# Temperature Performance of a Thione Quinoxaline Compound as Mild Steel Corrosion Inhibitor in Hydrochloric Acid Medium

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The inhibiting action of 3-methyl-1-prop-2-ynylquinoxaline-2(1*H*)-thione (Pr-N-Q=S) on mild steel in molar hydrochloric acid has been investigated in the temperature range from 35 to 80 °C using weight loss measurements. It was shown that the inhibition efficiency increased with Pr-N-Q=S concentration and remained constant and so higher close to 96 % at $10^{-3}$M though temperature rising. The apparent activation energies ($E_a$), enthalpies ($\Delta H^*$) and entropies of activation ($\Delta S^*$) values provided evidence of the inhibitory effect of Pr-N-Q=S. Langmuir isotherm model fitted well the adsorption of Pr-N-Q=S onto metallic surface in acidic media. Furthermore, spontaneity of the adsorption process, evaluated from the sign of free energy ($\Delta_{ads}G°$) values, showed a decrease upon temperature increase in the presence of Pr-N-Q=S.

## 1. INTRODUCTION

Corrosion of metals is a fundamental academic and industrial problem that has recently received more attention because metallic structures are easily destroyed through anodic dissolution [1-

3]. Among numerous of corrosion prevention, the use of inhibitors is one of the most applied alternatives to protect metals against corrosion, especially in acidic media due to its advantages of economy, high efficiency, and wide applicability [4-6]. The existing data show that most of the well-known corrosion inhibitors are organic compounds containing heteroatoms, such as sulphur, phosphorus, nitrogen, or oxygen, and multiple bonds, which act through a process of surface adsorption [7-9]. The adsorption occurs on the basis of interaction of the lone pair or $\pi$-orbitals of inhibitor molecules with d-orbitals of the metal surface atoms. The adsorption characteristics of inhibitors which determine the corrosion efficiency depends not only on some physicochemical and electronic properties of inhibitor molecules, including functional groups, the molecular size, the electronic density of donor atoms, etc., but the characteristics of the environment, such as the nature and surface charge of the metal and the type of the corrosion medium as well [10-13].

With increasingly stringent environmental policies, it is very urgent to search for effective, safe, and environmentally friendly corrosion inhibitors. Quinoxaline is a heterocyclic aromatic organic compound which consists of the fusion of benzene and pyrazine. Quinoxaline is commercially available, and the usual synthesis involves cyclization of o phenylenediamine with glyoxal. Quinoxaline and its derivatives play a vital role in various fields such as dyes, pharmaceuticals, pesticides, and feedstuff [14,15]. Among these activities, quinoxaline derivatives are also undertaken as corrosion inhibitors in our laboratory and by other co-workers [16-20]

The aim of the present work is to investigate the effect of 3-methyl-1-prop-2-ynylquinoxaline-2(1*H*)-thione denoted hereafter Pr-N-Q=S and shown in Figure 1, as novel synthesized product, on mild steel corrosion in 1 M HCl at different concentrations as well as temperatures. The thermodynamic and kinetic characterisation in the presence of Pr-N-Q=S is obtained and discussed.
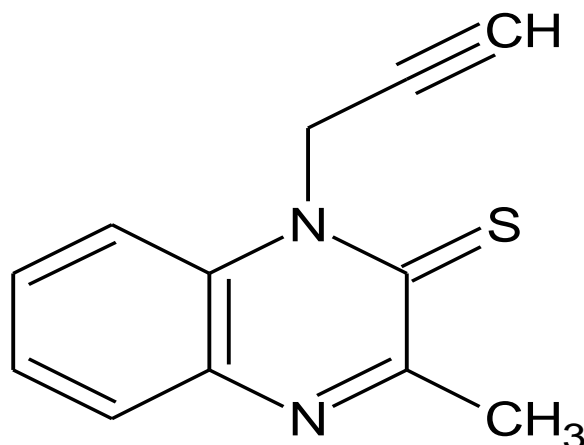


