Triphase catalysis: mass transfer and kinetic studies

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Triphase catalysis: 
Mass transfer and kinetic studies

by

Holger Jürgen Glatzer

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

Major Professor: L. K. Doraiswamy

Iowa State University

Ames, Iowa

1999

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has met the dissertation requirements of Iowa State University

Signature was redacted for privacy.

Major Professor

Signature was redacted for privacy.

For the Major Program

Signature was redacted for privacy.

For the Graduate College
To my parents,
who always taught me to aim high.
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ABSTRACT

The importance of phase transfer catalysis (PTC) in the production of high value chemicals has grown immensely over the past few years. PTC may be a suitable method to synthesize a product whenever each reactant is miscible in a different phase, e.g. the reaction of an organic compound miscible in one phase (usually an organic phase) with an inorganic salt miscible in the other (usually an aqueous phase). By addition of a PT catalyst, which functions as a ferrying agent and brings the reactants together in one phase, significant rate enhancements can be achieved.

The PT catalyst (e.g. a quaternary ammonium salt) is usually used in soluble form. Alternatively, it can be bound to a solid support. The latter technique is called triphase catalysis (TPC). It has operational advantages over conventional PTC due to its potential use in continuous processes. However, the solid support which is usually a porous polymer induces diffusional limitations and consequently reduces overall reaction rates.

The objective of the present research is to develop a method to determine external mass transfer coefficients since many TPC systems may be film diffusion limited under typical reaction conditions. A rotating disk contactor (RDC) has been specifically designed for this purpose. From the data obtained from this unit, it is possible to calculate mass transfer coefficients of several reaction systems and to suggest a general equation that correlates the Sherwood number to the Reynolds and Schmidt numbers.

In view of conflicting reports on the efficacy of supported PTC, a comparative assessment of heterogeneous and homogeneous catalysts has been made for different
mechanistic categories of PTC systems. It is possible to identify conditions under which the supported catalyst performs distinctly better than its soluble counterpart. The solubility of the homogeneous catalyst in the organic phase is found to be the most important factor in determining catalytic activity. Under certain conditions, polarity changes of the organic bulk phase induces autocatalytic behavior, an observation not hitherto made. In conclusion, it can be stated that certain categories of heterogenized catalysts perform better than their soluble counterparts for some reactions, notwithstanding their natural predilection to hinder reaction by diffusional limitation. This fact, coupled with the operational advantages of triphase catalysis, opens up the distinct possibility of its acceptance by industry. It is also noteworthy that operational advantages alone can justify the use of supported catalysts in selected cases.
CHAPTER 1. INTRODUCTION

1.1 General

Phase transfer catalysis (PTC) has been in use since the early 1970s and is today an established technique in organic synthesis. It is a technique to perform reactions between at least two reagents in two or more phases (usually inorganic salts in solid or aqueous form, acids, or bases and substrates in organic solvents). Whenever two phases are completely immiscible, rigorous stirring and heating of the two-phase mixture will lead to no more than minimal conversion (due to interfacial contact) simply because the reagents do not come together. The purpose of a PT catalyst is to transfer one of the reagents across the interface or into the interfacial boundary layer in a highly active state such that reaction can occur.

The origin of PTC goes back to the early 1950s when Jarousse (1951) reported the alkylation reaction of cyclohexanol and phenylacetonitrile in a two-phase system in the presence of quaternary ammonium salts. This was a major breakthrough in the field of displacement reactions which involve water soluble nucleophilic reagents and water insoluble electrophilic reagents. Traditionally, these reactions had been carried out by adding solvents with lipophilic as well as hydrophilic properties like ethanol but excessive solvation of the nucleophile caused minimal rate accelerations. Another alternative was the use of expensive dipolar aprotic solvents like dimethyl formamide or dimethyl sulfoxide which can dissolve both the nonpolar organic and the polar inorganic species. The separation and recovery of these solvents from the product constituted a difficult engineering task. The new method involved a
"phase transfer agent" which had to be added in only catalytic quantities and was able to transfer the reactants from one phase to the other. At the end of the 1960s, Brändström named this type of reaction mechanism "preparative ion pair extraction" (see also Brändström, 1977), but "phase transfer catalysis," first coined by Starks (1971), is now the accepted term.

According to Starks et al. (1994) there were over 700 new patents in the 1980s and early 1990s which involved phase transfer catalytic reactions. By then, an estimated 500 commercial PTC processes were being operated using more than 25 million pounds per year of catalyst. The total sales of products manufactured by processes involving at least one major PTC step was estimated to exceed $10 billion/year. The most important applications are in the synthesis of polymers, pharmaceuticals, agricultural chemicals and other specialty chemicals. A list of examples of industrially important reactions involving PTC was published by Naik and Doraiswamy (1998). Very recently, Yadav et al. (1999) have published a list of PTC promoted processes from agrochemical industry. The following examples are noteworthy: parathion (E 605), thionazin, ethion, fenvalerate, cypermethrin (all insecticides), methamitron, trichlorpyr (herbicides), captan, and triforine (fungicides).

Two types of PTC reactions have been reported in the literature, namely liquid-liquid (L-L) and solid-liquid (S-L) PTC. The classic PTC reaction process can be represented schematically for both cases as a catalytic cycle outlined in Figure 1.1. This mechanism was first proposed by Starks (1971) who studied the cyanide displacement reaction on 1-chlorooctane. The overall reaction consists of a reversible ion-exchange reaction in the aqueous phase and an irreversible reaction in the organic phase. The polymer bound phase transfer catalyst reacts with the inorganic reagent in the aqueous phase. In this reaction the anion of the inorganic reagent is extracted by the catalyst. The catalyst molecule with the
extracted anion can cross the liquid-liquid interface, enter the organic phase due to its lipophilic nature, and react there with the organic reagent to form the desired organic product. The reaction in the organic phase turns the catalyst back to its original form. The phase transfer catalyst also has hydrophilic properties which enables it to reenter the aqueous phase so that the reaction cycle continues.

\[
RX + Q^+Y^- \overset{k_2}{\rightarrow} RY + Q^+X^-
\]

Organic reactant \[ \text{Organic product (desired)} \]

\[
M^+X^- + Q^+Y^- \overset{k_1}{\rightarrow} M^+Y^- + Q^+X^-
\]

Inorganic product \[ \text{Inorganic reactant} \]

\( Q^+X^- \): Phase transfer catalyst
(Quaternary ammonium & phosphonium salts, crown ethers, cryptands, PEG's)

**Figure 1.1.** Classic mechanism of PTC promoted reactions.

When the phase transfer catalyst is immobilized to a solid support, the reaction system is called "triphasic catalysis" (TPC) as first coined by Regen (1975). Polymers are the most widely used supports (most commonly, polystyrene crosslinked with divinylbenzene). Depending on the type of reagents there are three types of three-phase systems that involve at least one solid phase, namely liquid-liquid-solid (L-L-S), liquid-solid-solid (L-S-S) and gas-
liquid-solid (G-L-S). Only the first two are commonly referred to as TPC systems in the literature. G-L-S systems are very different from all the other forms of PTC and TPC and are often categorized as two-phase systems denoted as G-L PTC (see Chapter 2, Section 2.1.4). In the literature the use of the term 'triphase' is different from 'three-phase' since it is restricted to systems with a supported PT catalyst. In some cases, a PT catalyst can form a third liquid phase resulting in a L-L-L PTC system. However, this type of insoluble PTC is commonly not referred to as triphase catalysis.

TPC has operational advantages over conventional PTC because of its potential for use in continuous reactors. Also, the TP catalyst can be separated from the product by a simple filtration step, subsequently regenerated and reused. However, high costs associated with catalyst synthesis with specific amounts of functional groups and the well-known lowering of reaction rates due to diffusional retardation have nearly all but prevented industrial acceptance.

1.2 Objectives

The project focuses on two main aspects: studies of mass transfer effects, and intrinsic kinetics of triphase catalytic systems. Figure 1.2 shows a stepwise magnification of a homogeneous and heterogeneous PTC system. The two intermediate levels for the triphase catalytic system, namely film diffusion and intraparticle diffusion, are responsible for the rate retardation associated with these systems. The mass transfer studies focus on the film diffusion level, while the kinetical studies focus on the active sites of the catalyst and their immediate surroundings. In view of the above, the present research was undertaken with the following objectives:
In the above case, since the catalyst is immobilized, it cannot move from one phase to the other, as in the homogeneous case. What perhaps happens is, at its fixed location, it is subject to alternating contacts with the organic and aqueous phases. The chemistry of the reaction is therefore preserved.

Figure 1.2. Diffusion-reaction scenario in heterogeneous and homogeneous PTC.
1. To design a contactor with constant and known interfacial area for three-phase systems (liquid-liquid-solid).

2. To develop a procedure to determine mass transfer coefficients for such systems.

3. To derive a general correlation for the estimation of mass transfer coefficients in L-L-S TPC systems.

4. To study the relative performances of polymer supported TP catalysts and their homogeneous analogs.

5. To determine conditions, if any, under which a triphase catalyst performs better than an analogous homogeneous species.

1.3 Dissertation Organization

Chapter 1 provides a general introduction to the subject matter, while in Chapter 2 a review of the literature on PTC and TPC is presented.

In Chapter 3 the design of a new rotating disk contactor (RDC) is presented. Data obtained with this equipment on the esterification of benzyl chloride to form benzyl acetate are presented as well as calculated mass transfer results. This chapter is the manuscript of a paper published in Chemical Engineering Science.

In Chapter 4 the general procedure for determining mass transfer coefficients in three-phase systems is outlined with special emphasis on its limitations when applied to certain systems.

In Chapter 5 a polymer supported catalyst, namely tributylmethylammonium chloride bound on polystyrene, is compared to its homogeneous analog with different reaction systems. Special emphasis is placed on the autocatalytic behavior of the homogeneous species that
occurs under certain circumstances. This chapter is the manuscript of the paper accepted for publication in *Journal of Molecular Catalysis*.

Chapter 6 continues more elaborate experimental work on RDC. A new test system, namely the esterification of octyl bromide with potassium acetate to yield octyl acetate, is chosen. At low agitation speeds, this system does not have a considerable reaction in the absence of a TP catalyst. The data is used together with the data from Chapter 3 to suggest a general equation that correlates the Sherwood number to the Reynolds and Schmidt numbers. This chapter constitutes the manuscript of the paper submitted for publication in *Chemical Engineering Science*.

Chapter 7 completes the dissertation with a statement of conclusions of the present study and recommendations for future work.

References and notation of the publications are listed at the end of each chapter. For Chapters 1, 2 and 4 these are listed at the end of the dissertation. In addition to the drawings of RDC in Chapter 3, there are more detailed ones of the machined PTFE-parts shown in Appendix A. Appendix B contains tables with the experimental data from Chapter 6.
CHAPTER 2. LITERATURE REVIEW

In the first section of this review, the literature on phase transfer catalysis is reviewed. The second section reviews triphase catalysis with special emphasis on modeling and mass transfer limitations.

2.1 Phase Transfer Catalysis

The appropriate choice of catalyst for a PTC mediated reaction is crucial from the economic standpoint. The properties and choices of available catalysts are discussed below. This is followed by a detailed discussion about reaction mechanisms of different categories of PTC. The section concludes with a discussion on diffusion and reaction in PTC.

2.1.1 PT catalyst: Properties and choices

PTC is characterized by two basic properties (Starks and Liotta, 1978): The agent needs to be cationic with a high enough organophilicity to partition between the two phases (transfer of the anion into the organic phase), and the anion must be in a highly reactive form (weak cation-anion binding equal to large interionic distance). Apart from the mechanistic enhancement due to PTC, the addition of a catalyst to a two-phase system results in various physical changes in the system: A reduced surface tension may facilitate mixing and mass transfer across the interface. In addition, a PT catalyst may increase the solubilities of the organic and inorganic reactants in the phases in which they are originally absent. PT catalysts
are surface active agents and by coordination with the reagents tend to increase the concentrations of these species at the interface in a manner similar to micellar catalysis. Factors like reactivity, selectivity, catalyst decomposition, ease of separation from the product, cost, availability, and toxicity need to be considered when choosing a PT catalyst for industrial application.

PT catalysts can be classified into two categories: Soluble PT catalysts and insoluble triphase catalysts. The latter will be described in the second section of this chapter. Typical PT catalysts are onium salts (usually N or P), macrocyclic polyethers (crown ethers), azamacrocyclic ethers (cryptates) and soluble polymers (polyethylene glycols and derivatives; polymers containing dipolar aprotic groups). A summary of PT catalysts is given by Starks et al. (1994) and Naik and Doraiswamy (1998).

Various phase transfer catalysts have been used commercially (e.g. Starks et al., 1994; Sharma, 1997). The most commonly used ones are quaternary ammonium and phosphonium salts. They combine high activity along with low costs and a wide range of applicability. Phosphonium salts are usually more reactive but also more expensive than their ammonium analogs. However, they have the disadvantage of low stability in the presence of bases. Phosphonium salts are much less stable in basic media than ammonium salts and decompose by Hofmann elimination where the hydroxide removes a β-proton to liberate a trialkylamine, an alkene, and water. Quaternary ammonium salts start to decompose at 50% NaOH and 25°C (usual half lives are in the range of 5 to 35 hours). Phosphonium salts are only stable under very mild conditions (<15% NaOH, 25°C). Onium salts can also degrade by nucleophilic substitution which is crucial for those species containing methyl groups in the presence of very strong nucleophiles (Starks et al., 1994).
Crown ethers and cryptands are very effective PT catalysts and also have a higher stability in basic media but are often not considered for industrial processes due to their high cost and toxicity. The latter is especially an issue when it comes to separation of product from catalyst.

Polyethylene glycols are also good catalysts, less expensive than onium salts, non-toxic and stable. They are mostly used in solid-liquid systems with hydroxide transfer due to their low solubility in aqueous phases which makes them poor catalysts for liquid-liquid systems.

In general, the overall reactivity in a PTC promoted displacement reaction is a function of both, the partition coefficient for extraction of the anion from the aqueous into the organic phase and the intrinsic reactivity of the transferred anion with the organic reactant. When it comes to selecting the right catalyst for a specific synthesis, the previously mentioned arguments may be helpful in selecting the appropriate catalyst category. If it is decided to use a quaternary ammonium salt, for example, the decision as to which specific molecule will be the most suitable catalyst mostly depends on the properties of the reaction system. A very small cation (e.g. tetramethylammonium chloride) will mostly partition in the aqueous phase due to its small organic structure. The overall reaction will be very slow since the catalyst concentration in the organic phase is very low. Increasing the size of the quaternary salt will result in a higher partition of $Q^+ Y^-$ in the organic phase where it drives the slow organic reaction. The partition of tetraoctylammonium chloride will mostly be in the organic phase causing maximum overall rates (especially for intrinsically slow organic phase reactions). Further increase in the chain lengths will usually not lead to a further increase in catalyst activity because those cations will not adequately interact with the aqueous phase. The partition coefficient is completely in favour of the organic phase and steric hinderance will also
prevent the cation from crossing the organic phase boundary. Thus the reaction is mass transfer limited by the rate of transfer of the reactive anion into the organic phase. It has to be noted that the polarity of the organic solvent also has an effect on the optimum catalyst choice. Polar organic solvents will already partition smaller quaternary salts efficiently in the organic phase pushing the optimum towards species with shorter chain lengths.

In reality, the choice of a phase transfer catalyst for a given reaction system is not a trivial decision. A simple empirical guideline is suggested by Starks et al. (1994). They present the concept of a 'PTC reaction rate matrix' for determining the rate-limiting step in a PTC system. The matrix consists of four quadrants represented in coordinates of the intrinsic organic reaction rate vs. the anion transfer rate two of which include slow and fast reactions without rate-determining steps. The other two quadrants represent the transfer rate limited region and the organic phase rate limited region. A more detailed guideline for choosing a quaternary ammonium salt for PTC systems has recently been published by Halpern (1997).

2.1.2 Mechanisms of liquid-liquid PTC

Extensive reviews of mechanisms of PTC have been published by Dehmlow and Dehmlow (1993), Starks et al. (1994), Starks (1997), Naik and Doraiswamy (1998) and many other authors.

2.1.2.1 Reaction under neutral or acidic conditions

Many PT catalyzed reactions like nucleophilic displacements, oxidations, and reductions are carried out under neutral or acidic conditions. Starks' extraction mechanism (see Chapter 1, Figure 1.1) for displacement reactions is the classic way to describe a PTC
promoted reaction under these conditions. It assumes that the PT catalyst is soluble in the aqueous phase in order to transfer the anion across the interface where the organic phase reaction occurs. Hence the PT catalyst partitions in both liquid phases and functions as an active carrier for the anions.

A significant solubility of the PT catalyst in the aqueous phase is not necessary to promote the reaction. In the case where the PT catalyst is very organophilic and exclusively partitions in the organic phase, the reaction mechanism is explained by the Brändström-Montanari modification of Starks' extraction mechanism (Brändström, 1977; Landini et al., 1977). Here, the ion exchange occurs at the interface or within an interfacial boundary layer. The PT catalyst is still actively involved in the anion transfer step with the restriction of not leaving the organic phase or interfacial region.

A third model involving PT catalysts with no solubility in the aqueous phase suggests that the metal salt is sparingly soluble in the organic phase and crosses the interfacial region (Starks et al., 1994). After the salt has transferred into the organic phase, an ion-exchange reaction with the PT catalyst occurs. Strictly speaking, this mechanism is not PTC since the PT catalyst is not an active carrier across the phase boundary. However, coordination of the anion with the PT catalyst may result in increased reactivity of the anion and thus of the overall rate enhancement.

2.1.2.2 Reaction under basic conditions

Numerous industrially relevant reactions are carried out in the presence of inorganic bases, namely C-, O-, and N- alkylations, isomerizations, hydrolysis reactions, additions, and α- and β-eliminations. The bases usually employed in these reactions are aqueous or solid
NaOH, aqueous or solid KOH, and solid K₂CO₃. The governing mechanism is not as clear-cut as in the case of a neutral reaction system since the hydroxide anion is among the most difficult ones to transfer into an organic phase. Its high charge-to-volume ratio and high degree of hydration make the direct OH⁻-transfer energetically almost unfeasible. In most cases, hydroxide is not transferred across the interface in the form of a $Q^{+}\text{OH}^-$ complex due to its low solubility in the organic phases. For many reactions, it can be assumed that the intermediate $Q^{+}\text{OH}^-$ promotes the reaction with the organic substrate at the interface of the liquid phases. A mechanistic picture of these reactions has recently been published by Makosza and Fedorynski (1997).

Asai et al. (1992) studied the PTC promoted alkaline hydrolysis of butyl acetate at 25°C. The reaction was carried out in an agitated vessel with flat interface to experimentally access mass transfer limitations of this fast reaction system. Aliquat 336 (methyltrioctylammonium chloride) was used as PT catalyst. For the organic phase no solvent was used. A model solution is proposed which assumes the noncatalytic reaction to take place in the aqueous phase and the catalytic reaction to take place in the organic phase. Since the overall reaction belongs to the fast reaction regime, it entirely takes place within the film. However, the film is divided into two layers by the interface and thus Starks' extraction mechanism is assumed to be valid for this reaction. Hence active transfer of $Q^{+}\text{OH}^-$ across the interface is a primary assumption of the model. Aliquat 336 is a very lipophilic PT catalyst and may have the ability to draw hydroxide ions into an organic phase. On the other hand, a less lipophilic PT catalyst is more likely to enhance the reaction rates by means of an interfacial mechanism with the species $Q^{+}\text{OH}^-$ exclusively residing in the aqueous phase or aqueous interfacial region. Thus the enhancement effect of a lipophilic catalyst for reactions involving hydroxide transfers
can be based on the fact that the locale of reaction changes from the aqueous phase to the organic phase where the driving force is much higher due to the high concentration of the ester. The reaction rates were enhanced 70-140 times by the PT catalyst. These large rate enhancements are probably due to the low temperature: The noncatalytic reaction usually has a higher activation energy and is therefore more temperature sensitive. Thus the ratio of catalytic and noncatalytic rates increases with decreasing temperature.

Makosza (1975) investigated the alkylation of phenylacetonitrile with n-butyl iodide in 50% aqueous hydroxide (see also Makosza and Bialecka, 1977). He suggested an interfacial mechanism which does not involve transfer of the anion via the PT catalyst complex, $Q^\text{+}OH^-$. Instead, formation of the carbanion and displacement of the iodide occur in the aqueous-organic interfacial region. The role of the PT catalyst is to coordinate with the carbanion and transfer it from the interfacial region into the bulk organic phase where the final step, the alkylation reaction, takes place. The fundamental difference between the extraction mechanism and the Makosza interfacial mechanism is the fact that in the latter case the cation of the PT catalyst does not assist the deprotonation of the organic acid, in this case phenylacetonitrile (see Starks et al., 1994). The extraction mechanism would involve the direct transfer of the hydroxide into the organic phase with subsequent formation of the carbanion and alkylation.

Starks et al. (1994) also describe a modified version of the interfacial mechanism where the PT catalyst is indeed involved in the formation of the carbanion. The PT catalyst partitions between the organic phase and the interfacial region. Within this region, the catalyst reacts with the hydroxide anion to form the hydroxide coordinated catalyst species which further reacts with the organic acid to form the catalyst species coordinated with the carbanion. This species is being transferred into the bulk organic phase to finally react with the alkyl halide.
Significant rate accelerations can be achieved by adding small amounts of water soluble alcohols as cocatalysts to the system. This is mainly due to the formation of the alkoxide anion, \( \text{RO}^- \), which is not as highly hydrated and thus more easily transferred into the organic phase. The alkoxide anion is a strong base and can replace the hydroxide anion in many reaction systems. A second reason for the cocatalytic enhancement effect is that the alcohol can solvate the hydroxide anion and thus increase its transfer rate. According to Dehmlow et al. (1985), 1,2 diols are most suitable cocatalysts for many alkoxide/hydroxide extraction experiments. The reaction mechanism shifts from an interfacial mechanism to an extraction mechanism with significant amounts of basic anions in the organic phase. When using quaternary ammonium salts as PT catalysts, Hofmann elimination is considerably retarded in the presence of alcohols as cocatalysts, since the cation is no longer coordinated with the hydroxide (Starks et al., 1994).

### 2.1.3 Mechanism of solid-liquid PTC

In these systems there is no aqueous phase, the inorganic salt being suspended in the organic phase. The advantage of such a system is the higher anion reactivity caused by its lower degree of hydration. However, these systems often suffer from lower reaction rates, probably due to the slow dissolution step of the sparingly soluble solid. In the literature there are only a few publications dealing with mechanistic studies in SLPTC. Melville and Goddard (1985) were among the first who investigated mass transfer in SLPTC. The authors obtained analytical solutions based on the film theory which agreed well with numerical solutions to the transport equations for the von Kármán rotating disk flow. For SLPTC, two general mechanisms can be distinguished, namely the homogeneous and heterogeneous solubilization
mechanisms (Melville and Goddard, 1988; Naik and Doraiswamy, 1997). Naik and Doraiswamy developed comprehensive models for both mechanisms that accounted for intrinsic reaction in the organic phase, ion exchange in the aqueous phase, dissolution of the solid, and mass transfer of the PT catalyst from the organic bulk through the film to the surface of the solid. Especially noteworthy is the methodology used for the homogeneous case where a series of four models is presented with increasing additions of complexity. While the simplest model (Model A) only considers the organic phase reaction with the ion-exchange reaction being at equilibrium, the most complicated model (Model D) considers all four resistances, namely organic and aqueous phase reactions, solid dissolution, and transport of $Q^+Y^-$ between the organic bulk and the film. Simulation results showed decreasing reaction rates as more and more resistances were considered in the models. Homogeneous solubilization is likely to occur when the salt possesses substantial solubility in the organic phase and the PT catalyst is sterically hindered to approach the solid surface closely. Thus location of the ion-exchange reaction and solubility of the salt in the organic phase are important mechanistic factors. The ion-exchange reaction can occur at the solid surface, within an interfacial area near the surface, or within the solid. The organic phase reaction always occurs in the bulk liquid. A more complex adsorption mechanism for these systems has been proposed by Yufit (1995). A detailed overview of SLPTC is given by Naik and Doraiswamy (1998), and specifically on mechanisms and applications by Liotta et al. (1997).

2.1.4 Mechanism of gas-liquid PTC

In GLPTC, a method developed by Tundo and several of his co-workers (1979; 1988; 1989; 1995), the organic substrate is present in gaseous form. Hence no organic solvent is
required. Strictly speaking, these systems are gas-liquid-solid systems since the gas phase is led over a bed either consisting of the inorganic solid or an inorganic support both of which are coated with the PT catalyst in its molten state. The reactions can be conducted continually and the PT catalyst can be recovered easily.

The mechanism is very different from the traditional PTC cycle and no general mechanism has been published so far. The reactant in the gas phase diffuses through the molten liquid film of the PT catalyst where reaction between the two species occurs. In addition, the inorganic solid needs to be transported into the liquid catalyst phase in order to react with the organic reactant or the PT catalyst - organic reactant complex that is formed.

