Kinetic Study of anodic corrosion of Copper in Phosphoric acid and Effects of Some Phenols Derivatives

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ARTICLE INFO	ABSTRACT
Article history: Received: 24 January 2013; Received in revised form: 5 December 2014; Accepted: 16 December 2014; **Keywords** Electropolishing of copper, Organic phenols, Limiting Current, Inhibition of corrosion, Thermodynamic parameters and adsorption isotherm.	Electropolishing of copper in phosphoric acid is considered as corrosion rate of copper and due to the economic importance of copper there are several researches deals with acceleration and inhibition of this process. From the previous studies this process may be controlled by the presence of some materials which may cause acceleration or inhibition of this process. In this paper the electropolishing process inhibited with different ratio by addition of some organic phenols derivatives by addition with concentration (10^{-5} - 10^{-2} mol. 1^{-1}).The results reveal that organic phenols have strongest inhibitive effect ranging from 4.92 to 40.98 % and the thermodynamic parameters and as well as adsorption isotherm were given.

Introduction

Due to its excellent thermal conductivity and good mechanical workability, copper is a material commonly used in heating and cooling systems. Scale and corrosion products have a negative effect on heat transfer, and they cause a decrease in the heating efficiency of the equipments. Therefore, periodic descaling and cleaning in hydrochloric acid pickling solution are necessary.

Many corrosion inhibitors can be used eliminate the undesirable destructive effect and prevent metal dissolution. Copper normally does not displace hydrogen from acid solutions and, therefore, is virtually unattached in non-oxidizing conditions. In fact, the uprising hydrogen bubbles induce a radial momentum transfer which enhances the rate of copper corrosion [1]. Copper dissolution in acidic medium has been studied by several researchers [2 – 7].

Corrosion inhibitors can be used to prevent copper dissolution. Amines are known to be very effective inhibitors for metal and alloys in different corrosion media. Benzotriazole, for instances, was studied and found to have excellent inhibition properties in several corrosion environments [8-11]. The molecule contains nitrogen atoms and it is also useful in preventing copper staining and tarnishing [12].

One of the most important methods in the protection of copper against corrosion is the use of organic inhibitors [13].

Organic compounds containing polar groups including nitrogen, sulfur, oxygen, and heterocyclic compounds with polar functional groups and conjugated double bonds have been reported to inhibit copper corrosion [14-22].

The inhibiting action of these organic compounds is usually attributed to their interactions with the copper surface via their adsorption. Polar functional groups are regarded as the reaction center that stabilizes the adsorption process, in general, the adsorption of an inhibitor on a metal surface depends on the nature and the surface charge of the metal, the adsorption mode, its chemical structure and the type of electrolyte solution [23].

The phenomenon of electropolishing is first discovered by Jaquet [24]. A lot of work has been done on this phenomenon owing to its important as metal finishing process. A great deal of work has been directed to study the mechanism of electro polishing as well as to establish conditions for different metals and alloys involved in the process.

Mechanistic studies have revealed that electro polishing is diffusion controlled process taking place at the limiting current which is attained most probably when the diffusion layer becomes saturated with Cu in, electropolishing of copper.

Therefore, the values of the limiting current which determined the polishing rate depends on the rate of mass transfer of Cu^{+2} from the diffusion layer to the bulk solution. The latter depends on the relative movement of the ions at the anode and in the electrolyte. Earlier works studied the factors affecting the limiting current have overlooked the effect of anode geometry as an important factor in determining the value of the limiting current.

The work of Heckerman and Simpson indicated that, electro polishing of copper in phosphoric acid results in the formation of a thin film of a phosphorous compound. The nature of solid film is not known. The radio tracer work suggested that, it a phosphorous containing compound. Other work based on electron diffraction showed .That, the film is an oxide. Hull cell studies by Lurking suggested that, copper oxides are formed during electro polishing of copper in H_3PO_4 [25].

It can be defined that, a viscous layer is present at the surface of copper anodes during electro polishing as shown by the work of Walton [26]. It is likely that, the viscous layer controls the rate of dissolution of the solid film and that electro polishing occurs in those electrolytes in which there is a relationship, between the rate of electro polishing and the

formation of the solid film and also between the rate of dissolution and diffusion of the solid product through the viscous layer. The objective of this study is to investigate the effect of some organic phenols (Phenol, *p*-amino phenol, *o*-amino phenol, *o*-cresol, *p*-cresol and *m*-cresol) on the inhibition of copper corrosion in phosphoric acid at different conditions. The rate of copper corrosion is determined by measuring the anodic limiting current.

Experimental Procedure

Chemicals

Analar grade H_3PO_4 (98% w/w) and double distilled water used to prepare the electrolyte. Phenols derivatives were used in this work are Phenol, *p*-amino phenol, *o*-amino phenol, *o*-cresol, *p*-cresol and *m*-cresol.
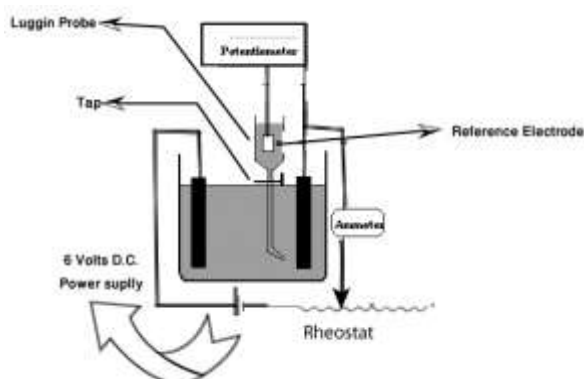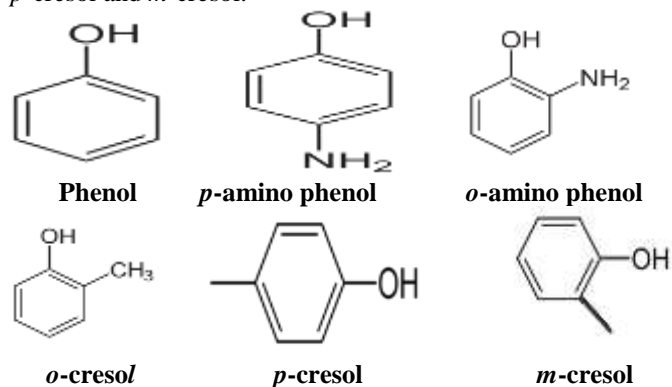

