LIQUID-LIQUID EXTRACTION WITH CHEMICAL REACTION IN AGITATED COLUMNS

by

SUKHAMOY SARKAR

A thesis submitted to the University of Aston
in Birmingham for the degree of Doctor of
Philosophy.

Department of Chemical Engineering
The University of Aston in Birmingham

September, 1976

TO MY MOTHER AND WIFE

SUMMARY

A study has been made of the hydrodynamics and mass transfer characteristics of liquid-liquid extraction with chemical reaction in both R.D.C and Oldshue Rushton contactor. The literature relating to these extractors and relevant phenomena, such as single drop mass transfer, droplet break-up and coalescence and phase inversion, has been reviewed. Consideration has also been given to published data on the rate controlling mechanism in mass transfer with and without chemical reaction.

Two 0.10 m diameter, 18 compartment, interchangeable columns were operated with model liquid-liquid systems, i.e. toluene-water and butyl acetate-water for hydrodynamic studies; and alkaline hydrolysis of butyl acetate, butyl formate and methyl dichloroacetate for mass transfer with chemical reaction. Drop size distribution and phase inversion phenomena were analysed using high speed still and cine photography. Solute concentrations were measured by chemical analysis.

Axial hold-up distribution increased to a maximum in the middle of the R.D.C and subsequently decreased but in the Oldshue Rushton the increase was maintained; this is explained in terms of the differing drop size distributions and end effects. The hold-up profiles were correlated by semi-theoretical models.

The effect of operating parameters, viz phase flow rates and energy input, upon phase inversion was investigated. Hold-up at inversion was correlated by,

$$Rr = 1 - \frac{a}{x_i} + \sum_{\substack{k=2\\ j=1}}^{\substack{k\\ j}} b^k/x_i^j$$

Phase inversion was a cyclic pseudo-steady state condition under which stable operation was possible. The time cycle was satisfactorily correlated by a mathematical model,

$$t = 0.048(Z)^{0.66}.(x)^{-0.33}.(D_{tr})^{-1.0}$$

With mass transfer involving a slow chemical reaction, two rate controlling regimes, e.g. diffusional and kinetic, were identified. Fast extraction-reaction systems were controlled by the diffusion process. The data were analysed in terms of film and penetration theory based models. Concentration profiles in the two contactors were correlated by mathematical models of the form,

$$\frac{d^2X}{dH^2} + Pe\,\frac{dX}{dH} = f(y_W, K_L, a, x_o, u, K_S, Pe, K_2, D, x_D, v)$$

A numerical technique was developed to solve these non-linear equations conditioned by the axial dispersion boundary values. Analyses are proposed for more complex situations in which both phases are impure and backmixing predominates in either, or both, phases.

Key words: 'Liquid-Liquid Extraction - Chemical Reaction - Agitated Contactors'

ACKNOWLEDGEMENTS

The author wishes to thank the following:

Professor G. V. Jeffreys for providing the facilities for this research and for his interest and encouragement throughout this study.

Dr. C. J. Mumford for his supervision, encouragement and constructive criticism.

The Technical Staff of the Department of Chemical Engineering for their assistance in fabricating the equipment.

Mrs. A. Mellings for her assistance with photographic work.

Mrs. H. Turner for her diligence in typing this thesis.

The Science Research Council for financial support.

CONTENTS

Page No.

Page No.

APPENDICES

1. Chemical Specifications
2. Kinetic Data
3. Description of Cine Film
4. Computer Program for Correlation of Hold-up in the R.D.C
5. Computer Program for Correlation of Hold-up in the Oldshue Rushton Column
6. Computer Program for Solution of Differential Models
7. Mass Transfer with Chemical Reaction.
    (a) Slow Reaction Data
    (b) Fast Reaction Data
    (c) Very Fast Reaction Data
8. Paper presented to the Institution of Chemical Engineers, 3rd Annual Research Meeting, University of Salford, 30-31 March, 1976.

1. INTRODUCTION

Liquid-liquid extraction involving interphase chemical reaction is an important operation in the chemical industry, for example in the recovery of metals from leach liquors and in aromatic nitrations. However there have been few fundamental studies in this field and, though there are many relevant publications, the phenomena involved are not well understood. This is due to its greater complexity compared with a conventional mass transfer operation and the uncertainty surrounding most of the chemical kinetics involved.

Individual studies have been concerned either with a specific application, or correlation of data for a specific duty, or the prediction of some specific characteristics related to a particular system. Some information is available from single drop studies, but no precise mechanism has as yet been established for extraction with chemical reaction involving a swarm of drops in a turbulent continuum. The complexities involved in this practical situation are discussed in Chapter 7.

Extraction with chemical reaction is a two-phase phenomenon with the two reactive species being present in two different and distinct phases, one continuous and the other dispersed. Hence the reactive species must diffuse to a reaction zone, or to an interface, and the reaction product must diffuse away to the selective phase, or phases, to allow fresh reactive elements to continue the process. The reaction zone may be in one phase or extend to both phases; in the extreme case it may reduce to a reaction plane dependent upon the reaction type and the mode of contacting.

The rate of extraction of such processes is controlled both by the kinetics of the reaction and the diffusional characteristics of the system. However, under certain circumstances, a process may either be entirely diffusion controlled or kinetically controlled. In the limiting case of a very slow reaction accompanied by high mass transfer rates, the overall extraction rate is dictated by the kinetics of reaction whilst in the case of a very fast reaction, the rate of diffusion controls the process. Originally most extraction processes were classified as entirely mass-transfer controlled and only more recently has the implication of kinetics received attention. Kinetic effects tended to be ignored because (1),

(a) Most extractors have been designed by calculation of the number of equilibrium stages required to effect a given separation. Design from equilibrium isotherms automatically neglects kinetic effects;

(b) Many processes involving chemical reactions have been carried out in mixer-settlers. The mixer comprised an agitated tank which has generally been over-designed so that the resultant long residence times ensured equilibrium between the phases;

and (c) Extractions carried out in differential contactors have been of the type involving a rapid chemical interaction, that is a mass transfer controlled process.

It follows that in the design of a differential contactor with a fixed time of contact neglect of kinetic effects could be a serious omission.

In the same way that the effect of reaction kinetics in these processes has only recently been recognised, the converse is equally true for many liquid-liquid reactions used in organic synthesis. These processes were classed as kinetically controlled. For example, the rates of aromatic nitration reactions, involving interaction between an aromatic hydrocarbon and an aqueous solution of nitric and sulphuric acids, were originally considered to be entirely dependent under all conditions on the kinetics of reaction. This is rather surprising since such reactions can be so rapid that control is difficult.

Recent work has revealed that most extraction processes involving interphase reaction in agitated systems will be diffusion-controlled under the influence of coalescence-redispersion phenomena; kinetic control will be limited to processes involving very slow reactions (2). It appeared worthwhile therefore to investigate the process in turbulent agitated continuous contactors in which diffusional resistances could be reduced to a significant degree thus yielding a high extraction rate. Of the several designs available, the Rotating Disc

Contactor and the Oldshue Rushton Contactor were selected to cover a range of energy input levels as discussed in Chapter 3. It was recognised at the outset that difficulties would arise since;

(a) Diffusion, convection and reaction proceed simultaneously. The nature of the convective movements of the liquids is ill-defined and to attempt to describe them completely would be impracticable (3);

(b) Although coalescence-redispersion would be expected to exert a profound influence, there is no realistic quantitative model for this phenomena.

(c) The creation of new species by chemical interaction may affect the physical properties of a system; in particular changes in interfacial tension may affect the transfer rate or create interfacial disturbances. The magnitude of these effects is unpredictable;

(d) In continuous columns additional complexities arise due to variation in hold-up across the column length and the effect of backmixing.

In the event an attempt has been made to obtain some insight into the rates of diffusion and kinetics of liquid-liquid extraction with chemical reaction using two practical rotary agitated columns and model systems i.e. a slow reaction (kinetically controlled) and a fast reaction (diffusion controlled). To facilitate useful predictions of the behaviour of such systems, it was necessary to use highly simplified models which simulate the situation sufficiently well for practical purposes without introducing a large number of parameters with unassignable values. Arising incidentially from observations of the column operating characteristics an attempt has also been made to define more precisely the limiting volumetric capacity of agitated columns in terms of an inversion point.

2. LIQUID-LIQUID REACTIONS

There are many heterogeneous liquid-liquid reactions of industrial importance, e.g. the winning of metals, aromatic nitration, sulphonation, alkylation and hydrolysis. The mechanism and practical applications of these processes are discussed fully in Chapter 7. However, a brief introduction is necessary to facilitate references in intermediate chapters to the significance of droplet phenomena and equipment characteristics.

The extraction of metals from leach liquors has been the subject of continuing research. This has covered both the common metals e.g., iron, cobalt, copper, nickel, silver and zinc, and the rare earth metals eg. uranium, plutonium, zinconium, neptunium, thorium, indium, rhenium and a host of other radioactive minerals. These investigations have been mainly concerned with finding the most efficient and economic extracting system and defining the related ion-exchange mechanism (4 - 7). For example a typical process is the extraction of uranyl nitrate by TBP (tri-n-butyl phosphate). The extraction reaction may be represented by,

$$UO_2^{2+} + 2NO_3^- + 2TBP_{org} \rightarrow UO_2(NO_3)_2\ 2TBP$$

However, different exchange reactions have been proposed. A dissociative mechanism has been suggested by Egozy and Weiss (4) for the formation of the activated complex,

$$UO_2(NO_3)_2\ 2TBP \rightleftarrows [UO_2(NO_3)_2TBP]^{\neq} + TBP$$

Amnon (5) however, considered the reaction to be best explained by an associative mechanism,

$$UO_2(NO_3)_2\ 2TBP + TBP \rightleftharpoons [UO_2(NO_3)_2\ 3TBP]^{\neq}.$$

Most metal extraction processes are classed as mass transfer controlled, but a close examination reveals that this generalisation is not strictly true since under certain conditions, for example in the case of a slow reaction the mass transfer and chemical reaction processes may be consecutive (8). Thus both effects should be accounted for. However, in the extraction of some metals with specific reagents, viz. uranium, cobalt, copper, cadmium, alkali metals and certain other rare earth metals, the reactions are so rapid that they may be classed as purely diffusion-controlled processes (1, 6 ,7).

Hanson et. al. (9 , 1) have reviewed the work on aromatic nitrations. These are used in the manufacture of intermediates for dyestuffs, pharmaceutical products, plastics and explosives, and provide an excellent example of the complex nature of industrially important two-phase reactions. The basic processes involved are the diffusion of the aromatic into the aqueous nitric acid phase, chemical reaction in that phase and finally diffusion of the products back into the organic phase. Nitric acid may be used either alone or mixed with sulphuric acid, depending upon the ease of nitration of the particular aromatic. If sulphuric acid is used, the rate of nitration is very sensitive to its concentration. In the past the function of the sulphuric acid was was considered to be the removal of the water formed during reaction i.e. to act as a dehydrating agent. However, current theories (10) have rejected this idea and consider the nitrating agent to be the nitronium ion formed by the dissociation of nitric acid; the role of sulphuric acid is to provide an ionising medium for this dissociation. However, there is still considerable uncertainty as to the mechanism of nitration processes (11). Accurate data on the rate processes involved, an essential prerequisite for reliable plant design, are still not available. An added incentive to obtaining a thorough understanding of the process is safety, since many nitrations are highly exothermic and run-away conditions can result in an explosion.

Work on aromatic sulphonation has been limited and the process mechanisms have not been established (12). Whilst basically similar to aromatic nitration, sulphonation differs in the important respect that the reaction products are water soluble. This results in (i) the phase ratio within a reactor being a function of the degree of conversion, and hence space time, as well as of feed ratio, and (ii) the reaction products remaining in the bulk aqueous phase instead of diffusing back across the interface into the organic phase, as in nitrations.

Albright (13) and Li et. al. (14) investigated the important industrial process of Alkylation, viz, the alkylation of isobutane with light olefins. The type of dispersion had a significant effect on the process i.e. mass transfer was dependent upon which phase was dispersed. The quantity of alkylate produced in an acid-continuous dispersion was much higher than in the hydrocarbon-continuous case. Further with increased agitation the mass transfer rate increased. These observations suggest that the rate controlling mechanism was the process of diffusion.

The hydrolysis of animal and vegetable fats is a classic example of mass transfer with chemical reaction in a liquid-liquid system. Originally this was a batch process involving saponification of animal fat with caustic alkali to produce soap and glycerine. Free fatty acids were obtained by acidifying the soap. However, in modern plants, the hydrolysis is carried out continuously under high pressure using hot water in a countercurrent spray tower. Jeffreys et. al. (15) studied the process in a pilot scale batch reactor, in a spray column and in a full-scale plant. The process was observed to be mass transfer controlled although the effect of chemical reaction was quite significant. Because of its importance this work and theoretical models developed for the system are discussed in Chapter 7.

An extremely interesting special class among heterogeneous reaction systems is that of liquid-liquid electron exchange. Scibona et. al. (16) and recently Mansoori and Madden (17) pointed out the potential for application of this type of system in the processing of aqueous solutions. For example, aqueous solutions of multivalent metallic ions can be reduced or oxidized by contact with an immiscible organic phase containing, appropriately, an organic soluble reducing or oxidizing species, the result being a change in the valence state of a species in the aqueous phase without introducing extraneous components, except for the addition or removal of a proton. For this to be effectively achieved the reactants and their oxidation/reduction products must be substantially insoluble in the opposite phase. Thus it would be possible for an analogous development in the general area of heterogenous electron exchange reactions to that which has occurred in the field of ion-exchange. In that area liquid-ion exchange has assumed an important processing role in recent years in metal extraction as mentioned earlier. Since the technique for conducting liquid ion-exchange operations is identical to that employed for general solvent extraction, the same advantage would accrue to liquid electron exchange operation. In particular, the ease of adoptation to continuous, counter current contacting would be a noteworthy operational advantage.

Rates of many reversible and irreversible reactions can be increased by the deliberate controlled addition to the reaction system of an immiscible extractive solvent phase. Such processes are termed pure extractive reactions. Reversible reactions can be made to go to completion by extracting one of the products from the reaction mixture. The classical example is the I.M.I. process for the manufacture of potassium nitrate (18) in which potassium chloride and nitric acid are equilibrated and the reaction made to go to completion by continuously extracting the hydrochloric acid as it is formed using amyl alcohol as the solvent. Furthermore, in competing reactions such as $A \begin{matrix} \rightleftarrows B \\ \rightleftarrows C \end{matrix}$, the conversion of A to B may be increased if an extractive reaction process is employed where $\alpha_B > \alpha_C$ where α_B and α_C are the partition coefficients for components B and C respectively. Thus for many complex reactions increased conversions to a desired product are possible provided a solvent system can be found with a favourable partition coefficient. It has been reported that this concept has not been widely used in industry because of lack of data regarding solubility relationship of solvents (8).

3. EQUIPMENT FOR LIQUID-LIQUID EXTRACTION WITH CHEMICAL REACTION

3.1 Equipment Classification

A wide variety of equipment is available for liquid-liquid extraction ranging from simple stagewise contactors, e.g. the mixer-settler, to differential contactors such as spray, packed and agitated columns (19). The former consist of discrete stages whereas the latter enable many stages to be incorporated in a single shell. The various contacting devices are listed in Table 3.1.

One of the prime considerations in the design of liquid-liquid extraction equipment is the creation of a suitable dispersion to give a large interfacial area. In non-agitated contactors this is obtained by converting pressure energy into droplet surface energy at a distributor. In rotary agitated contactors, however, dispersion is achieved by the transmission of kinetic energy from the agitator. This kinetic energy contributes to the surface energy, and to the potential and kinetic energy of the droplets in the dispersion. The rate of energy input per unit volume of the continuous phase may serve as a basis for the classification of contactors. They may also be classified into the two major categories already mentioned, viz, stagewise contactors and differential, continuous countercurrent, contactors. The most common design of contactor, and their gradation with respect to the degree of energy input, are listed in Figure 3.1.

3.2 Choice of Contactors

Although the choice of equipment for any specific duty is

Table 3.1

LIQUID-LIQUID EXTRACTION EQUIPMENT CLASSIFICATION (20)

Mode of Agitation	Discrete Stage Contact	Continuous Contact
None		Spray Column. Simple packed column Wetted-wall towers. Baffle Plate columns
Rotary Device	Pump-mix or KAPL mixer-settler. Holley-Mott mixer settler. Windscale mixer settler. Simple mixer-settler Mixer-settler by Hanson et.al. Colven mixer-settler	Rotating Disc Contactor. Scheibel column. Luwesta contactor Oldshue-Rushton column. Zhiel column Podbielniak extractor
Pulsing Device	Pulsed mixer-settler	Pulsed Packed column Pulsed Sieve-tray column.

Fig. 3.1 Liquid-liquid Extraction Equipment largely based on experience, the following factors should be considered,

(a) The number of effective contact stages required, determined from the desired terminal concentrations.

(b) The throughput and the residence time of the phases.

(c) The applicability of geometric, dynamic and kinematic similarity in scaling up.

(d) Capital investment and operating costs.

(e) The hold-up and the physical properties of the systems. This is particularly important when processing radioactive , flammable or low stability materials, where a low hold-up is desirable. (21)

(f) The ease of phase separation following extraction i.e. rapid coalescence is desirable, otherwise an excessive residence time is required resulting in reduced volumetric capacity.

In practice, selection of equipment is dependent on the overall economics of the process, that is, a compromise must be reached between the extraction rate and the capital and operating costs. Table 3.2 lists the characteristics of various contactors with reference to the factors discussed above.

3.3 Continuous Differential Contactors

Continuous countercurrent differential contactors may be categorised as,

(1) Gravity operated extractors
    (a) Non-agitated units
        (i) spray columns
        (ii) plate columns
        (iii) packed columns

Table 3.2

FACTORS DETERMINING THE CHOICE OF AN EXTRACTOR (22)

(b) Mechanically agitated units
  (i) rotary agitated columns
  (ii) pulsed columns

(2) Centrifugal extractors

In gravity operated columns, the phase flow rate is limited by the flooding characteristics of the extractor, that is, the maximum flow ratio at which countercurrent flow can be maintained. The agitated designs possess the obvious advantage over the non-agitated contactors of producing high mass transfer efficiencies due to smaller mean drop sizes and increased turbulence. The absence of mechanical agitation may result in inefficient dispersion leading to poor mass transfer efficiencies. For example, in a spray column the absence of any internals permits free circulation of the continuous phase so that the column does not behave as a true countercurrent contactor and has a low mass transfer efficiency.

The main features of the various continuous differential contactors are summarised in Table 3.3.

The present investigation comprises a study of mass transfer with chemical reaction. Now in general, apart from any involving a very slow chemical reaction, most of the systems which undergo two-phase mass transfer with simultaneous chemical reactions are diffusion controlled (39). For such diffusion controlled processes, agitated contactors are an appropriate choice; since, apart from generating high transfer area, agitation should also reduce the resistances of the individual phases. It is particularly applicable when most of the resistances are in the continuous phase. Only two rotary agitated contactors were in fact selected for use in this

Table 3.3

CONTINUOUS DIFFERENTIAL CONTACTORS

CONTACTOR	TYPE	COMMENT
1. R.D.C.(23)	Axially located discs in compartments separated by stator rings and driven by a central shaft.	Operation reasonably flexible; efficiency not much affected by phase flow ratio; H.E.T.S. is remarkably low, around 20 per cent of that for a simple packed tower. Hydrodynamics and mass transfer characteristics are well defined.
2. A.R.D.C.(24, 25)	Similar to the R.D.C. except that the rotar is off-set from the column axis; separation of phases take places in a shielded transfer section.	Mixing and separating zones claim to reduce backmixing; but phase entrainment does occur in settling zone reducing overall efficiency(29). No special advantages over R.D.C.
3. Oldshue Rushton(26)	Vertical column divided into compartments by horizontal stator rings with vertical baffles in each compartment. Impeller in each compartment driven by a central shaft.	Coalescence-redispersion is predominant. Stage efficiencies obtained by Oldshue and Rushton varied from 40 to 90%. H.E.T.S. was nearly half , that of a simple packed tower of same diameter.
4. Ziehl Extractor(27	Vertical column terminating at top and bottom in large vessels to assist settling. The stirring mechanism consists of a shaft fitted with a number of star-shaped impellers. Vertical, reciprocal, as well as rotary motion, is imposed on the impellers for effective mixing.	Theoretical efficiencies claimed to have been attained in the manufacture of phenol formaldehyde resin (27). No mass transfer data is available.

Table 3.3 (Continued)

CONTACTOR	TYPE	COMMENT
5. Scheibel Column(28)	Consists of alternate fully-baffled mixing sections and packed sections. Agitation is provided by centrally located impellers.	Coalescence-redispersion is predominant. Mass transfer coefficient is related by, $Ka = C(\frac{\Delta\rho}{\sigma})^{1.5}$. Capacity is limited by the permissible flow rate through the packing.
6. Khüni Extractor (30)	Incorporates the principles of R.D.C., Oldshue Rushton and sieve plate columns. The column is divided into compartments by plates perforated only at the centre so that flow from one compartment to the next is directed towards the agitator. Each compartment has four vertical baffles. Impeller agitator is provided. End sections are large for effective settling.	Published mass transfer data are limited. Capacity and scale-up are expressed by, $\frac{d}{D} = C.Re^{0.61}.We^{0.6}.Fr.^{0.05}$. The design allows for only low throughputs. Modified designs have found limited application(31).
7. Pulsed Columns(32)	Phases are interdispersed by inducing a pulsating motion either by means of diaphragm pump or a valveless piston. A variety of internal packing or baffles may be used. In one design the plates are pulsed.	Commercial application is limited. Employed in the extraction of metals from radioactive solutions. Power requirements are high. No published information is available for scale-up. Mass transfer data have been reported by various authors(32,33,34).
8. Centrifugal Extractor (35,36)	Rapid countercurrent flow of the phases is effected by inducing large centrifugal forces. The Podbielniak extractor belongs to this class and consists of a horizontal shaft on which is mounted a rotating drum containing perforated concentric cylinders.	Highly efficient contacting is obtained, but high costs have limited the use. Have found use in the pharmaceutical industry and in petroleum refining operations (37,38). No published mass transfer data is available.

investigation, viz, the Rotating Disc Contactor and the Oldshue Rushton Contactor. The reasons for this were,

1. As is clear from Figure 3.1, the R.D.C. is a low energy contactor and is therefore capable of handling liquid-liquid systems of low interfacial tension whilst the Oldshue Rushton Contactor, being essentially a high-energy device, is versatile in treating high interfacial tension systems. At the same **rotor** speed and diameter the energy dissipation in an R.D.C. is only about one eightieth of that in the Oldshue Rushton Contactor (40). Thus there was no restriction to the physical properties of the liquid-liquid systems within the range likely to be investigated.
2. The R.D.C. has found extensive industrial application and both column hydrodynamics and mass transfer phenomena have been reasonably established. Both past (26,41,42) and recent studies (40,43,44) have indicated that Oldshue Rushton Contactor is an efficient contactor; high mass transfer coefficients have been reported (40,44).
3. Little significant work has been reported for other rotary agitated contactors. Very little information is available as to their mass transfer characteristics.
4. Studies involving the R.D.C. and the Oldshue Rushton Contactor have so far been limited to physical extraction processes and no work has been reported regarding hydrodynamic phenomena and efficiencies when used for liquid-liquid extraction involving chemical reaction.

4. SELECTED ROTARY AGITATED CONTACTORS

4.1 Rotating Disc Contactor

The R.D.C. was first introduced by Reman (23) in 1951, and finds wide application in the petroleum industry. It was originally employed for the extraction of lubricating oils from crude oil using furfural as solvent(23);subsequently,it has been used in various petroleum extraction processes (45) and in the organic chemical industries (46).

It comprises a vertical cylindrical shell divided into a number of compartments by a series of stator rings. A rotating disc supported on a central shaft is located centrally in each compartment. The feed stream inlets are arranged tangentially in the direction of rotation at each end of the column; the outlets are via the top and bottom of the column. Countercurrent flow by gravity is effected by introducing the denser phase into the top and the lighter phase into the bottom of the column, generally via a distributor. One phase is dispersed by the action of the rotating discs. An interface is maintained either at the top or bottom of the column dependent upon which phase is dispersed. A typical R.D.C. is shown in Figure 4.1.

For optimum design the column dimensions have the following ratios (47,48,49,50,51),

$$\frac{S}{D_C} = 0.66 - 0.75$$

$$\frac{D}{D_C} = 0.5 - 0.66$$

$$\frac{H}{D_C} = 0.33 - 0.5.$$

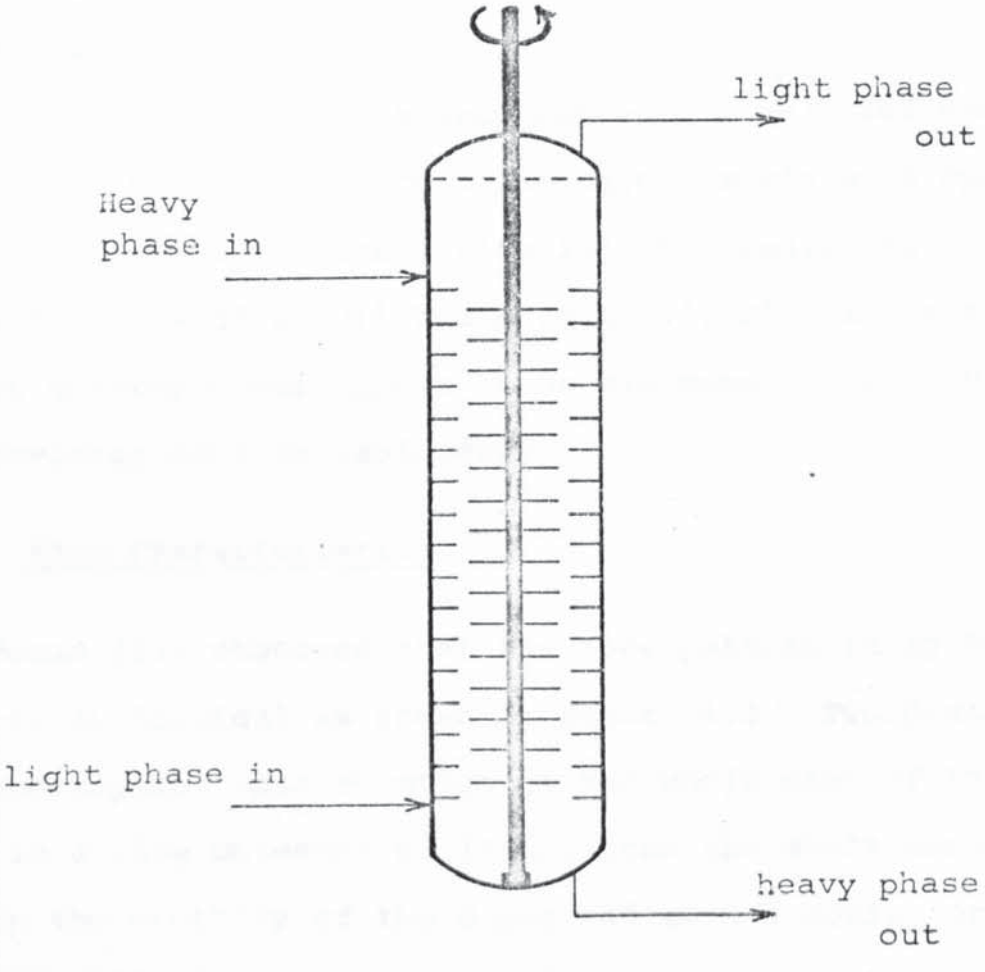


Fig. 4.1 Rotating Disc Contactor

The versatility of this contactor is established because of,

1. The power transmitted to the fluids need not be of a high order and is controllable. Therefore it is well suited for use with systems of low interfacial tension and density difference (51).
2. Ease of construction so that capital cost is low for a given capacity (23).
3. The flow pattern and hydrodynamics are well defined. The results of research on a laboratory scale unit have been used relatively successfully for the prediction of performance of a full scale unit (51,52). In fact, however, any discrepancies appear to be overcome in practice by the provision of a variable drive.

4.1.1 Flow Characteristics

Reman (53) observed that the flow pattern in an R.D.C. is essentially toroidal as shown in Figure 4.2. Two distinct flows are superimposed upon rotation of the whole mass of the liquid. There is a slow movement of liquid from the shaft towards the wall in the vicinity of the discs and also a motion originating from the wall of the column and flowing towards the shaft in the vicinity of the stator rings. These flow characteristics result in recirculation and backmixing of both liquids.

A similar flow pattern was also reported by Kung and Beckmann (48) but they observed that backmixing became insignificant below an impeller Reynold's number of 7.5×10^4. This is illustrated in Figure 4.3 and the backmixing flow pattern is shown in Figure 4.4.

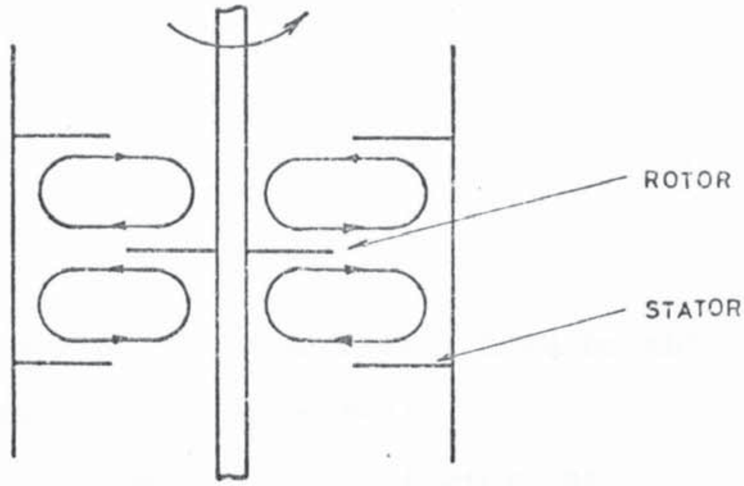


Fig. 4.2 Idealised flow pattern in a rotating disc contactor

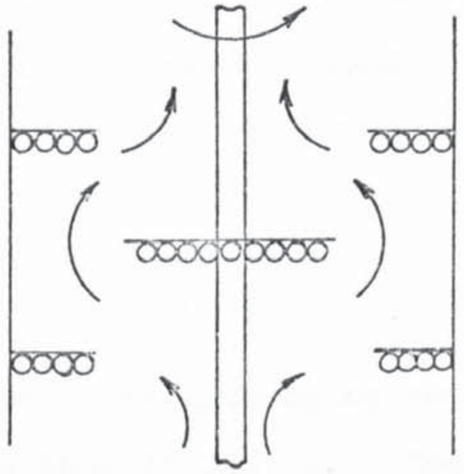


Fig. 4.3 Dispersed phase flow pattern ($Re<7.5x10^4$) in R.D.C. System Toluene-Water.

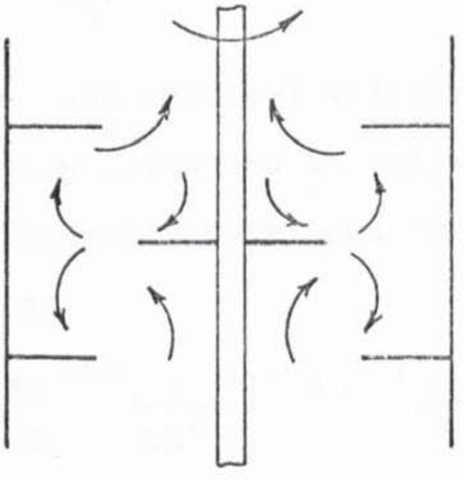


Fig. 4.4 Dispersed phase flow pattern ($Re>7.5x10^4$) in R.D.C. System: Toluene-Water

4.1.2 Hydrodynamics

4.1.2.1 Hold-up

In order to determine the interfacial area of the dispersion either of the following should be known:

(i) the drop residence time in the contactor, or

(ii) the fraction of the column volume occupied by the dispersed phase i.e. the dispersed phase hold-up. In agitated contactors, the residence time distribution is rather complex and dispersed phase hold-up is therefore usually used for the estimation of interfacial area. The interfacial area is expressed in terms of hold-up by;

$$a = 6 \frac{x}{d_{32}} \qquad 4.1$$

Hold-up increases with increasing rotar speed and dispersed phase flow rate (51,54,55). Logsdail et.al. (49) studied various two phase systems in the R.D.C. and related hold-up by,

$$\frac{V_d}{x_d} + \frac{V_c}{1-x_d} = V_N(1-x_d) \qquad 4.2$$

V_N is defined as the mean vertical velocity of the drops at substantially zero flow rates and at rotor speed N. A correlation was subsequently developed to relate V_N to system and column properties,

$$\frac{V_N \mu_c}{\sigma} = 0.012 \left(\frac{\Delta\rho}{\rho_c}\right)^{0.9} \left(\frac{\sigma}{DN^2}\right)^{1.0} \left(\frac{S}{D}\right)^{2.3} \left(\frac{H}{D}\right)^{0.9} \left(\frac{D}{D_c}\right)^{2.7} \qquad 4.3$$

In a later study, Kung and Beckmann (48) observed that hold-up increased with decreasing stator opening and compartment height and increasing disc diameter and rotor speed. A modified form of equation 4.2 was proposed,

$$\frac{V_d}{x_d} + \frac{K_1 V_c}{1-x_d} = V_N(1-x_d) \qquad 4.4$$

where K_1 is a geometric factor and has the value,

$$K_1 = 1.0 \text{ at } \frac{S-R}{D} > {}^1/24$$
$$= 2.1 \text{ at } \frac{S-R}{D} \leqslant {}^1/24.$$

At rotor speeds greater than 1.5m/sec, V_N was correlated by,

$$\frac{V_N \mu_c}{\sigma} = K_1 \left(\frac{\Delta\rho}{\rho_c}\right)^{0.9} \left(\frac{g}{DN^2}\right)^{1.0} \left(\frac{S}{D}\right)^{2.3} \left(\frac{H}{D}\right)^{0.9} \left(\frac{D}{D_c}\right)^{2.6} \qquad 4.5$$

where the value of $K_1 = 0.012 - 0.0225$.

Repeated droplet coalescence and break-up may occur in the R.D.C. dependent upon the energy input and system properties. The equations discussed above make no allowance for this effect. Misek (56) attempted to include the effect in the equation,

$$\frac{V_d}{x_d} + \frac{V_c}{1-x_d} = V_N(1-x_d)\exp\left[x_d(Z/M - 4.1)\right] \qquad 4.6$$

where Z = a coalescence coefficient strongly influenced by hold-up and hence the number of collisions resulting in coalescence. However, equation 4.6 found limited use owing to the strong dependence of the factor Z on the system properties. In a subsequent study, Misek (57) proposed a modified expression,

$$\ln\left(\frac{d}{d_o}\right) = 1.59 \times 10^{-2}(Re^*)^{0.5} x_d = Z x_d \qquad 4.7$$

where $Re^* = \left(\frac{D\mu_c}{\rho_c}\right)\left(\frac{\sigma}{\rho_c d_o}\right) \qquad 4.8$

However, the rate of drop interaction is very much influenced by the liquid-liquid system properties, column geometry and the level of energy transmission. At low hold-up, coalescence effects are significant even in the discharge region of the impeller (58). It appears therefore that the use of this Z factor is rather oversimplified and the applicability of equations 4.6 and 4.7 remains to be proven.

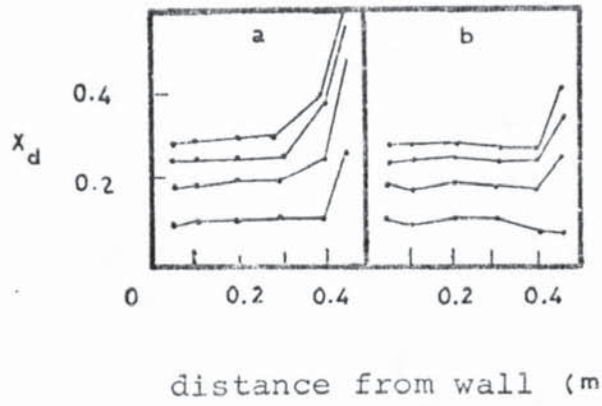
Hold-up Profile

Hold-up in the R.D.C. varies in both the radial and axial direction (47,48,49,50). The variation in the radial direction is generally insignificant in small columns(55).

Results from a 1.07m R.D.C., however, reproduced as Figures 4.5 and 4.6 showed that the hold-up in the radial direction remained fairly constant except in the vicinity of the rotor shaft (50). Hold-up in the axial direction was found to increase up the column, probably because a finite time is required for drop break-up. Hold-up decreased, however, towards the end of the column owing to the competing effects of axial diffusion of drops in the contact zone and of drop discharge into the settling zone.

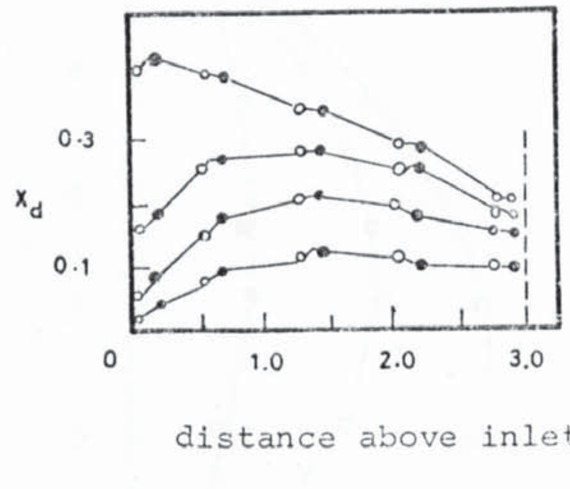
Rozkos (59) observed similar effects in an industrial R.D.C.; from the results reproduced in Figures 4.7 and 4.8, the maximum hold-up point corresponded to approximately the middle of the 'effective' column.

Rod (60) obtained similar results in subsequent work and derived a mathematical model on the basis that hold-up was determined by the twin effects of droplet break-up in the mixed section and longitudinal mixing of the dispersion. It



Compartment 9
a. 0.0625 m above stator
b. 0.0625 m below stator
rotor speeds 130, 150, 160 and 170 rpm

Fig. 4.5 Radial profile of hold-up, 1.08 m R.D.C, system: water-toluene



○- 0.0625 m above stators
●- 0.0625 m below stators
rotor speeds 130, 150, 160 and 170 rpm

Fig. 4.6 Axial profile of hold-up in 1.08 m R.D.C. system water-toluene

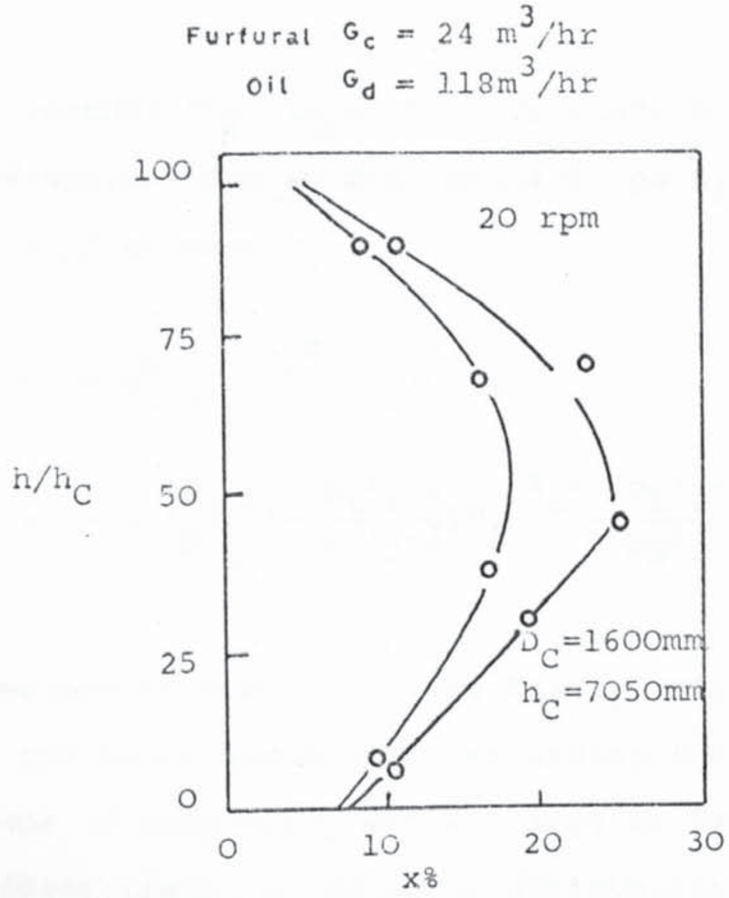


Fig. 4.7

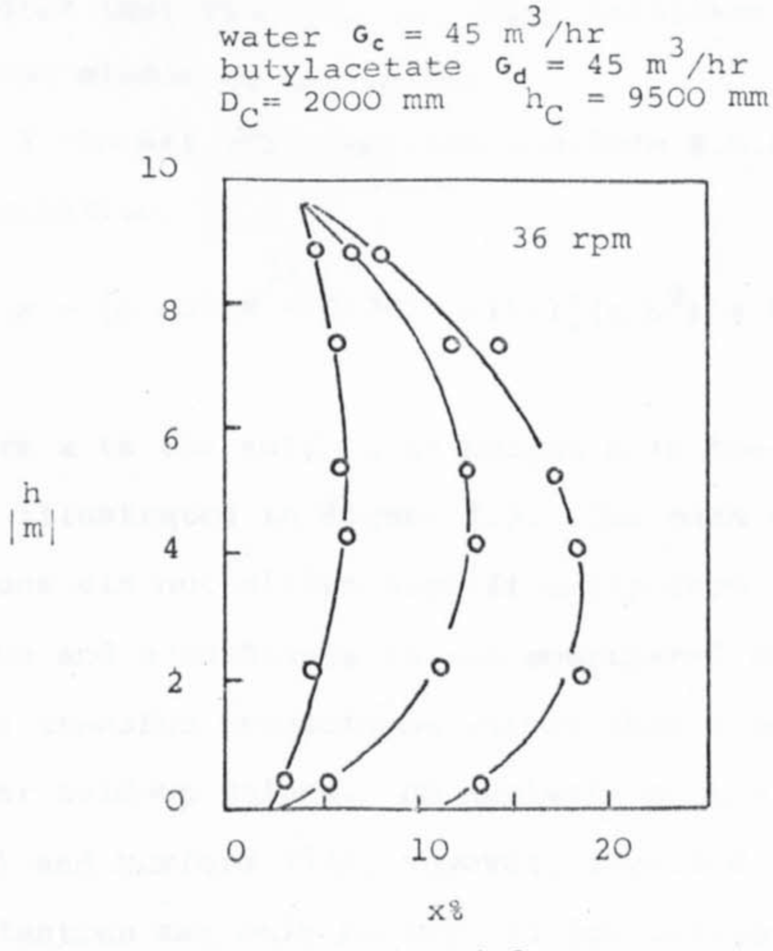


Fig. 4.8

Hold-up profile in an R.D.C.

was assumed that total hold-up consisted of two individual hold-ups, one due to the larger drops x_1 and the other due to the smaller ones x_2,

$$x_1 = x_1^o \left[C_1 e^{\lambda_1 Z} + C_2 e^{\lambda_2 Z}\right] \qquad 4.9$$

$$x_2 = x_1\left(\frac{p_2}{p_1}\right)\left[1-\left(\frac{p_1\lambda_1-1}{p_2\lambda_2-1}\right)C_1 e^{\lambda_1 Z}-\left(\frac{p_1\lambda_2-1}{p_2\lambda_2-1}\right)C_2 e^{\lambda_2 Z}+C_3 e^{-\left(\frac{1-Z}{p_2}\right)}\right] \qquad 4.10$$

Experimental results agreed fairly well with the above model but the basic assumption, regarding the presence of two groups of drop size, either large or small, is of doubtful validity since the dropsize distribution is not simple (54,55). It is interesting to note however, that the model appears to predict that flooding and phase inversion will occur first in the middle of the column.

Al-Hemeri (55) operated a 0.102m R.D.C. and proposed the correlation,

$$x = \left[0.0013N + 0.38(V_d-1)-1\right](h-h^2) + 0.076(1-1/V_d) \qquad 4.11$$

where x is the hold-up at height h in the column. The results are illustrated in Figure 4.9. The mean of point hold-up values did not differ significantly from the above hold-up value and accordingly it was considered suitable for use in mass transfer predictions rather than a consideration of point hold-up values. An analysis of the work done by Rod (60) and Mumford (54), however, revealed that the above contention may only be true at low values of dispersed phase flow rate and rotor speeds.

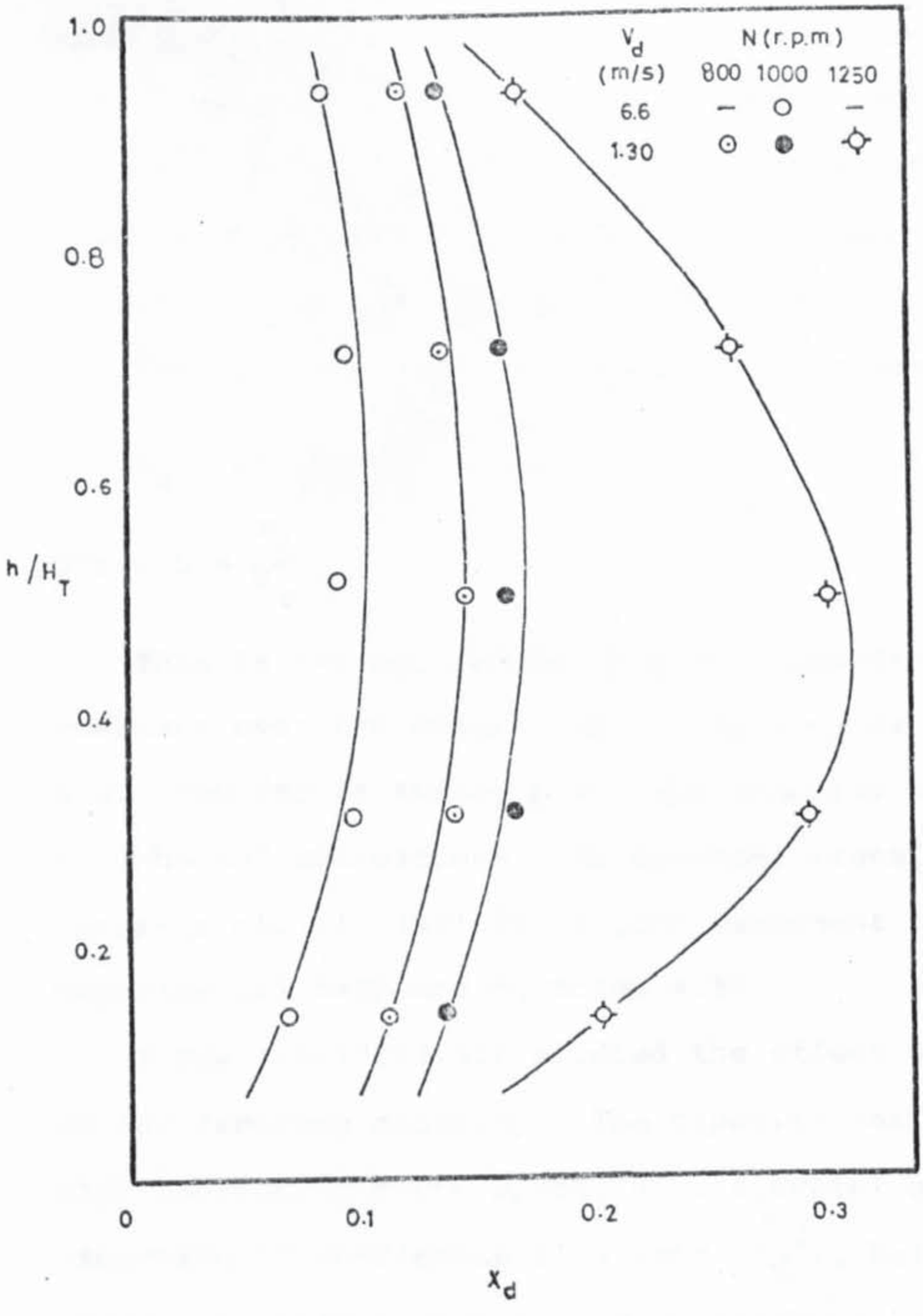


Fig. 4.9 Hold-up profiles in an R.D.C

4.1.2.2 Flooding

"Flooding" is a typical hydrodynamic phenomenon particularly associated with differential contactors. For each flow rate of one phase, there is a corresponding maximum practical flow rate of the other phase. This maximum depends upon the system properties and the design of the contactor. Flow in excess of the maximum causes either of the liquids to be rejected by the equipment. This is termed "flooding".

The hold-up values at flooding are given by (49),

$$x_d = \frac{(L^2 + 8L)^{0.5} - 3L}{4(1-L)} \qquad 4.12$$

where $L = \frac{V_d}{V_c}$.

This is not applicable when the mean dropsize is not constant over the entire hold-up region, as for example, when mass transfer is taking place and dropsize may increase owing to enhanced coalescence. In non-mass transfer studies, however, Thornton et. al. (49) found good agreement between their experimental data and equation 4.12.

Reman (23,47,53,61) studied the effect of system variables on the limiting capacity. The capacity was found to decrease with increasing rotor speed, disc diameter and ratio of dispersed to continuous flow rate $(\frac{V_d}{V_c})$, but to increase with increasing stator opening and compartment height. The capacity data obtained were correlated by considering energy input/volume (N^3D^5/HD_c^2) as determining the dropsize of the dispersed phase. A constriction factor C_R was introduced to allow for the effect of constrictions on settling of the drops. C_R was defined as the minimum of the three area ratios $(\frac{S}{D_c})^2, (1- \frac{D}{D_c})^2$

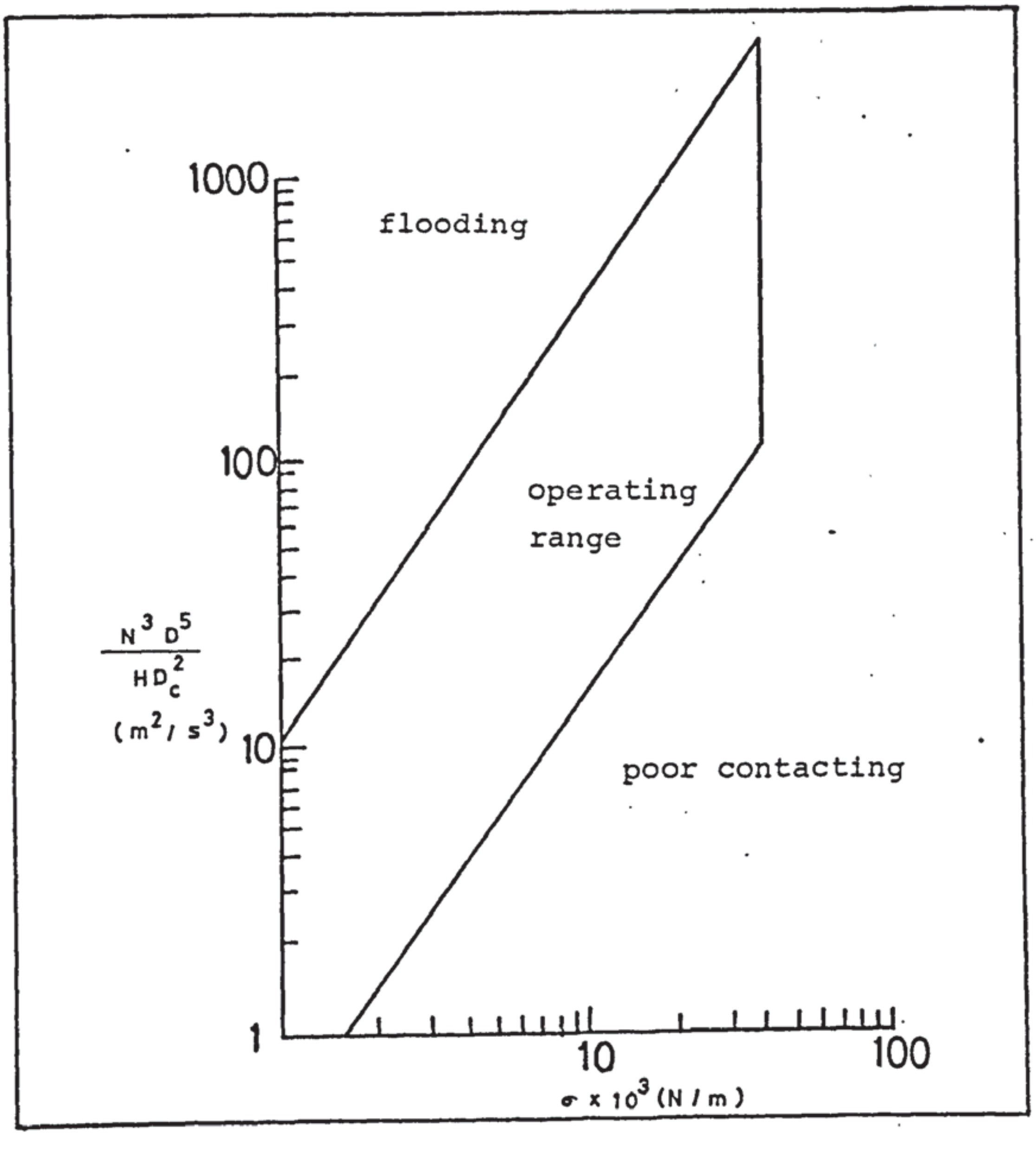


Fig. 4.10. R.D.C. power input group operating range

and $(\frac{S+D}{D_c})$ $\sqrt{(\frac{S-D}{D_c})^2+(\frac{H}{D_c})^2}$.

This correlation is inconclusive because physical properties are not included e.g., interfacial tension which is an important factor determining dropsize and hence settling rates and the volumetric capacity of the contactor. An approximate guide to operating range is presented in Figure 4.10.

4.1.2.3 Phase Inversion

Under certain conditions when the dynamic equilibrium between droplet break-up and coalescence is shifted towards the latter, phase inversion may occur. This is characterised by the continuous phase becoming dispersed and vice versa. Phase inversion characteristics of an R.D.C. are discussed in detail in Chapter 5.

4.1.3 MASS TRANSFER

The prediction of mass transfer performance of a differential column usually involves the evaluation of the height of a transfer unit and the number of transfer units. There are three definitions of a transfer unit (62),

(i) The true number of transfer units,

$$(N.T.U.)_t = \int_{x_o}^{x_1} \frac{Kadx}{G_c} \tag{4.13}$$

(ii) The apparent number of transfer units,

$$(N.T.U.)_a = \int_{x_o}^{x_1} \frac{dx}{x^1-x^*} \tag{4.14}$$

where $y = mx^*$.

(iii) The measured number of transfer units,

$$(\text{N.T.U.})_m = \int_{x_0}^{x_1} \frac{dx}{x-x^*} \qquad 4.15$$

The height of a transfer unit is given by the expression,

$$(\text{H.T.U.}) = \frac{G}{K_L aS} \qquad 4.16$$

The theoretical stage concept uses the fact that the amount of mass transfer taking place in a contactor may be regarded as a number of discrete equilibrium contacts. The height required for one contact is then analogous to height equivalent to a theoretical plate utilised in distillation column analysis. An efficiency may be used to express equipment performance, defined as the H.E.T.S., divided by the height of a practical stage. Although used in practice, this approach is of course fundamentally unsound when applied to a differential mass transfer operation.

In any event any attempt to calculate the equipment performance, expressed in terms of the terminal concentrations, will include any deviations from ideal behaviour. Thus, the $(\text{N.T.U.})_a$ and $(\text{N.T.U.})_m$ are only valid for the conditions prevailing at the time of measurement, and in the specific equipment used. The prediction of the interfacial area and the extent of both radial and longitudinal mixing involve many empiricisms which result in the estimation of contactor performance being only approximate.

Mass transfer studies in the R.D.C. have been carried out by various workers and the effect of different parameters on the overall efficiency assessed. Reman and Olney (47) observed that efficiency increased with increasing specific load, peripheral speed, and ratio of dispersed to continuous phase

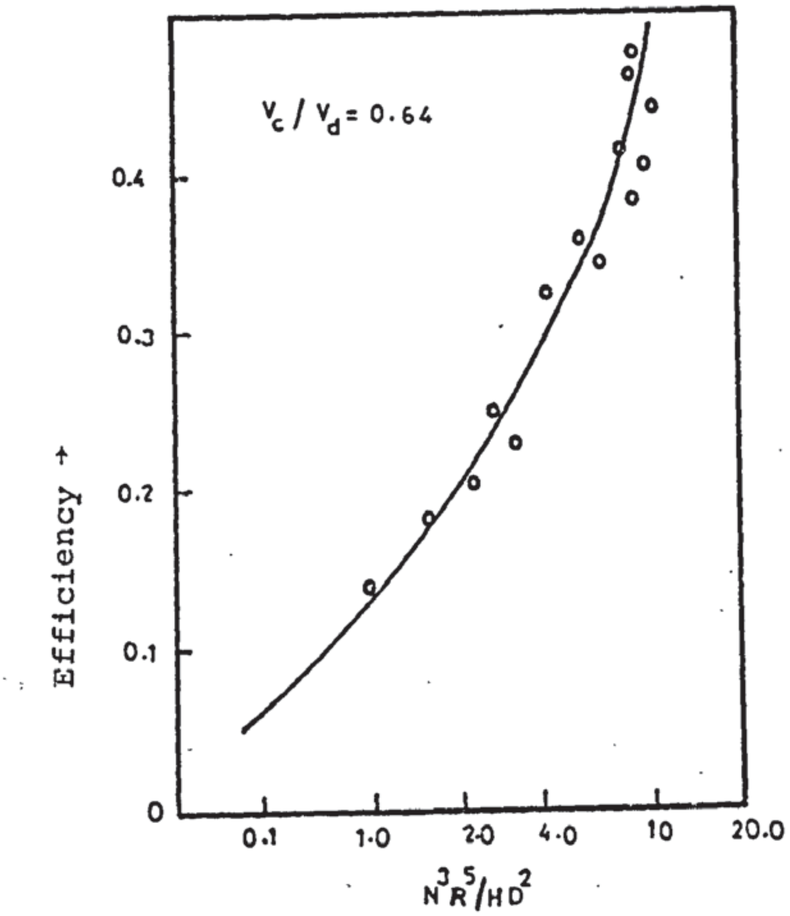


Fig. 4.11 Efficiency for system water - kerosene - butylamine

flow rate but decreased with decreasing stator opening and compartment height. They also found that enhanced backmixing reduced the efficiency at high rotor speeds and specific loadings. Data was interpreted by plotting efficiency against power input as illustrated in Figure 4.11. This is of doubtful validity, however, since system properties and the effect of axial mixing were not considered.

In subsequent work Logsdail et. al.(49) employed the systems toluene-acetone-water and butylacetate-acetone-water and produced a correlation of the form,

$$\left(\frac{(H.T.U.)_{oc}}{V_c}\right)\left(\frac{g^2\rho_c}{\mu_c}\right)^{1/3}(x_d) = \left(\frac{x_d}{K_{oc}a}\right)\left(\frac{g^2\rho_c}{\mu_c}\right)^{1/3} = K\left(\frac{\mu_c g}{V_N{}^3(1-x_d)^3\rho_c}\right)^{2m/3}$$

$$\times\left(\frac{\Delta\rho}{\rho_c}\right)^{\frac{2(m-1)}{3}} \qquad 4.17$$

The constant K, exponent m and velocity V_N were determined by experiment. An accuracy to within 20% was obtained. Unfortunately, this correlation is of little practical significance since it is specific to the equipment and experimental conditions used in the investigation.

In a recent study, Al-Hemeri (55) interpreted mass transfer data by comparing observed mass transfer coefficients with values calculated assuming the stagnant drop, circulating drop, oscillating drop and fresh surface models (63). Generally best agreement was obtained with the last two models. It was suggested that the total mass transfer comprised the net effect of a large number of oscillations and complete cycles of formation and coalescence. On this basis, he developed the expression,

$$\sum_{n=1}^{n}\left[\sum_{i=1}^{i}\int\left[\frac{dx}{x-x^*}\right]_i\right]_n = \sum_{n=1}^{n}\left[\sum_{i=1}^{i} A_i/V_i\int K_i dt\right]_n \qquad 4.18$$

where i refers to any particular phenomenon, i.e., drop formation, drop oscillation etc., and n is the compartment number. The above mass transfer model relies on the single drop correlations for transfer coefficients and therefore its application to an agitated interfacing multidrop system is of doubtful validity.

The importance of allowing for backmixing in all mass transfer calculations involving the R.D.C. has been realised for some time. Backmixing is either expressed by a dispersion coefficient or by a backmix ratio. A number of correlations by various authors are summarised in Table 4.1. The correlation by Miyauchi (67) is applicable to both the R.D.C. and Oldshue Rushton columns and the data of various workers has been tested against it and presented in the form of a graphical analysis in Figure 4.12.

Olney (69) introduced the concept of axial dispersion in the R.D.C. and the following mass transfer models were proposed,

(i) For the continuous phase,

$$E_c \frac{d^2y}{dZ^2} + \frac{V_c}{1-h}\frac{dy}{dZ} = -\frac{6h}{1-h}\int_{d_o}^{d_m} \frac{K_D(d)}{d} f(d)\left[x(d)-my\right]\delta(d) \qquad 4.27$$

(ii) For the dispersed phase,

$$E_d \frac{d^2}{dZ}\int_{d_o}^{d_m} x(d)\, f(d)\, \delta(d) - \int_{d_o}^{d_m} \frac{mK_D(d)}{d} f(d)\left[x(d)-my\right]\delta(d) \qquad 4.28$$

where f(d) is a function representing the drop size distribution in the column.

No analytical solution is available for the solution of equation 4.27 and 4.28 so that a numerical solution is necessary. The other limitations are the dependence on empiricisms for values of the dispersion coefficient and the drop size

Table 4.1

BACKMIXING CORRELATIONS

	AUTHOR	EQUATION NUMBER	EQUATION	COMMENT
1.	Strand et. al. (50)	4.19	$\frac{(1-x_d)E_c}{V_c H} = 0.5+0.09(1-x_d)(\frac{DN}{V_c})(\frac{D}{D_c})^2[(\frac{S}{D_c})^2-(\frac{D}{D_c})^2]$	Fair agreement in a 6 inch R.D.C. Misek found in an industrial R.D.C variation of 27-55% in E_c E_d values (68).
		4.20	$\frac{x_d E_d}{V_d H} = 0.5+0.09x_d(\frac{DN}{V_d})(\frac{D}{D_c})^2[(\frac{S}{D_c})^2(\frac{D}{D_c})^2]$	
2.	Stemerding (64)	4.21	$E_c = 0.5\ H\ V_c + 0.012\ D.N.H.(\frac{S}{D})^2$	Only applicable at high Reynold's number.
3.	Westerterp and Landsman(65)	4.22	$E_c = E_D\ [\frac{2n}{1+13x10^3\frac{ND}{F_c}}]$	When compared to values by Strand et.al.(50), E_c is 15% higher and values of E_d did not apply.
4.	Misek (66)	4.23	$f = ND[0.00434(\frac{S}{D_c})^2 + 0.0246(\frac{D}{D_c})^2 - 0.002]$	Agreement is worse for larger columns (66)
5.	Miyauchi et. al. (67)	4.24	$f = 4.3x10^{-3}ND\ (\frac{D_c}{H})^{\frac{1}{2}}(\frac{D_c}{S})^{\frac{1}{4}}$ for $\frac{ND^2\rho_m}{\mu_m}>1.2x10^5$	Compared reasonably with previous experimental work (50).
		4.25	$f = 4.5x10^{-2}ND(\frac{D_c}{H})^{\frac{1}{2}}(\frac{D_c}{S})^{\frac{1}{4}}$ for $\frac{ND^2\rho_m}{\mu_m}<1.2x10^5$	
		4.26	$f = 0.017\ ND\ (N_p)^{0.333}(\frac{D_c}{H})^{0.5}$	Suitable for both R.D.C. and Oldshue Rushton.

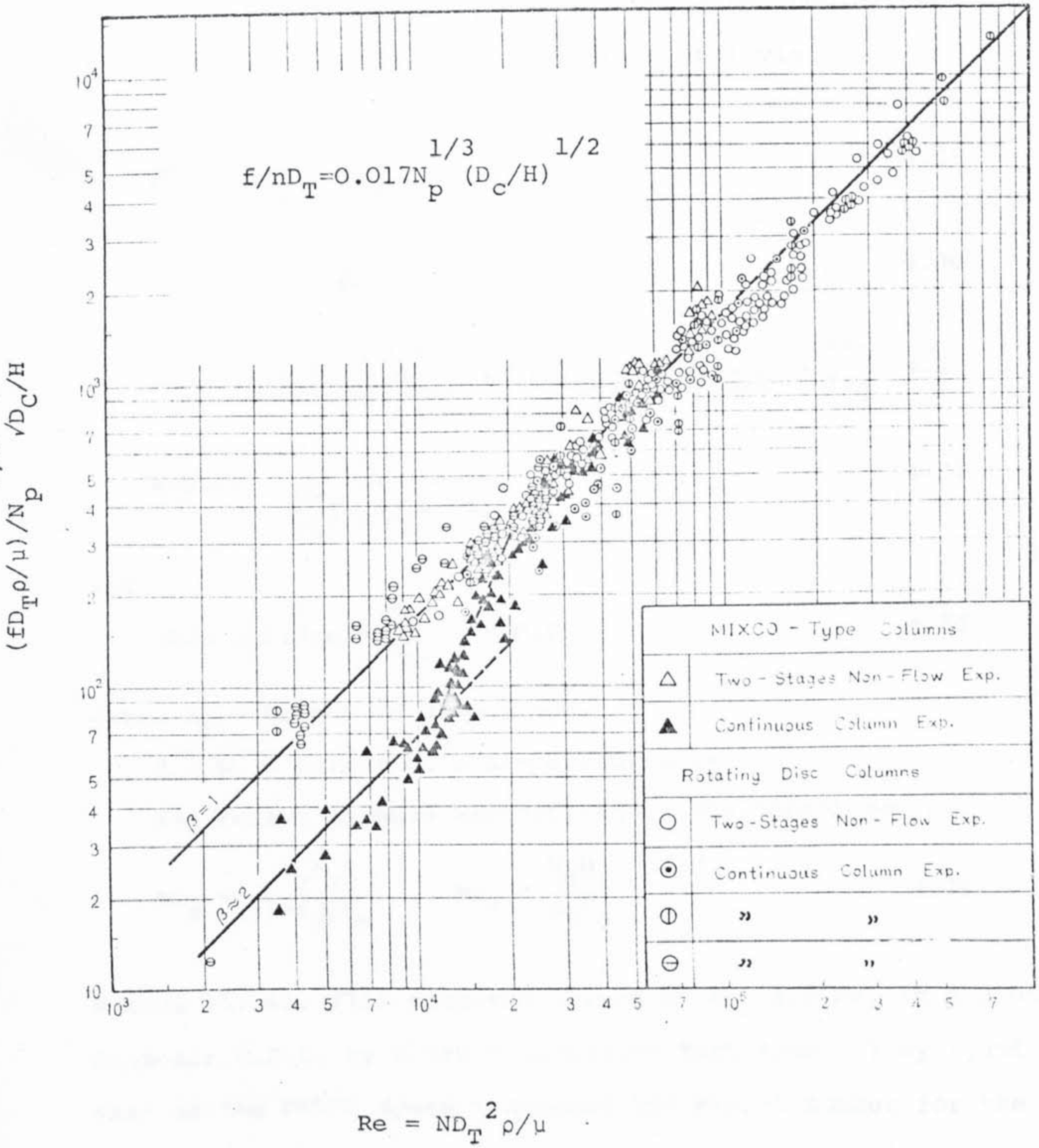


Fig. 4.12 Unified correlation for both of R.D.C and Mixco columns.

distribution, both of which are not accurately predictable.

More recently Bruin et. al. (70) calculated "true" H.T.U. values for cobalt extraction in a 0.06m diameter unit by modifying the values for plug flow using the Peclet number equations of Stemerding and Zuiderbeg (64) viz,

$$\frac{1}{Pe_1} = \frac{\varepsilon}{Pe_d} + \frac{1}{Pe_c} \qquad 4.29$$

$$\frac{1}{Pe_2} = \frac{1}{Pe_d} + \frac{\varepsilon}{Pe_c} \qquad 4.30$$

$$Pe_O = \left(\frac{(Pe_1)\ 0.1\ H}{(H.T.U.)\ true} + 1\right) / \left(\frac{0.1H}{(H.T.U.)\ true} + \frac{Pe_1}{Pe_2}\right) \qquad 4.31$$

$$H.D.U. = \frac{1}{\frac{Pe_O}{H} + \frac{0.8}{H_T}\,\frac{\ln\varepsilon}{\varepsilon-1}} \qquad 4.32$$

and

$$(H.T.U.)\,true = \frac{H_T}{N_{or}} - H.D.U. \qquad 4.33$$

where H_T = Height of dispersion.

H.D.U. = Height of a dispersion unit.

The Peclet numbers are defined in the normal way by,

$$Pe_c = \frac{V_c H_T}{(1-x_d)E_c} \quad , \quad Pe_d = \frac{V_d H_T}{x_d E_d} \qquad 4.34$$

Borrel et. al. (71) measured values of Pe_c and Pe_d in a 0.05m diameter R.D.C. by a trace injection technique. They found that as the rotor speed increased the Peclet number for the continuous phase increased, as expected, and that in two phase systems backmixing in the continuous phase was accentuated by the droplets present. The actual value of Pe_c varied between 40 and 20, depending upon rotor speed and flow rates.

From this review of the mass transfer characteristics, it is clear that allowance has never been made for hold-up variation along the contactor length which is rather important in predicting the effectiveness of an R.D.C. in mass transfer operations. Thus it would appear worthwhile to define and include this effect.

