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## Pyrazole Derivative as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Medium: Electrochemical and Theoretical Studies.

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### ABSTRACT

In this study, the inhibition effect of 3-phenyl-1H-pyrazole-4-carboxaldehyde (PP4C) on mild steel corrosion in 1.0 M HCl solution was studied. For this aim, electrochemical techniques such as potentiodynamic polarization (*PDP*) curves, electrochemical impedance spectroscopy (*EIS*) and weight loss (*WL*) were used. It was shown that, the PP4C has remarkable inhibition efficiency on the corrosion of mild steel in 1.0 M HCl solution. Polarization measurements indicated that the studied inhibitor acts as mixed type corrosion inhibitor. The inhibition efficiency depends on the concentration of inhibitor and reaches 96.33% at 5 mM PP4C. The remarkable inhibition efficiency of PP4C was discussed in terms of blocking of electrode surface by adsorption of inhibitor molecules through active centers. The adsorption of PP4C molecules on the mild steel surface obeys Langmuir adsorption isotherm. The adsorption characteristics of PP4C were theoretically evaluated by  $DMo^{\beta}$  method and confirm distinct adsorption of the inhibitor matter on the mild steel surface.

**Keywords:** Corrosion inhibition; Mild steel; *EIS*, 3-phenyl-1H-pyrazole-4-carboxaldehyde;  $DMo^{\beta}$

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## INTRODUCTION

Iron and its alloys are used as materials of choice in diverse industrial and structural applications. Acid solutions are often used in drilling operations in oil and gas exploration, as well as for cleaning, decaling and pickling of steel structure; processes which are normally accompanied by considerable dissolution of the metal and it is very important to add corrosion inhibitors to decrease the corrosion rate in such situations[1–4]. Organic heterogeneous compounds containing these elements have been reported to be efficient corrosion inhibitors[5–13]. These compounds contain nitrogen, oxygen, sulphur and aromatic ring in their molecular structures and function via adsorption of the molecules on the metal surface creating a barrier to corroding attack[14–16]. The main objective of theoretical research is to gain insight into the mechanisms by which inhibitor molecules added to aqueous environment retard the metal/corrosion interaction. Indeed, the effectiveness of the overall process is a function of the metal type, corrosion molecular and electronic structure as well as concentration of the inhibitor molecules while temperature and other environmental conditions have their contributions to the overall process[17–26]. Corrosion inhibition efficiency has been experimentally evaluated using gravimetric, electrochemical impedance, and potentiodynamic polarization techniques. We have also analyzed the adsorption structures of PP4C with acquiescent molecular structures, within the framework of the  $DMo^{\beta}$  to theoretically ascertain their possible adsorption modes and evaluate their individual contributions to the observed inhibiting effect.

## MATERIALS AND METHODS

### Electrodes, chemicals and test solution

Corrosion tests have been performed, using the gravimetric and electrochemical measurements, on electrodes cut from sheets of carbon steel with the chemical composition: 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu, and the remainder iron. The aggressive medium of molar hydrochloric acid used for all studies were prepared by dilution of analytical grade 37% HCl with double distilled water. The concentrations of PP4C used in this investigation were varied from 0.1 to 5 mM. The inhibitor molecule used in this paper was purchased from Sigma–Aldrich and have the structure presented in Fig. 1. As can be seen, they have different active groups, which can act as adsorption centers.

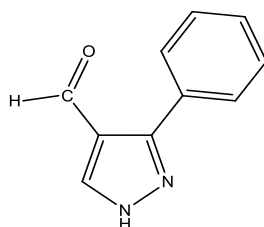


Figure 1. Chemical structure of 3-Phenyl-1H-pyrazole-4-carboxaldehyde

### Gravimetric measurements

Gravimetric measurements were realized in a double walled glass cell equipped with a thermostating condenser. The carbon steel specimens used have a rectangular form with dimension of  $2.5 \times 2.0 \times 0.2$  cm were abraded with a different grade of emery paper (320-800-1200) and then washed thoroughly with distilled water and acetone. After weighing accurately, the specimens were immersed in beakers which contained 100 ml acid solutions without and with various concentrations of PP4C at temperature equal to 303 K remained by a water thermostat for 6h as immersion time. The gravimetric tests were performed by triplicate at same conditions.

