LIQUID-LIQUID MASS TRANSFER
WITH SIMULTANEOUS CHEMICAL REACTION

by

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CONTENTS

ABSTRACT

A theoretical and experimental study was conducted of the liquid-liquid mass transfer with an instantaneous and a first-order chemical reaction in a stirred cell at various stirring speeds. The system used in both series of experiments was toluene/water. The neutralisation reaction between propionic acid and sodium hydroxide and the sulphonation of toluene were respectively chosen as the instantaneous and first-order reactions.

The pure mass transfer of propionic acid from toluene to water and vice versa was also investigated experimentally. Some correlations were discussed and tested so that a reference correlation could be established for the mass transfer coefficient of toluene in the sulphuric acid solution.

The presence of an interfacial resistance was detected for the transfer of propionic acid from toluene to the aqueous solution containing the product of the reaction and the other reactant.

It was also shown that the introduction of a simple chemical reaction could be useful in evaluating the intensification of mass transfer (increase in individual mass transfer coefficients) due to the presence of an instability.

The results obtained for the sulphonation indicated that above a certain sulphuric acid strength the presence of an interfacial reaction is observed in addition to a bulk reaction. The concentration range studied (between 68 and 84%-wt H_2SO_4) located the reaction in the slow diffusional regime for the three stirring speeds.

Provided that these secondary phenomena were taken into account, the general mechanism of simultaneous mass transfer and chemical

reaction outlined by Hatta was successfully employed when comparing the models presented with experimental data.

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Philippe Grosjean

CHAPTER 1

INTRODUCTION

Many industrial reactions such as nitration, sulphonation, ester saponification etc are often performed under conditions such that the reactants are initially present in mutually immiscible phases. For such conditions, the conversion of the reactant depends upon the flow patterns and velocities of the phases and the interface, the solubilities and diffusivities of the two reactants as well as the chemical kinetics of the reaction. For the reactions mentioned above, practically all the reaction occurs in the most polar phase because of the usually encountered low reaction rates and low solubilities of ionic reactants in the less polar phase. Diffusion and reaction therefore occur in the same region and the rate phenomena are coupled so closely that they have to be treated simultaneously in the same differential rate equations.

Generally, most chemical reactions which occur in a liquid-liquid system assist in removing the diffusing species from solution and hence increase the concentration gradient and the overall rate of mass transfer of the diffusing species. A chemical reaction is thus often introduced in order to enhance the rate and extent of solute separation. In consequence, because there is little place in industry for generous safety factors, it is necessary to formulate reliable models predicting, not only the rate of physical mass transfer, but also the effect of the chemical reaction on the rate of mass transfer. Until recently the major work in this field has been performed for gas-liquid or gas-solid reactions. In comparison with the above, chemical reactions occurring in liquid-liquid systems have received very little attention.

For many types of processes similar to uranium extraction the problem is simplified by the fact that the rate of chemical reaction is extremely rapid compared with the rate of transfer and so it is justifiable to treat the process as a simple mass transfer operation. The other extreme case is when the mass transfer is practically instantaneous, i.e. when the process is assumed to be kinetically controlled. The design of plants for such a process is consequently looked upon as a problem in reactor design rather than in mass transfer. These two situations can be modelled quite easily.

The problem is more complicated when both rates are comparable and for such reactions it is necessary to distinguish between the slow reaction diffusional regime and the fast reaction regime. The development of any such model clearly requires a knowledge of the kinetics of the reaction and of the conditions of diffusion.

It is the object of the present work to provide some understanding of the ways in which diffusion and reaction rates are coupled during mass transfer across a liquid-liquid interface, leading to an increase in the mass transfer coefficient. These relevant aspects of extraction have been studied in the case of mass transfer in a stirred cell accompanied by an instantaneous and a first-order reaction. For both types of reaction theoretical models have been established in order to represent the process.

Reference conditions, i.e. when no chemical reaction occurs, were also quantitatively and qualitatively investigated.

CHAPTER 2

LITERATURE SURVEY

The literature relevant to the reference conditions, i.e. to pure mass transfer, is extensive and will consequently be treated in Section 2.1 only with reference to the equipment used in the present work, i.e. the stirred cell. The choice and the description of such an apparatus will be discussed and presented later in Section 3.1 of Chapter 3. The liquid-liquid mass transfer with simultaneous chemical reaction is discussed in detail in Section 2.2.

In this chapter only experimental research is referred to. The theoretical work on the general subject of mass transfer is reviewed in Section 4.1.

2.1 Pure Mass Transfer in a Stirred Cell

LEWIS (1954) was the first to use a stirred transfer cell in which the interface formed an annulus between two baffles. He correlated the individual mass transfer coefficients of a few partially miscible binary systems in terms of their physical properties and Reynolds numbers of the phases. This correlation, when subsequently used to predict overall mass transfer coefficients for the transfer of a solute between two immiscible phases (1958), gave reasonable agreement in some cases and considerable deviation in others. Low coefficients were attributed to slow interfacial chemical reactions and the high coefficients to the observations of interfacial turbulence associated with the transfer.

Using a relationship of the form $K \alpha D^{\frac{1}{2}}$ and a stirred cell without a central baffle, GORDON and SHERWOOD (1954/55) successfully correlated the overall mass transfer coefficients as a function of the individual mass transfer coefficients for their reference system isobutanol/water + solute.

A stirred cell of the above type was also employed by McMANAMEY (1961a) in his studies on the interfacial resistances in liquid extraction of inorganic nitrates whilst a stirred cell of the type described by Lewis was used by DAVIES and MAYERS (1961) in their investigation of the effect of interfacial films on mass transfer rates in liquid-liquid extraction.

McMANAMEY (1961b) and MAYERS (1961) also re-correlated Lewis' data in a different form and added new results concerning binary and ternary systems.

Repeating many of Lewis' experiments but using a cell without any central baffles, OLANDER and BENEDICT (1962) found a change in the flow regime in the region of the principal transport resistance and thus correlated their data by using two similar equations taking into account the value of the Reynolds Number. The same cell was also employed by OLANDER and REDDY (1964) for an investigation of the effect of the concentration induced interfacial turbulence in several typical liquid-liquid systems.

AUSTIN (1966) followed the same idea as Olander and Benedict using a modified version of the Lewis cell. He also proposed two different correlations applicable for an undisturbed laminar interface (low Re) and for a surface-renewed interface (high Re).

JOHNSON and RAAL (1966) employed an extraction cell of the Lewis type for transfer of acetic acid and propionic acid from aqueous solutions into various solvents to study the concentration dependence of mass transfer coefficients. Observed variations of the latter could not be predicted by conventional mass transfer theory and the possibility that there exists an interfacial resistance was put forward.

It is worth noting that the model proposed by OLANDER (1963/64) for both phases stirred at the same speed was checked by LOOSEMORE and PROSSER (1963) in their work on the kinetics of liquid-liquid extraction of metals. Later it was extended to different stirring speeds in the phases by KIKINDAI and MOREL (1969).

The Levich model (LEVICH_1962) for the approach of an eddy to a free surface has been extended to mass transfer between turbulent liquids by DAVIES (1972). The derived correlation was satisfactorily used by McMANAMEY, DAVIES, WOOLLEN and COE (1973) and McMANAMEY, MULTANI and DAVIES (1975) in the study of the influence of molecular diffusion on liquid-liquid mass transfer using a cell of the type described by Davies and Mayers.

The influence of momentum transfer across the interface on the rate of mass transfer was taken into account by BULIČKA and PROCHÁZKA (1971/76) when developing their theoretical model which is, in fact, mainly based on the Kolář model (KOLÁŘ_1961). Their model was applied to mass transfer studies using a different version of the Lewis cell. The stability of the interface was improved by the introduction ot twelve vertical baffles and of a cylindrical grid in the proximity of the impellers.

ROD and STRNADOVÁ (1975) conducted studies in a mixed cell with flat interface in the arrangement due to Bulička and Procházka under conditions of simultaneous transfer of succinic acid and one of the solvents. The experiments have revealed a significant effect of transfer of the second component on the rate of extraction of succinic acid.

CULLINAN et al (1975a) studied isothermal mass transfer in a new stirred cell using water-acetone-glycerol as a ternary system. The cell was of the type described by Lewis but vertically movable interfacial ring and vertical baffles were introduced.

The classical Lewis cell was also used by CULLINAN and SETHY (1975b) to examine mass transfer during liquid-liquid extraction in the system acetonitrile-benzene-n-heptane. The mechanism of the mass transfer process, the relative importance of both diffusive interactions and interfacial activity were quantitatively assessed.

2.2 Mass Transfer with Chemical Reaction

2.2.1 General

Existing work dealing with mass transfer accompanied by chemical reaction in liquid-liquid systems was reviewed by HANSON and co-workers (1971/74a). Their main points can be summarised as follows:

(i) Until recently many of the industrial operations in liquid-liquid extraction have been classified as mass transfer controlled or chemical kinetic controlled processes, the influence of the other effect being generally ignored.

(ii) This assumption was discussed for several processes, e.g. aromatic nitrations, and was shown to be doubtful. The importance of the role of chemical kinetics or of mass transfer resistances was demonstrated.

(iii) The effect of various parameters, such as agitation, temperature, phase ratio, space time, phase inversion and surfactants was indicated (HANSON 1971) for purposes of easier recognition of type of control.

(iv) The case of interfacial reactions was briefly reported but attention was particularly drawn to a theoretical model developed for a fast reaction taking place in a reaction zone adjacent to the interface (HANSON et al. 1974a).

Another general review was published by SHARMA and NANDA (1968). The aspects of extraction accompanied by second-order reaction in a stirred cell and a spray column were considered. It was shown that the theory of absorption with second-order reaction was valid for extraction with reaction of the same order to predict the effect of reaction on the rate of extraction. The two types of reaction studied, i.e. alkaline hydrolysis of esters and formation of an oxime, were examined under six possible situations from the very slow reaction to the instantaneous reaction. The rate equations were also developed whenever possible.

RIETEMA et al (1958/62/64) studied drop interaction in mass transfer with chemical reaction in liquid-liquid systems. The degree of dispersion and its effect on mass transfer, the influence of surface active agents and of segregation on the overall reaction rate were analysed as a function of the order of reaction and of the stirring speed.

Mass transfer accompanied by a chemical reaction was also investigated by NAGATA and YAMAGUCHI (1960) in liquid-liquid agitated systems. It was found that the most marked effect of agitation is the increase in the interfacial area. The mass transfer resistance outside and inside the drops was not greatly affected by the increase of agitation.

In some processes an additional slow chemical reaction occurring at the interface was observed and the resistance due to this step determined. An example is the transfer of uranyl nitrate between water and the solvents dibutyl carbitol and methyl isobutyl ketone. It was shown by MURDOCH and PRATT (1953) in a wetted-wall column that the observed interfacial resistance was due to the reaction known to occur at the water-solvent interface between the uranyl nitrate, water and solvent molecules to form a nonionic complex, soluble in the solvent. The same conclusion was drawn by SMITH et al (1957) for the transfer of uranyl nitrate between water and methyl isobutyl ketones in a packed column and by LEWIS (1958) with a greater number of solvents in his stirred transfer cell. The investigations of these workers showed interfacial resistances of around 5-35% of the overall resistance or, for instance for Lewis' work, as high as 2000 s/cm.

An interfacial resistance of 40-60% of the total resistance was also observed by McMANAMEY (1961a) for the extraction of copper, cobalt and nickel nitrates from water by n-butanol in the stirred cell developed by the same author. BRISK and McMANAMEY (1967/69) in a kinetic study of the extraction of copper-cobalt mixtures made in the same stirred cell also found that the mass transfer rates between the phases are influenced by an interfacial resistance due to the extraction reaction of around 30-75% of the total resistance.

KLETENIK and NAVROTSKAYA (1967) studied the kinetics of iron III extraction by di-isoamyl phsphoric acid in benzene from several acid solutions using a quiescent interface. They established that the rate is controlled by a chemical reaction at the interface.

Recently RODDY and COLEMAN (1971) investigating the kinetics of metal extraction by organo-phosphorous acids also suggested that the rate controlling reactions are at the interface.

YAGODIN et al (1971) showed that the extraction by diethylhexyl phosphoric acid was accompanied by non ionic chemical reaction in the aqueous phase, preceded by the dissociation of the acid and that the extraction is also complicated by reactions connected with the existence of an equilibrium between the dimer and the monomer of the acid in the organic phase.

The extraction rate of uranium nitrate into a single drop of tricresyl phosphate studied by NABASHIO et al (1971) was shown to be controlled by the diffusion of the extracted species. When the drop was rising, the extraction rate was slightly influenced by an interfacial chemical reaction.

It is worth noting that TREUB (1918) noted in his investigation on saponification reactions that the reaction took place essentially at the surface of contact of both phases. The saponification rate was observed to be determined by the degree of adsorption of the reactants at the surface.

2.2.2 Instantaneous chemical reaction

In an attempt to study the applicability of the ion-diffusion theory (see Section 5.1.1.2) to the case of mass transfer between two stirred immiscible liquids with acid-base neutralisation of diffusing species, SHERWOOD and WEI (1957) investigated the extraction of acetic acid from an organic solvent by solutions of base in water. Their results can be compared with those of SEARLE and GORDON (1957), also obtained for a neutralisation reaction between sodium hydroxide and acetic acid. Neither the Hatta theory, nor the modification allowing for ion diffusion appeared to explain the observed high extraction rates which were, of course, due to interfacial turbulence. FUJINAWA and MARUYAMA (1957) studied the extraction of benzoic acid, butyric acid and monochloroacetic acid from benzene by aqueous solution of sodium or potassium hydroxide, and the extraction of I_2 from benzene by sodium hyposulphite solution. The rate of extraction was found to increase with the increase of the base concentration in water linearly up to a certain critical value beyond which it became constant and independent of the base concentration.

Experiments on dissolution of a rotating cylinder of benzoic acid into aqueous solution of sodium hydroxide were performed by SHERWOOD and RYAN (1959). The data were compared with the theories based on the film, penetration and turbulent boundary layer models. It was observed that the Hatta equation fitted the data somewhat better than any other theory.

A general analysis of chemical reactions in two-phase liquid systems was carried out by SCRIVEN (1961). The reaction zone movement for an instantaneous reaction was also estimated by solving the set of equations governing diffusion of the two reactants. TOOR (1962) studied mass transfer with rapid, homogeneous, irreversible reactions between dilute species with equal diffusivities using a device which reduced the system of mass transfer-reaction equations to the equations for mass transfer in the absence of reaction. Another mathematical treatment of the occurrence of interfacial turbulence in the case of diffusion accompanied by chemical reaction was due to RUCKENSTEIN and BERBENTE (1964). It was found by these authors that even small values of the reaction rate constant changed the conditions under which instability occurred.

Experiments on neutralisation reactions in one-dimensional, stagnant systems were performed by CHO and RANZ (1967) as part of their investigations of the diffusion-controlled reaction zone in two-phase liquid reactions. Analysis of zone movements revealed that, when there was interfacial turbulence, the reaction zone moved faster than predicted by theory. Otherwise the movement confirmed theoretical criteria set up by SCRIVEN (1961).

Some experiments on extraction with rapid chemical reaction carried out by BAKKER et al (1967) showed that at high concentrations of the reactant the interfacial instabilities die out because of the fact that the solute concentration at the interface becomes zero.

The kinetics of mass exchange was also investigated by RESPONDEK (1970) in terms of stirring speed, diffusion coefficient and stirrer dimensions using an aromatic hydrocarbon, carboxylic acid and aqueous sodium hydroxide.

BRUNSON and WELLEK (1970) demonstrated that the enhancement factor for simultaneous mass transfer and instantaneous chemical reaction is not dependent on the type of hydrodynamic model or the geometry of the system. Another theoretical analysis of mass transfer with an instantaneous chemical reaction across a liquid-liquid interface was carried out by SHIROTSUKA and MURAKAMI (1971). It gave results in good agreement with movement of the reaction front as measured in a capillary.

Experiments were also performed by ONDA et al (1971) with a diaphragm cell and for a certain number of acid-base systems. The analytical solution based on the film theory model was derived on the basis of ionic diffusion.

SAWANT and RAMACHANDRAN (1972) studied liquid-liquid extraction of 2-ethyl-hexoic acid in sodium hydroxide solutions in a stirred cell at two different stirring speeds. They observed the presence of interfacial turbulence which was believed to be caused by changes in the interfacial tension due to the product formed.

Mass transfer with an acid-base neutralisation in a falling drop was studied by FUJINAWA and NAKAIKE (1961) and NEKOVÁŘ and VACEK (1974). In the latter investigation visualisation of the various regions was obtained by using a dye technique.

2.2.3 First-order reaction

PIRET, PENNY and TRAMBOUZE (1960) for the dilute case and then TRAMBOUZE and PIRET (1960) for the concentrated case considered mass transfer between two fluid phases with a relatively slow, simultaneous first-order chemical reaction occurring in one or in both phases.

Design equations were presented for column as well as batch and continuous stirred tank operations by TRAMBOUZE et al (1961). Experimental data on the continuous hydrolysis of acetic anhydride in a benzene-water system operating in a pulsed sieve plate column and in a packed column were shown to fit the theory within 5%.

Experiments of alkaline hydrolysis of esters in emulsion with aqueous solutions of NaOH have been made by VIALLARD (1961) The reaction was shown to follow a homogeneous mechanism in the aqueous phase. It was also found that, if the interfacial area became smaller, the reaction became controlled by the slow process of dissolution of the ester.

The system toluene/water + sodium sulphite and dinitrochlorobenzene was studied by ABRAMZON and OSTROVSKII (1963). It was shown that the rate of the chemical reaction in the diffusion region was directly proportional to the interfacial area, the partition coefficient and the concentration of one of the reagents but was independent of the concentration and physicochemical properties of the other reagent.

CHO and RANZ (1967) estimated the rate constant of a slow pseudo-first-order reaction by measuring the zone thickness. When the process was diffusion-controlled, and when the rate constant was known, it was found that the movement of the reaction zone could have been predicted theoretically. The reactions investigated were hydrolysis of various esters by aqueous sodium hydroxide solutions.

The kinetics of fast alkaline hydrolysis of esters were studied by NANDA and SHARMA (1966/67) in stirred cells of known interfacial areas. The rate of extraction was found to be virtually independent of the stirring speed. This showed that the hydrodynamics were unimportant for these systems. SHARMA and co-workers (1967/68/69) also conducted studies of this type of fast pseudo-first-order reactions. They have shown that the values of the effective interfacial area in agitated liquid-liquid contactors can be evaluated by the method of liquid extraction with a fast pseudo-first-order reaction (1967/68).

After having critically considered the existing work on aromatic nitration, HANSON and co-workers (1966/71) suggested that mass transfer resistance may be of equal importance to kinetics in determining the overall rate in such liquid-liquid systems. The simple kinetic model adopted by previous workers for toluene nitration was shown to be inconsistent by HANSON, MARSLAND and WILSON (1971) since the diffusion resistance was found to play an important part in the overall rate process.

In order to explain these contradictory results HANSON (1971) has assumed that the reaction zone where the nitration species NO_2^+ is supposed to react can be extended into the organic phase if its depth is sufficiently large. The latter is a function of the kinetics of the reaction, of the rate of diffusion of reactants and products and of parameters such as agitation.

As concerns chlorobenzene nitration HANSON, MARSLAND and NAZ (1974) correlated the rate of reaction with only kinetic rates and so proved the absence of a diffusional resistance. However the experiments were performed at extremely low concentration levels and the possibility cannot be excluded of a diffusion resistance becoming significant at higher concentration levels.

A series of papers on the two phase nitration of chlorobenzene and toluene was published by COX and STRACHAN (1971/72a and b/74). In the first paper (1971) they studied the rate of nitration of chlorobenzene in 70.2%-wt H_2SO_4 and derived an equation for the rate of reaction. They also concluded that for low nitric acid concentrations the nitration was kinetically controlled. The two-phase nitration of toluene over a larger temperature range, using the same initial acid concentrations, showed that the nitration is kinetically or mass transfer controlled depending on the relative values of the kinetic or mass transfer rates which were in the present case of comparable magnitude (1972b). Their studies on toluene nitration were then extended to a much wider range of sulphuric acid concentrations (62-78%-wt) and higher nitric acid concentration (1972a). Three distinct regimes were obtained. At very low values of the rate constant k_2 there exists the kinetic regime whose reaction rate increases with k_2. At higher values of k_2, mass transfer takes over from kinetic control; a slow reaction diffusional regime is obtained and the reaction rate becomes constant. At still higher values of k_2 a fast reaction regime is obtained. The two-phase nitration of chlorobenzene has been studied under the same conditions with the stirred reactor and also with a stirred cell (1974) and similar conclusions have been drawn. Finally CHAPMAN, COX and STRACHAN (1974) extended the study of two-phase nitration of toluene to the stirred cell and concluded that "the formation of nitronium ions, rather than their attack on the toluene, is the rate limiting kinetic step under the experimental conditions".

GILES (1970) studied the heterogeneous nitration of toluene in a continuous flow stirred tank reactor and developed a mathematical model to represent the overall rate. This model has been verified by ISMAIL (1973) for the case of fast reaction.

SOHRABI (1972) carried out two-phase nitrations of both benzene and toluene in a batch reactor and found, like Cox and Strachan, that the rate of reaction could be diffusion, transition or kinetically controlled depending on mixed acid composition and condition of the reaction.

CERFONTAIN et al (1963b/64) studied the heterogeneous sulphonation of toluene with 81.9 and 95.9%-wt aqueous sulphuric acid at 25°C. Their finding was that for 95.9%-wt H_2SO_4 the toluene conversion is strongly dependent on the toluene to sulphuric acid volume ratio, the conversion being maximal at a one to one volume ratio. They therefore concluded that the toluene transport into the acid phase in which the entire reaction is assumed to occur is rate controlling under the experimental conditions employed. But, as shown by HANSON (1971), the phase ratio is a difficult criterion to employ. The lack of supplementary precisions concerning the experiments does not permit to draw obvious conclusions.

CHAUDHRY (1970) presented a critical review of literature on sulphonation. Except for the investigations of LEITMAN and co-workers (1959/61) on the kinetics of heterogeneous sulphonation of xylene isomers and ethylbenzene in concentrated sulphuric acid under batch conditions, many references concerning aromatic sulphonation are not easily available.

The analogy between nitration and sulphonation has been widely used to explain experimental results obtained in the case of sulphonation. Some specific studies have however been performed on sulphonation. Most of them have been conducted in continuous stirred tank reactors so that steady state conditions can be assumed in the reactor. The rate of consumption of aromatic as a function of agitation speed at constant temperature and space time has been measured in most investigations and has often been used to estimate which step is assumed to control the process. This reaction rate was shown to increase rapidly up to a certain agitation rate and then slow down beyond this value. A few workers found also that the relevant curve rose very slowly at low agitation rates before increasing very steeply as previously reported.

The presence of these three zones was explained in terms of agitation rate as follows:

(i) At low agitation rates the interfacial area remains constant and the process is mass transfer controlled.

(ii) When the agitation rate increases, the process is always mass transfer controlled but, with the degree of dispersion, the turbulence in each phase, the interfacial area and the surface renewal also growing, the reaction rate increases steeply.

(iii) At higher rates of agitation, the mass transfer resistances are reduced and it is assumed that the process is kinetically controlled.

As pointed out by HANSON (1971) for nitration and CHAUDHRY (1970) for sulphonation these explanations may be regarded as doubtful. Two reasons can be advanced in support of the latter statement:

(a) The rate of any true chemical reaction is independent of agitation rate. Hence if, as claimed under (iii), the process is kinetically controlled, there should be zero gradient for the variation of transfer rate with stirring speed. In fact, most workers observed a slight but definite increase.

(b) The interfacial area cannot increase indefinitely and thus must reach a maximum. Likewise, at high rates of agitation, the reduction of drop size reduces the internal circulation and the drop interaction which normally play an important part in the transfer process. This discussion shows that the rate of reaction cannot rise indefinitely with agitation rate and thus the same shape of curve can also be obtained in pure mass transfer operations.

The other criterion used by the previous workers as evidence in support of kinetic control was the effect of temperature . It was shown that, on changing the temperature up to 10°C, the rate changed by a factor of around 2 in accordance with the increase commonly encountered in chemical reactions. This cannot however be considered as an absolute proof since temperature will also affect other parameters of the system, such as partition coefficient, diffusion coefficients etc.

2.2.4 Other orders

BRIAN, BADDOUR and MATIATOS (1964) formulated the ionic penetration theory equations and solved them for mass transfer accompanied by a second-order chemical reaction. The ion diffusion effects were found to be qualitatively similar to those reported by SHERWOOD and WEI (1955) for their film theory analysis of an instantaneous chemical reaction but the ionic diffusion effects were smaller in magnitude in the penetration theory results.

KREMNEV et al (1965) showed that surface resistance together with the resistance of one of the phases can be determined with the aid of extraction accompanied by chemical reaction. The experiments were performed in a diffusion cell stirred in both phases with transfer of acetic acid, iodine or diethylamine between water and organic solvents.

KISHINEVSKII and KORNIENKO (1964) conducted an investigation into the kinetics of extraction complicated by a second-order reaction. The mathematical model developed for absorption with chemical reaction was extended to extraction accompanied by chemical reactions. Surface resistance occurring in the system benzene/water benzoic acid was observed for stirring speeds of 210 rev/min.

An investigation of the saponification of simple esters such as ethyl acetate, floating on aqueous sodium hydroxide solutions was performed by SETO and co-workers (1965/71) in both a stirred and an unstirred system. The effect of salting out of ethyl acetate by sodium hydroxide as well as by sodium acetate was incorporated into the equations. The mass transfer coefficients thus calculated were found to decrease with increasing sodium acetate concentration. This retardation was expressed in terms of interfacial resistance (1965). The effect of interfacial turbulence was later (1971) studied as well as the variation of concentration profiles of reactants and products in the aqueous laminar film near the interface.

A theoretical analysis giving the position of the reaction zone was also developed by CHO and RANZ (1967) for irreversible second-order reactions. Another theoretical consideration for extraction accompanied by second-order reaction has been developed by SHARMA and NANDA (1968) (see Section 2.2.1).

PORTER and ROBERTS (1969) suggested a theoretical model of mass transfer across an interface, which takes into account the expected presence of a velocity variation near the liquid surface in liquid-liquid extraction. For pseudo n-th order reaction, it was shown that, at sufficiently high values of reaction rate constant, the mass transfer rate will be independent of this velocity variation. The model was then used as a basis for general statements about predicting the performance of large scale equipment from laboratory experiments. Later GOTTIFREDI et al (1970) showed the limits of the Porter and Roberts' model.

The alkaline hydrolysis of formate or acetate in aqueous NaOH solutions which is known to be an irreversible, second-order reaction was also studied recently by ONDA et al (1975) in a diaphragm cell at 25°C. It was found that this type of cell can also be used for the investigation of mass transfer between liquid-liquid phases as well as gas-liquid phases.

Several investigators have studied liquid extraction with second-order chemical reaction inside the dispersed phase. SHARMA and NANDA (1968) investigated water drops, containing NaOH, as they rose in a spray column through methyl dichloroacetate and methyl trichloroacetate. They compared their data with the film theory approximation for second-order reaction, using experimentally determined physical mass transfer rates. TYROLER et al (1971) studied the position of the reaction shell for aqueous sodium hydroxide drops, falling through cyclohexanol containing acetic acid. They located the reaction surface photographically but did not report mass transfer rates. WELLEK and BRUNSON (1975) obtained experimental data for the diffusion of n-pentyl formate from the continuous phase into droplets of water containing NaOH and sodium sulphate and falling through a simple spray extractor. The film and penetration based models for mass transfer with second-order reaction were shown to be as accurate as the corresponding correlations for mass transfer with no chemical reaction in estimating extraction data.

CHAPTER 3

EXPERIMENTAL

The purpose of the experimental work is to study the effect of simultaneous reaction on the rate of mass transfer. This is best achieved by investigating the variation in the value of the mass transfer coefficient. Experiments and equipment must therefore be designed in such a way as to give accurate and reproducible values of this parameter. These requirements are discussed in Sections 3.1 and 3.4.

In addition to the choice of equipment and a suitable experimental technique it is also necessary to select suitable reactions and the relevant solvents. As the reaction kinetics plays an important role in the theoretical treatment of the results, it is necessary to employ reactions whose kinetics is reasonably well established even if their exact mechanism is not fully known. The choice of reactions is considered in Section 3.2 and Section 3.3 contains the properties of the selected systems.

3.1 Experimental Set-Up

In order to obtain accurate values of mass transfer coefficients, and hence of enhancement factors, the interfacial area of the apparatus must be known. Facilities must also exist for a simple and quick analysis of the various concentrations in the homogeneous bulks of the two phases.

Both these conditions are satisfied by a stirred cell in which the two phases are stirred and turbulent, yet the interface between the two fluids is smooth and well defined. AUSTIN (1966) selected and used such a cell for his liquid-liquid studies after having compared stirred extractors employed by several investigators working in this field. His modified version of the Lewis cell was used for the same reason in the present work and it is shown diagrammatically in Fig.3.1. Fig.3.2 represents a photograph of the cell.

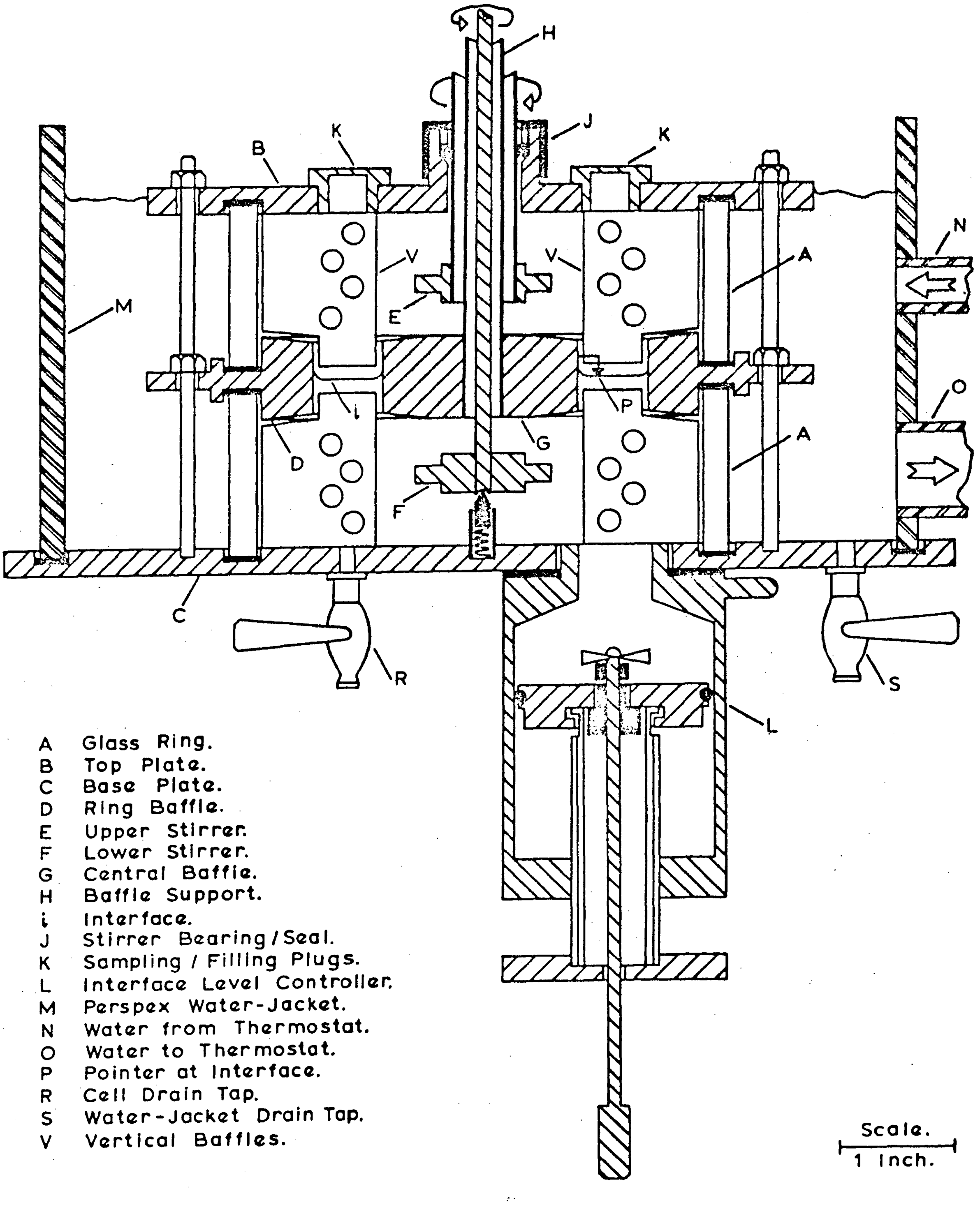
3.1.1 Description of apparatus

The cell consisted of two glass rings separated by an interfacial ring baffle support fastened tightly between a top plate and a base plate. Teflon gaskets were used throughout to provide good seals. In order to ensure a better stability at the interface, four perforated vertical baffles were fixed into both the base and the top plates. The base plate supported a perspex water jacket and the top plate had two filling and sampling plugs, each having a small hole drilled through it to provide access to the cell for the sampling needles.

Three concentric shafts were used to carry the stirrers and the fixed central baffle. Four annular baffles of depth 1/4", ½", 3/4" and 1", were available and either of them, as required, could be attached to the middle fixed tube. The outer and inner shafts were threaded so that flat-blade impellers could be attached to them and their position adjusted so that the blades were exactly equidistant from the centre of the central baffle.

The stirrers were driven through gears by variable speed motors controlled by PYE smooth-speed regulators. The speed was indicated on high accuracy tachometers reading with an accuracy of ± 2 rev/min. A reversing switch was incorporated in the circuit of the lower stirrer motors so that contra-rotating and co-rotating set-ups could be used if desired.

Water at 25.0 ± 0.1°C was pumped into the perspex water jacket from a large thermostat by a Tempunit unit manufactured



A	Glass Ring.
B	Top Plate.
C	Base Plate.
D	Ring Baffle.
E	Upper Stirrer.
F	Lower Stirrer.
G	Central Baffle.
H	Baffle Support.
i	Interface.
J	Stirrer Bearing / Seal.
K	Sampling / Filling Plugs.
L	Interface Level Controller.
M	Perspex Water-Jacket.
N	Water from Thermostat.
O	Water to Thermostat.
P	Pointer at Interface.
R	Cell Drain Tap.
S	Water-Jacket Drain Tap.
V	Vertical Baffles.

FIG. 3.1 THE STIRRED CELL

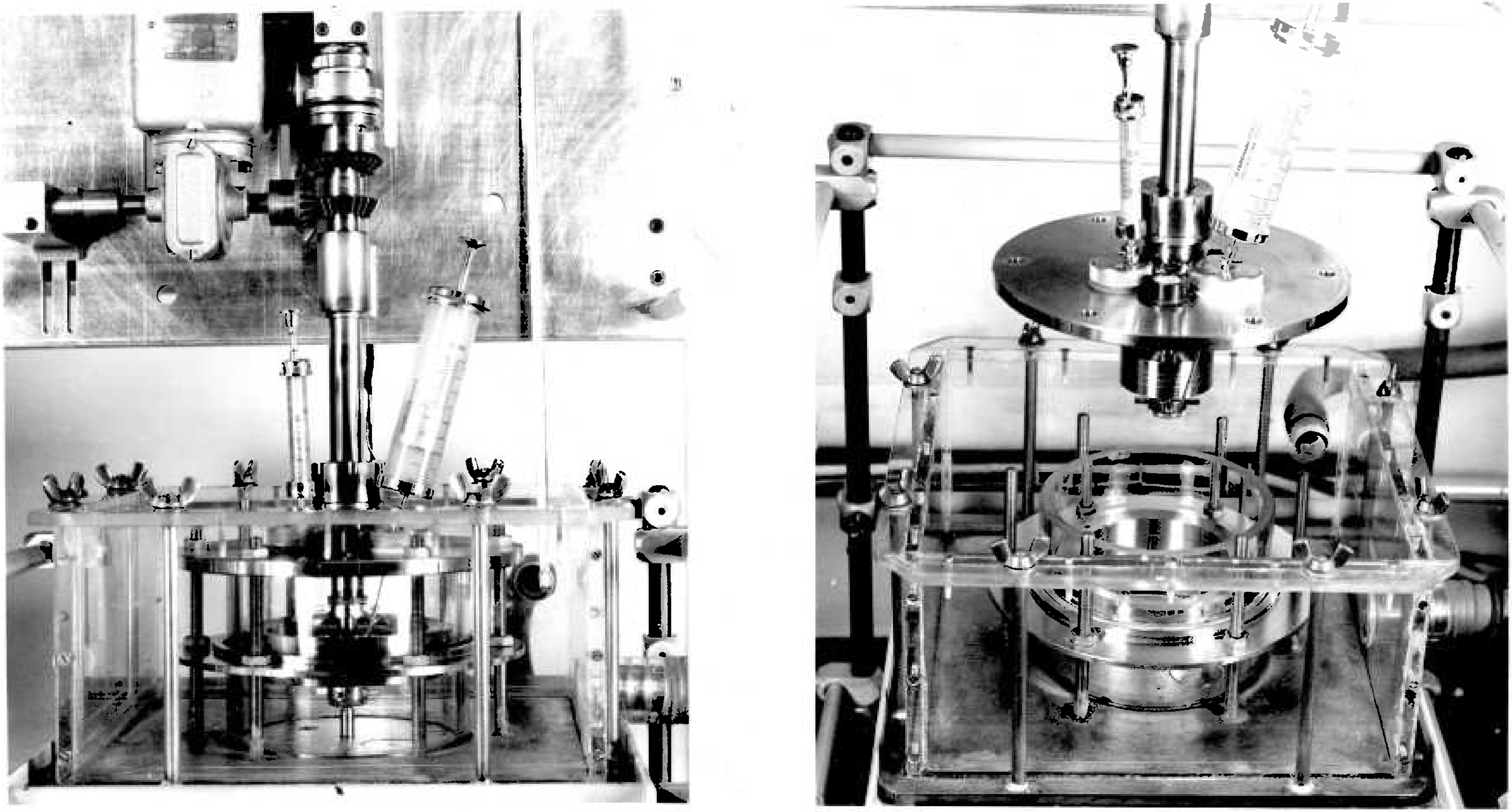


FIG. 3.2 : THE STIRRED CELL.

by TECHNE. The water level was controlled by a by-pass circuit and a screw clip in the water return line to the thermostat.

3.1.2 Operation of the cell

Austin analysed in his thesis the effects of the depths of various annuli on the mixing in the cell and on the stability of the interface. He found that the 3/4" annulus produced a flat and ripple-free interface for stirring speeds not exceeding 300-350 rev/min while maintaining good mixing in the bulk.

In order to establish the satisfactory range of operation of the cell, Austin performed control experiments using the system benzene/water, i.e. a system not very different from that used in the present work. The results and conclusions obtained by him and described below were considered to be equally valid for the present work.

The quality of bulk mixing was checked by dye injection. The mixing of the bulk at various stirring speeds was found to be instantaneous and no obvious dead spaces appeared in the cell.

The behaviour of the interface was tested by spreading talc particles on it. It was observed that, at low stirring speeds, the interface was stagnant. As the speed was increased, random movements could be seen, but it was not until a speed was reached of approximately 350 rev/min that ripples appeared in the interface.

In an attempt to prevent the rotation of the interface and improve the mixing at low stirring speeds, vertical baffles were introduced as described in Section 3.1.1.

These improvements were quantitatively checked by transferring propionic acid across the benzene-water interface at

$25^{\circ}C$. Here again experiments performed for 200 rev/min indicated that the best stability and mixing were obtained for the 3/4" annulus and vertical baffles.

On the basis of the above considerations the 3/4" annulus was selected for the present study. The main characteristics of the cell were therefore as follows:

- interfacial area (S): 30.25 cm^2
- volume of the upper phase (V_1): about 291 cm^3
- volume of the lower phase (V_2): about 290 cm^3
- tip-to-tip length of the stirrer blades: 3.16 cm
- distance of the interface from the horizontal axis passing through the impeller: 2.06 cm

3.1.3 Discussion

The technique of protecting the interface by an annular baffle, first introduced by Lewis, and the simultaneous use of vertical baffles has several important advantages over other cells. From a general point of view these are:

(i) a well defined ripple-free mass transfer area is produced;

(ii) the bulk phase can be assumed to be of uniform concentration and hence can be represented by a single and easily measured composition;

(iii) a visual observation of the interface is possible through the top plugs. This is useful for checking its stability and its position within the annulus.

Contrary to Austin's work, the small manually operated stirred cell of variable volume, denoted by L on Fig.3.1, was not inserted into the base of the transfer cell. It was designed originally for the purpose of controlling the level of the interface by manually adjusting its volume. However it is possible that this reserve volume can act as a dead space which is not isotropically mixed with phase 2. The errors due to a slight movement of the interface with respect to the plane of symmetry of the cell will probably be less important than those owing to the accumulation of solute in the small cell. Nevertheless each run was stopped if the interface moved beyond 0.3 cm into one of the phases. It should be pointed out here that only a change in volume of phase 2 results in movement of the interface. As will be seen later this movement has no significant influence on mass transfer coefficients.

The main disadvantage of the apparatus is that the values of mass transfer coefficients are somewhat sensitive to the distance of the impeller from the interface as pointed out by McMANAMEY, DAVIES, WOOLLEN and COE (1973).

Another difficulty is the cleaning of the cell. Between each experiment the cell was dismantled, carefully washed by concentrated acid solution and finally rinsed with distilled water. The cell was then re-assembled, filled with AnalaR acetone and dried until all traces of acetone had been removed from the cell.

3.2 Choice of Systems

Instantaneous and first-order reactions have been selected for experimental study because their kinetics is reasonably simple and thus easy to introduce into any theoretical model. Consequently, fairly simple reactions were chosen in these two categories so as to test the applicability of theoretical relations with a view to their possible extension to more complicated reactions.

Many typical examples of extraction with chemical reaction can be found in the chemical industry. Typical examples are nitration, sulphonation, extraction of uranium, hydrolysis, etc., but these were often of great complexity from the point of view of reaction mechanisms and reaction kinetics which, in some cases, are not yet entirely understood.

Because of these uncertainties, the reactions were selected not on account of their industrial importance, but rather to test the relevant models and to measure various parameters which make it possible to study the effects of chemical reaction.

3.2.1 Instantaneous reaction

The system required should have the following characteristics:

(i) the solvents and the solutes should be easily available in pure grade and be non-toxic;

(ii) the two solvents should be practically immiscible in order to lead to a maximum simplification of the mathematical treatment;

(iii) one of the two reactants should be soluble in both solvents whilst the other should be soluble in only one phase;

(iv) the common solute should be distributed roughly in the same proportion between the solvents;

(v) the solute and the active species should be chemically unreactive with the solvent pair;

(vi) the reaction must be instantaneous and irreversible;

(vii) it should be possible to measure the various concentrations accurately in a simple manner and using a very small sample of solution;

(viii) the system should be highly sensitive to changes in the hydrodynamics in the interfacial region so that all interfacial phenomena can be examined when introducing a chemical reaction.

Following the last requirement, the system should have a low density difference and a high interfacial tension. The toluene/water system can be considered as a suitable pair of solvents while propionic acid (subsequently abbreviated as HPr) fulfills the requirements as a solute. Its analysis can be carried out easily as shown in Section 3.4.1. The affinity of this weak acid for both phases is such that it is distributed almost equally between the two solvents at equilibrium.

The neutralisation of this acid by the sodium hydroxide, which is only soluble in water, gives a reaction whose properties are in agreement with the previous requirements. The chemical equation can be written as:

$$\mathrm{HPr} + \mathrm{NaOH} \longrightarrow \mathrm{NaPr} + \mathrm{H_2O}$$

One of the products is already a component of the system, which forms an additional simplification. As for the sodium propionate, it is very different in physical properties from the free acid, for it is partly inorganic and practically entirely ionic. Because of its ionic character, it is not soluble in the hydrocarbon solvent.

Otherwise this system is not very different from that used by AUSTIN (1966) for his investigation, of the cell characteristics (see also Section 3.1.2). It will therefore be interesting to compare Austin's results with those obtained in the present work.

3.2.2 Pseudo-first order reaction

In general, it is not easy to find homogeneous liquid-phase reactions, coupled with an extraction process, which are of first order kinetics. However, in the case of simple bimolecular reactions such as

$$A + B \longrightarrow \text{products}$$

they can often be treated as of pseudo-first order provided one of the reactants is present in excess.

Common reactions of this type are aromatic nitrations and sulphonations. The former have been widely studied by HANSON and co-workers (1966/71/74 a and b) and by COX and STRACHAN (1971/72 a and b/74). The latter have however received little attention.

