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# Study of corrosion inhibition of mild steel in acidic medium by 2-propargyl-5-p-chlorophenyltetrazole : Part I

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## Abstract

2-propargyl-5-p chlorophenyltetrazole (PCPT) was tested as corrosion inhibitor for mild steel in 1M HCl solution using electrochemical and weight loss measurements. Results obtained showed that this compound has a good inhibiting properties for mild steel corrosion in acidic medium, with inhibition efficiencies values reach 98% at $5\times10^{-4}$ M . The inhibition was assumed to occur via adsorption of the PCPT molecules on metallic surface. Adsorption of inhibitor molecules on steel surface showed Langmuir adsorption isotherms fit in acidic media. Potentiodynamic polarization curves showed that the inhibition is a cathodic nature. In addition, results obtained by weight loss and electrochemical measurements are in good agreement. Mechanism of physical adsorption is proposed from the apparent activation energy ($E_a$) and the thermodynamic parameters obtained. The adsorption of the PCPT on the mild steel surface is spontaneous.

**Keywords:** PCPT; Corrosion and inhibition; acidic medium, EIS

## 1. Introduction:

Mild steel has many industrial applications because of its easy availability, low cost, uncomplicated fabrication of it into water pipe lines **[1, 2]**, cooling water systems **[3]**, boilers etc.. However, they are susceptible to different forms of corrosion inducted by chloride and so on. Hydrochloric acid is the most difficult of the common acids to handle from the standpoints of corrosion and materials of constructions. Extreme care is required in the selection of materials to handle the acid by itself, even in relatively dilute concentrations or in process solutions containing appreciable amount of hydrochloric acid. This acid is very corrosive to most of the common metals and alloys **[4]**.

Due to their industrial applications, several inhibitors have either been synthesized or chosen from organic compounds having heteroatom in their molecular structures **[5]**. In addition, various protective methods have been adopted; one of the frequently used measures is the use of organic compounds containing nitrogen, oxygen and sulphur atoms **[6-10]**. These compounds either can form strong co-ordination bond with metal atom or form passive film on the surface **[11]**. There is still a continuous search for better inhibitors or blend of inhibitors to meet the demand of the industry. The selection criteria for various inhibitors include low concentration, stability in recirculation, cost effectiveness and low operational hazard.

We report here the effect of PCPT addition as corrosion inhibitor for mild steel in acidic medium and evaluation their performance to give the most effective blend for corrosion inhibition. Indeed, we studied the effect of some parameters on the performance of PCPT such as temperature and immersion time.

## 2. Experimental procedure:

The electrolysis cell was a pyrex of cylinder closed by cap containing five openings. Three of them were used for the electrodes.

The working electrode was ordinary mild steel with the surface area of 0.8 $cm^2$ and its chemical composition has previously defined **[12]**. Before each experiment, the electrode was polished using emery paper until 1200 grade. After this, the electrode was cleaned with distillate water. A saturated calomel electrode (sce) was used as a reference whose standard potential is 241 mV/HNE at 25 °C. All potentials were given with reference to this electrode. The counter electrode was a platinum plate of surface area of 2 $cm^2$.

The corrosive solution (1M HCl) was prepared by dilution of Analytical Grade 37 % HCl with distilled water. The inhibitor used in this experiment was 2-propargyl-5 –p-chlorophenyltetrazole (PCPT)**.** Its structure is shown in Fig. 1. The temperature was adjusted to 30± 2 °C.

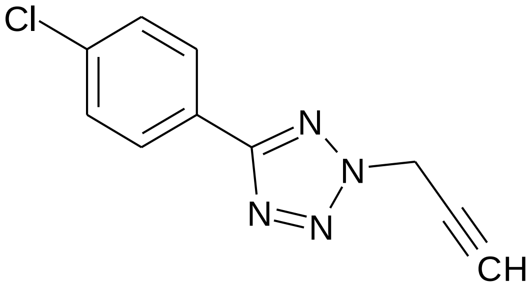

**Fig. 1.** Chemical structure of 2-propargyl-5-p-chlorophenyltetrazole.

The working electrode was immersed in test solution during one hour until a steady state open circuit potential ($E_{ocp}$) was obtained. The potentiodynamic polarization curve was recorded by polarization from the negative direction, under potentiodynamic conditions corresponding to 1 mV/s (sweep rate) and under air atmosphere, to positive direction using a VoltaLab PGZ 100, which was controlled by a personal computer.

