

Electrochemistry of C₆₀/Cationic Lipid Films on Electrodes in Aqueous Solution

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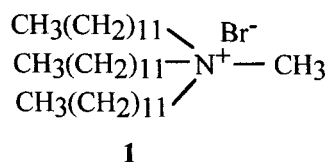
Fullerene C₆₀ was embedded in the cast films of an artificial lipid, tridodecylmethylammonium bromide (**1**) on electrodes. The electrochemistry of the obtained modified electrodes was examined in water containing a variety of electrolyte cations including K⁺, tetraethylammonium and tetra-n-butylammonium and of electrolyte anions including F⁻, Cl⁻, Br⁻, SO₄²⁻ and NO₃⁻. No cation dependence was observed during cyclic voltammetry of the modified electrodes. On the contrary, electrolyte anions except SO₄²⁻ were found to influence the CVs of the electrodes; that is, the cathodic peak potentials of the electrodes shifted in parallel with the hydration energy of the anions. Based on these results, one possible electron transfer mechanism for the first and second reduction processes of the embedded C₆₀ in the lipid films has been proposed.

Key words: fullerene, lipid, electron transfer mechanism, modified electrode, electrolyte dependence

1. INTRODUCTION

Fullerenes are novel and unique carbon nanocluster materials. Since the first discovery¹⁾, studies on the chemistry, physics and biochemistry of fullerenes and related compounds have been at the forefront of research.²⁾ The chemistry of fullerene anions is of particular interest in the field of fullerene science.³⁾ The electrochemistry of fullerene films is important from the aspects of both fundamentals and applications. The electrochemistry of cast films and Langmuir-Blodgett films of C₆₀ and C₇₀ on electrode surfaces are reported to be unstable and complex both in organic solvents⁴⁾ and in water⁵⁾. On the contrary, we have revealed that the electrochemistry of C₆₀ embedded in cast films of cationic lipids on electrodes are very stable.⁶⁻⁸⁾ Here we shed light on the electron transfer mechanism of C₆₀/lipids on electrodes. Kadish and coworkers⁹⁾ described the effects of electrolyte cations on the electrochemistry of C₆₀ in organic solution. Szucs and coworkers¹⁰⁾ reported a strong cation dependence on the aqueous electrochemistry of cast films of C₆₀ and of C₇₀ on electrodes. We have described the aqueous electrochemistry of a fullerene lipid on electrodes. We now propose a possible electron transfer mechanism for the C₆₀/lipid-modified electrodes based on the electrolyte cation and anion dependence of the electrodes. In this study, tridodecylmethylammonium bromide (**1**, Chart 1) that forms a molecular-bilayer structure was used as a cationic artificial lipid.

Chart 1.



2. EXPERIMENTAL

C₆₀ (+99.95%) was purchased from the Materials and Electrochemical Research Co. and used as received. Supporting electrolytes used in this study included KF, KCl, KBr, K₂SO₄, KNO₃, tetraethylammonium bromide (TEABr), and tetra-n-butylammonium bromide (TBABr). Tridodecylmethylammonium bromide (**1**) was available from our previous study⁸⁾. Milli Q water (Millipore Co., >18.2 M ohm) was used.

The preparation of the C₆₀/**1**-modified electrodes is as follows. A bare basal-plane pyrolytic graphite (BPG, Union Carbide Co.) electrode (geometric area, 0.196cm²) was polished with a 1500-grit SiC emery paper, followed by a rinse with water and then air-drying. A ten-microliter portion of C₆₀(0.8mM)/**1** (15.4mM) in toluene was placed on a polished BPG electrode surface and then dried in vacuo at 5hP for 1h.

Cyclic voltammogram (CV) measurements were conducted with a potentiostat (Seiko EG&G, Model 263A) in 0.1 M aqueous solution containing an electrolyte at 25 °C under an argon (99.9999%) atmosphere. A Pt plate (Nilaco, 99.98%) and a saturated calomel electrode (SCE) was used as the counter and reference electrodes, respectively.

3. RESULTS AND DISCUSSION

3.1 Effect of electrolyte cations on CVs

The cathodic peak potentials for C₆₀ cast on electrodes in aqueous solution have been reported to shift in the positive direction with a decrease in the hydration energy of the ions.¹⁰⁾ Differential pulse voltammograms of the cast films of fullerene lipid **2** (Chart 2) on electrodes showed a strong electrolyte cation dependence.¹¹⁾ In sharp contrast, the CVs for C₆₀/**1**-modified electrodes in water showed no electrolyte cation dependence. As demonstrated in Figure 1 and Table 1, the cathodic peak potentials (*E_{pc}*) for the first and second reduction of C₆₀ in the films are almost identical in three solutions containing KBr TEABr or TBABr. This result indicates that the C₆₀ anions

Chart 2.