4.2 OLDSHUE-RUSHTON COLUMN

This extractor was first designed by Oldshue and Rushton (26) in 1952. It consists of a vertical column divided into compartments by stator rings. Each compartment has four vertical baffles and a four-bladed turbine impeller driven by a central shaft. The overall view is a series of open-ended stirred tanks arranged in a vertical sequence. This is illustrated in Figure 4.13. The stators serve to minimise interstage mixing, and the smaller the diameter of stator, the less interstage mixing occurs. This, however, has an adverse effect in that it simultaneously reduces the volumetric capacity. Gutoff (72) and Ingham (73) observed that backmixing was small at low rates of agitation ($Re < 2.5 \times 10^4$) but increased linearly with speed and the latter contributed more towards interstage mixing. However, the typical column dimensions as recommended by Oldshue and Rushton are,

$D_T : D_c = 1:3$; $D_T : D_d = 4:3$; $D_T : B_W = 4:1$

$D_T : B_h = 5:1$; $D_c : A_S = 3:1$ to $2:1$

$D_c : H = 2:1$; $D_T : b = 4:1$.

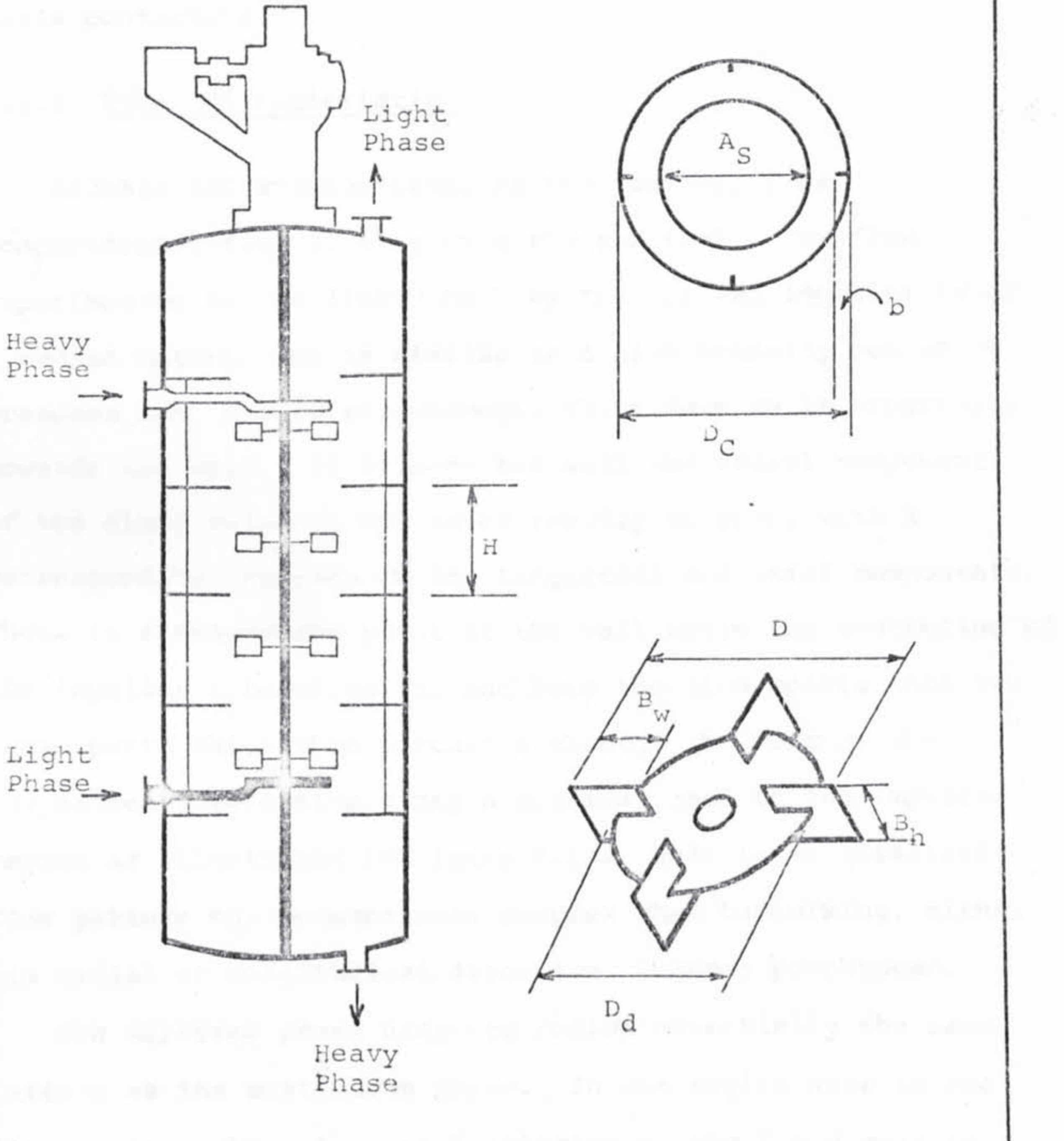


Fig. 4.13 Oldshue-Rushton Column

Industrial use of this contactor has been limited in the past owing to the lack of knowledge of mass transfer characteristics. The extraction of organics (43) and of Uranium (41,42)have been successfully carried out in large scale contactors.

4.2.1 Flow Characteristics

Oldshue and Rushton observed the similarity of compartmental flow to that in a stirred tank. The flow superimposed on the liquid mass by the turbine impeller is of a radial nature, and is similar to a high velocity jet which broadens and, due to entrainment, slows down as it progresses towards the wall. At or near the wall the radial component of the fluid velocity decreases rapidly to zero, with a corresponding increase in the tangential and axial components. There is a stagnation point at the wall where the centreline of the impeller intersects it, and here the flow splits into two equal parts which then circulate through the rest of the compartment, returning along a toroidal path to the impeller region as illustrated in Figure 4.14. This is an idealised flow pattern but becomes more complex when backmixing, either via radial or longitudinal direction, becomes pronounced.

The dipersed phase droplets follow essentially the same pattern as the continuous phase. In the region near to the stator ring, where the axial velocity of the fluid mass is low and the drop terminal velocity is in excess of the continuous phase flow, interstage flow of dispersed phase takes place. This sequence is repeated up the column and the droplets pass through the compartments and finally reach the coalescing

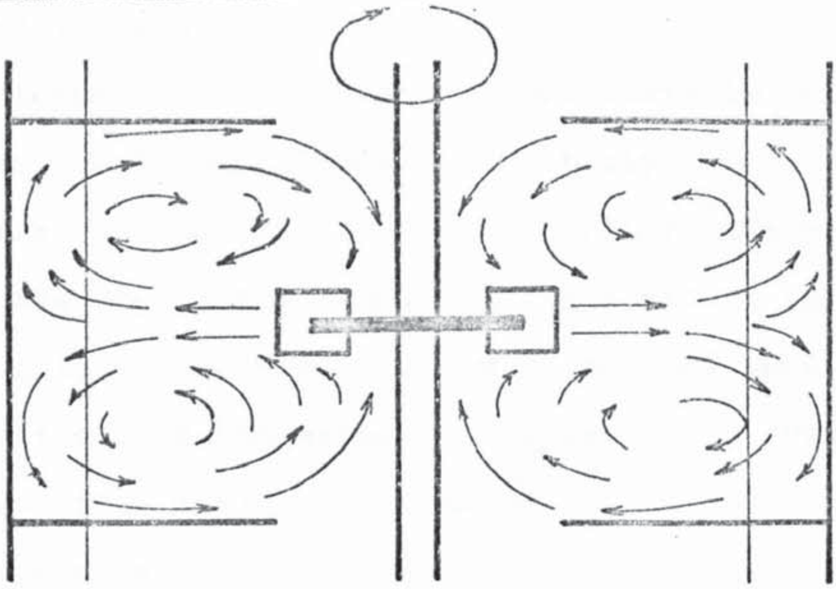


Fig. 4.14 Compartmental flow

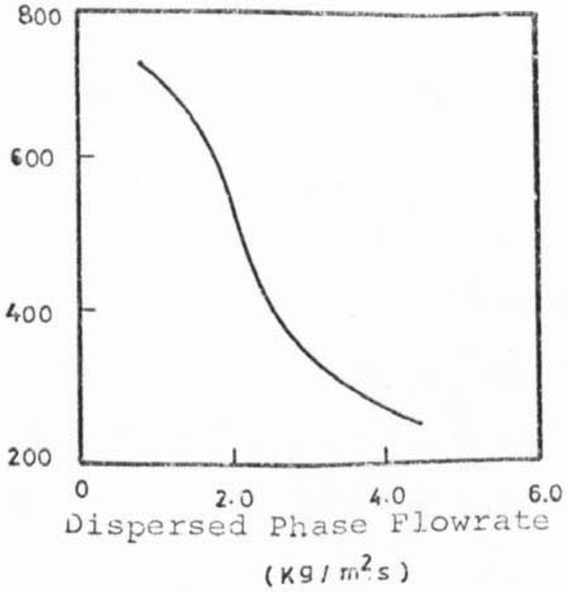


Fig. 4.15 Flooding in the O/R Column(26)

section of the contactor.

The Oldshue Rushton column cannot strictly be classed as either an ideal compartmental or a truly continuous differential contactor. As stated earlier, the compartments are separated by stator rings and the vertical component of drop velocity determines whether or not any specific drop will pass into the next compartment. Droplet size, system properties, flow ratio, power input and related factors e.g. coalescence effects control the life and motion of a drop through the contactor.

4.2.2 Hydrodynamics

4.2.2.1 Flooding

Oldshue and Rushton (26) found the flooding characteristics to be similar to those of other contactors such as the R.D.C. described earlier. In practice, for any particular total mass flowrate, the column should be operated at an impeller speed less than 90% of the "flooding" speed. Oldshue and Rushton found flooding to occur over a wide range of impeller speeds. Conversely Arnold (40) recently observed that at lower speeds capacity was limited because the relatively large drops (1 - 0.005m dia) were swept downwards from the distributor. by the high flowrate of continuous phase. Phase inversion at higher impeller speeds was caused by the formation of relatively smaller droplets having low terminal velocities and which could be swept downwards even by a relatively low continuous phase flow. The anomaly between these two studies was considerable. In fact phase inversion, a phenomenon discussed in Chapter 5, is a loading point with visual similarities to the onset of flooding. As a result it appeared possible that these phenomena had been confused in the detailed study by Oldshue and Rushton (26).

4.2.2.2 Hold-up and Drop Size

Hold-up in an Oldshue Rushton column was claimed to be correlated with column parameters by the equation 4.6,

$$\frac{V_d}{x_d} + \frac{V_c}{1-x_d} = V_N\ (1-x_d)\ \exp\left[x_d\left(\frac{Z}{M} - 4.1\right)\right] \qquad 4.6$$

Treybal (44) employed the familiar equation,

$$\frac{V_d}{x_d} + \frac{V_c}{1-x_d} = V_N\ (1-x_d) \qquad 4.2$$

where the characteristic velocity V_n was given by,

$$\frac{V_N \mu_c}{\sigma} = 1.77 \times 10^{-4}\ \left(\frac{g}{DN^2}\right)\left(\frac{\Delta\rho}{\rho_c}\right)^{0.9} \qquad 4.35$$

However, the above equations were found to be inapplicable in a later study (54).

Since drop size distribution is a major factor affecting hold-up characteristics of a column, some consideration must be given to it. There is a difference of opinion amongst various workers as to whether the drop size distribution in agitated columns is a log-normal or normal distribution. In a recent study Arnold(40) found the distribution to be log-normal in the case of Sauter mean diameters but normal for volume mean diameters. At low rotor speeds, the variation in the distribution was greater than at high speeds. Since there is a distribution of residence times for drops in each

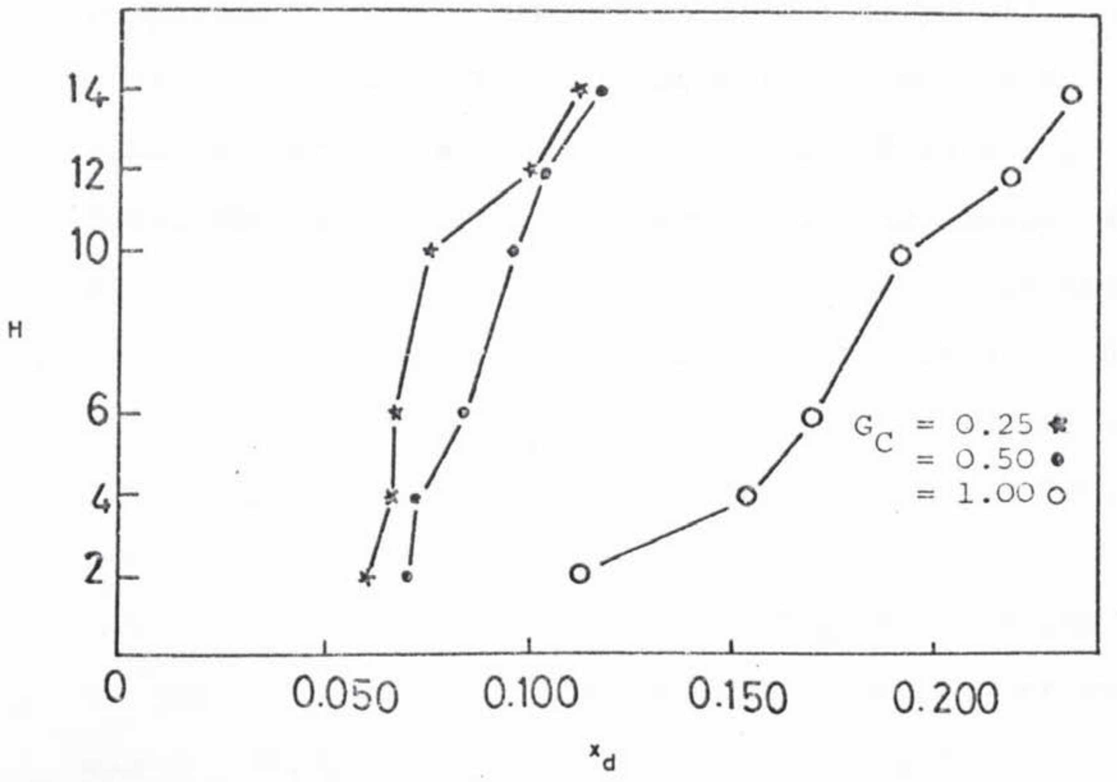


Fig. 4.16 Variation of hold-up with height, N = 350

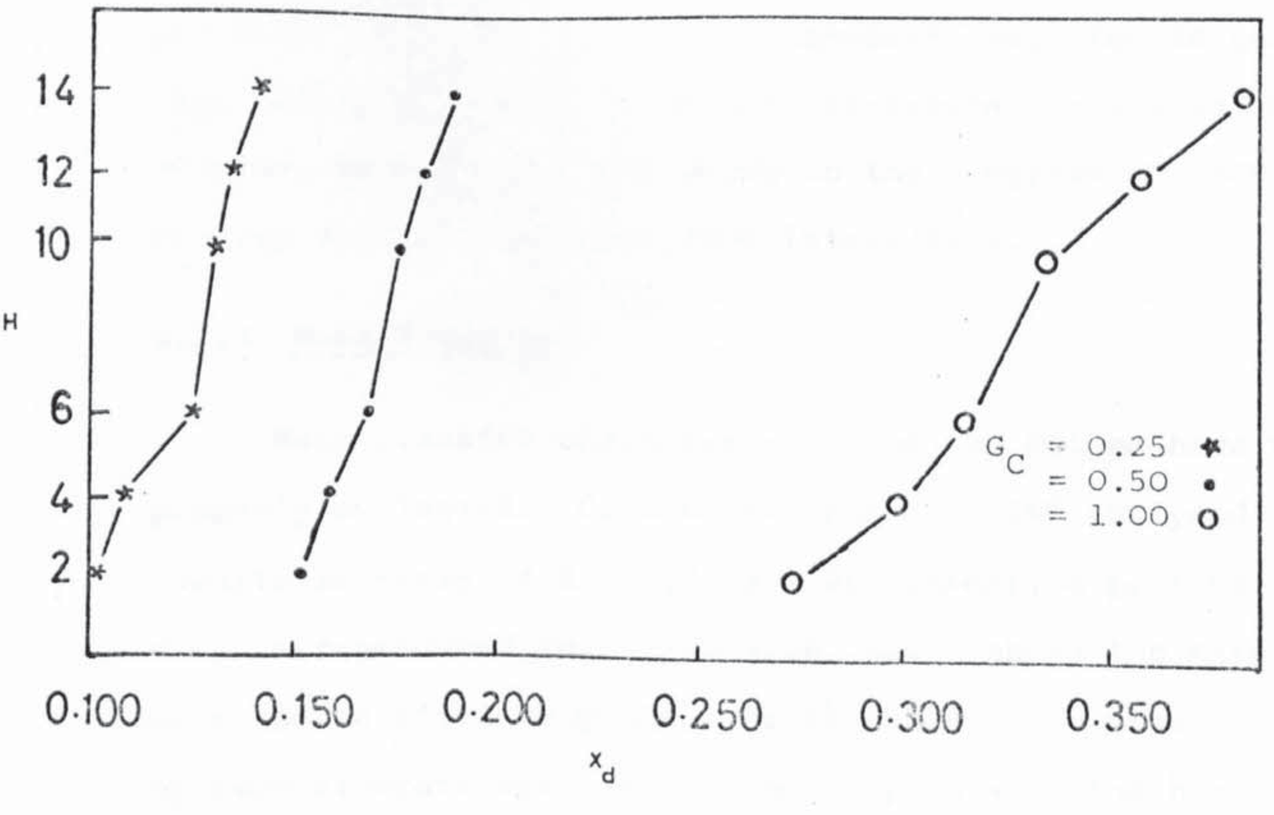
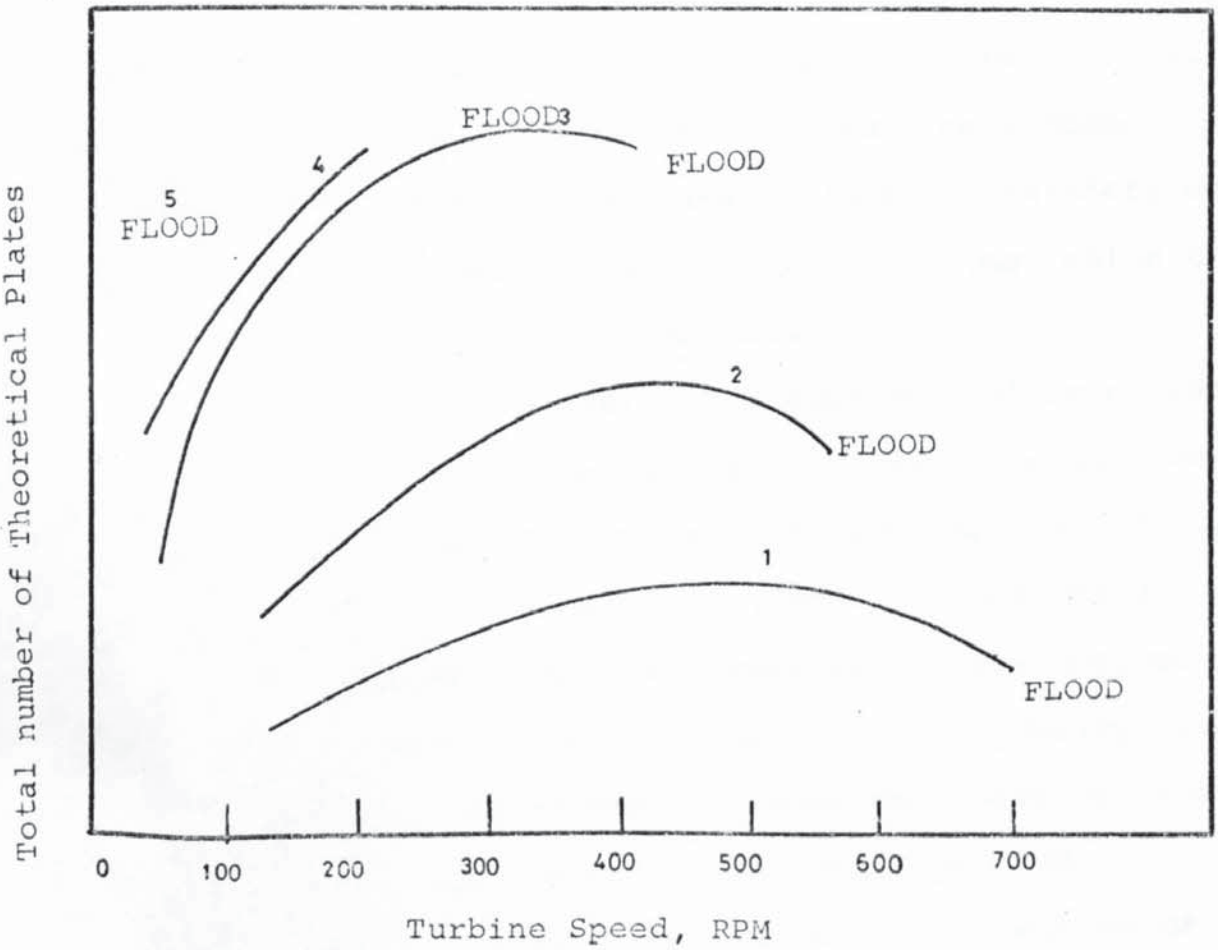


Fig. 4.17 Variation of hold-up with height, N = 500

compartment, only a proportion of the drops will spend a sufficient time in the discharge region of the impeller to cause break-up. When the impeller speed is high, the drop residence time in the discharge region is smaller than at lower speeds, but the number of drops passing through the region is much larger and the availability of energy for drop break-up is greater. That is, the hold-up is low at lower speeds but increases with increasing speed. A family of curves was obtained showing variation of hold-up with column height. Typical curves are illustrated in Figures 4.16 and 4.17. The hold-up was found to increase with column height in an erratic fashion but at higher impeller speeds the increase was approximately linear up the column. In the same study, hold-up values for mass transfer were found to be anomalous. In some cases hold-up was observed to decrease with column height whereas in others it increased. This inconsistency could not be explained. It is, however, expected in general that hold-up would increase with increasing height in an Oldshue Rushton contactor owing to the progressive decrease in drop size and enhanced drop-interaction.

4.2.3 Mass Transfer

Mass transfer characteristics of the column have not been properly evaluated. Oldshue and Rushton (26) analysed their results in terms of H.E.T.S. and efficiency; a plot of their data is reproduced in Figure 4.18, which shows the expected decrease in efficiency when the flowrate is decreased. The optimum flowrate was taken to correspond with the highest point in the family of curves provided flooding did not occur.



Flow rate increases from Run 1 to Run 5. Ratio of individual stream rates constant. All other conditions constant.

Runs 1,2 - Low flow rates. Maximum efficiency present
Run 3 - Optimum flow rate
Run 4 - Floods before maximum point is reached
Run 5 - Floods at no agitation

Fig. 4.18 Typical schematic diagram for effect of flow rate on stage efficiency (26)

These results alone are not adequate to predict the performance of a column. Furthermore, extrapolation from these results, obtained from specific experiment, would be valueless. In the above analysis, the dependent variables such as system properties, dropsize, coalescence and redispersion rates have not been considered. Evaluation of column performance is of no avail if the above factors are neglected. Further, no allowance was made for the effect of backmixing, which usually lowers the performance of a contactor.

Bibaud and Treybal (44) calculated the values of mass transfer coefficients K for the systems water-toluene and water-kerosine. The interfacial area was predicted from the dropsize correlation of Thornton (74). The results are thus of doubtful validity since this correlation was derived from an analysis of stirred tanks which differ significantly from a column. However, the calculated value of K were in reasonable agreement with those postulated for rigid spheres.

More recently, Arnold (40) studied the transfer of n-butyric acid between a two solvent system of water and toluene in a 0.15 m diameter contactor. Mass transfer coefficients were calculated on the basis of measured dropsizes. The number of transfer units measured from terminal concentrations were higher when transfer was from the continuous phase to the dispersed phase. It was pointed out that analysis of mass transfer is more meaningful in terms of area-free mass transfer coefficients since the H.T.U. concept is specific to the conditions prevailing during the experiment.

Recently, Oldshue (40) confirmed that there is no reliable data available for the prediction of mass transfer in the Oldshue Rushton column and that, without exception, pilot plant data must be obtained for specific systems.

As mentioned earlier, backmixing plays an important part in agitated contactors and its effect should be included in predicting the mass transfer characteristics of the contactor.

Investigations of this aspect have been carried out by a number of workers. A summary pertaining to work done with the Oldshue Rushton Column appears in Table 4.2. Although, some of the correlations exhibit a certain degree of accuracy, their application is limited because,

1) The use of mean values of hold-up which the correlations and models incorporate, is usually invalid. It has already been established that in both the Oldshue Rushton and R.D.C. the hold-up profile along the column is quite significant e.g., a variation of volumetric hold-up of upto four times is obtained between the top and bottom of an Oldshue Rushton Column under normal operating conditions (40).
2) Variation of dropsize in the contactor is quite significant and largely depends on the flowrate, impeller speed and system properties. The backmixing rate is obviously a function of dropsize distribution.
3) The so-called "coalescence redispersion" phenomena must have an effect on the extent of backmixing and vice-versa owing to the fluid energy interaction involved in such a process.

The above effects have not been included in the models presented in Table 4.2.

The situation is further complicated when mass transfer occurs, particularly if it is accompanied by a chemical reaction, and the effect of backmixing under such conditions has not been reported. The complexity arises since when a

Table 4.2

BACKMIXING CORRELATIONS

AUTHER	EQUATION NUMBER	EQUATION	COMMENT
1. Mecklenburg and Hartland (75)	4.36	$\frac{e_y}{U_y} + \varepsilon\frac{e_x}{U_x} = (H.T.U)_m - (H.T.U)_t - h^*$	The solution is complex
2. Misek (76)	4.37	$\frac{\varepsilon}{f_y}\frac{e_y}{U_y} + \frac{e_i}{\gamma_i U_i} = (H.T.U)_m - \Sigma\frac{\psi_i}{\partial_i}(H.T.U)_{ti}$	No end effects have been considered.
3. Bibaud and Treybal (44)	4.38	$\frac{e_x}{G_c H/\rho_c} = 0.449 + 0.01118\frac{DN}{G_c/\rho_c}$	Single phase backmixing
		$\frac{(1-x_d)e_x}{G_c/H/\rho_c} = -0.1400+0.0268\frac{DN(1-x_d)}{G_c/\rho_c}$	Continuous phase backmixing
		$\frac{D^2N}{e_y} = 3.39\times10^{-3}\left(\frac{D^3N^2\rho_c}{\sigma}\right)^{1.54}\left(\frac{\rho_c}{\Delta\rho}\right)^{4.18}\left(\frac{D^2N\rho_c}{\mu_c}\right)^{0.61}$	Dispersed phase backmixing no variation of e_y with flowrates is considered
4. Miyauchi et. al. (67)	4.39	$\frac{f}{ND} = 1.0 \times 10^{-2}\left(\frac{D_c}{H}\right)^{\frac{1}{2}}$	For a 0.15m diameter column
	4.40	$\frac{f}{ND} = 0.017(N_p)^{1/3}\left(\frac{D_c}{H}\right)^{\frac{1}{2}}$	Unified correlation for both R.D.C. and Oldshue Rushton Column.
5. Haug (77)	4.41	$\frac{f}{G_c A_s/\rho_c} = 0.0098\left[K_1\left(\frac{ND}{G_c}\right)\left(\frac{4D^2A_s}{\pi H D_c^3}\right)^{0.5}\right]^{1.24}$	Suits both single and two phase flow.
6. Ingham (78)	4.42	$\frac{e_x}{G_c H/\rho_c} = 0.0375\left[\frac{ND}{G_c/\rho_c}\right]\left[\frac{A_s}{D_c}\right]^2(1-x_d)$	Two phase flow backmixing agreed reasonably with Bibaud and Treybal(42)
7. Lelli (79)	4.43	$\frac{g}{ND3} = 0.038/\left[1+19.5\frac{q}{ND3}\right]$	Agreement with Miyauchi's correlation(67)is within7%

chemical reaction occurs, the reaction products change the overall physico-chemical properties of the fluid-system and the initial backmixing rate is altered. Added to this, physical transfer obviously has a secondary effect on backmixing via increased or hindered interdroplet coalescence resulting in a change of hold-up.

To sum up, the following factors must first be accurately determined quantitatively before an effective prediction of mass transfer performance is possible:-

1. The rate of drop-interaction i.e. frequency of coalescence-redispersion and the distribution of this rate across the column. Drop break-up usually leads to higher mass transfer coefficients due to an enhanced surface renewal effect (80). Again drop-drop coalescence has an obvious effect in reducing the area, thus causing less transfer but conversely it increases the internal turbulence in the drop leading to a higher coefficient. A balance is desirable, in theory, between these two phenomena i.e. the contactor should be operated at the optimum interaction rate for effective mass transfer.
2. The actual nature and amount of backmixing.

Published correlations are specific to the systems used and extrapolation of data to suit different systems is of doubtful validity. The general flow pattern in the Oldshue Rushton and the R.D.C. is plug flow but superimposed upon it is longitudinal/or radial mixing; evaluation of the extent of this effect is highly important. Thus experimental data is essential.

5. DROPLET PHENOMENA

The phenomenon of 'coalescence-redispersion' is highly pronounced in the Oldshue Rushton contactor and is present, to a lesser degree, in the R.D.C. It significantly controls the hydrodynamics and mass transfer characteristics of the columns. Thus a fundamental understanding of drop interaction, i.e. drop break-up and coalescence phenomena is important in the context of the present work. Current knowledge of the subject is summarised below.

5.1 Droplet Break-up Mechanisms in Turbulent flow

In turbulent systems deformation of drops is caused by various interacting forces e.g. energy transmitted by the impeller or impact against the container walls and internals. When the extent of deformation exceeds a certain limit, dependent upon the system properties, droplet break-up occurs. Hinze (81) identified various flow patterns and forces causing deformation and ultimately resulting in break-up. The following are the controlling forces for droplet break-up:

(a) Surface force (σ/d) arising from the interfacial tension (σ) and which resists drop deformation.

(b) The dynamic pressure (P)

(c) The viscous stress $[\frac{\mu_D}{d}(P/\rho_D)^{\frac{1}{2}}]$

Hinze selected the dimensionless groups:

Viscosity group: $N_{vi} = \dfrac{\mu_D/d}{\left(\dfrac{\rho_D\sigma}{d}\right)^{\frac{1}{2}}}$

Weber number $N_{We} = P/\frac{\sigma}{d}$

With increasing N_{We}, deformation increases and at a critical value of N_{We} break-up occurs.

Kolmogorov (82) postulated that a whole range of eddy dimensions exists in turbulent flow, the largest being the same order of magnitude as the impeller blade in the case of a stirred vessel whilst the smallest may be equal to the molecular dimensions. Energy from the impeller is transmitted into the fluid system by means of the primary, i.e. largest, eddies. These primary eddies are unstable and interaction with the fluid results in smaller eddies of higher frequency. This process continues until the energy is dissipated in the form of viscous shear. It was suggested that the smaller eddies are independent of the bulk motion at high values of a modified Reynold's number, Re_m, and their properties, viz, characteristic velocity and dissipation time are governed by the local energy dissipation per unit mass of fluid. The characteristic eddy length of the turbulent field was predicted by,

$$z = \left(\frac{\mu_c}{\rho_c}\right)^{3/4} (\varepsilon)^{-\frac{1}{4}} \qquad 5.1$$

and the eddy velocity was given by,

$$\nu = \left(\frac{\mu_c}{\rho_c} . \varepsilon\right)^{\frac{1}{4}}$$

Droplet break-up was considered to occur in two ways,

<u>Case I</u> If the eddy length is less than the droplet diameter, the fluctuations in the bulk motion of the continuous fluid are pronounced over the entire interface surrounding the drop. This results in break-up.

Case II If, however, the eddy length exceeds drop diameter, break-up results from viscous stresses, that is the contribution from inertial forces is negligible.

Hinze (81) considered the former case of droplet break-up when dynamic pressure fluctuation determines the largest drop size present in the system. The maximum drop size was related by,

$$(N_{we})_{crit} = \frac{\rho u^2 d_{max}}{\sigma} \qquad 5.2$$

where u = mean square fluctuating velocity. This was related to the maximum drop size and to the power dissipated per unit mass of the continuous phase E by,

$$u^2 = c_1 \; [E d_{max}]^{2/3} \qquad 5.3$$

d_{max} was given by,

$$d_{max} = c_2 \; E^{0.4} \; [\frac{\rho_c}{\sigma}]^{0.6} \qquad 5.4$$

where c_2 = a coefficient in the power number,

$$E = \frac{4c_3}{\pi} \; \frac{N^3 D^5}{HD_c^2} \; .$$

The above expression holds good for any Reynold's number >50,000. Sitaramayya and Laddha (83) investigated the applicability of equation 5.4 and observed the effect of E to be greater than that given by the exponent of 0.4. Considerable divergence was observed when the dispersed phase was viscous.

Shinnar and Church (84) proposed a similar expression relating the drop size to the energy input,

$$\frac{E}{\sigma d^2} \simeq 0.26 \qquad 5.5$$

where E = kinetic energy, equal to the difference between the total energy of the parent drop and the energy associated with the two daughter droplets formed upon break-up.

Equation 5.5 is based on the assumption that a drop having a similar viscosity and density to the continuous phase will oscillate with it. Thus it is only applicable to fluid systems for which the viscosity and density of both phases are of similar magnitude. For local isotropic turbulence, the kinetic energy is expressed as (84),

$$E_K = \rho \; u^2(d) d^3 \qquad 5.6$$

combining equation 5.5 and 5.6,

$$\frac{\rho_c u^2(d) d}{\sigma} = We \simeq 0.26 \qquad 5.7$$

The value of u(d) is difficult to determine in practical dispersions. However, equation 5.3 may be used. This incorporates the energy term E which for a fully baffled vessel is given by (85),

$$E \simeq N^3 D^2.$$

Therefore, by substitution equation 5.7 becomes,

$$We = \frac{K_3 N^2 D^{4/3} d^{5/3} \rho_c}{\sigma} \qquad d >> z \qquad 5.8$$

This refers to Case I in Kolmogorov's consideration of eddy characteristics mentioned earlier.

A similar treatment would result for Case II in,

$$We = \frac{K_4 N^{3/2} D d^{3/2} \rho_c}{\sigma} \qquad d << z \qquad 5.9$$

In the same work Shinnar and Church produced expressions for drop size in an agitated dispersion based on Kolomogorov's theory of isotropic turbulence.

At low hold-up,

$$\frac{d}{D} = C_4 N_{We}^{-0.6} \qquad 5.10$$

At high hold-up,

$$\frac{d}{D} = C_5 N_{We}^{-0.375} \left[\frac{A(h)}{\sigma L}\right]^{0.375} \qquad 5.11$$

Where A(h) = a function of the energy of adhesion between two drops each of unit diameter and separated by a distance h.

Vermeulen (86) developed a similar correlation and related the mean dropsize with hold-up

$$\frac{d}{D\phi} = C_6 N_{We}^{-0.6} \qquad 5.12$$

where ϕ = hold-up. The hold-up range considered was 10%-40%. Calderbank (87) also included hold-up considerations, up to 20%, in deriving the expression,

$$\frac{d}{D} = C_2 (1 + 9\phi) N_{We}^{-0.6} \qquad 5.13$$

Roger et. al. (85) investigated drop size in agitated dispersions at a fixed hold-up value of 0.50, and proposed the expression,

$$\frac{d}{D} = C_5 N_{We}^{-0.36} \left(\frac{D}{D_c}\right)^{a'} \qquad 5.14$$

where exponent $a' = 0.75 - 1.4$.

More recently, Giles et. al. (88) studied the drop size distribution in agitated systems involving simultaneous mass transfer amd chemical reaction. They concluded that two mechanisms are responsible for drop formation and break-up:

1. Interaction of interfacial tension forces, preventing the drop from deformation, and the external shear stress imposed by the turbulence, causing deformation. This has been observed to occur either at a low dispersed phase hold-up or in areas of high turbulence.

2. Deformation and subsequent break-up due to viscous forces occurs at high hold-up or in regions remote from the impeller where turbulent eddies decay. This observation confirms Kolmogorov's original postulations summarised earlier. The following correlation was developed to describe the drop size distribution,

$$y = 0.01 \exp\left(-4.0 \, \ell n^2 \left[\frac{d}{d_g}\right]\right) \qquad 5.15$$

where y = probability density

$d_g = 0.87 \, d_{32}$.

However, the applicability of this equation is limited to the specific reaction system used, viz., two-phase nitration of toluene.

So far discussion has been limited to the droplet break-up phenomena in stirred tanks. In a practical agitated column, a wide range of drop size exists owing to the repeated break-up and coalescence of drops moving up or down the column. While in the case of a stirred tank, the drop size distribution remains unchanged at equilibrium, each drop in a column must adjust to a new environment as it moves from one compartment to the next.

Misek (56) studied droplet break-up in an R.D.C. He followed the same approach as Hinze (81) and Shinnar and

Church (84) but incorporated the following assumptions appropriate to analysis of the R.D.C.,

(a) The continuous phase velocity in the rotor region is proportional to the pheripheral speed, and decays exponentially towards the wall of the column, thus

$$\frac{V_c}{V_o} = e^{-K_1 \Delta R} \qquad 5.16$$

(b) The dynamic pressure is highest in the region of the wall and is proportional to the square of continuous phase velocity.

(c) The compartment height is related to the Weber number through a power function,

$$N_{We} = K_5 \left(\frac{H}{D}\right)^a \qquad 5.17$$

He further defined three different regions of droplet break-up: turbulent, transitional and laminar regimes, and proposed the following expressions,

For break-up in the turbulent regimes ($Re > 6.5 \times 10^4$)

$$d = \frac{16.3[\sigma \exp\ (0.0887\ \Delta R)]\ [\frac{H}{D_c}]^{0.46}}{[N^2 D^2 \rho_c]} \qquad 5.18$$

For break-up in the transitional regime, ($Re < 6 \times 10^4$)

$$d = \frac{1.345 \times 10^{-6} [\sigma\ \exp(0.0887\ \Delta R)]\ [\frac{D^2 N \rho_c}{\mu_c}]^{1.42}}{[N^2 D^2 \rho_c]} \qquad 5.19$$

For break-up in the laminar regime ($Re \ll 10^4$)

$$d = 0.38 \left(\frac{\sigma}{\Delta \rho g}\right)^{\frac{1}{2}} \qquad 5.20$$

This laminar expression is analogous to that for break-up in packings. Mumford (54,89) tested the above equation and found reasonable agreement with experimental results if the numerical coefficient is replaced by 0.55, and provided Re $< 1.75 \times 10^4$ for a non-wetted disc. However contrary to the basis for derivation of equation 5.2, droplet break-up by impact on stators or discs was not considered a contributing factor in the actual mechanism. Indeed, Thomas and Mumford (90) observed that drops moving at terminal velocities did not rupture on impact with flat plates. However, small drops may rupture by impacts on the edge of the stators or discs as shown by Thornton (91).

Subsequently, the observed maximum drop diameter in an R.D.C was compared with the following Kolomogrov's relation for stable drop-size (92),

$$r_{sd} \simeq \sqrt{2} \left[\frac{\sigma}{K_f \rho} \right]^{0.6} \left[\frac{L^{0.4}}{V_c^{1.2}} \right] \qquad 5.21$$

where $K_f = 0.5$ for liquid drops falling in a gaseous medium. A reasonable agreement was obtained with most liquid-liquid systems, but it was concluded that it is rather difficult to predict the mean drop size in an R.D.C. from theoretical considerations because: (i) Levich (93) postulated that for a given velocity of a homogeneous isotropic flow, drops formed should be of a single size, whereas in practice, four or more unequal sized drops were formed on rupture of one drop.

(ii) In relatively small columns with large drops, the order of proportion of drops impinging vertically within one drop diameter of the disc or stator edge becomes significant.

(iii) In columns with large discs, there is a wide variation of velocity in the unstable region which results in a wide drop size distribution. It appears from the above review that although various drop size correlations are available, their application to rotary agitated columns is seriously limited for the following reasons,

(i) Most of the models published to-date predict mean drop sizes in stirred tanks. In an agitated column, there is always a distribution of mean drop sizes along the column length (40, 55, 69). Thus the assumption of a single mean drop size may lead to serious errors in the interpretation of mass transfer data in a column. Furthermore, application of drop size distribution characteristics in a stirred tank to such columns is invalid since they are specific to the particular geometry of the vessel and the impeller and the systems used.

(ii) In agitated systems, drop size is also a function of hold-up. This functional dependence is further complicated in an agitated coulmn where the hold-up itself is a function of the column height. This effect of hold-up variation on drop size distribution is not accounted for in analyses based on stirred tank data.

(iii) The phenomena of coalescence, discussed in the next section, has a pronounced effect on the drop size distribution. This effect has not been successfully quantified in the models.

(iv) In the presence of mass transfer, the mean drop size varies dependent upon the direction of transfer.

Unfortunately, it would be quite impracticable to derive a correlation to include this Phenomenon.

(v) Unlike stirred tanks, entrance and exit mechanisms are very important in rotary agitated columns (40). Larger drops have a greater vertical velocity than smaller ones and are less affected by small-scale disturbances in other directions. Some degree of classification therefore occurs between compartments resulting in a tendency for the smaller drops to remain in a compartment and larger ones to pass to the next.

Thus it appears that design of a rotary contactor, such as the R.D.C. or Oldshue Rushton column, based on a mean drop size throughout the length of the column and in which the drop size correlations are based on data from single stirred tanks is invalid. Without exception direct experimental investigation is necessary for precise design, although as already mentioned provision of a variable speed drive may overcome design uncertainties.

5.2 Coalescence

Coalescence phenomena have an important bearing on the hydrodynamics of any extraction column. A fundamental understanding of the subject is therefore useful since, via its effect on drop size distribution, drop-drop coalescence exerts such a great influence upon the operating characteristics of a column. Furthermore, drop coalescence followed by breakup affects mass transfer characteristics.

In general, coalescence is a simple fusion of two or more macroscopic quantities of the same substance. There are two distinct modes of coalescence namely drop-interface coalescence and drop-drop coalescence although the former is theoretically a limiting case of the latter. In both cases the basic mechanism involved is the approach of a drop to an interface followed by the entrapment of a film of continuous phase between the drop and interface; this film eventually drains away leading to rupture of the film and subsequent fusion of the drop with the homophase. Numerous investigations have been made of the mechanisms of drop-interface and drop-drop coalescence. Various physical situations of droplet coalescence have been investigated including studies of single drop coalescence (94,97) and large populations of drops in the presence or absence of mass transfer (94,95,98,99). Early work concentrated on the study of drop-interface coalescence in the absence of mass transfer to facilitate close inspection of the physical processes involved.

5.2.1 Drop-Interface Mechanism

Coalescence of a single drop at a plane interface consists of five distinct stages: (94, 97)

1. Approach of the drop to the interface and the subsequent deformation of the drop and interface profiles;
2. The damping of oscillations caused by the impact of the drop at the interface;
3. Formation and drainage of a continuous film between the drop and its bulk interface;
4. Rupture of the film; and
5. Drop contents deposition into the interface.

The sum of stages 1 and 2 is referred to as the pre-drainage time. This is generally of the order of 0.1 secs and the post-drainage stage, i.e. stage 5, takes about 0.05 seconds. Thus the coalescence time may be considered as the sum of the times taken by stages 3 and 4, and is of the order of several seconds. A distribution in the coalescence time for identical drop sizes has been reported in all the investigations. This distribution has been found to be approximately Gaussian.

Although a number of correlations for coalescence time have been proposed by various workers in terms of the ratio of number of drops not coalescing in time t to the total number of drops examined, controversy has arisen over their validity and reproducibility (100). This is probably because studies have been carried out under varying conditions (101,102). Presence of electrolytes or surfactants is expected to affect the interfacial tension which in turn may reduce or increase the film drainage process. Thus some knowledge is necessary of the factors affecting rate of coalescence.

5.2.2 Factors Affecting Coalescence

As the coalescence time depends on the drainage and rupture of the continuous phase film, factors affecting these steps control the coalescence process. These factors have been well documented by Lawson (97) and are summarised in Table 5.1. It is clear from this table that for parameters numbers 5 to 13 there is some agreement on the physical process taking place; this is, however, not the case for parameters numbers 1 to 4. Agreement generally occurs where the parameter under investigation is externally induced viz, temperature effects, vibrations, surfactants, mass transfer and electrical effects. The disagreements recorded for parameters numbers 1 - 4 are apparently related to the more fundamental properties of the system, e.g. density difference and interfacial tension, and as such are more difficult to isolate. The probable reasons for these discrepancies may be,

(i) The effect of a particular parameter not being constant for all immiscible liquid-liquid systems;

(ii) The different experimental techniques employed during investigation.

More recently Hitit (103) has shown that impurities may have a far more significant effect on coalescence time than any of the factors discussed.

Most of the studies mentioned above have been of drop-interface coalescence but the same factors will also affect drop-drop coalescence. In general, increase in interfacial

Table 5.1

FACTORS AFFECTING COALESCENCE TIME

No.	Variable (increasing)	Effect on coalescence time	Explanation in terms of effect on continuous film drainage rate.	Comments
(1)	Drop Size	(i) Increases $t_{\frac{1}{2}} \propto d^n$ n varied with conditions (ii) Independent of drop size	More of the continuous phase film	In stepwise coalescence smaller size daughter drops have a longer life at the interface than the original larger drops
(2)	Distance of fall	(i) Increase $t \propto H^n$ where n is constant depending upon drop size or $n = 11\times10^{-5}\left(\frac{\sigma^{2}}{\mu_c^{0.5}}\right)^{0.91}$	Drop 'bounces' and film is replaced.	Discrepancy of results was due to apparatus dimension and particularly the dimension of the cup that receives the drop.
		(ii) Independent of distance travelled.		
		(iii) Either increases or decreases.	Depending on thermal or mechanical disturbances produced.	
(3)	Interfacial tension	Decreases	More rigid drop, force causing drainage acts on smaller area.	
		Increases	Increases strength of film resistance to rupture.	
(4)	Phase $\Delta\rho$	Increases $\Delta\rho^n$ $n = 1.2, 0.32, 0.25$	More drop deformation, more continuous phase film.	
		Decreases	Greater hydrostatic forces act on drainage.	
(5)	Curvature of interface towards drop: (a) Concave	Increases	More continuous phase in film.	
	(b) Convex	Decreases	Less continuous phase in film.	

Table 5.1 continued

No.	Variable (increasing)	Effect on coalescence time	Explanation in terms of effect on continuous film drainage rate	Comments
(6)	Viscosity Ratio $\frac{\mu_c}{\mu_d}$	Decreases	Either less continuous phase film or higher drainage rate	
(7)	Temperature	Decreases $t_{\frac{1}{2}}=(\frac{T}{25})^{-0.7}\mu_d^{0.5}$	Increases μ ratio	Overall coalescence time, however,as distinct from first step time, may on occasions show an increase with increase in temperature because of transition from single step to stepwise coalescence
(8)	Temperature gradients	Decreases	Film distorts	
(9)	Vibrational effects	Decreases	Assists in film rupture	
(10)	Electrostatic effects	Decreases	Increase in effective gravitational force	Causes formation of twin secondary drops.
(11)	Applied Electric fields	(i)Decreases (ii)Independent	Increase in effective gravitational field	The efficiencies of electrostatic coalescers are dependent on this fact.
(12)	Presence of a third component (a)Surfactants	Increases $t_m \propto c_1^n$ $0.3<n<0.45$	'Skin' formation around the drop, film drainage inhibited.	

Table 5.1 continued

no.	Variable (increasing)	Effect on coalescence time	Explanation in terms of effect on continuous film drainage rate.	Comments
(12)	(b) Mass transfer into drop	Increases	Sets up interfacial tension gradients which oppose film flow.	Coalescence times are almost independent of solute concentration only primary step being affected for transfer from the drop
	(c) Mass transfer out of drop	Decreases	Sets up interfacial tension gradients which assist flow of film.	
(13)	Impurities	Varies in an unpredictable way.		All researchers found it necessary to clean the interface, otherwise reproducible results were unobtainable.

tension, increase in temperature and decrease in dispersed phase viscosity would increase the ease of separation at the upper or lower phase boundary of a contactor.

5.2.3. Drop-Drop Mechanism

Interdroplet coalescence occurs frequently in agitated contactors like the R.D.C. and Oldshue Rushton column though the effect is more pronounced in the latter.

The analysis of drop-drop coalescence, which represents a more dynamic situation in agitated systems is rather difficult on two counts. Firstly, it is difficult to reproduce a controlled collision between two drops which have not been restrained in some way. Secondly, there is an inherent randomness in the manner in which the drops rebound or coalesce. Thus drop-drop coalescence studies necessitate consideration of both collision theory and the coalescence process. It follows that the prediction of coalescence frequency requires a knowledge of both collision frequency and coalescence probability.

From the above considerations, Howarth (104) derived a mathematical model to relate the frequency of coalescence with hold-up in a homogenous isotropic turbulent flow,

$$\psi = \left[\frac{24x_d \; r \; \bar{u}_r^{\,2}}{d^3}\right] \exp\left[-3W^{*2}/4\bar{u}_r^{\,2}\right] \qquad 5.22$$

This is based on a simplified picture of coalescence taking place in a monodispersion having drops smaller than the characteristic length of the turbulent field and with most of the collisions resulting in cohesion or immediate coalescence.

This is however, consistent with the observation made by Madden and Damerell (105)who estimated the coalescence frequency of drops of an aqueous dispersion in toluene and observed that it increased markedly with increase in impeller speed and to a lesser extent with increase in the dispersed phase volume. However, doubt has been expressed as to the applicability of Howarth's model to real situations (54) due to the restrictive assumptions made in the derivation.

In a subsequent study, Misek (57) applied the theory of turbulent coalescence of drops, due to Levich (93), to the case of drop coalescence in agitated vessels, and derived the following models,

(i) For coalescence in the bulk,

$$\ln \frac{d}{d_o} = K_5 (n^1 d^3) V_o^{\frac{1}{2}} \left(\frac{D}{\gamma}\right)^{\frac{1}{2}}$$

$$= K_6 X \left(\frac{\sigma}{d_o \rho}\right)^{0.5} \left(\frac{D}{\gamma}\right)^{0.5} = Z_1 X \qquad 5.23$$

(ii) For coalescence at the vessel wall,

$$\ln \frac{d}{d_o} = K_7 \; (n' d^3) \; V_o \; \left(\frac{D}{\gamma}\right)$$

$$= K_6 X \left(\frac{\sigma}{d_o \rho}\right)^{0.5} \left(\frac{D}{\gamma}\right) = Z_2 X \qquad 5.24$$

The values of Z_1 and Z_2 were determined from equation 4.6 and d_o was calculated from the terminal velocities of falling solid spheres (56).

The above theoretical model was tested experimentally for a number of binary systems e.g. water/toluene, water/kerosene, water/butyl acetate, and water/amyl alcohol in various column designs like the R.D.C., A.R.D.C., Oldshue Rushton column and Scheibel column. Only a fair agreement was obtained between experimental and predicted results. In the derivation of the above expression, it was assumed that each interdroplet collision results in coalescence and that the dispersion may be characterised by a hydraulic mean drop diameter. Both of these assumptions are rather unrealistic and furthermore these equations make no allowance for any variation in the ease of coalescence with drop size. Their application to columns like the R.D.C. and Oldshue Rushton contactor, where the coalescence characteristics are so different, is also questionable (54).

Davies et.al.(106) observed that the extent of drop-drop coalescence in an R.D.C. was not significant upto a hold-up of 10% with the system kerosene-water. Misek (51), however, asserted that interdrop coalescence in an R.D.C. may be significant at hold-up values of about 18% or more. From fundamentals it would be expected that the prerequisites for a significant coalescence frequency are a high drop collision frequency and a high hold-up of the dispersed phase. Thus in a subsequent study of the R.D.C., interdroplet coalescence was only significant at conditions approaching flooding (54). More recently, Arnold (40) found significant interdroplet coalescence in a 0.15 m Oldshue Rushton column operating with a mutually saturated water-toluene system even at an average hold-up of 15%. However, the extent of coalescence was balanced by simultaneous redispersion, that is, a dynamic equilibrium existed between interdroplet coalescence and subsequent break-up.

Coalescence may also take place in a contactor by drop-solid surface interaction. This depends upon the wetting properties of the dispersed phase system and may properly be classed as a "Wetting Effect" rather than coalescence. Although a detailed treatment of wetting effects is beyond the scope of the present work, it may be important when the dispersed phase wets the internals of a column. However, Al Hemeri (55) has shown that it has no significant effect on the overall mass transfer efficiency in an R.D.C.

It appears from the above review that although drop-interface coalescence is well understood, knowledge on drop-drop coalescence is very limited. This is due to the inherent complexity of the process and it has not, as yet, been possible to observe in detail the behaviour of a swarm of drops in a turbulent field.

5.3 Phase Inversion

Phase inversion refers to the phenomenon of interchange of phases in a dispersion i.e. the dispersed phase becoming continuous and vice-versa under conditions dictated by system properties, phase ratio and the energy input. Its importance with regard to extraction efficiency and ease of separation has not been fully realised in the past. Theoretical modelling has been very limited, both with regard to batch and continuous systems, and there is no convincing set of experimental data, more particularly in the case of flow systems.

Phase inversion is likely to occur whenever the equilibrium between coalescence and redispersion under steady state conditions is disturbed and is accompanied by a shift in the equilibrium towards the former. As the stability of a dispersion is least at the point of inversion,the phenomenon may be effectively used for the separation of two immiscible liquids. Conversely, in the creation of a dispersion the opposite effect is desired, so that a knowledge of the point of inversion will enable it to be avoided to ensure that the preferred direction of mass transfer is maintained. From a recent study of the Oldshue Rushton column , Arnold (40) suggested that, because of the intense mixing of the phases during cyclical inversion, mass transfer may be enhanced. However, studies to-date, whether under flow or non-flow conditions, have been mostly of a qualitative nature. These are reviewed below.

5.3.1. Inversion In Stirred Tanks

Phase inversion studies using stirred tanks have mainly been concerned with analysis of the phenomenon in terms of its dependence on energy input, phase ratio and system properties. There are no reports regarding its effect on mass transfer.

In a study of batch operation with an oil/water system, Quinn and Sigloh (107) observed that inversion could be characterised by the expression,

$$\phi = \phi_o + {}^{b}/_{p} \qquad 5.25$$

where ϕ = Inversion concentration expressed as volume fraction in the organic phase.

ϕ_o = Asymptotic value of hold-up for high energy input
p = Energy input.
b = A constant

The constant b is related to the physical properties of the dispersion and is roughly proportional to the ratio of interfacial tension to the mean density. This confirms that surface energetics are one criteria determining inversion characteristics. However, it was concluded that the available data were insufficient for detailed analysis. The influence of energy input on the inversion concentration is illustrated in figure 5.1. The concentration of the organic phase at inversion decreased with increasing impeller speed and the volume fraction at phase inversion became independent of impeller speed at values of N two to three times the minimum necessary for complete dispersion.

Luhning and Sawistowski (108) studied phase inversion in greater detail under non-flow conditions in a stirred tank. They observed an increase in mean drop-size with increasing conentration of the dispersed phase, which is the probable outcome of an increased drop collision frequency. This trend was most significant at lower speeds and close to the inversion point drops of the continuous phase were contained within dispersed phase drops. It appears that at high dispersed phase loading the coalescence-redispersion process was responsible for this entrainment of the continuous phase. Quinn and Sigloh (107) observed similar phenomena in concentrated dispersions.

The phase that will be continuous in any particular case

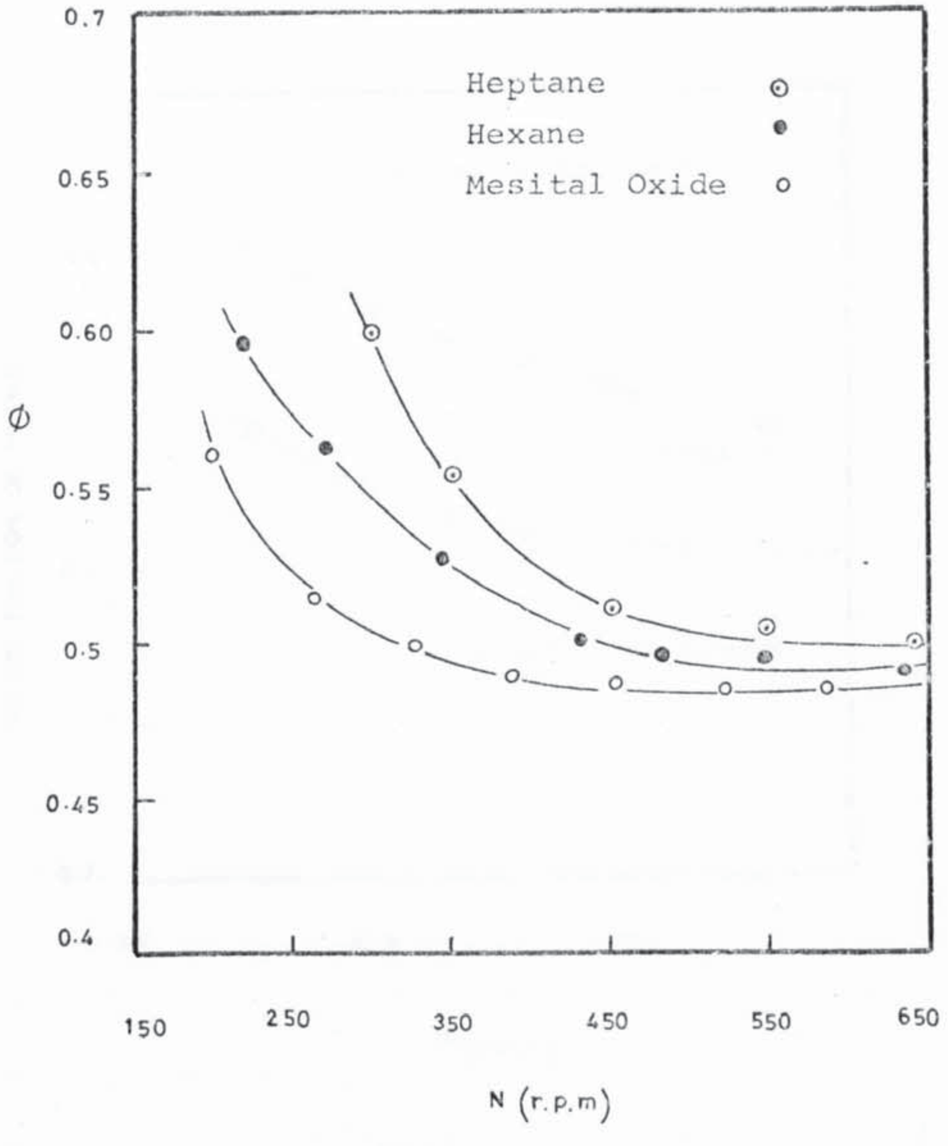


Fig. 5.1 Phase inversion curves for a four-bladed flat paddles impeller.

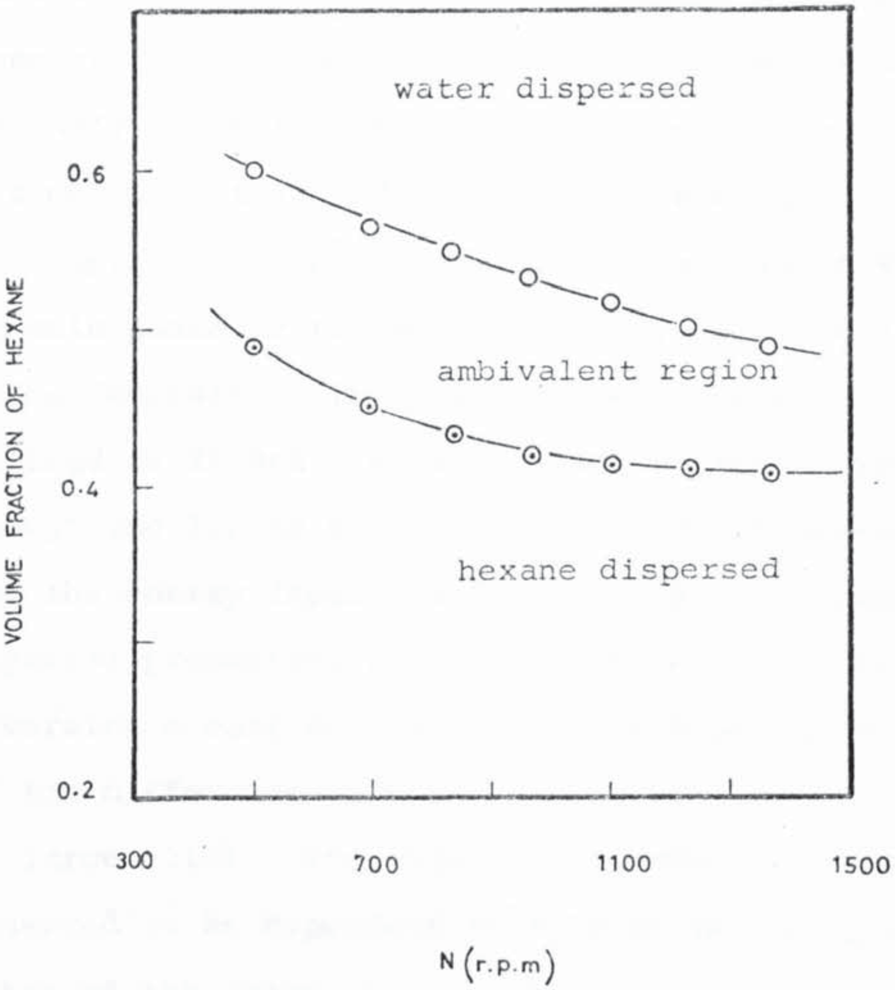


Fig. 5.2 Inversion characteristics for the Hexane-water system

Inversion from O/W to W/O
Inversion from W/O to O/W

is dictated by the upper limit of hold-up under a given set of conditions. In this respect both Selker and Sleicher (109) and later Lunhing and Sawistowski (108) characterised phase inversion by the existence of a hysteresis loop or ambivalent region. Figure 5.2 shows the ambivalent or metastable region within which either component would remain dispersed with remarkable stability. In their investigation with an aqueous/organic system, it was observed that upto 75% of volume of an aqueous phase could be dispersed in the organic phase, and about 90% of the organic phase in the aqueous phase, before the onset of phase inversion. The range of ambivalence could then be defined as 25-90% organic phase or 10-75% aqueous phase, though the limits may well be influenced by vessel geometry and the energy input. A characteristic dependence on fluid physical properties is to be expected. For example, phase inversion occurs most readily in systems in which the ratio of the difference in densities to continuous phase density is large (110). The width of the ambivalent region was observed to be dependent to a large degree upon the viscosity ratio of the phases i.e. as the viscosity of a phase increased its tendency to become dipersed increased. However, a large ratio of viscosities can cause dual dispersion (111). Furthermore the presence of a solute under conditions of phase equilibirum increases the range of ambivalence (108).

The influence of energy input to a system has been well demonstrated by Roger et. al. (112) who concluded that instability in a dispersion, leading to phase inversion, would occur at high energy input values. This is in agreement with the observations of Quinn and Sigloh (107) and McClarey and Mansoori (113).

The effect of impeller geometry and position on phase inversion has been studied by several authors in non-flow systems. Quinn and Sigloh (107) observed that by altering the position of the impeller the inversion concentration for a specific energy input could be raised or lowered. In the same study, changes in impeller geometry produced a significant change in the inversion point; this is to be expected since it would considerably alter the mixing characteristics. Similar observations have been made by Luhning and Sawistowski (108). Selker and Sleicher (109), however, observed that once a dispersion had formed, changing impeller position did not cause phase inversion provided there was no settling of the phases. Treybal (114) found that when the impeller was located at the interface, either of the phases could be dispersed and it was impossible to predict which phase would be the dispersed one.

The effect of interfacial tension on phase inversion has not been quantified. However, it is generally understood that if no other forces were present decrease in interfacial tension would permit phase inversion to occur only for equi-volume mixtures of immiscible liquids (108). Recently McClarey and Mansoori (113) concluded that the magnitude of the interfacial tension would affect the width of the ambivalence range. The effect, however, could not be correlated owing to lack of data.

The presence of impurities could exert a great influence on the shift in dispersion and make the ambivalent range larger than would be predicted (108).

Theoretical explanations for phase inversion are based either on surface energetics or geometric considerations. Yeh et. al. (115) predicted a maximum dispersed volume of around 74% at inversion based on the latter. Minimisation of surface energy at inversion is the basis of the energetics approach and leads to a predicted dispersed phase hold-up of 50% at inversion. However, Luhning and Sawistowski (108) have shown that inversion can be accompanied by either an increase or a decrease in interfacial energy, which negates the assumption of surface minimisation as a criterion for phase inversion. As a result, consideration of surface energy minimisation as a theoretical approach would need additional assumptions regarding the nature and hydrodynamics of the dispersion. In this regard Kolomogorov's theory of local isotropy may hold with the drop diameter as the characteristic linear dimension of the turbulent field upon which diffusion rate may be calculated (108).

5.3.2 Inversion In Flow Systems

Phase inversion studies in flow systems have to-date been very limited.

Al Hemeri (55) investigated the phenomenon using a 0.10 m R.D.C. with mutually saturated water-toluene as the operating system. The onset of phase inversion occurred in the bottom compartment giving rise to a very large 'slug',

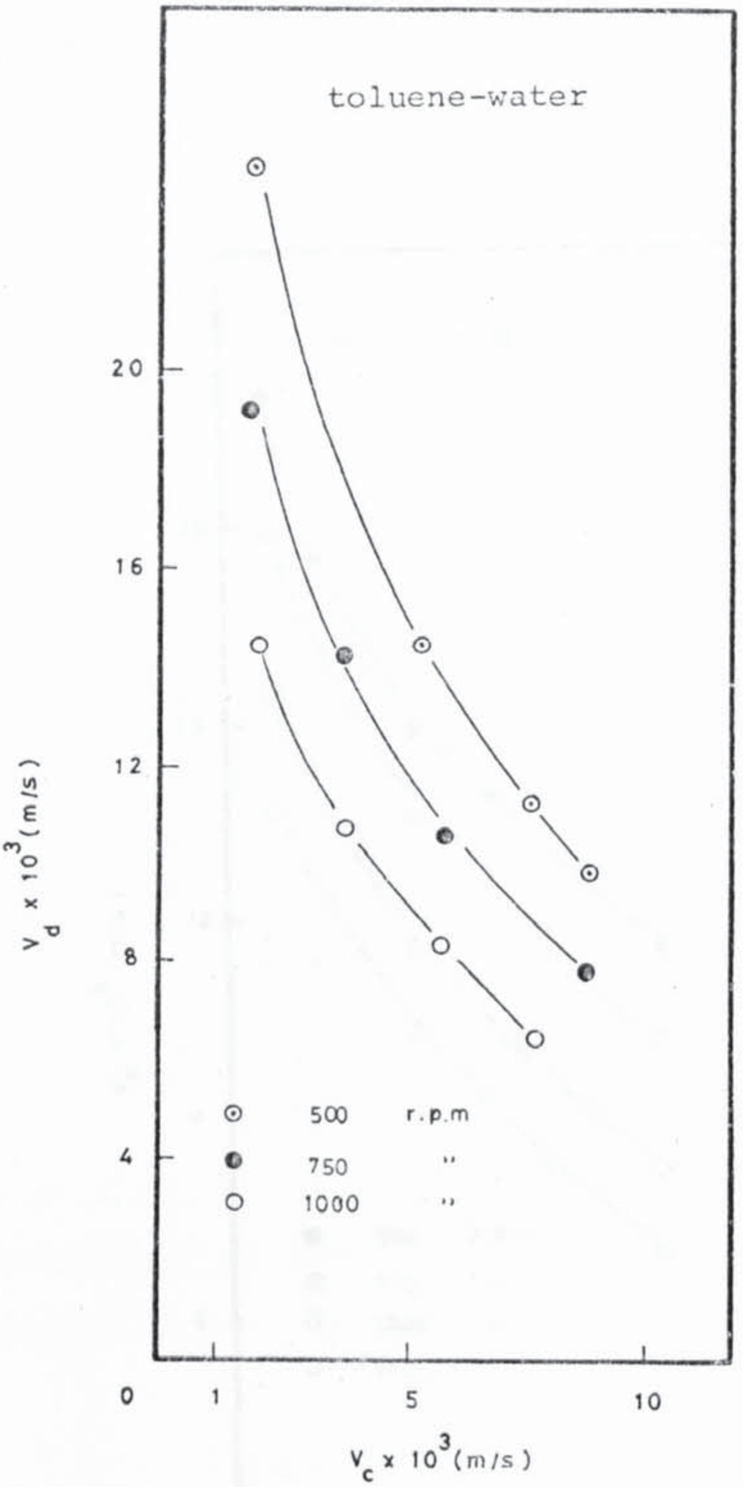


Fig. 5.3(a) Phase inversion curves for a non-wetted disc column

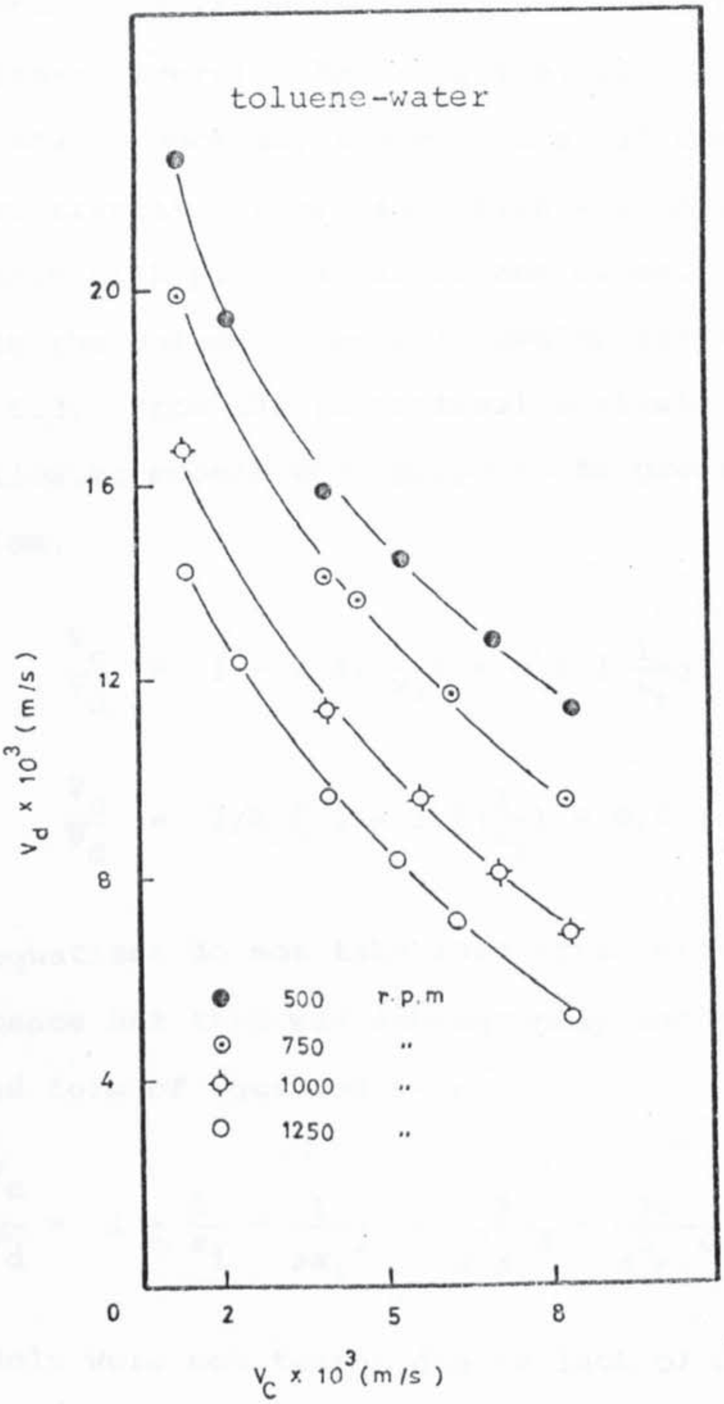


Fig. 5.3(b) Phase inversion curves for a wetted disc column

possessing a high terminal velocity, which travelled up the column and eventually dispersed in upper compartments. This phenomenon was demonstrated by the increased intensity of an oil-soluble dye added to the dispersed phase. With further increase in dispersed phase flow the effect was repeated at an increased frequency until all other compartments reached their phase inversion hold-ups i.e. complete inversion obtained in the mixing section; the column still operated countercurrently. Phase inversion was found to be more easily attainable with p.t.f.e. discs and cones, than with steel discs in the column. Typical results are illustrated in Figure 5.3. From the theoretical analysis of the phenomenon, the following models were proposed to predict the hold-up at inversion,

$$\frac{V_c}{V_d} = 1 - 1.5\left(\frac{1}{x_i}\right) + 0.5\left(\frac{1}{x_i}2\right) \qquad 5.26$$

$$\frac{V_c}{V_d} = 1/K_1\left[1 - 1.5\left(\frac{1}{x_i}\right) + 0.5\left(\frac{1}{x_i^2}\right)\right] \qquad 5.27$$

These equations do not take into consideration the effect of coalescence but this was subsequently included by use of a modified form of equation 4.6,

$$\frac{V_c}{V_d} = 1 - \frac{1}{x_i} - \frac{1}{ax_i^2} + \frac{2}{a^2x_i^3} + \frac{2b}{a^3x_i^4} + \ldots$$

The models were not tested due to lack of data. However, examination of the equations indicates that they all predict hold-up values much below those determined experimentally.

