

## Thermodynamic characterisation of steel corrosion in HCl in the presence of 2-phenylthieno (3, 2-b) quinoxaline

I. El Ouali <sup>1</sup>, B. Hammouti <sup>1</sup>, A Aouniti <sup>1,\*</sup>, Y. Ramli <sup>2,3</sup>, M. Azougagh <sup>3</sup>,  
E.M. Essassi <sup>2</sup>, M. Bouachrine <sup>4</sup>

<sup>1</sup> LCAE-URAC18, Faculté des Sciences, Université Mohammed Premier, B.P. 717, 60000 Oujda, Morocco

<sup>2</sup> Laboratoire de Chimie Hétérocyclique, Faculté des sciences, Université Mohammed V, Rabat, Morocco.

<sup>3</sup> Laboratoire Nationale de Contrôle des Médicaments, BP 6206, Rabat, Morocco

<sup>4</sup> Faculté Polydisciplinaire, Université Mohammed Ben Abdellah, Taza, Morocco.

\* Corresponding author. Tel. +212 5 36 500 602, Fax. +212 5 36 500 602, E-mail: [aouniti@yahoo.fr](mailto:aouniti@yahoo.fr)

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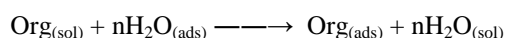
**Abstract-** The influence of inhibitor concentration and temperature on the corrosion behaviour of steel in molar HCl solution has been investigated by weight loss method. Results obtained show that the inhibitory effect of 2-phenylthieno(3, 2-b)quinoxaline (P4) increases with increasing P4 concentration to attain the highest value (95%) at 5 10<sup>-4</sup>M. The determination of the corrosion rate at the temperature range (308 - 353K) indicates that E% decreases with rise of temperature. Arrhenius law and its transition equation lead to estimate activation parameters of corrosion process. P4 inhibits well steel at moderate temperature and adsorbs according to the Langmuir isotherm. Plots of logarithm of corrosion rate function of the reciprocal of temperature as well as Van't hof and Gibbs equations facilitated the access to thermodynamic parameters such as equilibrium constant, adsorption heat and adsorption entropy. The various parameters of activation and adsorption may be a good tool to discuss manner of adsorption of organic compound. Attempt to correlate molecular structure to quantum indices was made.

*Keywords :* Corrosion ; inhibition ; quinoxaline ; Activation ; Adsorption.

### 1. Introduction

During acid picking process of steel temperature required is up to 60 °C, efficient inhibitors are required to limit metal dissolution as well as acid consumption. The corrosion is accelerated in elevated temperature, then inhibitors were selected to resist to elevated temperatures.

The effect of temperature on the corrosion inhibition of various organic compounds was treated by several works [1-3]. Investigations attempt to describe the corrosion phenomena of metals in aggressive media in the presence and absence of inhibitor. Also, the possible structural modifications of the double layer and the partial action of inhibitor on the electrochemical reactions are discussed [3-5]. The most effective and efficient inhibitors are organic compounds having heteroatoms and/or  $\pi$  bonds in their structures. An efficient organic compound possesses the ability to be adsorbed on the metal surface by displacing water molecule from a corroding interface as follow:



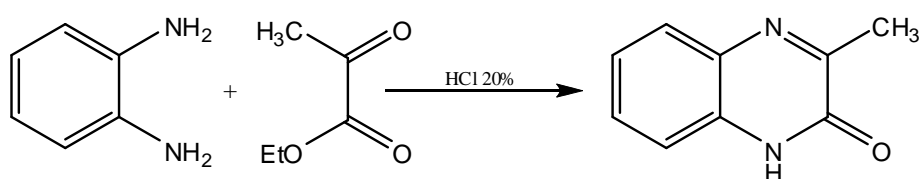
The reactivity of an inhibitor called “adsorption” is mainly influenced by the electronic structure of the inhibiting molecules [6]. The recognition of any molecule against a metal surface is ensured by active centers such as heteroatoms or functional groups such as C=NH, -N=N-, -CHO, R-OH, C=C, etc. The role of adsorption is to create a barrier against the arrival of aggressive ions which are responsible of corrosion. Then, active sites are blocked and corrosion rate is retarded or stopped. In this optic, in our laboratories, various molecules as azoles [7-

9], pyridines [10-12] and quinoxalines [13-15], are tested to protect steel. In this study, a new quinoxaline derivative, 2-phenylthieno(3, 2-b)quinoxaline (P4), was synthesised and tested as inhibitor of the steel corrosion in HCl solution. The determination of corrosion rate of steel in HCl with and without P4 by weight loss technique was made at different temperatures varying from 308 to 353 K. The various parameters describing the kinetic of corrosion as well as adsorption process inhibitor concentration are evaluated and discussed. Calculations of quantum parameters were used to explain efficiency in relation with molecular structure.

