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Electrochemical Formation of Thin Film of Viologen by Disruption of Micelles

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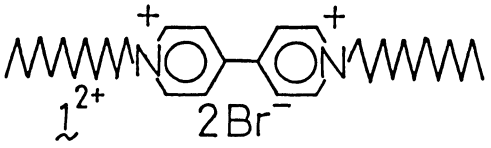
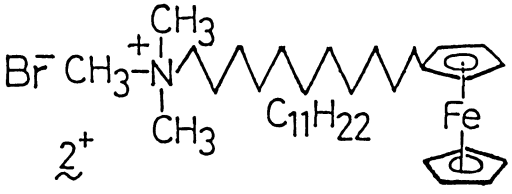
A novel electrochemical method for preparing organic thin film is reported. The thin film of a solubilizate, 1,1'-didodecyl-4,4'-bipyridinium dibromide, on glassy-carbon is prepared by electrochemical disruption of micelles formed by the surfactants with ferrocenyl moiety. The film is consisted of a dense skin region and a fiber-like region about 0.47 μm thickness.

Thin organic films have received considerable interest in recent years because of their potential applications to microelectronic devices such as molecular memory, molecular switch, resists, etc.[1,2] Several techniques for film formation have been presented, which involve Langmuir-Blogett's,[3] vaccum deposition,[4] plasma coating,[5] electrochemical polymerization,[6] and casting[7] methods. Recently, we demonstrated that micelles formed by surfactants with ferrocenyl moiety could be broken up into the monomers when the surfactants were oxidized and that a solubilizate was released from the micelles as the micelles were broken up.[8,9] In our previous paper,[10] an uncharged organic substance, 1-phenylazo-2-naphthol, was found to deposit on an electrode, to form the thin film by making use of this finding of micellar disruption. The purpose of this paper is to see if this new technique of film formation is also used for preparing thin films of charged substances. As a charged substance, 1,1'-didodecyl-4,4'-bipyridinium dibromide (1^{2+}) was used because 1,1'-disubstituted 4,4'- bipyridinium ions known as viologen have been used as candidate for electrochromic displays.[11]

The solubilizate, 1^{2+}, was prepared by the similar method described in the literature,[12] and identified by elemental analysis. Found: C, 62.05; H, 8.82; N, 4.14%. Calcd for $C_{34}H_{58}N_2Br_2$: C, 62.38; H, 8.93; N, 4.28%. The surfactant used was (11-ferrocenylundecyl)trimethylammonium bromide (2^+). The preparation of 2^+ was reported in our previous paper.[8] Electrochemical





measurements were carried out at 25 °C under a nitrogen atmosphere. A glassy-carbon electrode (GC) and a saturated calomel electrode (SCE) were used respectively as working and reference electrodes.

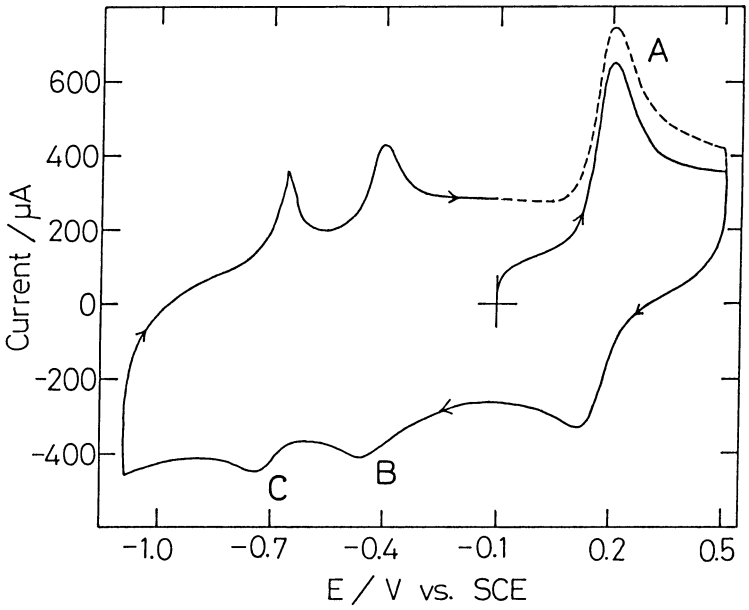


Fig. 1. Cyclic voltammogram for an aqueous solution containing 2.0 mM $\underset{\sim}{2}^{+}$, 0.8 mM $\underset{\sim}{1}^{2+}$, and 0.2 M Li_2SO_4 at a glassy-carbon electrode. Scan rate: 100 mV s^{-1}. Working electrode area: 1.9 cm^2.

