Published in

Chemical Engineering Science *62 (***2007)** 805-813.

Reduction of *o*-Nitroanisole to *o*-Anisidine by H_2S-rich Aqueous Diethanolamine: A Novel Process for Utilization of H_2S-laden Gas Streams

Sunil K. Maity, Narayan C. Pradhan*, Anand V. Patwardhan

Department of Chemical Engineering, Indian Institute of Technology,

Kharagpur-721302, India.

Abstract

H_2S-rich aqueous diethanolamine (DEA) solution, which could be obtained from amine treatment units (ATUs) of refineries, was utilized to prepare a value-added chemical, *o*-anisidine from *o*-nitroanisole (ONA) with co-production of elemental sulfur. The reduction of ONA was carried out under liquid-liquid mode in presence of phase transfer catalyst, tetrabutylammonium bromide (TBAB). The effects of DEA concentration and elemental sulfur loading on the conversion of ONA were suitably utilized to establish the stoichiometry and mechanism of the so-called Zinin reduction using H_2S-rich aqueous DEA. The reaction was found to be kinetically controlled with apparent activation energy of 63.6 kJ/mol. The rate of reaction of ONA was also found to be proportional to the concentration of catalyst, to the cube of the concentration of ONA, and to the 1.63 power of the concentration of sulfide. An empirical kinetic model based on experimental observations was developed to correlate the experimentally obtained conversion *versus* time data. The present work has a very high commercial importance as it can replace the conventional Claus process, which gives elemental sulfur as the only product.

Keywords: *o*-Anisidine; Claus process; Hydrogen sulfide; Kinetics; Multiphase reactions; Phase transfer catalysis; Reaction engineering.

1. Introduction

Reduction of nitroarenes to the corresponding aryl amines is a useful chemical transformation since many aryl amines find a multitude of industrial applications, being important intermediates in the production of many pharmaceuticals, photographic materials, agrochemicals, polymers, dyes and rubber materials. *o*-Anisidine is an important precursor of dye and pharmaceutical intermediates (Yadav et al., 2003; Haldar and Mahajani, 2004).

Varieties of methods are employed for the reduction of nitroarenes. For example, Bechamp reduction, which is the oldest industrially practiced method, involves the use of stoichiometric amounts of finely divided iron metal and water in the presence of small amount of acid. This method has a distinct disadvantage of formation of iron sludge that is difficult to filter and dispose of in an environmentally acceptable manner. Additionally, this method cannot be used for reduction of a single nitro group in a polynitro compound, nor can it be used on substrates harmed by acid media (e.g., some ethers and thioethers). Catalytic hydrogenation on the other hand requires expensive equipment and hydrogen handling facility; additional problems arise due to catalyst preparation, catalyst poisoning hazards and the risk of reducing other groups. Metal hydrides like lithium aluminum hydride generally converts nitro compounds to a mixtures of azoxy and azo compounds, besides being expensive. In the present work, the sulfide reduction is employed as it has considerable practical value and it enables chemoselective reduction of nitro compounds in the presence of C=C, azo and other nitro compounds.

The reduction reaction of nitroarenes by negative divalent sulfur (sulfide, hydrosulfide and polysulfides) is popularly known as Zinin reduction (Dauben, 1973).

Several researchers studied the kinetics of the reduction of nitroarenes using sodium sulfide and sodium disulfide both in the absence and in the presence of phase transfer catalyst (PTC) and also under different modes (solid–liquid and liquid-liquid) (Hojo et al., 1960; Bhave and Sharma, 1981; Pradhan and Sharma, 1992; Pradhan, 2000; Yadav et al., 2003a; 2003b). There are some reports, mostly very old, on the preparation of aryl amines using three different types of ammonium sulfide: (i) aqueous ammonium sulfide (Gilman, 1941), (ii) alcoholic ammonium sulfide (Cline and Reid, 1927; Lucas and Scudder, 1928), and (iii) ammonium sulfide prepared from an equivalent amounts of ammonium chloride and crystalline sodium sulfide dissolved in ammonium hydroxide or alcohol (Murray and Waters, 1938; Meindl et al., 1984). However, a detailed kinetic study using ammonium hydroxide and also the use of industrially relevant alkaline medium such as aqueous diethanolamine (DEA) for such an important reaction are never reported in the literature. The present work is, therefore, not only interesting from academic point of view, it is also relevant from commercial perspective as well.

During the course of many processes in the petroleum, coal, and natural gas processing industries, one or more gaseous byproducts containing hydrogen sulfide (H_2S) are quite commonly produced. The H_2S contents of the byproduct gas streams are to be brought down to a specified level before being used in further applications to meet the stringent environmental regulations. The H_2S from these gas streams is conventionally removed through amine treating unit (ATU) and the H_2S-rich gas obtained from the regenerator of the ATU is then oxidized in the Claus unit (Kohl and Nielsen, 1997) to produce elemental sulfur. However, there are several disadvantages of air oxidation of H_2S which include loss of valuable hydrogen source, requirement of precise air rate control, removal of trace sulfur compounds from spent air, and a limit on the concentration of H_2S in the gas stream to name a few. Therefore, the development of a viable alternative process for the conversion of H_2S to produce commercially important chemicals (aryl amines) with the co-production of elemental sulfur (as obtained in the Claus process) is very much welcome in the process industry, particularly in the refineries handling sour crudes.

Aqueous monoethanolamine (MEA) and diethanolamine (DEA) are most commonly used for the removal of acid gases (H_2S and CO_2) from various gas streams. Aqueous MEA has been widely used due to its high reactivity, low solvent cost, ease of reclamation, low absorption of hydrocarbons, and low molecular weight (which results high solution capacity at moderate concentrations). On the other hand, DEA, which is less corrosive than MEA, is a better choice for treating gas streams containing appreciable amounts of COS and CS_2 as it is much less reactive with these impurities compared to primary amines like MEA. Several researchers studied the equilibrium solubility of pure H_2S (Lee et al., 1974a, 1974b; Lawson and Garst, 1976; Lee et al., 1976; Isaacs et al., 1980), mixture of acid gases (H_2S and CO_2) (Lee et al., 1975; Lawson and Garst, 1976; Isaacs et al., 1980), and the mathematical representation of the experimental solubility data for H_2S, CO_2 and their mixture (Deshmukh and Mather, 1981; Astarita and Savage, 1982; Austgen et al., 1989; Weiland et al., 1993; Al-Baghli et al., 2001; Kaewsichan et al., 2001) using aqueous MEA. Much work was also reported on the use of aqueous DEA (Lee et al., 1973a, 1973b; Lee et al., 1974a, 1974b; Lawson and Garst, 1976; Lal et al., 1985; Austgen et al., 1989; Weiland et al., 1993; Vallée et al., 1999; Al-Baghli et al., 2001; Sidi-Boumedine et al., 2004). However, no attempt is made in the past to utilize the H_2S-rich aqueous alkanolamine to produce value-added chemicals such as *o*-anisidine. Considering the importance of the system, the present work was undertaken using aqueous DEA.

Phase transfer catalysis (Starks and Liotta, 1978; Dehmlow and Dehmlow, 1983) is now an attractive technique for organic synthesis because of its advantages of simplicity, reduced consumption of organic solvent and raw materials, mild operating conditions, and enhanced reaction rates and selectivity. Among several varieties of phase transfer catalysts, quaternary ammonium salts are most preferred for their better activity and ease of availability. Tetrabutylammonium bromide (TBAB) has been reported to be the most active PTC among six different catalysts used to intensify the reaction of benzyl chloride with solid sodium sulfide (Pradhan and Sharma, 1990). The present work was, therefore, carried out using TBAB as the phase transfer catalyst.

2. Experimental

2.1 Chemicals

Toluene (≥99%) and diethanolamine (≥98%) of synthesis grade were procured from Merck (India) Ltd., Mumbai, India. o-Nitroanisole (99%) was purchased from Alfa Aesar, Karlsruhe, Germany. Tetrabutylammonium bromide (TBAB) was obtained from SISCO Research Laboratories Pvt. Ltd., Mumbai, India.

2.2 Equipment

The reactions of ONA with H_2S-rich aqueous DEA were carried out batch-wise in a fully baffled mechanically agitated glass reactor of capacity 250 cm^3 (6.5 cm i.d.). A 2.0 cm-diameter six-bladed glass disk turbine impeller with the provision of speed regulation, located at a height of 1.5 cm from the bottom, was used for stirring the reaction mixture. The reactor assembly was kept in a constant temperature water bath whose temperature could be controlled within ±1K.

