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Electropolymerization of 2-Methoxyaniline: Kinetic Studies, Mechanism, Characterization of the Polymer and Applications as Corrosion Protection for Mild Steel in Acid Medium

S. M. Sayyah^a; M. M. El-Rabiey^b; H. El-Feky^b; A. F. Gaber^b

^a Polymer Research Laboratory, Chemistry Department, Faculty of Science, Beni-Suef University, Beni-Suef, Egypt ^b Chemistry Department, Faculty of Science, El-Fayum University, El-Fayum, Egypt

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Electropolymerization of 2-Methoxyaniline: Kinetic Studies, Mechanism, Characterization of the Polymer and Applications as Corrosion Protection for Mild Steel in Acid Medium

S. M. Sayyah

Polymer Research Laboratory, Chemistry Department, Faculty of Science, Beni-Suef University, Beni-Suef, Egypt

M. M. El-Rabiey

H. El-Feky

A. F. Gaber

Chemistry Department, Faculty of Science, El-Fayum University, El-Fayum, Egypt

Electropolymerization of 2-methoxyaniline on platinum electrode in acid medium was carried out under different reaction conditions as temperature, current density, hydrochloric acid, and monomer concentrations with reaction duration time. The initial rate of the electropolymerization reaction is small and the orders are found to be 1.18, 1.25, and 0.88 with respect to current density, HCl, and monomer concentrations, respectively. The apparent activation energy (E_a) is found to be 56.87 kJ/mol. The obtained polymer films are characterized by $^1\text{H-NMR}$, elemental analysis, and IR spectroscopic studies. The mechanism of the electropolymerization reaction has also been discussed. The thermogravimetric analysis (TGA) was used to confirm the proposed structure and determination of the number of water molecules associated with each polymeric chain unit. X-ray and scanning electron microscopic analysis were used to investigate the surface morphology. The corrosion behavior of uncoated and coated mild steel electrode with poly (2-Methoxyaniline) in 1M HCl at 25°C was investigated potentiodynamically. The various electrochemical parameters (I_{corr} , E_{corr} , and $P\%$) were calculated from Tafel plots for uncoated and coated electrodes. The influence of some coating conditions as duration time, current density of the electropolymerization, and monomer concentrations were investigated. The data reveal that the presence of coated polymer films on the electrode surface increase the cathodic and anodic polarization compared to the uncoated sample.

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Address correspondence to S. M. Sayyah, Polymer Research Laboratory, Chemistry Department, Faculty of Science, Beni-Suef University, Beni-Suef 62514, Egypt. E-mail: smsayyah@hotmail.com

Keywords: corrosion characterization, cyclic voltammetry, electropolymerization, 2-methoxyaniline, mild steel

INTRODUCTION

The electropolymerization of conducting polymers on different electrode surfaces has been a very active research area in electrochemistry because of their outstanding properties, which allow polymer modified electrodes to be used as sensors, catalysts, electrochromic materials, batteries, and microelectronic devices [1–11] and also as corrosion inhibitors to protect semiconductors and metals [12–18].

From an application point of view, polyaniline is considered as one of the best organic conducting materials. Its synthesis is performed generally either chemically or electrochemically because of its many promising properties such as fast switching rate (the ability to switch reversibly from the insulating to the conducting state either by electrochemical or chemical doping) [19–22]. In recent years, several reviews on polyaniline have been published [23–25].

In a search for new conducting polymers of the aniline type, investigations have been directed toward aniline modified by substituents in the ring [26–29] or at the nitrogen atom [30–32]. Electropolymerization of aniline and its derivatives has usually been carried out at low pH acidic aqueous solutions (e.g., HCl or H₂SO₄ aqueous solution) [33].

Electropolymerization of aniline in 0.5 M H₂SO₄ aqueous perchlorate and nitrate solutions has been studied [34–35]. Also, polyaniline and poly (3-Methoxyaniline) were obtained by the electropolymerization in tetra-*n*-butylammonium salt and 1,2-dichloroethane solution [36–38].

The kinetics of the chemical and electrochemical polymerization of some substituted aniline, pyrrole, and thiazole in aqueous acidic solutions and characterization of the obtained polymers by IR, UV-visible, X-ray, scanning electron microscopy, thermal gravimetric analysis, and cyclic voltammetry have been investigated by Sayyah et al. [39–47].

Polyaniline and its derivatives have been known as one of the best conducting polymers in corrosion protection because of its environmental stability and also because of the cheap raw materials. Polyaniline was used as an electroactive coating on steel in H₂SO₄ solution [48]. The authors found that the anodic deposition of polyaniline films protects the steel by maintaining the metal in the passive state and repassivating the damaged area. Sathiyarayanan [49] studied the electrochemically deposited polyaniline and polyethoxyaniline as inhibitors for iron corrosion in HCl solution by Tafel extrapolation, linear polarization, impedance, and weight loss techniques. The results show that the prepared polymers minimize the corrosion of iron in HCl solution.

J. Camalet et al. [50] studied the use of polyaniline for corrosion protection of mild steel in a solution containing 0.1 M HCl + 0.4 M NaCl by cyclic voltammetry and constant potential techniques. They found that the corrosion current is divided by 10 min and suggest that the polymer coats could be used for corrosion protection of mild steel.

The objective of the present work is to investigate the kinetic and optimum conditions for the electrochemical preparation of 2-methoxyaniline in aqueous hydrochloric acid medium and characterization of the obtained polymer film. The surface morphology of the obtained polymer is characterized by scanning electron microscopy and X-ray diffraction. The effect of electrodeposited poly (2-Methoxy aniline) film on the corrosion protection of mild steel in 1 M HCl by Tafel extrapolation should be investigated.

EXPERIMENTAL

Materials

2-Methoxyaniline, (vacuum distilled and stored in the absence of light before use), hydrochloric acid solution, anhydrous sodium sulphate are of analytically pure grade provided by Merck, Germany. All solutions were freshly prepared using double distilled water.

Cell and Electrodes

The experimental setup used was described previously [44–47] and consisted of rectangular Perspex cell provided with two parallel platinum foil electrodes. Each electrode had a dimension of 1 cm length and 0.5 cm width. Before each run, the platinum anode was cleaned and washed with distilled water, rinsed with ethanol, dried and weighed. The experiments were conducted at the required temperature $\pm 1^\circ\text{C}$ with the help of circular water thermostat. At the end of the experiment, the anode was withdrawn, washed with distilled water, dried, and weighed. The polymerization current was supplied by constant potential-power supply (Thurby-Thandar PL 330).

Electrochemical Polymerization of 2-Methoxyaniline

Anodic oxidative electropolymerization of 2-methoxyaniline was carried out in aqueous solution containing monomer (concentration range between 0.04–0.1 M) using 0.1 M Na_2SO_4 as the supporting electrolyte and with current densities in the range between 1 and 5 mA cm^{-2} . Electropolymerization was carried out in hydrochloric acid solution (concentration range between 0.2 and 0.8 M) at different temperatures in the range between 288 and 318° K.

