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Corrosion Behaviour of Mild Steel in Acidic Medium in Presence of Different Inhibitors

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ABSTRACT

The inhibitive effect of Formazan derivative of *p*-dimethyl amino benzaldehyde (FD) and an aqueous extract of *Allamanda blanchetii* (AB) from on the corrosion of mild steel in 2M Sulphuric acid was investigated using weight loss method ,Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The results obtained show that FD and AB could serve as effective inhibitors for the prevention of mild steel in acidic environment. The percentage inhibition increases with increasing the concentration of the inhibitors at room temperature. The corrosion rates of mild steel and inhibition efficiencies of the inhibitors was obtained from impedance and polarization measurements were in good agreement. Potentiodynamic polarization studies clearly reveal that the inhibitors predominantly as a cathodic inhibitor. From this comparison studies it reveals that in mild steel corrosion, FD acts as best inhibitor than AB in 2M H_2SO_4 acid solutions at room temperature for 2 hrs.

Keywords: Mild steel; Formazan derivative of *p*-dimethyl amino benzaldehyde; Allamanda blanchetii; AC impedance, potentiodynamic polarization.

1. Introduction

The use of corrosion inhibitors is very popular in controlling the mild steel corrosion in various manufacturing industries [1-3]. Inhibitors are substances which are added in small amount of concentrations to the corrosive environment decrease or prevent the rate of the reaction in metal with the media [3-6]. Many effective inhibitors contain heteroatom such as O, N, and S and multiple bonds in their molecular arrangement through which they are adsorbed on the metal surface [6-8].

It is experimentally verified that the adsorption mainly depends on the properties of inhibitor like functional groups, electron density at the donor atom, π-orbital character, and the electronic structure of the molecule [8-11]. The attention of researcher was paid in order to develop non-toxic inhibitors to reduce both acid attack and protection aspects in Mild steel [12-15]. Natural products like lignin and tannin [16], cinchona alkaloids [17] and pomegranate alkaloids [18] have been evaluated as very effective acid corrosion inhibitors in standard as well as in stringent conditions. Inhibition of corrosion was studied with the extracts of Antrographis paniculata [19], Thespesia populnea [20], Mangifera indica [21], Datura metal [22], Mentha pulgeium [23], Sesbania grandiflora seeds [24], Ficus benghalensis bark [25], Psidium gerajanra (bark) and Callistemos (leaves) [26], Canavalia ensiformis [27] etc. The natural inhibitors studied have been found to be highly ecofriendly and possess no threat to the environment. Extraction from the plant now become an important due to environmentally acceptable, inexpensive, readily available and renewable sources of materials, and ecologically acceptable. The extraction is carried out by means of simple procedures with minimum cost. In the present work, the authors have reviewed literature on green corrosion inhibitors. Therefore, in this investigation, the corrosion inhibition of mild steel in 2M H_2SO_4 solution is studied and compared in the presence and absence of Formazan of *p*-dimethyl amino benzaldehyde (FD) and in *Allamanda blanchetii* (AB) for two hours at room temperature.

2. Experimental

2.1 Material preparation

Prior to all measurements, the mild steel specimens, having composition (in wt%) 0.016 C, 0.010 P, 0.012 Si, 0.196 Mn, 0.050 Cr, 0.014 Ni and the remainder iron, were polished successively with fine grade Emery papers from 400 to 1200 grades. The specimens were pickled and washed thoroughly with double-distilled water and finally degreased with acetone and dried at room temperature. The aggressive solution 2M H_2SO_4 was prepared by dilution with double-distilled water, and all experiments were carried out in unstirred solutions.

2.2 Preparation of Solutions:

Inhibitor- (Formazan Derivatives)

Aniline (0.02 M) in glacial acetic acid and HCl (0.5ml) was diazotized with sodium nitrite (0.2g) in water (2ml) at (0-5^{o}C). This solution was added continuously with constant stirring to this 0.01 M of semicarbazone in pyridine in the cold and left over night. It was then poured into cold water with stirring when a coloured solid separated out. This was filtered, washed repeatedly with water and recrystalised from ethanol. The reaction scheme for the preparation of the compound is as follows.

