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Adsorption and corrosion inhibition of new synthesized quinoline on mild steel in HCl and H_2SO_4 solutions

A. Elyoussfi[1], A. Dafali[1], H. Elmsellem[1*], H. Steli[2], Y. bouzian[3], K. Cherrak[1],
Y. El Ouadi[1], A. Zarrouk[1], B. Hammouti[1]

[1] *Laboratoire de chimie analytique appliquée, matériaux et environnement (LC2AME), Faculté des Sciences, B.P. 717, 60000 Oujda, Morocco*

[2] *Laboratoire mécanique & énergétique, Faculté des Sciences, Université Mohammed Premier, Oujda, Maroc*

[3] *Laboratoire de Chimie Organique Hétérocyclique, URAC 21, Pôle de Compétences Pharmacochimie, Université Mohammed V, Faculté des Sciences, Av. Ibn Battouta, BP 1014 Rabat, Morocco*

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**Corresponding author. E-mail : h.elmsellem@yahoo.fr; Tel : +212670923431*

Abstract

2-oxo-1,2-dihydroquinoline-4-carboxylic acid (Q=O) was synthesized and its inhibiting action on the corrosion of mild steel in 1 M hydrochloric acid and 0.5 M sulfuric acid was examined by different corrosion methods, such as weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The experimental results suggest that this compound is an efficient corrosion inhibitor and the inhibition efficiency increases with the increase in inhibitor concentration. Adsorption of this compound on mild steel surface obeys Langmuir isotherm. Correlation between quantum chemical calculations and inhibition efficiency of the investigated compound is discussed using the Density Functional Theory method (DFT).

Keywords: Mild steel, Quinoline, EIS, Corrosion, Weight loss, EIS, DFT.

1. Introduction

Corrosion of steel is a fundamental academic and industrial concern, which has received a considerable amount of attention. Corrosion of metals usually occurs in an environment that can be considered as an electrolyte. Electrolytes encountered in corrosion are usually liquids containing dissolved ionic species. The use of inhibitors is one of the most practical methods for protection against corrosion. As acidic media, the use of HCl and H_2SO_4 acids, in pickling of metals, acidification of oil wells and in cleaning of scales is more economical, efficient and trouble-free, compared to other mineral acids.

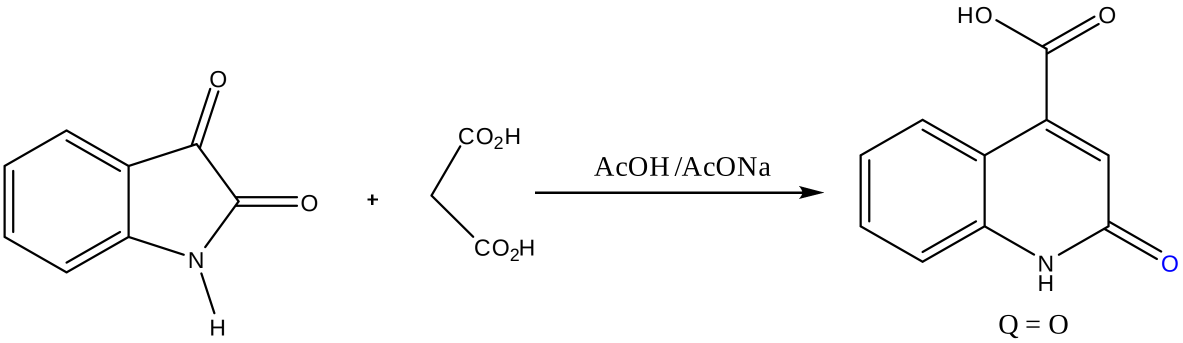
The use of organic compounds containing nitrogen, oxygen or sulphur as inhibitors to reduce corrosion attack has received detailed attention. These compounds act at the interphase created by the corrosion product between the metal and the aqueous aggressive solution, and their interaction with the corroding metal surface, usually via adsorption, often leads to amodification in either the mechanism of the electrochemical process at the doubled layer or in the surface available to the process [1-3].

