

Studies on Methylated β -Cyclodextrins and C_{60} Inclusion Complexes

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Abstract. Solid, water-soluble inclusion complexes: $DM\beta CD/C_{60}$ (1 : 1) and $DM\beta CD/C_{60}$ (2 : 1) can be obtained by kneading. Their formation has been confirmed by UV-vis spectroscopy, X-ray diffraction and DSC studies. UV-vis studies also reveal the transformation between the two complexes in aqueous solution. $TM\beta CD$ has also been studied as the host of an inclusion complex with C_{60} .

Key words: C_{60} , $DM\beta CD$, water-soluble inclusion complex.

1. Introduction

The carbon cluster C_{60} (buckminsterfullerene) has been widely studied in terms of its structure, preparation, properties, and reactions [1]. The structure of C_{60} , known to be a highly symmetric truncated icosahedral structure (football or soccerball) was finally determined by Hawkins' X-ray crystal structure [2] (Figure 1). The nearest-neighbour distance is (by X-ray diffraction) 10.02\AA [3] and the diameter calculated for the carbon cage itself is 7.1\AA . Although C_{60} is called a 'soluble all-carbon molecule' [4], the solubility of C_{60} , poor in most organic solvents and negligible in water, has been one of the main impediments to studying its properties [6].

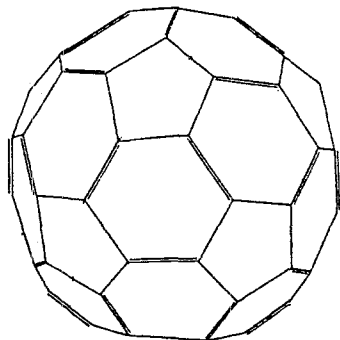


Fig. 1. Sketch of C_{60} structure.



Fig. 2. Possible structures of CD-C₆₀ complexes in aqueous solution. (a) 1 : 1 complex, (b) 2 : 1 complex.

The cyclodextrins (CDs) are quite promising agents for making C₆₀ soluble in water. Cyclodextrins, which, respectively, consist of six (α -CD), seven (β -CD), or eight (γ -CD) sugar molecules joined together in a ring, always act as the hosts of inclusion complexes. The internal annular diameters of α -, β -, γ -CD are respectively, 5–6, 7–8, and 9–10 Å [6,7]. The systematic variation of the annular diameter of these CDs and their derivatives provides an opportunity to test their selectivity in the formation of inclusion complexes [8,9]. If the diameter of the cavity is suitable for C₆₀, the nonpolar C₆₀ would probably sit in the cavity and the inclusion complex would form.

Recently, Wennerström and coworkers [10] treated C₆₀ with an aqueous solution of γ -CD under reflux and obtained a water-soluble γ -CD-C₆₀ inclusion complex. The highest concentration of C₆₀ in water reached by their procedure is 8×10^{-5} mol dm⁻³, but the stoichiometry was not reported. According to the simple molecular modeling performed by Wennerström [10], there are two possible structures of CD-C₆₀ inclusion complexes: 1 : 1 and 2 : 1 complexes (Figure 2).

However, the structure of CD-C₆₀ complexes have not been demonstrated by experimental studies until now.

As a β -CD derivative with high solubility in water [11], DM β CD (heptakis-(2,6-di-*O*-methyl)- β -cyclodextrin) has a cavity larger than that of β -CD and more hydrophobic than that of γ -CD (Figure 3). We treated C₆₀ with DM β CD by the kneading method and obtained, for the first time, two distinct solid inclusion complexes between DM β CD and C₆₀. In this paper we described the high-yield production of the complexes and proof for determination of their structures.

Since DM β CD is cheaper than γ -CD, the aqueous solution of DM β CD and C₆₀ complexes, with little excess of the host and a higher concentration of C₆₀, might be more useful in a study of the reaction of C₆₀ in water. More important, knowing the structure of the complex will be essential to understanding the reaction of C₆₀ in water. As a result, it is likely that the reaction of C₆₀ in water could be explored in more detail with the use of our method.

