

Research Article

The Inhibition Effect of Potassium Iodide on the Corrosion of Pure Iron in Sulphuric Acid

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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. The inhibition effect of potassium iodide on the corrosion of pure iron in 0.5 M H₂SO₄ has been studied by weight loss. It has been observed from the results that the inhibition efficiency (IE%) of KI increases from 82.17% to 97.51% with the increase in inhibitor concentration from 1·10⁻⁴ to 2·10⁻³ M. The apparent activation energy (E_a) and the equilibrium constant of adsorption (K_{ads}) were calculated. The adsorption of the inhibitor on the pure iron surface is in agreement with Langmuir adsorption isotherm.

1. Introduction

Corrosion is the deterioration of materials by chemical interaction with their environment [1]. Corrosion can cause disastrous damage to metal and alloy structures causing economic consequences in terms of repair, replacement, product losses, safety, and environmental pollution [2]. Several protective measures are taken to control and prevent corrosion. One of these is the use of corrosion inhibitors, which are usually chemical substances; when added in a small concentration to a corrosive medium, they reduce effectively the corrosion of the metal and/or alloy [3, 4]. The use of corrosion inhibitors constitutes one of the most economical ways to mitigate the corrosion rate [5]. The corrosion and corrosion protection of iron in corrosive environments have attracted the attention of many investigators [6–8]. Iron plays a central role as one of the most widely used materials in our daily life because of its so many applications [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]. Sulphuric 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 inhibitor molecules get bonded to the metal surface

by chemisorption, physisorption, or complexation with the polar groups acting as the reactive centers in the molecules [13].

2. Experimental

2.1. Materials. The weight loss experiments were conducted in a 150 mL beaker; the electrolyte volume is 100 mL. Julabo thermostat brand keeps the electrolyte at the desired temperature ($\pm 0.1^\circ\text{C}$).

The test pieces were mechanically polished with emery paper (a coarse paper was used initially and then progressively finer grades were employed, 400 to 1200 grade). The specimens were weighed by electronic digital analytical balance with five decimal accuracies before and after exposure.

2.2. Electrolyte. The corrosive solution, 0.5 M H₂SO₄, was obtained by dilution of analytical grade 98% sulphuric acid with bidistilled water. The concentration range of inhibitor employed was 1·10⁻⁴ to 2·10⁻³ M in the sulphuric acid.

2.3. Weight Loss Method. The test pieces were washed with bidistilled water, degreased with acetone, washed again

with bidistilled water, dried between two filter papers, and weighed. After specified periods of time, 3 test pieces were taken out of the test solution, rinsed with bidistilled water, dried as before, and weighed again. The average weight loss at a certain time for each set of three samples was taken. The weight loss experiments were performed after an exposure of 2 h. The inhibition efficiency of potassium iodide was expressed in terms of percentage inhibition, calculated using

$$IE (\%) = \left(\frac{w_{\text{corr}} - w_{\text{inh}}}{w_{\text{corr}}} \right) \times 100, \quad (1)$$

where W_{corr} is the corrosion rate of blank sulfuric acid and W_{inh} is the corrosion rate after adding inhibitor.

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

$$w = \left(\frac{m_1 - m_2}{S \cdot t} \right), \quad (2)$$

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

The degree of surface coverage (Θ) was calculated using the following equation:

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

3. Results and Discussion

3.1. Effect of Inhibitor Concentration. The values of percentage inhibition efficiency (IE%) and corrosion rate (w) at different concentrations of KI at 303 K are summarized in Table 1. Figure 1 shows the results obtained from weight loss measurements for pure iron in 0.5 M H_2SO_4 solutions in the absence and presence of different concentrations of KI. It has been observed from the results that the IE% of KI increases from 82.17% to 97.51% with the increase in inhibitor concentration from $1 \cdot 10^{-4}$ to $2 \cdot 10^{-3}$ M. The optimum concentration of this effect is $2 \cdot 10^{-3}$ M.

Figure 2 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.

