Int. J. Electrochem. Sci., 7 **(2012)** 5779 - 5797

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Anodic Corrosion of Copper in Presence of Organic Compounds

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Received: 14 April 2012 / *Accepted:* 8 May 2012 / *Published:* 1 July 2012

The electropolishing setting for the inhibiting the rate of anodic corrosion of copper plates in phosphoric acid were achieved using potentiodynamic studies including different factors such , plate height, conc of additives ,type of additives and temperature. The results reveal that benzoic acid derivatives have strongest inhibitive effect ranging from 11.4% to 42.8% depending on the type of additives and their concentrations. The adsorption obeys languimir, flory-Huggines and kinetic isotherm. The order of inhibition efficiency is Salicylic acid > anthranilic > m-Chlorobenzoic > m-hydroxy benzoic >Benzoic≈ P-hydroxybenzoic. Thermodynamic parameters were given

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Keywords: electropolishing , anodic corrosion , copper

1. INTRODUCTION

Due to its excellent electrical and thermal conductivities and good mechanical workability Copper is a material commonly used in heating and cooling systems. Scale and corrosion products have negative effect on heat transfer and cause decrease in the heating efficiency of equipment, which requires periodic descaling and cleaning in hydrochloric acid pickling solution are necessary.

Most corrosion inhibitors can eliminate the undesirable destructive effect and prevent metal dissolution. Copper normally doesn't displace hydrogen from acid solutions and therefore, is virtually not attacked in non-oxidizing conditions. In fact, if hydrogen bubbled through a solution of copper salts, it reduces as fast as the process occurs [1].

Copper dissolution in acidic medium has been studied by several researchers [2-7]. Corrosion inhibitors can be used to prevent copper dissolution. Benzotriazole and for instance, were reported to have been studied and found to have excellent inhibition properties in several corrosion environments [9-11]. The molecules contain nitrogen atoms and it is also usually in preventing copper, by 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 [14-22] and heterocyclic compounds with polar functional groups and conjugated double bonds have been reported to inhibit copper corrosion [23-27]. 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 [28]. 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. Among various nitrogen containing organic compounds, anilines are known to be very effective inhibitors for metal and alloys in different corrosion media.

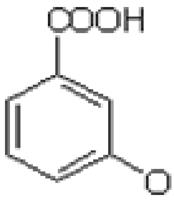
The objective of this study was to investigate the effect of some benzoic acid derivatives for the inhibition of copper corrosion in 8 M H_3PO_4 at different conditions. The rate of copper corrosion is determined by measuring the anodic limiting current.

2. PROCEDURE

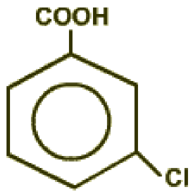
2.1. Materials

Analar BDH chemicals were used:

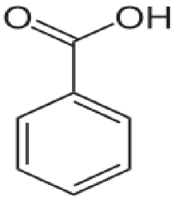
Benzoic acid, salicylic acid, m-hydroxy benzoic, p-hydroxy benzoic, Anthranilic acid and m-chlorobenzoic.



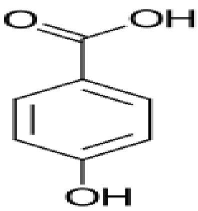
(I) m-Hydroxy Benzoic acid



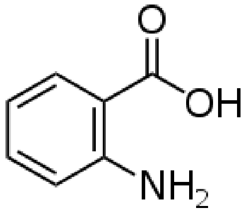
(II) m-Chlorobenzoic



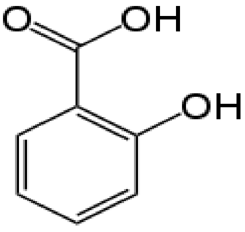
(III) Benzoic Acid



(IV)p-Hydroxy Benzoic



(V) Anthranilic Acid



(VI) Salicylic Acid

Chemically pure H_3PO_4 and double distilled water used to prepare solutions.

Electrode treatment is similar to that used by Wilke[29].

The rate of copper corrosion under different conditions is determined by measuring the limiting Current at 25°C.

Seven different concentrations of organic compound with 8M H_3PO_4 are used ranging from (0.5×10^{-4} - 5.0×10^{-4} M).

2.2. Apparatus and procedure

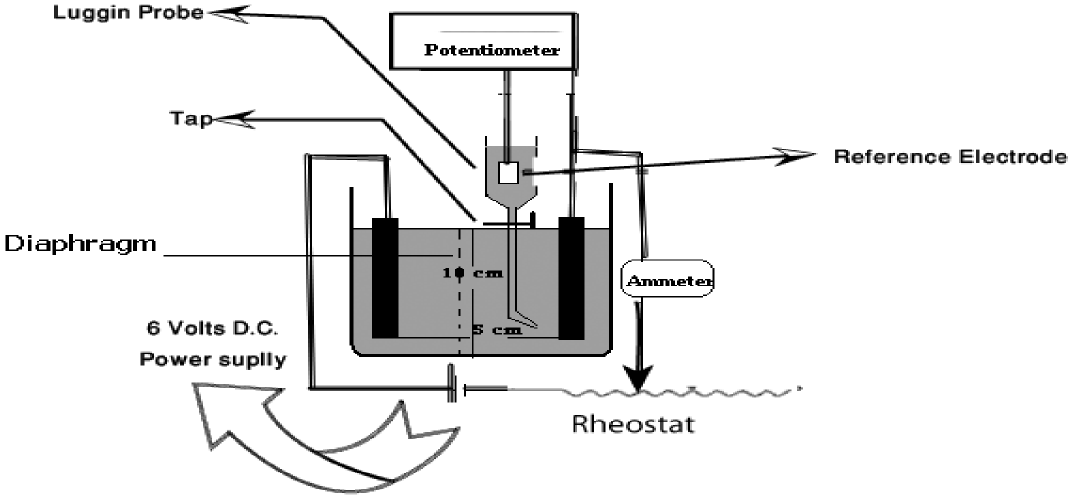


Figure 1. The electrolytic cell and the electrical circuit.