2.3 Preparation of H_2S-rich aqueous DEA

For the preparation of H_2S-rich aqueous DEA solution**,** around 36 wt% DEA solution was prepared first by adding suitable quantity of DEA in distilled water. Then H_2S gas was bubbled through this aqueous DEA in a 250 cm^3 standard gas-bubbler. The gas bubbling was continued until the desired sulfide concentration was obtained in the aqueous DEA.

2.4 Experimental procedure

In a typical run, 50 cm^3 of the aqueous phase containing a known concentration of sulfide was charged into the reactor and kept well agitated until the steady-state temperature was reached. Then 50 cm^3 of the organic phase containing measured amount of ONA, catalyst (TBAB) and solvent (toluene), kept separately at the reaction temperature, was charged into the reactor. The reaction mixture was then agitated at a constant speed. About 0.5 cm^3 of the organic layer was withdrawn at a regular interval after stopping the agitation and allowing the phases to separate.

2.5 Analysis

All samples from the organic phase were analyzed by gas-liquid chromatography (GLC) using a 2 m × 3 mm stainless steel column packed with 10% OV-17 on

Chromosorb W (80/100). A Chemito Model 8610 GC interfaced with Shimadzu C-R6A Chromatopac data processor was used for the analysis. The column temperature was programmed with an initial temperature of 423K and increased at 15K/min to 553K. Nitrogen was used as the carrier gas with a flow rate of 15 cm^3/min. An injector temperature of 553K was used during the analysis. An FID detector was used at a temperature of 573K. Initial sulfide concentrations were determined by the standard iodometric titration method (Scott, 1966).

3. Results and Discussion

3.1 Stoichiometry of the Zinin reduction

In H_2S-rich aqueous DEA, equilibria among H_2S, DEA and water result two active anions, sulfide (S^{2-}) and hydrosulfide (HS^-), as represented by following reactions (Weiland et al., 1993).

(a) Dissociation of DEA:

$$R_2NH + H_2O \rightleftharpoons R_2NH_2^+ + HO^- \ [R= HOCH_2CH_2]$$

(b) Dissociation of water:

$$H_2O \rightleftharpoons H^+ + HO^-$$

(c) Dissociation of hydrogen sulfide:

$$H_2S \rightleftharpoons H^+ + HS^-$$

(d) Dissociation of hydrosulfide:

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

A similar ionic equilibrium exists in the aqueous ammonium sulfide as well (Rumpf et al., 1999). Therefore, the behavior of H_2S-rich aqueous DEA is expected to be similar to that of ammonium sulfide. However, due to the existence of two different ions (sulfide and hydrosulfide) in the H_2S-rich aqueous DEA (and also ammonium sulfide), the properties of these reducing agents are expected to be different from the other sulfides such as sodium sulfide and disulfide.

The overall stoichiometry of the Zinin's original reduction of nitrobenzene by aqueous ammonium sulfide is given by Eq. 1 (Dauben, 1973). The same stoichiometry was also used for reduction of nitroarenes by sodium sulfide (Bhave and Sharma, 1981; Pradhan and Sharma, 1992; Pradhan, 2000; Yadav et al., 2003a, 2003b).

$$4ArNO_2 + 6S^{2-} + 7H_2O \rightarrow 4ArNH_2 + 3S_2O_3^{2-} + 6HO^- \qquad (1)$$

For the preparation of p-aminophenylacetic acid from p-nitrophenylacetic acid using aqueous ammonium sulfide, it was reported that the sulfide ions were oxidized to elemental sulfur instead of thiosulfate following stoichiometry of Eq. 2 (Gilman, 1941). A similar stoichiometry was reported for the reduction of 2-bromo-4-nitrotoluene by alcoholic ammonium sulfide (Lucas and Scudder, 1928). The formation of elemental sulfur was reported for the preparation of 3-amino-5-nitrobenzyl alcohol using ammonium sulfide prepared from ammonium chloride and crystalline sodium sulfide dissolved in methanol (Meindl, 1984).

$$ArNO_2 + 3HS^- + H_2O \rightarrow ArNH_2 + 3S + 3HO^- \qquad (2)$$

The overall stoichiometry of the reduction reaction using disulfide as the reducing agent is as follows (Hojo et al., 1960; Bhave and Sharma, 1981):

$$ArNO_2 + S_2^{2-} + H_2O \rightarrow ArNH_2 + S_2O_3^{2-} \qquad (3)$$

Therefore, two different reactions leading to the formation of either elemental sulfur or thiosulfate may be operative for the reduction of nitroarenes with H_2S-rich aqueous DEA.

3.2 Mechanism of the Reaction

In order to establish the exact stoichiometry and mechanism of the Zinin reduction using H_2S-rich aqueous DEA, the following effects (DEA concentration and elemental sulfur loading) were studied.

Effect of DEA concentration. Although DEA as such does not take part in the reaction with ONA, it does affect the equilibrium among DEA, H_2S, and water, which results in two active anions, sulfide (S^{2-}) and hydrosulfide (HS^-), in the aqueous phase as shown earlier. These two active anions participate in two different reactions (reactions 1 and 2). In presence of the base, DEA, dissociation equilibrium shifts toward more ionization and the concentration of sulfide ions relative to hydrosulfide ions in the aqueous phase increases with increase in DEA concentration. Therefore, only by changing the DEA concentration with constant sulfide concentration in the aqueous phase, one can easily prove the existence of two different reactions.

To study the effect of DEA concentration, H_2S-rich aqueous DEA of different DEA concentrations (but constant sulfide concentration) was prepared by taking 30 cm^3 of H_2S-rich aqueous DEA (with known sulfide and DEA concentration) and then adding various proportions of pure DEA and distilled water to it in such a way that the total volume became 50 cm^3 in all the cases.

The effect of DEA concentration on the conversion of ONA is shown in Fig. 1. With increase in concentration of DEA, conversion of ONA was found to decrease up to a certain reaction time, beyond that opposite trend was observed, i.e., with increase in DEA concentration, conversion of ONA was found to increase (Fig. 1).

Based on stoichiometry of reaction 1, the expected ONA conversion is around 51% for complete conversion of sulfide in the aqueous phase and it will be around 25.5% if the stoichiometry of reaction 2 is considered. However maximum ONA conversion achieved is about 32.5% with the maximum DEA concentration used in this study as shown in the figure. The maximum ONA conversion is far from expectation based on reaction 1. From this result, it is also clear that the first reaction is also operative in the Zinin reduction as proposed by Zinin in 1842 (Dauben, 1973). These results are in complete disagreement with some works with ammonium sulfide (Lucas and Scudder, 1928; Gilman, 1941; Meindl and Angerer, 1984) that propose reaction 2 as the solely operative one. Since the maximum ONA conversion is closer to the expected ONA conversion based on reaction 2, the course of reduction follows reaction 2 predominantly. It can also be concluded from this results that it is preferred to carry out the reaction with high sulfide loading (low DEA concentration) in the aqueous phase in order to get the elemental sulfur predominantly instead of thiosulfate. The existence of reaction 2 (formation of elemental sulfur) will be confirmed when the effect of elemental sulfur loading will be discussed.

Since, the formation of elemental sulfur was not reported anywhere in the literature for the reduction of nitroarenes with sodium sulfide, it could be thought that the reaction via the transfer of sulfide ions follows reaction 1. The concentration of sulfide ion (S^{2-}) increases with increase in the concentration of DEA, for a fixed total sulfide concentration. Thus, with increase in DEA concentration, there is an increase in the reaction via the transfer of sulfide ions following the stoichiometry of reaction 1, which results higher conversion of ONA at higher DEA concentration.

One thing to be noted here is that the nature of the curve obtained in this reaction is '*S*' type which is typical of an autocatalytic reaction where the rate of reaction increases with increase in the concentration of catalyst formed by the reaction and then the rate of reaction decreases with the depletion of the reactants as observed in the figure. This phenomenon was only observed for low concentration of one of the components: ONA, sulfide and catalyst or the conditions that favor low initial reaction rate (high DEA concentration, low temperature, etc.). However, for high concentration, this phenomenon could not be observed as it occurred within a very short period of time. The exact reason for this nature of curve is explained below under the heading of effect of elemental sulfur loading on the reaction.

Effect of elemental sulfur loading. Elemental sulfur in the solution of ammonia and hydrogen sulfide is known to form ammonium polysulfides (Dubois et al., 1988), $(NH_4)_2S_n$ where $2 \leq n \leq 6$, which is also one of the reducing agents of the Zinin reduction. A similar behavior is also expected with aqueous DEA. Since, the formation of elemental sulfur was reported for this reaction (Lucas and Scudder, 1928; Gilman, 1941; Meindl and Angerer, 1984), here we examined the effect of externally added elemental sulfur on the reaction rate and conversion of ONA.

