A New Mechanistic Model for Liquid-Liquid Phase Transfer Catalysis: Reaction of Benzyl Chloride with Aqueous Ammonium Sulfide

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Abstract

A new mechanistic model for reactions involving two liquid phases and a homogeneous phase transfer catalyst (PTC) has been developed based on extraction mechanism considering the equilibrium of catalyst and active catalysts at the interface. The proposed kinetic model considers thermodynamic framework based aqueous phase ionic equilibrium and the separate contributions of non-PTC and PTC-enhanced reactions towards the overall reactions. The developed model was then applied to an industrially important reaction of benzyl chloride with aqueous ammonium sulfide for synthesis of dibenzyl sulfide and benzyl mercaptan. The kinetic parameters of the developed model were estimated at different temperatures using an indigenously developed non-linear regression technique based on modified Levenberg-Marquardt algorithm. Sensitivity analysis was then performed under various experimental conditions using the estimated parameters and the results were compared with experimental observations. A good agreement was observed between experimental and calculated values with proper trends of the results.

Keywords: Phase transfer catalysis; Dynamic simulation; Reaction engineering; Multiphase reactions; Dibenzyl sulfide; Hydrogen sulfide.

1. Introduction

Phase transfer catalysis (PTC) is an attractive technique for synthesis of organic chemicals from two immiscible reactants existing in two different phases, which otherwise normally cannot react with each other due to their low mutual solubility in other phase and hence their low interaction (Dehmlow and Dehmlow, 1993; Starks et al., 1994). Now-a-days, this technique is widely practiced for large-scale production in industry as well because of its additional advantages of milder operating conditions, reduced consumption of solvents and raw materials, and enhanced selectivity over the conventional processes. The PTC technique has been applied successfully for a large
number of reactions of varied categories such as alkylation, arylation, condensation, elimination, polymerization, etc.

The liquid–liquid phase transfer catalysis (LL-PTC) is a process of favoring 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 aqueous phase to organic phase, where the reaction with the lipophilic substrate takes place (Starks et al., 1994; Dehmlow and Dehmlow, 1983; Starks and Owens, 1973). This mechanism as suggested by Starks is known as extraction mechanism (Scheme 1a) and is applicable when the PTC is not highly lipophilic one and hence can distribute themselves between the phases. When the PTC is a highly lipophilic one, interfacial mechanism (Scheme 1b) is generally used to explain the LL-PTC (Starks et al., 1994). According to this mechanism, the PTC remains entirely in the organic phase and exchanges nucleophile with hydrophilic reactant through aqueous-organic interface only. Extensive reviews have been published in the area of LL-PTC in the form of monographs and papers in peer reviewed journals (Dehmlow and Dehmlow, 1993; Starks et al., 1994; Sasson and Neumann, 1997; Halpern, 1997).

Although much effort has been devoted to the kinetic study and synthesis of organic chemicals, very little attention has been paid in the past for development of kinetic models for LL-PTC reactions of commercial importance. This is due to the fact that the modeling of the dynamic behavior of LL-PTC is quite complex one as it involves the consideration of reactions in both aqueous and organic phases and transfer of catalyst and active catalysts between the phases. Moreover, the physical parameters of the catalyst (or active catalysts) such as distribution coefficients, mass transfer coefficients, and dissociation equilibrium constants are difficult to obtain experimentally as organic-soluble PTC (or active catalyst) cannot be isolated or identified during the reaction in most of the cases (Wang and Yang, 1991; Wang and Chang, 1994).

The consideration of mass transfer factor in the kinetic modeling is important when the phase transfer catalyzed reactions in the organic phase are very fast compared to the mass transfer of the active catalysts. The examples of mass transfer controlled reactions are however limited in literature (Lele et al., 1983) and in most of the cases the organic phase reactions are found to be rate-determining step under intense agitation of the reaction mixture. The kinetic models developed in the past were mostly based on the two-film theory of mass transfer (of the catalysts and active catalysts) between two phases and the kinetics of the organic phase reactions (Wang and Wu, 1991; Wang and Yang, 1991). Wang and Yang, 1991a latter on analyzed the same reaction system using a simplified model based on the pseudo-steady-state hypothesis. It was revealed from the analysis that the mass-transfer resistance of active catalysts from the aqueous phase to the organic phase needs no consideration in the kinetic model as the contribution is
negligible compared to the chemical reaction rate either in the organic phase or in the aqueous phase.

\[
\begin{align*}
RX + Q^+Y^- &\rightleftharpoons RY + Q^+X^- & \text{Organic phase} \\
M^+X^- + Q^+Y^- &\rightleftharpoons M^+Y^- + Q^+X^- & \text{Aqueous phase}
\end{align*}
\]

