

# MATHEMATICAL MODELING OF A LIQUID-LIQUID PHASE-TRANSFER CATALYZED REACTION SYSTEM

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This paper presents a new mathematical model for the dynamics of a liquid-liquid phase-transfer catalyzed batch reaction system. The model is formulated as a system of coupled nonlinear differential and algebraic equations in which the differential equations describe the slow reactions in the organic phase, whereas the algebraic ones describe the rapidly established dissociation equilibria in the aqueous phase and the mass balances of the species. A two-stage optimal parameter estimation method is used to estimate the values of the model parameters, such as the reaction rate constants, the overall mass transfer coefficients, the distribution coefficients, and the dissociation constants, from the experimental data. The reversible reaction between organic-phase benzyl chloride and aqueous-phase sodium bromide, with tetrabutylammonium bromide as a catalyst, was carried out to verify the mathematical model. Simulation results reveal that by the proposed model one can successfully make a correct judgement as to whether the quaternary onium salts in the two phases are in extractive equilibrium. Also, one can explicitly determine the respective contributions of the reaction and the mass transfer to the overall rate. Moreover, the fact that a high-concentration inorganic salt in the aqueous phase salts out the quaternary onium salts into the organic phase and thereby alters the distribution coefficients of the phase-transfer catalysts can be explained by our model.

## Introduction

Chemical reactions between nonelectrolyte substrates dissolved in organic phase and ionic reagents dissolved in aqueous phase are generally inhibited by the boundary between the two phases, which separates the reactants and prevents them from access to each other. Traditionally, such a barrier is overcome by the use of an appropriate mutual solvent that solubilizes both inorganic salt and substrate. Typical solvents are polar or aprotic solvents, such as acetonitrile or dimethylformamide (DMF), which greatly increase the reaction rate since they only weakly solvate the nucleophile. However, the use of mutual solvents is not always convenient, and is frequently expensive on an industrial scale. To avoid these disadvantages, an alternative method known as phase-transfer catalysis (PTC) has been developed over the last two decades.

In a two-phase PTC system, the chemical reaction is brought about by the use of a small amount of phase-transfer agent, such as tetrabutyl onium salt, which transfers reactants across the phase boundary so that the reaction can proceed. The phase-transfer catalyst is not consumed but performs the above

transport function repeatedly. Many previous researches have shown that PTC not only promotes chemical reaction between reagents in different phases but also offers a number of important process advantages, such as mild reaction conditions, low energy requirements, high selectivity, and by-product suppression<sup>7,12</sup>.

Since PTC was pioneered by the early work of Starks<sup>15</sup> and others, the phase-transfer technique has received a great deal of attention from preparative chemists, and several articles and books on phase-transfer catalysis have appeared<sup>4,16,18</sup>. This is particularly true of liquid-liquid PTC, since it is the most common two-phase reaction process. Much experimental work has been done in pursuit of an understanding of the mechanism and kinetics of PTC. However, the mathematical description of a two-phase PTC reaction system has received inadequate consideration. Starks and Liotta<sup>16</sup> have proposed a model for a PTC reaction system by making an assumption that the two phases are in extractive equilibrium and thus the mass transfer resistance between phases can be neglected. Their assumption is based on the observation that the apparent rates of laboratory PTC reactions are often independent of the effectiveness of contact between the phases over a

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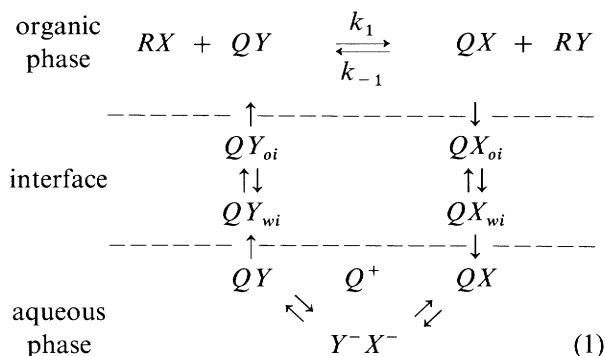
broad range of stirring speeds. However, as pointed out by several authors<sup>5,9,10)</sup>, the PTC reaction is strongly mediated by the mass transfer of the phase-transfer catalysts. Hence, the simple model of Starks and Liotta does not cover the complete range of operating conditions. Besides, it is not adequate to account for the salting-out and common-ion effects on the rate of PTC reactions.