Phenol   ***p*-amino phenol**   ***o*-amino phenol**

o*-creso*l   ***p*-cresol***   ***m*-cresol**

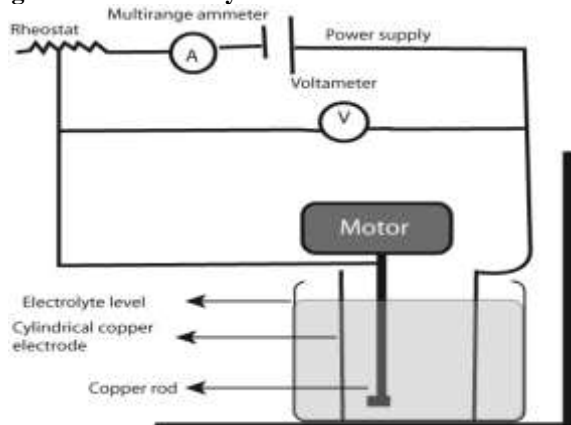**Figure 1 The electrolytic cell and the electrical circuit**

Figure 2 The electrolytic cell and electrical circuit

Measurements of the Limiting Current

Polarization curves were obtained by increasing the cell current step wise and the steady state anode potential against a reference electrode consisted of a wire immersed in a cup of Luggin tube   filled with phosphoric acid concentration similar to that in the cell, the tip of the Luggin tube was placed 0.5-from the anode. The potential difference between the anode and the

reference was measured by high impedance potentiometer. Five phosphoric acid concentrations (6, 8, 10, 12 and 14 M) were prepared from Analar grade phosphoric acid distilled water. The anode height varied from 1-5 cm. Before each run, the back part of the anode was insulated with polystyrene lacquers and the active surface of the anode was polished with fin emery paper, degreased with trichloroethylene, washed with alcohol and finally rinsed in distilled water. Electrode treatment was similar to that used by Wilke [27]. Organic acid concentration were 10^{-5} – 10^{-2} mol. l^{-1}. The rate of electro polishing of copper was determined at 25°C.

Rotating Cylinder Electrode (R.C.E.) Cell and Circuit

Figure 2 is a block diagram of the apparatus which permits the rotating of a cylinder electrode at accurately controlled angular velocities. The shaft was driven by a variable speed motor. The frequency of rotation, recorded as revolution per minute-, was counted by an optical tachometer. The glass vessel which holds electrolyte is 13 cm diameter. The electrical circuit consists of 6 volts D.C. power supply, a multirange ammeter connected in series with the cell to measure the current, and voltmeter is connected in parallel with the cell to measure its voltage.

The anode consists of a copper metal cylinder 2 cm diameter and 7 cm length. The sides and back of the cylinder as well as the drive shaft are insulated by epoxy- resin. The cathode is made of a cylinder copper metal electrode of 12 cm diameter; it's also acted as the reference electrode by virtue of its high surface area compared to that of the anode.

Results And Discussion

Leveling process

Figures 3 shows a typical polarization curves obtained using different concentration of *p*-cresol as divided cell at 25°C and 8M H_3PO_4. The limiting current at which polishing take place was determined from those polarization curves and used to calculate the mass transfer coefficient (K) of copper polishing in H_3PO_4 from the equation:

$$K = I / zFC_o \tag{1}$$

C_o: bulk concentration, z: valence and F: Faraday number.

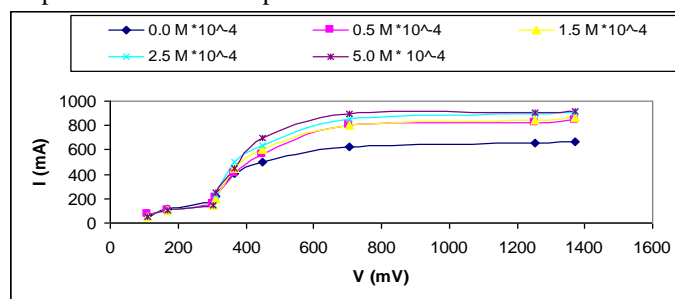Table 1 gives the values of limiting current at all temperatures for all compounds.

Figure 3 The relation between I (mA) and V (mV) in presence of *p*-cresol at 25ºC and 8 M H_3PO_4 for divided cell at 2 cm height.

Leveling is the principle process in electropolishing [28]. Mayer [29] explained the necessity to separate between anode and cathode by non-conductive slit to prevent the gas bubbles transfer to the anode surface and enhance the homogenous distribution of electric current [2]. The study of leveling based on the classical current voltage curves of electropolishing as shown in Figures 3 a typical polarogram obtained in this study for Phenols derivatives in case of divided and undivided cell.

