

# A New Synthesized Corrosion Inhibitor for Mild Steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>

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## ABSTRACT

The inhibition effect of a new synthesized organic inhibitor , namely 1-(3-Nitrobenzylidene) Thiosemicarbazide (A) on the corrosion of mild steel in 0.5 M sulphuric acid have been investigated at room temperature using weight loss, electrochemical impedance spectroscopy(EIS) and Tafel polarization measurements. The inhibition efficiencies obtained from all methods employed are in good agreement with each other. The obtained results show that compound (A) is a very good inhibitor with efficiency of 98% at 100 ppm additive concentration in acid solution. Generally the inhibition efficiency increased with increase of inhibitor concentration. Changes in impedance parameters (  $R_{ct}$  and  $C_{dl}$  ) were indicative of adsorption of compound (A) on the metal surface, leading to the formation of a protective film. Tafel polarization measurements showed that the inhibitor (A) is a mixed type. The adsorption of the inhibitor on the surface of mild steel in 0.5 M sulphuric acid was found to obey Langmuir's adsorption isotherm. Scanning electron microscopy (SEM) observation, confirmed the existence of an adsorbed protective film on the metal surface. The free energy of adsorption process was calculated and discussed.

**Key Words:** inhibitor, mild steel, AC impedance, corrosion inhibition

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## 1. INTRODUCTION

The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic solution [1].The organic compounds are widely used as acid inhibitors in industrial operations, such as pickling, cleaning, acidization of oil wells, to protect metals and alloys[2-3]. The organic substances contain mainly oxygen, sulfur, nitrogen atoms, and multiple bonds in the molecules that facilitate the adsorption on the metal surface are strongly polar [4-5]. The polar unit is regarded as the reaction center for the adsorption process. Thus, polar organic compounds are adsorbed on the metal surface, forming a charge transfer complex bond between their polar atoms and the metal. The size, orientation,

shape and electric charge on the molecule determine the degree of adsorption and hence the effectiveness of the inhibitor [6-8]. Synthesized organic compounds such as Schiff bases have been previously reported as effective corrosion inhibitors for steel, copper and aluminum [9-13].

In the present work, the efficiency of a new synthesized organic compound (A) as inhibitor for the corrosion of mild steel in 0.5 M sulphuric acid is discussed on the basis of weight loss, electrochemical impedance spectroscopy(EIS),Tafel polarization data and scanning electron microscopy (SEM). The structure of synthesized organic compound (A) is shown in Figure 1

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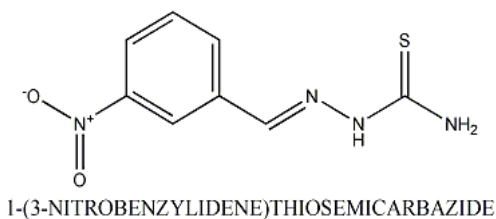


Figure 1. structure of synthesized organic inhibitor (A).

## 2. EXPERIMENTAL

### 2.1. Materials Preparation

AR grade  $H_2SO_4$  (Merk) and double distilled water were used for preparing test solutions of 0.5 M  $H_2SO_4$  for all experiments. The inhibitor compound was synthesized in laboratory and recrystallized. Inhibitor compound with structure shown in Figure 1 was dissolved in absolute ethanol to obtain 1000ppm concentration, then from this concentration by adding to corrosive electrolyte were prepared designated concentration of inhibitor (25, 50, 75 and 100ppm). All tested were performed at room temperature.

### 2.2. Electrodes

For all experiments, mild steel coupons with composition (wt %) C 0.34%, Si 0.3%, Ni 0.1%, Mn 0.76%, P 0.02%, S 0.02% and Fe(balance) were used. The electrode was polished to mirror finish, using fine grain emery paper of (120-2400) grade under water flow, washed with double distilled water and acetone and dried prior to the experiments.

### 2.3. Weight-loss Measurements

Gravimetric corrosion measurements were carried out at room temperature according to the ASTM standard procedure described in literature [14]. The mild steel coupons with dimensions ( $1 \times 1 \times 0.1$  cm<sup>2</sup>) in triplicate were immersed in 100 mL of 0.5 M  $H_2SO_4$  with and without inhibitor. The mass of coupons before and after immersion was determined using an analytical balance accurate to 0.1 mg. For further data processing, the average of the three replicate values was used.