The present project, we had synthesized a new 2-oxo-1,2-dihydroquinoline-4-carboxylic acid (Q = O) containing N and O heteroaromatic compound as substituent in its structure, was used for the first time for a comparative study of mild steel corrosion in hydrochloric and sulfuric acid media using weight loss measurements, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS). In addition, quantum chemical calculations were made to add theoretical support to experimental results.

2. Experimental

2.1. Synthesis of 2-oxo-1,2-dihydroquinoline-4-carboxylic acid (Q = O)

To a solution of isatin (10 mmole) and malonic acid (10 mmole) in acetic acid 30 ml, was added sodium acetate (1 mmole). The mixture was refluxed for 24 hours. After cooling ice-water (100ml) was added. The obtained precipate washed several time with ethanol, to lead compound Q=O.



Rdt = 87 %.F > 250 °C (EtOH). Spectre de RMN 1H (DMSOd6): 7.14(s, 1H, CH); 7.68-8.63(m, 4H, CHAr). Spectre de RMN 13C (DMSOd6) : 120.6 (=CH); 117.1, 117.6, 126.7, 133.7 (CHAr); 118.3, 137.0, 142.7 (Cq); 163.5 (C=O); 169.5 (CO2H). Spectre IR (cm-1) 3210 νN−H ; 2900-3100 νO-H ; 1705 νC=O. Spectre de masse (IE) M (m/z) = 189.

2.2. Materials

The steel used in this study is a mild steel with a chemical composition 0.09 wt. % P; 0.38 wt. % Si; 0.01 wt. % Al; 0.05 wt. % Mn; 0.21 wt. % C; 0.05 wt. % S and the remainder iron (Fe).

2.2.1. Preparation of Solutions

The aggressive solutions were HCl (1 M) prepared by HCl 37% (E. Merck) and H_2SO_4 (1 M) prepared by H_2SO_4 98% (E.Merck), with bi-distilled water. The concentration range of used inhibitor was 10^{-3} to 10^{-6} M of acid media. All experiments were performed at temperature 308k.

2.2.2. Gravimetric Study

Gravimetric experiments were performed according to the standard methods, the mild steel specimens (1.5 cm × 1.5 cm × 0.05 cm) were abraded with a series of emery papers SiC (120, 600, and 1200 grades) and then washed with distilled water and acetone. After weighing accurately, the specimens were immersed in a 100 mL of 1.0 M HCl solution with and without addition of different concentrations of inhibitor Q=O. All the aggressive acid solutions were open to air. After 6 hours of acid immersion, the specimens were taken out, washed, dried, and weighed accurately. In order to get good reproducibility, all measurements were performed few times and average values were reported.

3. Results and Discussion

3.1. Weight loss measurements

In general, the efficiency of an organic substance as an inhibitor for metallic corrosion depend on structure and the concentration of inhibitor, nature of the metal and the other experimental conditions, such as concentration of the medium [4]. In order to study the action of these parameters on mild steel corrosion, some experiments were carried out. The corrosion rate W (mg cm^{-2} h^{-1}), the surface coverage (θ) and the values of inhibition efficiency Ew (%) obtained from weight loss measurements of mild steel after 6 h immersion in 1 M HCl and 0.5 M H_2SO_4 solutions with and without the addition of various concentrations of the investigated 2-oxo-1,2-dihydroquinoline-4-carboxylic acid(Q = O) at different concentrations are shown in Table 1. The values of W_{corr}, θ and Ew were calculated using the following equations [5]:

$$W = \frac{\Delta m}{S\,t} \qquad (1)$$

$$\mathrm{Ew}\,\% = \frac{W_0 - W}{W_0} \times 100 \qquad (2)$$

where W is the average weight loss (mg), S is the surface area of the specimen (cm^2), t is the immersion time (h), W_0 and W are corrosion rates in the absence and presence of the inhibitor, respectively.
Data in Table 1 reveals that the addition of Q = O decreases the corrosion rate of mild steel, while inhibition efficiency (Ew) and surface coverage (θ) increase with increasing inhibitor concentration at temperature 308K, At a concentration of 10^{-3}M the 2-oxo-1,2-dihydroquinoline-4-carboxylic acid(Q = O) exhibits maximum inhibition efficiency (91% in 1 M HCl and 76% in 0.5 M H_2SO_4) at 308K, which represents efficient inhibitive ability. This can be due to the inhibitor molecules act by adsorption on the metal surface [6].

