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Original scientific paper

P(o-chlorophenol–co-o-hydroxyphenol): kinetic formation studies and pH-sensor application

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Abstract

Electrochemical copolymerization of o-chlorophenol (o-ClPh) with o-hydroxyphenol (o-HOPh) was conducted in aqueous H_2SO_4 *using cyclic voltammetry technique at the Pt electrode. The reaction rate was found to be of the second order in the monomer concentration and first order in the acid concentration. The activation energy, enthalpy, and entropy for the copolymerization were found to be 20.20 kJ* mol^{-1}*, 19.24 kJ* mol^{-1} *and -281.47 J* K^{-1} mol^{-1}*, respectively. The obtained copolymer films show smooth feature with amorphous nature. Copolymer films adhere Pt electrode very well and show less reactivity in the* H_2SO_4 *medium. The pH sensitivity of the poly(oClPh-co-HOPh)-modified electrode has been investigated potentiometrically using different polymer thicknesses. The potentiometric responses to pH change of the poly(oClPh-co-HOPh)-modified electrode appeared reversible and linear in the range from pH 2-11 with a maximum sub-Nernstian potentiometric response slope of 40.7 mV/pH (30 °C). The slope became close to 56.2 mV/pH in the range from pH 4 to 9 at (30 °C). The poly(oClPh-co-HOPh)-modified electrode readily responded to pH change but was not stable with time.*

Keywords

Pt-anode; poly(o-chlorophenol-co-o-hydroxyphenol); electrocopolymerization; kinetic study; activation parameters; potentiometric pH sensor

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Introduction

Phenolic compounds (Phs) are a class of pollutants which, when absorbed through the skin and/or mucous membranes, can cause damage to numerous organs of living bodies, like the lungs, liver, kidney, and genitourinary tract [1]. Phs are widely used in wood preservatives, textiles, herbicides and pesticides, and released into the ground and surface water. The identification and quantification of these compounds represent an important issue in the environmental monitoring. o-hydroxyphenol (o-HOPh) and o-chlorophenol (o-ClPh) are two phenolic compounds, which are present as contaminants in medical, food and environmental matrices. Different methods were used for identification and clearing of them. Some of these methods are time-consuming, of low sensitivity with complicated pretreatments and expensive. Electrochemical methods, however, provide an easy and fast alternative for the analysis of such materials [2,3].

Electropolymerization is a good approach for preparing polymer-modified electrodes by adjusting the electrochemical parameters that control film thickness, permeation, and charge transport characteristics. In the field of electropolymerization, two topics are of great importance: the first is the study of the electropolymerization kinetics [4–9], which provides information about the nature of the reactions taking place at the electrode surface and the chemical structure of the polymer film, while the second is the potential use of polymer modified electrodes as sensors for qualitative and quantitative analyses of hazardous and biologically active compounds [4–6, 9-11].

There have already been a few reports on the kinetics and mechanism of the electrochemical polymerization [12-18]. Sayyah *et. al.* [19] studied the kinetics of homopolymerization of o-HOPh and o-ClPh by cyclic voltammetry (CV) in aqueous H_2SO_4 solution at the Pt anode. These authors used different tools for characterization of the obtained films. The obtained films with a smooth lamellar surface were characteristic for poly(o-chlorophenol), P(o-ClPh), and a smooth feature with uniform thickness for poly(o-hydroxyphenol), P(o-HOPh). In addition, they discussed the possible applications of P(o-ClPh) in the field of sensors and P(o-HOPh) in the field of dye removal from water. Previously, we showed that a block copolymer film was deposited by polymerizing o-ClPh with o-HOPh using CV methods [20]. The copolymer formation was directly affected by monomer and acid concentrations and temperature. The copolymer consisted of higher fraction of o-HOPh than o-ClPh units suggesting that o-HOPh is much more reactive than o-ClPh.

Determination of pH is one of the most common measuring procedure in a wide variety of industries and industrial applications [21]. A glass pH electrode, as one of the traditional pH electrodes, has excellent electrode performances with respect to response slope straightforward operation, selectivity, and long-term stability. However, the electrode with the internal liquid system exhibits some drawbacks, such as mechanical fragility, high cost, and limited miniaturization for use in clinical or biological applications [22, 23]. Much interest in the development of pH sensors based on polymers has been created [24]. The positive charges in the oxidized state of the polymer are compensated by counter-ions from the solution, giving ion-exchange properties of the polymer films. Therefore, polymers are applicable in potentiometric pH sensors [25]. The conducting polymer-based pH sensors, however, have suffered from long response time, non-reproducibility and salt effect [26].

The aim of the present work is to study the kinetics of electrooxidation of the binary mixture of o-HOPh and o-ClPh in the aqueous acid solution. The reaction orders with respect to the electrolyte and monomer will be determined from electrochemical data and the prepared films/electrode will be tested as a potentiometric pH sensor.

Experimental

Materials

o-ClPh (+97 %, Hopkin & Williams, *Dagenham, Essex, UK*), sulfuric acid, K_2HPO_4, potassium hydrogen phthalate (KHP) , Borax, NaOH, hydrochloric acid, $NaHCO_3$ (Merck, *Darmstadt, Germany*) and o-HOPh (99 %, Aldrich, *Germany*). All chemicals were of analytical pure grade and used as received. All solutions were prepared by using freshly double-distilled water.

Instrumentation

Electrochemical experiments were performed using a Potentiostat/Galvanostat Wenking PGS 95. The *i-E* curves were recorded by the computer software from the same company (Model ECT). All experiments were conducted at a given temperature (± 0.5 °C) with the help of circular water thermostat.

Electrochemical polymerization was carried out in a home-made three-electrode single-compartment cell with platinum plates as working and counter electrodes and a saturated calomel electrode (SCE) as the reference electrode. The control temperature (± 0.5 °C) was achieved by means of a jacketed cell through which water was circulated from a Polytemp thermostat. All electrochemical reactions were carried out at 25 °C unless otherwise specified in the text. The areas of the working and counter electrodes were 0.5 cm^2 each. The oxidation potentials were measured by linear sweeping voltammetry as the anodic peak values ($i_{p(II)}{}^a$).

The obtained copolymer was peeled off from Pt electrode and washed with H_2SO_4 (0.6 M), then washed with bi-distilled water and finally heated to 95 °C for 3 h and stored for further characterization.

