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# Quinazoline Derivatives as Green Corrosion Inhibitors for Carbon Steel in Hydrochloric Acid Solutions

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The inhibiting effect of some quinazoline derivatives on the corrosion of carbon steel in 2 M HCl was studied by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) techniques. The results showed that the inhibition efficiency increases with increasing the inhibitor concentration, while it decreases with increasing the temperature. The adsorption of quinazoline derivatives on the carbon steel surface obeys Temkin adsorption isotherm. Some thermodynamic parameters were calculated and discussed. Polarization curves show that quinazoline derivatives are mixed-type inhibitors but the cathode is more polarized than the anode. The results obtained from chemical and electrochemical techniques are in good agreement.

**Keywords:** acid corrosion, carbon steel, EIS, EDS, SEM, quinazoline derivatives

## 1. INTRODUCTION

Corrosion is a fundamental process playing an important role in economics and safety, particularly for metals. The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media [1]. Most well-known acid inhibitors are organic compounds which have π bonds and contains hetero atoms such as sulphur, nitrogen, oxygen and phosphorous which allows the adsorption of compounds on the metal surface [2-6].

The most of the organic inhibitors are toxic, highly expensive and environment unfriendly. Research activities in recent times are geared towards developing the cheap, non-toxic and environment friendly corrosion inhibitors. However, the use of these organic compounds has been questioned lately, due to the several negative effects they have caused in the environment [7]. Thus, the development of the novel corrosion inhibitors of natural source and non-toxic type has been considered to be more important and desirable [8]. Because of their natural origin [9-11], as well as their non-toxic characteristics [12] and negligible negative impacts on the aquatic environment [13], drugs (chemical medicines) seem to be ideal candidates to replace traditional toxic corrosion. These inhibitors decrease the corrosion rate by adsorbing on the metal surface and blocking the active sites by displacing water molecules and form a compact barrier film on the metal surface.

The present paper describes a study of corrosion protection of some drugs on carbon steel in 2 M HCl using chemical (weight loss), electrochemical techniques (EIS, potentiodynamic polarization) and surface examination studies. These drugs are antibiotics and are of particular interest because of their safe use, high solubility in water, containing π-electrons and electronegative atoms such as N & O in their molecules. These factors favour the interaction of these drugs with the metal. As far as we know no concrete report has been published so for these drugs in 2 M HCl with use of electrochemical, chemical techniques and surface examinations, hence the present study. The structure of these drugs is shown in the Figure 1.

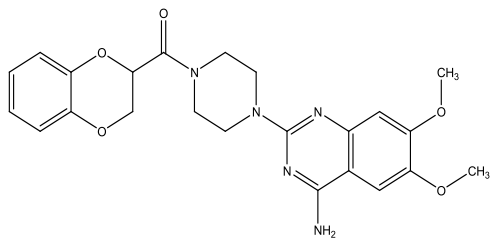
## 2. EXPERIMENTAL METHODS

### *2.1. Materials*

Tests were performed on carbon steel specimens of the following composition (weight %): 0.200 C, 0.350 Mn, 0.024 P, 0.003 S, and the remainder Fe.

### *2.2. Inhibitors*

The investigated drugs (quinazoline derivatives) have been purchased from Pfizer Company, Egypt and used as received.

| Inhibitor | Structure | IUPAC Name | Molecular weight | Active center | Chemical formula |
|---|---|---|---|---|---|
| (1) |  | (4-(4-amino-6,7-dimethoxy quinazolin-2-yl)piperazin-1-yl)(2,3-di hydrobenzo [b][1,4]dioxin-2-yl) methanone | 451.5 | 5O 5N | $C_{23}H_{25}N_5O_5$ |

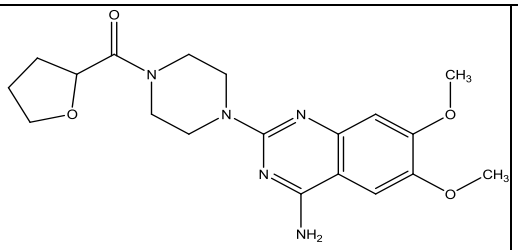
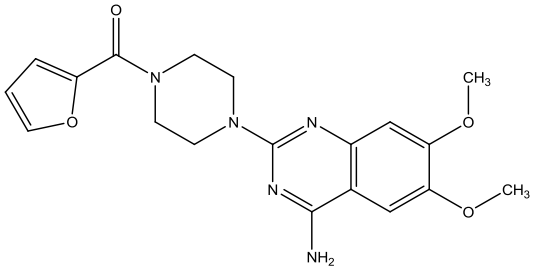
| | | | | | |
|---|---|---|---|---|---|
| (2) |  | (4-(4-amino-6,7-dimethoxy quinazolin-2-yl)piperazin-1-yl)(tetra hydro furan-2-yl)methanone | 387.4 | 4O 5N | $C_{19}H_{25}N_5O_4$ |
| (3) |  | (4-(4-amino-6,7-dimethoxy quinazolin-2-yl)piperazin-1-yl)(furan-2-yl)methanone | 383.4 | 4O 5N | $C_{19}H_{21}N_5O_4$ |

**Figure 1.** The molecular structures, names, molecular weights, molecular formula and active centers of investigated compounds

*2.3. Solutions*

The aggressive solutions 2 M HCl were prepared by dilution of analytical grade (37%) HCl with bi-distilled water. The concentration range of the inhibitors used was $3X10^{-6}$-$18X10^{-6}$ M

*2.4. Weight loss measurements*

Seven parallel carbon steel sheets of 2.5 × 2.0 × 0.06 cm were abraded with emery paper (grade 320–500–800) and then washed with bi-distilled water and degreased with acetone. After accurate weighing, the specimens were immersed in a 250 ml beaker, which contained 100 ml of HCl with and without addition of different concentrations of investigated inhibitors.

All the aggressive acid solutions were open to air. After 3 hours, the specimens were taken out, washed, dried, and weighed accurately. The average weight loss of seven parallel carbon steel sheets could be obtained. The inhibition efficiency (% IE) and the degree of surface coverage, θ, of these drugs (quinazoline derivatives) for the corrosion of carbon steel were calculated from equation 1[14]:

$$\% IE = \theta \times 100 = [1 - (W / W^{o})] \times 100 \quad (1)$$

where $W^{o}$ and W are the values of the average weight losses without and with addition of the inhibitor, respectively.

*2.5. Polarization measurements*

Polarization experiments were carried out in a conventional three-electrode cell with a platinum foil as counter electrode and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as reference electrode. The working electrode was in the form of a square cut from carbon steel embedded in epoxy resin of polytetrafluoroethylene (PTFE) so that the flat surface (1 $cm^2$) was the only surface of the electrode. Tafel polarization curves were obtained by changing the electrode potential automatically from -500 to +500 mV at open circuit potential with a scan rate of 1 $mVs^{-1}$. Stern-Geary method [15] used for the determination of corrosion current is performed by extrapolation of anodic and cathodic Tafel lines to a point which gives log $i_{corr}$ and the corresponding corrosion potential ($E_{corr}$) for inhibitor free acid and for each concentration of inhibitor. Then $i_{corr}$ was used for calculation of inhibition efficiency and surface coverage (θ) as in equation 2:

$$\% IE = \theta \times 100 = [1- (i_{corr(inh)} / i_{corr(free)}) ] \times 100 \quad (2)$$

where $i_{corr(free)}$ and $i_{corr(inh)}$ are the corrosion current densities in the absence and presence of inhibitor, respectively.

