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Noboru Oyama^a; Takeo Ohsaka^a; Masahiro Nakanishi^a

^a Department of Applied Chemistry for Resources, Tokyo University of Agriculture and Technology Koganei, Tokyo, Japan

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ELECTROCHEMICALLY POLYMERIZED *N,N*- DIMETHYLANILINE FILMS CONTAINING TRIS- (BATHOPHENANTHROLINE DISULFONATO)IRON(II/III) COMPLEXES

NOBORU OYAMA, TAKEO OHSAKA, AND MASAHIRO NAKANISHI

Department of Applied Chemistry for Resources
Tokyo University of Agriculture and Technology
Koganei, Tokyo 184, Japan

ABSTRACT

The electropolymerization of *N,N*-dimethylaniline (DMA) was carried out in an aqueous CF_3COONa solution (pH 1.0) containing DMA in the presence of tris(bathophenanthroline disulfonato)iron(II), $\text{Fe}(\text{bphen})_3^{4-}$. Poly(*N,N*-dimethylanilinium trifluoroacetate) (PDMA) film was formed on electrode surfaces and, at the same time, $\text{Fe}(\text{bphen})_3^{4-}$ ions were stably confined in the formed PDMA film by electrostatic interaction between them and the positively charged quaternary ammonium sites of the PDMA film. The PDMA- $\text{Fe}(\text{bphen})_3^{4-/3-}$ film thus prepared displayed well-defined reversible electroactivity and electrochromic properties ascribable to those of the $\text{Fe}(\text{bphen})_3^{4-/3-}$ couple confined in the film. The PDMA- $\text{Fe}(\text{bphen})_3^{4-}$ film is red, and the PDMA- $\text{Fe}(\text{bphen})_3^{3-}$ film is colorless. The response rate of the color change to a potential pulse was found to be correlated with the kinetic parameters characterizing the rate of the overall charge-transfer reaction at the PDMA- $\text{Fe}(\text{bphen})_3^{4-/3-}$ film-coated electrode, that is, the apparent diffusion coefficient (D_{app}) for the homogeneous charge-transport process within the film and the standard rate constant (k°) of the heterogeneous electron-transfer reaction at the electrode/film interface. For the PDMA- $\text{Fe}(\text{bphen})_3^{4-/3-}$ film with larger k° and D_{app} values, the response rate of the color change was larger. Further, k° , D_{app} , and response rate de-

pended on the concentration (C°) of the $\text{Fe}(\text{bphen})_3^{4-}$ (or $\text{Fe}(\text{bphen})_3^{3-}$) confined in the PDMA film; and at a given film thickness, the lower C° , the higher were k° , D_{app} , and response rate. At a given C° , the thinner the film thickness, the greater was the response rate.

INTRODUCTION

In a series of recent papers [1-8] we reported the preparation of polymer films by electropolymerization of aromatic compounds (e.g., aniline, phenol and their derivatives, polynuclear aromatic compounds), the electrochemical and spectroscopic characterization of the films prepared, and the various functions of the films themselves and/or the film-coated electrodes. More recently, it has been found that the electropolymerization of *N,N*-dialkylaniline derivatives such as *N,N*-dimethylaniline and *N,N*-diethylaniline leads to poly(*N,N*-dimethylanilinium trifluoroacetate) with quaternary ammonium sites in the polymeric backbone and that the resulting polymer films are electroinactive and insoluble in the commonly used organic solvents and H_2O [6, 7, 9]. These polymer films have an anion-exchange character over a wide range of pH, irrespective of the pH of the solution. Further, films coated on electrode surfaces can concentrate multiply-charged anion (e.g., $\text{Fe}(\text{CN})_6^{3-}$, $\text{Mo}(\text{CN})_8^{4-}$) from solutions as dilute as $\sim 10^{-9} M$ and, therefore, possess potential utility for performing electroanalysis in solution.

In the present paper we report the preparation of the "composite" poly(*N,N*-dimethylanilinium trifluoroacetate) (PDMA) film with electroactive and electrochromic properties by the electropolymerization of *N,N*-dimethylaniline (DMA) in the presence of tris(bathophenanthroline disulfonato)iron(II) ion ($\text{Fe}(\text{bphen})_3^{4-}$). It is shown that, during the electrolysis, formation of the PDMA and incorporation of $\text{Fe}(\text{bphen})_3^{4-}$ ions into the formed PDMA film occur concurrently, and consequently, the $\text{Fe}(\text{bphen})_3^{4-}$ (and/or $\text{Fe}(\text{bphen})_3^{3-}$)-containing PDMA "composite" films are prepared on electrode surfaces. In addition, the electrochemical and electrochromic properties of these composite polymer films will be shown.