Characterizion by UV–Vis spectrum was achieved using Shimadzu UV spectrophotometer (M160 PC) at room temperature in the range 200–700 nm. Dimethylformamide (DMF) was used as a solvent and reference (200 µL of the solution was diluted to 3 mL in a quartz cuvette of 1.0 cm optical path). IR-spectra was recorded using a Shimadzu FTIR-340 Jasco spectrophotometer (Japan) from 400 to 4,000 cm^{-1} with a spectral resolution of 4 cm^{-1} using KBr tablets (Merck, *Darmstadt, Germany*, 99 %) with 1:100 sample: KBr proportion. TGA was performed using a Shimadzu DT-30 thermal analyzer (Shimadzu, *Kyoto, Japan*) - the weight loss was measured from ambient temperature up to 600 25 °C, at the rate of 20 °C min^{-1} and nitrogen flow rate of 50 ml min^{-1} to determine the degradation rate of the copolymer. SEM is performed by a JXA-840A Electron Probe Microanalyzer (JEOL, *Tokyo, Japan*). XRD was done using (Philips 1976 Model 1390, *Netherlands*) - X-ray tube: Cu; current: 30 mA; preset time: 10 s; scan speed: 8°min^{-1}; voltage: 40 kV. The pH measurements were carried out using a pHS-3B pH meter and a commercial SCE. A series of buffer solutions were used for solutions of various pHs. The buffers were adjusted by adding diluted HCl or NaOH solution to the solution of KH phthalate, KH_2 phthalate, borax and/or $NaHCO_3$.

Results and discussion

Electrochemical copolymerization

The first cycle cyclic voltammogram (CV) recorded during the copolymerization a mixture of o-ClPh and o-HOPh with a molar feed ratio kept at 1:1 in the potential range from 0 to 1.7 V *vs.* SCE in the absence and presence of monomers is represented in Figure 1. From this figure, the adsorption peak of H_2 gas on Pt surface was observed at -0.3 V *vs.* SCE [19] in absence or presence of monomers, peak (I), whiile the oxidation peak of comonomers to yield copolymer, peak (II) was developed at

0.70 *vs.* SCE. By increasing number of cycles $i_{p(I)}$ was not changed while $i_{p(II)}$ decreased significantly and disappeared after 20 cycles.

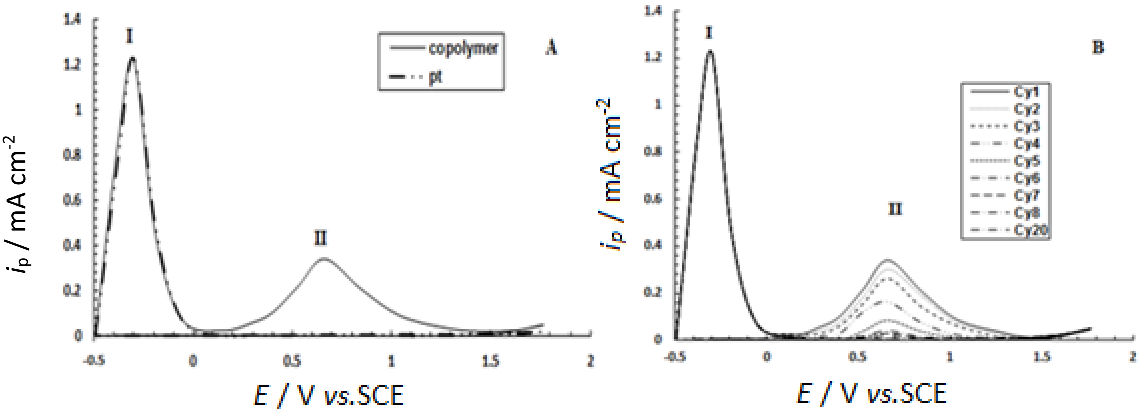

Figure ***1****: Cyclic voltamigrams of Pt electrode in aqueous solution containing 0.6 M H_2SO_4 at 303 K using 25 mV s^{-1} in absence and presence of 0.05 M comonomer (1:1 molar ratio) ,* ***A*** *- first cycle and* ***B*** *- repetative cycling up to 20 cycles.*

The mechanism of polyphenol formation was proposed elsewhere [20,27-30]. Similarly, we could propose that a removal of an electron from hydroxyl groups (O-atoms) to form free radicals adsorbed on the Pt electrode surface occurs at 0.70 *vs.* SCE. Adsorbed radicals react with each other or with a comonomer molecules via head-to-tail (C-O)-coupling to form dimeric radical what is followed by formation of the copolymer film.

On reversing the potential scan, the anodic current is very small indicating the presence of a copolymer film well adhered to the Pt surface [30,31]. The absence of any cathodic peaks indicates totally irreversible system as a result of the strong adhesion of the copolymer film to Pt surface. Insulating property of the copolymer film, no electroactive species, and/or the nature and kind of oxide species formed on the Pt surface during the electrooxidation is the reason of observed irreversibility [32,33].

CVs recorded for o-ClPh polymerization showed one oxidation peak at 0.86 V and one reduction peak at 0.25 V *vs.* SCE) while CVs for o-HOPh polymerization showed one oxidation peak at 0.62 V and one reduction peak at 0.20 V *vs.* SCE, respectively [19,20]. As seen in Figure 1, the obtained CVs for their mixtures differ, while no reduction peaks confirmed the copolymer formation.

By increasing the number of cycles repetitively (*i.e.* see Figure 1B), a fouling of Pt electrode is seen as in other poly phenols [30,33,34]. The reason of this phenomenon may be due to the formation of insulating and good adhered films on Pt surface which causeed a decrease of the peak current densities $i_{p(II))}$ with repetitive cycling [35]. E_p^a of the formation process does not shift with increasing number of cycles, indicating that the oxidation reactions were independent of the copolymer thickness [31,36,37].

Effect of the scan rate

The influence of the scan rate on the anodic current density $i_{p(II)}$ of the Pt electrode was studied in the range from 15 to 40 V *vs.* SCE for 0.05 M co-monomer (1:1 molar ratio) in an aqueous solution containing 0.6 M H_2SO_4 at 303 K. It is obvious from Figure 2 that almost linear relationship was observed for the dependence of $i_{p(II)}$ on both scan rate (v) and the square root of the scan rate ($v^{0.5}$). This behavior may be explained as the mixed diffusion-kinetically controlled process [20]. According to Randless [38] and Sevick [39] (relation between i_{pII} and ($v^{0.5}$ is linear see Fig 2B), the average diffusion coefficient (D^{diff}) is calculated to be 6.53 10^{-7} m^2s^{-1}. The values of D^{diff} are seen to be constant over the range of sweep rates, which again shows that the oxidation process is diffusion-controlled [33,40-43].

