

## Study Of The Protection Of Mild Steel Corrosion With Piperidin -4-One And Its Semicarbazones

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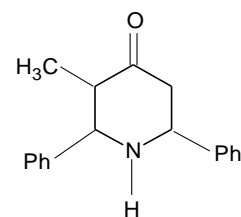
### Abstract

Three new Schiff bases viz r-2 c-6 Diphenyl-t-3-methyl piperidine-4-one [S<sub>1</sub>],r-2,c-6-diphenyl-t-3-methyl-N-methyl piperidine-4-one semicarbazone [S<sub>2</sub>] and r-2 c-6-Diphenyl-t-3-methyl piperidine-4-one semicarbazone [S<sub>3</sub>] have been investigated as corrosion inhibitors for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> using weight loss, Tafel polarization, electron chemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The three Schiff bases function as good inhibitors reaching inhibition efficiencies of ~ 93-94% at 7mM concentration. The fraction  $\theta$  of the metal surface covered by the inhibitor is found to increase with inhibitor concentration of the three Schiff bases, the S<sub>2</sub> shown better efficiency than the other two Schiff bases. The adsorption of the inhibitor follows Longmuir isotherm. Thermodynamic calculations indicate the adsorption to be physical in nature.

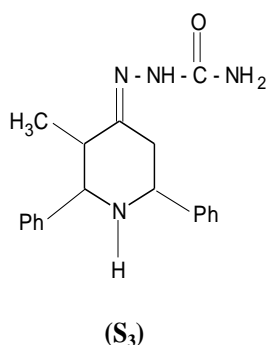
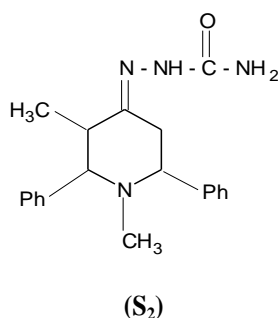
Semicarbazone moiety in addition to Nitrogen of piperidone ring [1]. The previous considerations led us to synthesizing the inhibitor molecules with structures depicted in Fig(1), namely. r-2, C-6 Diphenyl-t-3-methyl piperidine-4-one[S<sub>1</sub>],r-2,C-6-Diphenyl-t-3-methyl-N-methylpiperidine-4-one semicarbazones[S<sub>2</sub>] to compare the reactivity of three inhibitors, its order of reactivity is S<sub>1</sub><S<sub>3</sub><S<sub>2</sub>. The S<sub>3</sub> compared to that of S<sub>1</sub> has better inhibitor efficiency, due to the presence of CO-and -NH group which is present in semicarbazone, where as in the case of inhibitor S<sub>2</sub> in addition to -CO and -NH group an hydrogen attached to the ring nitrogen of S<sub>3</sub> has been replaced by CH<sub>3</sub> group enhances the inhibition efficiency. In the present paper the efficiency of S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub> as inhibitors for the corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> discussed on the basis of weight loss, Tafel polarization, AC Impedance spectroscopy and scanning electron microscopy (SEM) data.

### “1. Introduction”

The inhibiting influence of piperidine and its semicarbazones has been investigated this influence is attributed to the adsorption of these compounds through-NH and C=O group of piperidone to the metal surface. In the case of piperidin-4-one semicarbazones the inhibition efficiency was found to increase. This shows the involvement of -NH and -CO groups in



(S1)



“ Figure 1. Structure of the inhibitors S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub>”

## “2. Experimental”

### 2.1. Electrodes

Working electrodes were prepared using mild steel specimens of size (5cm x 2.5 cm x 0.1cm). The plates were washed, dried and polished successively using emery sheets of 1/0, 2/0, 3/0 and 4/0 grades to remove adhering impurities finally degreased with acetone and dried using a drier. For electrochemical study the cylinder of the mild steel having diameter 5mm were embedded in a Teflon holder with an exposed area of 1sq cm was used for the present study. The mild steel electrode, counter electrode and saturated calomel electrodes were used.

