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# Corrosion Inhibition of Carbon Steel (XC 38) in Hydrochloric Acid by Potassium Iodide

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**Abstract.** The corrosion inhibition of XC38 carbon steel in 1 M hydrochloric acid solutions by iodide potassium was studied at temperature range (293-333K) by gravimetric measurements. The inhibition efficiency decreases with increasing temperature. The adsorption of iodid potassium takes place according to Langmuir's adsorption isotherm. Kinetic parameters (activation energy  $E_a$ , enthalpy of activation  $\Delta H_a$  and entropy of activation  $\Delta S_a$ ) as well as thermodynamic parameters (enthalpy of adsorption  $\Delta H_{ads}$ , entropy of adsorption  $\Delta S_{ads}$  and Gibbs free energy  $\Delta G_{ads}$  were calculated and discussed; on the bases of these parameters both physisorption and chemisorption were suggested for this inhibitor. The adsorption of the inhibitor on the carbon steel surface is in agreement with Langmuir adsorption isotherm.

**Keywords:** Adsorption isotherm, Corrosion inhibition, Carbon steel, Potassium iodide, Thermodynamic parameters.

# **1. Introduction**

Corrosion of metals and alloys are defined as the spontaneous destruction or deterioration of alloys in the course of their chemical, electrochemical or biochemical interactions with the environment.

Some of the typical corrosive media are humid air, water, acids, bases as well as soil, steam, and gases. Strong acids such as hydrochloric and sulphuric acids are widely used in industries for many purposes, especially in cleaning, descaling, and pickling procedures [1].

The successful control of corrosion develops the life of mechanical hardware. Nowadays corrosion inhibitors have more significant, due to their usage in industries [2].

Corrosion inhibitors are substances added in small quantities to protect metals against corrosion by decreasing the rate of corrosion processes. The inhibition efficiency depends on the various parameters (corrosive medium, pH, temperature, duration of immersion, metal composition and on the nature of the inhibitor). Industrial corrosion inhibitors are generally of organic or inorganic compounds. The use of inorganic inhibitors as an alternative to organic compounds is based on the possibility of degradation of organic compounds with time, nature of medium and temperature [3, 4].

The objective of the present work is to study the inhibition of carbon steel corrosion in 1 M HCl solution by potassium iodide using weight loss method.

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### 2. Materials and Method

### **2.1.** Material preparation

The test solutions of 1 M of hydrochloric acid were prepared by the dilution of analytical grade 37% HCl with bi-distilled water. The carbon steel specimens having composition (wt.%) : 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 Fe is the remainder. The electrode was polished using different grades of emery papers (320 to 1200) and degreased. The specimens were weighed by analytical balance with five decimal accuracy before and after exposure. The weight loss experiments were performed after an exposure of two hours.

#### 2.2. Weight loss methods

Polished specimens were initially weighed in an analytical balance. Weighed samples are immersed in 50 mL of the acid 1 M HCl both in absence and presence of inhibitor for concentrations range from  $510^{-5}$  to  $5 \ 10^{-3}$  M. The specimens were taken out, washed with bi-distilled water, dried and weighed once again. The weight loss studies were made in triplicate and the loss of weight was calculated by taking an average of these values [5].

The inhibition efficiency (IE%) of potassium iodide was calculated using the formula (1).

$$IE(\%) = 100^{*}(w_{corr} - w_{inh})/w_{corr}$$
 (1)

Where  $W_{corr}$  corrosion rate of blank hydrochloric acid and  $W_{inh}$  corrosion rate after adding inhibitor. The corrosion rate (*w*) was calculated from the formula (2):

$$w = (m_1 - m_2)/S.t$$
 (2)

Where  $m_1$  is the mass of the specimen before corrosion,  $m_2$  the mass of the specimen after immersion in solution, S the total area of the specimen, t the corrosion time and w the corrosion rate.

