CHAPTER-III
MATERIALS AND METHODS

Corrosion of mild steel in 1 N sulphuric acid and substituted piperidin-4-one with semicarbazone and thiosemicarbazone as inhibitors in combating the corrosion have been investigated. For this purpose weight loss and electrochemical (potentiodynamic polarization and A.C. impedance methods) techniques have been employed.

3.1 Materials
3.1.1 Mild Steel Specimens

Mild steel specimens of the following composition have been used throughout the present investigation.

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.07</td>
</tr>
<tr>
<td>Sulphur</td>
<td>Nil</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>0.008</td>
</tr>
<tr>
<td>Silicon</td>
<td>Nil</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.34</td>
</tr>
</tbody>
</table>

3.1.2 Acids

Sulphuric acid used for weight loss and electrochemical measurements were of L.R. Grade. For the preparation of 1N sulphuric acid double distilled water was used.

3.2 Synthesis of inhibitor

Semicarbazones and thiosemicarbazones of variously Substituted 2,6-diphenylpiperidin-4-one [(01SC), (02SC), (03SC), (01TS), (02TS) and (03TS)] have been chosen as inhibitors for the present investigation. The chemicals used were of AnalaR grade.
3.2.1 Synthesis of $r$-2, c-6-diphenyl-$r$-3-methylpiperidin-4-one (01)

The procedure adopted was essentially that of Balasubramanian and Padma\textsuperscript{181}. To a solution of ethanol, benzaldehyde, butanone and dry ammonium acetate were added. The mixture was heated to boil and allowed to stand overnight at room temperature. Then concentrated hydrochloric acid was added. The precipitated hydrochloride was collected and washed with ethanol-ether. Crystallization from ethanol-ether yielded the pure hydrochloride mp 223-225 °C (lit\textsuperscript{181} 224-226 °C).

The base liberated by suspending the hydrochloride in acetone and adding ammonia till the hydrochloride dissolved. Dilution with water afforded the free base which was crystallized from ethanol, mp 96-97°C (lit\textsuperscript{181} 96-97°C).

3.2.2 Synthesis of $r$-2, c-6-diphenyl-$r$-3-ethyl-N-methyl piperidin-4-one (02)

The procedure was adopted by Noller and Baliah\textsuperscript{182}. A mixture of 2-pentaone, with benzaldehyde in the presence of dry ammonium acetate in ethanol was heated to boil and allowed to stand overnight at room temperature. Then concentrated hydrochloric acid was added. The precipitated hydrochloride was collected and washed with ethanol-ether. Crystallization from ethanol-ether yield the pure hydrochloride.

A suspension of the hydrochloride in acetone was treated with ammonia and the free base was obtained by diluting with large amount of water. Crystallization of the product from petroleum ether gave t-2, C-6-Diphenyl-t-3-ethyl piperidin-4-one, mp 94-95°C (lit\textsuperscript{182} 92-94°C).

$\gamma$-2,C-6-Diphenyl-t-3-ethyl piperidin-4-one was subjected to methylation. The piperidin-4-one was dissolved in acetone. To this solution was added anhydrous potassium carbonate, and methyl iodide. The mixture was refluxed over a water bath for about 3 hours and most of the acetone
was removed by distillation. Dilute with water, followed by treatment with ammonia gave the N-methylated product which was filtered, washed with water. Crystallization of the crude product from petroleum ether yield the methylated compound. mp 115-117°C (lit \textsuperscript{181} 115-117°C).

3.2.3 Synthesis of \textit{r-}2, \textit{c-}6 –diphenyl-\textit{r-}3-ethylpiperidin-4-one (03)

A mixture of 2-pentanone with benzaldehyde in the presence of dry ammonium acetate in ethanol, according to the procedure of Noller and Baliah\textsuperscript{182} and crystallization of the product from petroleum ether gave the piperidin-4-one (03), mp 94-95°C (lit \textsuperscript{182} 92-94°C).

