

Kinetic modelling of mass transport limited phase transfer catalysed reactions[☆]

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Abstract

A simple but general mathematical model has been developed for analysing the rate data for displacement type liquid–liquid PTC reactions in laboratory reactors. The present model accounts for interphase mass transfer effects when present in a *regime-independent* manner. The model has been validated against published experimental rate data obtained by several workers in a number of reaction systems and in two different laboratory apparatus.

The model predicts the time variation of the concentration of all the concerned species in either phase, given the initial composition of the two-phase reaction mixture, the type and the design of the reactor. The model can be used to study the sensitivity of the reaction rate towards the initial charge composition (PTC, organic/aqueous phase reactants, base, salt, if any), agitation speed, and phase hold-up ratio. It can also help to decide if mass transfer effect, in a given reaction under specified experimental conditions, is relevant and if so identify the regime. Finally, the model can be used to estimate the kinetic and distribution equilibria parameters that are of practical importance. This should be a useful tool for the design/scale-up of reactors for industrial PTC-based processes with a displacement reaction as the key step. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Kinetic modelling; Phase transfer catalysed reactions; Organic synthesis; Transport limitation

1. Introduction

The use of phase transfer catalysed (PTC) reactions has made a major impact in the area of organic synthesis for facilitating reactions between reactants occurring in two different immiscible liquid phases. Large number of reactions of varied categories, such as displacement, alkylation, arylation, condensation, elimination, polymerisation, etc., have seen application of

the PTC techniques. It is estimated by Starks et al. [1] that PTCs are perhaps used in over 500 commercial processes, with sales of products manufactured by processes consisting of at least one major PTC step being at least \$ 10 billion a year, and with applications in the pharmaceuticals, agro-based chemicals and the polymer industries.

Many biphasic reactions involving displacement of a functional group from an organic reactant by a nucleophile from the aqueous phase have been carried out under phase transfer conditions. Quite often in such reactions transport of various species, especially the quaternary ammonium cation bearing ion-pair containing the key reactant anion from the aqueous phase as well as the one having the displaced or the leaving

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Nomenclature

a_{ll}	liquid–liquid interfacial area per unit volume of dispersion (m^{-1})
c^a, c^o	bulk phase concentration ($kmol/m^3$)
c^i	concentration at liquid–liquid interface ($kmol/m^3$)
D	diffusivity (m^2/s)
E_{QJ}	extraction constant for species Q^+J^- , as defined in Eq. (9) ($m^3/kmol$)
k_i, k_2	second order rate constant for displacement reaction in organic phase ($m^3/(kmol\ s)$)
K_{QJ}	dissociation constant for species Q^+J^- ($kmol/m^3$)
$K_{QJ-J_i^-}$	interaction parameter as defined in Eq. (10)
m_{QJ}	distribution coefficient for species Q^+J^- , as defined in Eq. (2)
N^{aion}	number of all anions in the aqueous phase
N^{ion}	number of anions J^- taking part in phase transfer process
N^o	number of reaction steps in the organic phase
r	net rate of a reaction step within a given PTC reaction scheme ($kmol/(m^3\ s)$)
R	specific reaction rate ($kmol/(m^2\ s)$)
S	selectivity constants as defined in Eqs. (11) and (12)
t	time (s)
x	diffusion length co-ordinate (m)

Greek letters

δ	diffusion film thickness (m)
ε_1	fractional phase hold-up
ν	stoichiometric coefficient for a given PTC reaction scheme

Subscripts

i	i th reaction step
j	j th species
j_0	species j at $t = 0$
J	anion species ($J = X^-, Y^-, Z^-$)
J_0^-	anion J^- at $t = 0$
QJ	ion-pair Q^+J^-

Q^+	quaternary cation (e.g., Bu_4N^+)
Q_0^+	quaternary cation at $t = 0$
RX	organic phase reactant

Superscripts

a	aqueous phase
o	organic phase
w	pure water

group in the reverse direction, are involved. Typically, these transport steps are followed, in either phase, by one or more irreversible or reversible reactions, some of them are equilibrium reactions (such as the ionic equilibria in the aqueous phase).

In the past, a number of the so-called ‘faster’ PTC-mediated displacement reactions (e.g., alkaline hydrolysis of formates and acetates [2,3], synthesis of esters such as triphenyl phosphate (TPP) and benzyl benzoate [4], oxidation using hypochlorite ion, e.g., that of benzyl alcohol to benzaldehyde [5]) have been carried out, in the batch mode, in stirred cells. These studies have provided evidence indicating that the concerned reactions were controlled mainly by the rate of interphase transfer of the active form of the PTC (bearing the reacting anion) from the aqueous to the organic side of the interface.

Analytical approximations were derived and used [3–5] for calculating the rate of interphase mass transport for a number of PTC reactions. While for the specific experimental data generated in stirred cells this analytical approximation seemed satisfactory, the treatment had focussed almost exclusively to prove the fast-pseudo-first order reaction regime for the studied reactions. As such, the method does not lead to a model for a batch reactor (conducting a PTC reaction such as above) that can predict the time variation of the measured concentrations of both the ionic species and the ion-pairs apart from the organic reactant or the product.

There has been other published works generating rate data in laboratory scale mechanically agitated reactors (MARs) [6,7], using synthesis of TPP, benzyl alcohol oxidation as model systems. Importance of mass transfer effects in these reactions has been clearly demonstrated. However, there has been no effort to develop a model suitable for interpreting kinetic data from these reactors.

On the other hand, in an earlier communication from this laboratory [8], a simple but generalised model framework of wider applicability for analysing the batch kinetic data for liquid–liquid PTC reactions was provided. This model also included the mass transfer resistances, though in a lumped fashion effectively ignoring the reactions close to the interface region, if any.

In this paper, it is shown that it is possible to achieve a suitable generalisation of the treatment of interphase transport (coupled as it is with the displacement reaction along with the associated ionic equilibria) as well as an explicit variation of the bulk (measurable) liquid composition in both phases. This has provided a general enough model for analysing kinetic data obtained from a batch reactor carrying out a PTC-based displacement reaction including the mass transfer effects in a rigorous way.

The model is equally applicable to both stirred cells and MARs. Furthermore, for the model to handle various (experimentally achievable) combinations of PTC, inorganic salts, base, etc., there are built-in provisions to calculate (using appropriate estimation methods on a consistent basis) the necessary transport and hydrodynamic parameters as functions of physicochemical parameters apart from the process and operating variables. This has allowed prediction of the sensitivity of the reaction rate with respect to PTC, salt, base,

and the substrate concentrations, phase hold-up and the stirring.