Figure1. Represents the cell and the electrical circuit that has been used in this work. The cell consisted of a rectangular plastic container having the dimensions (5.1, 5.0, 10.0 cm) with electrodes fitting the whole section. Two electrodes, each as rectangular copper plate of 10 cm height and 5 cm width, are located 5.1 cm apart. A porous poly vinyl chloride diaphragm is used to prevent the effect of H_2 bubble. The electrical circuit during this work consisted of 6 Volt D.C. power supply of 6 volt with a voltage regulator and multi-range ammeter was connected in series with cell. Potential differences were obtained by increasing the cell current stepwise and measuring the steady state anode potential against a reference electrode which consisted of a copper wire immersed in a cup of Luggin probe filling with phosphoric acid solution containing organic compound at concentration similar to that in the cell, the tip of Luggin probe is placed 0.5 - 1 mm tube from the anode surface. The Potential difference between the anode and the reference electrode is measured by high impedance potentiometer. Ortho-phosphoric acid concentration is prepared from Analar ortho-phosphoric acid and distilled water. The anode height is 2 cm. before each run the block part of the anode is insulated with poly-styrene lacquers and the active surface of the anode is polished with fine emery paper, degreased with trichloroethylene, Washed with alcohols and finally rinsed in distilled water. Electrode treatment is similar to that used by Wilke[29]. The rate of copper corrosion under different conditions is determined by measuring the limiting Current at 25°C.

2.3. Leveling process

Leveling is the principle process in electro-polishing [30-32]. It can be explained by mass transfer mechanism [30]. A cell with a diaphragm is used for this study. The use of this cell eliminates the effect of hydrogen gas evolved at the cathode from affecting the rate of mass transfer at the anode, i.e. natural of free mass transfer by convection. A cell without diaphragm is used to study the effect of hydrogen gas evolved at the cathode on the rate of mass transfer at the anode, i.e. forced convection.

The study of leveling is based on the classical current voltage curves of electro-polishing as shown in Figures 2. A typical polarogram is obtained in this study for benzoic acid in case of divided and undivided cell.

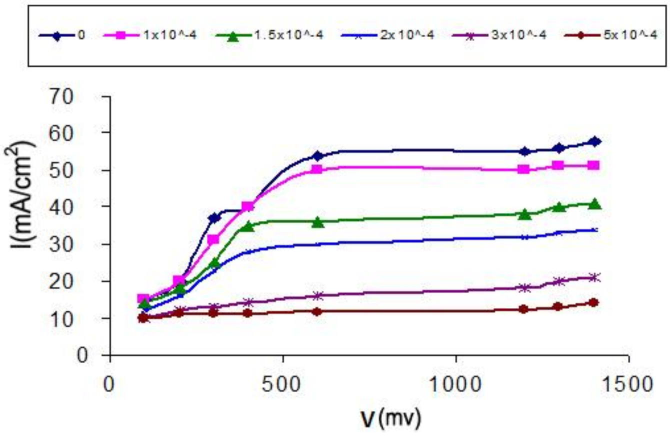


Figure 2. Current potential curves in presence and absence of benzoic acid (height 5 cm, 8 M H_3PO_4, 25°C).

The curve is 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 electro-polishing. In the first part, etching takes place and in the last part, some localized pitting occurs [31].

3. RESULTS AND DISCUSSION

3.1. Effect of electrode height on limiting current:

Figure3. Shows that, the limiting current 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 confirmed by visual observation during electro-polishing. The average limiting current density decreases with increase in the height according to the equation:

$$I_L = C/H^{0.33} \qquad (1)$$

Where C is constant, H is the height of electrode.

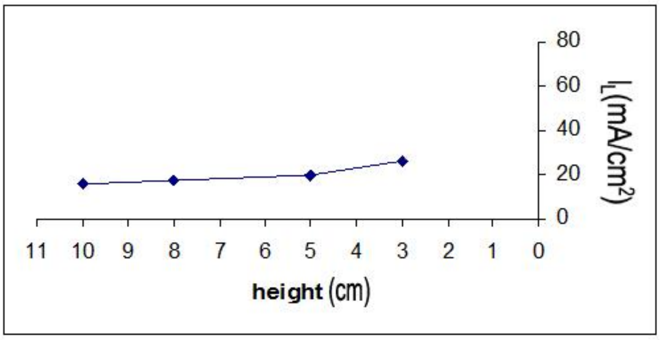


Figure 3. The relation between limiting current density and height at 25°C.

3.3. Effect of "benzoic acid derivatives" on the limiting current at anode:

Table1. Limiting current of different organic compounds (mA) at different temperatures

Organic compounds	C x 10^{-4} mol l^{-1}	Limiting current (Il) at different temperatures (mA)			
		25oC	30oC	35oC	40oC
(I)	5	350	370	390	410
	10	310	330	350	370
	15	300	310	320	330
	25	280	300	310	320
	30	250	260	270	280
	40	230	220	230	340
(II)	5	350	370	390	410
	10	300	320	340	350
	15	290	300	310	330
	25	270	280	290	300
	30	240	250	260	270
	40	220	230	240	250
(III)	5	350	370	390	410
	10	330	350	370	390
	15	310	330	350	370
	25	300	320	335	350
	30	280	290	310	330
	40	240	260	270	280
(IV)	5	350	370	390	410
	10	320	340	360	380
	15	310	325	340	360
	25	290	310	330	350
	30	270	280	290	300
	40	240	250	260	270
(V)	5	350	370	390	410
	10	290	310	330	350
	15	260	275	290	310
	25	240	245	260	275
	30	220	230	240	250
	40	210	220	230	240
(VI)	5	350	370	390	410
	10	270	280	300	320
	15	250	270	280	290
	25	240	250	260	270
	30	200	220	230	240
	40	200	210	220	230

The observed limiting current, represents the rate of anodic copper metal dissolution in Ortho-phosphoric acid at 25°C. It was found that, the limiting current decreased with increasing the concentration of organic compound additives. Table (1) shows the dependence of limiting current on the bulk concentration in absence and in presence of organic compound additives. It was found that, the limiting current decreased with increasing the concentration of organic compound. From the practical point of view, we infer that the results indicating decrease in I_l by organic test-additives could be extended to suggest similar inhibition of corrosion rate in 8 M H_3PO_4 by the type of organic additives under study. If the limiting current in absence of organic compound (I), and in the presence of organic compound is I_L, the percentage of inhibition can be calculated from the following equation:

$$\%\text{Inhibition} = \frac{\mathbf{I}-\mathbf{I}l}{\mathbf{I}l} \qquad (2)$$

The percent inhibition that caused by organic compound ranged from 11.4 % to 42.2 % depending on the type of organic compounds. These results in agreement with the finding of other workers who used same range of concentration for other anode geometries [32-36] . The decrease in the limiting current with increasing the concentration of benzoic acid derivatives could be attributed to:

(a) The decreasing solubility of dissolved copper phosphate in Ortho-phosphoric acid, (which is responsible for the limiting current), with increasing H_3PO_4 concentration.

