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2-oxo-N'-phenyl-1,2-dihydroquinoline-4-carbohydrazide as Corrosion Inhibitor for Mild Steel in Acidic Medium: Experimental Studies

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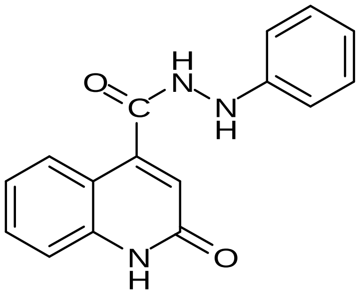
ABSTRACT

The title compound (P4) is studied for using as an interesting corrosion inhibitor for mild steel in acidic environment. The corrosion inhibition effect is investigated using weight loss, Tafel polarization, electrochemical impedance spectroscopy and DFT studies. The inhibitor showed 93% inhibition efficiency at 10^{-3} M concentration of P4. Potentiodynamic polarization suggests that it is a mixed type of inhibitor. Electrochemical impedance spectroscopy was used to investigate the mechanism of corrosion inhibition. The adsorption of this compound on mild steel surface obeys Langmuir adsorption isotherm. Quantum chemical studies were carried out in an attempt to rationalize this behavior.

Key words: corrosion inhibition, dihydroquinoline-4-carbohydrazide, polarization, adsorption, DFT.

INTRODUCTION

The development of new chemically synthesized molecules represents a major strategy for the discovery and preparation of new substances of biological interest. The quinolone heterocyclic is among the classic divisions of organic chemistry, which develop fastest. The quinolones are a family with a broad spectrum antibacterial agent with bactericidal activity [1-9]. Several classes of organic compounds like quinolones are widely used as corrosion inhibitors for metals in acid environments. These molecules have been reported to be effective inhibitors [10-14]; the choice of some molecules used as corrosion inhibitors is based on the following: (1) drug molecules contain oxygen and nitrogen as active centers, (2) molecules are reportedly environmentally friendly and important in biological reactions and (3) molecules can be easily produced and purified [15-18]. **Scheme 1**



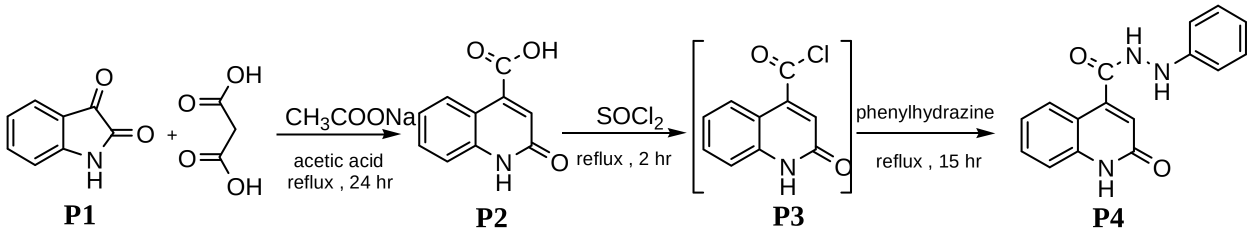
Scheme 1: 2-oxo-N'-phenyl-1,2-dihydroquinoline-4-carbohydrazide (P4)

The aim of this paper is to study the inhibiting action of P4 compound synthesized. The electrochemical behavior of mild steel in HCl media in the absence and presence of P4 has been studied by gravimetric method and electrochemical techniques such as potentiodynamic polarization and impedance spectroscopy (EIS). Quantum chemical studies were also carried out to propose an interpretation of the data.

MATERIALS AND METHODS

2.1. Synthesis of inhibitors

2-oxo-N'-phenyl-1,2-dihydroquinoline-4-carbohydrazide was synthesized and its possible inhibitory effects of the corrosion of mild steel in H_2SO_4 is studied using experimental methods.



Scheme 2: Synthesis of 2-oxo-N'-phenyl-1,2-dihydroquinoline-4-carbohydrazide (P4)

To a solution of 10 mmol of isatin and 10 mmol of malonic acid in 30 mL of acetic acid was added 1 mmol of sodium acetate. The mixture is refluxed for 24 hours. After cooling, 100 ml of water-ice was added. The precipitate obtained is washed several times with ethanol.

Compound P 2: **2-oxo-1,2-dihydroquinoline-4-carboxylic acid.**
Yield (%)= 90 %; Mp: >280 °C; ^1H NMR (300 MHz, DMSO-d6): 6.86 (s,1H, CH); 7.2-8.16 (m, 4H, CH_{arom}); 12.17(s, 1H, NH); 13.9 (s, 1 H, OH); ^{13}C NMR (75 MHz, DMSO-d6): 167.2 (COOH), 163. (C=O), 141.7-139.8 (Cq), 131.3 (CH_{arom}), 126.5 (CH_{arom}), 123.8 (CH), 122.6 (Cq), 116.2 (CH_{arom}).

To a sample of P**2** (1 g, 5.29 mmol) was added freshly distilled thionyl chloride (10 ml) at room temperature. The reaction mixture was heated under reflux for 1 h. The excess thionyl chloride was removed by distillation and co-distilled with dichloromethane (2×10 ml) to obtain **P3** in a quantitative yield. This compound was used immediately for next step without further purification. To excess of phenyl-hydrazine (10 mL) was added a solution of **P3** (0.9 g, 4.33 mmol) in 10 mL of acetone at 0 ˚C. The reaction mixture was stirred at room temperature for overnight. The solution was evaporated under reduced pressure and the residue obtained was washed several times with ether and dichloromethane and dried to obtain the compound P**4** as a yellow solid (0.81 g, 72%).