The applicability of the model has been tested by comparing the predicted indicators of the reactor performance against the published data for a number of experimental studies on PTC-mediated reactions such as mentioned above. The comparison shows that *the model can be used for interpreting laboratory batch kinetic data and for estimating the key model parameters*. It is hoped that the model will be found to be a useful component in an integrated and rational methodology of process development, reactor design and scale-up for PTC-based processes with a displacement reaction as the key step.

2. Mathematical model

2.1. Generalised reaction network

The displacement type PTC reactions being considered here, despite apparent variations follow the Starks mechanism, which can be generally represented as shown in Fig. 1.

With reference to the above network, Q^+Z^- is the original form of PTC added in the initial charge. By virtue of its distributability to both phases and furthermore, due to its partial dissociation in the aqueous

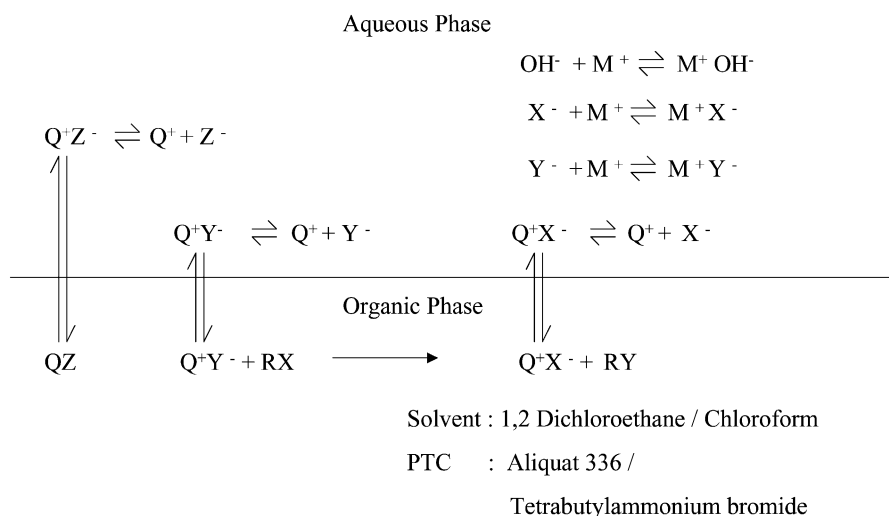


Fig. 1. Reaction network for PTC-based displacement reactions.

phase, the PTC may provide the quaternary cations to associate with the reactive anion Y^- available therein (generated in situ or supplied as a salt). This new and active form of the quaternary ion-pair (Q^+Y^-) then distributes to the organic phase and causes substitution on the organic substrate RX , while producing Q^+X^- , another ion-pair (with the leaving group). The latter partitions back to the aqueous phase and dissociates therein generating Q^+ to complete the catalytic cycle. As we shall see later in this paper, the specific reactions considered are instantiations of this general scheme.

In a well-designed catalytic system, the relative distributability of all the three quaternary ion pairs (Q^+Z^- , Q^+Y^- , Q^+X^-) are such that this cycle operates smoothly. Apart from the distribution equilibria, the interphase transport of the ion pairs between the two phases may in general, have an important bearing on the overall rate of reaction. It may be noted that in the common experimental protocols, the aqueous phase may sometimes contain alkalis and inorganic salts, the latter often being added to maintain a specified ionic strength or to alter it. All these species concentrations in the two-phase reaction mixture have shown, in some cases, remarkable influence on the observed reaction rate.

2.2. Model assumptions

The model to be presented is subject to the following assumptions:

1. The reaction steps in the above network are represented by bimolecular irreversible reactions governed by rate equations such as

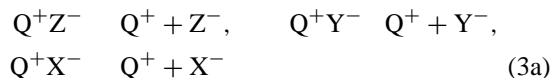
$$r_i = k_i \prod_j c_j \quad (1)$$

2. The quaternary ammonium/phosphonium cation bearing species, denoted as Q^+Z^- , Q^+Y^- and Q^+X^- are assumed to be distributed between the organic and the aqueous phases as

$$m_{QZ} = \frac{c_{QZ}^a}{c_{QZ}^o}, \quad m_{QY} = \frac{c_{QY}^a}{c_{QY}^o}, \quad m_{QX} = \frac{c_{QX}^a}{c_{QX}^o} \quad (2)$$

The distribution coefficient, m is, in general, a complex function of the ionic composition of the aqueous phase.

3. The ion pairs are assumed to be dissociated in the aqueous phase as



The ionic equilibria are characterised by the corresponding dissociation constants as follows:

$$\begin{aligned} K_{QZ} & = \frac{c_{Q^+}^a c_{Z^-}^a}{c_{Q^+Z^-}^a}, & K_{QY} & = \frac{c_{Q^+}^a c_{Y^-}^a}{c_{Q^+Y^-}^a}, \\ K_{QX} & = \frac{c_{Q^+}^a c_{X^-}^a}{c_{Q^+X^-}^a} \end{aligned} \quad (3b)$$

4. The interphase transport of the quaternary ion-pair species can be considered in terms of the film theory [9]. According to this theory, species transport from the liquid–liquid interface to the bulk liquid inside is mediated through a stagnant film of the concerned liquid, and that this passage may, in general, be accompanied by the pertinent liquid phase reaction(s). Use of this theory allows one to calculate the net rates of transport of the ion pairs across the interface into or out of the organic phase after accounting for the organic phase (substitution) reaction that may take place in both the film and the bulk region of the organic phase. For the present development, the transport resistance is considered significant only on the organic side of the interface. The ion pairs, alkali, and the salt, if any, in the aqueous phase are at equilibrium with the corresponding dissociated species.
5. The diffusivity, mass transfer coefficient and the interfacial area are calculated within the model using appropriate and consistent correlations with the pertinent physicochemical process and operating parameters.
6. A total of two liquid phases—one organic and one aqueous—are considered. The phase volumes remain unchanged during the reaction.
7. The reaction is assumed to be carried out in a standard laboratory reactor such as a stirred cell or an MAR.

2.3. Model equations

With reference to the generalised reaction network shown earlier and based on the assumptions listed

above, the following mathematical development is in order. Following the formalism used by Bhattacharya [8], mass balances pertinent to the bulk organic phase (denoted by the superscript ‘o’) and the aqueous phase (denoted by the superscript ‘a’) can be written as shown below.

