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EFFECT OF 1-BENZOYL-4-PHENYL-3-THIOSEMICARBAZIDE DERIVATIVES ON THE CORROSION INHIBITION OF COPPER IN NITRIC ACID

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ABSTRACT

The effect of 1-benzoyl-4-phenyl-3-thiosemicarbazide derivatives as inhibitors for the corrosion of copper in 3M HNO_3 acid has been studied using weight loss, galvanostatic polarization and C.V. techniques. The inhibition efficiency calculated from the three measurements are in good agreement and depends on the type and concentration of inhibitor. Application of Hammett equation supported the obtained results. The effect of temperature was studied over a temperature range 30-60°C using weight loss technique. The inhibitors appear to function through general adsorption following the Langmuir adsorption isotherm. Quantum calculations were performed to give a more general picture of the nature of corrosion inhibition.

Keywords: Copper, acid corrosion, Galvanostatic polarization, weight loss, 1-Benzoyl-4-Phenyl-3-thiosemicarbazide.

A large volume of literature exists on the use of organic compounds containing nitrogen, oxygen and/or sulphur functional groups, acting as inhibitors for the aqueous corrosion of metals such as aluminium, iron and copper[1-5]. The protection of metals against corrosion can be achieved either with inhibitors or with passivating agents[6]. The use of 2,4 dinitrophenylhydrazine as inhibitor for the corrosion of copper in sulphuric acid was studied by Siddagappo et al.[7] using weight loss and corrosion potential techniques. The inhibition effect of 3-benzamidorhodanine p- and o- substituted phenyl derivatives for copper corrosion in 3M HNO_3 acid solution was studied[8] by weight loss and galvanostatic polarization techniques. The rates of anodic dissolution of copper as well as hydrogen evolution in H_2SO_4 containing benzotriazoles were also examined[9] Inhibition effect of 1,5-diphenylcarbazide on the corrosion of copper in chloroacetic acids was also studied[10].

The aim of this paper is to study the influence of substituents of the 1-benzoyl-4-phenyl-3-thiosemicarbazide on the inhibition of copper corrosion.

2. EXPERIMENTAL PROCEDURE

Thiosemicarbazide derivatives were prepared[11,12] by slowly adding an appropriate volume of phenylisothiocyanate to the acid hydrazide solution in absolute ethanol. The thiosemicarbazide derivatives used were:
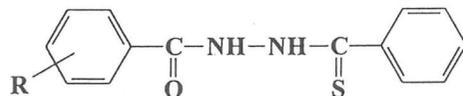
R = p-Methoxy   (a)   R = p-Methyl (b)
  = o-Methyl (c)   = o-Hydroxy(d)
  = o-Chloro (e)   = Hydrogen (f)
  = p-Nitro   (g)

These thiosemicarbazide derivatives are easily prepared from cheeply materials and are not toxic.

Copper test pieces of 99.9% purity (BDH grade) were used. All chemicals used were of A.R grade quality. Preparation of solutions, 3M HNO₃ and copper specimens (2x2x0.1 cm), for weight-loss measurements were performed as previously described[13]. The average weight loss at a certain time for each set of three samples was taken. Inhibition efficiencies (P) of additives were calculated as:

$$\%P = \frac{Wt.loss_{pure} - Wt.loss_{inh.}}{Wt.loss_{pure}} \times 100 \qquad (1)$$

For galvanostatic measurements, working electrodes were constructed from copper wire of 0.5 mm diam. and 1 cm long. Anodic and cathodic polarization experiments were carried out under unstirred conditions. Galvanostatic conditions were maintained using a potentiostat-galvanostat (Amel Model 549). A saturated calomel electrode and platinum wire were used as reference and auxiliary electrodes, respectively. the potentials were recorded using a PM 2517X multimeter. All experiments were carried out at 30±0.1°C. Polarization curves were obtained in absence and presence of the various inhibitors.

