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Der Pharmacia Lettre, 2013, 5 (2):43-53
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Inhibitive properties and thermodynamic characterization of quinoxaline derivative on carbon steel corrosion in acidic medium

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ABSTRACT

The inhibition of ethyl 2-(4-(2-ethoxy-2-oxoethyl)-2-p-tolylquinoxalin-1(4H)-yl)acetate (Q3) on the corrosion of carbon steel in 1.0 M HCl at 308-343 K was studied by gravimetric method. Results obtained show that Q3 acts as inhibitor for carbon steel in hydrochloric solution. The inhibition efficiency was found to increase with increase in Q3 but decreased with temperature, which is suggestive of physical adsorption mechanism although chemisorption may play a part. The adsorption of Q3 onto the carbon steel surface was found to follow the Langmuir adsorption isotherm. Both kinetic parameters (activation energy, pre-exponential factor, enthalpy of activation and entropy of activation) and thermodynamics of adsorption (enthalpy of adsorption, entropy of adsorption and Gibbs free energy) were calculated and discussed.

Keywords: Carbon steel, Corrosion, Thermodynamic, Inhibitor, Adsorption, Hydrochloric Acid.

INTRODUCTION

The development of inhibitors of steels in acid solutions has been the subject of great interest especially from the point of view of their efficiency and applications. Corrosion inhibitors may be divided into three broad classes, namely oxidizing, precipitation and adsorption inhibitors [1]. Compounds containing nitrogen, oxygen, sulphur and phosphorus in the conjugated system have particularly been reported as efficient corrosion inhibitors [2-17]. These compounds can adsorb on the metal surface by blocking the active sites and thereby decreasing the corrosion rate. The choice of inhibitors was based on the fact that these compounds contain π -electrons and heteroatom such as N, O and S which involve greater adsorption of the inhibitor molecules onto the surface of steel.

The corrosion of iron and its alloys and their inhibition by different organic inhibitors in acid solution has been studied by several authors [18-23]. A perusal of the literature on acid corrosion inhibitors acts by adsorption on the metal surface. This phenomenon could take place via (i) electrostatic attraction between the charged metal and the charged inhibitor molecules (ii) dipole-type interaction between uncharged electron pairs in the inhibitor with the metal, (iii) p electron-interaction with the metal, and (iv) a combination of all of the above [24]. The compounds containing nitrogen can provide excellent inhibition in acid media.

The object of the present work was to study the temperature effects on carbon steel corrosion in 1.0 M HCl solutions in the absence and presence of various additions of 2-(4-(2-ethoxy-2-oxoethyl)-2-p-tolylquinoxalin-1(4H)-yl)acetate (Q3) by using gravimetric method. Various thermodynamic parameters for inhibitor adsorption on carbon steel surface were estimated and discussed. Kinetic parameters for carbon steel corrosion in absence and presence of the studied inhibitor were evaluated and interpreted. On the light of inhibitor constituent, the inhibition mechanism for carbon steel in hydrochloric acid was suggested. The molecular structure of Q3 is shown in Fig. 1.

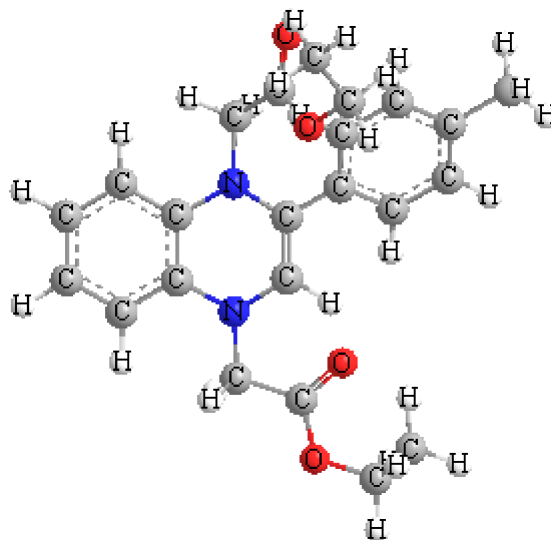


Figure 1. The chemical structure of the studied quinoxaline compound.

MATERIALS AND METHODS

Materials

The steel used in this study is a carbon steel (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu and the remainder iron (Fe). The carbon steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (120, 600 and 1200); rinsed with distilled water, degreased in acetone in an ultrasonic bath immersion for 5 min, washed again with bidistilled water and then dried at room temperature before use. The acid solutions (1.0 M HCl) were prepared by dilution of an analytical reagent grade 37 % HCl with double-distilled water. The concentration range of Q3 employed was 10^{-6} M to 10^{-3} M.

