

## Solubilization of $C_{70}$ into Water by Complexation with $\delta$ -Cyclodextrin

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**A water-soluble complex of  $C_{70}$  with  $\delta$ -cyclodextrin ( $\delta$ -CD) which was isolated and purified from cyclodextrin powder in our laboratory was investigated. The complex was characterized by its UV-VIS spectrum, which had higher aqueous solubility than that of the complex between  $C_{70}$  and  $\gamma$ -cyclodextrin ( $\gamma$ -CD). The aqueous solution had a red-brown color and resembled the color of  $C_{70}$  in toluene solution.**

**Key words**  $\delta$ -cyclodextrin; fullerene; solubilization

The conventional cyclodextrins (CDs), cyclic oligosaccharides of D-glucose, and their derivatives have been widely studied because of their excellent property as host compounds in molecular recognition. Large-ringed CDs composed of more than nine D-glucoses have not been well studied because of the difficulties in purification and preparation with reasonable yields. Recently, we established an isolation and purification method for several kinds of large-ringed CDs from commercially available CD powder and obtained a relatively large amount of  $\delta$ -CD, a cyclic oligosaccharide compound of nine  $\alpha$ -1,4-linked D-glucoses.<sup>1,2)</sup>

The  $C_{60}$  and  $C_{70}$  molecules are two important members of the fullerene family. Their availability in a high degree of purity has prompted many studies on their structures, properties, and reactions.<sup>3,4)</sup> However, the solubility of fullerenes, which is poor in most organic solvents and negligible in water, has been one of the greatest impediments to studying their reactions and possible biological functions.

Recently, several groups have focused on the complex formed by  $C_{60}$  with  $\gamma$ -CD in an aqueous solution,<sup>5,6)</sup> but that of  $C_{70}$  with CDs has rarely been reported.<sup>7,8)</sup> Herein, we describe  $C_{70}$  solubilized in an aqueous solution using  $\delta$ -CD.

The equipment and materials used in our investigations are as follows.

Initially, 20.2 mg of  $C_{70}$  ( $2.4 \times 10^{-5}$  mol) and 35.0 mg of  $\delta$ -CD ( $2.4 \times 10^{-5}$  mol) was ball-milled for about 3 days at room temperature.<sup>9,10)</sup> This procedure was carried out in the same

way as reported by Braun *et al.*<sup>9,10)</sup> After adding of 25 ml of water, the solution was incubated at 25 °C for about 3 days. The suspension was filtered through a membrane (0.45  $\mu$ m, KURABO INDUSTRIES LTD., Osaka, Japan) and centrifuged at 25 °C, 10000 rpm for 1 h. The supernatant was examined by UV-VIS spectroscopy.  $C_{70}$  and  $\gamma$ -CD were studied in the same manner. The solution of the  $C_{70}/\delta$ -CD system appeared red-brown, similar to the color of  $C_{70}$  in toluene solution shown in Fig. 1, although the  $C_{70}/\gamma$ -CD system is col-

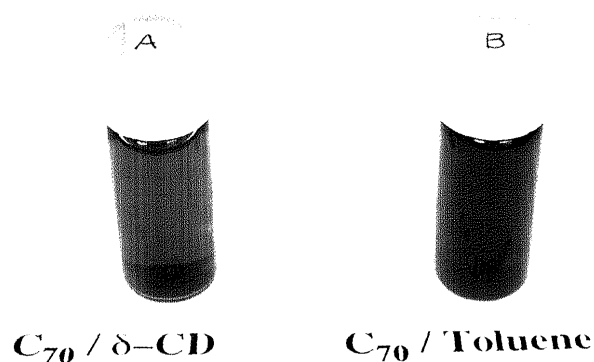


Fig. 1. The Color of  $C_{70}$  Solution

Left; complex of  $C_{70}$  and  $\delta$ -CD in aqueous solution. Right;  $C_{70}$  in toluene solution (0.5 mg/ml).

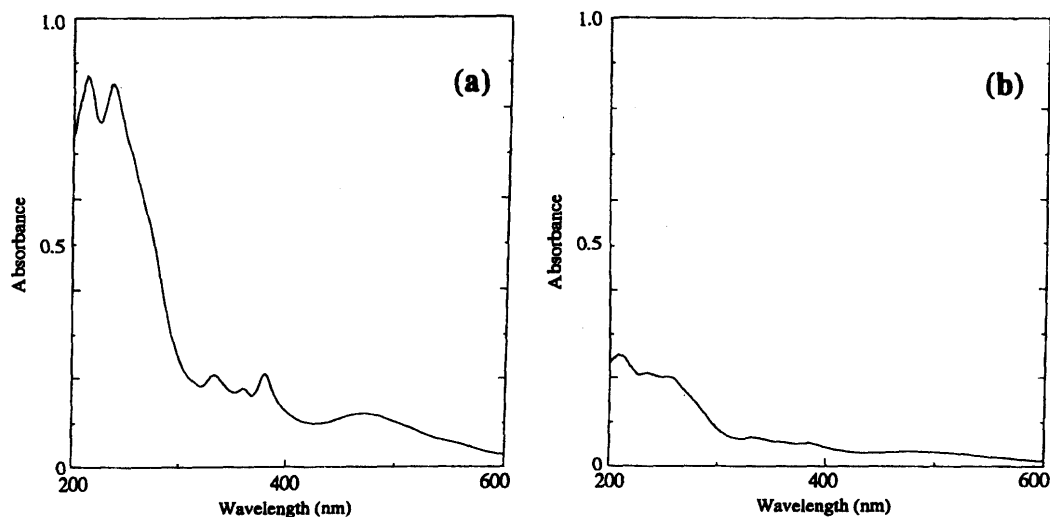


Fig. 2. UV-VIS Spectra of Aqueous Solution of (a)  $C_{70}/\delta$ -CD Complex (Diluted 12.5 Times) and (b)  $C_{70}/\gamma$ -CD Complex (Nondiluted)

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orless.

Figure 2 shows the UV-VIS spectra of the  $C_{70}/\delta$ -CD and  $C_{70}/\gamma$ -CD systems. The spectrum of  $C_{70}/\delta$ -CD is in agreement with that of  $C_{70}$  in hexane solution.<sup>11,12)</sup> The solubilization of  $C_{70}$  in water is believed to be due to the formation of a complex between  $C_{70}$  and  $\delta$ -CD. The concentration of  $C_{70}$  in water is *ca.*  $8.36 \times 10^{-5} M$  by measuring the absorbance at 332.5 nm using the UV absorption method. This concentration is almost the same as that of the  $C_{70}/\gamma$ -CD system reported by Andersson *et al.*<sup>8)</sup> The solubilization of  $C_{70}$  with  $\gamma$ -CD was achieved by use of a large excess of  $\gamma$ -CD.<sup>8,13)</sup> On the contrary, the spectral intensity of the  $C_{70}/\gamma$ -CD system under our experimental conditions is less than that of the  $C_{70}/\delta$ -CD system.

This difference results from the that  $\delta$ -CD has a larger cavity than  $\gamma$ -CD, so  $C_{70}$  is fitted better with  $\delta$ -CD than  $\gamma$ -CD. The details of the interaction mechanism between  $C_{70}$  and  $\delta$ -CD and its complex structure are being studied in our laboratory.

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