



Electrosynthesis of conducting polymer films from the azo dye methoxy red

H. H. REHAN*

Chemistry Department, College of Education for Girls, Malaz, Riyadh 11417, PO Box 27104,
Kingdom of Saudi Arabia

(*address for correspondence: Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt)

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Abstract

Anodic polymerization of the azo dye methoxy red (4-methoxybenzene azo-1,3-diaminobenzene) on platinum electrodes in 1 M HCl in 50% v/v ethanol/water was found to yield thin and stable polymeric films. The films were electroactive in acidic solutions and the activity diminished as the acidity decreased. The pair of symmetrical redox peaks at a formal redox potential, $(E^\circ)_{\text{pH}=0} = 0.61$ V vs SCE, with a Nernstian slope $dE/dpH = 0.06$ V, is attributed to a 1:1 proton + electron elimination (on oxidation)/addition (on reduction) at the amino/imino linkages which connect the aromatic nuclei. Chronocoulometric plots indicated that the transport of the solvated protons, and probably Cl^- ions, through the film is the rate-determining step of the above redox processes. The rate of electron transfer reactions of the redox couple $[\text{Fe}(\text{CN})_6]^{3-/4-}$ on poly-methoxy red-covered platinum electrodes decreased by a factor of more than two orders of magnitude, compared to the bare electrodes.

1. Introduction

Aromatic amine-based conducting polymers, especially polyanilines, are currently receiving attention [1–10]. This is because of their easy synthesis routes, the stability of the polymers against air and wet environments and the high electrical conductivity and capacitance of the oxidized forms. Polyaromatic amines can be formed either chemically via oxidation with oxidizing reagents, such as perchlorates [3, 8–10], or by anodic polarization [1, 2, 4–7]. The polymerization mechanism, involves the generation of reactive radical cations which, on coupling in a head-to-tail version with other radical cations or monomer molecules, yield more reactive dimers. The dimers and thereafter the trimers and oligomers repeat the oxidation and coupling steps until polymeric chains are formed [6, 10–12]. Generally, the electroactivity of polyaromatic amines requires the presence of protons in the medium, where electrons and protons must be exchanged during the redox processes, with switching in conductivity of the polymer (reduced form \equiv insulator and oxidized form \equiv conducting) [11, 13, 14]. It is clear that the domain of application of poly-aromatic amines expands when the monomer structure involves other reactive functional groups, such as hydroxyl, carboxyl, amino or azo group. Beside being a strong chromophoric group, the azo group may be involved in metal chelation. Very few aromatic amines containing azo group in their structures have been electropolymerized successfully to the corresponding conducting polymers [15–17].

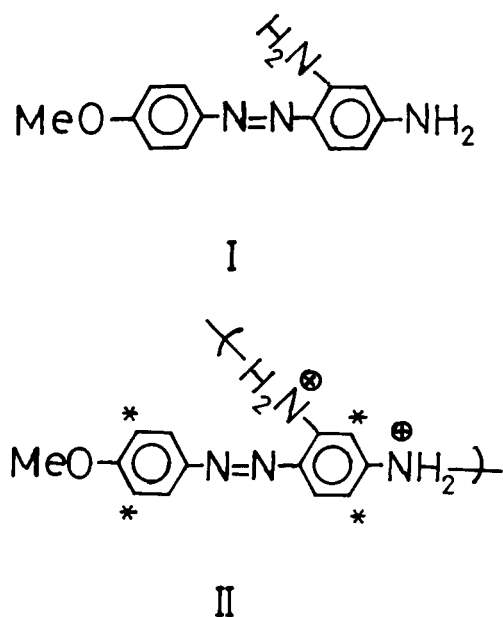
In the present study, anodic polymerization of methoxy red (4-methoxybenzene azo-1,3-diaminobenzene) on platinum electrodes in 1 M HCl in 50% v/v ethanol/water was done by cyclic voltammetry and the resulting polymer films were studied in acid chloride solutions.