Figure 1 shows the cyclic voltammogram for an aqueous solution containing 2.0 mM (1 M = 1 mol dm^{-3}) $\underset{\sim}{2}^{+}$, 0.8 mM $\underset{\sim}{1}^{2+}$, and 0.2 M Li_2SO_4. It exhibits redox waves assignable to (A) $\underset{\sim}{2}^{+}/\underset{\sim}{2}^{2+}$, (B) $\underset{\sim}{1}^{2+}/\underset{\sim}{1}^{+}$, and (C) $\underset{\sim}{1}^{+}/\underset{\sim}{1}^{0}$.[13,14] The half-wave potential for $\underset{\sim}{2}^{+}/\underset{\sim}{2}^{2+}$ was +0.15 V vs. SCE.[15] Almost all of $\underset{\sim}{1}^{2+}$ may be solubilized in the 2^+ micelles, because $\underset{\sim}{1}^{2+}$ is sparingly soluble in water. Most of $\underset{\sim}{2}^{+}$ may exist in the form of micelles with aggregation number of 230, owing to its negligible critical micelle concentration (below 0.1 mM).[8]

A white film was formed on GC by controlled-potential electrolysis of this solution at +0.30 V vs. SCE with stirring the solution. The amount of

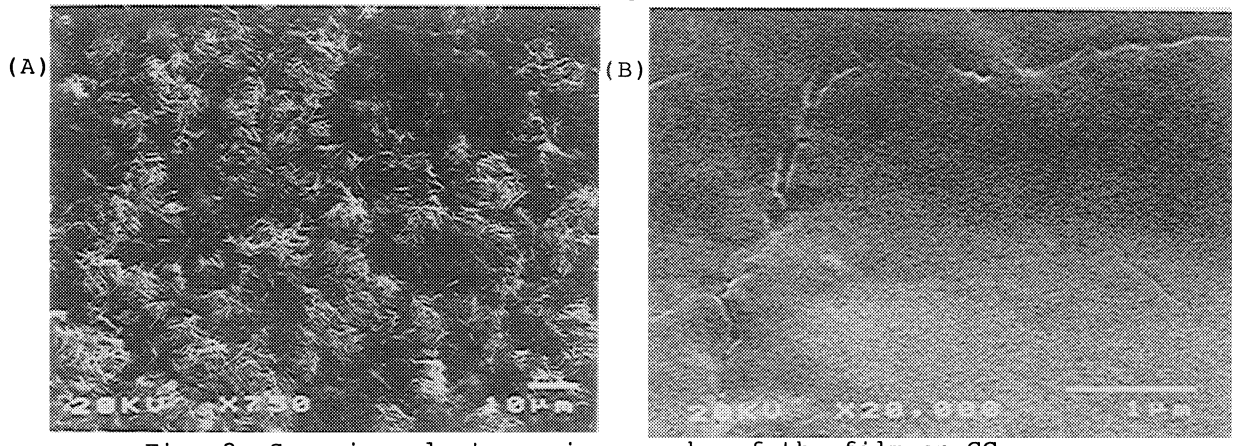


Fig. 2. Scanning electron micrographs of the film on GC.

electricity passed was 0.12 C cm^{-2}. While, no film was formed on GC by immersing GC in the micellar solution without electrolysis.