Cyclic Voltammetry Measurements

A standard three-electrode cell was used in the cyclic voltammetry measurements with saturated calomel electrode (SCE) as the standard reference electrode. The auxiliary electrode was a platinum wire. The platinum working electrode dimensions were $1 \times 0.5 \times 0.05$ cm. Before each run the platinum electrode was cleaned as mentioned earlier. The Electrochemical experiments were performed with Potentiostat/Galvanostat Wenking PGS 95 connected to the computer. The I-E curves were recorded by computer software (Moded ECT).

Infrared, Thermogravimetric, Elemental Analysis and H-NMR Spectroscopy

Infrared measurements were carried out using a Shimadzu FTIR-430 spectrophotometer. $^1\text{H-NMR}$ measurements were carried out using a Varian EM 360 L,60 MHz NMR spectrometer. NMR signals of the electropolymerized samples were recorded from their solutions in dimethylsulphoxide using tetramethylsilane as internal reference. Thermogravimetric analyses of the obtained polymers were performed using a Shimadzu DT-30 thermal analyzer. The weight loss was measured from ambient temperature up to 600°C , at the rate of $10^\circ\text{C min}^{-1}$ to determine the degradation rate of the polymer.

Elemental analysis was carried out in the micro-analytical center at Cairo University by oxygen flask combustion and dosimat E 415 titrator (Switzerland).

Scanning Electron Microscopy and X-Ray Diffraction

Scanning electron microscopic analysis was carried out using a JSM-T20 scanning electron microscope. (JEOL, Japan).

A X-ray diffractometer (Phillips 1976 Model 1390) was operated for the polymer film adhered on the platinum electrode under the following conditions, which were kept constant in all runs:

X-ray tube:

Preset time: 10 s

Voltage: 40 kV

Cu Current: 30 mA

Scan speed: 8 deg min^{-1}

Mild Steel Working Electrode for Corrosion Measurements

The working electrode employed in the present work was made from mild steel specimen (98.5% Fe, 0.33% C, 0.24% Si, 0.52% Mn, 0.04% Cr, and

0.02% S) axially embedded in an Araldite holder to offer an active flat disc shaped surface of a 2 cm^2 area. Prior to each experiment, the working electrode was polished successively with fine grade emery papers. The polished metal surface was rinsed with distilled water and acetone before electrodeposition of polymer film on its surface.

Preparation of Polymer Film on Mild Steel Working Electrode

Preparation of polymer film on the mild steel electrode was carried out using the same procedure previously mentioned by Sayyah et al. [44–47]. The electrical circuit used for the electrodeposition of the polymer consisted of an electropolymerization cell in which the steel working electrode acted as anode and a platinum foil electrode acted as cathode. These were immersed and fixed in their appropriate positions in the cell containing the test solution (aqueous/DMF (30:70 v/v)) containing $0.1\text{ M Na}_2\text{SO}_4$ as supporting electrolyte and the monomer. At the end of each experiment, the working electrode was picked up, washed with distilled water, and dried before use in the corrosion measurements. The obtained polymer films adhered well to the mild steel electrode surface.

Corrosion Measurements

The working electrode (polymer film coated on mild steel), platinum auxiliary electrode, and saturated calomel electrode as reference were introduced into the electrolytic cell containing 1 M HCl solution. Potentiodynamic polarization measurements were performed using the Potentiostat/Galvanostat Wenking PGS 95 connected to the computer.

The experiments were carried out by changing the electrode potential automatically with a scan rate of 25 mVs^{-1} from -580 to -520 mV and the I/E curves were recorded by computer software (Model ECT). For each run, a freshly prepared solution and new set of electrodes were used. Each run was conducted at constant temperature $\pm 1^\circ\text{C}$ using circular water thermostat.

RESULTS AND DISCUSSION

Anodic Oxidative Electropolymerization of 2-Methoxyaniline

Effect of Reaction Duration Time

Anodic oxidative electropolymerization of 2-methoxyaniline was studied under the influence of different plating and operating parameters.

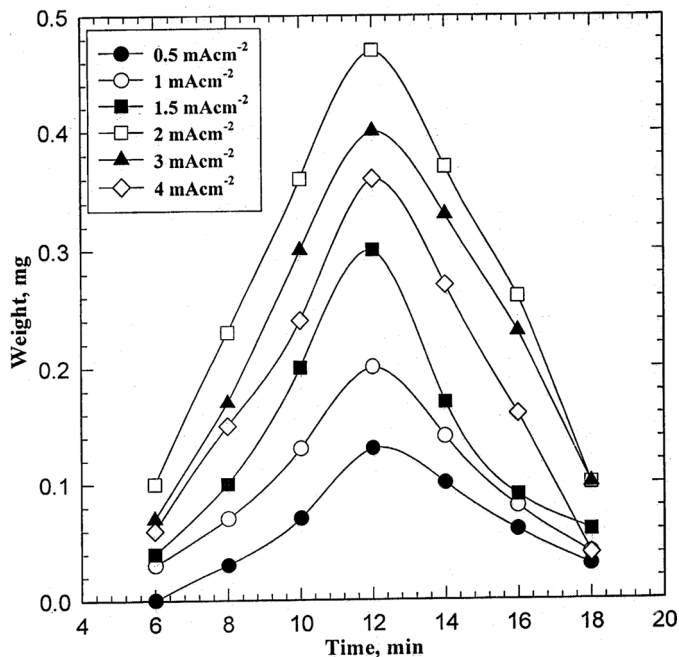


FIGURE 1 Effect of duration time on the electropolymerization of o-methoxyaniline from solution containing 0.1 M monomer, 0.5 M HCl, 0.1 M Na₂SO₄ at 30°C with different current densities.

The effect of duration time on the weight of the obtained polymer was studied with different values of current densities. The data reveal that the weight of obtained polymer increases with increased duration time up to 12 min and then tends to decrease as a result of degradation and solubility of the polymer film from the platinum surface in case of all investigated current densities. The data are graphically represented in Figure 1.