In reality, the mechanism and kinetics of a liquid-liquid phase-transfer catalyzed reaction system are extremely complicated. In general, a liquid-liquid phase-transfer catalyzed reaction involves the following steps: (1) chemical reaction in the organic phase; (2) fast dissociation equilibria and competition between the reactant and product anions for the quaternary cation in the aqueous phase; (3) transport of quaternary onium salts between the two phase; and (4) equilibrium partition of quaternary onium salt at the interface. Based on this mechanism and the two-film theory, we derive in this paper a new mathematical model for describing the dynamics of a liquid-liquid PTC reaction system. The model is formulated as a system of coupled nonlinear differential and algebraic equations in which the differential equations describe the slow reactions occurring in the organic phase, whereas the algebraic ones describe the rapidly established dissociation equilibria in the aqueous phase and the mass balances of species. This differential-algebraic system can be solved by the generalized third-order semi-implicit Runge-Kutta method<sup>6)</sup>. The parameters in the proposed model, such as the reaction rate constants, the overall mass transfer coefficients, the distribution coefficients, and the dissociation constants, are the major factors that govern the overall dynamic behavior of a liquid-liquid PTC reaction system. Since the chemical and physical properties of a PTC system change as the reaction proceeds, the parameters are often experimentally very difficult to measure and so they are not presently available<sup>16)</sup>. To obtain representative and physically meaningful parameters, a two-stage optimal parameter estimation scheme that combines the Sobol's systematic searching method<sup>14)</sup> with the DSC-Powell method<sup>1)</sup> is adopted to estimate the model parameters from the experimental data. To verify the proposed model, a reversible reaction of organic-phase benzyl chloride and aqueous-phase sodium bromide, in the presence of tetrabutylammonium bromide as a phase-transfer catalyst, was carried out. The experiment and simulation results reveal that the proposed model not only can cover a wide range of operating conditions but can also elucidate well several important phenomena involved in a liquid-liquid PTC reaction system.

## 1. Mathematical model

### 1.1 Model formulation

The following mechanism represents a general mathematical model of the dynamics of a liquid-liquid phase-transfer catalyzed reaction system.



It is assumed here that both  $RX$  and  $RY$  are insoluble in the aqueous phase and that quaternary onium salts  $QX$  and  $QY$  at the interface are in extractive equilibrium. Based on the mechanism in (1), the whole reaction system consists of the following steps:

1) Mass transfer step The quaternary onium salts can transfer back and forth between phases, with  $QY$  transferring from the aqueous phase to the organic phase and  $QX$  from the organic phase to the aqueous phase. Applying the two-film theory<sup>19)</sup>, we have the fluxes for  $QY$  and  $QX$  as follows:

$$J_{QY} = k_{QY,w}[(QY)_w - (QY)_{wi}] = k_{QY,o}[(QY)_{oi} - (QY)_o] \quad (2)$$

$$J_{QX} = k_{QX,o}[(QX)_o - (QX)_{oi}] = k_{QX,w}[(QX)_{wi} - (QX)_w] \quad (3)$$

2) Extractive equilibrium at interface We assume that  $QY$  and  $QX$  are, respectively, in extractive equilibrium at the interface but not in the two phases. This assumption implies that

$$m_{QY} = \frac{(QY)_{oj}}{(QY)_{wi}} \quad (4)$$

and

$$m_{QX} = \frac{(QX)_{oi}}{(QX)_{wi}} \quad (5)$$

With the substitution of Eqs. (4) and (5), we can eliminate  $(QY)_{oi}$ ,  $(QY)_{wi}$ ,  $(QX)_{oi}$ , and  $(QX)_{wi}$  from Eqs. (2) and (3). Hence, the fluxes of  $QY$  and  $QX$  between phases can be expressed in terms of their concentrations in the two phases:

$$J_{QY} = K_{QY}[m_{QY}(QY)_w - (QY)_o] \quad (6)$$

$$J_{QX} = K_{QX}[(QX)_o - m_{QX}(QX)_w] \quad (7)$$

where

$$K_{QY} = \left[ \frac{1}{k_{QY,w}} + \frac{m_{QY}}{k_{QY,o}} \right]^{-1}$$

$$K_{QX} = \left[ \frac{1}{k_{QX,o}} + \frac{m_{QX}}{k_{QX,w}} \right]^{-1}$$

3) Slow reactions in organic phase The rate equations for the slow organic-phase reactions are assumed to be:

$$\frac{d(RX)_o}{dt} = -k_1(RX)_o(QY)_o + k_{-1}(RY)_o(QX)_o \quad (8)$$

$$\frac{d(QY)_o}{dt} = -k_1(RX)_o(QY)_o + k_{-1}(RY)_o(QX)_o + V_o^{-1}AK_{QY}[m_{QY}(QY)_w - (QY)_o] \quad (9)$$

