CHAPTER 2
EXPERIMENTAL
2.0 MATERIAL

2.1 TEST SPECIMEN

The mild steel sheets used for the investigation had the following composition:

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.14</td>
<td>0.35</td>
<td>0.17</td>
<td>0.025</td>
<td>0.03</td>
<td>Rest</td>
</tr>
</tbody>
</table>

2.2 TEST SOLUTION

A. R. grade sulphuric and hydrochloric acids and double distilled water was used to prepare all the solutions required for the experiments. 1-2% ethanol or acetone was used to dissolve the inhibitors.

2.3 INHIBITORS USED

1. 2, 3, 9, 10 - tetraphenyl - 6, 13 - dithia - 1, 4, 5, 7, 8, 11, 12, 14 - octaaza-cyclotetradecane - 2, 4, 7, 8, 10, 12 - hexaene (PTAT)

2. 3, 4, 9, 10 - tetraphenyl - 7, 12 - dithia - 1, 2, 5, 6, 8, 11 - hexaaza-cyclobidecane-2, 4, 7, 8, 10, 12 hexaene (PTAB)

3. 3, 4, 9, 10 - tetraphenyl - 7, 12 - dioxa - 1, 2, 5, 6, 8, 11 - hexaaza-cyclobidecane - 2, 4, 7, 8, 10, 12 hexaene (POAB)

4. 7, 14 - dimethyl - 5, 12 - dioxo - 1, 4, 8, 11 - tetraaza - cyclotetradeca - 1, 7 - diene (MOAT)

5. 2, 3 : 9, 10 - dibenzo - 7, 14 - dimethyl - 5, 12 - dioxo - 1, 4, 8, 11 - tetraaza - cyclotetradeca - 1, 7 - diene (BMOAT)

6. 2, 5, 10, 13 - tetraoxo - 1, 6, 9, 14 - tetraaza - cyclohexadecane (OAH)

7. 7, 8 : 15, 16 - dibenzo - 2, 5, 10, 13 - tetraoxo - 1, 6, 9, 14 -tetraaza-
cyclohexadecane (BOAH)

8. 3, 4 : 11, 12 - dibenzo - 2, 5, 10, 13 - tetraoxo - 1, 6, 9, 14 - tetraaza-cyclohexadecane (DBOAD)

9. 3, 4 : 7, 8 : 11, 12 : 15, 16 - tetrabenzo - 2, 5, 10, 13 - tetraoxo - 1, 6, 9, 14 - tetraazacyclo-hexadecane (TBOAD)

10. Phenyl thiobisformamidine (PTBF)

11. Tolyl thiobisformamidine (TTBF)

12. Anisidyl thiobisformamidine (ATBF)

13. 4 - chlorophenyl thiobisformamidine (CPTBF)

14. 1, 5 - diphenyl - 2, 4 - dithiobiuret (DPDTB)

15. 1 - tolyl - 5 - phenyl - 2, 4 - dithiobiuret (TPDTB)

16. 1 - anisidyl - 5 - phenyl - 2, 4 - dithiobiuret (APDTB)

17. 1 - chlorophenyl - 5 - phenyl - 2, 4 - dithiobiuret (CPDTB)

18. 1 - benzylidene - 3 - thiocarbohydrazide (BTCH)

19. 1 - salicylidene - 3 - thiocarbohydrazide (STCH)

20. 1 - vanillidine - 3-thiocarbohydrazide (VTCH)

21. 1 - cinnamylidene - 3 - thiocarbohydrazide (CTCH)

22. 1 - furfurylidene - 3 - thiocarbohydrazide (FTCH)

2.4 SYNTHESES OF MACROCYCLIC COMPOUNDS

2.4.1 SYNTHESES OF PTAT, PTAB AND POAB

2.4.1.(A) PREPARATION OF THIOCARBOHYDRAZIDE [1]

To a vigorously stirred solution of 250 grams of 100% hydrazine hydrate (5 mol) in 150 ml of water, 76 grams (1 mol) of Carbon disulphide was added dropwise.
The reaction mixture was then heated at reflux for 30 minutes, cooled in ice bath for 30 minutes. The precipitated thiocarbohydrazide was filtered off, washed with ethanol and ether, air dried and crystallized from minimum amount of water acidified with a few drops of concentrated HCl: M.P. = 165°C.

