

Inhibition effect of potassium iodide on the corrosion of carbon steel (XC 38) in acidic medium

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Abstract

The effect of potassium iodide (KI) on the corrosion of carbon steel (XC38) in 0.5 M H₂SO₄ has been investigated in relation to the concentration of the inhibitor by weight loss measurement. It was found that the inhibition efficiency increases with an increase in concentration of inhibitors and temperature. The effect of temperature on the corrosion behavior with the addition of optimal concentration of KI was studied in the temperature range 293-323 K. The adsorption of the inhibitor on the XC38 surface is in agreement with Temkin adsorption isotherm. On the bases of thermodynamic adsorption parameters, it can be interpreted that the adsorption of this inhibitor on the carbon steel surface takes place through both chemical and physical adsorption.

Keywords: Corrosion Inhibition, Weight Loss, Carbon Steel, Adsorption Isotherm, Thermodynamic Parameters.

1. Introduction

Corrosion problems have received a considerable amount of attention because of their attack on materials (Abd El-Maksoud 2008). The use of inhibitors is 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 (Trabanelli 1991, Ali et al. 2003). A corrosion inhibitor is a substance which is added in small amounts to a corrosive medium to reduce its ability for corrosion (Dananjaya 2012). The selection of inhibitor is controlled by its capacity to inhibit corrosion of the substrate material, its environmental side effects and its economic availability. 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 (Antonijevic & Petrovic 2008, Tomić 2010). Carbon steel is a very prominent material of construction and frequently comes in contact with aqueous solution, which may be acidic in nature, as a part of industrial process (Deyab 2007). The investigation of corrosion of carbon steel is always a subject of high theoretical as well as practical interest (Fouda & Badr 2013). The study of carbon steel corrosion phenomena has become important particularly in acidic media because of the increased industrial applications of acid solutions (Hamdy & El-Gendy 2013). Among the acid solutions, 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 (Poornima et al. 2013, Kumar & Shetty 2013). Temperature dependence of the inhibitor efficiency and the comparison of the obtained thermodynamic data of the corrosion process both in absence and presence of inhibitors lead to some conclusions concerning the mechanism of inhibiting action (Noor 2007, Hammouti et al. 2011, Khadraoui 2014). The adsorption process depends upon the nature and surface charge of the metal, the type of aggressive media, the structure of the inhibitor and the nature of its interaction with the metal surface

(Solmaz et al. 2008, Chen 2011, Zaaafarany 2013). The adsorption of the inhibitors can be described by two main types of interaction: physical adsorption and chemisorptions (Larabi et al. 2004, 2006).

In the present work, the inhibitive effectiveness of potassium iodide has been studied in retarding corrosion of carbon steel (XC38) in 0.5 M H₂SO₄. Weight loss measurements were used to know the effect of inhibitor concentration, exposure time and temperature.

2. Materials and methods

2.1. Materials

Carbon steel (XC38) were used for the weight loss measurement contains C = 0.15-0.35%, Mn = 0.5-1%, Si = 0.15-0.35%, P = 0.015-0.035%, S = 0.035%, and iron is the remainder.

The electrode was polished using different grades of emery papers and degreased. The specimens were weighed by electronic digital analytical balance with five decimal accuracy before and after exposure.

2.1. Weight loss method

A known weight of carbon steel coupon was immersed in 100 ml of the test solution in an open beaker. The beaker was transferred into a water bath maintained at 303 K. Weight loss measurements were performed on carbon steel sample by immersing it in the absence and presence of different concentrations of inhibitor in 0.5M H₂SO₄ solution. The inhibition efficiency (% IE) of the inhibitor, degree of surface coverage (θ) and corrosion rates (w) were determined from the weight loss results, using equations (1), (2), and (3) respectively:

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

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

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

Where m_1 and m_2 are the weight losses of the specimen before and after corrosion, S is the area of the specimen, t is the time of immersion and w_{corr} , w_{inh} are the corrosion rates in the presence and absence of inhibitor respectively.

