Effect of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione on inhibition of mild steel corrosion in 1M HCl

Y. El Ouadi[1], H. Elmsellem[1*], M. El fal[2], N. K. Sebbar[2], A. Bouyanzer[1], R. Rmili[1], E. M. Essassi[2], B. El Mahi[1], L. Majidi[3] and B. Hammouti[1]

[1]*Laboratoire de Chimie Appliquée et environnement (LCAE-URAC18), Faculté des Sciences, Oujda, Morocco*
[2]*Laboratoire de Chimie Organique Hétérocyclique, URAC 21, Pôle de Compétences Pharmacochimie, Université Mohammed V, Faculté des Sciences, Av. IbnBattouta, Rabat, Morocco*
[3]*Laboratoire des Substances Naturelles & Synthese et Dynamique Moléculaire, Faculté des Sciences et Techniques, Errachidia, Morocco*

_____

ABSTRACT

The effect of addition of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) on the corrosion of steel in hydrochloric acid 1M has been studied by weight loss measurements, potentiodynamic and EIS measurements. The corrosion rates of the steel decrease with the increase of the inhibitor concentration, while the inhibition efficiencies increase. The addition of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) enhances the inhibition efficiency considerably. The presence of this inhibitor increases the degree of surface coverage. E (%) obtained from the various methods is in good agreement. Polarisation measurements show also that the 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione act as mixed type inhibitor.

Key words: corrosion, inhibition, mild steel, 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione, electrochemical system, HCl 1M.

_____

INTRODUCTION

The importance of inhibitive protection in acidic solutions is increased by the fact that steel materials, which are more susceptible to be attacked in aggressive media, are the commonly exposed metals in industrial environments. It is shown that the protective properties of such compounds depend upon their ability to reduce corrosion rate and are enhanced at higher electron densities around the nitrogen atoms [1–7]. Among these compounds, ketones are much known as good inhibitors in aggressive media [8–10].The inhibitive properties arise from their ability to be adsorbed onto the electrode surface. The relation between the adsorption inhibition mechanism and variation in the electronic structure of the inhibitor has been studied [11–15].
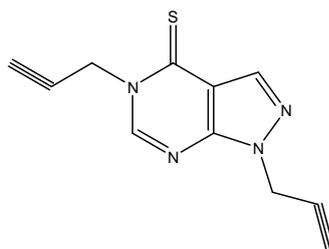
Scheme 1: 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione(P1)

_____

In this paper, electrochemical polarisation, EIS and gravimetric techniques are applied to study the ability of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) Scheme 1. to inhibit the corrosion of steel in 1M HCl. The effect of temperature is also studied.

## MATERIALS AND METHODS

2.1. Materials:
Corrosion tests were performed using coupons prepared from steel having the composition: 0.09%P; 0.38% Si; 0.01% Al; 0.05% Mn; 0.21% C; 0.05% S and 99.21 % Fe were polished with mery paper up to 1200 grade, washed thoroughly with double-distilled water, degreased with AR grade ethanol, acetone and dried at room temperature. MS samples of size 1.0 x 1.0x 1.0 cm and MS powder were used for weight loss studies. For electrochemical studies, specimens with an exposed area of 1 cm^2 were used. These specimens were degreased ultrasonically with 2-propanol and polished mechanically with different grades of emery paper to obtain very smooth surface.

2.2. Solutions:
The test solutions were prepared by the dilution of analytical grade 37 % HCl with distilled water up to the optimum inhibitor concentration of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1). For pH studies, the test solutions were prepared by the dilution of distilled water up to the optimum concentration, which was reached by adjusting the pH using HCl and NaOH. Inhibitor was dissolved in acid solution at required concentrations in (Mol/L) and the solution in the absence of inhibitor was taken as blank for comparison purposes. The test solutions were freshly prepared before each experiment by adding 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) directly to the corrosive solution. Experiments were conducted on several occasions to ensure reproducibility. Concentrations of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) were 10^{-6}, 10^{-5}, 10^{-4} and 10^{-3} Mol/L.

