CHAPTER I

INTRODUCTION

- General Aspects of Corrosion
- Aim of the Research Work
- Synthesis and Characterization of Schiff bases
General Aspects of Corrosion

In recent years corrosion by chemical and electrochemical reactions has assumed great economic importance throughout the world. The estimated annual loss due to corrosion is enormously large. Studies worldwide have shown that the overall cost of corrosion amount to at least 2-3% of the Gross National Product and that 20-25% of the cost could be avoided by using appropriate corrosion control technology [1]. The corrosion of a metal or a material is a global scientific problem as it affects different walks of life especially in metallurgical, chemical, materials and oil industries. Corrosion is defined as the degradation of materials or its properties due to a reaction with the environment. Corrosion exists in virtually all materials, but is most often associated with metals. Metallic corrosion is a naturally occurring process whereby the surface of a metallic structure is oxidized or reduced to a corrosion product such as “rust” by chemical and electrochemical reaction with the environment. The surface of metallic structures is attacked through the migration of ions away from the surface, resulting in material loss over time. The process of corrosion requires the presence of an anode, a cathode, an electrolyte and electrical circuit [2].

The problem of preventing the metallic corrosion is extremely complex but it is of great technological and economical importance. Corrosion of metals can be controlled by taking suitable preventive measures such as painting, plating, use of expensive alloys, use of inhibitors, etc. It is justifiable that several crores of rupees are spent on research for controlling corrosion [3].

Factors Influencing Corrosion:

The nature and extent of corrosion depend on the metal and the environment. The important factors which may influence the corrosion process are:

(i) Nature of the metal  (ii) Environment  (iii) Concentration of electrolyte  
(iv) Temperature  (v) Electrode potential  and  (vi) Hydrogen over voltage

Types of Corrosion:

Different types of corrosion, more or less visible to the naked eye, can occur on metal, such as uniform (generalized) corrosion, pitting corrosion, stress corrosion etc. The predominant type of corrosion will depend on a certain number of factors that are
intrinsic to the metal, the medium and the conditions of use. There is no form of corrosion that is specific to metal and its alloys.

⇒ **Uniform Corrosion**: This type of corrosion develops as pits of very small diameter, in the order of a micrometer, and results in a uniform and continuous decrease in thickness over the entire surface area of the metal. The rate of uniform corrosion can be easily determined by measuring the mass loss, or the quantity of released hydrogen [4].

⇒ **Pitting Corrosion**: This localized form of corrosion is characterized by the formation of irregularly shaped cavities on the surface of the metal. Their diameter and depth depend on several parameters related to the metal, the medium and service conditions. Unlike uniform corrosion, the intensity and rate of pitting corrosion can be assessed neither by determining the mass loss nor by measuring released hydrogen. In fact, these measurements do not make sense because a very deep and isolated pit results only in a small mass loss, whereas a very large number of superficial pits can lead to a larger mass loss. Pitting corrosion can be assessed using three criteria: the density, i.e. the number of pits per unit area, the rate of deepening and the probability of pitting.

⇒ **Transgranular and Intergranular (Intercrystalline) Corrosion**: Within the metal, at the level of the grain, corrosion may propagate in two different ways: (i) It spreads in all directions, corrosion indifferently affects all the metallurgical constituents; there is no selective corrosion. This is called transgranular or transcristalline corrosion because it propagates within the grains. (ii) It follows preferential paths: corrosion propagates at grain boundaries. Unlike transgranular corrosion, these forms of intercrystalline corrosion consume only a very small amount of metal, which is why mass loss is not a significant parameter for assessment of this type of corrosion. It is not detectable which naked eye but requires microscopic observation, typically at a magnification of 50. When penetrating into the bulk of the metal, intercrystalline corrosion may lead to a reduction of mechanical properties and even lead to the rupture of components [5].