(a)

\[
\begin{align*}
RX + Q^+Y^- &\rightleftharpoons RY + Q^+X^- & \text{Organic phase} \\
M^+X^- + Q^+Y^- &\rightleftharpoons M^+Y^- + Q^+X^- & \text{Interface} \\
M^+X^- &\rightleftharpoons M^+Y^- & \text{Aqueous phase}
\end{align*}
\]

(b)

**Scheme 1.** (a) Extraction mechanism (b) Interfacial mechanism

Wang and Yu, 1991 assumed that the concentration of the active catalyst in the organic phase remains constant during the course of reaction and the organic phase reactions are represented by pseudo first order reaction kinetics. Recently, the modeling of a variety of liquid-liquid phase transfer catalyzed nucleophilic substitution reactions were reported based on this assumption (Wang and Tseng, 2002, 2002a, 2003; Yadav and Jadhav, 2003; Yang and Lin, 2003). Wu, 1993 analyzed the dynamic behavior of a liquid-liquid phase transfer catalyzed reactions system using a phase-plane model based on the two-film theory. The analysis reveals that the assumption of pseudo first-order kinetics in the organic phase does not hold when mass transfer rates are comparable with the chemical reaction rates. Wu, 1996 reworked on the pseudo-steady-state hypothesis to avoid the assumption of the pseudo-first order reaction kinetics. It was demonstrated that the concentration of active catalyst in the organic phase decreased with the progress of the reaction. The model also suitably explained the concentration dependency of the apparent-first-order reaction rate coefficient \(k_{\text{app}} = k_o[QY]_o\) as observed by previous researchers (Wang and Wu, 1991).

In the past, the common approach was that the non-PTC reactions could either be ignored or incorporated in the PTC-enhanced reactions. With this approach, the correlation capability of the model will still remain unaffected as long as non-catalytic contributions relative to catalytic one remains constant. However, the conditions of reaction generally vary significantly with the progress of the reaction and the above assumption will therefore not remain valid throughout the course of the reaction. Separate consideration of these two contributions is therefore essential in order to develop a physically meaningful mechanistic model with a quite good parametric sensitivity. Recently, a kinetic model was developed considering separate contributions of both non-PTC and PTC-enhanced reactions and the effect of changes in electrolyte composition in
the aqueous phase and the developed model was then validated for the industrially important reaction of synthesis of benzaldehyde from benzyl chloride (BC) (Satrio and Doraiswamy, 2002).

The liquid-liquid phase transfer catalyzed reaction of BC with aqueous ammonium sulfide has enormous potential to utilize the hydrogen sulfide (H₂S) of various by-product gas streams and to produce value-added products, dibenzyl sulfide (DBS) and benzyl mercaptan (BM) (Maity et al., 2006). The aqueous ammonium sulfide based process has enormous commercial importance especially in the petroleum refineries dealing with large quantities of heavy crudes containing high amount of sulfur and nitrogen. During the process of reduction of the sulfur and nitrogen of the heavy crudes, large quantities of by-product gas streams containing H₂S and ammonia (NH₃) are commonly produced. Conventionally, the gas streams containing these gases are first scrubbed with either water or dilute sulfuric acid to remove NH₃ and then sent through amine treating unit to remove H₂S, which is further processed in the Claus unit to produce elemental sulfur (Kohl and Nielsen, 1997). One potential alternative of the conventional process is the simultaneous removal of both H₂S and NH₃ from the gas streams in a single step using dilute ammonium hydroxide to produce aqueous ammonium sulfide, which is then utilized to produce commercially important chemicals like DBS and BM. Moreover, the costly regeneration of H₂S-rich solution is not required in the proposed alternative process.

Considering enormous importance of the reaction system, the work was undertaken to develop a dynamic model following the actual reaction mechanism. The developed model considers the equilibrium of catalyst and active catalysts between the phases and the separation of non-PTC and PTC-enhanced contributions towards the overall reactions. Moreover, influence of complex aqueous phase ionic equilibrium on the reaction was considered for the first time in the developed kinetic model based on a thermodynamic framework. The reaction of BC with ammonium sulfide provides an ideal case study for development of kinetic model for multi-step LL-PTC systems as it involves more than one inorganic nucleophiles (HS⁻ and S²⁻) resulting from complex ionic equilibrium of NH₃-H₂S-H₂O in the aqueous phase, series-parallel reactions network in the organic phase, and significant non-PTC contribution (Scheme 2). The availability of a validated kinetic model for such kind of industrially important reaction with highly complex reaction mechanism is quite desirable one and is essential for the development, design, and scale-up of reactors.
2. Experimental

The reactions of BC with aqueous ammonium sulfide were carried out batch wise in a 6.5 cm i.d. fully baffled mechanically agitated glass reactor (capacity 250 cm³). A 2.0 cm diameter six-bladed glass disk turbine impeller with the provision for stirring speed regulation located at a height of 1.5 cm from the reactor bottom was used for stirring the reaction mixture. The reactor was kept in a constant temperature water bath whose temperature could be controlled within ±1°C.