Measurements

Weight loss measurements

The steel sheets of $1.6 \times 1.6 \times 0.07$ cm dimensions were abraded with different grades of emery papers, washed with distilled water, degreased with acetone, dried and kept in a desiccator. After weighing accurately by a digital balance with high sensitivity the specimens were immersed in solution containing 1.0 M HCl solution with and without various concentrations of the investigated inhibitor. At the end of the tests, the specimens were taken out, washed carefully in ethanol under ultrasound until the corrosion products on the surface of carbon steel specimens were removed thoroughly, and then dried, weighed accurately. Duplicate experiments were performed in each case and the mean value of the weight loss is reported. The immersion time for the weight loss is 1h. Weight loss allowed calculation of the mean corrosion rate in $\text{mg cm}^{-2} \text{h}^{-1}$. The corrosion rate (v) and the inhibition efficiency (η_{WL}) were calculated by the following equations:

$$v = \frac{W}{St} \times 100 \quad (1)$$

$$\eta_{\text{WL}} (\%) = \frac{v_0 - v}{v_0} \times 100 \quad (2)$$

where W is the three-experiment average weight loss of the carbon steel, S is the total surface area of the specimen, t is the immersion time and v_0 and v are values of the corrosion rate without and with addition of the inhibitor, respectively.

RESULTS AND DISCUSSION

Effect of immersion time

Fig. 2 shows the variation of the weight loss of carbon steel in HCl in the absence and presence of Q3, according to the time of immersion. We find that the two curves are almost linear; this implies that the metal surface is free of insoluble corrosion products. So, we can deduce that this quantity is almost constant from the first 4 hours of immersion, which allowed us to say that the immersion time has no significant effect on the corrosion inhibition of carbon steel in 1.0 M HCl by Q3 for optimum concentration of inhibitor.

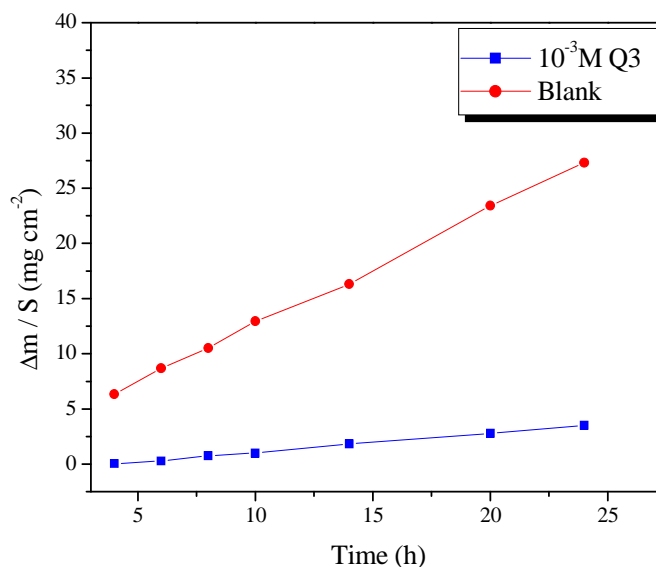


Figure 2. Weight loss as a function of immersion time of carbon steel in 1.0 M HCl without and with 10^{-3} M of Q3 at 308 K.

Table 1. The values of inhibition efficiency obtained from the weight loss for Q3 at different concentration in 1.0 M HCl and at different temperatures.

Temp (K)	Conc (M)	v (mg cm ⁻² h ⁻¹)	η_{WL} (%)	θ
308	10^{-3}	0.028	97.4	0.974
	10^{-4}	0.072	93.4	0.934
	10^{-5}	0.137	87.2	0.872
	10^{-6}	0.224	76.3	0.763
313	10^{-3}	0.103	93.1	0.931
	10^{-4}	0.191	87.2	0.872
	10^{-5}	0.307	79.4	0.794
	10^{-6}	0.459	69.2	0.692
323	10^{-3}	0.396	86.2	0.862
	10^{-4}	0.571	80.1	0.801
	10^{-5}	0.801	72.1	0.721
	10^{-6}	1.131	60.6	0.606
333	10^{-3}	1.089	79.1	0.791
	10^{-4}	1.427	72.6	0.726
	10^{-5}	1.834	64.8	0.648
	10^{-6}	2.542	51.2	0.512
343	10^{-3}	3.397	66.1	0.661
	10^{-4}	4.168	58.4	0.584
	10^{-5}	5.301	47.1	0.471
	10^{-6}	6.884	31.3	0.313

Effect of temperature

The influence of temperature on the corrosion behaviour of steel/acid in the presence and absence of the Q3 at various concentrations is investigated by weight-loss trend in the temperature rang 308-343K during 1h of immersion. The collected curves in Fig. 3 show the evolution of corrosion rate (v) with Q3 concentration (C) at different temperatures. Fig. 4 indicates that at a given Q3 concentration the corrosion rate of carbon steel increased with temperature. The increase is more pronounced at low concentrations. The results also indicate that for a given temperature, the corrosion rate of carbon steel decreased with increasing inhibitor concentration. The values of

inhibition efficiency obtained from the weight loss for different inhibitor concentrations and at various temperatures in 1.0 M HCl are given in Table 1 and Fig. 3. It is clear that inhibition efficiency increased with increase in inhibitor concentration. The maximum value of inhibition efficiency ($\eta_{WL}\%$) obtained for 10^{-3} M Q3 is 97.4% at 308K. It shows that inhibition efficiency decreased at higher temperatures. This behavior indicates desorption of inhibitor molecule [25].