Table 1: Corrosion parameters obtained from weight loss measurements of mild steel after 6 h immersions in 1 M HCl and 0.5 M H_2SO_4 solutions with and without addition of various concentrations of Q = O.

Medium	Conc (M)	W_{corr} (mg.cm^{-2}.h^{-1})	Ew(%)	θ
1M HCl	Blank	0.910	--	--
	10^{-3}	0.082	91	**0.91**
	10^{-4}	0.127	86	0.86
	10^{-5}	0.173	81	0.81
	10^{-6}	0.235	74	0.74
0.5M H_2SO_4	Blank	1.690	--	--
	10^{-3}	0.402	76	**0.76**
	10^{-4}	0.609	63	0.63
	10^{-5}	0.859	49	0.49
	10^{-6}	1.208	28	0.28

3.1.2. Adsorption isotherm and thermodynamic consideration

The adsorption isotherms are considered to describe the interactions of the inhibitor molecule with the active sites on the metal surface [7], several adsorption isotherms were attempted to fit θ values to standard isotherms including that of Fumkin [8], Temkin [9], Freundlich [10], Floy-Huggins [11] and Langmuir isotherm [12].
The degree of surface coverage(θ) values have been evaluated from the Weight loss measurements as a function of the concentration of the inhibitor (C) was tested graphically by fitting it to various isotherms to find the best fit which describes this study. Langmuir adsorption isotherm was found to give the best description 2-oxo-1,2-dihydroquinoline-4-carboxylic acid(Q = O) on mild steel. This isotherm can be represented as [13]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (3)$$

K_{ads} is the adsorptive equilibrium constant representing the interaction of the additive with the metal surface. The linear relationships of C/θ versus C, depicted in Fig. 1 suggest that the adsorption of (Q = O) on the mild steel in both the acids obeys Langmuir adsorption isotherm. This model assumes that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species [14]. The constant K_{ads} is related to the standard free energy of adsorption $\Delta G°_{ads}$ (kJ mol^{-1}) by the equation:

$$\Delta G°_{ads} = -RT.\ln(55{,}5.K) \qquad (4)$$

where R is universal gas constant; 8.3144 J K^{-1} mol^{-1}, T is the temperature in K. The value of 55.5 is the concentration of water in solution expressed in moles per liter.
The high values of K_{ads} and negative values of $\Delta G°_{ads}$ suggest that inhibitor molecules are strongly adsorbed onto mild steel surface. The $\Delta G°_{ads}$ values obtained for the inhibitor at studied temperature are between -38.04 kJ mol^{-1} and -42.47 kJ mol^{-1} in both acidic mediums.

These values indicate that the adsorption process of the evaluated inhibitor on the mild steel surface may involve chemical adsorption (it can be concluded that the adsorption is more chemical than physical adsorption).

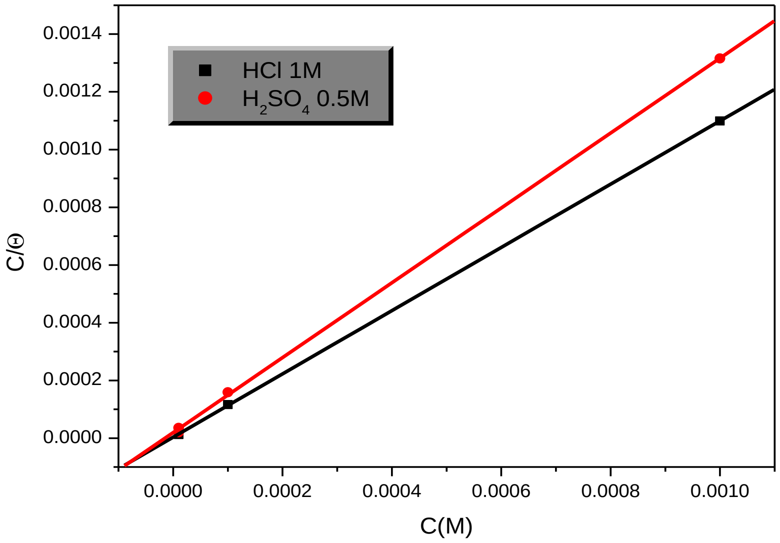


Figure 1: Langmuir adsorption isotherm of synthesized 2-oxo-1,2-dihydroquinoline-4-carboxylic acid(Q = O) on mild steel in 1 M HCl and 0.5 M H_2SO_4 at 308K.