The H₂S absorption experiments were carried out in a 250 cm³ standard gas-bubbler using ammonium hydroxide solution of suitable ammonia concentration. In a typical experimental run, 50 cm³ of the aqueous ammonium sulfide containing a known concentration of sulfide and catalyst, tetra-n-butylammonium bromide (TBAB) was charged into the reactor and kept well stirred until steady-state temperature was reached. Then the organic phase containing measured volume of BC and solvent (toluene) kept separately at the reaction temperature was charged into the reactor. Samples were withdrawn from the organic layer at regular intervals after stopping the stirring and

**Scheme 2.**
allowing the two phases to separate. All the samples from the organic phase were analyzed by gas-liquid chromatography using an FID detector and nitrogen as carrier gas. The initial sulfide concentration was determined by the standard iodometric titration method. The experimental details were reported in our earlier publication (Maity et al., 2006).

3. Modeling

3.1. Role of Mass Transfer Resistance

For discerning the true kinetics, the mass transfer resistance should be negligible during the reaction. To determine the role of mass transfer resistance, the effect of stirring speed on the rate of reaction of BC was studied in the range of 1000-3000 rev/min under otherwise identical experimental conditions in presence and absence of catalyst as shown in Fig.1. The variation of reaction rate of BC with the stirring speed was found to be negligibly small for both in the absence and presence of catalyst as observed from the figure. The reaction may, therefore, be considered as free from mass transfer resistance and controlled by kinetics only. Accordingly, effect of mass transfer was not considered in the developed model for this reaction. Moreover, the aqueous phase reactions and extraction of catalysts and active catalysts at the interface are assumed to remain in equilibrium. The overall rate of reaction in presence of a catalyst has two contributions: non-catalytic and catalytic as given by following equations.

\[
\frac{d[RX]}{dt}_{\text{overall}} = \frac{d[RX]}{dt}_{\text{non-catalytic}} + \frac{d[RX]}{dt}_{\text{catalytic}}
\]

\[
\frac{d[RSH]}{dt}_{\text{overall}} = \frac{d[RSH]}{dt}_{\text{non-catalytic}} + \frac{d[RSH]}{dt}_{\text{catalytic}}
\]

\[
\frac{d[RSR]}{dt}_{\text{overall}} = \frac{d[RSR]}{dt}_{\text{non-catalytic}} + \frac{d[RSR]}{dt}_{\text{catalytic}}
\]

3.2. Non-catalytic Contribution

Inorganic reagents are generally insoluble in the organic phase. It is therefore reasonable to assume that the non-catalytic reactions proceed at the aqueous-organic interface. Based on the product distribution, the mechanism of the non-catalytic reactions was represented by the reactions i-iv of Scheme 2. The ammonium hydrosulfide (NH4SH) and sulfide ((NH4)2S) in the aqueous phase non-catalytically react with organic phase benzyl chloride (RX) at the interface to yield benzyl mercaptan (RSH) and dibenzyl sulfide (RSR) respectively as represented by the reactions i-iii of Scheme 2. The nucleophilic substitution reactions are in general 2nd order overall. The direct reaction of BC with (NH4)2S was therefore assumed to proceed through an intermediate, RSNH4, which further reacts with RX to produce RSR. Since RSNH4 was not identified in GLC analysis, the net rate of its formation was approximated as zero based on pseudo-steady
state hypothesis. The RSH reacts further with RX to produce RSR (reaction iv of Scheme 2). This conclusion was reached from the concentration profile of a typical batch (Maity et al., 2006). The net rate of formation of RX, RSH, and RSR are represented by the following equations.

\[
\frac{d[RX]}{dt} = -k_{1}^{nc} [RX][NH_{4}SH] - 2k_{2}^{nc} [RX][(NH_{4})_{2}S] - k_{3}^{nc} [RX][RSH] \tag{4}
\]

\[
\frac{d[RSH]}{dt} = k_{1}^{nc} [RX][NH_{4}SH] - k_{3}^{nc} [RX][RSH] \tag{5}
\]

\[
\frac{d[RSR]}{dt} = k_{2}^{nc} [RX][(NH_{4})_{2}S] + k_{3}^{nc} [RX][RSH] \tag{6}
\]

3.3. Catalytic Contribution

In presence of a PTC, the reactions proceed through both non-catalytic and catalytic ways and needs consideration of both contributions in the overall rate expression. The contribution of non-catalytic reactions will be governed by the Eqs.4-6. The rate expression of the catalytic contribution is however quite complex and depends on the type of mechanism involved, which in turn depends on the lipophilicity of the PTC used in the reaction. The reaction of BC with aqueous ammonium sulfide was studied in presence of a PTC, TBAB, which is not highly lipophilic one and can distribute itself between aqueous and organic phase. Therefore, the catalytic reactions could be best represented by extraction mechanism of the LL-PTC as shown by the reactions a-d of Scheme 2. The dissociation equilibrium constants of the PTC, QX and active catalysts, QSH and QS, in the aqueous phase are defined as follows (VI-VIII of Scheme 2).

