Performance of Quinoxalinone Derivatives as a Potential Efficient Inhibitor of Ordinary Steel Corrosion in 1 M Hydrochloric Acid: DFT Calculations

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Abstract
Two quinoxalinone derivatives, namely 3- (p-tolyl)-3.4-dihydroquinoxalin-2-(1H)-one (Q1) and 3-(4-chlorophenyl)-4-methyl-3.4-dihydroquinoxalin-2-(1H)-one (Q2), were used and investigated as potential corrosion inhibitors for OS in a 1 M HCl solution, at C from $10^{-6}$ to $10^{-3}$ M, using PDP, EIS measurements and GQCD calculations. EIS results indicate that Q1 and Q2 IE(%) increased with higher C and reached maximum values of 86.2 and 92.5%, at $10^{-3}$ M, respectively. The inhibitors adsorption mechanism onto the OS surface was found to obey the Langmuir’s adsorption isotherm model. PDP data displayed that Q1 and Q2 acted as mixed inhibitors, predominantly of the cathodic type. The theoretical results showed that the obtained parameters were in good agreement with the experimental data. Q2 compound had better IE(%), due to the inductive effect of CH3 electro-donor group in dihydroquinoxaline position.

Keywords: corrosion inhibition, GQCD calculations, HCl, OS, PDP/EIS and Quinoxalinone derivatives.

Introduction *
Corrosion results from the environment chemical or electrochemical action on metals and alloys. Corrosion inhibitors are substances that are added to aggressive environments, such as acid pickling, chemical cleaning and oil wells acidification processes, since they can significantly reduce the attack rate of metals and alloys, by decreasing corrosion processes [1-4]. In spite of this, large amounts of steel are destroyed in acidic media, especially HCl, due to corrosion [5, 6]. Acidic solutions are more widely used in industrial fields (fertilizers manufacture, pickling and metal scaling) [7-9]. In a large number of articles, reviews and books, the use of heterocyclic

* The abbreviations and symbols definition lists are in pages 459-460.
compounds as corrosion inhibitors of metals in acidic media has been investigated [10-12]. Among the most emblematic works, there is the review published by Schmitt, in 1984, “Application of inhibitors for acid media” [13]. Thus, we will briefly describe recent works that deal, in particular, with the field of Fe and steel acidic corrosion protection by heterocyclic compounds containing several heteroatoms [14-17]. Steel corrosion in 1 M HCl has been studied by Elayyachy et al. [18]. Galai et al. have shown that the increase in N atoms electron density enhances IE(%) [1], while heterocyclic compounds containing N heteroatoms, such as pyridine, quinoline and various amines, have obtained good IE(%) in acidic media [19, 20]. H atom substitution by pyridine increases considerably its inhibitory action [21]. The authors evaluated the studied polymer IE(%), by using WL and electrochemical techniques, namely, PDP and EIS [22-24]. Due to quinoxalines (e.g. indeno-1-one [2, 3-b] quinoxaline, acenaphtho [1,2-b] quinoxaline, ethyl 2- (4-(2-ethoxy-2-oxoethyl)-2-p-tolylquinoxalin-1 (4H)-yl) acetate and 1- [4-acetyl-2- (4-chlorophenyl) quinoxalin-1(4H)-yl]acetone) excellent mechanical, thermal, viscometric and rheological properties[25-28], they have shown to be good inhibitors against acidic corrosion [20, 29-31]. Theoretical studies have been widely used to explain corrosion inhibition mechanism, interpret the experimental results, and also find a correlation between the organic compounds molecular structure and their IE(%). Global quantum chemical descriptors of the studied inhibitor molecules, such as HOMO, LUMO and μ, have been researched [32-40].

In the present work, Q1 and Q2 have been investigated as potential corrosion inhibitors for OS in a 1 M HCl medium, using electrochemical studies and theoretical calculations. Further, activation kinetic parameters, such as $E_a$, $\Delta H^0$, $\Delta S^0$ and $\Delta G^0$, have been calculated and thoroughly discussed. The geometry optimization of the studied molecules and the parameters calculation were carried out using DFT method level, at 6-31G(d,p) basis set.

