Electrodeposition of Poly(3-hydroxyaniline) from Acidic Aqueous/Acetonitrile Solution

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Electrodeposition of poly (3-hydroxyaniline) on platinum electrode from acidic/ acetonitrile medium was carried out using cyclic voltammetry technique. The kinetic parameters were calculated by means of ex-situ microgravimetric and electrochemical data. The experimentally obtained kinetic equations were $R_{P,W} = k_W$ [acid]$^{0.91}$ [monomer]$^{1.2}$ [electrolyte]$^{0.69}$ from microgravimetric data and $R_{P,E} = k_E$ [acid]$^{0.92}$ [monomer]$^{0.96}$ [electrolyte]$^{0.7}$ from the values of the anodic current density using cyclic voltammetry technique. The apparent activation energy was calculated by the two techniques and is found to be 145.5 and 143.6 kJ/mol from microgravimetric and electrochemical data, respectively. The mechanism of the electrochemical polymerization reaction has been discussed and thermogravimetric analysis (TGA) is used to confirm the proposed structure and determination of the number of water molecules in the polymeric chain unit.

INTRODUCTION

Electropolymerization of conducting polymers is a relatively new class in polymer science and has the potential of being used in a large number of different applications, in batteries [l–6], electrochromic devices [7–9], microelectronic devices [10], sensors [11–18], and as corrosion inhibitors to protect semiconductors and metals [19–24].

From an application point of view, polyaniline is one of the most studied conducting polymers due to its high stability and easy preparation from acidic aqueous solution. In a search for new conducting polymers of the aniline type, investigations directed their attentions toward aniline modified by substituents in the ring [25–28].

Sayyah et al. [29] studied the effect of monomer, acid concentrations, and current density on the kinetics of the electropolymerization of 3-chloroaniline on platinum electrode from DMF/H_2O (30:70 v/v) acid solution. They found that the kinetic rate equation is $Rp = k2 [D]^{0.99}. [acid]^{0.96}. [monomer]^{1.2}$ and the apparent activation energy was 41.6 kJ/mol.

The hydroxy derivatives of aniline as 4-hydroxyaniline have been studied [30–31]. The data show that the anodic oxidation gives benzoquinone as a product but no film formation was obtained.

Electropolymerization of 2-hydroxyaniline from aqueous acidic solution was carried out by Sayyah et al. [32] under different reaction conditions of temperature, current density, and hydrochloric acid and monomer concentrations. They found that the initial rate of electropolymerization was small and the orders were found to be 0.5, 1.125, and 1.2 with respect to current density, acid, and monomer concentrations, respectively. Also, the obtained polymer films were characterized by electrochemical and spectroscopic techniques.

Sayyah and El-Deeb [33] studied the kinetics of the electrocopolymerization of a binary mixture of pyrrole and 2-amino-4-phenylthiazole on platinum electrode from acidic medium by ex-situ microgravimetric and electrochemical techniques as function of acid and monomer concentrations. They found that the kinetic equations were $R_{P,W} = k_W [acid]^{1.16} [M]^{1.85}$ from microgravimetric data and $R_{P,E} = k_E [acid]^{1.1} [M]^{1.9}$ from the values of the anodic current density using cyclic voltammetry technique.

The objective of the present work was to investigate the electrodeposition of poly(3-hydroxyaniline) on platinum electrode from acidic acetonitrile solution by cyclic voltammetry technique. On the other hand, the monomer, acid, and electrolyte concentrations as well as the temperature influence are quantified in the electropolymerization reaction, attempting to obtain the ex-situ gravimetric reaction orders. At the same time the validity of the anodic current density to obtain the kinetic parameters will be evaluated.

EXPERIMENTAL

Materials

3-hydroxyaniline, hydrochloric acid solution, acetonitrile, and anhydrous sodium sulfate were analytically pure and were obtained from

Merck (Darmstadt, Germany). All solutions were freshly prepared with double distilled water.

Cell and Electrodes

Three Electrode Cell for Cyclic Voltammetry Technique

A standard three-electrode cell was used with saturated calomel electrode (SCE) as the standard reference electrode. The auxiliary electrode was a platinum wire. The platinum foil-working electrode was $1 \times 0.5 \times .05$ cm. Before each run, the platinum electrode is cleaned and washed with distilled water, rinsed with ethanol, and dried. The experiments were conducted at the required temperature $\pm 1°$C with the help of circular water thermostat.

The electrochemical experiments were performed using potentiostat/galvanostat Wenking PGS 95 connected to computer. The I–E curves were recorded by computer software (Model ECT).

Two Electrode Cell for Ex-Situ Microgravimetric Technique

The experimental setup used was described previously [29,32–37] and consists of rectangular Perspex cell provided with two platinum foil parallel electrodes. Each electrode has a dimension of 1 cm height 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 $\pm 1°$C with the help of a 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 d.c.-power supply (Thurby $\approx$ Thandar PL 330).

Infrared Spectroscopic, Elemental, and Thermal Analysis

IR measurements were carried out with a Shimadzu FTIR-340 Jasco spectrophotometer.

Elemental analysis was carried out in the microanalytical center at Cairo University by oxygen flask combustion and dosimat E415 titrator (Switzerland).

Thermogravimetric analyses (TGA) 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°C min^{-1} to determine the degradation rate of the polymer.

