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N-containing organic compound As An Effective Corrosion Inhibitor For Copper In 2M HNO_3 : Weight Loss and Quantum Chemical Study

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ABSTRACT

(2Z)-1-(4-chlorophenyl)-2-[(3E)-3-[2-(4-chlorophenyl)-2-oxoethylidene]-3,4dihydro quinoxalin-2 (1H)-ylidene]ethanone (Q4) was tested as inhibitor for the corrosion of copper in 2M HNO_3 *using gravimetric method at 303 – 343 K. The inhibitor (Q4) showed about 90% inhibition efficiency (E (%)) at an optimum concentration of* 10^{-3}*M. The inhibition efficiency increases with increase in inhibitor concentration but decrease with rise in temperature. Various parameters (*E_a*,* ΔG°_{ads}*,* K_{ads}*) for adsorption reveal a strong interaction between inhibitor and copper surface. The negative values of* ΔG°_{ads} *indicate the spontaneous adsorption of the inhibitor on copper surface. Kinetic parameters activation such as* E_a*,* ΔH°_a*,* ΔS°_a *and pre-exponential factor have been calculated and discussed. Further, theoretical calculations were carried out and relations between computed parameters and experimental inhibition efficiency were discussed.*

Keywords: Copper; Nitric Acid; Corrosion Inhibition; Quinoxaline; Weight Loss; Theoretical Calculations.

INTRODUCTION

The chemical industry employs copper and its alloys extensively for condensers, evaporators, fractionating columns, etc. Copper does not displace hydrogen from acid solutions and it is therefore unattacked in non-oxidising acid environments. Nevertheless, most acidic solutions contain dissolved air that enables some corrosion to take place. Many organic molecules are used to inhibit copper corrosion [1–15].

The primary step in the action of organic corrosion inhibitors in acid solutions is usually adsorption at the metal–solution interface. The adsorption process depends on the electronic characteristic of the molecules (adsorbate), the chemical composition of the solution, nature of the metal surface, temperature of the reaction and on the electrochemical potential at the metal–

solution interface [16]. The adsorption requires the existence of attractive forces between the adsorbate and the metal. According to the type of forces, adsorption can be physisorption or chemisorption or a combination of both [17]. Physisorption is due to electrostatic attractive forces between inhibiting organic ions or dipoles and the electrically charged surface of the metal. Chemisorption is due to interaction between unshared electron pairs or π electrons with the metal in order to form a coordinate type of bond. The adsorption occurs from active centers such as P, Se, S, N and O atoms, the double or triple bonds and also aromatic rings. This phenomenon may be reinforced by the formation of metallic complexes [1, 18–31]. This paper reported our attempt to use electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, weight loss and theoretical calculations to investigate the nature of adsorption of Quinoxaline on the copper surface. The structure of Q is shown in Fig. 1.

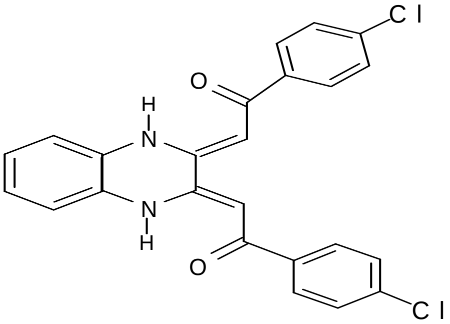

Fig .1 The molecular structure of Quinoxaline.

MATERIALS AND METHODS

2. Experimental Details

2.1. Materials and reagents

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.

2.3. Weight loss measurements

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 2 M HNO_3 with and without the addition of inhibitor was determined after immersion in acid for 1 h. The copper specimens were rectangular in the form (2 cm ×2 cm × 0.20 cm).

2.4. Quantum chemical calculations

Complete geometrical optimizations of the investigated molecules are performed using DFT (density functional theory) with the Beck's three parameter exchange functional along with the Lee–Yang–Parr nonlocal correlation functional (B3LYP) [32–34] with 6- 31G* basis set is implemented in Gaussian 03 program package [35]. This approach is shown to yield favorable geometries for a wide variety of systems. This basis set gives good geometry optimizations. The geometry structure was optimized under no constraint. The following quantum chemical parameters were calculated from the obtained optimized structure: the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), $\Delta E_{gap} = E_{HOMO} - E_{LUMO}$, the dipole moment (μ) and total energy (TE).

