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Synthesis, Characterization and Comparative Study of Functionalized Quinoxaline Derivatives towards Corrosion of Copper in Nitric Acid Medium

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Three quinoxalines named ethyl 2-(4-(2-ethoxy-2-oxoethyl)-2-*p*-tolylquinoxalin-1(4*H*)-yl)acetate (Q1), 1-[4-acetyl-2-(4-chlorophenyl)quinoxalin-1(4*H*)-yl]acetone (Q2) and 2-(4-methylphenyl)-1,4-dihydroquinoxaline (Q3) have been newly synthesised and tested as corrosion inhibitors for copper in 2M HNO_3. The investigation has been conducted at 303K using weight loss measurements, potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS) methods). The synthesis of quinoxaline functionalized was achieved by using quinoxaline. After purification, the products obtained are characterised using ^1H NMR and ^{13}C NMR spectroscopy. Results obtained show that Q1 is the best inhibitor and its inhibition efficiency (E %) increases with the increase of inhibitor concentration and reaches up to 97% at 10^{-3} M Q1. Potentiodynamic polarisation studies clearly reveal that the presence of inhibitors does not change the mechanism of hydrogen evolution and that they act predominately as cathodic inhibitors.

Keywords: Copper , Nitric acid, Quinoxalines, Polarisation curves, Impedance.

1. INTRODUCTION

Corrosion is spontaneous destruction of material due to its interaction with an aggressive environment. In liquid solutions, attack of metals is principally an electrochemical process [1]. To stop or retard corrosion in acidic environment, organic inhibitors are added to form a barrier against reaction to occur. Inhibitors act by adsorption facilitated by the presence of electronegative functional groups and л-electron in triple or conjugated double bonds as well as heteroatoms like sulphur, phosphorus, nitrogen and oxygen in their structure. Two modes of adsorption are generally exhibited separately or competitively [2-4].

A perusal of the literature on corrosion inhibitors reveals that most organic inhibitors employed as corrosion inhibitors contain nitrogen, oxygen, sulphur and/or aromatic ring in their molecular structure [5–7]. Among the organic compounds selected, azoles, amines… have been studied extensively because of their corrosion inhibition properties [7–11]. Quinoxaline derivatives recently receive more and more attention of researchers and provided on corrosion phenomenon efficiency which attained more than 97% [12-14].

In the present paper, three quinoxalines derivatives newly synthesised and investigated as corrosion inhibitors of copper in 2M HNO_3 by gravimetric, potentiokinetic polarization methods and electrochemical impedance spectroscopy (EIS). The chemical structures of the studied quinoxalines derivatives are given in Figure 1.

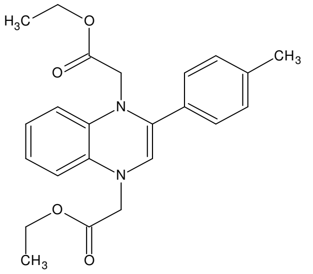
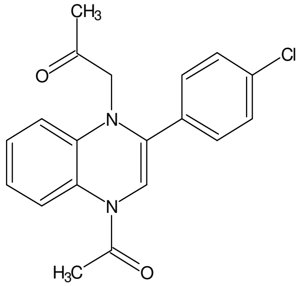
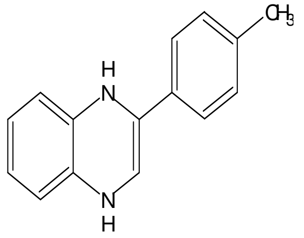
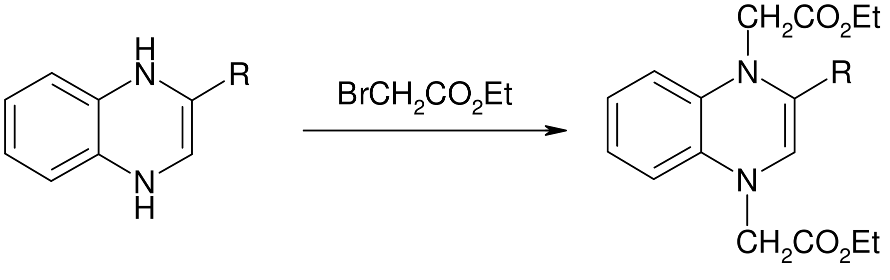
Structure			
name	ethyl 2-(4-(2-ethoxy-2-oxoethyl)-2-*p*-tolylquinoxalin-1(4*H*)-yl)acetate	1-[4-acetyl-2-(4-chlorophenyl)quinoxalin-1(4*H*)-yl]acetone	2-(4-methylphenyl)-1,4-dihydroquinoxaline
abbreviation	Q1	Q2	Q3

Figure 1. The molecular structure of the studied quinoxaline derivatives.