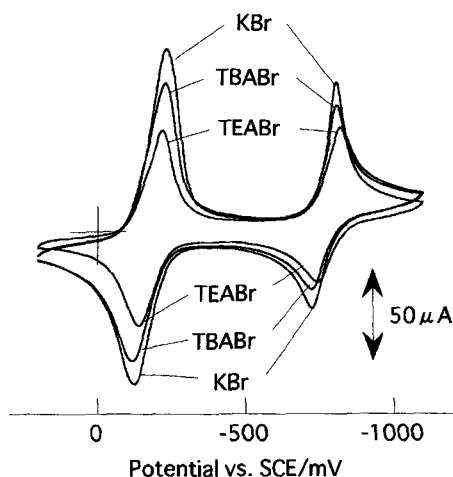
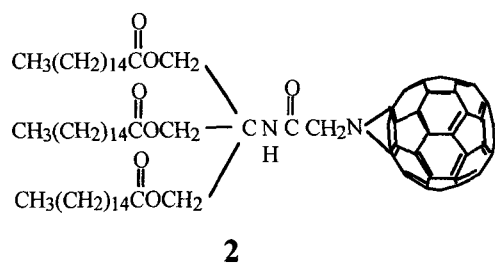


Figure 1. Typical cyclic voltammograms for $C_{60}/1$ -modified BPG electrodes in aqueous solution containing 0.1M KBr, TEABr or TBABr. Scan rate, 0.1 V/s.

Table 1. Cathodic peak potentials for cast films of $C_{60}/1$ on BPG electrodes.

Electrolytes	KBr	TEAB	TBAB
E_{pc_1} /mV	-224	-240	-234
E_{pc_2} /mV	-824	-808	-811

generated in the films do not bind to the electrolyte cations, instead, the cationic lipid **1** forms a complex with C_{60} radical monoanions and dianions.

3.2 Effect of electrolyte anions on CVs

Figure 2 shows the CVs for the $C_{60}/1$ -modified electrodes in water containing 0.1 M of a given electrolyte, in which the used electrolytes are KF, KCl, KBr, KNO_3 and K_2SO_4 . In sharp contrast with the cation dependence, the CVs showed a strong electrolyte anions dependence. Table 2 summarizes the E_{pc} , anodic peak potentials (E_{pa}), and formal potentials (E°) obtained from the CVs. In Figure 3, the obtained first and second cathodic potentials are plotted as a function of the hydration energies of the anions. For NO_3^- , Br $^-$, Cl $^-$ and F $^-$, both the first and second reduction potentials shift in parallel with the hydration energy of these anions as well as in parallel with the Hofmeister series of anions that exhibit an indication of the affinity of hydrophobic tetraalkylammonium cations in an organic phase and anions in an aqueous phase. This result suggests binding of electrolyte anions with the cationic lipid **1** in the films that results in a shift of the cathodic peak potentials. As can be seen in Figure 3, SO_4^{2-} exhibits large deviation

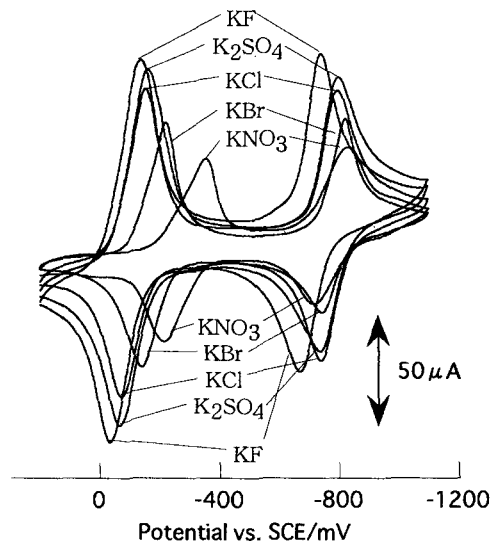


Figure 2. Typical cyclic voltammograms for $C_{60}/1$ -modified BPG electrodes in aqueous solution containing 0.1M KF, KCl, KBr, KNO_3 , or K_2SO_4 . Scan rate, 0.1 V/s.

Table 2. Cathodic peak potentials (E_{pc}), anodic peak potentials (E_{pa}) and formal potentials (E°) for cast films of $C_{60}/1$ on BPG electrodes in aqueous solution containing a given electrolytes.

