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RESEARCH ARTICLE

Electropolymerization of Ortho-bromophenol on Pt-Electrode from Aqueous Acidic Solution; Kinetics, Mechanism, Electrochemical Studies and Characterization of the Polymer Obtained

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Abstract

In this study electrochemical oxidation of o-bromophenol (OBP) on platinum electrode has been investigated using cyclic voltammograms in acid solutions under nitrogen atmosphere at different reaction conditions such as sulfuric acid concentration, monomer concentration and temperature

The experimentally obtained kinetic equation was $R_p = K_E [H_2SO_4]^{1.14} [M]^{0.96}$, which was deduced from the values of the first anodic current density (i_{pI}). A simplified mechanism for the electrochemical reaction of OBP is proposed and the apparent activation energy was determined.

The obtained polymer films were characterized by ^{1}H-NMR, elemental analysis, IR, UV spectroscopy, thermogravimetric analysis (TGA), X-ray and scanning electron microscopic (SEM) analysis.

Conventional electrochemical techniques for the obtained polymer such as open circuit potential measurements, polarization methods and electrochemical impedance spectroscopy (EIS) were used to investigate the application of the prepared polymer as corrosion inhibitors for mild steel in acid medium $P^H = 2$.

INTRODUCTION

One of the promising methods for waste water remediation is in the electrochemical oxidation of hazardous organic species [Fleszar&Jolanta, 1985; Comninellis, 1994]. Considered as one of the most promising methods for phenols due to their slow degradation, bioaccumulation and toxicity constitute a large group of organic pollutants. The quantitation of phenolic compounds in environmental, industrial and food samples is currently of great interest, which can be found in soils and groundwater [Wang et al., 1998]. Also, these compounds are important synthesis intermediates in chemical industry such as resins, preservatives, pesticides, etc. Another, the main sources of phenolic waste are in glass fiber insulation manufacture on petroleum refineries. Phenol and substituted phenolic compounds such as catechol, chlorophenol and hydroquinones are discharged from the effluent of chemical process industries. Today, these compounds are found in relatively high amount in domestic and industrial wastewater, discharged mainly from the chemical industries. Many treatment technologies are proposed for phenol recovery or destruction.

The electrooxidation of phenolic compounds can be occurs as follows: in the first step of electrooxidation of phenols, phenoxy radicals are generated, then these species can be either oxidized further or be coupled, forming ether and oligomeric or polymeric compounds [Wang et al ,1991; Iotov, &Kalcheva, 1998]. Electropolymerization of phenol beings with the formation of the phenoxy radical, or it can react with a molecule of phenol to give predominantly a para-linked dimeric radical. This radical may be further oxidized to form a neutral dimmer or it may attach another molecule. The dimer may be further oxidized creating oligomers or polymers. Formation of the insoluble polyphenol results in deactivation of electrode surface. The relative rates of the two pathways (polymerization and forming quinonic structure) depend on the phenol concentration, the nature of electrode, P^H, solvent, additives, electrode potential and current density [Gattrell& Kirk,1993]. Electropolymerization of phenols occur on different electrodes, such as Fe, Cu, Ni, Ti, Au, Pt and other type of electrodes [Iotov, &Kalcheva, 1998; Ezerskis&Jusys, 2002]. Deactivation of electrode due to the phenol polymerization is more characteristic in alkaline medium. Insoluble high molecular weight species block the electrode surface and prevent effective electrooxidation of phenol.

In the present work, we seek to contrast the electro-oxidation of o-bromophenol in aqueous H_2SO_4 medium as electrolyte using cyclic voltammetry technique. The kinetic study of the oxidation processes will be useful for optimization of the parameters affecting the electropolymerization reaction. Mechanism of the electrochemical polymerization will be discussed using electrochemical data. Also, the characterization of the obtained polymer films were carried out by elemental analysis, TGA, SEM, XRD, IR, UV, ^{1}H-NMR spectroscopy.

The obtained polymer at the investigated optimum conditions are tested to acts as corrosion inhibitor for mild steel in acid medium ($P^H = 2$).

2.Experimental

2.1. Materials:

O-bromophenol was obtained from (Merck.Schuchardt) ,Sulfuric acid and acetone were provided by Merck (Darmstadt, Germany). All chemicals are of analytical pure grade and used as received. All solutions were prepared by using freshly double-distilled water under N_2 gas.

2.2. Electropolymerization cell:

Electropolymerization of the o-bromophenol monomer was carried out using potentiodynamic technique. This cell is made from transparent Prespex trough, which has the inside dimensions of 8cm length, 2.5cm width and 3cm height.

2.2.1. Electrodes.

2.2.1.1. Working Electrode:

The working electrode (WE) was a platinum sheet with dimensions of 1cm length and 0.5cm width.

2.2.1.2. Auxiliary Electrode:

The auxiliary (counter) electrode (CE) was a platinum sheet with the same dimensions as the WE.

2.2.1.3. Reference Electrode:

A saturated calomel electrode (SCE) was used as a reference electrode. The values of the electrode potential in the present work are given relative to this electrode. The potential value for the SCE is 0.242V.

2.2.2. Procedure:

Potentiodynamic cyclic voltammetry measurements during the formation of the polymer films on the surface of the working electrode was carried out in the electrochemical cell .The cell was filled with the test solution (aqueous solution containing H_2SO_4 as supporting electrolyte, monomer and acetone as solvent). The working and counter electrodes were introduced in the cell. The reference electrode was attached to the cell by U-shaped salt bridge (SB) ended with a fine capillary tip (Luggin–Harber probe) where in the reference electrode was positioned very closed to the working electrode to minimize the over potential due to electrolyte resistance. The bridge was filled with the test solution. Before and during measurements a current of pure nitrogen gas was bubbled in the test solution to remove dissolved oxygen for 3minutes.

Electrochemical experiments were performed using the potentiostat/GalvanostatWenking PGS 95. I-E curves were recorded by computer software from the company (Model ECT). Except otherwise stated ,the potential was swept linearly from the starting potential vs. (SCE) into the positive direction up to a certain anodic potential with a given scan rate and then reversed with the same scan rate up to the starting cathodic potential. For each run, freshly prepared solutions as well as a cleaned and washed the cell, working reference and auxiliary electrodes were used thoroughly with ethanol, rinsed with doubly distilled water and then dried to remove any traces of the formed constituents in the reaction medium. All experiments were conducted at a given temperature with the help of circular water thermostat. The deposited polymer film was subjected to different experimental tests to characterize it.

2.3. Determination of the kinetic rate law of the electropolymerization reaction:

The amount of polymer electrodeposited on the electrode surface can be determined directly from the peak current density (i_p) [Sayah et al, 2010] therefore, The peak current density (i_p) is proportional to the electropolymerization rate (R_P,E) at a given concentration of the monomer and H_2SO_4. The kinetic equation was calculated from the value of anodic peak current density (i_p) measured at each concentration during the electroformation of polymer. In this case, we used the value of (i_p) instead of (R_P,E). Therefore, the kinetic rate law can be expressed as follows:

$$R_P, E = i_p = k_E\ [\text{Monomer}]^a\ [\text{Acid}]^b \qquad (1)$$

Where *a* and *b* are the reaction orders with respect to monomer and acid concentrations respectively and K_E is the kinetic rate constant calculated from the electrochemical measurements.

2.4. Characterization of the electro-prepared polymers.

2.4.1. UV, IR, ^{1}H-NMR Spectroscopy, Elemental Analysis and Theromogravemetic analysis:

UV absorption spectra of the prepared polymer sample was measured using Shimadzu UV spectrophotometer (M160 PC) at room temperature in the range 200-400nm using (ethanol) as a solvent and reference.

IR measurements were carried out using shimadzu FTIR-340 Jasco spectrophotometer (Japan) by KBr pellets disk technique.

^{1}H-NMR measurements were carried out using a Varian EM 360L,60-MHz NMR spectrometer. NMR signals of the electropolymerized sample were recorded in dimethylsulphoxide (DMSO) using tetramethylsilane as internal standard.

Theromogravemetic analysis (TGA) of the obtained polymer was performed using a Shimadzu DT-30 thermal analyzer (Shimadzu, Kyoto, Japan). The weight loss was measured from ambient temperature up to 600ºC, at the rate of 20ºC min^{-1} and nitrogen 50cc min^{-1} to determine the degradation rate of the polymer.

Elemental analysis was carried out in the micro-analytical center at Cairo University (Cairo, Egypt) by oxygen flask combustion and dosimet E415 titrator (Metrohm).

2.4.2. Scanning Electron Microscopy and X-ray Diffraction.

Scanning electron microscopic (SEM) analysis was carried out on the as prepared polymer film deposited on Pt-working electrode surface using a JSM-T20 Electron Probe Micro analyzer (JEOL, Tokyo, Japan).

