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Pyrazole Derivatives as Corrosion Inhibitor for C- Steel in Hydrochloric Acid Medium

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Abstract

5-Chloro-1-Phenyl-3-methyle Pyrazolo-4-methinethiosemicarbazone was investigated as corrosion inhibitors for carbon steel in HCl by chemical and electrochemical method. It has been observed that corrosion rate decreases and inhibition efficiencies and surface coverage degree increases with increasing in inhibitor concentration and temperature. The apparent activation energy (E_a) and other thermodynamic parameters have also been calculated. The recorded electrochemical data indicated the basic modification of steel surface as a result in a decrease in the corrosion rate. The polarization data indicated that the used compound act as mixed type inhibitors. The slopes of the cathodic and anodic Tafel lines (βc, βa) are approximately constant and independent of the inhibitor concentrations. The inhibition occurs through adsorption of the inhibitor molecules on the metal surface without modifying the mechanism of corrosion process. SEM studies revels the formation of passive film on the metal surface.

Keywords: Steel, Acid Corrosion, Weight loss, pyrazole derivatives, Polarization.

1- Introduction

Corrosion is a thermodynamically feasible process as it is associated with decrease in Gibb's free energy. Corrosion is an afflicting problem associated with every use of metals. The damage by corrosion results in highly cost for maintenance and protection of materials used. Development of methods to control corrosion is a challenge to scientists working in this area. Amongst various methods developed for corrosion protection, use of inhibitor is an attractive and most practical method for the protection of metals in contact with corrosion medium. Inhibitors reduce the corrosion of metallic materials by controlling the metal dissolution and consumption.

Metals generally tend to move to its original state by corrosion process. Mild steel is an alloy form of iron, which undergoes corrosion easily in acidic medium. Acidic solutions are extensively used in chemical laboratories and in several industrial processes such as acid pickling, acid cleaning, acid descaling and oil wet cleaning etc. **[1].** Also mild steel is used under different conditions in chemical and allied industries for handling alkaline, acid and salt solutions. Chloride, sulfate and nitrate ions in aqueous media are particularly aggressive and accelerate corrosion. Corrosion products are formed when a metal give its electrons to the oxidizing substances. This can be delayed by painting the metal,or other way of protecting these metals from corrosion is to use corrosion inhibitors. Many of the well known inhibitors are organic compounds containing nitrogen, sulfur and oxygen atoms **[2-5].** It has been observed that many of the organic inhibitors act by adsorption on the metal surface **[6].** This phenomenon is influenced by the nature and surface charge of metal, type of aggressive medium and chemical structure of inhibitors. The adsorption of corrosion inhibitor depends mainly on physico-chemical properties of the molecule such as functional groups, steric factor, molecular size, molecular weight, molecular structure, aromaticity, electron density of the donor atoms and π- orbital character of donating electrons **[7-11]** and also on the electronic structure of the molecules **[12, 13].** Many studies had been made on the corrosion and the inhibition of mild steel in acid media **[14-18].** Modified plastic waste was used as cheap and safe corrosion inhibitors for metals and alloys in different aqueous media **[19-22].**

The most efficient corrosion inhibitors used in hydrochloric acid contain heteroatoms such as sulfur, nitrogen and oxygen containing compounds **[23-28].**

survey of literature reveals that (i) pyrazole derivatives are effective corrosion inhibitors up to 80 °C (ii) thiosemicarbazide are effective acid corrosion inhibitors ,due to strong adsorption via the donation of the lone pair of electrons of S atom in C=S and N atom to metal surface **[29,30].**

So that the present work aimed to evaluate the corrosion inhibition efficiency of the product of the interaction between pyrazole and thiosemicarbazide in this respect the condensation reaction between pyrazole carboxaldehyde and thiosemicarbazide to gives the corresponding pyrazolothiosemicarbazone, **PS**.

The corrosion inhibition of **PS** towards carbon steel in 1 M HCl was studied using chemical and electrochemical techniques and the effect of temperature on the corrosion rate in order to calculate some thermodynamic parameters related to corrosion process.

2. Materials and methods

2.1. Synthesis and characterization of the inhibitor

To a solution of 1-phenyl-3-methylpyrazol-4-carboxaldehyde (0.1mmole) in ethanol (100 ml) add a solution of thiosemicarbazide (0.1mmole). Then reflux for 3 hours. The solid obtained was filterd, washed by ethanol and recrystalized to give the corresponding thiosemicarbazone (PS). The method of synthesis is summarized in **Figure (1).** The IR spectrum of (the synthesized inhibitor) showed the adsorption band at 3386, 3170 (NH_2, NH), 1490 cm^{-1} (CH=N) and 1249 cm^{-1} (C=S) while ^{1}HNMR spectrum (DMSO) of which exhibit signal at 4.7 (2H, br, NH; exchanged by D_2O), 7.4-7.66 (5H, m, ArH), 8.1 (1H, S, CH=N) and 11.4 ppm (2H, brs, 2NH) exchanged with D_2O.