### 2.4. Electrochemical Measurements

For electrochemical studies, the metal was embedded in epoxy resin, to expose geometrical surface area of 1cm<sup>2</sup> to electrolyte. The electrochemical impedance experiments were carried out using AC signals of amplitude 5mV peak to peak at the open circuit potential (OCP) in the frequency range 100 kHz to 10 mHz after 30 min immersion in the electrolyte cell. Polarization curves were recorded with scanning rate of 1 mV/s, after 30 min immersion from -250 to +250 mV with respect to the corrosion potential vs. SCE. The linear Tafel segments of the anodic and cathodic curves were extrapolated to

corrosion potential to obtain the corrosion current densities. The electrochemical experiments were carried out with a Potentiostat/Galvanostat 263A (EG&G) Princeton Applied Research HF response model 1025. For electrochemical measurements, the cell used was a conventional three electrodes Pyrex glass with a platinum counter electrode and a standard calomel electrode (SCE) as reference.

### 2.5. Scanning Electron Microscopy (SEM)

Immersion corrosion analysis of mild steel samples in the acidic solutions with and without the optimal concentration of the inhibitor was performed using SEM., immediately after the corrosion test, the samples were subjected to SEM studies to know the surface morphology. SEM (Cam Scan MV2300) was used for the experiments.

## 3. RESULT AND DISCUSSION

### 3.1. Gravimetric Measurements

The inhibition efficiencies ( $\eta_w$ %) of varying concentration of inhibitor (A) from the experimental weight loss data, were calculated as follows [15].

$$\eta_w \% = \frac{w_0 - w}{w_0} \times 100 \quad (1)$$

Where  $w_0$  and  $w$  are the values of weight loss of mild steel after immersing in electrolytes in the absence and presence of inhibitor (A) respectively. The obtained parameters were summarized in table 1.

Table 1. Inhibition efficiency for various conc. of inhibitor (A) for mild steel in 0.5M  $H_2SO_4$  obtained from weight loss measurements.

Inh. conc. (ppm)	$\eta_w$ %
25	73.88
50	92.34
75	96.08
100	97.68

As can be seen in table 1, the synthesized inhibitor (A) inhibit the corrosion of mild steel at all concentration in 0.5M  $H_2SO_4$ . Inspection of these data in table 1, reveals that the inhibition efficiency increased with increasing the concentration of the synthesized inhibitor (A).

### 3.2. Polarization Measurements

Anodic and cathodic polarization curves for mild steel in 0.5M  $H_2SO_4$  with various conc. of inhibitor (A) are shown in Figure 2. A decrease in both anodic and cathodic currents is noted.

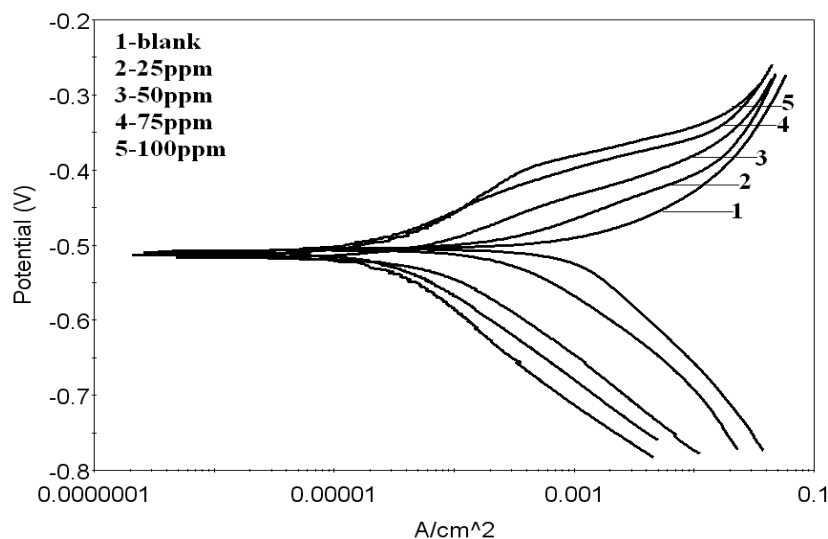


Figure 2. Polarization curves for mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> with various conc. of inhibitor (A).