2. Experimental details

Methoxy red (4-methoxybenzene azo-1,3-diaminobenzene), species **I**, was extra pure (>99.7%, Tokyo Kasei, Japan) and used without further purification. The chemicals: hydrochloric acid, potassium chloride and potassium hexacyanoferrate (**II**) were analytical grade (BDH, England). Triply distilled water was used for preparation of all solutions. Pure nitrogen gas (>99.9%) was used for deaeration of solutions before running the experiments. The working electrode was a platinum disc electrode of apparent area, about 0.125 cm^2 , and the counter electrode was a platinum sheet ($2 \text{ cm} \times 3 \text{ cm}$). The potential was measured and referred to a saturated calomel electrode (SCE). All experiments were conducted at 30°C . The electrochemical measurements were carried out on a computer-controlled potentiostat (AG&G PAR, model 273A).

Cyclic voltammetry was employed for the anodic polymerization. The polymerization solution was 0.05 M methoxy red + 0.1 M HCl dissolved in a 50% v/v ethanol/water medium. For IR analysis and conductivity, sufficient amounts of polymethoxy red were pre-

pared on platinum sheets (2 cm × 3 cm) by potential cycling from 0.0 to 1.0 V at a scan rate 0.1 V s⁻¹ for about 30 min. The experiment was repeated several times until enough polymer had been collected. IR spectra were recorded for the monomer and the as-formed polymer in KBr pellets. The electrical conductivity of pressed discs of the polymer was determined by a two-probe method using a digital electrometer (Keithley Instruments, model 614). The electroactivity of polymethoxy red was studied in acid chloride solutions of various pH, namely, 0.02, 0.60, 1.35 and 2.45, at a constant ionic strength of unity using HCl and KCl.



3. Results and discussion

3.1. Electropolymerization of methoxy red

Figure 1 shows the repetitive cyclic voltammograms (CVs) for the oxidative polymerization of methoxy red in alcoholic HCl. The oxidation peak at about 0.72 V is typical for the oxidation of primary aromatic amines [11, 15–18]. On repeating the scan, the magnitude of this peak decreases and a pair of redox peaks at about 0.5 V starts to appear and grows. This behaviour is attributed to the deposition and growth of an electroactive layer on the electrode surface. Following the regime of anodic polymerization of aromatic amines, the oxidation of methoxy red via NH_2 moiety leads to a head-to-tail dimerization with removal of protons. The head-to-tail coupling leads ultimately to the formation of the polymer through a progressively more facile oxidation of the dimer, trimer, tetramer, etc., and the consequent coupling and deprotonation. The decrease in the oxidation peak with the number of cycles and the slow growth of the redox peaks, indicate that the behaviour of the growing electroactive polymer film is predominantly inhibitive towards the polymerization process. The inhibition behaviour of the growing polymer film does not allow the preparation of thick layers. Previous trials to electropolymerize a variety of azo compounds lead to the same results [15–17, 19, 20]. It seems to be a rather general trend that the polymerization of structurally complicated compounds leads to thin inhibitive films. The inhibition action is due to the poor electronic conductivity of the films or/and the much lower diffusion coefficient of the reacting species through the films. The amount of polymethoxy red deposited as a function

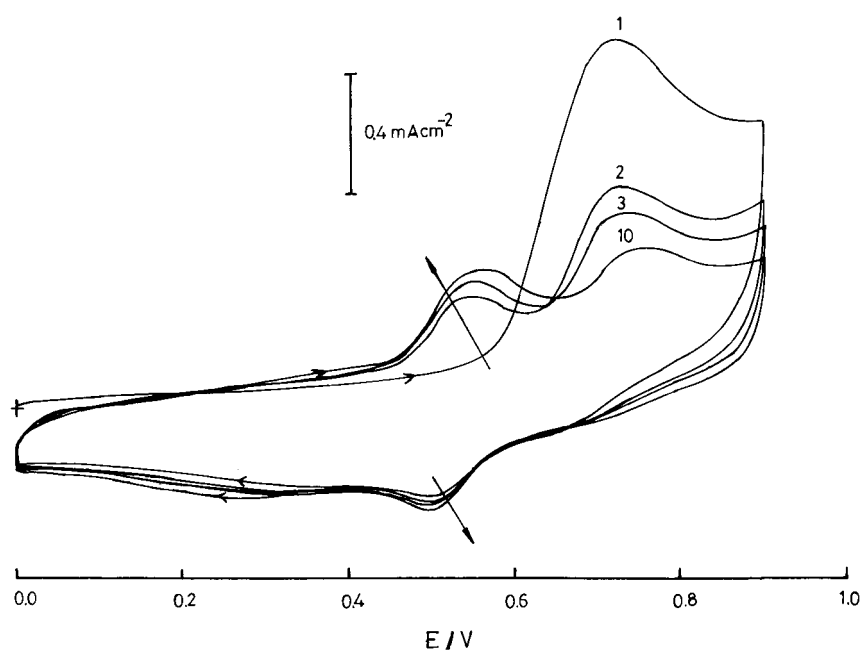


Fig. 1. Repetitive cyclic voltammograms for the oxidation of 0.05 M methoxy red + 0.1 M HCl in 50% ethanol/water. Scan rate 0.1 V s⁻¹. Numbers refer to the scan number and arrows indicate direction of change as scan rate increases.

