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## Corrosion inhibition of cold rolled steel in 0.5M H<sub>2</sub>SO<sub>4</sub> by potassium iodide

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### ABSTRACT

The inhibition of the corrosion of cold rolled steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution by potassium iodide has been investigated by using weight loss. The results show that KI as a good inhibitor, and its maximum inhibition efficiency is higher than 90% even at low concentration. The temperature effect on the corrosion behaviour of the cold rolled steel with and without the inhibitor was studied in the temperature range (293-323K). Some thermodynamic functions of dissolution and adsorption processes were also determined. The adsorption of the inhibitor on the cold rolled steel surface is in agreement with Langmuir adsorption isotherm.

**Keywords:** Adsorption isotherm, corrosion inhibition, potassium iodide, cold rolled steel, weight loss.

### INTRODUCTION

Corrosion can cause disastrous damage to metal and alloy structures causing economic consequences in terms of repair, replacement, product losses, safety, and environmental pollution [1]. The environmental consequence of corrosion is enormous, and its inhibition has been deeply investigated [2]. It has been found that one of the best methods of protecting metals against corrosion involves the use of inhibitors which are substances that slow down the rate of corrosion [3,4]. The corrosion inhibitor is widely used and acts as one of the most economical and effective ways [5-7]. The use of inorganic inhibitors as an alternative to organic compounds is based on the possibility of degradation of organic compounds with time and temperature [8,9]. The inhibition efficiency depends on the parameters of the corrosive system [pH, temperature, duration, metal composition, etc.] and on the nature of the inhibitor [10]. Sulfuric acid is one of the most aggressive acids for iron and its alloys and is often used during cleaning, pickling, descaling, acidizing, and so forth [11, 12]. The adsorption of the inhibitors can be described by two main types of interaction: physical adsorption and chemisorptions [13, 14]. The adsorption is also influenced by the structure and the charge of the metal surface, and the type of testing electrolyte [15-17].

The present work was designed to study the corrosion inhibition of cold rolled steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution using potassium iodide as corrosion inhibitors. Weight loss measurements were used to know the effect of time, temperature and concentration of KI on the inhibition properties. Adsorption and activation parameters were calculated to establish the kinetic behaviour of the inhibition process.

### MATERIALS AND METHODS

#### 2.1. Materials

Tests were performed on a cold rolled steel of the following composition (wt.%): 0.10% C, 0.5% Mn, 0.025% P, 0.025% S, and bal. Fe. The test pieces were polished with emery paper (grade 320–500–800–1200). The specimens were weighed by electronic digital analytical balance with five decimal accuracy before and after exposure.

## 2.2. Solution

The aggressive solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> was prepared by dilution of analytical grade 98% H<sub>2</sub>SO<sub>4</sub> with distilled water. The concentration range of inhibitor used is 10<sup>-4</sup> to 2.5x10<sup>-3</sup> M.

## 2.3. Weight loss method

Weight loss or gravimetric measurements were performed on cold rolled steel sample by immersing it in the absence and presence of different concentrations of KI at 303 K for 2h duration in 0.5M H<sub>2</sub>SO<sub>4</sub> solution. The inhibition efficiency of potassium iodide was expressed in terms of percentage inhibition, calculated using the equation:

$$IE(\%) = [(w_{\text{corr}} - w_{\text{inh}})/w_{\text{corr}}] \times 100 \quad (1)$$

where  $w_{\text{corr}}$  corrosion rate of blank sulfuric acid and  $w_{\text{inh}}$  corrosion rate after adding inhibitor.

The corrosion rate (W) was calculated from the following equation:

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

where  $m_1$  is the mass of the specimen before corrosion,  $m_2$  the mass of the specimen after corrosion, S the total area of the specimen and the corrosion time.

