

**SOLVENT FREE SYNTHESIS OF DIBENZYL SULFIDE USING
H₂S-RICH MONOETHANOLAMINE AND SOLUBLE PTC**

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THE DEGREE OF

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IN
CHEMICAL ENGINEERING**

**BY
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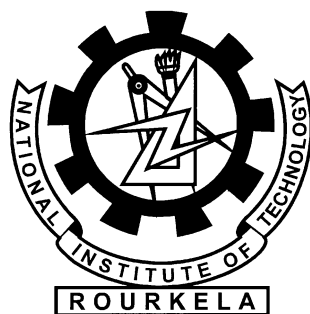
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2012



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CERTIFICATE

This is to certify that the seminar report titled “Solvent free synthesis of Dibenzyl Sulfide using H₂S rich Monoethanolamine under two phase transfer catalysis” submitted by Partha Pratim Panda bearing Roll no. 108CH019 in partial fulfillment of the requirements for the prescribed curriculum of Bachelor of Technology in Chemical Engineering Session 2008-2012 in the Department of Chemical Engineering, National Institute of Technology, Rourkela is an authentic work to the best of my knowledge and belief.

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Last but not the least, I offer my gratitude to the least acknowledged “Internet” without which this report would not have seen the light of the day.

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ABSTRACT

With the depletion of crude oil reserves, oil refineries are being forced to process sour crude which is high in sulfur content. Sulfur, if not removed from the system may corrode the system or may lead to unwanted side reactions which would entail consumption of reactants and energy. Usually the sulfur is removed by absorption in ammonia solution which is further processed in a Claus Unit to produce elemental sulfur which requires a high amount of energy. Also, the supply of elemental sulfur usually outstrips demand thereby eroding the profit margins. With a view to making more sophisticated fine chemicals which have higher usability and better market value, this project was undertaken to study the kinetics of the solvent-free synthesis of dibenzyl sulfide was carried out using H₂S-rich monoethanolamine under two phase transfer catalysis with a phase transfer catalyst (PTC), polyethylene glycol (PEG). The effects of different parameters, such as speed of agitation, temperature, monoethanolamine concentration, catalyst concentration, initial sulfide concentration and concentration of benzyl chloride, on the conversion and reaction rate of benzyl chloride were studied to establish the mechanism of the reaction.

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NOMENCLATURE

- MEA- Mono Ethanol Amine
- PTC- Phase Transfer Catalyst
- PEG- Polyethylene Glycol
- DBS- Dibenzyl sulfide
- BM- Benzyl Mercaptan
- BC- Benzyl Chloride

Chapter 1

Introduction

1. INTRODUCTION

1.1 Sources of Hydrogen Sulfide

Human activity accounts for about 10% of global H₂S emissions and this is rising at a steady pace. By far the largest contributor to these emissions is the petroleum industry which accounts for almost 80% of total emissions. Natural gas can contain up to 90% hydrogen sulfide. The hydrodesulfurization process is used to remove sulfur with the help of hydrogen gas in which large quantities of hydrogen sulfide and ammonia are produced. With the gradual decline of light and easy-to-process crude oils, refineries throughout the world are forced to process heavy crudes containing high amount of sulfur and nitrogen. In addition, refineries have to hydrotreat such crudes to bring down the sulfur levels to those prescribed by environmental protection agencies. During hydrotreatment of heavy and sour crude, large quantities of ammonium sulfide and ammonia are produced. Though coal gas contains very low amounts of hydrogen sulfide, the absolute quantities become significant in the wake of increase in coal gas production. Other man-made are tanneries, coke ovens and paper mills.

1.2 Need for treating H₂S laden gas

With increased environmental activism and sensitization, refineries all over the world are looking at decreasing their hydrogen sulfide emissions.

Table 1. Exposure Limits: US Department of Labour

Occupational Health and Safety Administration (OSHA) Permissible Exposure Limit (PEL) for general industry	10 ppm
American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV)	10 ppm

National Institute of Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL)	10 ppm
NIOSH Immediately Dangerous to Life or Health Concentration (IDLH)	100 ppm

Some of the compelling reasons for reducing the presence of hydrogen sulfide are:

- Hydrogen Sulfide is a toxic and highly flammable gas and being heavier than air, it tends to accumulate at the bottom of poorly ventilated spaces. Although very pungent at first, it quickly nullifies the smelling capability, thus afflicted victims may be unaware of its presence until its concentration becomes fatal. For safety issues related to handling, an appropriate material safety data sheet (MSDS) should be consulted. The prescribed standards by different American agencies are given in **Table 1**.
- H₂S is odiferous in nature, corrosive in the presence of water and poisonous in very small concentrations. Therefore, it must almost completely be removed from the gas streams before use and preferably before transport.
- The presence of H₂S in the refinery gas streams can cause a number of detrimental problems in subsequent processing steps such as corrosion of process equipment, deterioration and deactivation of the catalysts, undesired side reactions, increase in the process pressure requirements, and increase in the gas compressor capacity, etc.
- The supply of elemental sulfur highly outstrips the demand, therefore the price of sulfur is very low in the market and thus it doesn't make business sense to produce it by spending large amounts of men and money.

1.3 Industrial Processes for Removal and Recovery of H₂S

A number of industrial processes have been developed to remove hydrogen sulfide and bring it within acceptable limits to conform to strict environmental regulations. Hydrogen sulfide

being weakly acidic, its removal can be effected by the use of an alkaline solution. Since strong alkaline solutions like potassium hydroxide react irreversibly with hydrogen sulfide, it is prudent to use a weakly alkaline solution which can be regenerated and used again and again.

1.3.1 Ammonia-based Process

Use of aqueous ammonia in removal of H_2S (sometimes along with NH_3) from gas streams had been well practiced ^{[13][14]}. Gas streams containing both H_2S and NH_3 pass through a H_2S scrubber and an NH_3 scrubber in series. Stripped water is fed to the top of the NH_3 scrubber where it absorbs NH_3 from the gas. The resulting NH_3 solution is then used as absorbent for H_2S in the H_2S scrubber. The rich solution, from this unit containing ammonium sulfide in solution, is fed to a deacidifier, which decomposes the ammonium sulfide to produce H_2S rich vapor and NH_3 rich liquor. The use of ammonia to remove hydrogen sulfide and carbon dioxide from gas streams has declined in recent years; however, the process is still used to desulfurize coke-oven gas in a number of installations.

There are a few notable advantages with the NH_3 -based process over amine-based process ^[15].

- The NH_3 -based process is suitable for gas streams containing both H_2S and NH_3 , as simultaneous removal of NH_3 is obvious in this process. Moreover, for the gas streams containing both H_2S and NH_3 , the removal of both impurities could be done in a single step in the ammonia-based process instead of two steps as in the case of alkanolamine-based process (NH_3 removal by water scrubbing followed by H_2S removal through the amine treating unit).

- The rate of absorption of H₂S into aqueous NH₃ solution is rapid and dependent upon the concentration of NH₃. Therefore, with adequate NH₃ concentration at the interface, it is possible that the gas film resistance governs the rate of absorption of H₂S. On the other hand, absorption of CO in weak alkaline solution like aqueous NH₃ is considered typical of a liquid film controlled system. The result is that when gases containing both H₂S and CO₂ are contacted with aqueous NH₃ solution, the H₂S is absorbed much more rapidly than the CO₂. Yet another aspect is that once in solution, the CO₂ is stronger acid than H₂S and under equilibrium conditions, process would actually be expected to be selective for CO₂. Therefore, by using aqueous NH₃, the selective absorption of H₂S or CO₂ is possible from the gases containing both H₂S and CO₂. By the use of spray column in combination with short contact time can lead to the selective absorption of H₂S from the gas mixture containing both CO₂ and H₂S.
- NH₃ has the advantage for such applications being essentially unaffected by the presence of carbonyl sulfide (COS), carbon disulfide (CS₂) and hydrogen cyanide (HCN).

