STUDY OF LIQUID-LIQUID EXTRACTION
WITH SIMULTANEOUS CHEMICAL REACTION

by

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TO MY WIFE

SUMMARY

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A study has been made of liquid-liquid extraction with chemical reaction in a laboratory reactor and a rotating disc contactor. The esterification of n-butyl alcohol with acetic acid in the presence of sulphuric acid as catalyst and n-heptane as solvent was chosen for the study and the work was divided into four main areas, (i) The study of esterification kinetics for concentrated reactants and catalyst without solvent; (ii) Study of solutes distribution in multi-component two phase liquid-liquid systems; (iii) Study of the esterification reaction in the presence of n-heptane; (iv) Studies in the R.D.C.

A comprehensive literature survey on mass transfer with simultaneous chemical reaction and relevant phenomena, such as mass transfer in non-reacting systems and liquid equilibria has been made. The literature regarding liquid-liquid extraction equipment and R.D.C's operation was also reviewed.

The esterification of butanol at room temperature was feasible, when the reactants and catalyst were in concentrated form and a correlation has been derived for the reaction rate constant in terms of the catalyst and water concentrations.

Equilibrium data for the various ternaries and quaternaries, constituting the extractive-reactive system, were experimentally determined and the data for three component systems were correlated on the basis of Hand's formula. The two types of quaternary systems, viz the single and double binaries quaternaries were extensively studied and algebraic equations derived for both types. These equations are believed to be the first algebraic representation of distributions in liquid-liquid quaternary systems.

Batch esterification in the presence of n-heptane showed that a reversible reaction can go to completion by continuous removal of one of the products, as it is formed, by liquid extraction. A computer program was developed for predicting the conversion in the extractive-reactive system.

Studies in the R.D.C. showed that phase inversion phenomenon of the n-heptane/water system was unlike phase inversion so far described by research workers for other systems. Another interesting phase inversion phenomenon occurred when two solutes were transferred simultaneously in opposite directions. Both of these phenomena were explained, and recorded by cine films. The extraction-reaction process in the R.D.C. proved the R.D.C. to be a good equipment for this purpose.

Key Words:

n-BUTYL ALCOHOL ESTERIFICATION,

LIQUID-LIQUID EXTRACTION,

LIQUID EQUILIBRIA,

ROTATING DISC CONTACTOR OPERATION

PHASE INVERSION.

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CHAPTER 1

INTRODUCTION

Liquid-liquid extraction with simultaneous chemical reaction is an important operation in the chemical industry. It is similar in general aspects to other mass transfer operations involving interphase chemical reaction i.e. heterogeneous reacting systems. Whenever the components of a reaction mixture are present in more than one phase the reaction will not occur uniformly throughout the system(1). For such conditions, the rate of conversion of the reactants depends upon the flow patterns and velocities of the phases, the solubilities and diffusivities of the reactants and products as well as upon the chemical kinetics of the reaction(2).

Many heterogeneous chemical reaction processes are performed with one phase as the pure reactant which diffuses into and reacts in the other phase. On the other hand some processes involve extraction-reaction-separation where typically one of the reactants is dissolved in an organic solvent, immiscible with water; while the second reactant is in aqueous solution. The object of this research is the investigation of a reaction of the latter type.

One approach to the study of reactions in liquid-liquid systems has been the application of the hydrodynamic models of the gas-liquid interface discussed in Section (2.3.1) to the general theory of simultaneous diffusion and chemical reaction as in Section (3.1). However, liquid-liquid systems possess some peculiar characteristics due to interactions between drops of the dispersed phase(4,5). Attempts have been made to account for these characteristics by considering the effect of segregation in liquid-liquid systems. This is discussed in Section (3.2.5).

On the other hand, liquid-liquid systems have been studied on the basis of two distinct liquid phases, one dispersed and the other continuous. Consideration is given to the diffusion of the reactive species to a reaction zone, or to an interface and diffusion of the product to the selective phase, 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 of an infinitely fast reaction it may reduce to a reaction plane.