The X-ray diffraction analysis (XRD) (Philips 1976 Model 1390, Netherlands) was operated under the following conditions that were kept constant for all the analysis processes:

X-ray tube: Cu Scan speed: 8deg min^{-1} Current: 30mA Voltage: 40kV Preset time: 10sec.

2.5. Open Circuit Potential Measurements:

The potential of the working electrode under open circuit conditions was measured separately against the saturated calomel electrode ($Hg/Hg_2Cl_2/Cl^-_{sat}$) reference electrode [E^o = 242mV vs. the standard hydrogen (SHE)]. Open circuit potentials were following over 1hour using a high impedance autorangingmultimeter.

2.6. Electrochemical System:

The electrochemical impedance investigations and polarization measurements were performed using the Voltalab 10PGZ100 "All in-one " potentiostat / Galvanostat.

The instrument is interfaced to an external IBM 1200 CPU computer. The voltamaster4 software is designed to measured and analyzed corrosion quickly, easily and reliably using a variety of techniques, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) the experimental set up allows the direct application of any required techniques. In our experiments both linear and tafel polarization techniques were used after each impedance experiment which was always carried out open- circuit potential.

2.6.1. Potentiodynamic Polarization Techniques:

The corrosion rate can be obtained usually by the use of the linear polarization and Tafel extrapolation methods. Potentiodynamic measurements were conducted at a scan rate of 10mV/sec. The resulting current is linearly plotted versus the potential and the slope of this potential–current function at corrosion potential E_{corr}, is referred to as the polarization resistance R_p, and is used with the Tafel constants to determine the corrosion current density i_{corr}. The linear polarization technique is extremely rapid. This makes the measurements of the linear polarization very useful in the applied potential which is never far from the corrosion potential, so the surface of the specimen is not significantly affected by the experiment and can often be used for other studies.

2.6.2 Impedance Measurements:

The electrochemical impedance spectroscopy is a powerful technique for investigating electrochemical and corrosion systems. The main advantage of this technique is the use of a purely electronic model (equivalent circuits) to represent the electrode/electrolyte interface under different conditions. An interface undergoing an electrochemical reaction is typically analogous to an electronic circuit consisting of resistors, capacitors and/or conductors. Thus, an electrochemical system can be characterized in terms of its equivalent circuit. According to ac circuit theory, an impedance plot obtained for a given electrochemical system can be correlated with one or more equivalent circuits.

3. Results and discussion

3.1. Electropolymerization kinetics and mechanisms of o–bromophenol (OBP)

3.1.1. Electropolymerization:

Electropolymerization of o-bromophenol on platinum electrode from aqueous solution containing 0.4M H_2SO_4 at 298 ^{o}K in the absence and presence of monomer, was studied by cyclic voltammetry at potential range between –500 : +1500 mV(vs. SCE) with scan rate of 25 mVs^{-1}. The obtained voltammograms in absence and presence of monomer is represented in Figure (1A&B) respectively. The voltammogram in absence of the monomer is no oxidation or reduction peaks (c.f. figure (1A)).

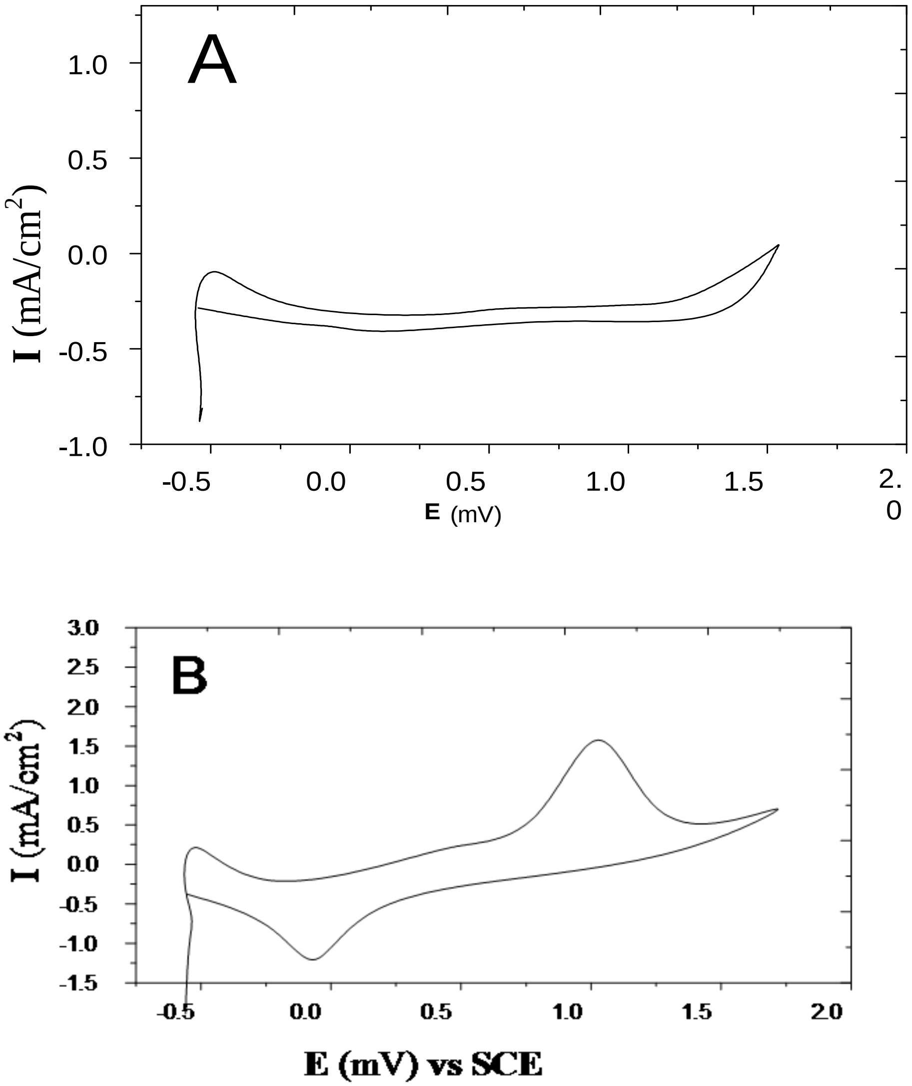


Figure (1): Cyclic voltammogram of solution containing 0.4M H_2SO_4 with scan rate 25mV/sec at 298^{o}K.

(A)Without Monomer **(B) With 0.04M Monomer**

While, the voltammogram in the presence of O-bromophenol exhibits two oxidation peaks (I and II) that progressively developed at -540 and +1030mV (vs.SCE) respectively and one reduction peak (II') at -13mV (vs. SCE) the first oxidation peaks (I) are a result of hydrogen reduction [Arslan et al, 2005] as mentioned above where, the second oxidation peaks (II) correspond to oxidation of monomer to give phenoxy radical which adsorbed on Pt - electrode [Gattrell& Kirk,1993]. The adsorbed radicals react with other monomer molecule via head-to-tail coupling to form predominantly a para-linked dimeric radical and so on to form oligomer and polymer film; this film is a

chain of isolated aromatic-electrons delocalizationrings between(polyethers)eachunitasshown in without scheme(1).

The oxidation occurs at more positive values ~+1030 mV vs. SCE where the presence of Bromine atom makes the oxidation process difficult. On reversing the potential scan from, the reversing anodic current is very smallindicating the presence of polymer layer adhered to the Pt-surface [Sayyah et al, 2010]. One cathodic peak (II') was found which could be ascribed to the reduction of the formed polymer films.

Figure (2): is illustrates that the effect of repetitive cycles on Pt-electrode in aqueous solution containing 0.4M H2SO4 with 0.04M monomer at 298oK. The data reveal that, the repetitive cycling show the oxidation peak (I). The current of this peak (ipI) is almost the same and not affected with cycling up to 7 cycles. This means that, surface area of electrode is not affected by the H2 adsorption while, the oxidation peak (II) the data reveal that, during the second cycle both the oxidation and the reduction peak currents decrease significantly with repetitive cycling. This behavior is observed else where as a result of fouling of electrode [Arslan et al,2005] where phenolic products block the electrode surface and the formed film hinders diffusion of further phenoxide ions to the electrode surface, there by causing a significant decrease in the anodic peak current and also decrease the cathodic peak current. The potential position of the redox peaks does not shift with increasing number of cycles, indicating that the oxidation and the reduction reactions are independent on the polymer thickness [Sayyah et al, 2010].