1. *Bulk organic phase equations:*

For any species j (e.g., QY, RX, QX and QZ):

$$(\varepsilon_1^o - a_{11}\delta) \frac{dc_j^o}{dt} = (\varepsilon_1^o - a_{11}\delta) \sum_{i=1}^{N^o} \nu_{ij} r_i^o + a_{11} D_j^o \left(\frac{dc_j}{dx} \right)_{x=\delta} \quad (4a)$$

subject to initial conditions:

$$t = 0, \quad c_j^o = c_{j0}^o \quad (4b)$$

2. *Bulk aqueous phase equations:*

For any anion J^- (e.g., Z^- , Y^- , X^-):

$$\varepsilon_1^a \frac{dc_{J^-}^a}{dt} = a_{11} D_{Q^+J^-}^o \left(\frac{dc_{Q^+J^-}}{dx} \right)_{x=0} \quad (5a)$$

subject to initial conditions:

$$t = 0, \quad c_{J^-}^a = c_{J0}^a \quad (5b)$$

For the quaternary cation Q^+ :

$$\varepsilon_1^a \frac{dc_{Q^+}^a}{dt} = \sum_{i=1}^{N^{ion}} a_{11} D_{Q^+J^-}^o \left(\frac{dc_{Q^+J^-}}{dx} \right)_{x=0} \quad (6a)$$

subject to initial conditions:

$$t = 0, \quad c_{Q^+}^a = c_{Q0}^a \quad (6b)$$

In the above equations N^o denotes the total number of reaction(s) in the organic phase and N^{ion} the number of anions in the aqueous phase directly involved in the phase transfer process (e.g., Z^- , Y^- and X^-). ν_{ij} is the stoichiometric coefficient (negative for the consumption and positive for the production of the j th species by the i th reaction). If any species j does not take part in any reaction i , ν_{ij} is zero (as in the case of Q^+Z^-). N^o for the reaction network under discussion is 1. However, the generality of the model would allow consideration of more complex reactions.

In developing these equations, one has to consider diffusional transport of all the species involved in the interphase transfer and/or those participating in the organic phase reaction (QZ, QY, QX and RX) across an intervening film region separating the bulk organic phase from the liquid–liquid interface. This entails accounting of mass balances for the above species simultaneously diffusing and reacting in the film region.

Organic side liquid film equations:

$$D_j^o \frac{d^2 c_j}{dx^2} = \sum_{i=1}^{N^o} -\nu_{ij} r_i \quad (7a)$$

subject to the boundary conditions:

$$x = 0, \quad c_j = c_{Q^+J^-}^i \quad (\text{for } J = Z, Y \text{ and } X) \quad (7b)$$

$$\frac{dc_j}{dx} = 0 \quad (\text{for the organic substrates like RX}) \quad (7c)$$

$$x = \delta, \quad c_j = c_j^o \quad (7d)$$

Solution of these equations requires specifications of the bulk organic phase species concentrations and the interfacial concentrations of the ion pairs. The former are obtained as solutions of the bulk phase equations and the latter are determined from the equations such as

$$c_{Q^+J^-}^i = E_{QJ} c_{Q^+}^a c_{J^-}^a \quad (\text{for } J = Z, Y \text{ and } X) \quad (8)$$

where E_{QJ} are the so-called composite extraction constants defined as

$$E_{QJ} = \frac{c_{Q^+J^-}^i}{c_{Q^+}^a c_{J^-}^a} = \frac{1}{m_{QJ} K_{QJ}} \quad (9)$$

Thus for the given reaction network, a set of Eqs. (4a), (5a) and (6a) can be solved simultaneously by providing the initial values (Eqs. (4b), (5b) and (6b)) for all the species, namely,

$$c_{RX}^o, c_{QY}^o, c_{QX}^o, c_{QZ}^o, \quad c_{Y^-}^a, c_{X^-}^a, c_{Z^-}^a, c_{Q^+}^a$$

The requisite interphase transport rate terms are obtained at each step of the integration by simultaneously solving the set of Eq. (7a) with the corresponding set of boundary conditions (Eqs. (7b)–(7d)). When all the physicochemical, thermodynamic, kinetic, transport, and the hydrodynamic parameters are specified or determined through estimation, the above model can be

completely solved. In this work, the ODEs are solved using standard solvers (IVPAG with the Gear method option and BVPFD) from the IMSL library.

This means that from an initially specified composition of the two-phase mixture in a specified agitated vessel (stirred cell or an MAR), the model would enable one to predict the time variation of the concentrations of the organic and the aqueous phase species of interest (including the ions, ion pairs, substrates, etc.).

2.3.1. Model parameter estimation

As mentioned above, the solution of the above equations for the purpose of predicting the concentration profiles, a number of parameters will have to be specified. This often requires estimating them by using well-known published correlations when experimentally measured values are not available which is more often than not the case. As a part of the above developmental effort, we have tested several correlations and tried to incorporate appropriate correlations in the model and to use them consistently for all the example systems considered in this paper.

The *diffusivities* of the ion pairs Q^+J^- in the organic phase are estimated in this work by using the Wilke–Chang correlation, wherever measured values are not available. As noted rightly by Asai et al. [3,4], the estimated values are usually somewhat underpredicted by this method. The *mass transfer coefficients* in the *stirred cell* apparatus (SCR) are computed by the correlations of Asai et al. [10], whereas for the MAR, Calderbank's correlation [11] is used. The *interfacial area* is generally considered known for a well-designed SCR, while for an MAR, we have chosen, from among a number of correlations available

in the literature, one suitable for the small sized laboratory reactors, namely, the Van Heuven-Beek correlation [12] to estimate the interfacial area. Table 1 summarises the estimated values of all these parameters used in performing the computations reported in this work.

All the above correlations involve, in turn, a number of physicochemical parameters like density and viscosity of one or both the phases, more importantly, the interfacial tension. For the given organic solvent/substrate and the composition of the two-phase mixture these properties are sometimes reported in the literature as experimentally measured values. In this work, we have used reported values when available, in other instances standard estimation procedures for both pure component and the mixture properties [13,14] were used. For the interfacial tension, the estimation procedure suggested by Yarranton and Masliyah [15] was found useful.