## 2. Experimental details

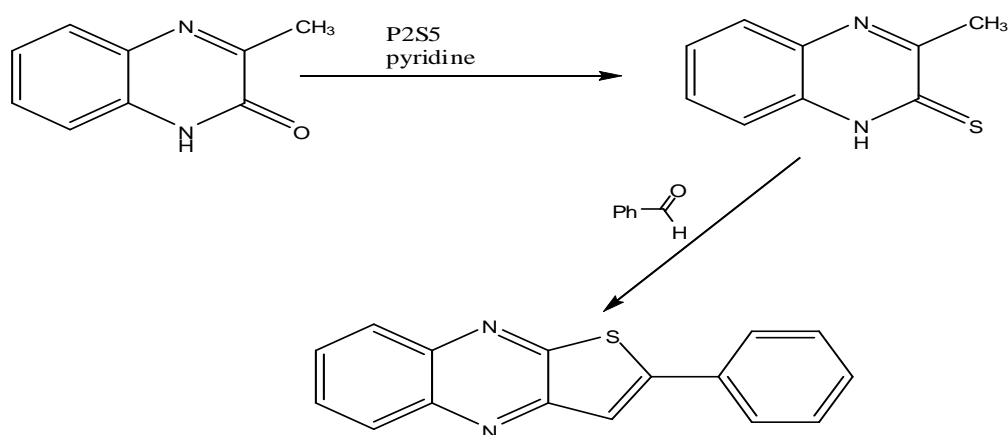
C38 Steel samples (0.09 % P; 0.38 % Si; 0.01 % Al; 0.05 % Mn; 0.21 % C; 0.05 % S and the remainder iron) was used. Prior to all measurements, are abraded with a series of emery paper from 180 to 1200 grade. The specimens are washed thoroughly with bidistilled water degreased and dried with acetone. The aggressive solution (1M HCl) was prepared by dilution of Analytical Grade 37 % HCl with double-distilled water.

Inhibitors studied are synthesized in our laboratory according to the procedure described in the schemes 1 and 2. In the literature, 3-methylquinoxalin-2-one is prepared according Philips method [16] [scheme 1](#);



**Scheme1:** Synthesis of, 3-methylquinoxalin-2-one

The treatment of the 3-methylquinoxaline-2 one with  $P_2S_5$  in the presence of the pyridine gave 3-methylquinoxaline-2-thione. The product obtained are merged with benzaldehyde gave 2-phenylthieno(3, 2-b)quinoxaline; [Scheme2](#). Cured product obtained was purified by recrystallization. The structure of compound was supported by  $^1H$  NMR,  $^{13}C$  NMR (Nuclear Magnetic Resonance), and mass spectrometry.



**Scheme2:** Synthesis of 2-phenylthieno (3, 2-b) quinoxaline

Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is  $50 \text{ cm}^3$ . The steel specimens used have a rectangular form ( $2\text{cm} \times 2\text{cm} \times 0.20\text{cm}$ ). The immersion time for the weight loss is 6h at 308K and 1h at other temperatures.

## 3. Results and discussion

The weight loss data made primarily at 6 hours of immersion at room temperature (308 K) were given in Table 1, where the inhibition efficiency was calculated using the following equation (1):

$$E_w \% = \left( 1 - \frac{W_{\text{corr}}}{W_{\text{corr}}^0} \right) 100 \quad (1)$$

$W_{\text{corr}}$  and  $W_{\text{corr}}^0$  are the corrosion rates of steel with and without organic compound, respectively.

It is clear that with the rise in P4 concentration, corrosion rate decreased and then the inhibition efficiency increased. The highest inhibiting efficiency attained 95% at  $5 \times 10^{-4}$  M. This excellent inhibitory effect merits to be studied at elevated temperatures.