3.2.4 Synthesis of Semicarbazones and Thiosemicarbazone of variously substituted Piperidin-4-ones

The variously substituted piperidin-4-one was dissolved in alcohol and distilled water. To this solution 1:1 ratio of sodium acetate and semicarbazide\textsuperscript{183} was added. The mixture was refluxed over a water bath for about 5 hours and most of the alcohol was removed by distillation. It was dried over P$_2$O$_5$. The crystallized product was washed with ice-cold alcohol and purity was checked by TLC. The same procedure was followed by variously substituted piperidin-4-ones with thiosemicarbazone.
3.3 Reaction Scheme of the Inhibitors

3.3.1 Semicarbazone of γ-2,c-6-diphenyl-t-3-methyl piperidin-4-one (01SC)

\[
\begin{align*}
\text{CHO} + \text{CH}_3\text{CONH}_4 & \rightarrow \text{H}_3\text{C} + \text{CH}_3\text{COONH}_4 + \text{CHO} \\
\text{CHO} \rightarrow \text{H}_3\text{C} + \text{CH}_3\text{COONH}_4 & \rightarrow \text{H}_3\text{C} + \text{CH}_3\text{COONH}_4
\end{align*}
\]

3.3.2 Semicarbazone of γ-2,c-6-diphenyl-N-methyl-t-3-ethyl piperidin-4-one (02SC)

\[
\begin{align*}
\text{CHO} + \text{CH}_3\text{CONH}_4 & \rightarrow \text{H}_3\text{C} + \text{CH}_3\text{COONH}_4 + \text{CHO} \\
\text{CHO} \rightarrow \text{H}_3\text{C} + \text{CH}_3\text{COONH}_4 & \rightarrow \text{H}_3\text{C} + \text{CH}_3\text{COONH}_4
\end{align*}
\]
3.3.3 Semicarbazone of γ-2, c-6-diphenyl-t-3-ethyl piperidin-4-one (03SC)

3.3.4 Thiosemicarbazone of γ-2, c-6-diphenyl-t-3-methyl piperidin-4-one (01TS)
3.3.5 Thiosemicarbazone of $\gamma$-2,c-6-diphenyl-N-methyl-t-3-ethyl piperidin-4-one (02TS)

\[
\begin{align*}
\text{CHO} + \text{CH}_3\text{COONH}_4 & \rightarrow \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CHO} + \text{CH}_3\text{COONH}_4 \rightarrow \text{N} \rightarrow \text{O} \\
& \rightarrow \text{K}_2\text{CO}_3, \text{CH}_3\text{I}, \text{(CH}_3\text{)_2O} \\
& \rightarrow \text{N} \rightarrow \text{O} \\
& \rightarrow \text{CH}_3\text{N}_3\text{S}, \text{CH}_3\text{COONa} \rightarrow \text{N} \rightarrow \text{O} \\
(E)-1-(3\text{-ethyl-1-methyl-2,6-diphenylpiperidin-4-ylidene})\text{thiosemicarbazide}
\end{align*}
\]

02TS

3.3.6 Thiosemicarbazone of $\gamma$-2, c-6-diphenyl-t-3-ethyl piperidin-4-one (03TS)

\[
\begin{align*}
\text{CHO} + \text{CH}_3\text{COONH}_4 & \rightarrow \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CHO} + \text{CH}_3\text{COONH}_4 \rightarrow \text{N} \rightarrow \text{O} \\
& \rightarrow \text{CH}_3\text{COONa} \rightarrow \text{N} \rightarrow \text{O} \\
& \rightarrow \text{CH}_3\text{N}_3\text{S} \rightarrow \text{N} \rightarrow \text{O} \\
(E)-1-(3\text{-ethyl-2,6-diphenylpiperidin-4-ylidene})\text{thiosemicarbazide}
\end{align*}
\]