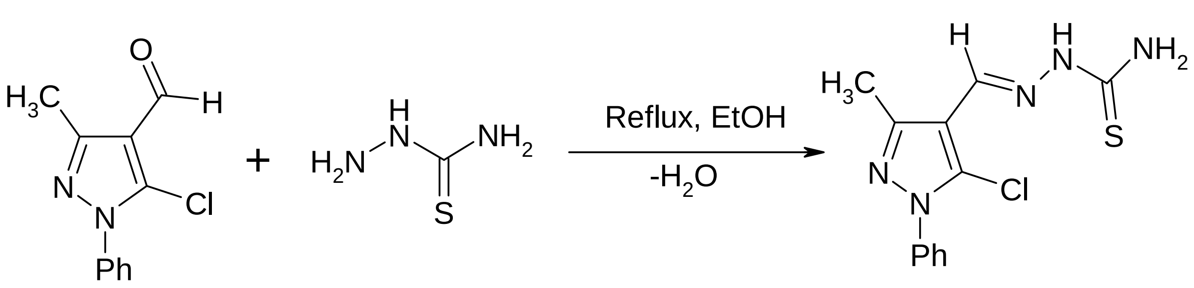

Fig.1. Chemical structure of 5-Chloro-1-Phenyl-3-methyle Pyrazolo-4-methinethiosemicarbazone (PS).

2.2. Preparation of aggressive solution

The aggressive solution (1 M HCl) was prepared by appropriate dilution of analytical grade 37% HCl with double distilled water.

2.3. Weight loss measurements

Carbon steel alloy with the dimensions of 2x2x0.05 (cm) with chemical composition (wt %) of 0.29 C, 1.25 Mn, 0.03 P, 0.03 Sn, 0.04 Cr, 0.04 Mo, and 0.027 Si and the remainder iron The samples were polished successively with fine grades (400,600 and800) emery papers, cleaned with acetone, washed with double distilled water, dried, weighed and then introduce into test solution. Weight loss measurements were carried out in a double wall glass cell equipped with a thermostat-cooling condenser.

2.4. Potentiodynamic polarization measurements

The working electrode was made from steel rod that has the same composition as mentioned in point 2.3. The rod was axially embedded in araldite holder to offer an active flat disc shaped surface of an area 1 cm^{-2}. Prior to each experiment, the working electrode was polished successively with fine grades (400,600 and 800) emery paper, rinsed with acetone, washed with double distilled water and finally dried before dipping into the electrolytic cell. A platinum wire was used as a counter electrode and a saturated calomel electrode (SCE) as the reference electrode to which all potentials are referred. The electrochemical experiments are performed using radiometer analytical, Volta master (PGZ301, DYNAMIC ELS VOLTAMMETRY). The experiments were carried out by changing the electrode potential automatically from the starting potential towards more positive values at the required scan rate(20 Mv S^{-1}) till the end of the experiments.

2.5. Open circuit potential

The potential of steel electrode was measured against saturated calomel electrode (SCE) in 1 M HCl solution in absence and presence of various concentrations of the used inhibitors at 25 °C. All measurements were carried out using Multi-tester until the steady-state potentials are reached.

2.6. Scanning electron microscopy (SEM)

In order to study the surface nature of the steel sample, the SEM images of steel specimen was taken after anodic polarization in presence and absence of the inhibitor.

3- RESULTS AND DISCUSSION

3. 1. Open Circuit Potential Measurements

The potential of carbon steel electrodes immersed in 1M HCl solution was measured as a function of immersion time in the absence and presence of various concentrations of **(PS)** as shown in **Figure (2).** It is clear that the potential of carbon steel electrode immersed in 1M HCl solution (blank curve) tends towards more negative potential firstly, giving rise to short step. This behavior was reported by West **[31],** which represents the breakdown of the pre-immersion air formed oxide film presents on the surface according to the following equation:

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O \qquad (1)$$

This is followed by the growth of a new oxide film inside the solution, so that the potential was shifted again to more noble direction until steady state potential is established. Addition of the inhibitor molecules to the aggressive medium shift the potential to more positive direction (less negative) and as the concentration of the inhibitor increases, the corrosion potential was shifted to more noble direction.