2.1.5 PTC: Diffusion and reaction

In PTC systems, reactants and products have to be transported across phase boundaries. The rate of transfer of these species is usually quantified by the mass transfer coefficient. An individual mass transfer coefficient can be defined for each side of the interface and the total transport across the interface expressed by the overall mass transfer coefficient which is calculated by using the concept of resistances in series. It is usually assumed that the interface is in equilibrium and hence no mass transfer resistance exists. It is important to understand the underlying mechanism of the PTC system because reaction and diffusion occur simultaneously in multi-phase systems and each step has its own contribution to the overall reaction rate.

For the case of gas-liquid reactions, Doraiswamy and Sharma (1984) developed a detailed theory of mass transfer and simultaneous chemical reaction. Assuming the ion-
exchange reaction to be very fast compared to the organic phase reaction and thus always being in equilibrium, the theory can be adapted to PTC systems.

The key issue is the classification of reaction systems into four main regimes, based on the relative rates of mass transfer and kinetic rate. Regime 1 is for very slow reactions which are completely kinetically controlled. There is no concentration gradient across the liquid film. Regimes 2, 3 and 4 are mass transfer controlled. In Regime 2 (slow reactions), the species $Q^+Y^-$ diffuses through the film and reacts in the bulk where it is totally consumed. There is no reaction within the film and the bulk concentration of $Q^+Y^-$ is zero. A reaction taking place in Regime 1-2 will result in a finite bulk concentration for species $Q^+Y^-$. Concentration gradients across the film are linear in Regime 2. In Regime 3 (fast reactions), the reaction takes place entirely within the liquid film. If there is reaction within the film and bulk, the corresponding regime is Regime 2-3 where the bulk concentration for species $Q^+Y^-$ is also finite. Simultaneous reaction and diffusion within the film results in curvilinear gradients across the film. In the case of an instantaneous reaction (Regime 4), $Q^+Y^-$ and $RX$ cannot coexist which results in a so-called reaction plane within the liquid film. The entire reaction occurs at this plane and the species concentrations are zero. The ratios of the amount of reactant reacting in the film to that in the bulk depends on the regime and can be quantified by the Hatta-number (for details see Doraiswamy and Sharma, 1984). In a triphase catalytic system, where a liquid-solid system reacts with an insoluble solid the reaction is restricted to the surface of the catalyst. Hence no reaction can take place within the liquid film. Thus for any regime the gradient within the film will be linear and any reaction system will take place in either regime one (very slow reactions), Regime 1-2 (very slow to slow reactions) or Regime 2 (slow to very fast reactions). This regime analysis is discussed in more detail in Chapter 3.
The analysis focuses on the transport of $Q^+Y^-$ from the phase boundary to the bulk organic phase and the reaction with $RX$. In most cases, the organic phase reaction is slow and takes place entirely in the bulk (Regimes 1, 1-2, and 2). Hence the role of the PT catalyst is to enhance the reaction rate by opening the possibility for the anion to enter the organic phase. PTC can also promote fast reactions, e.g. alkaline hydrolysis reactions of formate esters (Lele et al., 1983). These reactions are mass transfer limited even in the absence of a PT catalyst. The enhancement effect of the PT catalyst can be attributed to the fact that the reaction site is shifted from the aqueous phase into the organic phase where higher intrinsic rates are achieved due to the high concentration of the organic substrate $RX$ (see Asai et al., 1992; Naik and Doraiswamy, 1998). Recently, a modeling study for PTC promoted reactions in Regime 3 has been published by Yang (1998). It was assumed in the model that the dispersed organic phase droplets behave as rigid spheres. Simulation results were consistent with the experimental data (reaction of 2,4,6-tribromophenol with allyl bromide, see also Wang and Yang, 1991).

2.2 Triphase Catalysis

Phase transfer catalysis is a very attractive way of carrying out two-phase reactions, very often the only economically feasible one. However, one major problem is introduced by adding a phase transfer catalyst to the reaction mixture: separation of catalyst from product. Especially in the manufacture of high purity chemicals, like pharmaceuticals, the separation procedure can be very difficult and costly. The problem can be overcome by immobilizing the PT catalyst on a solid support. Separation can be achieved by a simple filtration step and hence the catalyst can be recycled. These features open the possibility for another process improvement: To perform PTC enhanced reactions in continuous reactors. Triphase catalysis
has roots which go back into the early 1950s (Schmidle and Mansfield, 1952) but the term itself was introduced by Regen (1975) who studied cyanide displacement reactions with solid supported quats.

In the present work, only the most common case of triphase catalysis, namely L-L-S TPC, is being discussed in detail. Liquid-solid-solid systems are more complicated since they involve reactions between two solids. Mechanistic studies on L-S-S TPC have been published by several researchers (e.g. Yanagida et al., 1979; MacKenzie and Sherrington, 1981; Kondo et al., 1994). However, no studies dealing with the modeling of such systems have been reported in the literature so far.

Immobilized PT catalysts have two main disadvantages compared to their homogeneous analogs: They are more expensive and are less active, mostly due to diffusional retardation. Consequently, triphase catalysis does not at present enjoy industrial acceptance. In fact, there is not a single important industrial application using a supported PT catalyst. If the problem with the low activity could by resolved or strategies found which could make a triphase catalyst competitive with its homogeneous analog, significant process improvements would be possible in many organic syntheses. Recent reviews on this subject have been published by Desikan and Doraiswamy (1995), Tomoi (1997), and Naik and Doraiswamy (1998).

2.2.1 TP catalyst: Support

Polystyrene - divinylbenzene resins which are often used as ion-exchange resins are the most commonly used supports in triphase catalysis. Several other resins have been used to immobilize phase transfer catalysts like crosslinked acrylate and methacrylate esters, glycidyl ether resins, and polyvinylpyridine resins. Commercially available ion-exchange resins (Arrad
and Sasson, 1989) as well as organophilic dextran crosslinked with epichlorohydrin or perfluoroethylene have also been used as supports.

There are several properties of a supported catalyst that have an effect on rates and selectivities of the overall reaction. These are the structure of the active sites, the structure of the polymer support (chemical composition, degree of crosslinking, porosity, etc.), percent ring substitution (active site density), and presence of spacer chains. These factors have been studied extensively by a number of researchers (e.g. Tomoi and Ford, 1981; Heffernan et al., 1982; Montanari et al., 1983).

One modification of supported catalyst which is especially noteworthy is the use of so-called spacer chains which separate the active site from the backbone of the polymer and also separates the ionic reaction centers away from each other. Very often the presence of such a spacer chain enhances the reactivity of the catalyst, especially for systems with intrinsically slow organic phase reactions. Tomoi (1997) states that some onium or macrocyclic TP catalysts have an increased activity which is comparable to analogous homogeneous catalysts when modified with medium or long alkylene spacer chains. The spacer chain is assumed to facilitate the reaction by oscillating between the organic and aqueous phases. Successful syntheses of supported catalysts with spacer chains have been conducted by Brown and Jenkins (1976), Chiles et al. (1980), Akelah and Sherrington (1982), Tomoi et al. (1982, 1985, 1986), and Idoux et al. (1983).

Also, inorganic materials like alumina (Tundo et al., 1982), silica (Arrad and Sasson, 1990), silica gel (Tundo and Venturello, 1981), and zeolites (Tundo et al., 1985) are known to serve as supports for PT catalysts. Inorganic supported PT catalysts are synthesized by physical adsorption methods or use of spacer chains.
2.2.2 Mechanism of triphase catalysis

In principle, a triphase catalytic reaction can be represented by the same catalytic cycle introduced earlier for homogeneous PTC (Molinari et al., 1979; Montanari et al., 1983). The physical scenario, however, is different in the case of a supported catalyst. It needs to be noted that the catalyst particle, with its support and catalytic sites, is much larger than the liquid-phase droplets of the dispersed (usually organic) phase. Thus the phase boundary of the system can no longer be considered a plane through which the catalyst transports the anions. Instead, a volume element within the porous catalyst particle needs to be considered which includes the continuous and the dispersed phases as well as the active catalytic sites. Since the catalyst is immobilized, it cannot move from one phase to the other, as in the homogeneous case. What perhaps happens is that, at its fixed location, it is subject to alternating contacts with the organic and aqueous phases. The chemistry of the reaction is therefore preserved, but mass transfer limitations exert very strong influences on such a system.

The overall reaction rate is influenced by the three processes outlined in Figure 1.2, Chapter 1:

1. External mass transfer of the reactants at the solid-liquid interfacial boundary.
2. a. Intraparticle mass transport of the dispersed and continuous phases
   (from catalyst surface to catalytic sites).
   b. Diffusion of the reactants and products within each bulk phase.
3. Intrinsic reaction (organic phase reaction usually rate limiting).

The additional factors 1 and 2a are characteristic of triphase catalytic systems and need to be considered in any comprehensive analysis. A major difference between the diffusion scenario of a TPC system and traditional heterogeneous catalysis is that in TPC both phases, the
continuous as well as the dispersed phase, need to be transported into the catalyst pores in order to drive the overall reaction cycle while in heterogeneous catalysis there is only one fluid phase involved in intraparticle diffusion. A complete picture of this diffusion-reaction scenario was published by Desikan and Doraiswamy (1995). The basic assumption is that the continuous phase fills the pores of the catalyst and that the organic phase droplets migrate through the pores to the catalytic sites.

Additional complications are caused by interactions between the support and liquid phases. Organic solvents like toluene cause a swelling of the polystyrene support, which is likely to increase the phase volume ratio in favour of the organic phase within the catalyst particle. Systems with intrinsically slow organic reaction might be enhanced by this phase volume increase around the catalytic sites.

Originally, two structural models for L-L-S triphase catalytic reactions had been proposed, namely the homogeneous model (Molinari et al., 1979) and the heterogeneous model (Ohtani et al., 1981). In the first, the catalyst particles are swollen with the organic phase with the hydrated active sites being dispersed therein. The reaction of the organic substrate with the anion takes place in the organic phase. This model is similar to conventional PTC and can explain the reactivity of the active sites. However, intraparticle diffusion cannot be fully explained by this model. In the heterogeneous model there is a pool of water in the catalyst particles swollen with the organic phase. The active sites are the ones at the liquid-liquid interphase within the particle where the reaction occurs. Mass transfer can be explained by this model but the reactivity of the active sites cannot be fully explained. The real scenario may be described best by assuming that the active sites from each model are present in an equilibrium state (see also Tomoi, 1997).
More detailed mechanisms for L-L-S triphase catalytic systems have been proposed by several research workers (e.g. Telford et al., 1986; Tomoi and Ford, 1981; Hradil et al., 1987, 1988; Svec, 1988). A summary of these mechanisms is given by Naik and Doraiswamy (1998).

2.2.3 TPC: Diffusion - reaction models

Naik and Doraiswamy (1998) discussed the kinetics and modeling of triphase catalysis in great detail. In view of the current work, it appears worthwhile to closely look at available diffusion - reaction models in TPC at this point.

First models for triphase catalytic systems were based on standard equations for heterogeneous catalysis with porous catalysts. Marconi and Ford (1983) developed such a model and quantified mass transfer resistances by means of an effectiveness factor. In such a model, the ion-exchange reaction in the aqueous phase is assumed to be fast and any mass transfer resistances from the bulk aqueous phase to the surface of the catalyst and subsequent diffusion within the catalyst not taken into account. In other words, such a model does not consider a chemical reaction across a liquid-liquid interface but simply a reaction within a heterogeneous catalyst which is exposed to an organic medium. The equations contain expressions for mass transfer resistance from the bulk organic phase to the surface of the catalyst, intraparticle diffusion and subsequent organic reaction.

As in traditional heterogeneous catalysis, Marconi and Ford (1983) defined a catalytic effectiveness factor for spherical pellets:

$$\eta_c = \frac{3}{\phi^2} (\phi coth \phi - 1)$$

(1)
An overall effectiveness factor for intraparticle diffusion and film diffusion resistances can be derived using the concept of resistances in series:

\[
\frac{1}{\eta_o} = \frac{1}{\eta_c} + \frac{1}{\eta_e}
\]  

(2)

For a reaction which is strongly limited by mass transfer through the film (i.e. the value of the Thiele modulus is large), the external effectiveness factor can be defined as

\[
\eta_e = \frac{3B_{im}}{\phi^2}
\]  

(3)

where \(B_{im}\) denotes the Biot number for mass transfer and \(\phi\) denotes the Thiele modulus:

\[
B_{im} = \frac{k_{RX}R}{D_{RX}}
\]  

(4)

\[
\phi = R\sqrt{\frac{k_c\rho_c C_{QX,0}}{D_{RX}}}
\]  

(5)

Hence we obtain an expression for the overall effectiveness factor:

\[
\eta_o = \frac{\eta_c}{1 + \eta_c \frac{\phi^2}{3B_{im}}}
\]  

(6)

In eqn. (3) the external effectiveness factor is assumed to be completely independent of the internal one. However, a more suitable assumption is that \(\eta_e\) also depends on \(\eta_c\). In this case we can write the following expression for \(\eta_e\):

\[
\eta_e = \eta_c \frac{3B_{im}}{\phi^2}
\]  

(7)

Hence we obtain a somewhat more general expression for the overall effectiveness factor (see also Marconi and Ford, 1983):
As already mentioned above, the kinetics and transport resistances of the ion-exchange reaction in the aqueous phase are completely ignored in this approach. Wang and Yang (1991) proposed a model that was more suitable for triphase catalytic systems since it considered mass transfer in both bulk phases, pore diffusion, and the intrinsic kinetics of aqueous and organic reactions. The pseudo-steady-state assumption was applied to the mass balance equations of the catalyst phase to yield the following expression for an apparent overall effectiveness factor:

\[ \eta_o = \frac{\eta_c \phi^2}{1 + \frac{3}{Bi_m}} \]  \hspace{1cm} (8)

The best available model to understand the process of diffusion-reaction of two liquid phases within a solid phase is probably the one developed by Desikan and Doraiswamy (1995). This dynamic model is an improved version of the one developed earlier by Wang and Yang (1992) (see also Wang, 1997) since it considers the ion-exchange reaction in the aqueous phase to be reversible. This had been clearly proven by Starks (see Starks, 1971 and also Starks et al., 1994). The model is dynamic in nature since the concentration of active sites inside the catalyst particles as well as the concentrations of the reactants in the catalyst and in the bulk phases are allowed to change with time. It is assumed in this model that all reactions are elementary and the reactions in each phase are independent. Furthermore, the diffusivities
are independent of concentration and the mass transfer coefficients are independent of the presence of the other phase. This model assumes isothermal behavior. An extension to nonisothermal behavior has been published recently by Desikan and Doraiswamy (1999a) and will not be discussed in great detail here.

The model considers mass balance equations for (a) the active catalytic sites, (b) the organic substrate and (c) the inorganic species within the catalyst phase:

(a) \[ \frac{\partial C_{QX}}{\partial t} = -k_1 \left( C_y C_{QX} - \frac{1}{K_{eq}} (C_{QX,0} - C_{QX})(C_{Y,0} - C_Y) \right) + k_2 C_{RX}(C_{QX,0} - C_{QX}) \]  
(b) \[ \varepsilon_{org} \frac{\partial C_{RX}}{\partial t} = D_{RX} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_{RX}}{\partial r} \right) - \rho_c k_2 C_{RX}(C_{QX,0} - C_{QX}) \]  
(c) \[ \varepsilon_{aq} \frac{\partial C_y}{\partial t} = D_y \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_y}{\partial r} \right) - \rho_c k_1 \left( C_y C_{QX} - \frac{1}{K_{eq}} (C_{QX,0} - C_{QX})(C_{Y,0} - C_Y) \right) \]

Initial conditions: \[ C_{RX} = 0 \quad C_Y = 0 \quad C_{QX} = C_{QX,0} \] (14)

Boundary conditions: At \( r = 0 \): \[ \frac{\partial C_{RX}}{\partial r} = \frac{\partial C_y}{\partial r} = 0 \] (15)
At \( r = R \): \[ D_{RX} \frac{\partial C_{RX}}{\partial r} = k_{RX}(C_{RX,b} - C_{RX,s}) \] (16)
\[ D_y \frac{\partial C_y}{\partial r} = k_Y(C_{Y,b} - C_{Y,s}) \] (17)

Relevant mass balance equations for bulk phases are:
\[ -V_{org} \frac{dC_{RX,b}}{dt} = k_{RX} a V_{cat}(C_{RX,b} - C_{RX,s}) \] (18)
\[ -V_{aq} \frac{dC_{Y,b}}{dt} = k_Y a V_{cat}(C_{Y,b} - C_{Y,s}) \] (19)

Initial conditions: \[ C_{RX,b} = C_{RX,0} \quad C_{Y,b} = C_{Y,0} \] (20)
In view of the scope of the current work we can see from the above equations that mass transfer coefficients are needed to relate the mass transfer from the catalyst particle to the bulk phases and to establish bulk phase mass balance equations. By means of physically relevant quantities like Biot number for mass transfer ($Bi_m$) and the Thiele modulus ($\phi$) the model equations were nondimensionalized (see Desikan and Doraiswamy, 1995, for details).

In this model the concentration of the active sites of the TP catalyst is a function of the radial position and of time. Obviously, an intraparticle effectiveness factor for such a reaction system will also change with time. Desikan and Doraiswamy (1995) derived an expression for an intraparticle effectiveness factor which takes this time dependence into account:

$$\eta_c = \frac{\int k_2 C_{RX}(C_{QX,0} - C_{QX})dV}{V}$$

In nondimensionalized form, this equation becomes:

$$\eta_c = \frac{3 \int C_{RX}^\ast (1 - C_{QX}^\ast) \omega^2 d\omega}{C_{RX,s}^\ast (1 - C_{QX,s}^\ast)}$$

The overall effectiveness factor for the entire cycle can then be obtained by equations (6) or (8). In the recently published paper by Desikan and Doraiswamy (1999a) which considers also nonisothermality, the intraparticle effectiveness factor is given by:

$$\eta_{c,noniso} = \frac{3 \int \exp \left[ \frac{\alpha_s \beta_m (C_{RX,s}^\ast - C_{RX}^\ast)}{1 + \beta_m (C_{RX,s}^\ast - C_{RX}^\ast)} \right] C_{RX}^\ast (1 - C_{QX}^\ast) \omega^2 d\omega}{C_{RX,s}^\ast (1 - C_{QX,s}^\ast)}$$

where $\alpha_s$ is the dimensionless Arrhenius parameter ($E/RT_s$) and $\beta_m$ the dimensionless adiabatic temperature rise within the catalyst particle which is defined as:
For the isothermal case, an expression for the apparent rate constant of the organic phase reaction was derived that considered internal as well as external mass transfer resistances:

\[
\beta_m = \frac{D_{RX}(-\Delta H_R) \rho_c C_{QX,0} \gamma_{RX}}{k_e T_s}
\]  

(24)

Results from the simulations revealed that the reversibility of the ion-exchange reaction had a significant (mostly negative) effect on effectiveness factors and conversions. Simulation results by Wang and Yang (1992) who considered the ion-exchange reaction to be irreversible, predicted higher conversions.

2.2.4 Activity of triphase catalysts: Polymer effect

Supported PT catalysts are known to have a reduced activity compared to their homogeneous analogs due to diffusional retardation. Under certain conditions, however, it is possible to observe higher reactivity with the supported PT catalyst. Desikan and Doraiswamy (1999b) did a comparative assessment of supported PT catalysts (polystyrene and silica gel were used as supports) and their homogeneous counterparts. If any support is used on a PT catalyst one would normally assume a lower activity than in homogeneous PTC under otherwise similar conditions. This was clearly observed with the inorganic support. With the polymer supported triphase catalyst, however, the authors report a positive "polymer effect" which accounts for the increase of activity of the polymer supported catalyst species. Hence the polymer support is not inert as in the case of an inorganic material. The effect is large.
enough to overcompensate the negative "diffusion effect" which results in higher conversions than those observed in homogeneous PTC. Desikan and Doraiswamy (1999b) conclude that the support structure can be manipulated to optimize conversion for a given reaction system. The polymer effect is the result of strong interactions between the support and the liquid phases. The formation of benzyl acetate from benzyl chloride with toluene as the organic phase solvent was studied. Polymer bound tributylmethyammonium chloride was compared to its homogeneous counterpart, benzyltributylammonium chloride, which is the more appropriate analogous form than tributylmethyammonium chloride. The immobilization adds a benzene ring from the support to the functional group which should also be considered in the homogeneous species. For all the reaction conditions used, significantly higher conversions were observed with the supported catalyst, a typical enhancement being 50%. There are other authors (MacKenzie and Sherrington, 1981; Kimura and Regen, 1983, Hradil and Svec, 1984) who have reported equal or higher activities by using immobilized PT catalysts. Tomoi (1997) concludes that polymer bound onium or macrocyclic TP catalyst with a proper lipophilic-hydrophilic balance shows the highest activity when modified with medium or long alkylene spacer chains. The reactivity is comparable to analogous soluble catalysts. However, reactivity is not the only criterion to accept or reject a TP catalyst for a chemical process. Stability and reusability (without loss of reactivity) are other important issues.

A strong enhancement due to immobilization is observed usually with hydrophilic catalysts like tetramethylammonium chloride or even benzyltributylammonium chloride (see Chapter 5 for more details). These catalysts partition mostly in the aqueous phase and hence cannot drive the organic phase reaction sufficiently. A nonpolar polymer support like polystyrene changes the physical properties of the catalyst enormously resulting in a much
more lipophilic structure. Thus the affinity of the supported catalyst to the organic phase becomes much higher than it is for the homogeneous counterpart, resulting in higher conversions. The phase volume ratio (organic phase to aqueous phase) within the pores of the catalyst is increased due to the lipophilicity of the support and thus the concentration of active sites available for reaction with the organic phase substrate may be higher than the concentration of a homogeneous catalyst in the organic phase droplets of a two-phase system. Naik and Doraiswamy (1998) conclude that for a typical lipophilic support a phase inversion should occur when the liquid phases enter the inside of the catalyst particle: in this case the organic phase is the phase that fills the pores of the TP catalyst with the aqueous phase being dispersed therein. However, models which address the complicated transport scenario in TPC usually suggest that the organic phase droplets migrate through the pores of the TP catalyst within the aqueous continuum but intraparticle diffusion terms in the models treat the liquids within the pores as one pseudo-homogeneous phase (Svec, 1988; Desikan and Doraiswamy, 1995). Svec studied the system bromooctane-toluene-supported catalyst and reported that the concentration of organic reactant was 2-4 times higher than in the bulk solution depending on the type of support used. Interactions between bromooctane and the support cause this concentration increase which can be quantified by the Flory solvent-polymer interaction parameter. His model was based on emulsion polymerization with the TP catalyst being at the phase boundary where it is in alternating contact with the two liquid phases. The presence of hydrophobic spacer chains between the polymer support and the catalytic sites leads to an enhanced performance of the TP catalyst in view of the alternating exposure of the active sites to the two bulk phases.
Since the diffusional resistances of triphase catalysts cannot be overcome, one cannot expect miracles by immobilization of PT catalysts. Whenever there is a strong enhancement caused by immobilization, the homogeneous catalyst is not likely to be the optimum choice. A highly lipophilic catalyst like aliquat 336 (methyltrioctylammonium chloride), which is a suitable catalyst for many reactions, is not likely to exhibit a strong polymer effect since it is already lipophilic from the beginning. By a good understanding of the effects influencing the performance of homogeneous and heterogeneous PT catalysts, it might be possible to open up possibilities where the supported species is indeed an industrial alternative. It should be noted at this point that even with slightly lower conversions the supported species can be economically more feasible than its homogeneous counterpart since operating costs, separation efforts, and catalyst recycling are all strong arguments in favor of supported catalysts.
CHAPTER 3. **TRIPHASE CATALYSIS: A NEW ROTATING DISK CONTACTOR FOR MEASURING MASS TRANSFER COEFFICIENTS**

A paper published in *Chemical Engineering Science*¹

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**Abstract**

Triphase catalysis (TPC) is a practically attractive way of carrying out phase transfer catalyzed reactions. The analysis of triphase catalytic systems requires a knowledge of mass transfer coefficients, but no correlations for estimating these are available. Therefore, a new rotating disk contactor (RDC) for measuring the external mass transfer coefficients of TPC systems has been designed and operated. Details of the design and construction of the contactor are discussed. In order to test the apparatus, experiments were carried out on a test system: synthesis of benzyl acetate from benzyl chloride and sodium acetate with polymer supported tributylmethylammonium chloride as the immobilized phase transfer catalyst. This reaction was found to be mass transfer controlled at low agitation speeds, and it was therefore possible to determine the external mass transfer coefficient as a function of the bulk agitation speed. The values ranged from $1.4 \times 10^{-3}$ to $2.0 \times 10^{-3}$ cm/min.

3.1 Introduction

Phase transfer catalysis (PTC) has been in use for close to three decades and is today an established technique in organic synthesis. Its origin goes back to the early fifties when Jarousse (1951) reported the alkylation reaction of cyclohexanol and phenylacetonitrile in a two-phase system in the presence of quaternary ammonium salts. This was a major breakthrough in the field of nucleophilic displacement reactions where the reactants are present in two immiscible phases. Traditionally, these reactions had been carried out by using expensive dipolar aprotic solvents like dimethyl formamide or dimethyl sulfoxide which can dissolve both the nonpolar organic and the polar inorganic species. The separation and recovery of these solvents from the product constituted a difficult engineering task. The new alternative method involved an agent which had to be added in only catalytic quantities and was able to transfer the reactants from one phase to the other. Brändström named this type of reaction mechanism "preparative ion pair extraction," but "phase transfer catalysis," first coined by Starks (1971), is now the accepted term.