Impedance measurements were carried out in frequency range from 100 kHz to 10 mHz with amplitude of 5 mV peak-to-peak using ac signals at open circuit potential. The experimental impedance were analyzed and interpreted on the basis of the equivalent circuit. The main parameters deduced from the analysis of Nyquist diagram are the resistance of charge transfer $R_{ct}$ (diameter of high frequency loop) and the capacity of double layer $C_{dl}$ which is defined as:

$$C_{dl} = 1/ (2 \pi f_{max} R_{ct}) \quad (3)$$

where $f_{max}$ is the maximum frequency

The inhibition efficiencies and the surface coverage (θ) obtained from the impedance measurements were calculated from equation 4:

$$\%IE = \theta \times 100 = [1- (R^{\circ}_{ct}/R_{ct})] \times 100 \quad (4)$$

where $R^{o}_{ct}$ and $R_{ct}$ are the charge transfer resistance in the absence and presence of inhibitor, respectively.

The electrode potential was allowed to stabilize 30 min before starting the measurements. All the experiments were conducted at 25 ± 1°C. Measurements were performed using Gamry (PCI 300/4) Instrument Potentiostat/Galvanostat/ZRA. This includes a Gamry framework system based on the ESA 400. Gamry applications include DC105 for corrosion measurements and EIS300 for electrochemical impedance spectroscopy along with a computer for collecting data. Echem Analyst 5.58 software was used for plotting, graphing, and fitting data.

## 3. RESULTS AND DISCUSSION

### *3.1. Weight loss measurements*

The weight loss-time curves of carbon steel with the addition of inhibitor (1) in 2 M HCl at various concentrations is shown in Fig. 1, (similar curves were obtained in presence of the other inhibitors, but not shown).

**Table 1.** Variation of inhibition efficiency (% IE) of various concentrations of all compounds at 120 min immersion and at 25$^{o}$C

| Compound | Conc., M | C.R. mg cm$^{-2}$ min$^{-1}$ | % IE |
|---|---|---|---|
| Blank | --- | 0.05 | ---- |
| 1 | 3X10$^{-6}$ | 0.021 | 58.8 |
| | 5X10$^{-6}$ | 0.018 | 63.6 |
| | 9X10$^{-6}$ | 0.016 | 67.6 |
| | 12X10$^{-6}$ | 0.014 | 71.9 |
| | 15X10$^{-6}$ | 0.013 | 77.8 |
| | 18X10$^{-6}$ | 0.011 | 81.7 |
| 2 | 3X10$^{-6}$ | 0.023 | 55.2 |
| | 5X10$^{-6}$ | 0.021 | 58.8 |
| | 9X10$^{-6}$ | 0.018 | 64.2 |
| | 12X10$^{-6}$ | 0.016 | 67.5 |
| | 15X10$^{-6}$ | 0.014 | 74.2 |
| | 18X10$^{-6}$ | 0.012 | 78.9 |
| 3 | 3X10$^{-6}$ | 0.026 | 47.3 |
| | 5X10$^{-6}$ | 0.023 | 53.5 |
| | 9X10$^{-6}$ | 0.021 | 58.6 |
| | 12X10$^{-6}$ | 0.018 | 63.9 |
| | 15X10$^{-6}$ | 0.016 | 67.5 |
| | 18X10$^{-6}$ | 0.013 | 73.4 |

The curves of Fig. 1 show that the weight loss values of carbon steel in 2 M HCl solution containing various concentrations of inhibitor (1) decrease as the concentration of the inhibitor increases; i.e., the corrosion inhibition strengthens with the inhibitor concentration, this is appear in the Table 1.

The linear variation of weight loss with time in uninhibited and inhibited 2 M HCl indicates the absence of insoluble surface films during corrosion. This trend may result from the fact that the adsorption of inhibitor molecules on the carbon steel surface increases with increasing the inhibitor concentration thus the carbon steel surface is efficiently separated from the medium by the adsorption of drugs molecules on carbon steel surface [16-17]**.**

The order of inhibition efficiency obtained from weight loss measurements (Table 1) is as follows: **1** > **2** > **3**

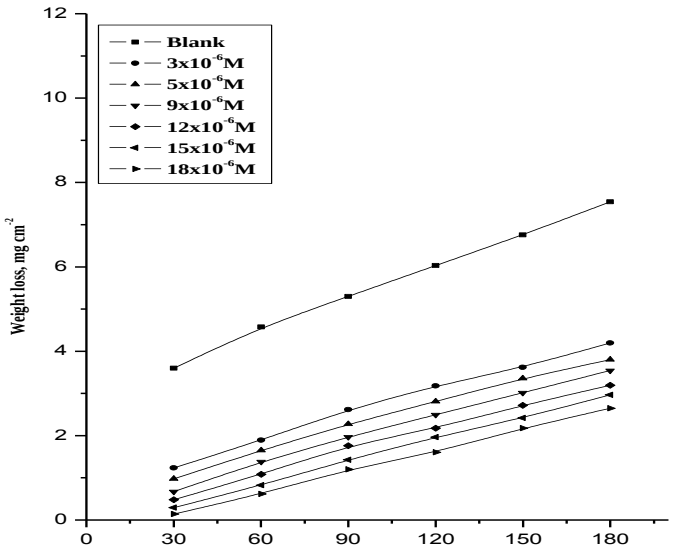



**Figure 1.** Weight-loss time curves for the dissolution of carbon steel in the absence and presence of different concentrations of compound (1) at 25°C

*3.2 Potentiodynamic polarization measurements*

Figure (2) shows the anodic and cathodic Tafel polarization curves for carbon steel in 2 M HCl in the absence and presence of varying concentrations of inhibitor 1 at 25°C (similar curves were obtained in presence of the other inhibitors, but not shown). From Fig. 2, it is clear that both anodic metal dissolution and cathodic hydrogen reduction reactions were inhibited when investigated inhibitors were added to 2 M HCl and this inhibition was more pronounced with increasing inhibitor concentration. Tafel lines are shifted to more negative and more positive potentials with respect to the blank curve by increasing the concentration of the investigated inhibitors. This behavior indicates that the undertaken additives act as mixed-type inhibitors [18-19]. The addition of quinazoline derivatives shifts the $E_{corr}$ values towards the negative potential. A compound can be classified as an anodic- or a cathodic-type inhibitor when the change in the $E_{corr}$ value is larger than 85 mV [20]. Since the largest displacement exhibited by quinazoline derivatives was less than this value (Table 1), it may be concluded that this molecule should be considered as a mixed-type inhibitor. The results show that the increase in inhibitor concentration leads to decrease the corrosion current density ($i_{corr}$), but the Tafel slopes ($\beta_a$, $\beta_c$),are parallel and approximately constant indicating that the retardation of the two reactions (cathodic hydrogen reduction and anodic metal dissolution) were affected without changing the dissolution mechanism[21-23]. The order of inhibition efficiency obtained from polarization measurements is as follows: **1** > **2** > **3**