EXPERIMENTAL

Materials

N,N-Dimethylaniline (DMA) of reagent grade was obtained from Wako Pure Chemical Industries (Osaka, Japan) and was purified by distillation using ordin-

ary techniques. Bathophenanthroline disulfonated ferrous sulfate solution (0.01 M in water) ($(C_{24}H_{14}N_2(SO_3Na)_2)_3 \cdot FeSO_4$, abbreviated $Fe(bphen)_3^{4-}$) was obtained from G.F.S. Chemical Co. (Ohio, U.S.A.). The supporting electrolyte solutions were 0.2 M CF_3COONa (or $NaClO_4$) (Aldrich) adjusted to pH 1.0 with CF_3COOH (or $HClO_4$). Aqueous solutions were prepared from doubly distilled water. Other chemicals were reagent grade and were used as received.

Apparatus and Procedures

A standard three-electrode electrochemical cell was used for all electrochemical experiments. The electrode assembly consists of an In_2O_3 electrode as a working electrode, a sodium chloride saturated calomel electrode (SSCE) as a reference electrode, and a platinum spiral as a counter electrode. The electrochemical polymerization of DMA was carried out by potential-sweep electrolysis and controlled-potential electrolysis. The electrolytic solutions were 0.2 M CF_3COONa (pH 1.0) containing 0.1 M DMA and 0.5-10 mM $Fe(bphen)_3^{4-}$. The thickness of the film prepared on electrodes was controlled by the charge passed during the anodic oxidation of DMA, and typically the films of PDMA (4.8 μm thick) were grown on an electrode by passing 10 C/cm² of charge [6]. The film thicknesses were measured with Surfcom 550A (Surface Texture Measuring Instrument, Tokyo Seimitsu Co.).

The amount (Γ) of $Fe(bphen)_3^{4-}$ (or $Fe(bphen)_3^{3-}$) confined in the films deposited on electrodes was estimated in units of mol/cm² by measuring the area of cyclic voltammograms (for the oxidation-reduction reaction of the confined $Fe(bphen)_3^{4-/3-}$ couple) obtained at a slow potential scan rate (2 mV/s) in a 0.2 M $NaClO_4$ aqueous solution (pH 1.0) [10, 11]. The molar concentration (in units of mol/cm³) of the confined $Fe(bphen)_3^{4-}$ (or $Fe(bphen)_3^{3-}$) was calculated from the Γ value thus obtained by using the dry thickness of the film. Absorption spectra were measured with a Hitachi Spectrophotometer 320. For cyclic voltammetry and normal pulse voltammetry, a home-made instrument was employed along with an X-Y recorder (Graphtec Co., Tokyo) [10, 11]. The estimation of the apparent diffusion coefficient (D_{app}) for the homogeneous charge-transport process within the film and the kinetic parameters (i.e., standard rate constant k^o and transfer coefficient α) of the heterogeneous electron-transfer reaction at the electrode-film interface was conducted according to the conventional analysis of normal pulse voltammograms [10-12]. All experiments were run under a nitrogen atmosphere at laboratory temperature ($25 \pm 1^\circ C$). Potentials were measured and are quoted with respect to SSCE.

RESULTS AND DISCUSSION

Electropolymerization of DMA in the Presence of $\text{Fe}(\text{bphen})_3^{4-}$

The cyclic voltammograms shown in Fig. 1(A) are typical of those obtained for DMA at an In_2O_3 electrode in a 0.2 M CF_3COONa solution (pH 1.0) containing 0.1 M DMA and 5 mM $\text{Fe}(\text{bphen})_3^{4-}$. The anodic peak at ~ 1.1 V vs SSCE corresponds to the oxidation of DMA to the cation radical, $\text{DMA}^{\bullet+}$ [6]. The corresponding cathodic peak is not observed, indicating the fast consumption of the electrogenerated $\text{DMA}^{\bullet+}$ by the subsequent chemical reactions. The anodic peak current corresponding to the oxidation of DMA decreases with each succeeding potential scan. This is due to the formation of the electroinactive PDMA polymer films on electrode surfaces, as reported previously [6, 7].