By far the most important among the model parameters are the extraction constants. As defined (Eq. (9)), E_{QJ} , in turn, depends on both the partition coefficient m_{QJ} denoting the equilibrium distribution of Q^+J^- between the two phases and the dissociation equilibrium constant K_{QJ} . While in the PTC literature [1,16], extraction constants for a number of pairs of anion and quaternary cation are reported, these are often available for a solvent and quaternary cation combination not immediately relevant to the particular chemical system at hand. Also these values refer to equilibrium distribution of a quaternary ion-pair between a pure solvent and water. In typical PTC reaction investigations, the aqueous phase contains several ionic species. The concentrations of the latter are widely variable due to different concentrations of the base (say, NaOH),

Table 1
Parameter values used in the simulations^a

Process (apparatus)	Solvent/PTC	$D_{Q^+Z^-}$ ($\times 10^9$ m ² /s)	$D_{Q^+X^-}$ ($\times 10^9$ m ² /s)	$D_{Q^+Y^-}$ ($\times 10^9$ m ² /s)	k_1 ($\times 10^4$ m/s)	a ($\times 10^{-2}$ m ⁻¹)
TPP synthesis (SCR)	1,2-DCE/TBAB	1.8203	1.8783	1.336	1.697	0.125
TPP synthesis (MAR)	Chloroform/aliquot 336	–	3.847	2.736	2.262	80–320
BA oxidation (SCR)	Toluene/CTMAB	2.847	2.855	2.823	0.443	0.125
BA oxidation (MAR)	DCM/TBAC	–	2.842	2.804	7.0	169.3
BB synthesis (SCR)	1,2-DCE/TBAB	1.8203	1.8783	1.239	0.118	0.125
<i>n</i> -BA hydrolysis (SCR)	<i>n</i> -BA/aliquot 336	3.74	3.61	3.784	0.169	0.125

^a 1,2-DCE: 1,2-dichloroethane; DCM: dichloromethane; *n*-BA: *n*-butyl acetate; TBAB: tetrabutyl ammonium bromide; TBAC: tetrabutyl ammonium chloride; CTMAB: cetyltrimethyl ammonium bromide.

Table 2
Estimated values of extraction constants and rate constants

Process (apparatus)	Solvent/PTC	E_{Q+X^-} (m ³ /kmol)	E_{Q+Y^-} (m ³ /kmol)	k_2 (303 K) (m ³ /kmol/s)
TPP synthesis (SCR)	1,2-DCE/TBAB	3.551 ($I = 1$)	4.385 ($I = 1$)	2.33×10^6
TPP synthesis (MAR)	Chloroform/aliquot 336	2.0 ($I = 0.5$)	1.7 ($I = 0.5$)	2×10^5
BA oxidation (SCR)	Toluene/CTMAB	0.44	1.75	22.7
BB synthesis (SCR)	1,2-DCE/TBAB	3.55	8.45	2.56

the anionic reactant (Y^-) used in practice. Inorganic salts are sometimes used to alter the ionic strength of the aqueous phase keeping identical base and/or reactant concentrations. Under such conditions, the extraction constants are known to vary depending on the ionic composition. For a limited number of systems that they investigated, Asai et al. [17,18] used experimentally determined (in separate static experiments) values of m_{QJ} and K_{QJ} and correlated these with the ion concentrations.

Considering the degree of uncertainty in estimating all these parameters related to equilibria from a separate experiment it was felt that often a better alternative (in the absence of data) would be a direct estimation of the extraction constants, as relevant to the batch PTC experiments, using the initial rate data, when available, from these runs themselves and the integral conversion–time behaviour predicted by the model. Table 2 presents values of E_{QX} and E_{QY} estimated for a number of systems dealt with in this work. As we shall see from the results later, these estimates are generally consistent with other *independent* and reported estimates. Wherever ionic composition is known to affect the extraction constants, the following correlation [17] was used to represent this feature:

$$E_{QJ} = E_{QJ}^w \exp \left(\sum_{i=1}^{N_{\text{aion}}} K_{QJ-J_i^-} c_{J_i^-}^a \right) \quad (10)$$

in which the superscript w refers to the extraction constant value in pure water. The summation in the above equation extends over all the anions, including the, often present, OH^- ion that may or may not directly participate in the phase transfer process. The model thus allows, if required, the possible variation of the distribution coefficients with the changes in the ionic concentration ($c_{J_i^-}^a$), if any, over the batch time period. However, for the initial rate measurements made by various workers in the past with which the results in

this work were compared, E_{QJ} 's are determined based on the initial charge composition and held constant over the batch time.

The model application to various cases simultaneously generated very good estimates of the second order substrate consuming reaction in the organic phase (see Table 2) that came close to the values published in the literature.

3. Results and discussion

The above model was applied systematically to four different PTC-based displacement reactions carried out in the past by different research groups in two common forms of laboratory reactors (namely, SCR and MAR). The model predictions of the experimentally observed initial rates and the conversion–time data (where available) under a variety of experimental conditions have been successfully made. In what follows, selected results of the applications are presented and discussed.

3.1. Synthesis of triphenyl phosphate

The reaction which has been projected as a typical example of an alternative, cheap, environmentally benign PTC-based route for making aryl esters having diverse uses [4,6], can be represented as shown in Fig. 2.

The PTC denoted as Q^+Br^- (tetrabutyl ammonium bromide or TBAB) at first distributes itself into both the phases. In the aqueous phase, Q^+Br^- partially dissociates. The free phenoxide ion ($\text{C}_6\text{H}_5\text{O}^-$), sourced from the initially charged sodium phenoxide in the aqueous phase, then associates with the quaternary cation (Bu_4N^+ or Q^+) as a new ion-pair $\text{Q}^+\text{C}_6\text{H}_5\text{O}^-$ that has a reasonably high lipophilicity. When transferred to the organic phase the latter

