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Studies on γ-cyclodextrin inclusion complexes with C_{60}

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Treatment of γ-cyclodextrin and C_{60} by kneading allows the formation of two distinct water-soluble inclusion complexes: γ-CD/C_{60}(1:1) and γ-CD/C_{60}(2:1). Their formation and structures have been indicated by UV-VIS spectroscopy and X-ray powder diffraction. Transformations between the two complexes, shown in the UV-VIS spectra, have been performed under certain conditions.

INTRODUCTION

In September, 1990, Huffman and Krätschmer successfully prepared a measurable quantity of C_{60} (Buckminsterfullerene), which led to the extensive studies on the structure, properties and chemical reactions of C_{60}.[1] The structure of C_{60}, which was determined by the X-ray crystal structure of Hawkins,[2] is that of a highly symmetric truncated icosahedral (Fig 1). The nearest-neighbour distance is 10.02 Å[3] and the calculated diameter of the carbon cage is 7.1 Å. The solubility of C_{60}, poor in most organic solvents and negligible in water, has been one of the main impediments in studying the properties of C_{60}.[4]

To make C_{60} soluble in water, CDs(cyclodextrins) and their derivatives are quite promising. Cyclodextrins consist of six(α-CD), seven(β-CD) or eight(γ-CD) sugar molecules, joined together in a ring by α-1,4-glucosidic bonds.[5,6] With a hydrophobic cavity inside the molecule, CD may act as the host of organic molecules. The diameters of the cavities of α-, β- and γ-CD at 5–6, 7–8 and 9–10 Å, respectively. If the diameter cavity of a CD is comparable with that of C_{60}, the non-polar C_{60} might sit in the cavity and an inclusion complex with certain solubility in water might form.

Recently, Wennerström *et al.*[7] treated C_{60} with a boiling aqueous solution of γ-CD (Fig 2) and obtained a water-soluble γ-CD/C_{60} inclusion complex. The highest concentration of C_{60} in water reached by their procedure is 8×10^{-5} mol·dm^{-3}. According to the simple molecular modeling performed by Wennerström,[7] there are two possible structures of the γ-CD/C_{60} inclusion complexes: 1:1 and 2:1 (Fig 3). However, until now the structures of the two complexes have not been demonstrated by experimental studies.

Considering the specific characteristics of C_{60} as a guest of CD in an inclusion complex, we prepared the complexes between γ-CD and C_{60} by the method called kneading and, for the first time, obtained two

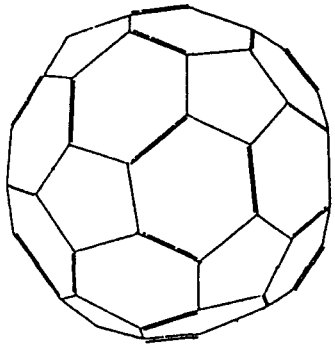

Figure 1 Sketch of C_{60} structure.

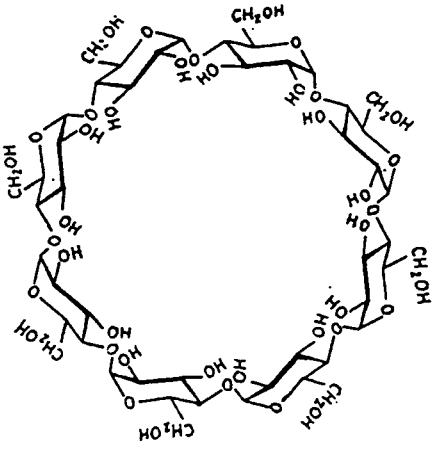

Figure 2 Chemical structure of γ-CD.