**Figure 1.** Molecular structure of the investigated Pr-N-Q=S inhibitor

## 2. EXPERIMENTAL DETAILS

Mild steel specimens having the chemical composition of 0.21% C; 0.38% Si; 0.09% P; 0.01 %Al; 0.05% Mn; 0.05% S and the remainder iron were used. The specimens used for weight loss measurements were cut into 2cm×2cm×0.05cm. Prior to all measurements, the mild steel specimens were ground with different emery papers (grades 400, 600, 800, and 1200), rinsed with double-distilled

water, degreased in ethanol, and then dried at room temperature. The acid solutions (1 M HCl) were prepared by dilution of analytical grade 37% HCl with double distilled water. The concentration range of the inhibitor employed was $5.10^{-5}$ - $10^{-3}$ M.

Weight loss measurements were performed at different temperatures from 35 to $80 \pm 1$ °C for an hour by immersing the mild steel coupons into acid solutions (100 mL) without and with various amounts of Pr-N-Q=S. After 1 h of hold time immersion, the electrode was withdrawn, rinsed with double-distilled water, washed with acetone, dried, and weighed accurately. All experiments were performed in triplicate, and average values were reported. The reproducibility of the experiment was higher than 95%. The inhibition efficiency ($IE_w\%$) and the degree of surface coverage ($\theta$) were determined by using the following equations:

$$IE_W\% = \frac{W_{corr} - W_{corr/inh}}{W_{corr}} \times 100 \tag{1}$$

$$\theta = \frac{W_{corr} - W_{corr/inh}}{W_{corr}} \tag{2}$$

where $W_{corr}$ and $W_{corr/inh}$ are the weight loss values in the absence and presence of Pr-N-Q=S, respectively.

## 3. RESULTS AND DISCUSSION

### 3.1. Temperature and concentration effects

The effect of Pr-N-Q=S addition at various concentrations on mild steel corrosion in 1 M HCl solution is investigated by weight loss measurements in the range of temperature 35-80 °C after 1 h of immersion in the aggressive electrolyte. The corrosion parameters such as inhibition efficiency $IE_W\%$, surface coverage $\theta$ are collected in Table 1.

As can be seen, that corrosion rate, at fixed temperature, decreases with concentration increase, whereas $IE_W\%$ remains almost constant with rise of temperature in acidic medium for all concentrations of Pr-N-Q=S. The values of inhibiting efficiency, at $10^{-3}$ M, remain constant and higher close to 96 % though temperature rising (Fig. 2). The investigated compound inhibits the corrosion of mild steel at all concentrations in 1 M HCl and at all temperatures and the inhibition action is pronounced at higher concentrations. Inspection of these data reveals that inhibition efficiency increases and corrosion rate decreases with increasing the concentrations at different temperature. This behaviour can be attributed to the increased adsorption and coverage of inhibitor on the mild steel surface with increase in the inhibitor concentration.

**Table 1.** Influence of temperature on the corrosion rate and inhibition efficiency of mild steel in 1 M HCl at different concentrations of Pr-N-Q=S

