PARAMETRIC STUDIES ON THE REDUCTION OF METACHLORONITROBENZENE (MCNB) USING HYDROGEN SULPHIDE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

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Submitted by

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CERTIFICATE

This is to certify that the thesis entitled **“PARAMETRIC STUDIES ON THE REDUCTION OF METACHLORONITROBENZENE (MCNB) USING HYDROGEN SULPHIDE”** submitted by **Mr. Abhijeet Anand**, Roll no. **111CH0519** in partial fulfilment of the requirements for the award of degree of Bachelor of Technology in Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance. Mr. Abhijeet Anand has worked on this topic from August, 2014 until April, 2015 and the thesis, in my opinion, is worthy of consideration for the award of the degree of “Bachelor of Technology” in accordance with the regulations of this Institute. To the best of my knowledge, the matter embodied in the report has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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Place: Rourkela

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I also take this opportunity to express my sincere thanks to my seniors Mr. Ujjal Mondal and Ms. Devipriya Gogoi for his help during the experiments.

Finally I thank my parents for their support and encouragement without which this project would not have been possible.

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ABSTRACT

H_2S gas is a greenhouse gas. So if we can use this gas to produce anything commercially profitable instead of releasing this gas into the open environment, it will be agreat boon for us. In my project, I am using H_2S gas to reduce metachloro nitro benzene to produce meta chloro aniline. But we cannot simply react H_2S gas with metachloro nitro benzene. So we absorbed the H_2S gas in alkanolamine and then react with metachloro nitro benzene. But both chemicals are in different phases so they cannot react with each other. Thus we need a phase transfer catalyst which will facilitate the interface transfer of species, making the reaction possible between reagent of two immiscible phases.

Aromatic amines are most widely used as the intermediates for the synthesis of dyes, pharmaceuticals and agro chemicals. That's why they are of significant industrial importance.

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ABBREVIATIONS

MCNB- meta chloro nitro benzene

MCA- meta chloro aniline

TBPB- tetra butyl phosphonium bromide

MDEA- methyl di ethanol amine

PTC- phase transfer catalysis

LLPTC – Liquid liquid phase transfer catalysis

GLPTC - Gas liquid phase transfer catalysis

SLPTC – Solid liquid phase transfer catalysis

Chapter 1

INTRODUCTION

1.1 SOURCES OF GENERATION OF H_2S GAS

Human activities are one of the most significant reasons of H_2S emission. More or less 90 percent of the sources that discharge hydrogen sulfide into the air are natural. Hydrogen sulfide is discharged into the environment as a result of the disintegration of dead plant and creature material, particularly when this happens in wet conditions with restricted oxygen, for example, in marshy lands. Hot springs, volcanoes, and other geothermal sources additionally radiate H_2S. Anthropogenic arrivals of H_2S into the air result from modern courses of action, fundamentally from the extraction and refining of oil and from paper and pulp fabricating industries. This gas is also present at sewage treatment plants, compost handling plants, tanneries, and coke oven plants.

1.2 MOTIVE BEHIND TREATING H_2S GAS

Human Health get effected from the exposure of Hydrogen Sulfide. Human wellbeing gets a huge impact due to introduction of hydrogen sulfide into the environment. The intensity of the impact depend on the concentration of the gas and the length of exposure. Our surrounding levels of H_2S gas in urban region territory varies from 0.11 to 0.33 ppb, while in rural it’s ranges can be as low as 0.02 to 0.07 ppb. A rotten egg smell can tell us H_2S presence, and very few people can distinguish the gas by its smell at concentration as low as 0.5 ppb. About 50% of the population can smell H_2S at fixations as low as 8 ppb, and more than 90% can notice it at levels of 50 ppb. Hydrogen sulfide, on the other hand, is odourless at concentration over 150 ppb because of the fact that it rapidly disfunctions the sensing organs. This effect of disfunctioning the sense of odour at the level that pose serious health danger and conceivably are life-endangering are one particular aspect of hydrogen sulfide exposure. Smell is not so much a dependable warning sign that you are present in the vicinity of H_2S gas.

Now we come to some commercial losses happening due to the presence of H_2S gas. Because of its corrosive nature, presence of H_2S gas in the gas pipelines of oil and natural gas refineries can bring about a number of issues like disintegration of internal parts of equipment, unwanted side reactions resulting in the synthesis of side products as well as deactivation of the catalyst, and so forth.

As H_2S gas is a greenhouse gas, it has a great potential to become a major constituent of the acid rain. Acid rain can cause great degradation to the soil. Acid rain causes several skin diseases and also spoils the water stored in wells or in any storage component.

Henceforth H_2S ought to be absorbed in alkanolamines and treated with fine chemicals to produce mixture of chemicals of commercial significance.

Table 1. Health Effects Associated with Hydrogen Sulfide

Concentration (ppm)	Effects	Sources
0.0057	Eye and nasal symptoms. Coughs, headaches and migraines	Partti-pellinen p.316
0.03-0.02	Detectable odour	EPA report 1993, p. iii-5
0.01	Neurophysiological abnormalities	Legator, p.124
0.1-1	Abnormal balance with closed eyes, delayed verbal recall, impaired color discrimination, decreased grip strength	Kilburn, 1999, p. 210
0.2	Detectable odour	Fuller, p. 940
0.25-0.30	Nuisance due to odour from prolonged exposure	Milby, p. 194
1-5	Abnormal balance with open and closed eyes, delayed verbal recall, impaired colour discrimination,	Kilburn 1999, p.210

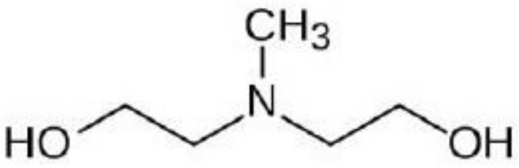
	decreased grip strength, abnormal simple and choice reaction time	
2-8	Malaise, irritability, headaches, insomnia, nausea, throat irritation	EPA report 1993 p.32
10	Eye irritation, chemical changes in blood and muscle tissue after 10 minutes	New York state report
>30	Fatigue, paralysis of olfaction from prolnged exposure	Snyder, p.200
50	Eye and respiratory irritation	Fuller, p. 940
50-100	Prolonged exposure leads to eye irritation (painful conjunctivitis, sensitivity to light, tearing, clouding of vision) and serious eye injury	Milby, p.194;EPA report 19
150-200	Olfactory nerve paralysis	EPA report 93,p 6
200	Respiratory and other mucous membrane irritation	Snyder, p.200
320-530	Damage to organs and nervous system, depression of cellular metabolism	EPA report 1993, p iii-6
250	Possible pulmonary edema from prolonged exposure	Milby, p.193
320-530	Pulmonary edema with risk of death	Kilburn,p.212
500	Systematic symptoms after 30 minutes	Fuller, p.940
500-1000	Stimulation of respiratory system, leading to hyperpnoea, followed by apnea	EPA report 1993,p iii-5
750	Unconsciousness, death	Fuller, p. 940
1000	Collapse, respiratory paralysis, followed by death	Fuller, p. 940
750-1000	Abrupt physical collapse, with possibility of recovery if exposure is terminated	Milby, p. 192
1000-2000	Immediate collapse with paralysis of respiration	Kilbun(1999),p.212

1.3 INDUSTRIAL PROCESS FOR REMOVAL OF H_2S GAS

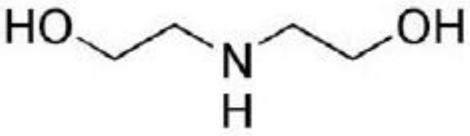
- Hydrogen sulphide absorption using alkanolamine
- Ammonia based process
- Crystasulf process
- Wet oxidation LO-CAT process

In my project, I am using the method which is the absorption of hydrogen sulfide using alkanolamine. Here are the structural formulas of several alkanolamines used for absorption of H_2S gas.

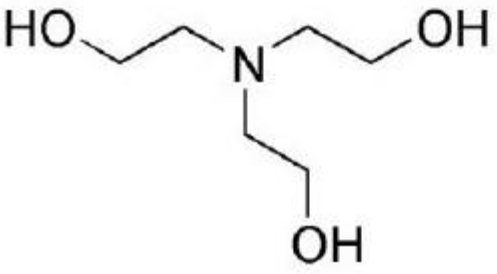
Monoethanolamine



Methyldiethanolamine



Diethanolamine



Triethanolamine

I am using MDEA as an alkanolamine for the absorption of Hydrogen Sulfide.

1.4 PHASE TRANSFER CATALYSIS

Phase transfer catalysis is a type of reaction in which the catalyst facilitates the interface transfer of species from one phase to another phase for making the reaction possible between two immiscible phases. Suppose there is an aqueous phase and an organic phase. The ions of organic phase is not dissolvable in aqueous phase and also the ions of organic phase will not be dissolvable in aqueous phase. The figure given below will give a brief explanation.