2.4.1. (B) SYNTHESIS OF PTAT, PTAB AND POAB (SCHEME 1.1) [2]

A solution of benzil (0.04 mol) in 30 ml ethanol was added dropwise to a refluxing solution of thiocarbohydrazide or thiosemicarbohydrazide or semicarbohydrazide (0.04 mol) in 30 ml of ethanol, followed by the addition of Conc. HCl (1ml). The mixture was refluxed for 4 - 6 hours and the solution was left for overnight. The precipitate thus obtained was filtered off and then recrystallized with ethanol. Their TLC were obtained in benzene + acetone + ethylacetate (6 : 3 : 1) mixture of solvents. The macrocyclic compounds thus prepared are: -

1. 2, 3, 9, 10 - tetraphenyl - 6, 13 - dithia - 1, 4, 5, 7, 8, 11, 12, 14 - octaaza - cyclotetradecane - 2, 4, 7, 8, 10, 12 - hexaene (PTAT) M.P. = 185°C, R_f = 0.51.
   IR (KBr) Cm^-1, 1590 (C = N, stretch), 1080 (C = S, stretch)

2. 3, 4, 9, 10 - tetraphenyl - 7, 12 - dithia - 1, 2, 5, 6, 8, 11 - hexaaza - cyclobidecane - 2, 4, 7, 8, 10, 12 hexaene (PTAB) M.P = 100°C, R_f = 0.53.

3. 3, 4, 9, 10 - tetraphenyl - 7, 12 - dioxa - 1, 2, 5, 6, 8, 11 - hexaaza - cyclobidecane - 2, 4, 7, 8, 10, 12 - hexaene (POAB) M.P = 198°C, R_f =0.63.

2.4.2 SYNTHESIS OF MOAT, BMOAT, OAH, BOAH, TBOAD AND DBOAD (SCHEME 1.2) [3]

To the 1, 2 - diaminoethylene or 1, 2 - diaminophenylene (0.01 mol) in 50 ml methanol, ethylacetoacetate or succinic acid or pthallic acid (0.01 mol) in 50 ml methanol was added dropwise while stirring continuously for 7 hours. The resultant solid product was then filtered, washed with methanol and dried in air. These compounds are crystallized by the mixture of methanol and ethanol. Their R_f values were obtained in benzene + ethylacetate (7 : 3) mixture. The macrocyclic compounds thus prepared are: -
4. 7, 14 - dimethyl - 5, 12 - dioxo - 1, 4, 8, 11 - tetraaza - cyclotetradeca - 1, 7 - diene (MOAT) M. P. = 114°C, R_f = 0.57.

5. 2, 3 : 9, 10 dibenzo - 7, 14 - dimethyl - 5, 12 - dioxo - 1, 4, 8, 11 - tetraaza - cyclotetradeca -1, 7 - diene (BMOAT), M.P. = 176°C, R_f = 0.62. IR (KBr) cm^{-1}, 1591 (C = N), 3245 (–NH), 1621 (C = O, cyclic).

6. 2, 5, 10, 13 - tetraoxo - 1, 6, 9, 14 - tetraaza-cyclohexadecane (OAH), M.P. = 144°C, R_f = 0.48.

7. 7, 8 : 15, 16 - dibenzo - 2, 5, 10, 13 - tetraoxo - 1, 6, 9, 14 - tetraaza - cyclohexadecane (BOAH), M.P. = 160°C, R_f = 0.56.

8. 3, 4 : 11, 12 - dibenzo - 2, 5, 10, 13 - tetraoxo - 1, 6, 9, 14 - tetraaza - cyclohexadecane (DBOAD), M.P. = 169°C, R_f = 0.60.