Reactions in liquid-liquid systems are controlled by both the kinetics of the reaction and the diffusional characteristics of the system. Under certain circumstances, a process may be either entirely diffusion controlled or kinetically controlled. Hence some classical examples of liquid-liquid reactions have been treated either as simple mass transfer operations, when the rate of the chemical reaction is extremely rapid compared with the rate of transfer between the two phases e.g. in most metal extraction processes; or as simple chemical reactions notably aromatic nitrations and alkylations for which the mass transfer rates are relatively much larger than chemical reaction rates. Another group of reactions in liquid-liquid systems usually referred to as "extractive reactions" comprises the various organic reactions carried out in the presence of a solvent; e.g. hydrolysis of esters in alkaline solutions and the hydrolysis of animal fats and vegetable oils. Neither the chemical reaction rate nor the mass transfer rate controls the overall rate of conversion. Early attempts at analysing these reactions were based on graphical methods(234,235). However, the advent of digital computers has made the solution of the differential equations describing the diffusion, according to the various gas-liquid interface models, and the accompanying chemical reactions possible. Various numerical techniques have further simplified the explicit reaction rate equations to simple implicit ones(326), and this has facilitated greatly the application of these equations. The computer has been utilised further in directly following the course of liquid-liquid reactions, a technique pioneered by Jeffreys and co-workers(150) in the study of hydrolysis of animal fats and vegetable oils. It appeared worthwhile to apply this technique to a "true" extractive reaction where typically one reactant is in water and the second one in an organic solvent.

It was recognised at the outset that difficulties would arise since;

(a) The various geometrical methods available in the literature for the representation of distributions in multicomponent two phase liquid-liquid systems are unsuitable for numerical computation and algebraic equations were not available. Therefore the study would have to be restricted to dilute reacting systems, where it is usually assumed that the distribution of two solutes is independent of each other, or a mathematical distribution model would have to be developed.

(b) The distribution of reactants/products in the extractive/reactive system will have to be such that the reaction can take place in one phase only or the reaction kinetics will have to be studied for both phases.

(c) However slow the reaction may be, there can be no guarantee that mass transfer effects can be completely ignored particularly if the reaction is reversible in which case slow extraction of the product from the reactive phase can initiate partial reversability. Therefore the

(c) contd.

numerical computation technique may have to take into consideration this mass transfer effect.

(d) Mass transfer rate is greatly influenced by the physical properties of the system; in particular the creation of new species by chemical reaction may cause interfacial disturbances, the magnitude of which and influence on mass transfer may be unpredictable.

(e) The interfacial area is also influenced by physical properties of the system and application of the various laws, predicting droplet sizes in turbulent flow, may not give the required accuracy due to the changing physical properties.

In the event an attempt has been made to study an extractive reaction using a laboratory reactor and a pilot plant scale rotating disc contactor. The esterification of butyl alcohol-acetic acid was selected as the system for study and a model was built systamatically on the basis of experimentally determined correlations or well established formulae previously published.

The experimental work undertaken in the R.D.C. started with hydrodynamic and mass transfer studies to determine equipment and system characteristics. Arising incidentally from this work two interesting phase inversion phenomena were recorded and explained.

CHAPTER 2

FUNDAMENTALS OF THE MASS TRANSFER PROCESS

Any multiphase system, not at equilibrium, will be altered spontaneously until it reaches a state of equilibrium where the temperature and the chemical potential of each component is the same throughout. When the temperature is constant, the chemical potential of any substance is related to its concentration, and spontaneous migration of components results ultimately in uniform concentration of each component throughout each phase. The spontaneous approach to uniformity on a molecular scale is known as molecular diffusion. This process is normally very slow. It can be accelerated by agitation which superimposes another type of migration as a result of bulk motion or fluid convection.

The phrase "mass transfer" is used when the motion of molecules or fluid elements is caused by some form of "driving force". It includes not only molecular diffusion but also transport by convection and sometimes simple mixing(57).

2.1) Mass Transfer with Laminar Flow.

Mass transfer occurs in only a few systems in which the fluid is in laminar flow. The principal reason for this is that most mass-transfer systems contain more than one fluid phase, so that stable laminar boundary layers cannot be built up in that part of the system in which mass transfer is important(58).

However, there are situations of engineering importance where mass transfer in laminar flow is encountered. There is no mixing in laminar flow, hence transport of components is accomplished by molecular diffusion superimposed on the bulk flow at any point in the stream.

The most important case of mass transfer with laminar flow is the falling film encountered in wetted-wall gas absorbers, condensers and other process equipment. The partial differential equation describing this type of absorption is of the form:

$$(1-y^2)\ \frac{\partial c}{\partial z} = \frac{\partial^2 c}{\partial y^2} \qquad (2.1)$$

where $y = \frac{x}{\Delta}$

This equation has been solved numerically by Olbrich and others(31).