2.3. Synthesis of inhibitors
(0,54 g, 3.04 mmol) of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-one and (0,84 g, 3.65 mmol) of phosphorus pentasulfide were refluxed in pyridine for 4 h. Then the solvent is evaporated under reduced pressure; the precipitate formed is washed with hot water and recrystallized from ethanol solution to afford the title compound as yellow blocks [16-18].
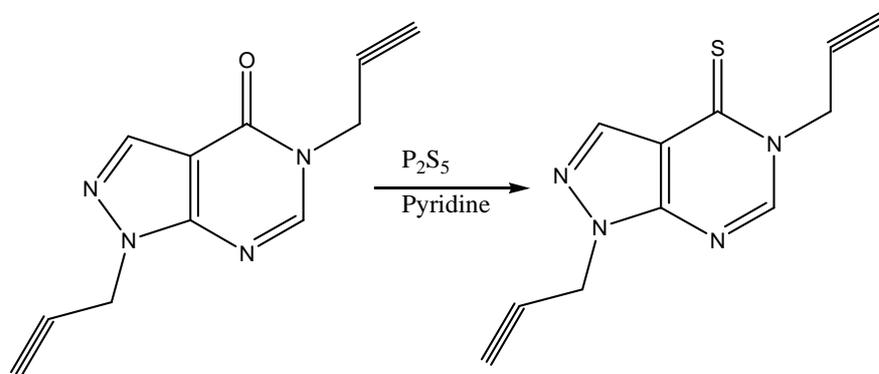
Scheme 2: Characterization of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1)

The analytical and spectroscopic data are conforming to the structure of compound formed.

(P1):Yield = 45%; Spectre de RMN^{1}H (DMSO) :δ 8.1 (s,1H,CH), 8.34 (s,1H,CH), 4.59 (dd, 2H, N5CH2,^{3}J=4.59, ^{4}J=4.57Hz), 4.89 (dd, 2H, N$_1$CH$_2$, ^{3}J=4.9, ^{4}J=4.68Hz), 4.94 (m, 2H, =CH$_2$, ^{3}J=4.9, ^{4}J=4.6), 5.1 (m, 2H, =CH$_2$, ^{3}J=5.1, ^{4}J=4.8), 5.95 (m, 1H, =CH, ^{3}J=5.93 ,^{4}J=5.63), 6.02 (m, 1H, =CH, ^{3}J=5.91, ^{4}J=5.71Hz). Spectre de RMN^{13}C (DMSO) : 35.22, 37.06 NCH$_2$; 76.1, 76.2≡CH ; 78.3, 79.1, 105.4, 135.6, 150.8, 151.3 Cq ; 169.9 C=S. Spectre de masse (IE) M$^+$(m/z) =216.

RESULTS AND DISCUSSION

3.1.Weight Loss Measurements
The gravimetric method (weight loss) is known to be the most widely used method of monitoring inhibition efficiency [19-22]. Weight loss is measured on sheets of steel of apparent surface area of 2 cm^2. These sheets are abraded successively with fine emery paper until 1200 grade. The sheets are then rinsed with distilled water,

_____

degreased and dried before being weighed and immersed in 50mL of the corrosive medium. The immersion time for the weight loss is 6h at room temperature 308°K in air without bubbling in a double walled glass cell equipped with a thermostat-cooling condenser. Corrosion rate was determined by hanging the steel coupon in acid solution with and without inhibitor. Each value is the mean of triplicate experiences.

The percent inhibition, E% for the weight loss method, is calculated as follows:

$$E (\%) = \frac{w_0 - w_i}{w_0} \times 100 \qquad\qquad (1)$$

wi and w$_0$ are the corrosion rates of steel samples with and without inhibitor, respectively.

Table 1. Weight loss mesurements of different concentration with and without presence of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) in HCl 1M medium

Inhibitor	Concentration (M)	w (mg.cm^{-2}h^{-1})	E (%)
1M HCl	-	0.3200	---
Inhibitor (P1)	10-6	0.0370	88.42
	10-5	0.0233	92.17
	10-4	0.0183	94.26
	10-3	0.0130	95.92

Steel samples were immersed for 6h at 308 °K in aerated 1M HCl at various contents of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1). Table 1collects the variation of the corrosion rate of steel with the inhibitor concentration. The calculated inhibition efficiencies of the naturally oil are also given in Table 1.

it is clear that 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) showed a best inhibitive effect, the efficiency reach until 95.92 % in 1M HCl medium.

This result could be explain by the presence of molecular structure containing heteroatoms having higher basicity and electron density on the hetero atoms such as N and substituents have tendency to resist corrosion.

3.2. Adsorption isotherm
Metal Surface providing us several information about the adsorption mechanism of the inhibitors on the surface by studying the relationship between the concentration and the surface coverage. Many isotherms are employed to fit the experimental data such as Langmuir, Temkin, Frumkin etc...