The corrosion rates ( $C_R$ ) and the inhibition efficiency ( $\eta_{wL}\%$ ) of carbon steel have been evaluated from mass loss measurement using the following equations:

$$C_R = \frac{w}{S_t} \quad (1)$$

$$\eta_{WL} \% = \frac{C_R^0 - C_R}{C_R^0} \times 100 \quad (2)$$

Where  $w$  is the average weight loss before and after exposure, respectively,  $S$  is the surface area of sample,  $t$  is the exposure time,  $C_R^0$  and  $C_R$  is the corrosion rates of steel without and with the PP4C inhibitor, respectively.

### Electrochemical tests

The potentiodynamic polarization curves were conducted using an electrochemical measurement system PGZ 100 Potentiostat/Galvanostat controlled by a PC supported by the Voltmaster 4.0 Software. The electrochemical measurements were performed in a conventional three electrode glass cell with carbon steel as a working electrode, platinum as counter electrode (Pt) and a saturated calomel electrode used as a reference electrode. The working electrode surface was prepared as described above gravimetric section. Prior to each electrochemical test an immersion time of 30 min was given to allow the stabilization system at corrosion potential. The polarization curves were obtained by changing the electrode potential automatically from -800 to -200 mV/SCE at a scan rate of 1 mV s<sup>-1</sup>. The temperature is thermostatically controlled at desired temperature  $\pm 1$  K. The percentage protection efficiency ( $\eta_{PDP}$  %) is defined as:

$$\eta_{PDP} (\%) = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100 \quad (3)$$

Where,  $i_{corr}^0$  are corrosion current in the absence of inhibitor,  $i_{corr}$  are corrosion current in the presence of inhibitor.

Electrochemical impedance spectroscopy (EIS) measurements were carried out with same equipment used for potentiodynamic polarization study (Voltalab PGZ 100) at applied sinusoidal potential waves of 5mV amplitudes with frequencies ranging from 100 KHz to 10 mHz at corrosion potential. The impedance diagrams are given in the Nyquist representation. The charge transfer resistance ( $R_{ct}$ ) was determined from Nyquist plots and double layer capacitance ( $C_{dl}$ ) was calculated from CPE parameters of the equivalent circuit deduced using Zview software. In this case the percentage protection efficiency ( $\eta_{EIS}$  %) is can be calculated by the value of the charge transfer resistance ( $R_{ct}$ )

$$\eta_{EIS} (\%) = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100 \quad (4)$$

Where  $R_{ct}^0$  and  $R_{ct}$  were the polarization resistance of uninhibited and inhibited solutions, respectively.

### DMo<sup>β</sup> method detail

$E_{HOMO}$  (highest occupied molecular orbital energy),  $E_{LUMO}$  (lowest unoccupied molecular orbital energy) and Fukui indices calculations were performed using  $DMo^{\beta}$  module in Materials Studio version 6.0[27]. These calculations employed an *ab initio*, gradient-corrected functional (GGA) method with a double numerical plus polarization (DNP) basis set and a Becke One Parameter (BOP) functional. It is well-known that the phenomena of electrochemical corrosion appear in aqueous phase.  $DMo^{\beta}$  includes certain COSMO controls, which allow for the treatment of solvation effects[28,29].