2.2) Mass Transfer in Turbulent Flow.

Mass transfer in turbulent flow is essentially a mixing process. The secondary velocities that characterise turbulent flow are random and fluctuate with both time and position. It is not possible to describe quantitatively the size and motion of the small elements i.e. eddies of fluid. Hence one approach to the study of turbulence has been statistical.

Much empirical information exists of relevance to practical engineering problems(57).

Another approach is to follow the pattern of molecular diffusion and define a diffusion coefficient as the ratio of molar flux of the species to the concentration gradient of the same species. This approach leads to an equation of the form(19):

$$J_{AT} = - \epsilon \frac{\partial c_A}{\partial z} \qquad (2.2)$$

where J_{AT} is the turbulent flux of A, and ϵ represents an eddy or turbulent diffusivity. If molecular diffusion is also considered, then:

$$J_{AT} = - (D_A+\epsilon) \frac{\partial c_A}{\partial z} \qquad (2.3)$$

$(D_A+\epsilon)$ is the total diffusivity due to both molecular and turbulent mass transport.

Various authors have determined values of eddy diffusivities for various materials diffusing in fluids flowing in pipes and flat ducts(63-65).

2.3) Mass Transfer Between Two Phases.

Liquid-liquid extraction, whether accompanied by a chemical reaction or not, involves mass transfer from one phase to another, across a phase boundary. Conditions in the immediate region of an interface are difficult to observe experimentally. In most practical situations the flow is turbulent, involving both molecular and eddy diffusions, and this makes rigorous treatment impossible. Hence in such situations mathematical models of the process are developed. These start with the known basic facts and results of mathematical analysis of the model are compared with experimental measurements. Good agreement suggests a realistic model.

2.3.1) Mathematical Models of Mass Transfer Between Two Phases.

2.3.1.1) The Two-Film Model:

This model was postulated by Whitman to explain the principles of gas absorption into a liquid$^{(6-8)}$. It is based on the assumption of stationary films of gas and liquid respectively on the two sides of the interface. It was assumed that the motion by convection of the respective phase through its film is practically zero, while in the main body of either liquid or gas, mixing by convection is so rapid that the concentration of solute in the fluid is essentially uniform at all points. The two films were assumed to be very thin so that the actual amount of solute contained in them at any one time is negligible compared to the amount diffusing through them. It follows that all the solute which passes through one film must also pass through the other, and the two films may be considered as two diffusional resistances in series.

The rate of absorption was expressed mathematically as follows:

$$N = Ak_g(C_{og}-C_{ig}) = Ak_\ell(C_{i\ell}-C_{o\ell}) \qquad (2.4)$$

Equation (2.4) was applied to the study of comparative absorption rates of widely differing solubilities(8). It was claimed that absorption rates could be predicted with an accuracy of 15% or better.

The two-film model, as developed originally by Whitman and coauthors, predicted that k_ℓ varies as the first power of diffusivity. However, other workers have subsequently postulated other correlations for k_ℓ. Thus data of Sherwood and Holloway(9) for a packed tower and of Peaceman(10) for a short wetted-wall column indicated that it varies as the square root of diffusivity.

2.3.1.2) Higbie's Penetration Model:

In 1935, Higbie(11) while studying the absorption of carbon dioxide in water, noted that the liquid-film coefficient was increased by shortening the time of exposure. This was in contradiction to the basic assumption of Whitman's film theory which stated that: "Since the surface films are very thin, the actual amount of solute in them at any one time is negligible compared to the amount diffusing through them". Higbie accepted the films theory with this "steady flow" assumption for cases where "steady flow" was for a period of contact much longer than the "penetration period". However, he challenged its validity during very short periods of exposure e.g. in cases where "surface renewal" occurs. Such conditions prevail practically under the hydrodynamic conditions in many industrial contactors.