Compound P4: 2-oxo-N'-phenyl-1,2-dihydroquinoline-4-carbohydrazide
Rdt (%)= 72%; Mp: >280 °C; ^1H NMR (300 MHz, DMSO-d6): 6.62-6.7 (m, 1H,CH_{arom}); 6.76 (s,1H, CH);6.84(d,1H, ^3J = 8.1 Hz, CH_{arom});7.02-7.55 (m, 8H,6CH_{arom},2NH);8.12 (d,1H, ^3J = 8.1 Hz, CH_{arom});11.97(s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d6): 161.2 (C=O), 150.6 (C=O), 143.84-139.87 (Cq, Cq), 131.05, 129.11, 126.88, 122.45, 118.79, 118.31(CH_{arom}), 116.6 (Cq), 116.1, 113.00, 112.76(CH_{arom}).

2.2. Solutions

The aggressive solutions of 1.0 M HCl were prepared by dilution of an analytical grade 37% HCl with double distilled water. The concentration range of inhibitor P4 employed was 10^{-6}-10^{-3} (mol/l).

2.3. Weight loss measurements

Coupons were cut into 1.5× 1.5 × 0.05 cm^3 dimensions having composition (0.09%P, 0.01 % Al, 0.38 % Si, 0.05 % Mn, 0.21 % C, 0.05 % S and Fe balance) used for weight loss measurements. Prior to all measurements, the exposed area was mechanically abraded with 180, 400, 800, 1000, 1200 grades of emery papers. The specimens are washed thoroughly with bidistilled water degreased and dried with ethanol. Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 100 cm^3. The immersion time for the weight loss is 6 h at (308±1) K. In order to get good reproducibility, experiments were carried out in duplicate. The average weight loss was obtained. The corrosion rate (**v**) is calculated using the following equation:

$$\mathbf{v = W / S}.t \qquad \textbf{(1)}$$

Where W is the average weight loss, S the total area, and t is immersion time. With the corrosion rate calculated, the inhibition efficiency (E_w) is determined as follows:

$$Ew\ \% = \frac{V0 - V}{V0}\ X\ 100 \qquad \textbf{(2)}$$

Where $\mathbf{V_0}$ and **V** are the values of corrosion rate without and with inhibitor, respectively.

2.4. Electrochemical tests

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltamaster soft-ware. This potentiostat is connected to a cell with three electrode thermostats with double wall. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. Anodic and cathodic potentiodynamic polarization curves were plotted at a polarization scan rate of 0.5mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarisation curves are obtained from −800 mV to −200 mV at 308 K. The solution test is there after de-aerated by bubbling nitrogen. Inhibition efficiency (Ep%) is defined as:

$$Ep\% = \frac{\mathrm{icor(0) - icor(inh)}}{\mathrm{icor(0)}}\ \mathrm{x}\ 100 \qquad \textbf{(3)}$$

Where icorr(0) and icorr(inh) represent corrosion current density values without and with inhibitor, respectively.

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system, which included a digital potentiostat model Voltalab PGZ100 computer at Ecorr after immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 308 K. The impedance diagrams are given in the Nyquist representation.

Inhibition efficiency (E_R%) is estimated using the relation:

$$ER\% = \frac{\mathrm{Rt(inh) - Rt(0)}}{\mathrm{Rt(inh)}}\ \mathrm{x}\ 100 \qquad \textbf{(4)}$$

Where Rt(0) and Rt(inh) are the charge transfer resistance values in the absence and presence of inhibitor, respectively.

2.5. Computational Chemistry

All the quantum chemical calculations have been carried out with Gaussian 09 programme package [19-20]. In our calculation we have used B3LYP, a hybrid functional of the DFT method, which consists of the Becke’s three parameters; exact exchange functional B3 combined with the nonlocal gradient corrected correlation functional of Lee-Yang-Par (LYP) has been used along with 6-31G(dp) basis set. In the process of geometry optimisation for the fully relaxed method, convergence of all the calculations has been conirmed by the absence of imaginary frequencies. The aim of our calculation is to calculate the following quantum chemical indices: the energy of highest occupied molecular orbital (E_{HOMO}), the energy of lowest unoccupied molecular orbital (E_{LUMO}), energygap (ΔE), hardness (η), sotness (σ), electrophilicity index (ω), the fraction of electrons transferred (ΔN) from inhibitor molecule to the metal surface, and energy change when both processes occur, namely, and correlate these with the experimental observations. The electronic populations as well as the Fukui indices and local nucleophilicities are computed using different populations analysis MPA (Mulliken population analysis) and NPA (natural population analysis) [21-23]. The cationic systems, needed in the calculation of nucleophilic Fukui indices, are taken in the same geometry as the neutral system. Our objective, in this study, is to investigate computationally inhibitory action of quinoline derivative **P4** with chloridric acid in gas and in aqueous phase using B3LYP method with 6-31G(d,p) basis set.