It is found that the adsorption of studied inhibitors on steel surface obeys the Langmuir adsorption isotherm equation:

$$\frac{c}{\theta} = \frac{1}{K} + C \qquad\qquad (2)$$

Where C is the concentration of inhibitor, K the adsorption equilibrium constant, and θ is the surface coverage.

Plots of C/θ against C yield straight lines as shown in Figure 1, and the corresponding linear regression parameters are listed in Table 2. These parameters indicating the adsorption of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) on steel surface obeys Langmuir adsorption isotherm.

Furthermore, the adsorption equilibrium constant (K) is related to the standard free energy Δ**G°** by the following equation:

$$\Delta G^0{}_{ads} = -RT.ln(55,5.K) \qquad\qquad (3)$$

Where R is the gas constant (8.314 J K^{-1} mol^{-1}), T the absolute temperature (K), and the value 55.5 is the concentration of water in the solution.
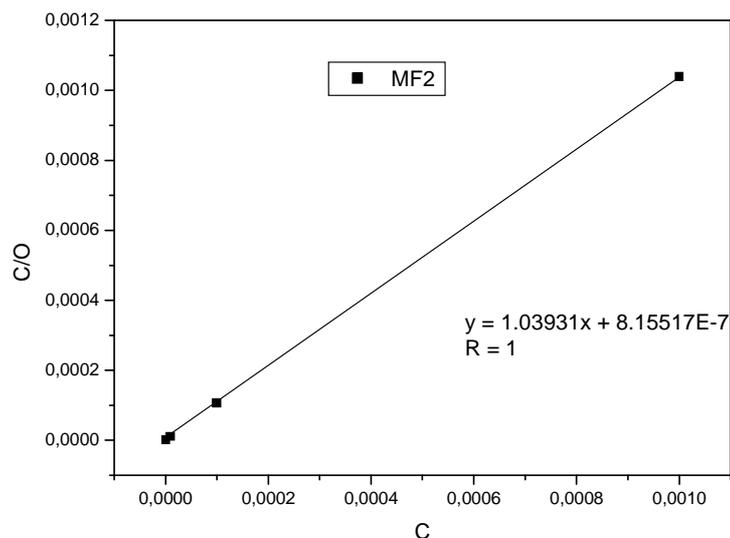
_____

Figure 1. Langmuir adsorption of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) on the mild steel in HCl 1M medium

Table 2 : Thermodynamics parameters adsorption of inhibitors (P1) on the steel mild in HCl 1M media

Measurements	Inhibitor	K_{ads}	ΔG°_{ads} kJ mol^{-1}	Linear coefficient regression (r)
Weigh tloss	(P1)	12.26 10^5	-8.64	1

The table 2 represent the ΔG^0_{ads} values, the negative values of the free energy means that the inhibitor was spontaneously adsorbed on mild steel–electrolyte interface. It has been reported that values of ΔG^0_{ads} up to -20 kJ/mol are consistent with the physisorption; those around -40 kJ/mol or higher are consistent with chemisorptions [23]. In the present study, the value of ΔG^0_{ads} is -8.64 kJ mol-1, probably means that the adsorption of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) on the steel surface exhibits is physical adsorption.

3.3. Electrochemical measurements
3.3.1. Potentiodynamic polarization curves
Potentiodynamic anodic and cathodic polarization plots for mild steel specimens in 1 M HCl solution in the absence and presence of different concentrations of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) at 308 °K are shown in Figure 2. The respective kinetic parameters including corrosion current density (I_{corr}), corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (βc, βa) and inhibition efficiency (E%) are given in Table 3.
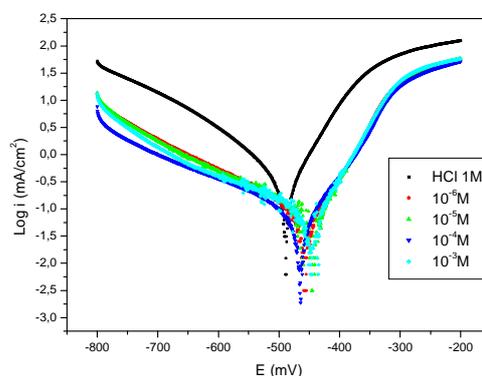

Figure 2. Tafel polarization curves in HCl 1M with and witout1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) at different concentrations

It is clear from Figure 2 that the addition of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione(P1) has an inhibitive effect in the both anodic and cathodic parts of the polarization curves. This indicates a modification of the mechanism of cathodic hydrogen evolution as well as anodic dissolution of steel, which suggest that inhibitor

_____

powerfully inhibits the corrosion process of mild steel, and its ability as corrosion inhibitor is enhanced as its concentration is increased. In addition, the parallel cathodic Tafel curves in Figure 2 show that the hydrogen evolution is activation-controlled and the reduction mechanism is not affected by the presence of this inhibitor.