Since toluene has already been used as solvent, the sulphonation of toluene was selected for the present study. As will be seen in Section 3.3.5, toluene is slightly soluble at the high concentrations considered in sulphuric acid. The reaction will thus take place in the lower phase. In addition, kinetic data for this reaction are available in literature and are reviewed in Section 3.3.6.

The product obtained by this reaction is the toluene sulphonic acid (subsequently referred to as TSA) which is present in a rather small quantity in the H_2SO_4 solution and can be easily analysed spectrophotometrically.

The use of concentrated sulphuric acid necessitated safety precautions such as the use of rubber gloves, an overall and goggles in order to ensure the operator's personal safety during manipulations of the acid solution, particularly when samples were removed from the acid phase.

3.3 Physical Properties

Except for the coefficients of diffusion which are given in Section 5.1, the physical properties of both solutes and solvents are summarised below.

For the study of the system toluene/water + HPr + NaOH small concentrations of solutes are assumed throughout. This means that, except for the refractive index and the interfacial tension, most physical properties of these dilute solutions will be taken as those of the pure solvents.

This does not apply to the highly concentrated sulphuric acid solution whose characteristics differ from those of water. It is therefore considered under a separate heading.

3.3.1 Materials

In his investigations GOLTZ (1960) checked the effect of purity of benzene on interfacial phenomena in liquid-liquid extraction. He concluded that no purification of the AnalaR benzene was needed for most experiments.

In the present work, the toluene used was of analytical reagent quality and the same conclusions were expected to apply. The water was freshly distilled and hence also regarded as sufficiently pure. Before each experiment, both phases were mutually saturated in the thermostat controlled at 25.0 ± 0.1°C.

Propionic acid, sodium propionate and toluene sulphonic acid were of laboratory reagent quality and were used without further purification.

The sodium hydroxide solutions were prepared from sodium hydroxide pellets of laboratory reagent grade whilst the sulphuric acid solutions were obtained by dilution of AnalaR sulphuric acid available at concentration of around 98% by weight.

3.3.2 General properties of pure substances

These are given in Table 3.1. It can be seen that the densities and refractive indices of toluene and water refer to the state of mutual saturation and hence approximate experimental conditions.

The solubilities of toluene in water and of water in toluene at 20°C are respectively 0.055 and 0.045 g/100 g saturated solution. Propionic acid is soluble in all proportions in water and toluene. The sodium salt is very different in physical properties from the free acid, for it is partly inorganic and is ionic. Because of its ionic character, it is not soluble in the aromatic solvent.

On titration with standard sodium hydroxide solution, propionic acid consumes an equivalent amount of base.

TABLE 3.1

PHYSICAL PROPERTIES OF AVAILABLE SUBSTANCES(25°C)

Component	Formula	Molecular Weight (g/g mol)	Density (g/cm³)	Viscosity (cP)	Refractive Index
Toluene	C_7H_8	92.14	0.864	0.555	1.49373
Water	H_2O	18.02	0.997	0.894	1.33295
Propionic Acid	$C_3H_6O_2$	74.08	0.988	1.025	
Sodium Hydroxide	NaOH	40.00	-	-	-
Sodium Propionate	$NaO_2C_3H_5$	96.06	-	-	-
Sulphuric Acid	H_2SO_4	98.08	1.84 (98%wt)	20.8 (98%wt)	-
Toluene Sulphonic Acid	$C_7H_7SO_3H$	172.22	-	-	-

3.3.3 Equilibrium data

In this section the influence is studied of the presence of the salt on the equilibrium of HPr between toluene and water. Two separate systems were investigated:

(i) toluene/water + propionic acid.

The equilibrium data for this system are available in literature (SEIDELL.1941). However experimental values were determined as a check on literature data.

(ii) toluene/water + propionic acid + sodium propionate.

Due to the lack of data, it has been necessary to determine experimentally the influence of the salt which is in solution in the water phase.

Procedure: The reagents were placed in 250 cm^3 flasks in sufficient quantities to cover the required concentration range. The flasks were shaken frequently and kept in a thermostat at 25°C. Equilibrium was assumed when the refractive index of the toluene phase reached a constant value. Its composition was then determined by measuring the refractive index. The concentration of acid in the aqueous phase was analysed by titration with phenolphthalein as indicator. The salt solutions used were of 1M and 0.5M concentrations.

Discussion: The influence on equilibrium data of a salt in aqueous solution has so far been represented only by the introduction of arbitrary empirical correlations. Most of them originated in the investigation of the solubilities of gases in liquids. Although many theories based on intensive thermodynamic studies have been developed, no theoretical relation predicts solubilities for gas-aqueous salt solution systems with sufficient accuracy.

Some empirical correlations have been presented by SETCHENOW (1892), LONG and McDEVIT (1952), MARKHAM and KOBE (1941), VAN KREVELEN and HOFTIJZER (1948) and ONDA et al(1970 a and b).

According to Setchenow

$$\log \frac{S_i^{\,o}}{S_i} = k_s C_s \qquad (3.1)$$

where S_i and $S_i^{\,o}$ are respectively the solubilities of the non-electrolyte in salt solution and in pure water, C_s is the concentration of the salt and k_s a temperature-dependent constant.

Using the fugacities of the non-electrolyte, Long and McDevit developed the same equation, The constant k_s was found to be a parameter for ion/non-electrolyte interaction.

Van Krevelen and Hoftijzer regarded this parameter as the sum of constants, denoted by i, which are characteristic of gases, cations and anions, i.e.

$$k_s = i_G + i_+ + i_- \qquad (3.2)$$

Moreover they assumed that i_+ and i_- are independent of temperature while i_G is dependent on it. They also proposed that ionic strength, I, should be used instead of C_s. The final equation is therefore:

$$\log \frac{S_i^{\,o}}{S_i} = k_s I \qquad (3.3)$$

As for Markham and Kobe and Onda et al, they complicated this equation by introducing a second parameter:

$$\frac{S_i}{S_i^{\,o}} = a\, m_s + \frac{1}{1 + b\, m_s} \qquad (3.4)$$

where m_s is the molality of the salt.

NANDA and SHARMA (1966/67/68/69) extended Van Krevelen and Hoftijzer's correlation to liquid-liquid system, the quantity i_G referring to the gas being replaced by i_s referring to the solute.

For the system toluene/water + HPr, the ratio of the solubilities in Eqn.3.3 is the ratio of the equilibrium concentrationsof propionic acid in the aqueous phase (C_w^* in presence of salt; C_w^{*o} in pure water).

As sodium proprionate decomposes into two ions of valence equal to one and if the dissociation of the weak acid HPr, present only in small quantities, is neglected, the ionic strength, I, will be equal to the salt concentraion C_s. It thus follows that

$$\log \frac{C_w^{*o}}{C_w^*} = k_s C_s \qquad (3.5)$$

which is of the same form as the Setchenow equation. The results obtained are plotted in Fig.3.3 and are tabulated in Appendix A3, Table 1. The data were fitted using the least square method and yielded a mean value of k_s equal to 0.106 l/gmol.

This value is compared in Table 3.2 with those found in the literature for species of the same kind. The effect of temperature acting only on i_s can be assumed as insignificant within the range considered.

TABLE 3.2

Solute	Salt	Temperature (^oC)	k_s (l/gmol)
n-propyl formate	NaCl	32.5	0.103
isoamyl formate	NaCl	32.5	0.100
p-nitroethyl benzoate	NaCl	30	0.090
p-nitromethyl benzoate	NaCl	30	0.080
isoamyl formate	Na_2SO_4	32.5	0.110

Ref: NANDA and SHARMA (1966/67/68/69).

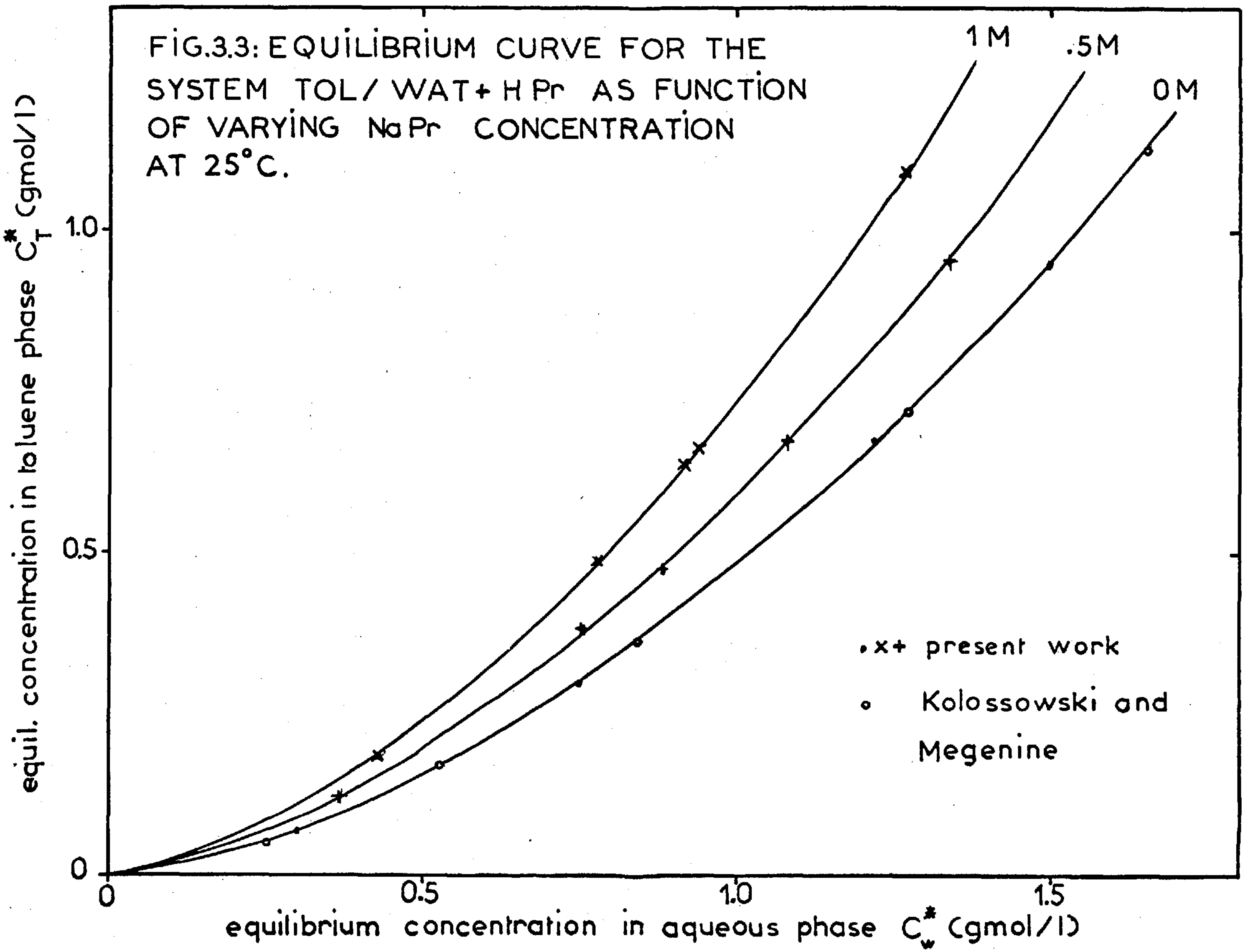


FIG.3.3: EQUILIBRIUM CURVE FOR THE SYSTEM TOL/WAT+HPr AS FUNCTION OF VARYING NaPr CONCENTRATION AT 25°C.

For molecules with long chains, or for molecules with large metallic atoms, k_s may rise up to about 0.180 l/gmol.

If the contribution of the cation Na^+ is taken as 0.091 (DANCKWERTS.1970), it follows that

$$i_{Pr^-} + i_s = 0.015$$

The mean value of i_- for anions of a size comparable to Pr^-, such as Cl^-, SO_4^{--} or CO_3^{--}, is 0.021.

It seems therefore that the contribution due to the solute is very small. This can be explained by the fact that it is of the same "quality" as two of the ions already present in the solution. The temperature should not have a significant influence on the value of k_s as was mentioned above.

3.3.4 Interfacial tension

The variation of interfacial tension is considered here as a function of concentration of the various species. For the toluene/water + HPr + NaOH system, it is essentially the effect of the salt produced by the instantaneous reaction. Experimental measurements were therefore made on the system toluene/water + NaPr. For the toluene/aqueous H_2SO_4 solution, no experiments could be carried out because of the occurrence of the sulphonation reaction and thus of the continuous change in the acid concentration in the zone near the interface. Nevertheless an estimation has been made of this effect.

System toluene/water + NaPr

Procedure: The interfacial tensions were roughly measured using a Torsion Balance WHITE at room temperature, i.e. about 22°C. This apparatus is a Du Noüy ring-detachment-type tensiometer with a sensitivity of 0.05 mN/m at the temperature considered. The platinum-iridium ring, 4cm in diameter, was thoroughly cleaned by rinsing in acetone, then in distilled water and finally dried in a reducing flame. Before measurements the graduated dial was adjusted for zero reading with the ring suspended in air.

A preliminary test was made to check the tensiometer by measuring the surface tensions of the pure samples of water and toluene.

The ring method was originally developed for surface tension measurement, but it can be applied to determine interfacial tensions provided that the lower liquid preferentially wets the platinum ring, which was the case with the present system. The results are presented below in Table 3.3.

The difference between observed and literature value for the system toluene/water was not considered to be important, as for the purpose of this investigation, the relative and not the absolute value is the important variable. The results however are not different from those found with the same type of apparatus by MURPHY, LASTOVICA and FALLIS (1957). As already pointed out, the error observed is certainly due to the method used.

From Table 3.3 it can be noticed that the presence of the salt, whatever its concentration, increases the interfacial tension by about 0.3 mN/m.

TABLE 3.3

NaPr Concentration (gmol/l)	Interfacial Tension (mN/m)	
	Experimental 22°C	Literature 25°C
0.0	29.2	36.1
0.20	29.5	
0.565	29.5	
0.625	29.6	
0.97	29.5	
1.00	29.6	
1.285	29.5	

A constant increase of 0.4 mN/m has been observed for a 1.0 normal solution of sodium acetate on the surface tension of water (RIDEAL.1926). This is of the same order of magnitude as that obtained in this work.

Discussion: The increase of interfacial tension caused by the addition of salts has been studied by RIDEAL (1926), by DAVIES and RIDEAL (1961) and by ADAMSON (1967). They pointed out that, in the case of molecules which do not dissociate or which are only partially dissociated, the orientation of the molecules in the interface layers affects the value of the interfacial tension. The organic chain of the substance is attracted by the organic phase whilst the charged part remains in the water phase. The adsorption of fatty acids at any oil/water interface can be taken as an example of this phenomenon.

The ionic character of the corresponding sodium salt will have an influence on the dielectric constant of the medium at the interface and thus disturb the existing equilibrium. The fact that the surface tension of water is raised by the addition of the salt indicates that repulsion of the salt as a whole from the surface must take place.

This discussion emphasises the importance of the interfacial behaviour of molecules which may even affect the chemical reaction kinetics if the reaction, as happens often in the present study, takes place at or near the interface.

System toluene/aqueous H_2SO_4 solution

Because the two phases react when brought into contact, it is difficult to obtain stable experimental results for the interfacial tension. Experiments can however be carried out for low H_2SO_4 concentrations and their results extended for the H_2SO_4 concentration range considered using a method described below and based on Antonoff's rule.

Since only the relative value of the interfacial tension with respect to H_2SO_4 mass fraction, i.e. $\frac{d\sigma}{dw}$ (see Section 6.2.2.3), is being considered the applicability of the rule is reasonably justified.

However it is obvious that Antonoff's rule will not be valid for the pure system toluene/water. A constant of about 8 mN/m will have to be substracted at 25°C in order to obtain the experimental value of 36.1 mN/m.

In spite of that, the analysis of values obtained for H_2SO_4 concentrations of 0.5, 2.5 and 5.0 gmol/l with the system benzene/aqueous H_2SO_4 solution and reported by DAVIES and RIDEAL (1961) shows a good agreement between calculated and experimental values provided that Antonoff's rule takes into account this constant of subtraction which is around 10 mN/m when benzene is used as the organic phase.

The estimation of the interfacial tension σ at any H_2SO_4 concentration is carried out with the following relation:

$$\sigma = \sigma_o + \sigma_2 - \sigma_w \qquad (3.6)$$

where σ_o is the interfacial tension of the system toluene/water, i.e. 36.1 mN/m at 25°C, σ_2 the surface tension of the relevant aqueous solution and σ_w the surface tension of pure water, i.e. 72 mN/m at 25°C.

In the derivation of the above equation it was assumed that the surface tension of toluene is not affected by the presence of sulphuric acid molecules. For 25°C Eqn.3.6 gives:

$$\sigma = \sigma_2 - 36 \qquad (3.7)$$

The International Critical Tables give the surface tension of aqueous H_2SO_4 solution at various temperatures. An extrapolation was however necessary for 25°C. It can be noted that at low H_2SO_4 concentration the surface tension σ_2 increases with mass fraction and reaches a maximum for 49%-wt H_2SO_4.

The estimated values of the interfacial tension σ over the range 68 to 84%-wt H_2SO_4 are tabulated in Appendix A4, Table 4.

3.3.5 Properties of the aqueous sulphuric acid solution

The density and the viscosity of such solution can be found in the International Critical Tables. The viscosity which is not a simple function of composition at high percentage of sulphuric acid is represented in Fig.3.4 for the considered range (see also Appendix A4, Table 5).

The toluene content is neglected and it is assumed that the toluene sulphonic acid dissolves without any change in the volume of the solution. It may also be assumed with reasonable accuracy that the small quantity of toluene sulphonic acid present in the solution does not affect its viscosity.

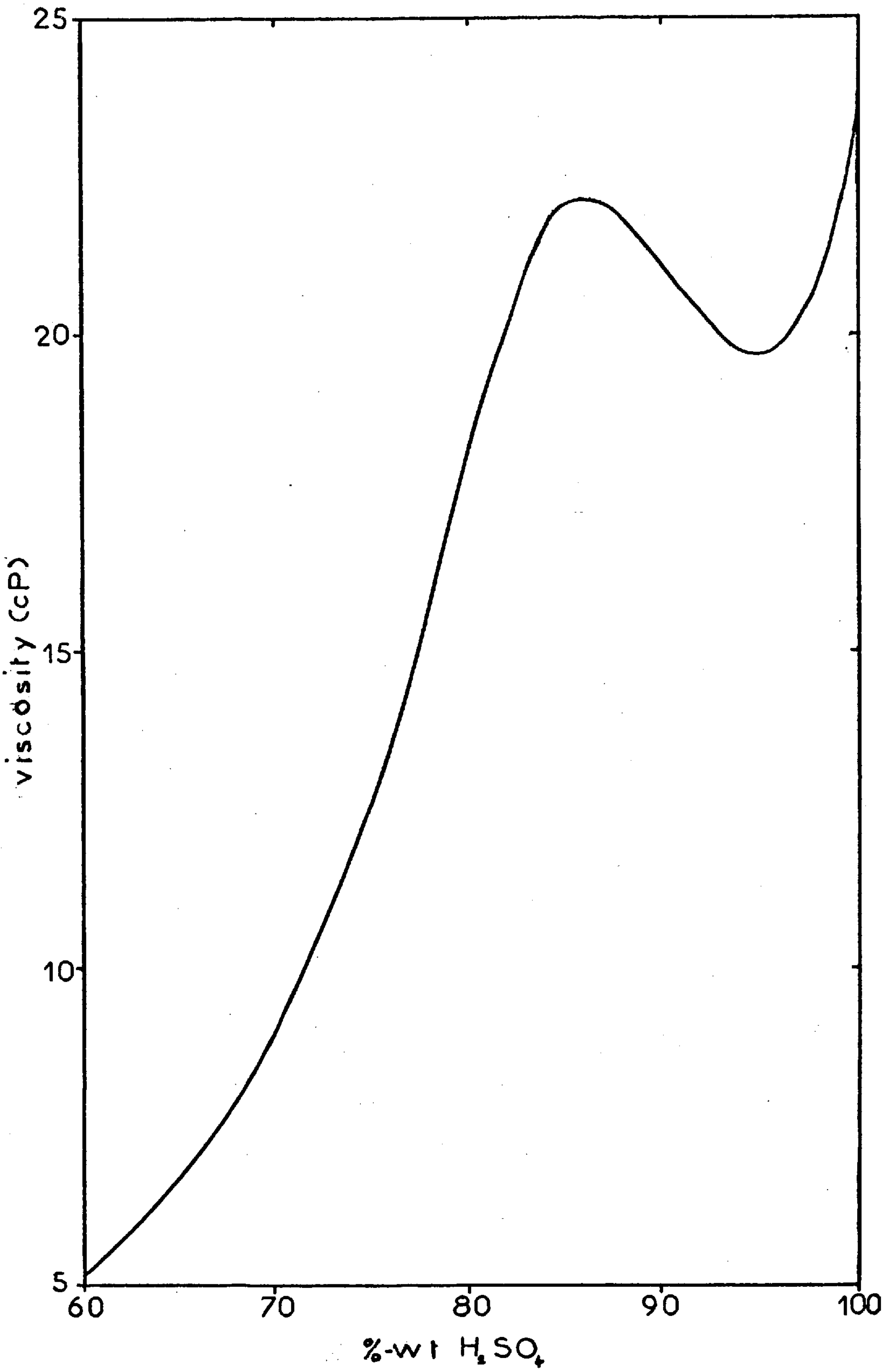


FIG.3.4 : VISCOSITY OF AQUEOUS SULPHURIC ACID SOLUTION AT 25°C

The data concerning the solubility of toluene at 25°C in aqueous sulphuric acid have been reviewed and presented by CERFONTAIN and TELDER (1965) under various concentrations. The acid range studied was 0-83%-wt H_2SO_4, but their results are plotted in Fig.3.5 only for the values which have any relevance to the present work.

3.3.6 Kinetics of toluene sulphonation

A general review of aromatic sulphonation was presented by SAUNDERS (1971). Toluene sulphonation was studied in detail by CERFONTAIN and co-workers (1965/68) under both heterogeneous (1964) and homogeneous (1961/63 a and b) conditions. Their study concerned the measurement of the rate of sulphonation of toluene and the isomer distribution in various aqueous sulphuric acid solutions particularly at 25°C, but also at some other temperatures.

CERFONTAIN, SIXMA and VOLLBRACHT (1964), studying the heterogeneous conditions, suggested that the reaction takes place mainly, if not solely, in the aqueous phase and that the content of p-toluene sulphonic acid is higher (about 68%) under those conditions than under homogeneous conditions, whereas the amount of the meta-isomer is about the same for both types of sulphonation.

With reference to the homogeneous conditions the main work is that of CERFONTAIN, KAANDORP and SIXMA (1963 a). The kinetics has been studied extensively for 5°, 25° and 45°C over the range of sulphuric acid concentrations 70 to 95.9%-wt. The sulphonation reaction was found to be of pseudo-first order with respect to toluene so that the rate of consumption of toluene can be written as

$$R_T = k_1 C_T \qquad (3.8)$$

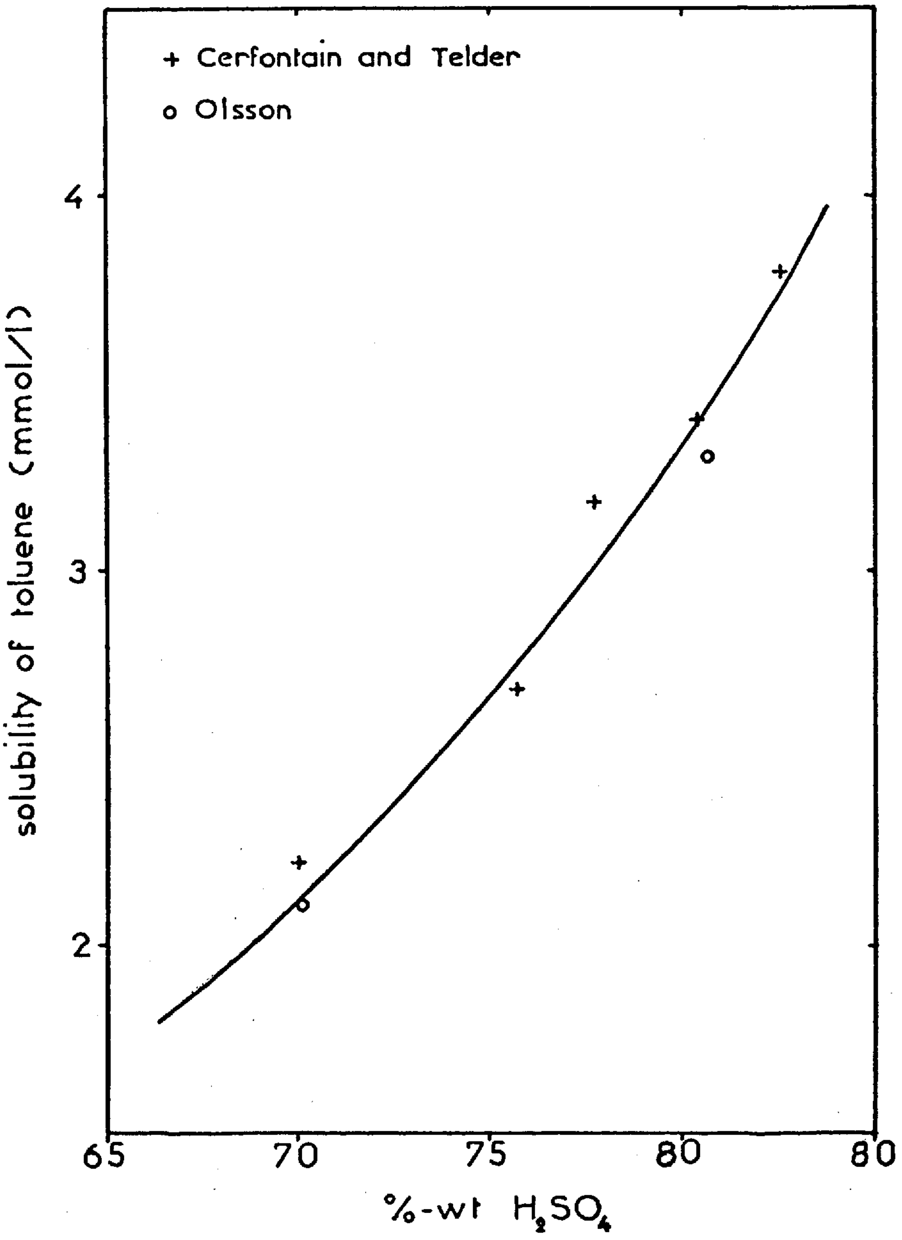


FIG.3.5: SOLUBILITY OF TOLUENE AT 25°C IN AQUEUS SULPHURIC ACID SOLUTION.

where C_T is the toluene concentration. The experimental data have been compared with other kinetic studies and summarised by SAUNDERS (1971) for 25°C to give the relation

$$\ln k_1 = -64.32 + 67.50\, w_2 \qquad (3.9)$$

where w_2 is the mass fraction of H_2SO_4 in the aqueous solution.

It was also found by previous workers that sulphone formation and disulphonation were negligible (CERFONTAIN, SIXMA and VOLLBRACHT.1963 b) and that the isomer distribution at 25°C for example in 82.3%-wt H_2SO_4 was 65.1% para-, 2.9% meta- and 32.0% ortho-isomer (CERFONTAIN, VOLLBRACHT, SIXMA.1961) for the homogeneous conditions. Moreover, the percentage of the meta-isomer in the product was low under all conditions and the ratio of the para- and ortho-isomer decreased with increasing sulphuric acid concentration.

Finally it should be noted that SAUNDERS (1971) estimated the activation energy of sulphonation E_s (kcal/gmol) by assuming that it depends linearly upon sulphuric acid concentration. Experimental data obtained over a large range of temperature led to:

$$E_s = 66.02 - 52.59\, w_2 \qquad (3.10)$$

for w_2 ranging from 78 to 86.2%-wt H_2SO_4.

3.4 Measurement Techniques

For the analysis of propionic acid in toluene, the measurement of the refractive index proved to be a quick and accurate method.

The quantitative analysis of small amounts of toluene sulphonic acid present in a large excess of concentrated sulphuric acid was more difficult to perform. The possibility of solving this problem by ultra-violet spectroscopy was therefore investigated.

All other analyses concerning the acid or base solutions were conducted by titration with the corresponding base or acid using phenolphthalin or bromothymol blue as indicator.

3.4.1 Refractive index measurements

The refractive indices of samples taken from the toluene phase were measured with a high accuracy Abbe 60 refractometer whose prism boxes were mounted in water jackets controlled at 25.0 ± 0.1°C by circulation of water from a thermostat. A sodium lamp was used as the light source and the refractometer angle converted, if necessary, to refractive index by means of calibration tables. The zero of the refractometer was adjusted by using a quartz block of known refractive index and monobromonaphthalene and checked with water.

The angle of refraction could be measured to an accuracy of ± 0.5' corresponding to ± 0.01 gmol/l of propionic acid. Vaporisation of propionic acid was minimised by injecting the solution quickly into the prism box with the syringe used to withdraw the sample of phase 1.

In order to obtain thecalibration curve measurements were performed with solutions of known concentration prepared in standard flasks using a precision balance. The calibration curve is presented in Fig.3.6.

The method has the advantage of requiring a small quantity of the organic phase and therefore of having a negligible effect on the variation of volume in the stirred cell.

3.4.2 Ultra-violet spectroscopy

A spectrophotometric determination of the total amount of toluene sulphonic acid in excess sulphuric acid was first described by PINCHAS and AVINUR (1958). CERFONTAIN et al and

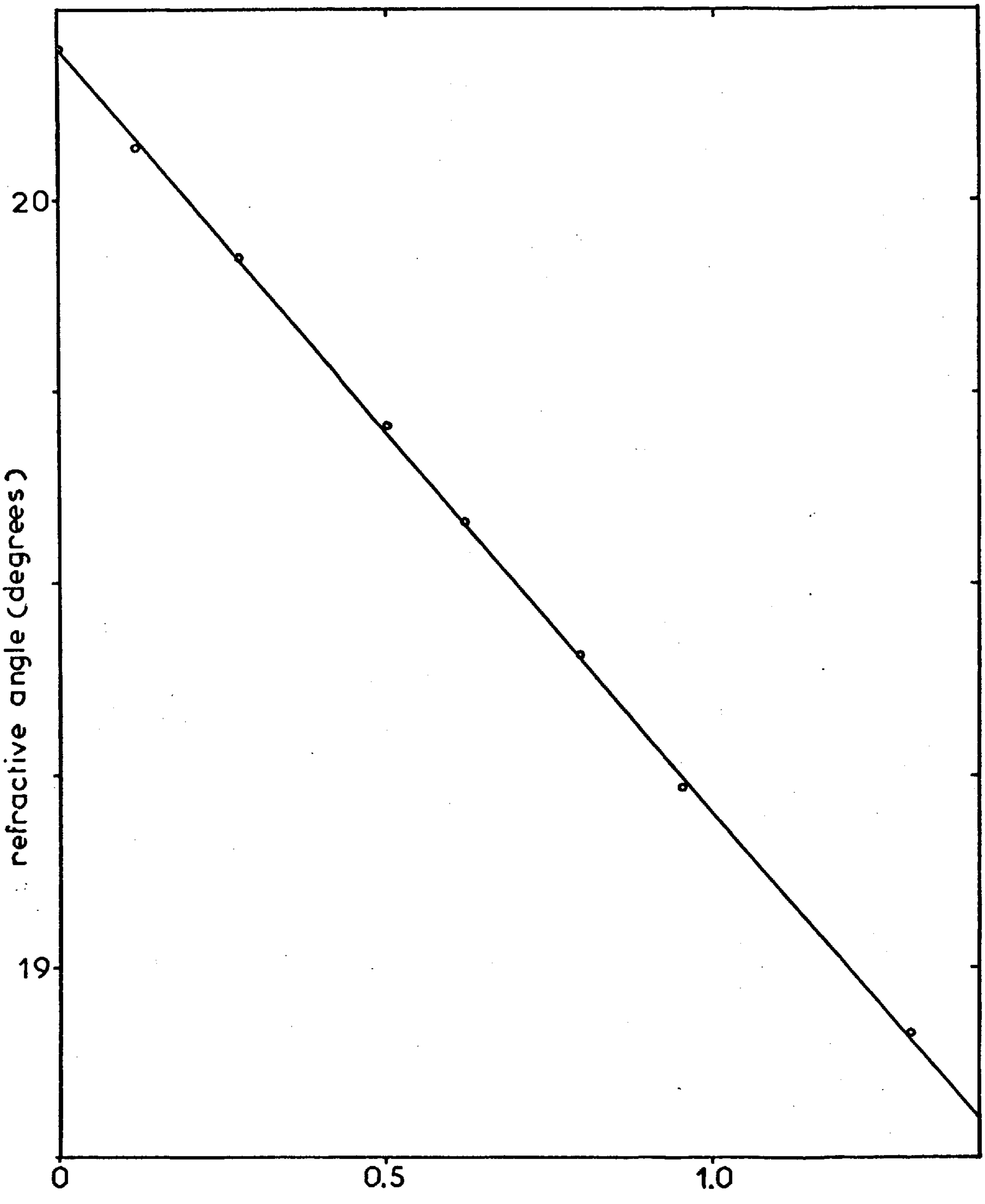


FIG. 3.6: REFRACTIVE ANGLE CALIBRATION CURVE AT 25°C.

SAUNDERS used this method in connection with their studies on kinetic rates of sulphonation. It was also employed by COX and STRACHAN in their investigation of two-phase nitration of toluene.

In order to study the composition of mixtures of the three isomers in the excess of concentrated aqueous sulphuric acid CERFONTAIN et al (1963 c) determined the absorbance of the unknown mixture and of its constituents at a large number of wavelengths and calculated the isomeric repartition using a least square treatment performed by a computer over the whole range of the spectrum.

SAUNDERS (1971) quantified only the total toluene sulphonic acid in samples. An accurate determination of the absorptivity at a reference wavelength was therefore essential. He observed from the absorption spectra of the three isomeric toluene sulphonic acids in aqueous sulphuric acid, obtained by the previous workers, that at 256 nm the absorptivity of the ortho-isomer equalled that of the para-isomer.

It has already been shown in Section 3.3.6 that the partial rate factor for the meta-isomer is small compared to the factors of the two other isomers. The assumption that the products of sulphonation are only the ortho- and para-isomers is justified and does not lead to serious errors.

Comparison of the spectrum of toluene with those of its sulphonic acids emphasises the importance of removing all traces of toluene by repeated washing with n-hexane. It should also be pointed out that sulphuric acid does not absorb between 245 and 280 nm.

The method developed by SAUNDERS seems to be suitable for the present work. The absorptivity of the BDH micro-analytical grade hydrated para-toluene sulphonic acid was calculated by using samples of known concentration in excess sulphuric acid. The same solution of sulphuric acid was employed in the reference cell in order to reduce the errors due to the absorption of interfering molecules. This procedure was adopted for the whole analysis.

The HITACHI-PERKIN-ELMER 139 UV-Spectrophotometer was used throughout this work. The dilute solutions of toluene sulphonic acid obeyed the Beer-Lambert Law up to TSA concentration of 1.2 g/l. The absorptivity of the three isomers, measured at 256 nm is calculated to be 1.613 $g^{-1}.l.cm^{-1}$.

The concentration of toluene sulphonic acid in excess sulphuric acid is related to absorbance A by:

$$C_{TSA} = 0.620\ A \tag{3.11}$$

where C_{TSA} is expressed in g/l.

In order to make full use of the accuracy and sensitivity of the UV spectrometer, the 1cm matched precision optical cells used in this work had to be carefully cleaned. Cleaning procedures varied with the accuracy required and with the type of contamination arising from previous use. Because the solution to be analysed is always the same, the latter can be ignored. The cleaning method employed in the ultra-violet region consisted of instant immersion of the cell in concentrated nitric acid and of repeated rinsing with distilled water and absolute ethanol. Correct application of this method should give transmission variations of less than 1.5% at 240 nm.

Finally it should be noted that samples analysed in this way can be injected again into the cell so that the volume remains constant.

CHAPTER 4

THEORETICAL MODEL FOR MASS TRANSFER WITH CHEMICAL REACTION

The purpose of this chapter is to obtain simple equations using a model selected from those reviewed in Section 4.1 and to interpret the effect of chemical reaction on the mass transfer process (Section 4.2).

In what follows, the superscript 'o' will indicate mass transfer conditions for the case of mass transfer in the absence of chemical reaction (the reference conditions) and the indices 1 and 2 will respectively refer to the upper and lower phases.

The values of the reference mass transfer coefficients are predicted in Chapter 5 and it is subsequently assumed that they are known.

4.1 Mass Transfer Models and Effect of Chemical Reaction

In order to study the process of homogeneous mass transfer with simultaneous chemical reaction, models have been developed by various workers. The three simplest and best known are: (1) the film theory, (2) the penetration theories, and (3) the generalised mass transfer theory.

Simultaneously with the diffusion of the reactants to the reaction zone, the reaction products must diffuse away. It is considered in literature that the diffusion of reaction products can be disregarded, except when ionic diffusion has to be taken into account, as will be seen in Section 5.1.1.2. It should however be remembered that strictly speaking such statements are only applicable to dilute solutions.

More complete discussions of the subject matter of this chapter have been given by ASTARITA (1967), DANCKWERTS (1970) and SHERWOOD, PIGFORD and WILKE (1975). They all summarised very adequately the general state of knowledge on gas absorption with chemical reaction, but quoted only a few references concerning liquid-liquid extraction accompanied by chemical reaction.

As pointed out by HANSON (1971), the little attention received by liquid-liquid reactions is not due to the lack of theoretical treatment, but rather to the great complexity and the uncertainty of their chemistry. In the present work it will however be assumed that the reaction kinetics is known so that the methods of approach developed for gas absorption can be applied to liquid-liquid systems.

In what follows, the available models are first reviewed, and then their behaviour studied when a chemical reaction is introduced. Finally the choice of the model leading to the best simulation of the process is made taking into account its degree of complication.

4.1.1 Mass transfer models based on film theory

The film theory deals with mass transfer between a turbulent medium and the interface. It assumes the presence of a stagnant layer of the fluid at the interface. The thickness of this fictitious film is calculated by assuming that the flux through it is due to molecular diffusion only. This thickness is usually small enough for the transfer to be treated as steady state diffusion through a stagnant medium.

WHITMAN (1923) assumed that the turbulence in the liquid is damped out near the interface. He visualised that the scale of turbulence and the eddy diffusivity got progressively smaller as the interface is approached until the transport by the eddy diffusion becomes of negligible importance. This simple model leads to:

$$N = K\ (C^{*} - C) \qquad (4.1)$$

and

$$K = \frac{D}{x} \qquad (4.2)$$

where N is the mass flux, K the mass transfer coefficient, D the diffusion coefficient, C^{*} and C respectively the concentration at the interface and in the bulk. The hydrodynamic properties of the system are accounted for by the film thickness x which depends on the geometry, liquid agitation, physical properties, etc.

4.1.2 Mass transfer models based on penetration theories

HIGBIE (1935) applied the concepts of transient diffusion to the solution of a mass transfer problem and this, in fact, introduced the idea of thepenetration theory with regular surface renewal (the Higbie model). This was later considerably modified by DANCKWERTS (1951) by the assumption of random surface renewal (the Danckwerts model).

In its present interpretation the penetration theory contains the postulate that large eddies penetrate to the liquid interface and are thus constantly bringing elements of fluid from the bulk to the interface where they are exposed for a finite time before being replaced. In the Higbie model it is assumed that every element is exposed for the same length of time θ whilst Danckwerts assumes a random distribution of surface ages in which the surface age frequency distribution function is given by $\phi\ (\theta) = s\ e^{-s\theta}$. It thus follows for the Higbie model that

$$N = 2\sqrt{\frac{D}{\pi\theta}}\,(C^* - C) \qquad (4.3)$$

and for Danckwerts model:

$$N = \sqrt{Ds}\,(C^* - C) \qquad (4.4)$$

PERLMUTTER (1961) modified the surface renewal model by considering the interface as consisting of a cascade of two-dimensional stirred tanks. This introduced n, the number of stirred tanks, as an additional parameter to s, the fractional rate of surface renewal. Value of $n = 1$ gives the Danckwerts model and $n = \infty$ the Higbie model. However, the whole range of variation in n only predicts a 13% change in the mass transfer coefficient.

Regarding the limitations of the film and the penetration models, TOOR and MARCHELLO (1958) showed that for purely physical absorption the two models are not separate unrelated concepts, but rather provide limiting cases of a more general model, the film-penetration model, and that the two theories are complementary and not mutually exclusive. It could be shown that mass transfer into new elements reaching the surface follows the penetration theory whilst mass transfer into old elements is approximated by the film theory. The elements of intermediate age have the characteristics of both theories.

MARCHELLO and TOOR later (1963) modified the film-penetration model, postulating layers of definite thickness, not necessarily in contact with the interface, which are uniformly mixed at random time intervals. Mass transfer from one layer to another then takes place by molecular diffusion.

4.1.3 Mass transfer models based on generalised mass transfer theory

So far molecular diffusion was considered as the only process by which molecules can reach the interface. However, it can be visualised that for conditions of high intensity turbulence, even energy-dissipating eddies are not damped out by the interface and eddy diffusivity, ϵ, is added to molecular diffusivity throughout the whole diffusion path.

KING (1966) has considered that ϵ is proportional to some power, m, of the distance from the surface. It is clear that the mass transfer coefficient K will be proportional to m and that it will therefore be difficult to calculate.

KISHINEVSKII et al (1949/55/56) has assumed ϵ to be a constant. The turbulence is supposed to extend to the surface, the new effective diffusion coefficient being the sum of the molecular and eddy diffusivities.

In general, in order to integrate the rate equation obtained i.e.

$$N = - (D + \epsilon) \frac{dC}{dx} \tag{4.5}$$

where x is the distance from the phase boundary, it is necessary to relate ϵ and x. For the turbulent regime, the usual approach is to use the various analogies relating mass, heat and momentum transfer. ϵ can thus be obtained indirectly through its relation to the eddy viscosity which is derived from velocity profiles. The basis of this turbulent boundary-layer model is developed in reference (SHERWOOD, PIGFORD, WILKE - 1975).

4.1.4 Other mass transfer models

HARRIOT (1962) envisaged eddies replacing fluid at varying distances from the surface, thus not necessarily renewing, but modifying the concentration profile near the interface. This leads to the surface rejuvenation model which resembles most closely the actual conditions of transfer, but is much too complicated for standard application.

KOLÁŘ (1961) and LEVICH (1962) were concerned with the fact that the turbulent disturbances penetrating from the bulk phase towards the interface cause a turbulent flow near the surface and also its periodic renewal. The first author assumed, in accordance with Higbie, that the controlling step is unsteady molecular diffusion into the elements forming the interface whilst the second assumed steady molecular diffusion into a boundary layer whose thickness depended on the depth of the zone of deformed turbulence corresponding to the characteristic size of the eddies causing surface renewal.

A simple model based on the theory of Levich was set up by DAVIES (1972). It will be studied in more detail in Section 5.2.3.

Based on the assumptions of Kolář, PROCHÁZKA and BULIČKA (1971) took into account momentum transfer between two liquids and assumed that the mean residence time of a liquid element at the interface was proportional to the Kolmogoroff length scale for isotropic turbulence divided by the corresponding velocity scale. However it has been pointed out that this model which predicts that

$$\frac{K_1}{K_2} = \left(\frac{D_1 \mu_1}{D_2 \mu_2}\right)^{\frac{1}{2}} \tag{4.6}$$

does not agree with most experimental results. In a subsequent paper (1976) the same authors revised their theory on the assumption that disturbances affect both layers simultaneously in view of the perfect mobility of the interface. This gives a more acceptable relation:

$$\frac{K_1}{K_2} = \left(\frac{D_1}{D_2}\right)^{\frac{1}{2}} \qquad (4.7)$$

4.1.5 Effect of chemical reaction

The development of a satisfactory theoretical model for the case of a chemical reaction will depend mainly on the precise knowledge of the reaction involved. If predictions are to be made about the behaviour of the system in such a case, it is necessary to use simplified models which simulate the situation sufficiently well so that conclusions can be drawn about the influence of the chemical reaction on the mass transfer process.

This aim was followed by most investigators. Nearly all of them studied the gas absorption process accompanied by chemical reaction because of its industrial importance and its suitability for theoretical treatment. In order to retain a simplicity of treatment they evaluated their results in terms of either the film model or the penetration model. Although the validity of the models may seem debatable, nevertheless it was proved that they lead to accurate predictions of the effects of chemical reaction.

There are basically two models based on the film theory: the Hatta model and the Sherwood-Wei ion diffusion model.

HATTA (1928) modified the two-film model for the case of absorption with chemical reaction by assuming that the reaction took place in the liquid film. He then derived an expression for the liquid phase mass transfer for a rapid irreversible reaction as a function of the molecular diffusivities, the concentrations of the reactants and the film thickness. Later on, he extended his analysis to first-order irreversible reactions (1932).