2.5.1. Theory and computational details

Theoretical study of quinoline derivative with chloridric acid as corrosion inhibitors was done by using the Density Functional Theory (DFT) with the B3LYP [24] /6-31G(d,p) method implemented in Gaussian 09 program package. In this study, some molecular properties were calculated such as the frontier molecular orbital (HOMO and LUMO) energies, energy gap (E_{Gap}), charge distribution, electron affinity (A), ionization

Popular qualitative chemical concepts such as electronegativity [25, 26] (χ) and hardness [27] (η) have been provided with rigorous definitions within the purview of conceptual density functional theory [28-30] (DFT). Electronegativity is the negative of chemical potential defined [31] as follows for an N-electron system with total energy E and external potential $v(\vec{r})$

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \qquad (5)$$

μ is the Lagrange multiplier associated with the normalization constraint of DFT [32, 33].

Hardness (η) is defined [34] as the corresponding second derivative,

$$\eta = -\left(\frac{\partial^2 E}{\partial N}\right)_{v(r)} = -\left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \qquad (6)$$

Using a finite difference method, working equations for the calculation of χ and η may be given as [28]:

$$\chi = \frac{I+A}{2} \quad \text{or} \quad \chi = -\frac{E_{HOMO}+E_{LUMO}}{2} \qquad (7)$$

$$\eta = \frac{I-A}{2} \quad \text{or} \quad \eta = -\frac{E_{HOMO}-E_{LUMO}}{2} \qquad (8)$$

Where I = $-E_{HOMO}$ and A= $-E_{LUMO}$ are the ionization potential and electron affinity respectively.

Local quantities such as Fukui function f(r) defined the reactivity/selectivity of a specific site in a molecule. The Fukui function is defined as the first derivative of the electronic density q(r) of a system with respect to the number of electrons N at a constant external potential v(r) [35].

$$f(r) = \left[\frac{\partial \rho(r)}{\partial N}\right]_{v(r)} = \left[\frac{\delta \mu}{\delta v(r)}\right]_{N} \qquad (9)$$

Using left and right derivatives with respect to the number of electrons, electrophilic and nucleophilic Fukui functions for a site k in a molecule can be defined [36].

$$f_k^+ = P_k(N+1) - P_k(N) \quad \textit{for nucleophilic attack} \qquad (10)$$

$$f_k^- = P_k(N) - P_k(N-1) \quad \textit{for electrphilic attack} \qquad (11)$$

$$f_k^+ = [P_k(N+1) - P_k(N-1)]/2 \quad \textit{for radical attack} \qquad (12)$$

Where, $P_k(N)$, $P_k(N+1)$ and $P_k(N-1)$ are the natural populations for the atom k in the neutral, anionic and cationic species respectively.

The fraction of transferred electrons ΔN was calculated according to Pearson theory [37]. This parameter evaluates the electronic flow in a reaction of two systems with different electronegativities, in particular case; a metallic surface (Fe) and an inhibitor molecule. ΔN is given as follows:

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \qquad \textbf{(13)}$$

where χFe and χinh denote the absolute electronegativity of an iron atom (Fe) and the inhibitor molecule, respectively; ηFe and ηinh denote the absolute hardness of Fe atom and the inhibitor molecule, respectively. In order to apply the eq. 8 in the present study, a theoretical value for the electronegativity of bulk iron was used χFe = 7 eV and a global hardness of ηFe = 0, by assuming that for a metallic bulk I = A because they are softer than the neutral metallic atoms [37].

The electrophilicity has been introduced by Parr et al. [38], is a descriptor of reactivity that allows a quantitative classification of the global electrophilic nature of a compound within a relative scale. They have proposed the ω as a measure of energy lowering owing to maximal electron flow between donor and acceptor and ω is defined as follows.

$$\omega = \frac{\chi^2}{2\eta} \qquad \textbf{(14)}$$

The Softness σ is defined as the inverse of the η [39]

$$\sigma = \frac{1}{\eta} \qquad \textbf{(15)}$$

RESULTS AND DISCUSSION

3.1. Weight loss studies

The values of inhibition efficiency (E_w%) and the corrosion rate (C_R) obtained from weight loss method at different concentrations of P4 are summarized in **table 1.** It follows from the data that the weight decreased and therefore corrosion inhibition increased with increase in inhibitor concentration. It was also observed that corrosion rate decreased with increase in inhibitor concentration.

It is evident from the table that P4 inhibits the corrosion of mild steel in HCl solution at all the concentrations used in the study i.e. 10^{-6} to 10^{-3}. Maximum inhibition efficiency was obtained at the concentration 10^{-3}. The increased inhibition efficiency and decreased corrosion rate might be due to the increased adsorption and increased surface coverage (θ) of inhibitor on mild steel surface with increase in concentration.

Table 1. Corrosion parameters obtained from weight loss measurements for mild steel in 1 M HCl containing various concentrations of P4 at 308 K

Inhibitor	**Concentration** (M)	**w** (mg.cm^{-2} h^{-1})	**E_w** (%)
1M HCL	**--**	0.82	--
Inhibitor P4	**10^{-6}**	0.21	74
	10^{-5}	0.19	77
	10^{-4}	0.15	82
	10^{-3}	0.06	**93**

3.2. Adsorption Isotherm

The degree of Surface Coverage (θ) for different concentrations of inhibitor in 1M HCl has been calculated from weight loss. The obtained data was tested graphically for fitting suitable isotherm. Almost a straight line was obtained by plotting C/θ Vs C shown in **figure 1**, which proves that the adsorption of this compound obeys Langmuir isotherm.