Note that the response for the dimeric compound (i.e., N,N,N',N' -tetramethylbenzidine) that can be formed by cation radical ($\text{DMA}^{\bullet+}$) coupling with the loss of two protons is not observed [6, 7, 13-15]. This is different from the electropolymerization of DMA in acidic media in the absence of $\text{Fe}(\text{bphen})_3^{4-}$ [6], where the anodic peak corresponding to the oxidation of N,N,N',N' -tetramethylbenzidine was observed at ~ 0.6 V vs SSCE and the corresponding cathodic peak at ~ 0.5 vs SSCE. The cyclic voltammetric response shown in Fig. 1(A) seems to be similar to that obtained for the electropolymerization of DMA in alkaline media in the absence of $\text{Fe}(\text{bphen})_3^{4-}$ [6]. No reasonable explanation for these facts has been given. However, from a phenomenological point of view, the presence of $\text{Fe}(\text{bphen})_3^{4-}$ in the electrolytic solution seems to block the formation of N,N,N',N' -tetramethylbenzidine substantially, and as a result the PDMA formation proceeds more efficiently.

The electrode used in Fig. 1(A) was washed, replaced in the pure supporting electrolytic solution containing no DMA and $\text{Fe}(\text{bphen})_3^{4-}$, and then the cyclic voltammogram was measured. Figure 1(B) shows such a cyclic voltammetric response for the $\text{Fe}(\text{bphen})_3^{4-/3-}$ couple confined in the PDMA film. The PDMA film is substantially electroinactive under the experimental conditions used here [6]. The electrochemically reversible oxidation-reduction response corresponding to the redox reaction of the $\text{Fe}(\text{bphen})_3^{4-/3-}$ couple confined in the PDMA film is almost equal to that obtained for solution-dissolved $\text{Fe}(\text{bphen})_3^{4-/3-}$ couple at an uncoated In_2O_3 electrode (see Fig. 1C). The peak height and wave shape of the cyclic voltammogram remained substantially unchanged after several hours when the electrode potential was scanned between 0.4 and 1.4 V vs SSCE at 50 mV/s. The stable binding of

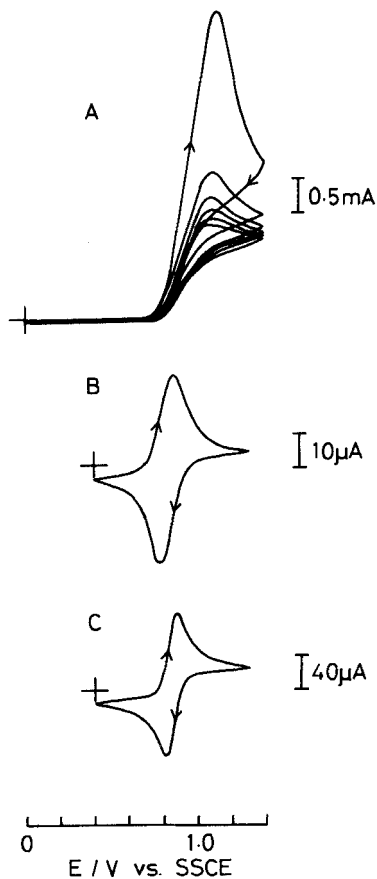
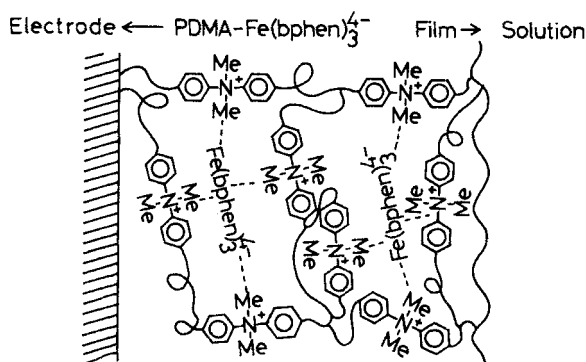
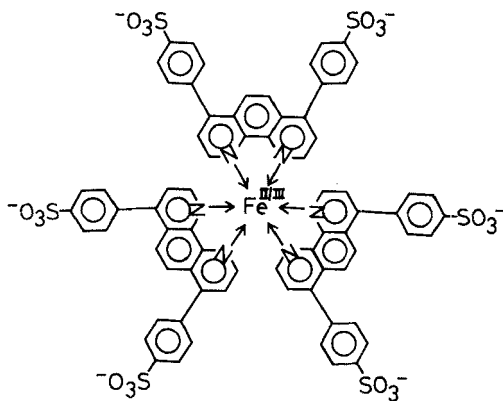