## RESULTS AND DISCUSSION

### Weight loss study

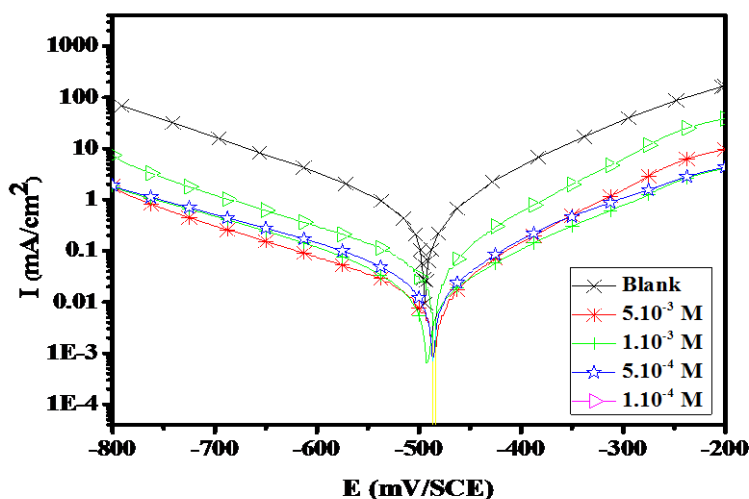
The weight loss of mild steel specimens after exposure to 1.0 M HCl solution with and without addition of various concentrations of PP4C was calculated in mg cm<sup>-2</sup> h<sup>-1</sup> and the data obtained were given in Table 1. It is clear from Table 1 that, the addition of inhibitor to the aggressive solution reduces dissolution rate of mild steel efficiently. The  $CR$  was reduced with increasing inhibitor concentration indicates that the inhibitor molecules act by adsorption on the metal surface[30–32].

**Table 1: Inhibition efficiency of various concentrations of PP4C for corrosion of MS in 1M HCl obtained by weight loss measurements at 303K.**

Inhibitors	Concentration (M)	$C_R$ ( $\text{mg cm}^{-2} \text{h}^{-1}$ )	$\eta_w$ (%)	$\Theta$
Blank	1.0	1.135	-	-
PP4C	$5.10^{-3}$	0.0472	95.84	0.9584
	$1.10^{-3}$	0.0678	94.03	0.9403
	$5.10^{-4}$	0.0886	92.19	0.9219
	$1.10^{-4}$	0.1335	88.24	0.8824

### Polarization results

The inhibition effects of PP4C on the corrosion of mild steel in 1 M hydrochloric acid solutions, studied by potentiodynamic polarization technique at different concentrations are shown in Table 2. The corrosion potential ( $E_{corr}$ ), corrosion current density ( $i_{corr}$ ), and cathodic ( $\beta_c$ ) slope are obtained by the cathodic region of the Tafel plots. The corrosion current density ( $i_{corr}$ ) can be obtained by extrapolating of the Tafel lines to the corrosion potential ( $E_{corr}$ ). It can be seen from the polarization curves (Fig. 2) and their fitted results that there is a smaller shift in the corrosion potential ( $E_{corr}$ ) and a drastic reduction in corrosion current density ( $i_{corr}$ ). The small shift in corrosion potential indicates that PP4C is a mixed type inhibitor[30]. Potentiodynamic polarization studies showed that the inhibition action is also considerable at low concentration, which is an indication of the high inhibition performance of PP4C in HCl medium.


**Figure 2. Polarisation curves of MS in 1 M HCl for various concentrations of PP4C at 303K.**
**Table 2. Corrosion parameters for corrosion of MS with selected concentrations of PP4C in 1M HCl by Potentiodynamic polarization method at 303K.**

Inhibitor	Concentration (PP4C)	$-E_{corr}$ (mV/SCE)	$-\beta_c$ ( $\text{mV dec}^{-1}$ )	$I_{corr}$ ( $\mu\text{A cm}^{-2}$ )	$\eta_{Tafel}$ (%)	$\Theta$
Blank	-	496	162.0	564.0	-	-
PP4C	$5.10^{-3}$	488	161.2	14.2	97.48	0.9748
	$1.10^{-3}$	494	165.3	26.85	95.24	0.9524
	$5.10^{-4}$	489	183.4	35.7	93.67	0.9367
	$1.10^{-4}$	487	159.7	56.7	89.95	0.8995

