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Some quinazoline derivatives as corrosion inhibitors for copper in HNO_3 solution

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ABSTRACT

The inhibition effect of some quinazoline derivatives on the corrosion of copper in 2 M HNO_3 has been investigated by weight loss and polarization studies. The inhibition efficiency increased with increase in inhibitor concentration but decreased with the increase in temperature. The thermodynamic functions of dissolution and adsorption processes were calculated. The polarization measurements indicated that the inhibitors are of mixed-type. The kinetic parameters of corrosion of copper in HNO_3 solution have been determined. The adsorption of the compounds was found to obey Frumkin's adsorption isotherm. It is observed that the combination between these quinazoline derivatives and halide ions shows good inhibition efficiency. The results obtained from weight loss and galvanostatic polarization are in good agreement.

Keywords: Corrosion; Copper; HNO_3; Quinazoline derivatives

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1. Introduction

Copper is widely used in various industrial operations due to its good properties. It is used in electronics, for production of wires, sheets, tubes, and also to form alloys. So, the study of its corrosion 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 [1]. The reaction of corrosion inhibitors at the metal/solution interface has been evaluated by adsorption characteristics and also by the thermodynamics of adsorption [2–4]. Hydrazone derivatives [5,6], caffeine [7], amines [8–11], substituted phenols [12] and azoles [13–20] have been used as effective corrosion inhibitors for copper.

The aim of the present study is to: i) determine the effect of some quinazoline derivatives towards the corrosion of copper in HNO_3 ii) throw some light on the mechanism of inhibition and iii) study the effect of the temperature on the inhibition of corrosion.

The quinazoline derivatives used in this study are available, easily prepared as before [21] and with low toxicity and their structures were identified by elemental analysis, IR, m.p., and NMR analysis. The quinazoline derivatives used as inhibitors have the structures as shown in Fig. 1.

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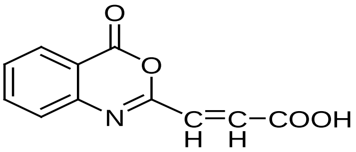
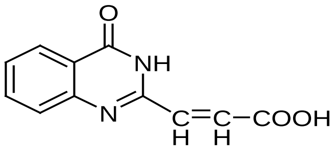
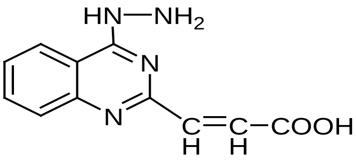
a) β-(4-oxo-benzo[d]oxozin-2-yl)-acrylic acid (BOA)



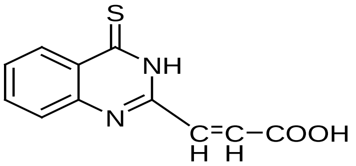
b) β-(4-oxo-3, 4-dihydro-quinazolin-2-yl)-acrylic acid (QA)



c) β-(4-hydrazino-quinazolin-2-yl) acrylic acid (HQA)



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



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

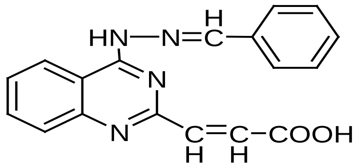


Fig. 1. Structures of the quinazoline derivatives.

It obvious that these derivatives contain nitrogen atoms which are easily protonated in acidic solution, oxygen and sulfur atoms and a great deal of π-electrons exist in these molecules.

2. Experimental method

2.1. Materials

The experiments were performed with copper specimens with the following composition (weight %): 0.001 Sn, 0.001 Ag, 0.01 Fe, 0.0005 Bi, 0.002 Pb, 0.0002 As and Cu remainder.

2.2. Solutions

The aggressive solutions used were made of AR grade HNO_3 (6 M) and its concentration was checked using standardized NaOH. Appropriate concentration (2 M) of acid was prepared by dilution using bidistilled water. 100 ml stock solutions (10^{-3} M) of investigated compounds were prepared by dissolving an accurately weighed quantity of each material in an appropriate volume of absolute ethanol, then the required concentrations (1×10^{-6}–17×10^{-6} M) were prepared by dilution with bidistilled water.