The various electrochemical parameters such as  $E_{corr}$ ,  $I_{corr}$  and  $\eta_p\%$  obtained by extrapolation of the Tafel lines were given in table 2. As was expected both anodic and cathodic reactions of mild steel electrode corrosion were inhibited with the increase of the synthesized inhibitor (A) concentration. This result suggests that the addition of this compound (A) reduces anodic dissolution and also retard the hydrogen evolution reaction. The inhibition efficiency,  $\eta_p\%$  were calculated as follows [16].

$$\eta_p \% = \frac{I_{0corr} - I_{corr}}{I_{0corr}} \times 100 \quad (2)$$

Where  $I_{0corr}$  and  $I_{corr}$  are uninhibited and inhibited current densities, respectively. This inhibitor causes change in the anodic and cathodic branch and no definite trend was observed in the shift of  $E_{corr}$  values in the presence of different concentrations of the synthesized inhibitor (A), suggesting that this compound behaves as mixed-type inhibitor.

Table2. Electrochemical parameters for mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> with various conc. of inhibitor (A) obtained from polarization curves.

Inh.c onc. (ppm)	$E_{corr}$ vs SCE/mv	$I_{corr}$ $\mu A/cm^2$	% $\eta_p$
0	-	118	-
25	504.5	2.00	7
50	-	283.	6.00
75	506.0	10	9
100	-	67.3	4.30
	516.5	3	9
	-	31.5	7.32
	509.5	9	9
	-	22.8	8.07
	513.0	0	

### 3.3. Electrochemical Impedance Measurements

Nyquist plots for mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> with various conc. of inhibitor (A) are shown in Figure 3.

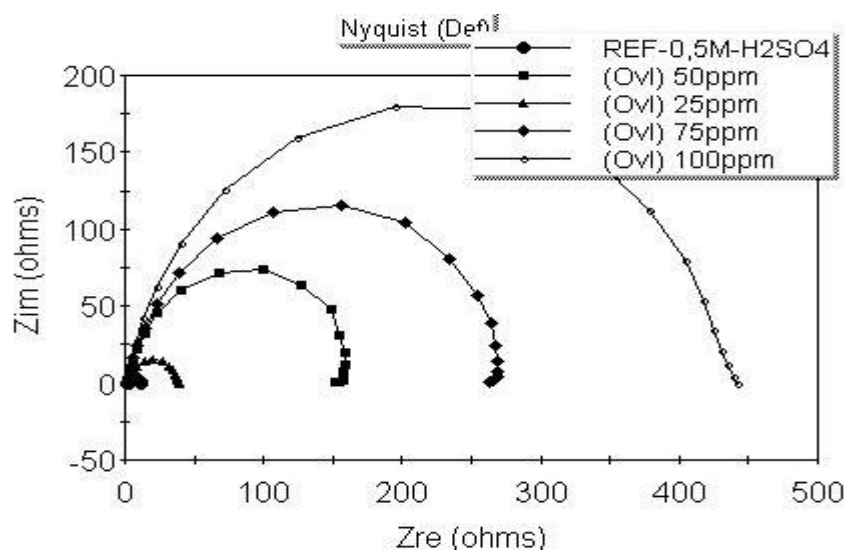


Figure 3. Nyquist plots for mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> with various conc. of inhibitor (A).

The impedance spectrums show a clear and slightly depressed semicircular shape in the complex impedance plane, with the center under the real axis. The equivalent circuit for this kind of complex impedance plane is plotted in Figure 4. by using Zsimpwin3.21 software.

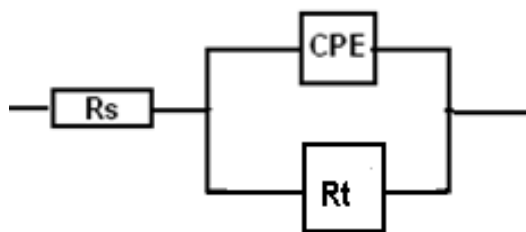


Figure 4. The suggested equivalent circuit model for the studied system.