03TS
### 3.4 Structure of the inhibitors

<table>
<thead>
<tr>
<th></th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1SC</td>
<td>H</td>
<td>CH$_3$</td>
<td>&gt; N – NH – CONH$_2$</td>
</tr>
<tr>
<td>O2SC</td>
<td>CH$_3$</td>
<td>C$_2$H$_5$</td>
<td>&gt; N – NH – CONH$_2$</td>
</tr>
<tr>
<td>O3SC</td>
<td>H</td>
<td>C$_2$H$_5$</td>
<td>&gt; N – NH – CONH$_2$</td>
</tr>
<tr>
<td>O1TS</td>
<td>H</td>
<td>CH$_3$</td>
<td>&gt; N – NH – CSNH$_2$</td>
</tr>
<tr>
<td>O2TS</td>
<td>CH$_3$</td>
<td>C$_2$H$_5$</td>
<td>&gt; N – NH – CSNH$_2$</td>
</tr>
<tr>
<td>O3TS</td>
<td>H</td>
<td>C$_2$H$_5$</td>
<td>&gt; N – NH – CSNH$_2$</td>
</tr>
<tr>
<td>Compound</td>
<td>Name and Molecular Weight (Mol.wt)</td>
<td>Structure</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>(01SC)</td>
<td>Semicarbazone of γ-2,c-6-diphenyl-t-3-methyl piperidin-4-one Mol.wt : 323</td>
<td><img src="image1" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>(02SC)</td>
<td>Semicarbazone of γ-2,c-6-diphenyl-N-methyl-t-3-ethyl piperidin-4-one Mol.wt : 351</td>
<td><img src="image2" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>(03SC)</td>
<td>Semicarbazone of γ-2,c-6-diphenyl-t-3-ethyl piperidin-4-one Mol.wt : 337</td>
<td><img src="image3" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>(01TS)</td>
<td>Thiosemicarbazone of γ-2,c-6-diphenyl-t-3-methyl piperidin-4-one Mol.wt : 339</td>
<td><img src="image4" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>(02TS)</td>
<td>Thiosemicarbazone of γ-2,c-6-diphenyl-N-methyl-t-3-ethyl piperidin-4-one Mol.wt : 366</td>
<td><img src="image5" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>(03TS)</td>
<td>Thiosemicarbazone of γ-2,c-6-diphenyl-t-3-ethyl piperidin-4-one Mol.wt : 352</td>
<td><img src="image6" alt="Structure" /></td>
<td></td>
</tr>
</tbody>
</table>
3.5 Experimental methods

3.5.1 Weight loss measurement

This method is the most reliable method. Mild steel specimen of 5 × 2.5 cm² has been used. It was polished using 110 to 410 grade emery papers and lastly degreased with the organic solvent trichloroethylene. The specimens were weighed. After weighing the specimens were immersed in 1 N sulphuric acid with and without inhibitor. After 1 hour, the specimens were washed with distilled water, dried and again weighed. The weight loss was noted. From this weight loss value, corrosion rate and inhibition efficiency were determined.

Corrosion rate has been determined from the following relationship.

\[
\text{Corrosion rate (mmpy)} = \frac{87.6 \times W}{(D\times A\times T)}
\]

Where

- \(A\) = Area of exposure in cm²
- \(W\) = Weight loss in mg
- \(D\) = Density in g/cc
- \(T\) = Time in hours

Inhibitor efficiency has been resolved by using the following relationship.

\[
\text{Inhibitor efficiency (%) } = \left( \frac{W_0 - W_e}{W_0} \right) \times 100
\]

Where

- \(W_0\) is the weight loss without inhibitor and
- \(W_e\) is the weight loss with an inhibitor.

3.5.2 Temperature studies

The inhibition efficiencies of substituted piperidin-4-one with semicarbazone and thiosemicarbazone at room temperature and higher temperatures (313, 323 and 328 K) have been determined for optimum inhibitor concentration of their inhibitor (0.2mM) by using weight loss
experiments. This study gives details about the nature of adsorption and activation energy.

3.6 Electrochemical studies

Electrode surface preparation

The mild steel rod with an exposed of 0.785 cm² were pickled with pickling solution. The pickled specimens were washed, dried, polished using 110 to 410 grade emery papers and finally degreased with the organic solvent trichloroethylene and immediately used for the experiments.

Electrode cell assembly

Electrochemical measurements were accomplished in a glass cell with a volume of 100 ml. A platinum electrode and a saturated calomel electrode were utilized as a counter electrode and a reference electrode accordingly. The mild steel electrode was then fixed in the test solution (uninhibited and inhibited solutions) for 10-15 minutes earlier electrochemical measurements.

Electrochemical study

Electrochemical impedance spectroscopy (EIS) and Tafel polarization were operated by an electrochemical measurement unit (Model 1280 B Solartron, UK). The electrochemical impedance spectroscopy measurements were built at corrosion potentials over a frequency area of 10 kHz to 0.01 Hz with signal amplitude of 10 mv. The Tafel polarization measurements were built after EIS for a potential range of -200 mv to +200 mv with respect to open circuit potential, at a scan rate of 1mv/Sec. The $I_{corr}$, $E_{corr}$, $R_t$ and $C_{dl}$ values were attained from the data using the corresponding “Corr view” and “Zview” softwares.