$$\frac{d(QX)_o}{dt} = k_1(RX)_o(QY)_o - k_{-1}(RY)_o(QX)_o - V_o^{-1}AK_{QX}[(QX)_o - m_{QX}(QX)_w] \quad (10)$$

$$\frac{d(RY)_o}{dt} = k_1(RX)_o(QY)_o - k_{-1}(RY)_o(QX)_o \quad (11)$$

4) Dissociation equilibrium in aqueous phase In the aqueous phase, dissociation equilibria for  $QX$  and  $QY$  are rapidly established. Hence, the competition between  $X^-$  and  $Y^-$  for quaternary cation  $Q^+$  and the common-ion effect of  $Q^+$  can be represented by the following dissociation equilibrium equations:

$$K_{QY}^D = \frac{(Q^+)_w(Y^-)_w}{(QY)_w} \quad (12)$$

$$K_{QX}^D = \frac{(Q^+)_w(X^-)_w}{(QX)_w} \quad (13)$$

5) Mass balances of species The mass balances for  $Y^-$ ,  $X^-$ , and  $Q^+$  are given below:

$$V_o[(RY)_o + (QY)_o] + V_w[(Y^-)_w + (QY)_w] = V_o(RY)_o^o + V_w[(QY)_w^o + (Y^-)_w^o] \quad (14)$$

$$V_o[(RX)_o + (QX)_o] + V_w[(X^-)_w + (QX)_w] = V_o(RX)_o^o + V_w[(QX)_w^o + (X^-)_w^o] \quad (15)$$

$$V_o[(QY)_o + (QX)_o] + V_w[(Q^+)_w + (QX)_w + (QY)_w] = V_w[(QY)_w^o + (QX)_w^o] \quad (16)$$

The dynamic behaviour of a liquid-liquid PTC reaction system is now described by Eqs. (8)–(16). These equations can be further simplified to the following system of three differential equations and one algebraic equation:

$$\frac{dy_1}{dt} = -p_1y_1y_2 + p_2(N_R^o - y_1)y_3 \quad (17)$$

$$\frac{dy_2}{dt} = -p_1y_1y_2 + p_2(N_R^o - y_1)y_3 - p_3 \left\{ y_2 - p_5 \frac{1}{1 + \frac{p_7}{y_4}} [N_Y^o - \alpha(N_R^o - y_1 + y_2)] \right\} \quad (18)$$

$$\frac{dy_3}{dt} = p_1y_1y_2 - p_2(N_R^o - y_1)y_3 - p_4 \left\{ y_3 - p_6 \frac{1}{1 + \frac{p_8}{y_4}} [N_X^o - \alpha(y_1 + y_3)] \right\} \quad (19)$$

$$0 = -N_Q^o + \alpha(y_2 + y_3) + y_4 + \frac{1}{1 + \frac{p_7}{y_4}} [N_Y^o - \alpha(N_R^o - y_1 + y_2)] + \frac{1}{1 + \frac{p_8}{y_4}} [N_X^o - \alpha(y_1 + y_3)] \quad (20)$$

where

$$[y_1, y_2, y_3, y_4] = [(RX)_o, (QY)_o, (QX)_o, (Q^+)_w]$$

$$[p_1, p_2, p_3, p_4, p_5, p_6, p_7, p_8] = [k_1, k_{-1}, V_o^{-1}AK_{QY}, V_o^{-1}AK_{QX}, m_{QY}, m_{QX}, K_{QY}^D, K_{QX}^D]$$

$$\alpha = \frac{V_o}{V_w}$$

$$N_R^o = (RX)_o^o + (RY)_o^o$$

$$N_Y^o = (QY)_w^o + (Y^-)_w^o + \alpha(RY)_o^o$$

$$N_X^o = (QX)_w^o + (X^-)_w^o + \alpha(RX)_o^o$$

$$N_Q^o = (QY)_w^o + (QX)_w^o$$

## 1.2 Admissible initial conditions

Before reaction, the species  $QX$ ,  $QY$ ,  $Y^-$ , and  $X^-$  are in the aqueous phase, while  $RX$  and  $RY$  are in the organic phase. Hence, the initial conditions of  $(RX)_o$ ,  $(QY)_o$ , and  $(QX)_o$  are given by  $[y_1(0), y_2(0), y_3(0)] = [(RX)_o^o, 0, 0]$ . The initial concentration of  $Q^+$ ,  $y_4(0)$ , cannot be a arbitrary value or the system will show impulsive (jump) behaviour at the initial state<sup>2,13</sup>. To avoid impulsive behaviour, the initial values of  $y_i(0)$  for  $i=1,2,3,4$  should satisfy the admissible initial condition. In other words,  $y_4(0)$  should be determined from Eq. (20).