**Table 1.** Gravimetric results of steel in acid at different concentrations of P4 at 6h and 308 K

Inhibitor	Concentration (M)	W (mg.cm <sup>-2</sup> .h <sup>-1</sup> )	E (%)
Blank	0	0.964	-
P4	10 <sup>-6</sup>	0.653	32
	5 x10 <sup>-6</sup>	0.550	43
	10 <sup>-5</sup>	0.302	69
	5x10 <sup>-5</sup>	0.137	86
	10 <sup>-4</sup>	0.069	93
	5 x10 <sup>-4</sup>	0.048	<b>95</b>

3.1. Kinetic parameters of activation.

The effect of temperature (313-353 K) was conducted at 1 hour at various concentration of P4. Table 2 collects data obtained by weight loss measurement and the corresponding inhibition efficiencies.

In acidic media, the increase of temperature leads to increasing corrosion rate of steel. It is well-known that corrosion rate increases with the rise of temperature. At each temperature, the inhibition corrosion increases with inhibitor concentration. But at a given inhibitor concentration, the inhibitory effect ceases more and more to jump from 95% at 308 K to 76% at 343 K. Apparently, the results obtained postulate that the inhibitor function through adsorption on the steel surface by the blocking the active sites to form a screen onto the steel surface from acidic solution. As the temperature increases, we notice the desorption rate manifests parallel to that of adsorption; the surface becomes less protected and then the inhibitor gradually loss its effectiveness.

**Table 2.** The effect of P4 concentration on the weight loss of steel/HCl and efficiency at different temperatures.

T (K)	Concentration (M)	W (mg.cm <sup>-2</sup> .h <sup>-1</sup> )	E (%)
313	0	1.087	-
	10 <sup>-5</sup>	0.420	61
	5x10 <sup>-5</sup>	0.159	85
	10 <sup>-4</sup>	0.112	90
	5x10 <sup>-4</sup>	0.073	<b>93</b>
323	0	2.823	-
	10 <sup>-5</sup>	1.287	54
	5x10 <sup>-5</sup>	0.457	84
	10 <sup>-4</sup>	0.325	88
	5x10 <sup>-4</sup>	0.275	<b>90</b>
333	0	4.802	-
	10 <sup>-5</sup>	2.431	49
	5x10 <sup>-5</sup>	1.129	76
	10 <sup>-4</sup>	0.786	84
	5x10 <sup>-4</sup>	0.724	<b>85</b>
343	0	9.963	-
	10 <sup>-5</sup>	5.397	46
	5x10 <sup>-5</sup>	2.509	75
	10 <sup>-4</sup>	1.998	80
	5x10 <sup>-4</sup>	1.698	<b>83</b>
353	0	17.95	-
	10 <sup>-5</sup>	10.021	44
	5x10 <sup>-5</sup>	5.697	68
	10 <sup>-4</sup>	5.119	71
	5x10 <sup>-4</sup>	4.327	<b>76</b>

The influence of temperature on the kinetic process of corrosion in free acid and in the presence of inhibitor leads to get more information on the behaviour of the steel/HCl interface. The Arrhenius law may be presented as a straight line of the logarithm of the corrosion rate (W) and 1/T according to the following relation:

$$\ln W = \frac{-E_a}{R} \times \frac{1}{T} + \ln A \tag{2}$$

where  $E_a$  represents the apparent activation energy,  $R$  is the universal gas constant,  $T$  is the absolute temperature and  $A$  is the pre-exponential factor.

The linear regression plots of  $\ln(W)$  and  $1/T$  are presented in Fig.1. The calculated activation energies,  $E_a$ , and pre-exponential factors,  $A$ , at different concentrations of the inhibitor are collected in Table 3. The change of the values of the apparent activation energies may be explained by the modification of the mechanism of the corrosion process in the presence of adsorbed inhibitor molecules [17].