In this experiment, elemental sulfur was first dissolved in the H_2S-rich aqueous DEA and then used for the reaction following the same procedure as described earlier. The color of the H_2S-rich aqueous DEA is greenish yellow. However, after dissolution of elemental sulfurs to this solution, the color of the solution became reddish brown. During the experimental run also, initially the color of the solution was unaffected but later on it changed rapidly from greenish yellow to reddish brown. This color change indicates the formation of elemental sulfur (and polysulfides) during the reaction. The characteristic reddish brown color of the polysulfide, which develops as the reaction proceeds, is useful in indicating the extent of the reaction.

The effect of elemental sulfur loading on conversion of ONA is shown in Fig. 2. It is clearly observed from the figure that the conversion of ONA increases with increase in elemental sulfur loading up to a certain reaction time. However, the overall conversion of ONA decreases with increase in the elemental sulfur loading. As it is observed from the nature of the curves in the figure, the reaction rate gradually decreases with conversion of ONA in the presence of elemental sulfur whereas the nature of the curve is '*S*' type in the absence of elemental sulfur.

These observations confirm the formation of elemental sulfur and can also be used to explain the '*S'* type of curve as discussed in the previous section. Therefore, it can be said that the reaction rate increases with the build up of elemental sulfur concentration (reaction 2) as the reaction proceeds and then falls gradually with the depletion of the reactants resulting in '*S'* type of curve.

The rise in rate of reaction with elemental sulfur loading may be due to the fact that the reaction via the transfer of hydrosulfide and sulfide ions is slow compared to polysulfide ions formed by the reaction of elemental sulfur with H_2S-rich aqueous DEA. As reported by Hojo et al. (1960), disulfide reduces nitrobenzene much more rapidly than sulfide.

The overall conversion of ONA decreases with increase in elemental sulfur loading as observed from the figure. This may be due to the formation of polysulfide in addition to disulfide (which is only transferred and reacts with ONA according to reaction 3) (Lucas and Scudder, 1928).

3.3 Effect of Speed of Agitation

The effect of speed of agitation on the rate of reaction of ONA was studied in the range 1000-2500 rev/min under otherwise identical experimental conditions in presence of PTC, TBAB as shown in Fig. 3. It is evident from the figure that the variation of reaction rate with speed of agitation is so small that the reactions may be considered as free from mass transfer resistance. All other experiments were performed at 1500 rev/min to ensure the absence of mass transfer resistance in the reaction system.

3.4 Effect of Temperature

The effect of temperature on the conversion of ONA was studied in the range of 313-343 K under identical experimental conditions in the presence of catalyst, TBAB, as shown in Fig. 4. The conversion of ONA increased with temperature as expected. The initial rates were calculated at different temperatures and Arrhenius plot of Ln (initial rate) against 1/T (K^{-1}) was made. The apparent activation energy was calculated from the slope of the best-fitted straight line as 63.6 kJ/mol (with the regression coefficient (r^2) = 0.99). The high value of apparent activation energy confirms that the reaction system is kinetically controlled.

3.5 Effect of TBAB Loading

The effect of catalyst (TBAB) loading on conversion of ONA is shown in Fig. 5. The study was also conducted in the absence of catalyst as shown in the same figure. The conversion of ONA increases with increase in TBAB loading. As it is observed from the figure, the conversion of ONA is only about 1.5 % in the absence of catalyst whereas it is around 38% with maximum concentration of catalyst tried after 125 minutes of reaction time under otherwise identical experimental conditions. This shows the importance of PTC in enhancing the rate of the reaction under investigation.

In order to determine the order of the reaction with respect to TBAB concentration, the initial reaction rate was calculated at different TBAB concentration and the plot of Ln(initial rate) against Ln(TBAB concentration) was made. From the slope of the linearly fitted line ($r^2 = 0.99$), the order of the reaction with respect to TBAB concentration was obtained as 0.99, which is close to unity. Yadav et al. (2003a) also reported similar observation for the reduction of p-nitroanisole by sodium sulfide in presence of PTC, TBAB.

3.6 Effect of ONA Concentration

The effect of concentration of ONA on its conversion was studied in the presence of TBAB under otherwise identical experimental conditions as shown in Fig. 6. The conversion of ONA increases with increase in its concentration up to a certain reaction time. However, overall conversion of ONA decreases with increase in ONA concentration. This is due to limited quantity of sulfide in the aqueous phase. From the plot of Ln(initial rate) against Ln(initial ONA concentration) ($r^2 = 0.98$), the order of the reaction with respect to ONA concentration was obtained as 3.2 (which is close to 3). However, for the reduction of nitroarenes by aqueous sodium sulfide, the reported order is unity with respect to the concentration of p-nitroanisole (Yadav et al., 2003a) and nitroaromatics (Bhave and Sharma, 1981). The rate was also reported to be proportional to the concentration of nitrobenzene for its reduction with sodium disulfide under two-phase conditions (Hojo et al., 1960).

3.7 Effect of Sulfide Concentration

The effect of sulfides (total) concentration on the conversion of ONA is shown in Fig 7. It is evident from this figure that the conversion of ONA increases with increase in the concentration of total sulfides. From the plot of Ln(initial rate) against Ln(initial sulfide concentration) ($r^2 = 0.97$), the order of the reaction with respect to the sulfide concentration was obtained as 1.63. However, for the reduction of nitroarenes with aqueous sodium sulfide, the reaction rate was reported to be first order with the sulfide concentration (Bhave and Sharma, 1981; Yadav et al., 2003a). The rate was also reported to be proportional to the square of the concentration of sodium disulfide (Hojo et al., 1960).

3.8 Kinetic Modeling

The modeling of a variety of phase transfer catalyzed SN^2 type of reactions, in liquid-liquid (Yang, 1998; Satrio and Doraiswamy, 2002), liquid-liquid-liquid (Yadav and Reddy, 1999; Yadav and Naik, 2001), and solid-liquid (Naik and Doraiswamy, 1997) modes, and some oxidation reactions (Yadav and Haldavanekar, 1997; Satrio and Doraiswamy, 2002) are well documented. Much works were also reported on the Zinin reduction. However, very limited attempt has been made so far to investigate the mechanism of this important reduction reaction and to study the kinetics in details. Probably, the first product is a nitroso compound, which is rapidly reduced to hydroxylamine and then to amine (Dauben, 1973). The attack of negative sulfur on the nitro group is considered to be the rate-determining step as no intermediate compounds are observed to be formed during the reaction. The mechanism and kinetic scheme developed by Yadav et al. (2003a) for the reduction of *p*-nitroanisole by aqueous sodium sulfide under liquid-liquid mode in presence of PTC, TBAB was found to be not applicable in the case of reduction of ONA by H_2S-rich aqueous DEA.

The hydrosulfide (HS^-) and sulfide (S^{2-}) ions present in the aqueous phase readily form ion pairs ($[Q^+HS^-]$ and $[Q^+S^{2-}Q^+]$) with quaternary cation, $[Q^+]$ and are transferred to the organic phase and reduce ONA following the stoichiometry of reactions 1 and 2, respectively. The polysulfide is formed by the reaction of elemental sulfur (reaction 2) with H_2S-rich aqueous DEA. It has been mentioned in the earlier discussion that the overall conversion of ONA decreases with increase in elemental sulfur loading because of the formation of higher amount of polysulfides (other than disulfide), which are not easily transferred to the organic phase. Only disulfide ions form ion pair, $[Q^+S_2^{2-}Q^+]$ and are transferred to the organic phase and reduce the ONA following reaction 3.