Inhibitor solution of Formazan of p-dimethyl amino benzaldehyde (FD) solutions were prepared and its structure is shown in Figure-1

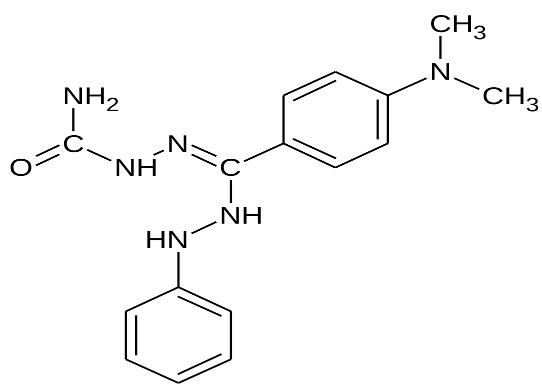

Figure 1- Formazan of p-dimethyl amino benzaldehyde (FD)

2.3 Weight loss measurement:

Mild steel specimens were immersed 2M H_2SO_4 for 2 h at room temperature for each inhibitor concentration. Then the specimens were removed, rinsed in double distilled water, acetone and the loss in weight of the specimen was determined. From this, the inhibiton efficiency (IE %) was calculated using the formula,

$$IE\ \% = \frac{W_o - W_i}{W_o} \times 100 \qquad (1)$$

Where, W_O and W_i (in g) are the values of the weight loss observed of mild steel in the absence and presence of inhibitor respectively.

2.4 Electrochemical Studies:

All the electrochemical measurements were performed using the Electrochemical Workstation (Model No: CHI 600D, CH Instruments, USA) at a constant room temperature which maintained with 2M H_2SO_4 electrolyte. A platinum electrode and a saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively, while the working electrode comprised of mild steel specimen with $1cm^2$ exposed area. The tip of the reference electrode was carefully positioned very close to the surface of the working electrode by the use of a fine Luggin capillary in order to minimize the ohmic potential drop.

The remaining uncompensated resistance was also reduced by the electrochemical workstation. Potentiodynamic polarization studies were carried out at a scan rate of $0.01mV\ s^{-1}$ and at a potential range of -800 to -200 mV for optimum concentration of the inhibitors. The electrochemical impedance studies were carried out in the same setup as that of potentiodynamic polarization studies and the applied ac perturbation signal was about 10 mV within the frequency range 1Hz to 1 KHz. All the electrochemical impedance measurements were carried out at open circuit potential.

The percentage of the inhibition efficiency is calculated from the values of the current density (I_{corr}) with aid of the following formula,

$$IE\% = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100 \qquad (2)$$

I_{corr} = Corrosion current density in the absence of inhibitor

$I_{corr(i)}$ = Corrosion current density in the presence of inhibitor.

3. Results and Discussion

3.1 Weight loss method

The comparison graph of corrosion behaviour of mild steel in 2M H_2SO_4 with Formazan of *p*-dimethyl amino benzaldehyde (FD) and Allamanda Blanchetii (AB) was given in **Figure 2** and inhibitor efficiency of FD and AB was given in **Figure 3** which was studied by weight loss method at 2 h at room temperatures. From the graph, it was observed that the weight loss of mild steel in the acid decreases with increasing concentration of additives and the values were tabulated in **Table 1** from which it was clear that the corrosion rate has decreased with increasing concentration of inhibitor and inhibition efficiency increased with increasing the concentration of the inhibitor. In addition, the maximum corrosion inhibition efficiency of Formazan of *p*-dimethyl amino benzaldehyde (FD) at 31.70 mM was 74.21% respectively in Allamanda Blanchetii (AB) at 52.05mM the inhibition efficiency was 54.41% in 2M H_2SO_4.

Table 1- Corrosion parameters in absence and presence of Formazan of *p*-dimethyl amino benzaldehyde (FD) and Allamanda Blanchetii (AB) with 2M H_2SO_4.