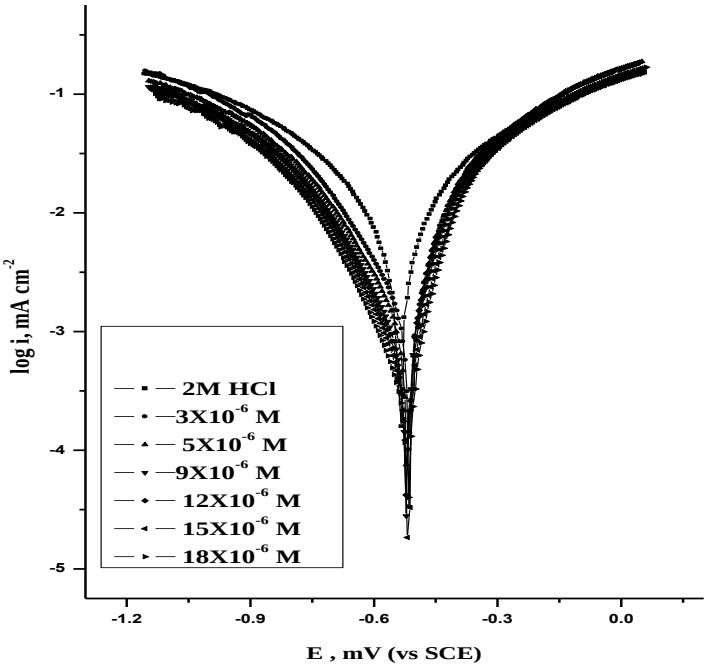


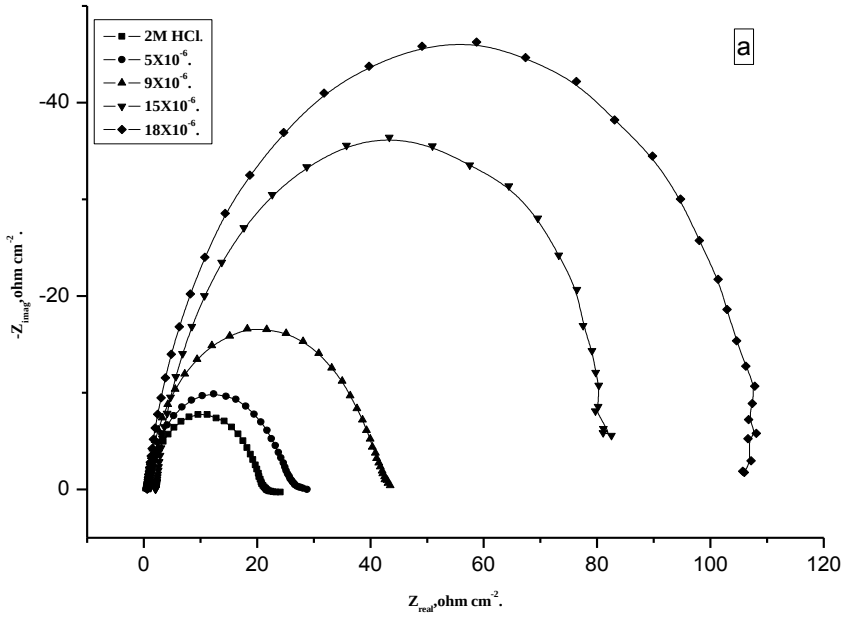

**Figure 2.** Potentiodynamic polarization curves for corrosion of carbon steel in 2 M HCl in the absence and presence of different concentrations of inhibitor (1) at 25ºC

**Table 2.** Corrosion parameters obtain from potentiodynamic polarization of carbon steel in 2 M HCl containing various concentrations of investigated inhibitors at 25 ºC

| Comp. | Conc., M | $-E_{corr}$ mV , vs. SCE | $i_{corr}$ mA $cm^{-2}$ | $\beta_c$ mV $dec^{-1}$ | $\beta_a$ mV $dec^{-1}$ | θ | % IE |
|---|---|---|---|---|---|---|---|
| 1 | 0.0 | 479 | 10.2 | 305 | 274 | ----- | ----- |
| | 3 x $10^{-6}$ | 566 | 9.4 | 154 | 153 | 0.078 | 7.8 |
| | 5 x $10^{-6}$ | 559 | 8.4 | 168 | 138 | 0.176 | 17.6 |
| | 9 x $10^{-6}$ | 555 | 6.9 | 146 | 159 | 0.323 | 32.3 |
| | 12 x $10^{-6}$ | 548 | 6.5 | 157 | 128 | 0.362 | 36.2 |
| | 15 x $10^{-6}$ | 544 | 5.6 | 139 | 114 | 0.450 | 45.0 |
| | 18 x $10^{-6}$ | 543 | 2.5 | 133 | 143 | 0.754 | 75.4 |
| 2 | 3 x $10^{-6}$ | 551 | 9.7 | 167 | 140 | 0.049 | 4.9 |
| | 5 x $10^{-6}$ | 549 | 8.9 | 165 | 127 | 0.127 | 12.7 |
| | 9 x $10^{-6}$ | 555 | 7.5 | 167 | 129 | 0.264 | 26.4 |
| | 12 x $10^{-6}$ | 547 | 6.6 | 158 | 129 | 0.352 | 35.2 |
| | 15 x $10^{-6}$ | 544 | 5.9 | 134 | 125 | 0.421 | 42.1 |
| | 18 x $10^{-6}$ | 525 | 4.1 | 128 | 133 | 0.598 | 59.8 |
| 3 | 3 x $10^{-6}$ | 553 | 8.8 | 173 | 145 | 0.033 | 3.3 |
| | 5 x $10^{-6}$ | 545 | 7.9 | 160 | 177 | 0.131 | 13.1 |
| | 9 x $10^{-6}$ | 543 | 6.7 | 177 | 155 | 0.270 | 27.0 |
| | 12 x $10^{-6}$ | 548 | 5.7 | 159 | 130 | 0.374 | 37.4 |
| | 15 x $10^{-6}$ | 554 | 5.0 | 142 | 145 | 0.452 | 45.2 |
| | 18 x $10^{-6}$ | 534 | 4.6 | 140 | 111 | 0.498 | 49.8 |

*3.3-Electrochemical impedance spectroscopy (EIS)*

The effect of inhibitor concentration on the impedance behavior of carbon steel in 2 M HCl solution at 25 ºC is presented in Fig. 3 (a, b). The curves show a similar type of Nyquist plots for carbon steel in the presence of various concentrations of inhibitor (1). Similar curves were obtained for other inhibitors but not shown. The existence of single semi-circle showed the single charge transfer process during dissolution which is unaffected by the presence of inhibitor molecules. Deviations from perfect circular shape are often referred to the frequency dispersion of interfacial impedance which arises due to surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, and formation of porous layers and in homogenates of the electrode surface [24-25]. Inspections of the data reveal that each impedance diagram consists of a large capacitive loop with one capacitive time constant in the Bode–phase plots (Fig.3b). The electrical equivalent circuit model is shown in (Fig. 4). It used to analyze the obtained impedance data. The model consists of the solution resistance ($R_s$), the charge-transfer resistance of the interfacial corrosion reaction ($R_{ct}$) and the double layer capacitance ($C_{dl}$). Excellent fit with this model was obtained with our experimental data. EIS data (Table 3) show that the $R_{ct}$ values increases and the $C_{dl}$ values decreases with increasing the inhibitor concentrations. This is due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface, decreasing the extent of dissolution reaction. The higher ($R_{ct}$) values, are generally associated with slower corroding system [26-27]. The decrease in the $C_{dl}$ can result from the decrease of the local dielectric constant and/or from the increase of thickness of the electrical double layer suggested that the inhibitor molecules function by adsorption at the metal/solution interface [28]. The %IE obtained from EIS measurements are close to those deduced from polarization measurements. The order of inhibition efficiency obtained from EIS measurements is as follows: **1** > **2** > **3**



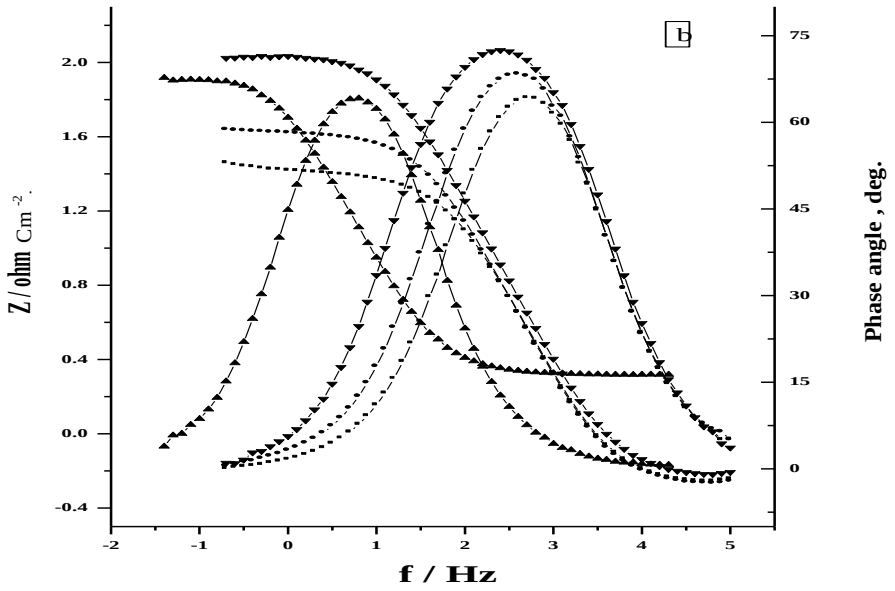



**Figure 3.** The Nyquist (a) and Bode (b) plots for corrosion of carbon steel in 2 M HCl in the absence and presence of different concentrations of compound (1) at 25°C