3. Results and discussion

3.1. Effect of inhibitor concentration

The effect of the inhibition efficiencies obtained from the weight loss with different inhibitor concentrations are presented in Figure 1. It is clear from data in Figure 1 that the increase of the inhibitors concentrations from 10^{-4} to 10^{-3} M decreased the corrosion rates of the carbon steel in 0.5 M H_2SO_4 solution. The results show that inhibition efficiency increases as the concentration of inhibitor. The maximum inhibition efficiency for potassium iodide inhibitor was found to be about 48.46 %.

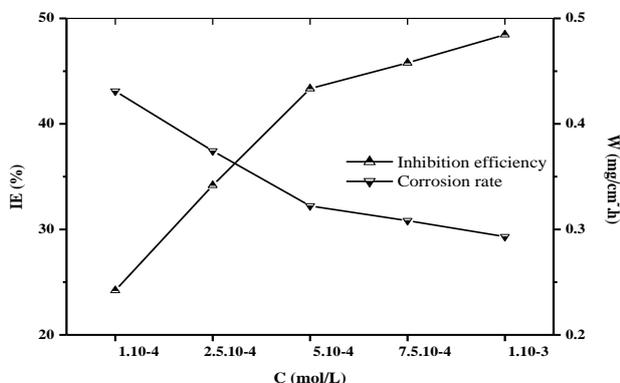


Fig. 1: Variation of Inhibition Efficiency and Corrosion Rate Vs Inhibitor Concentration for Carbon Steel after 2 Hrs of Exposure.

3.2. Effect of exposure time

Immersion time analysis of carbon steel samples in the acidic solutions with and without the optimal concentration of the inhibitor was performed using weight loss at 303 K. The weight loss of XC38 steel in 0.5 M H_2SO_4 is nearly varied linearly with immersion period in the absence and presence of different concentrations of potassium iodide as shown in Figure 2.

The variation of the inhibition efficiency of this inhibitor with time is shown in Figure 3. This shows that inhibition efficiency of the potassium iodide was increased with increasing immersion time. These results indicate a stabilization of the inhibition rate from 2 hours of immersion.

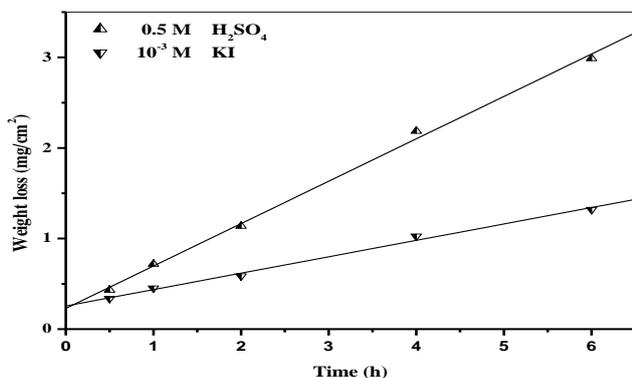


Fig. 2: Weight Loss as a Function of Immersion Time of XC38 Steel in 0.5 M H_2SO_4 without and With 10^{-3} M of KI At 303 K

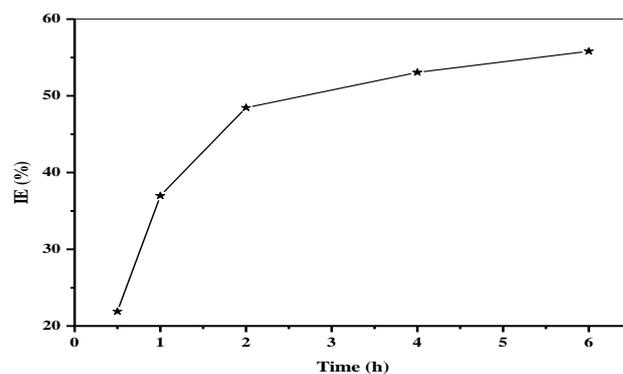


Fig. 3: Variation of Inhibition Efficiency of KI At 10^{-3} M With Immersion Time.

