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Effects of Supporting Electrolyte and pH on Charge Transport within Electropolymerized Poly(*o*-phenylenediamine) Films Deposited on Graphite Electrodes

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The homogeneous charge-transport process within electropolymerized electroactive poly(*o*-phenylenediamine) (PPD) films on graphite electrodes in various supporting electrolytic solutions (i.e., NaCl, $NaClO_4$, Na_2SO_4, LiCl, CF_3COONa, tetraethylammonium chloride (TEACl) and sodium *p*-toluenesulfonate (NaPTS)) at various pH's was examined by potential-step chronoamperometry and chronocoulometry. The overall charge-transport process was found to obey Fick's diffusion laws and thus the apparent diffusion coefficients (D_{app}) for the diffusion-like charge-transport process were estimated. The D_{app} values for the oxidation and reduction processes (i.e., D^a_{app} and D^c_{app}) were almost the same at pH 1.0 irrespective of the thickness of PPD films and were actually independent of the supporting electrolytes except for NaPTS. As pH was increased from 1 to 7, the D^a_{app} values decreased slightly from ca. 5.6×10^{-8} to 1.6×10^{-8} $cm^2 s^{-1}$ and the D^c_{app} values did more largely from ca. 5.6×10^{-8} to 2.2×10^{-9} $cm^2 s^{-1}$. This behavior was essentially common to all the supporting electrolytes examined. Such pH dependences of D^a_{app} and D^c_{app} are discussed on the basis of the fact that the charge-transport process within PPD films involves the intrinsic electron-transfer process between adjacent electroactive sites as well as the proton addition-elimination process, the charge-compensating counterion motion, the motion of solvent and the segmental motion of the polymeric chain. Especially, it is demonstrated that in this system the proton addition-elimination process must necessarily occur in order for the charge-transport process to proceed.

A large amount of work is devoted at present to a new class of organic polymers (in most cases obtained as films on electrode surfaces) produced by electropolymerization of various kinds of aromatic compounds (e.g., NH_2 and/or OH groups-containing aromatic compounds, heterocyclic aromatic compounds, polynuclear aromatic compounds and vinyl group-containing aromatic compounds), owing to the large field of potential applications of the resulting polymers themselves as well as the "composite" electrode materials composed of electrode substrates and the polymer films.[1] The property-dependent applications of electropolymerized film-coated electrodes have been suggested in various fields.[1]

On the other hand, some basic problems concerning electropolymerizations and the resulting films remain to be fully understood, e.g., the chemical composition and structure of films, the conductivity of films, the mechanism of electropolymerization and the rate of charge (ion and/or electron) transport through films. Especially in the case where polymer film-coated electrodes are used under a "wet" state (e.g., as electron-transfer catalysts (or mediators) for the redox reaction of a dissolved redox species) the rate of charge transport within films is one of the important factors which define the usefulness of film-coated electrodes as materials or devices with desired properties.

This paper deals with a potential-step chronoamperometric and chronocoulometric study of the charge transport within electroactive poly(*o*-phenylenediamine) (PPD) films which can be prepared by electropolymerization of *o*-phenylenediamine in an acidic solution.[2] There are relatively many papers concerning the functions of PPD films, e.g., protection against photo-corrosion of n-type semiconductor electrodes,[3] anticorrosion of metals,[4] pH response,[5–7] permselectivity,[8] and electrochemical diode property.[9] Such different properties of PPD films depend on the electrolytic conditions in their preparation. Recently, we[10] have examined the kinetics of the electrode reaction of PPD films deposited on graphite electrodes in an aqueous supporting electrolytic solution, and reported that the heterogeneous electron-transfer reaction obeys the conventional Butler-Volmer equation and the homogeneous charge-transport process within films can be treated as a Fickian diffusion process. Also, we have revealed that the PPD prepared from an acidic aqueous solution is a ladder polymer with phenazine rings.[2] The rates of the charge-transport within PPD films in aqueous solutions containing various supporting electrolytes at various pH's have been estimated as apparent diffusion coefficients (D_{app}) for the diffusion-like charge transport within the films. The results reveal that the proton addition-elimination process involved in the oxidation-reduction reaction of the PPD film as well as the motion of supporting electrolyte ions which is necessarily, for charge neutrality, coupled to electron transfer are closely related to the rate of the overall charge-transport process within the films.

