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# Bicapped Water-Soluble Inclusion Complexes of C70

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Solid, water-soluble inclusion complexes between C70 and DM $\beta$ CD or  $\gamma$ -CD have been prepared by kneading. The complexes have been characterized by their UV/VIS spectra, IR spectra and X-ray powder diffraction patterns. The decomposition kinetics of these complexes has also been studied.

## INTRODUCTION

Like C60, the larger C70 molecule is also an important member of the fullerene family. It is available in smaller quantity and in lower purity than C60. The technique of isolating pure C70 has developed quickly<sup>1</sup> and based on many results obtained for C60, the properties of C70 have clearly deserved more and more attention. The negligible solubility of the fullerenes in water has been an impediment in studying their reactions and possible biological activity. We have reported that C60 can be solubilized in water by complexation with  $\gamma$ -CD or DM $\beta$ CD (heptakis-(2,6-di-O-methyl)- $\beta$ -cyclodextrin)<sup>2,3</sup> (Figure 1) by our method of kneading. By this means we have obtained a solid inclusion complex between C70 and DM $\beta$ -CD. We have also prepared a solid complex between

C70 and  $\gamma$ -CD whose aqueous solution has been obtained by Wennerstroem by means of boiling.<sup>4</sup> The two solid complexes prepared by kneading are 2:1 complexes. In this paper, we describe the high yield production of the complexes and the proof for the determination of the formation of their structures.

## RESULT AND DISCUSSION

**UV-VIS spectra** Since C70 has strong absorption features in the ultraviolet region<sup>5</sup>, the presence of C70 in aqueous solution can be detected by UV-VIS spectroscopy.<sup>6</sup> At first, we homogenized an equivalent of DM $\beta$ -CD and C70 and kneaded for 2 h (sample 1). Then, 2 equiv. of DM $\beta$ CD and 1 equiv. of C70 were treated as above, to obtain sample 2. We found that in the first case, the solution was very turbid and a C70 precipitate was apparent in the aqueous solution of the product, while in the second case the product was completely dissolved in water, without any C70 precipitate (the solution is dark purplish).

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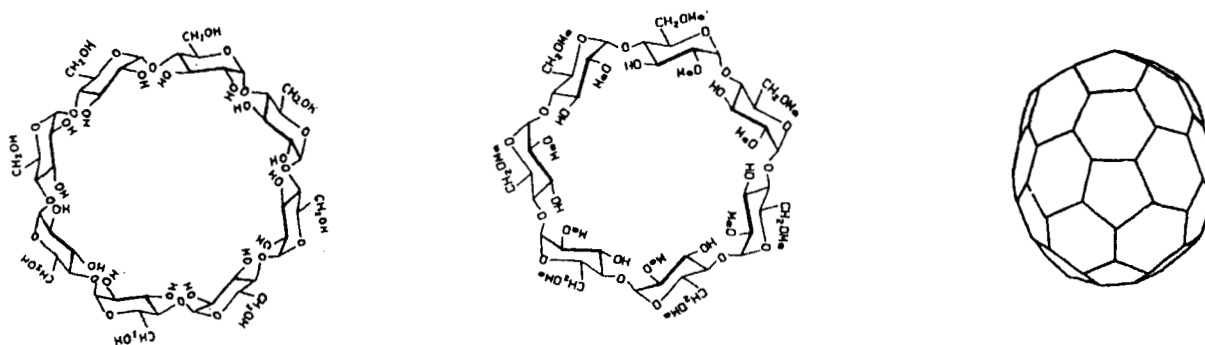


FIGURE 1 (a) Structure of  $\gamma$ -CD, (b) Structure of DM $\beta$ CD, (c) Sketch of C70 structure.

By comparing their UV-VIS spectra, we found that the spectrum of sample 1 was the same as that of sample 2. Furthermore, when we treated 3, 4, or more equiv. of DM $\beta$ CD and 1 equiv. of C70 by kneading, their spectra were the same. Relating this result to the size of C70 and the conclusion of Wennerstroem concerning the complex between  $\gamma$ -CD and C70, we think that the inclusion complex has a bicapped structure. One could conclude that the 1:1 complex might not exist. Result from complexation studies between

C70 and  $\gamma$ -CD done by the same method could lead to the same conclusion and this might coincide with Wennerstroem's report. The UV-VIS spectrum of DM $\beta$ CD<sub>2</sub>/C70 is shown in Figure 2. Its maximum absorption frequencies are at 240 nm, 338 nm, 386 nm and 486 nm. It is slightly red-shifted compared to data for C70 obtained in cyclohexene solution (238 nm, 332 nm, 378 nm, and 468 nm), due to the intermolecular interaction between the cavity of DM $\beta$ CD and the  $\pi$ -system of C70.