9. 3, 4 : 7, 8 : 11, 12 : 15, 16 - tetrabenzo - 2, 5, 10, 13 - tetraoxo - 1, 6, 9, 14 - tetraazacyclo-hexadecane (TBOAD), M.P. = 203°C, R_f = 0.63.

2.6 SYNTHESIS OF SUBSTITUTED THIOBISFORMAMIDINE
(SCHEME - 2)

2.5.1 PREPARATION OF P - SUBSTITUTED ARYLTHIOUREA [4, 5]

An appropriate p - substituted aniline (0.1 mol) was dissolved in a mixture of concentrated HCl (9 ml) and water (25 ml) by warming on a water bath. The solution of amine hydrochloride thus obtained was cooled and solid ammonium thiocyanate (0.1 mol) was added. The reaction mixture was then heated for 5 hours on a water bath. Thereafter, the reaction mixture was cooled and the precipitated crude product was filtered, washed with water, dried and crystallized from aqueous ethanol. p - substituted arylthiourea thus prepared are Phenyl thiourea : M.P. = 148°C, p - tolyl thiourea: M.P. = 180°C, p - anisidyl thiourea : M.P. = 209°C, p - chlorophenyl thiourea : M.P. = 174°C.
SCHEME 1.1

(1) 1. \( R = C_6H_5, X = S \) (PTAT)
(II) 2. \( R = C_6H_5, X = S \) (PTAB)
            3. \( R = C_6H_5, X = O \) (POAB)

SCHEME 1.2

(III) 4. \( X = (CH_2)_2, Y = (CH_2)_2 \) (OAH)
5. \( X = C_6H_4, Y = (CH_2)_2 \) (BOAH)
6. \( X = (CH_2)_2, Y = C_6H_4 \) (DBOAD)
7. \( X = C_6H_4, Y = C_6H_4 \) (TBOAD)

(IV) 8. \( X = (CH_2)_2, R = C_6H_5 \) (MOAT)
9. \( X = C_6H_4, R = C_6H_5 \) (BMOAT)
2.5.2 SYNTHESIS OF SUBSTITUTED THIOBISFORMAMIDINES
(SCHMIE 2) [6, 7]

To the alkaline solution of p - substituted arylthiourea (0.65 mol), lead acetate
(0.5 mol) was added, this mixture was heated with reflux on water bath for 30 minutes
to desulfurize the respective arylthioureas. Black precipitate of sulphur was filtered
off and to the filtrate ice cold glacial acetic acid was added dropwise to obtain the
precipitate. To this precipitate dry ether was added. To the ethereal layer HCl gas
was bubbled to get yellow oily layer. This oily layer was extracted. Thiourea
(0.11 mol) and dry acetone was added to this oily layer dropwise to get the precipitate
of the substituted thiobisformamidines, after keeping the contents to about half an
hour. The precipitate thus obtained was crystallized from the solvent. Their TLC
were obtained in the mixture of benzene + ethylacetate (7 : 3). The substituted
thiobisformamidine thus prepared are: –

10. Phenyl thiobisformamidine (PTBF) M. P. = 126°C, R, = 0.44.

IR (KBr) C m⁻¹: 3245 - 3455 (NH, NH₂), 1590 (C = N, stretch), 1320 (=C-S-C=).

11. Tolyl thiobisformamidine (TTBF), M. P. = 125°C, R, = 0.51.


13. 4 - chlorophenyl thiobisformamidine (CPTBF), M. P. = 165°C, R, = 0.64.