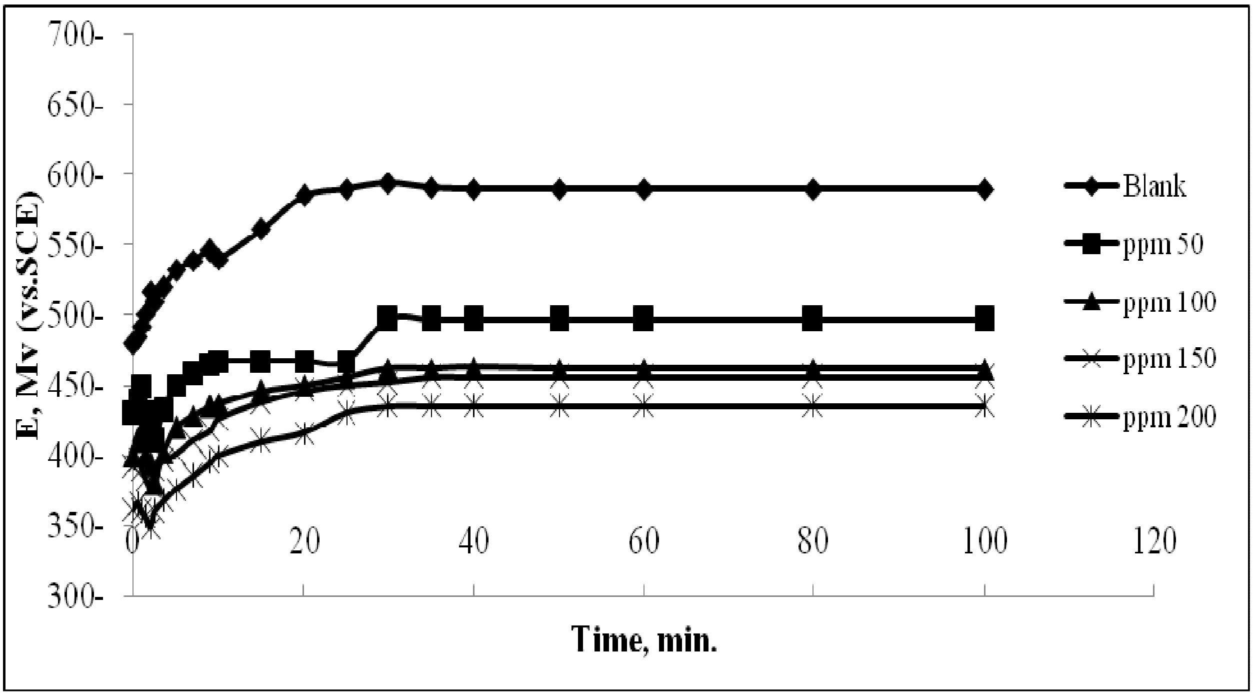

Fig.2. Potential–time curves for carbon steel immersed in 1M HCl solution in the absence and presence of different concentrations of **(PS).**

In all curves the steady-state values are always more negative than the immersion potential suggesting that before the steady state condition is achieved the steel oxide film has to dissolve. The results of final steady state potential (E_s) without inhibitor is -590 mV (vs. SCE) while that using the best dose (200 ppm) of the used inhibitor **(PS)** is -378 mV (vs. SCE) .

3.2. Potentiodynamic Polarization Measurements

Anodic and cathodic polarization curves for carbon steel in 1 M HCl with and without various concentrations (50-200 ppm) of the used inhibitor at 25°C were represented in **Figures (3).** The curves were swept from –500 to 0.00 mV (SCE) with scan rate of 20 mVs^{-1}. **Figure (3)** illustrate that the addition of the inhibitor decreases the corrosion current densities (I_{corr}). Furthermore, it was also found that the inhibitors behave as mixed-type, i.e. both cathodic and anodic polarization curves are affected by the inhibitors **[32]**. The variable values of the cathodic Tafel slopes suggest that the inhibition action of such compound occurs by simple blocking of the electrode surface area **[32]**. The cathodic current–potential curves give rise to parallel Tafel lines, which indicated that hydrogen evolution reaction was controlled **[33]**. The obtained results indicated that Pyrazol thiosemicarbazone **(PS)** products inhibit HCl corrosion of carbon steel via their adsorption on both anodic and cathodic active sites without modifying the mechanism of corrosion reaction. This means that the adsorbed inhibitor molecules block the surface active sites and decrease the area available for hydrogen evolution and metal dissolution reactions **[33].**

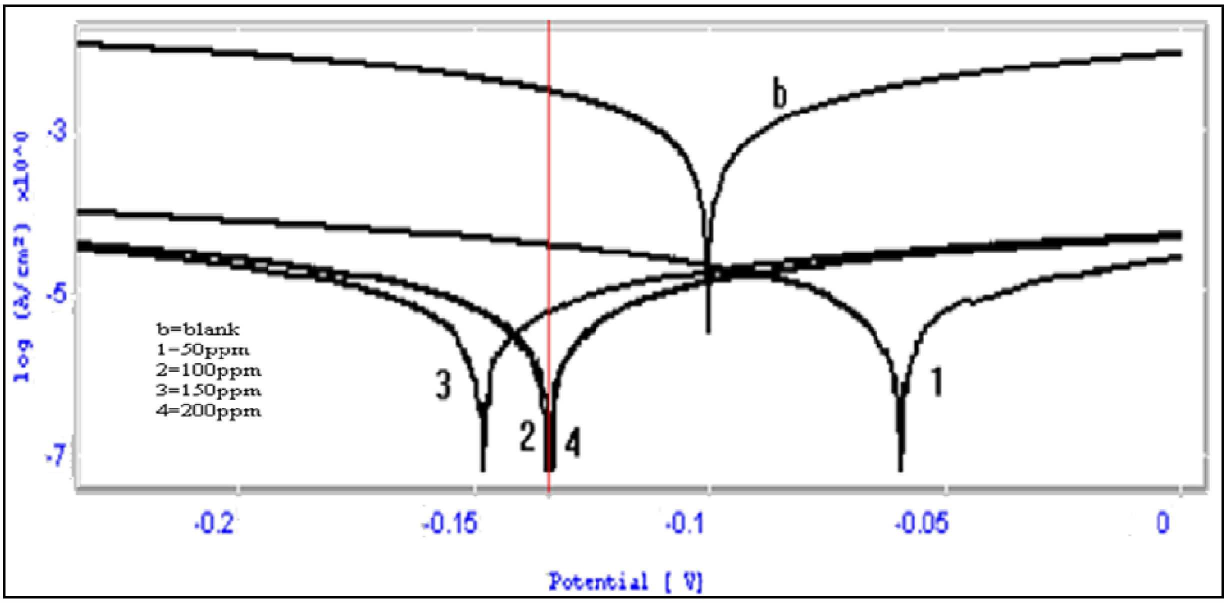

Fig.3. Potentiodynamic polarization curves of C-steel in 1 M HCl in absence and presence of different concentrations of inhibitor **PS** at 303 K,