For the irreversible second-order reaction, an approximate result was obtained by van KREVELEN and HOFTIJZER (1948) from the assumptions of the film theory of Hatta. KISHINEVSKII and co-workers (1965) proposed similar approximate relations applicable only when the substance is removed by a single molecular mechanism during the period of contact time.

SHERWOOD and WEI (1955) modified the Hatta model correcting the diffusivities of the ions for the presence of other ions. Using the treatment of VINOGRAD and McBAIN (1941) for diffusion in mixed electrolytes, they derived diffusion equations for each ion imposing the condition of electrical neutrality on the ion mixture. From these equations an expression was derived for the mass transfer coefficients as a function of diffusivities of individual ions and their concentrations (see Section 5.1.1.2). Their test of this model showed excellent results when used in a diffusion cell, but it has not been tested in a stirred cell or in a flow system where eddy diffusion is also important.

SHERWOOD and RYAN (1959) proposed the turbulent boundary layer model for a flow system. This leads to results similar to those of HATTA with the important difference that the resistance per unit length varies with the distance from the interface.

In the case of models based on the penetration theories of either Higbie and Danckwerts, several developments have been proposed according to the kind of chemical reaction studied. Most results were obtained and summarised by DANCKWERTS (1970).

To this list should be added the contribution of SCRIVEN (1961) for the case of a rapid second-order irreversible reaction and the ionic penetration theory of BRIAN, BADDOUR and

MATIATOS (1964). The latter, based on the ionic diffusion of reactants already mentioned, solves the problem of mass transfer accompanied by an irreversible second-order reaction using the penetration theory.

As far as the generalised mass transfer theory is concerned, little attempt has been made to couple it with a chemical reaction. This is certainly due to the complicated aspect of the models. If both a molecular and a turbulent mechanism are involved in removal of the substance, the mathematical problem is greatly complicated even for simple absorption. KISHINEVSKII and ARMASH (1965) showed that the theoretical equations derived with the aid of the renewal model and of the film model are equally valid for calculations relating to absorption accompanied by chemical reaction in mechanically stirred absorbers and wetted-wall columns.

As regards other models, KOLÁŘ (1961) tried to apply his theory to the case of first-order reaction. The mass transfer coefficient was found to be dependent on the local degree of turbulence.

4.1.6 Discussion

It was noticed by several authors that different models give solutions for several kinds of chemical reactions which are in close agreement. The comparison (SHERWOOD, PIGFORD and WILKE, 1975, p.321) of Hatta, Higbie and Danckwerts theories in the case of interfacial mass transfer accompanied by first-order irreversible chemical reaction is a good example of this agreement.

SHERWOOD and RYAN (1959), when developing their boundary turbulent layer model had pointed out that the Hatta equation fitted the data somewhat better than the other theories, including the Danckwerts model. Later, BRIAN, HURLEY and HASSELTINE (1961) introduced a penetration-theory solution for the effect of a second-order irreversible chemical reaction on the absorption rate which was calculated numerically on a computer. Their results were compared with the film-theory solution and it was shown that the solutions agreed within 16% if they were compared for similar conditions.

Finally BRIAN, BADDOUR and MATIATOS (1964) studied the magnitude of ionic diffusion effects in the penetration model for simultaneous chemical reaction. It was concluded that the maximum deviation of 4%, which was observed with respect to the film theory, was not significant because film theory approximation can be obtained much more simply than results of the ionic penetration theory.

4.1.7 Conclusions

The problem of predicting the effect of a simultaneous chemical reaction on the mass transfer rate has often been approached by adopting a simplified model of the liquid flow pattern which could then be treated mathematically. In the years since Hatta first used the simple film theory to analyse the effect of an infinitely fast irreversible bi-molecular reaction, a number of models have been developed. However most chemical reactions have been treated from the viewpoint of the film theory and of the penetration theories in order to find the best agreement with experimental results.

It is interesting to note that it was often found that the predicted answer to this problem was surprisingly insensitive to the liquid flow pattern model which was chosen. In view of its simplicity, it is therefore preferable to use the film model rather than any of the other models.

In general, the difference between expressions provided by the film theory and the penetration theory frequently comes down the difference between the ratios D_A/D_B and $(D_A/D_B)^{\frac{1}{2}}$. As the diffusivities of the reacting species in the liquid solvent are not substantially different, it is often difficult to draw conclusions concerning models from experiments of mass transfer with chemical reaction. If in such a situation the film model is preferred, it must be pointed out that the latter predicts that K is proportional to D, or to $D^{2/3}$ in its modified form while, according to AUSTIN (1966) it seems that, except at low stirring speed, it varies with $\sqrt{D}$.

However, apart from prediction of the mass transfer coefficient in the absence of a chemical reaction (the reference coefficient), the present work is not concerned with the effect of D on K. It is solely concerned with the effect of chemical reaction on K.

4.2 Application of Theoretical Model Based on Film Theory to Stirred Cell

4.2.1 Instantaneous reaction

The present theory on mass transfer with instantaneous chemical reaction is based on the assumptions that the fluid dynamics of the situation is unchanged by the reaction and that there is no change in the fine structure of the fluid dynamics in the region close to the interface.

In addition, in order to simplify the mathematical treatment and to draw the necessary conclusions for a better understanding of the problem, it will be assumed in this section that the equilibrium curve can be approximated by a straight line over the range of concentrations studied. Further developments concerning this point can be found in Section 5.2.1.

4.2.1.1 General

The model considered here is the oversimplified film model, i.e. more precisely the Hatta model, which is derived from the two-film theory for the case of absorption with chemical reaction by assuming that the reaction takes place in the liquid film.

The effect of chemical reaction on mass transfer is measured by the ratio of the mass fluxes with and without chemical reaction. This is called the enchancement factor and can be written as:

$$E = \frac{N_A}{N_A^o} \qquad (4.8)$$

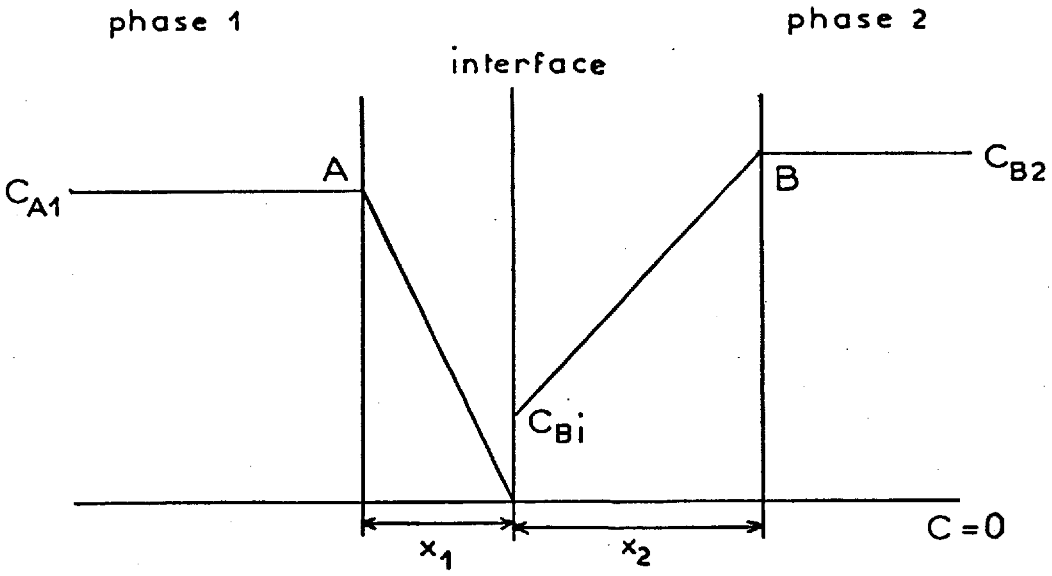
where N_A and N_A^o are the mass fluxes with and without chemical reaction respectively for the case of zero concentration of solute in the bulk.

To derive this ratio a rapid irreversible batch reaction

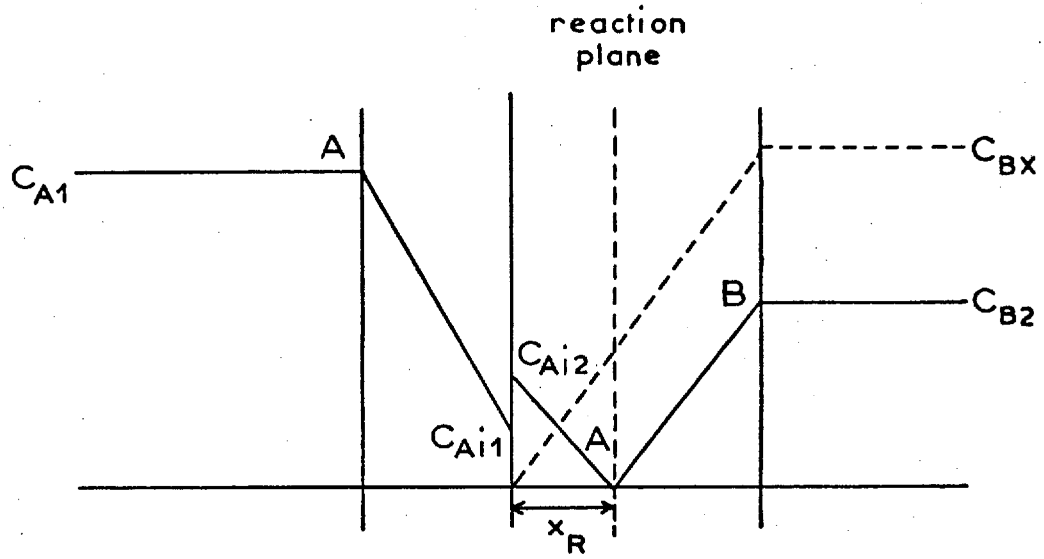
$$aA + bB \rightarrow cD + dD \text{ in a solvent S}$$

is considered.

The substance A is soluble in all proportions in both phases whilst B, C and D are soluble only in one phase (phase 2). Component A is initially present only in phase 1. After contact between the two phases, provided that concentration of B is sufficiently high (see later), there is transfer of A and B from the bulk towards the interface in phases 1 and 2 respectively (Fig.4.1.a).



a. Case I



b. Case II

FIG. 4.1: CONCENTRATION PROFILES OF THE REACTANTS IN THE CASE OF INSTANTANEOUS CHEMICAL REACTION.

Subsequently, as concentration of B decreases with time, the reaction plane moves away from the interface. Substance A then diffuses from the interface to the reaction plane and substance B reaches the same plane by diffusion from the bulk (Fig.4.1.b).

The products of the reaction, C and D, which are assumed insoluble in phase 1 are transported out of the reaction zone into the bulk of phase 2.

The concentration profiles of the reactants will be similar to those shown in Fig.4.1. It is clear that two different cases have to be considered:

Case I: the reactants react at the interface; A diffuses only in phase 1.

Case II: the reaction plane moves towards the bulk of phase 2; the reactant A diffuses also in phase 2 from the interface to the reaction plane.

The position of the reaction plane depends on the ratio of initial concentrations $\frac{C^i_{A1}}{C^i_{B2}}$, the stoichiometric ratio $\frac{a}{b}$ and the ratio of diffusivities D_{AS}/D_{BS}.

For a given C^i_{A1} let C_{BX} be the critical value of concentration of B for which the reaction zone leaves the interface. Then

- if $C^i_{B2} < C_{BX}$, Case I applies
- if $C^i_{B2} > C_{BX}$, Case I applies first, followed by Case II

when $C_B(t) < C_{BX}$.

4.2.1.2 Main assumptions

As seen previously in Fig.4.1 and with the purpose of establishing some mathematical formulationsit has been necessary to make a number of assumptions which are:

(i) component A is throughout in phase equilibrium at the interface

(ii) the properties of dilute solutions and of zero-nett-flux transfer are applicable

(iii) the chemical reaction which takes place only in phase 2 or at the interface does not affect the resistance to transfer in phase 1

(iv) the bulk phases are completely mixed and therefore of uniform concentration

(v) for mass balance purposes the capacities of the films are small in comparison to the volumes of the bulk phases

(vi) the mass transferred has a negligible effect on the volumes of the phases which remain constant

(vii) the molecular diffusivities of A and B which are assumed to be given by the binary diffusivities through the solvent are also taken to be independent of concentrations

(viii) interfacial phenomena, such as Marangoni or gravitational instabilities, are absent

(ix) the products C and D do not influence the equilibrium at the interface and the rate of reaction.

The first five assumptions are basic assumptions valid during the whole work. The last four are employed only in the theoretical approach in order to simplify it.

4.2.1.3 General forms of equations

The molar flux in the absence of chemical reaction is given by:

$$N_A^o = K_{o1}^o \left(C_{A1} - C_{A1}^{o*}\right) \qquad (4.9)$$

where K^o_{o1} is the overall mass transfer coefficient based on phase 1 in the case of transfer without chemical reaction.

According to the definition of E that no A component be present in phase 2, it follows from the above equation:

$$N^o_A = K^o_{o1} \; C_{A1} \tag{4.10}$$

When a chemical reaction occurs, it is necessary to consider the two cases already mentioned:

Case I. The reaction takes place at the interface.

The flux is given by

$$N_A = K_1 \; C_{A1} \tag{4.11}$$

where K_1 is the individual mass transfer coefficient in phase 1.

According to assumption (iii)

$$K_1 = K^o_1 \tag{4.12}$$

Combining 4.8, 4.10, 4.11 and 4.12, the enchancement factor becomes:

$$E_I = \frac{K^o_1}{K^o_{o1}} \tag{4.13}$$

If the distribution coefficient is constant, it follows that:

$$\frac{1}{K^o_{o1}} = \frac{1}{K^o_1} + \frac{m}{K^o_2} \tag{4.14}$$

where m is the distribution coefficient as defined by the equation $C^*_1 = m \; C^*_2$. In this case E_I is given by:

$$E_I = (E_C)_I = 1 + m \frac{K^o_1}{K^o_2} \tag{4.15}$$

The conclusions drawn from this relation are:

(i) the theoretical value of E_I is constant and can be written as a function of the equilibrium constant and of the ratio of the individual mass transfer coefficients determined without chemical reaction.

(ii) $(E_C)_I$ is therefore dependent on the system, on the temperature, on the ratio of the diffusivities of the solute in both solvents.

(iii) it is not affected by the concentration and the physical properties of reactant B.

Case II: The reaction plane is located inside the film of phase 2.

Using the concepts of the film theory it can be shown that for this case

$$N_A = K_2^o \left(C_{Ai2} + \frac{a}{b}\frac{D_{B2}}{D_{A2}} C_{B2}\right) \tag{4.16}$$

If the distribution coefficient is constant, it follows that

$$N_A = K_{o1}^o \left(C_{A1} + m \frac{a}{b}\frac{D_{B2}}{D_{A2}} C_{B2}\right) \tag{4.17}$$

The expression giving the enhancement factor is thus

$$E_{II} = 1 + m \frac{a}{b}\frac{D_{B2}}{D_{A2}}\frac{C_{B2}}{C_{A1}} \tag{4.18}$$

This factor obviously depends on the system, on the temperature and on all the reactants and their concentrations. It is also apparent that the enhancement factor is always greater than one; the chemical reaction accelerates the process.

The critical concentration, C_{BX}, defined previously, can be obtained from:

$$E_I = E_{II} \tag{4.19}$$

This assumes a continuous transition from case I to case II and vice versa. From equations 4.15 and 4.18,

$$C_{BX} = \frac{b}{a}\frac{D_{A2}}{D_{B2}}\frac{K_1^o}{K_2^o} C_{AX} \qquad (4.20)$$

If C_{B2} is plotted against C_{A1}, the above equation is represented by a straight line which is called the critical line.

4.2.1.4 Stoichiometric operating relation

In the stirred cell in which the overall mass transfer coefficients were determined, the volumes of the two phases, the concentrations of the reactants in each phase at any time and the interfacial area are well known. It is therefore possible to analyse the situation in greater detail.

For the transfer of solute from phase 1 to phase 2, the following material balance equation applies:

$$d(V_1 C_{A1}) = - N_A \; S \; dt \qquad (4.21)$$

where S is the interfacial area, t the time measured from contacting the phases and V_1 the volume of phase 1.

According to assumptions (v) and (vi) (Section 4.2.1.2), the following equation can be written directly from the overall stoichiometric balance equation on solute A:

$$V_1 \; dC_{A1} = \frac{a}{b} V_2 \; dC_{B2} \qquad (4.22)$$

After integrating it follows that at any time A during the experiment

$$C_{B2} - C_{B2}^i = \frac{b}{a}\frac{V_1}{V_2}(C_{A1} - C_{A1}^i) \qquad (4.23)$$

where C_{A1}^i and C_{B2}^i are the values of the concentrations of A and B in phases 1 and 2 respectively at time equal to zero. This stoichiometric operating relation can be represented on the graph of C_{B2} versus C_{A1} by a straight line.

4.2.1.5 Concentration profile and enhancement factor

Assuming that the mass transfer coefficients, the partition coefficient m and the diffusivities are constant, the general equations can be integrated for the two basic cases I and II.

Case I: The combination of 4.11 and 4.21 leads to the following relation:

$$N_A = K_1 C_{A1} = -\frac{V_1}{S}\frac{dC_{A1}}{dt} \qquad (4.24)$$

which gives on integration:

$$C_{A1} = C^i_{A1}\, e^{-\frac{K_1 S}{V_1} t} \qquad (4.25)$$

This can be written as:

$$K_1 = K^o_1 = \frac{V_1}{St} \ln \frac{C^i_{A1}}{C_{A1}} \qquad (4.26)$$

This form of the above relation indicates that the resistance in phase 2 and the initial concentration of component B do not affect the mass transfer coefficient for phase 1 and this is in agreement with assumption (iii). This equation will also be used elsewhere for calculating K^o_1, the individual mass transfer coefficient for phase 1 when no chemical reaction occurs.

Case II: If the value of C_{B2}, given by equation 4.23, is substituted into equation 4.17, it follows that:

$$N_A = K^o_{o1}\left[\left(1 + m\frac{V_1}{V_2}\frac{D_{B2}}{D_{A2}}\right)C_{A1} + m\,\frac{a}{b}\frac{D_{B2}}{D_{A2}}\left(C^i_{B2} - \frac{b}{a}\frac{V_1}{V_2}C^i_{A1}\right) \right] \qquad (4.27)$$

Combining with 4.21 and after integrating between t = 0 and t, it gives:

$$C_{A1} = \frac{m\frac{D_{B2}}{D_{A2}}\left(\frac{V_1}{V_2}C^i_{A1} - \frac{a}{b}C^i_{B2}\right) + \left(C^i_{A1} + m\frac{a}{b}\frac{D_{B2}}{D_{A2}}C^i_{B2}\right)\exp\left[-\frac{K^o_{o1}S}{V_1}\left(1 + m\frac{V_1}{V_2}\frac{D_{B2}}{D_{A2}}\right)t\right]}{1 + m\frac{V_1}{V_2}\frac{D_{B2}}{D_{A2}}}$$

(4.28)

Using equations 4.18 and 4.23, a simple expression for the enhancement factor is obtained:

$$E_{II} = 1 + m \frac{D_{B2}}{D_{A2}} \left[\frac{V_1}{V_2} + \frac{1}{C_{A1}} \left(\frac{a}{b} C^i_{B2} - \frac{V_1}{V_2} C^i_{A1} \right) \right] \qquad (4.29)$$

From this, it can be seen that both the concentration profile and the enhancement factor are dependent on C^i_{B2} .

In order to draw the relation representing the variation of E_{II} with t, it is necessary to differentiate equation 4.29. Appropriate substitutions lead to:

$$\frac{dE_{II}}{dt} = m \frac{a}{b} \frac{D_{B2}}{D_{A2}} \left(C^i_{B2} - \frac{b}{a} \frac{V_1}{V_2} C^i_{A1} \right) \frac{E_{II}\ K^o_{o1}\ S}{V_1} \frac{1}{C_{A1}} \qquad (4.30)$$

At this stage, three regions have to be considered:

1. $C^i_{B2} > \frac{b}{a} \frac{V_1}{V_2} C^i_{A1}$, E_{II} is a monotonically increasing function up to $C_{B2} = C_{BX}$.

2. $C^i_{B2} < \frac{b}{a} \frac{V_1}{V_2} C^i_{A1}$, E_{II} is a monotonically decreasing function.

3. $C^i_{B2} = \frac{b}{a} \frac{V_1}{V_2} C^i_{A1}$, E_{II} is constant and equal to:

$$(E_C)_{II} = 1 + m \frac{V_1}{V_2} \frac{D_{B2}}{D_{A2}} \qquad (4.31)$$

Fig.4.2 shows how E_{II} is related to t depending on the relative values of C^i_{A1} and C^i_{B2}. It has been found from equations 4.29 and 4.30 that in region 2 the slopes of the tangents at $E_{II} = 1$ are constant and equal to $- m \frac{D_{B2}}{D_{A2}} \frac{K^o_{o1} S}{V_2}$ whatever C^i_{A1} and C^i_{B2}. Equations 4.28 and 4.29 make it also possible to calculate the values of E_{II} at t = 0, i.e. :

$$E^i_{II} = 1 + m \frac{a}{b} \frac{D_{B2}}{D_{A2}} \frac{C^i_{B2}}{C^i_{A1}} \qquad (4.32)$$

The behaviour of E_{II} will thus be a function of the point representing the initial concentrations in the graph C_{B2} versus C_{A1}. In such a graph regions 1 and 2 will be separated by a straight line whose equation is:

$$C_{B2} = \frac{b}{a}\frac{V_1}{V_2} C_{A1} \qquad (4.33)$$

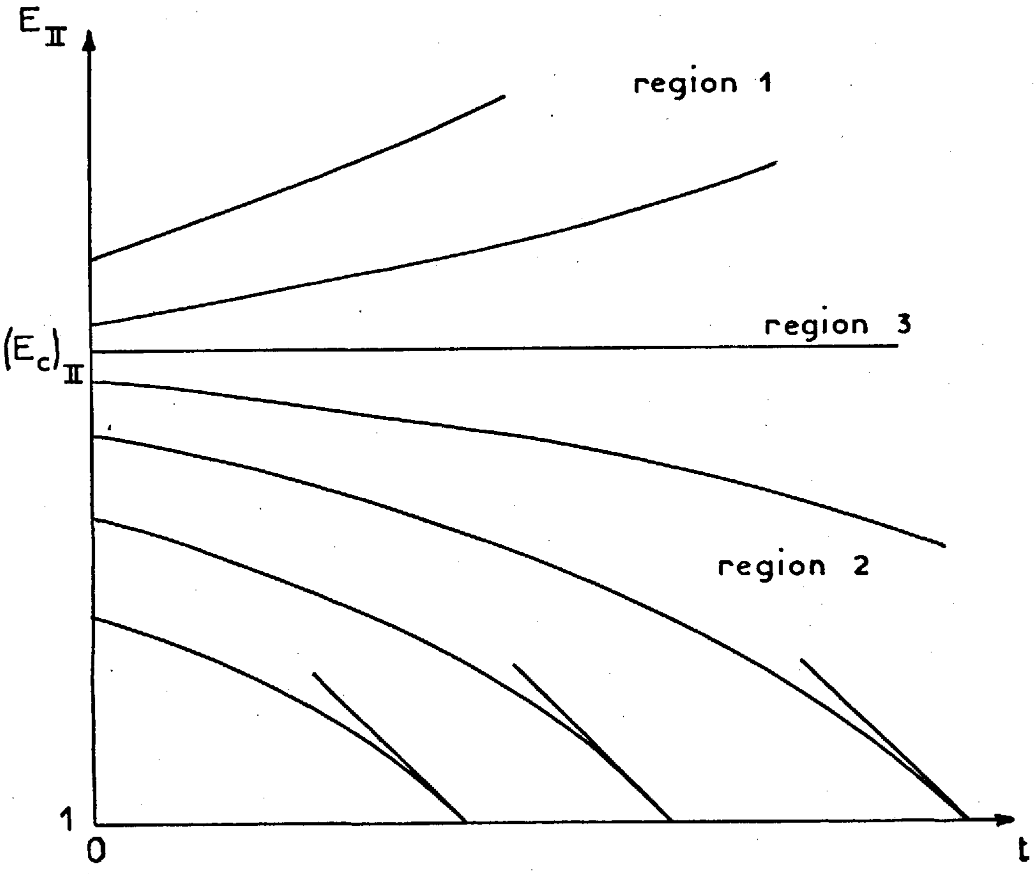


FIG.4.2 Variation of enhancement factor with time for case II

4.2.1.6 <u>Analysis</u>

In order to simplify the previous treatment and to summarise it without always referring to two different cases, a graph has been introduced of C_B versus C_A which relates the two characteristic sets of values obtained during the experiments.

In such a representation the behaviour of the system is seen to be controlled by three straight lines. These are:

- the stoichiometric operating line (see Eqn.4.23)
- the critical line (see Eqn.4.20)
- the line which represents the boundary of regions 1 and 2 as previously defined (see Eqn.4.33).

The two last lines divide the plane in three parts: two of them are such that any operating line starting in them will be entirely included in the regions corresponding to case I or II. An experiment starting in the third one will cut the critical line and it will be necessary to change the set of equations which describe the mass transfer process on account of passing from one case to another. The comparison of the slopes of the first two lines will give three main situations illustrated in Fig.4.3.

(i) Case A: $\frac{V_1}{V_2}\frac{D_{B2}}{D_{A2}}\frac{K_2^o}{K_1^o} > 1$

The slope of the operating line is greater than the slope of the critical line. The figure shows that three zones are defined:

- zone I_a: the equations of case I apply
- zone I_b: the process is in case I up to C_{BX}, then it moves into case II
- zone II: case II situation.

(ii) Case B: $\frac{V_1}{V_2}\frac{D_{B2}}{D_{A2}}\frac{K_2^o}{K_1^o} < 1$

The slope of the operating line is now smaller than the slope of the critical line.

- zone I : case I
- zone II_a: case II, then case I after C_{BX}
- zone II_b: case II.

(iii) Case C: $\frac{V_1}{V_2} \frac{D_{B2}}{D_{A2}} \frac{K_2^o}{K_1^o} = 1$

The two lines have merged and the simple situation, considered in Section 4.2.1.3 applies with only cases I and II present.

If the enhancement factor is being considered, it is necessary to draw curves which give its variation as a function of time. This has been done for the three previous cases in Fig.4.4.

From these graphs, several conclusions can be drawn:

(i) the enhancement factor E cannot be greater than $E_I = 1 + m \frac{K_1^o}{K_2^o}$ on condition that there is no interfacial or gravitational instability.

(ii) the function E versus t has no inflection point.

(iii) the two constant values of E are independent of the initial concentrations. They only depend on the properties of the cell and of the system.

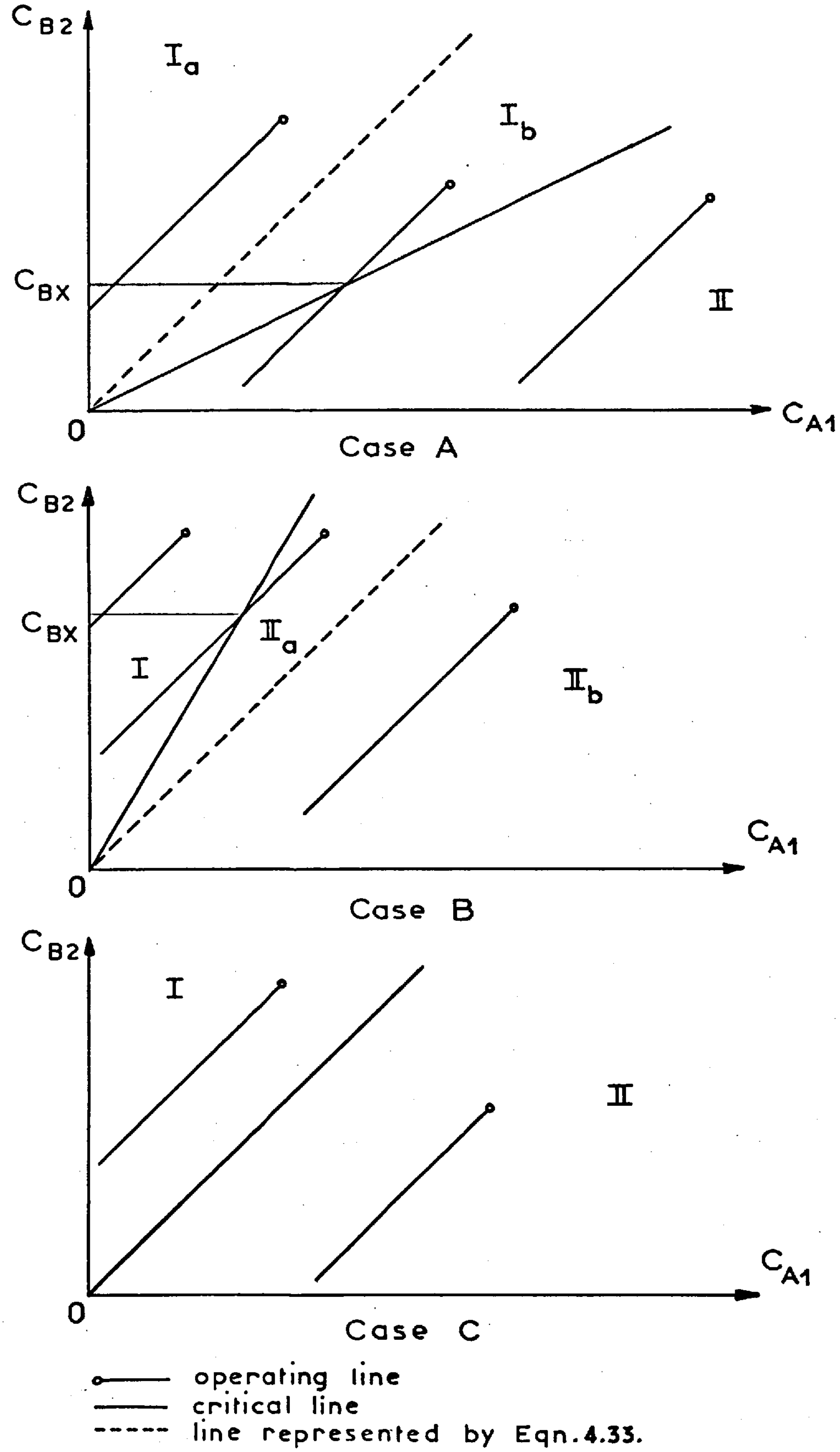


FIG.4.3: ZONES WHERE THE DIFFERENT CASES ARE APPLICABLE TAKING THE STARTING POINT AS A PARAMETER.

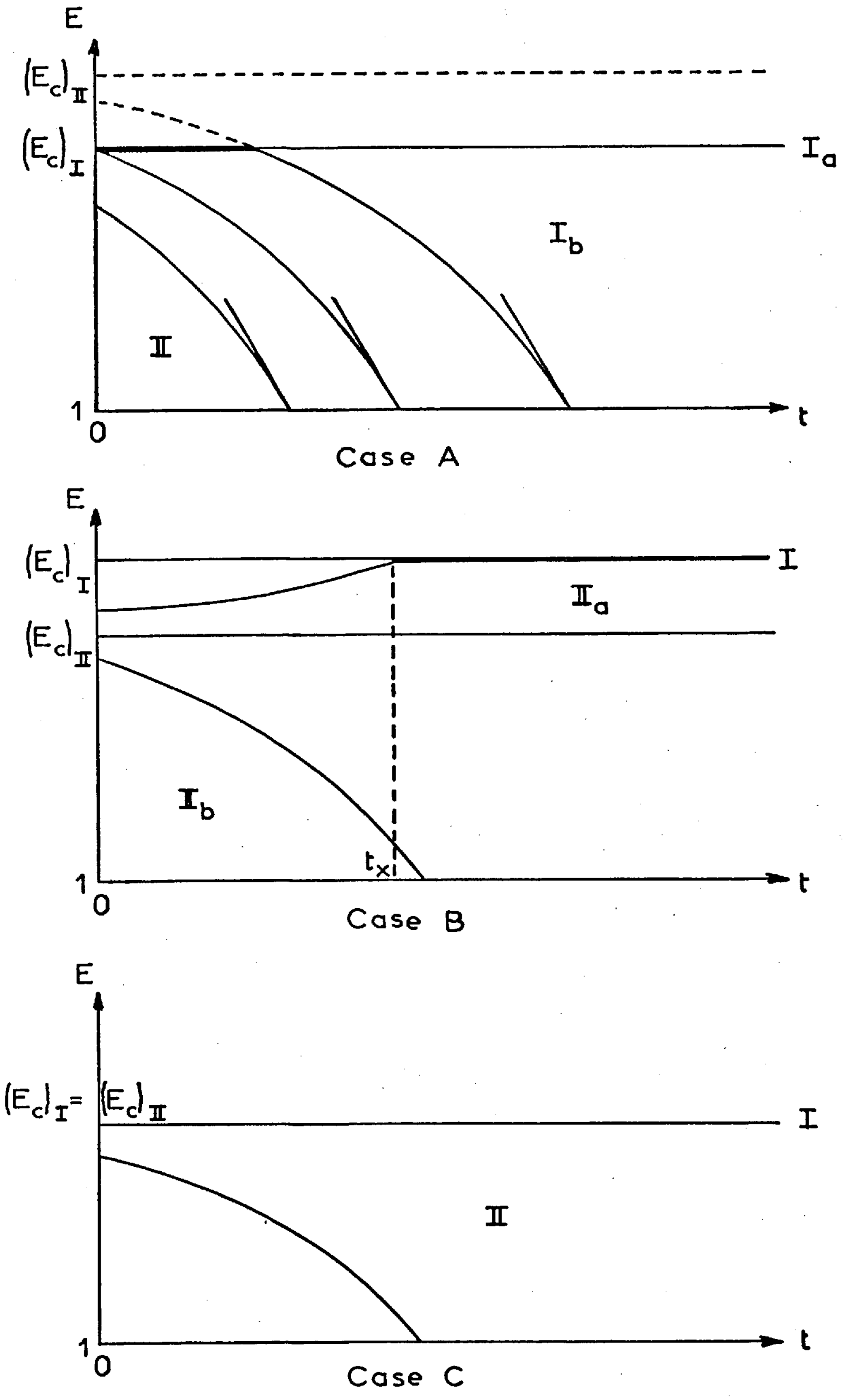


FIG. 4.4: VARIATION OF E VERSUS t AS A FUNCTION OF THE ZONES DEFINED IN FIG. 4.3.

4.2.2 Pseudo-first order reaction

In the preceding treatment the kinetic term does not occur due to the fact that the reaction is instantaneous. It was thus possible to consider a generalised case of mass transfer without reference to a particular system. In a similar way, generalised correlations can be developed for mass transfer with a simultaneous first-order reaction. However, in the present case it was considered advisable to deal immediately with the specific case of sulphonation of toluene.

This system presents special conditions by the high concentration of sulphuric acid, particularly at the interface, and by the slight solubility of toluene. Consequently measurements will be difficult.

4.2.2.1 Main assumptions

The total amount of toluene sulphonic acid (TSA) present in excess sulphuric acid was determined by a spectrophotometric analysis as described in paragraph 3.4.2. The salt concentration C_{TSA}(g/l) can be considered as the only data available after the experiments. The variation of this quantity as a function of time should provide information on the characteristics of the process. In order to achieve this, a certain number of assumptions were necessary:

(i) the reaction takes place in the aqueous (i.e. acid) phase

(ii) the salt is only soluble in the acid phase and it is not adsorbed in large quantities at the interface

(iii) the volumes can be considered as constant

(iv) no interfacial instabilities occur in phase 2

(v) the physical properties of the aqueous sulphuric acid solution such as viscosity, density etc. are not affected by the very small quantity of toluene and/or TSA present in the solution.

4.2.2.2 Theoretical approach

It has been seen with the instantaneous reaction that it is convenient to define an enhancement factor which will describe quantitatively the improvements of extraction by the action of the chemical reaction. As far as toluene transfer is concerned, it is suggested to express it as the ratio of the real molar flux of toluene passing through the interface when a chemical reaction occurs in phase 2 to the transfer which would exist without chemical reaction assuming that toluene concentration in the bulk is small enough to be taken as zero. This can be written as:

$$E = \frac{N_T}{N_T^o}$$

with $N_T^o = K_2^o \; C^*_{T2}$

where K_2^o is the individual mass transfer coefficient in phase 2 when no chemical reaction is present and C^*_{T2} the equilibrium value at the interface.

In the first approximation and within the range of sulphuric acid concentration studied, it looks as if the order of magnitude of both diffusion and reaction rates is comparable under most conditions.

The mechanism of the process is certainly represented by the following sequence of events:

1. Transfer of toluene from the organic to the acid phase.
2. Reaction of the aromatic somewhere in the acid phase.
3. Transfer of the product from the reaction zone to the bulk.

This envisages a certain amount of solute dissolving in phase 2 at the interface, then diffusiong towards the bulk and reacting either on the way or in the bulk depending on the relative magnitude of the diffusion and reaction rates.

According to the kinetic data, the rate of consumption of toluene can be written in a general form as:

$$R_T = k_1 C_{T2} \tag{4.34}$$

where C_{T2} is the concentration of toluene.

Let us compare the order of magnitude of diffusion and reaction rates.

(i) $\underline{N_T S \ll R_T V_2}$ (4.35)

Because the reaction rate is much more rapid than the rate of diffusion, the reaction takes place in the zone adjacent to the interface and the limit of toluene penetration is the depth of this reaction zone. The toluene concentration is thus zero in the bulk.

The depth of the reaction zone will depend on the kinetics of the reaction and on the rate of diffusion of toluene. It is equal or smaller than the thickness of the hydrodynamic film previously defined.

As the reaction occurs in the diffusion film, the reaction rate will influence the concentration gradient of toluene and hence N_T. For this condition, the flux can be represented by the simple expression:

$$N_T = K_2 C^*_{T2} \tag{4.36}$$

and the enhancement factor by:

$$E = \frac{K_2}{K^o_2} \tag{4.37}$$

Inequality 4.35 thus becomes:

$$K_2 C^*_{T2} S \ll k_1 C_{T2} V_2$$

and with $C_{T2} < C^{*}_{T2}$

$$K_2 \; S \ll k_1 \; V_2 \tag{4.38}$$

The problem at this stage is that K_2 is not easily available. It will be shown later how it can be evaluated.

(ii) $\underline{N_T \; S \gg R_T \; V_2}$ (4.39)

The reaction is now slow and takes place only in the bulk. The concentration of toluene in the bulk of phase 2 is probably low enough to be neglected if compared with C^{*}_{T2}. The conclusions of the next section will confirm this assumption.

The concept of slow reaction means that the diffusion rate is not affected by the chemical reaction and the rate equation can thus be written as:

$$N_T = K^{o}_{2} \; C^{*}_{T2} \tag{4.40}$$

It follows that:

$$E = 1 \tag{4.41}$$

Because of $R_T = k_1 \; C_{T2}^{\;b}$ and $C^{*}_{T2} > C_{T2}^{\;b}$ where $C_{T2}^{\;b}$ is the bulk concentration of toluene, the previous condition of having a slow reaction can be written as follows:

$$K^{o}_{2} \; S \gg k_1 \; V_2 \tag{4.42}$$

It can be seen from the above considerations that the relative magnitudes of K^{o}_{2} S or K_2 S and k_1 V_2 represent convenient quantities to decide whether the reaction occurs in the film near the interface or in the bulk.

This can be summarised as follows:

(i)	$K^{o}_{2} \; S \gg k_1 \; V_2$	slow reaction diffusional regime (bulk reaction)
(ii)	$K^{o}_{2} \; S < k_1 \; V_2$	transition and fast reaction regime (reaction in the film)

At 100 rev/min for instance the value of K_2^oS is about $1.5\ 10^{-3}cm^3/s$. In 70%-wt H_2SO_4, $k_1 = 3.86\ 10^{-8}s^{-1}$, so that $k_1\ V_2 = 1.1\ 10^{-5}cm^3/s$. In such circumstances $k_1\ V_2$ is considerably smaller than K_2^oS and toluene reacts in the bulk.

However the value of k_1 increases by a factor of 1.96 for each 1%-wt increase in the sulphuric acid strength, so that at higher sulphuric acid strengths $R_T\ V_2$ should become greater than N_TS and the reaction should occur in the film adjacent to the interface.

In view of this complexity and for a better understanding of the process, it is better to develop a mathematical model which will take into account that the rates of diffusion and reaction are comparable over the concentration range studied in this work.

4.2.2.3 Equations and analysis

The mathematical statement of the problem is given by the conservation equation written with respect to the solute, in this case toluene:

$$D_{T2}\frac{d^2C_{T2}}{dx^2} - k_1\ C_{T2} = 0 \qquad (4.43)$$

D_{T2} is the diffusion coefficient of toluene in phase 2 and x the distance in phase 2 from the interface at which the toluene concentration is C_{T2}. If x_2 is the thickness of the stagnant film which corresponds to the diffusional resistance K_2^o, the concentration of toluene in the bulk $C^b_{T_2}$ is related to the process by:

$$V_2\frac{dC^b_{T2}}{dt} = -\ S\ D_{T2}\left(\frac{dC_{T2}}{dx}\right)_{x=x_2} - k_1V_2C^b_{T2} \qquad (4.44)$$

The boundary conditions are:

(i) for $x = 0$ $\quad C_{T2} = C^{*}_{T2} = \text{constant}$

(ii) for $x > x_2$ $\quad C_{T2} = C^{b}_{T2} = f(t)$

(iii) at $t = 0$ $\quad C^{b}_{T2} = 0$

Using boundary conditions (i) and (ii) and introducing

$$q = \sqrt{\frac{k_1}{D_{T2}}} \tag{4.45}$$

the solution of equn.4.43 can be written as

$$C_{T2} = \frac{C^{b}_{T2} \sin h\,(qx) + C^{*}_{T2} \sin h\,[q(x_2 - x)]}{\sin h\,(qx_2)} \tag{4.46}$$

Appropriate substitutions into eqn.4.44 followed by its integration using boundary condition (iii) lead to:

$$C^{b}_{T2} = \frac{M}{M + k_1} \frac{C^{*}_{T2}}{\cos h\ \beta} \left[1 - e^{-(M+k_1)t}\right] \tag{4.47}$$

with:

$$M = \frac{S}{V_2} K^{o}_{2}\ Ha \tag{4.48}$$

$$Ha = \frac{\beta}{\tan h\ \beta} = \text{Hatta number} \tag{4.49}$$

$$\beta = q\ x_2 = \frac{\sqrt{k_1 D_{T2}}}{K^{o}_{2}} \tag{4.50}$$

The molar flux of toluene through the interface is given by the following relationship

$$N_{Ti} = -\ D_{T2} \left(\frac{dC_{T2}}{dx}\right)_{x=0} \tag{4.51}$$

and it becomes:

$$N_{Ti} = K^{o}_{2}\ Ha\ C^{*}_{T2} \left[1 - \frac{1 - e^{-(M + k_1)t}}{(1 + \frac{k_1}{M})\ \cos h^{2}\ \beta}\right] \tag{4.52}$$

It can be noticed that the dimensionless number β is a combination of kinetic and diffusion terms and thus it will be considered as the sole parameter able to describe the characteristics of the process. Two main cases have to be considered:

Case (a) = Fast reaction ($\beta > 3$).

It can be seen from Section 5.2. that the mass transfer coefficient K_2^o used in the present work is of the order 5×10^{-5} to 30×10^{-5} cm/s. If the average value of D_{T2}, i.e. 10^{-6} cm²/s, is employed in calculations, it follows that for a fast reaction

$$0.02 s^{-1} < k_1 < 0.80 \ s^{-1}$$

M being smaller than $10^{-4} s^{-1}$ in this case, it may be concluded that:

$$M \ll k_1$$

If the duration of the runs does not exceed two hours, the exponential term is very small and the second part of the expression in brackets in eqn.4.52 can be neglected with respect to 1. Hence,

$$N_{Ti} = \sqrt{k_1 D_{T2}} \ C^*_{T2} \qquad (4.53)$$

The mass transfer coefficient K_2^o does not appear in the above equation. This is due to the fact that the reaction takes place in the film where normally the diffusion resistance is concentrated. The process is therefore considerably improved and the enhancement factor is equal to β.

Case (b) = Slow reaction ($\beta < 0.2$).

This case is likely to cover the present work as can be seen in Appendix A4, Table 5. In the range for which a slow reaction is expected, the order of magnitude of M varies between $5 \times 10^{-6} s^{-1}$ and 3×10^{-5} whilst that of k_1 does between $10^{-8} s^{-1}$ and $5 \times 10^{-4} s^{-1}$. M and k_1 are thus in the same order of magnitude and no direct conclusion can be drawn. However, calculations worked out for a maximum time of contact of two hours have shown that the second term of the expression can also be neglected with respect to 1. The errors involved thereby are 6% for 100 rev/min, 10% for 200 rev/min and 13% for 300 rev/min.