FIG. 1. (A) Cyclic voltammograms of DMA at an In_2O_3 electrode in 0.2 M CF_3COONa aqueous solution (pH 1.0) containing 0.1 M DMA and 5 mM $\text{Fe}(\text{bphen})_3^{4-}$. (B) Cyclic voltammogram obtained when the electrode used in (A) was washed with water and transferred to a 0.2 M NaClO_4 solution (pH 1.0). (C) Cyclic voltammogram obtained at a bare In_2O_3 electrode in 0.2 M NaClO_4 aqueous solution (pH 1.0) containing 5 mM $\text{Fe}(\text{bphen})_3^{4-}$. In every case: scan rate, 50 mV/s; electrode area, 0.25 cm^2 . The arrows indicate the direction of potential scan.



(A)



(B)

FIG. 2. (A) Schematic depiction of the electrostatic binding of $\text{Fe}(\text{bphen})_3^{4-}$ in the PDMA film on electrodes. The symbols \sim , N^+ , and $-\text{Me}$ show the polymeric backbone, the positively charged quaternized ammonium site in the film, and the methyl group, respectively. (B) Structure of the $\text{Fe}(\text{bphen})_3^{4-/3-}$ complex.

the $\text{Fe}(\text{bphen})_3^{4-/3-}$ couple for such long periods can be considered to result from the strong electrostatic interaction between multiply-charged anions (i.e., $\text{Fe}(\text{bphen})_3^{4-}$ and $\text{Fe}(\text{bphen})_3^{3-}$) and the positively-charged sites (i.e., quaternized ammonium sites) of the PDMA film. A schematic depiction of

the electrostatic binding of $\text{Fe}(\text{bphen})_3^{3-}$ in the PDMA film on electrodes is shown in Fig. 2.

Such an electrostatic trapping of highly-charged redox ions into polycationic and polyanionic polymer films on electrodes was originally suggested by us [16-18], and since then, a number of researchers have reported many examples of such electrostatic trapping [19]. Most of such electrostatic trappings previously reported [19] are based on the "two-step method": after the introduction of the electroinactive polymer films with ion-exchange properties onto electrode surfaces by an appropriate procedure (e.g., by dipping an electrode into a polymer solution and then evaporating the solvent in the polymer coating on the electrode), the multiply-charged ionic redox compounds are incorporated into the polymer films by ion exchange. In contrast, the above-mentioned procedure may be regarded as a "one-step method" because the film coating of the electrode surfaces and the trapping of multiply-charged redox compound into the film occur substantially simultaneously.

Homogeneous Charge-Transport Process within the PDMA Films Confining $\text{Fe}(\text{bphen})_3^{3-}$ (or $\text{Fe}(\text{bphen})_3^{4-}$) and Heterogeneous Electron-Transfer Process between Electrode and $\text{Fe}(\text{bphen})_3^{3-}$ (or $\text{Fe}(\text{bphen})_3^{4-}$) Confined in the PDMA Films

Figure 3 shows cyclic voltammograms for the oxidation-reduction of the $\text{Fe}(\text{bphen})_3^{4-/3-}$ couple confined in the PDMA film on an In_2O_3 electrode in a 0.2 M NaClO_4 solution (pH 1.0). Plots of the anodic and cathodic peak currents (i_p^a and i_p^c) vs the square root of the potential scan rate, $v^{1/2}$, were nearly linear from 20 mV/s to 1 V/s, indicating that the charge-transport through the PDMA film is "apparently" diffusional and obeys Fick's law [10, 11, 20]. The cyclic voltammograms in Fig. 3 reflect the overall electrode reaction at the $\text{Fe}(\text{bphen})_3^{4-/3-}$ -containing PDMA film-coated electrode, that is, (1) the homogeneous charge-transport process within the PDMA film containing $\text{Fe}(\text{bphen})_3^{3-}$ (or $\text{Fe}(\text{bphen})_3^{4-}$) and (2) the heterogeneous electron-transfer reaction between the electrode and $\text{Fe}(\text{bphen})_3^{3-}$ (or $\text{Fe}(\text{bphen})_3^{4-}$) confined in the PDMA film (see Fig. 4).