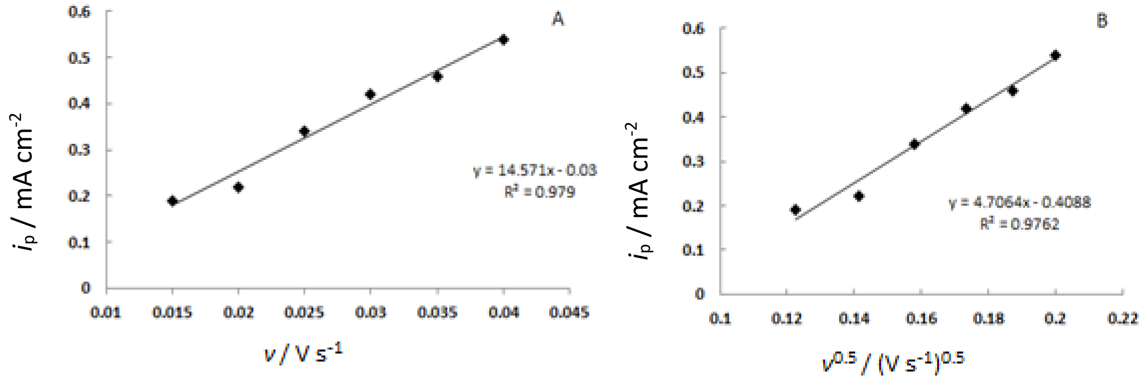

Figure 2. *Relation between* i_{pII} *and* ***A*** *- scan rate,* ***B*** *- square root of scan rate for Pt electrode and 0.05 M comonomer (1:1 molar ratio) in aqueous solution containing 0.6 M* H_2SO_4 *at 303 K.*

Increasing the temperature by 35 °C, the D^{diff} increased by a factor of ~6. The Walden product (the product of diffusion coefficient and the viscosity, $D \times \eta$) was constant over the temperature range studied suggesting that decrease of viscosity at higher temperature caused the observed increase of D^{diff}. Similarly to the Arrhenius law, the following equation allows the activation energy of diffusion, E^{diff}, to be calculated using a linear plot of Ln D^{diff} versus T^{-1}:

$$D + D^{\circ} e^{-\frac{E_a^{\mathrm{diff}}}{RT}}$$

Depending on the above equation and data obtained from Figure 3 the linearity of relation >0.95 confirm good stimulation of Arrhenius relation and E_a^{diff} was found to be 38.25 kJ mol^{-1} at 25 mV s^1.

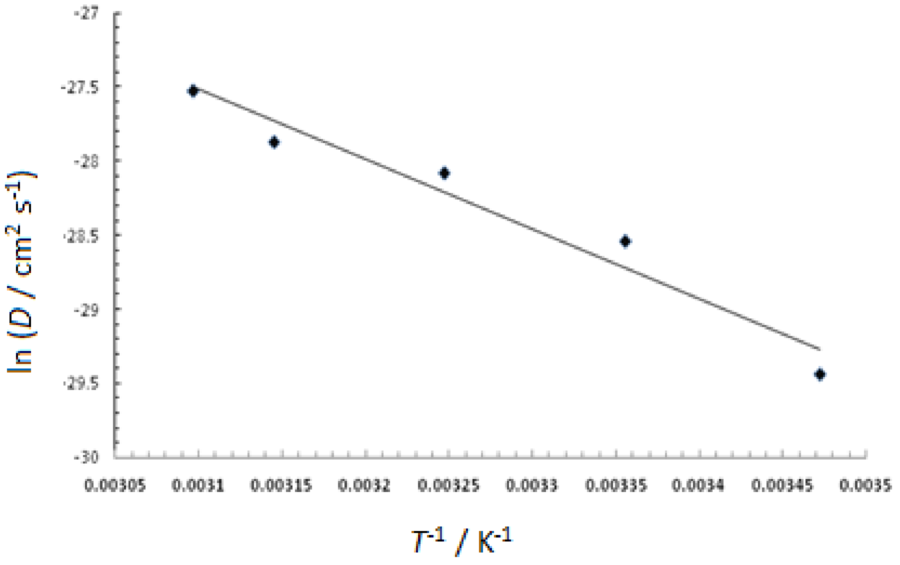

Figure 3. *Plot of ln* D versus T^{-1}.

Kinetics of the electropolymerization process

The electropolymerization kinetics was evaluated using deoxygenated aqueous solution containing monomer in the concentration range between 0.03 and 0.08 M and H_2SO_4 concentration in the range between 0.2 and 0.6 M at 303 K.

Assuming that the polymerization follows the following equation:

$$M+E\rightarrow P$$

where M is the monomer, E is the electrolyte and P is the polymer, then the kinetic equation can be formulated as follows:

$$R_{\mathrm{p}}=\frac{\mathrm{d}[W]}{\mathrm{d}t}=k[E]^{a}[M]^{b}$$

where R_p is the polymerization rate, which represents the polymer weight, W, per unit time and cm^2 of the electrode surface area, a and b are the reaction orders with respect to the electrolyte and monomer, respectively, and k is the specific rate constant of the electropolymerization process.

The electrochemical study of the copolymer formation is used instead of gravimetric study since the polymer yield on Pt electrode is so small to be used in kinetic studies.

The value of the anodic current density $i_{\mathrm{p(II)}}$ is proportional to the electropolymerization rate (R_p) at given concentrations of the monomer, acid, and electrolyte, and then we can replace the electropolymerization rate by the anodic current density [31,44-46]:

$$R_{\mathrm{p}}=\frac{\mathrm{d}[W]}{\mathrm{d}t}=i_{\mathrm{p}}=k[E]^{a}[M]^{b}$$

or expressed in logarithmic form as:

$$\log i_{\mathrm{p}}=\log k+a\log[E]+b\log[M]$$

For the electropolymerization of the comonomer in aqueous solutions, the kinetic equation can be represented by:

$$R_{\mathrm{p}}=k[H_2SO_4]^{a}[comonomer]^{b}$$

Comonomer mixture and sulfuric acid concentrations were varied keeping one of them constant to evaluate their respective reaction orders. The comonomer concentration varied from 0.04 to 0.08 mol L^{-1} (1:1 molar ratio) at a constant 0.6 mol L^{-1} H_2SO_4 concentration. Then, the H_2SO_4 concentration varied from 0.2 to 0.6 mol L^{-1} at a constant comonomer concentration of 0.08 mol L^{-1} (1:1 molar ratio).

Figure 4A presents the polymerization *i-E* plots corresponding to the copolymer formation from a constant 0.6 mol L^{-1} H_2SO_4 concentration and varying monomer concentrations (with 1:1 molar ratio). The log $i_{\mathrm{p(II)}}$ *versus* log $c_{\mathrm{comonomer}}$ relation is presented in Figure 4B. The slope of the linear relation was found to be 1.80 which means that the polymerization reaction is of the second order with respect to the comonomer concentration.