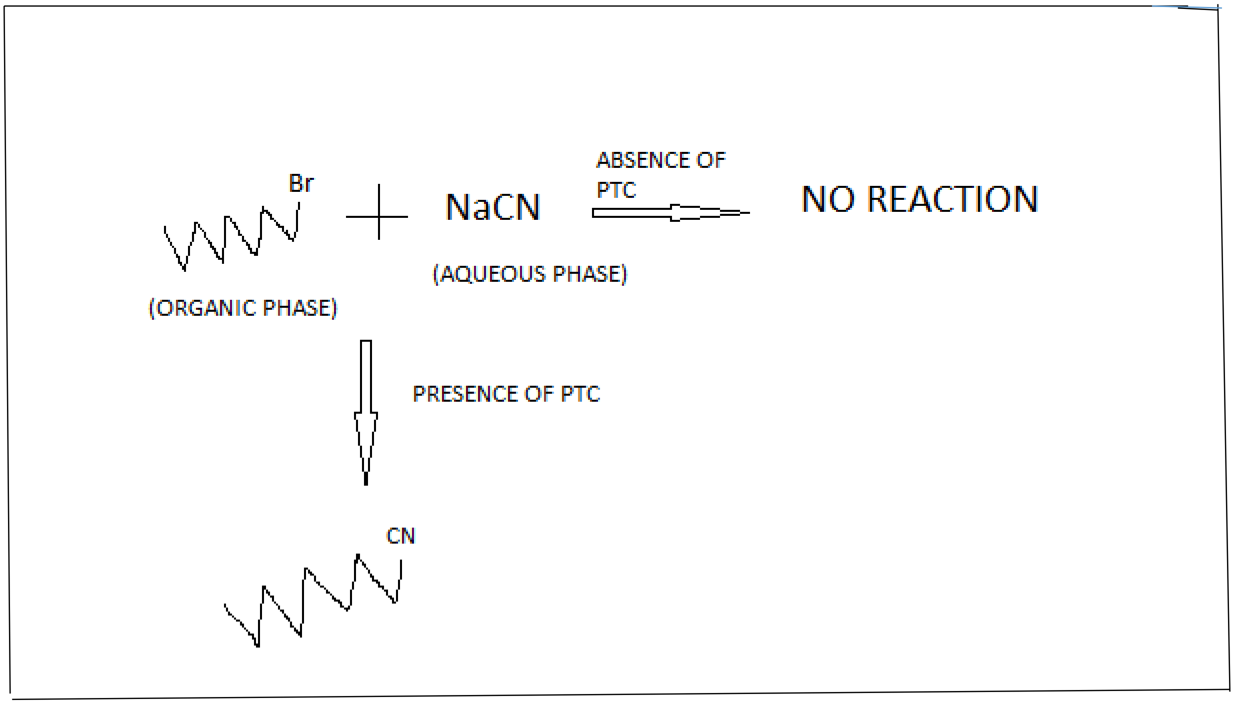


Figure 1.1: Reaction in presence of phase transfer catalyst.

In the above figure, the reaction doesn't occur readily but in the presence of phase transfer catalyst "tetra butyl phosphonium chloride", the reaction has occurred. $C_8H_{17}Br$ is soluble in organic solution while NaCN is soluble in aqueous solution. When we will mix the both the solution, the solution with lower density will be on upper side and with higher density at lower side. Both the reactant will not be able to meet each other except at interface. So there will be almost negligible reaction. But after adding the phase transfer catalyst, the reaction rate increases. Phase transfer catalyst carries the CN^- ion from aqueous phase to the organic phase and reaction occurs.

1.5 CLASSIFICATION OF PHASE TRANSFER CATALYSIS

There are two types of phase transfer catalysis. First one is insoluble and second one is insoluble. These types are also further classified. Let's see their classification and their mechanism through which they proceed through reaction.

