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Time and Temperature Elucidation on Steel Corrosion Inhibition by 3-methyl-1-prop-2-ynylquinoxalin-2(1H)-one in Molar Hydrochloric Acid: Part 2

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Abstract

The corrosion rate in the presence of a new synthesized quinoxaline derivative namely 3-methyl-1-prop-2-ynylquinoxalin-2(1h)-one and denoted Pr-N-Q=O as mild steel corrosion inhibitor in molar hydrochloric acid, was studied by weight loss method, in the range of temperature from 308 to 353 K. Results obtained revealed that the inhibition efficiency of this compound decreased relatively with increasing temperature and its value reached 80.0% at 353 K at 10^{-3}M. The inhibition was assumed to occur via adsorption of the quinoxaline molecules on metallic surface. Adsorption of Pr-N-Q=O obeyed to Langmuir adsorption isotherm model fit. The apparent activation energies E_a, enthalpy ΔH^* and entropy of activation ΔS^* values provided evidence of the inhibitory effect of Pr-N-Q=O. Furthermore, spontaneity of the adsorption process, through free energy $\Delta_{ads}G°$ values showed a drastic decrease upon temperature increase in the presence Pr-N-Q=O.

Keywords: Quinoxaline; Adsorption process; Corrosion inhibition; Thermodynamic proprieties; Activation energies.

1. INTRODUCTION

Treatments with organic compounds, as corrosion inhibitors, are frequently proposed in order to improve anticorrosion protection [1-6] in acidic media especially 1 M HCl. However, much attention is carefully attached when selecting inhibitors for investigation or application to ensure environmental regulations. The inhibitor must be environmentally friendly to replace the older [7], which is more toxic and harmful to the environment. When applying the ideas of green chemistry to the area of corrosion inhibitors, the major improvement is in the aim of eliminating environmentally toxic compounds. Several organic molecules containing sulphur, oxygen, and nitrogen hetero-atoms are suggested as inhibitors for steel in acidic medium [7-9]. Many investigators have reported the use of antibacterial drugs as corrosion inhibitors [10,11]. Sulfa drugs have been reported also as corrosion inhibitors by several authors [12,13]. The synthesis and chemistry of quinoxaline derivatives have attracted considerable attention in the past ten years [14,15]. Some of them exhibit biological activities including anti-viral [16], anti-bacterial [17], anti-inflammatory [18], anti-protozoal [19], anti-cancer [20,21] anti-depressant [22], anti-HIV [23], and as kinase inhibitors [24]. They are also used in the agricultural field as fungicides, herbicides, and insecticides [25].

In the present study, the choice of this drug as corrosion inhibitor is based on the fact that it is healthy reportedly and very important in biological reactions (environmentally friendly); its molecule has an oxygen and nitrogen atom as active centres as well as aromatic rings and triple bonds. Quinoxaline derivatives have already been studied as corrosion inhibitors in our laboratory and by other co-workers [26-31].

The objective of the present study is to study the thermodynamic and the kinetic characterisation of mild steel corrosion in 1 M HCl in the range of temperature from 308 to 353 K at different concentrations, in the presence of 3-methyl-1-prop-2-ynylquinoxalin-2(1*H*)-one denoted hereafter Pr-N-Q=O.

2. EXPERIMENTAL DETAILS

Prior to all measurements, the mild steel samples (0.21% C; 0.38% Si; 0.09% P; 0.01 %Al; 0.05% Mn; 0.05% S and the remainder iron) was used in squarer form of sheets with 2×2×0.05 cm^3 dimensions which were degreased with acetone, polished with different emery paper up to 1200 grade, dried, and weighed until used. The aggressive solution (1 M HCl) was prepared by dilution of analytical grade 37% HCl with bidistilled water. Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 100 cm^3. The molecular formula of the quinoxaline derivative is shown in Fig. 1.