## 2. Solution of nonlinear differential-algebraic equations

A model composed of nonlinear differential and algebraic equations can be expressed in the general form

$$\frac{dy_1}{dt} = f_1(y, p, t) \quad (21a)$$

$$0 = f_2(y, p, t) \quad (21b)$$

with the admissible initial condition  $y(0)$ , where  $y$  is the  $n$ -dimensional state vector

$$y = [y_1^T | y_2^T]^T \\ \equiv [y_1, y_2, \dots, y_m | y_{m+1}, y_{m+2}, \dots, y_n]^T,$$

$p$  is the  $r$ -dimensional parameter vector

$$p = [p_1, p_2, \dots, p_r]^T,$$

and  $f_1$  and  $f_2$  on the right-hand side of Eq. (21) are

$$f_1 = [f_1, f_2, \dots, f_m]^T \\ f_2 = [f_{m+1}, f_{m+2}, \dots, f_n]^T$$

The differential-algebraic system of Eq. (21) can also be written in the compact form

$$E\dot{y} = f \quad (22)$$

where

$$E = \begin{bmatrix} I_{m \times m} & 0_{m \times (n-m)} \\ 0_{(n-m) \times m} & 0_{(n-m) \times (n-m)} \end{bmatrix}$$

and

$$f = \begin{bmatrix} f_1 \\ f_2 \end{bmatrix}$$

It is noted that not all systems described by coupled differential and algebraic equations are solvable. Let the vector-valued function  $f$  be continuously differentiable with respect to  $y$ , and let the Jacobian matrix be partitioned as

$$\frac{\partial f}{\partial y^T} = \begin{bmatrix} J_{11[m \times m]} & J_{12[m \times (n-m)]} \\ J_{21[(n-m) \times m]} & J_{22[(n-m) \times (n-m)]} \end{bmatrix} \quad (23)$$

Then the sufficient condition for the solvability of Eq. (21) or Eq. (22) is<sup>3)</sup>

$$\det J_{22} \neq 0 \quad \forall t \quad (24)$$

It can be verified that Eqs. (17)–(20) are solvable. Hence the system with admissible initial conditions can be favorably solved by the generalized third-order semi-implicit Runge-Kutta method<sup>6)</sup>. This scheme is based on the Richardson extrapolation technique<sup>11)</sup> and has the advantages of increasing the solution accuracy by one order, retaining the stability properties of the algorithm, and providing a simple method for step-size control.

### 3. Optimal parameter estimation

To estimate the optimal parameters of the model, we assume that observation errors at different time points are uncorrelated. The following simple least-square function is chosen as the objective function:

$$\min_p J = \sum_{u=1}^{nexp} \sum_{v=1}^{v_u} \sum_{w=1}^{w_v} e_{uvw}^2(p) \quad (25)$$

where

$e$  : error between simulated result and experimental data

$nexp$  : number of runs

$v_u$  : number of observable components ( $v_u \leq n$ ) in run  $u$

$w_v$  : number of sampled data of component  $v$

It is well known that success in solving an optimal parameter estimation problem relies heavily on selecting a set of meaningful starting guesses for the parameters. The most obvious method for choosing a set of initial guesses is that by means of *a priori* knowledge. For PTC reaction systems, however, parameters are experimentally very difficult to measure and so they are not presently available<sup>16)</sup>. Hence, it is hard to find a set of feasible starting guesses for the parameters from experimental work or from *a priori* knowledge. Fortunately, this shortcoming can be overcome by a systematic search technique proposed by Sobol<sup>14)</sup>. In applying Sobol's method, we need only confine all the parameters to a hypercube which is formed with the possible parameter order from a *priori* knowledge. A boundary contraction algorithm<sup>17)</sup> can be used to adjust the parameter space, which thus avoids requiring many searching points. Because the searching points constructed by Sobol's method are distributed very uniformly in a certain region of parameter space, Sobol's method is found to be efficient and superior to the traditional random-search approach. After finding feasible starting points from Sobol's systematic searching method and boundary contraction algorithm, the DSC-Powell direct search method<sup>1)</sup> is then used for further refining the optimal parameters. The DSC-Powell method consists of two search techniques. The first, known as the DSC search, can bracket the optimal value of a parameter. The second is the Powell search method, by which the parameter can rapidly reach an optimal one after that parameter is bracketed.