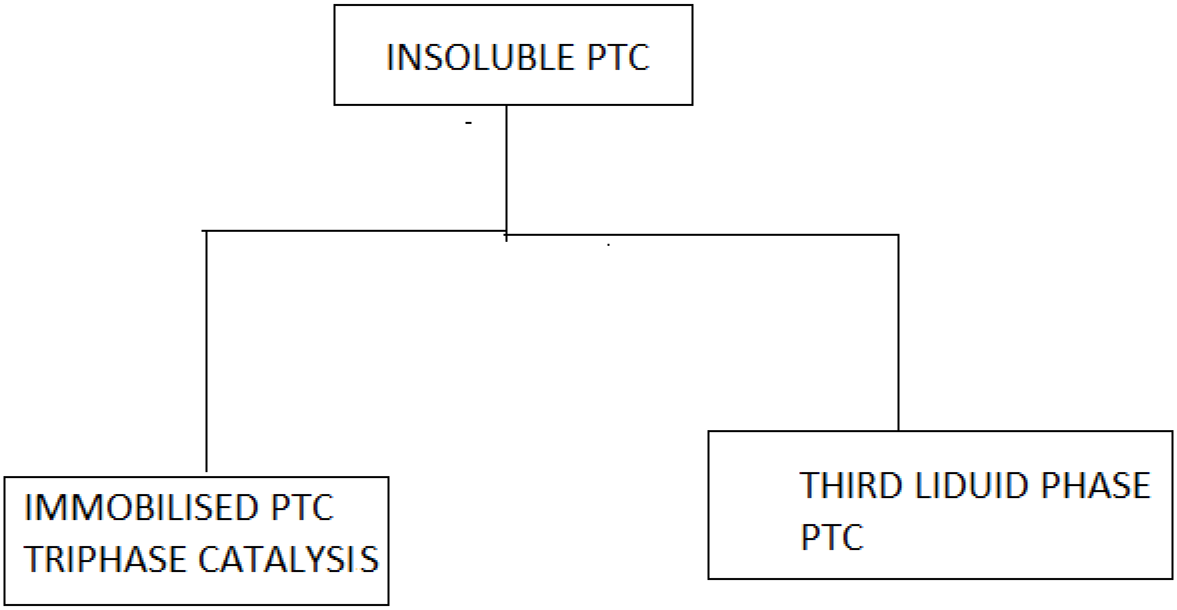


Figure 1.2: classification of insoluble PTC

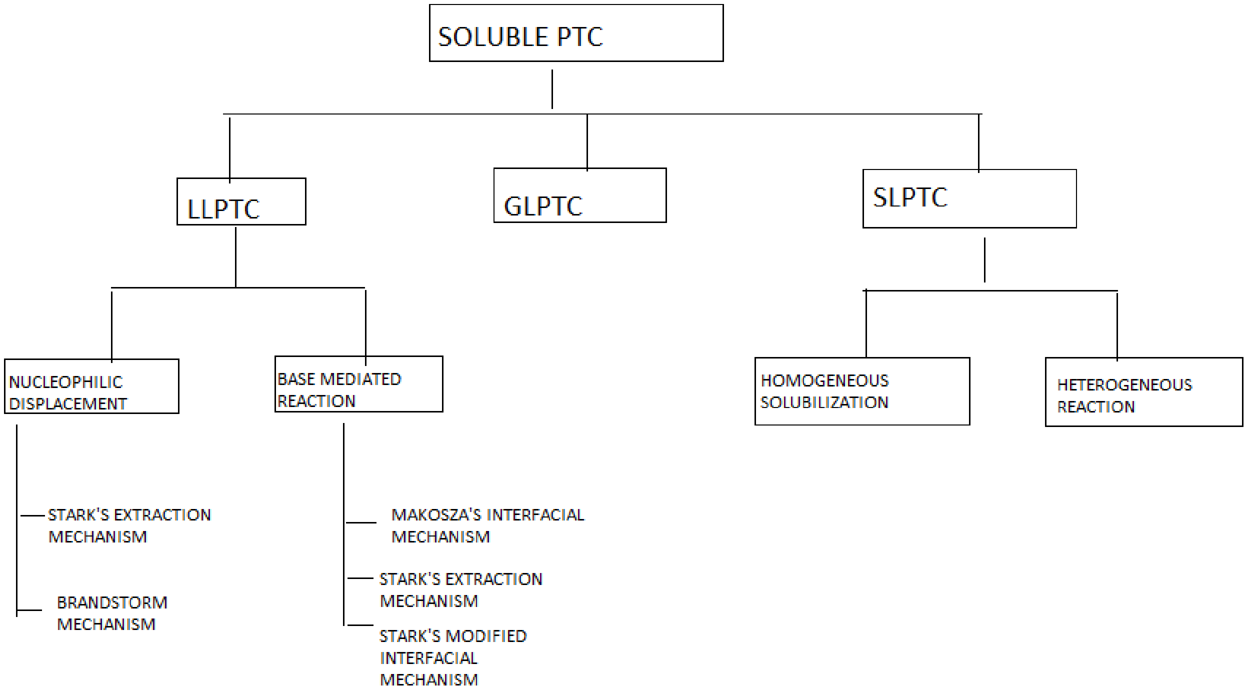


Figure 1.3: classification of soluble PTC

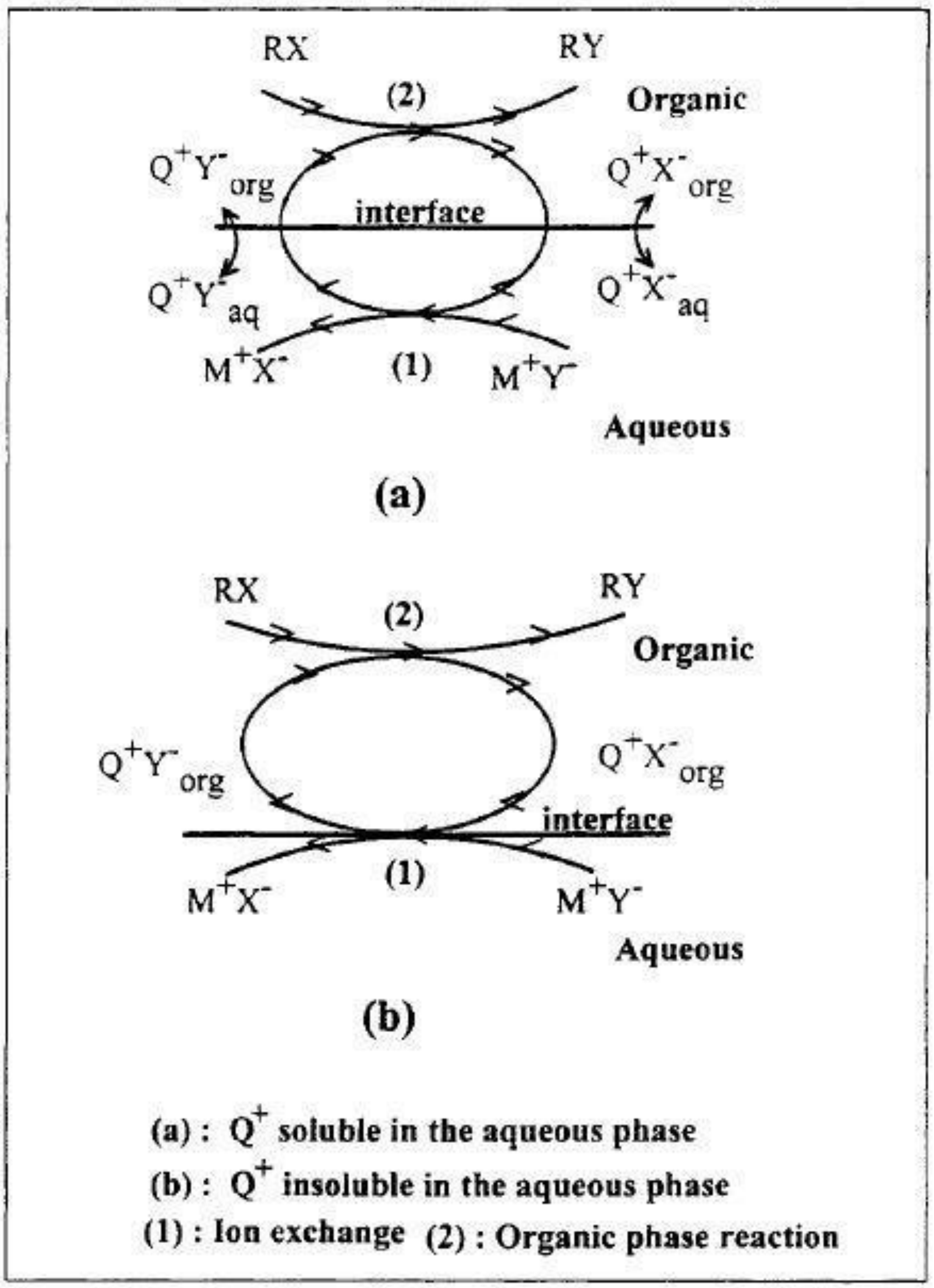
1.6 MECHANISM OF L-L PHASE TRANSFER CATALYSIS

In my project, I am doing liquid liquid phase transfer catalysis. The mechanism for the liquid liquid phase transfer catalysis is of two steps.

In step 1, anion transfer or delivery of anions from aqueous phase to organic phase takes place. The sequence of reaction that cause anions to be transferred into organic phase is called transfer step, represented by three equilibria.

a. Transfer of phase transfer catalyst from organic phase to aqueous phase.
b. Exchange of ions attached to catalyst for ion present in aqueous phase.
c. Transfer of reactant ion attached to catalyst from aqueous phase to organic phase

In step 2, the intrinsic reaction or organic phase starting with transferred anions which results in the formation of product is intrinsic reaction or phase reaction.



(a) : Q^+ soluble in the aqueous phase

(b) : Q^+ insoluble in the aqueous phase

(1) : Ion exchange (2) : Organic phase reaction

Mechanism of LLPTC.

Figure 1.4: Mechanism of L-L PTC

Reference: p. 617 Phase Transfer Catalysis: Chemistry and Engineering, **Sanjeev D. Naik and L. K. Doraiswamy** Dept. of Chemical Engineering, Iowa State University, Ames, **IA** SO011

1.7 OBJECTIVE OF MY PROJECT

My present work is devoted for better utilization of H_2S gas. The aim of my present project is to study the reduction of meta chloronitrobenzene using hydrogen sulphide absorbed alkanolamine in the presence phase transfer catalyst and to analyse the effect of temperature, catalyst loading, concentration of reactants and stirring speed on the conversion of the product.

My present experiment involves:

1. Synthesis of value-added fine chemicals like chloroanilines using the H_2S-rich aqueous alkanolamines under liquid-liquid phase conditions in the presence of a phase transfer catalyst (PTC), TBPB.
2. Analyse how the experimental process variables (stirring speed, catalyst loading, concentration of reactant, and temperature) affects the conversion of organic reactants.

Chapter 2

LITERATURE SURVEY

The mechanism as well as kinetics of liquid-liquid phase transfer catalysis is very hard to understand and will take very long time for completion. Both the oxidation and reduction in phase transfer catalysis are quite complex (Yadav & Haldavanekar, 1997; Yadav & Mistry, 2001). Heterogeneous synthetic responses between two responding species situated in immiscible stages are regularly hindered because of the experience issue. Customary systems to bypass this shared insolubility issue depend on the utilization of quick fomentation and the utilization of cosolvent, which shows both lipophilic and hydrophilic properties. In the event that the response happens at the stage limit, it is normal that the quick disturbance may have an quickening impact by expanding the interfacial contact (Phase transfer catalysis fundamentals, Jing Jer Wo, National Cheng kung University, Tainan, Taiwan).The expansion of cosolvent may dispose of the stage partition and give a homogeneous blending state to the response to happen. The cosolvents normally utilized are the protic solvents, for example, methanol and ethanol, and dipolar aprotic solvents, for example, acetonitrile, dimethyl formamide, and dimethyl sulfoxide. In spite of the fact that these cosolvents may resolve the common insolubility issue, they render certain detriments, for example, the issue of advancing contending hydrolysis pathways and the challenges in their filtration and evacuation. A conceivable method now generally known as "stage exchange catalysis" (PTC) created for succeeding the experience issue because of the shared insolubility of solvents showed up in the late 1960s. In a PTC response, an included stage exchange impetus is fit for exchanging one of the reactants from its typical stage into an alternate stage where it can regularly experience also, respond under an actuated state with the second reactant.

The most straightforward and broadly utilized system is L–L PTC, and the energy what's more, instruments of a mixed bag of SN2 sort of L–L PTC responses what's more, some alkylation responses are all around report. (Dehmlow & Dehmlow, 1993; Doraiswamy, 2001;Starks, Liotta, & Halpern, 1994).

Various edifices have been accounted for to elevate or to catalyze diminishment and carbonylation of nitro mixes, with the most productive metals being palladium, rhodium, and ruthenium. Only restricted consideration has been given to the investigation of iron buildings as promoters for these reactions. Several iron mixes are known to advance the stoichiometric
decrease of nitro mixes, yet couple of reactant courses of action have been accounted for. (reduction of nitrobenzene to aniline by iron carbonyl complexes, Fabio Ragaini, Milano, Italy).

Prof. Sunil K. Maity, Narayan C. Pradhan and Anand V. Patwardhan completed the diminishment responses of nitrochlorobenzenes (NCBs) with watery ammonium sulfide in toluene, under fluid mode with stage exchange impetus, tetrabutylammonium bromide (TBAB). The item compound was chloroanilines and its selectivity was 100%. The response rate of m-nitrochlorobenzene (MNCB) was discovered to be most noteworthy among the three NCBs took after by o- and p- nitrochlorobenzene (ONCB and PNCB). The response was discovered to be actively controlled with enactment energies of reactants in the particular responses discovered to be 22.8, 19.6 and 9.4 kcal/mol for ONCB, PNCB and MNCB, individually. The impacts of distinctive parameters, for example, centralization of NCB, TBAB focus, sulfide fixation, smelling salts focus, and essential sulfur stacking on the response rate and transformation were contemplated to build the instrument of the response. The rate of response of NCBs was discovered to be relative to the centralization of impetus and NCBs and to the block
of the convergance of sulfide.

Prof. Sunil K. Maity, Narayan C. Pradhan and Anand V. Patwardhan mulled over the energy of decrease of Nitrochlorobenzenes under fluid –liquid stage exchange impetus. Toluene was utilized as a dissolvable and the impetus utilized was TBAB (tetrabutyl ammonium bromide). General change of PNCB declines with expansion in centralization of PNCB. Request of the response was gotten to be 1.2. Response rate expanded with increment in sulfide focus. General transformation of PCNB (after delayed response run) was found to increment with expansion in alkali focus. ([6], [7] & [8]).