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

$$\theta = 1 - w_{\text{inh}}/w_{\text{corr}} \quad (3)$$

## RESULTS AND DISCUSSION

### 3.1. Effect of Inhibitor concentration

The variation of the inhibition efficiencies obtained from the weight loss with different inhibitor concentrations in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 303 K are summarized in Table 1. The results show that inhibition efficiency increases as the concentration of inhibitor increases from 10<sup>-4</sup> to 2.5x10<sup>-3</sup> M (Figure 1). The maximum inhibition efficiency for potassium iodide inhibitor was found to be about 97.40 %. The optimum concentration of this effect is 2.5x10<sup>-3</sup> M. The figure 1 shows that the corrosion rate decreases with increasing concentration of inhibitor, which explains the effect of protection against the corrosion by the type of inhibitor selected.

**Table 1: Corrosion parameters for cold rolled steel in aqueous solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence and absence of different concentrations of KI at 303 K for 2 h**

	C (mol/L)	w (mg/cm <sup>2</sup> .h <sup>1</sup> )	IE (%)
H <sub>2</sub> SO <sub>4</sub>	0.5	2.31360	-
KI	10 <sup>-4</sup>	1.83115	20.85
	2.5x10 <sup>-4</sup>	1.34740	41.76
	5x10 <sup>-4</sup>	0.91848	60.30
	7.5x10 <sup>-4</sup>	0.49180	78.74
	10 <sup>-3</sup>	0.16514	92.86
	2.5x10 <sup>-3</sup>	0.06013	97.40

### 3.2. Effect of immersion time

The weight loss measurements were performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> in absence and presence of inhibitor at 2.5x10<sup>-3</sup> M concentration for 30 min to 6 h immersion time at temperature 303 K.

Inhibition efficiency of KI is plotted against immersion time as seen from Figure 2.

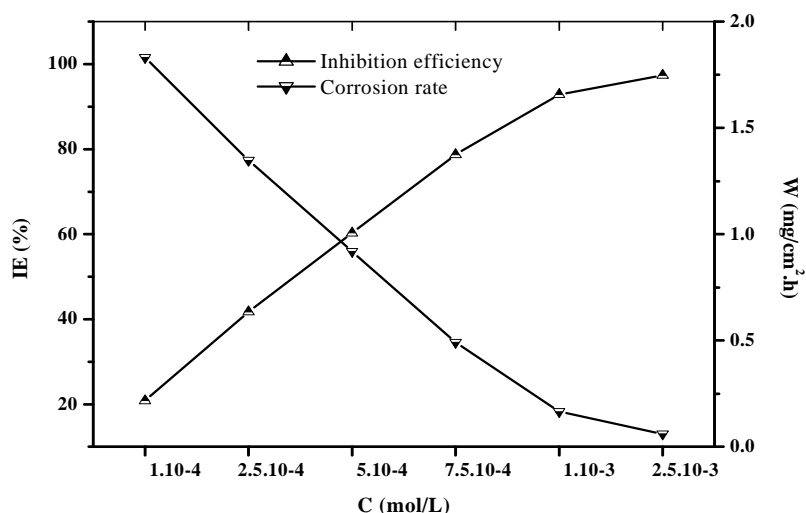


Fig. 1: Variation of inhibition efficiency and corrosion rate vs inhibitor concentration for cold rolled steel after 2 hrs of exposure

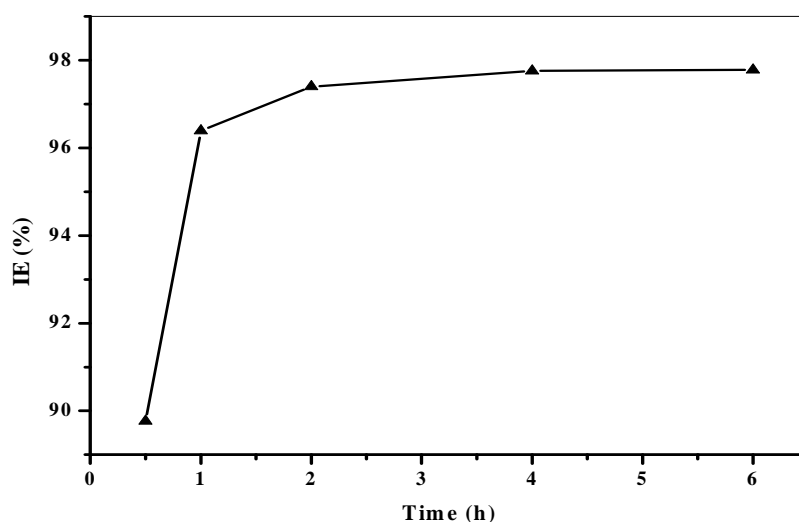


Fig. 2: Variation of inhibition efficiency of KI at  $2.5 \times 10^{-3}$  M with immersion time