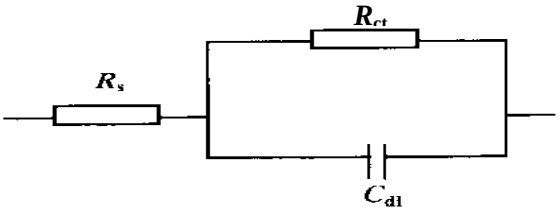


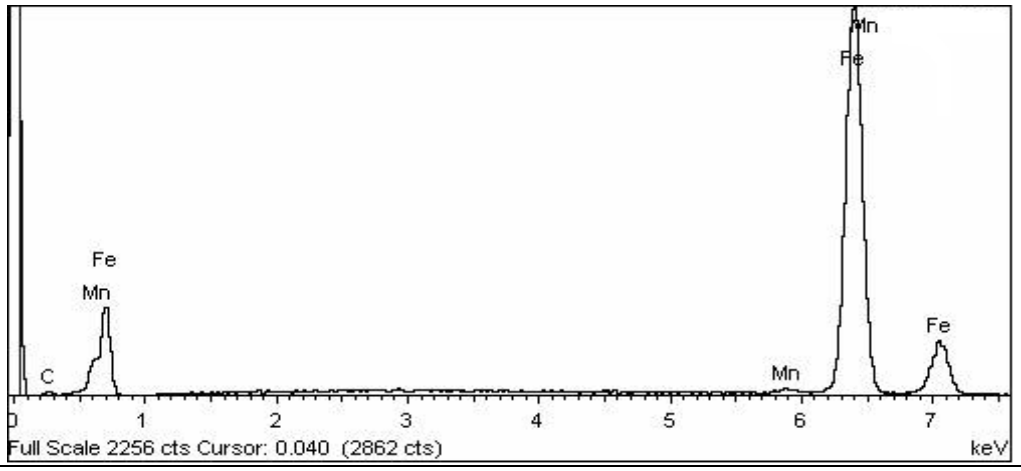

**Figure 4.** Electrical equivalent circuit model used to fit the results of impedance

**Table 3.** EIS data of carbon steel in 2 M HCl and in the absence and presence of different concentrations of investigated inhibitors at 25 ºC

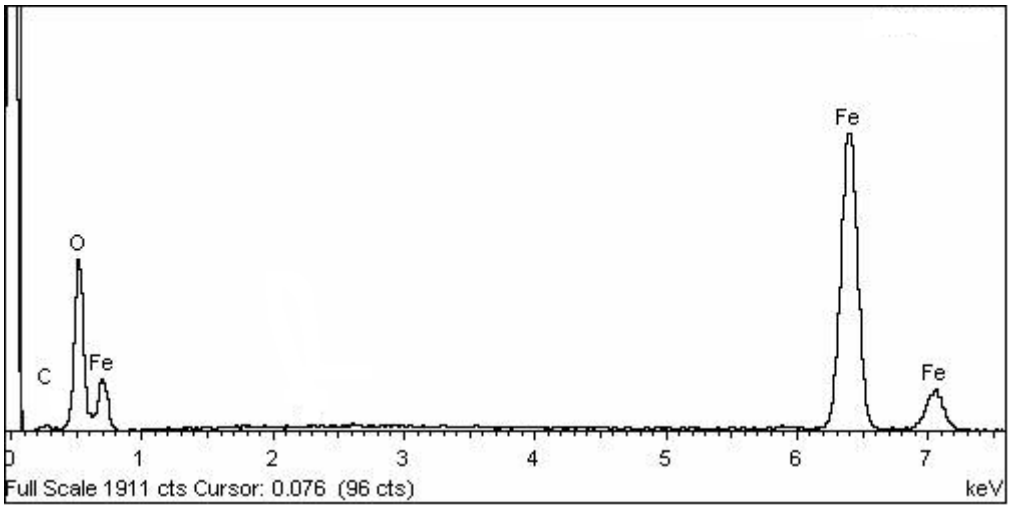
| Comp. | Conc., M | $C_{dl}$,x$10^{-3}$ µF $cm^{-2}$ | $R_{CT}$ x $10^{-4}$ Ω $cm^2$ | θ | % IE |
|---|---|---|---|---|---|
| Blank | --- | 96.32 | 22.1 | ---- | ---- |
| Inhibitor 1 | $5 \times 10^{-6}$ | 93.60 | 32.5 | 0.320 | 32.0 |
| | $9 \times 10^{-6}$ | 93.31 | 50.7 | 0.564 | 56.4 |
| | $15 \times 10^{-6}$ | 87.66 | 118.4 | 0.813 | 81.3 |
| | $18 \times 10^{-6}$ | 83.76 | 134.2 | 0.835 | 83.5 |
| Inhibitor 2 | $5 \times 10^{-6}$ | 92.75 | 29.7 | 0.256 | 25.6 |
| | $9 \times 10^{-6}$ | 90.40 | 43.2 | 0.488 | 48.8 |
| | $15 \times 10^{-6}$ | 86.43 | 98.1 | 0.775 | 77.5 |
| | $18 \times 10^{-6}$ | 82.31 | 125.3 | 0.824 | 82.4 |
| Inhibitor 3 | $5 \times 10^{-6}$ | 92.01 | 27.8 | 0.205 | 20.5 |
| | $9 \times 10^{-6}$ | 90.21 | 42.5 | 0.480 | 48.0 |
| | $15 \times 10^{-6}$ | 85.60 | 85.2 | 0.674 | 67.4 |
| | $18 \times 10^{-6}$ | 81.04 | 111.3 | 0.801 | 80.1 |