Phase Transfer catalysis (PTC) utilizes reactant measures of stage exchange specialists which encourage interphase exchange of species, making responses between reagents in two immiscible stages conceivable. PTC is utilized broadly as a part of the blend of various natural chemicals in both fluid and strong fluid frameworks. Existing writing on PTC is science intensive and a negligible modest bunch of late articles constitute the whole data on designing investigation. This article audits the field comprehensively by joining the existing information from science with experiences into unthinking and dynamic investigation what's more, numerical displaying of solvent and insoluble PTC. By its very nature, PTC includes a progression of balance and mass-exchange ventures, adjacent to the two fundamental responses. Disregard of mass-exchange impacts can horribly over predict the conversion of a PTC intervened response. A down to earth method for utilizing PTC, which empowers simple partition, is to immobilize the impetus on a strong backing. Mass-exchange impediments and higher expenses, however, have blocked its business utilize as such, obliging further investigation of mass-exchange confinements in these perplexing three-stage frameworks. The utilization of PTC, joined with other rate upgrade strategies like sono chemistry, microwaves, electro organic amalgamation, what's more, photochemistry, is in effect progressively investigated. Applications here in the assembling of natural intermediates and fine chemicals appear to be just about boundless. (Sanjeev D. Naik and L. K. Doraiswamy Dept. of Chemical Engineering, Iowa State University, Ames, IA SO01 1)

For most responses which continue by a bimolecular system, the change happens just when the reactants are in the same stage and proximate to each other. There are unquestionably samples of fruitful heterogeneous responses, cottage these by and large rely on upon some slight solubility of one reactant in the other or of both in a mutual cosolvent. For instance, phenyl acetonitrile would he be able to hydrolyzed by warming a heterogeneous mixture of it and 10% fluid sodium hydroxide arrangement together for two hours (I). As the hydrolysis happens, phase Transfer Catalysis Part I: General principles smelling salts is discharged and the phenyl acetic corrosive salt breaks up in the fluid stage. The achievement of this response relies on upon the slight cabin noteworthy solubility of phenyl acetonitrile in the fundamental watery stage. The perception that 1-chlorooctane would he be able to warmed for quite a long time with a concentrated watery arrangement of sodium cyanide without any result is a case of the disappointment of a heterogeneous response.(George W. Gokel The Pennsylvania State University University Park. 16802**and** William **P.** Weber University of Southern California Los Angeles. 90007]

Chapter 3

EXPERIMENTAL

3.1 CHEMICALS AND CATALYST

Kipp's apparatus which is used in the laboratory for the production of Hydrogen sulphide by reacting ferrous sulphide with sulphuric acid which is further absorbed in MDEA solution. Sulphide content of the particular solution is calculated by iodometric titration method. Other chemicals, including toluene (≥ 99.5 %) was acquired from Merck (India) Ltd., Mumbai. Tetra butyl phosphonium bromide, the catalyst used for the reduction of metachloronitrobenzene was obtained from Sigma Aldrich (India) Ltd., Mumbai. Methyl di ethanolamine (≥98 %) and metachloronitrobenzenes were obtained from Merck (India) Ltd., Mumbai, India. Iron (II) sulphide (FeS) sticks were obtained from Sigma Aldrich, Mumbai, India. Also, the chemicals used for iodometric titration for the calculation of sulphide content i.e., sodium thiosulphate, potassium iodate, potassium iodide, starch powder, sulphuric acid (98 % pure) and sodium hydroxide pellets of analytical grade were obtained from Merck (India) Ltd., Mumbai.

3.2 PREPARATION OF HYDROGEN SULFIDE ABSORBED ALKANOLAMINE

Initially, for getting a H_2S-rich aqueous methyldiethanolamine (MDEA) of approx 30-35 wt% aqueous alkanolamine solution, there is to be added a suitable quantity of desired alkanolamine in distilled water. Then the hydrogen sulfide gas produced in the Kipp's apparatus as shown in the figure, was released into this aqueous alkanolamines in a 250 mL standard gas bubbler. Hydrogen sulfide gas was prepared at laboratory scale in Kipp's apparatus via reacting FeS sticks with H_2SO_4. The concentration of H_2SO_4 was taken as 1 M and the reaction is carried out in Kipp's apparatus.

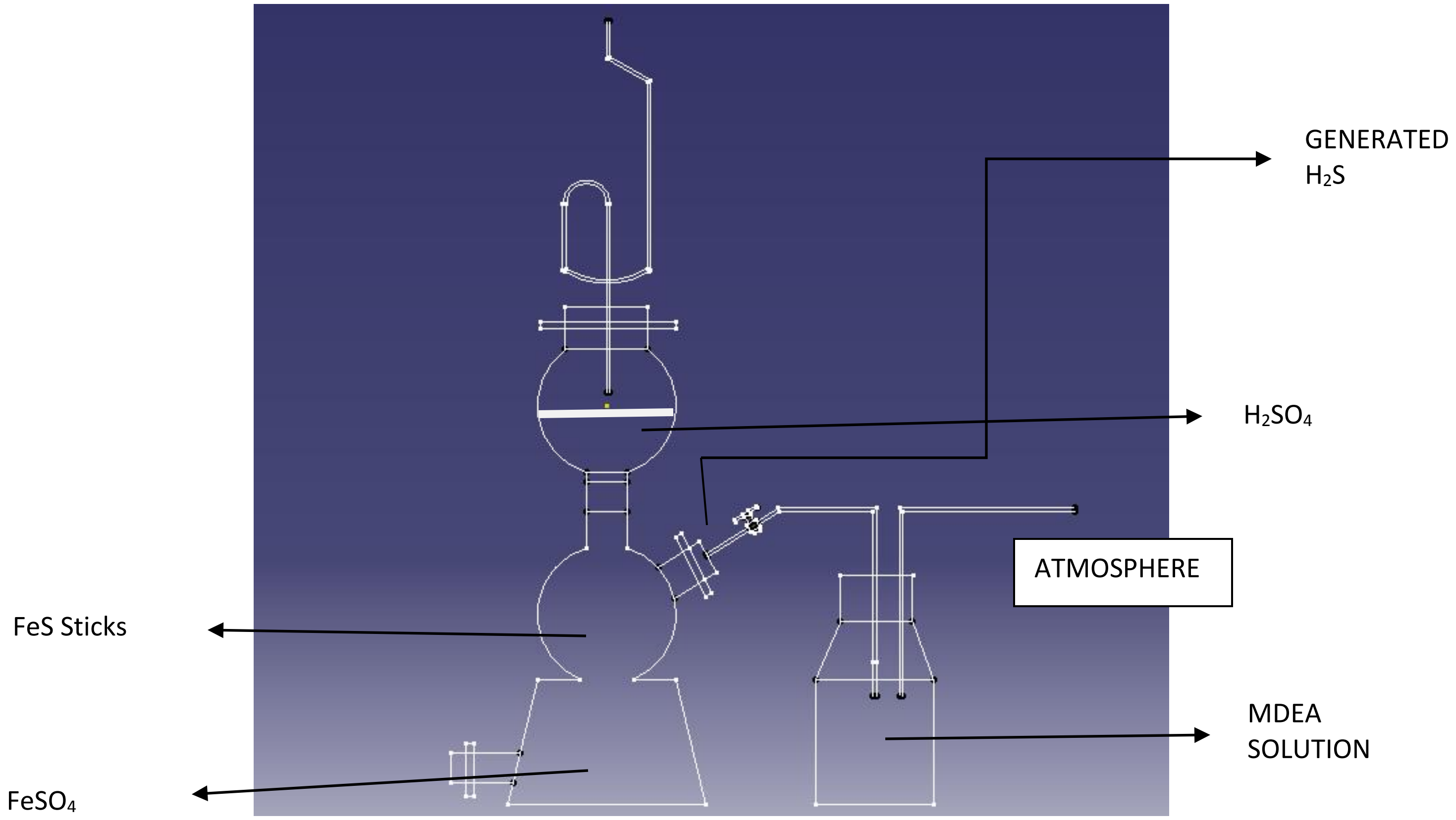


Figure 3.1: Schematic diagram of Kipp's apparatus

The reaction is as follows:

$$FeS + H_2SO_4 \xrightarrow{\text{exothermic reaction}} H_2S\,(g) + FeSO_4$$

As the reaction is an exothermic reaction, it releases a lot of heat. So the bubbler containing alkanolamine should be kept in ice or any cold region in order to prevent the oxidation of sulphide which results in the formation of disulphide. The unabsorbed H_2S gas from the first bubbler was sent to another bubbler containing ~ 1M MDEA solution whose outlet was open to the atmosphere. Liquid samples were withdrawn from at regular intervals of time after the bubbling of gas stopped and the samples were analysed for sulphide content. The quality of sulphuric acid should be checked at regular interval in the kipp's apparatus. As time progresses, the quality of sulphuric acid degrades. So for better production of hydrogen sulfide gas, sulphuric acid should be changed after 2-3 hours.

3.3 DETERMINATION OF SULFIDE CONCENTRATION

Initial sulphide concentrations were determined by standard iodometric titration method (Scott, 1966) as given:

Preparation of standard (0.025 M) KIO_3 solution:

A standard solution is prepared by weighing 4.28 gm of KIO_3 on digital weighing machine and dissolving it in distilled water. The volume was completed up to 1 litre in a graduated volumetric flask.

Preparation of standard (0.1 M) sodium thiosulphate solution:

A standard sodium thiosulphate solution is prepared by weighing 25 gm of $Na_2S_2O_3.5H_2O$ crystals and dissolving it in distilled water. The volume is completed up to 1 litre in a graduated volumetric flask by adding distilled water. About 0.1 g of sodium carbonate or three drops of chloroform is added to this solution to keep the solution for future use up to a few days.

