

## **Corrosion resistance properties of Benzhydrylidene-(3, 4, 5-trimethoxy-phenyl)-amine on mild steel in 0.5M sulphuric acid media**

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### **Abstract**

New Schiff base Benzhydrylidene-(3, 4, 5-trimethoxy-phenyl)-amine has been evaluated as effective corrosion inhibitor for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The inhibition action of the this compound has been investigated by using galvanostatic polarisation. The maximum inhibition efficiency (99.13% ) was observed for 10<sup>-1</sup> moles/litre BHTPA at 25<sup>0</sup>C. Polarization studies showed that BHTPA acts as a mixed type inhibitor. The number of water molecules (X) replaced by a molecule of Schiff base adsorbate was determined from the langmuir isotherms applied to the data obtained from the gravimetric experiments performed on mild steel specimen in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at 298.The kinetic and adsorption parameters for mild steel in the presence and absence of BHTPA were evaluated and thermodynamic parameter  $\Delta G$  was found to be negative which indicates spontaneous process.

### **1. Introduction**

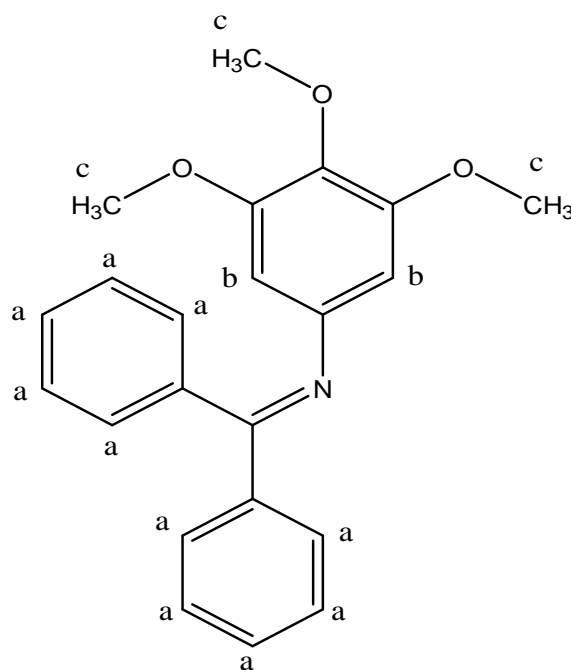
Carbon steel is used in mass amounts in marine applications, chemical processing, petroleum production and refining, construction and metal processing equipment [1–4], despite it has a relatively high cost. These applications usually induce serious corrosive effect on equipment's, tubes and pipelines made of iron and its alloys [5–7]. A huge cost is invested to control corrosion in oil and gas industry, usually corrosion inhibitors are used to inhibit corrosion. Corrosion inhibitors are organic compounds having polar groups including nitrogen, sulphur and/or oxygen atoms and heterocyclic compounds with polar functional groups and conjugated double bonds [8-10]. Inhibition appears as a result of adsorption of molecules and ions on the metal surface [11]. In the literature, several Schiff bases have reported as effective corrosion inhibitors for different metals and alloys in acidic media [12–15]. Increasing

popularity of Schiff bases in the field of corrosion inhibition science based on the ease of synthesis from relatively inexpensive starting materials and their eco-friendly or low toxic properties [16, 17]. The high inhibitory performance of these compounds results from the substitution of different heteroatoms (e.g. N, O, Cl and Br) and p-electrons in their structure besides the presence of imine (-C=N-) functional group [18, 19]. These molecules normally form a very thin and persistent adsorbed film that lead to decrease in the corrosion rate due to the slowing down of anodic, cathodic reaction or both [20–22]. In the present work BHTPA has been synthesized to investigate their inhibition effect on the corrosion of carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions by electrochemical techniques.