*3.4- Energy Dispersion Spectroscopy (EDS) Studies*

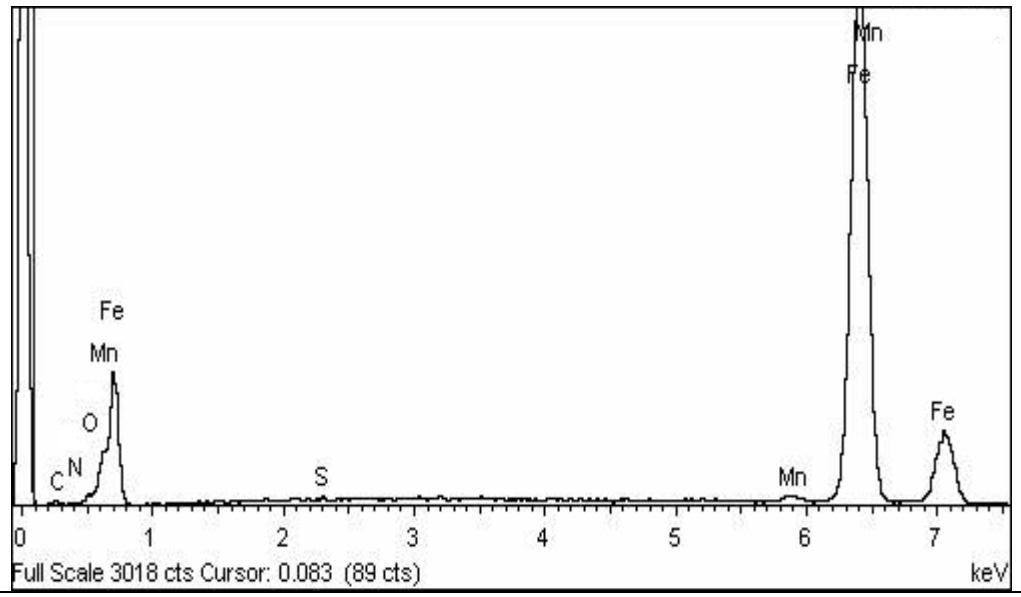
carbon steel alone




Blank




Inhibitor 1



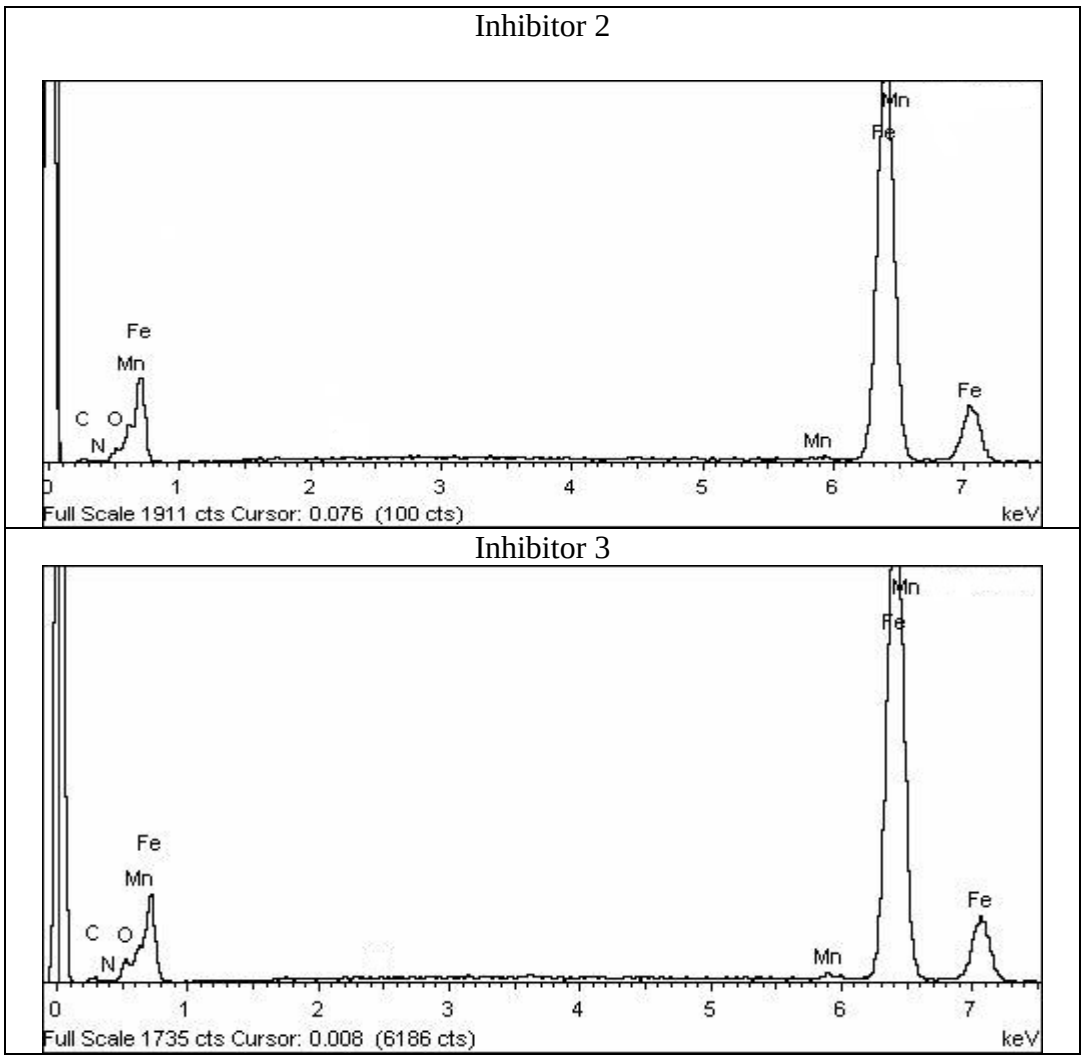



**Figure 5.** EDS analysis on C-steel in presence and absence of drugs (quinazoline derivatives) for 3 days immersion

The EDS spectra were used to determine the elements present on the surface of carbon steel and after 3 days of exposure in the uninhibited and inhibited 2 M HCl. Figure 5 shows the EDS analysis result on the composition of carbon steel only without the acid and inhibitor treatment. The EDS analysis indicates that only Fe and oxygen were detected, which shows that the passive film contained only $Fe_2O_3$.

Figure (5) portrays the EDS analysis of carbon steel in 2 M HCl only and in the presence of $18x10^{-6}$ M of drugs (quinazoline derivatives). The spectra show additional lines, demonstrating the existence of C (owing to the carbon atoms of quinazoline derivatives). These data shows that the carbon and N atoms covered the specimen surface. This layer is entirely owing to the inhibitor, because the carbon and N signals are absent on the specimen surface exposed to uninhibited HCl. It is seen that, in addition to Mn, O, C. and N were present in the spectra. A comparable elemental distribution is shown in Table (4).

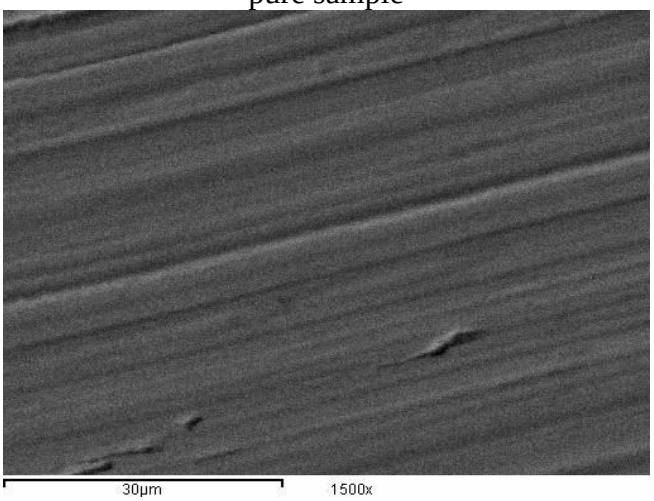
**Table 4.** Surface composition (weight %) of carbon steel alloy after 3hours immersion in 2 M HCl without and with 18 x $10^{-6}$ M of the studied inhibitors

| (Mass %) | Fe | Mn | C | O | N |
|---|---|---|---|---|---|
| carbon steel alone | 96.78 | 0.66 | 2.56 | -- | -- |
| Blank | 55.74 | -- | 2.34 | 41.92 | -- |
| Inhibitor 1 | 74.08 | 0.72 | 7.11 | 15.13 | 1.98 |
| Inhibitor 2 | 71.37 | 0.63 | 6.45 | 19.88 | 1.67 |
| Inhibitor 3 | 68.89 | 0.61 | 4.45 | 25.04 | 1.01 |

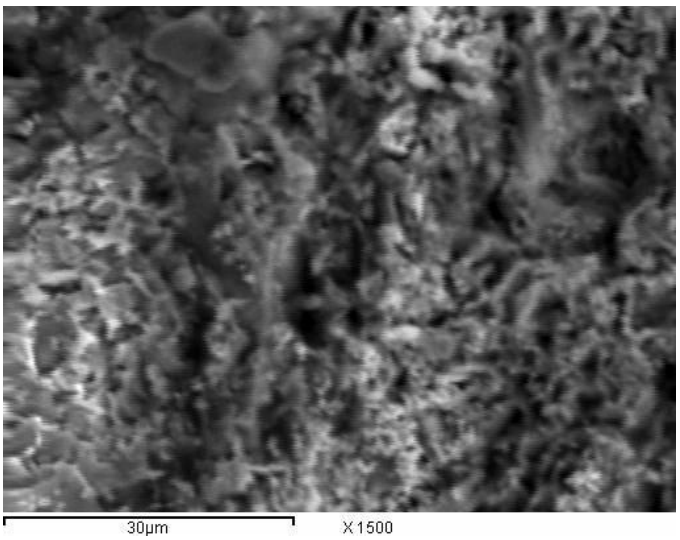
*3.5. Scanning Electron Microscopy (SEM) Studies*

Figure (6) represents the micrography obtained for carbon steel samples in presence and in absence of 18 x 10-6 M drugs (quinazoline derivatives) after exposure for 3 days immersion. It is clear that carbon steel surfaces suffer from severe corrosion attack in the blank sample.

