CHAPTER I

SCREENING OF THE EXCELLENT SCHIFF BASES AS CORROSION INHIBITORS FOR ZINC IN HYDROCHLORIC ACID
1.1 GENERAL ASPECTS OF CORROSION

The term “corrosion” has its origin from Latin word “corrodere” where *rodere* means “gangwing” and *corrodere* means “gangwing to pieces”. Corrosion is an irreversible interfacial reaction of a material (metal, ceramic and polymer) with its environment which results in consumption of the material or its dissolution into the material of a component of the environment. The annual loss due to corrosion has been estimated at about 6% of the country’s Gross Domestic Product (GDP) and that 20-25% of the cost could be avoided by using appropriate corrosion control technology [1]. Corrosion awareness in India is shown graphically.

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 exists in virtually all materials, but is most often associated with metals. In metals, corrosion is produced by the loss of actual material, which leaves the piece as an ion in solution, and is carried away by an electrolyte, resulting in material loss over time. The process of corrosion requires the presence of an anode, a cathode, an electrolyte and electrical circuit [2].

1. An anode. This is where the damage occurs. Oxidation takes place.
2. A cathode. Here’s where the reduction reaction takes place.
3. An electrolyte. (Almost any moisture will do.)
4. Electrical circuit. A current path between cathode and anode.
The destructive effects and high cost of corrosion prompted the researchers to develop methods to prevent corrosion. Many methods to prevent corrosion were invented and developed that tend to produce corrosion resistant materials, painting, coating and cathodic protection [3].

1.2 FACTORS INFLUENCING CORROSION

The nature and rate 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

1.3 TYPES OF CORROSION

- Uniform - common surface effect.
- Pitting Corrosion.
- Transgranular and Intragranular.
- Exfoliation
- Stress Corrosion.
- Crevice corrosion.
- Galvanic Corrosion.
- Errosion 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.

1.3.1 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].
1.3.2 Pitting Corrosion

It is a form of localized attack that results in holes in a corroding metal. It is a serious type of corrosion: though the extent of the reaction may be small, the damage may be severe, particularly when the metal concerned is used as a container for fluid.

Generally, a pit may be described as a cavity or hole whose surface diameter is about the same as or less than the depth. 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; where as 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.

1.3.3 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 transcrystalline 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 consumes 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 with
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].

1.3.4 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. This type of corrosion is observed mostly in wrought products.

1.3.5 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.

1.3.6 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. They are created by surface deposits of corrosion products, scratches in paint films etc.

1.3.7 Galvanic Corrosion

When two dissimilar metals in electrical contact with each other are exposed to an electrolyte, a current, which is called a galvanic current, flows from one to the other. Galvanic corrosion is that part of the corrosion which occurs on the anodic member of such a couple and is directly related to the galvanic current by Faraday’s law. Under a galvanic corrosion condition, the simultaneous additional corrosion taking place on the anode of the couple is called the local corrosion or the self-corrosion. The local corrosion may or may not equal the corrosion taking place when the two metals are not electrically connected, called the normal corrosion. The difference between the local corrosion and the normal corrosion is called the difference effect and may be positive, if the local corrosion decreases when galvanic current flows, or negative. A galvanic current generally causes a reduction in the total rate of corrosion of the cathodic member of the couple. In this case the cathodic member is cathodically protected.

1.3.8 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].
1.4 AIM OF THE RESEARCH WORK

The aim of the research work is to find excellent corrosion inhibitors in acidic media. Many compounds have been tried in the past. Aldehydes and amines are fairly good inhibitors for metals and alloys in acids and other corrosive media. Many of the corrosion inhibitor formulations for acid solutions include aldehydes and amines [6-31]. The use of Schiff bases as corrosion inhibitors has attracted considerable attention because through their functional groups they form complexes with metal ions and these complexes occupy a large surface area on the metal thereby protecting the metal from corrosive environment.

Previous research work [32-36] reveals the use of various Schiff bases for Zn, Al, Al-Mg alloy and mild steel in acidic medium and it was observed that the inhibition efficiency of Schiff bases is much greater due to the presence of a \( \text{C} = \text{N} \) group in azomethine. From this point of view, the following inhibitors have been synthesized and their performance in retarding the corrosion of zinc in hydrochloric acid has been studied.