2. EXPERIMENTAL PART

The synthesis of quinoxalines functionalized were synthesised according to Scheme 1 [15-17]. To a solution of quinoxaline 0.44 g (2 mmol) in acetonitrile (20 mL) was added 14 mL of ethyl bromoacetate. The mixture was refluxed for 1h30. After cooling, the quinoxaline functionalized was filtered and recrystallised in acetonitrile.



Scheme 1. The schematic diagram for the synthesis of quinoxaline functionalized R = (4-$CH_3C_6H_4$)

In the ^1H NMR spectrum , in addition to the appearance of aromatic protons between 7.59 and 8.22 ppm, the signals at 5.30 (s, CH_2N_1), 4.13 (s.CH_2N_4), 2.50 (s, CH_3), 1.22 (t. CH_3), 4.15 (q, CH_2) and 7.4 (s, CH) ppm were observed .

The proton decoupled ^{13}C NMR spectrum, The signals due to aromatic and ethylenic carbons at 114.2, 117.5, 127.8, 130.3, 130.9, 131.7, 144.4 and 152.4 ppm and the signals at 167.9 (CO), 21.7 (CH_3), 14.3 ($\underline{CH_3}CH_2$), 27.7 (OCH_2), 62.3 (CH_2N_1), 47.8 (CH_2N_4) were observed.

Copper strips containing 99.5 wt.% Cu, 0.001wt.% Ni, 0.019 wt.% Al, 0.004 wt.% Mn, 0.116 wt.% Si and balance impurities were used for electrochemical and gravimetric studies. The Copper samples were mechanically polished using different grades of emery paper, washed with double distilled water, and dried at room temperature. Appropriate concentration of aggressive solutions used (2M HNO_3) was prepared using double distilled water.

Gravimetric experiments were carried out in a double walled glass cell. The solution volume was 50 cm^3; the temperature of 303 K was controlled thermostatically. The weight loss of copper in 2M HNO_3 with and without the addition of inhibitor was determined after immersion in acid for 1h. The copper specimens were rectangular in the form (2 cm×2 cm × 0.20 cm).

The electrolysis cell was Pyrex of cylinder closed by cap containing five openings. Three of them were used for the electrodes. The working electrode was copper with the surface area of 0.28 cm^2. Before each experiment, the electrode was polished using emery paper until 2000 grade. After this, the electrode was cleaned ultrasonically with distillate water. A saturated calomel electrode (SCE) was used as a reference whose standard potential is 241 mV/HNE at 30 °C. All potentials were given with reference to this electrode. The counter electrode was a platinum plate of surface area of 1 cm^2. The aggressive medium used here is HNO_3 solution. The organic compound tested is quinoxaline. Its molecule formula is shown in Fig. 1. The concentration range of this compounds was 10^{-3} to 10^{-6} M.

The working electrode was immersed in test solution during 30 minutes until a steady state open circuit potential (E_{ocp}) was obtained. The polarization curve was recorded by polarization from -150 mV to 150 mV under potentiodynamic conditions corresponding to 1 mV/s (sweep rate) and under air atmosphere. The potentiodynamic measurements were carried out using equipment Tacussel Radiometer PGZ 301, which was controlled by a personal computer.

The electrochemical impedance spectroscopy measurements were carried out using a transfer function analyser (Tacussel Radiometer PGZ 301), with a small amplitude ac. Signal (10 mV rms), over a frequency domain from 100 KHz to 10 mHz at 30°C and an air atmosphere. The polarization resistance R_p, is obtained from the diameter of the semicircle in Nyquist representation.

3. RESULTS AND DISCUSSION

The corrosion tests were conducted on the corrosion of copper in 2M HNO_3 solution in the absence and presence of addition of Q1, Q2 and Q3 at different concentrations was monitored by weight loss at 1 h. The inhibition efficiency (E%) is estimated by the following equation:

$$E_w\% = \frac{(W_{corr}^0 - W_{corr})}{W_{corr}^0} \times 100 \qquad (1)$$

where W_{corr} and W^o_{corr} are the corrosion rates (CR) of copper with and without inhibitor, respectively.

Table 1. Gravimetric results of copper in 2M HNO_3 without and with addition of inhibitors at 303 K.