(b) The increasing viscosity of the test solution with increasing H_3PO_4 concentration with consequent decrease in the diffusivity of' Cu^{2+} according to stokes-Einstein equation [37] as reported elsewhere.

Also the increase in solution viscosity with increasing phosphoric acid concentration could lead to an increase in the diffusion layer thickness which represents the resistance to the rate of mass transfer of Cu^{2+} from anode surface to the bulk solution.

The viscosity of organic additives water- H_3PO_4 mixture was observed higher than water- H_3PO_4 mixture; this possibly resulted in decrease in diffusivity of Cu^{2+}. Also, the solubility of copper phosphate in test solutions with organic additives was lower than water phosphoric acid mixture, so the saturation of solution could be attained quickly, this decreasing the limiting current.

3.4. Adsorption isotherm

It is generally assumed that the adsorption isotherm of the inhibitor at the metal solution interface is the First step to be considered for mechanism of organic compounds in aggressive acid media. Four types of adsorption may take place in the inhibiting phenomena involving organic molecules at the metal-solution interface, namely:

a) Electrostatic attraction between charged molecules and the charged metal.
b) Interaction of uncharged electron pairs in the molecules with the metal.
c) Interaction of electron with metal.
d) A combination of the above [38].

Chemisorptions involve sharing or charge transfer from the inhibitor molecule to the surface in order to form coordinate bond. In fact, electron transfer is typical for transition metals having vacant low energy electron orbital.

Concerning inhibitors, electron transfer can be expected with compounds having relatively loosely bound electron. This situation may arise because of the presence (in the adsorbed inhibitor) of multiple bonds or aromatic rings with a π character [39-57].

The inhibition efficiency of homogenous series of organic substances, differing only in the hetero atom, is usually in the following sequence:

P>Se>S>N>O

The degree of surface coverage (θ) at constant temperature was determined from following expression as reported elsewhere [58].

$$\theta = \frac{\mathbf{I}-\mathbf{I}_{l}}{\mathbf{I}_{l}} \qquad (5)$$

Langmuir adsorption isotherm is donated by

$$KC = \theta/1 - \theta \qquad (6)$$

Where K is the equilibrium constant of adsorption process, C is the concentration and θ is the Surface coverage.

From Eq. 5 a plot of (θ /1- θ) against C should yield a straight line has slope unite which verify langmiur adsorption isotherm see Fig (4-9), also Figure (4-9) Shows adsorption isotherm for all compounds, in 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 obtained with slope X and intercept log xK.

Table 2. The relation between C ($mol.l^{-1}$) and % inhibition at 25°C

	% inhibition at 25°C					
	Organic compounds					
C x 10^4 $mol.l^{-1}$	I	II	III	IV	V	VI
10	11.40	14.20	51.70	8.60	17.40	2.00
15	14.20	17.40	11.20	11.40	25.70	28.57
25	20.20	22.85	14.20	14.20	31.40	31.40
30	25.57	31.40	20.00	22.85	37.10	40.00
40	34.20	37.14	31.40	31.40	40.00	42.80