At the instant when the gas and liquid are brought together, the liquid film is itself at the concentration of the body of the liquid, as shown by the dotted line in figure (2.1). The first stage in the absorption process is the penetration of the liquid film by the dissolved gas. The history of this in terms of successive concentration-depth curves is shown approximately by the dash-lines in figure (2.1). If the penetration process is not interrupted,

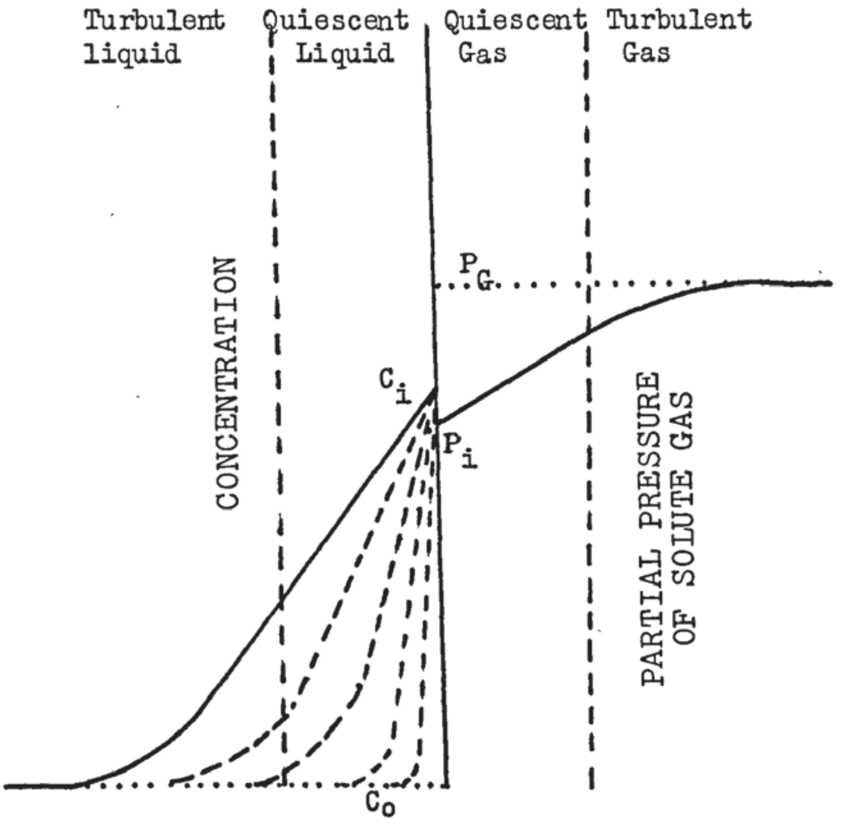


Fig.2.1 Concentration profiles at gas-liquid interface according to Higbie's penetration model(11)

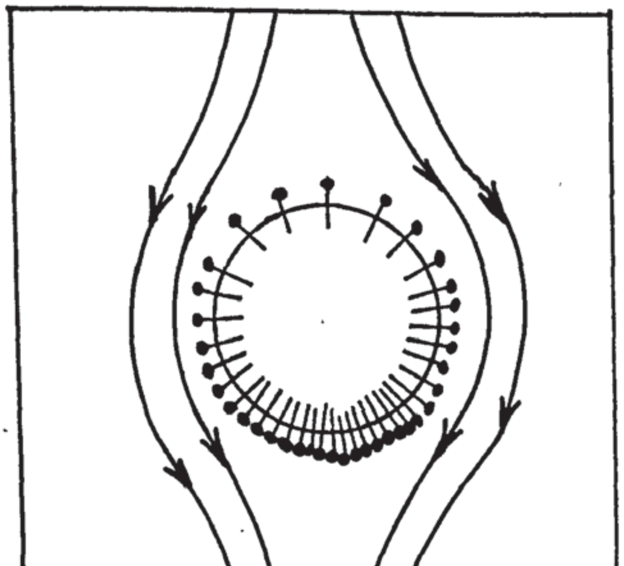


Fig.2.2 Influence of surface active agents on the internal circulation within a droplet(35).

the condition indicated by the full line is attained which does in fact correspond to the Whitman film theory. However, for the period before this condition is attained, which was termed "penetration period", the film theory is not valid.

Higbie based his mathematical derivations on Ficks Law. He derived an expression for concentration under isothermal conditions, constant diffusivity and infinite depth:

$$C = C_o + \frac{C_e - C_o}{\sqrt{\pi D t_e}} \int_x^{\infty} e^{-x^2/4Dt_e}\, dx \qquad (2.5)$$

The amount of gas absorbed up to time t_e is given by:

$$f = 2(C_e - C_o)\sqrt{\frac{Dt_e}{\pi}} \qquad (2.6)$$

and the liquid film coefficient is

$$k_L = 2\sqrt{\frac{D}{\pi t_e}} \qquad (2.7)$$

On testing the validity of equations 2.5 and 2.6, for periods of 0.01 to 0.1 seconds, Higbie found that the amount of gas absorbed consistently fell below the theoretical values. This deviation from the penetration theory was progressively greater with shorter periods of exposure which seemed to indicate an additional resistance to absorption which was especially effective for shorter periods. Higbie explained this by rejecting the usual assumption of equilibrium at the surface and assuming instead that the gas in passing through the surface undergoes a "first order process" i.e. a process whose rate is proportional to the degree of unsaturation or removal from equilibrium at the surface. Results predicted on the basis of "first-order process" fitted all data within experimental error.

