M. Tech (Dual Degree) Thesis

On

“Parametric Studies on the Reduction of 4-Nitroacetophenone using Hydrogen Sulfide and Phase Transfer Catalyst.”

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CERTIFICATE

This is to certify that the thesis entitled **"Parametric Studies on the Reduction of 4-Nitroacetophenone using Hydrogen Sulfide and Phase Transfer Catalyst."** submitted by **Mohamed Aslam Husein** to National Institute of Technology Rourkela, India for the award of degree of **Master of Technology (Dual Degree)** in engineering, is a bonafide record of investigation carried out by him in the Department of Chemical Engineering, under the guidance of **Prof. Sujit Sen**. The report is up to the standard of fulfilment of M. Tech (Dual Degree) degree as prescribed by regulation of this institute.

Prof. Sujit Sen

Date:

Dept. of Chemical Engineering

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LIST OF SYMBOLS

Q^+X^-	Phase Transfer Catalyst
Q^+	Quaternary Ammonium Cation
MY	Aqueous Phase Reactant
RX	Organic Product
RY	Desired Product

LIST OF ABBREVIATIONS

NAP	4-Nitroacetophenone
AAP	4-Aminoacetophenone
GC-MS	Gas chromatography-Mass spectroscopy
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
PTC	Phase Transfer Catalysis
TBPB	Tetrabutylphosphonium Bromide
DEA	Diethanolamine
DGA	Diglycolamine
DIPA	Di-isopropanolamine
TEA	Tri-ethanolamine
RPM	Revolutions per minute
TBAB	Tetrabutylammonium Bromide

ABSTRACT

Hydrogen Sulfide (H_2S) is more often than not, found in the gas streams of Oil and Gas Industry. This is due to the fact that crude oil has in its composition, a small percentage of sulfur. Subduing the amount of sulfur in the crude oil is of paramount importance because it can cause corrosion of equipments and pipelines and also leads to unwanted side reactions leading to additional use of reactant and power. Conventionally, reduction in sulfur levels is achieved by subjecting the gas stream to ammonia absorption followed by Claus Process, the latter which converts H_2S to elemental sulfur which is more productive (less poisonous) and used in rubber vulcanization and sulfuric acid production. The problem associated with Claus Process is that it is very expensive and the demand for elemental sulfur in the market is not as high to redeem the cost. So alternatively, H_2S is absorbed into an aqueous alkanolamine and used in the reduction of Nitroarenes following the Zinin Reduction mechanism. Since the alkanolamine and Nitroarene are in two different phases, a phase transfer catalyst (PTC) is used to help increase the reaction rate, conversion of reactant and selectivity of products.

This work is focused on the reduction of 4-Nitroacetophenone (NAP) to 4-Aminoacetophenone (AAP) using H_2S rich N-Methyldiethanolamine (MDEA) and Tetrabutylphosphonium bromide (TBPB) as the PTC under Liquid-Liquid Phase transfer catalysis, and to study the process parameters involved to maximize the conversion of NAP to AAP. The parameters studied are variation in Stirring speed, Catalyst concentration, Temperature, Sulfide concentration, MDEA concentration etc.

This Method can be used as an alternative to Claus Process to produce value added fine chemicals which have better use, in this case being Aminoacetophenone having applications in clinical microbiology, in the synthesis of Pyrimidines, Coumarins, as a drug metabolite. It also has antibacterial properties and used in the synthesis of HIV-1 growth inhibitors and selective antagonists at human adenosine receptors.

Keywords: Hydrogen Sulfide, Liquid-Liquid Phase transfer catalysis, Aminoacetophenone, Nitroacetophenone, N-methyldiethanolamine.

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CHAPTER 1:

INTRODUCTION

1.1 HYDROGEN SULFIDE: ITS SOURCES

Hydrogen sulfide is found naturally in crude petroleum and natural gas. It is also produced through the bacterial breakdown of organic matter. Hydrogen sulfide can be produced by decomposing human and animal waste, and is found in sewage treatment plants and livestock areas. Hydrogen sulfide in the atmosphere is often from refineries, natural gas plants and food processing plants. Automobiles emit hydrogen sulfide in their exhaust. About 11 % of the global Hydrogen Sulfide (H_2S) can be attributed to human practices. The natural breakdown of organic matter and subsequent release of H_2S occur mostly in deep sea vents, thermal geysers, volcanoes, swamps etc, where the decomposition occurs in the absence of or inadequate oxygen conditions. In general, H_2S is produced when elemental sulfur is contacted with organic matter at very high temperatures.

Apart from petroleum refineries, other industries involved in H_2S emission includes coke oven plants, paper and pulp industry, leather tannery, waste water treatment plants and textile industry (Toxological Profile of hydrogen sulfide, 2006). However, the most prominent contribution to the increasing global concentration of H_2S rests in the oil and gas industry, in the hydrotreatment of natural gas and processing for refined crude oil. There is growing concern regarding the issue of public health with the rate of such increase in the atmospheric H_2S concentration given the dangers involved of prolonged exposure even at low levels.

Statistics explain that the reserves of easy to process crude oil is declining day by day and refiners are now forced to work with heavy crude i.e. which has higher amount of sulfur and nitrogen. To comply with the stringent environmental regulations, rigorous hydrotreatment of the crude is followed leading to the removal of H_2S and NH_3 to the atmosphere in greater proportions than before. On the other hand in the coal processing industry, it is generally seen that H_2S gas is given out as by-product when any kind of treatment is done to reduce the ash content of coal. Coal gas has nearly about 0-3.5% of H_2S as prominent non-hydrocarbon impurity.

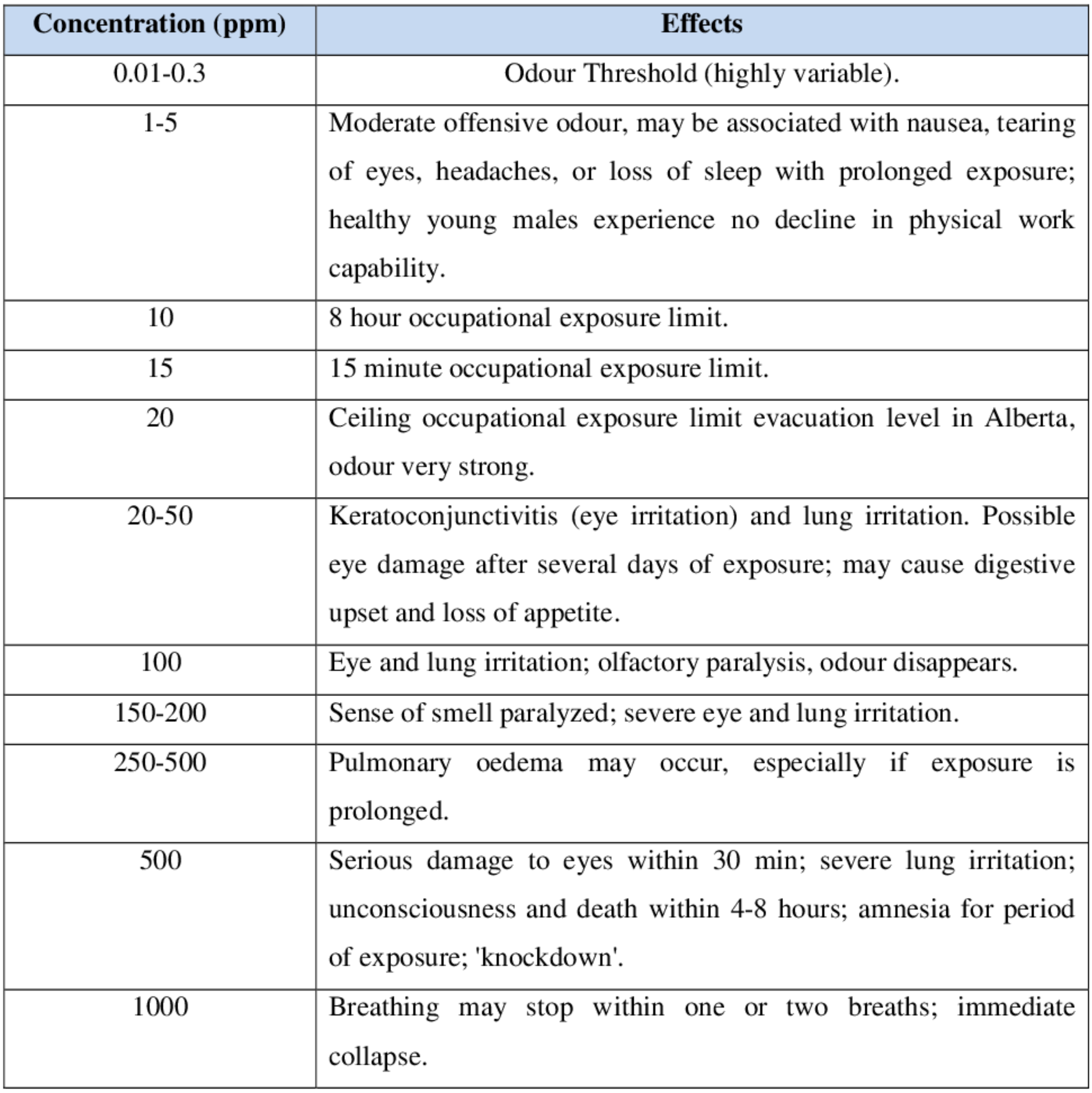
H_2S composition in natural gas in most cases is too high for it to be used as obtained naturally. Although the composition varies from area to area, natural gas generally has H_2S concentration in the range of 0.5 ppm to 175000 ppm.

1.2 NEED FOR THE TREATMENT OF H_2S-RICH GAS STREAMS:

With the advent of global environmental establishments and activists, the chemical industries are now compelled to dump, dispose and vent toxic substances in a very safe scale. H_2S, which is a by-product of many industries, need to dispose it in a very controlled manner due to the following reasons:

- Hydrogen sulfide is a colourless, flammable, extremely hazardous gas with a “rotten egg” smell. As it is denser than air, H_2S has a tendency of accumulating at poorly ventilated areas and voids. Although the smell is quite obvious in the beginning, the victim is left unaware of its presence after some time (olfactory fatigue). Such unaware prolonged low level exposure can cause inflammation of respiratory system after affecting the eyes, nose and throat. The effects can be delayed for several hours, or sometimes several days, when working in low-level concentrations. High level exposure can lead to difficulty in breathing and in certain cases, coma and death. Therefore, it is imperative to monitor the H_2S levels at regular intervals and compare it with the material safety data sheet of H_2S.
- From an industrial point of view, H_2S can cause extensive damage due to its corrosive nature leading to serious monetary repercussions. This is the reason it needs to be removed as much as possible before passing it through pipelines. In many countries, the H_2S concentration is limited to $0.25 g/100 ft^3$ of gas when being transported through pipelines.
- Apart from corrosion of process equipment, H_2S can also hamper the activity of catalysts by its poisoning and deactivation.
- Unwanted side reactions take place and it also increases the pressure sustenance of process equipments.
- Being a combustible gas and having an explosion limit of 4.3-46%, it also poses threats of fire and explosion. With the help of a suitable ignition source or spark, H_2S can burn with oxygen to produce noxious vapours and gases, like sulfur dioxide.

The people most prone to the dangerous effects of H_2S include sewage treatment plant workers, workers in manholes, tunnel workers, well diggers and chemical laboratory analysts.



Concentration (ppm)	Effects
0.01-0.3	Odour Threshold (highly variable).
1-5	Moderate offensive odour, may be associated with nausea, tearing of eyes, headaches, or loss of sleep with prolonged exposure; healthy young males experience no decline in physical work capability.
10	8 hour occupational exposure limit.
15	15 minute occupational exposure limit.
20	Ceiling occupational exposure limit evacuation level in Alberta, odour very strong.
20-50	Keratoconjunctivitis (eye irritation) and lung irritation. Possible eye damage after several days of exposure; may cause digestive upset and loss of appetite.
100	Eye and lung irritation; olfactory paralysis, odour disappears.
150-200	Sense of smell paralyzed; severe eye and lung irritation.
250-500	Pulmonary oedema may occur, especially if exposure is prolonged.
500	Serious damage to eyes within 30 min; severe lung irritation; unconsciousness and death within 4-8 hours; amnesia for period of exposure; 'knockdown'.
1000	Breathing may stop within one or two breaths; immediate collapse.

Table 1.1: Health effects of H_2S at various levels of exposure

The Hydrogen Sulfide exposure limits set by various safety establishments give us an idea of the seriousness of the threat posed by the gas on human health. Globally, every 1 of 4 deaths associated with chemical vapours is from H_2S poisoning.

	8hr TWA (ppm)	**STEL (ppm)**	**Ceiling (ppm)**	**Acceptable Max Peak above Ceiling for an 8hr shift.**	
				Concentration (ppm)	**Max Duration**
Federal OSHA PEL	NA	NA	20	50	10 minutes once only if no other measurable exposure occurs during shift
NIOSH REL	10	15	NA	NA	NA
TLV (2010)	1	5	NA	NA	NA

Table 1.2: H_2S exposure limits

1.3 INDUSTRIAL PROCESSES FOR H_2S RECOVERY AND RECLAMATION:

It is required by the industries to reduce the H_2S concentration in the flue and by-product gas stream in order to create a safe work environment for the workers and also for the overall benefit of the global environment. Over the years, a number of processes have been designed for the removal and retrieval of H_2S from gas mixtures. Because of the acidic nature of H_2S (weak acid), most of the removal methods involve the use of alkaline solutions. However, strong alkaline solutions are not preferred for the removal of H_2S from gas streams because they form irreversible products due to other chemical reactions. This tendency (of forming irreversible products) is enhanced when the gas mixture contains both H_2S and CO_2 and the concentration of CO_2 is more than 4% (Robin, 1999). This is the main reason why weak alkaline solutions such as ammonia and alkanolamines are used for the removal and reclamation of H_2S (Vago et al., 2011; Huertas et al., 2001).

1.3.1 AMMONIA-BASED PROCESS:

This method of using ammonia for the removal of H_2S from a gas mixture has been used extensively since long (Hamblin, 1973; Harvey and Makrides, 1980). The procedure followed in this process is as follows:

- The gas mixture consisting of H_2S and NH_3 is allowed to pass through a H_2S scrubber and NH_3 scrubber.
- The NH_3 scrubber was provided with a water stripper from the top to absorb the NH_3 from the gas as ammonium hydroxide. This ammonium hydroxide solution acts as the absorbent for the H_2S scrubber.
- Thus ammonium sulfide rich solution produced in the H_2S scrubber is sent to a deacidifier, where the ammonium sulfide is separated to obtain H_2S rich vapour and NH_3 rich liquor. The reactions are :

$$NH_3 + H_2O \rightarrow NH_4OH$$

$$NH_3 + H_2S \rightarrow NH_4HS$$

$$2\mathrm{NH_3} + \mathrm{H_2S} \rightarrow [\mathrm{NH_4}]_2S$$

The main advantages of NH_3-based process are as follows:

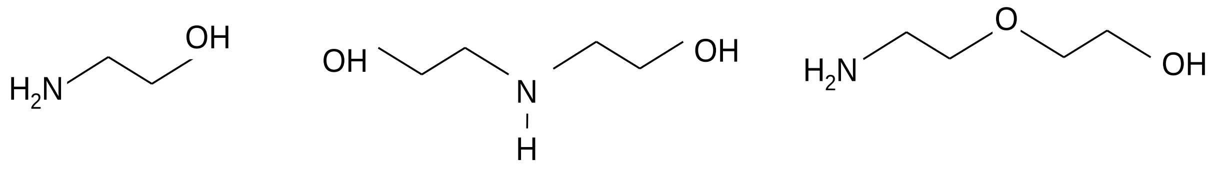
- This process is well suited for gas mixtures comprising of both H_2S and NH_3. The removal of both H_2S and NH_3 is achieved in a single step whereas separate steps are required for alkanolamines based process.
- If a gas containing H_2S and CO_2 is contacted with the ammonium hydroxide solution in the H_2S scrubber, then it is found there is an extensive absorption of H_2S. We can selectively absorb H_2S and CO_2 by altering the concentration of the ammonium hydroxide solution. Selective absorption of H_2S can be achieved by using a spray column and providing a short contact time.
- Ammonia is one of the largest produced chemicals globally and hence a cheap solvent. It also has the properties of not degrading or decomposing in the presence of oxygen or any other component in the flue gas like carbonyl sulfide (COS), carbon disulfide (CS_2) and hydrogen cyanide (HCN). Ammonia is also found to have high CO_2 removal efficiency and low regeneration energy. It is less toxic to the environment and human health than other amines.

Despite of these advantages, this process has lost popularity over the years and is now used very remotely. It is not considered as a feasible way to remove H_2S from a gas mixture because of the following operational problems (Hamblin, 1973):

- Because of the high partial pressure of ammonia (NH_3), we are compelled to use a dilute NH_3 solution in the scrubbing step, or a relatively high pressured NH_3 solution, or introduce a separate wash with water step after the NH_3 scrubbing in order to separate all the NH_3 from the gas mixture. Furthermore, using dilute NH_3 solutions will considerably elevate the regeneration costs as the regeneration step is operated at a higher temperature than the scrubbing step.
- The regeneration step involves the use of catalysts (like hydroquinone). The ammonium sulfide poses a risk of poisoning and deactivation of the catalyst by forming ammonium sulfate and thiosulfate. This will cause loss of both the catalyst and the scrubbing NH_3 solution (which is recycled).

1.3.2 ALKANOLAMINE PROCESS:

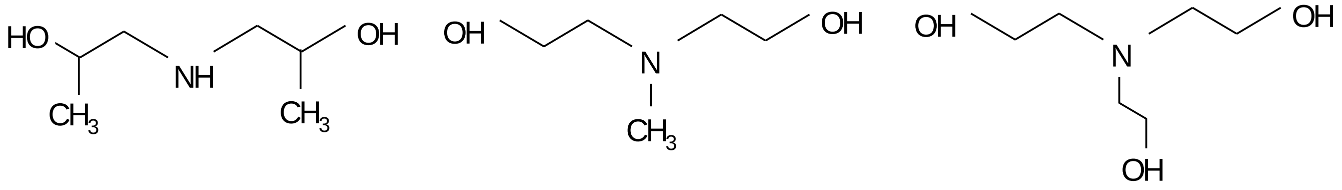
The alkanolamine process gained acceptance over the past decade for the removal of acid gas like H_2S and CO_2 from gas mixtures as compared to the ammonia process due to its advantages of low vapour pressure (high b.p.) and ease of reclamation. Because of the low vapour pressure of alkanolamines, the operation becomes flexible in terms of pressure, temperature and concentration of alkanolamine. In the early days, Triethanolamine (TEA) was considered for use in gas treating plants and it became the first commercially available alkanolamine (R. R. Bottoms, 1930). Today, the amines that are of particular interest to gas treatment are Monoethanolamine (MEA), Diethanolamine (DEA) and Methyldiethanolamine (MDEA). Triethanolamine (TEA) was replaced because of its low reactivity, low capacity and poor stability. MEA, DEA and MDEA have the advantages of larger capacity of absorption and lower molecular mass. In our work MDEA has been used because of its ability of selective absorption of H_2S from a gas.



Monoethanolamine (MEA)

Diethanolamine (DEA)

Diglycolamine (DGA)



Di-isopropanolamine (DIPA)

Methyldiethanolamine (MDEA)

Triethanolamine (TEA)

Figure 1.1: Commonly used Alkanolamine

If an amine group is attached to the alkanol, then the aqueous solution becomes basic in nature in order to dissolve acid gases like H_2S. On the contrary if a hydroxyl group is attached to the amine, then vapour pressure is reduced and water solubility is increased. The advantages and disadvantages of commonly used alkanolamine are shown in the Tables below.

