CORROSION INHIBITORS FOR COPPER IN ACIDIC MEDIA

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ABSTRACT

The inhibition effect of some quinazoline derivatives on the corrosion of copper in acidic media has been investigated by weight loss. galvanostatic and potentiodynamic anodic polarization techniques. Results obtained reveal that these quinazoline derivatives are good inhibitors. It is observed that the combination between these quinazoline derivatives and halide ions shows good inhibition efficiency. Galvanostatic polarization studies showed that these compounds are mixed-type inhibitors. The adsorption of these derivatives on the copper surface obeys Frumkin's adsorption isotherm. The effect of temperature on the corrosion behavior of copper in nitric acid in presence of definite concentration of the inhibitors was studied in the temperature range (30–50°C). Also, some thermodynamic data for corrosion and adsorption processes are calculated and discussed.

1. INTRODUCTION

Copper is widely used in various industrial operations and the study of its corrosion and its inhibition is a subject of practical significance. The use of organic compounds containing nitrogen as corrosion inhibitors is widely spread for many metals and alloys, little is known of their functions because of the complexity of the process. Several mechanisms have been proposed to explain the function of corrosion inhibitors of which the adsorption theory is the most pertinent

[Hackerman et al., (1962)]. The reaction of corrosion inhibitors at the metal/solution interface has been evaluated by adsorption characteristics and also by the thermodynamics of adsorption [Rudresh et al., (1977); Mayanna (1975) and Dinnappa et al., (1981)]. 2-hydroxyacetophenone aroyl hydrazone derivatives [Fouda et al., (2000)], Caffeine [Ahmed et al., (1977)], n-decylamine [Rudresh et al., (1977)], substituted phenols [Fouda et al., (1988)], benzoyl benzaldehyde hydrazone derivatives [Abdel Maksoud et al., (1995)] and ethylamine [Fouda et al., (1990)] have used as effective corrosion inhibitors for copper.

The purpose of the present paper is to determine the effect of some quinazoline derivatives towards the corrosion of copper in nitric acid, to throw some light on the mechanism of inhibition and to study the effect of the temperature on the rate of corrosion.

The quinazoline derivatives used in this study are available, easily prepared as before [Williamson (1957)] and non-toxic and their structures were identified by elementary, IR, m.p., and NMR analysis. The structures of the inhibitors are listed below:
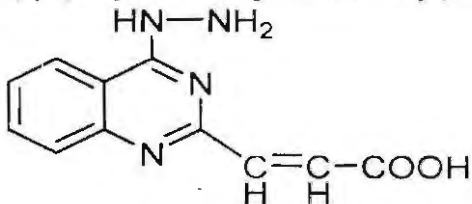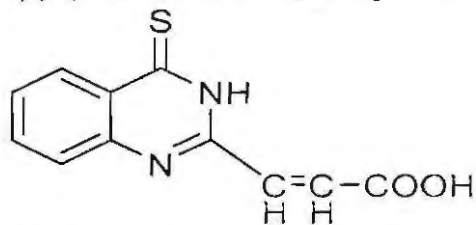
a) β-(4-oxo-benzo[d]oxozin-2-yl)-acrylic acid.
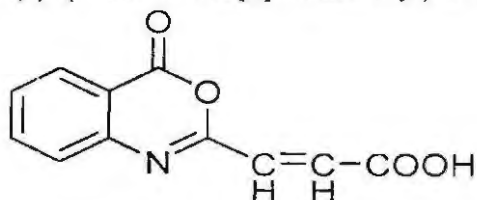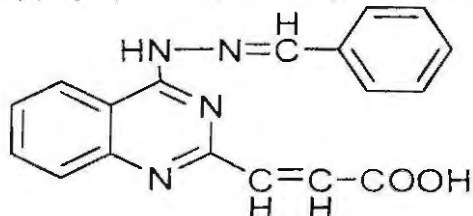

b) β-(4-oxo-3, 4-dihydro-quinazolin-2-yl)-acrylic acid.
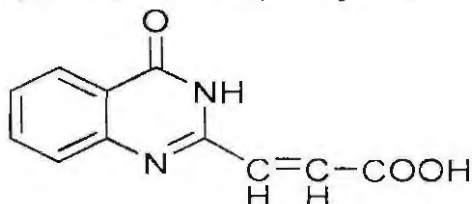
c) β-(4-hydrazino- quinazolin-2-yl) acrylic acid.

d) β-(4-thioxo-3, 4-dihydro-quinazolin-2-yl) acrylic acid.

e) β -[4-(N-benzylidine-hydrazno) - quinazolin-2-yl]-acrylic acid.