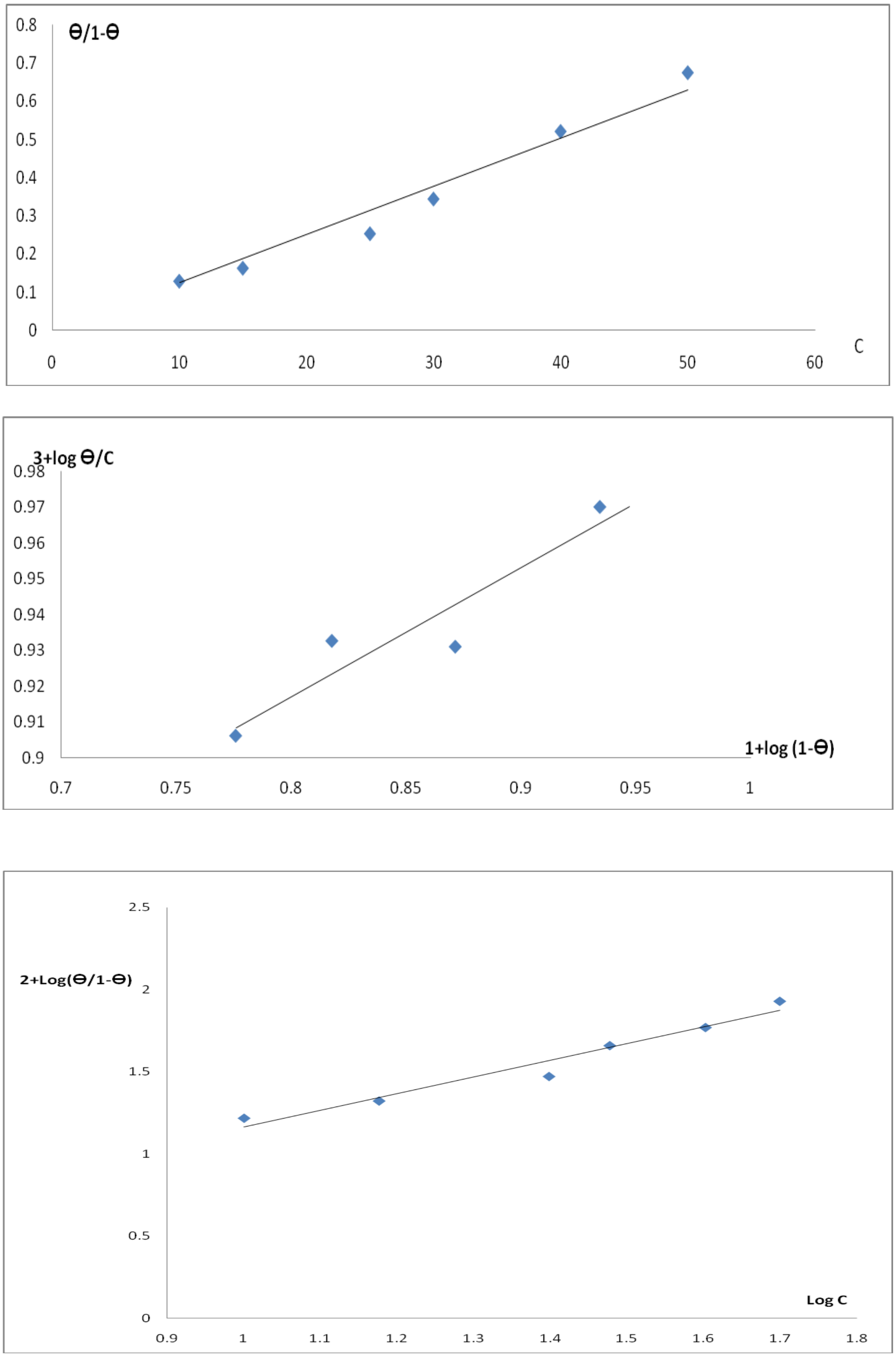


Figure 4. Adsorption isotherm for compound I; i) Langmuir ii) Flory-Huggins iii) Kinetic isotherm

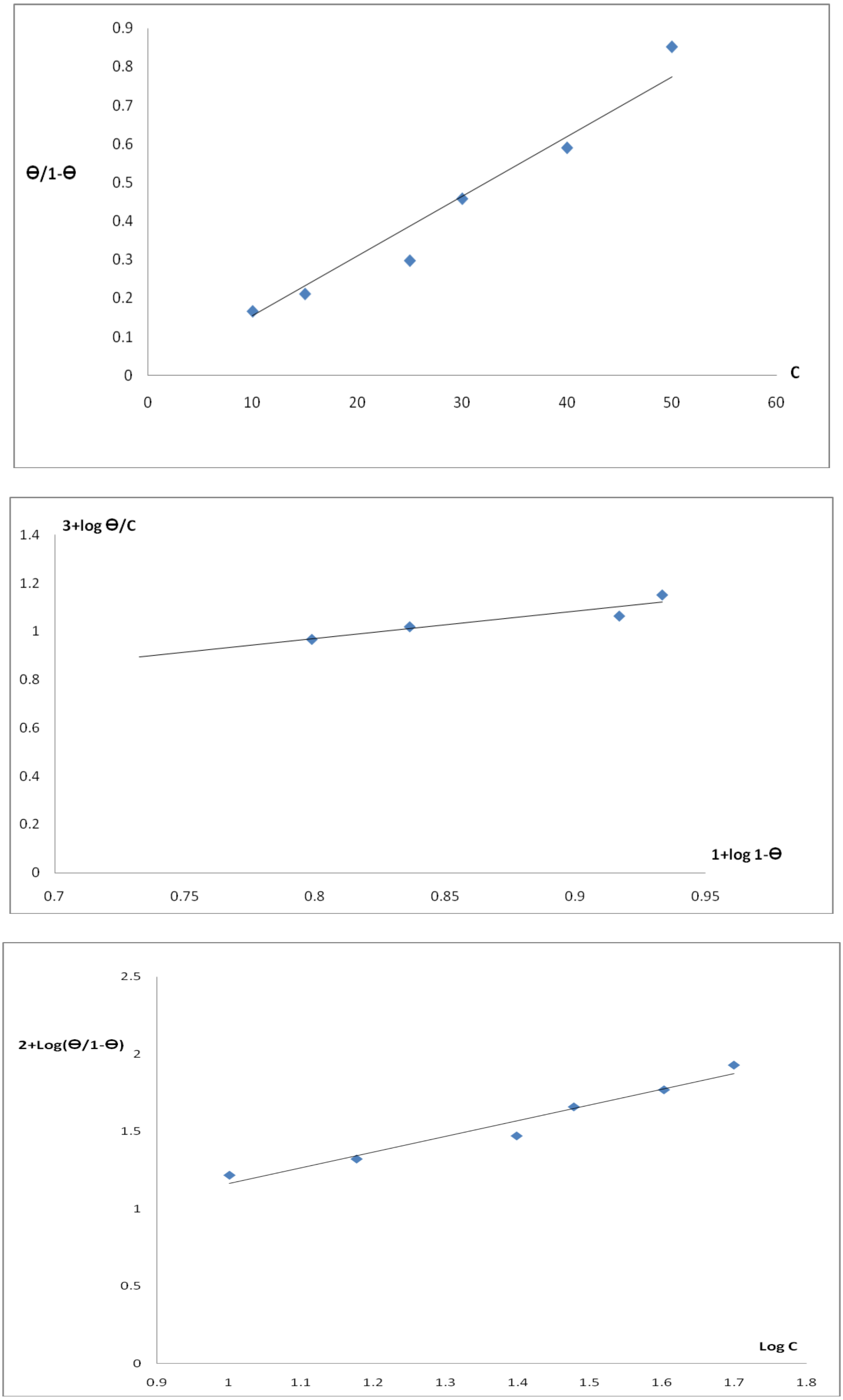


Figure 5. Adsorption isotherm for compound II; i) Langmuir ii) Flory-Huggins iii) Kinetic isotherm

