



Corrosion Inhibition of Cefuroxime Axetil on Mild Steel with Acid Solution

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ABSTRACT

The inhibition of corrosion on mild steel in 1M H₂SO₄ by a heterocyclic compound namely cefuroxime axetil has been studied by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy methods. The adsorption characters of the inhibitor on mild steel, free energy change and energy of activation of the inhibition process have been calculated from the results. The inhibition efficiency increases with inhibitor concentration and decreases with temperature. The adsorption of the inhibitor on the mild steel surface obeys Langmuir adsorption isotherm. Potentiodynamic polarization studies show that the inhibitor behaves as mixed type. Addition of halide ions enhances the inhibition efficiency.

Key words: Corrosion inhibition, mild steel, Cefuroxime axetil, Inhibition efficiency, Langmuir adsorption.

INTRODUCTION

Mild steel is one of the alloy which find applications for making the entire machinery in industries and for construction of industrial buildings. The surface of the mild steel must be freed from oxide by acid pickling and subjected to surface treatment such as painting enamelling etc. Organic heterocyclic compounds containing azole nucleus have been found to be effective inhibitors for steel in different corrosive media¹⁻³. Some of the organic compounds reported as inhibitors for mild steel in acid media were pyrrolidine dithiocarbamate⁴, beta phenylethylamine⁵, 5-hydroxyindole and nitroindole⁶⁻⁸, triazole derivatives⁹⁻¹², substituted dithiobiurets¹³, tetrazine derivatives¹⁴, hydrazine

and substituted hydrazines¹⁵, quinoline derivatives¹⁶, thiourea derivatives¹⁷, pyridine derivatives¹⁸. In this part of the present work, corrosion of mild steel in 1M H₂SO₄, the effect of cefuroxime-axetil as inhibitor in combating the corrosion have been investigated.

EXPERIMENTAL

The mild steel specimens of the following composition have been used for weight loss, polarization and impedance studies. Carbon: 0.06, Sulphur: Nil, Phosphorous: 0.009, Silicon: Nil, Manganese: 0.32. The sulphuric acid used is of A.R. grade for the preparation of 1M H₂SO₄ solution using double distilled water. The inhibitor used is

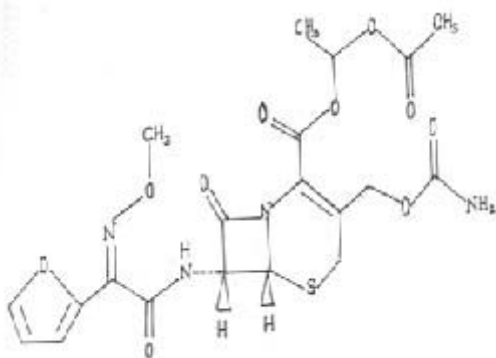


Fig.1. Structure of cefuroxime axetil

cefuroxime axetil prepared by dissolving in acetone. The inhibitor is available as an anti-inflammatory drug. Mild steel panel of 1.5 cm x 2.5 cm has been used for weight loss measurements, while for the polarization experiments a cylindrical rod embedded in teflon with an exposed area of 0.5 cm x 0.5 cm was used. Before each experiment the electrodes were polished with different grade emery papers, degreased with tetrachloroethylene rinsed under running water and finally dried.

Weight loss method

The polished and pre-weighed mild steel specimen were carefully hanged in hooks and suspended in 100 mL test solutions with and without inhibitors of different concentration at 298 K. The temperature was controlled by an aqueous thermostat. After 3 h of immersion in the corrosive solution, the specimen was carefully washed in double distilled water dried and then weighed. The percentage of inhibition efficiency (IE%) for various concentrations of the inhibitor were calculated as

$$\text{Inhibition efficiency, \%} = \frac{W_2 - W_1}{W_3} \times 100$$

Where W_2 = weight loss without inhibitor and W_1 = weight loss with inhibitor

Temperature studies

The effect of temperature on the inhibitory action of the inhibitor was determined by weight loss method with various concentrations at different temperature (308, 313 & 318 K) for a fixed immersion time of 1 h.