2.6 SYNTHESIS OF 1 - SUBSTITUTED DITHIOBIURETS

2.6.1 PREPARATION OF PHENYL ISOTHIOCYANATE [8]

To a round bottomed flask fitted with a mechanical stirrer and surrounded by
an ice - salt cooling bath carbon disulphide (0.71 mol) and aqueous ammonia (1.3
mol) were added. Aniline (0.6 mol) was added dropwise while stirring for about 20
minutes. The reaction mixture was allowed to stand for another thirty minutes. To it
lead nitrate (0.6 mol) and water (400 c.c.) was added. Thus obtained black mixture
was distilled with steam in to a receiver containing 5 - 10 c.c. of 1N sulphuric acid.
The distillate (oil) was separated from water and dried over calcium chloride and
distilled under reduced pressure B.P. 121°C.
(i) NaOH / (Pb)₂Ac  (ii) HCl

R—(NH—C—S—C—NH₂)

10. R = H  (PTBF)
11. R = CH₃  (TTBF)
12. R = OCH₃  (ATBF)
13. R = Cl  (CPTBF)

SCHEME 2
Phenylisothiocyanate (0.025 mol) was added dropwise to the solution of p-
substituted arylthiourea (0.025 mol) and powdered sodium hydroxide (0.025 mol) in
acetonitrile (15 ml). The reaction mixture was heated to about 60°C and stirred at
this temperature for another 30 minutes when a clear solution resulted. The reaction
mixture was diluted with water (150 ml) and filtered. The filtrate was acidified with
conc. hydrochloric acid (4 ml, 33%) and the precipitated product was collected and
redissolved in the minimum quantity of 4% aqueous alkali to remove any unreacted
thiourea and filtered. The alkaline filtrate on acidification at 0°C afforded 1 -
substituted, 5 - phenyl 2, 4 - dithiobiurets which were recrystallized as needles from
ethanol. The TLC were obtained in benzene + acetone + ethylacetate (6 : 3 : 1).
Thus prepared substituted dithiobiurets are:

14. 1, 5 - diphenyl - 2, 4 - dithiobiuret (DPDTB), M.P. = 130°C, R, = 0.48.
   IR (KBr) Cm⁻¹, 3320 - 3160 (- NH), 1350 (C - N), 1100 (C = S, stretch)
15. 1 - tolyl - 5 - phenyl - 2, 4 - dithiobiuret (TPDTB), M.P. = 130°C, R, = 0.56.
16. 1 - anisidyl - 5 - phenyl - 2, 4 - dithiobiuret (APDTB) M.P. = 83°C, R, = 0.62.
17. 1 - chlorophenyl - 5 - phenyl -2, 4 - dithiobiuret (CPDTB), M.P. = 138°C, R, = 0.52.

2.7 SYNTHESIS OF SUBSTITUTED THIOCARBOHYDRAZIDES
(SCHEMЕ 4)[11]

To the warm aqueous solution of thio-carbohydrazide (0.1 mol) alcoholic
solution of benzaldehyde, salicylaldehyde, vanillin, cinnamaldehyde or furfuraldehyde
(0.1 mol) was added dropwise while stirring magnetically for about 30 minutes without
further heating. After keeping the mixture overnight precipitate was filtered off and
air dried. The compounds were crystallized from alcohol. The compounds thus
prepared are:

18. 1 - benzylidene - 3 - thiocarbohydrazide (BTCH), M.P. = 191°C, R, = 0.47. IR
   (KBr) Cm⁻¹, 3245 - 3455 (NH, NH₂) stretch 1100 (C = S) and 1689 (C =N).
19. 1 - salicylidene - 3 - thiocarbohydrazide (STCH), M.P. = 193°C, R, = 0.53.
R-\textbf{NH}_2 + C_6H_5\textbf{C}=\textbf{S} \\
\textbf{NaOH} \\
R-\textbf{NH}_C-\textbf{NH}_C-\textbf{HN} \\
\textbf{CH}_3\textbf{C}=\textbf{N} \\

14. \( R = H \) (DPDTB) \\
15. \( R = CH_3 \) (TPDTB) \\
16. \( R = OCH_3 \) (APDTB) \\
17. \( R = Cl \) (CPDTB) \\

\textbf{SCHEME 3}
\[
\begin{align*}
\text{(I)} & \quad 18. \ n = 0, R_1 = H, \ R_2 = H \quad \text{(BTCH)} \\
19. \ n = 0, R_1 = \text{OH}, \ R_2 = H \quad \text{(STCH)} \\
20. \ n = 0, R_1 = \text{OH}, \ R_2 = \text{OCH}_3 \quad \text{(VTCH)} \\
21. \ n = 1, R_1 = H, \ R_2 = H \quad \text{(CTCH)} \\
\text{(II)} & \quad 22. \quad (\text{FTCH}) \\
\end{align*}
\]