To obtain the stabilized open circuit potential (OCP), the samples were immersed 20-30 min in the solution before EIS and Tafel polarization measurements.

### 2.2 Inhibitors

The inhibitors with structures shown in Fig.1 were synthesized according to the procedure that of Balasubramanian and Padma [2]. Briefly S<sub>1</sub>,

prepared by just heating the mixture of dry ammonium acetate in glacial acetic acid, benzaldehyde and butanone and allowed to stand overnight then, conc. HCl was added and then the precipitate washed with ethanol ether. The inhibitor S<sub>2</sub> and S<sub>3</sub> were prepared from S<sub>1</sub>. The r-2, c-6 diphenyl-t-3-methyl piperidine-4-one was dissolved in acetone, then potassium carbonate and dimethyl sulphate salts were added. The mixture refluxed over a water bath, dilution with water followed by treatment with ammonia gave S<sub>2</sub> r-2, c-6-diphenyl,-t-3- methyl N-methyl piperidine-4-one and it is added with semicarbazide hydrochloride and sodium acetate dissolved in ethanol. This mixture shaken well for about 15 min to obtained inhibitor S<sub>2</sub>. The inhibitor S<sub>3</sub> was prepared by adding semicarbazide hydrochloride and sodium acetate in hot ethanol and mixed with inhibitor S<sub>1</sub>. The solution was shaken well for about 15 min. The product formed was filtered and washed with water.

All chemicals were of analytical reagent grade and were used without future purification, and inhibitor solutions were prepared in 1M H<sub>2</sub>SO<sub>4</sub> to which 5% ethanol was added for solubility reasons.

### 2.3 Equipment

Mild steel specimens of size 5cm x 2.5cm x 0.1cm, 200 ml glass beaker and glass hooks were used for weight loss method, electrochemical impedance. Spectroscopy (EIS) and Tafel Polarization were calculated in an electrochemical measurement unit (Model 1280 B solar ton, Ok). The EIS measurements were made at corrosion potentials over a frequency range of 10 KHz to 0.01 KHz with a signal amplified of 10mv. The Tafel polarization measurements were made after EIS studies for a potential range of -200 mv to +200 mv with respect to open circuit potential (OCP), at a scan rate of 1mv/Sec.

The I<sub>corr</sub>, E<sub>corr</sub>, R<sub>t</sub> and C<sub>dl</sub> values were obtained from the data using the corresponding Corrview and Zview software's. Surface of mild steel specimens were examined using scanning electron microscope (SEM) in order to understand the surface morphology of the mild steel. The surface morphology was taken using JEOL Scanning electron microscope.

### “3. Results and Discussion”

#### 3.1 Weight Loss Studies

The weight loss method was carried out using various concentrations (i.e. 0.5mM -7mM) of the inhibitors namely S<sub>1</sub>,S<sub>2</sub> and S<sub>3</sub> in 1M H<sub>2</sub>SO<sub>4</sub>. In this study the parameters like corrosion rate (mpy), surface coverage (θ), inhibition efficiency and adsorption isotherm were calculated. The above results were given in Table (1).

**“Table 1. Inhibition efficiencies of various concentrations of inhibitor (S<sub>2</sub>) for the corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> obtained by weight loss measurements at room temperature”**

Name of the inhibitor	Inhibitor Conc. (mM)	Weight loss (gms)	Inhibition efficiency (%)	Corrosion rate (mpy)	Degree of Coverage (θ)
S <sub>2</sub>	Blank	0.3672	-	8379.69	-
	0.5	0.0547	85.1	1248.28	0.8510
	1	0.0487	86.74	1111.36	0.8674
	1.5	0.0457	87.55	1042.89	0.8755
	2	0.0397	89.19	905.97	0.8919
	2.5	0.0348	90.52	794.15	0.9052
	3	0.0318	91.34	725.69	0.9134
	5	0.0262	92.86	597.89	0.9286
	7	0.0203	94.47	462.26	0.9447

The effect of concentration of inhibitor on inhibition efficiency was determined by using the following relationship.

$$I.E (\%) = \frac{W_0 - W_i}{W_0} \times 100$$

Where W<sub>0</sub> is the weight loss without inhibitor and W<sub>i</sub> is the weight loss with inhibitor. From this the inhibition efficiency was found to increase with increasing inhibitor concentration.