Inhibitor	Conc. of inhibitor (mM)	Corrosion Rate (mm/y)	Inhibitor Efficiency (%)
		2M H_2SO_4	2M H_2SO_4
Formazan of *p*-dimethyl amino benzaldehyde (FD)	Blank	38.8961	---
	6.34	28.5312	26.64
	12.68	23.7389	38.96
	19.02	17.4977	55.01
	25.36	13.8198	64.46
	31.70	10.0305	74.21
Allamanda Blanchetii (AB)	Blank	38.7709	---
	10.41	26.7343	17.00
	20.82	18.4870	28.66
	31.23	13.2488	36.06
	41.64	7.2305	44.56
	52.05	6.7664	54.41

It was also concluded that the inhibitors were very efficient for mild steel corrosion in 2M H_2SO_4. **Figure 2** revealed the comparison of corrosion rate (CR) with concentration of FD and AB (%) in 2M H_2SO_4 solution at two hour at room temperature. Comparison of inhibition efficiency (IE) with concentration of FD and AB(%) in 2M H_2SO_4 solution for two hours at room temperature is shown in **Figure 3.**

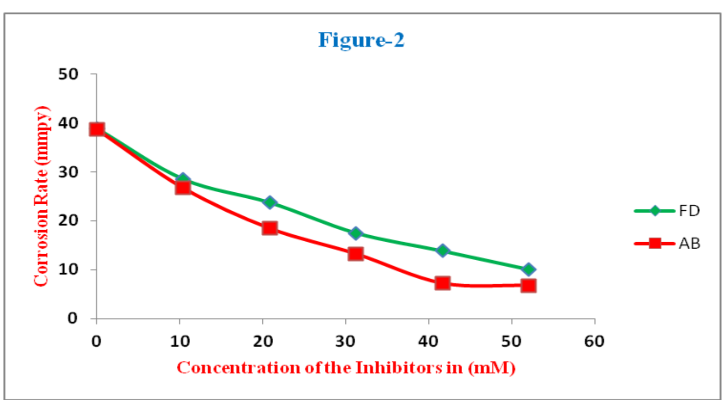

Figure2 – Comparison of corrosion rate (CR) with concentration of FD and AB (%) in 2M H_2SO_4

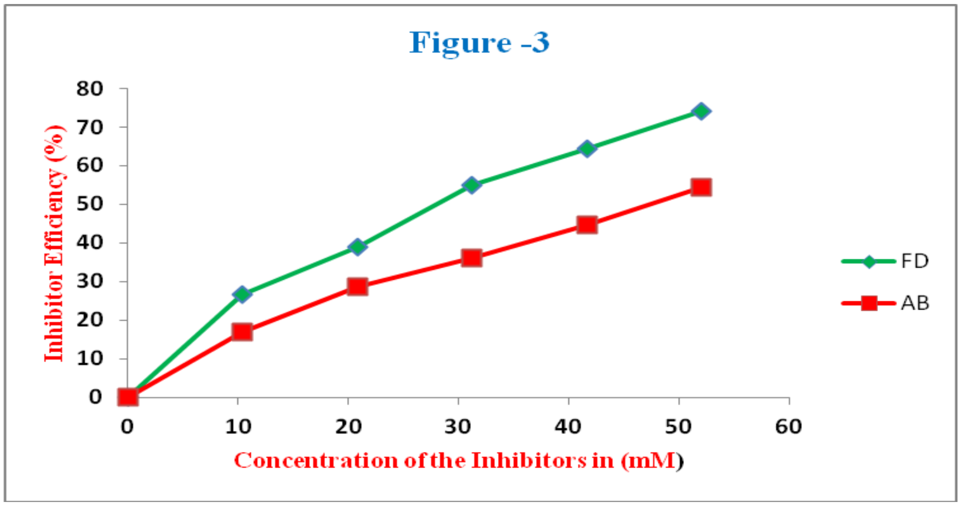

Figure 3 – Comparison of inhibition efficiency (IE) with concentration of FD and AB(%) in 2M H_2SO_4

3.2 Potentiodynamic polarization studies:

Potentiodynamic polarization results obtained for the inhibitory effect of Formazan of *p*-dimethyl amino benzaldehyde FD and AB on mild steel corrosion in 2M $H_2SO_4$are depicted clearly in **Figure 4**. The various polarization parameters such as corrosion current (I_{corr}), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (-βa and -βc) were derived from potentiodynamic polarization studies on mild steel in both acid media.