**SCHEME 4**
20. 1 - vanillidine - 3 - thiocarbohydrazide (VTCH), M.P. = 199°C, R_I = 0.62.
21. 1 - cinnamylidine - 3 - thiocarbohydrazide (CTCH), M.P. = 166°C, R_I = 0.48.
22. 1 - furfurylidine - 3 - thiocarbohydrazide (FTCH), M.P. = 185°C, R_I = 0.50.

2.8 TECHNIQUES EMPLOYED

The experimental work was carried out with the help of the following techniques:

1. Weight loss
2. Potentiodynamic polarization
3. Electrochemical AC impedance
4. Hydrogen permeation
5. Auger electron spectroscopy
6. Scanning electron microscopy

2.8.1 WEIGHT LOSS METHOD

The specimens of the size 2 x 2 x 0.025 cm. were cut from the mild steel sheet and mechanically polished with the 1 / 0, 2 / 0, 3 / 0 and 4 / 0 grades of emery papers. After polishing the specimens were washed with trichloroethylene. The specimens were stored in the dessicator over silica gel. The weight of the specimen was measured before exposing it to corrodent on the single pan Saritiorius balance. Weight loss experiments were conducted following the procedures given in the literature [12,13]. During experiments the specimens were fully immersed in 160 ml test solution using beaker of 200 ml capacity. After a definite exposure time the specimens were taken out and washed with distilled water. If there was any corrosion product on mild steel surface it was removed from the surface by mechanical rubbing with a rubber cork. The specimens were then dried and loss in weight was recorded. The thermostatic water bath was used for carrying out the weight loss experiments at higher temperatures. Thermostat was maintained within an accuracy of ± 2° C. The corrosion rates (C R), inhibition efficiencies (I E) and surface coverage (θ) of different concentrations of the inhibitors were calculated using the following equations: —
Corrosion rate (C.R.) = \( \frac{87.6 \times w}{d \times a \times t} \) (mmpy)

\[ IE(\%) = \frac{\text{uninhibited corrosion rate} - \text{inhibited corrosion rate}}{\text{uninhibited corrosion rate}} \times 100 \]

\[ \theta = \frac{\text{uninhibited corrosion rate}\text{-inhibited corrosion rate}}{\text{uninhibited corrosion rate}} \]

Where,

- \( w \) = weight loss (in grams)
- \( d \) = density of mild steel (7.86 cm\(^3\))
- \( a \) = area of the sample (in cm\(^2\))
- \( t \) = time of immersion (in hours)

2.8.2 POTENTIODYNAMIC POLARIZATION STUDIES

Polarization curves were recorded potentiodynamically using an EG & G PARC model 173 potentiostat/galvanostat, a model 175 universal programmer and a model RE 0089 X-Y recorder at 35 ± 2°C using the ASTM standards [14]. The cell assembly consists of a mild steel as working electrode, a platinum as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode of 1 cm X 1 cm with a tag of 5 cm were cut from the mild steel sheet and polished with the 1 / 0 to 4 / 0 grade of emery papers. The specimens were then thoroughly washed with distilled water and finally with trichloroethylene. Unwanted area of the electrode was coated with the lacquer to get a well defined working area of 1 cm\(^2\). Various parameters such as corrosion potential (\( E_{corr} \)), corrosion current (\( I_{corr} \)) and Tafel constant (\( b_a \) and \( b_c \)) were calculated from Tafel plot. All the potentials were measured against a saturated calomel electrode. The inhibition efficiencies were calculated using the following equations :-
\[
IE(\%) = \frac{I_{ocorr} - I_{corr}}{I_{ocorr}} \times 100
\]

Where,
- \( I_{ocorr} \) = Corrosion current density without inhibitor
- \( I_{corr} \) = Corrosion current density with inhibitor

