

Corrosion Inhibition Performance of Safranin Towards Mild Steel in Acidic Corrosion

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Abstract

The corrosion inhibition performance of safranin toward mild steel in 0.5M H₂SO₄ solution was studied at different inhibitor concentration and temperature levels using weight loss method. The results obtained showed that safranin exhibited a very good performance as an inhibitor for mild steel corrosion in 0.5M H₂SO₄ solution. Inhibition efficiency was found to have increased with increase in inhibitor concentration and decreased with increase in temperature. Adsorption of the inhibitor on the mild steel surface followed Langmuir adsorption isotherm. Thermodynamic adsorption parameters (ΔH_{ads} , ΔS_{ads} and ΔG_{ads}) showed that the studied inhibitor adsorbed on the mild steel surface by physisorption, exothermic and spontaneous processes.

Keywords: corrosion, mild steel, safranin, inhibition efficiency, thermodynamic parameters.

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1.0 Introduction

Pickling process of steel includes using a strong acid such as hydrochloric acid or a mixture of hydrochloric acid and nitric acid [1]. Residual acid on steel surface after the pickling process causes steel to corrode. One way of overcoming the major issue is the use of an inhibitor [2-6]. The use of inhibitors for the control of corrosion for metals and alloys which are in contact with aggressive environment is an accepted practice [7]. Most inhibitors used for corrosion inhibition are organic based materials containing coordination sites for metal coordination [1].

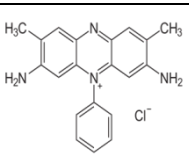
These heterocyclic compounds contain the widespread conjugation in terms of non-bonding electrons of P, S, O, and N, and π -electrons of the multiple bonds through which they can form co-ordination bonding with the d-orbitals of the surface metallic atoms [8, 9]. These heteroatoms mostly exist in the form of polar functional groups such as $-\text{OCH}_3$, OH , $-\text{NH}_2$, $-\text{NO}_2$, $-\text{COOC}_2\text{H}_5$, $-\text{NMe}_2$, $-\text{O}-$, $-\text{CONH}_2$ and $-\text{NHMe}$ that act as adsorption centers during metal inhibitor interactions [10, 11].

The choice of a suitable inhibitor relies on the kind of acid, its temperature and dose. Availability, toxicity and cost of the inhibitor are also significant factors in the utilization and choice of these inhibitors [12].

Unfortunately, most of the reported inhibitors are either toxic or pose an environmental concern. For this reason, an inhibitor that is free of these drawbacks will be very attractive. Safranines are well known in medical field and are commonly used as a counterstain in some staining protocols.

The aim of this research work is to study the inhibition performance of safranin on the corrosion of mild steel in acidic environment using weight loss method.

Table 1: Physical and Chemical Properties of Safranin

Structure	Iupac Name	Common Name	Molecular Formula	Molecular Weight
	3,7-diamino-2,8-dimethyl-5-phenyl-chloride	Safranin	$\text{C}_{20}\text{H}_{19}\text{ClN}_4$	350.85

2.0 Experimental

2.1 Materials

Specimens of mild steel were cut from a commercially available sheet of mild steel with area of 2.64cm^2 . The chemical composition of the mild steel as given by the supplier in wt% C 0.03%, Mn 0.51%, S 0.048%, P 0.08%, Cr 0.3%, Mo 0.05%, Cu 0.1% and the balance in wt% was Fe.

H_2SO_4 98% (analar grade). Double distilled water was used.

2.2 Gravimetric Analysis

Gravimetric analysis was performed following the guidance of the ASTM method G31-72 [13]. Mild steel sheets with total area of 2.64cm^2 were scraped with emery papers (600-1000 grade), washed with double distilled water to remove scales and rusts and then washed with acetone in order to degrease the surfaces and stored in moisture free dessicator. After weighing them on an analytical balance, the specimens were immersed in a 250ml beaker containing 100ml of H_2SO_4 (0.5M) solution with and without the addition of inhibitor solutions. All solutions were kept under an ambient condition except for the temperature study. After the immersion time of 2 days interval for inhibition concentration study and 2 hours for temperature study, the steel samples were removed, washed with plenty of double distilled water, dried in acetone and re-weighed. The corrosion rate (CR), percentage inhibition efficiency (%IE) and surface coverage (θ) of metal steel samples were calculated according to equations (1) - (3) [8, 14]:

$$C_R \text{ (mmpy)} = \frac{87.6 \times w}{DAT} \quad (1)$$

$$\%IE = \frac{C_{R(o)} - C_{R(i)}}{C_{R(o)}} \times 100 \quad (2)$$

$$\theta = \frac{C_{R(o)} - C_{R(i)}}{C_{R(o)}} \quad (3)$$

Where $C_{R(o)}$ is the weight loss (mg), D is density (gm/cm^3), A is the metallic surface area (cm^2) and T denotes the immersion time (h). $C_{R(o)}$ and $C_{R(i)}$ are the mild steel corrosion rates in the absence and presence of safranin inhibitor molecule.

