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Quinoline and its Derivatives as Effective Corrosion Inhibitors for Mild Steel in Acidic Medium

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Quinoline (QL) and its derivatives namely quinaldine (QLD) and quinaldic acid (QLDA) were tested as inhibitors for the corrosion of steel in 0.5 M HCl by weight loss method at 30 and 40 ^{o}C. Inhibition efficiency increased with increase in the concentration of of the studied compounds but decreased with increase in temperature. Results show that the order of inhibition efficiency is QLDA > QLD > QL. The adsorption of the inhibitors on the steel surface obey Langmuir and kinetic thermodynamic models.

Keywords: Quinoline derivatives, mild steel, hydrochloric acid, thermodynamics.

1. INTRODUCTION

The corrosion of steel is a fundamental academic and industrial concern that has received a considerable amount of attention [1]. Acid solutions are widely used in industry. Some of the important fields of application being acid pickling of iron and steel, chemical cleaning and processing, ore production and oil well acidification. In acidic media, the use of hydrochloric acid in pickling of metals, acidization of oil wells and in cleaning of scales is more economical, efficient and trouble-free compared to other mineral acids [2].Thus the use of corrosion inhibitors is one of the most practical methods for corrosion protection of steel especially in acidic media [3-5]. Organic compounds containing electronegative functional groups and π-electrons in triple or conjugated double bonds are usually good corrosion inhibitors. Heteroatoms such as sulphur, phosphorus, nitrogen and oxygen as well as aromatic rings in their structure are the major adsorption centers. The compounds used as corrosion inhibitors act through a process of surface adsorption. The efficiency of an inhibitors depends on the characteristics of the environment in which it acts, the nature of the metal surface and electrochemical potential at the interface. The structure of the inhibitor itself, which includes the number of adsorption active centers in the molecule, their charge density, the molecule size, the mode of adsorption, the formation of metallic complexes and the projected area of the inhibitor on the metallic surface also has effect on the efficiency of inhibitors [6-14].

Perusal of literature reveals that many N-heterocyclic compounds such as pyrimidine derivatives [15], triazole derivatives [16], tetrazole derivatives [17], pyrazole derivative [18], bipyrazole derivatives [19], indole derivatives [20], pyridazine derivatives [21], benzimidazole derivatives [22] to mention but a few, have been used for the corrosion inhibition of iron or steel in acidic media. The effectiveness of quinoxaline derivatives (N-heterocyclic compounds) as effective corrosion inhibitors for mild steel in sulphuric acid media has been reported[23-25].

Quinolines and their derivatives are important constituents of pharmacologically active synthetic compounds [26], including biological activities such as DNA binding capabilities [27], antitumor [28] and DNA- intercalating carrier [29]. Several 8-aminoquinoline compounds, for instance Primaquine, have been applied as chemotherapeutics for teatment of malaria disease [30]. Recently, the first quinoline-based structure (GS-9137) with very strong antiretroviral activity for HIV tratment has been synthesized [31]. Although some quinoline derivatives has been reported as corrosion inhibitors for steel in sulphuric acid medium [32], no work to the best of our knowledge has been documented on the corrosion inhibition potentials of quinoline derivatives namely: quinoline (QL), quinaldine (QLD) and quinaldic acid (QLDA) on mild steel in hydrochloric acid.

The aim of this paper therefore is to further explore the use of quinoline derivativs as an acid corrosion inhibitor for mild steel surface in sulphuric acid solution using weight loss measurements. The effect of temperature and molecular structure on the inhibition efficiency was also discussed.

2. EXPERIMENTAL METHOD

2.1. Material

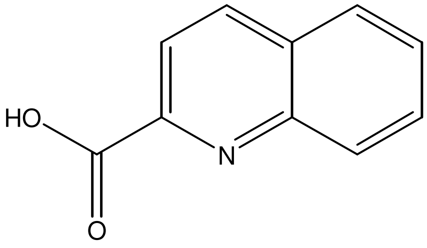
Test were performed on a freshly prepared sheet of mild steel of the following composition (wt.%): 0.13% C, 0.18% Si, 0.39% Mn, 0.40% P, 0.04% S, 0.025% Cu, and bal Fe. The metal specimen were prepared, degreased and cleaned as previously described [22, 23].