2.3. Gravimetric method

Prior to the experiment, the copper sheets of 20 × 20 × 1 mm were abraded with a series of emery paper of 1/0, 2/0, 3/0 and 4/0 grades. Then the specimens were washed several times with distilled water then degreased with methanol [13] and dried using a stream of dry air. After weighing accurately, the specimens were immersed in 100 ml beaker, which contained 100 ml of 2 M HNO_3 with and without addition of different concentrations of investigated compounds. All the aggressive acid solutions were open to air. After 3 h, the specimens were taken out, washed, dried and weighed accurately. The weight loss is recorded to the nearest 0.0001 gram and the reproducibility of the results is more than 96%. Then the tests were repeated at different temperatures. The degree of surface coverage (θ) and percentage inhibition efficiency (IE(%)) were calculated from the following equations:

$$\theta = \left[\left(W_0 - W\right)/W_0\right] \quad (1)$$

$$\left(\mathrm{IE}(\%)\right) = \left[\left(W_0 - W\right)/W_0\right]\times 100 \quad (2)$$

where W_0 and W are the weight losses in the absence and presence of inhibitors, respectively.

2.3.1 Corrosion rate measurements

The annual correction rate (CR) in mmy^{-1} can be calculated using the following equation [22]:

$$\mathrm{CR} = \left(k x W\right)/ATD \quad (3)$$

where k is a constant and is equal to 8760, W corrosion mass in mg, A is the surface area in cm^2, T is the immersion time in h and D is the density of Cu in g/cm^2 (8.96 g/cm^2).

2.4. Electrochemical measurements

For electrochemical measurements 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. A platinum foil was used as an auxiliary electrode. The reference electrode was Ag/AgCl electrode coupled to a Luggin capillary whose tip was located between the working electrode and the auxiliary electrode. All experiments were conducted at 30°C. All polarization measurements were performed using potentiostat/galvanostat model Amel 549. The potential at any given current under the similar experimental condition was reproducible with ± 7%. The degree of surface coverage (θ) and percentage inhibition efficiency (IE(%)) was calculated from the following equations:

$$\theta = \left[\left(j_{\text{corr}} - j_{\text{inh}} \right) / j_{\text{corr}} \right] \tag{4}$$

$$\left(\text{IE}(\%) \right) = \left[\left(j_{\text{corr}} - j_{\text{inh}} \right) / j_{\text{corr}} \right] \times 100 \tag{5}$$

where j_{corr} and j_{inh} are the uninhibited and inhibited corrosion current densities, respectively, determined by extrapolation of Tafel lines to the corrosion potential.

2.4.1. Corrosion rate measurements

The corrosion rate (CR) in mm y^{-1} in polarization method can be calculated using the following equation [23]:

$$\text{CR} = 3.268 \times 10^3 \times \left(j_{\text{corr}} \times \text{MW} \right) / \left(z\, x\, \rho \right) \tag{6}$$

where j_{corr} is the corrosion current in A/cm^2, MW is the molecular weight of Cu in g, ρ is the density of Cu in g/M and z is the number of electrons transferred in corrosion reaction ($z = 2$) in the case of Cu reaction.

3. Results and discussion

3.1. Weight loss method

Fig. 2 shows the weight loss-time curves for copper in 2 M HNO_3 and in presence of different concentrations of inhibitor (SHQA), curves are characterized by gradual rise in weight loss with time. The curves indicate that, the corrosion rate (CR) 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 in Table 2. The order of increasing inhibition efficiency (IE(%)) of these quinazoline derivatives is: BOA < QA < HQA < ThQA < SHQA.

3.2. Effect of temperature

The effect of temperature on the corrosion rate of copper in 2 M nitric acid solution in the absence and presence of 1×10^{-6}–17×10^{-6} M of these inhibitors was studied at different temperatures (30–50°C) by weight loss method. The data of Table 2 show that (IE (%)) decreases as the temperature increases due to the desorption of inhibitor molecules from the copper surface, and hence low surface coverage was obtained. Also, (IE (%)) increases with increasing inhibitor concentration.