Normal pulse voltammetric experiments [10-12] were carried out in order to examine the overall electrode reaction quantitatively. Figure 5 shows typical normal pulse voltammograms for the oxidation of the $\text{Fe}(\text{bphen})_3^{4-}$ confined in the PDMA film on an In_2O_3 electrode at various sampling times. According to the conventional analysis [10-12] of such normal pulse voltammograms, the apparent diffusion coefficient (D_{app})

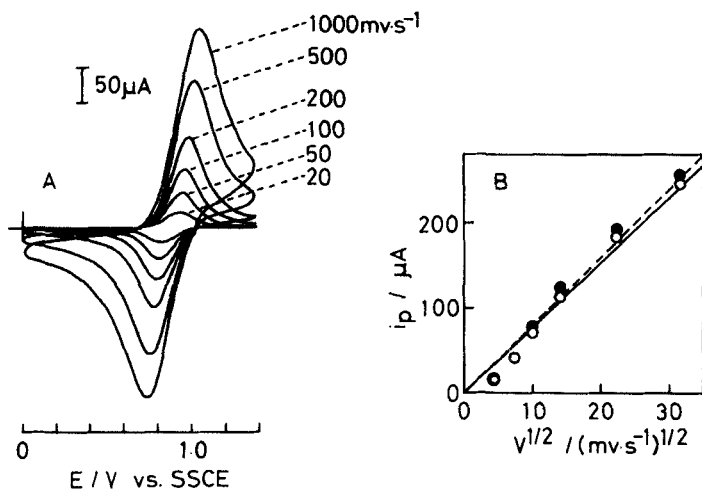


FIG. 3. (A) Cyclic voltammograms for oxidation-reduction of the $\text{Fe}(\text{bphen})_3^{4-/3-}$ redox couple confined in PDMA film on In_2O_3 electrode (area: 0.25 cm^2) in 0.2 M NaClO_4 solution (pH 1.0). The $\text{Fe}(\text{bphen})_3^{4-}$ -containing PDMA film-coated electrode was prepared in the same manner as in Fig. 1. (B) Dependence of the anodic and cathodic peak currents upon $(\text{scan rate})^{1/2}$. (○) Anodic peak currents; (●) cathodic peak currents.

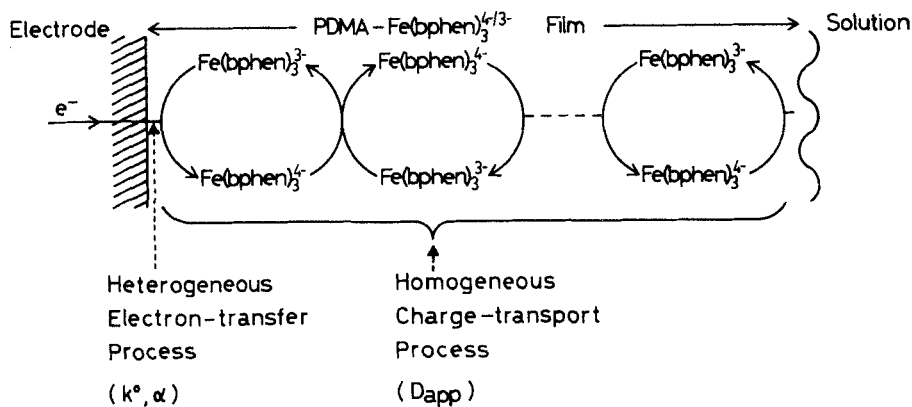


FIG. 4. Schematic depiction of the overall charge-transfer processes on the $\text{Fe}(\text{bphen})_3^{4-/3-}$ -containing PDMA film-coated electrode. k° and α are the standard rate constant and the transfer coefficient, respectively, of the heterogeneous electron-transfer process at the electrode/film interface. D_{app} is the apparent diffusion coefficient for the diffusionlike charge-transport process within the $\text{Fe}(\text{bphen})_3^{4-/3-}$ -containing PDMA film. Note that heterogeneous and homogeneous charge-transfer processes are associated with charge-compensating counterion motion.