The degree of surface coverage  $(\Theta)$  was calculated using following equation (3):

$$\Theta = 1 - (w_{inh}/w_{corr}) \tag{3}$$

### 3. Results and Discussion

There are many factors affecting on the corrosion rate, like concentation of inhibitor, temperature and time of immersion.

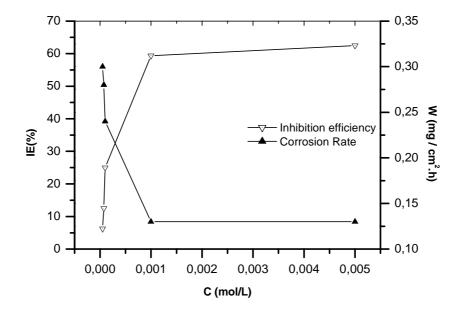
#### 3.1. Effect of inhibitor concentration

Corrosion inhibition efficiency of the inorganic inhibitor (potassium iodide) solution has been calculated using weight loss measurement after two hours of immersion. The tests were carried out in different concentration range from to  $5.10^{-5}$ M to  $5.10^{-3}$ M.

Table 1 collects the corrosion rates and Fig. 1 shows the variation of inhibition efficiencies and corrosion rates for different concentrations of inhibitor (KI) in hydrochloric acid 1 M at 303 K. The corrosion rate decreases with increasing inhibitor concentration and in turn the inhibition efficiency (IE%) increases to attain 62.5% at  $5.10^{-3}$  M.

**Table 1**.Corrosion parameters obtained from weight loss measurements for carbon steel XC38 in 1 M HCl containing various concentrations of the inhibitor at 303 K.

Inhibitor concentration	W (mg/cm <sup>2</sup> .h <sup>1</sup> )	IE (%)
0.0	0.32	-
5.10 <sup>-5</sup>	0.30	6.25
7.5 10 <sup>-5</sup>	0.28	12.50
10 <sup>-4</sup>	0.24	25.00
10 <sup>-3</sup>	0.13	59.37
<b>5</b> 10 <sup>-3</sup>	0.12	62.50



**Fig.1.** Variation of inhibition efficiency (IE%) and corrosion rate (w) with the concentration of potassium iodide for carbon steel (XC38) in 1 M HCl.

### **3.2. Effect of temperature**

The effect of temperature is an important parameter on the inhibited acid–metal reaction is highly complex, Further- more many changes occur on the metal surface such as rapid etching, adsorption/desorption of inhibitor and the inhibitor itself may undergo decomposition and/or rearrangement [6,7]. The collected curves in Fig. 2 show the evolution of corrosion rate with of inhibitor concentration at different temperatures (293 to 333K). It is indicates that at a given of inhibitor concentration the corrosion rate of XC38 increased with temperature. The increase is more pronounced at low concentrations.

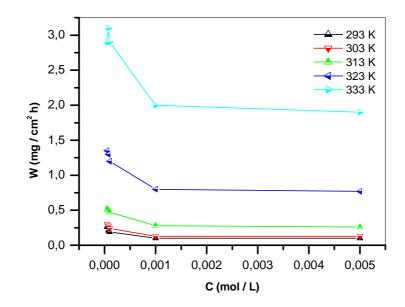
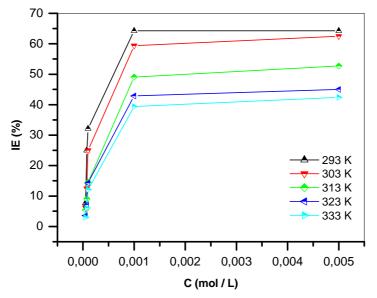


Fig.2. Variation of corrosion rate with the concentrations of KI for carbon steel in 1 M HCl at different temperatures.

It showed in the figure 3 that the inhibition efficiency decreases with increasing temperature indicating that higher temperature dissolution of carbon steel predominates on adsorption of inhibitor molecules at the mettalic surface.