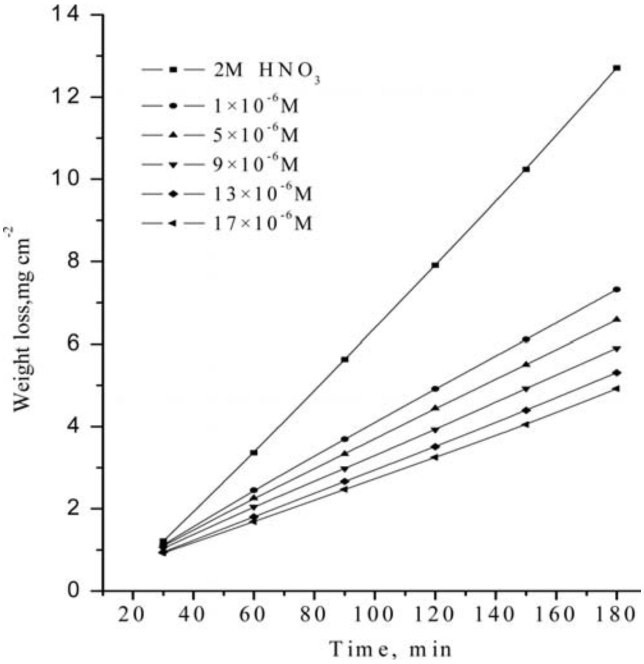


Fig. 2. Weight loss-time curves for copper in 2 M HNO_3 in the absence and presence of different concentrations of compound (SHQA) at 30°C.

Table 1
Corrosion rate (CR mm/y) at different concentrations of all investigated compounds calculated from weight loss method at 120 min immersion and 30°C

Comp. conc., M	BOA	QA	HQA	ThQA	SHQA
1×10^{-6}	7.5	7.2	6.5	6.6	6.1
5×10^{-6}	6.8	6.6	6.3	6.1	5.5
9×10^{-6}	6.2	6.2	5.8	5.5	4.8
13×10^{-6}	5.9	5.7	5.2	4.9	4.3
17×10^{-6}	5.7	5.4	4.8	4.7	4.0

The thermodynamic functions for the dissolution of copper in 2 M HNO_3 in the absence and presence of 13×10^{-6} M of inhibitors were obtained by applying the Arrhenius equation [Eq. (7)] and transition state equation [Eq. (8)] respectively:

$$\ln k = \left(-E_a^* / RT \right) + \ln A \tag{7}$$

$$k = \left(RT / Nh \right) \exp\left(\Delta S_a^* / R \right) \exp\left(-\Delta H_a^* / RT \right) \tag{8}$$

where E_a^* represents the apparent activation energy, R the gas constant, T the absolute temperature, A the pre-exponential factor, k is the corrosion rate, ΔS_a^* is the entropy of activation, ΔH_a^* is the enthalpy of activation, h is Planck's constant and N is the Avogadro's number.

Table 2
Inhibition efficiency (IE(%)) of some quinazoline derivatives for copper dissolution in 2 M HNO_3 at different temperatures and at different concentrations of investigated compounds and at 120 min immersion

Conc., M	Temp., °C	(IE(%))				
		BOA	QA	HQA	ThQA	SHQA
1×10^{-6}	30	23.0	26.1	33.1	32.7	37.9
	35	20.7	23.2	26.6	32.0	36.0
	40	19.6	22.5	25.5	30.5	34.9
	45	18.4	21.6	25.5	29.0	33.7
	50	16.3	19.6	22.6	25.7	31.8
5×10^{-6}	30	30.3	32.1	35.4	37.5	43.8
	35	27.6	29.2	31.9	35.8	42.7
	40	25.3	28.9	29.7	33. 5	40.6
	45	23.7	26.5	27.8	31.7	38.4
	50	21.6	24.7	27.4	30.6	36.4
9×10^{-6}	30	36.1	37.3	40.6	43.5	50.4
	35	32.3	35.1	37.7	41.1	46.8
	40	30.9	32.7	35.4	39.4	44.3
	45	28.9	29.7	32.6	36.5	42.0
	50	26.6	29.1	32.8	34.2	39.0
13×10^{-6}	30	40.0	42.0	46.5	49.5	55.6
	35	36.7	39.0	42.7	45.9	51.7
	40	35.8	38.2	40.5	43.8	48.5
	45	33.8	35.7	37.4	40.5	45.2
	50	30.6	32.5	35.9	37.6	42.2
17×10^{-6}	30	42.0	45.0	50.4	52.0	58.9
	35	40.8	43.2	46.7	50.9	57.6
	40	39.6	41.9	44.9	47.4	53.4
	45	37.5	39.4	42.3	44.8	49.6
	50	34.4	36.6	39.7	42.5	45.5