**Materials and methods**

**OS used**

OS chemical composition (% by wt.) is shown in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Al</th>
<th>Cu</th>
<th>V</th>
<th>W</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass(%)</td>
<td>0.11</td>
<td>0.24</td>
<td>0.47</td>
<td>0.12</td>
<td>0.02</td>
<td>0.1</td>
<td>0.03</td>
<td>0.14</td>
<td>&lt;0.003</td>
<td>0.06</td>
<td>rest</td>
</tr>
</tbody>
</table>

The OS surface was a rectangle of 1 cm$^2$, which was prepared, before immersion, by polishing it with an abrasive paper up to a grain size of 2000. It was rinsed with distilled water and acetone, and dried with hot air. The corrosive medium was a 1 M HCl solution, prepared from the commercial solution (37%), using bi-distilled water. The C range used for the two tested inhibitors was from $10^{-6}$ to $10^3$ M, which was determined after studying their solubility in the corrosive medium.

**Used inhibitors**

Quinoxalinone derivatives compounds were synthesized, as characterized by Lalami et al. [41], and their structures are listed in Table 2.
Table 2. Structures, masses and molecular formulas of the studied quinoxalinone derivatives.

<table>
<thead>
<tr>
<th>Quinoxalinone derivatives</th>
<th>Abbreviation</th>
<th>Molecular structures</th>
<th>Molecular weight and chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-(p-tolyl)-3,4-dihydroquinoxalin-2(1H)-one</td>
<td>Q1</td>
<td><img src="image1" alt="Structure Q1" /></td>
<td>238.28 C₁₅H₁₄N₂O</td>
</tr>
<tr>
<td>3-(4-chlorophenyl)-4-methyl-3,4-dihydroquinoxalin-2(1H)-one</td>
<td>Q2</td>
<td><img src="image2" alt="Structure Q2" /></td>
<td>272.73 C₁₅H₁₃ClN₂O</td>
</tr>
</tbody>
</table>

**Electrochemical measurements**

The electrochemical experiments were carried out in a conditioned cell equipped with a conventional three-electrode arrangement: OS as WE, Pt as AE and Ag/AgCl as RE. Electrochemical methods for the study of corrosion can be classified into two main groups: the so-called stationary (classical) and non-stationary (transient) methods. In the first one, the intensity-E curves are obtained in a PDP mode, where the E applied to the sample varies continuously, with a SR of 1 mV/S⁻¹. The measurements were made by a PGZ100 Potentiostat-Galvanostat, associated with Voltamaster 4 software. Before the curves were drawn, the WE was maintained at its E, for 30 min. EIS measurements were made under the same conditions as those of the PDP plotting, at the frequency interval from 100 to 10 KHz.

**DFT calculations**

Optimization of the quinoxalinones compounds geometric structure was performed by the DFT method, with the non-local Lee-Yang-Parr correlation function (B3LYP), at 6-31G (d,p) basis set, using 09W Gaussian software [42]. The various GQCD parameters, such as χ, Pi and ΔE, are expressed by the following relations [43-46]:

\[
\Delta E = E_{LUMO} - E_{HOMO} \tag{1}
\]

\[
Pi = -E_{HOMO} \tag{2}
\]

\[
A = -E_{LUMO} \tag{3}
\]

\[
\chi = \frac{Pi + A}{2} \tag{4}
\]

η and σ are given by the following equations [47]:

\[
\eta = \frac{Pi - A}{2} \tag{5}
\]

\[
\sigma = \frac{1}{\eta} = -\frac{2}{E_{HOMO} - E_{LUMO}} \tag{6}
\]