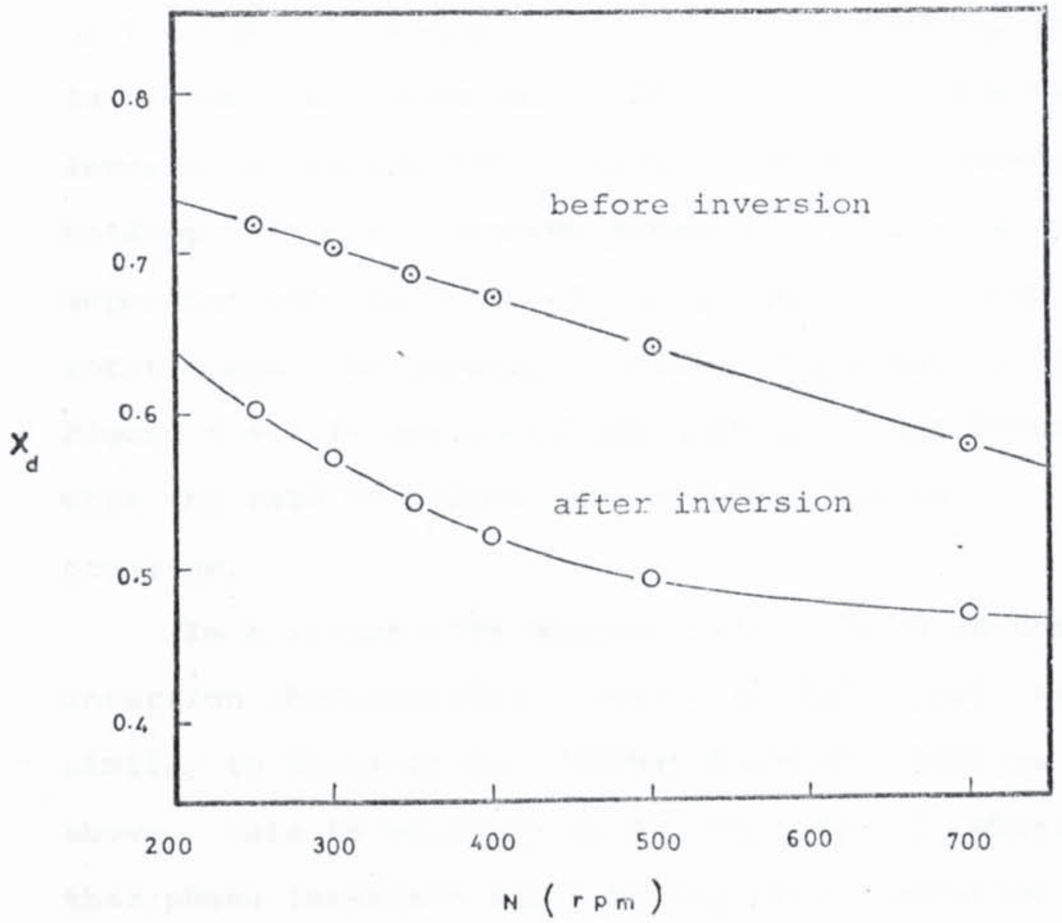


Fig. 5.4 Variation of inversion hold-up with impeller speed.

Arnold (40) subsequently studied phase inversion with the system water-toluene in a 0.15 m Oldshue Rushton column. Contrary to Al Hemeri's observations, inversion occurred on a cyclic basis. When one particular compartment had inverted, the inversion passed to the next compartment and proceeded up the column. Normal conditions were restored immediately in the initial compartment. After a finite time this compartment inverted again and the whole sequence was repeated. The hold-up values at inversion ranged from 0.55-0.80 and were very dependent upon the rate of energy input. With increasing rotor speed, the inversion hold-up decreased as illustrated in Figure 5.4. It was suggested that the phase inversion occurred when the rate of coalescence exceeded the rate of droplet break-up.

In a recent work McSween (116) indicated that phase inversion characteristics within an R.D.C. were rather similar to those of the Oldshue Rushton column as discussed above. This is contrary to Al Hemeri's (55) observation that phase inversion was a steady state operation in the R.D.C. The anomalous observation could be due to the difference in the design of the two contactors.

6. MASS TRANSFER FUNDAMENTALS OF NON-REACTING SYSTEMS

In a two-phase liquid-liquid system, one phase generally remains in the form of a dispersion of droplets in the other. Therefore, the mechanism of solute transfer from or to a single drop is fundamental to the overall transfer process in practical equipment.

In considering mass transfer, the life span of a drop may be broadly divided into three stages: (a) time of formation, (b) residence time in the continuous phase, and (c) time for coalescence with some degree of mass transfer occurring at each stage. In agitated columns the magnitude of the contributions from (a), (b) and (c) will be dependent on the rate and frequency of droplet coalescence and redispersion.

6.1 Mass Transfer During Drop Formation

Various workers have measured the extent of mass transfer during drop formation. Sherwood (117) observed that 40% of the overall transfer occurred during the formation period but recent investigations (80, 118, 119) have shown the amount to be around 10%. Sawistowski (119), has shown however, that the prediction of precise extraction rates during drop formation is difficult because of the rapid changes in interfacial tension which occur during this period. Nevertheless, many mathematical expressions have been proposed to predict dispersed phase mass transfer rates during drop formation. These are summarised in Table 6.1. All these expressions, in which mass transfer is assumed to be entirely controlled by diffusion, are based on one of the following models, (55)

Table 6.1

MODELS FOR MASS TRANSFER DURING DROP FORMATION

Authors	Correlation	Equation Number
Licht and Pansing (120)	$K_{df} = \frac{6}{7}(D_d/\pi t_f)^{\frac{1}{2}}$	6.1
Heertjes et. al. (118)	$K_{df} = \frac{24}{7}(D_d/\pi t_f)^{\frac{1}{2}}$	6.2
Groothuis and Kramer (63)	$K_{df} = \frac{4}{3}(D_d/\pi t_f)^{\frac{1}{2}}$	6.3
Coulson and Skinner (121)	$K_{df} = \frac{2\sqrt{3}}{5}\ (D_d/\pi t_f)^{\frac{1}{2}}$	6.4
Heertjes and de Nie (122)	$K_{df} = 2[a_o/a_r + 2/3][D_d/\pi t_f]^{\frac{1}{2}}$	6.5
Heertjes and de Nie (134)	$K_{df} = \frac{14}{3}[a_o/a_r + 1/3]D_d/\pi t_f]^{\frac{1}{2}}$	6.6
Ilkovic (123)	$K_{df} = 1.31\ (D_d/\pi t_f)^{\frac{1}{2}}$	6.7
Angelo et. al. (80)	$K_{df} = \frac{2}{\tau}\ \sqrt{\tau}\ (D_d/\pi t_f)^{\frac{1}{2}}$	6.8

(i) The model of an ageing rigid boundary layer which increases in surface area.

(ii) In the ageing boundary layer, the concentration gradient increases because of the increase in surface area due to stretching; this is known as the 'balloon model'.

(iii) The 'fresh surface' model. Here the boundary layer ages as with a rigid layer.Surface is increased by addition of fresh surface elements.

(iv) For the boundary layer a flow pattern has been developed in which a varying rate of stretching occurs.

Further the following conditions have been assumed to hold in the derivation of the expressions in all cases,

(i) The interfacial concentration is that at saturation,

(ii) Mass is transported by diffusion perpendicular to the interface.

(iii) The process of diffusion is slow compared with the process of drop growth.

(iv) Variations in the diffusion coefficient in the direction of flow may be neglected.

Skelland and Minhas (124) concluded that the above models are unrealistic because they fail to allow for the effects of internal circulation, interfacial turbulence and disturbances caused by drop detachment. A modified expression was proposed for the mass transfer coefficient,

$$K_{df} = 0.0432\left(\frac{d}{t_f}\right)\left(\frac{V_n^2}{dg}\right)^{0.089}\left(\frac{d^2}{t_f D_d}\right)^{-0.334}\left(\frac{\mu_d}{\sqrt{\rho_d d\sigma}}\right)^{-0.60} \qquad 6.9$$

Around 25% deviation was obtained from the observed values.

This correlation represents the overall mass transfer occurring during drop formation, which includes mass transfer during drop growth, during the detachment of the drop and the influence of the rest drop.

The model did not however consider the rate of formation as one of the variables affecting mass transfer whereas Heertzes et. al. (122) and Coulson and Skinner (121) observed enhanced mass transfer at higher frequencies of drop formation.

Mass transfer studies in connection with different rates of formation have to-date been limited. The only siginificant work in this regard is due to Popovich et. al. (125). Based on the fresh surface model and associated diffusion mechanism of transport, he derived the following expression for the prediction of mass transfer rate,

$$E_F V_{dr} = \frac{4n}{2n+1} \int_0^1 \{(1-y^2)\,dy\,(C^*-C^o)(D/\pi)^{0.5} B_p t^{(2n+1)/2}\} \qquad 6.10$$

where $B_p = A/t^n$, $y = (1-t/t_1)^{0.5}$ and t is the time at which a fresh surface element is formed and t_1 that when the mass transfer is considered.

This model is applicable to drops with a moderate rate of formation given by,

$$1.286 \times 10^4 < \left(\frac{d^2}{t_f D_d}\right) < 12.31 \times 10^4.$$

In a subsequent study, Heertjes and de Nie (134) proposed two modified forms of the above equation to fit their data.

In the case of formation at high speed, i.e. Re> 40, large contributions to mass transfer are caused by strong circulation in the drop. For circulating drops, Johnson (119) showed that the amount of transfer taking place during formation could be estimated by the expression,

$$E_F = \left(\frac{20.6}{d}\right) \left(\frac{\pi}{Dt_f}\right)^{0.5} \qquad 6.11$$

Although several studies (122, 80) in this regard have been reported, no theory has yet been advanced to take account of the mechanism of transfer involved in the process.

Mass transfer at low rates of formation has not been studied in detail. The only information available suggests that mass transfer in these circumstances is comparable to that with drops formed at moderate speed on which is superimposed the contribution of free convection (134). Quantitative data on this phenomenon is still lacking.

6.2 Mass Transfer During Drop-Rise

Mass transfer during the drop-rise period is significantly influenced by the hydrodynamic state of the drop i.e. whether it is circulating, oscillating or rigid. The mechanism of transfer differs in each case. Circulation or oscillation induces intense mixing inside the drop resulting in a high mass transfer rate to, or from, the drop. Conversely a rigid drop, in which internal mixing is completely inhibited, has a lower mass transfer rate. Oscillations commence in regimes of flow for which droplet Re > 200, below this circulation predominates (129). A good agreement however, has often been found between the rates of mass transfer for oscillating drops and those with rapid internal circulation, although in several instances (89, 80), the rates were considered to be much higher for oscillating drops. Since strongly developed oscillation leaves no room for any predictable circulation, a sharp distinction should be made between droplets with vigorous internal circulation and oscillating drops.

Thus in single drop studies of non-reacting systems mass transfer characteristics have been interpreted in terms of the above hydrodynamic regimes of the drop. These are summarised in Tables 6.2 and 6.3.

Although mass transfer is dependent on the hydrodynamic state of the drops, as discussed above, the presence of a wake behind the moving drop may considerably affect the overall transfer rate (133, 136, 139). Thus a fundamental understanding of wake phenomena is necessary. Whenever mass transfer occurs to or from moving drops, in addition to the mass transfer of solute, portions of continuous phase are transported in a direction opposite to that of the main flow of that phase. This transport is brought about by the existence of wakes which trail behind the moving drops. Each wake is visualised as continually picking up and shedding liquid to the non-wake portion of the continuous phase. This process results in wakes of constant volume but of changing composition, the composition of each wake being that of the non-wake continuous phase at some lower plane in the column. Therefore shedding of part of the wake constitutes backmixing of continuous

Table 6.2

MASS TRANSFER IN THE DISPERSED PHASE

Author	Equation Number	Correlation	Hydrodynamic State of Drop	Comment
Newman (126)	6.12	$E = \frac{C_o - C_f}{C_o - C^*}$ $= 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty} \frac{1}{n^2} \exp[-n^2\pi^2 \frac{D_D t}{a^2}]$	Rigid	Model based on non-stationary diffusion; applicable only to small drops.
Kronig & Brink(127)	6.13	$E = 1 - \frac{3}{8}\sum_{n=1}^{\infty} A_n{}^2 \exp[-\lambda_n \frac{16 D_D t}{a^2}]$	Circulatory	Applicable to regime of laminar circulation with Re<1; no resistance in the continuous phase.
Handlos & Baron(128)	6.14	$E = 1 - 2\sum_{n=1}^{\infty} (A_n)^2 \exp[\frac{\lambda_n U_t}{128(1+\frac{\mu_D}{\mu_C}) d}]$	Oscillatory	Drop with turbulent circulation; no resistance in the continuous phase.
*Rose & Kintner (129)	6.15	$E = 1 - \exp[-\frac{2\pi D_E}{V} \int_{t_o}^{t_f} F(t)\,dt]$	Oscillatory	Based on interfacial stretch model; deviation from experimental results is only 15%.
Skelland & Minhas(124)	6.16	$K_{dr} = \frac{S_{drc}}{t_{cr} a_r [\frac{1}{2}(C_{di} + C_{df}) - C_d{}^*]}$	Rigid	Suitable for transfer during free fall period.
Olander (130)	6.17	$K_d = 0.972\ K_{HB} + 0.075\ \frac{d}{t}$	Circulatory	Improvement on Handlos and Baron's model (128); K_{HB} being calculated from the same model.
Angelo et. al.(80)	6.18	$K_d = [\frac{4 D_d W (1+\varepsilon_O)}{\pi}]^{\frac{1}{2}}$	Circulatory	Based on surface-stretch and internal mixing concepts.

$$^*F(t) = \frac{1}{F'(t)}\{[\frac{3V}{4\pi(a' + a'\,|\mathrm{Sin}W't|)^2}]^2 \frac{1}{2\alpha} \ln \frac{1+\alpha}{1-\alpha} + (a_o + a_p[\mathrm{Sin}W't])^2\}$$

Table 6.3

MASS TRANSFER IN THE CONTINUOUS PHASE

Author	Equation Number	Correlation	Hydrodynamic State of Drop	Comment
Linton and Sutherland(131)	6.19	$Sh = 0.0582(Re)^{\frac{1}{2}}(Sc)^{1/3}$	Rigid	Validity is doubtful owing to the lack of allowance for transfer mechanism.
Rowe et.al. (132)	6.20	$Sh = 2+0.76(Re)^{\frac{1}{2}}(Sc)^{1/3}$	Rigid	Accounts for diffusion process but ignores implication due to wake formation
Kinard et.al. (133)	6.21	$Sh = 2+(Sh)_n +0.45(Re)^{\frac{1}{2}}(Sc)^{1/3}$	Rigid	Includes diffusion process with superimposed wake phenomena.
Boussinesq(134)	6.22	$Sh=1.13(Re)^{\frac{1}{2}}(Sc)^{\frac{1}{2}}$	Circulatory	Claimed to be valid for many systems.
Garner and Tayeban(135)	6.23	$Sh = 0.6(Re)^{\frac{1}{2}}(Sc)^{\frac{1}{2}}$	Circulatory	Inapplicable to Re>450
Garner and Tayeban(135)	6.24	$Sh = 50+0.0085(Re)(Sc)^{0.7}$	Oscillatory	Thorsen (138) has successfully employed the correlation in single drop studies.
Hughmark(136)	6.25	$Sh = 2+0.084[(Re)^{0.484}(Sc)^{0.339}(dg^{1/3}/D^{2/3})^{0.072}]^{3/2}$	Oscillatory	Includes eddy contribution from the wake at high Re No. (>500)
Treybal et.al. (137)	6.26	$K_C=K_S + 3.9(^{D}A/\theta_C)^{0.5}$	Mixed Regime	Drops in agitated vessel; suitable for drops in a coalescing environment. Most experimental results were correlated to within 20%.

phase from a higher to a lower concentration plane. Few attempts have been made to quantify this effect which may be pronounced in quiescent flow. The only significant work is due to Kinard et. al. (133) who developed equation 6.21 to account for the modification of the driving force due to the entrainment of a wake behind the drop. Recently, Forsyth et. al. (139) has proposed a theoretical analysis of the effect in spray columns. Wake phenomena have little significance in turbulent flow systems however because the continuous phase is continually renewed and the wake is not allowed to develop. Furthermore in agitated systems the wake contents are readily mixed with the continuous phase.

Finally, none of the correlations discussed so far make any allowance for the interfacial effects on solute transfer e.g. Marangoni Effect, discussed in the next section, which is known to affect significantly the mass transfer to or from the drop. Thus according to Sawistowski (140) the equations should only be applied to conditions away from the interface, that is where interfacial instabilities have been damped out. Further, all the correlations were derived assuming the drop to be a spheriod whereas, Nekovar and Vacek (141) found recently that in drop motion through the continuous phase, the drop shape periodically changes. Drop shapes are complex and reveal complicated flow fields inside as well as outside the drop. In a detailed investigation of the transfer of acetic acid from water drops to benzene, an area variation was found compared to a spheroid approximation. Thus in the evaluation of experimental and theoretical mass transfer data some allowance may be necessary for the effect.

6.3 Mass Transfer And Interfacial Effects

The main resistance to mass transfer in a two-phase agitated system lies in the immediate vicinity of the interface. Thus, the hydrodynamic conditions in the interface have an important effect on the mass transfer rate. Considering the mobility of the interface, it may be assumed that there will be an interaction between the hydrodynamic conditions on both sides of it, though the extent will depend upon the physical properties of the phases. It is well established that in mass transfer operations, the interface itself can be a source of interfacial turbulence. This phenomenon, reported by Marangoni (142) and named accordingly, is due to momentum transfer caused by a surface tension driving force. Other phenomena can also occur, which affect the mass transfer rate other than by a change in the hydrodynamic conditions e.g. the so-called interfacial resistance induced by a slow chemical reaction or by diminished diffusivity in the interface due to the presence of surface-active agents which form a barrier to solute diffusion.

Sternling and Scriven (143) studied the interfacial instability and the related Marangoni effect in mass transfer operations. They showed that some systems may be stable with solute transfer in one direction yet unstable with transfer in the opposite direction. It was suggested that interfacial turbulence may be enhanced by the following factors: (i) Solute transfer out of the phase of higher viscosity; (ii) Solute transfer out of the phase in which its diffusivity is lower; (iii) Large differences in kinematic viscosity and solute diffusivity between the two phases; (iv) Steep concentration gradients near the interface; (v) Interfacial tension highly sensitive to solute concentrations; (vi) Low viscosities and diffusivities in both phases. (vii) Absence of surface active agents, and (viii) Interfaces of large extent.

Maroudas and Sawistowski (144) in their work on the simultaneous transfer of two solutes across liquid-liquid interfaces found that both solutes produced spontaneous interfacial disturbances, termed 'eruptions', during mass transfer in either direction. This is contrary to the stability criteria of Sternling and Scriven (143). Mass transfer in the eruptive regime, however, can not be explained by penetration and surface renewal theories.

Rates of mass transfer tend to be very high in those extraction systems in which interfacial turbulence occurs. Transfer rates may be several times higher than those predicted from measured single phase rate coefficients.

Finally, although Marangoni effects and related interfacial turbulence have a profound effect upon the efficiency of interphase mass transfer operations and negate the classical theories of mass transfer, there has been no significant mathematical analysis of the phenomena. The theoretical approached by Sternling and Scriven (143) and Marsh et. al. (145) have limited practical application.

Recent work by Sawistowski and co-workers (140, 146-148) has however assisted qualitative appreciation of the subject. Allowance for Marangoni effects during equipment design will remain impracticable in the near future owing to the inherent uncertainties and difficulties encountered in explaining the phenomena.

6.4 Mass Transfer And Coalescence

Mass transfer in a coalescing environment is a rather complex process. As outlined in Chapter 5, numerous studies have been made of coalescence mechanisms but there is little information as to the effects of mass transfer on coalescence and vice versa.

Various workers have found that coalescence rates are greatly affected by the presence of mass transfer. The rates were also dependent on the direction of transfer. Groothuis and Zuiderweg (149) observed enhanced coalescence when the transfer was from the dispersed to the continuous phase. This was considered to be due to the Marangoni Effect which was subsequently confirmed by Jeffreys and Lawson (95), Sawistowski (150) and from work in agitated columns by Al-Hemeri (55) and Arnold (40). This observation is only applicable however if the solute decreases the interfacial tension, since McFerrin and Davidson (151), using the system water-di-isopropylamine-salt, in which the solute salt increased the interfacial tension, found that transfer into the drop aided coalescence and out of the drop hindered it. Heertjes and de Nie (134) recently concluded that the effect of mass transfer on the rate of coalescence of drops in binary systems could not be entirely explained by interfacial phenomena alone as suggested by previous workers.

Even less is known about the effect of coalescence on mass transfer. For the simple case of a drop coalescing immediately on reaching the phase boundary Johnson and Hamielee (152) proposed,

$$K_{dc} = (D_d/\pi t_f)^{0.5} \qquad 6.27$$

Penetration theory was assumed to hold for the process. Similar results were reported by Licht and Conway (153) and Coulson and Skinner (121) but, Skelland and Minhas (124) subsequently criticised the above models and concluded that the amount of mass transfer during coalescence is insignificant compared to that during drop-formation. Therefore for all practical purposes transfer during coalescence might be ignored though they proposed an expression of the form,

$$K_{dc} = \frac{2V_d}{a_c t_f}\left[\frac{2I_{f,c} + (K_{df}/V_d)a_f t_f(I_{f,c} - 4V_d)}{8V_d - 2I_{f,c} - (K_{df}/V_d)a_f t_f I_{f,c}}\right] \qquad 6.28$$

where K_{dc} = mass transfer coefficient during coalescence. The experimental data was correlated by,

$$\frac{K_{dc}t_f}{d} = 0.1727\left(\frac{\mu_d}{\rho_d D_d}\right)^{-1.115}\left(\frac{\Delta\rho g d^2}{\sigma}\right)^{1.302}\left(\frac{V_t^2 f_t}{D_d}\right)^{0.146} \qquad 6.29$$

The average deviation from the data was around 25%.

Skelland and Minhas's (124) observation of insignificant mass transfer on coalescence at the interface has been recently confirmed by Heertjes and de Nie (134, 154) who argued that drainage of drop-contents in a homophase does not allow entrainment of continuous phase in the homophase. Further since coalescence on impact with an interface is almost instantaneous (of the order of 3 x 10^{-2} sec), very little mass transfer is expected. This is particularly true in the case of agitated columns where efficient mass transfer occurs in the column proper.

The above discussion summarises data for the case of drop-interface coalescence. Unfortunately no substantial work has been performed with regard to mass transfer during interdroplet coalescence. This effect is expected to be highly significant in agitated columns which exhibit the coalescence-redispersion phenomenon. In fact, in a study with agitated vessels, Mok and Treybal (137) found the value of K_c to be approximately twice as large and $K_c a$ approximately five times as large, for the unbaffled vessel as for the baffled vessel at the same impeller power. This was attributed to the greater coalescence frequency in the unbaffled vessel.

6.5 Application Of Single Drop Mass Transfer Data To Agitated Extraction Columns

Although studies of mass transfer in agitated contactors are an extension of single drop behaviour to swarms, the direct application of single drop data is of limited value because of the complex interaction between drops of different sizes in a swarm. The basic differences may be summarised as;

1. In single drop studies, the hydrodynamic state of the drop is assumed to remain unchanged from its release to eventual coalescence with the interface. Whilst this may be true in quiescent flow it does not apply to agitated systems. Drop hydrodynamics change as it moves up, or down, the column. For example, an initially rigid drop may be transformed into a non-rigid drop during passage, owing to a gain in the total energy content transmitted from the turbulent eddies of the continuous phase. Thus in agitated columns the dispersed phase consists of a distribution of drops spanning different hydrodynamic regimes (55). Therefore interpretation of mass transfer data in terms of a specific hydrodynamic state of any dispersion is rather misleading.

2. Unlike a single drop, whose residence time in a contactor is clearly defined, drops in a swarm within an agitated continuum exhibit a spread of residence times, a larger drop having a lower residence time than a smaller one. The calculation of residence time is therefore complicated.

3. In the case of single drop mass transfer the driving force may be evaluated to a reasonable degree of accuracy. Difficulties arise in the estimation for an agitated column owing to axial mixing effects, discussed earlier.

4. Mass transfer coefficients predicted from single drop studies are usually considerably lower than values obtained in agitated systems. This is due to the phenomena of coalescence-redispersion and associated surface renewal effects which predominate in an agitated system. Drop-drop coalescence has a significant effect by reducing surface area but increasing internal mixing; the net effect on mass transfer is difficult to predict from fundamentals. Further new drops are generated continuously in an agitated system and the mode of formation is different to that of single drops. Thus the amount of transfer during break-up cannot be estimated from single drop hydrodynamics.

It follows from the above that application of single drop mass transfer correlations to the prediction of mass transfer efficiency in column contactors, as is the general practice, gives only a broad approximation. When the complexities of a chemical reaction are added the situation becomes even worse.

7. MASS TRANSFER WITH CHEMICAL REACTION

The phenomenon of mass transfer with chemical reaction comprises some combinations of the following steps: (3,155)

(a) Diffusion of one or more reactants from the bulk of phase I to the interface between the phases. Physical equilibrium may be assumed to prevail at the interface; whenever the concentration of the reactant at the interface is finite in one phase it is also finite in the other.

(b) Diffusion of the reactant from the interface towards the bulk of phase II.

(c) Chemical reaction within phase II.

(d) Diffusion of reactants initially present within phase II, and/or of reaction products within phase II, due to concentration gradients which are set up by the chemical reaction.

Steps (b), (c), (d) may take place simultaneously, and thus mutually interfere. The overall phenomenon resulting from steps (b), (c) and (d) takes place in series with step (a). If step (a) is rate controlling the overall rate is not influenced by the chemical reaction, that is the process may be regarded as a simple mass transfer process unaffected by the reaction rate. Of course, the chemical reaction may itself be the cause of an overall high mass transfer rate within phase II, resulting in step (d) being rate controlling.

A number of workers (1, 2, 3, 15) have considered generalised cases of mass transfer with simultaneous chemical reaction and developed theoretical models for specific conditions. Modelling appears to be a feasible proposition for any process which is either entirely controlled by the chemical kinetics of the reaction or entirely controlled by mass transfer rate. The situation is more complex when steps (a), (b) and (c) all contribute significantly to the determination of the overall rate of conversion. It may be further complicated by the reaction zone being present in both phases. Generally, the phases exhibit some mutual solubility however slight and as a result the reaction zone may be in either or both phases dependent upon other considerations e.g. diffusivity and concentrations of the species. However if the two phases are completely immiscible, or the reactants do not distribute at all between the phases, the reaction will be purely interfacial. Whilst such reactions are very common in heterogeneous systems where one of the phases is a solid the necessary criteria are unlikely to be satisfied in liquid-liquid systems. The probable situation when one phase is an aqueous solution is of reaction in a zone in the aqueous phase adjacent to the interface. The mechanism in this case involves dissolution of a certain amount of extractant in the aqueous phase at the interface and then its diffusion into the bulk phase and reaction with the solute in transit; this is followed by diffusion of one or more reaction products back into the solvent phase.

7.1 Reaction Kinetics and Extraction Mechanism

As discussed in the last section, the extraction rate is dependent on various interacting mechanisms. In most cases, however, the overall transfer rate is a function of both the kinetics of the chemical reaction and the rates of diffusion (molecular and eddy) of one or more of the species between the two phases. The only true exception to this is when either the reaction or mass transfer is instantaneous. Nevertheless, it is usual to classify a process as either 'kinetic-controlled' or 'diffusion-controlled' if one rate virtually determines the transfer resistance. Astarita (155), Danckwerts (3) and Sherwood and Pigford (156) have published work with regard to this which, though particularly concerned with gas absorption processes, may be equally applicable to liquid-liquid systems (155). A full review is beyond the scope of this work but according to their analysis, two phase reaction systems may be kinetically divided into,

(i) Slow reaction systems
(ii) Fast reaction systems
(iii) Instantaneous reaction systems.

The transfer process is analysed on the basis of either the film, penetration or Danckwerts' models which involves the solution of the equation,

$$\frac{\partial A}{\partial t} = D \frac{\partial^2 A}{\partial x^2} - r\ (x,t) \qquad 7.1$$

with appropriate boundary conditions related to the specific transfer mechanism. Detailed mathematical analyses are given in their work (3, 155) but only the relevant transfer rate models will be discussed in the following sections with regard to the model reaction

$$A + B \rightarrow \text{Products},$$

in which the component A from a phase diffuses into the phase containing B with which it reacts in the same phase.

7.1.1 Slow Reaction System

In a slow reaction system the kinetics are such that an appreciable amount of transferred solute reacts in the bulk and a negligible proportion in the diffusion film. The process is essentially one of physical diffusion followed by reaction in the bulk. Under these conditions the rate of transfer for the reaction is given by,

For Flow Systems,

$$Ra = k_L a \ (y^* - y^o) = \frac{1}{\tau} (y^o - y_i) + r(y^o, x_o) \qquad 7.2$$

In the case of a first-order irreversible reaction, the rate may be expressed in terms of the inflowing concentration of component A,

$$Ra = k_L a \frac{\frac{1}{\tau}(y^* - y_i) + K_1 y^*}{K_L a + K_1 + \frac{1}{\tau}} \qquad 7.3$$

A necessary condition for the above equation to be valid is no reaction in the film i.e.,

$$D_A K_1 << K_L^2 \qquad 7.4$$

<u>For a Batch System,</u>

$$Ra = K_L a \ (y^* - y^o) = \frac{dy^o}{dt} + r \ \{y^o, x^o\} \qquad 7.5$$

In case of a batch system, if y^o does not change appreciably the process will tend to a steady state and the corresponding rate expression for a first-order, or pseudo-first order, will be,

$$Ra = \frac{y^*}{[\frac{1}{K_1} + \frac{1}{K_L a}]} \ [1 + \frac{K_L a}{K_1} \exp\{-(K_L a + K_1) \ t\}] \qquad 7.6$$

The condition for no reaction in the film will be,

$$\frac{D_A K_1}{K_L^2} << \frac{K_1}{K_L a + K_1} \qquad 7.7$$

7.1.2 Fast Reaction System

In this case, the reaction is sufficiently fast that a substantial amount of the dissolved solute reacts in the diffusion film rather than being transferred unreacted into the bulk phase. In general, this results in enhancement of the overall rate. It is convenient to express the effect of chemical reaction in terms of an enhancement factor, which is the factor by which the reaction increases the transfer rate compared to the rate of physical transfer. Clearly in the case of a fast reaction this factor must be >1.

The rate of transfer for fast irreversible reactions in which a substantial amount of solute reacts in the film may be expressed as,

$$Ra = \phi K_L a y^* = \frac{1}{z\tau} (x_i - x^o) \qquad 7.8$$

where the enhancement factor ϕ is given by,

(i) for a first order reaction based on the film model (3),

$$\phi = \sqrt{D_A K_1}/K_L \quad \text{for} \quad \sqrt{M} >> 1 \qquad 7.9$$

(ii) for a second order reaction based on the film model (157),

$$\phi = \frac{\sqrt{M \frac{\phi_i - \phi}{\phi_i - 1}}}{\tanh\sqrt{M \frac{\phi_i - \phi}{\phi_i - 1}}} \quad \text{for } y^o = 0 \qquad 7.10$$

$$\text{where } \phi_i = 1 + \frac{D_B x^o}{z D_A y^*} \qquad 7.11$$

(iii) for any mass transfer system, based on the penetration model (158),

$$\phi = \frac{R_c \phi_1^{\,2}}{2} \left[\sqrt{\frac{1}{\phi_1^2}\left[1 + \frac{4}{R_c} \left(1 + \frac{1}{R_c}\right)\right]} -1\right] \qquad 7.12$$

where R_c is the ratio of interfacial concentration of

Fig. 7.1 Enhancement factors for second order reaction(157) transferring solute A to the bulk concentration of B.

(iv) For m,n^th^ order reaction $(r = K_{mn} \{A\}^m \{B\}^n)$ based on the film model (159),

$$\phi = \sqrt{M}\left\{\frac{\phi_i - \phi}{\phi_i - 1}\right\}^{n/2} \tanh \sqrt{M}\left\{\frac{\phi_i - \phi}{\phi_i - 1}\right\}^{n/2}$$

$$\text{when } y^o = 0 \qquad 7.13$$

Equation 7.10 for a second order reaction, reproduced in Fig. 7.1, was developed by Van Krevelen and Hoftizer (157) and successfully tested against experimental data by various workers. In most cases the data could be correlated to an accuracy of 90%. The general shape of the curves in Fig. 7.1 suggests that for a given ϕ_i the enhancement is initially small due to the slow rate of reaction and the process approximates to purely physical diffusion. However, with increasing $\sqrt{M}$, the effect of chemical reaction becomes appreciable. The reaction rate then becomes very fast indeed as $\phi \rightarrow \phi_i$ and is controlled by the relative diffusion rates of A and B.

Fig. 7.1 has been found useful for both quiescent and agitated absorbers in gas-liquid reactions. Danckwerts

(3) has successfully applied it to describe the absorption of carbon dioxide in sodium hydroxide solution in a packed column. Its application in liquid-liquid reactions has not been investigated in detail, although the validity of such an approach has been reported (183) and Wellek and Brunson (174) used a similar approach for single droplets in a spray tower. However it is open to question whether the approach applies to bubbles or droplets in a continuum equally as well as for gas passing over a film. In the case of droplets in an agitated contactor the presence and degree of coalescence-redispersion would be an important factor.

Different rate expressions may be deduced dependent upon the circumstances under which the transfer process occurs. These are summarised below:

(a) m,n^th^ order reaction ($r = K_{mn}\{A\}^m\{B\}^n$) with the rate of transfer being independent of K_L (159),

$$R = \sqrt{\left\{\frac{2K_{mn}D_A(y^*)^{m+1}(x^o)^n}{m+1}\right\}} \qquad 7.14$$

This is the case when $\phi >> 1$, i.e. when all the transferred solute reacts in the film and none diffuses in the unreacted state into the bulk of the phase.

(b) Fast pseudo-first order reaction where the concentration of the reactant is maintained virtually undepleted (3),

$$R = y^* \sqrt{D_A K_2 x^o} \qquad 7.15$$

The condition to be satisfied is from film model considerations,

$$\sqrt{[D_A K_1 x^o]} > 3K_L \qquad 7.16$$

(c) First-order irreversible reaction under conditions such that the concentrations of the reacting species other than the transferred solute are virtually uniform (3),

$$R = K_L y^* \sqrt{\left[1 + \frac{D_A K_1}{K_L^2}\right]} \qquad 7.17$$

The criterion for the concentrations to be uniform (apart from that of A) is given by,

$$y^* \sqrt{D_A K_1} << \frac{K_L x^o}{z} \qquad 7.18$$

The corresponding rate equation based on the film model is,

$$R = (y^*/K_L) \left[\frac{\sqrt{[D_A K_1]}}{\tanh\left[\sqrt{D_A K_1}/K_L\right]}\right] \qquad 7.19$$

(d) Danckwerts (3) analysed second order reaction systems and suggested a model for the limiting case in which the reaction may be regarded as pseudo-first order,

$$R = y^* \surd [D_A K_2 x^o + K_L^2] \qquad 7.20$$

The reaction will be pseudo-first order if,

$$\frac{\surd [D_A K_2 x^o]}{K_L} << 1 + \frac{x^o}{zy^*} \qquad 7.21$$

7.1.3 Instantaneous Reaction Systems

When the reaction is instantaneous, the transferring component and the reactant in the reactive phase obviously cannot co-exist in the same region. Under such circumstances the reaction may be so fast that the interface is starved of both the reactants. The term 'instantaneous' is an idealised one since all reactions proceed at a finite rate. However, 'instantaneous' reactions are characterised by a high specific reaction rate together with a low value of K_L. Thus the rate of reaction is entirely controlled by the diffusion mechanism; the rate of reaction is sufficient to maintain equilibrium at all points and the kinetics are therefore irrelevant.

The general rate expression according to the film model as derived by Hatta (160) is given by,

$$R = K_L y^* \phi = K_L y^* [1 + \frac{D_B x^o}{z D_A y^*}] \qquad 7.22$$

When $ZD_Ay^* << D_Bx^o$, the rate will be given by,

$$R \approx K_L \frac{D_Bx^o}{ZD_A} \quad \text{i.e. when } y^* << x^o \qquad 7.23$$

Danckwerts (3) and Sherwood (156) solved equation 7.1 for the enhancement factor E as,

$$\phi = 1/\operatorname{erf}(\beta/\sqrt{D_A}) \qquad 7.24$$

where β is obtained by,

$$\exp[\beta^2/D_B]\operatorname{erfc}[\beta/\sqrt{D_B}] = (\frac{x^o}{Zy^*})(\frac{D_B}{D_A})^{\frac{1}{2}}\exp[\beta^2/\sqrt{D_A}]\operatorname{erf}[\beta/\sqrt{D_A}]$$

for $\phi >> 1.0$ i.e. in the instantaneous reaction regime, this may be approximated to,

$$\phi_i = [\frac{D_A}{D_B}]^{\frac{1}{2}} + \frac{x^o}{Zy^*}[\frac{D_B}{D_A}]^{\frac{1}{2}} \qquad 7.25$$

The rate expression is then given by,

$$Ra = K_La[\{\frac{D_A}{D_B}\}^{\frac{1}{2}}y^* + \{\frac{D_B}{D_A}\}^{\frac{1}{2}}\frac{x^o}{Z}] \qquad 7.26$$

All the models given in sections 7.1.1 to 7.1.3 assume that the transfer resistance is restricted to one phase, that is, the phase where chemical reaction takes place. Thus they will only be applicable to those systems in which the transferring solute itself constitutes a phase, or where most of the resistance lies in the reactive phase. There are numerous cases in practice e.g. hydrolysis, esterification and nitrations. No modifications of the models have yet been published to account for the detailed hydrodynamics of many other examples in which there are significant resistances in both phases. Indeed the number of parameters involved in such cases, when system hydrodynamics are also included, may preclude useful modelling (3).

7.2 Extraction with Chemical Reaction in Single Drops

Although the mass transfer mechanism in multiparticle systems, that is in practical applications, differs from that to or from a single drop, studies of the latter help to elucidate the more complex process. Unfortunately, however, fundamental single drop studies of extraction with chemical reaction have been very limited.

Tyroler et. al. (171) investigated experimentally and theoretically mass transfer to single stagnant and circulating drops during the steady fall period. They studied the position of the reaction shell in aqueous sodium hydroxide drops falling through cyclohexanol containing acetic acid. The reaction surface was located from photographs. It was concluded that a study of the time-variant position of the reaction shell could enable prediction of local mass transfer rates in drops under the influence of chemical reaction. Mathematical analysis involved solution of transport phenomena equations. The study was however essentially qualitative since changes of physical properties of the dispersed phase with the progress of reaction were neglected and further resistance to transfer was assumed to be entirely within the dispersed phase. The latter is inapplicable when the continuous phase is not a pure reactant.

Watada (172) studied aqueous sodium hydroxide drops, falling through and reacting with butyl lactate or ethyl acetate. These systems underwent interfacial turbulence which could be observed visually and some of the drops even broke up, probably due to Marangoni type instability. The phenomena could not be explained.

A detailed study of transfer into the drop has recently been carried out by Nakashio et. al. (173). The extraction of uranium nitrate by tricresyl-phosphate (TCP) and of hydrochloric acid by n-lauryltrialkylmethylamine (Amerlite-LA-2) were investigated in a column. The reactions were interfacial and of pseudo first order. The diffusion model of Heertjes and de Nie (122) was modified to interpret the mass transfer mechanism during drop formation. Mass transfer rate during drop-rise was correlated by Newman's (126) model. The following expressions were proposed,

(i) <u>Transfer during drop formation</u>

The average extraction rate $\bar{N}_f$ is represented by,

$$\bar{N}_f = (1/A_o t_f)\int_o^{t_f} \bar{N}\, t\, F_f(t)\,dt \qquad 7.27$$

where $\bar{N} = K\bar{\eta}\, C_{A_O}\, C_{B_O}^{\ Z}$

$$\bar{\eta} = (1/\tau^2)\int_o^{\tau} 2\tau \exp(\tau^2)\mathrm{erfc}(\tau)\,d\tau.$$

$F_f(t)$ = the life time distribution of the drop surface elements.

$= A_O/t_f$ for $0 \leqslant t \leqslant t_f$

A_O = drop surface area.

(ii) Transfer during drop-rise

The average extraction rate $\bar{N}_r$,

$$\bar{N}_r = K \, \bar{\eta}_r \, C_{A_O} \, C_{B_O}^{\,z} \qquad 7.28$$

The interfacial reaction did not influence the extraction rate during drop formation and had only a slight effect during drop-rise. The experimental data for both systems during drop-rise agreed well with Newman's model for a rigid sphere. The results cannot however be generalised since a drop's hydrodynamics change continually during its passage through the continuous phase due to the progressive change in surface and internal conditions caused by the unsteady-state diffusion, and counter diffusion, of reaction species. The assumption of the rigid drop model is thus of doubtful validity.

More recently Wellek and Brunson (174) studied liquid-liquid extraction involving chemical reaction in greater detail. Experimental data were obtained for the diffusion of n-pentyl formate from the continuous phase into aqueous sodium hydroxide droplets falling in a single stream through a simple spray extractor. The process involved consecutive diffusion and reaction in the dispersed phase. Semitheoretical models based on penetration theory and film theory were developed to interpret the mass transfer data. The film theory based model generally gave a better approximation to the experimental data. However, the average absolute deviations of the experimental mass transfer data from both the models were remarkably high, viz, the deviation from the film model was in the range 11.2% - 53.4% and from the penetration model 9.1% - 74.3%. Deviation was more marked for drop sizes >0.15 cm probably because drops greater than this size would be expected to oscillate and may exist in the mixed regime of oscillation and circulation, discussed in greater detail in Chapter 6. The net effect of these complex hydrodynamics is difficult to predict from theoretical considerations.

This brief review illustrates the complexities involved in mass transfer with simultaneous chemical reaction. In the absence of a valid model, a prediction may be obtained by combining the film theory for mass transfer with chemical reaction and the mass transfer results for the case of no reaction. This appears to be the only alternative at present.

7.3 Mass Transfer with Chemical Reaction in Practical Systems

Studies of mass transfer with chemical reaction in practical systems have been very limited. Progress has been slow owing to the complex nature of the phenomena already discussed. Various workers have proposed simplified models each with its own special characteristics. However each model applies only to a particular scheme, order and rate of reaction and takes into account only a selection of process variables. Investigations have considered mainly batch systems, although a few important processes have also been studied in flow systems. These investigations are discussed in the following sections.

7.3.1 Batch Processes

Numerous studies have been made with two-phase metal extraction systems (1, 4-7). As stated earlier, these investigations were mainly concerned with the kinetics and the distribution mechanism of the metal complex in the aqueous and organic phases. Calculation of overall rate is generally based on the evaluation of the metal distribution factor which is related to the concentrations of the various species and the equilibrium constant. For example in the extraction of Copper (II) from chloride solution using LIX64N in kerosene, the distribution coefficient (D) of the metal is given by, (4),

$$D = K.\ \frac{[HA]^n}{[H^+]^n}\ .\ \frac{1}{1+\beta_1[C\ell^-] + \beta_2[C\ell^-]^2} \qquad 7.29$$

where $|HA|$ = LIX concentration

β_1, β_2 = Formation constants of the metal complexes.

There have been no significant investigations of the effect of hydrodynamics on the extraction rate. Furthermore controversy exists as to the locale of the reaction zone i.e. whether the reaction is purely interfacial or occurs in the bulk (6). Recently Hanson (1) suggested that with most metal extraction systems, reaction may be presumed to take place in a zone in the aqueous phase adjacent to the interface. That the reaction occurs in the aqueous phase is in agreement with Abramzon and Kogan's (175) postulation which suggests that a liquid-liquid reaction involving ionic and non-ionic reactants would proceed in the aqueous phase. This situation is more likely in the case of metal extraction than the converse, i.e. a reaction zone in the solvent, as the latter would assume free cations transferring into an organic phase. Based on the above postulation of the reaction zone in the aqueous phase and using the film model Hanson derived a mathematical expression for the rate of transfer of an elementary metal extraction system,

$$M^{n+} + nHR \underset{k_2}{\overset{k_1}{\rightleftarrows}} MR_m + nH^+$$

The rate is given by,

$$R_{MR_n} = -\frac{1}{n}\left\{\frac{[HR]_{org}}{m}\right\}^{\frac{n+1}{2}} \sqrt{\frac{2D_{HR}.k_1.[M^{n+}]_b}{n+1}} \qquad 7.30$$

This assumes that the effect of the reverse reaction is negligible, but may be extended to include both the forward and reverse reaction schemes. The model has not been tested experimentally and its application to practical systems is apparently limited by the assumption made in the derivation that the extractant is in phase equilibrium at the interface; this can only be true in the case of an extracting phase which is itself a pure reactant.

Mansoori and Madden (178) studied interphase chemical reaction whilst determining the oxidation-reduction rates in an agitated liquid-liquid system in which tetravalent cerium ions were reduced by tetrachlorohydroquine (TCH). The reduction rate of cerium was found experimentally to be directly proportional to the TCH concentration and to $N^{1.4}$. This suggested that the rate was directly proportional to the interfacial area. Two possible rate limiting mechanisms were considered:

(a) Assuming that the solute tetrachlorohydroquinone was at physical partition equilibrium at the interface, the rate of reduction of cerium may be expressed as,

$$-V_C\frac{dc}{dt} = K_p\,[TCH]S\sqrt{DK} = K'[TCH]S \qquad 7.31$$

This is based on the theory of extraction accompanied by a rapid first order chemical reaction. The constant K' is independent of the system hydrodynamics and related only to the physico-chemical properties. However owing to the lack of proper kinetic data for TCH-Ce reaction in a homogeneous system, the above mechanism may not be convincing since it presupposes that the reaction is zero-order in Ce(IV); and

(b) Assuming that the rate of chemical reaction is very fast compared with the rate of passage of TCH across the interface, so that the rate is independent of the kinetics of reaction. The rate expression proposed was,

$$- V \frac{dc}{dt} = K_{OW}[TCH]S \qquad 7.32$$

Whilst the rate equations 7.31 and 7.32 are similar, the distinction is that K_{OW} is independent of the chemical reaction rate. Since fortuitously either of the models suit the experimental results, a clear-cut choice of mechanism is rather difficult. The first mechanism, apart from uncertain kinetics, is clearly however of doubtful validity as the TCH would not in reality be at physical partition equilibrium at the interface.

Searle and Geordon (179) investigated the sodium hydroxide-acetic acid reaction in a system which comprised a layer of alcohol-saturated water containing sodium hydroxide beneath a layer of water saturated isobutanol

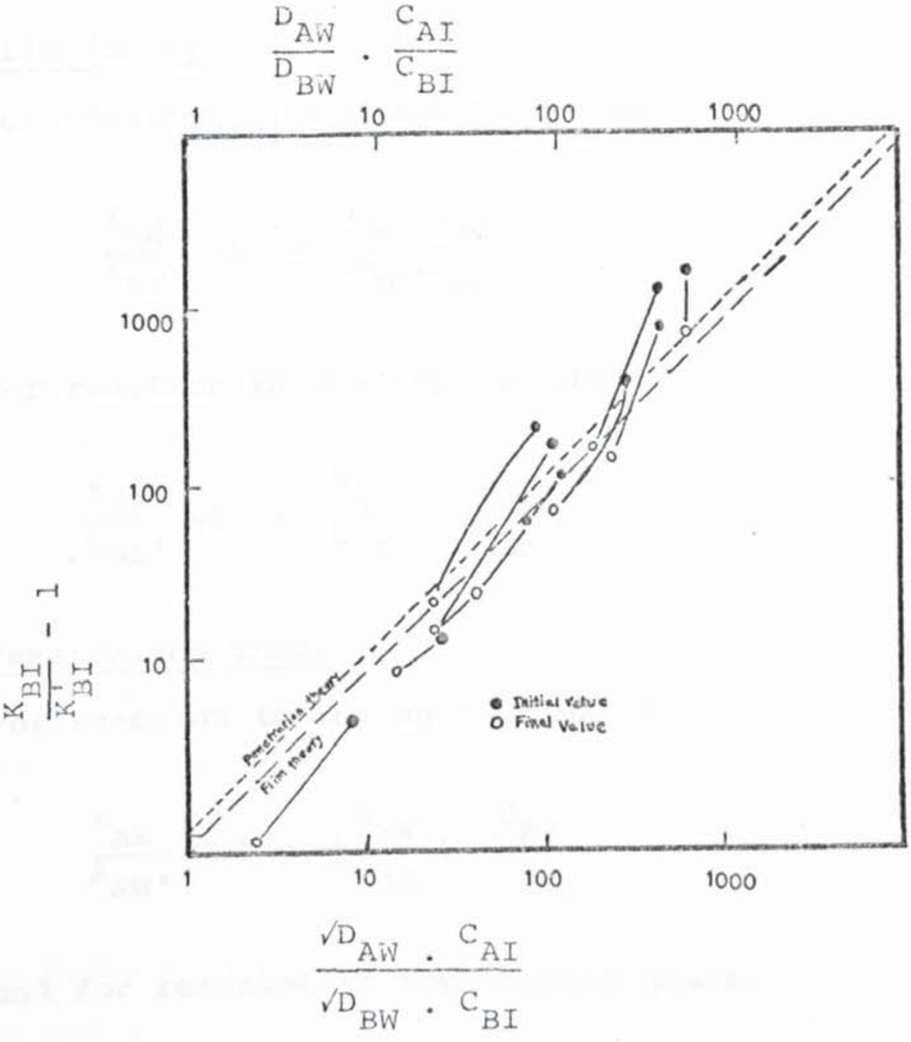


Fig. 7.2 Experimental increase of alcoholic-phase mass transfer coefficient vs theoretical increase.

containing acetic acid. Both phases were agitated such that there was minimum practicable disturbance of the interface. The investigation was to ascertain if film theory and/or penetration theory were valid for the prediction of mass transfer rates with chemical reaction. The following set of equations were considered,

Film Theory

For reaction in the aqueous phase:

$$\frac{K_{AW}}{K_{AW'}} - 1 = \frac{D_{BW}.C_{BW}}{D_{AW}.C_{AW_i}} \qquad 7.33$$

For reaction in the organic phase,

$$\frac{K_{BI}}{K_{BI'}} - 1 = \frac{D_{AI}}{D_{BI}} \cdot \frac{C_{AI}}{C_{BI'}} \qquad 7.34$$

Penetration Theory

For reaction in the aqueous phase:

$$\frac{K_{AW}}{K_{AW'}} - 1 = \sqrt{\left(\frac{D_{BW}}{D_{AW}}\right)} \cdot \frac{C_{BW}}{C_{AW_i}} \qquad 7.35$$

and for reaction in the organic phase,

$$\frac{K_{BI}}{K_{BI'}} - 1 = \sqrt{\left(\frac{D_{AI}}{D_{BI}}\right)} \cdot \frac{C_{AI}}{C_{BI_i}} \qquad 7.36$$

The considerable scatter of experimental data when compared with the models is illustrated in Fig. 7.2. The penetration theory predicts values of $|(K/K')-1|$ which are about 100% high at 0.005N bulk concentration of acetic acid, correct values at about 0.1N and values about 60% low at 1N. Likely explanations for the above discrepancies between theoretical and calculated transfer coefficients would lead to theoretical coefficients higher than experimental values, whereas analysis of data reveals that the reverse is true at concentrations above about 0.1N. This is contrary to the fact that at higher concentration the viscosity would be increased and molecular diffusivity decreased. From these effects the experimentally observed values should be less than the theoretically calculated values and not the converse. The anomaly cannot be explained. Sherwood and Wei (180), however, obtained a high mass transfer rate with the same system, viz, the rate was 2.4 times the value predicted from film theory at low concentrations of sodium acitate. Clearly therefore film theory,and the penetration model, is only applicable to a narrow range of concentrations.

Piret, Penny and Trambouze (8) developed a mathematical model to predict the concentration of one of the reacting components in a batch system ,

$$-\frac{dx_A}{dt} = \frac{[bK'+ak]n_T a_{AO} - K'(bn_{AO}+an_{BO})}{an_T e^Y} \qquad 7.37$$

where,

a,b → stoichiometric coefficient

n_T → total mols in reactive phase.

$\frac{K}{K'}$ → equilibrium constant

y → characteristic root.

This is of limited application since a basic assumption is that the two phases are dilute solutions mixed so effectively that they are in equilibrium at all times, giving a system which is reaction rate controlled. The model was not tested experimentally.

Trambouze and Piret (184), however, extended the work to concentrated solutions. Here again it was assumed that there was homogeneity between the two phases and that the overall process was kinetically controlled. Subsequently, Trambouze et. al. (185) proposed a model for a first order slow reaction on the assumption that the solute transfers and reacts consecutively,

$$\frac{V_1}{VK_A}\ \frac{d^2a_1}{dt^2} + \frac{da_1}{dt}\left[\alpha_A + \frac{KV_1}{VK_A} + \frac{V_1}{V_2}\right] + K\alpha_A a_1 = 0 \qquad 7.38$$

This model of consecutive diffusion and reaction has not been verified experimentally but might prove useful if the reaction rate constant is very low, i.e. of the order of $K < 4 \times 10^{-3}$ ℓ/sec, when the mechanism may be applicable (186).

The effect of phase ratio on the apparent reaction rate was investigated by Koen and Trambouze (187). A reduced velocity constant was derived in terms of the true velocity constant, the distribution coefficient for the reactant and its concentration and conversion. An investigation using the system n-heptane-acetic anhydride water showed that this reduced velocity constant was greatly dependent on phase ratio and was a maximum at a phase ratio of 0.7 (water: organic).

Cho and Ranz (188) investigated slow and instantaneous reactions in two phase systems. Two-phase liquid reactions were found to be complicated by spontaneous physico-chemical phenomena in the interfacial region. With a second-order instantaneous reaction, mass transfer rates were observed to be approximately twice as large as predicted by theory. This suggests that the theory of diffusion and reaction is not applicable when interfacial turbulence is present. Similar observations were made earlier by Sherwood and Wei (180) who studied instantaneous reactions experimentally in stirred vessels but were unable to compare their results and reaction theory because of the effects of interfacial turbulence.

In the important practical case of two phase aromatic nitration processes there is divergence of opinion between various workers as to the rate controlling mechanism i.e. whether the process is diffusion or kinetic controlled (1). Giles (189) studied the process in detail and considered it to be diffusion-controlled, that is reaction kinetics were of no practical significance in the determination of the overall rate of transfer. A rate model was proposed,

$$R = \frac{[TOL]_{org}}{\phi_{TOL}} \sqrt{DK_2 |HNO_3|_{aq}} \qquad 7.39$$

where $[TOL]_{org}$ = concentration of toluene in organic phase.

ϕ_{TOL} = partition coefficient of toluene in the aqueous and organic phases.

The model was later verified by Ismail (190) under conditions in which (a) the sulphuric acid concentration in the aqueous phase was sufficiently high to give a fast reaction, and (b) the diffusion process was solely by molecular diffusion. In a turbulent system, D would be the sum of molecular and eddy diffusivities with the latter dominating; thus uncertainty as to the eddy diffusion component renders such models difficult to use for quantitative prediction of transfer rates. Cox and Strachan (191) however observed for toluene nitration that whether the process was kinetically or mass transfer controlled depended on the relative values of $K_2|HNO_3|$ and K_La. It was concluded that in a practical agitated contactor, the value of K_La even with efficient stirring is unlikely to exceed 0.5 sec^{-1}. Evidently if the value of $K_2|HNO_3|$ is very much smaller than this, the rate will be kinetically controlled whereas if it is very much greater, the rate will be mass transfer controlled.

Cox and Strachan subsequently studied the nitration of chlorobenzene to determine the influence of chemical reaction on the rate of surface renewal at a liquid-liquid interface. Nitration was carried out under 'mass transfer control' conditions in a stirred reactor and in a stirred cell. In both cases the fast reaction diffusional regime was observed with the reaction rate influencing the concentration gradient of chloro-benzene in the acid phase at the interface, and hence the rate at which chloro-benzene was transferred into the acid phase and nitrated. In the case of the stirred reactor as the reaction rate constant decreased transition occurred to the slow reaction diffusional regime and then to the kinetic regime. However, with the stirred cell, the expected 'levelling off' of the mass transfer rate with decreasing reaction rate, corresponding to the onset of the slow reaction diffusional regime, did not occur. On the contrary, the mass transfer rate fell continuously as illustrated in Fig. 7.3 . It was concluded that chemical reaction promoted good surface renewal within the stirred cell which agitation alone was insufficient to maintain. It is of particular interest that whilst the mass transfer coefficient without reaction was approximately 1.73×10^{-6} m/sec, with reaction it was 2.10×10^{-5} and 2.29×10^{-5} m/sec for the stirred reactor and stirred cell respectively. This demonstrates the considerable influence which chemical reaction may have on the rate of surface renewal.

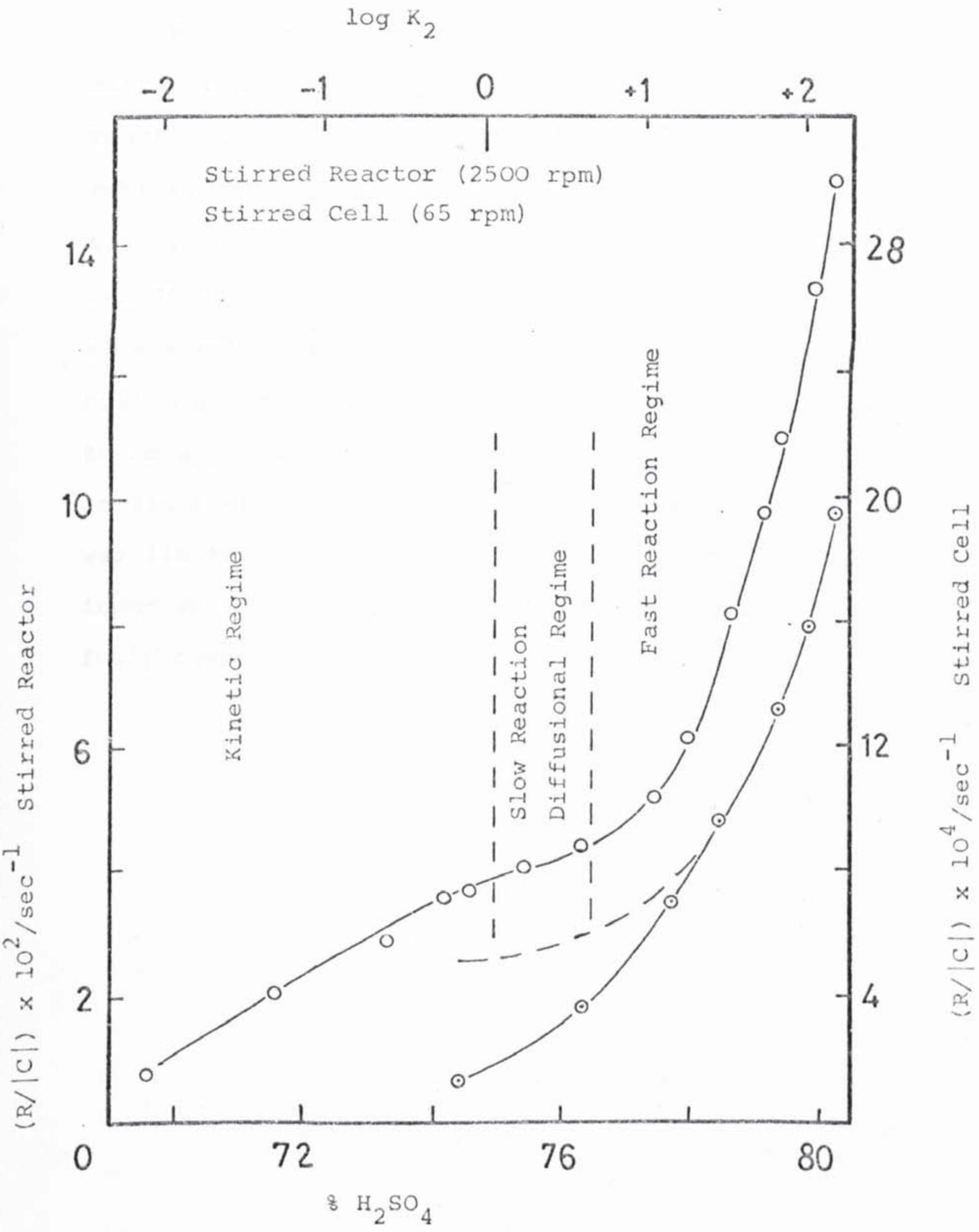


Fig. 7.3 Kinetic and diffusional regimes

Sharma and co-workers (181 - 183) studied the extraction of various esters in alkaline solutions. The reactions were in general second order but could under certain circumstances be considered as pseudo-first order. One phase comprised pure esters so that the resistance in that phase could be neglected. The theory of absorption with second order reaction in a gas -liquid system based on film or penetration models was found to be applicable to extraction with second order reaction in liquid-liquid systems. However, their investigation was limited to a narrow range of concentrations and energy input and, as such, the effect of hydrodynamics was not fully covered.

7.3.2 Continuous Processes

A theory for the design of a continuous chemical reactor for two-phase chemical reaction processes was developed by Trambouze et. al. (192). The following design equations were proposed,

For a C.S.T.R. Chain,

$$(C_A)_i = \frac{1}{K_A V}\Big[\big(\frac{F_1}{\rho 1} - F_1 - K_1 V_1 - K_A \alpha_A V\big) G_1 \rho_1{}^i + \big(\frac{F_1}{\rho_2} - F_1 - K_1 V_1 - K_A \alpha_A V\big) G_2 \rho_2{}^i\Big] \qquad 7.40$$

where $(C_A)_i$ = concentration of the solute in the ith stage.

For a column,

$$\left[\frac{F_1 F_2}{K_A S^2 \alpha_A}\right] \frac{d^2 a_2}{dx^2} + \frac{1}{S}\left[\frac{F_1}{\alpha_A}\left(1 + \frac{k.r}{K_A}\right) - F_2\right] \frac{da_2}{dx} - kra_2 = 0 \qquad 7.41$$

Experimental data obtained for continuous hydrolysis of acetic anhydride in a benzene-water system during countercurrent operation of a pulsed sieve plate column and in a packed column were in good agreement with the theory as is demonstrated in Fig. 7.4 ; the data obtained were within 5% of the predicted values. The model is however limited to slow reaction systems ($K=1.87 \times 10^{-3}$ ℓ/sec), in which the diffusion and reaction processes are consecutive.

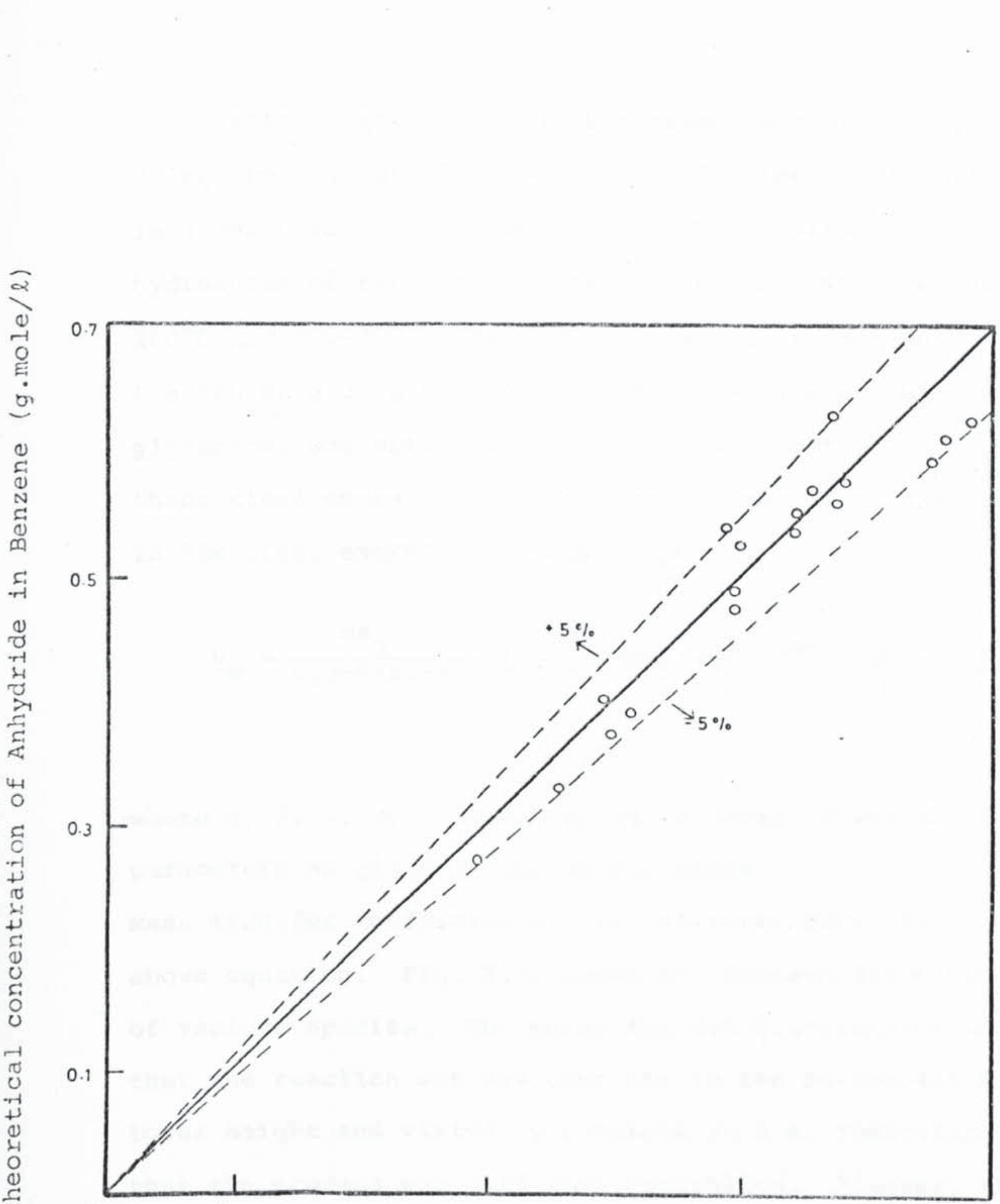


Fig. 7.4 Experimental and calculated values.