RESULTS AND DISCUSSION

Electrodeposition of Poly(3-hydroxyaniline)

Electrodeposition of poly(3-hydroxyaniline) film on platinum electrode from solution containing 1.0 M HCl, 0.05 M monomer, and 0.1 M Na_2SO_4 at 298°K in acetonitrile/water mixture (10:90 v/v) by cyclic voltammetry in the potential range between 540 and 2000 mV (vs. SCE) with scan rate of 25 mVs^{-1} was studied and the obtained voltammogram is represented in Figure 1. In the absence of the monomer, the basic curve is drawn in Figure 1a while in the presence of monomer, in Figure 1b the voltammogram exhibits two oxidation peaks at 870 and 1400 mV. The first oxidation peak corresponds to the oxidation of 3-hydroxyaniline monomer and removal of an electron from the amine nitrogen atom to give a radical cation that interacts with another monomer molecule to form a dimer radical cation, trimer radical cation, and so on. Finally, the semiquinone radical cation (Polaron State) was formed as shown in Scheme 1.

The presence of hydroxy group in the meta position retards the first oxidation process and the formation of the radical cation towards a high potential (870 mV) comparative to ortho position in case of 2-hydroxyaniline (−300 mV) [32].

The second oxidation peak at 1400 mV was assigned to the oxidation of the semiquinone radical cation (polaron) to the quinine imine (bipolaron state) as shown in Scheme 2.
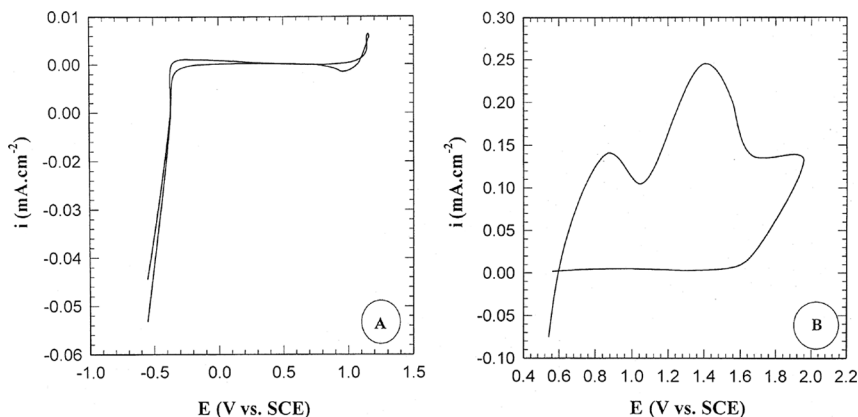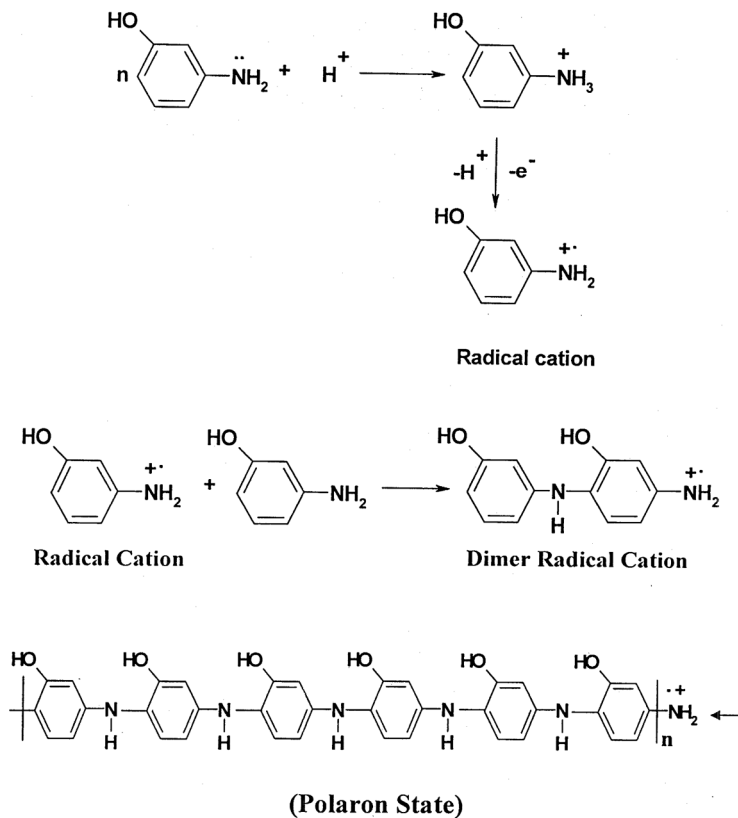
FIGURE 1 Cyclic voltammogram of Pt electrode from solution containing 1.0 M HCl and 0.1 M Na_2SO_4 at 298°K with scan rate of 25 mVs^{-1} in (A) absence of monomer, (B) 0.05 M monomer.

Radical cation

Radical Cation   **Dimer Radical Cation**
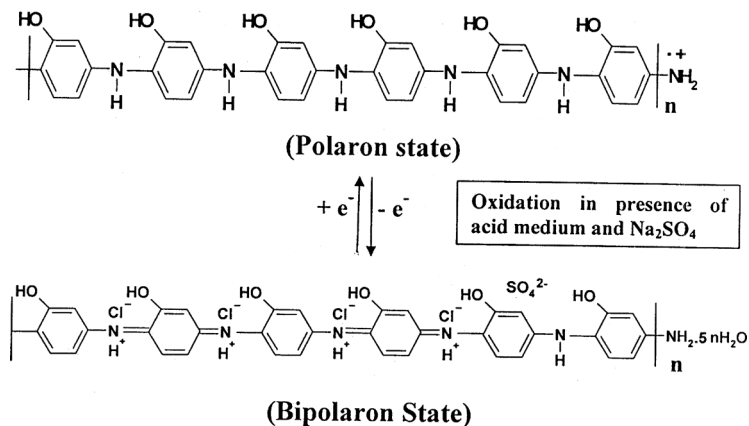
(Polaron State)

SCHEME 1 Formation of semiquinone radical cation.