Table 3. Electrochemical parameters of mild steel at various concentrations of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione(P1) HCl (1M)

Inhibitor	Concentration (M)	$-E_{corr}$ (mV/ECS)	I_{corr} (μA/cm^2)	$-\beta_c$ (mV/dec)	E (%)
1M HCl	-	490	5779	74.8	--
Inhibitor (P1)	10^{-6}	456	89	63.2	85
	10^{-5}	445	488	53.1	92
	10^{-4}	456	468	70.3	92
	10^{-3}	447	404	49.7	93

From Table 3, it is clear that increasing concentration of the inhibitor resulted in a decrease in corrosion current densities (I_{corr}) and an increase in inhibition efficiency (**E**%), reaching its maximum value, 93.01 %, at 10^{-3}Mol/L.

This behavior suggests that the inhibitor adsorption protective film formed on the carbon steel surface tends to be more and more complete and stable. The presence of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) caused a slight shift of corrosion potential towards the positive values compared to that in the absence of inhibitor. In literature, it has been also reported that if the displacement in E_{corr} is > 85 mV the inhibitor can be seen as a cathodic or anodic type inhibitor and if the displacement of E_{corr} is < 85 mV, the inhibitor can be seen as mixed type [24]. In our study, the maximum displacement in E_{corr} value was 45 mV which indicates that the inhibitor acts as mixed type inhibitor.

3.3.2. Electrochemical impedance spectroscopy (EIS)
The corrosion of mild steel in 1 M HCl solution in the presence of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) was investigated by EIS at room temperature after an exposure period of 30 min. Nyquist plots for mild steel obtained at the interface in the absence and presence of the inhibitor at different concentrations is given in Figure 3.
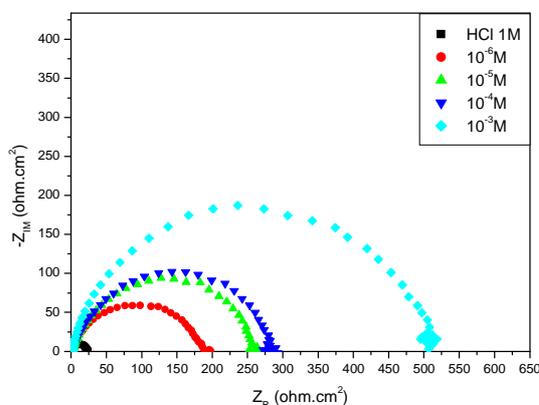

Figure 3: Nyquist plots in absence and presence of different concentrations of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) in HCl 1M

As shown in Figure 3, in uninhibited and inhibited 1 M HCl solutions, the impedance spectra exhibit one single capacitive loop, which indicates that the corrosion of steel is mainly controlled by the charge transfer process [25]. It is noted that these capacitive loops in 1 M HCl solutions are not perfect semicircles which can be attributed to the frequency dispersion effect as a result of the roughness and inhomogeneous of electrode surface [26]. Furthermore, the diameter of the capacitive loop in the presence of inhibitor is larger than that in blank solution, and enlarges with the inhibitor concentration. This means that the impedance of inhibited substrate increases with the inhibitor concentration, and leads to good inhibitive performance.

The EIS results of these capacitive loops are simulated by the equivalent circuit shown in Figure 3 to pure electric models that could verify or rule out mechanistic models and enable the calculation of numerical values corresponding to the physical and/or chemical properties of the electrochemical system under investigation. In the electrical equivalent circuit, R_s is the electrolyte resistance, R_t the charge transfer resistance and C_{dl} is the double layer capacitance.
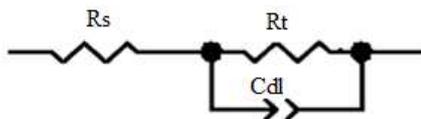
_____

Figure 4: Equivalent circuit used to fit the EIS data of mild steel in 1 M HCl without and with different concentrations of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1)

The electrochemical parameters of R_t, C_{dl} and f_{max} derived from Nyquist plots and inhibition efficiency E(%)are calculated and listed in Table 4.

