



**Advances in Hydrogen Sulphide Utilization: Phase Transfer
Catalysed Selective Reduction of Nitronaphthalene**

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ARTICLE

Advances in Hydrogen Sulphide Utilization: Phase Transfer Catalysed Selective Reduction of Nitronaphthalene

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ABSTRACT

The current study demonstrated the selective reduction of 1-Nitronaphthalene (1-NN) by Hydrogen Sulphide (H₂S) absorbed in aqueous N-Methyldiethanolamine (MDEA), which is a commonly encountered process in Amine treating unit (ATU) of petroleum refinery. The modified Zinin reduction has been carried out using Tetra-n-butylphosphonium Bromide (TBPB) as Phase Transfer Catalyst under Liquid-Liquid (L-L) biphasic mode. The selectivity of product 1-aminonaphthalene was found to be 100% and the reaction was kinetically controlled with the activation energy of 20.77 kJ/mol. The influence of the process parameters like stirring speed, concentration of 1-NN, concentration of aqueous sulphide, concentration of catalyst, MDEA concentration, elemental sulphur loading at different reaction time on the reactant conversion and the reaction rate of 1-NN were studied for establishment of the reaction mechanism. The kinetic model and mechanism of complex L-L phase transfer catalytic process has been developed and then the same has been validated against the experimental data. This approach of reducing 1-NN by H₂S –rich MDEA can substitute the energy-expensive Claus process, which gives no other product than sulphur.

1. INTRODUCTION

Hydrogen sulphide (H₂S) gas is often present as a major impurity in petroleum, coal, biogas and natural gas processing industries - which are the preeminent anthropogenic sources of H₂S gas in the Earth's atmosphere.^{1,2} H₂S is a poisonous gas for environment and corrosive gas for technological processes if it is present at more than 3ppm.³⁻⁵ H₂S content of little more than 1ppm is sufficient to poison catalyst used in fuel processing unit (FPU) and electrolytes of fuel cells (FCs).^{6,7} In recent years, petroleum refineries are compelled to process heavy crude oil that contains a higher amount of sulphur and Nitrogen, due to the unavailability of light crude oil. So H₂S is one of the main by-products of the petroleum refinery industry. H₂S gas from these industries is removed in Amine treating unit (ATU) and the regenerated H₂S gas from the regenerator of ATU unit is then oxidised to produce elemental sulphur in conventional Claus unit.⁸ Stringent environment regulation and less demand for elemental sulphur in comparison to its production have made experimentalists to think of an alternative for better utilisation of H₂S. H₂S gas is a major source of hydrogen and sulfur. During recent years, in approach to recover hydrogen and sulfur from H₂S gas, a variety of methods has been adopted, like absorption of H₂S in some absorbent followed by

electrochemical process⁹⁻¹¹. Acid gases (H₂S, CO₂) generated from the petroleum industries can be pyrolysed to produce Syngas (H₂ & CO). Gas engines can be run using syngas and valuable chemicals such as ammonia, liquid fuels are produced from Syngas.¹² All these processes for better utilisation H₂S gas are also disadvantageous due to difficult and expensive mode of operation, stringent environmental condition and less demand for the production of elemental sulphur. All these have made modern researchers to think of an alternative and better technology for removal and utilisation of H₂S gas.

Some techniques are available for removing H₂S gas including an aqueous solution of NaCl, activated carbon, sewage sludge, metal oxides, iron-based sorbents, FeOOH, Fe₂O₃ and aqueous solutions.¹³ In industries, the usual practice is to use an aqueous solution of alkanolamines or ammonia to remove sour gases (H₂O, CO₂) present in the gas stream. Alkanolamine based separation process is commercially well-adopted as it has several advantages over the ammonia-based process. Alkanolamines have less vapour pressure that favours flexible process operation (in terms of pressure, temperature, concentration of alkanolamine). Also, its recycling is easy and loss of solution due to vapourisation is minimum.¹⁴ There were lots of studies on the equilibrium solubility of both pure H₂S^{13,15-17} and mixture of acid gases (H₂S and CO₂).^{16,17} Different mathematical models have also been developed based on experimental solubility data for H₂S, CO₂ and a mixture of both the gases^{18,19} in Monoethanolamine (MEA) and Diethanolamine (DEA) solution. H₂S gas can be absorbed selectively from natural gas, refinery off-gases and gases from

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the coal gasification unit by aqueous methyldiethanolamine (MDEA).²⁰ The advantage MDEA over other alkanolamines is the selective absorption of H_2S in the presence of other gases like CO_2 .^{20–22} The present work was therefore undertaken using MDEA.

Selective reduction of the nitro group present in the aromatic ring along other multifunctional groups is a commercially important reaction but is a challenging work. Several methods for reducing aromatic nitro compounds have been documented in the literature, among those the Bechamp reduction,²³ catalytic hydrogenation²⁴ and Zinin reduction²⁵ are most familiar. Since our focus is the utilisation of H_2S in the synthesis of value added fine chemicals like aromatic amines from aromatic nitro compounds; literature review was restricted to Zinin reduction only. Negative divalent sulphur in the form of sulphide, hydrosulphide (both exists in H_2S -laden aqueous alkanolamine solution) and polysulphide are known to reduce aromatic nitro compounds effectively and it is called Zinin reduction.²⁶ Sodium sulphide/ disulphide have been used as a reducing agent to reduce o-chloronitrobenzene and p-chloronitrobenzene to the corresponding amino derivatives using polar solvents such as N-methylpyrrolidone (NMP) and dimethyl formamide (DMF).²⁷ p-chloronitrobenzene was reduced with sodium sulphide under a different mode of phase transfer catalysis such as (L-L), (L-S) and (L-L-L) processes.²⁸ Novelties of kinetics and mechanism of liquid–liquid phase transfer catalysed the reduction of p-nitroanisole to p-anisidine has been reported with 100% selectivity.²⁹ Kinetics of the reduction of nitrotoluenes by aqueous ammonium sulphide was studied under liquid–liquid phase transfer catalysis and selectivity of toluidine was 100%.²² Several researchers have worked with tetra-n-butylammonium bromide (TBAB) as PTC for reducing CNBs and they got high conversions.^{3,28} In our studies, reduction of 1-nitronaphthalene (1-NN) to 1-naphthylamine (1-NA) was carried out using H_2S -laden MDEA under L-L PTC.

Aromatic amines such as aminonaphthalenes are used as an intermediate for direct dyes, azoic dyes, disperse dyes, acid dyes and it is the essential raw material for the production of rubber antioxidants, pesticides, etc. It is also used as a reagent for thin layer chromatography to test nitro compounds, fluorescence chromatography, stationary phase of gas chromatography and used in organic synthesis. The 1-naphthylamine sulfonic acids are used for the preparation of azo dye, these dyes possessing the unique property of dyeing unmordanted cotton. The most important is naphthionic acid, 1-amino-4-sulfonic acid, produced by heating 1-naphthylamine and sulfuric acid to 170–180 °C with about 3% of crystallised oxalic acid. It forms small needles, very sparingly soluble in water. With diazotized benzidine, it gives Congo red.