3.3. Effect of temperature

The effect of rising temperature on the corrosion rate of carbon steel in 0.5 M H_2SO_4 containing 10^{-3} M of potassium iodide was studied in temperature range from 20 to 50°C by weight loss measurements. Table 1 shows the effect of temperature on the corrosion rate of carbon steel in absence and presence of inhibitor. It is evident from this Table that inhibition efficiency increases with increasing temperature.

Table 1: Effect of Temperature on the Corrosion Rate and Inhibition Efficiency for the Corrosion of XC (38) in 0.5 M H_2SO_4 Solution in Absence and Presence of Inhibitors.

T (K)	w_0 (mg/cm ² .h)	w_{inh} (mg/cm ² .h)	IE (%)
293	0.26876	0.18264	32.04
303	0.56877	0.29313	48.46
313	1.31803	0.64454	51.09
323	3.39625	1.22182	64.02

3.4. Adsorption isotherm

To understand the mechanism of corrosion inhibition, the adsorption behavior of the inhibitors adsorbents on the metal surface must be known. The most usually used adsorption isotherms are Langmuir, Temkin, Frumkin and other various isotherms (Shukla 2011, Hmamou et al. 2012). The adsorption is also influenced by the structure and the charge of the metal surface, and the type of testing electrolyte (El Ashry et al. 2006, Kissi et al. 2006, Obot et al. 2009). Adsorption isotherms provide information about the interaction of the adsorbed molecules with the electrode surface (Noor & Al-Moubaraki 2008). This adsorption isotherm can be put in linear form from Equation 4 as follows (Bilgic & Caliskan 2001, Umoren et al. 2008, Ebenso et al. 2009):

$$K_{\text{ads}} C_{\text{inh}} = \exp(-2a\theta) \quad (4)$$

$$\ln(C_{\text{inh}}) = -2a\theta - \ln(K_{\text{ads}}) \quad (5)$$

Where C_{inh} is the concentration of inhibitor, K_{ads} is the equilibrium constant of adsorption, a is lateral interaction parameter which describe the molecular interactions in the adsorbed layer.

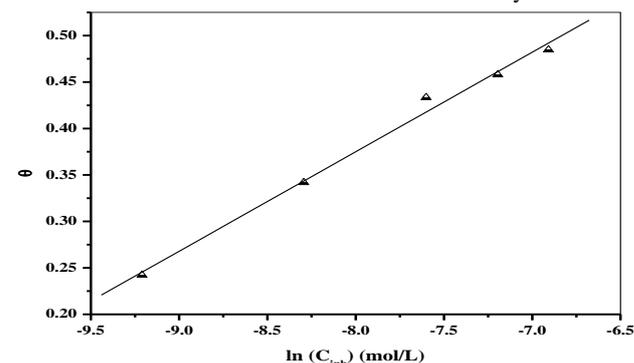


Fig. 4: Temkin Adsorption of KI on the Carbon Steel Surface in 0.5 M H_2SO_4 Solution.

Plots of θ against $\ln(C_{inh})$, as presented in Figure 4, gave linear relationship, which shows that adsorption data fitted Temkin adsorption isotherm. Adsorption parameters obtained from Temkin adsorption isotherms are recorded in Table 2. The values of attractive parameter (a) are negative, indicating that repulsion exists in the adsorption layer.

The equilibrium constant K_{ads} is related to the standard free energy of adsorption (ΔG_{ads}) with the following equation (Fekry & Ameer 2010):

$$K_{ads} = (1/55.5) \exp(-\Delta G_{ads}/RT) \quad (6)$$

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^3 (Olivares et al. 2006).

Table 2: Adsorption Parameters from Temkin Isotherm for XC38 in 0.5 M H_2SO_4 Solutions Containing 10^{-4} M Inhibitor At 303K.

Inhibitor	R^2	A	K_{ads}	ΔG_{ads}
KI	0.99	-4.63	9.59×10^4	-39.01

The negative values of ΔG_{ads} showed that the adsorption of inhibitor molecules on the metal surface is spontaneous (Dabrowski 2001). If the values of ΔG_{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 (Dahmani et al. 2010).

3.5. Thermodynamic parameters

Kinetic and thermodynamic parameters of dissolution process are important to understand the inhibition mechanism, 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 (Okafor et al. 2008, Quraishi et al. 2010).