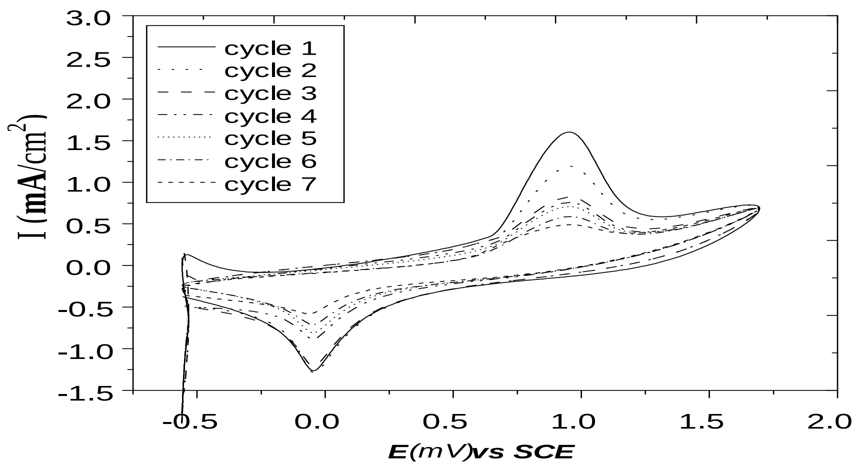


Figure (2): Repetitive cycling on the cyclic voltamograms for electropolymerization of O-bromophenol from solution containing 0.04M monomer, 0.4M H_2SO_4 concentration at 298^{o}K with scan rate 25mV/sec.

Figure (3A): illustrates the influence of the scan rate(5–30mVs^{-1}) on the potentiodynamic anodic polarization curves for o-bromophenol from aqueous solution containing 0.4M H_2SO_4 and 0.04M monomer at 298^{o}K on platinum electrode. It is obvious that both the anodic and cathodic peak current densities (i_{pII} and $i_{pII'}$) increases with the increasing of the scan rate. This behavior may be explained as follows, when an enough potential is applied at Pt- surface causing oxidation of species in solution, a current arises due to the depletion of the species in the vicinity of the Pt-surface. As a slope (dc/dx) imposed (i=dc/dx). As the scan rate increases the gradient increase and consequently the current (i_p).consequence, a concentration gradient appears in the solution. The current (i_p) is proportional to the gradient

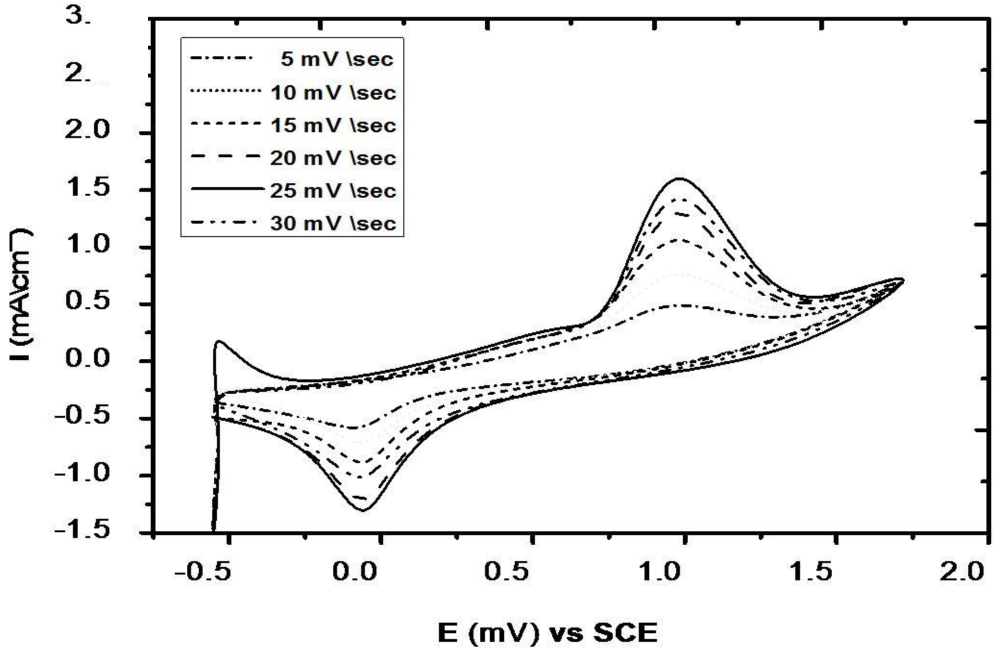


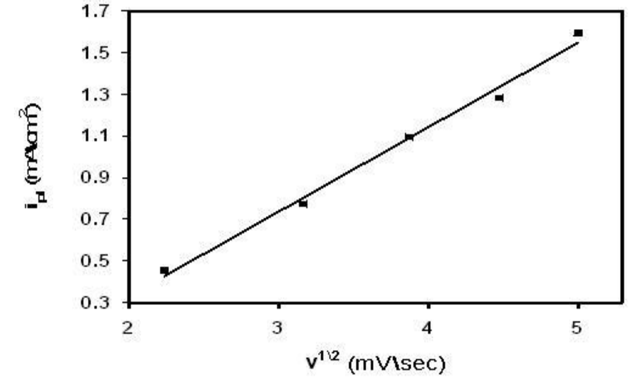
Figure (3A): Effect of scan rate on the cyclic voltammograms for electropolymerization of O-bromophenol from solution containing 0.04M monomer, 0.4M H_2SO_4 concentration at 298^{o}K.

Figure (3B): shows the linear dependency of the anodic peak current densities (i_{pII})-which is corresponding to the formation of the polymer film poly(o-bromophenol) versus the square root of scan rate ($v^{½}$). This linear relation suggests that the oxidation of o-bromophenol to poly (o-bromophenol) may be described by a partially diffusion-controlled process (diffusion of reacting species to the polymer film/solution interface) where the correlation coefficients (r^2) is higher than 0.9 but not equal to 1.0 suggesting the non-ideal simulation relation (i.e: the process is not completely diffusion control but it is exactly a partially diffusion control). Values of I_p are proportional directly to $v^{½}$ according to Randless [Randless, 1984] and Sevick [Sevick, 1948] equation:

$$i_{pII} = 0.4463\, n\, F\, A\, C\, (n\, F\, v\, D / R\, T)^{1/2} \qquad (4)$$

where n is the number of exchanged electron in),A is the mec the electrode area (cm^2), C is the bulk concentration, D is the analyst diffusing coefficient ($cm^2 s^{-1}$), and v is the

scan rate Vs^{-1}). R is the universal gas constant (8.314 $Jmol^{-1}K^{-1}$), T is the absolute temperature (^oK).



Figure(3B): Relation between I_{pi} and $v^{½}$.

The calculated values of D (at 0.4M H_2SO_4 and 0.04M monomer at 298^{o}K with scan rate from 5 to 30mVs^{-1}) are shown in Table (1):

Table 1.Calculated values of Diffusion Coefficient.

Diffusing coefficient, (D) ($m^{2}\ s^{-1}$)	**Scan rate,** (Vs^{-1})
0.8034×10^{-7}	0.005
2.0977×10^{-7}	0.010
3.7432×10^{-7}	0.015
5.4028×10^{-7}	0.020
7.5307 X 10-7	0.025

The values of D are seen to be increase over the range of sweep rate, which again shows that the oxidation process is diffusion-controlled [Sayyah et al, 2010]. It seems that, initially the electroformation of radical cations is controlled by charge transfer process. When the polymers become thick, the diffusion of the reactant inside the film becomes the slowest step, the process changed to diffusion transfer, which confirms the data in Figure 3A.

The intercept in Figure (3B) is small, -0.48, which could be attributed to a decrease of the active area of the working electrode during the positive scan [Zanartu et al, 2002] or the increase of the covered area of working electrode by the adhered polymer sample, which confirm the data of Figure (3A).

3.1.2. Kinetic Studies

The electropolymerization kinetics was investigated by using aqueous solution containing (different monomer concentrations in the range between 0.01 and 0.05M where H_2SO_4 concentration in the range between 0.1 and 0.5M at $298^{O}K$. The cyclic voltammogram for each monomeric systems and the relation between the $\log I_{pII}$vslog[monomer] or $\log I_{p11}$ vs. log[H_2SO_4] are plotted from which linear relation was obtained.

3.1.2.1. Effect of monomer concentration on the electropolymerization processes.

The influence of OBP concentrations on the CV behavior was studied using aqueous solution containing 0.4M H_2SO_4 at $298^{O}K$ scan rate of $25mVs^{-1}$ is shown in Figure (4A). The voltammograms show that, the anodic peak current densities (i_{pI1}) increase with the increasing of the monomer concentration in the range between 0.01 and 0.05M. This is obvious due to the increased availability of the electroactive species, OBP in solution, which is again in accordance with Eq. (4). At higher monomer concentrations (i.e. concentration >0.04M), no noticeable increase in the peak current was observed. This suggests that, at higher concentration (more than 0.04M), the oxidation reaction is not limited by diffusion alone. A double logarithmic plot of the current density related to oxidation peak (II) against monomer concentrations are graphically represented in Figure (4B), straight line with slope of 0.96 was obtained. Therefore, the reaction order with respect to monomer concentration is a first-order reaction.

