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Effect of Some Organic Aldehydes on the Electropolishing of Copper in Phosphoric Acid

Nabila M. Elmalah[1], *S.M.Abd Elhaliem*[2], *A.M.Ahmed*[1] *and, S .M.Ghozy*[2,*]

[1] Chemistry Department Faculty of Science Alexandria University
[2] Chemistry Department Faculty of Science Elzagazig University
[*]E-mail: msghozy@yahoo.com

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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 aldehydes (formaldehyde, acetaldehyde, paraldehyde, benzaldehyde, salicylaldehyde, anisaldehyde, and tolualdehyde) by addition with concentration (10^{-5} - 10^{-2} mol. l^{-1}).The results reveal that organic aldehydes have strongest inhibitive effect ranging from 14.3 – 61.9 % and the thermodynamic parameters and dimensionless group were present.

Keywords: Electropolishing of copper, organic aldehydes, Limiting Current, Inhibition of corrosion. Thermodynamic parameters and dimensionless group.

1. 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 denied 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 aldehydes (formaldehyde, acetaldehyde, paraldehyde, benzaldehyde, salicylaldehyde, anisaldehyde, and o-tolualdehyde.) 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.

2. EXPERIMENTAL PROCEDURE

2.1. Chemicals:

Analar grade H_3PO_4 (98% w/w) and double distilled water used to prepare the electrolyte. The organic aldehydes were used in this work are Formaldehyde, Acetaldehyde, Paraldehyde, Benzaldehyde, Salicylaldehyde, Anisaldehyde and O-Tolualdehyde.

2.2. Apparatus and Procedure:

Fig (1.a) shows the cell and electrical circuit used in the present work.

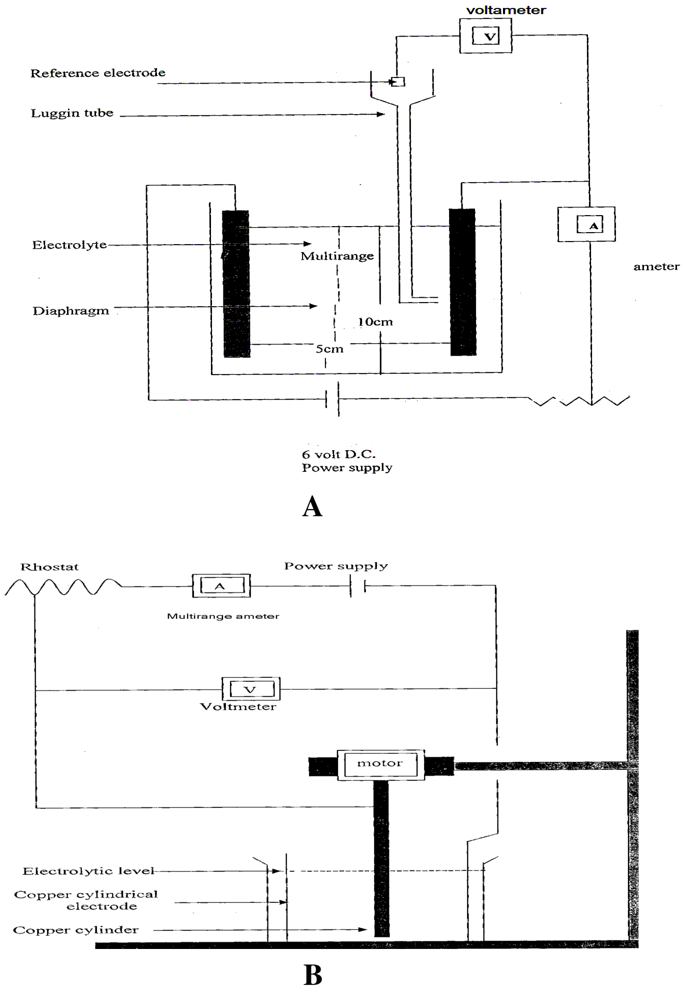


Figure 1. a) Shows the cell and electrical circuit, **b)** Shows the cell and electrical circuit in the rotating system

The cell consists of a rectangular plastic container having the dimensions 5.1x5x10 cm with electrodes filing the whole cross section. The electrodes were rectangular copper sheets of 10 cm height and 5 cm width. Electrodes separation was 5 cm. A porous PVC diaphragm was used to prevent the effect due to H_2 bubbles. The electrical circuit consists of 6V D.C. power supply, while a voltmeter is connected in parallel with the cell to measure the voltage and multirange ammeter connected in series with cell to measure the current.

2.3. 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 concentration (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.

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

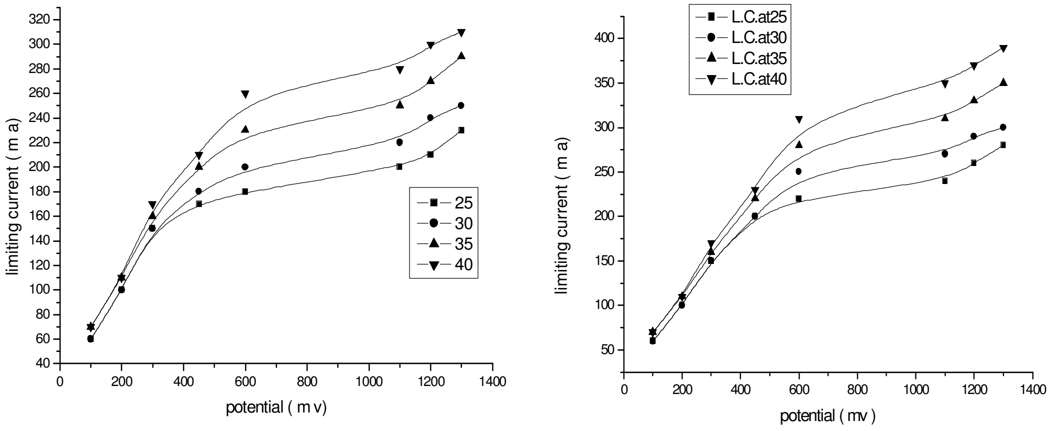
Fig (1.b) is a block diagram of the apparatus which permits the rotating of a cylinder electrode at accurately controlled angular velocities. The shaft was driven by a variable speed motor. The frequency of rotation, recorded as revolution per minute-, was counted by an optical tachometer. The glass vessel which holds electrolyte is 13 cm diameter. The electrical circuit Fig (1.b) 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 (4.76 cm) diameter and 2 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.

3. RESULTS AND DISCUSSIONS

3.1.Electropolishing using Divided and Undivided Cell:

Figure (2.a) show the limiting current measured using undivided cell for the blank solution (H_3PO_4) at different temperatures. Figure (2.b) show the limiting current measured using divided cell at the same temperatures. The data indicate that on used undivided cell, cathodic H_2 evolution increases the anodic limiting current. This increase is attributed in part to the fact that, the uprising hydrogen bubbles induce a radial momentum transfer which enhances the rate of polishing at the anode. Also indicated that on increasing the temperature the limiting current increase, this refers Figure to the high temperature catalyze the electro polishing process.



A B

Figure 2. Show the relation between the limiting current and temperature, H_3PO_4= 8M, (a: with and b : without diaphragm)

3.2. Effect of aldehydes concentration on the limiting current density:

The observed limiting current density , which represents the rate of copper metal corrosion in phosphoric acid at 25 ° C , decrease with increasing the concentration of the organic aldehydes under studying.