2. EXPERIMENTAL

Copper test samples containing 0.001% Sn, 0.001% Ag, 0.01% Fe, 0.0005% Bi, 0.002% Pb, 0.0002% As and Cu is the remainder were used throughout this investigation. All chemicals were from an analytical reagent grade. A solution of 2M HNO_3 was prepared from concentrated HNO_3 (BDH grade) by dilution with double-distilled water and its concentration was checked using standardized NaOH. For weight loss measurements the tested specimens were used in the form of sheets of dimensions 2 × 2 × 0.1 cm. The specimens were polished using emery papers of 1/0, 2/0, 3/0 and 4/0 grade then degreased with methanol [Bonhoeffer et al., (1956)], then washed with double distilled water, and finally dried between two filter papers and weighed. This treatment was carried out immediately before each measurement. For electrochemical measurements EG and G model 173 potetiostat / galvanostat was used. Tree compartment cell with was used in this measurments .The electrodes used were cut from a wire of diameter 0.037 cm. A copper wire was fixed at one end by mechanical jamming, and the electrode was fixed into a pyrex glass tubing by means of araldite (Ciba-Geigy-Switzerland) leaving an exposed length of 1 cm in contact with the solution. Ag/AgCl electrode and platinum electrodes were used as reference and auxiliary electrodes, respectively. All experiments were

conducted at 30°C. The percentage inhibition efficiency (%I) was calculated from corrosion current density values using the equation:

$$\%I = \left[1 - \frac{i_{add}}{i_{free}} \right]100$$

3. RESULTS AND DISCUSSION

Figure 1 shows the weight loss-time curves for copper in 2M HNO_3 and in presence of different concentrations of inhibitor (e),(similar curves are obtained in presence of the other inhibitors, but not shown). Curves are characterized by gradual rise in weight loss with time. The curves indicate that, the weight loss of copper depends on the concentration and the type of additives (Table 1). Increase in bulk concentration and consequently increase of surface coverage by the additive increases their inhibition efficiency as indicated by the decrease in weight loss per cm^2.

Table 1 shows the effect of concentrations of quinazoline derivatives on percentage inhibition efficiency. From these data one can say that the order of increasing inhibition efficiency of these quinazoline derivatives is:
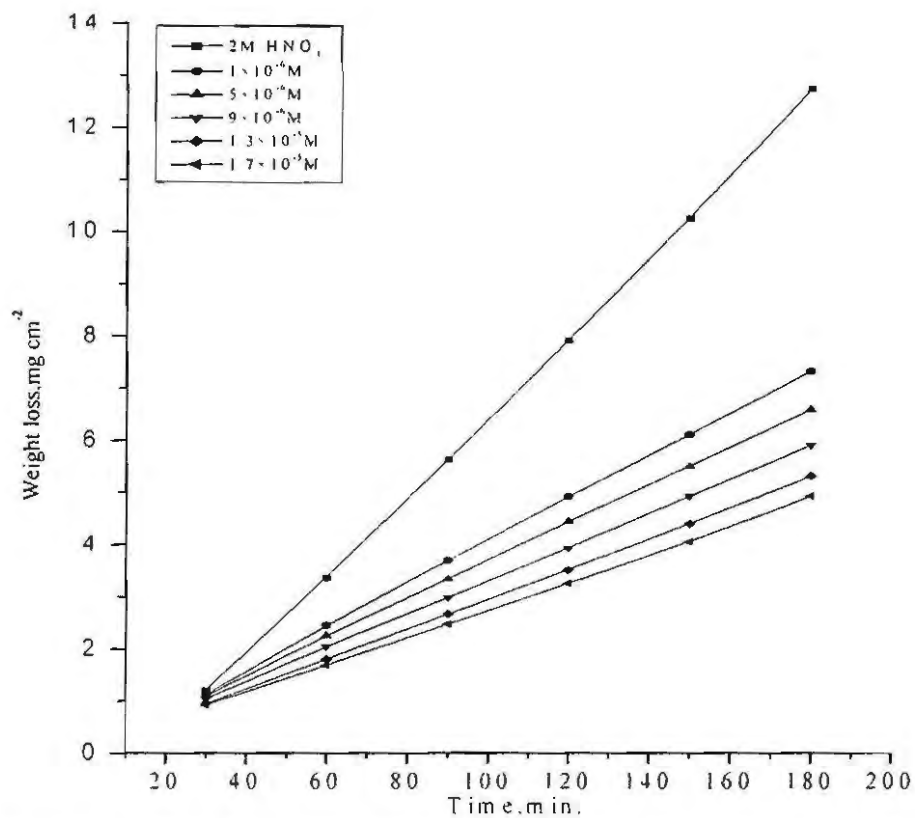
a < b < c < d < e

Fig. (1): Weight loss-time curves for copper in 2M HNO_3 in absence and presence of different concentrations of compound (e) at 30°C.

Table (1): Inhibition efficiency (I %) of some and quinazoline derivatives for copper dissolution in 2 M HNO_3 at different temperatures and at different concentrations of inhibitors (at 120min. immersion).