Table 1 The values of limiting current at different temperatures for all compounds used in case of divided cell

Conc. M×10⁶	Phenol				o-cresol			
	25°C	30°C	35°C	40°C	25°C	30°C	35°C	40°C
0.0	710	750	800	860	710	750	800	860
0.5	650	670	720	730	570	585	600	620
1.0	580	600	630	640	540	540	555	570
1.5	550	570	590	610	490	510	530	545
2.0	510	530	540	550	460	480	500	520
2.5	470	485	500	530	420	435	450	470
3.0	430	445	460	500	390	405	420	430
5.0	405	420	435	450	275	290	310	330

Conc. M×10⁶	p-amino				p-cresol			
	25°C	30°C	35°C	40°C	25°C	30°C	35°C	40°C
0.0	710	750	800	860	710	750	800	860
0.5	620	640	660	680	550	570	585	600
1.0	565	585	600	620	520	540	555	570
1.5	530	545	560	580	490	500	510	520
2.0	485	500	515	570	430	445	450	465
2.5	460	470	480	490	410	425	440	450
3.0	425	440	455	470	370	380	390	405
5.0	385	400	410	420	210	230	250	280

Conc. M×10⁶	o-amino				m-cresol			
	25°C	30°C	35°C	40°C	25°C	30°C	35°C	40°C
0.0	710	750	800	850	710	750	800	860
0.5	590	610	630	650	510	530	550	570
1.0	550	470	580	600	480	495	510	530
1.5	510	525	540	550	420	435	450	470
2.0	470	480	490	500	370	385	400	420
2.5	450	460	470	480	300	320	340	350
3.0	400	410	420	440	240	260	280	300
5.0	350	370	385	400	145	160	180	200

Table 4 The limiting current and surface coverage in 8M phosphoric acid with different phenols derivatives concentrations for divided cell

| Conc. M*10⁴	% Inh.	log C	Θ	Θ /1- Θ	log(Θ /1- Θ)	1- Θ	log(1- Θ)	log Θ /C
Phenol (I)								
0.5	9.72	-4.30	0.097	0.108	-0.97	0.92	-0.04	3.29
1.0	19.44	-4.00	0.194	0.241	-0.62	0.81	-0.09	3.28
1.5	23.61	-3.82	0.236	0.309	-0.51	0.76	-0.12	3.20
2.0	29.17	-3.70	0.292	0.412	-0.39	0.71	-0.15	3.16
2.5	34.72	-3.60	0.347	0.532	-0.27	0.65	-0.19	3.14
3.0	40.28	-3.52	0.402	0.674	-0.17	0.60	-0.22	3.13
5.0	43.75	-3.30	0.438	0.778	-0.11	0.56	-0.25	2.94
p-amino (II)								
0.5	13.89	-4.30	0.139	0.161	-0.79	0.85	-0.07	3.44
1.0	21.53	-4.00	0.215	0.274	-0.56	0.78	-0.11	3.33
1.5	26.39	-3.80	0.264	0.358	-0.45	0.74	-0.13	3.25
2.0	32.64	-3.70	0.326	0.485	-0.315	0.68	-0.17	3.21
2.5	36.11	-3.60	0.361	0.565	-0.25	0.65	-0.19	3.16
3.0	40.97	-3.52	0.409	0.694	-0.16	0.60	-0.22	3.13
5.0	46.53	-3.30	0.465	0.870	-0.06	0.54	-0.27	2.97
o-amino (III)								
0.5	9.72	-4.30	0.097	0.108	-0.97	0.92	-0.04	3.29
1.0	19.44	-4.00	0.194	0.241	-0.62	0.81	-0.09	3.28
1.5	23.61	-3.82	0.236	0.309	-0.51	0.76	-0.12	3.20
2.0	29.17	-3.70	0.292	0.412	-0.39	0.71	-0.15	3.16
2.5	34.72	-3.60	0.347	0.532	-0.27	0.65	-0.19	3.14
3.0	40.28	-3.52	0.402	0.674	-0.17	0.60	-0.22	3.13
5.0	43.75	-3.30	0.438	0.778	-0.11	0.56	-0.25	2.94
o-cresol (IV)								
0.5	13.89	-4.30	0.139	0.161	-0.79	0.85	-0.07	3.44
1.0	21.53	-4.00	0.215	0.274	-0.56	0.78	-0.11	3.33
1.5	26.39	-3.80	0.264	0.358	-0.45	0.74	-0.13	3.25
2.0	32.64	-3.70	0.326	0.485	-0.315	0.68	-0.17	3.21
2.5	36.11	-3.60	0.361	0.565	-0.25	0.65	-0.19	3.16
3.0	40.97	-3.52	0.409	0.694	-0.16	0.60	-0.22	3.13
5.0	46.53	-3.30	0.465	0.870	-0.06	0.54	-0.27	2.97
p-cresol (V)								
0.5	9.72	-4.30	0.097	0.108	-0.97	0.92	-0.04	3.29
1.0	19.44	-4.00	0.194	0.241	-0.62	0.81	-0.09	3.28
1.5	23.61	-3.82	0.236	0.309	-0.51	0.76	-0.12	3.20
2.0	29.17	-3.70	0.292	0.412	-0.39	0.71	-0.15	3.16
2.5	34.72	-3.60	0.347	0.532	-0.27	0.65	-0.19	3.14
3.0	40.28	-3.52	0.402	0.674	-0.17	0.60	-0.22	3.13
5.0	43.75	-3.30	0.438	0.778	-0.11	0.56	-0.25	2.94
m-cresol (VI)								
0.5	13.89	-4.30	0.139	0.161	-0.79	0.85	-0.07	3.44
1.0	21.53	-4.00	0.215	0.274	-0.56	0.78	-0.11	3.33
1.5	26.39	-3.80	0.264	0.358	-0.45	0.74	-0.13	3.25
2.0	32.64	-3.70	0.326	0.485	-0.315	0.68	-0.17	3.21
2.5	36.11	-3.60	0.361	0.565	-0.25	0.65	-0.19	3.16
3.0	40.97	-3.52	0.409	0.694	-0.16	0.60	-0.22	3.13
5.0	46.53	-3.30	0.465	0.870	-0.06	0.54	-0.27	2.97