In general, by using phase transfer catalysts much milder reaction conditions can be employed. But adding a phase transfer catalyst to the reaction mixture introduced a major problem: separation of catalyst from product. This problem can be overcome by immobilizing the phase transfer catalyst to a solid support. Although solid supported phase transfer catalysis does have roots which go nearly as far back as the very beginning of phase transfer catalysis itself (Schmidle and Mansfield, 1952), intensive research in this field is of much more recent origin. The term "triphase catalysis" for reaction systems where the phase transfer catalyst is bound to a solid support was first introduced by Regen (1975) who studied cyanide
displacement reactions in the presence of solid supported quaternary salts. The solid support
can be a polymer, silica gel, or alumina. However, polymers are the most widely used
supports. A summary of the commonly used polymer-bound phase transfer catalysts is given
by Ford (1984). Based on the form of the inorganic reagent there are three types of triphase
catalytic systems, namely liquid-liquid-solid (L-L-S), solid-liquid-solid (S-L-S) and gas-
liquid-solid (G-L-S). The type of triphase catalysis covered in the present work involves a
liquid-liquid reacting system along with a polymer supported PTC.

Triphase catalysis does not at present enjoy industrial acceptance for a number of
reasons. It is commonly believed that the polymer bound catalyst has a reduced activity
compared to its homogeneous analog in a two-phase system due to diffusional retardation. In
addition, it is very costly to synthesize large quantities of triphase catalysts with specific
concentrations of functional groups. However, if one could overcome these problems, there
would be a great potential for triphase catalysts as already indicated above. Heterogeneous
catalysts can be used in continuous reactors and can be separated from the products by one
simple filtration step without contaminating the desired products. Thus no costly separation
techniques are required to recover the catalyst. It can be regenerated to its original activity and
reused until it loses its mechanical stability.

Extensive work has been done on the synthesis and characterization of polymer
supported triphase catalysts (e.g., Montanari and Tundo, 1981; Ford et al., 1982; Tomoi et al.,
1985). Detailed mechanistic investigations on liquid-liquid-solid TPC systems have also been
published (e.g., Regen, 1976, 1979; Tomoi and Ford, 1981; Montanari and Tundo, 1983;
Balakrishnan et al., 1990, 1993).
Triphase catalysis, by its very nature, is strongly influenced by mass transfer. There are only a few publications on triphase catalysis which deal in detail with mass transfer effects (e.g. Marconi and Ford, 1983; Wang and Yang, 1991, 1992; Dutta and Pangarkar, 1994). TPC reactions are industrially carried out under well agitated conditions (usually mechanical). The reaction mixture forms a slurry in which the organic phase is dispersed in the aqueous phase. The organic phase droplets are transported into the pores of the TP catalyst. For the reaction to occur the inorganic and organic reactants have to come in contact with the active sites of the catalyst. This implies that the two species diffuse in their respective bulk phases to the active sites of the catalyst where the reaction occurs. Then the products diffuse back to their bulk phases and the organic phase droplets are transported out of the pores of the TP catalyst. Since these phenomena have to be taken into account in any model describing TPC reactions the diffusion-reaction scenario becomes highly complicated. A comprehensive theoretical model to understand the process of diffusion-reaction in an immobilized phase transfer catalyzed system has been developed and described in detail by Desikan and Doraiswamy (1995). This dynamic model involves rate constants as well as mass transfer and diffusion coefficients and is an extension of the one developed earlier by Wang and Yang (1992) and considers the ion-exchange reaction in the aqueous phase to be reversible. Starks (1994) has clearly shown that the aqueous phase ion-exchange reaction is reversible and hence the model for a TPC system should take this into account. The parameters of the model need to be determined experimentally in order to validate it, since there are no correlations available in the literature that correspond to this complex diffusion-reaction situation.

There are many correlations available to estimate mass transfer coefficients in two-phase systems (e.g. Oldshue, 1983; Cussler, 1997). For the case of gas-liquid systems, there
are various models of contactors with known interfacial area for mass transfer. A summary is given by Doraiswamy and Sharma (1984). Construction details of stirred contactors with undisturbed gas-liquid interface are given by Levenspiel and Godfrey (1974), Danckwerts and Alper (1975), Sridharan and Sharma (1976) and Yadav and Sharma (1979). All these contactors are good for two-phase systems but cannot be used for three-phase systems such as triphase catalysis.

The concept of a rotating disk to study mass transfer in two-phase systems is also well known in the literature (Melville and Goddard, 1985, 1988; Hammerschmidt and Richarz, 1991). Mass transfer coefficients for two-phase systems with the solid reactant dissolving into the liquid can be obtained from available correlations (Levich, 1962; Comet et al., 1969). In the case of TPC, the physical scenario is different since there is a second liquid phase and the solid is an insoluble catalyst.

### 3.2 Objective of Present Study

The present work focuses on the determination of external mass transfer coefficients from the liquid bulk phases to the surface of the catalyst in triphase catalytic systems. Special emphasis is placed on the equipment which has been conceived and designed for this purpose. Details of design and construction of this new rotating disk contactor (RDC) are discussed. Although developed specifically for TPC, use of this interphase reactor is not restricted to these systems; it can be used in general for any L-L-S three-phase system up to a temperature level of approximately 150°C. For gas-liquid-solid reaction systems like hydrogenation reactions, minor modifications will be necessary to account for the flow of the gas phase.
The synthesis of benzyl acetate from benzyl chloride and sodium acetate with polymer supported tributylmethylammonium chloride as the phase transfer catalyst has been used as the model system. This esterification reaction has been studied in detail for two-phase systems like liquid-liquid PTC (Hwu et al., 1990) and solid-liquid PTC (Yadav and Sharma, 1981) as well as for triphase catalytic systems (Tomoi et al., 1983). From the data obtained from experiments on this unit, mass transfer coefficients as well as the intrinsic rate constant for the chosen reaction conditions will be determined.

3.3 Design of Rotating Disk Contactor (RDC)

3.3.1 Main features of RDC

RDC is a stirred contactor with constant interfacial area. A disk carries the supported phase transfer catalyst and is rotated about the horizontal axis which is located exactly at the level of the liquid-liquid interface. The position of the disk is perpendicular to the liquid-liquid interface since any catalyst particle should be equally exposed to both bulk phases during one revolution. This ensures that the catalyst is equiaccessible to both liquid phases. RDC has the following features:

1. Independent manipulation of the variables influencing mass transfer
2. Constant and known liquid-solid interfacial area
3. Equiaccessibility of the catalyst to both bulk phases

In liquid-liquid-solid systems there are two mass transfer coefficients, one for mass transfer from the organic phase to the surface of the catalyst, and the other from the aqueous phase to
the surface of the catalyst. This apparatus has been designed to obtain the two mass transfer coefficients independently. Samples of both phases can be taken from the reactor during a reaction run. In this work the reactor has only been used to determine the mass transfer coefficient for transport from the organic phase to the surface of the catalyst because equilibrium could be assumed in the aqueous phase (see Section 5.1.). In general, this reactor is a much more versatile apparatus than its use in this study would indicate.

3.3.2 Construction details

Figure 3.1 shows a detailed cross sectional view of the reactor, and Figure 3.2 a three-dimensional view. In addition, the entire unit is shown as photograph in Figure 3.3.

The reactor has a total volume of two liters, one liter for each liquid phase. The top and bottom ends of the reactor consist of two circular Teflon plates 8.0 inches in diameter and 1.25 inches in thickness. In the middle there is a Teflon ring with the same dimensions as the two plates. The ring has an inner opening of 4.5 inches. In between these three Teflon bodies there are two sets of glass cylinders 8.0 cm in height which form an annulus 0.5 inch in thickness. Thermostatic fluid can be pumped through the annulus providing for constant temperature within the reactor. Teflon was chosen to minimize heat losses through the bottom and top of the reactor and to achieve maximum chemical resistance. Viton-A O-rings are used to seal the reactor between Teflon plate and glass cylinder. Viton-A is a fluorocarbon material with sufficient resistance to aromatic solvents. The Teflon plate at the bottom has two ports: One for emptying the reactor and the other for taking samples from the bottom phase. The Teflon ring in the middle of the reactor is necessary to hold the rotating disk which carries the phase transfer catalyst. A glass plate can be inserted into this Teflon ring to cover the liquid-
liquid interface and prevent dispersion at moderate agitation speeds of the stirrers in the bulk phases.

The two circular stainless steel plates 11.0 inches in diameter can be tightened up with four threaded rods to seal the reactor. This can be done with standard nuts but it is advantageous to use quick release skewers since this makes it more convenient to take the reactor apart for cleaning purposes after each reaction run.

Each bulk phase can be stirred independently by a stirrer connected to an electromotor. The position of each stirrer within its bulk phase can be varied vertically. The motors are connected to two drives (ministepping system with 400 steps/rev). The disk is rotated by a similar electromotor which is connected to another drive (microstepping system: 50,800 steps/rev). The microstepping systems were chosen to account for smooth movement at very low speeds. All three drives are connected to a four-axis indexer which is attached to a personal computer. Slow rotary seals made from Teflon are used to seal the rotating axises from the motors against the Teflon bodies of the reactor.

The crucial design piece is the disk. Figure 3.4 shows three-dimensional views of this disk, and Figure 3.5 a detailed cross sectional view. Its body is made of Teflon, 3.5 inches in diameter and 0.5 inch in thickness. The Teflon body has recesses of depth 2 mm for placing the supported catalyst. Solid catalyst particles can be held on the disk by a screen consisting of a mesh sieve and a support sieve. These two sieves are mounted on a stainless steel frame which can be fixed on the Teflon body with four small screws. There are pockets on both sides of the disk, one side has one pocket with a diameter of 5.7 cm, the other side has three pockets with each having a diameter of 2.4 cm which are symmetrically located on the disk. This design is necessary since the Teflon body of the disk is connected to a motor on one side.
The total area of these pockets is 39.0 cm². The percentage of open area of the mesh sieve increases with increasing width of opening. Therefore, the particle size distribution of the catalyst material should be determined first before choosing the mesh sieve. The width of opening should be marginally smaller than the smallest particle size in order to maximize the open area and to ensure that the catalyst particles do not go through the mesh sieve.

3.4 Determination of Mass Transfer Coefficients

In this section we present the rationale behind the determination of mass transfer coefficients for three-phase systems. This involves an analysis of the various regimes of solid-liquid systems with the solid not soluble in the liquid phase. Concentration profiles for the different regimes are shown in Figure 3.6. An analogous type of regime analysis for gas-liquid systems is discussed in great detail by Doraiswamy and Sharma (1984). It must be noted that the physical scenario is much different for a gas-liquid system: The gaseous reactant diffuses into the film and simultaneously reacts within the liquid film and/or the bulk. The ratios of the amount of reactant reacting in the film to that in the bulk depends on the regime and can be quantified by the Hatta-number. In the case of a liquid-solid system with insoluble solid the reaction is restricted to the surface of the catalyst. Hence no reaction can take place within the liquid film. For any regime the gradient within the film will be linear. Thus there are only three different regimes possible:

<table>
<thead>
<tr>
<th>Regime</th>
<th>Reaction Description</th>
<th>Control Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regime 1</td>
<td>Very slow reaction</td>
<td>Kinetic control</td>
</tr>
<tr>
<td>Regime 1-2</td>
<td>Very slow to slow reaction</td>
<td>Mixed control</td>
</tr>
<tr>
<td>Regime 2</td>
<td>Slow to very fast reaction</td>
<td>Mass transfer control</td>
</tr>
</tbody>
</table>
Regime 1:

Here the reaction is completely kinetically controlled and is independent of the agitation speed. Diffusional factors are unimportant in this regime. The condition to be satisfied is given by:

\[ k_L a[A_o] \gg k'_{\text{cat}}[A_o] \quad (1) \]

Regime 2:

The condition to be satisfied for this regime is the opposite of (1), i.e.

\[ k_L a[A_o] \ll k'_{\text{cat}}[A_o] \quad (2) \]

Regime between 1 and 2:

In this regime, neither of the two control mechanisms can be neglected. The concentration of the reactant on the surface of the catalyst will be finite. The mass transfer resistance \( k_{LR} \) in the presence of a first-order reaction is the sum of the intrinsic mass transfer resistance and the resistance due to the reaction rate, i.e.

\[ \frac{1}{k_{LR} a} = \frac{1}{k_L a} + \frac{1}{k'_{\text{cat}}} \quad (3) \]

The criterion for a reaction to be in regime 1-2 can thus be stated as:

\[ k_L a[A_o] = k'_{\text{cat}}[A_o] \quad (4) \]

3.5 Experimental

3.5.1 Reaction system

The reaction of benzyl chloride and sodium acetate promoted by the phase transfer catalyst tributylmethylammonium chloride bound on polystyrene polymer was chosen as a
model system. The catalyst is commercially available from Fluka Chemical Corp. and was not further modified. 1.0 g of the catalyst are equivalent to 0.85 mmol. All the chemicals were of analytical grade. The reaction is shown schematically in Figure 3.7.

In this reaction system, the organic reagent benzyl chloride is dissolved in toluene and the inorganic reagent sodium acetate is dissolved in water. The reactant in the aqueous phase, sodium acetate, undergoes an ion-exchange reaction with the chloride form of the phase transfer catalyst to form sodium chloride and the acetate form of the catalyst. Due to the lipophilic properties of the polymer resin the catalyst can cross the liquid-liquid interface to react with the reactant in the organic phase, benzyl chloride. The desired product is benzyl acetate. Since the recovered chloride form of the PTC also has hydrophilic properties it can cross the liquid-liquid interface back into the aqueous phase and the reaction cycle continues. The ion-exchange reaction in the aqueous phase is very fast compared to the reaction in the organic phase, and the concentration of the aqueous phase reactant is much higher than that of the organic reactant. Hence, the ion-exchange reaction can be considered to be at equilibrium. In addition, the concentration of sodium acetate in the aqueous phase is very high (five times the concentration of benzyl chloride in the organic phase) so that the aqueous phase reaction is not rate limiting. Thus the focus of this study was on the determination of the organic liquid side mass transfer coefficient.

3.5.2 Analysis of samples

The concentrations of benzyl chloride and benzyl acetate were determined using a gas chromatograph. A Perkin Elmer gas chromatograph (PE 3000 Autosystem) with FID was used. Each analysis was isothermally run for 10 min. at 150 °C. A packed column from
Supelco was used for the analysis (Carbopack: 10% SP-2250) with a length of 2.0 m and a
diameter of 1/8 inch. The concentration values of benzyl acetate were used to determine the
conversion.

3.5.3 **Studies with slurry reactor**

Different series of experiments were carried out in a slurry reactor prior to the
experimental work with RDC. Results obtained from this reactor were used to generally characterize the reaction system and will also be used for a comparison of the results obtained from RDC. The main difference here is that the PTC is not immobilized on a rotating disk, but is present as free catalyst particles in solution. A 600 ml agitated vessel from PARR Instruments was used.

A series of experiments at different agitation speeds was carried out to determine the kinetic plateau. The temperature was held constant at 90°C. The initial concentration of benzyl chloride was 1 mol/l, and of sodium acetate 5 mol/l. The total volume was 485 ml with equal contributions of both phases. The equivalent of 1 mmol polymer bound tributylmethylammonium chloride (1.2g) was added. The Arrhenius parameters were estimated with a number of runs at different temperatures (60, 70, 80, 85 and 90°C). All other parameters remained unchanged. Finally the dependence of the conversion on catalyst concentration was evaluated with catalyst loadings of 0.5, 1.0, 2.0 and 3.0 mmol at 90°C.

3.5.4 **Studies with rotating disk contactor**

A series of experiments was first carried out at different disk speeds. Three different levels were chosen, 1.200, 12.000 and 36.000 rpm. The agitation speed in the bulk phases
was kept constant at 360 rpm. It is important to know whether full displacement of the films can be achieved when the rotating disk moves from one phase into the other. There would appear to be an optimum disk speed: Above the optimum the films are not fully displaced when moving from one phase into the other, and below the optimum the exposure of the catalyst in each phase is longer than the reaction demands. This question will be more fully addressed in Section Results and Discussion: RDC: Effect of disk speed.

The main goal of the experimental work with RDC was to obtain conversion vs. time data under well defined mass transfer controlled conditions in order to calculate mass transfer coefficients for the organic phase reaction. The key to this achievement is equiaccessibility of the catalyst to the bulk phases and exact knowledge of the surface area of the catalyst. This implies the fundamental assumption that the reaction only takes place on this known surface. Conversion vs. time data under these conditions provide information that enables one to obtain the rate constants per unit surface area of the catalyst. These rate constants need to be obtained as a function of agitation speed under mass transfer limited conditions. Thus the following seven levels of agitation were selected: 120, 180, 240, 300, 360, 420 and 480 rpm. Below 120 rpm stirring was not high enough to make the phases homogeneous. Beyond 480 rpm the organic phases became fully dispersed within the aqueous phase. At this level the equiaccessibility assumption would no longer be valid. With increasing agitation speed the rates will increase till a point where external mass transfer is no longer controlling, and conversion vs. agitation speed data reach a plateau. In this plateau the reaction is kinetically controlled, and experiments under these conditions will give the intrinsic rate constant. A regime analysis is then necessary to mathematically derive an expression which defines the true mass transfer coefficient.
The bulk phases can be stirred independently in the rotating disk contactor. However, it was decided to use the same stirring rates within each bulk phase at any level. The temperature was held constant at 85°C throughout the experiments. The initial concentration of benzyl chloride in the organic phase was 1.0 mol/l, the one of sodium acetate in the aqueous phase 5.0 mol/l. The pockets on the disk hold 2.0 mmol of the triphase catalyst, tributylmethylammonium chloride polymer bound, which is equivalent to 2.40 g.

3.6 Results and Discussion

3.6.1 Slurry reactor

The esterification of benzyl chloride with sodium acetate to form benzyl acetate also proceeds to a considerable extent in the absence of any phase transfer catalyst at temperatures above 50°C. This noncatalytic reaction will be denoted as base reaction throughout this paper. The base reaction can be attributed to the fact that sodium acetate has a certain solubility in toluene. This implies that the conversion due to the base reaction be proportional to the liquid-liquid interfacial area.

A plot of the data obtained from the experiments at different agitation speeds is shown in Figure 3.8. A regression analysis was done with the constraint that there is no intercept. The data points clearly suggest a linear trend. This means that the reaction is pseudo first order with respect to the benzyl chloride concentration. Furthermore, we can see from the data that the reaction occurs within the kinetical plateau at agitation speeds beyond 400 rpm. At 200 rpm the reaction seems to be mass transfer controlled. In fact, the organic phase is not fully dispersed within the aqueous phase at low agitation speeds causing a smaller liquid-liquid
interfacial area. Hence increasing the agitation speed at very low levels mainly results in an enhancement of the base reaction.

Arrhenius plots for reaction runs with and without phase transfer catalyst are shown in Figure 3.9. For the reaction runs in the presence of the catalyst:

\[
\frac{dC_{RX}}{dt} = -k_{obs}C_{RX}
\]  

(5)

For the base reaction only:

\[
\frac{dC_{RX,base}}{dt} = -k_{base}C_{RX}
\]  

(6)

<table>
<thead>
<tr>
<th>Amount of TPC [mmol]</th>
<th>Activation energy $E$ [kJ/mol]</th>
<th>Frequency factor $k_o$ [1/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>92.7</td>
<td>$2.8 \times 10^{10}$</td>
</tr>
<tr>
<td>0</td>
<td>126.5</td>
<td>$1.3 \times 10^{15}$</td>
</tr>
</tbody>
</table>

The concentration dependence of the catalyst is shown in Figure 3.10. These data clearly suggest a linear dependence.

\[
\frac{dC_{RX}}{dt} = (a + bC_{QX,a})C_{RX}
\]  

(7)

At 90.0°C:

\[
\frac{dC_{RX}}{dt} = (0.00080 + 0.00043 \cdot C_{QX,a})C_{RX}
\]  

(8)

$k_{base}$ at 90.0°C was determined to be 0.00086 min$^{-1}$ which is close to the value of 0.00080 min$^{-1}$ obtained from the concentration dependence data. Hence for the catalytic reaction alone:
\[
\frac{dC_{RX}}{dt} = (k_{\text{base}} + k_{\text{cat}} \cdot C_{QX,o}) C_{RX} = k_{\text{obs}} C_{RX}
\]  \quad (9)

\[
k_{\text{cat}} = \frac{2.8 \cdot 10^{10} \cdot e^{-11136/T} - 1.3 \cdot 10^{15} \cdot e^{-15202/T}}{C_{QX,o}}
\]  \quad (10)

Even though we do not know the Arrhenius parameters of \( k_{\text{cat}} \) explicitly, we can obtain them at different temperatures by substitution into the right hand side of equation (10).

For \( T=85.0^\circ \text{C} \):
\[
k'_{\text{cat}} = k_{\text{cat}} C_{QX,o} = 3.9 \cdot 10^{-4} \frac{1}{\text{min}}
\]  \quad (11)

All experiments with RDC were carried out at this temperature.

### 3.6.2 RDC: Effect of disk speed

The conversion vs. time data obtained at different disk speeds are shown in Table 3.1. The conversion due to the base reaction increases with increasing disk speed, due to an increase in the liquid-liquid interfacial area. The data from the experiments in the presence of the catalyst do not show this tendency. The highest conversion was obtained at the speed of 12 rpm; lower and higher disk speeds led to lower conversions. This implies that at the high disk speed of 36 rpm there is no complete displacement of the films while entering from one phase to the other. At the very low disk speed, although there is full displacement, the exposure of the PTC on the disk to each of the phases is longer than the reaction actually demands. Reducing the disk speed only affects the organic phase reaction since it is rate limiting. At a level far below the optimum disk speed, the active sites of the PTC completely
react with benzyl chloride well before the disk reenters the aqueous phase. The resulting time
lag causes the conversion to be lower than at the higher speed. The optimum will be the
maximum disk speed where there is still full displacement of the films. At this speed the
conversions will be the highest given a certain agitation speed in the bulk phases. For this
reaction system the optimum disk speed is very close to 12 rpm. Thus, all the experiments for
the determination of the mass transfer coefficients were carried out at this speed.

3.6.3 RDC: Effect of agitation speed in the bulk phases

The conversion vs. time data obtained at different agitation speeds in the bulk phases
are shown in Table 3.2. The results are somewhat surprising. Up to an agitation speed of 300
rpm increasing the agitation speed results in slight increases of the rates. At an agitation speed
of 360 rpm the organic phase gets dispersed into the aqueous phase. The result is an increase
of the rates due to an increase in the base reaction (larger liquid-liquid interfacial area). The
differences in the conversions of two corresponding runs with and without catalyst give the
purely catalytic effect. Theoretically these catalytic rates should increase till a certain point and
then level off. The increase in the rates is very small between 120 and 300 rpm, but beyond
300 rpm the rates increase enormously. This is due to the so-called dispersion effect which
will be addressed shortly. Figures 3.11 and 3.12 show plots of -ln(1-conversion) vs. time for
the runs with and without catalyst at agitation speeds not affected by dispersion. The slopes
were obtained by regression analysis with the constraint that there is no intercept. This
analysis is reasonable since a non-zero intercept does not have a physical meaning. It can be
seen from the data that the fit is not good for the points up to 660 min. The conversion values
are consistently below the regression line. It is believed that the reason for this is the limitation
of the GC to detect very low quantities of benzyl acetate accurately. The detected peaks were shifted to longer retention times for those points. From the studies with the slurry reactor we know that this reaction follows pseudo-first-order kinetics and there is no evidence for assuming a different reaction kinetics in this apparatus. Kinetical control of the reaction can be assumed at an agitation speed of 300 rpm. Below 300 rpm there is additional mass transfer limitation. The slopes from the corresponding runs with and without catalyst were subtracted. Hence the base reaction was taken out of the analysis. The value from the experiments at 300 rpm is the intrinsic pseudo-first-order rate constant per unit volume for the catalytic reaction alone. The following values for the slopes were obtained:

\[
\begin{align*}
120 \text{ rpm:} & \quad k_{LR}a = 7.1 \cdot 10^{-6} \text{ m/s} \\
180 \text{ rpm:} & \quad k_{LR}a = 7.2 \cdot 10^{-6} \text{ m/s} \\
240 \text{ rpm:} & \quad k_{LR}a = 7.4 \cdot 10^{-6} \text{ m/s} \\
300 \text{ rpm:} & \quad k'_{cat} = 8.5 \cdot 10^{-6} \text{ m/s}
\end{align*}
\]

### 3.6.4 Dispersion effect

The rate of the base reaction is proportional to the liquid-liquid interfacial area. With increasing agitation speed there is a higher extent of dispersion thus increasing this area. Pictures were taken from the organic phase which clearly showed that the degree of dispersion of the organic phase in the aqueous phase is a function of the presence of the phase transfer catalyst. Here the rates of the base reaction cannot be quantified in the presence of the catalyst, and the difference in the conversions of any two reaction runs with and without PTC will give a value which is much too high for the chemical effect of the catalyst alone. The dispersion
effect only exists at agitation speeds at which considerable dispersion of the organic phase in 
the aqueous phase comes into play. At higher agitation speeds where the organic phase is fully 
dispersed in the aqueous phase the difference in the conversions of two corresponding runs 
will indicate the chemical effect of the phase transfer catalyst alone. A breakdown of the 
apparent effects for this reaction system at different agitation speeds is given in Table 3.3. Up 
to an agitation speed of 300 rpm there is no dispersed phase in the reactor.