Figure 2 shows the effect of repetitive cycling on the formation of the polymer film. The data reveal that the peak current densities Ip_1 and Ip_2 for the first and second anodic peak, respectively, decrease with repetitive cycling.

Figure 3A illustrates the influence of the scan rate $(5–100 \, \text{mVs}^{-1})$ on the potentiodynamic anodic polarization curves for 3-hydroxyaniline from solution containing 0.05 M monomer, 1.0 M HCl, and 0.1 M Na_2SO_4 at 298°K on platinum electrode. It is obvious that the anodic peak current (Ip) increases with increasing scan rate.

Figure 3B shows the linear dependency of Ip versus $v^{1/2}$. This linear relation suggests that the electropolymerization of 3-hydroxyaniline may be described partially by a diffusion controlled process (diffusion of reacting species to the polymer film/solution interface).

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(Polaron state)

$+ e^-$ ↑↓ $- e^-$

Oxidation in presence of acid medium and Na_2SO_4

(Bipolaron State)
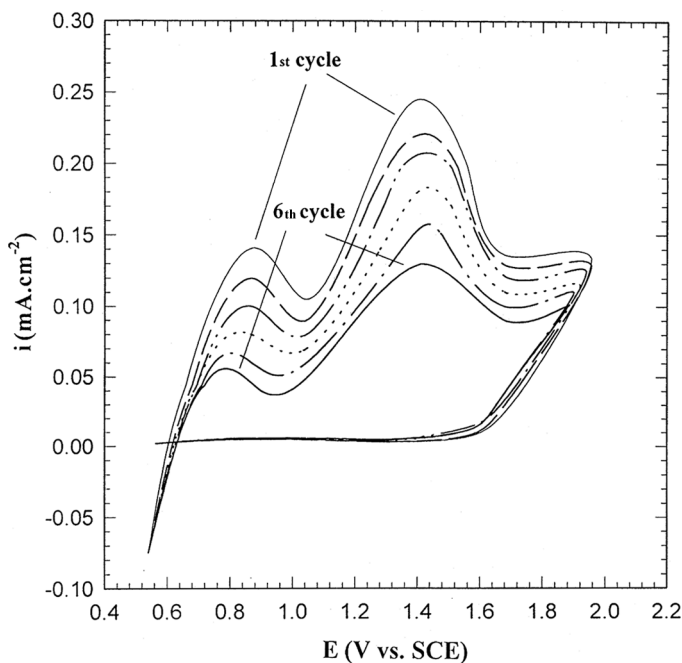
SCHEME 2 Formation of quinine imine.

FIGURE 2 Repetitive cycling of electrodeposition of poly(3-hydroxyaniline) from solution containing 0.05 M monomer, 1.0 M HCl, and 0.1 M Na_2SO_4 at 298°K with scan rate of 25 mVs^{-1}.
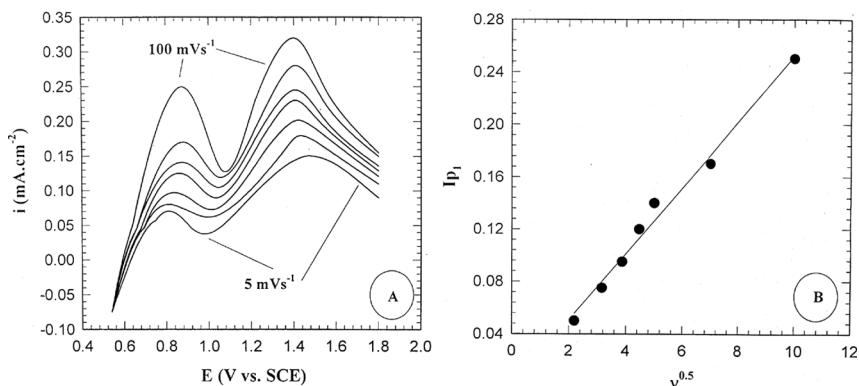
FIGURE 3 (A): Effect of scan rate on the electrodeposition of poly(3-hydroxyaniline) from solution containing 0.05 M monomer, 1.0 M HCl, and 0.1 M Na_2SO_4 at 298°K. (B): Relation between Ip_1 versus $\nu^{0.5}$.

Kinetic Studies

The electropolymerization kinetics were evaluated using aceto-nitrile/H_2O mixture (10:90 v/v) solutions containing monomer (concentration range between 0.01 and 0.09 M), hydrochloric acid (concentration range between 0.2 and 1.4 M), and Na_2SO_4 (concentration range between 0.02 and 0.16 M) at 298°K. The kinetic equation was calculated from two different sets of data: (1) by means of ex-situ microgravimetric study (two electrode cell), and (2) by means of electrochemical study from the values of the anodic current densities (three electrode cell).

Ex-Situ Microgravimetric Study

Effect of monomer concentration. The effects of monomer concentrations on the electro-deposition of poly(3-hydroxyaniline) were studied by keeping the acid concentration fixed at 1.0 M, Na_2SO_4 at 0.1 M and temperature at 298°K but the monomer concentrations were varied in the range between 0.01 and 0.09 M. The weight of the obtained polymer film in each case was determined.