It found that the limiting current decreases with increasing the concentration of aldehydes. From the practical point of view and on the basis of results obtained the uses of aldehydes studied in the concentration range between (10^{-5} - 10^{-2} mol.l^{-1}) inhibit the corrosion of copper metal in 8 M H_3PO_4 acid[28,29]. The limiting current in absence of organic aldehydes (I), and in the presence of organic aldehydes (I_L), the percentage inhibition can be calculated from the following equation**:**

$$\% \text{ inhibition} = \frac{I - I_L}{I} * 100 \quad \rightarrow (1)$$

Table (1) show that the percentage inhibition caused by organic aldehydes range from 14.3 – 63.6 % depending on the aldehyde type, concentration and temperature. The limiting current decreases with increasing the concentration of aldehydes and temperature which agree with other previous work [30,31]. The decreasing in the limiting current densities with increasing the concentration of aldehydes may be due to the following

1- The solubility of the dissolved copper phosphate in the orthophposphoric acid, which is responsible for the limiting current, decreases with increasing the phosphoric acid concentration.

2- The increase in the diffusion layer thickness, which relates the resistance of electrolyte to the rate of mass transfer of copper ion from anode surface to the bulk solution.

Table 1. Give the effect of aldehyde concentration on the percentage inhibition of copper electrode in the presence of 8M H_3PO_4 at 25 ° C.

C. *10-5	1	5	10	50	100	500	1000
Formaldehyde	23.8	26.2	28.6	33.7	42.9	52.4	61.9
Acetaldehyde	14.3	19	23.8	31	35.7	47.6	52.4
Paraldehyde	28.6	33.3	38.1	40.5	42.9	54.8	59.5
Benzaldehyde	23.8	28.6	33.3	35.7	38.1	52.4	61.9
Salicylaldehyde	31.8	34.1	36.4	38.6	40.9	54.5	63.6
Anisaldehyde	31	33.3	35.7	40.5	42.9	59.5	61.9
Tolualdehyde	31.8	36.4	38.6	40.9	43.2	56.8	61.4

3.3. Adsorption Isotherm

The adsorption of the inhibitor molecules from aqueous solutions can be regarded as substitution adsorption process between the organic compounds in the aqueous phase and water molecules adsorbed on the electrode surface ($H2O_{(s)}$).

$$\mathrm{Org}_{(aq)} + x\mathrm{H_2O}_{(s)} = \mathrm{org}_{(s)} + x\,(\mathrm{H_2O}) \qquad \rightarrow (2)$$

Where x (the size ratio) is the number of water molecules displaced by one molecule of inhibitor. The above process reaches equilibrium when the chemical potential on the left hand equal to that of the right hand side.

Adsorption isotherms are very important in determining the mechanism of electrochemical reactions. the most frequently used isotherms are those of Langmuir . Frumkin, Parsons, Temkin, Flory-Huggins, and Bockris-Swinkels [32].

These entire isotherms are of the general form:

$$f(\Theta,x)\exp^{(-a\Theta)} = KC \qquad \rightarrow (3)$$

Where f (Θ, x) is the configuration factor which depends essentially on the physical model and assumption underlying the derivation of the isotherm. The mechanism of inhibition is generally believed to be due to the formation and maintenance of a protective film on the metal surface [33,34].

3.4.Application of Isotherm:

The degree of surface coverage (ϴ) at constant temperature was determined from the following equation[35,36].

$$\Theta = \frac{I - I_L}{I} \rightarrow (4)$$

Figs (3.a – 3.g) show 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 x K. The experimental data fits the Flory-Huggins adsorption isotherm which represented by:

$$\log \Theta /C = \mathrm{Iog}\ xk + x\log(1- \Theta) \rightarrow (5)$$

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 electrostatic or covalent bonding between the adsorbates and the metal surface [37]. The kinetic adsorption isotherm may be written in the form [38]:

$$\mathrm{Iog}\ \Theta /1- \Theta = \mathrm{Iog}\ k' + y \rightarrow (6)$$

From equation (6) a plot of log ϴ /1- ϴ against log C should yields a straight line with intercept of log K\` and slop = y , where y is the number of inhibitor molecules occupy one active site. The binding constant of adsorption K= k'l/y, where 1/y is the number of the active surface sites occupied by one molecule of the inhibitor, and k is the binding constant. Figs (4.a– 4.g) indicate linear relationship between log ϴ / 1- ϴ and log C at 25°C, and the calculated values of 1/y and K are given in Table (2). And from this table,. it is obvious that the value of 1/y for all compounds are higher than one indicating that, the given inhibitors molecules are attached to more than one active site. The free energy of adsorption (ΔG_{ads}). at different concentration of the aldehydes as calculated from the following equation:

$$\Delta G_{ads} = -RT\ \mathrm{In}\ (55.5\ K) \rightarrow (7)$$

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

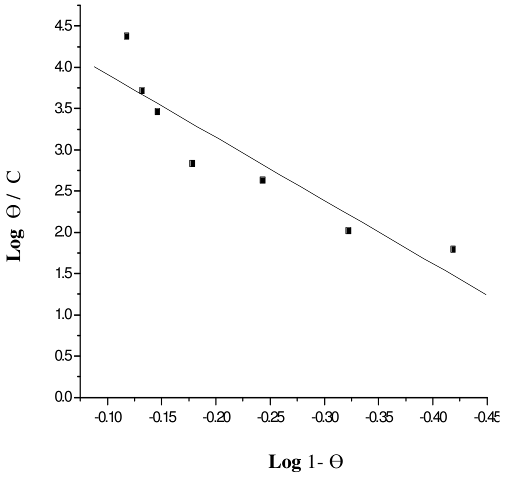
The values of ΔG_{ads} are given in Table (3). In all cases, the (ΔG_{ads}) values are negative and lie in the range of 22.01 – 36.35 KJ/mol. The most efficient inhibitor shows the most negative (ΔG_{ads}) value. This suggests that, they are strongly adsorbed on metal surface. The negative values of (ΔG_{ads}) indicate that the spontaneous ion of the inhibitors. It's found that (ΔG_{ads}) values are more positive than (- 40) indicating that the inhibitors are physically adsorbed on the metal surface. similar results have also been reported by Talati [38].

Table 2. Gives the values of K,X and 1/Y of H3PO4 of some organic aldehydes to Flory – Huggins, and Kinetic Adsorption Isotherm constants at 25 ° C.