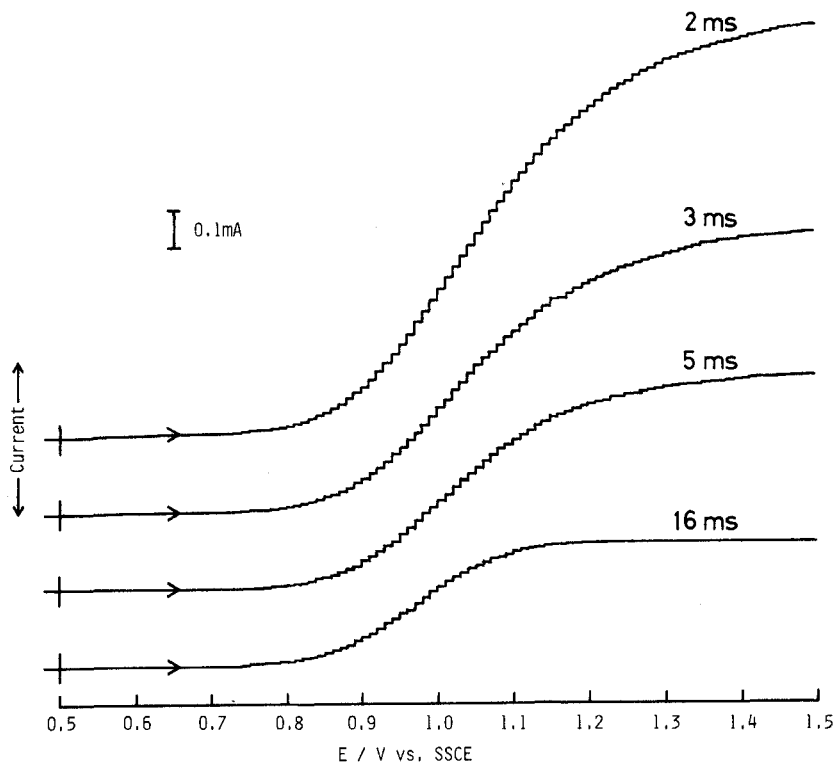


FIG. 5. Typical normal pulse voltammograms for the oxidation of $\text{Fe}(\text{bphen})_3^{4-}$ confined in PDMA film on an In_2O_3 electrode at various sampling times in $0.2\text{ M CF}_3\text{COONa}$ solution (pH 3.0). The concentration of $\text{Fe}(\text{bphen})_3^{4-}$ confined in the PDMA film: 0.23 M . Sampling times are given on each voltammogram. The arrows indicate the direction of the normal pulse voltammetric potential step.

for the charge-transport process within the film and the kinetic parameters (i.e., standard rate constant (k°) and transfer coefficient (α)) of the heterogeneous electron-transfer reaction between the electrode and the bound $\text{Fe}(\text{bphen})_3^{4-}$ species were evaluated (D_{app} from the dependence of the anodic limiting current on the sampling time and k° and α by analysis of the rising part of the current-potential curves shown in Fig. 5). It is apparent from Table 1 that the k° and D_{app} values decrease considerably with increasing concentration (C°) of the $\text{Fe}(\text{bphen})_3^{4-}$ (or $\text{Fe}(\text{bphen})_3^{3-}$) confined

TABLE 1. Dependence of the Standard Rate Constant, k° , and the Transfer Coefficient, α , of Heterogeneous Electron Transfer at the In_2O_3 Electrode/PDMA Film Interface and the Apparent Diffusion Coefficient, D_{app} , for the Process of Charge Transport within the PDMA- $\text{Fe}(\text{bphen})_3^{4-}$ (or $\text{Fe}(\text{bphen})_3^{3-}$) Films on the Concentration, C° , of $\text{Fe}(\text{bphen})_3^{4-}$ (or $\text{Fe}(\text{bphen})_3^{3-}$) Confined in the PDMA Film and the Thickness, ϕ , of the PDMA Film^a

C°, M	$\phi, \mu\text{m}$	$k^\circ, \text{cm/s}^1$	α_a^b	α_c^b	$D_{\text{app}}^{a,c}, \text{cm}^2/\text{s}$	$D_{\text{app}}^{c,c}, \text{cm}^2/\text{s}$
0.021	1.63	6.7×10^{-5}	0.73	0.23	3.1×10^{-9}	5.3×10^{-9}
0.070	1.06	5.7×10^{-5}	0.74	0.23	2.6×10^{-9}	2.7×10^{-9}
0.23	0.35	2.4×10^{-5}	0.71	0.25	2.0×10^{-10}	1.3×10^{-10}

^aSupporting electrolyte: 0.2 M CF_3COONa (pH 3.0).

