



Electrochemical, gravimetric and theoretical evaluation of (4Z)-2,5-dimethyl-4-(4-methylpyrimido[1,2-a]benzimidazol-2(1H)-ylidene)-2,4-dihydro-3H-pyrazol-3-one (P1) as a corrosion inhibitor for mild steel in 1 M HCl solution

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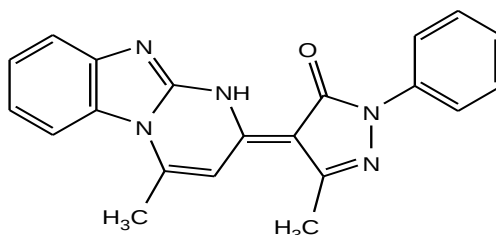
Abstract

The effect of (4Z)-2,5-dimethyl-4-(4-methylpyrimido[1,2-a]benzimidazol-2(1H)-ylidene)-2,4-dihydro-3H-pyrazol-3-one (P1) on the corrosion inhibition of mild steel (MS) in 1 M HCl solution was investigated by linear polarization resistance, electrochemical impedance spectroscopy (EIS) and weight loss measurements in the presence of different concentrations of P1 ranging from 10^{-6} M to 10^{-3} M. The adsorption of P1 on the MS surface was described very well by the Langmuir adsorption model and quantum chemical calculations (DFT).

Keywords: 4-methylpyrimido-[1,2-a]Benzimidazole, Mild steel, Polarization, Electrochemical impedance spectroscopy, Quantum chemical calculations (DFT).

1. Introduction

Over the years, benzimidazoles have constituted an important class of heterocyclic which, derivatives are very useful intermediates/subunits for the development of molecules of pharmaceutical or biological interest [1]. They are an important class of bioactive molecules in the field of drugs and pharmaceuticals and have found applications in diverse therapeutic areas including antitumor [2] antibacterial [3–6], antifungal [7], antiviral [8–12], anticonvulsant [13], antidepressant [14], analgesic [15], anti-inflammatory [16] and antidiabetic properties [17]. Furthermore pyrazole is an important kind of nitrogen heterocyclic compound [18–20], which derivatives exhibit a wide range of biological activities, such as antifungal [21], insecticidal [22], herbicidal [23], anticancer [24], antiinflammatory [25]. All these properties have motivated us to synthesize a compound with two entities benzimidazole and pyrazole in the same structure (P1) **Scheme 1**.



Scheme 1: Chemical Structure of (4Z)-2,5-dimethyl-4-(4-methylpyrimido[1,2-a]benzimidazol-2(1H)-ylidene)-2,4-dihydro-3H-pyrazol-3-one (**P1**).

In continuation of the previous work on the development of benzimidazole derivatives as corrosion inhibitors in acidic environment [26], the effect of (**P1**) on the corrosion inhibition of MS in 1 M HCl was studied using polarization measurements, impedance techniques, weight loss measurements and quantum chemical calculations. The relationship between calculated quantum chemical parameters and experimental inhibition efficiencies of the inhibitor (**P1**) was discussed.

2. Experimental details

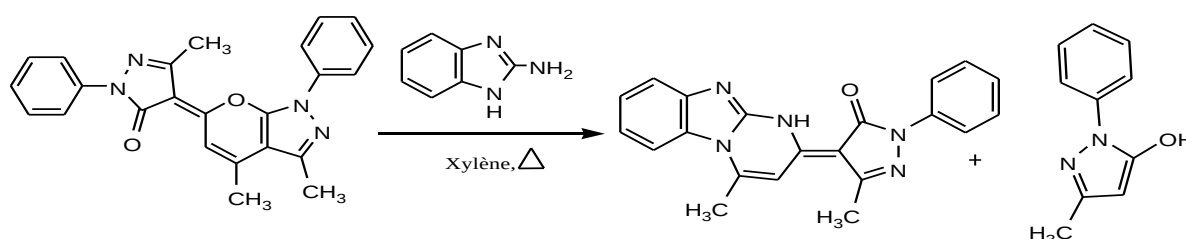
2.1. Materials and sample preparation

The composition (wt.%) of **MS** samples used for all the experiments was as follows: C = 0.253; Si = 0.12; P = 0.013; S = 0.024; Cr = 0.012; Mn = 0.03; and 99.548 Fe. Coupons cut into 1.5 x 1.5 x 0.05 cm³ size were used for gravimetric measurements. On the other hand specimens with exposed surface areas 1 cm² were used as working electrode for polarization and (**EIS**) measurements. At first, the specimens were mechanically abraded with 320, 400, 600, 800, 1000 and 1200 grade of emery papers. Then they were degreased with acetone, washed with double distilled water, and dried in air before use.

The 1.0 M HCl solution was prepared by dilution of analytical grade HCl of predetermined molarity with double distilled water. The concentration range of the inhibitor (**P1**) was 10⁻⁶ M to 10⁻³ M. The volume of the solution used in each experiment was 100 mL.