Table 4. Corrosion parameters obtained by impedance measurements for mild steel in HCl 1M at various concentrations of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1)

Inhibitor	Concentration (M)	R_t (Ω cm^2)	f (Htz)	C_{dl} ($\mu f/cm^2$)	E (%)
1M HCl	-	21.08	100	75.5	--
Inhibitor (P1)	10^{-6}	185	20	43.01	89
	10^{-5}	260.9	20	30.5	92
	10^{-4}	198.1	20	26.69	93
	10^{-3}	509.6	20	15.61	96

From the impedance data Table 4, it was clear that:
→R_t values in the presence of the inhibitor were always greater than their values in the absence of the inhibitor molecules. This means that, this inhibitor was acting as adsorption inhibitor;
→ Charge transfer resistance R_t, values were increased in the presence of the inhibitor and consequently the inhibition efficiency (**E%**) increases to 95.86% at 10^{-3}M, which indicates a reduction in the steel corrosion rate;
→ Values of double layer capacitance C dl, are also brought down to the maximum extent in the presence of inhibitor (15.61 μF.cm^2 at 3 10^{-3}M) and the decrease in the values of C_{dl} follows the order similar to that obtained for I_{corr} in this study.

3.4. Effect of temperature
In order to study the effect of temperature on the inhibition efficiencies of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1), weight loss measurements were carried at four temperatures values: 318, 328,338 and 348°K and during 1 hour of immersion in absence and presence of inhibitor at optimum concentration (10^{-3}Mol/L) determined in electrochemical measurements.

The various corrosion parameters obtained are listed in Table 5. Figure 5 illustrates the Variation of CR in 1M HCl on steel surface without and with of optimum concentration of inhibitor studied at different temperatures. From the weight loss results, the corrosion rate (CR), the inhibition efficiency (E %) of inhibitors and degree of surface coverage (Θ) were calculated using equations 4, 5 and 6[27] :

$$CR = \left(\frac{\Delta W}{Sxt}\right) \tag{4}$$

$$E(\%) = \left(1 - \frac{W_{corr}}{W^o_{corr}}\right)x100 \tag{5}$$

$$\theta = \left(1 - \frac{W_{corr}}{W^o_{corr}}\right) \tag{6}$$

Where W_{corr} and W^o_{corr} are the weight losses for mild steel in the presence and absence of the inhibitor in HCl solution and θ is the degree of surface coverage of the inhibitors. ΔW is the difference of weight loss for mild steel with and without inhibitors, S is the exposure area of the metallic specimens and t is the immersion time of the metal in corrosive solution.

The fractional surface coverage (θ) can be easily determined from the weight loss measurements by the ratio E%:100, where E % is inhibition efficiency and calculated using equation (6).The data obtained suggest that 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) get adsorbed on the steel surface at all temperatures studied and corrosion rates increased in absence and presence of inhibitor with increase in temperature in 1M HCl solutions. In acidic media, corrosion of metal is generally accompanied with evolution of H$_2$ gas; rise in temperature usually accelerates the corrosion reactions which results in higher dissolution rate of the metal.

_____

Table 5. Corrosion parameters for mild steel in HCL 1M in absence and presence of optimum concentration of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) at different temperatures

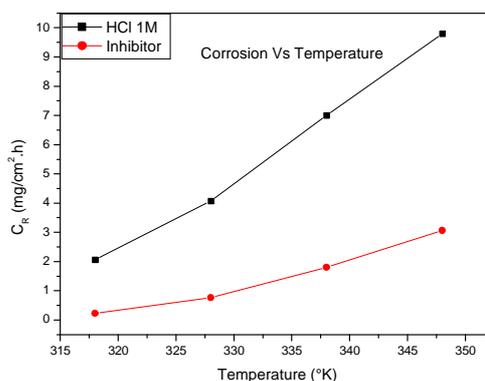| Temperature (K)	Inhibitor	C_R(mg/cm².h)	θ	E (%)
318	HCL 1M	2.0649	---	---
	Inhibitor*(P1)*	0.2267	0.89	89
328	HCL 1M	4.0689	---	---
	Inhibitor*(P1)*	0.7621	0.81	81
338	HCL 1M	6.9998	---	---
	Inhibitor*(P1)*	1.8038	0.74	74
348	HCL 1M	9.7914	---	---
	Inhibitor*(P1)*	3.0637	0.68	69

Figure 5. Variation of C_R in 1M HCl on steel surface without and with of optimum concentration of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) at different temperatures