The corrosion potential (E_{corr}), the corrosion current density (I_{corr}) were determined from extra-pollation of cathode I_c and anodic Tafel lines. The values of E_{corr}, I_{corr}, R_p, Tafel slopes (b_c, b_a), degree of surface coverage (θ) and inhibition efficiency (I.E %) were calculated for each sample and listed in **Table (1)**. It is clear that at high concentration of the inhibitor the values of corrosion potentials E_{corr} remain almost unchanged and indicate that the prepared inhibitor act mainly as mixed type inhibitors **[34].** Addition of the prepared inhibitor to HCl solution decreases the values of I_{corr} and increases the values of R_p for carbon steel alloy.
The inhibition efficiency IE % of inhibitors was calculated from polarization measurements by using the following equation:

$$IE\ \% = 1 - (I_{inh} / I_{uninh}) \times 100 \qquad (2)$$

Where: I_{uninh} and I_{inh} are the corrosion current densities in the absence and presence of inhibitor respectively. Also, the polarization resistance (R_p) can be calculated using Stren-Geary equation.

$$R_p = (b_a \times b_c) / (2.303\ i_{corr}\ (b_a + b_c)) \qquad (3)$$

The results revealed that, the inhibition efficiency increases with increasing the concentration of inhibitors.

Table 1: Polarization data of the prepared inhibitor.

Sample	Conc., ppm	I_{corr}., mA/cm^2	-E_{corr}., mV	Rp, ohm.cm^{-2}	β_a, mV/decade	-β_c, mV/decade	IE %	θ	Coeff.
Blank	0	425.80	101.1	11.2	118.2	346	0	0	0.9946
PS	50	24.2	60	177	335	264	94	0.94	0.9991
	100	22.9	135	212	311	342	94.6	0.946	0.9994
	150	21.4	149	241	302	362	95	0.95	0.9991
	200	19.6	134	268	312	362	95.5	0.955	0.9991

3.3. Weight Loss Measurements

3.3.1. Effect of Temperature:

Effect of temperatures on the corrosion behavior of carbon steel immersed in 1 M hydrochloric acid for 7 days was studied by the weight loss method over temperature range (303–333 K). **Figure (4)** indicated that the weight losses of carbon steel in 1 M HCl increase with increase immersion time. The results of carbon steel inhibition efficiency of 200 ppm (the best concentration) of the prepared inhibitor at different temperatures show that the weight losses decrease (corrosion rate) with increasing temperature from 303 – 333K which indicate chemical adsorption **[35].**