Synergistic effects of halide ions

The synergistic effect was studied in the presence of 2 mM KCl and KI to the steel specimen immersed for 3 hours in 1 M sulphuric acid containing 2 mM concentration of the inhibitor. The same weight loss method procedure has been followed to study the synergistic effect. From the weight loss data, the corrosion rate and the inhibition efficiency were calculated.

Polarisation and impedance studies

Electrochemical studies were carried out using the potentiostat model 1280 B solartron (U.K). They were carried out in a glass cell with a capacity of 100 mL. A platinum electrode and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode respectively. The polarisation measurements were carried out with a scan rate of 1 mV/Sec in the range of -200 mV to +200 mV vs corrosion potential of the working electrode measured against SCE. The AC impedance measurements are shown as Nyquist plots and polarisation data as Tafel plots. The impedance measurements were made at a corrosion potentials with the AC voltage amplitude 10 mV in the frequency range 10 KHz to 10 MHz. The I_{corr} , E_{corr} , R_t and C_{dl} values were obtained from the data using the corresponding "corr view" and "Z view" softwares.

RESULTS AND DISCUSSION

Weight loss studies

The cefuroxime axetil was tested for six different concentrations (0.001mM to 2.0mM). The corrosion rate and inhibition efficiency calculated based on weight loss data are given in Table 1. Table 1 reveals that inhibition efficiency increase with an increase in the concentration of the inhibitor reaching a maximum of 79 to 97 % at 2mM (Fig.1). At the same time the corrosion rate decreases with increase in inhibitor concentration. The increase in inhibition efficiency with increase in concentration may be attributed to the increase in surface coverage (θ) by the adsorption of inhibitor on the steel surface.

To investigate the mechanism of inhibition and to determine the activation energies of the corrosion process, the weight loss studies were carried out at higher temperatures from 308-318 K.

Table 1: Inhibition efficiency of cefuroxime axetil on mild steel in 1M H₂SO₄

S.No	Inhibitor concentration (mM)	Weight loss(g)	Corrosion rate (mmpy)	Inhibitor efficiency (%)	Surface coverage (θ)
1	Blank	0.1776	270.31	-	-
2	0.001	0.0341	51.90	79.4	0.7940
3	0.01	0.0207	31.50	87.5	0.8750
4	0.1	0.0187	28.46	88.7	0.8870
5	1.00	0.0110	16.74	93.0	0.9300
6	2.0	0.0066	10.04	97.0	0.9700

Table 2: Inhibition efficiency (%) of 2mM concentration of cefuroxime axetil and corrosion rate of mild steel in corrosion in 1 M H₂SO₄ at different temperature

S. No.	Temperature(K)	Weight loss(g)	Corrosion rate(mmpy)	IE(%)
1	308	0.0208	31.65	88.49
2	313	0.0335	50.98	81.79
3	318	0.0534	81.27	72.16