\[
K_{VI} = \frac{[Q^{+}][X^{-}]}{[QX]} \tag{7}
\]

\[
K_{VII} = \frac{[Q^{+}][HS^{-}]}{[QSH]} \tag{8}
\]

\[
K_{VIII} = \frac{[Q^{+}]^{2}[S^{2-}]}{[QS]} \tag{9}
\]

The equilibrium distribution coefficients of the PTC and active catalysts are defined as follows.

\[
m_{QX} = \frac{[QX]}{[QX]} \tag{10}
\]

\[
m_{QSH} = \frac{[QSH]}{[QSH]} \tag{11}
\]

\[
m_{QS} = \frac{[QS]}{[QS]} \tag{12}
\]
The total sulfide concentration \( (T_S) \) expressed as kmol/m\(^3\) of aqueous phase at any reaction time is the sum of the sulfides present in the aqueous phase in the form of molecular and ionic sulfur species and active catalysts and organic phase in the form of active catalysts as given by the following equation.

\[
T_S = [H_2S] + [HS^-] + [S^{2-}] + [QSH]_a + [QSO]_a + f([QSH]_a + [QSO]_a)
\]  

where, \( f = \frac{\text{volume of organic phase}, V_o}{\text{volume of aqueous phase}, V_a} \)

The total initial amount of PTC added in the reaction mixture, \( Q_0 \), expressed as kmol/m\(^3\) of organic phase, is distributed between the aqueous and organic phases. The PTC in the aqueous phase remains in the form of ionic, molecular, and active catalysts, whereas it is present as molecular and active catalysts form in the organic phase.

\[
Q_0 = [QX]_o + [QSH]_o + 2[QSO]_o + \frac{1}{f}([Q^-] + [QX]_a + [QSH]_a + 2[QSO]_a)
\]  

Combining Eqs.10-12 with Eq.14, the following expression is obtained.

\[
Q_0 = [QX]_a(m_{QX} + \frac{1}{f}) + [QSH]_a(m_{QSH} + \frac{1}{f}) + 2[QSO]_a(m_{QSO} + \frac{1}{f}) + \frac{1}{f}[Q^+]
\]  

The concentration of \( X^- \) ions generated from the ionization of the PTC (reaction VI of Scheme 2) in the aqueous phase is given by following equation.

\[
[X^-] = [Q^+] + [QSH]_a + 2[QSO]_a + f([QSH]_o + [QSO]_o)
\]  

(Using Eq.11&12)

The concentration of \([Q^+], [X^-], [QX]_a, [QSH]_a, \) and \([QSO]_a \) are obtained by solving the set of five non-linear equations, Eqs.7-9,15,16 provided the sulfide and hydrosulfide ions concentration in the aqueous phase are known. The calculation steps followed are (1) Assume a value of \([Q^+]\), (2) calculate \([QSH]_a\) and \([QSO]_a\) using Eqs.8&9 respectively, (3) calculate \([X^-]\) using Eq.16, (4) calculate \([QX]_a\) using Eq.7, (5) calculate \(Q_0\) using Eq.15, (6) If the \(Q_0\) calculated from Eq.15 is not equal to the \(Q_0\) added in the reaction mixture; repeat the steps from 1. (7) calculate the concentration of \([QSH]_o\) and \([QSO]_a\) using Eq.11&12. The sulfide and hydrosulfide ions concentration in the aqueous phase are calculated based on a thermodynamic framework developed by Edwards et al., 1975 as described in the subsequent section.

The reaction of BC with QSQ was assumed to proceed through an intermediate of RSQ. The rate of formation of RSQ is given by

\[
\frac{d[RSQ]}{dt} = k_1^+] [RX] [QSQ]_o - k_2^- [RX] [RSQ]
\]  

The RSQ was not identified in GLC analysis. The concentration of RSQ was therefore expressed assuming pseudo steady state hypothesis as given by the following equation.
The rate of formation of benzyl chloride (RX), benzyl mercaptan (RSH), and dibenzyl sulfide (RSR) by catalytic pathway is expressed by the following equations. The concentration of RSQ as appeared in the rate expression was replaced by using Eq. 18.

\[
\frac{d[RX]}{dt} = -k_1^c [RX][QSH]_o - 2k_2^c [RX][QSO]_o - k_3^c [RX][RSH]
\]

(19)

\[
\frac{d[RSH]}{dt} = k_1^c [RX][QSH]_o - k_4^c [RX][RSH]
\]

(20)

\[
\frac{d[RSR]}{dx} = k_2^c [RX][(NH_4)_2S] + k_5^c [RX][RSH]
\]

(21)