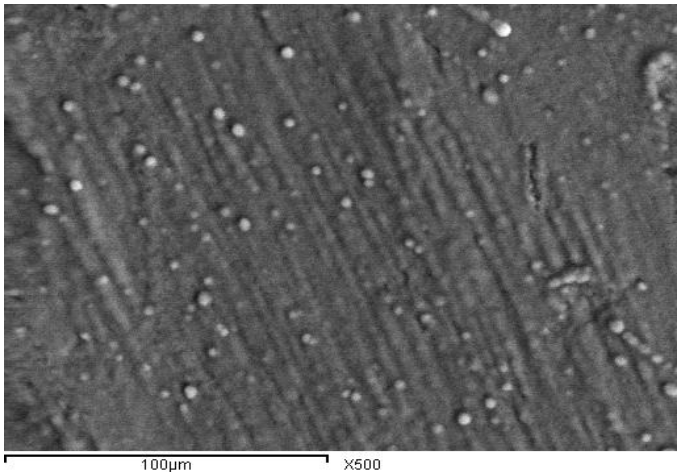
pure sample



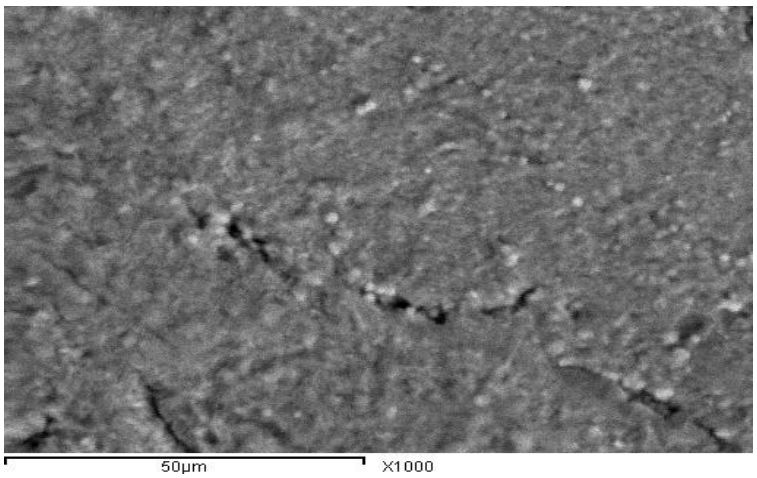

Blank



Inhibitor 1




Inhibitor 2




Inhibitor 3

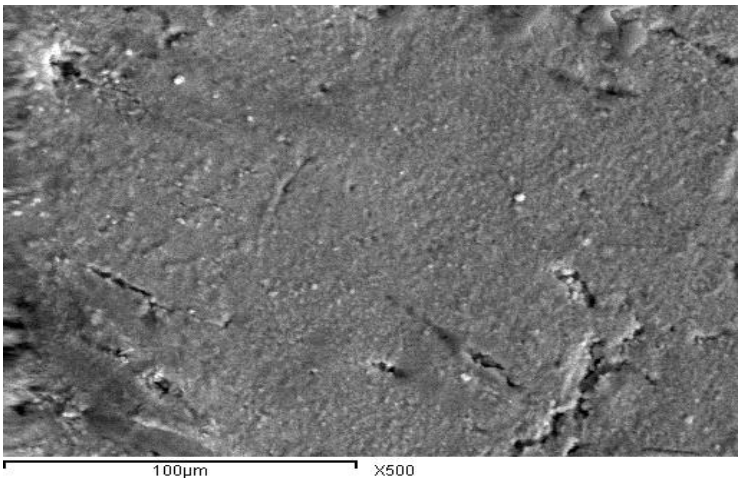



**Figure 6.** SEM micrographs for carbon steel in absence and presence of $18x10^{-6}$ M of drugs (quinazoline derivatives)

It is important to stress out that when the compound is present in the solution, the morphology of carbon steel surfaces is quite different from the previous one, and the specimen surfaces were smoother. We noted the formation of a film which is distributed in a random way on the whole surface of the carbon steel. This may be interpreted as due to the adsorption of the drugs (quinazoline derivatives) on the carbon steel surface incorporating into the passive film in order to block the active site present on the carbon steel surface. Or due to the involvement of inhibitor molecules in the interaction with the reaction sites of carbon steel surface, resulting in a decrease in the contact between carbon steel and the aggressive medium and sequentially exhibited excellent inhibition effect [29, 30].

### *3.6. Adsorption Isotherm*

Organic molecules inhibit the corrosion process by the adsorption on metal surface. Theoretically, the adsorption process can be regarded as a single substitutional process in which an inhibitor molecule, I, in the aqueous phase substitutes an "x" adsorbed on the metal surface [31-32] vis,

$$I_{(aq)} + xH_2O_{(sur)} \longrightarrow I_{(sur)} + xH_2O_{(aq)} \quad (5)$$

where x is known as the size ratio and simply equals the number of adsorbed water molecules replaced by a single inhibitor molecule. The adsorption depends on the structure of the inhibitor, the type of the metal and the nature of its surface, the nature of the corrosion medium and its pH value, the temperature and the electrochemical potential of the metal-solution interface. Also, the adsorption provides information about the interaction among the adsorbed molecules themselves as well as their interaction with the metal surface.

The values of surface coverage, θ, for different concentration of the studied compounds at different temperatures have been used to explain the best isotherm to determine the adsorption process.

By far the results of investigated inhibitors were best fitted by Temkin adsorption isotherm. Figure (7) show the plotting of θ against log C at 25$^o$C for investigated inhibitors. These plots gave straight lines indicating that the adsorption of investigated compounds on carbon steel surface follows Temkin adsorption isotherm [31]**.** In all cases the values of $R^2$ were near to unity indicating a Temkin adsorption isotherm.

$$\theta = (1/f) \ln K_{ads}C \quad (6)$$

where C is the concentration of inhibitor, θ the fractional surface coverage and $K_{ads}$ is the adsorption equilibrium constant related to the free energy of adsorption $\Delta G_{ads}$ as:

$$K_{ads} = 1/ 55.5 \exp (-\Delta G_{ads}/ RT) \quad (7)$$

Where R is the universal gas constant, T is the absolute temperature. The value 55.5 is the concentration of water on the metal surface in mol/ l.