For evaluation corrosion kinetic parameters a fitting by Steren -Gery equation was used such as presented previously **[13]**. The inhibition efficiency was evaluated from the measured $i_{corr}$ values using the relationship:

$$IE\% = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \qquad (1)$$

Where $i^0_{corr}$ and $i_{corr}$ are the corrosion current densities values without and with inhibitor, respectively.

The electrochemical impedance spectroscopy measurements were carried out using a transfer function analyser (VoltaLab PGZ 100), with a small amplitude ac. Signal (10 mV.rms), over a frequency domain from 100 KHz to 10 mHz at 30°C and an air atmosphere. The results were then analyzed in terms of equivalent electrical circuit using Bouckamp program **[14]**. The inhibition efficiency of the inhibitor has been found from the relationship:

$$IE = \frac{R_{ct} - R^0_{ct}}{R_{ct}} \times 100 \qquad (2)$$

Where $R^0_{ct}$ and $R_{ct}$ are the polarization resistance values in the absence and the presence of inhibitor, respectively.

## 3. Results and discussion :

### *3.1. Gravimetric study:*

The weight loss measurements are conducted in 1M HCl at 30°C for 8h of immersion time. The values of corrosion rate ($W_{corr}$), coverage surface (ϴ) and inhibition efficiency (IE%) containing PCPT at different concentrations are represented in table 1. It is shown that PCPT acts as effective corrosion inhibitor. This inhibition can be explained by increasing of the effective electron density in the ring by the functional group. In aromatic or heterocyclic ring compounds, the effective electron density at the functional group can be varied by introducing different substituent in the ring leading to variations of the molecular structure.

**Table 1.** Corrosion rate, coverage surface and inhibition efficiency values obtained by weight loss measurements

| Concentration (M) | $W_{corr}$ (mg /cm$^2$.h) | ϴ | IE% |
|---|---|---|---|
| 00 | 1.66 | 0 | 0 |
| $10^{-5}$ | 0.498 | 0.70 | 70 |
| $5\times10^{-5}$ | 0.398 | 0.76 | 76 |
| $10^{-4}$ | 0.332 | 0.80 | 80 |
| $5\times10^{-4}$ | 0.270 | 0.83 | 83 |

### *3.2. Potentiodynamic polarization curves:*

The polarization behaviour of mild steel in 1M HCl containing different concentrations of PCPT is shown in Fig. 2. Electrochemical parameters extracted from this curves are given in Table 2. These results show that the PCPT bring down $i_{corr}$ value at all concentrations suggesting that these compounds are effective corrosion inhibitors. Moreover, we note that this compound causes a significant shift in $E_{corr}$ to negative values indicating that it is cathodic type inhibitors in 1M HCl and the change in cathodic Tafel slope conducting a change in evolution hydrogen mechanism. In other hand, for higher values of potential (higher than -0.300V/sce approximately), the various polarization curves tend to converge, with the high currents densities. This convergence is often explained by the fact that at high anodic potentials, the glass compounds are desorbed and the dissolution of mild steel then takes place on an almost naked metal surface **[15, 16]**.