3.1.2.2. Effect of acid concentration on the polymerization process

The influence of acid concentration in the range between (0.1 and 0.4M) on the CV using 0.04M monomer at $298^{O}K$ with scan rate of $25mVs^{-1}$ is represent in Figure (5A). Voltammograms show that, the anodic peak current densities (I_{pI1}) increase with the increasing of the acid concentration. At higher acid concentrations (i.e. concentration >0.4M), no noticeable increase in peak current was observed but, it began to decrease as a result of degradation and the solubility of the polymer film from the platinum surface.

A double logarithmic plot of the current density related to oxidation peak (II) against acid concentrations in the range between 0.1 and 0.4M is graphically represented in Figure (5B), straight line with slope of 1.14 was obtained. Therefore, the reactions order with respect to acid concentration is a first-order reaction.

The kinetic rate laws obtained from this method can be written as:

$$R_P, E = k_E\,[\text{monomer}]^{0.96}\,[\text{acid}]^{1.14}$$

Where R_P,E is the electropolymerization rate and k_E is kinetic rate constant.

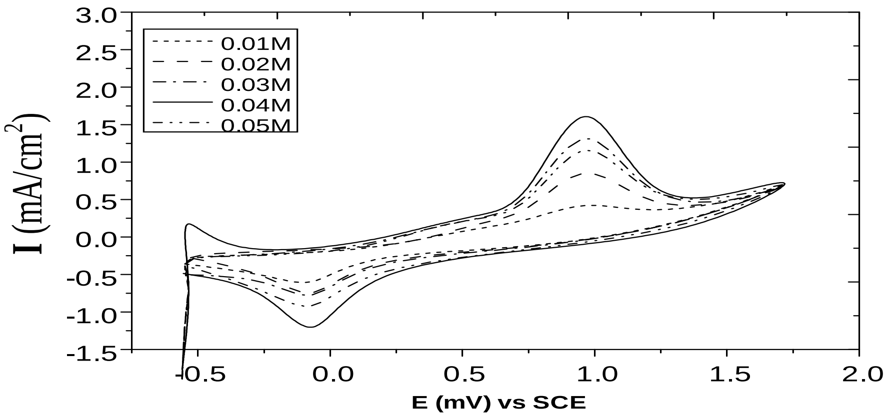


Figure (4A): **Effect of monomer concentration on the cyclic voltamograms for electropolymerization of O-bromophenol from solution containing 0.4M H_2SO_4 at $298^{0}K$ with scan rate 25mV\sec.**

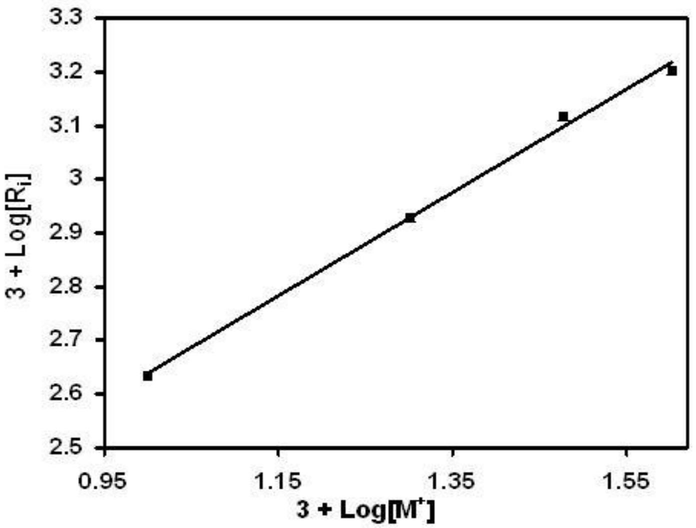


Figure (4B): **Douple logarithmic plot of the initial rate for electropolymerization reaction versus different monomer concentration values.**

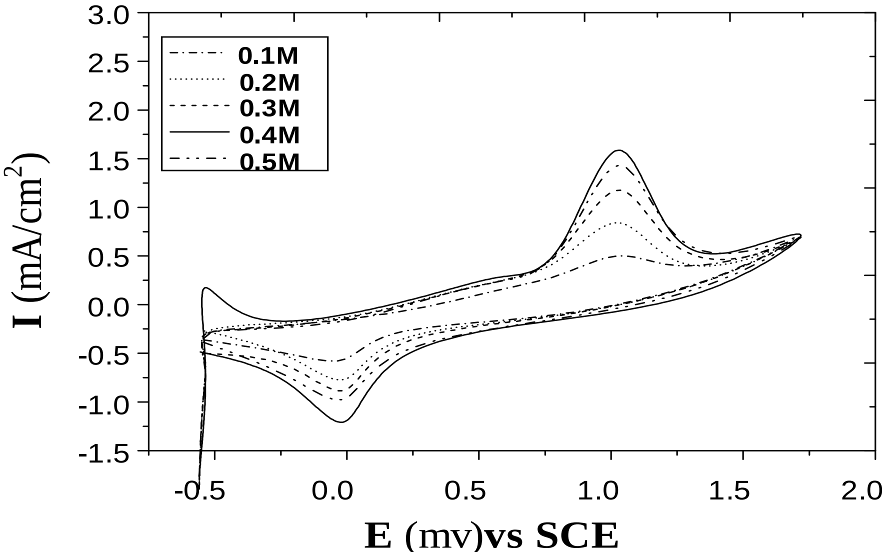


Figure (5A): **Effect of acid concentration on the cyclic voltammograms for electropolymerization of O-bromophenol from solution containing 0.04M monomer at 298^{0}K with scan rate 25mV/sec.**

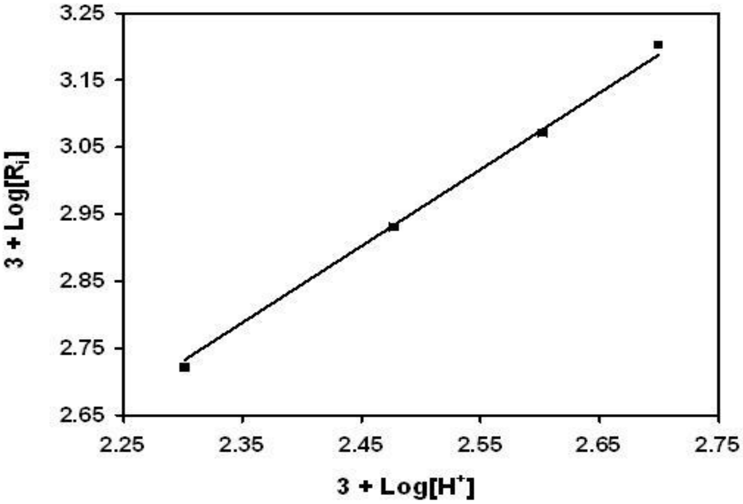


Figure (5B): Douple logarithmic plot of the initial rate for electropolymerization reaction versus different acid concentration values.

3.1.2.3. Effect of temperature and calculation of thermodynamic parameters:

The potentiodynamic polarization curves as a function of the solution temperature in the range between 283 and 303^{O}K under the optimum experimental conditions as mentioned above (i.e.0.04M monomer concentration and 0.4M acid concentration) was illustrated in Figure (6A). From this figure, it is clear that, an increase of the reaction temperature resulted in a progressive increase of the charge included in the anodic peaks. The plot of the log(I_{p1}) versus 1/T is represented in Figure(6B). Obtained straight line with slope equal to -2.166. The apparent activation energy was calculated using Arrhenius equation and it is found to be 41.48kJ mol^{-1}.

The enthalpy ΔH* and entropy ΔS* of activation for from Eyring equation plot at different temperatures (Figure 6C) we obtained linear relationship with slope of -ΔH*/2.303Rand intercept oflog {(R/Nh)+ΔS*/2.303R}. From slope and interceptfound tobe 39.06kJmol^{-1}and -49.64JK^{-1}mol^{-1} respectively.

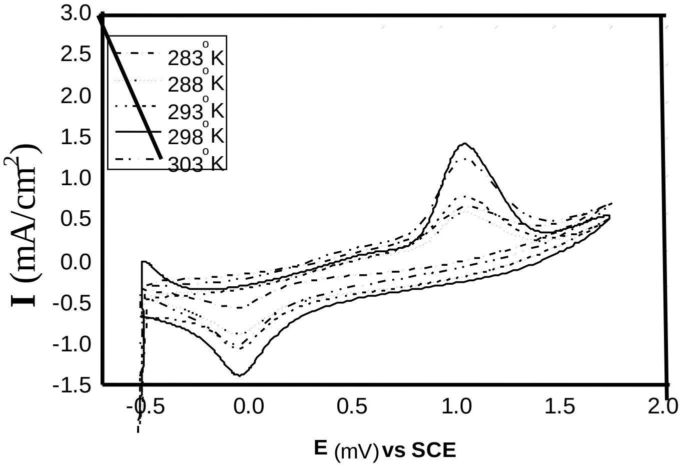


Figure (6A): Effect of temperature on the cyclic voltamograms for electropolymerization of O-bromophenol from solution containing 0.4M acid, 0.04M monomer concentrations with scan rate 25mV\sec.