Standardization of sodium thiosulphate solution by standard potassium iodate solution:

25mL of 0.025M KIO_3 solution is taken and 1 gm (excess) of potassium iodide (KI) was added to it followed by 3 mL of 1 M sulphuric acid. The liberated iodine (I_2) was titrated with thiosulphate solution. When the colour of the solution became a pale yellow, it was diluted to 200 mL with distilled water. 2 mL of starch solution is added, and the titration is continued until the colour changed from blue to colourless. The chemical reaction involved in this titration is given below.

$$KIO_3 + 5KI + 3H_2SO_4 \rightleftharpoons 3I_2 + 3H_2O + 3K_2SO_4$$

$$2Na_2S_2O_3 + I_2 \rightleftharpoons Na_2S_4O_6 + 2NaI$$

Therefore, 1 mole of $KIO_3 \equiv 3\times2$ mole of $Na_2S_2O_3$.

$$\therefore Strength\ of\ thiosulfate\ soluton = \left(\frac{6 * strength\ of\ KIO_3 * volume\ of\ KIO_3}{volume\ of\ thiosulfate\ consmed}\right)$$

Estimation of sulphide concentration:

15 mL of standard (0.025M) potassium iodate solution was taken in a conical flask. 10 mL of sulphide solution containing about 2.5 mg of sulphide was then added to it followed by the addition 10 mL of 10M sodium hydroxide solution. The mixture was boiled gently for about 10 minutes, cooled, and 5 mL of KI solution and 20 mL of 4M sulphuric acid solution were added to it. The liberated iodine was titrated, which was equivalent to the unused potassium iodate, with a standard 0.1M sodium thiosulphate in the usual manner. The potassium iodate in the alkaline medium oxidizes the sulphide to sulphate as given by the following reaction. For sulphide solution having sufficiently high sulphide concentration, suitable dilution was made before the estimation of sulphide by above mentioned procedure.

$$4IO_3^- + 6OH^- + 3S^{2-} = 3SO_4^{2-} + 4I^- + 6H_2O$$

$$4\ mole\ of\ IO_3^- \equiv 3\ mole\ of\ S^{2-}$$

$$H_2S\ concentration = \left\{\left[(15 * S_{iodate}) - \frac{(V_{thiosulfate} * S_{thiosulfate})}{6}\right] * \frac{3}{4} * \frac{N_d}{10}\right\}$$

Where S_{iodate}= Strength of KIO_3

$V_{thiosulfate}$ = Volume of thiosulfate

$S_{thiosulfate}$= Strength of thiosulfate

N_d= Number of times of dilution

3.4 REACTOR SETUP

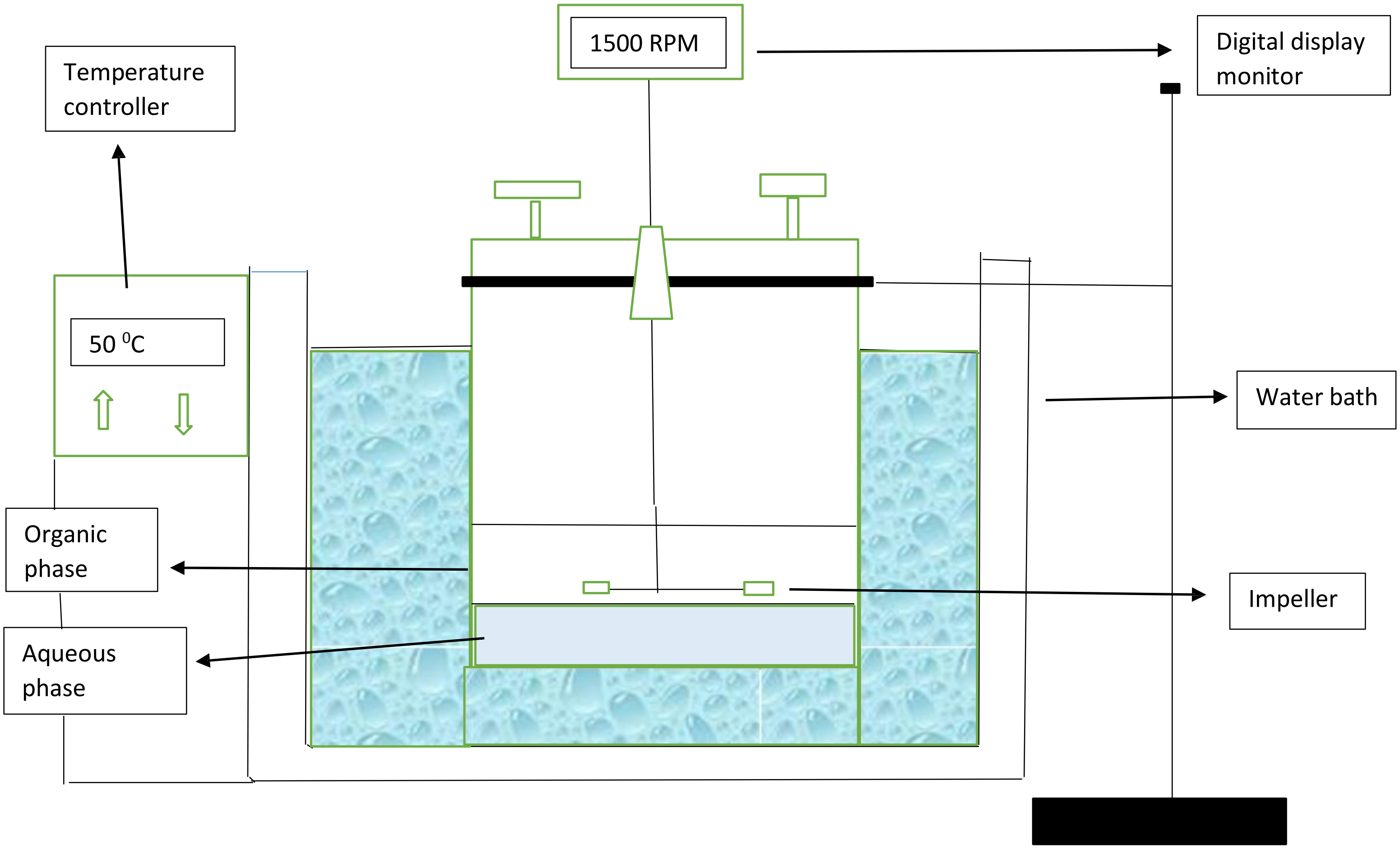


Figure 3.2: Schematic diagram of Reactor

The design of a typical reactor is as shown in the above figure. All the reactions are to be carried out in a thermostated (± 0.5 ^{0}C) three-necked 250-ml (6.5 cm I.D.) in a batch mode equipped in a fully baffled mechanically stirred glass reactor. The reactor is mechanically agitated using a 2.0 cm-diameter six-bladed glass disk turbine impeller the speed of which can be regulated manually. The blades of the stirrer are positioned at a height of 1.5 cm from the bottom which ensures efficient stirring of the reaction mixture. Borosilicate glass beaker would be used as the contactor and three-necked flask, a dropping funnel serving the purposes of agitating the solution, inserting the thermometer, taking samples, and feeding the feed. The motto is to reduce the building up of mass transfer resistance. This arrangement ensures excellent solid-liquid mixing for high mass transfer rate. The reactor assembly is to be kept in a constant temperature water bath whose temperature could be controlled within ± 0.5 ^{0}C and mechanically stirred at a known speed with an electric motor.

3.5 REACTION PROCEDURE

Reaction procedure for meta chloro nitrobenzene reduction:

1. Hydrogen sulfide gas was prepared in the laboratory using Kipp's Apparatus followed by absorption in MDEA solution. The MDEA solution of 30-35 weight% was prepared adding required amount of distilled water to MDEA.

2. Iodometric titration was performed to find out the sulphide ion concentration of hydrogen sulfide absorbed MDEA.

3. Organic phase was prepared by adding toluene to 5 grams of MCNB so that the volume becomes 50 ml.

4. Aqueous phase was prepared by dissolving in 50 ml of H_2S-MDEA solution, along with 0.75 grams of TBPB was taken in the reactor.

5. The organic phase, aqueous phase and the catalyst were fed into the reactor. Aqueous phase was added first followed by organic phase.

6. The reactor was immersed in an isothermal water bath containing balls which will lessen the amount of heat loss.

7. The temperature was maintained at 50 ^{0}C and stirring speed is gradually increased to 1500RPM after the system was switched on.

8. 9 samples of volume 0.1 ml each were collected at 5 min, 10 min, 15 min, 30 min, 60 min, 120 min, 240 min, 360 min and 480 min time duration from the starting time. Before the

collection of the sample, stirring is to be stopped and 5 min time should be allowed for the chemicals inside to settle down into two phases. Then very small amount of organic phase (containing product) should be taken with the help of micro pipette.

9. The product we got must be analysed in the gas chromatograph with great precaution and attention.

10. One variable at a time approach was followed for each experiment. Catalyst concentration, reactant concentration, temperature and stirring speed are varied one at a time for each experiment and all the above steps were repeated for each of the experiment.

3.6 GAS CHROMATOGRAPHY

Chromatography is an advanced analytical device of modern era with the fact that it permits the scientist to partitioned components in a particular mixture for resulting utilization or measurement of the concentration of the compound. Most specimens that scientific experts need to investigate are likely to be mixtures. On the off chance that the strategy for measurement is particular for a given segment in the mixture, detachment is not needed. Nonetheless, it is frequently the case that the indicator is not sufficiently particular, then a separation of constituents should first be performed. Today there are several different types of chromatography techniques, depending on the type of sample involved, are available. The gas chromatograph makes it conceivable to particular the unstable parts of a little sample and to measure the concentration of every part exhibit. The basic components required for the process of gas chromatography to operate are an injection port through which samples are put in to the gas chromatography, a "column" on which the components of sample are separated, a regulated and steady flow of a carrier gas (generally helium or N_2) which conveys the sample through the gas chromatograph, a detector and a data analyser. In gas chromatograph, the particular temperature of the injection port, column, and detector are controlled by thermo-stated radiators.