From the Table 5, it is clear that corrosion rate increased with increasing temperature both in uninhibited and inhibited solutions while the inhibition efficiency of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) decreased with temperature. A decrease in inhibition efficiencies with the increase temperature in presence of the inhibitor might be due to weakening of physical adsorption. In order to calculate activation parameters for the corrosion process, Arrhenius equation. (7) and transition state equation (8) were used [28].

$$CR = A\exp(\frac{-E_a}{RxT}) \tag{7}$$

$$CR = \frac{RxT}{Nxh}\exp(\frac{-\Delta S_a}{R})\exp(\frac{-\Delta H_a}{RxT}) \tag{8}$$

where CR is the corrosion rate, R the gas constant, T the absolute temperature, A the pre-exponential factor, h the Plank's constant and N is Avogrado's number, E_a the activation energy for corrosion process, ΔH_a the enthalpy of activation and ΔS_a the entropy of activation. The apparent activation energy (E_a) at optimum concentration of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) was determined by linear regression between Ln(CR) and 1/T (Figure 6) and the result is shown in Table 6.
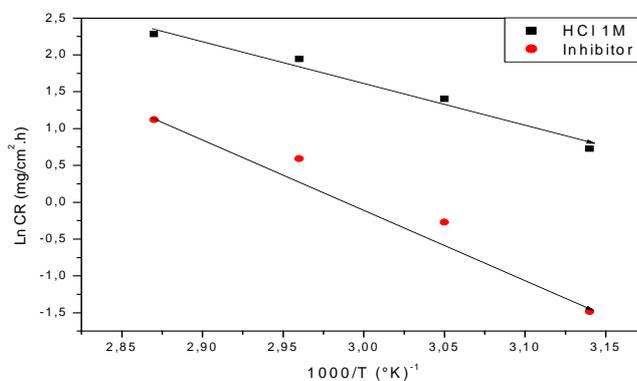

Figure 6. Arrhenius plots of ln CR vs. 1/T for mild steel in 1M HCl in the absence and the presence of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) at optimum concentration (10⁻³Mol/L)

_____

Inhibitor	Ea(J/mol)	ΔHa(KJ/mol)	ΔSa(J/mol.K)
1M HCL	48.13	45.61	-95.79
Inhibitor (P1)	80.15	77.85	-12.367

Inspection of Table 6 showed that the value of Ea determined in 1M HCl containing 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) is higher (80.15 J/mol) than that for uninhibited solution (48.13 J/mol). The increase in the apparent activation energy may be interpreted as physical adsorption that occurs in the first stage. The increase in activation energy could be attributed to an appreciable decrease in the adsorption of the inhibitor on the steel surface with increase in temperature. As adsorption decreases more desorption of inhibitor occur because these two opposite processes are in equilibrium. Due to more desorption of inhibitor molecules at higher temperatures the greater surface area of steel comes in contact with aggressive environment, resulting increased corrosion rates with increase in temperature [29-36].
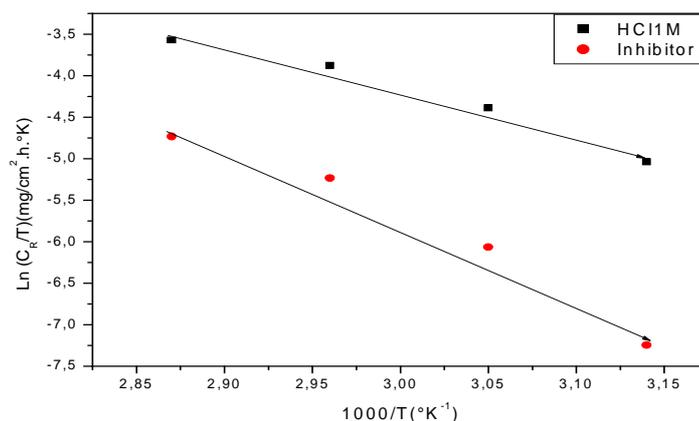

Figure 7.Arrhenius plots of ln CR/T vs. 1/T for steel in 1M HCl in the absence and the presence of 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) at optimum concentration (10⁻³Mol/L)

Figure 7 showed a plot of Ln (CR/T) versus 1/T. The straight lines are obtained with a slope ($\Delta H_a/R$)and an intercept of (Ln R/Nh +ΔS_a /R) from which the values of the values of ΔH_a and ΔS_a are calculated for 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) of   analyzed and are given in Table 6. Inspection of these data revealed that the thermodynamic parameter (ΔH_a) for dissolution reaction of steel in 1M HCl in the presence of inhibitor is higher (77.85 kJ/mol) than that of in the absence of inhibitors (45.61 kJ/ mol). The positive sign of ΔH_a reflect the endothermic nature of the steel dissolution process suggesting that the dissolution of steel is slow in the presence of inhibitor. Negative value of entropy (ΔS_a) imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactant to the activated complex.