Despite these advantages, the use of ammoniacal scrubbing has not been universally accepted in the gas treating art as the preferred method for removing H₂S from a gas stream. This is primarily because of a number of operational difficulties associated with its implementation^[13], such as:

- High partial pressure of NH₃ forces the scrubbing step be conducted with relatively dilute NH₃ solutions or at relatively high pressures or a separate water wash step after the NH₃ scrubbing step in order to remove NH₃ from the treated gas stream. In addition, the use of dilute scrubbing solutions typically increases substantially the

regeneration costs where the regeneration step is conducted at a considerably higher temperature than the scrubbing step.

- Another difficulty is associated with the regeneration of the rich absorbent solution withdrawn from the scrubbing step. Several regeneration procedures have been proposed but they typically involve the use of soluble catalysts such as hydroquinone and have had problems such as contamination of the sulfur product with the catalyst, excessive formation of side products such as ammonium sulfate and thiosulfate and loss of scrubbing solution and catalyst during the periodic purges that are generally required to remove side products from the system. Other difficulties have been associated with the recovery of the elemental sulfur from the regeneration step where it has been customary to form a froth of sulfur, which then must be skimmed off and filtered.

1.3.2 Alkanolamine-based process

Although both ammonia and alkanolamine-based processes are in use for the removal of acid gas constituents (H_2S and CO_2) from gas streams, alkanolamine-based process got wide commercial acceptance as the gas treating art because of its advantages of low vapor pressure (high boiling point) and ease of reclamation. The low vapor pressure of alkanolamines makes the operation more flexible in terms of operating pressure, temperature, and concentration of alkanolamine in addition to the negligible vaporization losses.

The basic flow diagram of amine-based acid gas removal process is shown in Figure 1. Treatment with alkanolamines involves circulating gas stream upward through the absorber, countercurrent to the stream of aqueous alkanolamine solution. The rich solution from the bottom of the absorber is heated by heat exchange with lean solution from bottom of the stripping column and is then fed to the stripping column where the absorbed gases are

stripped off from the alkanolamine solution. The regenerated alkanolamine is then recycled to the absorber. The concentrated hydrogen sulfide off gas obtained from the top of the stripping column is then subjected to S recovery or disposal.

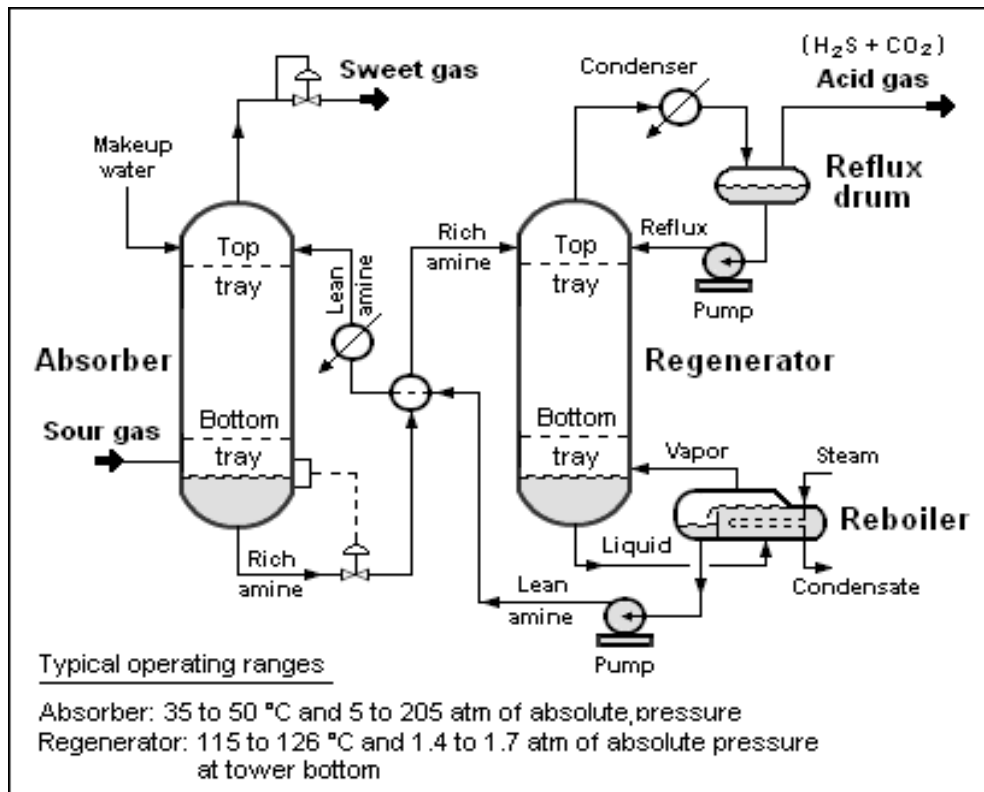


Figure 1: Schematic flow diagram of the amine gas treating process

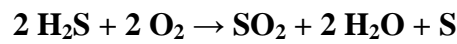
1.4 Sulfur recovery from H₂S

1.4.1 The Claus Process

The Claus process is the most significant gas desulfurizing process, recovering elemental sulfur from gaseous hydrogen sulfide. First patented in 1883 by the scientist Carl Friedrich Claus, the Claus process has become the industry standard.

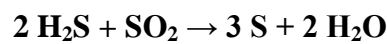
H₂S gas separated from the host gas stream using amine extraction is fed to the Claus unit (Figure 2), where it is converted in two steps:

- 1. Thermal Step:** The H₂S-laden gas reacts in a sub-stoichiometric combustion with air. This is done in a reaction furnace at high temperatures (1000 – 1400°C). Claus gases (acid gas) with no further combustible contents apart from H₂S are burned in burner by the following chemical reaction:



This is a strongly exothermic free-flame total oxidation of hydrogen sulfide generating sulfur dioxide that reacts away in subsequent reactions. The air to the acid gas ratio is controlled such that in total 1/3 of all hydrogen sulfide (H₂S) is converted to SO₂. This ensures a stoichiometric reaction for the Claus reaction in the second catalytic step.

- 2. Catalytic Step:** The reaction gases leaving the sulfur condenser are reheated to 200-350°C and fed to a series of catalytic converters and sulfur condenser where H₂S react with SO₂ to produce elemental sulfur:



The catalyst used in the catalytic converter is normally either activated aluminum (III) or titanium (IV) oxide.

Inevitably a small amount of H₂S remains in the tail gas. This residual quantity, together with other trace sulfur compounds, is usually dealt with in a tail gas unit. The latter can give overall sulfur recoveries of about 99.8%, which is very impressive indeed. Sulfur is used for manufacturing sulfuric acid, medicine, cosmetics, fertilizers and rubber products. Elemental sulfur is used as fertilizer and pesticide.