Fig. 3 shows the Arrhenius plot of ln k vs. $1/T$ in the absence and presence of 1.3×10^{-5} M from all inhibitors. The E_a^*can be obtained from the slopes of these lines. Moreover, a plot of log (k/T) against $1/T$ should give straight lines (Fig. 4) with slope of ($-\Delta H_a^*/2.303\ RT$) and intercept of [log (RT/Nh) – $\Delta S_a^*/2.303\ R$]. The calculated parameters are given in Table 3. Inspection of these data reveals that the apparent activation energy in HNO_3 solution in the absence of inhibitors was 72 kJ mol^{-1} which is in good agreement with the values obtained by Fouda et al. [24] in which he found that the activation energy of copper in 3 M HNO_3 is 72.4 kJ mol^{-1}. Also, since the activation energy (E_a^*) is more than 40 kJ mol^{-1}, the process is diffusion controlled. The increase of E_a^* in the presence of the inhibitor indicates the physical adsorption or weak chemical bonding between the inhibitor molecules and copper surface [25]. The entropy of activation in the absence and presence of inhibitor is large and negative. This implies that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on

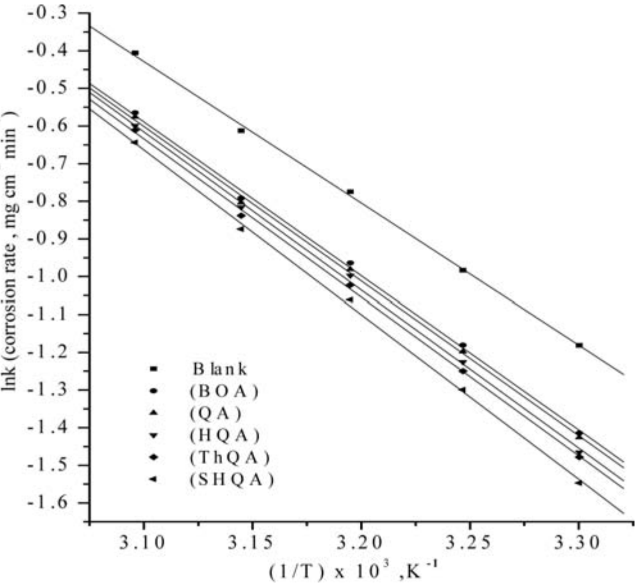


Fig. 3. log k vs. $1/T$ curves for copper dissolution in the absence and presence of 13×10^{-6} M inhibitors.

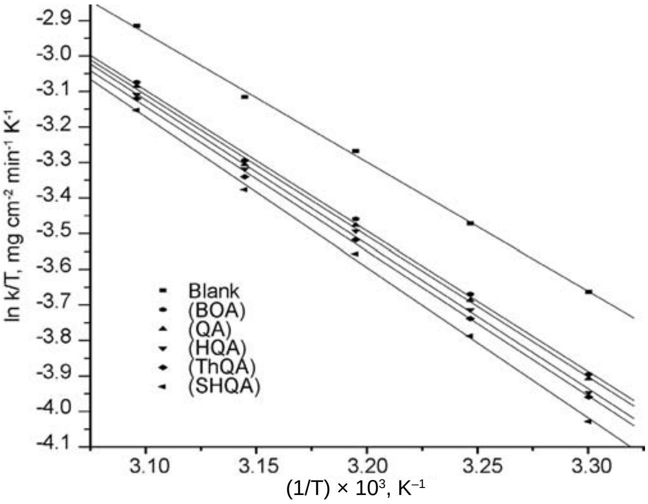


Fig. 4. log k/T vs. $1/T$ curves for copper dissolution in the absence and presence of 13×10^{-6} M inhibitors.