A reaction run under similar conditions with inactive polymer material led to 
conversions which were only slightly higher compared to the one with no catalyst on the disk. 
A reaction run with another triphase catalyst, tributylmethylphosphonium chloride polymer 
bound, was carried out towards the end of this work. Although the two catalysts are 
chemically analogous, the latter did not show this effect to any larger extent than the inactive 
polymer material. At this point we do not know the reason for this phenomenon. All we can 
say is that some PTC's induce dispersion at moderate agitation speeds thus making it 
impossible to quantify their chemical effect in reaction systems with base reaction.

The dispersion effect shows that phase transfer catalysts can have strong physical 
effects on the reaction system. The name phase transfer agent is then much more suitable. 
This finding cannot be exploited in industry since reactions with catalyst particles are carried 
out in a slurry where the organic phase is fully dispersed in the aqueous one. Under these 
conditions a base reaction proceeds at its maximum rate and the catalyst has only a chemical 
effect. The dispersion effect becomes very important in laboratory studies to determine mass 
transfer coefficients. Without taking this effect into account any mass transfer values reported 
for a triphase catalytic system would be questionable.
3.6.5 Comparison of slurry reactor and rotating disk contactor

Concentration vs. time data as a function of agitation speed at a fixed time are shown qualitatively in Figure 3.13 for RDC and slurry reactor. For each reactor type there are three curves, one for experiments in the presence of the phase transfer catalyst (base+cat) and one for those in the absence of the catalyst (base). The difference between the two curves shows the observed chemical effect of the PTC.

In RDC the triphase catalyst is immobilized on a disk which results in a much smaller available surface area and the liquid-liquid interface is covered by a glass plate. The curves for two corresponding runs with and without PTC have been discussed in detail in the previous section. Taking the difference of the two curves leads to the interesting result that the catalytic effect apparently goes through a strong maximum. This is due to the lag between the two curves caused by the dispersion effect. Otherwise this curve would follow the dashed line. In this case the conversions decrease with increasing dispersion since the catalyst is not equiaccessible to the two liquid phases when one phase is dispersed in the other.

In the slurry reactor the liquid-liquid interface is not kept smooth by a glass plate. Therefore, full dispersion will already be reached at much lower agitation speeds. In addition, the surface area of the catalyst available for reaction is much larger. Consequently, the curve for the catalytic effect has a large slope at low agitation speeds and the maximum due to the dispersion effect shows up much weaker.

The intrinsic rate constants obtained from the two reactors can be compared by converting them into rate constants per unit area of the catalyst. It must be pointed out that a slurry reactor is not necessarily the best device to obtain the kinetic parameters of a reaction system due to the fact that the catalyst is not equiaccessible to the two liquid phases.
Slurry reactor:
The specific surface area of the catalyst is $0.40 \text{ m}^2 \text{ g}^{-1}$ (BET method). The volume of the slurry was $485 \text{ cm}^3$. From this the surface area per unit volume of the reactor $a$ can be calculated:

$$a = 9.70 \text{ cm}^2 \text{ cm}^{-3}$$

The rate constant per unit surface of the catalyst is given by:

$$k_s = \frac{k_y}{9.70} = \frac{3.9 \cdot 10^{-4}}{9.70} = 4.0 \cdot 10^{-5} \text{ cm min}^{-1}$$ \hspace{1cm} (12)

Rotating disk contactor:
The spherical catalyst particles have a diameter of approximately $63 \mu\text{m}$. From this it can be concluded that the porosity of the particles increases the surface area by a factor 4.5. The total volume of the reactor is $2000 \text{ cm}^3$, the open area of the mesh sieve covering the catalyst is $12.6 \text{ cm}^2$. Knowing these values we can determine the surface area of the catalyst per unit volume of the reactor:

$$a = 0.03 \text{ cm}^2 \text{ cm}^{-3}$$

The rate constant per unit surface of the catalyst is given by:

$$k_s = \frac{k_y}{0.03} = \frac{8.5 \cdot 10^{-6}}{0.03} = 2.8 \cdot 10^{-4} \text{ cm min}^{-1}$$ \hspace{1cm} (13)

We can see that the rate of reaction is higher in RDC. The reason for this is that there is complete displacement of the phases in the rotating disk contactor at the rotating disk speed used. As a result the two reactions, namely the reaction in the organic phase and in the aqueous phase, take place as distinct reactions each with its own mass transfer and reaction characteristics. In fact, RDC has been specifically designed to permit such an operation. It
will be noticed that under these "ideal PTC conditions" the reaction rate is nearly seven times higher than in the conventional slurry reactor. Obviously, in the slurry reactor the two phases are fully mixed and there is no clear-cut separation between reaction and mass transfer associated with each of the phases. Consequently, the reaction rate is lower. In practical terms this can be expressed by the statement that only a certain percentage (in this case 15%) of the catalytic surface in the slurry mode is operative as a PT catalyst.

3.6.6 Mass transfer coefficients

From equation (3) the following mass transfer coefficients as a function of the bulk agitation speed were obtained:

120 rpm: \( k_L a = 4.3 \cdot 10^{-5} \frac{1}{\text{min}} \quad k_L = 1.4 \cdot 10^{-3} \frac{\text{cm}}{\text{min}} \)

180 rpm: \( k_L a = 4.5 \cdot 10^{-5} \frac{1}{\text{min}} \quad k_L = 1.5 \cdot 10^{-3} \frac{\text{cm}}{\text{min}} \)

240 rpm: \( k_L a = 5.9 \cdot 10^{-5} \frac{1}{\text{min}} \quad k_L = 2.0 \cdot 10^{-3} \frac{\text{cm}}{\text{min}} \)

Comparing the values of \( k_L a \) and \( k_{cut} \) we see that the mass transfer rates are approximately five times the kinetic rate. The values are within one order of magnitude and we conclude that the reaction takes place in the overlapping regime 1-2.

In Figure 3.14 the dependence of the mass transfer coefficient on the agitation rate is shown graphically. The graph shows that the mass transfer coefficients increase with increasing agitation rate. There are only a few data points available. This is mainly due to the presence of the dispersion effect which narrows the range of possible agitation speed levels. Furthermore, the levels for the agitation speeds need to differ by approximately 60 rpm in order to overcome the random error and see differences among the chosen levels for this reaction system.
3.6.7 Reproducibility

The concentration vs. time data obtained from experiments in the RDC could be replicated to within ±5% for times beyond 660 min. For samples taken at 180, 300, 420 and 540 min. the error was sometimes as high as ±15%. At extremely low conversions the GC analysis gives high variability and also tends to underestimate the true concentration value. However, these data points do not have a large impact on the regime analysis since the slopes calculated from the -ln(1-conversion) vs. time plots were obtained by using a regression analysis with the constraint that there is no intercept. Data points close to the origin will not affect the regression line as much as values far away from the origin. The regime analysis itself is highly sensitive to the variation in the raw data, especially when the rate constants are very low.

3.7 Conclusion

The objective of this research is the development of a contactor for studying mass transfer in three-phase systems in the presence of reaction. No such apparatus exists today. The main concept is that a rotating disk which is equiaccessible to both bulk phases carries the solid catalyst. The surface area of the catalyst is known and the physical factors influencing mass transfer can be controlled independently. The apparatus is a very versatile equipment and can be used to study mass transfer in any three-phase system subject to minor modifications of the contactor, like providing for gas flow for a gas-liquid-solid system.

Experiments were carried out on a liquid-liquid-solid triphase catalytic system, namely esterification of benzyl chloride with sodium acetate to yield benzyl acetate with polymer
supported tributylmethylammonium chloride as the phase transfer catalyst. This reaction is mass transfer controlled at low agitation speeds. It was found to be characterized by considerable noncatalytic reaction and effects due to dispersion associated with the catalyst. However, mass transfer coefficients as a function of agitation speed could be determined. The values ranged from $1.4 \times 10^{-3}$ cm/min to $2.0 \times 10^{-3}$ cm/min for agitation speeds ranging from 120 to 240 rpm.

It is important to note that for systems with base reaction, such as the present one, mass transfer coefficients cannot be determined in the presence of the dispersion effect. Consequently, the range of values for the agitation speed is narrowed down to a level where there is no dispersion at all. In addition, for a reaction system in regime 1-2, it becomes difficult to estimate the intrinsic rate constant. While the present study has demonstrated the use of the proposed RDC for determining mass transfer coefficients in L-L TPC systems, it has also brought out the importance of the dispersion effect in such systems. Thus further studies will be continued on mass transfer in three-phase systems using a reaction with negligible base reaction.

3.8 Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>liquid-phase species</td>
</tr>
<tr>
<td>$[A]$</td>
<td>local concentration of $A$, mol/cm$^3$</td>
</tr>
<tr>
<td>$[A_o]$</td>
<td>bulk concentration of $A$, mol/cm$^3$</td>
</tr>
<tr>
<td>$[A^*]$</td>
<td>concentration of $A$ on the surface of the solid catalyst, mol/cm$^3$</td>
</tr>
<tr>
<td>$a$</td>
<td>liquid-solid interfacial area per unit volume of the reactor, cm$^2$/cm$^3$ and also parameter, l/min</td>
</tr>
<tr>
<td>$b$</td>
<td>parameter, cm$^3$/mol min</td>
</tr>
<tr>
<td>$C_{RX}$</td>
<td>concentration of reactant (benzyl chloride), mol/cm$^3$</td>
</tr>
</tbody>
</table>
\( C_{QX, o} \) = concentration of triphase catalyst, mol/cm\(^3\)
\( D \) = diffusion coefficient, m\(^2\)/s
\( E \) = activation energy, kJ/mol
\( k_{\text{base}} \) = first-order rate constant of base reaction, 1/min
\( k'_{\text{cat}} \) = pseudo-first-order rate constant of catalytic reaction, 1/min
\( k_{\text{cat}} \) = second-order rate constant of catalytic reaction, cm\(^3\)/mol min
\( k_L \) = true liquid-side mass transfer coefficient, cm/min
\( k_{LR} \) = liquid-side mass transfer coefficient in the presence of reaction, cm/min
\( k_0 \) = frequency factor, 1/min
\( k_{\text{obs.}} \) = observed first-order rate constant, 1/min
\( k_s \) = first-order rate constant per unit surface of the catalyst, cm/min
\( k_v \) = first-order rate constant per unit volume of the reactor, 1/min
\( r \) = radius of disk, m
\( R_A \) = specific rate of mass transfer for species A, mol/cm\(^2\)
\( Re \) = Reynolds number = \( 2\pi r^2/v \), dimensionless
\( Sc \) = Schmidt number = \( v/D \), dimensionless
\( Sh \) = Sherwood number = \( k_L r/D \), dimensionless
\( T \) = absolute temperature, K
\( t \) = time, min

Greek symbols
\( \nu \) = kinematic viscosity, m\(^2\)/s
\( \omega \) = number of revolutions per second, 1/s

3.9 Literature Cited


Table 3.1. Conversion vs. time data for different disk speeds with and without catalyst (polymer bound tributylmethylammonium chloride) on the disk.

<table>
<thead>
<tr>
<th>Catalyst on disk [mmol]</th>
<th>Time [min.]</th>
<th>Conversion [%] as a function of disk speed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1.20 rpm</td>
</tr>
<tr>
<td>2.0</td>
<td>180</td>
<td>0.32</td>
</tr>
<tr>
<td>2.0</td>
<td>300</td>
<td>0.69</td>
</tr>
<tr>
<td>2.0</td>
<td>420</td>
<td>1.12</td>
</tr>
<tr>
<td>2.0</td>
<td>540</td>
<td>1.38</td>
</tr>
<tr>
<td>2.0</td>
<td>660</td>
<td>1.79</td>
</tr>
<tr>
<td>2.0</td>
<td>840</td>
<td>2.33</td>
</tr>
<tr>
<td>2.0</td>
<td>960</td>
<td>2.56</td>
</tr>
<tr>
<td>2.0</td>
<td>1080</td>
<td>3.01</td>
</tr>
<tr>
<td>2.0</td>
<td>1200</td>
<td>3.21</td>
</tr>
<tr>
<td>0</td>
<td>180</td>
<td>0.10</td>
</tr>
<tr>
<td>0</td>
<td>300</td>
<td>0.27</td>
</tr>
<tr>
<td>0</td>
<td>420</td>
<td>0.43</td>
</tr>
<tr>
<td>0</td>
<td>540</td>
<td>0.57</td>
</tr>
<tr>
<td>0</td>
<td>660</td>
<td>0.71</td>
</tr>
<tr>
<td>0</td>
<td>840</td>
<td>0.99</td>
</tr>
<tr>
<td>0</td>
<td>960</td>
<td>1.13</td>
</tr>
<tr>
<td>0</td>
<td>1080</td>
<td>1.28</td>
</tr>
<tr>
<td>0</td>
<td>1200</td>
<td>1.43</td>
</tr>
</tbody>
</table>
Table 3.2. Conversion vs. time data for different bulk agitation speeds with and without catalyst (polymer bound tributylmethyammonium chloride) on the disk.

Mass transfer controlled: 120 / 180 / 240 rpm  
Kinetically controlled: 300 rpm  
Dispersion effect: 360 / 420 / 480 rpm

<table>
<thead>
<tr>
<th>Catalyst on disk [mmol]</th>
<th>Time [min.]</th>
<th>Conversion [%] as a function of bulk agitation speed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>120 rpm</td>
<td>180 rpm</td>
</tr>
<tr>
<td>2.0</td>
<td>180</td>
<td>0.15</td>
</tr>
<tr>
<td>2.0</td>
<td>300</td>
<td>0.25</td>
</tr>
<tr>
<td>2.0</td>
<td>420</td>
<td>0.37</td>
</tr>
<tr>
<td>2.0</td>
<td>540</td>
<td>0.48</td>
</tr>
<tr>
<td>2.0</td>
<td>660</td>
<td>0.66</td>
</tr>
<tr>
<td>2.0</td>
<td>840</td>
<td>0.92</td>
</tr>
<tr>
<td>2.0</td>
<td>960</td>
<td>1.00</td>
</tr>
<tr>
<td>2.0</td>
<td>1080</td>
<td>1.17</td>
</tr>
<tr>
<td>2.0</td>
<td>1200</td>
<td>1.37</td>
</tr>
<tr>
<td>0</td>
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<td>0</td>
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</tr>
<tr>
<td>0</td>
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<td>0</td>
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</tr>
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</tr>
<tr>
<td>0</td>
<td>960</td>
<td>0.35</td>
</tr>
<tr>
<td>0</td>
<td>1080</td>
<td>0.41</td>
</tr>
<tr>
<td>0</td>
<td>1200</td>
<td>0.44</td>
</tr>
</tbody>
</table>
Table 3.3. Apparent effects at different levels of bulk agitation for the catalyst, tributylmethylammonium chloride (polymer bound).

<table>
<thead>
<tr>
<th>Stirring speed (rpm)</th>
<th>Catalytic effect</th>
<th>Mass transfer effect</th>
<th>Dispersion effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>360</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>420</td>
<td>✓</td>
<td></td>
<td>✓✓</td>
</tr>
<tr>
<td>480</td>
<td>✓</td>
<td></td>
<td>✓✓✓</td>
</tr>
</tbody>
</table>
Note: All dimensions in inches.

1. Stirrers (coil paddles), one for each phase
2. Bottom port for emptying the cell
3. Rotating disc covered with phase transfer catalyst
4. Corrosion resistant steel plates
5. Bottom, middle, and top plates (PTFE)
6. Glass cylinders
7. Inlet and outlet for thermostatic water circulation
8. Sampling port
9. Glass plate covering liquid-liquid interphase

Figure 3.1. Cross-sectional cut of rotating disk contactor (RDC).
Figure 3.2. Three-dimensional view of RDC.
Figure 3.3.  Photograph showing entire unit.
Figure 3.4. Three-dimensional views of the rotating disk. Underneath the support sieve there is a mesh sieve which holds the catalyst particles in pockets in the Teflon body.
Figure 3.5. Cross-sectional cut of the rotating disk.
Figure 3.6. Possible regimes of a liquid-liquid-solid reaction system with the solid insoluble in the liquid phases.
Figure 3.7. Triphase catalytic system under study: Esterification of benzyl chloride with sodium acetate to form benzyl acetate and sodium chloride.
Figure 3.8. Plot of $-\ln(1 \text{- conversion})$ vs. time for different bulk agitation speeds in a slurry reactor.
Figure 3.9. Arrhenius plot $\ln (k)$ vs. $1/\text{temperature}$, with 1 mmol catalyst (polymer bound tributylmethylammonium chloride) and with no catalyst, both in slurry mode. With PTC: activation energy $E = 92.7$ kJ/mol. Without PTC: activation energy $E = 126.5$ kJ/mol.
Figure 3.10. Plot of rate constant vs. amount of catalyst in slurry mode: $T = 90 \, ^\circ\mathrm{C}$, bulk agitation speed: 700 rpm.
Figure 3.11. Plot of -ln(1-conversion) vs. time for different bulk agitation speeds in the rotating disk contactor with 2 mmol polymer bound tributylmethylammonium chloride on the disk.
Figure 3.12. Plot of $-\ln(1-X)$ vs. time for different bulk agitation speeds in the rotating disk contactor with no catalyst on the disk (base reaction).
Figure 3.13. Comparison of the conversions obtained in the slurry reactor and in the rotating disk reactor with and without triphase catalyst. This plot illustrates the effect of dispersion induced by some PTC's.
Figure 3.14. Plot of mass transfer coefficient vs. agitation speed.
Catalyst: 2mmol polymer bound tributylmethylammonium chloride.
CHAPTER 4. LIMITATIONS OF THE ROTATING DISK CONTACTOR (RDC) FOR REACTION SYSTEMS INVOLVING TRANSFER OF HYDROXIDE IONS

4.1 General

The rotating disk contactor has been specifically designed to determine external mass transfer coefficients of systems with and without reaction which involve two liquid phases and one solid phase. The basic principle of this technique is that both reactions, for a PTC system namely the ion-exchange reaction in the aqueous phase and the displacement reaction in the organic phase, are decoupled under RDC conditions allowing for independent determination of mass transfer coefficients for each phase. It is important to note that the chemistry of the overall reaction is preserved. In Chapter 3 the method was demonstrated with a triphase catalytic system involving an organic and an aqueous phase as well as a polymer bound PT catalyst. In analogy, this could be done with a system without reaction which involves two immiscible liquid phases and a slowly dissolving solid, e.g. naphthalene. From concentration vs. time data the mass transfer of the dissolved solid can then be quantified.

4.2 RDC: Reactions Involving Hydroxide Transfer

The esterification of benzyl chloride to form benzyl acetate involves the transfer of acetate into the organic phase which follows Starks' extraction mechanism. Two other reaction systems have been investigated, namely the alkaline hydrolyses of hexyl acetate and octyl acetate to form hexanol and octanol, respectively. The reactions were carried out at 65°C. An
analogous reaction involving butyl acetate as the ester was initially also considered (Asai et al., 1992) but the noncatalytic reaction was too fast to be investigated in RDC. This base reaction is due to the relatively high solubility of butyl acetate in the aqueous phase (solubility of butyl acetate in water at 20 °C: 14,000 mg/l). Without the base reaction, the system would have been a suitable reaction, since the reaction is fast and thus mass transfer limited. The initial concentrations of hexyl acetate and octyl acetate were 0.86 and 0.83 mol/l, respectively, and the initial hydroxide concentration in the aqueous phase was 2.0 mol/l. Sodium sulfate was added to the aqueous phase to obtain an ionic strength of 5.0 mol/l in order to suppress the noncatalytic reaction. The idea was adopted from Lele et al. (1983) who reported that a high salt content in the aqueous phase reduces the solubility of the ester in this phase substantially.

These PTC promoted reactions involve the transfer of hydroxide into the organic phase. However, hydroxide is one of the ions most difficult to transfer into an organic phase due to its high degree of hydration and its high charge-to-volume ratio. It is commonly known that PTC reactions with strong inorganic bases follow interfacial mechanisms, i.e. no active transfer of the anion across the phase boundary by the catalyst complex $Q^+OH^-$ is involved in the reaction.

Rigorous stirring in both of the hydrolysis systems led to high conversions in the slurry mode. Conversions were significantly higher in the presence of a TP catalyst than in the case with no catalyst (due to noncatalytic base reaction) (see Chapter 5, Figures 5.2 and 5.3). However, when the hydrolysis reactions were conducted in RDC, there was no clearly detectable difference in the conversions between corresponding runs with and without catalyst. The conversions were very low, especially for the octyl acetate system which has very little base reaction. It was concluded that the conversions obtained had been caused by the noncatalytic reaction alone in both cases. Experimental data (for disk speed: 12 rpm) from
hydrolysis reactions and, as a reference, for the previous esterification of benzyl chloride are shown in Figure 4.1. Experiments conducted with both the hydrolysis systems at a disk speed of 120 rpm showed higher conversions in the presence of the catalyst, but replication was poor. This was assumed to be the result of the dispersion effect of the TP catalyst which became significant at high disk speeds. The high speed of the rotating disk caused the organic phase to get dispersed into the aqueous one, and corresponding runs with and without catalyst at fixed agitation and disk speeds proved that there was significantly more dispersion in the presence of the TP catalyst. The increase in the liquid-liquid interfacial area led to higher conversions due to the base reaction. The data are shown in Figure 4.2.

The key issue is the question whether a reaction following an interfacial mechanism can be decoupled in the way it is done in RDC. The intermediate \(Q^{+}OH^{-}\) has simultaneous contact with both liquid phases in the slurry mode, and the entire reaction takes place at the liquid-liquid interface. In RDC, the overall reaction is divided into two separate two-phase reactions. Consequently, the formation of the intermediate \(Q^{+}OH^{-}\) and the displacement reaction with the organic substrate are reaction steps in series. What perhaps happens is, due to the high hydrophilicity and high degree of hydration of the intermediate \(Q^{+}OH^{-}\), the formation of a thin aqueous film around the TP catalyst when passing the organic phase. This aqueous film completely blocks off the organic (and strongly lipophilic) substrate from the TP catalyst. The displacement of a film of the other phase, which is assumed to be a function of the disk speed for systems with neutral aqueous phases (see Chapter 3) is not likely to occur in the presence of a strongly hydrophilic anion like hydroxide.
Figure 4.1. Concentration vs. time for several reaction systems in RDC with and without TP catalyst (polymer bound tributylmethylammonium chloride). Reaction conditions: agitation rate in each bulk: 300 rpm, rotating disk speed: 12 rpm.

**Benzyl chloride system:** 0.90 mol/l benzyl chloride in toluene; 5.0 mol/l sodium acetate in water; temperature: 85°C.

**Octyl acetate system:** 0.83 mol/l octyl acetate in toluene; 2.0 mol/l sodium hydroxide, 1 mol/l sodium sulfate in water; temperature: 65°C.

**Hexyl acetate system:** 0.86 mol/l hexyl acetate in toluene; 2.0 mol/l sodium hydroxide, 1 mol/l sodium sulfate in water; temperature: 65°C.
**Figure 4.2.** Concentration vs. time for hexyl acetate and octyl acetate systems in RDC with and without TP catalyst (polymer bound tributylmethylammonium chloride).

**Reaction conditions:** Organic phase: 0.86 mol/l hexyl acetate / 0.83 mol/l octyl acetate in toluene; aqueous phase: 2.0 mol/l sodium hydroxide, 1mol/l sodium sulfate in water; temperature: 65°C, agitation rate in each bulk: 300 rpm, rotating disk speed: 120 rpm.
4.3 Extraction Mechanism - Interfacial Mechanism

Starks et al. (1994) name different criteria for distinguishing between an extraction mechanism and an interfacial mechanism. For an extraction mechanism, increased organophilicity of the quat leads to increased rates, the rates are independent of stirring speed above a certain level, and pseudo-first-order or second-order kinetics is observed if reaction in the organic phase is rate limiting (zero order when diffusion across the interface is limiting). On the other hand, an interfacial mechanism is characterized by increasing rates with increasing hydrophilicity of the quat, by reaction rates that are dependent on the agitation speed, and by more complex kinetics. These criteria can only be considered as very general guidelines. In systems with a noncatalytic base reaction, the rate will be dependent on the agitation rate regardless of the mechanism governing the catalytic reaction, since increasing agitation increases the liquid-liquid interfacial area of the system. The noncatalytic reaction depends strongly on the hydrodynamics, since its contribution to the overall rate is a function of the solubility, mainly of the organic species in the aqueous phase, and of the interfacial surface area which provides direct contact of the reacting species. For the classic PTC reaction system, namely the cyanide displacement of 1-chlorooctane, there is no measurable base reaction reported in the literature (Starks, 1971; 1997). This is due to the low solubility of 1-chlorooctane in aqueous phases and to the high interaction energy of the NaCN, the reactant in the aqueous phase. Above a certain agitation speed, the rates are independent of the stirring speed; below this level they are proportional to the square of the stirring speed. This suggests different mechanisms at different agitation speeds and is not useful information for the understanding of what is really happening. A reaction which has an extraction mechanism will
be mass transfer controlled at low agitation speeds simply because the limited mass transfer
cannot provide a large enough flux for the organic phase reaction. The bulk concentrations
will not be uniform anymore, and the locale of the reaction shifts from the organic bulk phase
towards the interface. The chemistry is fully preserved and the reaction still has an extraction
mechanism. If full mixing of the bulk phases is fully achieved and the locale of the reaction is
the interface or interfacial region, which can be assumed for most PTC reactions involving
strong inorganic bases, the mechanism of the reaction will be an interfacial mechanism. Thus,
not all of the above criteria will give suitable information about the governing mechanism of a
given reaction system.