Excellent fit with the model is obtained for all experimental data. Electrically equivalent circuits are generally used to model the electrochemical behavior and to calculate the parameters of interest such as electrolyte resistance ( $R_s$ ), charge transfer resistance ( $R_{ct}$ ) and double layer capacitance ( $C_{dl}$ ) [17]. When a non ideal frequency response is present such as a depressed semicircular shape in the complex impedance plane in our experiments, it is commonly accepted to employ distributed circuit elements in an equivalent circuit. The most widely used is constant element (CPE) [18], which has a non-integer power dependence on the frequency and take account local non-homogeneous nature of the electrode. The impedance of a CPE is described by the expression

$$Z_{CPE} = Y^{-1} (i\omega)^{-n} \quad (3)$$

Where  $Y$  is a proportional factor,  $i$  is  $\sqrt{-1}$ ,  $\omega$  is  $2\pi f$  and  $n$  has the meaning of a phase shift [19]. Often a CPE is used in a model in place of a capacitor to compensate for non-homogeneity in the system. For example, a rough or porous surface can cause a double-layer capacitance to appear as a CPE with an  $n$  value between 0.9 and 1 [20]. For  $n=0$ ,  $Z_{CPE}$  represents a resistance with  $R=Y^{-1}$  For  $n=1$ , a capacitance with  $C=Y$ , for  $n=0.5$  a Warburg element and for  $n=-1$  an inductance with  $L=Y^{-1}$ .

Figure 4. Shows the electrical equivalent circuit employed to analyze the impedance plots. From the equivalent circuit  $R_s$  is the electrolyte resistance ( $\Omega \text{ cm}^2$ ) and  $Y$  ( $\Omega^{-1} \text{ cm}^2 \text{ S}^n$ ) and  $n$  are the parameters depicted for  $Z_{CPE}$  in Eq.(3). Excellent fit with the model was obtained for all experimental data. Circuit parameters for mild steel in absence and presence of synthesized inhibitor (A) were listed in table 3.

The inhibition efficiency was calculated by following equation

$$\eta_Z \% = \frac{R_{ct} - R_{0ct}}{R_{ct}} \times 100 \quad (4)$$

Where  $R_{ct}$  and  $R_{0ct}$  are values of charge transfer resistance observed in presence and absence of inhibitor.

Table 3. Circuit parameters for mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> with various conc. of inhibitor (A).

Inh.C. (ppm)	R <sub>s</sub> (Ω cm <sup>2</sup> )	R <sub>ct</sub> (Ω cm <sup>2</sup> )	C <sub>dl</sub> (μF/cm <sup>2</sup> )	Y (Ω <sup>-1</sup> cm <sup>-2</sup> S <sup>n</sup> )×10 <sup>5</sup>	n	η <sub>Z</sub> %
0	2.22	8.88	348.0	44.09	0.86	-
25	2.74	36.11	345.3	27.23	0.89	75.68
50	2.38	167.90	117.4	6.50	0.90	94.71
75	2.25	274.60	106.0	6.93	0.89	96.76
100	2.93	431.70	75.66	5.46	0.90	97.94

#### 4. CORROSION INHIBITION MECHANISM

From the obtained results of various experimental techniques used, it was concluded that the synthesized inhibitor (A) inhibit the corrosion of mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> by adsorption at the metal/electrolyte interface. The essential effect of this compound as corrosion inhibitor is due to the presence of free electron pairs in the sulphur and the nitrogen atoms, π-electrons on the aromatic rings, molecular size, mode of interaction with the metal surface and the formation of metallic complexes [21-23].

The unshared and π-electrons interact with d-orbital of Fe provide a protective film. The inhibitive properties of such

compounds depend on the electron densities around the active center, the higher the electron density at the active center, the more effect is the inhibitor. Skeletal representation of the mode of adsorption of the synthesized inhibitor (A) is shown in Figure 5 and clearly indicates the adsorption centers. From the obtained results it is clear that this compound (A) exhibits a good inhibition effect due to its molecular size that may facilitate surface coverage and its adsorption through active centers which enhance the delocalized π-electrons on the active centers of the compound.

