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### Using antibiotic as corrosion inhibitor of carbon steel in acidic media

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#### Abstract

The inhibiting effect of some antibiotic such as amoxicillin on the corrosion of carbon steel in 1 M HCl was studied by weight loss. The results showed that the inhibition efficiency increases with increasing the inhibitor concentration, while it decreases with increasing the temperature. The adsorption of amoxicillin on the carbon steel surface obeys langmire adsorption isotherm. Some thermodynamic parameters were calculated and discussed amoxicillin is mixed-type inhibitors but the cathode is more polarized than the anode. The results obtained from chemical techniques are in good agreement.

**Key words:** Antibiotics, corrosion, carbon steel.

#### Introduction

Corrosion inhibition of carbon steel in acid solutions has become one of the most urgent and severe challenges in acid pickling process to prevent undesirable metal dissolution and excess acid consumption [1–7]. Recent interests for corrosion inhibition focus on non-toxic and environmental-friendly inhibitors due to more stringent environment quality requirements [8–10]. Various effective inhibitors have been reported to inhibit steel corrosion in various acid solutions, which are commonly organic compounds having  $\pi$ -bonds and hetero atoms [11–16].

Amoxicillin as a heterocyclic compounds have aromaticity,  $\pi$ -bonds and functional groups such as =NH, R=OH, R=R, etc. amoxicillin is readily available, nontoxic and biodegradable.

In the present work, the inhibitive effects and mechanism of amoxicillin have been studied for carbon steel in 1 M HCl in the concentration range  $4 \times 10^{-6}$  to  $10 \times 10^{-6}$  M at 25–55°C. Weight loss were performed on amoxicillin as inhibitor for carbon steel corrosion in 1 M HCl

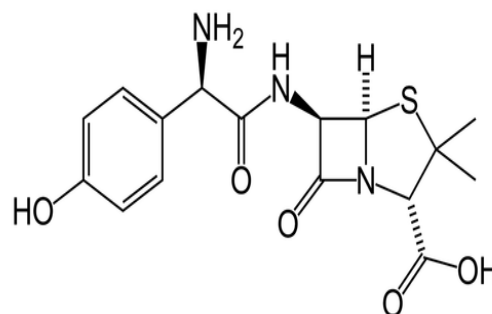
#### Material and Methods

##### Material and Solutions

Carbon steel strips (BDH grade) containing (weight %): 0.2 C, 0.024 P, 0.003 Si, 0.35 Mn, and rest Fe were used in this investigation. All chemicals used were of AR grade. Specimens of C-steel strips were abraded successively by emery papers of different grades, i.e. 320, 400, 600, 800 and 1000 finally polished with a 4/0 emery paper to obtain mirror like finish, then degreased ultrasonically with ethyl alcohol and rinsed with bidistilled water several times and dried between two filter papers. AR grade hydrochloric acid (37 %) was used for preparing the corrosive solutions.

Appropriate concentration of aggressive solutions used (1 M HCl) was prepared by dilution using bidistilled water.

##### The structure of amoxicillin:



##### Weight loss measurements

For weight loss measurements, rectangular C-steel specimens of size 20 x 20 x 2 mm were immersed in 100 ml inhibited and uninhibited solutions and allow

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to stand for several intervals at  $25 \pm 1^\circ\text{C}$  in water thermostat. Therefore, the weight losses ( $W$ ) given by:

$$W = (m_1 - m_2) \quad (1)$$

where  $m_1$  and  $m_2$  are the weights of metal before and after exposure to the corrosive solution, respectively. The percentage inhibition efficiency (% IE) and the degree of surface coverage ( $\theta$ ) of the investigated compounds were calculated from the following equations:

$$\%IE = \theta \times 100 = \left(1 - \frac{W_{(inh)}}{W_{(free)}}\right) \times 100 \quad (2)$$

where,  $W_{free}$  and  $W_{inh}$  are the weight loss in the absence and presence of inhibitor, respectively.

