CHAPTER 3
EXPERIMENTAL

3.1 INTRODUCTION

The process instrumentation, cell systems, analytical procedures adopted for the present investigation is well known in electroorganic synthesis. Hence, a general outline of the experimental set up in preparative scale experiments, large scale experiments, divided cell, undivided cell, flow cells and chemical oxidation experiment procedures adopted in this research programme are presented in this chapter.

The main objective of the present investigation is to study the following for the electrochemical preparation of cerium(IV) methanesulphonate in methanesulphonic acid medium and to prepare aldehydes and quinones from aromatic compounds using the electrochemically generated cerium(IV) methanesulphonate as an oxidant. Experiments were classified and carried out in the following titles.

i. Electrochemical preparation of cerium(IV) methanesulphonate
ii. Process optimisation study on Ce(III)/Ce(IV) system
iii. Process kinetic study for Ce(III)/Ce(IV) system:
iv. Factorial design of experiments for Ce(III)/Ce(IV) system
v. Electrochemical cells for Ce(III)/Ce(IV) system
vi. Mediated electrochemical synthesis of aromatic quinones
vii. Mediated electrochemical synthesis of aromatic aldehydes

In these studies, the reaction/experiment contains two parts. In the first step the oxidant cerium(IV) methanesulphonate was generated by electrochemical method. The second step consists of oxidation of aromatic compounds using the electrochemically generated cerium(IV) methanesulphonate oxidant.
3.2 Electrochemical preparation of cerium(IV) methanesulphonate

3.2.1 Preparation of cerium(III) methanesulphonate

Solutions of cerium(III) methanesulphonate in aqueous methanesulphonic acid were prepared by making a slurry of cerous carbonate \[ \text{Ce}_2(\text{CO}_3)_3 \] in water, adding calculated quantity of concentrated methanesulphonic acid to convert cerous carbonate to cerous methanesulphonate and also to maintain the desired methanesulphonic acid concentration in electrolyte. After the reaction, the solution was filtered to remove the insolubles and the clear filtrate was estimated to find out the cerium(III) ion content in cerium(III) methanesulphonate volumetrically.

\[
\begin{align*}
\text{Ce}_2(\text{CO}_3)_3 + 6\text{CH}_3\text{SO}_3\text{H} & \rightarrow 2\text{Ce}^{2+}(\text{SO}_3\text{CH}_3)_3 + 3\text{H}_2\text{O} + 3\text{CO}_2 \\
\text{Cerous carbonate} & \quad \text{methanesulphonic acid} & \quad \text{Cerous methanesulphonate}
\end{align*}
\]

\[
\begin{align*}
\text{Ce}^{2+}(\text{SO}_3\text{CH}_3)_3 + \text{CH}_3\text{SO}_3\text{H} & \rightarrow \text{Ce}^{4+}(\text{SO}_3\text{CH}_3)_4 + \text{H}_2 \\
\text{Cerous methanesulphonate} & \quad \text{methane-sulphonic acid} & \quad \text{Ceric methanesulphonate}
\end{align*}
\]

Scheme 3.1 Electrochemical generation of Cerium(IV)methanesulphonate

Constant current electrolysis was carried out to oxidize cerium(III) methanesulphonate. Electrolysis was conducted galvanostatically by varying parameters like, current density, temperature, acid concentration, degree of agitation, etc. During the electrolysis the cerium(IV) ion formed was estimated by the standard titrimetric method. The current efficiency and yield for the oxidation were calculated as the ratio of cerium(IV) ion formed during reaction to the cerium(IV) ion expected based on the current passed.

Studies on process parameters like current density, temperature, concentration of methanesulphonic acid etc were conducted in similar conditions. Studies were also conducted to evaluate the different anodes, cathodes and diaphragms for maximum current efficiency and yield.
3.2.2 Preparation of Cerium(IV) methanesulphonate

Cerium(IV) methanesulphonate was prepared galvanostatically using electrochemical batch cell. The cell (Figure.7.1) consists of two compartments with a holding capacity of 500 ml electrolytes. The batch cell was made up of PVC material and has an anolyte volume of 250 ml and a catholyte volume of 250 ml and a total capacity of 500 ml. The electrolyte in the cell is agitated by a glass stirrer connected to fractional horse power (FHP) motor provided with a speed control unit (dimmerstat).

In batch cell, Nafion 324 series cationic exchange membrane is fixed between the two compartments to prevent the mixing of anolyte and catholyte and to enhance the reaction rate. For preparative scale Dimensionally stable oxygen evolution anode [DSA-O₂] and stainless steel cathode were used. In anolyte chamber, the cerous methanesulphonate and in the catholyte chamber methanesulphonic acid were taken. The reaction temperature was maintained at 50°C.