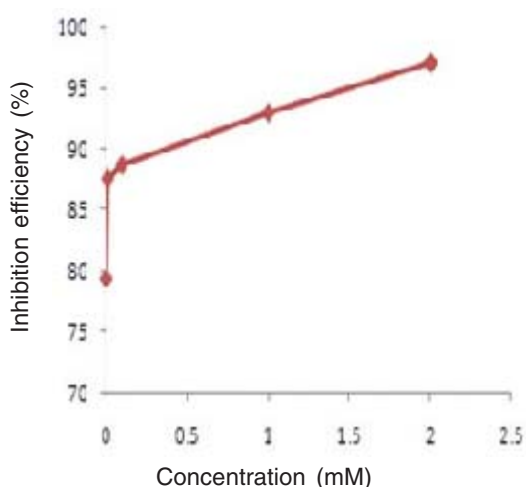
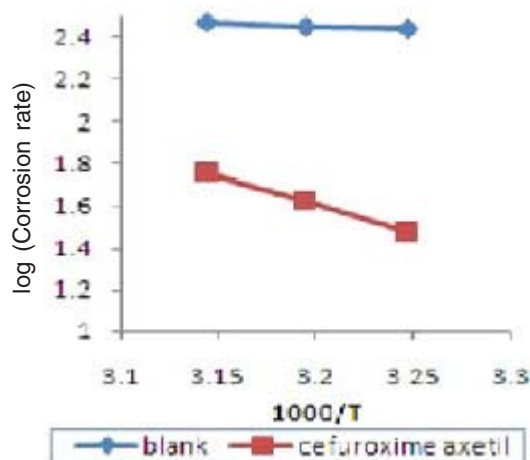
**Fig. 1. Plot of Inhibition efficiency (%) Vs concentration (mM) for the inhibition of cefuroxime axetil on mild steel in 1M H₂SO₄ Effect of Temperature****Fig. 2. Arrhenius plot of corrosion rate of mild steel in 1 M H₂SO₄ solution in the absence and presence of 1 mM concentration of the cefuroxime axetil.**

Table 2 reveals that the rate of corrosion of mild steel increases with increase in temperature in the presence of the inhibitor.

It is observed that inhibition efficiency decreases with increase in temperature from 308-

318 K. The decrease in inhibition efficiency with temperature may be attributed to desorption of the inhibitor molecules from metal surface at higher temperature¹⁹.

Fig. 1 presents the Arrhenius plots of log corrosion rate vs. 1/T for 1 M H₂SO₄ with and without

the addition of the inhibitor and the slopes of the straight lines permit the calculation of Arrhenius activation energy, E_a . The value of E_a (76.80 kJ/mol) increases in the presence of inhibitor. Szauer, Brandt²⁰ and Foroulis²¹ proposed that the lower activation energy value of the process in the presence of the inhibitor compared to that in its absence is attributed to chemisorptions, while the opposite is attributed to physical adsorption. The increase in E_a in the presence of cefuroxime axetil indicates physical or weak bonding between the molecules of the inhibitor and the mild steel surface. The standard free energy of adsorption ΔG_{ads} can be calculated using the relation

$$\log C = \log \theta / (1 - \theta) - \log B$$

$$\text{where, } \log B = -1.74 - (\Delta G / 2.303 RT)$$

θ = Surface coverage, C = Concentration, R = Gas Constant and T = Temperature

The negative values of ΔG_{ads} (Table 4) ensure the spontaneity of the adsorption process and the stability of the adsorbed layer. The value of ΔG , indicates that the inhibitor function by physically adsorbing on the surface of the mild steel. Generally values of ΔG up to -20 kJ mol^{-1} are consistent with electrostatic interaction between charged molecules and charged metal (which indicates physisorption) while those more negative than -40 kJ mol^{-1} involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (which indicates chemisorptions)²².

Synergistic effects of halide ions

Synergism between the organic inhibitor and halide ions on metal corrosion in acidic solution has been researched by many authors²³. Many studies indicate that nitrogen and sulphur containing

Table 3: Effect of anions on corrosion rate for 2mM of Cefuroxime Axetil in 1M H₂SO₄

Name of the anion	Concentration of anion (mM)	Weight loss (g)	Corrosion rate (mmpy)	Inhibition efficiency (%)
Cl ⁻	2	0.0066	10.0452	96
I ⁻	2	0.0020	3.0440	99

organic compounds have been found to behave better for the steel corrosion in hydrochloric acid than in sulphuric acid. The possible reason is that there is a synergistic inhibition between chloride ion and such organic compounds²⁴. In the present study, an attempt has been made to study the influence of halide ions on the corrosion inhibition of cefuroxime axetil for mild steel in 1 M H₂SO₄, by weight loss measurements. It is clear from the Table 3 that addition of halide ions enhanced the inhibition efficiency of the inhibitor.