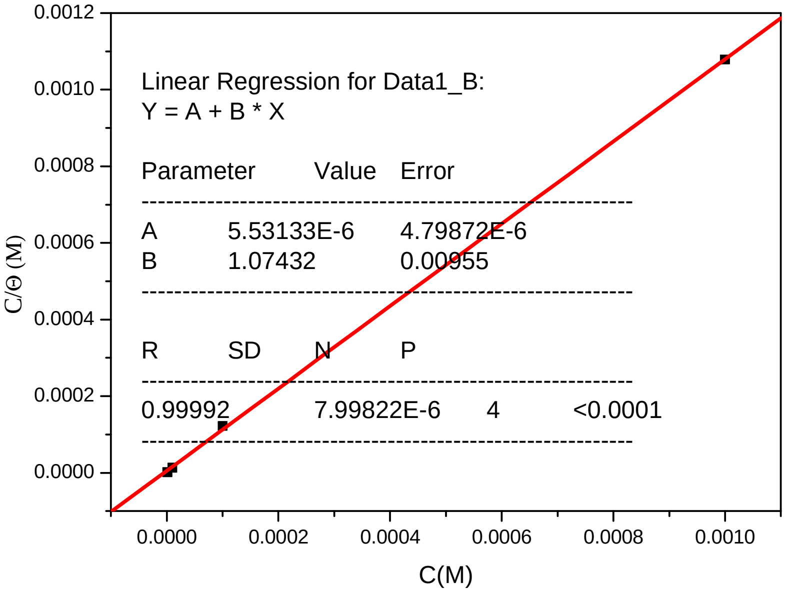
$$\frac{C}{\theta} = \frac{1}{k} + C \qquad \textbf{(16)}$$

Where, C is the concentration of inhibitor, θ is surface coverage on the metal surface and K_{ads} is the equilibrium constant of adsorption process.

The free energy of adsorption ΔG°ads, also can be calculated using the following equation:

$$K = \frac{1}{55.55}\exp\left(-\frac{\Delta G^{0}_{ads}}{RT}\right) \qquad \textbf{(17)}$$

Where R is the universal gas constant, T the thermodynamic temperature and the value 55.5 is the molar concentration of water in the solution.



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Linear Regression for Data1_B:
Y = A + B * X

Parameter         Value         Error
------------------------------------------------------------
A         5.53133E-6         4.79872E-6
B         1.07432            0.00955
------------------------------------------------------------