Based on the moles of cerium(III) methanesulphonate taken, the charge (F) was passed. After passing the required charge, the cerium(III) methanesulphonate was converted to cerium(IV) methanesulphonate in the anolyte chamber. The change of colourless cerium(III) methanesulphonate to orange coloured cerium(IV) methanesulphonate was observed visually. The cerium(IV) ion content in cerium(IV) methanesulphonate solution was estimated by titration with ferrous ammonium sulfate [FAS] using ferroin indicator.

3.2.3 Quantitative estimation of cerium(III) & cerium(IV) ion

3.2.3.1 Estimation of cerium(III)

Diluted solution of cerium(III) methanesulphonate was chemically oxidized to cerium(IV) ion by adding an oxidising agent such as ammonium persulphate with silver nitrate as the catalyst. Oxidised cerium(IV) species were titrated against
standard ferrous ammonium sulphate solution with ferroin as the indicator. The appearance of a red colour was the end point.

3.2.3.2 Estimation of cerium(IV)

A known amount of electrolyte was acidified by adding 10-15 ml of 1:1 sulphuric acid and then titrated against standard ferrous ammonium sulphate using ferroin as the indicator. The appearance of a red colour was the end point.

3.3 Chemical Oxidation

The chemical oxidation of substrate was carried out in a chemical reactor. The reactor comprises of a three necked round bottom reactor of 1000 ml capacity. The reactor was provided with a glass stirrer for agitating the reactor contents. The speed of agitator was controlled by means of a dimmerstat. The reactor was also provided with the reflux condenser for condensing the solvent vapours and to condensate back to the reactor. Aqueous solution of cerium(IV) methanesulphonates obtained from the electrochemical reactor was charged to the chemical reactor.

Reactants to be oxidised were dissolved in a suitable organic solvent 1,2-dichloroethane and added to the reactor. The reactor contents were stirred well using the mechanical glass stirrer and the reaction was conducted till there was no more reactant. The temperature of the reaction was controlled using a thermostatic bath.

3.4 Isolation of the product

After the completion of the chemical oxidation, reactor contents were transferred to a separating funnel. Aqueous and organic layers were separated. The aqueous layer was repeatedly extracted with a fresh solvent 1,2-dichloroethane and the extracts were added to the organic layer. The organic layer was washed with water and dried over anhydrous sodium sulphate then distilled to recover the
solvent. The residue obtained after distillation was further purified by vacuum distillation or by crystallization.

3.5 Analysis of the product

The product analysis was carried out using FTIR spectra photometer and High pressure Liquid Chromatography (HPLC). Analytical conditions of the above instruments are given below.

**FTIR ANALYSIS**

Analytical Condition:

- **Model**: Paragon-500
- **Make**: Perkin Elmer, England
- **Mode**: Transmittance
- **Wave length**: 400 to 4000 cm$^{-1}$
- **Sampling**: Neat liquid/solid (KBr)

**HPLC ANALYSIS**

Analytical Condition:

- **Model**: Class.VP.10
- **Make**: Shimadzu, Japan
- **Column**: shimpack ODS-18
- **Mobile phase**: Methanol : water (70:30)
- **Detector**: UV
- **Flow rate**: 1 ml/min
- **Wave length**: 254 nm

3.5.1 Infra Red Spectroscopy

IR spectroscopy seems as an important tool for identification of several compounds. This technique is especially used for the identification of different functional groups. When Infrared light is passed through a sample of an organic compounds some of the frequencies are absorbed while other frequencies are transmitted through the sample without being absorbed. If the percent absorbance or percent transmittance is plotted against frequency the result is an infrared
Transitions involved in infrared absorption are associated with vibrational changes within molecules. Basically it is called vibrational spectroscopy.

IR spectra contain much absorption associated with the complex interacting vibrating systems in the molecule and the pattern of vibrations. Since it is uniquely characteristic of each molecule it gives rise to a uniquely characteristic set of absorption bands in the spectrum. This band pattern serves as a fingerprint of molecules, the region that contains a particularly large number of unassigned vibrations is from 900-1400 cm\(^{-1}\) and this area is often called as "the fingerprint region". To identify an unknown compound we need only to compare its IR spectrum with a set of standard spectra recorded under identical conditions. Substances that give the same IR spectra are identical.

### 3.5.2 High Pressure Liquid Chromatography [HPLC]

HPLC is used for the separation and purification of a wide variety of compounds. This technique can be applied for non-volatile, reactive, highly polar, polymers and complex compounds. In this method, a mixture of compounds passed through a stationary phase gets separated depending upon their interactions with this stationary phase.