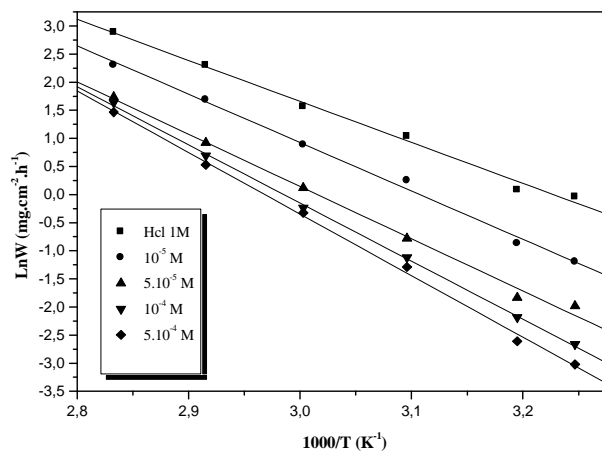
The variation of the apparent activation energy  $E_a$  in the presence and absence of inhibitor is largely discussed in the literature [1-3, 17,18]. Values of  $E_a$  were found to increase or decrease in the presence of inhibitors. The apparent activation energy was lower in the presence of inhibitor than that in the absence of inhibitor [17,18]. In our study,  $E_a$  increases with increasing the P4 concentration, and all values of  $E_a$  were higher than that in its absence. This type of inhibitor retards well corrosion at ordinary temperatures but inhibition is diminished at elevated temperature.

Arrhenius law predicts that corrosion rate increases with the temperature and  $E_a$  and  $A$  may vary with temperature (Eq. 2). The obtained values seem that  $A$  and  $E_a$  increase continuously with the inhibitor's concentration.

Other kinetic data (enthalpy and entropy of corrosion process) are accessible using the alternative formulation of Arrhenius equation:

$$W = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a^\circ}{R}\right) \exp\left(-\frac{\Delta H_a^\circ}{RT}\right) \tag{3}$$

where  $h$  is plank's constant,  $N$  is Avogrado's number,  $\Delta S_a^\circ$  and  $\Delta H_a^\circ$  are the entropy and enthalpy of activation, respectivel. Plots of  $\ln(W/T)$  vs. the reciprocal of temperature show straight lines with a slope equal to  $(-\Delta H_a^\circ/R)$  and an intercept of  $(\ln R/Nh + \Delta S_a^\circ/R)$ . The values of  $\Delta H_a^\circ$  and  $\Delta S_a^\circ$  are also presented in Table 3.



**Fig.1.** Arrhenius plots of steel in acid with and without different P<sub>4</sub> concentrations

Examination of the kinetic values shows that the increase of inhibitor concentration leads to increase all the parameters of corrosion process (Table 3). The positive sign of the enthalpy ( $\Delta H_a^\circ$ ) is an endothermic nature of the steel dissolution in HCl solution. The entropy of activation  $\Delta S_a^\circ$  in the absence of inhibitor is negative and tends to become positive at higher concentration. The increase of  $\Delta S_a^\circ$  is generally interpreted by increase in disorder taking place on going from reactants to the activated complex [19].

**Table 3.** Kinetic parameters of activation as function of inhibitor concentration.

Concentration of P <sub>4</sub> (M)	E <sub>a</sub> (kJ/mol)	ΔH <sub>a</sub> <sup>°</sup> (kJ/mol)	E <sub>a</sub> - ΔH <sub>a</sub> <sup>°</sup>	ΔS <sub>a</sub> <sup>°</sup> (J/mol.K)
Blank	60.70	57.97	2.73	-58.33
10 <sup>-5</sup>	71.63	68.89	2.74	-31.65
5x10 <sup>-5</sup>	77.40	74.66	2.74	-20.84
10 <sup>-4</sup>	86.00	83.27	2.73	2.52
5x10 <sup>-4</sup>	91.14	88.40	2.74	16.28

The value of  $E_a$  for mild steel corrosion in free molar HCl solution ( $60.7 \text{ kJ mol}^{-1}$ ) is in the same order of magnitude of some literature data for steel [19–21]. values of  $E_a$  obtained in the presence of inhibitor are higher than that for the uninhibited one, indicating a strong inhibitive action for the studied compounds by increasing the energy barrier for the corrosion process, emphasizing the electrostatic character of the inhibitor’s adsorption on mild steel surface [22]. According to Riggs and Hurd [23], the decrease in apparent activation energy at higher level of inhibition arise from a shift of the net corrosion reaction from that on the uncovered surface to one involving the adsorbed sites directly.

The increase of  $E_a$  and  $\Delta H_a^\circ$  accompanying the increase in the inhibitor concentration is explained by an increase of the energy barrier of corrosion reaction. In case of endothermic H adsorption, with a high activation energy barrier for the transition between strongly bonded  $H_{ads}$  and  $H_{diss}$  [23]. The higher activation energy in the inhibitor’s presence further supports the proposed physisorption mechanism. Unchanged or lower values of  $E_a$  in inhibited systems compared to the blank to be indicative of chemisorption mechanism, while higher values of  $E_a$  suggest a physical adsorption mechanism.