The curve divided into three parts: in the first part, the current density (c.d.) is proportional to the voltage. At the second part of the curve, the metal undergoes electropolishing.

Effect of electrode height on limiting current

Figure 4 show that, the limiting current density decreases with the increase in height. In electro-polishing and generally for anodic dissolution of metal, the direction of flow of the thermodynamic boundary layer and the diffusion layer increase in the downward direction , i.e. the resistance to mass transfer increases in the downward direction. Accordingly, the local limiting current density increases in the up-ward direction of the anode. This explains why polishing is attained at the upper parts of the electrode before the lower parts at the limiting current region. This was confirming by visual observation during electropolishing. The average limiting current density decreases with increase in the height according to the equation [30]:

$$I_l = C/H^a \qquad (2)$$

where C is constant, H is the height of electrode, a is constant depends on the type of solution, [a = 0.502 for undivided cell].
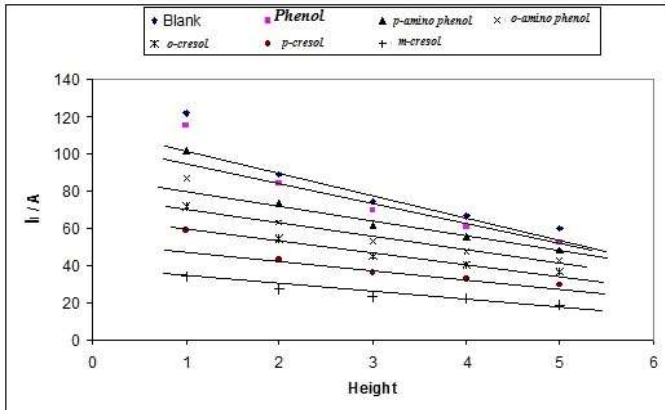
Figure 3 The relation between current density and height for blank solution and in presence of all compounds.

Effect of organic compounds Concentration the limiting current

Table (1) gives the observed limiting current at all concentrations of phenol and at all temperatures. The observed limiting current, which represent the rate of copper metal corrosion in phosphoric acid, are found that, the limiting current rate of electropolishing decrease with increasing the concentration of phenols derivatives additives as shown in Table 1. we can recommended on the basis of results that, it may use in this range of concentration to inhibit the corrosion of copper metal in 8 M H_3PO_4 acid in all type of phenols derivatives to be used in this work [31]. The mass transfer coefficient of polishing process, which used in data correlation, calculated from the limiting current using the equation (1).

The above equation based on the finding of previous studies [32]. If the limiting current in absence of organic compounds (I), and in the presence of organic compounds (I_l), the percentage of inhibition can be calculated from the following equation:

$$\% \text{ Inhibition} = I-I_l/I \times 100 \qquad (3)$$

Table 2 and Figure 4 shows that the percent inhibition caused by organic compounds ranges from 4.92 to 40.98 % depending on the organic phenols derivatives and their concentrations.

The limiting current decreases with increasing the concentration of organic compounds this agree with the finding of other authors who worked within the same range of concentration using other inhibitors [33]. The deceasing in the

limiting current with increasing the concentration of organic phenols derivatives is attributing to:

(a) The solubility of dissolved copper phosphate in phosphoric acid, which is responsible for the limiting current, decreases with increasing phosphoric acid concentration.

(b) The viscosity of the solution increases with increasing phenols derivatives concentration with consequence decrease in the diffusivity of' Cu^{2+} according to stokes-Einstein equation [34].

Table 3 The relation between percentage inhibition and concentration of all compounds at 25°C

C x 10^5 mol.l^-1	% Inhibition					
	Phenol (I)	p-amino (II)	o-amino (III)	o-cresol (IV)	p-cresol (V)	m-cresol (VI)
0.5	9.7	13.9	18.1	20.8	23.6	29.2
1.0	19.4	21.5	23.6	25.0	27.8	33.3
1.5	23.1	26.4	29.2	31.9	40.3	48.6
2.0	29.2	32.6	34.7	36.1	40.3	48.6
2.5	34.7	36.1	37.5	41.7	43.1	58.3
3.0	40.2	40.9	41.7	45.8	48	66.7
5.0	43.8	46.5	51.4	61.8	70.8	80.1
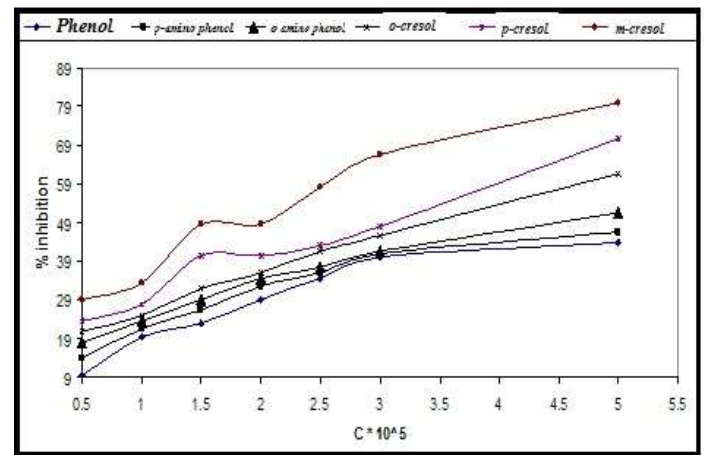
Figure 4 The relation between % inhibition and concentration of all compounds at 25°C.