| Temperature T / °C | Concentration C / M | Weight loss $W_{corr}$ / mg cm$^{-2}$ h$^{-1}$ | $IE_W$ % | Surface coverage $\theta$ |
|---|---|---|---|---|
| 35 | 00 | 1.15 | – | – |
|    | $5 \times 10^{-5}$ | 0.29 | 74.8 | 0.748 |
|    | $1 \times 10^{-4}$ | 0.15 | 86.9 | 0.869 |
|    | $5 \times 10^{-4}$ | 0.08 | 93.0 | 0.930 |
|    | $1 \times 10^{-3}$ | 0.05 | 95.6 | 0.956 |
| 40 | 00 | 1.30 | – | – |
|    | $5 \times 10^{-5}$ | 0.32 | 75.4 | 0.754 |
|    | $1 \times 10^{-4}$ | 0.18 | 86.2 | 0.862 |
|    | $5 \times 10^{-4}$ | 0.08 | 93.5 | 0.935 |
|    | $1 \times 10^{-3}$ | 0.05 | 95.8 | 0.958 |
| 50 | 00 | 3.47 | – | – |
|    | $5 \times 10^{-5}$ | 0.86 | 75.2 | 0.752 |
|    | $1 \times 10^{-4}$ | 0.49 | 85.9 | 0.859 |
|    | $5 \times 10^{-4}$ | 0.23 | 93.4 | 0.934 |
|    | $1 \times 10^{-3}$ | 0.14 | 96.0 | 0.960 |
| 60 | 00 | 6.72 | – | – |
|    | $5 \times 10^{-5}$ | 1.66 | 75.3 | 0.753 |
|    | $1 \times 10^{-4}$ | 0.94 | 86.0 | 0.860 |
|    | $5 \times 10^{-4}$ | 0.44 | 93.4 | 0.934 |
|    | $1 \times 10^{-3}$ | 0.33 | 95.1 | 0.951 |
| 70 | 00 | 10.8 | – | – |
|    | $5 \times 10^{-5}$ | 2.66 | 75.4 | 0.754 |
|    | $1 \times 10^{-4}$ | 1.50 | 86.1 | 0.861 |
|    | $5 \times 10^{-4}$ | 0.70 | 93.5 | 0.935 |
|    | $1 \times 10^{-3}$ | 0.43 | 96.0 | 0.960 |
| 80 | 00 | 19.2 | – | – |
|    | $5 \times 10^{-5}$ | 4.72 | 75.5 | 0.755 |
|    | $1 \times 10^{-4}$ | 2.65 | 86.2 | 0.862 |
|    | $5 \times 10^{-4}$ | 1.23 | 93.6 | 0.936 |
|    | $1 \times 10^{-3}$ | 0.82 | 95.7 | 0.957 |
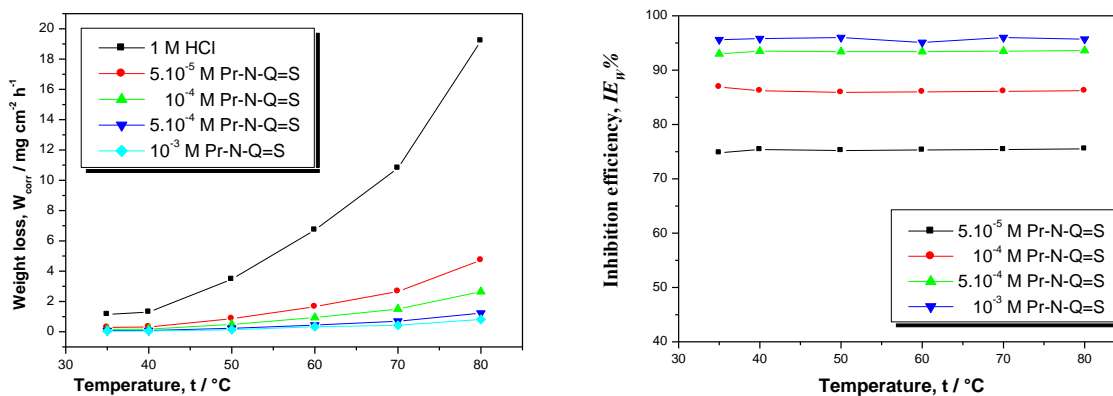


**Figure 2.** Variation of corrosion rate and inhibition efficiency with temperature for mild steel in 1 M HCl in the presence of Pr-N-Q=S at various concentrations

*3.2. Kinetic parameters of activation of the corrosion process*

It is considered worthwhile to study the effect of temperature as it can modify the interaction between the mild steel electrode and the acidic medium in the presence and the absence of Pr-N-Q=S. The influence of temperature on the kinetic of corrosion process in free acid and in the presence of adsorbed inhibitor leads to get more information on the behaviour of metallic materials in aggressive media. The corrosion reaction, in 1 M HCl solutions with and without different concentration of Pr-N-Q=S, can be regarded as an Arrhenius type process, the rate of which is given by equation (3) [21].

$$W_{corr} = A \exp(-\frac{E_a}{RT}) \tag{3}$$

where $A$ is the Arrhenius pre-exponential constant, $E_a$ is the apparent activation energy of the corrosion process, $R$ the gas constant ($R = 8.314$ J K$^{-1}$ mol$^{-1}$) and $T$ the absolute temperature.