However, the Claus process has a number of inherent disadvantages ^{[16] [17] [18]}. For example:

- It operates at high temperatures.
- It requires exact process control over the ratio of oxygen to H₂S in the feed.
- The valuable hydrogen energy is lost in this process.
- It requires expensive pretreatment of the feed gas if CO₂ is present in high concentrations. At least a portion of the CO₂ must be removed from the byproduct gas by pretreatment before oxidizing the H₂S to maintain the efficiency of the oxidation process.
- The sulfur content of Claus process tail gas released to the atmosphere is generally too high to meet stringent environmental regulations. To comply with these regulations, it is necessary to add more Claus stages and/or employ a separate tail gas cleanup process at great expense.

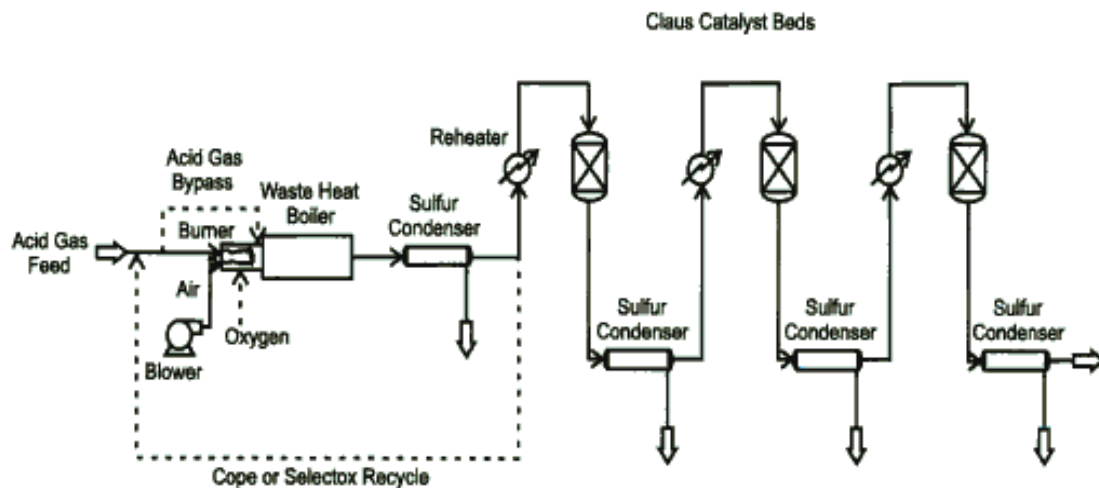


Figure 2: Claus Process

1.4.2 CrystaSulf Process

CrystaSulf is a chemical process used for removing hydrogen sulfide from natural gas, synthesis gas and gas streams in refineries and chemical plants. CrystaSulf uses a liquid phase Claus reaction to convert the hydrogen sulfide (H_2S) into elemental sulfur which is then removed from the process by filtration. This process is used in the energy industry as a one-step alternative to Amine–Claus process.

1.4.3 Wet-oxidation LO-CAT Process

In the LO-CAT process, hydrogen sulfide is converted to elemental sulfur using an environmentally safe chelated iron catalyst. The iron catalyst is held in solution by organic chelating agents that wrap around the iron ions in a claw like fashion, preventing precipitation of either iron sulfide (FeS) or iron hydroxide ($\text{Fe}(\text{OH})_3$). According to this process, the hydrogen sulfide, absorbed into the slightly alkaline, aqueous LO-CAT solution (pH 8.0-8.5), is oxidized to elemental sulfur by reducing the iron ions from the ferric to the ferrous state. The reduced iron ions are then transferred from the absorber to the oxidizer where the ferrous iron is re-oxidized to ferric iron by atmospheric oxygen, absorbed into the LO-CAT solution, thus regenerating the catalyst.

1.5 Present Work

The present work was undertaken to develop an alternative process (alternative to Claus or LO-CAT process) for better utilization of H_2S present in various gas streams. The present work deals with the production of value-added chemicals utilizing the H_2S present in various byproduct gas streams obtained from different chemical industries. In accordance with the present process, value-added chemicals were produced from the H_2S -rich aqueous ammonia or alkanolamine that could be obtained from scrubbing step of the corresponding ammonia-

or alkanolamine-based process. In other words, the removal of H₂S was assumed to be done by conventional process. The present investigations are devoted to:

- Synthesis of value-added fine chemicals like dibenzyl sulfide, benzyl mercaptan, and aryl amines using the H₂S-rich aqueous ammonia and/or alkanolamines under two phase (liquid-liquid) conditions in the presence of a phase transfer catalyst (PTC), polyethylene glycol (PEG).
- Study the influence of process variables (stirring speed, catalyst loading, concentration of reactant, and temperature, alkanolamine concentration, elemental sulfur loading) on the conversions organic reactants and selectivity of various products.
- Establish a suitable mechanism or stoichiometry utilizing the effects of various parameters on the reaction rate and conversion, to explain the course of the reaction.
- Kinetic modeling of the above mentioned commercially important reactions and estimation of the model parameters.

1.6 Phase Transfer Catalysis

Phase transfer catalysts (PTC) are widely used to intensify otherwise slow heterogeneous reactions involving an organic substrate and an ionic reactant, either dissolved in water (liquid-liquid) or present in solid state (solid-liquid).

Phase transfer catalysis is now an attractive technique for organic synthesis because of its advantages such as

- Simplicity of process
- Reduced consumption of organic solvent and raw materials
- Mild operating conditions
- Enhanced reaction rates

- Better selectivity

Among several varieties of PTCs, quaternary ammonium salts have been reported to be the most active PTC among different catalysts used. But the usage of Poly-Ethylene Glycol (PEG) for the synthesis of Dibenzyl Sulfide has not been reported in literature. Present study was therefore carried out using PEG as PTC.

Two mechanisms, interfacial and extraction, are generally used to explain the liquid-liquid phase transfer catalysis based on the lipophilicity of the quaternary cation. The extraction mechanism (Figure 3) is applicable to catalysts that are not highly lipophilic or that can distribute themselves between the organic and the aqueous phase, such as benzyltriethylammonium, dodecyltrimethylammonium, and tetrabutylammonium salts ^{[19] [20]}. In the interfacial model, catalysts such as tetrahexylammonium and trioctylmethylammonium salts remain entirely in the organic phase because of their high lipophilicity, and exchange anions across the liquid-liquid interface ^[21].

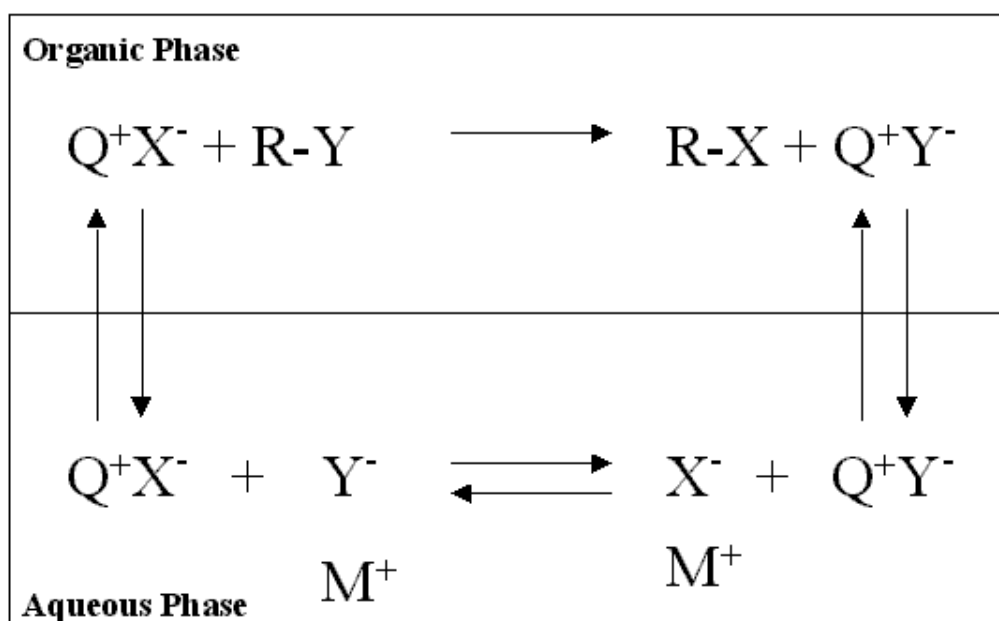


Figure 3: Schematic representation of extraction mechanism

Table 2. Commonly used PTCs^[12]