The total sulfide and ammonia concentration in the aqueous phase decreases as the reaction proceeds. Therefore, the total sulfide \( T_S \) and ammonia \( T_{NH_3} \) concentration in the aqueous phase at any reaction time were obtained from overall mass balance as given by the following equations.

\[
T_S = T_{S0} - f([RSH]+[RSR])
\]

(22)

\[
T_{NH_3} = T_{NH_30} - f([RX]_0 - [RX])
\]

(23)

where \([RX]_0\) is the initial concentration of BC

4. Modeling of Aqueous Phase Ionic Equilibrium

Edwards et al., 1975 developed a thermodynamic framework for calculation of vapor-liquid equilibrium for aqueous solutions containing one or more volatile weak electrolytes: NH₃, CO₂, H₂S, SO₂, and HCN and successfully applied the developed model for two ternary systems: NH₃-H₂S-H₂O and NH₃-CO₂-H₂O. In the present study, this framework was used to represent the ionic equilibrium of NH₃-H₂S-H₂O (Eqs. I-IV of Scheme 2) in the aqueous phase.

The ionic equilibrium of NH₃-H₂S-H₂O results seven (molecular and ionic) species (in addition to water) in the aqueous phase namely, NH₃, H₂S, NH₄⁺, H⁺, HS⁻, S²⁻, and OH⁻ as represented by Scheme 2. The ionic equilibrium of I-IV can be represented by the dissociation equilibrium constants \( K \) in terms of molar concentration (m) and activity coefficients \( \gamma \) of the species as represented by Eq. E1-E4.

\[
K_I = \frac{a_{NH_4} a_{OH^-}}{a_{NH_3}} = \frac{m_{NH_4} m_{OH^-}}{m_{NH_3}} \times \frac{\gamma_{NH_4} \gamma_{OH^-}}{\gamma_{NH_3}} = K_I^m K_I^\gamma
\]

(E1)
\[
K_{II} = \frac{a_{H^+}a_{HS^-}}{a_{H_2S}m_{HS^-}} = \frac{m_{H^+}m_{HS^-}}{m_{H_2S}} \times \gamma_{H_2S}^{-} \gamma_{HS^-} = K_{II}^m K_{II}^y 
\]

(E2)

\[
K_{III} = \frac{a_{H^+}a_{S^{2-}}}{a_{HS^-}m_{S^{2-}}} = \frac{m_{H^+}m_{S^{2-}}}{m_{HS^-}} \times \gamma_{H^+}^{-} \gamma_{S^{2-}} \gamma_{HS^-} = K_{III}^m K_{III}^y 
\]

(E3)

\[
K_{IV} = a_{H^+}a_{OH^-} = m_{H^+}m_{OH^-} \times \gamma_{H_2O}^{-} \gamma_{OH^-} = K_{IV}^m K_{IV}^y 
\]

(E4)

Where \(a_i\) (\(a_i = m_i \gamma_i\)) is the activity of the species \(i\). The dissociation equilibrium constants of Eqs. I-IV at a given temperature are calculated using the correlation reported by Beutier and Renon, 1978.

As observed from Eqs. E1-E4, the calculation of concentrations of seven species in the aqueous phase involves fourteen variables (concentration and activity coefficients of each of the seven species) and fourteen independent equations are therefore needed to solve these equations. In addition to above four equations, three more balance (mass and charge) equations can be written as given by the Eqs. E5-E7.

**Mass Balance for NH$_3$:**

\[
T_{NH_3} = m_{NH_3} + m_{NH_4^+} 
\]

(E5)

**Mass Balance for sulfide:**

\[
T_{S} = m_{H_2S} + m_{HS^-} + m_{S^{2-}} 
\]

(E6)

**Electroneutrality/ Charge Balance:**

\[
m_{NH_4^+} + m_{H^+} = m_{HS^-} + 2m_{S^{2-}} + m_{OH^-} 
\]

(E7)

The activity coefficients \((\gamma_i)\) for each of seven species were expressed based on the model developed by Edwards et al., 1975 as given by the following equations (Eqs. E8-E14).

\[
\ln \gamma_i = -\frac{aZ_i^2\sqrt{I}}{1 + \sqrt{I}} + 2\sum_{k=1}^{7} \beta_{ik} m_k 
\]

(E8-E14)

Where, \(\alpha\) is the Debye-Hückel proportionality factor defined by \(\alpha = 2.303 A_r\) where \(A_r\) is the Debye-Hückel constant for activity coefficient = 0.511 (kg/mol) \(1/2\) at 25\(^{\circ}\)C (Bromley, 1973), \(z_i\) is the ionic charge of species \(i\), \(I\) is the ionic
strength of the solution defined by $I = \frac{1}{2} \sum_{i=1}^{n} Z_i^2 m_i$, and $\beta_{ik}$ is the specific interaction parameter for species i and k and obtained from the works of Edwards et al., 1975.