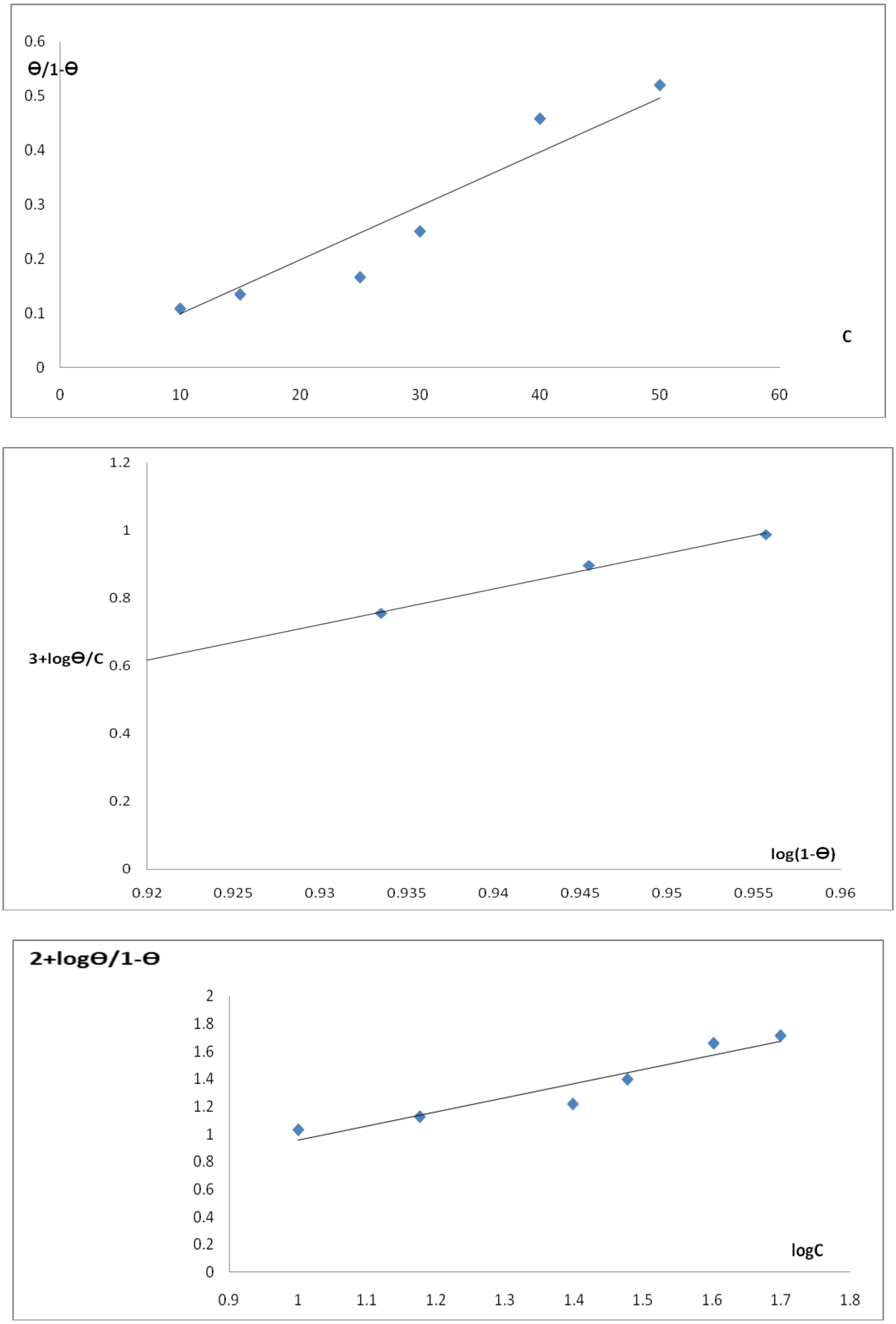


Figure 6. Adsorption isotherm for compound III; i) Langmuir ii) flory-Huggins iii)Kinetic isotherm