Explanation for synergism

The compound contains nitrogen with unshared electron pair and p-electrons. In strongly acidic solution, they may be surface contains positive charge due to $E_{corr} - E_q = 0 > 0$ [where $E_q = 0$ = potential of zero charge]²⁵. Thus, it is difficult for the positively charged inhibitor molecules to approach the positively charged steel surface due to electrostatic repulsion. Addition of halide ions

causes their specific adsorption on the steel and causes the steel surface negatively charged. The protonated organic inhibitor is then adsorbed by coulombic attraction on the metal surface and therefore their inhibition efficiency is increased. The synergistic effect increases in the order Cl⁻ < I⁻. This is because iodide ion is the most adsorbable of halide ions on steel.

Adsorption isotherm

Adsorption isotherms are very important in determining the mechanism of organic electrochemical reactions. The most frequently used isotherms are Langmuir, Temkin and Frumkin. The compounds follow Langmuir adsorption isotherm, which is given as

$$\theta / (1 - \theta) = KC$$

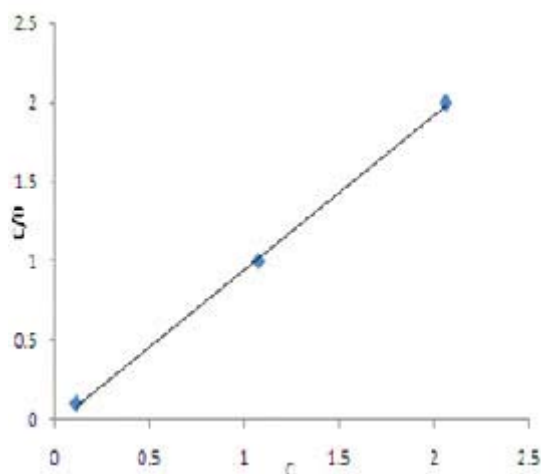
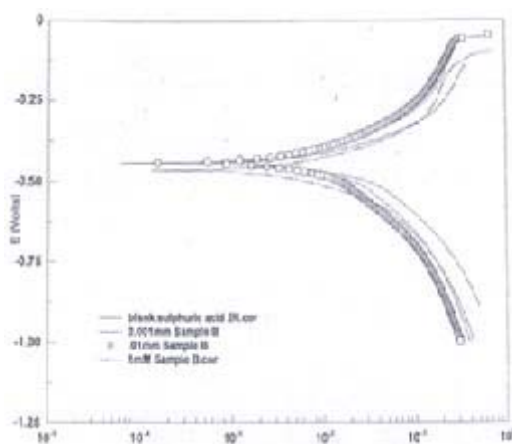
Rearranging this equation

$$C / \theta = 1 / K + C$$

where θ is the surface coverage degree, K the equilibrium constant of the adsorption process

Table 4: Activation energy E_a and free energy of adsorption (ΔG_{ads}) for the corrosion of mild steel in 1 M H_2SO_4 concentration of cefuroxime axetil.

S.No	Concentration (mM)	E_a (kJ/mol)	ΔG_{ads}		
			308 K	313 K	318 K
1	Blank	4.874	-	-	-
2	2	76.80	-15.2341	-14.3382	-13.3202

**Fig.3. Langmuir plot of cefuroxime axetil****Fig.4. Potentiodynamic polarization curves for mild steel in 1 M H_2SO_4 in the absence and presence of selected concentrations of cefuroxime axetil****Table 5: Potentiodynamic polarization parameter for mild steel in 1M H_2SO_4 with various concentration of Cefuroxime Axetil**

Concentration of the Inhibitor (mM)	Tafel slope		E_{corr} (mV/sec)	i_{corr} (A/cm^2)	Corrosion rate (mmpy)	I.E(%)
	b_a (mV)	b_c (mV)				
Blank	146.16	128.71	-442	107	4962.2	-
0.001	126.75	103.68	-464	49	2260.8	54
0.1	138.0	107.28	-457	43	1996.1	60
1	90.85	86.558	-481	7.8	363.05	93

and C is the inhibitor concentration. It was found that a plot of C/θ vs. C is a straight line for cefuroxime axetil. Fig.3 depicts the graph of the Langmuir adsorption isotherm for the studied compound. As adsorption is of Langmuir character, the organic molecules are attached as a monolayer and through a physical mechanism.