**Fig.3.** Variation of inhibition efficiency (IE%) with concentration of KI for carbon steel in 1 M HCl at different temperatures.

The decrease of inhibition efficiency at elevated temperatures indicates than of the strength of the adsorption processes, suggesting a physical adsorption mode [8].

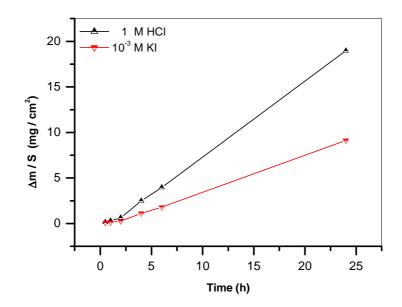
### 3.3. Immersion time

Weight loss and inhibition efficiency versus immersion time was described in the Table 2. As the immersion time increases, the inhibition performance also increases. The maximum inhibition efficiency value was found for 2 h (59.37%), after that slight decrease in efficiency was observed. The variation of the weight loss of carbon steel in 1 M HCl is nearly varied linearly with immersion period

in the absence and presence of  $10^{-3}$  M of potassium iodide, during an immersion time between one half hour and 24 hours at 303 K as shown in Fig. 4.

Time (h)	$\Delta m_{\rm corr}/{\rm S}~({\rm mg/cm}^2)$	$\Delta m_{inh}/S (mg/cm^2)$	IE (%)
1/2	0.14	0.08	42,85
1	0.30	0.13	55
2	0.64	0.26	59.37
4	2.48	1.12	54,83
6	3.96	1.80	54,54
24	18.96	9.12	51,89

**Table 2.** Effect of immersion time on inhibitor performance for carbon steel in 1 M HCl for 10<sup>-3</sup>M at 303 K



**Fig.4.** Weight loss versus immersion time of XC38 in 1 M HCl without and with 10<sup>-3</sup> M of KI at 303 K.

#### 3.4. Activation parameters

The Arrhenius equation was used to investigate the relationship between the rate of corrosion of carbon steel X38 and the activation energy, in the presence of various concentrations of inhibitor KI. It has been reported that the natural logarithm of the corrosion rate is a linear function with 1/T, where T is the absolute temperature, for the corrosion of carbon steel in acidic conditions [9, 10]. The equation can be written as follows [11, 12].

$$ln(w) = (-E_a / RT) + A \tag{4}$$

Where *w* is the corrosion rate of carbon steel, *A* is Arrhenius constant, *R* is the universal gas constant, *T* is the temperature and  $E_a$  is the activation energy. The plots of ln(w) against 1/T were linear, as shown in Figure 5. Simplification of Equation (4) yields Equation (5) [13]

$$w = (RT/Nh) \exp \left( \Delta S_a/R \right) \exp \left( -\Delta H_a/RT \right)$$
(5)

Where, h is Planck's constant, N the Avogadro's number, the apparent entropy of activation and the enthalpy of activation. A plot of ln (w/T) versus 1/T is shown in Figure 6. Straight lines were obtained with slope  $(-\Delta H_a/R)$  and intercept of  $((\Delta S_a/R) + ln (R/Nh))$ , from which the values of  $E_a$ ,  $\Delta H_a$  and  $\Delta S_a$  were calculated and listed in table 3.

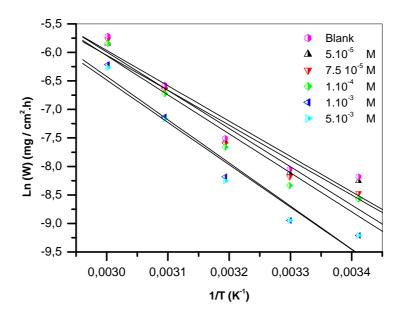


Fig.5. Arrhenius plot for the dissolution of carbon steel in 1 M HCl with and without inhibitor at various temperatures

 Table 3. Activation parameters for the carbon steel dissolution in 1 M HCl in absence and presence of different concentrations of KI