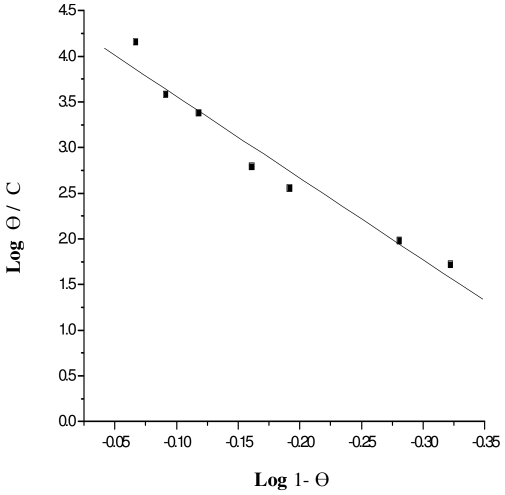
Compound	Flory - Huggins		Kinetic Adsorption Isotherm			
	X	K	K'	Y	1/Y	K
Formaldehyde	7.63	6200.6	3.99	0.239	4.2	322.4
Acetaldehyde	8.96	3198.9	3.84	0.276	3.6	130.04
Paraldehyde	10.37	38715.6	3.036	0.181	5.5	361.8
Benzaldehyde	8.03	7862.3	3.55	0.2204	5.54	312.7
Salicylaldehyde	8.5	17705.7	3.023	0.1785	5.6	493.97
Anisaldehyde	8.499	20201.3	3.55	0.1955	5.11	654.98
O-Tolualdehyde	9.86	42444	3.012	0.1709	5.85	632.5

Table 3. Gives the calculated values of free energy of adsorption (K.J. mol -1) of H_3PO_4 in the presence of the aldehydes

Compound	**Flory - Huggins**	**Kinetic Adsorption Isotherm**
	$-\Delta G_{ads}$	$-\Delta G_{ads}$
Formaldehyde	31.59	24.26
Acetaldehyde	29.95	22.01
Paraldehyde	36.13	23.15
Benzaldehyde	32.18	24.19
Salicylaldehyde	34.19	25.32
Anisaldehyde	34.51	26.02
O-Tolualdehyde	36.35	25.93

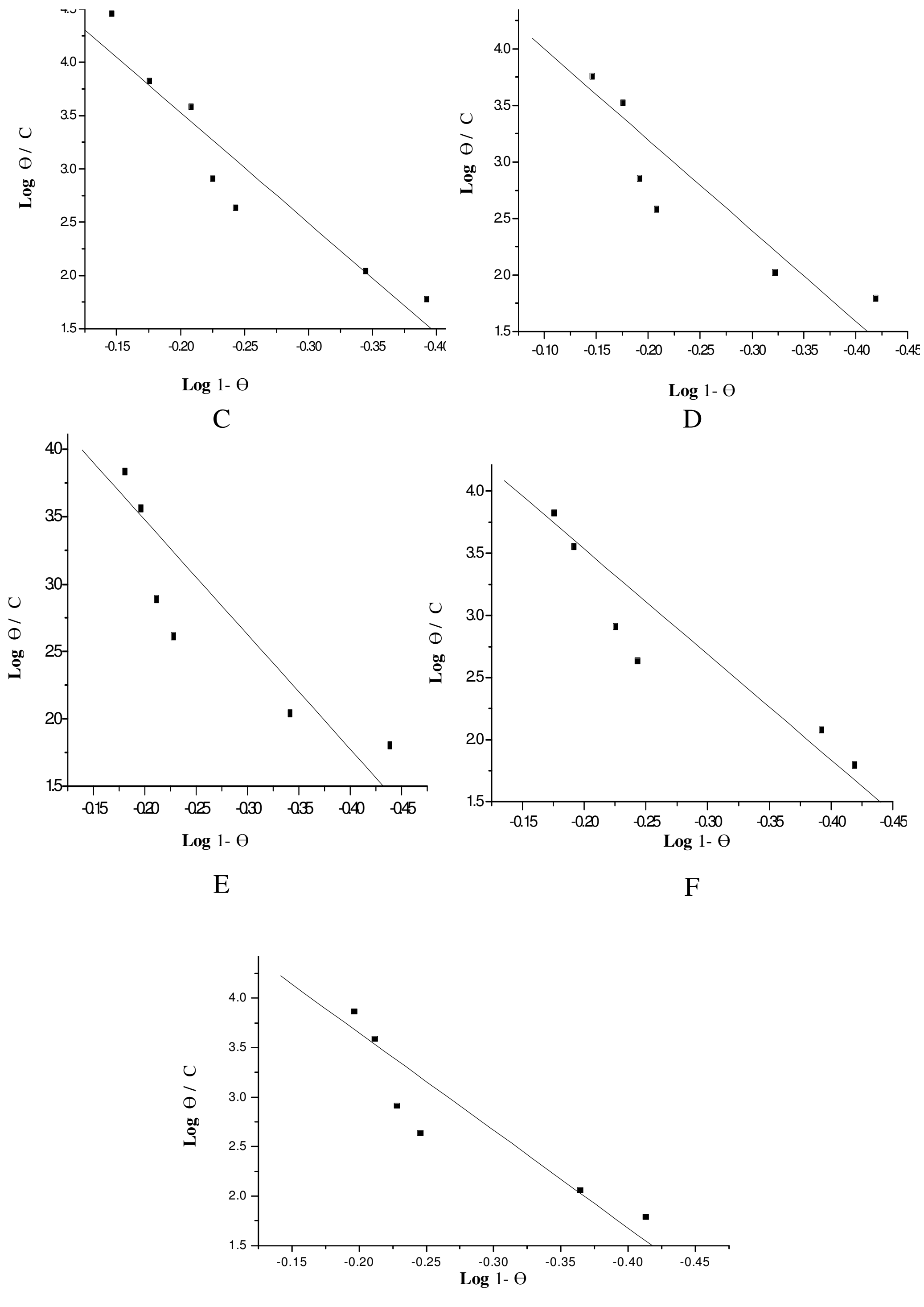


A



B

Θ



C

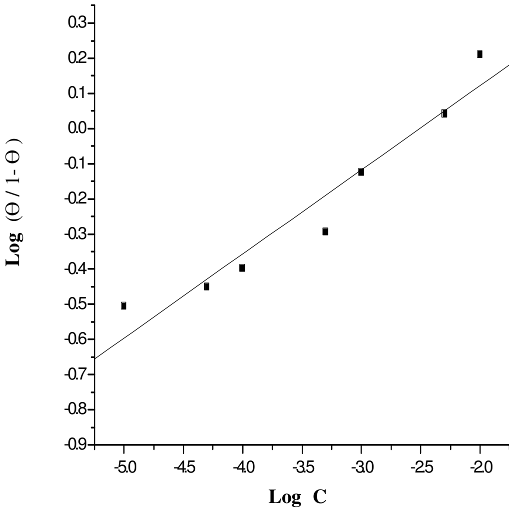
D

E

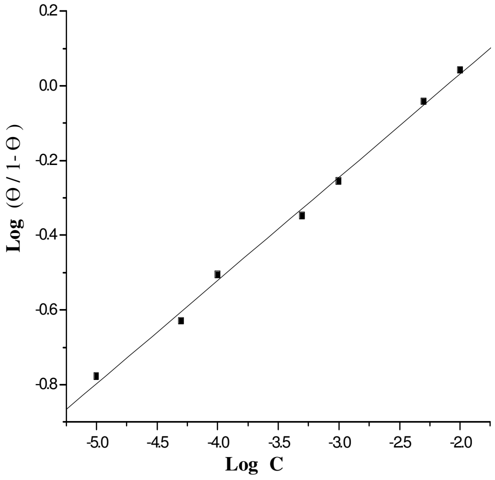
F

G

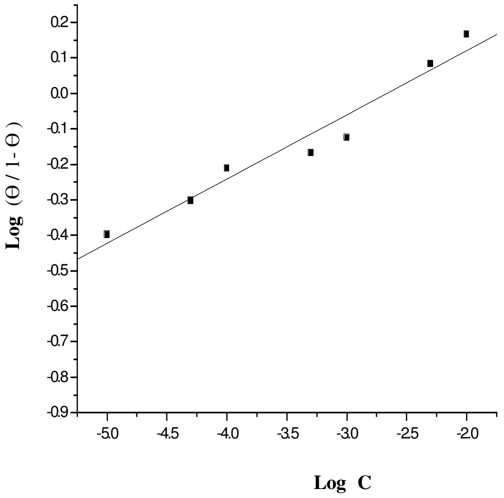
Figure 3. Show the relation between Log (Θ / C) and Log (1- Θ) at 25 ° C in case of all aldehydes.where (a: for formaldehyde b: for acetaldehyde, c: for paraldehyde, d: for benzaldehyde, e: for salicylaldehyde, f : for anisaldehyde, and g: for tolualdehyde)