Inhibitor		Inhibition efficiency (I%)				
	Conc.,M / Temp.,$^{\circ}$C	1×10^{-6}	5×10^{-6}	9×10^{-6}	1.3×10^{-5}	1.7×10^{-5}
a	30	23.00	30.25	36.08	40.00	42.01
	35	20.73	27.64	32.26	36.66	40.83
	40	19.57	25.32	30.88	35.75	39.61
	45	18.36	23.70	28.85	33.8	37.47
	50	16.25	21.57	26.57	30.64	34.35
b	30	26.09	32.06	37.32	42.00	44.98
	35	23.22	29.21	35.12	39.02	43.21
	40	22.46	28.85	32.66	38.2	41.87
	45	21.57	26.48	29.67	35.69	39.44
	50	19.55	24.66	29.12	32.46	36.55
c	30	33.09	35.36	40.55	46.50	50.35
	35	26.55	31.93	37.68	42.73	46.73
	40	25.47	29.68	35.36	40.48	44.9
	45	25.47	27.79	32.56	37.37	42.26
	50	22.57	27.41	32.84	35.88	39.66
d	30	32.67	37.50	43.5	49.50	52.01
	35	31.95	35.78	41.1	45.87	50.91
	40	30.46	33.45	39.44	43.77	47.36
	45	28.98	31.65	36.49	40.47	44.83
	50	25.69	30.64	34.19	37.62	42.53
e	30	37.85	43.82	50.35	55.60	58.90
	35	36.00	42.74	46.78	51.71	57.60
	40	34.91	40.63	44.25	48.54	53.37
	45	33.66	38.37	41.96	45.22	49.55
	50	31.79	36.38	38.98	42.21	45.45

The effect of temperature on the corrosion rate of copper in 2M nitric acid solution in absence and presence of 1×10^{-6} to 1.7×10^{-5}M of these inhibitors was studied at different temperatures (30–50°C) by weight loss measurements. The data of Table 1 show that the percentage inhibition efficiency decreases as the temperature increases and the concentration of these compounds decreases.

The effect of Cl⁻ and Br⁻ ions on the corrosion inhibition of copper in 2M HNO_3 solution in presence and absence of the quinazoline compounds was studied by weight loss method. The values of inhibition efficiency (%IE) for various concentrations of inhibitors in the presence of specific concentrations of these anions (Br⁻ & Cl⁻) are given in Tables (2 &3).

Table (2): Inhibition efficiency at different concentrations of inhibitors + 1 x 10^{-4} M KBr as determined from weight loss method at 30°C.

Conc.. M	%Inhibition				
	Compound (a)	Compound (b)	Compound (c)	Compound (d)	Compound (e)
1×10^{-6}	68.38	70.48	73.12	75.76	76.81
5×10^{-6}	71.05	73.91	76.55	79.18	80.24
9×10^{-6}	73.48	75.08	77.69	80.45	81.38
1.3×10^{-5}	75.27	75.99	79.01	81.63	83.22
1.7×10^{-5}	76.02	78.13	80.24	83.40	85.24

Table (3): Inhibition efficiency at different concentrations of inhibitors +
1 x 10^{-4} M KCl as determined from weight loss method at
30°C.

Conc., M	%Inhibition				
	Compound (a)	Compound (b)	Compound (c)	Compound (d)	Compound (e)
1x10^{-6}	59.77	61.88	64.51	65.56	68.20
5x10^{-6}	63.13	65.21	66.80	68.38	72.59
9x10^{-6}	66.97	68.55	70.13	71.71	74.35
1.3x10^{-5}	70.11	70.66	72.24	74.88	77.51
1.7x10^{-5}	73.91	74.96	75.21	78.65	80.23

Arrhenius plot of logarithmic of corrosion rate against the reciprocal of absolute temperature (1/T) is shown graphically in Fig. 2 at 1.3 × 10^{-5}M of the inhibitors.

The values of activation energies, E_a^*, were calculated and given in Table 4. These values indicate that the presence of these inhibitors increases the activation energy of the metal dissolution reaction and that the process is diffusion controlled ($E_a^* > 40$ kJ mol^{-1}).

The activation energy for the corrosion of copper in 2M HNO$_3$ is 71.99 kJ mol^{-1} which is in good agreement with the values obtained by Mansour et al. [**El Sayed et al., (1989)**] in which he found that the activation energy of copper in 3M HNO$_3$ is 72.4 kJ mol^{-1}. The adsorption of the inhibitors was assumed to occur on the higher energy sites [**Riggs**