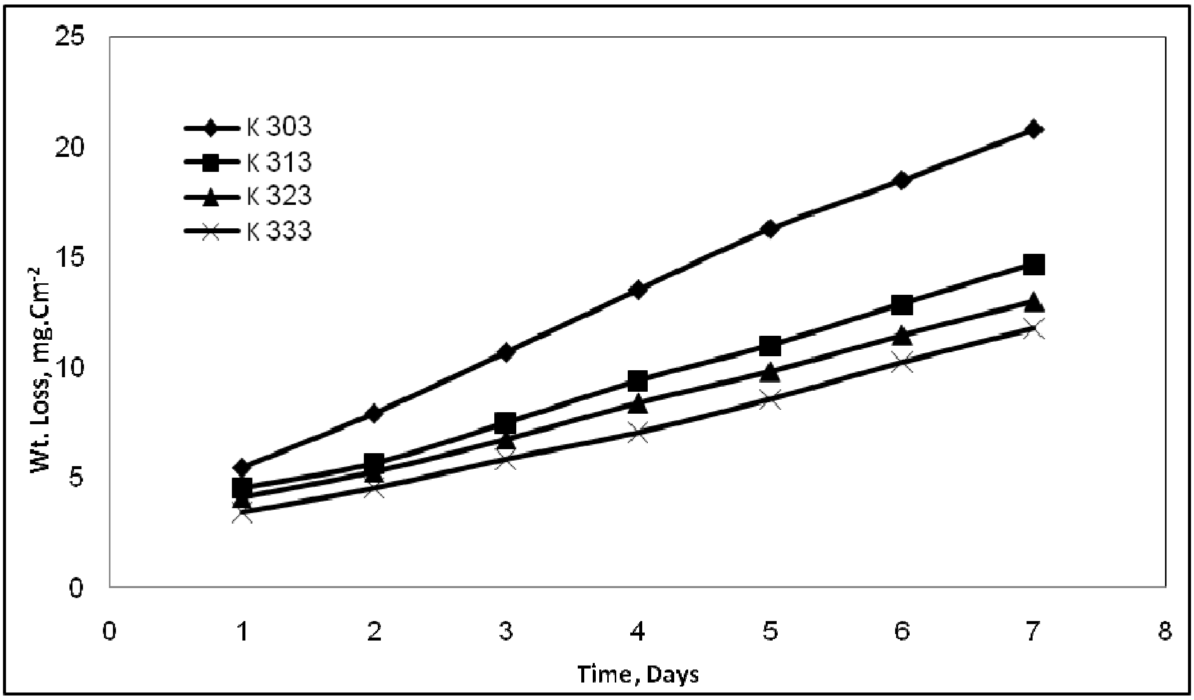

Fig. 4. Weight loss-time curves of C-steel alloy in 1 M HCl in the presence of 200 ppm of inhibitor **PS** at different temperatures

Table 2: Degree of surface coverage (θ) and percentage of inhibition efficiency (IE %) of the Inhibitor PS in 1M HCl at different temperatures calculated from weight loss data.

Compound	T, K	(1/T)x10^{-3}	CR, mg.cm^{2}.day^{-1}	-Log CR	IE, %	θ	E $*_{active}$, k.J.mol^{-1}
PS	303	3.30	0.489	0.311	92.5	0.925	71.5
	313	3.19	0.439	0.358	93.6	0.936	
	323	3.18	0.369	0.433	95	0.95	
	333	3.01	0.352	0.453	96.7	0.967	

The corrosion inhibition efficiency (IE %) was calculated by the following equation:

$$IE\% = ((\Delta W - \Delta W_i)/ \Delta W) X100 \qquad (4)$$

Where, ΔW and ΔW_i are the weight loss per unit area in absence and presence of the inhibitor respectively. ΔW can be calculated from the following equation:

$$\Delta W = W_b - W_a \qquad (5)$$

Where, W_b and W_a are the weight of the specimen before and after reaction, respectively. The obtained data of (%IE) and rate of corrosion (C.R.) of **PS** were summarized and listed in **Table (2).** The data show that CR value was decreased with increase of temperature. On the other hand, the inhibition efficiency was increased with increasing of temperature. So that the inhibitors compounds may be chemically adsorbed on the steel surface and cover some sites of the electrode surface.

The chemical adsorption can be explained on the basis of the effect of chemical structure of inhibitors on its inhibition efficiency. In this respect, the pyrazol ring, benzene ring, NH, NH_2, CH=N, and the thiocarbonyl group (C=S) of **PS** can form a big (π) bond accordingly, not only the (π) of benzene, pyrazol and (CH=N) enter unoccupied orbital of iron, but also, the π^* orbital can accept the electron of d orbital of iron to form feed back bonds, which produce more than one center of chemical adsorption on the steel surfaces **[22].**

3.3.2. Activation Energy of corrosion:

Corrosion is an electrochemical phenomenon and consequently follows the laws in chemical kinetics. The corrosion rate increases with temperature as a result of decreasing the apparent activation energy, Ea, of the charge transfer reactions. The increase of temperature enhances the rate of H^+ ion diffusion to the metal surface beside the ionic mobility, which increases the conductivity of the electrolyte. The effect of temperature on the inhibition efficiency of corrosion inhibitors is important in elucidation of the mechanism and kinetics of their action **[36].**

Analysis of the effect of temperature on the protection efficiencies (IE %) **Figure (5) and Table (3),** shows that the inhibition efficiency increases with an increase in temperature. This is due to formation of co ordination bond. This suggests that chemical adsorption may be the type of adsorption of inhibitor on the metal surface. **Figure (6)** shows the relation between corrosion rate (CR) of carbon steel and temperature in both acid solutions and with inhibitor according to Arrhenius plot:

$$\text{Log CR} = (\text{Ea} / 2.303RT) + A \qquad (6)$$

Where, E_a is the apparent activation energy and A is a constant.

Table (3) shows the apparent activation energies (E_a) of steel in HCl is 37.3 in the presence of **PS** molecules higher activation energies is observed (71.5). **Table 3** shows that the apparent activation energies (E_a) increase by increasing the concentrations of the used inhibitor. It is also indicated that the whole process is controlled by surface reaction, since the energy of activation corrosion process is over 20 KJ/mol **[37].**

An alternative form of Arrhenius equation is the transition state equation.

$$\text{Corrosion rate} = (RT/Nh) \exp(\Delta S^o/R) \exp(-\Delta H^o/RT) \qquad (7)$$

Where R is the ideal gas constant, h the Plank's constant, N the Avogadro's number, ΔS^o and ΔH^o are respectively the entropy and the enthalpy of activation.