### 4. Experiment

The system chosen for study is the reaction of organic-phase benzyl chloride with aqueous-phase sodium bromide in the presence of tetrabutylammonium bromide as catalyst. The experimental procedure is described as follows: First, the desired amount of reactant sodium bromide, phase-transfer catalyst tetrabutylammonium bromide and water were poured into a  $3.0 \times 10^{-4} \text{ m}^3$ , two-neck, round-bottomed flask reactor. These aqueous components were heated and mixed with a magnetic stirrer. The constant stirring speed was controlled by a Heidolph MR 2002 and the temperature was controlled by a Kontakt thermostat. The organic phase was composed on the solvent toluene, reactant benzyl chloride, and

a small amount of naphthalene, which was used as an internal standard for analysis. The organic phase was preheated and kept at a present reaction temperature. The reaction starts as soon as the organic phase is added into the reactor.

Samples of  $1.0 \times 10^{-7} \text{ m}^3$  of organic phase were withdrawn from the reactor at the present sampling time and each sample was diluted by  $1.0 \times 10^{-6} \text{ m}^3$  of toluene. The contents of the organic phase were analyzed by a Shimadzu GC-7A gas chromatograph with a Shimadzu C-R2A integrator. The GC column is of  $3 \text{ m} \times 3 \text{ mm}$  ID and was packed with 5% SE-30 as liquid phase and 80–100 mesh Chromsorb W AW-DMCS as solid support. The column temperature was programmed from  $120^\circ\text{C}$ , maintained for 1 minute, to  $270^\circ\text{C}$  at a heating rate of  $32^\circ\text{C}/\text{min}$ . The analysis conditions were as follows: injection-port temperature was  $270^\circ\text{C}$ , the flow rate of carrier gas  $\text{N}_2$  was  $5.0 \times 10^{-7} \text{ m}^3/\text{s}$ , the pressure of  $\text{H}_2$  was  $5.9 \times 10^4 \text{ N/m}^2$ , and that of air was  $4.9 \times 10^4 \text{ N/m}^2$ . Under these conditions, the retention times of benzyl chloride, benzyl bromide and naphthalene were found to be 2.41, 2.76, and 3.28 minutes respectively.

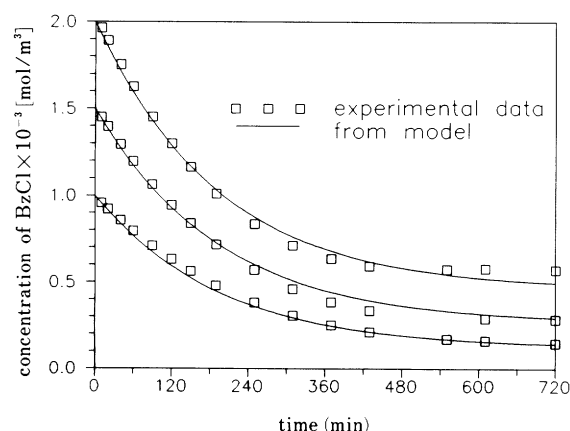
## 5. Results and Discussion

To have accurate and reliable experimental data, only benzyl chloride was actually measured. It seems that the data from a single experiment are insufficient to estimate all the parameters of our model. For the purpose of searching a set of representative and physically meaningful parameters, three runs with different initial concentrations of benzyl chloride but under the same operating conditions were carried out. To check whether tetrabutylammonium bromide and tetrabutylammonium chloride in the two phases were in extractive equilibrium or not, a sufficiently high stirring speed was set to eliminate the effect of stirring rate on the reaction.

By applying the optimal parameter estimation technique described in the previous section, the starting guesses obtained from Sobol's systematic searching method and the optimal parameters refined by the DSC-Powell searching technique were determined and are listed in **Table 1**. Referring to Table 1, the starting guesses from the Sobol searching stage is good enough for the DSC-Powell searching stage to refine the optimal parameters. After the DSC-Powell searching stage, the parameter  $p_4$  becomes extremely large. It is evident that tetrabutylammonium chloride is in an extractive equilibrium between two phases such that the corresponding mass transfer is very fast. This is reasonable since tetrabutylammonium chloride is more hydrophilic than lipophilic<sup>12)</sup> and transfers into aqueous phase rapidly until the concentrations in the two phases reach a condition established by the distribution coefficient