Development of fundamental kinetic model for this system is a difficult task because of these complexities involved and poor knowledge of the system. In this work, an empirical kinetic model was, therefore, developed to correlate the experimentally obtained time *versus* conversion data. Since, the concentration of DEA in the aqueous phase was kept around 36 wt%, its effect was not incorporated in this kinetic model. Based on the experimental facts, the rate of reduction of ONA $(-r_A)$ is expressed by the following equation.

$$-r_A = k_1 C_A^3 C_S^{\ 1.63} C_C + k_2 C_A^3 C_S^{\ 1.63} C_C C_B \qquad (4)$$

where C_A and C_C are the concentrations of ONA and catalyst, TBAB in the organic phase, respectively. The 2nd term in the above rate expression takes care of *'S'* nature of the curve due to the formation of elemental sulfur during the reaction as discussed previously. Since, the course of reduction follows the stoichiometry of Eq. 2 predominantly; the concentration of sulfide (C_S) and elemental sulfur (C_B) in the aqueous phase are obtained from the overall mass balance based on the same stoichiometry as given by the following expressions.

$$C_S = C_{SO} - 3f(C_{AO} - C_A) \tag{5}$$

$$C_B = 3f(C_{AO} - C_A) \tag{6}$$

where C_{SO} and C_{AO} represent the initial concentrations of sulfide and ONA, respectively and f is the ratio of volume of organic phase to that of aqueous phase. A non-linear regression algorithm was used for parameter estimation. The optimum values of the rate constants (k_1 and k_2) at different temperatures were estimated by minimizing the objective function (E) as given by the equation

$$E = \sum_{i=1}^{n} \left[\left\{ (-r_A)_{pred} \right\}_i - \left\{ (-r_A)_{\exp t} \right\}_i \right]^2 \tag{7}$$

The optimum values of the rate constants, k_1 and k_2, at different temperatures are listed in Table 1. The activation energy and pre-exponential factor of the rate constants were evaluated from the slope and intercept of the Arrhenius plot of Ln (k) against 1/T, as shown in Table 2. Fig. 8 represents the comparison of the calculated conversions of ONA at different temperatures based on these rate constants and experimentally obtained conversions. Good agreement was observed with a maximum deviation of ±5% between the calculated and experimental conversions.

4. Conclusions

H_2S-rich aqueous diethanolamine (DEA) was successfully used for the production of value-added chemical, *o*-anisidine from *o*-nitroanisole (ONA), together with elemental sulfur. The reduction reaction was studied under liquid–liquid mode in the presence of PTC, TBAB. The selectivity of o-anisidine was 100%. The process was found to follow a complex mechanism involving three different reactions. The reduction reaction was observed to be kinetically controlled with an apparent activation energy of 63.6 kJ/mol. The rate of reduction of ONA was established to be proportional to the concentration of catalyst, to the cube of the concentration of ONA, and to the 1.63 power of the concentration of sulfide. Based on the detailed kinetic study and a proposed mechanism, an empirical kinetic model was developed. The developed model, predicted the conversions of ONA reasonably well. The present process could be considered as a viable alternative to the Claus process that gives elemental sulfur as the only product with the loss of valuable hydrogen energy.

Acknowledgment

Sunil K. Maity is thankful to the All India Council for Technical Education (AICTE), New Delhi, India, for the award of the National Doctoral Fellowship during the tenure of this work.

References

Al-Baghli, N. A., Pruess, S. A., Yesavage, V. F., Selim, M. S., 2001. A Rate-based Model for the Design of Gas Absorbers for the Removal of CO_2 and H_2S Using Aqueous Solutions of MEA and DEA. Fluid Phase Equilibria 185, 31–43.

Astarita, G., Savage, D. W., 1982. Simultaneous Absorption with Reversible Instantaneous Chemical Reaction. Chemical Engineering Science 37(5), 677-686.

Austgen, D. M., Rochelle, G. T., Peng, X., Chen, C., 1989. Model of Vapor-Liquid Equilibria for Aqueous Acid Gas-Alkanolamine Systems Using the Electrolyte-NRTL Equation. Industrial & Engineering Chemistry Research 28, 1060-1073.

Bhave, R. R., Sharma, M. M., 1981. Kinetics of Two-Phase Reduction of Aromatic Nitro Compounds by Aqueous Solutions of Sodium Sulphides. Journal of Chemical Technology and Biotechnology 31, 93-102.

Cline, E. L., Reid, E. E., 1927. Some Derivatives of Ethylbenzene. Journal of American Chemical Society 49, 3150-3156.

Dauben, W. G., 1973. Organic Reactions, John Wiley & Sons, Inc.: New York, Vol. 20, p455-481.

Dehmlow, E. V., Dehmlow, S. S., 1983. Phase Transfer Catalysis, 2nd ed., Verlag Chemie Weinheim.

Deshmukh, R. D., Mather, A. E., 1981. A Mathematical Model for Equilibrium Solubility of Hydrogen Sulfide and Carbon Dioxide in Aqueous Alkanolamine Solutions. Chemical Engineering Science 36 (2), 355-362.

Dubois, P., Lelieur, J. P., Lepoutre, G., 1988. Identification and Characterization of Ammonium Polysulfides in Solution in Liquid Ammonia. Inorganic Chemistry 27, 1883-1890.

Gilman, H., 1941. Organic Syntheses, Collective volume 1, John Wiley & Sons, Inc., NewYork, p-52.

Haldar, P., Mahajani, V.V., 2004. Catalytic transfer hydrogenation: *o*-nitroanisole to *o*-anisidine, Some Process Development Aspects. Chemical Engineering Journal 104, 27–33.

Hojo, M., Takagi, Y., Ogata, Y., 1960. Kinetics of the Reduction of Nitrobenzene by Sodium Disulfide. Journal of American Chemical Society 82, 2459-2462.

Isaacs, E. E., Otto, F. D., Mather, A. E., 1980. Solubility of Mixtures of H_2S and CO_2 in a Monoethanolamine Solution at Low Partial Pressures. Journal of Chemical and Engineering Data 25, 118-120.

Kaewsichan, L., Al-Bofersen, O., Yesavage, V. F., Selim, M. S., 2001. Predictions of the Solubility of Acid Gases in Monoethanolamine (MEA) and Methyldiethanolamine (MDEA) Solutions Using the Electrolyte-UNIQUAC Model. Fluid Phase Equilibria 183–184, 159–171.

Kohl, A. L., Nielsen, R. B., 1997. Gas Purification, Gulf Publishing Company Houston: Texas.

Lal, D., Otto, F. D., Mather, A. E., 1985. The Solubility of H_2S and CO_2 in Diethanolamine Solution at Low Partial Pressure. Canadian Journal of Chemical Engineering 63, 681-685.

Lawson, J. D., Garst, A. W., 1976. Gas Sweetening Data: Equilibrium Solubility of Hydrogen Sulfide and Carbon Dioxide in Aqueous Monoethanolamine and Aqueous Diethanolamine Solutions. Journal of Chemical and Engineering Data 21(1), 20-30.

Lee, J., Otto, F. D., Mather, A. E., 1973a. Solubility of Hydrogen Sulfide in Aqueous Diethanolamine Solutions at High Pressures. Journal of Chemical and Engineering Data 18(1), 71-73.

Lee, J., Otto, F. D., Mather, A. E., 1973b. Partial Pressures of Hydrogen Sulfide over Aqueous Diethanolamine Solutions. Journal of Chemical and Engineering Data 18(4), 420.

Lee, J., Otto, F. D., Mather, A. E., 1974a. The Solubility of H_2S and CO_2 in Aqueous Monoethanolamine Solutions. Canadian Journal of Chemical Engineering 52, 803-805.

Lee, J., Otto, F. D., Mather, A. E., 1974b. The solubility of Mixture of Carbon Dioxide and Hydrogen Sulfide in Aqueous Diethanolamine Solutions. Canadian Journal of Chemical Engineering 52, 125-127.

Lee, J., Otto, F. D., Mather, A. E., 1975. Solubility of Mixtures of Carbon Dioxide and Hydrogen Sulfide in 5.ON Monoethanolamine Solution. Journal of Chemical and Engineering Data 20 (2), 161-163.

Lee, J., Otto, F. D., Mather, A. E., 1976. Equilibrium in Hydrogen Sulfide-Monoethanolamine-Water System. Journal of Chemical and Engineering Data 21(2), 207-208.

Lucas, H. J., Scudder, N. F., 1928. The Preparation of 2-Bromo-9-Cresol from p-Nitrotoluene. Journal of American Chemical Society 50, 244-249.

Meindl, W. R., Angerer, E. V., Schonenberger, H., Ruckdeschel, G., 1984. Benzylamines: Synthesis and Evaluation of Antimycobacterial Properties. Journal of Medicinal Chemistry 27, 1111-1118.

Murray, M. J., Waters, D. E., 1938. Ammonium Chloride-Sodium Sulfide Solutions for Organic Nitro Reductions and for Inorganic Qualitative Analysis. Journal of American Chemical Society 60, 2818-2819.

Naik, S. D., Doraiswamy, L. K., 1997. Mathematical Modeling of Solid-Liquid Phase-Transfer Catalysis. Chemical Engineering Science 52(24), 4533-4546.