Electrolytes	KF	KCl	K_2SO_4	KBr	KNO_3
E_{pc_1} /mV	-143	-158	-166	-225	-376
E_{pa_1} /mV	-34	-72	-66	-140	-216
E_1° /mV	-89	-115	-116	-183	-296
E_{pc_2} /mV	-743	-798	-801	-821	-832
E_{pa_2} /mV	-668	-738	-736	-742	-716
E_2° /mV	-706	-768	-769	-782	-774

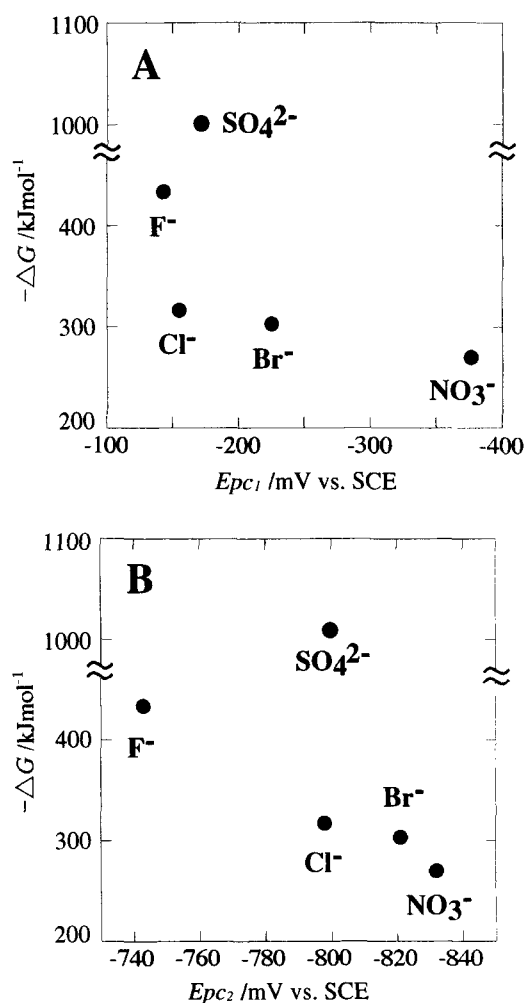


Figure 3. Relationship between the hydration energy of anions (ΔG) and the cathodic peak potentials (A: first reduction process, B: second reduction process) of the $C_{60}/1$ -modified electrodes.

from the plot. This is probably due to the 1:2 complex formation between SO_4^{2-} and lipid **1** in the films.

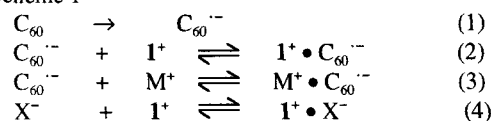
3.3 A proposed electron transfer mechanism

We have described elsewhere the theoretical treatment (thermodynamics) for the binding of electrolyte cations (tetraalkylammonium) to the radical anion and the dianion of the fullerene moieties in a **2** film cast on a BPG electrode in aqueous solution, where the binding of the anions of the C_{60} moiety with electrolyte cations determines the cathodic peak potentials of the C_{60} moiety.¹¹ Szucs and coworkers¹⁰ described the aqueous electrochemistry of films of C_{60} solely on electrodes to have a strong anion dependence.

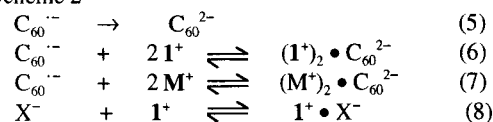
The following is the proposed electron transfer mechanism for $C_{60}/$ lipid **1**-coated electrodes. For the first reduction process (eq 1) of C_{60} embedded in films of **1**, the cathodic peak potentials in the CVs shift to a positive direction compared with those of C_{60} in organic solutions^{3a}, indicating the complex formation of a C_{60} radical monoanion and cation. For the $C_{60}/$ **1**-modified electrodes, no electrolyte cation dependence on the CVs

suggests that the counter cation of the C_{60} anion is not an electrolyte cation but the ammonium cation of lipid **1** (eq 2). Therefore, the contribution of eq 3, where M denotes the electrolyte cation, for the cathodic potentials is almost negligible. Unfortunately, the determination of the binding constant between the C_{60} radical monoanion and **1** was not possible since **1** is not an electrolyte but a film component. Important feature is the anion dependence on the cathodic potentials. As was described in section 3.2, the cathodic peak potentials for the $C_{60}/$ **1** electrodes shifted negatively in the presence of electrolyte anions with smaller hydration energies. This shift is due to the formation of a complex between an electrolyte anion and ammonium moiety on **1**, as expressed by eq 4, where X denotes the electrolyte anion. That is, the negative shift is explained by the competitive binding of the C_{60} radical monoanion and electrolyte anion toward the lipid cation. The proposed electron transfer mechanism is quite different from those of **2**-coated electrodes¹¹ and of C_{60} -coated electrodes¹⁰. The same electron transfer mechanism for the second reduction process (Scheme 2) would be proposed since both the cation and anion dependences on the CVs (see Figures 1 and 3) for the second reduction were almost similar to those of the first reduction.

Scheme 1



Scheme 2



4. CONCLUSION

In conclusion, we have revealed the electron transfer reactions of C_{60} embedded in lipid cast films on electrodes. The proposed mechanism would be applicable for the electron transfer reactions of higher fullerenes incorporated in lipid films on electrodes. Detailed analyses of the modified electrodes using the electrochemical quartz crystal microbalance are currently underway in our laboratory.

5. ACKNOWLEDGMENTS

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