ω was introduced by Parr [48, 49], and it is given by:

\[
\omega = \frac{\mu^2}{2\eta} \tag{7}
\]
This index measures the propensity of chemical species to accept electrons. A more reactive nucleophilic is characterized by \( \mu \) and \( \omega \) lower values; conversely, a good electrophile is characterized by \( \mu \) and \( \omega \) greater values. \( \Delta N \) was calculated as follows [50]:

\[
\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})}
\]

where \( \chi_{Fe} \) and \( \chi_{inh} \) represent Fe absolute \( \chi \) and the inhibitor molecule, respectively; \( \eta_{Fe} \) and \( \eta_{inh} \) denote Fe absolute \( \eta \) and the inhibitor molecule, respectively; and \( \chi_{Fe} = 7.0 \) eV and \( \eta_{Fe} = 0 \) theoretical values were used to calculate \( \Delta N \) [49].

**Results and discussion**

**EIS analysis**

In order to understand OS corrosion mechanisms, after 30 min of immersion in 1 M HCl, at 303 K, EIS diagrams obtained at \( E_{corr} \), without and with Q1 and Q2, in different C, are shown in Figs. 1 and 2.

**Figure 1.** Nyquist diagram for OS in 1 M HCl, without and with Q1, in different concentrations.

**Figure 2.** Nyquist diagram for OS in 1 M HCl, with and without Q2, in different concentrations.
From the analysis of Figs. 1 and 2, we note that there is a large increase in the loop, in Q1 and Q2 presence and, consequently, an increase in $R_{ct}$, which is inversely proportional to $CR$. Corrosion IE(%) and OS $C_{dl}$ were calculated by the following equations [51-54]:

$$C_{dl} = \frac{1}{2\pi R_{ct}f_{max}}$$  \hspace{1cm} (9)

$$\eta \% = \frac{R'_{ct} - R_{ct}}{R_{ct}} \times 100$$  \hspace{1cm} (10)

$R'_{ct}$ and $R_{ct}$ are values without and with the inhibitor, respectively. $C_{dl}$ values are also expressed by the Helmholtz relation [55].

$$C_{dl} = \frac{\varepsilon^0 \varepsilon}{\delta} S$$  \hspace{1cm} (11)

where $\delta$ is the double layer capacity thickness, $S$ is the OS electrode surface, and $\varepsilon^0$ and $\varepsilon$ are vacuum and solution dielectric constants, respectively.

The electrochemical parameters associated with the impedance diagrams are recorded in Table 3.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>Conc (M)</th>
<th>$R_{ct}$ (ohm/cm²)</th>
<th>$C_{dl}$ (µF/cm²)</th>
<th>IE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank HCl</td>
<td>1</td>
<td>44</td>
<td>294</td>
<td>-</td>
</tr>
<tr>
<td>Q1</td>
<td>$10^{-6}$</td>
<td>148</td>
<td>296</td>
<td>72.2</td>
</tr>
<tr>
<td></td>
<td>$10^{-5}$</td>
<td>161</td>
<td>227</td>
<td>73.0</td>
</tr>
<tr>
<td></td>
<td>$10^{-4}$</td>
<td>225</td>
<td>200</td>
<td>80.5</td>
</tr>
<tr>
<td></td>
<td>$10^{-3}$</td>
<td>319</td>
<td>133</td>
<td>86.2</td>
</tr>
<tr>
<td>Q2</td>
<td>$10^{-6}$</td>
<td>99</td>
<td>266</td>
<td>55.5</td>
</tr>
<tr>
<td></td>
<td>$10^{-5}$</td>
<td>189</td>
<td>183</td>
<td>77.0</td>
</tr>
<tr>
<td></td>
<td>$10^{-4}$</td>
<td>380</td>
<td>93</td>
<td>88.5</td>
</tr>
<tr>
<td></td>
<td>$10^{-3}$</td>
<td>579</td>
<td>51</td>
<td>92.5</td>
</tr>
</tbody>
</table>