### Electrochemical impedance spectroscopy study

In Fig. 3, the Nyquist plots of mild steel in 1.0 M HCl solution is seen. It is apparent from Fig. 3 that, the Nyquist plot of mild steel yields a slightly depressed semicircular shape and only one time constant was

observed. This observation indicates that the corrosion of mild steel in 1.0 M HCl solution is mainly controlled by charge transfer process[33,34]. The deviation from ideal semicircle is generally attributed to the frequency dispersion as well as to the inhomogeneities of surface and mass transport resistant[31,32]. As it was illustrated graphically in Fig. 3, the diameter of semicircle increased after the addition of PP4C to the aggressive solution. This increase more and more pronounced with increasing inhibitor concentration. This result may be indicative of adsorption of inhibitor molecules on the metal surface. The impedance spectra were fitted to the  $R_s(R_{ct}CPE)$  equivalent circuit of the form in Fig. 4. Where  $R_s$  is the solution resistance,  $R_{ct}$  denotes the charge-transfer resistance and  $CPE$  is constant phase element. The introduction of  $CPE$  into the circuit was necessitated to explain the depression of the capacitance semicircle, which corresponds to surface heterogeneity resulting from surface roughness, impurities, and adsorption of inhibitors[35,36]. The impedance of this element is frequency-dependent and can be calculated using the Eq. 5[35]:

$$Z_{CPE} = \frac{1}{Q(j\omega)^n} \tag{5}$$

Where  $Q$  is the  $CPE$  constant (in  $\Omega^{-1} S^n cm^{-2}$ ),  $\omega$  is the angular frequency (in  $rad s^{-1}$ ),  $j^2 = -1$  is the imaginary number and  $n$  is a  $CPE$  exponent which can be used as a gauge for the heterogeneity or roughness of the surface.

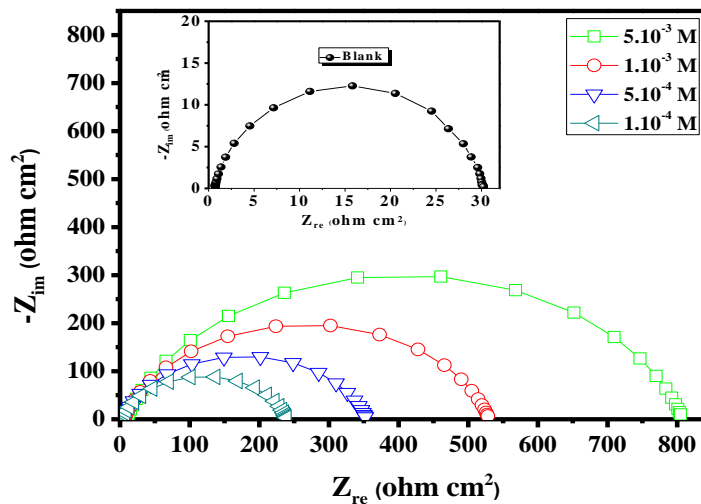


Figure 3. Nyquist curves for mild steel in 1 M HCl for selected concentrations of PP4C at 303K.

In addition, the double layer capacitances,  $C_{dl}$ , for a circuit including a  $CPE$  were calculated by using the following Eq. 6[37]:

$$C_{dl} = (Q \cdot R_{ct}^{1-n})^{1/n} \tag{6}$$

As it was shown in Table 3, the addition of PP4C reduces the  $CPE$  values and increases  $R_{ct}$ . The decrease in the  $CPE$ , which can result from a decrease in local dielectric constant and/or an increase in the thickness of double layer was attributed to the gradual replacement of water molecules and other ions originally adsorbed on the surface by the adsorption of inhibitor molecules on the metal surface[37]. The adsorption of larger PP4C molecules also reduces the capacitance through the increase in the double layer thickness[38]. The adsorption of inhibitor molecules at the metal/solution interface results in an increase of  $R_{ct}$ , which reduces the corrosion rate of mild steel.

Table 3. AC-impedance parameters for corrosion of mild steel for selected concentrations of PP4C in 1M HCl at 303K.