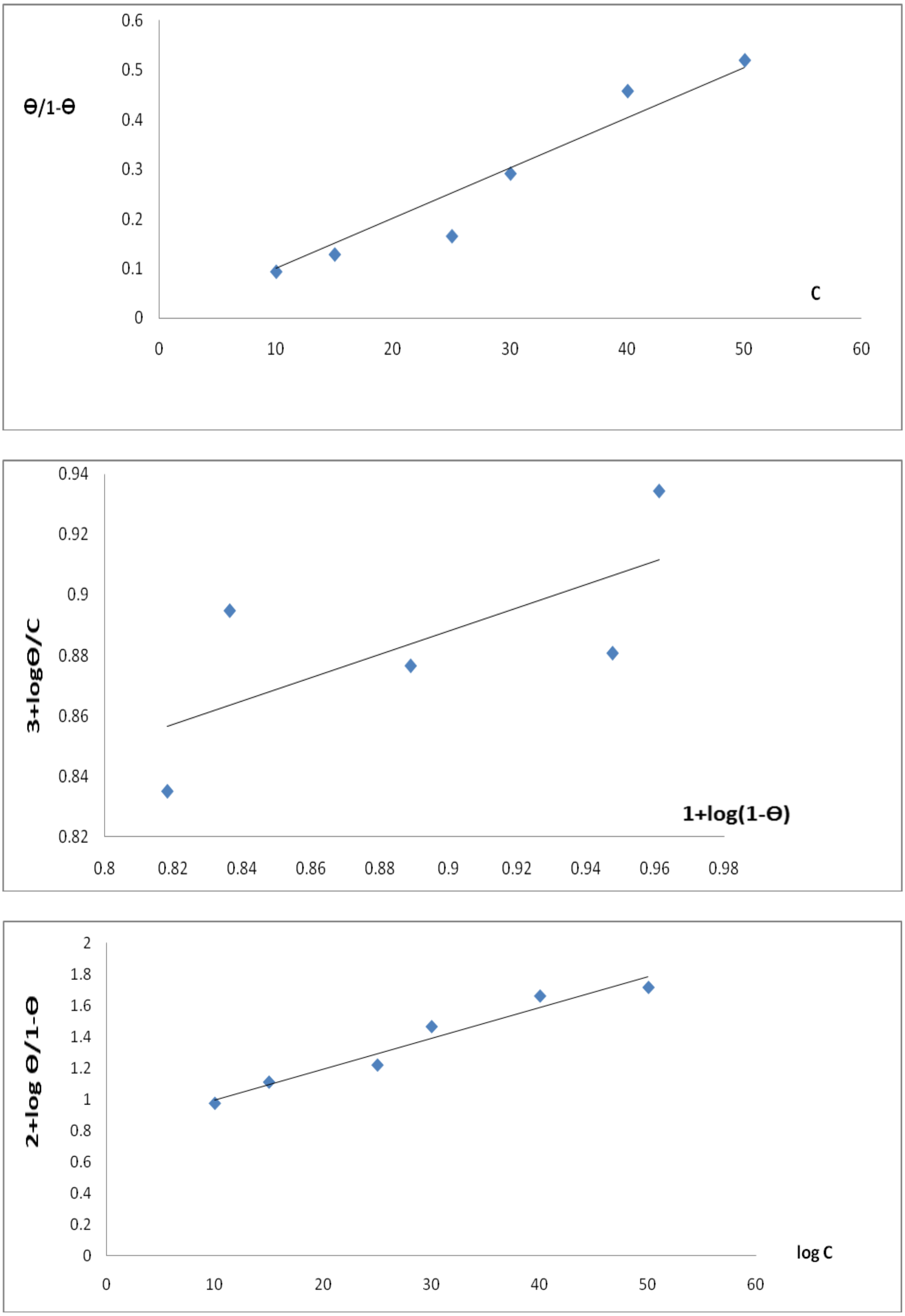


Figure 7. Adsorption isotherm for compound IV; i) Langmuir ii) flory-Huggins iii) Kinetic isotherm

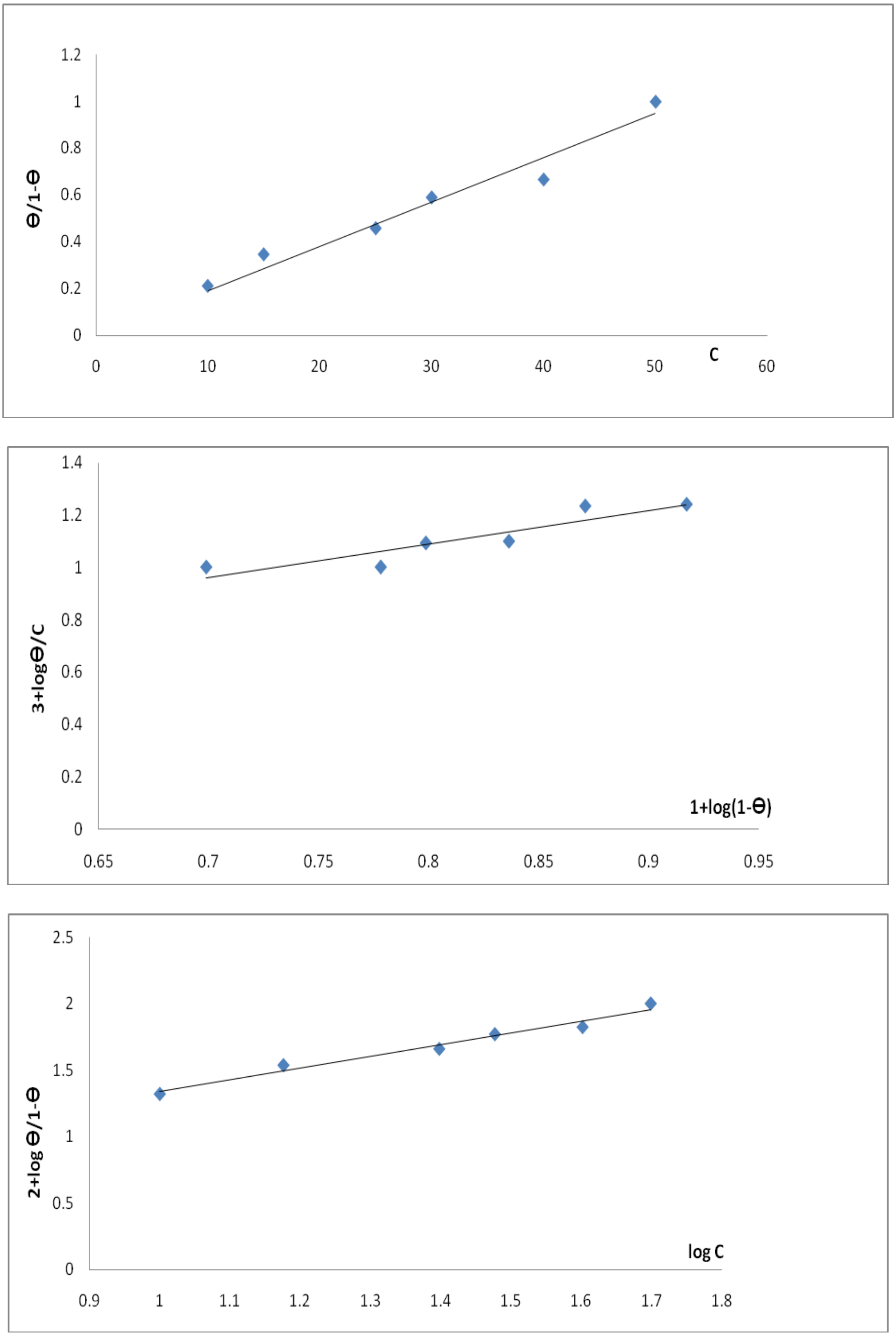


Figure 8. Adsorption isotherm for compound V; i) Langmuir ii) Flory-Huggins iii) Kinetic isotherm