## 2. Experimental details

### 2.1 Materials

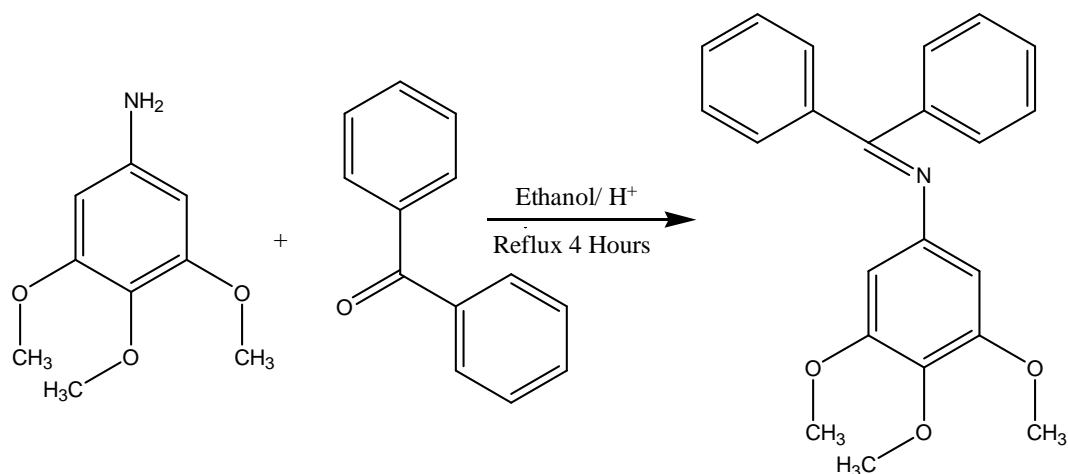
The mild steel samples of dimensions 5 cm × 1 cm × 1 cm were prepared from rectangular rod having composition (C = 0.15%, Si = 0.08%, S = 0.025%, P = 0.025% and Mn = 1.02%). These rectangular steel samples was mounted with polyester in such a way that only 1 cm<sup>2</sup> area of rod was exposed to electrolyte. Prior to any test, the exposed area of mild steel working electrode was mechanically abraded by emery papers of various grits (400, 600, 1000). Finally the steel samples were rinsed in acetone and dried. For each test, a freshly abraded electrode was used. Solution of 1 N H<sub>2</sub>SO<sub>4</sub> were prepared from analytical grade reagents using double distilled water. Test solution were 1N H<sub>2</sub>SO<sub>4</sub> with and without inhibitor in the concentration range  $1 \times 10^{-1}$  to  $1 \times 10^{-4}$  M.



**Fig.1.** The chemical structure Structure of Schiff base prepared.

## 2.2. Synthesis of Schiff base

3, 4, 5-Trimethoxy-phenylamine was refluxed with Diphenyl-methanone in ethanol at 65 °C for 4 hours to form Benzhydrylidene-(3, 4, 5-trimethoxy-phenyl)-amine. The product, “an symmetric Schiff’s base” BHTPA (the structure of which is shown in Fig. 1), was separated by vacuum distillation and purified by vacuum distillation in hexane and ethyl acetate medium. The ethanol solution of the product obtained was distilled to remove the unreacted reactants.