Phase transfer catalysis (PTC) is a well-matured technique in the area of research and as well as in industries like dyes, pharmaceuticals, flavours, agrochemicals, perfumes, etc. There are different types of phase transfer catalysed systems

depending upon the number and type of phases they are involved. Liquid–Liquid (L-L), Liquid-Solid (L-S), Liquid-Liquid-Solid (L-L-S), Liquid-Liquid-Liquid (L-L-L) are among the different PTCs^{30–39} available in the literature. Among these, the most simple and widely accepted system is L-L PTC system because of its simplicity, low requirement of solvent and raw materials, user-friendly operating conditions, high selectivity and high reaction rate. PTC intensifies the reaction rate by transferring inorganic anions from the aqueous phase to the organic phase.⁴⁰ The kinetics and mechanism of L-L PTC systems have been discussed in the literature, which includes mainly SN_2 type reactions and alkylation reactions. Very few discussion can be found on the kinetics and mechanism of reduction reaction of nitroarenes.^{28,29,41} The liquid–liquid phase transfer catalysis (L-LPTC) is a process of favouring reactions between a lipophilic substrate dissolved in an organic phase with a hydrophilic reactant solubilized in water. The PTC facilitates the transfer of nucleophile of a hydrophilic reactant (via formation of a lipophilic ion-pair) from the aqueous phase to organic phase, where the reaction with the lipophilic substrate takes place.^{42,43} This mechanism as suggested by Starks is known as extraction mechanism and is applicable when the PTC is not highly lipophilic one and hence can distribute itself between the phases. When the PTC is a distinctly lipophilic one, the interfacial mechanism is used to explain the L-LPTC.⁴³ According to this mechanism, the PTC remains entirely in the organic phase and exchanges nucleophile with hydrophilic reactant through aqueous-organic interface only. The distribution of PTC in a biphasic (organic-aqueous phase) reaction condition is dependent upon the distribution coefficient (D_Q) of the PTC. Extractive properties of several Quaternary salts, like TBPB in two-phase system is studied by Wu et al., 2002⁴⁴. The use of TBPB as PTC is available in several literatures^{45–47}. Phosphonium cation of TBPB and thiolate anions (HS^-) are soft bases. According to the Pearson's HSAB theory the phosphonium cations can combine with HS^- ion and transfer it to the organic phase more effectively than ammonium quaternary salts (TBAB)⁴⁷. However, there is no work on use of phosphorous containing PTC on Zinin reduction. The present work is carried out using tetra-n-butylphosphonium bromide (TBPB) which is efficient, thermally stable and mutually soluble in both the phases.

2. Experimental

2.1. Chemicals

Toluene ($\geq 99\%$) and N-Methyldiethanolamine (MDEA) ($\geq 99\%$) of analytical grade were produced by Sigma-Aldrich (France) Ltd. Tetra-n-butylphosphonium bromide obtained from Sigma-Aldrich (China) Ltd., 1-nitronaphthalene (1-NN) was purchased from Sigma-Aldrich (USA) Ltd. Potassium iodate (KIO_3), Potassium iodide (KI), Sodium hydroxide pellets (NaOH) and Sodium thiosulphate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) of AR grade were obtained from Rankem (India) Ltd., New Delhi, India. Starch soluble and Sulphuric acid ($\geq 98\%$) acquired from Merck (India), Ltd., Mumbai, India. Ferrous sulphate sticks

(FeS) obtained from Thermo Fisher Scientific India Pvt., Ltd., Mumbai, India.

2.2. Experimental set-up

All the reactions were carried out with a 6.5 cm internal diameter, fully baffled mechanically agitated glass batch reactor of capacity 150 cm³. 2 cm diameter six-bladed glass disk turbine impeller with digital speed regulation system, kept at a height of 1.5 cm from the bottom of the reactor, was used for stirring the reaction mixture. The reactor was placed in an isothermal water bath ($\pm 1^\circ\text{C}$) having PID controller.

2.3. Preparation of H₂S-laden Aqueous Alkanolamines

35 wt% aqueous MDEA solution was prepared by adding an adequate quantity of raw MDEA in the measured amount of distilled water. Then H₂S gas was then bubbled through the aqueous MDEA solution in the gas bubbler, placed in the ice bath. This gas bubbling process was continued till desired sulphide concentration was attained. Sulphide concentration was estimated using conventional iodometric titration.⁴⁸

2.4 Experimental Procedure

In each experimental run, 30 cm³ of aqueous alkanolamine solution containing a known concentration of sulphide was taken into the 150 cm³ glass reactor. It was then kept well agitated by a six-bladed turbine stirrer until the steady state temperature was reached. Then 30 cm³ of the organic phase containing measured quantity of organic reactant (1-nitronaphthalene) dissolved in a solvent (toluene) and the catalyst (TBPB) were added into the reactor. The reaction mixture was then agitated at a constant speed of stirring. A Minimal amount of sample from the organic phase was withdrawn by micropipette at regular time intervals after stopping the agitation and allowing the phases to separate. A few runs were repeated for each type of parameter variation to check the reproducibility of the results.

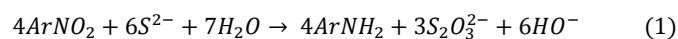
2.5 Analysis of Organic Phase

Samples collected from the organic phase were analysed by gas liquid chromatography on Agilent GC 7890B model. Capillary column DB-5MS, 2 m x 3 mm with nitrogen as a carrier gas was used at a flow rate 1.6 cm³/min for analysis in conjunction with a flame ionisation detector. Formation of the product is further confirmed by GC-MS (Agilent 5977A model). The conversion is defined with respect to the limiting reactant m-CNB.

3. RESULTS AND DISCUSSION

3.1. Proposed mechanism of reduction of aromatic nitro compounds under L-L PTC.

The overall stoichiometry of the Zinin's original reduction of nitrobenzene by aqueous ammonium sulphide, as proposed by Zinin in 1842, is given by Equation (1).²⁶ Reduction of nitroarenes by sodium sulphide follows same stoichiometry.^{22,23,34,39–52}

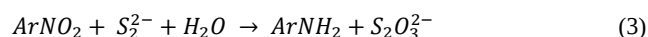


Some other reports show that elemental sulphur can be produced as a by-product instead of thiosulphate when aqueous ammonium sulphide used as a reducing agent in the reaction. P-Aminophenylacetic acid is prepared from p-nitrophenylacetic acid using aqueous ammonium sulphide and it is reported that the sulphide ions are oxidised to elemental sulphur instead of thiosulphate following stoichiometry of Equation (2).⁵³



Above reactions (Equation (1) and (2)) show that two different anions (S^{2-} & HS^-) have participated in those reduction reactions and elemental sulphur or thiosulphate is produced as a by-product respectively. 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.²²

