

## Side Chain Chlorination of 1- Methyl Naphthalene by an Electro Chemical Method

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**Abstract** – Electrochemical side chain chlorination of 1- Methyl Naphthalene has been carried out in a two compartment cell with a conversion of 80 to 85% with an yield of 99%. Uses of varies electrode at different current density under different solvent has been carried out and results are reported in the paper.

**Keywords:** Electrochemical Chlorination, Aromatic compounds, current densities, Electrolyte, Two Compartment divided electrochemical cell, 1- chloro methyl Naphthalene

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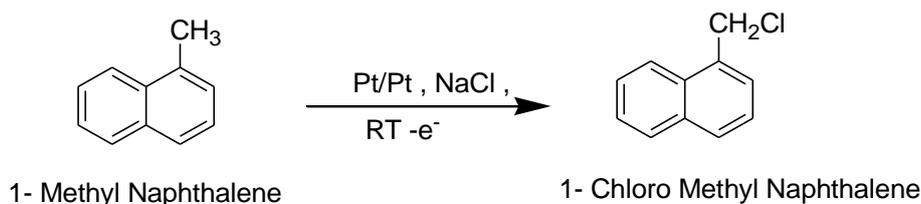
### I. Introduction

The conversion of methyl group in 1- methyl naphthalene is a fundamental reaction in the synthesis of a variety of organic compounds[1,2]. This forms the basis of organic electrosynthesis and condition have been devised for selective and useful chemical conversions. Two phase electrolysis has distinct advantages over conventional homogeneous electrolysis [3,4]. With electrochemical technology it is possible to carry out desired reaction via two-phase electrolytic reaction resulting in high yields and selectivity. In the case of electrochemical chlorination in homogeneous systems less selectivity is observed due to oxidation of the substrate on the surface of the electrode giving a mixture of nuclear (ortho/para isomers) and side chain chlorination products [5].

Substitution of C-H bonds in alkyl aromatic compounds by radical chlorination is one of the most important reactions for functionalization of alkyl aromatics. In this case 33 percentage of NaCl solution as the supporting electrolysis at room temperature in a two Compartment electrochemical cell. Electrochemical chlorination produces chlorine in vivo as an intermediate from non-corrosive chlorides and it can be easily controlled. Selective chlorination can be achieved in electrochemical technique .

Electrochemical reaction has advantages over conventional chemical method, because it does not require be used of large quantity of noxious or corrosive reagents. Electrochemical chlorination produces chlorine in vivo as intermediate from non-corrosive chlorides and it can be easily controlled. Selective chlorination can be achieved in electrochemical technique[6]. Similarly type of chlorination was reported in the literature [7-11]. In continuation of our earlier work [12], now we wish to report a simple and efficient electrochemical method for chlorination of 1 methyl naphthalene to 1- chloro methyl naphthalene by electrolytic method.

The  $\alpha$  – chlorination of 1- methyl naphthalene to 1- Chloro Methyl Naphthalene was carried out by two compartment electrolysis using an 33% of NaCl solution as the supporting electrolyte at room temperature in a H shape – type cell. Electrochemical chlorination has been investigated in different solvents [13-19]. We observed formation of side chain chlorination without formation of any poly chlorinated product.



### II. Experimental

#### 2.1. Materials and analysis

All the employed chemicals are commercially available and were used as received. Deionised water was used for preparing sodium chloride solution. Aplab power source was