2.2 Inhibitors

Quinoline derivatives were purchased from SIGMA-ALDRICH and used as inhibitors without further purification. Stock solutions were made in 10:1 water: methanol mixture to ensure solubility [33]. These stock solutions were used for all experimental purposes. Fig.1 shows the molecular structures of the quinoline derivatives studied..

Quinoline

Quinaldine



Quinaldic acid

Figure 1. Names and molecular structures of inhibitors studied.

2.3. Solutions

The aggressive solutions, 0.5 M HCl were prepared by dilution of analytical grade 37% HCl with distilled water. The concentration range of the inhibitors prepared and used were 1×10^{-3}–1×10^{-1}M.

2.4. Gravimetric measurements

The gravimetric method (weight loss) is the most widely used method of inhibition assessment [34 - 37]. The simplicity and reliability of the measurement offered by the weight loss method is such that the technique forms the baseline method of measurement in many corrosion monitoring programmes [38, 39]. Weight loss measurements were conducted under total immersion using 250 mL capacity beakers containing 200 mL test solution at 303 and 313 K maintained in a thermostated water bath. The mild steel coupons were weighed and suspended in the beaker with the help of rod and hook. The coupons were retrieved at 2 h interval progressively for 10 h, washed thoroughly in 20% NaOH solution containing 200 g/l of zinc dust [10] with bristle brush, rinsed severally in deionized water, cleaned, dried in acetone, and re-weighed. The weight loss, in grammes, was taken as the difference in the weight of the mild steel coupons before and after immersion in different test solutions. Then the tests were repeated at different temperatures. In order to get good reproducibility, experiments were carried out in triplicate. In this present study, the standard deviation values among parallel triplicate experiments were found to be smaller than 5%, indicating good reproducibility. A visual examination was carried out after the weight loss measurements were over. It was observed that in the absence of inhibitor, a the uniform corrosion attack was observed, while on the other hand in the presence of quinoline derivatives, such an attack was not observed: therefore the surface area was bright and did not present any corrosion form which is an indication that no attack has occurred on the surface area of mild steel.

The corrosion rate (ρ) in g cm^{-2} h^{-1} was calculated from the following equation [40]:

$$\rho = \frac{\Delta W}{St} \qquad (1)$$

where W is the average weight loss of the mild steel sheets, S the total area of the mild steel specimen, and t is the immersion time (10 h) . With the calculated corrosion rate, the inhibition efficiency *(%I)* and the degree of surface coverage *(θ)* were calculated as follows [41, 42]:

$$\%I = \left(\frac{\rho_1 - \rho_2}{\rho_1} \right) x100 \qquad (2)$$

$$\theta = \left(\frac{\rho_1 - \rho_2}{\rho_1} \right) \qquad (3)$$

where ρ_1 and ρ_2 are the corrosion rates of the mild steel coupons in the absence and presence of inhibitor, respectively.

3. RESULTS AND DISCUSSION

3.1. Gravimetric measurements

The loss in weight of mild steel coupons in 0.5 M HCl in the absence and presence of different concentrations of QL, QLD, and QLDA was determined after 10 h immersion period at 30 and 40 °C respectively. The percentage inhibition efficiency (*%I*) and the degree of surface coverage *(θ)* were calculated and presented in Table 1. In the three cases, it can be observed from the table that the inhibition efficiency increases with increase in the concentration of each compound and the used compounds act as very good inhibitors for corrosion of mild steel in HCl. Maximum efficiency (*%I*) for each compound was achieved at 10^{-1} M and a further increase in concentration did not cause any appreciable change in the performance of the inhibitors. The parameter *(θ),* which represents the part of the metal surface covered by the inhibitor molecules increases as the inhibitor concentration is increased. The corrosion inhibition can be attributed to the adsorption of the quinoline derivatives at the steel/acid solution interface. However, the corrosion inhibition ability of the compounds studied follows the sequence: QLDA > QLD > QL.