The percentage inhibition efficiency (P_I) is given by:

$$\%P_I = \frac{I - I`}{I} \times 100 \qquad (2)$$

where I and I` are the corrosion currents in absence and presence of the investigated compounds, respectively. The corrosion current density was obtained by extrapolating

the Tafel lines to the experimentally measured free corrosion potential. The free corrosion potential $E_{corr.}$ is defined as the potential at zero current density. the degree of surface coverage by the adsorbed molecules was calculated from the equation:

$$\theta = 1 - \frac{I`}{I} \qquad (3)$$

3. RESULTS AND DISCUSSION

i- Gravimetric measurements

Weight loss in mg per cm² of the surface area for copper was determined at various time intervals (every 15 min. till 120 mins.) in absence and presence of the additives at 30°C. These inhibitors had a marked inhibitive effect on the copper corrosion in HNO₃.

Table 1 gives values of inhibition efficiency from the weight loss measurements of copper for 3M different concentrations of all tested compounds in HNO₃ at 30°C after 2 h of immersion.

Table 1. Inhibition efficiency for different concentrations of all tested compounds for copper corrosion in 3M HNO₃ after 2 h. of immersion.

Inhibitor	Inhibition efficiency (%)						
conc. in M	a	b	c	d	e	f	g
1.0x10⁻⁶	19.9	17.0	17.3	12.5	12.1	10.5	6.6
5.0x10⁻⁶	41.3	33.4	31.3	27.9	24.9	23.2	22.0
1.0x10⁻⁵	53.9	55.9	49.4	41.2	39.9	38.1	34.9
5.0x10⁻⁵	65.2	63.6	56.7	53.7	54.3	51.1	49.1
1.0x10⁻⁴	73.3	72.6	64.8	62.6	63.3	60.5	58.8
5.0x10⁻⁴	81.5	78.4	76.6	73.5	71.2	68.6	63.6

All tested compounds inhibit the corrosion of copper. Inspection of Table 1 reveals that inhibition efficiency increases with an increasing inhibitor concentration. This behaviour could be attributed to the increase of the surface coverage (θ). The order of inhibition efficiencies of the additive compounds over most of the concentration range used (1x10⁻⁶ – 5x10⁻⁴M) is: a > b > c > d > e > f > g.

ii- Polarization measurements

The results of anodic and cathodic polarization of copper in presence and absence of different concentrations of compound (a) are plotted in Fig. 1. The addition

of inhibitors induced parallel displacements in Tafel curves to more +ve and –ve values for anodic and cathodic polarizations, respectively. Thus, the compounds influence both anodic and cathodic processes. The data of Table 2 suggest that the additives act as mixed type inhibitors. The value of measured corrosion potential in absence of inhibitors vs S.C.E. is in good agreement with that published before[15]. The plots of log $(\theta/1-\theta)$ vs. log C for all the additives are reasonably linear (Fig. 2 for compound a). This indicates that these compounds are adsorbed on the copper surface according to Langmuir adsorption isotherm.
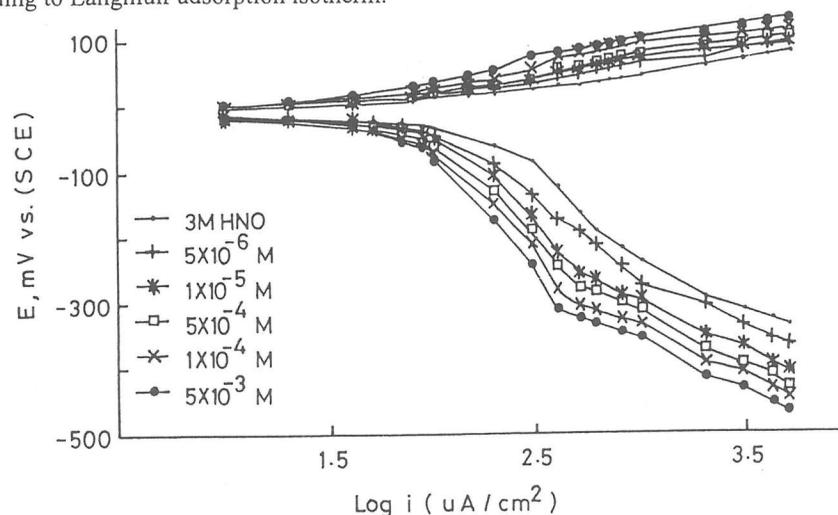