The Schiff bases studied are:
1. Aniline-N-(p-methoxybenzylidene) (ANPMB)
2. Benzylamine-N-(p-methoxybenzylidene) (BANPMB)
3. 2-Phenylethylamine-N-(p-methoxybenzylidene) (2-PANPMB)
4. o-Chloroaniline-N-(p-methoxybenzylidene) (o-CANPMB)
5. m-Chloroaniline-N-(p-methoxybenzylidene) (m-CANPMB)
6. p-Chloroaniline-N-(p-methoxybenzylidene) (p-CANPMB)

The following parameters have been considered to evaluate the effectiveness of each Schiff base as inhibitors:
(a) The effect of inhibitor concentration on inhibitor efficiency.
(b) The effect of acid concentration on inhibitor efficiency.
(c) The effect of exposure period on inhibitor 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 \( (\Delta G^\circ_A) \), entropy of adsorption \( (\Delta S^\circ_A) \) and heat of adsorption \( Q_A \) of an inhibitor.
(h) Action mechanism of an inhibitor by Galvanostatic Polarization method.
1.5 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 zinc in hydrochloric acid solutions. This chapter describes the synthesis of azomethines investigated as corrosion inhibitors.

1.5.1 Synthesis of Azomethines

There are several reaction pathways to synthesize Schiff bases. The most common is an acid catalyzed reaction of amine and aldehyde or ketone under refluxing conditions. The first step in this reaction is an attack of nucleophilic nitrogen atom of an amine on the carbonyl carbon resulting in a normally unstable carbinolamine intermediate. The reaction can reverse to the starting materials, or when the hydroxyl group is eliminated and a >C=N bond is formed, an imine is formed. Many factors affect the condensation reaction, for example the pH of the solution as well as the steric and electronic effects of the carbonyl compound and amine. As amine is basic, it is mostly protonated in acidic conditions and thus cannot proceed. Furthermore, in very basic reaction conditions the reaction is hindered as sufficient protons are not available to catalyse the elimination of the carbonilamine hydroxyl group. In general, aldehydes react faster than ketones in Schiff base condensation reactions as the reactions centre of an aldehyde is sterically less hindered than that of a ketone. Furthermore, the extra carbon of ketone donates electron density and thus makes the ketone less electrophilic as compared to aldehyde.

Different types of Schiff bases were synthesized by using different amines and different carbonyl compounds [37].
Condensation of carbonyl compounds with amines is the general reaction to prepare Schiff bases (azomethines).

\[
\begin{align*}
R - C = O + R' NH_2 & \quad \rightarrow \quad R - C = NR' + H_2O \\
\left| \quad \quad \quad \quad \quad \quad \right| \quad \quad \quad \quad \quad \quad \left| \quad \quad \quad \quad \quad \quad \quad \right|
\end{align*}
\]

This work was planned to investigate inhibition of corrosion of zinc in hydrochloric acid by azomethines. These are the derivatives of p-methoxybenzaldehyde with aromatic amines such as aniline, monochloro substituted Aniline, Benzylamine, 2-Phenylethylamine.

Using the above aldehyde and amines, respective Schiff bases have been synthesized. Their important physical properties have been obtained and the structures are given below. The compounds were characterized through Infra-red spectroscopy and their purity was confirmed by thin-layer chromatography.

1.5.2 Preparation of Aniline-N-benzylidene

In a 500 c.c. three necked round bottom flask provided with a mechanical stirrer, one mole of p-methoxybenzaldehyde 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 [38]. The yield of pure Aniline-N-(p-methoxybenzylidene) is 84 – 87 % and the melting point is 63°C.
1.6 DATA ABOUT SCHIFF BASES

The salient features of the Schiff bases investigated as corrosion inhibitors in the present work are specified in this section:

[1.6.1]

Name of the inhibitor : *Aniline-N-(p-methoxybenzylidene)* [ANPMB]  
Synonyms : N-(4-methoxybenzylidenel)aniline  
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 : 