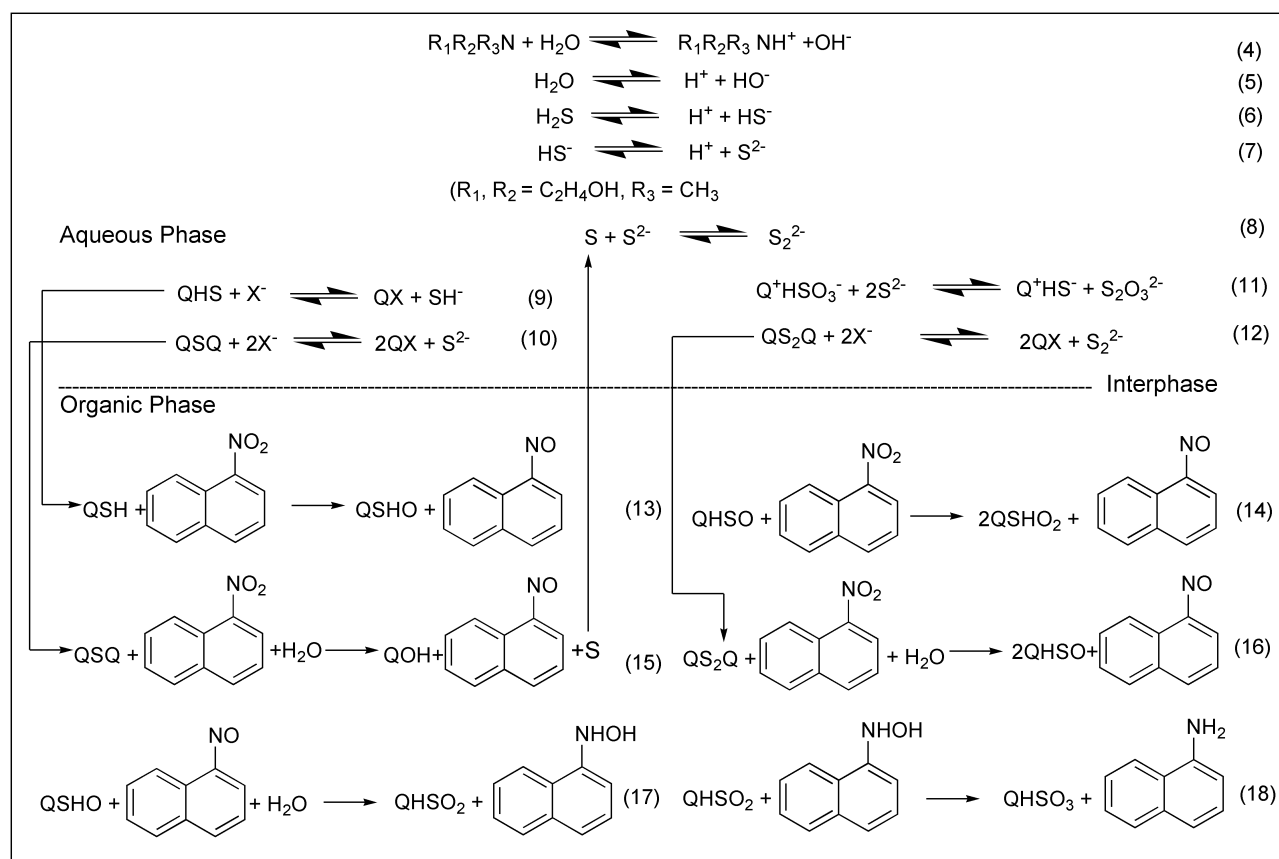
The overall stoichiometry of the reduction reaction using sodium disulphide as the reducing agent follows stoichiometry of Equation (3).¹⁹



Ionic equilibrium of sulphide ions (S^{2-}) and hydrosulphide ions (HS^-) in H₂S-laden aqueous alkanolamine (MDEA for example) solution should follow the same trend as H₂S-laden aqueous ammonium sulphide solution⁵⁴, as represented by Equation (4) to Equation (7) in the Scheme 1. These two ions are responsible for the formation of elemental sulphur or thiosulphate in the process of reduction of nitroarenes by H₂S-laden aqueous MDEA solution. The presence of both ions (sulphide, hydrosulphide) makes H₂S-laden aqueous alkanolamine and aqueous ammonium sulphide solutions different from other reducing agent like sodium sulphide, sodium disulphide.⁵⁵

Based on the current study and some earlier studies on reactions of reduction of nitroaromatic compounds by sodium sulphide^{28,29,37,56}, a general reaction mechanism has been proposed (Scheme 1). Sulphur can exist in multiple valence states ranging from (-2) to (+6) and, therefore, can form different anions (HS^- , HSO^- , HSO_2^- , HSO_3^-) which are capable of pairing with quaternary cations in a rapid manner than other anions that require multiple quaternary cations (Q_n^+X^-).²⁹ The nitro group present in the aromatic nitro compounds is reduced by the transfer of an electron from sulphide ions during reduction of nitro-aromatic compounds by aqueous sulphide solution.

Current reaction system is a liquid-liquid PTC system, which consists of an organic phase (organic substrate dissolved in solvent), an aqueous phase (H_2S absorbed in an aqueous solution of MDEA) and quaternary phosphonium salt, partitioned into both the phases. The organic reactant (1-NN)



Scheme 1. Proposed mechanism of reduction of 1-NN by H₂S-laden MDEA under L-L PTC.

and product (1-NA) are organophilic in nature.⁵⁷ According to Starks extraction mechanism, after the distribution of catalyst in both the phases, nucleophiles (anions) present in the aqueous phase get attached to catalyst cations and then move to the organic phase for taking part in the reaction with organic substrates.

The aqueous phase reaction of H₂S and MDEA is a reversible reaction and instantaneous in nature with respect to mass transfer. H₂S-MDEA equilibrium exists in the aqueous phase as well in the interfacial liquid film and five ion species are formed (HS^- , S^{2-} , OH^- , H^+ , $R_1R_2R_3NH^+$) in the aqueous phase (Scheme 1)^{58–62}. Quaternary cations (Q^+) present at the interphase readily form Q^+HS^- ion pair as soon as it comes into contact with the aqueous phase. Then, a series of reactions take place in the organic phase as shown in Scheme 1. Reactions also occur near the interphase between anions present in the aqueous phase and organic substrate on the organic phase side as the substrate has limited solubility in the aqueous phase. It is confirmed by the fact that products form even in the absence of the catalyst.

The contribution of several elementary reactions in the organic phase to the overall rate of the reaction is elaborated by the following mechanism. In a series of complex elementary reactions, 1-NN is converted to 1-naphthylamine (1-NA) through

the formation of intermediates (1-nitrosonaphthalene and 1-hydroxyaminonaphthalene), both of which have not been detected by GC-MS analysis. The existence of these two intermediates during Zinin reduction has long been established.^{29,56} Those intermediates remain undetected which may be due to the faster disappearance of the intermediates in the organic phase. While the catalyst cations are pairing with the HS^- anions, some water molecules transfer to the interphase and taking part in the reaction (Equation (16) to Equation (17)). After a series of elementary reaction the ion pair $Q^+HSO_3^-$ formed in the organic phase transfers to the aqueous phase and reacts with S^{2-} to regenerate Q^+HS^- Equation (8). The regenerated quaternary cations transferred to the organic phase again for the reduction reaction and that completes a typical catalytic cycle.