The enthalpy and entropy parameters of corrosion process can be evaluated from the effect of temperature. To do so, an alternative formulation of Arrhenius equation is called transition state [22], eq. (4):

$$W_{corr} = \frac{k_B T}{h} \exp(\frac{\Delta S^*}{R}) \exp(-\frac{\Delta H^*}{RT}) \tag{4}$$

where $k_B$ is Boltzmann's constant ($k_B = 1.38066 \ 10^{-23}$ J K$^{-1}$), $h$ is Planck's constant ($h = 6.6252 \ 10^{-34}$ J s), $\Delta H^*$ and $\Delta S^*$ the enthalpy and entropy of activation, respectively.
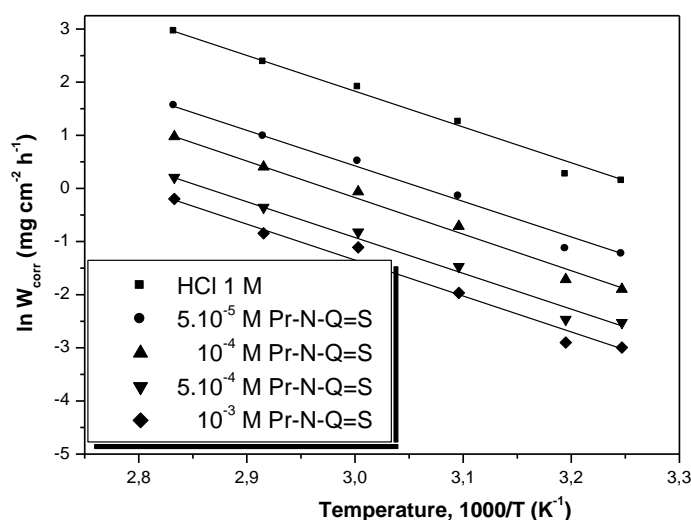


**Figure 3.** Arrhenius plots of mild steel in 1 M HCl at different concentrations of Pr-N-Q=S.

Figure 3 illustrates the dependence of the corrosion rate in Arrhenius coordinates for mild steel in the corrosive medium with and without addition of Pr-N-Q=S at different temperatures. Straight

lines are obtained with a slope of $(-E_a/R)$. Figure 4 shows the plots of $\ln W_{corr}/T$ against $1/T$. Straight lines are obtained with a slope of $(-\Delta H*/R)$ and an intercept of $(\ln(k_B/h) + \Delta S*/R)$, which give the values of $\Delta H*$ and $\Delta S*$.
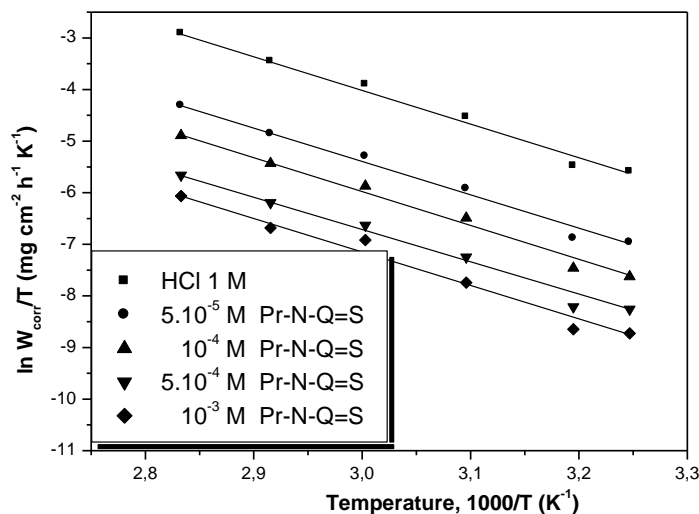


**Figure 4.** Relationship between $\ln W_{corr}/T$ vs. $1/T$ for mild steel at different concentrations of Pr-N-=S

Table 2 collects the values of activation parameters ($E_a$, $\Delta H*$ and $\Delta S*$) for mild steel in the corrosive medium with and without addition of Pr-N-Q=S at different concentrations. Generally, the increase of energy barrier of corrosion reaction with concentration rise of inhibitor is often regarded as physical adsorption leading to the formation of an adsorptive film of electrostatic character (physisorption) [23]. Whereas, a decrease in $E_a$ values when compared to the blank can often be interpreted as an indication of chemisorption [24].