**Table 1.** Estimated parameters

	Sobol	DSC-Powell	reduced model
$p_1$ [ $\text{m}^3/\text{mol} \cdot \text{s}$ ]	$4.202 \times 10^{-4}$	$4.172 \times 10^{-4}$	$4.188 \times 10^{-4}$
$p_2$ [ $\text{m}^3/\text{mol} \cdot \text{s}$ ]	$2.845 \times 10^{-3}$	$2.840 \times 10^{-3}$	$2.799 \times 10^{-3}$
$p_3$ [ $\text{mol}/\text{m}^3 \text{s}$ ]	$2.503 \times 10^3$	$2.433 \times 10^3$	$2.361 \times 10^3$
$p_4$ [ $\text{mol}/\text{m}^3 \text{s}$ ]	$1.063 \times 10^5$	$3.198 \times 10^{14}$	$\infty$
$p_5$ [—]	0.699	0.700	0.696
$p_6$ [—]	0.063	0.063	0.066
$p_7$ [ $\text{mol}/\text{m}^3$ ]	$6.895 \times 10^5$	$6.878 \times 10^5$	$6.892 \times 10^5$
$p_8$ [ $\text{mol}/\text{m}^3$ ]	$8.282 \times 10^5$	$8.241 \times 10^5$	$8.373 \times 10^5$



**Fig. 1.** Fitness of the model

The experiments were carried out under the following conditions: benzyl chloride ( $\text{BzCl}$ ):  $1.0 \times 10^3$ ,  $1.5 \times 10^3$  and  $2.0 \times 10^3 \text{ mol/m}^3$ , sodium bromide ( $\text{NaBr}$ ):  $2.0 \times 10^3 \text{ mol/m}^3$ , tetrabutylammonium bromide ( $\text{TBABr}$ ):  $1.0 \times 10^2 \text{ mol/m}^3$ , volume ratio =  $1/2$  ( $V_0 = 7.5 \times 10^{-5} \text{ m}^3$ ,  $V_w = 1.5 \times 10^{-5} \text{ m}^3$ ), reaction temperature =  $70^\circ\text{C}$ , stirring rate = 700 rpm

$m_{QX} \cdot \Omega$ .

From the above result, we can set the term in brackets on the right-hand side of Eq. (19) to zero. This gives the following equation:

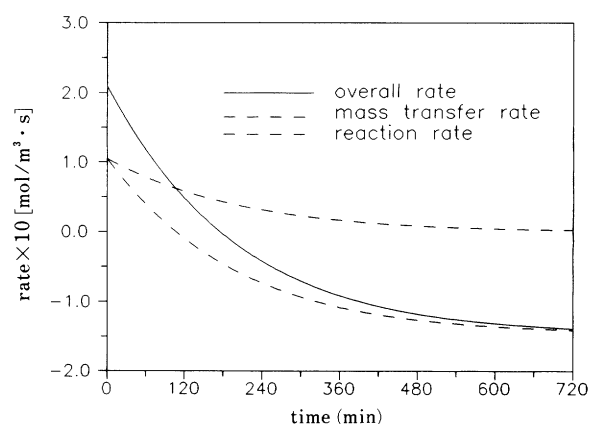
$$y_3 = \frac{p_6(N_X^0 - \alpha y_1)y_4}{\alpha p_6 y_4 + y_4 + p_8} \quad (26)$$

By substituting Eq. (26) into Eqs. (17), (18) and (20), a new model, which will be referred to as the reduced model, is obtained. Applying the DSC-Powell searching method to the reduced model with the starting points being the final results of the original model, as in the third column in Table 1, we obtained the optimal parameters for the reduced model as shown in the last column of Table 1. It is noted here that the parameter  $p_5$  still represents the distribution coefficient of tetrabutylammonium bromide at the interface, whereas the parameter  $p_6$  now denotes the distribution coefficient of tetrabutylammonium chloride between the two phases. The test of the set of optimal parameters is shown in **Fig. 1**. The estimated parameters reveal that the mass transfer of tetrabutylammonium bromide has a significant effect on

the behavior of the system, whereas the mass transfer resistance of tetrabutylammonium chloride can be neglected. To investigate the contributions of the mass transfer and the reaction to the overall formation rate of tetrabutylammonium bromide in the organic phase, the mass transfer rate, the reaction rate, and the overall rate are plotted **Fig. 2** for the second run. It can be seen from Fig. 2 that the contributions of reaction and mass transfer are both positive before 110 min. At 110 min, the overall rate is contributed merely by the reaction since the mass transfer rate is zero. Later on, the mass transfer gives a negative contribution to the overall rate. This implies that tetrabutylammonium bromide is transferring back into the aqueous phase.