The effect of concentration of inhibitor on weight loss measurements were obtained by plotting weight loss Vs inhibitor concentration as shown in Fig (2). This reveals that the metal loss progressively decreased with the increasing inhibitor concentrations. The corrosion rate in 1M H<sub>2</sub>SO<sub>4</sub> for various concentrations of the inhibitors (S<sub>1</sub>, S<sub>2</sub>, and S<sub>3</sub>) was determined by using the formula.

$$\text{Corrosion Rate (mpy)} = \frac{534 \times \text{Weight Loss in mgm}}{\text{Density} \times \text{Area} \times \text{time in hours}}$$

Where

W - Weight loss in mg

D - Density in g/cc

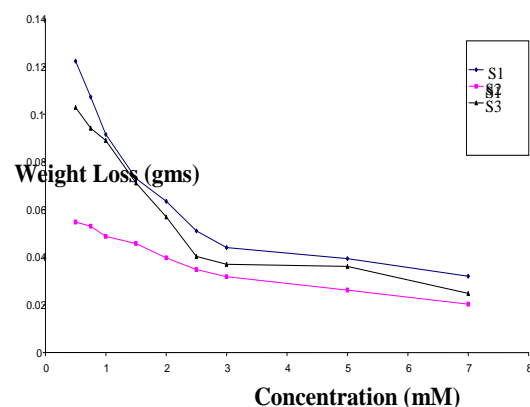
A - Area of Exposure in cm<sup>2</sup> and

T - Time in hours

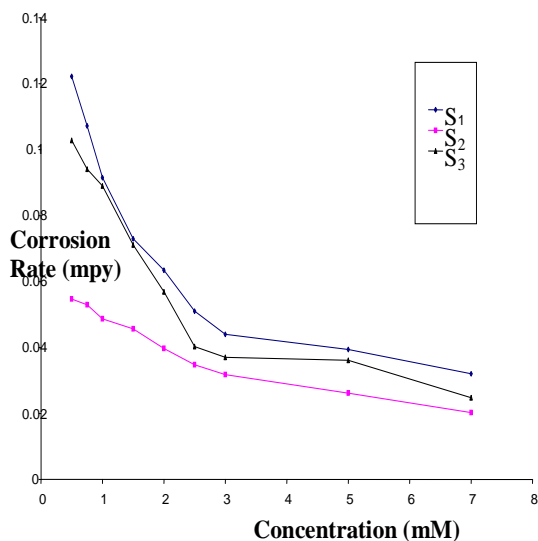
The corrosion rate expressed in mpy decreased with increasing inhibitor concentration as evident from table (1) and shown in Fig (3). The surface coverage θ for different inhibitor concentrations were calculated by using the formula

$$\theta = \frac{W_b - W_i}{W_b}$$

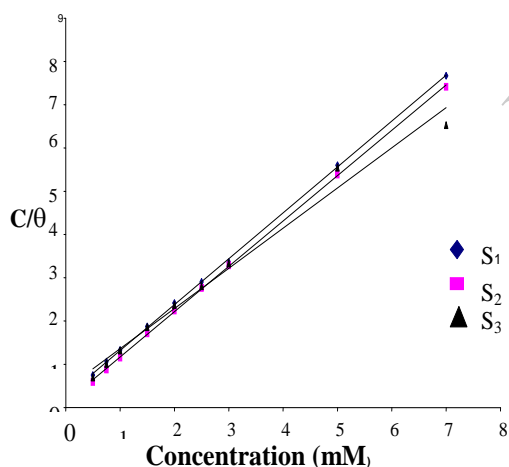
from this a graph was drawn between C/θ Vs C as shown in Fig(4). From this fig a straight line confirming that the piperidine-4-one semicbazones obeyed Langmuir adsorption isotherm.