The plots of log CR/T versus 1/T of the used inhibitor **Figure (7)** shows linear variation with a slope of ($-\Delta H^o/2.303R$) and the intersection of (log R/Nh + ($\Delta S^o/2.303R$)). The values of ΔH^o and ΔS^o were calculated and tabulated in **Table (3)**. This table indicates that the addition of **PS** to the corrosive medium leads to an increase in the ΔH^o values; so these molecules increase the highest of energy barrier for the corrosion process. In addition, the values of entropy of activation ΔS^o are large and negative. This implies that the activated complex in the rate determining step represent association rather than dissociation meaning that the decrease in a disordering takes place on going from reactants to activated complex **[38, 39].**

Table 3. The values of activation parameters E_a, ΔS^o, ΔH^o for carbon steel in 1 M HCl in the absence and presence of different concentrations of **PS.**

Techniques	**Concentration (ppm)**	**E_a ($KJmol^{-1}$)**	**ΔH^o ($KJmol^{-1}$)**	**$-\Delta S^o$ ($J K^{-1}mol^{-1}$)**
Weight loss	Blank	37.2715	30.5095	245.571
	50	55.4645	33.833	226.021
	100	59.1905	38.801	209.795
	150	65.389	43.033	202.239
	200	71.461	45.816	186.829

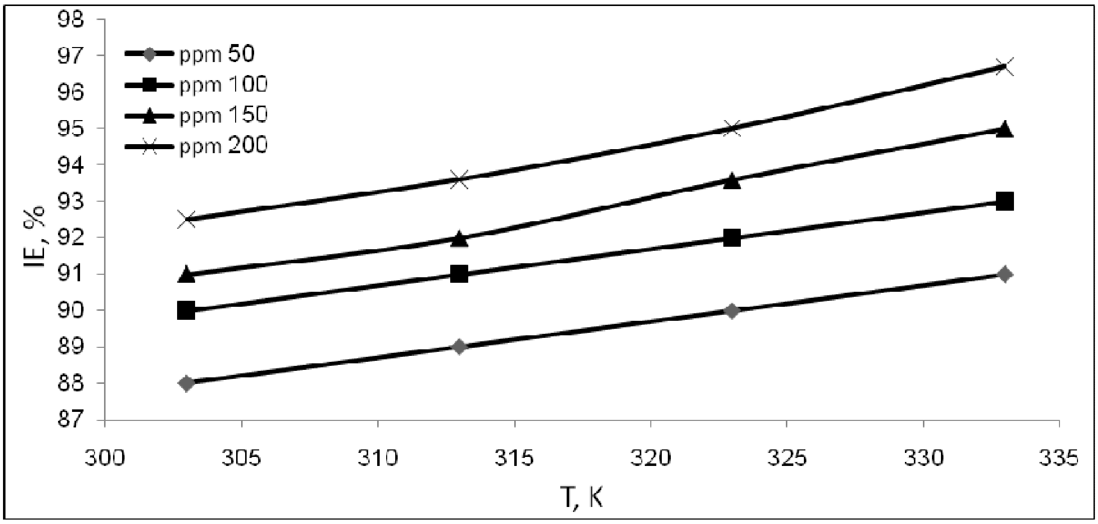

Fig.5. Effect of temperature on IE for C- Steel in 1M HCl in the presence of different concentrations of the inhibitor **PS.**

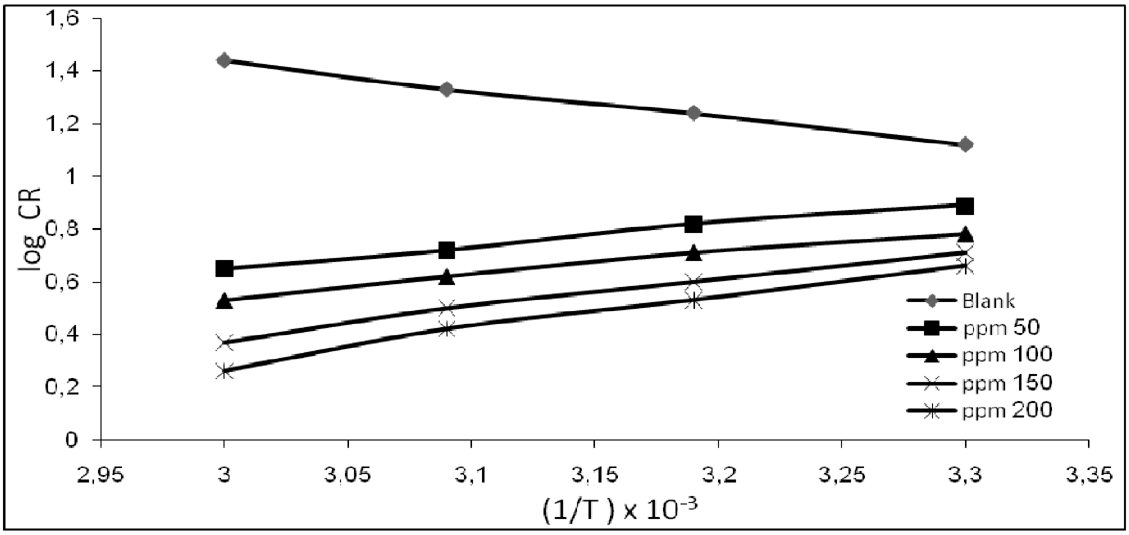

Fig.6. Arrhenius plot for C- Steel in 1M HCl solution in the absence and presence of different concentrations of the inhibitor **PS**.