of the number of cycles, N , or the final potential, E_f , was estimated from the amount of the redox charge, q_{redox} . For this purpose, the polymer-covered electrode was washed by 1 M HCl and transferred to a fresh 1 M HCl solution, where q_{redox} was estimated from the CV in the potential range 0.0–0.8 V. Figure 2 shows CVs for the redox processes of polymethoxy red films formed by 20 cycles at different E_f values. The origin of the redox peaks will be discussed in Section 3.3. The dependence of q_{redox} on E_f and N is shown in Figure 3. The increase in E_f leads to an increase in q_{redox} up to 0.9 V, then further E_f increase causes a slight decrease in q_{redox} . Thus, $E_f = 0.9$ V seems to be the optimum final potential for the electropolymerization of methoxy red in alcoholic HCl solutions. Increasing the number of cycles leads to an increase in q_{redox} up to $N = 20$, then further increase in N has a negligible effect.

3.2. Characterization of polymethoxy red films

Polymethoxy red films were insoluble in water, ethanol, methanol, acetone, methyl cyanide, carbon disulfide and carbon tetrachloride. Under the optical microscope, the as-formed films appeared reddish brown, amorphous and compact. The average electrical conductivity of pressed discs of polymethoxy red was about $70 \mu\text{S cm}^{-1}$ and 0.9 mS cm^{-1} for the reduced and oxidized forms, respectively. The reduced and oxidized forms were obtained by holding the potential after formation for about 10 min at 0.0 and 0.8 V, respectively, before collecting the polymer. To make a comparison with the best aromatic amine-based conducting polymer, namely, polyaniline, the conductivity of polyaniline was 10^{-3} – $10^{-1} \text{ S cm}^{-1}$ for the oxidized form and 10^{-7} – 10^{-4}

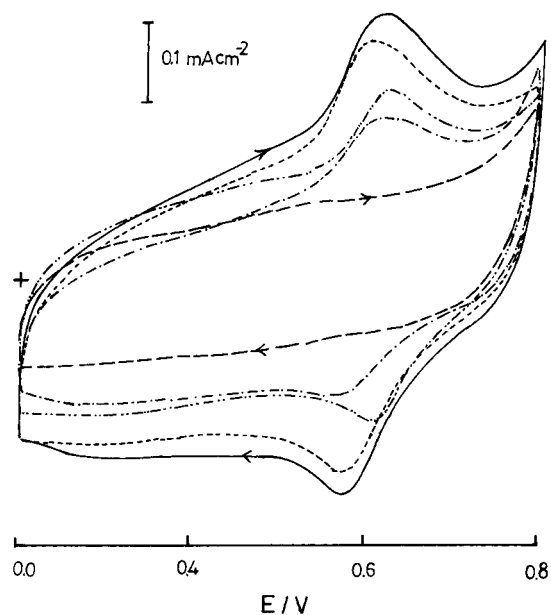


Fig. 2. Cyclic voltammograms for the redox processes of polymethoxy red films formed by 20 cycles at different final potential values, E_f , in 1.0 M HCl. E_f values are: (---) 0.7, (- · - ·) 0.8, (—) 0.9, (---) 1.05 and (- - -) 1.2 V. Scan rate 0.1 V s^{-1} .