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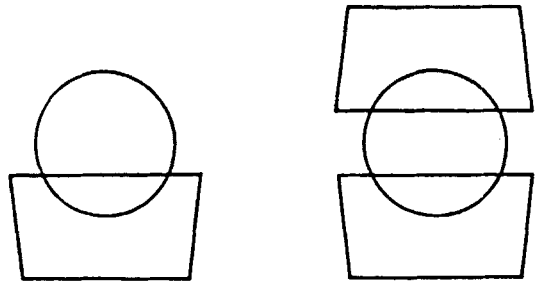


(a) 1:1 complex (b) 2:1 complex

Figure 3 Possible structures of γ-CD/C_{60} complexes. In aqueous solution.

discernible solid inclusion complexes of γ-CD and C_{60}. The transformation between the two complexes, as well as their UV-VIS spectra, provides significant evidence for the structures of the complexes.

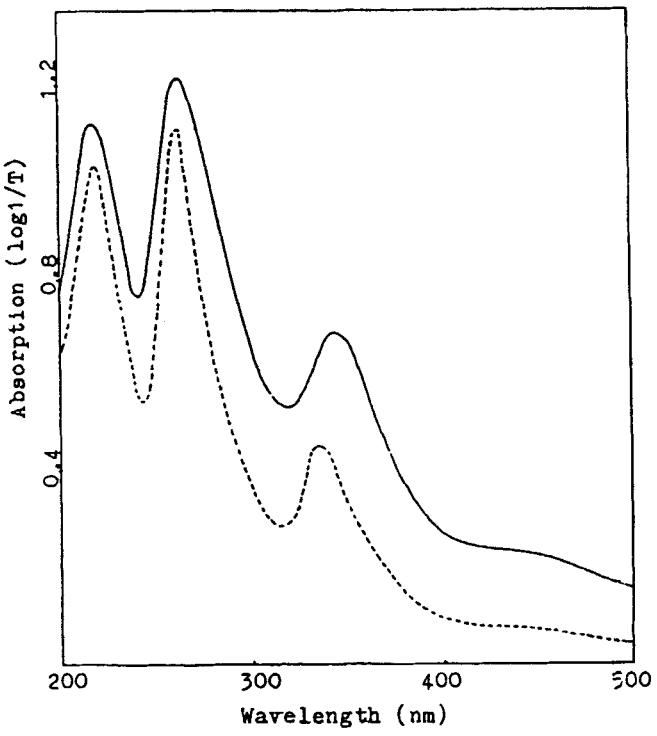
The aqueous solution of γ-CD and the C_{60} complexes obtained by our procedures, with little excess of the host molecules and higher concentration of C_{60}, might be more helpful for further studies on the properties of C_{60} in water. More important, knowing the structure of the complex is essential to understand the mechanism of reaction of C_{60} in water. Consequently, water-soluble-C_{60} is likely to extend the range of study on reactions of C_{60}.

RESULTS AND DISCUSSION

UV-VIS spectra studies

To our delight, γ-CD/C_{60}(1:1) and γ-CD/C_{60}(2:1) are both completely soluble in water and give yellowish, transparent solutions. The UV-VIS spectra of γ-CD/C_{60}(1:1) and γ-CD/C_{60}(2:1) (Fig 4) indicate the formation of the complexes. γ-CD/C_{60}(1:1) was prepared at the molar ratio of γ-CD/C_{60} = 1:1 and there is no C_{60} precipitate in the aqueous solution of the product. So the product should be a relatively pure complex: every host(γ-CD) includes one guest(C_{60}).

The UV-VIS spectra of γ-CD/C_{60}(1:1) and γ-CD/C_{60}(2:1) exhibit differences which are consistent with the formation of two distinct inclusion complexes corresponding to the two different structures: 1:1 and 2:1. The main UV-VIS absorptions of three solutions containing C_{60} are listed in Table 1. One can observe that the spectrum of γ-CD/C_{60}(2:1) in aqueous solution is slightly blue-shifted as compared to that of γ-CD/C_{60}(1:1) in aqueous solution and slightly red-shifted as compared to that of a C_{60} cyclohexane solution. This observation could be explained by solvent effects. C_{60} is essentially a three-dimensional π-electron system with thirty inter-pentagonal π-type C-C bonds,[8,9] while the polarity of the hydrophobic



(a) —— γ-CD/C_{60}(1:1) (b) – – – γ-CD/C_{60}(2:1)

Figure 4 UV-VIS spectra of γ-CD/C_{60}(1:1) and γ-CD/C_{60}(2:1).