An additional criterion, one and perhaps more suitable to distinguish between a PTC
reaction following Starks' extraction mechanism and another following an interfacial
mechanism, can be obtained by looking at the dependence of the pseudo-first-order reaction
rate on the amount of catalyst. Thus, experiments were conducted with the octyl acetate
system in the slurry mode at 65°C. The data from this system and corresponding data from the
benzyl chloride system are shown in Figure 4.3. The trend lines clearly indicate a linear
relationship for the benzyl chloride system and a curvilinear one for the octyl acetate system.
As already mentioned, the PTC reaction of benzyl chloride to form benzyl acetate proceeds
within both liquid bulks with the catalyst being the transfering agent. Increasing catalyst
concentrations lead to a linear increase of the reaction rate, which can be explained as being due
to full utilization of the catalyst in a three-dimensional space. In the interfacial mechanism, the
scenario is different. The reaction is restricted to the liquid-liquid interface or interfacial area.
In this two-dimensional space, an increase in the catalyst concentration will lead to a hindrance
among the catalyst particles, and not all particles may be simultaneously utilized for chemical
Figure 4.3. Pseudo-first-order rate constants as a function of the amount of TP catalyst (polymer bound tributylmethylammonium chloride). Reaction conditions:

**Benzyl chloride system:** 0.90 mol/l benzyl chloride in toluene; 5.0 mol/l sodium acetate in water; temperature: 90°C, agitation rate: 700 rpm.

**Octyl acetate system:** 0.83 mol/l octyl acetate in toluene; 2.0 mol/l sodium hydroxide, 1 mol/l sodium sulfate in water; temperature: 65°C, agitation rate: 700 rpm.
reaction. Consequently, the increase in the rates is less than linear with increasing amount of catalyst.

4.4 RDC: Possible Design Modifications

It might be possible to use RDC for the determination of mass transfer coefficients of hydroxide systems, but design modifications would be necessary. If it is possible to place a disk horizontally at the liquid-liquid interface such that either the top surface or the bottom surface of the disk exactly coincides with the interface, one could calculate the mass transfer coefficients from the concentration vs. time data in the same manner as was done with the current design. Let us denote the top liquid (1) and the bottom liquid (2). When the disk is in liquid (2) and its upper surface exactly coincides with the interface, we get the mass transfer coefficient in liquid (1). If the disk is immersed in liquid (1) such that the bottom surface coincides exactly with the interface, we will get the mass transfer coefficient in liquid (2). The liquid phase in which the disk is immersed would have to be pumped (periodically) or pulsed along the catalyst surface in order to renew the interface. Another possibility would be a pulsed movement of the disk away from the interface in order to assure the renewal of the interface with the immersed phase. The challenge in this design is to assure equal and simultaneous accessibility of the TP catalyst to the two liquid bulk phases. This work will not focus on such a design modification. Instead, the focus will be on the collection of data of a few more neutral TPC systems in order to suppose a general correlation for mass transfer coefficients of liquid-liquid-solid systems.
CHAPTER 5. RATE ENHANCEMENTS DUE TO AUTOCATALYSIS AND HETEROGENIZATION IN PHASE TRANSFER CATALYSIS: A COMPARATIVE STUDY

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Abstract

Reactions mediated by phase transfer catalysts (PTCs) can be carried out with either a homogeneous or a heterogeneous PT catalyst. Heterogeneous catalysts are usually bound to a polymer support and have the potential to be used in continuous processes. However, polymer bound catalysts do not enjoy industrial acceptance mainly because of the traditional circumstance that the reaction rates are lower in solid bound catalysts due to diffusional retardation. In this work polymer bound tributylmethylammonium chloride is compared to its homogeneous analog, benzyltributylanmionium chloride, for different reaction systems: esterification of benzyl chloride to benzyl acetate, and alkaline hydrolysis of hexyl acetate and octyl acetate. Their performance is distinctly superior to that of their homogeneous analogs at lower conversions. An unusual observation, however, is the "autocatalytic" behavior of the hydrolysis reactions which makes it possible for them to proceed faster than their heterogeneous counterparts as more product builds up with the progress of reaction (i.e. at higher conversions). This is because the autocatalytic product increases the solubility of the PT catalyst in the organic phase (where the reaction occurs) with consequent enhancement of the reaction rate. Kinetic analyses of all the systems have been carried out and rate constants for the noncatalytic, homogeneous, and heterogeneous components of the reactions determined.
5.1 Introduction

Phase transfer catalysis (PTC) is an important technique in organic synthesis. In the production of fine chemicals and pharmaceuticals PTC is a powerful tool that can be used in general whenever the reactants are present in two immiscible phases, liquid-liquid or solid-liquid. By adding a "phase transfer agent" which can be a quaternary ammonium salt, phosphonium salt, crown ether, polyether or cryptant, the anion from one of the phases, aqueous or solid, can be transferred into the other phase. PTC has been used for hundreds of reactions, and in many cases it is the only economically feasible way to synthesize a product.

In phase transfer catalytic systems the catalyst can either be homogeneous or heterogeneous. In the latter case the phase transfer catalyst is bound to a solid support which usually is a polymer, silica gel, or alumina. The term "triphase catalysis" (TPC) for these reaction systems was first introduced by Regen [1]. Based on the form of the reagents we can distinguish among three different types of TPC systems: liquid-liquid-solid (L-L-S), liquid-solid-solid (L-S-S) and gas-liquid-solid (G-L-S). The latter is very different from all the other forms of PTC and TPC and is often categorized as two-phase system in the literature denoted as G-L PTC. The type of triphase catalysis covered in the present work involves a liquid-liquid reaction system along with a polymer supported PTC.

PTC reactions are industrially carried out almost exclusively with homogeneous phase transfer catalysts since it is commonly believed that polymer bound catalysts have a reduced activity compared to their homogeneous analogs in two-phase systems due to diffusional retardation. According to Starks et al. [2] reactions with slow intrinsic (organic phase) reactions rates are much slower with a TP catalyst than with its homogeneous counterpart. In
addition, the synthesis of large quantities of TP catalysts with specific concentrations of functional groups is very expensive. On the other hand, TP catalysts do have a great potential since they can be readily separated from the products by filtration and thus be used in continuous reactors. They can be regenerated to their original activity and reused until they lose their mechanical stability.

5.1.1 Mechanisms under neutral and acidic conditions

The mechanism of this type of PTC reaction was first proposed by Starks [3]. The phase transfer catalyst undergoes an ion-exchange reaction and forms an ion pair which can cross the liquid-liquid interface due to its lipophilic nature. In the organic phase this ion pair undergoes a nucleophilic displacement reaction with the organic reagent to form the product. The new ion pair returns to the aqueous phase and the cycle continues. It is a fundamental requirement that the ion pair formed in the aqueous phase have a certain solubility in the organic phase and that this ion pair is transferred in a highly active state.

5.1.2 Mechanisms in the presence of inorganic bases

For PTC reactions performed in the presence of strong inorganic bases the scenario is not as clearcut. The hydroxide anion is one of the most difficult anions to transfer into an organic phase because of its great propensity for hydration and high charge-to-volume ratio. Consequently, the transfer of hydroxide anions is energetically much more difficult than of halides. Only a small fraction of the phase transfer catalyst dissolved in the organic phase will be associated with the hydroxide anion, the large majority with the chloride. This should result in extremely slow reactions, which is not observed. Interfacial mechanisms can explain fast
reactions involving hydroxide anions in PTC reactions. Such a mechanism was first proposed by Makosza and Bialecka [4]. The interfacial mechanism is not an extraction mechanism since the phase transfer catalyst does not carry the hydroxide anion into the organic phase. Details of this interfacial mechanism and its modifications are given for several organic reactions involving hydroxide ions by Starks et al. [2], Dehmlow and Dehmlow [5] and Naik and Doraiswamy [6].

5.2 Problem Definition

In view of the conflicting reports on the efficacy of supported PTC (heterogeneous catalyst), it is desirable to make a comparative assessment of heterogeneous and homogeneous catalysts for different categories of PTC systems. Thus consider the following model systems:

1. Alkaline hydrolysis:
   1 a. Hexyl acetate with sodium hydroxide.
   1 b. Octyl acetate with sodium hydroxide.

2. Esterification of benzyl chloride with sodium acetate.

Reactions 1a and 1b occur in the presence of a base. In reaction 1a the polarity of the organic phase increases during the course of reaction since hexanol has a higher polarity than hexyl acetate. Furthermore, the hydroxide anion can be solvated by the alcohol in the organic phase making it more easily transferable. PTC promoted alkaline hydrolysis reactions have been investigated by Lele et al. [7] for different formate and acetate esters in two-phase systems with homogeneous catalysts. Reaction system 1b is similar to 1a: polarity changes, but solvation effects caused by the formation of octanol are weaker than those observed for hexanol.
Reaction system 2 has already been investigated [8, 9, 10, 11, 12]. Desikan and Doraiswamy [11] report faster reaction rates obtained with the heterogeneous catalyst than with its soluble analog. There is a positive "polymer effect" which overcompensates the negative "diffusion effect" which was normally expected for a reaction system with porous catalyst particles. It needs to be pointed out that the polarity of the organic phase does not change significantly during the course of this reaction.

Preliminary experimental data obtained on the three reactions showed some unusual behavior, particularly for reactions la and lb. These reactions were conspicuous by the autocatalytic nature of the reactions clearly indicated by the S-shaped curve which was obtained for conversion as a function of time, while reaction 2 showed consistently higher conversions for the supported catalyst [11]. Based on these preliminary observations, it was decided to study all the three systems in some detail with particular reference to the nature of autocatalysis in PT catalyzed reactions. To the best of the authors' knowledge, autocatalysis in phase transfer mediated reactions has not been reported so far.

5.3 Experimental

5.3.1 Materials

All three reaction systems were either promoted by tributylmethylammonium chloride bound on polystyrene, or its homogeneous analog benzyltributylammonium chloride. Desikan and Doraiswamy [11] argue that due to the observed polymer effect of polymer bound triphase catalysts, benzyltributylammonium chloride is the more appropriate analogous homogeneous form than tributylmethylammonium chloride. The immobilization adds a benzene ring to the
functional group which is illustrated in Figure 5.1. Hence, the functional group of the polymer bound catalyst is best represented by benzyltributylammonium chloride.

Both catalysts are commercially available from Fluka Chem. Corp. and were not further modified. 1.0 g of the heterogeneous catalyst (corresponds to 0.277 g of homogeneous catalyst) are equivalent to 0.85 mmol. As a comparison aliquat 336 (methyltrioctylammonium chloride) was used. Toluene was used as the organic phase solvent. All the chemicals were of analytical grade.

5.3.2 Analysis of samples

The concentrations of products and reactants in the organic phase were determined using a gas chromatograph. A Perkin Elmer gas chromatograph (PE 3000 Autosystem) with FID was used. Each analysis was run isothermally (150°C for the benzyl chloride system, 130°C the for hexyl acetate system, and 160°C for the octyl acetate system). A packed column from Supelco was used for the analysis (Carbopack: 10% SP-2250) with a length of 2.0 m and a diameter of 1/8 inch. The obtained results were consistent and could be replicated to within ±4%.

5.3.3 Procedure

The experiments were carried out in two different agitated vessels, a 500 ml stainless steel reactor from PARR Instruments and a 2000 ml PTFE reactor with built-in glass cylinders which is a modified form of a special reactor developed by the authors earlier [12]. The catalyst concentration was $4.0 \times 10^{-3}$ mol/l slurry.
The alkaline hydrolysis reactions were carried out at 50°C and 65°C. The initial concentrations of hexyl acetate and octyl acetate were 0.86 and 0.83 mol/l, respectively, and the initial hydroxide concentration in the aqueous phase was 2.0 mol/l. In addition, sodium sulfate was added to the aqueous phase to obtain an ionic strength of 5.0 mol/l. Lele et al. [7] report that the noncatalytic reaction can be suppressed by a high salt content in the aqueous phase since the solubility of the ester is reduced substantially.

The esterification reaction of benzyl chloride was carried out at 85°C. The initial concentration of benzyl chloride was 0.90 mol/l and that of sodium acetate 5 mol/l.

By conducting preliminary experiments, it was determined that the reactions were kinetically controlled at stirring speeds of 700 rpm and 900 rpm in the PARR and PTFE reactors, respectively.

5.4 Results and Discussion

We will first consider the case where the reactions are promoted by a homogeneous PT catalyst. The results from experiments with the analogous heterogeneous species as well as a comparison of the two cases are discussed later in this section.

5.4.1 PTC systems with homogeneous catalyst

In the beginning of this section, results from experiments on the alkaline hydrolysis systems are discussed. A general mathematical procedure to determine the kinetic parameters of reaction systems that exhibit autocatalytic behavior is then described and adopted to the present case. The section concludes with a discussion of the results from the neutral reaction system, namely the esterification of benzyl chloride with sodium acetate.
5.4.1.1 Alkaline hydrolysis: Systems 1a and 1b

Conversion vs. time plots are shown in Figures 5.2 (a), (b) and (c) for the hexyl acetate system at 50°C, 65°C and 85°C, respectively, and in Figures 5.3 (a), (b) and (c) for the octyl acetate system at the same temperature levels. The plots reveal an S-shape in each case, i.e. the rate initially increases, reaches a maximum, and finally decreases as the ester is being depleted. Thus the hydrolysis reactions of hexyl acetate and octyl acetate clearly exhibit autocatalytic behavior.

Solubility studies showed that at room temperature 7.5 g of benzyltributylanammonium chloride could be dissolved in 100 ml of aqueous phase, while there was virtually no solubility in the organic phase. At 100 °C approximately 1.0 g of catalyst could be dissolved in 100 ml of organic phase. The addition of hexanol or octanol increased the solubility of the catalyst in the organic phase dramatically. Adding 5 ml of hexanol to 100 ml of organic phase at room temperature led to a solubility of 6.0 g of catalyst in the organic phase. If the homogeneous catalyst was added to the two-phase system, a third liquid layer was observed at a high enough catalyst concentration at the location of the liquid-liquid interface. Adding hexanol to the systems resulted in elimination of this third liquid layer indicating that the catalyst was dissolved in the organic phase. The difference in the extraction constants of $Cl^-$ and $OH^-$ is very high and should not permit a high concentration of hydroxide in the organic phase. Thus most of the catalyst dissolved in the organic phase should be paired with the chloride ion. This is not the case since the alcohol is able to hydrate the hydroxide ion making it more organophilic. A key role in this solvation process is played by the hydrogen bonds. In fact, the addition of hexanol will result in an inversion of the extractibility of $Cl^-$ and $OH^-$, thus preferably pairing the catalyst with the hydroxide rather than with the chloride in the organic
phase. For the same reason alcohols like methanol and ethanol are sometimes added to the aqueous phase where they act as cocatalysts.

When the reaction starts there is no product and the organic phase has a very low polarity, which prevents the phase transfer catalyst from crossing the interface. The reaction can only proceed by an interfacial mechanism, and is thus restricted to the organic-aqueous interfacial boundary layer. The concentration of PT catalyst in this layer is very high and so is the concentration of activated hydroxide ions. This explains the observed enhancement due to the homogeneous catalyst even in the absence of the product. As the reaction proceeds alcohol is formed and the PT catalyst paired with hydroxide ions can cross the interface into the organic bulk. The mechanism changes and proceeds according to Starks’ extraction mechanism which takes place in the bulk phase and results in increased rates due to the high solubility of the hydroxide paired PT catalyst.

When alcohol is added to the reaction system initially, the reaction proceeds at much higher rates due to the higher solubility of the catalyst in the organic phase. Figure 5.4 shows the effect of added alcohol to the reaction system. At very large initial concentrations the reaction will approach pseudo-first-order kinetics. These results confirm the autocatalytic nature of the reaction.

The same reaction was performed with a much more lipophilic catalyst, namely aliquat 336. The result was a fast pseudo-first-order reaction which is shown in Figure 5.5. Consequently, autocatalysis only occurs in phase transfer catalysis when a hydrophilic PT catalyst is used and changes in polarity of the organic phase allow the catalyst to dissolve more and more in the organic phase as the reaction proceeds.
5.4.1.2 Kinetics and mechanism: Autocatalytic behavior

Tamhankar et al. [13] derived a general expression for the treatment of autocatalytic reactions. The rate expression accounts for both reaction steps, namely the noncatalytic and autocatalytic. Adopting this analysis to the present case, the overall reaction can be written in the following form:

\[ Ester + Sodium\ hydroxide \xrightarrow{PTC} Alcohol + Sodium\ acetate \]

or, in general notation,

\[ A + 5P + <2 \]

where \( A \) is the ester, \( B \) is sodium hydroxide, \( P \) is the alcohol and \( Q \) sodium acetate. The reaction also proceeds in the absence of phase transfer catalyst, this noncatalytic reaction being expressed as

\[ \frac{dC_A}{dt} = k^*C_AC_B. \]

Since \( B \) is in excess and the ion-exchange reaction is very fast compared to the reaction in the organic phase, the ion-exchange reaction can be considered to be at equilibrium and thus not rate limiting. The rate can then be expressed as

\[ R_{nc} = -\frac{dC_A}{dt} = k^*_nC_A. \]

As already pointed out, the concentration of homogeneous catalyst increases with time, thus increasing the reaction rate. The effect of the increasing catalyst concentration is reflected in the amount of hexanol formed. Hence the kinetics can be treated as autocatalysis with respect to hexanol. The autocatalytic step can be represented as

\[ A + B + P \rightarrow 2P + Q \]
and the corresponding rate expressed as

\[ R_{ac} = -\frac{dC_A}{dt} = k_A C_A C_p. \]  

(6)

The total rate of reaction is given by

\[ R = R_{ac} + R_{ac} = k_u C_A + k_A C_A C_p. \]  

(7)

Equation (7) can be expressed in terms of fractional conversion as

\[ R = \frac{d\alpha}{dt} = k_o(1 - \alpha) + k\frac{A}{A_0} \alpha(1 - \alpha) \]  

(8)

which can be rearranged to give

\[ \frac{d\alpha}{dt} = k_o + (C_A k_{ac} - k_o) \alpha + (-C_A k_{ac}) \alpha^2. \]  

(9)

On integration this gives

\[ \ln \frac{\alpha + k_1}{1 - \alpha} = k_2 t + \ln k_1 \]  

(10)

with

\[ k_1 = \frac{k_o}{C_A k_{ac}} \]  

(11)

and

\[ k_2 = k_o + C_A k_{ac}. \]  

(12)

The constant \( k_1 \) can be obtained by differentiating eqn. (9) and equating to 0.

\[ \frac{dR}{dt} = C_A k_{ac} - k_o - 2C_A k_{ac} \alpha_{max} = 0 \]  

(13)

Hence

\[ k_1 = \frac{k_o}{C_A k_{ac}} = 1 - 2\alpha_{max} \]  

(14)

\( \alpha_{max} \) represents the value of \( \alpha \) at which the maximum rate is obtained. This value can be determined from the conversion vs. time plots by locating the point of inflection of the S-
shaped curve. The corresponding conversion will be the value of $\alpha_{max}$. The value of $k_1$ can then be obtained from eqn. (14), and that of $k_2$ by plotting $\ln \left( \frac{\alpha + k_1}{1 - \alpha} \right)$ vs. time according to eqn. (10). Once $k_1$ and $k_2$ are known, the rate constants $k_0$ and $k_{ac}^-$ can be calculated using the relations

$$ k_0 = \frac{k_1 k_2}{k_1 + 1} $$

and

$$ k_{ac}^- = \frac{k_2}{C_{A0}(k_1 + 1)}. $$

Figures 5.6 (a) and (b) show plots of $\ln \left( \frac{\alpha + k_1}{1 - \alpha} \right)$ vs. time at three different temperatures, 50°, 65° and 85°C for the hydrolysis of hexyl acetate and octyl acetate. The values of $k_2$ were determined from these plots and then $k_0$ and $k_{ac}^-$ were calculated from eqns. (15) and (16). These are shown in Table 5.1 for all three temperatures.

The low value of $k_1$ for the octyl acetate system indicates that the noncatalytic reaction is of little significance. The noncatalytic reaction is caused by the solubility of the acetate ester in the aqueous phase which is lower in the case of octyl acetate. A value of $\alpha_{max} = 0.5$ corresponds to a $k_1$ value of 0 which means that there is no base reaction.

Values of $k_0$ were also obtained independently from reaction runs without the phase transfer catalyst, and data for the hexyl acetate system at 65°C are plotted in Figure 5.8. Exactly similar plots were also obtained for the other temperatures and for the octyl acetate system. The values of $k_0$ obtained from this analysis are shown in Table 5.2; they agree very well with those obtained from the above analysis. The value of the noncatalytic reaction obtained in the PTFE-reactor is lower. The reason for this is the less effective mixing in the large PTFE-reactor which is only apparent in the absence of a PT catalyst which acts as a
surfactant. The droplet size of the dispersed phase is much more dependent on the agitation speed in the absence of a PT catalyst.

Values of the activation energy for all reaction steps were obtained for the alkaline hydrolysis reactions. The data are shown in Table 5.3 and plotted in Figures 5.7 (a) and (b) for hexyl acetate and octyl acetate, respectively. For the noncatalytic reaction and reaction with heterogeneous catalyst, pseudo-first-order kinetics was assumed. The values of $k_o$ were subtracted from the corresponding slopes of the experiments with heterogeneous catalyst to obtain $k_{cat}$. Comparing the values of the activation energies of the catalytic and the noncatalytic reaction steps, we see that the activation energies are slightly lower in the presence of a PT catalyst. This result is in conformity with earlier findings by the authors [12]. However, a much larger decrease in the activation energies for the esterification of benzyl chloride with sodium acetate was reported by the authors when a PT catalyst was added to the reaction mixture. Hence, no general conclusions for the lowering of activation energies can be drawn at this stage since the values from this work appear to be of the same order of magnitude for all the three reaction steps.

5.4.1.3 Esterification: System 2

Experiments were carried out on the benzyl chloride system with different amounts of hexanol added to the organic phase. The conversion vs. time data are shown in Figure 5.9. Within each run the polarity of the organic phase does not change significantly, and hence autocatalytic behavior is not observed. The data show, however, that the reaction rates do increase as more hexanol is added to the system. This can be explained by the higher amount of catalyst dissolved in the organic phase in the presence of the alcohol. As a reference the
conversions obtained with aliquat 336 (methyltrioctylammonium chloride) are included in Figure 5.9. This catalyst is much more lipophilic than benzyltributylammonium chloride and most of the catalyst will be dissolved in the organic phase. The benzyl chloride system has a slow reaction in the organic phase and thus lipophilic catalysts tend to give greater enhancements.

5.4.2 PTC systems with heterogeneous catalyst

All the three reactions studied in the previous section with homogeneous catalyst were carried out in the presence of heterogeneous catalysts. Polymer bound tributylmethylammonium chloride was used as the analogous heterogeneous PT catalyst. The results which are given in Figures 5.8 and 5.9 clearly show that there is no autocatalytic effect. The rates follow pseudo-first-order kinetics in all cases. As already mentioned above, the polymer bound catalyst is more organophilic due to its nonpolar polymer backbone. The diffusion scenario is complicated in systems with porous catalyst particles and two liquid phases. The droplets of the dispersed phase have to diffuse into the pores of the catalyst to the active sites for reaction to occur. The more lipophilic these droplets are the higher their affinity to the catalyst will be since it is the polymer structure and not the catalytic site that primarily influences the physical properties of the TP catalyst. Hence the use of cosolvents to increase the polarity of the organic phase should have a negative effect on the conversion. The fraction of the organic phase within the pores of the catalyst should decrease. It can be seen from Figure 5.9 that this is indeed the case for the benzyl chloride system. Reaction runs with 20% hexanol in the organic phase had 15% lower conversions than the corresponding runs without any hexanol. But the effect is small and for the alkaline hydrolysis systems there was no effect
at all because of the observed first-order kinetics despite increasing hexanol concentration which is shown in Figure 5.8. One can also argue on a more macroscopic scale that in heterogeneous PTC systems the catalyst particles are much larger than the droplets of the dispersed phase. Hence the liquid phases can be regarded as forming a single one pseudo-homogeneous phase. Polarity changes of this pseudo-homogeneous phase are not an issue for the reaction rate because they do not have an influence on the access of the catalyst to the reactants.