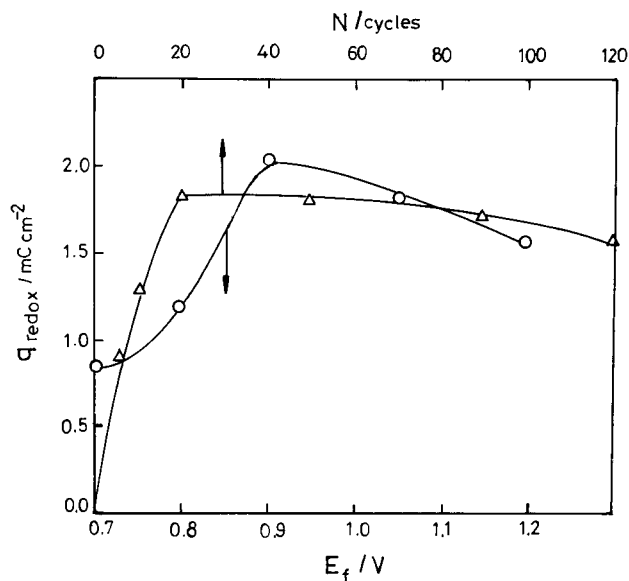


Fig. 3. Dependence of the redox charge, q_{redox} , for polymethoxy red on the polymerization conditions; (O) Final potential at $N = 20$ and (Δ) Number of cycles, N , at $E_f = 1.2$ V. Solution is 1.0 M HCl.

S cm^{-1} for the reduced form, depending on the preparation and doping methods [21–24].

The significant IR bands for the as-formed polymethoxy red are given in Table 1. The bands at 3410 – 3200 cm^{-1} due to N-H stretching for the monomer were replaced by a broad multiband peak at 3500 – 3350 cm^{-1} for the polymer. This is attributed to the transformation of the primary amine in the monomer to the secondary amine in the polymer, as usually observed for aniline-based conducting polymers [15, 16, 18, 25, 26]. The bands at 1320 – 1235 cm^{-1} , due to $\text{C}_{\text{aromatic}}-\text{N}$ stretching of secondary amine, together with the band at 1645 cm^{-1} , due to $\text{C}_{\text{aromatic}}-\text{N}$ stretching (absent for the monomer), confirm the presence of the linkage $\text{C}=\text{N}=\text{C}$ in the polymer [15, 16, 18, 25]. The presence of the methoxy group in the polymer was confirmed by the stretching bands of the $\text{C}_{\text{aryl}}-\text{O}-\text{C}_{\text{aliphatic}}$ linkage at 1255 and 1045 cm^{-1} . The bands at 1460 – 1435 cm^{-1} of $\text{N}=\text{N}$ stretching confirm the retention of the azo group after polymerization. According to IR data, species II is the proposed polymeric unit for poly-methoxy red,

Table 1. Assignment of IR data for methoxy red and polymethoxy red

Vibration mode*	Wave number/ cm^{-1}	
	Polymethoxy red	Methoxy red
(N-H) _s	3500–3350	3410, 3320, 3200
(C-H) _s	2980	2980
(C=C) _s	1590, 1570, 1465	1595, 1580, 1460
(C=N) _s	1645	—
(C-N) _s	1320, 1240	1310, 1235
(N=N) _s	1455, 1435	1460, 1430
(C-O-C) _s	1255, 1045	1255, 1040
(C-H) _b	950, 840	950, 840

* Subscripts 's' and 'b' refer to the stretching and bending modes of vibration, respectively

where the asterisks denoted the probable positions for the propagation of polymerization.

3.3. Electroactivity of polymethoxy red films

After polymer formation, the electrodes were transferred to a test solution for study of the electroactivity by cyclic voltammetry. The poly-methoxy red-covered electrodes showed a pair of redox peaks in acid chloride solutions at $\text{pH} < 3$, while the redox peaks disappeared completely in 1 M KCl. Thus, protons are essential for electroactivity of polymethoxy red. The dependence of the redox processes on pH is shown in Figure 4. It is clear that the magnitude and the position of the peaks depend on pH. As pH increases, the magnitude of the peak diminishes and the peak potential, E_p , shifts to less anodic values. The increase in peak current, i_p , for the anodic and cathodic peaks with pH decrease indicates that the kinetics of the oxidation and reduction processes depend on the concentration of H^+ ions in solution. In other words, the transport of protons is involved in the rate-determining step of the redox processes. As can be seen in Figure 5, E_p decreases linearly with pH increase, with a slope $dE_p/d\text{pH} = 0.060 \text{ V}$ and 0.064 V for the anodic and cathodic peaks, respectively. This indicates that the electroactivity of polymethoxy red involves a proton + electron elimination in the oxidation processes and a proton + electron addition in the reduction process. The situation is