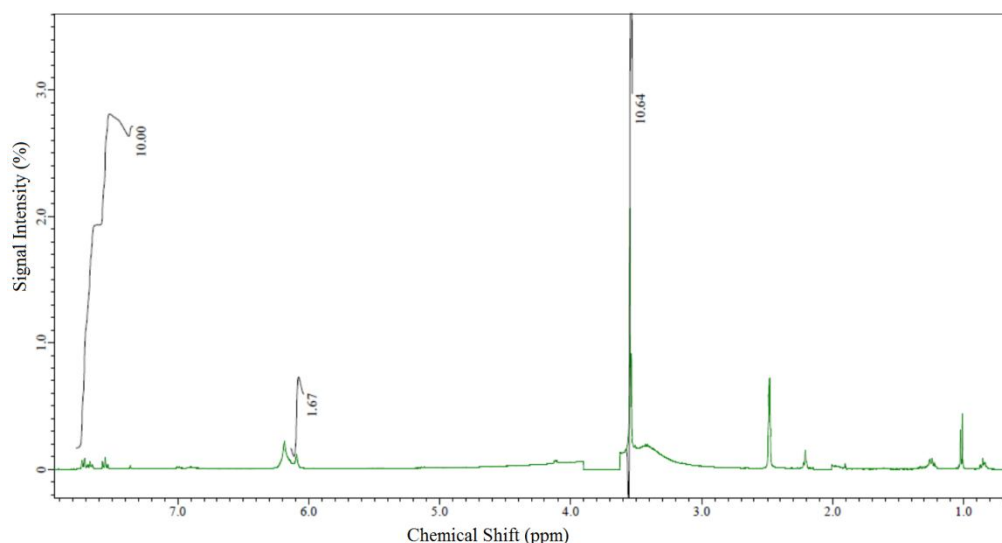


**Fig.** Scheme of synthesis of BHTPA.

The structures of the compounds were confirmed by <sup>1</sup>H nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR).

<sup>1</sup>H NMR data of BHTPA (in DMSO): 7.5-7.8 ppm (10 H, m), 6.1-6.2 ppm (2H, s), 3.4-3.6 ppm (9H, s)

The multiplet peak at 7.5 to 7.8ppm is for Ten H of two phenyl rings numbered as a in fig 1. The Singlet peak at 6.1-6.2ppm is of Two equivalent hydrogens numbered as b in fig 1. The singlet at 3.4-3.6ppm is for nine H numbered as c in fig 1.



**Fig.3.** The  $^1\text{H}$  NMR spectra of BHTPA.

The data of  $^1\text{H}$  NMR spectrum confirmed the expected hydrogen proton distribution in the synthesized Schiff base BHTPA.

### 2.3. Electrochemical measurements

Electrochemical measurements were carried in conventional three-electrode cell with mild steel as working electrode, a Pt wire counter electrode and Ag/AgCl as reference electrode. A computer controlled chi 760 model electrochemical analyzer was used for measurements. The working mild steel electrode was immersed in test solution for 4 hours to establish steady state open circuit potential  $E_{\text{ocp}}$ . All reported potentials were with respect to SCE. For Tafel measurements, the potential-current curves were recorded at a scan rate of  $0.001 \text{ Vs}^{-1}$  in the potential range obtained by adding  $-0.2$  and  $+0.2 \text{ V}$  to open circuit potential (OCP) value. The corrosion parameters such as corrosion potential ( $E_{\text{corr}}$ ), corrosion current ( $I_{\text{corr}}$ ) cathodic Tafel slope ( $b_c$ ), and anodic Tafel slope ( $b_a$ ) were obtained from the instrument.