C (M)	Q1		Q2		Q3	
	W(mg/cm^2.h)	E_w (%)	W(mg/cm^2.h)	E_w (%)	W(mg/cm^2.h)	E_w (%)
Blank	1.78	-	1.78	-	1.78	-
10^{-3}	0.053	**97.0**	0.147	**91.8**	0.306	**82.8**
5×10^{-4}	0.071	96.0	0.278	85.9	0.380	78.6
10^{-4}	0.155	91.2	0.466	73.8	0.561	68.5
5×10^{-5}	0.740	58.4	1.001	51.0	0.870	51.1
10^{-5}	1.255	29.5	1.337	24.9	1.396	21.6
10^{-6}	1.350	24.1	1.427	19.7	1.515	14.9

Table 2. Polarisation data of Copper in 2M HNO_3 without and with addition of inhibitors at 303 K.

	C (M)	E_{corr} (mV/SCE)	$-b_c$ (mV/dec)	I_{corr} (μA/cm^2)	IE (%)
HNO_3	2	34.0	304	365.1	-
Q1	10^{-3}	-50.9	209	25.9	**92.9**
	10^{-4}	-21.7	193	55.7	84.7
	10^{-5}	3.5	213	279.2	23.5
	10^{-6}	16.4	190	289.1	20.8
Q2	10^{-3}	-8.0	172	47.9	**86.9**
	10^{-4}	6.1	201	119.9	67.2
	10^{-5}	25.7	246	275.2	24.6
	10^{-6}	26.2	242	291.1	20.2
Q3	10^{-3}	4.9	196	79.1	**78.3**
	10^{-4}	8.5	155	122.0	66.6
	10^{-5}	8.8	200	295.0	19.2
	10^{-6}	13.4	211	323.6	11.4

Results obtained are collected in Table 1 and indicate that the CR values fall down in the presence of quinoxalines tested. The lower value is obtained at 10^{-3}M Q1. This inhibitory action is better shown by the inhibition efficiency which grows with inhibitor concentration to attain 97.0% for Q1, 91.8% for Q2 and 82.8% for Q3 at 10^{-3}M. Then, the three inhibitors investigated exhibit on the copper corrosion in 2M HNO_3, but Q1 may be selected as the best one. The inhibitory action of these quinoxalines may be classified as:

$$Q1 > Q2 > Q3$$

Polarisation essays were undertaken to show the partial action of inhibitors on anodic and cathodic polarization branches. Figures 2–4 regroup the i-E curves for copper in 2M HNO_3 with and without various concentrations of inhibitors used.

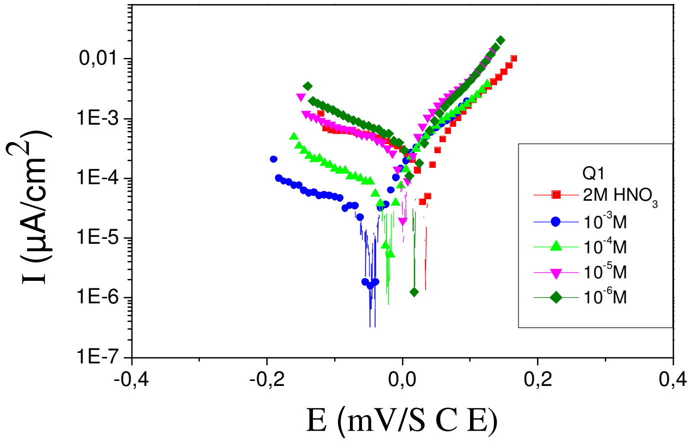


Figure 2. Polarisation curves for Copper in 2M HNO_3 containing different concentrations of Q1

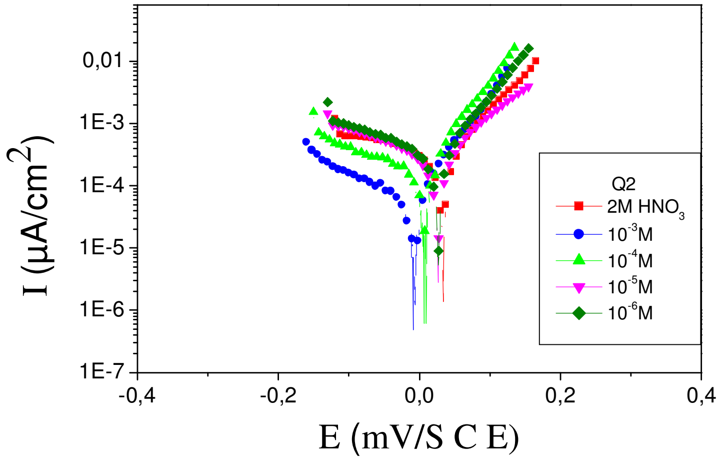


Figure 3. Polarisation curves for Copper in 2M HNO_3 containing different concentrations of Q2