Polarization studies

The inhibition process of the cefuroxime axetil for the corrosion of mild steel in 1 M H_2SO_4 was analyzed by polarization experiments. Fig. 4 shows the Tafel anodic and cathodic polarization plots for the inhibitor cefuroxime axetil. Table 5 gives the values of electrochemical corrosion parameters.

The lower corrosion current density (I_{corr}) values in the presence of inhibitors without causing significant changes in corrosion potential (E_{corr}) and Tafel slopes b_a and b_c suggests that the compound is mixed type inhibitor and are adsorbed on the surface there by blocking the corrosion reaction.

Electrochemical Impedance Spectroscopy studies

The anticorrosive performance of the inhibitor was also studied by electrochemical impedance spectra at $30 \pm 1^\circ\text{C}$ for various concentrations of the inhibitor in 1 M H_2SO_4 . The data obtained are given in Table 6. The R_{ct} is increased in the presence of cefuroxime axetil. Maximum increase was observed for at 4 mM concentration. The double layer capacitance C_{dl} decreased, as concentration is increased. This decrease may be due to the adsorption of the

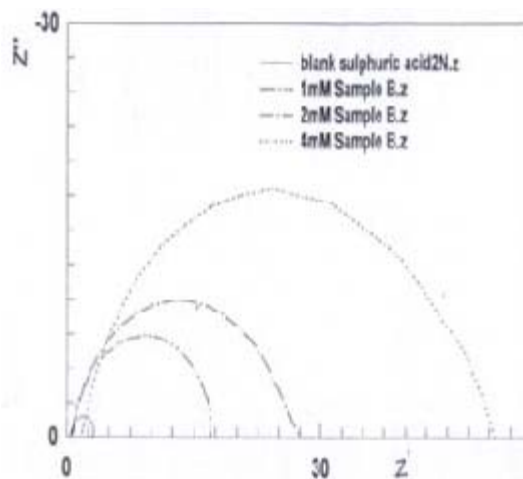


Fig.5. Nyquist plots for mild steel in 1 M H_2SO_4 in the absence and presence of selected concentrations of cefuroxime axetil

Table 6: Impedance parameter for mild steel in 1M H_2SO_4 with various concentration of cefuroxime axetil

Concentration (mM)	R_{ct} (ohm.cm ²)	$C_{dl} \times 10^{-5}$ (Farads)	Inhibition Efficiency(%)
Blank	1.20	40.90	-
1.00	15.86	23.78	92
2.00	28.76	24.93	96
4.00	49.13	17.19	98

compounds on the metal surface leading to a film formation. The corresponding Nyquist diagram for cefuroxime axetil is shown in Fig. 5. As can be noticed, the impedance diagrams are perfect semicircles, indicating a charge transfer process mainly controlling the corrosion of the steel.

CONCLUSION

- Inhibition efficiencies of the inhibitor increase with increase in inhibitor concentrations. The optimum inhibitor efficiency of cefuroxime axetil has been achieved even at very low concentration of the inhibitor (2mM).
- Temperature has significant in corrosion rate

and inhibitor efficiency. Efficiency decreases with increase in temperature shows the desorption of the inhibitor at higher temperature from the metal surface.

- The inhibition of corrosion by cefuroxime axetil is due to physisorption of the inhibitor on the metal surface. The greater E_a value in the presence of inhibitor and the less negative ΔG_{ads} values support this point.
- The variation of Tafel constants b_a and b_c and E_{corr} values with increase in the concentration of inhibitor suggests that this compound acts as mixed type inhibitor.
- The adsorption of inhibitor on the metal surface follows Langmuir isotherm.

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