⇒ **Exfoliation Corrosion**: Exfoliation corrosion is a type of selective corrosion that propagates along a large number of planes running parallel to the direction of
rolling or extrusion [6]. Between these planes are very thin sheets of sound metal that are not attacked, but gradually pushed away by the swelling of corrosion products, peeling off like pages in a book; hence the term exfoliation corrosion. The metal will swell, which results in the spectacular aspect of this form of corrosion.

⇒ **Stress Corrosion** : This type of corrosion results from the combine action of a mechanical stress (bending, tension) and a corrosive environment. Each of these parameters alone would not have such a significant effect on the resistance of the metal or would have no effect at all.

⇒ **Crevice Corrosion** : Crevice corrosion is a localized corrosion in recesses: overlapping zones for riveting, bolting or welding, zones under joints and under various deposits. These zones also called crevices, are very tiny and difficult to access for the aqueous liquid that is covering the rest of the readily accessible surfaces. This type of corrosion is also known as deposit attack.

⇒ **Galvanic Corrosion** : When two dissimilar metals are in direct contact in a conducting liquid, experience shows that one of the two may corrode. This is called galvanic corrosion. The other metal will not corrode; it may even be protected in this way. This corrosion is different in its kind and intensity from the one that would occur if they were placed separately in the same liquid. Unlike other types of structural corrosion, galvanic corrosion does not depend on the metal’s texture, temper, etc. Galvanic corrosion may occur with any metal, as soon as two are in contact in a conductive liquid. It works like a battery. The appearance of galvanic corrosion is very characteristic. It is not dispersed like pitting corrosion, but highly localized in contact zone with the other metal. The zone affected by galvanic corrosion often has a shinier aspect than the rest of the surface.

⇒ **Erosion** : Corrosion by erosion occurs in moving media. This type of corrosion is related to the flow speed of the fluid. It leads to local thinning of the metal, which results in scratches, gullies, and undulations, which are always oriented in the same direction, namely the flow direction. Avoiding erosion corrosion on aluminium
does not require any specific precautions, only those commonly applied to other metals [5].

**Aim of the Research Work**

The main purpose of the research work that has been described in the thesis centers around the possibility of finding excellent inhibitors for aggressive corrosive media. It has been our experience that it is difficult to find or to come across excellent effective inhibitors for metals corroding extensively in aggressive corrosive medium, e.g. for systems such as zinc in concentrated hydrochloric acid and sulphuric acid or aluminium in concentrated hydrochloric acid or in concentrated sodium hydroxide solutions. Aldehydes and amines are fairly good inhibitors for metals and alloys in acids and other corrosive media. Many of the commercial inhibitor formulations for acid solutions include aldehydes and amines [7-32].

Some previous research work [33] reveals that the inhibition efficiency of Schiff bases is much greater than corresponding aldehydes and amines. This is likely to be due to the presence of a >C=\text{N}– group in Schiff bases. From this point of view, the following inhibitors have been synthesized and the performance of these inhibitors in retarding the corrosion of Al-Mg alloy in hydrochloric acid has been studied. The Schiff bases studied are:

1. Aniline-N-(p-methoxy benzylidene) (ANPMB)
2. Benzylamine-N-(p-methoxy benzylidene) (BANPMB)
3. 2-Phenylethylamine-N-(p-methoxy benzylidene) (2PANPMB)
4. o-chloroaniline-N-(p-methoxy benzylidene) (o-CANPMB)
5. m-chloroaniline-N-(p-methoxy benzylidene) (m-CANPMB)
6. p-chloroaniline-N-(p-methoxy benzylidene) (p-CANPMB)
7. Aniline-N-benzylidene (ANB)
8. Benzylamine-N-benzylidene (BANB)
9. D(+)-\alpha-Phenylethylamine-N-benzylidene (DANB)
10. o-chloroaniline-N-benzylidene (o-CANB)
11. m-chloroaniline-N-benzylidene (m-CANB)
12. p-chloroaniline-N-benzylidene (p-CANB)
The effectiveness of each Schiff base has been evaluated by investigating the following parameters which shall be discussed in Chapter – IV:

a. The effect of inhibitor concentration on inhibition efficiency.
b. The effect of acid concentration on inhibition efficiency.
c. The effect of exposure period on inhibition efficiency.
d. Adsorption isotherm followed by the inhibitor.
e. The effect of temperature on the performance of the inhibitor.
f. Activation energy in the presence and absence of an inhibitor.
g. Evaluation of the thermodynamic parameters such as free energy of adsorption ($\Delta G_{\text{ads}}$), entropy of adsorption ($\Delta S_{\text{ads}}$) and heat of adsorption ($Q_{\text{ads}}$) of an inhibitor.
h. Evaluation of Tafel parameters of the inhibitor and the calculation of efficiency of the inhibitor from Tafel plots.
i. The effect of external cathodic polarization on the efficiency and the adsorption characteristics of an inhibitor.
j. Investigation of the influence of inhibitor by Electrochemical Impedance Spectroscopy (EIS) technique.
k. Investigation of the surface morphology by Scanning Electron Microscopy (SEM) technique.
l. An attempt has been made to suggest a probable action mechanism of an inhibitor from the results obtained by above investigation.
Synthesis and Characterization of Schiff bases

In the present work, systematic investigations have been carried out with several Schiff bases to study their efficiency as inhibitors for the corrosion of Al-Mg alloy in hydrochloric acid solutions. This chapter describes the synthesis of azomethines investigated as corrosion inhibitors.

Synthesis of Azomethines

Condensation of carbonyl compounds with amines is the general reaction to prepare Schiff bases (azomethines).

\[
R\text{——}C=O + R'\text{—}NH_2 \rightarrow R\text{——}C=NR' + H_2O
\]

Both aliphatic and aromatic aldehydes can be condensed with primary amines (aliphatic, carbocyclic or aromatic) to form N-substituted azomethines. As the aim of synthesis of these compounds was to develop new, efficient and stable corrosion inhibitors, such compounds were of little interest in the present work.

On the other hand, Schiff bases derived from aromatic aldehydes such as benzaldehyde or substituted benzaldehydes and aliphatic or aromatic amines, are more stable and could be interesting as corrosion inhibitors [34]. The benzaldehyde entity may carry a halo, hydroxyl, methoxy, dialkylamino or nitro-group as a substitutent. Usually, an immediate reaction occurs upon mixing the two reactants either without a solvent or in dilute alcohol. The reaction between an aromatic aldehyde and an aromatic amine is an exothermic reaction.

The present work was planned to investigate inhibition of corrosion of Al-Mg alloy in hydrochloric acid by azomethines. These are the derivatives of p-methoxy benzaldehyde and benzaldehyde with aromatic amines such as aniline, monochloro substituted aniline, benzylamine, D(+)-Phenylethylamine and 2-Phenylethylamine.

Using the above aldehydes and amines, respective Schiff bases have been synthesized. Their important physical properties have been obtained and the structures are given on page no.9 to 20. The compound was characterized through its structure data (IR-data) and its purity was confirmed by thin-layer chromatography (TLC).
The general methods for preparation of these derivatives was to prepare separately solutions containing the required amount of aldehyde and amine in alcohol and slowly mix the reactants at 0-5°C by immersing the flask in an ice salt bath; and after mixing, reflux the mixture on a water bath for a time ranging from thirty minutes to two hours. After the reaction is complete, the reaction mixture is treated with ice-cold distilled water, when the crude solid product separates. It is first washed with water and then with very dilute hydrochloric acid and finally washed with water and purified by repeated re-crystallization from ethanol. With liquid Schiff bases, after reaction is complete, the reaction mixture is treated with ice-cold water, where the two layers get separated and the one with liquid Schiff base is separated from water with help of separating funnel. The procedure followed is illustrated by the preparation of Aniline-N-(p-methoxy benzyldene) [35].

