

# Process Optimisation Studies on the Electrochemical Preparation of Monochlorotoluene.

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The process optimization studies were conducted in a batch cell on the electrochemical chlorination of toluene using DSA-Cl<sub>2</sub> type electrode (Dimensionally stable Anode = DSA) in aqueous hydrochloric acid medium. Different experimental conditions like concentration and current density were tried to maximise the product yield.

**Key words:** Optimization study, electrochemical chlorination, concentration, and yield.

## Introduction

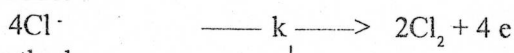
Process investigation consists in finding kinetic parameters to get an optimum value for a given function. Before an optimum property can be estimated, an optimisation criterion has to be chosen. This may be a process variable, say, yield of product per unit volume of reactor, a minimum cost of product for a specified output etc. On the basis of the optimisation criterion, one has to develop an objective function, which relates the optimisation criterion to the dominant parameters [1-4]. The goal of optimisation is to maximise or minimise the objective function as the case may be.

Since electrochemical methods are simple and avoid environmental pollution considerably, many organic compounds are synthesised by such methods [5]. In any electrochemical process, electrochemical reactor has a central role to play. As wide range of conditions are required in the reactor system, the selection of an optimum cell design is usually difficult. A comprehensive treatment of laboratory cells has been published as well as several reviews on electrochemical cells.

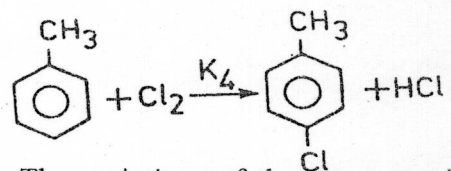
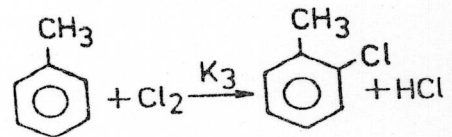
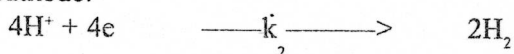
## Theory

The electrochemical chlorination of toluene to monochlorotoluene has been carried out by many workers [5-12]. In the present work, both the reaction kinetic modeling and the influence of concentration and current density on electrochemical preparation of monochlorotoluene in batch reactor have been studied. During electrolysis chlorine is formed in-situ at the anode and further chlorination of toluene occurs according to the reaction

At the anode:



At the cathode:



The variations of the amount of specific species in a cell is due to particular electrochemical or chemical reaction. The reactor can be assumed to behave as ideal stirred tank batch reactor. Denoting reaction rate as 'r<sub>i</sub>' corresponding to each reaction in the scheme, the mass balance can be written as

$$\frac{d[\text{Cl}^-]}{dt} = (-4r_1 + r_2' + r_4) \dots\dots\dots (1)$$

$$\frac{d[\text{Cl}_2]}{dt} = (2r_1 - r_3 - r_4) \dots\dots\dots (2)$$

$$\frac{dC_A}{dt} = -(r_3 + r_4) \dots\dots\dots (3)$$

$$\frac{dC_B}{dt} = r_3 \dots\dots\dots (4)$$

$$\frac{dC_C}{dt} = r_4 \dots\dots\dots (5)$$

where, A = toluene, B = o-chlorotoluene, C = p-chlorotoluene, r<sub>1</sub> = rate of chlorine formation, r<sub>2</sub> = rate of hydrogen formation, r<sub>3</sub> = rate of orthochloro toluene formation and r<sub>4</sub> = rate of parachlorotoluene formation.

Further pseudo steady state theory can be applied to production and consumption of Cl<sub>2</sub>. The rate of formation of Cl<sub>2</sub> is practically identical to its rate of disappearance. Then,

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$$2r_1 = r_3 + r_4 \quad \dots\dots\dots (6)$$

Writing the rate expression for this system

$$-r_1 = \frac{-dC_A}{dt} = (k_3 + k_4)C_A \quad \dots\dots\dots (7)$$

$$r_3 = \frac{dC_B}{dt} = k_3 C_A \quad \dots\dots\dots (8)$$

$$r_4 = \frac{dC_C}{dt} = k_4 C_A \quad \dots\dots\dots (9)$$

The reactor is ideal stirred tank batch reactor; the equation (7) can be integrated to give

$$C_A = C_{A0} \exp [ - (k_3 + k_4) t ] \quad \dots\dots\dots (10)$$

equation (8) can be divided by equation (9) to give

$$\frac{r_3}{r_4} = \frac{k_3}{k_4} \quad \dots\dots\dots (11)$$

$$\frac{dC_B}{dC_C} = \frac{k_3}{k_4} \quad \dots\dots\dots (12)$$

and upon integration,

$$C_B = (k_3 / k_4) C_C \quad \dots\dots\dots (13)$$

where,

$C_A$  = is the concentration of toluene in the reactor,  
 $C_B$  = is the concentration of o-chlorotoluene in the reactor and  $C_C$  = is the concentration of p-chlorotoluene in the reactor

