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Voltammetric behavior of C₆₀-*p*-*tert*-butylcalix[8]arene inclusion complex film

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Abstract The C₆₀-*p*-*tert*-butylcalix[8]arene inclusion complex film has been directly formed on the surface of a glassy carbon electrode, and its electrochemical behavior in acetonitrile containing tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte studied. The film has a two-electron reduction wave at -1.0 V (vs Ag/AgCl), but limits to the first cathodic potential scan.

Key words C₆₀-*p*-*tert*-butylcalix[8]arene · Inclusion complex · Film · Cyclic voltammetry

Introduction

The third allotropic modification of Carbon, C₆₀, has attracted much attention because of its peculiar closed-cage structure, and its electrochemistry has been studied extensively in solution as well as in the film state [1–9]. Calixarenes [10] are cavity-shaped cyclic molecules made up of phenol units linked via alkylidene groups, and these have been regarded as the third generation of supramolecules after cyclodextrins and crown ethers.

In 1994, Atwood et al. [11] and Suzuki et al. [12] found that, from their solutions in toluene, C₆₀ and *p*-*tert*-butylcalix[8]arene formed a 1:1 inclusion complex, which was a novel and useful purification method for obtaining C₆₀ in large quantity and in high purity, since this complex was sparingly soluble in most organic solvents. The interaction between C₆₀ and *p*-*tert*-butylcalix[8]arene has been confirmed by ¹³C CP-MAS NMR, IR spectroscopy and UV-visible spectroscopy [11–14]. Castillo et al. [15] made the Langmuir film of fullerene/

calix[8]arene complex. Chen et al. [16] studied the effects of calixarenes on the electrochemical reduction of C₆₀ in toluene, mixed toluene and acetonitrile and mixed toluene and DMSO, and found that *p*-*tert*-butylcalixarenes could interact or react with C₆₀ⁿ⁻ anions; the products of these reactions were insoluble or poorly soluble in the solvent mixture and adsorb or precipitate onto the electrode surface. As we have studied the electrochemical behavior of C₆₀- γ -cyclodextrin inclusion complex [2, 3], and the structure of C₆₀-*p*-*tert*-butylcalix[8]arene is similar to that of C₆₀- γ -cyclodextrin, we became interested in studying the electrochemical behavior of *p*-*tert*-butylcalix[8]arene. However, when the complex was solubilized in some solvents such as chloroform, dichloromethane and 1,2-dichloroethane, it dissociated to form the two components [11]. Although it is stable in carbon tetrachloride [11], the resultant brown/yellow solution is turbid even at 1×10^{-6} M, and we could not get the voltammetric response in mixed solution of tetrachloride and acetonitrile containing tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte, so that the electrochemical behavior of this complex has not been studied so far. In this paper, we describe how the C₆₀-*p*-*tert*-butylcalix[8]arene inclusion complex film was directly formed on the surface of a glassy carbon (GC) electrode and its electrochemical behavior studied.

Experimental

Cyclic voltammetry (CV) experiments were performed on an EG&G PAR 273 potentiostat/galvanostat with an EG&G PAR 270 universal programmer. The working electrode was a glassy carbon disk of diameter 4 mm insulated in Teflon rods of diameter 8 mm. The auxiliary electrode consisted of a platinum wire. Ag/AgCl was used as reference electrode. Acetonitrile (MeCN) and tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) were used as the solvent and supporting electrolyte respectively. TBAPF₆ was from Sigma; toluene and MeCN were distilled from P₂O₅ prior to use. All other reagents were of analytical grade. Water was triply distilled from an all-quartz still. High purity nitrogen was used for

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deacration. To prevent the organic solvent from evaporating, all CV experiments were carried out in an ice bath. The IR spectra (KBr disk) were recorded by means of a Magna-IR750 spectrophotometer.

The synthesis of C_{60} (99.9%) is described elsewhere [17, 18], and *p*-*tert*-butylcalix[8]arene (99%) was prepared in our laboratory according to the literature [19]. C_{60} and *p*-*tert*-butylcalix[8]arene were dissolved in toluene to give 1×10^{-3} M solutions respectively.

The glassy carbon (GC) electrode surface was polished with alumina to produced a mirror-like surface, and then washed with water and ethanol in an ultrasound bath and left to dry.

To prepare the C_{60} film, 3 μ L of 1×10^{-3} M C_{60} solution in toluene was dropped onto the surface of a GC electrode using a 10- μ L syringe, and dried under an infra-red lamp.