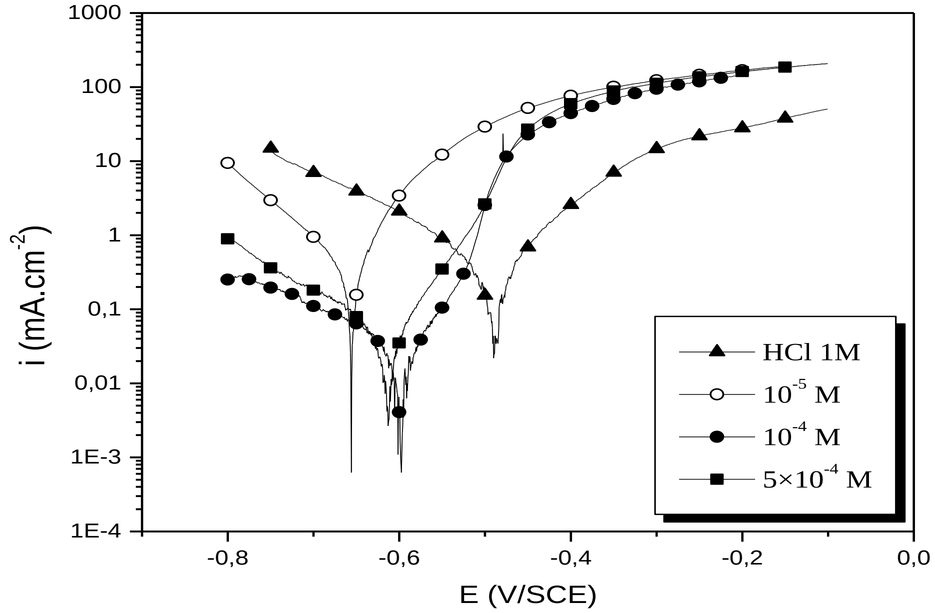

**Fig.2:** Potentiodynamic polarization curves of mild steel in 1M HCl containing different concentration of PCPT.

**Table 2:** Potentiodynamic electrochemical parameters obtained of mild steel in 1M HCl containing different concentrations of PCPT

| Concentration (M) | $E_{corr}$ (mV/sce) | $i_{corr}$ (μA/cm$^2$) | $-b_c$ (mV/dec) | IE% |
|---|---|---|---|---|
| 00 | -490 | 530 | 132 | - |
| $10^{-5}$ | -656 | 375 | 104 | 30 |
| $10^{-4}$ | -613 | 30 | 62 | 94 |
| $5\times10^{-4}$ | -600 | 20 | 88 | 96 |

### *3.3. Electrochemical impedance spectroscopy (EIS) measurements:*

Fig. 3 shows Nyquist plots obtained from impedance measurements of mild steel in 1M HCl containing different concentrations of PCPT. The results can be interpreted using equivalent circuit presented in Fig. 4, which has been used previously to model the iron/acid interface **[9]**. Various parameters such as charge-transfer resistance ($R_{ct}$) and double layer capacitance ($C_{ct}$) obtained from impedance measurements are shown in Table 3.

It is apparent from these plots that the impedance in all cases corresponds to a capacitive loop. The semicircle diameters depend on the PCPT concentration and they increase with increasing of PCPT concentration. This indicates that the impedance of inhibited substrate increases with increasing inhibitor concentrations and consequently the inhibition efficiency increases.

However, the addition of inhibitor improves $R_{ct}$ values and brings down $C_{ct}$ values. These observations clearly bring out the fact that the corrosion of mild steel in 1M HCl is controlled by a charge transfer process and the corrosion inhibition occurs through the adsorption of PCPT on mild steel surface. Decrease in the $C_{ct}$ values, with can result from a decrease in local dielectric constant and/or an increase in courant density, the thickness of the electrical double layer, suggested that the PCPT molecules function by adsorption at the metal-solution interface **[17]**.

The effectiveness of a compound as corrosion inhibitor mainly depends on the size and the active centers of the compound **[18]**. The improved performance of inhibitor PCPT can be attributed to heterocyclic structure and the biggest size of the compound.

