CHAPTER III

EXPERIMENTAL METHODS
III.1 Materials

Preparation of carbon steel specimens

The carbon steel specimens were chosen from the same sheet of the following composition:

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>Si</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition %</td>
<td>0.098</td>
<td>0.179</td>
<td>0.012</td>
<td>0.024</td>
<td>0.01</td>
<td>0.0023</td>
<td>0.018</td>
<td>&lt;0.001</td>
<td>99.57</td>
</tr>
</tbody>
</table>

Carbon steel specimens of the above compositions were analysed by using vaccum emission spectrometer DV-4 (supplied by BAIRD Corporation of India) and of the dimensions 1.0 cm × 4.0 cm × 0.2 cm were polished to mirror finish using emery sheets, (No. 0/2 and 0/3) washed with double distilled water, degreased with trichloroethylene, dried and were used for the weight-loss and surface examination studies. The specimens were stored in a desiccator and used for all investigations. Carbon steel rod encapsulated in Teflon with an exposed cross section of 1 cm² diameter was used as the working electrode (WE) in potentiostatic polarisation studies. The surface of working electrode was polished to mirror finish and degreased with trichloroethylene.

Chemicals

Analar samples of sulphuric acid, sodiumgluconate, sodium salt of diethylenetriaminepentamethylene phosphonicacid (Na₃DTPMP), sodiumchloride, sodium molybdate, sodiumpotassiumtartrate, trisodiumcitrate, zinscsulphate, sodium hydroxide, N-cetylpyridinium chloride (CPC), N-cetyl-N,N,N-trimethylammonium
bromide (CTAB) and trichloroethylene were used for the experimental investigations.

III.2 Preparation of stock solutions

III.2.1 Conductivity water

Alkaline potassium permanganate was used to distill demineralized water and the water so obtained was redistilled without using any further additives using all glass apparatus. The double distilled (DD) water was used for cleaning the cell and the electrodes. The preparations of all solutions were with DD water only.

III.2.2 Sodium hydroxide solution (1 N)

About 13 gm of sodium hydroxide was dissolved in 250 ml double distilled water in order to make a solution of normality slightly greater than 1 N. Its exact strength was determined by titrating with a standard oxalic acid solution using phenolphthalein indicator. Then 1 N sodium hydroxide solution was prepared by transferring the required volume of NaOH into a 250 ml standard measuring flask and making up to the mark with double distilled water.

III.2.3 Acid

1.33 N sulphuric acid was prepared from concentrated sulphuric acid. By using this solution exactly 1 N acid was prepared by taking required volume in a 250 ml standard flask and its normality was determined by titrating with standard sodium hydroxide.
III.2.4 Solutions of sodium salt of phosphonic acid

1 gm of diethylenetriaminepentamethylene phosphonic acid was dissolved in dilute sodium hydroxide solution, neutralized and then made up to 100 ml in a standard flask. 1 ml of this solution was diluted to give 100 ml of 100 ppm of DTPMP.

III.2.5 Sodium chloride solution

A stock solution of sodium chloride was prepared by dissolving 9.8 gm of sodium chloride in double distilled water and making up to 1 liter. A hundred-fold dilution yields 60 ppm of chloride solutions.

III.2.6 Zinc sulphate solution

4.4 gm of zinc sulphate was dissolved in doubledistilled water and made up to 1 liter. A hundred-fold dilution yields 10 ppm of Zn$^{2+}$ ion concentration.

III.2.7 Sodium gluconate solution

1 gm of sodium gluconate was dissolved in double distilled water and made up to 100 ml in a standard flask. 1 ml of this solution was diluted to give 100 ml of 100 ppm of sodium gluconate.

III.2.8 Sodium potassiumtartrate

1 gm of sodiumpotassiumtartrate was dissolved in double distilled water and made unto 100 ml in a standard flask. 1 ml of this solution was diluted to give 100 ml of 100 ppm sodium potassiumtartrate.
III.2.9 Sodium molybdate

1 gm of sodium molybdate was dissolve in doubled distilled water and made up to 100 ml in a standard flask. 1 ml of this solution was diluted to give 100 ml of 100 ppm of sodium molybdate.

III.2.10 N-cetyl-N,N,N-trimethylammonium bromide (CTAB) solution

1 gm of CTAB was dissolved in double distilled water and made up to 100 ml in a standard flask. 1 ml of this solution was diluted to give 100 ml of 100 ppm CTAB.