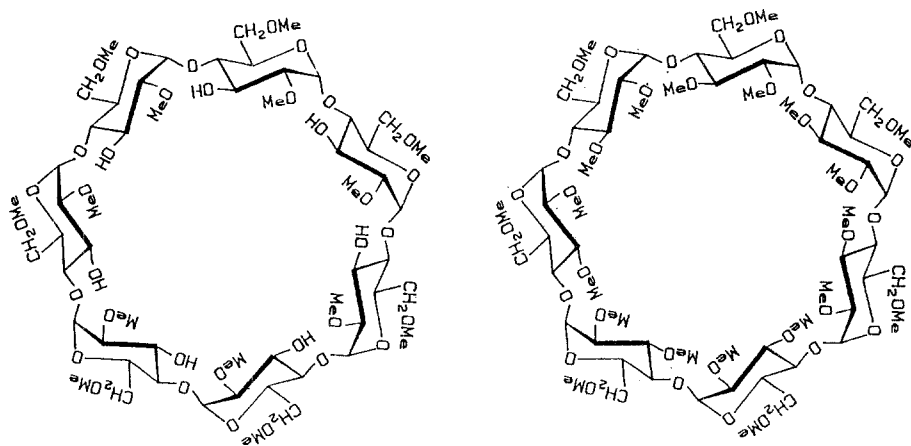


Fig. 3. Chemical structure of $DM\beta CD$ and $TM\beta CD$.

2. Experimental

2.1. MATERIALS

$DM\beta CD$ and $TM\beta CD$ are products of Chinoin Pharmaceutical and Chemical Works Ltd., Budapest. The fullerene C_{60} was produced by the contact-arc method and purified by the standard procedure [12]. The purity of C_{60} is 99.5% or higher. Distilled water was used throughout the study.

2.2. PREPARATION OF THE INCLUSION COMPLEXES

$DM\beta CD-C_{60}$ (1 : 1): 7.0 mg (9.7×10^{-6} mol) C_{60} and 13.6 mg (1.0×10^{-5} mol) $DM\beta CD$ were homogenized at a 1 : 1 molar ratio and kneaded for 1 h with dropwise addition of *n*-hexane. The product formed was vacuum-dried at $117^\circ C$ for 2 h. Yield: 18.1 mg. C_{60} content: 34%.

$DM\beta CD-C_{60}$ (2 : 1): 5.1 mg (2.4×10^{-6} mol) $DM\beta CD-C_{60}$ (1 : 1) and 3.4 mg (2.5×10^{-6} mol) $DM\beta CD$ were homogenized and kneaded for 1 h with dropwise addition of water. The product was vacuum-dried at $117^\circ C$ for 2 h. Yield: 7.5 mg. C_{60} content: 20%.

C_{60} in the complex was extracted by toluene and chromatographed on a Polygram Sil G/UV254 pre-coated plastic sheet, developer: hexane, R_f : 0.78, the same as pure C_{60} .

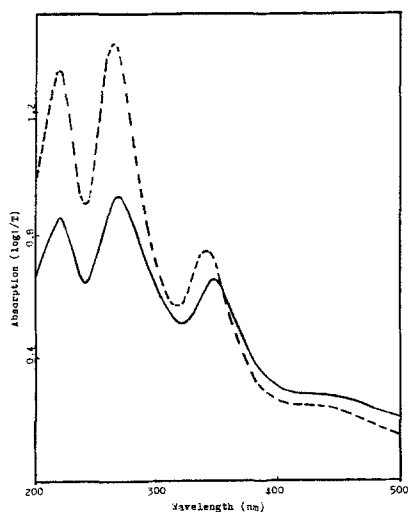


Fig. 4. UV-vis spectra of (a) — $DM\beta CD-C_{60}$ (1 : 1), (b) - - - - $DM\beta CD-C_{60}$ (2 : 1) in aqueous solution.

2.3. 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 $CuK\alpha$ radiation: instrumental parameters: 40 kV and 30 mA at a scan rate of $8^\circ/\text{min}$.

DSC curves were obtained on a Du Pont model 1090 DSC-TGA system at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere.

3. Results and Discussion

3.1. UV-VIS SPECTRA

Since C_{60} has strong absorption features in the ultraviolet region [3,13], the aqueous solution containing C_{60} can be detected by UV-vis spectroscopy [10]. The UV-vis spectra of $DM\beta CD-C_{60}$ (1 : 1) and $DM\beta CD-C_{60}$ (2 : 1), shown in Figure 4, indicated the formation of the complexes. The maximum absorption frequencies are listed in Table I.