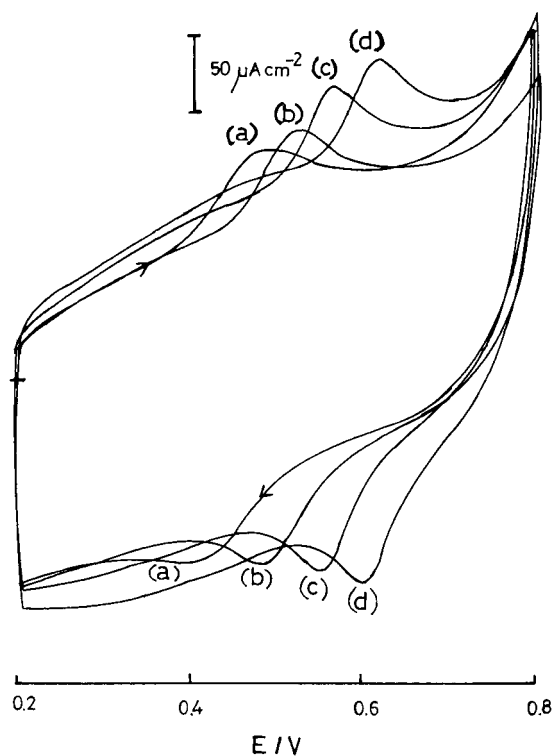


Fig. 4. Cyclic voltammograms for the redox processes of polymethoxy red films in acid chloride solutions of different pH: (a) 2.45, (b) 1.35, (c) 0.60 and (d) 0.02. Films were formed by 20 cycles at $E_r = 1.2 \text{ V}$. Scan rate 0.1 V s^{-1} .

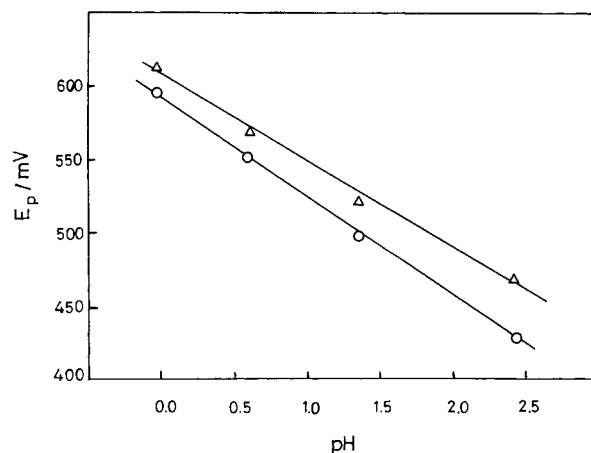


Fig. 5. Dependence of the peak potential, E_p , for the redox processes of polymethoxy red films on pH. (Δ) Anodic E_p and (\circ) cathodic E_p . Details are given in Figure 4.

usually met in the examination of the electroactivity of aromatic amine-based conducting polymers such as polyanilines [6, 13, 16, 27, 28]. The behaviour is attributed to the transformation of the protonated amino linkages into protonated imino linkages on oxidizing the polymer, and vice versa on reducing the polymer. Previous studies on aromatic amine-based conducting polymers showed that not only protons are exchanged but also anions, to compensate for the extra charge involved in the capacitive processes [14, 28, 29]. A formal redox potential, E° , for the redox processes of polymethoxy red in acid chloride solutions was estimated as: $E^\circ = (E_p^a + E_p^c)/2 = 0.61 \text{ V}$ vs SCE. E° values for poly-*p*-aminoazo-benzene [15] and 4(5-chloro-2-pyridylazo-1,3-diaminobenzene [16] in the same solution were 0.52 and 0.30 V, respectively. It should be mentioned that the electroactivity of poly-methoxy red films in acid chloride solutions is quite stable, in the potential range 0.0–0.8 V, against repetitive cycling, that is, the films do not suffer from degradation.

Figure 6 shows the effect of scan rate on the redox peaks of polymethoxy red films in 1 M HCl. It is clear that the peak current increases as the scan rate, ν , increases, while the peak potential is practically insensitive to the change in ν and the peak separation, ΔE_p , is nearly 0.00 V. Within the tested ν range (0.005 – 0.12 V s^{-1}), i_p varies linearly with ν as can be seen in Figure 7. This indicates that the electroactivity of polymethoxy red films in 1 M HCl is similar to that of surface-attached electroactive sites [30, 31]. Similar behaviour was reported for many electroactive polymer films [15, 16, 32, 33].