R         SD         N         P
------------------------------------------------------------
0.99992         7.99822E-6     4         <0.0001
------------------------------------------------------------
```

Figure 1. Langmuir Adsorption isotherm for different concentrations of P4 in 1M HCl

Figure 1 illustrates the dependence of the fraction of the concentration and the surface covered C/θ as function of the concentration of the P4. The obtained plot of inhibitor is linear with a slope 1.03668 to close to unity. The regression coefficient is R = 0.99992 the intercept permit the calculation of the equilibrium constant K which is 180788.346 M^{-1} which leads to evaluate $\Delta G°_{ads}$ = -41.36 kJ/mol.

The large negative values of ensure the spontaneity of the adsorption process and the stability of the adsorbed layer on the mild steel surface as well as a strong interaction between the P4 molecules and the metal surface [40-43]. This value indicates also that inhibitor interacts on the steel surface by electrostatic effect. These results indicate that the presence of P4 increases the inhibition efficiency without change in adsorption mechanism. The results suggest that the experimental data are well described by Langmuir isotherm.

3.3. Polarisation measurements

Current–potential characteristics resulting from cathodic and anodic polarisation curves of steel in 1M HCl in presence of the P4 at various concentrations are evaluated. The cathodic Tafel plots of P4 are shown in Figure 2, Table 2, collects electrochemical parameters and inhibition efficiencies (EP).

The cathodic and anodic polarisation curves of steel in hydrochloric acid in the absence and presence of P4 at different concentrations of the tested inhibitor are shown in Figure 2. Table 2 gives the corresponding electrochemical parameters values of corrosion potentials E_{corr}, corrosion current Icorr, cathodic Tafel slope βc and inhibition efficiencies Ep% for different concentrations of compound derived from the potentiodynamic polarisation curves.

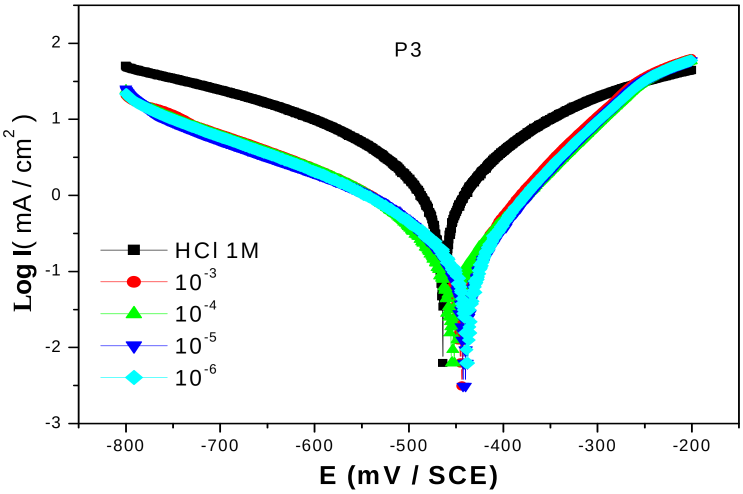


Figure 2. Cathodic and anodic polarisation curves of mild steel in 1M HCl at different content of P4

Table 2. Polarisation parameters and the corresponding inhibition efficiency of mild steel corrosion in 1M HCl containing different concentrations of P4 at 308 K

Inhibitor	**Concentration** (M)	**-E_{corr}**	**I_{corr}** (µA/cm^2)	**-βc**	**E_P** (%)
1M HCl	--	465	1386	184	--
Inhibitor P4	**10^{-3}**	460	132	180	90
	10^{-4}	463	212	188	85
	10^{-5}	466	401	185	71
	10^{-6}	458	581	175	**58**

All concentration of P4 not affect significantly E_{corr}. It reported out that if the inhibition is due to the geometric blocking effect the shift of corrosion potential will be negligible (ΔE_{corr} will be zero) as the inhibitor is added to the solution [44-45].

The inhibition for this system cannot be caused by the active sites blocking effect, but may be due in the main to the geometric blocking effect. Positive values of Ep% indicated corrosion inhibition, and negative values showed corrosion acceleration [46-47].

The parallel Tafel curves obtained indicate that hydrogen evolution reaction is activation controlled and the addition of P4 does not modify the mechanism of this process.

We conclude that the P4 has effect on the cathodic and anodic behaviour of mild steel. Then, we may conclude that P4 acts as a mixed inhibitor.

3.4. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) becomes a very important tool in the study of the inhibition of corrosion of metals. This method permits to impose a small sinusoidal excitation to an applied potential and then the electrochemical interface metal/solution offers impedance. From the various impedance data, interfaces are often described by equivalent circuits involving resistors, capacitors and sometimes inductances. The various electrochemical reactions involve the formation of electrical double layer.