According to this mechanism, the quaternary cations are pairing with different anions during the reactions but the majority of the catalyst cations remains in Q^+HS^- form and the catalysis cycle goes on. Nine reactions (Equation (4) – Equation (12)) took place in the aqueous phase and rest of the reactions (Equation (13)–Equation (18)) occurred consecutively in the organic phase. During the reaction, 100% selectivity of 1-NA was obtained at the end of the reaction.

3.2 Kinetic modelling

From the mechanism shown in Scheme 1, it can be said that Q^+HS^- active ion pair forms in large excess although other anions are also present. A few assumptions are made as follows- (1) all the aqueous phase reactions have reached equilibrium fast, (2) modelling of the whole PTC reaction have done, is based on the mechanism proposed above and (3) the reactions occur in the interphase region are negligible in comparison to aqueous phase and organic phase reactions.

It was assumed to be an L-L PT catalytic reaction where 1-NN dissolved in toluene is reduced by H_2S -laden aqueous MDEA solution to yield 1-NA and $S_2O_3^{2-}$ as a by-product in their respective phases as shown in above Scheme 1. The overall reaction can be expressed in a single reaction shown in Equation (1).

The reaction medium was agitated with a stirrer at 1500 rpm to make the reaction as kinetically controlled and mass transfer effects can be ignored. With the progress of the reaction, the first ion exchange reaction took place between HS^- and Q^+X^- ($X^- = Cl^-$ for 1st ion exchange reaction) to form an active ion pair (Q^+HS^-). During reduction reaction, different transition anions were brought into existence in the organic phase and finally those ions become the inactive ion-pairs when HSO_3^- ions get attached to quaternary cations. The inactive sites underwent a redox reaction with S^{2-} ions and active sites Q^+HS^- were regenerated.

Steps as indicated in the mechanism in Scheme 1 are:

1. Transfer of in-active PT catalyst from organic phase to aqueous phase with equilibrium constant K_1 ,

$$K_1 = \frac{[QSHO_3]_a}{[QSHO_3]_o} \quad (19)$$

2. Ion exchange reactions are shown in Scheme 1 (Equation (9) -Equation (12)). Reaction (11) is the catalyst regeneration reaction, from which we can write,

$$K_2 = \frac{k_1}{k'_1} = \frac{[Q^+HS^-]_a[S_2O_3^{2-}]_a}{[Q^+HSO_3^-]_a[S^{2-}]_a^2} \quad (20)$$

3. Transfer of initially added catalyst QX from organic phase to aqueous phase and the active catalysts Q^+HS^- , QSQ and QS_2Q from aqueous phase to organic phase with equilibrium constant K_3 , K_4 , K_5 , K_6 ,

$$K_3 = \frac{[QX]_a}{[QX]_o} \quad (21)$$

$$K_4 = \frac{[QHS]_o}{[QHS]_a} \quad (22)$$

$$K_5 = \frac{[QSQ]_o}{[QSQ]_a} \quad (23)$$

$$K_6 = \frac{[QS_2Q]_o}{[QS_2Q]_a} \quad (24)$$

4. The overall rate is controlled by organic phase reactions. Among all elementary reactions (Equation (13) to Equation (18)), reaction shown in the Equation (13) is the slowest and rate determining step, where the first intermediate product ArNO is produced.²⁹ The presence of elemental sulphur as one of the byproduct has made reactions shown in Equation (15) and Equation (16) as a contributor also to overall reaction. During the transfer of ion pairs from the aqueous phase to the organic phase, some water molecules also got transferred.

As $ArNO_2$ is the limiting reactant, it can be taken as a basis of reaction. Rate of disappearance of $ArNO_2$ can, therefore, be expressed as,

$$-\frac{d[ArNO_2]}{dt} = k_2[ArNO_2]_o[QHS]_o + k_3[ArNO_2]_o[QSQ]_o[H_2O]_o + k_4[ArNO_2]_o[QS_2Q]_o[H_2O]_o \quad (25)$$

As the number of water molecules transferred to the organic phase are very less in comparison to that of Q^+HS^- ion pairs, it can be assumed that the reaction in Equation (13) is the main rate determining step. Reactions shown in Equation (15) and Equation (16) can, therefore, be ignored.

Therefore, Equation (25) can be rewritten as

$$-\frac{d[ArNO_2]}{dt} = k_2[ArNO_2]_o[QHS]_o \quad (26)$$

The mole balance for the catalyst is given by,

$$V^o [QX]^* = V^a \{ [QX] + [QHS] + [QSQ] + [QS_2Q] + [QHSO_3] \}_a + V^o \{ [QX] + [QHS] + [QSQ] + [QS_2Q] + [QHSO_3] \}_o \quad (27)$$

$[QX]^*$ is the concentration of catalyst initially fed to the organic phase., V^a and V^o are the volume of aqueous the phase and organic phase. Therefore,

$$[QX]^* = \frac{V^a}{V^o} \{ [QX] + [QHS] + [QSQ] + [QS_2Q] + [QHSO_3] \}_a + \{ [QX] + [QHS] + [QSQ] + [QS_2Q] + [QHSO_3] \}_o \quad (28)$$

Substituting Equation (19), (21), (22), (23) and (24) in the above reaction, we get

$$[QX]^* = \frac{V^a}{V^o} \left\{ K_3 [QX]_o + \frac{[QHS]_o}{K_4} + \frac{[QSQ]_o}{K_5} + \frac{[QS_2Q]_o}{K_6} + [QHSO_3]_o \right\}_a + \{ [QX] + [QHS] + [QSQ] + [QS_2Q] + [QHSO_3] \}_o \quad (29)$$

The total catalyst concentration in the organic phase is given by,

$$[Q^T] = [QX]_o + [QHS]_o + [QSQ]_o + [QS_2Q]_o + [QHSO_3]_o \quad (30)$$

$$1 = \frac{[QX]_o}{[Q^T]} + \frac{[QHS]_o}{[Q^T]} + \frac{[QSQ]_o}{[Q^T]} + \frac{[QS_2Q]_o}{[Q^T]} + \frac{[QHSO_3]_o}{[Q^T]} \quad (31)$$

Let us consider,

$$\frac{[QHS]_o}{[Q^T]} = \eta_1; \frac{[QSQ]_o}{[Q^T]} = \eta_2; \frac{[QS_2Q]_o}{[Q^T]} = \eta_3; \frac{[QHSO_3]_o}{[Q^T]} = \eta_4;$$