1. Monoethanolamine (MEA)

Advantages	**Disadvantages**
• Low cost. • Degradation products can be reclaimed. • Low molecular weight increases solution capacity at moderate concentration.	• Not selective in presence of CO_2. • CO_2, COS and CS_2 can irreversibly degrade the amine. • Products are very corrosive. • Used amine has lower acid gas removal capacity. • Large energy required for its regeneration. • High vaporization losses due to high vapour pressure.

Table 1.3: Advantages and Disadvantages of MEA (Typical Concentration: 15-18 wt %)

2. Diethanolamine (DEA)

Advantages	Disadvantages
• Moderate Cost. • Selection less with CO_2 and COS than MEA. • Used products are less corrosive than MEA. • Purification achieved by vacuum distillation. • Less energy required for its regeneration than MEA.	• Not selective in presence of CO_2. • CO_2, COS irreversibly damage the amine. • Used amine has lower acid gas removal capacity.

Table 1.4: Advantages and Disadvantages of DEA (Typical Concentration: 25-30 wt %)

3. Diglycolamine (DGA)

Advantages	Disadvantages
• Low specification achieved under critical conditions. • Degradation products can be reclaimed.	• High Cost. • Not selective in presence of CO_2. • CO_2, COS irreversibly damage the amine. • Products are very corrosive. • High solubility of the aromatic, olefins and heavy hydrocarbons in the DGA. • Extremely high energy required for regeneration.

Table 1.5: Advantages and Disadvantages of DGA (Typical Concentration: 50wt %)

4. Di-isopropanolamine (DIPA)

Advantages	Disadvantages
• Moderate selectivity in the presence of CO_2. • Purification achieved by vacuum distillation. • Relatively moderate energy is required for regeneration.	• High Cost. • CO_2, COS irreversibly damage the amine.

Table 1.6: Advantages and Disadvantages of DIPA (Typical Concentration: 27wt %)

5. Methyl-diethanolamine (MDEA)

Advantages	Disadvantages
• High selectivity to absorb H_2S. • Higher acid gas removal capacity at moderate concentration. • Does not get damaged with CO_2 or COS. • Non-corrosive at the concentration of use. • Little energy required for regeneration.	• Higher cost than MEA, DEA and DIPA. • More soluble than DEA in liquid hydrocarbons.

Table 1.7: Advantages and Disadvantages of MDEA (Typical Concentration: 35-50 wt %)

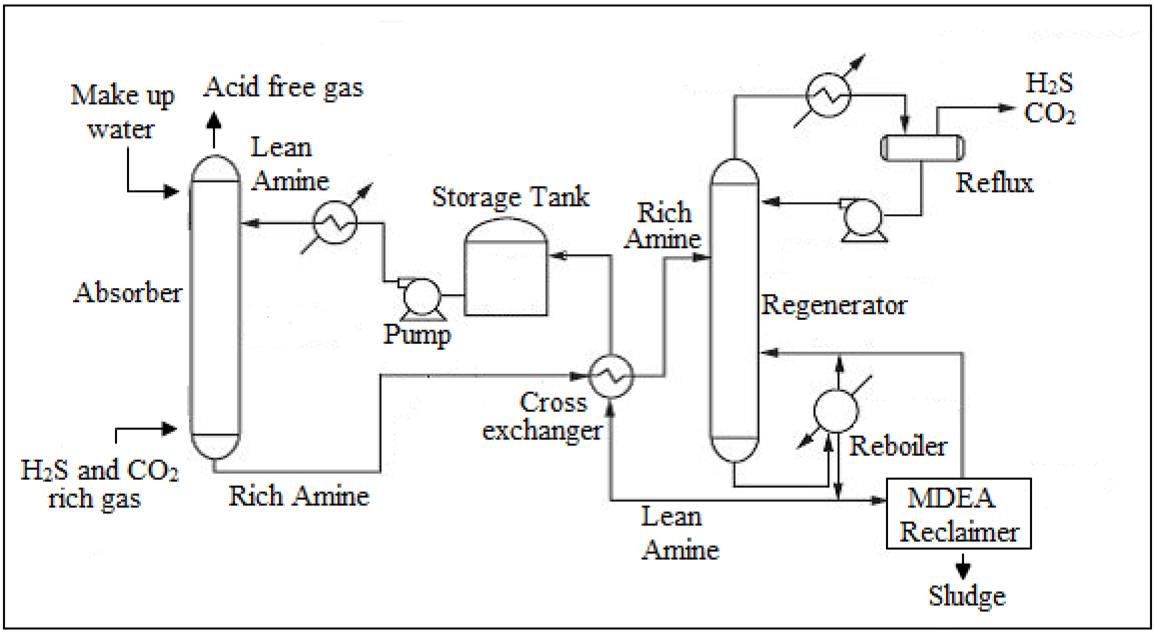


Figure 1.2: Flow Diagram of Amine Treating Process

The sour gas from the industries is fed from the bottom of the absorber where it is contacted with lean aqueous alkanolamine in a counter-current manner. The gas mixture free from acid gases is taken out from the top and the solution from the bottom of the absorber containing H_2S rich amine is heated along with the lean amine from the bottom of the regenerator (stripping column) with the help of a heat exchanger. In the regenerator, the absorbed gases (H_2S) are stripped off from the alkanolamine solution and taken from the top. The concentrated H_2S gas is then sent for elemental sulfur recovery or disposal. The regenerated lean amine is then sent back to the absorber as shown in Fig 1.2.

Reactions with H_2S:

Sulfide formation: $2RNH_2 + H_2S \leftrightarrow [RNH_3]_2S$

Hydrosulfide formation: $RNH_2 + H_2S \leftrightarrow RNH_3SH$

Reactions with CO_2:

Carbonate formation: $2RNH_2 + CO_2 + H_2O \leftrightarrow [RNH_3]_2CO_3$

Bicarbonate formation: $RNH_2 + CO_2 + H_2O \leftrightarrow RNH_3CO_3H$

Carbamate formation: $2RNH_2 + CO_2 \leftrightarrow RNH - CO - ONH_3R$

1.4 CLAUS PROCESS TO RETRIEVE SULFUR FROM H_2S:

More poisonous hydrogen sulfide gas is converted to less poisonous and more useful elemental sulfur through the Claus process. This standard procedure is followed in industries producing H_2S as by-products since a long time. H_2S is obtained as by-product mainly during the treatment of natural gas in refineries, gasification plants etc. If any Hydrocarbons, sulfur dioxide or ammonia and hydrogen cyanide are present in these by-product gases, then they are separated from the H_2S using amine extraction. Only H_2S gas is supplied to the Claus unit, the process of which comprises of two steps: Thermal and Catalytic.

In the Thermal step, the H_2S gas is burned in a reaction furnace in a sub-stoichiometric combustion process in the presence of air at temperatures between 1000 - 1400 °C. Claus gases (acid gas) with no further combustible contents apart from H_2S are burned in burner. The ratio of air to the acid gas, in this strongly exothermic oxidation reaction, is controlled in such a way that one third of all H_2S is converted to SO_2. This facilitates the stoichiometric reaction in the catalytic step.

Thermal step reaction: $2H_2S + 2O_2 \rightarrow SO_2 + 2H_2O + S$

In the Catalytic step, the gases leaving the thermal step are cooled in a sulfur condenser and reheated to about 200-350°C before being fed to a series of catalytic converters and sulfur condensers where H_2S reacts with SO_2 to produce elemental sulfur. Usually, the catalyst used in the catalytic converter is either activated aluminium (III) or titanium (IV) oxide. A small amount of H_2S remains in the tail gas. This remaining quantity, together with other trace sulfur compounds, is generally processed in a separate tail unit. It can give overall sulfur recoveries of about 99.8%. Sulfur is used for manufacturing sulfuric acid, medicine, cosmetics, fertilizers and rubber products. Elemental sulfur is used as fertilizer and pesticide.

Catalytic step reaction: $2H_2S + SO_2 \rightarrow 3S + 2H_2O$

However, the Claus process has a number of disadvantages (Plummer, 1994; Plummer and Beazley, 1986; Plummer and Zimmerman, 1986) namely:

- It operates at high temperatures.
- It requires exact process control over the ratio of oxygen to H_2S in the feed.
- The valuable hydrogen energy is lost in this process.

- The feed would require expensive pre-treatment if it contains CO_2 in high concentration. In order to maintain the efficiency of the process, at least a portion of the CO_2 must be removed from the by-product gas by pre-treatment before oxidizing the H_2S.
- The sulfur content of the tail gas in the Claus process is too high for it to be released to the atmosphere. In order to comply with the stringent environmental regulations, a lot more of the Claus stages would be needed to be added, thereby increasing the cost of the process to a great extent.

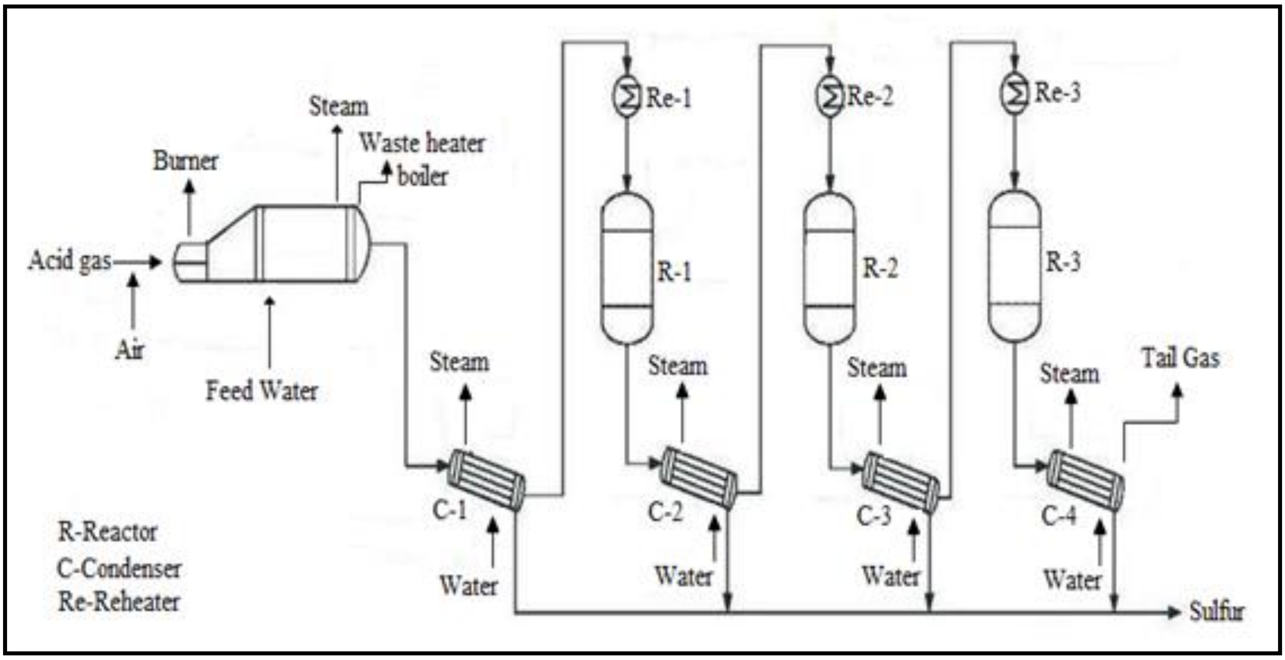


Figure 1.3: Flow Diagram of Claus Process

1.5 ALTERNATIVES FOR PROCESSING H_2S-RICH GAS:

Since it is not possible to treat gases containing H_2S and high amounts of CO_2 by amine extraction, a separate process called ‘CrystaSulf’ or ‘SulFerox’ or ‘ARI-LO-CAT’ is used. It is a liquid reduction-oxidation process used for the treatment of natural gas. In this process, instead of air, a liquid solution containing oxidised iron is used for the redox reactions. A new technique called H_2S splitting process is being developed to isolate both hydrogen and sulfur from H_2S. Hydrogen is used to store energy in fuel cells and also used in the oil industry and for the production of ammonia and methanol.

1.5.1 CRYSTASULF PROCESS:

A non-aqueous solution in which elemental sulfur has a good solubility is used for Crystasulf Process. Due to the fact that elemental sulfur remains dissolved in the solution, the liquid circulated to the absorber will have no solids. The advantage of CrystaSulf is that it avoids the problems related to aqueous sulfur recovery systems and make them suitable for direct treatment of high-pressure sour gas.

According to the process, a conventional tray absorber is used to remove H_2S from the sour gas. Dissolved elemental sulfur is produced from the reaction of H_2S with sulfur dioxide SO_2. No solids are left in the absorber, flash tank, or solution lines, which reduces the chances of plugging. From the absorber, the rich solution passes to a flash step in which the flash gas is compressed and recycled to the inlet stream. After this, the solution is taken to a crystallizer where the temperature is lowered to form solid elemental sulfur crystals. The only location where sulfur solids exist within the process is in the crystallizer/filter area. The leaner liquid is transferred back to the absorber by a pump when it overflows from the slurry tank to a surge tank.

There are two different ways to add SO_2. Liquid SO_2 can be obtained and injected into the lean solution line; this option is economically viable when SO_2 is readily available for purchase and sulfur throughputs are small. In the second method, a part of the product sulfur is burned and the resulting SO_2 absorbed into the solution through a separate, small SO_2 absorber.

In Crystasulf process, SO_2 binds with species in the non-aqueous solution. Since this bond is strong, it would be impossible to detect even small concentration of SO_2 in the gas phase anywhere within the system, including the sweetened gas. Operational flexibility is obtained as a large excess of SO_2 can exist within the solution, and this background concentration causes a buffering effect. The CrystaSulf process provides the inherent capital cost benefit of a single step approach and avoids the operating problems of the aqueous-based processes. CrystaSulf is advantageous to operators who have avoided natural gas due to its H_2S content, or who are drilling gas wells in areas that tend to produce sour gas containing moderate amounts of CO_2.

Process Advantages

- Elemental sulfur is dissolved in the solution and so, solids are absent (except in the crystallizer/filter section).
- There is no foaming in the solution because of the absence of surfactants or particles present.
- There is no need for tail gas treating because the circulations rates are controlled and there is complete removal of H_2S.
- Non-corrosive solution.

1.5.2 WET OXIDATION LO-CAT PROCESS:

This is a liquid phase oxidation process that uses solution that is a little alkaline (but not noxious) containing an iron chelate complex as a reduction-oxidation catalyst. This process takes into account the environmental repercussions while converting H_2S to elemental sulfur. Gas mixture comprising H_2S is treated with aqueous LOCAT solution in a venture-scrubber. In the solution, the H_2S is absorbed and instantaneously converted to elemental sulfur by reacting with oxygen. Subsequently the iron ions are reduced from ferric to ferrous state, which are then transported to an oxidizer from the absorber to regenerate the ferric ion by contacting with atmospheric oxygen. These ions are then absorbed into the LOCAT solution thereby replenishing the catalyst. Sulfur can be removed from the underside of the oxidizer and thus from the circulating solution. Elemental sulfur can be obtained from the sulfur slurry by centrifuge or by melting. The process has an efficiency of removing 99.9% of H_2S from a gas mixture comprising any concentration of H_2S.

1.6 PHASE TRANSFER CATALYSIS:

Many valuable reactions do not occur due to the constraint of insoluble nature of reactants in one solvent. Conventionally we use a solvent that can dissolve all the reactants but in most cases, these solvents are very expensive. Also, other factors like low rate of reaction (due to excessive solvation of the nucleophile) and difficulty in separation of the product from the reaction mixture adds to the disadvantages. In order to overcome this problem, we allow the reactants to dissolve in their respective organic and aqueous phases and then, a particular type of catalyst is added which facilitates the transfer of the reactant from the aqueous phase or solid phase to the organic phase where the reaction occurs. Such type of catalysts are called phase transfer (PT) catalyst and the phenomenon in named phase transfer catalysis (PTC).

PTC helps in the elevation of the environmental performance by improving pollution prevention, green chemistry and pollution treatment. Because of its mild operating condition, use of cheaper reagents, high selectivity of product in shorter time and suppression of unwanted side reactions, PTC has proved to be better than the traditional synthesis method (Weber and Gokel, 1977; Selvi et al., 2012). Effectively, what the phase transfer catalysis involves is dissolving a nucleophilic reagent into water and electrophilic reagent into organic solvent and then employing PTC on catalytic amounts to transfer active anion from solid or aqueous phase into organic phase where the reaction takes place. It is necessary for the transferred active ion pair to remain in an active form for necessary phase transfer catalytic action, and to be reclaimed during the reaction in the organic phase.

1.6.1 CLASSIFICATION OF PTC:

PTC reactions are categorized into two major classes: soluble and insoluble Phase Transfer Catalysis. Each category is then again divided into a number of classes. Soluble PTC is further divided into liquid-liquid (L-LPTC), gas-liquid (G-LPTC) and solid-liquid (S-LPTC) phase transfer catalysis according to the aqueous and organic phases present. Separation of product and recovery of catalyst is difficult in case of soluble PTC. Hence, for increasing the recovery and reuse of phase transfer catalyst, a catalyst rich layer is formed in between aqueous and organic phase, and this kind of PTC is known as insoluble PTC.

In L-L PTC, the nucleophile (M^+Y^-) is dissolved in an aqueous phase whereas in S-L PTC, it is a solid suspended in the organic phase. S-L PTC is mostly used to avoid undesirable side reactions like hydrolysis and to increase selectivity of product.

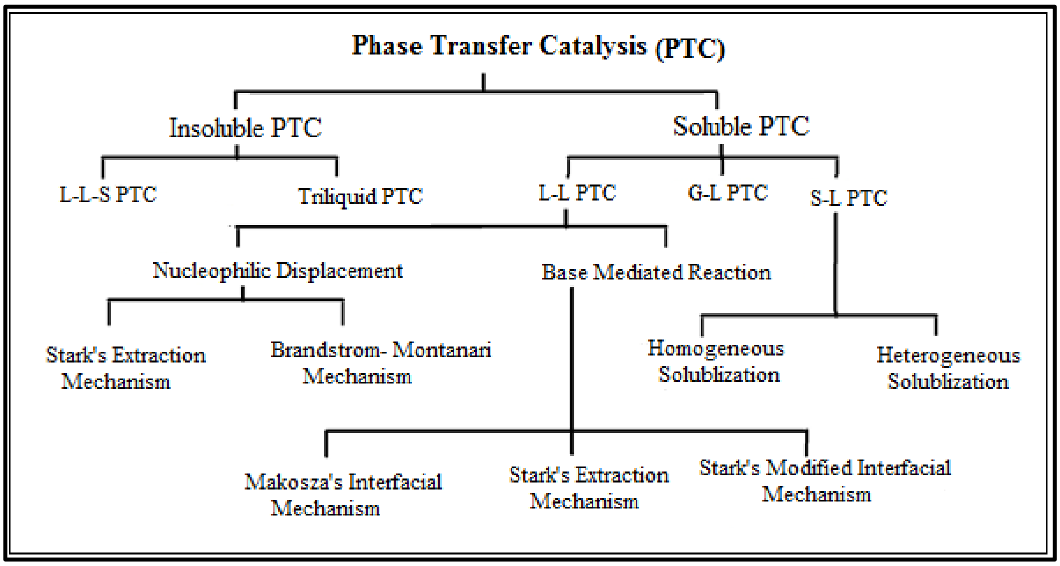


Figure 1.4: Classification of PTC

1.6.2 MECHANISM:

1.6.2.1 L-L Phase Transfer Catalysis:

There are basically two mechanisms: interfacial and extraction, which are used to describe the L-L PTC depending on the lipophilicity of the quaternary cation. Stark's extraction mechanism is applied in case of low lipophilic catalysts. In the interfacial mechanism, the catalysts remain in the organic phase because of their high lipophilicity. In this phase, anions are also exchanged across the liquid-liquid interface.

