Research Article

Evaluation of a Green Inhibitor for Corrosion of Mild Steel

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Abstract

The inhibitive characteristics of 7-hydroxyflavone for corrosion of mild steel are described. The anticorrosive efficiency was evaluated by weight loss and potentiodynamic polarization studies at 300 K. The inhibitor showed a maximum of 90% inhibition efficiency at 50 ppm concentration. The Tafel polarization study showed that the inhibitor behaves likely as a mixed type. The corrosion inhibition effect measured by weight loss method and electrochemical studies were in good agreement with each other. The surface of the mild steel both in presence and absence of inhibitor were observed by SEM. The negative value of ΔG_{ads} indicates the spontaneous adsorption of the inhibitor on mild steel surface.

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Introduction

Corrosion inhibition is one of the important academic and industrial research topics. Several substances ranging from synthetic compounds to natural products were studied for corrosion inhibition of metals/alloys at different corrosive environments [1–10]. The heavy metal based inhibitors exhibited high inhibition efficiencies at very low concentrations. Due to the issues of toxicity and other environmental concerns, alternatives for metal inhibitors are in demand. Much attention has been given to organic substances, especially, on plant extracts/natural products due to biocompatibility [11].

Plant extracts contain several kinds of organic compounds including alkaloids, flavonoids, terpenoids, glycosides and so on [12]. Our research group has a strong background for identification and isolation of flavonoids and for their biological activities [13–16]. Also we studied the corrosion inhibitive characteristics of several synthetic and natural organic substances against corrosion of mild steel in hydrochloric acid medium [1–7]. Since the plant extracts contains different compounds, understanding the mechanism of inhibition is still not so clear. Previously, our research group studied 2,3-dihydroxyflavonone [4] as representative compound for plant extracts. In this study, we examined another simple compound, 7-hydroxyflavone for its anti-corrosion properties. The weight loss, potentiodynamic polarization techniques, and SEM were employed to obtain the inhibition results. The weight loss results were subjected to different isotherms to draw an outline on the mechanism of inhibition. The unusual results exhibited by the phenolic hydroxyl group also discussed in the following sections.

Experimental

The mild steel specimens having compositions 0.10% C, 0.34% Mn, 0.08% P, and the remainder being Fe with dimensions 3 cm x 2 cm x 0.3 cm were used for weight loss experiments. 7-hydroxyflavone (M_w, 238.24 g/mol) was purchased from Research Organics, Madras, India. The acid and inhibitor solutions were prepared using double distilled water. Weight loss experiments were performed at varying temperatures 300 K, 310 K, 320 K, and 330 K. The weight loss (WL) was calculated. From the WL values, corrosion rate (CR), surface coverage (θ), and inhibition efficiency percentage (IE%) were calculated. The values of activation energy (E_a), Gibbs free energy (ΔG_{ads}), entropy (ΔS_{ads}), enthalpy (ΔH_{ads}) of adsorption at different temperatures were calculated. A CH electrochemical analyzer model 650B was used to record Tafel polarization curve. Mild steel specimen having 1 cm^2 of exposed area was used as a working electrode for electrochemical studies. A detailed experimental procedure for weight loss studies and electrochemical measurements are available in our previous reports [2, 7]. The surface of the mild steel specimens in presence and absence of inhibitors were observed under a Hitachi 300H Scanning Electron Microscope (SEM).

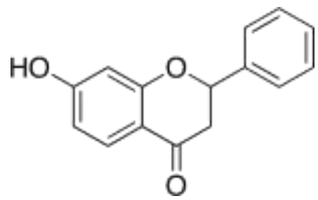


Figure 1 Chemical Structure of 7-Hydroxyflavone.

Result and discussion

Weight loss study

The values of IE%, CR, θ, were calculated from weight loss values and are summarized in Table 1. The inhibitor greatly decreases the corrosion rate at the concentration of 50 ppm in 1 M HCl. While, increase in inhibitor concentration increases the corrosion rate. This peculiar behavior of this inhibitor is discussed in later sections. As expected, upon increasing the acidity of the corrosion medium to 2 M and 3 M, corrosion rate increases to 1.4–1.8 fold than at 1 M concentration. Elevation of immersion time and temperature showed a similar trend for corrosion rate. These results suggest that the adsorption of inhibitor molecules on the surface of the mild steel specimen may be predominantly via physical interactions. Because physical adsorption, for instant Van der Waals forces, between the inhibitor and the metal surface disappears at elevated temperatures.