Table 1. Calculated values of inhibition efficiency and the degree of surface coverage for mild steel in 0.5 M HCl in the absence and presence of quinoline derivatives studied at 30 and 40 °C

System/concentration	Inhibition efficiency (%I)		Surface coverage (θ)	
	30 °C	40 °C	30 °C	40 °C
QLDA				
0.001 M	76.72	67.51	0.77	0.68
0.005 M	80.48	71.00	0.80	0.71
0.01 M	83.61	74.21	0.84	0.74
0.05 M	89.42	81.34	0.89	0.81
0.1 M	94.21	84.00	0.94	0.84
QLD				
0.001 M	73.41	62.10	0.73	0.62
0.005 M	76.98	68.00	0.77	0.68
0.01 M	81.28	72.10	0.81	0.72
0.05 M	88.25	80.21	0.88	0.80
0.1 M	91.38	83.64	0.91	0.84
QL				
0.001 M	70.11	61.00	0.70	0.61
0.005 M	73.18	63.71	0.73	0.64
0.01 M	78.24	70.20	0.78	0.70
0.05 M	85.42	76.59	0.85	0.77
0.1 M	88.71	80.24	0.89	0.80

The fact that inhibition efficiencies increase with increasing concentration (Fig. 2 for example for quinaldic acid at 30 and 40 °C) suggests that the molecules may first be adsorbed on the surface and cover some sites of the steel surface, then probably form monomolecular layers on which the insoluble products (by forming a complex) of the iron ions form and the inhibitor grows, thereby protecting these sites from attack by chloride ions. Similar report have been documented elsewhere [44].

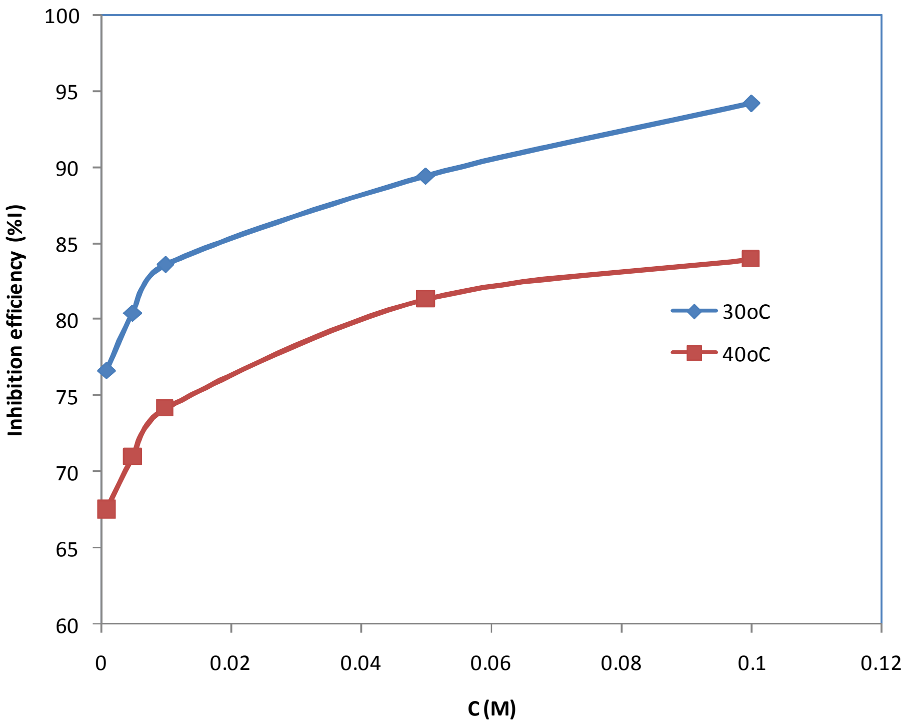


Figure 2. Variation of inhibition efficency(%I) versus different concentrations of quinaldic acid (QLDA) at 30 and 40^{o} C

3.2. Adsorption isotherm and thermodynamic parameters

The interaction between the inhibitors and the steel surface can be described by the adsorption isotherm. During corrosion inhibition of metals, the nature of the inhibitor on the corroding surface has been deduced in terms of adsorption characteristics of the inhibitor. Futhermore, the solvent (H_2O) molecules could also be adsorbed at metal/solution interface. So the adsorption of organic inhibitor molecules from aqueous solution can be regarded as a quasi-substitution process between the organic compounds in the aqueous phase [$Org_{(sol)}$] and water molecules at the electrode surface [$H_2O_{(ads)}$] [45]:

$$Org_{(sol)} + xH_2O_{(ads)} \leftrightarrow Org_{(ads)} + xH_2O_{(sol)} \quad (4)$$