After substituting $\eta_1, \eta_2, \eta_3, \eta_4$ in the Equation (31) we get,

$$[QX]_o = (1 - \eta_1 - \eta_2 - \eta_3 - \eta_4) [Q^T] \quad (32)$$

The following equation can be obtained from Equation (29) and Equation (30) as

$$[QX]^* = \frac{v^a}{v^o} \left\{ K_3 \frac{[QX]_o [Q^T]}{[Q^T]} + \frac{[QHS]_o [Q^T]}{[Q^T]} K_4 + \frac{[QSQ]_o [Q^T]}{[Q^T]} K_5 + \frac{[QS_2Q]_o [Q^T]}{[Q^T]} K_6 + K_1 \frac{[QHSO_3]_o [Q^T]}{[Q^T]} \right\}_a + [Q^T] \quad (33)$$

Combining Equation (32) and Equation (33) yields,

$$[QX]^* = \frac{v^a}{v^o} \left\{ K_3 [Q^T] (1 - \eta_1 - \eta_2 - \eta_3 - \eta_4) + \eta_1 \frac{[Q^T]}{K_4} + \eta_2 \frac{[Q^T]}{K_5} + \eta_3 \frac{[Q^T]}{K_6} + \eta_4 K_1 [Q^T] \right\}_a + [Q^T] \quad (34)$$

Rearranging we get,

$$[Q^T] = \frac{[QX]^*}{\frac{v^a}{v^o} \left\{ K_3 (1 - \eta_1 - \eta_2 - \eta_3 - \eta_4) + \frac{\eta_1}{K_4} + \frac{\eta_2}{K_5} + \frac{\eta_3}{K_6} + \eta_4 K_1 \right\}_a + 1} \quad (35)$$

According to the overall reaction (Equation (1)), the conversion can be calculated as,

$$\text{Conversion (X)} = 1 - \frac{[ArNO_2]_o}{[ArNO_2]^*} \quad (36)$$

[Where $ArNO_2^*$ is the total reagent added in the organic phase]

$$\text{So, } [ArNO_2]_o = (1 - X) [ArNO_2]^* \quad (37)$$

As it is mentioned before that the reaction (Equation (13)) presented in Scheme 1 is rate-limiting step in the organic phase, the rate (r_A) of the reaction can be written as,

$$-\frac{d[ArNO_2]}{dt} = k_2 [ArNO_2]_o [QHS]_o \quad (38)$$

Now substituting $\eta_1 [Q^T]$ in the place of $[QHS]_o$ and Equation (38) in the above equation, we have

$$[ArNO_2]^* \frac{dX}{dt} = k_2 [ArNO_2]_o \eta_1 [Q^T] \quad (39)$$

$$[ArNO_2]^* \frac{dX}{dt} = k_2 \eta_1 (1 - X) [ArNO_2]^* [Q^T] \quad (40)$$

Substituting Equation (35) in the above equation, the following is obtained.

$$\frac{dX}{dt} = \frac{k_2 \eta_1 (1 - X) [QX]^*}{\frac{v^a}{v^o} \left\{ K_3 (1 - \eta_1 - \eta_2 - \eta_3 - \eta_4) + \frac{\eta_1}{K_4} + \frac{\eta_2}{K_5} + \frac{\eta_3}{K_6} + \eta_4 K_1 \right\}_a + 1} \quad (41)$$

$$\frac{dX}{(1 - X)} = k_{app} dt, \quad (42)$$

Where $k_{app} = \frac{k_2 \eta_1 [QX]^*}{\frac{v^a}{v^o} \left\{ K_3 (1 - \eta_1 - \eta_2 - \eta_3 - \eta_4) + \frac{\eta_1}{K_4} + \frac{\eta_2}{K_5} + \frac{\eta_3}{K_6} + \eta_4 K_1 \right\}_a + 1}$, since all terms are constant and can be calculated experimentally.

$$-\ln(1 - X) = k_{app} \cdot t, \quad (43)$$

From the Equation (43) it is clear that the reaction follows Pseudo first order.

3.3. Parametric studies

3.3.1. Effect of stirring speed

The effect of mass transfer resistance on reaction kinetics at different stirring speed have been investigated in the range of 500-2500 rev/min under otherwise identical experimental conditions in the presence of TBPB as phase transfer catalyst. It is ascertained from the Figure 1 that, there is no substantial increase in conversion due to the rise of stirring speed beyond stirring speed of 1000 rev/min. During further studies, the stirring speed has been maintained at 1500 rev/min for the complete elimination of mass transfer resistance.

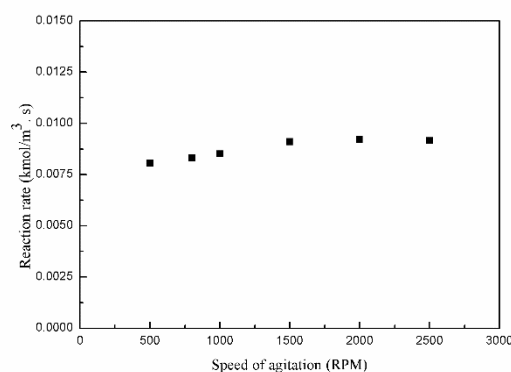


Figure 1. Effect of stirring speed on the conversion of 1-NN. Operating conditions: Volume of organic phase = $3 \times 10^{-3} \text{ m}^3$, volume of aqueous phase = $3 \times 10^{-3} \text{ m}^3$, [1-NN] = 0.577 kmol/m^3 in org. phase, [toluene] = 8.17 kmol/m^3 in org. phase, [catalyst] = 0.046 kmol/m^3 in org. phase, [sulphide] = 2.5 kmol/m^3 , [MDEA] = 3.04 kmol/m^3 , temperature = 333 K.

3.3.2. Effect of temperature.

The influence of temperature on the conversion of 1-NN catalysed by TBPB, as phase transfer catalyst was studied under various reaction temperatures in the range of 313–343K under otherwise similar reaction conditions as shown in Figure 2.

As per the transition state theory, the rates of most organic reactions increase with the rise in temperature. Increasing temperature is likely to enhance the rate of slow organic phase reactions under the PTC system. From the figure 2, it is clear that the reactivity (conversion) of 1-NN augments with an increase in the temperature. The reason is, with the rise in temperature, the activation energy of the molecules is overcome and more molecules can react to form the product.

On the other hand, collision among reactant molecules at a higher temperature has also resulted in the increase in reaction rate with increasing temperature.

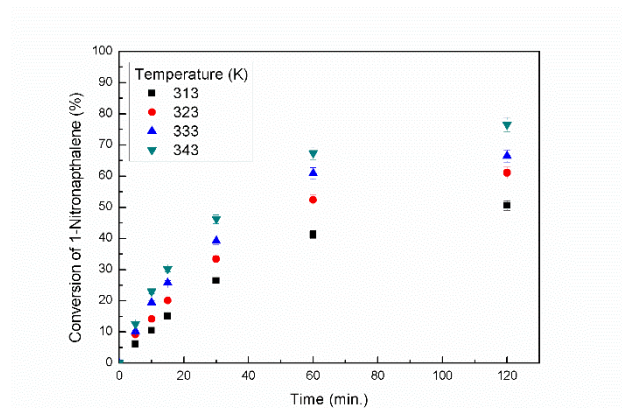


Figure 2 Effect of temperature on the conversion of 1-NN. Operating conditions: Volume of organic phase = $3 \times 10^{-3} \text{ m}^3$, volume of aqueous phase = $3 \times 10^{-3} \text{ m}^3$, [1-NN] = 0.577 kmol/m^3 in org. phase, [toluene] = 8.17 kmol/m^3 in org. phase, [catalyst] = 0.046 kmol/m^3 in org. phase, [sulphide] = 2.5 kmol/m^3 , [MDEA] = 3.04 kmol/m^3 , temperature = 333 K .