^b α_a : anodic transfer coefficient; α_c : cathodic transfer coefficient.

^c D_{app}^a : D_{app} for anodic process; D_{app}^c : D_{app} for cathodic process.

in the PDMA film. For example, when C° is increased from 0.021 to 0.23 M, k° decreases from 6.7×10^{-5} to 2.4×10^{-5} cm/s and D_{app}^a from 3.1×10^{-9} to 2.0×10^{-10} cm²/s. This is remarkable since the rate of the overall charge-transfer reaction at the $\text{Fe}(\text{bphen})_3^{4-/3-}$ -containing PDMA film-coated electrode can be expected to be controlled arbitrarily by changing C° . The values of D_{app}^a and D_{app}^c are almost the same at any given C° . The values of α_a and α_c are independent of C° , and the sum of α_a and α_c is almost equal to 1, as expected from the theory [20] for simple heterogeneous electron-transfer reactions.

Electrochromic Properties of PDMA- $\text{Fe}(\text{bphen})_3^{4-/3-}$ Thin Film

PDMA- $\text{Fe}(\text{bphen})_3^{4-/3-}$ thin film displayed electrochromic character: the PDMA- $\text{Fe}(\text{bphen})_3^{4-}$ film is red and the PDMA- $\text{Fe}(\text{bphen})_3^{3-}$ film is colorless. From the data shown in Fig. 6 it is apparent that the electrochromic character of the PDMA- $\text{Fe}(\text{bphen})_3^{4-/3-}$ film originates from that of the $\text{Fe}(\text{bphen})_3^{4-/3-}$ couple (i.e., $\text{Fe}(\text{bphen})_3^{4-}$ is red and $\text{Fe}(\text{bphen})_3^{3-}$ is colorless). A reversible color change of the film between red and colorless was observed when the electrode potential was cycled between 0.0 and 1.4 V vs SSCE.

As Fig. 7 shows, both oxidation (decolorization process) and reduction (coloration process) currents showed a very rapid response to the potential step, and the color change was complete within 200 ms. The rate of the color

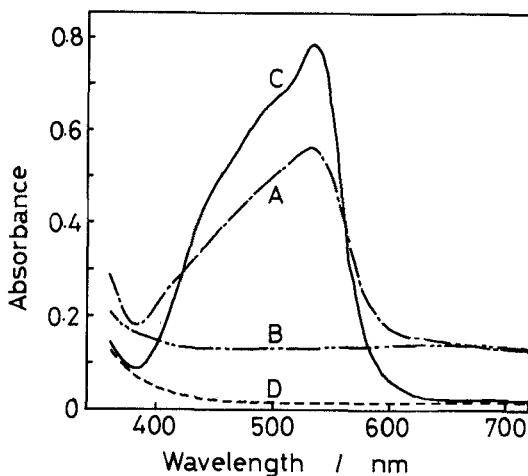


FIG. 6. Absorption spectra of (A) $\text{Fe}(\text{bphen})_3^{4-}$ -containing PDMA film on In_2O_3 electrode, (B) $\text{Fe}(\text{bphen})_3^{3-}$ -containing PDMA film on In_2O_3 electrode, (C) $\text{Fe}(\text{bphen})_3^{4-}$ solution, and (D) $\text{Fe}(\text{bphen})_3^{3-}$ solution.

TABLE 2. Response of the Color Change of PDMA- $\text{Fe}(\text{bphen})_3^{4-/3-}$ Film-Coated In_2O_3 Electrodes to a Potential Pulse between 0 and 1.4 V vs SSCE^a

$C^c, {}^b M$	$\phi, {}^c \mu\text{m}$	Response time of color change, s	
		Decolorization process ^d	Coloration process ^e
0.088	0.06	0.12	0.12
0.53	0.06	0.20	0.20
1.09	0.06	1.1	1.3
0.22	0.42	0.85	0.77
0.30	0.32	1.4	1.1
0.42	0.50	4.2	3.8

^aSupporting electrolyte: 0.2 M NaClO_4 (pH 1.0).