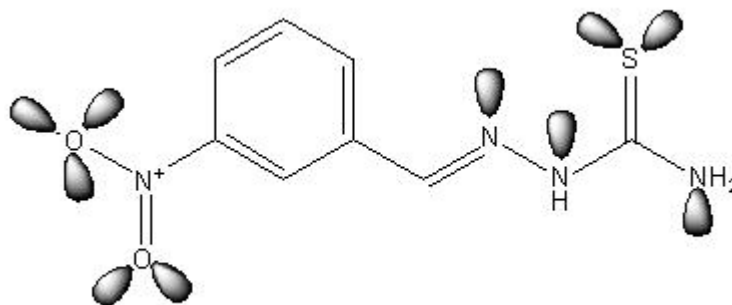


Figure 5. Skeletal representation of the mode of adsorption of synthesized inhibitor (A).

#### 5. ADSORPTION ISOTHERM

In general, two models of adsorption can be considered. The proceeding of physical adsorption requires presence of electrically charged metal surface and charged species in the bulk of solution. Chemisorption process involves charge sharing or charge transfer from the inhibitor molecules to the metal surface. The presence of an inhibitor molecule having relatively loosely bound electrons or heteroatoms with lone-pair electrons with a transition metal having vacant and low-energy electron orbital facilitates this adsorption [24]. Assuming the corrosion inhibition was caused by the absorption of the synthesized inhibitor (A) and the values of surface coverage ( $\theta = \eta\%/100$ ) for different concentrations of inhibitors in 0.5M H<sub>2</sub>SO<sub>4</sub> were evaluated from three used methods. Adsorption isotherms are very important in determining the mechanism of organic electrochemical reactions. The most frequency used adsorption isotherms are Langmuir. It was found that adsorption of the synthesized inhibitor on mild steel surface in 0.5M H<sub>2</sub>SO<sub>4</sub>

solution obeys Langmuir adsorption isotherm by the following equations [25]

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

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \quad (6)$$

Where C is the inhibitor concentration,  $\theta$  is the fraction of the surface covered,  $K_{ads}$  is the equilibrium constant of the inhibitor adsorption process, the value 55.5 is the molar concentration of water in solution in mol dm<sup>-3</sup>, R is the gas constant, T is absolute temperature and  $\Delta G_{ads}$  is the standard free energy of adsorption process.

Figure 6 shows the dependence of the fraction of surface covered C/θ as a function of the concentration (C) of the synthesized inhibitor (A).

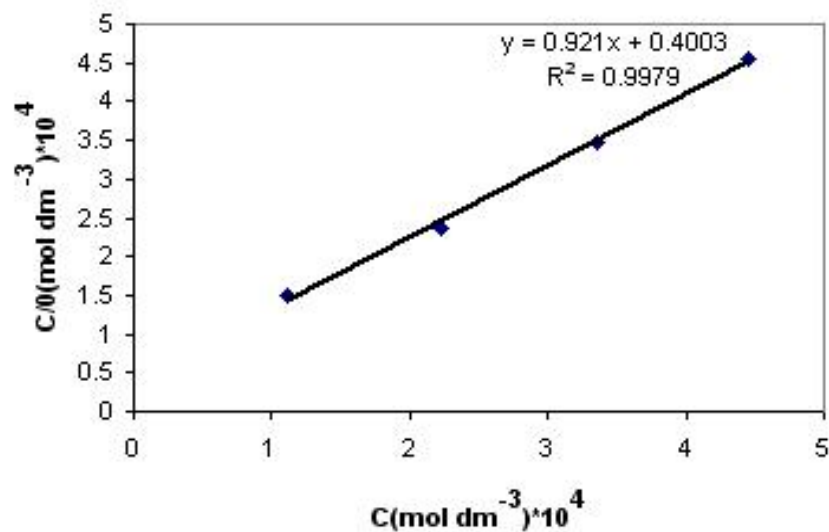


Figure 6. Langmuir's adsorption plot for inhibited mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> with various conc. of inhibitor (A).