In a 500 c.c. three necked round bottom flask provided with a mechanical stirrer, one mole of p-methoxy benzaldehyde is placed and one mole of aniline is added with rapid stirring. After a few seconds a reaction occurs with evolution of heat and separation of water. The mixture is allowed to stand for fifteen minutes and it is then poured, with vigorous stirring into 165 c.c. of 95 percent alcohol in a 500 c.c. beaker. Crystallization begins in about five minutes, and the mixture is allowed to stand first for ten minutes at room temperature and then for thirty minutes in ice water. The solid mass is filtered using Buchner funnel, by suction, and air-dried. The yield of pure Aniline-N-(p-methoxy benzyldene) is 84 – 87 % and the melting point is 63°C.
The salient features of the Schiff bases investigated as corrosion inhibitors in the present work are specified in this section:

[1] Name of the inhibitor: Aniline-N-(p-methoxy benzylidene)
Synonyms: Benzenamine-N[(4-methoxy-phenyl)methylene]
C. A. Registry number: 836-41-9
Physical properties: Light yellowish crystalline substance, m.p. 63°C, insoluble in water, soluble in ethanol.

Structure of ANPMB:

\[
\text{IR spectral data of ANPMB:}
\]

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3110 cm(^{-1})</td>
<td>–C–H stretching aromatic ring</td>
</tr>
<tr>
<td>1631 cm(^{-1})</td>
<td>&gt;C=N– stretching in iminic group</td>
</tr>
<tr>
<td>1254 cm(^{-1})</td>
<td>–C–O–C– stretching in aromatic ring</td>
</tr>
</tbody>
</table>
Name of the inhibitor: *Benzylamine-N-(p-methoxybenzylidene)*

**Synonyms**: Benzenemethanamine,N-[(4-methoxyphenyl)methylene]

**C. A. Registry number**: 622-72-0

**Physical properties**: Dark yellowish liquid, b.p.: 225.1°C, 0.5268 mW/mg from DSC graph, insoluble in water, soluble in ethanol.

**Structure of BANPMB**:

![Structure of BANPMB]

**DSC graph**:

![DSC graph]

**IR spectral data of BANPMB**:

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3080</td>
<td>−C–H stretching aromatic ring</td>
</tr>
<tr>
<td>1647</td>
<td>&gt;C=N– stretching in iminic group</td>
</tr>
<tr>
<td>1258</td>
<td>−C–O–C– stretching in aromatic ring</td>
</tr>
</tbody>
</table>
Name of the inhibitor: 2-Phenylethylamine-N-(p-methoxy benzylidene)

Synonyms: Benzeneethanamine,N-[(4-methoxyphenyl)methylene]

C. A. Registry number: 3240-96-8

Physical properties: Yellowish liquid, b.p.: > 350°C from DSC graph, insoluble in water, soluble in ethanol.

Structure of 2ANPMB:

![Structure of 2ANPMB]

DSC graph:

![DSC graph]

IR spectral data of 2ANPMB:

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3072</td>
<td>–C–H stretching aromatic ring</td>
</tr>
<tr>
<td>1645</td>
<td>&gt;C=N– stretching in iminic group</td>
</tr>
<tr>
<td>1232</td>
<td>–C–O–C– stretching in aromatic ring</td>
</tr>
</tbody>
</table>
**Name of the inhibitor**: *o-chloroaniline-N-(p-methoxy benzylidene)*

**Synonyms**: Benzenamine, 2-Chloro-N-[(4-methoxyphenyl)methylene]

**C. A. Registry number**: Not available.

**Physical properties**: Dark reddish liquid, b.p.: 362.4°C, 0.8165 mW/mg from DSC graph, insoluble in water, soluble in ethanol.