2.2. Synthesis of inhibitor

A 40 ml xylene solution of 5-[1-phenyl-3-methyl-5-oxo-pyrazol-4-ylidene]-1,7-dimethyl-3-phenylpyrano [2,3-c] pyrazole (0.005 mole) was added to another 40 ml xylene solution 2-amino-benzimidazole (0.01 mol) in a round-bottomed flask. The resulting reaction mixture was stirred and refluxed for 6 hrs. The precipitate formed after cooling the reaction mixture to room temperature was filtered and then recrystallized from ethanol (**Scheme 2**).



Scheme 2: Synthesis of (4Z)-2,5-dimethyl-4-(4-methylpyrimido[1,2-a]benzimidazol-2(1H)-ylidene)-2,4-dihydro-3H-pyrazol-3-one (**P1**)

The following physical and spectroscopic NMR data are in consistant for the structure of the synthesized compound (P1):

(P1): Yield = 70%; M.p.: 535-537K; **NMR1H (DMSO-d6) δ ppm:** 2.67(s, 3 H, CH₃), 3.07 (s, 3H, CH₃), 7.21(s, 1H, CH), 7.28-8.11 (m, 10H, CH ar); **NMR13C (DMSO-d6) δ ppm:** 14.30(CH₃), 20.81 (CH₃), 162.04(C=O), 100.4(Cq), 125.7-160.85(Cq), 109.9-129.54 (CH ar).

2.3. Weight loss measurements

The weight loss measurements were performed in a glass vessel containing 100 mL of 1 M HCl solution with and without addition of different concentrations of **P1** at temperature 308 K for 6 hrs. immersion time without bubbling. The mild steel specimens were withdrawn, rinsed with doubly distilled water, washed with acetone, dried and weighed. The experiments were done in triplicate and the average value of the weight loss was noted. The inhibition efficiency ($E_w\%$) was calculated according to the following equation [27]:

$$E_w \% = \frac{V_0 - V}{V_0} \times 100 \quad (1)$$

Where 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 was 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. The potential was stabilized at free potential during 30 mins., before conducting any run. The polarization 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 ($E_p\%$) is defined as:

$$E_p \% = \frac{i_{cor}(0) - i_{cor}(inh)}{i_{cor}(0)} \times 100 \quad (2)$$

Where $i_{cor}(0)$ and $i_{cor}(inh)$ represent corrosion current density values without and with the inhibitor **P1**, respectively.

The electrochemical impedance spectroscopy (EIS) measurements were carried out with the electrochemical system, which included a digital potentiostat model Volta lab PGZ100 computer at E_{cor} 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 ($E_R\%$) was determined using relation (3):

$$E_R \% = \frac{R_t(inh) - R_t(0)}{R_t(inh)} \times 100 \quad (3)$$

Where $R_t(0)$ and $R_t(\text{inh})$ are the charge transfer resistance values in the absence and presence of the inhibitor **P1**, respectively.

2.5. Computational Chemistry

The quantum chemical calculations reported in this work for the inhibitor **P1** were performed at the B3LYP/6-31G (d, p) level of theory using GAUSSIAN 09 series of programs [28]. The optimizations of equilibrium geometric of the inhibitor **P1** were performed using the Berny analytical gradient optimization method [29, 30]. The electronic populations and the Fukui indices as well as local nucleophilicities were computed using different population analysis MPA (Mulliken population analysis) and NPA (natural population analysis) [31-34]. The cationic systems, needed in the calculation of nucleophilic Fukui indices, were taken in the same geometry as the neutral system.

Our objective, in this study, is to investigate computationally the inhibitory action of compound **P1** with hydrochloric acid in the gaseous and in aqueous phases using B3LYP method with 6-31G(d,p) basis set.

2.5.1. Theory and computational details

Theoretical study of quinoline derivative with hydrochloric acid as corrosion inhibitor was done by using the Density Functional Theory (DFT) with the B3LYP[35]/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), and ionization.

Popular qualitative chemical concepts such as electronegativity [36, 37] (χ) and hardness [38] (η) have been provided with rigorous definitions within the purview of conceptual density functional theory [39-41] (DFT). Electronegativity is the negative of chemical potential defined [42] as follows for an N-electron system with total energy E and external potential $v(\vec{r})$

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \quad (4)$$

μ is the Lagrange multiplier associated with the normalization constraint of DFT [43, 44].

Hardness (η) is defined [45] as the corresponding second derivative,

$$\eta = -\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} = -\left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \quad (5)$$

Using a finite difference method, working equations for the calculation of χ and η may be given as [39]:

$$\chi = \frac{I+A}{2} \quad \text{or} \quad \chi = -\frac{E_{\text{HOMO}} + E_{\text{LUMO}}}{2} \quad (6)$$

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

Where $I = -E_{\text{HOMO}}$ and $A = -E_{\text{LUMO}}$ 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 $v(r)$ [46].

$$f(r) = \left[\frac{\partial \rho(r)}{\partial N} \right]_{v(r)} = \left[\frac{\delta \rho}{\delta v(r)} \right]_N \quad (8)$$

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 [47].

$$f_k^+ = P_k(N+1) - P_k(N) \quad \text{for nucleophilic attack} \quad (9)$$

$$f_k^- = P_k(N) - P_k(N-1) \quad \text{for electrophilic attack} \quad (10)$$

$$f_k^+ = [P_k(N+1) - P_k(N-1)]/2 \quad \text{for radical attack} \quad (11)$$

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 [48]. This parameter evaluates the electronic flow in a reaction of two systems with different electronegativity, in particular case; a metallic surface (Fe) and an inhibitor molecule. ΔN is given as follows:

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \quad (12)$$

Where χ_{Fe} and χ_{inh} denote the absolute electronegativity of an iron atom (Fe) and the inhibitor molecule, respectively; η_{Fe} and η_{inh} denote the absolute hardness of Fe atom and the inhibitor molecule, respectively. In order to apply the eq. 12 in the present study, a theoretical value for the electronegativity of bulk iron was used $\chi_{Fe} = 7$ eV and a global hardness of $\eta_{Fe} = 0$, by assuming that for a metallic bulk $I = A$ because they are softer than the neutral metallic atoms [48].

The electrophilicity which introduced by the authors in reference [49], 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.

$$\omega = \frac{\chi^2}{2\eta} \quad (13)$$

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

$$\sigma = \frac{1}{\eta} \quad (14)$$

3. Results and Discussion

3.1. Weight loss measurements

3.1.1. Effect of inhibitor concentration on corrosion of mild steel

The effect of addition of **P1** at various concentrations in 1 M HCl solution on the **MS** corrosion was studied by weight loss measurements at 308 K after 6 hrs immersion. Sometimes the highest concentration is limited by the solubility of the compound. The values of inhibition efficiencies (Ew%) and corrosion rates (v) obtained from weight loss measurements for **P1** at different concentrations in 1 M HCl are listed in (Table 1).

It is found that inhibition efficiency increases with increasing inhibitor concentration, while corrosion rate decreases with inhibitor concentration. The inhibition of mild steel corrosion can be attributed to the adsorption of the inhibitor at the mild steel/HCl solution interface. All Mannich bases are good inhibitors showing more

than 92% inhibition efficiency at 300 ppm concentrations. The good performance of **P1** as corrosion inhibitor for **MS** in 1 M HCl solution may be due to the presence of aromatic rings and hetero-atoms [50-51].

Table 1. Corrosion parameters obtained from weight loss measurements for **MS** in 1 M HCl containing various concentrations of (**P1**) at 308 K.

Inhibitor	Concentration (M)	v (mg.cm ⁻² h ⁻¹)	E_w (%)	θ
1 M HCl	--	0.82	--	--
P1	10⁻⁶	0.42	49	0.49
	10⁻⁵	0.25	70	0.70
	10⁻⁴	0.16	80	0.80
	10⁻³	0.08	90	0.90

3.1.2. Effect of immersion time on corrosion of mild steel

In order to assess the stability of inhibitive behaviour of inhibitor on a time scale, weight loss measurements were performed in 1 M HCl in the absence and presence of **P1** at 10⁻³M concentration for 4–48 hrs immersion time at temperature 308 K. Inhibition efficiencies were plotted against immersion time as seen in (**Figure 1**).

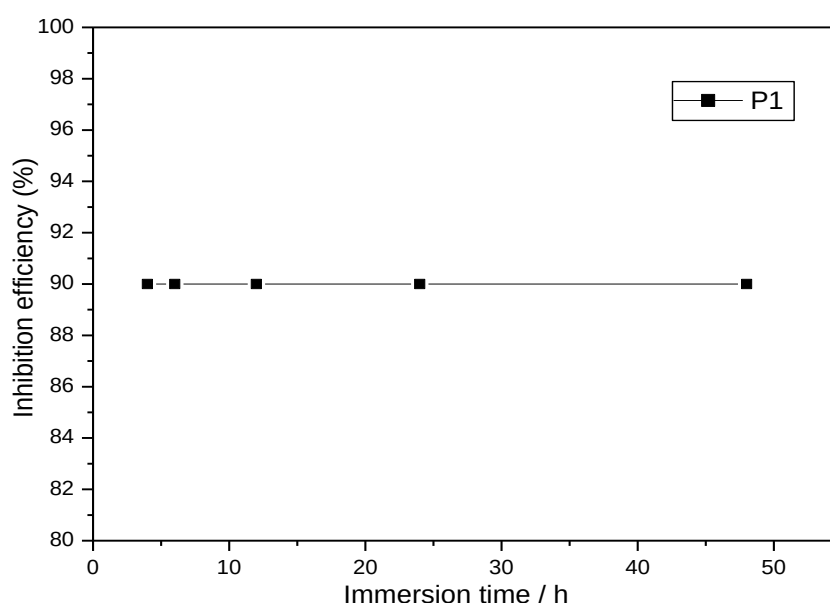


Figure 1. Effect of immersion time on the performance of inhibitor **P1** on **MS** in 1 M HCl at 308 K.

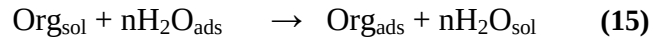
The inhibition efficiency of **P1** was nearly constant after 4 hrs. immersion in the inhibited solution. This means that P1 strongly adsorbed on the MS surface, resulting in a more protective layer.

From these observations, it can be concluded that **P1** is efficient corrosion inhibitor for **MS** in 1 M HCl solution.