III.2.11 N-cetyldpyridinium chloride (CPC) solution

1 gm of CPC was dissolved in double distilled water and made up to 100 ml in a standard flask. 1 ml of this solution was diluted to give 100 ml of 100 ppm of N-cetyldpyridinium chloride.

III.3 Preparation of the environments for weight loss method

The preparation of various environments used for weight loss method in the present study is explained in Table III.1 for one set of solutions. In the same way, other test solutions were prepared.
Table III.1. Preparation of the environments for weight loss method.

<table>
<thead>
<tr>
<th>NaCl solution</th>
<th>Sodiumphosphonate solution</th>
<th>ZnSO₄ solution</th>
<th>Total volume made up with distilled water</th>
</tr>
</thead>
<tbody>
<tr>
<td>ml</td>
<td>ml</td>
<td>ml</td>
<td>ml</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>1</td>
<td>10</td>
</tr>
</tbody>
</table>

III. 4 Experimental techniques

Weight loss method

III.4.1 Determination of surface area of the specimens

The length, breadth and thickness of carbon steel specimens, the radius of the hole was determined with the help of vernier callipers of high precision and the surface areas of the specimens were calculated.

III.4.2 Weighing the specimens before and after corrosion

Weighing of the carbon steel specimens before and after corrosion were carried out using a Mettler analytical balance-AE 240 Mettler instrument AG, CH-8606 Grefensee, Switzerland with readability of 0.01 mg in 40 gm range and 0.1
mg in 200 gm range. The balance has reproducibility (standard deviation) of 0.02 mg in 40 gm range and 0.1 mg in 200 gm range.

III.4.3 Determination of corrosion rate

The weighed specimens in triplicate were suspended by means of glass or plastic hooks in 100 ml beakers containing 100 ml of various test solutions. After three days of immersion, the specimens were taken out, washed with distilled water running water, dried and weighed. From the change in weight of the specimens, corrosion rates were calculated using the following relationship:\(^\text{1,2}\):

\[
\text{Corrosion rate} = \frac{\text{Loss in weight (mg)}}{\text{Surface area of the specimen (dm}^2\text{)} \times \text{Period of immersion (days)}}
\]

The corrosion rate is expressed in mdd units [mdd = mgm/(dm\(^2\)) (day)].

Corrosion inhibition efficiency (I.E.) was then calculated using the equation\(^\text{3-7}\):

\[
\text{I.E.} = 100 \left[1 - \frac{W_2}{W_1}\right] \%
\]

where \(W_1\) = Corrosion rate in the absence of inhibitor and \(W_2\) = Corrosion rate in the presence of inhibitor.

III.4.4 Synergism parameters (\(S_I\))

The synergism parameters (\(S_I\)) were calculated using the relation as stated below\(^\text{8-12}\):

\[
S_I = \frac{1 - I_{1+2}}{1 - I_{1+2}}
\]

Where \(I_{1+2} = (I_1 + I_2) - (I_1 \cdot I_2)\)

\(I_{1+2}\) = combined inhibition efficiency of substance 1 and substance 2.
If the resultant values of $S_I$ are greater than 1, the result confirms the synergistic effect between the inhibitor and the additives.

### III.5 Polarization study

The polarization measurements\(^{13-20}\) were carried using corrosion measurement system (EG & G Model 6310 Electrochemical Impedance Analyzer) (Fig. III.1). A three-electrode cell assembly was used. The working electrode (WE) used was a rectangular specimen of carbon steel with one face of the electrode of 1 cm\(^2\) area exposed and the rest being shielded with red lacquer. A rectangular platinum foil was used as the counter (CE) electrode. The area of the counter electrode was much larger when compared to the area of the WE. This can exert a uniform potential field on the WE and minimize the polarization effect on the CE. The reference electrode (RE) used was saturated calomel electrode (SCE). The RE was placed close to the WE to minimize iR contribution. A time interval of about 5 to 10 min was given for the WE to attain a steady state open circuit potential\(^{21-24}\) (Fig. III.2). The results such as inhibition efficiency, Tafel slopes, $E_{corr}$ and $I_{corr}$ values were presented.
Figure III.1. EG & Electrochemical Analyser Model 6310.
Figure III.2. General configuration of test equipment, electrochemical cell, test electrode and electrical connections in electrochemical tests. RE: calomel reference electrode, WE: working electrode, CE: Platinum counter electrode.
III.6 Surface analysis by FTIR spectroscopy

After the immersion period of 3 days in various environments, the specimens were taken out of the solutions and dried. The film formed on the surface was scratched carefully and it was thoroughly mixed so as to make it uniform throughout. FTIR spectrum\textsuperscript{25-32} of the powder (KBr pellet) was recorded using Perkin-Elmer 1600 FTIR spectrometer.