In the Stark's extraction mechanism, the quaternary onium halide (Q^+X^-) present in the aqueous phase exchanges anion with the reactant (MY) present in the aqueous phase. The ion-pair formed thus (Q^+Y^-) passes through the liquid-liquid interface because of its low lipophilic nature and goes into the organic phase. Phase transfer occurs in this step. In the organic phase the ion-pair (Q^+Y^-) undergoes nucleophilic substitution reaction with the reagent (RX) forming the product (RY). Then the catalyst goes into the aqueous phase and the process is repeated.

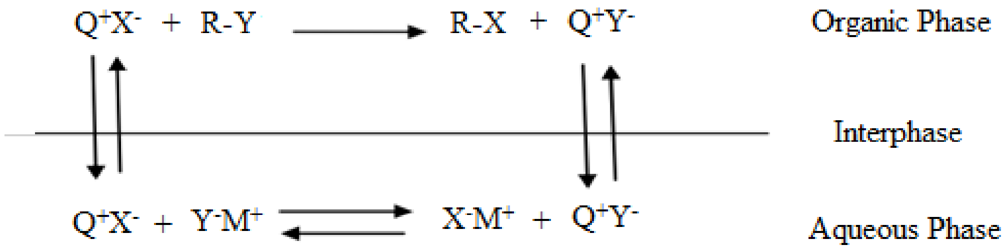


Figure 1.5: Stark's Mechanism of PTC

As mentioned before, the Stark's mechanism applies when the PT catalyst is hydrophilic in nature whereas if it lipophilic in nature, then the PT catalyst cannot dissolve in the aqueous phase. In such a case, the Brandstorm Montanari mechanism applies where the anion exchange of the nucleophile with catalyst takes place at or near the interphase

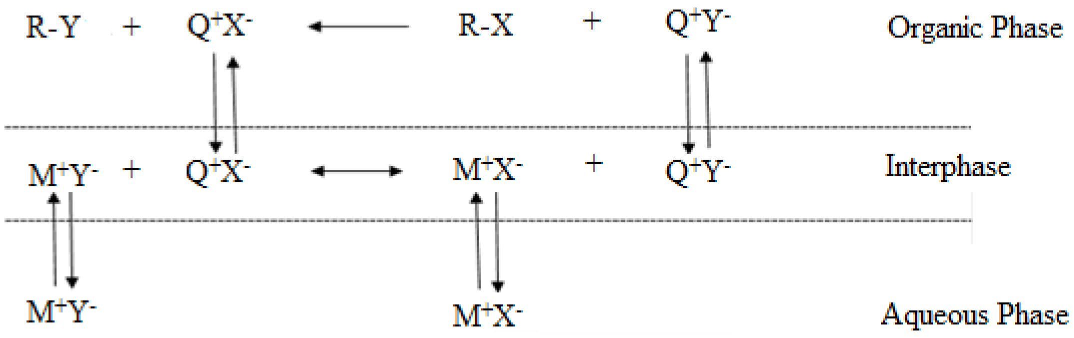


Figure 1.6: Brandstorm Montanari Mechanism

1.6.2.2 S-L Phase Transfer Catalysis:

We find that there are more industrial applications associated with L-L PTC but it has the disadvantage of unwanted side reaction due to hydrolysis. In order to avoid this, the nucleophile is taken in solid form suspended in organic phase, and it is called solid-liquid (S-L) PTC. Thus, more yield and selectivity can be achieved through S-LPTC than L-LPTC.

During the reaction, the quaternary ion (Q^+X^-) first move to solid nucleophile for the ion exchange reaction near the solid surface and active form of catalyst (Q^+Y^-) is formed. Two mechanisms have been proposed for S-L PTC (Starks and Liotta, 1978, Yadhav and Sharma 1981), one among which is fit for conditions when the inorganic salt has finite solubility in the given solvent. This mechanism is called homogeneous solubilisation. The other mechanism where the inorganic salt is insoluble in the given solvent is called heterogeneous solubilisation. Therefore in homogeneous solubilisation, the quaternary ion (Q^+X^-) does not come in direct contact with the solid surface of the nucleophile (KY) and the ion exchange takes place with the dissolved KY at the interphase. In heterogeneous solubilisation, the quaternary ion (Q^+X^-) has to go to surface of solid crystal lattice of the nucleophile (KY) for ion exchange and then comes back to organic phase. The reaction of QY with organic substrate RX takes place in bulk of organic phase (Melville and Goddard, 1988).

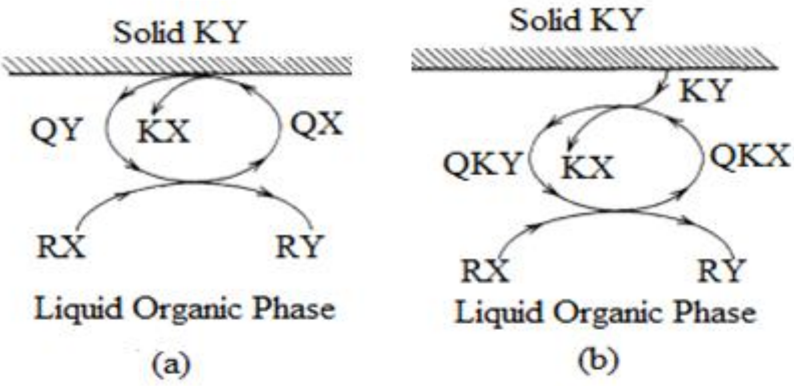


Figure 1.7: (a) Heterogeneous (b) Homogeneous S-L PTC

1.6.2.3 G-L Phase Transfer Catalysis:

When phase transfer catalysis occurs in a gas-liquid-solid mode, it is called gas-liquid phase transfer catalysis (G-L PTC). In this process, the organic substrate (RX) is in the gaseous form and is allowed to pass over a bed of solid inorganic reagent (coated with PT catalyst) in molten liquid form.

Due to constant flow of organic gaseous reactant over solid bed, G-L PTC has the advantage of continuous mode of operation. PT catalyst can be easily replenished as it is directly loaded on inorganic solid bed and unlike L-L PTC; there is increased selectivity as there are no unwanted side reaction of hydrolysis.

A disadvantage related to G-L PTC is that in order to reclaim the organic substrate in the gaseous form, the process needs to be carried out at high temperature. This may lead to the fractional volatilization and thermal decomposition of the PT catalyst (Tundo et al., 1989).

1.6.3 TYPES OF PHASE TRANSFER CATALYSTS:

There are many types of phase transfer catalysts such as quaternary onium salt (ammonium, phosphonium, arsonium salts), crown ethers, cryptands, polyethylene glycol etc. Ionic liquids have also been used in areas of phase transfer catalysis. Among several varieties of PTCs, quaternary ammonium salts (Quats) are the most preferred for their better activity and ease of availability. Among six different catalysts used to intensify the reaction of benzyl chloride with solid sodium sulfide, Tetrabutylammonium bromide (TBAB) had been seen to be the most active PTC (Pradhan and Sharma, 1990). Present study was carried out using TBPB (Tetrabutylphosphonium bromide) as PTC as it is more stable at higher temperatures and performs better than TBAB in adverse conditions also.

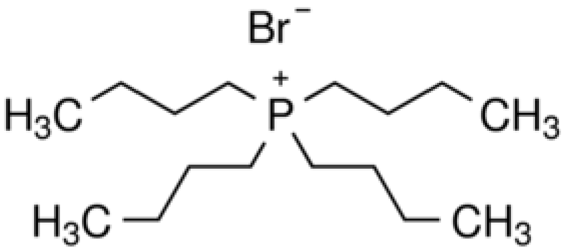


Figure 1.8: Structure of TBPB (Tetrabutylphosphonium bromide)

The qualities of a good PT catalyst are

- Lipophilicity of the catalyst should be high for better transfer of nucleophilic anion to organic phase from aqueous phase.
- There must be a good partition coefficient between organic and aqueous phase.
- For the cation to be easily available for anion exchange reaction in aqueous phase, the catalyst should form loose cation-anion bonding.

The commonly used phase transfer catalysts are onium salts (ammonium and phosphonium salts), crown ethers, cryptands and open chain polyethers like polyethylene glycols (PEG) shown in Fig. 1.9 in the next page (Nathan, 2011).

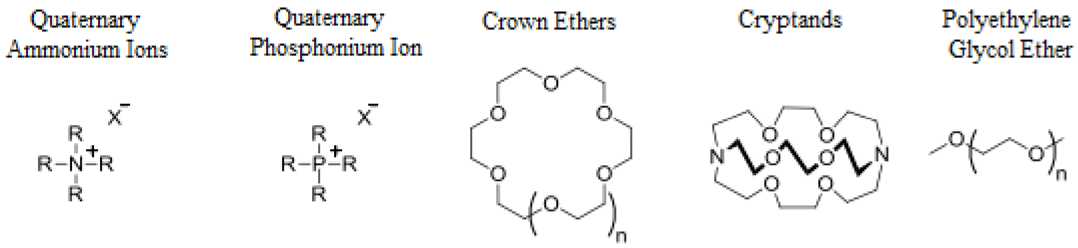


Figure 1.9: Commonly used effective PT Catalyst

Phase transfer catalysis is an attractive technique for synthesis of organic chemicals from two reactants existing in two or three different phases, which normally cannot react with each other due to their low mutual solubility in other phase and their low interaction (Dehmlow and Dehmlow, 1983; Starks et al., 1994).This technique is widely practised for large scale production in industry as well as because of its additional advantages of milder operating conditions, reduced consumption of solvents and raw materials, and enhanced selectivity over the conventional process.

Catalyst	Cost	Stability and activity	Use and recovery of catalyst
Ammonium Salt	Cheap	Moderately active.	Commonly used but difficult to recover.
Phosphonium salt	Costlier than ammonium salts	Moderately active. Thermally more stable than ammonium salt but decomposes under basic condition.	Commonly used but difficult to recover.
Crown ethers	Expensive	Highly active. Stable at both high temperature and basic condition.	Often used. Difficult to recover due to toxicity.
Cryptands	Expensive	Highly active. Stable at both high temperature and basic condition.	Used sometimes due to high activity. Recovery is difficult due to toxicity.
PEG	Very cheap	Lower activity but more stable than onium salts.	Rarely used where high concentration of catalyst does not affect the synthesis reaction. Easy to recover.

Figure 1.10: Properties of Commonly Used PT Catalyst (Naik and Doraiswamy, 1998)

PEG (Polyethylene glycol) is the cheapest among the usual PT catalysts unlike crown ethers and cryptands which are very expensive. All of them are steady at high temperatures (150-200ºC) and it should be kept in mind that various applications of phase transfer catalysis require temperatures ranges between 50-120 ºC. As discussed before, quaternary onium salts remains active and steady under these specified conditions. But PEG's, crown ether and cryptands have higher stability to basic conditions as compared to quaternary onium.

1.6.3.1 Insoluble Phase transfer catalysis:

The separation and recovery of catalyst is an important challenge. Conventional processes like absorption, distillation and extraction are used for the separation of catalyst and product from reaction mixture. If the relative volatility between solvent, product and catalyst are too low, distillation becomes an energy consuming process. For extraction and absorption, more solvent is required which is to be distilled off again (Yadav and Lande, 2005; Yadav and Desai; 2005). Therefore, catalyst is generally treated as waste because of being in very less quantity than the product (Jin et al., 2003). Also, complete separation of catalyst from the product need not be possible leaving the product less pure.

These problems can be solved by converting biphasic PTC to tri-phasic system namely liquid-liquid-solid (L-L-S) PTC and liquid-liquid-Liquid (L-L-L) PTC (Yadav and Motirale, 2010).

1.6.3.2 Liquid-Liquid-Solid PTC:

The L-L-S PTC consists of an organic phase with the substrate, an aqueous phase with the reagent and a solid supported PT catalyst. The mechanism involved is similar to that of stark's extraction mechanism, which involves ion exchange in the aqueous phase and synthesis reaction step in the organic phase, except for the fact that in L-LPTC, catalyst is free to move between aqueous and organic phase while in L-L-S PTC, movement of catalyst is restricted and aqueous and organic phase travels inside the catalyst to react with catalyst cation (Satrio et al., 2000).The advantages of L-L-S PTC over normal PTC are:

- Increase in reaction rates by orders of magnitude.
- Easier catalyst recovery and reuse.
- The reaction can be carried out in a continuous reactor by continuously separating the catalyst.
- Better selectivity.

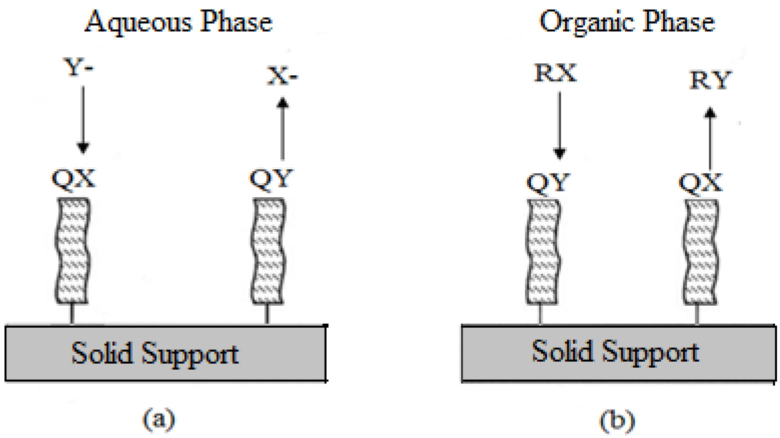


Figure 1.11: (a) Aqueous Phase Reaction (b) Organic Phase Reaction Mechanism of L-L-S PTC

Due to the limitations of diffusion and high cost, L-L-S PTC has not been extensively industrialized. Also, the fact exists that there has been very little understanding of the complex interactions between the three phases involved in L-L-S PTC.

The common examples of L-L-S PTC are Quaternary onium salts, crown ethers, cryptands, and polyethylene glycol on various kinds of supports including polymers (most commonly methylstyrene-co-styrene resin cross-linked with divinylbenzene), alumina, silica gel, clays and zeolites.

1.6.3.3 Liquid-Liquid-Liquid PTC:

Although the PT catalyst in L-L-S PTC can be easily separated from reaction mixture by filtration and reused as it is bound on a solid matrix like polymer or inorganic support, the rate of the reaction is slowed considerably because of intra-particle diffusion limitations. Also, L-L-S PTC has a high cost of installation and catalyst preparation. In L-L-L PTC, a middle catalyst rich phase (liquid) is formed in between aqueous and organic phase where the reaction occurs.

There are several ways of creating this third liquid phase. It can be made by increasing catalyst concentration above critical value or through saturation of aqueous phase. Studies show that presence of such a third phase is accompanied by a sudden increase in reaction rate with 100% selectivity of desired product in relatively less reaction time. Since the catalyst rich phase is immiscible with the aqueous and organic phases, it can be easily separated and reused. The high selectivity of product in L-L-L PTC is because of the fact that the organic phase never comes in contact with the aqueous phase and so, unwanted side reactions of hydrolysis are avoided.

The main advantages of L-L-L PTC are:

- Even in mild operating conditions, it gives a high conversion.
- The catalyst can be easily replenished to reuse.
- As unwanted reactions are avoided, a high yield of the desired product is obtained.
- The catalyst does not require any solid support.

L-L-L PTC requires high quantity of catalyst requirement making the initial cost of operation very high but eventually, the catalyst can be separated and reused easily. Catalyst recovery can be done by either reuse of only catalyst rich phase or reuse of catalyst rich phase along with aqueous phase. There is always decrease in catalyst activity through each run due to loss catalyst in aqueous and organic phase distribution (Yadav and Badure, 2007). However, this method is not used for systems that require very high temperatures to carry out the reaction. This is due to the fact that the stability of third liquid phase decreases as the temperature increases.

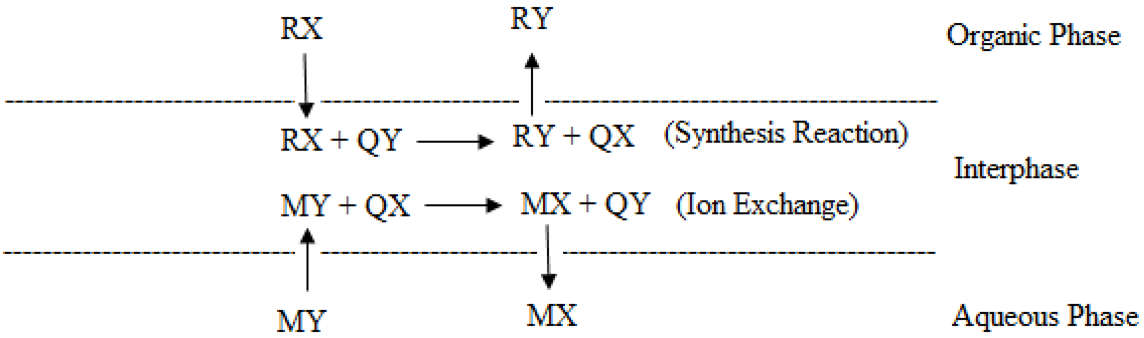


Figure 1.12: Mechanism of L-L-L PTC

CHAPTER 2:

LITERATURE SURVEY

2.1 USE OF AQUEOUS ALKANOLAMINES FOR THE REMOVAL OF H_2S:

Presently, aqueous alkanolamines are being widely used in industries that produce H_2S as by-product for its removal. The amines mostly being used are Diethanolamine (DEA), Monoethanolamine (MEA), and Methyldiethanolamine (MDEA). Using MEA has the advantages of relatively low cost, high reactivity, ease of retrieval, low molecular weight (which results high solution capacity at moderate concentrations) and low absorption of hydrocarbons. MDEA is also used extensively because of regeneration ease, high selectivity towards removal of just H_2S or both H_2S and CO_2 (Zicarai et al., 2003).

Kohl and Nielsen (1997) studied the removal of H_2S and its reclamation from gas mixtures using ammonium hydroxide.

Hamblin (1973) established a method for the removal of hydrogen sulfide from gas mixtures using ammonium hydroxide, producing ammonium hydrosulfide which was oxidised further using a air stream to obtain ammonium polysulfide. This ammonium sulfide is then treated to get elemental sulfur.

Asai et al. (1989) studied the rates of absorption of H2S and ammonia in water with a flat interface in an agitated vessel.

Rumpf et al. (1999) studied the solubility of ammonia and hydrogen sulfide in water varying the temperature from 313 to 393 K and pressure up to 0.7 MPa.

2.2 SYNTHESIS OF ARYL-AMINES USING AMMONIUM SULFIDE:

Such synthesis is done using three kinds of ammonium sulfide (i) aqueous ammonium sulfide (ii) alcoholic ammonium sulfide (iii) ammonium sulfide. They are prepared by dissolving equal amounts of ammonium chloride and crystalline sodium sulfide in alcohol or ammonium hydroxide.

Lucas and Scudder (1928) studied the reduction of 2-bromo-4-nitrotoluene to 2-bromo-4-aminotoluene in a solution of ammonium sulfide dissolved in alcohol.

Idoux and Plain (1972) reduced 1-Substituted 2,4 Dinitrobenzenes using ammonium sulfide or sodium hydrosulfide. It was found that the reduction took place at the position to which electron donation is the least by 1- substituent.