Catalyst	Cost	Stability and Activity	Use and Recovery of Catalyst
Ammonium Salts	Cheap	Moderately stable under basic conditions and up to 100°C. Moderately active	Widely used. Recovery is relatively difficult.
Phosphonium Salts	Costlier than ammonium salts	More stable thermally than ammonium salts, although less stable under basic conditions.	Widely used. Recovery is relatively difficult.
Crown ethers	Expensive	Stable and highly active catalysts both under basic conditions and at higher temperatures up to even 150-200 °C	Often used. Recovery is difficult and poses environmental issues due to their toxicity.
Cryptands	Expensive	Stable and highly reactive, except in the presence of strong acids.	Used sometimes despite high costs and toxicity, due to higher reactivity.
PEG	Very cheap	More stable than quaternary ammonium salts, but lower activity.	Often used. Can be used when larger quantities of catalyst cause no problems. Relatively easy to recover.

1.7 Polyethylene Glycol (PEG)

Environment has become the buzzword in the past decade and no field of science has remained untouched. These days the focus has shifted to not only increase the productivity but also doing it in such a way so as to have minimum adverse impact on the environment. Organic reactions without the use of harmful organic solvents are now of great interest in organic synthesis. Attempts have been made to develop solvent-free chemistry, which to some extent have been successful in a few transformations. PTCs like TBAB are very difficult to recover and reuse and are harmful to the environment. With that concern in view,

the focus has been the use of environment friendly catalysts such as polyethylene glycol. ^[11] PEG and its monomethyl ethers are inexpensive, thermally stable, recoverable, and nontoxic media for phase-transfer catalysts. PEG, a biologically acceptable polymer used extensively in drug delivery and in bioconjugates as tool for diagnostics, has thus far not been widely used as a PTC but has been used as a support for various transformations. ^[11]

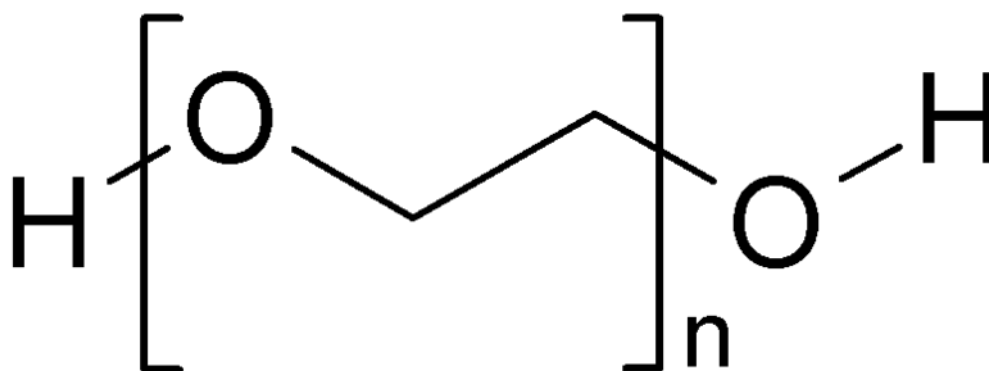
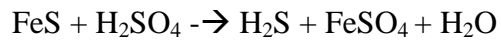


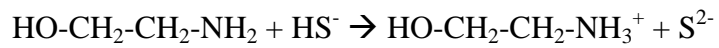
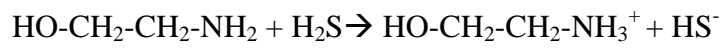
Figure 4: Structure of Polyethylene Glycol (PEG)

1.8 Reactions

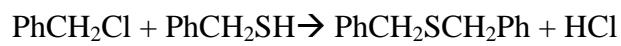
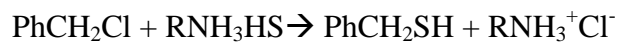
Generation of H₂S:



H₂S absorption in MEA:



Reactions:



Chapter 2

Literature Survey

2. LITERATURE SURVEY

Maity et al. (2006) have synthesized toluidine by the reduction of nitrotoluenes using aqueous ammonium sulfide under liquid–liquid phase transfer catalysis in the presence of TBAB as catalyst. They also studied the kinetics of reduction of nitrotoluenes by H₂S rich ethanolamine using TBAB and also carried out reduction of o-nitroanisole to o-anisidine by H₂S-rich aqueous diethanolamine.

Yadav and Badure (2007) studied the role of third phase in the intensification of reaction rates and selectivity in phase transfer catalyzed synthesis of benzyl phenyl ether.

Pradhan and Sharma (1992) studied the solid-liquid reactions of benzyl chloride with Solid sodium sulfide catalyzed by alumina and ion exchange resin.

Maity et al. (2007) studied the effects of various process parameters on conversion and selectivity associated with the synthesis of dibenzyl sulfide by the reaction between benzyl chloride and aqueous ammonium sulfide using TBAB as a phase transfer catalyst.

Sen et al. developed a mechanistic model for the reaction of benzyl chloride with aqueous ammonium sulfide in the presence of TBAB as a phase transfer catalyst.

It is evident from the above discussion that there is hardly any information in the literature on the reduction of benzyl chloride by the use of H₂S rich MEA and PEG as a phase transfer catalyst. Considering the importance of the system, a detailed study was therefore performed, and is reported in the present work, on the reduction of benzyl chloride to produce commercially important dibenzyl sulfide. The effects of various parameters on the reaction rate and conversion were studied to establish the mechanism and the stoichiometry of the

reaction. A generalized empirical kinetic model applicable for all the benzyl chloride was also developed to correlate the experimental data.

Chapter 3

Experimental Setup

3. EXPERIMENTAL SETUP

3.1 Chemicals

Toluene ($\geq 99\%$) was procured from RFCL Limited, New Delhi, India. Monoethanolamine was procured from Loba Chemie (India) Pvt. Ltd., Mumbai, India. Benzyl Chloride ($>99\%$) was obtained from Merck (India) Ltd., Mumbai, India. PEG-600 ($> 99\%$) was procured from ThermoFisher Scientific India Ltd., Mumbai, India. H_2SO_4 (98%) and NaOH pellets (97%) were procured from Merck (India) Ltd., Mumbai, India. $\text{Na}_2\text{S}_2\text{O}_3$ ($\geq 99\%$), KI ($\geq 99.2\%$) and KIO_3 ($\geq 99.5\%$) were also obtained from Merck (India) Ltd., Mumbai, India.