Results gathered merit to verify the known thermodynamic relation between  $E_a$  and  $\Delta H_a^\circ$  characterizing unimolecular reaction [21]:

$$E_a - \Delta H_a^\circ = RT \tag{4}$$

The calculated value (2.77 at 333 K) is too close to those estimated in Table 3. Then, the inhibitor affected by the same manner on  $E_a$  and  $\Delta H_a^\circ$ .

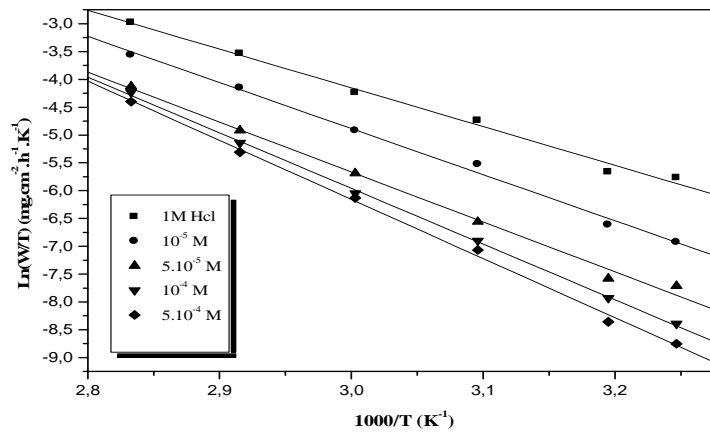


Fig.2. The relation between Ln (W/T) and 1/T for different P<sub>4</sub> concentrations

### 3.3. Parameters of adsorption.

Attempts were made to fit values of  $\theta$  to many isotherm including Langmuir, Temkin Frumkin and Freundlich. The organic compound seems that follows well the Langmuir adsorption isotherm written in the rearranged form:

$$\frac{C}{\theta} = \frac{1}{K} + C \text{ with } K = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^\circ}{RT}\right) \tag{5}$$

where  $C$  is the concentration of inhibitor,  $K$  is the adsorptive equilibrium constant,  $\theta$  is the surface coverage and the standard adsorption free energy ( $\Delta G_{ads}^\circ$ ).

The relationship between  $C/\theta$  and  $C$  presents linear behaviour at all temperatures studied (Fig. 3) with slopes equal to unity.

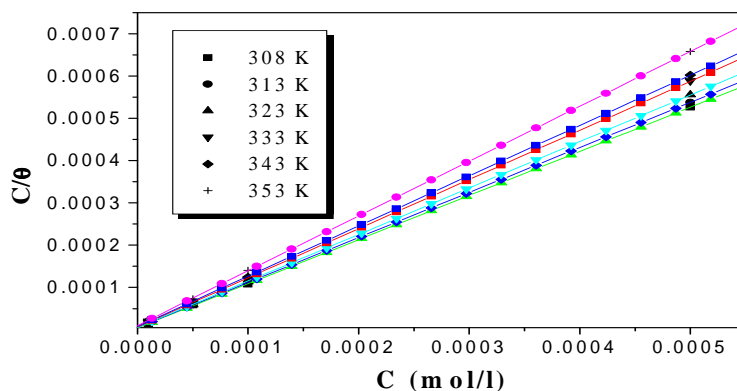


Fig. 3. The relation between C/θ and C of P<sub>4</sub> at various temperatures

To get more adsorption enthalpy,  $\Delta H^{\circ}_{ads}$ , the Van't Hoff equation was used [25]:

$$\ln(K) = -\frac{\Delta H^{\circ}_{ads}}{RT} + Constant \quad (6)$$

Fig. 4 shows the straight line obtained between  $\ln(K)$  and  $1/T$  leads to  $\Delta H^{\circ}_{ads} = -14.71 \text{ kJ.mol}^{-1}$ . This value is also equal to that estimated by the Gibbs–Helmholtz equation, expressed by:

$$\left[ \frac{\partial(\Delta G^{\circ}_{ads}/T)}{\partial T} \right]_P = -\frac{\Delta H^{\circ}_{ads}}{T^2} \quad (7)$$

and written in the following equation.

$$\frac{\Delta G^{\circ}_{ads}}{T} = \frac{\Delta H^{\circ}_{ads}}{T} + A \quad (8)$$

The standard adsorption entropy  $\Delta S^{\circ}_{ads}$  may be deduced using the thermodynamic basic equation:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \quad (9)$$

