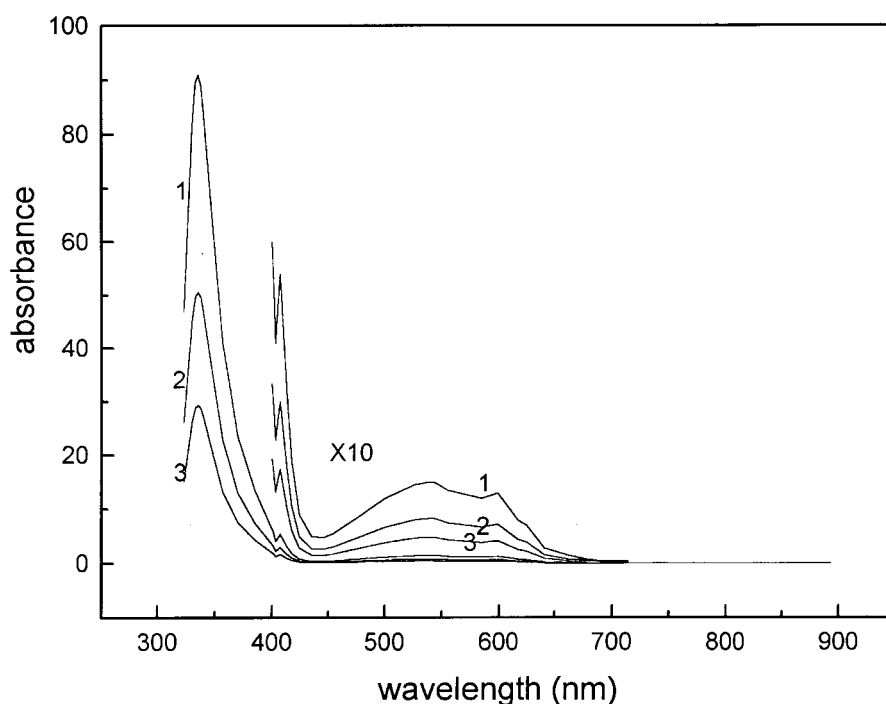
Figure 1. Typical changes in optical absorption of C_{60}:C[8]A solution in toluene at low reaction rate. Initial concentrations of C_{60} and C[8]A are 10^{-4} and 5×10^{-4} M, respectively. (1) spectrum of as-prepared solution; (2) the same solution after one week aging and (3) after two weeks aging.

the band at 330 nm and the spike at 407 nm, remained in the spectra. These peculiarities indicate that the C_{60} undergoes specific interactions different from the fullerene-fullerene ones which are observed in aggregates of pure C_{60}.

The bands in the region at wavelengths greater than 410 nm are normally assigned to the forbidden transitions in the highly symmetrical C_{60} structure [12]. The region of 420 to 520 nm overlaps with that of orbitally forbidden singlet-singlet transitions which undergo Jahn–Teller distortions and appear through Herzberg–Teller vibronic interactions. The peak at 680 nm is one of the spin forbidden singlet-triplet transitions and requires spin-orbital and vibronic interactions for its appearance. It is also subjected to Jahn–Teller effects. Therefore, the appearance of C_{60} absorption bands in the regions mentioned above suggests that interaction between C_{60} and C[8]A occurs which causes distortion of the C_{60} symmetry and polarization of the molecule.

3.3. IR ABSORPTION OF THE C_{60}/C[8]A COMPLEX

IR spectra of the C_{60}/C[8]A precipitate revealed changes of vibrational modes of both the C_{60} and C[8]A constituents. It is known that the highly symmetrical cage-
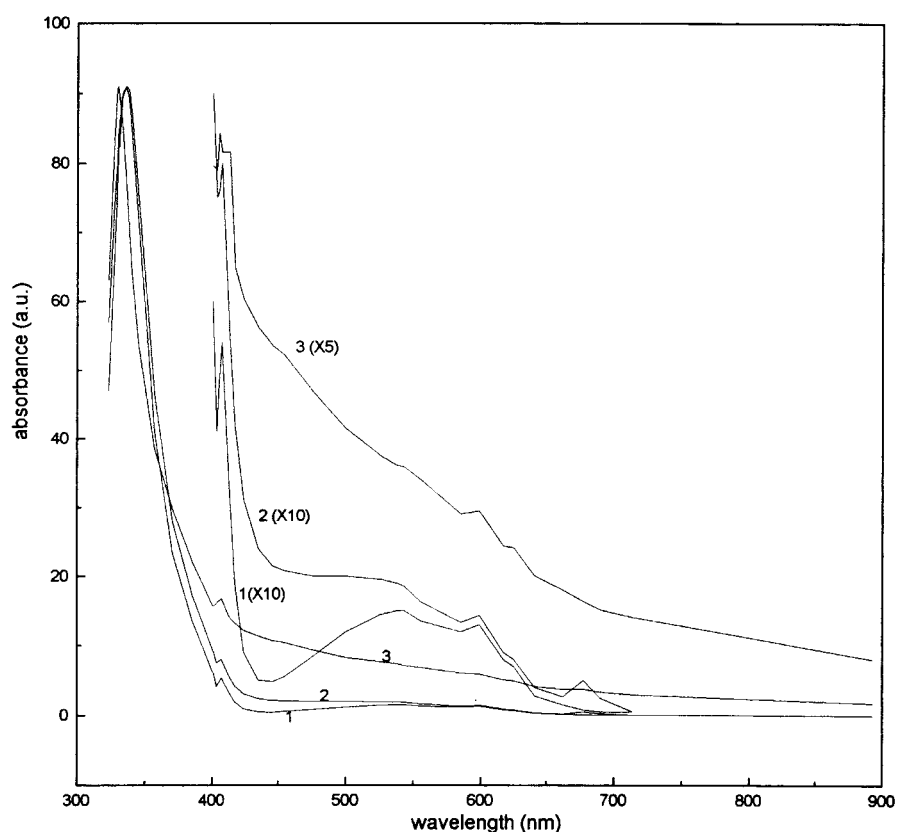
Figure 2. Electronic absorption spectra of stable C_{60}/C[8]A clusters formed at a high reaction rate: (1) as-prepared C_{60}:C[8]A solution in toluene; (2) clusters formed in a toluene solution; (3) C_{60}:C[8]A dry sediment re-dissolved in CCl_4. All the spectra are normalized to give the same maximum absorption of the near-UV absorption band.