Pradhan, N. C., 2000. Reactions of Nitrotoluenes with Sodium Sulphide: Phase Transfer Catalysis and Role of Ω Phase. Indian Journal of Chemical Technology 7, 276-279.

Pradhan, N. C., Sharma, M. M., 1990. Kinetics of Reactions of Benzyl Chloride/p - Chlorobenzyl Chloride with Sodium Sulfide: Phase-Transfer Catalysis and the Role of the Omega Phase. Industrial & Engineering Chemistry Research 29, 1103-1108.

Pradhan, N. C., Sharma, M. M., 1992. Reactions of Nitrochlorobenzenes with Sodium Sulfide: Change in Selectivity with Phase-Transfer Catalysts. Industrial & Engineering Chemistry Research 31, 1606-1609.

Rumpf, B., Kamps, Á. P., Sing, R., Maurer, G., 1999. Simultaneous solubility of Ammonia and Hydrogen Sulfide in Water at Temperatures from 313 K to 393 K. Fluid Phase Equilibria158–160, 923–932.

Satrio, J. A. B., Doraiswamy, L. K., 2002. Phase Transfer Catalysis: A New Rigorous Mechanistic Model for Liquid–Liquid Systems. Chemical Engineering Science 57, 1355-1377.

Scott, W. W., 1966. Standard Methods of Chemical Analysis, Van Nostrand: New York, 6th ed., Vol. IIA, p 2181.

Sidi-Boumedine, R., Horstmann, S., Fischer, K., Provost, E., Fürst, W., Gmehling, J., 2004. Experimental Determination of Hydrogen Sulfide Solubility Data in Aqueous Alkanolamine Solutions. Fluid Phase Equilibria 218, 149–155.

Starks, C. M., Liotta, C. L., 1978. Phase Transfer Catalysis Principles and Techniques, Academic: New York.

Vallée, G., Mougin, P., Jullian, S., Fürst, W., 1999. Representation of CO_2 and H_2S Absorption by Aqueous Solutions of Diethanolamine Using an Electrolyte Equation of State. Industrial & Engineering Chemistry Research 38, 3473-3480.

Weiland, R. H., Chakravarty, T., Mather, A. E., 1993. Solubility of Carbon Dioxide and Hydrogen Sulfide in Aqueous Alkanolamines. Industrial & Engineering Chemistry Research 32, 1419-1430.

Yadav, G. D., Haldavanekar, B. V., 1997. Mechanistic and Kinetic Investigation of Liquid-Liquid Phase Transfer Catalyzed Oxidation of Benzyl Chloride to Benzaldehyde. Journal of Physical Chemistry A 101, 36-48.

Yadav, G. D., Jadhav, Y. B., Sengupta, S., 2003a. Novelties of Kinetics and Mechanism of Liquid–Liquid Phase Transfer Catalysed Reduction of *p*-Nitroanisole to *p*-Anisidine. Chemical Engineering Science 58, 2681-2689.

Yadav, G. D., Jadhav, Y. B., Sengupta, S., 2003b. Selectivity Engineered Phase Transfer Catalysis in the Synthesis of Fine Chemicals: Reactions of *p*-Chloronitrobenzene with Sodium Sulphide. Journal of Molecular Catalysis A: Chemical 200, 117–129.

Yadav, G. D., Naik, S. S., 2001. Novelties of Liquid–Liquid–Liquid Phase Transfer Catalysis: Alkoxylation of *p*-Chloronitrobenzene. Catalysis Today 66, 345-354.

Yadav, G. D., Reddy, C. A., 1999. Kinetics of the *n*-Butoxylation of *p*-Chloronitrobenzene under Liquid-Liquid-Liquid Phase Transfer Catalysis. Industrial & Engineering Chemistry Research 38, 2245-2253.

Yang, H., 1998. Dynamic Model for Mass Transfer and Reaction in Liquid-Liquid Phase Transfer Catalysis. Industrial & Engineering Chemistry Research 37, 398-404.

Table 1 . Rate constants of the Model Equation 4.

Rate Constants	Temperatures (K)			
	313	323	333	343
$k_1 \times 10^5$ $(\text{kmol/m}^3)^{-4.63}\text{s}^{-1}$	1.70	3.80	8.34	12.5
$k_2 \times 10^4$ $(\text{kmol/m}^3)^{-5.63}\text{s}^{-1}$	1.67	3.80	12.0	25.0

Table 2 . Activation energies and pre-exponential factors of the rate constants.

$k_1 = A_{10}Exp(-\frac{AE1}{RT})$ ($r^2 = 0.99$)		$k_2 = A_{20}Exp(-\frac{AE2}{RT})$ ($r^2 = 0.99$)	
A_{10} $[(\text{kmol/m}^3)^{-4.63}\text{s}^{-1}]$	AE1 (kJ/mol)	A_{20} $[(\text{kmol/m}^3)^{-5.63}\text{s}^{-1}]$	AE2 (kJ/mol)
2.35×10^5	60.61	1.02×10^{10}	82.72

Figure Captions

Fig. 1. Effect of DEA concentration on conversion of *o*-nitroanisole. Volume of organic phase = 5×10^{-5} m^3; ONA concentration = 1.31 kmol/m^3; TBAB concentration= 9.31×10^{-2} kmol/m^3 of org. phase; volume of aqueous phase = 5×10^{-5} m^3; sulfide concentration = 1.01 kmol/m^3; temperature = 333 K; speed of agitation =1500 rev/min.

Fig. 2. Effect of elemental sulfur loading. Volume of organic phase = 5×10^{-5} m^3; ONA concentration = 1.31 kmol/m^3; volume of aqueous phase = 5×10^{-5} m^3; sulfide concentration = 1.68 kmol/m^3; TBAB concentration = 9.3×10^{-2} kmol/m^3 of org. phase; concentration of DEA = 3.45 kmol/m^3; temperature = 333 K; speed of agitation =1500 rev/min.

Fig. 3. Effect of speed of agitation. Volume of organic phase = 5×10^{-5} m^3; ONA concentration = 1.31 kmol/m^3; TBAB concentration= 9.3×10^{-2} kmol/m^3 of org. phase; volume of aqueous phase = 5×10^{-5} m^3; sulfide concentration = 1.68 kmol/m^3; concentration of DEA = 3.45 kmol/m^3; temperature = 333 K; speed of agitation =1500 rev/min; Matching ONA conversion =20%.

Fig. 4. Effect of temperature on conversion of ONA. Volume of organic phase = 5×10^{-5} m^3; ONA concentration = 1.04 kmol/m^3; TBAB concentration= 6.20×10^{-2} kmol/m^3 of org. phase; volume of aqueous phase = 5×10^{-5} m^3; sulfide concentration = 1.17 kmol/m^3; DEA concentration =3.45 kmol/m^3; speed of agitation =1500 rev/min.

Fig. 5. Effect of TBAB concentration on conversion of ONA. Volume of organic phase = 5×10^{-5} m^3; ONA concentration = 1.31 kmol/m^3; volume of aqueous phase = 5×10^{-5} m^3; sulfide concentration = 1.68 kmol/m^3; concentration of DEA = 3.45 kmol/m^3; temperature = 333 K; speed of agitation =1500 rev/min.

Fig. 6. Effect of ONA concentration on conversion of ONA. Volume of organic phase = 5×10^{-5} m^3; TBAB concentration = 6.2×10^{-2} kmol/m^3 of org. phase; volume of aqueous phase = 5×10^{-5} m^3; sulfide concentration = 1.17 kmol/m^3; concentration of DEA = 3.45 kmol/m^3; temperature = 343 K; speed of agitation =1500 rev/min.

Fig. 7. Effect of sulfide concentration on conversion of ONA. Volume of organic phase = 5×10^{-5} m^3; ONA concentration = 1.31 kmol/m^3; TBAB concentration= 9.3×10^{-2} kmol/m^3 of org. phase; volume of aqueous phase = 5×10^{-5} m^3; concentration of DEA = 3.45 kmol/m^3; temperature = 333 K; speed of agitation =1500 rev/min.

Fig. 8. Comparison of calculated and experimental conversions of ONA. All conditions are the same as in Fig. 4.