Fig. 1. Galvanostatic polarization curves of copper in 3M HNO₃ in absence and in presence of different concentrations of compound (a).
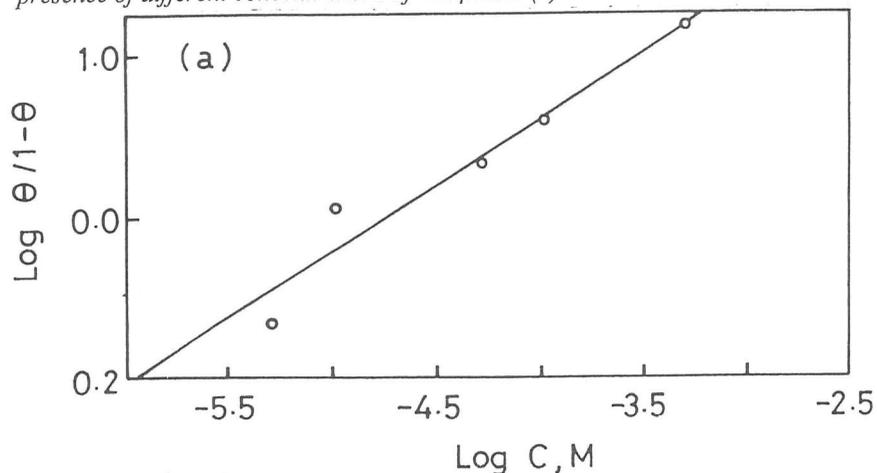

Fig. 2. log $\left(\dfrac{\theta}{1-\theta}\right)$ vs. log C curve for compound (a).

Table 2. Effect of compound (a) concentrations on the open circuit potential $(E_{o.p})$, free corrosion potential $(E_{corr.})$, Tafel slopes (β_a, β_c), corrosion current density $(i_{corr.})$, inhibition efficiency (p) and degree of surface coverage (θ) of copper in 3M HNO₃ at 30°C.

Concentration M	$-E_{o.p.}$ (mV)	$-E_{corr.}$ (mV)	$i_{corr.}$ (μA cm⁻²)	p %	β_a mV/current decade	β_c mV/current decade	θ
0.00	7.0	9.7	155.9	--	3.9	35.6	--
5.0×10^{-6}	7.0	2.9	130.0	16.6	4.0	33.1	0.166
1.0×10^{-5}	9.0	19.4	102.1	34.5	3.2	39.8	0.345
5.0×10^{-5}	12.0	32.4	45.7	70.7	4.2	35.0	0.511
1.0×10^{-4}	12.0	35.6	65.1	58.2	3.9	36.9	0.582
5.0×10^{-4}	12.0	32.4	45.7	70.7	4.2	35.0	0.707

iii- Voltammetric studies

A demonstration of the adsorption of the inhibitor molecules on the surface of noble metals was achieved by studying cyclic voltammetric current-potential diagrams for Pt in 0.1M H₂SO₄ solution as shown in Fig. 3. The voltammogram for the oxidation of adsorbed compounds was taken by dipping the electrode into a solution containing 0.1M H₂SO₄ and 1.0×10^{-5}M of inhibitor for 2 min. at 0.4V, then the solution is replaced by 0.1M H₂SO₄ only and a sweep starts towards the cathodic direction. the current obtained during the anodic sweep is higher than that in the case of H₂SO₄ only, the difference being due to the oxidation of inhibitor adsorbed on the surface. If a second sweep is taken just after the first, the anodic current is decreased, showing that the adsorbate has been desorbed from the surface and the time has been too short for readsorption to take place. The fractional surface area covered by the organic inhibitor $(\theta_{org.})$ was calculated from the hydrogen region according to the following equation[16]:

$$\theta_{org.} = \frac{Q_{hy.} - Q_{hy,org.}}{Q_{hy.}} \qquad (4)$$

Where $Q_{hy.}$ is the charge for the deposition of a monolayer of hydrogen on the electrode in the absence of the organic compound and $Q_{hy.org.}$ is the charge for the deposition of hydrogen in the presence of the adsorbed organic compound. $\theta_{org.}$ was