The apparent activation energy E_a for carbon steel corrosion in uninhibited and inhibited acid solution was evaluated from Arrhenius equation (Quraishi & Khan 2005, Singh et al. 2012):

$$\ln(w) = (-E_a/RT) + A \quad (7)$$

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 E_a values were calculated from the slope, equals to $-E_a/R$ of each straight line. Arrhenius plots are shown in Figure 5.

The apparent activation energy obtained for the corrosion process in the inhibitor-free, uninhibited acid solution was found to be 66.34 and 50.94 kJ/mol in presence of the inhibitor. The energy barrier of the corrosion reaction decreased in the presence of the inhibitor, which can be due to the adsorption of the inhibitor on the steel surface (Valle-Quitana 2014).

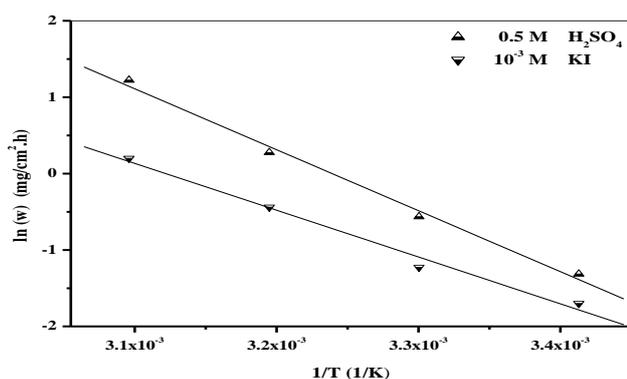


Fig. 5: Adsorption Isotherm Plots for $\ln(W)$ Versus $1/T$

$$k = (\mu RT/Nh) \exp(-\Delta G_{ads}/RT) \quad (8)$$

Where, k is the constant rate and μ 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 (Singh & Ebenso 2013):

$$w = (\mu RT/Nh) \exp(\Delta S_a/R) \exp(-\Delta H_a/RT) \quad (9)$$

Where h is plank's constant, N Avogadro's number, ΔS_a the entropy of activation, and ΔH_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 6) with a slope of $-\Delta H_a/R$ from which the value of ΔH_a was calculated.

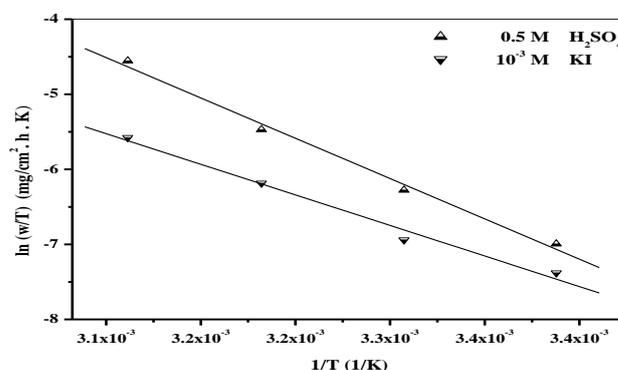


Fig. 6: Adsorption Isotherm Plots for $\ln(W/T)$ Versus $1/T$

The calculated values of enthalpy are 63.79 kJ/mol and 48.38 kJ/mol in the absence and presence of inhibitor respectively. The positive signs of enthalpy reflect the endothermic nature of dissolution process (Sorkhabi et al. 2006, Singh et al. 2014). Moreover, the average difference value of the $E_a - \Delta H_a$ is 2.55 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 (Lebrini et al. 2011, Attar et al. 2014).

$$E_a - \Delta H_a = RT \quad (10)$$

4. Conclusion

The main conclusions of the study may be presented in the following points:

- In 0.5 M H_2SO_4 , the inhibition efficiency of potassium iodide increases with increasing the inhibitor concentration.
- The negative value of ΔG_{ads} is a sign of spontaneous adsorption on the metal surface.
- The adsorption of the inhibitor molecule was consistent with Temkin adsorption isotherm.
- Thermodynamic data for the inhibitor adsorption lead to suggest the occurrence may be both physical and chemical adsorption.

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