Log (Θ / 1- Θ)
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-5.0
-4.5
-4.0
-3.5
-3.0
-2.5
-2.0
Log C

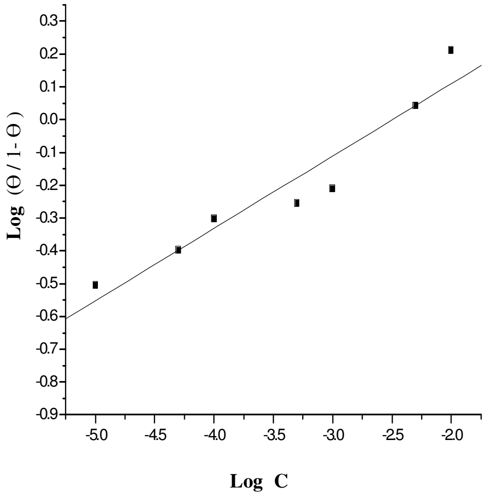
A


Log (Θ / 1- Θ)
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-5.0
-4.5
-4.0
-3.5
-3.0
-2.5
-2.0
Log C

B


Log (Θ / 1- Θ)
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-5.0
-4.5
-4.0
-3.5
-3.0
-2.5
-2.0
Log C

C


Log (Θ / 1- Θ)
0.3
0.2
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0.0
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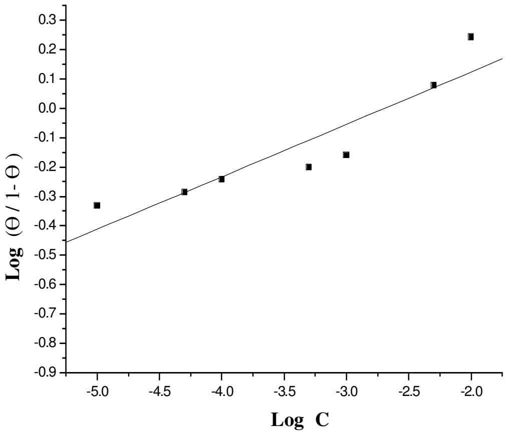
-0.7
-0.8
-0.9
-5.0
-4.5
-4.0
-3.5
-3.0
-2.5
-2.0
Log C

D


Log (Θ / 1- Θ)
0.3
0.2
0.1
0.0
-0.1
-0.2
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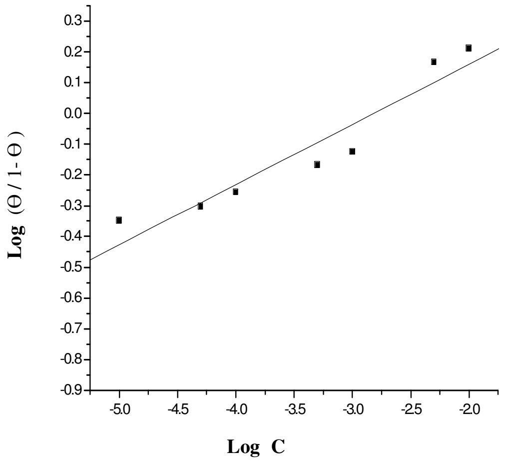
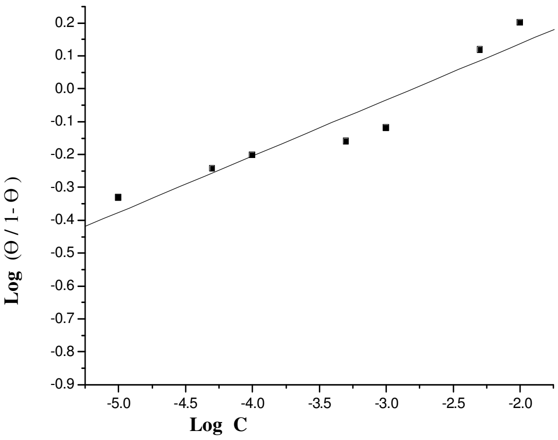
-0.6
-0.7
-0.8
-0.9
-5.0
-4.5
-4.0
-3.5
-3.0
-2.5
-2.0
Log C

E


Log (Θ / 1- Θ)
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-5.0
-4.5
-4.0
-3.5
-3.0
-2.5
-2.0
Log C

F



G

Figure 4. Show the relation between Log (Θ / 1- Θ) and Log C at 25 ° C in case of all aldehydes where (a: for formaldehyde, b: for acetaldehyde, c: for paraldehyde, d: for benzaldehyde, e: for salicylaldehyde, f : for anisaldehyde, and g: for tolualdehyde)

3.5.Effect of temperature and thermodynamic treatment of the reaction

The effect of temperature on the Cu electro polishing rate in absence and presence of organic additives was determined in the temperature ranges between (25 - 40℃) . It was observe that the electro polishing rate increases with temperature for different concentrations of organic additives. Values of Ea that have been derived from the slopes of Arrhenius [39].

It is obviously seen that the Ea values in absence and presence of organic additives are less than < 40 k J mol-1, also indicating that the diffusion processes are controlling the electropolishing reaction[40]. In this research, the thermodynamic parameters such as change in free energy ΔG*, enthalpy ΔH* and entropy ΔS* were calculated in same way as the related researches did in literature [41 – 44]. From transition state equation [45] a straight line was obtained, from which can ΔH* and ΔS* be calculated from the slope and intercept, respectively. The free energy change, ΔG*, can be represented as follows:

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad \rightarrow (8)$$

The result indicated of that the tested compounds acted as inhibitors through adsorption on copper surface, which resulted in formation of a barrier to mass and charge transfer. The values of ΔH* reflect the strong adsorption of these compounds on copper surface. The negative values of ΔS* pointed to a greater order produced during the process of activation.

This can be achieved by the formation of activated complex representing the association or fixation with consequent loss in the degree of freedom of the system during the process. ΔG* values showed limited increase with rise in the concentration of organic additives revealing that weak dependence of ΔG* on the composition of the organic additives can be attributed largely to the general linear composition between ΔH* and ΔS* for the given temperature [39,46].

3.6.1. The isokinetic relationship

Table 4. The values of E* and all thermodynamic parameters For all different concentration of the organic aldehydes.