![Structure of ANPMB](image)  

IR spectral data of ANPMB:

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Description</th>
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<tbody>
<tr>
<td>3110</td>
<td>–C–H stretching aromatic ring</td>
</tr>
<tr>
<td>1631</td>
<td>&gt;C=N– stretching in iminic group</td>
</tr>
<tr>
<td>1254</td>
<td>–C–O–C–stretching in aromatic ring</td>
</tr>
</tbody>
</table>
1.6.2

Name of the inhibitor: *Benzylamine-N-(p-methoxybenzylidene)* [BANPMB]

Synonyms: N-(4-methoxybenzylidene)benzylamine

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:

```
N
O
C
H
```

DSC graph:

IR spectral data of BANPMB:

<table>
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<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Description</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-methoxybenzylidene) [2-PANPMB]

Synonyms: N-(4-methoxybenzylidenel)-2-phenylethylamine

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

Physical properties: Yellowish liquid, insoluble in water, soluble in ethanol.

Structure of 2-PANPMB:

DSC graph:

IR spectral data of 2-PANPMB:

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Interpretation</th>
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<td>3072</td>
<td>–C–H stretching aromatic ring</td>
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<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-methoxybenzylidene) [o-CANPMB]

Synonyms: 2-Chloro-N-(4-methoxybenzylidene)aniline

C. A. Registry number: Not available.

Physical properties: Dark reddish liquid, b.p.: 362.4°C, insoluble in water, soluble in ethanol.

Structure of o-CANPMB:

\[
\begin{align*}
\text{H}_3\text{CO} & \quad \text{N} \\
& \quad \text{Cl} \\
& \quad \text{N} \\
\end{align*}
\]

DSC graph:

IR spectral data of o-CANPMB:

<table>
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<tr>
<th>Wave Number (cm(^{-1}))</th>
<th>Description</th>
</tr>
</thead>
<tbody>
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<td>3120</td>
<td>–C–H stretching aromatic ring</td>
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<tr>
<td>1642</td>
<td>&gt;C=N– stretching in iminic group</td>
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<tr>
<td>1263</td>
<td>–C–O–C– stretching in aromatic ring</td>
</tr>
<tr>
<td>744</td>
<td>–C–Cl stretching in aromatic ring</td>
</tr>
</tbody>
</table>
**[1.6.5]**

*Name of the inhibitor*: *m*-Chloroaniline-\(N\)-(p-methoxybenzylidene)

*Synonyms*: 3-Chloro-N-(4-methoxybenzylidenel)aniline

*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 m-CANPMB*:

![Structure of m-CANPMB](image)

*DSC graph*:

![DSC graph](image)

*IR spectral data of m-CANPMB:*

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Description</th>
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<tr>
<td>3164</td>
<td>–C–H stretching aromatic ring</td>
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<tr>
<td>1634</td>
<td>&gt;C=N– stretching in iminic group</td>
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<tr>
<td>1240</td>
<td>–C–O–C– stretching in aromatic ring</td>
</tr>
<tr>
<td>737</td>
<td>–C–Cl stretching in aromatic ring</td>
</tr>
</tbody>
</table>
**Name of the inhibitor**: \( p\text{-Chloroaniline-N-}(p\text{-methoxybenzylidene}) \)  
**[P-CANPMB]**

**Synonyms**: 4-Chloro-N-(4-methoxybenzylidenel)aniline

**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 p-CANPMB**:

![Structure of p-CANPMB](image)

**DSC graph**:

![DSC graph](image)

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

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Description</th>
</tr>
</thead>
<tbody>
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<td>3131</td>
<td>( \text{C–H stretching aromatic ring} )</td>
</tr>
<tr>
<td>1648</td>
<td>( \text{&gt;C=N– stretching in iminic group} )</td>
</tr>
<tr>
<td>1257</td>
<td>( \text{C–O–C– stretching in aromatic ring} )</td>
</tr>
<tr>
<td>766</td>
<td>( \text{C–Cl stretching in aromatic ring} )</td>
</tr>
</tbody>
</table>
REFERENCES

5. Roberts C.W., Journal of Institute of Metals 81(1953) 301.