The initial rates were calculated at different temperatures and Arrhenius plots of $\ln$ (initial rate) vs. $1/T$ were made (Figure 3). The apparent activation energy for the kinetically controlled reaction was calculated from the slope of best fitted the straight line as 20.77 kJ/mol . The high values of apparent activation energies again confirm the reaction systems to be kinetically controlled. The reduction of 1-NN by aqueous ammonium sulphide catalysed by Tetra-n-butylammonium bromide (TBAB) as phase transfer catalysis have been studied, which requires activation energy of 9.4 kJ/mole .²⁸

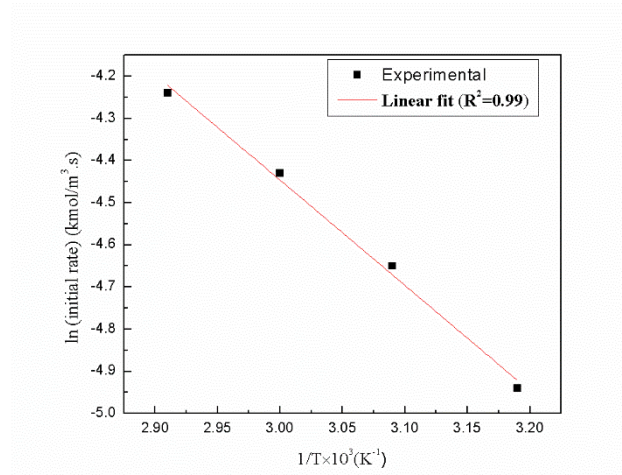


Figure 3. Arrhenius Plot (Plot of $\ln$ (initial rate) vs. $1/T$). All other conditions are same as Figure 2.

3.3.3. Effect of Catalyst (TBPB) loading.

The effect of catalyst (TBPB) loading on the conversion of 1-NN by H_2S -laden aqueous MDEA was studied in the range of $0.000 - 0.093 \text{ kmol/m}^3$ under otherwise identical experimental conditions, as shown in Figure 4. As the catalyst load increases, the conversion of 1-NN as well as the reaction rate increases. Only by increasing the catalyst concentration, reactant conversion of more than 75.4% was achieved with 0.093 kmol/m^3 of catalyst loading whereas it was about 23% without added catalyst even after 2 hours of reaction under otherwise identical conditions. Enhancement factors, which is the ratio of the rate of reaction in the presence of the catalyst to that in the absence of the catalyst, are calculated at different catalyst loadings has shown in Table 1. A highest enhancement factor of 75 was observed with 0.093 kmol/m^3 of catalyst loading.

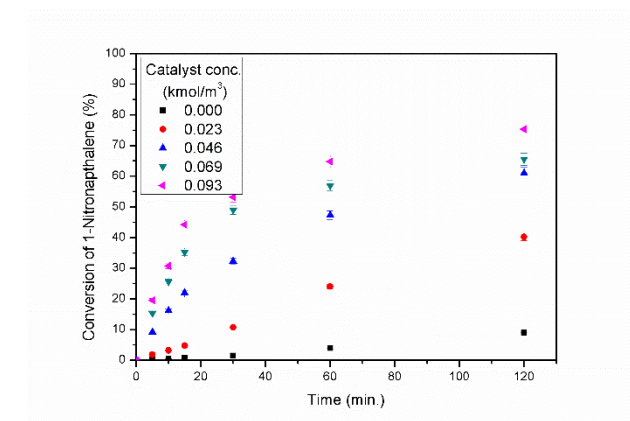


Figure 4. Effect of catalyst concentration on the conversion of 1-NN. Operating conditions: Volume of organic phase = $3 \times 10^{-3} \text{ m}^3$, volume of aqueous phase = $3 \times 10^{-3} \text{ m}^3$, [1-NN] = 0.577 kmol/m^3 in org. phase, [toluene] = 8.17 kmol/m^3 in org. phase, [catalyst] = 0.046 kmol/m^3 in org. phase, [sulphide] = 2.5 kmol/m^3 , [MDEA] = 3.04 kmol/m^3 , temperature = 333 K

Table 1. Effect of catalyst loading on Initial reaction rate^a

Conc. of TBPB (kmol/m³ org phase)	Initial reaction rate (kmol/m³s)	Enhancement factor
0.000	0.0003	1.0
0.023	0.0022	7.3
0.046	0.0090	30.0
0.069	0.0165	55.0
0.093	0.0225	75.0

^aAll other conditions are same as Figure 5.

To determine the order of reaction with respect to the catalyst concentration, the initial reaction rate was calculated at different catalyst concentrations. A plot of $\ln$ (initial rate) against $\ln$ (TBPB concentration) was made and shown in Figure 5. From the slope of the linear fit line, the order of reaction was determined. The order of the reaction was found out to be 1.4 with respect to TBPB concentration. Similar observations were made for the reduction of nitrochlorobenzenes by aqueous ammonium sulphide by PTC, TBAB.³

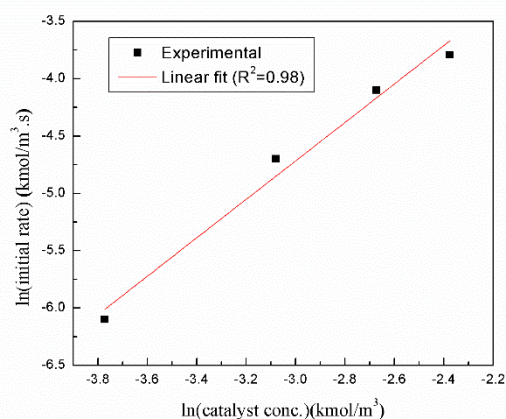


Figure 5. Plot of $\ln$ (initial rate) vs. $\ln$ (catalyst concentration). All other conditions are same as Figure 4.

3.3.4. Effect of 1-nitronaphthalene concentration.

The effect of concentration of 1-NN on its conversion was considered at four different concentrations in the range of 0.288 to 1.155 kmol/m³ in the presence TBAB under otherwise identical experimental conditions, as shown in Figure 6.