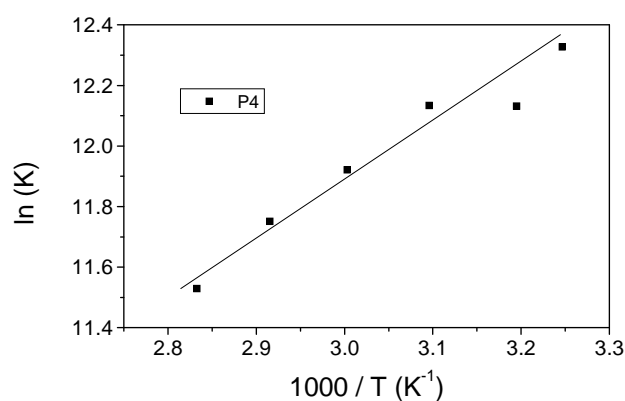


Fig. 4. The relationship between  $\ln(K)$  and  $1/T$  for P4

The variation of  $\Delta G^{\circ}_{ads}/T$  with  $1/T$  gives a straight line with a slope that equals  $\Delta H_{ads} = -14.53 \text{ (kJ/mol)}$  (Fig. 5). It can be seen from the figure that  $\Delta G^{\circ}_{ads}/T$  decreases with  $1/T$  in a linear fashion.

**Table 4.** Thermodynamic parameters of adsorption of P<sub>4</sub> on the steel surface at different temperatures

T(K)	K	$\Delta G^{\circ}_{ads}$ (kJ.mol <sup>-1</sup> )	$\Delta H^{\circ}_{ads}$ (kJ.mol <sup>-1</sup> )	$\Delta S^{\circ}_{ads}$ (J.mol <sup>-1</sup> .K <sup>-1</sup> )
308	225607.84	-41.88	-14,71	88,21
313	185712.75	-42.05		87,35
323	186084.59	-43.40		88,82
333	150411.45	-44.15		88,42
343	126907.42	-45.05		88,30
353	101643.89	-45.66		87,66

The adsorption parameters gathered in Table permit to clarify the interaction of organic compound with metallic surface. In general, two kinds of adsorption can be considered. Physical adsorption or chemisorption and sometimes both of these kinds were considered. The negative values of  $\Delta H^{\circ}_{ads}$  indicate that the adsorption of inhibitor is an exothermic process [26]. Literature pointed out that an exothermic process signifies either physisorption while endothermic process is associated to chemisorption [27]. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of a physisorption process is lower than  $40 \text{ kJ mol}^{-1}$  while the adsorption heat of a chemisorption process approaches  $100 \text{ kJ mol}^{-1}$  [28]. The  $\Delta H^{\circ}_{ads}$  obtained  $-14.71 \text{ kJmol}^{-1}$  reinforces that a comprehensive adsorption (physical adsorption) might occur. The adsorption of inhibitor molecules is accompanied by positive values of  $\Delta S^{\circ}_{ads}$ . The positive values of  $\Delta S^{\circ}_{ads}$  might be explained by an ordered layer onto the steel surface.

The values of  $\Delta G^{\circ}_{ads}$  were negative at temperatures studied, which indicate that the adsorption process of P4 occurs spontaneously. Usually, the adsorption is regarded as physisorption if the value of  $\Delta G^{\circ}_{ads}$  lower than  $-40 \text{ kJ.mol}^{-1}$ . The inhibition of the metal corrosion is due to the electrostatic interaction between the charged molecules and the

charged metal (physisorption); those around  $-40 \text{ kJ.mol}^{-1}$  or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [29,30]. The estimated  $\Delta G_{\text{ads}}^{\circ}$  values oscillating around  $-40 \text{ kJ.mol}^{-1}$  indicate that the adsorption mechanism of the quinoxaline tested may be a mixed type of physisorption and chemisorption. This phenomenon is often encountered in the literature [31,32].