Figure 5A shows the effect of the change of H_2SO_4 concentration on the polymerization $i_{\mathrm{p(II)}}$ at a constant concentration of comonomer 0.08 mol^{-1} using (1:1 molar ratio). The plot of log $i_{\mathrm{p(II)}}$ against log $c_{\mathrm{H_2SO_4}}$ is presented in Figure 5B. The linear relation has a slope of 0.80 which means that the polymerization reaction is of the first order with respect to H_2SO_4 concentration.

Based on the above data, the kinetic equation of the copolymerization process is defined as:

$$R_{\mathrm{p}}=k[H_2SO_4]^{0.80}[comonomer]^{1.8}$$

From the above equation, the order of the copolymerization reaction is first order with respect to H_2SO_4 and second order with respect to comonomer concentration.

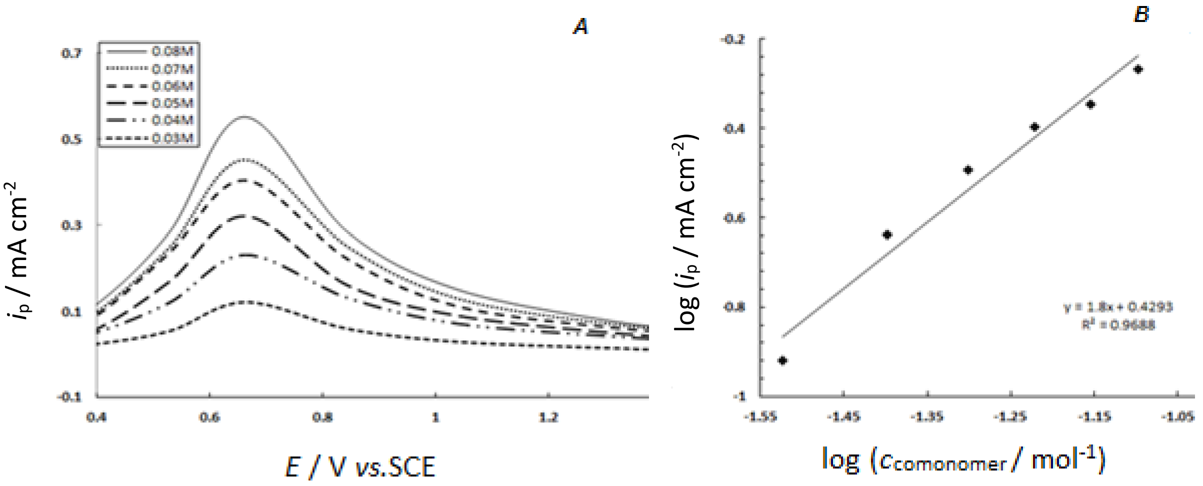

Figure 4. A- i-E *curves for the effect of comonomer concentration on the electropolymerization of oHP and oCP from solution containing 0.6M H_2SO_4 at 303K with scan rate 25 mV s^{-1} on Pt electrode;* ***B*** *- Double logarithmic plot of* $j_{p(II)}$ versus *comonomer concentrations).*

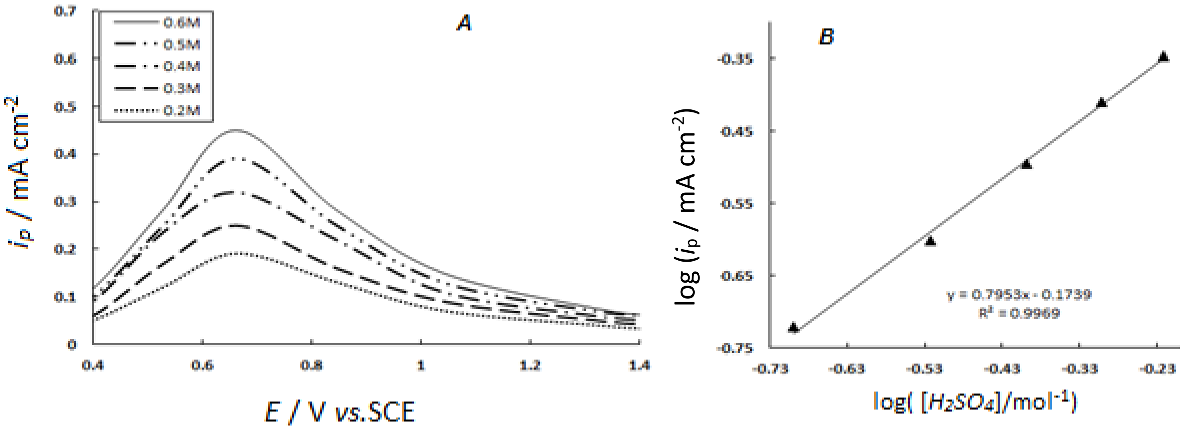

Figure 5. A - i-E *curves for the effect of acid concentration on the electropolymerization of oHP and oCP (1:1molar ratio) from solution containing 0.08M comonomer at 303 K with scan rate 25 mV s^{-1} on Pt electrode;* ***B*** *- Double logarithmic plot of* $i_{p(II)}$ versus *acid concentrations*

Effect of temperature

Figure 6A shows the potentiodynamic polarization curves as a function of the solution temperature in the range between 288 and 323 K. *i-E* curves were recorded in the solution of 0.6 M H_2SO_4 and 0.09 M monomer concentration using scan rate of 25 mV s^{-1}. From Figure 6A it appears that an increase of the reaction temperature resulted in a progressive increase of the charge included in the anodic peaks.

In general, the rate of polymerization increases with the increase of the reaction temperature. The Arrhenius-like plot exhibits a linear relationship between the logarithm of the rate constant of the electropolymerization reaction (log $i_{p(II)}$) and inverse absolute temperature (T^{-1}),

$$\ln i_p = \ln A - \frac{E_a}{RT} .$$

According to the Arrhenius equation, the apparent activation energy (E_a) and pre-exponential factor (A) can be determined from the slope and intercept of the plot respectively [47].