et al., (1967)] and the presence of the inhibitors, which results in the blocking of the active sites must be associated with an increase in the activation energy of copper corrosion in the inhibited state.
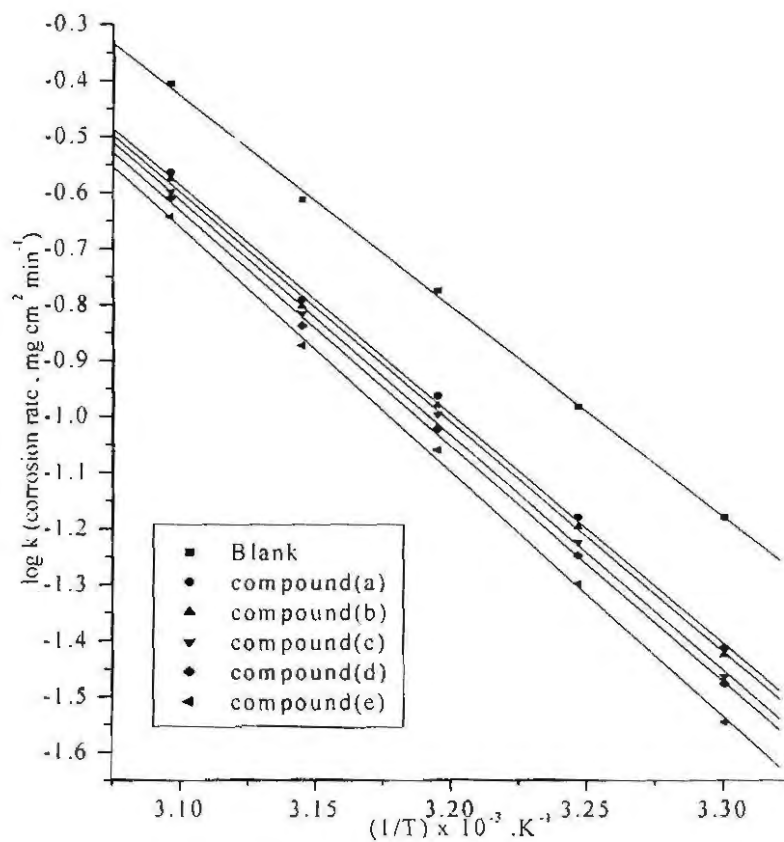

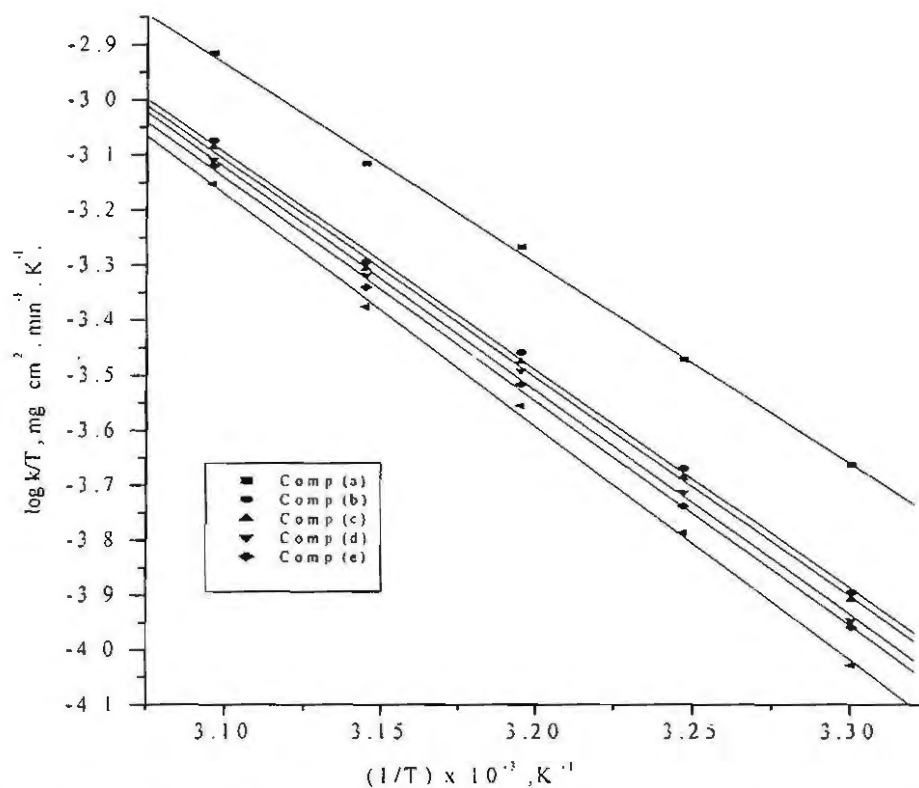**Fig.(2):** log k vs.1/T curves for copper dissolution in absence and presence of 1.3×10^{-5} M inhibitors

Fig. (3): log k/T vs.1/T curves for copper dissolution in absence and presence of 1.3×10^{-5}M inhibitors.

Table (4): Activation parameters of the copper in 2M HNO_3 in absence and presence of 1.3×10^{-5}M of different inhibitors.