3.2. Adsorption Isotherm

Basic thermodynamic information on the connections between inhibitor molecules and the metal surface can be provided by the adsorption isotherm. The efficiency of both molecules as a successful corrosion inhibitor mainly

relied on their adsorption ability of the **MS** surface. The adsorption procedure contains the alternative of water and P1 molecules at the MS surface/solution interface according to the following equation [52]:



Where $\text{Org}_{(\text{sol})}$ and $\text{Org}_{(\text{ads})}$ are the organic molecules studied in the solutions and adsorbed on the **MS** surface, respectively, and n is the number of water molecules replaced by the organic molecules. To obtain the isotherm, the surface-covered (θ) values as a function of inhibitor concentration must be obtained. The surface coverage (θ) at different concentrations of **P1** in 1M HCl solution was calculated from the inhibition efficiencies using the following equation: $\theta = (E_{\text{w}}\%)/100$.

Then, efforts were created to fit the θ values to various isotherms such as Langmuir, Temkin, and Frumkin. Among all these adsorption isotherms, the Langmuir adsorption isotherms were discovered to be the best information for the adsorption behavior of the inhibitors studied. Langmuir adsorption isotherm can be indicated by the following equation:

$$\frac{\theta}{1-\theta} = C_{\text{inh}} \cdot K_{\text{ads}} \quad (16)$$

By rearranging equation (16), the following equation was obtained (17):

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \quad (17)$$

Where K_{ads} is the equilibrium constant of the inhibitor adsorption process and C is the inhibitor concentration. Plots of C/θ versus C yielded a straight line as shown in Figure 2. In both the cases, the linear regression coefficients (R^2) were almost similar to 1, showing that the adsorption of P1 followed the Langmuir adsorption isotherm. Further, the K_{ads} values were measured from the intercept of the straight lines on the C/θ -axis. The continuous of adsorption (K_{ads}) has been relevant to the standard free energy of adsorption, $\Delta G^{\circ}_{\text{ads}}$ with the following equation:

$$\Delta G^{\circ}_{\text{ads}} = -RT \ln (K_{\text{ads}} 55.5) \quad (18)$$

The K_{ads} value obtained from the Langmuir adsorption isotherm is tabulated in (**Table 2**), together with the Gibbs free energy of adsorption $\Delta G^{\circ}_{\text{ads}}$. The high value of K_{ads} for **P1** indicates that **P1** molecules are very well adsorbed on the **MS** surface in 1M HCl solution.

Table 2. Thermodynamic parameters for the corrosion of **MS** in 1 M HCl in the absence and presence of different concentrations of **P1**.

Inhibitor	Linear correlation (coefficient R)	Slope	K (M ⁻¹)	$\Delta G^{\circ}_{\text{ads}}$ (kJ.mol ⁻¹)
P1	0.99994	1.10601	$1.69 \cdot 10^5$	-41.09

The addition of inhibitors caused negative values of $\Delta G^{\circ}_{\text{ads}}$, which verified that the inhibitor P1 was adsorbed spontaneously. It has been usually accepted that for $\Delta G^{\circ}_{\text{ads}}$ values up to -20 kJmol⁻¹, the type of adsorption was regarded for physisorption because the inhibitors acted due to the electrostatic interactions between the charged

molecules and the charged metal surface, while those around -40 kJmol^{-1} were considered for as chemisorption [53], which was due to the charge sharing or a transfer from the inhibitor molecules to the metal surface to form a covalent bond. In the present study, the value of $\Delta G^{\circ}_{\text{ads}}$ was found to be equal to $-41.09 \text{ kJmol}^{-1}$ for **P1** at 308 K. This value is very close to -40 kJmol^{-1} . Therefore, it can be concluded that the adsorption of **P1** on the **MS** surface is more likely chemisorption rather than physisorption [54].

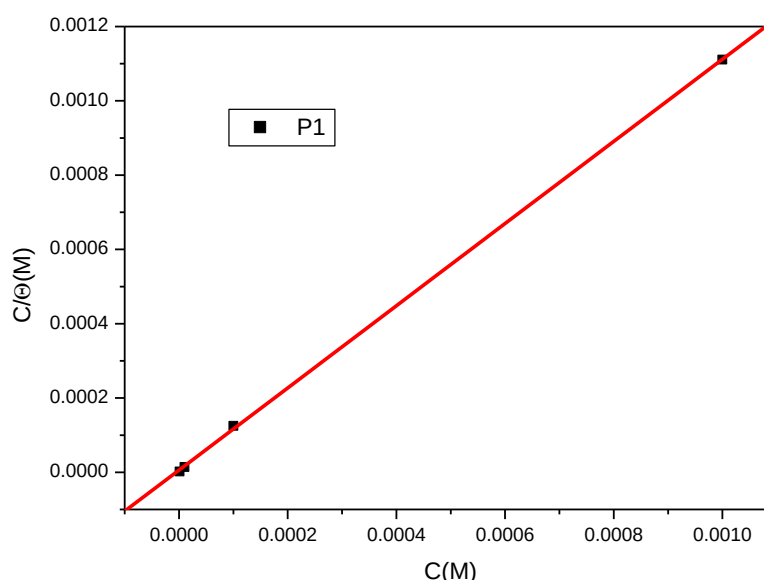


Figure 2. Langmuir adsorption isotherm of **P1** on **MS** in 1M HCl at 308K.