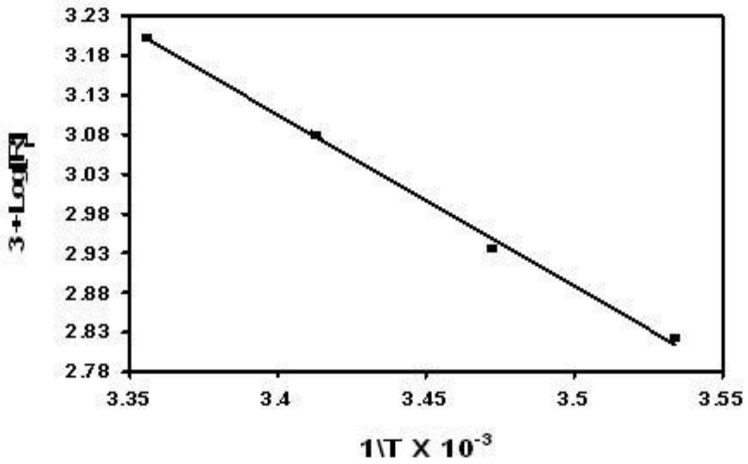


Figure (6B): Arrhenus plot of the anodic oxidative of the electropolymerization of o-bromophenol from solution containing 0.04 M monomer and 0.4 M acid concentration with scan rate25mV/Sec.

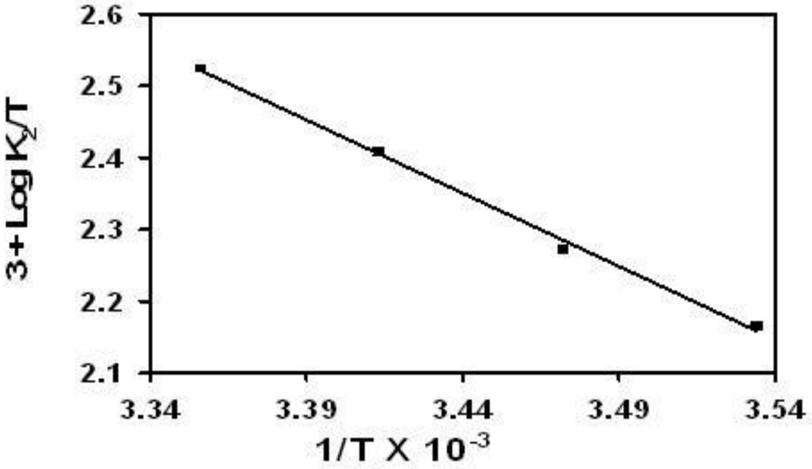
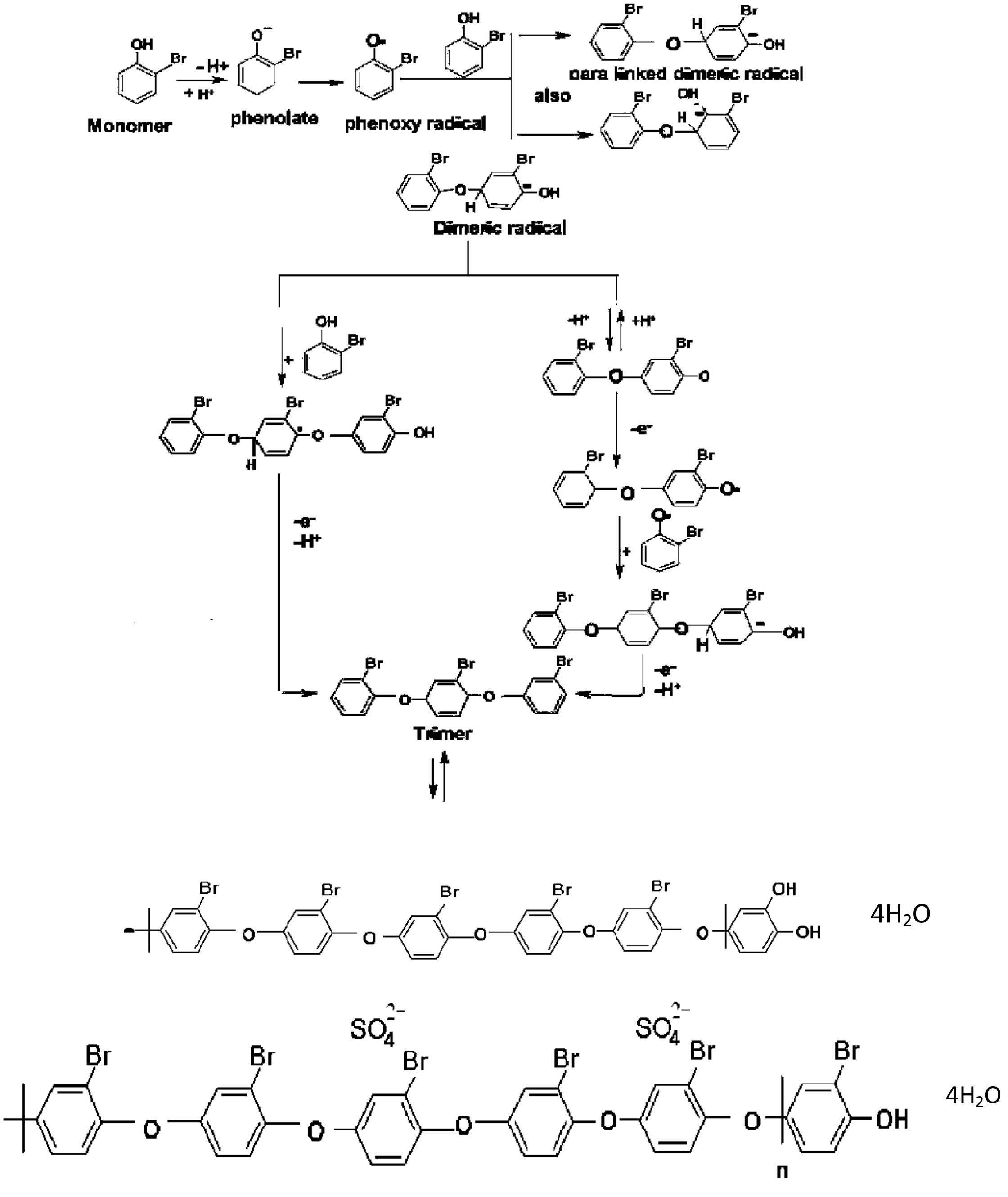


Figure (6C): Eyrring plot of the anodic oxidative electropolymerization of o-bromophenol from solution containing 0.04 M monomer and 0.4 M acid concentration with scan rate25mV/Sec.

3.2. Mechanisms of electropolymerization

The anodic oxidative polymerization of OBP is preceded in different steps as follows:



Scheme (1): The Mechanism of electropolymerization of the polymer.

3.3. Structure determination of the obtained polymers by elemental and spectroscopic analysis.

3.3.1. Elemental analysis:

Elemental analysis of the obtained polymers by anodic oxidative Electropolymerization of OBP was carried out in the micro-analytical laboratory at Cairo University. The percentage Carbon, Hydrogen, Bromine and Sulfur for investigated polymer sample are summarized in Table 2.

The found elemental analyses are in a good agreement with the calculated data for the above suggested structure in scheme 1.

Table 2.Elemental analytical data of the prepared homopolymer.

Elemental analysis				
Element Type	**C**	**H**	**Br**	**S**
Percentage	**(%)**			
Calculated	**33.46**	**2.09**	**37. 18**	**4.96**
Found	**32.92**	**1.58**	**37. 89**	**4.65**

3.3.2. Spectroscopic analysis.

3.3.2.1. Ultraviolet-Visible spectroscopic studies:

The UV spectra of OBP and its homopolymer POBP is shown in Figure (7). The absorption bands shown in the spectra are summarized in Table 3**.**

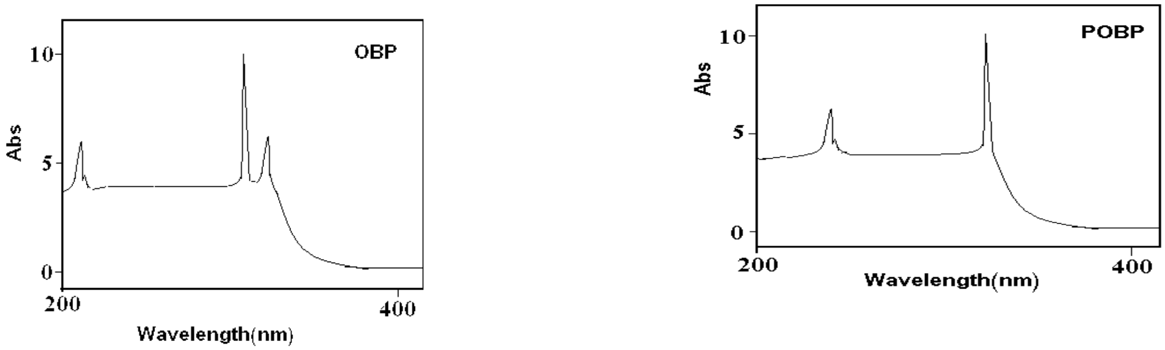


Figure (7): The UV- assignments of OBP and POBP.