The UV-vis spectra exhibit variations which are consistent with the formation of two distinct inclusion complexes corresponding to the two different structures: 1 : 1 complex and 2 : 1 complex.

To our delight, $DM\beta CD-C_{60}$ (1 : 1), with the molar ratio of $DM\beta CD : C_{60} = 1 : 1$, is completely soluble in water. This means that C_{60} molecules are all embedded in $DM\beta CD$ cavities and the structure should be the 1 : 1 complex. Table I reveals

TABLE I. UV data of the samples

C_{60} cyclohexane solution	λ max (nm)	
	DM β CD- C_{60} (2 : 1) aq. solution	DM β CD- C_{60} (1 : 1) aq. solution
220	220	222
258	266	270
330	344	350

that the UV-vis spectrum of DM β CD- C_{60} (1 : 1) in water is slightly red-shifted compared to that of DM β CD- C_{60} (2 : 1) in water, and the latter is also red-shifted compared to that of a cyclohexane solution of pure C_{60} . Fullerene C_{60} is, in its totality, a three-dimensional π -electron system with thirty inter-pentagonal π -type C-C bonds [14,15], while the polarity of the CD hydrophobic cavities was proved to be analogous to that of cyclohexane [16]: non-polar in comparison with water. We believe 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 DM β CD- C_{60} (2 : 1) solution, to aqueous DM β CD- C_{60} (1 : 1) solution. This suggests that DM β CD- C_{60} (2 : 1) should have a structure with less surface exposed to water than DM β CD- C_{60} (1 : 1). In conclusion, DM β CD- C_{60} (2 : 1) should be the 2 : 1 complex.

3.2. TRANSFORMATION BETWEEN DM β CD- C_{60} (1 : 1) AND DM β CD- C_{60} (2 : 1)

Both DM β CD- C_{60} (1 : 1) and DM β CD- C_{60} (2 : 1) can be dissolved in water to give yellowish, transparent solutions. At room temperature, DM β CD- C_{60} (2 : 1) is so stable in water that it shows no change in the UV-vis spectrum after several weeks, while DM β CD- C_{60} (1 : 1) decomposed slowly, but not completely, in water. However, DM β CD- C_{60} (2 : 1) decomposed under reflux. Figure 5 shows the process of the decomposition of DM β CD- C_{60} (2 : 1) in aqueous solution. The red shift of the spectrum corresponds to the relative decrease of DM β CD- C_{60} (2 : 1) and increase of DM β CD- C_{60} (1 : 1). Five hours later, the complexes had decomposed thoroughly and the solution showed no significant absorptions in the UV-vis spectrum. This result is perfectly consistent with the proposed structure of

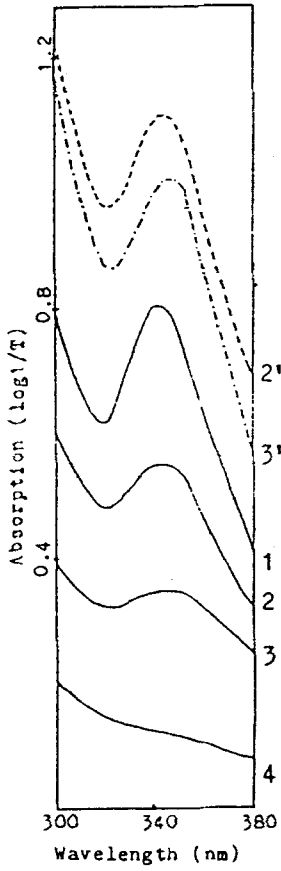


Fig. 5. UV-vis spectrum of DM β CD-C₆₀ (2 : 1), aq. solution under reflux after (1)0, (2)1.5, (3)4 and (4)5 h. (2' and 3' are enlargements of 2 and 3).