used as a direct current source for the electrolysis. In a 150 ml capacity two compartment electrochemical cell, 31.5ml of 2M H<sub>2</sub> SO<sub>4</sub>, 50 ml of saturated solution of NaCl and 7 ml of Acetonitrile containing 1.5 g of 1-Methyl Naphthaene (0.01M) were taken as anolyte and the catholyte was the equal volume of 2M H<sub>2</sub> SO<sub>4</sub> (90 ml) are taken the solution as mentioned above without depolariser. 150 ml capacity two-compartment electrochemical cell with porous glass frit as separator. The cell was placed on a magnetic stirring unit. The electrolyte was stirred throughout the electrolysis using Teflon magnetic stirrer was used for the electrolysis. In electrochemical chlorination two platinum electrodes were used as electrodes (4 cm x 2.5 cm) and a charge of 2F was passed. In some cases more amount of current (4F, 6F) was passed to get maximum conversion. Saturated solution of sodium chloride containing catalytic amount of sulphuric acid (2M) and acetonitrile was used as electrolyte. The electrolysis was monitored by HPLC (Shimadzu, Japan, Model. no. CLASS. VP-10) using Shimpack ODS-18 column (125mm×4.5 mm) as stationary phase. The eluent consisted of methanol/water (70:30) at a flow rate of 1 ml/min. Samples were analysed at a wavelength of 254 nm with a UV detector (Shimadzu UV-vis detector) coupled to a printer.

## 2.2 Experimental Procedure

An amount of 1.5 gm of 1- Methyl Naphthalene (0.0105M) was dissolved in 7 ml of Acetonitrile and the solution was transferred into the electrolytic cell. 50 ml of saturated sodium chloride solution and 31.5ml of 2M H<sub>2</sub> SO<sub>4</sub> was added over the above solution in a 150 ml capacity two compartment electrochemical cell. The organic phase alone was stirred with magnetic stirrer at a rate of 40 rpm. After electrolysis the aqueous electrolyte solution was extracted twice with 25ml of diethyl ether in order to remove the organic phase. The ether layer was then washed with water (2X10 ml) and dried over anhydrous sodium sulphate. Then the filtered organic extract was distilled to get the crude product. The material yield and current efficiency were calculated for the isolated products based was analyzed and characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR(400 MHz, BRUKER), FT-IR spectra(Perkin Elmer model paragon 500).

## III. Product Analysis

The product analysis was carried out by high performance liquid chromatography using Shimadzu Model LC8A preparative liquid chromatography along with Shimadzu SPD6A UV detector. 100% methanol was used as the eluent. ODS (Octa Dodecyl Silance) column was used as stationary phase. Chromatograms of the experimental samples were compared with authentic samples.

The product identification was also confirmed by FT-IR spectrophotometer using Perkin Elmer model paragon 500. Neat liquid was used for recording FT-IR measurements in the range of 400 - 4000cm<sup>-1</sup>. Product analysis was also done by recording proton NMR spectra using 400 MHz Bruker NMR spectrometer.

## 3.1 Chemicals and Solvents Used

The following chemicals and solvents were used for the present study.

1. 1- Methyl Naphthalene, (AR)
2. Sulphuric acid (LR)
3. Diethyl ether (LR)
4. Acetonitrile (LR)
5. n-Hexane (LR)
6. Anhydrous sodium sulphate (LR)
7. TLC Silica gel 60 F<sub>254</sub> plates.

## IV. Results and Discussion

Galvanostatic electrolysis was carried out for the synthesis of 1- Chloro Methyl Naphthalene from 1- Methyl Naphthalene. The experimental parameters such as current density, solvent, current passed (F/mol) and anode material for the chlorination of 1- Methyl Naphthalene to 1- Chloro Methyl Naphthalene was studied and the results are summarized in Table. At the optimum electrolytic condition platinum electrodes were used at a current density of 5A/dm<sup>2</sup> in acetonitrile solvent medium.

### 4.1 Effect of Solvent:

A total charge of 2F/mol was passed at different current densities of 3, 5 and 7mA/cm<sup>2</sup> using graphite electrode and acetonitrile as a solvent. The yield of product 1- Chloro Methyl Naphthalene obtained is of 72%, 81%, and 60% with 3, 5,7 A/dm<sup>2</sup> respectively.

When the electrolysis was carried out using Dichloromethane as a solvent with a current density of 3, 5 & 7 A/dm<sup>2</sup> and the product is obtained with an yield of 65%, 73% & 57% respectively.

