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Electrochemical Study of Inclusion Complexes of Fullerene

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Fullerenes' (C60 and C70) inclusion complexes of γ-CD and DMβCD were modified on the glassy carbon electrode and the behavior of their cyclic voltammograms was studied. The results show that CD inclusion complexes have large effects on the fullerene's electrochemical properties. The different effects of γ-CD and DMβCD on the electrochemical properties of C60 and C70 were also compared.

Keywords: Fullerene, inclusion complex, cyclic voltammograms

INTRODUCTION

The discovery by Huffman and Kratschmer of a technique to produce and separate fullerene has promoted a flurry of research into its structure, properties and reactivity [1, 2]. But fullerene reactions and property studies in polar solvents, particularly aqueous solution, are generally hampered by the low solubility of this carbon modification [3].

To make C60 and C70 soluble in water, cyclodextrins (CDs) and their derivatives are quite promising. Cyclodextrins consist of six (α-CD), seven (β-CD), or eight (γ-CD) sugar molecule*s, joined together in a ring by α-1, 4-glucosidic bonds (Fig. 1) [4]. With a hydrophobic cavity inside the molecule, CDs may act as the host for organic molecules. We have succeeded in preparing fullerene inclusion complexes of γ-CD and DMβCD by our method of kneading [5, 6]. At the same time, UV/VIS spectra, IR spectra and X-ray powder diffraction patterns of these inclusion complexes have been studied in detail [5, 6].

Some recent reports [2, 7] have been concerned with the electrochemical properties of fullerene, particularly the cyclic voltammogram (CV) study of films [8] of fullerenes which has helped to understand the electrochemical properties of C60 and C70. Thus, for the first time, we carried out the cyclic voltammogram study of the films of these inclusion complexes. Modified on the glassy carbon (GC) electrode and in TBAP (Bu_4NClO_4)/MeCN, these inclusion complexes show distinct positive shifts of the reduction peak potentials of C60 and C70, which suggests the

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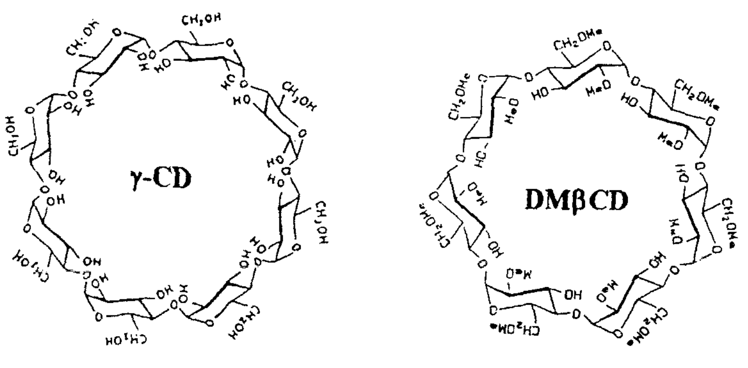

FIGURE 1 Chemical structure of γ-CD and DMβCD.

effects of CDs-inclusion on the electrochemical behavior of C60 and C70.

RESULTS AND DISCUSSION

Similar Cyclic Voltammogram Behavior of C60 and C70

In 1991, Bard [7] reported the first electrochemical study of a film of C60 on a platinum electrode, where he observed four reduction peaks with cathodic peak potentials (Epc) at −1.17, −1.39, −1.88 and −2.24 V *vs* Fc/Fc$^+$ (Fc is ferrocene). In order to investigate the electrochemical properties of inclusion complexes of C60 and C70, for the first time, we studied the CV behavior of their films on an electrode. It was difficult to modify these complexes on the platinum electrode so we cast their films on the surface of a GC electrode.

For the sake of convenience to compare the CV behavior between the pure fullerene and the inclusion complexes, we also prepared films of pure C60 and C70 on the GC electrode under the same conditions. In TBAP/MeCN, typical voltammograms for the reduction of C60 film (Fig. 2) show three reduction peaks with cathodic peak potentials (Epc) at −1.15, −1.48 and −2.08 V *vs* Ag/AgCl. They are close to the first three reduction peak potentials reported by Bard [7]. We have also obtained the first CV data of the film of C70 on GC electrode (Fig. 3). This system shows three reduction peaks with cathodic peak potentials (Epc) at −1.00, −1.50, −1.85 V vs Ag/AgCl and two oxidation peaks with anodic peak potentials (Epa) at 1.35, 1.80 V vs Ag/AgCl (Tab. I).