Jeffreys et. al. (193) investigated hydrolysis, using the concept of consecutive diffusion and reaction, in a countercurrent spray column. The continuous hydrolysis of fat was performed by feeding water at 220-280^{o}C and 600-700 lb/in pressure through sprays into the top of a 22 m high tower. The reaction product, glycerine, was obtained in solution with water. A theoretical expression for the concentration of glycerine in the final extract (y_o) was proposed,

$$y_o = \frac{mz_o}{\omega[\alpha - \exp(-\gamma H)]}\left[1 + \left(\frac{\lambda-1}{\alpha-\lambda}\right)\exp(-\gamma H) - \left(\frac{\alpha-1}{\alpha-\lambda}\right)\exp(-\beta H)\right] \tag{7.42}$$

where α, β, λ, ω, γ were defined in terms of system parameters as given in the Nomenclature.
Mass transfer coefficients were estimated from the above equation. Fig. 7.5 shows the concentration profiles of various species. The curve for fat distribution shows that the reaction was 95% complete in the bottom 4.5 m of tower height and virtually complete in 9 m, indicating that the process was diffusion controlled. However, the mass transfer driving force did not reach its maximum until the fat had passed 3 m up the tower, which implies that in the lower part of the column the mass transfer process must await the chemical reaction process. This suggests poor mass transfer conditions in the contactor and the values of H.T.U. and H.E.T.S. obtained were indeed very much greater than would be expected for a spray column

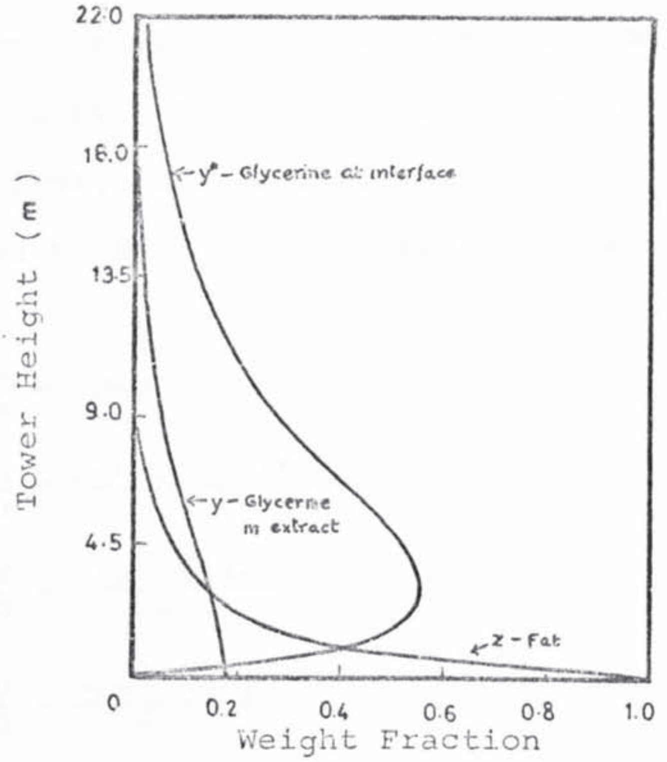


Fig. 7.5 Concentration distributions in column

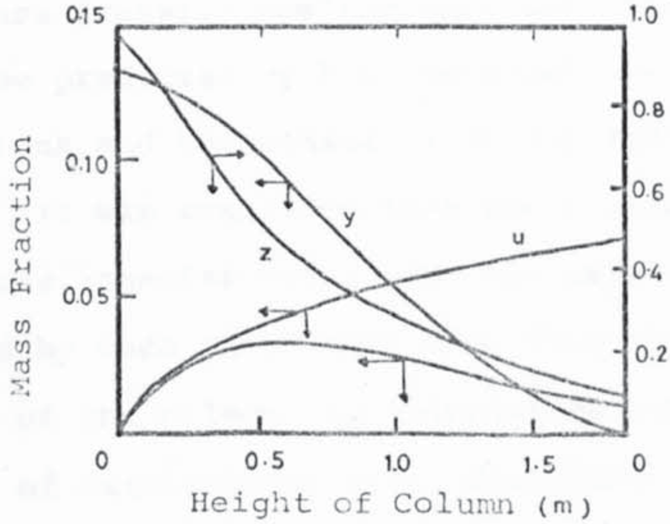


Fig. 7.6 Computed composition profiles in a continuous hydrolyser.

performing a conventional duty. Subsequently, Jeffreys and co-workers(194) studied the process mechanism in greater detail in a 0.075 m diameter, 2.5 m long pilot scale plant. The following set of equations were proposed to define the entire process,

$$\frac{dG}{dh} = \beta-\alpha \qquad 7.43$$

$$\frac{du}{dh} = \frac{\beta-0.587\gamma-(\beta-\alpha)u}{L} \qquad 7.44$$

$$\frac{dx}{dh} = \frac{\gamma-\alpha-(\beta-\alpha)x}{L} \qquad 7.45$$

$$\frac{dy}{dh} = \frac{-\alpha-(\beta-\alpha)y}{G} \qquad 7.46$$

where α, β, γ were defined in terms of process variables as given in the Nomenclature. These equations were solved by a numerical technique. Fig. 7. 6 shows the concentration distribution of various reaction species. High mass transfer coefficients were reported compared to those predicted by the empirical correlation of Calderbank and Korchinski (194) for fully circulating drops. It was concluded that one possible reason for high mass transfer rates was the effect of the wake carried by each individual drop from the top to the bottom of the column; an interesting example of a limited amount of axial mixing being desirable since water initiated the reaction at the bottom of the column. Possible coalescence effects at high dispersion concentration may also influence the mass transfer rates. Apart from the above factors however chemical reaction itself is likely to have contributed in enhancing the observed mass transfer rates.

Recently, Bruin et. al. (195) investigated the potential of the R.D.C. for extraction involving interphase chemical reaction. The system examined was the extraction of cobalt chloride from aqueous process streams by extractants including tri-iso-octylamine and alkyl sulphonium compounds in toluene. The height of a transfer unit was used as a measure of the mass transfer rate. The results reproduced in Fig. 7.7 and 7.8 illustrate that at very low power inputs $(H.T.U.)_{true}$ was so high that long slender columns were needed whilst at high power inputs it was so low that axial mixing effects which increase with increasing power input and column diameter became length-determining and dependent upon the flooding velocities a large-diameter column was needed. Both situations imply a relatively large volume of contactor. Optimum volume of the contactor was for a continuous phase flow rate of 4 m^3/hr and a dispersed phase flow rate of 12 m^3/hr, corresponding to a power input of roughly 0.15 m^2/s^3. Further efforts to reduce the mass transfer limitation, by increasing the power input, were thwarted by increased axial mixing.

The investigation did not however include any detailed study of the variation in transfer mechanism with various degrees of turbulence in the R.D.C.; this

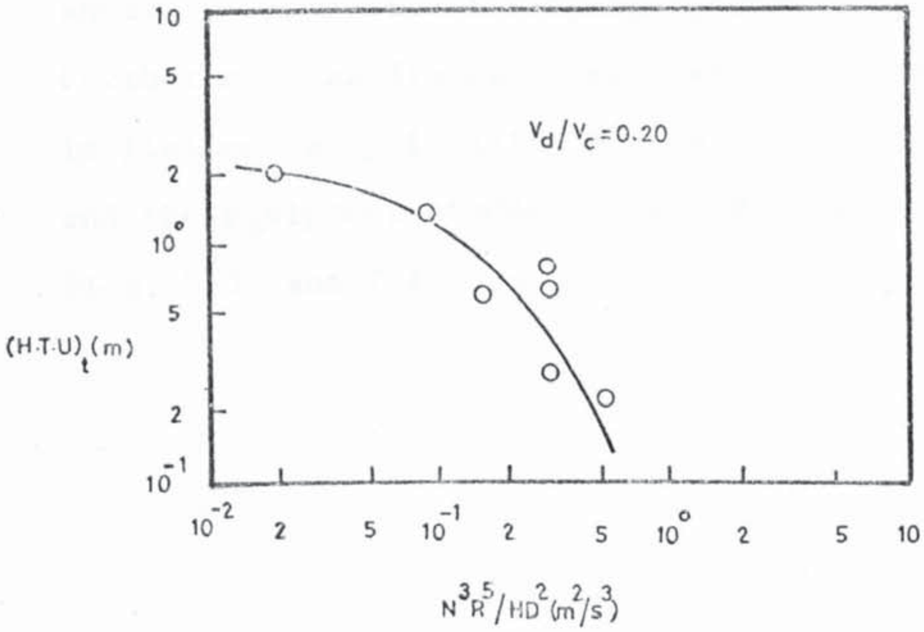


Fig. 7.7 $(H.T.U)_{true}$ against specific power input

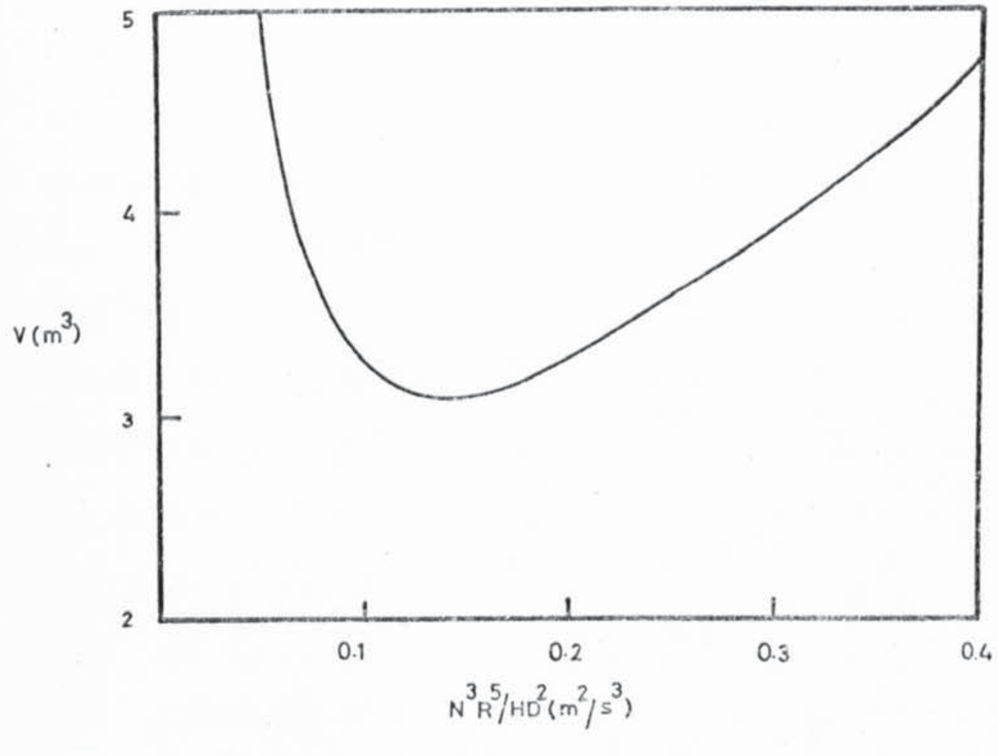


Fig. 7.8 Typical calculation of column volume

should be accounted for in optimising a system. Furthermore, as discussed earlier the H.T.U.-concept is limited in application to the particular system and the equipment studied. Thus for design purposes Figs. 7.7 and 7.8 can only serve as a qualitative guide.

7.4 Kinetic Studies In Solvent Extraction

The only appreciable kinetic studies in heterogeneous reactions have been concerned with extraction of metals such as Uranium and Plutonium and a few other rare earth metals (5 , 7 , 6). The extraction of common metal chelates has received some attention, typical of these being extraction of copper by LIX reagents- α-hydroxy oxime/β-hydroxybenzophenone oxime mixtures (161); nickel, cobalt by α-hydroxy oxime/lauric acid mixtures (162) and some other transition metals by D2EHPA, a phosphoric acid complex. There has been an upsurge of interest in this field recently with the extraction of iron, zinc, cadmium, manganese, silver and alkali metals, all being studied with various extracting agents, viz, carboxylic, salicylic and bromo-lauric acids, tri-n-butyl phosphate (TBP), LIX, KELEX and D2EHPA (4,6).

The different techniques and equipment used for the evaluation of kinetic data are, (1)

(a) Use of the 'dip-sample' technique which involves sampling from a stirred cell at suitable time intervals;

(b) Use of an AKUFVE apparatus. This is normally used for the continuous measurement of the distribution factor of a solute in liquid-liquid extraction. It consists of a mixer, a centrifuge for absolute phase separation and on-line detectors, which are either connected in a once-through or in a closed cycle arrangement;(163).

(c) Use of a wetted-wall column;

(d) Measurement of the rate of transfer in stirred cells having constant interfacial areas;

and (e) Measurement of the rate of transfer to or from single drops of known volume in a vertical column.

The 'dip sample' technique is best suited to slow reactions and has been widely used in industry where only an approximate estimate of extraction rate is required. Ryon and Johnson (164) employed this method for uranium extraction from leach liquors. One of its limitations is that area-free mass transfer coefficients can not be obtained.

Alimarin et.al.(165) and Flett et.al(161) investigated the kinetics of solvent extraction of metal chelates and reviewed the state of the art. Opinions differ as to whether a chelating extraction reaction should be considered in terms of complex formation in a homogeneous aqueous solution or in terms of the heterogeneous kinetics of the species absorbed at the aqueous-organic interface (1). Flett et. al. employed the AKUFVE apparatus to determine the kinetics of copper extraction by LIX reagent. A tracer technique was employed to follow the rate of extraction. The extraction rate was found to become constant above an impeller Reynolds number of 2.5×10^4. It was established that the reaction was first order with respect to the copper concentration and that an increase in pH increases the rate of extraction. These observations suggest that the reaction takes place in the bulk of the aqueous phase, contrary to their postulation of an interfacial reaction. It was concluded, however, that with the extractants used, the aqueous solubility was such that the molarity of the extractant in the aqueous phase, and in particular the molarity of the extractant anion, was so low that a homogeneous aqueous rate-controlling complexing reaction was unlikely.

Spink and Okuhara (166) have recently studied the distribution of copper using KELEX-100, a proprietary alkyl β-hydroxy quinoline, in various diluents in an AKUFVE apparatus and correlated the extraction constants with the solubility parameters of the organic diluents. The work revealed that the nature of the metal complex being extracted was greatly dependent on the diluent. For example, rate of extraction was greater with the diluents isooctane or n-heptane than with benzene, toluene or xylene. This occurs since the degree of stability of the metal complex varies with the type of diluent used.

Murdoch and Pratt (167) studied the distribution of uranyl nitrate between water and the solvents dibutyl carbitol and methyl isobutylketone in a wetted-wall column with well-defined system hydrodynamics. The method, however, is not applicable to phases having higher density differences and lower interfacial tension owing to the interfacial instability in the wall-water phase film.

Most kinetic studies have been performed in constant interfacial area cells, in particular in the Lewis cell. Lewis (168,169,176) investigated extraction of uranyl nitrate and various organic solutes. Interfacial turbulence was observed in the case of uranyl nitrate, giving transfer rates higher than predicted. The limitation of this cell is its low interfacial area-volume ratio giving long diffusion paths thus reducing the rate of transfer of the reacting species to the interface. Typically, the interfacial area in such cells is of the order of $3 \times 10^{-3} m^2$ and the volume of each phase is of the order of $3 \times 10^{-2} m^3$. However, a cell with a higher interfacial area-volume ratio has been designed by Keisch (177) to facilitate the process of diffusion. In metal extraction, it is generally observed that the rate increases initially but gradually slows down. This has been observed by various authors (161,162,176,177) and is due to the creation of an interfacial barrier. Thus Lewis (176) has concluded that in the extraction of Uranyl nitrate by TBP an interfacial barrier is formed by the association of $(UO_2)^{++}$ and $(NO_3)^-$ ions giving $UO_2(NO_3)_2$ which subsequently reacts with the extractant molecule. Flett et. al.(162) while investigating the extraction of nickel with a α-hydroxy amine/lauric acid mixture observed that the slow rate of extraction is caused by the formation of a solid interfacial phase containing nickel which acts as a barrier to mass transfer. The other recent work in constant interfacial cells is due to Roddy and Colman (196) who examined the kinetics of iron(III) extraction by D2EHPA and explained the data in terms of an interfacial reaction. This is in concert with the recent observation by Flett et. al. (162).

Single drop kinetic studies has been made by Baumgartner and Finsterwalder (197). The principle lies in the creation of single drops in which internal circulation is completely inhibited so that mass transfer is controlled by the kinetics of the reaction. However, recent work (200) has revealed that k-values obtained by this method are about double the true values because of the neglect of end effects. Baumgartner and Finsterwalder supported the argument advanced by Nitsch (199) that at high throughputs the formation and removal times of the drops at the end of the column tend towards zero, so that end-effects become negligible. According to Farbu et. al.(200) however the magnitude of turbulence and other disturbances increases with increasing throughput and thus the above argument is invalid. A similar investigation has recently been carried out by Farbu et.al. They employed the rising drop technique (201) to study transfer of uranyl nitrate between an aqueous continuum and rising droplets of tri-n-butyl phosphate (TBP) under constant hydrodynamic conditions. End-effects were measured by a graphical technique. It was observed that the continuum → drops rate constant k varied as $|TBP|^2$ while the drops → continuum rate constant k was independent of $|TBP|$. They suggested that the rate-determining step involves formation or break-up of the complex $UO_2(NO_3)_2$ 2TBP. The values of the experimentally determined rate constants compared reasonably with published values.

It is apparent from the above discussion that most work has been in the field of metal extraction. Kinetic data regarding other heterogeneous liquid-liquid systems are very limited and the only significant work has been carried out by Nanda and Sharma (182) who studied the reaction kinetics of the alkaline hydrolysis of several esters. They employed stirred cells of known interfacial area and claimed that the method may be adopted to determine second-order rate constants in the range 0.2 - 10,000 ℓ/gmole.sec.. The method has since been successfully tested by Kothari and Sharma (202).

Finally, in view of the industrial importance of liquid extraction with chemical reaction, it is surprising that so little attention has been paid to kinetic studies, prior knowledge of which is fundamental to an understanding of any process.

7.5 Segregation In Liquid-Liquid Extraction With Chemical Reactions

Danckwerts (203) introduced the concept of segregation to illustrate that within a homogeneous system in any vessel there will be zones of fluid with different concentrations due to incomplete mixing. Such a system is termed 'segregated'. Two quantities have been assigned to the state of segregation: (i) the scale of segregation, i.e. whether it is micro or macro and (ii) the degree of segregation, i.e. the rate of interaction. Both affect the rate of chemical conversion. When the scale of segregation is small, the process is greatly influenced by the degree of segregation provided the residence time distribution remains constant.

This concept of segregation may be described more precisely in a bi-phase system in which one phase remains in a state of dispersion in the other. In continuous operation a dispersed phase droplet may during its passage through the contactor either lead its own segregated, isolated life or interact with the neighbouring drops. Thus a dispersed phase particle may in theory be fully segregated if there is no interaction. At the other extreme, in the event of infinite drop interaction, segregation could be totally absent. In liquid-liquid extraction with conditions of complete segregation the dispersed phase droplets will possess different concentrations owing to the spread in residence times. Whilst the concentration distribution will be narrower within an interacting environment its magnitude will depend upon the intensity of interaction induced by diffusion, coalescence-redispersion or the Marangoni effect.

From theoretical considerations, Rietema (204) postulated that segregation increases the overall conversion rate for reactions of an order >1 and decreases the rate when the order is <1. The following models were proposed to account for the effect of segregation on the conversion rate of interphase chemical reaction in a continuous stirred tank reactor.

(a) Zero-order drop conversion

Consider a chemical reaction to take place in a CSTR in a dispersed phase system between two reactants A and B, where A is dissolved in the dispersed phase and B in the continuous phase. It is assumed that there is no segregation in the continuous phase. The rate equation may be represented by,

$$-\frac{dA}{dt} = kA^{n}B \qquad 7.47$$

when $n = 0$,

$$-\frac{dA}{dt} = kB$$

or

$$A = A_o - kBt \qquad 7.48$$

and

$$A = 0 \text{ for } t > {}^{A}o/kB,$$

where A_o = feed concentration of reactant A.
If there is no segregation in the dispersed phase, then the rate of interaction is so high that all drops have the same concentration, and the overall conversion is a linear function of the average residence τ_n. This is given by,

$$f_n = \tau_n \left(k \frac{B}{A_o} \right) \tag{7.49}$$

Conversely, if the system is completely segregated, i.e. there is no drop-interaction whatsoever, all drops will have different concentrations depending upon their age in the reactor. Assuming the reactor to be ideally mixed, the residence time distribution will be given by,

$$g(t) = e^{-t/\tau_c} \tag{7.50}$$

where τ_c = mean residence time,
Therefore, the average concentration of A is,

$$\bar{A} = \int_0^{A_o/Bk} (A/\tau_c) g(t) dt.$$

$$= A_o - Bk\tau_c (1 - e^{-A_o/Bk\tau_c}) \tag{7.51}$$

and overall conversion is given by,

$$f_c = \frac{Bk\tau_c}{A_o} (1 - e^{-A_o/Bk\tau_c})$$
$$= K (1 - e^{-1/K}) \tag{7.52}$$

where $K = \frac{Bk\tau_c}{A_o}$ = drop-conversion modulus.

For the same conversion in both cases, a relation may be obtained between residence times by combining equations 7.49 and 7.52,

$$\frac{1}{f} = \frac{\tau_c}{\tau_n} \ln \left(\frac{\tau_n}{\tau_c} - 1 \right) \qquad 7.53$$

(b) Half-order drop conversion

A similar treatment leads to the following equations for half-order conversion;
for complete segregation,

$$f_c = \frac{Bk\tau_c}{A_o^{\frac{1}{2}}} - \frac{B^2k^2\tau_c^2}{2A_o} \left[1 - \exp\left(- \frac{2A_o^{\frac{1}{2}}}{Bk\tau_c}\right)\right] \qquad 7.54$$

for no segregation,

$$\frac{f_n}{\sqrt{1-f_n}} = \frac{Bk\tau_n}{A_o^{\frac{1}{2}}} \qquad 7.55$$

Equations 7.54 and 7.55 may be combined as before to relate the residence times in both cases of segregation.

Graphs representing equations 7.54 and 7.55 , that is for no segregation and complete segregation, are reproduced in Figure 7.9 . This illustrates that for the same conversion, the residence time needed in the case of a completely segregated system is much longer than for a system with infinite interaction. Thus high mass transfer rates would be expected in agitated systems exhibiting coalescence-redispersion phenomenon. Further, it may be

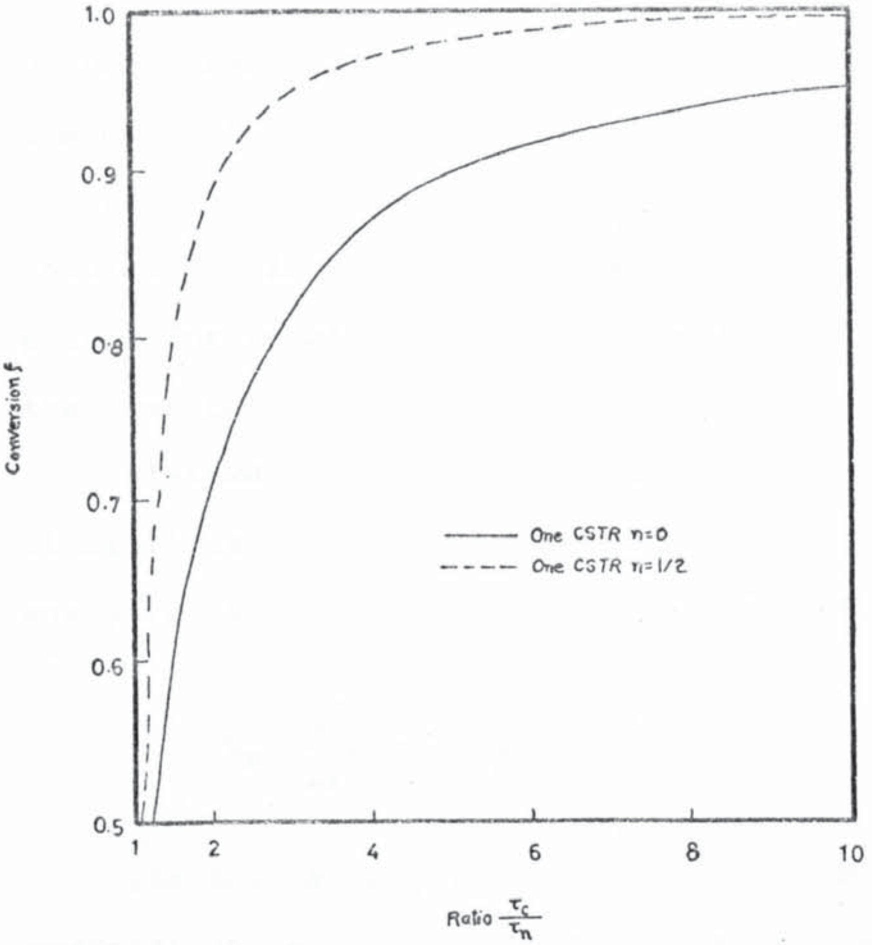


Fig. 7.9 Degree of conversion with ratio of residence time

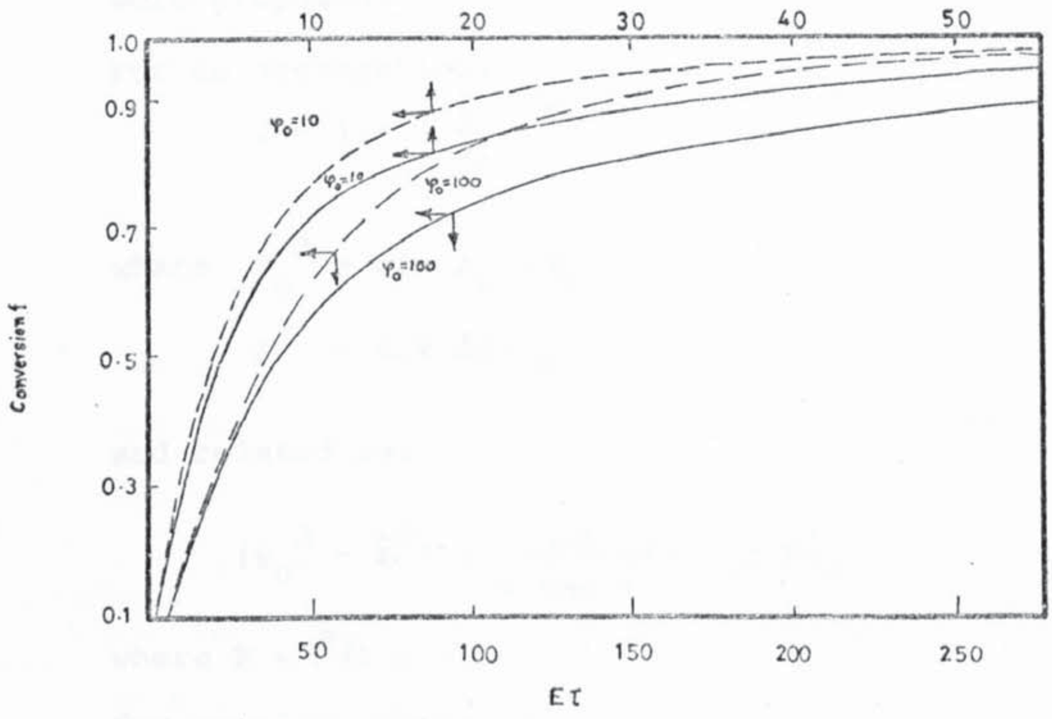


Fig. 7.10 First-order reaction with mass transfer limitation: solid lines, no interaction; dotted lines no segregation.

deduced from Figure 7. 9 that the order of reaction affects the overall conversion, for example the effect of segregation for half-order being lower than zero-order. However, theoretical investigation showed that segregation has no effect for reactions of order one and for orders higher than one the situation is very complex (204).

Rietema further considered the effect of mass transfer limitations on overall conversion rate. The mathematical analysis involved was the solution of the diffusion equation,

$$D_B\left(\frac{d^2B}{dr^2} + \frac{2}{r}\frac{dB}{dr} \right) - kAB = 0 \qquad 7.56$$

The two extreme cases of 'no segregation' and 'complete segregation' were treated as before and the effects were calculated for a C.S.T.R., for which a first order reaction occurred in the dispersed phase. The following expressions were proposed,

For no segregation,

$$f = 1 - \left(\frac{\bar{\psi}}{\psi_o} \right)^2 \qquad 7.57$$

where $\psi_o{}^2 = d.k.A_o/4D_B$

$\psi^2 = d.k.\bar{A}/4D_B$

and related by,

$$(\psi_o{}^2 - \bar{\psi}^2)\left(\frac{\tanh \bar{\psi}}{\bar{\psi} - \tanh\bar{\psi}} \right) = 2\ E\tau_n$$

where $E = {}^3/2\ m\ B\ k$

for complete segregation,

$$f = 1 - \frac{1}{\psi_o^2} \int_o^{\infty} \psi^2 \, e^{-t/\tau_c} \frac{1}{\tau_c} \, dt \qquad 7.58$$

Figure 7.10 demonstrates that although the reaction is of first order, it may still be influenced by the effect of segregation when the process is mass transfer controlled.

Although the above models show qualitatively the effect of segregation, their application to real situations is limited because of deviations from assumptions 1 to 3 below:

1. All drops are equal in size. This means that when there is segregation, it is only the age distribution which causes a concentration distribution in the dispersed phase. Although in later models variation in drop size has been considered, only highly simplified distributions have been included. In a practical contactor, complicated distribution functions exist (40).

2. In the case of 'no segregation' as the interaction rate is infinite compared with conversion rate, the concentration of the dispersed phase reactant is the same in all drops and equal to the outlet concentration. In real systems, segregation is finite and infinite interaction is difficult to achieve. Therefore, the above assumption is not valid as the drops tend to exhibit a concentration distribution function.

3. The continuous coalescence and redispersion of the drops does not influence the mass transfer into them. This may be true in the case of a very slow interphase

reaction, in which the process is entirely controlled by the kinetics of the reaction, but diffusion controlled processes would be affected by the above phenomenon.

7.5.1 Interaction Models

Discussion in Section 7.5 was limited to the two extreme cases of interaction. However, neither of these two extremes exists in real situations but interaction is finite in practical contactors. This necessitates evaluation of data relating to the rate and extent of interaction for mass transfer predictions.

Various interaction models have been proposed. These are - (a) The Homogeneous model (205), (b) The Circulation model (206), (c) The Dead-Corner model (204), and (d) The Harada model (207). The Circulation model is based on predictions of the total number of small drops which during one circulation unite to one large drop, and the average number of circulations which a molecule of the dispersed phase experiences during its stay in the reactor. However, it is rather difficult to predict these parameters. The Dead-Corner model holds that interaction is not homogeneously distributed in a baffled stirred tank and as a consequence, the segregation is not pure microscale segregation, but a combination of micro and macroscale segregation. The mathematical analysis of this model is complex. In the Harada model each drop of the dispersed phase enters into the interaction process at a regular time interval. During interaction, the drop exchanges matter with an imaginary drop of the same size, but of average concentration. After this interaction, the original drop starts to react again during the same time interval. Each drop, therefore, keeps its own identity. The model is of doubtful validity since drop interaction occurs continuously and not at regular intervals. Of these models only the homogeneous interaction model has received any attention and this is discussed below in the light of past and recent investigations in the field of droplet interaction.

Homogeneous Interaction Model

The model is based on the following assumptions:

(a) The dispersion consists of drops of equal size.

(b) The probability of coalescence of a drop with a neighbouring drop is the same throughout the vessel and independent of the concentration distribution of the drops and the age distribution function.

(c) Coalescence is immediately followed by redispersion.

(d) The phenomenon of coalescence-redispersion has no effect on mass transfer.

With the above considerations, Curl (205) investigated interphase chemical reaction in a C.S.T.R. An interaction mechanism was suggested in which the change of a fraction of drops in the dimensionless concentration interval between α and $\alpha + \Delta\alpha$ during a short dimensionless time $\Delta\xi$ is caused by,

(i) Chemical reaction. Drops with a concentration parameter higher than $\alpha + \Delta\alpha$ will move into the interval while other drops will move out of the interval.

The total effect is given by,

$$\Delta g_1 = K \frac{d}{d\alpha} \{\alpha^n g(\alpha)\} \Delta\alpha \; \Delta\xi$$

where $g(\alpha)$ = concentration distribution function in the drops

K = conversion parameter.

(ii) Carry-off with the product stream

This contribution is,

$$\Delta g_2 = - g\,(\alpha) \; \Delta\alpha \; \Delta\xi$$

(iii) Coalescence and redispersion effects

$$\Delta g_3 = 4 \; I \; \Delta\xi \; \Delta\alpha \int_{2\alpha-1}^{\alpha} g(\beta) g(2\alpha-\beta) d\beta$$

where $2\alpha-1<\beta<\alpha$

and I = interaction modulus.

(iv) Carry-off by coalescing. All drops of the considered interval continuously have a chance, by coalescing with drops of other concentrations, to disappear out of the interval. This concentration is,

$$\Delta g_4 = - I \; g(\alpha) \; \Delta\alpha \; \Delta\xi$$

Combining all the effects the total must be equal to the change with time,

$$(\Delta g)_{\text{total}} = \frac{dg}{d\xi} \Delta\alpha \; \Delta\xi$$

i.e.,

$$\frac{dg}{d\xi} = K \; \frac{d}{d\alpha}\{\alpha^n g(\alpha)\} - (1+I)g(\alpha) + 4I \int_{2\alpha-1}^{\alpha} g(\alpha)g(2\alpha-\beta)\,d\beta \qquad 7.59$$

The steady state solution may be obtained by putting $\frac{dg}{d\xi}=0$ when n, K, I, τ and A_o are kept constant.

Veltkamp (208) later confirmed the theory of Curl and solved equation 7.59 for the interaction rate in a C.S.T.R. Recently, Spielman (209) calculated the influence of interaction by Monte Carlo method, which is in fact a direct simulation of the physical process happening in a C.S.T.R. Results were in reasonable agreement with those of Cure and Veltkamp.

Madden and Damerell (105) studied interaction rates experimentally in a system undergoing interphase reaction

$$(2S_2O_3^{--} + I_2 \rightarrow S_4O_6^{--} + 2I^-)$$

and proposed the following expression for the concentration time relationship under interacting conditions,

$$\ell n \; \frac{c_0}{c} = \frac{KaN}{V_t\theta} \quad \ell n \; \frac{1+Xe^{\theta t}}{1+X} \qquad 7.60$$

where N = total number of drops.

θ = coalescence frequency.

X = initial rate of hypo to inert drops.

The derivation is based on the Homogeneous Interaction Model with a simplified coalescence mechanism. The model was found to be of approximate validity and the only conclusion to be drawn from this work is that the interaction frequency increases markedly with increase in impeller speed and to a lesser extent with increase in dispersed phase volume.

Matsuzawa and Miyauchi (210) also measured interaction rate by means of a chemical reaction and interpreted the data by the homogeneous interaction model. However, experimentation was limited to controlled conditions of negligible interaction rate. In agitated systems the degree of interaction is always high and thus the work is of limited significance to real situations.

Miller et. al.(211) and Groothuis and Zuiderweg (212) measured interaction rates by a light transmission technique under non-mass transfer conditions and in both cases the interaction rate was observed to increase with an increase in energy input. Groothuis and Zuiderweg also studied the influence of mass transfer on the interaction rate and observed that when 1.37% acetic acid was added to the dispersed phase, the interaction rate increased by a factor of 20.

From the work based on the stochastic description of concentration distribution in a drop population furnished by Curl (205,) Komasawa et al (213) proposed the following expression for concentration distribution under finite interaction with no chemical reaction in a C.S.T.R.,

$$P_o(c)-P(c) + I\left[4\int_0^c P(c+\alpha)P(c-\alpha)\,d\alpha-P(c)\right]=0 \qquad 7.61$$

where,

$P(c)$ = Frequency function of drops of concentration c in a tank.

$P_o(c)$ = Frequency function of feed drops.

I = Average number of interaction of drops during their residence in a tank.

α = Dummy variable.

The interaction rates could not be compared directly with previous workers, since any traces of surface active contaminant can alter the fractions of collisions resulting in coalescence. However, the effect of both impeller speed and volume fraction of dispersed phase on interaction rate were in good agreement with those of others (105, 211).

In a practical dispersion, unlike the basic assumption in the Homogeneous Interaction Model, there is a distribution of drop diameters. Both coalescence and breakage processes are related strongly to the variation in drop-size and consequently interaction rate is also a function of drop-size. Keneth et. al. (214) developed a mathematical model to relate interaction rate in a two-phase system to the steady state distribution of droplet sizes in a continuous system. The expression is of the form,

$$NA(m) = \Big[n_A a(m) + \int_m^L v(\mu) g(\mu) \beta(m{:}\mu) NA(\mu) d\mu$$
$$+ \int_0^{m/2} \lambda(m-\mu) h(m-\mu) h(\mu) NA(m-\mu) NA(\mu) d\mu\Big]$$
$$/ \left| f(m) + g(m) + h(m) W(m) \right| \qquad 7.62$$

where $W(m) = \int_0^{L-m} \lambda(m,\mu) h(\mu) NA(\mu) d\mu$.

$A(m)$ = droplet size distribution in vessel.

$a(m)$ = droplet size distribution in feed.

N = Number of droplets in vessel.

n_A = Number of feed rate of droplets.

$\upsilon(\mu)$ = Number of drops formed upon breakage of drop of mass μ.

$g(\mu)$ = Breakage frequency

$\beta(m{:}\mu) d\mu$ = Fractional number of droplets with mass between μ and $\mu + d\mu$.

$f(m)$ = Escape frequency.

$g(m)$ = Breakage frequency.

$h(m)$ = Collision frequency.

$\lambda(m,\mu)$ = Coalescence efficiency.

The above integral model consists of two drop size distribution functions and a kernel describing the breakage mechanism. The authors have proposed a numerical approach to the solution of the model with a highly simplified drop size distribution function. This has however not been verified experimentally and thus the validity of the model remains to be proven.

A number of interaction models based on theoretical investigations have been discussed above. Unfortunately, there has been no direct confirmation of the theories in two phase reacting systems. Although the effect of segregation and interaction on the overall conversion rate has been recognised, an experimental approach to the problem is extremely difficult as both the conversion rate and interaction rate have to be measured at the same time in the same system (203).

8. EXPERIMENTAL INVESTIGATION

It is clear from the literature reviewed in Chapter 7, that co-ordinated data is lacking as to the effect of hydrodynamics upon liquid-liquid reaction rates in continuous agitated systems. In particular, no design data are available for continuous countercurrent agitated contactors. This is surprising since although most industrial extraction-reaction systems are diffusion controlled, kinetic effects cannot be entirely ignored in the design of continuous contactors. The present investigation was therefore undertaken to analyse the comparative influence of the two rate-controlling parameters using model systems under varying degree of turbulence. The study was therefore carried out in two pilot scale agitated contactors, the R.D.C and the Oldshue Rushton column. Incidental to this study, investigations were also carried out to determine the criterion for maximum volumetric capacity of the two contactors.

8.1 Description of Equipment

A flow diagram of the equipment is shown in Figure 8.1 and a general arrangement in Figure 8.2. The process lines and the feed and effluent vessels were arranged so that the column was accessible from all sides, to facilitate sampling and photography, and all valves were within easy reach. Drain points were incorporated at the lowest points in the system. Two interchangeable columns were used viz an R.D.C. and an Oldshue Rushton contactor.

8.1.1 Rotating Disc Contactor.

The basic equipment was that described by Al Hemeri (55). However, the whole column section was redesigned to eliminate internal steady bearings which can act as flow restrictions. The process lines were also altered and new Q.V.F. control valves installed as appropriate. The column shown in FIgure 8.3 consisted of a 0.101 m diameter 0.92 m long Q.V.F. glass section divided into 18 compartments each 0.05 m high. The diameter of the discs was 0.05 m and that of the stator openings 0.076 m. These dimensions were determined from the design specifications recommended by Reman (23). A phase ratio of 0.5-4.0 to 1.0 was assumed for design purposes. Five sampling points were provided at 0.15 m intervals along the column length. Each point comprised a 10 mm diameter hole

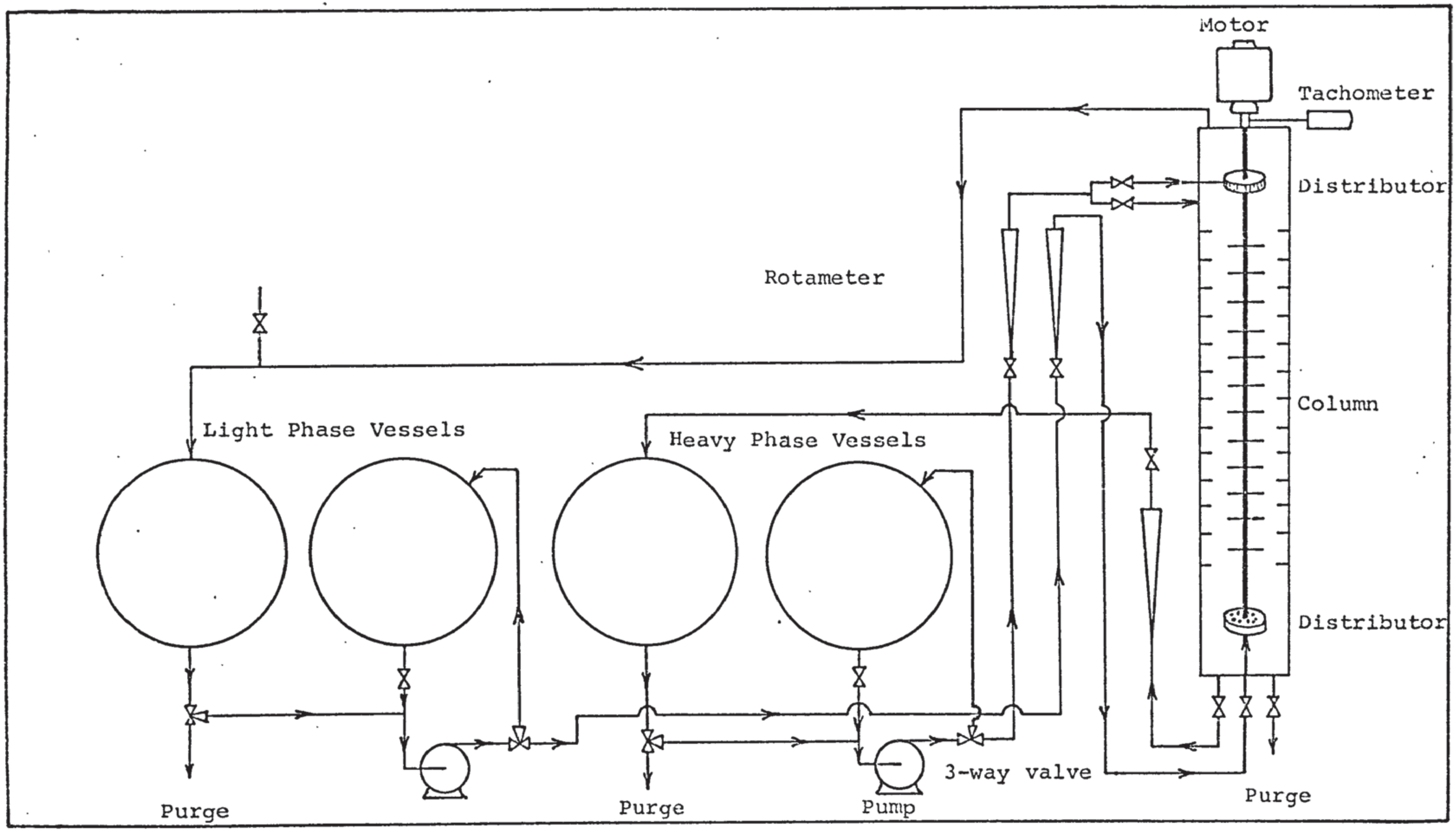


FIG. 8.1 Flow Diagram

FIG. 8.2 General Arrangement

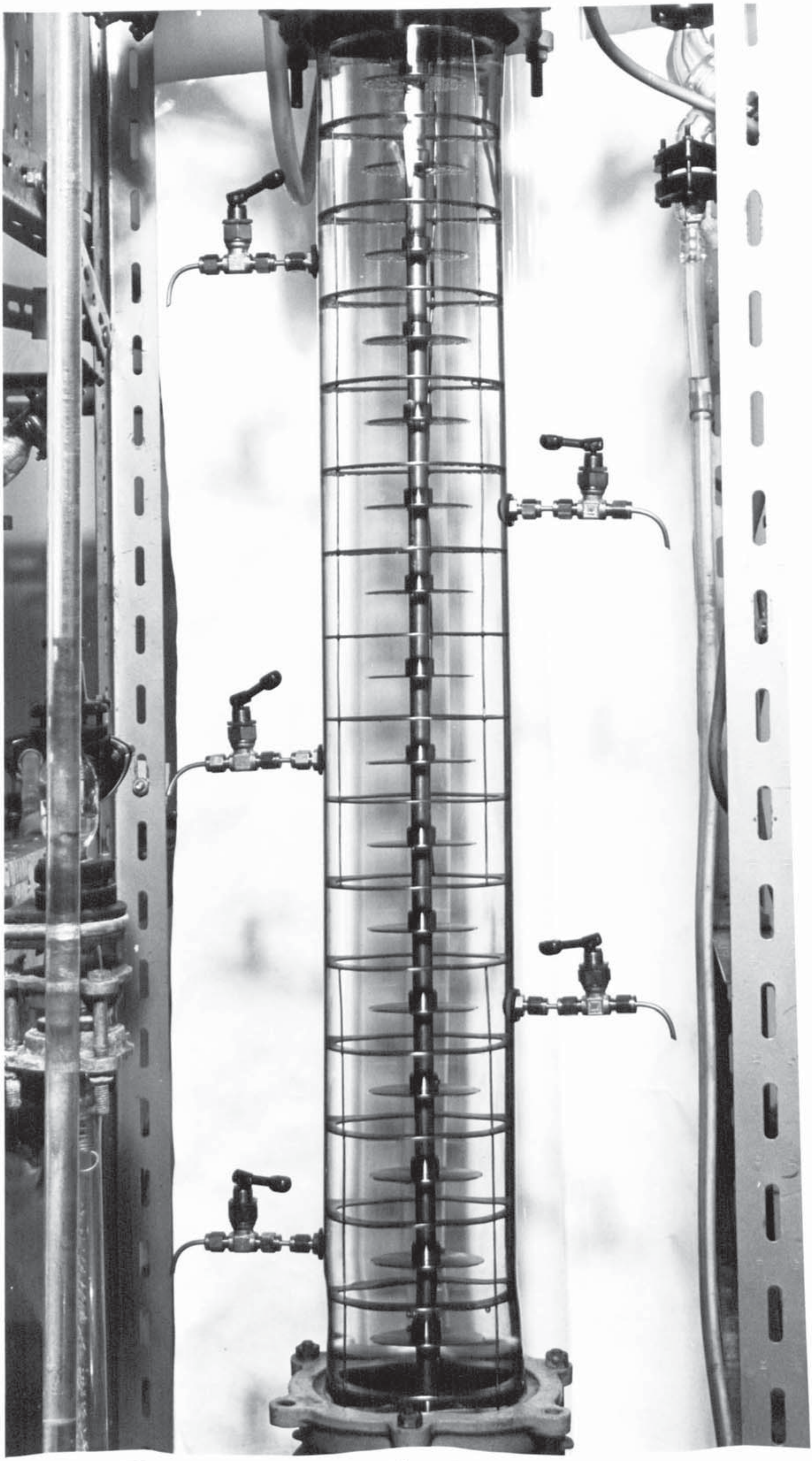


FIG. 8.3 Rotating Disc Contactor

fitted with a quick-acting toggle valve. Additional sampling points were provided at the respective phase inlets and outlets.

The column internals were fabricated entirely from 18/8 stainless steel, and were machined to obtain a close fit at the column walls, since the uncharacteristic performance of many laboratory columns may be attributable to phase flows between the column wall and the edge of the stator rings (54). The stators were supported by means of three equispaced lengths of 1 mm S/S wire. This was found to be rigid enough to support the stators without introducing extraneous baffling effects. The thickness of the discs and stators was 2 mm. The discs were supported by means of a grub screw through the collar of the disc; this was countersunk into the collar so as to eliminate any effect on the pattern of agitation. In any event, the neighbourhood of the collar is effectively a dead zone and any disturbances caused by protruding screws would be very small (54). The discs had straight edges, since discs with sharp or tapered peripheries would have increased the axial mixing effects (51). The rotor shaft, was fabricated from 9.6 mm stainless steel rod and was supported by bearings at three points throughout the column length. There was no support bearing within the effective column length, this being a significant improvement over earlier designs.

The heavy phase was introduced into the column at a point just above the top compartment, through a

FIG. 8.4 Top Distributor And Bearing Assembly

stainless steel distributor plate, and left via a pipe above the coalescence zone situated at the top of the column. The heavy phase inlet was designed such that, if desired, the stream could pass through the stainless steel disperser illustrated in Fig. 8.4 and hence constitute the dispersed phase. Provision was made for initial dispersion of the lighter phase via a distributor plate to facilitate a rapid approach to equilibrium hydrodynamic considerations in the contactor by simulating the initial break-up stages which would otherwise occupy useful column height. The two distributors were designed according to the method of Treybal (32). Each consisted of 46, 2 mm dia holes arranged on 6 mm triangular pitch inside a 0.10 m dia circle. The holes were drilled undersize (1.5 mm) and then counterpunched to the correct size to provide a small upward projection around the periphery of each hole.

The column end plates were fabricated from 8 mm thick 18/8 stainless steel plate. The bottom plate supported the distributor and a P.T.F.E. end step bearing. The top end plate housed a P.T.F.E. bearing and a stuffing box filled with 'T-Seal' P.T.F.E. granules. The necessary inlet and outlet pipes were integral with the end plates.

8.1.2 Oldshue Rushton Column

The design of the column was based on the original of Oldshue and Rushton (26). The column illustrated in Fig. 8.5 was of similar dimensions to the R.D.C., but with

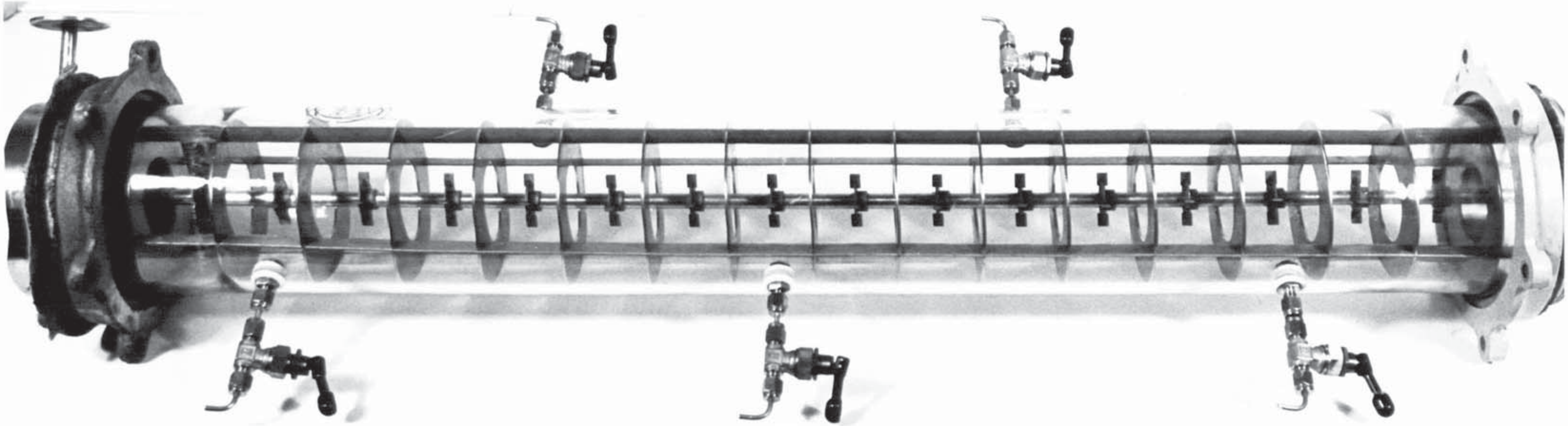


FIG. 8.5 Oldshue Rushton Contactor

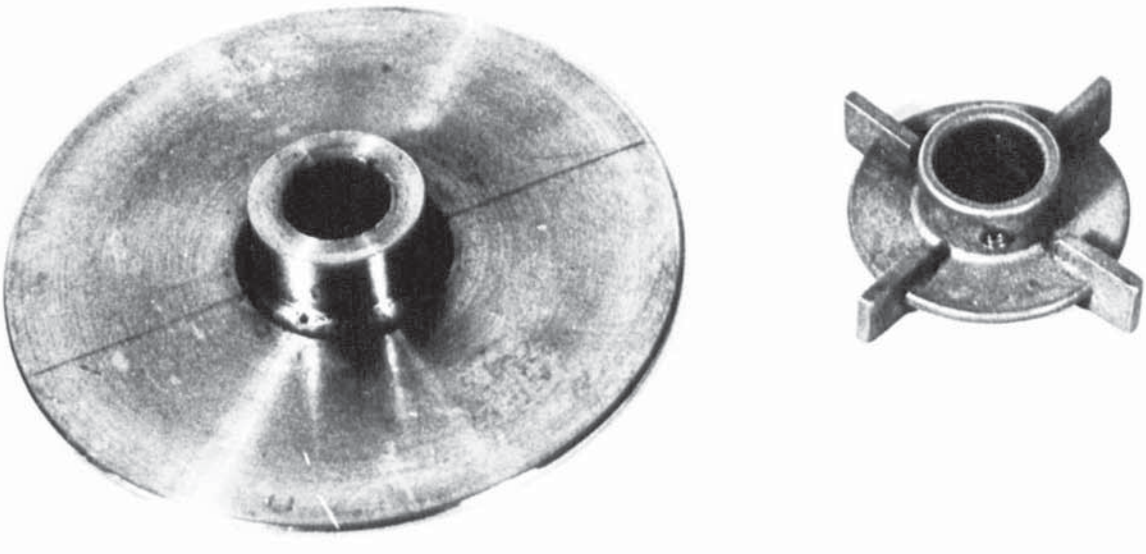


FIG. 8.6 Impeller Details

different column internals. There were 18 compartments each 0.05 m high. Each 4-bladed standard disc turbine of 33 mm diameter was fabricated from 2 mm thick stainless steel elements and secured to the shaft by grub screws as shown in Figure 8.6. Four vertical baffles each 8.5 mm wide and 2 mm thick were slotted into the 34 mm internal diameter stator rings before assembly of the column. The two end sections of internals were then screwed into the two support bearings situated at the top and bottom of the effective column length.

8.1.3 Associated Equipment

The agitator shaft was driven by a 1/4 h.p. A.C. Voss motor, controlled by a 'Torovolt' variable voltage mains transformer. The effective speed range was 0-3000 r.p.m. The drive shaft of the motor was coupled to the column shaft via a flexible rubber joint. The other end was initially attached via a flexible drive to a permanent 0-3000 r.p.m. tachometer mounted on the Control Panel. This was later replaced by a high precision Comark Type 2101 electronic tachometer.

Process fluids were stored in any of four 50 litre Q.V.F. spherical glass vessels mounted on special supports. Two of these served as reservoirs and two as receivers. Pipe work was mainly of 16 mm i.d. borosilicate glass but P.T.F.E. tubing was used in certain sections. Flow rates were measured by independently calibrated rotameters with stainless steel floats. Flow control valves were of glass with a P.T.F.E. stem and seat, ex Q.V.F. Ltd. The remaining valves were of the all-glass stopcock type. Drainpoints were incorporated in the pipework to allow complete draining of the system. Provision was made for the circulation of the liquids within one vessel, or between two vessels containing the same liquid, by means of by-passes on the pumps.

Fluids were transferred by means of two Stuart-Turner centrifugal pumps, type No.10 and No. 12 capable of handling 1.25/0.45 m^3s^{-1} against a hydrostatic head of 2.0/10.0 m. Stainless steel casings and impellers were incorporated in these pumps together with graphite and 'Viton A' seals. Immersion tests confirmed that 'Viton A' was unaffected by the process systems selected for investigation. The speed of each pump could be varied by means of a 'Torovolt' variable voltage unit. Drip covers were provided on pump motors to protect them from any leakage of process fluids. Drip trays were placed underneath the process vessels.

No provision was made for temperature control of the equipment environment but temperature was always within 18.5 - 20°C. The equipment was in fact located in an isolated pilot plant room provided with flameproof switchgear and lighting and an efficient low level air extraction system.

8.2 Selection of Reaction Systems

Following the classification given by Chapter 7, three types of reaction were selected for study - a slow reaction, a moderately fast reaction and a very fast reaction. The chemical reaction in each case is represented by

$$RCOOR' + OH^- \rightarrow RCOO^- + R'OH^-$$

The reaction schemes are described below:

(i) Slow Reaction: The slow reaction scheme was the alkaline hydrolysis of butyl acetate. The butyl acetate itself constituted a pure phase and diffusion into an aqueous solution of sodium hydroxide was followed by chemical reaction in that phase. This system was chosen as representative of a slow reaction since the reaction rate constant is small,of the order of 0.08 ℓ/g mole sec at 20°C (181).

(ii) Slow to Fast Reaction : To typify a moderately fast reaction the butyl acetate phase in (i) was replaced by butyl formate, with the reaction scheme remaining the same. The reaction rate constant of this system is approximately 22 ℓ/gm-mole sec at 20°C (215).

(iii) Very Fast Reaction: The alkaline hydrolysis of methyl dicholoroacetate was chosen to typify a very fast reaction. The reaction rate constant is of the order of 220 ℓ/mole-sec (216).

The above systems have been chosen for the following reasons:

(a) Favourable reaction rate constants.

(b) All the components were readily available to fixed specifications at reasonable cost. The specifications are given in Appendix 1.

(c) Some data are available from other studies for comparison purposes.

(d) Very low volatility and toxicity (217).

Many heterogeneous chemical reaction processes are conducted with one phase as the pure reactant which diffuses into and reacts in the dispersed phase. The above type of heterogeneous chemical reaction system is simpler to study theoretically and experimentally than an extraction-reaction separation process where typically the phase from which a solute is extracted is usually a dilute solution of some solute. This arises because in the case of a heterogeneous chemical reaction it may be assumed that in general all the resistance to mass transfer is in the phase were the reaction occurs. However, for the extraction-reaction process the analysis is very complex since resistance usually exists in both phases. Because of the complexity of the situation, even in single drop studies one phase is usually selected as a pure reactant (174).

Thus in the present investigation, the ester phase in each reactant scheme was a pure reactant.

8.3 Measurement Techniques

8.3.1 Chemical Analysis

In the alkaline hydrolysis of esters, the solutions were analysed either for the amount of alkali remaining or the amount of sodium salts of ester formed. The alkali content was estimated by simple acid-base titration. When the normality of alkali in the exit stream was very low (< .05 N) estimation of sodium salts of ester by oxidation with potassium permanganate was preferred. Formates or acetates in aqueous solution were analysed by a simple saponification method.

8.3.2 Interfacial Area

Droplet size distributions were measured by direct photography. The semi-automatic counting of drops from 180 prints was performed using the Zeiss T G 3 Particle Counter.

8.3.3 Photographic technique

8.3.3.1 Still Photography

Photographs of the dispersions were taken on Kodak Plus-X panchromatic 35 mm film, 120 ASA, using an Asahi Pentax Spotmatic still camera with a No. 1 single extension ring at a shutter speed of 1×10^{-3}S. This high speed virtually 'froze' the movement of the drops. The distance between the column wall and the camera was maintained constant using a spacing adaptor. Lighting was provided by a twin Kobold SR2 Cine light, the two quartz-iodine bulbs of which had an output of 1250 W at 125 V. Light was directed into the compartment under study at an angle of 90° to the camera. Two to three photographs were taken for each event. Initially, to eliminate any distortion and magnification caused by viewing through the curvature of the glass column, a perspex box jacket was erected around the column section to be photographed. This jacket was in two-halves which were pressed together and against the column by means of a clamp and then filled with the continuous phase. However, analysis of photographs taken with and without the jacket revealed no significant difference. This was in agreement with other observations (40, 55) and the jacket was therefore discarded.

8.3.3.2 Cine Photography

Cine film was taken to record, and enable qualitative analysis of the phenomenon of phase inversion. Kodak 16 mm Tir-X Reversa- roll film, type 7278 was used in a Milliken R16 with P3 Type, f 0.75 camera. Lighting was provided by two 500 W photoflood lamps in addition to the Kobold lamp. The film was taken at 200 f.p.s.

8.3.4 Physico - Chemical Data

8.3.4.1. Viscosity

Viscosity was determined by timing the passage of the fluid through a capilliary immersed in a constant temperature bath (20 ± .1°C), i.e. by Cannon Fenske Viscometer.

8.3.4.2 Interfacial Tension

Interfacial tension was measured by using the standard Wilhelmy Plate method on a 'Cambridge' torsion balance.

8.3.4.3 Diffusivity determination

Wilke and Chang (218) correlation was employed for the calculation of diffusivity

$$D = 7.4 \times 10^{-8} \frac{(xm)^{\frac{1}{2}}T}{nV^{0.6}}$$

8.3.4.4 Kinetic Data

Kinetic data for the alkaline hydrolysis of esters of formic and acetic acids and are presented in the Appendix 2.

8.3.5 Cleaning Procedure

A 1% aqueous solution of Decon-90 decontaminant was used to clean the column, vessels and the process lines. Owing to the nature of contacting, there was a tendency for dirt and other impurities to be deposited on the column internals in preference to the rest of the equipment so that great attention was paid to cleaning. The whole system was filled with Decon solution for at least 12 hours and this was then circulated throughout the system with the agitator on for about an hour and then drained away.The system was then flushed through with tap water. Since it is widely accepted that surface active agents affect mass transfer rates (102, 135), hot water was circulated through the system to get rid of any possible traces of Decon.

The whole equipment was then washed with distilled water. Care was taken to ensure that all the sample ports were well-flushed. Finally, checks were made by measuring the surface tension of distilled water in the column.

9. EXPERIMENTAL PROCEDURES AND RESULTS

9.1 NON-MASS TRANSFER STUDIES

The non-mass transfer investigations were performed in support of the main study and were not extensive to avoid mere repetition of the observations of earlier workers (40, 55) using different systems. Preliminary work to establish the hydrodynamics of the modified R.D.C. and the new Oldshue Rushton contactors, was performed with the well-defined toluene-water system. However, novel phase inversion phenomena observed were subsequently studied with the butyl acetate-water system whilst toluene-water was used in a parallel study (116).

9.1.1 FLOODING

As discussed in Chapter 4, flooding rates represent the maximum volumetric capacity of a contactor under a given set of conditions. In this work flooding was characterised by the complete rejection of the dispersed phase as a dense layer of droplets.

The operating procedure was as follows:

The column was filled with the continuous phase upto the plane to be occupied by the interface, generally a distance of 0.16 m from the top of the column. With the agitator stationary and with no continuous phase flow, the lighter dispersed phase was admitted to the column. When the build-up of bulk dispersed phase above the interface was sufficiently high, it recycled back to the reservoir. The agitator was then started and its speed adjusted to the required value. The dispersed phase hold-up steadily increased, and the continuous phase which it displaced was allowed to flow out of the column via the outlet valve. The continuous phase was then admitted to the top of the column at the desired rate. Careful control of the outlet flow rate of the continuous phase was necessary to maintain the interface at a constant level at the top of the column throughout start-up, that is whilst the hold-up was increasing. Steady state was indicated by the interface level remaining steady. The dispersed phase flow rate was then increased incrementally until flooding occurred Sufficient time was allowed for steady state conditions to be re-established following each increase which was found to be about five minutes. On occasions temporary incremental increases in the continuous phase outlet flow were necessary to maintain a constant interface position during the re-establishment process.

Steady state was achieved in either column after approximately three column volumes total flow had passed through it. This conformed with previous experience (26,55).

Both the dispersed phase and continuous phase flow rates were recorded at the flooding point. As a check, the dispersed phase flow rate was then decreased by about ten per cent to allow the column to revert to normal operation, and then increased until flooding reoccurred. Intense mixing was observed immediately prior to the onset

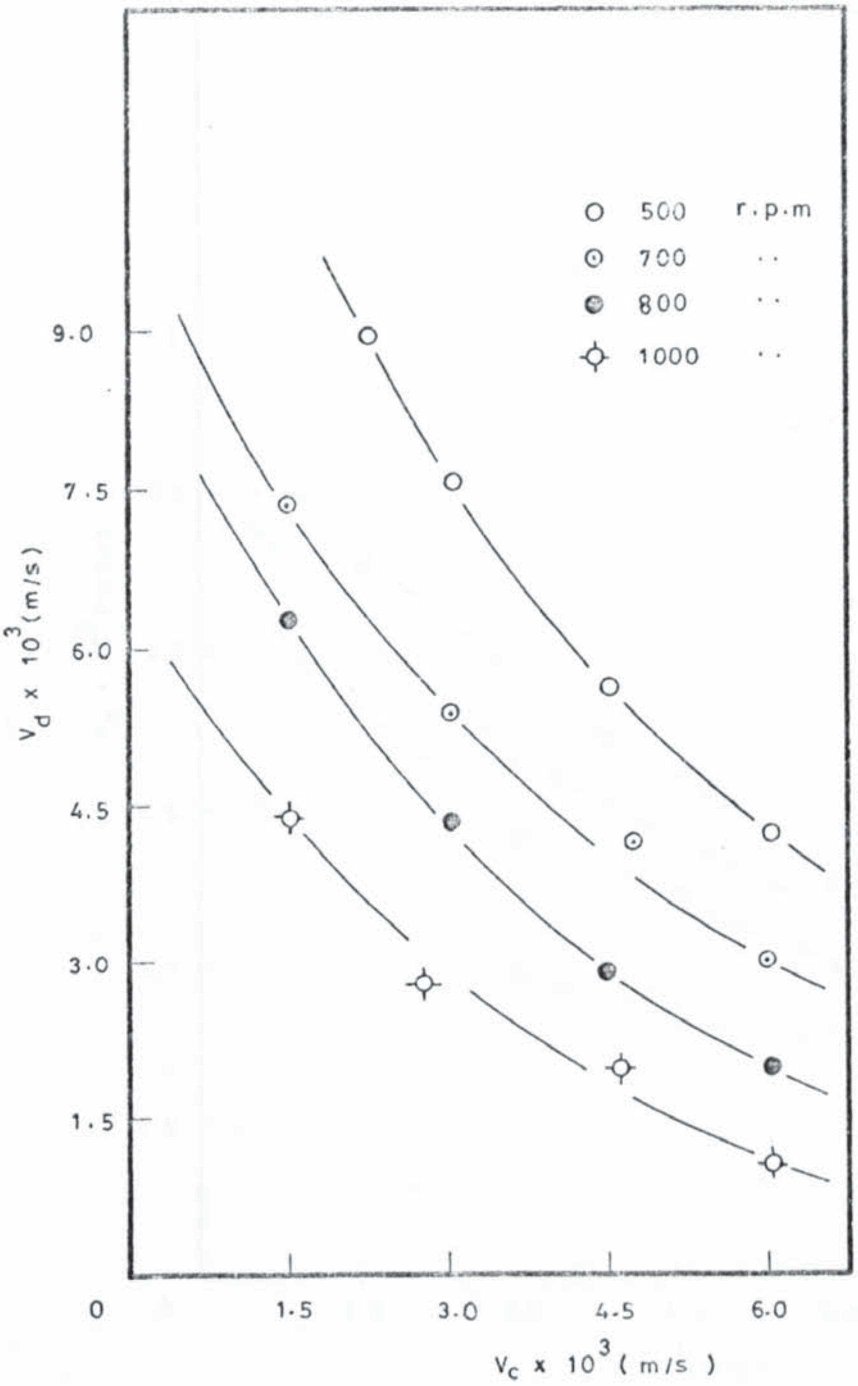


Fig. 9.1 Flooding data for the R.D.C

|System: toluene-water|

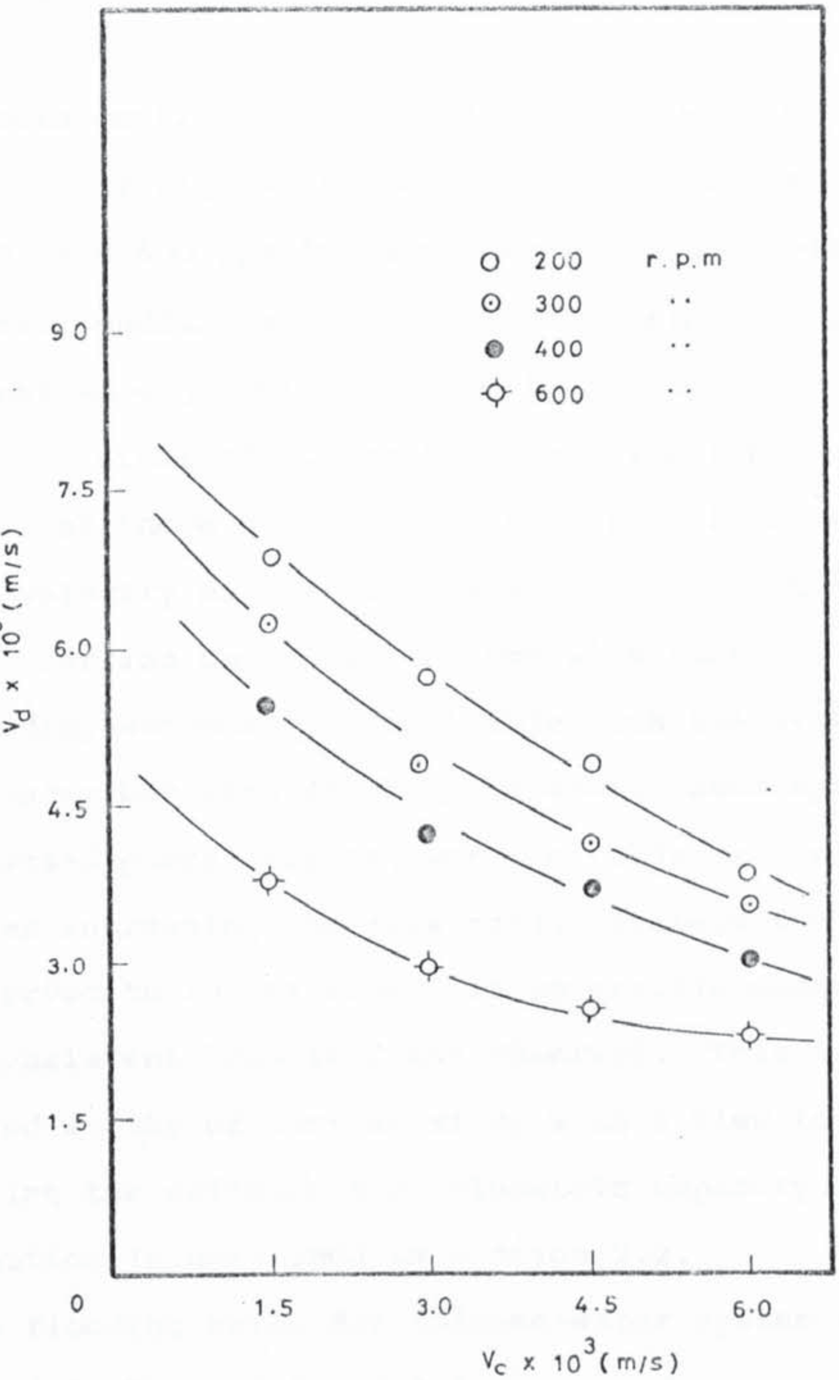


Fig. 9.2 Flooding data for the Oldshue Rushton contactor.

|System: toluene-water|

of flooding; this was also reported by previous workers (40, 55).