3.2. Effect of Immersion Time. The weight loss measurements were performed in 0.5 M H_2SO_4 in absence and presence of KI at $2 \cdot 10^{-3}$ M concentration for 30 min to 6 h immersion time at temperature of 303 K. Inhibition efficiencies were plotted against immersion time as seen in Figure 3. This figure shows that inhibition efficiency of the potassium iodide was increased with increasing immersion time. The increase in inhibition efficiency up to 2 h reflects the inorganic inhibitor adsorption of constituents on the pure iron surface. This result indicates 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 pure iron in H_2SO_4 0.5 M because after an immersion time of half an hour the power of protection already achieved 94.91%.

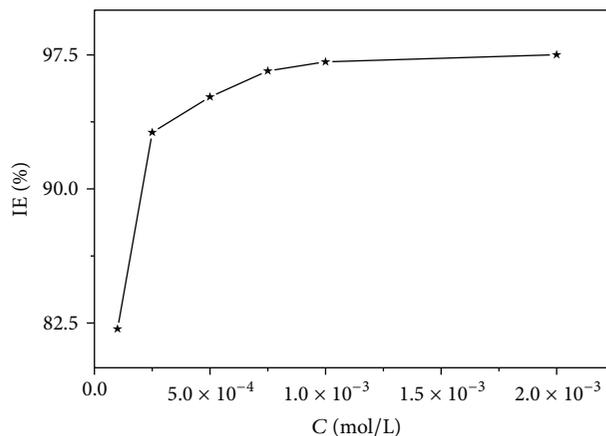


FIGURE 1: Variation of inhibition efficiency with KI concentration.

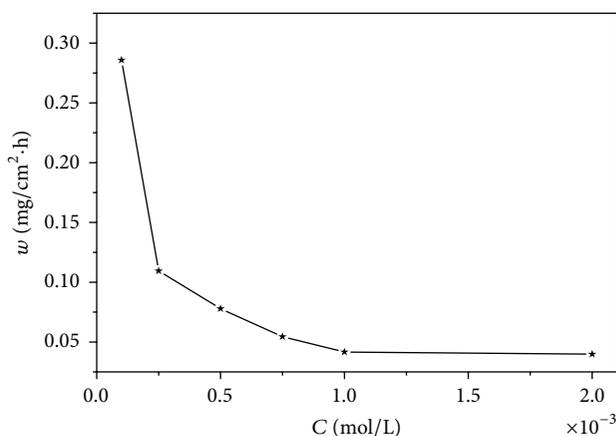


FIGURE 2: Plot of corrosion rate versus inhibitor concentration for pure iron test specimens after 2 hrs of exposure.

3.3. Effect of Temperature. In order to study the effect of temperature on the inhibition efficiencies of potassium iodide, weight loss measurements were carried out in the temperature range 293–323 K in absence and presence of inhibitor at optimum concentration during 2 hours of immersion. Table 2 shows the effect of temperature on the corrosion rate of pure iron in absence and presence of inhibitor. It is evident from this table that inhibition efficiency increases with increasing temperature.

The apparent activation energy E_a for pure iron corrosion in 0.5 M H_2SO_4 in the absence and presence of inhibitors was evaluated from Arrhenius equation [14]:

$$\ln(w) = -\frac{E_a}{RT} + A, \quad (4)$$

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); E_a values were obtained from the slope and are as presented in Table 3.

TABLE 1: Corrosion parameters for pure iron in aqueous solution of 0.5 M H₂SO₄ in presence and absence of different concentrations of KI at 303 K for 2 h.

	C (mol/L)	w (mg·cm ⁻² ·h ⁻¹)	IE (%)
H ₂ SO ₄	0.5	1.60383	—
KI	1 · 10 ⁻⁴	0.28593	82.17
	2.5 · 10 ⁻⁴	0.10956	93.16
	5 · 10 ⁻⁴	0.07787	95.15
	7.5 · 10 ⁻⁴	0.05445	96.60
	1 · 10 ⁻³	0.04169	97.11
	2 · 10 ⁻³	0.03986	97.51

TABLE 2: Effect of temperature on pure iron in the presence and absence of KI, at 2 h.

T (K)	w ₀ (mg/cm ² ·h ¹)	w _{inh} (mg/cm ² ·h ¹)	IE (%)
293	0.15107	0.00622	95.88
303	0.34152	0.01329	96.10
313	1.32256	0.05035	96.19
323	3.43109	0.11280	96.71

TABLE 3: The values of activation parameters for pure iron in 0.5 M H₂SO₄ in the absence and the presence of inhibitor of 2·10⁻³ M concentration at 2 h.