3.4. Diffusion characteristics of polymethoxy red films

The diffusion characteristics of polymethoxy red films were studied by chronocoulometry. Regardless of the nature or the mechanism of the mass and charge transport processes, which control the kinetics of the redox processes, it is customary to use a large-potential

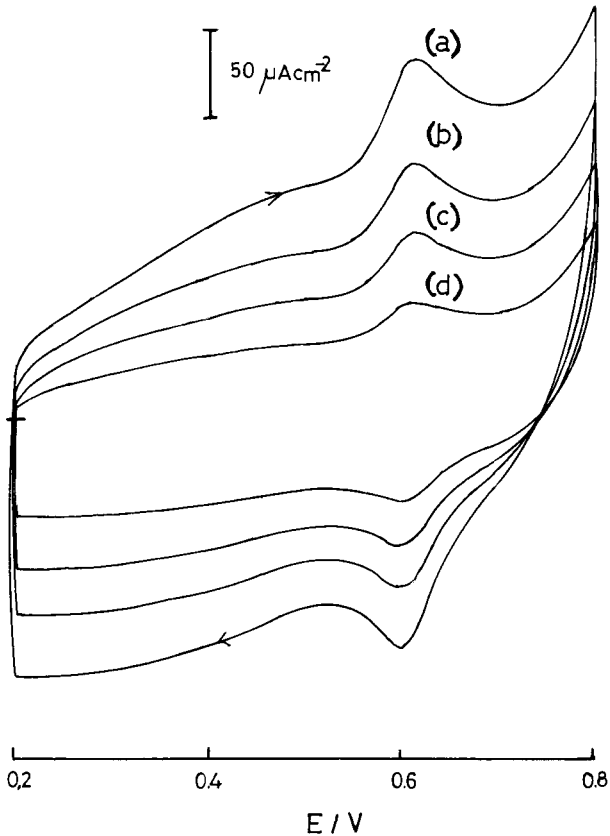


Fig. 6. Cyclic voltammograms for the redox processes of polymethoxy red films in 1.0 M HCl at different scan rates: (a) 100, (b) 70, (c) 50 and (d) 30 mV S^{-1} . Films were formed by 20 cycles at $E_f = 1.2$ V.

step chronocoulometry within a time interval < 1 s to deduce the diffusion coefficient, D , according to the following relation [15, 16, 34]:

$$q = q_{\text{dl}} + 2nFCD^{1/2}\pi^{-1/2}t^{1/2} \quad (1)$$

where q (C cm^{-2}) is the charge density passed in time t , q_{dl} (C cm^{-2}) is the charge density consumed in charging

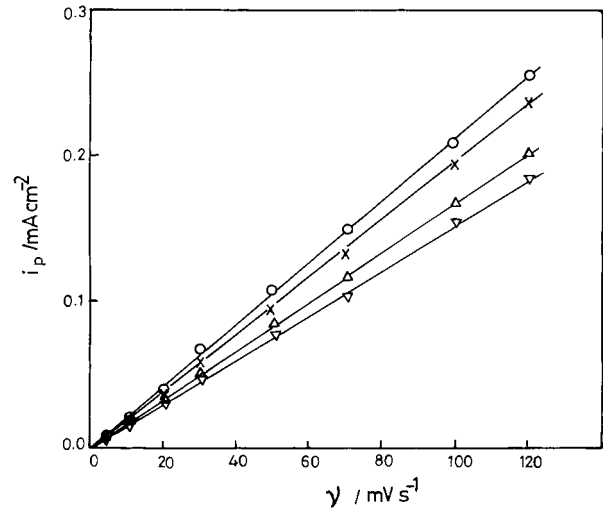


Fig. 7. Dependence of the peak current, i_p , for the redox processes of polymethoxy red films on the scan rate, v , in acid chloride solutions of pHs: (O) 0.02, (X) 0.60, (Δ) 1.35 and (∇) 2.45.