In the case of 1-Butanol as a solvent, with a current density of 3, 5 & 7 A/dm<sup>2</sup> the product is obtained with an yield of 58%, 69% & 47% respectively. From the above set of experiments the maximum yield of product.

**4.2 Effect of Electrode:**

The electrochemical chlorination of 1- Methyl Naphthalene was carried out using different electrodes of platinum and graphite under various solvents of acetonitrile, Dichloromethane and 1-Butanol as solvent the following results are observed.

When the electrolysis was carried out with platinum as electrode and acetonitrile as solvent, the product 1- Chloro Methyl Naphthalene was obtained with a yield of 85%, 99%, and 79% at different current densities of 3, 5 and 7A/dm<sup>2</sup> respectively. In the case of Dichloromethane as a solvent, the yield obtained was 75%, 87%, and 63% at the current densities of 3, 5 and 7 A/dm<sup>2</sup> respectively.

Similarly when 1-Butanol was used as solvent, the yield obtained was 62%, 77%, and 53% at the current densities of 3, 5 and 7A/dm<sup>2</sup> respectively. From the above results it is concluded that usage of platinum electrodes gives a maximum yield of 99% product.

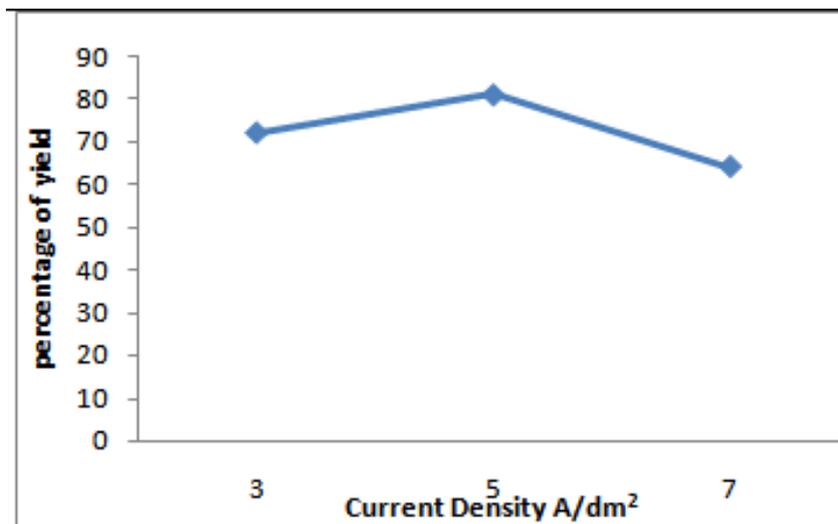
**Electrochemical chlorination of 1- Methyl Naphthalene to 1- Chloro Methyl Naphthalene**

**Effect of current density using Graphite electrode in Acetonitrile**

- Electrolytic cell : Two – compartment electrochemical cell
- Electrolyte : 31.5ml of 2M H<sub>2</sub>SO<sub>4</sub> + 7ml of acetonitrile
- Electrode : Cathode Graphite & Anode Graphite (Area = 4 cm x 2.5 cm)
- Temperature : Room Temperature.
- Cell Voltage : 2.0- 5.0 V

**Table 1**

No.	Weight of 1- Methyl Naphthalene taken for chlorination (g)	Current density (A/dm <sup>2</sup> )	Current passed (F/mole)	Weight of the product obtained (g)	Material yield %	Current efficiency %
1	1.50	3.0	2.0	1.34	72	72
2	1.50	5.0	4.0	1.51	81	41
3	1.50	7.0	6.0	1.11	60	20