Encouraging results obtained by weight loss and stationary methods have incited us to study the inhibitory effect of P4 in mild steel in 1M HCl solution by the use of EIS measurements. The corrosion behaviour of steel, in the absence and presence of P4 compound is also investigated by the electrochemical impedance spectroscopy (EIS) at 308 K after 30 min of immersion. The charge-transfer resistance (R_t) values are calculated from the difference in impedance at lower and higher frequencies.

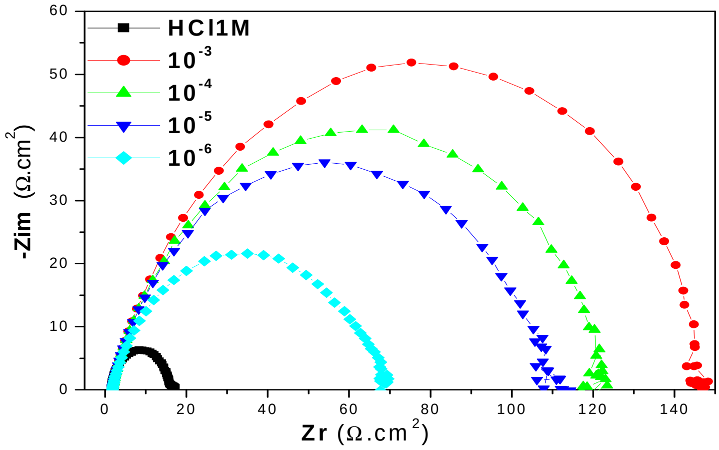


Figure 3. Impedance diagrams of iron in 1M HCl at Ecorr with and without P4 at different concentrations

Typical Nyquist diagrams obtained in the presence of P4 compound at 10^{-3}M are shown in Figure 3. the deduced impedance parameters as transfer-resistance R_t (Ω.cm^2), frequency f_m (Hz), double layer capacitance C_{dl} (F/cm^2) and corresponding inhibition efficiency (E_{Rt}%) are gathered in table 3. It is seen from this figure 3, the impedance diagrams does show perfect semi-circles. We remark that the increase of R_t and decrease of double-layer capacitance (C_{dl}) and the efficiency increases when the concentration P4 increases.

The obtained impedance diagrams almost a semi-circular appearance, indicating a charge transfer process mainly controls the corrosion of mild steel. In fact, the presence of P4 compound enhances the value of R_t in acidic solution. Values of double layer capacitance are also brought down to the maximum extent in the presence of P4 and the decrease in the values of C_{dl} follow the order similar to that obtained for I_{corr} in this study.

The decrease in C_{dl} may be due to the adsorption of this compound on the metal surface leading to the formation of film from acidic solution [48-50].

Table 3.Characteristic parameters evaluated from EIS diagrams with and without P4 at different concentrations

Inhibitor	**Concentration** (M)	**R_{ct}** (Ω cm^2)	**C_{dl}** (µf/cm^2)	**E_{Rt}** (%)
1M HCl	-	15	200	--
Inhibitor P4	**10^{-6}**	57	88	74
	10^{-5}	68	80	78
	10^{-4}	88	73	83
	10^{-3}	101	71	**86**

3.5. Theoretical calculations

The FMOs (HOMO and LUMO) are very important for describing chemical reactivity. The HOMO containing electrons, represents the ability (E_{HOMO}) to donate an electron, whereas, LUMO haven't not electrons, as an electron acceptor represents the ability (E_{LUMO}) to obtain an electron. The energy gap between HOMO and LUMO determines the kinetic stability, chemical reactivity, optical polarizability and chemical hardness–softness of a compound [51].

Firstly, in this study, we calculated the HOMO and LUMO orbital energies by using B3LYP method with 6-31G(d,p). All other calculations were performed using the results with some assumptions. The higher values of E_{HOMO} indicate an increase for the electron donor and this means a better inhibitory activity with increasing adsorption of the inhibitor on a metal surface, whereas E_{LUMO} indicates the ability to accept electron of the molecule. The adsorption ability of the inhibitor to the metal surface increases with increasing of E_{HOMO} and decreasing of E_{LUMO}. The HOMO and LUMO orbital energies and image of P4 were performed and were shown in Table 4 and Figure 4.

The number of electrons transferred (ΔN) was also calculated and tabulated in Table 4. The $\Delta N < 3.6$ and indicate the tendency of surface [52-53].

Table 4. Quantum chemical descriptors of the studied inhibitor at B3LYP/6-31G(d,p) in gas, G and aqueous, A phases

	Phase	
Prameters	**Gas**	**Aqueous**
Total Energy *TE* (eV)	-25366.7	-25367,3
E_{HOMO} (eV)	-6.2564	-5.9149
E_{LUMO} (eV)	-0.5679	-1.7763
Gap ΔE (eV)	5.6885	4.1386
Dipole moment μ (Debye)	3.9945	6.1221
Ionisation potential *I* (eV)	6.2564	5.9149
Electron affinity *A*	0.5679	1.7763
Electronegativity χ	3.4121	3.8456
Hardness η	2.8443	2.0693
Electrophilicity index ω	2.0467	3.5733
Softness σ	0.3516	0.4833
Fractions of electron transferred ΔN	0.6307	0.7622

The calculated values of the f_k^+ for all inhibitors are mostly localized on the quinoline ring (table 5). Namely C_9, C_{13}, C_{15}, C_{16}, and O_{19} indicates that the quinoline ring will probably be the favorite site for nucleophilic attacks [54-55]. The results also show that O_{15} and O_{21} atoms are suitable sites to undergo both nucleophilic and electrophilic attacks, probably allowing them to adsorb easily and strongly on the mild steel surface.