Effect of Current Density

The effect of applied current density on the anodic oxidative electropolymerization of 2-methoxyaniline was studied in the range between 1 to 5 mA cm⁻² at equal duration times (12 min) using 0.07 M monomer concentration, 0.1 M Na₂SO₄ in dimethyl formamide/water mixture (30:70 v/v), and 0.5 M HCl at 303 K, which were kept constant. The data reveal that, as the applied current density increases, the weight of obtained polymer increases up to 2 mA cm⁻² and then tends to decrease. This finding implies that an oxygen and chlorine evolution

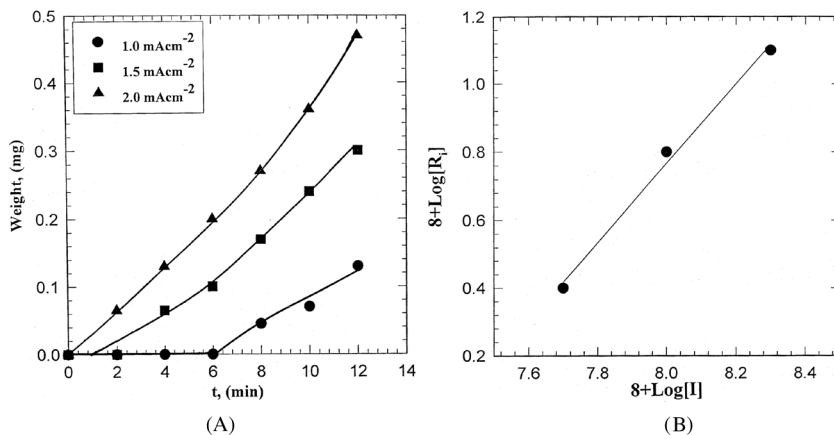


FIGURE 2 (A): Yield-time curve for the effect of current densities. (B): Double-logarithmic plot of the initial rates of the electropolymerization versus different current density values.

takes place as a side reaction, especially at high current densities. Each value of the used current density (1, 1.5, and 2 mA cm⁻²) was studied with different time intervals and the yield-time curve was estimated. The data are graphically represented in Figure 2A, from which the initial rate of the electropolymerization was determined. The reaction exponent with respect to the current density was determined from the slope of the straight line presented in Figure 2B. The exponent was found to be 1.18.

Effect of HCl Concentration

Anodic oxidative electropolymerization of 2-methoxyaniline was carried out using 0.07 M monomer concentration, 0.1 M Na₂SO₄ in dimethyl formamide/water mixture (30/70v/v), current density = 2 mA cm⁻² at 303°K, which were kept constant. But the hydrochloric acid concentration was varied in the range between 0.2 and 0.8 M. The obtained polymer film in each experiment was weighed. The results show that the maximum weight is obtained when 0.5 M HCl concentration is used. The effect of HCl concentrations in the range between 0.2 and 0.5 M on the electropolymerization rate was studied. The weight of the obtained polymer film on the platinum electrode in each experiment was plotted against the duration time as shown in Figure 3A.

The initial rate of the electropolymerization reaction was calculated and the double logarithmic plot of the initial rate versus hydrochloric acid concentration is represented in Figure 3B. A straight line was

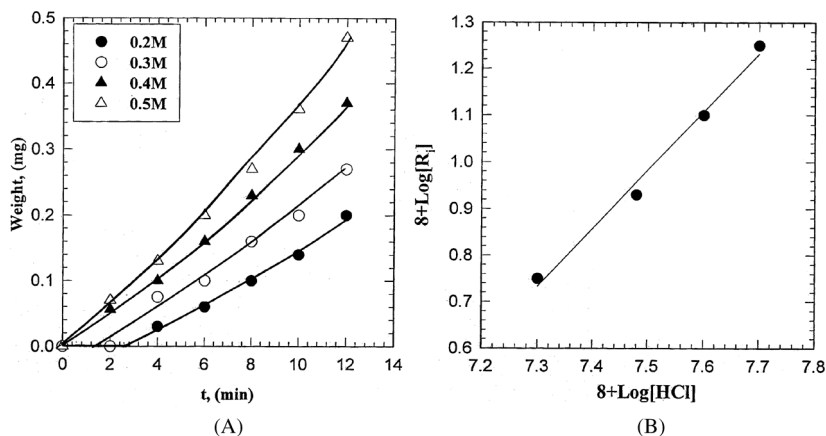


FIGURE 3 (A): Yield-time curve for the effect of HCl concentrations. (B): Double-logarithmic plot of the initial rates of electropolymerization versus HCl concentrations.

obtained that has a slope of 1.25. This means that the order of the electropolymerization reaction with respect to HCl is a first order reaction.

Effect of Monomer Concentration

Anodic oxidative electropolymerization of 2-methoxyaniline was carried out by keeping all the aforementioned conditions constant at 0.5 M HCl, 0.1 M Na₂SO₄ in dimethyl formamide/water mixture (30/70v/v), current density = 2 mA cm⁻² at 303°K, but the monomer concentrations were varied in the range between 0.04 and 0.1 M. The weight of the obtained polymer film in each experiment was calculated. The obtained results show that the maximum weight is obtained when 0.07 M monomer concentration is used. It was also noticed that the weight of the polymer film decreases at higher concentrations >0.07 M of the monomer, which means that polymer degradation may be occurring.

The electropolymerization of 2-Methoxyaniline was studied using different monomer concentrations in the range between 0.04 and 0.07 M. The weight of obtained polymer film on the platinum electrode in each experiment was plotted against the duration time as shown in Figure 4A. The initial rate of the electropolymerization reaction was calculated and the double logarithmic plot of the initial rate of electropolymerization versus the monomer concentration is represented in Figure 4B. A straight line was obtained with a slope equal to 0.88,

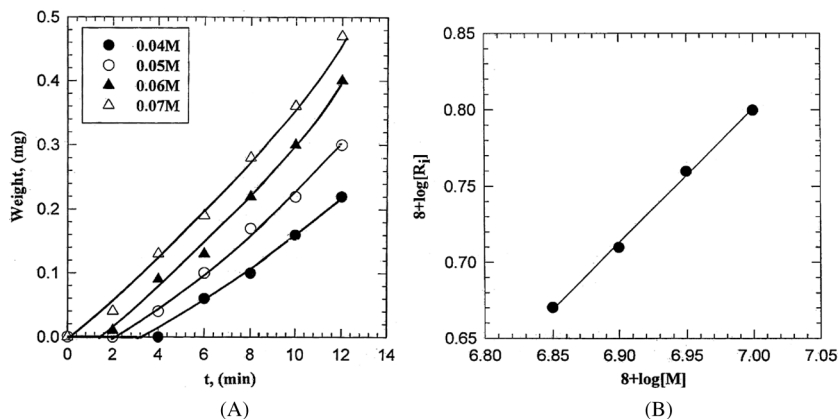
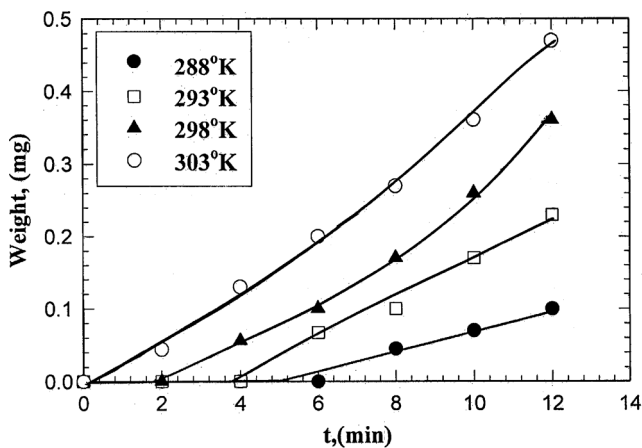


FIGURE 4 (A): Yield-time curve for the effect of monomer concentration. (B): Double-logarithmic plot of the initial rates of electropolymerization versus different monomer concentrations.