3.2 Equipment

All the reactions were carried out in batch mode in a fully baffled mechanically agitated glass reactor of capacity 250 cm³ (6.5 cm i.d.). A 2.0 cm-diameter six-bladed glass disk turbine impeller with the provision of speed regulation, located at a height of 1.5 cm from the bottom, was used for stirring the reaction mixture. The reactor assembly was kept in a constant temperature water bath whose temperature could be controlled within $\pm 1^\circ\text{C}$. The schematic diagram of the experimental setup is as shown in Figure 6.

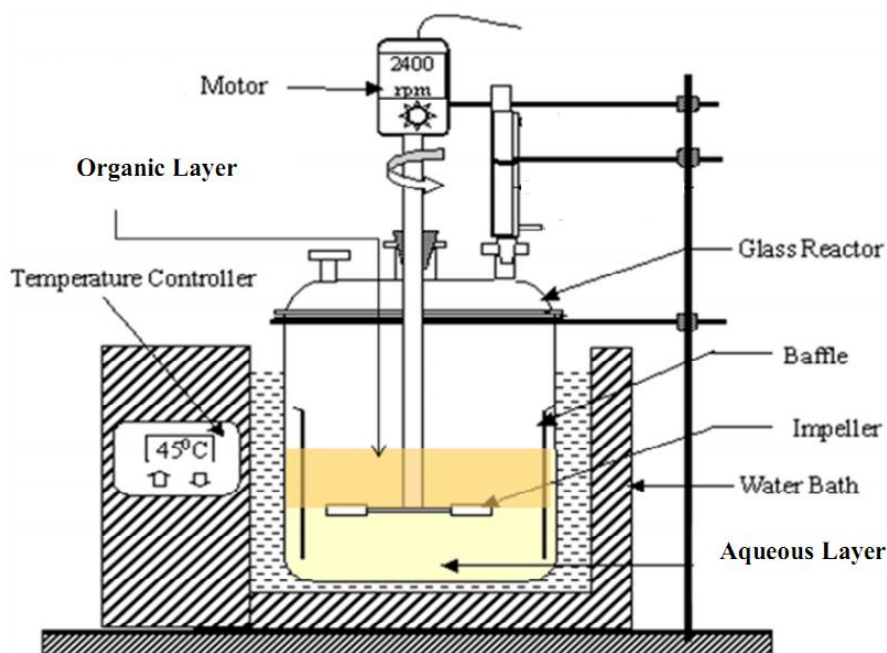


Figure 5. Batch Reactor Assembly

3.3 Preparation of H₂S-rich Monoethanolamine

For the preparation of H₂S-rich aqueous monoethanolamine (MEA), around 30-35wt% aqueous alkanolamine solution was prepared first by adding a suitable quantity of desired alkanolamine in distilled water. Then H₂S gas was bubbled through this aqueous ammonium sulfide or aqueous alkanolamines in two 50 cm³ standard gas bubblers connected in series. Since the reaction of H₂S with ammonium hydroxide and with alkanolamines is exothermic (Kohl and Nielsen, 1997), the gas bubbler containing aqueous alkanolamine was kept immersed in an cold water bath in order to prevent the oxidation of sulfide and thus to prevent the formation of disulfide. The unabsorbed H₂S gas from the first bubbler was sent to another bubbler containing 1M sodium hydroxide solution whose outlet was open to the atmosphere. The gas bubbling was continued until the bubbling had stopped in both the gas bubblers.

3.4 Experimental Procedure

In a typical experimental run, 50 cm³ of aqueous phase containing a known concentration of H₂S-rich Monoethanolamine was charged into the reactor and kept well agitated until the steady state temperature was reached. Then 50 cm³ of the organic phase containing measured amount of organic reactant (benzyl chloride) and catalyst (PEG) kept separately at the reaction temperature, was charged into the reactor. The reaction mixture was then agitated at a constant speed of stirring. About 0.5 cm³ of the organic layer was withdrawn at a regular time interval after stopping the agitation and allowing the phases to separate.

3.5 Analysis

3.5.1 Analysis of organic phase

All samples from the organic phase were analyzed by gas liquid chromatography (GLC) using a 2 m × 3 mm stainless steel column packed with 10% OV-17 on Chromosorb W (80/100). A Chemito Model 8610 GC was used for the analysis. An FID detector was used with nitrogen as the carrier gas during the analysis.

3.6 Determination of Sulfide Concentration

Initial sulfide concentrations were determined by standard iodometric titration method (Scott, 1966) as given below.

Preparation of standard (0.025 M) KIO₃ solution

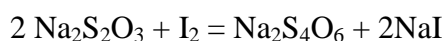
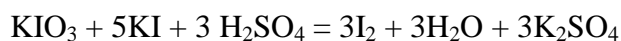
4.28g of KIO₃ was weighed accurately and dissolved in distilled water and was made up to 1 L in a graduated volumetric flask.

Preparation of standard (0.1 M) sodium thiosulfate solution

25g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ crystals was weighed and dissolved in distilled water and made up to 1 litre in a graduated volumetric flask with distilled water.

Standardization of sodium thiosulfate solution by standard potassium iodate solution

25 cm³ of 0.025M KIO_3 solution was taken and 1g (excess) of potassium iodide (KI) was added to it followed by 3 cm³ of 1M sulfuric acid. The liberated iodine (I_2) was titrated with thiosulfate solution. When the color of the solution became a pale yellow, it was diluted to 200 cm³ with distilled water. 2 cm³ of starch solution was added, and the titration was continued until the color changed from blue to colorless. The chemical reaction involved in this titration is given below.



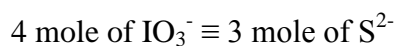
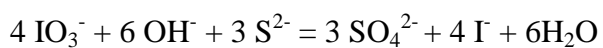
Therefore, 1 mole of $\text{KIO}_3 \equiv 3 \times 2$ mole of $\text{Na}_2\text{S}_2\text{O}_3$

$$\text{Strength of thiosulfate solution} = \frac{6 * \text{Strength of } \text{KIO}_3 * \text{Volume of } \text{KIO}_3}{\text{Volume of } \text{Na}_2\text{S}_2\text{O}_3}$$

Estimation of sulfide concentration

Hydrogen sulfide and soluble sulfides can be determined by oxidation with potassium iodate in an alkaline medium. 15 cm³ of standard (0.025M) potassium iodate solution was taken in a conical flask. 10 cm³ of sulfide solution containing about 2.5 mg of sulfide was then added to it followed by the addition 10 cm³ of 10M sodium hydroxide solution. The mixture was boiled gently for about 10 minutes, cooled, and 5 cm³ of KI solution and 20 cm³ of 4M sulfuric 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 thiosulfate in the usual manner. The potassium iodate in the alkaline medium oxidizes the sulfide to sulfate as

given by the following reaction. For sulfide solution having sufficiently high sulfide concentration, suitable dilution was made before the estimation of sulfide by above mentioned procedure.



$$\text{H}_2\text{S concentration} = [15 * S_{\text{iodate}} - (V_{\text{thiosulfate}} * S_{\text{thiosulfate}})/6] * 3/4 * N_d/10$$