CONCLUSION

The principal finding of present work can be summarized as follows:

✓ Steady state electrochemical measurements have shown that 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione act as mixed inhibitor for the corrosion of steel in HCl 1M without modifying the mechanism of hydrogen evolution reaction.
✓ The increase in the charge transfer resistance and decrease in double layer capacitance values, with the increase in the inhibitor concentration, showed that 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) formed protective layers on the mild steel surface, covering areas where HCl solution degrades and corrodes rapidly.
✓ Inhibition efficiency increases with increase in the concentration of the inhibitor studied but decreases with rise in temperature.
✓ The corrosion process was inhibited by adsorption of the organic matter on the mild steel surface, obtaining the formation of the film on the metal/acid solution interface, decreasing the degradation of the material.
✓ Results obtained through weight loss measurements and electrochemical tests demonstrated that 1,5-di(prop-2-ynyl)-1H-pyrazolo[3,4-d]pyrimidine-4(5H)-thione (P1) act as efficient corrosion inhibitors of the mild steel in 1 M HCl solution.

_____

REFERENCES

[1] W.J. Lorenz, F. Mansfeld, *Corros. Sci*, **1986**, 3, 467.

[2] H. Elmsellem, H. Nacer, F. Halaimia, A. Aouniti, I. Lakehal, A .Chetouani, S. S. Al-Deyab, I. Warad, R. Touzani, B. Hammouti, *Int. J. Electrochem. Sci*, **2014**, 9, 5328 – 5351

[3] D. Bouzidi, S. Kertit, B. Hammouti, M. Brighli, J. *Electro-chem. Soc. India* , **1997**, 46, 23.

[4] H. Elmsellem, A. Elyoussfi, N. K. Sebbar, A. Dafali, K. Cherrak, H. Steli, E. M. Essassi, A. Aouniti and B. Hammouti, *Maghr. J. Pure & Appl. Sci*, **2015**, 1, 1-10.

[5] K. Bekkouch, A. Aouniti, B. Hammouti, S. Kertit, *J. Chim. Phys*, **1999**, 96, 838.

[6] Y. Abed, Z. Arrar, A. Aouniti, B. Hammouti, S. Kertit, A. Mansri, *J. Chim. Phys*, **1999**, 96 ,1347.

[7] H. Elmsellem, N. Basbas, A. Chetouani, A. Aouniti, S. Radi, M. Messali, B. Hammouti, *Portugaliae. Electrochimica. Acta*, **2014**, 2,77.

[8] H. Elmsellem, A. Aouniti, Y. Toubi, H. Steli, M. Elazzouzi, S. Radi, B. Elmahi, Y. El Ouadi, A. Chetouani, B. Hammouti ,*Der Pharma Chemica,* **2015**, 7, 353-364

[9] I.M. Issa, M.N.H. Moussa, M.A.A. Ghandour, *Corros. Sci*, **1973** , 13, 791.

[10] H. Elmsellem, T. Harit, A. Aouniti, F. Malek, A. Riahi, A. Chetouani , and B. Hammouti. *Protection of Metals and Physical Chemistry of Surfaces,* **2015**, 51(5), 873–884

[11] H. Elmsellem, A. Aouniti, M. Khoutoul, A. Chetouani, B. Hammouti, N. Benchat, R.Touzani, M. Elazzouzi. *Journal of Chemical and Pharmaceutical Research*, **2014**, 6(4), 1216-1224.

[12] A. Popova, M. Christov, S. Raicheva, E. Sokolova, *Corros. Sci*, **2004**,46,1333.

[13] T. Szauer, A. Brandt, *Electrochim. Acta*, **1981**,26,1209.

[14] A. Aouniti, H. Elmsellem, S. Tighadouini, M. Elazzouzi, S. Radi, A. Chetouani, B. Hammouti, A. Zarrouk, *Journal of Taibah University for Science,***2015**, http://dx.doi.org/10.1016/j.jtusci.2015.11.008

[15]H. Elmsellem, K. Karrouchi, A. Aouniti, B. Hammouti, S. Radi, J. Taoufik, M. Ansar, M. Dahmani, H. Steli and B. El Mahi, *Der Pharma Chemica*, **2015**, 7(10),237-245.