Adsorption Isotherms

Different adsorption isotherms such as Langmuir, Temkin, Frumkin, Frendlich isotherms were plotted for the weight loss values and the results are given in Figures 1a–1d. It is observed that plot obeys Langmuir and Temkin adsorption isotherms through surface coverage of adsorbed inhibitor on mild steel surface. The higher inhibitive property of 7-Hydroxyflavone is attributed due to the presence of π electrons, in oxygen and the larger molecular size, which ensures greater coverage of the mild steel surface.

The expected linear relationship for Langmuir and Frumkin adsorption isotherms were well approximated with correlation coefficient values greater than 0.99. Especially for Langmuir isotherm the R^2 and the slope values were 1.255. The deviation of the slope from the unity on one hand is attributed to the size of the inhibitor molecules that adsorbed on the metal is more or less than a typical adsorption site. On the other hand, involvement of other mechanisms of adsorption is also assumed from the R^2 values for Freundlich (0.9782) and Temkin (0.9715). These results indicated that the mechanism of inhibition is more pronounced in terms of physical adsorption rather than chemical adsorption.

The thermochemical parameters such as ΔH_{ads}, ΔS_{ads}, and ΔG_{ads} were calculated from the weight loss data and were presented in Table 2. The negative signs of ΔS_{ads} indicated that the activated complex in the rate-determining step could be represented by an association than a dissociation step [17]. Generally the adsorption process which exhibits ΔG_{ads} values between -20 to -40 kJ/mol are categorized into physical adsorption, where as more than -40 kcal/mol are for chemical adsorption processes. In the present case, the ΔG_{ads} was -38.5 kJ/mol indicating that the inhibitors molecules on the surface of mild steel are physically adsorbed [17–21].

Table 1 Effect of different inhibitor concentrations on inhibition efficiency

Inhibitor Concentration (ppm)	WL (mg/cm^2)	CR ($mg/cm^2/hr$)	θ	IE%	σ
0	5.804	2.902	-	-	-
50	0.565	0.283	0.903	90.3	0.05
100	0.744	0.372	0.872	87.2	0.01
150	0.893	0.446	0.846	84.6	0.03
200	1.042	0.521	0.821	82.1	0.02
Acid Concentration (M)					
1	0.565	0.283	0.903	90.3	0.05
2	0.804	0.402	0.826	82.6	0.06
3	1.131	0.565	0.755	75.5	0.03
Immersion Time (hr)					
2	0.565	0.283	0.903	90.3	0.05
3	1.012	0.506	0.839	83.9	0.09
4	2.083	1.042	0.689	68.9	0.01
5	3.810	1.905	0.460	46.0	0.01
Temperature (K)					
300	0.565	0.283	0.903	90.3	0.05
310	3.542	1.771	0.660	66.0	0.02
320	11.76	5.878	0.499	49.9	0.03
330	27.92	13.96	0.386	38.6	0.01

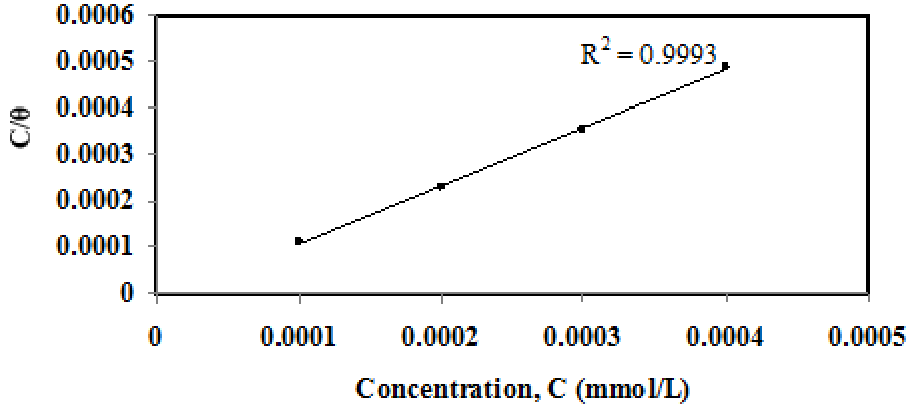
WL - weight loss (mg/cm^2); CR - corrosion rate (mg/cm2/hr)
θ - Surface Coverage ; IE% - Inhibition Efficiency Percent
σ - Standard Deviation for IE%