3. 3. Electrochemical impedance spectroscopy measurements

The corrosion behavior of **MS** in the acidic solution in the absence and presence of inhibitor **P1** was also investigated by the **EIS** technique at 308 K. The results of **EIS** experiments in the Nyquist representation are shown in (**Figure 3**). All the obtained spectra are similar in shape and consist of a single capacitive loop, which suggests that the geometric blocking effect is the inhibition mode of **P1**. The diameter of Nyquist plots increased on increasing the concentration of **P1** indicating strengthening of inhibitive film [55]. The above impedance diagram (Nyquist) contains a depressed semicircle with the centre under the real axis, such behavior is characteristic for solid electrode which is attributed to surface roughness and heterogeneities of the steel electrodes.

It is obvious that addition of inhibitor **P1** resulted in an increase in diameter of the semicircular capacitive loop (**Figure 3**) and in the impedance of the double layer impedance. Based on the shape of Nyquist plots (**Figure 3**), the simplest equivalent circuit was decided to be used for a system in which the Warburg impedance is not important to fit the impedance measurements.

This equivalent circuit (Figure 5) includes the solution resistance (R_s), the charge-transfer resistance (R_{ct}) whose value is a measure of electron transfer across the surface and is inversely proportional to corrosion rate and a constant phase element (CPE), instead of the double layer capacitor (C_{dl}), in order to take into account the

electrode surface heterogeneity resulting from surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, formation of porous layers [56, 57]. The impedance of the CPE is expressed by (19):

$$Z_{CPE} = (1/Q) * (1/(j\omega)^n) \quad (19)$$

where Q is the CPE coefficient, n the CPE exponent (phase shift), ω the angular frequency ($\omega = 2\pi f$, where f is the AC frequency), and j here is the imaginary unit. When the value of n is one, the CPE behaves like an ideal double-layer capacitance (C_{dl}) [58]. For the case of a CPE in parallel with a resistance, Hsu and Mansfeld [59] have given this equation for calculating the capacitance (C_{dl}) using the following relation:

$$C_{dl} = Q(\omega_{max})^{n-1} \quad (20)$$

where ω_{max} is angular frequency and $\omega = 2\pi f$. The f_{max} is the frequency at the top of the depressed semicircle, and it is also the frequency at which the real part (Z_r) is midway between the low and high frequency x-axis intercepts.

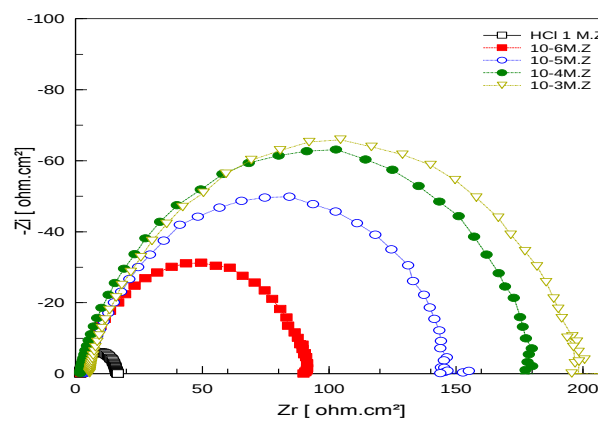


Figure 3. Nyquist impedance diagrams for **MS** obtained at 308K in 1 M HCl solution containing different concentrations of **P1**.

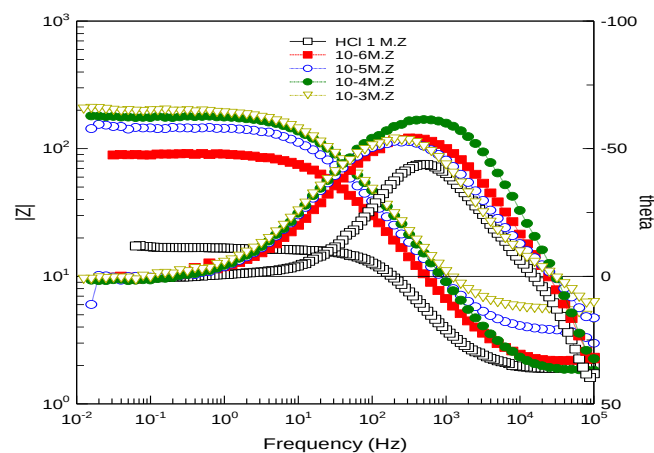


Figure 4. Bode and Phase angle plots of **MS** in 1 M HCl in the absence and presence of different concentrations of (**P1**) at 308K.

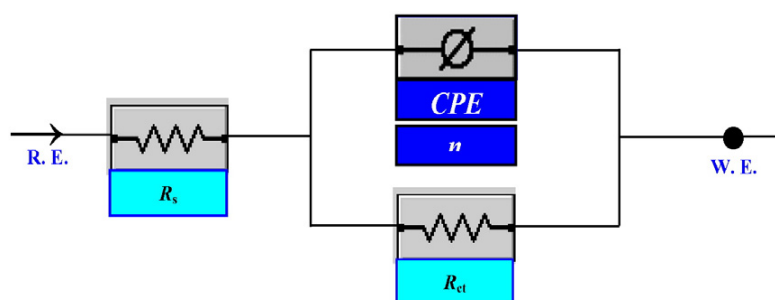


Figure 5. Electrochemical equivalent circuit used in fitting impedance data for **MS** corrosion in 1 M HCl in the absence and presence of different concentrations of the studied inhibitor (**P1**).