Table 3.The Ultraviolet- Visible assignments.

Assignment	λ_{mas}	
	OBP	**POBP**
π- π*transition	**210**	**---**
	---	**236**
	306	**306**
	329	**---**

3.3.2.2. ^{1}HNMR spectroscopic studies.

The ^{1}HNMR spectrum of the prepared POBP is represented in (Figure 8). The figure shows three solvent signals at δ = 1.22ppm, δ = 2.1ppm and δ = 2.54ppm. Th in the region from eδ singlet=6.89 tosignalδ= 8appears.5ppm. That δ = 9.5 water of salvation. The singlet signal appears at δ = 5.2ppm is attributed to OH proton attached to for benzene ring.

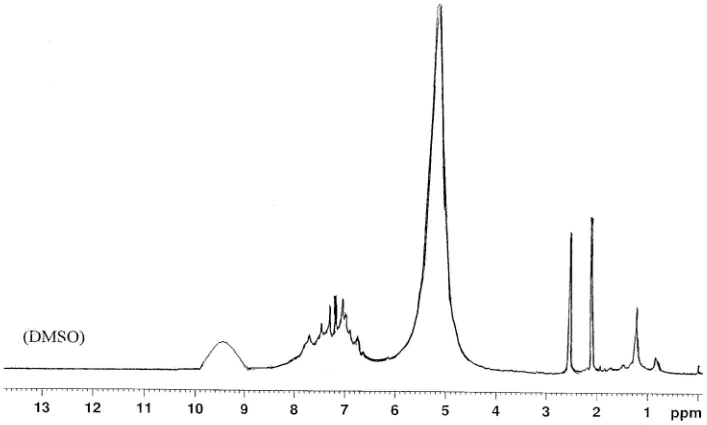


Figure (8): ^{1}HNMR Spectra of Poly (O-bromophenol)(POBP) in Dimethylsulphoxide(DMSO).

3.3.2.3. Infrared spectroscopic studies.

The infrared spectra of OBP monomer and its prepared homopolymer POBP are represented in Figure (9). The IR absorption bands and their assignments are given in Table 4.

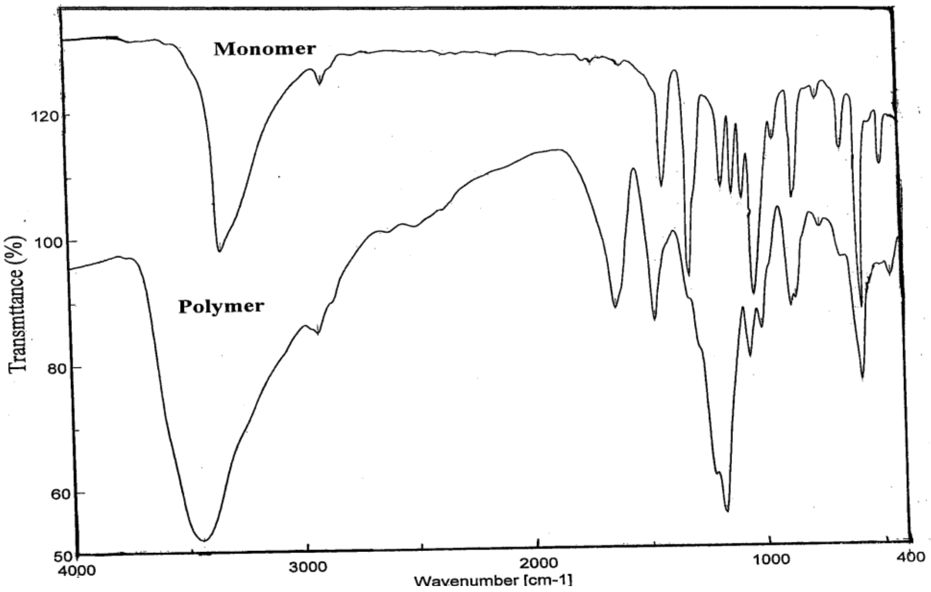


Figure (9): The infrared Spectra of O-bromophenol(OBP) and Its Homopolymr(POBP).

Table 4. IR adsorption bands and their assignments for monomer (OBP) and its polymer.

Assignments	**Wave number** (cm^{-1})	
	Monomer	**Polymer**
CH out of plane bending for 1, 2 di-substituted benzene ring.	749^{s}	752^{w}
	826^{m}	--
CH out of plane bending for 1, 2, 4 tri-substituted benzene ring.	---	860^{s}
	---	879^{s}
Stretching vibration for C-Br group.	934^{w}	1009^{w}
Stretching vibration for C-O group.	1030^{s}	1062^{m}
Stretching for incorporation in the polymer sulfate group.	1189^{s}	1183^{s}
Stretching vibration of C=C in benzene ring	1475^{s}	1486^{m}
	1588^{s}	---
	---	1637^{s}
	1777^{w}	---
Stretching vibration for CH aromatic	3069^{w}	2927^{w}
Stretching vibration intermolecular hydrogen solvated OH group or end group OH of polymeric chain.	3499^{b}	3445^{b}

(Where; s: strong, w: weak, b: broad, m: medium)

3.3.2.4. Thermogravimetric Analysis (TGA).

Thermogravimetric analysis (TGA) for the electrochemically prepared POBP. The sample has been investigated and the

TGA-curve is represented in (Figure 10) from which it is shown that there are four stages during thermolysis

The first stage: including the loss of 4H_2O molecules in the temperature range between 35.99^{O}C and87.42^{O}C, The weight loss was found to be (6.403%) which is in good agreement with the calculated value (5.577%) water release [Sayyah et al 2010].

The second stage: includes the loss of the dopant species, **2**SO_3+Hydroxyl radical in ring at the temperaturerange between 88.44^{O}C and 232.07 ^{O}C , the weight loss for this step was found to be (14.721%) which is in good agreement with the calculated value (13.710%).

The third stage: includes the loss of the dopant species, 2Br and one benzenoide in the range oftemperature between 233.09^{O}C and 397.06^{O}C, the weight loss for this step was found to be (19.50%) which is in good agreement with the calculated value (21.379%).

The fourth step: the remaining part of the polymer decomposition, was found to be (59.38%) in the range400 - 600^{O}C and the calculated value is equal to 59.334 %.(c.f. Table.5.) of the POBP sample.

Table 5.**Thermogravimetric (TGA) analysis of POBP.**

Temperature (^{0}C)	Cal/found(%)	The released molecules or radicals
35.99^{0}C and 85.42^{0}C	5.577 / 6.403	Four water molecules
88.44^{0}C and 232.07^{0}C	13.710 / 14.72	2SO$_3$+ Hydroxyl radical
233.09^{0}C and 397.06^{0}C	21.379 / 19.5	2Br + Two benzenoide molecule.
400^{0}C –600^{0}C	59.334 / 59.38	The remained polymeric chain.

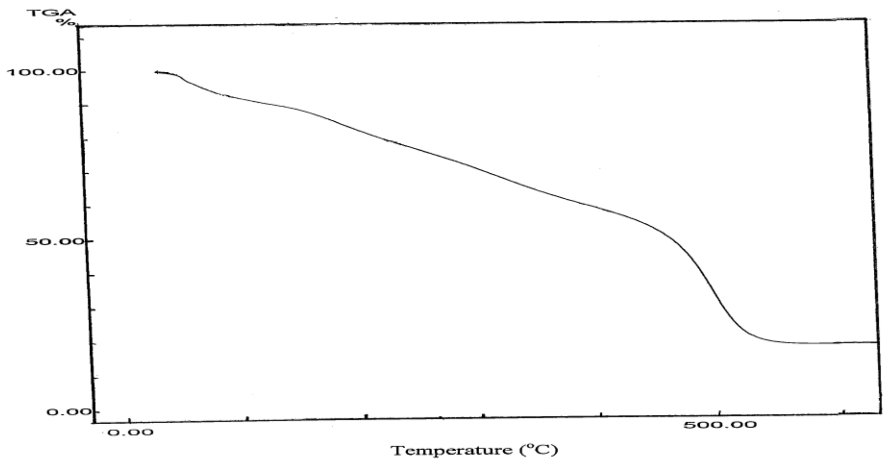


Figure (10): Thermogravimetric Analysis (TGA) of Poly (O-bromophenol)(POBP).