Where S_{iodate} = Strength of KIO_3

$V_{\text{thiosulfate}}$ = Volume of thiosulfate

$S_{\text{thiosulfate}}$ = Strength of thiosulfate

N_d = Number of times of dilution

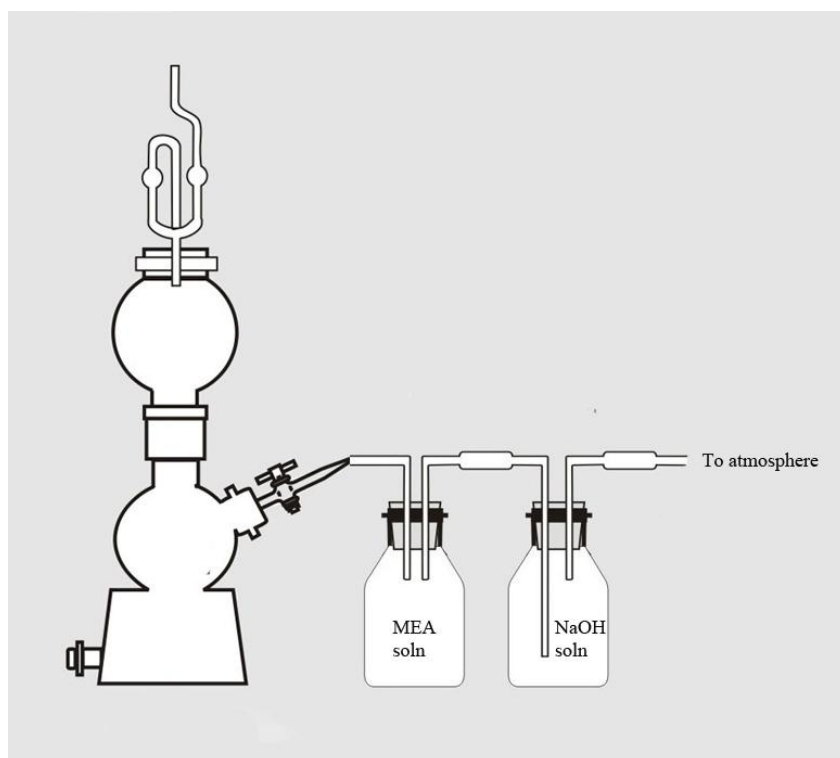


Figure 6. Kipp's Apparatus

Chapter 4

Results and Discussion

RESULTS AND DISCUSSION

4.1 Introduction

In refining and other petrochemical industries, hydrogen sulfide is usually removed from by absorption in aqueous alkanolamines. Amines are regenerated in the strippers releasing H_2S , which is further subjected to the Claus process releasing elemental sulfur.

In the present study, the reaction of benzyl chloride (BC) with H_2S -rich aqueous monoethanolamine (MEA) was carried out in batch mode under two-phase conditions (liquid-liquid) both in the absence and in the presence of phase transfer catalyst (PTC), namely, Polyethylene Glycol (PEG). Dibenzyl sulfide (DBS) and benzyl mercaptan (BM) were detected as the products from the reaction mixture by gas liquid chromatography (GLC). The commercial importance of these compounds has been mentioned in Conclusion. Although there is a possibility of formation of benzyl alcohol by alkaline hydrolysis of benzyl chloride and N-benzyl monoethanolamine by substitution of chlorine atom by MEA, neither of them was detected in the reaction mixture even after a batch time of 6 hours. Accordingly, the overall reaction may broadly be represented by Figure 8.

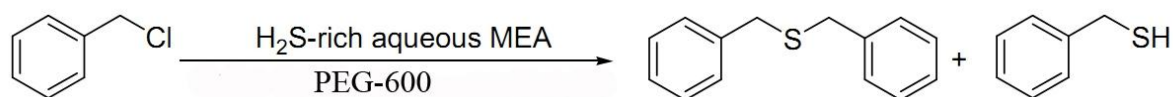


Figure 7. Overall Reaction

Parametric studies were performed following one-variable-at-a-time (OVAT) approach to see the effect of various parameters such as stirring speed, temperature, aqueous sulfide concentration, MEA concentration, catalyst loading and BC concentration on BC conversion and DBS selectivity. From the detailed study of the effects of various parameters on the reaction, a suitable mechanism was established which could explain the course of the reaction.

4.2 Parametric Study

4.2.1 Effect of stirring speed

To evaluate the role of mass transfer resistance in this system, the stirring speed was varied and corresponding reaction rates were observed and plotted on a graph. The chart shows that the conversion rate of BC is nearly independent of the stirring speed. Thus we can conclude that in the present system, mass transfer factors do not affect the conversion rate which is almost purely controlled by kinetics. Hence, all the other experiments were performed at a stirring speed of 1500 rpm.

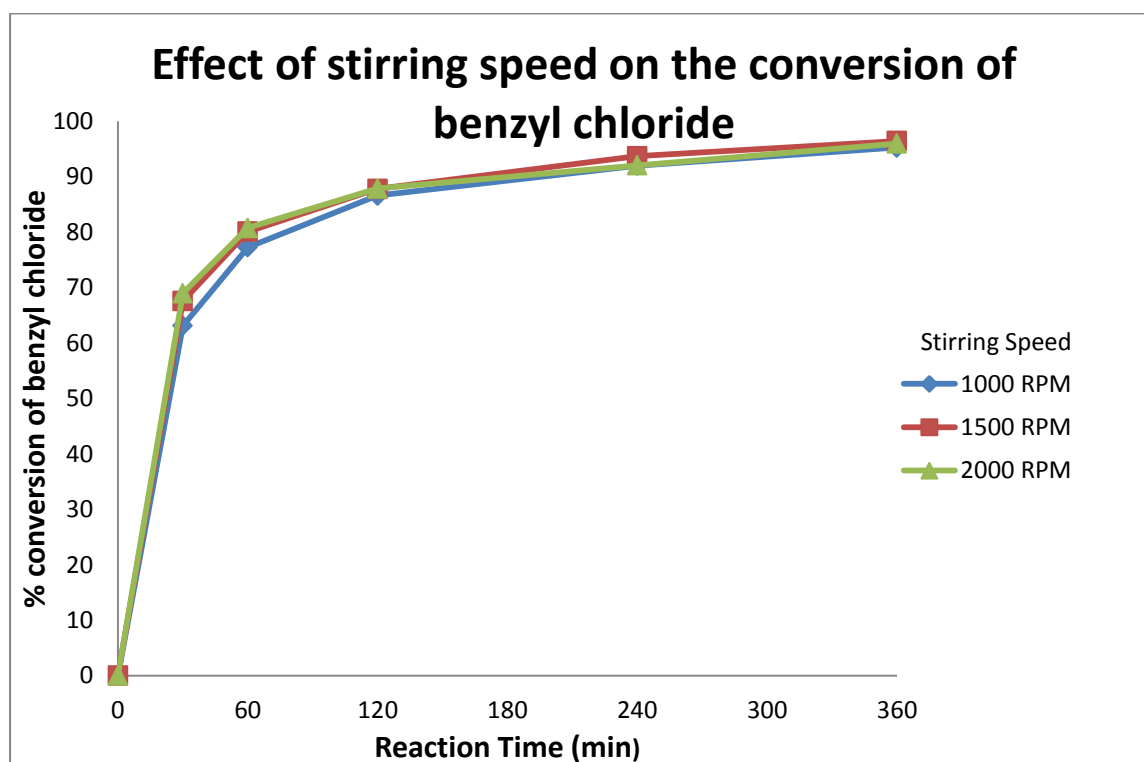
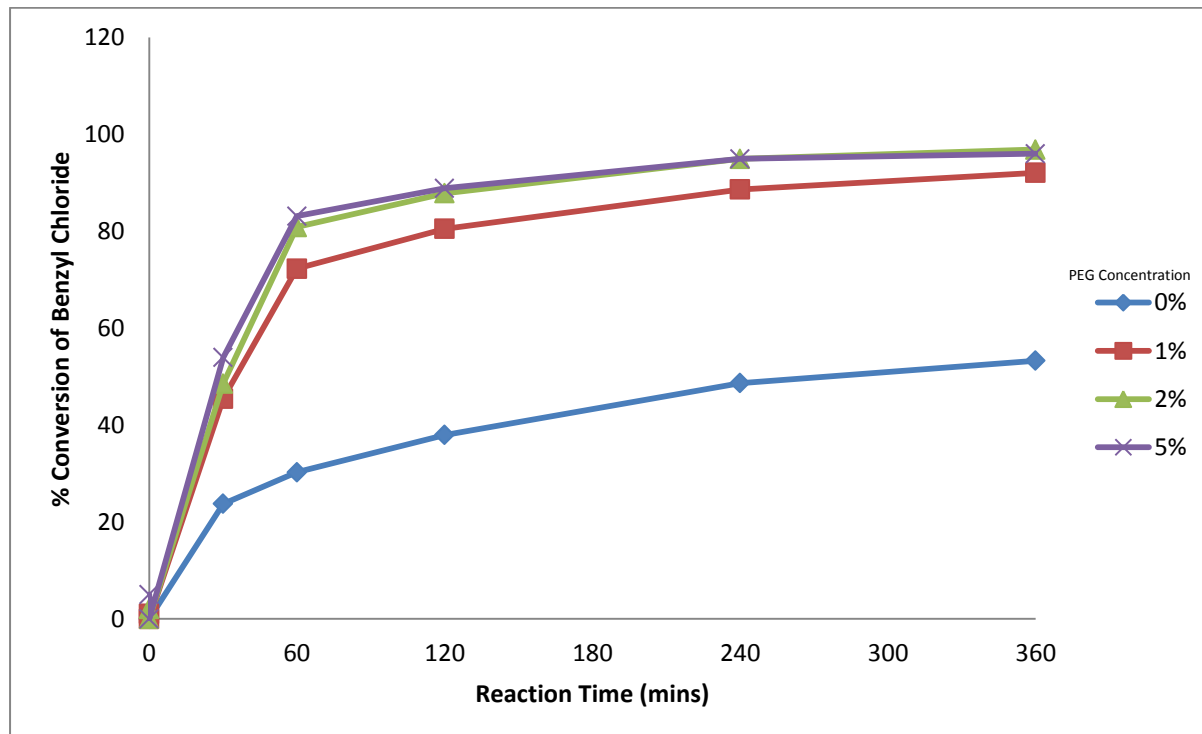