Results and discussion

Solutions of C_{60} and *p*-*tert*-butylcalix[8]arene solutions in toluene (30 μ L, 1×10^{-3} M) were mixed in a small test tube, and 6 μ L of the mixed solution was then dropped onto the surface of GC electrode using a 10 μ L syringe and dried under an infra-red lamp. A brown/yellow film was obtained. As a mixture of C_{60} and *p*-*tert*-butylcalix[8]arene becomes turbid after a little while, it should be added to the GC surface as soon as it is mixed.

Since the brown/yellow substance on the GC electrode surface was insufficient to allow an infra-red (IR) adsorption experiment to be carried out, 1 mL 1×10^{-3} M C_{60} and *p*-*tert*-butylcalix[8]arene solution in toluene were mixed in a watch glass and left to dry under the infra-red lamp. Figure 1 displays the IR spectra (KBr) of the resulting brown/yellow powder and solid-state *p*-*tert*-butylcalix[8]arene, which indicate that the intramolecular hydrogen bonding normally present in the calixarene is partially disrupted (indicated by a shift

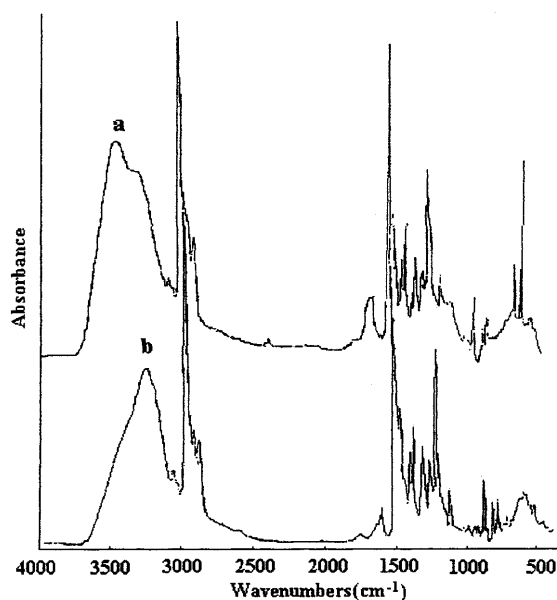


Fig. 1 Infrared spectra (KBr discs) of *a* C_{60} -*p*-*tert*-butylcalix[8]arene complex, *b* *p*-*tert*-butylcalix[8]arene

from 3250 to 3450 cm^{-1}). This is in agreement with the IR spectrum of the C_{60} -*p*-*tert*-butylcalix[8]arene complex synthesized using the literature method [11, 13, 14], indicating that the brown/yellow substance is C_{60} -*p*-*tert*-butylcalix[8]arene inclusion complex. Therefore, we can conclude that the brown/yellow film on GC electrode is undoubtedly the C_{60} -*p*-*tert*-butylcalix[8]arene film.

The voltammogram of the C_{60} -*p*-*tert*-butylcalix[8]arene film in the MeCN solution containing 0.1 M TBAPF₆ between 0 and -2.0 V (vs Ag/AgCl) (Fig. 2a) shows three reduction peaks (P_1 , P_2 , P_3) and no oxidation peak. When the potential range was changed to 0 to -1.3 V, when only P_1 appeared, two reoxidation peaks (Pa_1 , Pa_1') could be seen (Fig. 3a) in the reverse scan, and the reduction peak separated into two in the second scan (Fig. 4). Thus, only the cathodic wave of the first scan (P_1) corresponds to the reduction the C_{60} -*p*-*tert*-butylcalix[8]arene film, and this was studied extensively in the next experiment.

A mixed solution of C_{60} and *p*-*tert*-butylcalix[8]arene (2 μ L, 4 μ L, 6 μ L, 8 μ L, 10 μ L 1:1) was dropped onto the GC surface. CVs in MeCN containing 0.1 M TBAPF₆ showed that the reduction peak currents increased as the surface coverage increased, but increased