These fourteen equations (Eq. E1-E14) constitute model of Edwards et al., 1975 for calculation of concentrations and activity coefficients of each of the seven species in the aqueous phase. The concentrations of different sulfur species in the aqueous phase at 333 K were calculated from this model for varying total ammonia and sulfide concentration in the aqueous phase as shown in Fig. 2. It is clear from this figure that hydrosulfide ions are the dominating sulfur species and its concentration increases with total sulfide concentration in the aqueous phase (Fig. 2a). It is also observed from the figure that the concentration of hydrosulfide ions is in the same order of magnitude as that of total sulfide concentration. The concentration of sulfide ions (Fig. 2b) on the other hand was only significant at high total ammonia concentration and the concentration of molecular $H_2S$ (Fig. 2c) was found to be significant at high total sulfide concentration and low total ammonia concentration. From this result it may be concluded that at high ammonia concentration the dissociation equilibria of I-IV of Scheme 2 shift towards more ionization that results low molecular $H_2S$ concentration and high sulfide ion concentration in the aqueous phase.

5. Regression Analysis and Parameters Estimation

It is worthy to mention here that the reaction of BC with BM apparently seems to be non-catalytic one. If the above reaction was assumed to proceed non-catalytically only, even in presence of a PTC, the appropriate trend of conversion of BC and selectivity of DBS was not observed during the regression analysis. This observation clearly indicates that the above reaction proceeds catalytically as well. However, exact catalytic mechanism for this reaction is still not clear.

The required model parameters, distribution coefficient and dissociation constants of the TBAB were taken from the work of Wu et al., 1998 measured in chlorobenzene solvent at different temperature in the range of 283-323 K as it closely resembles the present reaction system. However, the values of these constants for the active catalysts, QSH and QSQ, could not be obtained experimentally as these catalysts could not be isolated during the reaction. Therefore, the values of these parameters for the active catalysts were assumed to be same as that of catalyst.

5.1. Non-catalytic Contribution

The kinetic constants for non-catalytic contribution were estimated using the experimental data of independent experiments in absence of any catalyst at four different temperatures in the range of 303-333 K. The non-catalytic model consisting of three ordinary differential equations, Eqs.4-6, algebraic equations, Eqs.22-23, and model of aqueous phase ionic equilibrium, Eqs.E1-E14, were regressed using an indigenously
developed non-linear regression algorithm based on modified Levenberg-Marquardt algorithm. The optimum values of the parameters were estimated by minimizing the objective function as given by the following equation.

\[
E = \sum_{i=1}^{n} \left[ (\{[RX]_{\text{exp}}\}_i - ([RX]_{\text{pred}})_i)^2 + (\{[RSH]_{\text{exp}}\}_i - ([RSH]_{\text{pred}})_i)^2 \right] + \left( ([RSH]_{\text{exp}})_i - ([RSH]_{\text{pred}})_i \right]^2 \]  

(24)

The optimized non-catalytic rate constants at different temperatures were reported in Table 1. It was observed from the table that with increasing temperature, the values of the rate constants increase as expected. The Arrhenius plot of ln(k) against 1/T was made and the activation energy and pre-exponential factor were obtained from the slope and intercept of the Arrhenius plot as shown in Table 2.

The initial rate of reaction at different temperatures were calculated from experimental data and the experimental activation energy was calculated from the slope of the Arrhenius plot of ln(initial rate) versus 1/T as shown in Table 2. As it is observed from the table, the activation energy calculated from the estimated rate constants was comparable with the experimental activation energy. The conversion of BC and selectivity of DBS at various reaction times were calculated using the estimated rate constants at different temperatures and compared with those of experimental values as shown in Fig. 3. Quite a good agreement was observed with average absolute deviation of about 5.1%, 4.2%, 4.3%, and 5.2% at 303, 313, 323, and 333 K, respectively.

5.2. Catalytic Contribution

In order to estimate the kinetic constants corresponding to the catalytic contribution, experiments were conducted in presence of a catalyst, TBAB, under otherwise identical experimental conditions as that of non-catalytic reactions as shown in Fig. 4. The entire kinetic model corresponding to both catalytic and non-catalytic contributions was regressed using the previously estimated non-catalytic kinetic constants as before. The optimized catalytic kinetic constants at different temperature are shown in Table 3. The estimated rate constants corresponding to catalytic contribution are found to be higher compared to the rate constants corresponding to the non-catalytic contribution as one can observe from the Table 1&3. This indicates the importance of rate enhancement by PTC in the reaction of present study. The activation energy and pre-exponential factor of the rate constants were obtained from the slope and intercept of the Arrhenius plot of ln(k) against 1/T as shown in Table 4. The conversion of BC and selectivity of DBS at various reaction times were calculated using the estimated rate constants at different temperatures and compared with those of experimental values as shown in Fig. 4. Quite a good agreement was observed with average absolute deviation of about 5.8%, 4.7%, 4.4%, and 4.1% at 303, 313, 323, and 333 K, respectively.