Experimental

Materials. *o*-Phenylenediamine (Tokyo Kasei Co.) was purified three times by recrystallization from water and dried under reduced pressure. Sodium chloride (NaCl), sodium sulfate (Na_2SO_4), sodium perchlorate ($NaClO_4$) (Wako Chemical Co.), lithium chloride (LiCl), tetraethylammonium chloride (TEACl), sodium *p*-toluenesulfonate (PTSNa) (Kanto Chemical Co.), and sodium trifluoroacetate

(CF_3COONa) (Aldrich), which were reagent grade, were used as supporting electrolytes without further purification. In each supporting electrolytic solution, the concentration of supporting electrolyte was 0.2 M (1M=1 mol dm^{-3}). At pH<2, no buffer solutions were used and at pH 3—7, a citric acid-disodium hydrogenphosphate buffer (20 mM) was used. The basal plane pyrolytic graphite (BPG) (Union Carbide Co.) disk electrodes (area: 0.2 cm^2) were prepared and mounted into glass tube with heat-shrinkable polyolefin tube. Fresh electrode surfaces were produced by cleaving the disk with a scalpel. Aqueous solutions were prepared from doubly distilled water. All other chemicals were reagent grade and were used as received.

Preparation of Poly(*o*-phenylenediamine) (PPD) Films. The PPD films were prepared on BPG or In-Sn oxide conducting glass (ITO) electrodes by scanning (at 50 mV s^{-1}) the electrode potential between −0.8 and 1.2 V vs. SSCE in a 0.5 M Na_2SO_4-H_2SO_4 solution (pH 1.0) containing 50 mM *o*-phenylenediamine, as previously described.[2] The films prepared on BPG (or ITO) electrodes were rinsed with H_2SO_4 solution (pH 1.0) and then with distilled water, and used for further study without removing them from the electrode surfaces. The thicknesses of the films were controlled by the amount of charge passed during the electrochemical polymerization. The film thicknesses (ϕ) were measured with a Surfcom 550 A (Surface Texture Measuring Instrument, Tokyo Seimitsu Co.) as previously described.[2,9]

Apparatus and Procedures. A standard three-electrode electrochemical cell was used for all electrochemical experiments. The electrode assembly consisted of a bare or PPD-coated BPG (or ITO) as working electrode, a sodium chloride saturated calomel electrode (SSCE) as reference electrode and a spiral platinum electrode as counter electrode.

The surface concentration (Γ_p°) of the electroactive site in PPD films was estimated in mol cm^{-2} by measuring the area of cyclic voltammograms (for the oxidation-reduction reaction of PPD films themselves) obtained at scan rate of 2 mV s^{-1} in a 0.2 M $NaClO_4$-$HClO_4$ solution (pH 1.0). The molar concentration (C_p°) (in mol cm^{-3}) of the electroactive site was calculated from the Γ_p° thus obtained using the thicknesses (ϕ) of the films. It was found that there is a linear relationship between ϕ and Γ_p° at $\Gamma_p^\circ < 1.0 \times 10^{-7}$ mol cm^{-2} and that the C_p° values are $(7.8 \pm 0.8) \times 10^{-4}$ mol cm^{-3} irrespective of ϕ at $\phi < 2 \times 10^{-4}$ cm.

For cyclic voltammetry, potential-step chronoamperometry and potential-step chronocoulometry, a home-made instrument was employed along with a Nicolet digital oscilloscope (model 3091) and X-Y recorder (Graphtec Co., Tokyo). Positive feedback circuitry was employed to compensate the resistances (these were typically ca. 20—50 Ω) associated with the polymer coatings as much as possible. All experiments were run under nitrogen atmosphere at laboratory temperature (25±1 °C). Potentials were measured and are quoted with respect to SSCE.

Results

Figure 1 shows a typical cyclic voltammogram representing the electrochemical response for the oxidation-reduction reaction of the PPD film deposited on BPG electrode in a 0.2 M $NaClO_4$-$HClO_4$ aqueous solution (pH 1.0). The wave shape resembles that for the ordinary electrode reaction of a solution-phase redox species at an uncoated electrode,[11] that is, the wave has "diffusion tails" and its shape is unsymmet-