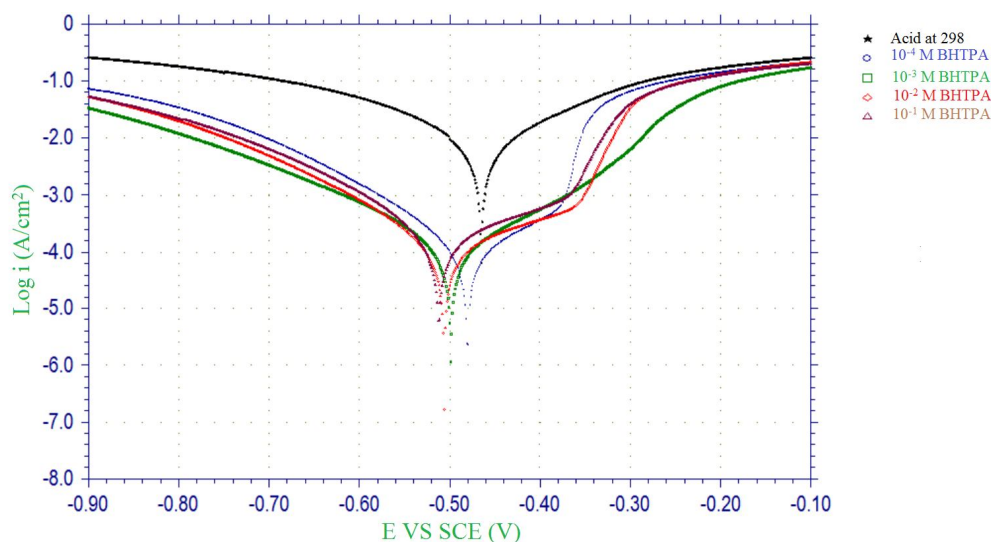
## 3. Results and discussion

### Potentiodynamic polarisation curves:

Fig. 4. Shows the cathodic and anodic polarization curves of mild steel in  $0.5 \text{ M H}_2\text{SO}_4$  solutions at  $25^\circ\text{C}$  in the presence of different concentrations of BHTPA. It follows tafel behaviour. The corresponding Electrochemical parameters i.e. corrosion potential ( $E_{\text{corr}}$  versus SCE), corrosion current density ( $i_{\text{corr}}$ ) and cathodic and anodic tafel slopes ( $\beta_a$ ,  $\beta_c$ ) were calculated from these curves and are listed in table 1. Inhibition Efficiency (IE %) was calculated using the relationship (1)

$$IE \% = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}}} \times 100 \quad (1)$$

Where  $I_{\text{corr}}$  and  $I_{\text{corr(inh)}}$  represent the corrosion current density values without and with inhibitor, respectively.



**Fig.4.** Tafel polarisation curves for mild steel in 0.5M  $\text{H}_2\text{SO}_4$  solution in the presence and in the absence of the BHTPA at various concentrations.

The degree of surface coverage ( $\theta$ ) values for different concentrations is calculated by following equation. (2)[23]

$$\theta = 1 - (I_{\text{corr}}/I_0) \quad (2)$$

Galvanostatic polarisation studies on mild steel in 0.5M sulphuric acid solution containing various concentrations reveal that BHTPA influences the corrosion parameters (table 1). This inhibitor has produced a noticeable decrease in the corrosion current density at all the concentrations. The inhibitive action is better expressed by inhibition efficiency which increases with BHTPA concentration (Table 1). The inhibitor efficiency attains the maximum value of 99.13 % at  $10^{-1}$  M BHTPA.

As it was expected both anodic and cathodic reactions of mild steel electrode corrosion were inhibited by the increase of concentration of the synthesized Schiff base. This result suggests that the addition of the synthesized inhibitor reduces anodic dissolution and also retards the hydrogen evolution reaction [24].

The irregular trends of  $b_a$  and  $b_c$  values indicates the involvement of more than one type of species adsorbed on the metal surface. Therefore, the adsorption of the  $\pi$ -electron system of BHTPA possibly overlaps with the vacant d-orbitals of the surface of iron resulting in a strong  $d\pi$ - $p\pi$  interaction. This electrostatic interaction probably leads to a stronger adsorption of the inhibitor and formation of a barrier between the metal surface and reactive sites. At lower concentration ( $10^{-4}$  M) surface coverage drops considerably because of the inability of BHTPA to block the active sites, hydrogen permeation onto the metal surface.

There is no remarkable change in the OCP of inhibited solutions from that of uninhibited solution (fig.4) but there is shift in OCP values towards more negative potential in the presence of higher concentrations of the synthesized inhibitor, suggesting that this compound behave as mixed-type anodic inhibitor.

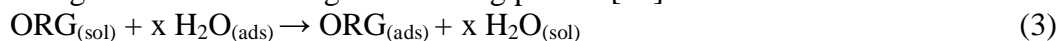
**Table.1.** Electrochemical parameters for the corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with and without different concentrations of inhibitors at 25 °C.

Temp	Conc (M)	$I_{corr}$ (mA/cm <sup>2</sup> )	$-E_{corr}$ Vs SCE(mV)	$b_a$ (mV/dec)	$b_c$ (mV/dec)	I.E. %	Q
298	Blank	8.805	465	70.59	60.89	-	-
	10 <sup>-4</sup>	0.364	479	75.15	82.66	95.86	0.9586
	10 <sup>-3</sup>	0.225	499	82.15	90.47	97.74	0.9774
	10 <sup>-2</sup>	0.130	504	76.49	79.84	98.52	0.9852
	10 <sup>-1</sup>	0.076	510	166.78	95.89	99.13	0.9913

### Adsorption isotherm

The corrosion inhibitive action of the Schiff's base molecules in the acid media on mild steel is due to its adsorption at the metal–solution interface. The adsorption isotherm can be determined if the inhibitor effect is due mainly to the adsorption on the metal surface (i.e. to its blocking).