Table 2 Thermochemical parameters for adsorption of 7-hydroxyflavone on mild steel in 1 M hydrochloric acid

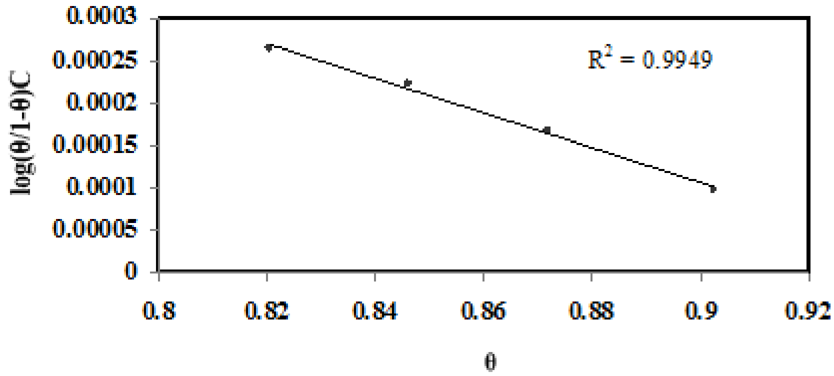
Thermodynamic parameters	Blank (1 M HCl)	1 M HCl + Inhibitor
ΔH_{ads} (kJ/mol)	-54.80	-31.0
ΔS_{ads} (J/K mol)	-33.91	-196
ΔG_{ads} (kJ/mol)	-	-38.5

3.3 Potentiodynamic polarization studies

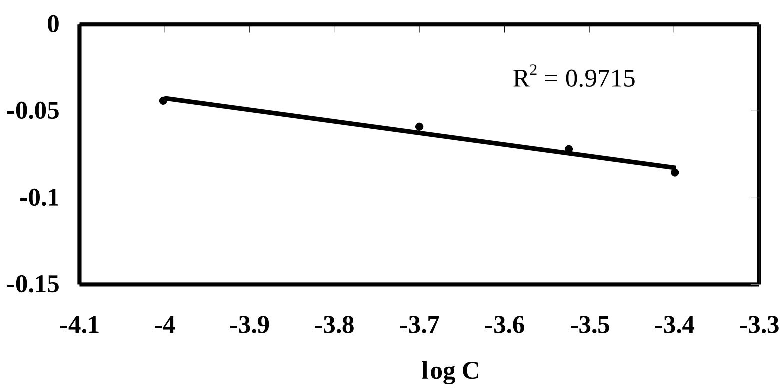
The Tafel curves of mild steel both in presence and absence of various concentrations of inhibitor in 1 M HCl were shown in Figure 3. The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), and tafel constants (b_a and b_c) obtained from cathodic and anodic curves were given in Table 3. From the results inhibitor predominantly inhibits cathodic reaction. It was observed that the current density increased along with the inhibitor concentration indicating the increase in corrosion rate. As seen from Figure 3, the inhibitor affects both anodic and cathodic reactions.


R² = 0.9993
C/θ
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0
0
0.0001
0.0002
0.0003
0.0004
0.0005
Concentration, C (mmol/L)