**Table 2**. Activation parameters of the dissolution reaction of mild steel in 1 M HCl in the absence and presence of different concentrations of Pr-N-Q=S

| Concentration C / M | A mg cm$^{-2}$ h$^{-1}$ | $E_a$ kJ mol$^{-1}$ | $\Delta H*$ kJ mol$^{-1}$ | $\Delta S*$ J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|
| 00 | $9.650 \times 10^9$ | 58.7 | 56.0 | -62.9 |
| $5 \times 10^{-5}$ | $2.130 \times 10^9$ | 58.4 | 55.6 | -75.6 |
| $1 \times 10^{-4}$ | $1.720 \times 10^9$ | 59.4 | 56.7 | -77.3 |
| $5 \times 10^{-4}$ | $0.413 \times 10^9$ | 57.5 | 54.8 | -89.2 |
| $1 \times 10^{-3}$ | $0.039 \times 10^9$ | 58.6 | 55.8 | -89.6 |

The values found of the apparent activation energy of the corrosion process indicate that the presence of Pr-N-Q=S inhibitor at all concentrations in acidic solution apparently do not affect the $E_a$ value of the corrosion reaction. Similar results have been reported by our laboratories using pyridazine

derivatives and lavender oil in acidic solutions [25,26]. Popova [27] has discussed the impact of indole molecules tested as corrosion inhibitor in acidic media. He has concluded the fact that $E_a$ remains almost constant and the decrease of the inhibiting efficiency as well as the pre-exponential term A is in favour of electrostatic type adsorption. In our case, notwithstanding the decrease of $A$, the values of inhibiting efficiency remain constant and higher close to 96 % though temperature rising. Hence it seems reasonable and highly probable to suggest that Pr-N-Q=S adsorb on the metal surface forming strong chemisorption bonds.

The positive values of $\Delta H^*$ mean that the dissolution reaction is an endothermic process and that the dissolution of mild steel is difficult [28]. The entropy $\Delta S^*$ increases negatively in the presence of Pr-N-Q=S with increasing of inhibitor concentration. This reflects the formation of an ordered stable layer of Pr-N-Q=S onto the mild steel surface electrode [29]. The decrease of $\Delta S^*$ in inhibited medium implies that the activation of Pr-N-Q=S in the rate-determining step represents a dissociation rather than an association step, meaning a decrease in disordering takes place on moving from reactants to activated complex [30].

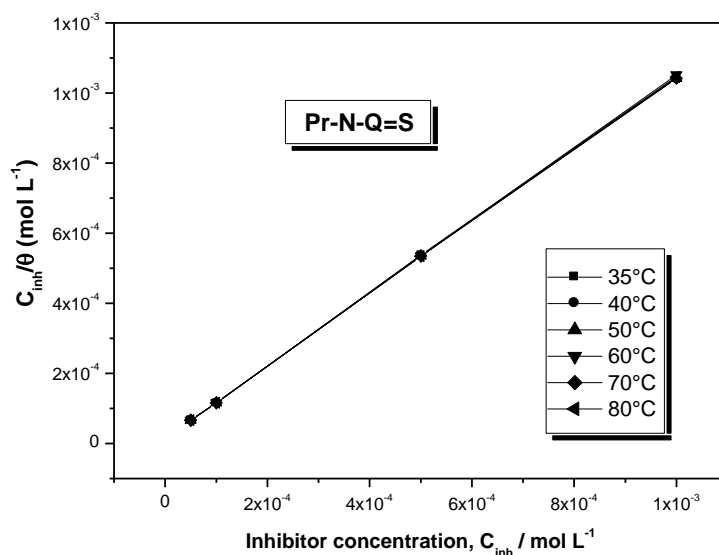*3.3. Thermodynamic parameters of the adsorption process*