calculated for the different derivatives. The order of decrease in the degree of surface coverage (at 1×10^{-4} M inhibitor) is as follows: a (0.69) > b (0.65) > c (0.59) > d (0.56) > e (0.51) > f (0.45) > g (0.41). This order is in agreement with that obtained from weight loss and polarization techniques. Moreover, $\theta_{org.}$ was found also to increase with increasing inhibitors concentrations.
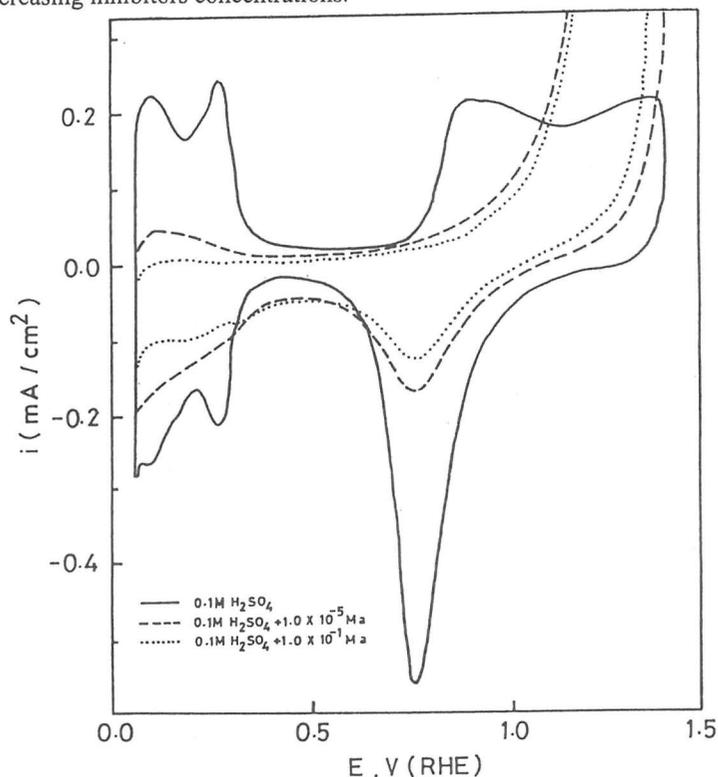

Fig. 3. Cyclic voltammogram of a Pt electrode (25 °C, 100 mVs⁻¹) in absence and in presence of compound (a)

iv- Effect of temperature:

The corrosion of copper in 3M HNO₃ acid was studied by weight loss in the range 30-60°C in absence and in presence of 1×10^{-4} M concentration of the compounds. Generally, the specific rate constants of copper dissolution increase with increase in acid concentration as well as in temperature[17] and the lower values of the activation energies (less than 50 KJ mol⁻¹). This behaviour proves that the inhibition of corrosion occurs through physical adsorption of the additives on the metal surface.

Plots of log k (rate of corrosion) against 1/T for the additives are shown in Fig. 4. The Arrhenius activation energy, E_a^* is calculated according to the following equation:

$$Log\ k = \frac{E_a^*}{2.303\ RT} + constnat \qquad (5)$$

Table 3 exhibits the values of enthalpy, entropy, energy and free energy of activation for the corrosion of copper in 3M HNO₃ solution in absence and presence of inhibitors. Free energy and entropy of activation (ΔG_a^* and ΔS_a^*) were calculated using the transition state theory relation.

$$\Delta G_a^* = RT(\ln\frac{KT}{h} - \ln k) \qquad (6)$$

For reaction in solution

$$\Delta H_a^* = \Delta E_a^* + RT \qquad (7)$$

$$\Delta S_a^* = \frac{\Delta H_a^* - \Delta G_a^*}{T} \qquad (8)$$

where K is the Boltzmann constant, h is the plank constant R is the gas constant and T is the absolute temperature.