It can be pointed out that this error decreases with time and with the stirring speed and becomes quite negligible particularly for 100 and 200 rev/min. The error is of the same order of magnitude as the experimental error for most conditions of experimental work and certainly much smaller than that of the correlations giving the individual mass transfer coefficients which were used in the calculation of M.

The assumption of neglecting the time-dependent term is equivalent to assuming $C_{T2}^{b} = 0$ as can be seen from eqns.4.47 and 4.52. This assumption was anyway necessary in order to be able to use the enhancement factor as previously defined, i.e. with zero concentration of solute in the bulk.

It was also noticed that absorbance measurements were not greatly affected when samples taken directly from phase 2 without any treatment were used instead of samples washed with n-hexane in order to remove all traces of toluene. This supports the conclusion reached previously.

Eqn.4.52 can therefore be written as:

$$N_{Ti} = K_2^o C_{T2}^* \qquad (4.54)$$

The above equation shows that transfer of toluene across the film is not affected by the reaction and the whole reaction takes place in the bulk. As expected, the enhancement factor is equal to 1.

If W_T and W_{TSA} are respectively the molar amounts of toluene and TSA present in phase 2 at time t, the following relation applies:

$$\frac{dW_{TSA}}{dt} = -\frac{dW_T}{dt} = S\ N_{Ti} = \text{constant} \qquad (4.55)$$

Integration will give simply:

$$W_{TSA} = S\ N_{Ti}\,t \qquad (4.56)$$

If C_{TSA} (g/l) is the concentration of toluene sulphonic acid at instant t in phase 2, it follows that:

$$C_{TSA} = M_{TSA}\,\frac{S}{V_2}\,N_{Ti}\,t \qquad (4.57)$$

The concentration of TSA in phase 2 versus time is thus represented by a straight line whose slope is equal to $M_{TSA}\,\frac{S}{V_2}\,N_{Ti}$. This will permit us to calculate from the experimental results the molar flux of toluene and thus to verify the theoretical model in detail.

4.3 Conclusions

The general model proposed for a bimolecular instantaneous reaction which applies to a system of constant partition coefficient permits us to draw several conclusions applicable to the system under consideration. This will be analysed later in Chapter 6.

However, from now on, reservations have to be made concerning some assumptions. Thus, on account of the transfer of solute and the collection of samples, the volumes of both phases will change slightly during the experiments and appropriate corrections will be made. In addition, it can no longer be forgotten that the salt produced by the reaction has an influence on on the interfacial tension and on the equilibrium at the interface. It will therefore be impossible to assume subsequently the constancy of m during an experiment. Finally the various instabilities which improve the transfer of HPr can be considered as quite important with such a system and will have to be taken into account.

As far as the sulphonation of toluene is concerned, most assumptions can be considered as valid. Unlike in the previous case, the small rate of transfer and the sampling technique do not involve significant changes in the volumes. Because the solute concerned in the transfer is already the solvent of the upper phase and the concentration of the reaction product in the lower phase is very low, neither Marangoni nor gravitational instabilities are likely to arise.

The only problem which can arise is, as will be seen later in Chapter 6, that of a chemical reaction occurring at the interface. The occurrence of such a reaction and of any other interfacial phenomenon cannot be completely ignored, particularly if their rates are of the same order of magnitude as the necessarily small transfer rates observed in the present work.

CHAPTER 5

PREDICTION OF MASS TRANSFER COEFFICIENTS

In order to be able to relate the effects of chemical reaction and of mass transfer, it is necessary to know the characteristics of the system in the absence of chemical reaction.

Hence, in this chapter, mass transfer coefficients are predicted for the stable diffusional regime. The predictions were verified by conducting experiments using the system toluene/water + propionic acid. At the same time, instabilities affecting mass transfer were qualitatively and quantitatively estimated.

5.1 Estimation of Coefficients of Diffusion

The part played by molecular diffusion has been outlined in Chapter 4. The necessity of knowing the coefficients of diffusion to estimate the individual mass transfer coefficients was also indicated in the literature survey.

This section will consequently deal with molecular diffusivities such as will be encountered in the systems under consideration.

5.1.1 System toluene/water + HPr + NaOH

5.1.1.1 Diffusion of propionic acid in toluene and water

A few experimental values are available in literature at 25°C. WARD and BROOKS (1952) in particular investigated the free diffusion of acetic, propionic, n-butyric and n-valeric acids across the water-toluene interface using a Lamm scale method without stirring. There was good agreement between their theoretical and experimental values which can therefore be directly applied to the present system.

The values employed were, in addition, checked using the Sitaraman equation:

$$D_{AB} = 5.4\ 10^{-8} \left[\frac{M_B^{\frac{1}{2}} \quad \Delta H_B^{1/3}\ T}{\mu_B\ V_A^{0.5}\ \Delta H_A^{0.3}} \right]^{0.93} \tag{5.1}$$

where M_B(g) is the molecular weight of the solvent

T(K) the temperature

μ_B(cP) the viscosity of the solvent

V_A(cm^3/gmol) the molecular volume of the solute at the normal boiling point

ΔH_B and ΔH_A(cal/g) the latent heat of vaporisation measured at the boiling point of the solvent and of the solute respectively.

Sitaraman correlated experimental data of 115 binary systems without any restriction. He found that his correlation applied with a standard deviation of 26% for organic solvents and 12% for water. Propionic acid in toluene or in water was not included in the tested systems.

The accuracy of his correlation is shown in Table 5.1.

TABLE 5.1

Comparison of literature values and calculated values for the diffusion coefficients of HPr in toluene and water at 25°C

References	D_{HPr} in toluene x 10^5 (cm^2/s)	D_{HPr} in water x 10^5 (cm^2/s)
WARD and BROOKS (1952)	2.04	1.11
ROSSI, BIANCHI and ROSSI (1958)	-	0.90
BIDSTRUP and GEANKOPLIS (1963)	-	1.01
Sitaraman's correlation	2.15	1.13

5.1.1.2 Ion diffusion in water

Although the diffusion of dissolved electrolytes does not differ in principle from that of dissolved non-electrolytes, two related factors should be taken into account which are absent in solutions of non-electrolytes. One of them is the electric potential gradient, caused by ions of different mobilities, which markedly alters the rate of the diffusion of ions by means of cross-effects. The other one is due to the electrostatic interaction between ions which does not allow macroscopic separation of ions of opposite charge. Both of them influence the mobility of ions.

Molecules of an electrolyte, such as NaOH, in solution dissociate into cations and anions, which because of their smaller size, diffuse more rapidly than the undissociated molecules. In solutions containing not more than one electrolyte, despite differences between the sizes of the positively and negatively charged ions, both types diffuse at the same rate, so that the electrical neutrality of a given solution is preserved. In the presence of other ions already in the solution, individual ions may diffuse at rates which are quite different from those of the previous case.

Until recently most investigators have ignored the complications introduced by differences in ionic diffusivity. The difference between the results is likely to be greatest when H^+ or OH^- are involved, as these have much greater mobilities than other species of ions. It is thus necessary to take into account these various influences, particularly when transfer is diffusion-controlled.

1. If no salt is present, anions OH^- must diffuse at the same rate as Na^+ to maintain neutrality at any plane in the solution. Under such circumstances it is permissible to define a molecular diffusivity of the compound NaOH, even though ions rather than molecules are diffusing. In this case NaOH diffuses as if it obeyed Fick's Law with an apparent diffusivity (DANCKWERTS.1970) equal to:

$$D_{NaOH} = \frac{u_+ u_-}{u_+ + u_-} \frac{y_+ + y_-}{y_+ y_-} \frac{RT}{F} \tag{5.2}$$

This equation was first obtained by Nernst and assumes ideality of the solution.

The mobility of any ion is given by:

$$u_i = \frac{\lambda_i}{F} \tag{5.3}$$

where λ_i is the limiting ionic conductance relative to this ion. Using Eqn.5.2 and values given in Table 5.2, it was calculated that:

$$D_{NaOH} = 2.12\ 10^{-5} cm^2/s \tag{5.4}$$

TABLE 5.2

Limiting equivalent ionic conductance at 25°C (Ref. LANGE)

ion	λ_{ion} mho cm^2/g equiv.
H^+	349.82
Na^+	50.11
OH^-	198.6
Pr^-	35.8

2. In the case of neutralisation involving ionic reactions as in the present work, it is the diffusion of ions which is important. Following Nernst's theory, diffusion in mixed electrolytes has been discussed by several authors (VINOGRAD and McBAIN 1941; SHERWOOD and WEI 1955). The concentration profiles of ions are represented in Fig.5.1. The treatment used here relates to the model described previously in Section 4.2.1.1, the reaction being now the neutralisation reaction between H^+ and OH^-.

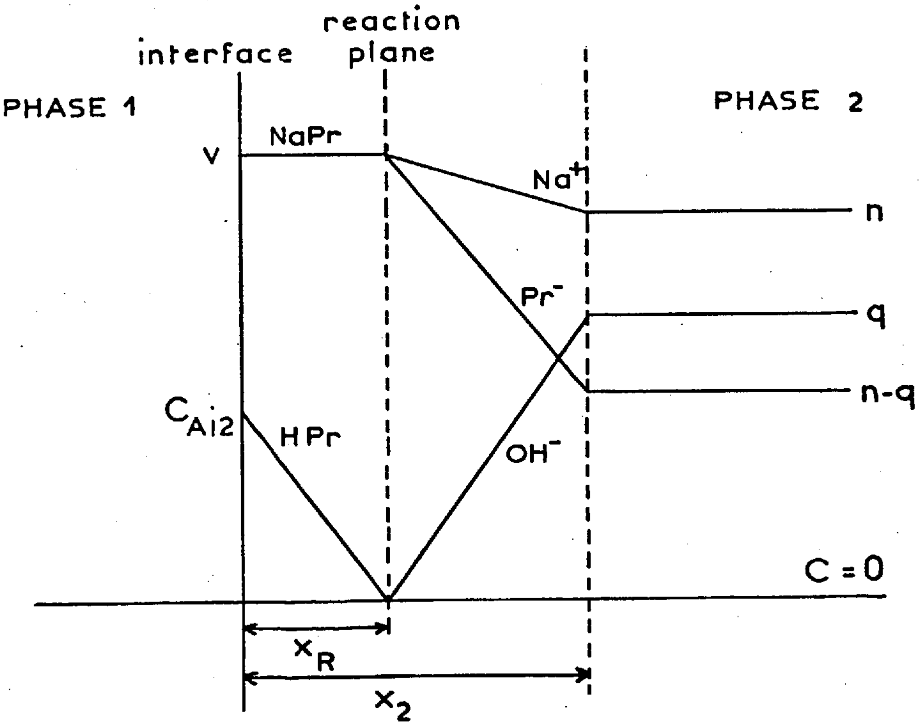


FIG.5.1 Concentrations in phase 2 of the various components involved in the reaction

Since the reaction takes place at the reaction plane, it has been assumed that in the film of thickness x_R the ionisation of HPr can be neglected.

As shown in Appendix A1, the general diffusion equation can be written for each ion, the diffusion potential for each involving both the concentration gradient of the particular ion and the gradient of the electrical potential in the solution. Imposing the condition of electrical neutrality upon the ion mixtures, the following equation for diffusion of cations is obtained:

$$y_+N_+ = -\frac{RT}{F}\frac{u_+}{y_+}\left(G_+ - y_+C_+\frac{\Sigma u_+G_+/y_+ - \Sigma u_-G_-/y_-}{\Sigma u_+C_+ + \Sigma u_-C_-}\right) \qquad (5.5)$$

N_+ is the ion flux of a particular cation of valence y_+, concentration C_+ and mobility u_+. G_+ is the concentration gradient $\frac{dC_+}{dx}$ of this cation in the direction of diffusion. The minus signs as subscripts refer to anions whilst the plus denotes cations.

As can be noticed, activity coefficients and collision effects are ignored, as are the effects of ion pairs or ionic complexes. Such approximations are well within the precision of the stagnant film model. It may also be pointed out that the factor $\frac{RT}{F}\frac{u_+}{y_+}$ in Eqn.5.5 is the diffusion coefficient of the ion in its free state and that the factor in parenthesis is the concentration gradient of that ion corrected for the presence of the other ions.

In the case of weak acids and NaOH, SHERWOOD and RYAN (1959) have shown that Eqn.5.5 can be integrated to give an exact solution without any approximation involving concentrations. Calculations are worked out in Appendix A2. They permit us to define the apparent diffusion coefficient of anion OH^- in presence of other ions. The defining equation can be written as follows:

$$D'_{app} = \frac{2\,D'_-}{1 + \sqrt{1 + \left(\frac{u'_-}{u_-} - 1\right)\frac{q}{n}}} \qquad (5.6)$$

where u'_- and u_- are respectively the mobilities of OH^- and Pr^-

ions, q and n the bulk concentrations of OH^- and Na^+ ions (see Fig.5.1) and D'_- is the diffusion coefficient of OH^- in its free state, i.e:

$$D'_- = \frac{RT}{F} u'_- \qquad (5.7)$$

If there is a large excess of sodium propionate in the solution, so that

$$\frac{q}{n} \to 0$$

Eqn.5.6 becomes:

$$D'_{app} = D'_- \qquad (5.8)$$

OH^- will thus diffuse independently with a diffusivity of $5.28\ 10^{-5}$ cm²/s.

Generally D'_{app} will be smaller than this value, but also greater than the 2.12×10^{-5} of the NaOH diffusivity calculated previously.

It can thus be seen that the error will be important if the diffusivities are calculated with respect to the molecules without taking into account the ionic motion. The diffusivity called D_{B2} in Section 4.2.1 will therefore be replaced by D'_{app} when computing experimental results.

5.2.2 System toluene/aqueous sulphuric acid solution

The diffusion coefficient of toluene in the aqueous sulphuric acid solution has been estimated from viscosity data by means of the modified Wilke and Chang equation proposed by PERKINS and GEANKOPLIS (1969):

$$D_{T2} = \frac{7.4 \quad 10^{-8} \ (\bar{\phi}\bar{M})^{\frac{1}{2}} T}{\mu_2 \ V_T^{0.6}} \qquad (5.9)$$

V_T(cm³/g mol) is the molal volume of toluene at its normal boiling point and $\bar{\phi}\bar{M}$ is defined by the relationship:

$$\phi\bar{M} = x_w \phi_w M_w + x_s \phi_s M_s \qquad (5.10)$$

The symbols x, ϕ and M denote mole fraction, association factor and molecular weight and the subscripts w and s refer to water and sulphuric acid respectively.

In their work on two-phase nitration of toluene and chlorobenzene, COX and STRACHAN (1972, 1974) already used this method and calculated that the association number ϕ_s relative to sulphuric acid was 2.0. The usual value of 2.6 was taken for the association factor of water.

If w_2 is the percentage-weight of sulphuric acid in water, Eqn.5.10 becomes:

$$\phi\bar{M} = M_w \frac{\phi_w \left(\frac{1}{w_2} - 1\right) + \phi_s}{\frac{1}{w_2} - 1 + \frac{M_w}{M_s}} \qquad (5.11)$$

The diffusion coefficient D_{T2}(cm^2/s) of toluene in the acid phase can thus be written as follows:

$$D_{T2} = \frac{53.37 \quad 10^{-7}}{\mu_2} \left(\frac{2.6 - 0.6w_2}{1 - 0.826w_2}\right)^{\frac{1}{2}} \qquad (5.12)$$

where μ_2(cP) is the viscosity of the aqueous sulphuric acid solution. This solution is only valid at 25°C and for high sulphuric acid strengths.

Although Wilke and Chang's correlation has often been shown not to be very accurate when the solvent is highly viscous, it has been employed in this work as the diffusivities calculated by Cox and Strachan using the same method gave results which agreed well with those obtained experimentally.

The calculated values are tabulated in Appendix A4, Table 5.

5.2 Predicted Mass Transfer Coefficients

As can be seen in the literature, several correlations are applicable to the stirred cell employed in the present work. Only those of AUSTIN (1966) and DAVIES (1972) are however considered, the latter presenting the advantage of taking into account the value of the interfacial tension which is likely to be of a great importance in the mass transfer process.

In order to relate individual mass transfer coefficients obtained in this manner with overall mass transfer coefficients, it became necessary to define carefully either these mass transfer coefficients or particularly the partition coefficient which appears in most relations.

5.2.1 General

For the purpose of measuring mass transfer rates and correlating results, the most commonly used method is the mass transfer coefficient K defined by:

$$K = \frac{\text{Mass flux}}{\text{Driving force}} \tag{5.13}$$

The rate of mass transfer per unit area of interface is thus proportional to the mass transfer coefficient and the driving force. In terms of individual mass transfer coefficients K_1^o and K_2^o, respectively based on phases 1 and 2, this gives, if the transfer from phase 2 to phase 1 is taken as an example,

$$N = K_1^o \, (C_{1i} - C_1) = K_2^o \, (C_2 - C_{2i}) \tag{5.14}$$

where C_{1i} and C_{2i} are the interfacial concentrations whilst C_1 and C_2 are those of the bulk.

For the overall mass transfer coefficients K_{o1}^o and K_{o2}^o applicable to the two-phase system, it can similarly be written:

$$N = K_{o1}^o \, (C_1^* - C_1) = K_{o2}^o \, (C_2 - C_2^*) \tag{5.15}$$

The asterisk denotes the equilibrium values with respect to the solute concentration in the bulk of the adjoining phase.

According to the two-film theory, the interfacial concentrations C_{1i} and C_{2i} are equilibrium concentrations and the resistances to mass transfer in the two phases, as measured by the reciprocals of K's, are additive. Equilibrium at the interface means no resistance across it. These definitions are applicable independentaly of the mass transfer theory used to interpret the K's. The significance of this is shown in Fig.5.2. Point M represents the bulk solute concentration in the liquids and I the equilibrium interfacial concentration. Any line MI (or PJ) has a slope equal to:

$$\frac{C_{1i} - C_1}{C_{2i} - C_2} = -\frac{K_2^o}{K_1^o} \qquad (5.16)$$

If K is considered to be proportional to $D^{\frac{1}{2}}$, then for propionic acid as solute in the system toluene/water:

$$\frac{K_2^o}{K_1^o} = \left(\frac{D_2}{D_1}\right)^{\frac{1}{2}} = 0.738 \qquad (5.17)$$

In a stirred cell, the following overall material balance applies:

$$V_1\, dC_1 + V_2\, dC_2 = 0 \qquad (5.18)$$

This equation leads to an expression of the slope of the operating line AB (or DE)

$$\frac{dC_1}{dC_2} = -\frac{V_2}{V_1} \qquad (5.19)$$

which is approximately equal to -1 if $V_1 \simeq V_2$.

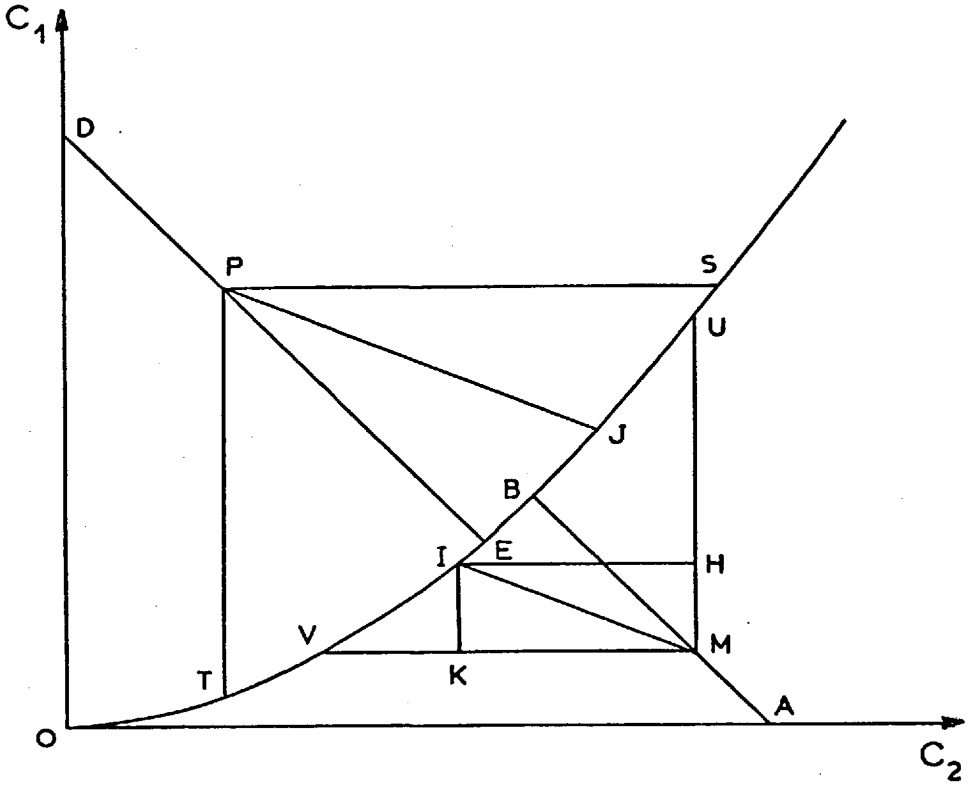


FIG.5.2

At any time, if m_2' and m_2'' are respectively the slopes of the lines IU and IV of Fig.5.2, then

$$|UM| = |HM| + m_2' \ |IH|$$

i.e. $$\frac{1}{K^o_{o1}} = \frac{1}{K^o_1} + \frac{m_2'}{K^o_2} \qquad (5.20)$$

Similarly:

$$|VM| = |KM| + \frac{|IK|}{m_2''}$$

i.e. $$\frac{1}{K^o_{o2}} = \frac{1}{K^o_2} + \frac{1}{m_2'' K^o_1} \qquad (5.21)$$

If the equilibrium curve is straight so that $m_2 = m_2' = m_2''$, it can also be written that

$$K^o_{o2} = m_2 \ K^o_{o1} \qquad (5.22)$$

Likewise it is possible to show that, if mass transfer occurs from phase 1 to phase 2, m_1' and m_1'' defined with the same type of equations as 5.20 and 5.21 are respectively the slopes of the lines TJ and JS. Eqn. 5.22 is still applicable, but with m_1 instead of m_2.

In what follows, the overall mass transfer coefficient will be based on phase 1. Two reasons are offered for this choice:

- as the chemical reaction takes place in phase 2 (see Chapter 6), C_{A2} is equal to zero in the bulk and the second part of Eqn.5.15 cannot be used;

- when pure mass transfer is considered, the measurements are more accurate if samples are taken from phase 1. The experimental error in K_{o1}^{o} is thus smaller than that in K_{o2}^{o}.

Fig.3.3 shows that the constancy of m is not valid for the present system. Therefore for the initial concentrations used in runs 1-15, it is plausible to assume a mean value for m_1', m_1'', m_2' and m_2''. They are obviously dependent on the position of D and A, i.e. on the initial acid concentrations in phases 1 and 2 respectively.

For C_{A1}^{i} and C_{A2}^{i} equal to 0.95 gmol/l, the values of m were estimated to be between 0.50 and 0.80. It should be pointed out that, at 100 rev/min, K_1 is proportional to D_{A1} (see later) and consequently the slope of the lines MI and PJ is no longer equal to -0.738 (Eqn.5.16) but to -0.545. However the initial acid concentrations were greater in this case than those for 200 and 300 rev/min and the partition coefficients have approximately the same values as mentioned above.

The error introduced by using a mean value of m in the calculations of mass transfer coefficients has been estimated to be about 13%. It has also been noticed that the chosen value, i.e. $m = 0.65$, will give good agreement between predicted and experimental values of overall mass transfer coefficients and thus confirm the validity of its use in what follows.

Eqn.5.20 combined with Eqn.5.17 gives for 200 and 300 rev/min and for the stable direction of transfer (i.e. from phase 2 to phase 1 in the presence of a surfactant):

$$K^o_{o1} = 0.53\ K^o_1 \qquad (5.23)$$

$$K^o_{o1} = 0.72\ K^o_2 \qquad (5.24)$$

For 100 rev/min, the equivalent equations are:

$$K^o_{o1} = 0.455\ K^o_1 \qquad (5.25)$$

$$K^o_{o1} = 0.835\ K^o_2 \qquad (5.26)$$

As can be pointed out from the four previous relationships, the knowledge of the individual mass transfer coefficients will permit us to predict the overall mass transfer coefficients. The determination of the former can be conducted with the correlations already developed in the literature and checked by experiments.

5.2.2 Austin's correlations

Austin's study (1966), conducted in the same stirred cell as used in the present work, has shown that there exists two different transfer regimes. The first regime is characterised by the presence of a boundary layer and the second by surface renewal. The change in the mode of transfer was indicated by a sharp change in the slope of the curve of mass transfer coefficient versus stirring speed.

Austin's experiments were performed by using partially miscible, interfacially stable, two-component systems. In order to eliminate the complicating effect of having the second phase interacting with the transfer in the phase under investigation, this second phase was saturated with the first and unstirred.

For a laminar interface, coefficients were well correlated by the following equation:

$$Sh = 1.5\ Re^{\frac{1}{2}} \cdot Sc^{1/3} - 400 \qquad (5.27)$$

for the range

$$300 < Re^{\frac{1}{2}} \cdot Sc^{1/3} < 800 \qquad (5.28)$$

As regards surface-renewed interface, they were correlated by an equation of the form:

$$\ln \frac{K^{o}}{D^{\frac{1}{2}}} = \frac{N}{300} - a \qquad (5.29)$$

Assuming, in accordance with the Danckwerts model, that $K^{o} = \sqrt{Ds^{o}}$, it followed:

$$\ln s^{o} = \frac{N}{150} - 2a \qquad (5.30)$$

where s^{o} is the fractional rate of surface renewal for stirring in one phase only. The final constant was found to vary between 1.25 and 1.6 for various liquid pairs.

Eqn.5.30 is in good agreement with the form of the equation given by DAVIES and KHAN (1965). With various oils in unstirred layers a few millimeters thick overlying a turbulent water phase, they observed, using the talc method, that:

$$\ln s^{o} = 0.0033\ N - 2.9 \qquad (5.31)$$

Although these systems oil/water had interfacial tensions which varied over a large range and the viscosities of phases differed sometimes by a factor of 20, the final constant was practically unchanged.

For six systems out of eight studied by Austin, 'a' had the constant value of 1.25. If this value is used in Eqn.5.30, it can be shown that for speeds between 200 and 300 rev/min the values of s calculated from both equations are of the same order of magnitude.

Although the surface renewal rate should depend on the physical properties of phases, in particular on their kinematic viscosity, it is assumed that 'a' can be taken as a constant. Its value, which is considered to be the most suitable to fit Eqns.5.29 and 5.30, is 1.25.

The mass transfer process may be affected by the hydrodynamic conditions of the adjacent phase if both phases are stirred. It was found that the film correlation holds quite well up to certain critical Reynolds number. This conclusion is satisfactory with respect to the undisturbed film concept developed by Austin for low stirring speeds. From 120-180 rev/min onwards according to the system, when the regime changes to surface renewal the influence of the stirring in the other phase is much too complicated to be correlated easily. AUSTIN and SAWISTOWSKI (1967) proposed that the surface renewal rate s_T is to be taken as equal to the sum of individual contributions s_1^o and s_2^o based on phases 1 and 2 respectively and obtained from Eqn.5.30, i.e. when only the relevant phase is stirred, i.e.

$$s_T = s_1^o + s_2^o \qquad (5.32)$$

All along this work, the two phases will be agitated at the same stirring speed N. It follows, according to Eqn.5.30, that $s_1^o = s_2^o$ and consequently that:

$$s_T \simeq 2\ s_1^o \qquad (5.33)$$

This means that the frequency of renewal is the same for both phases on account of symmetry of the cell, equal stirring speeds and with the assumption of neglecting the influence of kinematic viscosity.

The individual mass transfer coefficient K_1^o should therefore be corrected, when both phases are equally stirred, as follows:

$$\ln \frac{K_1^o}{(2\ D_1)^{\frac{1}{2}}} = \frac{N}{300} - 1.25 \qquad (5.34)$$

It can be noticed that the above equation does not take into account the physical properties of the system, which is certainly a deficiency of this correlation.

For the system toluene/water + propionic acid Eqns.5.23 to 5.27 and 5.34 permit us to calculate the individual mass transfer coefficients K_1^o and K_2^o (cm/sec) in the case of:

1. laminar interface:

$$1000\ K_1^o = 0.335\ N^{\frac{1}{2}} - 2.580 \qquad (5.35)$$

$$1000\ K_2^o = 0.208\ N^{\frac{1}{2}} - 1.410 \qquad (5.36)$$

2. surface renewed interface:

$$1000\ K_1^o = 1.83\ e^{N/300} \qquad (5.37)$$

$$1000\ K_2^o = 1.35\ e^{N/300} \qquad (5.38)$$

where N is the stirring speed expressed in rev/min.

Calculations can be compared with experimental results from Tables 5.3 and 5.5. It can be seen that the agreement is not very good.

Austin's correlations were established for systems whose interfacial tension is very low. If conditions existing at the interface between liquids are taken into account, we can no longer neglect the influence of the high interfacial tension which exists in the present system.

5.2.3 Davies' correlation

The interpretation of the present results (see Section 5.4) is based on an extension to liquid-liquid mass transfer of the Levich model for the approach of an eddy to a free surface. A full derivation of the mass transfer relationship for this model is given by DAVIES (1972).

5.2.3.1 Introduction

LEVICH (1962) postulated a three-zone model, comprising a freely turbulent zone, then a zone of restricted turbulence and finally the diffusional sublayer near the interface in which molecular diffusion dominates. The thickness of the latter depends on that of the zone near the interface within which turbulence is damped. It is assumed that in this zone the fluctuation velocity decreases linearly as the eddy approaches the deformable liquid-liquid interface and that the horizontal fluctuation component is constant whatever its position.

In order to calculate the thickness of the surface zone of damped turbulence, DAVIES (1972) considered the forces which damp an eddy at the gas-liquid surface. He pointed out that the approach of an eddy to the surface is restrained by surface tension and gravitational pressures. Assuming that the transfer resistance is located mainly in the mathematically equivalent diffusion layer mentioned above, he formulated a relation giving the liquid-side mass transfer coefficient as a function of $D^{0.5}$ and of various other parameters, such as the characteristic eddy dimension, the surface tension, the turbulence fluctuation velocity outside the zone of damped turbulence and the density.

He then applied it to liquid-liquid systems on the assumption that there is no great difference in the basic mechanism of mass transfer at the gas-liquid and liquid-liquid interfaces so that the relation derived for the liquid-side mass transfer coefficient can be used for the individual mass transfer coefficient.

If both the liquid phases are agitated, the total fluctuation velocity in the plane of the liquid-liquid interface will be increased when the turbulent fluctuations happen to be synchronised. The interaction of the turbulent fields in both phases which is particularly significant for liquid-liquid systems in a stirred cell, will affect the radius of curvature at certain regions of the interface and therefore the mass transfer rate.

5.2.3.2 Equation

It is assumed that the turbulence fluctuation velocity outside the zone of damped turbulence is proportional to the stirring speed N and to the characteristic length L which is taken as the tip-to-tip length of stirrer blades.

The resulting equation can be presented in dimensionless form as follows:

$$Sh_1 = B\Lambda \qquad (5.39)$$

where

$$\Lambda = (Sc_1)^{\frac{1}{2}}\, We_1'\, [Re_1 + \frac{\nu_2}{\nu_1} Re_2]^{\frac{1}{2}} [1 + \frac{\rho_2 \nu_2^2}{\rho_1 \nu_1^2} \left(\frac{Re_2}{Re_1}\right)^2]^{\frac{1}{2}}$$

and B is a constant.

The modified Weber number We_1' is defined by

$$We_1' = N_1 L \left(\frac{\rho_1 L}{\sigma_e}\right)^{\frac{1}{2}} \qquad (5.40)$$

where σ_e which represents the interfacial tension and gravitational forces opposing the movement of an eddy so the interface is given by:

$$\sigma_e = \sigma + \ell^2 \times \left|\Delta\rho\right| \times \frac{g}{16} \qquad (5.41)$$

In this expression σ is the interfacial tension, ℓ the eddy length, $|\Delta\rho|$ the absolute value of density difference between the two solvents and g the acceleration due to gravity.

Eqn.5.39 can be written for both phases and thus always predicts that:

$$\frac{K_1^o}{K_2^o} = \left(\frac{D_1}{D_2}\right)^{\frac{1}{2}}$$

A simplification of Eqn.5.39 can be made if the stirring speeds in both phases are equal to the same value N. The individual mass transfer coefficient K_1^o is then

$$K_1^o = B\sqrt{2}\left(\frac{(NL)^3 D_1(\rho_1 + \rho_2)}{\sigma_e}\right)^{\frac{1}{2}} \qquad (5.42)$$

The total surface renewal s_T can be expressed as:

$$s_T = 2\ B^2\ \frac{(NL)^3(\rho_1 + \rho_2)}{\sigma_e} \qquad (5.43)$$

When only the reference phase is stirred, i.e. when $Re_2 = 0$, it follows from the general correlation that

$$K_1^o = B\left(\frac{(NL)^3\ D_1\rho_1}{\sigma_e}\right)^{\frac{1}{2}} \qquad (5.44)$$

The renewal rate s_1^o produced by stirring of phase 1 alone is therefore

$$s_1^o = B^2\ \frac{(NL)^3\ \rho_1}{\sigma_e} \qquad (5.45)$$

The above equation is similar to that derived by DAVIES (1972) for the liquid-side renewal in the case of absorption, i.e. when the second phase is gaseous.

At this stage it must be pointed out that:

(i) the various surface renewal rates obtained in this section are not the same as those of Section 5.2.2. This disagreement is confirmed by the following equation obtained from Eqns.5.43 and 5.45:

$$s_T = 2\ (s_1^o + s_2^o) \qquad (5.46)$$

Equations 5.32 and 5.46 differ by the constant factor of 2. This seems to indicate that the total rate of surface renewal cannot be taken as the sum of individual contributions of the two phases obtained under conditions of only one phase being stirred. The factor 2 is therefore a measure of the coupling effect arising from transfer of momentum across the interface.

(ii) results obtained by Austin for the systems hexane-aniline and isobutanol-water deviated from those of other systems. This can perhaps be explained by the fact that the densities of hexane and isobutanol are significantly different from the densities of the other solvents. Following Eqn.5.44, this difference should have an influence on the value of $K_1^o/\sqrt{D_1}$.

5.2.3.2 Estimation of the constant B

In order to obtain predicted values of the individual mass transfer coefficients from Davies' correlation, the numerical constant B was determined using the existing experimental results of Austin. To achieve this, the systems hexane-aniline and isobutanol-water were chosen.

As pointed out by McMANAMEY, DAVIES, WOOLLEN and COE (1973) the eddy length ℓ is related to the scale of turbulence. It has been assumed that any change in stirring speed affected only the intensity of turbulence, so that ℓ was assumed to be constant.

Arbitrary values of ℓ between 0.1L and L (L being the tip-to-tip stirrer length) were tried in the σ_e term of Eqn.5.39 using a computer. The interfacial tension of the systems chosen is, as a matter of fact, insignificant with respect to the second term of Eqn.5.41. $\ell = 0.2L$ was found to produce the most consistent values of B for the results obtained by Austin when phases were stirred independently at various speeds.

The mean length of the eddies is consequently estimated to be about 0.63cm. The magnitude of ℓ suggests that mass transfer is mainly influenced by the largest eddies. It may be significant that perforations made in the vertical baffles at the level of the impellers have also a diameter of 0.634cm. It therefore appears that the large-scale flows propelled by the impeller blades through these holes produce large eddies whose length is equal to the diameter of the perforations.

Fig.5.3 shows the Sherwood numbers plotted against Λ (see Eqn.5.39) calculated by using $\ell = 0.63$cm. Austin's results are well correlated to within 18% if constant B is taken as 0.019.

The values of B and ℓ calculated by McManamey (McMANAMEY et al.1973) for a similar cell are about twice those of the present work. The reason for this difference is probably that their cell did not have vertical baffles and so the movement of eddies to the interface was less restricted.

Similar treatment was applied to Austin's results for the mass transfer process when only one phase was stirred. The correlation does not hold so well and the value of B, estimated to be 0.039 with an error of 55%, is surprisingly quite different from the previous value.

The fact must therefore be emphasised that, as indicated by the form of Eqn.5.39, it is applicable perhaps only to the mass transfer process occurring under conditions of both phases being stirred. This finding supports the previous conclusions based on the study of the surface renewal rates.

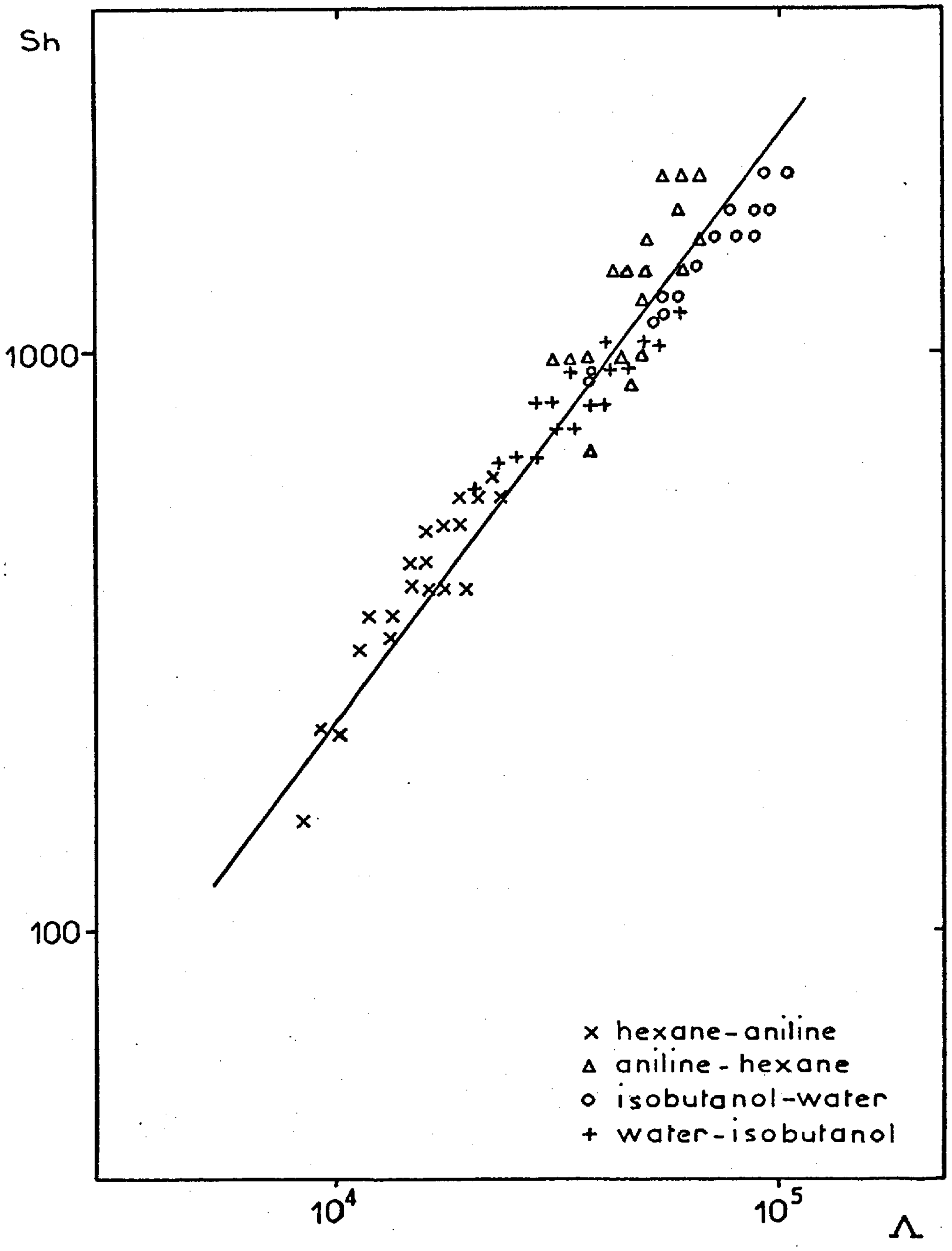


FIG.5.3: AUSTIN'S RESULTS PLOTTED ON A LOG-LOG SCALE USING EQN 5.39.

In addition, it should be pointed out that B which is strongly dependent on the hydrodynamic conditions in the cell is very sensitive to the distance of the impellers from the interface. It is therefore important for purposes of reproducibility to carry out the experiments with the same positioning of the impeller. This may be a further explanation of the differences observed between the results of various workers.

5.2.4 Comparison of correlations

The correlations of Austin and Davies were used to predict overall mass transfer coefficients for transfer of HPr in the toluene/water system and for transfer in the toluene/H_2SO_4 system.

Eqns. 5.35 and 5.36 were used for 100 rev/min and Eqns.5.37 and 5.38 for 200 and 300 rev/min in the case of Austin's correlation. For Davies' correlation, Eqn.5.42, as well as its corresponding form for K_2^o, was used at all stirring speeds. The predicted values will be compared with experimental results in Section 5.4. The calculated results for the system toluene/water with propionic acid as solute are shown in Table 5.3.

As predicted, Davies' correlation compares favourably with experimental results presented later in Table 5.5. For this reason, this correlation was also employed to calculated the individual mass transfer coefficient which needs to be predicted for the diffusional transfer of toluene into aqueous sulphuric acid.

Because of the variation of the physical properties of phase 2 and of the dependence of diffusion coefficient on H_2SO_4 concentrations (see Table 5 , Appendix A4), the individual mass transfer coefficients must be determined in terms of the acid mass fraction, as shown in Table 5.4.

TABLE 5.3

Comparison of estimated mass transfer coefficients for the system toluene/water + HPr in the case of stable transfer from water to toluene

Common Stirring Speed (rev/min)	Austin's Correlations (cm/s) x 10^3			Davies' Correlation (cm/s) x 10^3		
	K_1^o	K_2^o	K_{o1}^o	K_1^o	K_2^o	K_{o1}^o
100	0.77	0.67	0.44	0.32	0.29	0.19
200	3.73	2.75	1.98	0.90	0.66	0.48
300	4.97	3.66	2.64	1.70	1.20	0.88

Calculations using Austin's equations were also worked out and are presented in the same table. The disagreement between both correlations is much more marked than encountered previously. This is certainly due to the high density and viscosity of phase 2.

The reasonable agreement in the values of K between Davies' correlation and experimental results provides further support for the validity of its use in the present work.

TABLE 5.4

Comparison of estimated individual mass transfer coefficients K_2^o for the system toluene/H_2SO_4 solution

Mass Fraction %	K_2^o for Austin's Correlation			K_2^o for Davies' Correlation		
	100	200	300	100	200	300
68	2.27	6.82	9.51	0.475	1.33	2.46
70	2.12	6.50	9.07	0.45	1.28	2.35
72	1.95	6.12	8.55	0.425	1.21	2.22
74	1.79	5.76	8.04	0.41	1.15	2.11
76	1.63	5.40	7.53	0.38	1.08	1.99
78	1.48	5.04	7.04	0.365	1.02	1.88
80	1.36	4.78	6.67	0.35	0.975	1.79
82	1.28	4.57	6.38	0.33	0.94	1.73
84	1.24	4.49	6.26	0.33	0.935	1.72

Note: K_2^o is expressed in 10^4 x cm/s, the stirring speed in rev/min and the mass fraction in %-wt H_2SO_4.

5.3 Qualitative Estimation of Instability Conditions

In the previous section, mass transfer coefficients were predicted for systems in which no interfacial activity was supposed to be present, i.e. for the so-called diffusional transfer. In subsequent sections, the influence of gravitational and Marangoni instabilities on the rate of mass transfer is considered to estimate roughly their effect on the values of mass transfer coefficients.

5.3.1 Gravitational instability

The effect of solute density on the mass transfer process in a ternary system will depend on its relative value as compared to the two solvents and on the direction of transfer. All the possible combinations of these parameters were shown by AUSTIN in his thesis (1966) together with the resulting stability of the phases in each case.

Austin observed in particular that, for transfer of HPr from water to benzene, the system was stable on both sides of the interface, which was contrary to his previous prediction. On the other hand, transfer in the opposite direction, i.e. benzene to water, produced an unstable interface. This behaviour would probably have been the same if toluene were used instead of benzene.

This apparent anomaly was explained by considering the variation of the density of the aqueous solution as a function of the HPr concentration. This density did not decrease with increase in the concentration, as predicted by the mixing law, but increased for solutions up to approximately 50% by weight.

For the order of magnitude of HPr concentrations used in the present work, the density of solutions was around that of water. Consequently, whatever the direction of transfer, a very slight gravitational instability was expected in the aqueous phase. In the toluene phase, the large density difference between toluene and propionic acid resulted in natural convection for transfer from toluene to water only.