### Results and Discussion

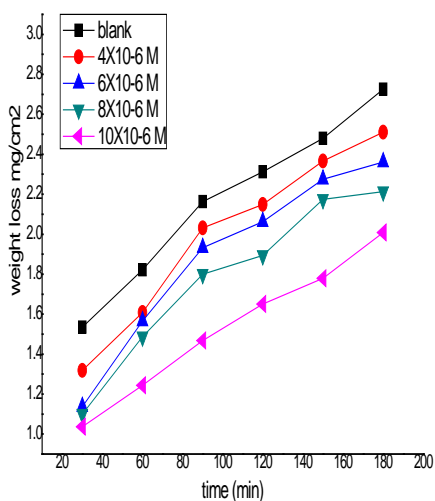


Figure 1. Weight loss-time curves for the corrosion of C-steel in 1 M HCl in the absence and presence of different concentrations of inhibitor at  $25^\circ\text{C}$ .

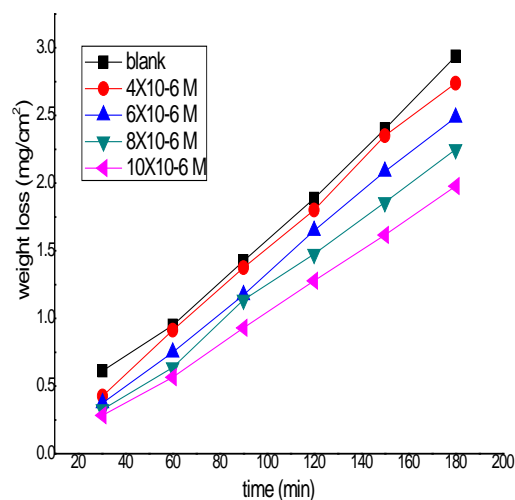


Figure 2. Weight loss-time curves for the corrosion of C-steel in 1 M HCl in the absence and presence of different concentrations of inhibitor at  $35^\circ\text{C}$ .

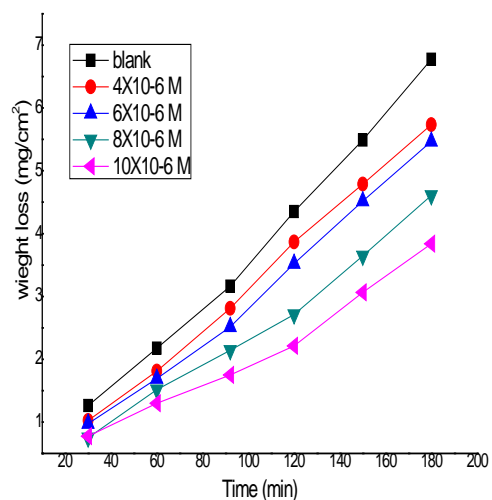
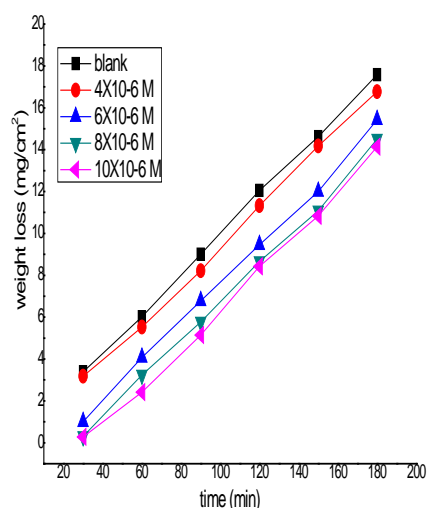


Figure 3. Weight loss-time curves for the corrosion of C-steel in 1 M HCl in the absence and presence of different concentrations of inhibitor at  $45^\circ\text{C}$ .



**Figure 4. Weight loss-time curves for the corrosion of C-steel in 1 M HCl in the absence and presence of different concentrations of inhibitor at 55°C.**

Weight loss Figure 1-4 shows the effect of concentration of inhibitor on the weight loss vs. time of C-steel at 25°C-55°C.. It is obvious that the weight loss of C-steel in presence of inhibitors varies linearly with time, and is much lower than that obtained in blank solution. The linearity obtained indicated the absence of insoluble surface film during corrosion and that the inhibitors were first adsorbed onto the metal surface and, therefore, impede the corrosion process [17].

The calculated values of the percentage inhibition efficiency (% IE) at different concentrations of amoxicillin in 1 M HCl at different temperatures (25- 55°C) are given in Tables 1, 2. From these Tables, the inhibition efficiency increases by increasing the concentrations of inhibitor and decreases by raising the temperature. This behavior could be attributed to the increase of the number of adsorbed molecules at the metal surface and by raising the temperature there is a desorption of inhibitor molecules from the metal surface.