	$C*10^{-5}$	Ea* ($K.J.mol^{-1}$)	H*Δ ($K.J.mol^{-1}$)	- Δ S * ($J.mol^{-1}. K^{-1}$)	G*Δ ($K.J.mol^{-1}$)
Formaldehyde	0	23.2	20.74	131	**59.8**
	1	30.4	27.9	109.2	**60.4**
	5	27.9	25.4	117.7	**60.5**
	10	25.9	23.4	124.7	**60.6**
	50	29.7	27.2	112.9	**60.9**
	100	30	27.5	112.4	**61.1**
	1000	39.4	29.4	108	**61.6**
Acetaldehyde	1	19.3	16.8	145.4	**60.2**
	5	20.2	17.8	142.7	**60.3**
	10	21.3	18.8	139.8	**60.5**
	50	24.1	21.6	131.3	**60.7**
	100	25	22.6	128.6	**60.9**
	1000	24.31	21.83	133.31	**61.58**
Paraldehyde	1	24.9	22.4	128.1	**60.6**
	5	23.3	20.8	134.1	**60.8**
	10	24.7	22.2	130	**60.9**
	50	23.2	20.7	135.3	**61.1**
	100	22.2	19.8	138.8	**61.15**
	1000	25.3	22.9	131.1	**61.97**
Benzaldehyde	1	21.3	18.8	139.8	**60.46**
	5	22.4	19.95	136.4	**60.62**
	10	23.7	21.24	132.7	**60.79**
	50	20.2	17.8	144.7	**60.9**
	100	19.7	17.2	146.9	**60.98**
	1000	31.4	28.9	111.4	**62.11**
Salicylaldehyde	1	14.8	12.3	162.2	**60.64**
	5	15.2	12.7	161	**60.73**
	10	14.4	11.97	163.8	**60.8**
	50	14.9	12.4	162.6	**60.89**
	100	15.4	12.9	161.2	**60.99**
	1000	24.9	22.4	133.3	**62.1**
Anisaldehyde	1	19	16.5	147.6	**60.65**
	5	18	15.5	151.6	**60.7**
	10	16.14	13.7	158.2	**60.83**
	50	18.5	16	150.8	**60.99**
	100	19.2	16.7	149.1	**61.13**
	1000	23.1	20.6	139.3	**62.14**
Tolualdehyde	1	17	14.5	154.7	**60.63**
	5	18.5	16	150.2	**60.8**
	10	18.6	16.1	150.22	**60.89**
	50	16.7	14.2	156.8	**60.96**
	100	17.3	14.8	155.3	**61.1**
	1000	**23.7**	**21.24**	**136.72**	62

Variation in the rate within series may be caused by changes in either, or both, the enthalpy or the entropy of activation the correlation of ΔH^* with ΔS^* is linear relation ship may be stated algebraically :

$$\Delta H^* = \beta \Delta S^* + \text{constant} \qquad \rightarrow (9)$$

$$\delta \Delta H^* = \beta \Delta S^* \qquad \rightarrow (10)$$

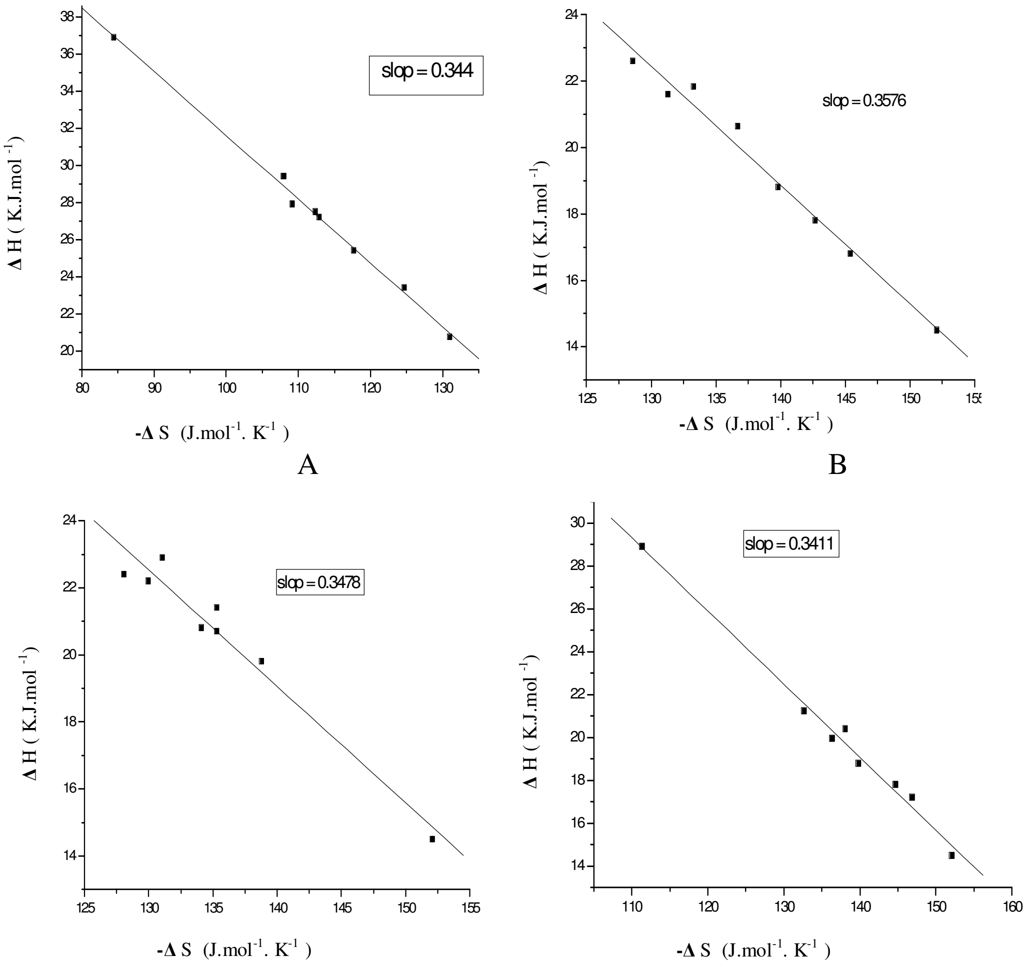
The operator, δ, concerns difference between any two reactions in the series. Substituting from the equation (11) into the familiar relationship:

$$\delta\,\Delta\,H^{*} = \delta\,\Delta\,G^{*} + T\,\delta\,\Delta\,S^{*} \qquad \rightarrow (11)$$

We obtain

$$\beta\,\delta\,\Delta\,S^{*} = \delta\,\Delta\,G^{*} + T\,\delta\,\Delta\,S^{*} \qquad \rightarrow (12)$$

Where $\delta\,\Delta\,G^{*} = \text{zero}$, $\beta = T$. In other words , the slop in a linear plot of $\Delta\,H^{*}$ versus $\Delta\,S^{*}$ is the temperature at which all reactions that conform to the line occur at the same rate. β there for known as the isokinetic temperature . The isokinetic plot of ΔH* and ΔS* for different concentration of the organic aldehydes, fig (5.a – 5.g) and table (4) was found to be linear and the isokinetic temperature (β) was computed from the slop of the plot as 344K, 357.6K, 347.8K, 341.1K, 357.1K, 384K and 355K. These values are much higher than that of the experimental temperature 298 K indicating that the rate of the reaction is enthalpy controlled [47- 49].