Murray and Waters (1938) studied the reduction of *p*-Nitrobenzoic acid using ammonium sulfide which was prepared by dissolving equal amounts of ammonium chloride and crystalline sodium sulfide in alcohol or ammonium hydroxide.

Cline and Reid (1927) studied the reduction of 2,4-dinitroethylbenzene using alcoholic ammonium sulfide. 50gm of 2,4-dinitroethylbenzene was taken in 150ml of ethyl alcohol and reacted with 150ml of concentrated aqueous ammonia. The solution is then saturated with H2S and boiled until there was found a 30gm increase in weight. The amine was separated by pouring the solution over ice. The solution was then filtered off and dissolved in dilute HCl. The acid solution was boiled with animal charcoal, filtered and cooled to separate the hydrochloride. It was purified by recrystallizing several times with dilute acid, using animal charcoal each time. The base was removed by NH3 and recrystallized from dilute alcohol, which melts at 45^0C.

Meindl et al. (1984) studied the reduction of 3,5-dinitrobenzyl alcohol to 3-amino-5-nitrobenzyl alcohol using ammonium sulfide solution. This ammonium sulfide solution was prepared by reacting a solution of Na2S.9H20 (0.4 mol, 96g) and MeOH (250 ml) with a solution of NH4Cl (1.6 mol, 85.6g) and MeOH (250 ml), and the NaCl is separated. The solution so obtained was added to a solution of 3,5-dinitrobenzyl alcohol (0.2 mol, 39.6gm) after 30 minutes in 700 ml of boiling MeOH, and the mixture was refluxed for 5 hours. The mixture was allowed to cool at room temperature and the precipitate of sulfur was removed. HCl (2N) was added and the solvent was distilled off. The aqueous solution was alkalized and the product extracted with ether after the removal of starting material with ether. The results found were : yield 62%; M.P. 91.5^0C.

Maity et al. (2006a, 2006b, 2008a, 2008b) have performed a lot of work in the reduction of nitrotoluene and nitrochlorobenzenes using aqueous ammonium sulfide and TBAB as catalyst. They also studied the reduction of p-nitrotoluene using aqueous ammonium sulfide, and anion-exchange resin as the catalyst.

2.3 SYNTHESIS OF ARYL-AMINES USING SODIUM SULFIDE/DISULFIDE:

Hojo et al. (1960) worked on the kinetics of the reduction of nitrobenzene to aniline using sodium disulfide in methanolic solution form. It was found that the rate of reaction was proportional to the concentration of nitrobenzene and to the square of the concentration of sodium disulfide.

Bhave and Sharma (1981) worked on the kinetics of three aromatic nitro compounds *m*-chloronitrobenzene, *m*-dinitrobenzene and *p*-nitroaniline in two phase using aqueous solutions of sodium disulfide and sodium monosulfide. The order of the reaction with respect to the concentration of nitroaromatics and sulfide was found to be first order.

Pradhan and Sharma (1992b) studied the reduction of Chloronitrobenzenes to Chloroanilines using sodium sulfide in the absence and presence of a Phase Transfer Catalyst (PTC). The reactions of *o*-chloronitrobenzene and *p*-chloronitrobenzene gave 100% conversion to chloroanilines in the absence of a PTC and 100% conversion to dinitrodiphenyl sulfides in the presence of a PTC, in solid-liquid mode phase transfer catalysis whereas *m*-chloronitrobenzene gave *m*-chloroaniline as the only product even in the presence of a PTC. All the three reactants gave amine as the only product in the presence and absence of a PTC in liquid-liquid mode phase transfer catalysis.

Pradhan (2000) studied the reduction of *o*-, *m*-, and *p*-nitrotoluenes to the corresponding toluidines using sodium sulfide (as aqueous phase) in the liquid-liquid and solid-liquid modes. TBAB acted as the Phase Transfer Catalyst. It was found that all the nitrotoluenes were kinetically controlled in the liquid-liquid mode whereas in the solid-liquid mode, it was found that *o*- and *p*-nitrotoluenes were kinetically controlled and *m*-nitrotoluene was mass transfer controlled.

Yadav et al. (2003a) worked on the kinetics and mechanism of reduction of *p*-nitroanisole to *p*-anisidine under liquid-liquid Phase transfer catalysis. The reaction rate was found to be proportional to the concentration of sodium sulfide, *p*-nitroanisole(reactant) and TBAB (catalyst). They have also reported on the detailed kinetics mechanism of the complex liquid–liquid Phase Transfer Catalysis.

Yadav et al. (2003b) studied the reduction of *p*-chloronitrobenzene using sodium sulphide under liquid-liquid, liquid-solid, and liquid-liquid-liquid forms of Phase transfer catalysis. They found that There are two ways to get p-AP either we have to reduce p-NP by aqueous Sodium Sulphide or first converting p-CNB to p-NP in situ under L-L PTC followed by neutralization of aqueous phase and subsequent reduction with Sodium Sulphide under L-L PTC.

2.4 NITROARENE REDUCTION:

Rode et al. (1999) found a new method to prepare *p*-aminophenol by hydrogenation of nitrobenzene (acid medium) in a single step when the conventional method involved a two-step iron-acid reduction of *p*-nitrophenol.

Jiang et al. (2001) studied a two phase (aqueous/organic) CO selective reduction of nitroarenes catalyzed by Ru3(CO)9(PEO-DPPSA)3 {PEO-DPPSA- poly(ethylene oxide)-substituted 4 (diphenylphosphino)benzenesulfonamide}, a thermoregulated phase-transfer catalyst. It was found that there was good activity and selectivity towards nitro group when carbonyl, cyano or halogen groups were present in the substrates.

Yadav et al. (2003) worked on the reduction of nitroaromatics and nitroanisoles to the corresponding amines. They found that the reduction was affected by aqueous inorganic sulfides, polysulfides and the rates of these biphasic reductions are responsive to intensification under phase transfer catalysis.

Xiaozhi Liu, Shiwei Lu(2003) designed a new and efficient method for the production of aromatic amines by catalytic reduction of aromatic nitro compounds. Selenium was used as the catalyst. It was found that aromatic nitro compounds are reduced by H_2O/CO to form the corresponding amines under atmospheric pressure. Irrespective of the functional groups present on the aromatic ring, the reduction was found to be highly selective to the desired product.

Yadav et al. (2004) worked on the reduction of nitroaromatics to the corresponding amines. The reduction was carried out in two-phase i.e. the nitroaromatics were first dissolved in organic solvents and reduced using aqueous sodium sulfide and TBAB as the phase transfer catalyst. This was liquid-liquid phase transfer catalysis and they compared it to liquid-liquid-liquid phase transfer catalysis. It was found that the latter produced better selectivity and higher rates of reaction.

Maity et al. (2006) worked on the reduction of all nitrotoluene isomers. The organic solvent used was toluene and an aqueous ammonium sulfide acted as the reducing agent. TBAB was the phase transfer catalyst and the experiments were done under liquid-liquid phase transfer catalysis. The highest reaction rate was found for m-nitrotoluene, followed by p- and o-nitrotoluene.

Maity et al. (2007) worked on the reduction of nitrochlorobenzenes (NCBs) under liquid–liquid mode using toluene as the organic solvent,TBAB as the phase transfer catalyst and aqueous ammonium sulfide as the reducing agent.

Yadav at al. (2009) synthesised nitrophen from potassium 2,4-nitrophenolate and *p*-nitrochlorobenzene under solid-liquid mode of phase transfer catalysis using PEG-400 as a phase transfer catalyst. Xylene was used as the solvent and the experiment was done under microwave irradiation. It was found that the participation of microwave activation and using Solid-Liquid PTC (PEG 400) as the catalyst results in enhancement of reaction rate and selectivity of nitrophen.

Farhadi et al.(2010) synthesised NiO nanoparticles by the thermal decomposition of bis(dimethylglyoximato) nickel(II) complex, which was a reusable heterogeneous catalyst for rapid and efficient microwave-assisted reduction of nitroarenes with ethanol.

Robert Kaplanek, Viktor Krchnak(2013) studied the parameters for a rapid and efficient reduction of aromatic nitro compounds to hydrophobic polystyrene-based Wang and Ring resins. They used sodium dithionite in dichloromethane–water under PTC conditions. Tetrabutylammonium hydrogen sulfate (TBAHS) was the phase transfer catalyst found effective for the reduction of nitro groups to amino groups under mild conditions with 100% conversion. This method proved to be a better alternative to tin (II) chloride-based reduction.

Kiasat, Ali Reza (2011) devised an eco-friendly and simple method for the reduction of Nitroarenes wherein Polyethylene glycol was easily grafted to silica gel and used as a phase transfer catalyst under solid-liquid mode. This silica-grafted polyethylene glycol along with zinc powder in water was found to be an efficient heterogeneous catalyst in reducing nitroarenes to the corresponding aromatic amines. The reduction reaction did not affect other sensitive functional groups and proved to have good chemoselectivity.

The methods used in the reduction of Nitroarenes are:

Bechamp reduction: Being the oldest method practiced industrially, it uses stoichiometric amounts of finely divided iron metal (tin, zinc, and aluminium can also be used) and water in the presence of small amount of acid. The main disadvantage associated with this process is the formation of iron sludge, which is difficult to separate and dispose off in the environment. Furthermore, this method cannot be used for substrates harmed by acid media or for the reduction of a single nitro group in a polynitro compound.

Catalytic hydrogenation: In this method, metal hydrides like lithium aluminum hydrides are used for reduction. Besides being expensive due to the requirement of expensive equipment and facility to handle the hydrogen, it may also pose problems due to the risk of preparation of catalyst, poisoning hazards due to catalyst, and the risk of reducing other groups too. Moreover, the metal hydrides tend to convert the nitro compounds to a mixture of azoxy and azo compounds.

Sulfide reduction: It enables chemoselective reduction of nitro compounds in the presence of C=C, azo and other nitro compounds. The sulfide reduction of nitroarenes is commonly carried out by sodium sulfide, disulfide, hydrosulfide, and ammonium sulfide.

Zinin reduction: The reduction reaction of nitroarenes by negative divalent sulfur (sulfide, hydrosulphide and polysulphide) is called Zinin reduction.

The overall stoichiometry of the Zinin's original reduction of nitrobenzene by aqueous ammonium sulfide is given below (Dauben, 1973). This stoichiometry is also applicable for the reduction of nitroarenes by sodium sulfide (Bhave and Sharma, 1981; Pradhan and Sharma, 1992; Pradhan, 2000; Yadav et al., 2003b, 2003c).

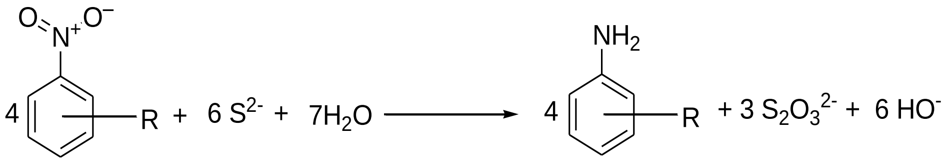


Figure 2.1: Stoichiometry of Zinin’s original reduction**.**

CHAPTER 3:

EXPERIMENTAL WORK

3.1 CHEMICALS AND CATALYST:

Hydrogen sulfide (H_2S)-rich alkanolamine was prepared in the laboratory using Kipp's apparatus. The chemicals used for its preparation and estimation of sulfide content present in it are as follows. Toluene (≥ 99.5 %) of analytical grade (used as solvent), N-Methyldiethanolamine was acquired from Sigma-Aldrich (France) Ltd. The iron sulfide (FeS) sticks were obtained from Thermo Fisher Scientific India Pvt., Ltd., Mumbai, India. Sodium thiosulfate, Potassium iodide, Starch powder, Sulfuric acid (98 % pure) and Sodium hydroxide pellets of analytical grade used for the iodometric titration for the estimation of sulfide content in the H_2S rich N-Methyldiethanolamine (MDEA) were purchased from Rankem (India) Ltd., New Delhi, India. The reactant and PT catalyst used, 4-Nitroacetophenone (NAP) and Tetra-n-butylphosphonium bromide (TBPB) respectively, were acquired from Sigma-Aldrich (USA) Ltd. The water used here was distilled using a distillation column.

3.2 PREPARATION OF H_2S RICH ALKANOLAMINE:

H_2S-rich aqueous N-methyldiethanolamine (MDEA) was prepared by firstly making a 30-35% solution of aqueous alkanolamine by adding suitable amount of N-methyldiethanolamine in distilled water. H_2S gas is then produced in the Kipp's apparatus as shown in Fig. 3.1 in the next page, by reacting FeS sticks with 1 molar H_2SO_4. The produced gas is then taken from the apparatus through a tube to a 250 mL standard gas bubbler containing the prepared N-methyldiethanolamine solution.

Such a reaction between H_2S and N-methyldiethanolamine (MDEA) is exothermic (Kohl and Nielsen, 1997) and so, the gas bubbler containing the N-methyldiethanolamine was kept on top of an ice water bath. This helps to prevent the oxidation of sulfide and consequent formation of disulfide. The outlet of this bubbler was open to the atmosphere. The H_2S gas was bubbled into the MDEA solution until the required concentration of sulfide content was achieved, which was ensured by taking out samples at regular intervals of time and subjecting them to iodometric analysis.

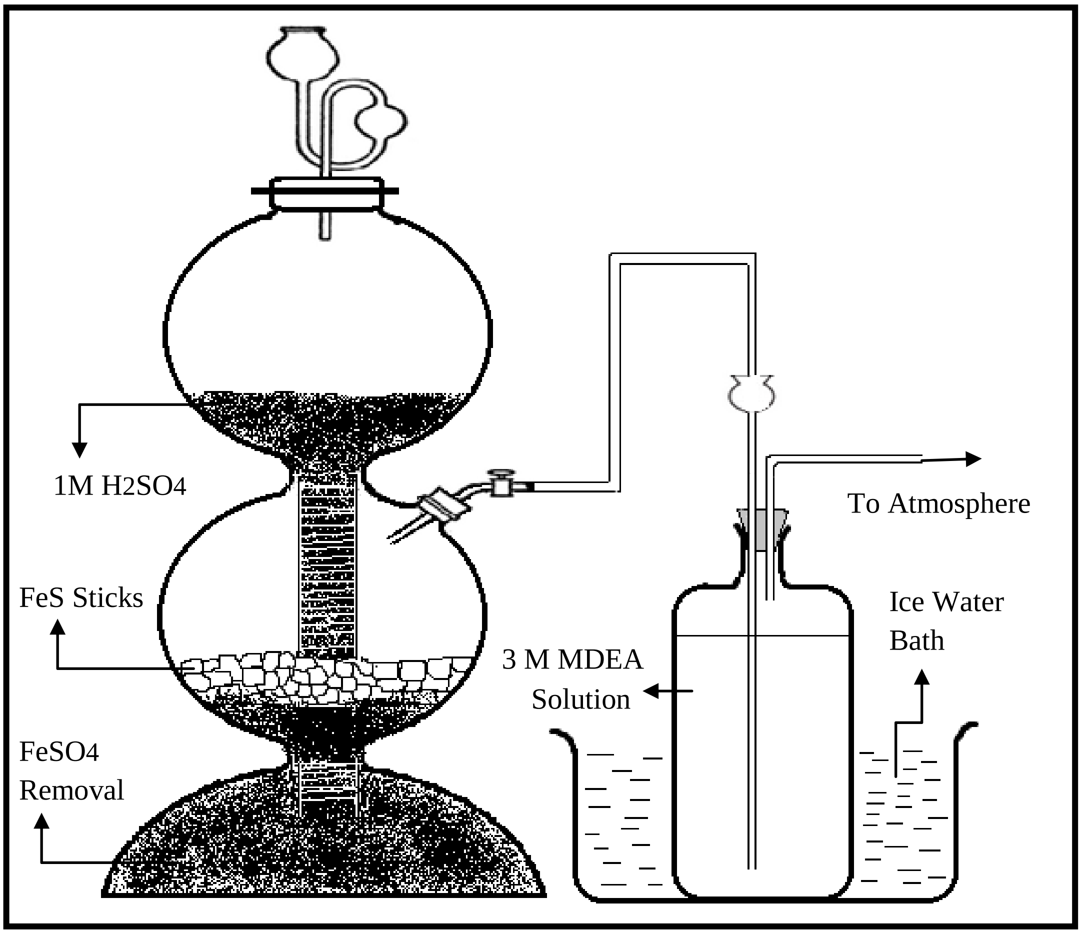


Figure 3.1: Schematic Diagram for Absorption of H_2S in MDEA Solution

3.3 APPARATUS:

The reactions were carried out in a batch reactor (250 cm^3), the temperature of which was controlled using a thermostat. It also consisted of a mechanically agitated glass reactor that was fully baffled and three-necked. The borosilicate glass beaker of the reactor was where the solutions were contacted and the three-necked flask served purposes for agitating the solution, inserting the thermometer, taking solution samples and feeding the solutions. In order to agitate the solution mixture, there was provided a six bladed glass impeller of 2.0 cm diameter at a height of 1.5 cm from the bottom of the glass reactor. Provision for speed regulation is also included. Such an arrangement led to excellent solid-liquid mixing and high mass transfer rates. Water was poured into the batch reactor around the glass reactor forming a constant temperature water bath, the temperature of which could be controlled within ±1°C, by mechanical stirring using an electric motor. The diagram of the experimental arrangement is as shown in Fig.3.2 in the next page.