Figure 8. Effect of stirring speed on BC conversion. Volume of organic phase = 5.0×10^{-5} m³; volume of aqueous phase = 5.0×10^{-5} m³; concentration of BC = 8.69 kmol/m³; concentration of catalyst = 2%; concentration of sulfide = 1.23 kmol/m³; temperature = 303K;

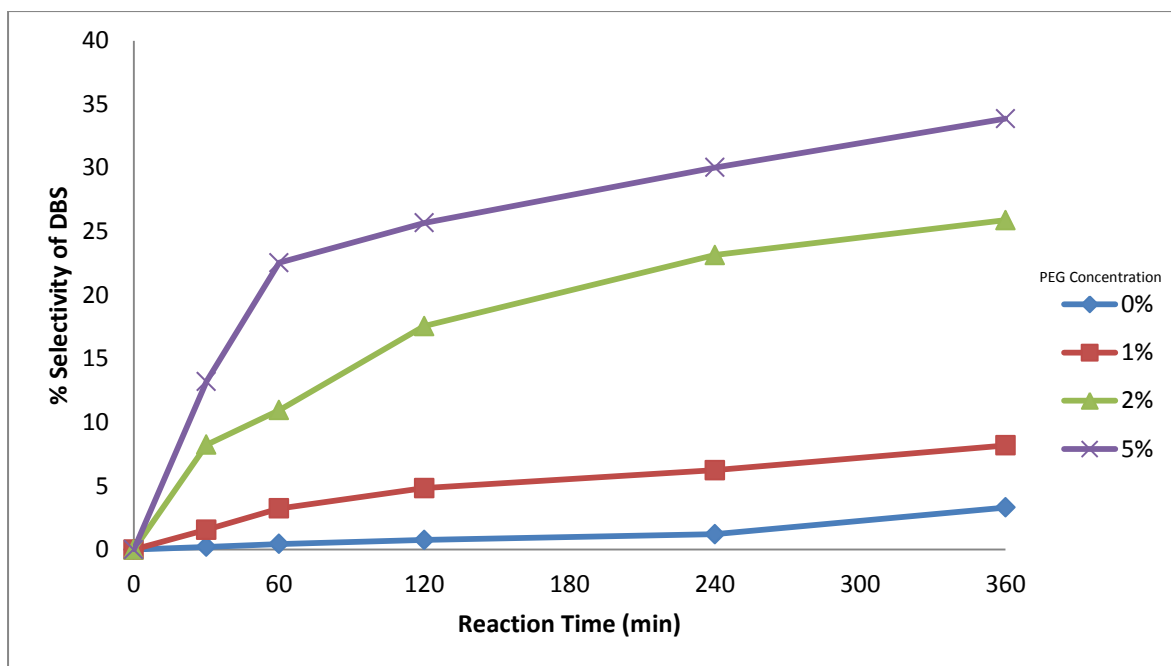
4.2.2 Effect of catalyst concentration

The effect of catalyst (PEG) concentration on BC conversion was studied in the concentration range of 0 – 5 % of organic phase, as shown in Fig. 9(a). With increase in catalyst concentration, BC conversion as well as reaction rate increases. Only by increasing the catalyst concentration, BC conversion of about 96% was achieved whereas it was about 53% without catalyst even after 360 min of reaction under otherwise identical conditions. Fig. 9(a) also shows that over 2 % concentration of the catalyst, the conversion of BC becomes constant.

This can be explained by the fact that the mass transfer of the active species into organic phase reaches a maximum value. The selectivity of DBS increases with increase in catalyst concentration as shown in Fig. 9(b). Therefore, the selectivity of BM decreases with increase in catalyst concentration.



(a)



(b)

Figure 9. Effect of catalyst concentration on (a) BC conversion (b) DBS selectivity.

Volume of organic phase = $5.0 \times 10^{-5} \text{ m}^3$; volume of aqueous phase = $5.0 \times 10^{-5} \text{ m}^3$; concentration of sulfide = 1.23 kmol/m^3 ; concentration of BC = 8.69 kmol/m^3 ; temperature = 303 K; stirring speed = 1500 rpm.