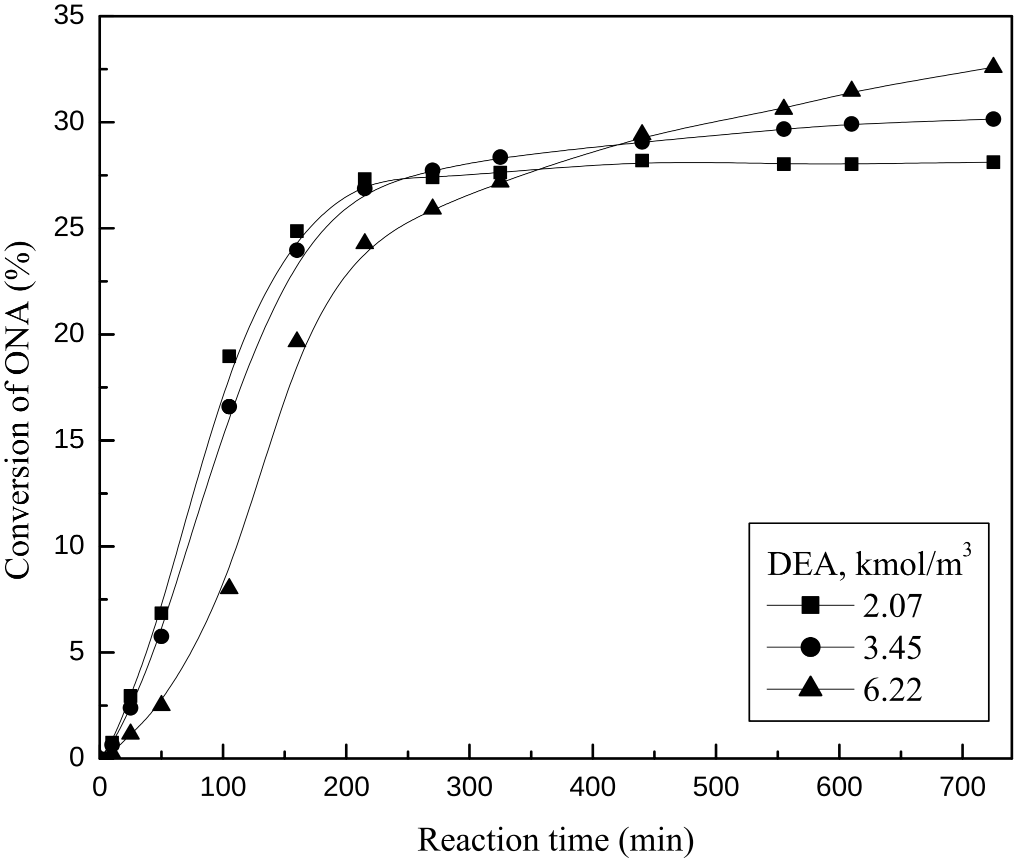

Fig. 1. Effect of DEA concentration on conversion of *o*-nitroanisole. Volume of organic phase = 5×10^{-5} m^3; ONA concentration = 1.31 kmol/m^3; TBAB concentration= 9.31×10^{-2} kmol/m^3 of org. phase; volume of aqueous phase = 5×10^{-5} m^3; sulfide concentration = 1.01 kmol/m^3; temperature = 333 K; speed of agitation =1500 rev/min.

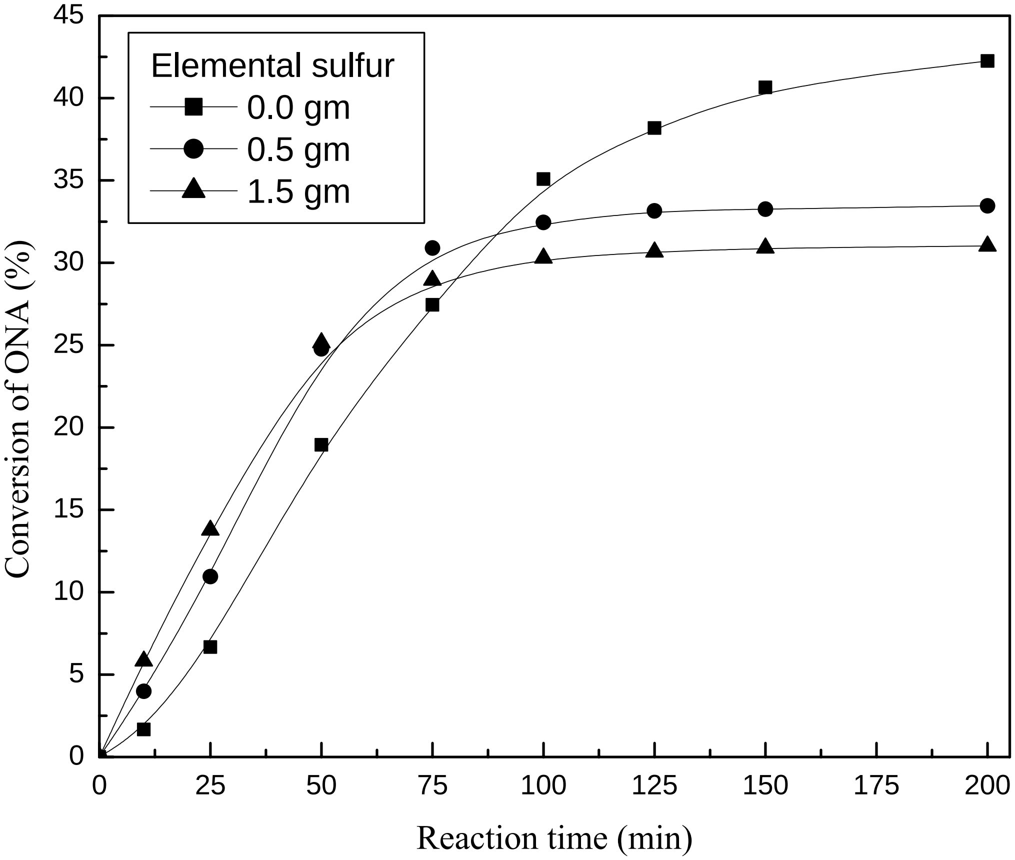

Fig. 2. Effect of elemental sulfur loading. Volume of organic phase = 5×10^{-5} m^3; ONA concentration = 1.31 $kmol/m^3$; volume of aqueous phase = 5×10^{-5} m^3; sulfide concentration = 1.68 $kmol/m^3$; TBAB concentration = 9.3×10^{-2} $kmol/m^3$ of org. phase; concentration of DEA = 3.45 $kmol/m^3$; temperature = 333 K; speed of agitation =1500 rev/min.

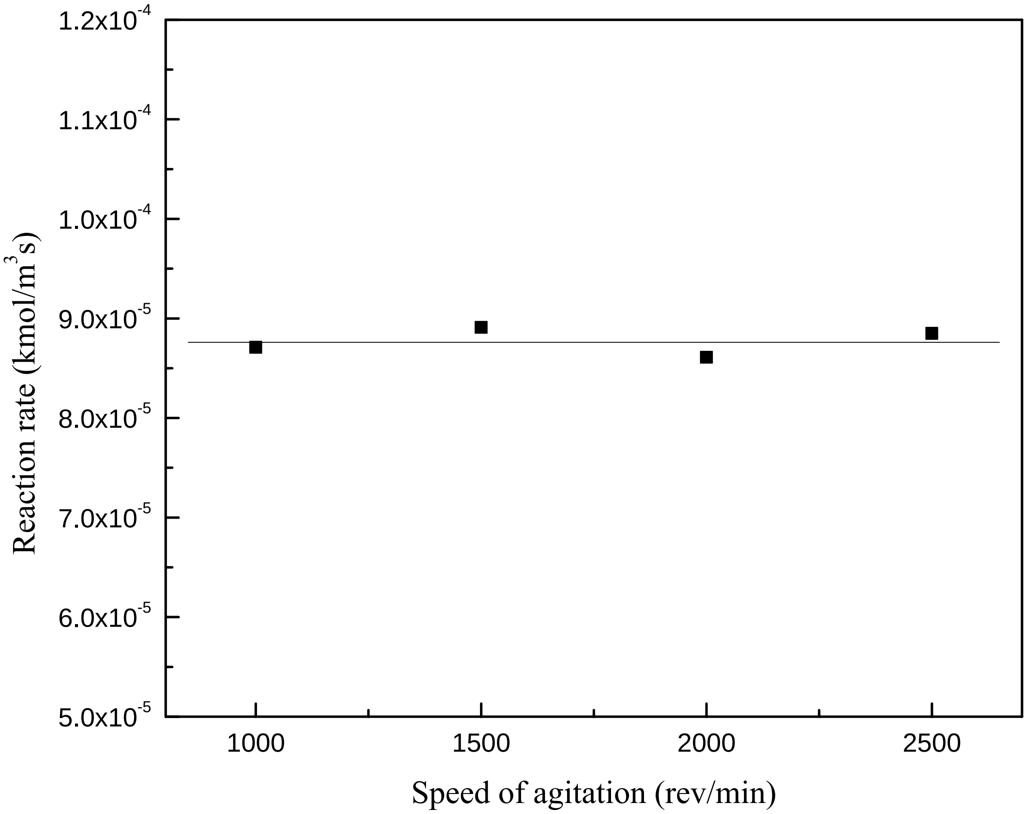

Fig. 3. Effect of speed of agitation. Volume of organic phase = 5×10^{-5} m^3; ONA concentration = 1.31 kmol/m^3; TBAB concentration= 9.3×10^{-2} kmol/m^3 of org. phase; volume of aqueous phase = 5×10^{-5} m^3; sulfide concentration = 1.68 kmol/m^3; concentration of DEA = 3.45 kmol/m^3; temperature = 333 K; speed of agitation =1500 rev/min; Matching ONA conversion =20%.