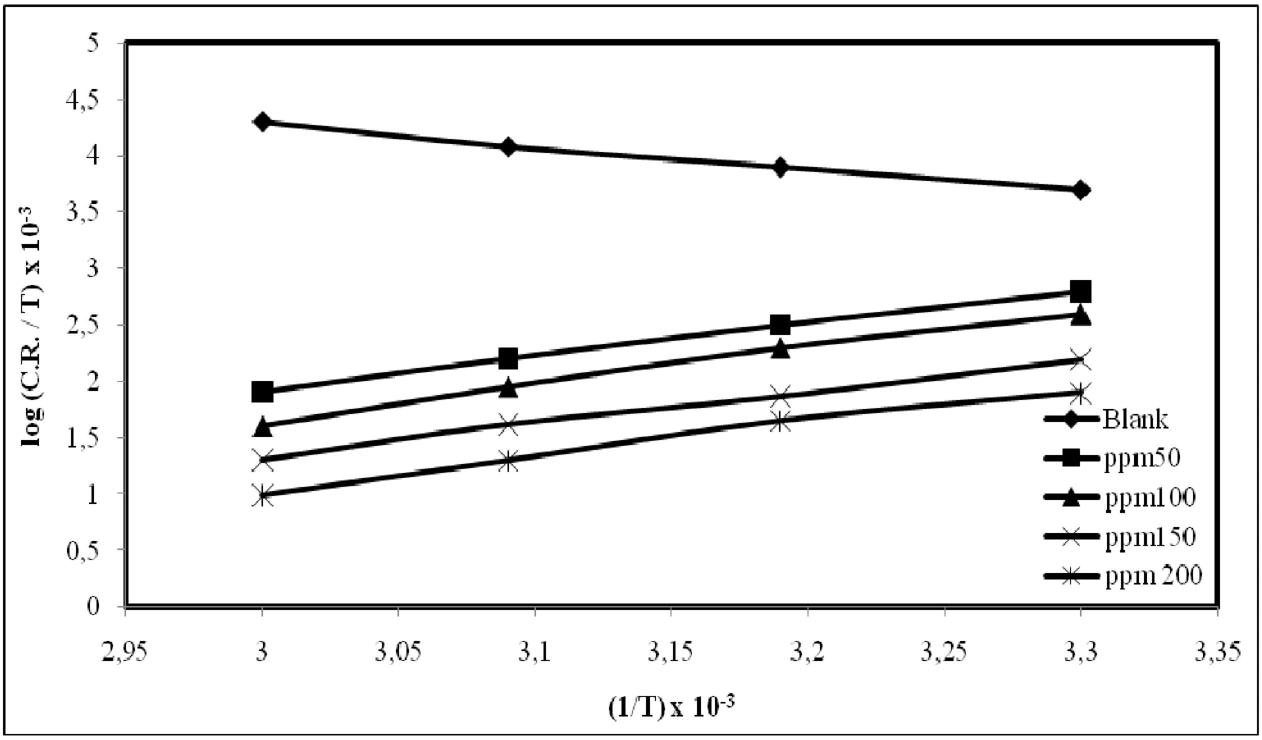

Fig.7. Transition state plot for C-Steel in 1M HCl solution in the absence and presence of different concentrations of the inhibitor **PS.**

3.4. Mechanism of corrosion inhibition:

The organic compounds containing N, S and O are known to be effective inhibitors. Its effectiveness depends on the electron density at the functional groups. The electron density can be varied with the help of suitable constituents and thus the inhibition action of an inhibitor **[40].** The corrosion inhibition property of the used Pyrazol derivatives **(PS)** can be attributed to the presence of heteroatom and π-electrons on pyrazol and benzene ring. These factors play the vital role in the adsorption of the inhibitor and the formation of co-ordinate bond with metal. The adsorption of inhibitor on the steel surface can occur either directly by the interactions between the π-electrons of the inhibitor and the vacant d-orbitals of metal surface atoms. Also there may be an interaction of inhibitor with adsorbed chloride ions leads to the adsorption of inhibitor **[41, 42].** The adsorption of inhibitor on steel may also be due to the interaction of nitrogen, sulfur and oxygen with the surface atoms of metal. The interaction causes the adsorption of **PS** on corroding sites of metals and prevents the anodic reaction. As inhibitor concentration increases, it covers more and more surface area and results in the reduction of corrosion rate.

3.5. SEM analysis

The surface morphology of steel surface was studied by scanning electron microscopy (SEM). **Figure (8 a and b)** shows the SEM photograph of the steel surface without and with inhibitor after immersion in hydrochloric acid corrosive media. The SEM photographs showed that the surfaces of metal have pits and corrosion product, but in presence of inhibitor they are minimized on the metal surface. It indicates the formation of passive layer on the metal surface. So the corrosion rate is decreased in the presence of inhibitor and reduces the electrochemical reaction.