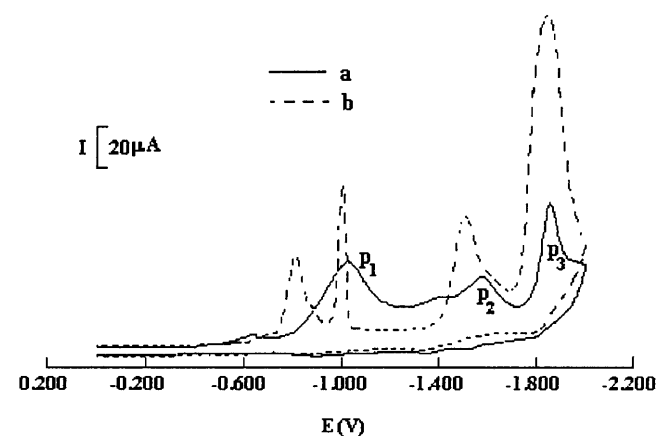


Fig. 2 CVs of *a* C_{60} -*p*-*tert*-butylcalix[8]arene film, *b* C_{60} film in MeCN solution containing 0.1 M TBAPF₆ at the scan rate of 100 mV s^{-1}

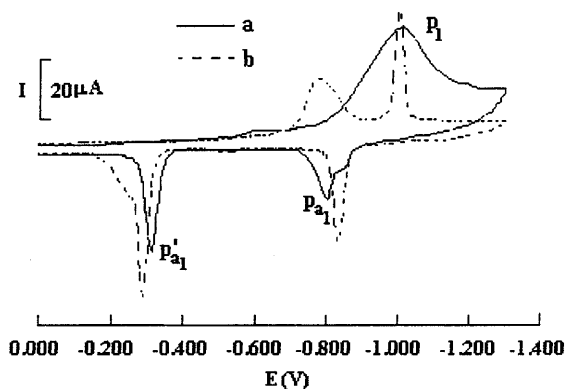


Fig. 3 CVs of *a* C_{60} -*p*-*tert*-butylcalix[8]arene film, *b* C_{60} film in MeCN solution containing 0.1 M TBAPF₆ at the scan rate of 100 mV s^{-1}

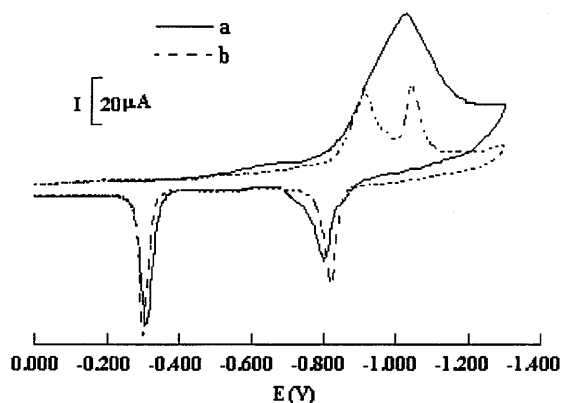


Fig. 4 CVs of C_{60} -*p*-*tert*-butylcalix[8]arene film in MeCN solution containing 0.1 M TBAPF₆ at the scan rate of 100 mV s⁻¹: a first, b second scan

slowly when the volume was more than 6 μ L. This might be because the reduction is less complete when the film is thicker. It is therefore preferable to drop 6 μ L mixed solution on the GC electrode. That is, the surface coverage of the C_{60} -*p*-*tert*-butylcalix[8]arene complex is 2.4×10^{-8} mol cm⁻².

The reduction peak current was unchanged as the concentration of TBAPF₆ changed from 0.02 to 0.5 M; 0.1 M TBAPF₆ was used in this work. C_{60} and *p*-*tert*-butylcalix[8]arene (each 1×10^{-3} M) were mixed in the ratio 1:0.5, 1:1, 1:1.5 respectively, and 4.5 μ L, 6 μ L, and 7.5 μ L were dropped onto the GC surface respectively to ensure that the amounts of C_{60} on the electrode surface were the same. Figure 5 shows the CVs of these films, which indicate that the cathodic wave distorts when the amount of C_{60} is excess; while excess *p*-*tert*-butylcalix[8]arene causes a slightly larger peak current than that for 1:1 mixing; this might be because the complexing reaction is more complete.

The potential scan rate also had an influence on the CV behavior of C_{60} -*p*-*tert*-butylcalix[8]arene film. The higher