Table 3
Activation parameters of the copper in 2 M HNO_3 in the absence and presence of 13×10^{-6} M of investigated compounds

Inhibitor	Activation parameter		
	E_a^* (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	$-\Delta S^*$ (J mol^{-1} K^{-1})
Blank	72.0	69.4	38.6
BOA	78.2	75.6	22.3
QA	78.5	75.9	21.8
HQA	80.3	77.7	16.5
ThQA	80.4	77.8	16.4
SHQA	83.6	81.0	7.0

going from reactants to the activated complex [26,27]. The positive sign of ΔH_a^* indicates that the corrosion process is endothermic one.

3.3. Synergistic effect of halide anions

The effect of Cl^- and Br^- ions on the corrosion inhibition of copper in 2 M HNO_3 solution in the 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^- and Cl^-) are given in Table 4. The data in Table 4 indicates that the addition of halide ions to the system resulted in a significant increase in (IE(%)). This may be attributed to the stabilization of adsorbed halide ions by means of electrostatic interaction with the inhibitor which leads to greater surface coverage and hence inhibition [28,29]. The extent of the effect follows the order: $Br^- > Cl^-$. Similar observations have been reported [30,31]. This order depends on electronegativity and ionic radii of the halide ions (electronegativity decreases from $Cl^- = 3.0$ to $Br^- = 2.8$ and ionic radii increase in the order $Cl^- = 0.09$ nm, $Br^- = 0.114$ nm). It is clear that halide anions play a dominate role in the corrosion inhibition of copper in the presence of quinazoline derivatives. The inherent reason is that the copper surface has positive charge and it is difficult for the positively charged quinazoline molecules to approach this positively charged copper surface. However, the specific adsorption of halide anions on the positively charged copper surface by means of electrostatic attraction results in a negatively charged surface layer. Thus cationic molecules can be adsorbed readily on copper surface by electrostatic interaction between halide layer and the cationic inhibitor molecules, thus leading to a significant decrease in corrosion rate.

Table 4
Inhibition efficiency at different concentrations of inhibitors + 1×10^{-4} M KBr and KCl as determined from weight loss method at 30°C and at 120 min immersion

Halide anions	Concentration (M)	(IE (%))				
		(BOA)	(QA)	(HQA)	(ThQA)	(SHQA)
KBr	1×10^{-6}	68.4	70.5	73.1	75.8	76.8
	5×10^{-6}	71.1	73.9	76.6	79.2	80.2
	9×10^{-6}	73.5	75.1	77.7	80.5	81.4
	13×10^{-6}	75.3	76.0	79.0	81.6	83.2
	17×10^{-6}	76.0	78.1	80.2	83.4	85.2
KCl	1×10^{-6}	59.9	61.9	64.5	65. 6	68.2
	5×10^{-6}	63.1	65.2	66.8	68.4	72.6
	9×10^{-6}	67.0	68.6	70.1	71.7	74.4
	13×10^{-6}	70.1	70.7	72.2	74.9	77.5
	17×10^{-6}	73.9	75.0	75.2	78.7	80.2

3.4. Adsorption isotherm

Attempts were made to fit θ values to various isotherms including Frumkin, Langmuir and Temkin. By far the best fit was obtained with Frumkin isotherm. This Frumkin model has been used for other inhibitor systems [32]. According this isotherm θ is related to concentration inhibitor via:

$$\left[\theta/(1-\theta)\exp(-2a\theta)=KC\right] \tag{9}$$

or its linear form:

$$\ln\left[\theta/(1-\theta)C\right]=\ln K+2a\theta \tag{10}$$

where θ is the degree of surface coverage, *C* the inhibitor concentration, *a* is the parameter of interaction between molecules adsorbed on the metal surface and *K* the equilibrium constant of adsorption.