3.0 Results and Discussion

3.1 Effect of Inhibitor Concentration

The values of corrosion rate (mmpy), percentage inhibition efficiency and surface coverage obtained from gravimetric analyses method at various inhibitor concentrations of safranin and time of exposure are given in Table 2, 3 and 4 respectively. The results show that inhibition performance of safranin increases with concentrations and as the time of exposure increases. The result shows significant increase in inhibition efficiency from 6 days and there was no significant change in inhibition efficiency between safranin concentration of 100mg/L and 200mg/L as the corrosion

studies progressed indicating that 100mg/L is the optimum concentration.

The inhibition performance of safranin on metal steel may be attributed to increase in the effective surface coverage [15]. It was observed that increase in immersion time increases the inhibition efficiency suggesting that safranin is effective in acid solution over the immersion range. The inhibition performance of safranin may be attributed to the presence of Nitrogen atoms that can coordinate with the metallic d-orbitals and strengthen the metal-inhibitor interactions [8].

Table 2: Corrosion rates for mild steel in 0.5 M H₂SO₄ in the absence and presence of Safranin at 28°C.

Conc. (mg/l)	Corrosion Rate (mmpy)					
	2	4	6	8	10	12
0.00	1.34	0.59	0.45	0.94	1.02	1.0
50	0.87	0.25	0.13	0.16	0.01	0.07
100	0.56	0.24	0.12	0.095	0.09	0.07
200	0.55	0.22	0.12	0.088	0.086	0.07
300	0.55	0.21	0.11	0.073	0.058	0.06
400	0.48	0.20	0.90	0.066	0.051	0.05

Table 3: % Inhibition Efficiency for Mild Steel in 0.5 M H₂SO₄ in the Absence and Presence of Safranin at 28°C.

Conc. (mg/l)	Percentage Inhibition Efficiency					
	2	4	6	8	10	12
50	35.07	57.09	71.11	82.98	90.20	93.00
100	58.21	58.63	73.33	89.89	91.18	93.00
200	58.96	63.25	73.33	90.64	91.57	93.00
300	58.96	63.93	75.56	92.23	94.31	94.00
400	64.18	66.15	80.00	92.98	95.00	95.00

Table 4: Surface coverage (θ) for mild steel in 0.5M H₂SO₄ in the absence and presence of safranin at 28°C.

Conc. (mg/l)	Surface Coverage					
	2	4	6	8	10	12
50	0.35	0.57	0.71	0.83	0.90	0.93
100	0.58	0.59	0.73	0.90	0.91	0.93
200	0.59	0.63	0.73	0.91	0.92	0.93
300	0.59	0.64	0.76	0.92	0.94	0.94
400	0.64	0.66	0.80	0.93	0.95	0.95

3.2 Effect of Temperature

The weight loss experiments were also performed at different temperatures ranging from 303K to 343K and concentration of inhibitor (50,100 and 400mg/L) in order to study the effect of temperature on the performance of safranin. The results are shown in Table 5 indicating that inhibition performance of safranin decreases with increase in solution temperatures. The decrease in inhibition efficiency on increase in solution temperature might be due to increase in the mobility of the inhibitor molecules which in turn decrease the interaction between metallic surface and inhibitor molecules [15]. Moreover, rapid etching, molecular rearrangement, fragmentation and desorption at elevated temperatures may also decrease the inhibition efficiency [16].

The effect of temperature on the protection ability of safranin molecule can be described in using Arrhenius equation [8, 11, 15].

$$\log(C_R) = \frac{-E_a}{2.303RT} \times \log A \quad (4)$$

In the equation, R, T and A are the gas constant, the absolute temperature and Arrhenius pre-exponential factor respectively. E_a is the activation energy for corrosion process and C_R is the corrosion rate. The value of activation energy (E_a) for blank (11.26 kJ/mol), 50, 200 and 400mg/L were 12.35, 17.23 and 22.98 kJ/mol respectively. It can be seen from the results that magnitude of E_a in the presence of inhibitor molecules were greater than the blank which indicated that corrosive dissolution of mild steel in acidic medium becomes difficult or slows down owing to the formation of inhibitor protective films, which eventually decreases the corrosion rate [8,17]. Moreover, the relatively low value of E_a which were below 80KJ/mol suggested a physisorption process [18].

Table 4: Variation of C_R, % IE and (θ) with temperature for mild steel in the absence and presence of safranin in 0.5M H₂SO₄.