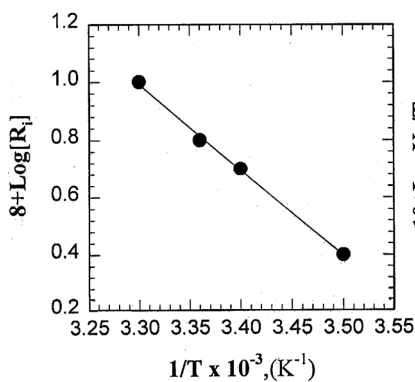
which means that the order of the electropolymerization reaction of 2-methoxyaniline is first order with respect to the monomer concentration.

Effect of Temperature

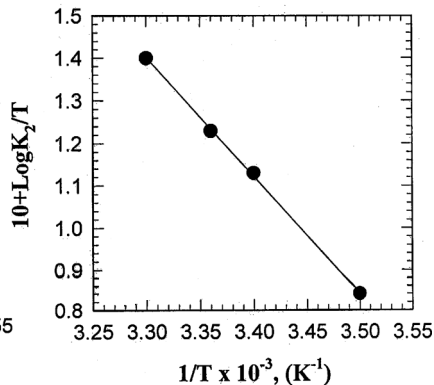
Anodic oxidative electropolymerization of 2-Methoxy aniline was carried out using 0.5 M HCl concentration, 0.1 M Na_2SO_4 in dimethyl formamide/water mixture (30/70 v/v), current density = 2 mA cm^{-2} at 0.07 M monomer concentration, which were kept constant, but the reaction was carried out at different temperatures in the range between 288 and 318° K. The maximum weight of the polymer film was recorded at 303° K. It was noticed during the experiments that at higher temperature than 303° K some polymers are formed in the solution near the anode and do not adhere to the electrode, which means that at temperatures higher than 303° K the adhesion of the film to the electrode is decreased. The electropolymerization of 2-methoxyaniline was carried out at different temperatures 288, 293, 298, and 303° K for different time intervals. At each temperature the weight of the formed polymer at the anode was plotted versus the duration time and the yield-time curve is represented in Figure 5A. The initial rate of the electropolymerization was calculated for each investigated temperature and the logarithm of the initial rate was plotted versus $1/T$ (cf. Figures 5B), which gives a straight line with a slope



(A)



(B)



(C)

FIGURE 5 (A): Yield-time curve for the effect of temperature. (B): Arrhenius plot for the electropolymerization. (C): Eyring equation plot for the electropolymerization.

-2.972. By applying Arrhenius equation, the apparent activation energy was calculated and found to be 56.87 kJ/mol.

Calculation of Thermodynamic Parameters

The enthalpy and entropy of activation energy for the electropolymerization reaction can be calculated from the k_2 values of the following equation:

$$\text{Reaction rate} = k_2[\text{HCl}]^{1.25}[\text{D}]^{1.18}[\text{M}]^{0.88}$$

The values of k_2 at different temperatures were calculated and the enthalpy (ΔH^*) and entropy (ΔS^*) of the activation associated with k_2 were calculated using Eyring equation:

$$k_2 = \frac{RT}{Nh} e^{\Delta S^*/R} e^{-\Delta H^*/RT}$$

where k_2 is the rate constant, R is the universal gas constant, N is avogadro's number and h is Planck's constant. By plotting $\log k_2/T$ versus $1/T$ (cf. Figure 5C), a linear relationship is obtained with a slope of $-\Delta H^*/2.303R$ and an intercept of $\log (R/Nh) + \Delta S^*/2.303R$. From the slope and intercept, the values of ΔH^* and ΔS^* were found to be $57.44 \text{ kJ mol}^{-1}$ and $-168.09 \text{ kJmol}^{-1}$, respectively.

Cyclic Voltammetry Characterization

Cyclic voltammograms of polymerization of 2-methoxyaniline on platinum electrode from solution containing 0.5 M HCl and 0.1 M Na_2SO_4 at 303°K with and without 0.07 M monomer in the potential range from -450 to 1800 mV (vs SCE) with scan rate of 25 mVs^{-1} are shown in Figure 6A and B, respectively. The voltammogram in the presence of monomer exhibits three oxidation peaks, which progressively developed at -300 , 900 , and 1000 mV . The first oxidation peak corresponds to the removal of the electron from the nitrogen atom of amine group to give radical cation. The formed radical cation reacts with other monomer molecule to form dimer radical cation that followed by further reaction with monomer molecule to give trimer radical cation and so on. Finally, the semiquinone radical cation (polaron state) is formed as shown in Scheme 1A.

The presence of methoxy group in the ortho position of the amino group facilitates the first oxidation process and formation the radical cation, which occurs immediately at low potential (-300 mV). This indicates that the aromatic chain is rapidly charged by isolated, delocalized, polarons. This potential is lower than the first oxidation peak potential exhibited by 2-chloroaniline [46] at -80 mV due to the presence of methoxy group (as electron donating group), whereas chlorine atom acts as electron withdrawing group.

On the other hand, the second oxidation process during the electropolymerization appears at high potential as a split peak (900 & 1000 mV vs SCE), which is assigned to the oxidation of the semiquinone radical (polaron state) to quinone imine (bipolaron), as shown in Scheme 1B.

In other words, the second oxidation process is attributed to the conversion of the radical cations to the fully oxidized form (quinoid structure). The polymer chain consists mainly of para coupling of