The obtained plot of the inhibitor (A) is linear with correlation coefficient higher than 0.99. The intercept permits the calculation of the equilibrium constant  $K_{ads}$  which is  $2.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$  respectively. The value of  $K_{ads}$  which indicate the binding power of the inhibitor to the mild steel surface leads to calculation of adsorption energy. Value of  $\Delta G_{ads}$  is  $-35.02 \text{ kJmol}^{-1}$  respectively.

The negative value of  $\Delta G_{ads}$  means that the adsorption of the synthesized inhibitor (A) on mild steel surface is a spontaneous process and also show a strong interaction of the inhibitor molecule onto the mild steel surface [26].

Generally, values of  $\Delta G_{ads}$  around  $-20 \text{ kJmol}^{-1}$  or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption). While those more negative than  $-40 \text{ kJmol}^{-1}$  involve

charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) [27]. The calculated  $\Delta G_{ads}$  value indicated that the adsorption mechanism of the synthesized inhibitor (A), on mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> is a mixed form physical and chemical adsorption [28].

## 6. SCANNING ELECTRON MICROSCOPY (SEM)

The SEM micrographs of the corroded mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of inhibitor are shown in fig.7 (a - b).

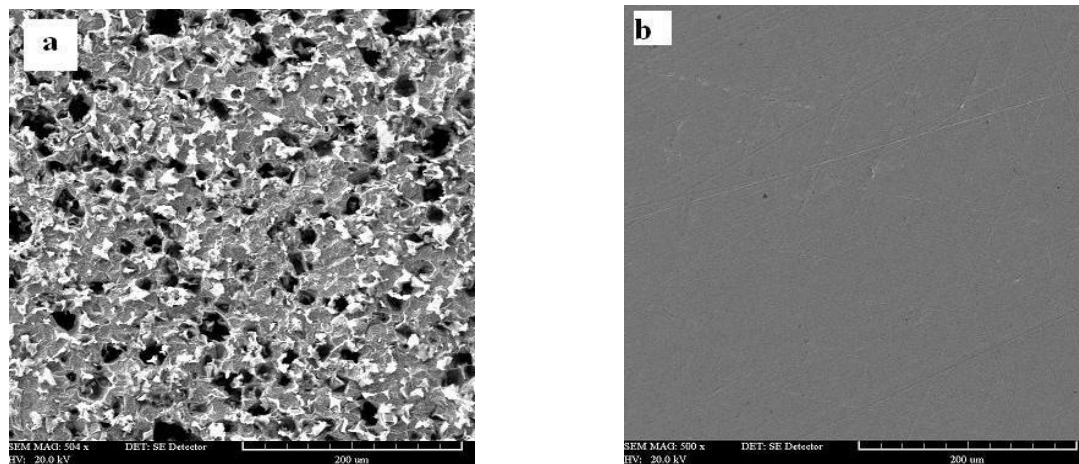


Figure 7. SEM micrographs of mild steel samples after immersion in 0.5M H<sub>2</sub>SO<sub>4</sub> solution (a) without inhibitor, (b) with 100 ppm synthesized inhibitor (A).

In Figure 7a of bare mild steel electrode surface, defects and notches were observed, while a layer of closely packed film was obtained in Figure 7b, and the surface was free from pits and it was smooth. It can be concluded from Figure 7a-b that corrosion does not occur in presence of inhibitor (A) and hence corrosion was inhibited strongly when the inhibitor was present in the solution, then scanning electron microscopy (SEM) observation, confirmed the existence of an adsorbed protective film on the metal surface.

## 7. CONCLUSION

- 1- The synthesized inhibitor (A), has been found to perform well as corrosion inhibitor for mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> solution.
- 2- Electrochemical studies and weight loss measurements have been given similar results.
- 3- From the polarization measurements has been found that the inhibitor (A) to behave as a mixed type inhibitor.
- 4- This compound (A) was found to inhibit the corrosion of mild steel by adsorption on the metal surface.
- 5- Adsorption of this inhibitor on mild steel surface has been found to obey Langmuir's isotherm.
- 6- The investigated inhibitor (A) has been suggested to be mixed form physical and chemical adsorption on the mild steel electrode surface.

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