From the obtained data, it was noticed, that the maximum weight of the polymer film was obtained when a monomer concentration of 0.05 M was used (cf. Figure 4A). The electropolymerization was performed with different monomer concentrations in the range between 0.01 and 0.05 M at different electro-polymerization time intervals and the data are represented in Figure 4B. The initial rate of the electropolymerization reaction (R_i) was calculated and the double
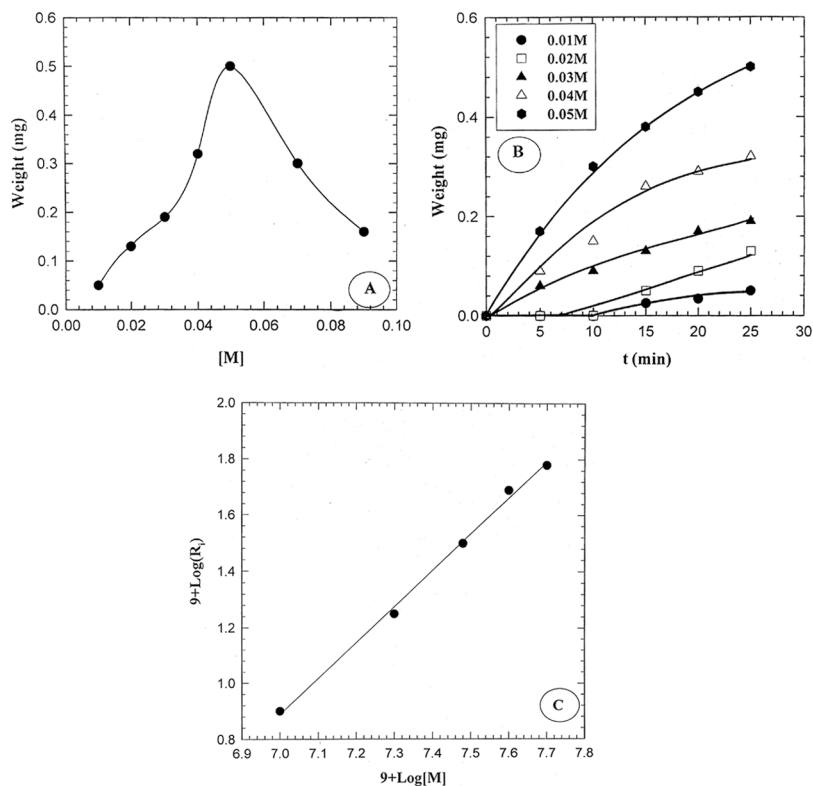
FIGURE 4 (A): Effect of monomer concentration on the electrodeposition of poly(3-hydroxyaniline) from solution containing 1.0 M HCl, 0.1 M Na$_2$SO$_4$ at 298°K. (B): Yield-time curves showing the effect of monomer concentrations on the reaction rates. (C): Double logarithmic plot of the initial rates of the electrodeposition reactions versus monomer concentrations.

logarithmic plot of the (R_i) versus the monomer concentration is represented in Figure 4C. This relation gave a straight line with slope equal to 1.2. This means that the order of the reaction with respect to the monomer concentration is a first order.

Effect of HCl concentration. The electropolymerization of 3-hydroxyaniline from acetonitrile/water mixture (10:90 v/v) solution containing 0.05 M monomer, 0.1 M Na$_2$SO$_4$ at 298 K using different HCl concentrations in the range between 0.2 M and 1.4 M at constant time (25 min). The maximum weight of the good adherent polymer film on platinum electrode was found when 1.0 M HCl was used. The electropolymerization reactions were carried out for each investigated HCl

concentration (0.2, 0.4, 0.6, 0.8, and 1.0 M) at different time intervals. The weight of the deposited polymer film on the platinum electrode in each concentration is plotted against the electropolymerization time and the electropolymerization rate was calculated (cf. Figure 5A). The double logarithmic plot of the electropolymerization rate versus HCl concentration is represented in Figure 5B. A straight line was obtained with a slope of 0.91. Therefore, the reaction order with respect to HCl concentration is a first-order reaction.

Effect of electrolyte concentration. Electrodeposition of poly-(3-hydroxyaniline) was carried out from solution containing 1.0 M HCl and 0.05 M monomer at 298°K in acetonitrile/H_2O (10:90 v/v) mixture at 25 min but the electrolyte concentrations were varied in the range between 0.02 to 0.16 M. The weight of the deposited polymer film on the platinum electrode in each electrolyte concentration (0.02, 0.04, 0.06, 0.08, and 0.1 M where 0.1 M is the optimum concentration) is plotted against the duration time and the electropolymerization rate was calculated (cf. Figure 6A). The double logarithmic plot of the electropolymerization rate versus Na_2SO_4 concentrations is represented in Figure 6B. A straight line was obtained with a slope of 0.69. Therefore, the reaction order with respect to the electrolyte concentration is a first-order reaction.

Therefore, the kinetic rate law obtained from an ex-situ microgravimetric study for the electropolymerization of 3-hydroxyaniline on
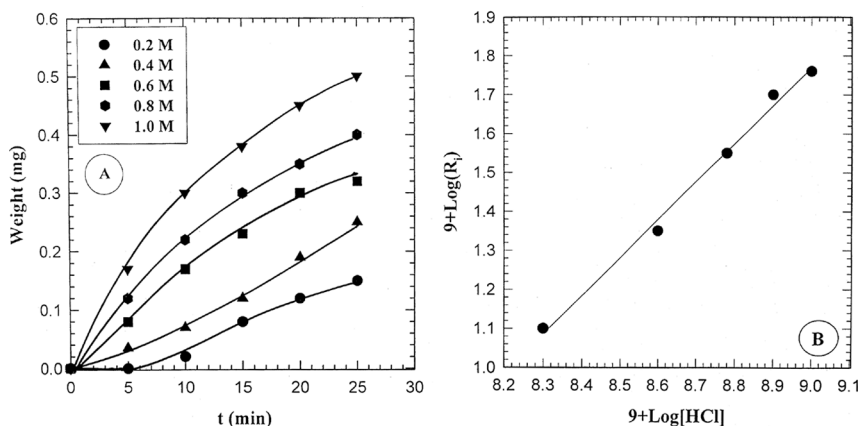