The Table 2 and figure 2 show that inhibition efficiency of the potassium iodide was increased with increasing immersion time. However, the results indicate a stabilization of the inhibition rate from 2 hours of immersion. According to this study, it was found that KI is a very effective inhibitor for cold rolled steel in  $\text{H}_2\text{SO}_4$  0.5M because after an immersion time of half an hour, the power of protection already achieved 89.77%.

Table 2: Effect of immersion time on inhibitor performance for cold rolled steel in 0.5 M  $\text{H}_2\text{SO}_4$  at 30°C for the KI at  $2.5 \times 10^{-3}$  M

Time (hours)	$w_{\text{corr}}$ (mg/cm <sup>2</sup> .h)	$w_{\text{inh}}$ (mg/cm <sup>2</sup> .h)	IE (%)
1/2	0.76690	0.07839	89.77
1	1.40702	0.05072	96.39
2	2.31360	0.06013	97.40
4	2.30380	0.05150	97.76
6	2.19789	0.04888	97.78

### 3.3. Effect of temperature

In order to study the effect of temperature on the inhibition efficiency of potassium iodide, weight loss measurements were carried out in the temperature range (293-323K) in absence and presence of inhibitor at optimum concentration during 2 hours of immersion. Table 3 shows the effect of temperature on the corrosion rate of cold rolled steel in absence and presence of inhibitor. It is evident from this Table that inhibition efficiency decreases slowly with increasing temperature.

Table 3: Effect of temperature on cold rolled steel in the presence and absence of KI, at 2 h

T (K)	w <sub>0</sub> (mg/cm <sup>2</sup> .h)	w <sub>inh</sub> (mg/cm <sup>2</sup> .h)	IE (%)
293	1.14468	0.02576	97.74
303	2.31360	0.06013	97.40
313	3.59440	0.11070	96.92
323	5.59957	0.18345	96.72

### 3.4. Adsorption isotherm

Adsorption isotherms provide information about the interaction of the adsorbed molecules with the electrode surface [18]. The most usually used adsorption isotherms are Langmuir, Temkin, Frumkin and other various isotherms [19, 20]. These are influenced by the chemical structure of the inhibitor, the type of the electrolyte, pH, the charge and nature of the metal and temperature [21]. The phenomenon of interaction between the metal surface and the inhibitor can be better understood in terms of adsorption isotherm. The plots of  $C_{inh}/\theta$  against  $C_{inh}$  (Figure 3) yield a straight line with approximately unit slope, indicating that the inhibitor under study obeys Langmuir adsorption isotherm. According to this isotherm,  $\theta$  is related to  $C_{inh}$  by [22]:

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \quad (4)$$

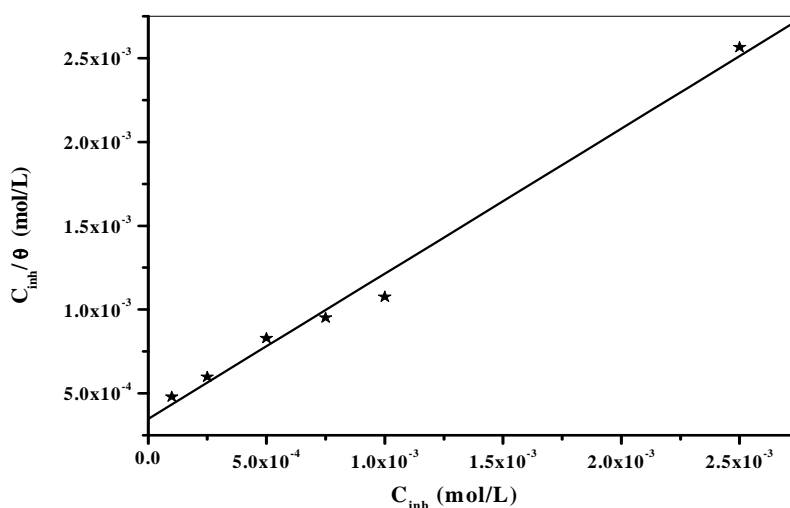


Fig. 3: Langmuir adsorption isotherm for the cold rolled steel corrosion in the presence of KI at 303 K

The  $K_{ads}$  values can be calculated from the intercept lines on the  $C_{inh}/\theta$  -axis. This is related to the standard free energy of adsorption ( $\Delta G_{ads}$ ) with the following equation [23]:

$$K_{ads} = (1/55.5)exp(-\Delta G_{ads}/RT) \quad (5)$$

where R is the gas constant and T is the absolute temperature. The constant value of 55.5 is the concentration of water in solution in mol/dm<sup>3</sup> [24].

The intercept permits the calculation of the equilibrium constant  $K_{ads}$  which is  $2.87 \times 10^3$  L/mol. The value of  $K_{ads}$  which indicates the binding power of the inhibitor to the cold rolled steel surface leads to calculation of adsorption energy. Value of  $\Delta G_{ads}$  is -30.19 kJ/mol. The negative values of  $\Delta G_{ads}$  showed that the adsorption of inhibitor molecules on the metal surface is spontaneous [25]. If the values of  $\Delta G_{ads}$  is in the order of -20 kJ/mol or less this would indicate a physical adsorption, while those values of -40 kJ/mol or higher imply chemical adsorption. We can conclude that adsorption acts simultaneously by chemisorptions and physical adsorption [26].

### 3.5. Kinetic and thermodynamic parameters of dissolution

Kinetic and thermodynamic parameters of dissolution process are important to understand the inhibition mechanism, The apparent activation energy  $E_a$  for cold rolled steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of inhibitors was evaluated from Arrhenius equation [27, 28]:

$$\ln(w) = (-E_a/RT) + A \quad (6)$$

where w is the corrosion rate determined from gravimetric measurements, A is the Arrhenius frequency factor, R is the molar gas constant and T is the absolute temperature.

The plots of  $\ln(w)$  against  $1/T$  were linear, as shown in Figure 4, from which the values of  $E_a$  for the inhibited corrosion reaction of cold rolled steel have been calculated and recorded in Table 4.

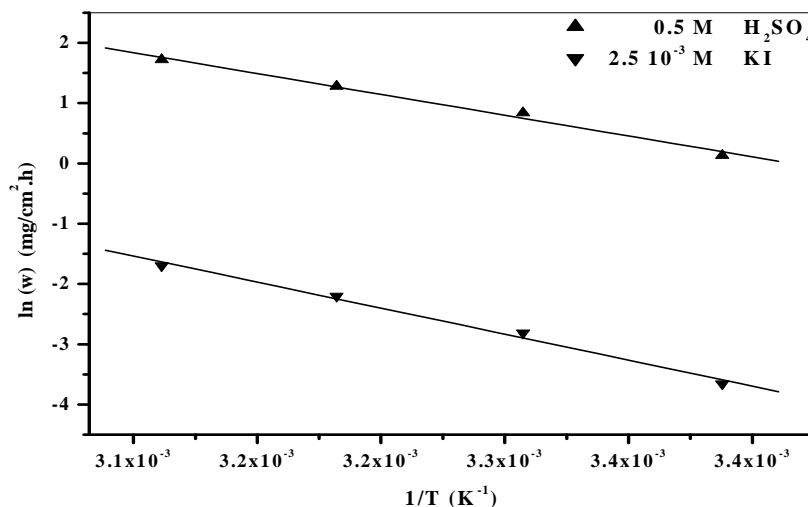


Fig. 4: Adsorption isotherm plots for  $\ln(w)$  versus  $1/T$

$$k = (\mu RT/Nh) \exp(-\Delta G_a/RT) \tag{7}$$

Where,  $k$  is the constant rate and  $\mu$  the transmission coefficient which represents a distance and can take a value from zero to unity. If we suppose that the corrosion rate is proportional to the constant rate, the alternative formulation of Arrhenius equation is [29]:

$$w = (\mu' RT/Nh) \exp(\Delta S_a/R) \exp(-\Delta H_a/RT) \tag{8}$$

where  $h$  is plank's constant,  $N$  Avogadro's Number,  $\Delta S_a$  the entropy of activation, and  $\Delta H_a$  the enthalpy of activation and  $\mu' = B\mu$  ( $B$  is the coefficient of proportionality). A plot of  $\ln(w/T)$  versus  $1/T$  gave a straight line (Figure 5) with a slope of  $-\Delta H_a/R$  from which the value of  $\Delta H_a$  was calculated and listed in Table 4.

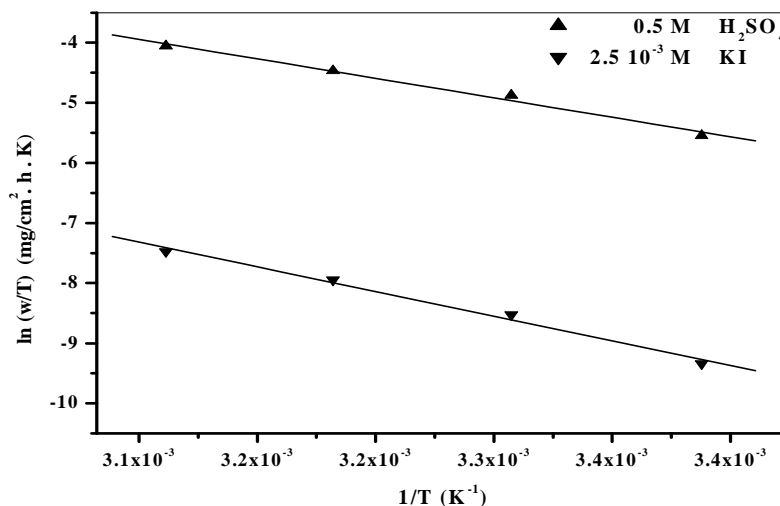


Fig. 5: Adsorption isotherm plots for  $\ln(w/T)$  versus  $1/T$

It is evident from the Table 4 that the activation energy increased on addition of KI in comparison to the uninhibited solution. The increase in the apparent activation energy value interpreted as the decrease in the inhibition efficiency with the increase in the temperature.

The value of  $\Delta H_a$  increased in the presence of inhibitor than in the absence of inhibited solution indicating the higher inhibitive efficiency. The positive signs of enthalpy  $\Delta H_a$  reflect the endothermic nature of dissolution process [30]. Moreover, the average difference value of the  $E_a - \Delta H_a$  is 2.56 kJ/mol, which is approximately equal to the average

value of RT (2.52 kJ/mol). Therefore, it is indicated that the corrosion process is a unimolecular reaction as it is characterized by the following equation [31].

$$E_a - \Delta H_a = RT \quad (9)$$

**Table 4: Thermodynamic parameters for cold rolled steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and the presence of inhibitor at 303 K**

Concentration of Inhibitor (M)	E <sub>a</sub> (kJ/mol)	ΔH <sub>a</sub> (kJ/mol)	E <sub>a</sub> -ΔH <sub>a</sub> (kJ/mol)
0	41.03	38.47	2.56
2.5x10 <sup>-3</sup>	51.26	48.70	2.56

## CONCLUSION

The principal conclusions are:

1. The inhibition efficiency of KI increases by increasing the inhibitor concentration, but it decreases with increase in temperature.
2. The adsorption of KI on cold rolled steel obeyed Langmuir adsorption isotherm.
3. The negative value of ΔG<sub>ads</sub> is a sign of spontaneous adsorption on the metal surface.

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