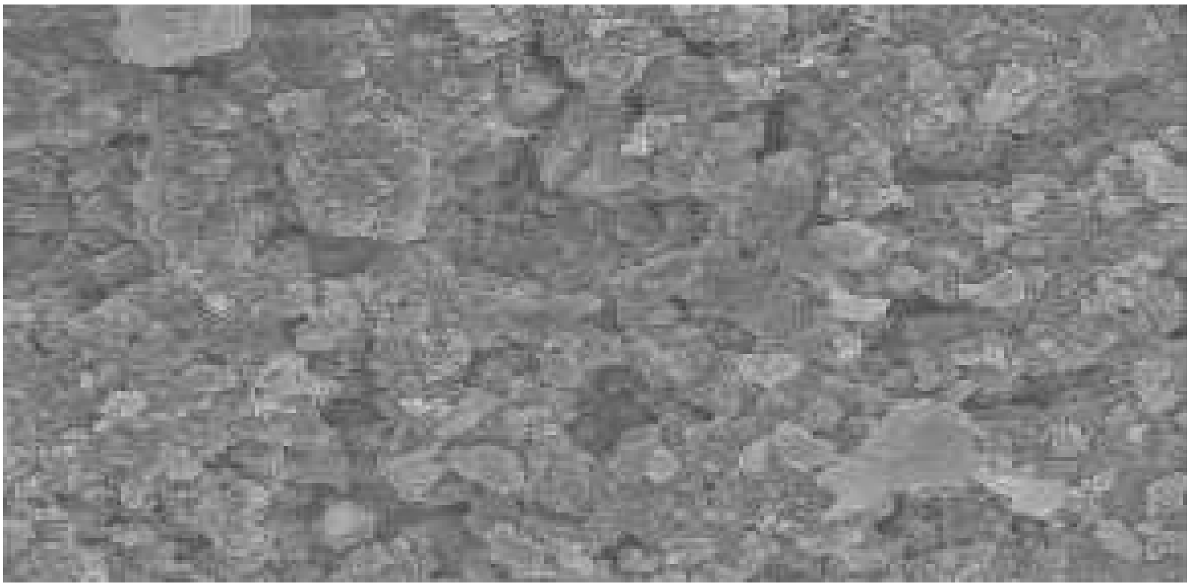

Figure 8a). SEM images of C- Steel immersed in 1M HCl in absence of inhibitor

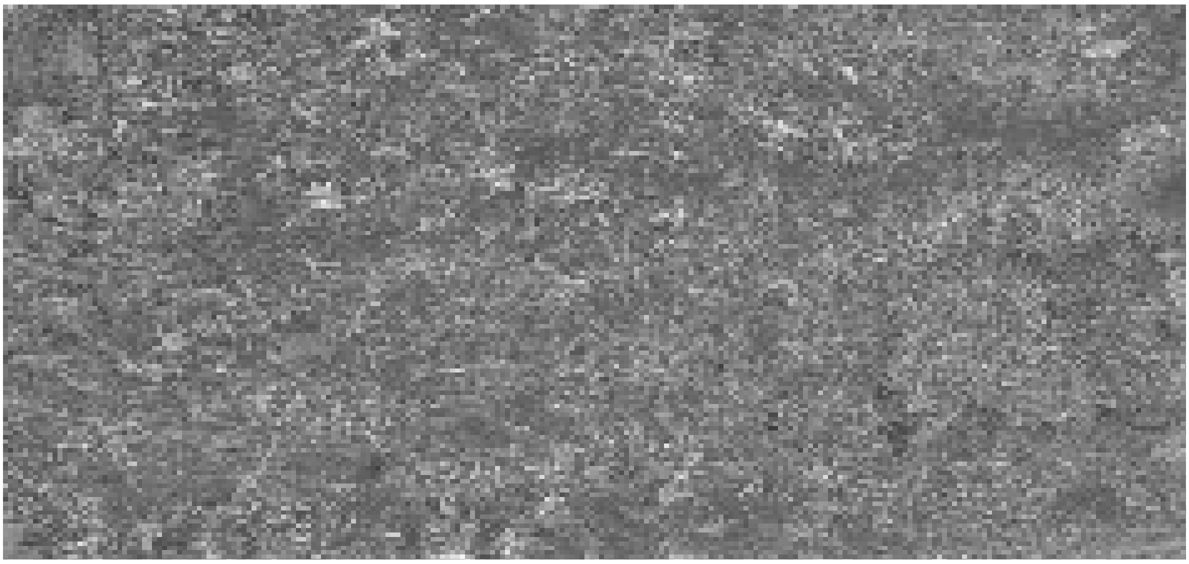

Figure 8b). SEM images of C- Steel immersed in 1M HCl in presence of 200 ppm of the used inhibitor (**PS**).

Conclusion

1- Results obtained from the experimental data shows that Pyrazolthiosemicarbazone **(PS)** is a good inhibitor for the corrosion of carbon steel in 1M HCl and inhibition efficiency was more pronounced with increase in the inhibitor concentration.
2- The inhibition efficiency increase with increase in temperature, leading to the conclusion that the protective film of these compounds formed on the carbon steel surface is stable at higher temperature.
3- The potentiodynamic polarization curves imply that, **(PS)** acts as a mixed type inhibitor, but under prominent cathodic control.

4- The polarization resistance (R_p) value increased with increase in the concentration of the inhibitor.
5- The addition of **PS** to the corrosive medium leads to an increase in the ΔH^o values; so these molecules increase the highest of energy barrier for the corrosion process
6- , the values of entropy of activation ΔS^o are large and negative. This implies that the activated complex in the rate determining step represent association rather than dissociation.
7- Results obtained from polarization, open circut and weight loss measurements are in good agreement with each other.

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