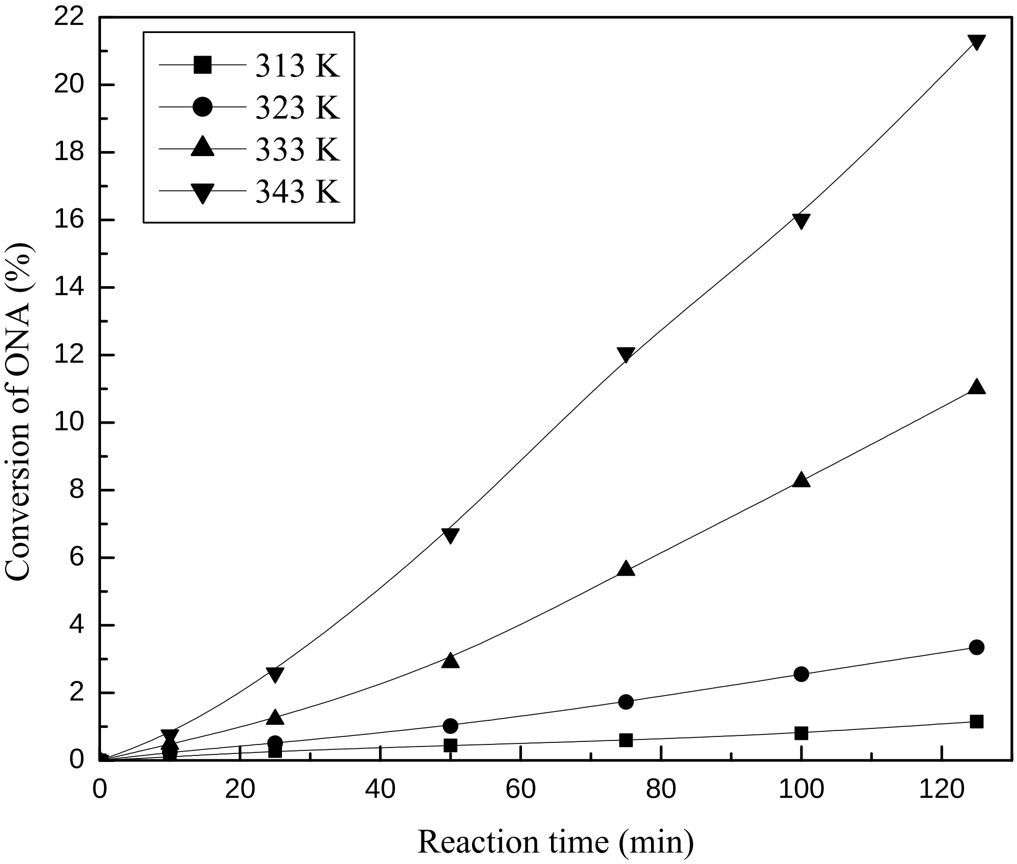

Fig. 4. Effect of temperature on conversion of ONA. Volume of organic phase = 5×10^{-5} m^3; ONA concentration = 1.04 kmol/m^3; TBAB concentration= 6.20×10^{-2} kmol/m^3 of org. phase; volume of aqueous phase = 5×10^{-5} m^3; sulfide concentration = 1.17 kmol/m^3; DEA concentration =3.45 kmol/m^3; speed of agitation =1500 rev/min.

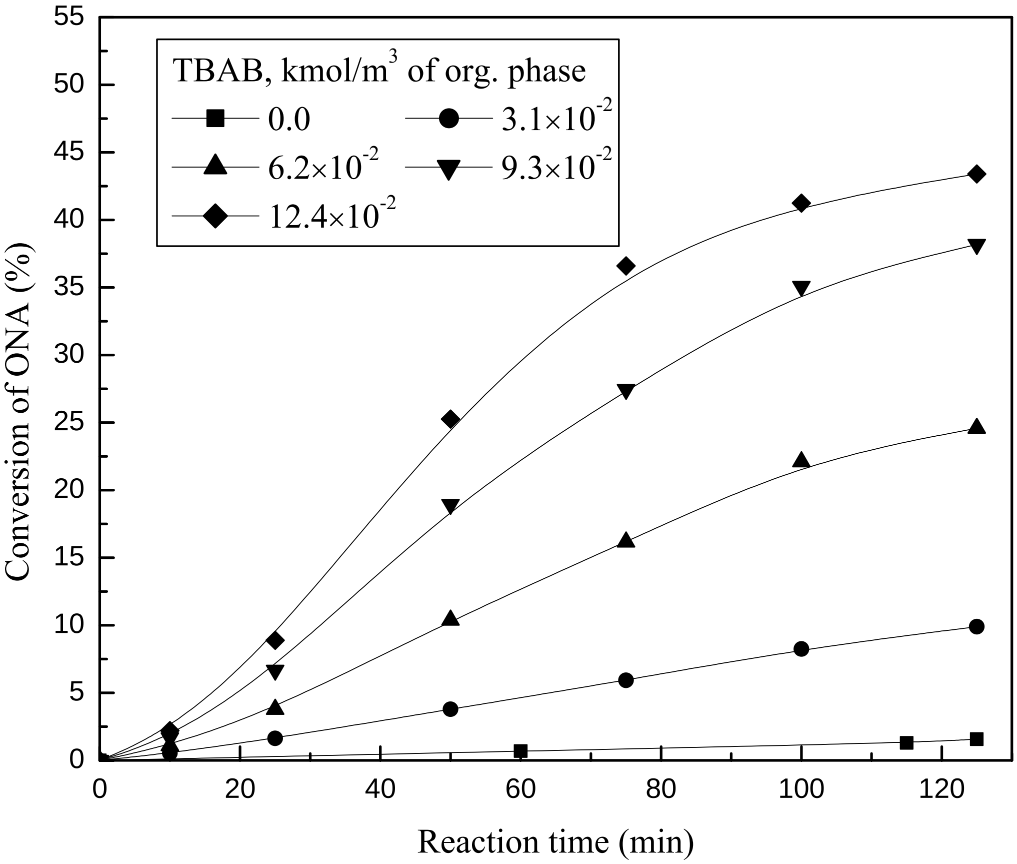

Fig. 5. Effect of TBAB concentration on conversion of ONA. Volume of organic phase = 5×10^{-5} m^3; ONA concentration = 1.31 kmol/m^3; volume of aqueous phase = 5×10^{-5} m^3; sulfide concentration = 1.68 kmol/m^3; concentration of DEA = 3.45 kmol/m^3; temperature = 333 K; speed of agitation =1500 rev/min.