From the above, one can observe that the three reduction peak potentials (E_R1, E_R2, E_R3) of pure C60 are close to the corresponding reduction peak potentials for pure C70 (Tab. I). Furtheremore, in Table I we discovered that γ-CD inclusion complexes (2:1) affects the CV

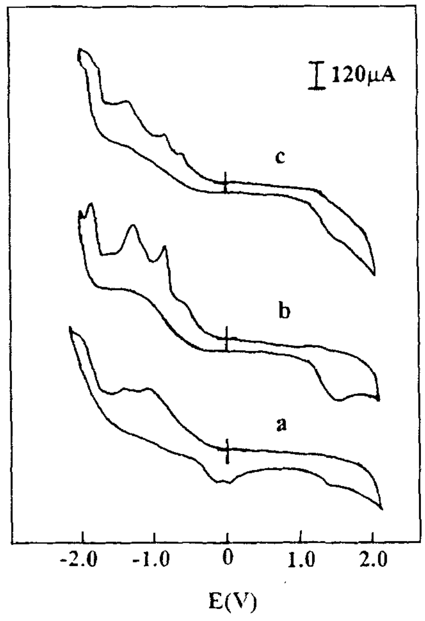

FIGURE 2 Cyclic voltammograms of C60 and its γ-CD inclusion complexes in TBAP/MeCN, glassy carbon electrode, scan rate, 200 mv/s. (a) pure C60; (b) γ-CD/C60 (1:1) (c) γ-CD$_2$/C60 (2:1).

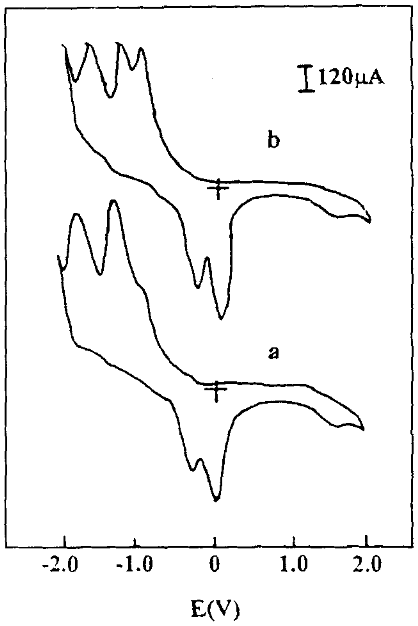

FIGURE 3 Cyclic voltammograms of inclusion complexes of C60 and DMβCD in TBAP/MeCN, glassy carbon electrode, scan rate, 200 mv/s. (a) DMβCD/C60 (1:1): (b) DMβCD$_2$/C60 (2:1).

behavior of C60 and C70 in a similar fashion. DMβCD inclusion complexes (2:1) also show a similar effect on the CV behavior of C60 and C70. These results coincide with Wudl's report [9] that both fullerenes have essentially the same CV behavior in different solvents. He interpreted the observation in terms of strain and pyracylene-type electronic character of the fullerenes.

In Figures 2 and 3, it is shown that no reduction peak for pure C60 or C70 was associated with the corresponding oxidation peaks, suggesting the chemical-irreversibility of the reaction on the electrode surface under our experimental conditions. These inclusion complexes give similar results.

Effects on the Reduction Peak Potentials

By comparing the CV curves of inclusion complexes and pure C60 and C70 (Figs. 2–4), we found that inclusion complexes showed an obvious positive shift of reduction peak potential. On the other hand, γ-CD and DMβCD affect the CV behavior of C60 and C70 to varying degrees as discussed below.

γ-CD Inclusion Complexes

Qualitatively, the same trend (Figs. 5a, 5c) is observed for the γ-CD inclusion complex effects on the CV behavior of C60 and C70. Figure 5a shows that compared with pure C60, the reduction peak potential E_R1 and E_R3 for inclusion complexes γ-CD$_2$/C60 (2:1) shift + 270 mv and +180 mv respectively. While E_R2 shifts only −20 mv. In Figure 5c, the same trend is observed: E_R1 and E_R3 of inclusion complexes γ-CD$_2$/C70 (2:1) shift +220 mv, +100 mv respectively, E_R2 shifts +50 mv. The positive shifts of other inclusion complexes also show clearly in Table I. These results might be contributed to the fact that C60 and C70 have been partly included inside the cavity of γ-CD. The hydrophobic cavity and the three-dimensional π-electron system affect each other, which help to delocalize the electrons. Thus, adding electrons to the fullerenes included in CD's cavity would be easier and the reduction peaks move to more positive potentials [10].