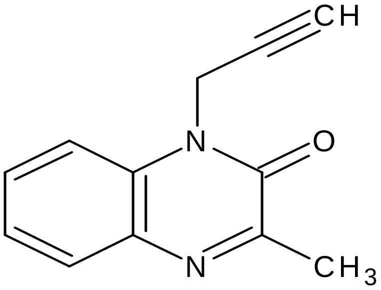

Figure 1. 3-methyl-1-prop-2-ynylquinoxalin-2(1*H*)-one (Pr-N-Q=O)

3. RESULTS AND DISCUSSION

3.1. Effect of immersion time

The effect of increasing immersion time on the weight loss of mild steel in uninhibited and inhibited acid solutions is shown in Fig. 2 by addition of Pr-N-Q=O at 10^{-3} M in 1M HCl solution at 308 K. It is obvious that the weight loss varies linearly with immersion period in plain acid and inhibited acid, showing the absence of eventual insoluble products on the mild steel surface [32]. The curve obtained in the presence of the additive falls significantly below that of free acid. The relatively large divergence of plots indicates the increase of $IE_w\%$ with time as shown in Fig. 3. It is noteworthy that the inhibition efficiency attains 92.2% since 6 h and decrease slightly to 90.5% at 24 h at 308 K. This result promises also the use of Pr-N-Q=O even during a long period.

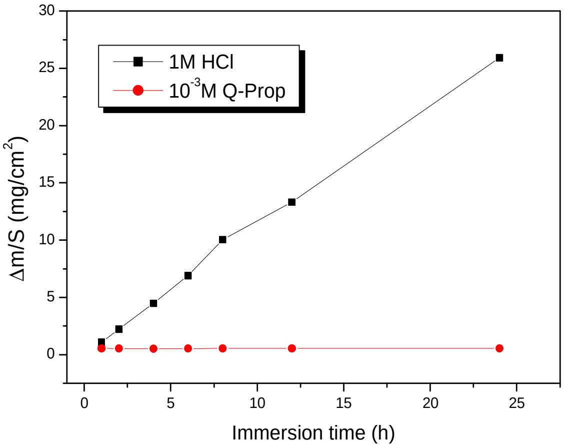

Figure 2. Weight loss versus immersion time of mild steel in 1 M HCl without and with 10^{-3} M of Pr-N-Q=O at 308 K.

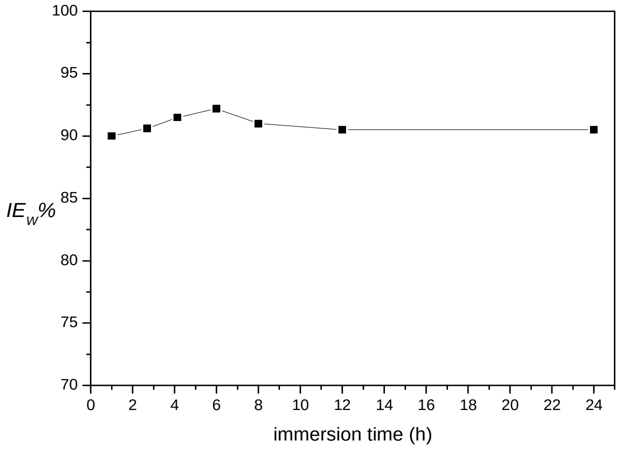

Figure 3. Variation of $IE_w\%$ versus immersion time of mild steel in 1 M HCl without and with 10^{-3} M of Pr-N-Q=O at 308 K.

3.2. Effect of temperature

To evaluate the adsorption of the studied quinoxaline Pr-N-Q=O and to extract the activation parameters of corrosion process of mild steel in acidic medium, weight loss measurements are used. The inhibition efficiency $IE_w\%$ is calculated as follows:

$$IE_{WL}\% = \frac{W_{corr} - W_{corr/inh}}{W_{corr}} \times 100 \quad (1)$$

where W_{corr} and $W_{corr/inh}$ are the corrosion rates of mild steel in the absence and presence of Pr-N-Q=O, respectively.

Table 1 collects the values of corrosion rate of mild steel at different concentrations of Pr-N-Q=O determined by weight loss measurements at various temperatures (308-353 K) as well as the corresponding inhibition efficiencies and surface coverage.

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=O.