The electrochemical parameters R_s , R_t , C_{dl} and $E_R\%$ are listed in (**Table 3**). Inspection of (**Figure 3**) reveals that addition of the inhibitor P1 increases the capacitive loop diameter of the Nyquist plots without affecting their characteristic features. This means that the inhibition action of this inhibitor is due to its adsorption on the metal surface without altering the corrosion mechanism.

Table 3. Electrochemical parameters for **MS** in 1 M HCl without and with different concentrations of (**P1**) at 308K.

Concentration (M)	HCl 1M	10^{-6}	10^{-5}	10^{-4}	10^{-3}
Parameters					
Real Center	9.2572	46.77	75.47	90.32	102.46
Imag. Center	1.6279	15.335	24.503	28.859	39.784
Diameter	15.134	94.03	150.9	185.6	210.72
Deviation	0.15828	0.86227	2.1549	1.8151	1.4932
Low Intercept $R_s (\Omega \cdot \text{cm}^2)$	1.8673	2.3266	4.1115	2.1242	4.896
High Intercept $R_t (\Omega \cdot \text{cm}^2)$	16.647	91.214	146.83	178.52	200.02
Depression Angle	12.423	19.037	18.951	18.119	22.185
$\omega_{\max}$	929.6	175.86	123.37	127.88	103.27
Estimated $R_t (\Omega \cdot \text{cm}^2)$	14.78	88.887	142.72	176.39	195.12
Estimated $C_{dl} (\text{F} \cdot \text{cm}^{-2})$	$7.11 \cdot 10^{-5}$	$6.1 \cdot 10^{-5}$	$5.4 \cdot 10^{-5}$	$4.5 \cdot 10^{-5}$	$4.3 \cdot 10^{-5}$
$E_R(\%)$	--	83	89	91	93

Table 3 shows that values of solution resistance (R_s) are very small as compared to R_t values. The magnitude of R_t increases while the values of C_{dl} decreases, with addition of inhibitor **P1** in 1 M HCl at different concentration, which causes an increase in $E\%$ and θ .

The high R_t values are generally associated with slower corroding system [60-61]. The double layer between the charged metal surface and the solution is considered as an electrical capacitor.

The adsorption of inhibitor P1 on the **MS** electrode surface decreases its electrical capacity as they displace the water molecules and other ions originally adsorbed on the surface. The decrease in this capacity with inhibitors

may be attributed to the formation of a protective adsorption layer on the electrode surface [62-63]. The thickness of this protective

layer(d) is related to C_{dl} in accordance with Helmholtz model, given by the following equation [64]:

$$C_{dl} = \epsilon \epsilon_0 A / d \quad (21)$$

Where ϵ is the dielectric constant of the medium and ϵ_0 is the permittivity of free space ($8.854 \times 10^{-14} \text{ Fcm}^{-1}$) and A is the effective surface area of the electrode.

3.4. Potentiodynamic (Tafel) polarization measurements

Furthermore, potentiodynamic polarization curves have been recorded for **MS** steel in 1 M HCl solution with and without different concentrations of the inhibitor **P1**. The representative curves are shown in (**Figure 6**). Electrochemical parameters determined from polarization curves as corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic Tafel slopes(β_c), and the corrosion rate ($E_p\%$) are given in (**Table 4**). As it is clearly seen from (**Figure 6**), the corrosion potential values of **MS** were almost the same. The displacement in E_{corr} (ΔE_{corr}) between the absence and presence of the inhibitor **P1**, was less than 85 mV.

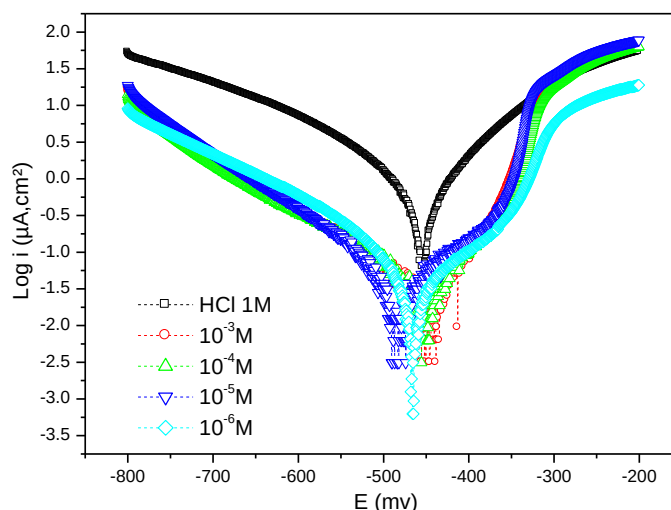


Figure 6. Tafel polarization curves for **MS** obtained at 308K in 1 M HCl solution containing different concentrations of (**P1**).

Table 4. Tafel polarization parameters obtained at different concentrations of (**P1**).