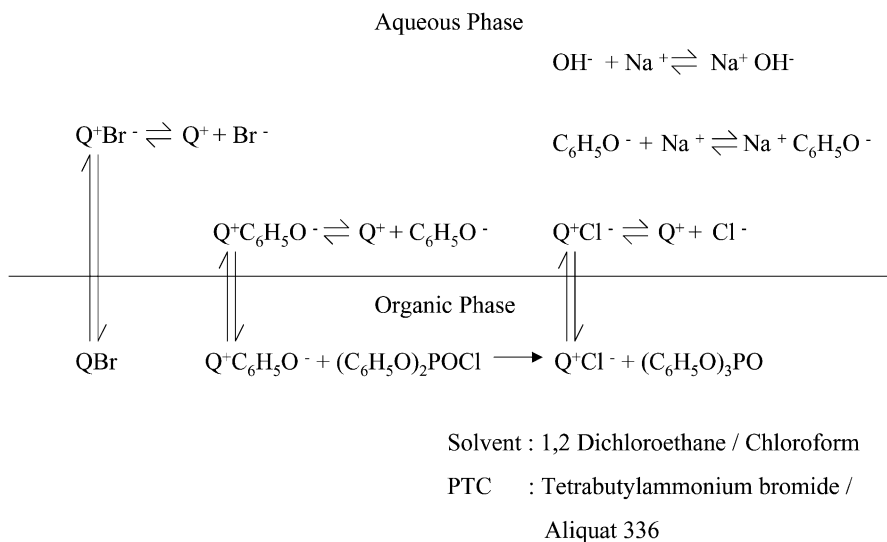


Fig. 2. Reaction mechanism for the synthesis of TPP.

ion-pair causes substitution on the organic substrate, namely, diphenylphosphoryl chloride (DPPC) to produce TPP. On the other hand, Q^+ associates with the leaving group to form another ion-pair Q^+Cl^- that distributes more favourably to the aqueous phase, where it again dissociates to make Q^+ available for the catalytic cycle to complete.

While in terms of Starks' original mechanism, the operation of the cycle can be represented as an extraction equilibrium, it has been shown by Bhattacharya [8] that it is more appropriate to interpret the observed results, in general, in terms of a dynamic balancing of several kinetic and transport steps occurring in both the phases. It is quite another matter that under practical process and operating conditions, in some cases, one or the other among these rate processes turns out to be predominant.

3.1.1. Stirred cell reactor data

For instance, Asai et al. [4] generated initial rate data for this system in an SCR. They had also interpreted their data in terms of an a priori assumed fast-pseudo-first order film reaction regime (so-called 'regime 3' in the parlance common in the literature on mass transfer with chemical reaction). In effect, this means that the overall rate of the displacement reaction is governed by the rate of transport of $\text{Q}^+\text{C}_6\text{H}_5\text{O}^-$ across the organic side film, which was perhaps very

well the case under which their data were generated. The *model presented here does not make any such assumption about the regime*. However, when it was applied to this case under varied experimental conditions used, based on the model calculations a characteristic regime 3 (linear) plot such as shown in Fig. 3 was *independently* obtained in this work.

This plot combines a range of variations in the concentrations of DPPC, $\text{C}_6\text{H}_5\text{O}^-$, Q^+Br^- and also OH^- at various ionic strengths. The model predictions seem to fit the data very well. The value of the slope of this straight line, $2.3 \times 10^6 \text{ m}^3/(\text{kmol s})$, is very close to the estimate of the rate constant (k_2) for the second order substitution reaction in the organic phase as reported by Asai et al. [4].

More significantly, it was observed that the ratios of the estimated extraction constants are relatively invariant for constant ionic strengths. These ratios termed as the selectivity constants and defined as

$$S_{\text{C}_6\text{H}_5\text{O}^-/\text{Cl}^-} = \frac{c_{\text{Q}^+\text{C}_6\text{H}_5\text{O}^-}^{\text{o}} c_{\text{Cl}^-}^{\text{a}}}{c_{\text{Q}^+\text{Cl}^-}^{\text{o}} c_{\text{C}_6\text{H}_5\text{O}^-}^{\text{a}}} \quad (11)$$

$$S_{\text{Br}^-/\text{Cl}^-} = \frac{c_{\text{Q}^+\text{Br}^-}^{\text{o}} c_{\text{Cl}^-}^{\text{a}}}{c_{\text{Q}^+\text{Cl}^-}^{\text{o}} c_{\text{Br}^-}^{\text{a}}} \quad (12)$$

in the PTC literature have been reported for many ions with Cl^- as the reference ion. We made some

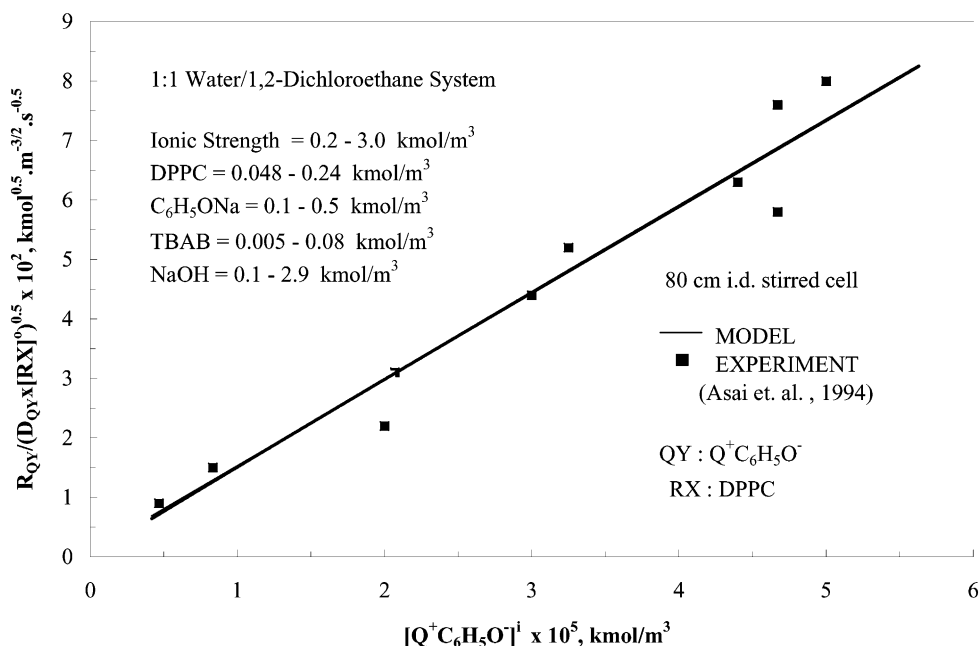


Fig. 3. Regime 3 plot for the synthesis of TPP.

comparison of these quantities as estimated in our work with those reported in the literature. Asai et al. [17] has tabulated values for $m_{Q^+C_6H_5O^-}$, $m_{Q^+Cl^-}$, $m_{Q^+Br^-}$ (with 1,2-dichloroethane as the solvent and Bu_4N^+ as Q^+) as a function of the ionic strength of the aqueous phase. Using these values and the corresponding dissociation constants, $K_{Q^+J^-}$, the selectivity constants can be evaluated at a given ionic strength pertinent to the experimental conditions in [4]. For the cases with the ionic strength of 1 kmol/m³ extraction constants for $Q^+C_6H_5O^-$ and Q^+Cl^- estimated in this work are 4.385 and 3.551, respectively. This leads to a value of 1.2348 for $S_{C_6H_5O^-/Cl^-}$ which is very close to the one calculated from the values of $m_{Q^+C_6H_5O^-}$ and $K_{Q^+C_6H_5O^-}$ reported in [17] at the same ionic strength. The value of the selectivity constant for the same $C_6H_5O^-$ ion with (the chloride reference ion) has also been reported elsewhere as 1.19 [1] for Bu_4N^+ as the quaternary cation and in chloroform solvent. With the ionic strength falling to 0.5 and 0.2, the above selectivity constant fell to 0.853 and 0.635, respectively, as the distribution coefficient (m) increased [17].