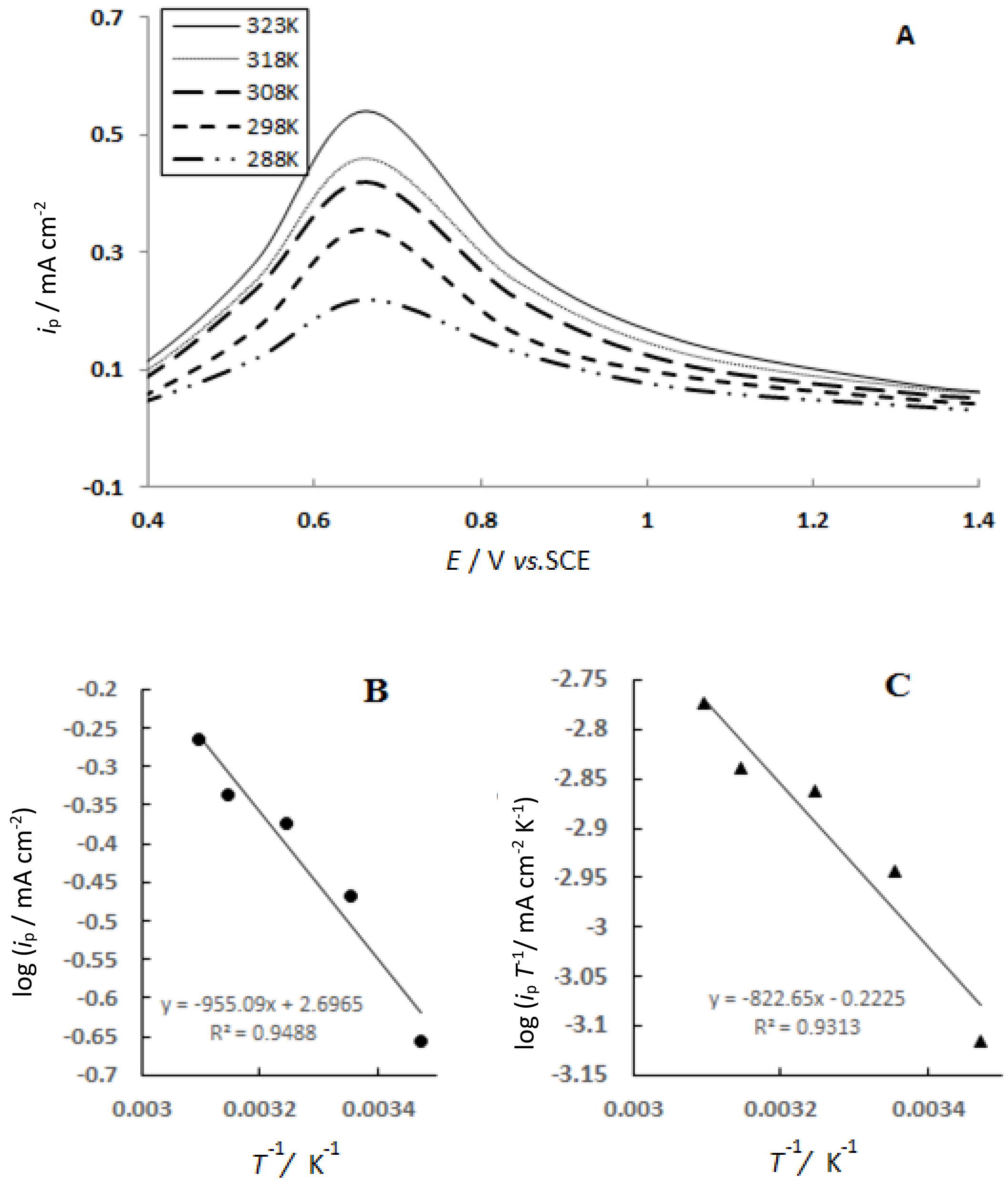

Figure 6. A - i-E *curves for the effect of temperature on the electropolymerization of oHP and oCP (1:1 molar ratio) from solution Containing 0.09 M comonomer and 0.6 M H_2SO_4 at 303 K with scan rate 25 mV s^{-1} on Pt electrode;* ***B*** *- Arrhenius plot of the electropolymerization of oHP and oCP (1:1 molar ratio);* ***C*** *- Eyring equation plot of the electropolymerization of a binary mixture of oHP and oCP (1:1 molar ratio).*

At temperatures higher than 323 K the log $i_{p(II)}$ deviates slightly from the straight line (*i.e.* the value is lower than expected) owing probably to the excessive diffusion of radicals away from the vicinity of the electrode. Such diffusion is evidenced by the color change in the electrolyte solution at higher temperatures.

The plot of log $i_{p(II)}$ *versus* T^{-1} yields a straight line (Figure 6B), indicating that the copolymerization also obeys the Arrhenius equation. The apparent activation energy was calculated using Arrhenius equation and found to be 20.2 kJ mol^{-1}.

Other activation parameters, *i.e.* activation enthalpy (ΔH^*) and activation entropy (ΔS^*) were determined from the slope and intercept of the plot of log ($i_{p(II)}$ T^{-1}) against T^{-1}, respectively, according to the following equation [48]:

$$\ln\frac{i_{\mathrm{p}}}{T}=-\frac{\Delta H^{*}}{RT}+\frac{\Delta S^{*}}{R}+\ln\frac{k}{h}$$

where *R* is the gas constant, *k* is Boltzmann's constant, and h is Planck's constant. The change in ΔH^* and ΔS^* of activation for the electropolymerization reaction can be calculated from the Eyring equation plot at different temperatures (Figure 6C). We obtained a linear relationship with a slope of $-\Delta H^*/2.303\ R$ and intercept of $\{\log (k/h) + \Delta S^*/2.303\ \mathrm{R}\}$. From the slope and intercept the values of ΔH^* and ΔS^* were found to be 19.24 kJ $\mathrm{mol^{-1}}$ and -281.47 kJ $\mathrm{mol^{-1}}$, respectively.

The negative ΔS^* value suggests the formation of ordering activated complexes. There are several possible reasons for the negative ΔS^* which are consistent with the proposed mechanism [49]. First, the radicals generated during the polymerization are much more solvated in the media in comparison with the corresponding neutral reactants. Second, the polymer chain growth involves bimolecular reactions between the radicals and the incoming monomers. Both factors may have contributed to the observed entropy decrease in the activated complexes.

Electroactivity of the Pt-copolymer film

The obtained polymer film prepared on Pt electrode at the optimum conditions (0.08 M comonomer and 0.6 M H_2SO_4 at 303 K using 25 mV s^{-1}) was transferred to another cell with only 0.6M H_2SO_4 and cycled from - 600 to +2000 mV, *vs.* SCE (Figure 7). Figure7 shows that both oxidation peak (developed at +700 mV *vs.* SCE) and the H_2 peak (developed at -300 mV *vs.* SCE) disappeared completely.