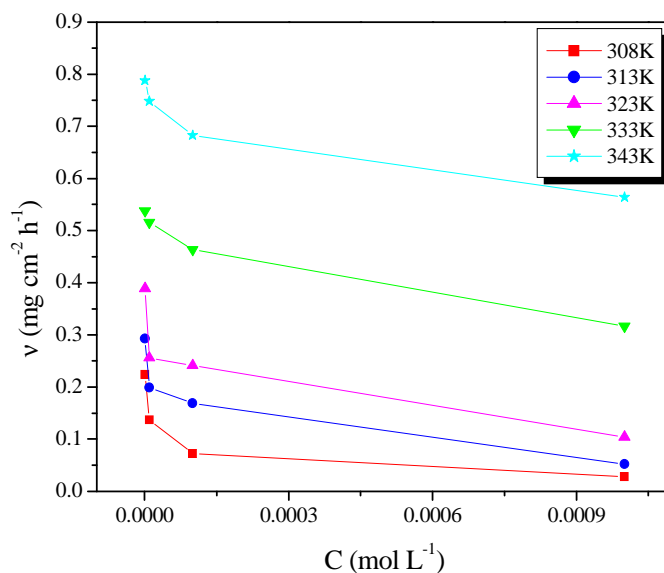


Figure 3. The relationship between corrosion rate and inhibitor concentration of Q3.

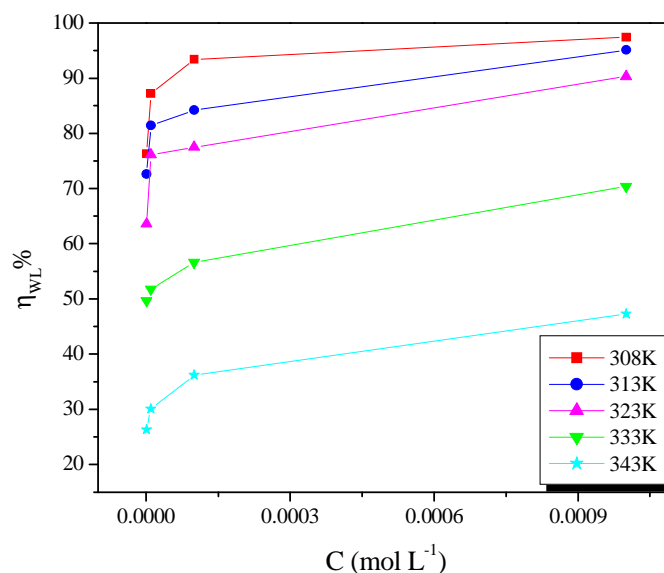


Figure 4. Variation of inhibition efficiency ($\eta_{WL}\%$) with concentration of Q3 for carbon steel in 1.0 M HCl at different temperatures.

Thermodynamic activation functions of the corrosion process

In order to calculate activation thermodynamic parameters of the corrosion reaction such as activation energy E_a , activated entropy ΔS_a and enthalpy ΔH_a , the Arrhenius equation and its alternative formulation called transition state equation were employed [26]:

$$v = A \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

$$v = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(-\frac{\Delta H_a}{RT}\right) \quad (4)$$

where v is the corrosion rate, A is a constant depends on a metal type and electrolyte, E_a is the apparent activation energy, h is the Planck's constant (6.626176×10^{-34} Js), N is the Avogadro's number (6.02252×10^{23} mol⁻¹), R is the universal gas constant and T is the absolute temperature, ΔH_a the enthalpy of activation, and ΔS_a entropy of activation.

The activation energy can be calculated from the slope $-E_a/R$ by plotting the logarithm of corrosion rate versus $1/T$. Fig. 5 shows the variations of logarithm of the corrosion rate with the presence and absence of inhibitor with the reciprocal of absolute temperature. The calculated activation energies, E_a , and pre-exponential factors, A , at different concentrations of the inhibitor are collected in Table 2.

From Table 2, it is evident that the value of E_a in the presence of Q3 is higher than that in the uninhibited acid solution. According to equation (3), it is clear that the lower A and the higher E_a lead to the lower corrosion rate (v). For the present study, the value of A in the presence of Q3 is higher than that in uninhibited solution and so the decrease in steel corrosion rate is determined by the apparent activation energy (E_a). Similar report has been documented previously [27]. The relationships between the temperature dependence of $\eta_{WL}\%$ of an inhibitor and the E_a can be classified into three groups according to temperature effects [28];

1. $\eta_{WL}\%$ decreases with increase in temperature, E_a (inhibited solution) $>$ E_a (uninhibited solution).
2. $\eta_{WL}\%$ increases with increase in temperature, E_a (inhibited solution) $<$ E_a (uninhibited solution).
3. $\eta_{WL}\%$ does not change with temperature, E_a (inhibited solution) = E_a (uninhibited solution).