Inhibitors	Activation parameter		
	E_a^* , k J mol^{-1}	ΔH^* , k J mol^{-1}	$-\Delta S^*$, J mol^{-1} K^{-1}
Free acid	71.99	69.39	38.58
Compound (a)	78.22	75.62	22.34
Compound (b)	78.47	75.87	21.8
Compound (c)	80.26	77.66	16.52
Compound (d)	80.42	77.83	16.36
Compound (e)	83.62	81.02	7.02

By plotting log k/T vs. 1/T at 1.3 $\times 10^{-5}$M of these inhibitors, straight lines were obtained as shown in Fig.3. The values of ΔH^* and ΔS^* can be calculated from the slope and intercept of the above plot. Examination of these data reveals that the values of ΔH^* and ΔS^* in the presence of the additives increase over that of the uninhibited solution. This implies that energy barrier of the corrosion reaction in the presence of the additives increases which is expected. It is evident that the values of ΔH^* and ΔS^* increase with increasing temperature in presence of different concentrations of the tested compounds. ΔS^* in the presence of additives is larger. meaning that a decreasing in disordering takes place in going from reactants to the activated complex **[Gomma et al., (1995) and Marsh (1988)]**. The results of Table 4 show that by increasing the temperature the percentage inhibition of the tested compounds decreases. This indicates that the adsorption of these compounds on copper surface is physically. By plotting the surface coverage. θ vs. log C for all the tested compounds and for copper in 2M HNO$_3$. S-shape curves were obtained in all cases. thereby clearly proving that the adsorption of these compounds on copper surface in 2M HNO$_3$ obeys Frumkin's adsorption isotherm [Fig. 4].
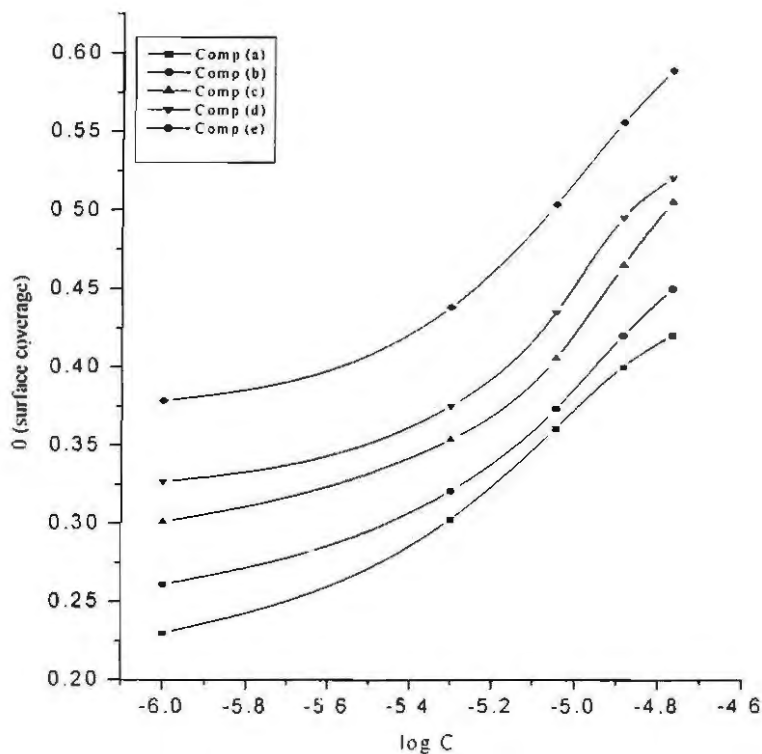
Fig. (4): Frumkin adsorption isotherm of investigated compounds on Cu surface from HNO_3 solution at 30 °C.

Both the anodic and cathodic polarization curves of copper in 2M HNO_3 in absence and presence of different concentrations of compound (e) are shown in Fig. 5. Similar polarization curves are obtained in the presence of other compounds, but not shown. It is clear that the polarization behavior of copper in this media follows almost similar pattern. Various corrosion kinetic parameters such as corrosion potential ($E_{corr.}$), corrosion current ($i_{corr.}$), and Tafel slopes β_a and β_c derived from the polarization curves are given in Table 5. From these data one can say that these compounds behave as mixed-type inhibitors, but the cathode is more polarized when an external current density was applied ($\beta_c > \beta_a$). The data of Table 6 shows the variation of the percentage inhibition efficiency of these compounds with their concentrations obtained from polarization method at 30°C. The order of increasing inhibition efficiency of these compounds is :   a <b< c< d <e
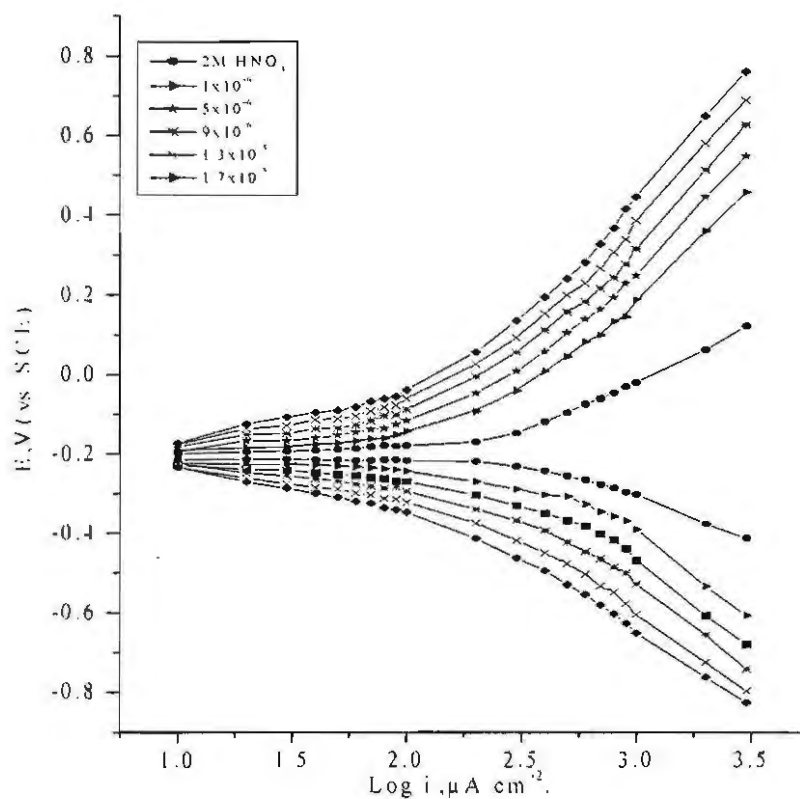
Fig. (5): galvanostatic polarization curves of copper in 2M HNO₃ alone and containing different concentrations of compound (e) at 30°C.