It is worthy to mention here that the experimental activation energy in presence of catalyst has been found to be significantly smaller than that of calculated from the
estimated rate constants. This is due to the fact that the experimental activation energy in presence of catalyst reflects the reactions of both catalytic and non-catalytic contributions. The activation energy of rate constants corresponding to the catalytic contribution is found to be significantly higher than that of the non-catalytic contribution as one can observe from Tables 2&4. From this results, it can therefore be concluded that that the reaction in presence of catalyst is much more temperature sensitive than the reactions in absence of catalyst. Moreover, the high values of activation energies (Table 2&4) further confirms the fact that the reaction is kinetically controlled and provides further justification of neglecting the mass transfer resistances in developed model.

6. Sensitivity Study
The parametric sensitivity of the validated mechanistic model was further tested using the above estimated rate constants to understand the effect of various process parameters on conversion of BC and selectivity of DBS. The results obtained from the above analysis were then compared with that of experimental observations under different experimental conditions as shown in the Figs. 5-8. The discussions of the results thus obtained are presented below.

6.1. Effect of PTC Concentration
The effect of catalyst loading on conversion of BC and selectivity of DBS was studied at four different catalyst concentrations in the range of 0.0–0.093 kmol/m³ and compared with the model based calculations as shown in Fig. 5. Both conversion of BC and selectivity of DBS at a fixed reaction time were found to increase with increasing PTC concentration as observed from the figures. A reasonably well correlation was obtained with proper trends as observed from the figure. It is worthy to mention here that the developed model is capable of correlating data even in the absence of any catalyst, which is otherwise not possible if the non-PTC reactions are incorporated in the PTC-enhanced reaction.

6.2. Effect of Benzyl Chloride Concentration
The effect of BC concentration on conversion of BC and selectivity of DBS is shown in Fig. 6. With increase in concentration of BC the conversion of BC decreases because of the limited quantity of sulfide in the aqueous phase as observed from the figure. However, the selectivity of DBS increases with increase in concentration of BC. It is also observed from the figure that the model prediction is reasonably close to that of experimental observations.

6.3. Effect of Sulfide Concentration
Fig. 7 shows comparison of the model-based predictions and experimental results of the effect of sulfide concentration on the conversion of BC and selectivity of DBS. The
conversion of BC increases with increase in sulfide concentration in the aqueous phase as expected (Fig. 7a). However, the selectivity of DBS was found to be higher for lower sulfide concentration in the aqueous phase as observed from the Fig. 7b. Also, as evident from the figures, quite a good agreement was observed between experimental and calculated results with proper trends of the parameters.

6.4. Effect of Ammonia Concentration

The concentration of sulfide ions relative to hydrosulfide ions vary significantly with ammonia concentration in the aqueous phase which in turn affect the conversion of BC and selectivity of DBS. Therefore, the effect of ammonia concentration on this reaction can be used to test the suitability of the model of Edwards et al., 1975 for predicting the concentration of sulfide and hydrosulfide ions in the aqueous phase. The experimental result of the effect of ammonia concentration on the conversion of BC and selectivity of DBS was compared with that of model based prediction as shown in Fig. 8. The appropriate trend of results was obtained from the model. However, the calculated results based on developed mechanistic model were found to deviate slightly from the experimental observations because of the inaccuracy of the model of Edwards et al., 1975. The more appropriate model is therefore needed to represent the aqueous phase ionic equilibrium.

7. Conclusions

A kinetic model based on extraction mechanism was developed for the liquid-liquid phase transfer catalyzed reaction of BC with aqueous ammonium sulfide considering separate contribution of non-PTC and PTC-enhanced reactions, the complex ionic equilibrium of NH$_3$-H$_2$S-H$_2$O in the aqueous phase, and equilibrium of catalyst and active catalysts between the phases. A thermodynamic framework developed by Edwards et al., 1975 was used to represent the aqueous phase ionic equilibrium. The rate constants and equilibrium constants of the developed kinetic model were estimated at different temperatures using a modified Levenberg-Marquardt algorithm. The frequency factors and activation energies of the rate constants were determined from the intercept and slope of the Arrhenius plot of $\ln$(rate constants) versus 1/T. Sensitivity analysis was then performed using the estimated parameters under various experimental conditions and then the results were compared with experimental ones. A reasonably good agreement was observed between the calculated results obtained from the developed model and the experimental observations.