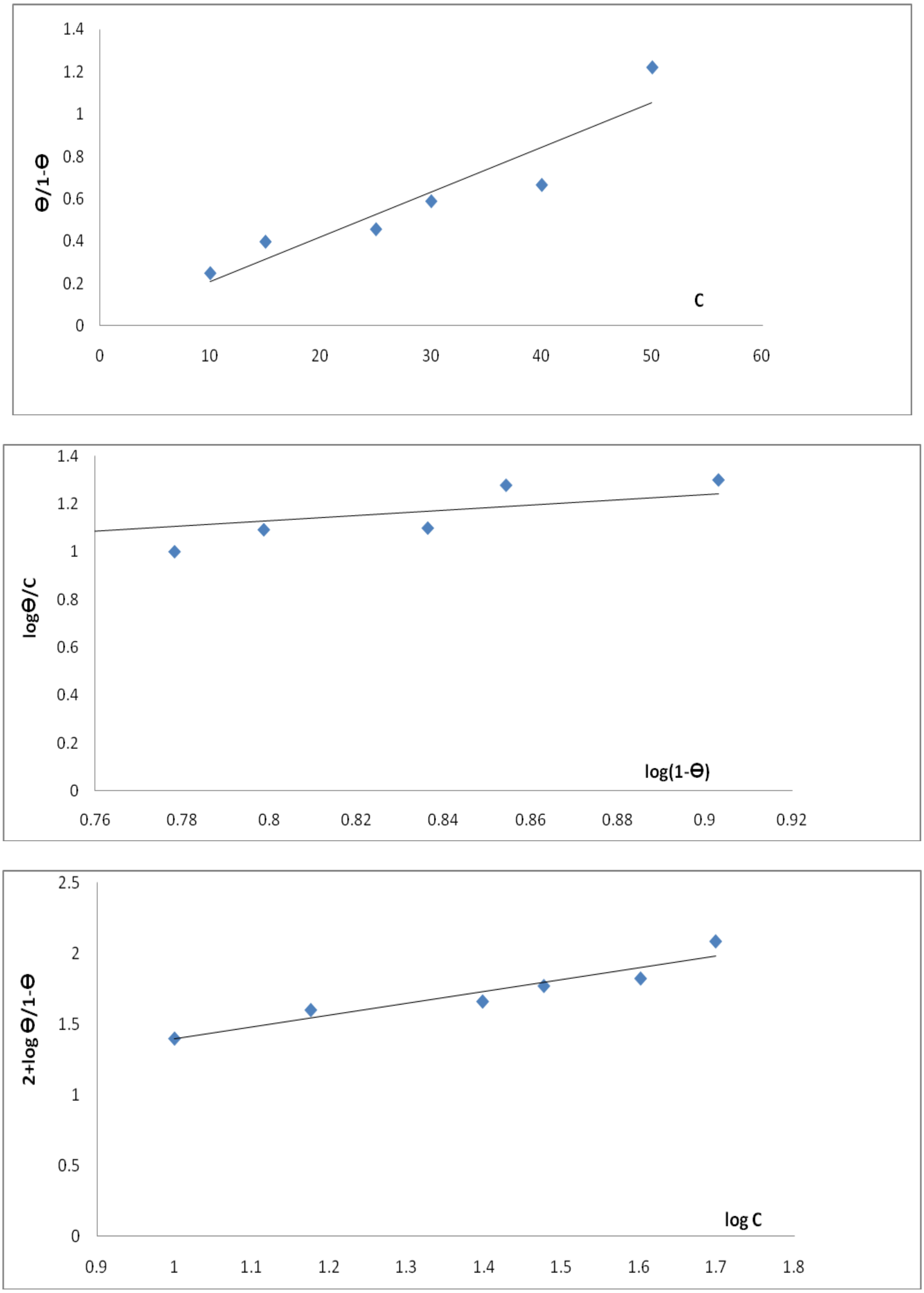


Figure 9. Adsorption isotherm for compound VI; i) Langmuir ii) Flory-Huggins iii) Kinetic isotherm

The experimental data fits the Flory-Huggins adsorption isotherm which represented by:

$$\log \theta / C = \log xk + x \log (l- \theta) \qquad (7)$$

Where x is the number of' water molecules replaced by one molecule of the inhibitor . The adsorption of' inhibitors at metal-solution interface might be due to the formation of either electrostatic or covalent bonding between the adsorbate and the metal surface atoms [59].

The kinetic adsorption isotherm may be written in the form [60].

$$\log \theta /1- \theta =\log k'+ y \log C \qquad (8)$$

Where y is the number of inhibitor molecules that 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[60]. Also figure (4-9) shows linear relation of the inhibitor molecules between log θ and log (1- θ) at 25°C, and the calculated values of $1/y$ and K are given in table (3).

Table3. Gives calculated value of free energy of adsorption ($KJ.mol^{-1}$) of H_3PO_4 in presence of different carboxylic acids additives to Flory-Huggins and Kinetic isotherm.

Compound	Flory-Huggins			Kinetic isotherm			
	X	K	-Δ G $KJmol^{-1}$	Y	1/Y	K	-Δ G $KJmol^{-1}$
I	0.359	$2.670x 10^{-2}$	0.98	1.054	0.950	$1.00x 10^{-2}$	1.46
II	1.131	$1.390x10^{-2}$	0.64	1.014	0.986	$1.40x 10^{-2}$	0.63
III	10.51	$0.332x10^{-2}$	1.50	1.024	0.976	$8.57x 10^{-2}$	3.87
IV	0.387	$2.180x 10^{-2}$	0.47	1.000	1.000	$1.58x 10^{-2}$	0.37
V	1.277	$2.213x 10^{-2}$	0.51	0.885	1.130	$2.80x 10^{-2}$	1.09
VI	2.440	$1.480x 10^{-2}$	0.48	1.557	0.640	$2.88x 10^{-2}$	1.16

The values of $1/y$ depend on the type of acid derivatives. From Table 3 it is obvious that, the value of.' $1/y$ for compounds II, III, IV is approximately one. Suggesting that, the compound is attached to one active site per inhibitor molecule.

For other inhibitors 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 calculated from the following equation:

$$\Delta G_{ads} = - RT \text{ In } (55.5K) \qquad (9)$$

The value 55.5 is the concentration of water in the Solution mol 1^{-1}.

The values of Δ G_{ads} are given in Table 3. In all cases the Δ G_{ads} values were negative and lay in the range of 0.3-3.87 kJ mol^{-1}. The most efficient inhibitor showed the most negative value. This suggested that, they were strongly adsorbed on the metal surface. The negative values of Δ G_{ads} indicate that, the spontaneous adsorption of the inhibitor. It's found that, the Δ G_{ads} values were more positive than - 40 kJ mol^{-1}indicating that the inhibitors were physically adsorbed on the metal surface. Similar results also been reported by Talati et.al[61].

