Synthesis, Aggregate Structure and Electrochemical Properties of a Water-Soluble Fullerene-Bearing Ammonium Amphiphile

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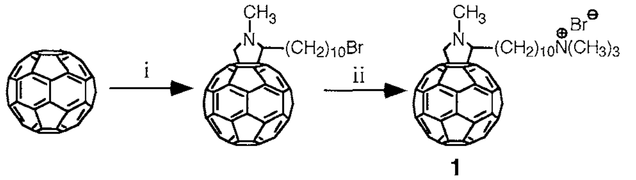
A water-soluble C_{60}-terminating ammonium surfactant, **1**, was synthesized. Electron microscopy revealed that **1** forms a fibrous aggregate in an aqueous solution. Electronic interaction between the fullerene moieties in **1** in the aqueous solution was observed. Electrochemistry for **1** aqueous solutions was found to be quite different from that of **1** in the film states.

Studies on both fullerene chemistry and the chemistry of molecular assemblies are currently at the forefront of researching. Our interest is focused on the coupling of these two fields.[1] We recently synthesized a fullerene-lipid possessing many unique characteristics.[2] Although fullerenes can be solubilized in water by several means,[3] there is no report describing a water-soluble fullerene-bearing surfactant. Here we synthesized a water-soluble C_{60}-terminating ammonium amphiphile, **1**, and examined its properties by using spectral and electrochemical techniques.

Compound **1** was synthesized according to the following scheme (Scheme 1). C_{60} was reacted with *N*-methylglycine and 11-bromoundecanal in toluene, followed by the quarternarization of the terminal bromide with trimethylamine in THF to produce **1** as a dark-brown solid (37 %, decomp. >300 °C), which was identified with ^{1}H NMR and ^{13}C NMR spectroscopies and elemental analysis.[4] The compound was soluble in DMF, DMSO, hot chloroform and hot alcohols, but was insoluble in THF, acetonitrile, ethylacetate, hexane and toluene.



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i) N-methylglycine, 11-bromoundecanal, toluene, reflux, 18 h, 50 %; ii) trimethylamine, THF, 25 °C, 45 h, 73 %.

Scheme 1.

A transparent light-brown aqueous solution was obtained by sonicating a film which was cast from hot methanol solution of **1**. Electron microscopy revealed that **1** forms a nanometer-sized fibrous aggregate in the aqueous solution (Figure 1). The UV-visible absorption maximum for an aqueous solution of **1** was observed at 271 nm (Figure 2, line a); the peak maximum is being shifted to longer wavelength by 3- and 5 nm, respectively, compared to those in micellar solutions (lines b and c) of hexadecyltrimethylammonium bromide (CTAB) or sodium dodecylsulfate (SDS), indicating the electronic interaction[2] of the fullerene moieties in the aqueous solution of the single component of **1**.

Although fullerenes dissolved in organic solutions form multiply charged anions upon reduction because of their high degrees of degeneracy of LUMO, the electrochemistry of fullerene films is rather complicated.[5] We have recently found that C_{60} incorporated in a molecular-bilayer film of tetradecyldimethylammonium poly(styrene sulfonate) (**2**) cast on an electrode shows stable and reversible electron transfer reactions with the underlying electrode.[6]

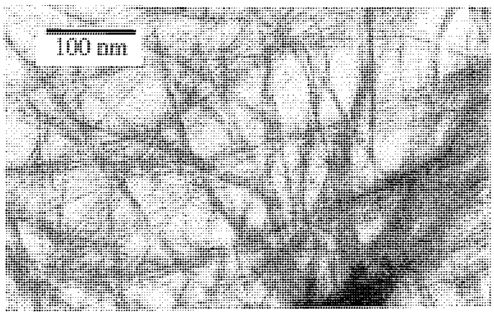

Figure 1. Transmission electron microscopic image of an aqueous solution of **1** stained by uranyl nitrate.