As for the other ion-pair, Q^+Br^- , which is known to be distinctly more lipophilic, from the data reported by Asai et al. [17], S_{Br^-/Cl^-} in pure water/1,2

dichloroethane turns out to be 10.25. From the estimates in the present work, the same constant is found to have a value of 6.3.

The same reaction system (TPP synthesis) was studied earlier by Krishnakumar and Sharma [6] in an SCR, but with chloroform as the organic solvent and aliquot 336 as the PTC. The predicted values of the specific reaction rate $R_{Q^+C_6H_5O^-}$ (R_{QY}) have been compared with the experimental data in Fig. 4. The fit seems excellent. The estimated values of the rate constant k_2 turns out to be 2×10^5 m³/(kmol s). For the conditions of the experiment, slightly different values for E_{QJ} 's had to be used than in the previous case, though it was found that $S_{C_6H_5O^-/Cl^-}$ is still 0.85 at an ionic strength of 0.5. For the different solvent (1,2-dichloroethane/chloroform) and PTC (TBAB/aliquot 336) combinations the value of k_2 can be different due to the difference in the structure of the active catalytic species Q^+Y^- and the nature of their solvation.

The important aspect about the results in Fig. 4 is that this demonstrates the apparent linear relation between the reaction rate and the initial PTC loading, despite strong mass transfer effect. Similar observations have been routinely made with many PTC reactions following the extraction mechanism.

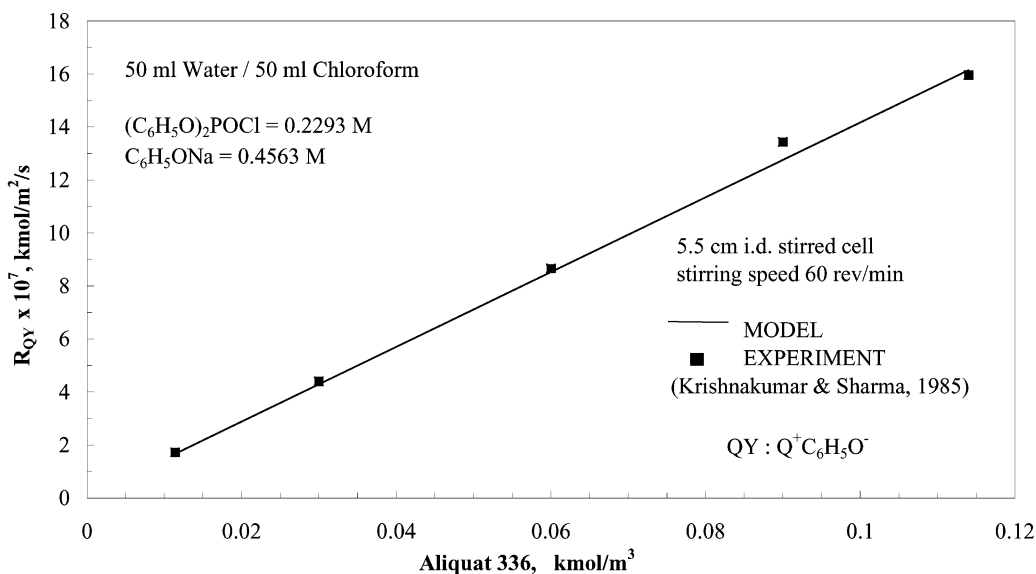


Fig. 4. Effect of initial PTC loading on the reaction rate in the synthesis of TPP.

However, it has been pointed out by us, elsewhere [19] by using the present model, that for cases *where mass transfer limitation is present*, there are pitfalls in using this linear relationship in estimating the true value of k_2 . A consistent and safe way is to use the regime 3 plot as we have shown above.

3.1.2. Mechanically agitated reactor data

In the same paper, Sharma and coworkers [6] also studied the TPP synthesis reaction in an MAR using the same solvent and the PTC combination as in their SCR experiment. The model was applied to this case using substantially the same set of parameters (k_2 and E_{QJ} 's) as used in interpreting their SCR data. The comparison of the model predictions with the experimental rate data is shown in Fig. 5. The model seems to simulate the data trends fairly well. This is a characteristic plot for MAR, where the volumetric rate of reaction is directly proportional to the agitation speed over quite a wide range, showing the clear evidence of the mass transfer effect.

3.2. Oxidation of benzyl alcohol using hypochlorite ion

This has been a model reaction used by many workers demonstrating the facilitation of the trans-

port of the hypochlorite ion to the organic phase in pursuance of the objective of oxidation of organic substrates with this and other such oxidising inorganic ions. The reaction scheme proposed in the literature [5] can be represented as in the generalised network shown earlier in Fig. 1, with Q^+Z^- as cetyltrimethyl ammonium bromide (CTMAB) or TBAB and the anions Z^- , Y^- and X^- being Br^- , OCl^- (supplied in the aqueous phase, say, as calcium hypochlorite) and Cl^- , respectively. Experimental protocols [5] do not suggest separate addition of alkalis. The same oxidation reaction had been studied in SCR [5] with toluene as the solvent and CTMAB as the PTC, as well as in an MAR [7] with dichloromethane as the solvent and TBAB as the PTC. In what follows, we present the results of the model application to both the cases.