DM β CD-C₆₀ (1 : 1) and DM β CD-C₆₀ (2 : 1). The process of decomposition of DM β CD-C₆₀ (2 : 1) could be described as below:

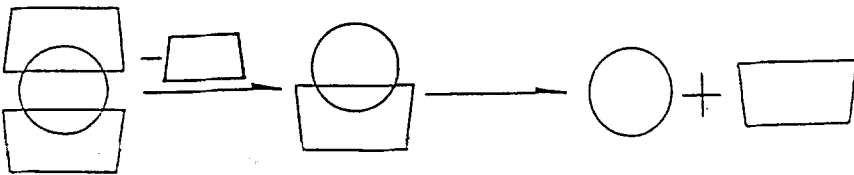


TABLE II. Solubilities of the samples

Samples	Solubility of the complex (mg/100 mL)	Highest concentration of C in aq. solution (mol dm ⁻³)
DM β CD- C_{60} (1 : 1)	11	5×10^{-5}
DM β CD- C_{60} (2 : 1)	64	2×10^{-4}

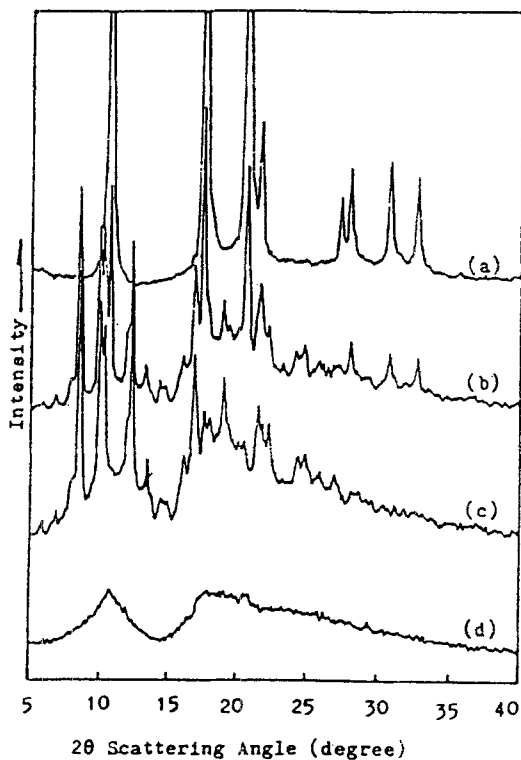


Fig. 6. X-ray diffraction patterns (a) C_{60} , (b) physical mixture, (c) DM β CD and (d) DM β CD- C_{60} (2 : 1).

3.3. SOLUBILITY OF DM β CD- C_{60} (1 : 1) AND DM β CD- C_{60} (2 : 1)

The solubility of DM β CD- C_{60} (1 : 1) and DM β CD- C_{60} (2 : 1) were measured by spectrophotometric analysis in aqueous solution with determination at 270 nm and 266 nm, respectively. The results are listed in Table II.

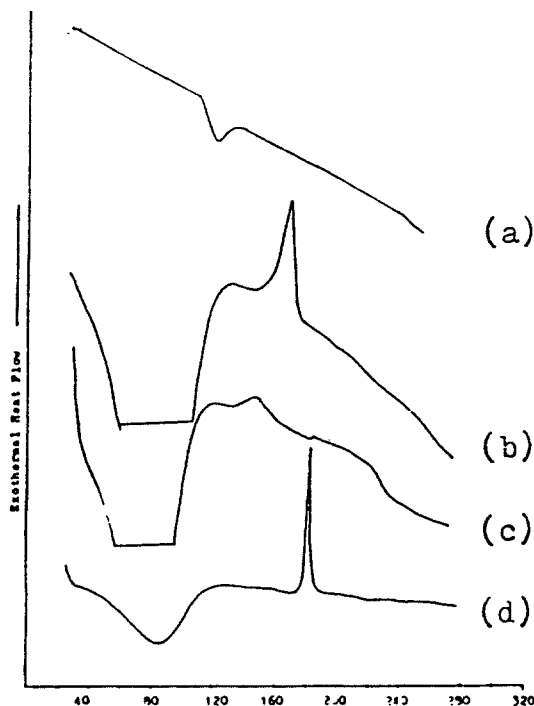


Fig. 7. DSC curves. (a) C₆₀, (b) DMβCD, (c) physical mixture and (d) DMβCD-C₆₀ (2 : 1).