FIGURE 5 (A): Yield-time curves showing the effect of HCl concentrations on the reaction rates. (B): Double logarithmic plot of the initial rates of the electrodeposition reaction versus HCl concentrations.
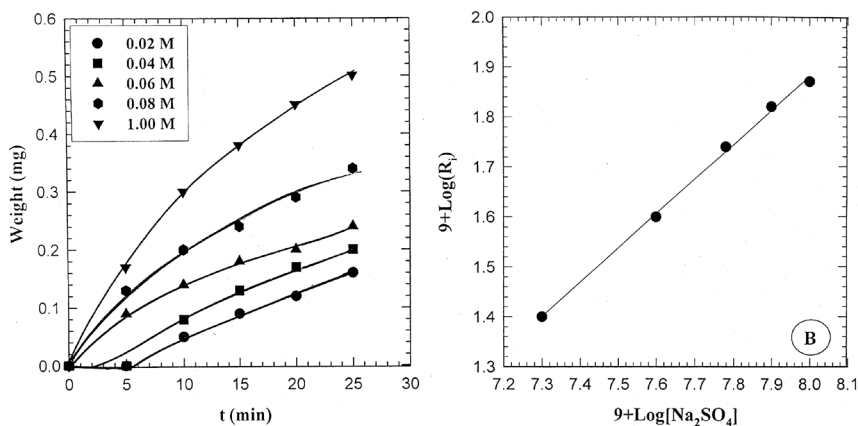
FIGURE 6 (A): Yield-time curves showing the effect of Na_2SO_4 concentrations on the reaction rates. (B): Double logarithmic plot of the initial rates of the electrodeposition reaction versus Na_2SO_4 concentrations.

platinum electrode can be expressed as follows:

$$R_{P,W} = k_W[monomer]^{1.2}[acid]^{0.91}[electrolyte]^{0.69}$$

where $R_{P,W}$ is the electrodeposition rate and k_W is the kinetic rate constant calculated from ex-situ microgravimetric study.

Effect of temperature. The effect of temperature on the electropolymerization of 3-hydroxyaniline was elucidated by ex-situ microgravimetric study under the following constant conditions: 1.0 M HCl, 0.05 M monomer, and 0.1 M Na_2SO_4 but the reaction was carried out at different temperatures in the range between 288 and 313°K. The maximum weight of the polymer film was recorded at 298°K. It was noticed during the experiments that, at temperatures higher than 298°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 298°K, the adhesion of the film to the electrode is decreased. The electrodeposition of poly(3-hydroxyaniline) was carried out at different temperatures 288, 293, and 298°K for different time intervals as shown in Figure 7A. The rate of the electro-deposition was calculated at each investigated temperature and the logarithm of the electrodeposition rate was plotted versus 1/T (cf. Figure 7B), which gives a straight line with a slope equal to -7.6. By applying Arrhenius equation, the apparent activation energy was calculated to be 145.5 kJ/mol.
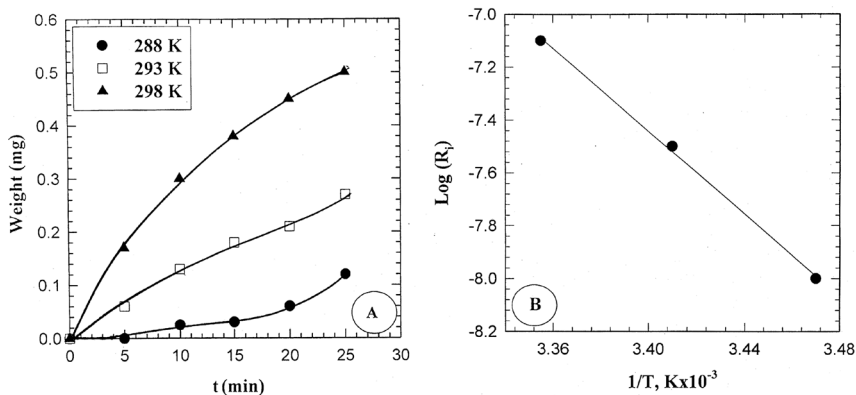
FIGURE 7 (A): Yield-time curves showing the effect of temperature on the reaction rates. (B): Arrhenius plot of the electrodeposition of poly(3-hydroxyaniline) from solution containing 0.05 M monomer, 1.0 M HCl, 0.1 M Na_2SO_4 and i = 6 mAcm^{-2}.

Electrochemical Study

The kinetic equation was calculated from the values of the anodic current densities produced at each concentration during the electrodeposition of the polymer. The values of the anodic current density (I_{Pa}) are proportional to the electropolymerization rate ($R_{P,E}$) at a given concentration of the monomer, acid, and electrolyte concentrations. Thus one can replace the electropolymerization rate with the anodic current density [33,38].

Effect of monomer concentration. Figure 8A represents the potentiodynamic polarization curves obtained at 0.01, 0.02, 0.03, 0.04, and 0.05 M monomer solutions in the potential range between 540 and 1800 mV (vs. SCE) with scan rate of 25 mVs^{-1}. From the figure, it is clear that the anodic peak current obtained at each concentration was enhanced by increasing the monomer concentration. A double logarithmic plot of the current density at the first anodic peak against the monomer concentration gives a straight line with a slope of 0.96 (cf. Figure 8B). Therefore, the reaction with respect to monomer concentration is a first-order reaction.