A

B

C

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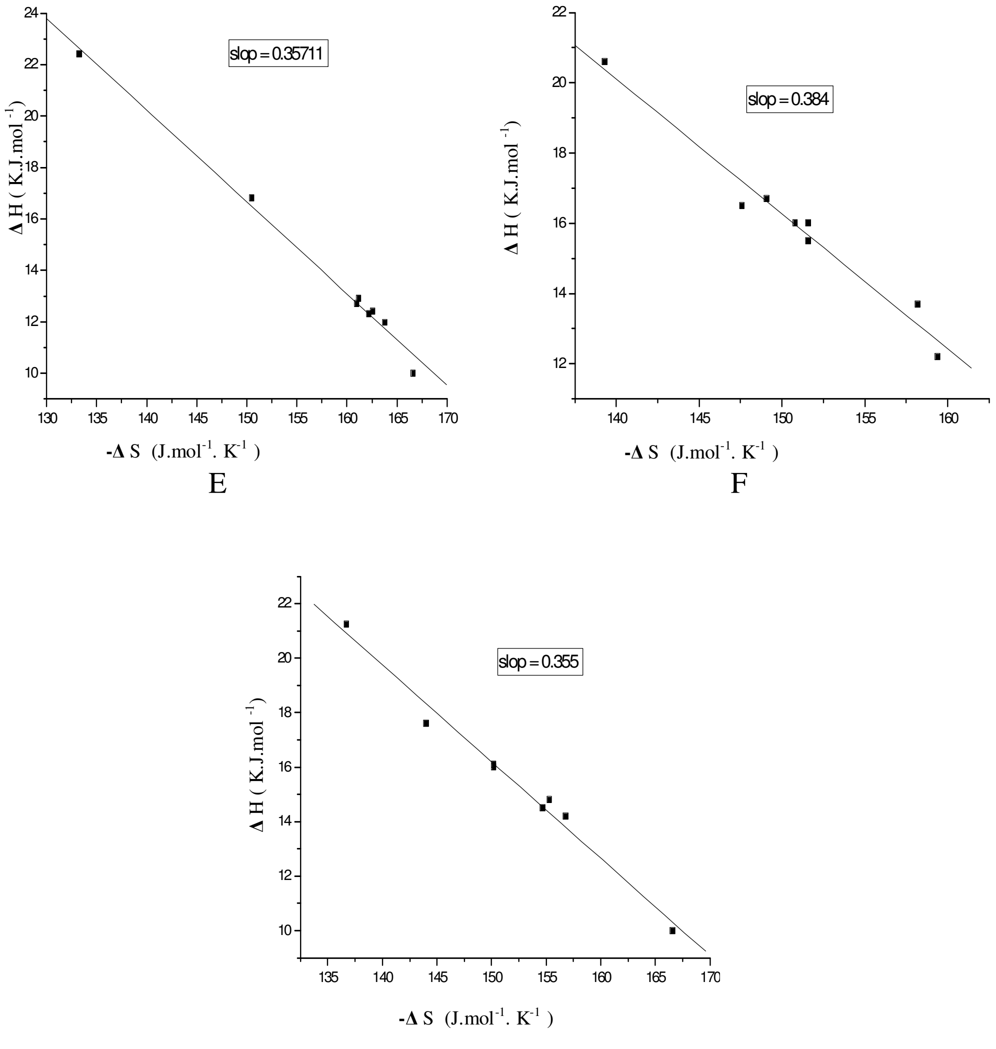


E F

G

Figure 5. Show the relation between Δ H^{*}(k j mol $^{-1}$) and -Δ S^{*}(j mol $^{-1}$ K $^{-1}$) for different concentration of organic aldehydes where (a: for formaldehyde, b: for acetaldehyde, c: for paraldehyde, d: for benzaldehyde, e: for salicylaldehyde, f : for anisaldehyde, and g: for tolualdehyde)

3.7. Effect of Stirring and Application of Dimensionless Analysis:

The effect of the speed-of rotation on the rate of electro polishing of copper in presence of organic Aldehydes additives can also be used to determine whether the electro polishing process is diffusion or chemically controlled process. If the rate of electro polishing increases by increasing the speed of rotation, then the reaction is diffusion controlled. However, if the rate of electro polishing is independent of the rotation it is likely to be a chemically controlled process.

The angular velocity to is given by:

W =2Π rpm → (13)

where r is the radial distance in cm , rpm is revolution per minute

Figure (6.a – 6.g): Show the relation between the limiting current density and the angular velocity $W^{0.7}$ at different compositions of the organic aldehydes at 25°C. Straight lines were obtained and the limiting current increases with increasing rotation, which indicates that the electro-polishing is a diffusion controlled process.

Figure (6.a – 6.g): Show the effect of the speed of rotation on the limiting current density in absence and in the presence of organic aldehydes. The data satisfy the Eisenberg equation. The 'diffusion coefficient of copper ions (D) in the different solutions was determined from the values of the limiting current densities according Eisenberg equation [50, 51].

$$I_L=0.079nFC_b\, v^{0.7} d^{-0.3} U^{0.344} D^{0.644} \qquad \rightarrow (14)$$

Where: n is the number of exchanged electrons

F is the Faraday s constant; n F is called "Faradic equivalence

C_b is the bulk concentration ($mol.cm^{-3}$).

U is the peripheral velocity = w r in cm. $rad.s^{-1}$

And where, w is the angular velocity in $rad.s^{-1}$, r is the radial distance in cm

or U= 2 Π W r in cm s^{-1}

d is the characteristic length for the rotating cylinder = the diameter of the cylinder in cm , D is the diffusion coefficient for the metal ions(Cu^{+2} ion in the present case) in $cm^2\ S^{-1}$, and v is the kinamatic viscosity in Stoke (ט= η/ρ).

Values of (D) and (ט) for all solutions under different conditions are also recorded. The diffusion coefficient, D, of Cu^{+2} ions in solutions containing organic aldehydes decreases due to the increase in the viscosity η according to Stokes-Einstein equation(52):

η/ T = constant → (15)

where: η is the viscosity of the solution ($g.cm^{-1}\ .s^{-1}$).

D is the diffusion coefficient of Cu^{2+} ($cm^{2.}\ S^{-1}$).

And T is the absolute temperature (K).

The dimensionless groups most often used in convection mass transfer were$^{(53)}$:

Sherwood number Sh = kd/D → (16)

Schmidt number Sc = v/D → (17)

Reynolds number Re= ud/v → (18)

Where k mass transfer coefficient.

D, diffusion coefficient

V, kinematics viscosity and.

d, distance from the entrance or leading edge.

Reynolds number was used in forced convection problem, while Groasshof number was used in the case of natural of dimensional analysis [53]. To obtain an overall mass transfer correlation under the present conditions by using the method of dimensional analysis it is supposed that:

$$Sh = a\, Re^{b} (Sc)^{0.33} \qquad \rightarrow (19)$$

Where: (a, b) are constants.

By plotting log {Sh /(Sc $^{0.33}$) } against log (Re), a straight line is obtained, its slope gives the constant b,. while the intercept gives the constant a, and C = 0.33 (indication forced convection).

Figure (7.a – 7.g): show the overall mass transfer correlations for all organic aldehydes used.

