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PROCESS KINETIC STUDIES ON THE ELECTROCHEMICAL PREPARATION OF MONOCHLOROTOLUENE

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The process kinetic studies has been investigated for the electrochemical chlorination of toluene under different experimental conditions like concentration and current density to maximize the product yield and to study the reaction kinetic modelling. These studies conducted in a batch reactor using DSA type electrode (Titanium Substrate Insoluble Anode = TSIA) in aqueous hydrochloric acid medium.

Keywords: Process kinetic study, batch reactor, current density, concentration and kinetic modelling.

INTRODUCTION

The success of an electrochemical system requires not only an understanding of the basic chemistry and electrochemistry, but also the way these couple with engineering design and development of reactors. Feasibility of the electrochemical system is related to many factors such as the design, performance of cell components and parts, and operating conditions such as current density, temperature and electricity [1].

The electrochemical chlorination of toluene to monochlorotoluenes has been carried out by many workers [2-5]. However there are wide variations in the operating conditions in the processes referred to. It was therefore, considered necessary to study the optimum conditions such as better cell design, mass transfer, electrode, current density and temperature [6-7].

In this paper, we present our work on the process kinetic studies conducted in a batch reactor on the electrochemical chlorination of toluene using DSA electrode (TSIA = Titanium Substrate Insoluble Anode) in aqueous hydrochloric acid medium in high yield and low energy consumption. The process conditions have been optimised and detailed material balance studies have been carried out.

However, for large scale electrochemical cells it was necessary to devise a better electrochemical cell. This electrochemical cell has the narrow and constant inter-electrode gap, good agitation, good mass transfer and efficient heat removal. This cell can be used for the synthesis of various chloro aromatic compounds.

In our present work we have made efforts to study both the reaction kinetic modelling and the influence of concentration and current density on electrochemical preparation of monochlorotoluenes in a batch reactor using a factorial 2^2 design and derived the empirical equation.

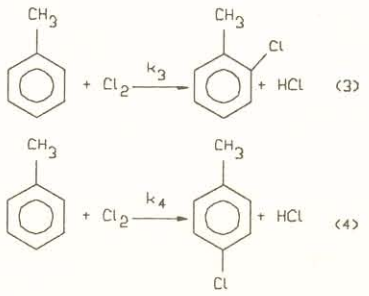
Theoretical

During electrolysis the following reactions occur in the reactor. Chlorine is formed anisette at the anode and further chlorination of toluene occurs according to the reaction given below

$$\text{At the anode } 4Cl^- \xrightarrow{k_1} 2Cl_2 + 4e \qquad (1)$$

$$\text{At the cathode } 4H^+ + 4e \xrightarrow{k_2} 2H_2 \qquad (2)$$

Reaction with toluene



The variations of the amount of specific species in a reactor is due to particular electrochemical or chemical reaction. The reactor can be assumed to behave as an ideal stirred tank batch reactor.

Experimental details

Experiments were carried out in a 500 ml capacity glass cell. The cell cover was equipped with openings for introducing the electrodes, porous diaphragm, thermometer and stirrer. The anode was TSIA and a graphite placed inside a porous diaphragm was used as a cathode. Hydrochloric acid was used as anolyte and the same solution was used as catholyte.

The anolyte was stirred by means of a glass stirrer. The electrolysis was carried out under constant current conditions in a temperature range 293-298 K at four different experimental conditions. After each experiment, the electrolyte was analyzed.

RESULTS AND DISCUSSION

The results are presented in Figs. 1, 2 and 3 and Tables I and II. Fig.1 shows the variation of concentration of toluene (C_A), o-chlorotoluene (C_B) and p-chlorotoluene (C_C) with time. It can be seen from the figures that the concentration 'C_A' decreases steadily with time whereas the concentration of the product 'C_B' and 'C_C' increases with time.

The linearity of ln 'C/Co' Vs 't' indicates the exponential variation with respect to time, indicating the first order reactions. Fig.2 is a derived graph which shows the linear variations of 'C_E' with respect to 'C_C'. The yield of 'B' is

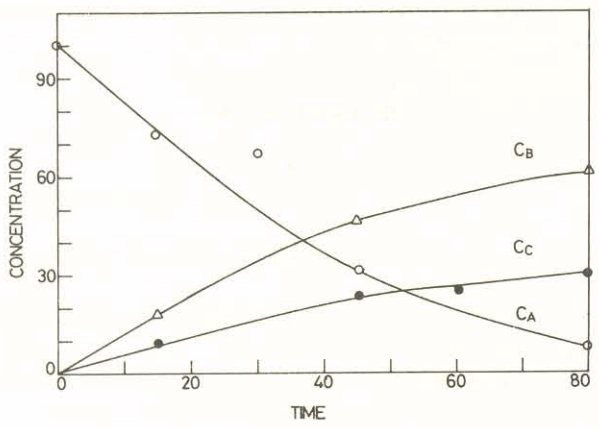


Fig. 1: Variation of concentration of reactants (A) and products (B & C)
Toluene (○) 0-chlorotoluene (△) P-chlorotoluene (●)

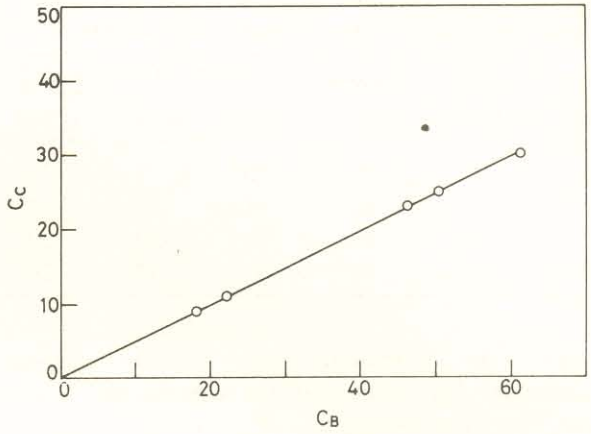


Fig. 2: Linear variation of C_B with respect to C_C

twice the yield of 'C' and the ratio of k_3/k_4 is 0.5. The values of the rate constants are presented in the Table II.