**“Figure 2. The effect of concentration of inhibitor on weight loss in 1M H<sub>2</sub>SO<sub>4</sub>”**



“Figure 3. The effect of concentration of inhibitor on corrosion rate in 1M H<sub>2</sub>SO<sub>4</sub>”



“Figure 4. The effect of concentration of inhibitor on C/θ”

### 3.2. Adsorption Isotherm and Thermodynamic Calculations.

In 1M H<sub>2</sub>SO<sub>4</sub> the dissolution of metal increases with rise in temperature both in presence and absence of inhibitor and efficiency of the inhibitor decrease with increase in temperature indicating weak adsorption this is shown in Table(2).

The values of activation energy (E<sub>a</sub>) were calculated from the plot of log (corrosion rate) Vs 1000/T. The free energy of adsorption (ΔG<sup>o</sup><sub>ads</sub>) at various temperatures was calculated using the following equation.

$$\Delta G^{\circ}_{ads} = - RT \ln (55.5K)$$

Where K is the equilibrium constant and it is given by

$$K = \theta/C (1-\theta) \text{ (from, Langmuir equation)}$$

θ = Degree of coverage on the metal surface.

C = Concentration of inhibitor in mM.

R = Gas constant and

T = Temperature

The decrease in IE with temperature indicates the fact that the inhibitor film formed on the metal surface is less protective in nature at higher temperature [3]. The values of E<sub>a</sub> and ΔG<sup>o</sup><sub>ads</sub> are given in Table (2). The less negative values of ΔG<sup>o</sup><sub>ads</sub> with increase in temperature indicate the physical adsorption of Schiff bases of piperidin-4-one and its semicarbazones on the metal surface [4]. The values of E<sub>a</sub> in the inhibited acid solution are appreciable for greater than those obtained in the uninhibited acid solutions. This suggests that the presence of reactive centers on the inhibitors, block the active sites for corrosion resulting in an increase in E<sub>a</sub> [5].

“Table.2 Activation energies (E<sub>a</sub>) and free energies of adsorption (ΔG<sup>o</sup><sub>ads</sub>) for the corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> at selected concentration of the inhibitors”

Name of the Inhibitor	E <sub>a</sub> 40°C - 60°C KJ	ΔG <sup>o</sup> <sub>ads</sub> at various temperature KJ		
		40°C	50°C	60°C
Blank	17.998	-	-	-
S1	24.125	-4.28	-2.05	-1.08
S2	32.162	-7.73	-2.75	-1.3
S3	23.359	-6.01	-2.43	-1.25

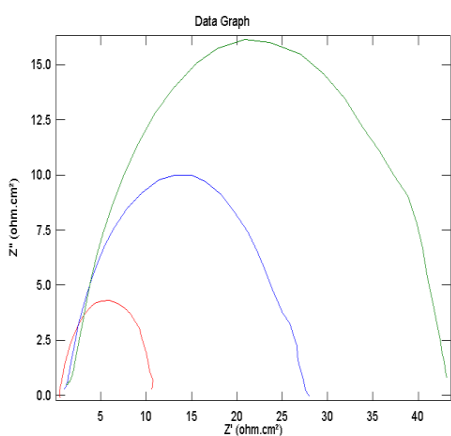
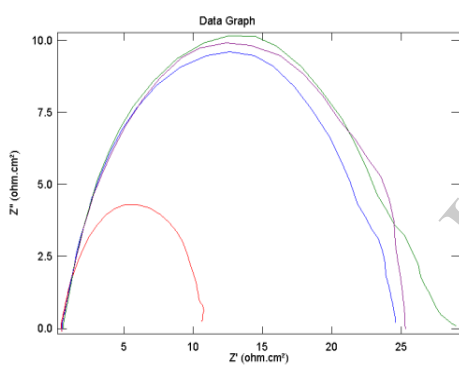
### 3.3 Electrochemical Studies