Inhibitor	Concentration (M)	$R_{ct}$ ( $\Omega \text{ cm}^2$ )	$n$	$Q \times 10^{-4}$ ( $\text{s}^n \Omega^{-1} \text{cm}^{-2}$ )	$C_{dl}$ ( $\mu\text{F cm}^{-2}$ )	$\eta_{EIS}$ (%)	$\theta$
Blank	1.0	29.35	0.910	1.7610	91.6	-	-
PP4C	$5.10^{-3}$	799.2	0.82	0.1665	6.45	96.33	0.9633
	$1.10^{-3}$	524.5	0.81	0.2856	10.66	94.40	0.944
	$5.10^{-4}$	349.7	0.87	0.4743	25.70	91.61	0.9161
	$1.10^{-4}$	235	0.85	0.6978	33.78	87.51	0.8751

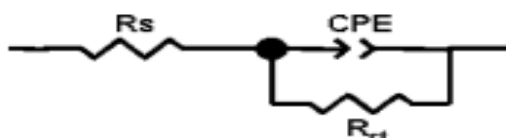


Figure 4. Equivalent electrical circuit corresponding to the corrosion process on the carbon steel in hydrochloric acid.

### Adsorption isotherm

In order to clarify the nature of adsorption, the gravimetric data in 1 M HCl at 303 K were fitted to a series of adsorption isotherms including Frumkin, Langmuir, and Temkin isotherms and the best fit was obtained with the Langmuir isotherm (Fig. 5) as per Eq.7[23,24]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (7)$$

Where, C is the concentration of the inhibitor,  $K_{ads}$  is the equilibrium constant of adsorption and  $\theta$  is the surface coverage. The Langmuir approach is based on a molecular kinetic model of the adsorption-desorption process. On the other hand, the adsorption equilibrium constant ( $K_{ads}$ ) is related to the standard free energy of adsorption ( $\Delta G^{\circ}_{ads}$ ) of the inhibitor molecules by the following Eq. 8[8,9]:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \quad (8)$$

Where R is the universal gas constant, T the absolute temperature in K, and 55.5 represents the molar concentration of water in the solution. A plot of  $C/\theta$  versus C (Fig. 5) gives a straight line with an average correlation coefficient of 0.9999 and a slope of nearly unity (1.04) suggests that the adsorption of PP4C molecules obeys Langmuir adsorption isotherm.

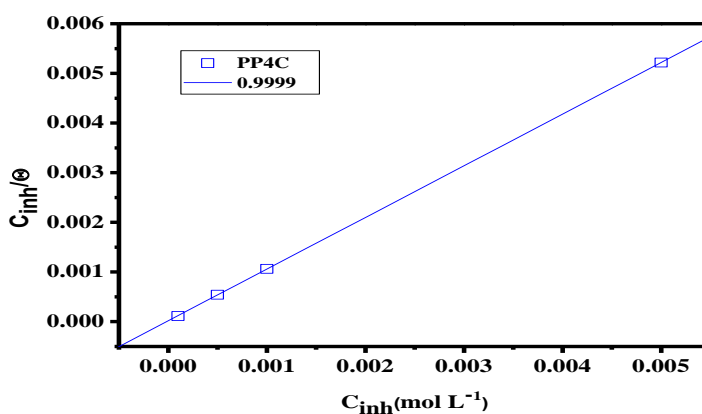


Figure 5. Langmuir adsorption of inhibitor on the MS surface in 1.0 M HCl solution at 303K.

The value  $K_{ads}$  calculated from the reciprocal of intercept of isotherm line as  $55933 \text{ M}^{-1}$ . The high value of the adsorption equilibrium constant reflects the high adsorption ability of this inhibitor on mild steel surface[39]. The  $\Delta G^{\circ}_{ads}$  was calculated as  $-37.64 \text{ kJ mol}^{-1}$ . The negative value of standard free energy of adsorption indicates spontaneous adsorption of inhibitor molecules on mild steel surface and also the strong interaction between inhibitor molecules and the metal surface[14]. Generally, the standard free energy values of  $-20 \text{ kJ mol}^{-1}$  or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface (physical adsorption). Those of  $-40 \text{ kJ mol}^{-1}$  or more negative involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (chemical adsorption)[37,40]. The calculated standard free energy of adsorption value is  $-37.64 \text{ kJ mol}^{-1}$ , it can be concluded that the adsorption is obey by chemical and physical interaction[41].