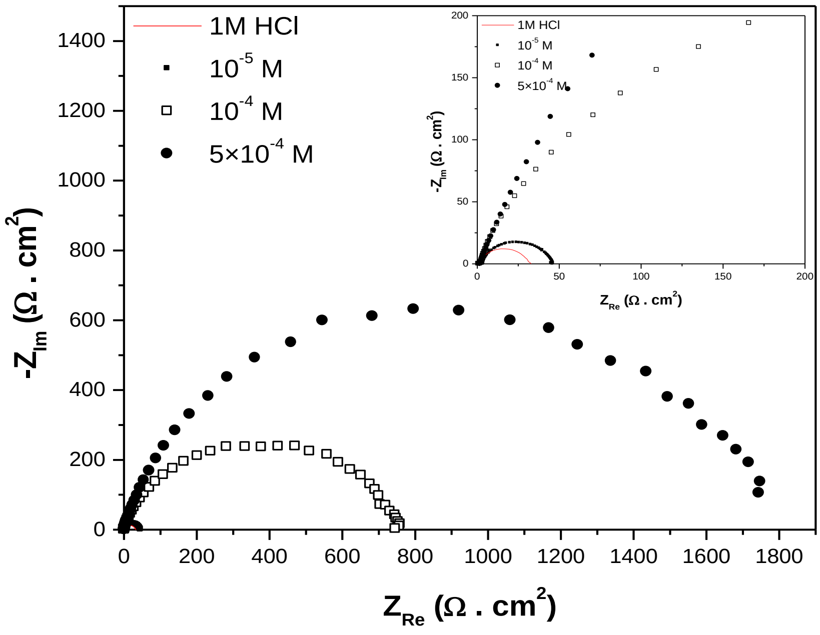

**Fig. 3:** Nyquist plots for mild steel in 1M HCl containing different concentrations of PCPT at over open circuit potential.

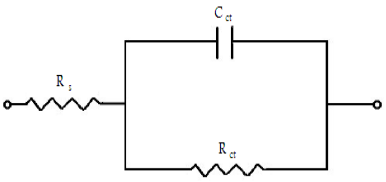

**Fig.4**. Equivalent circuit

**Table 3:** Corrosion parameters obtained by impedance measurements for mild steel in 1M HCl at various concentrations of PCPT.

| Concentration (M) | $R_{ct}$ ($\Omega$.cm$^2$) | $C_{ct}$ ($\mu$F.cm$^{-2}$) | IE% |
|---|---|---|---|
| 00 | 30 | 147 | - |
| $10^{-5}$ | 45 | 84 | 33 |
| $10^{-4}$ | 760 | 33 | 96 |
| $5\times10^{-4}$ | 1809 | 21 | 98 |

*3.4. Effect of temperature:*

Table 4 shows weight loss measurements of mild steel in 1M HCl containing $5\times10^{-4}$ M of PCPT at different temperatures ranging from 30°C to 60°C for 8h of immersion time. It can be seen that the inhibition efficiency of PCPT was reduced at higher temperature suggesting that the adsorption mechanism of PCPT on metallic surface is physical adsorption **[18-20]**.

In addition, the activation energy ($E_a$) for mild steel corrosion in the absence and the presence of PCPT was calculated using Arrhenius theory. Assumptions of Arrhenius theory is expressed by Equation 3:

$$W_{corr} = K \exp(\frac{-E_a}{RT}) \qquad (3)$$

where $W_{corr}$ is the corrosion rate, T the absolute temperature, R is the universal gas constant and K is the Arrhenius pre-exponential factor.

**Table 4.** Inhibition efficiencies obtained from weight loss data in 1 M HCl solution in the presence and the absence of $5\times10^{-4}$ M of PCPT at different temperatures range

| Inhibitor | Temperature (°C) | $W_{corr}$ (mg.cm$^{-2}$.h$^{-1}$) | IE% |
|---|---|---|---|
| Blank solution | 30 | 1.66 | _ |
| | 40 | 2.14 | _ |
| | 50 | 2.71 | _ |
| | 60 | 3.35 | _ |
| $5\times10^{-4}$ of PCPT | 30 | 0.27 | 83 |
| | 40 | 0.43 | 80 |
| | 50 | 0.65 | 76 |
| | 60 | 0.92 | 72 |

Plots of the logarithm of corrosion rate vs. l000/T are given in Fig. 5. The plots obtained are straight lines and the slope of each straight line gives its activation energy $E_a$. It notes that the value in presence of PCPT (10.43 KJ/mol) was higher than value obtained for blank (5.97 KJ/mol) indicating an increasing of inhibitor adsorption with rising concentration. Also the activation energy values were found to be lower than the threshold value of 80 KJ/mol required for chemical adsorption indicating that a physical adsorption mechanism is applicable for PCPT on metallic surface **[18,19]**.

### 3.5. Effect of immersion time:

Fig. 6 shows the variation of corrosion rate versus immersion time of corrosion mild steel in 1M HCl solution containing $5\times10^{-4}$ M of PCPT at 25°C. It is found that the corrosion rate decrease with increase immersion time. This can be explained by increasing in the chlorides quantity which will be adsorbed on metallic surface helping the inhibitor layer formation. However, the entire active sites become saturated with inhibitor molecules.