It is known that  $Cl^-$  from the bulk is transported to the electrode surface where it undergoes conversion to chlorine and it is transported back to bulk for reaction and similarly toluene is transported from bulk to surface for reaction. Assuming the Tafel behaviour is applicable

$$\frac{i_1}{2F} = k_{1s} S (Cl_{2s}) \exp (\beta E) \quad \dots\dots\dots (14)$$

$$\frac{i_1}{2F} = k_{1s} (C_{As}) \exp (\beta E) \quad \dots\dots\dots (15)$$

and

$$\frac{i_1}{2F} = k_L S (C_A - C_{As}) \quad \dots\dots\dots (16)$$

Elimination of  $C_{As}$ , the surface concentration by combining equation (15) and (16),

$$\frac{i_1}{2F_s} = 1/k_{1s} \exp (\beta E) + 1/k_L = C_A \quad \dots\dots\dots (17)$$

$$\frac{i_1}{2F} = k_{3s} C_A \quad \dots\dots\dots (18)$$

where,

$$1/k_3 = 1/k_L + 1/k_{1s} \exp (\beta E) \quad \dots\dots\dots (19)$$

and similarly,

$$1/k_4 = 1/k_L + 1/K_{2s} \exp(\beta E) \quad \dots\dots\dots (20)$$

where,  $i_1$  = limiting current density,  $K_{2s}$  = reaction rate constant of surface reaction

### Experimental

A batch cell was constructed with a glass body, the anode was DSA- $Cl_2$  and graphite sheet placed inside a porous diaphragm and placed in center of the cell was used as cathode. Electrical connections to each electrode was given through the cell cover. The glass stirrer was placed in the middle of the cell. The thermometer and sampling port were in the top cover.

The electrolysis was carried out under galvanostatic condition (constant current) at a temperature range of 20-25 °C and at atmospheric pressure. Aqueous phase of the electrolytic solution was 2 N hydrochloric acid, which acts as a supporting electrolyte and a  $Cl^-$  source. The organic phase is LR grade toluene. The anolyte was stirred by a mechanical glass stirrer at 200 - 250 rpm.

The product monochlorotoluene, having a higher density, settled at the bottom of the cell, which was easily separated from the electrolyte. The product was distilled and analysed further for its contents by gas chromatography and liquid chromatography.

### Results and discussions

Electrochemical reactions are quite complex due to the possibility of innumerable side reactions. Hence, the importance of proper optimization study is imperative. The experiments are designed for the production of o- and p- chlorotoluene from toluene by using the batch cell and for optimum current density, concentration. The results from the experiments are used to model the reactor for maximum yield of desired products and to determine optimum experimental conditions.

The main emphasis has been on the design and development of electro chemical reactor for the preparation of o- and p-chlorotoluene in high yield. The chief advantage of electrochemical preparation of monochlorotoluene has been high yield, conversion and current efficiency in aqueous medium. The additional advantages are selective chlorination, absence of bye-products and freedom from chlorine gas handling and pollution.

The broad conclusions that are drawn from study are as follows. A batch electrochemical cell has been developed for the preparation of o- and p-chlorotoluene from toluene. The main advantage of this cell is the electrochemical generation of chlorine in aqueous medium in a divided cell. During electrolysis, the generated chlorine species which could be fully absorbed easily by the organic phase. In general the rate of conversion increases with mass transfer as the reaction moves from a predominantly mass transfer controlled region to a mixed control region. This could be achieved using this cell.

The important variable that affected the yield and conversion of monochlorotoluene from toluene in the electrochemical process are electrolyte concentration, current density and temperature. The effect of above parameters have been investigated and the current efficiency, space time yield, energy consumption, conversion and yield have been determined.