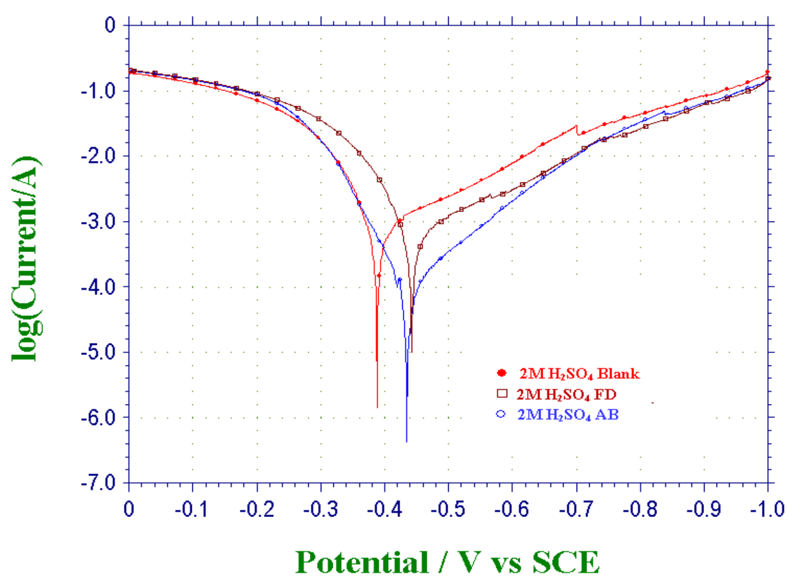

Figure 4 -Potentiodynamic polarization curves of mild steel in 2M H_2SO_4in the absence and presence of the inhibitor.

It could be observed from the Table that the E_{corr} values have shifted slightly towards negative side in presence of inhibitors suggesting that the inhibitors inhibit the corrosion of mild steel in acids solution by controlling cathodic reactions due to the blocking of active sites on the metal surface. It is evident that inhibitors bring about considerable polarization of the cathode. It was, therefore inferred that the inhibitive action of FD is of mixed type. The corresponding results of potentiodynamic polarization parameters are represented in **Table 2**.

Table 2 - Polarization parameters of mild steel electrode immersed in the absence and presence of the optimum concentration of the inhibitors.

Name of the Acid	Inhibitors	β_c (V dec^{-1})	β_a (V dec^{-1})	E_{Corr} (V)	I_{Corr} x10^{-4} (A)	Corrosion Rate (mmpy)	Inhibition Effeciency (%)
2M H_2SO_4	Blank	4.086	11.235	-0.478	3.784	17.481	---
	FD	4.235	8.053	-0.594	0.8457	4.658	74.59
	AB	4.102	9.205	-0.521	0.9987	6.587	60.23

The non-constancy of Tafel slopes for different inhibitor at optimum concentration reveals that the inhibitor action due to the interference in the mechanism of the corrosion processes at cathode. The I_{corr} values have decreased when comparing with different inhibitors at optimum concentration. The inhibition efficiencies determined from the values of corrosion current density and the inhibition efficiency were found to show good agreement with those obtained from weight loss measurements. In 2M H_2SO_4 FD shows maximum inhibition efficiency 74.59 % whereas 60.23% inhibition efficiency in AB. This result suggests that the addition of inhibitors retards the hydrogen evolution reaction [23]. Hence the FD acts as good inhibitor than AB system due to the higher electrostatic attraction of FD and metal surface by the high electron density of the nitrogen (N-H group) atom in the inhibitor molecule.

3.3 Electrochemical impedance spectroscopy (EIS)

The corrosion of mild steel in 2M H_2SO_4 solution in the absence and presence of FD and AB which was investigated by EIS measurements at open circuit potential condition. Nyquist plots for mild steel obtained at the interface of electrode and electrolyte in the absence and presence of optimum concentration of inhibitors is given in **Figure 5**. The Nyquist diagram obtained with 2M H_2SO_4 shows only one capacitive loop and the diameter of the semicircle increases on the increasing the electrostatic attraction of the inhibitor suggesting that the formed inhibitive film was strengthened by the addition of such inhibitors. All the obtained plots show only one semicircle and they were fitted using one time constant equivalent model (Randle's model) with capacitance(C) and charge transfer resistance (R_{ct}). The main parameters deduced from the impedance technique are given **Table 3**.