Table 3 indicates that $P_r$ increased with higher $C$ of the studied inhibitors. Further, Q1 and Q2 IE(%), at inhibitors optimal $C$ of $10^{-3}$ M, reached the maximum values of 86.2 and 92.5%, respectively. $C_{dl}$ was inversely proportional to $R_{ct}$. $C_{dl}$ values calculated in the 1 M HCl medium without inhibitors were lower than of those with Q1 and Q2. This decreases can be attributed to the organic molecules adsorption onto the metallic surface [56, 57]. From these observations, it can be said that Q2 adsorption performance onto the metallic surface was higher than that of Q1. The equivalent electrical circuit used to output the electrochemical parameters is shown in Fig. 3.

**Figure 3.** Equivalent electrical circuit of inhibitors/OS interface in 1 M HCl.
**PDP investigation**

Figs. 4 and 5 show the cathodic and anodic polarization curves of OS in 1 M HCl without Q1 and Q2 and with them in different C, at 298 K. The electrochemical parameters taken from these curves are grouped in Table 3. Figs. 4 and 5 show that the increases in C of the tested inhibitors led to a shift in $I_{\text{corr}}$, in the two anodic and cathodic domains, to lower values.

![Figure 4. PDP of OS in 1 M HCl without and with Q1 at different concentrations, at 298 K.](image)

![Figure 5. PDP of OS in 1 M HCl without and with Q2 in different concentration, at 298 K.](image)

The cathodic slope is in the form of Tafel line, for the entire range of examined $E$, indicating that H reduction on the OS surface took place through a pure activation mechanism [58-60].

IE(%) was calculated by the following equation:

$$\eta_{\text{IE}} \% = \frac{I_{\text{corr}} - I_{\text{corr}}}{I_{\text{corr}}} \times 100$$

(12)

The electrochemical parameters determined from the polarization curves, such as $E_{\text{corr}}$, $\beta_c$, $i_{\text{corr}}$ and IE(%), are grouped in Table 4.
Table 4. IE(%) and electrochemical parameters obtained from the curves of OS in 1 M HCl without and with inhibitors at different concentrations.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>C (M)</th>
<th>$E_{corr}$ (mV/Ag/Agcl)</th>
<th>$i_{corr}$ (µA/cm²)</th>
<th>$\beta_c$ (mV/dec⁻¹)</th>
<th>IE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank HCl</td>
<td>1</td>
<td>478</td>
<td>470</td>
<td>240</td>
<td>-</td>
</tr>
<tr>
<td>Q1</td>
<td>$10^{-6}$</td>
<td>556</td>
<td>140</td>
<td>194</td>
<td>70.2</td>
</tr>
<tr>
<td></td>
<td>$10^{-5}$</td>
<td>530</td>
<td>129</td>
<td>111</td>
<td>72.5</td>
</tr>
<tr>
<td></td>
<td>$10^{-4}$</td>
<td>520</td>
<td>92</td>
<td>103</td>
<td>80.5</td>
</tr>
<tr>
<td></td>
<td>$10^{-3}$</td>
<td>491</td>
<td>61</td>
<td>99</td>
<td>87.1</td>
</tr>
<tr>
<td>Q2</td>
<td>$10^{-6}$</td>
<td>530</td>
<td>194</td>
<td>177</td>
<td>58.0</td>
</tr>
<tr>
<td></td>
<td>$10^{-5}$</td>
<td>531</td>
<td>104</td>
<td>156</td>
<td>78.1</td>
</tr>
<tr>
<td></td>
<td>$10^{-4}$</td>
<td>550</td>
<td>52</td>
<td>121</td>
<td>89.0</td>
</tr>
<tr>
<td></td>
<td>$10^{-3}$</td>
<td>516</td>
<td>30</td>
<td>100</td>
<td>93.6</td>
</tr>
</tbody>
</table>

From the analysis of Table 3, we observed that, for all Q1 and Q2 C, $i_{corr}$ decreased with higher inhibitor C and, consequently, IE% increased, reaching a maximum value of 87.1 and 93.6%, respectively. In general, this behavior is due to the active sites blocking by the formation of a protective layer on the OS surface.