3.2. Electrochemical impedance spectroscopy (EIS)

In order to better define the effect of our additive and concentration on the corrosion process, Nyquist plots of mild steel in uninhibited and inhibited acidic solutions containing various concentrations of 2-oxo-1,2-dihydroquinoline-4-carboxylic acid(Q = O) are shown in Fig. 2 and 3.

The existence of a single semicircle shows a single charge transfer process during dissolution which is unaffected by the presence of inhibitor molecules. Deviations from perfect circular shape are often referred to the frequency dispersion of interfacial impedance which arises due to surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, and formation of porous layers and inhomogenates of the electrode surface [15, 16]. Transfer resistance R_t, double layer capacitance C_{dI} and the inhibitor efficiency values E_{Rct}(%) are given in Table 2. Double layer capacitance values were obtained at maximum frequency (f_{max}) at which the imaginary component of the Nyquist plot is maximum and calculated using the following equation:

$$C_{dI}=1/2\pi f_{max}R_{ct} \qquad (5)$$

The inhibition efficiency E_{Rct} was calculated using the polarization resistance as follows:

$$E_{Rct}\% = \frac{R_{ct(inh)}-R_{ct(0)}}{R_{ct(inh)}} \text{ x } 100 \qquad (6)$$

where $R_{ct(0)}$ and $R_{ct(inh)}$ are the charge transfer resistance values in the absence and presence of inhibitor, respectively

As seen from Fig. 2 and 3, the diameter of the semicircle increases after the addition of 2-oxo-1,2-dihydroquinoline-4-carboxylic acid (Q = O) to the aggressive solution. This increase more and more pronounced with increasing inhibitor concentration. It is evident from these results that 2-oxo-1,2-dihydroquinoline-4-carboxylic acid (Q = O) inhibits the corrosion of mild steel in 1 M H_2SO_4 and 1 M HCl at all the concentrations used, and the inhibition efficiency (E_{Rct}) increases continuously with increasing concentration at 308K. EIS results (Table 2) show that the R_{ct} values increase and the C_{dI} values decrease with increasing the inhibitor concentration.

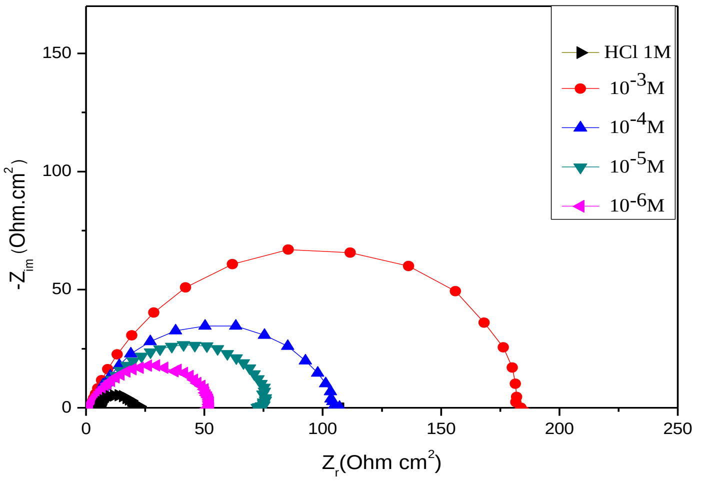


Figure 2: Nyquist impedance diagram for mild steel in 1M HCl with inhibitor Q=O.