**Table 1. Corrosion rate (C.R.) in (mg cm<sup>-2</sup> min<sup>-1</sup>) and inhibition efficiency data obtained from weight loss measurements for carbon steel in 1 M HCl solution in the absence and presence of different concentrations of inhibitor at 25°C.**

| Conc.X<br>10 <sup>-6</sup> M | Corrosion Rate<br>(CR) mg cm <sup>-2</sup><br>min <sup>-1</sup> | θ     | IE%   |
|------------------------------|---|-------|-------|
| 1 M HCl                      | 0.05  | ----- | ----- |
| 4                            | 0.0163  | 0.674 | 67.4  |
| 6                            | 0.0148  | 0.704 | 70.4  |
| 8                            | 0.0125  | 0.75  | 75    |
| 10                           | 0.009   | 0.82  | 82    |

**Table 2. Data of weight loss measurements for carbon steel in 1 M HCl solution in the absence and presence of different concentrations of inhibitor at 35-55°C.**

| Conc.X<br>10 <sup>-6</sup> M | 35°C  |      | 45°C   |       | 55°C   |       |
|------------------------------|-------|------|--------|-------|--------|-------|
|                              | θ     | IE%  | θ      | IE%   | θ      | IE%   |
| 4                            | 0.653 | 65.3 | 0.6025 | 60.25 | 0.4801 | 48    |
| 6                            | 0.686 | 68.6 | 0.645  | 64.5  | 0.6205 | 62.05 |
| 8                            | 0.691 | 69.1 | 0.674  | 67.4  | 0.60   | 60    |
| 10                           | 0.777 | 77   | 0.7408 | 74.08 | 0.697  | 69.7  |

### Adsorption isotherm

Basic information on the interaction between the inhibitors and the C-steel can be provided by the adsorption isotherm. Two main types of interaction can describe the adsorption of the compound: physical adsorption and chemical adsorption. These are influenced by the chemical structure of the inhibitor, the type of the electrolyte, the charge and nature of the metal. The surface coverage, θ, of the metal surface by the adsorbed inhibitor was evaluated from weight loss measurements using equation (2). The θ values of different inhibitor concentrations at 25 °C were tested by fitting to various isotherms including, Frumkin, Langmuir, Temkin and Flory-Huggins. By far the best fit was obtained with the Langmuir isotherm is given as [18].

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (3)$$

where C is the inhibitor concentration and K<sub>ads</sub> is the equilibrium constant of adsorption

A plot of (C /θ) against C, for all concentrations of inhibitor (Figure 5) a straight line relationship was

obtained in all cases with correlation coefficients ( $R^2$ ) in more than 0.994. The standard free energy of adsorption  $\Delta G_{ads}^\circ$  can be calculated from Eq. (4):

$$K_{ads} = \frac{1}{55.5} e^{\frac{-\Delta G_{ads}^\circ}{RT}} \quad (4)$$

The value of 55.5 is the concentration of water in solution expressed in mole per liter, R is the universal gas constant and T is the absolute temperature.

The deviation of the slope from unity as observed from this study could be interpreted that there are interactions between adsorbed species on the metal surface as well as changes in adsorption heat with increasing surface coverage [19, 20], factors that were ignored in the derivation of Langmuir isotherm. The negative  $\Delta G_{ads}^\circ$  values (Table 3) are consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the C-steel surface [21].

It is generally accepted that the values of  $\Delta G_{ads}^\circ$  up to  $-20 \text{ kJ mol}^{-1}$  the types of adsorption were regarded as physisorption, the inhibition acts due to the electrostatic interaction between the charged molecules and the charged metal, while the values around  $-40 \text{ kJ mol}^{-1}$  or larger, were seen as chemisorption, which is due to the charge sharing or a transfer from the inhibitor molecules to the metal surface to form covalent bond [22, 23]. The  $\Delta G_{ads}^\circ$  values obtained in this study range from  $-36.2$  to  $-36.7 \text{ kJ mol}^{-1}$ . It suggested that the adsorption mechanism of investigated inhibitors on C-steel in 1 M HCl solution was typical of physisorption and chemisorption (mixed one).