Table 3.a.   Enthalpy, entropy, energy and free energy of activation for dissolution of copper in 3.0M HNO₃ in absence of inhibitors at different temperatures.

Temp. °C	E_a^* Kcal.mol⁻¹	ΔH_a^* Kcal.mol⁻¹	ΔG_a^* Kcal.mol⁻¹	$-\Delta S_a^*$ cal.mol⁻¹ K⁻¹
30		4.83	18.46	44.9
40	5.44	4.81	18.93	45.1
50		4.79	19.39	45.2
60		4.77	19.82	45.2

It is evident that the presence of inhibitors increase the activation energy of copper dissolution reaction. The free energy of activation increases with increasing temperature in absence and in presence of various inhibitors and is higher for the latter case. The order of decreasing inhibition efficiency as gathered from the increase in E_a^* for the additives is: a > b > c > d > e > f > g.

Table 3.b. Enthalpy, entropy, energy and free energy of activation for dissolution of copper in 3.0M HNO$_3$ in presence of 1x10^{-4}M inhibitors (a) at different temperatures.

Temp. °C	E_a^* Kcal.mol^{-1}	ΔH_a^* Kcal.mol^{-1}	ΔG_a^* Kcal.mol^{-1}	$-\Delta S_a^*$ cal.mol^{-1} K^{-1}
30		11.81	19.51	25.4
40	12.41	11.79	19.61	25.2
50		11.77	19.99	25.4
60		11.75	20.23	25.5

Inhibition of corrosion of copper in acid solution by weight loss and galvanostatic polarization was found to depend on the concentration and nature of the inhibitors. The results indicate that the corrosion inhibition takes place by adsorption of the inhibitors at the electrode solution interface[18].

v- Mechanism of inhibition:

Variation in the structure of the indicated compounds (a→g) takes place through the benzoyl side chain, the thiosemicarbazide moiety being the same. The electron charge density of the adsorption centers would depend on substituents in the phenyl ring conjugated with the carbonyl group.

Adsorption most probably takes place through the carbonyl oxygen, secondary amine nitrogen and thioketo sulphur[19]. Also, some substituents on the phenyl ring may participate in adsorption. Compound (a) has the highest inhibition efficiency due to the high electron releasing effect of 4-OCH$_3$ (σ = -0.28) and its higher molecular size than the other subsatituents. Moreover, oxygen of methoxy group acts as an additional center of adsorption. 4-Methyl substituted inhibitor (b) (σ = -0.17) follows suit as the number of adsorption centers is decreased by one. A substituted methyl group at the 4-position would donate charge through hyperconjugation (a long range effect through the π-bonds) and by inductive effect (a short range effect through σ-bonds). Methyl substituted inhibitor in 2- position (c) is less effective than 4-methyl substituent (b). The presence of the hydroxyl group in 2-position to the carbonyl group in compound (d) allows for hydrogen bonding to operate leading to a decrease in the availability of electrons[17] on the carbonyl oxygen adsorption site. The 2-chloro derivative (e) comes next, due to the dual nature of Cl (a measomeric +M effect involving pairs of electrons on Cl which can operate in opposite direction to the –I effect) and its more bulky size than the succeeding H which would increase the surface area coverage than the parent compound (f). the NO$_2$ group with the highest –I

effect among the substituents imparts the lowest inhibition efficiency to inhibitor (g). Coplanarity of the 4-NO$_2$ group with the phenyl ring brings about maximum electron withdrawal. Moreover, the nitro group is easily reduced in acid medium and the evolved heat of hydrogenation aids the desorption of the additives.