SAWISTOWSKI (1973) indicated that cellular convection resulting from gravitational instability increased the mass transfer by a factor of 4 relative to its diffusional value.

The neutralisation reaction occurring in phase 2 should not affect its gravitational stability.

As concerns the sulphonation of toluene, the concentrations of both toluene and TSA in phase 2 were sufficiently low, so that gravitational instabilities were again unlikely to arise.

5.3.2 Marangoni instabilities

According to the Sternling-Scriven instability criterion, the appearance of such instabilities is determined by four factors:

1. direction of mass transfer
2. sign of interfacial tension/concentration gradient
3. ratio of molecular diffusivities
4. ratio of kinematic viscosities.

From the interfacial tension versus solute concentration curve for benzene/water + HPr, it may be seen that the present system has an interfacial tension which decreases with increase in solute concentration, i.e. $\frac{d\sigma}{dC} < 0$. Such a system will be convectionally unstable for mass transfer out of phase of higher kinematic viscosity and lower molecular diffusivity, but stable in the opposite direction of transfer.

Consequently, for the transfer of propionic acid from toluene to water, the system will be stable whilst from water to toluene it will be unstable.

If the driving force is not too large, roll-cell formation will be expected in the unstable direction. The mass transfer coefficient will thus be enhanced by a factor which depends on the intensity of this surface movement, i.e. on the driving force. At high driving forces, this stationary instability will turn into interfacial turbulence.

At sufficiently high driving forces eddies arriving at the interface may produce an interfacial tension gradient which is even high enough to overcome the resistance to surface movement in Marangoni stable system. The resulting Marangoni-type disturbances, known as eruptions at moderate driving forces, also result in increased mass transfer coefficients. At high driving forces the individual eruptions lose their identity and the system exhibits interfacial turbulence. It follows therefore that, whatever the direction of transfer, interfacial turbulence is expected at high driving force.

The number of eddies arriving at the interface decreases with the stirring speed and becomes very small when a stagnant film is supposed to be present. The contribution due to eruptions could be considered as negligible at 100 rev/min.

5.3.3 Summary

The previous considerations for the system toluene/water + HPr may be summarised as follows:

	Gravitational instability	Marangoni instability
toluene $\xrightarrow{\text{HPr}}$ water	unstable	stable
toluene $\xleftarrow{\text{HPr}}$ water	stable	unstable

IYER (1971) observed that for the transfer of HPr from a 1M solution in water into initially acid-free toluene the system was weakly unstable whilst for the opposite direction of transfer using a 0.5M solution in toluene convection currents produced by gravitational instability were seen on both sides of the interface.

SAWISTOWSKI (1973) also reported that for low driving forces if gravitational instability is present in the Marangoni stable direction of transfer and absent in the unstable direction, the mass transfer coefficient for the Marangoni stable direction will be 1.3 to 2.5 times greater than its value in the unstable direction.

5.4 Experimental Results for System Toluene/Water + HPr

The mass transfer process in the absence of chemical reaction has been investigated quantitatively by transferring propionic acid across the toluene-water interface.

The overall mass transfer coefficients calculated by the previous correlations can now be compared with the experimental results so that the effect of instabilities mentioned above can be assessed.

5.4.1 Procedure

The cleaned cell was carefully filled with the mutually saturated solvents, previously brought to 25°C, and the exact volumes of toluene and water used were recorded. The volume corresponding to HPr to be injected was removed before filling so that, once the acid has been introduced, the cell would be full and the interface correctly positioned. For transfer from the lower to the upper phase, care had to be taken not to go beyond the lower part of the central baffle in order to avoid toluene drops creeping into phase 2. To achieve this, the initial HPr concentrations in aqueous phase had to be lower than approximately 1.5 gmol/l.

The stirrers were rotated slowly to ensure thermal equilibrium between the phases before setting them at the desired speed.

The acid was then injected with a hypodermic syringe into the plane of the stirrer blades to obtain, as far as possible, instantaneous mixing. The exact weight of acid was found by weighing the syringe before and after the injection.

Samples of 0.1 ml were removed from the toluene phase at regular intervals of time to be analysed by refractometer. At the end of the run the concentration of acid in the aqueous phase was determined by titration.

The run was stopped when the interface had advanced more than 0.3cm into one of the phases with respect to the centre of the annulus. Generally such runs had a duration of about 100-120 min.

5.4.2 Results

The overall mass transfer coefficient based on the toluene phase K^o_{o1} was calculated using the equation

$$-\frac{1}{S}\frac{d(V_1C_1)}{dt} = K^o_{o1}\ (C_1 - C_1^*) \tag{5.47}$$

where C_1 and C_1^* are the bulk and equilibrium HPr concentrations of the toluene phase respectively.

The volumes V_1 and V_2 depend on the solute transfer and on the number of samples taken. Hence they were corrected as follows:

$$V_1 = \frac{V_1^i\ (1 - \frac{M}{\rho}\ C_1^i) - nv}{1 - \frac{M}{\rho}\ C_1} \tag{5.48}$$

$$V_2 = V_2^i + \frac{M}{\rho}\ (C_1^iV_1^i - C_1V_1) \tag{5.49}$$

where respectively M and ρ are the molecular weight and density of propionic acid, n and v the number and the volume of samples taken. The superscript 'i' refers to initial conditions.

The concentration in aqueous phase 2 was found using the simple mass balance equation

$$C_1^iV_1^i - C_1V_1 = C_2V_2 - C_2^iC_2^i \qquad (5.50)$$

From this value, the equilibrium concentration C_1^* was determined with the help of the equilibrium curve (Fig.3.3).

All calculations have been performed using the Imperial College computer. The available Departmental Library subroutines have been widely used particularly for fitting of the equilibrium curve and the experimental data V_1C_1 versus time by means of the least squares method.

Fig.5.4 shows an extract from a typical output. The variation of the various physical properties is indicated as well as that of the overall mass transfer coefficients based on the toluene phase and denoted by KOT. Its variation in the last two lines was due to the least squares method and these values were not taken into account when analysing the results.

Experiments were divided according to the direction of transfer and to the direction of stirring as follows:

1. Figs.5.5a and b show the variation of the overall mass transfer coefficient with the driving force, both based on toluene phase, for, respectively, contra-rotating and co-rotating stirrers operating at 100, 200 and 300 rev/min in the case of transfer of HPr from toluene to water.
2. Figs.5.5c and d correspond to the transfer of HPr from water to toluene. In Fig.5.5c, the broken lines represent the curves of Fig.5.5a.
3. The effect of the addition of teepol is shown in Fig.5.6 for the transfer of HPr from water to toluene with contra-rotating stirrers.

```
**RUN14**

TRANSFER OF PROPIONIC ACID FROM WATER TO TOLUENE AT 25°C

STIRRING SPEED  200 rev/min  ⇄  SURFACTANT.

TIME(MIN),CONCENTRATION(GMOL/L),VOLUME(ML),KOT(CM/SEC)

  T   CT    CW   CT*  CT*-CT  LOG(CT*-CT)  DC/DT    VT      VW   1000KOT


  0.    0 .918 .419   .419       -.377       .5887 291.00 290.00     .773
  2. .004 .914 .417   .413       -.384       .5577 290.89 289.91     .745
  5. .009 .909 .413   .403       -.395       .5161 290.81 289.79     .705
 10. .018 .901 .407   .389       -.410       .4575 290.79 289.61     .648
 20. .032 .888 .396   .364       -.438       .3715 290.90 289.30     .562
 30. .044 .877 .388   .344       -.463       .3171 290.95 289.05     .507
 40. .054 .867 .381   .327       -.486       .2925 290.98 288.82     .493
 50. .064 .858 .374   .311       -.508       .2837 290.99 288.61     .503
 60. .073 .850 .368   .295       -.530       .2618 290.98 288.42     .488
 70. .082 .841 .362   .280       -.552       .2571 290.98 288.22     .505
 80. .090 .833 .356   .266       -.576       .2465 290.97 288.03     .511
 90. .099 .825 .350   .252       -.599       .2322 290.95 287.85     .508
100. .106 .818 .345   .239       -.621       .2129 290.91 287.69     .490
110. .112 .812 .341   .229       -.640       .1474 290.85 287.55     .354
120. .116 .809 .339   .223       -.652       .0648 290.73 287.47     .160
```

FIG.5.4: TYPICAL PRINT-OUT

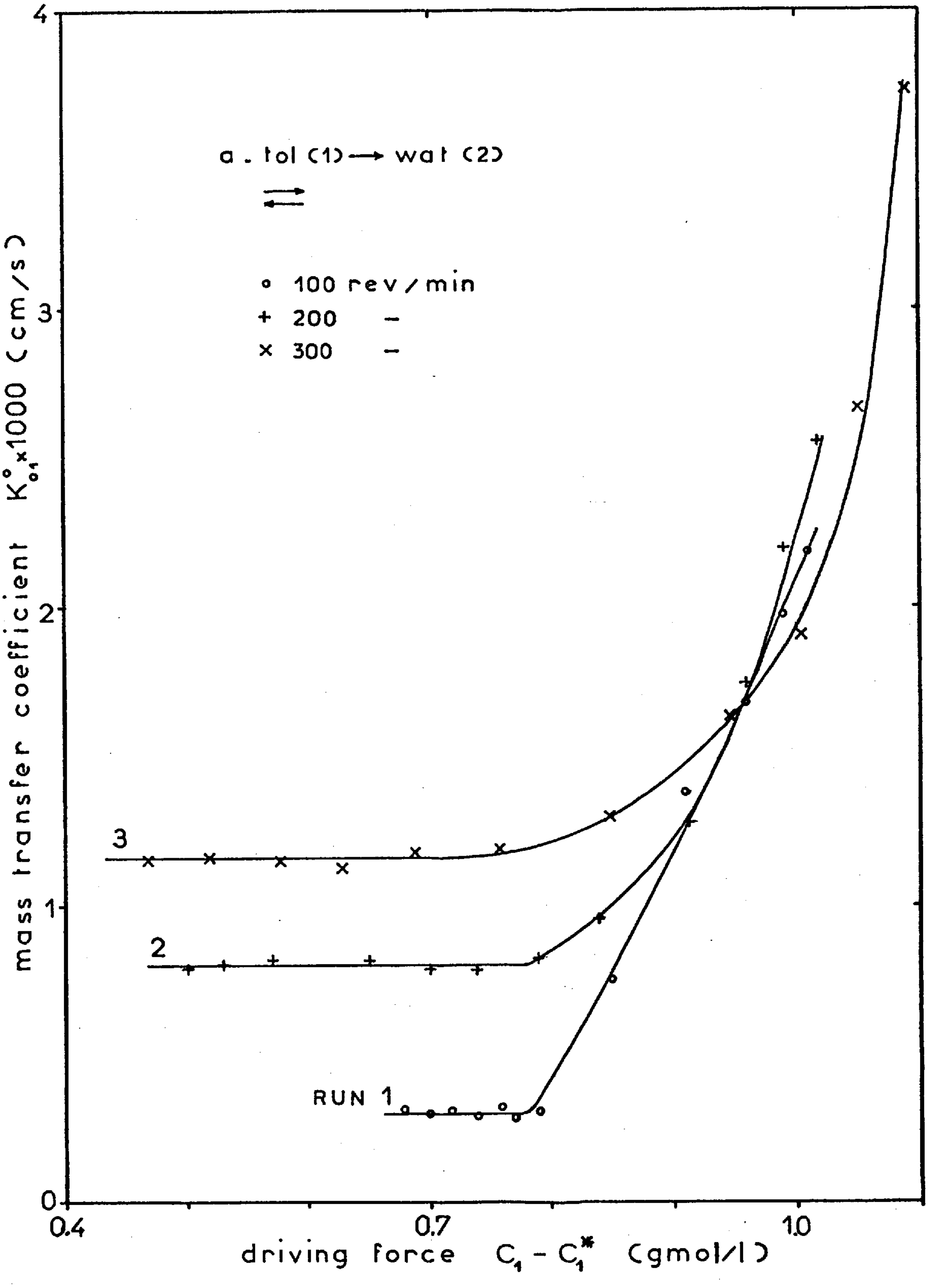
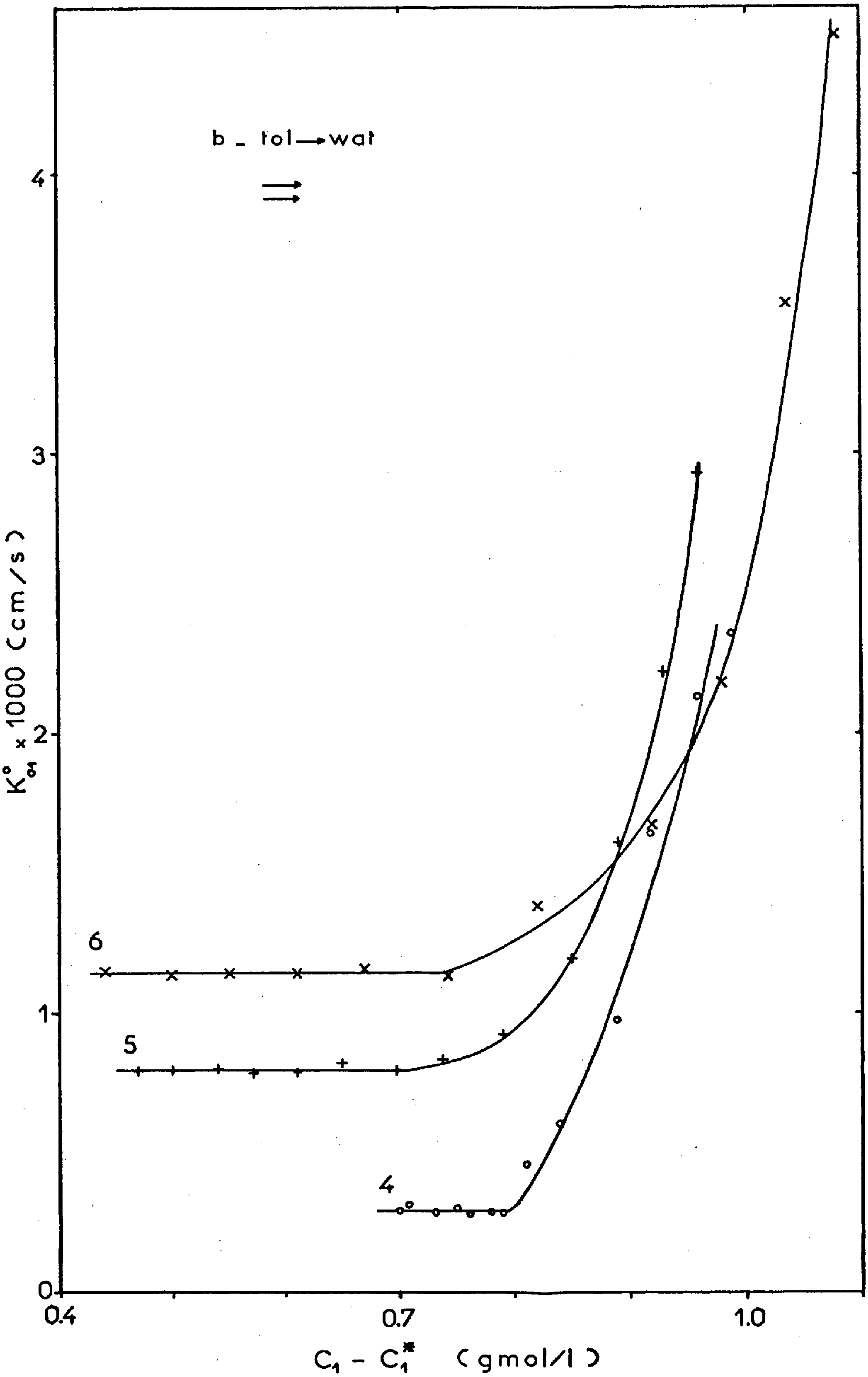
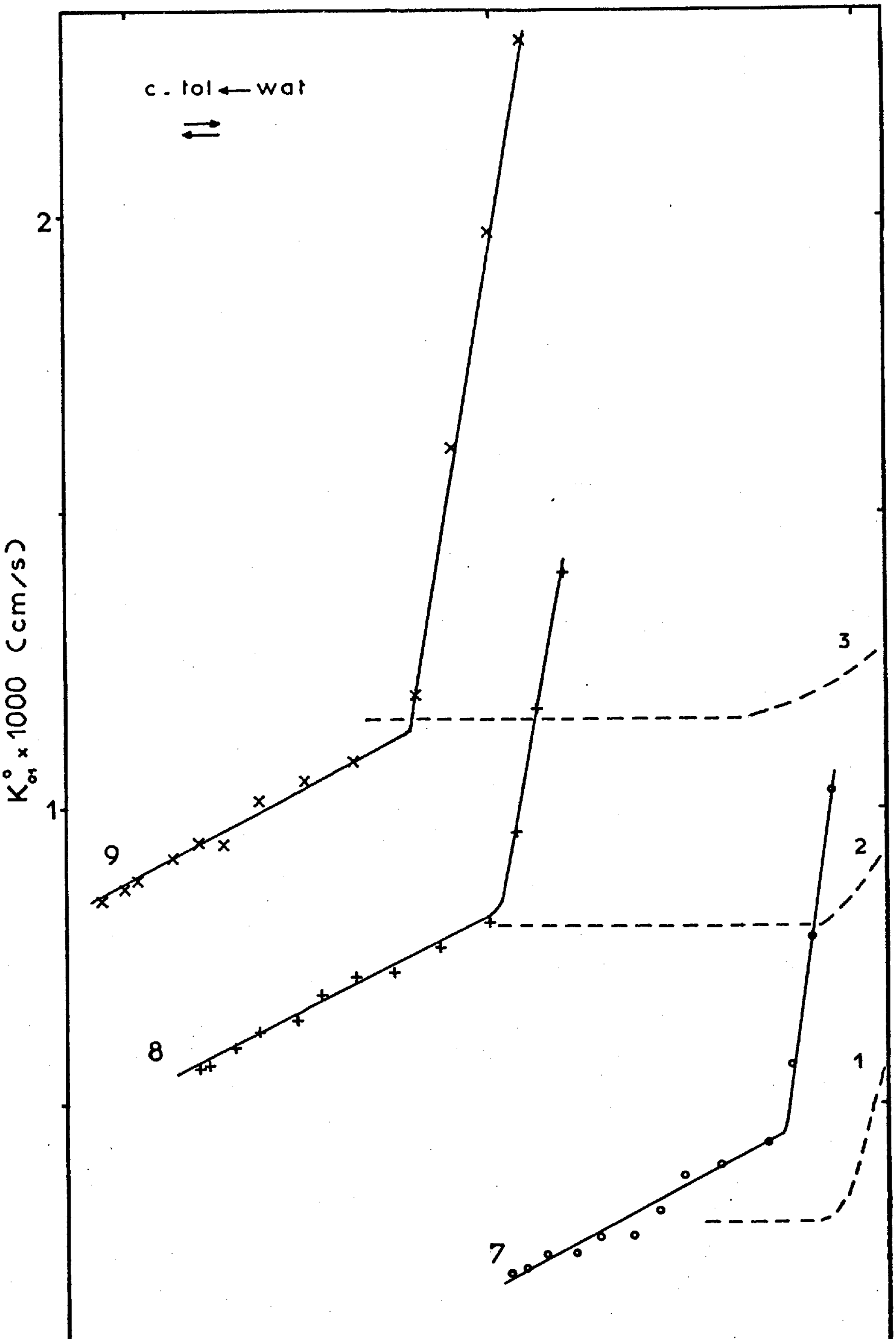
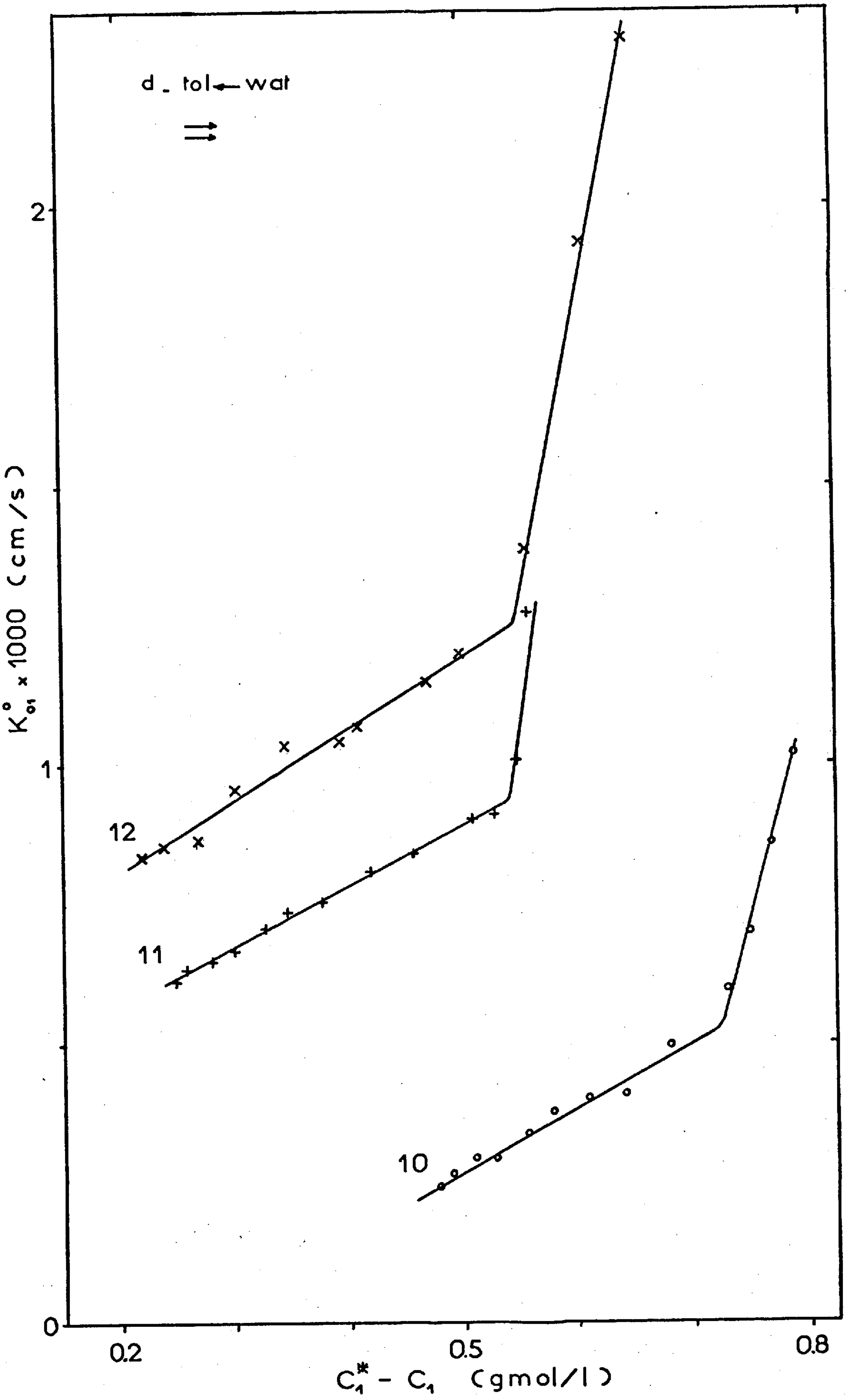


FIG. 5.5: MASS TRANSFER COEFFICIENT AS A FUNCTION OF DRIVING FORCE FOR THE TRANSFER OF HPr BETWEEN TOLUENE AND WATER AT 25°C.


b _ tol → wat
6
5
4
0
1
2
3
4
$K^{\circ}_{o1} \times 1000$ (cm/s)
0.4
0.7
1.0
$C_1 - C_1^*$ (gmol/l)


c - tol ← wat
2
1
0
0.2
0.5
0.8
$K^{\circ}_{o1} \times 1000$ (cm/s)
$C_1^* - C_1$ (gmol/l)
9
8
7
3
2
1


d _ tol ← wat
⇉
K^{o}_{o1} x 1000 (cm/s)
0
1
2
$C_1^* - C_1$ (gmol/l)
0.2
0.5
0.8
12
11
10

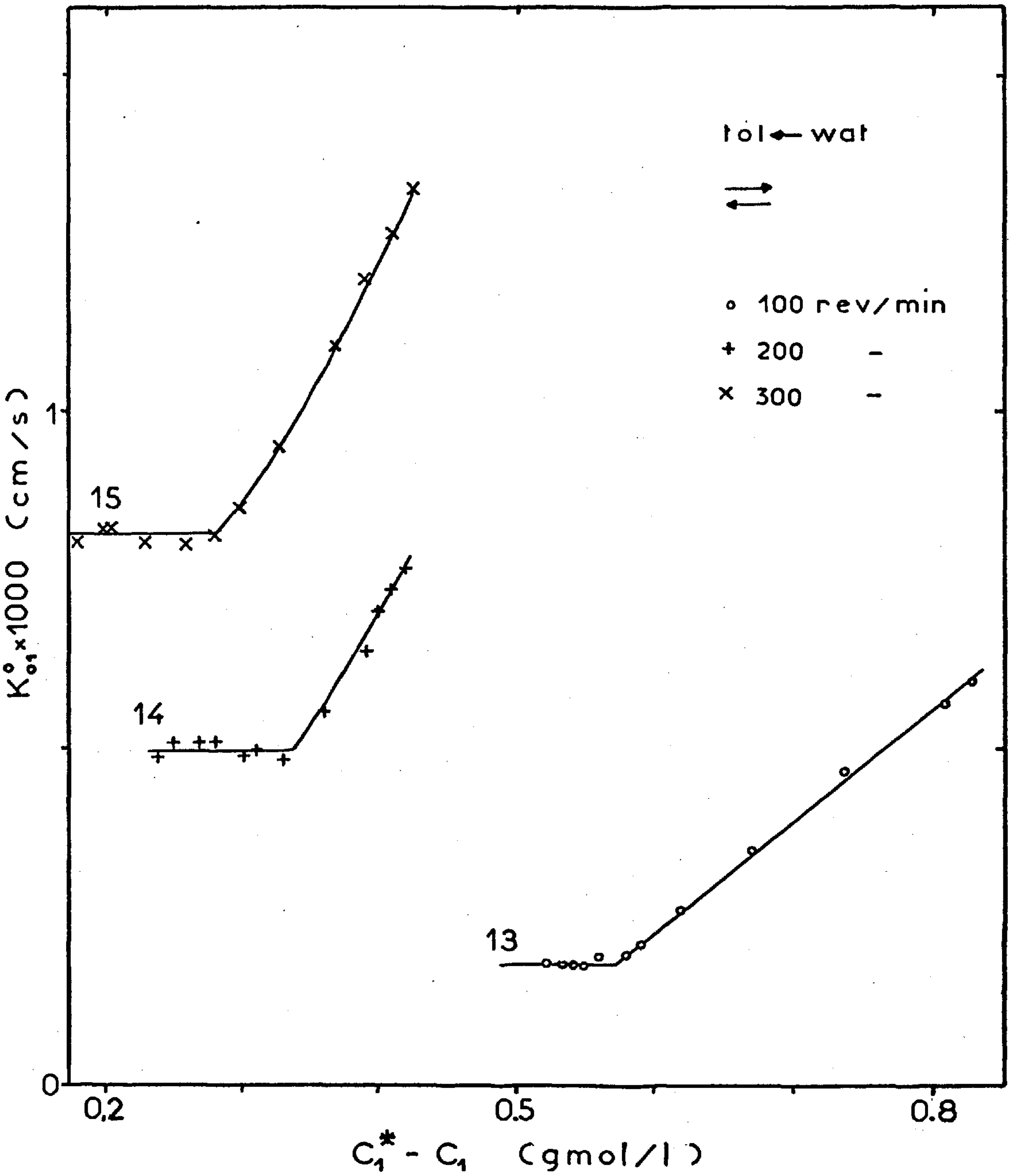


FIG. 5.6: MASS TRANSFER COEFFICIENT AS A FUNCTION OF DRIVING FORCE WITH ADDITION OF SURFACTANT AT 25°C.

In runs 1-6 and 7-12 the coefficients were compared for different stirring conditions and for, respectively, gravitationally unstable and Marangoni unstable transfers. Data can be found in Appendix A3, Table 2.

Runs 13-15, represented in Fig.5.6 and tabulated in Appendix A3, Table 3, give the experimental diffusional values of the overall mass transfer coefficients for the transfer of propionic acid from water to toluene.

As far as possible, the initial concentrations have been taken in the 1 gmol/l region in order to be able to compare results. However, at 100 rev/min and for the transfer from water to toluene, higher initial concentrations have been employed so that the regime of cellular convection be better defined.

The most interesting values are summarised in Table 5.5 and discussed in Section 5.4.3. In what follows, the overall mass transfer coefficients for the Marangoni stable direction (i.e. from toluene to water) and for the stable transfer (i.e. with a surfactant) are respectively denoted K_{STABLE} and K_{DIFF}. The transition value of K when interfacial turbulence dies out for the Marangoni unstable direction is K_{TRANS}.

Comparison with values obtained by SAWISTOWSKI (1973) at 200 rev/min for the system benzene/water + propionic acid shows good agreement provided m_2 in Eqn.5.22 has a value of around 0.5.

TABLE 5.5

Comparison of mass transfer coefficients

	Tol → Wat		Wat → Tol	Wat → Tol + surfactant
N (rev/min)	K_{STABLE} x 1000(cm/s)	$\frac{K_{STABLE}}{K_{DIFF}}$	$\frac{K_{TRANS}}{K_{DIFF}}$	K_{DIFF} x 1000(cm/s)
100	0.30	1.67	2.5	0.18
⇄ 200	0.80	1.60	1.64	0.50
300	1.15	1.40	1.38	0.82
100	0.29	1.61	2.89	-
⇉ 200	0.79	1.58	1.86	-
300	1.14	1.39	1.51	-

5.4.3 Discussion

In Figs.5.5 and 5.6, the regimes of diffusional transfer, Marangoni stable transfer accompanied by gravitational instabilities, cellular convection and interfacial turbulence are clearly discernible. As predicted, interfacial turbulence is observed for high driving forces in each run. As the driving force decreases, the roll-cell pattern gradually evolves from this interfacial turbulence in the case of transfer from water to toluene. If teepol is present, the diffusional state is very quickly established.

The transfer from toluene to water is Marangoni stable but, due to gravitational instability, the resulting mass transfer coefficients are higher than the diffusional value.

The effect of direction of stirring on pure mass transfer was also investigated because of the contradictory statements made by Austin and by Lewis. The former showed in his thesis (1966) that the mass transfer coefficients were dependent on the direction of stirring whilst he also reported the findings of Lewis who stated that co-rotating stirrers gave coefficients which were "if anything, slightly higher" than when the stirrers were contra-rotating.

It can be seen from this work that for the transfer of solute between two solvents no significant difference was observed. Once again Davies' treatment is consistent with the experimental results. Most of the eddies reaching the interface have an isotropic turbulent behaviour whatever the direction of stirring. This is to be expected by the introduction of vertical baffles in order to prevent the rotation of the interface. Consequently horizontal components of turbulence were produced which, according to Davies, play the most significant part in the transfer process.

As far as pure mass transfer is concerned, the following conclusions can be drawn from Table 5.5:

(i) at the same initial concentration, the overall mass transfer coefficient for the Marangoni stable but gravitationally unstable direction is 1 to 1.67 times greater than its value in the Marangoni unstable but gravitationally stable direction;

(ii) the above ratio decreases when the stirring speed increases; this is explained by the larger depth of penetration of gravitational instability (density eddies) than of Marangoni instability. Hence the relative contribution to mass transfer of the former decreases faster than of the latter with increasing stirring speed.

(iii) if the initial concentration is higher, as with runs 7 and 10, the Marangoni unstable transfer becomes faster than the stable transfer observed with a lower initial concentration;

(iv) at constant initial concentration, the higher the stirring speed, the stronger is the interfacial turbulence;

(v) in spite of the presence of a surfactant slight interfacial turbulence occurs initially (at high driving force) in runs 13-15;

(vi) as seen in Fig.5.5c the transition to interfacial turbulence occurs at a lower driving force for Marangoni unstable direction of transfer than for the Marangoni stable direction; this is connected with the resistance to surface renewal encountered in Marangoni stable systems;

(vii) the transition to interfacial turbulence is approximately independent of the stirring speeds for the gravitational unstable system; this can be explained by the fact that the phenomenon is only due to a particular property of the system, i.e. the density difference.

5.5 Conclusions

The main conclusions from this chapter can be summarised as follows:

(i) comparison of experimental overall mass transfer coefficients with those predicted by Davies correlation in the diffusional regime shows reasonable agreement for the whole range of stirring speeds.

(ii) interfacial instabilities of varying degree are observed for the system toluene/water + HPr depending on the magnitude of the driving force and the direction of transfer. The explanation of such phenomena is suggested in terms of surface tension induced interfacial convection for the transfer from water to toluene and of gravitational instability for the transfer in opposite direction.

(iii) the direction of stirring is found to have no significant effect on the transfer process.

(iv) when the activity of the interfacial regions can be ignored, it is assumed that, in accordance with Austin, at 100 rev/min the interface is laminar whilst at 200 and 300 rev/min a surface-renewal interface is likely to be present.

(v) Davies' correlation and Austin's observations show that the momentum transfer across the interface cannot be neglected; this also applies to the part played by the high interfacial tension of the present system.

(vi) comparison of mass transfer coefficients at various stirring speeds indicates that the formation of a laminar interface does not suppress Marangoni instabilities. However both interfacial turbulence and cellular convection are strongly affected by the surface renewal by eddies.

(vii) because of the impossibility of determining experimentally at least one of the individual mass transfer coefficients, no direct conclusion concerning the quantitative analysis of the instabilities in each phase can be drawn. It is only possible to estimate them using Eqns.5.23 to 5.26 and the experimental overall coefficients obtained for the diffusional transfer. The results are tabulated in Table 5.6.

TABLE 5.6

Values of K_1^o and K_2^o estimated from experimental results for stable diffusional transfer from water to toluene with propionic acid as solute at 25°C

$N_{(rev/min)}$	K_1^o x 1000 (cm/s)	K_2^o x 1000 (cm/s)
100	0.39	0.22
200	0.94	0.70
300	1.54	1.14

CHAPTER 6

EXPERIMENTAL RESULTS AND DISCUSSION

In Chapter 5 information was provided on pure mass transfer. In the present chapter the effect of the introduction of a chemical reaction is investigated.

The first part will be concerned with the system toluene/ water + propionic acid, which has already been studied in detail, but on which a neutralisation reaction will be superimposed (Section 6.2.1). The second part (Section 6.2.2) will deal with the simple sulphonation of toluene using sulphuric acid solution in the concentration range of 68 to 84%-wt H_2SO_4.

The experimental procedure common to both sets of experiments will be described in Section 6.1 and conclusions will be presented in Section 6.3.

6.1 Experimental Procedure

All the experiments were performed at 25°C and the operation was similar to that described in Section 5.4.1.

For the neutralisation reaction the experiments were started by filling the cell first with the heavier phase and then with the lighter liquid after bringing the phases and the equipment to the same temperature. Great care was taken not to leave drops of the aqueous solution in the upper compartment during the first operation of filling. The initial interface level was chosen so as to remain within ± 0.3cm with respect to the plane of symmetry of the cell throughout the experiment.

The experiments were also carried out at various sodium hydroxide concentrations, the initial acid concentrations being kept at the same value as far as possible. After starting the impellers and injecting the necessary acid volume into the toluene phase, the time was noted and the relevant phase was regularly sampled by a syringe as previously described. The samples were analysed by means of the refractometer.

A few runs were also conducted with transfer of HPr into a 0.5M sodium propionate solution for the purpose of comparison with runs 1-3. These experiments were performed at the stirring speeds for which any supplementary contribution to the transfer resistances was the most noticeable, i.e. at 200 and 300 rev/min. The experimental procedure and the calculations of the overall mass transfer coefficients were the same as described in Section 5.4.

For the case of sulphonation, the problem was complicated by the fact that the chemical reaction begins immediately when one phase comes into contact with the other. For this reason time was recorded arbitrarily as being zero at the beginning of the filling. The disturbance created by the filling cannot unfortunately be avoided. The resulting consequences will be discussed in Section 6.2.2.2.

Periodically a 3ml sample was withdrawn from the acid phase; its absorbance A was quickly measured at 256nm and the sample was then returned to the stirred cell. A loss of about 0.25ml was noted for every measurement. However, as only 6 samples were taken for each run, this return of samples ensured that no significant change in the volume of phase 2 and consequently in the level of the interface occurred during the run.

Both measurement techniques were described in detail in Section 3.4.

6.2 Experimental Results

All the results presented below were obtained at 25°C and with contra-rotating stirrers. Three stirring speeds were investigated: 100, 200 and 300 rev/min.

As the results of the experiments were to be compared with those estimated from correlations, frequent references to Chapter 5 have been made, particularly as concerns Davies' correlation which was proved to be the best for the present system.

6.2.1 Instantaneous reaction

6.2.1.1 Equations and computational procedure

It was desirable to obtain a computing program for the calculation of various mass transfer parameters, particularly mass transfer coefficients and enhancement factors. As demonstrated in Section 4.2.1, many different cases can exist so that it was necessary to simplify the equations to be used and to define the regions of their applicability.

In fact, due to ignorance concerning the real value of the individual mass transfer coefficients, when gravitational instabilities arose, and of the values of the ratio of diffusion coefficients, it was practically impossible to obtain correct positioning of the critical line at the first attempt. Hence, the calculations which did not depend on the position of the latter were worked out first:

(i) The flux, for instance, was easily available using Eqn.5.47. The volume of phase 2 was calculated by assuming that it did not change during the reaction and thus that equation 5.49 could be used. This assumption was questionable, but the error so introduced was negligible since the maximum total variation of the volume was as low as 4% of the total volume of the phase.

(ii) The concentrations of NaOH and sodium propionate were also calculated using the stoichiometric equation 4.23 for the former and the equation

$$C_s = \frac{V_1^i C_{A1}^i - V_1 C_{A1}}{V_2} + C_s^i \qquad (6.1)$$

for the latter. The concentration of the salt was estimated to be constant whatever the distance from the interface and thus equal to the sum of the initial concentration and that corresponding to the amount of NaPr produced by the chemical reaction. This assumption is strictly valid for case I, but is not exactly valid for the runs performed under conditions of case II (see Fig.5.1).

(iii) For the purpose of calculating E_{EXP} using Eqn.4.8 it was necessary to know N_A^o. To achieve this, Eqn.4.10 was used with the values of K_{o1}^o given in Table 5.5 for the transfer from toluene to water. It may be pointed out that this estimation of N_A^o does not take into account the initial interfacial turbulence and that thus E_{EXP} will be abnormally high for its first assumption. However, when the turbulence dies out, E_{EXP} can be considered as reliable. Another possibility of calculating E_{EXP}, which would only be strictly valid in the case I, was to use Eqn.4.13, but this presupposes a known value of K_1^o. The restrictions applicable to the present part of the work will be discussed later.

At this stage and before envisaging how the position of the critical line could be estimated the behaviour at the interface will first be considered. One of the two following assumptions had to be chosen:

1. There is no interfacial resistance so that the concentrations of HPr at the interface can be considered at equilibrium. In such a case assumption (i) of Section 4.2.1.2 is valid as well as the equations established in the relevant section.

2. There is an interfacial resistance and the interfacial concentrations of HPr assumed to be at equilibrium are no longer reliable. Such a case will be discussed later as far as the electrolytic properties of the aqueous solution are likely to be modified by the presence of the salt produced by the reaction.

If assumption 2 is retained, Eqn.4.14 will consequently have to be changed. On the assumption that K_1^o is not affected by the presence of a salt which is only soluble in the aqueous phase, it becomes:

$$\frac{1}{K_{o1}^{o'}} = \frac{1}{K_1^o} + \frac{1}{K_R} + \frac{m'}{K_2^{o'}} \qquad (6.2)$$

where the prime indicates the presence of the salt.

This will not affect the validity of Eqn.4.17 provided interfacial resistance is incorporated into the value of the overall mass transfer coefficient.

For the determination of the critical line, i.e. the estimation of the diffusion coefficients, D_{B2} and D_{A2}, and of the mass transfer coefficients, K_1^o and K_2^o, there exist several possibilities. Thus two approaches were available for the estimation of diffusion coefficients: the first took into account the diffusion of ions as outlined in Section 5.1.1.2, while the second consisted in neglecting their influences and considering only molecular diffusion. The selected approach will be discussed subsequently. For K_1^o, the difficult was removed by calculating it for each run using Eqn.4.26. It was obvious that its correct value was found only for the runs whose operating lines were situated in the region corresponding to case I. This condition was verified by drawing the critical line once all parameters were estimated.

However, it must be pointed out that this coefficient was obtained from Eqn.4.11 and was valid only if the concentration of solute was zero at the interface. When an interfacial resistance was present, this calculated K_1^o, denoted by $(K_1^o)_c$, could be used to calculate the slope of the critical line, but did not give the real coefficient K_1^o which could be derived from

$$\frac{1}{(K_1^o)_c} = \frac{1}{K_1^o} + \frac{1}{K_R} \tag{6.3}$$

The enhancement factor defined by Eqn.4.13 becomes consequently:

$$E_I = \frac{(K_1^o)_c}{K_{o1}^o} \tag{6.4}$$

The value of K_2^o was estimated using the system of equations consisting of Eqns. 6.2 and 6.3. This could be solved only if it was assumed that the salt had a negligible influence on the gravitational instability of the aqueous phase, i.e. that

$$K_2^o \simeq K_2^{o'} \tag{6.5}$$

This last assumption seems questionable, but the resulting error is certainly very low since gravitational instability due to the presence of the solute HPr is expected to have only a small effect on K_2^o (see Section 5.3.1). The similar compound NaPr present in the same range of concentrations should not have a more marked influence. Finally, when their chemical reaction occurs, it can be estimated that in fact each molecule of HPr arriving in the interfacial layer is immediately converted to a molecule of NaPr and thus the density of this medium is not strongly altered.

From Eqns.6.2 and 6.3, it follows that

$$\frac{m'}{K_2^o} = \frac{1}{K_{o1}^{o'}} - \frac{1}{(K_1^o)_c} \qquad (6.6)$$

where m' can be calculated using the following equation

$$m' = m \exp(2.3\ k_s C_s) \qquad (6.7)$$

m is the coefficient of partition defined in Section 5.2.1, k_s the constant calculated in Section 3.3.3 and C_s the concentration of the salt present in phase 2. For the sake of simplicity a mean value of C_s has been chosen, i.e. 0.5 gmol/l. This assumes that m' is approximately equal to 0.735 if m = 0.65.

Since the various parameters affecting the slope of the critical line could now be calculated, its position was estimated and cases I and II demarcated.

For case I, the calculations have already been worked out since only $(K_1^o)_c$ needed to be estimated. The problem was a little more complicated for case II. The aim of the mathematical treatment of this case was to calculate K_R for the purpose of checking its value against that found from runs 29 and 30.

The relevant calculations have been worked out as follows:

(i) C_{Ai1} was calculated using the following equation (derived from Eqn.5.14)

$$C_{Ai1} = C_{A1} - \frac{N_{Ai}}{K_1^o} \qquad (6.8)$$

(ii) C_{Ai2} was obtained in a similar manner from Eqn.4.16.

(iii) C^*_{Ai1} was evaluated using the equilibrium curve and taking into account the influence of the salt.

(iv) C_{Ai1} and C^*_{Ai1} were finally employed to give K_R using the equation

$$N_{Ai} = K_R\ (C_{Ai1} - C^*_{Ai1}) \qquad (6.9)$$

It was known that the equilibrium curve was not a straight line and thus that Eqns.4.17 and 4.18 were not strictly speaking valid. Nevertheless $K^{o'}_{o1}$ and E were calculated using the relevant equations for the purpose of estimating the error which would be introduced when employing such simple equations for the quick evaluation of the enhancement factor.

The computer program written for this series of runs calculated the variation of all these parameters. The outputs can be found in Appendix A4, Tables 1 and 2. According to the positioning of a run on the graph of C_B versus C_A, i.e. according to the case of operation, some columns are applicable while others are not. This is discussed in the subsequent section.

6.2.1.2 Results

The experiments can be divided into three groups:

1. Runs 16 to 26 were performed over a large range of NaOH concentrations and an initial concentration of the salt equal to zero (Appendix A4, Table 1).
2. For runs 27 and 28, the experimental conditions were similar except that a concentration of 0.5 gmol/l was already present in phase 2 at t = 0 (Appendix A4, Table 1).
3. In runs 29 and 30, the transfer of HPr into a 0.5M NaPr solution was studied without any chemical reaction (Appendix A4, Table 2).

The stoichiometric operating lines of these runs are shown in Fig.6.1. It may be noticed that their slopes were taken as unity on the assumption that $V_1 \simeq V_2$.

It was considered that runs whose initial concentration was high enough could be assumed to satisfy case I conditions.