III. 7 AC Impedance measurement

AC Impedance measurements\textsuperscript{33-43} were carried out using EG & G Model 6310 Electrochemical Impedance Analyzer (Fig. III.1). Cell set up was the same as that used for polarization measurements. A time interval of 5-10 min was given for the system to attain a steady state open circuit potential. Then over this steady state potential, an AC potential of 10 mV was superimposed. The AC frequency was varied from 100 MHz to 100 kHz. The real part ($z'$) and the imaginary part ($z''$) of the cell impedance were measured in ohms for various frequencies. The $R_{ct}$ and $C_{dl}$ values were calculated.

III.8 Surface analysis by optical microscopy

Polished specimens prior to the initiation of all corrosion experiments were examined through an optical microscope\textsuperscript{44-47} (Fig. III.3) to find out any surface defects such as pits or noticeable irregularities like cracks, etc. only those specimens which had a smooth pit free surface, were subjected to experimental exposure. After completion of these tests, the specimens were thoroughly washed in double distilled
water, dried in a desiccator and thereafter subjected to study surface morphological studies of the metal in the absence and presence of inhibitors.

![Optical microscope](image)

**Figure III.3.** Optical microscope

### III.9 Surface analysis by Atomic Force Microscopy

Atomic Force Microscope (AFM) is an exciting new technique that allows surface to be imaged at higher resolutions and accuracies than ever before.\(^{48-51}\) The microscope used for the present study was (Shimadzu SPM 9500 Scanning Probe Microscope) Polished specimens prior to the initiation of all corrosion experiments were examined through an optical microscope to find out any surface defects such as pits or noticeable irregularities like cracks, etc. Only those specimens, which had a smooth pit free surface, were subjected AFM examination. The protective films formed on the mild steel specimens after immersion in the inhibitor systems for different time durations were examined for a scanned area of \(5 \times 5 \ \mu \text{m}^2\). The two-dimensional and three-dimensional topography of surface films gave various roughness parameters of the film.
III.10 Determination of biocidal efficiency of the system

The phosphonic acid–Zn$^{2+}$ formulation that offered the best corrosion inhibition efficiency was selected for biocidal study. The biocidal efficiency of N-cetyl-N,N,N-trimethylammoniumbromide (CTAB)$^{52-60}$ and N-cetylpyridinumchloride (CPC)$^{53,58,61}$ in DTPMP-Zn$^{2+}$ inhibitor system with synergists Zn$^{2+}$, TSC, SG, SM and SPT were determined.

Various concentrations of CTAB (10 ppm, 50 ppm, 100 ppm, 150 ppm and 200 ppm) were added to the formulation consisting of the inhibitor system. Polished and degreased carbon steel specimens in triplicate were immersed in these environments for a period of 7 days. After 7 days, easy to use BACTASLYDE was dipped in each test solution containing phosphonic acid and synergists viz., Zn$^{2+}$, TSC, SG, SM and SPT for 20-25 sec. The slydes were then incubated in a warm place for 24 hours to ensure rapid growth of microbial bacteria present in the inhibitor system, which caused microbial corrosion. After incubation the slydes were matched with density chart and the total bacterial colonies formed for each ml of the solution was calculated and used for calculating biocidal efficiencies of the biocides CTAB and CPC. The biocidal efficiencies of the formulations consisting of the inhibitor in the presence of various concentrations of CTAB were determined in the same way. Similarly the experiment was done with N-cetylpyridiniumchloride.

III.11 Surface analysis by X-ray diffraction (XRD) technique

The XRD patterns were recorded by using a computer controlled X-ray powder diffractometer JEOL JDX 8030 with Cu K$_\alpha$ (Ni-filtered) radiation
\( \lambda = 1.5418 \text{Å} \) at a rating of 40kV, 20 mA. The scan rate was 0.05-20° per step and the measuring time was 1 sec per step.
References