where x is the size ratio, that is, the number of water molecules replaced by one organic inhibitor. Basic information on the interaction between the inhibitor and the mild steel surface can be provided by the adsorption isotherm. In order to obtain the isotherm, the linear relation between the degree of surface coverage (θ) and inhibitor concentration (C) must be found. Attempts were made to fit the θ values to various isotherms including Langmuir, Temkin, Frumkin and Flory-Huggins. By far the best fit was obtained with the Langmuir isotherm. The Langmuir isotherm is based on the assumption that all adsorption sites are equivalent and that particle binding occurs independently from nearby sites, whether occupied or not [46]. According to this isotherm, θ is related to C by:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{5}$$

where K_{ads} is the equilibrium constant of the adsorption process.

Fig. 2 shows the plots of C/θ against inhibitor concentration C at 303K and the expected linear relationship is obtained for all compounds with excellent correlation coefficents (R^2) (Table 2), confirming the validity of this approach. The slopes of the straight lines are unity , suggesting that adsorbed inhibitor molecules form monolayer on the mild steel surface and there is no interaction among the adsorbed inhibitor molecules.

Table 2. Some parameters from Langmuir model for mild steel in 0.5 M HCl at 30 °C.

Inhibitors	R^2	**Slope**	K_{ads} (M^{-1})	ΔG^o_{ads} (kJ mol^{-1})
QLDA	**0.999**	**1.006**	**2×10^2**	**-23.46**
QLD	**0.999**	**1.085**	**1×10^3**	**-27.52**
QL	**0.999**	**1.227**	**5×10^4**	**-37.37**

On the other hand, it was found that the kinetic thermodynamic model [47] is valid to operate the present adsorption data. The following equation represents the model [48]:

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

The equilibrium constant of adsorption $K_{ads}= K^{(1/y)}$, where 1/y is the number of the surface active sites occupied by one inhibitor molecule and C is the bulk concentration of the inhibitor. Values of 1/y less than unity imply the formation of multilayers of the inhibitor on the surface of the metal. However, values of 1/y greater than unity indicate that a given inhibitor will occupy more than one active site. The plot of $\log\frac{\theta}{1-\theta}$ versus log C at 303 K (Fig. 3), gives straight lines with good correlation coefficients (R^2) suggesting the validity of this model for the present study. It is worth nothing that the value of 1/y is more than unity which means that the inhibitor molecule will occupy more than one active site displacing three water molecules in the case of QLDA and QLD and about four water molecules in the case of QL respectively (Table 3).

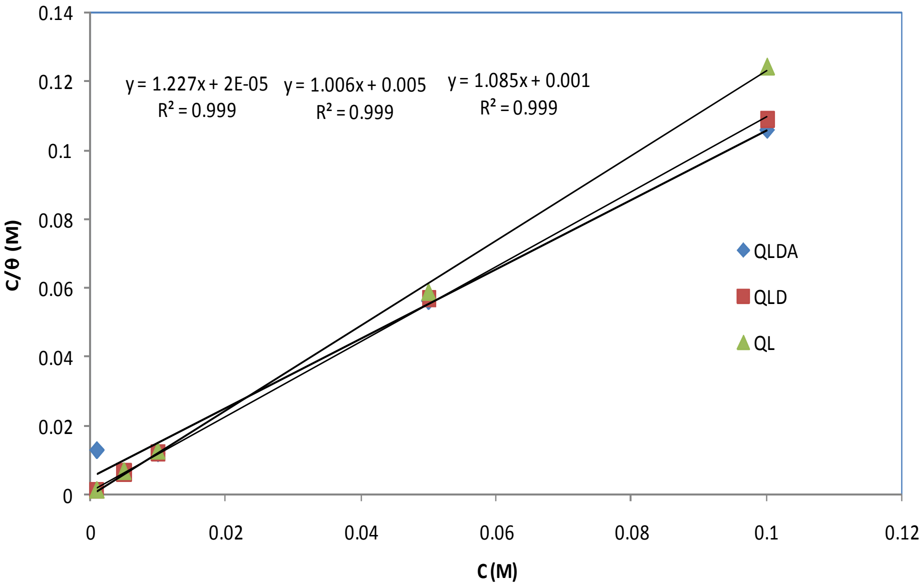


Figure 3. Curve fitting (Langmuir adsorption isotherm) of corrosion data for mild steel in 0.5 M HCl at different concentrations of quinoline derivatives at 30 °C.