3.2.1. Stirred cell reactor data

Fig. 6 shows the model prediction of the effect of the hypochlorite concentration on the specific rate of oxidation at two levels of initial PTC loading. The model seems to have predicted both the qualitative and the quantitative trends of the experimental data rather well. Fig. 7 presents the regime 3 plot for all the dozen odd data sets representing various experimental conditions. The linearity of the plot

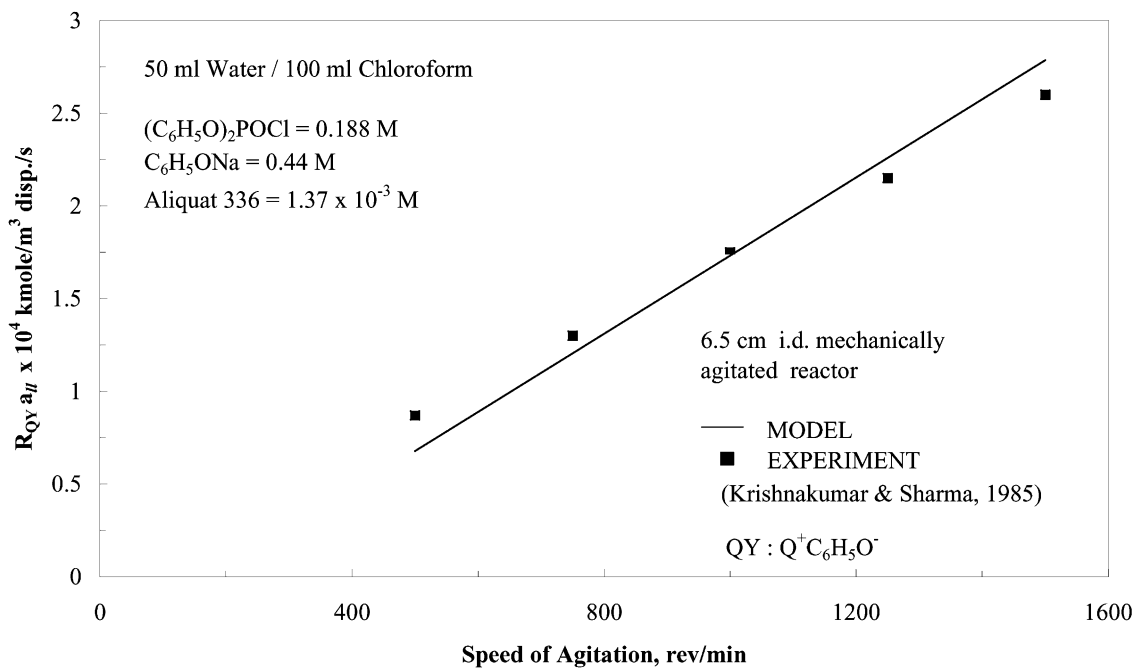
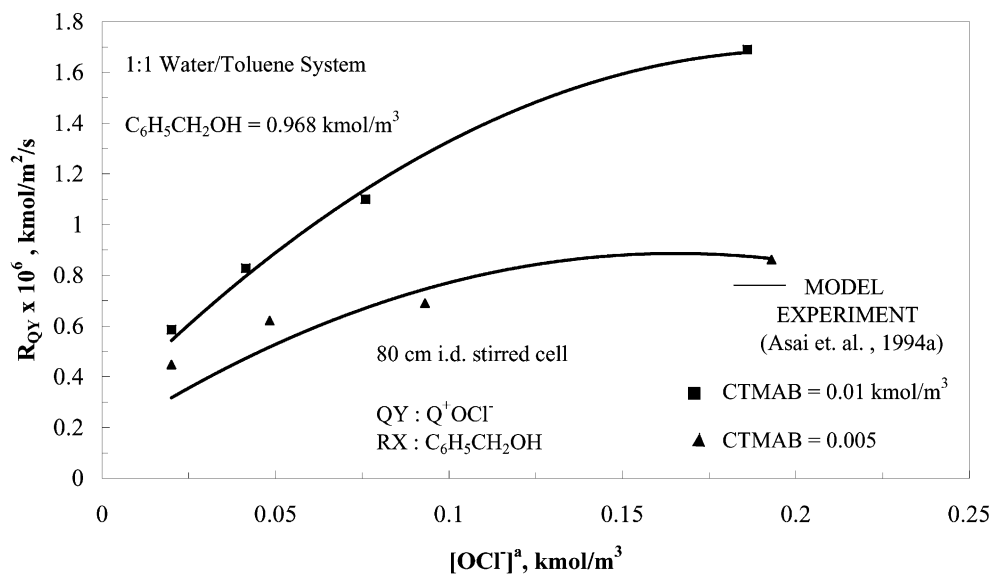


Fig. 5. Effect of agitation on the reaction rate in the synthesis of TPP.

Fig. 6. Effect of bulk concentration of OCl^- ion in aqueous phase on the benzyl alcohol oxidation rate.

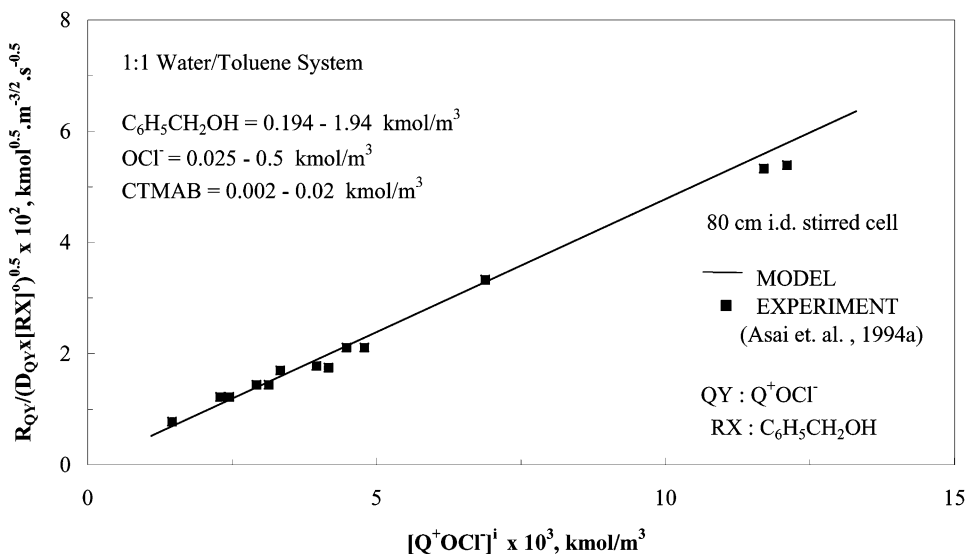


Fig. 7. Regime 3 plot for benzyl alcohol oxidation with hypochlorite.

strongly suggests the importance of the mass transfer effect on the rate. The slope of the plot provides a value of $22.7 \text{ m}^3/(\text{kmol}\cdot\text{s})$ (at 303.2 K) for the rate constant k_2 for the oxidation step in the organic phase.