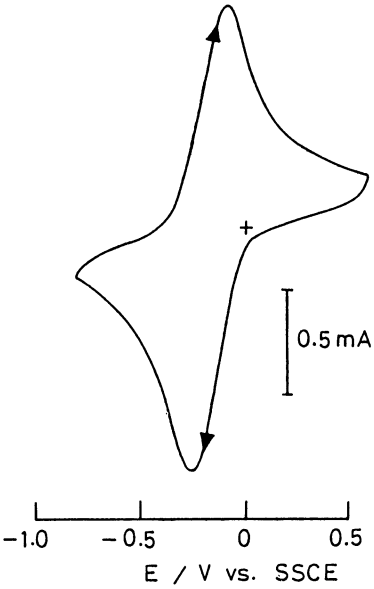


Fig. 1. A typical cyclic voltammogram for the oxidation-reduction reaction of the PPD film deposited on BPG electrode in a 0.2 M $NaClO_4$+$HClO_4$ solution (pH 1.0) at 500 mV s^{-1}. Film thickness: 1.9 µm. C_p°: 7.8×10^{-4} mol cm^{-3}.

Table 1. Apparent Diffusion Coefficients for the Diffusional Charge-Transport Process within PPD Films in a 0.2 M $NaClO_4$+$HClO_4$ Solution (pH 1.0)[a]

ϕ[b] µm	$10^8 \Gamma_p^\circ$[c] mol cm^{-2}	Reaction[d]	Method[e]	$10^8 D_{app}$ cm^2 s^{-1}
0.19±0.02	1.5±0.2	Ox	CA	2.3±0.2
		Ox	CC	1.9±0.2
		Red	CA	2.6±0.3
		Red	CC	3.0±0.4
0.38±0.04	3.0±0.3	Ox	CA	1.7±0.2
		Ox	CC	1.6±0.2
		Red	CA	1.9±0.2
		Red	CC	2.3±0.2
0.59±0.02	4.6±0.2	Ox	CA	2.9±0.3
		Ox	CC	2.6±0.3
		Red	CA	3.2±0.3
		Red	CC	3.3±0.3
1.08±0.02	8.4±0.2	Ox	CA	3.6±0.4
		Ox	CC	3.2±0.3
		Red	CA	3.1±0.3
		Red	CC	3.1±0.3
1.40±0.03	10.9±0.3	Ox	CA	3.2±0.3
		Ox	CC	2.9±0.3
		Red	CA	2.8±0.3
		Red	CC	2.9±0.3

a) Values averaged with several electrodes. b) Film thicknesses. c) Surface concentrations of the electroactive site in PPD films. d) Ox: oxidation process, Red: reduction process. e) CA: potential-step chronoamperometry, CC: potential-step chronocoulometry.

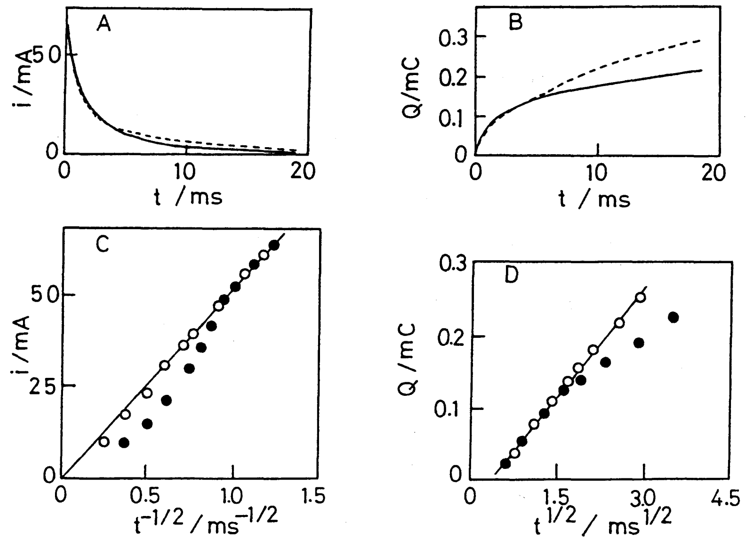


Fig. 2. (A) Potential-step chronoamperometric current–time responses for the oxidation and reduction processes of the PPD film. (B) Potential-step chronocoulometric charge–time responses corresponding to the current–time responses in A. (C) Cottrell plots of i vs. $t^{-1/2}$ for the data in A. (D) Cottrell plots of Q vs. $t^{1/2}$ for the data in B. Supporting electrolyte: 0.2 M $NaClO_4$+$HClO_4$ (pH 1.0). Film thickness: 0.20 μm. C_p^o: 7.8×10^{-4} mol cm^{-3}. (----, ○): reduction process; (——, ●): oxidation process. The electrode potentials were stepped from −0.50 V to 0.40 V vs. SSCE and from 0.40 V to −0.50 V vs. SSCE for the oxidation and reduction processes, respectively.