Skeletal representation of the mode of adsorption of the compounds is given by the following Fig.:
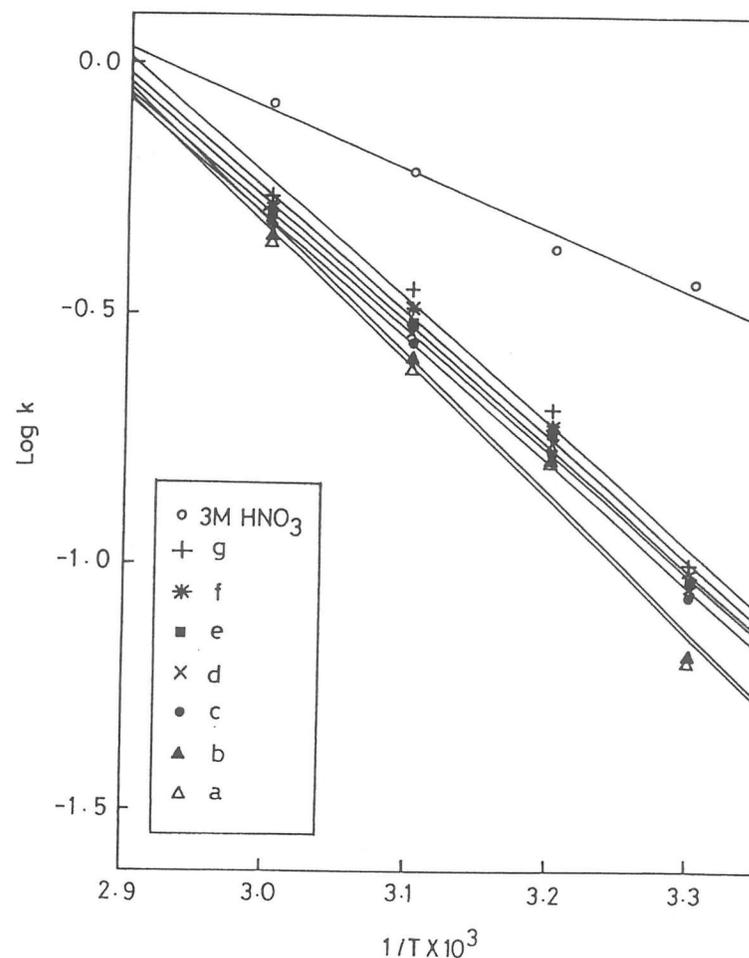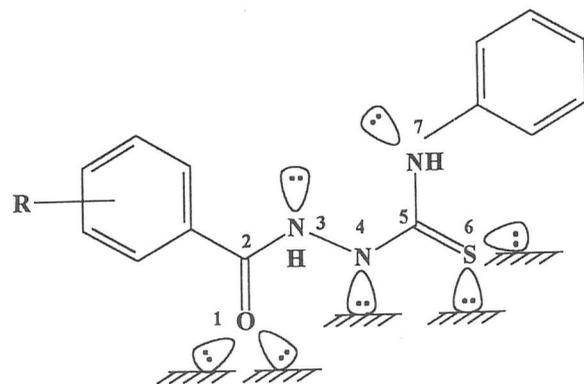

Fig. 4. Log k vs. 1/T curves for copper in 3M HNO$_3$ in absence and in presence of inhibitors.

R = p-OCH$_3$ (a)   R = p-CH$_3$ (b)
R = o-CH$_3$`   (c)   R = o-OH   (d)
R = o-Cl   (e)   R = H   (f)
R = p-NO$_2$ (g)

Quantum calculations[20] were performed to asses the validity of the above mentioned explanation of corrosion inhibition efficiency of the various additives. Results of Table 4 indicate, high negative charge density at two of the proposed adsorption centers, the carbonyl and the thioketo groups. Moreover, from highest occupied molecular orbital (HOMO), the highest atomic contribution is observed at the thioketo sulphure which should be considered the most active adsorption center. The order of HOMO energies increases on going from (a) to (g). Lower HOMO energy values corresponding to lower ionization potential refer to enhanced Lewis base character and consequently to higher adsorption probability and increased inhibition efficiency. This supports the experimentally observed order of inhibition efficiency.

Table 4. Quantum chemical parameters of the investigated compounds.