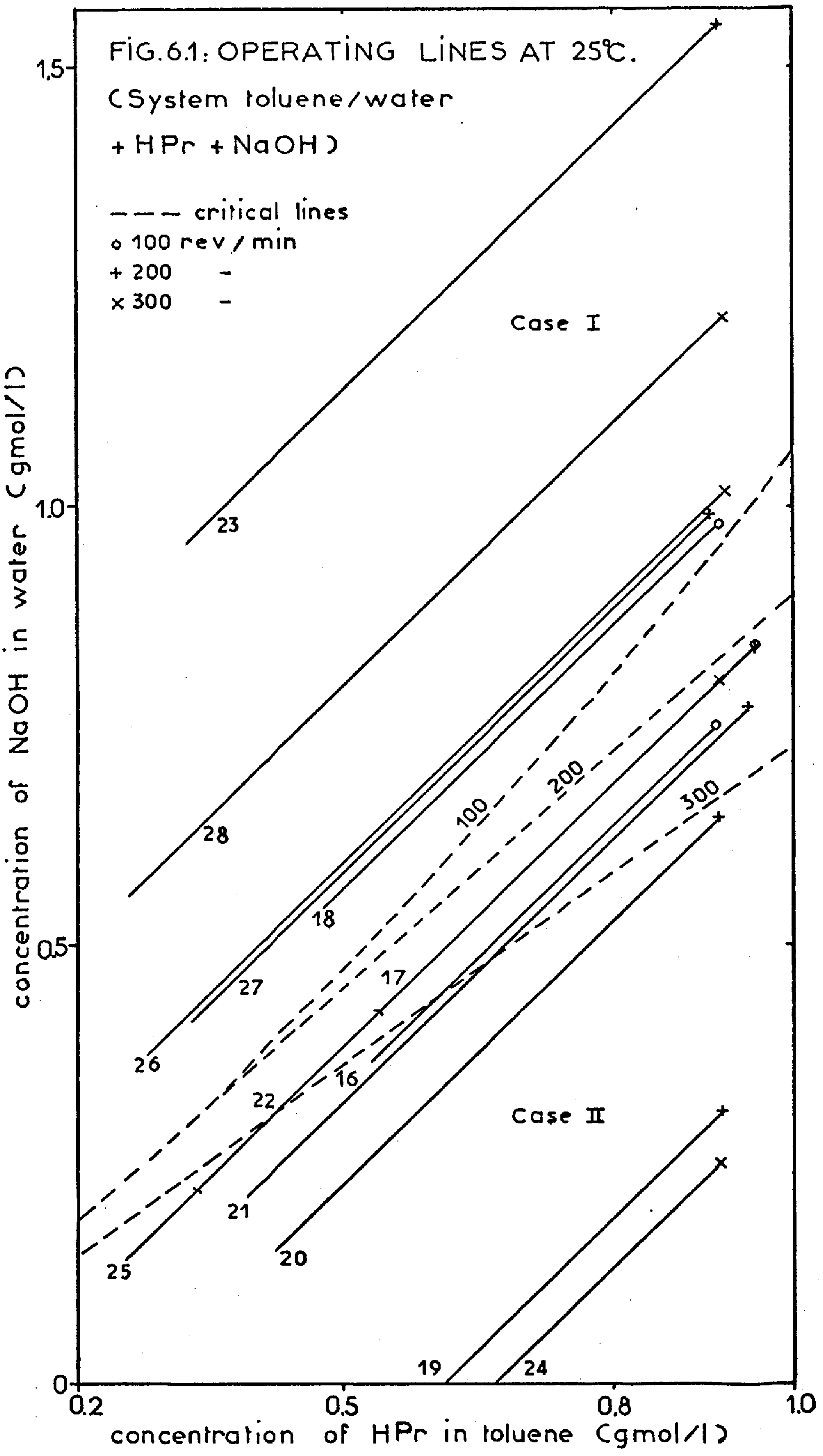


FIG.6.1: OPERATING LINES AT 25°C.
(System toluene/water
+ HPr + NaOH)

Fig.6.2 shows the variation of the mass transfer coefficient $(K_1^o)_c$ as a function of C_{A1} for runs 18, 23, 26 and partly 25 ($C_s^i = 0$), 27, 28 ($C_s^i = 0.5$ gmol/l). From this graph it was taken that $(K_1^o)_c$ at 100, 200 and 300 rev/min was respectively equal to 0.93, 1.5 and 1.8 x 10^3cm/s.

It can thus be seen that at this stage two main difficulties may be removed:

- the value of the apparent diffusion coefficient of the reacting species originally present in the bulk of the phase 2.
- the problem of the presence of an interfacial resistance.

Preliminary calculations neglecting the interfacial resistance have shown that the best results obtained for $K_{o1}^{o\,'}$ with the experiments carried out at low concentrations of NaOH were procured by considering an ionic diffusion as described in Section 5.1.1.2 at 100 rev/min and molecular diffusion of undissociated NaOH at 200 and 300 rev/min.

The same sets of calculations also showed that, if the K_2^o's are calculated from the concentration profiles, their values so found were too low to be acceptable. The ratio was approximately 1:2 with respect to the diffusional values of Table 5.6. An interfacial resistance was thus assumed and calculations according to the above section worked out.

Runs 29 and 30 which involved pure mass transfer from toluene into a 0.5M NaPr solution gave $K_{o1}^{o\,'}$ at 200 and 300 rev/min as shown in Fig.6.3. The relevant characteristics of these runs are tabulated in Appendix A4, Table 2.

From Eqn.6.6 K_2^o is easily obtained. Substituting its value into Eqn.4.14, it gives K_1^o and then from Eqn.6.3 K_R is evaluated. These values are all collected in Table 6.1. In these calculations

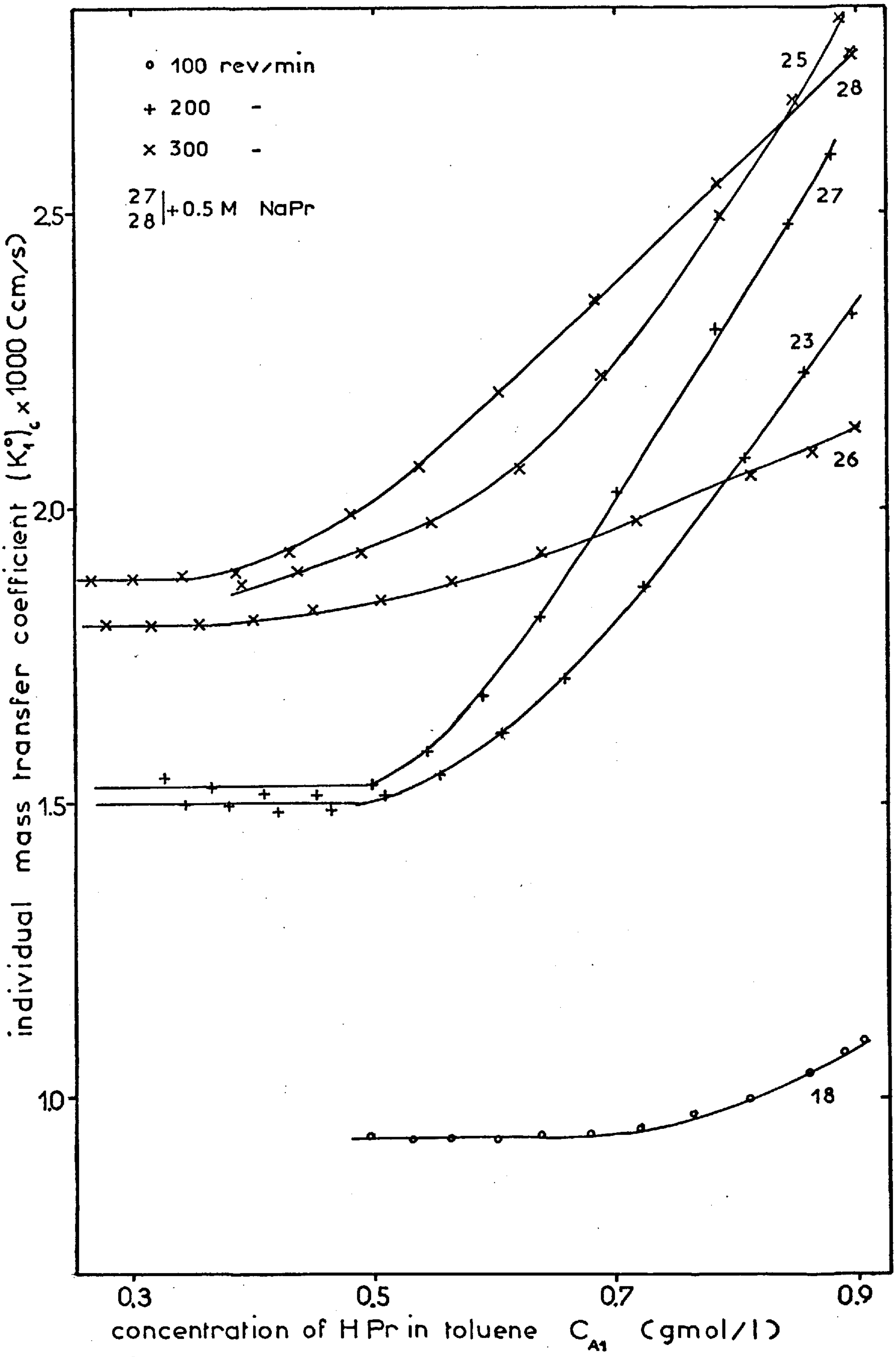


FIG.6.2 : VARIATION OF $(K_1^o)_c$ AS A FUNCTION OF C_{A1} AT 25°C.

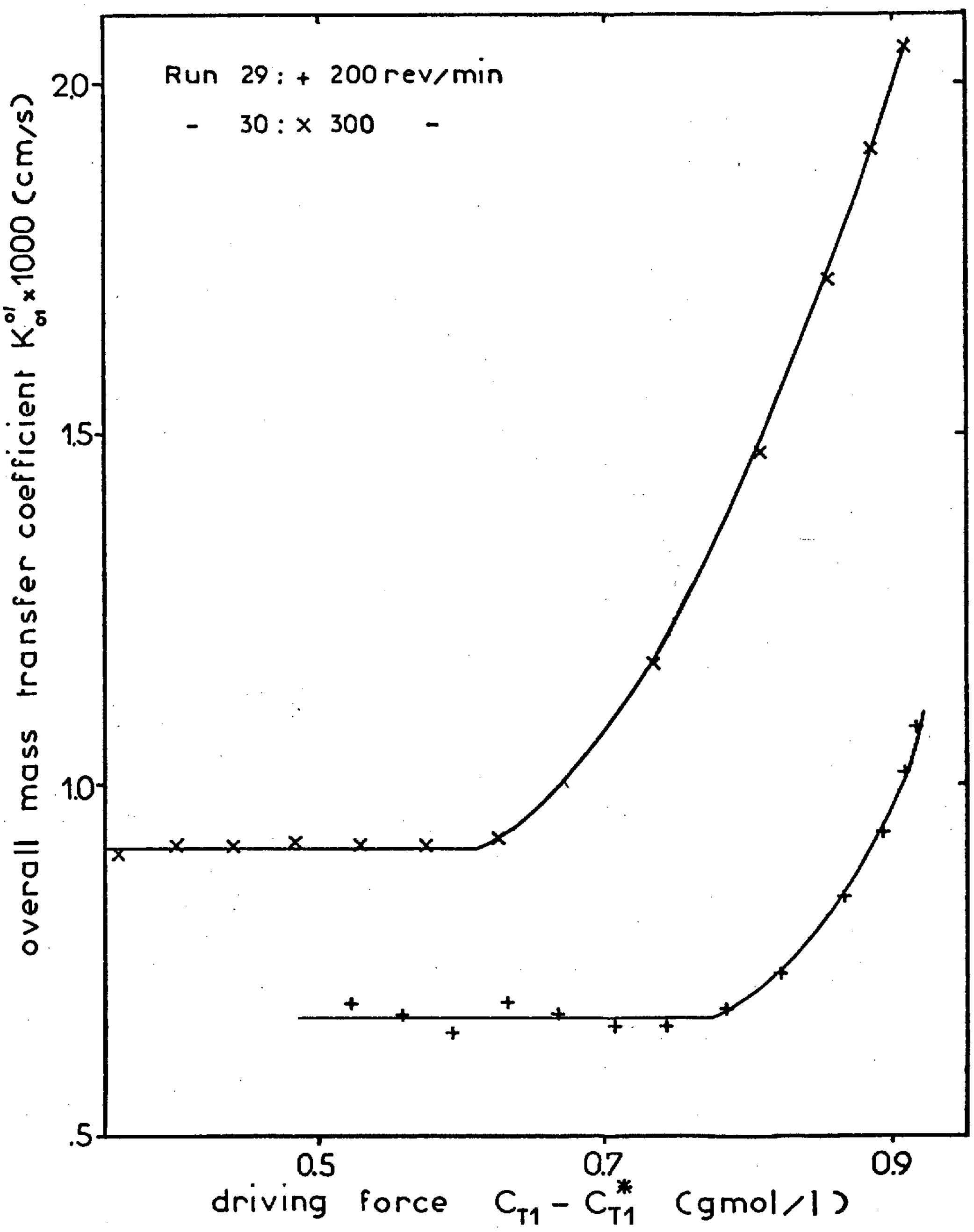


FIG. 6.3 : TRANSFER OF HPr FROM TOLUENE TO AQUEOUS SOLUTION OF 0.5 M NaPr AT 25 °C.

TABLE 6.1

N (rev/min)	$(K_1^o)_c$	K_1^o	X (-)	K_2^o	Y (-)	$K_{o1}^{o\prime}$	K_R	D_{B2} x 10^5 (cm^2/s)	Slope of the Critical Line (-)
100	0.93	1.09	2.80	0.29	1.32	0.31 (estimated)	-	varying	varying
200	1.50	1.94	2.06	0.885	1.26	0.67	6.45	2.12	0.89
300	1.80	2.56	1.66	1.35	1.18	0.91	6.06	2.12	0.70

All K's are expressed in 1000 x cm/s.

it was shown that K_R is approximately the same for 200 and 300 rev/min. Its mean value of 6.25 was used for calculating K_1^o at 100 rev/min.

K_1^o and K_2^o were compared with their diffusional values and the ratio of these values, respectively called X and Y, is represented in Fig.6.4.

The critical lines were consequently drawn on Fig.6.1 and the assumption, according to which runs 18, 23, 26, 27 and 28 were in case I region, was subsequently verified. As D_{B2} was a function of C_{B2} and C_s, the critical line for 100 rev/min could only be estimated around a mean value of D_{B2} taken as 3.60×10^{-5} cm²/s. Run 25 cuts the critical line and is therefore common to both cases.

The variations of the enhancement factor E determined by Eqn.4.18 are compared with E_{EXP} in Table 6.2. In this table two different values of E_{EXP} are reported. The question is to know how N_A^o has to be defined. If the interfacial resistance is negligible, as for 100 rev/min, i.e. when no significant change is observed between K_{o1}^o and $K_{o1}^{o'}$, any of these can be used for calculating N_A^o. However, as pointed out above, when the influence of the interfacial resistance becomes important, $K_{o1}^{o'}$ has to be used rather than K_{o1}^o. Calculations performed initially with K_{o1}^o and tabulated in Appendix A4, Table 1 have been consequently adjusted as can be seen in Table 6.2.

The variation of the enhancement factor E_{EXP}, so modified, with the initial concentration of NaOH in the phase 2 is also shown in Fig.6.5. It may be noticed that this enhancement factor is about 1.5 times greater at 100 rev/min than at 200 and 300 rev/min. This increase is due to the difference in the

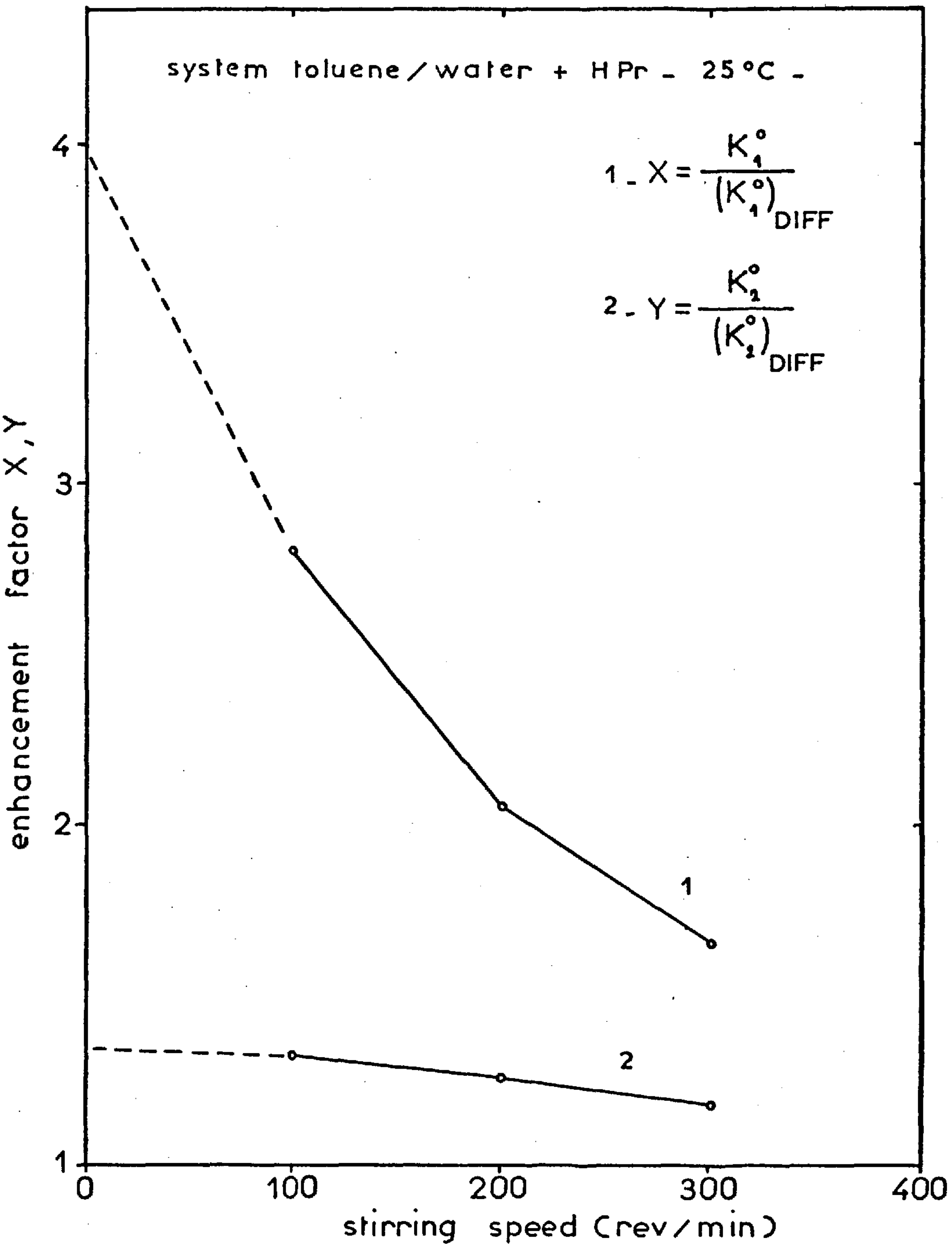


FIG. 6.4: VARIATION OF THE ENHANCEMENT FACTORS RELATIVE TO THE INDIVIDUAL MASS TRANSFER COEFFICIENTS AS A FUNCTION OF THE STIRRING SPEED.

diffusion regimes of the reactants as has been previously explained. Provided that a mean value is used for C_{A1}, Eqn.4.29 can be employed to describe the phenomenon in case II. When case I is reached, Eqn.6.4 must be used. The value of E_{EXP} is thus constant and equal to 3.14, 2.13 and 2.02 for 100, 200 and 300 rev/min. The average error with respect to the predicted value calculated from Eqn.6.4 is less than 5%.

TABLE 6.2

N (rev/min)	C^i_{B2} (gmol/l)	E_{EXP} based on K^o_{o1}	E_{EXP} based on $K^{o\prime}_{o1}$	E
100	0.747	2.65	2.53	2.61
	0.838	2.86	2.67	2.81
	0.979	3.23	3.13	-
200	0.311	1.11	1.33	1.12
	0.645	1.41	1.68	1.66
	0.771	1.59	1.90	1.86
	0.838	1.56	1.86	2.02
	0.991	1.77	2.11	-
	1.551	1.80	2.15	-
300	0.249	0.88	1.11	1.09
	0.801	1.59	2.01	(1.94)
	1.017	1.61	2.03	-
	1.215	1.60	2.02	-

The agreement between the mean values of E_{EXP} and E is generally very good (see Table 6.2) except for run 19. It is easy to understand that for low initial concentrations of NaOH the enhancement factor E will vary considerably and that a mean value will thus be difficult to define.

Likewise the calculated values of $K^{o\prime}_{o1}$ (using Eqn.4.17) are correct. This shows that the value of m adopted gives satisfactory results in spite of the fact that it does not describe the real situation as shown in Section 5.2.1.

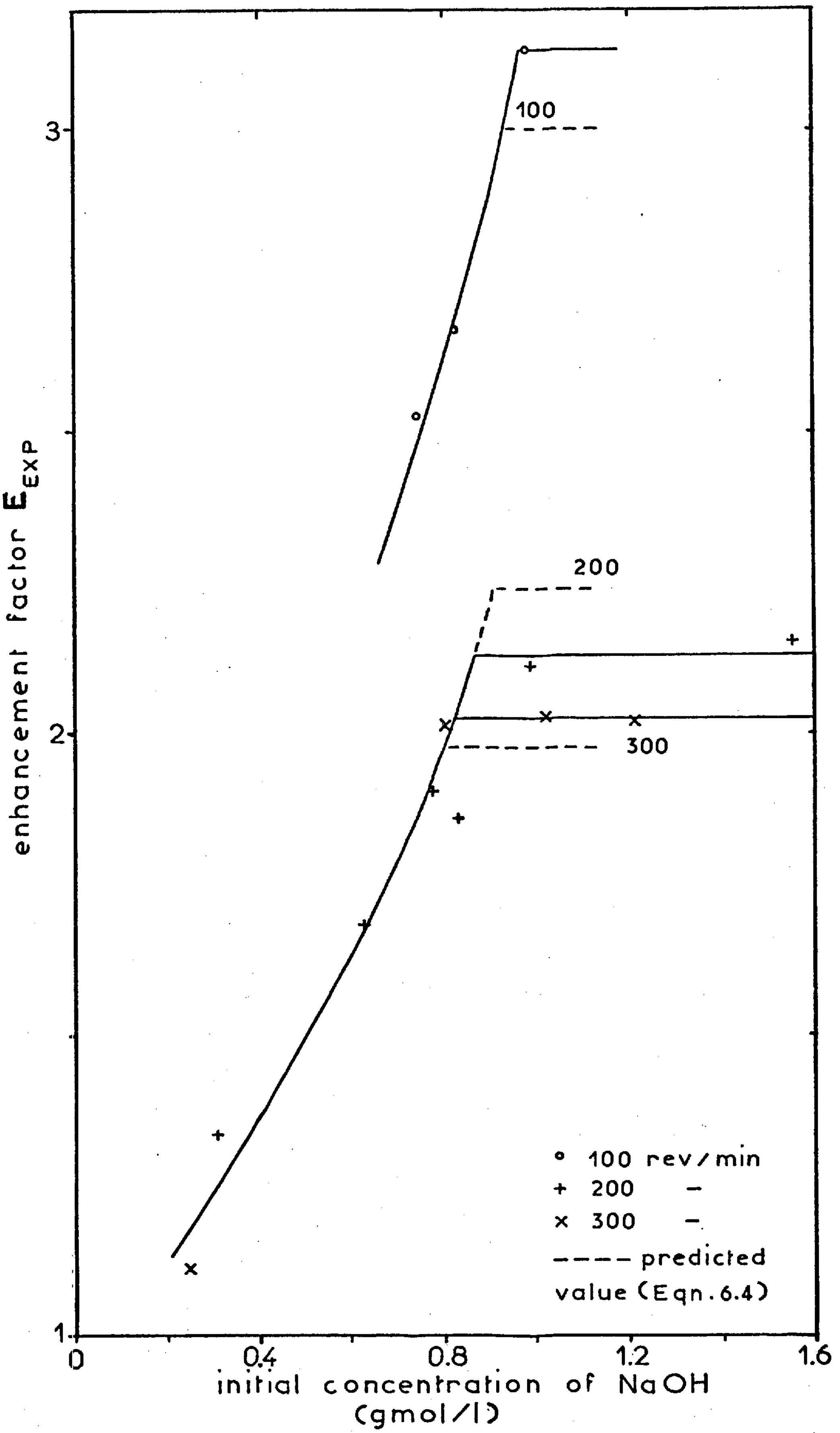


FIG.6.5: VARIATION OF E_{EXP} (based on $K_{o1}^{o'}$)

On account of the many manipulations and of the large error introduced in estimating the diffusion coefficients, the value of K_R is subject to a much greater error than any other calculated parameter. For this reason only its mean value was calculated for each run. It can be seen from Fig.6.6 that for runs situated in case I region, $K_R = 6.61 \times 10^{-3}$ cm/s is within 25% the relevant values whilst for those situated in case II region $K_R = 3.86 \times 10^{-3}$ cm/s seems to be a better value, the maximum deviation being about 12% if runs 18 and 24 are excluded. It should be remembered that the value found from runs 29 and 30 was of the same order of magnitude, i.e. 6.25 10^{-3} cm/s.

6.2.1.3 Discussion

The good agreement observed for the order of magnitude of most experimental and predicted parameters shows the consistency of the adopted assumptions and calculations. The most relevant remarks are:

(i) interfacial turbulence observed at the beginning of each experiment continues to be present when a chemical reaction is introduced. This also applies to the gravitational instabilities which occur later.

(ii) the diffusion phenomenon of the reacting species of phase 2 is strongly affected by the hydrodynamic condition of the layer situated near the interface. In fact, the diffusion coefficient of the reacting species, D_{B2}, at 100 rev/min will be that of OH^- as described in Fig.5.1, i.e. when the concept of laminar diffusion is applicable. On the contrary, when the surface is continually renewed by eddies, as at 200 and 300 rev/min, the influence of the other ion on the rate of diffusion of anion OH^- becomes negligible, because of the strong internal

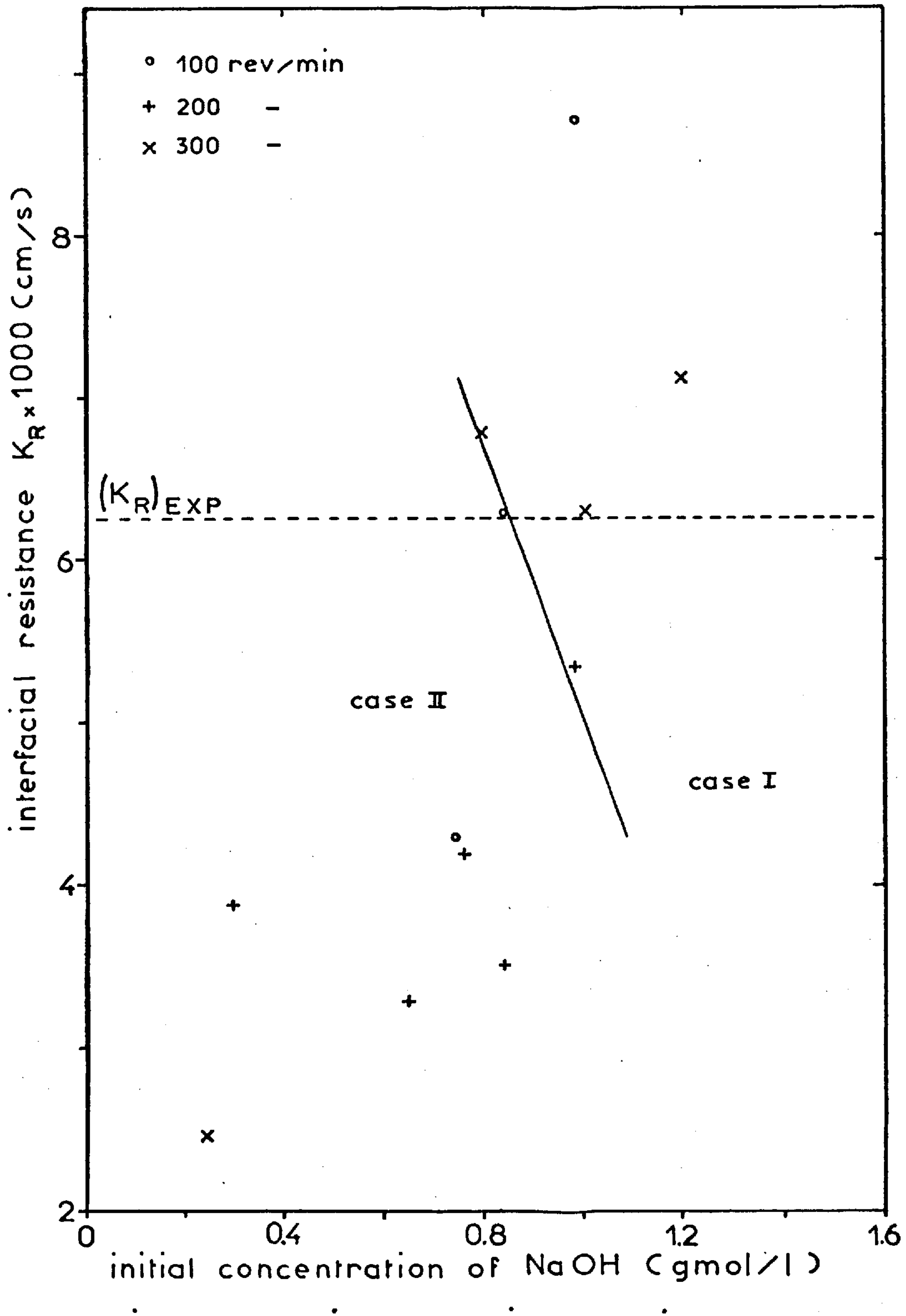


FIG.6.6: THE INTERFACIAL RESISTANCE AS A FUNCTION OF THE INITIAL CONCENTRATION OF NaOH AT 25 °C.

turbulence inside each eddy. The diffusion coefficient of the molecule NaOH has to be taken into account in this case for, according to the neutrality law applied to the eddy, Na^+ will have to follow OH^-.

(iii) it seems that for the system toluene/water + propionic acid an interfacial resistance is set up at the interface. This resistance is probably due to a slow process of re-solvation of the molecule HPr. This additional term was not observed by DAVIES and WIGGILL (1960) and HARADA et al (1975) in their investigations on the transfer of acetic acid from toluene or benzene to water but was detected by the latter for the system benzene/water + propionic acid. The order of magnitude of this resistance, approximately 100 s/cm, was low enough to be neglected if pure water is considered as the solvent. The error so introduced is of the same order of magnitude as the experimental error for 100 and 200 rev/min but is slightly higher for 300 rev/min. This could explain why in Chapter 5 the experimentally observed overall mass transfer coefficient was also 10% lower than the predicted value. The change due to this additional term is not very sensitive because of the relative order of magnitude of K^o_{o1} and is not easy to detect under usual conditions. It is also more marked for the carboxylic acids whose chain is longer as pointed out by HARADA et al (1975). The value of the resistance observed in the present work, i.e. when a salt is present, is higher (approximately around 200 s/cm) than the value obtained by Harada and co-workers. This tends to prove that the process of re-solvation of the molecules HPr is more marked in the presence of anions and cations OH^-, Na^+ and Pr^-.

The resistance to motion inherent in the interface is probably connected with the polarity and the orientation of molecules at the interface. For the carboxylic acids whose chain is long, a high degree of orientation is probable at the interface and molecules approaching the interface must have a favourable orientation or a high kinetic energy to overcome the repulsion. The addition of dissociated electrolytes may increase this repulsion so that the value of the interfacial resistance will be approximately multiplied by 2.

(iv) the abnormally low value of K_R observed for the runs performed in case II could be due to an error in D_{A2} which could be dependent on the concentration of NaPr in the layer of thickness x_R (see Fig.5.1). This is the most probable explanation. Alternatively it is due to the fact that NaPr is not really dissociated in this part of the film. This last assumption is questionable, for it is known that the salt is easily dissociated as pointed out in Section 3.3.2.

(v) the enhancement factor E calculated on the assumption that the equilibrium curve is a straight line is of the same order of magnitude as E_{EXP} for the non-turbulent transfer if $K^{o\prime}_{o1}$ is taken instead of K^{o}_{o1} when calculating N^{o}_{A}. The value of 0.65 chosen for the coefficient of partition provides good agreement in the above calculation and thus can be considered as reliable for the range of concentrations of HPr studied.

(vi) the neutralisation reaction enhances the transfer by a factor whose order of magnitude is strongly dependent on the hydrodynamic regime of the layer situated near the interface, i.e. of the region where the reaction occurs, and on the initial strength of one of the reacting species, the other being kept approximately constant to be able to carry out the

the comparison. This enhancement factor is within the range 1.0 to 3.5 and is constant for the concentrations of NaOH greater than about 0.9 gmol/l according to Eqn.6.4. These constant values are independent of the initial concentration of HPr. It can also be noticed that once the stirring speed has been reached for transition from the film regime to the surface-renewed regime, the variation of E_{EXP} versus C^i_{B2} will follow the same curve (provided that C^i_{A1} = constant) for the experiments situated in case II.

(vii) the introduction of a chemical reaction has allowed the calculation of the enhancement factor relative to the individual mass transfer coefficients when gravitational instabilities play an important part in the transfer. This part is diminished when the stirring speed, i.e. also the surface renewal, is increased as can be seen in Fig.6.4. It seems thus that at high speeds the transfer process is controlled by the artificially produced eddies rather than by those resulting from the difference in densities. If an extrapolation is carried out, enhancement factors of 4 and 1.35 can be estimated for instabilities in phases 1 and 2 respectively, when no stirring occurs, in accordance with predictions of Section 5.3.1.

The problem of a temperature increase at the interface due to the reaction as well as due to the re-solvation of HPr has not been forgotten but was considered to be negligible because of the small concentrations of reactants employed in the present work and on account of the efficiency of the stirring which maintained the temperature at 25°C everywhere in the cell and resulted in high heat transfer coefficients at the interface. Anyway, a slight increase of temperature in the reaction zone would only have a slight effect on the instabilities.

The least square method has given acceptable values of the experimental flux as has also been seen in Section 5.4. However, the use of the various assumptions necessary for the calculations of the ratio of the diffusion coefficients has introduced a large error which can be estimated as 40-50%. It is not surprising therefore that such high deviations should occur in the calculated value of K_R.

6.2.2 Pseudo first-order reaction

As in this section sulphuric acid is the important compound of phase 2, all relevant notations concerning this reactant, such as density, viscosity, interfacial excess, etc, will be characterised by the subscript 2. For toluene and water, the notations will remain unchanged. The superscript s will refer to surface conditions.

6.2.2.1 Equations and computation procedure

The salt concentration in phase 2 was determined by UV absorbance measurements. These measurements were converted directly into TSA concentrations by means of Eqn.3.11.

The TSA concentration-time curves were consequently available. In order to calculate the slope of the straight line which was predicted in Section 4.2.2.3, data were computed using a least square linear curve fitting.

According to Eqn.4.55, the molar transfer rate of toluene per unit interfacial area can be calculated as a function of the slope $\frac{dC_{TSA}}{dt}$, i.e.

$$N_T = \frac{1}{M_{TSA}} \frac{V_2}{S} \frac{dC_{TSA}}{dt} \qquad (6.10)$$

Assuming that the mean value of V_2 is 290 cm³, it follows that

$$N_T = 0.5634\ 10^{-4} \frac{dC_{TSA}}{dt} \qquad (6.11)$$

if N_T is expressed in gmol/cm² s, C_{TSA} in g/l and t in s.

Further, according to Chapter 4, the individual mass transfer coefficient based on phase 2 is given by:

$$K_2 = \frac{N_T}{C^*_{T2}} \qquad (6.12)$$

This equation combined with Eqn.6.11makes it possible to calculate K_2 in a very simple manner.

During the work on the system toluene/sulphuric acid solution, yellow coloration of the acid phase was observed when using concentrations equal to or higher than 84%-wt H_2SO_4. This phenomenon was already reported by GILES (1970) in his studies on heterogeneous nitration of toluene. He attributed the coloration to formation of impurities and by-products.

It is clear that spectroscopic analysis of the samples taken in the aqueous phase will be perturbed by such impurities or by-products. Consequently no experiment was carried out beyond 84% acid strength.

6.2.2.2 Results

Typical experimental concentration—time profiles for the system toluene/H_2SO_4 solution are shown in Figs.6.7a, b and c for different stirring speeds and sulphuric acid strengths. For the sake of clarity the experimental points have been omitted but the results are listed in Appendix A4, Table 3.

Data are quite well fitted by a straight line within the experimental error. The curves can be divided into two parts

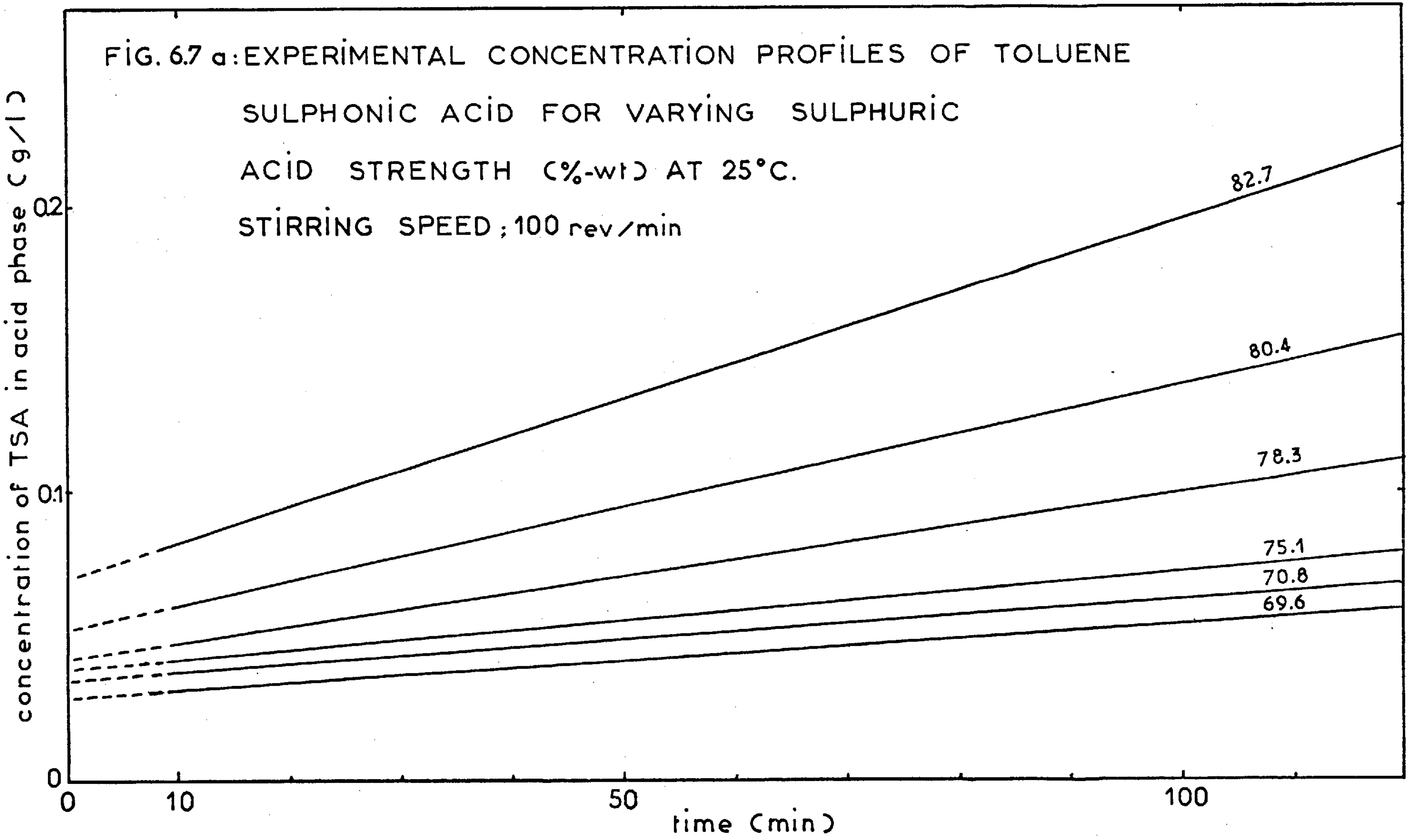


FIG. 6.7 a: EXPERIMENTAL CONCENTRATION PROFILES OF TOLUENE SULPHONIC ACID FOR VARYING SULPHURIC ACID STRENGTH (%-wt) AT 25°C.

STIRRING SPEED ; 100 rev/min

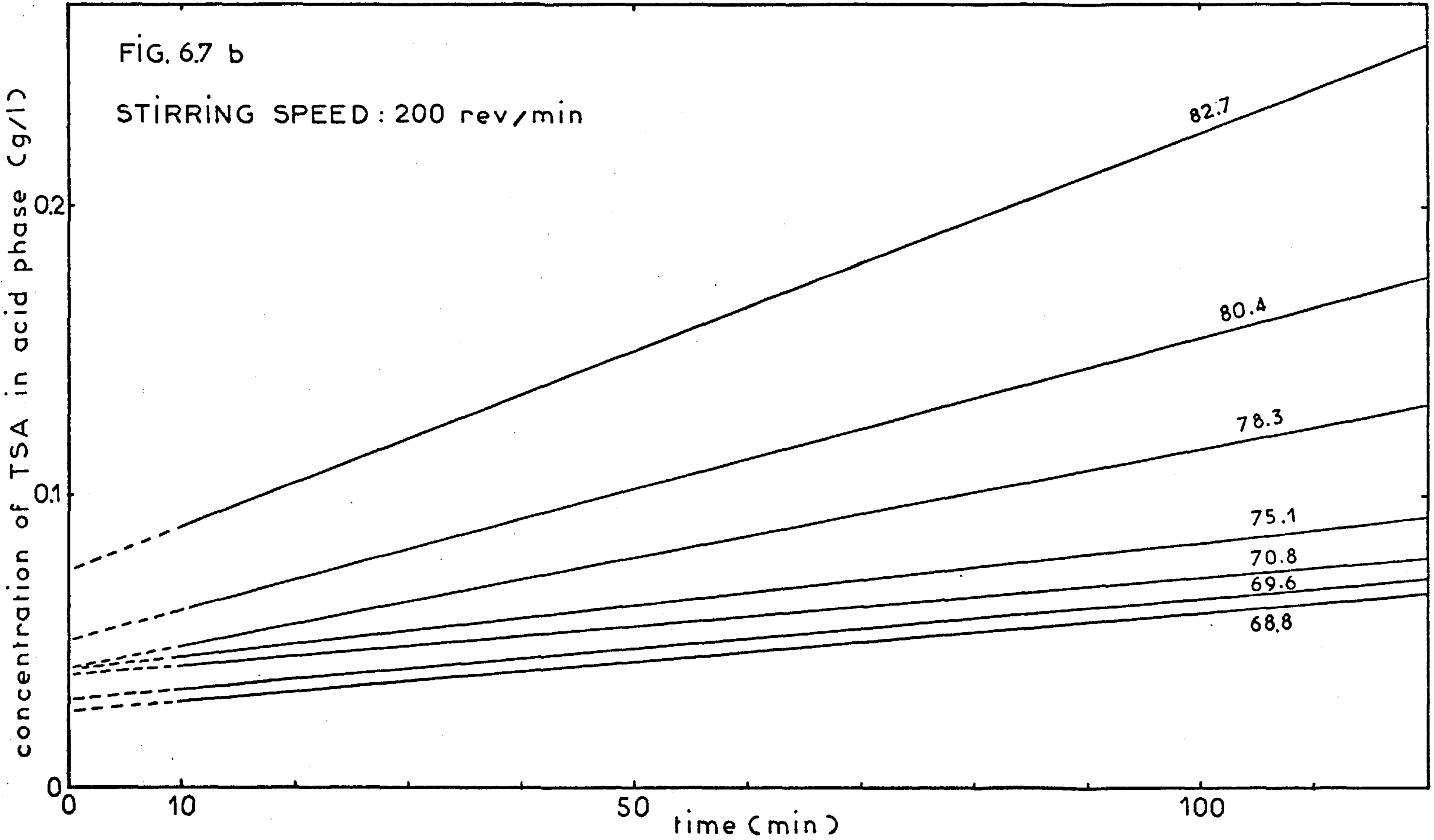
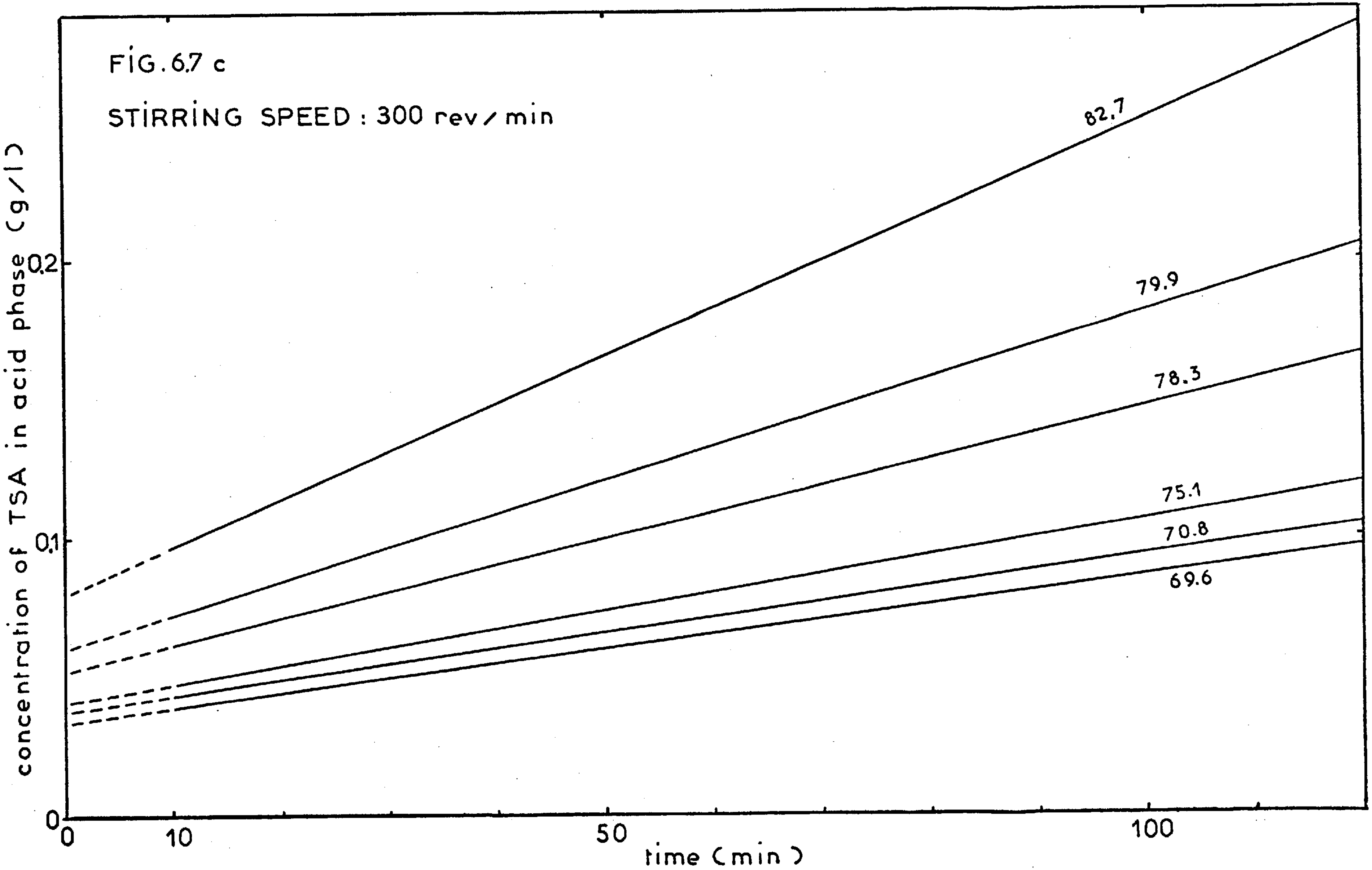


FIG. 6.7 b

STIRRING SPEED: 200 rev/min

FIG. 6.7 c

STIRRING SPEED : 300 rev / min



- a straight line beyond 10 minutes which permits to calculate N_T and then K_2
- a section under 10 minutes.