Concentration of inhibitor (M)	E _a (kJ/mol)	ΔH _a (kJ/mol)	E _a - ΔH _a (kJ/mol)
0.5 H ₂ SO ₄	84.32	81.65	2.67
2 · 10 ⁻³ KI	78.89	76.22	2.67

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 ΔH_a was calculated and listed in Table 3.

The E_a values in the presence of inhibitor are lower than in the absence of inhibitor indicating that the inhibition efficiency increases with increases in temperature. The positive sign of enthalpy of activation reflects the endothermic nature of the steel dissolution process.

3.4. Adsorption Isotherm. Adsorption isotherms provide information about the interaction of the adsorbed molecules with the electrode surface [15]. The adsorption of the inhibitors can be described by two main types of interaction: physical adsorption and chemisorptions [16, 17]. 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 [18]. 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}/θ against C (Figure 6) yield a straight line with approximately unit slope, indicating that the inhibitor under study obeys Langmuir adsorption isotherm. According to this isotherm, θ is related to C_{inh} by [19]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (5)$$

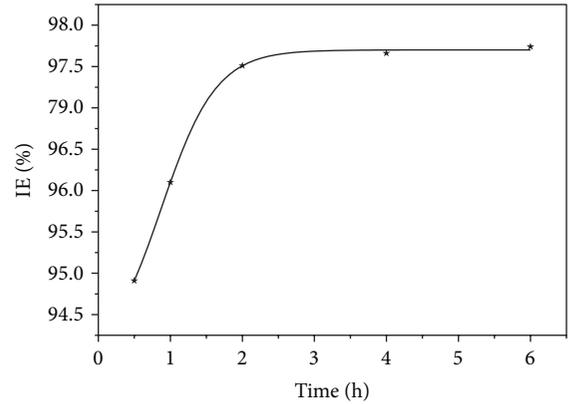


FIGURE 3: Variation of inhibition efficiency of KI with immersion time.

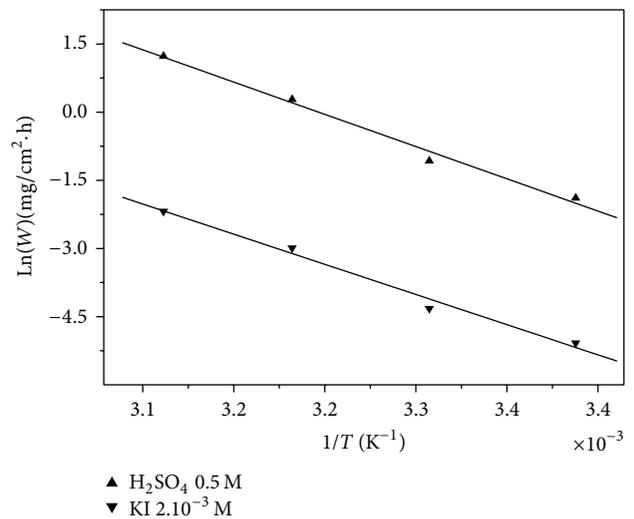


FIGURE 4: Adsorption isotherm plots for $\ln w$ versus $1/T$.

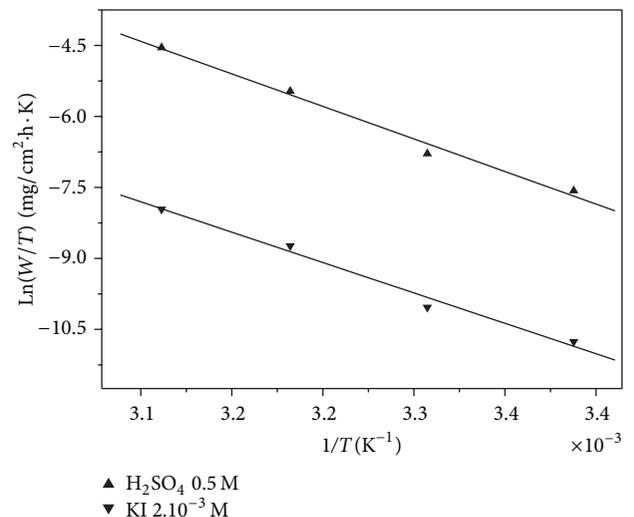


FIGURE 5: Adsorption isotherm plots for $\ln(w/T)$ versus $1/T$.