Table 5. Pertinent natural populations and Fukui functions of the studied inhibitors calculated at B3LYP/6-31G(d,p) in gas, G and aqueous, A phases

Atom k	*Phase*	*P(N)*	*P(N+1)*	*P(N-1)*	f_k^+	f_k^-	f_k^0
C_9	G	6,1037	6,2051	6,0676	0,1014	0,0361	0,0688
	A	6,0668	6,1969	6,0943	0,1302	-0,0275	0,0513
C_{13}	G	6,2201	6,3948	6,2283	0,1748	-0,0082	0,0833
	A	6,2792	6,3848	6,2633	0,1057	0,0159	0,0608
O_{15}	G	8,6036	8,7098	8,4969	0,1061	0,1068	0,1064
	A	8,6603	8,7391	8,6398	0,0788	0,0206	0,0497
C_{16}	G	5,3283	5,3486	5,3189	0,0203	0,0093	0,0148
	A	5,3035	5,4091	5,2942	0,1056	0,0093	0,0574
O_{19}	G	8,5736	8,6769	8,5556	0,1033	0,0181	0,0607
	A	8,6349	8,7121	8,5630	0,0772	0,0719	0,0745

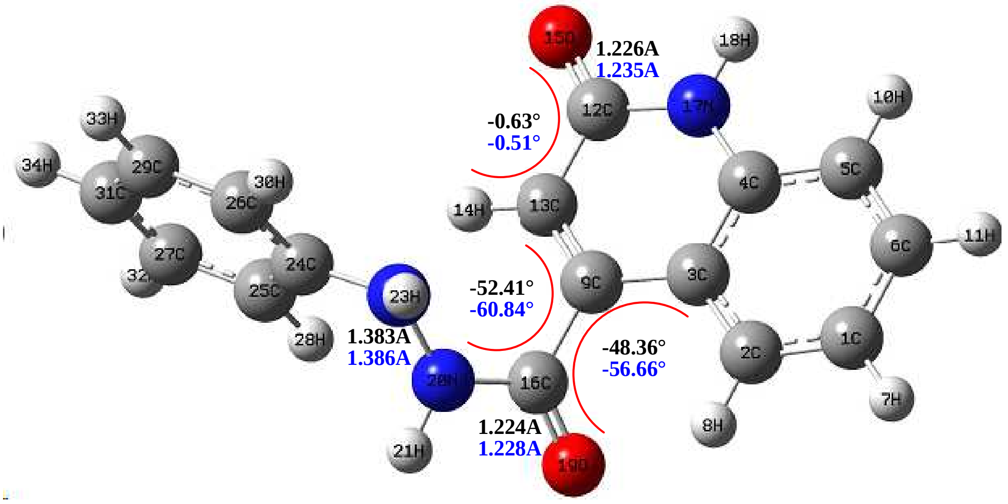
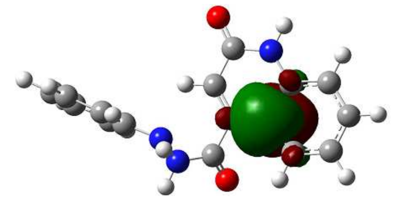
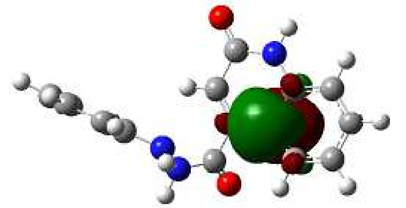
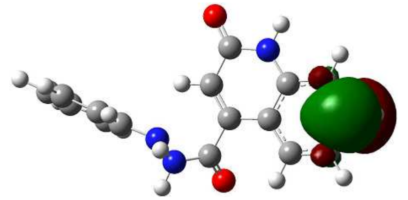
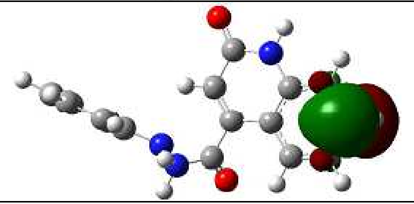


Figure 4. Optimized molecular structures and pertinent dihedral angles and bond lengths of the studied inhibitors calculated in gas (black) and aqueous (blue) phases at B3LYP/6-31G(d,p) level of P4

After the analysis of the theoretical results obtained, we can say that the molecule P4 have a non-planar structure.

Table 6. The HOMO and the LUMO electrons density distributions of the studied inhibitors computed at B3LYP/6-31G (d,p) level in gas and aqueous phases

Phase	Gas	Aqueous
HOMO		
LUMO		

CONCLUSION

The principal finding of the present work can be summarized as follows:
i) P4 acts as a good inhibitor for the corrosion of mild steel in 1M HCl.
ii) Potentiodynamic curves reveal that P4 is a mixed type of inhibitor.
iii) The results obtained from weight loss, impedance and polarization studies are in good agreement with each other.
iv) The adsorption of P4 on mild steel surface obeyed Langmuir adsorption isotherm.
vi) The calculated quantum chemical parameters such as HOMO-LUMO gap, E_{HOMO}, E_{LUMO}, dipole moment (μ) and total energy (TE) were found to give reasonably good correlation with the efficiency of the corrosion inhibition.

REFERENCES

[1] C. Spinorin, *Ann. Rev. Microbiol,* **1989**, 43, 60.
[2] J.J. Pocidalo, « Les nouvelles quinolones », *éd. Arnette. Paris*, **1985**.
[3] H. Beruer, "Atlas de la chimie", *1ere éd. Edition la Pochothèque, France*, **2000**, 411.
[4] C. Spinorin, *Ann. Rev. Microbiol*, **1989**, 43,601.
[5] H. Beruer, "Atlas de la chimie", *1ere éd. Edition la Pochothèque, France*, **2000**, 412.
[6] A. Korolhovas, J. H. Burckhaltre, «Essentials of medicinal chemistry». *éd. Wiley Interscience Pub, New york*, **1983**, 404.
[7] J. J. Poccidalo, "Les nouvelles quinolones", *éd. Arnnette, Paris*, **1985**.
[8] J. C. Bergh, A. Lazovios, G. Somogyi, L. Feher, *Cancer invest*, **1997**, 15, 204.
[9] R. Khunt, N. Datta, F. Bharmal, A. R. Rarikh, *J. Ind. Chem. Soc*, **2001**, 78, 47.
[10] N.O. Eddy and S.A. Odoemelam, *Adv. Nat. & Appl. Sci*, **2008**, 2(1), 35.
[11] I.B. Obot, N. O. Obi-Egbedi, S.A. Umoren, *Int. J. Electrochem. Sci*, **2009**, 4, 863.
[12] E.E. Ebenso, H. Alemu, S.A. Umoren, I.B.Obot, *Int. J. Electrochem. Sci*, **2008**, 3, 1325.
[13] S.A. Umoren, I.B. Obot, E.E. Ebenso, N. O. Obi-Egbedi, *Int. J. Electrochem. Sci*, **2008**, 3, 1029.
[14] E. E. Ebenso, N. O. Eddy and A. O. Odiongenyi, *Portugaliae Electrochimica. Acta*, **2009**, 27(1), 13.
[15] N.O. Eddy, E.E. Ebenso, *Int. J. Electrochem. Sci*, **2010**, 5, 731.
[16] N.O. Eddy , 'Inhibition of corrosion of mild steel by some antibiotics' PhD Thesis,University of Calabar, Nigeria, **2008**.
[17] N.O. Eddy, S.A. Odoemelam and A.J. Mbaba, *Afri. J. Pure & Appl. Chem*, **2008**, 2 (12), 132.
[18] N. O. Eddy, E. E. Ebenso and U. J. Ibok, *J. Appl. Electrochem*, **2010**, 40(2), 445.
[19] M.J.Frisch,G.W.Trucks,H.B.Schlegeletal., Gaussian 09, Revision A.1, Gaussian, *Inc.,Wallingford, Conn, USA*, **2009**.
[20] H. Elmsellem, M. H.Youssouf, A. Aouniti, T. Ben Hadd, A. Chetouani, B. Hammouti. Russian, *Journal of Applied Chemistry*, **2014**, 87(6), 744−753.