The latter is not represented in the figure because no experimental points were available for this period. Some measurements have however been carried out, but no plausible results were obtained.

Contrary to what was predicted by Eqn.4.57, the straight lines do not pass through the origin. With the present type of stirred cell it is impossible to prevent the upper region of phase 2 from being mixed with the toluene when the latter is poured even carefully at the beginning of the experiment. It follows that during a very short time there is a heterogeneous stirred region instead of a plane interface dividing the two homogeneous liquids. The mass transfer conditions are thus completely changed and both mass transfer and reaction rates are multiplied by a large factor depending on the interfacial area, the degree of mixing and the sulphuric acid strength. It can be easily understood that during this short time of unsteady state no precise calculation can be done.

The interfacial equilibrium is reached instantaneously as soon as the separation of the two immiscible phases is effected and the uniform mass transfer process can start as is described in the theoretical model.

No effect on the measurements and thus on the mass transfer rates was observed with TSA already present in phase 2 at $t = 0$, apart from improvements in the accuracy of the UV determinations.

The variation of the experimental values of mass transfer coefficients with sulphuric acid strength is shown in Fig.6.8 for the three studied speeds. Results are tabulated in Appendix A4, Table 6. The broken lines represent the predicted values obtained in Section 5.2.4 and tabulated in Table 5.4.

It can be seen that the curves consisted of two parts:
(a) the section under about 74.5%-wt H_2SO_4 representing the bulk reaction or the slow reaction diffusional regime. It is at 300 rev/min that the agreement with calculated values of mass transfer coefficient, K_2^o, is best (2%). For 100 and 200 rev/min the experimental values are greater than those obtained with Davies' correlation, the ratio being respectively 1.96 and 1.17. The latter value is well within the error generally acceptable for correlations of mass transfer coefficients. The magnitude of the former is perhaps not surprising, as at 100 rev/min the physical conditions at the interface are not really well described by Davies' assumptions;
(b) the section above 74.5% should be a continuation of the former according to Chapter 4 but shows an increase which disagrees with predicted values. The increase due to the transition of the slow reaction diffusional regime to the fast reaction regime should take place for values greater than 82%-wt H_2SO_4 (see β in Appendix A4, Table 5). The only explanation of this phenomenon is that, in addition to the mass transfer process, a chemical reaction occurs at the interface. This interfacial chemical reaction depends mainly on the sulphuric acid strength and must be independent of the stirring speed. It was certainly already present in the concentration range previously described,

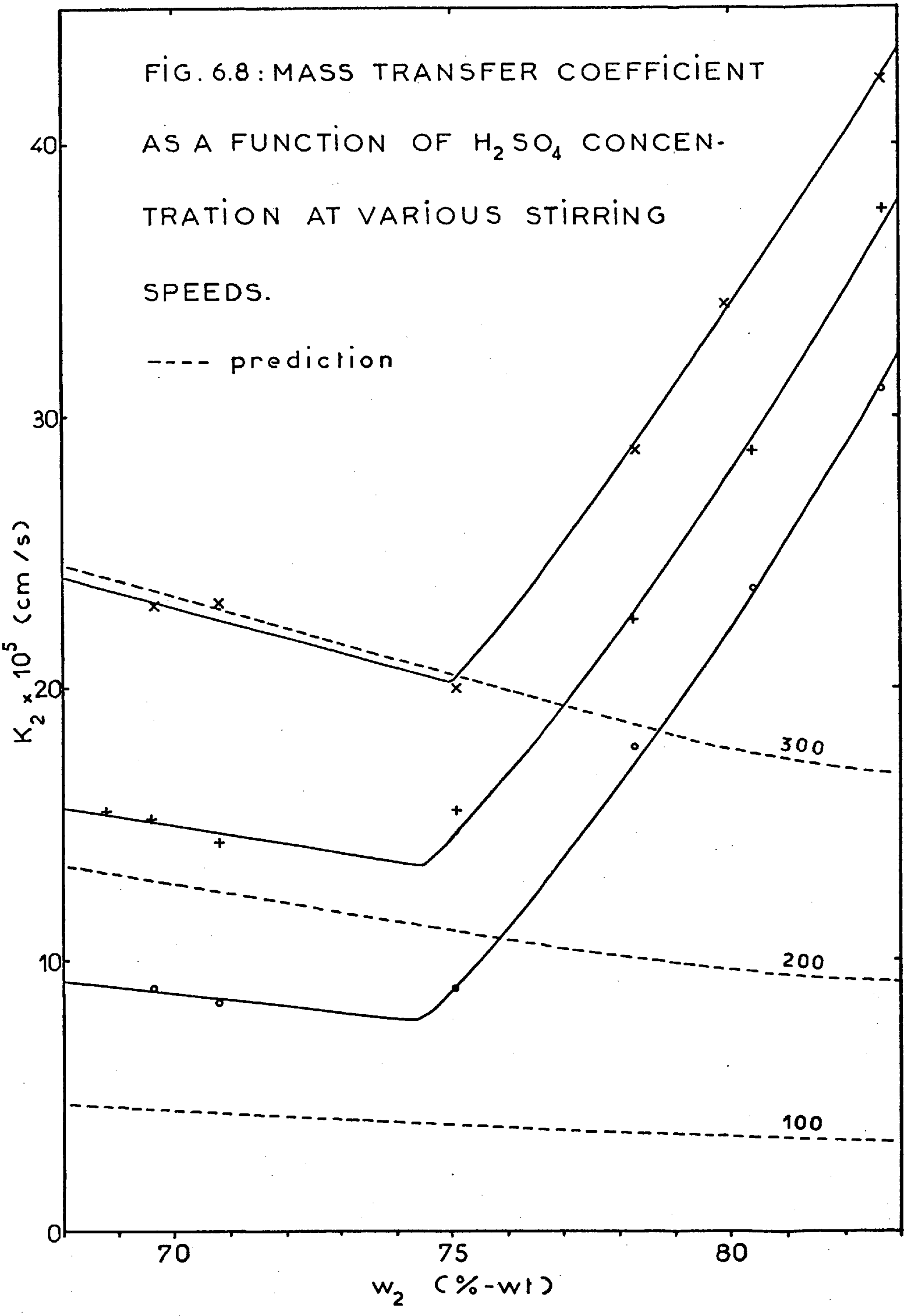


FIG. 6.8: MASS TRANSFER COEFFICIENT AS A FUNCTION OF H_2SO_4 CONCENTRATION AT VARIOUS STIRRING SPEEDS.

but its effect was negligible as its rate was very small with respect to the mass transfer rate.

Since a phenomenon other than mass transfer takes place at the interface, it appears that the mass transfer coefficient K_2, as previously defined, cannot be reliable any longer. Consequently, the choice of N_T as a parameter is more satisfactory.

Experimental values of N_T are plotted in Fig.6.9 and tabulated in Appendix A4, Table 6.

6.2.2.3 Interfacial chemical reaction

Equations

An expression giving the rate of generation of TSA or of consumption of toluene has been derived in Section 4.2.2.3 without taking into account the possibility of an interfacial chemical reaction. It was assumed that if the concentration of toluene in the bulk is taken as zero, toluene molecules penetrate and then react in phase 2 to give TSA. molecules in a stoichiometric ratio of 1:1.

If an interfacial chemical reaction interferes with this process, it is necessary to add a term giving the amount of toluene consumed (or of TSA generated) at the interface on the assumption that TSA molecules will leave the interface instantaneously without affecting the equilibrium and the transfer process of toluene. It has been seen elsewhere that the range of sulphuric acid concentrations studied located the process in the slow reaction diffusional regime and hence the molar flux of toluene due to the transfer process was put equal to $K_2^o C^*_{T2}$. In such circumstances the total flux of toluene consumed (or of TSA generated) will be

$$N_T = K_2^o\, C^*_{T2} + R_{Ti} \qquad (6.13)$$

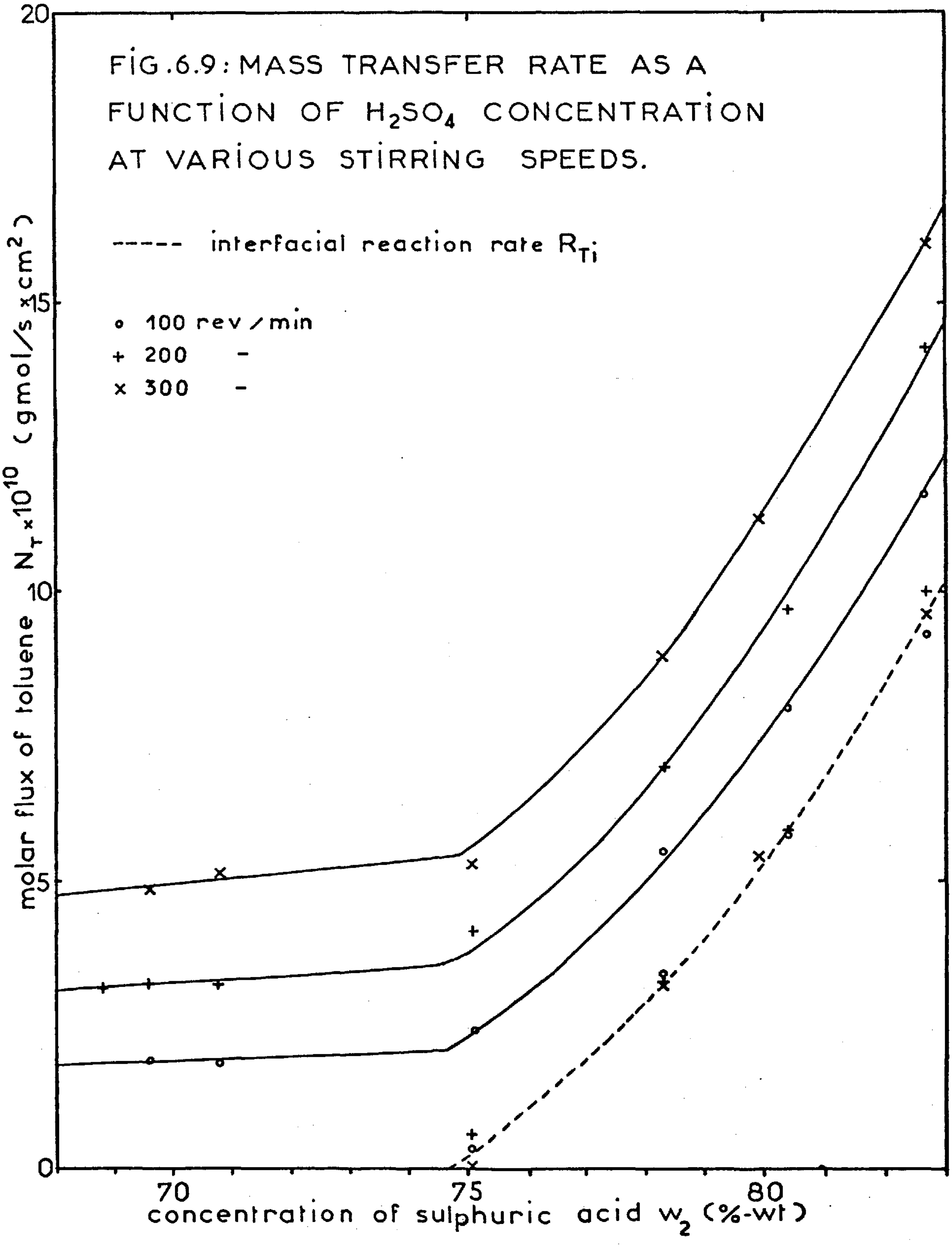


FIG.6.9: MASS TRANSFER RATE AS A FUNCTION OF H_2SO_4 CONCENTRATION AT VARIOUS STIRRING SPEEDS.

where R_{Ti} is the interfacial chemical reaction rate per unit area.

It thus follows for the enhancement factor that

$$E = 1 + \frac{R_{Ti}}{K_2^o \, C_{T2}^*} \qquad (6.14)$$

The interfacial reaction rate R_{Ti} can easily be calculated using Eqn.6.13. N_T is known experimentally whilst $K_2^o C_{T2}^*$ will be calculated by multiplying the predicted mass transfer coefficients derived from Davies' correlation by the factors already mentioned under (a). These were respectively 1.96, 1.17 and 0.98 for 100, 200 and 300 rev/min.

The variation of the values of R_{Ti} with respect to w_2 is represented by the broken line on Fig.6.9 and the calculations tabulated in Appendix A4, Table 6.

Interfacial excess

ADAMSON (1967) showed the tendency of solutes to form a thin and in most cases monomolecular film at the surface of the solution when surface tension tends to decrease with increasing solute concentration. The equilibrium is reached when the "energy" of the surface is at its lowest possible value. The thermodynamic treatment of this problem is due to Gibbs and is reported by Adamson for the gas-liquid surface.

At this stage it is necessary to develop Gibbs' analysis on the assumption that the thermodynamics of liquid-liquid systems are in principle the same as those of gas-liquid systems.

If two liquids in equilibrium are considered, there is no sharp transition from one to the other at the interface, but there exists a region over which the concentrations vary and over which molecules of the two liquids are intimately mixed.

The thickness of this region can be between about 1nm and 10nm. It is in this film that the previously called interfacial reaction will occur because of the contact of the relatively large number of molecules of both toluene and sulphuric acid present in such an interfacial film.

The amount of any component i present in this region per unit area, i.e. the surface concentration, will be

$$n_i^s = n_i + \Gamma_i \tag{6.15}$$

where Γ_i denotes the interfacial excess per unit area and n_i the normal interfacial distribution per unit area contributed by the bulk concentration. As phase 1 is a pure liquid it follows that

$$n_T^s = n_T \tag{6.16}$$

For phase 2, there can exist an excess of sulphuric acid and hence:

$$n_2^s = n_2 + \Gamma_2 \tag{6.17}$$

A general thermodynamic treatment leads to the Gibbs equation which, if the temperature and the interfacial area are constant and if no change in the mass of the interfacial region occurs, can be written as

$$d\sigma = - \sum_i \Gamma_i \, d\mu_i \tag{6.18}$$

where μ_i is the chemical potential of component i whilst σ is the interfacial tension.

Neglecting the TSA effect and considering that no toluene excess is present, Eqn.6.18 reduces to:

$$d\sigma = -\Gamma_w \, d\mu_w - \Gamma_2 \, d\mu_2 \tag{6.19}$$

By the use of the Gibbs-Duhem equation:

$$x_w d\mu_w + x_2 \, d\mu_2 = 0 \tag{6.20}$$

$d\mu_2$ can be eliminated and one obtains:

$$- d\sigma = d\mu_2 \, [\Gamma_2 - \frac{x_2}{x_w} \Gamma_w] \qquad (6.21)$$

It was shown above that the contact region between phases 1 and 2 is not sharply defined. Consequently it is convenient to invent a mathematical dividing interface. Γ_w and Γ_2 will obviously depend on that choice and so will the term into square brackets of Eqn.6.21.

It was decided to choose the location of the dividing interface so that the gravitational stability does not change because of the presence of interfacial excesses. This can be represented by the following relationship:

$$M_w \Gamma_w + M_2 \Gamma_2 = 0 \qquad (6.22)$$

where M_i is the molecular weight of component i. Γ_2 can thus be regarded as the excess of sulphuric acid in the interfacial region over the moles that would be present in a bulk region of the same total mass as the interfacial region.

Eqns.6.21 and 6.22 may be combined to give:

$$- \frac{d\sigma}{d\mu_2} = \Gamma_2 \left(1 + \frac{x_2 M_2}{x_w M_w}\right) \qquad (6.23)$$

or

$$- \frac{d\sigma}{d\mu_2} = \frac{\Gamma_2}{w_w} \qquad (6.24)$$

Otherwise if the chemical potential μ_2 is expressed as usual by:

$$\mu_2 = \mu_2^o + RT \ln \gamma_2 x_2$$

where μ_2^o is a constant, γ_2 the activity coefficient and x_2 the mole fraction, it follows:

$$- \frac{d\sigma}{dx_2} = \Gamma_2 \frac{RT}{w_w} \left(\frac{1}{x_2} + \frac{d \ln \gamma_2}{dx_2}\right) \qquad (6.25)$$

or, using mass fraction w_2,

$$-\frac{d\sigma}{dw_2} = \Gamma_2 \frac{RT}{w_w}\left(\frac{1}{w_2[1 - w_2(1 - \frac{M_w}{M_2})]} + 2.3\frac{d \log \gamma_2}{dw_2}\right) \tag{6.26}$$

This equation allows to calculate the variation of Γ_2 with w_2 on the assumption that the relation $\gamma_2 = f(w_2)$ is known.

The thermodynamic properties of aqueous sulphuric acid solutions have been studied at 25°C by GIAUQUE (1960). In activity coefficient γ_2 is given with respect to the molality in sulphuric acid and its value is equal to $\gamma_2 = 0.130$ for a molality equal to 1. Anyway the absolute value of γ_2 does not matter since only its relative value is of interest to the present work.

The various calculations are tabulated in Appendix A4, Table 4 and the results are shown in Fig.6.10.

Otherwise the quantities n_T and n_2 have been calculated on the assumption that a molecule of the liquid occupies a cubic volume a^3 defined as $a^3 = \frac{M}{\mathcal{N} V}$ where $\mathcal{N}$ is the Avogadro Number.

In this case the number of molecules present per unit interfacial area will be $\frac{1}{a^2}$, that is $\left(\frac{\mathcal{N} V}{M}\right)^{2/3}$. It follows that for toluene:

$$n_T = \frac{1}{\mathcal{N}}\left(\frac{\rho_T \mathcal{N}}{M_T}\right)^{2/3} = 5.26\ 10^{-10}\ \text{gmol/cm}^2 \text{ and}$$

and for pure sulphuric acid:

$$n_{SA} = 8.33\ 10^{-10}\ \text{gmol/cm}^2$$

Furthermore, it is assumed that the distribution of molecules in the three-dimensional space remains the same in the

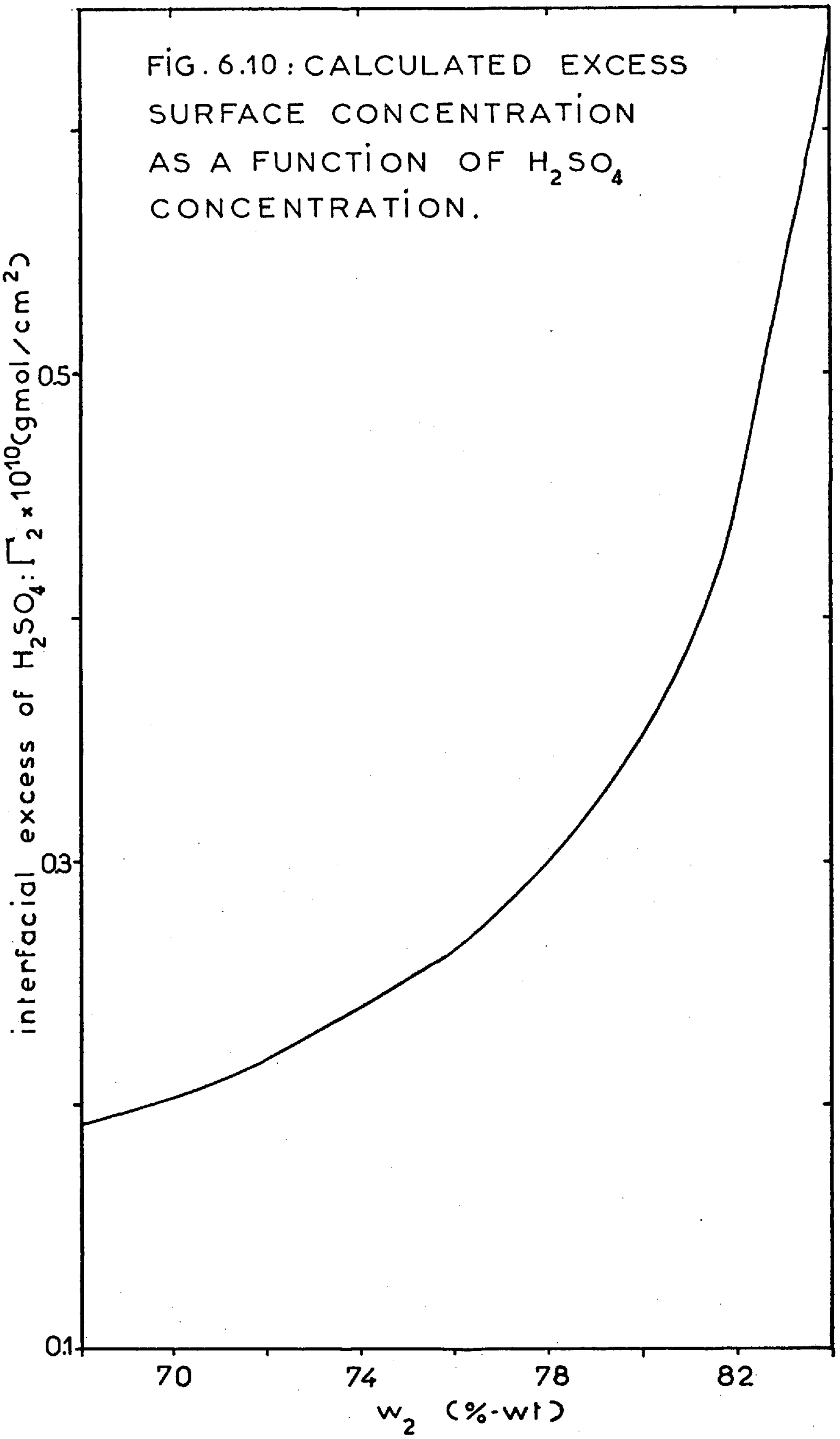


FIG. 6.10: CALCULATED EXCESS SURFACE CONCENTRATION AS A FUNCTION OF H_2SO_4 CONCENTRATION.

two-dimensional scale. Hence the number of H_2SO_4 molecules per unit interfacial area can be written as

$$n_2 = x_2 \, n_{SA} \tag{6.27}$$

where x_2 is the mole fraction of H_2SO_4 in phase 2. Calculations tabulated in Appendix A4, Table 6 show that the value of Γ_2 is around 10% of the theoretical number of molecules H_2SO_4 already present at the interface.

Reaction rate

The interfacial reaction due to the high strength of the H_2SO_4 solution at the interface will follow reaction kinetics which cannot be the same as those previously defined.

The stoichiometric ratio of the toluene sulphonation suggests a second-order reaction rate such as:

$$R_{Ti} = k_2^s \, n_T^s \, n_2^s \tag{6.28}$$

where n_T^s and n_2^s are respectively the amount of moles of toluene and sulphuric acid per unit interfacial area in contact at the interface as was previously defined in Eqns.6.16 and 6.17.

In order to verify all assumptions already made R_{Ti} obtained from Eqn.6.13 was plotted against n_2^s (Fig.6.11).

It can be noted that the results are in good agreement with Eqn.6.28 whatever the stirring speed. The value of the slope is approximately 8 s^{-1} and that of the rate constant k_2^s is 1.52 x 10^{10} cm²/s gmol. The latter is strictly speaking a two-dimensional rate constant and hence cannot be compared with volume-based rate constants.

6.2.2.4 Discussion

The classical theory of mass transfer with chemical reaction does not adequately describe all experimental results

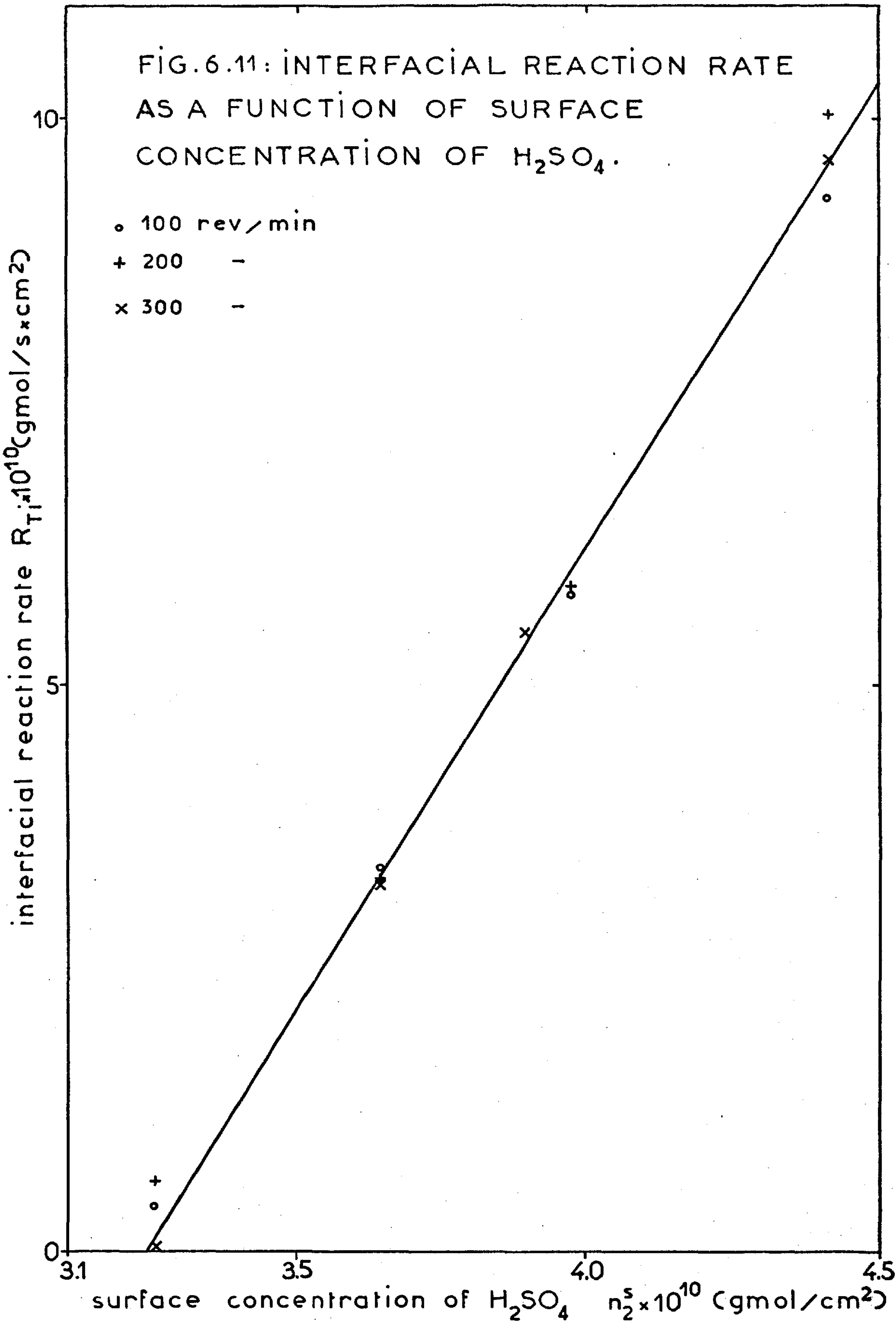


FIG. 6.11: INTERFACIAL REACTION RATE AS A FUNCTION OF SURFACE CONCENTRATION OF H_2SO_4.

over the studied range of H_2SO_4 concentrations. Hence it has been necessary to emphasise the role played by the interfacial chemical reaction. The other contributions which could have intensified mass transfer such as Marangoni effect, increase of temperature due to the reaction, seemed to be negligible.

The calculations which are outlined in the above section present a simplified attempt at evaluating the number of molecules involved in the interfacial reaction. In spite of that, good agreement is reached and this confirms the model and the various assumptions previously presented. If a factor for variations in packing is to be introduced in order to estimate more correctly n_T^s and n_2^s, the straight line obtained in Fig. 6.11 will only be shifted.

Returning to the discussion on the existence of an interfacial reaction, it can be pointed out that a single Hatta number cannot by itself explain the experimentally observed increase in the curve N_T versus w_2. If it is assumed that this increase is only due to the transition from the slow reaction diffusional regime to the fast reaction regime in absence of any other phenomenon, it is necessary to multiply β by 20, i.e. to divide K_2^o by $\frac{1}{20}$ or to multiply k_1 or D_{T2} by 400. Thus it can be seen that neither interfacial instabilities which will, on the contrary, increase K_2^o, nor an error in D_{T2} can explain the shift of the curve. On the other hand the logarithmic variation of the rate constant k_1 suggests a kinetic explanation of this phenomenon.

Besides the similar shapes of the curves after 74% on Fig.6.8 and the fact that R_{Ti} is independent of stirring speed, as can be seen on Fig.6.11, suggest that the behaviour of molecules involved in the reaction at the interface is not affected by surface renewal. This is not surprising as according to the Gibbs definition of the interface it is a mathematical region whose total thickness is no more than 10 nm and in which toluene, sulphuric acid and water molecules are in close contact. It is clear that if this region is kept hydrodynamically stable, it will not be disturbed by eddies coming from the bulk. The properties of the interface are thus unchanged whatever the stirring speeds as well as the interfacial reaction rate.

On the other hand the interface is deeply disturbed when phase 1 is poured at time equal to zero and relatively large quantities of TSA is produced. That quantity depends on the manner of introducing the organic liquid into the cell.

Finally, similarly to the neutralisation reaction and for the same reasons, the temperature increase due to the reaction at or near the interface was considered low enough to be neglected.

CHAPTER 7

GENERAL CONCLUSIONS

The main conclusions of the present work can be summarised as follows.

7.1 Theoretical Results

(i) Theoretical models based on Hatta's treatment were derived for the case of mass transfer in a stirred cell accompanied by instantaneous and first-order reactions and the appropriate enhancement factors determined.

(ii) The relevant equations indicate the importance of accurate determination of the diffusion and partition coefficients for the instantaneous reaction and of the rate constant, the individual mass transfer coefficient, the solubility and diffusion coefficient of the solute for the first-order reaction. With the accuracy of measurements of bulk concentrations being satisfactory, the correct value of the enhancement factor will strongly depend on satisfactory knowledge of the relevant parameters.

7.2 Mass Transfer Without Chemical Reaction

(iii) During transfer of propionic acid from toluene to water and vice versa interfacial instabilities of varying degree were observed. An explanation was suggested in terms of gravitational and Marangoni instabilities.

(iv) The overall mass transfer coefficients were experimentally determined in the absence of instabilities and compared with the predicted values obtained from individual mass transfer coefficients calculated by Davies' correlation. The agreement was found to be satisfactory. The estimated individual mass transfer coefficients applicable to the case of sulphonation were consequently derived using this correlation.

(v) The direction of stirring was found to have a very slight influence on the transfer process. Contra-rotating stirrers were used throughout the present work.

(vi) For the case of physical mass transfer, because of the impossibility of determining experimentally one of the individual mass transfer coefficients, no conclusions could have been drawn concerning the presence of an interfacial resistance or the value of the individual mass transfer coefficients when enhanced by instabilities.

7.3 Mass Transfer with Chemical Reaction

(vii) Experiments with system toluene/water + HPr + NaOH showed that the model developed in the present work was applicable and that the enhancement factor could be estimated from it within limits of an acceptable error.

(viii) The mathematical treatment must take into account the two different cases which exist according to the relative values of concentrations of reactants. In one case the reaction occurs at the interface and in the other in the film near the interface.

(ix) The influence of the salt as reaction product on interfacial equilibrium was studied and the relevant corrections introduced when necessary.

(x) Ionic diffusion was taken into account for the case of a non-renewable interface (transfer across a laminar sublayer) but molecular diffusion was assumed to describe the transfer satisfactorily in the surface renewal regime.

(xi) Individual mass transfer coefficients were experimentally obtained and the relevant enhancement factors derived. It was thus possible to observe quantitatively the influence of agitation on gravitational instabilities.

(xii) The calculations have indicated the presence of an interfacial resistance. This resistance was undetectable when pure mass transfer took place, i.e. when no salt was present, because it represented only a few percent of the overall resistance. As shown by experiments performed without chemical reaction but with a salt solution as phase 2, the interfacial resistance seems to be affected by the presence of the salt.

(xiii) The sulphonation of toluene was studied for sulphuric acid concentration in the range 68-84%-wt. It was expected to follow the pattern of mass transfer with slow chemical reaction, i.e. practically pure diffusion across the film followed by reaction in the bulk. The model so developed was shown to be consistent with experiments up to a certain sulphuric acid concentration.

(xiv) The sharp increase of the consumption of toluene beyond this value was attibuted to an interfacial reaction due to an increase of the interfacial concentration of sulphuric acid and thus to an important change in the value of the kinetics term. A rough estimation of the reaction rate using Gibbs' adsorption law was worked out in order to verify this assumption.

(xv) The two studies have emphasised the important part played by the interface and the interfacial phenomena. The above results have shown, for instance, that two opposing effects may occur in the interfacial region: namely, a retardation of transfer due to an interfacial resistance and an acceleration due to an interfacial reaction or to interfacial turbulence. It is possible that, in some other cases, the two effects more or less cancel out. It appears consequently that, in order to predict with accuracy the extraction rate when a chemical reaction occurs, it is necessary to verify if such interfacial phenomena exist. To achieve this, the stirred cell seems to be the most suitable apparatus.

7.4 Suggestions for Future Work

The presence of the salt appears to play an important part in the transfer process. Its role, particularly at the interface, should be investigated in greater detail. It is, for instance, possible that toluene sulphonic acid influences the solubility of aromatics in a similar way as sodium propionate affected the partition of propionic acid between the two phases. Although, in the present work, the solubility of toluene was assumed constant, this should be more closely verified.

The assumption concerning the occurrence of a chemical reaction at the interface in the case of sulphonation could easily be checked by using variable interfacial area. For this purpose the stirred cell would have to be appropriately modified.

APPENDIX A1

THE ION FLUX EQUATION

Consider diffusion in medium containing a dilute solution. The concentration of the dissociated electrolyte is C (g equiv/cm^3). In the diffusion process let C + dC be the concentration at a distance dx from the plane containing solution of concentration C.

Also let u_+ and u_- be the mobilities of the cation and anion respectively. The rate of migration of ions per unit cross-sectional area (the ion flux) for the two ions of valence y_+ and y_- are:

$$N_+ = - D_+ \frac{dC_+}{dx} \qquad (A1.1)$$

and

$$N_- = - D_- \frac{dC_-}{dx} \qquad (A1.2)$$

with

$$D_\pm = \frac{RTu_\pm}{Y_\pm F} \qquad (A1.3)$$

The electrostatic forces that come into play as a result of such a gradient will be a function of the electric field strength: $-\frac{d\psi}{dx}$ and $+\frac{d\psi}{dx}$ (V/cm) for cation and anion respectively. The rates of migration of ions through the cross section as a result of these forces of attraction and repulsion are:

$$N_+ = - u_+ C_+ \frac{d\psi}{dx} \qquad (A1.4)$$

and

$$N_- = + u_- C_- \frac{d\psi}{dx} \qquad (A1.5)$$

The rates of diffusion for the two ions under the combined influence of the concentration and of the electrostatic potentials can be written as follows:

for cation $$N_+ = - D_+ \frac{dC_+}{dx} - C_+ u_+ \frac{d\psi}{dx} \qquad (A1.6)$$

and for anion $$N_- = - D_- \frac{dC_-}{dx} + C_- u_- \frac{d\psi}{dx} \qquad (A1.7)$$

Equations A1.6 and A1.7 are similar to the diffusion law for ions in dilute solution given by the Nernst-Planck equation.

Consider macroscopically immobile solutions in which there is no electrolytic current. The electric current density resulting from the mass flux must thus be equal to zero:

$$F \sum_i N_i = 0 \tag{A1.8}$$

thus:

$$\sum_{i+} N_{i+} - \sum_{i-} N_{i-} = 0 \tag{A1.9}$$

$\frac{d\psi}{dx}$ can be eliminated by subtracting the sum of equation A1.7 for all anions from the corresponding sum of equation A1.6 for all cations and the following expression is obtained:

$$\frac{d\psi}{dx} = \frac{RT}{F} \alpha \tag{A1.10}$$

where

$$\alpha = \frac{\Sigma\, u_+ G_+ / y_+ - \Sigma\, u_- G_- / y_-}{\Sigma\, u_+ C_+ + \Sigma\, u_- C_-} \tag{A1.11}$$

G_+ and G_- are the concentration gradients $\frac{dC_+}{dx}$ and $\frac{dC_-}{dx}$ in the direction of diffusion.

On substitution into equations A1.6 and A1.7:

$$N_+ = -\frac{RT}{F} \frac{u_+}{y_+} \left(G_+ - y_+ C_+ \alpha \right) \tag{A1.12}$$

and

$$N_- = -\frac{RT}{F} \frac{u_-}{y_-} \left(G_- + y_- C_- \alpha \right) \tag{A1.13}$$

APPENDIX A2

THE APPARENT DIFFUSION COEFFICIENT

According to SHERWOOD and WEI (1955), there is no net diffusion of Na^+ in the region of thickness $x_2 - x_R$ near the interface (Fig.5.1). The Na^+ flux is set equal to zero:

$$N_+ = -\frac{RT\,u_+}{F}\,(G_+ - C_+\,\alpha) = 0 \qquad (A2.1)$$

with

$$\alpha = \frac{u_+G_+ - u_-G_- - u'_-G'_-}{u_+C_+ + u_-C_- + u'_-C'_-} \qquad (A2.2)$$

where the subscripts refer to the anion and cation of the salt, and the prime to OH^-.

The condition of electrical neutrality requires the C_+ to be equal to the sum of C_- and C'_-:

$$C_+ = C_- + C'_- \qquad (A2.3)$$

and thus

$$G_+ = G_- + G'_- \qquad (A2.4)$$

Using the above relations, C_- and G_- in equation A2.1 can be obtained and the following expression obtained:

$$C_+G'_- + G_+C'_- = \frac{2\,u_-}{u_- - u'_-}\,G_+C_+ \qquad (A2.5)$$

which becomes:

$$\frac{u_-}{u_- - u'_-}\,d(C_+^2) = d(C_+C'_-) \qquad (A2.6)$$

This is integrated and gives:

$$C_+\sqrt{1 + \left(\frac{u'_-}{u_-} - 1\right)\frac{C'_-}{C_+}} = K \qquad (A2.7)$$

The constant K is evaluated in terms of the concentrations at the two boundaries using the model shown in Fig.5.1. This leads to the following equation:

$$\sqrt{1 + \left(\frac{u'_-}{u_-} - 1\right)\frac{q}{n}} = \frac{v}{n} \qquad (A2.8)$$

The equation for N'_-, similar to equation A2.1, is written as follows:

$$N'_- = - \frac{RT\, u'_-}{F} \, (G'_- + C'_- \, \alpha) \qquad \text{(A2.9)}$$

From relation A2.1, it also follows that:

$$\alpha = \frac{G_+}{C_+} \qquad \text{(A2.10)}$$

Substituting the above into equation A2.9 and then relation A2.5 into the equation obtained:

$$N'_- = \frac{2\, D'_-}{\frac{u'_-}{u_-} - 1} \; \frac{dC_+}{dx} \qquad \text{(A2.11)}$$

with

$$D'_- = \frac{RT\, u'_-}{F}$$

From equation A2.8, it follows that:

$$\frac{u'_-}{u_-} - 1 = \frac{v^2 - n^2}{n\,.q}$$

Hence

$$N'_- = \frac{2\, n\, q}{v^2 - n^2} \; \frac{dC_+}{dx} \qquad \text{(A2.12)}$$

Integration and substitution of limits leads to the equation:

$$N'_- = - \frac{2\, n\, q\, D'_-}{(v + n)(x_2 - x_R)} \qquad \text{(A2.13)}$$

On introducing D'_{app}, the apparent diffusion coefficient of anion OH^- in presence of other ions, and taking into account that N'_- has an algebraic value, it can be written:

$$N'_- = \frac{D'_{app}\; q}{x_2 - x_R} \qquad \text{(A2.14)}$$

Combining equations A2.8, A2.13 and A2.14, it follows that:

$$D'_{app} = 2\, D'_- \left(1 + \sqrt{1 + \left(\frac{u'_-}{u_-} - 1\right) \frac{q}{n}}\right)^{-1} \qquad \text{(A2.15)}$$

APPENDIX A3

EXPERIMENTAL RESULTS. CHAPTERS 3 and 5

TABLE 1

Experimental Equilibrium Values (25°C)

System tol/wat + HPr			
Kolossowski and Megenine (Seidell.1941)		Present work	
C_W^*	C_T^*	C_W^*	C_T^*
.2508	.04918	.30	.070
.528	.172	.75	.305
.8396	.3604	1.23	.679
1.2701	.7299	1.50	.948
1.6664	1.1326		
System tol/wat + HPr + NaPr			
NaPr M/2		NaPr M	
.370	.120	.43	.185
.755	.380	.78	.488
.88	.476	.92	.640
1.08	.675	.94	.665
1.34	.961	1.27	1.10

Note: All concentrations are in gmol/l.