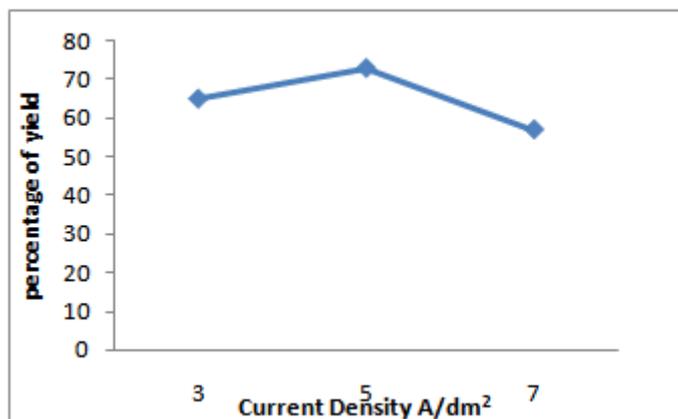


**Effect of current density using Graphite electrode in Dichloromethane**

- Electrolytic cell : Two – compartment electrochemical cell
- Electrolyte : 31.5ml of 2M H<sub>2</sub>SO<sub>4</sub> + 7ml of Dichloromethane
- Electrode : Cathode Graphite & Anode Graphite (Area = 4 cm x 2.5 cm)
- Temperature : Room Temperature.
- Cell Voltage : 2.0- 5.0 V

**Table 2**

No.	Weight of 1- Methyl Naphthalene taken for chlorination(g)	Current density (A/dm <sup>2</sup> )	Current passed (F/mole)	Weight of the product obtained (g)	Material yield %	Current efficiency %
1	1.50	3.0	2.0	1.21	65	65
2	1.50	5.0	4.0	1.36	73	37
3	1.50	7.0	6.0	1.06	57	19

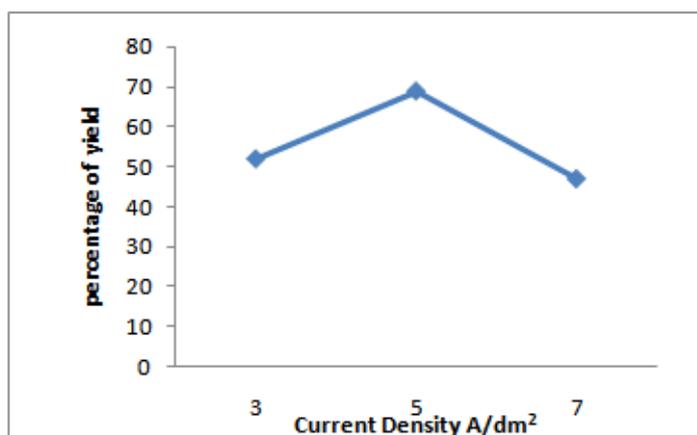


**Effect of current density using Graphite electrode in 1- Butanol**

Electrolytic cell : Two – compartment electrochemical cell  
 Electrolyte : 31.5ml of 2M H<sub>2</sub>SO<sub>4</sub> + 7ml of 1- Butanol  
 Electrode : Cathode Graphite & Anode Graphite (Area = 4 cm x 2.5 cm)  
 Temperature : Room Temperature.  
 Cell Voltage : 2.0- 5.0 V

**Table 3**

No.	Weight of 1- Methyl Naphthalene taken for chlorination (g)	Current density (A/dm <sup>2</sup> )	Current passed (F/mole)	Weight of the product obtained (g)	Material yield %	Current efficiency %
1	1.50	3.0	2.0	1.08	58	58
2	1.50	5.0	4.0	1.28	69	35
3	1.50	7.0	6.0	0.87	47	16



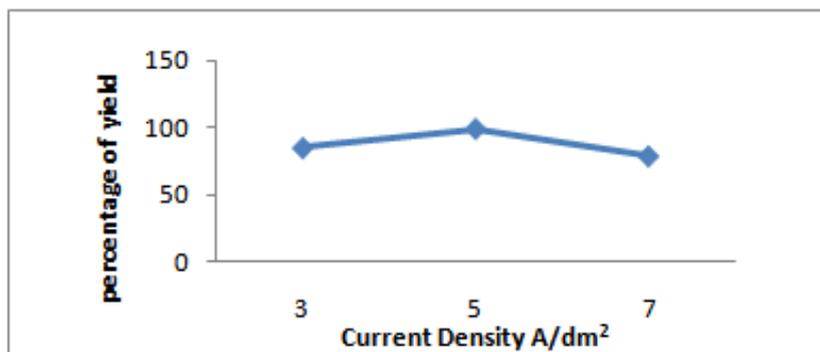
**Effect of current density using Platinum electrode in Acetonitrile**