Table 1 UV-VIS data for the samples

	λ max(nm)	
C_{60} cyclohexane solution	*γ-CD/C_{60}(2:1) aq. solution*	*γ-CD/C_{60}(1:1) aq. solution*
220	218	218
258	262	264
330	334	344

cavity of the CD was proved to be analogous to that of cyclohexane,[10] non-polar compared with water. It is thought that the increasing surface available for contact with water is responsible for the systematic red-shift of the UV-VIS spectra, from pure C_{60} in cyclohexane, through aqueous γ-CD/C_{60}(2:1) solution, to aqueous γ-CD/C_{60}(1:1) solution. This means that γ-CD/C_{60}(2:1) should have a structure with less surface exposed to water than that of γ-CD/C_{60}(1:1). In conclusion, γ-CD/C_{60}(2:1) should be, at least in large part, the 2:1 complex.

TRANSFORMATION BETWEEN THE TWO COMPLEXES

At room temperature, γ-CD/C_{60}(2:1) is so stable in water that it shows no change in the UV-VIS spectrum after several weeks, while γ-CD/C_{60}(1:1) decomposes

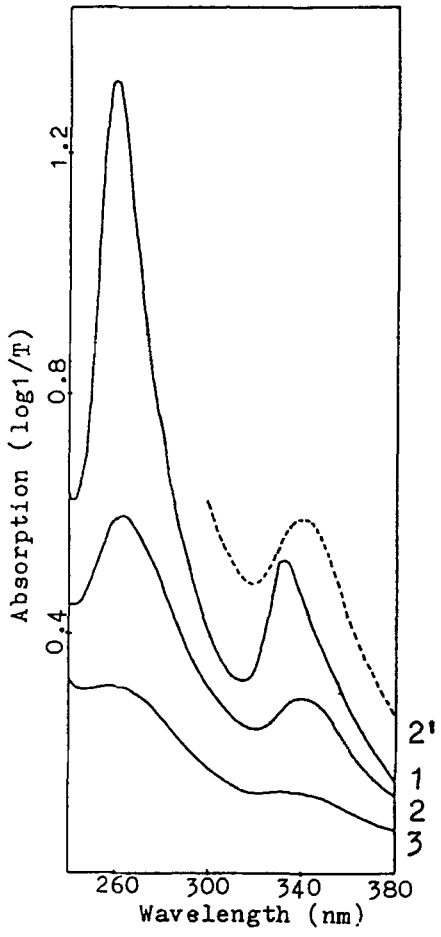
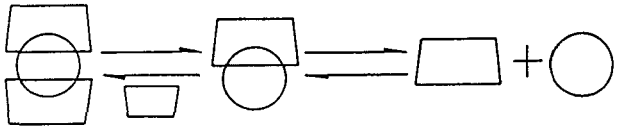


Figure 5 UV-VIS spectrum of γ-CD/C_{60}(2:1) aqueous solution under reflux after 1) 0, 2) 0.5 and 3) 2 h (2' is the enlargement of 2).

slowly, but not completely in water. However, γ-CD/C_{60}(1:1) and γ-CD/C_{60}(2:1) may be transformed into each other under proper conditions. We recorded, with respect to time, the changes of the UV-VIS spectrum of γ-CD/C_{60}(2:1) in boiling aqueous solution and obtained Fig 5. The red-shift of the spectrum with respect to time, which corresponds to the relative decrease of γ-CD/C_{60}(2:1) and increase of γ-CD/C_{60}(1:1), reveals the decomposition of the former and the formation of the latter. Fig 5 also indicates the subsequent decomposition of γ-CD/C_{60}(1:1), which finally resulted in no significant absorptions in the spectrum. Fig 6 records the UV-VIS spectrum of γ-CD/C_{60}(1:1) in aqueous solution with excess of the host (γ-CD) under reflux. It shows a blue-shift of the spectrum with respect to time. Finally, the absorption bands came to be consistent with those of γ-CD/C_{60}(2:1). The transformation could be described as below:



SOLUBILITIES

Solubilities of γ-CD/C_{60}(1:1) and γ-CD/C_{60}(2:1) were measured at room temperature by spectrophotometric analysis in aqueous solution with determination at 264 nm and 262 nm, respectively. The results are listed in Table 2.