Temperature T / K	Concentration C / M	Weight loss W_{corr} / mg cm^{-2} h^{-1}	IE$_{WL}$ %	Surface coverage θ
308	00	1.15	–	–
	5×10^{-5}	0.33	71.3	0.731
	$1 \text{ x } 10^{-4}$	0.19	83.5	0.835
	5×10^{-4}	0.11	90.4	0.904
	$1 \text{ x } 10^{-3}$	0.09	92.2	0.922
313	00	1.30	–	–
	5×10^{-5}	0.41	68.5	0.685
	$1 \text{ x } 10^{-4}$	0.26	80.0	0.800
	5×10^{-4}	0.16	87.7	0.877
	$1 \text{ x } 10^{-3}$	0.13	90.0	0.900
323	00	3.47	–	–
	5×10^{-5}	1.24	64.3	0.643
	$1 \text{ x } 10^{-4}$	0.83	76.1	0.761
	5×10^{-4}	0.52	85.0	0.850
	$1 \text{ x } 10^{-3}$	0.41	88.2	0.882
333	00	6.72	–	–
	5×10^{-5}	2.63	60.9	0.609
	$1 \text{ x } 10^{-4}$	1.88	72.0	0.720
	5×10^{-4}	1.2	82.1	0.821
	$1 \text{ x } 10^{-3}$	1.0	85.1	0.851
343	00	10.8	–	–
	5×10^{-5}	4.5	58.3	0.583
	$1 \text{ x } 10^{-4}$	3.18	70.5	0.705
	5×10^{-4}	2.26	79.1	0.791
	$1 \text{ x } 10^{-3}$	1.8	83.3	0.833
353	00	19.2	–	–
	5×10^{-5}	8.6	55.2	0.552
	$1 \text{ x } 10^{-4}$	6.0	68.8	0.688
	5×10^{-4}	4.3	77.6	0.776
	$1 \text{ x } 10^{-3}$	3.84	80.0	0.800

The evolution of corrosion rate and inhibition efficiency with temperature for mild steel in 1 M HCl of Pr-N-Q=O at different concentrations is shown in Fig. 4. It is well-known that corrosion rate increases with the rise of temperature in acidic media. It is noticed a decrease in the inhibition efficiency with temperature rising at all concentrations whereas an opposite progression is registered when varying concentration at a fixed temperature. Moreover, the increase of W_{corr} is more pronounced in free solution and in less concentrations of Pr-N-Q=O when compared to those at higher concentrations.

Apparently, the results obtained postulate that the inhibitor function through adsorption on the metal surface blocking the active sites to form a barrier onto the mild steel surface against infiltration of the aggressive electrolyte solution. As the temperature increases, desorption of the inhibitor film takes place and manifests in parallel to adsorption [33]; the surface becomes less protected and then the inhibitor gradually losses its effectiveness.

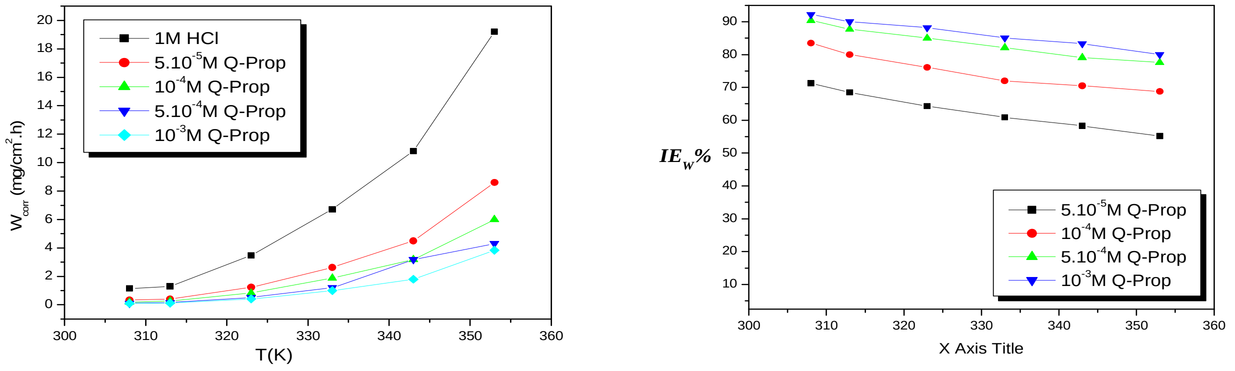

Figure 4. Variation of corrosion rate and inhibition efficiency with temperature for mild steel in 1 M HCl at different concentrations of Pr-N-Q=O.

3.2.1. Kinetic parameters of activation corrosion process

The influence of temperature on kinetic process of corrosion in free acid and in the presence of adsorbed Pr-N-Q=O inhibitor leads to get more information on the behaviour of mild steel in aggressive media. To calculate kinetic and thermodynamic activation parameters at different concentrations of Pr-N-Q=O such as activation energy E_a, entropy ΔS^* and enthalpy ΔH^* of activation, Arrhenius Eq. (2) and its alternative formulation called transition state Eq. (3) are used:

$$W_{corr} = A e^{-\frac{E_a}{RT}} \qquad (2)$$

$$W_{corr} = \frac{RT}{hN}\exp(\frac{\Delta S^*}{R})\exp(-\frac{\Delta H^*}{RT}) \qquad (3)$$

where T is the absolute temperature, A is a constant and R is the universal gas constant, h is Plank's constant, N is Avogadro's number.