It is clear from Table 2, that case (i) is applicable in this work, i.e. E_a in the inhibited solution is higher than that obtained for the free acid solution indicating that the corrosion reaction of carbon steel is inhibited by Q3 [29], hence supports the phenomenon of physical adsorption [30,31]. Higher values of E_a in the presence of inhibitor can be correlated with increasing thickness of the double layer which enhances the E_a of the corrosion process [32]. It is also an indication of a strong inhibitive action of Q3 by increasing energy barrier for the corrosion process, emphasizing the electrostatic character of the inhibitor's adsorption on the carbon steel surface (physisorption) [33].

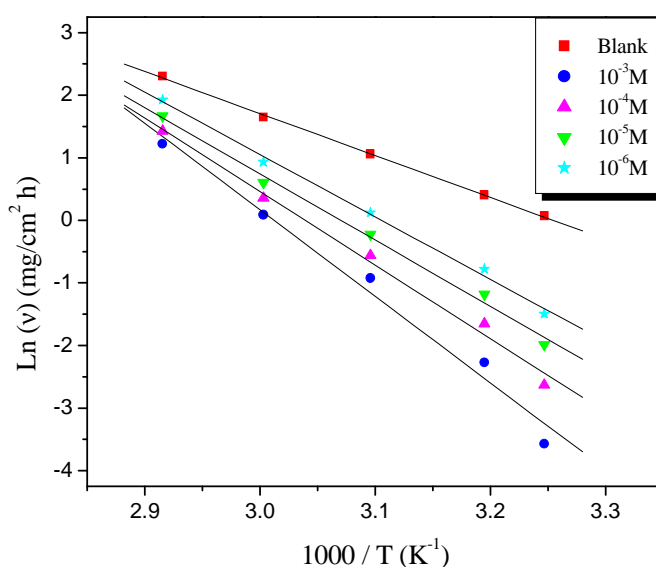
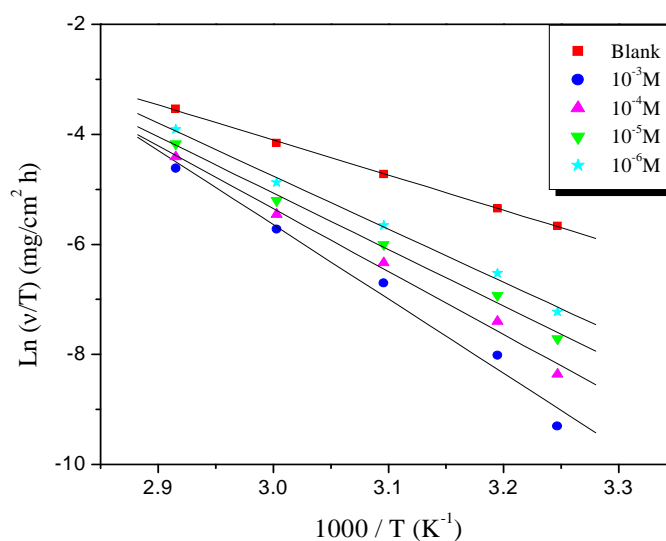


Figure 5. Arrhenius plots of copper in acid with and without different concentrations of Q3.

Table 2. Activation parameters of the dissolution of carbon steel in 1.0 M HCl in the absence and presence of different concentrations of Q3.

Conc (M)	A (mg/cm ² h)	Linear regression coefficient (r)	E_a (kJ/mol)	ΔH_a (kJ/mol)	ΔS_a (J/mol K)	$E_a - \Delta H_a$ (kJ/mol)
Blank	3.0066×10^9	0.9996	55.75	53.05	-72.49	2.7
10^{-3}	1.9030×10^{16}	0.9996	115.01	112.31	92.49	2.7
10^{-4}	3.2987×10^{15}	0.9959	97.75	95.05	43.14	2.7
10^{-5}	1.2911×10^{14}	0.9971	87.99	85.29	16.19	2.7
10^{-6}	2.8029×10^{13}	0.9979	82.90	80.20	03.49	2.7

The values of enthalpy of activation ΔH_a and entropy of activation, ΔS_a were obtained from the transition state equation (4). A plot of $\ln(v/T)$ as a function of $1/T$ (Fig. 6) was made for carbon steel corrosion in 1.0 M HCl in the absence and presence of different concentrations of Q3. Straight lines are obtained with a slope $(-\Delta H_a/R)$ and intercept $(\ln R/Nh + \Delta S_a/R)$ from which the ΔH_a and ΔS_a values are calculated (Table 2).