5.4.3 Comparison of homogeneous and heterogeneous PT catalysts

Experiments with both catalysts, homogeneous benzyltributylammonium chloride and polymer bound tributylmethylammonium chloride, were conducted earlier by Desikan and Doraiswamy [11] on the benzyl chloride system and the heterogeneous catalyst was found to consistently perform better. In this case, there is a perceptible increase in the conversions due to the immobilization of the catalyst. This in itself is an interesting observation since it is commonly believed that the immobilized catalyst is always inferior due to diffusional resistances.

In order to explain this fully, two more reaction systems, namely alkaline hydrolysis of hexyl acetate and octyl acetate, were studied with respect to the effect of heterogenizing the PT catalyst. In these cases, there is no such clearcut conclusion. Initially, the heterogeneous catalyst performs better, but after a certain time the homogeneous catalyst becomes superior due to the autocatalytic effect.

It is possible to find a homogeneous catalyst like aliquat 336 (methyltrioctylammonium chloride) to improve the conversions of all three reactions significantly. This catalyst is much
more lipophilic than benzyltributylammonium chloride and is a good choice for reaction systems with nonpolar organic phases.

Furthermore, it is possible to improve the performance of a PT catalyst with reasonable or little solubility in the organic phase by heterogenizing it. Depending on the polymer, a certain degree of organophilicity will be added to the catalyst. Although the heterogenized form of the catalyst still has a lower performance than aliquat 336, it can be considered industrially feasible because it is in solid form with its inherent operational advantages (use in continuous reactors, easy separation of the catalyst from the product). Figure 5.10 illustrates a methodology for an economic choice of catalyst. A reasonably soluble catalyst which is immobilized on a polymer with a strong positive polymer effect should be a viable candidate, and not one to be rejected because of a sole perceived effect of diffusion.

5.5 Conclusion

The objective of this research is to investigate the relative reactivities of homogeneous and heterogeneous phase transfer catalysts. Polymer bound tributylmethylammonium chloride and its homogeneous analog, benzyltributylammonium chloride, are chosen as the catalysts for three different reaction systems.

In most cases, the homogeneous PT catalyst has a higher activity than its heterogeneous analog because of diffusional retardation. In some cases, when a hydrophilic catalyst is used in systems with organic phases with very little polarity, the polymer bound PT catalyst will perform better as shown by Desikan and Doraiswamy [11]. This is due to the polymer effect induced by the polymer backbone which increases the organophilicity of the catalyst. Even in
these cases, the homogeneous catalyst can overcome the reactivity of the corresponding polymer bound species, if the reaction system shows autocatalytic behavior. A hydrophilic PT catalyst tends to autocatalyze the reaction in systems with increasing polarity of the organic phase caused by the formation, and dissolution in the organic phase, of a product of reaction. In these systems, the polymer bound catalyst is not greatly influenced by polarity changes in the organic phase, and the system will exhibit simple kinetics (usually pseudo first order).

5.6 Notation

\( A, B, P, Q \) = particular species
\( C \) = concentration, mol/cm\(^3\)
\( C_A \) = concentration of species \( A \), mol/cm\(^3\)
\( C_{A_0} \) = initial concentration of species \( A \), mol/cm\(^3\)
\( k'' \) = second-order rate constant, cm\(^3\)/mol min
\( k_o \) = pseudo-first-order rate constant for the noncatalytic step, 1/min
\( k_{ac}^* \) = second-order rate constant for the autocatalytic step, cm\(^3\)/mol min
\( k_1 \) = \( k_o / C_{A_0} k_{ac}^* \), a dimensionless constant
\( k_2 \) = \( k_o + C_{A_0} k_{ac}^* \), the overall rate constant, 1/min
\( R \) = total rate of reaction, mol/cm\(^3\) min
\( R_{nc} \) = rate of reaction of the noncatalytic reaction step, mol/cm\(^3\) min
\( R_{ac} \) = rate of reaction of the autocatalytic reaction step, mol/cm\(^3\) min
\( R' \) = total rate of reaction, 1/min
\( t \) = time, min

Greek symbols
\( \alpha \) = fractional conversion
\( \alpha_{max} \) = fractional conversion at maximum rate
5.7 References


Table 5.1. Experimental values of rate constants for the noncatalytic and autocatalytic steps for different reaction systems.

<table>
<thead>
<tr>
<th>Reaction system</th>
<th>Reactor</th>
<th>$k_i$ [1/min]</th>
<th>$k_o$ [cm$^3$/mole·min]</th>
<th>$k_{uc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexyl acetate, 50°C</td>
<td>PARR</td>
<td>0.10</td>
<td>7.87x10^{-4}</td>
<td>9.16</td>
</tr>
<tr>
<td>Hexyl acetate, 65°C</td>
<td>PARR</td>
<td>0.12</td>
<td>1.46x10^{-3}</td>
<td>14.15</td>
</tr>
<tr>
<td>Hexyl acetate, 65°C</td>
<td>PTFE</td>
<td>0.12</td>
<td>1.47x10^{-3}</td>
<td>14.30</td>
</tr>
<tr>
<td>Hexyl acetate, 85°C</td>
<td>PARR</td>
<td>0.12</td>
<td>4.64x10^{-3}</td>
<td>45.04</td>
</tr>
<tr>
<td>Octyl acetate, 50°C</td>
<td>PARR</td>
<td>0.02</td>
<td>9.41x10^{-5}</td>
<td>5.64</td>
</tr>
<tr>
<td>Octyl acetate, 65°C</td>
<td>PARR</td>
<td>0.02</td>
<td>2.37x10^{-4}</td>
<td>14.22</td>
</tr>
<tr>
<td>Octyl acetate, 85°C</td>
<td>PARR</td>
<td>0.02</td>
<td>5.17x10^{-4}</td>
<td>30.99</td>
</tr>
</tbody>
</table>
Table 5.2. Experimental values of the rate constant $k_o$ from first-order analysis of the noncatalytic reaction.

<table>
<thead>
<tr>
<th>Reaction system</th>
<th>Reactor</th>
<th>$k_o$ [l/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexyl acetate, 50°C</td>
<td>PARR</td>
<td>$7.67 \times 10^{-4}$</td>
</tr>
<tr>
<td>Hexyl acetate, 65°C</td>
<td>PARR</td>
<td>$1.69 \times 10^{-3}$</td>
</tr>
<tr>
<td>Hexyl acetate, 65°C</td>
<td>PTFE</td>
<td>$1.15 \times 10^{-3}$</td>
</tr>
<tr>
<td>Hexyl acetate, 85°C</td>
<td>PARR</td>
<td>$4.52 \times 10^{-3}$</td>
</tr>
<tr>
<td>Octyl acetate, 50°C</td>
<td>PARR</td>
<td>$1.01 \times 10^{-4}$</td>
</tr>
<tr>
<td>Octyl acetate, 65°C</td>
<td>PARR</td>
<td>$2.18 \times 10^{-4}$</td>
</tr>
<tr>
<td>Octyl acetate, 85°C</td>
<td>PARR</td>
<td>$5.40 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Table 5.3. Values of the activation energy of the alkaline hydrolysis systems for various reaction steps.

<table>
<thead>
<tr>
<th>Reaction system</th>
<th>Activation energy $E$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reaction step with homogeneous catalyst</td>
</tr>
<tr>
<td>Hexyl acetate</td>
<td>44.3</td>
</tr>
<tr>
<td>Octyl acetate</td>
<td>46.6</td>
</tr>
</tbody>
</table>
**Heterogenous catalyst:**

![Chemical structure]

Polymer bound tributylmethylammonium chloride

**Homogeneous analogous candidates:**

![Chemical structure]

Benzyltributylammonium chloride

![Chemical structure]

Tributylmethylammonium chloride

---

**Notation:**

\[ CH_3-(C_4H_9)_3-N^+ Cl^- \]

Polymer backbone

**Figure 5.1.** Polymer bound tributylmethylammonium chloride and its soluble analogs.
Figure 5.2a. Alkaline hydrolysis of hexyl acetate (PARR reactor): Conversion vs. time plots: (□) Heterogeneous PT catalyst; (●) Homogeneous PT catalyst; (▲) No catalyst. T = 50°C.
Figure 5.2b. Alkaline hydrolysis of hexyl acetate (PARR reactor): Conversion vs. time plots: (□) Heterogeneous PT catalyst; (●) Homogeneous PT catalyst; (▲) No catalyst. T = 65°C.
Figure 5.2c. Alkaline hydrolysis of hexyl acetate (PARR reactor): Conversion vs. time plots: (□) Heterogeneous PT catalyst; (●) Homogeneous PT catalyst; (▲) No catalyst. T = 85°C.
Figure 5.3a. Alkaline hydrolysis of octyl acetate: (PARR reactor): Conversion vs. time plots: (□) Heterogeneous PT catalyst; (●) Homogeneous PT catalyst; (▲) No catalyst. T = 50°C.
Figure 5.3b. Alkaline hydrolysis of octyl acetate: (PARR reactor): Conversion vs. time plots: (□) Heterogeneous PT catalyst; (●) Homogeneous PT catalyst; (▲) No catalyst. T = 65°C.
Figure 5.3c. Alkaline hydrolysis of octyl acetate: (PARR reactor): Conversion vs. time plots: (□) Heterogeneous PT catalyst; (●) Homogeneous PT catalyst; (▲) No catalyst. T = 85°C.
**Figure 5.4.** Alkaline hydrolysis of hexyl acetate, $T = 65^\circ$C (PTFE reactor): Conversion vs. time: (■) Homogeneous PT catalyst (50% hexanol initially added, based on molar quantity of hexyl acetate); (○) Homogeneous PT catalyst (20% hexanol added); (▲) Homogeneous PT catalyst (10% hexanol added); (●) Homogeneous PT catalyst; (□) Heterogeneous PT catalyst; (×) No catalyst.
Figure 5.5. Alkaline hydrolysis of hexyl acetate, $T = 65^\circ\mathrm{C}$ (PTFE reactor): Plot of $-\ln(1-\alpha)$ vs. time. PT catalyst: Aliquat 336 (methyltrioctylammonium chloride).
Figure 5.6a. Alkaline hydrolysis of hexyl acetate: Plot of $\ln \left( \frac{\alpha + k_1}{1 - \alpha} \right)$ vs. time to determine the rate constants of the noncatalytic and autocatalytic steps simultaneously: (■) $T = 85^\circ C$, (○) $T = 65^\circ C$, (▲) $T = 50^\circ C$. 
Figure 5.6b. Alkaline hydrolysis of octyl acetate: Plot of $\ln \left( \frac{\alpha + k_i}{1 - \alpha} \right)$ vs. time to determine the rate constants of the noncatalytic and autocatalytic steps simultaneously: (■) $T = 85^\circ$C, (●) $T = 65^\circ$C, (▲) $T = 50^\circ$C.
Figure 5.7a. Alkaline hydrolysis of hexyl acetate: Arrhenius plot, \( \ln(k) \) vs. 1/temperature: (•) Reaction with homogeneous PT catalyst; (□) Reaction with heterogeneous PT catalyst; (▲) Noncatalytic reaction.
Figure 5.7b. Alkaline hydrolysis of octyl acetate: Arrhenius plot, ln (k) vs. 1/temperature: (●) Reaction with homogeneous PT catalyst; (□) Reaction with heterogeneous PT catalyst; (▲) Noncatalytic reaction.
Figure 5.8. Alkaline hydrolysis of hexyl acetate, T = 65°C (PTFE reactor): Plot of \(-\ln (1-\alpha)\) vs. time: (□) Reaction with heterogeneous PT catalyst; (▲) Noncatalytic reaction.
Figure 5.9. Esterification of benzyl chloride with sodium acetate, $T = 85^\circ C$ (PTFE reactor): Conversion vs. time plots: ($\times$) Aliquat 336; ($\square$) Heterogeneous PT catalyst; ($\bigcirc$) Heterogeneous PT catalyst (20% hexanol initially added, based on the volume of the organic phase); ($\blacktriangle$) Homogeneous PT catalyst (20% hexanol); ($\bullet$) Homogeneous PT catalyst (5% hexanol); ($\blacksquare$) Homogeneous PT catalyst.
Homogeneous PT catalyst

Highly soluble catalyst (e.g. aliquat 336)

HETEROGENIZING

TP catalyst with lower conversion because of diffusion

Reasonably or less soluble catalyst

TP catalyst with lower conversion because of diffusion

TP catalyst with higher conversion because of polymer eff.

Economical choice:
Compromise between slightly lower conversion and operational advantage

Figure 5.10. A methodology for economic choice of PT catalyst.
CHAPTER 6. TRIPHASE CATALYSIS: A CORRELATION FOR SHERWOOD NUMBER USING THE ROTATING DISK CONTACTOR (RDC) DEVELOPED EARLIER

A paper submitted to Chemical Engineering Science

Holger J. Glatzer and L. K. Doraiswamy

Abstract

Triphase catalysis (TPC) has the potential for conducting phase transfer catalyzed reactions in the continuous mode. However, there is so far no industrial acceptance of this possibility since the achieved reaction rates are usually low due to diffusional limitations. Triphase catalytic systems are strongly influenced by mass transfer, and thus an experimental technique using a rotating disk contactor that was specifically designed for this purpose [Glatzer, Desikan, and Doraiswamy (1998) Chem. Engng Sci. 53 13, 2431-2449] has been developed by the authors to estimate mass transfer coefficients. The key to precise measurements is the choice of the model system which should have an almost negligible noncatalytic reaction but yet a high enough rate to be mass transfer controlled at low agitation speeds. The synthesis of octyl acetate from octyl bromide and potassium acetate has these attributes and was used as the test system. The reaction was mediated by polymer supported tributylmethylammonium chloride or the corresponding phosphonium chloride. Mass transfer coefficients could be determined as a function of the agitation speed. Despite limited available data, an equation that correlates the Sherwood number to the Reynolds and Schmidt numbers has been proposed.
6.1 Introduction

Phase transfer catalysis (PTC) is an important tool in the manufacture of pharmaceuticals and fine chemicals. Whenever the overall reaction is inhibited because its reactants are soluble in different phases, PTC offers a convenient way to bring the reactants together. The key to PTC is the addition of a phase transfer catalyst (Starks, 1971) which is able to transfer the reactants across the phase boundaries. The most common PT catalysts are quaternary ammonium or phosphonium salts but crown ethers and cryptands are also known to be suitable catalysts. When the phase transfer catalyst is immobilized to a solid support, the reaction is termed triphase catalysis (Regen, 1975). The most widely used solid supports are polymers like polystyrene which are also common ion-exchange resins. However, silica gel and alumina have been used as solid supports as well (Ford, 1984). Triphase catalysis can be categorized under three major groups, namely liquid-liquid-solid (L-L-S) which will be covered in this work, liquid-solid-solid (S-L-S), and gas-liquid-solid (G-L-S). However, the latter is commonly referred to as a two-phase G-L PTC system in the literature.

The advantages of triphase catalysis over conventional PTC are evident: The catalyst can be easily separated from the product stream, thus making the reaction suitable for continuous operation with attendant lower operating costs. The TP catalyst can be recovered, regenerated to its original activity, and reused until it loses its mechanical stability. Despite these advantages, triphase catalysis does not enjoy industrial acceptance at present. In fact, there is no single major process operating in industry that uses a TP catalyst in the key synthesis step. The main reasons are reduced activities due to diffusional limitation of the
supported catalysts compared to their homogeneous analoges. Furthermore, the synthesis of large quantities of triphase catalysts with specific concentrations of functional groups tends to be expensive.

Mass transfer plays an important role in triphase catalysis. Therefore, mass transfer effects in TPC systems cannot be neglected and any detailed modeling of triphase catalytic systems will require a knowledge of mass transfer coefficients. So far, no correlations for estimating these are available. The number of publications dealing in detail with mass transfer effects in TPC systems is limited (Marconi and Ford, 1983; Wang and Yang, 1991, 1993; Dutta and Pangarkar, 1994; Desikan and Doraiswamy, 1995; Naik and Doraiswamy, 1998; Glatzer et al., 1998). Dutta and Pangarkar (1994) used the standard theory for porous catalysts to estimate an average mass transfer coefficient for the aqueous and organic phases. The authors found the mass transfer coefficient to be dependent on agitation speed and particle size. Wang and Yang (1992) suggested a dynamic model which contained separate mass transfer coefficients for the two liquid phases to describe the complex diffusion-reaction scenario in TPC systems. This model was later significantly improved by Desikan and Doraiswamy (1995, 1999). The modifications accounted for reversibility of the ion-exchange reaction in the aqueous phase and also for nonisothermal effects. In order to validate these models mass transfer as well as diffusion coefficients need to be estimated. Naik and Doraiswamy (1998) give a summary of PTC and TPC that emphasizes both their chemistry and engineering aspects. The authors discuss available models for soluble and insoluble PTC in great detail. At about the same time, Glatzer et al. (1998) published an experimental procedure to determine the mass transfer coefficients for the two liquid phases of a TPC system simultaneously. A rotating disk contactor (RDC) was specifically designed for this
purpose. The authors reported organic-phase mass transfer coefficients for the esterification of benzyl chloride with sodium acetate mediated by polymer bound tributylmethylammonium chloride as the immobilized PT catalyst.

6.2 Previous Studies on Mass Transfer in Two-Phase Systems for Well-Defined Hydrodynamics

For the case of gas-liquid systems, there are various models of contactors with known interfacial areas for mass transfer. A summary is given by Doraiswamy and Sharma (1984). The authors classify the contactors in two groups, those with and without well established hydrodynamics. Among the latter, the stirred contactor is particularly noteworthy. It is a stirred vessel with an undisturbed gas-liquid interface where the gas and liquid phases can be stirred independently. Construction details are given by Levenspiel and Godfrey (1974), Danckwerts and Alper (1975), Sridharan and Sharma (1976) and Yadav and Sharma (1979). Levenspiel and Godfrey proposed a unique double mixed contactor and studied mass transfer with and without reaction. Interface plates with different numbers of holes were used to control the surface area and to keep the gas-liquid interface undisturbed at high agitation speeds. Mass transfer coefficients as a function of agitation speed were determined for different systems in various kinetic regimes.

Melville and Goddard (1985) studied mass transfer enhancement in a solid-liquid phase transfer catalytic system. They obtained analytical solutions for the stagnant film model which agreed well with numerical solutions to the transport equations for the von Kármán rotating disk flow. In 1988 Melville and Goddard reported the development of a rotating disk contactor for studying mass transfer with reaction. Experimental results for a solid-liquid PTC system
obtained from this unit contributed to identifying the underlying mechanism. A rotating disk of potassium acetate was used to contact it with a solution of benzyl chloride and the quaternary ammonium salt Aliquat 336 as catalyst in acetonitrile. The disk was designed such that a cylindrical pellet of potassium acetate was inserted in the center of an aluminum disk. They conclude that the first step of the solid-liquid PTC (SLPTC) mechanism is dissolution of potassium acetate. This is followed by a fast reaction on Aliquat 336 to yield aliquat acetate which subsequently reacts with benzyl chloride to yield benzyl acetate.

Many correlations have been suggested to estimate mass transfer coefficients in two-phase systems for various types of physical scenarios. Oldshue (1983) gives a summary of available correlations for liquid-solid, liquid-liquid and gas-liquid mass transfer, and also an estimate of the mass transfer rate of a G-L-S system, namely, the oxidation of sodium sulfite in water. Cussler (1997) gives selected mass transfer correlations for different physical situations for fluid-fluid and fluid-solid interfaces. Of these, four are particularly noteworthy for the current work:

\[ k \left( \frac{1}{V_g} \right)^{1/3} = 0.0051 \left( \frac{V_o}{aV} \right)^{0.67} \left( \frac{D}{V} \right)^{0.50} (ad)^{0.4} \]  

This equation is used to estimate the mass transfer coefficient at liquid-solid interfaces in packed towers. According to Cussler (1997), it might be the best available correlation for liquids. Note that in this equation the reciprocal Schmidt number is raised to a positive fractional power.

\[ \frac{kd}{D} = 0.026 \left( \frac{dV_o}{V} \right)^{0.8} \left( \frac{V}{D} \right)^{1/3} \]
This correlation is used for turbulent flow through tubes and horizontal slits. As in many correlations, the Schmidt number is raised to the power 1/3. In turbulent flow, the Sherwood number can often be correlated by the Reynolds number raised to the power 0.8.

\[
\frac{kd}{D} = 0.62 \left( \frac{d^2 \omega}{2v} \right)^{1/2} \left( \frac{v}{D} \right)^{3/4} \tag{3}
\]

This correlation was suggested by Levich (1962) for the estimation of the mass transfer coefficient at a solid-liquid interface with the solid being a rotating disk. Here, \(d\) is the disk diameter and \(\omega\) the disk rotation in radians/time. The equation should be used for laminar flow around the disk but is valid for Reynolds numbers as high as 20,000 (Cussler, 1997).

(d) For higher Reynolds numbers, the following correlation should be used instead (Cornet et al., 1969):

\[
\frac{kd}{D} = 0.0198 \left( \frac{d^2 \omega}{2v} \right)^{0.8} \left( \frac{v}{D} \right)^{3/4} \tag{4}
\]

Hammerschmidt and Richarz (1991) studied Grignard reagent formation from the reaction of a rotating disk of magnesium with bromocyclopentane. They report that this reaction is strongly mediated by mass transfer at a temperature of 25°C up to a rotating disk speed of 6300 rpm. Mass transfer coefficients as a function of the disk speed were obtained from equations (3) and (4).

It may be noted from equations (1), (2) and (4) that small factors (0.0051, 0.026 and 0.0198) are usually typical of turbulent flow.
6.3 Objective of Present Study

The present work focuses on the determination of external mass transfer coefficients from the organic bulk phase to the surface of the catalyst in TP catalytic systems. Details of design and construction of an RDC were discussed in a previous publication by the authors (1998). It was shown in that paper that it is advantageous to use a model system with negligible noncatalytic reaction. The synthesis of octyl acetate from octyl bromide and potassium acetate has a very slow noncatalytic component. This reaction will be denoted as "base reaction" throughout this paper. The large alkyl group of the reactant causes the base reaction to be slow since the solubility in the aqueous phase and the intrinsic reactivity are reduced. This reaction system is investigated in the present work with polymer supported tributylmethylammonium and -phosphonium chloride as the phase transfer catalysts. Mass transfer coefficients as well as the intrinsic rate constant for the chosen reaction conditions are determined. All the available data are then used to propose a general correlation for mass transfer coefficients in TPC systems.

Experimental work with RDC revealed certain limitations of the method. These are either operational or inherent to certain reaction systems. The latter occurred with systems that involved the transfer of hydroxide ions. Data obtained from RDC with ester hydrolysis reactions on hexyl acetate and octyl acetate raise the question whether it is possible to decouple the organic and inorganic reaction steps of a PTC cycle in the way it is accomplished in RDC.

6.4 Determination of Mass Transfer Coefficients

The rationale behind the determination of mass transfer coefficients for three-phase systems has been presented in an earlier publication by the authors (1998). This involves an
analysis of the various regimes of solid-liquid systems with the solid not soluble in the liquid phase. Doraiswamy and Sharma (1984) have discussed an analogous regime analysis for gas-liquid systems in great detail. However, in the case of a liquid-liquid-solid system with the solid insoluble in the liquids, only three different regimes are possible since the reaction is restricted to the surface of the catalyst:

- **Regime 1**: Very slow reaction, Kinetic control
- **Regime 1-2**: Very slow to slow reaction, Mixed control
- **Regime 2**: Slow to very fast reaction, Mass transfer control

The criteria for the different regimes are:

**Regime 1**

\[ k_L a[A_o] \gg k'_{\text{cat}} [A_o] \quad (5) \]

**Regime between 1 and 2**

\[ k_L a[A_o] = k'_{\text{cat}} [A_o] \quad (6) \]

**Regime 2**

\[ k_L a[A_o] \ll k'_{\text{cat}} [A_o] \quad (8) \]

**6.5 Experimental**

In this section, we will shortly discuss the visualization of flow patterns in RDC under typical operating conditions. In addition, the chosen reaction system as well as the analysis of
samples are described. These are followed by a brief description of the experimental work with the slurry reactor and RDC.

6.5.1 Hydrodynamics: Flow patterns within the contactor

A few words on the visualization of the flow patterns in RDC would be relevant at this stage. This could be accomplished by use of a dye or solid particles. At agitation speeds beyond 180 rpm both bulk phases are well mixed and governed by a characteristic radial flow pattern in which the fluid particles are discharged to the vessel wall in a horizontal direction. Below 120 rpm there are regions which are not well mixed and the flow appears random. Rotating coil paddles cause low pressure zones directly above and below the coils. The fluid particles circulate toward these zones, flow into the coil and are centrifugally thrown outward from the rotating coil ends toward the glass cylinder walls where the stream is divided into upward and downward flows. The perturbations at the liquid-liquid phase are small when the flows are in the same direction near the interface in each bulk, i.e. when the flow patterns in the top phase are the mirror image of the ones in the bottom phase. The opposite case leads to countercurrent flow near the interface in each bulk which induces waves and draws droplets of one phase into the other bulk phase resulting in a high degree of dispersion. The upward flow of the bottom phase and the downward flow of the top phase are deflected by the glass plate and then flow is tangential along the rotating disk. Thus the region surrounding the disk is well mixed.

