Inhibition of Mild Steel Corrosion in Hydrochloric Acid Solutions by Adsorption Using Safranin O Dye

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Abstract

In this paper, the adsorption and corrosion inhibition of Safranin O dye on mild steel in 0.5 M hydrochloric acid solutions were studied at the temperature range of 30 °C to 60 °C using weight loss technique. The results indicate that Safranin O dye acts as an inhibitor by adsorption on the metal surface. It has been noticed that the inhibition efficiency increases by increase in dye concentration while it decreases by increase in temperature. The adsorption of the studied Safranin O dye on mild steel surface involves the Langmuir adsorption isotherm involves physical adsorption mechanism. The change of Gibbs energy, enthalpy, and entropy of adsorption, have been also evaluated for the adsorption of Safranin O dye mild steel surface.

Keywords: Mild steel; corrosion; inhibition; weight loss; safranin; dye.

1. Introduction

The use of metals is always associated with an afflicting problem called corrosion. Corrosion damage requires high costly maintenance. Improvement of corrosion is a challenging task faces scientists working in this area [1]. Steel is considered the most important metal in engineering applications. Steel is used in each aspect of our life [2]. Mild steel has excellent mechanical properties and it is relatively cheap, so, it is widely used in industry [3]. Mild steel is an iron alloy, which corrode easily in acidic medium. Acidic solutions such as hydrochloric acid, which are widely used in chemical laboratories and in several industrial processes such as acid pickling and acid cleaning, is also used for the removal of undesirable oxide films and corrosion products [4]. In several industrial applications, mild steel is used is in places which are easily subjected to corrosion in the presence of acids, such as the fabrication of reaction vessels and storage tanks [5]. Inhibitors are compounds that reduce corrosion rate of metals in two different ways. In the first way, the inhibitor is absorbed on the surface of the metal through the transfer of charge from charge of inhibitor molecule to a charged metal surface (physical adsorption process). In the second way, the inhibitor is absorbed on the surface of the metal by electron transfer from the inhibitor's molecule to the vacant d-orbital of the metal (chemical adsorption process) [6]. Inhibitors are considered as one of the most practical methods for corrosion protection, especially in acidic media [7]. Organic inhibitors have been widely studied for the use as an inhabitant of mild steel in acid media. It has been revealed in the literature that most organic compounds have been used as corrosion inhibitors. These compounds adsorb on the metal surface through hetero atoms such as nitrogen, oxygen, sulfur and phosphorus, multiple bonds or aromatic rings; they block the active sites leading to corrosion rate decrease [1]. Methyl orange, Azorubine dye, Sunset Yellow, Fast Green, reactive blue, Chrysoidine, which are organic dyes, have been used as corrosion inhibitors for mild steel in hydrochloric acid solutions [2, 8, 9]. The present work investigates the corrosion inhibition of mild steel in 0.5 M hydrochloric acid solutions by Safranin O dye as corrosion inhibitors using by "weight loss" technique.

Table 2.1: Characteristics of Safranin-O Dye

Parameter	Value
Chemical formula	$C_{20}H_{19}$ Cl N_4
Molecular weight	350.84 (g/mol)
Abb	SFO
Physical form	Reddish brown powder
Soluble in solvents	Water
λ_{max}	530 - 534 nm
C.I. Name	Cationic Dye

2. Material and Methods

2.1. Materials

The materials used in this paper are as follows: Hydrochloric acid from BDH and Safranin-O dye (Sigma Aldrich chemical company, USA) without further purification.

2.2. Corrosion Medium

0.5 (mol/L) Hydrochloric acid solution was prepared by dilution with double distilled water.

2.3. Dye Solution Preparation

Table 2.1 shows the characteristics of the Safranin-O dye (SFO). Figure 2.1 shows the Chemical structure of Safranin O dye. Stock solution (1.0 x10^{-3} M) has been prepared by dissolving a precisely weighed quantity of the dye (0.351 g) in double distilled water. The stock solution is used in the experiments in order to obtain the desired concentration by successive dilutions, which ranges from 1.0 $\times 10^{-6}$ to 1.0 $\times 10^{-3}$ M. The Safranin O dye (SFO) has been used as a Corrosion Inhibitor in this paper.