the double layer, n is the number of faradays, F , involved and C (mol cm^{-3}) is the concentration of the redox sites in the polymer film; $C = q_{\text{redox}}/nFd$, where d (cm) is the polymer film thickness. Equation 1 is applicable for electroactive polymers under the condition that the time scale of the experiment is sufficiently short to allow the diffusion process to be totally within the polymer film, that is, the film thickness must be larger than the diffusion layer thickness (δ). With a typical D value of 10^{-10} – 10^{-8} $\text{cm}^2 \text{s}^{-1}$ for this type of polymer films [15] and a time interval of 0.1 s ($\delta \approx (\pi t D)^{1/2} \approx 10^{-5}$ cm), a film thickness of 1 μm is sufficient for the application of Equation 1. Figure 8 shows typical chronocoulometric plots for the redox processes of poly-methoxy red films formed by 20 cycles in 1 M HCl. As can be seen, straight $q-t^{1/2}$ lines can be distinguished at $t > 10$ s. The nonlinear portion of $q-t^{1/2}$ curves at $t < 10$ s is predominantly attributed to the

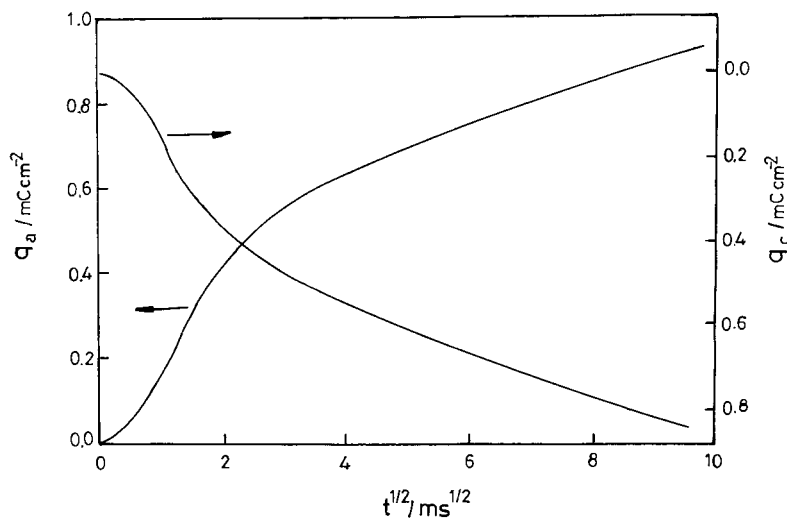


Fig. 8. Chronocoulometric plots for the redox processes of polymethoxy red films in 1.0 M HCl. Films were formed by 20 cycles at $E_f = 0.9$ V. For the oxidation, the potential was stepped from 0.0 to 0.8 V and for the reduction, the potential was stepped from 0.8 to 0.0 V.

charging of the metal/polymer/electrolyte interfaces. Extrapolation of $q-t^{1/2}$ lines to $t = 0$ gave q_{dl} values of 4.3 and 3.4 mC cm^{-2} for the oxidation and reduction processes, respectively. The q_{dl} values are not the same due to the change in conductivity of the polymer film on oxidation or reduction. Since an accurate estimation for the film thickness could not be made in the present study, the diffusion characteristics were reported in terms of $D^{1/2}C$, which is directly proportional to the slope of the chronocoulometric plot, $dq/dt^{1/2}$. The $D^{1/2}C$ values for the oxidation and reduction processes were 15.9 and 17.2 $\text{nmol s}^{-1/2} \text{cm}^{-2}$, respectively. The fact that the two values are close signifies the diffusion of the same species in the oxidation and reduction processes. The charge transport in the oxidation (charge propagation in an insulating film) and reduction (charge propagation in a conducting film) of electroactive polymer films are expected to be significantly different [24, 33]. Thus, it may be assumed that the reported $D^{1/2}C$ values are due to the diffusion of solvated protons and Cl^- ions in the redox processes of polymethoxy red. To make a comparison between the diffusion characteristics of polymethoxy red films and similar electroactive polymers derived from azo compounds, $D^{1/2}C$ values for poly-*p*-aminoazobenzene and 4(5-chloro-2-pyridyl azo-1,3-diamino-benzene) were calculated from the D and C values reported in the literature. The $D^{1/2}C$ values for poly-*p*-aminoazobenzene [15] and 4(5-chloro-2-pyridyl azo-1,3-diamino-benzene) were 11.2 and 2.2 $\text{nmol s}^{-1/2} \text{cm}^{-2}$, respectively. The average D and C values for aniline based-conducting polymers were, respectively, 10^{-10} – $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ and 10^4 – $10^{-3} \text{ mol cm}^{-3}$ [15], that is, $D^{1/2}C \approx 1$ – $100 \text{ nmol s}^{-1/2} \text{ cm}^{-2}$. Thus, the diffusion characteristics of polymethoxy red films lie within the range of aniline based-conducting polymers.