Table 2. Apparent Diffusion Coefficients for the Diffusional Charge-Transport Process within PPD Films in Various Supporting Electrolytic Solutions of pH 1.0[a,b]

Supporting electrolyte	$10^8 \Gamma_p^o$ [c)] mol cm^{-2}	$10^4 C_p^o$ [f)] mol cm^{-3}	Reaction[d)]	Method[e)]	$10^8 D_{app}$ cm^2 s^{-1}
$NaClO_4$	2.8±0.3	7.8±0.8	Ox	CA	3.2±0.4
			Ox	CC	2.9±0.3
			Red	CA	4.0±0.4
			Red	CC	3.7±0.4
NaCl	2.8±0.3	7.8±0.8	Ox	CA	6.0±0.7
			Ox	CC	5.7±0.6
			Red	CA	4.8±0.5
			Red	CC	4.6±0.5
CF_3COONa	2.3±0.3	6.4±0.7	Ox	CA	4.1±0.4
			Ox	CC	3.4±0.4
			Red	CA	4.0±0.4
			Red	CC	3.5±0.4
Na_2SO_4	2.2±0.2	6.1±0.6	Ox	CA	4.4±0.4
			Ox	CC	4.0±0.4
			Red	CA	6.0±0.6
			Red	CC	5.9±0.6
PTSNa	1.7±0.2	4.7±0.5	Ox	CA	1.7±0.2
			Ox	CC	2.1±0.2
			Red	CA	2.5±0.2
			Red	CC	2.2±0.2

a) Values averaged with several electrodes. b) Film thicknesses (ϕ) of the PPD films: 0.36±0.03 μm. c—e) see Table 1 for the definitions of column headings. f) Volume concentrations of the electroactive site in PPD films were calculated as Γ_p^o/ϕ.

ric, although in general electropolymerized electroactive polymer films display the complicated redox responses as being reported for the electropolymerized polyaniline film.[12,13] Based on our recent studies[2] concerning the structure of the PPD film, the electroactive sites in PPD films are considered to be phenazine rings.

In order to estimate the kinetic parameters characterizing the charge-transport process within the films, the potential-step chronoamperometric and chronocoulometric responses for the oxidation and reduction of the PPD films were examined. A typical example of such an examination is shown in Fig. 2. The Cottrell plots (i.e., i-$t^{-1/2}$ and Q-$t^{1/2}$ plots) are linear at short times. The deviation from the linearity indicates that currents in longer times become controlled by finite diffusion.[14,15] These facts indicate that the charge-transport process within the PPD films follows Fickian diffusion laws. Thus, the slopes of the linear plots shown in Fig. 2 yielded the apparent diffusion coefficients (D_{app}) for the diffusion-like charge-transport process within the films. The obtained D_{app}'s are summarized in Tables 1 and 2 and Fig. 3. The D_{app}

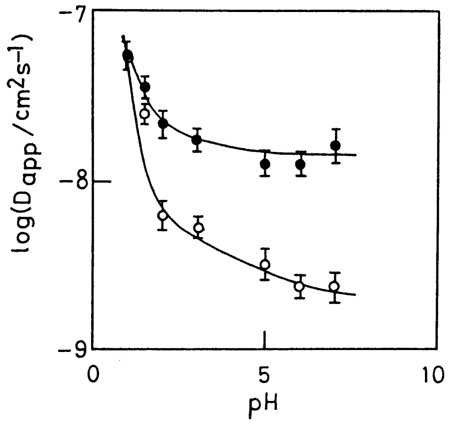


Fig. 3. pH dependences of D^{a}_{app} and D^{c}_{app}. (●): for the oxidation process (D^{a}_{app}); (○): for the reduction process (D^{c}_{app}). Supporting electrolyte: 0.2 M NaCl. At pH<2, no buffer solutions were used and at pH 3—7 a citric acid–disodium hydrogenphosphate buffer (20 mM) was used.