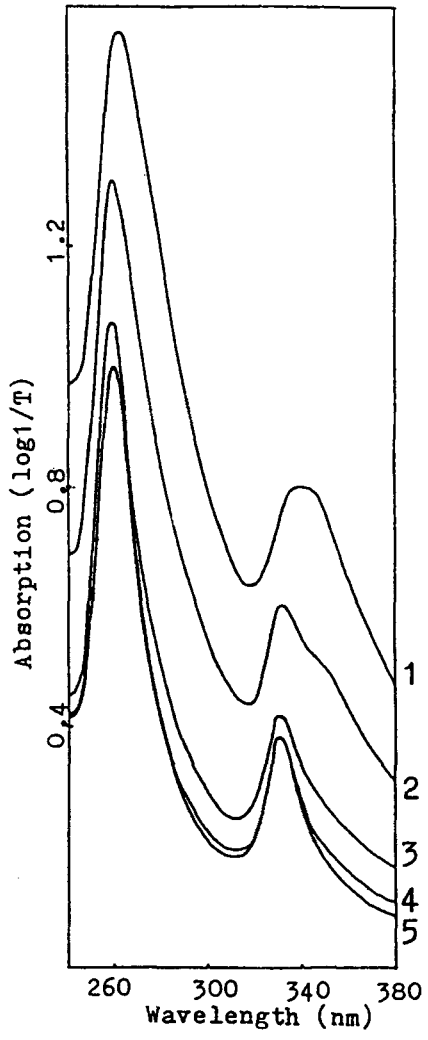


Figure 6 UV-VIS spectrum of γ-CD/C_{60}(1:1) in γ-CD aqueous solution (0.0067 mol·dm^{-3}) under reflux after 1) 0, 2) 0.5, 3) 1, 4) 2 and 5) 5.5 h.

Table 2 Solubilities of γ-CD/C_{60}(1:1) and γ-CD/C_{60}(2:1) in water

Samples	*Solubility (mg/100 ml)*	*Highest concentration of C_{60} in aqueous solution (mol·dm^{-3})*
γ-CD/C_{60}(1:1)	63	3×10^{-4}
γ-CD/C_{60}(2:1)	44	1×10^{-4}

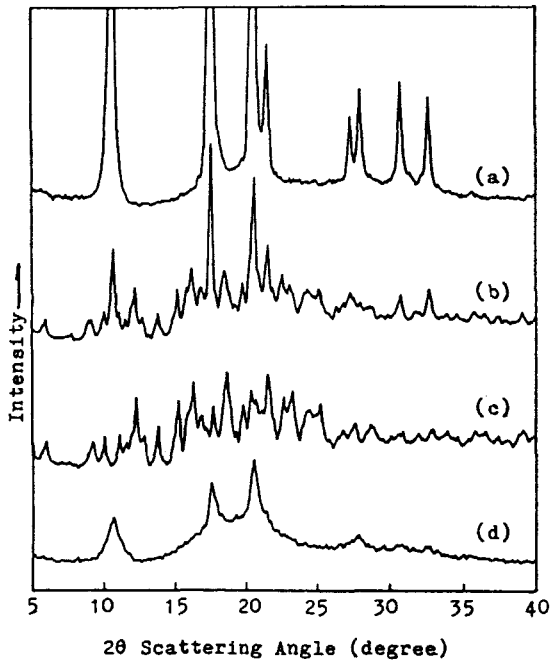


Figure 7 X-ray diffraction patterns of (a) C_{60}, (b) physical mixture of γ-CD and C_{60}, (c) γ-CD and (d) γ-CD/C_{60}(1:1).