Temperature (K)	Corrosion Rate (mmpy), Inhibition Efficiency (%) and Surface Coverage (θ)									
	Blank	50 (mg/l)			200 (mg/l)			400 (mg/l)		
		C _R	C _R	%I _E	θ	C _R	%I _E	θ	C _R	%I _E
303	0.81	0.45	44.44	0.44	0.23	71.60	0.72	0.18	77.77	0.78
313	2.13	1.69	20.66	0.21	0.78	63.38	0.63	0.80	62.63	0.63
323	2.26	1.86	17.70	0.18	0.90	60.35	0.60	0.86	61.86	0.62
333	2.45	2.03	16.94	0.17	1.15	52.86	0.53	1.15	53.06	0.53
343	2.91	2.47	15.12	0.15	1.47	49.35	0.49	1.20	58.76	0.59

313	1724.14	29.85	29.50	40
323	1470.59	30.35		
333	1470.59	31.34		
343	1250	31.79		

3.3 Adsorption Studies

Adsorption of inhibitors molecules to the interfaces manifests information related to the electric double layer created in the form of various thermodynamic parameters [8]. The types of interaction that occur between an organic inhibitor and a surface of mild steel could be calculated from studying adsorption isotherms [1].

The degree of surface coverage (θ) for the organic inhibitor in 0.5M H₂SO₄ at 303- 343K for 2 hours immersion time were evaluated using Langmuir Isotherm equation [1].

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

Where θ is the surface coverage obtained from equation (3), K_{ads} is the adsorption-desorption equilibrium constant, C is the inhibitor concentration. By plotting the values C/ θ versus C and the values of K_{ads} were calculated from the intercepts.

Table 6: Variation of Adsorption Constant and Thermodynamic Parameters for Inhibitor Molecules at Different Temperatures

Temp (K)	K_{ads} (M ⁻¹)	$-\Delta G^\circ$ (kJ/mol)	$-\Delta H$ (kJ/mol)	$-\Delta S$ (J/mol/K)
303	4545.45	31.34		

The results are summarized in Table 6. The results indicate a stable protective layer of safranin on the metal surface and hence good anticorrosion properties. The Langmuir adsorption equilibrium constant reveals that there is no interaction between the adsorbed species. In this study, adsorption of safranin molecules obeyed Langmuir adsorption isotherm model.

3.4 Thermodynamic Studies

The equilibrium constant of adsorption of safranin on the surface of the metal is related to the free energy of adsorption (ΔG_{ads}) by the following equation [8].

$$\Delta G^\circ = -2.303RT \log (55.5K_{ads}) \quad (6)$$

Where R is the gas constant, T is the temperature and K_{ads} is the equilibrium constant of adsorption. The arithmetical magnitude of 55.5 signifies the aqueous concentration in bulk acidic solution.

The values of ΔG° for safranin suggests that the adsorption of safranin onto metal surface is a spontaneous process and the adsorbed layer is a more stable [14,18]. In the present study, ΔG° values are between -29.85 and -31.34 kJ/mol. Literature shows that, the standard Gibbs free energy of adsorption in aqueous solution with a value up to -20kJ/mol or more positive indicates physisorption while if the value is close to -40kJ/mol or more negative indicates chemisorption. However, this conclusion should be considered with some caution, since the enthalpy of adsorption is the parameter that reflects the adsorption bond strength, rather than the standard Gibbs free energy of adsorption [1,19]. The adsorption of safranin molecules on mild steel surface in H₂SO₄ solution was physisorption.

The Gibbs free energy of adsorption (ΔG°) at different temperatures were used in equation (7) to obtain the ΔH° and ΔS° [20].

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ \quad (7)$$

Where ΔH° is the standard enthalpy change which determines exothermic or endothermic process, ΔS° is the standard entropy change which determines the degree of randomness of the adsorption. A plot of ΔG° versus T gave

straight lines which are used in the computation of ΔH° and ΔS° from the intercept and slope respectively.

From the result shown in Table 6, it can be seen that values of ΔH° and ΔS° in our present study were -29.50kJ/mol and -40J/mol/K respectively. The negative sign of ΔH° indicates adsorption of inhibitor molecule onto metal surfaces is an exothermic process. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of ΔH_{ads} . For the physisorption process, ΔH is lower than 40kJ/mol while that of chemisorption process approaches 100kJ/mol [21]. In the present case, ΔH value was lower than 40kJ/mol, once again emphasizing that physisorption took place. The ΔS of the adsorption process was obtained as -40J/mol/K, the negative value of ΔS reveals a decrease in randomness at metal-inhibitor interfaces during adsorption of safranin on the metal surface [20]. The low ΔS might be explained by the fact that before the adsorption of inhibitors molecules onto the metal surface, inhibitor molecules might freely move in the bulk solution but with the progress in the adsorption, inhibitor molecules orderly adsorbed on the steel surface, as a result low negative entropy is observed. Equally, from the thermodynamic principles, since the adsorption is an exothermic process, it must be accompanied by a decrease in entropy [21].

4.0 Conclusion

The following conclusions can be drawn from the results of the study.

The safranin molecule functioned as corrosion inhibitor for mild steel in 0.5M H₂SO₄ solution.

The inhibition efficiency of the studied inhibitor increases with increase in concentration of the inhibitor and decreases as temperature of the acid solution increases.

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

The thermodynamic adsorption parameters (ΔH_{ads} , ΔS_{ads} , and ΔG_{ads}) shows that the studied inhibitor are adsorbed on mild steel surfaced by physisorption, exothermic and spontaneous process.

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