The activation energy E_a is calculated from the slope of the plots of $\ln W_{corr}$ vs. $1/T$ (Fig. 5). Plots of $\ln W_{corr}/T$ vs. $1/T$ give straight lines with slopes of $\Delta H^*/R$ and intercepts of $(\ln(R/Nh)+ \Delta S^*/R)$ as shown in Fig. 6. From equation 3, the values of ΔH^* and ΔS^* can be calculated.

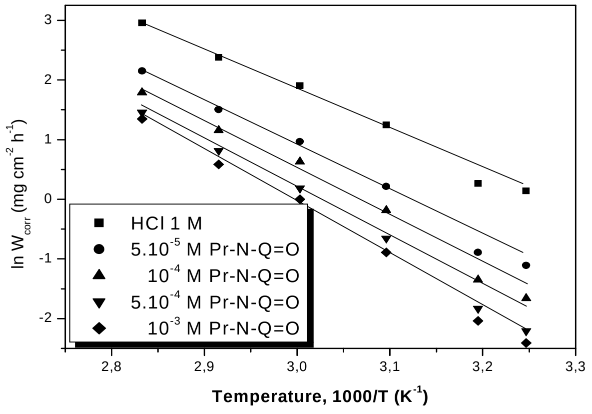

Figure 5. Arrhenius plots of mild steel in 1 M HCl at different concentrations of Pr-N-Q=O.

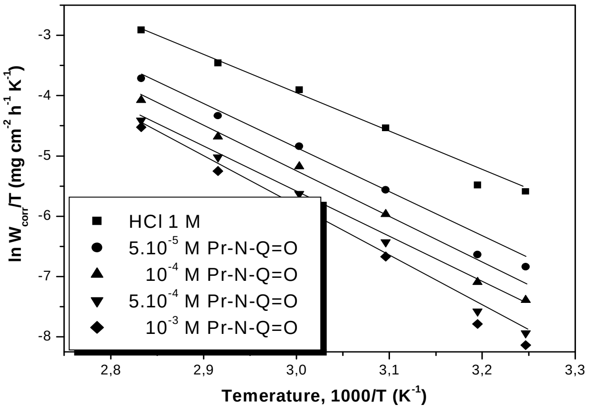

Figure 6. The relationship between ln W_{corr}/T and $1/T$ for mild steel at different concentrations of Pr-N-Q=O.

The calculated parameters at different concentrations of the inhibitor are collected in Table 2. The activation energy E_a as well as the pre-exponential factor A increase in the presence of Pr-N-Q=O. Generally, the inhibitive additives cause a rise in activation energy value when compared to the blank solution. 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 [34] and can be often interpreted as an indication of adsorptive film formation by a physical (electrostatic) mechanism [35].

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

Concentration C / M	A mg cm^{-2} h^{-1}	E_a kJ mol^{-1}	ΔH* kJ mol^{-1}	ΔS* J K^{-1} mol^{-1}
00	9.65 10^9	58.71	55.97	-62.94
5 × 10^{-5}	8.54 10^{10}	67.4	64.67	-44.84
1 x 10^{-4}	2.16 10^{11}	71.07	68.33	-37.07
5 × 10^{-4}	1.99 10^{12}	75.24	72.51	-27.98
1 x 10^{-3}	3.50 10^{12}	76.46	73.72	-25.90

Inspection of kinetic data obtained in Table 2 show that all parameters of corrosion process increases with Pr-N-Q=O concentration. Literature reports that the positive sign of the enthalpy ΔH^* is an endothermic nature of mild steel dissolution process and that the dissolution of steel is difficult [36]. The entropy of activation ΔS^* in the absence of inhibitors is negative and this value increases with the Pr-N-Q=O concentration. The increase of ΔS^* implies that an increase in disordering taking place on going from reactants to the activated complex [37].