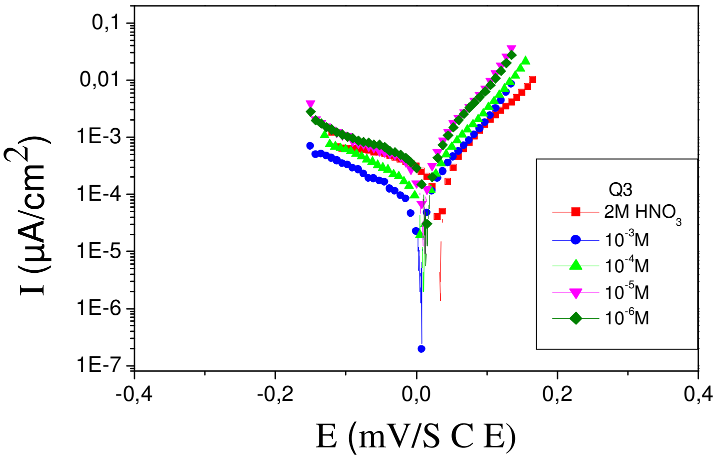


Figure 4. Polarisation curves for Copper in 2M HNO_3 containing different concentrations of Q3

Deduced corrosion parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), Tafel slopes (b_c) and the inhibition efficiency (E%) were determined by Tafel extrapolation method and are given in Table 2. E% was calculated using the equation 2:

$$E\% = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} \times 100 \qquad (2)$$

It is clear that I_{corr} values decreased in the presence of inhibitors and decreased significantly with increasing inhibitors concentration. The maximum E% (93%) is obtained at 10^{-3}M Q1. This result agrees that obtained by gravimetric method. The characteristics of curves revealed that quinoxalines acted as cathodic inhibitors while Q1-3 acted principally on cathodic branche with a remarkable shift of E_{corr} to more negative values. This observation means that quinoxaline molecules acted on cathodic sites to block the reduction of hydrogen ion onto copper surface. The cathodic current versus potential curves gave rise to Tafel lines indicating that the hydrogen evolution reaction is activation-controlled, b_c values is widely modified and then the addition of inhibitors modifies the mechanism of the proton discharge reaction. The anodic branches are slightly affected in the presence of these inhibitors. Explanation of efficacy may be based on the molecular structure of inhibitors, the substitution of two hydrogen atoms of nitrogen of Q3 by two ester groups ($CH_2COOCH_2CH_3$) in Q1 has major role in adsorption by increasing of E% from 78 to 93% at 10^{-3}M. In other hand, the replacement of methyl group in Q1 by chloride in Q2 in para position provokes a decrease of efficiency.

Figure 5 shows the Nyquist plots of copper in nitric acid obtained in the absence and presence of Q1 at different concentrations. The impedance parameters estimated are given in Table 3. The charge-transfer resistance values (R_{ct}) were calculated from the difference in impedance at lower and higher frequencies as suggested by Tsuru et al. [18]. The values of C_{dl} were obtained from the equation 3 using the maximum frequency (−Zimax):

$$f(-Zi\max) = \frac{1}{2\pi C_{dl} R_t} \qquad (3)$$

In this case, the inhibition efficiency is calculated using charge transfer resistance from equation 4:

$$E_Z \% = \frac{R_{t(inh)} - R_t}{R_{t(inh)}} \times 100 \qquad (4)$$

where $R_{t(inh)}$ and R_t are the charge transfer resistance in the presence and absence of Q1, respectively.

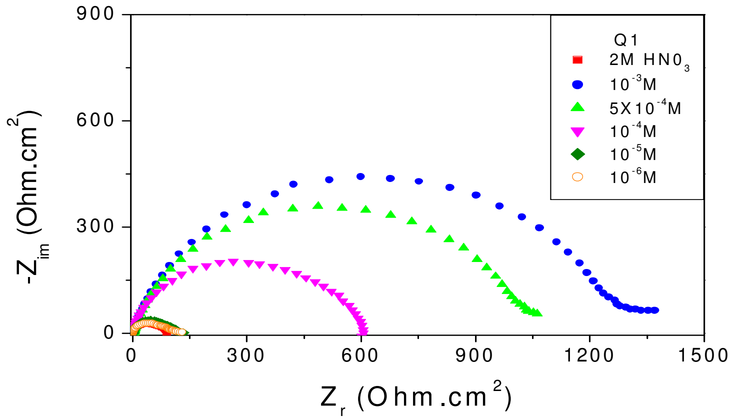


Figure 5. Nyquist diagrams Copper in 2M HNO_3 without and with different concentrations of Q1