TABLE 2

TRANSFER OF PROPIONIC ACID BETWEEN TOLUENE AND WATER AT 25°C

Toluene $\xrightarrow{HPr}$ Water			Toluene $\xleftarrow{HPr}$ Water		
N(rev/min) C_T^i(gmol/l)	K^o_{01} x 1000 (cm/s)	$C_1-C_1^*$ (gmol/l)	N(rev/min) C_W^i(gmol/l)	K^o_{01} x 1000 (cm/s)	$C_1^*-C_1$ (gmol/l)
Run 1	2.19	1.01	Run 7	1.03	0.78
	1.97	0.99		0.78	0.77
100	1.68	0.96	100	0.57	0.75
	1.38	0.91		0.44	0.73
→	0.75	0.85	→	0.40	0.69
←	0.49	0.81	←	0.38	0.66
	0.30	0.79		0.32	0.64
1.01	0.28	0.77	1.31	0.28	0.62
	0.31	0.76		0.28	0.59
	0.29	0.74		0.25	0.57
	0.30	0.72		0.25	0.55
	0.30	0.70		0.22	0.53
	0.30	0.68		0.21	0.52
Run2	2.56	1.02	Run 8	1.40	0.56
	2.20	0.99		1.17	0.54
200	1.75	0.96	200	0.96	0.52
	1.28	0.91		0.81	0.50
→	0.96	0.84	→	0.77	0.46
←	0.83	0.79	←	0.73	0.42
	0.79	0.74		0.72	0.39
1.02	0.79	0.70	1.08	0.69	0.36
	0.81	0.65		0.65	0.34
	0.78	0.61		0.63	0.31
	0.81	0.57		0.60	0.29
	0.80	0.53		0.57	0.27
	0.79	0.50		0.57	0.26
Run 3	3.74	1.09	Run 9	2.30	0.53
	2.67	1.05		1.98	0.50
300	1.92	1.01	300	1.61	0.47
	1.63	0.95		1.19	0.44
→	1.30	0.85	→	1.08	0.39
←	1.19	0.76	←	1.05	0.35
	1.17	0.69		1.02	0.31
1.09	1.13	0.63	1.05	0.94	0.28
	1.15	0.58		0.94	0.26
	1.15	0.52		0.92	0.24
	1.15	0.47		0.88	0.21
	1.12	0.42		0.86	0.20
	1.18	0.39		0.85	0.18

TABLE 2 (cont.)

Run 4	2.37	0.99	Run 10	1.04	0.79
	2.14	0.96		0.86	0.77
100	1.65	0.92	100	0.71	0.75
	0.99	0.89		0.60	0.73
→	0.60	0.84	→	0.50	0.68
→	0.45	0.81	→	0.41	0.64
	0.28	0.79		0.40	0.61
0.99	0.28	0.78	1.33	0.38	0.58
	0.28	0.76		0.34	0.56
	0.29	0.75		0.30	0.53
	0.28	0.73		0.30	0.51
	0.30	0.71		0.27	0.49
	0.29	0.70		0.25	0.48
Run 5	2.93	0.96	Run 11	1.27	0.56
	2.22	0.93		1.01	0.55
200	1.61	0.89	200	0.91	0.53
	1.20	0.85		0.90	0.51
→	0.92	0.79	→	0.86	0.46
→	0.83	0.74	→	0.81	0.42
	0.79	0.70		0.76	0.38
0.96	0.80	0.65	1.09	0.74	0.35
	0.78	0.61		0.71	0.33
	0.77	0.57		0.67	0.30
	0.79	0.54		0.65	0.28
	0.79	0.50		0.64	0.26
	0.79	0.47		0.62	0.25
Run 6	4.50	1.08	Run 12	2.54	0.72
	3.21	1.03		2.30	0.65
300	2.19	0.98	300	1.94	0.61
	1.68	0.92		1.39	0.56
→	1.38	0.82	→	1.20	0.50
→	1.13	0.79	→	1.15	0.47
	1.15	0.67		1.07	0.41
1.08	1.14	0.61	1.25	1.04	0.37
	1.14	0.55		1.03	0.34
	1.14	0.50		0.95	0.30
	1.15	0.44		0.86	0.27
	1.17	0.40		0.85	0.24
	1.10	0.37		0.83	0.22

Note: Data represents, in the decreasing order, samples taken at 0, 2, 5, 10 min and then every 10 min.

TABLE 3

TRANSFER OF HPr FROM WATER TO TOLUENE WITH ADDITION OF TEEPOL AT 25°C

K^o_{o1} x 1000 (cm/sec)	0.60	0.59	0.57	0.54	0.47	0.41	0.35	0.30	0.26
$C^*_1-C_1$ (gmol/l)	0.83	0.82	0.81	0.78	0.74	0.70	0.67	0.64	0.62
K^o_{o1} x 1000 (cm/sec)	0.23	0.21	0.19	0.19	0.18	0.18	0.18	0.18	
$C^*_1-C_1$ (gmol/l)	0.60	0.59	0.58	0.56	0.55	0.54	0.53	0.52	

Run 13 - 100 rev/min - C^i_w = 1.38 gmol/l

K^o_{o1} x 1000 (cm/sec)	0.77 0.51	0.74 0.51	0.71 0.51	0.65 0.49	0.56	0.51	0.49	0.50	0.49
$C^*_1-C_1$ (gmol/l)	0.42 0.28	0.41 0.27	0.40 0.25	0.39 0.24	0.36	0.34	0.33	0.31	0.30

Run 14 - 200 rev/min - C^i_w = 0.92 gmol/l

K^o_{o1} x 1000 (cm/sec)	1.33 0.83	1.27 0.83	1.20 0.81	1.10	0.95	0.86	0.82	0.81	0.81
$C^*_1-C_1$ (gmol/l)	0.42 0.21	0.41 0.20	0.39 0.18	0.37	0.33	0.30	0.28	0.26	0.23

Run 15 - 300 rev/min - C^i_w = 0.92 gmol/l

APPENDIX A4

EXPERIMENTAL RESULTS. CHAPTER 6

TABLE 1: Print-outs of experiments with a neutralisation reaction.

System: toluene/water + HPr + NaOH.

Temperature: 25°C.

Contra-rotating stirrersat 100, 200, 300 rev/min.

Notation:

T = time (min)

CA = concentration of HPr in toluene (gmol/l)

CB = concentration of NaOH in water (gmol/l)

$(K^{o}_{1})_{c}$ = mass transfer coefficient in phase 1 taking into account the interfacial resistance and only valid in case I (cm/s)

$CAO-CA$ = salt concentration in water (gmol/l)

FLUX = experimental flux; also denoted later by N (10^{7} x gmol/cm^{2}s)

VT,VW = respectively volume of the toluene and aqueous phase (cm^{3})

$K^{o'}_{o1}$ = overall mass transfer coefficient calculated from Eqn.4.17 and only valid in case II (cm/s)

E = enhancement factor calculated from Eqn.4.18 and only valid in case II (-)

N/NO = experimental enhancement factor, E_{EXP}, obtained by using K^{o}_{o1} (or K_{STABLE}) of Table 5.5 (-)

X = interfacial resistance (10^{3}cm/s)

DB = diffusion coefficient of the reacting species present in phase 2 ($10^{5}cm^{2}/s$)

K^{o}_{2} = individual mass transfer coefficient in phase 2 and estimated from Table 6.1 (cm/s)

100 rev/min

```
**RUN 16**

  T     CA     CB 1000(K°1/c) CAO-CA  LOG(CAO-CA)  FLUX     VT       VW    1000K°'01   E   N/NO     X    DB   1000K°2

  0.   .915   .747     0        0    *            11.874 289.00 288.00    .517   2.51 4.33      I 3.16   .290
  2.   .902   .734  1.114     .013  -1.894        10.992 288.49 288.31    .484   2.52 4.06      I 3.17   .290
  5.   .884   .717  1.075     .031  -1.515         9.924 287.86 288.74    .444   2.53 3.74      I 3.20   .290
 10.   .858   .690  1.019     .057  -1.243         8.611 287.04 289.36    .395   2.54 3.35      I 3.23   .290
 20.   .812   .645   .935     .103   -.989         7.046 285.78 290.42    .338   2.57 2.89      I 3.29   .290
 30.   .774   .606   .877     .141   -.849         6.219 284.68 291.32    .310   2.59 2.68   5.01 3.35   .290
 40.   .738   .570   .838     .177   -.753         5.735 283.67 292.13    .298   2.61 2.59   3.43 3.40   .290
 50.   .705   .537   .812     .210   -.678         5.455 282.71 292.89    .295   2.62 2.58   3.29 3.46   .290
 60.   .673   .505   .795     .242   -.616         5.273 281.79 293.61    .297   2.64 2.61   3.62 3.51   .290
 70.   .641   .473   .785     .274   -.563         5.120 280.88 294.32    .301   2.65 2.66   4.30 3.57   .290
 80.   .611   .443   .779     .304   -.517         4.959 279.99 295.01    .305   2.66 2.71   5.23 3.63   .290
 90.   .581   .413   .775     .334   -.476         4.723 279.13 295.67    .305   2.67 2.71   5.32 3.69   .290
100.   .553   .385   .772     .362   -.441         4.410 278.31 296.29    .299   2.67 2.66   4.29 3.75   .290
110.   .527   .355   .766     .388   -.411         3,853 277.54 296.86    .274   2.67 2.44   2.37 3.81   .290
120.   .505   .337   .755     .410   -.387         3.956 276.85 297.35    .294   2.67 2.61   3.75 3.86   .290
```

```
**RUN 17**

  T     CA     CB 1000(K°1/c) CAO-CA  LOG(CAO-CA)  FLUX     VT       VW    1000K°'01   E   N/NO     X    DB   1000K°2

  0.   .960   .838     0        0    *            15.532 289.00 288.00    .619   2.61 5.39        3.16   .290
  2.   .943   .821  1.387     .017  -1.779        14.118 288.40 288.40    .570   2.63 4.99      I 3.18   .290
  5.   .921   .798  1.321     .039  -1.406        12.410 287.66 288.94    .510   2.64 4.49      I 3.20   .290
 10.   .888   .766  1.229     .072  -1.143        10.349 286.69 289.71    .437   2.67 3.88      I 3.24   .290
 20.   .835   .713  1.095     .125   -.903         8.030 285.26 290.94    .356   2.70 3.21      I 3.31   .290
 30.   .791   .669  1.008     .169   -.772         6.942 284.05 291.95    .321   2.73 2.92  13.49 3.36   .290
 40.   .752   .629   .952     .208   -.681         6.380 282.94 292.86    .307   2.76 2.83   5.90 3.42   .290
 50.   .714   .592   .917     .246   -.610         6.068 281.90 293.70    .305   2.79 2.83   5.66 3.47   .290
 60.   .679   .556   .894     .281   -.551         5.843 280.89 294.51    .306   2.81 2.87   6.60 3.53   .290
 70.   .644   .521   .879     .316   -.500         5.619 279.91 295.29    .308   2.84 2.91   7.93 3.58   .290
 80.   .610   .488   .870     .350   -.456         5.354 278.96 296.04    .307   2.86 2.92   8.33 3.64   .290
 90.   .578   .456   .861     .382   -.418         4.986 278.06 296.74    .300   2.88 2.87   6.00 3.70   .290
100.   .549   .427   .853     .411   -.386         4.516 277.21 297.39    .285   2.89 2.74   3.75 3.76   .290
110.   .523   .401   .840     .437   -.360         3.778 276.44 297.96    .249   2.90 2.41   2.14 3.81   .290
120.   .502   .379   .821     .458   -.339         3.714 275.77 298.43    .254   2.91 2.47   2.31 3.86   .290
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**RUN 18**

  T     CA     CB 1000(K°1)c  CAO-CA  LOG(CAO-CA)  FLUX     VT       VW    1000K°'01   E   N/NO     X    DB   1000K°1

  0.   .921   .979     0        0    *            11.632 290.00 288.00    .426   2.97 4.21      I 3.16   .290
  2.   .908   .966  1.095     .013  -1.900        11.016 289.49 288.31    .407   2.98 4.04      I 3.17   .290
  5.   .890   .948  1.075     .031  -1.514        10.279 288.86 288.74    .385   3.00 3.85      I 3.19   .290
 10.   .862   .920  1.046     .059  -1.231         9.368 287.99 289.41    .358   3.04 3.62      I 3.21   .290
 20.   .811   .869  1.003     .110   -.959         8.222 286.60 290.60    .327   3.10 3.38      I 3.27   .290
 30.   .765   .822   .973     .156   -.806         7.512 285.33 291.67    .310   3.17 3.27  12.82 3.32   .290
 40.   .722   .779   .953     .199   -.700         6.991 284.15 292.65    .300   3.23 3.23   9.14 3.36   .290
 50.   .681   .739   .940     .240   -.620         6.601 283.03 293.57    .294   3.30 3.23   8.79 3.41   .290
 60.   .642   .700   .933     .279   -.555         6.285 281.95 294.45    .291   3.36 3.26   9.59 3.46   .290
 70.   .605   .662   .929     .316   -.500         5.925 280.91 295.29    .289   3.43 3.27   9.68 3.51   .290
 80.   .569   .626   .928     .352   -.453         5.524 279.91 296.09    .289   3.50 3.24   8.89 3.56   .290
 90.   .534   .592   .929     .387   -.413         5.134 278.95 296.85    .288   3.57 3.20   8.12 3.61   .290
100.   .501   .559   .931     .420   -.377         4.725 278.02 297.58    .286   3.65 3.14   7.00 3.66   .290
110.   .470   .527   .934     .451   -.345         4.425 277.13 298.27    .276   3.72 3.14   6.96 3.71   .290
120.   .440   .498   .936     .481   -.318         3.932 276.29 298.91    .312   3.80 2.98   4.95 3.76   .290
```

200 rev / min

RUN19

T	CA	CB	$1000(K_1^0)_c$	CAO-CA	LOG(CAO-CA)	FLUX	VT	VW	$1000K_{01}^{0'}$	E	N/NO	X	DR	$1000K_2^0$
0.	.925	.311	0	0	*	15.474	290.00	288.00	1.180	1.42	2.09	I	2.12	.885
2.	.908	.295	1.446	.017	-1.779	14.168	289.40	288.40	1.111	1.40	1.95	I	2.12	.885
5.	.886	.272	1.385	.039	-1.404	12.585	288.65	288.95	1.027	1.38	1.78	I	2.12	.885
10.	.852	.238	1.300	.073	-1.137	10.653	287.67	289.73	.924	1.35	1.56	I	2.12	.885
20.	.797	.183	1.173	.128	-.893	8.400	286.19	291.01	.814	1.29	1.32	5.87	2.12	.885
30.	.751	.137	1.089	.174	-.760	7.226	284.93	292.07	.778	1.24	1.20	4.02	2.12	.885
40.	.710	.096	1.031	.215	-.668	6.497	283.80	293.00	.777	1.18	1.14	3.70	2.12	.885
50.	.673	.059	.990	.252	-.599	5.973	282.75	293.85	.795	1.12	1.11	3.83	2.12	.885
60.	.638	.024	.959	.287	-.543	5.510	281.77	294.63	.821	1.05	1.08	4.11	2.12	.885
70.	.606	.000	.933	.319	-.497	5.035	280.86	295.34	.830	1.00	1.04	3.93	2.12	.885

RUN20

T	CA	CB	$1000(K_1^0)_c$	CAO-CA	LOG(CAO-CA)	FLUX	VT	VW	$1000K_{01}^{0'}$	E	N/NO	X	DR	$1000K_2^0$
0.	.921	.645	0	0	*	17.724	290.00	286.00	1.030	1.87	2.41	I	2.12	.885
2.	.902	.625	1.682	.019	-1.716	16.359	289.34	286.46	.973	1.87	2.27	I	2.12	.885
5.	.875	.599	1.622	.046	-1.338	14.685	288.50	287.10	.903	1.86	2.10	I	2.12	.885
10.	.836	.559	1.538	.085	-1.069	12.592	287.38	288.02	.815	1.85	1.88	13.52	2.12	.885
20.	.770	.493	1.410	.151	-.820	10.010	285.66	289.54	.712	1.83	1.63	4.50	2.12	.885
30.	.715	.438	1.321	.206	-.686	8.537	284.21	290.79	.663	1.80	1.49	3.30	2.12	.885
40.	.667	.390	1.258	.254	-.595	7.575	282.91	291.89	.641	1.77	1.42	2.88	2.12	.885
50.	.623	.347	1.213	.298	-.526	6.901	281.73	292.87	.636	1.74	1.38	2.73	2.12	.885
60.	.582	.306	1.180	.339	-.470	6.388	280.63	293.77	.642	1.71	1.37	2.73	2.12	.885
70.	.545	.268	1.155	.376	-.424	5.975	279.59	294.61	.657	1.67	1.37	2.84	2.12	.885
80.	.509	.232	1.138	.412	-.385	5.637	278.60	295.40	.681	1.63	1.39	3.11	2.12	.885
90.	.475	.198	1.126	.446	-.350	5.333	277.65	296.15	.712	1.58	1.40	3.53	2.12	.885
100.	.442	.166	1.118	.479	-.320	5.078	276.75	296.85	.754	1.52	1.44	4.34	2.12	.885
110.	.411	.135	1.114	.510	-.292	4.732	275.87	297.53	.788	1.46	1.44	5.04	2.12	.885
120.	.382	.105	1.112	.539	-.268	5.190	275.04	298.16	.978	1.39	1.70	I	2.12	.885

RUN21

T	CA	CB	$1000(K_1^0)_c$	CAO-CA	LOG(CAO-CA)	FLUX	VT	VW	$1000K_{01}^{0'}$	E	N/NO	X	DR	$1000K_2^0$
0.	.955	.771	0	0	*	30.627	292.00	288.00	1.602	2.00	4.01	I	2.12	.885
2.	.922	.738	2.796	.033	-1.485	27.183	291.01	288.79	1.472	2.00	3.68	I	2.12	.885
5.	.879	.695	2.639	.076	-1.120	22.955	289.79	289.81	1.305	2.00	3.26	I	2.12	.885
10.	.820	.636	2.410	.135	-.871	17.767	288.22	291.18	1.085	2.00	2.71	I	2.12	.885
20.	.735	.551	2.059	.220	-.658	11.786	286.06	293.14	.809	1.98	2.00	18.87	2.12	.885
30.	.674	.490	1.817	.281	-.552	8.948	284.47	294.53	.675	1.97	1.66	4.34	2.12	.885
40.	.625	.441	1.652	.330	-.481	7.573	283.16	295.64	.622	1.95	1.51	3.24	2.12	.885
50.	.581	.397	1.541	.374	-.427	6.910	281.98	296.62	.616	1.93	1.49	3.09	2.12	.885
60.	.540	.356	1.468	.415	-.382	6.562	280.87	297.53	.638	1.91	1.52	3.34	2.12	.885
70.	.500	.316	1.422	.455	-.342	6.318	279.79	298.41	.673	1.88	1.58	3.92	2.12	.885
80.	.462	.278	1.393	.493	-.307	6.056	278.75	299.25	.712	1.84	1.64	4.85	2.12	.885
90.	.425	.241	1.374	.530	-.276	5.657	277.75	300.05	.738	1.80	1.66	5.64	2.12	.885
100.	.391	.207	1.359	.564	-.249	5.062	276.82	300.78	.737	1.75	1.62	5.19	2.12	.885
110.	.362	.178	1.339	.593	-.227	4.056	275.99	301.41	.656	1.71	1.40	2.97	2.12	.885
120.	.340	.156	1.303	.615	-.211	3.466	275.31	301.89	.613	1.66	1.27	2.31	2.12	.885

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**RUN22**

  T     CA     CB 1000(K°1)c CAO-CA  LOG(CAO-CA)  FLUX      VT        VW    1000K°'01   E    N/NO     X    DB   1000K°2

  0.   .960   .838      0        0   *            18.715 289.00 288.00      .936   2.08 2.44        I 2.12    .885
  2.   .940   .818  1.697     .020   -1.692       17.228 288.31 288.49      .879   2.09 2.29        I 2.12    .885
  5.   .912   .790  1.634     .048   -1.316       15.410 287.45 289.15      .809   2.09 2.11    20.89 2.12    .885
 10.   .870   .748  1.545     .090   -1.047       13.160 286.28 290.12      .723   2.09 1.89     7.02 2.12    .885
 20.   .801   .680  1.414     .159    -.800       10.467 284.49 291.71      .624   2.09 1.63     4.00 2.12    .885
 30.   .744   .622  1.326     .216    -.665        9.043 282.97 293.03      .581   2.09 1.52     3.26 2.12    .885
 40.   .692   .570  1.269     .268    -.572        8.204 281.61 294.19      .567   2.09 1.48     3.05 2.12    .885
 50.   .644   .522  1.233     .316    -.500        7.675 280.33 295.27      .571   2.09 1.49     3.09 2.12    .885
 60.   .598   .476  1.212     .362    -.441        7.284 279.11 296.29      .586   2.08 1.52     3.28 2.12    .885
 70.   .554   .432  1.201     .406    -.391        6.935 277.94 297.26      .605   2.07 1.56     3.53 2.12    .885
 80.   .512   .390  1.197     .448    -.349        6.573 276.82 298.18      .625   2.06 1.61     3.80 2.12    .885
 90.   .472   .350  1.197     .488    -.312        6.123 275.76 299.04      .637   2.04 1.62     3.96 2.12    .885
100.   .435   .313  1.197     .525    -.280        5.573 274.76 299.84      .635   2.02 1.60     3.84 2.12    .885
110.   .402   .280  1.193     .558    -.253        4.748 273.85 300.55      .593   1.99 1.48     3.02 2.12    .885
120.   .374   .252  1.180     .586    -.232        4.556 273.06 301.14      .619   1.97 1.52     3.33 2.12    .885
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**RUN23**

  T     CA     CB 1000(K°1)c CAO-CA  LOG(CAO-CA)  FLUX      VT        VW    1000K°'01   E    N/NO     X    DB   1000K°2

  0.   .920  1.551      0        0   *            24.397 291.00 288.00      .858   3.09 3.31        I 2.12    .885
  2.   .894  1.524  2.329     .026   -1.578       22.159 290.17 288.63      .792   3.13 3.10        I 2.12    .885
  5.   .858  1.488  2.229     .062   -1.206       19.397 289.12 289.48      .710   3.19 2.83        I 2.12    .885
 10.   .806  1.437  2.085     .114    -.945       15.958 287.73 290.67      .604   3.27 2.47        I 2.12    .885
 20.   .726  1.356  1.867     .194    -.711       11.832 285.67 292.53      .475   3.43 2.04    10.23 2.12    .885
 30.   .662  1.292  1.718     .258    -.588        9.695 284.02 293.98      .409   3.58 1.83     5.99 2.12    .885
 40.   .607  1.238  1.618     .313    -.504        8.514 282.59 295.21      .376   3.73 1.75     5.07 2.12    .885
 50.   .557  1.188  1.553     .363    -.440        7.839 281.28 296.32      .362   3.89 1.76     5.12 2.12    .885
 60.   .510  1.141  1.514     .410    -.387        7.410 280.04 297.36      .357   4.07 1.82     5.77 2.12    .885
 70.   .465  1.096  1.495     .455    -.342        6.524 278.86 298.34      .357   4.27 1.75     5.06 2.12    .885
 80.   .422  1.053  1.489     .498    -.303        6.024 277.71 299.29      .357   4.50 1.78     5.41 2.12    .885
 90.   .380  1.011  1.494     .540    -.268        5.513 276.62 300.18      .352   4.76 1.81     5.73 2.12    .885
100.   .342   .972  1.503     .578    -.238        5.106 275.58 301.02      .338   5.07 1.87     6.52 2.12    .885
110.   .306   .937  1.511     .614    -.212        4.802 274.64 301.76      .303   5.41 1.96     8.16 2.12    .885
120.   .277   .908  1.508     .643    -.192        4.221 273.81 302.39      .295   5.76 1.91     7.12 2.12    .885
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300 rev / min

RUN24

T	CA	CB	1000$(K_1^o)_c$	CAO-CA	LOG(CAO-CA)	FLUX	VT	VW	1000$K_{o1}^{o'}$	E	N/NO	X	DB	1000K_2^o
0.	.921	.249	0	0	*	18.427	290.00	287.00	1.498	1.34	1.74	I	2.12	1.350
2.	.901	.229	1.727	.020	-1.704	16.554	289.32	287.48	1.395	1.32	1.60	I	2.12	1.350
5.	.875	.202	1.634	.046	-1.336	14.281	288.50	288.10	1.265	1.29	1.42	23.26	2.12	1.350
10.	.838	.165	1.501	.083	-1.079	11.532	287.43	288.97	1.101	1.25	1.20	5.67	2.12	1.350
20.	.780	.108	1.308	.141	-.850	8.480	285.89	290.31	.924	1.18	.95	2.64	2.12	1.350
30.	.734	.062	1.184	.187	-.728	7.149	284.64	291.36	.878	1.11	.85	2.17	2.12	1.350
40.	.693	.021	1.108	.228	-.643	6.599	283.51	292.29	.916	1.04	.83	2.28	2.12	1.350
50.	.654	.000	1.063	.267	-.574	6.433	282.43	293.17	.983	1.00	.86	2.68	2.12	1.350

RUN25

T	CA	CB	1000$(K_1^o)_c$	CAO-CA	LOG(CAO-CA)	FLUX	VT	VW	1000$K_{o1}^{o'}$	E	N/NO	X	DB	1000K_2^o
0.	.920	.801	0	0	*	29.701	291.00	285.00	1.552	2.08	2.81	I	2.12	1.350
2.	.888	.769	2.834	.032	-1.494	26.555	290.04	285.76	1.436	2.08	2.60	I	2.12	1.350
5.	.845	.726	2.693	.075	-1.127	22.782	288.83	286.77	1.292	2.09	2.34	I	2.12	1.350
10.	.785	.666	2.499	.135	-.871	18.532	287.24	288.16	1.118	2.09	2.03	29.91	2.12	1.350
20.	.692	.573	2.228	.228	-.643	13.559	284.92	290.28	.938	2.09	1.70	8.33	2.12	1.350
30.	.618	.499	2.067	.302	-.520	11.398	283.04	291.96	.887	2.08	1.60	6.60	2.12	1.350
40.	.552	.433	1.976	.368	-.434	10.155	281.38	293.42	.890	2.07	1.60	6.53	2.12	1.350
50.	.493	.373	1.924	.427	-.369	9.185	279.86	294.74	.912	2.04	1.62	6.86	2.12	1.350
60.	.438	.319	1.895	.482	-.317	8.260	278.48	295.92	.935	2.02	1.64	7.15	2.12	1.350
70.	.389	.270	1.876	.531	-.275	7.162	277.21	296.99	.955	1.98	1.60	6.62	2.12	1.350
80.	.345	.226	1.863	.575	-.240	6.165	276.07	297.93	.983	1.94	1.55	6.03	2.12	1.350
90.	.305	.186	1.856	.615	-.211	5.344	275.02	298.78	1.037	1.88	1.52	5.75	2.12	1.350
100.	.268	.145	1.860	.652	-.186	4.932	274.04	299.56	1.161	1.81	1.60	7.43	2.12	1.350
110.	.232	.113	1.883	.688	-.162	4.822	273.07	300.33	1.411	1.71	1.81	24.35	2.12	1.350
120.	.193	.074	1.946	.727	-.139	4.732	272.07	301.13	2.247	1.57	2.13	I	2.12	1.350

RUN26

T	CA	CB	1000$(K_1^o)_c$	CAO-CA	LOG(CAO-CA)	FLUX	VT	VW	1000$K_{o1}^{o'}$	E	N/NO	X	DB	1000K_2^o
0.	.925	1.017	0	0	*	22.148	289.00	288.00	1.012	2.37	2.08	37.00	2.12	1.350
2.	.900	.993	2.137	.025	-1.609	20.937	288.21	288.59	.978	2.38	2.02	25.36	2.12	1.350
5.	.865	.958	2.104	.060	-1.225	19.396	287.19	289.41	.936	2.39	1.95	18.00	2.12	1.350
10.	.812	.904	2.056	.113	-.945	17.329	285.75	290.65	.882	2.42	1.86	12.87	2.12	1.350
20.	.718	.810	1.981	.207	-.683	14.354	283.40	292.80	.809	2.47	1.74	9.15	2.12	1.350
30.	.637	.730	1.924	.288	-.541	12.247	281.40	294.60	.761	2.52	1.67	7.71	2.12	1.350
40.	.567	.660	1.882	.358	-.446	10.627	279.65	296.15	.727	2.58	1.63	6.99	2.12	1.350
50.	.505	.596	1.851	.420	-.377	9.355	278.09	297.51	.705	2.63	1.61	6.69	2.12	1.350
60.	.450	.542	1.829	.475	-.323	8.322	276.69	298.71	.690	2.68	1.61	6.66	2.12	1.350
70.	.400	.493	1.815	.525	-.280	7.461	275.42	299.78	.681	2.74	1.62	6.87	2.12	1.350
80.	.355	.447	1.807	.570	-.244	6.429	274.25	300.75	.677	2.80	1.58	6.19	2.12	1.350
90.	.314	.406	1.806	.611	-.214	5.361	273.18	301.62	.674	2.87	1.49	5.13	2.12	1.350
100.	.277	.369	1.808	.648	-.188	4.840	272.20	302.40	.670	2.94	1.52	5.53	2.12	1.350
110.	.243	.336	1.813	.682	-.166	4.744	271.30	303.10	.645	3.02	1.70	8.18	2.12	1.350
120.	.214	.307	1.816	.711	-.148	4.778	270.50	303.70	.717	3.11	1.94	17.46	2.12	1.350

200 rev/min 0.5 M NaPr

RUN27

T	CA	CB	$1000(K_1^{\circ})_c$	CAO-CA	LOG(CAO-CA)	FLUX	VT	VW	$1000K_{01}^{\circ\prime}$	E	N/NO	X	DB	$1000K_2^{\circ}$
0.	.910	.991	0	.500	-.301	26.895	290.00	288.00	1.169	2.53	3.69	I	2.12	.885
2.	.881	.962	2.602	.529	-.276	24.295	289.10	288.70	1.085	2.54	3.45	I	2.12	.885
5.	.841	.923	2.484	.569	-.245	21.041	287.98	289.62	.975	2.56	3.13	I	2.12	.885
10.	.786	.867	2.309	.624	-.205	16.901	286.50	290.90	.829	2.59	2.69	I	2.12	.885
20.	.702	.783	2.025	.708	-.150	11.778	284.38	292.82	.634	2.65	2.10	12.40	2.12	.885
30.	.640	.721	1.826	.770	-.114	9.114	282.78	294.22	.530	2.69	1.78	5.35	2.12	.885
40.	.589	.670	1.684	.821	-.086	7.782	281.44	295.36	.485	2.73	1.65	4.14	2.12	.885
50.	.543	.625	1.591	.867	-.062	7.223	280.23	296.37	.481	2.76	1.66	4.22	2.12	.885
60.	.499	.580	1.536	.911	-.041	7.070	279.06	297.34	.505	2.80	1.77	5.24	2.12	.885
70.	.455	.536	1.513	.955	-.020	6.321	277.90	298.30	.545	2.85	1.74	4.88	2.12	.885
80.	.411	.492	1.513	.999	-.000	5.812	276.74	299.26	.588	2.90	1.77	5.22	2.12	.885
90.	.367	.449	1.529	1.043	.018	5.486	275.60	300.20	.616	2.95	1.87	6.49	2.12	.885
100.	.327	.408	1.548	1.083	.035	5.025	274.54	301.66	.605	3.02	1.92	7.42	2.12	.885
110.	.292	.374	1.554	1.118	.048	4.560	273.61	301.79	.506	3.08	1.95	7.95	2.12	.885
120.	.269	.350	1.526	1.141	.057	3.156	272.92	302.28	.374	3.13	1.47	2.97	2.12	.885

300 rev/min 0.5 M NaPr

RUN28

T	CA	CB	$1000(K_1^{\circ})_c$	CAO-CA	LOG(CAO-CA)	FLUX	VT	VW	$1000K_{01}^{\circ\prime}$	E	N/NO	X	DB	$1000K_2^{\circ}$
0.	.925	1.215	0	.500	-.301	28.792	289.00	288.00	1.095	2.84	2.71	I	2.12	1.350
2.	.893	1.183	2.771	.532	-.274	26.535	288.05	288.75	1.035	2.87	2.58	I	2.12	1.350
5.	.849	1.139	2.689	.576	-.240	23.653	286.83	289.77	.955	2.92	2.42	I	2.12	1.350
10.	.786	1.075	2.565	.639	-.194	19.847	285.15	291.25	.846	2.99	2.20	193.16	2.12	1.350
20.	.683	.973	2.359	.742	-.130	14.709	282.63	293.57	.691	3.12	1.87	13.56	2.12	1.350
30.	.604	.893	2.198	.821	-.085	11.581	280.66	295.34	.591	3.24	1.67	7.66	2.12	1.350
40.	.539	.828	2.076	.886	-.052	9.633	279.03	296.77	.531	3.37	1.56	5.93	2.12	1.350
50.	.483	.772	1.988	.942	-.026	8.441	277.60	298.00	.500	3.50	1.52	5.52	2.12	1.350
60.	.432	.722	1.929	.993	-.003	7.698	276.31	299.09	.489	3.64	1.55	5.86	2.12	1.350
70.	.385	.675	1.896	1.040	.017	7.172	275.10	300.10	.490	3.80	1.62	6.84	2.12	1.350
80.	.341	.630	1.883	1.084	.035	6.678	273.95	301.05	.491	3.99	1.70	8.37	2.12	1.350
90.	.300	.589	1.881	1.125	.051	6.020	272.89	301.91	.477	4.21	1.75	9.34	2.12	1.350
100.	.264	.553	1.879	1.161	.065	5.059	271.93	302.67	.431	4.46	1.67	7.68	2.12	1.350
110.	.235	.525	1.858	1.190	.076	3.515	271.14	303.26	.318	4.70	1.30	3.59	2.12	1.350
120.	.218	.508	1.791	1.207	.082	2.074	270.59	303.61	.195	4.88	.83	1.51	2.12	1.350

TABLE 2: Print-outs of the experiments performed without reaction and with a 0.5 M NaPr solution.

T = time (min)

CT,CW: concentrations of HPr in toluene and water respectively (gmol/l)

CT*: equilibrium concentration of HPr (gmol/l)

DC/DT: $= \frac{dC}{dt}$ (gmol/l min)

KOT: overall mass transfer coefficient based on the toluene phase (cm/s)

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**RUN29**

TRANSFER OF PROPIONIC ACID FROM TOLUENE TO WATER AT 25°C

STIRRING SPEED   200 rev/min   -   0.5M NaPr  -

TIME(MIN),CONCENTRATION(GMOL/L),VOLUME(ML),KOT(CM/SEC)

 T     CT     CW    CT*   CT-CT*  LOG(CT-CT*)  DC/DT    VT      VW        1000KOT

  0.  .921    -0     0     .921        -.036     -1.8054 290.00 288.00     1.080
  2.  .910  .012  .001     .910        -.041     -1.6756 289.54 288.26     1.015
  5.  .896  .029  .002     .893        -.049     -1.5191 288.98 288.62      .937
 10.  .873  .053  .005     .869        -.061     -1.3257 288.25 289.15      .841
 20.  .835  .094  .011     .824        -.084     -1.0918 287.15 290.05      .730
 30.  .802  .129  .018     .784        -.106      -.9642 286.19 290.81      .678
 40.  .772  .160  .027     .745        -.128      -.8877 285.29 291.51      .656
 50.  .744  .190  .037     .708        -.150      -.8440 284.45 292.15      .657
 60.  .717  .218  .047     .670        -.174      -.8161 283.63 292.77      .671
 70.  .691  .244  .058     .633        -.199      -.7922 282.82 293.38      .690
 80.  .665  .270  .070     .595        -.225      -.7036 282.04 293.96      .651
 90.  .640  .295  .081     .559        -.252      -.6801 281.28 294.52      .670
100.  .617  .318  .092     .525        -.280      -.6583 280.56 295.04      .691
110.  .597  .338  .102     .495        -.306      -.5469 279.90 295.50      .609
120.  .581  .355  .111     .470        -.328      -.5523 279.33 295.87      .648
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**RUN30**

TRANSFER OF PROPIONIC ACID FROM TOLUENE TO WATER AT 25°C

STIRRING SPEED   300 rev/min   -   0.5M NaPr  -

TIME(MIN),CONCENTRATION(GMOL/L),VOLUME(ML),KOT(CM/SEC)

 T     CT     CW    CT*   CT-CT*  LOG(CT-CT*)  DC/DT    VT      VW        1000KOT

  0.  .910    -0     0     .910        -.041     -3.3955 289.00 288.00     2.056
  2.  .890  .022  .002     .888        -.052     -3.0786 288.32 288.48     1.910
  5.  .862  .052  .005     .858        -.067     -2.6838 287.47 289.13     1.724
 10.  .823  .094  .011     .813        -.090     -2.1828 286.36 290.04     1.480
 20.  .763  .156  .026     .738        -.132     -1.5608 284.78 291.42     1.166
 30.  .718  .203  .042     .677        -.170     -1.2276 283.55 292.45     1.000
 40.  .681  .241  .057     .624        -.205     -1.0466 282.50 293.30      .924
 50.  .648  .274  .071     .577        -.239      -.9548 281.56 294.04      .912
 60.  .617  .305  .086     .531        -.275      -.8800 280.66 294.74      .913
 70.  .587  .334  .100     .486        -.313      -.8130 279.79 295.41      .921
 80.  .558  .363  .115     .442        -.354      -.7309 278.94 296.06      .910
 90.  .530  .390  .129     .401        -.397      -.6630 278.13 296.67      .912
100.  .505  .414  .142     .363        -.441      -.5930 277.38 297.22      .901
110.  .485  .433  .153     .332        -.479      -.4794 276.74 297.66      .796
120.  .473  .445  .160     .313        -.505      -.3445 276.27 297.93      .607
```

TABLE 3

EXPERIMENTAL CONCENTRATION OF TOLUENE SULPHONIC ACID IN THE ACID PHASE AS A FUNCTION OF TIME

w_2 (%-wt)	N (rev/min)	C_{TSA} in phase 2 (g/l) as a function of t (min)					
		10	30	50	70	90	110
68.8	200	0.028	0.036	0.043	0.049	0.056	0.062
69.6	100	0.030	0.037	0.040	0.047	0.050	0.056
	200	0.032	0.040	0.050	0.053	0.060	0.063
	300	0.038	0.050	0.061	0.069	0.079	0.093
70.8	100	0.036	0.042	0.048	0.052	0.060	0.064
	200	0.040	0.053	0.056	0.060	0.068	0.076
	300	0.043	0.054	0.066	0.079	0.088	0.098
75.1	100	0.044	0.046	0.056	0.064	0.070	0.072
	200	0.044	0.053	0.062	0.072	0.078	0.088
	300	0.048	0.061	0.073	0.087	0.098	0.113
78.3	100	0.050	0.058	0.070	0.083	0.093	0.106
	200	0.047	0.063	0.080	0.094	0.100	0.124
	300	0.062	0.080	0.098	0.119	0.135	0.156
79.9	300	0.071	0.096	0.120	0.146	0.170	0.193
80.4	100	0.060	0.078	0.094	0.112	0.128	0.147
	200	0.056	0.084	0.104	0.121	0.141	0.166
82.7	100	0.081	0.106	0.133	0.158	0.183	0.208
	200	0.088	0.120	0.151	0.180	0.209	0.242
	300	0.096	0.130	0.164	0.200	0.233	0.269

TABLE 4

w_2 %wt	γ_2	$\frac{d\log\gamma_2}{dw_2}$	$\sigma \times 10^3$ (mN/m)	$-\frac{d\sigma}{dw_2}$ (N/m)	$\Gamma_2 \times 10^{10}$ (gmol/cm^2)
68	2.21	3.51	38.5	0.0170	0.193
70	2.62	3.44	38.1	0.0191	0.204
72	3.04	3.33	37.6	0.0216	0.220
74	3.54	3.26	37.2	0.0244	0.240
76	4.10	3.08	36.7	0.0290	0.267
78	4.74	2.89	36.1	0.0351	0.300
80	5.37	2.64	35.1	0.0437	0.351
82	6.04	2.19	34.3	0.0546	0.452
84	6.56	1.42	32.9	0.0685	0.630

TABLE 5

w_2 (%wt)	D_{T2} x 10^7 (cm^2/s)	μ_2 (cP)	ρ_2 (gcm^3)	σ_e (mN/m)	k_1 x 10^7 (s^{-1})	β_{100} x10^2 (-)	β_{200} x 10^2 (-)	β_{300} x 10^2 (-)
68	14.9	8.0	1.583	56.0	0.1	0.23	0.09	0.05
70	13.6	8.9	1.606	56.3	0.4	0.50	0.17	0.09
72	12.0	10.3	1.629	56.4	1.5	0.99	0.35	0.19
74	10.6	11.8	1.652	56.5	5.7	1.93	0.68	0.38
76	9.4	13.7	1.676	56.6	22.2	3.76	1.33	0.72
78	8.2	16.0	1.699	56.5	85.5	7.33	2.58	1.41
80	7.3	18.2	1.722	56.2	330	14.1	5.03	2.74
82	6.7	20.3	1.744	55.8	1270	27.7	9.80	5.33
84	6.5	21.6	1.763	55.0	4910	53.7	19.0	10.3

Note: the dimensionless coefficient β is calculated for 100, 200, 300 rev/min using the coefficients estimated from Davies' correlation (Table 5.4).

TABLE 6

w_2 %-wt	N rev/min	x_2 %-molar	N_T $\times 10^{10}$ gmol/cm^{2}s	C^*_{T2} $\times 10^6$ gmol/cm^3	K_2 $\times 10^5$ experimental cm/s	K^0_2 $\times 10^5$ corrected cm/s	R_{Ti} $\times 10^{10}$ gmol/cm^2	n_2 $\times 10^{10}$ gmol/cm^2	Γ_2 $\times 10^{10}$ gmol/cm^2	n^s_2 $\times 10^{10}$ gmol/cm^2
68.8	200	28.9	3.13	2.02	15.5	15.4	0	2.41	0.20	2.61
69.6	100	29.7	1.88	2.10	8.35	8.82	0	2.47	0.20	2.67
	200		3.20		15.2	15.2	0			
	300		4.85		23.1	23.2	0			
70.8	100	30.9	1.88	2.22	8.47	8.55	0	2.57	0.21	2.78
	200		3.20		14.4	14.8	0			
	300		5.15		23.2	22.6	0			
75.1	100	35.8	2.42	2.66	9.10	7.60	0.40	2.99	0.26	3.25
	200		4.14		15.6	13.1	0.66			
	300		5.31		20.0	20.1	0.04			
78.3	100	40.1	5.55	3.10	17.9	6.93	3.40	3.34	0.30	3.64
	200		6.98		22.5	11.9	3.29			
	300		8.92		28.8	18.3	3.25			
79.9	300	42.5	11.32	3.32	34.1	17.6	5.48	3.54	0.35	3.89
80.4	100	43.2	8.05	3.39	23.7	6.60	5.82	3.60	0.37	3.97
	200		9.74		28.7	11.4	5.88			
82.7	100	46.8	11.70	3.78	31.0	6.43	9.28	3.90	0.51	4.41
	200		14.25		37.7	11.1	10.05			
	300		16.07		42.5	17.0	9.64			

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LIST OF MAIN SYMBOLS

Only symbols used repeatedly are shown in this list; other symbols are fully explained in the text.

A	absorbance
C	concentration
D_{ij}	diffusion coefficient of species i in phase j
E	enhancement factor
F	Faraday constant
g	gravitational constant
HPr	propionic acid
k_1	first-order rate constant
K	individual phase mass transfer coefficient
K_o	overall mass transfer coefficient
$1/K_R$	interfacial resistance
ℓ	characteristic eddy dimension
L	length (tip-to-tip) of stirrer blade
m	partition coefficient
M_i	molecular weight of species i
n_i^S	surface concentration of species i
$\mathcal{N}$	Avogadro number
N	stirring speed
NaPr	sodium propionate
N_i	molar flux of species i
Pr^-	propionate anion
R_i	reaction rate of species i per unit volume of solution
s	fractional rate of surface renewal (Danckwerts model)
S	interfacial area
t	time
T	absolute temperature
TSA	toluene sulphonic acid

V	phase volume
w_2	mass fraction of H_2SO_4 in phase 2
x	distance from the interface
x_i	molar fraction of species i
y_i	valence of species i

Greek letters:

β	as defined by Eqn.4.50
ϵ	eddy diffusivity
γ	activity coefficient
μ	viscosity
ν	kinematic viscosity
ρ	density
Γ_i	excess surface concentration of species i
σ	interfacial tension

Dimensionless groups:

Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
We	Weber number
We'	modified Weber number (Eqn.5.40)

Subscripts:

1,2	upper and lower phases respectively
T	toluene phase
W,w	water phase
SA	pure sulphuric acid
S,s	salt (i.e. product of the reaction)

A,B	reactants
I,II	cases described in Section 4.2.1
X	critical value
i	interfacial condition
EXP	experimental
c	calculated

Superscripts:

o	reference condition (pure mass transfer)
*	equilibrium condition
i	initial condition
s	surface condition