3.2.2. Thermodynamic parameters of adsorption process

The temperature elevation has an opposite effect on adsorption process, where inter and/or intra molecular forces such as, electrostatic bond, coordinative bond, and even weaker interactions such as, π–π stacking interactions. For this, it is widely acknowledged that adsorption isotherms provide useful insights into the mechanism of corrosion inhibition. In order to obtain the isotherm type model, one assumes that Pr-N-Q=O acts via a simple adsorption mode. Thus, the apparent corrosion rate of the inhibited mild steel electrode is proportional to the ratio of the surface covered θ and that not covered $(1- \theta)$ by Pr-N-Q=O molecules. The surface coverage, θ, is calculated according to the following equation 4:

$$\theta = \frac{W_{corr} - W_{corr/inh}}{W_{corr}} = \frac{IE_{WL}\,\%}{100} \qquad (4)$$

Surface coverage values for Pr-N-Q=O are obtained from the weight loss measurements at various concentrations and different temperatures (308–353 K), as shown in Table 1. It is necessary to determine empirically which adsorption isotherm gives the best fitting for the surface coverage data in order to use the corrosion rate measurements to calculate the thermodynamic parameters of Pr-N-Q=O adsorption.

Careful investigation performed for Temkin [38], Langmuir [39], Frumkin [40] and Freundlich [41] isotherms (equations 5-8) would show the most fitting isotherm with maximum regression coefficients, R^2, using the following relationships:

Temkin isotherm $\exp(f.\,\theta) = K_{ads}\,C_{inh}$ (5)
Langmuir isotherm $\theta / (1-\theta) = K_{ads}\,C_{inh}$ (6)
Frumkin isotherm $\theta / (1-\theta)\,.\,\exp(-2f.\,\theta) = K_{ads}\,C_{inh}$ (7)
Freundlich isotherm $\theta = K_{ads}\,C_{inh}$ (8)

where K_{ads} is the equilibrium constant of the adsorption process, C_{inh} is the inhibitor concentration and f the heterogeneous factor of metal surface.

The best fitted straight line is obtained for the plot of C_{inh}/θ versus C_{inh} with slopes around unity. The correlation coefficient (R^2) is used to choose the isotherm that fit well the experimental data. This suggests that the adsorption of Pr-N-Q=O on the metal surface obeyed to the Langmuir's adsorption isotherm (Fig. 7).

Equilibrium constant K_{ads} of adsorption process determined using 9 can be further used to determine free energy of adsorption as follows:

$$\Delta_{ads} G^{\circ} = -R\,T\,\ln(55.55\,K_{ads}) \qquad (9)$$

where 55.5 is the molar concentration of water, R is the universal gas constant, and T is the thermodynamic temperature. Table 3 summarizes the equilibrium constant and free energy of adsorption values in presence and absence of Pr-N-Q=O.

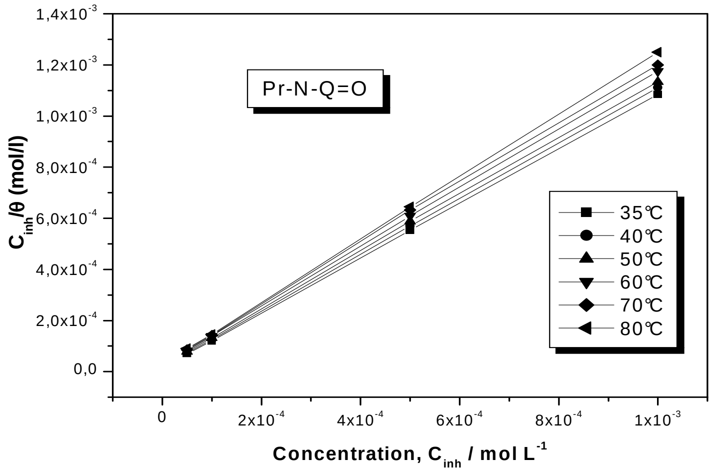

Figure 7. The relationship between C_{inh}/θ and C_{inh} of Pr-N-Q=O at various temperatures.