Electron transfer reaction of the couple $[\text{Fe}(\text{CN})_6]^{3-/4-}$ on polymethoxy red covered electrodes were studied by cyclic voltammetry and chronocoulometry to explore the diffusion characteristics of the polymer films towards the transport of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ species. Figure 9 shows CVs for the couple $[\text{Fe}(\text{CN})_6]^{3-/4-}$ on bare and polymethoxy red covered electrodes. As can be seen, the redox processes of the couple are significantly inhibited in the presence of the polymer films and the degree of inhibition for films formed by 20 cycles is higher than that formed by five cycles. The presence of polymethoxy red films decreased the current and increased ΔE_p significantly. The large ΔE_p in the presence of the polymer film is attributed to an iR (ohmic) drop due to the low conductivity of the polymer film. [33, 35]. Thus, the electron transfer reactions of the couple $[\text{Fe}(\text{CN})_6]^{3-/4-}$ seems to occur by charge injection through the polymer film in parallel with diffusion of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ species through the film. Consequently, the measured D value is assumed to be given by $D = D^\circ + D_{ct}$, where D° is the diffusion coefficient of the species through the film (as physical barrier) and D_{ct} is the diffusion coefficient of the charge transport in the film (as an electronic resistance). The diffusion coefficient for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ species on polymethoxy red-covered electrodes were calculated from the chronocoulometric plots according to Equation 1 using a large-potential step (-0.8 to 0.8 V for the oxidation and 0.8 to -0.8 V for the reduction). The average D values were 1.6×10^{-8} and $2.5 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for the films formed by 5 and 20 cycles, respectively. Using an average $D^\circ = 1.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for the diffusion coefficient of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ species on the bare electrode, the presence of polymethoxy red films formed by 5 and 20 cycles retard the diffusion of

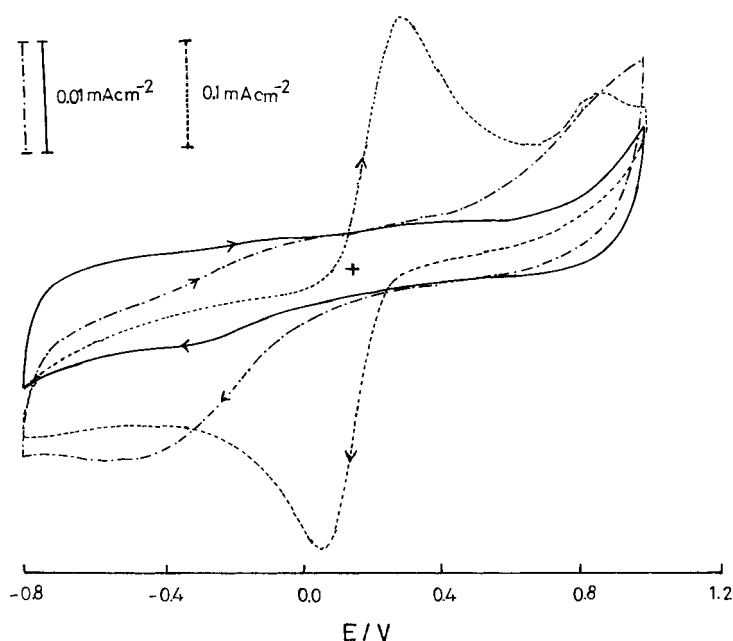


Fig. 9. Cyclic voltammograms for the redox $[\text{Fe}(\text{CN})_6]^{3-/4-}$ on (---) bare and (—), (— · —) polymethoxy red-covered Pt electrodes. Films were formed by (· · ·) 5 cycles and (—) 20 cycles at $E_f = 1.2 \text{ V}$. Scan rate 0.1 V s^{-1} . The solution was $1 \text{ mM K}_4[\text{Fe}(\text{CN})_6] + 0.5 \text{ M KCl}$.

$[\text{Fe}(\text{CN})_6]^{3-/4-}$ species by at least 106 and 680 times, respectively.

4. Conclusion

Anodic polymerization of methoxy red in alcoholic HCl solutions yielded thin polymeric films which were electroactive in acid chloride solutions. The characteristics of polymethoxy red films were comparable to those of polyaromatic amines.

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