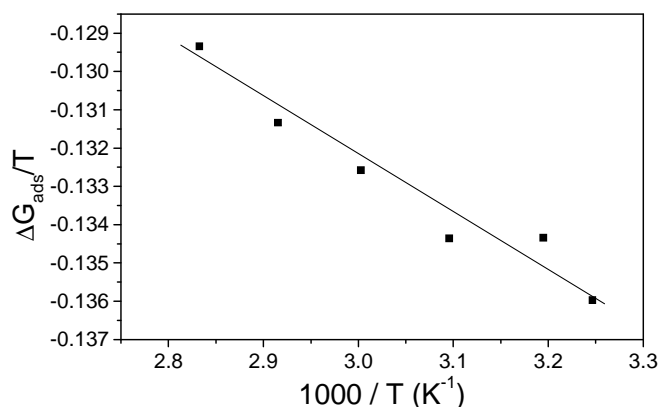


Fig. 5. Relationship between  $\Delta G_{\text{ads}}^{\circ}/T$  and the reverse of absolute temperature

### 3.4. Quantum chemical calculations

To correlate experimental data obtained from weight loss, quantum indices of P4 are computed using B3LYP/6-31G (d). Among the calculated parameters, we cite energy of highest occupied molecular orbital ( $E_{\text{HOMO}}$ ), energy of lowest unoccupied molecular orbital ( $E_{\text{LUMO}}$ ), HOMO-LUMO energy gap ( $\Delta E_{\text{L-H}}$ ), molecular band gap ( $\Delta E_{\text{MBG}}$ ) and total energy (TE). The finding data are grouped in the Table 5:

Table 5. Quantum indices of P4

$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	DE (eV)	$\sigma$ (Debye)	TE (kCal/mol)
-5.967	-2.222	3.744	1.451	1123.43

$E_{\text{HOMO}}$  is often associated with the electron donating ability of a molecule, whereas  $E_{\text{LUMO}}$  indicates its ability to accept electrons. The high values of  $E_{\text{HOMO}}$  (-5.9666 eV) are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy and empty molecular orbital. The optimized minimum energy structure of P4 is shown in Fig. 6.

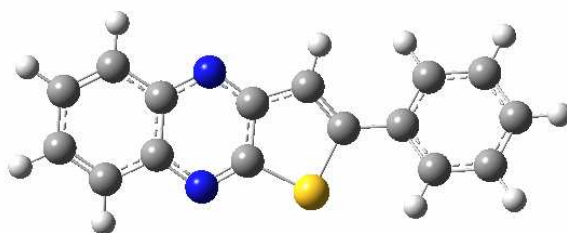


Fig.6. Optimised Structure of P4 obtained by B3LYP-6-31g(d) method.

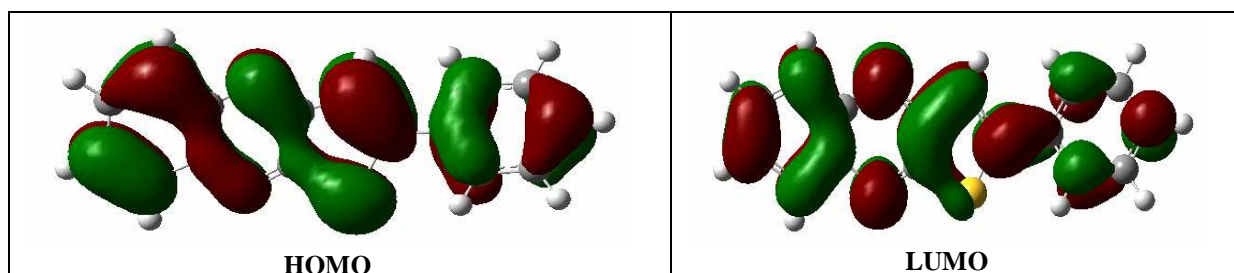


Fig. 7. HOMO and LUMO orbitals of P4.

The calculated HOMO-LUMO energy gap is 3.744 eV mol<sup>-1</sup>, indicates that P4 is a soft molecule and this results in high corrosion inhibition implying soft-soft interaction [33]. Regarding also the total energy as well as the moment dipolar, P4 may be classified as an efficient inhibitor for C38 steel corrosion in molar hydrochloric acid solution.

#### 4. Conclusion

- \* Results obtained qualified that quinoxaline tested is an efficient inhibitor.
- \* Inhibiting effect increased with the inhibitor concentration to attain the maximum (95%) at 5 10<sup>-4</sup>M.
- \* At elevated temperatures, efficiency decreased with an increase of the activation energy.
- \* P4 acted according to the Langmuir isotherm model and the negative value of  $\Delta G^{\circ}_{\text{ads}}$  is a sign of spontaneous adsorption on the metal surface.
- \* Kinetic and adsorption parameters were evaluated and discussed.

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