TABLE I Potentials of reduction and oxidation of pure fullerene and inclusion complexes

	Reduction			Oxidation		
	E_R1	E_R2	E_R3	E_O1	E_O2	E_O3
C60	−1.15	−1.48	−2.08	−0.20	−0.02	1.38
γ-CD/C60 (1:1)	−0.82	−1.32	−1.88			1.42
γ-CD$_2$/C60 (2:1)	−0.88	−1.50	−1.90			1.40
DMβ-CD/C60(1:1)	−0.78	−1.09	−1.66	−0.21	0.09	1.65
DMβ-CD$_2$/C60 (2:1)	−0.90	−1.16	−1.57	−0.32	0.06	1.59
C70	−1.00	−1.50	−1.85		1.35	1.80
γ-CD$_2$/C70 (2:1)	−0.78	−1.45	−1.75		1.35	
DMβ-CD$_2$/C70 (2:1)	−0.85	−1.01	−1.47		1.59	

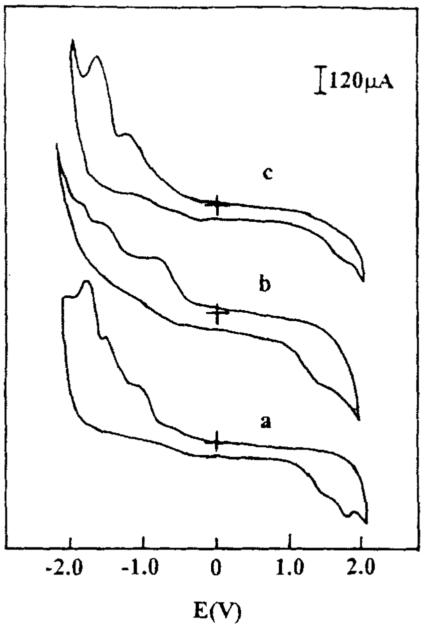

FIGURE 4 Cyclic voltammograms of C70 and its inclusion complexes in TBAP/MeCN, glassy carbon electrode, scan rate, 200 mv/s. (a) pure C70; (b) γ-CD_2/C70 (2:1); (c) DM$\beta$$CD_2$/C70 (2:1).

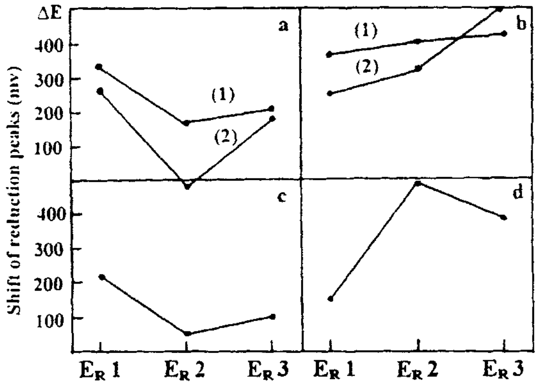

FIGURE 5 Shift of reduction peaks (ΔE) (mv) $\Delta E = E_{\text{inclusion complex}} - E_{\text{pure fullerene}}$ (mv) (a) Inclusion complexes of C60 and γ-CD inclusion complexes: (1) γ-CD/C60 (1:1); (2) γ-CD_2/C60 (2:1); (b) Inclusion complexes of C60 and DMβCD inclusion complexes: (1) DMβCD/C60 (1:1); (2) DM$\beta$$CD_2$/C60 (2:1); (c) γ-CD_2/C70 (2:1); (d) DM$\beta$$CD_2$/C70 (2:1).

On the other hand, the γ-CD inclusion complexes (1:1 and 2:1) do not affect the CV behavior of C60 identically. To our surprise we found that the reduction peak potentials of inclusion complexes γ-CD_2/C60 (2:1) shifted less than that of inclusion complexes γ-CD/C60 (1:1). From Table I, one can see the reduction peak potentials E_R1, E_R2 and E_R3 of inclusion complexes γ-CD/C60 (1:1) shift +330, +160 and +200 mv respectively. The difference is obvious. These results lead us to consider that the effects of inclusion complexes on C60's electron affinity could be ascribed to two factors. On the one hand, the CD's hydrophobic cavity act on the π-electron system and help C60 to delocalize the electrons that causes the positive shift of reduction peaks. On the other hand, CDs-inclusion seals off part of fullerenes' surface and hinders the electron transfer between fullerenes during electrolysis. It is possible that both effects operate and cancel each other to produce the observed results.