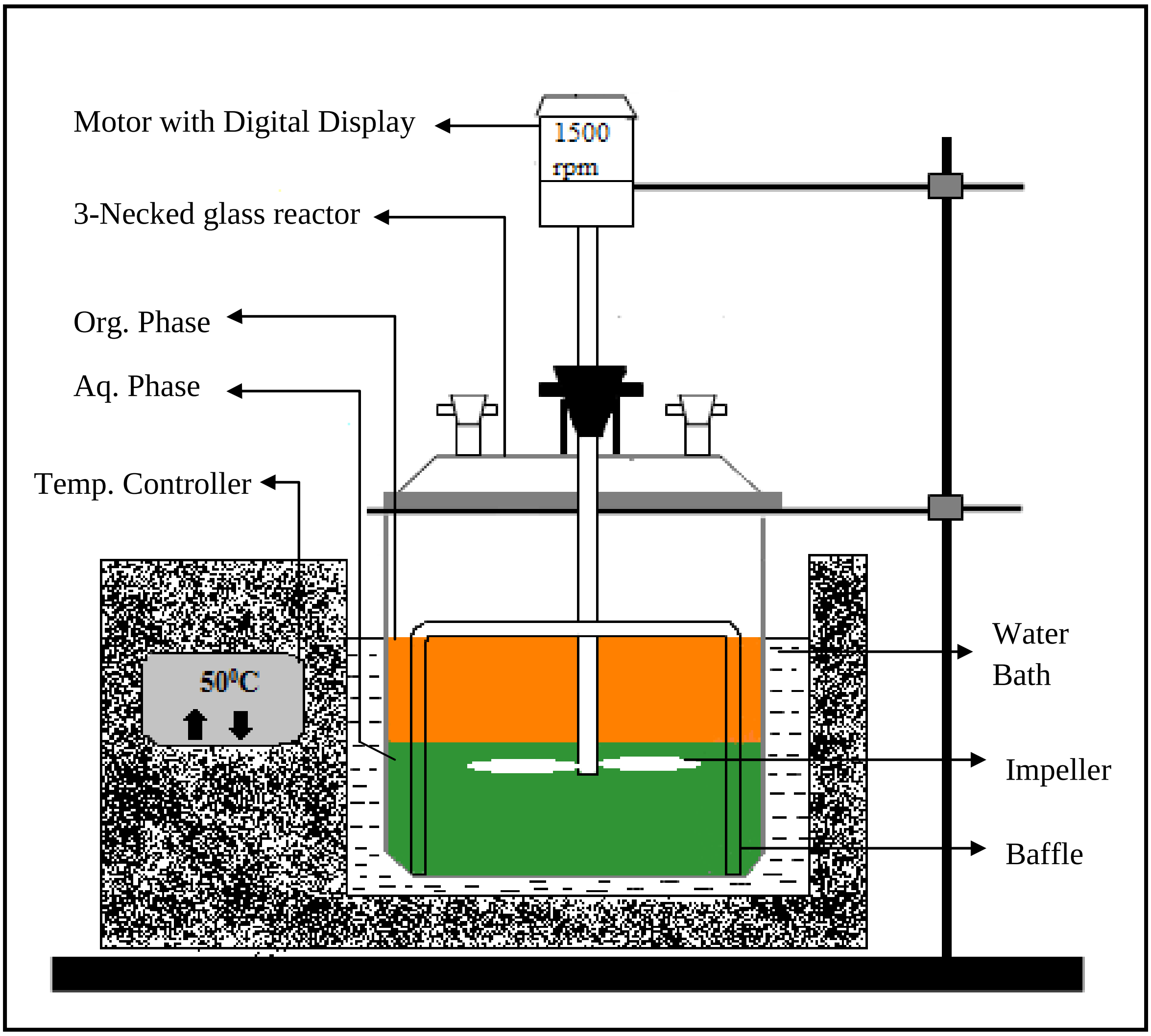


Figure 3.2: Batch Reactor Assembly

3.4 EXPERIMENTAL PROCEDURE:

At first, 30 ml of aqueous phase with a known sulfide concentration was poured into the three-necked glass reactor. The thermostat in the batch reactor was switched on with the reactor well stirred to attain a steady state temperature. After attaining the required steady state temperature, organic phase containing prescribed amounts of organic reactant (4-Nitroacetophenone) and phase transfer catalyst (TBPB) dissolved in 30 ml toluene (organic solvent) was transferred to the three-necked glass reactor. Since both phases were immiscible, two layers were formed in the glass reactor, the organic phase above the aqueous phase. In order to initiate the reaction, the glass reactor was kept in a constant temperature water bath and mechanically agitated using the stirrer at constant speed. After regular known intervals of time, the agitation was stopped and the phases were allowed to separate. About 0.1 ml of the organic phase was pippeted out of the glass reactor. The samples were taken at intervals of 5, 10, 15, 30, 60, 120, 240, 360 and 480 minutes. Therefore the reaction extended for a total of 8 hours wherein 9 samples of the organic phase were taken out. The samples were transferred into glass vials.

3.5 METHOD OF ANALYSIS:

3.5.1 Determination of Sulfide Concentration

Determination of initial sulfide concentration was done by standard iodometric titration method (Scott, 1966) as given below.

3.5.2 Preparation of standard (0.025 M) KIO_3 Solution:

0.535 gm of KIO_3 was weighed accurately and dissolved in 100 ml of distilled water and kept in a graduated volumetric flask.

3.5.3 Preparation of standard (0.1 M) sodium thiosulfate Solution:

24.818 ~ 25 gm of $Na_2S_2O_3.5H_2O$ crystals was weighed and dissolved in 1000 ml of distilled water and kept in a graduated volumetric flask. Approximately, 0.1 g of sodium carbonate or three drops of chloroform was added to this solution to retain the solution for more than a few days.

3.5.4 Preparation of standard (5% w/v) KI Solution:

5 gm of KI was weighed accurately and dissolved in 100 ml of distilled water and kept in a graduated volumetric flask.

3.5.5 Preparation of standard (1 M) Sulfuric acid Solution:

53.26 ml of concentrated (98%) H_2SO_4 was taken and dissolved in distilled water to make up 1000 ml and kept in a graduated volumetric flask. Since this is an extremely exothermic reaction, the Sulfuric acid must be added slowly to the distilled water under a cool water bath.

3.5.6 Preparation of standard (10M) NaOH Solution:

40 gm of NaOH pellets were weighed accurately and dissolved in 100 ml of distilled water and kept in a graduated volumetric flask.

3.5.7 Standardization of Sodium Thiosulfate Solution by standard Potassium Iodate Solution:

25 ml of 0.025M KIO_3 solution was taken. To it, 1 gm (excess) of potassium iodide (KI) was added along with 3 ml of 1 M Sulfuric acid. According to the reaction below, the iodine was liberated and titrated against thiosulfate solution (in the burette) until the colour of solution changed from brown to pale yellow. Then the solution was made up to 200 ml using distilled water and few drops of 0.2% iodine starch solution were added to it, changing the colour of the solution to violet. After this, the titration was continued until colour changed from violet to colourless. Readings of the burette during the colour changes were noted.

The starch solution was prepared by boiling 100 ml of distilled water and then adding 0.2 g starch powder to the 100 ml boiled distilled water. The solution was again boiled for 2 minutes and then cooled and 2.5 gm of KI was added to make it 0.2% iodine starch solution. The chemical reaction involved in this titration is given below.

$$\mathrm{KIO_3 + 5KI + H_2SO_4 \leftrightarrow 3I_2 + 3H_2O + 3K_2SO_4}$$

$$\mathrm{2Na_2S_2O_3 + I_2 \leftrightarrow Na_2S_4O_6 + 2NaI}$$

Therefore, 1 mole of KIO_3 ≡ 3×2 mole of $Na_2S_2O_3$.

$$\therefore \text{ Strength of Thiosulfate Solution} = \frac{6 \times \text{Strength of KIO}_3 \times \text{Volume of KIO}_3}{\text{Volume of Thiosulfate Consumed}}$$

3.5.8 Estimation of Sulfide Concentration:

Hydrogen sulfide and soluble sulfides oxidise with potassium iodate in an alkaline medium. This is used for sulfide estimation. 1 ml of the aqueous phase (H_2S-rich MDEA) was taken from the gas bubbler to a graduated volumetric flask and then made up to 100 ml using distilled water to form the sulfide solution. A conical flask was taken and to it was added 10 ml of the diluted aqueous phase along with 15 ml of standard 0.025M potassium iodate solution and 10 ml of 10M sodium hydroxide solution. The resulting mixture was then boiled for about 10 minutes. After cooling, 20 ml of 4M Sulfuric acid solution and 5 ml of 5% KI solution were added to the conical flask. The iodine liberated was titrated with 0.1 M Sodium thiosulfate. When the colour in the conical flask turned pale yellow, it was diluted to 200 ml using distilled water. This is followed by the addition of a few drops of 0.2% iodine starch solution, changing the colour of the solution in the conical flask to violet. After adding starch solution, the titration was continued until colour changes from violet to colourless. Readings of the burette during the colour changes were noted.

The oxidation of sulfide to sulfate by potassium iodate in the alkaline medium is given by reaction below.

$$4IO_3^- + 6OH^- + S^{2-} \rightarrow 4SO_4^{2-} + 4I^- + 6H_2O$$

$$4 \text{ moles of } IO_3^- = 3 \text{ moles of } S^{2-}$$

$$\therefore \; H_2S \text{ Concentration} = \left[15 \times S_{\text{iodate}} - \frac{V_{\text{thiosulfate}} \times S_{\text{thiosulfate}}}{6}\right] \times \frac{3}{4} \times \frac{N_d}{10}$$

Where, S_{iodate} = Strength of KIO_3

$V_{thiosulfate}$ = Volume of thiosulfate

$S_{thiosulfate}$ = Strength of thiosulfate

N_d = Number of times of dilution

3.5.9 Analysis of organic phase:

The conversion of 4-Nitroacetophenone (NAP) to 4-Aminoacetophenone (AAP) in the different sample vials were evaluated using gas liquid chromatography (GLC). GC is mainly used as an analytical technique in industrial laboratories for the measurement and identification of quantity of compounds present in a sample mixture. The working of a Gas chromatography or GC is simple. It consists of a mobile phase and a stationary phase. The mobile phase may be any inert gas like Helium or non-reactive gas like nitrogen. The Stationary phase is essentially a very thin (microscopic) layer of liquid coated over the column.

In the process, firstly a pre-determined quantity of sample is injected with a microsyringe onto the chromatographic column of the GC. The carrier gas carries the sample through the stationary phase (coated column). Depending on the adsorption properties of different components of the sample, they elute and have different retention time in the column. A detector at the outlet of the column determines the retention time and amount of components leaving the column.

Flame Ionization Detector (FID) is the most common detector for organic components. In FID, we find electrodes at the end of the column along with burning fuel of air/hydrogen. When the organic compounds exit the column, the flam pyrolizes the carbon compound and with this, +ve and –ve ions are produced. This creates and electrical pulse between the electrodes. The electrical pulse is instantaneous and appears in the form of peaks on the graph (chromatogram) at the retention time of the component.

In present work, GC-MS from Agilent Technology of model 7890B was used with FID detector.

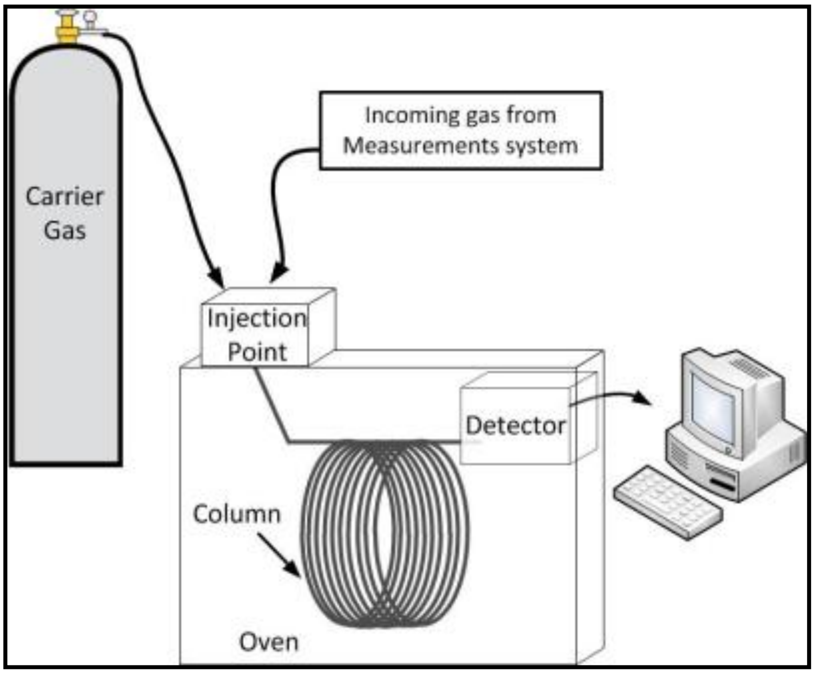


Figure 3.3: A Gas Chromatography Assembly

Program for MS and FID was evaluated given below:

MS PROGRAM

Injection Volume = 1μl

Inlet

Heater = 250^{0}C

Pressure = 14.306 psi

Total Flow = 84.6 ml/min

Purge Flow = 3 ml/min

Mode = Split

Split Ratio = 50:1

Column

Agilent DB-5ms

Flow = 1.6 ml/min

Pressure = 14.306 psi

Holdup Time = 1.0793 min

Avg Velocity = 46.325 cm.sec

Oven

Oven Temperature = 60^{0}C

Maximum Oven Temperature = 324^{0}C

	Rate (^{0}C/min)	Value (^{0}C)	Hold Time (min)	Run Time (min)
Initial		60	0	0
Ramp 1	30	190	0	4.3333
Ramp 2	15	230	0	7

FID PROGRAM

Injection Volume = 1µl

Inlet

Heater = 250^0C

Pressure = 16.724 psi

Total Flow = 44.6 ml/min

Purge Flow = 3 ml/min

Split Ratio = 25:1

Column

Agilent DB-5ms

Flow = 1.6 ml/min

Pressure = 16.724 psi

Holdup Time = 1.3436 min

Oven

Oven Temperature = 60^0C

Maximum Oven Temperature = 324^0C

	Rate (^{0}C/min)	Value (^{0}C)	Holdup Time (min)	Retention Time (min)
Initial		60	0	0
Ramp 1	30	190	0	4.3333
Ramp 2	15	220	0	6.3333

Detector

Heater = 300^0C

Air Flow = 400 ml/min

H_2 Flow = 30 ml/min

Make up Flow (N_2) = 25 ml/min

Column Flow (N_2) = 1.6 ml/min

The chromatogram of NAP system is shown in Fig.3.4. From the chromatogram, we learn that toluene is not participating in the reduction reaction and act as a solvent.

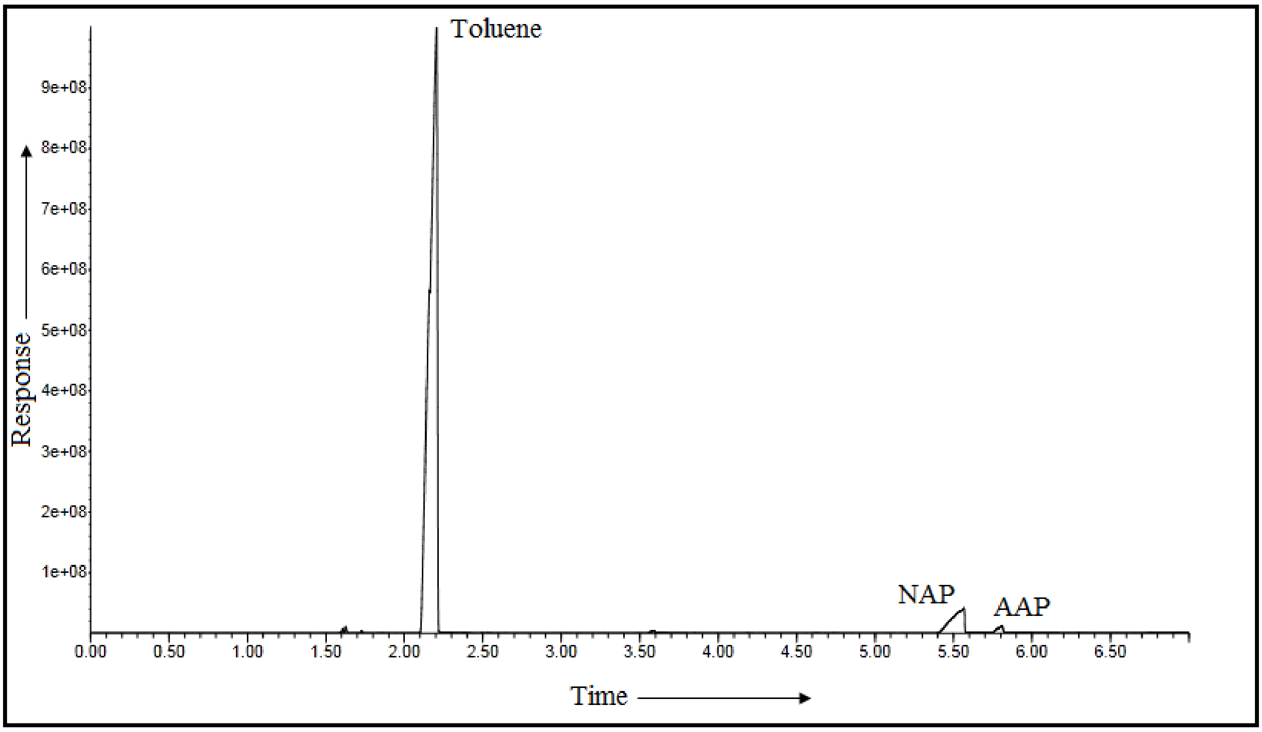


Figure 3.4: Chromatogram of NAP Synthesis

CHAPTER 4:

REDUCTION OF NAP WITH H_2S-RICH MDEA UNDER L-L PTC

4.1 ZININ REDUCTION:

In Scheme 1 given below, the equations (1) to (4) explains the ionic equilibrium between sulphide ions (S^{2-}) and hydrosulphide ions (HS^{-}) in H_2S-rich Alkanolamine solution. During the reduction of NAP by H_2S-rich aqueous MDEA solution, (S^{2-}) and (HS^{-}) ions help in the formation of elemental sulfur or thiosulphate. The presence of both these ions makes H_2S laden aqueous alkanolamine solution different than conventional reducing agents.

$$R_1R_2R_3N + H_2O \rightleftharpoons RNH^+ + OH^- \quad (1)$$

$$H_2O \rightleftharpoons H^+ + HO^- \quad (2)$$

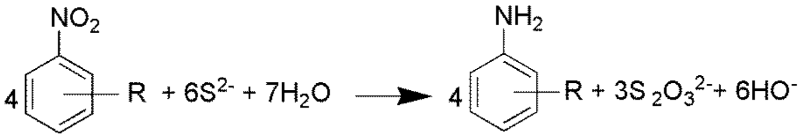
$$H_2S \rightleftharpoons H^+ + HS^- \quad (3)$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \quad (4)$$

$R_1R_2 = CH_2OH$, $R_3 = CH_3$

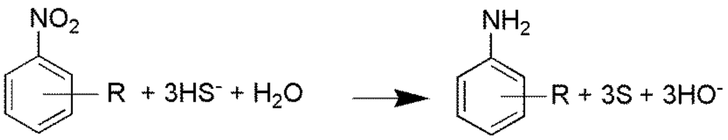
Scheme1. Ionic equilibria in H_2S-MDEA-H_2O system (Maity et al., 2007)

Eq. (5) explains the overall stoichiometry of the Zinin's original reduction of nitrobenzene by aqueous ammonium sulphide, as proposed by Zinin in 1842. The same stoichiometry is followed by reduction of nitroarenes by sodium sulphide [17,30,31,33].



(5)

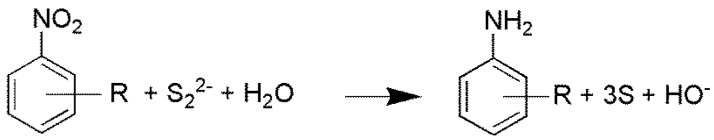
It was seen from literatures that instead of thiosulphate, elemental sulfur can be produced as a by-product if aqueous ammonium sulphide is used as a reducing agent when p-nitrophenylacetic acid is reduced to p-aminophenylacetic acid as shown in Eq. (6) (H.Gilman, 1941).