Table. (5): Corrosion parameters obtained from galvanostatic
polarization of copper in 2M HNO₃ containing various
concentrations of inhibitor (e) at 30° C.

Conc., M	$-E_{corr.}$ mV,	I_{corr}, $\mu A\ cm^{-}$	βa mV dec^{-1}	$-\beta c$ mV dec^{-1}	θ	% IE
0.0	0.20	1.92	244	142	---	------
1×10^{-6}	0.20	1.18	388	193	0.38	38.36
5×10^{-6}	0.20	1.02	426	249	0.47	46.54
9×10^{-6}	0.18	0.92	450	320	0.52	52.00
1.3×10^{-5}	0.22	0.85	527	346	0.55	55.27
1.7×10^{-5}	0.25	0.75	579	343	0.61	60.93

Table(6): Variation of the percentage inhibition efficiency (I%) of some
quinazoline derivatives with their concentrations obtained
from polarization method at 30°C.

Concentration,(M)	Inhibition efficiency, (I %)				
	a	b	c	d	e
1×10^{-6}	24.85	29.44	28.34	35.13	38.36
5×10^{-6}	31.67	33.43	34.09	39.10	46.54
9×10^{-6}	36.14	38.56	41.59	43.78	52.00
1.3×10^{-5}	40.86	41.86	47.65	50.05	55.27
1.7×10^{-5}	42.83	46.59	50.21	53.82	60.93

Fig.(6) represents the effect of the addition of increasing
concentrations of compound (e) on the potentiodynamic anodic
polarization curves of copper electrode in 0.1M HNO₃ + 0.001M NaCl at
a scanning rate of 1mV/sec. Similar potentiodynamic anodic polarization
curves are obtained in presence of the other inhibitors, but not shown. It
was found that the pitting potential of the copper electrode is shifted to

more positive (noble) direction with increasing the concentration of additives. This indicates that increased resistance to pitting attack.

Fig. (7) represents the relationship between pitting potential and the logC of the added compounds. Straight lines were obtained and the following conclusion can be drawn:

a) An increase of inhibitor concentration causes the shift of the pitting potential to more positive values in accordance with the following equation:

$$E_{pitt.} = a_2 + b_2 \log C_{inh}$$

where a_2 and b_2 are constants which depend on both the nature of the additives and the nature of the electrode.