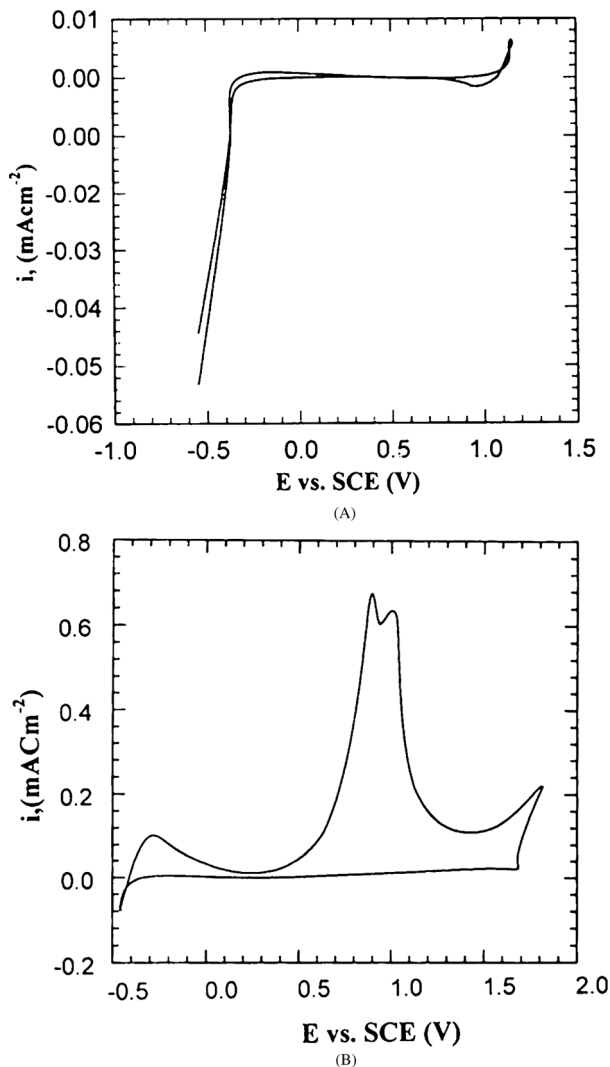
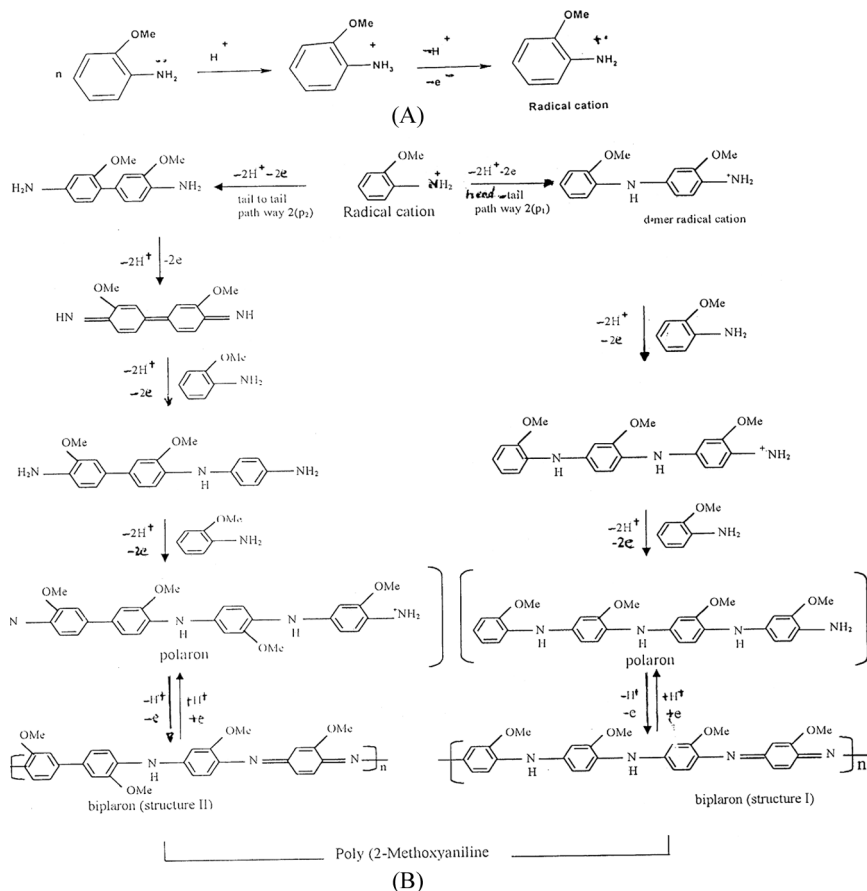


FIGURE 6 (A): Cyclic voltammogram in absence of monomer. (B): Cyclic voltammogram in presence of 0.07 M monomer.

semiquinone, quinone, and benzene rings in ratio depending on the applied potentials as mentioned by Buzarovska et al. [28] in case of *o*-toluidine. The second oxidation state appears at lower potential than that in case of 3-methoxyaniline (1100 mV) [51] due to the presence of the substituted methoxy group in the meta position of aniline moiety,



SCHEME 1 Structures and mechanisms of the products.

which facilitates the polymerization process. However, as soon as polymerization is initiated, a thick, highly adherent and brown polymer film rapidly deposits on the electrode surface.

On the other hand, the second oxidative peak at 2-chloroaniline voltamogram appears at 1120 mV [46], which is higher than the second oxidation peak of 2-methoxyaniline at (900 & 1000 mV). This is due to the nature of the substituent group, as mentioned earlier. The data reveal that the two oxidation processes are irreversible, and no cathodic peaks appear upon reversing the potential sweep up to 1800 mV.

Figure 7 represents the influence of repetitive cycling on the voltamogram of electropolymerization of 2-methoxyaniline. The data show that upon repetitive cycling the height of the anodic peaks (I) (which

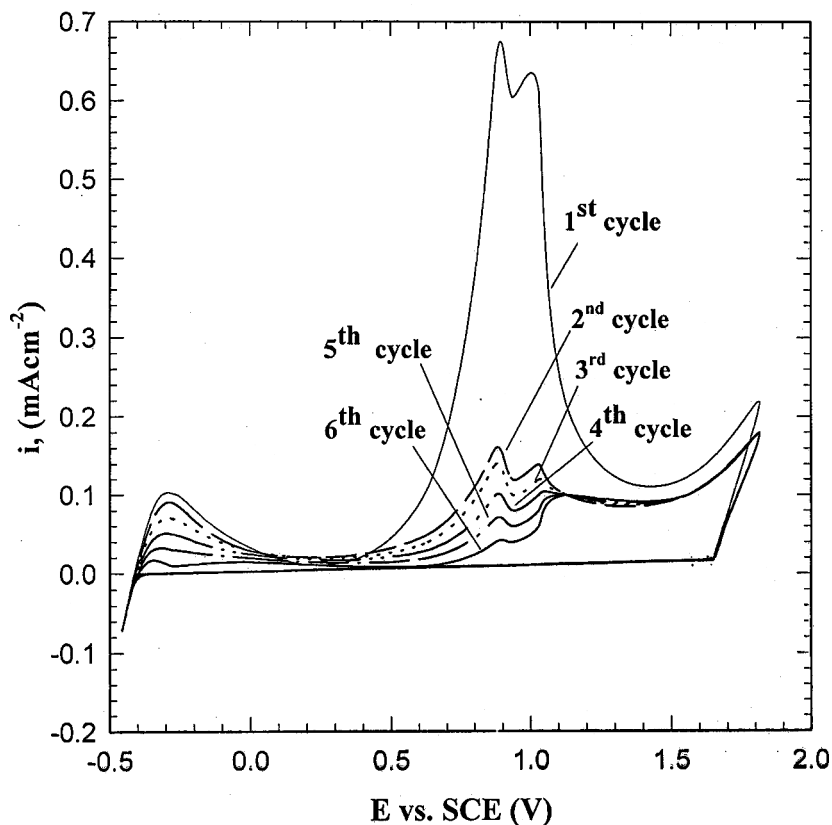


FIGURE 7 Repetitive cycling of electropolymerization of 2-methoxyaniline from solution containing 0.07 M monomer, 0.5 M HCl, and 0.1 M Na_2SO_4 at 303°K with scan rate of 25 mV s^{-1} .