Adsorption Isotherm

It generally assumed that the adsorption isotherm of the inhibitor at the metal solution interface is the first main role the mechanism of inhibitors action in aggressive acid media. Table 4 shows the relation between limiting current and surface coverage in 8M H_3PO_4 for all phenols used:

a) Electrostatic attraction between charged molecules and the charged metal.

b) Interaction of lone pairs of electron in the molecules with the metal.

c) Interaction of electron with metal.

d) A combination of the above [35].

Figures 5 to 10 shows the Flory-Huggins adsorption isotherm for copper electrode in H_3PO_4 plotted as log Θ/C against log (1-Θ) at 25°C. A straight line is obtained with a slope x and intercept log xK. The experimental data fits the Flory-Huggins adsorption isotherm which represented by:

$$\log Θ/C = \log xK + x\log (1-Θ) \qquad (4)$$

where x is the number of water molecules replaced by one molecule of the inhibitor. It is clear that, the surface coverage data are useful for discussing adsorption characteristics. The adsorption of inhibitors at metal solution interface may be due to

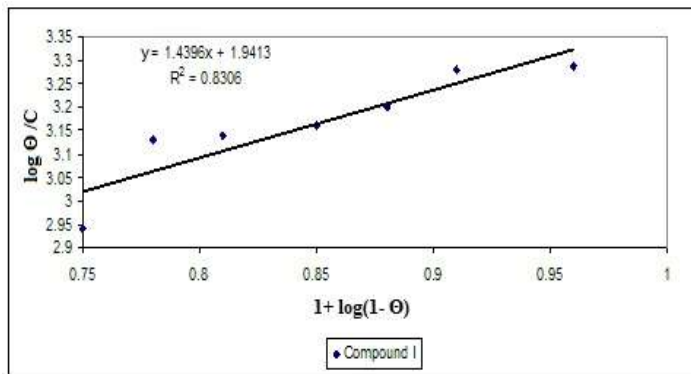the formation of either electrostatic or covalent bonding between the adsorbents and the metal surface atoms [36].

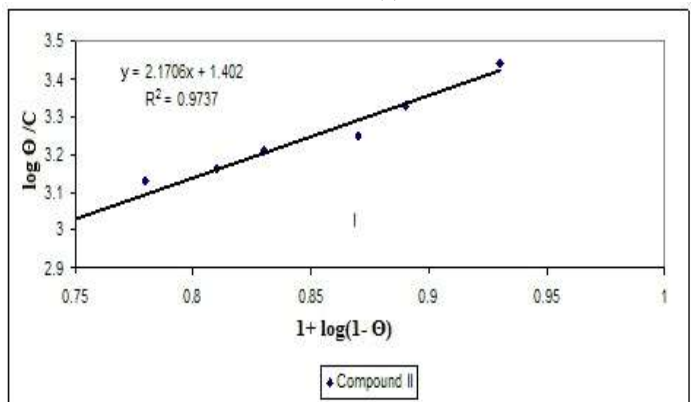**Figure 5 Flory-Huggins adsorption isotherms at 25ºC for Phenol (I).**

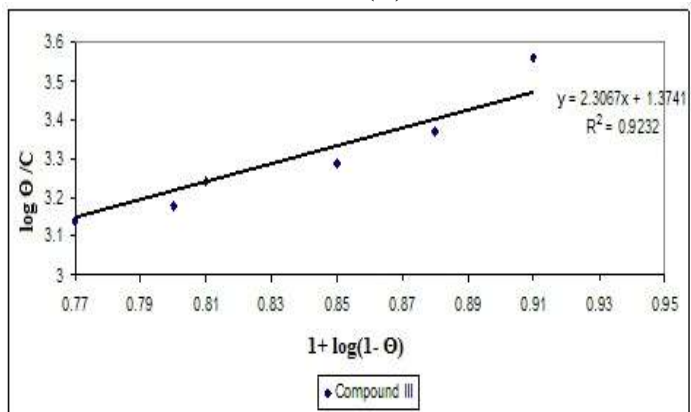**Figure 6 Flory-Huggins adsorption isotherms at 25ºC for *p*-amino (II).**

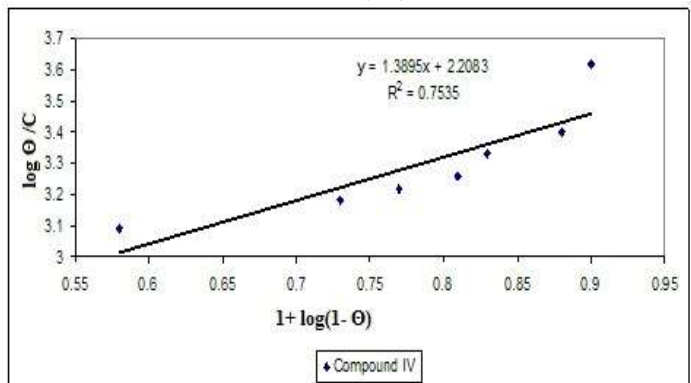**Figure 7 Flory-Huggins adsorption isotherms at 25ºC for *o*-amino (III).**