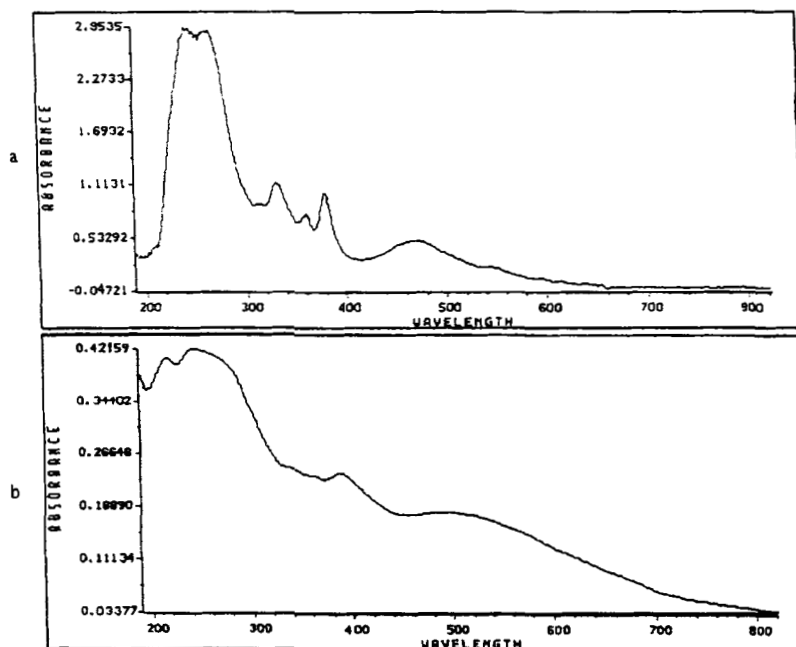


FIGURE 2 UV-VIS Spectra (a) cyclohexane solution of C70 (b) aqueous solution of DM $\beta$ CD<sub>2</sub>/C70.

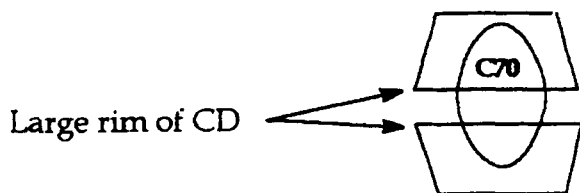


FIGURE 3 Possible structure of the inclusion complexes.

### Solubilities

The solubilities of  $\gamma$ -CD<sub>2</sub>/C70 and DM $\beta$ CD<sub>2</sub>/C70 were measured at  $25 \pm 0.5^\circ\text{C}$  by spectrophotometric analysis in aqueous solution with determination at 240 nm. The solubilities of  $\gamma$ -CD<sub>2</sub>/C70 and DM $\beta$ -CD<sub>2</sub>/C70 are  $1.3 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$  and  $6.0 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ .

### IR spectra

Infrared spectra for  $\gamma$ -CD<sub>2</sub>/C70,  $\gamma$ -CD, DM $\beta$ CD<sub>2</sub>/C70, DM $\beta$ CD, C70 were also obtained. The few absorption peaks observed for C70 are not strong and not much affected by cyclodextrin inclusion. The spectra of these complexes show little change compared with  $\gamma$ -CD and DM $\beta$ CD except for a small peak shift due to the stretching vibration of OH bonds and the absorption peak ( $1429 \text{ cm}^{-1}$ ) of C70. Compared with pure  $\gamma$ -CD, the peak due to the stretching vibration of the hydroxyl groups of  $\gamma$ -CD<sub>2</sub>/C70 moved a little to the right from  $3401 \text{ cm}^{-1}$  to  $3345 \text{ cm}^{-1}$ . DM $\beta$ CD<sub>2</sub>/C70 is analogous to  $\gamma$ -CD<sub>2</sub>/C70 (from  $3429 \text{ cm}^{-1}$  to  $3415 \text{ cm}^{-1}$ ). This phenomenon that only OH bond vibrations show apparent change after inclusion while other vibrations of cyclodextrin show no apparent change might be explained by the bicapped structure of the complexes (See Figure 3). In the inclusion complexes, the hydroxyl groups situated at the large rims of the cyclodextrins are more strongly affected by the C70.