In both contactors flooding was more easily recognizable at high agitator speeds, viz 1000 rpm for the R.D.C. and 600 rpm for the Oldshue Rushton column. Under these conditions the droplets entering the first compartment were quickly ruptured to produce very small drops of the order of 0.5 mm to 1 mm. The terminal velocities of these droplets was very much less than the downward velocity of the continuous phase, and they were therefore carried out of the column with that phase.

Flooding was easily recognisable with the system toluene-water but with the butyl acetate-water system the dispersed phase droplets were not rejected easily even after increasing the flow rate. Instead the phases were observed to invert albeit in an erratic manner and no consistent behaviour was observed. This was considered worthy of further study with a view to determining the criteria for volumetric capacity. This investigation is described in section 9.2.

The flooding rates for toluene-water system are reproduced in Figs. 9.1 and 9.2.

9.1.2. Hold-Up

Hold-up measurement involved operating the column under the desired steady state conditions and then rapidly closing the inlet and outlet valves. After stopping the agitator and allowing time for complete phase

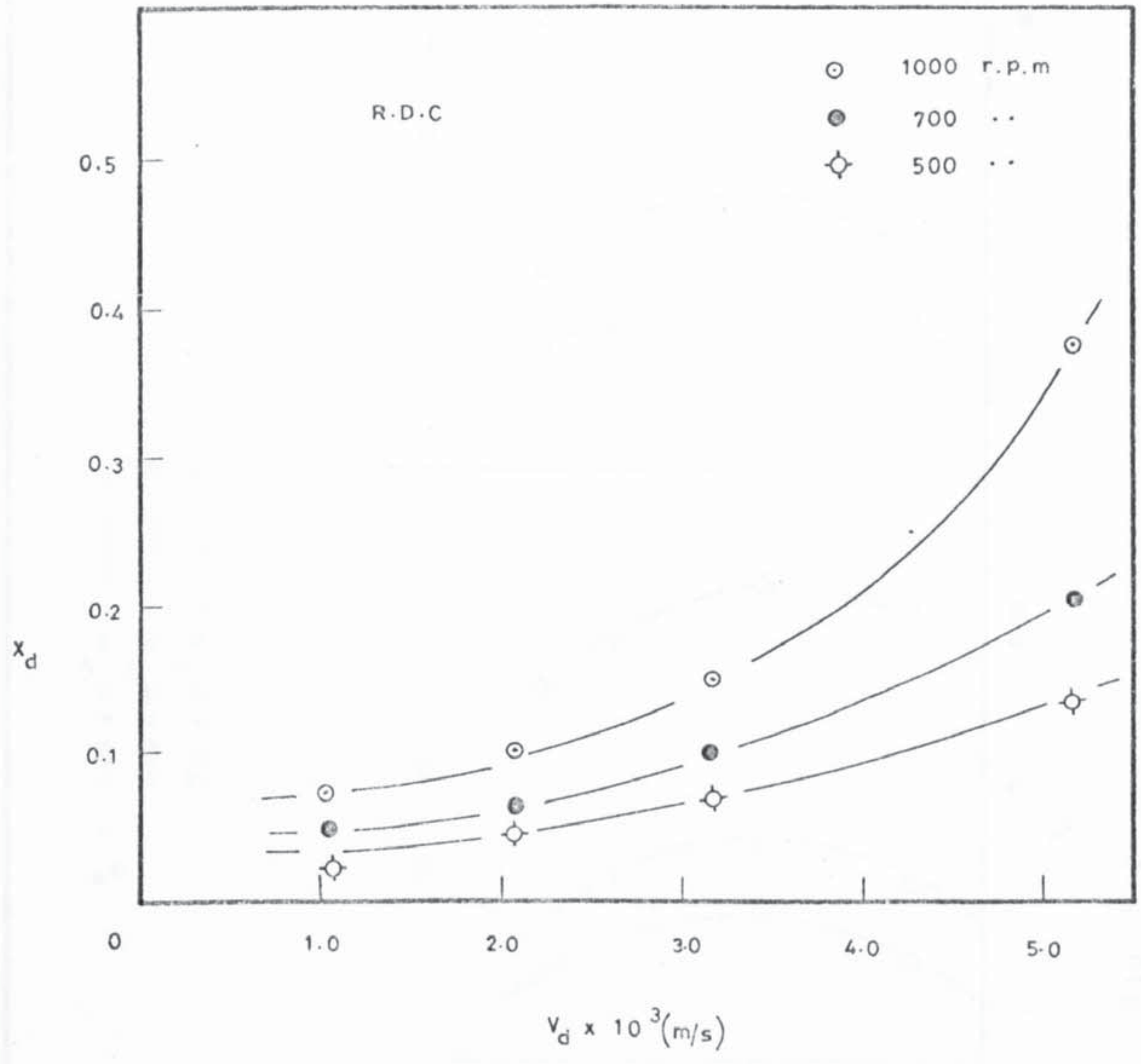


Fig. 9.3 Hold-up vs dispersed phase flow rate (System: toluene-water)

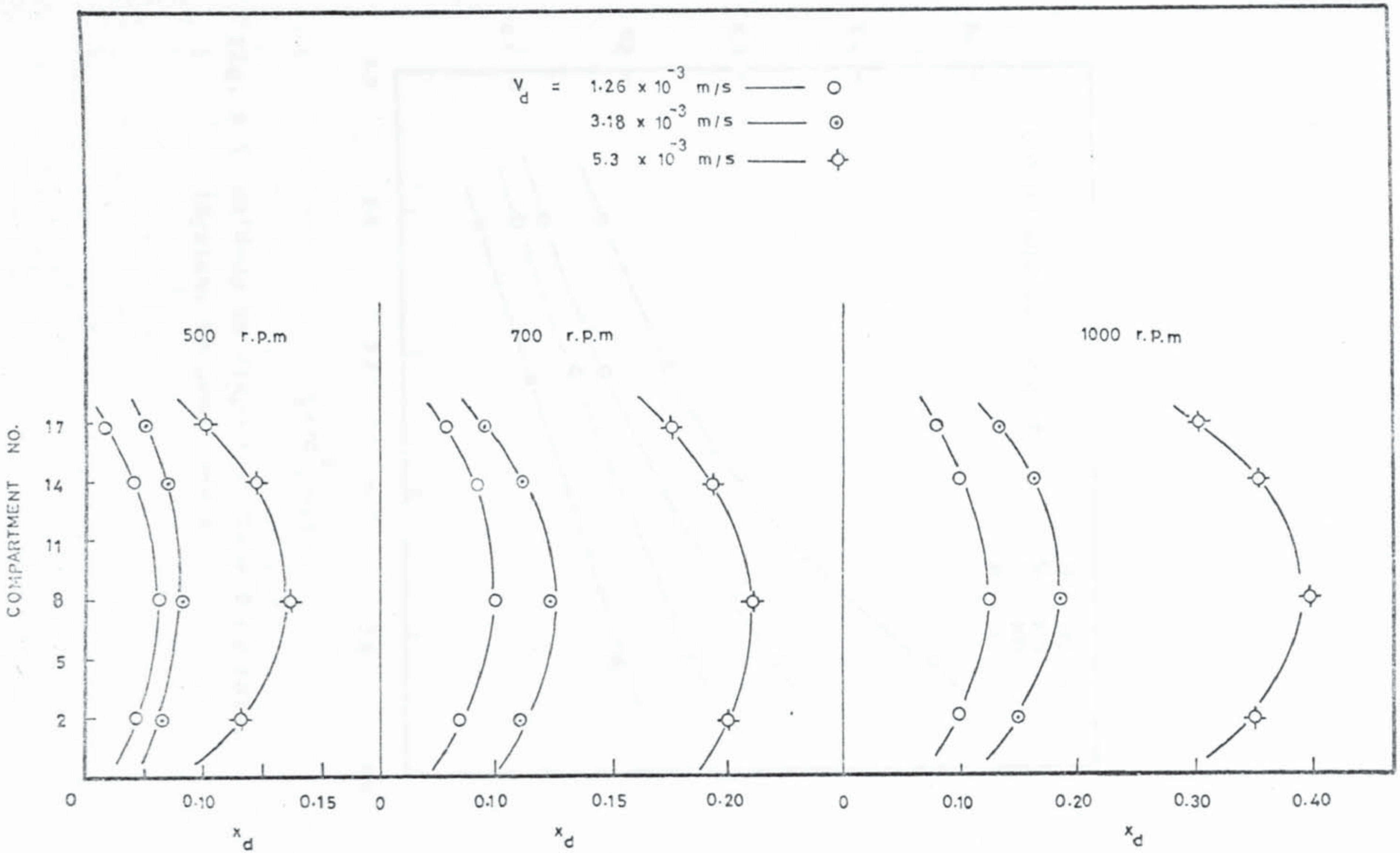


Fig. 9.4 Hold-up profile in the R.D.C
(System: toluene-water)

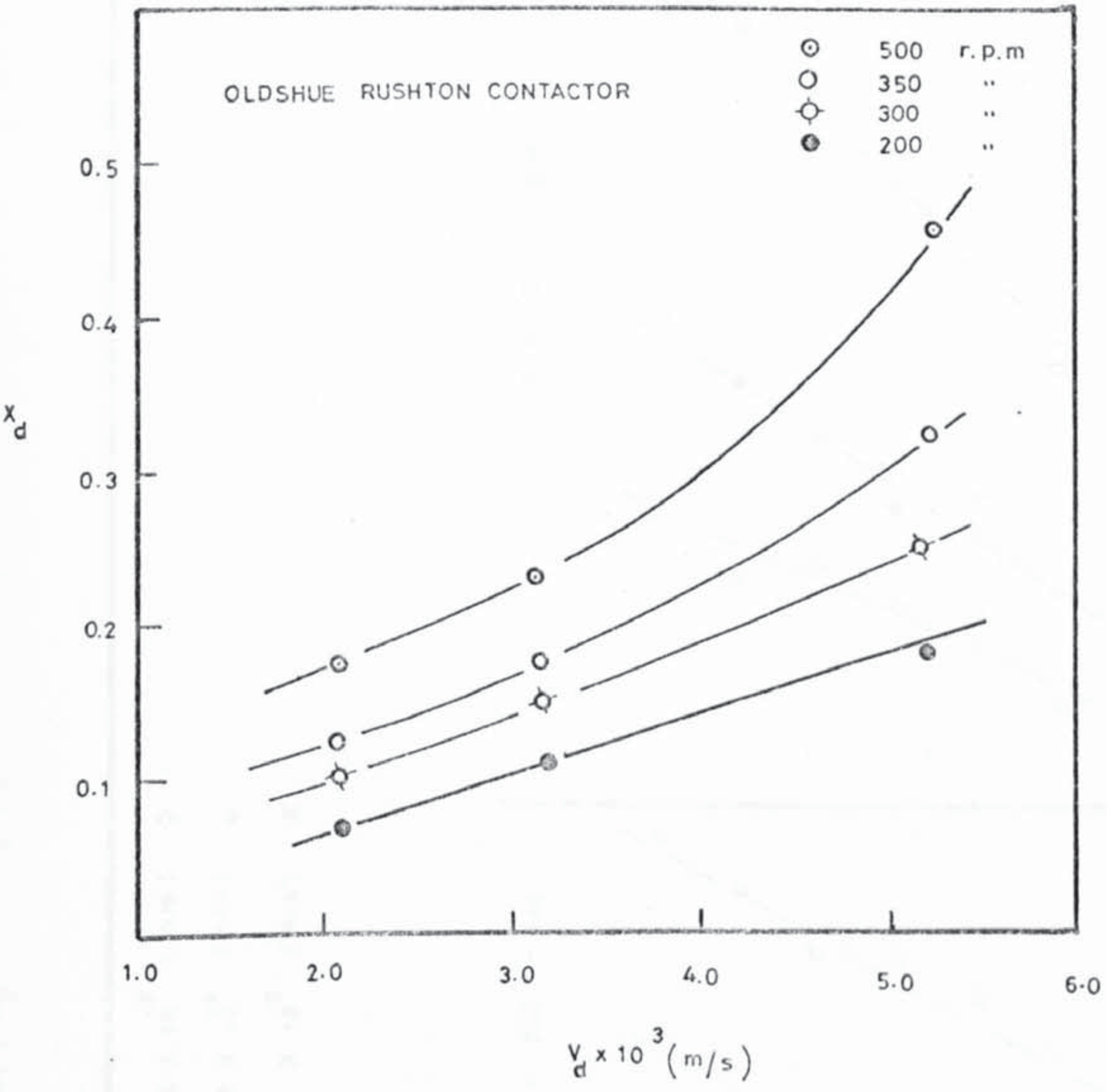


Fig. 9.5 Hold-up vs dispersed phase flow rate.
(System: toluene-water)

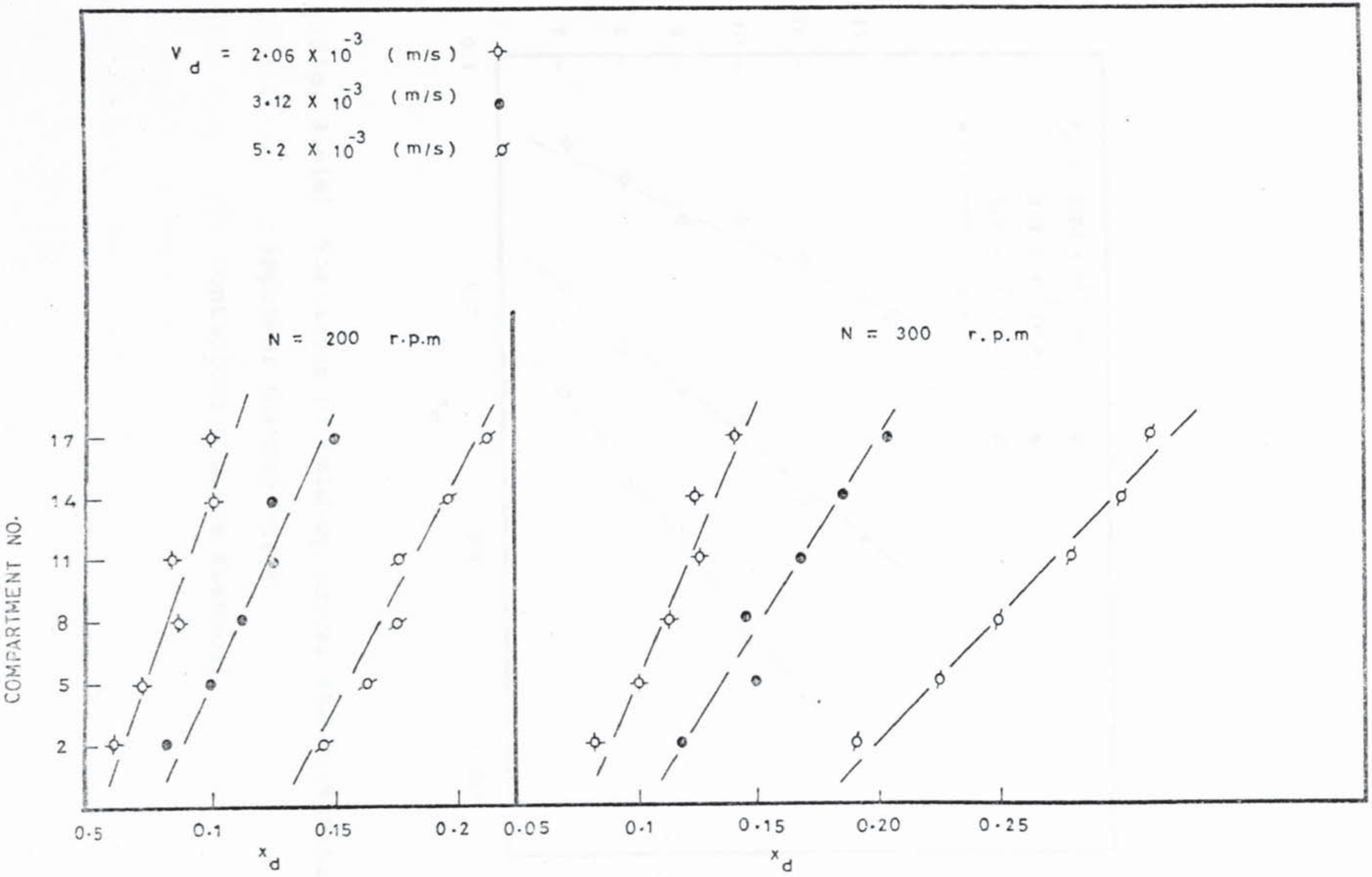


Fig. 9.6 Variation of hold-up across the contactor length.
| System: toluene-water
Contactor: Oldshue Rushton|

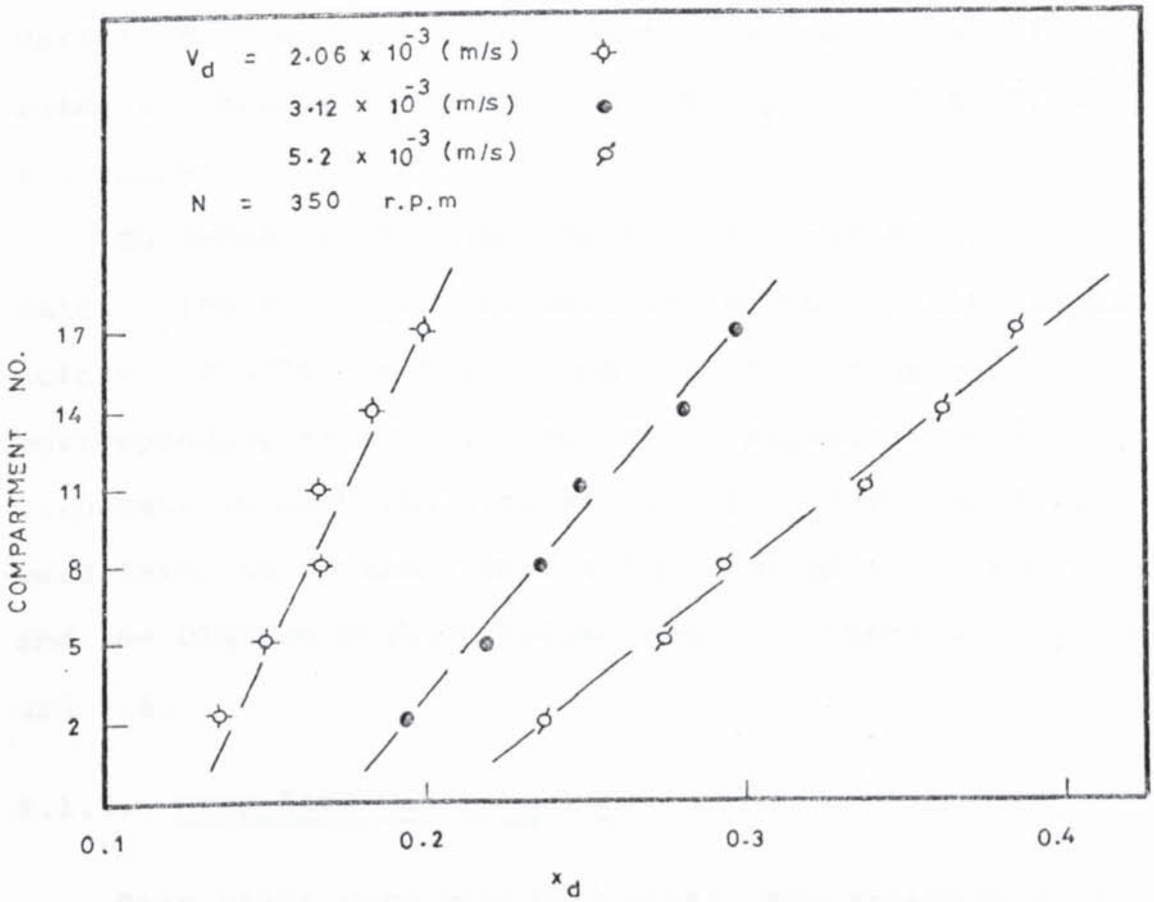


Fig. 9.6(a) Variation of hold-up across the contactor length.
|System: toluene-water
Contactor: Oldshue Rushton|

separation, the height of the dispersed phase below a previously marked interface and the overall operating height of the column were measured by reference to a fixed graticule.

This method (55) was found to be satisfactory in the present work since the hold-up associated with the free-rise zones was relatively small. Typical results showing the variation of average hold-up with dispersed phase flow rates at various rotor speeds, are reproduced in Figs. 9.3 and 9.5.

To determine the variation of hold-up along the column axis, point hold-ups were measured,using the five sample points installed in the column. 50 ml samples, corresponding to 12% of compartment capacity, were withdrawn in each instance and at least three readings were taken to obtain a mean value. Results for the R.D.C. and the Oldshue Rushton column are reproduced in Figs. 9.4 and 9.6.

9.1.3. Drop Size Distributions

Drop sizes were measured within compartments 2, 5, 8, 11, 14 and 17. Preliminary observations confirmed that, as reported by other workers (54, 56), drop size distribution was not directly affected by continuous phase flow rate. Therefore, observation and photography of droplet phenomena and drop size were carried out with a stationary continuous phase.

The criterion for equilibrium was taken as a steady interface level and its attainment normally required about 5 minutes. Duplicate photographs were then taken of each compartment. Enlargement of the negative to give an overall magnification of four times the true drop size and printing, on Kodak grade 4 'Bromesko' paper, gave sufficient magnification and contrast for counting. At least 300 drops were counted for each print. The ranges of impeller speed employed were 200-600 rpm for the Oldshue Rushton column and 500-1000 rpm for the R.D.C. The photographs were analysed as discussed in section 8.3.2.

Santer mean diameter was evaluated from,

$$d_{32} = \frac{\Sigma nd^3}{\Sigma nd^2}$$

The variation of drop size with hold-up is illustrated in Figs. 9.8 and 9.10 and the variation with compartment height in Figs. 9.9 and 9.11.

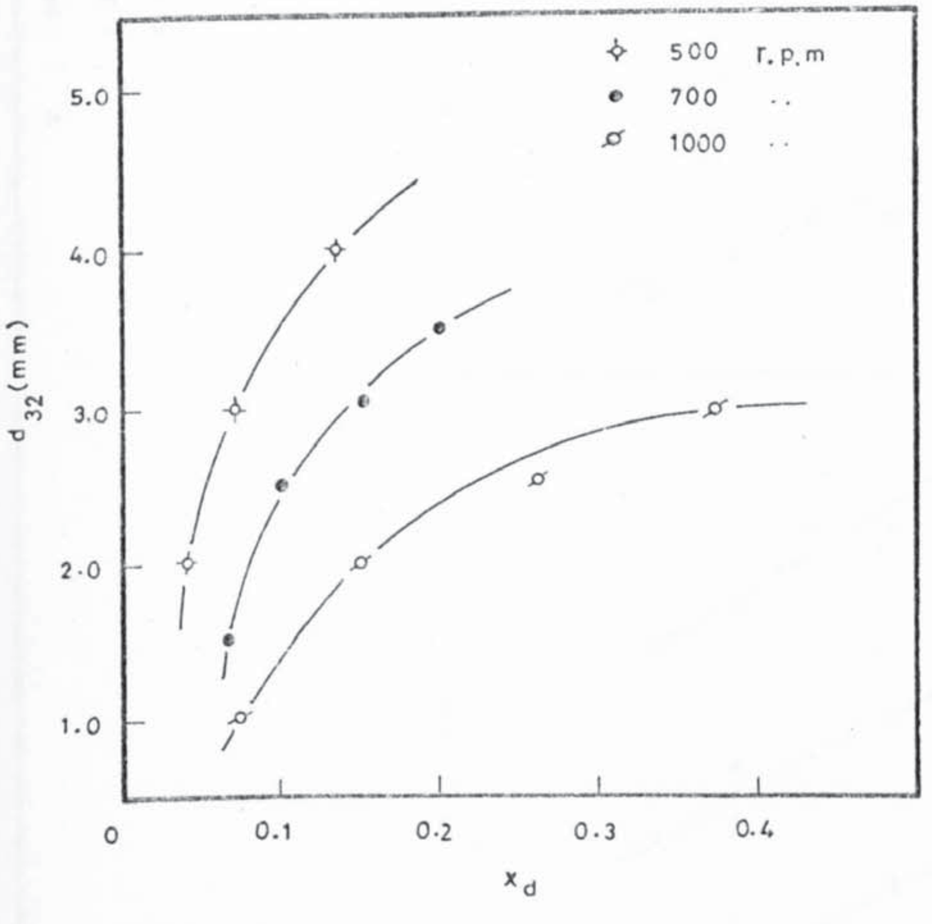


Fig. 9.8 Variation of drop size with hold-up.

|System: toluene-water
Contactor: R.D.C|

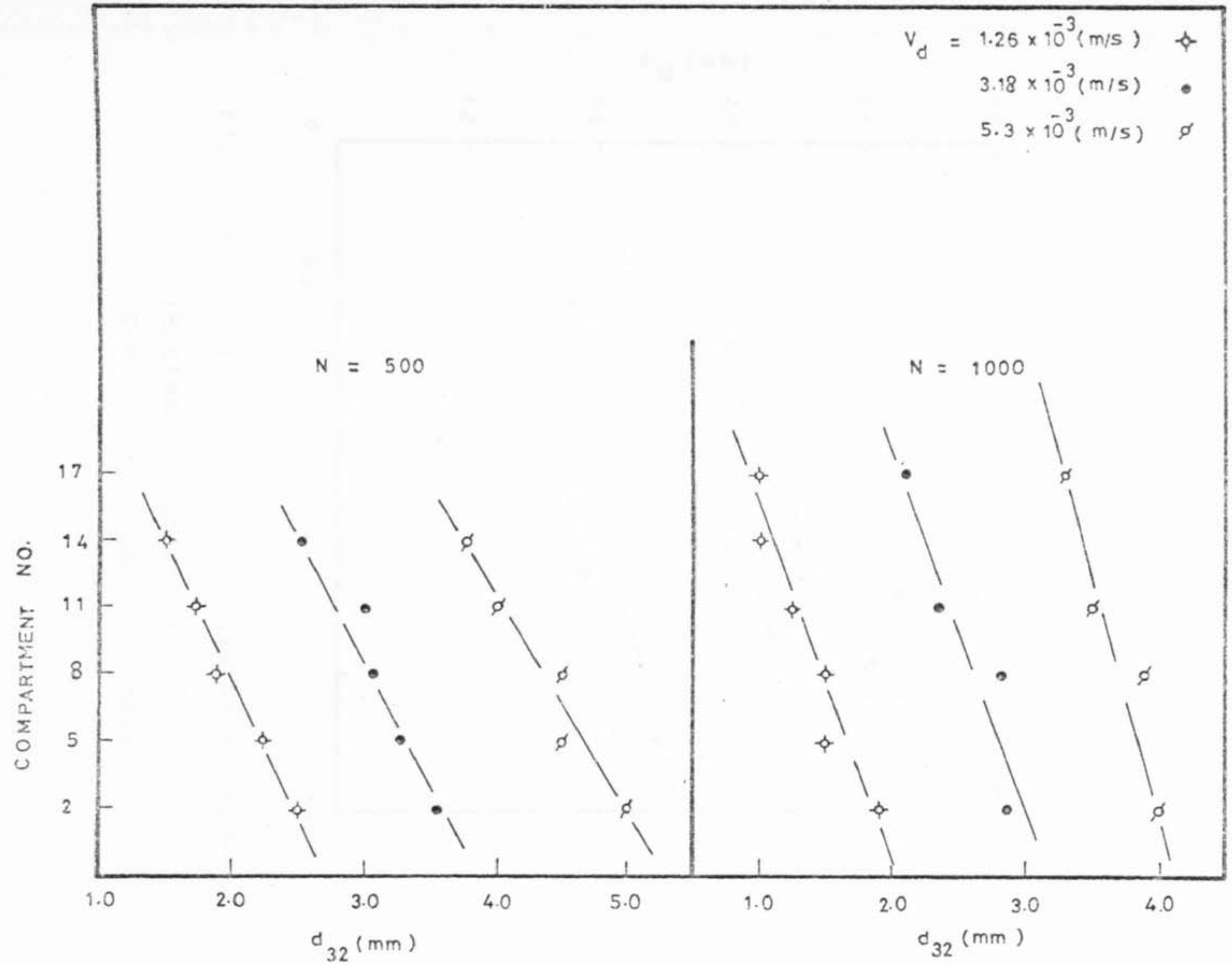


Fig. 9.9 Variation of drop size across the contactor length.
|System: toluene-water|

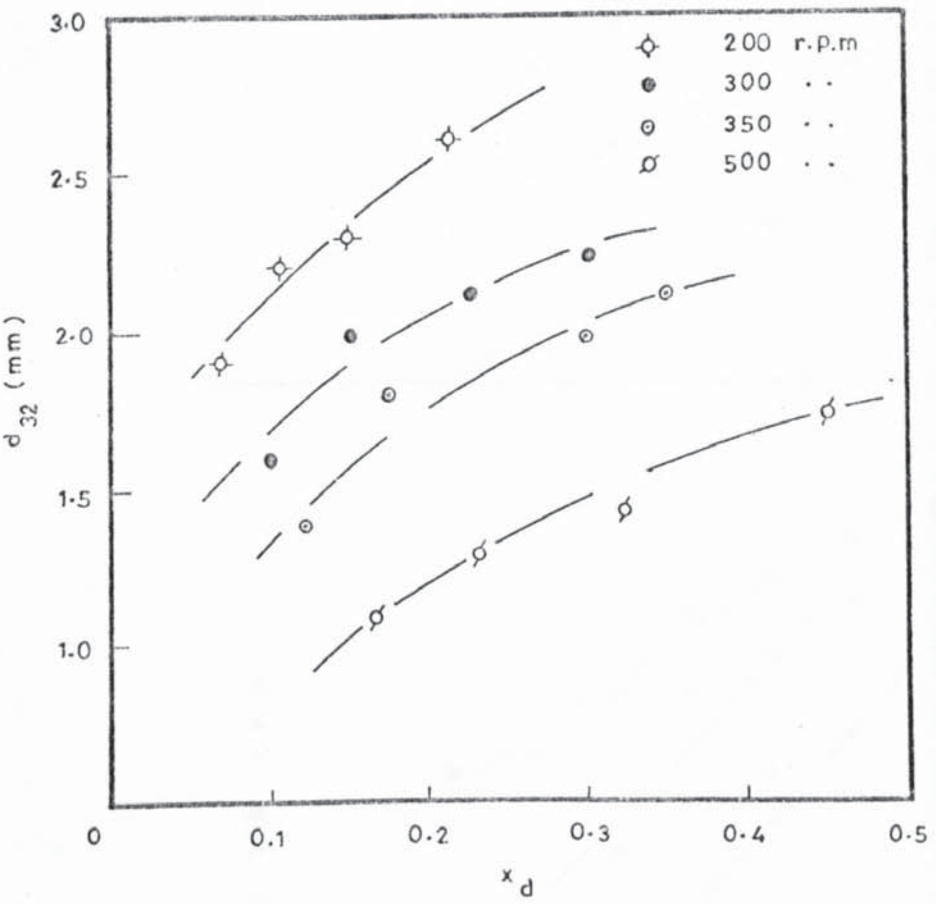


Fig. 9.10 Variation of drop size with hold-up.

|System: toluene-water
Contactor: Oldshue Rushton|

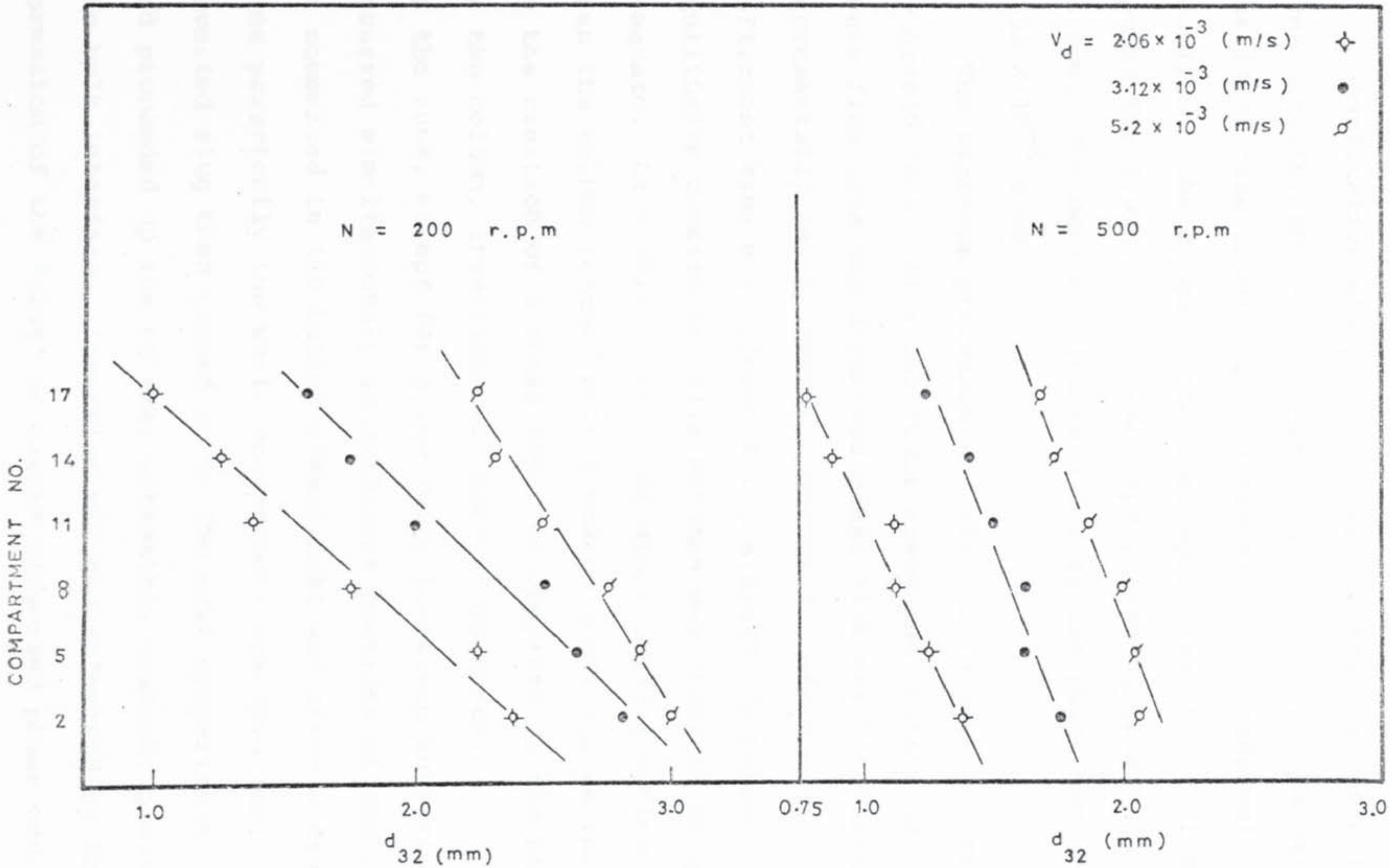


Fig. 9.11 Variation of drop size across the column length.
|System: toluene-water|

9.2 PHASE INVERSION

Quantitative study was limited to the systems butyl acetate-water and butyl acetate-aqueous sodium hydroxide, the later case involving mass transfer with chemical reaction. The range of impeller speeds was 500 to 1000 rpm in the R.D.C. and 250-600 rpm in the Oldshue Rushton column. The maximum flow rate for either phase was 7.85×10^{-5} m^3/s.

The start-up procedure was similar to that described by Arnold (40). At a set rotor speed and continuous phase flow rate the dispersed phase flow was increased incrementally until inversion occurred. After each increase, sufficient time was allowed for the system to reach equilibrium conditions; five minutes was found to be quite adequate. At a certain value of dispersed phase flow rate, when the column reached near flooding condition as indicated by the creation of a dense layer of droplets at the base of the column, inversion was observed to occur. In most of the runs, except for a few where localised inversion occurred simultaneously in different sections of the column, it commenced in the bottom compartment and after a finite time practically the whole compartment was inverted. This inverted slug then passed on to the next compartment and proceeded up the column, ultimately coalescing with the bulk interface. Inversion was characterised by the formation of the 'slug' of parent dispersed phase and normal operating conditions were restored soon after it left

FIG. 9.12(a) Phase Inversion Characteristics - R.D.C

a. Slugs of inverted lighter dispersed phase entering the upper settling zone.

b. Formation of a slug of lighter dispersed phase in one compartment.

c. Intense mixing prior to phase inversion in one compartment.

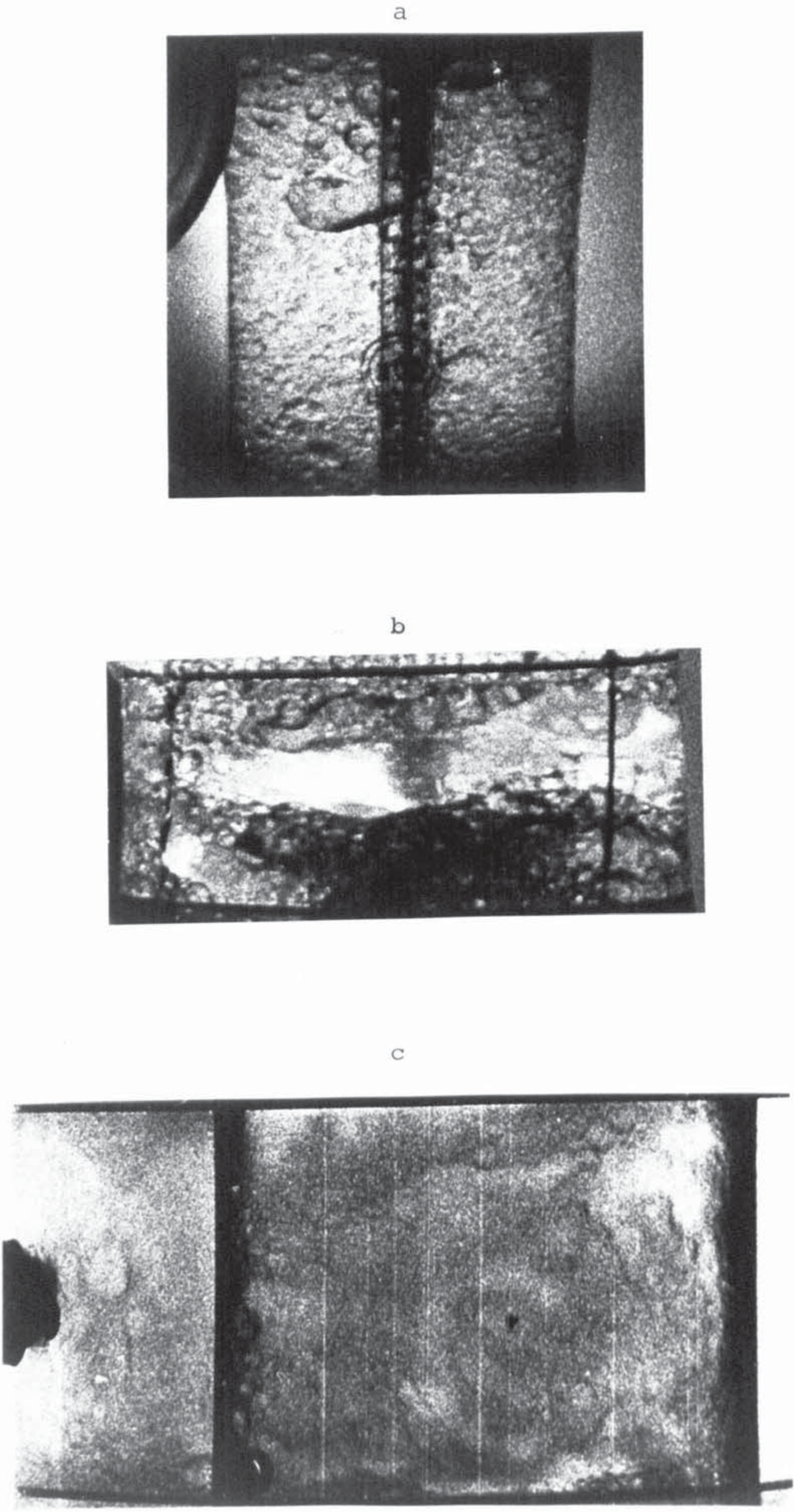


FIG. 9.12(a) Phase Inversion Characteristics - R.D.C

FIG. 9.12(b) Cyclical Phase Inversion - R.D.C

This illustrates a slug of inverted lighter dispersed phase travelling up the column.

a. Compartments 1 - 5

b. Compartments 6 - 9

c. Compartments 10 - 13

d. Inversion in a single compartment (enlarged).

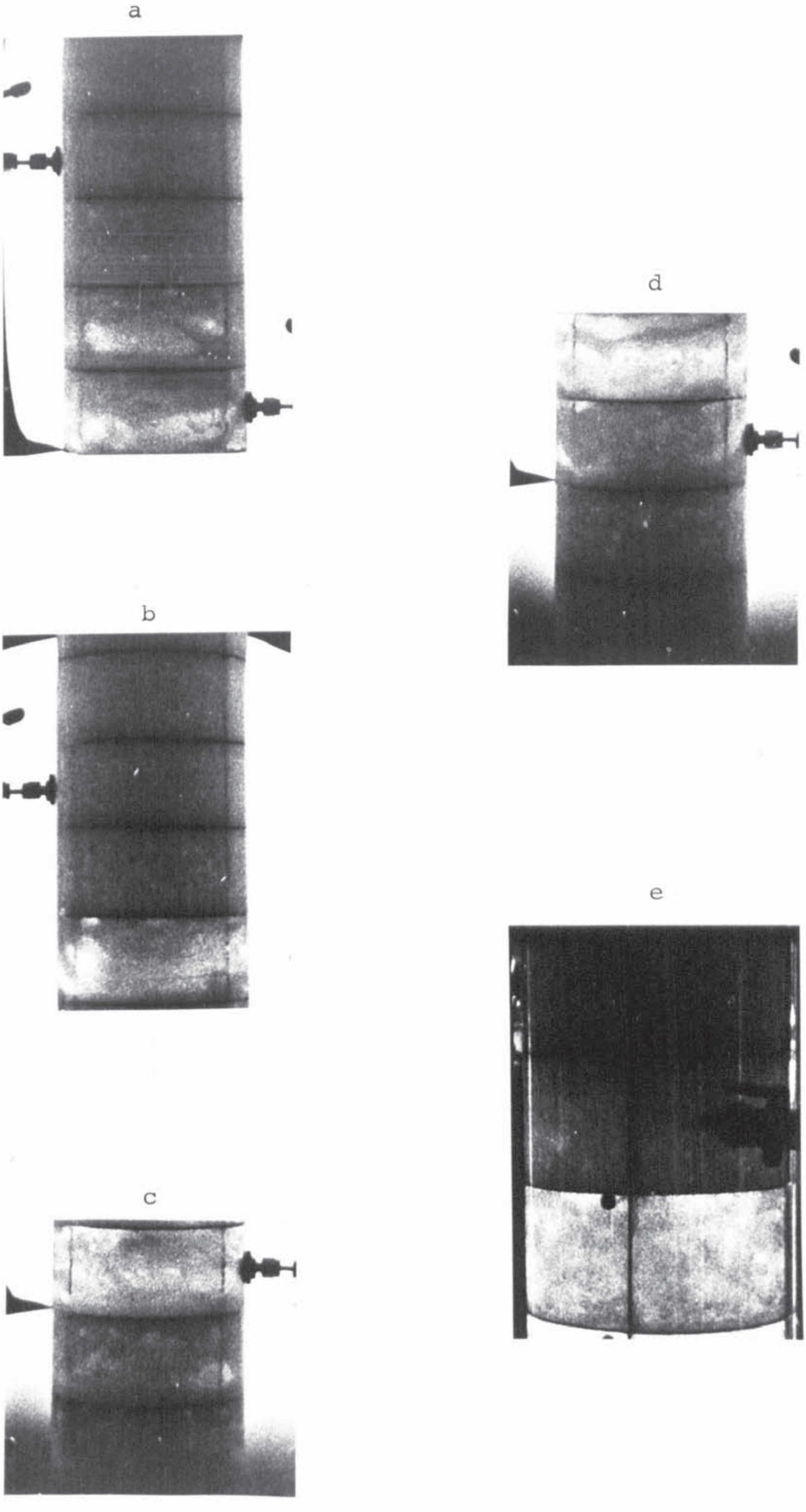


FIG.9.12(b) Cyclical Phase Inversion - R.D.C

any particular compartment. Re-inversion occurred in this compartment after a finite time with the whole process being repeated indefinitely. The process is typified by Fig. 9.12, consisting of prints selected from a cine film taken at 200 fps using a Milliken Camera (This film has been deposited in the Departmental Library). A description of the film sequence is given in Appendix 3.

Inversion was hence cyclical and the time cycle varied with the dispersed phase hold-up and energy input. At any given set of system parameters the inversion point was found to be very specific. A slight disturbance in the form of a minor change of the order of 2-3% in phase flow rate or stirrer speed was sufficient to disturb the inversion equilibrium and inversion ceased to occur.

Inversion hold-up values were measured by extraction of samples both prior to, and immediately after, inversion. Both values were approximately equal and the average value was considered as the inversion hold-up. The results are plotted in Figs. 9.13 and 9.14.

The phenomenon was observed to be cyclical in both the contactors. A detailed study of this time cycle was made for the Oldshue Rushton contactor only. Time of inversion, that is the time taken by the dispersed phase droplets to coalesce en masse to form a homophase, was recorded for each run.

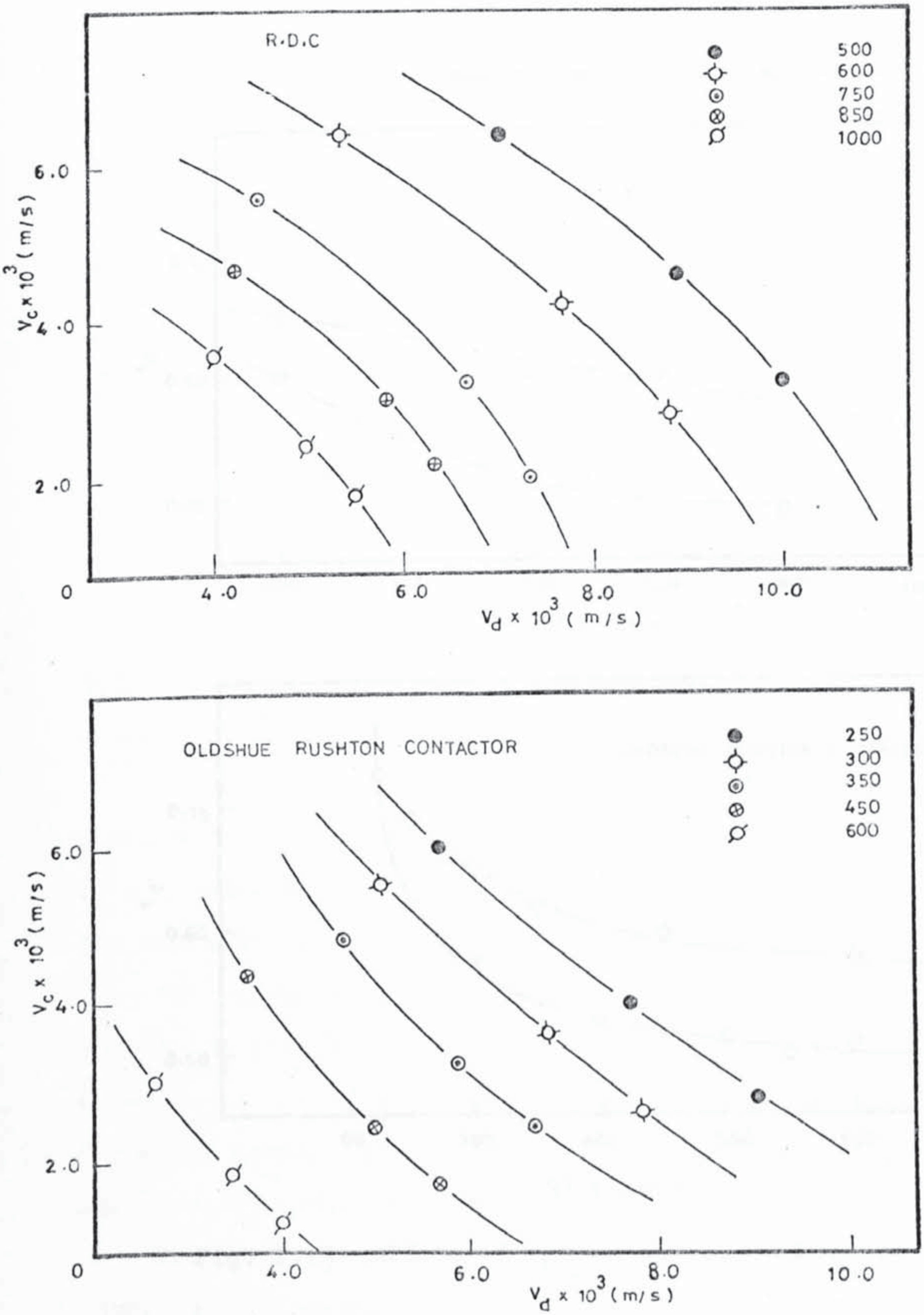


Fig. 9.13 Continuous vs dispersed phase flow at inversion (System: butyl acetate-water)

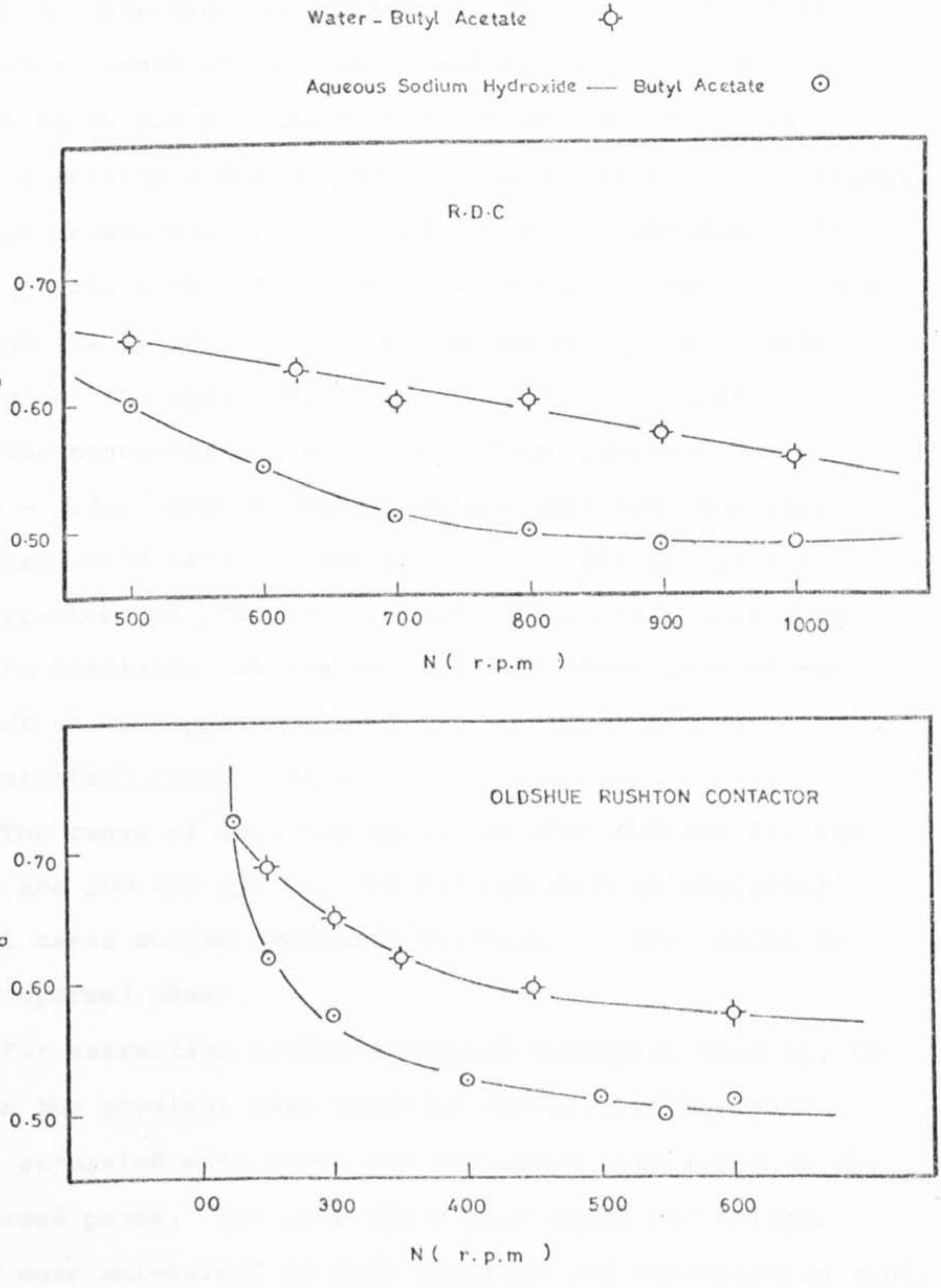


Fig. 9.14 Effect of rpm on inversion hold-up

9.3 Mass Transfer With Chemical Reaction

Initial investigations were carried out using each system to determine the approximate time taken for both columns to reach steady-state conditions. This was done by taking 20 c.c of sample at 3 minute time intervals until identical values of solute concentration were obtained. In most cases, equilibrium conditions were attained after the equivalent of 3-4 column volumes total flow had passed through the system. Subsequent measurements were taken only after the approximate minimum time had elapsed.

The concentration range of sodium hydroxide was 0.25N - 0.8N. Higher concentrations were not considered as these would have created significant changes in the physico-chemical properties, particularly diffusivity and kinetic constant. It was assumed that these properties did not change appreciably within the experimental concentration range (181).

The range of agitator speed was 500-1000 rpm for the R.D.C and 200-400 rpm for the Oldshue Rushton contactor. In all cases sodium hydroxide solution was maintained as the dispersed phase.

For extraction without chemical reaction, that is, to obtain the physical mass transfer coefficient K_L, each ester saturated with water was contacted with water as the dispersed phase. The same phase flow rates and stirrer speed were maintained in both reaction and non-reaction runs.

The slow reaction was studied in both contactors. The investigation suggested that higher K_L values were obtainable with the Oldshue Rushton column. Thus, for the fast reaction system, characterised by diffusion control, runs were carried out in the latter contactor. For the very fast reaction system the R.D.C was selected since a rapid extraction-reaction, being essentially interfacial in nature is difficult to analyse at high interaction rate (204). Thus runs were performed in the R.D.C at 500 rpm to ensure a limited droplet interaction rate. The effective height of dispersion was equivalent to twelve compartments in case of fast reactions.

The results are tabulated in Appendix 7(a), 7(b), and 7(c).

10. DISCUSSION OF RESULTS

10.1 NON-MASS TRANSFER STUDIES

10.1.1 FLOODING

To assist interpretation of the flooding data for the R.D.C, a plot of V_d vs $x_f^2(1-x_f)$ (49) is shown in Fig. 10.1. These straight lines are clearly capable of extrapolation through the origin. This suggests that the 'Characteristic Velocity' approach is satisfactory for the correlation of flooding data. Although not a discrete drop contactor, droplet interaction in the R.D.C is not pronounced within the normal range of operating characteristics. Hence the above approach would be expected to be appropriate for the prediction of flooding rates. However, deviations would be expected at higher flow rates and energy input levels, that is under conditions when the extent of drop-interaction becomes appreciable. The difference in design characteristics also influences the flooding rates to a significant degree. The present design exhibited 30-40% higher capacities than some other designs (55, 54) having different constriction factors and arrangements of column internals.

With the system butyl acetate-water it was difficult to recognise flooding because of the enhanced coalescence effects. Instead of flooding in the usual way, the phases were observed to invert, giving rise to a dynamic phenomena

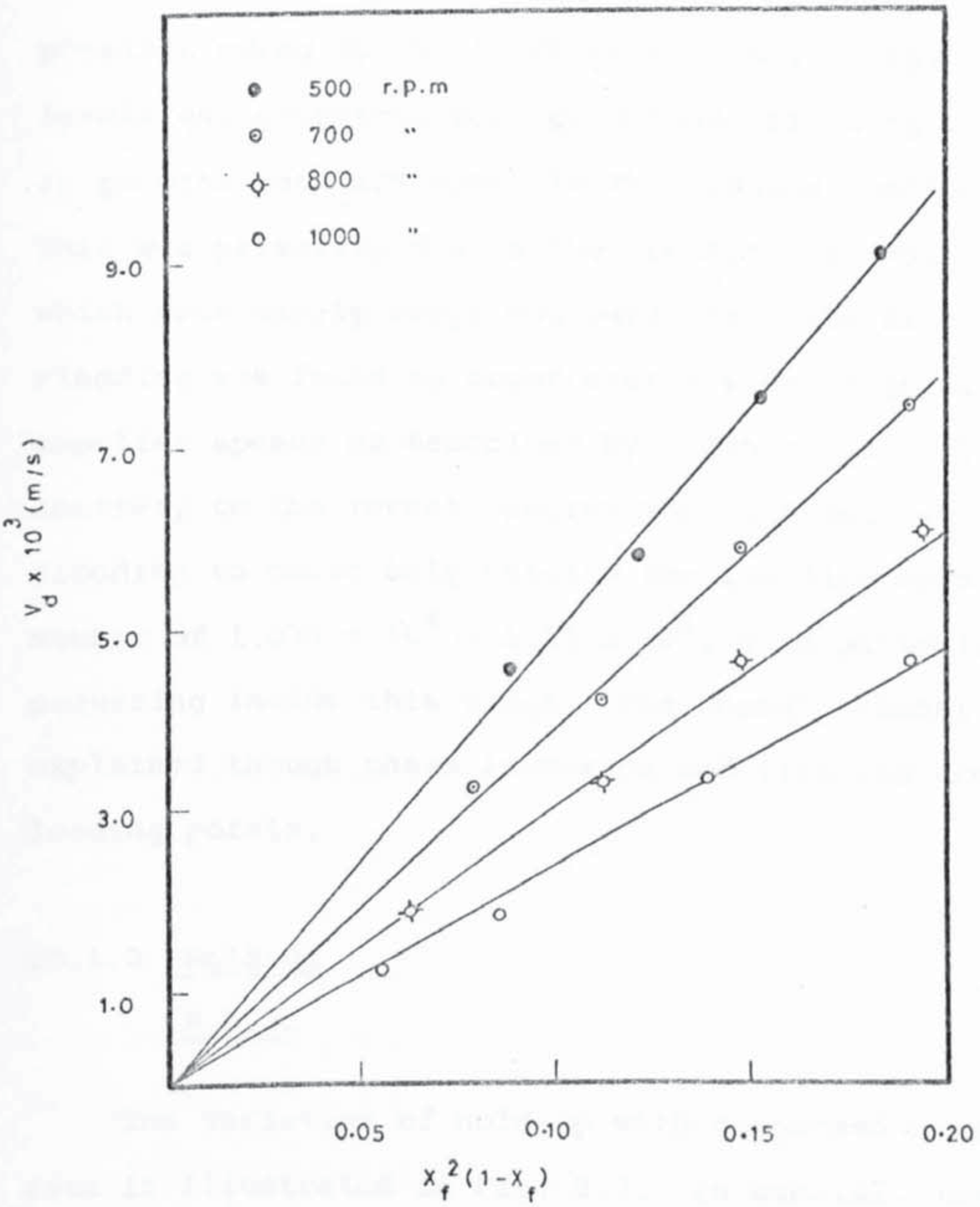


Fig. 10.1 Correlation of flooding data.

|System: toluene-water|

discussed in section 10.2.

Flooding rates in the Oldshue Rushton column are illustrated in Fig. 9.2. Although a direct comparison with the flooding characteristics of the R.D.C. is not possible owing to the difference in the energy input levels and geometric configurations, flooding rates in general were 12% lower in the Oldshue Rushton column. This was primarily due to the creation of smaller drops which were easily swept downwards from the distributor. Flooding was found to occur over a wide range of impeller speeds as described by Oldshue (26). This is however contrary to the recent observation of Arnold who reported flooding to occur only outside the impeller Reynold's number of $1.075 \times 10^4 - 2.15 \times 10^4$, with phase inversion occurring inside this range. The anomaly cannot be explained though phase inversion and flooding are close loading points.

10.1.2 Hold-Up

R.D.C.

The variation of hold-up with dispersed phase flow rate is illustrated in Fig. 9.3. In general, hold-up increased gradually with increasing dispersed phase flow rate at a fixed rotor speed. However, at high rotor speeds the rate of increase was very sharp. The data obtained were in general lower, in some cases by as much as 35%, than those reported by Al Hemeri (55). This may be attributed to the multiple constrictions, i.e. bearings, inside the earlier column.

The hold-up profile along the column is shown in Fig. 9.4. The hold-up increased gradually to a maximum value at a point approximately midway up the column and subsequently decreased. This is in agreement with the earlier findings of Rod (60), Strand et. al. (50) and Al Hemeri (55). Theoretically, the hold-up profile would be expected to be the inverse of the drop-size profile. The data suggests, therefore that the characteristic drop-size first decreased to a minimum value at a point corresponding to a maximum hold-up value and then increased towards the exit. This was not so in practice however; the drop size in fact decreased progressively up the column owing to the increased number of impacts. The reason for the unexpected downturn in hold-up at the dispersed phase outlet is the removal of restriction upon droplets flowing into the settler.

An attempt has been made to model the point hold-up values and so provide a means of predicting the profile in practical columns.

Experimentally the variation of dispersed phase hold-up at any fixed continuous phase flow was found to be dependent on height, dispersed phase flow rate and the impeller speed.

Thus, $$x_d = f(h, V_d, N_s) \qquad 10.1$$

Treating the function as a polynomial in h upto square terms as a first approximation,

$$x_d = a'_o + a'_1 h + a'_2 h^2 + \ldots\ldots. \qquad 10.2$$

where a'_o, a'_1, a'_2, are functions of V_d and N_s. Under these circumstances, the right-hand side of equation 10.2 is a polynomial having rings of polynomials (219). Thus expansion of the polynomial involves a large number of terms.

At zero height there is no column volume and hence no hold-up. Thus, $h = 0$; $x_d = 0$. Substitution of this boundary condition in Equation 10.2 gives,

$$a'_o = 0$$

Clearly the hold-up in any plane in the extraction section x_h, is related to the hold-up at the end of the section x_H, since there is a continuous change in hold-up from the bottom of the column. Intuitively, it is reasonable therefore to express equation 10.2 in the form

$$x_d = a'_2 \{h^2 - H\ h\}$$

where

$$a'_2 = f(V_d, N_s)$$

following from above (219) it would be reasonable to express $f(V_d, N_s)$ in the form $(a_o + a_1 N_s V_d + a_2 N_s {V_d}^2)$. Therefore,

$$x_d = (a_o + a_1 N_s V_d + a_2 N_s {V_d}^2)(h^2 - H\ h) \qquad 10.3$$

The values of coefficients in equation 10.3 were obtained by regression analysis as,

$a_o = +0.0131$

$a_1 = -0.162$

$a_2 = +0.0151$

Examination of equation 10.3 shows that it applies within the limit,

$$a_1 N_s V_d + a_2 N_s V_d^2 \leqslant 0$$

i.e.

$$a_1 + a_2 V_d \leqslant 0$$

but,

$$a_1 \approx -10a_2$$

therefore

$$V_d \leqslant 10 \text{ cm/s.}$$

This is within the practicable operating limits for agitated columns. The detailed computer programme is given in Appendix 4. The R^2 value obtained was 0.9 and sum squares of residuals was 0.005. This correlation gave a very close fit to the experimental data as shown in Fig. 10.2 Hence given the operating parameters equation 10.3 enables hold-up profile to be predicted.

Oldshue Rushton Column

The 'average hold-up' characteristics of the Oldshue Rushton Column were similar to those of the R.D.C in that the hold-up increased with increasing rotor speed and dispersed phase flow rate, as shown in Fig. 9.5. Although at higher rotor speeds the residence time of the drops within the discharge region of the impeller is smaller than at lower speeds, the number of drops passing through the region is much larger. The

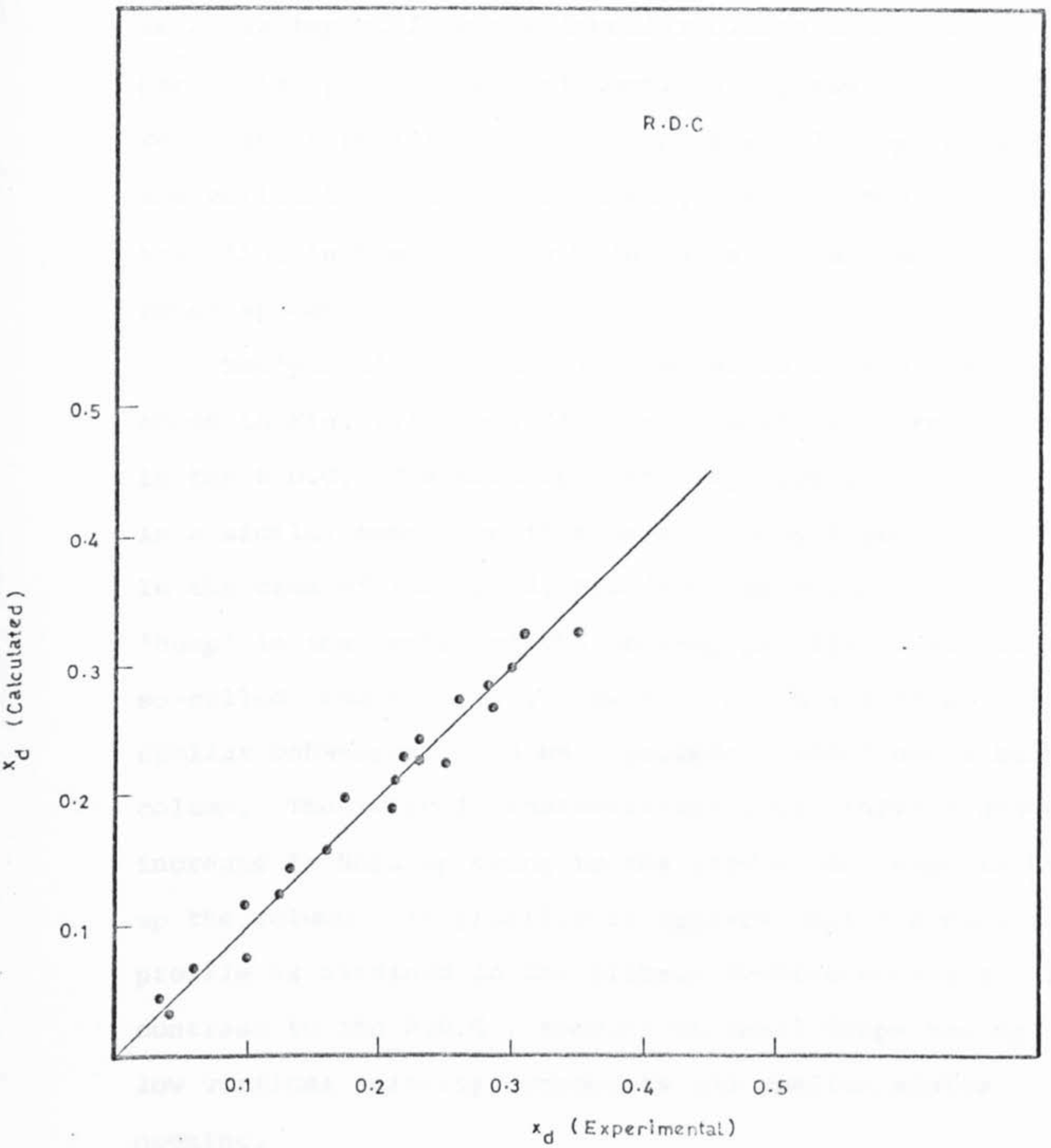


Fig. 10.2 Calculated vs measured dispersed phase point hold-up.
(System: Toluene-water)

energy available to rupture the drops is also larger, both via impact from the impeller blades and more particularly the turbulent continuous phase eddies. The resultant effect is the creation of small drops having low vertical velocity components. This is the mechanism resulting in high average hold-up values at the higher rotor speeds.