2.8.3 ELECTROCHEMICAL AC IMPEDANCE STUDIES

Electrochemical AC Impedance studies were carried out using an electrochemical impedance analyzer EG & G PARC system model M6310 with software M398 according to known procedure [15]. The cell assembly having mild steel as working electrode, platinum as auxiliary and reference electrodes was used. The block diagram of impedance set up is shown in Fig 2.0. The working electrodes were polished, degreased before each experiment and immersed in the test solution. Nyquist plots were drawn for the uninhibited and inhibited test solutions employing a frequency of 100 mHz to 10 KHz range. The real part (Z') and the imaginary part (Z") of the cell impedance were measured for various frequencies. The charge transfer resistance value (R_t) were determined by taking the difference in impedance values of high and low frequency intercepts of the real axis.

Various parameters such as double layer capacitance (C_{dl}), corrosion current density (I_{corr}) and Inhibition efficiency (IE) were calculated by using the following equations:

\[
C_{dl} = \frac{1}{2 \pi f_{max}} \times \frac{1}{R_t}
\]

\[
I_{corr} = \frac{b_a \cdot b_c}{2.3 (b_a + b_c)} \times \frac{1}{R_t}
\]

\[
IE = \frac{1}{R_{to}} - \frac{1}{R_t} \times 100
\]

\[
IE(\%) = \frac{I_{ocorr} - I_{corr}}{I_{ocorr}} \times 100
\]
FIGURE 2.0 Block diagram of impedance setup

F.R.A. = Frequency Response Analyser
W.E., R.E. = Working electrode
S.E. = Counter electrode
R.E. = Reference electrodes
E.I. = Electrochemical interface
Where

\[ f_{\text{max}} = \] the frequency at which the imaginary component of impedance \((Z_{\text{im}} \text{ max})\) is maximum.

\[ b_a & b_c = \] anodic & cathodic Tafel constants

\[ R_{to} = \] charge transfer resistance without inhibitor

\[ R_t = \] charge transfer resistance with inhibitor

### 2.8.4 HYDROGEN PERMEATION STUDIES

Hydrogen Permeation Studies were carried out using an adaptation of the modified Devanathan and Stachurski’s two compartment cell [14,15] and the hydrogen permeation curves were recorded using X - Y - T (Rikadenki) recorder at 30 ± 2°C. The complete permeation setup is shown in Fig. 2.1.

Mild steel specimens of the same composition with 1 cm² working area were used after mechanically polishing and degreasing with trichloroethylene. G R grade NaOH and BDH grade palladium chloride were used. Conductivity water was used for the solution preparation. In this method steel membrane functions as bipolar electrode in the cell. The cathodic side of the membrane remained in contact with experimental solution and the anodic side of the membrane was electroplated with a thin layer of palladium (palladised) by the following procedure:–

Specimens were polished, degreased, cathodically cleaned at the ambient temperature (35 ± 2°C) in the cleaning solution containing sodium hydroxide (35 gms / litre) and in sodium carbonate (25 gms / litre) at a current density of 150 mAcm⁻² for 5 minutes with mild steel as anode, then specimens were gently washed with double distilled water. The steel membrane was electroplated with a thin layer of palladium from the solution of the following composition:–

100 ml of double distilled water was heated to 80°C to this 1 gm of PdCl₂ was added followed by NaNO₂, until the PdCl₂ reacted completely to form a yellow solution of the complex \( \text{Na}_2[\text{Pd} (\text{NO}_2)_4] \). This complex salt solution was added to 1000 c.c. of 0.2 M NaOH solution prepared from double distilled water and AR grade NaOH pellets.
FIGURE 2.1 Complete Permeation cell setup

1. Steel membrane  2. Teflon bushings
3. PVC Coupling  4. Reference electrode
5. Counter electrode  6. Tap
7. Water circulation  8. Anode
The steel membrane was fitted in between the PVC disc clamp with teflon bushing (Fig 2.1), with a circular 1 cm² exposed area and this prepared solution was filled in cell assembly. After coating palladium solution is removed at low current density 100 μ Acm⁻² this solution gave a bright coherent yellow coloured coating of palladium on the steel membrane for 90 minutes duration using platinum as the anode.