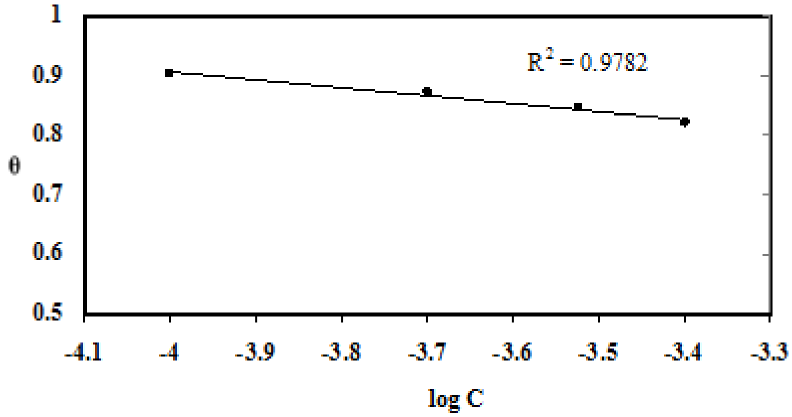
2a


R² = 0.9949
log(θ/1-θ)C
0.0003
0.00025
0.0002
0.00015
0.0001
0.00005
0
0.8
0.82
0.84
0.86
0.88
0.9
0.92
θ

2b


R² = 0.9715
0
-0.05
-0.1
-0.15
-4.1
-4
-3.9
-3.8
-3.7
-3.6
-3.5
-3.4
-3.3
log C

2c



2d

Figure 2 Adsorption isotherms for corrosion inhibition of mild steel in 1 M HCl by 7-hydroxyflavone. 2a) Langmuir, b) Frumkin, c) Temkin, and d) Freundlich adsorption isotherms.

3.4 SEM analysis

The morphologies of the mild steel in 1 M HCl both in presence and absence of inhibitor were recorded by SEM (Figures 4a and 4b) to establish the interaction of inhibitor molecules with the mild steel surface. Figure 4a shows the effect of aggressive acidic solution. Figure 4b Whereas Figure 4b showed the adsorption of inhibitor molecules on the surface. The SEM images revealed that the specimens immersed in the inhibitor solutions are in better conditions having smooth surface while the metal surface immersed in 1 M HCl is rough and covered with corrosion products and appeared like full of pits and cavities. This indicated that the inhibitor molecules hinder the dissolution of iron by adsorption on the steel surface and there by reduced the rate of corrosion.

Table 3 Tafel polarization parameter values for the corrosion of mild steel in the absence and presence of inhibitor in 1 M HCl

Concentration of inhibitor (ppm)	I_{corr} (μA cm^{-2})	E_{corr} (mV)	b_c	b_a	I.E (%)
0 (Blank)	565	477	4.03	5.76	-
50	67	495	7.31	8.45	88
100	91	488	6.90	8.11	83
150	99	487	6.59	7.40	82
200	102	482	6.21	7.10	77

3.7. Mechanism of Inhibition

The discussions based on weight loss measurement, polarization study, isotherms, and SEM morphologies; the physical adsorption of the inhibitor molecules is proposed to be the preferable mechanism. Earlier, Kesavan et al examined an Schiff base derived from phenylpropanolamine and salicylaldehyde for corrosion inhibition of mild steel. The authors found that the presence of phenolic hydroxyl group increased the corrosion rate at higher concentrations of inhibitor. Similar results were observed in the present study. The presence of hydroxyl group on the 7th position of 7-hydroxyflavone (Scheme 1) is regarded to be highly acidic in nature [22], which obviously increased the corrosion rate upon increasing the inhibitor concentration. Although, the inhibitor exhibits significant IE% which is more than 80%. The presence of H^+ ions in 1 M HCl is expected to shift the equilibrium more towards the original structure shown in the left side than to the ketone, which is assumed to be the reason for the persisting IE% values of the inhibitor.