Inhibitor	Concentration (M)	$-E_{corr}$ (mV/SCE)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	$-\beta_c$	E_p (%)
1M HCl	--	454	1386	164	--
Inhibitor P1	10^{-6}	462	425	157	69
	10^{-5}	467	368	155	73
	10^{-4}	453	217	139	84
	10^{-3}	452	129	131	91

Therefore, the inhibitor was defined as mixed type [65-67]. It could be observed from Figure 6, that the anodic and cathodic reactions affected by the addition of P1. The anodic and cathodic current densities decreased with increasing P1 concentration. Furthermore, the I_{corr} values were sharply decreased in the presence of P1. The I_{corr} value was decreased from $425 \mu\text{A}/\text{cm}^2$ to $129 \mu\text{A}/\text{cm}^2$ as the concentration of P1 increased from 10^{-6} M to 10^{-3} M (**Table 4**). This can be attributed to its adsorption and formation of a barrier film on the MS surface. The maximum $E_p\%$ was obtained (91%) for the maximum **P1** concentration (10^{-3} M) (**Table 4**). Furthermore the cathodic Tafel slopes decreased in the presence of P1. The addition of P1 to the 1 M HCl solution may modify the mechanism of hydrogen evolution reaction.

Percentage inhibition efficiencies obtained from potentiodynamic polarization measurements are comparable and run parallel with those obtained from weight loss and impedance measurements.

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 which is empty, 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 [68]. At first, in this study, the HOMO and LUMO orbital energies were calculated 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 values of HOMO and LUMO energies are given in (**Table 5**), while the image of P1 is shown in (**Figure 7**).

Table 5. Quantum chemical calculations of the studied inhibitor **P1** at B3LYP/6-31G(d,p) in the gaseous (G) and aqueous (A) phases.

Parameters	Phase	
	Gas	Aqueous
Total Energy TE (eV)	-31550,29	-31550.75
E_{HOMO} (eV)	-5.3147	-3.1591
E_{LUMO} (eV)	-2.1550	-1.5787
Gap ΔE (eV)	3.1596	1.5804
Dipole moment μ (Debye)	7.9902	11.5669
Ionisation potential I (eV)	5.3147	3.1591
Electron affinity A	2.1550	1.5787
Electronegativity χ	3.7348	2.3689
Hardness η	1.5798	0.7902
Electrophilicity index ω	4.414	3.551
Softness σ	0.633	1.265
Fractions of electron transferred ΔN	1.033	2.930

The number of electrons transferred (ΔN) was also calculated and tabulated in (Table 6). The $\Delta N < 3.6$, indicates that the tendency of **P1** to be adsorbed on the MS surface is very high [69-70].

The calculated values of the f_k^+ for all elements in the inhibitor **P1** are mostly localized on the imidazo[1,2-a]pyrimidine ring. Namely N₁₆, O₂₁, C₂₂, O₂₆, and N₄₂, indicating that the imidazo[1,2-a]pyrimidine ring is most probably the favorite site for nucleophilic attack.

The results also show that N₁₆ and O₂₁ 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 6. Pertinent natural populations and Fukui functions of the studied inhibitor **P1** calculated at B3LYP/6-31G(d,p) in the gaseous (G) and aqueous (A) phases.

Atom <i>k</i>	Phase	<i>P(N)</i>	<i>P(N+1)</i>	<i>P(N-1)</i>	f_k^+	f_k^-	f_k^0
N ₁₆	G	7,2823	7,3728	7,2256	0,0905	0,0567	0,0736
	A	7,3332	7,3900	7,2241	0,0568	0,1091	0,0829
O ₂₁	G	8,6566	8,7169	8,5465	0,0603	0,1101	0,0852
	A	8,6897	8,7609	8,5549	0,0712	0,1348	0,1030
C ₂₂	G	5,7627	5,8424	5,7245	0,0797	0,0382	0,0589
	A	5,7170	5,8545	5,7015	0,1375	0,0155	0,0765
C ₂₆	G	5,7179	5,8890	5,7004	0,1711	0,0175	0,0943
	A	5,7015	5,8695	5,6699	0,1680	0,0316	0,0998
N ₄₂	G	7,5951	7,6043	7,5368	0,0092	0,0583	0,0338
	A	7,5539	7,6182	7,5274	0,0643	0,0265	0,0454

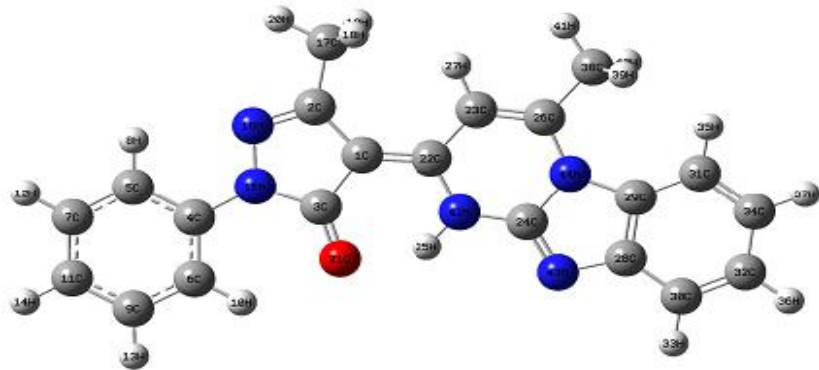


Figure7. Optimized molecular structure of **P1** at B3LYP/6-31G(d,p) level

From the analysis of the above theoretical results, it seems that the molecular structure of **P1** is planner and very well adsorbed on the MS surface attaining a large coverage surface area (θ) (i.e. high corrosion inhibition), which is in good agreement with the results obtained from the weight lost measurements.