**Figure 5**. Relationship between $C_{inh}/\theta$ and $C_{inh}$ of Pr-N-Q=S at various temperatures.

The adsorption isotherm provides useful insights into the mechanism of corrosion inhibition. The surface coverage, given in Table 1, is calculated according to the equation 2. Surface coverage values for the Pr-N-Q=S are obtained from weight loss measurements at different concentrations of Pr-N-Q=S in the temperature range from 35° to 80 °C. Several adsorption isotherms are assessed. The best fitted straight line (Fig. 5) is obtained from the plot of $C_{inh}/\theta$ versus $C_{inh}$ with slopes around unity. The regression coefficient $r^2$ is also circa unity. This suggests that the Pr-N-Q=S adsorption on the metal surface obeyed to the Langmuir's adsorption isotherm, eq. 5 [31].

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}, \quad with \quad K_{ads} = \frac{1}{55,55} \exp(-\frac{\Delta_{ads}G°}{RT}) \tag{5}$$

where $K_{ads}$ is the adsorption coefficient or adsorption equilibrium constant and $\Delta_{ads}G°$ is the standard free energy of adsorption, 55.5 is the molar concentration of water in the solution, $R$ is the universal gas constant, and $T$ is the thermodynamic temperature.

The thermodynamic parameters for adsorption process obtained from Langmuir adsorption isotherm for the studied Pr-N-Q=S molecules are given in Table 3.

**Table 3.** Thermodynamic parameters of adsorption of Pr-N-Q=S on the mild steel surface at different temperatures

| Temperature T/ K | Slope | Adsorption constant $K_{ads}$ | $\Delta_{ads}G°$ kJ mol$^{-1}$ | $\Delta_{ads}H°$ kJ mol$^{-1}$ | $\Delta_{ads}S°$ J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|
| 308 | 1.03 | 67186.43 | -38.75 | | |
| 313 | 1.03 | 67210.73 | -39.38 | | |
| 323 | 1.02 | 63840.62 | -40.50 | 0.44 | 127.17 |
| 333 | 1.03 | 72081.64 | -42.09 | | |
| 343 | 1.02 | 65249.75 | -43.07 | | |
| 353 | 1.03 | 68772.41 | -44.48 | | |

The values of free energy of adsorption, $\Delta_{ads}G°$ are negative which reveals the spontaneity of adsorption process and stability of the adsorbed layer on the steel surface [32]. It is well known that the absolute values of $\Delta_{ads}G^0$ of order of 20 kJ mol$^{-1}$ or lower indicate a physisorption; while those of order of 40 kJ mol$^{-1}$ or higher are associated with chemisorption [33]. It is shown that the calculated $\Delta_{ads}G°$ values are ranging from about -44.48 to -38.75 kJ mol$^{-1}$, indicating, therefore, that the adsorption mechanism of the Pr-N-Q=S on mild steel surface in 1 M HCl solution as typical of chemisorption. The possible mechanism of chemisorption can be attributed to the donation $\pi$-electron by the aromatic rings, the nonbinding electron pair of two nitrogen and sulphur in quinoxaline group as well as the presence the propyne group with triple bonds. Moreover, the chemisorption can be favoured by the Pr-N-Q=S planarity [34].

The corrosion inhibition of Pr-N-Q=S for mild steel may be well explained by using a thermodynamic model, so, the heat, the free energy and the entropy of adsorption are calculated to elucidate the phenomenon for the inhibition action of Pr-N-Q=S (Table 3). According to Gibbs–Helmholtz equation defined as follows in equation 6 and which can be arranged to give equation 7:

$$\left[\frac{\partial(\Delta_{ads}G°/T)}{\partial T}\right]_P = -\frac{\Delta_{ads}H°}{T^2} \tag{6}$$

$$\frac{\Delta_{ads}G^{\circ}}{T} = \frac{\Delta_{ads}H^{\circ}}{T} + cte \tag{7}$$

where $\Delta_{ads}H^{\circ}$ is the heat of the adsorption process considered temperature-independent in the range of studied temperature.