Electrolytic cell : Two – compartment electrochemical cell

Electrolyte : 31.5ml of 2M H<sub>2</sub>SO<sub>4</sub> + 7ml of acetonitrile  
 Electrode : Platinum (Cathode) & Platinum (Anode) (Area = 4 cm x 2.5 cm)  
 Temperature : Room Temperature.  
 Cell Voltage : 2.0- 5.0 V

**Table 4**

No.	Weight of 1- Methyl Naphthalene taken for chlorination(g)	Current density (A/dm <sup>2</sup> )	Current passed (F/mole)	Weight of the product obtained (g)	Material yield %	Current efficiency %
1	1.50	3.0	2.0	1.58	85	85
2	1.50	5.0	4.0	1.84	99	49
3	1.50	7.0	6.0	1.47	79	26

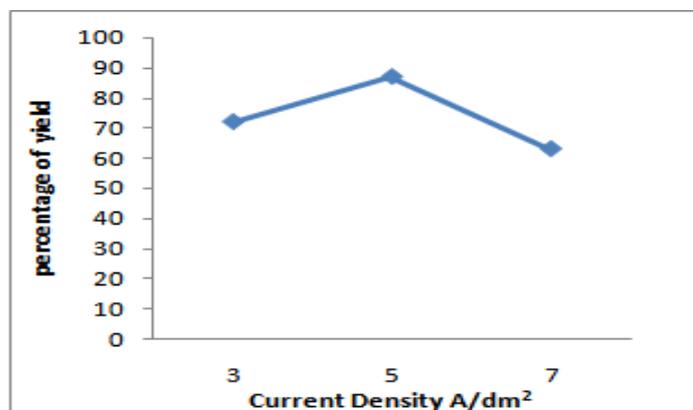


**Effect of current density using Platinum electrode in Dichloromethane**

Electrolytic cell : Two – compartment electrochemical cell  
 Electrolyte : 31.5ml of 2M H<sub>2</sub>SO<sub>4</sub> + 7ml of Dichloromethane  
 Electrode : Platinum (Cathode) & Platinum (Anode) (Area = 4 cm x 2.5 cm)  
 Temperature : Room Temperature.  
 Cell Voltage : 2.0- 5.0 V

**Table - 5**

No.	Weight of 1- Methyl Naphthalene taken for chlorination (g)	Current density (A/dm <sup>2</sup> )	Current passed (F/mole)	Weight of the product obtained (g)	Material yield %	Current efficiency %
1	1.50	3.0	2.0	1.34	72	72
2	1.50	5.0	4.0	1.62	87	44
3	1.50	7.0	6.0	1.17	63	21



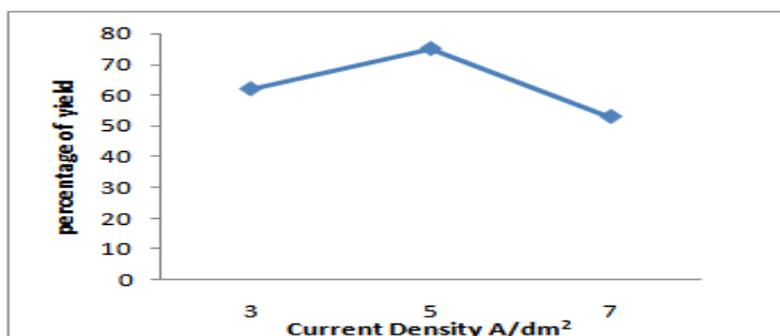
**Effect of current density using Platinum electrode in 1- Butanol**

Electrolytic cell : Two – compartment electrochemical cell  
 Electrolyte : 31.5ml of 2M H<sub>2</sub>SO<sub>4</sub> + 7ml of 1- Butanol  
 Electrode : Platinum (Cathode) & Platinum (Anode) (Area = 4 cm x 2.5 cm)  
 Temperature : Room Temperature.