## 6. Salting-out effect on distribution coefficients

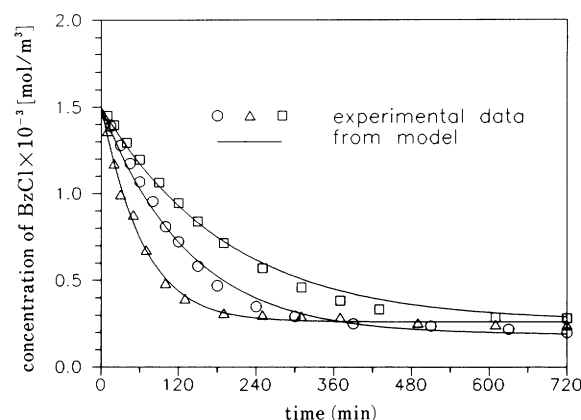
Heriott and Picker<sup>8)</sup> have found that increasing the concentration of inorganic salts in the aqueous phase tends to accelerate the overall reaction. They concluded that increasing the ionic strength in the aqueous phase salts out the organic salts, driving them into the organic phase and, therefore altering their distribution coefficients. To investigate the salting-out effect on the distribution coefficients, two additional experiments were carried out with different concentration of sodium bromide but under the same operating conditions as before. The DSC-Powell searching technique is applied to find the optimal parameters  $p_5$  and  $p_6$  for each additional run, while keeping other parameters in the values as shown in the last column of Table 1. The estimated distribution coefficients are shown in **Table 2**. The simulation results as well as the experimental data are plotted in **Fig. 3**. From Table 2, it is evident that the increase of the concentration of sodium bromide in the aqueous phase results in increases of the distribution coefficients of both tetrabutylammonium bromide at the interface and tetrabutylammonium chloride between the two phases. When the concentration of NaBr is increased to  $3.0 \times 10^3 \text{ mole/m}^3$ , the distribution coefficient of tetrabutylammonium chloride becomes about three times larger than that in the case of  $2.5 \times 10^3 \text{ mole/m}^3$ . These data show that there a great amount of tetrabutylammonium chloride accumulates in organic phase as the reaction proceeds. The accumulation of tetrabutylammonium chloride in the organic phase inhibits the forward reaction and lowers the circulation rate of the phase-transfer catalysts between the two phases. Hence, the final conversion is lower. This is so called "catalyst poisoning." From Fig. 3, it is clear that our model can well explain the salting-out effect on the distribution coefficients.



**Fig. 2.** Contributions of mass transfer and reaction to overall rate

**Table 2.** Salting-out effect on distribution coefficients

NaBr	$2.0 \times 10^3 \text{ mole/m}^3$	$2.5 \times 10^3 \text{ mole/m}^3$	$3.0 \times 10^3 \text{ mole/m}^3$
$p_5$	0.696	0.864	1.383
$p_6$	0.066	0.067	0.215



**Fig. 3.** Salting-out effect

The experiments were carried out under the following conditions: sodium bromide (NaBr):  $2.0 \times 10^3$ ,  $2.5 \times 10^3$  and  $3.0 \times 10^3 \text{ mol/m}^3$ , benzyl chloride (BzCl):  $1.5 \times 10^3 \text{ mol/m}^3$ , tetrabutylammonium bromide (TBABr):  $1.0 \times 10^2 \text{ mol/m}^3$ , volume ratio = 1/2 ( $V_o = 7.5 \times 10^{-5} \text{ m}^3$ ,  $V_w = 1.5 \times 10^{-5} \text{ m}^3$ ), reaction temperature =  $70^\circ\text{C}$ , stirring rate = 700 rpm.  $\square$ ,  $\circ$  and  $\triangle$  represent the experimental data for NaBr  $2.0 \times 10^3$ ,  $2.5 \times 10^3$  and  $3.0 \times 10^3 \text{ mole/m}^3$  respectively.

## Conclusions

A new mathematical model, formulated as a system of coupled nonlinear differential and algebraic equations, has been presented from describing the dynamics of a liquid-liquid phase-transfer catalyzed reaction system. The model not only contains all the factors that influence the behaviour of a phase-transfer catalyzed reaction system but also accounts for the common-ion and salting-out effects. Moreover, the model can cover the whole range of operating

conditions.

Through the help of a parameter estimation technique, the estimated model parameters provide more information for understanding the behaviour of the reaction system. It should be pointed out that since the chemical and physical properties of the aqueous phase and the organic phase change as the reaction proceeds, the values of parameters may not be constant for a real PTC system. Hence, the estimated parameters can be considered as characteristic properties of a PTC system in the range of reaction conditions. In general, the estimated parameters would be more representative if more components could be measured accurately and reliably. Also, if some parameters can be estimated from published correlations, the accuracy of the obtained model becomes higher.

The stimulation and experimental results reveal that the suggested model can elucidate well the phenomena involved in a liquid-liquid phase-transfer catalyzed system. Hence, it is confirmed that the proposed model can be adopted for reactor design for a liquid-liquid phase-transfer catalyzed reaction system.