The different C of the studied inhibitors slightly modified $\beta_c$ values, with respect to the blank HCl.

Thus, these compounds are mixed inhibitors, predominantly cathodic, because there was a displacement in the $E_{corr}$ values, in both cathodic and anodic domains, with Q1 and Q2 different C in 1 M HCl. This maximum displacement was 78 mV/Ag/AgCl for Q1. $\beta_c$ and $\beta_a$ were extensively changed by Q1 and Q2. This modification indicates that the organic compounds derivatives, which were elaborated as potential inhibitors, were adsorbed onto the OS surface, by blocking the active centers through the chemical bonds.

Cathodic and anodic reactions for OS substrates were inhibited by Q1 and Q2. PDP results confirmed the data obtained by EIS measurements.

**T effect**

T effect on Q1 and Q2 IE(%) for OS corrosion in a 1 M HCl solution without and with them, in a C of $10^{-3}$ M, at a range from 298 to 318 K, was obtained by PDP measurements. Table 5 lists all the electrochemical parameters, as a function of the different T.

Table 5. PDP parameters of OS in 1 M HCl without and with Q1 and Q2 ($10^{-3}$M), at different T.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>T (K)</th>
<th>$-E_{corr}$ (mV/Ag/Agcl)</th>
<th>$i_{corr}$ (µA/cm²)</th>
<th>IE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank HCl</td>
<td>298</td>
<td>498</td>
<td>470</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>491</td>
<td>1200</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>475</td>
<td>1450</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>465</td>
<td>2500</td>
<td>-</td>
</tr>
<tr>
<td>Q1</td>
<td>298</td>
<td>491</td>
<td>61</td>
<td>87.1</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>478</td>
<td>210</td>
<td>82.5</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>456</td>
<td>285</td>
<td>80.2</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>503</td>
<td>533</td>
<td>79.0</td>
</tr>
<tr>
<td>Q2</td>
<td>298</td>
<td>526</td>
<td>30</td>
<td>93.6</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>493</td>
<td>132</td>
<td>89.0</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>491</td>
<td>201</td>
<td>86.1</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>490</td>
<td>410</td>
<td>84.0</td>
</tr>
</tbody>
</table>
IE(%) underwent a decrease, while CR increased with higher T, in the absence of Q1 and Q2 and in their presence (10^{-3} M).

Activation kinetic parameters, such as $E_a$, $\Delta H^\circ$ and $\Delta S^\circ$, were calculated. $E_a$ (kJ/mol^{-1}) relative to the corrosion process was calculated from Arrhenius equation:

$$k = E_a e^{E/RT}$$

(13)

where $R$ is the perfect gas constant and $T$ is absolute.

Fig. 6 shows the $i_{corr}$ logarithm variations, as a function of $T$ inverse.

$$\ln(i_{corr}) = f(1/t)$$

(14)

where $\ln$ is the natural logarithm, $f$ is the frequency and $t$ is the time period.

Figure 6. Arrhenius lines calculated from PDP for OS in 1 M HCl without and with Q1 and Q2 inhibitors.

The $i_{corr}$ logarithm variations enabled to calculate $E_a$ values from the slope of each one of the obtained straight lines. $E_a$ values are listed in Table 6, which shows that this parameter, in HCl without Q1 and Q2 is higher than of that with them. This result is interpreted as an indication of an electrostatic character of the inhibitors adsorption. It can be said that the studied inhibitors were adsorbed onto the steel surface by forming physical bonds (physisorption) [6].

Another formulation of the Arrhenius equation is [61]:

$$\ln(i_{corr}/T) = \frac{RT}{Nh} \exp \left( \frac{\Delta S^\circ_a}{R} \right) \exp \left( \frac{\Delta H^\circ_a}{RT} \right)$$

(15)

where $h$ is the Plank constant and $N$ is the Avogadro number.