The equations obtained are as the following:

I- For formaldehyde : $Sh = 0.1935\ Re^{0.7176}$ → (20)

2- For acetaldehyde : $Sh = 0.2608\ Re^{0.7175}$ → (21)

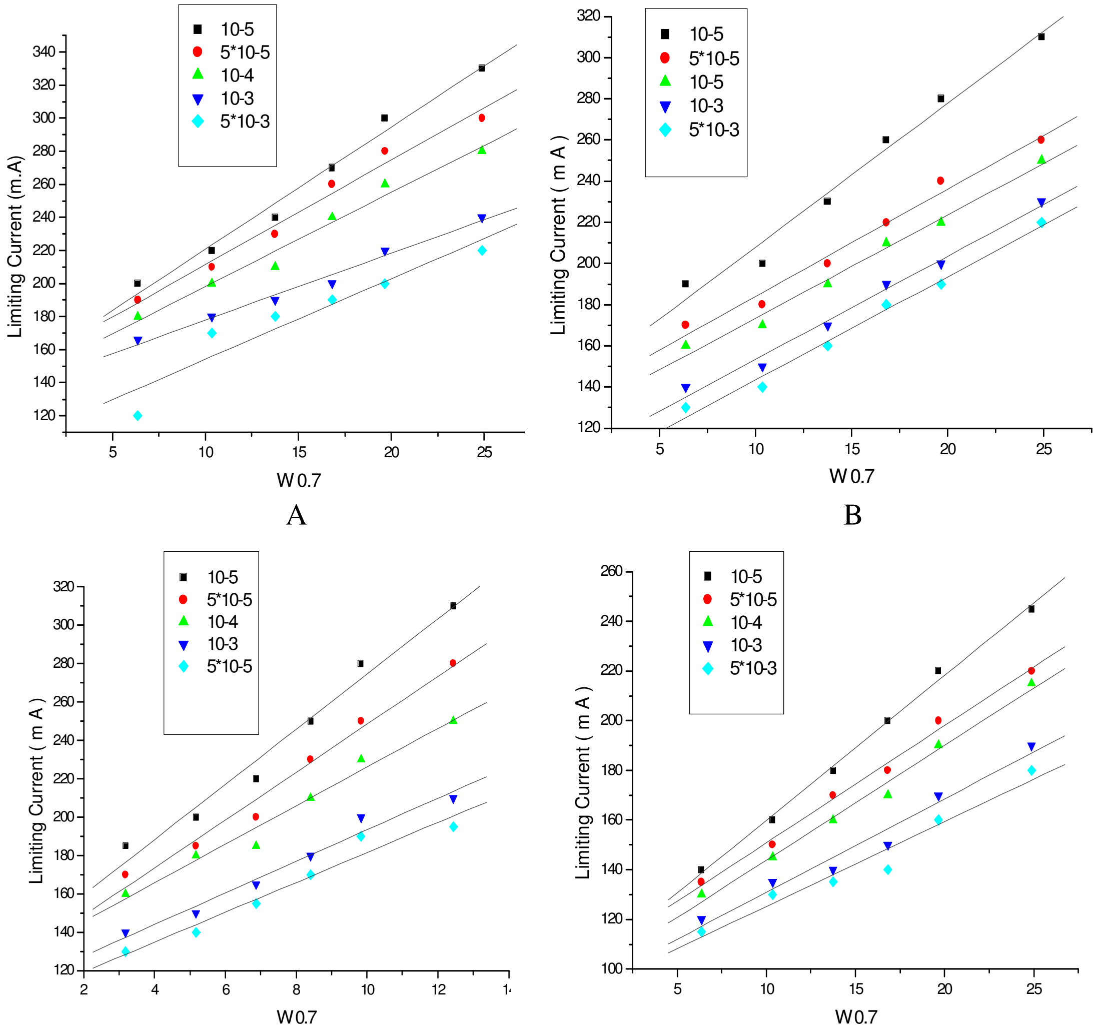
3-For paraldehyde : $Sh = 0.2541\ Re^{0.7171}$ → (22)

4-For salicyladehyde : $Sh = 0.2465\ Re^{0.7164}$ → (23)

5- For benzaldehyde : $Sh = 0.2615\ Re^{0.7202}$ → (24)

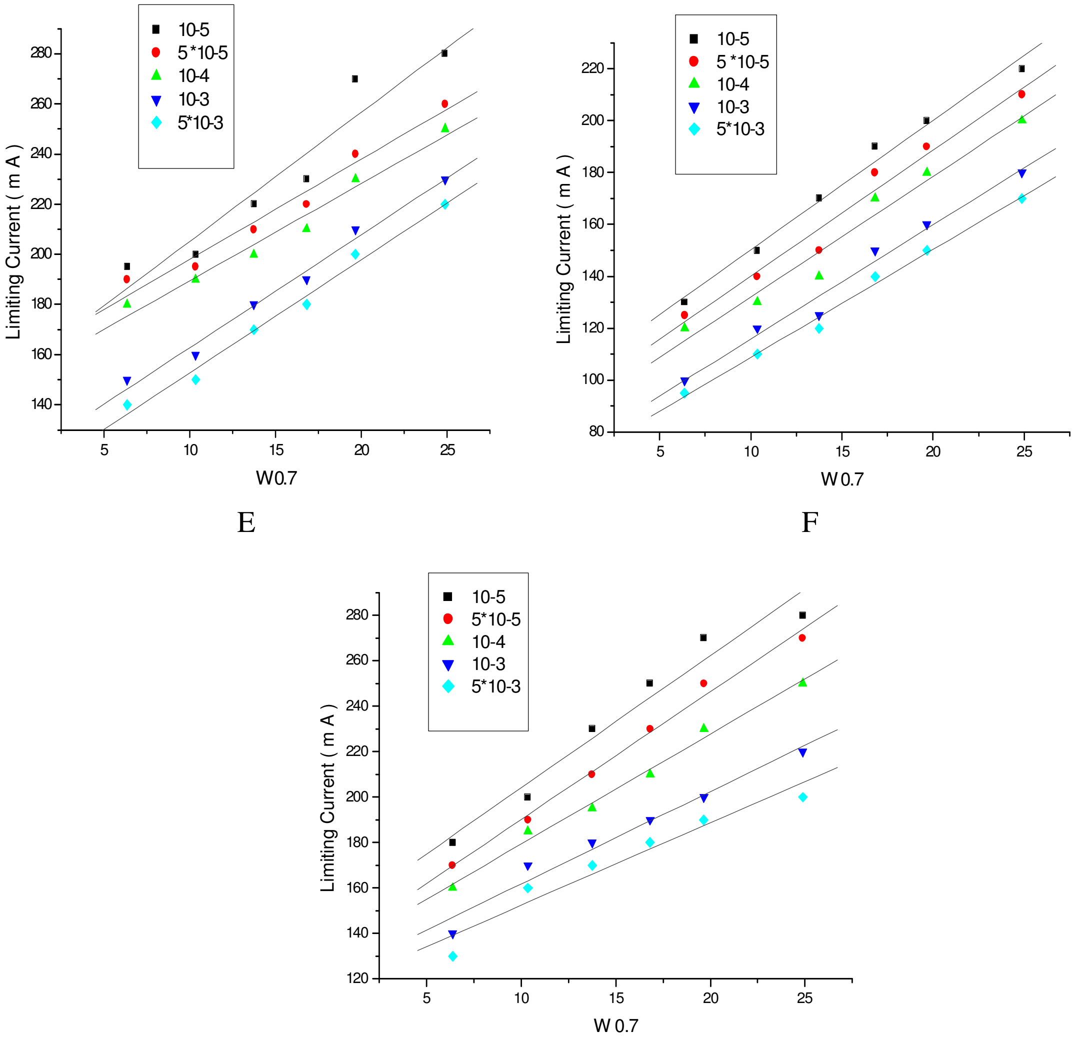
6- For anisaldehyde : $Sh = 0.2451\ Re^{0.717}$ → (25)