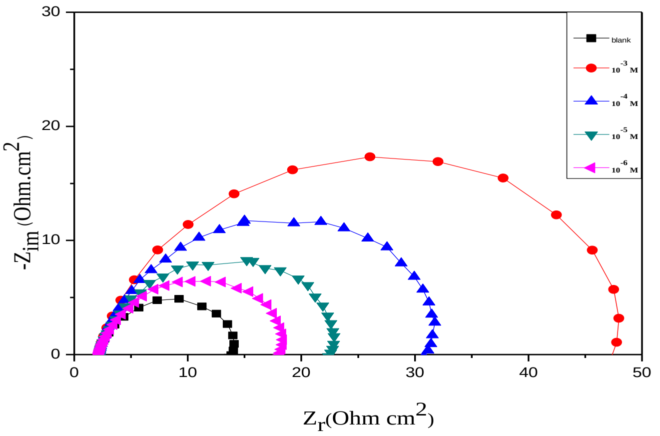


Figure 3: Nyquist impedance diagram for mild steel in 0.5 M H_2SO_4 with inhibitor Q=O.

Table 2: Impedance parameters for corrosion of steel in 1.0 M HCl and 0.5M H_2SO_4 in the absence and presence of different concentrations of Q=O at 308 K.

Medium	**Concentration (M)**	**R_t (Ω.cm^2)**	**C_{dl} (μf/cm^2)**	**E (%)**
1M HCl	Blank	16.58	200	--
	10^{-3}	183	54.94	**91**
	10^{-4}	103	61.50	84
	10^{-5}	71	70.76	77
	10^{-6}	51	78.70	67
0.5M H_2SO_4	Blank	12	134	--
	10^{-3}	47	85.80	**74**
	10^{-4}	30	123	60
	10^{-5}	21	130	43
	10^{-6}	16	150	27

The increase in Rct value can be attributed to the formation of protective film on the metal/solution interface. In fact, the decrease in C_{dl} values can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer. It can be assumed that the decrease of C_{dl} values is caused by the gradual replacement of water molecules by adsorption of inhibitor molecules on the mild steel surface [17]. The increase in values of R_{ct} and the decrease in values of C_{dI}

with increasing the concentration also indicate that the 2-oxo-1,2-dihydroquinoline-4-carboxylic acid(Q = O) acts as primary interface inhibitor and the charge transfer controls the corrosion of mild steel under the open circuit conditions. The impedance study also gave the same efficiency trend as found in Tafel polarization and weight loss methods

3.3. Tafel polarization study

Fig. 4 and 5 shows anodic and cathodic polarization plots recorded on mild steel electrode in 1 M HCl and in 0.5 M H_2SO_4 in absence and presence of different concentrations of (Q = O) inhibitor. Electrochemical corrosion parameters, such as corrosion potential E_{corr} (mV/SCE), cathodic slopes βc (mV/dec), the corrosion current density I_{corr} and inhibition efficiency Ep (%) are given in Table 2. The percentage of inhibition efficiency Ep was calculated following this equation [18]:

$$Ep\% = \frac{I_{cor(o)} - I_{cor(inh)}}{I_{cor(o)}} \text{ x } 100 \qquad (7)$$

where $I_{corr(0)}$ and $I_{corr(inh)}$ are the corrosion current densities in the absence and presence of the inhibitor, respectively.

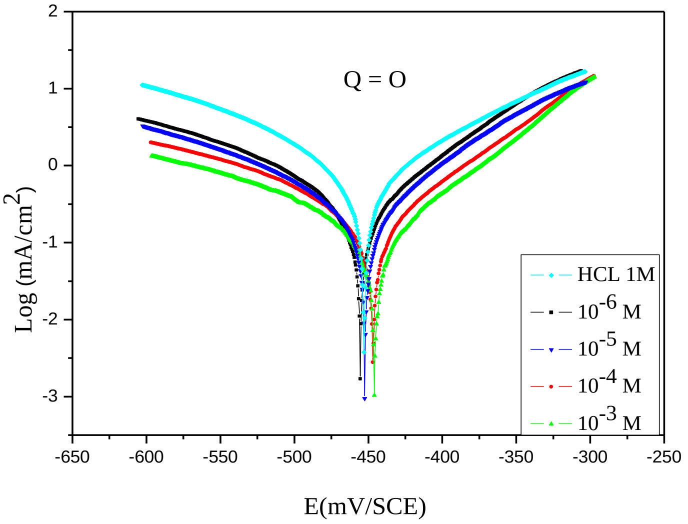


Figure 4: polarization curves for mild steel in 1 M HCl for various concentrations of Q = O at 308 K.