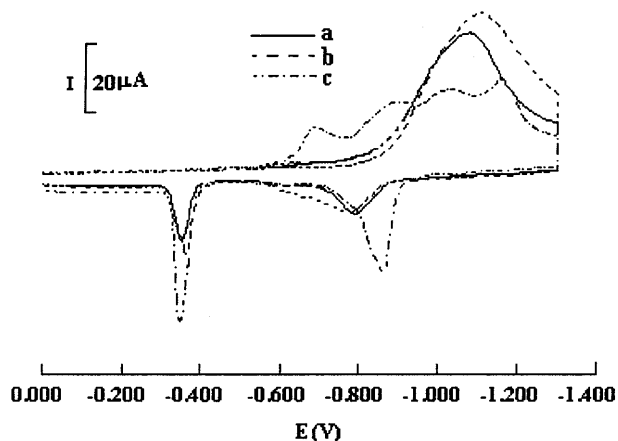


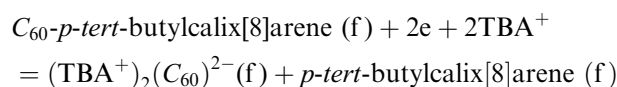
Fig. 5 CVs of a 1:0.5, b 1:1, c 1:1.5 (v/v) of C_{60} /*p*-*tert*-butylcalix[8]arene film in MeCN solution containing 0.1 M TBAPF₆ at the scan rate of 100 mV s⁻¹

scan rate resulted in higher current flow, but the peak current increased slowly when the scan rate was more than 200 mV s⁻¹, while the wave shape became worse. Therefore the scan rate was chosen to be 100 mV s⁻¹.

Comparing the CVs of C_{60} -*p*-*tert*-butylcalix[8]arene film and C_{60} film (Fig. 2), it can be seen that the latter two peaks, P₂ and P₃, of the C_{60} -*p*-*tert*-butylcalix[8]arene film are similar to those of the C_{60} film, indicating the decomposition of the C_{60} -*p*-*tert*-butylcalix[8]arene complex. When the potential range was reduced to 0 to -1.3 V, the two reoxidation peaks Pa₁, Pa₁' (Fig. 3a) in the reverse scan were also similar to those of the C_{60} film (Fig. 3b), and the reduction peak separated into two in the subsequent scan (Fig. 4); this confirmed the decomposition of C_{60} -*p*-*tert*-butylcalix[8]arene complex when the potential scanned from 0 V to -1.3 V in which P₁ appeared.

Since the reoxidation peaks of the C_{60} film (Fig. 3b) corresponded to successive one-electron transfers [4], we conclude that the reduction of C_{60} -*p*-*tert*-butylcalix[8]arene film is a two-electron transfer reaction. TBA⁺ ion diffuses into the film to balance the negative charges.

As the size of the inner cavity of *p*-*tert*-butylcalix[8]arene (8.6 Å when it adopts a regular cone conformation) is comparable with the size of C_{60} (7.1 Å) [12], one C_{60} molecule can be encapsulated in the cavity of *p*-*tert*-calix[8]arene and forms a 1:1 complex. The formation of the 1:1 adduct is determined by the interplay of the attractive (C)H... π interactions and repulsive π ... π interactions [20], which results in the relatively weakly bonded 1:1 C_{60} -calixarene system [14]. The interaction between TBA⁺ and (C_{60})²⁻ might be stronger than that between (C_{60})²⁻ and *p*-*tert*-butylcalix[8]arene, which makes (C_{60})²⁻ drop out of the cavity of *p*-*tert*-butylcalix[8]arene:



where "f" represents the film on the GC electrode. The anodic wave corresponds to the reoxidation of (C_{60})²⁻(TBA⁺)₂:

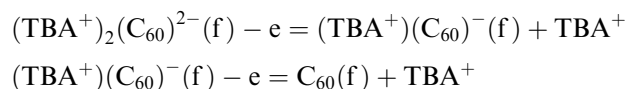
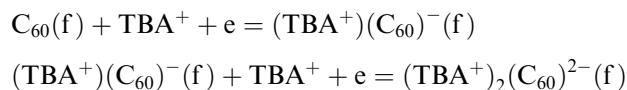


Figure 3 also shows the peak potential difference in the anodic wave of C_{60} -*p*-*tert*-butylcalix[8]arene film and C_{60} film, indicating that the existence of *p*-*tert*-butylcalix[8]arene in the film still affects the CV behavior of the film.

Since the C_{60} -*p*-*tert*-butylcalix[8]arene complex has decomposed, the cathodic wave of the second scan is the reduction of pure C_{60} in the film:



Conclusion

C₆₀-*p*-*tert*-butylcalix[8]arene inclusion complex film can be directly formed by dropping a 1:1 mixed solution of C₆₀ and *p*-*tert*-butylcalix[8]arene onto a GC surface and letting it dry quickly under the infra-red lamp. The film has an unsteady two-electron reduction wave in MeCN solution containing TBAPF₆, limited to the first scan.

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