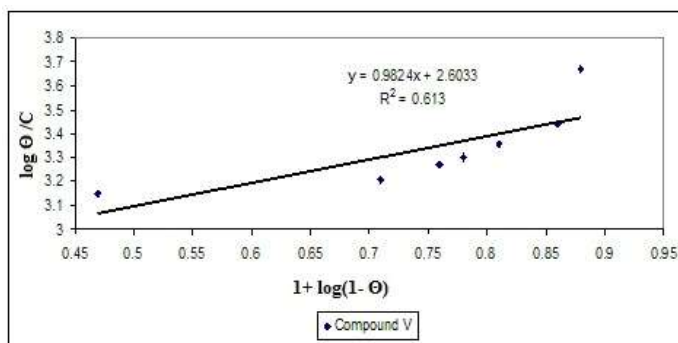**Figure 8 Flory-Huggins adsorption isotherms at 25ºC for *o*-cresol (IV).**

Figure 9 Flory-Huggins adsorption isotherms at 25ºC for *p*-cresol (V).
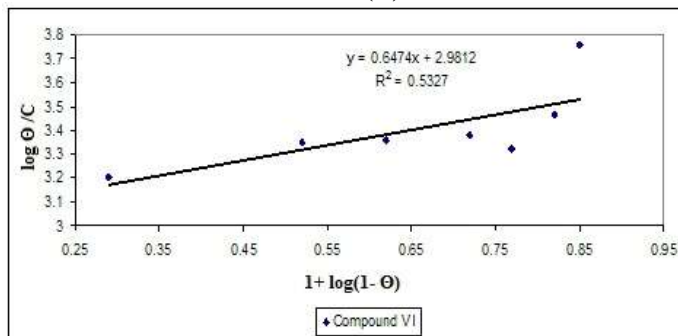

Figure 10 Flory-Huggins adsorption isotherms at 25ºC for *m*-cresol (VI).

The kinetic adsorption isotherm may be written in the form: [37]

$$\log \Theta /1- \Theta =\log k'+ y \log C \qquad (5)$$

where y is the number of inhibitor molecules occupy one active site. The binding constant of adsorption $K= k'^{1/y}$, where $1/y$ is the number of the surface active sites occupied by one molecule of the inhibitor, and k is the binding constant. Figures 11 to 16 linear relation of the inhibitor molecules between $\log \Theta/1-\Theta$ and log C at 25°C, and the calculated values of $1/y$ and K given in Table 4.
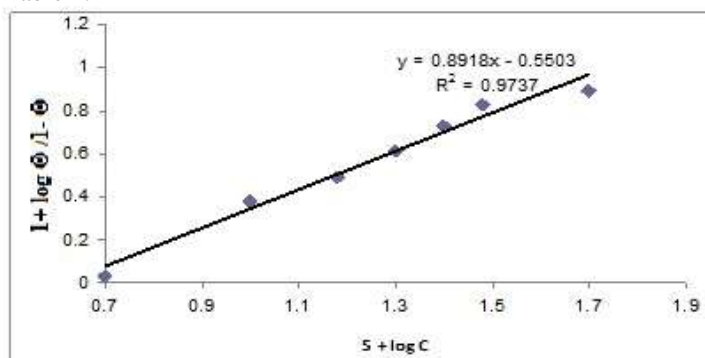

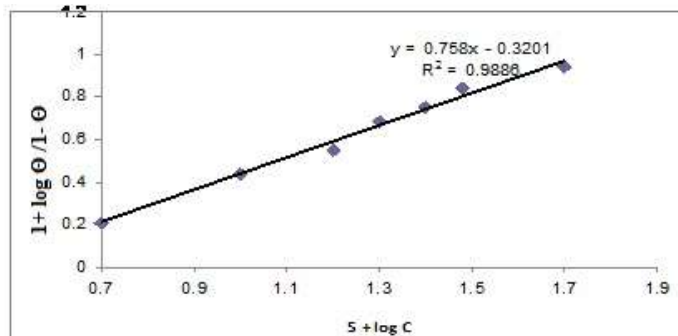**Figure 11 Kinetic adsorption isotherms for Phenol (I) at 25ºC**

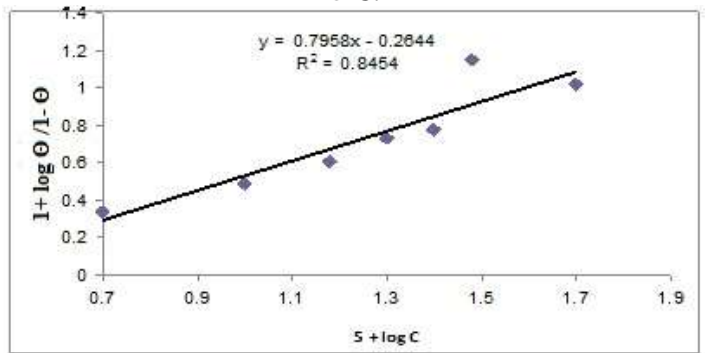**Figure 12 Kinetic adsorption isotherms for *p*-amino (II) at 25ºC.**