Scanning electron micrographic and interferometric measurements were carried out to investigate morphology and thickness of the film, respectively. Figure 2A shows a typical scanning electron micrograph of the whole image of the film on GC. A dense skin and a porous fiber-like regions were observed in the film, which correspond to the dark and the light areas in the micrograph, respectively. Under magnification of the dense skin region, it is so smooth that we could not perceive microcrystals forming the region (Fig. 2B). The thickness of the film was determined to be 0.47 μm on average by the usual interference technique.[16)]

Figure 3 shows the absorption spectra of (A) the methanol solution prepared by washing the film and (B) 26 μM $\underset{\sim}{1}^{2+}$ in methanol. The shape and the absorption maximum (263 nm) of spectrum A were the same as those of spectrum B. In the absence of $\underset{\sim}{1}^{2+}$, a film was not formed on GC by the electrolysis. The absorption spectrum of the methanol solution prepared by washing this GC exhibits no absorption peaks as shown in Fig. 3C. These results support that the thin film formed is made of $\underset{\sim}{1}^{2+}$. Furthermore, the film were formed on ITO and Pt electrodes.

Such a film formation may be explained by the following processes: (1) Mass transfer of the $\underset{\sim}{2}^{+}$ micelles containing $\underset{\sim}{1}^{2+}$ from the bulk solution to the electrode. (2) Oxidation of the $\underset{\sim}{2}^{+}$ micelles at the electrode surface. (3) Break-up of the $\underset{\sim}{2}^{+}$ micelles into the corresponding monomers ($\underset{\sim}{2}^{2+}$) and the subsequent release of $\underset{\sim}{1}^{2+}$ from the micelles. (4) Deposition of $\underset{\sim}{1}^{2+}$ on the electrode surface. (5) Mass transfer of $\underset{\sim}{2}^{2+}$ to the bulk solution.

The coverage of deposited $\underset{\sim}{1}^{2+}$, Γ, was 2.5 X 10^{-7} mol cm^{-2} determined by the spectrum A, while the calculated value of Γ, Γ_{calcd}, was 5.6 X 10^{-7} mol cm^{-2}, hence ca. 45% of $\underset{\sim}{1}^{2+}$ solubilized in the $\underset{\sim}{2}^{+}$ micelles deposited on GC. The value of Γ_{calcd} was derived by using the data of the amount of electricity through GC and the number of the $\underset{\sim}{1}^{2+}$ molecules solubilized per micelle.

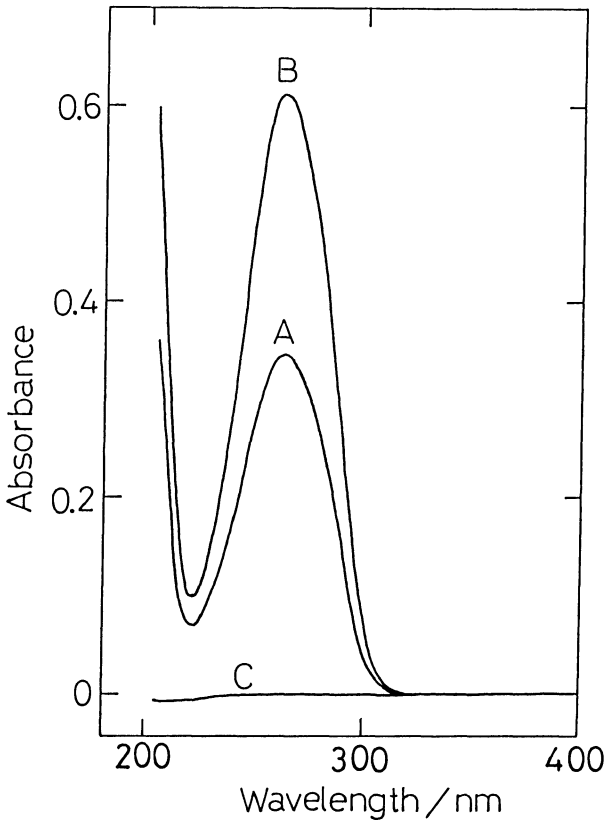


Fig. 3. Electronic absorption spectra of (A) the methanol solution prepared by washing the film and (B) 26 μM $\underset{\sim}{1}^{2+}$ in methanol. (C) shows the spectrum of the methanol solution prepared by washing GC obtained by the electrolysis of the $\underset{\sim}{2}^{+}$ solution not containing $\underset{\sim}{1}^{2+}$.

Present experiments show that such an electrochemical method also serves as a tool for preparing thin films of the charged materials which are soluble in a micellar solution.

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