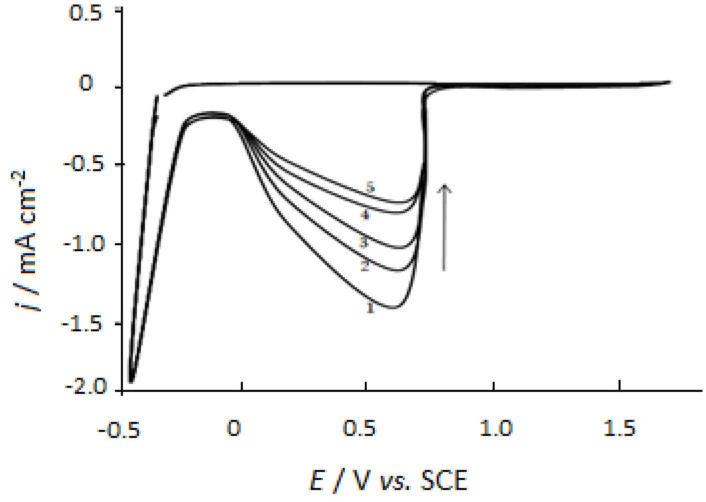

Figure 7. *Electroactivity behavior of copolymer coated Pt electrode in 0.6 M H_2SO_4 with different cycle numbers. Scan rate=25 mV s^{-1}.*

The lack of oxidation peaks confirms the insulating properties and the lack of active species inside the copolymer film. The appearance of a new broad reduction peak can be explained as follows: at the absence of other cations (comonomers cations) H^+ will accumulate on the copolymer/platinum surface forming local charge densities which are considered as a new copolymer form (Copolymer H). During the reduction process, the formed Copolymer H will reduce to Copolymer and H^+ *via* a chemical process. This phenomenon is the basis for the construction of polymeric pH sensors. By repetitive cycling, the current of cathodic peak decreases as a result of decreasing the copolymer amount on the Pt surface. For P(o-ClPh) and P(o-HOPh), adsorption peak of H_2 is observed and not affected by repeating cycles, no oxidation peaks were formed and one broad reduction peak is developed at -300 and -200 mV *vs.* SCE respectively [19].

UV-Vis and IR spectroscopy

The UV-Visible spectrum of P(o-HOPh -co-o-ClPh) shows that the π- π* transition ((E2 band) of the benzene ring and the β-band (A_1g to B_2u)) appear at 257, 307 and 317 nm where the π-polaron transition (conjugation of the aromatic polymeric chain) appears at 485 nm [20,45,50]. This band doesn't appear at both homopolymers [19] which confirm the copolymer formation.

The assignments of the absorption bands of the obtained infrared spectra (KBr pellets) of copolymer sample is recorded and represented in Table 1.

Table 1. *IR - wavenumbers and thier assignments for the prepared copolymer sample.*

Assignments	Wavenumber, cm^{-1}
Electronic transition from the valence band to the conduction band	3700 – 1800
O-H group (phenolic) streching vibration	3320 and 3420
Aromatic ring C–H stretching vibration	3044 and 3105
out-of- plane bending of =C–H bonds of an aromatic ring	830 and 860
C=C stretching vibration bands	1500 and 1665
C–O–C stretching frequency of phenyl ether [51]	1230
dopant SO_4^{-2} incorporation [20]	1180
stretching vibration of the C-Cl bond	912

Thermogravimetric analysis of the prepared sample

The presence of water molecules in the repeated unit is confirmed by the TGA. The TGA steps of the prepared P(o-ClPh-co-o-HOPh) are shown in Figure 8. From the Figure 8 the loss of (water and doped anions) in the temperature ranging between 25 and 220 °C can be observed. At higher temperatures the polymer begins to decompose. It is suggested that P(o-ClPh -co-o-HOPh) is thermally stable until ~220 °C where it starts to decompose resulting in only 27 % polymer weight remaining at 600 °C. However, the remaining amount of P(o-HOPh) at 600 °C is ~65 % and for P(o-ClPh) ~70 % [19] which confirms the copolymer formation.

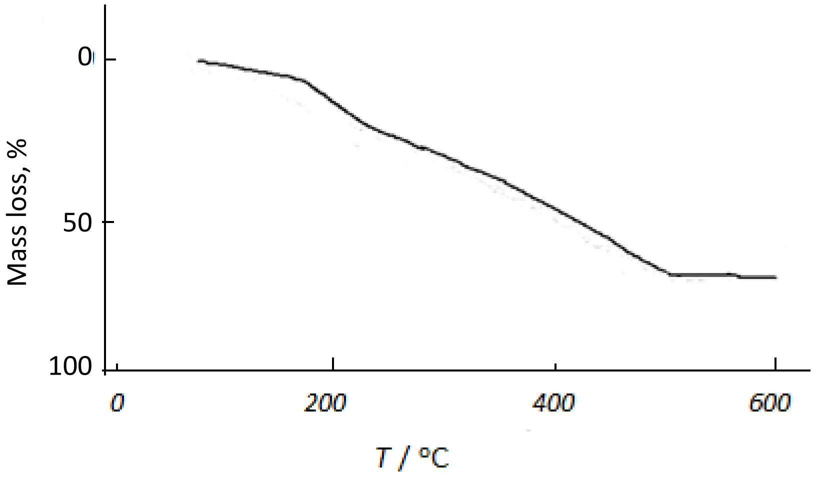

Figure 8. *TGA curve for P(o-ClPh-co-o-HOPh)*

Surface morphological studies

Based on data obtained from XRD and SEM techniques, we previously [19] showed that in a case of o-ClPh, a homogeneous, smooth, brown and well-adhering P(o-ClPh) films were electrodeposited on Pt electrode surface with a lamellar surface feature of the amorphous nature. In a case of o-HOPh, a smooth, black and well-adhering P(o-HOPh) films were electrodeposited on the Pt-surface with uniform thickness and amorphous structure.

In the case of the binary mixture, a homogeneous, smooth, black and well-adhering P(o-ClPh -co-o-HOPh) films were electrodeposited on the Pt- electrode surface. The XRD- pattern shows that the prepared copolymer was amorphous as shown in Figure 9A.

The surface morphology of the copolymer obtained at the optimum conditions was examined by SEM that shows smooth and amorphous in nature as seen in Figure 9B.

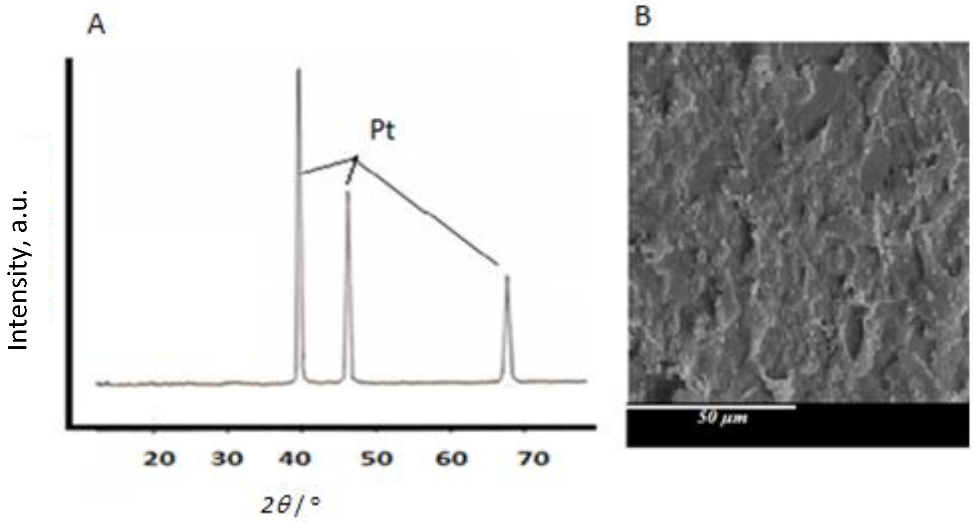

Figure 9. A *- XRD patterns of P(o-ClPh-co-o-HOPh);* ***B*** *- SEM image of P(o-ClPh-co-o-HOPh)*

The solubility of the obtained copolymer and the two homopolymers were examined in different solvents. Both P(o-HOPh) and P(o-ClPh) were found to be soluble well in DMSO, DMF and THF, while their copolymer is soluble in DMF, and HF but not soluble in DMSO. This confirmed the copolymer formation.