corresponds to the formation of radical cation) increases, whereas the second oxidation peak (II) (which corresponds to the polymer formation) decreases. The increasing of the height of peak I with each cycle reflects the growth of polymer film on the electrode surface and the increase in the anodic surface area as a result of increasing surface roughness. Moreover, repetitive cycling leads to splitting of peak (II) into two peaks (II_a and II_b). This splitting could be attributed to the possibility of two reaction pathways (P_1 and P_2) as shown in Scheme 1. The first pathway (P_1) leads to structure 1 formation (head to tail) corresponding to peak II_b , but the second pathway (P_2) leads to structure 11 formation (tail to tail) corresponding to peak II_a . It seems that the electropolymerization structure 1 (head to tail) is the dominant pathway (P_1) [52].

TABLE 1 The Elemental Analysis of the Prepared Poly(2-Methoxyaniline)

The element	C%	H%	N%	Cl%
% (found)	52.9	5.61	8.9	11.3
% (calculated)	53.59	5.74	8.9	11.37

Elemental and Spectroscopic Analysis

The percentages of C,H,N and Cl are in a good agreement with those calculated for the suggested structure given in Scheme 1. The elemental analysis data are given in Table 1.

The infrared absorption bands and the their assignments for poly(2-methoxyaniline) are summarized in Table 2. The medium bands appearing at 612 cm^{-1} may be attributed to the stretching vibration of C–H in CH_3 group. The medium adsorption band appearing at 750 is attributed to out of plane C–H deformation for the 1,2-disubstituted benzene ring. The broad absorption band at 3420 cm^{-1} is attributed to the stretching vibration of –NH group solvated by water molecules. Other absorption bands and their assignments are given in Table 2.

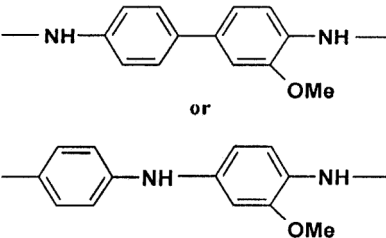
The $^1\text{H-NMR}$ spectrum of the prepared (2-methoxyaniline) shows a singlet signal at δ 3.04 ppm, which is characteristic for OCH_3 group, and a singlet signal at δ 7.02 ppm and a broad signal at δ 7.58 ppm, which are characteristic for the two types of benzene ring protons.

TABLE 2 Infrared Spectroscopic Analysis of the Prepared Poly(2-Methoxyaniline)

Wave number (cm^{-1})	Assignments [56]
612^m	Rocking vibration of C–H in CH_3 group
750^m	Out of plane deformation showing 1,2-disubstituted benzene ring
860^w	Out of plane deformation showing 1,4-disubstituted benzene ring
1012^m	In plane deformation of C–C aromatic
1046^m	Symmetric stretching vibration of C–N group in aryl–NH or
1116^s	Aryl–NH ₂ and C–O in Aryl–OCH ₃
1406^s	Stretching vibration of CH_3 group
1543^w	Symmetric stretching vibration of C=N in quinoid structure
1590^m	Symmetric stretching vibration of C=C in benzene ring
3031^m	Symmetric stretching vibration of C–H in aromatic moiety
3420^m	Symmetric stretching vibration of N–H in Aryl–NH or Aryl–NH ₂

^mmedium, ^sstrong, ^wweak.

TABLE 3 (TGA) of Poly(2-methoxyaniline)

Temperature range (°C)	Weight loss (%)		Removed molecules
	Found	Calculated	
25–105	11.90	11.48	4 H ₂ O
105–242	11.40	11.64	2 HCl
242–400	10.75	9.89	2OCH ₃
400–600	36.25	38.60	
>600	Remained (%)		Carbon residual + Na ₂ SO ₄
	29.70	28.44	

The singlet signal, which appears at δ 8.7 ppm, may be attributed to the NH group proton.

Thermal Analysis of the Electrochemically Prepared Poly(2-methoxyaniline) Sample

Thermogravimetric analysis (TGA) of the electrochemically prepared poly(2-methoxyaniline) sample revealed the thermal degradation steps shown in Table 3. From the table, it is clear that there are five stages:

1. The first stage includes the loss of water hydration (four molecules) in the temperature range 25–105°C. The estimated weight loss for this step was found to be 11.9% and the calculated one is 11.48%.
2. The second stage: The weight loss in the second stage, in the temperature range 105–242°C was found to be 11.66%, which is attributed to the loss of two molecules of hydrochloric acid. The calculated weight loss of this stage equals 11.64%.
3. The third stage: In the temperature range 242–400°C the weight loss was found to be 10.75%, indicating a loss of two methoxy groups from the polymeric chain. The calculated weight loss is equal to 9.89%.

4. The fourth stage: In the temperature range 400–600°C, the weight loss was found to be 36.25%, indicating a loss of N-phenyl-4-amino-3-methoxyaniline structure or 4,4-diamino-3-methoxybiphenyl from the polymeric chain (according to the mentioned possibilities of the two pathways in Scheme 1). The calculated weight loss for this step is 38.6%.
5. The fifth stage: above 600°C a residual polymer and carbon or supporting electrolyte materials remained and was found to be 29.44%.

Surface Morphology

Homogenous, smooth, brown, and well-adhering polymer films were electrodeposited on Pt surface in most conditions. The surface morphology of the electrodeposited poly(2-methoxyaniline) film at the optimum condition was examined by scanning electron microscopy and X-ray diffraction analysis. The data show that the film is amorphous structure and may contain a very small amount of crystallinity (cf. Figure 8A and B). The data are in good agreement with those obtained by Sayyah et al. in case of poly(3-methoxyaniline) [51].

Applications of the Prepared Polymer as Corrosion Protection of Mild Steel in Acid Medium

The corrosion behavior of steel without coat and coated with poly (2-Methoxyaniline) in 1M HCl at 25°C was investigated potentiodynamically from -580 to -520 mV with scan rate of 25 mV s^{-1} . The coated polymer film was electrodeposited on mild steel anode surface under different conditions such as duration time, current density of electropolymerization, and monomer concentration. The corrosion current (I_{corr}) was obtained by Tafel extrapolation method where large cathodic and anodic polarization provide the cathodic and anodic polarization curves for the respective corrosion process [53].