Effect of HCl concentration. Potentiodynamic polarization curves obtained at 0.2, 0.4, 0.6, 0.8, and 1.0 M HCl solutions in the potential range between 540 and 1800 mV (vs. SCE) with scan rate of 25 Vs^{-1} are shown in Figure 9A. The data show that the anodic peak current obtained during the electrodeposition reaction was enhanced by
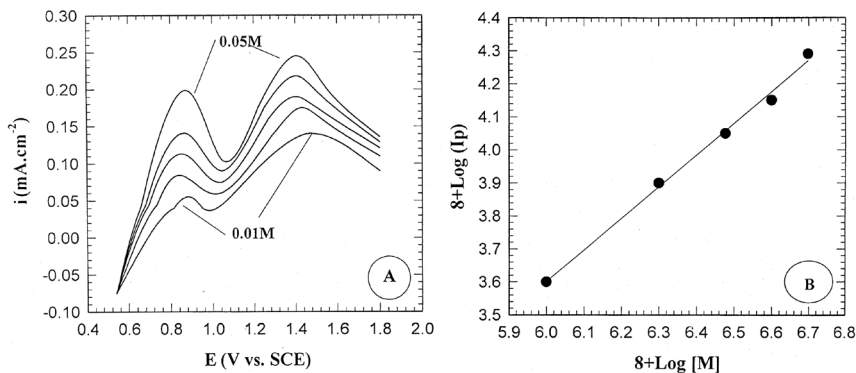
FIGURE 8 (A): Potentiodynamic polarization curves for the effect of mono-mer concentrations on the electrodeposition of poly(3-hydroxyaniline) from sol-ution containing 1.0 M HCl and 0.1 M Na_2SO_4 at 298 K with scan rate of $25\,\mathrm{m\,V\,s^{-1}}$. (B): Double logarithmic plot of the anodic current density versus monomer concentrations.

increasing the acid concentration. A double logarithmic plot of the current density at the first oxidation peak against HCl concentra-tions is graphically represented in Figure 9B. A straight line with slope of 0.92 was obtained. Therefore, the reaction with respect to HCl concentrations is a first-order reaction.
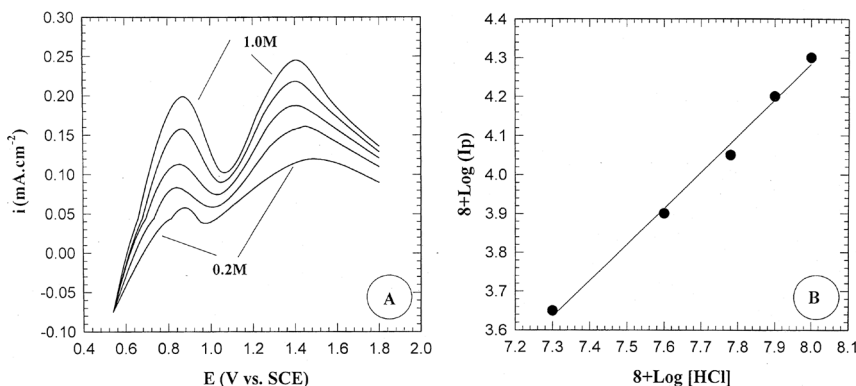

FIGURE 9 (A): Potentiodynamic polarization curves for the effect of HCl con-centrations on the electrodeposition of poly(3-hydroxyaniline) from solution containing 0.05 M monomer and 0.1 M Na_2SO_4 at 298 K with scan rate of $25\,\mathrm{mVs^{-1}}$. (B): Double logarithmic plot of the anodic current densities versus HCl concentrations.

Effect of electrolyte concentration. Figure 10A represents the potentiodynamic polarization curves obtained at 0.02, 0.04, 0.06, 0.08, and 0.1 M Na_2SO_4 in the potential rangey between 540 and 1800 mV with scan rate of $25\,mVs^{-1}$ The data show that the anodic peak current obtained was enhanced by increasing the electrolyte concentration. A double logarithmic plot of the current density at the first oxidation peak against the electrolyte concentrations gives a straight line with a slope of 0.7 (cf. Figure 10B).

Therefore, the kinetic rate law obtained from this method can be written as:

$$R_{P,E} = k_E[\text{monomer}]^{0.96}[\text{acid}]^{0.92}[\text{electrolyte}]^{0.7}$$

where $R_{P,E}$ is the electrodeposition rate and k_E is the kinetic rate constant calculated from electrochemical study.

By comparing both kinetic equations, calculated from ex-situ microgravimetric study and from electrochemical study, it can be concluded that there is a good agreement between the order of the reaction with respect to the acid, the monomer, and the electrolyte concentrations. Because this was determined by different techniques, it indicates that there is no significant parallel reactions occuring on the electrode and the current efficiency remains constant during the electrodeposition reaction [33,39].
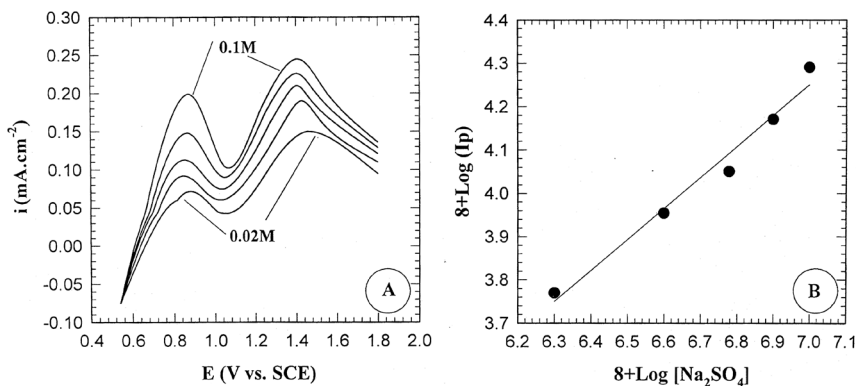