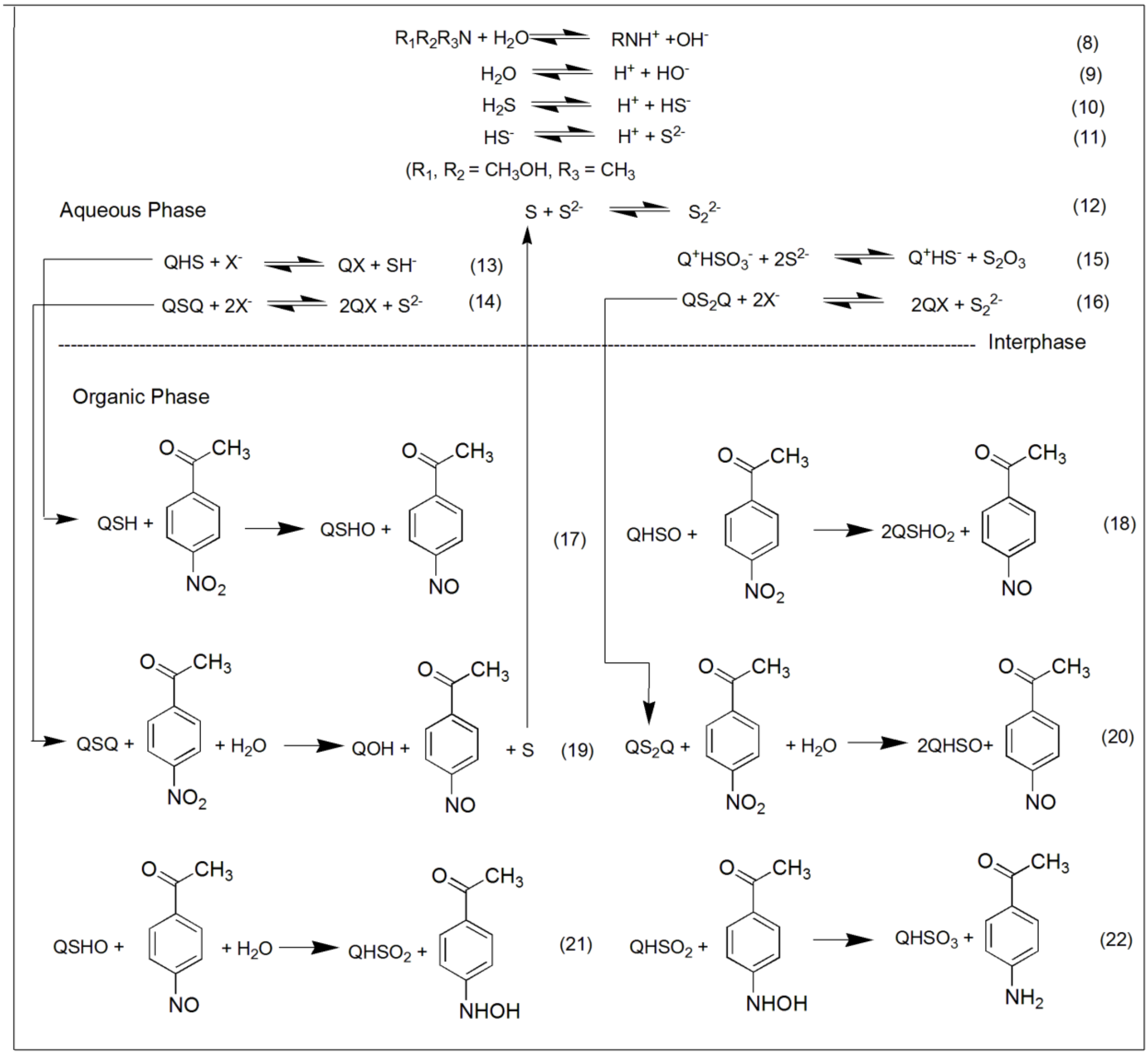
(6)

From the above two reactions, it is clear that S^{2-}& HS^{-} have reduced the reactant to give elemental sulfur or thiosulphate as by-products. In the presence of a base, ammonia, the dissociation equilibrium favours toward more ionization and the concentration of sulphide ions (S^{2-}) relative to hydrosulphide (HS^{-}) ions increases in the aqueous phase with the rise in the ammonia concentration (Maity et al., 2006b).

The overall stoichiometry of the reduction reaction using sodium disulphide as the reducing agent is as follows (H.Gilman, 1941).



(7)



Scheme 2. Proposed mechanism of reduction of NAP by H_2S-laden MDEA under L-L PTC

4.2 PROPOSED MECHANISM FOR REDUCTION OF NAP UNDER L-L PTC:

Based on literature studies on reactions of reduction of nitroarenes by sodium sulphide, a general reaction mechanism has been proposed (Scheme 2 in the previous page). Sulfur has the ability to exist in various valency states from (-2) to (+6) making it favourable for the formation of different anions ($HS^-, HSO^-, HSO_2^-, HSO_3^-$). These anions are capable of pairing with quaternary cations in a rapid manner than other anions which require multiple quaternary cations ($Q_n^+X^-$). During reduction of nitroaromatic compounds by aqueous sulphide solution, the nitro group present in the nitro aromatic compound is reduced by the transfer of an electron from sulphide ion.

Present system is a liquid-liquid PTC system, consisting of an organic phase (4-Nitroacetophenone dissolved in toluene solvent), an aqueous phase (H_2S absorbed in aqueous solution of MDEA) and quaternary phosphonium salt (TBPB), partitioned into both the phases. According to Starks extraction mechanism, nucliophiles (anions) present in the aqueous phase get attached to the catalyst cations and then are transported to the organic phase for taking part in reaction with organic substrates.

In the aqueous phase, hydrosulphide ions (HS^-) and sulphide (S^{2-}) anions are formed from the reaction of H_2S reacting with MDEA as shown in Scheme 1. As soon as the Quaternary cation(Q^+) comes into contact with the aqueous phase, it readily forms (Q^+HS^-) and ($Q^+S^{2-}Q^+$) ion pair. This is followed by a series of reactions taking place in the organic phase as shown in Scheme 2. Since the organic substrate has limited solubility in the aqueous phase, reactions occur near the interphase between anions present in aqueous phase and organic substrate on the organic phase. This is confirmed by the fact that products are formed in the absence of catalyst also.

The contribution of several elementary reactions in the organic phase to the overall rate of the reaction is elaborated by the above mechanism. In a series of complex elementary reactions, 4-Nitroacetophenone is converted to 4-Aminoacetophenone through the formation of intermediates (4-nitrosoacetophenone and 4-hydroxylaminoacetophenone), both of which haven’t been detected by the GC-MS. Although the existence of these intermediates during Zinin reduction have been established, the fact that they cannot be detected may be due to the fact that of faster disapperance of the intermediates in the organic phase. When the catalyst cations are pairing with the HS^- anions, some water molecules transfer to the interphase and they take part in the reaction (Eq.(19) to Eq. (21)). After a series of elementary reactions, we can see from Scheme 2 that the ion pair $Q^+HSO_3^-$ is formed in the organic phase and it is transferred to the aqueous phase where it reacts with S^{2-} to regenerate Q^+HS^- according to Eq. (15). The regenerated quaternary cations are transferred to the organic phase again for the reduction reaction and this completes a typical catalytic cycle.

As we can see from Scheme 2, the quaternary cations pair with different anions during the reactions but majority of the catalyst cations remain in Q^+HS^- form and the catalysis cycle goes on. Nine reactions (Eq. (8) – Eq. (16)) took place in the aqueous phase and rest of them (Eq. (17) – Eq. (22)) in the organic phase. 100% selectivity of 4-Aminoacetophenone is obtained at the end of the reaction.

4.3 PRESENT WORK:

In the present work, more valuable chemicals like 4-Aminoacetophenone was synthesised from 4-Nitroacetophenone dissolved in toluene using H_2S-rich MDEA in a batch reactor under L-L PTC in the presence of Tetrabutylphosphonium Bromide (TBPB). This process is considered to be lower in cost and more environment friendly as compared to the Claus process owing to the fact that H_2S gas (noxious) is being utilised and the gas is produced in plenty as byproduct gas in various industries.

Aminoacetophenone (AAP) is used used in clinical biology as a detector or marker for Pseudomonas Aeruginosa in the cystic fibrostic lung. It is also a drug metabolite as it helps in the biochemical modification of pharmaceutical substances by living organisms through enzymes. AAP plays a major role in the determination of vitamin B_6 and in the asymmetric total synthesis of pactamycin. It was used as a starting agent during the synthesis of curcumin mimics with substituted sulphonyl group. Also, it acts as a bifunctional coupling reagent during the synthesis of pyrimidines. It has potential antibacterial properties and is used in the synthesis of HIV-1 growth inhibitors and selective antagonists at human adenosine receptors. AAP is also used as an intermediate in organic synthesis of pharmaceutical products like Coumarins (benzopyrones).

The influence of process variables like stirring speed, elemental sulfur loading, concentration of reactant, temperature, sulphide concentration, catalyst loading on the conversion NAP was studied.

4.4 PARAMETRIC STUDIES:

4.4.1 *Effect of stirring speed:*

The main objective of examining the effect of stirring speed on the reaction is to find the effect of mass transfer resistance on the reaction kinetics. This is because along with the reaction kinetics, the mass transfer is also important in influencing the conversion or rate of the L-L PTC. The reaction was carried out at stirring speeds of 500, 1000, 1500 and 2000 revolutions/minute (rpm) under the exact same experimental conditions and in the presence of TBPB as the phase transfer catalyst. From Fig. 4.1 (a), it is clear that the conversion of 4-Nitroacetophenone is not influenced by the speed of agitation when it is above 1000 rpm. This kind of observation was found to be quite unique as other reaction systems required a high stirring speed to reach a more or less constant level of conversion.

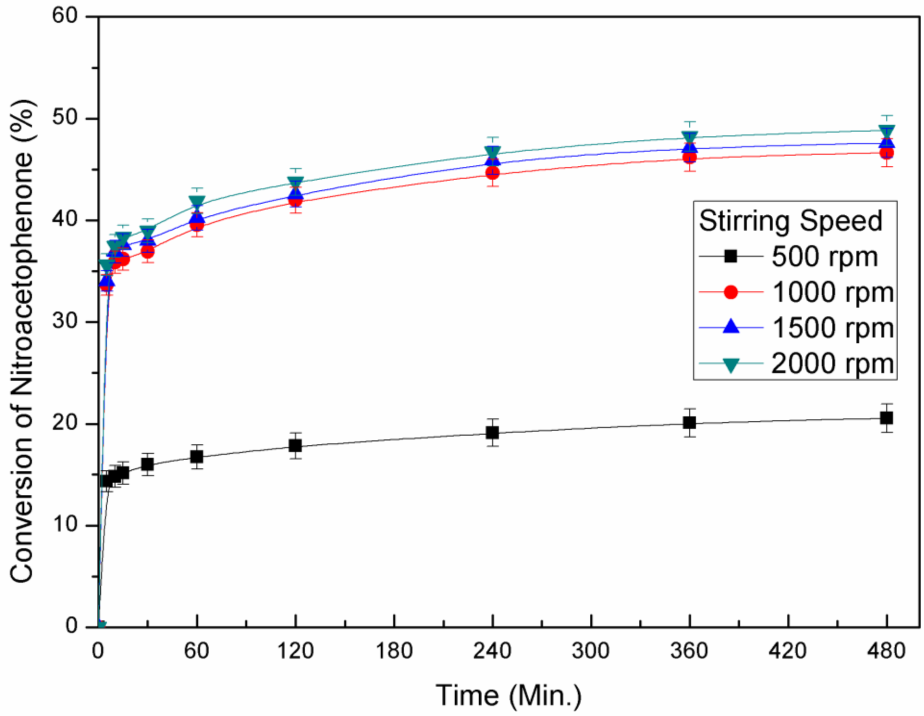


Figure 4.1 (a): Effect of stirring speed on conversion of NAP.

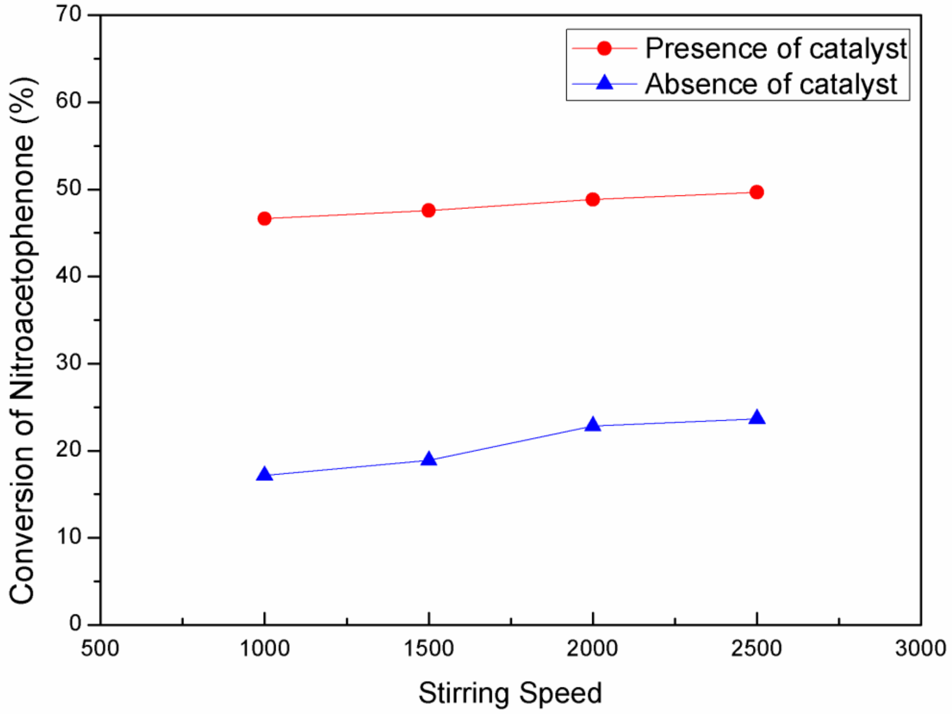


Figure 4.1 (b): Effect of stirring speed on conversion of NAP with and without catalyst. Operating conditions: Volume of organic phase = 30 ml, Volume of aqueous phase = 30 ml, Concentration of NAP = 0.9082 Kmol/m^3 in org. phase, Concentration of toluene = 4.721 Kmol/m^3 in org. phase, Concentration of catalyst = 0.0442 Kmol/m^3 in org. phase, Concentration of sulphide = 2.5 Kmol/m^3, Concentration of MDEA = 3.04 Kmol/m^3, Temperature = 323 K.

This is probably because the active intermediate of the catalyst (QSQ) is hydrophobic and favours to stay in the organic phase, wherein the interfacial area is not important, whereas other reaction systems require a larger interfacial area to increase the mass transfer rate. Thus we can conclude from the above figures that the variation of conversion of NAP with the speed of agitation is very small (in 1000-2000 rpm range) and so, the mass transfer resistance becomes unimportant and we can say that the reaction is purely kinetically controlled. All further experiments were carried out at a stirring speed of 1500 rpm to ensure there is no mass transfer resistance.

4.4.2 *Effect of Temperature:*

Experiments were carried out with NAP in toluene catalyzed by TBPB in the presence of H_2S rich MDEA under various reaction temperatures ranging from 40^0C to 70^0C. Rest of the operating conditions were exactly the same for the experiments. The effect of temperature on the conversion of NAP can be seen from the Fig. 4.2. From the transition state theory, we know that rates of organic reactions increase with increase in temperature. This is why it can be safely assumed that increasing temperature will elevate the rate of slow organic phase reactions in the PTC system as the activation energy of molecules is overcome and more molecules react to form the product when the temperature is increased. Furthermore, at higher temperature, collision of the reactants is also increased. Hence, the reaction rate undeniably increases with increase in temperature.

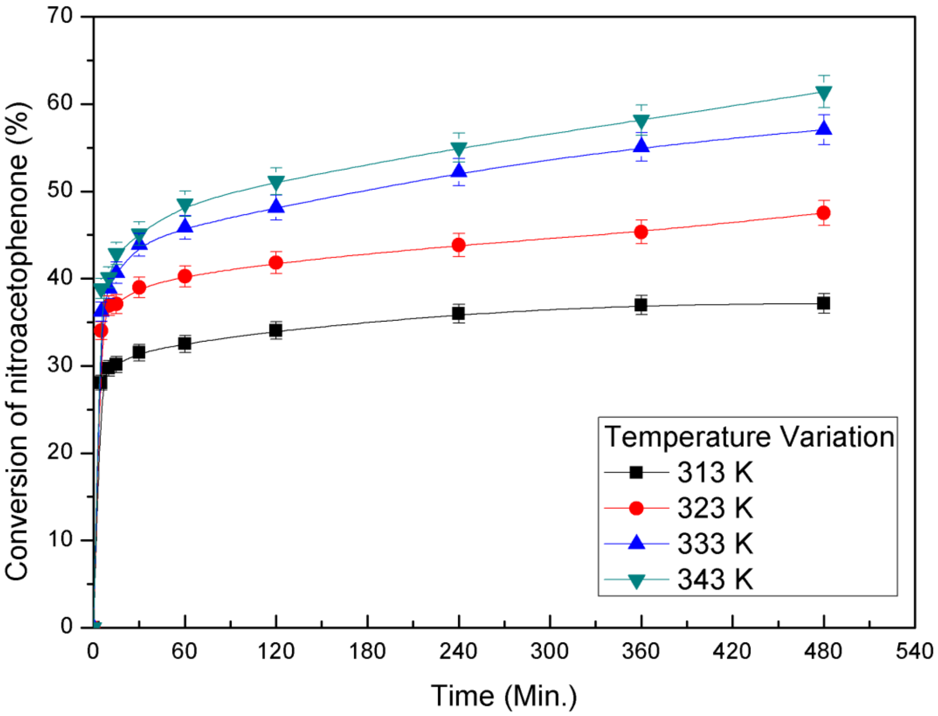


Figure 4.2: Effect of temperature on conversion of NAP.

Operating conditions: Volume of organic phase = 30 ml, Volume of aqueous phase = 30 ml, Concentration of NAP = 0.9082 $Kmol/m^3$ in org. phase, Concentration of toluene = 4.721 $Kmol/m^3$ in org. phase, Concentration of catalyst = 0.0442 $Kmol/m^3$ in org. phase, Concentration of sulphide = 2.5 $Kmol/m^3$, Concentration of MDEA = 3.04 $Kmol/m^3$, Stirring speed = 1500 rpm.

The initial rate of reaction of NAP was calculated for different temperatures and an Arrhenius plot of *ln* (initial rate) vs. 1/T was made. The apparent activation energy for the kinetically controlled reaction was calculated from the slope of best fitted the straight line as 9.645 KJ/mol.

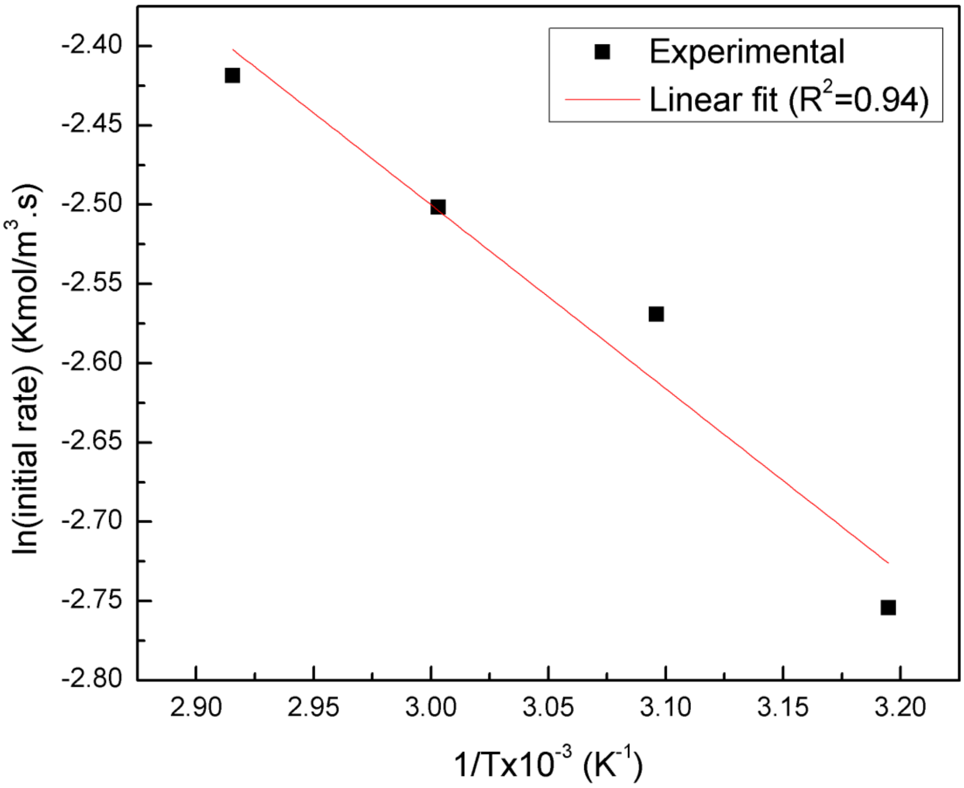


Figure 4.3: Arrhenius plot for activation energy.