**Figure 6. The relationship between $\ln(v/T)$ and T^{-1} for different concentrations of Q3.**

Examination of these data reveals that the ΔH_a values for dissolution reaction of carbon steel in 1.0 M HCl in the presence of Q3 are higher than that in the absence of Q3. The positive sign of ΔH_a show the endothermic nature of the solution process suggesting that the dissolution of carbon steel is slow [34], which indicates that inhibition efficiencies decrease with increase in temperature. It is also clear from Table 2 that E_a and ΔH_a increase with increase in Q3 concentration. From Table 2, it is seen that the value of activation energy and enthalpy of activation varied in the same way. This result verified the known thermodynamic relation between E_a and ΔH_a [35, 36]:

$$E_a - \Delta H_a = RT \quad (5)$$

The large negative value of ΔS_a for carbon steel in 1.0 M HCl implies that the activated complex is the rate-determining step, rather than the dissociation step. In the presence of the inhibitor, the values of ΔS_a increases and is generally interpreted as an increase in disorder as the reactants are converted to the activated complexes [37]. The positive values of ΔS_a reflect the fact that the adsorption process is accompanied by an increase in entropy, which is the driving force for the adsorption of the inhibitor onto the steel surface.

Adsorption isotherm and thermodynamic consideration

In order to get more information about the interaction of the studied inhibitor and metal surface at different temperatures, the values of surface coverage (θ) obtained from weight loss measurement at different concentrations of Q3 in 1.0 M HCl in the temperature range (308-343K) after 1h immersion were used to investigate the adsorption characteristics of the inhibitor. Four widely used adsorption isotherms (Langmuir, Temkin, Frumkin and Freundlich) were tested for their fit to the experimental data. The best fit was obtained with Langmuir's adsorption isotherm, given by Equation as following:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (6)$$

Where θ is the degree of surface coverage, C_{inh} is the inhibition concentration in the electrolyte and K_{ads} is the equilibrium constant of the adsorption process. Plots of C_{inh}/θ versus C_{inh} yield a straight line as shown in Fig. 7. In both cases the linear regression coefficients (R^2) are almost equal to 1 and the slopes are very close to 1, indicating that the adsorption of Q3 in 1.0 M HCl follows the Langmuir isotherm and exhibit single-layer adsorption characteristic. The equilibrium adsorption constant, K_{ads} , for the adsorption of the compound at different temperature were calculated from the slopes of straight lines and listed in Table 3.

Table 3. The thermodynamic parameters of adsorption of Q3 on the carbon steel surface.

T (K)	Linear regression coefficient (r)	K_{ads} (L/mol)	ΔG_{ads}° (kJ/mol)	ΔH_{ads}° (kJ/mol)	ΔS_{ads}° (J/mol K)
308	0.9999	515910.68	-43.97	-34.06	32.15
313	0.9999	320355.72	-43.44		29.96
323	0.9999	262170.61	-44.29		31.66
333	0.9999	205456.94	-44.99		32.80
343	0.9999	109075.16	-44.53		30.52

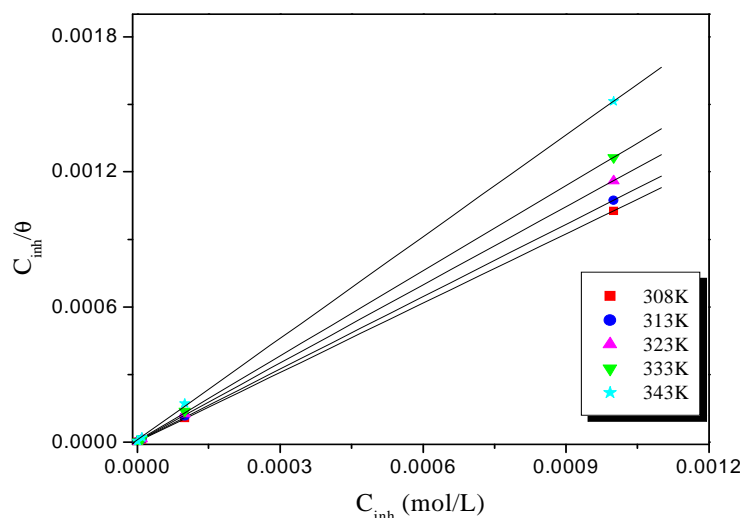


Figure 7. The relationship between C_{inh}/θ and C_{inh} of Q3 at various temperatures.

It is seen from the table that the correlation coefficients are very good and K_{ads} values decrease with an increase in temperature. Large values of K_{ads} mean better inhibition efficiency of the inhibitor, i.e., strong electrical interaction between the double-layer existing at the phase boundary and the adsorbing inhibitor molecules. Small values of K_{ads} , however, reveal that such interactions between adsorbing inhibitor molecules and the metal surface are weaker, indicating that the inhibitor molecules are easily removable by the solvent molecules from the metal surface [38].

K_{ads} is related to the free energy of adsorption ΔG_{ads}° by the equation:

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^{\circ}}{RT}\right) \quad (7)$$

where 55.5 is the concentration of water expressed in mol/L (the same as that of inhibitor concentration), R is the molar gas constant ($\text{kJ mol}^{-1}\text{K}^{-1}$) and T is the absolute temperature (K).