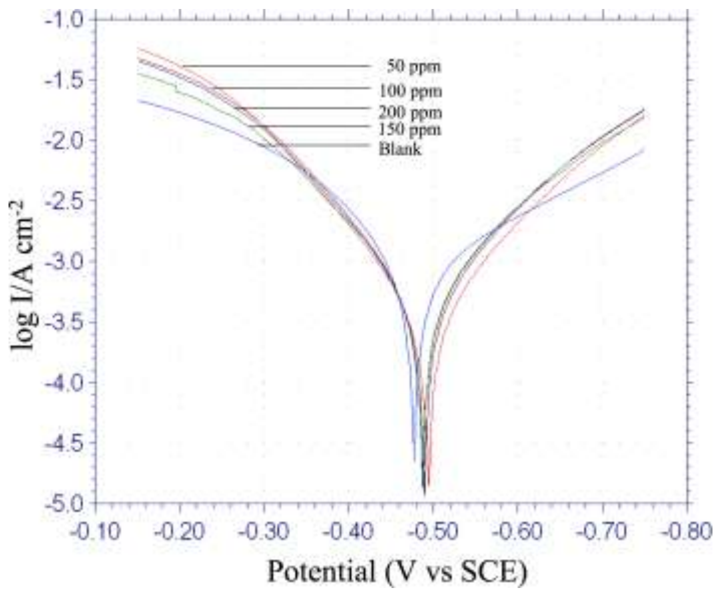
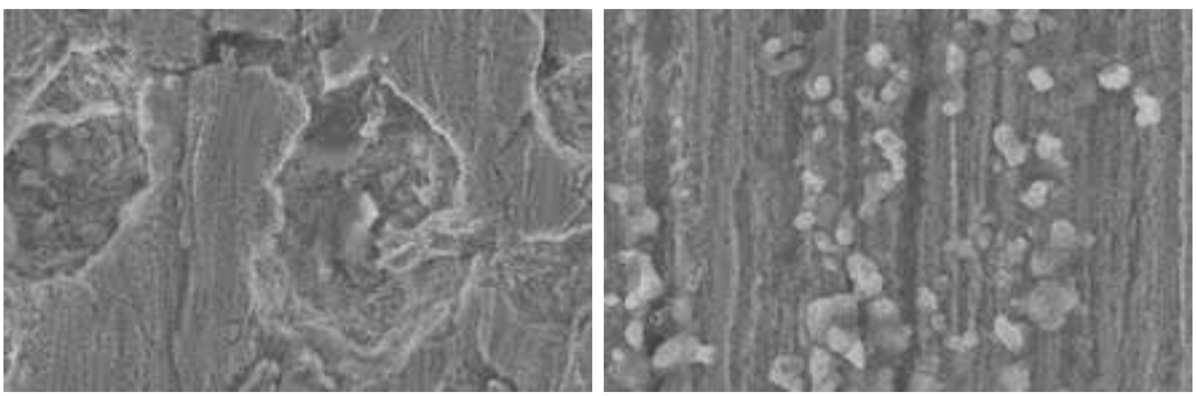
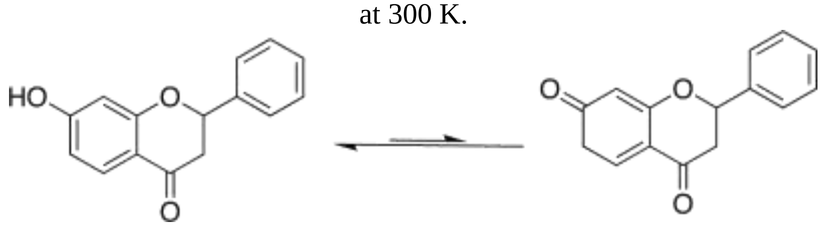


Figure 3 Tafel polarization curves for mild steel in 1 M hydrochloric acid in presence and absence of inhibitor



4a 4b

Figure 4 SEM morphologies of mild steel after immersion in 1 M HCl acid without inhibitor (a) and with inhibitor (b) at 300 K.



Scheme 1 Keto-enol tautomerism of phenolic hydoxyl group in 7-hydroxyflavone.

4. Conclusion

7-hydroxyflavone was examined as a representative natural product for corrosion inhibition of mild steel in 1 M HCl. The weight loss measurement, polarization technique, and adsorption isotherms were employed to evaluate the inhibitor's potential against corrosion. The results showed the inhibitor exhibits IE% ranging from 82–90% at varying concentrations. Langmuir adsorption isotherm of the weight loss data indicated that the inhibitor molecules adsorbed on the mild steel predominantly via physical adsorption. The unusual effect of the inhibitor concentration on IE% is attributed to the presence of phenolic hydroxyl group in 7-hydroxyflavone. By preparing suitable combination of synergistic factors, the flavone inhibitor is expected to show more higher inhibition efficiencies at different corrosive circumstances.

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