RESULTS AND DISCUSSION

3.1. Gravimetric measurements

- **Effect of temperature**

In the gravimetric experiment, a previously weighed metal (copper) coupon was completely immersed in 50 mL without and with quinoxaline at 10^{-3}M in different temperatures range (303K-343K) in an open beaker. From the weight loss results, the inhibition efficiency (%IE) of the inhibitor and degree of surface coverage (Θ) were calculated using equations 1 and 2 [36];

$$\%IE = \left(1 - \frac{W_1}{W_2}\right) \times 100 \qquad (1)$$

$$\Theta = 1 - \frac{W_1}{W_2} \qquad (2)$$

Where W_1 and W_2 are the weight losses for copper in the presence and absence of the inhibitor in HNO_3 solution and Θ is the degree of surface coverage of the inhibitor.

The corrosion process and protectiveness of an inhibitor are significantly dependent on the temperature. In this optic, effect of temperature is conducted in the absence and presence of Q studied at 10^{-3}M, in the range (303-343 K), during 1 hour of immersion. The data collected in Table 1, clearly show an increase of corrosion rate (W) at different temperatures. The increase is more pronounced for uninhibited acid. The values of inhibition efficiency obtained from the weight loss at various temperatures show that the inhibition efficiency decreases rapidly with increasing temperature indicating that higher temperature dissolution of copper predominates on adsorption of quinoxaline at the surface.

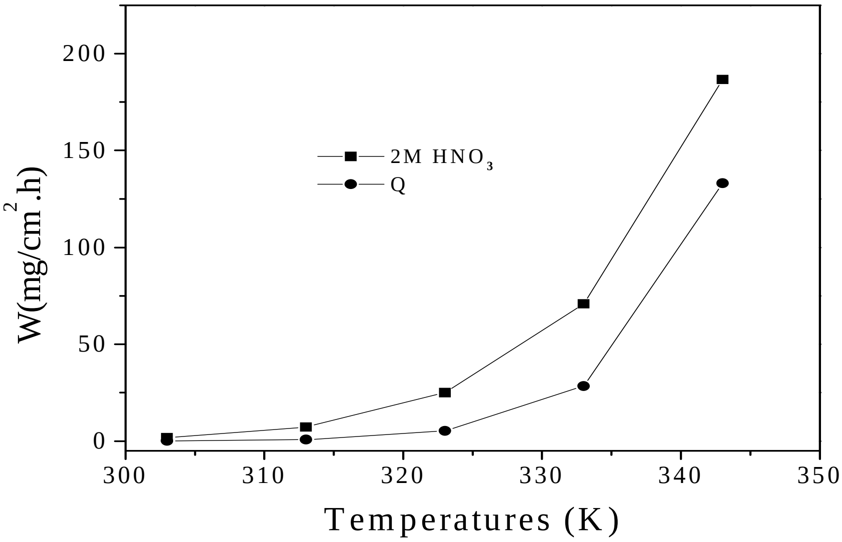

Fig 2. Variation of corrosion rate in 2M HNO_3 on copper surface without and with of optimum concentration of quinoxaline at different temperatures

- **Adsorption isotherm and thermodynamic activation parameters**

The adsorption isotherm study that describes the adsorptive behavior of organic inhibitor is important in order to know the mechanism of corrosion inhibition. Basic information dealing with interaction between inhibitor molecules and the metal surface can be provided by adsorption isotherms. The surface coverage (Θ) of different concentrations of inhibitor in acidic medium was calculated using the equation (2). In a previous study we showed that the adsorption of the inhibitor on the copper in the acid solution was found to accord with Langmuir adsorption isotherm [37].

Table 1. Various corrosion parameters for copper in 2M HNO_3 in absence and presence of optimum concentration of Q at different temperatures

Temperature (K)	Inhibitor	W(mg/cm^2.h)	E_w (%)	Θ
303	Blank	1.78	-	-
	Q	0.17	90.2	0.902
313	Blank	7.33	-	-
	Q	0.82	88.8	0.888
323	Blank	24.97	-	-
	Q	5.33	78.6	0.786
333	Blank	70.82	-	-
	Q	28.42	59.9	0.599
343	Blank	186.61	-	-
	Q	133.11	28.7	0.287

In this previous study we calculated $\Delta G°_{ads}$ and K_{ads} at different temperatures using the two equations 3 and 4. Free energy of adsorption was calculated using the relation:

$$\Delta G^{\circ}_{ads} = -2.303 RT log(55.55 K_{ads}) \qquad (3)$$

The value 55.55 is the molar concentration of water in solution [38], K_{ads} is the adsorption equilibrium constant and its value is given by

$$K_{ads} = \frac{\Theta}{C(1-\Theta)} \qquad (4)$$

The free energy of adsorption calculated from relation 6 is given in Table 2. The negative value of ΔG°_{ads} and the high values of the adsorption constant suggested that the adsorption of quinoxaline in 2M HNO_3 on the copper surface is a spontaneous process and the adsorbed layer is stable. Generally, for values of ΔG°_{ads} up to -20 kJ mol^{-1}, the type of adsorption is considered as physisorption. The adsorption process is due to electrostatic interactions between the charged molecules and the charged metal [39]. The calculated ΔG°_{ads} values are -28.57 to -33.84 kJ mol^{-1} indicated that adsorption mechanism of the investigated drug is typical of physical adsorption.