FIGURE 10 (A): Potentiodynamic polarization curves for the effect of electrolyte concentrations on the electrodeposition of poly(3-hydroxyaniline) from solution containing 0.05 M monomer and 0.1 M HCl at 298 K with scan rate of $25\,mVs^{-1}$. (B): Double logarithmic plot of the anodic current densities versus electrolyte concentrations.

Effect of temperature. The potentiodynamic polarization curves as a function of the solution temperature in the range between 288 to 298°K under the same experimental conditions, as mentioned earlier in case of ex-situ microgravimetric studies, are illustrated in Figure 11A. From the figure, it is clear that the anodic current densities increase with raising reaction temperature. The plot of log Ip versus 1/T is represented in Figure 11B. A straight line relationship is obtained with a slope of– 7.5. Then, the apparent activation energy was calculated using Arrhenius equation and was found to be 143.6 kJ/mol.

Elemental and Infrared Spectroscopic Analysis

The percentage of C, H, N, S, and Cl were in good agreement with those calculated from the suggested structure given in Scheme 2 and the data are summarized in Table 1. The presence of five molecules of water for each repeated unit is confirmed by thermogravimetric analysis (TGA).

The medium IR absorption bands appearing at 773 and 872 cm^{-1} assigned to out of plane C–H deformation for 1,3- and 1,4-disubstituted benzene ring, respectively. The two absorption bands at 1128 and 1176 cm^{-1} are attributed to the stretching vibration of SO_4^{2-} and Cl^-, respectively, which indicate that SO_4^{2-} and Cl^- anions are counter-ions to the polymeric chain [40–41]. But no evidence for the
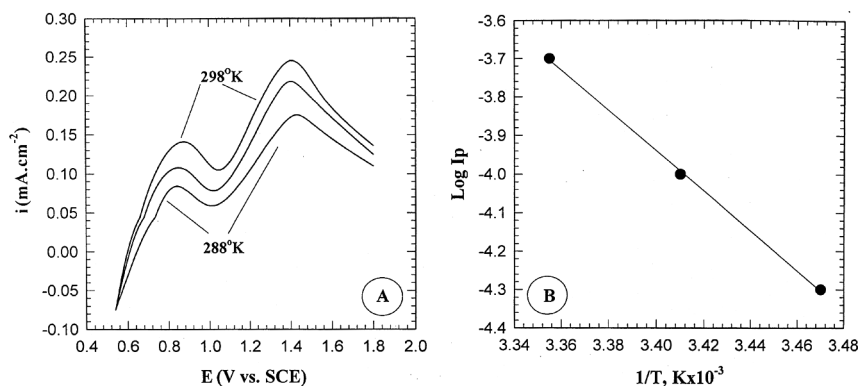

FIGURE 11 (A): Potentiodynamic polarization curves for the effect of temperature on the electrodeposition of poly(3-hydroxyaniline) from solution containing 0.05 M monomer and 0.1 M HCl, and 0.1 M Na_2SO_4 with scan rate of 25 mVs^{-1}. (B): Arrhenius plot of the electrodeposition of poly(3-hydroxyaniline).

TABLE 1 Elemental Analysis of the Prepared Poly(3-hydroxyaniline)

Element (%)									
C		H		N		Cl		S	
Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
45.24	45.70	4.08	4.50	7.33	6.90	14.87	15.20	3.35	3.40

formation of new bonds between the polymer chain. and the doped anions was observed, which means that the counter-anions near the polymeric chains exist in the ionic form [42] as shown in Scheme 2.

The two absorption bands appearing at 1461 and 1616 cm^{-1} are assigned to benzenoid and quinoid structures, respectively [41,43].
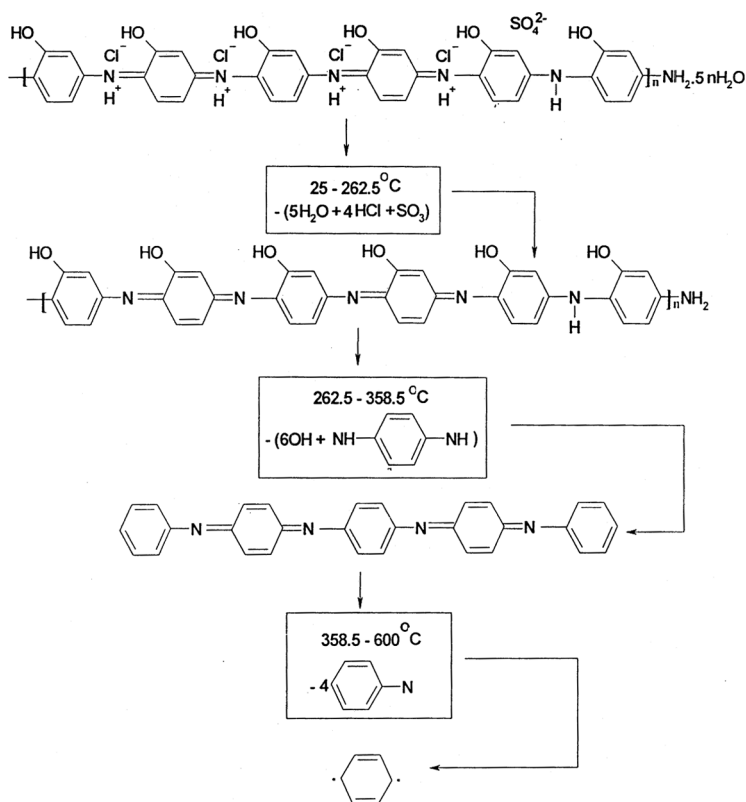

SCHEME 3 The four degradation stages of electrochemically prepared poly(3-hydroxyaniline).