In factorial design of the experiment, the various influence on a particular quantity is being investigated are referred to as factors. The values of these factors which are set for each experiment are called levels. For a study of the influence of 'n' factors at 'm' levels, a 'm^n' factorial design is employed, 'n' indicates the number of experiments required.

An example for the use of 2^2 factorial design is the study of the influence of current density, 'i' (factor A) and concentration of reactant 'C' (factor B) on the current efficiency 'O_e' of an electrochemical conversion. Each of the two factors (concentration and current density) is assigned a low level (a_0,b_0) and high level (a_1, b_1).

These four values give 2^2=4 combinations of 2 factors. The combinations of parameters are taken as settings for the

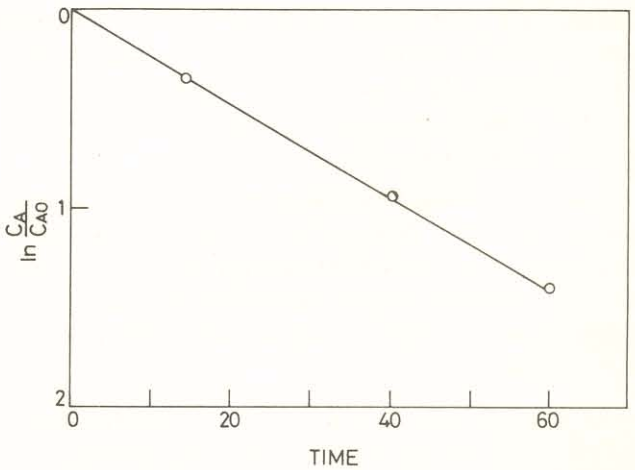


Fig. 3: Linear variation of ln C_A/C_A O with respect to time

TABLE I: Electrochemical chlorination of Toluene
Duration = 80 minutes Temp = 293 to 298 K

Experiment	C.D Amp/dm^2	Concn V/V	Current Efficiency (%)		
			Total	Ortho	Para
(1)	1	5	10	7	3
a	1	10	21	14	7
b	5	5	59	39	20
ab	5	10	85	57	28

experiments to determine the current efficiency experimentally. The results of the experiments (current efficiency) for each combination of levels are expressed by the following symbols.

Combination of factor (levels)	Symbol of the result
$a_0 b_0$	(1)
$a_1 b_0$	a
$a_0 b_1$	b
$a_1 b_1$	ab

The effect 'E_A' of factor 'A' on the result is derived from the difference between the mean values of results for high and low levels of factor 'A'.

$$E_A = \frac{1}{2}(a + ab) - \frac{1}{2}((1) + b) \quad (5)$$

The effect of factor 'B' is derived in a similar way

$$E_B = \frac{1}{2}(b + ab) - \frac{1}{2}((1) + a) \quad (6)$$

Besides these two main effects of the factors, there is often an interaction 'E_{AB}' between the factors. This is calculated according to the equation

$$E_{AB} + \frac{1}{2}(AB + (1)) - \frac{1}{2}(b + a) \quad (7)$$

In the presence of an interaction, the effect of a factor in the region between the lowest and highest levels on the result is inter-related with the level of the other factor. Taking the example of current efficiency, this interaction can also be explained physicochemically.

The current density at high concentration is lower than the limiting current density and it has no effect on the current efficiency. If on the other hand, the concentration is reduced the limiting current density is smaller than the current density. Current efficiency will decrease with increasing current density.

The experiments were carried out for the time specified in the Table I and the current efficiency was calculated using

TABLE II: The effect parameters for electrochemical chlorination of toluene

	Effect factor value		
	Total	Ortho	Para
E_A	18.5	12.5	6
E_B	56.5	37.5	19
E_{AB}	7.5	5.5	2

factors such as current density and concentration from Table I and the empirical equation for current efficiency has been predicted as follows

$$Y\ (total) = -38.05 - 1.0i + 9.05\ C + 0.75\ iC \quad (8)$$

$$Y\ (ortho) = -23.98 - 1.0i + 5.8\ C + 0.6\ iC \quad (9)$$

$$Y\ (para) = -20.00 - 0.4i + 4.0\ C + 0.25\ iC \quad (10)$$

and the rate of reaction also has been determined from the above data and figures [1-3].

The process conditions have been optimised and detailed materials balance studies have been carried out. This electrochemical cell has the narrow and constant inter-electrode gap, good agitation, good mass transfer, and efficient heat removal. This process can be used for the synthesis of various chloro-aromatic compounds.

CONCLUSION

The investigations have revealed that the current efficiencies for the four different experimental conditions were calculated and the mean current efficiency was found to be 44%. The parameters-effects E_A, E_B, E_{AB} are given in the Table II and the regression function for the electrochemical chlorination of toluene is equation (8).

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