Figure 13 Kinetic adsorption isotherms for *o*-amino (III) at 25ºC
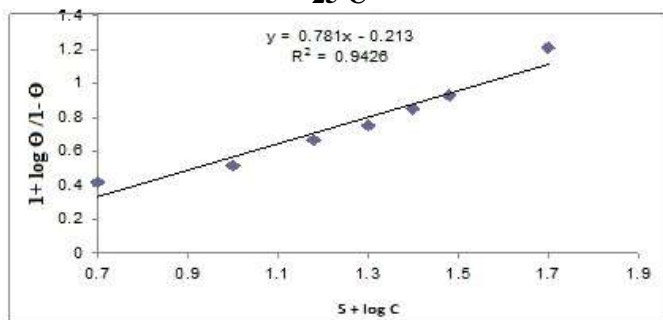

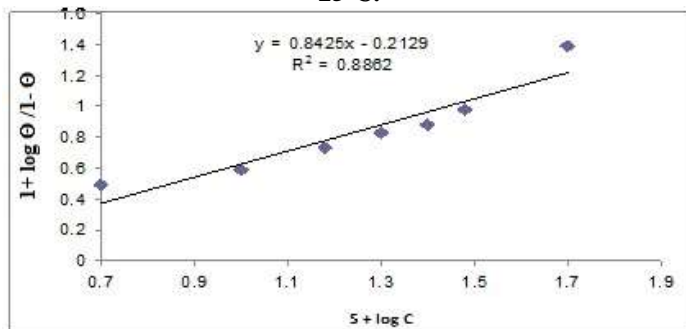**Figure 14 Kinetic adsorption isotherms for *o*-cresol (IV) at 25ºC.**

Figure 15 Kinetic adsorption isotherms for *p*-cresol (V) at 25ºC.
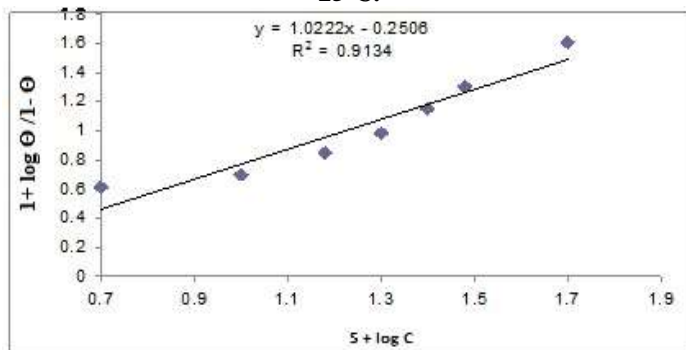

Figure 16 Kinetic adsorption isotherms for *m*-cresol (VI) at 25ºC.

The values of 1/y depend on the type of phenols derivative. From Table 5 it is obvious that, the value of 1/y for *m*-cresol (VI) is approximately one. Suggesting that, the compound attached to one active site per inhibitor molecule.

For other inhibitors (Phenol (I), *p*-amino (II), *o*-amino (III), *o*-cresol (IV) and *p*-cresol (V)) the Values of 1/y higher than one, indicating that, the given inhibitors Molecules are attached to more one active site.

The free energy of adsorption (ΔG_{ads}) at different Concentration was calculating from the following equation:

$$\Delta G_{ads} = - RTIn\ (55.5K) \tag{6}$$

The value 55.5 is the concentration of water in the Solution mol/1.

The values of ΔG_{ads} are given in Table 6. In all cases, the ΔG_{ads} values are negative and lie in the rank of 26.56 - 31.31 KJ/mol. the most efficient inhibitor shows the most negative value. This suggests that, they strongly adsorbed on the metal surface. The negative values of ΔG_{ads} indicate that, the spontaneous adsorption of the inhibitor. It's found that, the ΔG_{ads} values are more positive than - 40 K.J/mol indicating that the inhibitors are physically adsorbed on the metal surface. Similar results also had been reported [38].

Table 5 The values of k, x and 1/y of phosphoric acid in presence of different phenols derivatives to Langmuir, Flory-Huggins and Kinetic adsorption isotherm.

Compounds	Flory-Huggins		Kinetic adsorption isotherm		
	X	K	Y	1/y	k
Phenol (I)	1.4396	1669.39	0.8918	1.12	810.59
***p*-amino (II)**	2.1706	1721.95	0.7572	1.32	294.04
***o*-amino (III)**	1.8727	2027.83	0.6903	1.45	188.93
***o*-cresol (IV)**	1.4195	2913.83	0.7810	1.28	491.81
***p*-cresol (V)**	2.3713	2980.67	0.8425	1.19	997.01
***m*-cresol (VI)**	0.6374	2682.53	0.9858	1.01	5640.09

Table 6 The values of free energy of adsorption (kJ. mol⁻¹) of phosphoric acid in presence of different phenols derivatives using different methods.

Compounds	$-\Delta G_{ads}$, kJ.mol^{-1}	
	Flory-Huggins	**Kinetic adsorption isotherm**
Phenol (I)	28.35	26.56
***p*-amino (II)**	28.42	24.04
***o*-amino (III)**	28.83	22.95
***o*-cresol (IV)**	29.73	25.32
***p*-cresol (V)**	29.78	27.07
***m*-cresol (VI)**	29.52	31.36

Effect of temperature

The effect of temperature on the copper electropolishing rate in absence and presence of phenols derivatives was determined in the temperature range 25, 30, 35, 40°C and illustrated in Table 3. It observed that the electropolishing rate increases with temperature for different concentrations of organic compounds.

Thermodynamic treatment of the results

From the integrated form of the Arrhenius equation:

$$\ln I = - E_a/RT + \ln A \tag{7}$$

where R is the gas constant (8.314 kJmol⁻¹), E_a is the activation energy and A is the frequency factor. It can be seen that, the gradient is given by $-E_a/R$ and the intercept by ln A. tables (25-31) and Figs. (37-42) give the values of E for the compounds used.