In addition, the change in the corrosion rate may be caused by the gradual replacement of water molecules by the chloride anion and by the adsorption of the organic molecules on metallic surface, decreasing the extent of dissolution reaction.

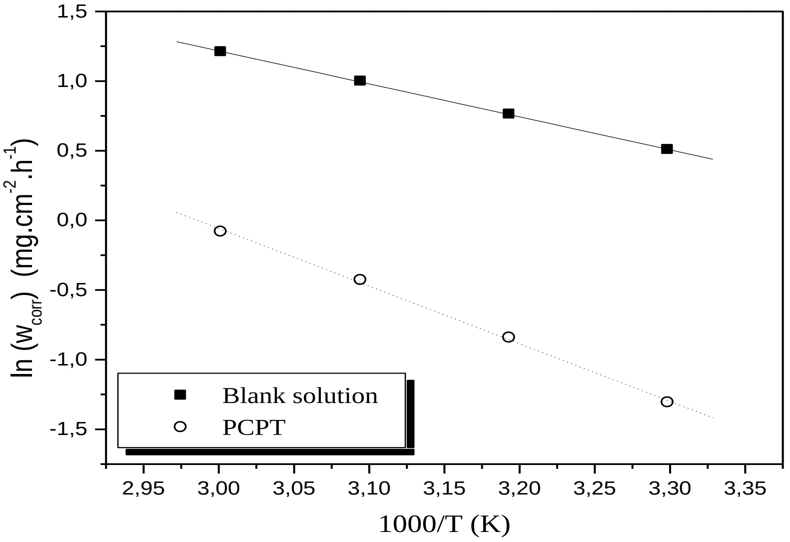

**Fig. 5:** Relation between corrosion rate and reciprocal temperature of mild steel in the presence and the absence of $5\times10^{-4}$ M of PCPT.

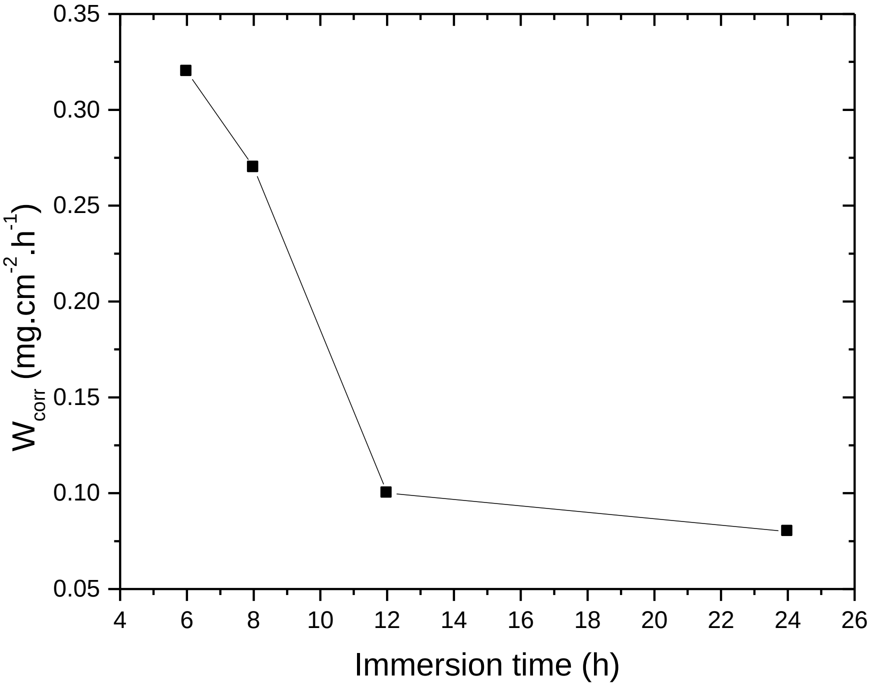

**Fig.6:** Variation of corrosion rate versus immersion time of ordinary mild steel in 1M HCl containing $5\times10^{-4}$ M of PCPT.