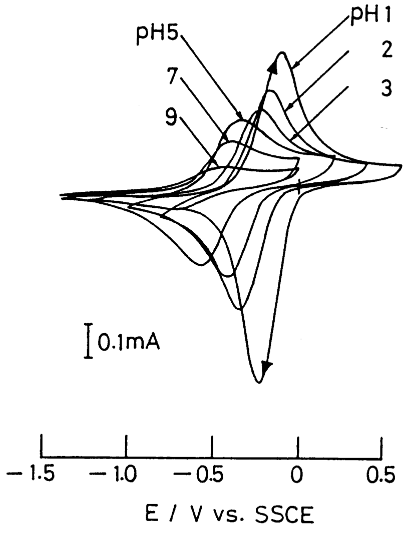


Fig. 4. Typical cyclic voltammograms for the oxidation–reduction reaction of the PPD film in buffered aqueous solutions of various pH's. Supporting electrolyte: 0.2 M NaCl. Film thickness: 0.36 μm. Scan rate: 200 mV s⁻¹.

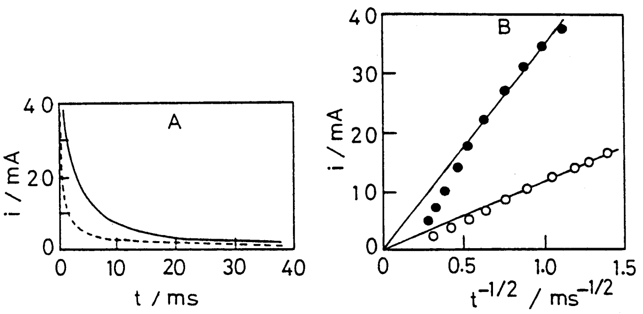


Fig. 5. (A) Typical potential-step chronoamperometric current–time curves for the oxidation and reduction processes of the PPD film deposited on BPG electrode in a 0.2 M NaCl+20 mM CH_3COONa/CH_3COOH solution (pH 5.0). (B) Cottrell plots of i vs. $t^{-1/2}$ for the data in A. The electrode potentials were stepped from −0.8 V to 0.10 V vs. SSCE and from 0.0 V to −0.90 V vs. SSCE for the oxidation and reduction processes, respectively. Film thickness: 0.34 μm. C°_{p}: 7.8×10^{-4} mol cm^{-3}. (----, ○): reduction process; (——, ●): oxidation process.

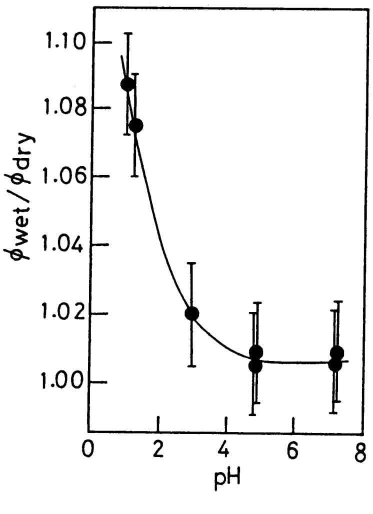


Fig. 6. pH dependence of the swelling of PPD films. The PPD films were prepared on ITO electrodes by a potential-sweep electrolysis between −0.6 and 1.2 V vs. SSCE at 50 mV s⁻¹ in 0.5 M Na_2SO_4 solution (pH 1.0) containing 50 mM *o*-phenylenediamine. The dry thicknesses (ϕ_{dry}) of the PPD films: 0.32 μm. The wet thicknesses (ϕ_{wet}) were measured after the immersion of each of the PPD film-coated electrodes in 0.2 M NaCl solutions of various pH's for an hour. The citric acid-phosphate solution (20 mM) was used as a buffer solution except at pH 1.0.

Table 3. Apparent Diffusion Coefficients for the Diffusional Charge-Transport Process within PPD Films in Various Supporting Electrolytic Solutions of pH 5.0[a,b)]

Supporting electrolyte	$10^8\,\Gamma^{\circ}_{\mathrm{p}}$ c)	$10^4\,C^{\circ}_{\mathrm{p}}$ f)	Reaction d)	Method e)	$10^8\,D_{\mathrm{app}}$
	$\mathrm{mol\,cm^{-2}}$	$\mathrm{mol\,cm^{-3}}$			$\mathrm{cm^2\,s^{-1}}$
$NaClO_4$	2.7±0.3	7.9±0.7	Ox	CA	2.9 ±0.3
			Ox	CC	2.5 ±0.3
			Red	CA	0.43±0.04
			Red	CC	0.37±0.04
NaCl	2.0±0.2	5.9±0.6	Ox	CA	3.6 ±0.4
			Ox	CC	2.9 ±0.3
			Red	CA	0.37±0.04
			Red	CC	0.29±0.03
CF_3COONa	2.1±0.2	6.2±0.6	Ox	CA	2.7 ±0.3
			Ox	CC	2.4 ±0.2
			Red	CA	0.42±0.04
			Red	CC	0.31±0.03
Na_2SO_4	1.9±0.2	5.6±0.5	Ox	CA	2.5 ±0.3
			Ox	CC	2.2 ±0.2
			Red	CA	0.62±0.06
			Red	CC	0.50±0.05
PTSNa g)	1.9±0.2	5.6±0.5	Red	CA	0.21±0.02
			Red	CC	0.19±0.02
LiCl	2.4±0.2	7.1±0.7	Ox	CA	1.7 ±0.2
			Ox	CC	1.2 ±0.1
			Red	CA	0.27±0.03
			Red	CC	0.21±0.02
TEACl	2.2±0.2	6.5±0.6	Ox	CA	2.2 ±0.2
			Ox	CC	1.5 ±0.2
			Red	CA	0.24±0.02
			Red	CC	0.19±0.02