We examined the electrochemistry of **1** in film states and in aqueous solution using cyclic voltammetry and differential pulse voltammetry (BAS-100B Electrochemical Analyzer, Bioanalytical Systems) in an argon atmosphere (99.998% purity). A saturated calomel electrode (SCE) and a Pt plate were used as the reference and the counter electrodes, respectively. Typical procedure for the preparation of a modified electrode is as follows. A twenty microliter portion of **1** in chloroform ($[\mathbf{1}] = 0.4$ mmol dm^{-3}) was placed on a homemade basal plane pyrolytic graphite (BPG) disk electrode (geometric area, 0.25 cm^2), and allowed to air-dry.

Figure 3 shows cyclic voltammograms (CVs) and a differential pulse voltammogram (DPV) for films of **1** or **1**/**2** (molar ratio, 1/19) cast on a BPG electrode in a 0.5 M tetraethylammonium chloride aqueous solution. While a cast film of C_{60} gave no faradaic current in the potential range of – 1000 – 0 mV (data not shown), **1** was found to give evident redox response in the CVs, though they are broad. The DPV of **1** shows a peak at – 725 mV together with a shoulder near –500 mV. The broad voltammograms suggest the inhomogeneity in the structure of **1** in

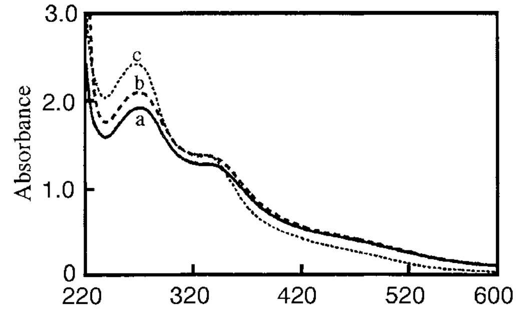

Figure 2. UV-visible absorption spectra of aqueous solutions of **1** (7.5×10^{-5} mol dm^{-3}) in the absence (a) or presence of 0.1 mol dm^{-3} CTAB (b) or 0.1 mol dm^{-3} SDS (c).

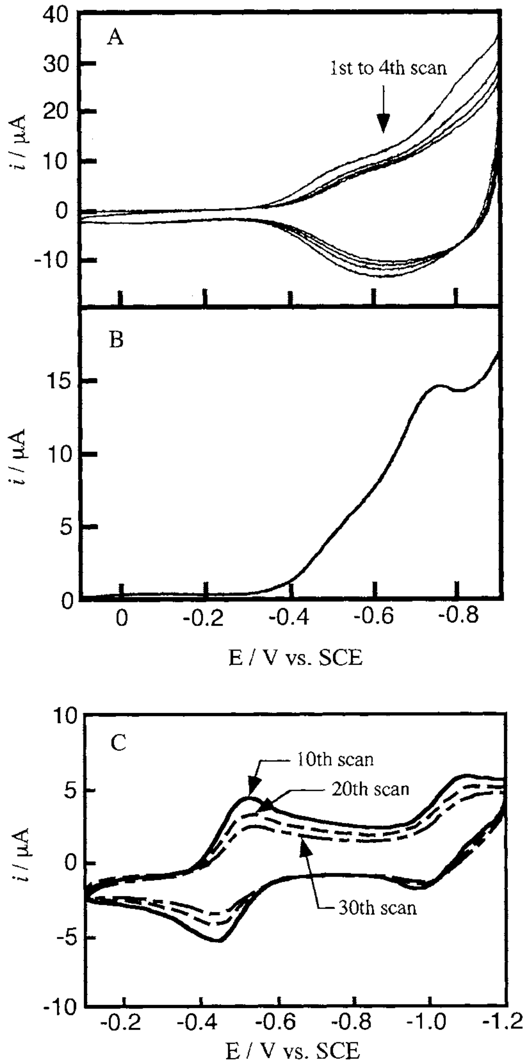

Figure 3. CVs (A) at a scan rate of 100 mV/s and a DPV (B) for cast films of **1** and CVs (C) at a scan rate of 100 mV/s for a cast film of **1**/**2** (molar ratio, 1/19) on BPG electrodes in water containing 0.5 M tetraethylammonium chloride as the supporting electrolyte. Scan rate, pulse amplitude and pulse width for the DPV are 10 mV/s, 50 mV and 50 ms, respectively. Temp:25 °C.

the film state. On the contrary, we could obtain well-defined voltammograms for a **1**/**2** film, leading to the generation of the fullerene dianion; this electrochemical behavior was very similar to that for C_{60}/**2** films on BPG[6]. That is, clear electrochemistry is possible for the fullerene derivative as well as for C_{60}, when the fullerenes are embedded in the lipid films on electrodes.