like structure of C_{60} possesses four IR modes, at 526, 576, 1182 and 1428 cm^{-1} (see, for example, [13]). In the C_{60}/C[8]A mixture only the first two modes can be analyzed because of the strong C[8]A absorption in the region of 1100 to 1500 cm^{-1}. We found a slight shift of the low-frequency vibrational mode of C_{60} in the C_{60}/C[8]A precipitate as compared to pure C_{60}. The band of C_{60} at 526 cm^{-1} was shifted to 528 cm^{-1} in the C_{60}/C[8]A complex, while the band at 576 m^{-1} remained unchanged. These results are quite similar to those reported in Reference [14].

The major changes in the IR spectra of C[8]A are noticeable in the fingerprint region, from 700 to 1000 cm^{-1} (Figure 3). In the C_{60}/C[8]A complex, some bands of C[8]A, observed at 943 (not shown), 784 and 728 cm^{-1}, lose their intensity relatively to the neighboring ones and undergo broadening. These bands should be assigned to out-of-plane bending vibrations of CCH groups of benzene units and C—CH_2—C groups bridging the benzene units in the C[8]A macrocycle [15].
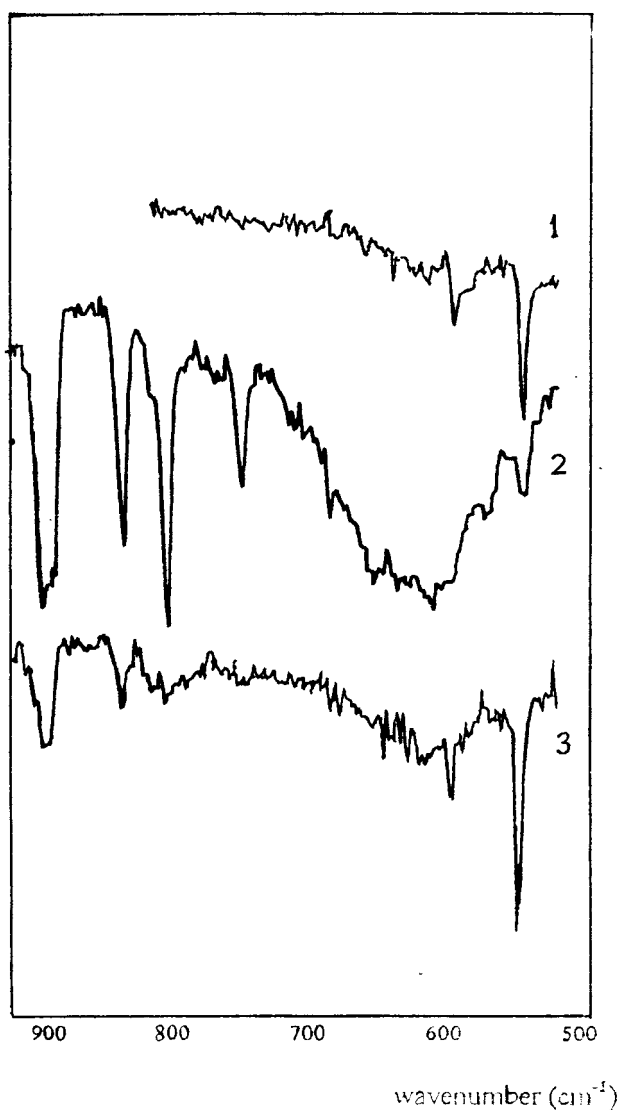
Figure 3. IR absorption spectra of (1) C_{60}, (2) C[8]A and (3) C_{60}/C[8]A complex.

The small changes in the IR spectra of the C_{60}/C[8]A complex as compared to the separated constituents show that rather weak intermolecular forces are responsible for the complexation. These spectral changes are consistent with the model of "a-ball-in-a-basket" of the C_{60}/C[8]A inclusion complex [1]. The low-frequency mode of C_{60} corresponds to vibrations with the major amplitude of a thin-wall fullerene sphere [16], so that its incorporation into a "basket" results in an increase of this vibrational frequency. On the other hand, the out-of-plane displacements in the "basket" will be suppressed when a "ball" is inserted in it.

4. Conclusions

A correlation between composition of C_{60}:C[8]A mixed solutions and the reaction rate of complex formation was demonstrated. In all cases an excess of C[8]A over C_{60} is needed to accelerate the reaction. These findings indicate that the C_{60}/C[8]A supermolecule can be further dissolved in C[8]A to a great extent. Spectral data clearly indicate the interaction between C[8]A and C_{60} due to the appearance of new bands in the forbidden region of the C_{60} absorption.

Acknowledgement

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