Inhibitor concentration (M)	E <sub>a</sub> (KJ/mol)	$\Delta H_a$ (KJ/mol)	$\Delta S_a (J/mol.K)$
0.0	50.903	48.307	-151.220
5.10 <sup>-5</sup>	51.719	49.124	-148.430
7.5 10 <sup>-5</sup>	55.734	53.139	-136.247
$10^{-4}$	56.870	54.274	-133.383
10 <sup>-3</sup>	62.932	60.336	-118.226
5 10 <sup>-3</sup>	61.768	59.172	-122.222

The increase in  $E_a$  in the presence of inhibitor indicates the physical adsorption that occurs on the electrode surface.

The positive sign of the enthalpies of activation in the absence and presence of various concentration of inhibitor reflects the endothermic nature of the steel dissolution process and that mean the dissolution of steel is difficult.

The entropy of activation increased in the presence of the inhibitor compared to free acid solution. The value of entropy is negative both in the absence and presence of inhibitor, and the increase of the entropy of activation is generally interpreted by the increase in disorder taking place in going from reactants to the activated complex [14, 15].

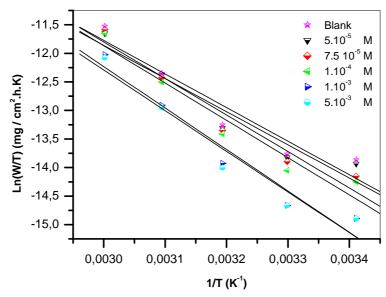


Fig.6. Transition Arrhenius plots of carbon steel in 1 M HCl with and without inhibitor at various temperatures

Moreover, the average difference value of the  $E_a-\Delta H_a$  is 2.59 kJ/mol, which is approximately equal to the average value of RT (2.60 kJ/mol) at 313 K. This indicates that the corrosion process is a unimolecular reaction as it is characterized by the following equation (6):.

$$E_a = \Delta H_a - RT \tag{6}$$

#### 3.5. Adorption isotherm

Adsorption isotherms furnish information about the interaction of the adsorbed molecules with the electrode surface [16]. The adsorption of the inhibitors can be described by two main types of interaction: Physisorption and/or chemisorption [17-19] : One is physical adsorption, which involves electrostatic forces between ionic charges or dipoles on the adsorbed species and the electric charge at the metal/solution interface. The heat of adsorption is low and therefore this type of adsorption is stable only at relatively low temperatures. The other is chemical adsorption, which involves charge transfer or sharing from the inhibitor molecules to the metal surface to form a coordinate type bond. This type of adsorption is known to have much stronger adsorption energy compared to the other mode of adsorption. Thus, such bond is more stable at higher temperatures.

The adsorption is also influenced by the structure and the charge of the metal surface, and the type of testing electrolyte [20-22].

The strong correlation ( $R^2$ >0.99) showed that the adsorption of the inhibitor molecules in 1M hydrochloric acid on the surface of electrode obeyed to the Langmuir's adsorption isotherm [23].

The plots of C/ $\Box$  versus C which is the Langmuir adsorption isotherm gives a straight line with an intercept of 1/K<sub>ads</sub> as shown in Fig. 7. Values of the equilibrium constant of adsorption calculated by fig 7, was use for the calculation of the standard free energy changes of adsorption ( $\Delta G_{ads}$ ) through according to Equation (7) [24,25].

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

Where

$$1G_{ads} = -RTln \left(55.5 K_{ads}\right) \tag{8}$$

Where R is the gas constant (8.314 J/mol.K) and T is the absolute temperature (k). The constant value of 55.5 is the concentration of water in solution in mol/L [28],  $K_{ads}$  is the adsorptive equilibrium constant (L/mol).