Compoun	Charge density for atom no.							HOMO*
	1	2	3	4	5	6	7	
a	-0.5514	0.2421	0.2139	0.1704	0.1222	-0.3896	0.2263	0.5253 B
b	-0.5465	0.2439	0.2168	0.1712	0.1222	-0.3892	0.2263	0.5268 B
c	-0.5468	0.2435	0.2166	0.1712	0.1222	-0.3892	0.2263	0.5270 B
d	0.5526	0.2422	0.2135	0.1704	0.1222	-0.3896	0.2263	0.5272 B
e	-0.5476	0.2437	0.2160	0.1711	0.1222	-0.3892	0.2263	0.5275 B
f	-0.5459	0.2441	0.2169	0.1713	0.1222	-0.3891	0.2263	0.5278 B
g	-0.5450	0.2441	0.2175	0.1716	0.1222	-0.3890	0.2263	0.5284 B

* B = 2.3 eV.

Evidence for the validity of the forgiven explanation is gathered from the application of the Hammet equation[21]:

Log k = Log k$_0$ + ρσ

where k and k$_0$ are corrosion rate constants of substituted and unsubstituted inhibitors and σ is the polar substituent constant. is a proportionality constant dependent upon the reaction conditions. It is a measure of the susceptibility of a given reaction series to polar substituents. a plot of log R vs. σ gives a straight line (Fig. 5), thus demonstrating the dependence of corrosion rate on the polar character of substituents in the inhibitor molecules.
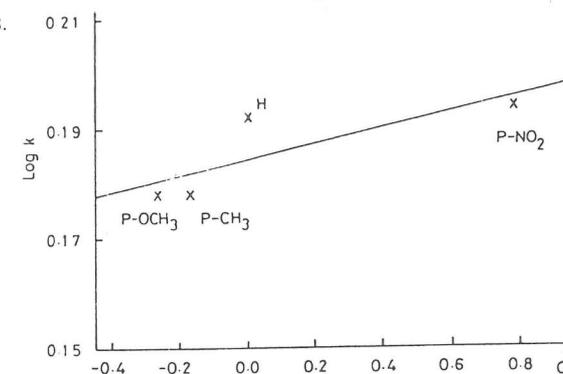

Fig. 5. Relationship between inhibitor efficiency (log k) and Hammett constants of all tested compounds (inhibitor concentration is 1x10^{-4}M).

4. CONCLUSION

The corrosion rate of copper depends on the nature and concentration of the inhibitors used as gathered from the results of weight loss, polarization and cyclic voltammetric techniques which supports each other. This refers the validity of the present measurements which show that these compounds act as mixed type inhibitors and that the corrosion inhibition has a greater effect on cathodic polarization as cathodic Tafel slopes (β$_c$) are greater than anodic (β$_a$). The inhibition action has been attributed to the adsorption of organic inhibitors on the oxide metal surface. This is supported by the observed suppression of the current on the hydrogen region in cyclic voltammogrmas recorded in H$_2$SO$_4$ using a Pt electrode dipped in inhibitor containing solution. The adsorption isotherms obey Langmuir isotherm as indicated from the plots of log θ/1-θ vs. log C. The same behaviour was observed by Moussa et al.[22] in their investigation on the effect of some substituted thiomseicarbazide derivatives on the corrosion of aluminium in hydrochloric acid solution.

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ROLE OF ALDEHYDES ON THE ELECTROCHEMICAL DEPOSITION AND DISSOLUTION OF ZINC: A CYCLIC VOLTAMMETRIC STUDY

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ABSTRACT

Electrochemical deposition and dissolution of zinc in acidic zinc plating bath solutions containing formaldehyde (FA), benzaldehyde (BA) or furfuraldehyde (FUA) has been studied by cyclicvoltammetric technique. Shapes of voltammograms, peak potentials and Tafel slopes are not affected by the presence of aldehydes in the plating bath solution. Aldehydes decreased the peak currents and the extent of decrease is in the order: FUA>BA>FA. This is accounted by Langmuir type of adsorption of aldehydes on zinc-solution interface and the electron density of oxygen atoms in aldehydes. SEM photographs of zinc deposits indicated the gradual decrease of grain size from FA to BA and FUA. Negative values of ΔS^{o}_{a} and ΔG^{o}_{a} suggested the considerable interaction of aldehydes on zinc surface with rigid adsorbed species.

Keywords: Cyclicvoltammetry, zinc-dissolution-deposition, aldehydes, surface adsorption.

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