a) Values averaged with several electrodes. b) Film thicknesses (ϕ) of the PPD films: 0.34±0.03 μm. c—f) see Tables 1 and 2 for the definitions of column headings. g) For the oxidation process, the linear i-$t^{-1/2}$ and Q-$t^{1/2}$ plots were not obtained.

values (i.e., $D^{\mathrm{a}}_{\mathrm{app}}$ and $D^{\mathrm{c}}_{\mathrm{app}}$) for anodic and cathodic processes in an acidic solution are almost the same irrespective of the film thicknesses and supporting electrolytes examined.

Figure 4 shows typical cyclic voltammograms of the PPD film at different pH's. As reported previously,[2)] the anodic and cathodic peak potentials ($E^{\mathrm{a}}_{\mathrm{p}}$ and $E^{\mathrm{c}}_{\mathrm{p}}$) shifted to negative values with increasing pH and the slopes of the formal redox potential ($E^{\circ\prime}$), estimated as the average of $E^{\mathrm{a}}_{\mathrm{p}}$ and $E^{\mathrm{c}}_{\mathrm{p}}$ values, vs. pH plots were about $-60\ \mathrm{mV\,pH^{-1}}$ in the examined range of pH 1 to 7. This suggests that the overall electrode reaction of the PPD film is a H^+/e^- (1/1) reaction. Then, the peak currents decreased slightly with an increase in pH. This was found to be not due to the decrease of the electroactive site number (N_{active}) in the PPD film, but due to the decrease in the apparent rate of the diffusion-like charge transport in the film. The concentrations (C°_{p}) of the electroactive site were almost constant ($7.8\times10^{-4}\ \mathrm{mol\,cm^{-3}}$) within experimental error irrespective of pH in the examined range of pH 1 to 7. In this case, N_{active}, i.e., C°_{p} values at various pH's were determined by the graphical integration of the cyclic voltammograms as described in Experimental section. Such a decrease of peak currents with increasing pH was found to be clearly reflected in the potential-step chronoamperometric (and chronocoulometric) behavior and as a result in the D_{app} values. The results are shown in Fig. 3. It is apparent that as pH increases both $D^{\mathrm{a}}_{\mathrm{app}}$ and $D^{\mathrm{c}}_{\mathrm{app}}$ decrease. Further, we can see that the difference between $D^{\mathrm{a}}_{\mathrm{app}}$ and $D^{\mathrm{c}}_{\mathrm{app}}$ values becomes larger with increasing pH. A typical example of the potential-step chronoamperometric data demonstrating the largely different D_{app} values for the oxidation and reduction processes at pH 5.0 is shown in Fig, 5. The slope of the i vs. $t^{-1/2}$ plot for the oxidation process is significantly larger than that for the reduction process, and thus in contrary to the D_{app}'s obtained in more acidic solutions (e.g., at pH 1.0) the $D^{\mathrm{a}}_{\mathrm{app}}$ value is much larger than the $D^{\mathrm{c}}_{\mathrm{app}}$ value. The related data are summarized in Table 3.

pH dependence of the swelling of PPD films was examined by measuring the wet thickness (ϕ_{wet}) of the films swollen in 0.2 M NaCl aqueous solutions of various pH's. The result is shown in Fig. 6. The $\phi_{\mathrm{wet}}/\phi_{\mathrm{dry}}$ values (ϕ_{dry}: dry thickness) decreased largely with an increase in pH in the range of pH 1 to 3, and at higher pH's they decreased slightly with increasing pH. This behavior is associated with the protonation of PPD film, as mentioned below.