3.5. Structure effect of organic additives:

It is known that many additives are usually capable of adsorption on the anodic substrate and even might get trapped within metal/solution interference. This may be due to either the need for the electron transfer to occur through the adsorbed layer or to a complex formation at the electrode surface. A complexation of the metal cation in the solution is also proposed .in many cases the use of additives is still done in an empirical way. Indeed, the number of such organic or non-organic substances is very large. Moreover, their action could be different in function of the substrate, the ion to reduce and the electrolytic conditions. For example, additive re-orientation on the electrode surface has been observed depending, on the surface coverage or as a function of pH.

In the case of copper, a very great number of researches have already been undertaken, because of the industrial interest. A complex in solution between benzoic acid derivatives and Cu^{+} or Cu^{2+} cation is formed as a result of transport of copper ions from the interface to the bulk and the work for the discharge of copper complex ion increases.

The inhibition action of acids depends on the number of functional groups taking part in the absorption of the inhibitor molecule and their electron charge density, molecular size, mode of interaction, heats of hydrogenation and complexing ability of additives. The order of inhibition efficiency for the monocarboxylic acids is: salicylic acid > anthranilic acid > m-chlorobenzoic acid > m-hydroxybenzoic acid > benzoic acid > p-hydroxybenzoic acid.

The presence of a substituent in ortho-, meta- or para positions affects the inhibition efficiency of these benzoic acids greatly especially the o-substituent as this provides better surface coverage by neighboring adsorption centers anchored to the copper surface. This may be imagined from the skeletal structure. Vertical orientation is more likely than the planar in view of the significant substituent effect on the inhibition ability. Salicylic acid is better restrainer is more strongly adsorbed than anthranilic because oxygen is a stronger Lewis base than nitrogen. Moreover, a probably copper complex could be formed and itegrated in the oxide layer, thus reinforcing it.

m-Chloro-benzoic acid has nearly the same efficiency as anthranilic acid and this may be due to the larger size (molecular weight) of the molecule. It is stronger inhibitor than them-OH one. Easy formation of a carboxylate complex accounts for its increased efficiency. m-Chlorobenzoic acid is stronger than them-hydroxybenzoic acid and the unsubstituted benzoic acid which comes last as a corrosion inhibitor in this group. The situation is quite different for the p-hydroxybenzoic acid which acts as a corrosion less inhibitor. Here, the efficiency is differently influenced by the p-hydroxy substituent. The electron attracting character of the carboxylic group is complemented by the electron releasing ability of the p-OH group. Most substituent in p-position undergo resonance with the reaction center.

3.6. Effect of temperatures

Table 4. The thermodynamic parameters for electropolishing of copper in presence of organic substance at 25^{o}C

Organic substances	Cx10^{-4} mol l^{-1}	Thermodynamic parameters			
		Ea KJ.mol^{-1}	ΔH^* KJ.mol^{-1}	$-\Delta S^*$ J.mol^{-1} K^{-1}	ΔG^* KJ.mol^{-1}
(I)	5	8194±52	5715±52	177	58598±103
	10	9165±76	6685±76	175	58799±150
	15	4934±2	2456±2	189	58881±4
	25	6745±928	3390±10	188	59027±1834
	30	5869±10	3390±10	188	59333±19
	40	18679±11242	16200±11242	146±37	59650±41
(II)	5	8194±52	5715±52	177	58498±103
	10	8141±846	5662±846	178±3	58866±1671
	15	6517±841	4038±841	184±3	58981±662
	25	5459±6	2981±6	188	59143±13
	30	6104±14	3625±14	187	59435±28
	40	6618±21	4139±21	186	59650±41
(III)	5	8194±52	5715±52	177	58644±124
	10	8650±63	6171±63	176	58799±151
	15	9165±76	6686±76	175	58870±918
	25	7905±76	5426±465	179	59076±1697
	30	8680±859	6201±859	177±3	59405±2151
	40	7794±1089	5315±1088	181±4	58644±124
(IV)	5	8194±52	3625±14	177	58598±103
	10	8899±70	6420±69	175	58720±137
	15	7661±358	5182±358	180±1	58807±707
	25	9737±92	7259±92	173	58963±183
	30	5459±6	2981±6	188	59143±13
	40	6104±14	5715±52	187	59435±28
(V)	5	8194±52	5715±52	177	58498±103
	10	9737±92	7258±92	173	58963±182
	15	7509±500	5030±500	182	59227±989
	25	7252±1053	4773±1053	183	59765±51
	30	6618±21	4139±21	186	59650±41
	40	6914±26	4435±26	186	59464±2081
(VI)	5	8194±52	5715±52	177	58498±103
	10	8971±884	6492±884	177	59167±1747
	15	7498±1044	5019±1044	182	59305±2062
	25	6618±21	4139±21	187	59650±41
	30	9208±1314	6730±1314	178	59851±2597
	40	9909±997	7430±997	176±3	59897±1970

The effect of temperature on the Cu electropolishing rate in absence and presence of all benzoic acid additives was determined in the temperature ranges between (25 - 40ºC) and illustrated in Table 1. It was observe that the corrosion rate increases with temperature for different concentrations of organic additives. Values of E_a that have been derived from the slopes of Arrhenius plots [39] are given in Table 4.

It is obviously seen that the E_a values in absence and presence of organic additives are less than < 28 k J mol^{-1}, also indicating that the diffusion processes are controlling the electropolishing reaction [40]. In this reach, 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]. Table 4 summarizes the values of these thermodynamic properties. From transition state equation [42] 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:

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad (10)$$

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 [64-65].

4. CONCLUSION

1-The rate of electropolishing of anodic dissolution is measured by measuring limiting current.

2-The electrode process on copper in phosphoric acid where finding to depend on benzoic acid derivatives as well as concentration and temperature.

3-It is found that the rate of anodic corrosion decreases in presence of benzoic acid derivatives and increases by temperature

3-Those compounds verifying Langmuir, Flory-Huggins, kinetic isotherm

4-Activation energy proves that reaction is diffusion controlled.

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