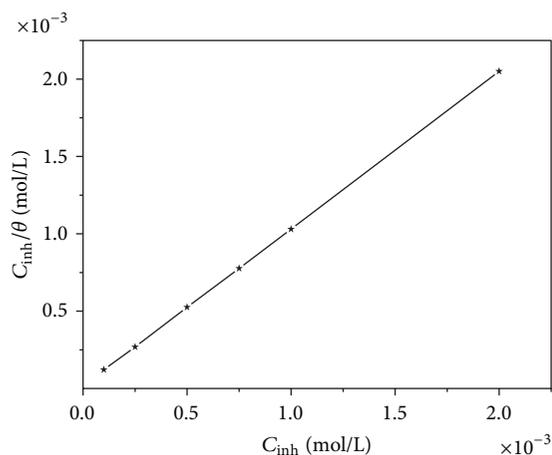


FIGURE 6: Relationship between (C_{inh}/θ) and inhibitor concentration C_{inh} .

The K_{ads} values can be calculated from the intercept lines on the C_{inh}/θ -axis. This is related to the standard free energy of adsorption (ΔG_{ads}) with the following equation [20]:

$$K_{ads} = \left(\frac{1}{55.5} \right) \exp \left(-\frac{\Delta G_{ads}}{RT} \right), \quad (6)$$

where

$$\Delta G_{ads} = -RT \ln(55.5K_{ads}), \quad (7)$$

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/dm³ [21].

The intercept permits the calculation of the equilibrium constant K_{ads} which is 6.17×10^4 L/mol, respectively. The value of K_{ads} which indicates the binding power of the inhibitor to the pure iron surface leads to calculation of adsorption energy. Value of ΔG_{ads} is -37.55 kJ/mol, respectively. The negative values of ΔG_{ads} showed that the adsorption of inhibitor molecules on the metal surface is spontaneous [22].

Generally, the standard free energy values of -20 kJ/mol or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface (physical adsorption); those of -40 kJ/mol or more negative involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (chemical adsorption).

Note that our measures were carried out without inert atmosphere. In $1M H^+$, the iodide ion becomes hydrogen iodide which reacts with oxygen to form molecule iodide I_2 . The formed molecule could be adsorbed onto iron and occupying the surface, it strikes the adsorption of iodide. At the end, a lower efficiency of adsorption of iodide was obtained but the inhibition efficiency of the studied inhibitor KI increases due to adsorption of I_2 .

Otherwise the value of ΔG_{ads} (-37.55 kJ/mol) near to -40 kJ/mol indicates that, in our case, the adsorption is neither typical chemisorption nor typical physisorption but

it is a complex mixed type. That is, the adsorption inhibitor molecule on the iron surface in the present study involves both chemisorption (of I_2) and physisorption (of I^-) but chemisorption is the predominant mode of adsorption. This assumption is supported by the data obtained from temperature dependence of inhibition process, reported in Tables 2 and 3, which show that the inhibition efficiency of the studied compound as inhibitor increases with increase in temperature and that the value of E_a in absence of the inhibitor is lower than that in its presence [23]. On the other hand it is known that the iron surface acquires positive charge in H_2SO_4 0.5 M [24], while iodide ion is negatively charged, as a result the physisorption (electrostatic attraction) of the iodide ion occurs onto iron surface.

4. Conclusion

On the basis of the experimental results obtained in the present study, the following conclusions can be drawn.

- (1) Potassium iodide is a good inhibitor for pure iron corrosion in 0.5 M H_2SO_4 solution. The inhibition efficiency increases with increased KI concentration to attain a maximum value of 97.51% at $2 \cdot 10^{-3}$ M.
- (2) The adsorption of KI on pure iron obeyed Langmuir adsorption isotherm.
- (3) At higher experimental temperature, inhibitor molecules are adsorbed into the metal surface.
- (4) The negative value of ΔG_{ads} is a sign of spontaneous adsorption on the metal surface.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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