The'point' hold-up values obtained in the column, as shown in Fig. 9.6, were distinctly different from those in the R.D.C. The hold-up gradually increased up the column in a similar manner to that described by Arnold (40). In the case of the R.D.C, Rod (60) has suggested that the 'hump' in the centre of the hold-up profile is due to the so-called 'end effects'. However, if this were so similar behaviour would be expected in the Oldshue Rushton column. Theoretical considerations would infer a gradual increase in hold-up owing to the gradual decrease in drop-size up the column. In practice it appears that the predicted profile is attained in the Oldhsue Rushton contactor, in contrast to the R.D.C , because of small drops having low vertical velocity components and smaller stator opening.

The hold-up values were compared with the data of Arnold (40) under identical conditions. Whilst there was good agreement under high agitation (>300 rpm), high negative deviations of the order of 30% were observed at low rotor speeds. This may be partly attributed to the uncertainties commonly encountered in withdrawing a

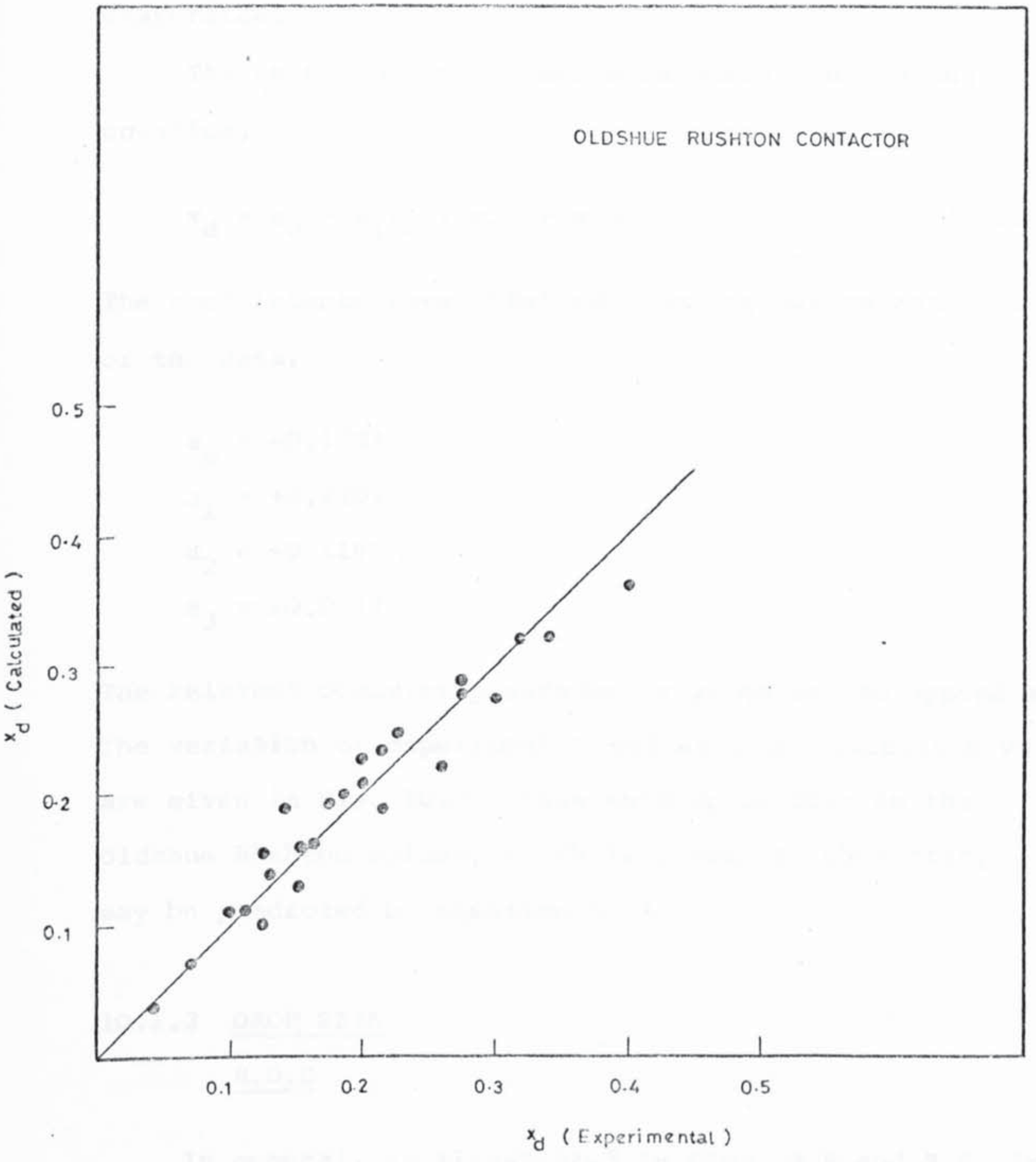


Fig. 10.3 Calculated vs measured dispersed phase point hold-up.
(System: Toluene-water)

representative sample of a non-uniform and dilute dispersion.

The point hold-up values were correlated by the equation,

$$x_d = a_o + a_1V_d + a_2h + a_3N_s \qquad 10.4$$

The coefficients were obtained from regression analysis of the data,

$a_o = -0.1728$
$a_1 = +0.4406$
$a_2 = +0.1185$
$a_3 = +0.0247$

The relevant computer programme is given in the Appendix 5. The variation of experimental values with calculated values are given in Fig. 10.3. Thus hold-up profile in the Oldshue Rushton column, which is linear in character, may be predicted by equation 10.4.

10.1.3 DROP SIZE

R.D.C

In general, as illustrated in Figs. 9.8 and 9.9, drop sizes increased with increasing hold-up and decreased with increasing rotor speed and column height. The range of drop sizes observed was between 1.0 mm and 5 mm which is characteristic of those commonly found in an R.D.C. under normal operating conditions (55).

The drop sizes were compared with those predicted by the correlations of Misek (56), discussed in Chapter 5.1. Although all experimentation was in the transition region ($10^4 < Re < 6x10^4$), all three correlations were considered. The values predicted were around 50% and 40% smaller than the drop size values, obatined for the turbulent and transition regions respectively. The laminar region correlation predicted values twice as large as the experimental values. The inapplicability of these correlations is not surprising since they take no account of the variation of drop size with hold-up, dispersed phase flow rate and column height.

The data were however in good agreement with the correlation of Al Hemeri (55). This is well illustrated in Fig. 10.4. A deviation of ±10% was obtained for the same system, viz, toluene and water.

Oldshue Rushton Column

The effect of dispersed phase flow rate and rotor speed on drop size were observed to be similar but not comparable in magnitude to that in the R.D.C. At low rotor speeds, i.e. in the range of 200-300 rpm, the variation of drop size with column height was greater than at the higher speeds. The range of drop sizes obtained was between 0.2 mm to 3 mm. Considering one compartment as a discrete mixer, the experimental data was compared with an identical stirred tank analysis of Hossain (220). An average variation of 70% was obtained which confirms that application of stirred tank data to columns is misleading(40).

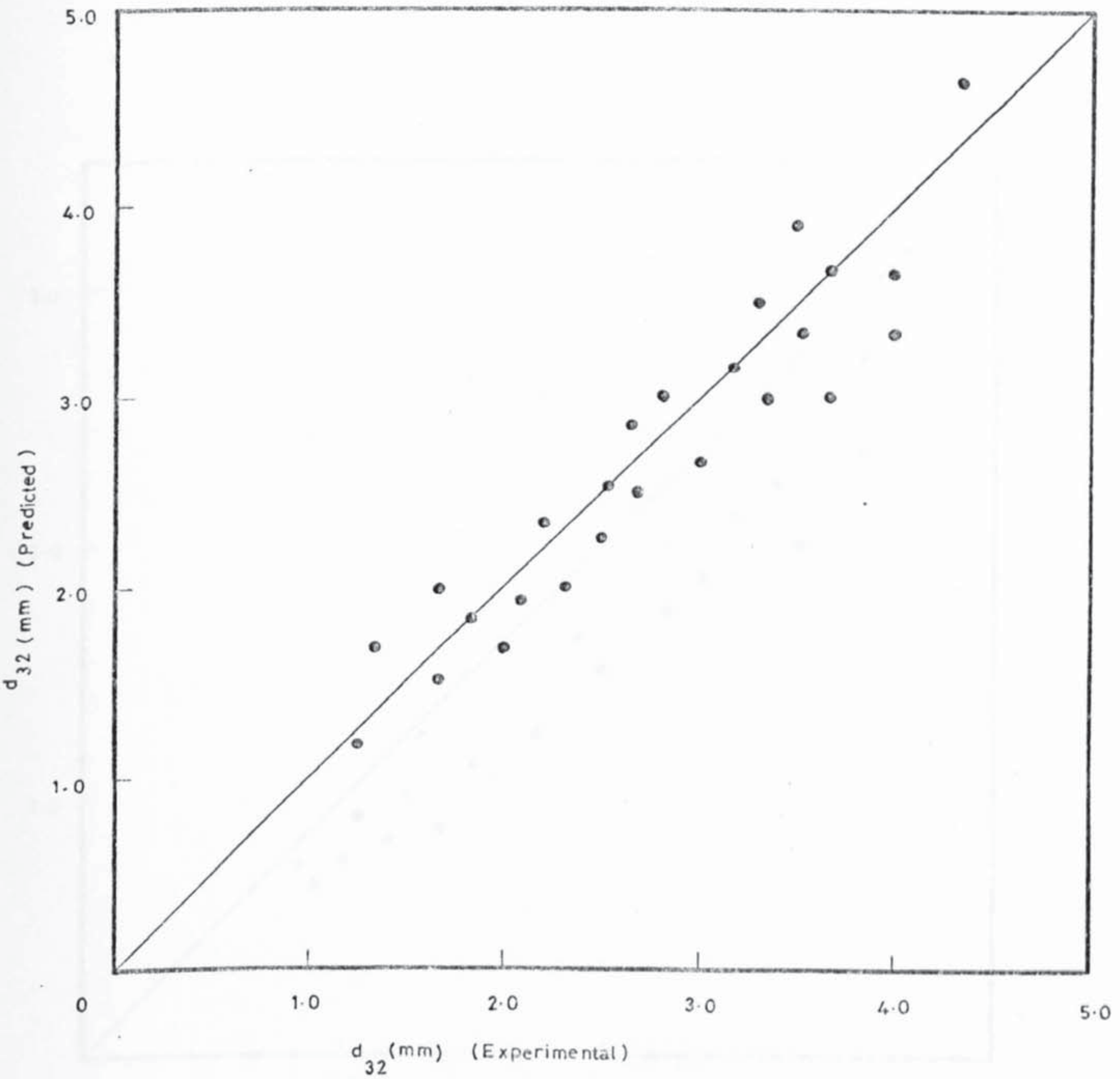


Fig. 10.4 Predicted vs experimental drop size in R.D.C
(System: Toluene-water)

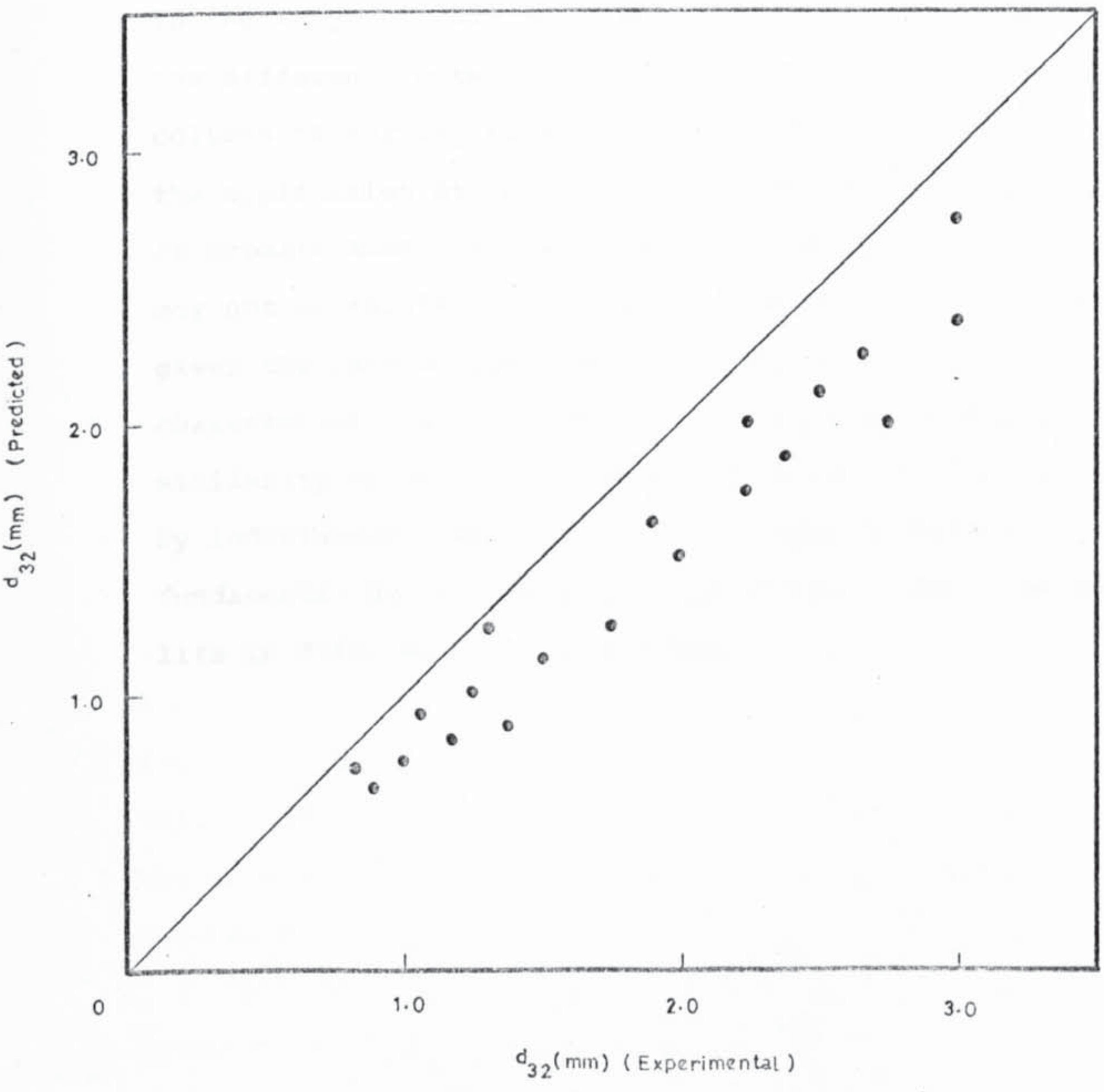


Fig. 10.5 Predicted vs experimental drop size in Oldshue Rushton contactor.
(System: Toluene-water)

The drop sizes were also compared with the correlation recently proposed by Arnold (40) from work on a 150 mm dia Oldshue Rushton Column. This comparison, reproduced in Fig. 10.5, shows experimental d_{32} values always greater than the predicted values. The deviation ranges from 10%-40% and is particularly marked at higher drop sizes, in the range of 1.75 to 3 mm. This is probably due to the difference between coalescence-redispersion rates in columns of varying size, and raises doubts regarding the application of laboratory data for scale-up purposes. It appears that the hydrodynamics of a small column may not be applicable to large-scale columns. For example, given the same energy input per unit volume, the characteristic eddy length may not meet any defined similarity criteria since the life of an eddy is controlled by indefinable viscous forces. Because of this a fundamental difference must exist between eddy size and life in different diameter columns.

10.2 PHASE INVERSION

10.2.1 MATHEMATICAL MODELS FOR PHASE INVERSION PHENOMENA

10.2.1.1 Inversion Hold-Up

From results in section 9.3 and as discussed in Chapter 4, a high hold-up (>40%) of the dispersed phase is an essential criterion for phase inversion. The hold-up in a counter-current contactor is related to the phase flow rates by the equation 4.2,

$$\frac{V_d}{x} + \frac{V_c}{1-x} = V_n(1-x) \qquad 4.2$$

V_n is a function of drop size and hence would be expected to be some function of x, the dispersed phase hold-up (51). Thornton et. al. (49), however, did not observe any such dependence of V_n on x and concluded that any tendency for V_n to increase with droplet size was offset by a progressive increase in hindrance of droplet movement with increased dispersed phase hold-up. This implies that high hold-up imposes a resistance to the upward flow of drops. However, this fails to take account of the effect of coalescence and thus may be applicable only to situations where coalescence effects are insignificant e.g. a spray tower.

In a detailed work Marchant-Williams (221) observed in an R.D.C. that V_n was a strong function of hold-up under conditions involving pronounced coalescence. Therefore, although the exact nature of the dependence is not known, V_n would be expected to increase with increasing

hold-up when the system exhibits a high coalescence rate owing to the decrease in resistance. The resistance to flow will decrease under 'strongly coalescing' conditions due to the formation of bigger drops, thus considerably shortening the mean length of the path an incoming drop may have to travel in comparison with a 'weakly' or non-coalescing situation where it has to suffer multiple collision before leaving the high hold-up zone. This is particularly true in the case of phase inversion. At phase inversion, drops exist which are far larger than Kolmogorov's predicted drop size (82). Thus in a pronounced 'coalescing environment', the resistance due to hold-up is insignificant compared with the upward momentum of big drops generated by high hold-up. In such an environment, particularly under conditions approaching inversion, any increase in hold-up increases the drop size which may range from the characteristic dimension of the turbulent field to mis-shaped slugs of dispersed phase fluid. Consequently V_n is increased.
Thus,

$$V_n \simeq f(d) \approx f(x) = Kx^n \qquad 10.6$$

According to Arnold (40) phase inversion occurs in an Oldshue Rushton column in the hold-up region of 0.6-0.8 and has the effect of relieving the imminent flooding situation in the contactor. Similar observations were made by Al Hemeri (55) in an R.D.C. although,phase inversion also occurred well below the flooding point at certain phase ratios, possibly due to the undetected presence of surfactants e.g. dirt or interfacial scum which are known to shift the inversion to a low hold-up (108). Thus, in the absence of mass transfer, the inversion hold-up may be assumed to be very near, or equal to, flooding hold-up values.

Substitution of V_n from equation 10.6 into equation 10.5 yields,

$$\frac{V_d}{x} + \frac{V_c}{1-x} = Kx^n(1-x) \qquad 10.7$$

The inversion hold-up may be obtained from equation by imposing the necessary conditions,

$$\frac{dV_c}{dx} = 0 \; ; \qquad \frac{dV_d}{dx} = 0$$

Differentiating equation 10.7 w.r.t. x, with V_c constant

$$-\frac{V_d}{x^2} + \frac{1}{x}\frac{dV_d}{dx} + \frac{V_c}{(1-x)^2} = K\left[nx^{n-1}(1-x) - x^n\right]$$

At inversion, $\frac{dV_d}{dx} \to 0$,

Therefore,

$$V_{d_i}\left[\frac{1}{x_i} + \frac{1}{1-x_i}\right] = K\left[(x_i)^{n+1} - nx_i^{\,n}(1-x_i) + x_i^{\,n+1}\right]$$

or

$$V_{d_i} = K(x_i)^{n+1}(1-x_i)\left[x_i(n+2)-n\right] \qquad 10.8$$

Similarly,

$$V_{c_i} = K(x_i)^n(1-x_i)^2\ [(n+1)-x_i(n+2)] \qquad 10.9$$

where subscript 'i' indicates the corresponding values at inversion. The value of exponent n may as a first approximation be taken as 2.0; this is from a study of the variation of V_n with drop size by Bouyatiotis et. al. (74), and the work of Thornton et. al. (49) in the R.D.C. Combining equations 10.8 and 10.9,

$$\frac{V_{c_i}}{V_{d_i}} = \frac{(1-x_i)(3-4x_i)}{x_i(4x_i-2)} \qquad 10.10$$

which may be expressed as the series,

$$Rr = 1-\frac{a}{x_i} + \sum_{\substack{k=2\\j=1}}^{\substack{k\\j}} (b)\ {}^{K}/(x_i)^j \qquad 10.11$$

where, $Rr = V_{c_i}/V_{d_i}$; $a = 1.5$; $b = 0.5$.

Examination of equation 10.10 suggests that when $V_c = 0$, either $x = 1.0$ at which condition the continuous phase would be completely absent, or, $x = 0.75$. The latter value may be interpreted as the maximum hold-up value when the continuous phase flow is zero. This is in good agreement with the experimental value of approximately 0.70 obtained by Arnold in an Oldshue Rushton Contactor. From theoretical considerations Clayton (222) has calculated the maximum value of dispersed phase hold-up in a stirred tank as 0.74 and this may be considered analogous to a single compartment. However, higher hold-up may be possible in practice. A dispersion of 96% Kerosene in water in a non-flow stirred system has been reported (55).

Al Hemeri (55) presented three speculative models of phase inversion, two of which rendered a maximum theoretical value of 0.5 hold-up at $V_c = 0$. This contrasts with the observation of Arnold (40) and also the present model. The third model is rather inconclusive and is not therefore discussed here.

Misek (51) proposed an expression for hold-up at flooding in an R.D.C.,

$$\frac{V_d}{V_c} = \frac{2x^2\left[(1-x)+(z/\alpha-4.1)(x-x^2/2-1/2)\right]}{(1-x)^2\left[(1-2x)+(z/\alpha-4.1)(x-x^2)\right]} \qquad 10.12$$

at z values ranging from 2.26 to 6.105. Unfortunately, this model gives unrealistic values of hold-up e.g. 0.123 at $V_c/V_d = 1.0$.

The present model gives reasonable hold-up values e.g. $x = 0.6-0.67$ at $V_c/V_d = 1:1-1:4$ which is the normal operating range of R.D.C. and Oldshue Rushton contactors.

10.2.1.2 Time For Phase Inversion

This work has confirmed that phase inversion in countercurrent agitated columns is a cyclic phenomenon (40). Inversion normally commenced in the bottom compartment and the inverted 'slug' gradually moved up the column. As soon as it left a compartment, the compartment reinverted to its original condition and a finite time then elapsed before it again started to invert. This time lag represented the time required for the inversion process to reach completion in the compartment starting again from initial conditions. An attempt has therefore been made to model the phenomenon and deduce an expression for the time cycle of this pseudo-steady state operation.

Sawistowski (108) observed that phase inversion in liquid-liquid systems is a fast process. Furthermore from observations in this work and by others (55, 40) the prerequisites for phase inversion are,

(i) An enhanced rate of coalescence i.e. the rate of coalescence far exceeds the rate of droplet break-up.

(ii) A high dispersed phase hold-up.

Since the process of inversion is rapid, it may be assumed that the rate controlling mechanism is the process of coalescence. The rate of inversion therefore, depends on the frequency of collision, determined by the concentration of dispersion, and the intensity of turbulence. The latter may be characterised by a turbulent diffusion constant. Hence to evaluate the dynamics of the process, it is first necessary to know the number of collisions taking place between droplets. Secondly, it is necessary to quantify the effect of these collisions i.e. the proportion of collisions leading to coalescence compared with the ineffective collisions which occur when the droplets again move away from each other primarily due to the impact of high frequency eddies. Presumably for a phase to invert, the number of successful encounters must far exceed the number of ineffective collisions, otherwise the system would remain in a state of dynamic equilibrium.

The situation is analogous to the coagulation of colloidal suspensions. The only fundamental difference between the two phenomena is that, whilst coagulation in colloidal dispersions is brought about by electrolytic forces, coalescence in liquid-liquid systems takes place by a surface interaction mechanism (97). Thus Smoluchowski's (223) theory of coagulation may be combined with the drop-growth mechanism discussed later to find an expression for the time required to invert a phase having the maximum hold-up defined by the hydrodynamics of the column. This basically involves predicting the number of collisions per unit time. In this context Fick's 2nd law of bulk diffusion is assumed to apply to macrodroplets under homogeneous turbulent conditions i.e.,

$$\frac{\partial c}{\partial t} = D_{tr}\left(\frac{\partial^2 c}{\partial \bar{a}^2} + \frac{2}{\bar{a}} \frac{\partial c}{\partial \bar{a}}\right) \qquad 10.13$$

where, C = dispersion concentration

$\bar{a}$ = distance from the centre of a sphere R.

D_{tr} = turbulent diffusion coefficient to characterise the eddy diffusion in a turbulent field.

The above equation may be assumed to describe the diffusion of drops towards a stationary drop and a collision will result as soon as any droplet approaches it so closely that the centre of both droplets is equal to 2r. This may be considered as diffusion of point masses towards a sphere of radius $R = 2r$. The concentration of droplets on the surface of this sphere is zero at any instant since single drops cease to exist here by virtue of the assumption of rapid coalescence.

The above mechanism allows for the following boundary condition,

$C = C_o$ at $t = 0$ for $\bar{a} > R$

$C = 0$ at $t > 0$ for $\bar{a} = R$.

Equation 10.13 may be solved with the above boundary conditions (93),

$$C = C_o\left[1 - \frac{R}{\bar{a}}\left\{1 - \frac{2}{\sqrt{\pi}} \int_o^{\frac{\bar{a}-R}{2\sqrt{D_{tr}t}}} e^{-\xi^2} d\xi\right\}\right] \qquad 10.14$$

when $t >> R^2/D_{tr}$,

$$C = C_o(1 - R/\bar{a}) \qquad 10.15$$

The number of droplets that pass the surface of radius R in 1 sec. is given by Fick's first law,

$$N = 4\pi R^2 D_{tr}\left(\frac{\partial c}{\partial \bar{a}}\right)_{\bar{a} = R} \qquad 10.16$$

From equation 10.15,

$$N = 4\pi R\, D_{tr}\, C_o \qquad 10.17$$

Equations 10.14 to 10.17 are based on collision with a stationary drop whereas in the real situation all drops are in motion. Under this condition, N is given by,

$$N = 8\pi D_{tr}\, C_o\, R \tag{10.18}$$

The flux $\dot{N}$ expresses the rate of coalescence with respect to one drop and will be C_o times greater with respect to all C_o drops in unit volume and is valid for any concentration, That is,

$$\frac{dc}{dt} = -8\pi R\, D_{tr} C^2 \tag{10.19}$$

Substituting R = d, the drop diameter

$$\frac{dc}{dt} = -8\pi D_{tr}\, d\, C^2 \tag{10.20}$$

Now the volume of a drop may be expressed as,

$$v = \frac{\pi}{6} d^3 = \frac{x}{C} \tag{10.21}$$

Differentiating equation 10.21, w.r.t. t, and substituting for $\frac{dc}{dt}$ in equation 10.20 yields,

$$\frac{dv}{dt} = 9.95\pi x D_{tr} v^{\frac{1}{3}} \tag{10.22}$$

which is an expression for the rate of change of drop volume with time t.

The collision mechanism is rather complex and it is rather difficult to predict the number of drops involved in any collision, particularly in the case of a concentrated dispersion. Multi-drop collision may frequently occur when the dispersed phase hold-up is very high i.e. in the region of 0.50-0.70. Since it is not yet possible to observe in detail the behaviour of drops in a turbulent field, it is only possible to speculate as to the mechanism of collision (104). In reality, at any time t drops of different sizes may exist in a coalescing medium under transient conditions and the whole mechanism of the droplet combination changes every instant with progressive increase in the number of drop species. The situation is rather complex and probably unpredictable but may be simplified if a drop growth concept is assumed to hold wherein a sphere is imagined to grow continuously with the addition of fresh surface elements (i.edroplets) from a drop volume v to the coalesced inversion volume V_i. The time taken for this growth may be taken as equal to the total time taken by droplets of different species to attain the inversion volume through a complex series of droplet combinations. By integrating equation 10.22,

$$\int_{v}^{V_i} \frac{dv}{v^{1/3}} = 9.95\pi x D_{tr} \int_{0}^{t} dt \qquad 10.23$$

from which

$$t = 0.048(z)^{0.66}(x)^{-0.33}(D_{tr})^{-1.0} \qquad 10.24$$

where z = volume of the vessel or compartment of a contactor.

The value of D_{tr} may be predicted from the expression (93),

$$D_{tr} = \alpha(\bar{\varepsilon})^{0.33}\ (\lambda)^{1.33} \qquad \lambda \geqslant \lambda_o \qquad 10.25$$

where α = constant dependent on the density of the continuous phase.

$\bar{\varepsilon}$ = Energy input / unit mass

λ_o =Characteristic eddy length.

10.2.2 DISCUSSION OF RESULTS

It has been observed that the creation of a high dispersed phase hold-up is a prerequisite for phase inversion. In counter-current operation, the maximum hold-up is limited by the hydrodynamics of the contactor; it varies with phase flow rates and the energy input per unit volume. It coincides with the condition termed the 'flooding point'. This is the highest hold-up value attainable under a given set of conditions.

In the present work inversion occurred when the column was operated at or near this flooding condition and in >95% of the runs it commenced within the bottom compartment. At this operating condition, the vertical velocity component of the majority of droplets at the base of the column approaches zero whereas there is a steady supply of the dispersed phase. Since the droplets do not escape at a sufficient rate a dense layer of droplets forms at the bottom compartment. Thus the inversion would be expected to occur firstly in the bottom compartment since the droplet concentration under these circumstances is a maximum and inversion is dependent on the rate of coalescence, which is related to the collision frequency. Arnold (40) earlier observed that in an Oldshue Rushton column phase inversion occurred to relieve the imminent flooding situation and although in his work inversion occurred in one or two compartments at a time irrespective of their position in the column, it was initiated in the bottom compartment. Al Hemeri (55) also observed that inversion always commenced at the bottom of the R.D.C. Observations in the present work therefore agree well with those of the above workers who used different liquid-liquid systems.

As shown in Fig. 9.14, hold-up values at inversion were between 0.57-0.69. Arnold (40) reported a similar range from his work in a larger Oldshue Rushton column but no comparable data are available for the R.D.C. However, in a preliminary study subsequent to the present work, maximum inversion hold-up was found to be 0.76 with the system toluene-water (116).

The theoretical model derived in the previous section to predict hold-up is in good agreement with the experimental values. However, because of other experimental restrictions it was only tested for $V_c/V_d < 1.0$. Clearly it will be necessary to test this over the normal limits for V_c/V_d in both columns, i.e. 0.5 to 2.0 or in some cases 4.0. However it appears that, as shown in Fig. 10.6, the rate of change of theoretical inversion hold-up decreases appreciably at high V_c/V_d values e.g., an increase of V_c/V_d from 1.5-3.0 only increases the hold-up by 0.05. Similar observations have been made in an earlier work (55). Thus although the present work was restricted to $V_c/V_d \leqslant 1.0$, it may well be applicable for higher phase ratios. If it does prove applicable over a wide range, then it will provide an accurate method for determining the maximum volumetric capacity of a contactor rather than 'flooding' which is generally not well-defined and specific.

The hold-up profiles obtained in experiments involving interphase mass transfer and chemical reaction are illustrated in Fig. 9.14. It follows a similar trend to that for inversion under non-mass transfer conditions but with lower values of inversion hold-up. It is difficult to explain this in quantitative terms because of the very complex nature of the conditions under which inversion occurs with simultaneous mass transfer and chemical reaction. However, it may be due to a change in interfacial energetics owing to the change of system properties i.e. the presence of products of reaction and concentration changes of the reactants . For example, Sawistowski (108) studied the effect of interfacial tension on the inversion hold-up in a stirred cell and observed a significant widening of the ambivalence range leading to low inversion

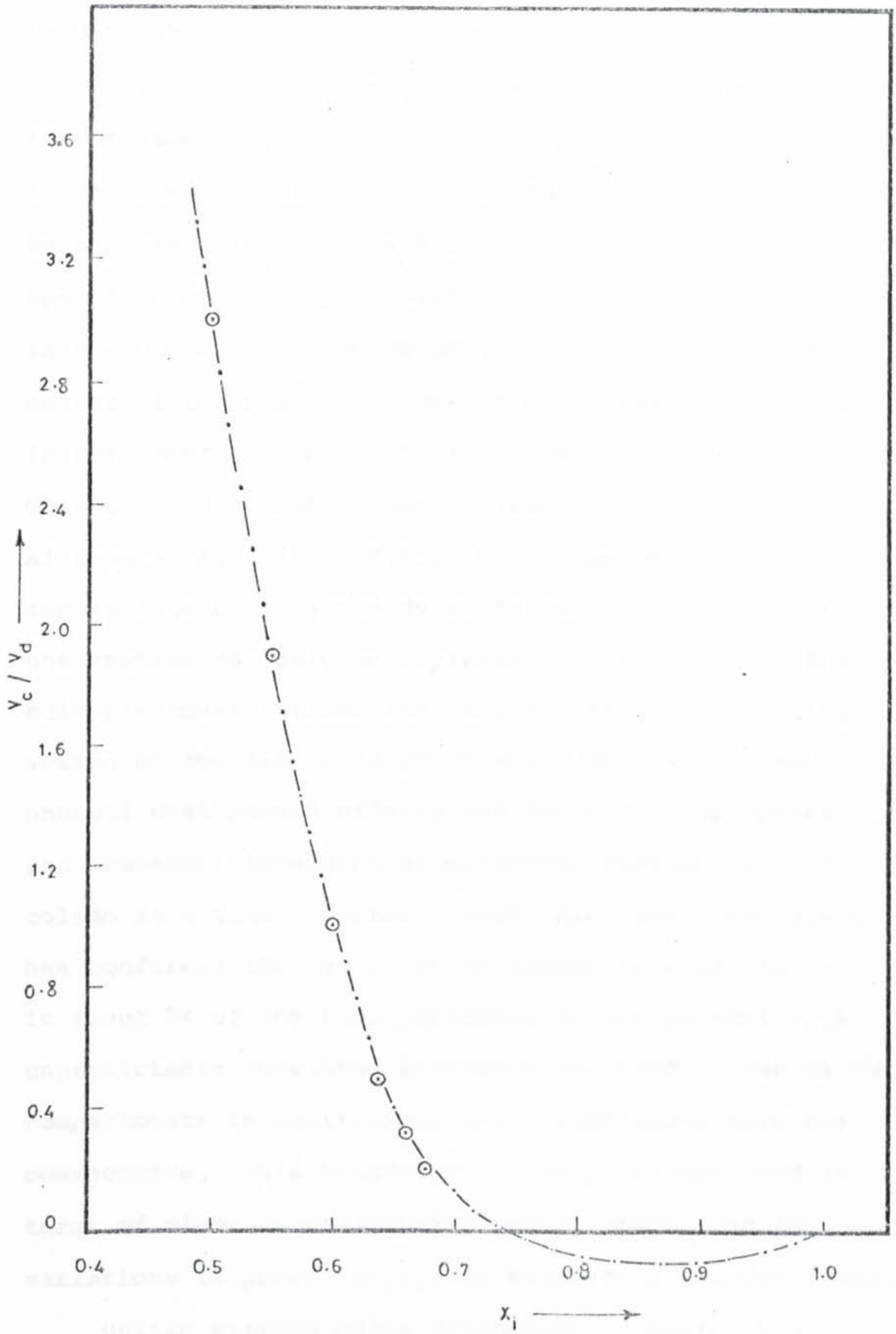


Fig. 10.6 Predicted phase inversion hold-up (Equation 10.11)

hold-up when mass transfer occurred.

Inversion characteristics were found to be similar in both the R.D.C. and Oldshue Rushton contactors but lower hold-ups were obtained in the former. This would be expected since in the R.D.C., in the normal range of operation, mean droplet size is significantly greater than in the Oldshue Rushton column. The pseudo steady state nature of inversion observed in both the conatactors is in agreement with Arnold's (40) observations on the Oldshue Rushton column but contrary to those of Al Hemeri (55) on the R.D.C where the operation was reported to be of a steady state nature. The anomalous observation can only be explained by reference to the multiple constrictions inside the latter column being wetted by the dispersed phase which may have caused unusual coalescence effects and hence hold-up 'peaks' and premature inversion at different sections of the column at a time. Further work (116) using the R.D.C has confirmed the cyclic phase inversion mode. In fact in about 5% of the runs performed in the present work unpredictable localised inversion occurred in one or two compartments in sections of the column which were not consecutive. This behaviour can only be explained in terms of minor fluctuations in rotor speed, due to variations in power supply, or volumetric pumping rates.

Unlike stirred cells discussed in Chapter 5.3, no ambivalence range was found to exist in counter-current contactors owing to the dynamic nature of the instability.

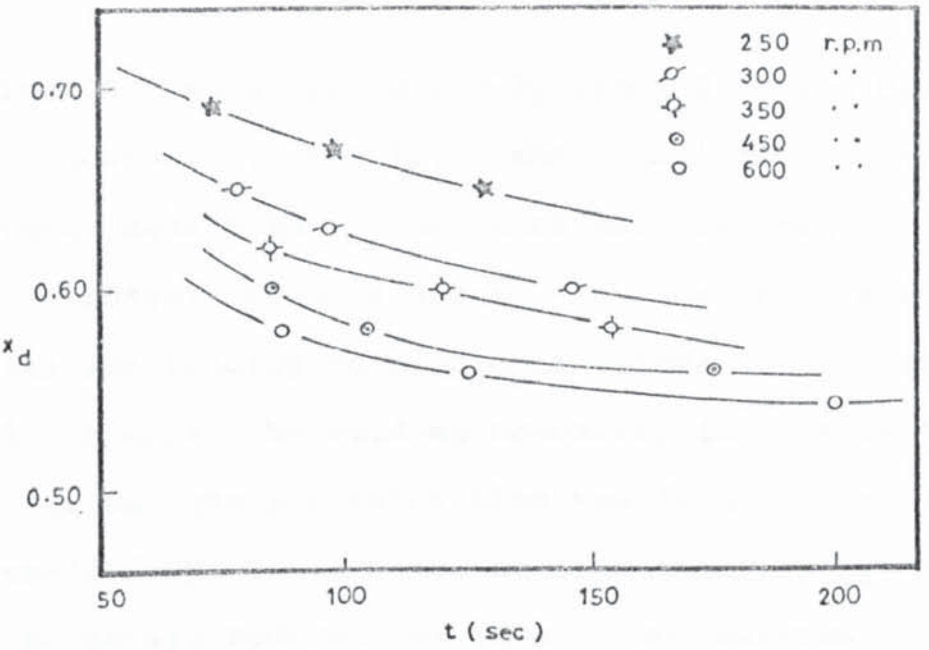


Fig. 10.7 Experimental variation of inversion time with hold-up

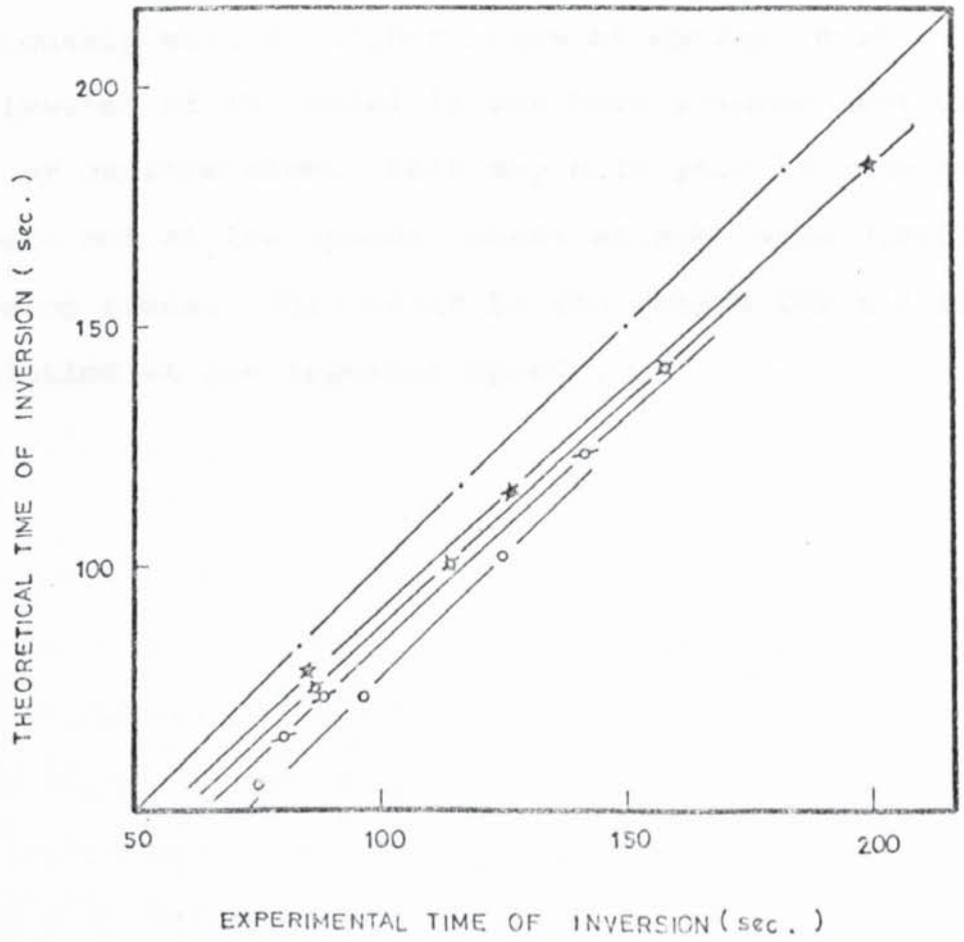


Fig. 10.8 Predicted vs experimental time of phase inversion
(System: butyl acetate-water)

The inversion time was only studied in the Oldshue Rushton contactor. Fig 10. 7 shows that the higher the dispersed phase hold-up, the less the time required to invert a phase. This is due to the increased frequency of collision leading to high coalescence rates. At high impeller speeds, the hold-up necessary for inversion decreases but the inversion time was found to increase. Very small drops are created at high impeller speeds which obviously reduces the rate of coalescence. A comparison between experimental and predicted 'inversion times' is shown in Fig. 10.8. It is seen that the deviation narrows as the energy input increases and at 600 rpm, it is approximately 10%. Thus the model predicts time reasonably well at higher rates of energy input. In the derivation of the model it has been assumed that drops are of uniform size. This may hold good at high impeller speeds but at low speeds, there exists a wide distribution of drop sizes. This could be the reason for the higher deviation at low impeller speeds.

10.3 MASS TRANSFER WITH CHEMICAL REACTION

10.3.1 MATHEMATICAL MODELS FOR INTERPHASE MASS TRANSFER WITH CHEMICAL REACTION IN AGITATED COLUMNS

Any mathematical description of interphase mass transfer and chemical reaction of the type discussed in Chapter 7, is further complicated if the process occurs in continuous countercurrent agitated columns. This is because,

1. Unpredictable end effects arise. The boundary conditions available to define these effects are largely arbitrary and a proper choice is rather difficult (155).

2. Diffusion mechanisms are ill-defined since it is not yet possible to isolate the contributions of molecular and eddy diffusion. Furthermore diffusion mechanisms vary along the column length due to varying eddy characteristics and concentration effects.

3. Although coalescence-redispersion and the related surface renewal effects were discussed in detail in Chapter 7, the uncertainty and complexity involved in their analysis make allowance in design impracticable.

4. The effect of backmixing has been discussed in Chapter 4. No detailed backmixing studies have been reported for cases involving mass transfer. Clearly since the departure of solute concentrations from their plug flow values is the manifestation of backmixing, this may be important. Additionally, mass transfer has a secondary effect on backmixing via increased, or hindered, interdroplet coalescence, and possibly coalescence on column internals, and

thus a change in hold-up. None of these factors can be accounted for analytically. However, backmixing can be controlled to some extent dependent upon the column design and the operating variables, e.g., agitator speed and the process variables e.g., if the continuous phase is pure.

In any case a detailed description of the hydrodynamics of motion within an agitated contactor is generally impracticable (3); it is also virtually impossible to take into account all the mutually interacting phenomena involved simultaneously in interphase mass transfer with chemical reaction. Therefore simplifying hypotheses are preferred in practice; these describe the process adequately for practical purposes rather than being mathematically precise.

The chemical reactions considered in the present work are of the form,

$$A_{org} + B_{aq} \rightarrow C_{org} + D_{aq} \qquad 10.26$$

The mathematical analysis of this diffusion-reaction scheme is based on the following assumptions,

(a) The organic phase mass transfer resistance is negligible. Most of the resistances lie in the aqueous phase where the reaction occurs.

(b) The molar flow is constant. This is justified provided the extent of reaction is not appreciable, large quantities of diluents are present or if there is no change in the number of moles on reaction.

(c) An isothermal steady state process.

(d) The axial mixing is limited to one phase only. This may apply when one of the phases is either a pure substance or the change in the concentration is small. The flow characteristics may be represented by the axial dispersion model. The radial dispersion is assumed to be negligible. However, any variation of concentration and velocity in the axial direction will be taken into account by the resulting Peclet number.

A steady state mass balance over a differential volume of the column then gives the following differential equations for the reaction schemes under consideration:-

(i) Very Slow Reaction

As discussed in Chapter 7, in the case of a very slow reaction, the rate of reaction is very much slower than the rate of transfer of one of the reacting components. Thus the reaction may be assumed to occur at the saturation concentration of the transferred component. The saturation concentration of a substance in ionic solutions may be related by, (224,225)

$$\log_{10}\left[\frac{y_\omega}{y^*}\right] = K_s\, I \qquad 10.27$$

where y_ω = solubility of the component in water at the temperature under consideration.

I = Ionic strength of the solution.

K_s = Sum of contribution of various ions.

y^* = Saturation concentration.

For the present investigation,

$$K_s = i_{Na^+} + i_{OH^-} + i_{acetate/formate}$$

The ionic contributions may be obtained from published values (226). The ionic concentration of NaOH is the molar concentration i.e. $I=x$. Substituting for I in equation 10.27,

$$y^* = y_\omega \exp[-2.303\ K_s x] \qquad 10.28$$

The differential balance gives,

$$S\ E_x \frac{d^2x}{dh^2} + L\frac{dx}{dh} = S\ x_d K_2\ x\ y^* \qquad 10.29$$

Substituting for y^* in equation 10.29,

$$S\ E_x\frac{d^2x}{dh^2} + L\frac{dx}{dh} = [y_\omega\ K_2\ x_d\ S]\ x\ \exp[-2.303\ K_s x]$$

Changing to dimensionless concentration X as a function of axial dimensionless co-ordinate H,

$$\frac{d^2X}{dH^2} + Pe\ \frac{dX}{dH} = Pe\left[\frac{K_2}{u}\ x_d\ y_\omega\ H_T\right]\ X\ \exp[-2.303\ K_s\ x_o X] \qquad 10.30$$

where $X = \dfrac{x}{x_o}$; $H = \dfrac{h}{H_T}$; $Pe = \dfrac{uH_T}{E_X}$

Equation 10.30 will hold provided, as discussed earlier,

$$K_L a >> K_2 x.$$

(ii) Slow Reaction

In the slow reaction scheme the reaction is too fast for the conditions for very slow reactions to be imposed. The bulk concentration of A is substantially smaller than y^* and is indeed virtually zero under certain conditions.

The transfer rate of A with negligible bulk concentration is given by equation 7.2.

$$Ra = K_L a y^* \qquad 7.2$$

This is subject to the usual conditions of no reaction in the film and negligible concentration of free A in the bulk of phase containing B.

That is,

$$K_L{}^2 >> K_2 D_A x$$

$$K_L a << K_2 x$$

A differential balance in dimensionless co-ordinates gives,

$$S\ E_x \frac{d^2x}{dh^2} + L \frac{dx}{dh} = K_L a S y^* \qquad 10.31$$

Substituting the value of y^* from equation 10.28, and reducing to dimensionless form, equation 10.31 becomes,

$$\frac{d^2X}{dH^2} + Pe \frac{dX}{dH} = Pe\left[\frac{y_\omega\ K_L\ a\ H_T}{x_o\ u}\right] \exp\left[-2.303\ K_s\ x_o X\right] \qquad 10.32$$

(iii) Fast Reaction

Danckwerts (3) has shown that for fast reactions in practical situations, the concentration of unreacted transferred component in the bulk may be neglected. Thus the rate of transfer may in general be represented by,

$$Ra = \phi\{K_L, y^*, x\}\ K_L\ a\ y^* \qquad 10.33$$

The rate models based on equation 10.33 have been discussed in Chapter 7. For the present investigation, the following transfer rate expressions will be considered for the axial dispersion differential model;

(a) Film model

The rate is given by,

$$R = y^* \sqrt{D_A K_2 x} \qquad 7.15$$

provided, $\sqrt{D_A K_2 x} > 3K_L$.

This is true provided the reaction rate is not great, or the physical mass transfer co-efficient is large, so that the concentration of the reactant is maintained virtually undepleted with its bulk concentration x^o right up to the surface. Under these circumstances the differential model is given by,

$$\frac{d^2X}{dH^2} + Pe\frac{dX}{dH} = Pe\ Q_1\sqrt{X}\ \exp[-2.303\ K_s\ x_o\ X] \qquad 10.34$$

where $Q_1 = \dfrac{y_\omega a\ \sqrt{K_2 D_A}\ H_T}{u\sqrt{x_o}}$

(b) Danckwerts Model

The rate is,

$$R = y^* \sqrt{D_A K_2\ x + K_L^2} \qquad 7.20$$

The condition to be satisfied is,

$$\frac{\sqrt{DK_2 x}}{K_L} \ll 1 + \frac{x}{zy^*}$$

This corresponds to a pseudo-first order reaction. The corresponding differential equation becomes,

$$\frac{d^2X}{dH^2} + Pe\ \frac{dX}{dH} = Pe\ Q_2 \sqrt{a_2 X + K_L^2}\ \exp\ (-2.303\ K_s x_o X) \qquad 10.35$$

where $Q_2 = \frac{y_\omega\ a\ H_T}{u\ x_o}$; $a_2 = D_A K_2 x_o$.

(c) Surface Renewal Model

In this case, the rate is given by equation 7.26

$$R = K_L[\sqrt{m}\ y^* + \frac{1}{\sqrt{m}} \frac{x}{z}] \qquad 7.26$$

where $m = D_A/D_B$

and the differential equation becomes,

$$\frac{d^2X}{dH^2} + Pe\ \frac{dX}{dH} = Pe\ Q_3[a_3 X + a_4\ \exp(-2.303\ K_s x_o X)] \qquad 10.36$$

where $Q_3 = \frac{K_L\ a\ H_T}{x_o\ u}$; $a_3 = x_o/\sqrt{m}$ and $a_4 = y_\omega \sqrt{m}$.

Solution of Equations

All the models are non-linear in character and where appropriate were solved by Runge-Kutta 4th order method along with the Golden Section Search optimisation technique (227). In brief the solution involved iterative numerical step by step integration along the column until the top boundary condition was satisfied. The calculation sequence started at the bottom with 'guess' values of dimensionless exit concentration in the range 0.1-0.99.

The dispersion coefficients for calculation of Peclet numbers were obtained from equations 4.20 and 4.38.

The boundary conditions allowing for axial mixing which were employed in the solution of the equations were those given by Wehner and Wilhelm (228) and discussed in detail by Jeffreys (229). These are,

$$\frac{dX}{dH} = 0; \quad H = 0$$

$$X(1-) + \frac{1}{Pe}\frac{dX}{dH}(1-) = 1; \quad H = 1.$$

The detailed computer programme is given in Appendix 6.

General Case of Extraction with Fast Second Order Reaction with Axial Dispersion in both Phases

Unlike previous reaction schemes where one of the reactants constituted a pure phase, analysis can now be extended to the general case where both phases are impure. Resistance to mass transfer however is assumed, as before, to be limited solely to the one phase in which the reaction occurs.

As discussed in Chapter 7, second order reactions are in general not amenable to analytical solution. However, under certain circumstances, they may be considered as pseudo-first order reactions. Therefore they may be described by the equation 7.20,

$$R = y^* \sqrt{D_A K_2 x + K_L{}^2} \qquad 7.20$$

The concentration distribution of each component (A and B) may now be represented by the equations,

$$\frac{d^2X}{dH^2} + Pe_x \frac{dX}{dH} = Pe_x M_1 \; Y \sqrt{M_2 X + M_3} \qquad 10.37$$

and

$$\frac{d^2Y}{dH^2} - Pe_y \frac{dY}{dH} = Pe_y M_4 Y \sqrt{M_2 X + M_3} \qquad 10.38$$

where

$$M_1 = \frac{a\ H_T\ y_o^*}{u\ x_o} \quad ; \quad M_2 = D_A\ K_2\ x_o ; \quad M_3 = KL^2$$

and $M_4 = \dfrac{a\ H_T\ y_o{}^*}{v\ y_o}$

The boundary conditions are,

$$\frac{dX}{dH} = 0; \quad H = 0 \qquad 10.39$$

$$X(1-) + \frac{1}{Pe_x} \frac{dX}{dH} (1-) = 1; \qquad H = 1 \qquad 10.40$$

$$\frac{dY}{dH} = 0; \quad H = 1 \qquad 10.41$$

$$Y(0+) - \frac{1}{Pe_y} \frac{dY}{dH}(0+) = 1; \qquad H = 0 \qquad 10.42$$

Equations 10.37 and 10.38 can be solved by the computational approach used earlier and given in Appendix 6 , provided a second 'Test' condition given by equation 10.42 is incorporated together with an additional function to account for Y.

Although the solution of equations 10.37 and 10.38 is complex, simpler practical cases are amenable to easy solution. These are,

(a) When $Pe_y \rightarrow \infty$, equation 10.38 reduces to

$$\frac{dY}{dH} = -M_4 \, Y\sqrt{M_2X + M_3} \qquad 10.43$$

combination of equation 10.37 and 10.43 leads to,

$$a_1 \frac{dY}{dH} = -\frac{1}{Pe_x}\frac{d^2X}{dH^2} - \frac{dX}{dH} \qquad \text{where } a_1 = \frac{M_1}{M_4}$$

$$\text{or,} \quad a_1 \frac{d}{dH}(Y) = -\frac{1}{Pe_x}\frac{d}{dH}\left(\frac{dX}{dH}\right) - \frac{d}{dH}(X) \qquad 10.44$$

Integrating,

$$a_1Y = -\frac{1}{Pe_x}\frac{dX}{dH} - X + C_1 \qquad 10.45$$

where C_1 is the integration constant.

Equation 10.42 reduces to,

$$Y(0+) = 1; \quad H = 0 \qquad 10.46$$

Combining equations 10.39, 10.45 and 10.46,

$$y = 1 + \frac{X(0)-X}{a_1} - \frac{1}{a_1Pe_x}\frac{dX}{dH} \qquad 10.47$$

Substituting y in equation 10.37,

$$\frac{d^2X}{dH^2} + Pe_x \frac{dX}{dH} = PeM_1\sqrt{M_2X+M_3}\left[1+ \frac{X(0)-X}{a_1} - \frac{1}{a_1Pe_x}\frac{dX}{dH}\right] \qquad 10.48$$

Thus, equations 10.37 and 10.38 have been reduced to a single equation in terms of the dimensionless concentration X only. A similar form of equation would be obtained for the case $Pe_x \to \infty$. Equation 10.48 may be solved by the same computational procedure as given in Appendix 6. The calculation sequence would start with an initial 'guess' value of X(0) and terminate when both the "Test" condition and the condition at the bottom of the column, given by $|X(0) - X| \to 0$, are satisfied simultaneously.

(b) For the case of a very slow reaction system with low solubility of the transferring component, the change in the reactant concentration of the reactive phase may not be appreciable. Equation 10.38 will then reduce to,

$$\frac{d^2Y}{dH^2} - Pe_Y \frac{dY}{dH} = Pe_Y\, M_5\, Y \qquad 10.49$$

This is again subject to the boundary conditions given by equation 10.41 and 10.42 .

Although the above reaction schemes were not considered in the present investigation, the analysis made, and the numerical technique developed earlier, may prove useful in practical cases.

10.3.2 DISCUSSION OF RESULTS

10.3.2.1 Slow Reaction System: Butyl Acetate - Aqueous Sodium Hydroxide.

Rotating Disc Contactor

The area-based mass transfer coefficient K_La increased with increasing energy input and dispersed phase flow rate, as shown in Fig. 10.9. However, K_La values did not approach an asymptotic maximum value at high speeds, as is usual , owing to the limitation imposed on the operating range by phase separation in the end settling zones. That is, at higher agitation rates difficulties were encountered in settling and coalescence of the very small dispersed phase droplets and with droplets being swept out via the continuous phase outlet. The K_L values obtained, are given in Appendix 7(a) and were in the range of $3.73 \times 10^{-5} - 6.35 \times 10^{-5}$ m/s. This was at flow rates of $1.0 \times 10^{-5} - 4.0 \times 10^{-5}$ m^3/s and agitator speeds between 650-1000 rpm, and may be compared with a value of 4.0×10^{-5} m/s at a flow rate of 1.0×10^{-5} m^3/s in a spray tower (181). Allowing for minor differences in physical properties of the system, due to differences in specification, this confirms that at low rotor speeds when droplet interaction is small, the R.D.C behaves in an analogous fashion to a discrete drop contactor. The values of K_L increased with increase in both energy input and dispersed phase flow rate. The effect of

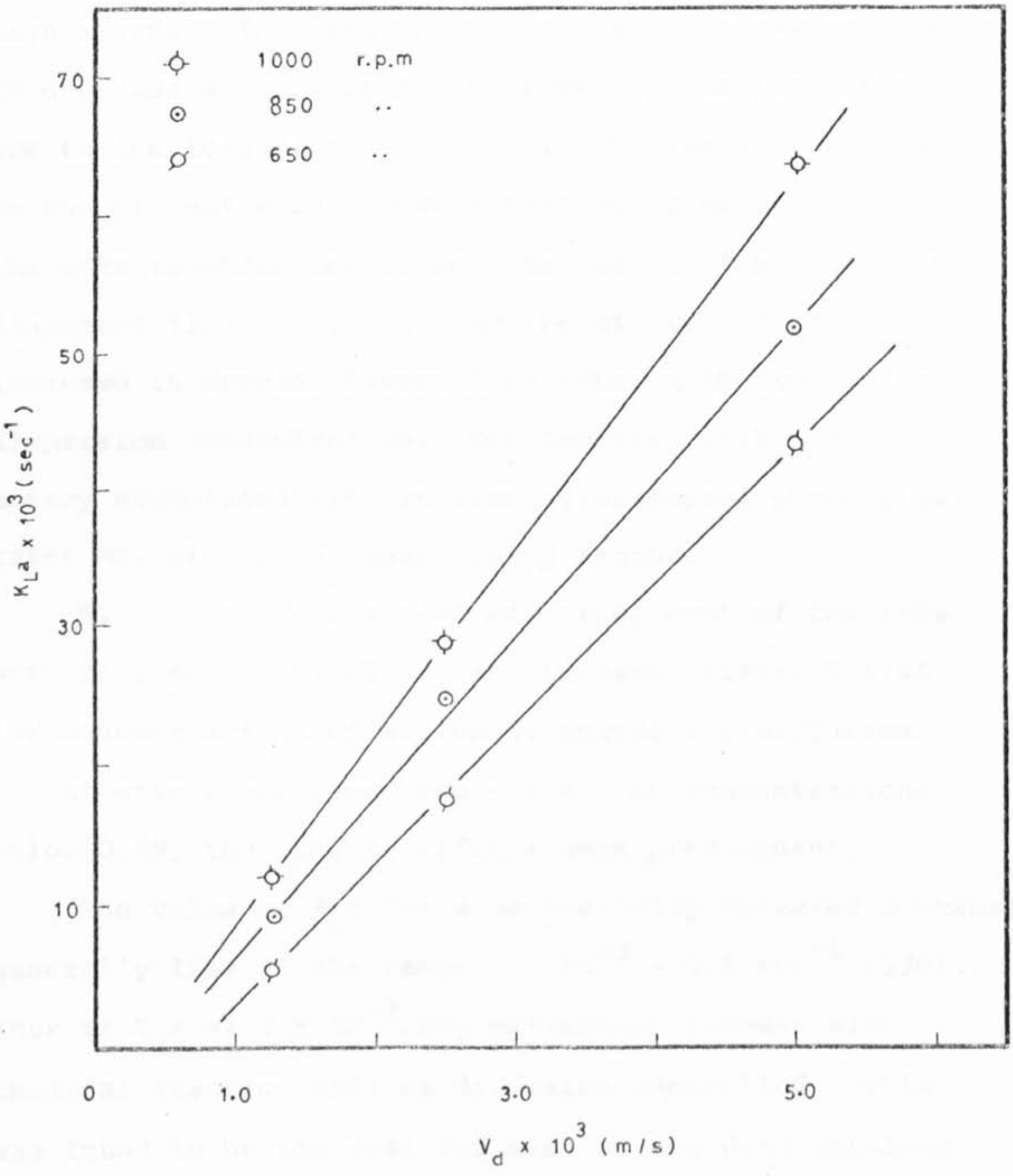


Fig. 10.9 Area-based mass transfer coefficient- vs dispersed phase flow rate.
|System: butyl acetate-water
Contactor: R.D.C|

increased agitation rate, apart from creating increased interfacial area, lies in the diminution of mass transfer resistance associated with the diffusion film outside a droplet and also in the increase of circulation inside the drop, although the latter decreases at very high speeds. The mass transfer coefficient was expected to decrease with increased dispersed phase flow rate due to the long diffusion paths. This was not obtained in the present work however; instead of decreasing the mass transfer coefficient increased with increasing dispersed flow rate. This may be attributed to an increase in droplet interaction rates with increasing dispersion concentration. The increase in kinetic energy associated with increasing dispersed phase flow rates may also be a contributing factor.

With chemical reaction occurring most of the runs were diffusion controlled, as discussed later, but at low concentrations of sodium hydroxide the diffusion and kinetic rates were comparable. At concentrations below 0.5N, the kinetic effects were predominant.

The value of K_La for a mechanically agitated contactor generally lies in the range $3 \times 10^{-3} - 0.4 \text{ sec}^{-1}$ (230). Thus if $K_2x \gg 3 \times 10^{-3}$, any extraction process with chemical reaction will be diffusion controlled. This was found to be the case for most of the data obtained in the present investigation.

Fig 10.10 shows the variation of the rate of extraction with K_La at a particular concentration of sodium hydroxide,

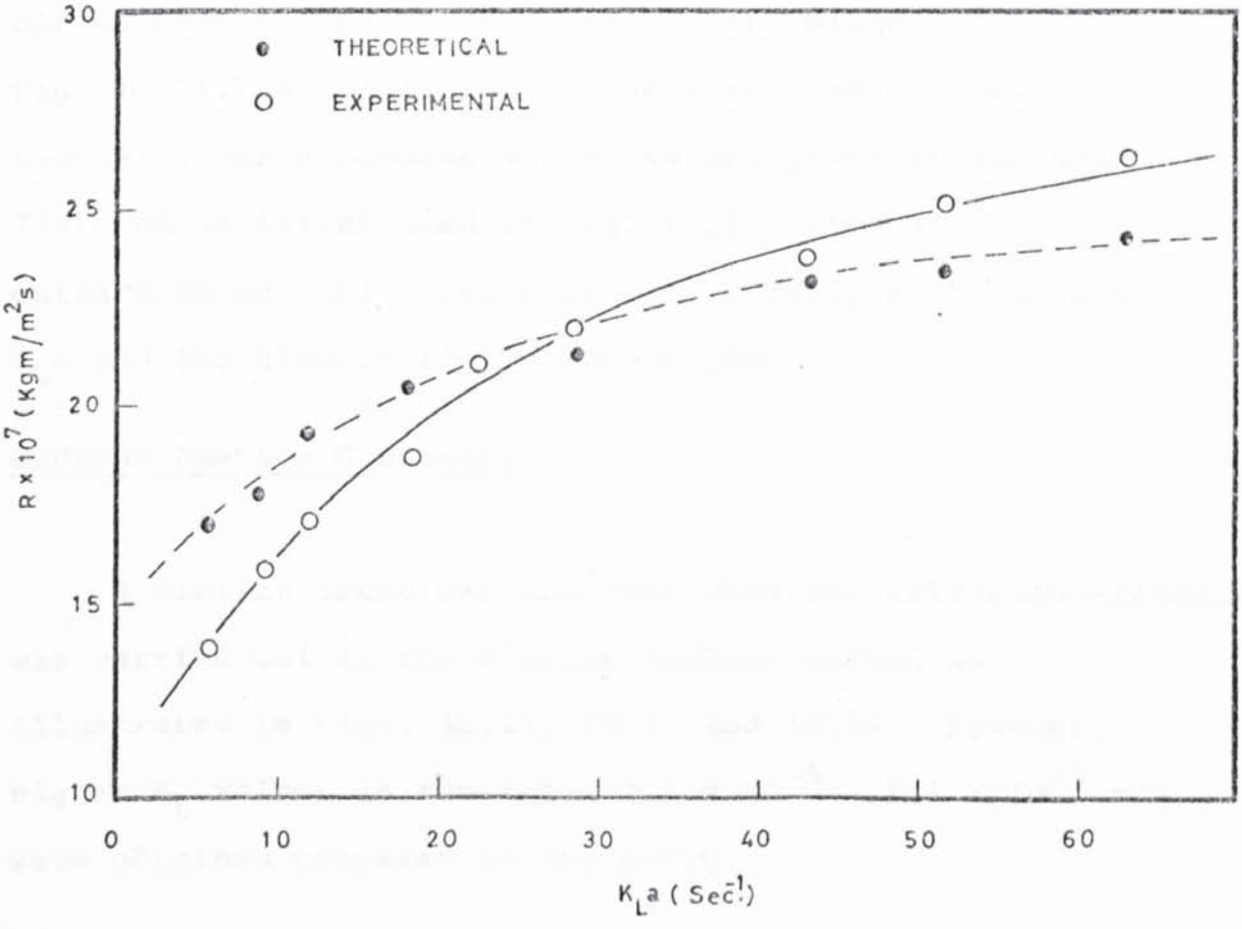


Fig. 10.10 Rate of extraction vs area-based mass transfer coefficient.

|System: butyl acetate - aq. NaOH

Contactor: R.D.C|

approximately 0.75N. The rate of extraction initially increased sharply with increasing K_La but the rate of increase then gradually waned corresponding to higher K_La values in the range 40 - 65 x 10^{-5} m/s. This suggests that at this stage a transition regime is approaching i.e $K_2x \simeq K_La$. In subsequent experiments in this region with sodium hydroxide concentration decreased, transition occurred to the very slow reaction diffusional regime as indicated by the plateau in Fig. 10.11. At still lower concentrations of sodium hydroxide corresponding to the values given in Appendix 7(a) and as illustrated in Fig. 10.11 rates of extraction per unit area decreased sharply with increased K_La and the kinetic regime was reached.

Oldshue Rushton Contactor

A similar trend was observed when the extraction-reaction was carried out in the Oldshue Rushton column as illustrated in Figs. 10.12, 10.13 and 10.14. However, higher K_L values in the range 3.2 x 10^{-5} - 8.1 x 10^{-5} m/s were obtained compared to the R.D.C.