The variation of $\Delta_{ads}G^{\circ}/T$ with $1/T$ gives a straight line with a slope that equals $\Delta_{ads}H^{\circ}$ (Fig. 6).
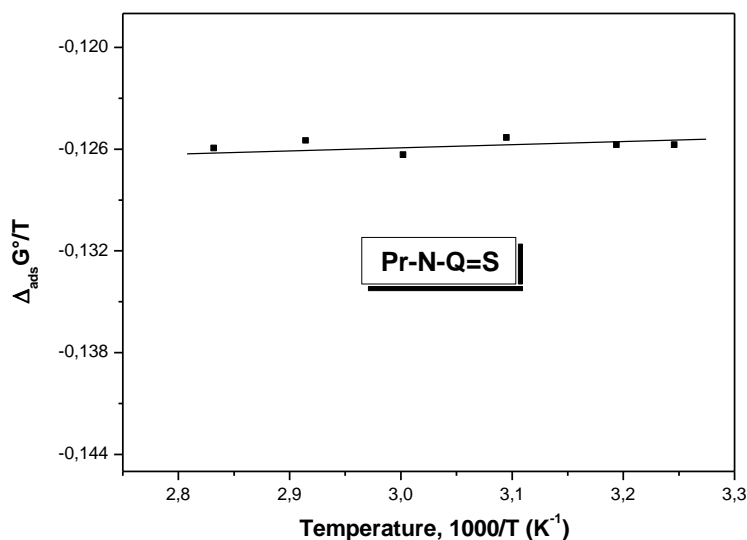


**Figure 6.** The variation of $\Delta_{ads}G^{\circ}/T$ with $1/T$ for the mild steel/Pr-N-Q=S/1M HCl system

It can be seen that $\Delta_{ads}G^{\circ}/T$ decreases slightly with $1/T$ in a linear manner. $\Delta_{ads}S^{\circ}$ can be deduced from the thermodynamic basic equation 8:

$$\Delta_{ads}G^{\circ} = \Delta_{ads}H^{\circ} - T\Delta_{ads}S^{\circ} \tag{8}$$

It is assumed that an exothermic process is attributed to either physical or chemical adsorption but endothermic process corresponds solely to chemisorption. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of $\Delta_{ads}H^{\circ}$. For a physisorption process $\Delta_{ads}H^{\circ}$ is lower than 40 kJ mol$^{-1}$ while the adsorption heat of a chemisorption process approaches 100 kJ mol$^{-1}$ [35]. In this study, the value of $\Delta_{ads}H^{\circ}$ is positive ($\Delta_{ads}H^{\circ}$=0.44 kJ mol$^{-1}$), reflecting the endothermic behaviour of adsorption on the steel surface and corresponds solely to chemisorption [36]. The adsorption of inhibitor molecule is accompanied by positive value of $\Delta_{ads}S^{\circ}$.


## 4. CONCLUSION

The following main conclusions are drawn from the present study:

- The results obtained showed the effectiveness of the Pr-N-Q=S investigated quinoxaline derivative as a good inhibitor of mild steel in 1 M HCl.

- The inhibiting efficiency increases with Pr-N-Q=S concentration and remains as high as 96 % even at higher temperatures.

- The presence of Pr-N-Q=S at all concentrations in acidic solution apparently does not affect the $E_a$ value of the corrosion reaction whereas a decrease of pre-exponential factor is registered with addition of Pr-N-Q=S at different concentrations.

- The most fitting isotherm in the adsorption of Pr-N-Q=S onto mild steel surface in acidic medium is Langmuir isotherm.

- The negative values of $\Delta_{ads}G°$ reflect the spontaneous adsorption of Pr-N-Q=S on the metal surface and their absolute values are globally higher than 40 kJ mol$^{-1}$. Moreover the heat enthalpy of adsorption $\Delta_{ads}H°$ is a positive value.

- The confrontation of kinetic process parameters of iron dissolution and those of thermodynamic adsorption process of Pr-N-Q=S, the authors confirm the performance of the undertaken inhibitor Pr-N-Q=O acting by chemisorption mechanism.

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