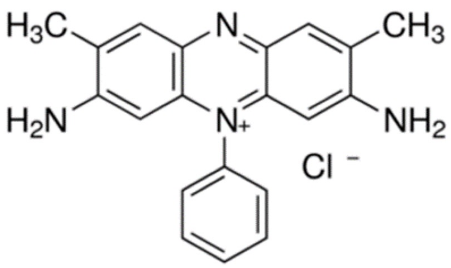

Figure 2.1: Chemical structure of Safranin-O Dye

2.4. Sample Preparation

Local mild steel sheets have been used in this study. The mild steel specimens have been chemically analyzed in the Libyan Iron and Steel Company. Results show the following percentages of chemical composition: 0.002% P, 0.288% Mn, 0.128 C, 0.0035% S, 0.014% Cr, 0.0005% Mo, 0.0195% Cu, 0.0027% V, 0.0001% B, 0.0027% Co , while the remainder is Fe. The sample sheets have been cut in size 4.2 $\times$1.2 $\times$ 0. 2 cm. A small hole has been drilled at one end of the sample to assist suspension inside the solution. Mild steel samples have been polished using emery papers, degreased with absolute ethanol, dried at room temperature, and stored in the moisture free desiccators.

2.5. Weight Loss Measurements

Firstly, mild steel samples have been weighed using an electronic balance. Next, the specimens were suspended and totally immersed in beakers of 250 mL capacity filled with 200 mL of 0.5 M Hydrochloric acid containing different inhibitor concentrations at fixed temperatures of 30, 40, 50 and 60 °C maintained by a thermostatic water bath for four hours. Similar experiments have been conducted in the absence of inhibitors. After that, the specimens were removed from the beakers and washed with water to remove any corrosion products, and then it was washed with acetone. Then, the specimens were dried and reweighed. Finally, mass loss measurements were performed as by ASTM method [10, 11]. Each experiment has been duplicated in order to guarantee the reliability of the results and the mean value of the weight loss has been used. Weight loss technique has been used for the estimation of the inhibition efficiency (IE %) of the extract. The corrosion rate (CR) of mild steel has been estimated using the equations below:

$$IE\,\% = \left(1 - \frac{W_2}{W_1}\right) \times 100 \tag{2.1}$$

$$CR\;(g\,h^{-1}cm^{-2}) = \frac{\Delta W}{AT} \tag{2.2}$$

Where: W_1 and W_2 are weight loss (mg) of mild steel in the absence and presence of the inhibitor respectively. A is the Surface area of the sample in cm^2, T is the period of immersion in hours and ΔW equals the difference between W_1 and W_2. Equation 2.3 has been used to calculate the degree of surface coverage (θ)

$$\theta = \left(1 - \frac{W_2}{W_1}\right) \tag{2.3}$$

3. Results and Discussion

3.1. Effect of Concentration and Temperature

Table 3.1 and 3.2 show that, the inhibition efficiency increases with increase in the inhibitor concentration while it decreases with rise in temperature. The percentage values of inhibition efficiency and corrosion rate have been calculated by the weight loss method at different concentrations of SFO dye in 0.5 M HCl at different temperature values. Figure 3.1 shows the relationship between the corrosion rate and inhibitor concentration while Figure 3.2 shows the relationship between the inhibitor efficiency and the inhibitor concentration. Table 3.2 shows the Percentage inhibition efficiency in 0.5 M HCl at various temperatures. It has been noticed that the corrosion rate decreases with increase in the inhibition efficiency.

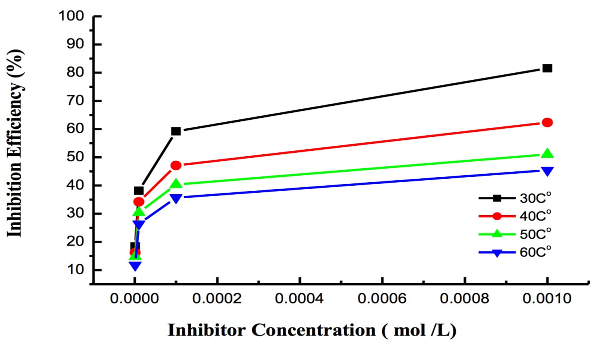

Figure 3.1: Variation of inhibition efficiency with concentration of SFO Dye at different temperature