Table 2. Thermodynamic parameters for copper corrosion in 2M HNO_3 in absence and presence of 10^{-3} M quinoxaline at different temperatures

Tem (K)	Free acid			Q (10^{-3}M)				
	E_a (KJ/mol	ΔH°_a (kJ/mol)	ΔS°_a (J/mol.K)	E_a (KJ/mol)	ΔH°_a (kJ/mol)	ΔS°_a (J/mol.K)	K_{ads} (M^{-1})	ΔG°_{ads} (kJ/mol)
303	100.21	097.53	082.36	145.29	142.61	210.06	9235.41	-33.13
313							7968.61	-33.84
323							3677.27	-32.84
333							1494.39	-31.36
343							403.90	-28.57

Activation parameters like activation energy (E_a), enthalpy (ΔH_a°) and entropy (ΔS_a°) for the dissolution of copper in 2M HNO_3 in the absence and presence of 10^{-3}M quinoxaline was calculated from the Arrhenius equation (Eq. (5)) and the transition state equation (Eq. (6)) [40]:

$$C_R = A\exp\left(\frac{-E_a}{RT}\right) \tag{5}$$

$$C_R = \frac{RT}{Nh}\exp\left(\frac{\Delta S_a^\circ}{R}\right)\exp\left(-\frac{\Delta H_a^\circ}{RT}\right) \tag{6}$$

Where C_R is the corrosion rate, R the gas constant, T the absolute temperature, A the pre-exponential factor, h the Plank's constant and N is Avogrado's number, E_a the activation energy for corrosion process , ΔH_a° the enthalpy of activation and ΔS_a° the entropy of activation. Fig. 3 showed the Arrhenius plot of Ln C_R versus 1/T which gave straight lines with slopes equal to $-E_a$ /R. Again the Arrhenius plots of Ln (C_R/T) versus 1/T gave straight lines (Fig. 4) with slope ΔH_a° /R and intercept (Ln R/Nh + $\Delta S°_a$ /R) from which ΔH_a° and ΔS_a° values were calculated. The activation parameters are given in Table 2.

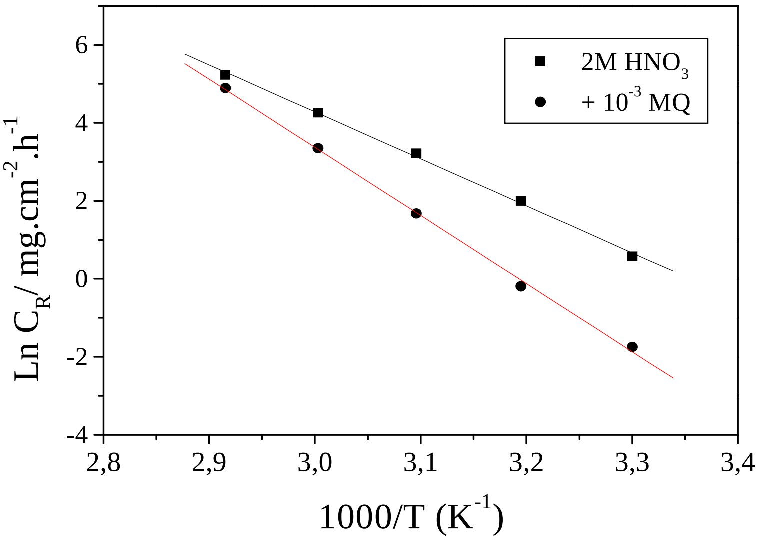

Fig. 3. Arrhenius plots of log C_R vs. 1/T for copper in 2M HNO_3 in the absence and the presence of quinoxaline at optimum concentration.

It was observed that the values of apparent activation energy E_a and enthalpy ΔH_a° are higher in presence of inhibitor than in its absence. This indicated that the energy barrier for the corrosion reaction increases in presence of inhibitor. The value of ΔS_a° is higher for inhibited solutions than that for free acid solutions. This suggested that an increase in randomness occurs on going from reactants to the activated complex. This increase in entropy of activation is attributed to the increase in solvent entropy [41].