Electrochemistry for **1** aqueous solutions (Figure 4) was found to be quite different from that of **1** in the film states. Aqueous solution of **1** showed a CV with evident cathodic current near -500 mV; however, anodic current for the solution did not appear. Similar voltammogram was obtained for the solution containing CTAB (line b). These voltammograms are not identical with that of a C_{60}/γ-cyclodextrim complex dissolved in aqueous solution, where the reversible electron transfer reaction of C_{60} appears.[3a] The absence of anodic current may come from dispropomation or non-electrochemical oxidation of the radical anion of **1**. On the

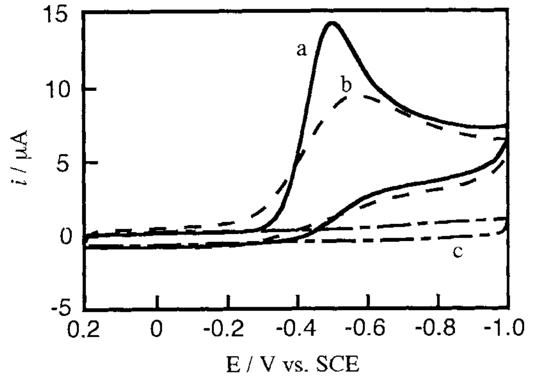

Figure 4. CVs at a bare BPG electrode for aqueous solutions of **1**(1×10^{-4} mol dm^{-3}) containing 0.02 mol dm^{-3} NaBr as the supporting electrolyte in the absence (a) or presence of 0.1 mol dm^{-3} CTAB (b) or SDS (c). Scan rate, 100 mV/s. Temp: 25 °C.

contrary, no faradaic current was observed for **1** in a SDS micellar solution (line c), suggesting that the cationic charge of **1** and CTAB plays a very important role for the electrochemistry of **1** in solution.[6,7] We cannot exclude the possibility of unknown catalytic reactions at the electrode system.

Detailed characterizations including the analysis of electrochemical behavior as well as the aggregated structure of aqueous solutions of **1** are now in progress in our laboratory.

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References and Notes

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4 Anal. Found: C, 82.39; H, 3.73; N, 2.56, Br, 7.17%. Calcd for $C_{76}H_{35}N_2Br + 2.9\ H_2O$: C, 82.36 ; H, 3.71; N, 2.53, Br, 7.21%. ^1H NMR (400 MHz, DMSO-d_6, TMS); δ 1.25 (m, 6H, $C^*C_3(CH_2)_3C_4N^+$), 1.45 (m, 2H, $C^*C_2CH_2C_7N^+$), 1.63 (m, 2H, $C^*C_6CH_2C_3N^+$), 1.77, m, 2H, $C^*CCH_2C_8N^+$), 1.85 (m, 2H, $C^*C_7CH_2C_2N^+$), 2.40 (m, 4H, $C^*CH_2C_9N^+$ and $C^*C_8CH_2CN^+$), 2.90 (s, 3H, NCH_3), 3.01, s, 9H, $N^+(CH_3)_3$), 3.62 (t, 2H, CH_2N^+), 3.98 (t, 1H, C*H), 4.18 (d, 1H, $NC\mathit{H}HC_{60}$), 7.90 (d, 1H, $NCH\mathit{H}C^{60}$). ^{13}C NMR (100 MHz, DMSO-d_6, TMS); δ 21.95, 25.03, 25.69, 26.51, 28.45, 28.65, 52.08, 65.27, 66.94, 98.32, 139.53, 141.17, 141.52, 142.06, 142.61, 143.77, 144.75, 145.49, 146.65.

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