$\ln(i_{corr}/T)$ variation, as function of $T$ inverse, is a straight line (Fig. 7), with a slope of $1000/R$ and an ordinate at the origin equal to $(\ln R/Nh + 1000/ R)$. Fig. 7 shows that the lines are almost straight, and that all $R^2$ values are close to 1. From the slopes and lines intersections, $E_a$, $\Delta H^\circ_a$ and $\Delta S^\circ_a$ values were computed and grouped in Table 6.
The endothermic reactions positive values were expressed on the OS dissolution process. Indeed, the increase in $\Delta S^\circ$ with Q1 and Q2 was 52.9 and 63.9 kJ/mol$^{-1}$, respectively, whereas in their absence it was 41.4 kJ./mol$^{-1}$, which corresponds to a decrease in the metal dissolution. The high and negative entropy values mean that there was an increase in disorder when the reactants were transformed into an activated Fe-molecule complex in the solution [1, 8, 35].

Table 6. $E_a$, $\Delta H^\circ_a$ and $\Delta S^\circ_a$ values without and with Q1 and Q2 inhibitors.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>$E_a$ (kJ/mol$^{-1}$)</th>
<th>$\Delta H^\circ_a$ (kJ/mol$^{-1}$)</th>
<th>$-\Delta S^\circ_a$ (J/mol$^{-1}$/K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank HCl</td>
<td>44.3</td>
<td>41.4</td>
<td>54.3</td>
</tr>
<tr>
<td>Q1</td>
<td>55.7</td>
<td>52.9</td>
<td>31.2</td>
</tr>
<tr>
<td>Q2</td>
<td>67.5</td>
<td>63.9</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**Adsorption isotherm**

The adsorption isotherm can give additional data on the compounds adsorption performance on the metal surface. $\theta$ values for different inhibitor C in a 1 M HCl solution were obtained according to the IE% ratio. There are several adsorption models, such as Langmuir’s, Temkin’s and Frumkin’s isotherms, based on $C_{inh}/\theta$. As a function of $C_{inh}$, we found that there were excellent experimental values for Q1 and Q2. For Langmuir’s isotherm, its $R^2$ coefficient was close to 1, relative to those found in Temkin’s and Frumkin’s isotherms, as shown in Fig. 8 [45, 46, 62]. Therefore, experimental results obeyed the Langmuir’s adsorption isotherm, where $\theta$ and $C_{inh}$ are linked to each other via the equation:

$$\theta = \frac{K_{ads} C_{inh}}{1 + K_{ads} C_{inh}}$$

(16)

The rearrangement gives:
\[
\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}
\]  \hspace{1cm} \quad (17)

\(K_{ads}\) can be calculated from the straight lines intersections.

Fig. 8 shows \(C_{inh}/\theta\) variation, as a function of the inhibitor \(C\), where the shown lines are close to one.

Figure 8. Langmuir’s adsorption isotherm of OS in 1 M HCl with Q1 and Q2 inhibitors.

\(\Delta G_{ads}^o\) is related to \(K_{ads}\) by relationship (16), and the corresponding results are listed in Table 7 [63].

\[
\Delta G_{ads}^o = -RT\ln\left(55.5K_{ads}\right) \quad (18)
\]