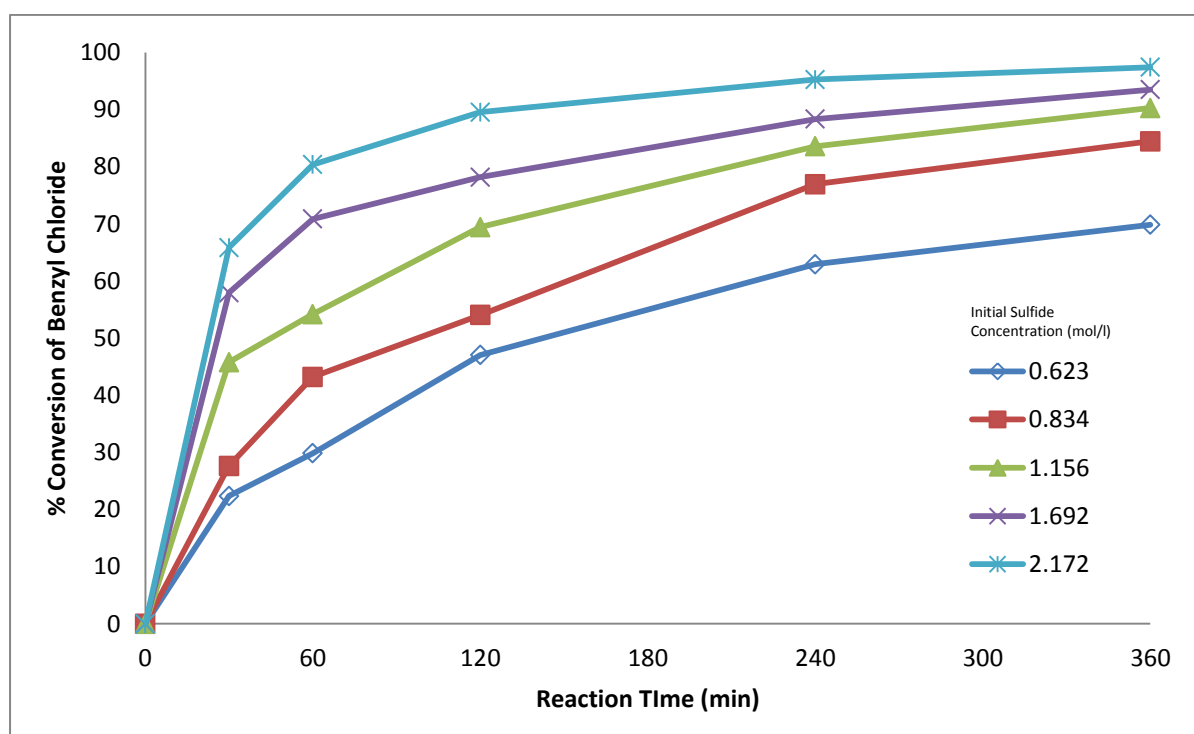
4.2.3 Effect of initial sulfide concentration

The effect of initial sulfide concentration on the conversion of BC and DBS selectivity was studied keeping the MEA concentration fixed at 4.97 kmol/m^3 .

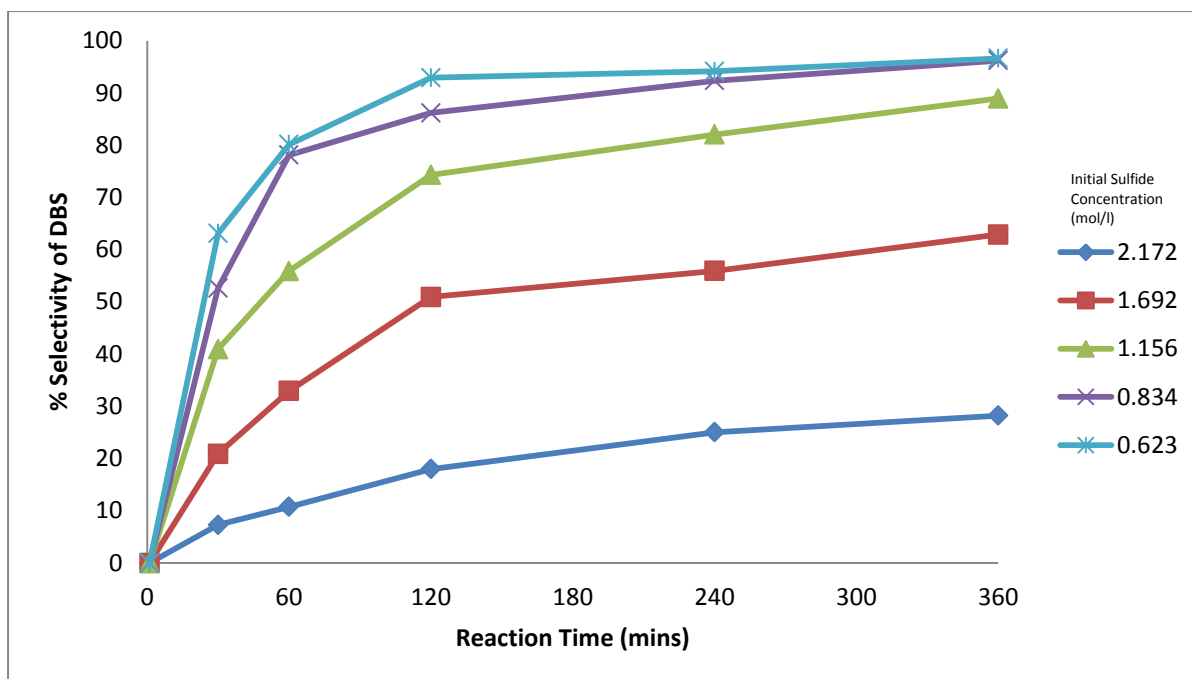
Keeping the MEA concentration constant, with the increase in initial sulfide concentration, percentage conversion increased because more sulfide ions were available for reaction, as shown in Figure 10(a). Conversion rates of up to 97% were achieved with initial sulfide concentration of 2.172 kmol/m^3 .

However an opposite trend was observed in case of DBS selectivity. Here the DBS selectivity actually decreased with an increase in initial sulfide concentration as shown in Figure 10(b).

This can be explained by considering the fact that although MEA as such does not participate in the reaction with BC, it does affect the equilibrium among MEA, H₂S, and water, which results in two active anions, sulfide (S²⁻) and hydrosulfide (HS⁻), in the aqueous phase. These two active anions participate in two different reactions. In the presence of a base (MEA), the dissociation equilibrium shifts toward more ionization and the concentration of sulfide ions, relative to hydrosulfide ions in the aqueous phase, increases as the MEA concentration increases. Therefore, only by changing the MEA concentration with constant sulfide concentration in the aqueous phase, it would be easy to prove the existence of two different reactions.



(a)



(b)

Figure 10. Effect of initial sulfide concentration on (a) BC conversion (b) DBS selectivity. Volume of organic phase = $5.0 \times 10^{-5} \text{ m}^3$; volume of aqueous phase = $5.0 \times 10^{-5} \text{ m}^3$; concentration of catalyst = 2%; concentration of BC = 8.69 kmol/m^3 ; temperature = 303 K; stirring speed = 1500 rpm.

Chapter 5

Conclusion

5. CONCLUSION

The reaction under study is an industrially important reaction as it produces products such as dibenzyl sulfide and benzyl mercaptan which have varied industrial applications.

DBS finds applications in:

- Additives for extreme pressure lubricants.
- Anti-wear additives for motor oils.
- Stabilizers for photographic emulsion.
- In refining and recovery of precious metals.
- Anticorrosive formulations

BM finds application in raw material for synthesis for herbicides in the thiocarbamate family such as esprocarb, prosulfocarb, tiocarbazil, etc.

This reaction was investigated thoroughly but a few parameters could not be studied due to technical handicaps. For the parameters that were examined, it was found that DBS can be preferentially produced by increasing the catalyst concentration and by decreasing the initial sulfide concentration. On the other hand, opposite trend was observed for BM which was the dominant product in lower catalyst concentration and higher initial sulfide concentration. When other factors such as temperature, BC concentration will be studied, we would enough data to optimize the process and suggest a suitable reaction mechanism along with kinetic model.

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