## CHAPTER 3

**EXPERIMENTAL**

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CHAPTER 3

EXPERIMENTAL

This chapter gives the details of the various experimental aspects such as the cells employed, set up used, preparation of the reagents and general experimental procedures used in the investigations.

3.1 THE CELLS

A standard all-glass electrolysis cell with three electrode assembly shown in Fig. (1) was used for cyclic voltammetric, linear polarisation, impedance, and potentiostatic measurements. It has provisions for introducing the working and counter electrodes, inlet and outlet for deaerating the solution used in the experimental set up and a reference electrode compartment with a luggin capillary. The electrolytic contact between the working electrode and the reference electrode was made through a luggin probe whose tip was kept very close to the working electrode. The temperature of the cell assembly was maintained at the required value by circulating methanol from a colora thermostat through the outer jacket of the cell.

3.2 ELECTRODE MATERIALS

Reference electrode

Unless otherwise stated, all potentials were referred to a Hg/HgO (1M KOH) reversible electrode and no correction was made for liquid junction potential.
1. REFERENCE ELECTRODE
2. WORKING ELECTRODE
3. COUNTER ELECTRODE
4. WATER INLET
5. WATER OUTLET
6&7. N₂ INLET FOR DEAERATION
8. BUBBLER FOR N₂ EXIT
**Counter electrode**

A large area platinum foil was used as the counter electrode.

**Working electrode**

The electrode was prepared from 99.99% pure tin metal (J & M, U.S.A) and made into cylindrical rods of 0.283 cm$^2$ cross section. A copper wire was soldered to one end of the rod. The specimen was then embedded into a teflon mount so that only the flat front surface was in contact with the solution in the vertical position. The test electrode was polished with emery papers from 1/0 to 4/0 grade, degreased with acetone and finally washed with doubly distilled water.

**3.3 INSTRUMENTATION**

A Tacussel Potentiostat (type PRT 20-2X) was used for all potentiostatic and potential sweep measurements. The output of the function generator (Wenking Model VSG 72) was connected to the external modulation input of the potentiostat to produce cyclic potential sweeps for cyclic voltammetric studies. Current-potential curves were recorded using a Digilog type 2000 X-Y recorder. The X-axis was connected directly to the output of the follower in the multipurpose instrument to monitor the potential of the working electrode. The current was measured by connecting the Y-axis of the recorder inputs to read the potential drop across a standard resistor in series with the auxiliary and working electrodes. Block diagram of cyclic voltammetry set up is given in Fig. (2).
6 - SCAN GENERATOR.
P - POTentiOSTAT.
R - RECORDER.
Ce- CELL.
W - WORKING ELECTRODE.
Re- REFERENCE ELECTRODE.
C - COUNTER ELECTRODE.

FIG:2. BLOCK DIAGRAM FOR CYCLIC VOLTAMMETRY SET UP
In the Linear polarisation measurements the same set up used for cyclic voltammetric studies was employed except for one additional unit namely Summing Amplifier. The circuit diagram of the set up used for linear polarisation measurements is shown in Fig.(3). The photographic view of the instrumental set up used for current-potential measurements is shown in Fig. (4).

Impedance measurements were carried out using Princeton Applied Research model 368 AC impedance measurement system. The block diagram and photograph of the impedance system are shown in Figs. (5) and (6).

3.4 EXPERIMENTAL PROCEDURE

3.4.1 Steady State Potential measurements

Polarisation studies have been carried out using potentiostatic technique in which the potential of the working electrode is adjusted to a specified value with the help of a Tacussal potentiostat and the current corresponding to the given potential is registered upto the moment when the constant potential is set up. Before carrying out the experiment, sufficient time is allowed for the electrode to reach steady state potential.

3.4.2 Cyclic Voltammetric measurements

The electrode was cathodically polarised for 10 minutes to reduce any oxide film present on the metal surface before carrying out the experiment. Cyclic voltammograms have been recorded by polarising the electrode anodically in the forward direction and reversing
FIG. 3. SET UP FOR LINEAR POLARISATION
FIG. 4. EXPERIMENTAL SET UP FOR POLARISATION MEASUREMENTS
Fig. 5. Block Diagram of the Model 368 Modular AC Impedance System
FIG. 6. EXPERIMENTAL SET UP FOR IMPEDANCE MEASUREMENTS
the sweep to record the cathodic response with the help of a potentiostat and scan generator. The experiments were carried out at different sweep rates and in different concentrations of sodium hydroxide in the presence and absence of additives.

The peak current was measured by making use of the zero current line as a reference line in all the cyclic voltammograms. It was noted that the cyclic voltammograms were well reproducible and exhibited sharp features in agreement with reported cyclic voltammograms on tin electrode in alkaline solutions. Similarly, cyclic voltammograms for various sweep rates were recorded after giving necessary pretreatment and taking precautions before each reading. Effect of concentrations of sodium hydroxide solution on the shape of the cyclic voltammograms was also studied. Repetitive cycling experiments were also carried out and the cyclic voltammograms for a number of subsequent cycles were recorded.

In order to establish relationship between the anodic and the corresponding cathodic process over various ranges of $E_{\text{cut}}$ (anodic cutting potential), voltammograms were obtained by progressively increasing the anodic potential limit, keeping the cathodic potential limit constant.

The effect of temperature and additives such as sodium stannate and stannous hydroxide on the behaviour of tin electrode in alkaline solution was investigated.

3.4.3 Linear polarisation measurements

In the linear polarisation method, polarisations were carried out to the extent of 20 mV on either side of the open circuit
potential that is -20 mV to +20 mV from equilibrium potential. A sum­ming Amplifier unit was included in the circuit in order to offset the equilibrium potential and feed the difference of 20 mV only to the recorder for sensitive recording. Sweeping experiments were carried out in different concentrations of sodium hydroxide solutions and at different sweep rates. The slope of the linear portion of the voltage­current plot \( \Delta E/ \Delta I \) gives the polarisation resistance \( R_p \) in ohms/cm\(^2\).

3.4.4 Impedance measurements

The a.c. impedance of a working electrode can be obtained by applying an alternating potential of known amplitude to the electrode relative to a reference electrode and measuring the amplitude and phase of the resulting alternating current. Impedance measurements were carried out using Princeton Applied Research Corporation Model 368 AC Impedance Measurement system. The frequency range used were from 10 KHz to 0.001 Hz. The real and imaginary components of response were measured in different concentrations of sodium hydroxide solution.

3.5 REAGENTS USED

**Sodium hydroxide**

Sodium hydroxide solutions of approximately 11M strength was prepared by dissolving AR grade NaOH pellets in double distilled water. This solution was pre-electrolysed using platinum foil electrodes for about 30 hours. Pure nitrogen gas was bubbled through the solution during the time of pre-electrolysis. The strength of this solution was
determined by titrating against standard hydrochloric acid using phenolphthalein as indicator. From this stock solution of sodium hydroxide the required concentrations were prepared by dilution.

**Stannous hydroxide**

Stannous hydroxide was prepared by adding required amount of sodium hydroxide to stannous chloride solution. The precipitated stannous hydroxide was filtered, washed well with double distilled water and dried. A.R. grade Tin (II) chloride (E.Merck) was used for the preparation of stannous chloride solution. Sodium hydroxide solutions of 2M strength containing 0.01M, 0.03M, 0.05M and 0.1M stannous hydroxide were prepared.

Solutions of 4M NaOH containing required quantities of sodium stannate, potassium chromate, sodium carbonate, borax and trisodium phosphate were prepared in double distilled water.