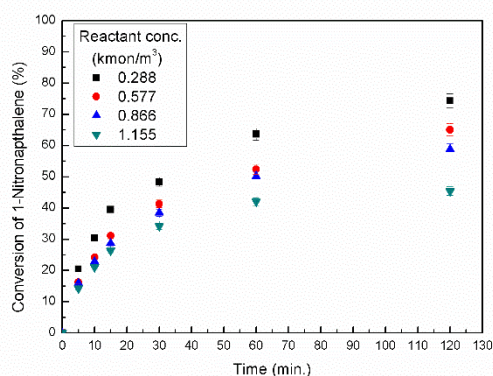


Figure 6. Effect of reactant concentration on the conversion of 1-NN. Operating conditions: Volume of organic phase = 3×10^{-3} m³, volume of aqueous phase = 3×10^{-3} m³, [1-NN] = 0.577 kmol/m³ in org. phase, [toluene] = 8.17 kmol/m³ in org. phase, [catalyst] = 0.046 kmol/m³ in org. phase, [sulphide] = 2.5 kmol/m³, [MDEA] = 3.04 kmol/m³, temperature = 333 K.

It is evident from the figure that with higher reactant concentration lower conversion of 1-NN was achieved. As expected, the increase in the reaction rate during the initial stage of the reaction is due to the increase in the concentration of 1-NN. Since the amount of sulphide in the aqueous phase has remained the same for all the experimental runs, the conversion of 1-NN dropped beyond a particular concentration as shown in Figure 6. For reduction of o-nitroanisole by H₂S rich diethanolamine, a similar observation was found.⁵⁴

Conversion and the reaction rate were found to increase with the decrease in 1-NN concentration at the end of 2 hours of reaction time. From the Figure 7, the order of reaction with respect to 1-NN concentration was obtained as 1.13. Hence, the reaction is first order with respect to the concentration of 1-NN. A similar observation was found elsewhere for the reduction of nitroarenes by aqueous sodium sulphide.²⁹

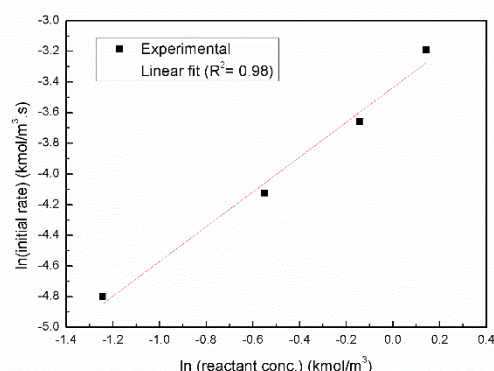


Figure 7. Plot of $\ln$ (initial rate) vs. $\ln$ (reactant concentration). All other conditions are same as Figure 6.

3.3.5. Effect of sulphide concentration.

Figure 8 shows the effect of sulphide concentration in the aqueous phase on the conversion of 1-NN. With an increase in the concentration of sulphide, the conversion of 1-NN and the reaction rate increases which is as expected. Sulphide concentration was varied in the range of 1.0 to 2.5 kmol/m³ under otherwise identical experimental conditions in the presence of catalyst TBPB. From the plot of $\ln$ (initial rate) against $\ln$ (sulphide concentration) (Figure 9), the slope of the linear fit line was found out to be 1.91. Studies on the reduction of nitrotoluenes with aqueous ammonium sulphide also reported the order of reaction to be 2nd with respect to sulphide concentration.²²

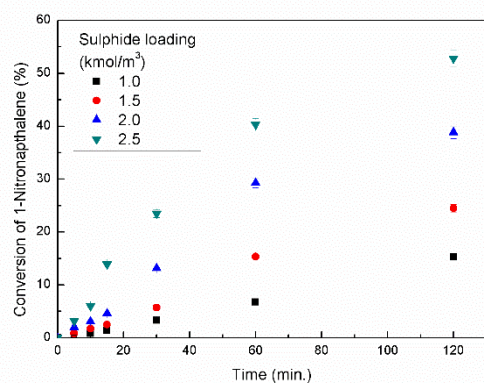


Figure 8. Effect of sulphide concentration on the conversion of 1-NN. Operating conditions: Volume of organic phase = 3×10^{-3} m³, volume of aqueous phase = 3×10^{-3} m³, [1-NN] = 0.577 kmol/m³ in org. phase, [toluene] = 8.17 kmol/m³ in org. phase, [catalyst] = 0.046 kmol/m³ in org. phase, [sulphide] = 2.5 kmol/m³, [MDEA] = 3.04 kmol/m³, temperature = 333 K.

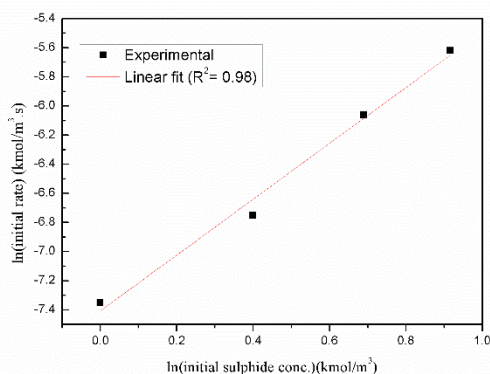


Figure 9. Plot of ln (initial rate) vs. ln (sulphide concentration). All other conditions are same as Figure 8.

3.3.7. Effect of MDEA concentration.

MDEA does not have the direct impact on reaction rate, but it does affect the equilibrium among MDEA, H₂S and water. As mentioned in Scheme 1, in aqueous phase, sulphide (S²⁻) and hydrosulphide (HS⁻) active anions are formed and these two active anions are responsible for two different reactions (Equation (1) & Equation (2)). Basic nature of MDEA favours more ionisation of H₂S and sulphide ions (S²⁻) dominates over hydrosulphide ions (HS⁻) in the aqueous phase. The existence of two reactions can be proven only by varying MDEA addition in the aqueous phase with a fixed sulphide concentration.

Various MDEA concentrations (sulphide concentration kept constant) were prepared by taking 20 cm³ of H₂S-laden aqueous MDEA (with known sulphide 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 cm³. During the course of the

reaction colour of the aqueous solution was changed from greenish yellow to orange and then to reddish brown that is useful in indicating the extent of reaction. With the progress of the reaction, polysulphide that is reddish brown in colour, formed. A similar phenomenon was observed by Lucas and Scudder.⁶³

In this study, after 12 hrs of run, 46% conversion of 1-NN was achieved with maximum MDEA concentration of 3.04 kmol/m³ as shown in Figure 10. It was observed that increase in MDEA concentration lowers the conversion of 1-NN. The reason is, with increase in MDEA concentration, concentration of HS⁻ decreases with respect to S²⁻, and consequently, conversion of 1-NN decreases as concluded from Equation (2).

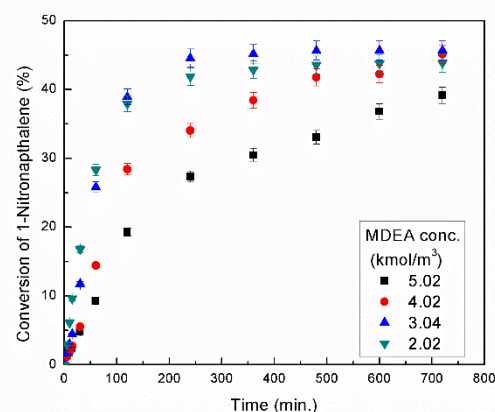


Figure 10. Effect of MDEA concentration on the conversion of 1-NN. Operating conditions: Volume of organic phase = 3×10^{-3} m³, volume of aqueous phase = 3×10^{-3} m³, [1-NN] = 0.577 kmol/m³ in org. phase, [toluene] = 8.17 kmol/m³ in org. phase, [catalyst] = 0.046 kmol/m³ in org. phase, [sulphide] = 2.5 kmol/m³, [MDEA] = 3.04 kmol/m³, temperature = 333 K.