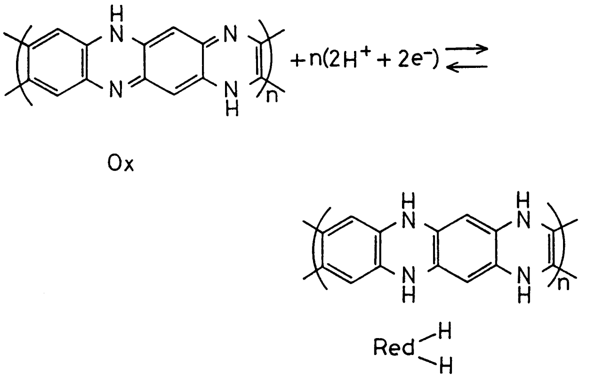
Discussion

From Table 1, it is apparent that $\Gamma^{\circ}_{\rm p}$'s are proportional to ϕ. This indicates that $C^{\circ}_{\rm p}$ values which are estimated as $\Gamma^{\circ}_{\rm p}/\phi$ are constant irrespective of ϕ, that is, the distribution of the electroactive sites in the PPD films is homogeneous. Further, we can see that the values of $D^{\rm a}_{\rm app}$ and $D^{\rm c}_{\rm app}$ are actually independent of ϕ in the examined range of ϕ from 0.19 to 1.4 μm and the $D^{\rm a}_{\rm app}$ and $D^{\rm c}_{\rm app}$ values are almost the same ($(2.7\pm 1.1)\times 10^{-8}$ cm^2 s^{-1}).

Table 2 shows the $D_{\rm app}$ values measured in different supporting electrolytic solutions at pH 1.0. The $\Gamma^{\circ}_{\rm p}$ values seem to slightly change with supporting electrolytes, probably suggesting the partially inhomogeneous distribution of the electroactive sites and the formation of electroinactive regions. Similar results have been also observed for other polymeric film-coated electrodes.[16,17] $D^{\rm a}_{\rm app}\approx D^{\rm c}_{\rm app}$ for a given supporting electrolyte. The $D_{\rm app}$'s obtained in $NaClO_4$, NaCl, CF_3COONa, and Na_2SO_4 electrolytic solutions are almost the same and those in PTSNa solution seem to be a little smaller. This may reflect the different rates of the diffusional motion of electrolytic ions which is necessarily coupled to electron transfer, as can be expected from the Stokes radii ($\gamma_{\rm s}$) of the electrolytic ions used: $\gamma_{\rm s}$ (PTS$^-$)$>\gamma_{\rm s}$ (Na$^+$)$\approx\gamma_{\rm s}$ (CF_3COO^-)$\approx\gamma_{\rm s}$ (SO_4^{2-})$>2\ \gamma_{\rm s}$ (Cl$^-$)$\approx 2\gamma_{\rm s}$ (ClO_4^-).[18]

Table 3 shows the $D_{\rm app}$'s obtained in various supporting electrolytes containing 20 mM CH_3COONa/CH_3COOH buffer solution (pH 5.0). For all the supporting electrolytes examined, $D^{\rm a}_{\rm app}$'s are largely different from $D^{\rm c}_{\rm app}$'s. For example, in the case of NaCl and TEACl electrolytes $D^{\rm a}_{\rm app}$'s are about one order of magnitude larger than $D^{\rm c}_{\rm app}$'s. This remarkable fact demonstrates the significantly different rates of the homogeneous charge transports within the films during the reduction and oxidation processes, and seems to be associated with the low concentration (i.e., 10^{-5} M) of hydrogen ion. The more detailed pH responses of $D^{\rm a}_{\rm app}$ and $D^{\rm c}_{\rm app}$ values are shown in Fig. 3. Both $D^{\rm a}_{\rm app}$'s and $D^{\rm c}_{\rm app}$'s decrease with increasing pH and the degree of the decrease is different each other: As pH was increased from 1 to 7, $D^{\rm a}_{\rm app}$'s decreased from ca. 5.6×10^{-8} to 1.6×10^{-8} cm^2 s^{-1} and $D^{\rm c}_{\rm app}$'s from 5.6×10^{-8} to 2.2×10^{-9} cm^2 s^{-1}. Such essentially different pH dependences of $D^{\rm a}_{\rm app}$ and $D^{\rm c}_{\rm app}$ may be ascribable to the fact that a proton addition-elimination process is involved in the homogeneous charge-transport process in the PPD films which can be regarded as a homogeneous oxidation-reduction process between electroactive sites, as mentioned below.