3.3.2.5. Surface Morphology Study.

In most conditions, a homogeneous, smooth and well-adhering brown POBP film was electrodeposited on platinum electrode surface.

Figure (11A) illustrates that the surface morphology of the polymer obtained at the optimum conditions were examined by scanning electron microscopy. The SEM micrographs show a smooth lamellar surface.

The X-ray diffraction pattern shows that the prepared polymer is crystalline as shown in (Figure 11B).

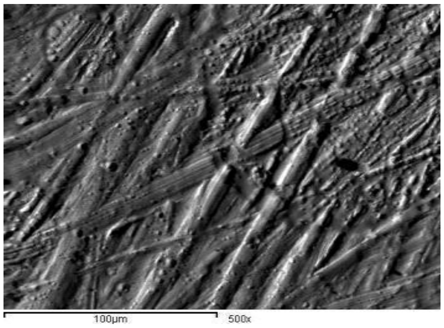


Figure (11A): The Scanning Electron Microscope (SEM) of Poly O-bromophenol (POBP).

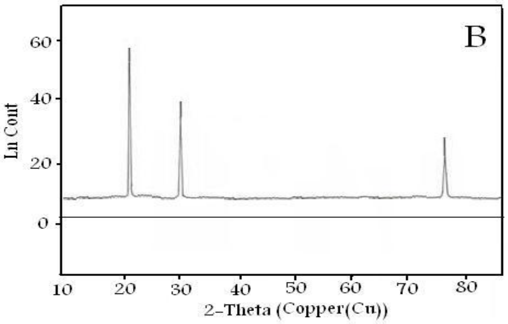


Figure (11B): The X- Ray Diffraction (XRD) of Poly O- bromophenol (POBP).

3.4. Application of Poly (O-Bromophenol) as Corrosion Inhibitors on Mild Steel in acid medium (PH=2).

3.4.1. Open Circuit Potential Measurements:

Open Circuit Potential of carbon steel in poly (o-bromophenol) was followed over 1hour in stagnant naturally aerated aqueous solution of pH=2. We obtained that the values of the steady state potentials were reached within 60min for carbon steel electrode immersion in the solution at blank and different concentrations of POBP (2ml , 5ml , 10ml) at pH=2. This data are presented in Figure (12). The results show that the presence of polymer shifts the steady state potentials to less negative values.

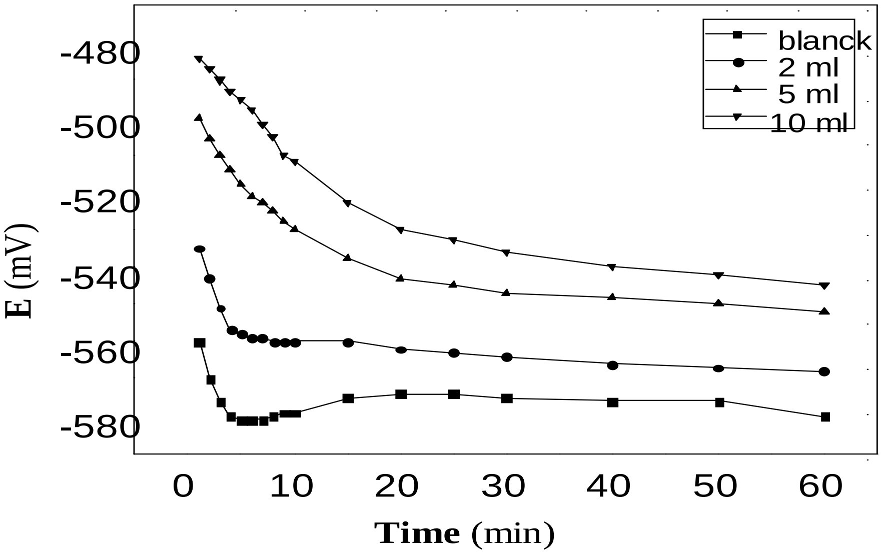


Figure (12): Variation of the open-circuit potential of mild steel alloy with time in stagnant naturally aerated aqueous solutions of pH=2 in the presence of poly (O- bromophenol) at 25^{0}C

3.4.2. The Corrosion Rates Measurements of Mild Steel:

The electrochemical behavior of carbon steel in different concentrations (blank, 2ml, 5ml, 10ml) of POBP at pH=2 were investigated under polarization conditions, the linear polarization and Tafel extrapolation techniques were used at scan rate $10mVs^{-1}$.

Figure(13): illustrated that the potentiodynamic polarization curves of different concentrations of POBP(blank, 2ml , 5ml , 10ml) after holding the carbon steel electrode at the open circuit potential for 60min in naturally aerated aqueous solution of pH=2. The values of corrosion α&β),corrosionparameter potential E_{corr} , corrosion current density i_{corr} and corrosion rate were calculated and presented in Table 6**.**

Table 6: Potentiodynamic polarization parameter of steel after 60min of electrode immersion in stagnant naturally aerated poly (o-bromophenol) solution at 25^{o}C.

Conc	E_{corr} / mV	R_p kΩ.^{2}c	i_{corr} μAcm^{-2}	β_a (mV)	β_c (mV)	Corrosion rate(my^{-1}	η %
blank	**-670.6**	**0.502**	**107.1**	**263.4**	**-345.1**	**1.33**	**0**
20ppm	**-668.5**	**1.23**	**62.2**	**309.8**	**-300.0**	**0.774**	**41.9**
50ppm	**-687.8**	**1.52**	**44.0**	**337.1**	**-233.1**	**0.547**	**58.9**
100ppm	**-695.2**	**2.24**	**21.6**	**283.3**	**-152.8**	**0.269**	**79.8**

We noted that from the table 6 The Tafel slopes (β_a&$_b$)βare in most cases increase with increasing the concentrations which indicate that the corrosion process is under activation control [12], the corrosion current density i_{corr} measured after 60min of carbon steel electrode immersion in the acidic solution of pH=2, decreases while, corrosion potential E_{corr} increases in negative direction and the corrosion rate deceases with increasing POBP concentrations up to 100ppm (Fig.13) this indicate that POBP is better corrosion resistance.

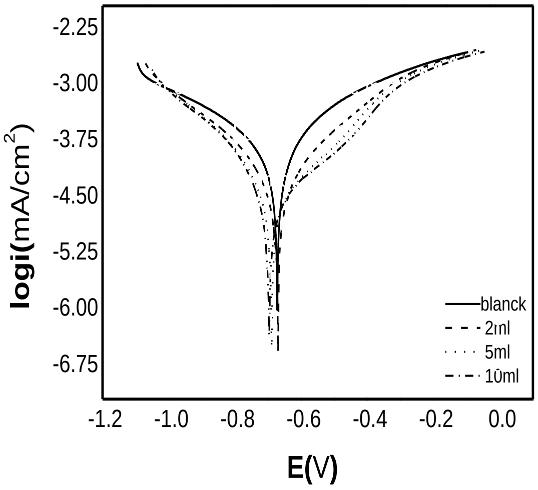


Figure (13): Potentiodynamic polarization curves of mild steel alloy in stagnant naturally aerated aqueous solutions of pH=2 in the presence of polybromophenol at 25^{o}C.

3.4.3. The Elelectrochemical Impedance Measurement:

The Elelectrochemical Impedance spectroscopy (EIS) is a powerful,non-destructive electrochemical technique for characterizing electrochemical reactions at metal/electrolyte interface and the formation of corrosion products. The impedance spectra are recorded at the open circuit potential for mild steel in different concentrations of POBP in naturally aerated acidic solutions of pH=2.

These results of the impedance measurements are illustrated if Figure (14) in the form of Nyquist plot (Fig.14A) and Bode plot (Fig.14B).The response of the system in the Nyquist complex plane (Fig.14A) consists of one semicircle. The time constant or diameter of the semi-circle decreased with the increase of immersion time.

Figure (14B): a show that on clear phase maximum is present for carbon steel electrode at intermediate frequency. This one time constant appears as well-defined capacitive loop in intermediate frequency region of Nyquist presentation (cf.Fig14A). The intermediate time constant is attributed to the presence of a protective surface film.

The mathematical formulation to measured of the electrode impedance (Z) as show:

$$Z = R_s + [R_{ct}/1 \quad + {}_{ct} (2\pi C_{dl})] f R \qquad {}^{\alpha} \qquad (5)$$

Where R_S is the solution resistance, connected to a parallel combination of R_{ct}, representing the charge transfer resistance at the electrode/electrolyte interface and C_{dl}, representing the double layer empirical parameter (0≤ α≤1).