General

The rates of extraction calculated from equations 7.2 and 10.27 using experimental data are represented by the dotted lines in Figs. 10.10, 10.11, 10.13 and 10.14. For the R.D.C rates of extraction were 12% higher

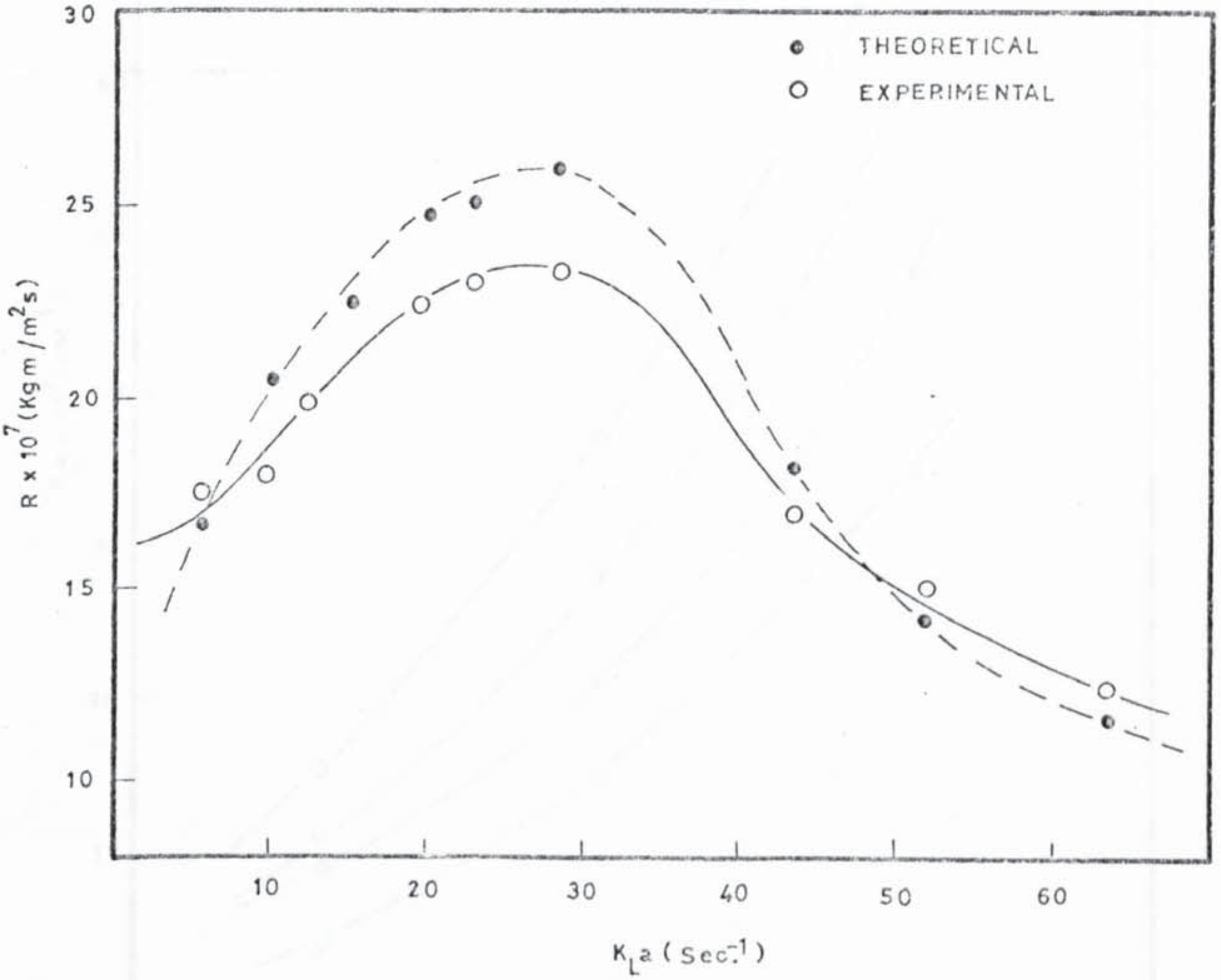


Fig. 10.11 Rate of extraction vs area-based mass transfer coefficients.

|System: butyl acetate - aqueous sodium hydroxide
Contactor: R. D. C|

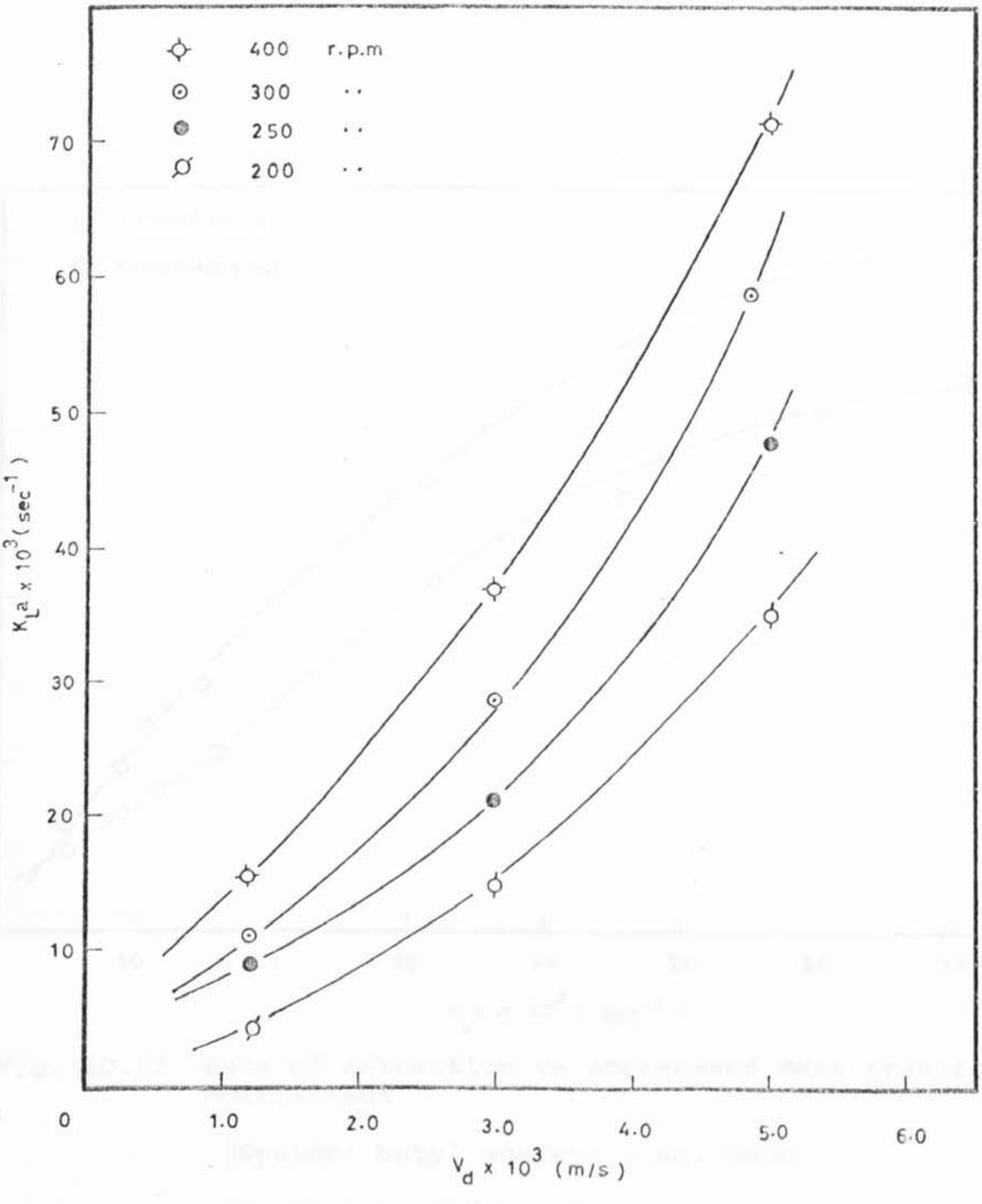


Fig. 10.12 Area-based mass transfer coefficient vs dispersed phase flow rate

|System: butyl acetate-water
Contactor: Oldshue Rushton|

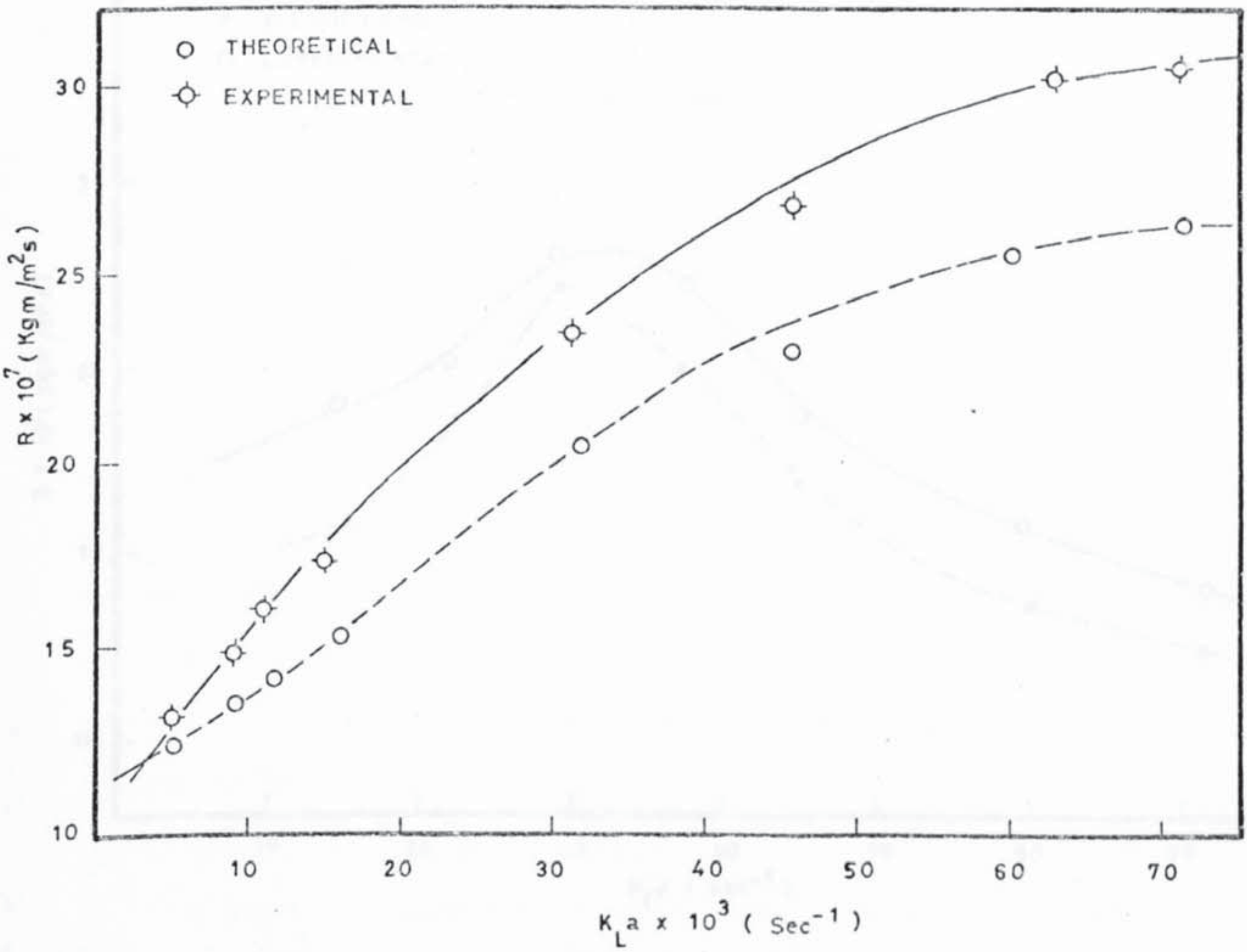


Fig. 10.13 Rate of extraction vs area-based mass transfer coefficient

|System: butyl acetate - aq. NaOH

Contactor: Oldshue Rushton|

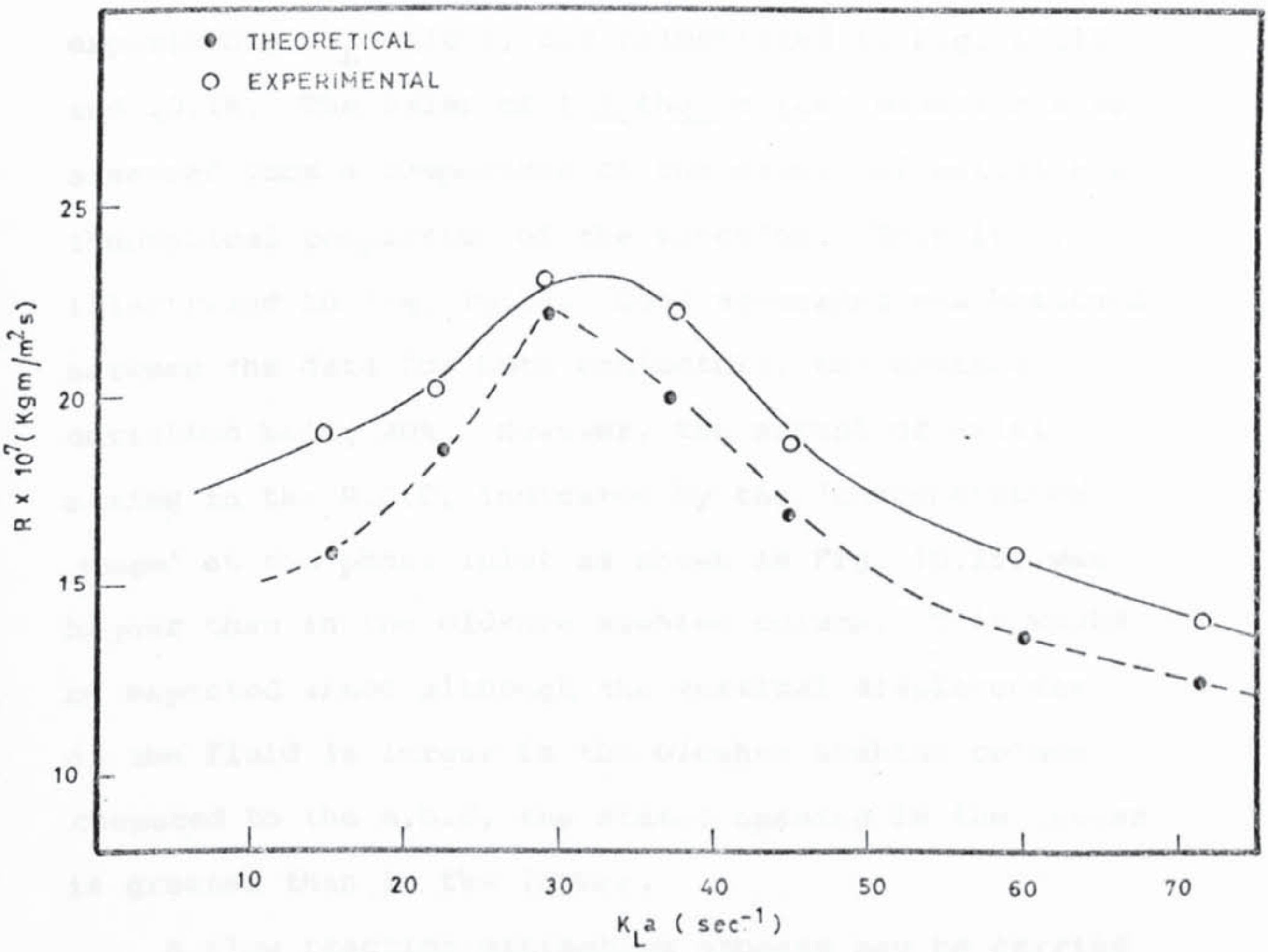


Fig. 10.14 Rate of extraction vs area-based mass transfer coefficient.

|System: butyl acetate - aq. NaOH

Contactor: Oldshue Rushton|

than experimental values whereas the contrary was observed for K_La values greater tahn 43×10^{-3} cm/s. An average positive deviation of 16% was obtained for the case of Oldshue Rushton column.

Concentration profiles along the column length, computed from model equations 10.4 and 10.6 using experimental K_L values, are illustrated in Fig. 10.15 and 10.16. The value of the theoretical models can be assessed from a comparison of the extent of actual and theoretical completion of the reaction. This is illustrated in Fig. 10.17. Good agreement was obtained between the data for both contactors, the maximum deviation being 20%. However, the extent of axial mixing in the R.D.C, indicated by the 'concentration jumps' at the phase inlet as shown in Fig. 10.15, was higher than in the Oldshue Rushton column. This would be expected since although the vertical displacement of the fluid is larger in the Oldshue Rushton column compared to the R.D.C, the stator opening in the latter is greater than in the former.

A slow reaction-extraction process may be carried out in a kinetic or a diffusional regime depending upon the process variables and contactor-type. A direct comparison between the R.D.C and the Oldshue Rushton column, for example on the commonly accepted basis of equal rates of energy input is not meaningful since the flow patterns and hydrodynamics are different.

In conclusion therefore for any extraction with a

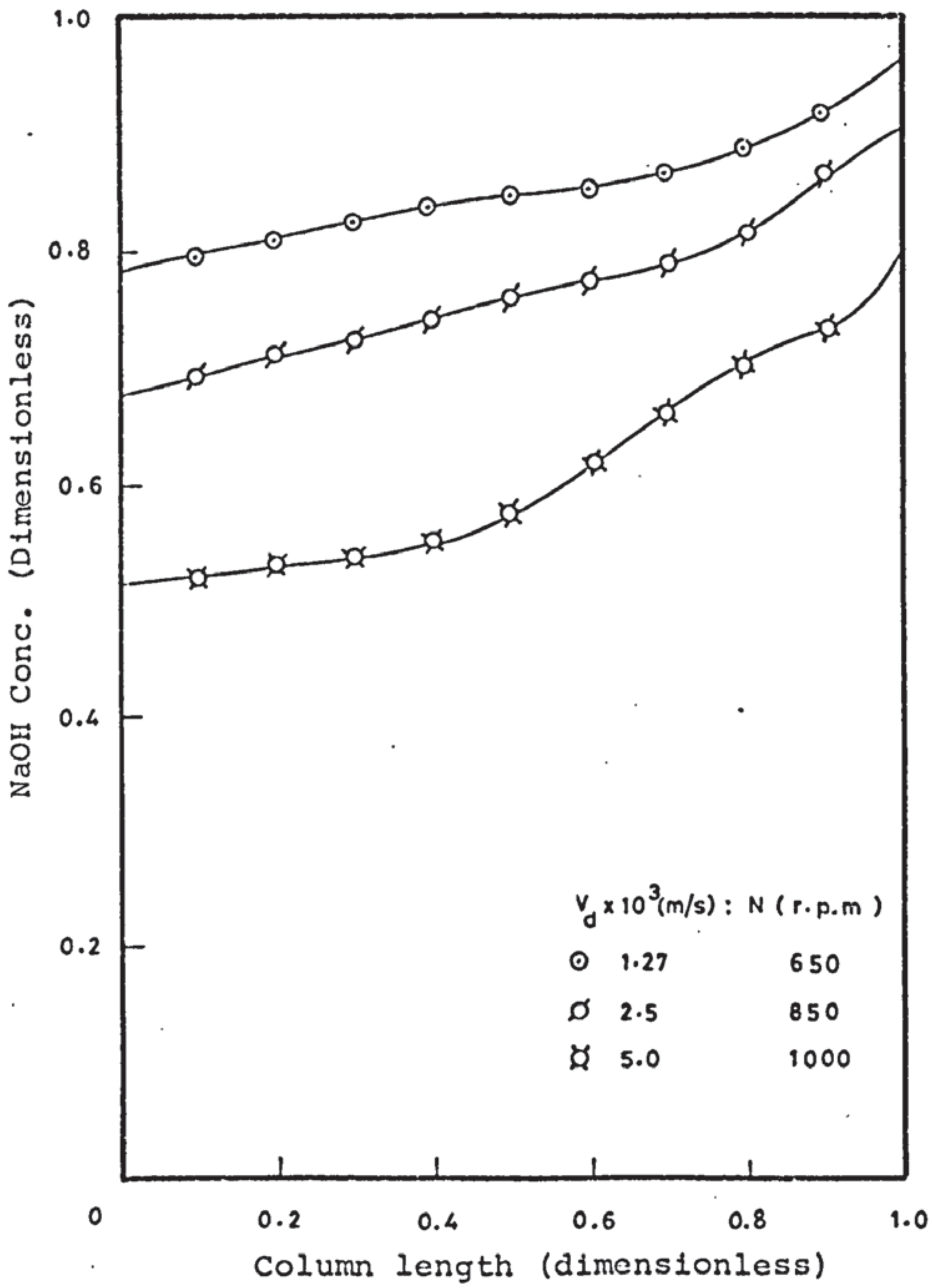


Fig. 10.15 Concentration profiles in the R.D.C |System: butyl acetate - aq. NaOH|

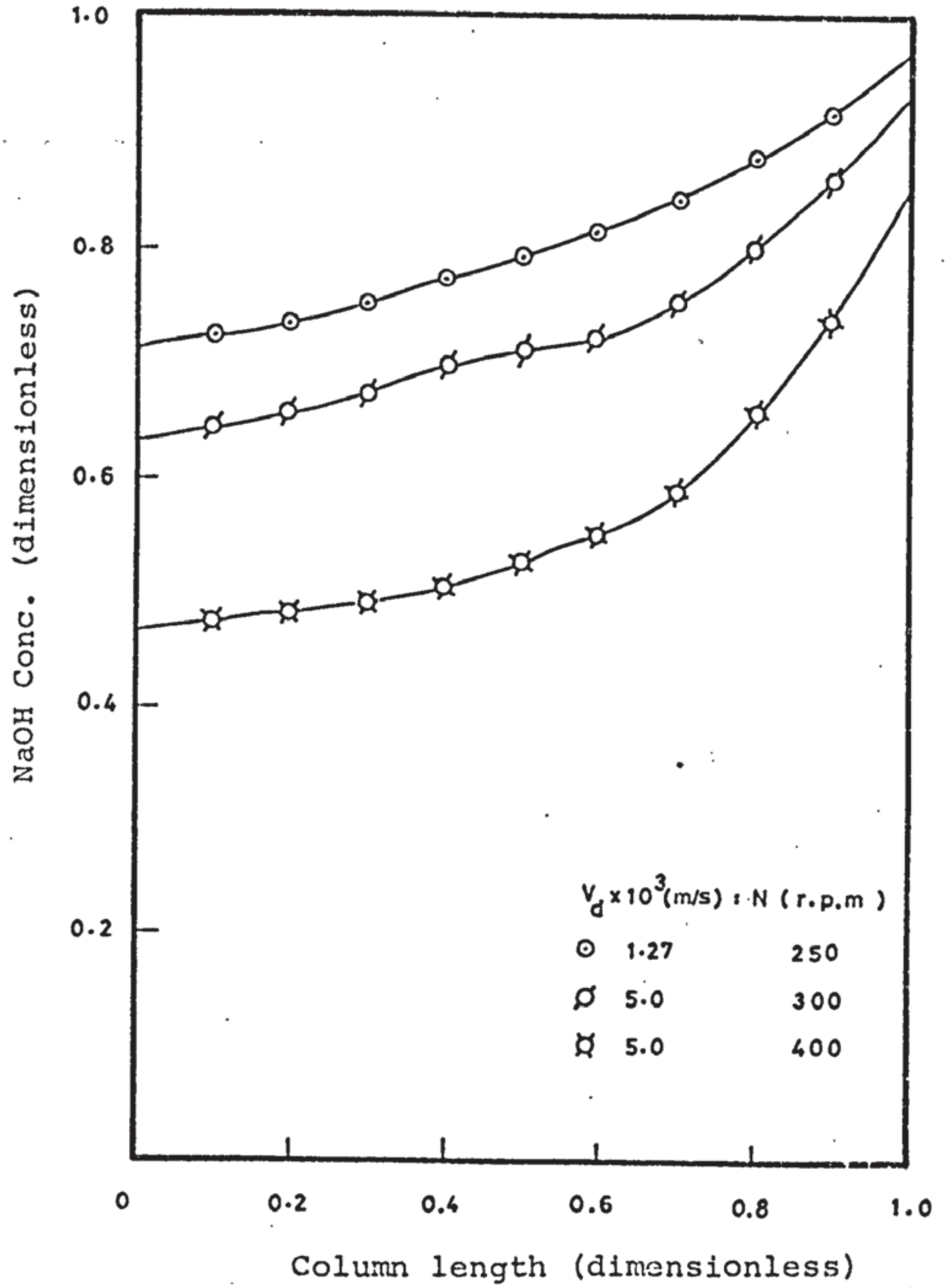


Fig. 10.16 Concentration profiles in the Oldshue Rushton column.

|System: butyl acetate - aq. NaOH|

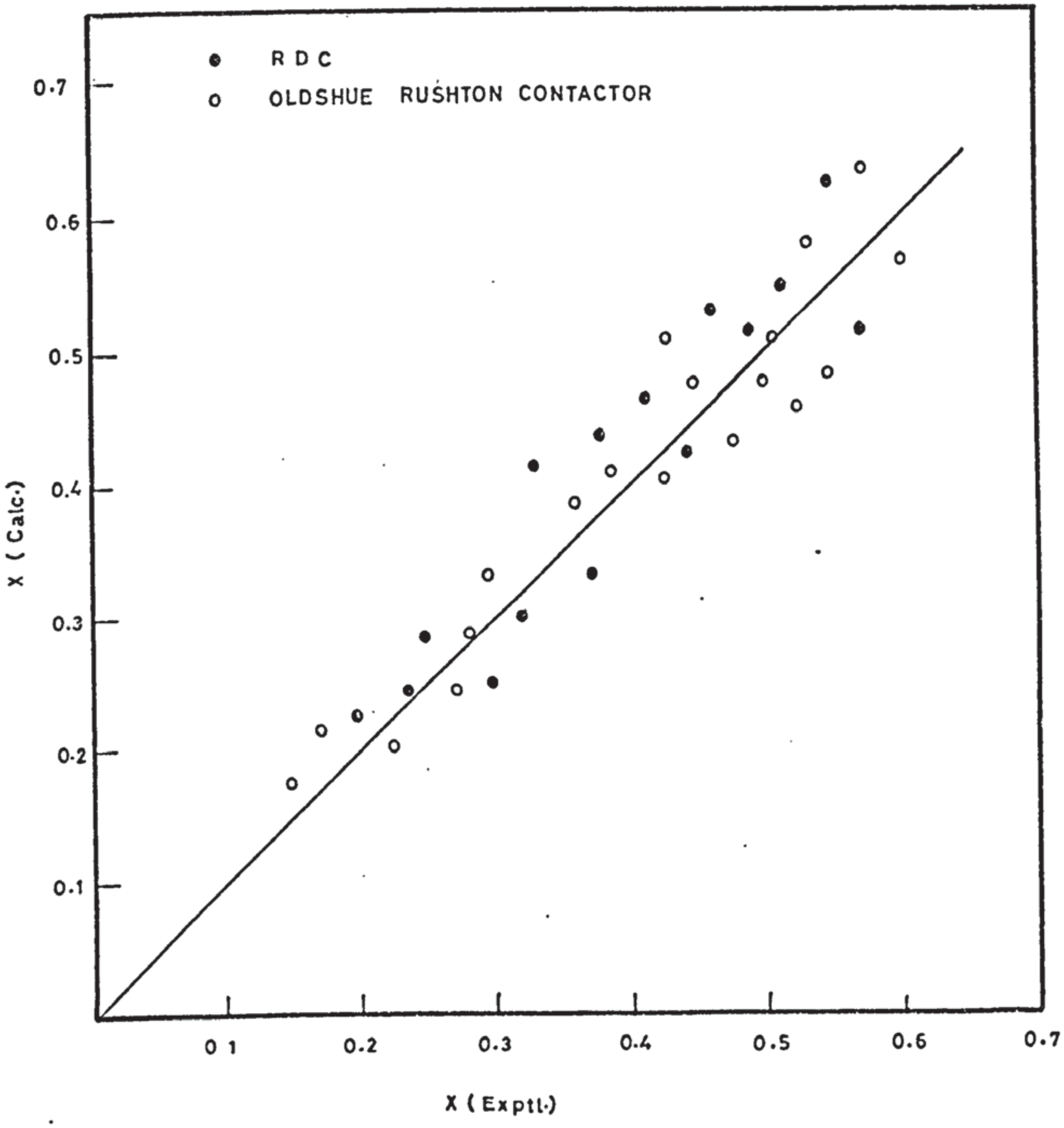


Fig. 10.17 Theoretical vs experimental outlet concentration of sodium hydroxide.

|System: butyl acetate-aqueous NaOH|

very slow reaction, there is nothing to choose between the R.D.C and the Oldshue Rushton contactor,. However, for the case of a moderately slow reaction, which is controlled by the process of diffusion, high energy contactors like the Oldshue Rushton would be preferable so that kinetic control becomes predominant. There is a limit however to the K_La values that can be generated in a practical contactor and thus diffusional resistances may not be altogether eliminated. Therefore it is difficult to identify a process as entirely diffusion or kinetically controlled. It appears however that since higher levels of agitation are more easily provided in batch or continuous stirred tank reactors and the condition of physical equilibrium is more easily attained in this type of equipment, it may be preferable for the operation of extraction systems involving slow reaction.

10.3.2.2 Fast Reaction System: Butyl Formate - Aqueous Sodium Hydroxide

Contactor: Oldshue Rushton Column

The data given in Appendix 7(b) suggests that within the concentration range 0.82 - 0.35 N of sodium hydroxide and the experimental conditions, i.e. flow rates and energy input,

$$\sqrt{D_A K_2 x} \;/\; K_L << 1 + \frac{x}{zy^*}$$

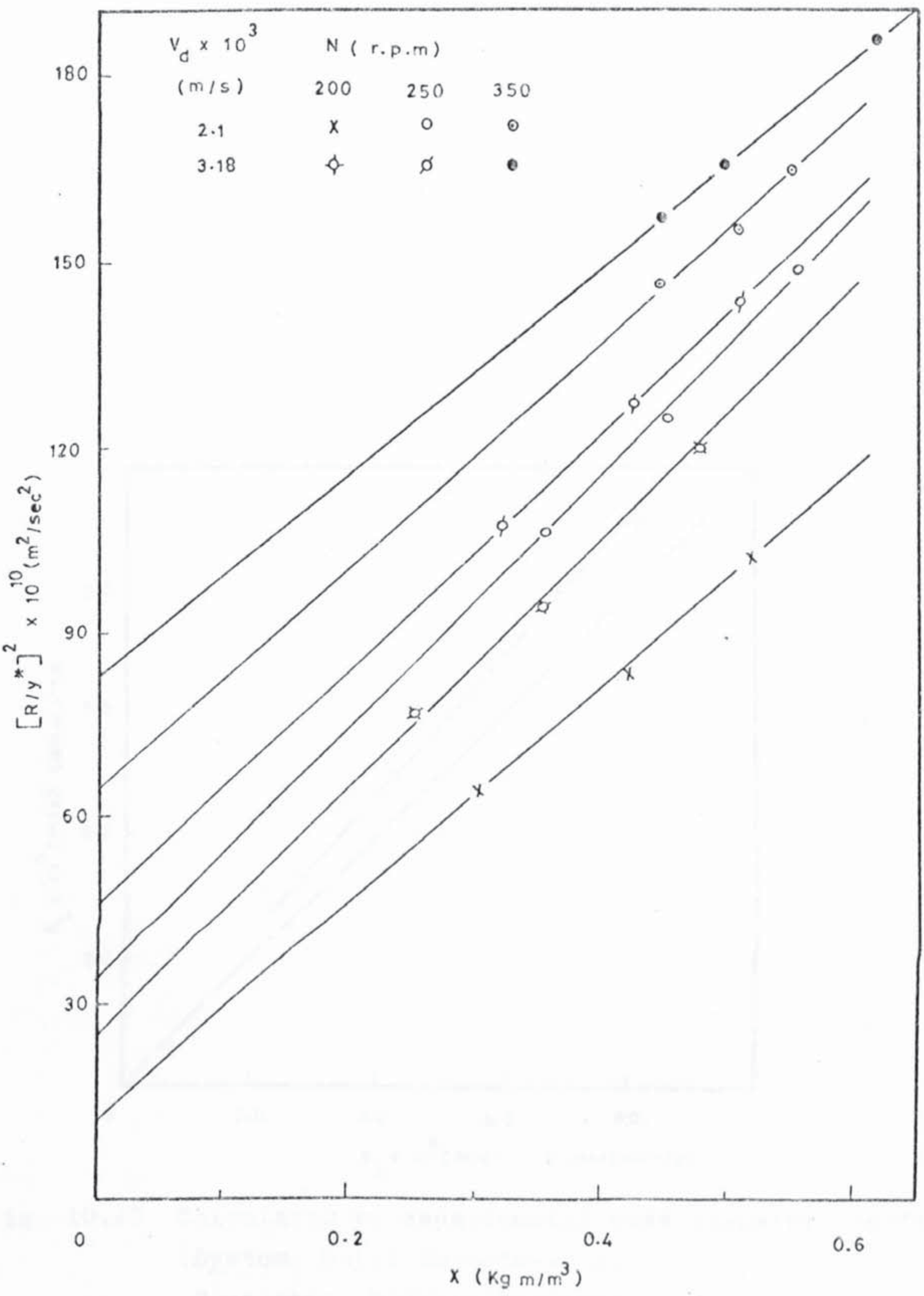


Fig. 10.18 Danckwerts' plot of $|R/y^*|^2$ vs x.
|System: butyl formate- aq. NaOH|

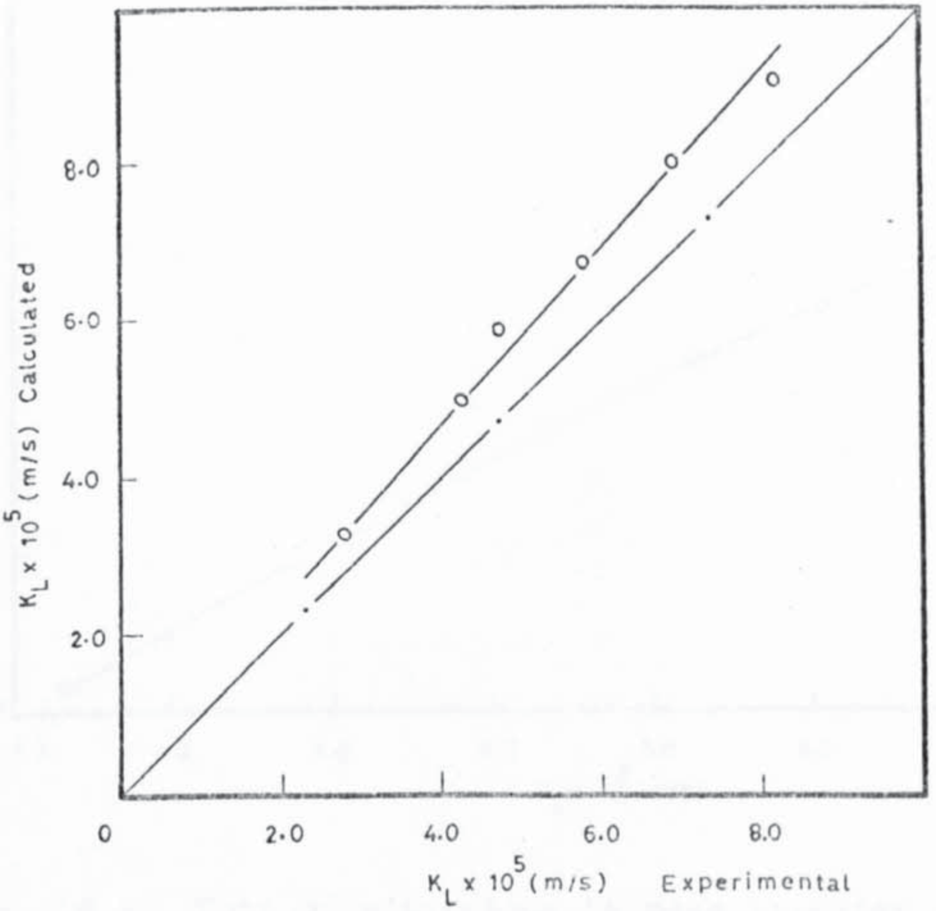


Fig. 10.19 Calculated vs experimental mass transfer coefficient.
|System: butyl formate-water
Contactor: Oldshue Rushton|

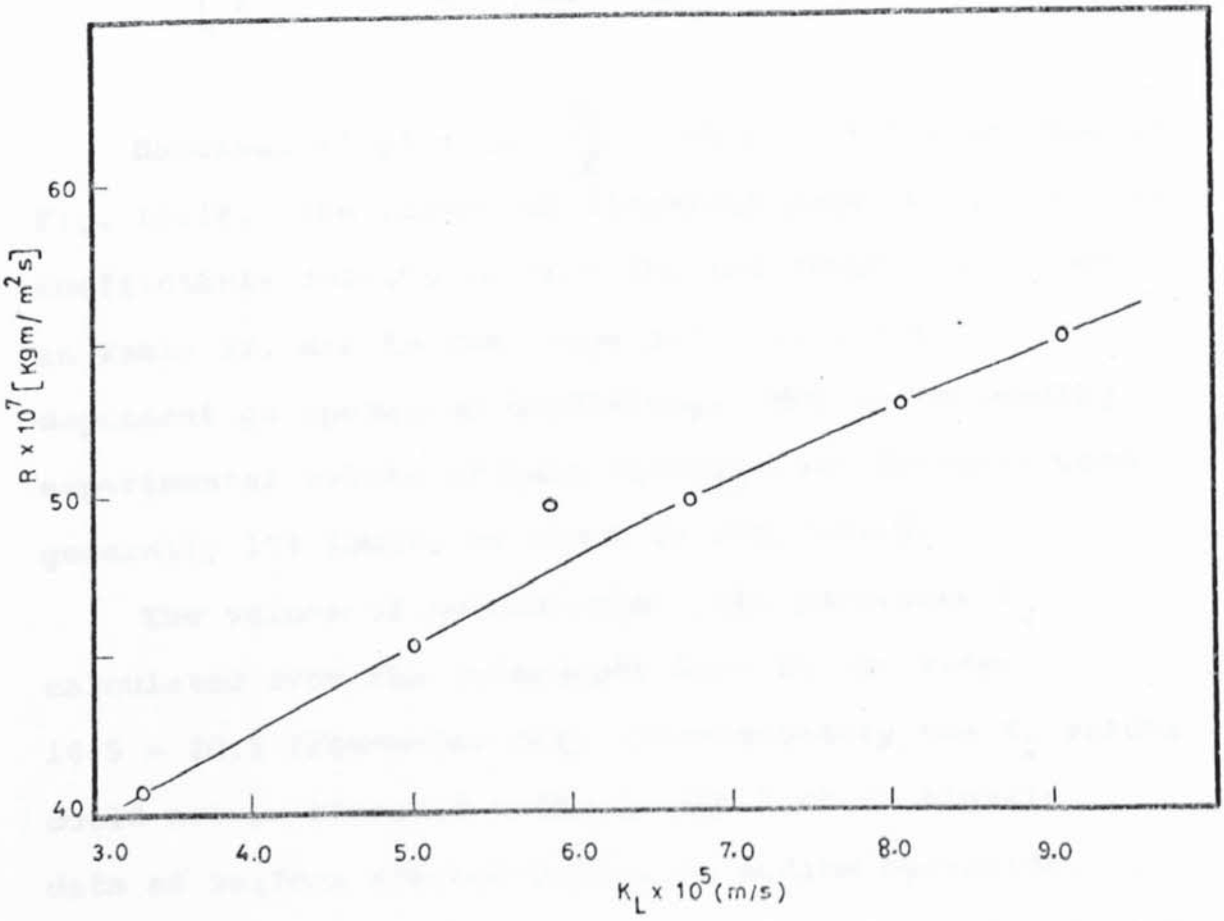


Fig. 10.20 Rate of extraction vs mass transfer coefficient |System: butyl formate-aqueous sodium hydroxide Contactor: Oldshue Rushton|

According to Danckwert's surface renewal theories, the reaction may therefore be regarded as of pseudo-first order. The corresponding rate of extraction will be given by the equation 7.20,

$$R = y^* \sqrt{D_A K_2 x + K_L^2} \qquad 7.20$$

$$\text{i.e.} \qquad \left[\frac{R}{y^*}\right]^2 = K_L^2 + D_A K_2 x \qquad 10.50$$

Danckwerts' plot of $\left[\frac{R}{y^*}\right]^2$ vs x is illustrated in Fig. 10.18. The values of dispersed phase mass transfer coefficients calculated from the intercepts, as given in Table II, are in the range 3.3 - 9.11 x 10^{-5} m/s dependent on operating conditions. The corresponding experimental values of mass transfer coefficients were generally 15% lower, as shown in Fig. 10.19.

The values of second-order rate constants K_2 calculated from the intercepts were in the range 16.5 - 20.5 ℓ/gm-moles sec. Unfortunately the K_2 values could not be compared owing to the lack of kinetic data at various concentrations of sodium hydroxide. However, the only value of the kinetic constant reported is 22.0 ℓ/gm-mole sec at 20°C and at practically zero ionic concentration (215).

Fig. 10.20 shows the variation of the rate of extraction per unit area with K_L. This indicates that the rate of extraction per unit area increases with increasing K_L, that is, within the range studied, the

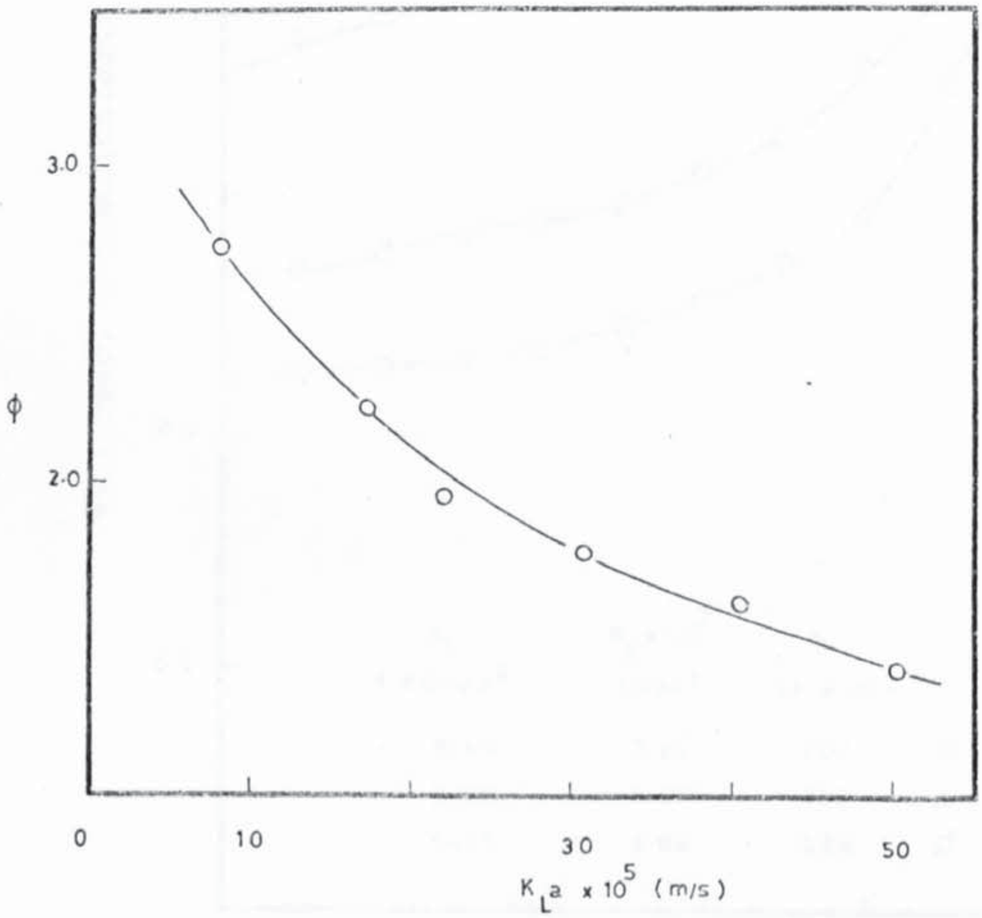


Fig. 10.21 Enhancement factor vs Mass Transfer Coefficient.

|System: butyl formate-aqueous sodium hydroxide
Contactor: Oldshue Rushton|

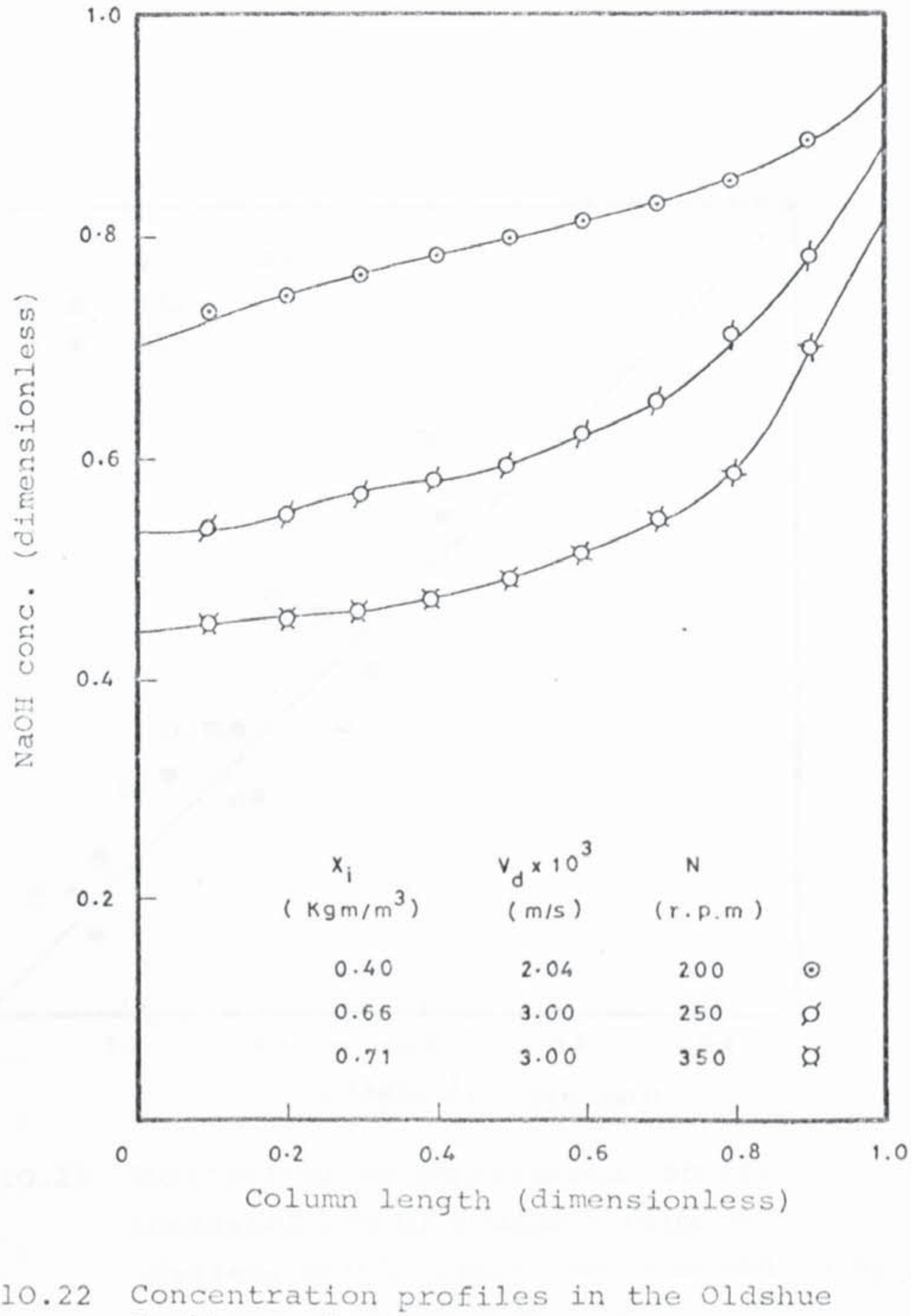


Fig. 10.22 Concentration profiles in the Oldshue Rushton column

|System: butyl formate - aqueous sodium hydroxide|

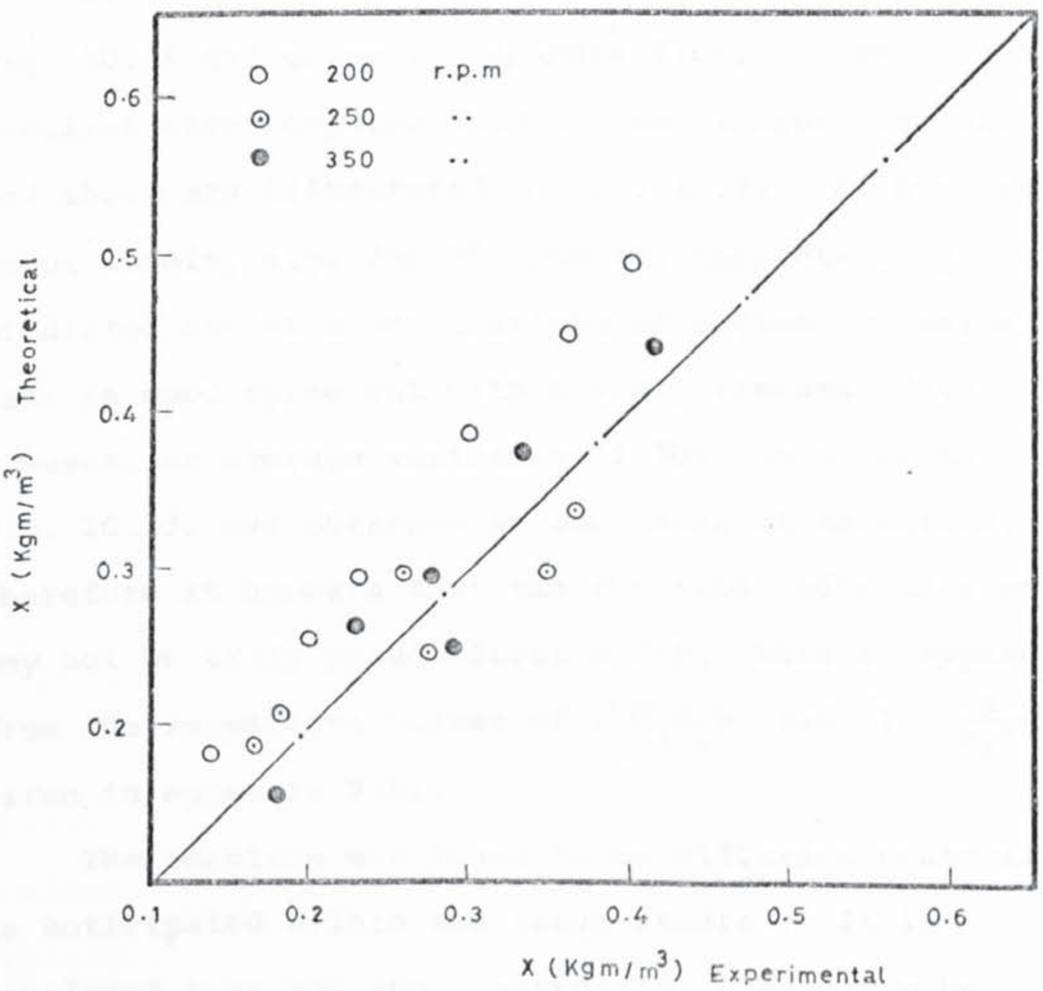


Fig. 10.23 Theoretical vs experimental outlet concentration of sodium hydroxide
|System: butyl formate-aqueous sodium hydroxide
Contactor: Oldshue Rushton|

process was controlled by diffusion. Fig. 10.21 however suggests that although the condition could not be attained in the equipment, at still higher K_La values the enhancement factor would tend to unity. Both kinetic and diffusion processes would then be comparable.

With K_L values obtained from the intercepts in Fig. 10.18 and given in Appendix 7(b), concentration profiles were computed from the model equation 10.9 and these are illustrated in Fig. 10.22. At high energy input levels, e.g. 250-350 rpm the theoretically predicted outlet concentrations of sodium hydroxide were in good agreement with the experimental data. However, an average variation of 30%, as shown in Fig. 10.23, was obtained at low rates of agitation. Therefore it appears that the reaction under this condition may not be truly pseudo-first order. This is apparent from the respective values of $\sqrt{D_A K_2 x}$ and $1 + \frac{x}{zy^*}$ given in Appendix 7(b).

The reaction was found to be diffusion-controlled as anticipated within the range studied. It is concluded that the above extraction scheme may be applicable in determining the kinetic data in two-phase reaction systems. Further, if the kinetic data is known, the interfacial area in agitated systems may be obtained. Similar approaches for interfacial area determination have been suggested by Danckwerts (3) in gas-liquid systems. Although it may be applicable in gas-liquid systems, where the interfacial tension does not vary appreciably between systems, it cannot be applied generally to liquid-liquid extraction since so many variables e.g. interfacial tension, coalescence-redispersion rates, directions of solute transfer, type of contacting devices are involved. The method will however apply for specific systems.

10.3.2.3 Very Fast Reaction System: Methyl Dichloroacetate - Aqueous Sodium Hydroxide

Contactor: R.D.C

The data given in Appendix 7(c) reveals that none of the conditions given by equations 7.16, 7.18 and 7.21 for a fast reaction were satisfied. Thus the reaction is a general second order reaction of finite speed and the reactant is probably depleted near the interface (3). Whilst there is no precise analytical solution available, a numerical approach to the problem may be attempted based on the analysis of Brian et. al. (231) for gas absorption processes. This involves evaluation of an approximate enhancement factor from equation 7.10 followed by correction for deviations from the Penetration theory. Unfortunately this correction could not be applied in the present work since Brian's correction factors are specific only to a few values of ϕ_i and cannot strictly be extrapolated. In any case, Van Krevelen and Hoftizer (157) showed that their data fitted within 10% of values predicted from equation 7.10. In fact, the deviation obtained by Brian et. al. (231) did not exceed 10% for $D_A/D_B>1$ and 12% for $D_B/D_A>0.1$. In the present investigation, $D_B/D_A>1$ and hence for all practical purposes, equation 7.10 may be applicable. The solution of Van Krevelen and Hoftizer based on the above equation is presented in Fig. 7.1 for equal diffusivities of both reactants; according to Danckwerts (3) the same approach would be applicable even when $D_A \neq D_B$. In the present work the diffusivities of the reacting species were different and the values of enhancement factor corresponding to instantaneous reaction (ϕ_i) obtained were much greater than unity as shown in Appendix 7(c). Therefore, $\phi_i \simeq (x/zy^*)\sqrt{D_B/D_A}$ (3) was considered for evaluation of data. Fig. 7.1 reproduced in Fig. 10.24 with the experimental data shown in points, gives a plot of enhancement factor ϕ vs $\sqrt{M}$ with $\frac{x}{zy^*}\sqrt{\left(\frac{D_B}{D_A}\right)}$ as the parameter. It can be seen from the graph that the experimental data are in good agreement with the theory. A plot of experimental vs theoretical enhancement factors is reproduced in Fig. 10.25. The data is shown to be within ±10%, the maximum deviation being 13%. Such a close fit between experimental data and theory is surprising and rather unexpected since the calculations were made by the use of the diffusivities of the pure components. Clearly this is an approximation since immediately the reaction starts an ionic reaction product is obtained, in this case sodium dichloroacetate. The diffusivity of sodium hydroxide, an ionic material, should be affected by the

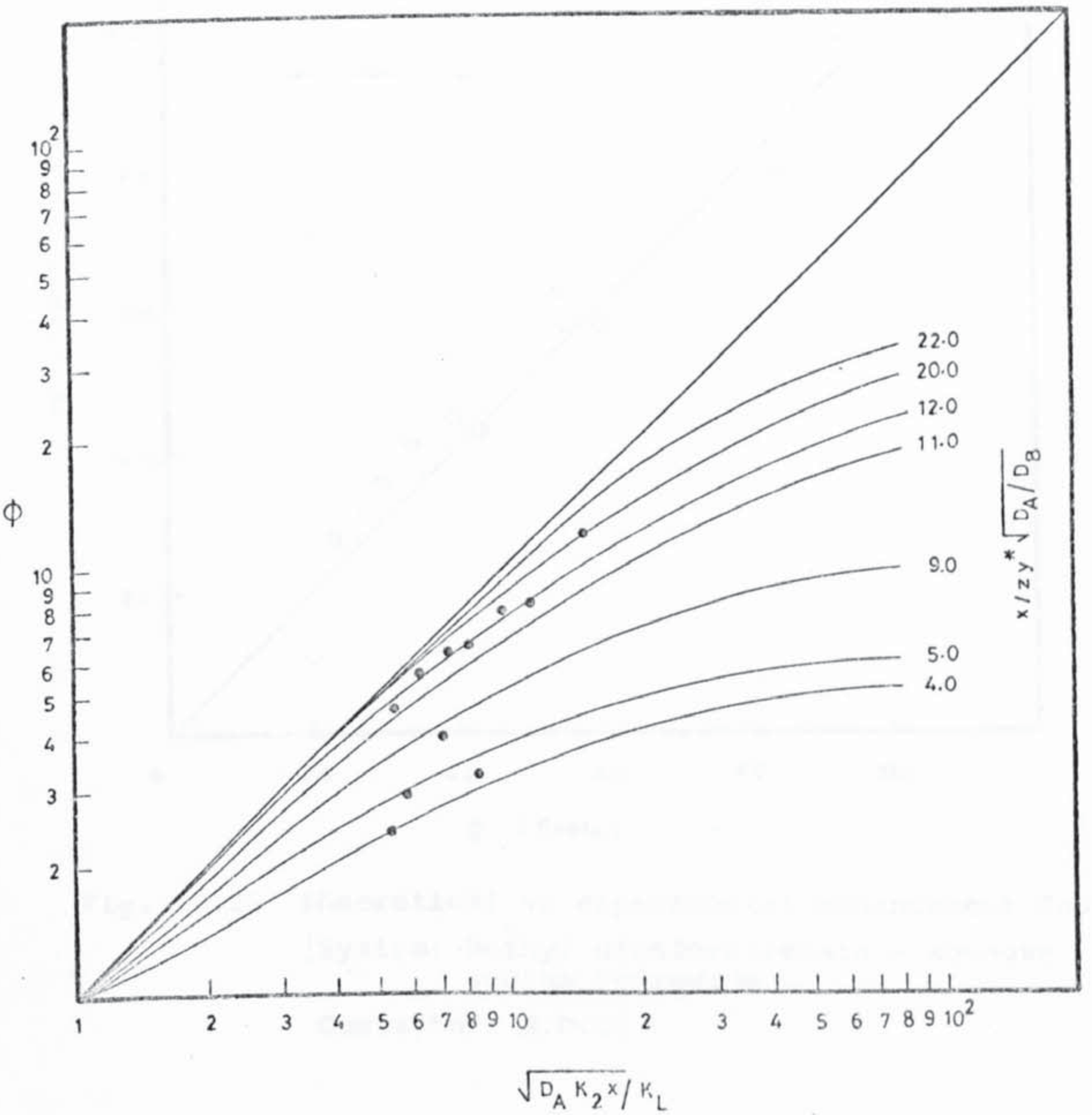


Fig. 10.24 Experimental enhancement factors for second order reaction.

|System: Methyl dichloroacetate - aqu. NaOH
Contactor: R.D.C|

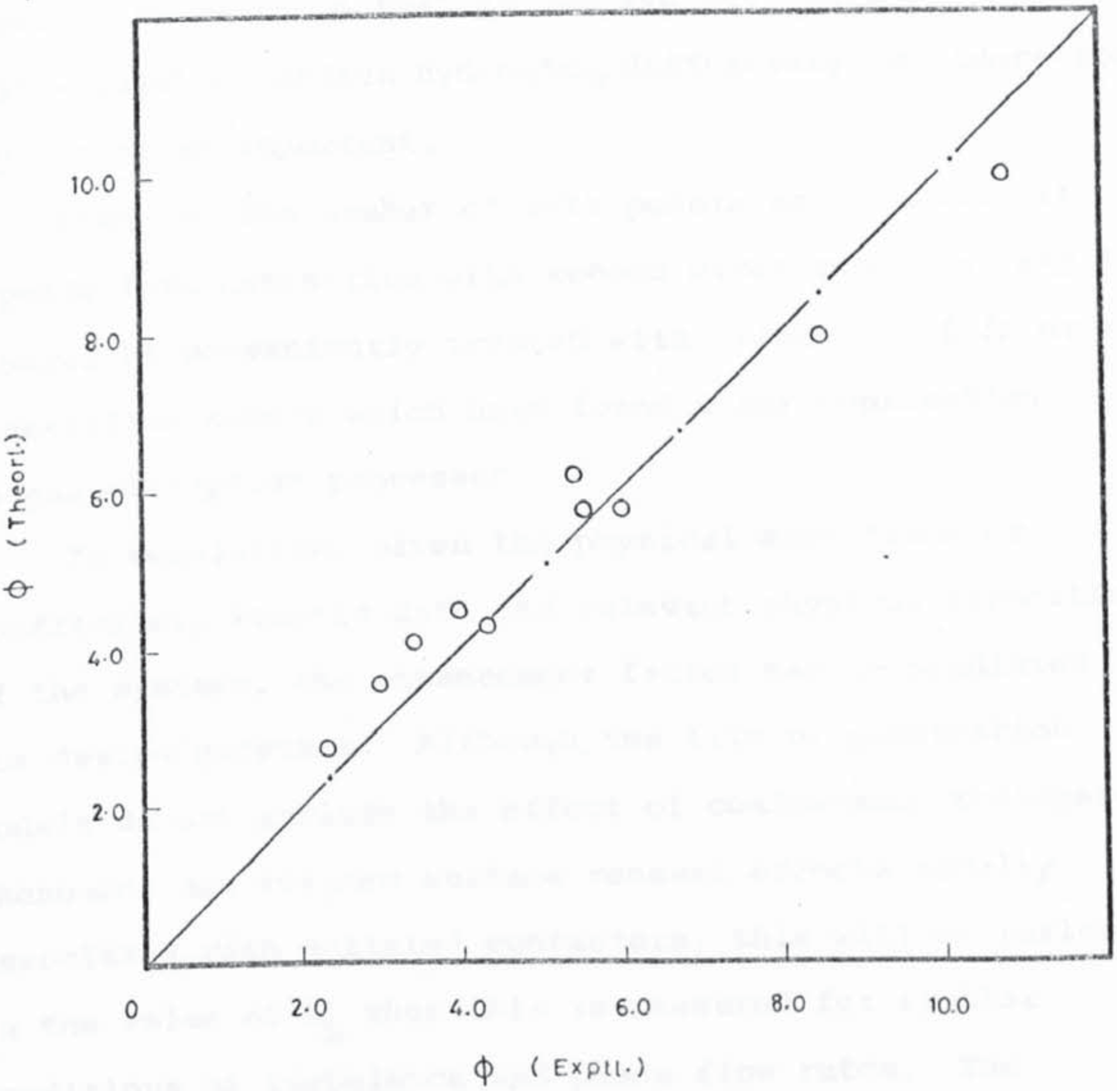


Fig. 10.25 Theoretical vs experimental enhancement factor
|System: Methyl dichloroacetate - aqueous sodium hydroxide
Contactor: R.D.C|

presence of sodium dichloroacetate, another ionic material. The hydroxide and acetate ions may be diffusing while the sodium ions may not be diffusing. Thus the ionic diffusivities may become important. However, it could be that at low average concentrations (.57 - .16N) of sodium hydroxide, diffusivity considerations may not be so important.

Although the number of data points are limited, it appears that extraction with second order reaction may in general be conveniently treated with either the film or penetration models which have found wider application in gas absorption processes.

In conclusion, given the physical mass transfer coefficient, kinetic data and relevant physical properties of the systems, the enhancement factor can be predicted for design purposes. Although the film or penetration models do not include the effect of coalescence-redispersion phenomena and related surface renewal effects usually associated with agitated contactors, this will be reflected in the value of K_L when this is measured for similar conditions of turbulence and phase flow rates. The difference in droplet interaction rates between physical transfer and transfer with chemical reaction, as discussed in Chapter 8, may not be significant provided the change in interfacial tension of the system caused by the formation of reaction products is not large, e.g. only 2.5 dyne cm^{-1} as in this work. Thus the above approach may serve as a guide to the design of contactors for extraction with second order chemical reaction.

11. CONCLUSIONS

The main conclusions arising from this work are as follows:-

1. Because of their different energy input levels, use of an R.D.C and Oldshue Rushton column provided an insight into the effect of hydrodynamics on the extraction mechanism of heterogeneous liquid-liquid systems undergoing simultaneous physical transfer and chemical reaction. For any practical extraction with chemical reaction, the choice of a contactor will depend on the physico-chemical properties of the system. For example, the Oldshue Rushton contactor will be appropriate, for a high interfacial tension systems e.g.>30 dyne/cm, whereas for very fast reactions, the R.D.C will be suitable.

2. With both columns the mean drop size produced in any compartment decreased with its number from the dispersed phase inlet. The mean drop size increased with increased dispersed phase flow rate but decreased with rotor speed. In the R.D.C. the hold-up distribution along the column length was similar to earlier observations, that is, the hold-up increased gradually to a maximum value in the middle of the column and subsequently decreased. In the Oldshue Rusthon column however the hold-up increased with increasing column height and this confirmed Arnold's(40) earlier results. Flooding rates were found to be better expressed in terms of an inversion point.

3. Phase inversion was observed to be a pseudo-steady

state phenomena and occurred at high ratios of the dispersed to the continuous phase. It was characterised by 'slugs' of coalesced dispersed phase rising up the column periodically. Equations 10.11 and 10.24 were derived to satisfactorily predict hold-up and the time required for a phase to invert under a given set of operating conditions. Phase inversion is considered a better criterion for the maximum volumetric capacity of a contactor than 'flooding'. The evaluation of capacity involves the calculation of the hold-up at inversion (x_i) from equation 10.11 followed by substitution of this value in equation 4.2. The characteristic velocity V_N for substitution in the latter equation may be predicted from an expression of the form suggested by Logsdail et. al. (49) and given by Equation 4.5.

4. Mathematical models i.e. equations 10.30, 10.32 and 10.35, and a numerical technique for their solution have been developed to satisfactorily predict the concentration profile in a column. However, practical values of mass transfer coefficient without reaction under the actual conditions of turbulence are necessary for the solution of the models. This may be obtained, as a first approximation, from laboratory investigations, as is the practice with gas-absorption processes, based on the usual concept of constant energy/volume ratios in both laboratory and full-scale plants. This approach however has limitations since surface renewal rates, which dictate

the eventual value of the mass transfer coefficient, will differ between the two scales.

5. A very slow reaction, that is when $K_La>>K_2x$, is practically controlled by the kinetics of reaction and the choice of a contactor for such extraction-reaction systems is dependent on other criteria, e.g. the provision of a sufficiently long residence time.

6. In a slow reaction system, defined by $K_L^2>>K_2D_Ax$ and $K_La<<K_2x$, either diffusion or both diffusion and kinetics may be controlling. In a practical contactor, diffusional resistances may not be altogether eliminated and thus it is difficult to identify a process as entirely diffusion or kinetically controlled.

7. A moderately fast reaction characterised by $\frac{D_AK_2}{K_L^2}>>1$ is controlled by the diffusion process and may under some circumstances be used to evaluate the kinetics of interphase chemical reaction or interfacial area in agitated contactors. Unlike in gas absorption processes the evaluation of interfacial area by the latter method is limited to the specific system.

8. Chemical reaction was found to enhance the rate of extraction significantly when the reaction was very fast i.e. when $\phi >> 1$. Under some conditions of concentration and energy input level, the rate of extraction with chemical reaction was enhanced by a factor of 10. This confirms that one effect of chemical reaction in a liquid extraction operation is to enhance the rate and extent of

solute separation.

By analogy with the treatment of gas-liquid absorption processes, the mechanism involved in extraction with interphase chemical reaction may be conveniently expressed in terms of film or penetration theory based models.

12. RECOMMENDATIONS FOR FURTHER WORK

1. The mathematical models developed to characterise phase inversion merit further investigation using systems with more extreme physical properties, particularly interfacial tension, which partially dictates the coalescence efficiency of a system. Since phase inversion has been shown to be governed by the rate of interdroplet coalescence, these studies should extend to mass transfer conditions and take account of the change in coalescence efficiency with the direction of transfer.
2. In modelling extraction involving chemical reaction, it has been assumed that the resistance to transfer is limited to one phase only. This may be extended to systems having resistances in both phases. The model and the numerical techniques proposed in Section 10.3 may be applicable. Initial investigations should be carried out in stirred cells and CSTR where the hydrodynamics are well-defined. The data would then serve as a basis for operation in differential contactors. Extraction systems recommended are - (i) Benzene- acetic anhydride - water for a slow reaction and (ii) Isobutanol - acetic acid - aqueous sodium hydroxide. These recommendations are based on the effects of physico-chemical properties, particularly interfacial tension and the kinetic constant, deduced from the present investigation.
3. There is a general lack of information on the kinetic

data of heterogeneous chemical reaction systems. Knowledge of kinetics is essential to define an extraction-reaction system. It is therefore recommended that kinetic studies should be performed before attempting to analyse further the phenomena of liquid-liquid extraction with chemical reaction. These studies may be carried out in constant interfacial cells using the obvious assumption of film or penetration theory for evaluating the rate of transfer. A study of a recent work by Nanda and Sharma (182) would be a useful starting point.

4. The correlations describing the hold-up profiles in the R.D.C and the Oldshue Rushton column developed in this work may be extended to include the effect of varying the continuous phase flow. It could then be incorporated in the differential models to account for the variation of hold-up along the contactor length.

APPENDIX 1

Chemical Specifications And Properties

Specifications	Systems			
	Toluene	Butyl Acetate	Butyl Formate	Methyl Dichloroacetate
Density $(kg/m^3)x10^{-3}$	0.863-0.866	0.878-0.88	0.90-0.885	0.89-0.895
B. Pt.	110°C	124°C	122°C	125°C
R. I	1.494-1.497	1.52-1.53	1.56-1.57	1.59-1.61
Dist. range	110-111°C	124-127°C	122-123°C	125-128°C
Impurities	0.5%	0.1%	0.15%	0.105%
K_S (ℓ/g.ion)	-	0.305	0.145	0.150
Interfacial tension (O/W) at 20°C	34.1	12.7	15.1	11.6
Solubility in water, 20°C (part/100parts of water)	Sparingly soluble	0.7	0.8	0.65
Viscosity (poise)	0.006	0.0075	0.008	0.0092

APPENDIX 2

Kinetic Data: Alkaline hydrolysis of Esters.

The rate constants refer to data at infinite dilution and at 20°C ± 1°C.

Ester	Rate Constant (ℓ/gm.mole.sec)
Butyl acetate	0.08
Butyl formate	22.0
Methyl dichloroacetate	220.0

APPENDIX 3

Description of Cine Film

System: Butyl acetate (dispersed) - water (continuous)

Ist Sequence

The column is operating with a hold-up of 0.60 and at an agitator speed of 700 rpm.

2nd Sequence

This sequence follows the first after the dispersed phase flow was increased by about 3%. Drops grow larger in the bottom compartment and after about a minute phase inversion occurs. This is indicated by the formation of a'slug' of dispersed phase which then passes on to the next compartment and gradually proceeds up the column, ultimately coalescing with the bulk interface. Normal operating conditions are restored soon after it leaves a particular compartment. Reinversion occurs in each compartment after a finite time. This sequential inversion of consecutive compartments is demonstrated as the 'slug' moves up the column.

3rd Sequence

This shows intense mixing in a single compartment at the onset of phase inversion.

4th Sequence

This is an enlarged view of the formation of a 'slug' in one compartment.

5th Sequence

This demonstrates very large drops, and mis-shaped masses, of dispersed phase coalescing with the interface in the settling section.

(This proves that phase inversion had occurred rather than froth formation).