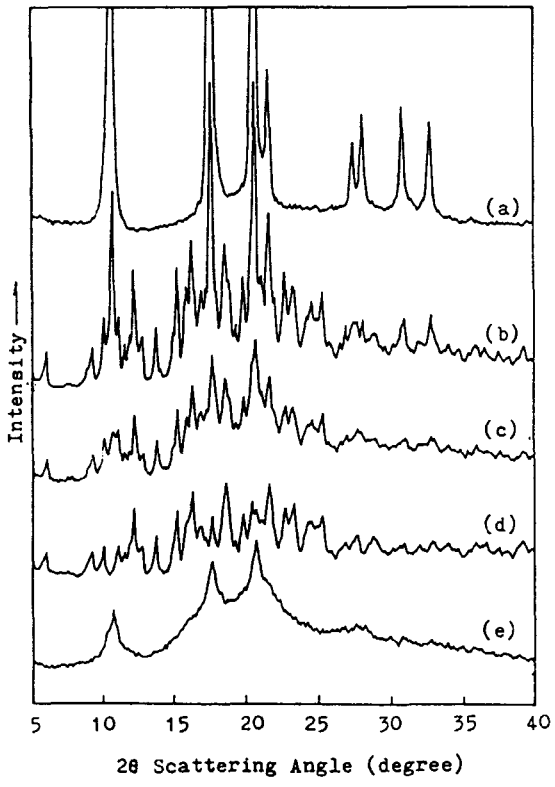


Figure 8 X-ray diffraction patterns of (a) C_{60}, (b) physical mixture of C_{60} and γ-CD, (c) physical mixture of γ-CD/C_{60}(1:1) and γ-CD, (d) γ-CD and (e) γ-CD/C_{60}(2:1).

X-RAY POWDER DIFFRACTION STUDIES

The X-ray powder diffraction patterns for the individual components, complex γ-CD/C_{60}(1:1) and physical mixture (molar ratio 2:1) are presented in Fig 7. A comparison of the γ-CD/C_{60}(1:1) pattern with that of the physical mixture, which can be interpreted as an approximate superposition of the components, shows that the pattern of γ-CD/C_{60}(1:1) does not correspond to those of the pure components. These observations prove that the solid product is a new crystalline phase associated with the formation of an inclusion complex. The differences in the X-ray diffraction patterns between γ-CD/C_{60}(2:1) and the physical mixture of γ-CD/C_{60}(1:1) and γ-CD at 1:1 molar ratio (shown in Fig 8) provides the proof for further inclusion of C_{60}.

EXPERIMENTAL SECTION

Materials

γ-CD is a product of Chinoin Pharmaceutical and Chemical Works Ltd., Budapest. The fullerene C_{60} was produced by the contact-arc method and purified by now-standard procedures.[11] The purity of C_{60} is above 99.5%. Redistilled water was used throughout the study.

Preparation of the inclusion complexes

γ-CD/C_{60}(1:1): 17 mg (2.4×10^{-5} mol) C_{60} and 30.9 mg (2.4×10^{-5} mol) γ-CD were homogenized and kneaded for 1 h with dropwise addition of n-hexane. The product was vacuum-dried at 117 °C for 2 h. Yield: 43.4 mg. C_{60} content: 35.5%.

γ-CD/C_{60}(2:1): 13.4 mg (C_{60} content: 6.6×10^{-6} mol) γ-CD/C_{60}(1:1) and 8.6 mg (6.6×10^{-6} mol) γ-CD were homogenized and kneaded for 3 h with dropwise addition of water. The product was vacuum-dried at 117 °C for 2 h. Yield: 17.6 mg. C_{60} content: 21.6%.

Physical measurements

UV-VIS spectra were recorded on a UV-730 spectrometer. Solvent and reference: water. X-ray powder patterns were obtained with a Rigaku-D/max-RB diffractometer with a monochromator of Ni utilizing CuKα radiation with 40 kV and 30 mA at scan rate of 8°/min.

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