7- For tolualdehyde : $Sh = 0.2535\ Re^{0.7183}$ → (26)



A B

C D

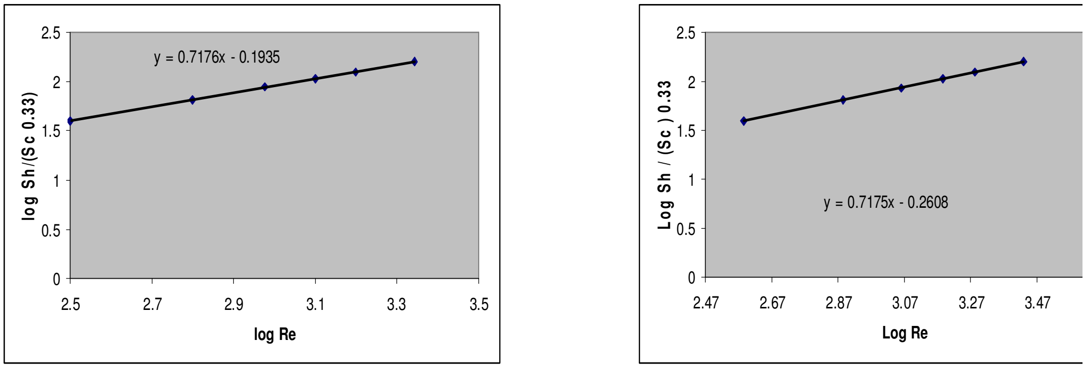


E

F

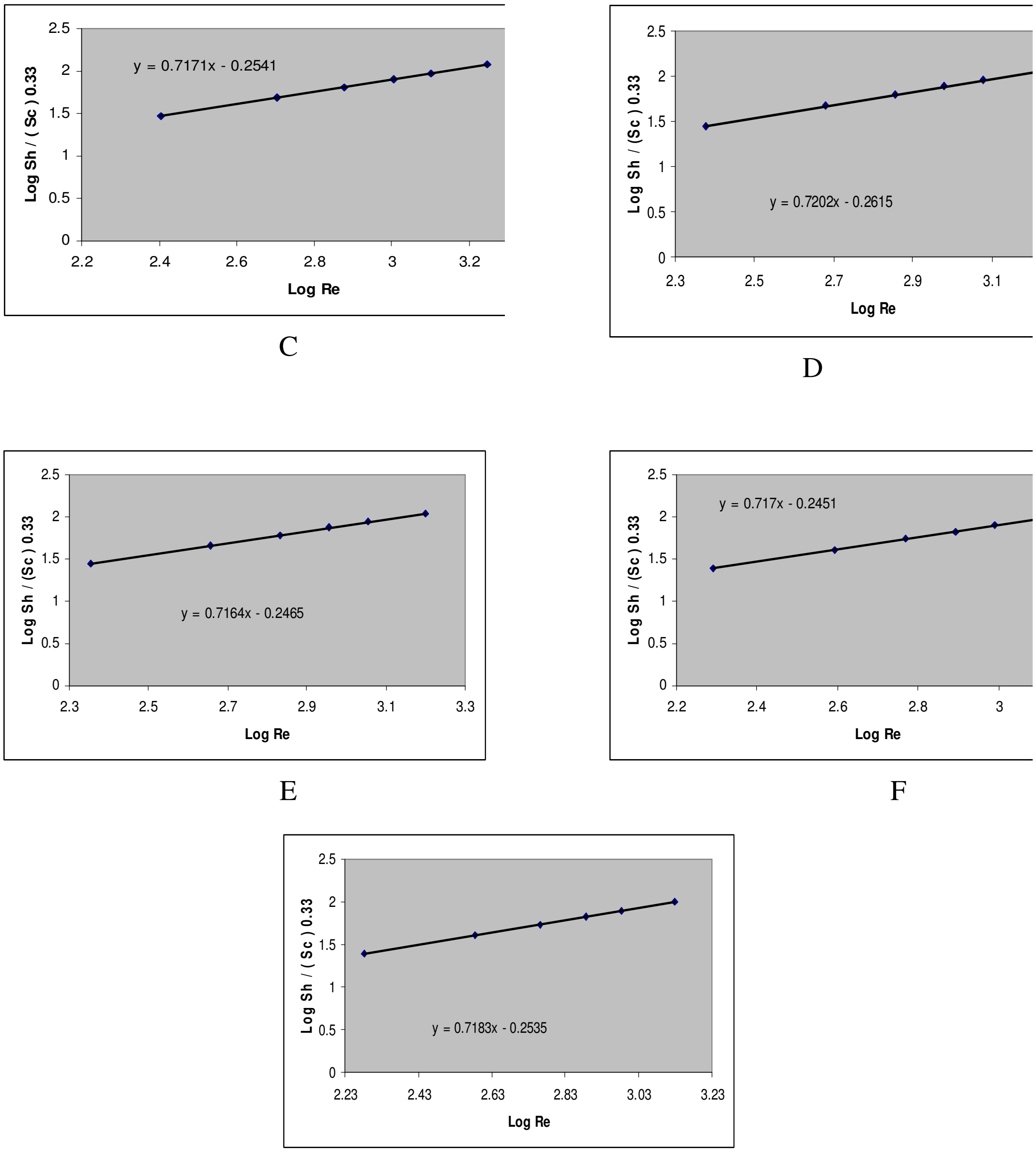
G

Figure 6. The relation between I_l and $W^{0.7}$ for aldehydes at different concentrations. Where (a: for formaldehyde, b: for acetaldehyde, c: for paraldehyde, d: for benzaldehyde, e: for salicylaldehyde, f : for anisaldehyde, and g: for tolualdehyde)



A

B



C

D

E

F

G

Figure 7. The relation between Log Re and Log Sh / (Sc) 0.33 for aldehydes at different concentrations where (a: for formaldehyde, b: for acetaldehyde, c: for paraldehyde, d: for benzaldehyde, e: for salicylaldehyde, f : for anisaldehyde, and g: for tolualdehyde)

4. CONCLUSION

Electropolishing of copper in phosphoric acid is considered as corrosion rate of copper. It is measured by measuring the limiting current .

- The rate of corrosion decreases by adding of organic aldehydes (formaldehyde, acetaldehyde, paraldehyde, benzaldehyde, salicylaldehyde, anisaldehyde, and tolualdehyde).

- The rate of inhibition ranged from 14.3 - 61.9 % depending on the type of the aldehyde and its concentration.
- The corrosion rate increases by increases the temperature and the activation energy of the reaction is less than 40 k. j. i.e. the reaction is diffusion controlled. All aldehydes verify Flory – Huggins and Kinetic Adsorption Isotherm.
- Dimensionless group were calculated which indicated that the corrosion process takes place by forced convection.

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