The higher the speed of the disk in one phase the more the fluid particles carried over into the other phase, mainly from the organic phase into the aqueous phase. This causes a high
degree of dispersion within the aqueous phase. An increased agitation speed of the stirrer in the aqueous has the same effect.

6.5.2 Reaction system

The reaction of octyl bromide with potassium acetate to yield octyl acetate was investigated. This reaction was promoted by either polymer bound tributylmethylammonium chloride or tributylmethylphosphonium chloride. Both catalysts are commercially available from Fluka Chemical Corp. and were not further modified. 1.0 g of tributylmethylammonium chloride is equivalent to 0.85 mmol (1.27 mmol for phosphonium catalyst). All the chemicals were of analytical grade.

This reaction has a very slow base component. The pseudo-first-order reaction rate constant in the slurry mode was found to be approximately $1.8 \times 10^{-6}$ l/min. Compared to the benzyl chloride system earlier investigated by the authors (1998), the base reaction of the current system is about 270 times slower.

In this reaction system, the organic reagent octyl bromide is dissolved in toluene and the inorganic reagent potassium acetate in water. The reaction proceeds according to Starks' extraction mechanism. Potassium acetate undergoes an ion-exchange reaction with the chloride form of the phase transfer catalyst to form potassium chloride which leaves the catalyst coordinated with the acetate. The catalyst can cross the liquid-liquid interface to react with octyl bromide in the organic phase to yield octyl acetate. After reaction has occurred, the PTC is coordinated with the bromide and crosses the liquid-liquid interface back into the aqueous phase and the reaction cycle continues.
The ion-exchange reaction in the aqueous phase is very fast compared to the reaction in the organic phase, and the concentration of the aqueous phase reactant is higher than that of the organic reactant. Hence the ion-exchange reaction can be considered to be at equilibrium and the organic phase reaction to be the rate limiting reaction step.

6.5.3 Analysis of samples

The concentrations of octyl bromide and octyl acetate were determined using a gas chromatograph. A Perkin Elmer gas chromatograph (PE 3000 Autosystem) with FID was used. Each analysis was run isothermally for 9 min. at 150 °C. A packed column from Supelco was used for the analysis (Carbopack: 10% SP-2250) with a length of 2.0 m and a diameter of 1/8 inch. The concentrations of octyl acetate were used to determine the conversion since these are very low in RDC and thus the relative changes in concentration are much higher for the product.

6.5.4 Studies with slurry reactor

A 600 ml agitated vessel from PARR Instruments was used as a slurry reactor. Results obtained from this reactor were used to compare the reactivities of the ammonium and phosphonium PT catalysts and to obtain the activation energies of the catalytic and noncatalytic reaction steps.

A series of experiments with different catalyst concentrations was carried out to determine the reactivities of the catalyst (catalyst loadings: 0.5, 1.0, 2.0 and 3.0 mmol). The temperature was held constant at 85°C. The initial composition of the organic phase was 69.5
ml octyl bromide + 165 ml toluene (~1.71 mol/l octyl bromide), and that of the aqueous phase 125 g potassium acetate + 250 ml water (~3.5 mol/l).

The Arrhenius parameters were estimated with a number of experiments at different temperatures (65, 75, 85 and 95°C for reactions with TP catalyst; 85, 90 and 95°C for the noncatalytic reaction). All other parameters remained unchanged.

6.5.5 Studies with RDC

Conversion vs. time data obtained from RDC contain information about the rate constants per unit surface area of the catalyst and allow us to calculate mass transfer coefficients for the organic phase reaction. In this unit the TP catalyst is equiaccessible to the bulk phases and the surface area of the catalyst is exactly known. It is assumed that the reaction can only take place on this surface. The rate constants are obtained as a function of agitation speed under mass transfer limited conditions. The levels of agitation were 120, 180, 240, 300, 360, 420, 480, 600 and 720 rpm. The rotation of the disk was held constant at 12 rpm for all reaction runs.

Mass transfer coefficients can be determined from experiments at low agitation speeds where external mass transfer is the controlling mechanism. The intrinsic reaction rate constant can be obtained from experiments at high enough agitation speed where mass transfer is no longer controlling (kinetical plateau). All experiments were conducted at 85°C. The initial concentration of benzyl chloride in the organic phase was ~1.71 mol/l, and that of potassium acetate in the aqueous phase ~3.5 mol/l (5.0 moles salt + 1000 ml water). The pockets on the disc hold 2.4 g of triphase catalyst.
6.6 Results and Discussion

First, the results from studies with the slurry reactor are discussed in detail. The activation energies from reaction systems from the current work as well as from earlier works by the authors (Glatzer et al., 1998; Glatzer and Doraiswamy, 1999) are comparatively assessed in this discussion. This is followed by a detailed discussion of the experimental data obtained from studies with RDC and the calculation of mass transfer coefficients. The section concludes with the suggestion of a general equation for TPC systems that correlates the Sherwood number to the Reynolds and Schmidt numbers.

6.6.1 Slurry reactor

The kinetics of the reaction system of octyl bromide with potassium acetate to yield octyl acetate reveals a complex mechanism which has been separately investigated by Satrio et al. (1999). A plot of the data obtained from the experiments with different catalyst loadings proved that the reactivity of the two TP catalysts was approximately equal to the ratio of the amounts of effective chloride bound to the resins.

Arrhenius plots for reaction runs with both TP catalysts are shown in Figure 6.1 and for the base reaction in Figure 6.2. The values for the activation energies and the frequency factor are given in Table 6.1.

The base reaction follows pseudo-first-order kinetics. For the reaction runs with TP catalyst, the initial rates were used to estimate the Arrhenius parameters. It is assumed that initially the reaction rates obey pseudo-first-order kinetics. The data show that the TP catalysts do not lower the activation energies significantly but do have an effect on the frequency factor
which is a measure for the number of collisions leading to reaction. A similar trend was observed by Glatzer and Doraiswamy (1999) with PTC mediated reactions involving the transfer of hydroxide. On the other hand, Glatzer et al. (1998) and Desikan and Doraiswamy (1999) studied the esterification of benzyl chloride with sodium acetate and reported a decrease in activation energy when a TP catalyst was added to the reaction mixture.

It was observed that octyl bromide is converted into octyl acetate much faster than octyl chloride. In fact, no appreciable conversions could be obtained under RDC conditions with octyl chloride as the reactant. In PTC reactions with nonpolar organic solvents the organic reaction step follows an $S_N2$ mechanism because the existence of free ions is not favorable. In the case of octyl bromide, the $S_N2$ reaction step is faster since the bromide is a much better leaving anion than the chloride. A substitution reaction at a saturated carbon atom cannot proceed without an agent solvating the leaving anion which can in these cases be the catalyst cation or water molecules at the liquid-liquid interface. The chloride anion has a larger charge-to-volume ratio than bromide which results in larger binding energies of the alkali chlorides. The coordination of the chloride anion with a quarternary ammonium or phosphonium ion significantly reduces the coulombic binding energies because of its much larger size and consequently larger cation-anion distances. This will result in a larger decrease in activation energy than observed in corresponding bromide substitutions. Iodide will form an even better leaving group but the high extraction constant and equilibrium constant observed with PT catalysts in the presence of free iodide ions will limit the amount of aqueous reactant to be transferred into the organic phase.

A strong decrease in the activation energy with PTC promoted reactions involving the transfer of hydroxide was most likely not observed due to the high degree of hydration of $OH^-$. 
The PTC assisted reaction is usually assumed to occur at the interface (Starks et al., 1994; Dehmlow and Dehmlow, 1993) because direct transfer of hydroxide into the organic bulk phases is not favored. However, Glatzer and Doraiswamy (1999) showed that the locale of reaction strongly depends on the solvent and under certain conditions autocatalytic behavior suggests a shift of the locale of reaction from the liquid-liquid interface to the bulk. The hydroxide anion will be transferred in hydrated form and the effective size of the anion will be much larger than its 'naked' form. Coulomb interaction energies are not reduced by coordination with a quarternary salt as strongly as one would expect with the naked hydroxide anion, and consequently the activation energy will not be reduced significantly in the presence of a PT catalyst.

6.6.2 RDC: Access to mass transfer data

Slurry reactor studies showed that the esterification of ocyl bromide does not follow simple power-law kinetics (Satrio et al., 1999). However, due to the low conversions achieved in RDC, the data can be approximated well by assuming pseudo-first-order kinetics.

Conversion vs. time data were obtained with both TP catalysts, namely polymer supported tributylmethylammonium chloride and the corresponding phosphonium chloride. The catalytic rate is the difference in the conversions between runs with and without catalyst. Below 360 rpm the reaction systems does not have any measurable base reaction, while beyond this speed the base reaction cannot be neglected. Hence, an increase in the rates can be solely attributed to an enlarged liquid-liquid surface area due to dispersion of the phases. Thus the purely catalytic effect increases till a certain point and then levels off (kinetic plateau). Figures 6.3 and 6.4 show plots of -ln(1-X) vs. time for the purely catalytic effect of the
phosphonium and ammonium catalysts, respectively. The slopes were obtained by regression analysis with the constraint that there is no intercept. At high agitation levels (>300 rpm) the slopes from corresponding runs with and without TP catalyst were subtracted. The controlling mechanisms of the overall reaction rate are shown in Figure 6.6. For the experiments with phosphonium catalyst, the average value from the experiments at 300 to 420 rpm was used as an estimate for the intrinsic pseudo-first-order rate constant per unit volume for the catalytic reaction alone. In this region, the values of the slopes were constant indicating that the reaction was under kinetic control. The ammonium catalyst had a significantly lower activity causing lower overall rates and a shift of the kinetically controlled region towards lower agitation speeds. At 240 rpm the reaction was already under kinetic control. The average value from experiments at 240 and 300 rpm was used to estimate the intrinsic rate constant in this case. Experiments with the ammonium catalyst revealed a large increase in the conversions at agitation speeds beyond 300 rpm. Glatzer et al. (1998) called this effect "dispersion effect" which can now be explained by the fact that at high agitation speeds a few catalyst particles penetrate the mesh sieve over time and cause higher conversions through their presence in the bulk phases. These tiny amounts of TP catalyst react through two mechanisms: The catalytic reaction cycle and the physical changes induced by the surface active properties of the catalyst which lead to a higher degree of dispersion and subsequently an enhanced base reaction rate. We can see in Figure 6.6 that the rates level off in the dispersion regime if we disregard data points from times larger than 660 minutes. For the full range (1560 min.), the conversion vs. time data show a trend with positive curvature and the slopes keep increasing due to a slow release of polymer beads from the disk which increases with agitation (see Figure 6.5, dashed line). Apparently, the physical influence of the catalyst on the bulk phases is not a strong
function of the catalyst concentration in contrast to the other mechanism, namely the catalytic reaction cycle. The esterification of benzyl chloride (Glatzer et al., 1998) has such a large base reaction component that the conversions due to the dispersion effect were mainly caused by the physical changes the free catalyst induced in the bulk phases and not so much by its catalytic activity. Consequently, the slopes of \(-\ln(1-X)\) vs. time data increased enormously but the trend remained linear. Although both TP catalysts were synthesized from the same polymer beads, the dispersion effect is much stronger when the ammonium catalyst was on the disk. The values for the slopes are given in Table 6.2.

6.6.3 Mass transfer coefficients

In RDC, the surface area of the catalyst per unit volume of the reactor is \(a = 0.03\text{cm}^{-1}\) (Glatzer et al., 1998). The mass transfer coefficients as a function of the bulk agitation speed were obtained from equation (7) and are given in Table 6.3 (P and N denote phosphonium and ammonium TP catalysts, respectively).

Comparing the values of \(k_La\) and \(k_{cat}'\) we see that the mass transfer rates are higher than the kinetic rate. Since the values are within one order of magnitude, we conclude that the reaction takes place in the overlapping regime 1-2. Figure 6.6 shows a plot of the mass transfer coefficients as a function of the agitation rate.

6.6.4 Generalization of mass transfer data

Before we can suggest a general correlation for mass transfer in triphase catalytic systems, it is crucial to estimate certain physical properties such as pure liquid and mixture viscosities and diffusion coefficients with the least possible error.
6.6.4.1 Estimation of viscosity and diffusion coefficient

In order to determine the Sherwood, Reynolds, and Schmidt numbers, knowledge of the viscosity of the liquid mixtures and the diffusion coefficient of the organic reactant in toluene is necessary. The data for the benzyl chloride - toluene system refer to data previously published by the authors (1998). The pure-liquid viscosities are as follows:

- **Toluene**: \( \eta_{\text{as} \cdot \text{c}} = 3.16 \times 10^{-4} \text{ Pa} \cdot \text{s} \)
- **Benzyl chloride**: \( \eta_{\text{as} \cdot \text{c}} = 5.16 \times 10^{-4} \text{ Pa} \cdot \text{s} \)
- **Octyl bromide**: \( \eta_{\text{as} \cdot \text{c}} = 6.61 \times 10^{-4} \text{ Pa} \cdot \text{s} \)

The values for toluene and benzyl chloride were obtained from ASPEN, and that for octyl bromide was estimated by Van Velzen, Cardoso, and Langenkamp's method (Van Velzen et al., 1972). Due to the low conversions in RDC, the viscosity changes introduced by the organic products can be neglected. The viscosities of the mixtures were obtained from:

\[
\ln \eta_m = \sum x_i \ln \eta_i
\]

(9)

where \( x_i \) is the volume fraction of component \( i \) in its mixture. The method of Grunberg and Nissan (1949) which involves mole fractions and an additional term with an interaction parameter led to virtually the same results. The interaction parameter was estimated by a group contribution method published by Isdale et al. (1985) (see also Reid et al.; 1986). The following values were obtained with equation (9):

- **Series A**: Benzyl chloride-toluene \( \eta_m = 3.324 \times 10^{-4} \text{ Pa} \cdot \text{s} \)
- **Series B**: Octyl bromide-toluene \( \eta_m = 3.930 \times 10^{-4} \text{ Pa} \cdot \text{s} \)

The diffusion coefficient \( D_{AB} \) was estimated from the Wilke-Chang correlation. The association factor was taken as 1.0, and the molar volumes of the solute at its normal boiling
temperature estimated from the additive volume table published by Le Bas (1915). Ideal behavior of the mixtures was assumed. The values for the diffusion coefficients were as follows:

Series A: Benzyl chloride-toluene \( D_{AB} = 3.984 \times 10^{-5} \text{ cm}^2/\text{s} \)

Series B: Octyl bromide-toluene \( D_{AB} = 2.644 \times 10^{-5} \text{ cm}^2/\text{s} \)

6.6.4.2 Development of a generalized correlation for mass transfer in TPC systems

Although the data obtained from experiments with RDC are limited in the sense that only three different reaction systems (two reactions with one of them using two catalysts) have been investigated, the authors believe that a first generalization can be suggested. The key idea for a general correlation for TPC systems is to break up the three-phase system (L-L-S) into two L-S systems and use the correlation for each "side" of the three-phase system separately. Figure 6.7 shows a plot of \( \log Sh vs. \log Re \). The plot contains data from all the three reaction systems and indicates that all the data points fall on one line.

The following equation correlating the Sherwood number with the Reynolds and Schmidt numbers was found to predict the mass transfer coefficient well:

\[
\frac{k_n d}{D} = 0.005 \left( \frac{d^2 \omega}{2v} \right)^{1/4} \left( \frac{D}{v} \right)^{1/3}
\]

(10)

where \( d \) is the stirrer diameter and \( \omega \) the disk rotation in radians/time. The factor and the exponents were not taken from the regression line in Figure 6.7 due to the limitation in the number of data points but empirically found by trial and error. The above equation shares some similarities with equation (1) which is used for a liquid flowing through a packed tower.
and according to Cussler (1997) supposed to be one of the best available correlations for liquids with the tendency to give lower estimates than other correlations. The factors are almost similar and both equations raise the reciprocal Schmidt number to a positive fractional power. The precise estimation of the diffusion coefficient is crucial to this equation since $D$ occurs on both sides of the equation, once in the numerator and once in the denominator. The experimentally determined and predicted Sherwood numbers are listed in Table 6.4. The equation is capable of predicting the Sherwood number to within 20% error. However, in most cases the prediction was significantly better. This is commonly an accepted level of uncertainty in the prediction of Sherwood number with these types of correlations.

6.7 Limitations of RDC

These will be discussed under two kinds of limitations, namely operational limitations and those inherent to reaction systems.

6.7.1 Operational limitations

The current design of RDC introduces certain operational difficulties: The surface area of the catalyst per unit volume of the reactor is very small which leads to very low conversions and long reaction times. Modern analytical techniques, however, enable us to precisely determine even very small quantities of a reagent. RDC, with its thin catalytic layer on the disk, is almost like a differential reactor, which has become very useful in the analysis of reaction systems involving heterogeneous catalysts. But at low conversions, a base reaction becomes difficult to subtract from the overall reaction in order to quantify the purely catalytic effect of the TP catalyst. Long reaction times, on the other hand, tend to soften the polymer
backbone of the catalyst which leads to a partial release of the catalyst from the disk into the bulk. A mesh sieve with smaller openings can prevent the extent of this slow release. On the other hand, it reduces the available surface area (already small) and thus the conversions, and might introduce an additional significant resistance when the mesh sieve starts to act like a membrane at a certain mesh size. The release of catalyst into the bulk phases causes large conversions with systems with significant base reaction which, as already noted, is referred to as "dispersion effect." Future work with RDC should involve design modifications to enhance the value of $a$ which is currently 0.03 cm$^{-1}$.

### 6.7.2 Limitations inherent to reaction systems

The authors found that the method to determine mass transfer coefficients with a rotating disk contactor does not work for certain reaction systems (Glatzer, 1999). The methods seems to fail with systems that involve the transfer of hydroxide ions. Hydroxide is one of the most difficult to transfer into an organic phase due to its high degree of hydration and its high charge-to-volume ratio. It is known that PTC-promoted reactions with strong inorganic bases follow interfacial mechanisms, i.e. no active transfer of the anion by the catalyst complex $Q^+OH^-$ occurs across the phase boundary (e.g. Dehmlow and Dehmlow; 1993; Starks et al., 1994). The alkaline hydrolysis reactions of hexyl acetate and octyl acetate to yield hexanol and octanol were investigated. In the slurry mode, the reaction proceeded fast and almost complete conversions were achieved within several hours. However, when the reactions were carried out in RDC, no clear difference in the conversions between corresponding experiments with and without TP catalyst on the disk could be discerned. The conversions with the octyl acetate system which has very little base reaction were almost
negligible. It may, therefore, be concluded that the conversion was due entirely to the base reaction for such systems.

Thus, it would seem that a reaction following an interfacial mechanism cannot be decoupled in the way it is done in RDC. The intermediate $Q^+OH^-$ has simultaneous contact with both liquid phases in the slurry mode, the entire reaction taking place at the liquid-liquid interface. In RDC, the overall reaction is divided into two separate two-phase reactions. Consequently, the formation of the intermediate $Q^+OH^-$ and the displacement reaction with the organic substrate are reaction steps in series. What perhaps happens is that due to the high hydrophilicity and high degree of hydration of the intermediate $Q^+OH^-$, the thin aqueous film that is formed around the TP catalyst during its passage through the aqueous phase is not displaced as it moves into the organic phase during a rotation. This aqueous film forms a barrier for the organic (and strongly lipophilic) substrate around the TP catalyst, leading to a significant fall in the reaction rate (almost to zero).

6.8 Conclusion

The objective of this research was the determination of single-phase mass transfer coefficients for triphase catalytic systems in order to develop a general correlation for such systems. The experiments were carried out in a rotating disk contactor (RDC) which had been designed earlier (Glatzer et al., 1998) specifically for this purpose.

The esterification of octyl bromide with potassium acetate to yield octyl acetate was chosen as the model system. The reaction was promoted by either polymer bound tributylmethyl ammonium chloride or its corresponding phosphonium species. The main advantage of this system is the fact that it has a negligible base reaction at low agitation levels.
This reaction was found to be mass transfer controlled at low agitation speeds. Mass transfer coefficients as a function of agitation speed could be determined for this model system. In an earlier work by the authors (Glatzer et al., 1998), mass transfer coefficients had been determined with the same equipment for the esterification of benzyl chloride with sodium acetate. With the available data from both reaction systems (actually three systems since two different catalysts were used for one of the reactions), a general correlation could be developed. This equation treats the three-phase system as two independent L-S systems (as achieved in RDC through decoupling of the two reactions in the bulk phases). The equation itself should be regarded as a preliminary one in view of the limited number of reaction systems studied.

### 6.9 Notation

- $A, B$ = liquid-phase species
- $[A_o]$ = bulk concentration of $A$, mol/cm$^3$
- $a$ = liquid-solid interfacial area per unit volume of the reactor, cm$^2$/cm$^3$
- $d$ = characteristic length (diameter of disk, nominal packing size), m
- $D$ = diffusion coefficient, m$^2$/s
- $D_{AB}$ = binary diffusion coefficient of species $A$ in solvent $B$, m$^2$/s
- $E$ = activation energy, kJ/mol
- $g$ = gravitational constant, m/s$^2$
- $k, k_L$ = true liquid-side mass transfer coefficient, cm/min
- $k_{LR}$ = liquid-side mass transfer coefficient in the presence of reaction, cm/min
- $k_o$ = frequency factor, 1/min
- $k'_{cat}$ = pseudo-first-order rate constant of catalytic reaction, 1/min
- $N$ = TP catalyst: tributylmethylammonium chloride
- $P$ = TP catalyst: tributylmethylphosphonium chloride
\[ Re = \text{Reynolds number} = d^2 \omega / 2v, \text{dimensionless} \]

\[ Sc = \text{Schmidt number} = v/D, \text{dimensionless} \]

\[ Sh = \text{Sherwood number} = k_d / D, \text{dimensionless} \]

\[ t = \text{time, min} \]

\[ T = \text{temperature, K} \]

\[ v^o = \text{superficial or average fluid velocity, m/s} \]

\[ X = \text{conversion} \]

\[ x_i = \text{volume fraction of component } i \]

**Greek symbols**

\[ \eta_i = \text{dynamic viscosity of component } i, \text{Pa-s} \]

\[ \eta_m = \text{dynamic viscosity of the mixture, Pa-s} \]

\[ \nu = \text{kinematic viscosity, } \text{m}^2/\text{s} \]

\[ \omega = \text{speed of disk, radians/s} \]

### 6.10 Literature Cited


Table 6.1. Activation energies and frequency factors for the catalytic steps (tributylmethylammonium chloride and -phosphonium chloride) and for the base reaction.

<table>
<thead>
<tr>
<th>TPC</th>
<th>Amount of TPC [mmol]</th>
<th>Activation energy $E$ [kJ/mol]</th>
<th>Frequency factor $k_o$ [$\frac{1}{\text{min}}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>2.0</td>
<td>74.4</td>
<td>$4.24 \times 10^7$</td>
</tr>
<tr>
<td>P</td>
<td>2.0</td>
<td>74.2</td>
<td>$6.41 \times 10^7$</td>
</tr>
<tr>
<td>None</td>
<td>0</td>
<td>76.1</td>
<td>$1.64 \times 10^5$</td>
</tr>
</tbody>
</table>
Table 6.2. Mass transfer and intrinsic reaction rate constants as functions of agitation speed for the esterification of octyl bromide with potassium acetate.

<table>
<thead>
<tr>
<th>Agitation speed [rpm]</th>
<th>Phosphonium catalyst (k_L\alpha) or (k'_{cat}) [min(^{-1})]</th>
<th>Ammonium catalyst (k_L\alpha) or (k'_{cat}) [min(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>(4.262 \times 10^{-6})</td>
<td>(2.168 \times 10^{-6})</td>
</tr>
<tr>
<td>180</td>
<td>(4.380 \times 10^{-6})</td>
<td>(2.282 \times 10^{-6})</td>
</tr>
<tr>
<td>240</td>
<td>(4.750 \times 10^{-6})</td>
<td>(2.482 \times 10^{-6})</td>
</tr>
<tr>
<td>300</td>
<td>(5.409 \times 10^{-6})</td>
<td>(2.558 \times 10^{-6})</td>
</tr>
<tr>
<td>360</td>
<td>(5.578 \times 10^{-6})</td>
<td>((4.187 \times 10^{-6}))</td>
</tr>
<tr>
<td>420</td>
<td>(5.491 \times 10^{-6})</td>
<td>((7.485 \times 10^{-6}))</td>
</tr>
<tr>
<td>480</td>
<td>((5.701 \times 10^{-6}))</td>
<td>-</td>
</tr>
<tr>
<td>600</td>
<td>((6.238 \times 10^{-6}))</td>
<td>-</td>
</tr>
<tr>
<td>720</td>
<td>((6.928 \times 10^{-6}))</td>
<td>-</td>
</tr>
</tbody>
</table>

Average \(k'_{cat}\) \(5.493 \times 10^{-6}\) \(2.520 \times 10^{-6}\)
### Table 6.3

Mass transfer rates and mass transfer coefficients as functions of agitation speed for the esterification of octyl bromide with potassium acetate (TP catalysts: tributylmethylammonium chloride and -phosphonium chloride).