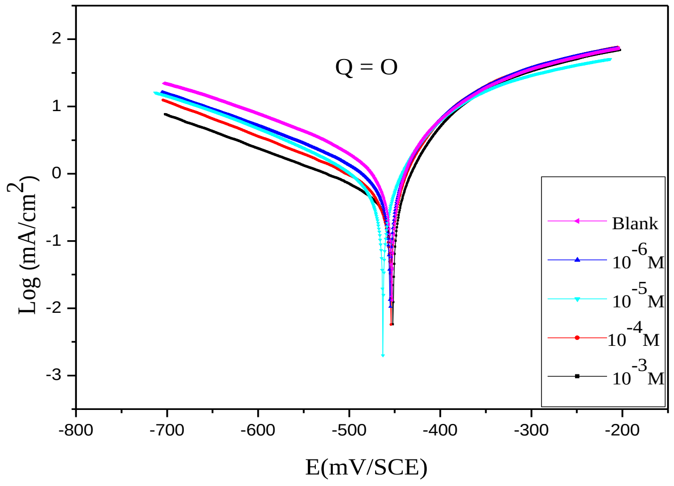


Figure 5: polarization curves for mild steel in 0.5 M H2SO4 $_{for}$ various concentrations of Q= O at 308 K.

It is clear from Fig. 3 and 4 that the presence of 2-oxo-1,2-dihydroquinoline-4-carboxylic acid(Q = O) decreases cathodic and anodic slopes with the increasing inhibitor concentration in both acids. As it can be seen from Table 3, in both solutions when the concentration of inhibitor increases the inhibition efficiencies increase, while corrosion current densities decrease. From Table 3 also can find that the corrosion potentials of inhibitor (Q = O) shift in the positive and negative direction in HCl and in H_2SO_4 solutions.

These results indicate that (Q = O) is a mixed type inhibitor (with predominant cathodic effectiveness in H_2SO_4 medium) acting on both the hydrogen evolution reaction and metal dissolution. The cathodic current–potential curves (Fig. 3 and 4) give rise to parallel lines indicating that the addition of (Q = O) to the HCl and H_2SO_4 solutions does not modify the hydrogen evolution mechanism and the reduction of H^+ ions at the mild steel surface which occurs mainly through a charge transfer mechanism.

The inhibitor molecules are first adsorbed onto mild steel surface and blocking the available reaction sites. In this way, the surface area available for H^+ ions decreases while the actual reaction mechanism remains unaffected [19]. These results are in good agreement with the results obtained from weight loss measurements. That is, the inhibition efficiency increases by increasing (Q = O) concentration. This may be due to the increase in (Q = O) concentration leads to increasing the surface coverage of the inhibitor and hence increase the adsorption on the mild steel surface.

Table 3: Polarization data of mild steel in 1.0 M HCl and 0.5M H_2SO_4 without and with addition of inhibitor at 308 K.

Medium	**Concentration (M)**	**-Ecorr (mV/SCE)**	**Icorr (µA/cm^2)**	**βc**	**βa**	**E_p (%)**
1M HCl	Blank	-453	1559	-143	143	--
	10^{-3}	-446	150	-101	75	**90**
	10^{-4}	-455	203.5	-81	67	87
	10^{-5}	-445	316	-242	81	80
	10^{-6}	-452	457	-173	145	71
0.5M H_2SO_4	Blank	-453	1647	-215	89	--
	10^{-3}	-451	392	-162	46	**76**
	10^{-4}	-454	649	-194	58	61
	10^{-5}	-459	1025	-202	81	38
	10^{-6}	-455	1168	-218	74	29

3.4. Computational theoretical studies

Quantum chemical computations were carried out by density function theory (DFT) with 6-31G (d, p) basis set for all atoms. All of the calculations were carried out with Gaussian 09W package [20].