^bVolume concentration of $\text{Fe}(\text{bphen})_3^{4-}$ (or $\text{Fe}(\text{bphen})_3^{3-}$) confined in the PDMA films.

^cDry thickness of the PDMA- $\text{Fe}(\text{bphen})_3^{4-}$ (or $\text{Fe}(\text{bphen})_3^{3-}$) films.

^dAnodic process.

^eCathodic process.

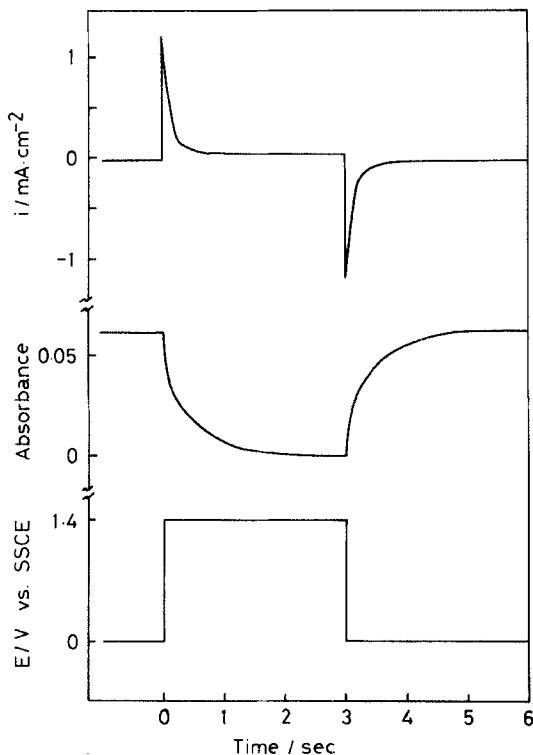


FIG. 7. The responses of current and absorbance at 540 nm of the $\text{Fe}(\text{bphen})_3^{4-/3-}$ -containing PDMA film-coated In_2O_3 electrode to a potential pulse between 0 and 1.4 V vs SSCE in 0.2 M NaClO_4 solution (pH 1.0). The concentration of the $\text{Fe}(\text{bphen})_3^{4-}$ confined in the PDMA film (thickness: $0.06 \mu\text{m}$): 0.53 M. Electrode area: 0.25 cm^2 .

change of the PDMA- $\text{Fe}(\text{bphen})_3^{4-/3-}$ films was found to depend on the concentration (C°) of $\text{Fe}(\text{bphen})_3^{4-}$ confined in the PDMA at a constant film thickness (see Table 2). Further, such a C° dependence of the rate of the color change parallels the C° dependences of k° and D_{app} . Thus, the attainment of a faster color change needs higher k° and D_{app} values. In other words, the lower C° is, the larger are k° and D_{app} and, thus, the faster is the color change. Lowering C° , on the contrary, weakens the contrast in color. Thus, the optimum C° should be sought for the practical use of the PDMA- $\text{Fe}(\text{bphen})_3^{4-/3-}$ film coated electrode as an electrochromic material. A further examination concerning this point is outside the scope of this study. However, it is worth-

while to note that even at C° as low as 0.005 M, a distinct color change is still recognizable to the naked eye. From Table 2, it is also apparent that the color change is faster for the thinner film.

CONCLUSION

It was found that, by the electropolymerization of DMA in the presence of $\text{Fe}(\text{bphen})_3^{4-}$, a PDMA film is formed on the electrode surface and, at the same time, $\text{Fe}(\text{bphen})_3^{4-/3-}$ anions are stably confined in this PDMA film by electrostatic interaction between $\text{Fe}(\text{bphen})_3^{4-}$ anions and the positively-charged quaternary ammonium sites of the PDMA film. The PDMA- $\text{Fe}(\text{bphen})_3^{4-/3-}$ film thus prepared displayed well-defined reversible electroactivity and the electrochromic properties. The electrochemical and electrochromic properties of PDMA- $\text{Fe}(\text{bphen})_3^{4-/3-}$ film prepared by the above-mentioned "one-step method" are superior to those of film prepared by the "two-step method," which showed ill-defined electroactivity and electrochromic properties. This example shows that the electropolymerization procedure used in this study may be useful as a new approach to the preparation of new "composite" polymer films and to a wide variety of modifications of electrode surfaces [19]. Studies with this objective are in progress.

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