A HPLC system is basically composed of, a pump, an injector, a column and a detector. The pump keeps the flow of carrier or mobile phase liquid flow through the stationary phase. The column acts as the stationary phase, which is filled with a packing material such as silica gel or resin. After a sample is loaded on the top of the column, with the help of the injector, it flows through the column with the carrier. Each component of the sample has specific interaction between the mobile phase and the stationary phase. A component, which has a strong interaction with the stationary phase, migrates slowly, while one that has a weak interaction migrates quickly through the column. In this way, each component is separated from the others on the column by its differential migration speed and each component was
detected separately from the bottom of the column. A detector detects components migrating from the column and detector’s output signal is recorded by a data processor. The plotted signal is called as a chromatogram.

3.6 PROCESS OPTIMISATION STUDY ON Ce(III)/Ce (IV) SYSTEM

As described in chapter-3.2, process optimisation studies were conducted galvanostically. The following process parameters were studied in electrochemical generation of cerium(IV) methanesulphonate in aqueous methanesulphonic acid medium.

- current density
- temperature
- concentration of cerium(III) methanesulphonate
- anode
- cathode
- diaphragm
- agitation

3.7 Electrochemical cells for Ce(III)/Ce(IV) redox system

Different types of electrochemical cells (Figure.7.1-7.3) were employed for the electrochemical generation of cerium(IV) methanesulphonate. Studies were performed with the above cells with and without diaphragm. Some studies were conducted in an undivided cell to investigate the cell performance for the generation of cerium(IV) methanesulphonate. All experiments were carried out galvanostically.

Following cells were designed and used for the electrochemical preparation of cerium(IV) methanesulphonate.

- Batch cell
- Batch cell with re-circulation
- Flow cell [Electro MP Cell - plate & frame type cell]
3.8 Mediated electrochemical syntheses of aldehydes

Electrochemical synthesis of aromatic aldehydes was carried out using the ceric methanesulphonate as an oxidant. The required amount of ceric methane sulphonate solution was taken in a two necked flask. Condenser and stirrer were placed at the two joints of the flask. The solution was heated to 70°C by a water bath. The substrate (substituted toluene) was then dissolved in 1,2 dichloro ethane (10% solution) and this solution was added at once to the stirred solution of cerium(IV) methanesulphonate solution, which was generated by electrochemical method.

After the completion of the reaction [change of orange coloured ceric methane sulphonate to colourless cerous methane sulphonate], the top organic phase was separated using a separating funnel and the aqueous phase was extracted twice using 1,2 dichloroethane. The combined organic phase was washed with ice water and dried over anhydrous sodium sulphate. After drying, the organic solvent was removed under reduced pressure and the residue was cooled to get the corresponding oxidised product. This was further purified by crystallization using Hexane as the solvent.

3.9 Mediated electrochemical syntheses of quinones

Electrochemical synthesis of aromatic quinones was carried out using the cerium(IV) methanesulphonate as an oxidant. As described in Chapter 3.8, quinones were synthesized using the cerium(IV) methanesulphonate.

3.10 Chemicals used

Following chemicals were used in the present work

1. Ceros carbonate AR grade Indian rare earths Ltd.
2. Methane sulphonic acid AR grade S.D.fine chemicals
3. Silver nitrate solution AR grade Merck India
4. Ammonium persulphate AR Merck India  
5. Sulfuric acid LR CDH chemicals  
6. Ferrion indicator Merck India  
7. Ferrous ammonium sulfate Merck India  
8. Naphthalene Merck India  
9. 2-methylnaphthalene Merck India  
10. 1-nitronaphthalene Merck India  
11. 1,4-naphthoquinone Merck India  
12. 2-methyl-1,4-naphthoquinone Merck India  
13. 5-nitro-1,4-naphthoquinone Merck India  
14. Benzaldehyde Merck India  
15. p-chlorobenzaldehyde Merck India  
16. o-chlorobenzaldehyde Merck India  
17. Toluene Merck India  
18. p-chlorotoluene Merck India  
19. o-chlorotoluene Merck India  
20. 1,2-dichloroethane SRL, India  
21. Hexane SRL, India

### 3.11 Apparatus and instruments

Following equipments were used in the present work.

a. Rectifier (power source)  
   Aplab Make, India, 0-20A, 0-32V, Digital display  

b. Divided cell – 500 ml capacity, PVC  

c. Cooling unit- Julabo Make, Germany, -25 to 100°C  

d. Mechanical stirrer- Remi Make, India, 0-1400 rpm, F.H.P.  

and  

e. Multimeter- Meco Make, India, digital display, portable model