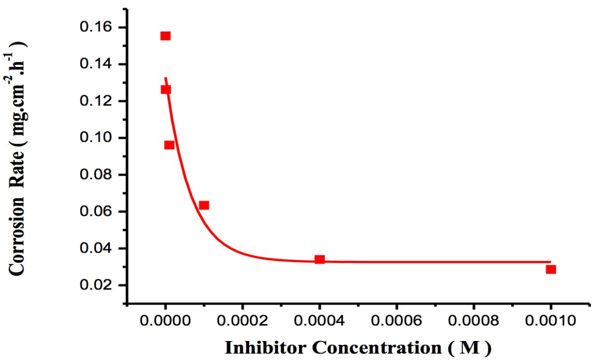

Figure 3.2: Corrosion rate against inhibitor concentration for mild steel corrosion in 0.5M HCl acid solution at 30 °C

3.2. Adsorption Study

The interaction between the corroding surface and the inhibitor can be described in terms of the adsorption characteristics [12]. Adsorption of the inhibitor molecules essentially depends on electronic characteristics of the metal surface, temperature adsorption of the solvent ionic species, the charge and the nature of the Metal surface and the electrochemical potential at the solution interface. The adsorption isotherms define the molecular interactions of the inhibitor molecules with the active sites on the metal surface [13 –15]. It also provides information about the mechanism of corrosion inhibition. Equation 3.1 gives the linear form of Langmuir isotherm as follows [16].

$$\frac{C_{inh}}{\theta} = \frac{1}{k_{ads}} + C_{inh} \tag{3.1}$$

Where θ is the degree of surface coverage, k_{ads} is the equilibrium constant of the adsorption/desorption process and C_{inh} is the concentration of the inhibitor. Figure 3.3 illustrates the application of Langmuir equation for the results of Safranin O dye adsorbing on the surface of mild steel at different values of temperature. It has been found the Langmuir adsorption isotherm provides the best description of the behavior of the investigated SFO dye with almost a unity correlation coefficient (R^2) value. Table 3.3 shows the Langmuir parameters of Safranin-O dye adsorption, which are estimated at different temperature range of 30 - 60 °C. It has been noted that K_{ads} decreases when temperature increases. This indicates that adsorption of SFO dye on the mild steel surface decreases at higher temperatures.

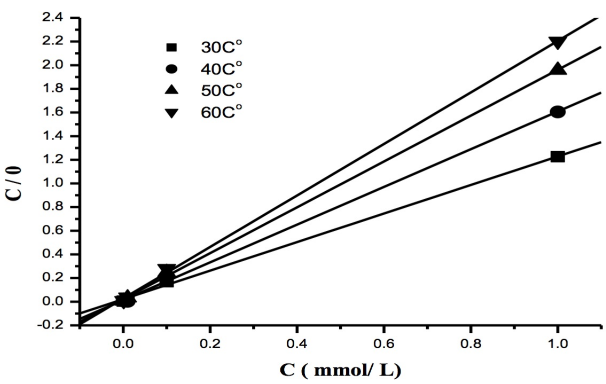

Figure 3.3: Langmuir isotherms for adsorption of SFO dye onto the mild steel at different temperatures

Table 3.1: Weight loss data for mild steel corrosion in the presence and absence for various concentrations of SFO Dye in 0.5 (mol\L) HCl at different temperatures

Conc. (mol/L)	Weight loss (g)				CR (mg cm^{-2} h^{-1})			
	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
Blank	0.0076	0.0087	0.0094	0.0135	0.1554	0.1779	0.1923	0.2761
1.0 X10^{-6}	0.0062	0.0072	0.0080	0.0119	0.1268	0.1490	0.1693	0.2435
1.0 X10^{-5}	0.0047	0.0057	0.0065	0.0099	0.0961	0.1170	0.1338	0.2034
1.0 X10^{-4}	0.0031	0.0045	0.0056	0.0086	0.0634	0.0940	0.1147	0.1755
1.0 X10^{-3}	0.0014	0.0032	0.0046	0.0073	0.0086	0.0669	0.0941	0.1506

Table 3.2: Percentage inhibition efficiency in 0.5 M HCl at various temperatures

Conc. (mol/L)	Inhibition efficiency (IE %)				Surface coverage (θ)			
	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
1.0 X10^{-6}	18.40	16.20	14.75	11.78	0.184	0.162	0.147	0.117
1.0 X10^{-5}	38.16	34.21	30.37	26.30	0.381	0.342	0.303	0.263
1.0 X10^{-4}	59.20	47.11	40.32	35.71	0.592	0.471	0.403	0.357
1.0 X10^{-3}	81.50	62.34	51.06	45.42	0.815	0.623	0.511	0.454

Table 3.3: Langmuir adsorption constants for adsorption of SFO dye for mild steel at different temperatures