3.3.8. Effect of elemental sulphur loading.

The dark greenish colour of H₂S-laden MDEA solution became orange when elemental sulphur was added to it, the change in colour is attributed to the formation of disulphide. A similar colour change was observed during other parametric studies. The effect of elemental sulphur loading on conversion of 1-NN is shown in Figure 11. It is evident from the figure that initially reaction rate has increased with elemental sulphur addition but after certain time reaction rate slowed down.

It was predicted that polysulphide (S_n²⁻, where 2 ≤ n ≤ 6) was produced along with disulphide that can readily transfer to the organic phase and reacts with aromatic nitro compounds as shown in Equation (3). A similar explanation was given by Lucas and Scudder (1928).⁶³ The transfer of hydrosulphide (HS⁻) and sulphide ions (S²⁻) to the organic phase is slower in comparison to disulphide ions and consequently disulphide ions can reduce nitroaromatic compounds faster.⁶⁴ Conversion

without elemental sulphur addition was found to be higher after 120 min of reaction. This crossover may be due to the fact that the reaction rate increases as elemental sulphur build up as the reaction proceeds (Equation (2)).

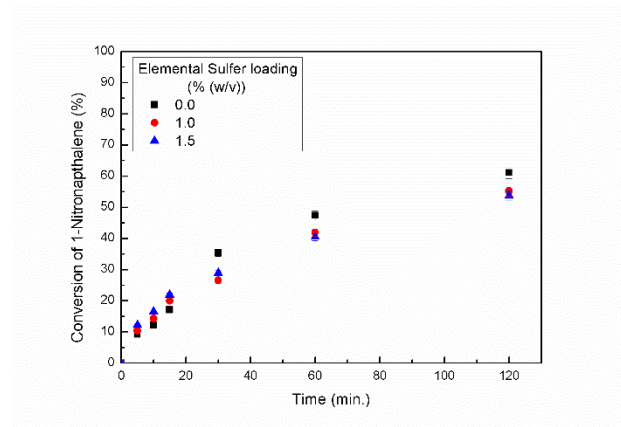


Figure 11. Effect of Elemental sulphur on the conversion of 1-NN. Operating conditions: Volume of organic phase = 3×10^{-3} m³, volume of aqueous phase = 3×10^{-3} m³, [1-NN] = 0.577 kmol/m³ in org. phase, [toluene] = 8.17 kmol/m³ in org. phase, [catalyst] = 0.046 kmol/m³ in org. phase, [sulphide] = 2.5 kmol/m³, [MDEA] = 3.04 kmol/m³, temperature = 333 K.

3.4. Validation of the kinetic model.

The kinetic model has been validated by considering Equation (43) to be valid at different catalyst concentrations and plotting of $-\ln(1-X)$ against time (Figure 12). The slope of each line gives apparent rate constant k_{app} at different catalyst concentrations as shown in Table 2.

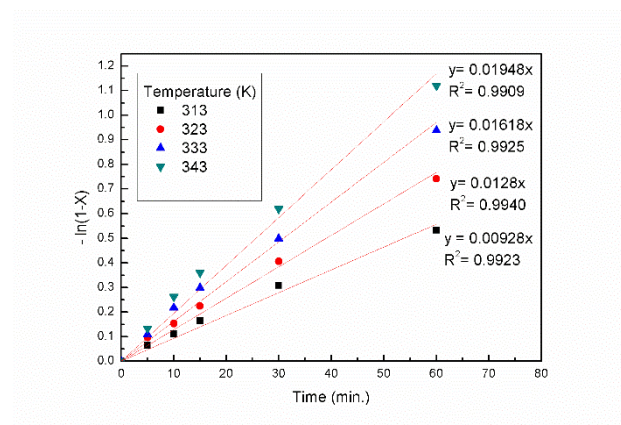


Figure 12. Validation of the kinetic model with experimental data at different catalyst concentrations. Operating conditions: Volume of organic phase = 3×10^{-3} m³, volume of aqueous phase = 3×10^{-3} m³, [1-NN] = 0.577 kmol/m³ in org. phase, [toluene] = 8.17 kmol/m³ in org. phase, [catalyst] = 0.046 kmol/m³ in org. phase, [sulphide] = 2.5 kmol/m³, [MDEA] = 3.04 kmol/m³, temperature = 333 K.

Table 2. Apparent rate (k_{app}) constants at different temperatures^b

Temperature (K)	313	323	333	343
k_{app} (min ⁻¹)	0.0092	0.0128	0.0161	0.0195

^b All considerations are the same as mentioned in Figure 12.

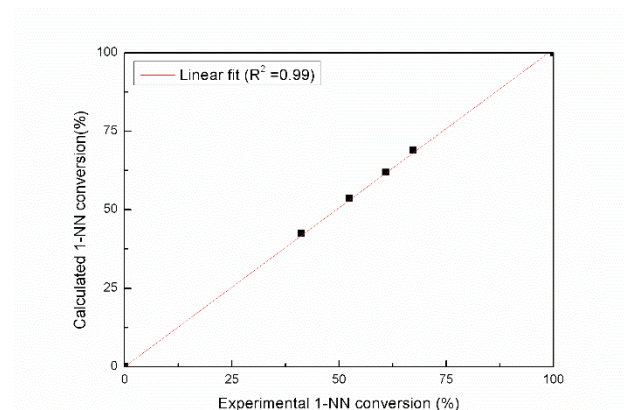


Figure 13. Comparison of calculated and experimental 1-NN conversions at 60 min at different temperatures and all considerations are the same as Figure 12.

Figure 13 represents a comparison of calculated conversions of 1-NN based on these rate constants and experimentally obtained conversions of 1-NN. Good agreement has been observed between calculated and experimental conversions.

3.5 CONCLUSION

H₂S-rich MDEA is successfully used as reducing agent for Zinin reduction of 1-NN in this work and 100% selectivity of 1-AN is achieved after the reaction. The reaction is kinetically controlled with an activation energy of 20.77 kJ/mol. This work addresses the novelties of the kinetics and mechanism of the selective reduction of 1-NN to respective amine using hydrogen sulphide absorbed in industrially significant sour gas absorber under L-L PTC. The effects of different parameters such as stirring speed, temperature, MDEA concentration, reactant concentrations (both sulphide and 1-NN), and sulphur loading were studied. The process was found to follow a complex mechanism involving different ions and molecules. Based on detailed kinetic studies and proposed mechanism, a kinetic model was developed considering Stark's extraction mechanism for L-L PTC. The developed model predicts the conversion of 1-NN reasonable well at all temperatures.

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Notes and References

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