Table 3. EIS parameters for the Copper corrosion in 2M HNO_3 at different concentrations of Q1

	Conc (M)	R_t (Ω.cm^2)	f_{max} (Hz)	C_{dl} (μF/cm^2)	E_{Rt} (%)
HNO_3	2	091.41	15.82	110.1	-
Q1	10^{-3}	1254.8	02.50	050.7	**92.7**
	$5x10^{-4}$	1021.1	02.81	055.4	91.1
	10^{-4}	606.9	04.46	058.8	84.9
	10^{-5}	122.8	12.50	103.7	25.6
	10^{-6}	118.9	12.50	107.0	23.2

It is clear from these plots that impedance response of copper in nitric acid has significantly changed after the addition of inhibitor. The results can be interpreted in terms of equivalent circuit of the electrical double layer which has been used to model the copper–acid interface [19]. As can be seen in Fig. 5, Nyquist plots are depressed into the real axis and not perfect semicircles as expected from theory of EIS for assumed equivalent circuit and this is generally attributed to the inhomogeneity of the metal surface arising from surface roughness or interfacial phenomena [20,21]. Table 3 indicates that, R_t value increases and C_{dl} value decreases with increasing Q1 concentration. The decrease in C_{dl} values is generally attributed to a decrease in local dielectric constant and/or an increase in the thickness of electrical double layer. This suggests that inhibitor molecules inhibit the corrosion rate by adsorption at metal/solution interface [22].

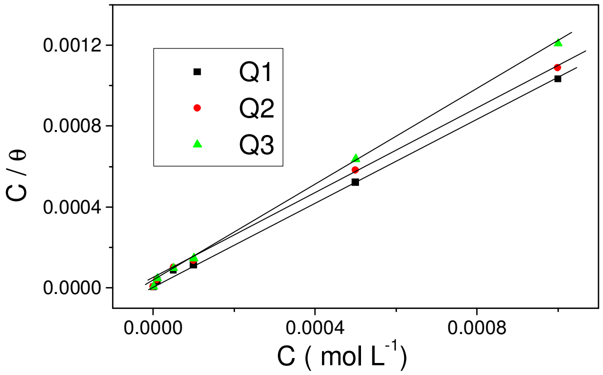


Figure 6. The Langmuir adsorption isotherm of quinoxaline tested

The adsorption isotherm study which describes the adsorptive behaviour of an organic inhibitor is important in order to get more data on the mechanism of corrosion inhibition. Interaction between inhibitor molecules onto the metal surface is formulated by adsorption isotherms. The wide used adsorption isotherms are Langmuir, Temkin, Frumkin and Freundluich. But the quite adequate and most encountered is the simplest one: Langmuir isotherm. The plots of C/θ against C are straight lines (Fig. 6) with slope close unity and regression coefficients, R^2, more than 0.999. This suggests Langmuir adsorption isotherm [23] for adsorption of inhibitor on the copper surface in nitric acid according to the following equation:

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{6}$$

where C is the concentration of inhibitor, K is the adsorptive equilibrium constant, and θ is the surface coverage.

The determined adsorption constants, K, are 58018.1, 34855.96 and 35586.4 for Q1, Q2 and Q3, respectively. To obtain the standard adsorption free energy (ΔG_{ads}), the following equation was employed:

$$K = \frac{1}{55.5}\exp\left(-\frac{\Delta G^{\circ}_{ads}}{\mathrm{RT}}\right) \tag{7}$$

The negative values of ΔG°_{ads} -37.7, -36.5 and -36.5 kJ mol^{-1} for Q1, Q2 and Q3, respectively, ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the copper surface. The more negative value for inhibitors indicates that this last is more strongly adsorbed on the copper surface [24].

Two modes of adsorption: chemisorption and physical adsorption are introduced in literature. A value of ΔG°_{ads} equals -40 kJ moll^{-1} is admitted as a threshold value between these modes of adsorption [25]. The estimated values for the adsorption of quinoxalines on Cu can be interpreted by physical adsorption.

4. CONCLUSIONS

These results obtained may lead to the following conclusions:

- Q1, Q2 and Q3 exhibited good inhibitory effect against copper corrosion in 2M HNO_3.
  Q1 is found to be more effective.
- The inhibition efficiencies are related to concentration and chemical structure of quinoxalines. The inhibition efficiencies increased with increasing inhibitor's concentration.
- They act principally as cathodic-type inhibitors.
  Quinoxalines adsorb according to Langmuir isotherm and physical adsorption is admitted.

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