2.3.1.3) Mass Transfer Coefficient and Diffusivity.

In the absence of any other resistances, the film theory predicts a first power dependence of the transfer rate on the diffusivity, and the penetration theory a square root dependence(28). However, a number of workers has shown this not to be so for a number of extractive systems.

Thus Murdoch and Pratt(20) and other workers(21-23) have shown that the solvent phase mass transfer coefficients for wetted wall columns vary approximately as the minus two-thirds power of the Schmidt number $\left(\frac{\mu}{\rho D}\right)$ i.e. it was correlated to $D^{2/3}$.

On the other hand, Lewis' data for a number of mass transfer systems(24-27) was correlated satisfactorily by a correlation between the transfer coefficients and Reynolds number and viscosities of the two phases i.e. the mass transfer coefficients were shown to be independent of D. However, a number of anomilies were found. Lewis(27) attributed positive deviations i.e. "fast" transfer rates to phenomena of interfacial turbulence. While the "slow" rates were explained by an assumed slow heterogeneous chemical reaction at the interface.

Hence, neither the film nor the penetration theories has been established as an authoritative description(19), this has promoted the development of further models.

2.3.1.4) Danckwerts Surface Renewal Model.

In 1951 Danckwerts(18) challenged the basic assumption of the "stagnant film" of liquid at the gas-liquid interface which is the main pillar of the film theory. Instead he advanced a theory based on the assumption that the surface is continually being replaced with fresh liquid. Hence the concept of an "age distribution function" was developed by Danckwerts to describe the absorption process. The average absorption, according to this concept is given by(3):

$$\overline{R} = \int_0^\infty \sqrt{\frac{D}{\pi t}}\,(C_i - C_o)\psi(t)\,dt \qquad (2.8)$$

where,

$\psi(t)dt$ = fraction of the total surface which is made up of surface elements whose age is between t and (t+dt)

$\psi(t)$ is the age distribution function and satisfies the condition:

$$\int_0^\infty \psi(t)\ dt = 1$$

Equation 2.8 cannot be integrated without assuming a specific form for the age distribution function. However, since the probability of a surface element disappearing from the surface in a given interval of time is independent of its age(18), then the rate of disappearance of surface elements of any given age is proportional to the number of elements of that age which are present, hence

$$-\frac{d\psi}{dt} = s\psi$$

$$\psi = s\ \exp(-st)$$

where s is a proportionality constant.

Substitution into equatioh 2.8 yields

$$\overline{R} = \sqrt{D\ s}\ (C_i - C_o) \qquad (2.9)$$

The quantity s has the physical meaning of a rate of surface renewal and $\frac{1}{s}$ may be regarded as an "average" life of surface elements. Values of s are not generally available(57). However, there has been some evaluations of s on the basis of experimentally determined rates of absorption. Thus Hutchinson and Sherwood(73), obtained values of s for the absorption of pure hydrogen in water. On the other hand,Lamb,Springer and Pigford(74) provided direct experimental measurement of surface renewal rate as gas absorption was occurring.

2.3.1.5) Other Models:

Toor and Marchello(28) have suggested that a combination theory, known as "film-penetration" model, which allows for both long time ($k \propto D$) and short time ($k \propto D^{0.5}$) exposure of various surface elements, may lead to better interpretation of the observed data. According to Toor and Marchello, the film and penetration theories are not separate unrelated concepts but are rather limiting cases of a more general model and the two theories, rather than being mutually exclusive, are actually complimentary.