Operating conditions: Volume of organic phase = 30 ml, Volume of aqueous phase = 30 ml, Concentration of NAP = 0.9082 Kmol/m^3 in org. phase, Concentration of toluene = 4.721 Kmol/m^3 in org. phase, Concentration of catalyst = 0.0442 Kmol/m^3 in org. phase, Concentration of sulphide = 2.5 Kmol/m^3, Concentration of MDEA = 3.04 Kmol/m^3, Stirring speed = 1500 rpm.

4.4.3 *Effect of catalyst (TBPB) loading:*

The effect of catalyst (TBPB) loading on the conversion of NAP by H_2S- laden aqueous MDEA was studied in the range of 0-0.0737 Kmol/m^3 under otherwise identical experimental conditions, as shown in Fig. 4.4. With the increase in catalyst quantity, the conversion of NAP as well as reaction rate increases. Only by increasing the catalyst concentration, NAP conversion of more than 80% was achieved whereas it was about 23% without catalyst after 480 minutes of reaction under otherwise identical conditions. This shows the importance of PTC and our work.

The overall reaction rate of a L-L PTC (such as the present system) is controlled by the transportation of anions (S^{2-}, HS^-, and S_2^-) from aqueous phase to organic phase. In presence of PTC, the transportation of these anions is facilitated and the reaction becomes organic-phase limited. In the aqueous phase, the anions readily form ion pairs [$Q^+HS^-$and $Q^+S^{2-}Q^+$] with the quaternary cations [Q^+]. The ion pairs are then transported to the organic phase in order to react with NAP as shown in Scheme 2. With increased catalyst concentration, more amount of [$Q^+HS^-$and $Q^+S^{2-}Q^+$] ion pairs are formed and transferred to the organic phase and reacts 4-Nitroacetophenone (NAP) to form 4-Aminoacetophenone (AAP).

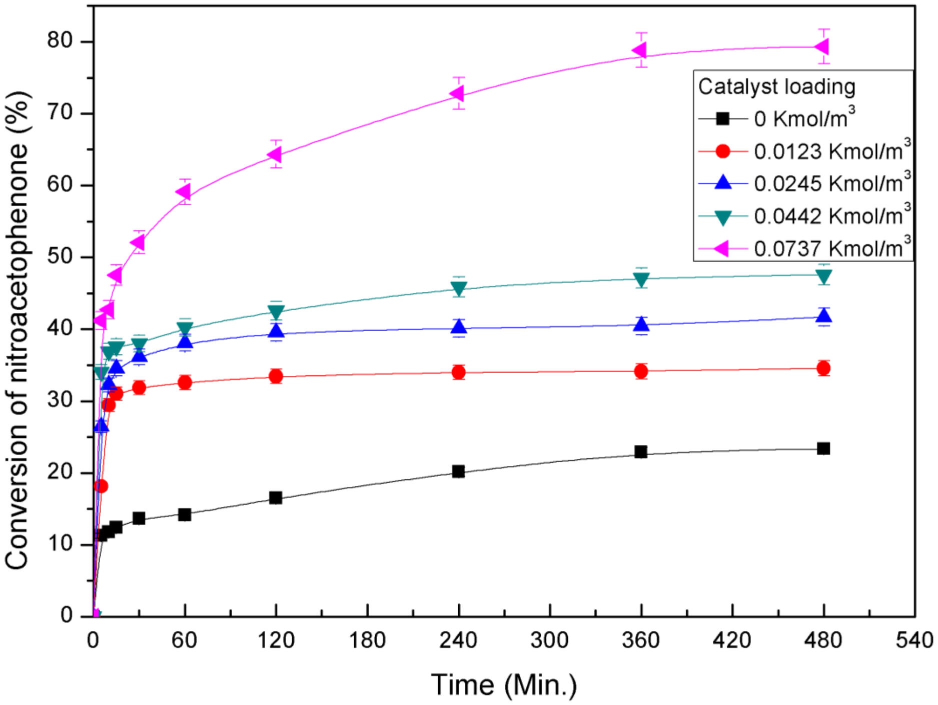


Figure 4.4: Effect of catalyst loading on conversion of NAP.

Operating conditions: Volume of organic phase = 30 ml, Volume of aqueous phase = 30 ml, Concentration of NAP = 0.9082 Kmol/m^3 in org. phase, Concentration of toluene = 4.721 Kmol/m^3 in org. phase, Concentration of sulphide = 2.5 Kmol/m^3, Concentration of MDEA = 3.04 Kmol/m^3, Stirring speed = 1500 rpm, Temperature = 323 K.

To find out order of reaction, the initial reaction rate at different TBPB concentration is calculated and its natural logarithm is plotted with natural logarithm of catalyst concentration as indicated in Fig. 4.5 below. From the slope of the linear fit line, the order of reaction was determined. The order of the reaction with respect to TBPB concentration is found out to be unity.

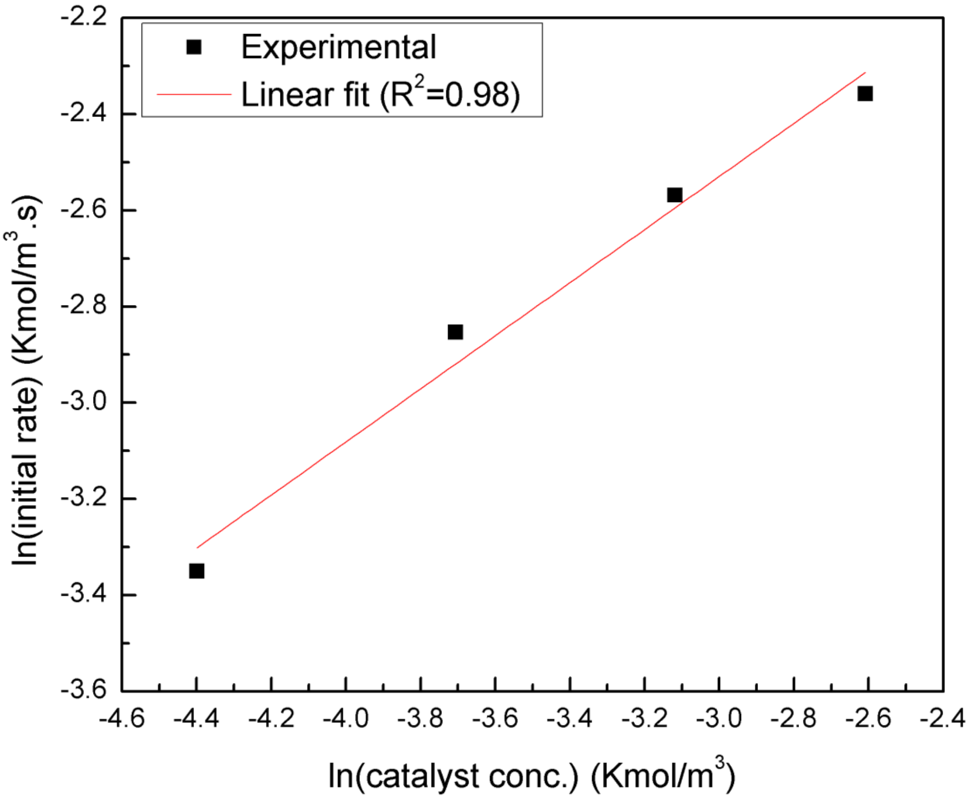


Figure 4.5: Plot of the natural logarithm of the initial rate vs the natural logarithm of the catalyst conc**.**

Concentration of TBPB ($kmol/m^3$ org phase)	**Initial reaction rate ($kmol/m^3s$)**	**Enhancement factor**
0	0.0257	0
0.0123	0.0351	1.36
0.0245	0.0577	2.245
0.0442	0.0767	2.98
0.0737	0.0946	3.68

Table 4.1: Initial reaction rate and enhancement factor.

4.4.4 *Effect of sulfide concentration:*

The effect of sulfide concentration in the aqueous phase on the conversion of NAP with TBPB as PT catalyst in the presence of H_2S rich MDEA was studied, by keeping the MDEA concentration in the aqueous phase constant at 3.04 M. The sulfide concentration was varied in the range of 1 $Kmol/m^3$ to 2.5 $Kmol/m^3$. It was found that for constant MDEA concentration, the reaction rate increased with an increase in the sulfide concentration in the aqueous phase, and a maximum of 47.5% conversion was achieved at the end of 480 minutes with 2.5 $Kmol/m^3$ of sulfide as shown in Fig.4.6.

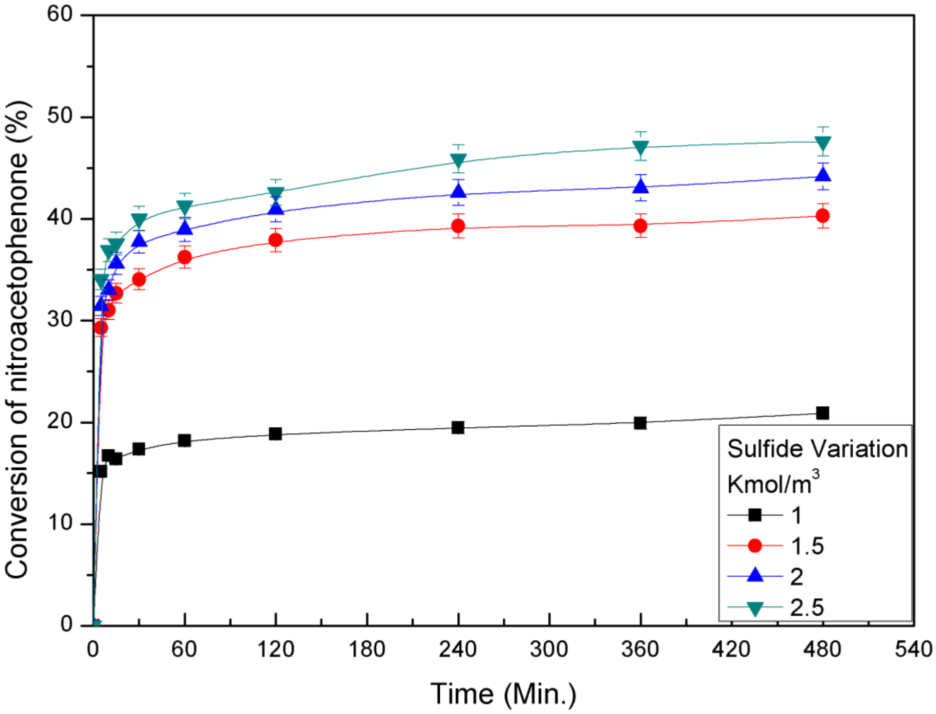


Figure 4.6: Effect of sulfide concentration on conversion of NAP.

Operating conditions: Volume of organic phase = 30 ml, Volume of aqueous phase = 30 ml, Concentration of NAP = 0.9082 Kmol/m^3 in org. phase, Concentration of TBPB = 0.0442 Kmol/m^3 in org. Phase, Concentration of toluene = 4.721 Kmol/m^3 in org. phase, Concentration of MDEA = 3.04 Kmol/m^3, Stirring speed = 1500 rpm, Temperature = 323 K.

This trend can be attributed to the fact that when more amount of sulfide is introduced, there will be more ionization in the aqueous phase to produce more HS^-, S^{2-}, and eventually S_2^{2-} ions as shown in Scheme 2. This leads to greater formation of ion pairs [$Q^+HS^-$and $Q^+S^{2-}Q^+$] with the Quaternary cations [Q^+]. These ion pairs are then transported to the organic phase to cause reduction of NAP to the desired product. Therefore, more the sulfide concentration, more the ion pairs which in turn increases the reduction and hence the reaction rate.

From the slope of the linear fit line, the order of reaction was determined. The order of the reaction with respect to sulfide concentration is found out to be unity.

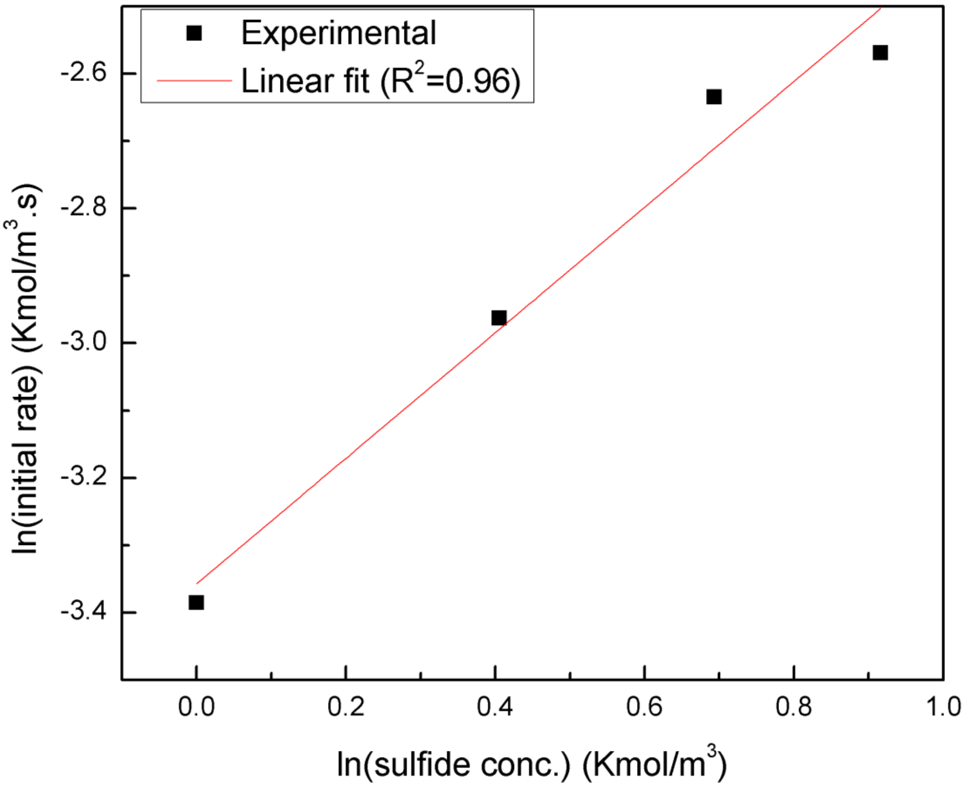


Figure 4.7: Plot of the natural logarithm of the initial rate vs the natural logarithm of the Sulfide conc.

Operating conditions: Volume of organic phase = 30 ml, Volume of aqueous phase = 30 ml, Concentration of NAP = 0.9082 Kmol/m^3 in org. phase, Concentration of TBPB = 0.0442 Kmol/m^3 in org. Phase, Concentration of toluene = 4.721 Kmol/m^3 in org. phase, Concentration of MDEA = 3.04 Kmol/m^3, Stirring speed = 1500 rpm, Temperature = 323 K.

4.4.5 *Effect of MDEA concentration:*

From literature, we find that MDEA does not have direct impact on reaction rate, but it does affect the equilibrium among MDEA, H_2S and water. As mentioned above in Scheme 1, in the aqueous phase, sulphide (S^{2-}) and hydrosulphide (HS^-) active anions are formed which are responsible for two different reactions (Eq. (5) & Eq. (6)). Basic nature of MDEA favours more ionization and hence, sulphide ions (S^{2-}) are more in number than hydrosulphide ions (HS^-) in the aqueous phase. The existence of two reactions can be proven only by varying MDEA addition in the aqueous phase and fixing the sulphide concentration.

Various MDEA concentrations (sulfide concentration kept constant) were prepared by taking 14.5cm^3 of H_2S-laden aqueous MDEA (with known sulfide and MDEA concentrations) solution and adding into it various proportions of pure MDEA and distilled water in such a way that the total volume was made up to 30 cm^3.

During the course of reaction colour of the aqueous solution was changed from greenish yellow to orange and then to reddish brown which is useful in indicating the extent of reaction. As reaction proceeds polysulphide formed which is reddish brown in colour. Similar phenomenon was observed by Lucas and Scudder, 1928.

In this study, after 8 hrs of long run, 32.86% conversion of NAP was achieved with maximum MDEA concentration of 6 Kmol/m^3 while sulphide concentration in aqueous phase was 1.20 Kmol/m^3, as shown in the Fig. 4.8 in the next page. Conversion of NAP obtained is much higher than we can get from Eq. (5) or Eq. (6). This leads to the conclusion that the Eq. (7) is dominant over other two reactions as reaction progresses and polysulphide (formed when elemental sulfur produced in Eq. (6) reacted with sulphide ions present in aqueous phase) ions were formed during the course of reaction.

Formation of elemental sulfur was not reported for the reduction of Nitroarenes with sodium sulphide (Pradhan and Sharma,1992; Yadav and Sengupta,2003b) and it can be assumed that this reaction follows the stoichiometry of Eq. (5) by transfer of sulphide ions. It was observed that initially with increase in MDEA concentration the conversion of NAP was low up to a certain reaction time but then opposite trend was observed and finally higher

NAP conversion was achieved. This may be because at first, the reaction followed Eq.(17) and Eq.(19) of Scheme 2. Eq.(19) was essential for the formation of elemental sulfur and subsequent formation of disulfide and polysulfide ions. Increase in MDEA concentration causes more ionisation of S^{2-} ions rather than HS^- ions. Since Eq.(17) is the main rate determining step, lower HS^- ions lowers the rate of reaction. But with time, disulfide ions are formed which reduce Nitroarenes at a faster rate, thus making up for the increased overall reaction rate. Therefore, for a fixed sulphide concentration in aqueous phase, the increase in MDEA concentration results higher sulphide ions and that boost up the conversion of NAP.

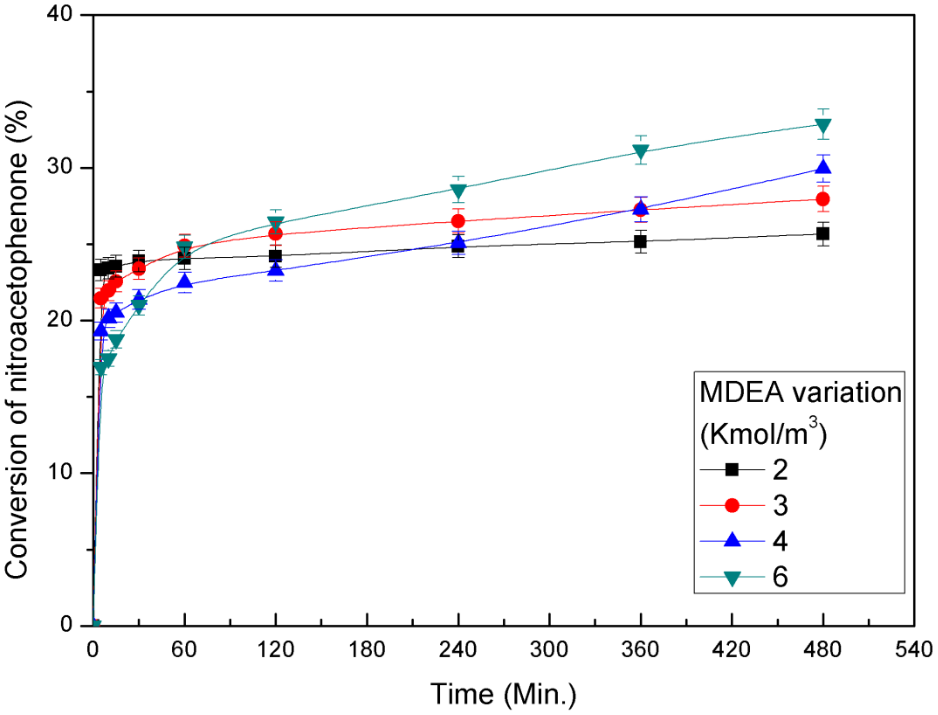


Figure 4.8: Effect of MDEA concentration on conversion of NAP.