The negative value of ΔG_{ads}° (Table 3) means that the adsorption of Q3 on steel surface is a spontaneous process, and furthermore the negative values of ΔG_{ads}° also show the strong interaction of the inhibitor molecule onto the

copper surface [39,40]. Generally, values of ΔG_{ads}° around -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption). Those more negative than -40 kJ mol^{-1} involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) [41,42]. The calculated values of ΔG_{ads}° are greater than -40 kJ mol^{-1} , indicating that the adsorption of mechanism of Q3 on steel in 1.0 M HCl solution at the studied temperatures may be a chemisorption [43].

The negative sign of ΔH_{ads}° indicates that the adsorption of Q3 molecules is an exothermic process. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of ΔH_{ads}° . For physisorption process, the enthalpy of adsorption is lower than 40 kJ mol^{-1} while that for chemisorption approaches 100 kJ mol^{-1} [44]. In the present case; the standard adsorption heat $-34.06 \text{ kJ mol}^{-1}$ shows that a comprehensive adsorption (physical adsorption) might occur [45]. The adsorption of inhibitor molecules is accompanied by positive values of ΔS_{ads}° .

$\Delta H_{ads}^{\circ} = -34.06 \text{ kJ mol}^{-1}$ found by the Van't Hoff equation, may be also evaluated by the Gibbs–Helmholtz equation, which is defined as follows :

$$\left[\frac{\partial(\Delta G_{ads}^{\circ} / T)}{\partial T} \right]_P = -\frac{\Delta H_{ads}^{\circ}}{T^2} \quad (8)$$

Which can be arranged to give the following equation:

$$\frac{\Delta G_{ads}^{\circ}}{T} = \frac{\Delta H_{ads}^{\circ}}{T} + A \quad (9)$$

The standard adsorption entropy ΔS_{ads}° may be deduced using the thermodynamic basic equation:

$$\Delta G_{ads}^{\circ} = \Delta H_{ads}^{\circ} - T\Delta S_{ads}^{\circ} \quad (10)$$

Thermodynamic model is very useful to explain the adsorption phenomenon of inhibitor molecule. The adsorption heat could be calculated according to the Van't Hoff equation:

$$\text{Ln}(K_{ads}) = -\frac{\Delta H_{ads}^{\circ}}{RT} + \text{Constant} \quad (11)$$

Where ΔH_{ads}° and K_{ads} are the adsorption heat and adsorptive equilibrium constant, respectively. To obtain the adsorption heat, the regression between $\text{Ln}(K_{ads})$ and $1/T$ was dealt with. Fig. 8 is the straight line $\text{Ln}(K_{ads})$ versus $1/T$. The adsorption heat (ΔH) can be approximately regarded as the standard adsorption heat (ΔH_{ads}°) under the experimental conditions [46, 47].

The variation of $\Delta G_{ads}^{\circ}/T$ with $1/T$ gives a straight line with a slope that equals $\Delta H_{ads}^{\circ} = -34.08 \text{ kJ.mol}^{-1}$ (Fig. 9). It can be seen from the figure that $\Delta G_{ads}^{\circ}/T$ decreases with $1/T$.

The value of the enthalpy of adsorption found by the two methods such as Van't Hoff and Gibbs–Helmholtz relations are in good agreement.

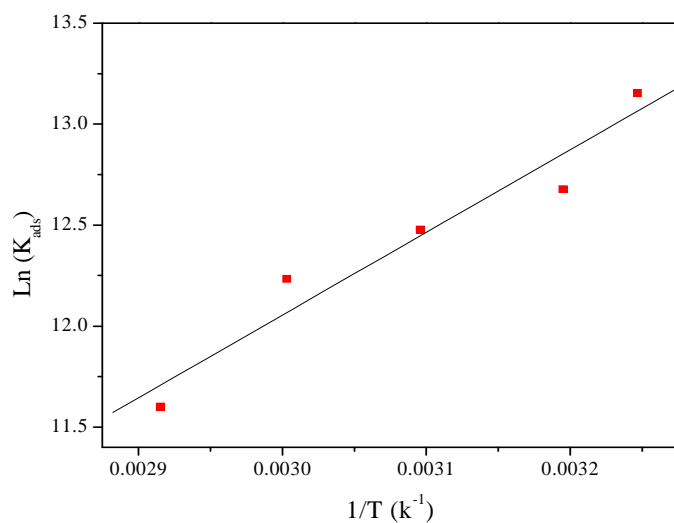


Figure 8. The relationship between Ln (K_{ads}) and $1/T$ for Q3.