The band intensity at $1461 \, \text{cm}^{-1}$ (Benzenoid form) is slightly stronger than that at $1616 \, \text{cm}^{-1}$ (Quinoid form) and thus it gives a good relation between the number of benzenoid to quinoid rings, as shown in Scheme 2.
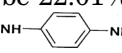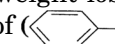
The two absorption bands at 3362 and $3300 \, \text{cm}^{-1}$ are assigned to the combination of OH and NH symmetric stretching vibration.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) for the electrochemically prepared poly(3-hydroxyaniline) sample has been investigated and the thermal degradation steps are shown in Scheme 3. From the scheme, it is clear that there are four stages:
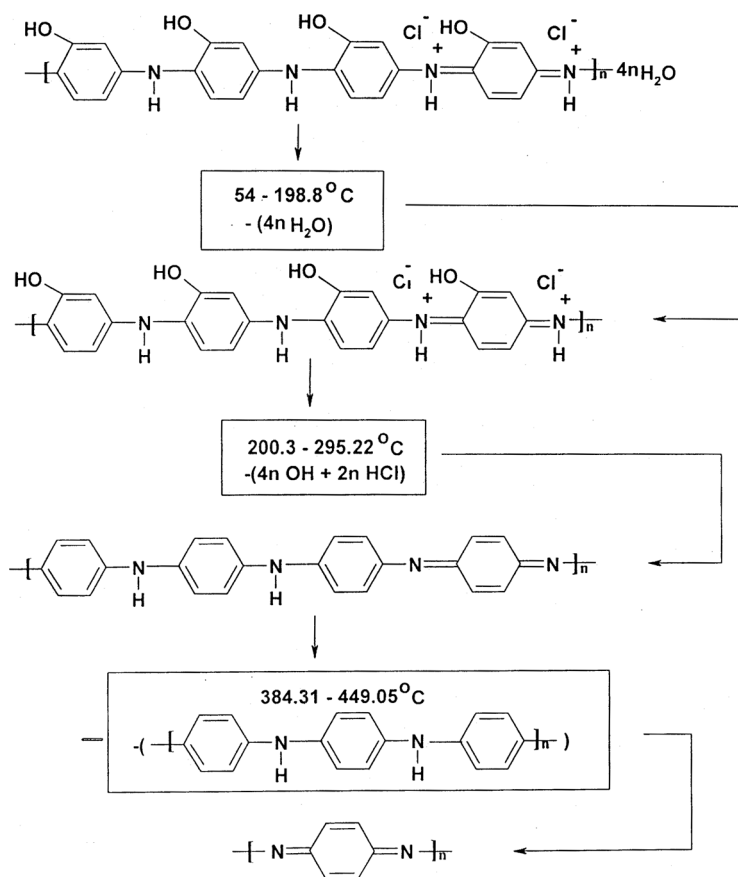
SCHEME 4 Degradation of chemically prepared poly(3-hydroxyaniline).

1. The first stage includes the loss of five molecules of H_2O, four molecules of HCl, and one molecule of SO_3 in the temperature range between 25 and 262.5°C. The estimated weight loss for this step is found to be 33.50% and the calculated one is 33.09%.
2. The weight loss in the second stage, in the temperature range between 262.5 and 358.5°C is found to be 22.01%, which is attributed to the loss of six OH and one NH—⟨⟩—NH. The calculated weight loss of this stage equals 21.8%.
3. In the third stage, in the temperature range between 358.5 and 600°C, the weight loss was found to be 36.9%, which is attributed to the loss of (⟨⟩—N)₄. The calculated weight loss of this stage is 36.2%.
4. The last stage, above 600°C, phenyl biradical (7.6%) remains.

The thermal degradation steps of the chemically prepared poly-(3-hydroxyaniline) by Sayyah et al. [44] are shown in Scheme 4. From Schemes 3 and 4, it is clear that electrochemically prepared poly-(3-hydroxyaniline) is more thermally stable than that prepared by chemical method.

CONCLUSIONS

1. The onset potentials for the oxidation of 3-hydroxyaniline monomer are 870 and 1400 mV (vs. SCE).
2. The electropolymerization of 3-hydroxyaniline monomer may be described partially by diffusion controlled process.
3. The kinetic rate law obtained from an ex-situ micro-gravimetric study for the electropolymerization reaction is: $R_{p,w} = k_w \, [\text{acid}]^{0.9} \, [\text{monomer}]^{1.2} \, [\text{electrolyte}]^{0.69}$, while that obtained from the potentiodynamic study is $R_{P,E} = k_E [\text{acid}]^{0.92} \, [\text{monomer}]^{0.96} \, [\text{electrolyte}]^{0.7}$.
4. The apparent activation energies were calculated from the two techniques and found to be 145.5 and 143.6 kJ/mol from microgravimetric and potentiodynamic measurements, respectively.
5. Electrochemically prepared poly(3-hydroxyaniline) is more thermally stable than that prepared by chemical method.

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