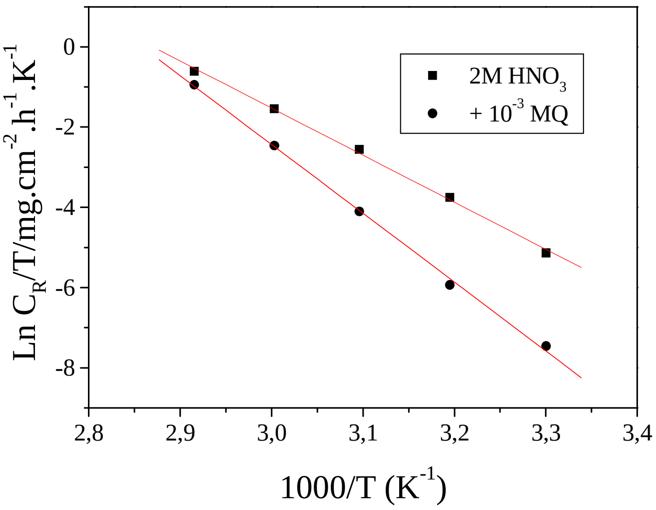

Fig. 4. Arrhenius plots of log C_R/T vs. 1/T for copper in 2M HNO_3 in the absence and the presence of quinoxaline at optimum concentration.

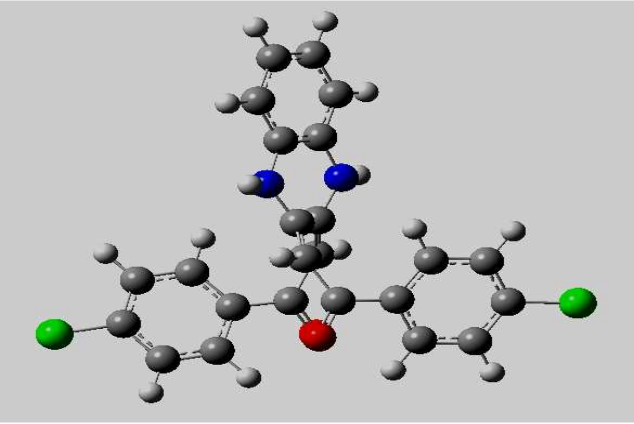

Fig .5. Optimized structure of the studied molecule obtained by B3LYP-6-31 G(d) method.

3.4. Theoretical study

Quantum chemical calculations have been widely used to study reaction mechanisms. They have also proved to be a very powerful tool for studying corrosion inhibition mechanisms [42]. Recently, theoretical prediction of the efficiency of corrosion inhibitors has become very popular in parallel with the progress in computational hardware and the development of efficient algorithms which assisted the routine development of molecular quantum mechanical calculations [43]. Some quantum chemical parameters, which are thought important to directly influence on electronic interaction between copper surface and inhibitor, are listed in Table 3. The energy of highest occupied molecular orbital (E_{HOMO}), the energy of lowest unoccupied molecular orbital (E_{HOMO}), the Gap energy of E_{LUMO} - E_{HOMO} (ΔE), the dipole moment (µ) and the total energy (TE). All these quantum chemical parameters were obtained after geometric optimization of the studied compound with respect to the all nuclear coordinates using Kohn–Sham approach at DFT level. The fully optimized structure of quinoxaline molecule is given in Fig. 5.

In order to construct a composite index of an inhibitor molecule it may be important to focus on parameters that directly influence the electronic interaction of the inhibitor molecules with the metal surface. These are mainly: energies of the molecular orbital, E_{HOMO}, E_{LUMO}, ΔE (E_{LUMO} - E_{HOMO}), dipole moment (μ) and total energy (TE). The values of these calculated quantum chemical parameters are listed in Table 3. Generally, the inhibition efficiency increases with decreasing E_{HOMO} and increasing of ΔE. It is known that in the chemical adsorption, an increase in E_{HOMO} causes significant increase in inhibition efficiency of organic compounds [44, 45] while the negative sign of E_{HOMO} coefficient has been interpreted by some researchers to be an indication of physical rather than chemical adsorption [46–48]. The inhibition efficiency also increases with decreasing LUMO energy of the inhibitors. It is known that E_{LUMO} indicates the ability of the molecule to accept electrons. Excellent corrosion inhibitors are usually those organic compounds, which are not only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal [49, 50]. The inhibition efficiency increases with the decreasing dipole moment of the inhibitors. As with energetic quantum parameters, some degree of confusion exists when dealing with dipole momentum data interpretation since scientific literature provides both positive [51, 52] as well as negative [45, 53] relationship between this factor and inhibition efficiency. Ju et al. Concluded that physical adsorption results from electrostatic interaction between the charged centers of molecules and charged metal surface, results in a dipole interaction of molecule and metal surface. Therefore, the positive sign of the coefficient of μ suggests that these inhibitors can be adsorbed on the alloy surface by physical mechanism [50]. Frontier orbital theory is useful in predicting the adsorption centers of the inhibitor molecules responsible for the interaction with surface metal atoms [54].