References


### Table 1. Variation of rate constants with temperature in the absence of catalyst

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$k_1^{nc}$, (kmol/m$^3$)$^{-1}$s$^{-1}$</th>
<th>$k_2^{nc}$, (kmol/m$^3$)$^{-1}$s$^{-1}$</th>
<th>$k_3^{nc}$, (kmol/m$^3$)$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>$3.30 \times 10^{-05}$</td>
<td>$1.61 \times 10^{-04}$</td>
<td>$4.88 \times 10^{-06}$</td>
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<tr>
<td>313</td>
<td>$9.63 \times 10^{-05}$</td>
<td>$5.63 \times 10^{-04}$</td>
<td>$7.89 \times 10^{-06}$</td>
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<tr>
<td>323</td>
<td>$2.45 \times 10^{-04}$</td>
<td>$6.03 \times 10^{-04}$</td>
<td>$1.60 \times 10^{-05}$</td>
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<tr>
<td>333</td>
<td>$3.17 \times 10^{-04}$</td>
<td>$1.26 \times 10^{-03}$</td>
<td>$2.27 \times 10^{-05}$</td>
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</tbody>
</table>

### Table 2. Frequency factor and activation energy of various rate constants in the absence of catalyst

<table>
<thead>
<tr>
<th>Rate constants</th>
<th>Frequency factor, $k_0$ (kmol/m$^3$)$^{-1}$s$^{-1}$</th>
<th>Activation energy, $E$ (kJ/mol)</th>
<th>Correlation factor, $R^2$</th>
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</thead>
<tbody>
<tr>
<td>$k_1^{nc}$</td>
<td>$6.53 \times 10^06$</td>
<td>65.20</td>
<td>0.95</td>
</tr>
<tr>
<td>$k_2^{nc}$</td>
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<td>52.54</td>
<td>0.90</td>
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<tr>
<td>$k_3^{nc}$</td>
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<td>0.99</td>
</tr>
<tr>
<td>Experimental</td>
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<td>62.17</td>
<td>1.0</td>
</tr>
</tbody>
</table>

### Table 3. Variation of rate constants with temperature in the presence of catalyst (TBAB)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$k_1^c$, (kmol/m$^3$)$^{-1}$s$^{-1}$</th>
<th>$k_2^c$, (kmol/m$^3$)$^{-1}$s$^{-1}$</th>
<th>$k_3^c$, (kmol/m$^3$)$^{-1}$s$^{-1}$</th>
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<td>333</td>
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<td>241.40</td>
<td>$5.39 \times 10^{-05}$</td>
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</table>

### Table 4. The frequency factor and activation energy of various rate constants in the presence of a catalyst

<table>
<thead>
<tr>
<th>Rate constants</th>
<th>Frequency factor, $k_0$ (kmol/m$^3$)$^{-1}$s$^{-1}$</th>
<th>Activation energy, $E$ (kJ/mol)</th>
<th>Correlation factor, $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1^c$</td>
<td>$1.22 \times 10^{15}$</td>
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<tr>
<td>$k_2^c$</td>
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</tr>
<tr>
<td>$k_3^c$</td>
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<td>61.28</td>
<td>0.96</td>
</tr>
<tr>
<td>Experimental</td>
<td>-</td>
<td>68.02</td>
<td>0.99</td>
</tr>
</tbody>
</table>
**Fig 1. Effect of speed of agitation on rate of reaction of benzyl chloride.** Volume of organic phase = 5.0×10⁻⁵ m³; concentration of benzyl chloride = 2.6 kmol/m³; volume of aqueous phase = 5.0×10⁻⁵ m³; concentration of sulfide = 1.20 kmol/m³; NH₃ concentration= 6.05 kmol/m³; temperature=333 K; Matching reaction time = 5 min.
**Fig. 2.** Concentration of different sulfur species in the aqueous phase. Simulation results are at 333 K.
**Fig 3.** Comparison of calculated and experimental results in the absence of catalyst. Volume of organic phase = $5.0 \times 10^{-5}$ m$^3$; concentration of benzyl chloride = 2.6 kmol/m$^3$; volume of aqueous phase = $5.0 \times 10^{-5}$ m$^3$; concentration of sulfide = 1.20 kmol/m$^3$; NH$_3$ concentration = 6.05 kmol/m$^3$; stirring speed = 1500 rev/min.

**Fig 4.** Comparison of calculated and experimental results in the presence of catalyst (TBAB). Concentration of TBAB = $9.3 \times 10^{-2}$ kmol/m$^3$ of org. phase; all other conditions are same as in Fig. 3.
Fig. 5. Effect of PTC concentration on conversion of benzyl chloride and selectivity of DBS. Temperature = 333 K; all other conditions are same as in Fig. 3.

Fig. 6. Effect of benzyl chloride concentration on conversion of benzyl chloride and selectivity of DBS. The experimental results are taken from Maity et al., 2006.
Fig. 7. Effect of sulfide concentration on conversion of benzyl chloride and selectivity of DBS. The experimental results are taken from Maity et al., 2006.

Fig. 8. Effect of ammonia concentration on conversion of benzyl chloride and selectivity of DBS. The experimental results are taken from Maity et al., 2006.