Moreover, the adsorption heat can be calculated according to the Van't Hoff equation (5) [24]:

$$\ln K = -\frac{\Delta H_{ads}^\circ}{RT} + \text{const} \quad (5)$$

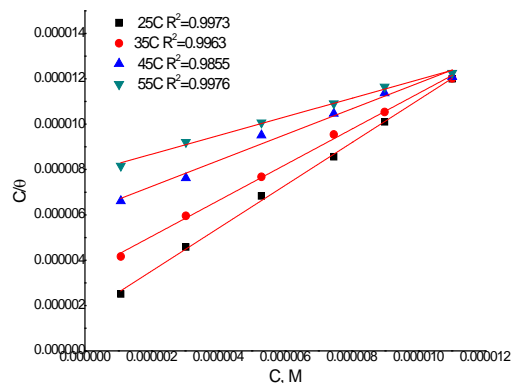
Figure 6 show the plot of  $\log K$  vs.  $1/T$  for carbon steel dissolution in 1 M HCl in the presence of inhibitor. The  $\Delta H_{ads}^\circ$  values (Table 3) are negative, which show that the adsorption is an exothermic process [25].

Finally, the standard adsorption entropy  $\Delta S_{ads}^\circ$  can be calculated by the equation (6):

$$\Delta S_{ads}^\circ = \frac{\Delta H_{ads}^\circ - \Delta G_{ads}^\circ}{T} \quad (6)$$

The  $\Delta S_{ads}^\circ$  values (Table 3) are negative, which show that the adsorption is an exothermic process and always accompanied by a decrease of entropy. The

reason can be explained as follows: the adsorption of organic inhibitor molecules from the aqueous solution. Table 3 lists all the above calculated thermodynamic parameters [26-27].



**Figure 5. Langmuir adsorption isotherm of inhibitor on C-steel surface in 1 M HCl at different temperatures.**

**Table 3. Thermodynamic parameters for the adsorption of the inhibitor on carbon steel surface in 1 M HCl at different temperatures**

| Temp. K | $K_{ads} \times 10^4 \text{ M}^{-1}$ | $\Delta G_{ads}^\circ$ ,<br>kJ mol <sup>-1</sup> | $\Delta H_{ads}^\circ$ ,<br>kJ mol <sup>-1</sup> | $-\Delta S_{ads}^\circ$ ,<br>J mol <sup>-1</sup> K <sup>-1</sup> |
|---------|--------------------------------------|--|--|--|
| 298     | 77.25                                | 42.99  | 76.23  | 108.59   |
| 308     | 52.87                                | 42.90  |  | 106.77   |
| 318     | 38.96                                | 42.36  |  | 105.34   |
| 328     | 17.26                                | 42.02  |  | 111.85   |
|         |                                      |  |  | 3  |

#### Kinetic-thermodynamic corrosion parameters

As noticed previously, the adsorption process was well elucidating by using a thermodynamic model, in addition a kinetic-thermodynamic model was another tool to explain the mechanism of corrosion inhibition for an inhibitor. The apparent effective activation energies ( $E_a^*$ ) for the corrosion reaction of C-steel in HCl in the absence and presence of different concentrations of this compound were calculated from Arrhenius-type equation (7) [28]:

$$\text{Rate } (k) = A e^{\frac{-E_a^*}{RT}} \quad (9)$$

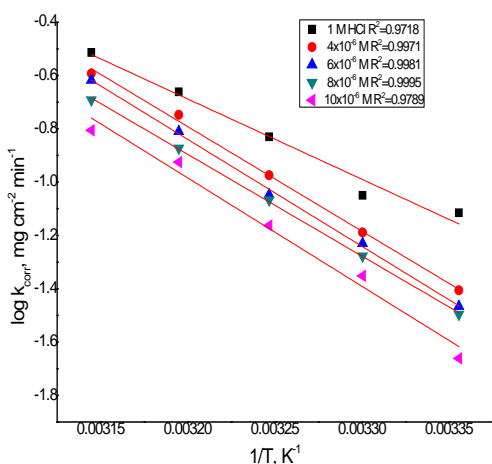
where A is the Arrhenius pre-exponential factor. A plot of  $\log k$  (corrosion rate) vs.  $1/T$  gave straight lines as shown in (Figure 4). The entropy of activation