b) Inhibition afforded by these compounds using the same different concentrations of the additives increases in the following order:
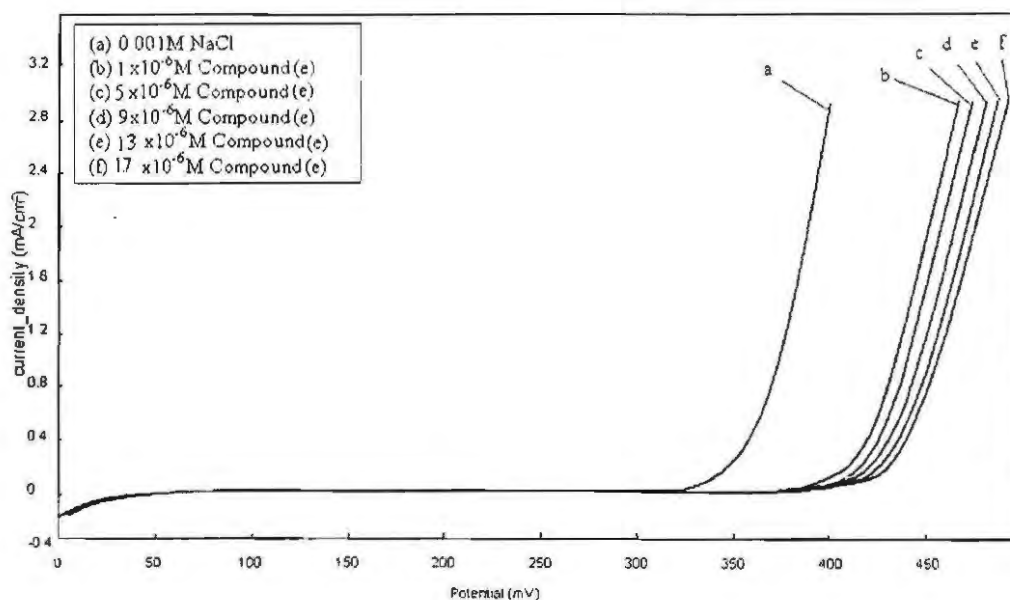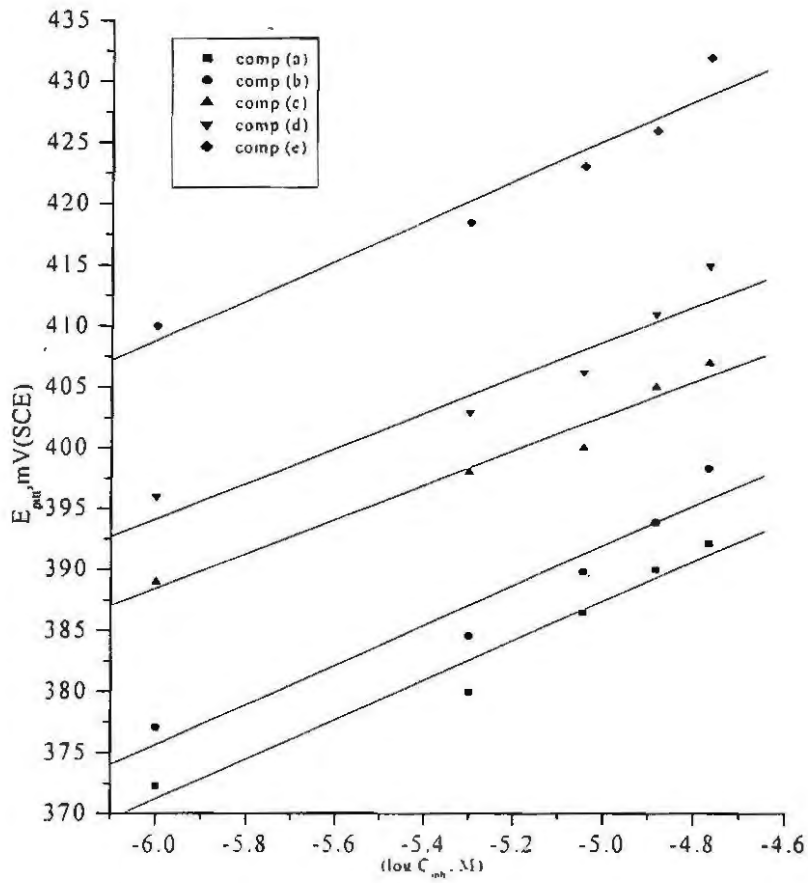
$$a < b < c < d < e$$

Fig.(6): Potentiodynamic anodic polarization curves of copper in 0.1M HNO$_3$ + 0.001M NaCl containing different concentrations of compound (e).

Fig(7): The relationship between pitting potential of copper and logarithm concentration of the inhibitors in presence of 0.001M NaCl.

All compounds have two adsorption active centers see Fig. (8), so, the numbers of active center have no effect. Compound (e) is the most efficient inhibitors because of increased molecular size (318) and presence of one more benzene ring in the molecule which contributes π electrons to the adsorption active centers and hence increases the electron density on the adsorption centers. Compound (d) comes next in the sequence of decreased inhibition efficiency, because of its lower molecular size (232). Compound (c) comes after compound (d) in the sequence of decreased inhibition efficiency. This is due to its lower molecular size (230) and N atom less basic than S atom in compound (d). Compound (b) has lower molecular size (216) than compound (c), so, it comes after it in inhibition efficiency. Compound (a) is the least effective inhibitor. This is due to its lower molecular size (217) and O atom is less basic than N atom in compound (b).