Fig. 5 represents the linear relationship of the Frumkin adsorption isotherm. By plotting ln [θ / (1 – θ) *C*] vs. θ straight lines were obtained for all investigated compounds (data obtained from weight loss method). The equilibrium constant (*K*) is related to the free energy of adsorption (ΔG^0_{ads}) by:

$$K=(1/55.5)\exp\left(-\Delta G^0_{ads}/RT\right) \tag{11}$$

where 55.5 is the molar concentration of water in solution in mol L^{-1}. The linear fitting slope for the Frumkin's isotherms gave the values of *a* and the intercepts gave the values of *K* for all investigated compounds. The results are given in Table 5. The increasing values of *K* from compound BOA to compound SHQA reflects the increasing capability, due to structural formation, on the metal surface [33], and the negative values of *a* indicates the presence of repulsive forces between the adsorbed species of investigated compounds. And also, the lower values of ΔG^0_{ads} indicate that these compounds are physically adsorbed on Cu surface.

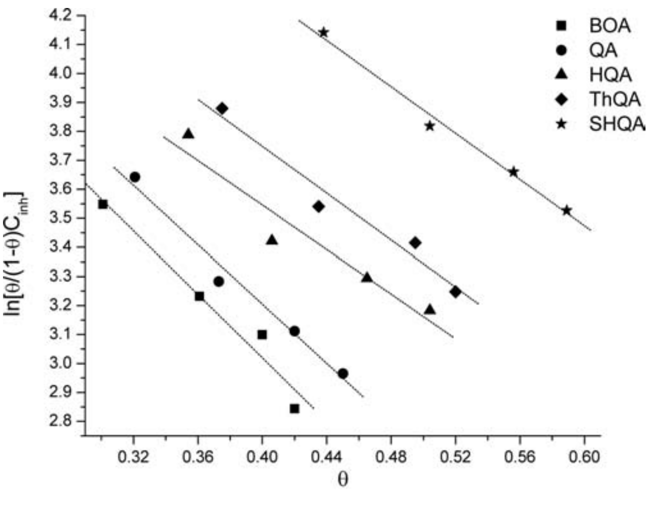


Fig. 5. The linear form of Frumkin adsorption isotherm of investigated compounds on Cu surface from in 2 M HNO_3 solution at 30°C.

Table 5
Interaction parameter (*a*), adsorption equilibrium constant (*K*), free energy (ΔG^o_{ads}) and regression constant (R^2) of Cu dissolution in the presence of investigated compounds at 30°C in 2 M HNO_3

Inhibitor	–*a*	K_{ads} (M^{-1})	$-\Delta G^o_{ads}$ (kJ mol^{-1})	R^2
BOA	2.7	182.5	23.2	0.9786
QA	2.6	190.6	23.3	0.9901
HQA	1.9	201.0	22.9	0.9608
ThQA	2.0	214.3	23.6	0.9810
SHQA	2.0	355.9	23.2	0.9950

It is generally assumed that the adsorption of the inhibitor at the metal-solution interface is the first step in the action mechanism of inhibitors in aggressive acid media. Four types of adsorption may take place involving organic molecules at the metal-solution interface: i) electrostatic attraction between charged molecules and the charged metal, (ii) interaction of unshared electron pairs in the molecule with the metal, (iii) interaction of π-electrons with the metal and (iv) a combination of the above [35].

3.5. Polarization studies

Both the anodic and cathodic polarization curves of copper in 2 M HNO_3 in the absence and presence of different concentrations of compound (SHQA) are shown in Fig. 6. 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 ($j_{corr.}$), and Tafel slopes β_a and β_c derived from the polarization curves are given in Table 6. From these data one can say that these compounds behave as mixed-type inhibitors (the presence of inhibitors does not prominently shift the corrosion potential) and also the presence of these additives cause a remarkable decrease in the corrosion rate (Hence increase in (IE (%)) i.e. shifts the anodic curves to more positive potentials and the cathodic curves to more negative potentials. This may attributed to adsorption of inhibitors over the corroded surface [35]. Both β_a and β_c change upon addition of inhibitors, which indicates that the inhibitors affect both anodic and cathodic reactions [36].The data of Table 7 shows the variation of the (IE (%)) of these compounds with their concentrations and the corrosion rate (CR) obtained from polarization method at 30°C. The order of increasing inhibition efficiency of these compounds is: BOA < QA < HQA < ThQA < SHQA

Furthermore, (*IE(%)*) obtained from gravimetric and electrochemical polarization curves are in reasonably good agreement.