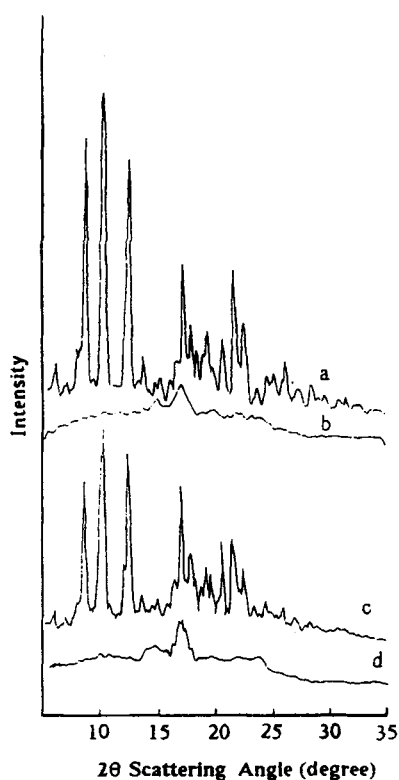


FIGURE 4.1 X-ray diffraction pattern of (a) DM $\beta$ CD (b) C70 (c) mixture of C70 and DM $\beta$ CD (d) DM $\beta$ CD<sub>2</sub>/C70.

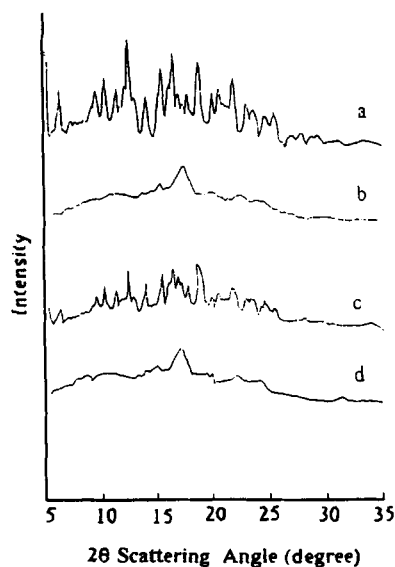


FIGURE 4.2 X-ray diffraction pattern of (a)  $\gamma$ -CD (b) C70 (c) mixture of C70 and  $\gamma$ -CD (d)  $\gamma$ -CD<sub>2</sub>/C70.

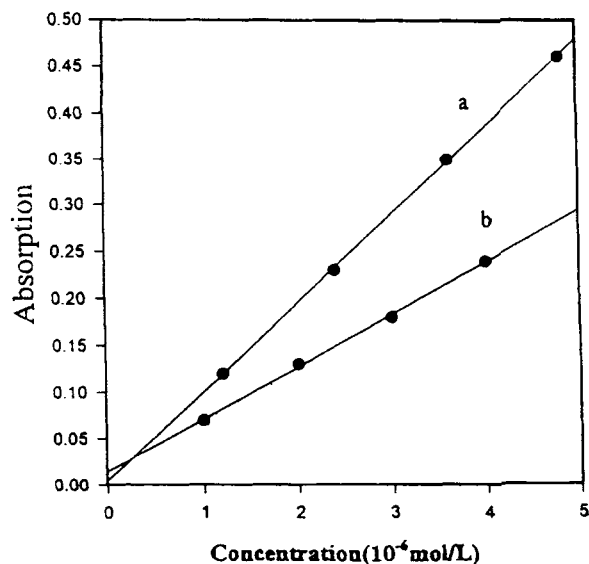


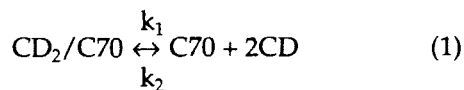
FIGURE 5 Standard Curve (A ~ C) (a)  $\gamma$ -CD (b) DM $\beta$ -CD.

### The X-ray Diffraction

The X-ray powder patterns for the individual components, the inclusion complexes, and the physical mixture are presented in Figure 4.1 and Figure 4.2. The pattern of the physical mixture can be interpreted as an approximate superposition of the components. These observations prove that the solid product is a new crystalline phase associated with the formation of an inclusion complex.