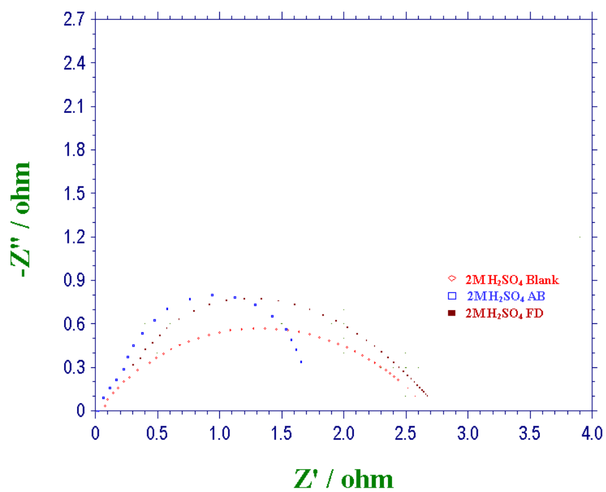

Figure 5 -A.C. Impedance curves of mild steel electrode immersed in 2M H_2SO_4in the absence and presence of the inhibitors.

Table 3 - A.C. Impedance parameters of mild steel electrode immersed in 2M H_2SO_4in the absence and presence of the inhibitors.

Name of the Acid	Inhibitors	Parameters		
		R_{ct} (ohm cm^2)	C_{dl} (µF $X10^{-5}$)	Inhibition Efficiency (%)
2M H_2SO_4	Blank	72.72	4.118	-
	FD	274.80	1.592	73.53
	AB	187.92	1.125	50.14

The lower double layer capacitance (C_{dl}) value for 2M H_2SO_4 mediums indicates that the homogeneity of the surface of the mild steel roughened due to corrosion. The double layer capacitance C_{dl} values have decreased on the effective addition of different inhibitors at the optimum concentration. The studied system indicates that the reduction of charge accumulated in the double layer due to formation of adsorbed inhibitor layer [24]. The inhibiting efficiencies show that the inhibitory actions may be due to the adsorption of the inhibitors on mild steel surface [25].

The compound investigated FD and AB has been found to give an excellent inhibition due to the electron density on the nitrogen of the N-H group. Generally on the metal side, electrons control the charge distribution whereas on the solution side is controlled by ions. Since ions are much larger than the electrons, the equivalent ions to the charge on the metal will occupy quite a large volume on the solution side of the double layer [26]. It can be obtained from **Table 3** that, the capacitance of the electrical double layer (C_{dl}) decreases in the presence of the inhibitors. Decrease in the (C_{dl}) which can result from a decrease in local dielectric constant and / or an increase in the thickness of the electrical double layer, suggests that the inhibitor molecule may act by adsorption at the metal/solution interface [27].

Conclusions:

The present study leads to the following conclusions in controlling the corrosion of mild steel by Formazan of p-amino benzaldehyde (FD) and *Allamanda blanchetii* (AB) in 2M H_2SO_4.

1. In 2M H_2SO_4 both the inhibitors Formazan of p-amino benzaldehyde (FD) and *Allamanda blanchetii* (AB) was found to be an effective inhibitor giving inhibition efficiency upto 74.21% in FD and 54.41 % respectively.
2. Polarization measurements demonstrate that the compound under investigation FD and AB inhibit both anodic and cathodic reaction and hence it act as mixed type inhibitors.
3. Impendance measurements indicate that, the presence of electron donating group on the inhibitor increase the charge transfer resistance and decreasing the double layer capacitance. The type of the substitutents group and the type of the functional atoms of the inhibitor molecule are found to play an important role in the inhibition process.

4. Results obtained from weight loss measurements and electrochemical measurements are in good agreement.
5. FT-IR analysis confirm that the inhibiton efficiency of the inhibitor in mild steel through electrostatic attraction of inhibitor molecule and the metal surface.
6. The morphological investigation also confirms the effective protection of mild steel, through the less damaged and minimum pits found in the inhibited surface.

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