On the basis of the fact that PPD is a ladder polymer with phenazine rings[2] and that the slope of the $E^{\circ\prime}$ .vs. pH plot is ca. −60 mV pH^{-1} in the range of pH 1—7, and with the assumption that the protonation constant (p$K_{\rm a}$) of PPD is ca. 1 based on the p$K_{\rm a}$ values of phenazine (p$K_{\rm a_1}$=1.2 and p$K_{\rm a_2}$=−4.3),[19,20] the heterogeneous electron-transfer reaction of PPD in aqueous solutions of pH ca. 1—7 may be written as:



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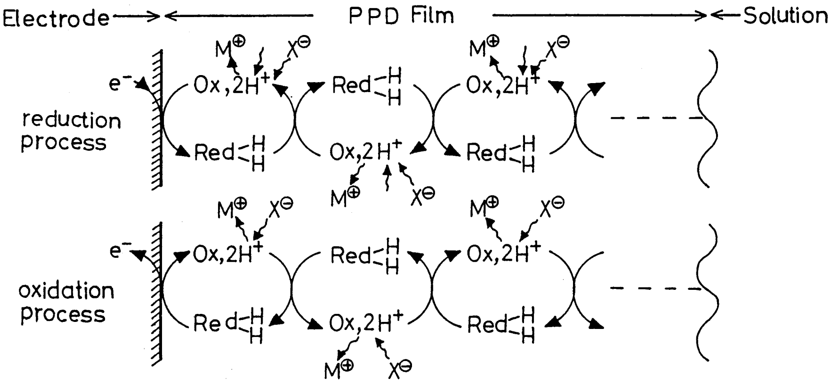

Fig. 7. Schematic depiction of homogeneous charge-transport process within PPD films on electrodes. The symbols Ox and Red$<^{\rm H}_{\rm H}$ represent the oxidized and reduced forms (see text), respectively, of the PPD, and M$^\oplus$ and X$^\ominus$ indicate supporting electrolytic cations and anions, respectively. H$^+$ is hydrogen ion. The symbol —▸ shows the diffusional motion of H$^+$, M$^\oplus$ and X$^\ominus$. The symbols ✕ and ✕ show the homogeneous oxidation-reduction (electron self-exchange) reaction between adjacent electroactive sites.

From the analogy with the heterogeneous electron-transfer reaction (Eq. 1), the mechanism of the homogeneous charge (ion and electron)-transport process within solvent-swollen PPD films undergoing electrolysis (i.e., oxidation and reduction of the electroactive sites) can thus be schematically represented as in Fig. 7. The charge-transport process is considered to involve the intrinsic electron-transfer process between adjacent electroactive sites, the proton addition–elimination process, the charge-compensating counterion motion, the motion of solvent and the segmental motion of the polymeric chain. The charge-transport rate, which will be determined by only the slower of these various processes, is characterized by the D_{app}'s mentioned throughout the paper.

The $D^{\mathrm{a}}_{\mathrm{app}}$'s tend to decrease slightly with increasing pH, especially in the range of pH between 1 and ca. 2 and are almost constant at pH 2—7. This may be explained as follows: The pK_{a} of PPD may be assumed to be ca. 1 as mentioned above. Thus, the degree of the protonation of PPD is thought to change with pH in the pH range where the decreasing of $D^{\mathrm{a}}_{\mathrm{app}}$ with an increase in pH was observed. Further, the swelling of the PPD film is associated with the protonation: The higher the degree of the protonation of PPD is, the larger is the swelling of its film (see Fig. 6). In a more swollen film, the motions of supporting electrolytic ions and solvents and/or the segmental motion of polymeric chains become easier and as a result larger $D^{\mathrm{a}}_{\mathrm{app}}$ values are obtained at lower pH's.

The same explanation seems to be also applicable to the decreasing of $D^{\mathrm{c}}_{\mathrm{app}}$'s with increasing pH. However, in this case, another important factor should be taken into account. That is to say, in order for the charge-transport process during the reduction process to proceed more rapidly, hydrogen ions are necessary to be sufficiently present in the vicinity of the oxidized sites (symbolized by "Ox" in Fig. 7). The apparent rate of the charge transport during the reduction process should decrease with decreasing the concentration of hydrogen ion. Thus, the $D^{\mathrm{c}}_{\mathrm{app}}$ values decrease with increasing pH.

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