The criteria used by Toor and Marchello is the Schmidt number. At low Schmidt numbers a steady gradient is set up very rapidly in any new surface element, so that unless the rate of renewal is high enough to remove a large fraction of the surface elements before they are penetrated, most of the surface is "old". Steady state transfer then takes place through what is essentially a film and the effect of surface renewal is negligible. As the Schmidt number increases, the time necessary to set up the steady gradient increases rapidly and even low rates of surface renewal are sufficient to keep most of the elements from being penetrated. Transfer then follows the penetration theory and the transfer rate is a function of the rate of surface renewal. When conditions are such that a surface contains appreciable quantities of young and old elements, as well as middle aged ones, the transfer characteristics are intermediate between the film and penetration types.

Subsequently, Marchello and Toor(66) modified the "film-penetration" model to include fluid elements which although in the vicinity of an interface are not necessarily adjacent to it.

Other models have been developed by various other workers, which are essentially modifications of the film or penetration models to special conditions(67-71).

The most recent model has been developed by Pincewski and

Sideman(72). This model is based on the assumption that complete fluid renewal near the wall occurs only occasionally, resulting in a thin fluid layer adjacent to the wall which is infrequently replenished. The effect of this is negligible at small Schmidt numbers but becomes increasingly important with increasing Sc.

2.4) Mass Transfer in Liquid-liquid Extractors.

The extraction process involves transfer of solute from the bulk of the raffinate phase to the interface and thence into the bulk of the solvent phase. The rate of this process depends on the resistance to diffusion, the interfacial area and the driving force(34,163). The diffusional resistance is a series resistance:

(a) inside the droplets

(b) at the interface

(c) in the liquid surrounding the droplet.

Relationships between overall and individual mass transfer coefficients have been derived on the basis of the two-film theory(172-174), to give

$$\frac{1}{K_{Gc}a} = \frac{1}{k_c a} + \frac{1}{mk_d a} + r_i \qquad (2.10)$$

$$\frac{1}{K_{Gd}a} = \frac{1}{k_d a} + \frac{m}{k_c a} + r_i \qquad (2.11)$$

if $r_i = 0$ and $m >> 1$ equation 2.10 becomes

$$k_{Gc} = k_c \qquad (2.12)$$

i.e. in this case the overall mass transfer coefficient is equal to the continuous phase mass transfer coefficient.

2.4.1) Mass Transfer Within Droplets:

When a drop is moving through the continuous phase, drag at the interface tends to set up internal circulation of the drop contents. Large drops also oscillate. Circulation increases with the droplet diameter and with the ratio of the viscosity of the continuous phase to that of the dispersed phase $^{(34,191)}$. Other factors influencing internal circulation within a drop are the interfacial tension between the dispersed and continuous phases$^{(164,165)}$, and the nature of the interface e.g. polarity or otherwise of solvent droplets in water$^{(167)}$.

Diffusion rates within the drop depend on transport both by molecular motion and fluid mixing. Very small drops are essentially stagnant, and transport is by molecular diffusion. Drops of intermediate size develop laminar toroidal internal circulation, which reduces the path length for molecular diffusion. In very large drops, the laminar circulation is replaced by what appears to be violent internal mixing, resulting from the kneading effect of drop oscillation$^{(57)}$.

2.4.1.1) The Rigid Drop:

For the rigid drop, which is a limiting case holding for small drops only, mass transfer occurs by molecular diffusion. Newman$^{(166)}$ has developed a theory for drying of porous spheres. The liquid concentration-time-locations relations, in the interior of such a sphere, while the surface is substantially dry, and evaporation takes place as rapidly as liquid can diffuse from the interior to the surface, is generally used for interpretation of mass transfer in rigid drops.

2.4.1.2) The Non-Rigid Drop:

In non-rigid drops, mixing can be by laminar and turbulent circulation. Reynolds number is generally taken as the criteria for laminar circulation within the drops. Hadamard$^{(168)}$ has shown that the liquid inside the droplet would circulate by laminar flow at Reynolds number less than 1.0. However, the work of Heertjes et al.$^{(169)}$ and Garner et al.$^{(170)}$ indicates that for up to Re = 10.0, the flow pattern is laminar. The Reynolds number at which circulation begins within the drop decreases with increasing viscosity of the continuous phase(191). For the case of complete liquid circulation inside the droplets, mass transfer amounts to 1.5 times that for rigid spheres(171). However, other workers have reported far greater increases(34).