3.2.2. Mechanically agitated reactor data

Do and Chou [7] had systematically carried out the same reaction in an MAR and presented, among many interesting and useful results, the conversion–time data at various PTC loadings. Fig. 8 shows a comparison

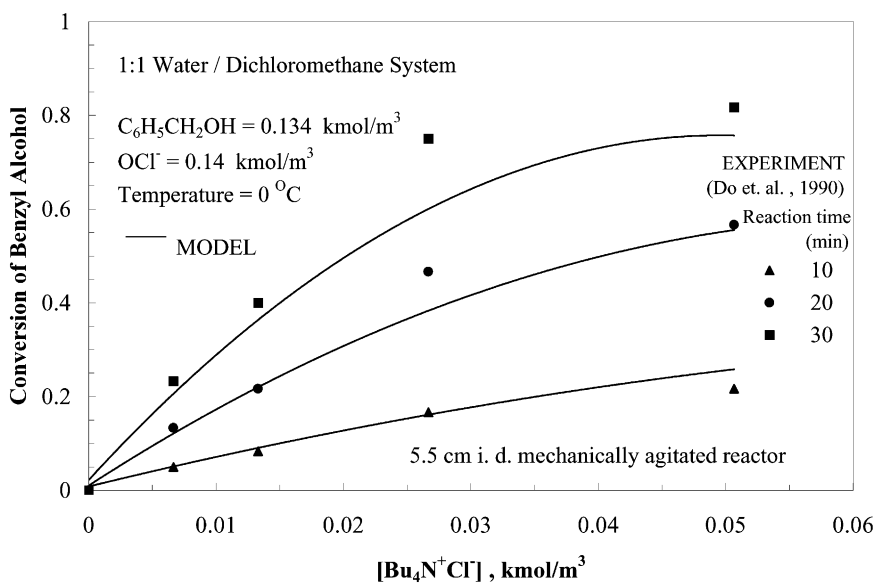


Fig. 8. Effect of PTC concentration on the conversion of benzyl alcohol in the oxidation by hypochlorite ion.

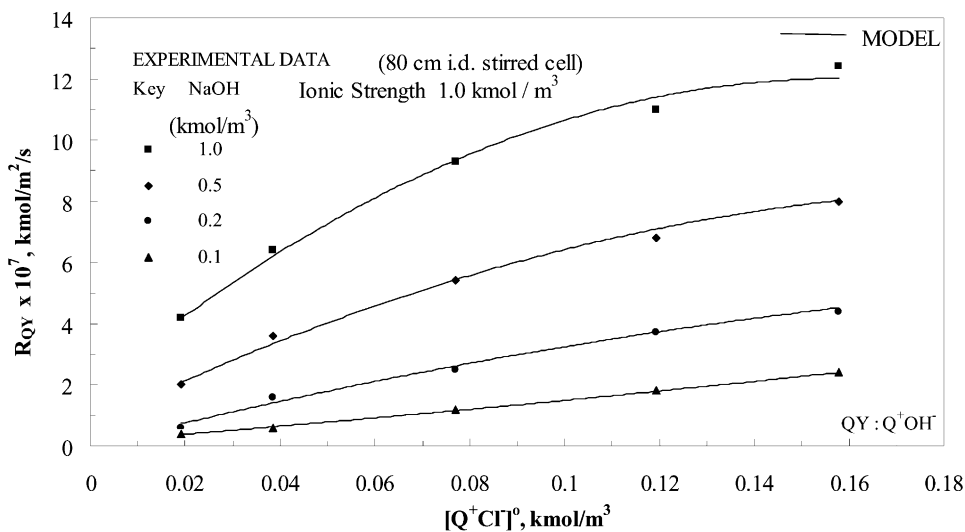


Fig. 9. Effect of bulk concentration of PTC and alkali loading on the reaction rate in the hydrolysis of *n*-butyl acetate.

between the experimental data and the model predictions of the benzyl alcohol conversion as a function of the PTC loading at various batch times. The model has not only predicted the observed initial rate data but the integral conversion–time behaviour as well for an MAR.

3.3. Additional applications

The model was also applied to two other systems such as the alkaline hydrolysis of *n*-butyl acetate using aliquot 336 as the PTC and the synthesis of benzyl benzoate by reacting benzyl chloride with sodium benzoate with TBAB as the PTC, both the reactions conducted in an SCR. In order to conserve space, the results for the second system will be skipped, as these are similar to those for the TPP synthesis. However, from a similar regime 3 plot obtained by using the model, the rate constant for the displacement reaction was estimated to be about six orders of magnitude less than that for the TPP synthesis (Table 2). For the hydrolysis *n*-butyl acetate, the model predictions of the initial rate as a function of the initial alkali and the PTC loading were compared with the published experimental data [3] in Fig. 9.

4. Conclusions

A simple but general mathematical model has been developed for analysing the rate data for PTC-based displacement reactions in MARs or stirred cells. The model has been validated by comparing the predicted indicators of the laboratory reactor performances against published experimental data in a number of reaction systems, in two different apparatus and by various workers. The values of the key parameters like the extraction constants and the displacement reaction rate constants estimated by the model match very well with those published in the literature.

The point of departure of this model is that the effects of interphase mass transfer in PTC reactions, when present, has been accounted for in a regime-independent manner, thus allowing the possibility to apply the model to wider set of reactions and/or the process/operating conditions than so far studied. The model can essentially predict the time variation of the concentrations of various species in either phase, once the starting composition of the two-phase reaction mixture and the type/design of the agitated reaction apparatus are specified.

The model can be used to predict the effect of the initial concentration of PTC, organic and aqueous phase reactants, alkali and the salt, if any, agitation

speed, phase hold-up ratio, etc. on the reaction rate. In particular, it can help to decide if for a particular reaction under a given set of experimental conditions mass transfer effect is present or predominant and if so identify the regime (rate controlling step). Last but not the least, the model can also be used to estimate the kinetic and the distribution equilibria parameters from a limited but well designed set of batch kinetic experiments.

It is hoped that the model presented here would be found to be a useful and practical tool by the practitioners of PTC-based processes using displacement reaction as a key step.

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