The values for enthalpy of activation ΔH^*, entropy of activation ΔS^*, and free energy of activation ΔG^* can be obtaining by using equations:

$$\Delta H^* = E_a - RT \tag{8}$$

$$\Delta S^* / R = \ln A - \ln (kTe/h) \tag{9}$$

$$\Delta G^* = \Delta H^* - T\ \Delta S^* \tag{10}$$

where k is Boltzmann's constant, e = 2.7183, h is Plank's constant, A is Arrhenius constant, T is absolute temperature and R is the universal gas constant. The adsorption is usually followed by liberation of heat of adsorption, so that $E_a < 0$, consequently the rate of adsorption decreases with temperature and as a result, the surface coverage at given concentration decreases with increasing temperature. It known that an increase in the heat of adsorption leads to an increase in the energy of adsorption forces, however rising of the temperature acts in the reverse direction, increasing the kinetic energy of the molecules, facilitating disruption (consequently in the physical adsorption).

Table 7 The thermodynamic parameters for electrodeposition of copper in presence of phenol, *p*-amino and *o*-amino at 25°C

Conc. (mol l^{-1})	E_a (kJ.mol^{-1})	ΔG^* (kJ.mol^{-1})	ΔS^* (J.mol^{-1} k^{-1})	ΔH^* (kJ.mol^{-1})
Phenol (I)				
1.00E-05	6.6642	57.26592	-0.17811	4.16364
5.00E-05	8.6161	57.4188	-0.17199	6.1373
1.00E-04	11.1814	57.629.5	-0.161977	9.33587
5.00E-04	12.5433	57.727.07	-0.159861	10.0645
1.00E-03	13.0243	57.786.68	-0.15844	10.5455
5.00E-03	11.5827	57.905.4	-0.16368	9.10395
1.00E-02	12.4715	57.854.9	-0.16053	9.99275
***p*-amino (II)**				
1.00E-05	13.5059	57.7883	-0.15683	11.02708
5.00E-05	11.7423	57.814	-0.1628	9.26352
1.00E-04	13.4603	58.00544	-0.1577	10.98148
5.00E-04	13.1846	58.11443	-0.159	10.70582
1.00E-03	14.9851	58.242	-0.1534	12.506
5.00E-03	16.0355	58.3668	-0.1503	13.5567
1.00E-02	18.6014	58.5231	-0.1422	16.1225
***o*-amino (III)**				
1.00E-05	6.6862	57.624	-0.17916	4.20738
5.00E-05	5.7894	57.720	-0.18249	3.31056
1.00E-04	7.0650	57.852	-0.1787	4.58618
5.00E-04	8.4720	58.0185	-0.17449	5.99325
1.00E-03	8.8610	58.13796	-0.1736	6.3822
5.00E-03	9.2864	58.2634	-0.1726	6.80756
1.00E-02	10.7887	58.4066	-0.16802	8.30989

In absence of organic substance, the results fit a straight line with an activation energy equals to 31.935 k.J.mol^{-1} which is higher than the values obtained when organic substance was used as inhibitor.

Thus, the high values of activation energy show that:

1- The rate of electropolishing of copper from phosphoric acid decreased by adding small amounts of the organic substances at temperature above 25°C.

2- The adsorption process is physical adsorption and molecules of organic substance disrupted at temperature above 30°C completely.

Table 7 and Table 8 show that, the entropy ΔS^* possess height negative values indicating a highly ordered organic species in the solution under investigation. These values found to be independent on the type of amide and dipolar aprotic solvents

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Table 8 The thermodynamic parameters for electrodeposition of copper in presence of *o*-cresol, *p*-cresol and *m*-cresol at 25°C

Conc. (mol l^{-1})	E_a (kJ.mol^{-1})	ΔG^* (kJ.mol^{-1})	ΔS^* (J.mol^{-1} k^{-1})	ΔH^* (kJ.mol^{-1})
***o*-cresol (IV)**				
1.00E-05	6.4438	57.5265	-0.17964	3.9649
5.00E-05	6.6862	57.62402	-0.17916	4.2073
1.00E-04	5.9713	57.68906	-0.18177	3.4925
5.00E-04	5.9027	57.773	-0.18228	3.42397
1.00E-03	6.4855	57.8762	-0.18067	4.0067
5.00E-03	6.7679	57.9888	-0.1801	4.28919
1.00E-02	6.5044	58.0854	-0.18131	4.0256
***p*-cresol (V)**				
1.00E-05	5.3584	57.379	-0.1828	2.8796
5.00E-05	5.6506	57.5179	-0.1823	3.17187
1.00E-04	5.7607	57.56616	-0.18207	3.28192
5.00E-04	5.8439	57.64404	-0.18205	3.36514
1.00E-03	5.3717	57.69218	-0.1838	28.9299
5.00E-03	5.0401	57.73919	-0.18506	2.56135
1.00E-02	5.4567	57.81215	-0.18391	29.77789
***m*-cresol (VI)**				
1.00E-05	7.0218	57.2553	-0.1767	4.5430
5.00E-05	6.2807	57.3180	-0.1794	3.8019
1.00E-04	6.3887	57.3624	-0.1792	3.9098
5.00E-04	7.3771	57.4404	-0.1762	4.8982
1.00E-03	7.7779	57.5266	-0.1751	5.2991
5.00E-03	6.8480	57.5705	-0.1784	4.3692
1.00E-02	5.8689	57.6152	-0.1818	3.3901

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