Potentiometric study of P(o-ClPh-co-o-HOPh)- Pt modified electrode

The pH measurements were carried out using a pHS-3B pH meter and a commercial SCE. A series of buffer solutions was used for various pH solutions which were adjusted by adding diluted HCl or NaOH solution to the solution of KH phthalate, KH_2 Phthalate, borax and/or $NaHCO_3$. Figure 10 shows that P(o-ClPh-co-o-HOPh)-Pt modified electrodes gave linear responses over the pH range from 2 to 12, with the slope values ranging from 32.5 to 56.7 mV/pH, and a linear correlation coefficients (R^2) with a value of > 0.93 as summarized in Table 2.

Table 2. *Slopes and R^2 values obtained from Figure 10*

No of cycles	pH range 2-12	
	-slope, mV pH^{-1}	R^2
3	56.29	0.99
5	48.80	0.99
10	44.90	0.97
15	29.71	0.99

Figure 10 and Table 2 show that the best slope value was obtained at a moderate thickness (no of cycles 3) while the smallest deviation of the straight line is found at pH < 4 and also at pH > 9. This suggests that the P(o-ClPh -co-o-HOPh)/Pt modified electrode may not be an effective pH sensor for more basic or more acidic solutions.

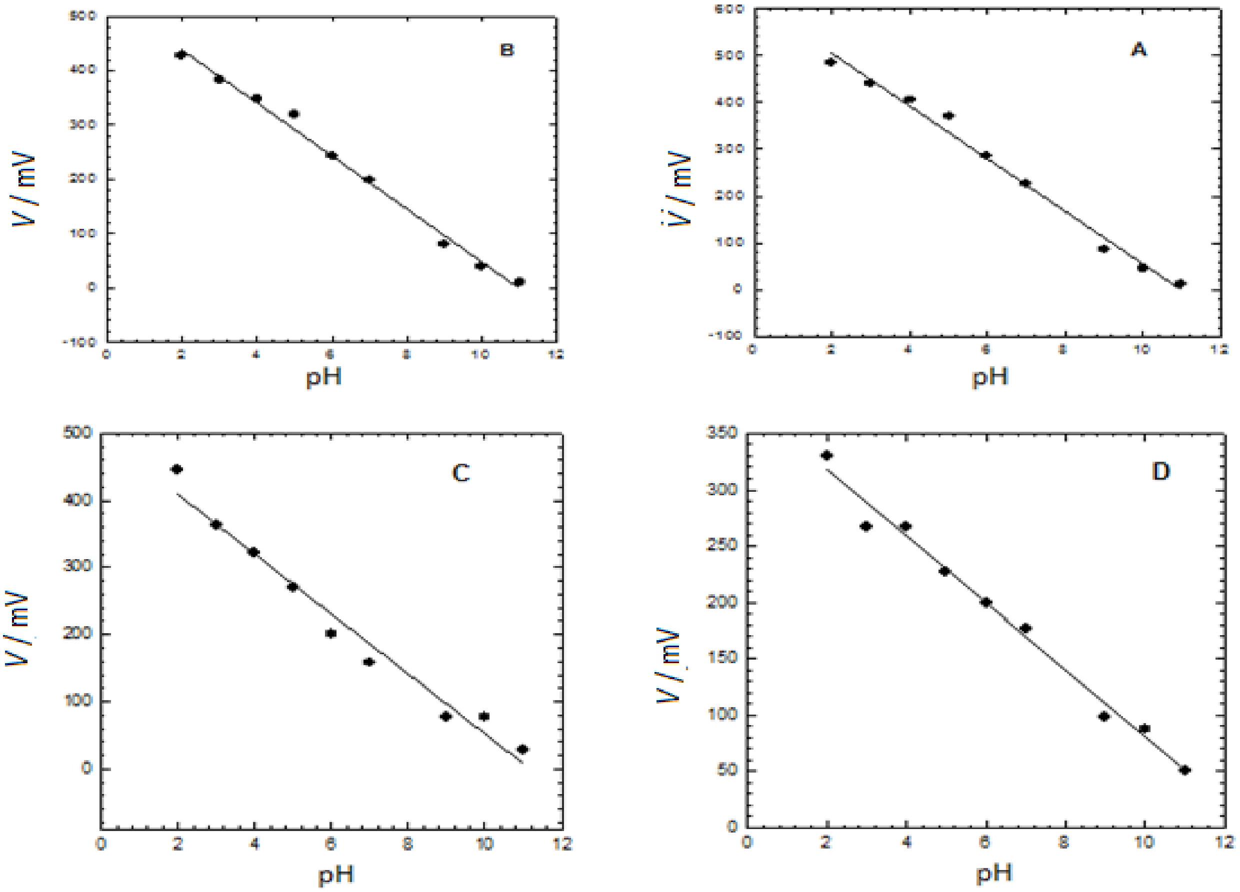

Figure 10. *P(o-ClPh-co-o-HOPh) response at different pH values, the prepared copolymer films after **A** - 3 cycles, **B** - 5 cycles, **C** - 10 cycles and **D** - 15 cycles*

Figure 11 shows the responses of P(o-ClPh-co-o-HOPh)-Pt modified electrode at different pH values (from 5 to 9). The best slopes were improved *i.e.* 56.19 mV pH^{-1} with R^2=0.98 for the film prepared after 3 cycles.