DMβCD Inclusion Complexes

The effect of DMβCD inclusion complexes on the CV behavior is shown clearly in Figures 5b and 5d. First, we observed that the reduction peak potentials of DMβCD inclusion complexes shift more than those of γ-CD inclusion complexes. For example, the reduction peak potentials of inclusion complexes DMβCD/C60 (1:1) shift +370, +390 and +420 mv respectively. Compared with the shift of inclusion complexes γ-CD/C60 (1:1), the change is obvious. DM$\beta$$CD_2$/C60 (2:1) and DM$\beta$$CD_2$/C70 (2:1) also showed the same trend as can be seen from Table I. There is also a great effect of DMβCD inclusion complexes on the second reduction peak potential, E_R. From the above, we know that γ-CD inclusion complexes have little or no effect on the second reduction peak potential E_R2, but the reduction peak potential E_R2 of DMβCD inclusion complexes moves to more positive potential. i.e., E_R2 of γ-CD_2/C70 (2:1) shift only +50 mv, while the E_R2 of DM$\beta$$CD_2$/C70 (2:1) shift +490 mv. The observation might prove that substitution of methoxyl for hydroxyl would strengthen the interaction of the hydrophobic cavity of CD and the π-electron system.

Effects on the Oxidation Peak Potentials

The effect of inclusion complexes on fullerene's electrochemical properties displayed not only on the reduction peaks but also on their oxidation peaks. Table I, Figures 2 and 4 show that γ-CD inclusion complexes have little effect on the fullerene's oxidation peak potentials except for the disappearance of the first two oxidation peaks of pure C60. While DMβCD inclusion complexes show a larger effect on the fullerene's oxidation peak potentials (Figs. 3, 4). Both 1:1 and 2:1 inclusion complexes of DMβCD and C60 show a negative shift of the first oxidation peak potential (E_O1), and a large positive shift of the second and third oxidation peak potentials (Fig. 5b). E_O2 of inclusion complexes of DMβCD and C70 also shifts +240 mv. The effects of DMβCD inclusion complexes on the CV behavior of fullerene also could be seem from the changes on the peak's shape (Fig. 3). This is currently under investigation in our laboratory.

In conclusion, by comparing the CV behavior of fullerene and their CDs inclusion complexes, we have found that CD-inclusion complexation affected the CV behavior of C60 and C70 greatly. At the same time, we also discovered that the DMβCD inclusion complexation effect on the CV behavior of C60 and C70 significantly differed from γ-CD inclusion complexes.

EXPERIMENTAL SECTION

Materials

γ-CD and DMβCD are products of Chinoin Pharmaceutical and Chemical Works Ltd., Budapest. Fullerenes C60 and C70 are products of the Department of Chemistry of Peking University and their purity is 99.0%. The preparation of these inclusion complexes was described in detail in reference [5, 6].

Cyclic Voltammogram Study

Cyclic voltammogram studies were carried out at a glassy carbon (GC) electrode (diameter 3 mm) in MeCN. Supporting electrolyte: 0.1 M TBAP (Bu_4NClO_4). Scan rate: 200 mv/s. A platinum wire served as the counter electrode and a silver wire was used as a reference electrode.

Preparation of the Films

To prepare the films of the fullerenes and their inclusion complexes, 2 mmol of complex was dissolved in 1 ml of $C_2H_2Cl_4$, obtaining the saturated solution. A few microliters of the saturated solution was dropped on a GC electrode and the solvent was evaporated under infrared lamp.

Acknowledgements

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References

[1] Kratschmer, W., Lamb, L. D., Fortiropoulos, K. and Huffman, D. R. (1990). *Nature*, **347**, 354.

[2] Xie, Q. S., Arias, F. and Echegoyen, L. (1993). *J. Am. Chem. Soc.*, **115**, 9818 and references therein.

[3] Sivaraman, N., Dhamodaran, I., Srinivasan, T. G., Vasudeva Rao, P. R. and Mathews, C. K. (1992). *J. Org. Chem.*, **57**, 6077.

[4] Saenger, W. (1980). *Angew Chem. Ed. Engl.*, **19**, 344.

[5] Zhang, D. D., Liang, Q., Chen, J. W. *et al.* (1993). *Supramol. Chem.*, **3**, 235.

[6] Zhang, D. D., Chen, J. W., Yang, Y., Cai, R. F., Shen, X. L. and Wu, S. H. (1993). *J. Inclusion Phenom.*, **16**, 245.

[7] David, E. and Bard, A. J. (1994). *J. Phys. Chem.*, **98**, 8140.

[8] Jchoulet, C., Bard, A. J. and Wudl, F. (1991). *J. Am. Chem. Soc.*, **113**, 5456.

[9] Allemand, P. M., Koch, A. and Wudl, F. (1991). *J. Am. Chem. Soc.*, **113**, 1050.

[10] Ohlendorf, V., Willnow, A., Hungerbuhler, H., Guldi, D. M. and Asmus, K. D. (1995). *J. Chem. Soc. Chem. Commun.*, 759.