### Theoretical calculations

In order to study the effect of molecular structure on the inhibition efficiency, quantum chemical calculations were performed by using *DMol<sup>3</sup>*. The calculations were carried out with the help of complete geometry optimization. The optimized geometry,  $E_{HOMO}$  and  $E_{LUMO}$  of PP4C is shown in Figure 5. As per the frontier molecular orbital theory, frontier molecular orbital's *HOMO* and *LUMO* are involved in the course of adsorption of the inhibitor molecules[37]. In general the higher the value of *HOMO*, the higher would be the electron donating capacity of the inhibitor to vacant d-orbital of the metal. Moreover, the lower the value of *LUMO*, the greater would be the electron accepting ability of the inhibitor from the filled metal orbitals. But the most important parameter is  $\Delta E$ , which is the energy difference between *LUMO* and *HOMO*. The lower the value of  $\Delta E$  the easier would be the release of electron and the stronger would the adsorption[42–44]. Thus to become a good corrosion inhibitor, easy donation of electron as well as easy acceptance of electron in their vacant orbital's is necessary[38,39]. The quantum chemical parameters for PP4C are represented in Table 4

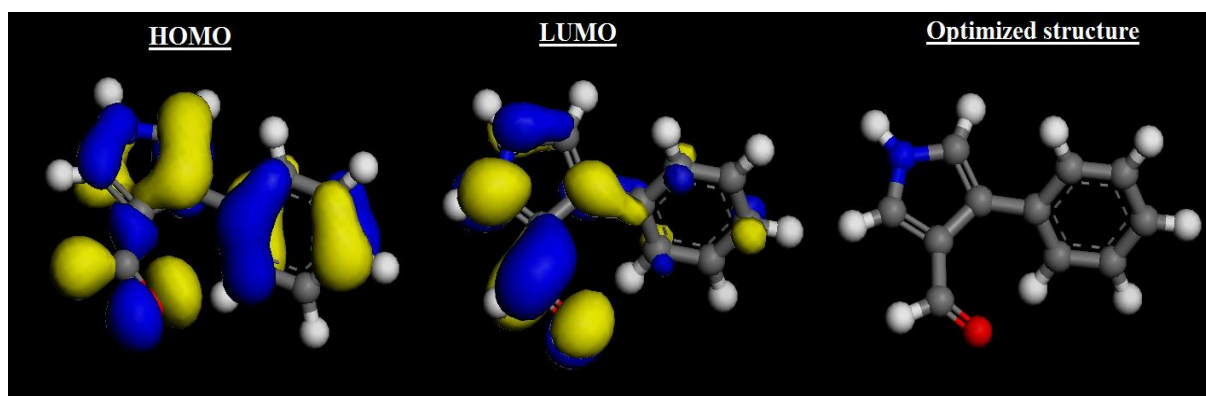


Figure 6. The frontier molecular orbital (*HOMO* and *LUMO*) and optimized molecular structures of the inhibitor.

Table 4. Calculated quantum chemical parameters of the inhibitor molecule

Inhibitors	$E_{HOMO}$ (eV)	$E_{LUMO}$ (eV)	$\Delta E_{gap}$
PP4C	-5.013	-1.764	3.249

### CONCLUSIONS

The 3-Phenyl-1H-pyrazole-4-carboxaldehyde act as good corrosion inhibitor for mild steel in 1 M HCl solution. Polarization studies showed that tested inhibitor is mixed type in nature. *EIS* study show that charge transfer resistance ( $R_{ct}$ ) increases and double layer capacitance ( $C_{dl}$ ) decreases in the presence of inhibitor, which suggested the adsorption of the inhibitor molecules on the surface of mild steel. The results obtained from Langmuir adsorption isotherm suggested that the mechanism of corrosion inhibition is occurring mainly through adsorption process. Quantum chemical results of PP4C showed higher value of  $E_{HOMO}$ , lower value of  $E_{LUMO}$ , and smaller value of  $\Delta E$ , indicating that the inhibitor is good corrosion inhibitor for mild steel in studied medium.



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