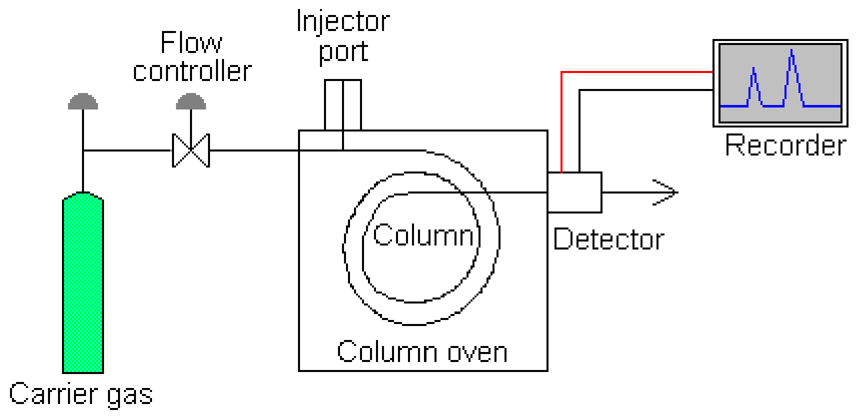


Figure 3.3: schematic diagram of gas chromatograph

Reference:
http://www.google.co.in/imgres?imgurl=http://teaching.shu.ac.uk/hwb/chemistry/tutorials/chrom/gcdiag.gif&imgrefurl=http://teaching.shu.ac.uk/hwb/chemistry/tutorials/chrom/gaschrm.htm&h=206&w=430&tbnid=mhBEA3kPrDUKKM:&zoom=1&tbnh=87&tbnw=184&usg=__pPkgBihslRkEozHsJa82nH0bpJQ=&docid=1Er4jwInNDkb2M&itg=1

In the separation column containing the stationary phase followed by a detector, and a data recording system, the organic compounds are separated due to differences in their partitioning behavior between the carrier gas or mobile gas and the stationary phase in the column. The principle behind it is that component having more affection to the stationary phase will be in the column for more time than the component of sample having less affection to stationary phase.

Chapter 4

OBSERVATION AND RESULTS

4.1 EFFECT OF CATALYST LOADING

OPERATING CONDITIONS:

Volume of organic phase = 50 ml, Volume of aqueous phase = 50ml, concentration of reactant =0.63kmol/m^3, Temperature = 50^{0}C, Stirring Speed = 1500 RPM, Sulphide Concentration = 2.5 kmol/m^3, MDEA concentration = 3.04 kmol/m^3, Concentration of toluene = 8.17 kmol/m^3 Catalyst (TBPB) loading varies from 0 gm to 1.25 grams per volume of organic phase.

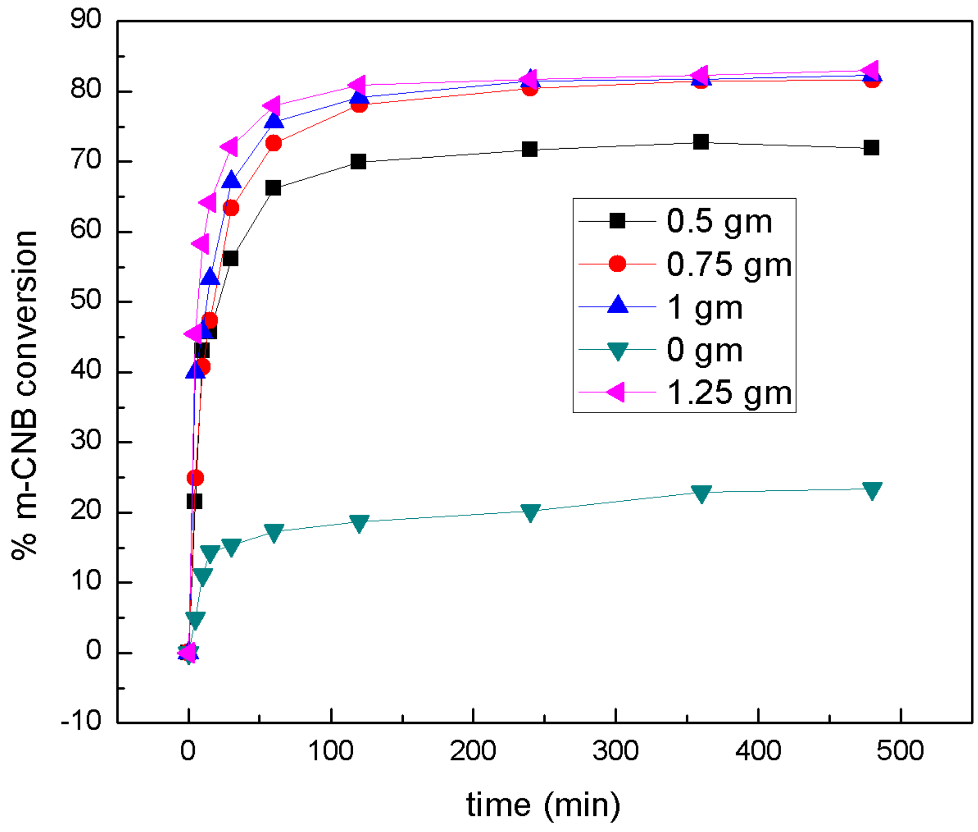


Figure 4.1: Plot of % conversion of m-CNB vs time

In order to find the order of the reaction with respect to catalyst concentration, keeping the concentration of reactant constant, we plot the graph between ln (initial rate of reaction) vs ln (catalyst concentration).

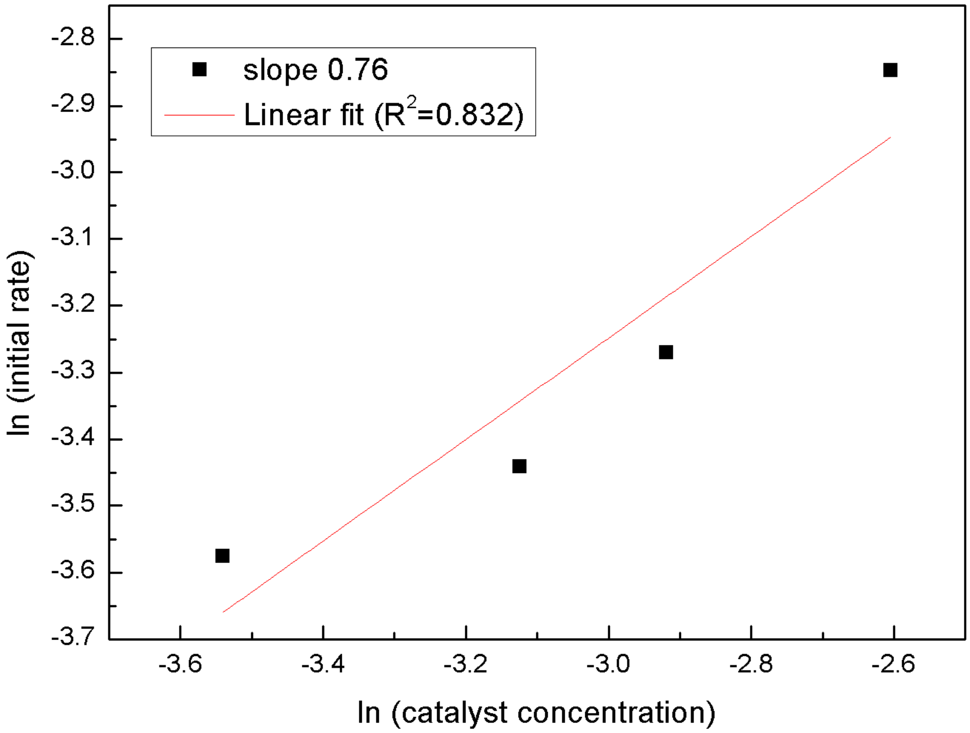


Figure 4.2: Plot between ln (initial rate) vs ln (catalyst concentration)

The slope of the above line comes to be 0.76 which can be approximated to 1. Thus we can say that the order of reaction is 1 with respect to catalyst concentration.

4.2 EFFECT OF REACTANT CONCENTRATION

OPERATING CONDITION:

Volume of organic phase = 50 ml, Volume of aqueous phase = 50ml, Temperature = 50^0C, Stirring Speed = 1500 RPM, Sulphide Concentration = 2.5 kmol/m^3, MDEA concentration = 3.04 kmol/m^3, Concentration of toluene = 8.17 kmol/m^3, Catalyst (TBPB) loading =0.044 kmol/m^3, Concentration of m-CNB varies from 1grams to 7.5 grams per volume of organic phase.