#### Nomenclature

$A$	= interfacial area	[m <sup>2</sup> ]
$J_{QX}, J_{QY}$	= fluxes of $QX$ and $QY$	[mol/m <sup>2</sup> s]
$K_{QX}, K_{QY}$	= overall mass transfer coefficients of $QX$ and $QY$	[m/s]
$K_{QX}^D, K_{QY}^D$	= dissociation constants of $QX$ and $QY$	[mol/m <sup>3</sup> ]
$k_{QX,w}, k_{QX,o}$	= mass transfer coefficients of $QX$	[m/s]
$k_{QY,w}, k_{QY,o}$	= mass transfer coefficients of $QY$	[m/s]
$k_1, k_{-1}$	= forward and backward reaction rates	[m <sup>3</sup> /mol·s]
$m_{QX}, m_{QY}$	= distribution coefficients of $QX$ and $QY$	[—]
$(QX), (QY)$	= concentrations of quaternary onium salts	[mol/m <sup>3</sup> ]
$(QX)_{oi}, (QX)_{wi}$	= concentrations of $QX$ at the interface	[mol/m <sup>3</sup> ]
$(QY)_{oi}, (QY)_{wi}$	= concentrations of $QY$ at the interface	[mol/m <sup>3</sup> ]
$(Q^+)$	= concentration of quaternary cation in the aqueous phase	[mol/m <sup>3</sup> ]
$(RX), (RY)$	= concentrations of organic reagents in the organic phase	[mol/m <sup>3</sup> ]
$(X^-), (Y^-)$	= concentrations of anions in the	

	aqueous phase	[mol/m <sup>3</sup> ]
$V_o, V_w$	= volumes of organic phase and aqueous phase	[m <sup>3</sup> ]

$\alpha$  = volume ratio ( $\alpha = V_o/V_w$ )

#### <Subscripts>

$o$	= organic phase
$w$	= aqueous phase
$i$	= interface

#### <Superscripts>

$o$	= total concentration at initial
$T$	= transpose of a vector or matrix

#### Literature Cited

- 1) Brantley, R. O., R. A. Schaefer and P. B. Deshpande: *Int. Eng. Chem. Process Des. Dev.*, **21**, 297 (1982).
- 2) Campbell, S. L.: "Singular Systems of Differential Equations," London: Pitman (1980).
- 3) Caracotsios, M. and W. E. Stewart: *Computers & Chem. Eng.*, **9**, 359 (1985).
- 4) Dehmlow, E. V. and S. S. Dehmlow: "Phase Transfer Catalysis," 2nd, Verlag Chemie, (1983).
- 5) Evans, K. J. and H. J. Palmer: *AIChE. Symp. Ser.*, No. 202, 104 (1981).
- 6) Feng, A. and C. D. Holland: *Comput. Chem. Eng.*, **8**, 51 (1984).
- 7) Freedman, H. H.: *Pure & Appl. Chem.*, **58**, 857 (1986).
- 8) Herriott, A. W. and D. Picker: *J. Am. Chem. Soc.*, **97**, 2345 (1975).
- 9) Kreysa, G. and C. Woebecken: *Chem. Eng. Sci.*, **41**, 307 (1986).
- 10) Melville, J. B. and J. D. Goddard: *Chem. Eng. Sci.*, **40**, 2207 (1985).
- 11) Michelsen, M. L.: *AIChE. J.*, **22**, 594 (1976).
- 12) Reuben, B. and K. Sjöberg: *CHEMTECH*, May, 315 (1981).
- 13) Sincovec, R. F., A. M. Erisman, E. L. Yip and M. A. Epton: *IEEE Tran. Aut. Contr.*, **26**, 139 (1981).
- 14) Sobol, I. M.: *SIAM J. Numer. Anal.*, **16**, 790 (1979).
- 15) Starks, C. M.: *J. Am. Chem. Soc.*, **93**, 195 (1971).
- 16) Starks, C. M. and C. Liotta: "Phase Transfer Catalysis, Principles and Techniques," Academic Press, New York, (1978).
- 17) Wann, J. C., "Nonlinear Optimization Software Design," MS Diss., National Taiwan University, Taiwan, R. O. C. (1986).
- 18) Weber, W. and G. W. Gokel: "Phase Transfer Catalysis in Organic Synthesis," Springer Verlag, Berlin (1977).
- 19) Welty, J. R., C. E. Wicks, and R. E. Wilson: "Fundamentals of Momentum, Heat, and Mass Transfer," 2nd edition, John Wiley & Sons (1976).