Figure 9 shows the potentiodynamic cathodic and anodic polarization curves of uncoated and coated steel electrode. The data reveal that the presence of polymer coat inhibits the corrosion of steel in 1M HCl because the value of I_{corr} decreases by coating the steel electrode with the polymer film. In the same time, the presence of the polymer film on the electrode surface slightly shifts the corrosion potential (E_{corr}) to more positive values. It is clear that the presence of the polymer film on the electrode surface increases the cathodic and anodic polarization compared to the free sample without coating and the increase in the anodic polarization is more pronounced than

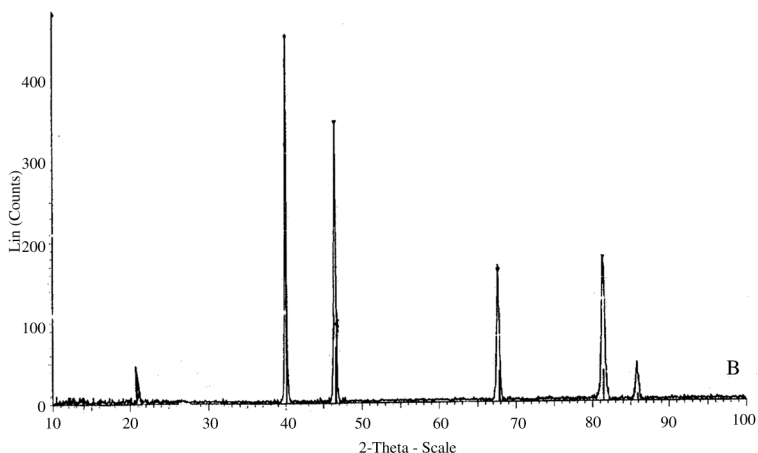
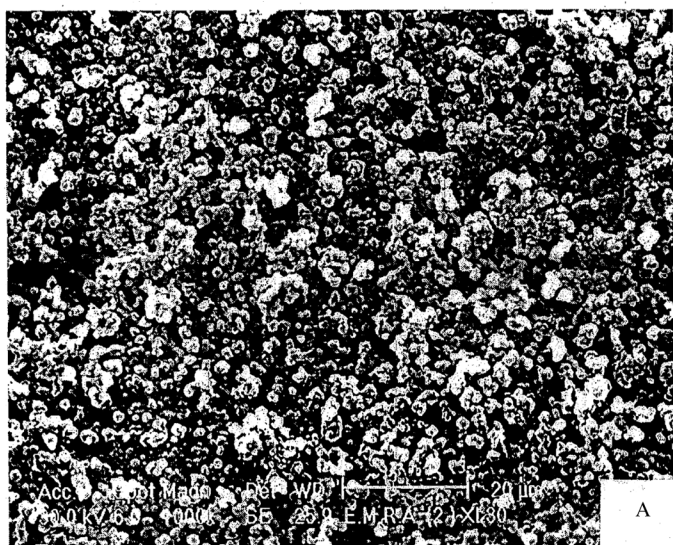


FIGURE 8 (A): Photomicrograph of the electropolymerized poly(2-methoxyaniline). (B): X-ray diffraction pattern of the electropolymerized poly(2-methoxyaniline) (peaks are from the metal substrate).

that in case of cathodic polarization. The inhibition of steel corrosion seems to be due to the presence of the barrier polymer film on the electrode surface, which increases the resistance to the charge transfer across the interface.

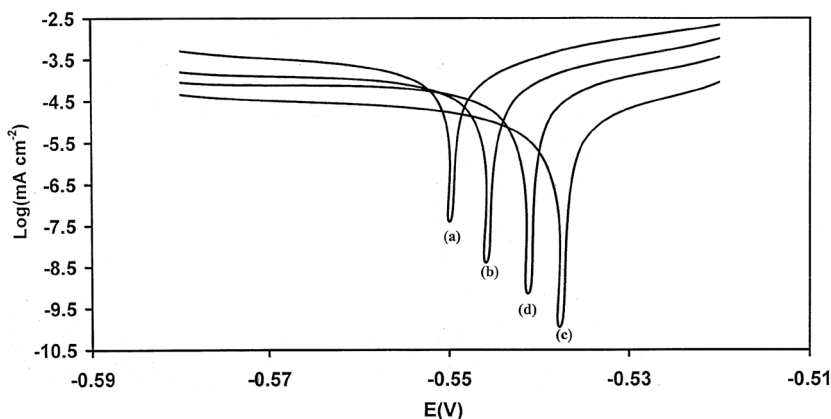


FIGURE 9 Cathodic and anodic potentiodynamic polarization curves of steel in 1 M HCl coated with poly(2-methoxyaniline). (a) blank without coat, (b–d) coated samples. The coat was deposited on steel from aqueous solution (30:70 DMF/H₂O v/v) containing 0.1 M monomer, 0.1 M Na₂SO₄ and $i = 1.5 \text{ mA cm}^{-2}$ under the influences of different duration time (a) blank, (b), 5, (c) 10, and (d) 15 min at 298° K.

Effect of Duration Time of Electropolymerization

The effect of duration time of the electropolymerization on the coated film protection function was measured. Figure 9 shows the potentiodynamic anodic and cathodic polarization curves of steel electrode coated with poly(2-Methoxyaniline) that was prepared at different duration times. The electrochemical parameters such as corrosion current (I_{corr}) and corrosion potential (E_{corr}) from these measurements are summarized in Table 4.

The protection efficiency (P%) for each polymer coat was calculated from the following equation [54]:

$$P\% = \frac{(I_{\text{corr}}^0 - I_{\text{corr}})}{I_{\text{corr}}^0} \times 100$$

TABLE 4 Electrochemical Parameters for Mild Steel Electrode in 1 M HCl at Different Duration Time of the Electropolymerization of 2-methoxyaniline Coat

Duration time (min)	$I_{\text{corr}} (\mu\text{A cm}^{-2}) \times 10^5$	E_{corr} mV (vs. SCE)	P%
Blank	10	-550	—
5	2.9	-545	71
10	2.1	-537	79
15	3.9	-541	61

where I_{corr}^0 and I_{corr} are the corrosion current for uncoated and coated steel electrode, respectively. The calculated values of P% are also listed in Table 4. The data reveal that in all cases, the protection efficiency increases with increasing the duration time of electropolymerization up to 10 min. Further increase in the duration time more than 10 min leads to a decrease of the protection efficiency.

The increase in the protection efficiency with duration time of electropolymerization could be attributed to the increase in the polymer weight and consequently the film thickness. These data are in a good agreement with the previously published data [44–47]. The decrease in the protection efficiency observed at a long time resulted from the decrease of the thickness of the coated film caused by the solubility or degradation of the coated film.