3.6. Mechanism of corrosion inhibition

It is well recognized that organic inhibitor molecules set up their inhibition action via the adsorption of the inhibitor molecules onto the metal/solution interface. The adsorption process is affected by the chemical structures of the inhibitors, the nature and charged surface of the metal and the distribution of charge over the whole inhibitor molecule. In general, owing to the complex nature of adsorption and inhibition of a given

inhibitor, it is impossible to be a single adsorption mode between inhibitor and metal surface. Organic inhibitor molecules may be adsorbed on the metal surface in one or more of the following ways:

- Electrostatic interaction between the charged molecules and the charged metal,
- Interaction of unshared electron pairs in the molecule with the metal,
- Interaction of Π -electrons with the metal and/or,
- A combination of types (a–c).

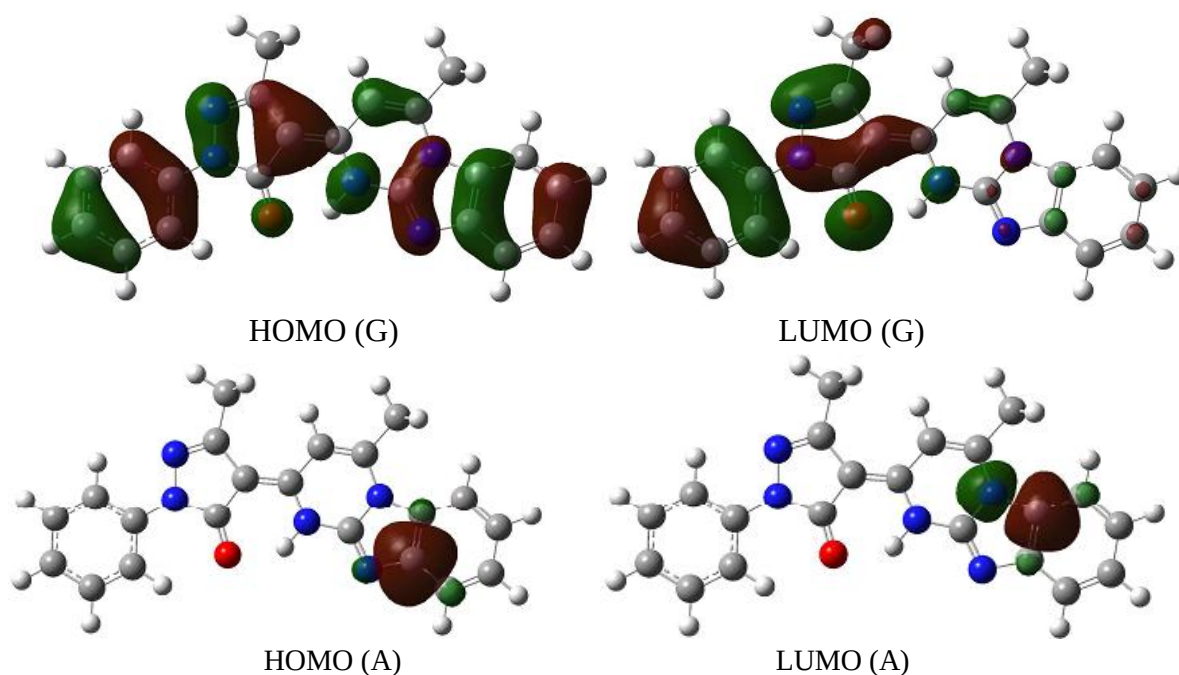


Figure 8. The HOMO and the LUMO electrons density distributions of the studied inhibitor **P1** computed at B3LYP/6-31G (d, p) level in the gaseous (G) and aqueous (A) phases.

The inhibition efficiency afforded by P1 may be attributed to the presence of electron rich N, O and aromatic rings. One benzimidazol group and imidazo-pyrimidine ring is common in the structure of P1. The presences of electron donating groups (methyl and aromatic ring) increase the electron density on nitrogen N42 of imidazo-pyrimidine group, resulting high inhibition efficiency. Furthermore, the better performance of P1 is also attributed to its planar structure (**Scheme 1**)

Conclusion

All the results showed that the P1 has excellent inhibition properties for the corrosion of **MS** in 1 M HCl solution. The weight loss measurements showed that at 10^{-3} M of **P1** in 1 M HCl solution yields a maximum inhibition efficiency of 90%. The Langmuir adsorption isotherm suggests that inhibitor has strong tendency to adsorb spontaneously on the **MS** surface. The inhibitor formulation acts as mixed in nature. **EIS** measurements indicate that thickness of electric double layer increases due to adsorption of inhibitor at metal / electrolyte interface, 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.

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