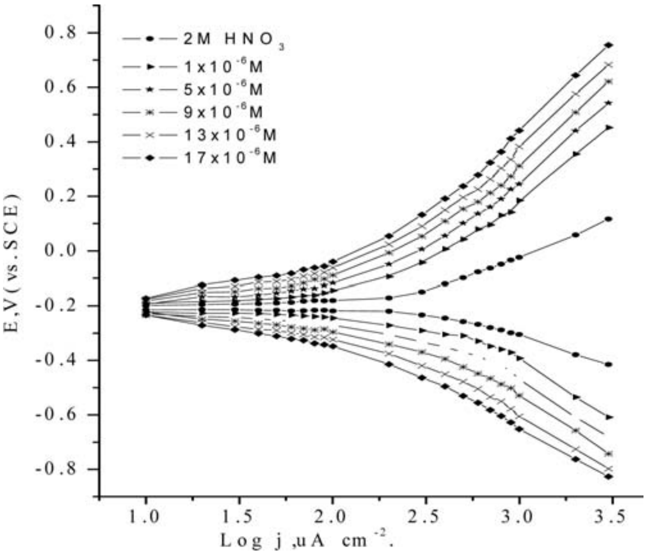


Fig. 6. Galvanostatic polarization curves of copper in 2 M HNO_3 alone and containing different concentrations of compound (SHQA) at 30°C.

3.6. Mechanism of inhibition

The polar organic compounds acting as corrosion inhibitors are adsorbed on the surface of metals, forming a charge transfer complex between their polar atoms and the metal. The size, shape and orientation of the molecule and the electronic charge on the molecule determine the degree of adsorption and hence the effectiveness of the inhibitor.

All the investigated compounds have two adsorption active centers (Fig. 7), so, the numbers of active center have no effect. Compound (SHQA) is the most efficient inhibitor because of its higher molecular size (318) and the 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 (ThQA) comes next in the sequence of decreased inhibition efficiency, because of its lower molecular size (232) than compound (SHQA). Compound (HQA) comes after compound (ThQA) in the sequence of decreased inhibition efficiency. This is due to its lower molecular size (230) than compounds (SHQA and ThQA) and the N atom in the molecule is less basic than S atom in compound (d). Compound (QA) has lower molecular size (216) than compound (HQA), so, it comes after it in inhibition efficiency. Compound (BOH) is the least effective inhibitor. This is due to its lower molecular

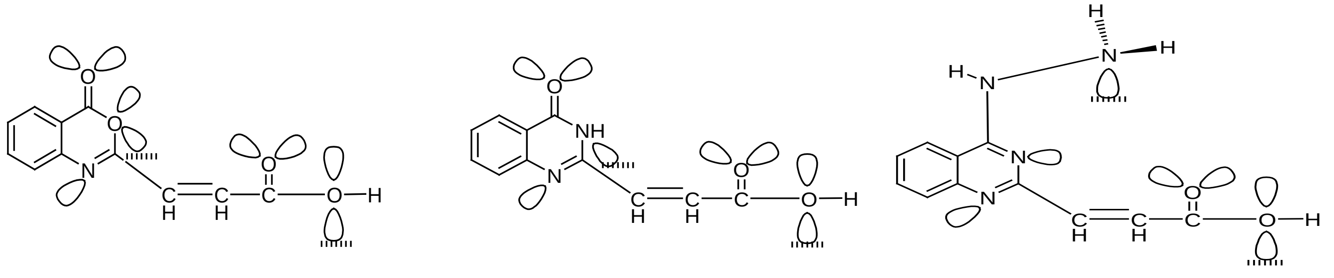
Table 6
Corrosion parameters obtained from galvanostatic polarization of Cu in 2 M HNO_3 containing various concentrations of inhibitor (SHQA) at 30°C