Operating conditions: Volume of organic phase = 30 ml, Volume of aqueous phase = 30 ml, Concentration of NAP = 0.9082 Kmol/m^3 in org. phase, Concentration of TBPB = 0.0442 Kmol/m^3 in org. Phase, Concentration of sulfide = 1.20 Kmol/m^3, Concentration of toluene = 4.721 Kmol/m^3 in org. phase, Stirring speed = 1500 rpm, Temperature = 323 K.

4.4.6 *Effect of Reactant variation:*

The effect of concentration of NAP on its conversion was studied at four different concentrations in the range of 0.3028-1.2110 Kmol/m^3 in the presence TBPB under otherwise identical experimental conditions, as shown in Fig. 4.9. It is clear that with the increase of concentration of NAP, its conversion is decreased. About 90% conversion of NAP was obtained for a reactant concentration of 0.3028 Kmol/m^3 and 45.6% conversion of NAP for reactant concentration of 1.2110 Kmol/m^3, after 480 minutes of reaction under otherwise identical experimental conditions.

The increase in the reaction rate during the initial stage of reaction can be attributed to increase in the concentration of the reactant NAP. Hence initially, when there is more number of molecules of NAP reacting with more number of molecules of TBPB and H_2S-rich MDEA, it leads to more conversion. But the amount of sulphide in the aqueous phase remained the same for all the experimental runs, which is why the conversion dropped beyond a certain concentration of NAP in the reaction. For reduction of o-nitroanisole by H_2S rich Diethanolamine, similar observation was found (Maity and Pradhan, 2007). Conversion and reaction rate were found to increase with decrease in NAP concentration at the end of 8 hours of reaction time.

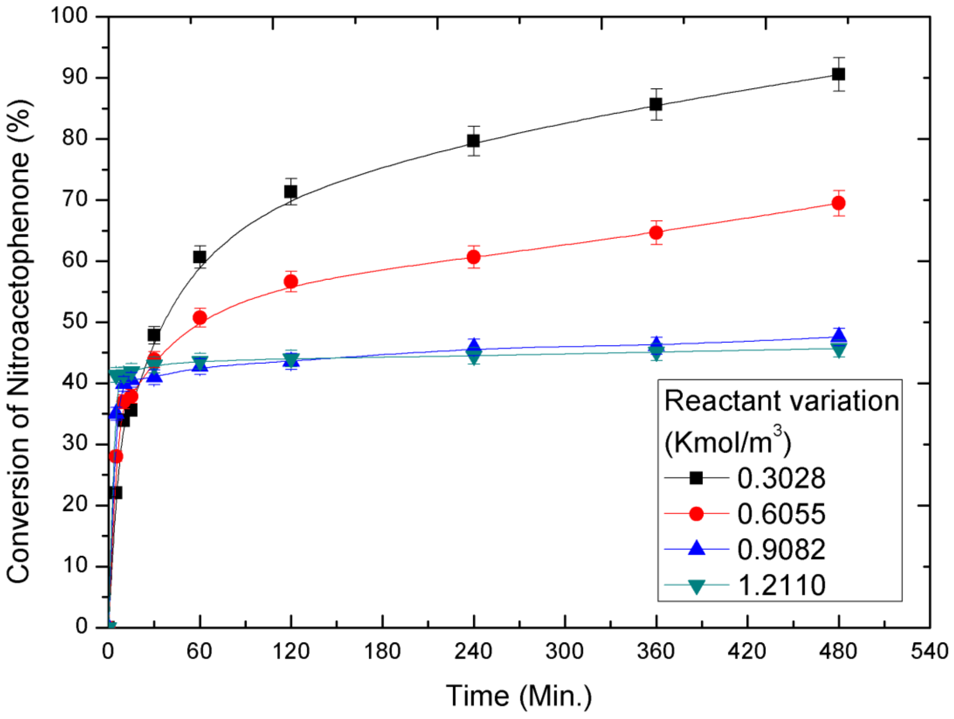


Figure 4.9: Effect of reactant concentration on conversion of NAP.

Operating conditions: Volume of organic phase = 30 ml, Volume of aqueous phase = 30 ml, Concentration of TBPB = 0.0442 Kmol/m^3 in org. Phase, Concentration of sulfide = 2.5 Kmol/m^3, Concentration of toluene = 4.721 Kmol/m^3 in org. phase, Concentration of MDEA = 3.04 Kmol/m^3, Stirring speed = 1500 rpm, Temperature = 323 K.

The order of reaction with respect to NAP concentration was obtained as unity. Hence the reaction is first order with respect to the concentration of reactant. A similar observation was found for reduction of Nitroarenes by aqueous sodium sulfide (Yadav and Sengupta, 2003b).

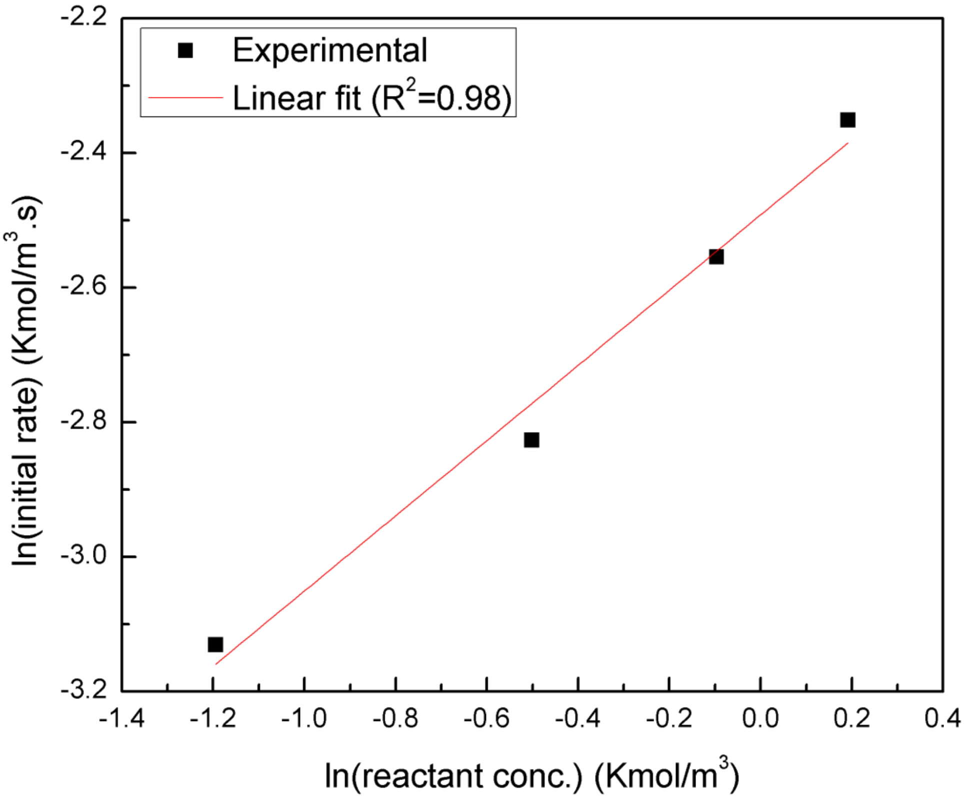


Figure 4.10: Plot of the natural logarithm of the initial rate vs the natural logarithm of the NAP conc.

Operating conditions: Volume of organic phase = 30 ml, Volume of aqueous phase = 30 ml, Concentration of TBPB = 0.0442 Kmol/m^3 in org. Phase, Concentration of sulfide = 2.5 Kmol/m^3, Concentration of toluene = 4.721 Kmol/m^3 in org. phase, Concentration of MDEA = 3.04 Kmol/m^3, Stirring speed = 1500 rpm, Temperature = 323 K.

4.4.7 *Effect of sulfur loading:*

The effect of elemental sulfur loading on conversion of NAP in the presence of H_2S rich MDEA and TBPB as the PT catalyst is shown in Fig. 4.11 in the next page. The elemental sulfur was introduced into the aqueous phase. The dark greenish colour of H_2S-laden MDEA solution became orange when elemental sulfur was added in it. As seen from Fig. 4.11, initially the reaction rate increased with elemental sulfur addition but after certain time, reaction rate slowed down. This can be attributed to the fact that with the elemental sulfur introduced, it can combine with sulfide ions present in the aqueous phase to form disulfide and polysulfide ion pairs. We know from literature that disulfide ion pairs can transfer to the organic phase from the aqueous phase in quicker pace and they are capable of reducing NAP at a faster rate than sulfide or hydrosulfide ion pairs. This is why initially; there is an increase in the reaction rate when more elemental sulfur is introduced. But after a certain reaction time, polysulfides increase in number having no effect on the conversion of NAP. Similar explanation was given by Lucas and Scudder (1928). Also, the reason for decrease in reaction rate may also be due to the reactants depleting with the elemental sulfur build up (which leads to disulfide and polysulfide formation). Hence, it is found that conversion for zero elemental sulfur addition is the highest at the end of 8 hour reaction time.

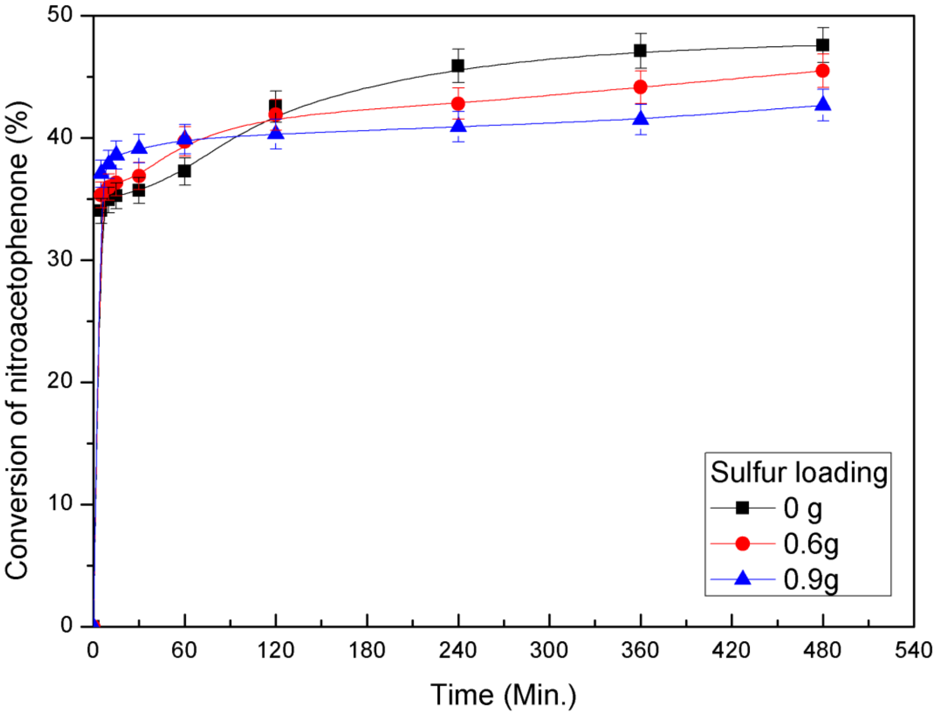


Figure 4.11: Effect of sulfur loading on conversion of NAP.

Operating conditions: Volume of organic phase = 30 ml, Volume of aqueous phase = 30 ml, Concentration of NAP = 0.9082 Kmol/m^3, Concentration of TBPB = 0.0442 Kmol/m^3 in org. Phase, Concentration of sulfide = 2.5 Kmol/m^3, Concentration of toluene = 4.721 Kmol/m^3 in org. phase, Concentration of MDEA = 3.04 Kmol/m^3, Stirring speed = 1500 rpm, Temperature = 323 K.

4.4.8 *Effect of Different catalysts:*

The effect of different catalysts on the conversion of NAP was studied for 3 different catalysts in otherwise identical conditions as shown in Fig. 4.12. TBAB and TBPB were introduced at 0.0442 Kmol/m^3 while Amberlite 400 was introduced at 0.29 Kmol/m^3. It was found that Tetrabutylammonium Bromide effected the highest conversion of 67%. This was followed by Amberlite 400 having effected a conversion of 60%. TBPB which is known to be more stable at adverse conditions effected a conversion of 44%.

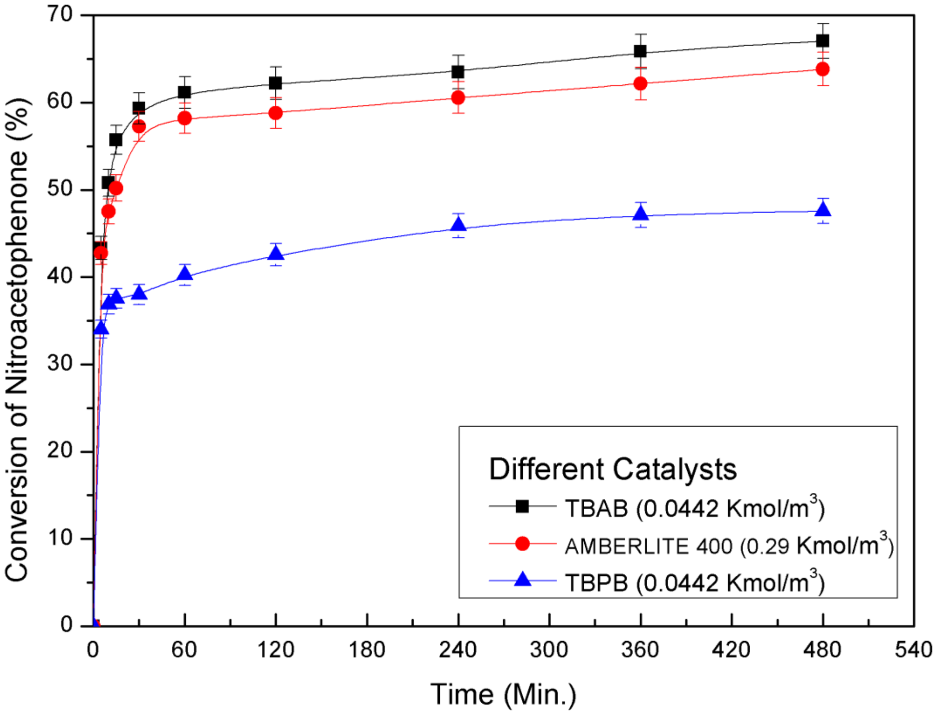


Figure 4.12: Effect of Different catalysts on conversion of NAP.

Operating conditions: Volume of organic phase = 30 ml, Volume of aqueous phase = 30 ml, Concentration of NAP = 0.9082 Kmol/m^3, Concentration of sulfide = 2.5 Kmol/m^3, Concentration of toluene = 4.721 Kmol/m^3 in org. phase, Concentration of MDEA = 3.04 Kmol/m^3, Stirring speed = 1500 rpm, Temperature = 323 K.

CHAPTER 5

CONCLUSION

5.1 CONCLUSION:

The present work is a green process owing to the fact that it consumes H_2S, which is a commonly produced by-product gas, to produce value-added chemicals. With the declining availability of easy-to-process crude oil, refineries are forced to use heavy oil containing high sulfur content leading to the emission of dangerously high levels of H_2S. The importance of this work is directly reflected in this fact.

H_2S is produced in Kipp's apparatus and then absorbed in aqueous MDEA. The sulfide concentration in the MDEA after the Kipp's absorption was measured using Iodometric technique. The samples drawn after the reaction was subjected to GC-MS.

4-Aminoacetophenone (AAP) was produced batch-wise by the reduction (Zinin reduction) of 4-Nitroacetophenone (NAP) using TBPB as phase transfer catalyst and H_2S-rich MDEA as the reducing agent. The effect of various process parameters like stirring speed, temperature, catalyst loading, sulfide concentration, elemental sulfur loading, MDEA concentration and reactant concentration were studied. Lastly Amberlite 400 and TBAB were used as phase transfer catalysts in different experiments to compare the conversion results with that of the ones with TBPB as the PTC.

A mechanism for the course of the reaction was determined from the results of the above studies. It was found that the regeneration of the catalyst took place when [$QHSO_2$] reacted with the nitroso intermediate to give amine and [$QHSO_3$] in the organic phase. This [$QHSO_3$] reacted with S^{2-} in the aqueous phase to give [Q^+HS^-], which is used again in the process.

It was found that between 1000-2000 rpm, there was no significant effect in the conversion of NAP, justifying the absence of any mass transfer effect on the reaction kinetics. As expected, the reaction rate increased with increase in temperature and catalyst concentration. From the studies of the effect of temperature on the conversion of NAP, the apparent activation energy of the kinetically controlled reaction was found to be 9.645 KJ/mol. This owes to why the reactions gave high conversion in short intervals of time. The enhancement factors were found out from the catalytic studies and tabulated. Increase in sulfide concentration increased the conversion of NAP. Although MDEA concentration did not have direct effects on the conversion of NAP, it was found that experiments with higher MDEA concentration eventually resulted in higher conversions (due to explained reasons in the appropriate sections). As the reactant concentration was increased, a trend of decline in the conversion of

NAP was observed. Although increase in sulfur loading increased the reaction rates initially, experiments with lower sulfur loading eventually gave higher conversions (as polysulfide ions were produced).

In the present work, it was observed that there was complete utilization of sulfide in the aqueous phase and therefore, no further treat was required for re-use. However, TBPB being a soluble phase transfer catalyst, it becomes very difficult for its reclamation and reuse. Nevertheless, there is a high probability for the present process to overthrow conventional processes for disposal of H_2S.

5.2 FUTURE WORK:

5.2.1 MECHANISTIC PATHWAY INVESTIGATION:

From section 4.2, we saw the mechanistic pathway for the reaction of NAP with H_2S- rich MDEA (Scheme 2). It was based on some earlier studies and observations from the present study. The Aqueous phase can be analyzed to find out the different species present in it. These species can be quantified in an MS to get a better understanding of the mechanistic pathway of the aqueous phase in L-L system. If this practice is followed, then it will help in getting a better insight into the reaction mechanism, and also to perform kinetic modelling. Statistical modelling can also be done in the “Design Expert” software, where certain additional experiments may be required to be performed at higher temperatures and catalytic concentrations. Such a modelling could help us get simultaneous interactive effect of two parameters on the NAP conversion.

5.2.2 EVALUATION OF EFFECT OF OTHER PARAMETERS:

Presently, Toluene is being used as the solvent for all the experiments as it is cheap and easily available. The physical properties of the solvent have an important part to play in the Phase transfer catalytic reactions. Not only do they carry out the reactions due to the presence of HS^-, S^{2-} and S_2^{2-}, they are also responsible for the transport of the phase transfer catalyst and active catalyst species (QSQ and QSH). Many other solvents like chlorobenzene, n-heptane, and dichloromethane can be tested for better conversion of NAP. Other co-catalyst and anion can also be tested for better conversion.

Most of the effluent gases from industries contain both H_2S and CO_2 as major acid gas impurities. Therefore we need to test H_2S absorption efficiency with different aqueous solutions. Although MDEA proved to be selective towards H_2S, it is next to impossible to get a 100% selective solvent. Since some CO_2 always remains in the aqueous phase, we also need to study the effect of CO_2 on our system.

5.2.3 LARGE SCALE APPLICATION OF PRESENT STUDY:

The present work needs to be scaled up and larger reactors should be utilized before the process is taken up to an industrial scale. An efficient method for product separation and purification should be designed. Although identification of the products are done through GC-MS, other techniques such as nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR) can also be used.

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