The adsorption process consists of the replacement of water molecules at a corroding interface according to following process[25].



where Org(sol) and Org(ads) are the organic molecules in the solution and adsorbed on the metal surface, respectively, and x is the number of water molecules replaced by the organic molecules. For organic compounds, which impede the metal dissolution reaction in acid media, the surface coverage can be evaluated as a function of the inhibitor efficiency (IE%). The link between the surface coverage and the inhibitor efficiency at constant temperature gives an insight into the adsorption process.

In the present study, various adsorption isotherms were tested and it was found that the adsorption of Schiff's base on the mild steel surface in acid media follows the Langmuir adsorption isotherm

According to Langmuir's isotherm, surface coverage is related to inhibitor concentration (C) by the following equation [26]

$$C/\theta = 1/K_{ads} + C \quad (4)$$

where  $K_{ads}$  is the equilibrium constant for adsorption process. The plot of  $C/\theta$  versus C yields a straight line (Fig. 5) with regression coefficient ( $R^2$ ) close to 1 (0.9997) suggests that the adsorption of inhibitor molecules follow Langmuir adsorption isotherm. The  $K_{ads}$  values can be calculated from line intercept on  $C/\theta$  axis and is related to standard free energy change of adsorption ( $\Delta G^\circ_{ads}$ ) as follows [27]

$$\Delta G^{\circ}_{\text{ads}} = -2.303RT \log (55.5 K_{\text{ads}}) \quad (5)$$

where R is molar gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), T is absolute temperature (K) and value 55.5 is the concentration of water (in  $\text{mol dm}^{-3}$ ) in the solution.

A second order polynomial of the adsorption free energy versus temperature is shown in following equation (6):

$$\Delta G = 0.1733T^2 - 206.45T + 19133 \quad (6)$$

The most common independent variables are T and P, and from Gibbs equations we can obtain temperature dependences of free energy, G, which is expressed as (7)

$$dG = -SdT + VdP \quad (7)$$

At constant P we write  $dP = 0$  and we can obtain Eq. (8)

$$\Delta S = - (dG/dT)_P \quad (8)$$

If the second order polynomial expression (6) is derived according to T at constant P, Eq. (9) is obtained.

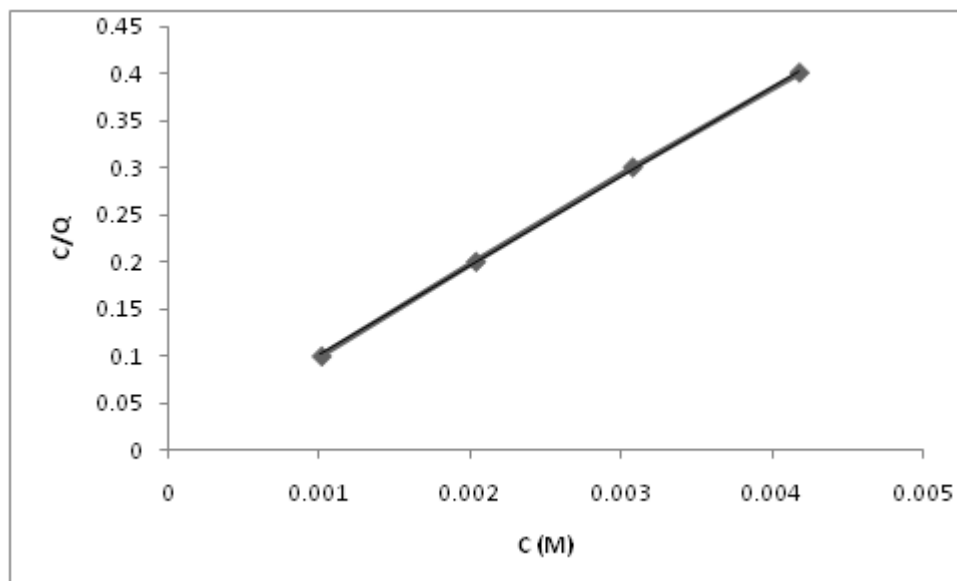
$$\Delta S = -0.3466T + 206.45 \quad (9)$$

Thus  $\Delta S_{\text{ads}}$  values can be calculated at all studied temperature from Eq. (9).