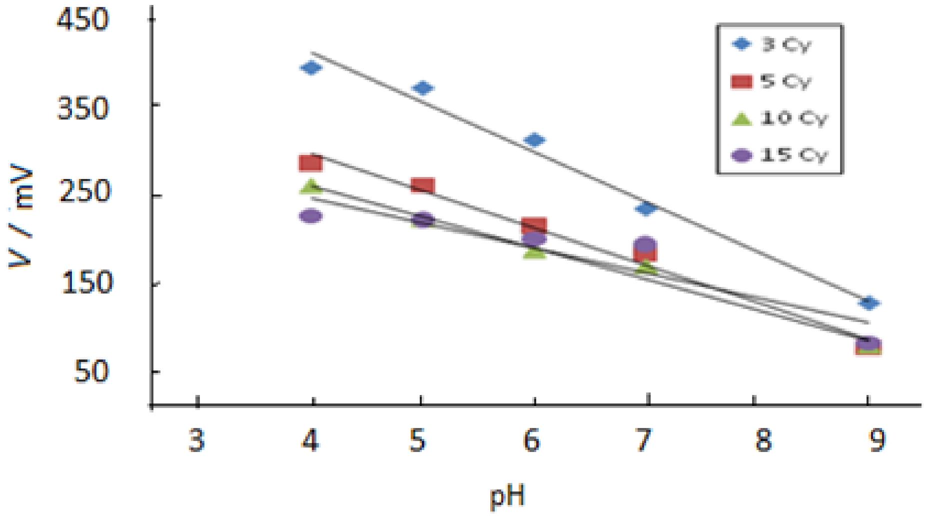

Figure 11. *The responses of P(o-ClPh-co-o-HOPh)-Pt modified electrode having different thicknesses at pH range (4-9).*

Electrode stability

Potentiometric response of the P(o-ClPh-co-o-HOPh)-Pt modified electrode was examined over a period of 9 days in order to study the stability of electrode. As seen in Figure 12 and Table 3, a significant decrease in the response slope is observed for the P(o-ClPh-co-o-HOPh)-Pt modified electrode. Also, the calibration curves of the P(o-ClPh-co-o-HOPh)-Pt modified electrode lost their linearity and were compared to the fresh electrode (1st day) even after repeatedly using it for 9 days.

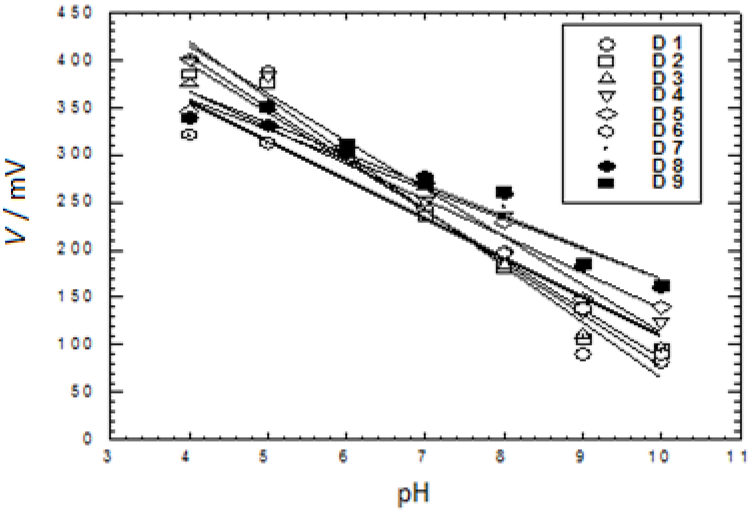

Figure 12. *P(o-ClPh-co-o-HOPh) response from the first to the ninth day*

Table 3. *Slopes and R^2 values obtained from Figs 12*

Time, day	-slope, mV pH^{-1}	R^2
1	58.7	0.97
2	54.5	0.97
3	51.5	0.97
4	49.9	0.97
5	37.9	0.95
6	40.9	0.91
7	40.5	0.91
8	31.3	0.94
9	32.5	0.93

Response mechanism

We have shown that the potentiometric responses to pH changes of the different modified electrodes are linear in the range 2-12. These responses must be mainly attributed to the copolymer films rather than the platinum substrate. Possible explanation is the affinity of the numerous hydroxyl groups and Cl atoms to the protons in solutions. The binding of H+ onto copolymer creates local charge density excess at the electrode surface. Surface reactions seemed to take place on the copolymer film, essentially protonation and deprotonation of superficial OH groups of the polymers as symbolically described by:

$$\text{Copolymer} + \text{H}^{+} \rightarrow \text{CopolymerH}^{+}.$$

When the equilibrium is attained at the copolymer/solution interface, we can write the equilibrium expression of the surface reaction and the equilibrium potential *E* as:

$$k = \frac{[\text{Copolymer}\,\text{H}^+]}{[\text{Copolymer}][\text{H}^+]}$$

$$E = E_\circ + \frac{RT}{F}\ln\frac{[\text{Copolymer}\,\text{H}^+]}{[\text{Copolymer}]} = E_\circ^{'} + \frac{RT}{F}\ln[\text{H}^+]$$

According to this mechanism of the reaction, we expect the slope of 59 mV pH^{-1} at 25 °C at all pH values. But our electrodes showed lower response slope. The presence of anionic and cationic species in the vicinity of the modified electrode surface such as (K^+, Na^+, Cl^-, *etc.*) in the buffer solutions which have an effect on the modified electrode response as mentioned in the literature [52–54].

Conclusion

P(o-ClPh-co-o-HOPh) films are prepared by the electropolymerization of a mixture of o-ClPh and o-HOPh (with 1:1 molar ratio) on Pt substrates from an aqueous medium. The process is fast and economic. The electropolymerization reaction was found to be first order with respect to the H_2SO_4 concentration, but of the second order for the comonomer concentration. The prepared P(o-ClPh-co-o-HOPh) films are stable up to 220 °C and exhibit amorphous and smooth structure with uniform distribution on the Pt substrate. IR and UV-Vis spectroscopy confirm the copolymer formation. The calculated activation energy, enthalpy, and entropy for the copolymerization were found to be 20.20 kJ mol^{-1}, 19.24 kJ mol^{-1} and -281.47 J K^{-1} mol^{-1}, respectively. The diffusion coefficient D is 6.53 10^{-7} m^2 s^{-1} in the scan rate of 15 up to 40 mV s^{-1} at 25 °C and increased with increasing temperature where E_a^diff was calculated to be 38.25 kJ mol^{-1} at 25 mV s^{-1}.

The potentiometric sensitivity to pH change of the P(o-ClPh-co-o-HOPh)-modified electrode exhibits a response slope of 52.16 mV/pH (30 °C), a linearity range from pH 4 to 9 and the response time less than 10 seconds. The electrode lost its response with time. The potentiometric responses to pH change were suggested to be related to the protonation and deprotonation of the polymer film atoms. Easy fabrication and low production cost of the P(o-ClPh-co-o-HOPh)-modified electrodes offer an alternative to other polymer-based pH sensors. Further development will focus on modification of the P(o-ClPh-co-o-HOPh) surfaces in order to improve the potentiometric responses to pH change and stability with time.

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