From Table 7, we find that \(K_{ads}\) values are high, indicating that Q1 and Q2 were readily adsorbed onto the OS surface [64]. In general, if \(\Delta G_{ads}^o\) values are close to or greater than -20 kJ/mol, they are linked to electrostatic interactions; those which are close to -40 kJ/mol or lower involve the formation of chemical nature bonds between the inhibitor molecules and the metal surface. For \(\Delta G_{ads}^o\) values in the range from -20 to -40 kJ/mol, the two phenomena apply at the same time [65]. However, these criteria remain insufficient in order to distinguish between the two phenomena (chemisorption and physisorption). The results in Table 8 indicate that the two inhibitors obeyed the order Q2> Q1. That is, Q2 adsorption performance onto the OS surface was higher than that of Q1, due to the existence of an electro-donor group on the N atom number four (N4) in the first compound.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>(K_{ads})</th>
<th>(R^2)</th>
<th>(-\Delta G_{ads}^o) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1</td>
<td>289070.8</td>
<td>0.9999</td>
<td>41.1</td>
</tr>
<tr>
<td>Q2</td>
<td>384714.5</td>
<td>0.9999</td>
<td>41.8</td>
</tr>
</tbody>
</table>
**DFT calculations**
Quantum chemistry calculation was carried out by the DFT 6-31G (d, p) method, and compared with experimental results. During this study, we calculated chemical quantum parameters. Also, HOMO and LUMO optimized geometric structures and electron density distributions for these inhibitors are presented in Fig. 9. It is seen that HOMO and LUMO were distributed over Q1 and Q2 entire surfaces. This indicates that these molecules are rich in electrons.

![HOMO and LUMO for Q1 and Q2 inhibitors](image)

**Figure 9.** Optimized structures, HOMO and LUMO for studied molecules using DFT/B3LYP at 6-31G (d, p).

Mulliken atomic charges on the Q1 and Q2 atoms, the μ vector direction, and the contour and surface representation of the electrostatic E are presented in Figs. 10 and 11.

![Mulliken load distribution and molecular electrostatic E](image)

**Figure 10.** Mulliken charge and electrostatic properties for Q1 inhibitor.

From these figures, it is evident that the N, O and some C atoms for the two inhibitors carry negative charges. So, they are responsible for a nucleophilic attack
towards the OS surface. The electrostatic E different values were given using red, yellow, green and blue. Red (electrophilic active regions) and blue (nucleophilic regions) represent MESP negative and positive parts and green depicts the zero region electrostatic E [66, 67]. Depending on the studied inhibitors ESP and MESP contour surfaces, the negative parts are electrophilic active regions mainly found on the O surface.

Mulliken charge and electrostatic properties for Q2 inhibitor.

\( E_{HOMO} \) indicates the molecule ability to give electrons to another empty molecular orbit; \( E_{LUMO} \) describes the ability of a compound to accept electrons. \( \Delta E \) is the energy difference between \( E_{HOMO} \) and \( E_{LUMO} \). The energy absorption between the inhibitors and the metal surface increases when \( \Delta E \) decreases, i.e., the energy to remove an electron from the last occupied orbit will be low [68-70]. The corresponding results of the quantum parameters are presented in Table 8, from which we note that the \( \Delta E \) values for Q1 and Q2 are 3.536 and 3.194 eV, respectively. Q2 had a weaker \( \Delta E \) than that of Q1. This indicates that Q2 adsorption performance was greater than that of Q1, in the order: \( \Delta E (Q1) > \Delta E (Q2) \).

Consequently, \( \eta \) and \( \sigma \) are important properties for measuring molecular stability and reactivity. Q1 and Q2 IE(%) increased with higher chemical reactivity [71-75]. Q2 had good chemical reactivity with the metal surface, due to the increase in the \( \sigma \) value (0.626 eV\(^{-1}\)) and the decrease in \( \eta \) (1.597 eV), according to the following order: \( \eta (Q2) > \eta (Q1) \).

Q2 maximum \( \mu \) value was 5.304 Debye, which shows that this is highly polarizable. So, Q2 is very reactive, which could be related to the \( \mu-\mu \) interaction between the inhibitor molecules and the metal surface [12, 76, 77].

Q2 had a minimum \( \Pi \) of 5.545 eV, indicating that it is more effective. On the other hand, the IE(%) was higher with an increase in the inhibitor electron donor capacity to the metal surface. The transferred electrons displacement from the inhibitor to the metal surface occurred in the following order: \( \Delta N = 0.955 \) (Q2) > \( \Delta N = 0.872 \) (Q1).