#### 3.3.1 A.C. Impedance Method

Fig (5) shows a typical set of complex plane plots of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of various concentrations of the shift bases to the acid media. Increasing the concentration of the inhibitor caused the values of charge transfer resistance to shift to elevated amounts this can be calculated using the formula.

$$I.E (\%) = \frac{R_{t(\text{blank})} - R_{t(\text{inh})}}{R_{t(\text{blank})}}$$

Where R<sub>t(inh)</sub> and R<sub>t(blank)</sub> is the charge transfer resistance in the presence and absence of inhibitor steel in 1M H<sub>2</sub>SO<sub>4</sub>. Of the three inhibitors the S<sub>2</sub> show better efficiency than the other two inhibitors. This can be related to the structure of the molecule and its more adsorption centers on metal surface.



“Figure 5. Impedance curve for the Inhibitor S<sub>1</sub> and S<sub>2</sub>”

From the table(3) the decrease in the double layer capacitance (C<sub>dl</sub>) values may be attributed to decrease in local dielectric constant or an increase in the thickness of the electrical double layer(6). The double layer capacitance (C<sub>dl</sub>) decreases with increasing inhibitor concentration. The decreases in C<sub>dl</sub> values in presence of inhibitors indicate the fact that these additives inhibit corrosion by adsorption on the metal surface (7).

“Table.3. A.C- Impedance parameters for mild steel for selected concentrations of the inhibitors S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub> in 1M H<sub>2</sub>SO<sub>4</sub>”

Name of the Inhibitor	Inhibitor concentration (mM)	R <sub>t</sub> (ohm cm <sup>2</sup> )	C <sub>dl</sub> (μFcm <sup>-2</sup> )	Inhibition efficiency (%)
S1	Blank	1.037	1.671	
	1.0	2.305	2.348	
	5.0	2.855	1.550	63.68
	7.0	3.464	1.441	70.06
S2	1.0	2.812	1.878	63.12
	7.0	4.669	1.667	77.79
S3	5.0	2.519	1.942	70.53
	7.0	4.172	1.765	75.14

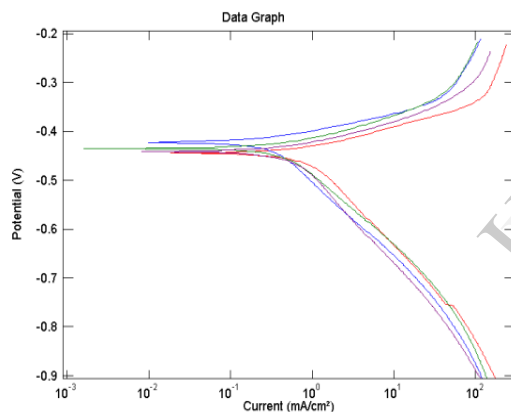
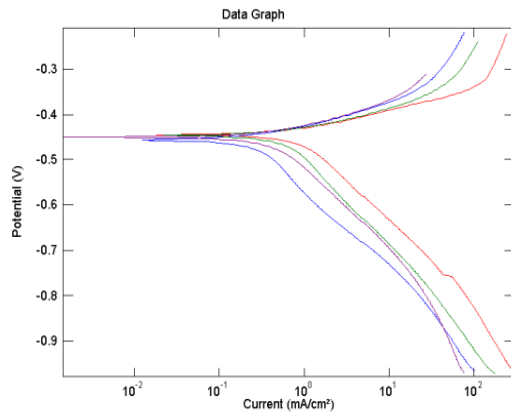
#### 3.3.2. Tafel polarization

Fig (8) shows a typical record of Tafel polarization measurement for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of the inhibitor. The inhibition efficiency is calculated from the value of I<sub>corr</sub> by using the formula

$$I.E (\%) = \frac{I_{\text{corr}(\text{blank})} - I_{\text{corr}(\text{inh})}}{I_{\text{corr}(\text{blank})}}$$

where I<sub>corr(blank)</sub> and I<sub>corr(inh)</sub> is the corrosion current in the presence and absence of the inhibitor. The corrosion current density (i<sub>corr</sub>) of blank mild steel electrode in this condition was 261.43 μA cm<sup>-2</sup>. It is clear that corrosion current density decreases with increasing the concentration of the inhibitors.