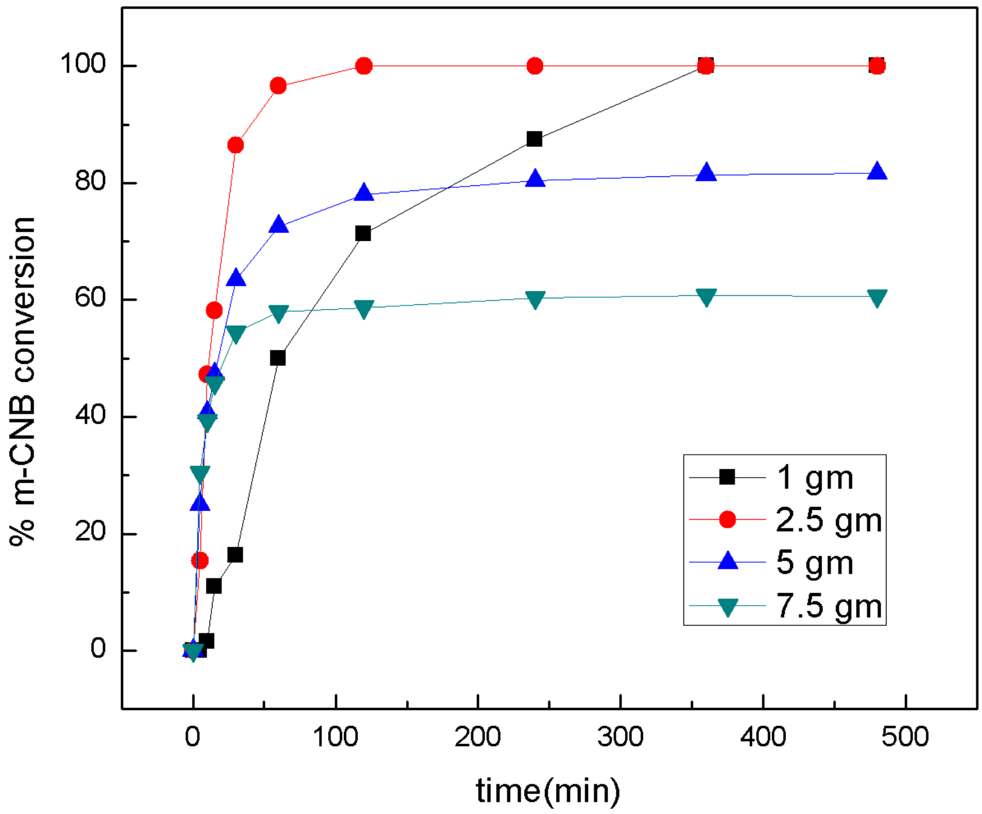


Figure 4.3: Plot of % conversion of m-CNB vs time

Now again in order to find the order of reaction with respect to reactant concentration, we will have to plot the graph between ln (initial rate of reaction) vs ln (reactant concentration).

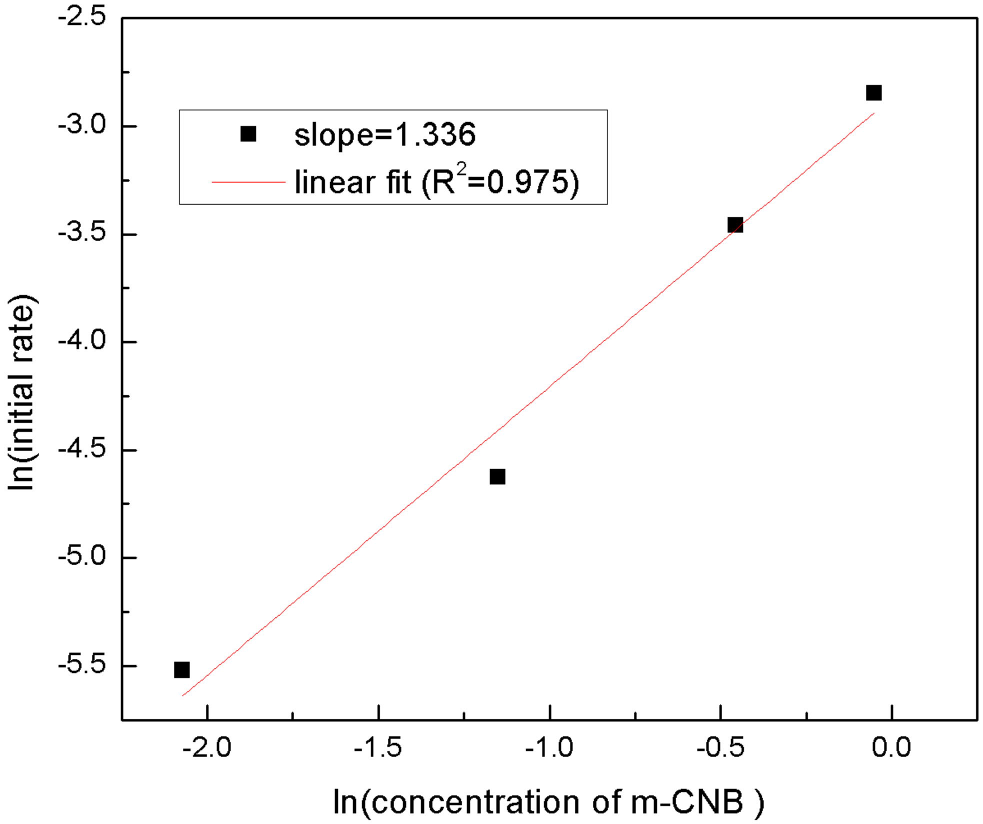


Figure 4.4: Plot between ln (initial rate) vs ln (concentration of m-CNB)

From the above graph, we came to know that the slope of the plot between ln (initial rate of reaction) vs ln (reactant concentration) is 1.336. It can be approximated to1. Thus we can say that the order of reaction is 1 with respect to reactant concentration, keeping the catalyst concentration constant.

4.3 EFFECT OF TEMPERATURE

OPERATING CONDITION:

Volume of organic phase = 50 ml, Volume of aqueous phase = 50ml, Stirring Speed = 1500 RPM, Sulphide Concentration = 2.5 kmol/m^3, MDEA concentration = 3.04 kmol/m^3, Concentration of toluene = 8.17 kmol/m^3, Catalyst (TBPB) loading =0.044 kmol/m^3, Concentration of m-CNB =.0.63 kmol/m^3 and Temperature varies 313 K to 343 K.

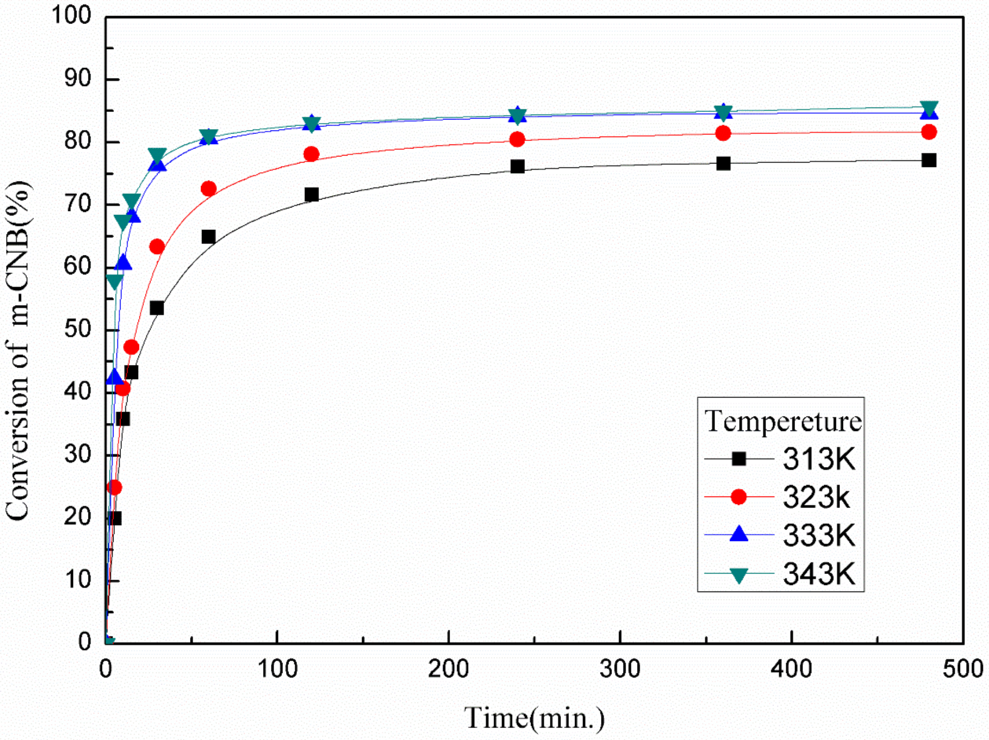


Figure 4.5: Plot of % conversion of m-CNB vs time

Now, the activation energy of the reactant in the reaction can be calculated with the help of Arrhenius plot. Initial rates of reaction were found out for reactions occurring at different temperatures. The ln (natural logarithm) of the initial rates were plotted against 1/T. The slope of the line obtained is negative and equal to E/R, where E is the activation energy and R is the universal gas constant.