APPENDIX 4

Computer program for regression analysis of data: Hold-Up profile in the R.D.C

```
      TRACE 1
      READ FROM (CR)
      MASTER
      DIMENSION X(50,10),Y(50),A(99),B(50),XBAR(50),YHAT(50),AA(50,50)
      N1=50.0
      NO=66.0
      READ(1,11) HT
   11 FORMAT(F0.0)


   10 READ(1,001) NA,NX,M
  001 FORMAT(8I0)
      NN= NA*NA
      IF(NA)999,999,20
   20 CONTINUE
      READ(1,002) (X(J,1),X(J,2),X(J,3),Y(J),J=1,M)
  002 FORMAT(4F0.0)
  100 CONTINUE
C     SECTION 1*** SET UP FUNCTIONS***
      DO 200 K=1,M
      XB=((X(K,3)**2)-HT*X(K,3))
      XA=X(K,1)*X(K,2)*XB
      XC=XA*X(K,2)*XB
      X(K,1)=XA
      X(K,2)=XC
  200 CONTINUE
  003 FORMAT(8F0.0)
      CALL LINREG (X,Y,NA,M,A,B,XBAR,YHAT,AA,NN,NO)
      GO TO 10
  999 STOP
      END

END OF SEGMENT, LENGTH   128, NAME  NONM

      SUBROUTINE LINREG (X,Y,N,M,A,B,XBAR,YHAT,AA,N2,NO)
      DIMENSION X(50,10),Y(50),A(99),B(50),XBAR(50),YHAT(50),AA(50,50)
      WRITE(2,001)
  001 FORMAT(1H1,10X,36HMULTIPLE LINEAR REGRESSION ALGORITHM)
C     CALCULATE AVERAGE X AND Y VALUES
      DO 200 I=1,N
      SUMX=0.0
      DO 100 J=1,M
  100 SUMX=SUMX+X(J,I)
  200 XBAR(I)=SUMX/FLOAT(M)
      SUMY=0.0
      DO 300 K=1,M
  300 SUMY=SUMY+Y(K)
      YBAR=SUMY/FLOAT(M)
      WRITE(2,003) (II,XBAR(II),II=1,N)
  002 FORMAT(//,2X,23HVARIABLE AVERAGE VALUES)
      WRITE(2,002)
  003 FORMAT(/,3(2X,5HXBAR(,I2,4H)=,1,E14.7))
      WRITE(2,004) YBAR
  004 FORMAT(/,2X,7HYBAR=,1,E14.7)
C     CALCULATE REGRESSION MATRICES
      KK=1
      DO 500 I=1,N
      DO 500 J=1,N
      SUMA=0.0
      SUMB=0.0
      DO 400 K=1,M
      SUMA=SUMA+(X(K,I)-XBAR(I))*(X(K,J)-XBAR(J))
  400 SUMB=SUMB+(Y(K)-YBAR)*(X(K,I)-XBAR(I))
      AA(I,J)=SUMA
      A(KK)=SUMA
      KK=KK+1
  500 B(I)=SUMB
      WRITE(2,005)
  005 FORMAT(//,10X,8HA MATRIX)
      DO 550 II=1,N
```

```
  550 WRITE(2,006) (AA(II,JJ),JJ=1,N)
  006 FORMAT(/,8(2X,E10.4))
      WRITE(2,007)
  007 FORMAT(//,10X,8HB MATRIX)
      WRITE(2,006) (B(KK),KK=1,N)
C     SOLVE REGRESSION MATRICES FOR COEFFICIENTS
      CALL SIMQ (A,B,N,KS,N2)
      SUMX=0.0
      DO 600 I=1,N
  600 SUMX=SUMX+B(I)*XBAR(I)
      AZERO=YBAR-SUMX
      WRITE(2,008)
  008 FORMAT(1H1,10X,37HVALUES OF THE REGRESSION COEFFICIENTS)
      WRITE(2,009) (JJ,B(JJ),JJ=1,N)
  009 FORMAT(/,2(2X,5HAHAT(,I2,4H)=,1,E16.8,8X))
      WRITE(2,010) AZERO
  010 FORMAT(/,2X,8HAZERO=,1,E16.8)
C     CALCULATE S AND R TEST VALUES
      STEST=0.0
      DO 800 J=1,M
      SUMS1=0.0
      DO 700 K=1,N
  700 SUMS1=SUMS1+B(K)*X(J,K)
      YHAT(J)=AZERO+SUMS1
      DIFF=(Y(J)-YHAT(J))**2
  800 STEST=STEST+DIFF
      SUMST=0.0
      DO 900 I=1,M
  900 SUMST=SUMST+(Y(I)-YBAR)**2
      SUMSR=SUMST-STEST
      RTEST=SUMSR/SUMST
      WRITE(2,011)
  011 FORMAT(////,5X,19HEXPERIMENTAL VALUES,18X,17HREGRESSION VALUES)
      DO 1000 KK=1,M
 1000 WRITE(2,012) KK,Y(KK),KK,YHAT(KK)
  012 FORMAT(/,2X,2HY(,I3,4H)=,1,E16.8,10X,5HYHAT(,I3,4H)=,1,E16.8)
      WRITE(2,013) SUMST,STEST,RTEST
  013 FORMAT(///,2X,8HSUMST=,1,E16.8,/,2X,4HS=,1,E16.8,10X,7HR**2=,1,E16
     1.8)
      RETURN
      END

END OF SEGMENT, LENGTH   452, NAME  LINREG

      SUBROUTINE SIMQ(A,B,N,KS,NS)
      DIMENSION A(NS),B(N)
C     FORWARD SOLUTION
      TOL=0.0
      KS=0
      JJ=-N
      DO 65 J=1,N
      JY=J+1
      JJ=JJ+N+1
      BIGA=0
      IT=JJ-J
      DO 30 I=J,N
C     SEARCH FOR MAXIMUM COEFFICIENT IN COLUMN
      IJ=IT+I
      IF(ABS(BIGA)-ABS(A(IJ))) 20,30,30
   20 BIGA=A(IJ)
```

```
      IMAX=I
   30 CONTINUF
C     TEST FOR PIVOT LESS THAN TOLERANCE(SINGULAR MATRIX)
      IF(ABS(RIGA)-TOL) 35,35,40
   35 KS=1
      RETURN
C     INTERCHANGE POWS IF NECESSARY
   40 I1=J+N*(J-2)
      IT=IMAX-J
      DO 50 K=J,N
      I1=I1+N
      I2=I1+IT
      SAVE=A(I1)
      A(I1)=A(I2)
      A(I2)=SAVE
C     DIVIDE FQUATION BY LFADING COEFFICIENT
   50 A(I1)=A(I1)/BIGA
      SAVE=B(IMAX)
      B(IMAX)=B(J)
      B(J)=SAVE/BIGA
C     ELIMINATE NEXT VARIABLE
      IF(J-N) 55,70,55
   55 IQS=N*(J-1)
      DO 65 IX=JY,N
      IXJ=IQS+IX
      IT=J-IX
      DO 60 JX=JY,N
      IXJX=N*(JX-1)+IX
      JJX=IXJX+IT
   60 A(IXJX)=A(IXJX)-(A(IXJ)*A(JJX))
   65 B(IX)=B(IX)-(B(J)*A(IXJ))
C     BACK SOLUTION
   70 NY=N-1
      IT=N*N
      DO 80 J=1,NY
      IA=IT-J
      IB=N-J
      IC=N
      DO 80 K=1,J
      B(IB)=B(IB)-A(IA)*B(IC)
      IA=IA-N
   80 IC=IC-1
      RETURN
      END

END OF SEGMENT, LFNGTH   306, NAME  SIMQ

                      FINISH

END OF COMPILATION -  NO ERRORS

S/C SUBFILE:               22 BUCKETS USED

PROGRAM FXXX
EXTENDED DATA (22AM)
COMPACT PROGRAM (DBM)
CORE                11968
```

APPENDIX 5

Computer program for regression analysis of data: Hold-Up profile in the Oldshue Rushton Column.

```
      TRACE 1
      READ FROM (CR)
      TRACE 2
      MASTER
      REAL NS(100)
      DIMENSION Y(100),X(100),Z(100),A(5,5),YCALC(100)
      READ(1,10) NP,NPAR
   10 FORMAT(2I0)
      READ(1,11) (Y(I),X(I),Z(I),NS(I),I=1,NP)
   11 FORMAT(4F0.0)
      S1=0.0
      S2=0.0
      S3=0.0
      S4=0.0
      S5=0.0
      S6=0.0
      S7=0.0
      S8=0.0
      S9=0.0
      S10=0.0
      S11=0.0
      S12=0.0
      S13=0.0
      DO 50 I=1,NP
      S1=S1+Y(I)
      S2=S2+X(I)
      S3=S3+Z(I)
      S4=S4+NS(I)
      S5=S5+X(I)**2
      S6=S6+Z(I)**2
      S7=S7+NS(I)**2
      S8=S8+Y(I)*X(I)
      S9=S9+X(I)*Z(I)
      S10=S10+X(I)*NS(I)
      S11=S11+Z(I)*NS(I)
      S12=S12+Y(I)*Z(I)
   50 S13=S13+Y(I)*NS(I)
      A(1,1)=NP*1.
      A(2,1)=S2
      A(3,1)=S3
      A(4,1)=S4
      A(1,2)=S2
      A(2,2)=S5
      A(3,2)=S9
      A(4,2)=S10
      A(1,3)=S3
      A(2,3)=S9
      A(3,3)=S6
      A(4,3)=S11
      A(1,4)=S4
      A(2,4)=S10
      A(3,4)=S11
      A(4,4)=S7
      A(1,5)=S1
      A(2,5)=S8
      A(3,5)=S12
      A(4,5)=S13
      NA=NPAR+1
      DO 51 J=1,NPAR
      DIV=A(J,J)
      DO 53 K=1,NA
   53 A(J,K)=A(J,K)/DIV
      DO 51 I=1,NPAR
      C=A(I,J)
      DO 51 K=1,NA
      IF(I.EQ.J) GOTO 51
      A(I,K)=A(I,K)-A(J,K)*C
   51 CONTINUE
      A0=A(1,5)
      A1=A(2,5)
      A2=A(3,5)
      A3=A(4,5)
      SUMSQ=0.
      DO 52 I=1,NP
      YCALC(I)=A0+A1*X(I)+A2*Z(I)+A3*NS(I)
   52 SUMSQ=SUMSQ+(YCALC(I)-Y(I))**2
      WRITE(2,54) A0,A1,A2,A3
   54 FORMAT(1H ,//5X,'A0',2X,F12.5,5X,'A1',2X,F12.5,5X,'A2',2X,F12.5,5X
     1,'A3',2X,F12.5//)
      WRITE(2,63)
   63 FORMAT(1H ,//5X,'RUN NO',10X,'YCALC',10X,'YEXTL',10X,'X(I)',12X,'Z
     1(I)',12X,'NS(I)'//)
      WRITE(2,55) (I,YCALC(I),Y(I),X(I),Z(I),NS(I),I=1,NP)
   55 FORMAT(1H ,3X,I3,8X, 8X,F10.3,8X,F10.3,8X,F10.3,8X,F10.3,8X,F10.3)
      WRITE(2,56) SUMSQ
   56 FORMAT(1H ,///40X,'SUM OF SQUARES OF RESIDUALS',F15.7)
      STOP
      END


 END OF SEGMENT, LENGTH   687, NAME   NONM
```

APPENDIX 6

Computer program for solution of non-linear differential models.

```
      TRACE 1
      READ FROM (CR)
      MASTER
      INTEGER PRINT
      COMMON Z,X,H,DH,FUN(2),A0,A1,A2,A3,A4,A5,A6,A7,A8,PECLET,KLA,KL,A,
     1U,XE,XD,X1,X2
      READ(1,10) ZA,XA,DH
      READ(1,10) A1
      READ(1,10) HMAX,X1,X2
      READ(1,10) A0,CONV
      READ(1,11) PRINT
      READ(1,11) NU
      X8=X1
      X9=X2
      NS=0
   42 READ(1,10) PECLET,U,XD,XE
      WRITE(2,71) PECLET
      ITERA=0
      X1=X8
      X2=X9
      X=XA
      Z=ZA
   71 FORMAT(1H ,//21X,'PECLET NO IS',F12,5//)
   10 FORMAT(4F0,0)
   11 FORMAT(I0)
   31 WRITE(2,20)

   20 FORMAT(1H ,//21X,'H',21X,'X',21X,'U',21X,'XD',21X,'XE'//)
   21 FORMAT(1H ,17X,F10,5,12X,F10,5,12X,F10,5,12X,F10,5,12X,F10,5)
      H=0,
   32 J=0
   30 CALL RUKU4
      IF(H,GE,HMAX) GOTO 33
      J=J+1
      IF(J,NE,PRINT) GOTO 30
      WRITE(2,21) H,X
      GOTO 32
   33 CONTINUE
      TEST=(1,0-X)*PECLET-Z
      A0=TEST
      TEST=ABS(TEST)
      IF(TEST,LE,CONV) GOTO 40
      CALL GOLD(XA)
      ITERA=ITERA+1
      IF(ITERA,GT,30) GOTO 40
      X=XA
      Z=ZA
      GOTO 31
   40 NS=NS+1
      WRITE(2,21) H,X,U,XD,XE
      IF(NS,LT,NU) GOTO 42
      STOP
      END

 END OF SEGMENT, LENGTH   209, NAME  NONM
```

```
      SUBROUTINE GOLD(XGUESS)
      REAL INTVAL
      COMMON Z,X,H,DH,FUN(2),A0,A1,A2,A3,A4,A5,A6,A7,A8,PECLET,KLA,KL,A,
     1U,XF,XD,X1,X2
      IF(A0.LT.0.0)GOTO 300
      X1=XGUESS
      GOTO 301
  300 X2=XGUESS
  301 INTVAL=X2-X1
      XGUESS=X1+(INTVAL/1.618)
      RETURN
      END

END OF SEGMENT, LENGTH    45, NAME  GOLD

      SUBROUTINE EQNS
      COMMON Z,X,H,DH,FUN(2),A0,A1,A2,A3,A4,A5,A6,A7,A8,PECLET,KLA,KL,A,
     1U,XE,XD,X1,X2
      FUN(1)=Z
      FUN(2)=PECLET*(A1/U)*XD*X*EXP(-0.7*XE*X)-PECLET*Z
      RETURN
      END

END OF SEGMENT, LENGTH    46, NAME  EQNS

      SUBROUTINE RUKU4
      REAL K(4)
      DIMENSION G(4)
      COMMON Z,X,H,DH,FUN(2),A0,A1,A2,A3,A4,A5,A6,A7,A8,PECLET,KLA,KL,A,
     1U,XF,XD,X1,X2
      X0=X

      Z0=Z
      DO 101 I=1,4
      CALL EQNS
      K(I)=DH*FUN(1)
      G(I)=DH*FUN(2)
      GOTO(103,103,104,105),I
  103 X=X0+K(I)/2.
      Z=Z0+G(I)/2.
      GOTO 102
  104 X=X0+K(I)
      Z=Z0+G(I)
      GOTO 102
  105 X=X0+(K(1)+2.*K(2)+2.*K(3)+K(4))/6.
      Z=Z0+(G(1)+2.*G(2)+2.*G(3)+G(4))/6.
  102 CONTINUE
  101 CONTINUE
      H=H+DH
      RETURN
      END
```

APPENDIX 7

This consists of data pertaining to mass transfer with and without chemical reaction.

APPENDIX 7(a) - I

System: Alkaline hydrolysis of butyl acetate

Contactor: Oldshue Rushton Column

$V_d \times 10^5$ (m^3/s)	$V_c \times 10^5$ (m^3/s)	x_i Kgm/m^3	$(K_L a) \times 10^3$ (sec^{-1})	x Kgm/m^3	$(K_2 x) \times 10^3$ (sec^{-1})	N (rpm)	$a \times 10^{-2}$ (m^2/m^3)	$K_L \times 10^5$ (m/s)	$R \times 10^6$ ($Kgm/m^2 s$)
1.0	1.0	0.75	4.8	0.67	53.6	200	1.5	3.2	1.34
1.0	1.0	0.75	8.58	0.645	51.7	250	2.2	3.9	1.49
1.0	1.0	0.755	11.70	0.60	48.0	300	2.6	4.5	1.64
1.0	1.0	0.75	15.5	0.56	44.8	400	3.1	5.0	1.75
4.16	1.0	0.75	31.8	0.625	50.0	200	6.0	5.3	2.48
4.16	1.0	0.75	45.5	0.59	47.1	250	7.0	6.5	2.72
4.16	1.0	0.745	59.94	0.55	44.0	300	8.1	7.4	3.01
4.16	1.0	0.75	71.28	0.505	40.4	400	8.8	8.1	3.05
2.5	1.5	0.50	15.17	0.4	32.0	200	3.7	4.1	1.93
2.5	1.5	0.50	22.36	0.375	30.0	250	4.3	5.2	2.07
2.5	1.5	0.55	28.8	0.345	27.0	300	4.8	6.0	2.3
2.5	1.5	0.50	37.7	0.32	25.56	400	5.8	6.5	2.21
4.16	1.5	0.40	31.8	0.29	23.2	200	6.0	5.3	2.18
4.16	1.5	0.40	45.5	0.30	23.0	250	7.0	6.5	1.87
4.16	1.5	0.40	59.94	0.29	23.25	350	8.1	7.4	1.61
4.16	1.5	0.40	71.28	0.30	23.0	400	8.8	8.1	1.48

APPENDIX 7(a) - II

System: Alkaline hydrolysis of butyl acetate

Contactor: R.D.C

$V_d \times 10^5$ (m^3/s)	$V_c \times 10^5$ (m^3/s)	x_i (Kgm/m^3)	$(K_L a) \times 10^3$ (sec^{-1})	x (Kgm/m^3)	$(K_2 x) \times 10^3$ (sec^{-1})	N (rpm)	$a \times 10^{-2}$ (m^2/m^3)	$K_L \times 10^5$ (m/s)	$R \times 10^6$ ($Kgm/m^2 s$)
1.0	1.0	0.755	5.95	0.675	47.84	650	1.5	3.73	1.4
1.0	1.0	0.75	9.66	0.615	49.2	850	2.3	4.2	1.6
1.0	1.0	0.75	12.32	0.57	45.6	1000	2.8	4.4	1.72
2.08	1.0	0.76	18.28	0.632	50.56	650	4.0	4.57	1.90
2.08	1.0	0.75	23.04	0.592	47.36	850	4.8	4.8	2.1
2.08	1.0	0.75	28.6	0.557	44.56	1000	5.5	5.2	2.2
4.16	1.0	0.75	43.6	0.60	64.0	650	7.5	5.8	2.4
4.16	1.0	0.752	51.85	0.572	45.76	850	8.5	6.1	2.54
4.16	1.0	0.75	63.5	0.525	42.0	1000	10.0	6.35	2.64
1.0	1.0	0.50	5.595	0.41	41.0	650	1.5	3.73	1.77
1.0	1.0	0.51	9.66	0.35	35.0	850	2.3	4.2	1.8
1.0	1.0	0.52	12.32	0.30	30.0	1000	2.8	4.4	2.0
2.08	1.5	0.50	18.28	0.35	35.0	650	4.0	4.57	2.23
2.08	1.5	0.50	23.04	0.305	30.5	850	4.8	4.8	2.3
2.08	1.5	0.50	28.6	0.29	29.0	1000	5.5	5.2	2.3
4.16	1.5	0.35	43.6	0.25	25.0	650	7.5	5.8	1.7
4.16	1.5	0.35	51.85	0.26	26.0	850	8.5	6.1	1.5
4.16	1.5	0.35	63.5	0.245	24.5	1000	10.0	6.35	1.24

APPENDIX 7(b)

System: Alkaline hydrolysis of butyl formate

Contactor: Oldshue Rushton Column.

$V_d x 10^5$ (m^3/s)	$V_c x10^5$ (m^3/s)	x_i (Kgm/m^3)	N (rpm)	$a \times 10^{-2}$ (m^2/m^3)	x (Kgm/m^3)	K_2 ($m^3/Kgm.s$)	$\|R/y^*\|^2 x10^{10}$ (m^2/s^2)	$\sqrt{D_A K_2 x}/K_L$	$1+ \frac{x}{zy^*}$	$K_L x 10^5$ (m/s)
1.66	1.0	0.401	200	2.5	0.30	17.65	65.0	2.34	7.25	3.316
1.66	1.0	0.527	200	2.5	0.42	17.65	83.0	2.75	10.33	3.316
1.66	1.0	0.626	200	2.5	0.515	17.65	103.0	3.04	13.4	3.316
2.5	1.0	0.357	200	3.5	0.25	20.0	77.0	1.4	6.0	5.0
2.5	1.0	0.463	200	3.5	0.35	20.0	94.0	1.656	8.36	5.0
2.5	1.0	0.59	200	3.5	0.475	20.0	120.0	1.93	12.17	5.0
1.66	1.0	0.534	250	3.75	0.355	20.5	106.0	1.41	8.7	5.916
1.66	1.0	0.64	250	3.75	0.45	20.5	125.0	1.59	11.32	5.916
1.66	1.0	0.754	250	3.75	0.56	20.5	149.0	1.775	15.0	5.916
2.5	1.0	0.476	250	4.5	0.32	19.0	107.0	1.168	7.66	6.78
2.5	1.0	0.585	250	4.5	0.425	19.0	127.0	1.346	10.44	6.78
2.5	1.0	0.665	250	4.5	0.51	19.0	143.0	1.47	13.0	6.78
1.66	1.0	0.728	350	5.0	0.45	17.8	145.0	1.156	11.22	8.12
1.66	1.0	0.785	350	5.0	0.51	17.8	155.0	1.23	13.1	8.12
1.66	1.0	0.825	350	5.0	0.55	17.8	164.0	1.278	14.4	8.12
2.5	1.0	0.824	350	5.5	0.62	16.5	185.0	1.210	17.0	9.11
2.5	1.0	0.662	350	5.5	0.45	16.5	157.0	1.03	11.32	9.11
2.5	1.0	0.71	350	5.5	0.50	16.5	165.0	1.07	12.76	9.11

APPENDIX 7(c)

System: Alkaline hydrolysis of butyl formate

Contactor: Oldshue Rushton Column

$V_d \times 10^5$ (m^3/s)	$V_c \times 10^5$ (m^3/s)	x_i (Kgm/m^3)	N (rpm)	$K_L \times 10^5$ m/s	$a \times 10^{-2}$ (m^2/m^3)	x (Kgm/m^3)	ϕ	$\sqrt{DK_2x}/K_L$	$\frac{x}{zy^*}\sqrt{(\frac{D_B}{D_A})}$
2.5	1.66	0.6	500	2.45	2.5	0.425	9.0	11.216	12.21
3.32	1.66	0.6	500	3.6	3.5	0.40	6.25	8.0	11.8
3.32	1.66	0.45	500	3.6	3.5	0.30	4.00	6.88	8.85
3.32	1.66	0.30	500	3.6	3.5	0.195	3.00	5.70	5.08
3.32	1.66	0.25	500	3.6	3.5	0.16	2.63	5.1	3.95
4.16	1.66	0.60	500	5.2	5.0	0.375	4.38	5.2	10.70
2.5	1.66	0.80	500	2.45	2.5	0.60	10.88	14.2	19.5
2.5	1.66	0.30	500	2.45	2.5	0.225	3.4	8.8	5.5
3.32	1.66	0.81	500	3.6	3.5	0.575	7.92	9.6	18.6
4.16	1.66	0.80	500	5.2	5.0	0.54	5.8	6.45	17.12
2.5	1.66	0.82	650	4.25	4.2	0.50	5.6	7.5	15.2

APPENDIX 8

Paper presented to the Institution of Chemical Engineers, 3rd Annual Research Meeting, University of Salford, 30-31 March, 1976.

PHASE INVERSION IN AGITATED COLUMNS

by Sarkar, S., Mumford, C.J., and Jeffreys G.V.

Department of Chemical Engineering
University of Aston in Birmingham

Phase inversion refers to the interchange of phases in a dispersion, that is the dispersed phase becoming continuous and vice-versa, under conditions dictated by system properties, phase ratio and the rate of energy input. It may occur whenever the equilibrium between droplet coalescence and redispersion is disturbed and accompanied by a shift in the equilibrium towards the former.

For liquid-liquid extraction operations in differential countercurrent contactors the maximum volumetric capacity of the contactor is generally defined by the 'flooding' rates. However, flooding is a rather ambiguous phenomenon whereas for specific values of the operating parameters the phase inversion point is well defined; thus the latter may serve as a capacity limit. In any event it is important to be able to predict which phase will be dispersed since this affects the mass transfer performance.

In the present work some observations regarding phase inversion have been made in two agitated continuous countercurrent extractors, an R.D.C. and Oldshue-Rushton column, as part of a study of liquid-liquid extraction with chemical reaction (9).

EXPERIMENTS

Phase inversion studies, under both non-flow and flow conditions, have to date been mainly qualitative. Several workers have carried out investigations with different systems in stirred cells (1,2,3,4). Limited observations have been reported for flow systems (5,6). There are no generally accepted mathematical models for phase inversion and no comprehensive experimental data, particularly for flow systems.

The present work was performed in 0.10m diameter x 1m long glass columns. Both the R.D.C. and the Oldshue-Rushton Contactor had 18 compartments each 0.05m high. The internals were of S/S and conformed to standard geometries (7,8). Five sampling points were provided at 15cm intervals along each column length. The heavy phase was introduced into a column at a point just above the top compartment, and left via a bottom outlet. One dispersed phase entered via a S/S distributor which consisted of 0.0016m holes arranged on 0.0048m triangular pitch inside a 0.10m diameter circle. The agitator shaft was fabricated from 0.01m S/S rod and was driven by a 0.25 mp A.C. Voss motor. The agitation was controlled by a 'Torovolt' variable voltage mains transformer. This part of the work, with mutually saturated phases i.e. under non-mass transfer conditions was performed with the system butyl acetate-water and subsequently toluene-water. Inversion rates were determined, by establishing steady state conditions at a fixed rotor speed and then increasing the flow of the dispersed phase slowly, with the continuous flow rate kept constant, until inversion occurred. At a certain value of dispersed phase flow rate, when the column reached near flooding conditions, as indicated by the creation of a dense layer of droplets at the base of the column, inversion was observed to occur. In most of the runs, it commenced in the bottom compartment and after a finite time practically the whole compartment was inverted. This inversion then passed into the next compartment and proceeded up the column, ultimately coalescing with the bulk interface. Inversion was characterised by the formation of a 'slug' of parent dispersed phase and normal operating conditions were restored soon after this left any particular compartment. Re-inversion occurred again in this compartment after a finite time, the whole process being repeated indefinitely. Inversion was hence cyclical in both the contactors. Inversion hold-up values were recorded. The effect of varying phase flow ratio and energy input was also investigated. Typical results are given in Figures 1 and 2.

RESULTS

A model predicting hold-up values at inversion is proposed,

$$Rr = 1 - \frac{a}{x_i} + \sum_{\substack{k=2 \\ j=1}}^{\substack{K \\ J}} b^k/x_i$$

where Rr = Phase flow ratio (continuous : dispersed)
a = 1.5 b = 0.5
x = hold-up, x_i = hold-up at inversion

The model was tested for $Rr < 1.0$ and found to be in good agreement with the experimental values.

As indicated earlier, phase inversion was a pseudo steady-state operation in both contactors. The time cycle of this mode has been investigated and a theoretical expression has been formulated,

$$t = 0.048(Z)^{0\cdot66}(x)^{-0\cdot33}(D_{tr})^{-1\cdot0}$$

where Z = volume of the vessel or compartment of a contactor
t = time
D_{tr} = drop diffusion coefficient

The deviation of experimentally determined times from those predicted by this equation was within 10% to 25%; at higher energy input rates the deviation was negligible. This work is being continued in columns up to 0.4m diameter, and in continuous mixer-settlers in which the hydrodynamics are fundamentally different.

REFERENCES

1. Luhning, R.W. and Sawistowski, J., Proc. I.S.E.C., 71, S.C.I., The Hague, (1971)

2. Quinn, J.A. & Sigloh, B., Can. J. Chem. Eng., 41, 15 (1963)

3. Selker, A.H. & Schleicher, C.A., Jnr. Can. J. Chem. Eng. 17, 298 (1965)

4. Yeh, G.C. et al, A.I.Ch.E. Jour., 10, 260 (1964)

5. Arnold, D., Ph.D. Thesis, 1973, University of Aston in Birmingham.

6. Al-Hemiri, A.A.A., Ph.D. Thesis, 1973, University of Aston in Birmingham.

7. Reman, G.H. and Olney, R.B., Chem. Eng. Prog., 51, 141 (1955)

8. Oldshue, J.Y., and Rushton, J.H., Chem.Eng.Prog. 48, 297 (1952)

9. Sarkar, S., Ph.D. Thesis, University of Aston in Birmingham, to be published 1976.

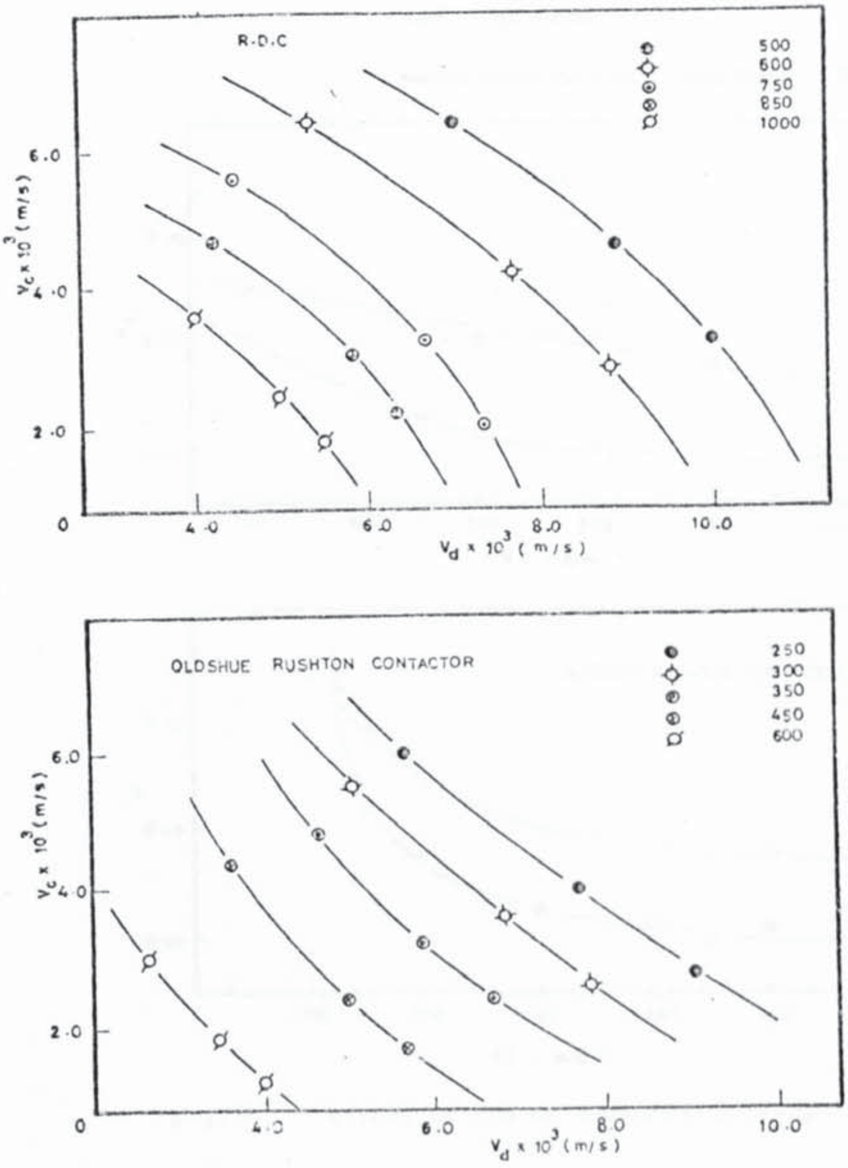


Fig. 1 Continuous vs dispersed phase flow at inversion (System: butyl acetate-water)

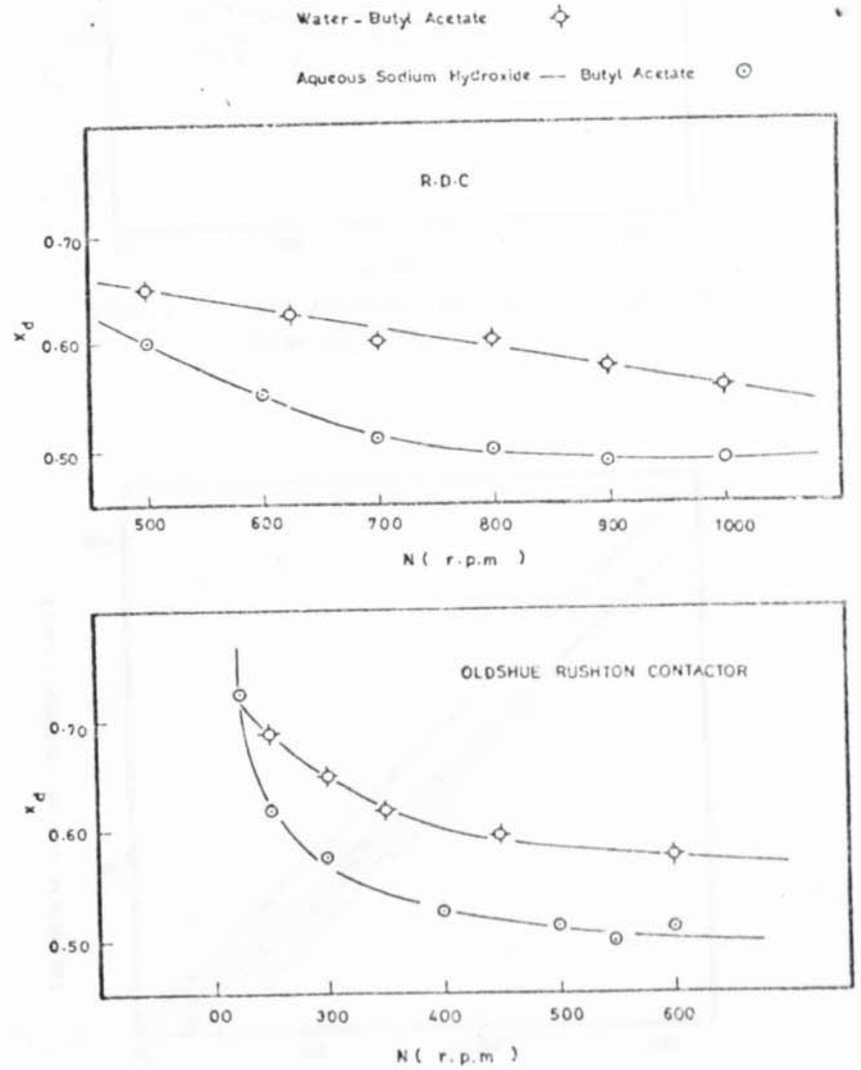


Fig. 2 Effect of rpm on inversion hold-up

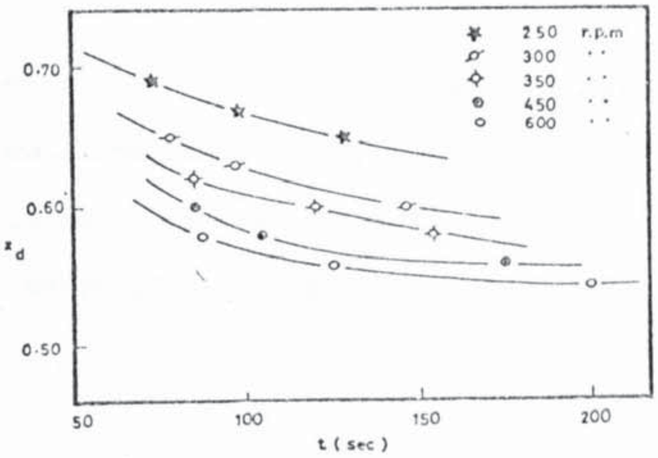


Fig. 3 Experimental variation of inversion time with hold-up

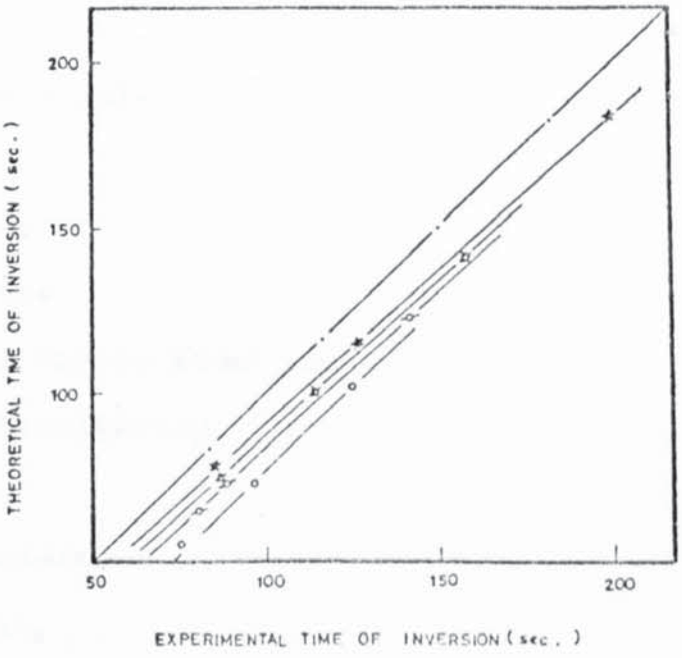


Fig. 4 Predicted vs experimental time of phase inversion
(System: butyl acetate-water)

NOMENCLATURE

$\bar{A}$	Average concentration
A	Reactant, Interfacial area in Eq.4.18, constant in Eq.6.10
A_s	Stator gap diameter in Oldshue Rushton Column
a, a_r	Interfacial area, exponent in Eq.5.17
a_1, a_2	Concentration in Eq.7.38 and Eq.7.41
a_o	Initial radius or half axis length
a_p	Amplitude
B	Reactant
B_w	Blade diameter
B_h	Blade height
b	Baffle width
C	Concentration
C, C_n	Constants (where n=1-7)
D	Diffusivity
D_C	Column diameter
D_T	Turbine diameter
D_d	DIsc diameter, Nozzle diameter
D_E	Equivalent diffusitivity
d	Drop diameter
d_{32}	Sauter mean diameter
E,e	Eddy diffusivity
E	Energy, efficiency
F	Harkin and Brown correction factor, Extraction factor or Flow rates
Fr	Froude No. $D_T N^2/g$
F_B	Superficial backmixing coefficient

f	actual rate of interstage back flow, overall conversion
f_h	Dispersed phase hold-up
G	Mass flow rate per unit area
g	Gravitational constant or interstage flow
Δg_1, Δg_2, Δg_3, Δg_4	Change in a fraction of drops during dimensionless time $\Delta\xi$
H	Compartment height
H_T, h_c	Column height, Height of dispersion
h	Distance, Height
H.T.U.	Height of transfer unit
hm	Height equivalent of a stage = h_c/n
I	Droplet interaction modulus
i	i^{th} stage
K, K_n	Constants (where n = 0-8)
K	Overall mass transfer coefficient
K_{df}	Mass transfer coefficient for forming drops
k',k	Individual mass transfer coefficient, or mass transfer coefficient with reaction.
K_1	First order reaction constant
K_2	Second Order reaction constant
k	Rate constant in Eq.7.47
K_L	Aqueous side mass transfer coefficient
K_s	Sum of contributions of various ions
L	Lagrangian macroscale of turbulence, or flow rate
M	Velocity exponent, mass of fluid in one compartment, $\frac{1}{K_L{}^2}(D_A k_1)$ for first order reaction,

	$\frac{1}{K_L^2}(D_A K_2 x)$ for second order reaction, or, Molecular weight
m	Equilibrium constant or exponent in Eq.4.17
N	Moles per unit time, RPM, number of drops
N_{we}	Weber number
N_{vi}	Viscosity group
N_{Pe}	Peclet number
(N.T.U)a	Apparent number of transfer units
(N.T.U)m	Measured number of transfer units
(N.T.U)t	True number of transfer units
N_p	Power number
n	Rotor speed, number of stages, number of moles, order of reaction
P	$\frac{DV}{uh_c}$ in Eq.4.10
P	Energy input
ΔP	Pressure drop
Pe	Peclet number
Q,q	Volumetric flow rate
Q_m	Mass flow rate
R	Disc diameter or extraction rate per unit area
R'	Extraction rate per unit volume
Re	Reynold's number
Rr	Phase ratio at inversion
r	Drop radius, disc radius, reaction rate or hold-up in Eq.7.41, distance in Eq.7.56
S	Cross-sectional area, stator diameter in the R.D.C.
S_o	Constant surface area

S_t or $S(\tau)$	Variable surface area
S_{drc}	Solute transferred per drop
Sc	Schmidt number $\frac{\mu}{D\rho}$
Sh	Sherwood number $K_L d/D$
T	Total number of drops, temperature
t	time
t_c	Circulation time
U,u	Phase velocity, or disc radial velocity
u*	Slip velocity
$\bar{u}_m$	Mean radial velocity of liquid along wall
U_t	Terminal velocity
V	Velocity
V_n	Characteristic drop velocity
V	Volume, molar volume
v	Coalescence frequency, velocity, drop volume, disc circumferential velocity, velocity scale of turbulence
We	Weber number $N^2D^3\rho/\sigma$
w^*	Critical approach velocity
w,w'	Oscillation frequency, angular velocity, axial velocity component
w	Mass fraction in Eq.7.42
X	Dimensionless concentration of reactant B
x,x^o	Concentration of reactant B in bulk
x_o	Inlet concentration of reactant B
x_i	Interfacial concentration, inversion hold-up
x,x_d	Dispersed phase hold-up
x	Solute concentration, distance

y, y^o	Concentration of reactant A in bulk of phase containing reactant B
y_i	Interfacial concentration of reactant A
y_ω	Solubility of reactant A in pure water
y^*	Solubility of reactant A in phase containing B, concentration of dissolved A at interface in equilibrium with A at interface.
Y	Probability density function
Z	Coalescence coefficient
z	Number of moles of reactant B reacting with each mole of A, h/h_c in Eq.4.10

Greek Letters

α	Major axis of an oscillating drop, back flow coefficient, partition coefficient in Eq.7.40
α	$\frac{mG}{L}$ in Eq.7.42 and $K_G a(mx-y)$ in Eq.7.43
β	Minor axis of an oscillating drop
β	$\frac{S\rho K_1}{L}$ in Eq.7.42 and $K_\omega as(1-y-nu)$ in Eq.7.43
γ	Surface tension, kinetic viscosity
γ	$\frac{K_E aS}{G}(\alpha-1)$ in Eq.7.42 and $(K_1 s\rho^2/\omega)\lvert uZ-x(1-z-x-u)/K\rvert$ in Eq.7.43
γ_1	Break-up coefficient
γ_2	Coalescence coefficient
δ_i	$\frac{fy}{\varepsilon}\frac{1}{\gamma_i} - (1-\varepsilon)\frac{(H.T.U)_t}{(H.T.U)_m}$ in Eq.4.37
ε	Amplitude of oscillation, Energy input per unit mass, Extraction factor
ε_o	$\varepsilon + (3/8)\varepsilon^2$

ξ	Dimensionless time, dimensionless concentration
	Microscale of turbulence
U	Viscosity
θ	Time
θ_c	Time between coalescence
λ_n	Eigen value, constant in Eq.6.13 and 6.14
λ	Constant in Eq.4.10
λ	$\frac{\gamma-\beta+\alpha\beta}{\gamma}$ in Eq.7.42
ρ	Density
σ	Interfacial tension
τ	Residence time, dimensionless time
ν	Kinematic viscosity
ψ	Rate of drop formation
ϕ	Enhancement factor, Hold-up
ϕ_1	Enhancement factor for a first order reaction
ϕ_i	Enhancement factor when rate is instantaneous
ω	Angular velocity
ψ	A function

Subscripts

c	Continuous phase, coalescence, column
A	Refers to phase A
B	Refers to phase B
av	Average
CD,c	Circulating drop
Crit	Critical
d,D	Dispersed

dr	Drop
e,E	Extract
F	Formation
f	Flooding, final, feed, formation
H.B	Harkin-Brown
h	Hold-up
i	Interfacial, initial, inside, I^{th} stage
k	Kinetic
m	Mean
Min	Minimum
Max	Maximum
o	Out, outside, inlet
o,OD	Oscillating drop
O.C	Overall value with respect to continuous phase
o.m	Overall mean
R	Raffinate
p	Particle
S	Solute, solvent, stagnant, slip
SD,s	Stagnant drop
s.d	Stable drop
vs	Refers to mean value
x	Refers to x phase
y	Refers to y phase
1	Refers to initial condition
2	Refers to final condition
ω	In the vicinity of column wall
BW	Reactant B in W-phase
AW	Reactant A in W-phase

BI	Reactant B in I-phase
AI	Reactant A in I-phase

Supercripts

o	Bulk condition
*	Equilibrium condition

REFERENCES

1. Hanson, C., Hughes, M. A., and Marsland, J. G., I.S.E.C. 1974, 3, 2401, Lyon (1974).
2. Rietema, K., Chem. Eng. Sci., 8, 103, (1958).
3. Danckwerts, P. V., 'Gas -liquid reactions', McGraw Hill, N.Y., (1970).
4. Paper Nos. 20, 40, 53, 87, 98, 135, 146, 147, 179, 183, 190, 208, Vol. I, I.S.E.C. 1971, The Hague,(1971).
5. Paper Nos. 59, 63, 132, 135, 183, 190, 192, 208, Vol. III, I.S.E.C. 1971, The Hague, (1971).
6. Paper Nos. 15, 49, 67, 107, 125, 126, 127, 131, 137, Vol. I, I.S.E.C. 1974, Lyon, (1974).
7. Paper Nos. 2, 14, 94, 129, 181, 228, 201, 246, 213, 257, 220, 187, 252, Vol. II & III, I.S.E.C. 1974, Lyon, (1974).
8. Trambouze, P., et. al., A. I. Ch. E. Jour., 6, 574, (1960).
9. Hanson, C., et. al., Chemy Ind., 675, (1966).
10. Gillespie, R. J. and Millen, D. J., Q. Rev. Chem. Soc., 2, 277, (1948).
11. Albright, L. F. and Hanson, C., Paper 26A, presented at 64th National Meeting, A. I. Ch. E., New Orleans, U.S.A., (1969).
12. Chaudhry, M.S.K.: M.Sc. Thesis, University of Bradford, (1970).
13. Albright, L. F., Chem. Eng., Albany, 73(14), 119, (1966).

14. Li, K. W. et. al., Paper presented in Division of Petroleum Chemistry, A.C.S. Meeting, N.Y., (1969).

15. Jeffreys, G. V. et. al., Trans. Instn. Chem. Engrs. 39, 389, (1961); Jenson, V. G. and Jeffreys, G. V., I. Chem. E. Symposium Series, No. 23, Instn. Chem. Engrs., (1967).

16. Scibona, G. et. al., J. Phys. Chem., 70, 3403, (1966).

17. Mansoori, G. A. and Madden, A. J., A.I.Ch.E.-JL, 15, 245, (1969).

18. I. M. I. Process, cited in 'Liquid-Liquid extraction with chemical reaction' by Hanson, C., in Hanson, C. (ed.), "Recent advances in liquid-liquid extraction", Pergamon, (1971).

19. Logsdail, D. H., and Lowes, L., 'Industrial Contacting Equipment' in Hanson, C(ed.), "recent advances in liquid-liquid extraction", Pergamon, (1971).

20. Hanson, C., Brit. Chem. Eng., 10, 1, 34, (1965).

21. Mumford, C. J., Brit. Chem. Eng., 13, (7), 981, (1968).

22. Salem, A. S. H., Ph.D. Thesis, University of Aston, U.K., (1975).

23. Reman, G. H. and Van der Vusse, J. G., Pet. Refiner, 34, 9, 129, (1955).

24. Misek, T., Chem. Eng., 68, 58, (1961).

25. Marek, J., Misek, T., and Windmer, F., Soc. Chem. Ind. Symp., University of Bradford, U.K., 31st Oct. (1967).

26. Oldshue, J. Y., and Rushton, J. H., Chem. Eng. Progr., 48, 297, (1952).

27. Simonis, H., Process Eng., Nov., 110, (1972).

28. Scheibel, E. G., U.S. Pat., 2,493, 265, (1950).

29. Marek, J., Mišek, T., Soc. Chem. Ind. Conf. on Solvent extraction, London, 27th March, (1969).

30. Kuhni, A. G., Verfahrens Technik and Apparateban, CH-4123, Allschwuil-Basel, Schweiz.

31. Shell Internationale research, Maatschoppig, N.V., Belgian Pat. 632926, 28th Nov, (1963).

32. Treybal, R.E., 'Liquid extraction', 2nd. Ed., McGraw Hill, (1963).

33. Thornton, J. D.,Trans. Instn. Chem. Engrs., 35, 316, (1957).

34. Coggan, G. C., Instn. Chem. Engrs., Symp. on Liquid-Liquid Extraction, April, (1967).

35. Podbielniak Inc., Division of Dresser Industries (G.B.) Ltd., London.

36. Eisenlohr, H., Ind. Chemist 27, 271, (1951).

37. Eisenlohr, H. and Scharlan, A., Pharm. Ind., 17, 207, (1955).

38. Jacobson, F. M. and Beyer, G. H., A.I.Ch.E.Jour.,2, 283, (1956).

39. Rietema, K. and Meyerinck, R., Chem. Eng. Japan, 26, 615, (1962).

40. Arnold, D. R., Ph.D. Thesis, University of Aston, U.K., (1974).

41. Dykstra, J., et. al., Ind. Eng. Chem., 50, 161, (1958).

42. Gutison, R. A., et. al., Chem. Eng. Prog. Symp. Series, No. 39, 58, (9), 8, (1959).

43. Lightnin' Mixers Ltd., Poynton, Stockport, Cheshire (U.K.), Sales Literature.

44. Bibaud, R. E., and Treybal, R. E., A.I.Ch.E. Jnl., 12, 472, (1966).

45. Brink, A. A., and Gericke, J. J., S. African Ind. Chemist, 18, 11, 152, (1964).

46. Westerterp, K. R. and Landsman, P., Chem. Eng. Sci., 3, 55, (1954).

47. Reman, G. H. and Olney, R. B., Chem. Eng. Prog., 51, 141, (1955).

48. Kung, E. Y., and Beckmann, R. B., A.I.Ch.E. Jnl., 7, 319, (1961).

49. Logsdail, D. H., et. al., Trans. Instn. Chem. Eng., 35, 301, (1957).

50. Strand, C. P., et. al., A. I. Ch. E. Jnl., 8, 525, (1962).

51. Misek, T., Rotacni Diskove Extraktory, Statni Nakadelstri Literatury, Prague, (1964).

52. Jeffreys, G. V., Chemical Eng. Practice, Vol. 9, Ed. Cremer and Watkins, Butterworths, London, (1965).

53. Reman, G. H., Proc. 3rd. World Petrol Congress, Hague, Section III, 1951, 121 and U.S. Patents 2,601, (1952); 2,729, 545, (1956); 2,912, 310, (1959).

54. Mumford, C. J., Ph.D. Thesis, University of Aston, U.K., (1970).

55. Al-Hemeri, A. A. A., Ph.D. Thesis, University of Aston U.K., (1973).

56. Misek, T,. Cool. Czech. Chem. COmm., 28,426, 570, 1631, (1963).

57. Misek, T. Call. Czech. Chem. Comm., 29, 2086, (1964).

58. Resnick, W., Paper presented to 3rd Int. Congr. on CHem. Eng., Marianske Lanze, (1969).

59. Rozkos, B., Research Rep. 918/69, VUCHZ Praha.

60. Rod, V., Brit. Chem. Eng., 16, 617, (1971).

61. Reman, G. H., Joint Symp - The Scaling-up of Chem. Plant and Processes, Instn. CHem. Engrs., 26,(1957); and Pet. Ref., 36, 9,269, (1967).

62. Schleicher, C. A., A.I.Ch.E. Jnl., 5, 145, (1959).

63. Groothuis, H., and Kramers, H., Chem. Eng. Sci., 4, 17 (1955).

64. Stemerding, S., et. al., Chemie Ingr. Tech., 35, 844, (1963).

65. Westerp, K. R., and Landsman, P., Chem. Eng. Sci., 17 , 363, (1962).

66. Misek, T. Paper presented at 2nd Chisa Congress, Marienbad, Czechoslovakia, (1965).

67. Miyauchi, T., et. al., A.I.Ch.E. Jnl., 12, 508, (1966).

68. Misek, T. and Roskos, B., Int. Chem. Eng., 6,130, (1966).

69. Olney, R. B., A.I.Ch.E. Jour, 10, 827, (1964).

70. Bruin, J. S., et. al., Paper 100, I.S.E.C.'74, Lyon, (1974).

71. Borrel, A., et. al., Paper 140, I.S.E.C., '74, Lyon, (1974).

72. Gutoff, E. B., A.I.Ch.E. Jnl., 11, 4,712, (1965).

73. Ingham, J., Paper presented to 3rd International Congress on Chem. Eng., Marianske Lazne, Sept. (1969).

74. Bouyatiotis, B. A., and Thornton, J. D., Instn. Chem. Engrs. Symp. Series, No. 26, (1967).

75. Hartland, S., and Mecklenburg, J. C., Chem. Symp. Series, No. 26, 115, (1967).

76. Misek, T., Chapter in 'Recent advances in liquid-liquid extraction', Hanson, C. (ed.), Pergamon, (1971).

77. Haug, H. F., A.I.Ch.E.Jnl., 17, 585, (1971).

78. Ingham, J., Trans. Instn. Chem. Engrs., 50, 372,(1972).

79. Lelli, U., et. al., Chem. Eng. Sci., 27, 1109, (1972).

80. Angelo, J.B., et. al., A. I. Ch. E. Jour., 12,571, (1966).

81. Hinze, J. O., A.I.Ch.E.Jour., 1, 289, (1955)

82. Kolmogorov, A. N., Doklady Acad. Nank, S.S.S.R., 30, 301, (1941); 66, 825, (1949).

83. Sitaramyya, T. and Laddha, G. S., Chem. Eng. Sci., 13, 263, (1960).

84. Shinnar, R. and Church, J. M., Ind. Eng. Chem., 52, 3, 253, (1960).

85. Roger, W. A., et. al., Chem. Eng. Prog., 52, 515,(1956).

86. Vermeulen, T., et. al., Chem. Eng. Prog., 51, 85F,(1955).

87. Calderbank, P. H., Trans. Instn. Chem. Engrs., 36, 443, (1958).

88. Giles, J. W., et. al., Proc. I.S.E.C.'71, The Hague, (1971).

89. Jeffreys, G. V. and Mumford, C. J., Paper presented at the 3rd CHISA Congress, Marianske Lazne, Sept. (1969).

90. Thomas, R. and Mumford, C. J., Paper presented at I.S.E.C., The Hague,(1971).

91. Thornton, J. D., I.Ch.Eng.Symp. Series, Nos. 26, 73 and 80, (1967).

92. Jeffreys, J. D., and Mumford, C. J., Paper presented at I.S.E.C., The Hague, (1971).

93. Levich, V. G., 'Physicochemical Hydrodynamics', Prentice Hall, New Jersey, (1962).

94. Jeffreys, G. V. and Davies, G. A., 'Recent advances in liquid-liquid extraction', C. Hanson(ed.), Pergamon Press, N.Y., (1971).

95. Jeffreys, G. V. and Lawson, G. B., Trans. Instn. Chem. Engrs., 43, T294, (1965).

96. Charles, G. E., and Mason, S. G., J.Coll.Sci., 15, 105, (1960).

97. Lawson, G. B., Ph.D. Thesis, Univ. of Manchester, (1967).

98. Davies, G. A., et. al. I.S.E.C., The Hague, (1971).

99. Davies, G. A., and Jeffreys, G.V., Filtration and Separation, Sept/Oct, 546, (1970).

100. Jeffreys, G. V., et. al., I.S.E.C., The Hague, (1971).

101. Jeffreys, G. V. and Hawkesley, J. L., J.Appl.Chem., 12, 329, (1962).

102. Elton, G. A. and Picknett, R. G., Proceedings of the 2nd International Congress on Surface Activity, Vol.1., 288-307, Butterworths, London, (1957).

103. Hitit, A., Ph.D. Thesis, Univ. of Aston, U.K., (1972).

104. Howarth, W. J., Chem.Eng.Sci., 19, 33, (1966).

105. Madden, A. J. and Damarell, G. L., A.I.Ch.E.Jour., 8, 233. (1962).

106. Davies, J. T., et. al., Trans. Instn. Chem. Engrs., 38, 331, (1960).

107. Quinn, J. A. and Sigloh, D. B., Can. J. Chem. Eng., 41, 15, (1963).

108. Luhning, R. W. and Sawistowski, H, Proc. I.S.E.C., '71, S.C.I., The Hague, (1971).

109. Selker, A. H., and Schleicher, C. A., Jnr.Can.J. Che. Eng., 17, 298, (1965).

110. Isemura, et. al., Memo. Inst. Sci. Res., Osaka, Univ., 6, 54-62, (1948).

111. Becher, P., J. Soc. Cosmetic Chemists, 9, 141, (1958).

112. Roger, W. A., et. al.,Chem. Eng. Prog., 52, 515, (1956).

113. Maclarey, M. J. and Mansoori, G. A., Paper presented to 79th Annual Meeting of A.I.Ch.E. in Houston, Texas, March, (1975).

114. Perry, R. H. and Chilton, C. H., "Chemical Engineers', Handbook", 5th Ed., McGraw-Hill, N.Y., (1973).

115. Yeh, G. C., et. al., A.I.Ch.E.J., Vol. 10, No.2., March, 260, (1964).

116. McSween, D., B.Sc. Project, Univ. of Aston, (1976).

117. Sherwood, T. K., et. al., Ind. Eng. Chem., 31, 1144, (1939).

118. Heertjes, P. M. and Holve, W. A., Chem. Eng. Sci., 3, 122, (1954).

119. Sawistowski, H. and Goltz, G. E., Trans. Instn. Chem. Engrs., 41, 174, (1963).

120. Licht, W., and Pansing, W. F., Ind. Eng. Chem., 45, 1885, (1953).

121. Coulson, J. H. and Skinner, S. J., Chem. Eng. Sci., 1, 197, (1951).

122. Heertjes, P. M. and de Nie, L. H., Chem. Eng. Sci., 21, 755, (1966).

123. Ilkovic, D., Colln. Czeck, Chem. Comm., 6,498,(1934).

124. Skelland, A. H. P. and Minhas, S. S., A.I.Ch.E. Jour., 17, 1316, (1971).

125. Popovich, A. T., et. al., Chem. Eng. Sci., 19, 357, (1964).

126. Newman, A. B., Trans. Am.Inst. Chem. Engrs., 27, 310, (1931).

127. Kronig, R. and Brink, J. C., Appl. Scient. Res. A2, 142, (1960).

128. Handlos, A. E. and Baron, T., A.I.Ch.E.Jour. 3, 127, (1957).

129. Rose, P. M. and Kintner, R. C., A.I.Ch.E.Jour., 12, 530, (1966).

130. Olander, D. R., A.I.Ch.E.Jour., 12, 1018, (1966).

131. Linton, M. and Sutherland, K. L., Chem. Eng. Sci., 12, 214, (1960).

132. Rowe, P. N., et. al., Trans. Instn. Chem. Engrs., 43, 14, (1965).

133. Kinard, G. E., et. al., Brit. Chem. Eng., 8, 326, (1963).

134. Heertjes, P. M. and de Nie, L. H., 'Mass transfer to drops', "Recent Advances in Liquid-liquid extraction", C. Hanson (ed), Pergamon, N.Y., (1971).

135. Garner, F. H. and Tayeban, H., An. R. Soc. Esp. Fis. Quim., 56B, 479, (1960); and Garner, F. H., and J. J. Lane, Trans. Instn. Chem. Engrs., 37. 162, (1959).

136. Hughmark, G. A., Ind. Eng. Chem. Funds., 6, 408, (1967).

137. Mok, Y. I. and Treybol , R. E., A.I.Ch.E.Jour., 17, 916, (1971).

138. Thorsen, G. et. al., Chem. Eng. Sci., 23, 413, (1968).

139. Forsyth, J. S., et. al., I.S.E.C.'74, Vol. 1, 417, Lyon, (1974).

140. Sawistowski, H. and Ying, W. E., Proc. I.S.E.C.'71, The Hague, (1971).

141. Nekobar, P. and Vacek, V., I.S.E.C.'74, VOl-2, 1047, Lyon, (1974).

142. Marangoni, C., Annln, Phys., 143, 337, (1871).

143. Sternling, C. V. and Scriven, L. E., A.I.Ch.E. Jour., 5, 514, (1959).

144. Maroudas, N. G. and Sawistowski, H., Chem. Eng. Sci., 19,919, (1965).

145. Marsh, et. al., Paper presented at 57th Annual Meeting, A.I.Ch.E., Philadelphia, (1965).

146. Austin, L. J. et. al., Chem. Eng. Sci., 21, 1109,(1966).

147. Sawistowski, H. and James, B. R., Proc. 3rd int. conf. Surface-active mater, 757-772, Berlin:Akademic-Verlag, (1967).

148. Atagunduz, et. al., Chemie-Ingr.-Tech., 40, 922, (1968).

149. Groothuis, H. and Zwiderweg, F. J., Chem. Eng. Sci., 12, 288, (1960).

150. Sawistowski,H., 'Recent advances in solvent extraction', edited by Hanson, C., Pergamon, (1971).

151. McFerrin, A. R. and Davidson, R. R., A.I.Ch.E. Jour., 17, 1021, (1971).

152. Johnson, A. I. and Hamielec, A. E., A.I.Ch.E. Jour., 6, 145, (1960).

153. Licht, W. and Conway, J.B., Ind.Eng.Chem., 42, 1151, (1950).

154. Heertjes, P. M. and de Nie, L. H., Chem. Eng. Sci., 26, 697, (1971).

155. Astarita, G., 'Mass Transfer with chemical reaction,' Elsevier, 1967.

156. Sherwood, T. K., and Pigford, R. L., 'Absorption and extraction', McGraw-Hill, (1952).

157. Van Krevelen, D. W. and Hoptizer, P. J.: Rec. Trav. Chim. 67, 563, (1948).

158. Yeramian, A. A. et. al., J. Chem, Eng. Sci., 25, 1622, (1970).

159. Hikita, H. and Asai, H, Intern. Chem. Eng., 4,5,(1964).

160. Hatta, S.: Technol.Repts. Tohoku Imp. Univ., 10, 119, (1932).

161. Flett, D. S., et. al., J. Inorg. Nucl. Chem., 35, 2471, (1973).

162. Flett, D. S., et. al., Paper presented to I.S.E.C.'74, Vol. 3, 2559, Lyon, (1974).

163. Rydberg, J., Acta. Chem. Scand., 23, 647, (1969).

164. Ryon, A. D. and Johnsson, K.O., ORNL-2213, (1956).

165. Alimarin, I. P., et. al., Pure, Appl. Chem., 25(4), 667, (1971).

166. Spink, D. R. and Okuhara, D. N., Paper presented to I.S.E.C'74, Vol. 3, 2527, Lyon, (1974).

167. Murdoch, R. and Pratt, H. R. C., Tran. Inst. Chem. Engrs., 31, 307, (1955).

168. Lewis, J. B., Chem. Eng. Sci., 3, 248, (1954).

169. Lewis, J. B., Chem. Eng. Sci., 3, 260, (1954).

170. McManamey, W. J., Chem. Eng. Sci., 15, 210, (1961).

171. Tyroler, G. et. al., Canadian Jour. Chem. Eng. p.56, Vol. 49, (1971).

172. Watada, H., Ph.D. Thesis, McMaster Univ.,,Hamilton, Ontario, (1968).

173. Nakashio, F. et. al., Proc. Int. Solvent. Extraction Conf., Vol. II, 831, (1971).

174. Wellek, R. M. and Brunson, R. J., Canadian Jour.Chem. Eng., Vol. 53, April, (1975).

175. Abramzon, A. A. and Kogan, N. A., J. Appl. Chem. (USSR); 36, 1949, (1963).

176. Lewis, J. B., Chem. Eng. Sci., 8, 295, (1958).

177. Davis, J. T., and Mayers, G. R. A., Chem. Eng. Sci., 16, 55, (1961).

178. Mansoori, G. A. and Madden, A. J., A.I.Ch.E. Jl., 15,245, (1969).

179. Searle, R. and Gordon, K. F., A.I.Ch.E. Jl., 3, 490, (1957).

180. Sherwood, T. K., and Wei, J. C., A.I.Ch.E. Jl, 1, 522,(1955).

181. Sharma, M.M. and Nanda, A.K., Trans. Instn. Chem. Engr., 46, 51, (1968).

182. Nanda, A. K. and Sharma, M. M., Chem. Eng. Sci., 22, 769, (1967).

183. Nanda, A. K., and Sharma, M.M., Chem. Eng. Sci., 21, 707, (1966).

184. Trambouze, P. J. and Piret, E. K., A.I.Ch.E. Jl., 6, 574, (1960).

185. Trambouze, P.J., et. al., A.I.Ch.E. Jl, 7, 138,(1961).

186. Law, C., M.Sc. Project, Univ. of Aston, U.K., (1975).

187. Koen, C. G. and Trambouze, P. J., Chem.Eng. Sci., 20, 141, (1965).

188. Cho, D. H. and Ranz, W. E., Chem.Eng. Prog. Symp. Series, 63 (72), 37 and 46, (1967).

189. Giles, J. W., Ph.D. Thesis, Univ. of Bradford, U.K., (1970).

190. Ismail, H. A. M., Ph.D. Thesis, Univ. of Bradford, U.K., (1973).

191. Cox, P. R. and Strachan, A. N., CHe. Eng. Sci., 27, 457, (1972) and I.S.E.C.'74, Vol. 3, 2415, Lyon, (1974).

192. Trambouze, P. J., et. al., A.I.Ch.E.Jl., 7, 138,(1961).

193. Jeffreys, G. V., et. al., Trans. Instn. Chem. Engrs., 39, 389, (1961).

194. Jenson, V. G., Jeffreys, G. V., and Edwards, R. E., Proc. 36th Internat. Cogr. Ind. Chem., Brussels, T32, VOl. 3, (1967).

195. Bruin, J. S., et. al., Paper 100, I.S.E.C.'74, Lyon, (1974).

196. Roddy, J. W. and Colman, C. F., Solvent Extraction Reviews, 1, 63, (1971).

197. Baumgartner, F. and Finsterwalder, L., J. Phys. Chem., 74 (1), 108, (1970).

198. McManamey, W. J., Ph.D. Thesis, Univ. of Sydney, (1959).

199. Nitsch, W., Dechema Monograph, 55, 143, (1965).

200. Farbu, L., et. al, I.S.E.C.'74, Vol. 3,2427, Lyon,(1974).

201. Mc.Kay, H.A.C. and Rees, D., AERE-C/R-1199, (1953).

202. Kothari, P.J. and Sharma, M. M.,Chem. Eng. Sci., 21, 391,(1966).

203. Danckwerts, P. V., Appl. Sci. Res., A3, 279, (1953).

204. Rietema, K., 'Advances in chemical Engg, Vol. 5, 237, Academic Press, N.Y., (1964).

205. Curl, R. L., A.I.Ch.E. Jour., 9, 175, (1963).

206. Vanderveen, J. H., Lawrence Radiation Lab., Rept., U.C.R.L. 8733, Univ. Calif., Berkley, (1960).

207. Harada, M., et. al., Mem. Foc. Eng., Kyoto Univ., 24(4), 431, (1962).

208. Veltkamp, G. W., Cited in Reference 204.

209. Spielman, L. A., Masters Thesis, Illinois Inst. of Technology, (1963).

210. Matsuzawa, H. and Miyauchi, T., Chem. Eng. (Tokyo), 25, 582, (1961).

211. Miller, et. al., A.I.Ch.E.Jour., 9, 196, (1963).

212. Groothuis, H. and Zuiderweg, F. J., Chem. Eng. Sci., 19, 63, (1964).

213. Komasawa, I. et. al., Jour. Chem. Eng. of Japan, Vol. 4. No. 4., 19, (1971).

214. Kenneth, et. al., I. and E.C. Fundamentals, Vol. 5., No. 4, 533, (1966).

215. Leimu, R. et. al., Acta. Che. Fenn, 19B, 93, (1964).

216. Tommila, E. and Sternberg, H., Acta, Chem. Fenn., 19B, 19, (1946).

217. Browning, E., Toxicity and Metabolism of Industrial Solvents, Elsevier, (1965).

218. Wilke,C. R., and Chang, P., A.I.Ch.E. Jour, 1,264,(1955).

219. Eames, W., The Elementary Theory of numbers, polynomials and rational functions,' Oldbourne, London.

220. Hossain, K. T., Ph.D. Thesis, Univ. of Aston, U.K., (1976).

221. Marchant-Williams, R. G., cited in Logsdail, D. H. and Thornton, J. D., Trans. Instn. Chem. Engrs., Vol. 35, 338, (1957).

222. Clayton, W., 'The theory of emulsions and their technical treatment', 4th Ed., J. and A. Churchill Ltd., London. (1943).

223. Smoluchowski, M., Z. Phys. Chem., 1917, 92, 129.

224. Long, F. A., and McDevit, W. F., Chem. REv., 51, 119, (1952).

225. Van Krevelen, D. W., and Hoftizer, P. J., Chim. Ind., 41, 168, (1948).

226. Van Krevelen, D. W., and Hoftizer, P. J., 'Sur la solubilite des gaz dans les solutions aqueuses', Inst. Chim. Ind., 21st Congress, (1948).

227. Wilde, J. D. and Beightler, S. C., Foundation of Optimisation, Prentice-Hall, (1967).

228. Wehner, J. F., and Wilhelm, R. H., Chem. Eng. Sci., 6, 89, (1956).

229. Cooper, A. R. and Jeffreys, G. V., Chemical kinetics and reactor design, Oliver and Boyd, Edinburgh, (1971).

230. Sharma, M. M. and Danckwerts, P. V., Br. Chem. Eng., 15, 522, (1970).

231. Brian, P. L. T., et. al., A.I.Ch.E. Jour., 7,226, (1961).