*3.6. Adsorption isotherm:*

Adsorption isotherms are very important in determining the mechanism of organoelectrochemical reaction **[20]**. The most frequently used isotherms are Langmuir, Frumkin, Hill de-Boer, Parsons, Temkin, Flory-

Huggin, Freundlich, Dhar-Flory-Huggin, Kinetic/Thermodynamic model of El-Awady et al. and Bockris-Swinkels **[22-33]**. All these isotherms are of the general form:

$$f(\theta, x)\exp(-2a\theta) = K_{ads}C \qquad (4)$$

Where f(θ, x) is the configurational factor which depends upon the physical model and the assumptions underlying the derivation of the isotherm, θ, the surface coverage, C, the inhibitor concentration in the electrolyte, x, the size factor ratio, a, the molecular interaction parameter and K the equilibrium constant of the adsorption process. In this study, Langmuir adsorption isotherm was found to be suitable for the experimental findings. The isotherm is described by equation (5):

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (5)$$

With $$K_{ads} = \frac{1}{55.55}\exp\left(\frac{-\Delta G_{ads}}{RT}\right) \qquad (6)$$

where C is the inhibitor concentration, $K_{ads}$ the adsorption equilibrium constant and $\Delta G_{ads}$ the standard free energy of adsorption. Though the plot of C/θ versus C was linear (Fig.7) (correlation 0.999), the deviation of the slopes from unity (for ideal Langmuir isotherm) can be attributed to the molecular interaction among the adsorbed inhibitor species, a factor which was not taken into consideration during the derivation of the Langmuir equation, The fit of the experimental data to this isotherm provides evidence for the role of adsorption in the observed inhibitive effect of PCPT.

The obtained value of $\Delta G_{ads}$ is -41.19 KJ.mol$^{-1}$. This value is low which suggest weak interactions (physisorption) of the active constituents present in PCPT the mild steel surface **[34]**.

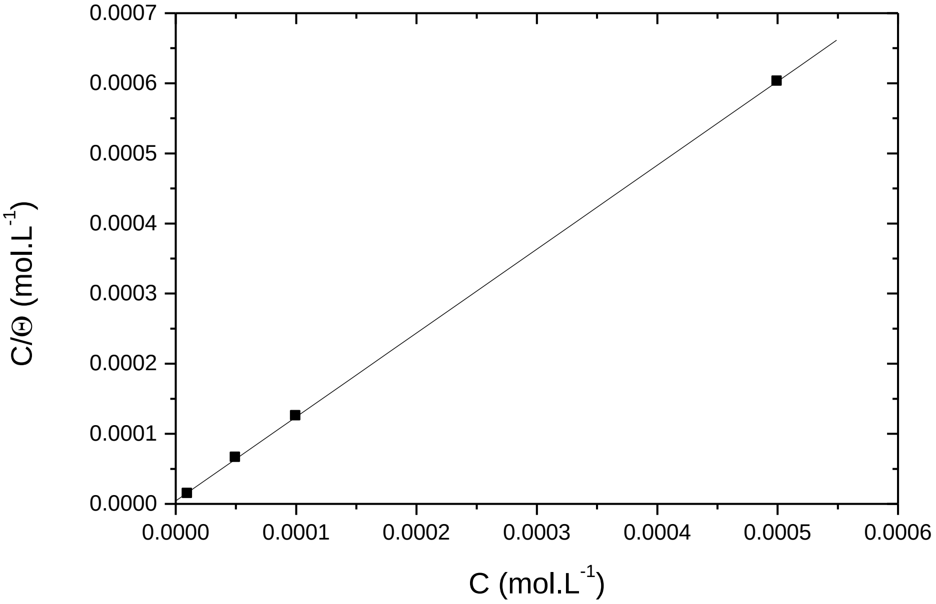

**Fig. 7.** Langmuir adsorption isotherm of mild steel corrosion in 1M HCl in the presence of of PCPT at 30 °C

## 4. Conclusion

The corrosion inhibition of mild steel in 1M HCl solution by PCPT has been studied by weight loss measurements, potentiodynamic polarization curves and electrochemical impedance spectroscopy. The obtained result shows that PCPT inhibit the corrosion of mild steel in acidic medium and its adsorption mechanism obeys to Langumiur isotherm. This inhibition may arise from the formation of protective film. The low $C_{ct}$ value obtained in the presence of PCPT indicates the formation of thicker inhibitor film on the metal surface.

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