3.4. X-RAY DIFFRACTION

The X-ray powder patterns for the individual components, the DMβCD-C₆₀ complex (2 : 1), and a physical mixture (molar ratio 2 : 1) are presented in Figure 6. A comparison of the DMβCD-C₆₀ (2 : 1) pattern with that of the physical mixture, which can be interpreted as an approximate superposition of the components, shows that the pattern of DMβCD-C₆₀ (2 : 1) does not correspond to those of the pure components. These observations prove that the solid product is of a new crystalline phase associated with the formation of an inclusion complex.

3.5. THERMAL ANALYSIS

Differential scanning calorimetry (DSC) curves for DMβCD, C₆₀, DMβCD-C₆₀ (2 : 1), and a physical mixture (molar ratio 2 : 1) are shown in Figure 7. The DSC pattern of the complex exhibits differences from that of the physical mixture, and this indicates the formation of a complex.

3.6. OTHER CDS

On attempting to embed C_{60} in the cavity of TM β CD (heptakis-(2,3,6-tri-*O*-methyl)- β -cyclodextrin) (Figure 3) by the same procedure, we found no significant evidence for the formation of an inclusion complex of C_{60} and TM β CD. Although TM β CD has a more hydrophobic cavity due to its 2-*O*-methyls, it is difficult for TM β CD to transform to a suitable conformation, in which the cavity can be consistent with the diameter of C_{60} . So C_{60} has difficulty in including in TM β CD. This, in conjunction with the observation that β -CD forms no inclusion complex with C_{60} and that γ -CD and DM β CD both form 1 : 1 and 2 : 1 complexes, demonstrates a substantial degree of selectivity in the formation of CD inclusion complexes.

4. Conclusion

Two different DM β CD and C_{60} inclusion complexes, consistent with two different structures, can be formed under proper experimental conditions. As relatively pure aqueous solutions of the complexes are available, the various physical and chemical properties of C_{60} in water can now be measured and speculations concerning its potential uses in water can be essayed.

Acknowledgements

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References

1. H.W. Kroto, A.W. Allaf, and S.P. Balm: *Chem. Rev.* **91**, 1213 (1991).
2. J.M. Hawkins, A. Myer, T.A. Lewis, S. Loren, and F.J. Hollander: *Science* **252** (91), 312.
3. W. Kratschmer, L.D. Lamb, K. Fostiropoulos and D.R. Huffman: *Nature* **347** (90), 354.
4. H. Ajie, M.M. Alvarez, S.J. Anz, R.D. Beck, F. Diederich, K. Fostiropoulos, D.R. Huffman, W. Kratschmer, Y. Rubin, K.E. Schriver, D. Sensharma, and R.L. Whetten: *J. Phys. Chem.* **14** (90), 8630.
5. N. Sivaraman, R. Dhamodaran, I. Kaliappan, T.G. Srinivasan, P.R. Vasuderva Rao, and C.K. Mathews: *J. Org. Chem.* **57** (92), 6077.
6. W. Saenger: *Angew. Chem. Int. Ed. Engl.* **19**, 344 (1980).
7. J. Szejtli: *Cyclodextrins and Their Inclusion Complexes*, Akademiai Kiado, Budapest (1982).
8. K. Kano, I. Takenoshita, and T. Ogawa: *Chem. Lett.*, 321 (1982).
9. A. Ueno, K. Takahashi, Y. Hino and T. Osa: *J. Chem. Soc., Chem. Commun.*, 194 (1981).
10. T. Anderson, K. Nilsson, M. Sundahl, G. Westman, and O. Wennerström: *J. Chem. Soc., Chem. Commun.*, 604 (1992).
11. J. Szejtli: *J. Incl. Phenom.* **1**, 135 (1983).
12. D.H. Parker, P. Wurz, K. Chatterjee, K.R. Lykke, J.B. Hunt, M.J. Pellin, J.C. Hemminger, D.M. Gruen, and L.M. Strock: *J. Am. Chem. Soc.* **113**, 7499 (1991).
13. J.P. Hare, H.W. Kroto, and R. Taylor: *Chem. Phys.* **177**, 394 (1991).
14. R.C. Haddon, L.E. Brus and K. Raghavachari: *Chem. Phys. Lett.* **125**, 459 (1986).
15. S. Satpathy: *Chem. Phys. Lett.* **130**, 545 (1986).
16. Y.-B. Jiang: *Chin. Sci. Bull.* **2**, 120 (1990).