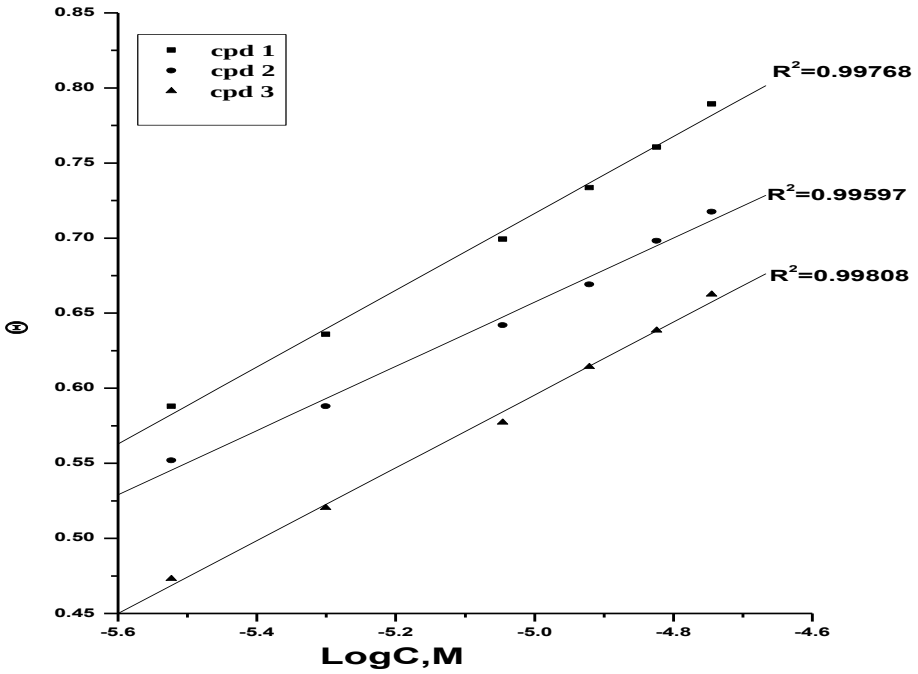



**Figure 9.** Temkin adsorption isotherm for investigated inhibitors for corrosion of carbon steel in 2 M HCl at 25°C

The values of $K_{ads}$ and $\Delta G^{o}_{ads}$ for drugs (quinazoline derivatives) were calculated and are recorded in Table (5). The low negative values of $\Delta G^{o}_{ads,}$ indicate that these derivatives are adsorbed physically on carbon steel surface, also ensures the spontaneity of the adsorption process and the stability of adsorbed layer on the carbon steel surface. The values of $K_{ads}$ were found to run parallel to the % IE ($K_1 > K_2 > K_3$). This result reflects the increasing capability, due to structural formation, on the metal surface [32].

**Table 5.** Equilibrium constant and adsorption free energy of the investigated drugs adsorbed on carbon steel surface at 25 ºC

| Inhibitors | Kinetic model | | | Temkin | | |
|---|---|---|---|---|---|---|
| | 1/y | K $M^{-1}$ | $-\Delta G^{\circ}_{ads.}$, kJ $mol^{-1}$ | f | K $M^{-1}$ | $-\Delta G^{\circ}_{ads.}$, kJ $mol^{-1}$ |
| (1) | 0.52 | 602.64 | 42.9 | 9.0 | 1.34 | 10.86 |
| (2) | 0.40 | 512.94 | 42.5 | 10.7 | 1.32 | 10.65 |
| (3) | 0.43 | 246.74 | 40.7 | 9.4 | 1.36 | 10.71 |

*3.7 Effect of temperature*

The effect of temperature on the rate of corrosion of carbon steel in 2 M HCl containing different concentrations from investigated inhibitors was tested by weight loss measurements over a temperature range from 25- 40$^{o}$C. The effect of increasing temperature on the corrosion rate and % IE obtained from weight loss measurements.

The results revealed that, the rate of corrosion increases as the temperature increases and decreases as the concentration of these compounds increases for all compound used. The activation energy ($E^{*}_{a}$) of the corrosion process was calculated using Arrhenius equation:

$$k=A \exp (-E_a^{*} / RT) \quad (8)$$

where k is the rate of corrosion and A is the Arrhenius constant. Figure 8 represents the Arrhenius plot in the presence and absence of compound (1) (similar curves are obtained in presence of the other inhibitors, but not shown). $E^{*}_{a}$ values determined from the slopes of these linear plots are shown in Table 5. The linear regression ($R^2$) is close to 1 which indicates that the corrosion of carbon steel in 2 M HCl solution can be elucidated using the kinetic model. Table 5 showed that the value of $E^{*}_{a}$ for inhibited solution is higher than that for uninhibited solution, suggesting that dissolution of carbon steel is slow in the presence of inhibitor and can be interpreted as due to physical adsorption[33]. It is known from Eq. 8 that the higher $E^{*}_{a}$ values lead to the lower corrosion rate. This is due to the formation of a film on the carbon steel surface serving as an energy barrier for the carbon steel corrosion [34].

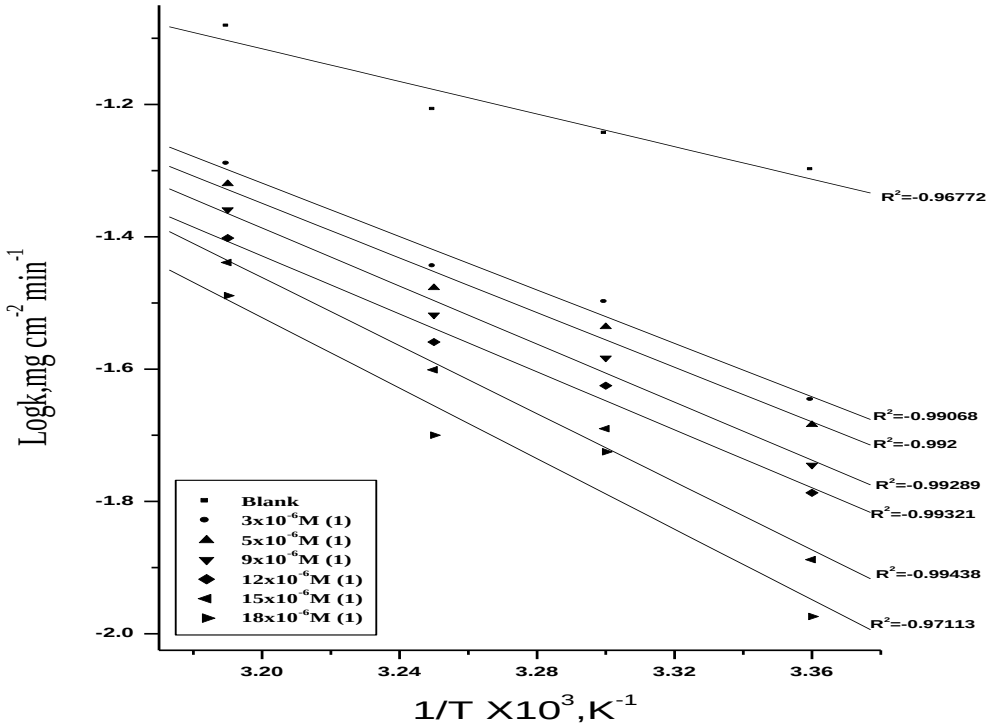



**Figure 8.** Log k – 1/T curves for carbon steel dissolution in 2 M HCl in the absence and presence of compound (1)

Enthalpy and entropy of activation ($\Delta H^*$, $\Delta S^*$) of the corrosion process were calculated from the transition state theory (Table 5):

$$Rate = (RT/ Nh) \exp (\Delta S^*/R) \exp (-\Delta H^*/RT) \quad (9)$$

where h is Planck's constant and N is Avogadro's number.

A plot of log (Rate/ T) vs. 1/ T for carbon steel in 2 M HCl at different concentrations from investigated compounds, gives straight lines as shown in Fig. 9 for compound (1) (similar curves are obtained in presence of the other inhibitors, but not shown). The positive signs of $\Delta H^*$ reflect the endothermic nature of the steel dissolution process. Large and negative values of $\Delta S^*$ imply that the activated complex in the rate-determining step represents an association rather than dissociation step, meaning that decrease in disordering takes place on going from reactants to the activated complex [35, 36].