Table 3. Calculated quantum chemical parameters of studied inhibitor

Compound	TE (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE_{gap} (eV)	μ (Debye)
Q	-2104.50436	-5.5462	-1.8794	3.666	6.8433

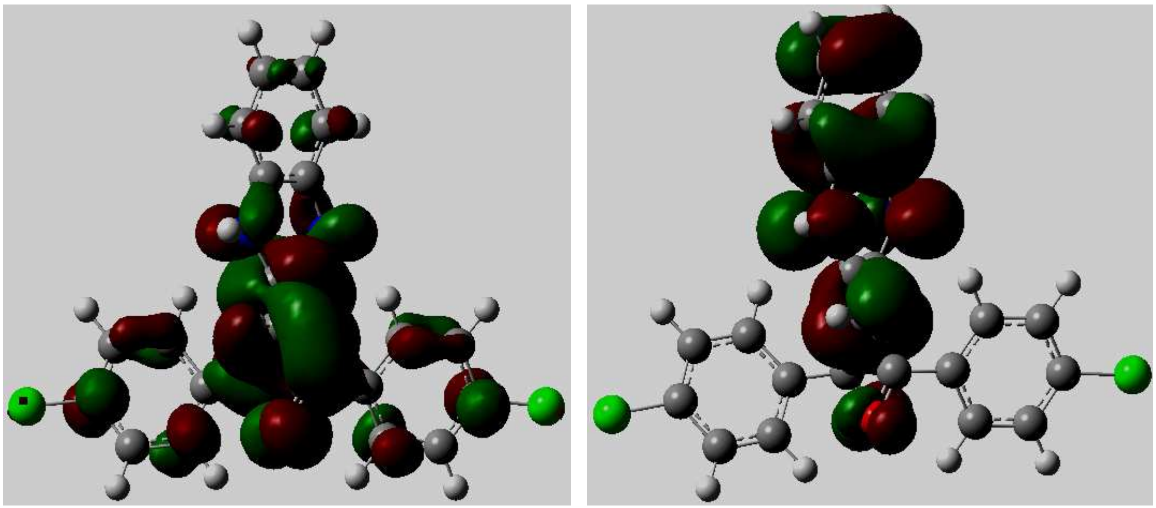

Fig .6 The frontier molecule orbital density distributions of ATA: HOMO (right); LUMO (left).

From the molecular orbital density distribution of the Q inhibitor (Fig. 6), we can see that the electron density of the HOMO location in the Q molecule is mostly distributed near the nitrogen (NH) and oxygen (= O) atoms and quinoxaline ring indicating that these are the favorite sites for adsorption, while the density LUMO was distributed around the entire molecule. The high value of E_{HOMO} (-5.5462 eV) has to indicate a tendency of the molecule to donate electrons to the appropriate acceptor molecules with low energy and empty molecular orbital, whereas the value of E_{LUMO} (-1.8794 eV) indicates its ability of the molecule to accept electrons. Consequently, the value of ΔEgap provides a measure for the stability of the formed complex on the metal surface.

The total energy of the quinoxaline is equal to -2104.50436 eV. This result indicated that quinoxaline is favourably adsorbed through the active centers of adsorption. Lower values of dipole moment (μ) will favour accumulation of the inhibitor in the surface layer and therefore higher inhibition efficiency [55].

CONCLUSION

The following conclusions can be drawn from this study:

❖ All measurements showed that the quinoxaline has excellent inhibition properties for the corrosion of copper in 2M HNO_3 solution. The weight loss measurements show that the inhibition efficiency decreases rapidly with increasing temperature and reaches its highest value (90.23%) at 10^{-3} M concentration at 303K.

❖ The negative values of ΔG°_{ads} indicate that the adsorption of the inhibitor molecule is a spontaneous process and an adsorption mechanism is typical of physisorption.

❖ The calculated quantum chemical parameters such as HOMO–LUMO gap ($\Delta E_{L\text{–}H}$), E_{HOMO}, E_{LUMO}, dipole moment (μ) and total energy (TE) were found to give good reasonably good correlation with the efficiency of corrosion inhibition.

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