### Kinetic Studies

In aqueous solution of these inclusion complexes, existed such a decomposition reaction



in which CD =  $\gamma$ -CD or DM $\beta$ -CD. Note that C70 is a solid substance that does not dissolve in water. We studied the kinetics of these reactions. First, we measured the UV absorption (at 240 nm) of

fresh aqueous solution of  $\gamma$ -CD<sub>2</sub>/C70 at different concentrations, to obtain the standard curve (A ~ C Figure 5). By means of measuring the UV absorption, we would know the concentration of the complex in its solution whenever necessary. Then we boiled its solution and found that the complex decomposed partly and finally got to a equilibrium (no concentration change was apparent), when we maintained the partly decomposed solution at a stable temperature (such as 50°C), the reaction acted from right to left, and finally reached a new equilibrium. We think the reaction is reversible. The complex decomposes only slightly at a common temperature and the time required for the reaction reach a balance from left to right is too transient for us to analyze, so we chose to study the reaction as it occurs in the right to left direction.

First we boiled a solution of  $\gamma$ -CD<sub>2</sub>/C70 whose concentration ( $C_0$ ) has been known to make it decompose in one hour, and maintained it a 50°C. From the standard curve and by the method of measuring the UV absorption (at 240 nm) every several minutes, we could obtain the complex concentration ( $[\text{CD}_2/\text{C70}]_t$ ). From (1) and  $C_0$  we could get

$$[\text{CD}]_t = 2(C_0 - [\text{CD}_2/\text{C70}]_t) \quad (2)$$

When the reaction reached equilibrium, from (1) we could get the equilibrium constant K

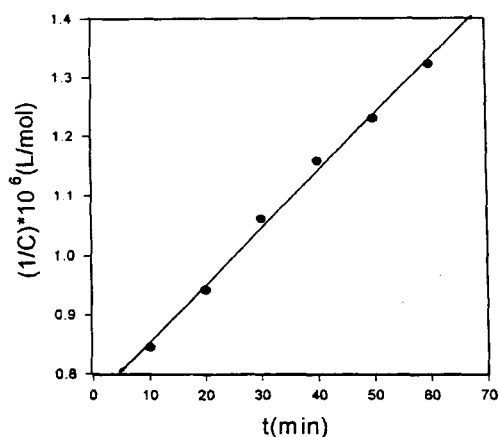
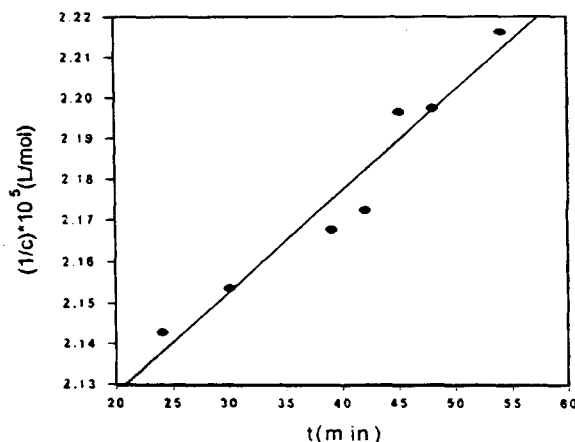
$$K = \frac{[\text{CD}]_{\text{eq}}^2}{[\text{CD}_2/\text{C70}]_{\text{eq}}} \quad (3)$$

From (2)

$$[\text{CD}]_{\text{eq}} = 2(C_0 - [\text{CD}_2/\text{C70}]_{\text{eq}}) \quad (4)$$

$$K = \frac{4(C_0 - [\text{CD}_2/\text{C70}]_{\text{eq}})^2}{[\text{CD}_2/\text{C70}]_{\text{eq}}} \quad (5)$$

And from


 FIGURE 6.1  $1/[\gamma\text{-CD}] \sim t$ .

 FIGURE 6.2  $1/[\text{DM}\beta\text{CD}] \sim t$ .

$$\Delta G = -nRT \ln K \quad (6)$$

We could obtain  $\Delta G$ .