Table 3. Some parameters from kinetic thermodynamic model for mild steel in 0.5 M HCl at 30 °C.

Inhibitors	R^2	1/y	K_{ads} (M^{-1})	ΔG^o_{ads} (kJ mol^{-1})
QLDA	**0.939**	**3.15**	**2.5×10^4**	**-35.60**
QLD	**0.971**	**3.42**	**1.6×10^4**	**-35.50**
QL	**0.967**	**3.66**	**1.3×10^4**	**-34.05**

The value of K_{ads} obtained from the Langmuir and the kinetic thermodynamic models are listed in Tables 2 and 3 respectively, together with the values of the Gibbs free energy of adsorption (ΔG^o_{ads}) calculated from the equation [49]:

$$K_{ads} = \frac{1}{55.5}\exp\left(\frac{-\Delta G^o_{ads}}{RT}\right) \tag{7}$$

where R is the universal gas constant, T the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution [50].

The high values of K_{ads} for studied quinoline derivatives indicate stronger adsorption on the mild steel surface in 0.5 M HCl solution. This can be explained by the presence of heteroatoms and π-electrons in the inhibitor molecules. Large values of K_{ads} imply more efficient adsorption hence better inhibition efficiency [51]. The large value of K_{ads} obtained for the quinoline derivatives agree with the high inhibition efficiency obtained.

The negative values of ΔG^{o}_{ads} calculated from Eq. (7), are consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the carbon steel surface. Generally, values of ΔG^{o}_{ads} up to -20 kJ mol^{-1} are consistent with physisorption, while those around -40 kJ mol^{-1} or higher are associated with chemisorption as a result of the sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate bond [52]. In the present study, the ΔG^{o}_{ads} values obtained for the quinoline derivatives on mild steel in 0.5 M HCl solution ranges between -23.46 and -37.37 kJ mol^{-1}, which are lower than -40 kJ mol^{-1} but higher than -20 kJ mol^{-1} (Tables 2 and 3). This indicates that the adsorption is neither typical physisorption nor typical chemisorption but it is complex mixed type. That is the adsorption of inhibitor molecules on the mild steel surface in the present study involves both physisorption and chemisorption (comprehensive adsorption) but physisorption is the predominant mode of adsorption. This assumption is supported by data obtained from temperature dependence of inhibition process (Table 1), which shows that the inhibition efficiency of the quinoline derivatives studied decreases with increase in temperature (physisorption) [53]. Thus, we conclude that the adsorption for all the quinoline derivatives studied on the mild steel in 0.5 M HCl is complex in nature and predominantly physisorption. Similar observation was reported by Ahamad et al. [54].

3.3. Effect of temperature

The importance of temperature variation in corrosion studies involving the use of inhibitors is to determine the mode of inhibitor adsorption on the metal surface [55, 56]. The influence of temperature on the corrosion behaviour of mild steel in 0.5 M HCl in the absence and presence of varying concentrations of quinoline derivatives were investigated using the weight loss method at 30 and 40°C. Thus in examining the effect of temperature on the corrosion process, an estimate of the heat of adsorption Q_{ads} was obtained from the trend of surface coverage with temperature as follows [57]:

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] x \left(\frac{T_{1X}T_2}{T_2 - T_1}\right) kJmol^{-1} \qquad (8)$$

where θ_1 and θ_2 are the degrees of surface coverage at temperatures T_1 and T_2, The calculated values for the parameter is given in Table 4.

The negative values of Q_{ads} signify the exothermic nature of the adsorption process of the studied inhibitors on steel surface. It also indicates that the degree of surface coverage decreased with rise in temperature, supporting the earlier proposed physisorption mechanism [58]. The average Q_{ads} values calculated follow the order: QLDA > QLD > QL, indicating that QLDA is likely to adsorbed more on the steel surface confirming its highest inhibition efficiency among the studied compounds.

Table. 4. Calculated values of heat of adsorption (Q_{ads}) for mild steel in 0.5 M HCl in the absence and presence of quinoline derivatives studied.