[16] M.El Fal, Y.Ramli, E. M.Essassi, M. Saadi & L.El Ammari, *Acta Cryst*, **2013**, E69, o1650.

[17] M.El Fal, Y.Ramli, E. M.Essassi, M.Saadi & L. El Ammari, *Acta Cryst*, **2015**, E71, o95–o96.

[18] M.El Fal, Y.Ramli, A.Zerzouf, A.Talbaoui, Y.Bakri & E.M. Essassi. *Journal of Chemistry,* **2015**, Article ID 982404, 6.

[19] A. Bouyanzer, L. Majidi, B. Hammouti, *Bull. Electrochem.***2006**; 22: 321.

[20] Y. El ouadi, A. Bouyanzer, L. Majidi, J. Paolini, J. M. Desjobert, J. Costa, A. Chetouani and B. Hammouti. Journal of Chemical and Pharmaceutical Research, **2014**, 6(7):1401-1416.

[21] Y. El Ouadi, A. Bouyanzer ,L. Majidi ,J. Paolini ,J.-M. Desjobert, J. Costa, A.Chetouani , B. Hammouti , S. Jodeh , I. Warad , Y. Mabkhot ,T. Ben Hadda. Res ChemIntermed DOI 10.1007/s11164-014-1802-7.

[22] M. Manssouri, Y. El Ouadi, M. Znini, J. Costa, A. Bouyanzer, J-M. Desjobert, L. Majidi. *Mater. Environ. Sci*, **2015**, 6 (3), 631-646.

[23] F. Bentiss, M. Outirite, M. Traisnel, H. Vezin, M. Lagrenee, B. Hammouti, SS. Al-Deyab, *International Journal of Electrochemical Science*, **2012**, 7, 1699-1723.

[24] A. K.Satapathy, G.Gunasekaran, S. C.Sahoo, K.Amit, P. V.Rodrigues, *Corros. Sci.* **2009**,5, 2848.

[25] A.Fouda, A.El-Bendary, M.Diabb, A.Bakra, *Mor. J. Chem*, **2014**, 2, 302-319.

[26] J.Saranya, P.Sounthari, A.Kiruthuka, K.Parameswari, S.Chitra, *J. Mater. Environ. Sci,* **2015***,* 6, 425-444.

[27] JR. Thompson, E. Scheetz, R. Schock, A. Lytl, J. Delaney, Abstracts, Water Quality echnology Conference, Denver, **1997**.

[28] F. Togue-Kamga, B.D. Btatkeu, C. Noubactep, P. Woafo, *Fresenius Environmental Bulletin*, **2012**,21,1992.

[29] I. Belfilali, A. Chetouani, B. Hammouti, S. Louhibi, A. Aouniti, SS.Al-Deyab, *Research on Chemical Intermediates,* **2014**,40,1069.

[30] K. Bouhrira, A. Chetouani, D. Zerouali, B. Hammouti, A. Yahyi, A. Et-Touhami, R. Yahyaoui, R.Touzani ,*Research on Chemical Intermediates*, **2014**,40,569.

[31] A. Ousslim, K. Bekkouch, A. Chetouani, E. Abbaoui, B. Hammouti, A. Aouniti, A. Elidrissi, F. Bentiss, *Research on Chemical Intermediates,* **2014**, 40,1201.

[32] D. Bouzidi, A. Chetouani, B. Hammouti, S. Kertit, M. Taleb, S.S. Al-Deyab. *International Journal of Electrochemical Science*, **2012**, 7, 2334.

[33] D. Ben Hmamou, R. Salghi, A. Zarrouk, B. Hammouti, S.S. Al-Deyab, L. Bazzi, H. Zarrok, A. Chakir, L. Bammou. *International Journal of Electrochemical Science,* **2012**,7, 2361.

[34] M. Abdallah, B.H. Asghar, I. Zaafarany, A.S.Fouda, *International Journal of Electrochemical Science*, **2012**,7,282.

[35] KF.Khaled, *Materials Chemistry and Physics,* **2008**,112, 290.

[36]Y. EL Ouadi, A. Bouratoua, A. Bouyenzer, Z. Kabouche, R. Touzani, H. Elmsellem, B. Hammouti, and A. Chetouani. *Der Pharma Chemica*, **2015**, 7(2),103-111.