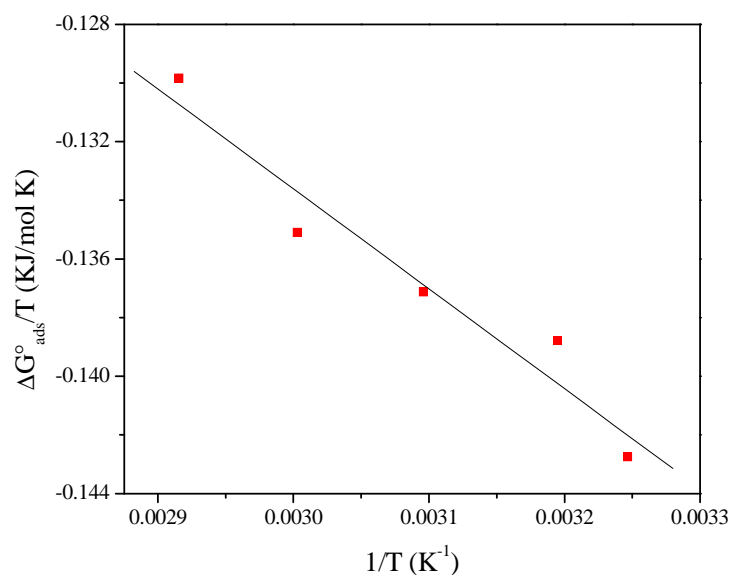


Figure 9. Relationship between $\Delta G_{ads}^{\circ} / T$ and the reverse of absolute temperature.

CONCLUSION

The following conclusions may be drawn from the study:

- Results obtained from the experimental data show that 2-(4-(2-ethoxy-2-oxoethyl)-2-p-tolylquinoxalin-1(4H)-yl)acetate (Q3) acts as an effective inhibitor of carbon steel corrosion in 1.0 M HCl.
- The corrosion process was inhibited by adsorption of the Q3 on the steel surface.
- Inhibition efficiency increases with increase in the concentration of Q3 but decreases with rise in temperature.
- The adsorption of Q3 on carbon steel surface from 1.0 M HCl obeys the Langmuir adsorption isotherm.
- From the free energy of adsorption ΔG_{ads}° values, it can be concluded that the adsorption process was spontaneous and chemically adsorbed (chemisorption) onto the carbon steel surface.
- Kinetic and adsorption parameters were evaluated and discussed.