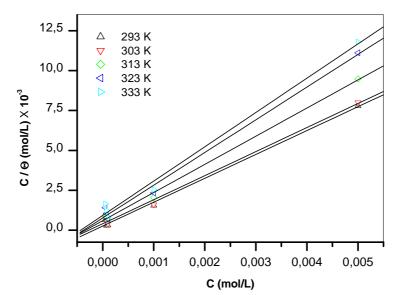


Fig.7. Langmuir isotherm for the adsorption of KI on XC 38 surface in 1M HCl

The negative values of the standard free energy of adsorption indicate the spontaneity of the adsorption process and the stability of the adsorbed species on the carbon steel surface [29, 30]. Usually, the energy values of -20 kJ/mol or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface, physisorption; those of -40 kJ/mol or more negative involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond, chemisorption [31, 32].

The values of thermodynamic parameters are listed in table 4.  $K_{ads}$  value decreased in this study with increase in the temperature indicating that adsorption of inhibitor on the carbon steel surface was unfavorable at higher temperature.

<b>Temperature (K)</b>	K <sub>ads</sub> (L/mol)	$\Delta H_{ads}(KJ/mol)$	$\Delta G_{ads}(KJ/mol)$	$\Delta S_{ads}(J/mol.K)$
293	3911.812		- 29.933	12.303
303	2477.455		- 29.804	11.472
313	1690.905	-26.328	- 29.794	11.076
323	1303.437		- 30.047	11.514
333	1073.933		- 30.441	12.351

 Table 4. Thermodynamic parameters of adsorption for carbon steel in 1 M HCl solution obtained from weight

 loss measurements

Inspection of Table 4 revealed that values the energy located - 29.933  $\square$   $\Delta G_{ads}$   $\square$  - 30.441 kJ/mol, less than the threshold value (-40 kJ/mol) required for chemical adsorption and the IE% decreased with increasing temperature. These support the mechanism of physical adsorption.

To calculate the enthalpy of adsorption and entropy of adsorption,  $lnK_{ads}$  was plotted against 1/T (Figure 8) and straight line was obtained with slope equal to (-  $\Delta H_{ads}/R$ ). According to the Van't Hoff equation [33]

$$lnK_{ads} = (-\Delta H_{ads}/RT) + const \tag{9}$$

The standard entropy of adsorption  $\Delta S_{ads}$  can be calculated from the thermodynamic basic equation as follows [34] :

$$\Delta G_{ads} = \Delta H_{ads} - T \,\Delta S_{ads} \tag{10}$$

The endothermic adsorption process ( $\Delta H_{ads} > 0$ ) is attributed unequivocally to chemisorption [35], while generally, an exothermic adsorption process ( $\Delta H_{ads} < 0$ ) may involve either physisorption or chemisorption or a mixture of both the processes [36]. In the present case, the negative values of the

enthalpy of adsorption indicate that the adsorption of the tested compounds is an exothermic process. The entropy of adsorption value is positive which attributed to the exothermic adsorption process.

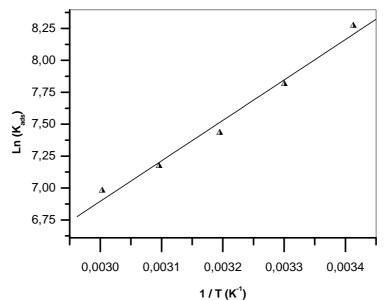


Fig.8. Relationship between Ln(K<sub>ads</sub>) and 1/T for carbon steel corrosion in 1M HCl solution with potassium iodide.

### 4. Conclusion

The following conclusions can be drawn from the results obtained from this study:

- The inhibition efficiency increased with the increasing concentration of inhibitor and decreased with increase in temperature and immersion time.

- The thermodynamic adsorption and activation parameters obtained support both physical and chemical adsorption mechanism.

- The negative sign of the standard free energy of adsorption indicates is a spontaneous adsorption of inhibitor on the metal surface.

- The adsorption of the studied inhibitors obeys the Langmuir adsorption isotherm at all investigated temperatures.

# 5. Acknowledgements

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