[21] J. Li, H. Li, M. Jakobsson, S. Li, P. Sjodin, M. Lascoux, *Mol. Ecol*, **2012**, 21, 28.
[22] H. Elmsellem, A. Aouniti, M. Khoutou, A. Chetouani, B. Hammouti, N. Benchat, R. Touzani and M. Elazzouzi, *J. Chem. Pharm. Res*, **2014**, 6, 1216.
[23] H. Elmsellema, T. Haritb, A. Aouniti, F. Malekb, A. Riahi, A. Chetouani, and B. Hammouti, *Protection of Metals and Physical Chemistry of Surfaces*, **2015**, 51(5), 873–884.
[24] K. Efil and Y. Bekdemir, *Canadian Chemical Transactions*, **2015**, 3(1), 85.

[25] L. Pauling, The nature of the chemical bond, 3rd edn. (Cornell University Press, Ithaca, **1960**).
[26] K.D. Sen, C. Jorgenson, Springer. Berlin, **1987**, 66.
[27] K.D. Sen, D.M.P. Mingos, Springer, Berlin, **1993**, 80
[28] R.G. Parr, W. Yang, Oxford University Press, Oxford, **1989**.
[29] P. Geerlings, F. de Proft, W. Langenaeker, *Chem. Rev*, **2003**,103, 1793
[30] H. Chermette, *J. Comput. Chem*, **1999**, 20, 129
[31] R.G. Parr, R.A. Donnelly, M. Levy, W. Palke, *J. Chem. Phys*, **1978**, 68, 3801
[32] P. Hohenberg, Kohn, *Phys. Rev. B*, **1964**, 136, 864
[33] W. Kohn, L. Sham, *J. Phys. Rev. A*, **1965**, 140, 1133
[34] R.G. Parr, R.G. Pearson, *J. Am. Chem. Soc*, **1983**, 105, 7512
[35] W. Yang, W. Mortier, J. Am. Chem. Soc, **1986**, 108, 5708
[36] R.K. Roy, S. Pal, K. Hirao, *J. Chem. Phys*, **1999**, 110, 8236
[37] R.G. Pearson, *Inorg. Chem*, **1988**, 27 734.
[38] V.S. Sastri, and J.R. Perumareddi, *Corrosion*, **1997**, 53, 671
[39] P. Udhayakala, T. V. Rajendiran, and S. Gunasekaran, *Journal of Chemical, Biological and Physical Sciences A*, **2012**, 2(3), 1151-1165.
[40] H. Elmsellem, M. H.Youssouf, A. Aouniti, T. Ben Hadd, A. Chetouani, B. Hammouti, Russian, *Journal of Applied Chemistry*, **2014**, 87(6), 744-753.
[41] H. Elmsellem, A. Elyoussfi, N. K. Sebbar, A. Dafali, K. Cherrak, H. Steli, E. M. Essassi, A. Aouniti and B. Hammouti, *Maghr. J. Pure & Appl. Sci*, **2015**, 1, 1-10.
[42] H. Elmsellem, H. Bendaha, A. Aouniti, A. Chetouani, M. Mimouni, A. Bouyanzer, *Mor. J. Chem*, **2014**, 2 (1), 1-9.
[43] N. K. Sebbar, H. Elmsellem, M. Boudalia, S. lahmidi, A. Belleaouchou , A. Guenbour, E. M. Essassi, H. Steli, A. Aouniti, *J. Mater. Environ. Sci*, **2015**, 6 (11), 3034-3044.
[44] H. Elmsellem, T. Harit, A. Aouniti, F. Malek, A. Riahi, A. Chetouani, B. Hammouti, *Protection of Metals and Physical. Chemistry of Surfaces*, **2015**, 51(5), 873.
[45] H. Elmsellem, A. Aouniti, M.H. Youssoufi, H. Bendaha, T. Ben hadda, A. Chetouani, I. Warad, B. Hammouti, *Phys. Chem. News*, **2013**,70, 84.
[46] A. Aouniti, H. Elmsellem, S. Tighadouini, M. Elazzouzi, S. Radi, A. Chetouani, B. Hammouti, A. Zarrouk, *Journal of Taibah University for Science*, **2015**, http://dx.doi.org/10.1016/j.jtusci.2015.11.008.
[47] H. Elmsellem, A. Elyoussfi, H. Steli, N. K. Sebbar, E. M. Essassi, M. Dahmani, Y. El Ouadi, A. Aouniti, B. El Mahi, B. Hammouti, *Der Pharma Chemica*, **2016**, 8(1), 248-256.
[48] H. Elmsellem, K. Karrouchi, A. Aouniti, B. Hammouti, S. Radi, J. Taoufik, M. Ansar, M. Dahmani, H. Steli and B. El Mahi, *Der Pharma Chemica*, **2015**, 7(10), 237-245.
[49] H. Elmsellem, H. Nacer, F. Halaimia, A. Aouniti, I. Lakehal, A .Chetouani, S. S. Al-Deyab, I. Warad, R. Touzani, B. Hammouti. *Int. J. Electrochem. Sci*, **2014**, 9, 5328.
[50] H. Elmsellem, N. Basbas, A. Chetouani, A. Aouniti, S. Radi, M. Messali, B. Hammouti, *Portugaliae. Electrochimica. Acta*, **2014**, 2, 77.
[51] M. Govindarajan, M. Karabacak, Spectrochim Acta Part A Mol Biomol Spectrosc, **2012**, 85, 251-60.
[52] I. Lukovits, E. Kalman, F. Zucchi, *Corrosion*, **2001**, 57, 3.
[53] S. Lahmidi, H. Elmsellem, A. Elyoussfi, N. K. Sebbar, E.M. Essassi, Y. Ouzidan, Y. Kandri Rodi, K. Dguigui, B. El Mahi and B. Hammouti, *Der Pharma Chemica*, **2016**, 8(1), 294.
[54] S. Kumar, D. G. Ladha , P. C. Jha, and N. K. Shah *International Journal of Corrosion* Volume **2013**, ID 819643, 10 http://dx.doi.org/10.1155/2013/819643
[55] K. F. Khaled., Applied *Surface Science*, **2010**, 256 (22), 6753.