Table 8 shows that Q2 had higher \( \omega \) than that of Q1 (9.626 eV). It was found that this inhibitor acts as an electrophile (electron acceptor). Finally, Q2 total energy was equal to -1223.76 a.u., which indicates that it was favorably adsorbed through the active adsorption centers.
Table 8. Chemical quantum parameters for studied inhibitors (Q1 and Q2).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Q1</th>
<th>Q2</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_LUMO (eV)</td>
<td>-2.147</td>
<td>-2.351</td>
</tr>
<tr>
<td>E_HOMO (eV)</td>
<td>-5.683</td>
<td>-5.545</td>
</tr>
<tr>
<td>ΔEgap (eV)</td>
<td>3.536</td>
<td>3.194</td>
</tr>
<tr>
<td>μ (debyes)</td>
<td>3.361</td>
<td>5.304</td>
</tr>
<tr>
<td>η (eV)</td>
<td>1.768</td>
<td>1.597</td>
</tr>
<tr>
<td>σ (e.V^(-1))</td>
<td>0.565</td>
<td>0.626</td>
</tr>
<tr>
<td>Pt (e.V)</td>
<td>5.683</td>
<td>5.545</td>
</tr>
<tr>
<td>χ (eV)</td>
<td>3.915</td>
<td>3.948</td>
</tr>
<tr>
<td>Λ (eV)</td>
<td>2.147</td>
<td>2.351</td>
</tr>
<tr>
<td>ΔN (eV)</td>
<td>0.872</td>
<td>0.955</td>
</tr>
<tr>
<td>ω (eV)</td>
<td>9.133</td>
<td>9.626</td>
</tr>
<tr>
<td>TE (u.a)</td>
<td>-764.18</td>
<td>-1223.76</td>
</tr>
</tbody>
</table>

The theoretical study showed that quantum parameters were in agreement with experimental observations.

Conclusion

Two quinoxalinone derivatives were used to inhibit OS corrosion in a 1 M HCl medium. The study was carried out using various experimental and theoretical approaches. The results of this study are as follows:

- Q1 and Q2 inhibitors were effective inhibitors for OS corrosion.
- Those molecules were mixed inhibitors, of predominantly the cathodic type.
- EIS results displayed that the Nyquist diagrams had a single capacitive loop, indicating that the corrosion inhibition was controlled by R_ct process.
- T effect suggested that IE(%) decreased with higher T.
- The studied inhibitors adsorption onto the OS surface in a 1 M HCl solution obeyed Langmuir’s adsorption isotherm.
- Theoretical approaches and experiments data were in good agreement.

Authors’ contributions

A. Benallal: collected the data. M. Galai: performed the analysis. F. Benhiba: performed the analysis; wrote the paper. N. M’hanni: wrote the paper. Rachid Hsissou: wrote the paper. S. Ibn Ahmed: conceived and designed the analysis. M. Ebn Touhami: conceived and designed the analysis. H. Oudda: other contributions. S. Boukhris: contributed with data or analysis tools. A. Souizi: conceived and designed the analysis.

Abbreviations

AE: auxiliary electrode
C: concentration
C_C: double layer capacity
CR: corrosion rate
DFT: density functional theory
E_a: activation energy
E: potential
E_corr: corrosion potential
EIS: electrochemical impedance spectroscopy
Symbols definition

\( \beta_c \): Tafel slope
\( \Delta E_{\text{gap}} \): gap energy
\( \Delta G^\circ \): activation free enthalpy
\( \Delta G_{\text{ads}}^\circ \): adsorption free energy
\( \Delta H^\circ \): activation standard enthalpy
\( \Delta S^\circ \): activation standard entropy
\( \eta \): chemical hardness
\( \mu \): dipole moment
\( \sigma \): chemical softness
\( \theta \): surface coverage rate values
\( \omega \): overall electrophile index
\( \chi \): electronegativity

References