2.8.4.1 MEASUREMENT OF PERMEATION CURRENT

The palladised steel membrane inserted in between clamp was fitted in two compartment cell assembly tightly fitted without any leakage of the solution. The compartment facing palladium plated side was filled with 0.2 N NaOH solutions which was pre - electrolysed for a period of 12 hours at a current of 2.5 mA. A Hg / HgO / 0.2 N NaOH reference electrode and platinum counter electrode were introduced to complete the circuit.

The cell was connected to a potentiostat (Wenking model : POS 73) and a constant potential of -300 mv was applied to the specimen. It has been reported by Srinivasan et.al. [16] that – 300 mv is the most suitable potential for ionizing the diffused hydrogen rapidly and efficiently at Pd / 0.2 N NaOH interface. Water was circulated through the double wall of the cell and the temperature was maintained at 35 ± 2°C. The potential was maintained steady and constant till a steady background current was obtained. In all these studies a residual current of very low value was obtained. After reaching the steady background current at the anode compartment, the test solution (acid or inhibited solution) was introduced into the cathode compartment and allowed to corrode the steel membrane. The permeation current was simultaneously recorded on the recorder.

2.8.5 AUGER ELECTRON SPECTROSCOPY

Auger electron spectroscopy is one of the most popular and powerful technique to analyze the chemical species within the outermost surface layers of the specimens. The presence of different elements species can be distinguished by their characteristic peaks in the auger spectra [17]. The auger analysis of the samples were accomplished
by using an auger electron spectrooscope (VARIAN CMA VT - 112 model), specimens were polished using different grades of emery papers and then dipped in the inhibited acid solution containing different concentrations of the inhibitors for 3 hours, rinsed with triple distilled water and dried at room temperature. The specimens were fixed onto a sample holder and introduced into a fast - entry air lock (FEAL) chamber maintained at a vacuum level of 10^-11 torr (1.33 X 10^9 pa). After degassing the specimens were transferred into the preparation chamber. Specimens again were kept for long enough to facilitate further degassing. The specimens then were introduced into the analyzer chamber. The area of interest was selected with the help of a scanning electron microscope (SEM) attached to the instrument and excited with a 3 Kev electron beam. The depth of the resolution was 2 Å to 20 Å. The appearance of peaks of different elements at specific ev confirms the presence of that element on the adsorbed surface of mild steel.

The atomic concentration of the element (X) present on the adsorbed layer is calculated by using the relation:

\[ C_x = \frac{I_x}{I_{Ag} \cdot S_x \cdot D_x} \]

Where

- \( I_x \) = peak - to - peak amplitude of the element X from the test specimen.
- \( I_{Ag} \) = peak - to - peak amplitude of the Ag standard.
- \( D_x \) = relative scale factor between the spectra for the test specimen and silver.
- \( S_x \) = relative sensitivity between any element X and silver.

2.8.6 SCANNING ELECTRON MICROSCOPY

To study the morphology of corroded surface of the specimen and formation of film at various stages in presence and absence of inhibitors Scanning electron microscope (SEM), model JEOL JSM 840, SM was used.

The specimens were polished with emery papers of different grades and washed with double distilled water and trichloroethylene. These specimens were then exposed to testing corrodent for 3 hours. After this these specimens were thoroughly
washed with double distilled water before putting them on the slide. These mild steel samples were cutted according to the size of the sample holder, fixed on the stub with carbon paste, coated with gold and then viewed. The micrographs have been taken from that portion of the specimen from where better information was obtained. They were photographed at the appropriate magnification.

To understand the morphology of the steel surface in absence and presence of inhibitors the following cases have been examined:

1. Polished mild steel specimens
2. Mild steel specimen dipped in 1N HCl
3. Mild steel specimen dipped in 1N HCl containing optimum concentration of inhibitors.
REFERENCES