To investigate the effect of molecular structure on the inhibition mechanism and inhibition efficiency, some quantum chemical calculations were performed. Quantum chemical parameters such as the energy of highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), HOMO–LUMO energy gap (ΔE_{gap}), the dipole moment (µ) of optimized molecular structure of the inhibitor 2-oxo-1,2-dihydroquinoline-4-carboxylic acid(Q = O) (Fig. 6) had been calculated (Table 4).

Frontier molecular orbital theory suggests that the formation of a transition state is due to an interaction between frontier orbitals (HOMO and LUMO) of reacting species. It is well known that low absolute values of the energy band gap gives good inhibition efficiencies, because the ionization potential will be low [21, 22]. The dipole moment (µ) is a measure of the polarity of a covalent bond, which is related to the distribution of electrons in a molecule [23, 24]. Although literature is inconsistent with the use of µ as a predictor for the direction of a corrosion inhibition reaction, it is generally agreed that the large values of μ favor the adsorption of inhibitor [25, 26]. As it is shown in Table 5, the 2-oxo-1,2-dihydroquinoline-4-carboxylic acid(Q = O) has a low ΔE_{gap} (7.37 eV), which implies the high ability to accept electrons from the d-orbital of Fe and a high stability of the [Fe–Q] complexes [27, 28]. Moreover, 2-oxo-1,2-dihydroquinoline-4-carboxylic acid(Q = O) has a rather high value of μ (4.69D), which implies the strong adsorption of molecule at the mild steel surface.

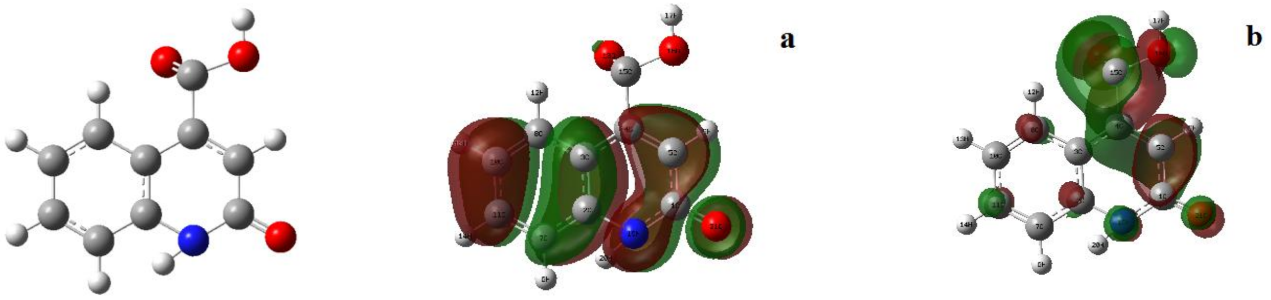


Figure 6: Optimized molecular structures of 2-oxo-1,2-dihydroquinoline-4-carboxylic acid(Q = O), HOMO (a), LUMO (b) orbitals.

Table 4: The calculated quantum chemical parameters Q = O

Pramaters	**Q = O**
E_{HOMO} (eV)	-9.24718184
E_{LUMO} (eV)	-1.87327408
ΔE (eV)	7.37390776
μ(debye)	4.6908

Conclusion

2-oxo-1,2-dihydroquinoline-4-carboxylic acid(Q = O) was synthesized and its chemical structure confirmed by elemental analysis, FT-IR and 1H NMR spectroscopy. The inhibition effect of this molecule on the corrosion of mild steel in 1 M HCl and 0.5 M H_2SO_4 was studied using chemical and electrochemical techniques. (Q = O) has a good inhibition effect for corrosion of mild steel in both acidic solutions to form a protective film, and it absorbs on the metal surface according to Langmuir adsorption isotherm. The inhibition efficiency increases with increasing inhibitor concentration. The polarization curves in 1 M HCl and 0.5 M H_2SO_4 indicate that (Q = O) behaves as mixed type inhibitor by inhibiting both anodic metal dissolution and cathodic hydrogen evolution reaction. The $\Delta G°_{ads}$ values suggest that this interaction may occur in both chemical adsorption. All the results obtained from EIS, polarization and weight loss agree with each other. Through the quantum chemical calculations, we have shown that the calculated parameters are correlated with the experimental results, and it was found that inhibition effect increased with the lower ΔE_{gap} and the higher μ values.

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