System/concentration	Q_{ads} (kJ mol^{-1})	Q_{ads}(average) (kJ mol^{-1})
QLDA		
0.001 M	**-35.85**	
0.005 M	**-38.71**	
0.01 M	**-48.28**	**-51.91**
0.05 M	**-50.53**	
0.1 M	**-86.22**	
QLD		
0.001 M	**-39.83**	
0.005 M	**-35.84**	
0.01 M	**-39.86**	**-43.00**
0.05 M	**-47.80**	
0.1 M	**-51.68**	
QL		
0.001 M	**-31.54**	
0.005 M	**-33.06**	
0.01 M	**-32.99**	**-38.93**
0.05 M	**-41.50**	
0.1 M	**-55.55**	

3.4. Correlation between inhibition action and molecular structure of the inhibitors

From the experimental data obtained from the weight loss study, the order of decreasing inhibition efficiency of the test compounds is QLDA > QLD > QL. This order can be accounted for in terms of the effect of the substituted groups on quinoline moiety (QL). It appears that the substitution of –H of the molecule QL by -CH_3 in QLD and by –COOH in QLDA increases the inhibitory efficiency.

This result is linked to the electron donating effect of the -CH_3 group which increases the electron density on the quinoline ring of QLD. Although –COOH is known to deactivate aromatic rings (electron withdrawing effect) [59], the increasing delocalization of electron density in the molecule, makes the molecule more stable than QLD and QL. The adsorption of QLDA is further stabilized by participation of π-electrons of quinoline ring. Electronagative oxygen atoms present in QLDA facilitate more efficient adsorption of the molecule on steel surface.

3.5. Explanation for adsorption and inhibition

From the experimental results obtained, the inhibition effect of quinoline derivatives herein reffered to as (QUIN) in 0.5 M HCl solution can be explained as follows:

$$\text{QUIN} + x\text{H}^+ \leftrightarrow [\text{QUINH}_x]^{x+} \quad (9)$$

Thus, in aqueous acidic solutions, the QUIN molecules exists either as neutral molecules or in the form of cations (protonated QUIN). Generally, two modes of adsorption could be considered. The neutral QUIN molecules may be adsorbed on the metal surface via the chemisorption mechanism involving the displacement of water molecules from the metal surface and the sharing of electrons between nitrogen, oxygen atom and iron. The QUIN molecules can be adsorbed also on the metal surface on the basis of donor-acceptor interactions between π-electrons of the heterocycle and vacant d-orbitals of iron. On the other hand, it is well known that the steel surface carries positive charges in acid solution [60], so it is difficult for the protonated QUIN molecules to approach the positively charged steel surface (H_3O^+/metal interface) due to the electrostatic repulsion. Since chloride ions have a smaller degree of hydration, being specifically adsorbed, they create an excess negative charge towards the solution and favour more adsorption of the cations [3]. The protonated QUIN molecules may adsorb through electrostatic interactions between the positively charged molecules and the negatively charged metal surface, i.e. there may be synergism between Cl^- and protonated QUIN molecules. Thus, the metal complexes of Fe^{2+} and QUIN molecules or protonated QUIN molecules might be formed as follows:

$$\text{QUIN} + \text{Fe}^{2+} \leftrightarrow [\text{QUIN-Fe}]^{2+} \quad (10)$$

$$[\text{QUINH}_x]^{x+} + \text{Fe}^{2+} \leftrightarrow [\text{QUIN}_x\text{-Fe}]^{(2+x)+} \quad (11)$$

These complexes might adsorb onto steel surface by Van der Waals force to form a protective film to keep the mild steel surface from corrosion. Similar mechanism have been documented elsewhere [61, 62].

4. CONCLUSIONS

Gravimetric measurements were employed to study the corrosion inhibition of mild steel in 0.5 M HCl solutions using some quinoline derivatives as corrosion inhibitors. The principal conclusions are:

1. Quinoline derivatives were found to be effective inhibitors for mild steel corrosion in 0.5 M HCl solutions.
2. The corrosion process is inhibited by the adsorption of these molecules on mild steel surface. Inhibition efficiency increased with increase in concentration of the quinoline derivatives but decreased with increase in temperature studied. Inhibition efficiency was found to be in the following order: QLDA > QLD > QL.
3. The data obtained from the weight loss technique for the studied inhibitors fit well into the Langmuir adsorption isotherm and the kinetic thermodynamic model. The values of the free energy for the adsorption process indicate that both physisorption and chemisorption (comprehensive adsorption) are involved in the adsorption of the quinoline derivatives studied on mild steel surface.

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