Addition of the inhibitor to acid media affects both the cathodic and anodic parts of the curves therefore these compounds behave as mixed inhibitors [8].



“Figure 8. Polarization curves for inhibitor  $S_1$  and  $S_2$ ”

Table (4) lists the polarization parameters for corrosion of mild steel in the presence of different concentrations of the investigated inhibitors. From this it is seen that the corrosion current density decreases when the concentration of the inhibitor increases, so the studied inhibitor cause a decrease in corrosion rate of steel in acid media by influencing both the anodic and cathodic reactions.

“Table.4. Corrosion parameters for the mild steel with selected concentrations of the inhibitors in 1M  $H_2SO_4$  by potentiodynamic polarization method”

Name of the Inhibitor	Inhibitor concentration (mM)	Tafel Slopes		$E_{corr}$ (mu)	$I_{corr}$ ( $\mu A/cm^2$ )	Inhibition efficiency (%)
		$b_a$	$b_c$			
$S_1$	Blank	1268	1391	-467.77	261.43	
	1.0	1011	1123	-457.66	99.26	62.03
	5.0	1016	1126	-462.29	90.92	65.47
	7.0	1012	1120	-455.91	86.47	66.92
$S_2$	1.0	1007	1119	-469.69	78.47	69.98
	5.0	1003	1112	-463.99	49.54	81.05
	7.0	1005	1115	-469.39	37.34	89.75
$S_3$	5.0	1003	1107	-461.23	76.79	70.62
	7.0	1007	1109	-467.89	56.23	78.49

### 3.4 Scanning Electron Microscopic Study [SEM]

Surface of polished mild steel specimen immersed in 1M  $H_2SO_4$  in the absence and presence of inhibitors such as  $S_1, S_2$  and  $S_3$  were examined using scanning electron microscope (SEM) it was shown in Fig(9). From this Fig (9a) in the case of blank corroded metal surface with etched grain boundaries the corrosion products are clearly seen. But in the presence of inhibitors, there is a formation of adsorption layer of inhibitors on the metal surface without any corrosion products, as seen in Fig (9b) only some original surface defects of the specimens are seen. Hence all the inhibitors having good inhibition efficiency is revealed.

### “4. Conclusion”

All these studied inhibitors are good inhibitors for mild steel corrosion in sulphuric acid solution, generating inhibition efficiencies in the order of 94% at a concentration of 7mM. For low concentrations  $S_1$  and  $S_3$  are indistinguishable in performance, as the concentration increases  $S_2$  shows an increasing inhibitive advantage over  $S_1$  and  $S_3$ .

The adsorption of the compounds on the metal surface is found to obey Langmuir adsorption isotherm.

The activation energy is higher for the inhibited acids than for the uninhibited acids showing the temperature dependence of inhibition efficiency and also the less negative  $\Delta G_{\text{ads}}^{\circ}$  values indicate spontaneous adsorption of the inhibitors on the metal surface.

Electrochemical impedance spectroscopy experiments have shown that an increase in inhibitor concentration cause an increase in polarization resistance  $R_p$  and a decrease in  $C_{dl}$  values, owing to the increased thickness of the adsorbed layer.

Tafel slopes obtained from potentiodynamic polarization curves indicates that the compounds behave as a mixed type indicator.

Scanning electron Microscope (SEM) study reveals the formation of a smooth, dense protective layer in presence of an effective inhibitor.

## “References”

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