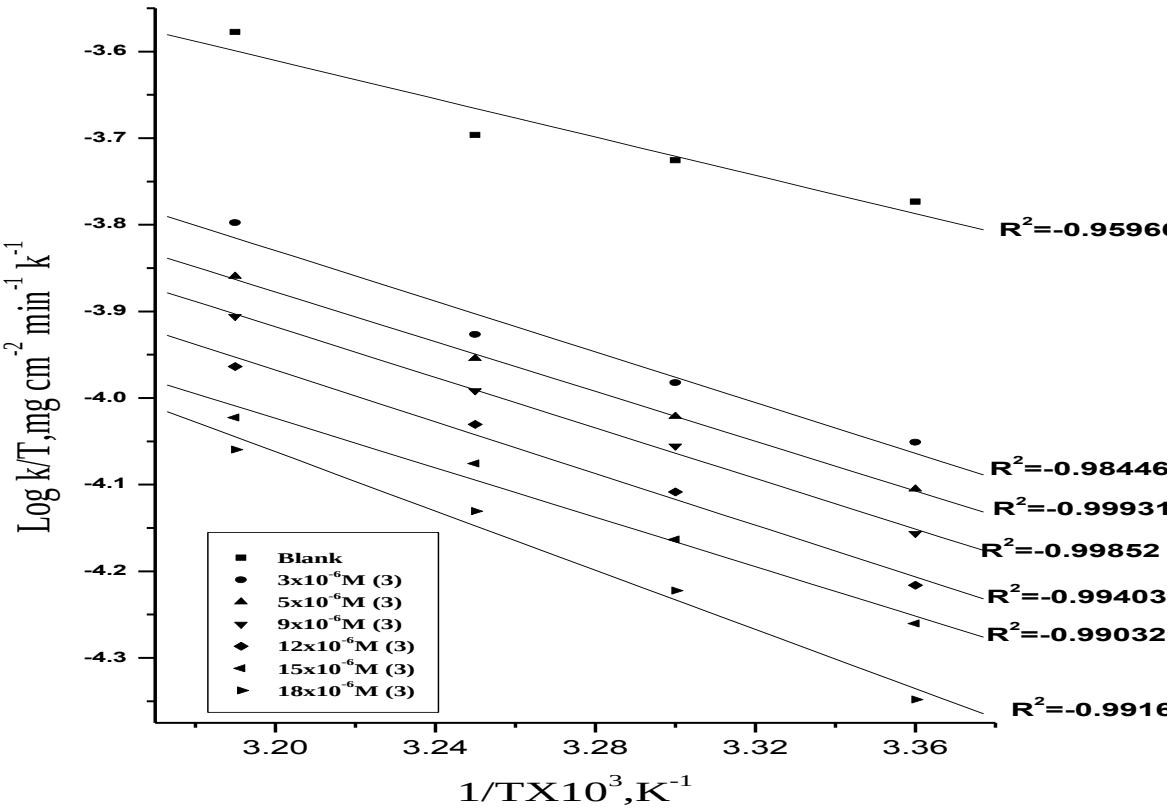



**Figure 9.** log k/T – 1/T curves for carbon steel dissolution in 2 M HCl in the absence and presence of different concentrations of compound (1)

**Table 5.** Activation parameters of the corrosion of carbon steel in 2 M HCl at $18X10^{-6}$ M for drugs (quinazoline derivatives)

| Comp. | Conc., M | $E_a^*$, kJ $mol^{-1}$ | $\Delta H^*$, kJ $mol^{-1}$ | $-\Delta S^*$, J $mol^{-1}K^{-1}$ |
|---|---|---|---|---|
| Blank | | 23.6 | 21.2 | 198.9 |
| 1 | $3X10^{-6}$ | 39.3 | 36.9 | 153.2 |
| | $5X10^{-6}$ | 42.4 | 40.1 | 143.7 |
| | $9X10^{-6}$ | 44.3 | 41.8 | 138.7 |
| | $12X10^{-6}$ | 47.2 | 52.0 | 106.8 |
| | $15X10^{-6}$ | 57.4 | 56.9 | 92.0 |
| | $18X10^{-6}$ | 65.9 | 64.6 | 68.8 |
| 2 | $3X10^{-6}$ | 38.7 | 36.2 | 154.6 |
| | $5X10^{-6}$ | 39.5 | 37.1 | 152.4 |
| | $9X10^{-6}$ | 42.0 | 39.6 | 145.2 |
| | $12X10^{-6}$ | 41.9 | 39.5 | 146.3 |
| | $15X10^{-6}$ | 49.3 | 46.8 | 123.4 |
| | $18X10^{-6}$ | 51.0 | 48.6 | 118.9 |
| 3 | $3X10^{-6}$ | 30.4 | 28.0 | 181.2 |
| | $5X10^{-6}$ | 29.9 | 27.5 | 183.7 |
| | $9X10^{-6}$ | 30.4 | 27.9 | 183.1 |
| | $12X10^{-6}$ | 31.0 | 28.6 | 182.1 |
| | $15X10^{-6}$ | 29.7 | 27.3 | 187.1 |
| | $18X10^{-6}$ | 35.2 | 32.7 | 170.6 |

The order of the inhibition efficiencies of quinazoline derivatives as gathered from the increase in $E_a^*$ and $\Delta H^*$ values and decrease in $\Delta S^*$ values are as follows: (1) > (2) > (3)

### *3.8. Chemical Structure of the Inhibitors and Corrosion Inhibition*

Inhibition of the corrosion of carbon steel in 2 M HCl solution by some drugs (quinazoline derivatives) is determined by weight loss, potentiodynamic anodic polarization measurements, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) studies, it was found that the inhibition efficiency depends on concentration, nature of metal, the mode of adsorption of the inhibitors and surface conditions. The observed corrosion data in presence of these inhibitors, namely: i) The decrease of corrosion rate and corrosion current with increase in concentration of the inhibitor ii) The linear variation of weight loss with time iii) The shift in Tafel lines to higher and lower potential regions iv) The decrease in corrosion inhibition with increasing temperature indicates that desorption of the adsorbed inhibitor molecules takes place and v) The inhibition efficiency was shown to depend on the number of adsorption active centers in the molecule and their charge density.

The corrosion inhibition is due to adsorption of the inhibitors at the electrode/ solution interface, the extent of adsorption of an inhibitor depends on the nature of the metal, the mode of

adsorption of the inhibitor and the surface conditions. Adsorption on carbon steel surface is assumed to take place mainly through the active centers attached to the inhibitor and would depend on their charge density. Transfer of lone pairs of electrons on the nitrogen atoms to the carbon steel surface to form a coordinate type of linkage is favored by the presence of a vacant orbital in iron atom of low energy. Polar character of substituent in the changing part of the inhibitor molecule seems to have a prominent effect on the electron charge density of the molecule. It was concluded that the mode of adsorption depends on the affinity of the metal towards the π-electron clouds of the ring system. Metals such as Cu and Fe, which have a greater affinity towards aromatic moieties, were found to adsorb benzene rings in a flat orientation. The order of decreasing the inhibition efficiency of the investigated compounds in the corrosive solution was as follow: 1 > (2) > (3)

Compound (1) exhibits excellent inhibition power due to:(i) its larger molecular size (451.47)that may facilitate better surface coverage, and (ii) the presence electron releasing groups (5O and5N atoms) which enhance the delocalized π-electrons on the active centers of the compound. Compound (2) comes after compound (1) in inhibition efficiency because it has lesser molecular size (387.47) and 4O and 5N atoms as active centers. Compound (3) has the lowest inhibition efficiency in spite of it has the same number of Active centers (4O and 5N atoms).This is due to it has the lowest molecular size (383.40)

## 4. CONCLUSIONS

1) The tested drugs (quinazoline derivatives) establish a very good inhibition for carbon steel corrosion in HCl solution

2) Drugs (quinazoline derivatives) inhibit carbon steel corrosion by adsorption on its surface and act better than the passive oxide film

3) The inhibition efficiency is in accordance to the order: 1 > 2 > 3

4) The inhibition efficiencies of the tested compounds increase with increasing of their concentrations

5) Double layer capacitances decrease with respect to blank solution when the inhibitor added. This fact may explained by adsorption of the inhibitor molecule on the carbon steel surface

6) The adsorption of these compounds on carbon steel surface in HCl solution follows Temkin adsorption isotherm

7) The values of inhibition efficiencies obtained from the different independent techniques showed the validity of the obtained results

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