The order of inhibition efficiency of the investigated compounds was revealed by the weight loss and further confirmed by galvanostatic polarization measurements. The agreement among these techniques proves the validity of results obtained and supports the explanation given for the effect of chemical structure on the inhibition action of the investigated compounds.
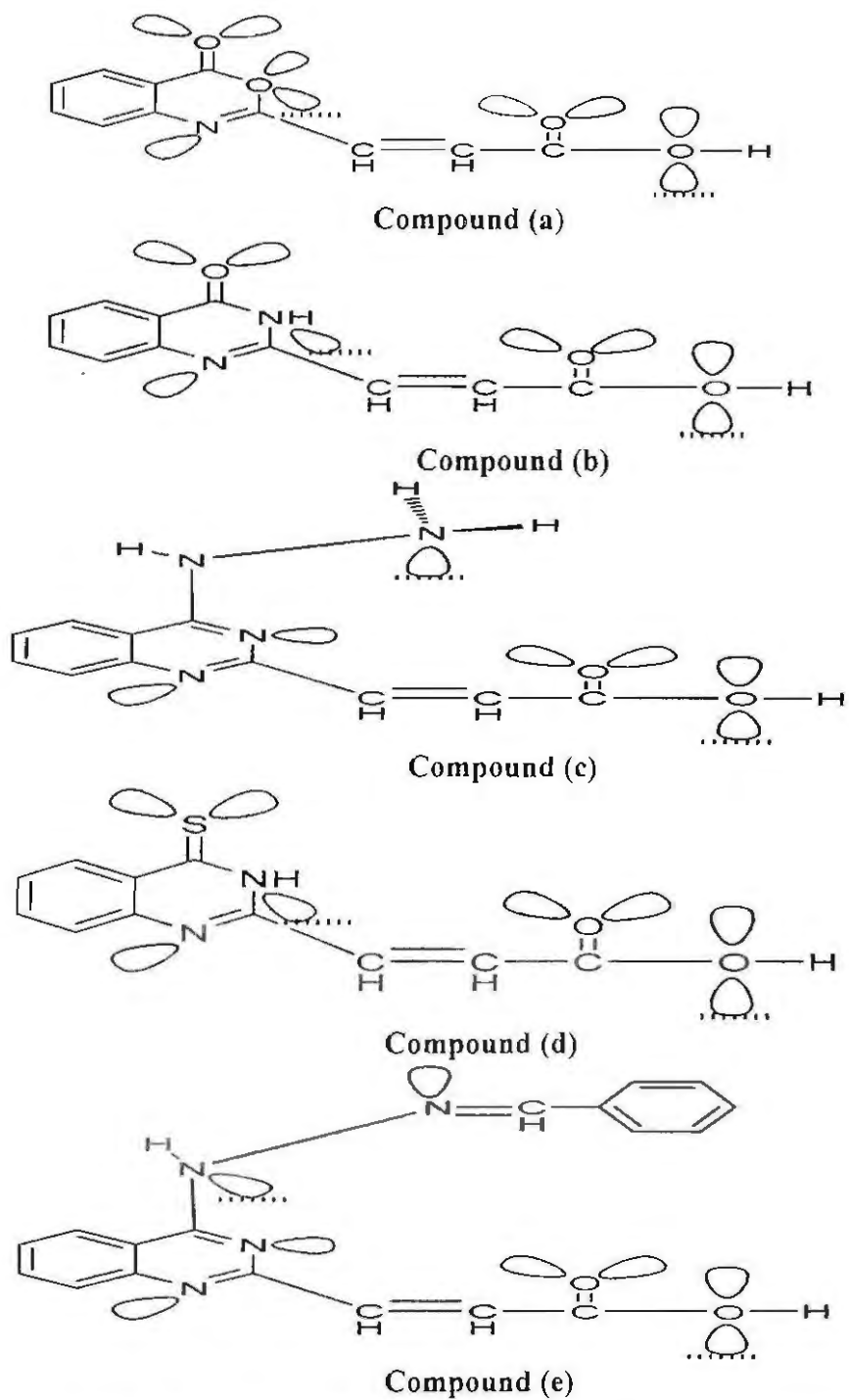
Compound (a)

Compound (b)

Compound (c)

Compound (d)

Compound (e)

Fig. (8): Skeletal representation of the mode of adsorption of all quinazoline compounds.

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مثبطات تآكل النحاس فى الوسط الحامضى

عبدالعزيز فودة ـ متولى عبدالله ـ رضا أبوالدهب

التآكل هو المشكلة الرئيسية التى تهدد فترة عمر صلاحية المعدن للاستخدام ؛وفهم ميكانيكية التآكل يمكنا من ايجاد حل لمشاكل التآكل الحالية ومنع المشاكل المستقبلية و هذا البحث يناقش تآكل النحاس في حامض النيتريك و كيفية حمايته.

تم مناقشة التركيب الكيميائي لمركبات الكينازولين و تاثيرها على كفاءة التثبيط ولوحظ أن كفاءة تثبيط المركبات يعتمد على الشكل الفراغي للمركبات و المراكز النشطة الموجودة في المركبات التى تحدد الكثافة الالكترونية على سطح النحاس و كذلك التأثير القطبي للمجموعات المستبدلة.وتمت الدراسات باستخدام الطرق التالية:

(طريقة الفقد في الوزن و الاستقطاب المهبطى و المصعدى و الاستقطاب البوتنشيو ديناميكي)

خلاصة القول أن قياسات الاستقطاب الكهربى و فقد الوزن تؤيد افتراض أن تثبيط التآكل يتم عن طريق ادمصاص المثبطات على سطح النحاس و الاتفاق بين وسائل القياسات المختلفة فى ترتيب كفاءة المثبطات المستخدمة و هذا يدل على صحة النتائج التي تم الحصول عليها.