Table 3. Thermodynamic parameters of adsorption of Pr-N-Q=O 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	1.07	65630	-38.69	-12.57	84.10
313	1.09	55675	-38.89		
323	1.11	43503	-39.47		
333	1.15	38867	-40.38		
343	1.17	36713	-41.43		
353	1.20	34436	-42.45		

The negative values of standard free energy of adsorption $\Delta_{ads}G°$ ensure the spontaneity of adsorption process [42] and stability of the adsorbed layer on the steel surface. It is shown that the calculated $\Delta_{ads}G°$ values, is ranging from about -40.27 to -36.29 kJ mol^{-1}, indicating, therefore, that the adsorption mechanism of the Pr-N-Q=O on mild steel surface in 1 M HCl solution involves both chemisorption and physisorption. However, physisorption seems to be more probable and predominantly favourable than chemisorption because of the decrease of the decrease of inhibition efficiency with rise of temperature beside the increase of activation energy in the presence of Pr-N-Q=O when compared to free acid solution. The possible mechanism for chemisorption can be attributed to the donation π-electron by the aromatic rings, the nonbinding electron pair of nitrogen in quinoxaline molecules as well as the oxo group. Moreover, the chemisorption can be favoured by the Pr-N-Q=O planarity [27,28].

The corrosion inhibition of Pr-N-Q=O 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=O (Table 3). According to the Van't Hoff equation [43]:

$$\ln K_{ads} = -\frac{\Delta_{ads}H^\circ}{RT} + cte \qquad (10)$$

$\Delta_{ads}H°$ and K_{ads} are the adsorption heat and adsorptive equilibrium constant, respectively.

The adsorption heat may be obtained from the linear regression between $\ln K_{ads}$ and $1/T$ shown in Fig. 8. $\Delta_{ads}S°$ can be deduced from the basic thermodynamic equation:

$$\Delta_{ads}G^\circ = \Delta_{ads}H^\circ - T\,\Delta_{ads}S^\circ \qquad (11)$$

The negative value of $\Delta_{ads}H°$ means that the adsorption process is an exothermic phenomenon [44]. 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 $\Delta_{ads}H°$.

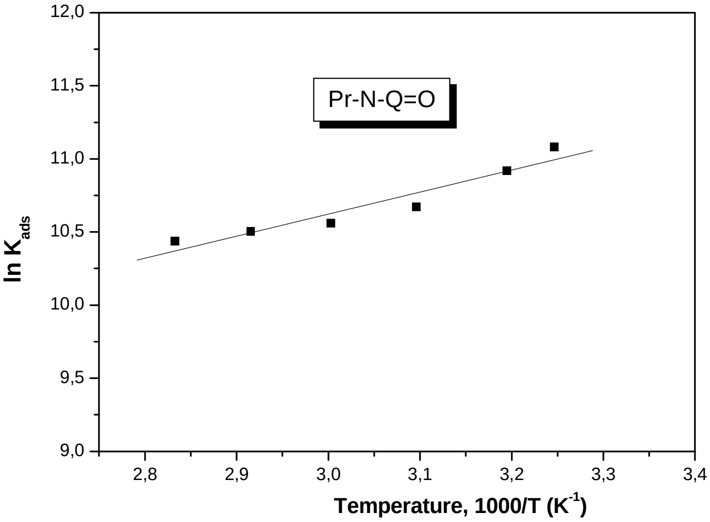

Figure 8. Vant'Hoff plot for the mild steel/Pr-N-Q=O/1M HCl system

For a physisorption process $\Delta_{ads}H°$ is lower than 40 kJ mol^{-1} while the adsorption heat of a chemisorption process approaches 100 kJ mol^{-1} [45]. In this study; the standard adsorption heat -12.57 kJ.mol^{-1} suggests that the adsorption mechanism of Pr-N-Q=O on mild steel surface in 1 M HCl solution might occur by physical adsorption [46]. The positive value of $\Delta_{ads}S°$ is generally explained by disorder of adsorbed molecules of inhibitor with the progress in the adsorption onto the mild steel surface [47].

4. CONCLUSION

The following conclusions are drawn from this study:

* 3-methyl-1-prop-2-ynylquinoxalin-2(1H)-one, Pr-N-Q=O presents good effectiveness at 10^{-3} M in 1 M HCl and even at higher temperatures.

* Inhibition efficiency increases with rise of concentration and decreases with temperature.

* Pr-N-Q=O adsorbs on mild steel according to Langmuir isotherm model.

* Taking into account the increase of both activation energy and pre-exponential factor for the kinetic process of iron dissolution and the values of Gibbs free energy and heat energy for thermodynamic process of Pr-N-Q=O adsorption on mild steel surface, the authors believe that the adsorption mechanism of Pr-N-Q=O maybe a combination of both chemisorption and physisorption with predominance of physisorption.

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