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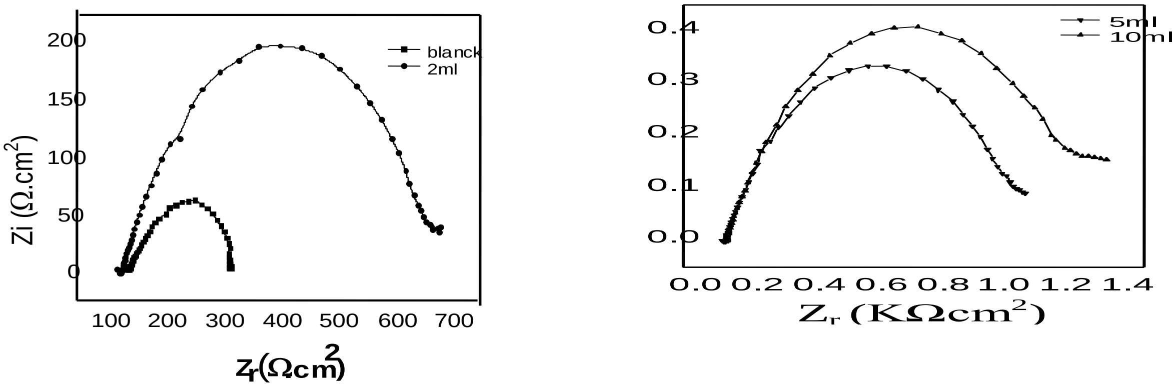


Figure (14A): Nyquiste plot of mild steel alloy in stagnant naturally aerated aqueous solutions of p^H=2 in the presence of poly(O-bromophenol) at 25°C .

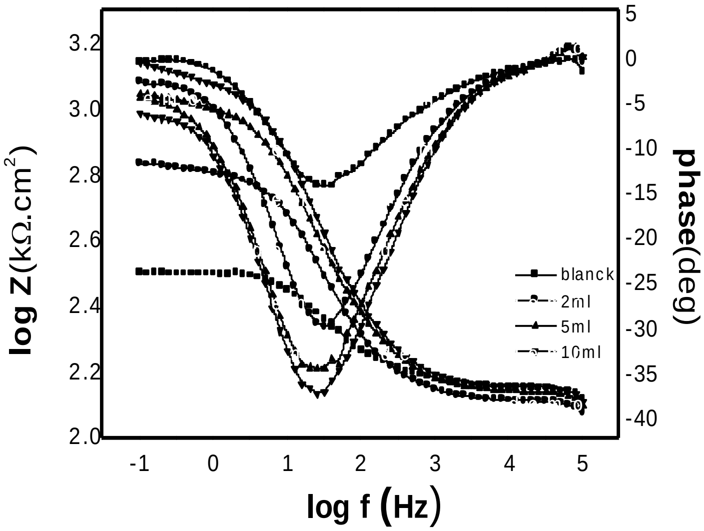


Figure (14B): Bode plot of mild steel alloy in stagnant naturally aerated aqueous solutions of p^H=2 in the presence of poly(O-bromophenol) at 25°C.

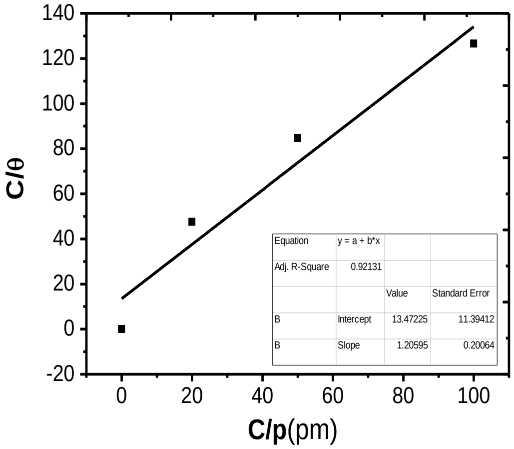
Table (7): indicated that the calculated equivalent circuit parameters from this data show the POBP formed passive layer on mild steel.

Table 7: Equivalent circuit parameters for steel recorded after 60min of electrode immersion in stagnant naturally aerated POBP solution at steady state potential at 25°C.

Conc	R_s (Ω.)cm^2	R_{ct} (kΩc)^2	C_{dl}(μFcm)$^{-2}$
blank	**143.1**	**0.183**	**34.8**
20ppm	**131.1**	**0.549**	**23.2**
50ppm	**138.6**	**0.994**	**25.3**
100ppm	**140.1**	**1.256**	**20.0**

3.4.4. Langmuir Adsorption Isotherm.

The representation of the data show that the adsorption process in accordance with Langmuir Adsorption Isotherm for solution of POBP on mild steel alloy in stagnant naturally aerated aqueous solution of P^{H} = 2 at $25^{o}C$ this data presented in (Figure 15).



Equation	y = a + b*x		
Adj. R-Square	0.92131		
		Value	Standard Error
B	Intercept	13.47225	11.39412
B	Slope	1.20595	0.20064

Figure (15): Langmuir isotherm plot for the adsorption of poly (O-bromophenol) on mild steel alloy in stagnant naturally aerated aqueous solutions of p^{H}=2 at 25^{o}C.

4. Conclusions

Cv is useful tool in oxidation of protective as phenols. The electropolymerization, by cyclic voltammetry, of phenols on Pt-surfaces is a notoriously complex process which depends on the phenols structure, the potential scan rate, the temperature and the phenols concentration. The voltammograms from the different monomer compound solutions, it was demonstrated that the polymer film resulting from OBP oxidation leads to the higher surface deactivation degree. This is probably due to the higher adhering properties of POBP to Pt-surface.

The proposed mechanisms are well confirmed by different tools and agree with that mentioned in literatures.

The oxidation processes are partially controlled processes with stable diffusion coefficients at different scan rates.

The Obtained polymers are crystalline with higher thermal stability with smooth lamellar surface feature for POBP.

More work must be done to improve that POBP is better corrosion resistance for mild steel at P^H = 2 at 25^oC.

4. References

1- Ardakani, M.M., Sadeghiane,A., Moosavizadeh, S, Karimi, M.A., Mashhadizadeh,M.H.(2009).Electrocatalytic Determination of Hydrazine using Glassy Carbon Electrode with Calmagates, Anal. Bioanal.Electrochem. 1(3): 224-338.

2- Arslan,G, Yazici, B & Erbil, M. (2005) . The effect of p^H, temperature and concentration on electrooxidation of phenol, Journal of Hazardous Materials B124: 37–43.

3-Comninellis, C. (1994).Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment, ElectrochimicaActa, 39 (11-12): 1857-1862.

4- Ezerskis Z., &Jusys, Z. (2002).Electropolymerization of chlorinated phenols on a Pt electrode in alkaline solution. Part IV: A gas chromatography mass spectrometry study,Journal of Applied Electrochemistry, 32 (5): 543-550.

5- Fleszar, B. &Jolanta, P. (1985), An attempt to define benzene and phenol electrochemical oxidation mechanism, ElectrochimicaActa, 30 (1) : 31-42.

6- Gattrell, M., & Kirk, D.W.(1993). Study of electrode passivation during aqueous phenol electrolysis, Journal of the Electrochemical Society, 140(4): 903-911.

7- Gutiérrez,C.(2002).Electrooxidation of 2,4-dichlorophenol and other polychlorinated phenols at a glassy carbon electrode, Electrochim.Acta, 47(15):2399.Iotov, P.I. &Kalcheva, S.V. (1998). Mechanistic approach to the oxidation of phenol at a Platinum/gold electrode in an acid medium, Journal of Electroanalytical Chemistry, 442(1-2) :19-26. Randles, J. E. B. (1948). A cathode ray polarograph. II. The current voltage curves, Trans. Faraday Soc, 44: 327-338.

8- Sayyah, S. M., Abd El-Rehim, S. S., El-Deeb, M. M., Kamal, S.M. &Azooz, R. E., (2010).Electropolymerization of P- Phenylenediamine on Pt-Electrode from Aqueous Acidic Solution :Kinetics, Mechanism ,Electrochemical Studies,and Characterization of the Polymer Obtained, J ApplPolymSci 117: 943–952.

9- Sevick, A. (1948), Oscillographic polarography with periodical triangular voltage, Collect.Czech. Chem. Commun., 13 349-377.

10- Wang, J.,Jiang, M. &Lu,F. (1998), Electrochemical quartz crystal microbalance investigation of surface fouling due to phenol oxidation,Journal of Electroanalytical Chemistry, 444(1, 5) :127-132.

11- Wang, J.,Martinez,T.Daphna, Y.R & McCormick, L.D.(1991). Scanning tunneling microscopic investigation ofsurface fouling of glassy carbon surfaces due to phenol oxidation, Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 313 (1-2): 129-140.