<table>
<thead>
<tr>
<th>Agitation speed [rpm]</th>
<th>Mass transfer rate $k_La$ [min$^{-1}$]</th>
<th>Mass transfer coefficient $k_L$ [cm/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>P-120</strong></td>
<td>$1.903 \times 10^{-5}$</td>
<td>$6.339 \times 10^{-4}$</td>
</tr>
<tr>
<td><strong>P-180</strong></td>
<td>$2.081 \times 10^{-5}$</td>
<td>$6.938 \times 10^{-4}$</td>
</tr>
<tr>
<td><strong>P-240</strong></td>
<td>$3.512 \times 10^{-5}$</td>
<td>$1.171 \times 10^{-3}$</td>
</tr>
<tr>
<td><strong>N-120</strong></td>
<td>$1.552 \times 10^{-5}$</td>
<td>$5.174 \times 10^{-4}$</td>
</tr>
<tr>
<td><strong>N-180</strong></td>
<td>$2.416 \times 10^{-5}$</td>
<td>$8.054 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Table 6.4. Experimental and predicted Sherwood numbers for several esterification reactions: benzyl chloride with sodium acetate (TP catalyst: tributylmethylammonium chloride); octyl bromide with potassium acetate (TP catalysts: tributylmethylammonium chloride and -phosphonium chloride).

<table>
<thead>
<tr>
<th>Reaction system</th>
<th>Agitation speed [rpm]</th>
<th>$Sh_{\text{experimental}}$</th>
<th>$Sh_{\text{predicted}}$</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl chloride (Glatzer et al., 1998)</td>
<td>N-120</td>
<td>2.050</td>
<td>1.753</td>
<td>-14.5</td>
</tr>
<tr>
<td></td>
<td>N-180</td>
<td>2.196</td>
<td>2.376</td>
<td>+8.2</td>
</tr>
<tr>
<td></td>
<td>N-240</td>
<td>2.928</td>
<td>2.948</td>
<td>+0.7</td>
</tr>
<tr>
<td>Octyl bromide</td>
<td>P-120</td>
<td>1.399</td>
<td>1.359</td>
<td>-2.9</td>
</tr>
<tr>
<td></td>
<td>P-180</td>
<td>1.531</td>
<td>1.842</td>
<td>+20.3</td>
</tr>
<tr>
<td></td>
<td>P-240</td>
<td>2.584</td>
<td>2.285</td>
<td>-11.6</td>
</tr>
<tr>
<td></td>
<td>N-120</td>
<td>1.142</td>
<td>1.359</td>
<td>+19.0</td>
</tr>
<tr>
<td></td>
<td>N-180</td>
<td>1.777</td>
<td>1.842</td>
<td>+3.7</td>
</tr>
</tbody>
</table>
Figure 6.1. Arrhenius plot ln (k) vs. 1/T for the catalytic steps. (TP catalysts: tributylmethylphosphonium chloride and tributylmethylammonium chloride).
Figure 6.2. Arrhenius plot $\ln(k)$ vs. $1/T$ for the base reaction.
Figure 6.3. Plot of $-\ln(1-X)$ vs. time for different bulk agitation speeds in the rotating disk contactor with 2 mmol polymer bound tributylmethylphosphonium chloride.
Figure 6.4. Plot of -ln(1-X) vs. time for different bulk agitation speeds in the rotating disk contactor with 2 mmol polymer bound tributylmethylammonium chloride.
Figure 6.5. Plot of catalytic rate constant $k_{cat}'$ vs. agitation speed for esterification of octyl bromide with potassium acetate (TP catalysts: tributylmethylammonium chloride and -phosphonium chloride). This plot identifies the controlling mechanisms (mass transfer or kinetic control; dispersion regime) at each level of the agitation speed. For the ammonium catalyst, the dashed line considers data of the full time range (1560 min.), the solid line only data up to 660 min.
Figure 6.6. Plot of mass transfer coefficient $k_L$ vs. agitation speed for several esterification reactions: benzyl chloride with sodium acetate (TP catalyst: tributylmethylammonium chloride); octyl bromide with potassium acetate (TP catalysts: tributylmethylammonium chloride and phosphonium chloride).
Figure 6.7. Plot of log (Sh) vs. log (Re) for several esterification reactions: benzyl chloride with sodium acetate (TP catalyst: tributylmethylammonium chloride); octyl bromide with potassium acetate (TP catalyst: tributylmethylammonium chloride and -phosphonium chloride).
CHAPTER 7. CONCLUSIONS AND RECOMMENDATIONS

7.1 General

Phase transfer catalysis (PTC) enjoys a wide range of applications in the manufacture of high-value chemicals like pharmaceuticals. PTC may be a suitable method to synthesize a product whenever each reactant is miscible in a different phase, e.g. the reaction of an organic compound miscible in one phase (usually an organic phase) with an inorganic salt miscible in the other (usually an aqueous phase). By addition of a PT catalyst, which functions as a ferrying agent and brings the reactants together in one phase, significant rate enhancements can be achieved. The PT catalyst which is most commonly a quaternary ammonium or phosphonium salt can be either added in soluble or supported form to the reaction mixture. In the first case we talk about homogeneous or conventional PTC, in the latter case about triphase catalysis (TPC). Triphase catalysis has huge operational advantages over homogeneous PTC due to its potential use in continuous operation with attendant lower operating cost: The catalyst can easily be separated from the product stream without the need for expensive separation techniques. In addition, the recovered TP catalyst can be regenerated to its original activity and reused until it loses its mechanical stability. However, TPC does not enjoy industrial acceptance at present due to the well-known fact that reactions which are mediated by a TP catalyst are significantly retarded by diffusional limitations. Another disadvantage is the fact that the production of TP catalysts with specific concentrations of functional groups tends to be costly. If one could overcome or limit the problem of reduced activity, triphase catalysis
would certainly become a superior alternative to homogeneous PTC due to the above mentioned operational advantages.

7.2 Conclusions

These are given under two different categories: conclusions with respect to mass transfer and with respect to catalyst efficacy.

7.2.1 Mass transfer studies

In the present study, an experimental procedure has been developed to determine external mass transfer coefficients for triphase catalytic systems since many TPC systems may be film diffusion limited under typical reaction conditions. A contactor generally referred to as a rotating disk contactor (RDC) has been specifically designed for this purpose. The main principle behind RDC is the fact that the two bulk phase reactions that together constitute a PTC cycle (ion-exchange reaction in aqueous phase and substitution reaction in organic phase) are decoupled and can therefore be treated as two reaction steps in series. Other features of RDC are equiaccessibility of the TP catalyst to both bulk phases and a precisely known surface area. From the data obtained from this unit it was possible to calculate mass transfer coefficients of several reaction systems. The following equation which correlates the Sherwood number to the Reynolds and Schmidt numbers has been suggested based on the data from this work:

\[
\frac{k_i d}{D} = 0.005 \left( \frac{d^2 \omega}{2v} \right)^{3/4} \left( \frac{D}{v} \right)^{1/3}
\]  

(1)
The key idea in this correlation is to break up the L-L-S TPC system into two L-S systems and use the correlation for each "side" of the three-phase system separately. For the reaction systems and reaction conditions that were investigated, the equation was capable of predicting the measured Sherwood number to within 20% error. This is commonly an accepted level of uncertainty in the prediction of the Sherwood number with these types of correlations.

7.2.2 Efficacy of TP catalyst

In view of conflicting reports on the efficacy of supported PTC, a comparative assessment of heterogeneous and homogeneous catalysts was made for different mechanistic categories of PTC systems. PT catalysts can be categorized into two major groups: those with predominantly lipophilic properties and those with predominantly hydrophilic properties. For the latter, it was possible to identify conditions under which the supported catalyst performed distinctly better than its soluble counterpart. The solubility of the homogeneous catalyst in the organic phase was found to be the most important factor in determining catalytic activity. Under certain conditions, polarity changes of the organic bulk phase induced autocatalytic behavior with a hydrophilic homogeneous catalyst, an observation not hitherto made. This autocatalytic behavior made it possible for them to proceed faster than their heterogeneous counterparts as more product built up with the progress of reaction. In conclusion, it can be stated that certain categories of heterogenized catalysts can perform better than the soluble counterparts for some reactions, notwithstanding their natural predilection to hinder reaction by diffusional limitation. This fact, coupled with the operational advantages of triphase catalysis, opens up the distinct possibility of its acceptance by industry. It is also noteworthy that operational advantages alone (even in cases where there is no enhancement in the rate due to
heterogenization or there is even a slight decrease in the rate) can justify the use of supported catalysts in selected cases.

7.3 Recommendations for Future Work

A generalized correlation for mass transfer in TPC systems has been proposed in the current work. In view of the limited number of reaction systems studied, this equation should be regarded as a preliminary one. The experimental data was obtained from a rotating disk contactor (RDC), a device with known catalytic surface area that exposes the catalyst equally to both liquid phases. The two reactions in the bulk phases, namely the ion-exchange reaction in the aqueous phase and the displacement reaction in the organic phase are decoupled in RDC. Hence the L-L-S three-phase system is treated as two independent L-S systems and the correlation can be used to estimate the Sherwood number for either "side" of the three-phase system.

The main problem in the design of RDC is the low ratio of catalytic surface area to reactor volume. This leads to extremely low conversions even after long reaction times. As a result, problems with chemical analysis are encountered, more replication may be needed, and propagation of errors may affect the results significantly. A modification of the current equipment therefore appears necessary before future experiments can be conducted. One possible way to increase the value of α is the use of multiple disks in the reactor which should be all mounted to the same axis. At the same time, the reactor volume should be reduced to its minimum size (determined by the space needed for the disks and the stirrers). The challenge in this design would be to ensure uniform mixing of the bulk liquid phases without the formation of pockets, especially in the spaces between the disks.
Since the value of $a$ was already very small, the present work was done with a mesh sieve that had the maximal allowable opening size and the largest percentage of open area. With a larger value of $a$ mesh sieves with smaller openings could also be used which should (a) reduce the dispersion effect since fewer particles might escape from the disk and (b) allow for calculation of mass transfer results from raw data obtained from reaction runs with different mesh sieves. Conversion vs. time data should correlate with different values of $a$ and result in the same mass transfer coefficients. With the currently low values of $a$ such a comparison cannot easily be made due to the natural variation in the raw data. However, if the openings of the mesh sieve are chosen too small, the mesh sieve itself will likely become a resistance in the system (like a membrane), in which case conversion vs. time data will be independent (or almost independent) of the bulk agitation.

The main focus in future work in this project will certainly be on access to conversion vs. time data from several more reaction systems to support the correlation that has been supposed in the present work or, if necessary, to derive a modified version. The present work investigated esterification reactions and an ester hydrolysis reaction which can both be classified as nucleophilic substitution reactions. However, PTC finds industrial application in a variety of reactions (usually key steps in multistep syntheses) like oxidations, reductions, addition reactions, condensations, synthesis of carbenes, and so on. It is therefore desirable to include mass transfer data from such reaction systems in the derivation of a generalized correlation. The most important key to this research will be the choice of model systems which should have fast intrinsic kinetics (i.e. mass transfer limitations over a wider range of agitation speeds than was observed in the current work), and, at the same time, negligible (or almost negligible) base reactions. It needs to be noted at this point that when high conversions are
obtained with RDC, the reaction rates may not necessarily obey pseudo-first-order kinetics. Satrio, Glatzer, and Doraiswamy derived a general hyperbolic model based on the Langmuir-Hinshelwood approach particularly of the Eley-Rideal type. The proposed rate law is as follows:

\[
\frac{dC_{RX}}{dt} = -k_{org} C_{RX} C_{QX,0} \frac{K_Y C_Y}{1 + K_Y C_Y + K_X C_X}
\]

(2)

where \(K_X\) and \(K_Y\) are constants describing the "degree of competitiveness" between the anions for coordination with the active sites of the TP catalyst. These constants are analogous to adsorption constants in Langmuir-Hinshelwood kinetics for traditional heterogeneous catalysis. The esterification of octyl bromide with potassium acetate is not a first-order reaction and could be described well by the above rate law. The rationale behind the model, simulation results, role of the anions etc. will not be discussed here but can be obtained from Satrio et al. (1999). It can be shown that in the beginning of the reaction, equation (2) reduces to a pseudo-first-order form if the inorganic salt is used in excess. In RDC, however, due to the low conversions, the entire rate data could be approximated by pseudo-first-order kinetics. Thus an integral approach could be applied to the data analysis. At higher conversions (due to larger surface area or much higher intrinsic reaction rates), however, an integral analysis for a first-order reaction may not be employed. Strictly, this approach is only applicable for a first-order reaction (equation (3) on page 42 only holds for this case). For reactions with non-first-order intrinsic kinetics a more rigorous approach requiring numerical solution would be necessary.

So far experimental work has been restricted to the investigation of the external mass transfer coefficient in the organic phase. However, transport limitations of the inorganic
reactant may also have a significant effect on the overall reaction rates. As already pointed out earlier, it is possible in RDC (without design modifications) to access mass transfer data for the aqueous phase as well. Since the aqueous phase usually has a higher specific gravity, sampling of the aqueous phase from RDC can be done through a port in the bottom PTFE plate. The interface should not change its original position through loss of sampled aqueous phase and therefore, the sampled volume should be replaced by fresh aqueous phase solution. Since the bulk phase reactions are decoupled in RDC, the procedure to determine the mass transfer coefficients in the aqueous phase and to derive a generalized correlation for the Sherwood number is completely analogous to the procedure outlined in the present work for the organic phase.

Due to the enormous potential of triphase catalysis for industrial application, it must always remain a goal to find a way to eliminate the disadvantages associated with supported PT catalysts. The present work shows a methodology for the economic choice of a PT catalyst. We know that there are conditions at which a polymer supported catalyst is superior to its homogeneous analog. These conditions which can be specific to the system (i.e. they can vary from system to system even if their chemistries are similar) need to be unveiled. The key factor seems to be the choice of catalyst support. By manipulation of the support structure it is possible to optimize catalytic activity of the triphase catalyst. As a recommendation for the development of a process where PTC is the key synthesis step, it can be stated that the possibility of using a supported catalyst should always be explored thoroughly before the final decision about the choice of catalyst is made.
APPENDIX A. ADDITIONAL CONSTRUCTION DETAILS FOR THE RDC

Three-dimensional drawings of the PTFE-parts of RDC are shown in Figures A1-A4. Figure A1 shows front and rear views of the rotating disk on a scale of 100%. Figure A2 shows the view of the top plate as seen from the inside of the reactor. Figure A3 shows the middle plate which is located at the interface and holds the rotating disk, and Figure A4 shows a view of the bottom plate as seen from the inside of the reactor. All the plates are shown on a scale of 70%.
Figure A1. Three-dimensional views of the Teflon body of the rotating disk. Both sides are shown on a scale of 100%. The recesses in the middle provide the space for the triphase catalyst.
Figure A2. Three-dimensional view of the top plate of RDC (Scale: 70%). The hole in the middle was machined for the stirrer in the organic phase, the off-centered hole is the sampling port for the organic phase. The hole on the side of the disk is for the outgoing flow of thermostatic fluid.
Figure A3. Three-dimensional view of the middle plate of RDC (Scale: 70%). The hole on the side of the plate was machined for the axis to which the rotating disk is mounted. The 24 holes between the recesses for the glass cylinders provide flow for the thermostatic fluid through the middle plate.
Figure A4. Three-dimensional view of the bottom plate of RDC (Scale: 70%). The hole in the middle was machined for the stirrer in the aqueous phase, the large off-centered hole is the port for emptying the reactor and the small one the sampling port for the aqueous phase. The hole on the side of the disk is for the incoming flow of thermostatic fluid.
APPENDIX B. RAW DATA

Conversion vs. time data of the esterification reaction of octyl bromide and potassium acetate to yield octyl acetate (see Chapter 6) are tabulated in Tables B1 and B2. The data were obtained from RDC and recorded as a function of the bulk agitation. Table B1 contains data from reaction runs with polymer bound tributylmethylphosphonium chloride on the disk, Table B2 those from the corresponding ammonium chloride.
Table B.1. Conversion vs. time data for different bulk agitation speeds with and without catalyst (polymer bound tributyl-methylphosphonium chloride) on the disk. Reaction system: Esterification of octyl bromide with potassium acetate.

Mass transfer controlled: 120 / 180 / 240 rpm
Kinetically controlled: 300 / 360 / 420 rpm
Dispersion effect: 480 rpm and higher

<table>
<thead>
<tr>
<th>TP catalyst on disk</th>
<th>Time [min.]</th>
<th>120 rpm</th>
<th>180 rpm</th>
<th>240 rpm</th>
<th>300 rpm</th>
<th>360 rpm</th>
<th>420 rpm</th>
<th>480 rpm</th>
<th>600 rpm</th>
<th>720 rpm</th>
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<td>P-2.0</td>
<td>180</td>
<td>0.075</td>
<td>0.077</td>
<td>0.069</td>
<td>0.084</td>
<td>0.105</td>
<td>0.082</td>
<td>0.077</td>
<td>0.097</td>
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<tr>
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<td>0.147</td>
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<td>0.750</td>
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<td>0.567</td>
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<td>0.843</td>
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<td>P-2.0</td>
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<td>0.601</td>
<td>0.624</td>
<td>0.677</td>
<td>0.778</td>
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</table>

The table continues with more data entries for different time values.
Table B.2. Conversion vs. time data for different bulk agitation speeds with and without catalyst (polymer bound tributyl-methylammonium chloride) on the disk. Reaction system: Esterification of octyl bromide with potassium acetate.
Mass transfer controlled: 120 / 180 rpm
Kinetically controlled: 240 / 300 rpm
Dispersion effect: 360 rpm and higher

<table>
<thead>
<tr>
<th>TP catalyst on disk</th>
<th>Time [mmol]</th>
<th>Conversion [%] as a function of bulk agitation speed</th>
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</tr>
<tr>
<td>N-2.0</td>
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<td>0.093</td>
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<tr>
<td>N-2.0</td>
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\textbf{NOTATION}\footnote{Note: Notations for chapters 3, 5 and 6 which appear or will appear as publications in Chemical Engineering Science and Journal of Molecular Catalysis have been given at the end of the individual chapters. The present list is therefore restricted to notations used in the other chapters, namely chapters 1, 2, 4 and 7.}

\begin{itemize}
\item \(a\) Area per unit volume of the catalyst, m\(^2\)/m\(^3\)
\item \(B_{im}\) Mass Biot number, dimensionless
\item \(C_{QX}\) Concentration of the inactive form of the catalyst, mol/g of catalyst
\item \(C_{QY}\) Concentration of the active form of the catalyst, mol/g of catalyst
\item \(C_{RX}\) Concentration of the organic reactant, mol/(cm\(^3\))\(_{\text{org}}\)
\item \(C_{Y}\) Concentration of the inorganic reactant, mol/(cm\(^3\))\(_{\text{aq}}\)
\item \(C_{QX}^*\) Dimensionless concentration of the inactive form of the catalyst
\item \(C_{RX}^*\) Dimensionless concentration of the organic reactant
\item \(C_{QX,0}\) Initial concentration of the inactive form of the catalyst, mol/g of catalyst
\item \(C_{Y,0}\) Initial concentration of the inorganic reactant, mol/(cm\(^3\))\(_{\text{aq}}\)
\item \(C_{RX,b}\) Concentration of the organic reactant in the bulk phase, mol/(cm\(^3\))\(_{\text{org}}\)
\item \(C_{Y,b}\) Concentration of the inorganic reactant in the bulk phase, mol/(cm\(^3\))\(_{\text{aq}}\)
\item \(C_{QX,s}\) Concentration of the inactive form of the catalyst on the surface of the catalyst particle, mol/g of catalyst
\item \(C_{RX,s}\) Concentration of the organic reactant on the surface of the catalyst, mol/(cm\(^3\))\(_{\text{org}}\)
\item \(C_{Y,s}\) Concentration of the inorganic reactant on the surface of the catalyst, mol/(cm\(^3\))\(_{\text{aq}}\)
\item \(d\) Diameter, m
\item \(D\) Diffusion coefficient, cm\(^2\)/s
\item \(D_{RX}\) Effective diffusivity of the organic reactant in the catalyst, (cm\(^3\))\(_{\text{org}}\)/(cm\(_{\text{cat}}\) s)
\item \(D_{Y}\) Effective diffusivity of the inorganic reactant in the catalyst, (cm\(^3\))\(_{\text{aq}}\)/(cm\(_{\text{cat}}\) s)
\item \(E\) Activation energy, kJ/mol
\item \(-\Delta H_R\) Heat of reaction (positive for exothermic reaction), J/(mol K)
\item \(k_1\) Intrinsic reaction rate constant of the forward reaction in the aqueous phase, (cm\(^3\))\(_{\text{aq}}\)/(mol s)
\end{itemize}
$k_{-1}$ Intrinsic reaction rate constant of the reverse reaction in the aqueous phase, $(\text{cm}^3)_{\text{aq}}/(\text{mol s})$

$k_2, k_{\text{org}}$ Intrinsic reaction rate constant of the organic phase reaction, $(\text{cm}^3)_{\text{org}}/(\text{mol s})$

$k_e$ Thermal conductivity of the solid support, $\text{W/(m K)}$

$K_{eq}$ Equilibrium constant for the aqueous phase reaction

$K_X$ "Attachment constant" for the inorganic product at triphase catalytic sites

$K_Y$ "Attachment constant" for the inorganic reactant at triphase catalytic sites

$k, k_L$ Liquid-solid mass transfer coefficient, $(\text{cm}^3)_{\text{org}}/[(\text{cm}^2)_{\text{cat}} \text{s}]$

$k_{RX}$ Mass transfer coefficient of organic reagent in bulk organic phase, $(\text{cm}^3)_{\text{org}}/[(\text{cm}^2)_{\text{cat}} \text{s}]$

$k_Y$ Mass transfer coefficient of inorganic reagent in bulk aqueous phase, $(\text{cm}^3)_{\text{aq}}/[(\text{cm}^2)_{\text{cat}} \text{s}]$

$M^+X^-$ Inorganic product in the aqueous phase

$M^+Y^-$ Inorganic reagent in the aqueous phase

$Q^+X^-$ Inactive form of phase transfer catalyst

$Q^+Y^-$ Active form of phase transfer catalyst

$R$ Radius, m

$Re$ Reynolds number

$RX$ Organic reagent in the organic phase

$RY$ Organic product in the organic phase

$Sc$ Schmidt number

$Sh$ Sherwood number

$T_s$ Surface temperature of catalyst, K

$t$ Time, s

$V$ Volume, cm$^3$

Greek symbols

$\alpha_s$ Dimensionless Arrhenius parameter, $E/RT_s$

$\beta_m$ Dimensionless adiabatic temperature rise (see Chapter 2, eqn. (24))

$\gamma_{RX}$ Ratio $C_{RX,0} / \rho_e C_{QX,0}$

$\varepsilon_{org}$ Volume fraction of the organic phase in the catalyst pore

$\varepsilon_{eq}$ Volume fraction of the aqueous phase in the catalyst pore

$\phi$ Thiele modulus (based on organic phase reaction)

$\phi_{app}$ Apparent Thiele modulus (based on organic phase reaction) as defined in Chapter 2, eqn. (10)
\(\eta_c\) Intraparticle effectiveness factor
\(\eta_{c,\text{noniso}}\) Intraparticle effectiveness factor, nonisothermal
\(\eta_e\) External effectiveness factor (film diffusion resistance)
\(\eta_o\) Overall effectiveness factor based on the organic reaction
\(\nu\) Kinematic viscosity, \(m^2/s\)
\(\rho_c\) Density of the supported catalyst, \(g/cm^3\)
\(\omega\) Dimensionless radius (Chapter 2), and also rotation (Chapter 7), radians/time

**Subscripts**

\(aq\) aqueous phase
\(b\) bulk phase
\(c,\,cat\) catalyst phase
\(org\) organic phase
\(s\) surface of the catalyst particle
\(0\) initial
REFERENCES


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1Note: References for chapters 3, 5 and 6 which appear or will appear as publications in *Chemical Engineering Science* and *Journal of Molecular Catalysis* have been given at the end of the individual chapters. The present list is therefore restricted to references used in the other chapters, namely chapters 1, 2, 4 and 7.


BIOGRAPHICAL SKETCH

Holger Jürgen Glatzer was born March 9, 1968 in Erwitte, Germany. He received the degree Diplomingenieur Fachrichtung Chemieingenieurwesen (diploma in chemical engineering) in 1994 from the Fachhochschule Hamburg, Hamburg, Germany. During the course of this program he was awarded two 6-month COMETT scholarships (COMmunity program for Education, Teaching, and Training) of the Commission of European Communities (EC), one for an engineering internship at AB Volvo, Gothenburg, Sweden in 1992, and one for a research assistantship at the Technical University of Graz, Graz, Austria in 1993.

From 1994 to 1999 he served as a Research Assistant and a Teaching Assistant in the Department of Chemical Engineering at Iowa State University. From 1997 to 1999 he also worked as a Teaching Fellow in the development of new teaching methods for chemical engineering thermodynamics.

His current research interests are rate enhancement techniques in organic synthesis engineering, with particular focus on the understanding of the role of mass transfer in multiphase reactions.