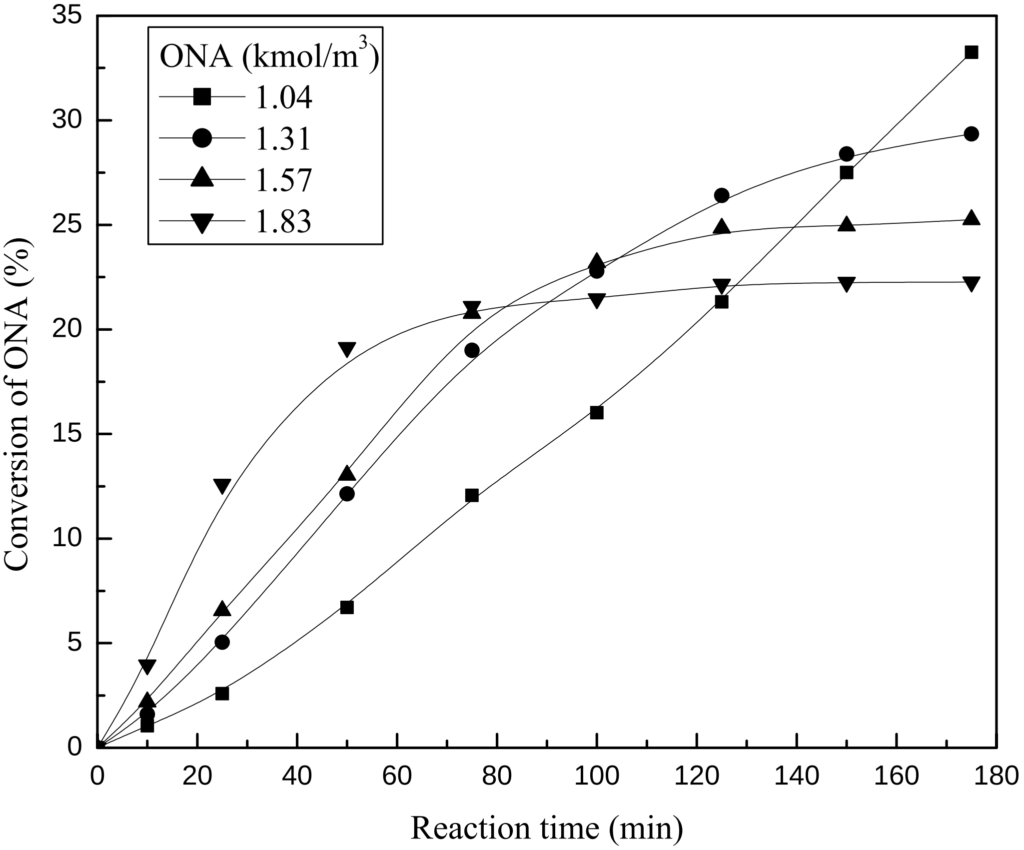

Fig. 6. Effect of ONA concentration on conversion of ONA. Volume of organic phase = 5×10^{-5} m^3; TBAB concentration = 6.2×10^{-2} kmol/m^3 of org. phase; volume of aqueous phase = 5×10^{-5} m^3; sulfide concentration = 1.17 kmol/m^3; concentration of DEA = 3.45 kmol/m^3; temperature = 343 K; speed of agitation =1500 rev/min.

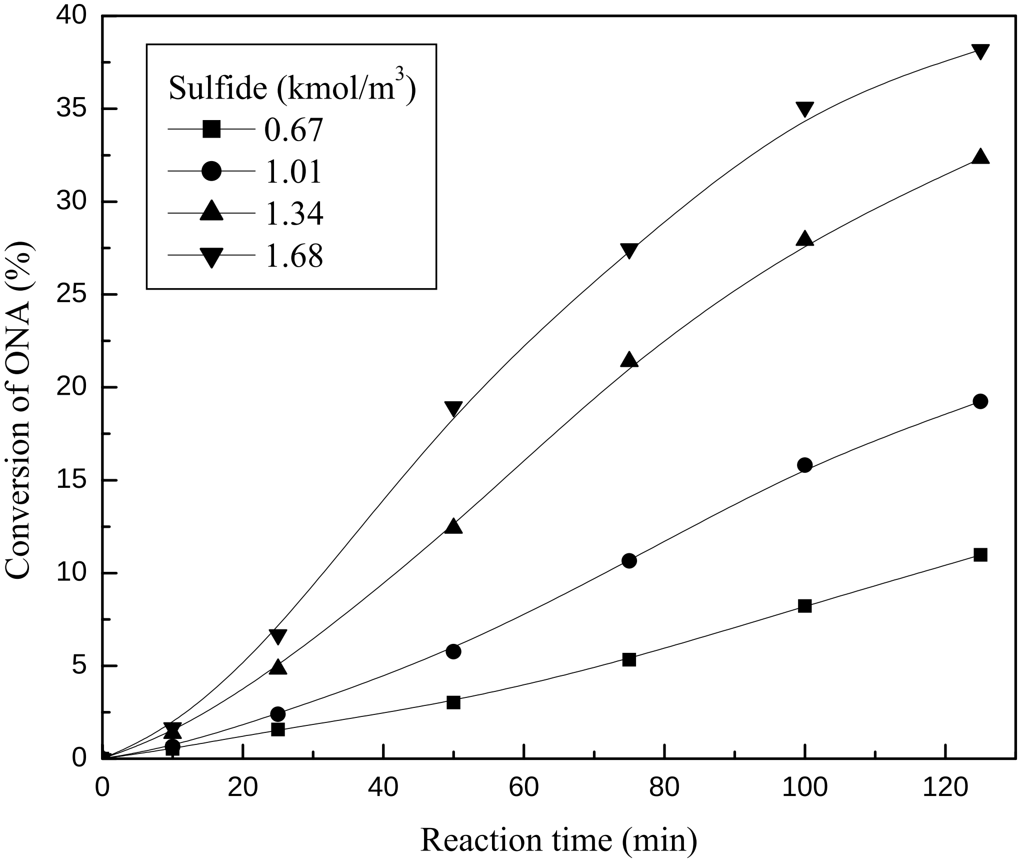

Fig. 7. Effect of sulfide concentration on conversion of ONA. Volume of organic phase = 5×10^{-5} m^3; ONA concentration = 1.31 kmol/m^3; TBAB concentration= 9.3×10^{-2} kmol/m^3 of org. phase; volume of aqueous phase = 5×10^{-5} m^3; concentration of DEA = 3.45 kmol/m^3; temperature = 333 K; speed of agitation =1500 rev/min.

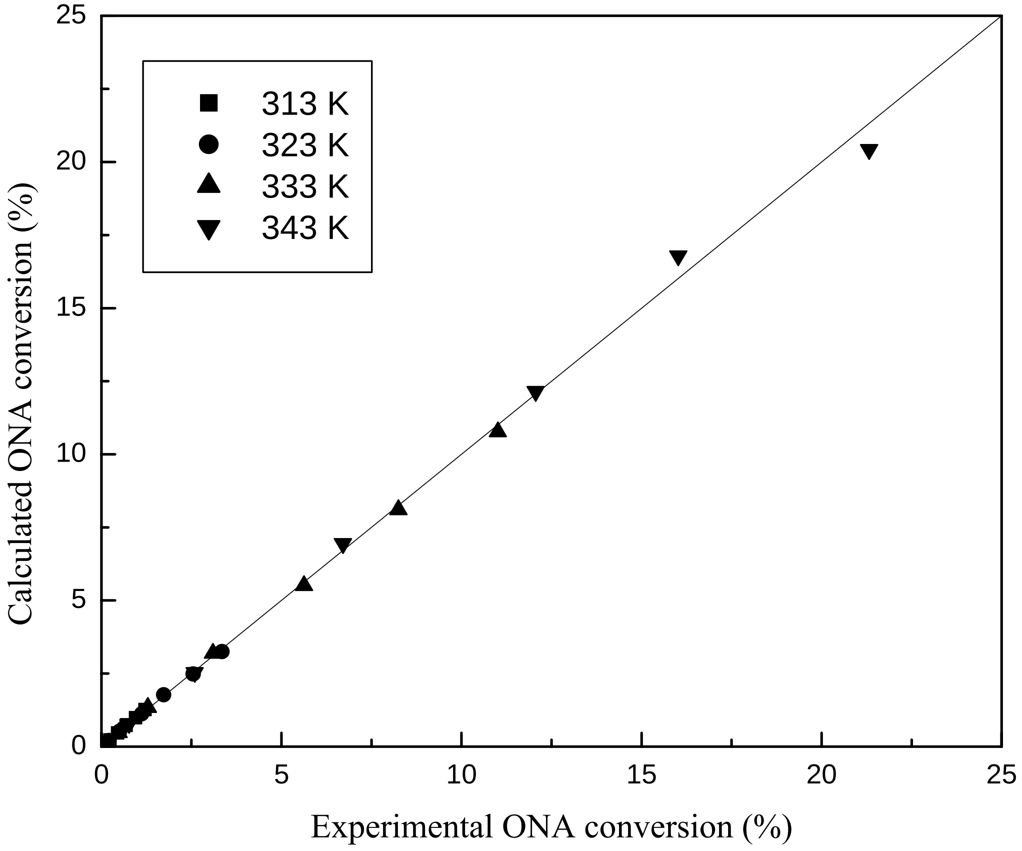

Fig. 8. Comparison of calculated and experimental conversions of ONA. All conditions are the same as in Fig. 4.