Effect of Current Density of Electropolymerization

The effect of current density of the electropolymerization on the coated polymer film protection efficiency was measured. Figure 10 shows the potentiodynamic cathodic and anodic polarization curves of steel electrode coated with poly(2-Methoxyaniline) prepared at different current density values. The electrochemical parameters (I_{corr} , E_{corr} , and P%) from these measurements are given in Table 5. The data show that the protection efficiency of these polymer coatings

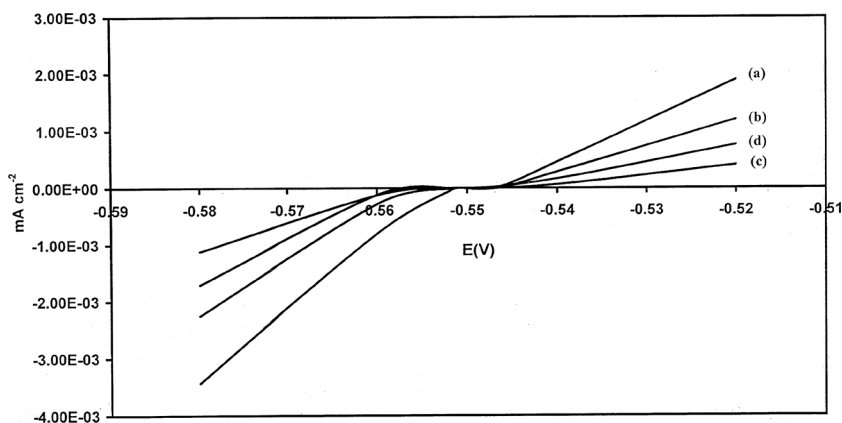


FIGURE 10 Cathodic and anodic potentiodynamic polarization curves of steel in 1 M HCl coated with poly(2-methoxyaniline). (a) blank without coat, (b–d) coated samples. The coat was deposited on steel from aqueous solution (30:70 DMF/H₂O v/v) containing 0.1 M monomer, 0.1 M Na₂SO₄ and duration time = 10 min under the influences of different current density values (a) blank, (b) 1, (c) 1.5, and (d) 2 mAcm⁻² at 298° K.

TABLE 5 Electrochemical Parameters for Mild Steel Electrode in 1 M HCl at Different Current Densities of the Electropolymerization of 2-methoxyaniline Coat

Current density (mA cm^{-2})	I_{corr} ($\mu\text{A cm}^{-2}$) $\times 10^5$	E_{corr} mV (vs. SCE)	P%
Blank	10	-550	—
1.0	3.1	-540	69
1.5	2.1	-537	79
2.0	3.5	-543	65

increases as the applied current density of electropolymerization reaction increases up to 1.5 mA cm^{-2} and then tends to decrease with further increase of current density values.

The increase in the protection efficiency of this film with increasing current density values could be attributed to the increase in the film thickness [44–47]. The decrease in the protection efficiency observed at high current density values resulted from the strong evolution of oxygen gas at the anode as a side reaction product. It is obvious that the oxygen evolution removes part of the deposited polymer and consequently the thickness of the polymer film will decrease.

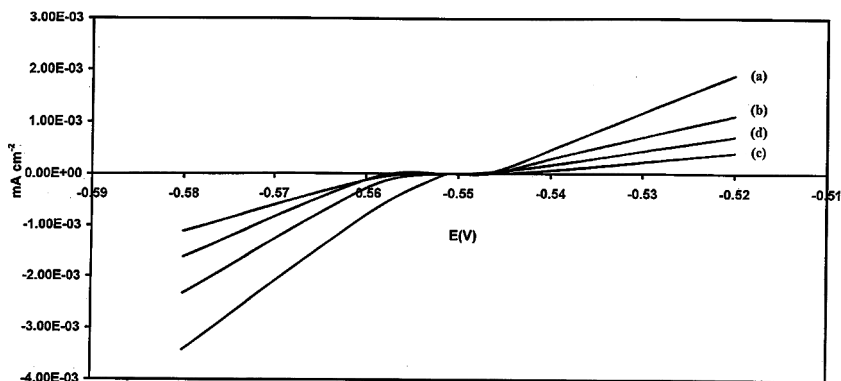


FIGURE 11 Cathodic and anodic potentiodynamic polarization curves of steel in 1 M HCl coated with poly(2-methoxyaniline). (a) blank without coat, (b–d) coated samples. The coat was deposited on steel from aqueous solution (30:70 DMF/H₂O v/v) containing 0.1 M Na₂SO₄, 1.5 mA cm^{-2} and duration time = 10 min under the influences of different monomer concentrations (a) blank, (b) 0.08, (c) 0.1, and (d) 0.12 mA cm^{-2} at 298°K.

TABLE 6 Electrochemical Parameters for Mild Steel Electrode in 1 M HCl at Different Monomer Concentrations of the Electropolymerization of 2-methoxyaniline Coat

[M] (mol/L)	$I_{\text{corr}} (\mu\text{A cm}^{-2}) \times 10^5$	E_{corr} mV (vs. SCE)	P%
Blank	10	-550	—
0.08	2.9	-539	71
0.10	2.1	-537	79
0.12	2.6	-541	74

Effect of Monomer Concentration

The effect of monomer concentration on the polymer film protection efficiency was studied. Figure 11 shows the potentiodynamic cathodic and anodic polarization curves of steel electrode coated with poly (2-Methoxyaniline) prepared with different monomer concentrations. The electrochemical parameters (I_{corr} , E_{corr} , and P%) are summarized in Table 6. It is obvious that the protection efficiency of the film increases with increasing monomer concentration up to 0.1 M and then starts to decrease with further increase in the monomer concentration.

This increase in the protection efficiency with increasing monomer concentration may be attributed to the increase in the film thickness [44–47] whereas the decrease in the protection efficiency observed at higher monomer concentrations (>0.1 M) results from polymer degradation. Moreover, the faster rate of the electropolymerization at high monomer concentrations leaves no sufficient time for polymer chains to stick smoothly on the electrode surface [55].

CONCLUSION

In conclusion, this article's data reveal the following:

1. The initial rate of the electropolymerization reaction of 2-methoxyaniline on platinum surface is relatively low. The fraction of the dissolved product may strongly depend on temperature, monomer, and HCl concentrations.
2. The orders of the electropolymerization reaction of 2-methoxyaniline are 1.18, 1.25, and 0.88 with respect to current density, hydrochloric acid, and monomer concentrations, respectively.
3. The apparent activation energy (E_a) is 56.87 KJ/mol.
4. Cyclic voltammogram exhibits three oxidation peaks at -300, 900, and 1000 mV (vs. SCE), the first oxidation peak corresponds to the formation of semiquinone radical cation (polaron state) whereas

the second and third may be assigned to the oxidation of semiquinone radical cation (polaron state) to quinone imine (bipolaron state).

5. The prepared poly(2-methoxyaniline) film is smooth, brown, and well adhered to the platinum electrode surface.
6. X-ray diffraction analysis and scanning electron microscopy picture show that the obtained polymer is amorphous with very small amounts of crystallinity.
7. The maximum protection efficiency for mild steel (79%) was found when the prepared polymer film was deposited at 10 min 1.5 mA cm^{-2} , and using 0.1 M monomer concentration.

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