The range of process parameters covered in this study are as follows:

Parameter	Process variables		
	Range	Yield	Conversion
1. Current density A/dm <sup>2</sup>	1-5	20-85%	35 - 95%
2. Electrolyte concentration V/V	5-10%	59-85%	68 - 95%
3. Temperature	20-38°C	85 - 55%	95 - 64%
4. Electrode -Anode			
a. Graphite	---	6%	15%
b. Platinum	---	55%	64%
c. DSA. - Cl <sub>2</sub>	---	85%	95%

Several electrodes including graphite, platinum and dimensionally stable anode (DSA-Cl<sub>2</sub>) were employed.

In the present study, aqueous hydrochloric acid was used as electrolyte, to provide the required chlorine reagent. The concentration of electrolyte used was varied from 5-10% V/V with corresponding monochlorotoluene yield of 59% and 85% respectively, indicating thereby that higher electrolyte concentration improves the yield. However, higher concentration of electrolyte could not be used as the rate of chlorine evolution was in excess of the consumption in the process, which in turn could lead to an unsafe and hazardous environmental condition.

Further the current density was varied in the range of 1- 5 A/dm<sup>2</sup> for determining its effect on yield and conversion of monochlorotoluene. Higher values of current density beyond the above range had to be avoided as the yield was adversely affected due to predominance of side reactions.

The influence of temperature on yield and conversion of monochlorotoluene was studied in the range of 20 - 38 °C. The maximum yield of 85% was observed at 20 °C. Increasing temperature beyond 20 °C decreased both yield and conversion.

The yield of monochlorotoluene in the early 1930 process of Hooker electrochemical company was less than 30% whereas in the present work a significant improvement in yield upto a level of 85% could be accomplished.

The results are presented in Figs. 1,2 and 3 and Table 1 and 2. The Fig. 1 shows the variation of concentration of toluene, o-chlorotoluene and p-chlorotoluene with time. It can be seen from figures that the concentration C<sub>A</sub> decreases steadily with time as the concentration of C<sub>B</sub> and C<sub>C</sub> increases with time. From the plot of ln {C<sub>A</sub> / C<sub>AO</sub>} vs 't' the slope gives (k<sub>3</sub> + k<sub>4</sub>) and from the plot of 'C'<sub>B</sub> vs 'C'<sub>C</sub> the value of the slope is k<sub>3</sub> / k<sub>4</sub>. From the two slopes, individual value of 'k<sub>3</sub> and 'k<sub>4</sub> can be computed.

The linearity of ln {C<sub>A</sub> / C<sub>AO</sub>} vs 't' (Fig. 3) indicates the exponential variation with respect to time, indicating the first order reactions. Figure 2 shows the linear variations C<sub>B</sub> with respect to 'C'<sub>C</sub>. The yield of 'B' is twice the yield of 'C' as the ratio of k<sub>3</sub> / k<sub>4</sub> is 0.5. The values of the rate constants are presented in the Table 2.

Table. 1 Electrochemical chlorination of toluene

Anode	: DSA-Cl <sub>2</sub>
Cathode	: Graphite
Electrolyte concentration	: 10% HCl
Temperature	: 20-25 °C

Sl. no	Type of cell	Current density	Cell voltage (V)	Yield (%)	
				total	ortho- para-
1.	divided	1	2.9	21.4	14.1 7.3
2.	divided	2	3.2	65.5	44.3 21.2
3.	divided	3	3.5	73.0	52.3 20.7
4.	divided	4	3.8	78.5	55.0 23.5
5.	divided	5	4.0	85.3	57.1 28.2
6.	divided	6	4.3	81.2	54.0 27.2

Table. 2. Rate constant for electrochemical chlorination of toluene

Sl.no	product	Rate constant (min <sup>-1</sup> )
1.	o-chlorotoluene ( $k_3$ )	$0.008 \times 10^{-3}$
2.	p-chlorotoluene ( $k_4$ )	$0.004 \times 10^{-3}$
3.	Total ( $k_3 + k_4$ )	$0.012 \times 10^{-3}$

### Conclusion

The investigations have revealed optimum process parameters for electrochemical chlorination of toluene and also revealed that the quantitative values of (i) rate constants for depletion of toluene (ii) rate constants for production of o-and p-chlorotoluene in this electrochemical batch reactor.

Presently the country meets its entire demand of chlorotoluene, which is nearly 5000 tonnes per year, by important due to lack of indigenous method of production. The process technology developed in the present investigation could go a long way in meeting this long felt need of the country. This, however, will require commercial trial and large scale industrial applications in the country.

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