**Structure of o-CANPMB**:

![Structure of o-CANPMB](image)

**DSC graph**:

![DSC graph](image)

**IR spectral data of o-CANPMB**:

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3120</td>
<td>(\text{C–H stretching aromatic ring})</td>
</tr>
<tr>
<td>1642</td>
<td>(\text{&gt;C=\text{N}– stretching in iminic group})</td>
</tr>
<tr>
<td>1263</td>
<td>(\text{–C–O–C– stretching in aromatic ring})</td>
</tr>
<tr>
<td>744</td>
<td>(\text{–C–Cl stretching in aromatic ring})</td>
</tr>
</tbody>
</table>
Name of the inhibitor: \textit{m-chloroaniline-N-(p-methoxy benzylidene)}

Synonyms: Benzenamine, 3-Chloro-N-[(4-methoxyphenyl)methylene]

C. A. Registry number: 24776-57-6

Physical properties: Brownish liquid, b.p.: 347.9°C, 0.8771 mW/mg from DSC graph, insoluble in water, soluble in ethanol.

Structure of \textit{m-CANPMB}:

\[
\begin{array}{c}
\text{Cl} \\
N \\
\text{OCH}_3
\end{array}
\]

DSC graph:

Peak: 347.9°C, 0.8771 mW/mg
Area: 110.5 J/g

IR spectral data of \textit{m-CANPMB}:

\begin{center}
\begin{tabular}{|c|c|}
\hline
3164 cm\textsuperscript{-1} & -\text{C–H stretching aromatic ring} \\
1634 cm\textsuperscript{-1} & -\text{C=N– stretching in iminic group} \\
1240 cm\textsuperscript{-1} & -\text{C–O–C– stretching in aromatic ring} \\
737 cm\textsuperscript{-1} & -\text{C–Cl stretching in aromatic ring} \\
\hline
\end{tabular}
\end{center}
Name of the inhibitor: \textit{p-chloroaniline-N-(p-methoxy benzylidene)}

Synonyms: Benzenamine, 4-Chloro-N-[(4-methoxyphenyl)methylene]

C. A. Registry number: 15485-22-0

Physical properties: White crystalline substance, m.p.: 335.9°C, 1.253 mW/mg from DSC graph, insoluble in water, soluble in ethanol.

Structure of \textit{p-CANPMB}:

\[
\begin{array}{c}
\text{Cl} \\
\text{N} \\
\text{OCH}_3
\end{array}
\]

DSC graph:

\[
\begin{array}{c}
\text{Area} = 88.32 \text{ J/g} \\
\text{Area} = 191.1 \text{ J/g}
\end{array}
\]

IR spectral data of \textit{p-CANPMB}:

\[
\begin{array}{c|c}
3131 \text{ cm}^{-1} & \text{–C–H stretching aromatic ring} \\
1648 \text{ cm}^{-1} & \text{–C=O– stretching in iminic group} \\
1257 \text{ cm}^{-1} & \text{–C–O–C– stretching in aromatic ring} \\
766 \text{ cm}^{-1} & \text{–C–Cl stretching in aromatic ring}
\end{array}
\]
**Name of the inhibitor**: Aniline-N-bezylidene

**Synonyms**: Benzeneamine-N-(phenylmethylene)

**C. A. Registry number**: 538-51-2

**Physical properties**: White crystalline substance, m.p. 52°C, insoluble in water, soluble in ethanol.

**Structure of ANB**:

![Structure of ANB](image)

**IR Spectral data of ANB**:

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3157</td>
<td>−C−H stretching in aromatic ring</td>
</tr>
<tr>
<td>1651</td>
<td>&gt;C=N− stretching in iminic group</td>
</tr>
</tbody>
</table>
**Name of the inhibitor**: Benzylamine-N-benzylidene

**Synonyms**: N-Benzylidene benzylamine

**C. A. Registry number**: 780-25-6

**Physical properties**: Yellowish liquid,

b.p. 143-144°C / 5mm Hg (lit),
insoluble in water,
soluble in ethanol.