( $\Delta S^*$ ) and the enthalpy of activation ( $\Delta H^*$ ) for the intermediate complex in the transition state for the corrosion of C-steel in HCl in the absence and presence of different concentrations of investigated compounds were obtained by applying the transition-state equation (8) [29-30]:

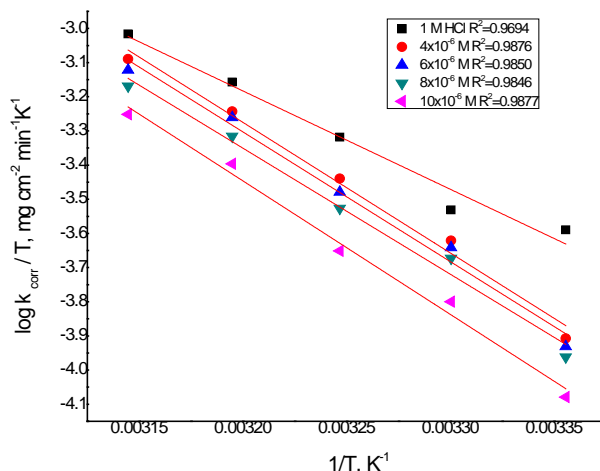
$$\text{Rate (k)} = \frac{RT}{Nh} e^{\frac{\Delta S^*}{R}} e^{\frac{-\Delta H^*}{RT}} \quad (10)$$

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

A plot of  $\log k$  (corrosion rate) /  $T$  vs.  $1/T$  should give a straight lines (Figure 5), with a slope of  $(-\Delta H^* / 2.303R)$ , and an intercept of  $[(\log(RT / Nh) + (\Delta S^* / 2.303R)]$  [31,32], from which the values of  $\Delta H^*$  and  $\Delta S^*$  were calculated, respectively. (Table 4) exhibited values of apparent activation energy, apparent enthalpies  $\Delta H^*$  and entropies  $\Delta S^*$  for C-steel dissolution in 1 M HCl solution in the absence and presence of different concentration of this compound. The presence of inhibitor increased the activation energies of C-steel indicating strong adsorption of the inhibitor molecules on the metal surface and the presence of these additives induces the adsorption of these additives on the surface of C-steel. Values of the entropy of activation  $\Delta S^*$  in the absence and in presence of the studied compounds are negative. This implies that the activated complex in the rate determining step represents an association rather than a dissociation step [33]. This means that the activated molecules were in higher order state than that at the initial stage [34, 35].



**Figure 6. Arrhenius plots for C-steel corrosion rates ( $k_{\text{corr}}$ ) after 120 minutes of immersion in 1 M HCl in the absence and presence of different concentrations.**



**Figure 7. Plots of ( $\log k_{\text{corr}}$ ) vs.  $1/T$  for corrosion of C-steel in 1 M HCl in the absence and presence of different concentration.**

**Table 4. Activation parameters for the dissolution of carbon steel in the presence and absence of different concentration of inhibitor in 1 M HCl.**

| Conc., x $10^{-6}$ M | Activation parameters |                             |                                       |
|----------------------|-----------------------|-----------------------------|---------------------------------------|
|                      | $E_a$ kJ mol $^{-1}$  | $\Delta H^*$ kJ mol $^{-1}$ | $-\Delta S^*$ J mol $^{-1}$ K $^{-1}$ |
| blank                | 54.60                 | 22.91                       | 77.18                                 |
| 4                    | 68.02                 | 31.25                       | 84.22                                 |
| 6                    | 74.25                 | 44.17                       | 91.07                                 |
| 8                    | 81.47                 | 57.46                       | 98.33                                 |
| 10                   | 93.01                 | 69.03                       | 101.25                                |

### Conclusion

From the overall experimental results the following conclusions can be deduced: The amoxicillin is good inhibitor and act as mixed type inhibitor for carbon steel corrosion in 1 M HCl solution. The results obtained from all measurements showed that the inhibiting action increases with the inhibitor concentration and decreases with the increasing in temperature. This fact confirms the adsorption of the compound molecules on the carbon steel surface. The adsorption of inhibitor on the carbon steel surface at different temperature was found to obey the Langmuir adsorption isotherm and this adsorption is physisorption. The values of inhibition efficiencies obtained from the different independent quantitative techniques used show the validity of the results.

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