Concentration (M)	$-E_{corr}$ (mV)	j_{corr} (μA cm^{-2})	β_a (mV dec^{-1})	$-\beta_c$ (mV dec^{-1})	(IE(%))	θ
0.0	0.20	192	244	142	—	—
1×10^{-6}	0.20	118	388	193	38.4	0.384
5×10^{-6}	0.20	102	426	249	46.5	0.465
9×10^{-6}	0.18	92	450	320	52.0	0.520
13×10^{-6}	0.22	85	527	346	55.3	0.553
17×10^{-6}	0.25	75	579	343	60.9	0.609

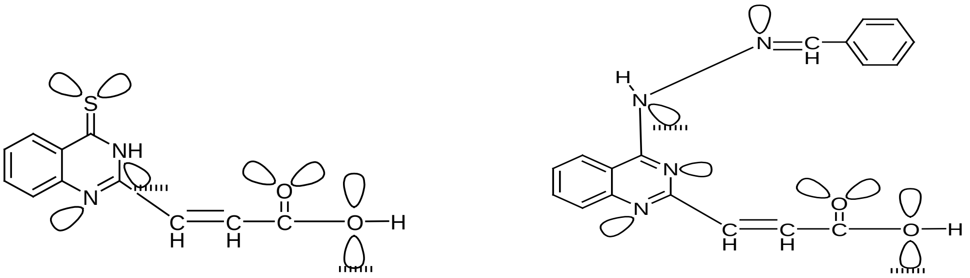
Table 7
Variation of the percentage inhibition efficiency (IE(%)) and rate of corrosion (CR) of some quinazoline derivatives with their concentrations obtained from polarization method at 30°C

Concentration (M)	(IE (%))				
	BOA	QA	HQA	ThQA	SHQA
1×10^{-6}	24.9 (1.974)	29.4 (1.569)	28.3 (1.594)	35.1 (1.443)	38.4 (1.366)
5×10^{-6}	31.7 (1.518)	33.4 (1.481)	34.1 (1.458)	39.1 (1.354)	46.5 (1.189)
9×10^{-6}	36.1 (1.420)	38.6 (1.365)	41.6 (1.298)	43.8 (1.249)	52.0 (1.067)
13×10^{-6}	40.9 (1.314)	41.9 (1.296)	47.7 (1.163)	50.1 (1.109)	55.3 (0.984)
17×10^{-6}	42.8 (1.272)	46.6 (1.187)	50.2 (1.107)	53.8 (1.027)	60.9 (0.869)

*The values in the parenthesis indicate the corrosion rate (CR in mm/y)



Compound (BOA) Compound (QA) Compound (HQA)



Compound (ThQA) Compound (AHQA)

Fig. 7. Skeletal representation of the mode of adsorption of all quinazoline compounds.

size (217) than compounds (SHQA, ThQA, HQA) and the O atom in the molecule is less basic than N atom in compound (QA). The order of inhibition efficiency of the investigated compounds revealed by the weight loss and galvanostatic polarization measurements is the same. 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.

4. Conclusions

The following can now be stated:

(i) Quinazoline compounds act as inhibitors for the corrosion of Cu in 2 M HNO_3 .

(ii) Inhibition efficiency increases with increase in inhibitor concentration and decreases with increase in temperature.

(iii) On addition of Br^- and Cl^- ions to 2 M HNO_3 containing inhibitors, a synergistic or cooperative effect occurred thus inhibiting Cu corrosion.

(iv) The Frumkin adsorption isotherm fits the experimental data obtained in this study.

(v) The values of E_a^* and ΔG^o_{ads} indicate the physical adsorption of these compounds on Cu surface.

(vi) Polarization results indicate that these compounds behave as mixed-type inhibitors.

(vii) Thermodynamic parameters also revealed that the adsorption process is spontaneous.

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