**Structure of BANB**:

![Structure of BANB](image)

**IR spectral data of BANB**:

<table>
<thead>
<tr>
<th>Wave Number (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3110</td>
<td>−C−H stretching aromatic ring</td>
</tr>
<tr>
<td>1620</td>
<td>&gt;C=N− stretching in iminic group</td>
</tr>
</tbody>
</table>
**Name of the inhibitor**: \( D(+)\alpha\text{-Phenylethylamine-N-}

**benzylidene**

**Synonyms**: Benzenemethanamine \( \alpha\text{-metyl-N-}

(phenylmethylene)

**C. A. Registry number**: 3129-98-4

**Physical properties**: Brownish liquid, b.p.: 247.1°C, 0.2886 mW/mg
from DSC graph, insoluble in water, soluble in ethanol.

**Structure of DANB**:

\[
\begin{align*}
\text{C. A. Registry number}: & \quad 3129-98-4 \\
\text{Physical properties}: & \quad \text{Brownish liquid, b.p.: 247.1°C, 0.2886 mW/mg from DSC graph, insoluble in water, soluble in ethanol.}
\end{align*}
\]

**DSC graph**:

**IR Spectral data of DANB**:

<table>
<thead>
<tr>
<th>( \text{cm}^{-1} )</th>
<th>( \text{IR Spectral data of DANB} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3157</td>
<td>(-\text{C--H stretching aromatic ring})</td>
</tr>
<tr>
<td>1640</td>
<td>(\text{&gt;C=N-- stretching in iminic group})</td>
</tr>
<tr>
<td>1256</td>
<td>(\text{&gt;C--CH}_3\text{ stretching})</td>
</tr>
</tbody>
</table>
Name of the inhibitor: o-chloroaniline-N-benzylidene

Synonyms: Benzenamine, 2-Chloro-N-(phenylmethylene)

C. A. Registry number: 884-29-7

Physical properties: Dark brownish liquid, b.p.: 327.3°C, 0.8938 mW/mg from DSC graph, insoluble in water, soluble in ethanol.

Structure of o-CANB:

DSC graph:

IR spectral data of o-CANB:

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Functional Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3162</td>
<td>–C–H stretching aromatic ring</td>
</tr>
<tr>
<td>1638</td>
<td>&gt;C=N– stretching in iminic group</td>
</tr>
<tr>
<td>745</td>
<td>–C–Cl stretching in aromatic ring</td>
</tr>
</tbody>
</table>
**Name of the inhibitor**: m-chloroaniline-N-benzylidene

**Synonyms**: Benzenamine, 3-Chloro-N-(phenylmethylene)

**C. A. Registry number**: 7519-65-5

**Physical properties**: Brownish liquid, b.p.: 334.3°C, 0.9452 mW/mg from DSC graph, insoluble in water, soluble in ethanol.

**Structure of m-CANB**:

![Structure of m-CANB][1]

**DSC graph**:

![DSC graph][2]

**IR spectral data of m-CANB**:  

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3128</td>
<td>−C–H stretching aromatic ring</td>
</tr>
<tr>
<td>1635</td>
<td>&gt;C=N– stretching in iminic group</td>
</tr>
<tr>
<td>741</td>
<td>−C–Cl stretching in aromatic ring</td>
</tr>
</tbody>
</table>
Name of the inhibitor: \textit{p-chloroaniline-N-benzylidene}

Synonyms: Benzenamine, 4-Chloro-N-(phenylmethylene)

C. A. Registry number: 780-21-2

Physical properties: Off white crystalline substance, m.p.: 307.5°C, 1.412 mW/mg from DSC graph, insoluble in water, soluble in ethanol.

Structure of \textit{p-CANB}:

\begin{center}
\includegraphics[width=0.5\textwidth]{structure.png}
\end{center}

DSC graph:

\begin{center}
\includegraphics[width=0.5\textwidth]{dsc_graph.png}
\end{center}

\textit{IR spectral data of \textit{p-CNAB}}:

\begin{center}
\begin{tabular}{|c|l|}
\hline
3122 cm\textsuperscript{-1} & –C–H stretching aromatic ring \\
1640 cm\textsuperscript{-1} & >C=N– stretching in iminic group \\
750 cm\textsuperscript{-1} & –C–Cl stretching in aromatic ring \\
\hline
\end{tabular}
\end{center}
REFERENCES