$\Delta H_{\text{ads}}$  values are also calculated at all studied temperatures applying the  $\Delta G_{\text{ads}}$  and  $\Delta S_{\text{ads}}$  values in Eq. 10 [28]

$$\Delta H_{\text{ads}} = \Delta G_{\text{ads}} + T\Delta S_{\text{ads}} \quad (10)$$

The calculated thermodynamic parameters are listed in Table 2. The positive values of  $\Delta H_{\text{ads}}$  led to interpretation that adsorption onto the mild steel surface through endothermic reaction. This could be explained in the following way: the adsorption of inhibitor from the aqueous solution can be regarded as quasi-substitution process between water molecules at the mild steel surface and the organic compound in the aqueous phase. Here, the adsorption of BHTPA molecules is accompanied by desorption of water molecules from the surface which results in positive enthalpy [29].  $\Delta S_{\text{ads}}$  values were positive, this can be explained as the inhibitor molecules were earlier free to move in bulk solution but after inhibitor molecules were orderly adsorbed onto steel surface, as a result, a decrease in entropy observed. The large negative  $\Delta G^{\circ}_{\text{ads}}$  and high  $K_{\text{ads}}$  values insure spontaneity of adsorption, stability of the adsorbed layer on the mild steel surface and hence better inhibition efficiency. It is well known that values of  $\Delta G^{\circ}_{\text{ads}}$  of the order of  $20 \text{ kJ mol}^{-1}$  or lower indicate a physisorption and those of order of  $40 \text{ kJ mol}^{-1}$  or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) [30, 31]. In accordance with this, it could be said that the interaction seems to be physical.



**Fig. 5.** Langmuir adsorption isotherm of the inhibitor in 1.0 M H<sub>2</sub>SO<sub>4</sub> at 25 °C:

**Table 2.** Thermodynamic adsorption parameters for BHTPA on mild steel in 1.0 M H<sub>2</sub>SO<sub>4</sub> solution at 298.

Compound	K <sub>ads</sub>	R <sup>2</sup>	-ΔG° <sub>ads</sub> (kJ/mol)	-ΔS <sub>ads</sub> (J/mol)	ΔH <sub>ads</sub> (J/mol)
BHTPA	1.66 × 10 <sup>2</sup>	0.9997	22.63	103.16	8111.68

## CONCLUSIONS:

The Schiff base Benzhydrylidene-(3, 4, 5-trimethoxy-phenyl)-amine was synthesized and Evaluated as possible corrosion inhibitor for mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> solution.

According to results obtained, the following points can be emphasized:

1. The BHTPA Schiff base has better corrosion inhibition efficiency than the corresponding amine group. The inhibition efficiency of Schiff base studied depends on its concentration. The excellent inhibition efficiency was attributed to the adsorption of inhibitor molecules and protective film formation on the metal surface.
2. The potentiodynamic polarization curves indicated that the BHTPA Schiff base inhibits both anodic metal dissolution and also cathodic hydrogen evolution reactions but OCP is becoming more negative with the increase in inhibitor concentration proving it a mix type cathodic inhibitor, with predominantly control of cathodic reaction..
3. The adsorption of BHTPA molecules on the metal surface from 0.5M H<sub>2</sub>SO<sub>4</sub> solution obeys Langmuir adsorption isotherm. The high value of adsorption equilibrium constant and the negative value of standard free energy of



adsorption suggested that, the BHTPA molecules were strongly adsorbed on mild steel surface and this adsorption took place spontaneously.

4. The standard free energy of adsorption has been found close to  $-22 \text{ kJ mol}^{-1}$  which indicated that the adsorption is seen more a physical form than chemical adsorption.

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