Temp (°C)	$k_{ads}10^3$ (L/mol)	$ln\, k_{ads}$	ΔG (kJ/mol)	R^2
30	56.674	10.945	-27.585	0.9994
40	82.760	11.323	-29.479	0.9993
50	84.607	11.345	-30.480	0.9997
60	90.400	11.411	-31.606	0.9997

3.3. Thermodynamic Parameters for Adsorption Process

The thermodynamic parameters for adsorption of an inhibitor have been estimated by Langmuir constant (k_{ads}) at different temperature values. Figure 3.4 shows the values ($ln\, k_{ads}$) vs. ($1/T$) for the estimation of thermodynamic parameters for adsorption of SFO dye onto the mild steel at different temperature. These parameters thermodynamic includes the change in free energy (ΔG), the change in enthalpy (ΔH) and the change in entropy (ΔS) associated with adsorption process.

Equation 3.2 is used for calculating the change in free energy (ΔG) associated with adsorption process as follows [17].

$$\Delta G = -RT\, ln\, k_{ads} \tag{3.2}$$

where: ΔG is change in free energy (kJ/mol), R is general gas constant , which equals 8.314 (J/mol K) , T is absolute temperature (K), k_{ads} is Langmuir constant (L/mol).

Equations 3.3 and 3.4 are used to calculate the values of ΔS and ΔH respectively [7]:

$$ln\, k_{ads} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{3.3}$$

$$\Delta G = \Delta H - T\,\Delta S \tag{3.4}$$

A graph of ($ln\, k_{ads}$) on the Y-axis and ($1/T$) on the X-axis has been plotted as shown in Figure 3.4. The relationship is linear with a slope equals $\left(\frac{-\Delta H}{R}\right)$. The slope value can be used for calculating the value of ΔH and then substitute in equation 3.3 to find the value of ΔS. Table 3.4 shows the quantitative thermodynamic data of the SFO dye on the adsorbent surface on the mild steel. Positive values of ΔH for SFO dye indicate that the adsorption process is an endothermic process while positive values of ΔS show the increase in randomness at the solid-solution interface during the adsorption process. The obtained value of the change in enthalpy, which equals 12.041 (kJ\mol), indicates that the adsorption process of the Inhibitor on the metal surface is a physical adsorption process. In addition, the negative value of ΔG has increased with temperature increase. This indicates that the adsorp-

Table 3.4: The thermodynamic parameters of SFO dye adsorption process on mild steel surface

Temp (K)	$^1/_T$ (K^{-1})	K_{ads} (L/mol)	$ln\ k_{ads}$	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J.mol/K)
303.15	0.00330	0.05567	10.945	-27.585	12.041	130.77
313.15	0.00319	0.08276	11.323	-29.479		
323.15	0.00309	0.08461	11.345	-30.480		
333.15	0.00300	0.09040	11.411	-31.606		

tion process of Safarin dye on the metal surface is the feasible.

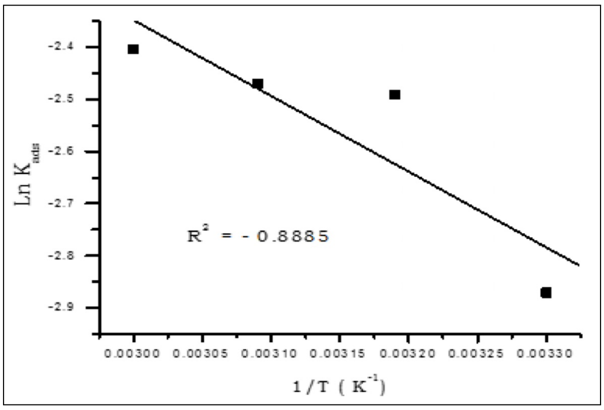

Figure 3.4: $ln\,k_{ads}$ vs. $^1/_T$ plot to estimate the thermodynamic parameters of SFO dye adsorption onto mild steel at different temperatures

4. Conclusion

The obtained results show that SFO dye acts as an excellent effective inhibitor for the corrosion of mild steel in 0.5 M HCl solution. The increase in the inhibitor concentration decreases the corrosion rate while the increase in temperature leads to an increase in the corrosion rate. It has been concluded that the adsorption of SFO Dye follows the Langmuir adsorption isotherm. In addition, it has been noticed that the inhibition efficiency increases with the increase in the concentration of SFO dye. The values of thermodynamic parameters show that the adsorption process is a physical adsorption process.

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