Cell Voltage : 2.0- 5.0 V

Table – 6

No.	Weight of 1- Methyl Naphthalene taken for chlorination (g)	Current density (A/dm <sup>2</sup> )	Current passed (F/mole)	Weight of the product obtained (g)	Material yield %	Current efficiency %
1	1.50	3.0	2.0	1.15	62	62
2	1.50	5.0	4.0	1.39	75	38
3	1.50	7.0	6.0	0.98	53	18



\* Experiment carried out in an Two compartment electrochemical cell

#### 4.3 Effect of Current Passed (F / mol)

The electrochemical chlorination of 1- Methyl Naphthalene is found to be quite facile, the theoretically required current of 2F/mole is quite sufficient for the conversion of 1- Methyl Naphthalene with maximum yield of 1- Chloro Methyl Naphthalene. When more than theoretical amount of current, 4F/ mole and 6F/mole were passed for electrolysis, low yield was obtained due to competitive O<sub>2</sub> evolution.

Hence the optimum conditions for the direct anodic oxidation of 1- Methyl Naphthalene to 1- Chloro Methyl Naphthalene is found to be 5.0 A/dm<sup>2</sup> current density, platinum electrode in acetonitrile solvent medium with theoretical amount of current.

## V. Product Analysis

### 5.1 High performance liquid chromatography (HPLC)

Typical HPLC graphs of standard and experimental samples of 1- Chloro Methyl Naphthalene were analysed.. The retention times of 1- Chloro Methyl Naphthalene in the synthesized product mixture was 4.823 min. The percentage purity of 1- Chloro Methyl Naphthalene in the product mixture was found out by HPLC as above 99% and the material yield of 1- Chloro Methyl Naphthalene was calculated based on the peak area.

### 5.2 FTIR Spectroscopy

The FT-IR Spectrum of 1- Chloro Methyl Naphthalene synthesized was analysed. The characteristic alkane C-H stretching absorption is found at 2970 cm<sup>-1</sup>, aromatic C-H stretching absorption is found at 3069 cm<sup>-1</sup> and C-Cl absorption of alkyl halide function is found at 776 cm<sup>-1</sup>. These values coincide well with the literature value and hence the 1- Chloro Methyl Naphthalene formation is confirmed.

### 5.3 Proton NMR Spectrum

Proton NMR Spectrum of prepared 1- Chloro Methyl Naphthalene was analysed. The chemical shift values ( $\delta$ ) observed in the product spectrum are compared with the literature value.

Compound Name	Chemical Shift $\delta$ values			
	H <sup>1</sup>		C <sup>13</sup>	
	Observed	Reported	Observed	Reported
	5.13	5.08	46.8	48.8
	7.50	7.35	123.8	123.9
	7.52	7.45	125.4	125.2
	7.53	7.46	126.2	125.4
	7.59	7.52	126.3	126.2
	7.73	7.76	126.6	126.4
	7.79	7.80	126.6	126.5
	8.10	8.09	128.9	128.9

1- Chloro Methyl Naphthalene			133.1 134.1	133.4 134.0
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The  $\delta$  values of aromatic protons are observed at 7.50 – 8.10, methyl protons at 5.13 are observed in our products. The  $\delta$  values of aromatic carbon are observed at 123.8 – 134.1, Methyl protons at 46.8 are observed in the product which compares well with the literature value.

## VI. Conclusion

The present research investigation has established a very good method for the direct anodic chlorination 1- Methyl Naphthalene using platinum electrode in a divided cell with aqueous sulphuric acid medium containing a solvent of acetonitrile to get 1- Chloro Methyl Naphthalene in excellent yield (99%). The optimum current density for the chlorination is at 5.0 A/dm<sup>2</sup>. Platinum electrodes gave maximum material yield than the graphites.

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