The inhibition efficiency from potentiodynamic polarization studies was determined from the value $I_{corr}$ by utilizing the formula.
Inhibition efficiency (%) = \( \frac{I_{\text{corr(blank)}} - I_{\text{corr(inh)}}}{I_{\text{corr(blank)}}} \times 100 \)

Where

- \( I_{\text{corr(inh)}} \) is the corrosion current in the presence of inhibitor.
- \( I_{\text{corr(blank)}} \) is the corrosion current in the absence of inhibitor.

The inhibition efficiency from impedance measurements was calculated using the formula

\[
\text{Inhibition efficiency} (%) = \frac{R_t(\text{inh}) - R_t(\text{blank})}{R_t(\text{inh})} \times 100
\]

Where

- \( R_t(\text{inh}) \) is the charge transfer resistance in the presence of inhibitor.
- \( R_t(\text{blank}) \) is the charger transfer resistance in the absence of inhibitor.

### 3.7 Synergistic effect

The synergistic effect was studied by Weight loss measurements and electrochemical techniques in the presence of 1 M KCl, KBr and KI to the steel specimen immersed in 1 N sulphuric acid containing 0.2mM concentrations of inhibitors for duration of 1 hour. From the weight loss data the corrosion rate and inhibition efficiency were calculated. The same procedure was repeated with the addition of 1M ZnSO$_4$ and CdSO$_4$.

### 3.8 FT-IR Spectral analysis

The FT-IR spectra of the inhibitors were recorded on a Shimadza FT-IR 8000 Spectrophotometer in the range 4000-400 cm$^{-1}$ using a KBr disc technique.

### 3.9 FT-Raman Spectral analysis

The FT-Raman spectrum was recorded on a computer interfaced BRUCKER IFS 66V model interferometer equipped with FRA-106 FT-Raman Accessories. The spectrum was measured in the region 4000-
100 cm\(^{-1}\) using Nd: YAG laser operating at 200mW power continuously with 1064 nm excitation. The spectra were recorded with scanning speed of 30 cm\(^{-1}\) min\(^{-1}\) of spectral width 2 cm\(^{-1}\). The frequencies of all sharp bands are accurate to ±1 cm\(^{-1}\).

### 3.10 \(^{13}\)C NMR and \(^{1}\)H NMR Spectral analysis

The \(^{13}\)C NMR and \(^{1}\)H NMR spectra of six synthesized organic compounds were recorded on an NMR spectrometer analysis ranging from 400 MHZ to 800 MHZ using CDCl\(_3\) as a solvent and TMS as an internal standard. The recorded spectrums were analyzed to confirm the structure of synthesized compounds.

### 3.11 Antibacterial activity

Antibacterial activity of (01SC), (02SC), (03SC), (01TS), (02TS) and (03TS) was determined using the disc diffusion method. The bacteria (\textit{Pseudomonas aeruginosa}, \textit{Salmonella sp. Klebsiella pneumonia}, \textit{Staphylococcus aureus}) was cultured in nutrient broth medium and these cultured bacteria kept in medium, and it poured into the centrifuge at 200 RPM and incubated overnight at 37\(^{\circ}\)C. The muller Hinton agar plates were prepared and microbial cultures were swabbed on the medium. After 5 min, the disc (5 mm size) was made using gel puncher and different concentrations (25 µg, 50 µg, 75 µg and 100 µg/ml) of samples were added to the disc. The positive control (10 µg/ml) (tetracycline) was used. The microbial culture plates were incubated at 310K for 24 hours. Afterwards incubation, the zone of inhibition was determined. Each screening test was performed with three replicates and the mean values are recorded.

### 3.12 Quantum chemical parameters calculation (Gaussian 09w program)

In the present investigation Quantum chemical calculations were carried out by means of the Gaussian 09w program package with Becke3-
Lee-Yang-Parr (B3LYP) DFT functional with standard basis sets. Scaling of the force fields was performed by the scaled quantum mechanical procedures with the selective scaling in the local symmetry coordinate representation using transferable scale factors available in the literature. The vibrational modes were allowed by method of visual inspection using the GAUSSVIEW program. The scaled frequencies were close agreement with the observed frequencies.