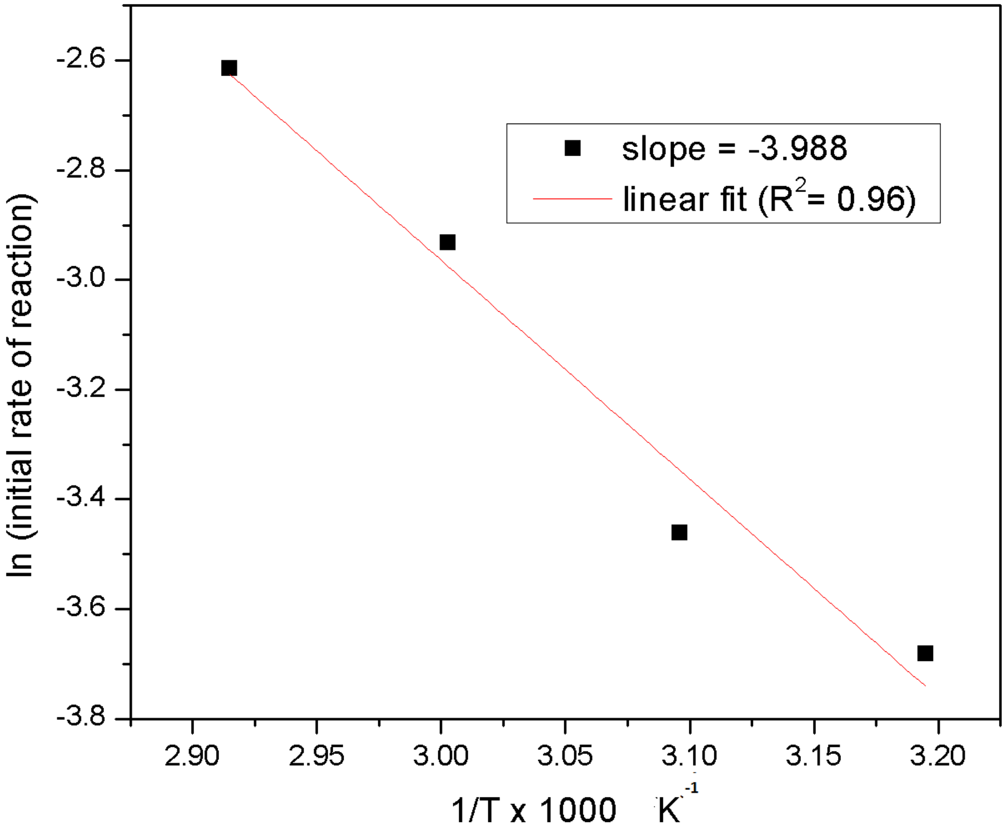


Figure 4.6: plot between ln (initial rate of reaction) vs 1/T x 10^3 K^{-1}

From the above graph, the slope is coming out to be -3.988. Now we multiply it with R (universal gas constant) = 8.31 KJ/mol to get the activation energy of reaction which is 33.14 KJ/mol.

4.4 EFFECT OF STIRRING SPEED

OPERATING CONDITION:

Volume of organic phase = 50 ml, Volume of aqueous phase = 50ml, Sulphide Concentration = 2.5 kmol/m^3, MDEA concentration = 3.04 kmol/m^3, Concentration of toluene = 8.17 kmol/m^3, Catalyst (TBPB) loading =0.044 kmol/m^3, Concentration of m-CNB =.0.63 kmol/m^3 and temperature = 323 K and stirring speed varies from 500 to 2500 RPM.

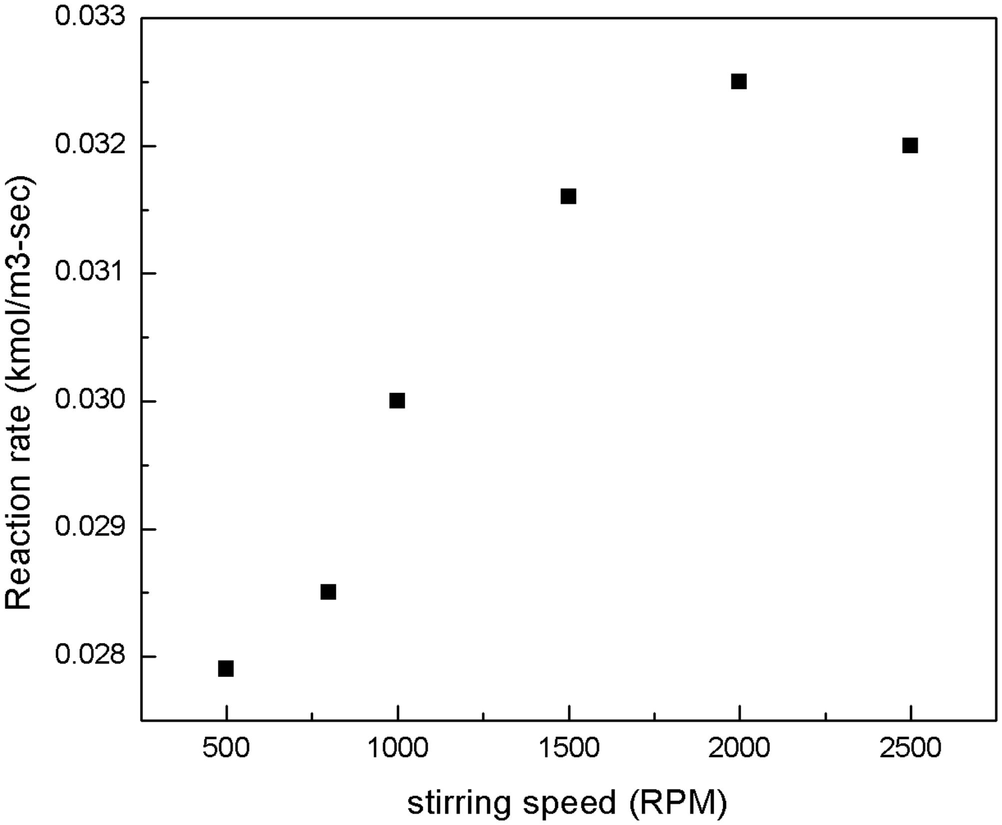


Figure 4.7: Plot of reaction rate vs stirring speed

From the above graph, it can be concluded that reaction rate is highest at 2000 RPM. After 2000 RPM, the reaction rate starts to decrease. So, we should the reaction with all other variation at

2000 RPM. But 2000 RPM is not ideal from survey. So I have taken 1500 RPM in all the reaction performed during the experiment.

Chapter 5

CONCLUSION

The reduction of metachloronitrobenzene by aqueous methyldiethanolamine solution to the corresponding chloroanilines under Liquid-liquid mode PTC in presence of TBPB phase transfer catalyst was experimented and analysed. The chloroanilines was our main product to be found in the organic phase after reaction.

The effect of various parameters on the rate of reactions and conversion of MCNB to MCA was studied in detail.

Figure 4.3 shows that the overall conversion decreases with increase in the reactant concentration except at 0.126 kmol/m^3 concentration whereas the initial rates of the reaction increases with increase in the reactant concentration for reactant concentration between 0.126 kmol/m^3 to 0.952 kmol/m^3. The graph of reactant concentration 0.126 kmol/m^3 has not came ideal. The conversion was initially slow and later it became fast or due to some error the graph has not came good.

From figure 4.7, stirring speed does not much affect the conversion of reactants. The reaction rate was observed to be maximum at 2000 RPM stirring speed. But it was low at lower stirring speed. Hence the mass transfer factor was negligible at lower stirring speed. But increasing the stirring speed above 2000 RPM will also results in lower reaction rate. It can be explained by collision theory that as we increase the stirring speed, the probability of collision of reactant molecule becomes less and less thus reducing the rate of reaction. Stirring speed of 1500 RPM was maintained for all other reactions with different parameters under observations.

The activation energy for metachloronitrobenzene was found to be 33.14 KJ/mol. It is minimum energy required for the reaction to take place. According to figure 4.5, with the increase in temperature from 313 K to 343 K, the conversion has increased. Increase in temperature might have caused the increase in molecular collision between reactants molecule thus increasing the conversion.

From figure 4.3, it is quite evident that increase in catalyst concentration increases the the conversion of reactant. The conversion for 0.75, 1.0, 1.5 grams catalyst per volume of organic phase is nearly same after 250 minutes. Thus it can be deduced that more the number of catalyst particle more will be the probability of interface transfer of ions thus reaction and thus conversion.

Removal of H_2S gas from environment is required for health and safety purpose. Corrosion during the transmission in oil refinery and distribution also. Hydrogen sulfide is also a greenhouse gas which can serious environmental as well as health problems.

Chloroanilines are important constituent chemicals used in the chemical industry for the manufacture of pesticides, drugs, and dyestuffs.

Therefore, the reduction of metachloronitrobenzene to chloroaniline using Hydrogen sulphide absorbed in alkanolamine via phase transfer catalyst will help us a get a very useful product and also saves the environment. That is why , this process is a green process.

Chapter 6

FUTURE SCOPE OF THIS PROJECT

This chapter will tell us on the future scope of the project and what are the parameter which has been left.

The reduction of metachloronitrobenzene was done with the help of H_2S rich aqueous alkanolamine (MDEA) solution in presence of a liquid-liquid phase transfer catalyst, Tetra butyl phosphonium bromide. The present work was carried out for the determination of the effects of process parameter like concentration of the reactant, catalyst concentration, temperature and stirring speed.

The effect of other parameters could have been found out which are also necessary for determining the dependence of reaction rate and conversion % on those parameters. Few of the other parameters which can be found out are

1. Effect of pH
2. Effect of sulphide variation
3. Effect of MDEA variation

Other people can use another solvent. In this work, toluene has been used as the solvent. The role of solvent is major in governing the rate of the reaction as it affects the interface transport properties of the phase transfer catalyst and the active reactant sites. Higher molecular weight hydro carbon or any hydrocarbon which is liquid at the room temperature can also be used as the solvents in future reactions.

Methyl di ethanolamine solution was used in the present work to absorb hydrogen sulphide. Other aqueous solutions of monoethanolamine and diethanolamine can also be used to absorb hydrogen sulphide to carry out the reaction.

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