Also, by analysis of this process, we found that at the start, the reaction followed second order kinetics

From (1), we could show that

$$\frac{-d[\text{CD}]_t}{2dt} = \frac{d[\text{CD}_2/\text{C70}]_t}{dt} = k_2[\text{CD}]_t^2 \quad (7)$$

$$\frac{d[\text{CD}]}{[\text{CD}]^2} = -2k_2 dt \quad (8)$$

from the integral transform,

$$1/[\text{CD}]_t = 2k_2 t + \text{Constant} \quad (9)$$

$$[\text{CD}]_t = 2(C_0 - [\text{CD}_2/\text{C70}]_t) \quad (2)$$

From  $1/[\text{CD}]_t \sim t$ , we can get  $k_2$ . (Figure 6.1 and Figure 6.2)

In this reaction, equilibrium constant

$$K = k_1/k_2 \quad (10)$$

So,

$$k_1 = K \times k_2 \quad (11)$$

By method above, we obtained  $k_1$ ,  $k_2$ ,  $\Delta G$  of  $\gamma\text{-CD}_2/\text{C70}$  (Table 1), and for  $\text{DM}\beta\text{-CD}_2/\text{C70}$ . The results are presented in Table 1.

From the data shown in Table I, we found that  $\gamma\text{-CD}_2/\text{C70}$  is more stable than  $\text{DM}\beta\text{-CD}_2/\text{C70}$  and this coincides with the fact that  $\gamma\text{-CD}$  could form inclusion complexes more easily with C70 than  $\text{DM}\beta\text{CD}$ ;  $\Delta G_{\gamma\text{-CD}_2/\text{C70}}$  is much larger than  $\Delta G_{\text{DM}\beta\text{-CD}_2/\text{C70}}$  being approximately twice of  $\Delta G_{\text{DM}\beta\text{-CD}_2/\text{C70}}$ . This result coincides with the complex structures. From a study of CPK molecular models, we think that the two complexes have a bicapped

 TABLE I The kinetic data ( $50^\circ \pm 0.5^\circ\text{C}$ )

	$\Delta G$ (KJ·mol)	$k_1$ ( $\text{s}^{-1}$ )	$k_2$ ( $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ )	$K$ ( $\text{mol}\cdot\text{L}^{-1}$ )
$\gamma\text{-CD}_2/\text{C70}$	40.41	$2.519 \times 10^{-5}$	83.08	$3.032 \times 10^{-7}$
$\text{DM}\beta\text{-CD}_2/\text{C70}$	22.37	$4.005 \times 10^{-6}$	2.596	$1.543 \times 10^{-6}$

structure in which the  $C_7$ -axis of DM $\beta$ -CD or  $C_8$ -axis of  $\gamma$ -CD coincides with the long axis ( $C_5$ ) of C70. The complexes are believed to contain a C70 molecule in two CDs, hydrogen bonded to each other at the larger rim<sup>5</sup> as reported by Wennerstroem. Each  $\gamma$ -CD<sub>2</sub>/C70 molecule contains  $16 \times 2$  secondary hydroxyl groups while each DM $\beta$ -CD<sub>2</sub>/C70 contains only  $7 \times 2$  secondary hydroxyl groups at the larger rims. The number of hydrogen bonds of  $\gamma$ -CD<sub>2</sub>/C70 is approximately double that of DM $\beta$ -CD<sub>2</sub>/C70 and this coincides with the measurement result of  $\Delta G$ . From these studies we concluded that the hydrogen bonds play an important role aside from the hydrophobic effect in the inclusion between C70 and cyclodextrins.

## EXPERIMENTAL SECTION

### Materials

$\gamma$ -CD and DM $\beta$ -CD are products of Chinoin Pharmaceutical and Chemical Works Ltd., Budapest. The fullerene C70 is a product of Department of Chemistry Peking University and its purity is 99.0% or higher. Distilled water was used throughout the study.

### Preparation of the Inclusion Complexes

$\gamma$ -CD<sub>2</sub>/C70: 12.50mg C70 and 44.10mg  $\gamma$ -CD were homogenized for 2 h with dropwise addition of water. The product was vacuum-dried at 117°C for 3 h. Yield 56.50 mg. DM $\beta$ -CD<sub>2</sub>/C70: 11.94 mg

C70 and 42.96mg DM $\beta$ -CD were homogenized and kneaded for 2 h with dropwise addition of water. The product was vacuum-dried at 117°C for 3 h. Yield 49.71 mg.

### Physical Measurements

UV-VIS spectra were recorded on a HP-8452A UV spectrometer. X-ray powder patterns were obtained with a Rigako-D/max-RB diffractometer with a monochromator of Niutilixing Cuka radiation with 40 kV and 30mA at scan rate of 8°/min. IR Spectra were recorded on a 5SXC-Nicolet FT-IR.

### Acknowledgements

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