REFERENCES

- [1] J. M. Sykes, Br. Corros. J., **1990**, 25, 175.
- [2] A. K. Singh; M. A. Quraishi; *J. Mater. Environ. Sci.*, **2010**, 1, 101.
- [3] M. Prajila; J. Sam; J. Bincy; J. Abraham; *J. Mater. Environ. Sci.* **2012**, 3, 1045.
- [4] U.J. Naik; V.A. Panchal ; A.S. Patel ; N.K. Shah ; *J. Mater. Environ. Sci.*, **2012**, 3, 935.
- [5] A. Zarrouk, H. Zarrok, R. Salghi, B. Hammouti, F. Bentiss, R. Touir, M. Bouachrine, *J. Mater. Environ. Sci.*, **2013**, 4, 177.
- [6] H. Zarrok, H. Oudda, A. Zarrouk, R. Salghi, B. Hammouti, M. Bouachrine, *Der Pharm. Chem.*, **2011**, 3, 576.
- [7] H. Zarrok, R. Salghi, A. Zarrouk, B. Hammouti, H. Oudda, Lh. Bazzi, L. Bammou, S. S. Al-Deyab, *Der Pharm. Chem.*, **2012**, 4, 407.
- [8] H. Zarrok, S. S. Al-Deyab, A. Zarrouk, R. Salghi, B. Hammouti, H. Oudda, M. Bouachrine, F. Bentiss, *Int. J. Electrochem. Sci.*, **2012**, 7, 4047.
- [9] D. Ben Hmamou, R. Salghi, A. Zarrouk, H. Zarrok, B. Hammouti, S. S. Al-Deyab, M. Bouachrine, A. Chakir, M. Zougagh, *Int. J. Electrochem. Sci.*, **2012**, 7, 5716.
- [10] A. Zarrouk, H. Zarrok, R. Salghi, B. Hammouti, S.S. Al-Deyab, R. Touzani, M. Bouachrine, I. Warad, T. B. Hadda, *Int. J. Electrochem. Sci.*, **2012**, 7, 6353.
- [11] A. Zarrouk, M. Messali, H. Zarrok, R. Salghi, A. Al-Sheikh Ali, B. Hammouti, S. S. Al-Deyab, F. Bentiss, *Int. J. Electrochem. Sci.*, **2012**, 7, 6998.
- [12] H. Zarrok, A. Zarrouk, R. Salghi, Y. Ramli, B. Hammouti, S. S. Al-Deyab, E. M. Essassi, H. Oudda, *Int. J. Electrochem. Sci.*, **2012**, 7, 8958.
- [13] D. Ben Hmamou, R. Salghi, A. Zarrouk, H. Zarrok, S. S. Al-Deyab, O. Benali, B. Hammouti, *Int. J. Electrochem. Sci.*, **2012**, 7, 8988.
- [14] A. Zarrouk, M. Messali, M. R. Aouad, M. Assouag, H. Zarrok, R. Salghi, B. Hammouti, A. Chetouani, *J. Chem. Pharm. Res.*, **2012**, 4, 3427.
- [15] D. Ben Hmamou, M. R. Aouad, R. Salghi, A. Zarrouk, M. Assouag, O. Benali, M. Messali, H. Zarrok, B. Hammouti, *J. Chem. Pharm. Res.*, **2012**, 4, 3489.
- [16] H. Zarrok, H. Oudda, A. El Midaoui, A. Zarrouk, B. Hammouti, M. Ebn Touhami, A. Attayibat, S. Radi, R. Touzani, *Res. Chem. Intermed* (2012) DOI 10.1007/s11164-012-0525-x
- [17] A. Zarrouk, B. Hammouti, H. Zarrok, R. Salghi, A. Dafali, Lh. Bazzi, L. Bammou, S. S. Al-Deyab, *Der Pharm. Chem.*, **2012**, 4, 337.
- [18] Y. Feug, K.S. Siow, W.K. Teb and A.K. Hsieh, *Corros. Sci.*, **1999**, 41, 829.
- [19] L. El Kadi, B. Mernari, M. Traisnel, F. Bentiss and M. Lagrenee, *Corros. Sci.*, **2000**, 42, 703.
- [20] M.S. Morad, *Corros. Sci.*, **2000**, 42, 1307.
- [21] M. Gajic, *Corros. Sci.*, **2001**, 43, 919.
- [22] S. Martinez, *J. Appl. Electrochem.*, 31, **2001**, 973.
- [23] M.A. Ameer, E. Khamis and G. Al-Senani, *J. Appl. Electrochem.*, 32, **2002**, 149.
- [24] D. Schweinsberg, G. George, A. Nanayakkawa and D. Steinert, *Corros. Sci.*, **1988**, 28, 33.
- [25] M. Schorr, J. Yahalom, *Corros. Sci.*, **1972**, 12, 867.
- [26] B. Hammouti, A. Zarrouk, S.S. Al-Deyab And I. Warad, *Orient. J. Chem.*, **2011**, 27, 23.
- [27] H. Ashassi-Sorkhabi, S.A. Nabavi-Amri, *Acta Chim. Slov.*, **2000**, 47, 512.
- [28] S.A. Umoren, I.B. Obot, *Surf. Rev. Lett.*, 15, **2008**, 277.
- [29] A.R.S. Priya, V.S. Muralidharam, A. Subramania, *Corrosion*, **2008**, 64, 541.
- [30] I.B. Obot, N.O. Obi-Egbedi, *Mater. Chem. Phys.*, **2010**, 122, 325.
- [31] I.B. Obot, N.O. Obi-Egbedi, *Corros. Sci.*, **2009**, 51, 276.
- [32] M.M. Solomon, S.A. Umoren, I.I. Udoso, A.P. Udoh, *Corros. Sci.*, **2010**, 52, 1317.
- [33] S.A. Umoren, M.M. Solomon, I.I. Udoso, A.P. Udoh, *Cellulose*, **2010**, 17, 635.
- [34] N. M. Guan, I. Xueming, I. Fei, *Mater. Chem. Phys.*, **2004**, 86, 59.
- [35] A. Zarrouk, B. Hammouti, H. Zarrok, S. S. Al-Deyab, I. Warad, *Res. Chem. Intermed.*, **2012**, 38, 1655.
- [36] A. Zarrouk, B. Hammouti, H. Zarrok, S.S. Al-Deyab, M. Messali, *Int. J. Electrochem. Sci.*, **2011**, 6, 6261.
- [37] I. El Ouali, B. Hammouti, A. Aouniti, Y. Ramli, M. Azougagh, E. M. Essassi, M. Bouachrine, *J. Mater. Environ. Sci.*, **2010**, 1, 1.
- [38] M.A. Amin, Q. Mohsen, O.A. Hazzazi, *Mater. Chem. Phys.*, **2009**, 114, 908.
- [39] M. Elachouri, M. S. Hajji, M. Salem, S. Kertit, J. Aride, R. Coudert, E. Essassi, *Corrosion*, **1996**, 52, 103.
- [40] B.V. Savitri, S. Mayanna, *Ind. J. Chem. Technol.*, **1996**, 3, 256.
- [41] F. M. Donahue, K. Nobe, *J. Electrochem. Soc.*, **1965**, 112, 886.
- [42] E. Khamis, F. Bellucci, R. M. Latanision, E. S. H. El-Ashry, *Corrosion*, **1991**, 47, 677.
- [43] A. H. Al Hamzi, H. Zarrok, A. Zarrouk, R. Salghi, B. Hammouti, S. S. Al-Deyab, M. Bouachrine, A. Amine, F. Guenoun, *Int. J. Electrochem. Sci.*, **2013**, 8, 2586.
- [44] A.M. Badiea, K.N. Mohana, *Corros. Sci.*, **2009**, 51, 2231.

- [45] L. B. Tang, G. N. Mu, G. H. Liu, *Corros. Sci.*, **2003**, 45, 2251.
[46] T. P. Zhao, G. N. Mu, *Corros. Sci.*, **1999**, 41, 1937.
[47] G. N. Mu, X. M. Li, F. Li, *Mater. Chem. Phys.*, **2004**, 86, 59.