The effect of circulation within the drop on the rate of mass transfer has been the subject of many analytical studies(175,188,189). Hadamard(168) described the flow field, and Kronig and Brink(208) applied the diffusion equation to obtain an expression for transfer rates from which the following equation was obtained for the dispersed phase mass transfer coefficient, in the absence of continuous-phase resistance(19,210)

$$k_d = \frac{17.9D}{d} \qquad (2.13)$$

Drop oscillation is to be expected in most systems if the drop Reynolds number is greater than 500 to 1000(57). Good agreement has often been found for mass transfer from drops with rapid internal circulation and oscillating drops(179-181). However, cases are known in which the effect of oscillations is much larger than the effect of circulation(190).

Rose and Kintner(178) reported that droplet oscillation causes interfacial stretch which break up internal circulation streamlines and a type of turbulent internal mixing is achieved. They developed a correlation for the mass transfer coefficient for an oscillating drop as follows:

$$k_d = 0.450\ (D\omega)^{\frac{1}{2}} \qquad (2.14)$$

The frequency of oscillation was predicted with the Schroeder and Kintner(211) modification of Lamb's(212) equation:

$$\omega^2 = \frac{\sigma b}{r^3} \frac{n(n+1)(n-1)(n+2)}{\{(n+1)\rho_d + n\rho_c\}} \qquad (2.15)$$

where

$$b = \frac{d_p^{\,0.225}}{1.242} \qquad (2.16)$$

2.4.2) Mass Transfer in the Continuous Phase.

For the continuous phase distinction is also made whether the dispersed phase is rigid or non-rigid.

2.4.2.1) Mass Transfer to and From Rigid Drops.

It is difficult to estimate the contribution to mass transfer from the wake of the drop. Therefore, the process is often described as an overall process over the whole drop. Thus Linton and Sutherland(182) correlated the overall transfer by

$$Sh = 0.582\ (Re)^{\frac{1}{2}}(Sc)^{\frac{1}{3}} \qquad (2.17)$$

Bayadzhiev and Elenkov(184,185) gave the following correlation for the mass transfer coefficient for the continuous phase in turbulent extraction in a tube, when the dispersed phase drops behave like rigid spheres:

$$k_c = 0.65\left(\frac{Du}{d}\right)^{\frac{1}{2}} \left(\frac{D}{\nu_c}\right)^{1/6} \qquad (2.18)$$

Various workers have endeavoured to include the influence of various processes contributing to the overall process(171). The most general formula is that of Kinard, Manning and Manning(186),

$$Sh = 2.0 + (Sh)_n + 0.450\ Re^{\frac{1}{2}}Sc^{\frac{1}{3}} + 0.0484(Re)(Sc)^{\frac{1}{3}} \qquad (2.19)$$

where the figure 2.0 stands for the contribution by diffusion, $(Sh)_n$ is the contribution for natural convection $((Sh)_n = f(Gr),(Sc))$, the third term is the contribution at the top and the last term for the wake effect at the rear.

2.4.2.2) Mass Transfer to and From Non-Rigid Drops.

Several investigators(190,192-194) have confirmed that the continuous-phase mass transfer coefficient is several times as great for circulating drops as for solid spheres. Mass transfer is enhanced by the slip of the drop surface which thins the boundary layer.

Several correlations have been derived for continuous phase mass transfer via Sherwood number. Thus Boussinesq(195) has derived

$$Sh = 1.13(Re)^{\frac{1}{2}} (Sc)^{\frac{1}{2}} \qquad (2.20)$$

However, the formula derived by Garner and Tayeban(190) is generally more accepted(178,179)

$$Sh = 0.6(Re)^{\frac{1}{2}}(Sc)^{\frac{1}{2}} \qquad (2.21)$$

For oscillating drops, Garner and Tayeban(190), derived the formula,

$$Sh = 50 + 0.0085\ Re\ Sc^{0.7} \qquad (2.22)$$

2.4.3) Resistance to Transfer at the Interface.

It has been suggested on many occasions that there is a positive resistance offered by the interface to mass transfer(34).

Chandrasekhar and Hoelscher(161) measured interfacial resistances of different systems using an analytical ultracentrifuge equipped with a schlieren optical system. Wide variations in interfacial resistance were reported for different systems. Thus while water/toluene system offered significant resistance to the transfer of solutes like acetic and propionic acids; the water/n butanol system offered no significant resistance to the transfer of acetic acid across the interface.

Brenner and Leal(162), theoretically calculated the interfacial resistance to solute mass transfer between two unstirred immisible fluids. Solute molecules were modelled as Brownian particles, bathed by homogeneous fluid continua when wholly immersed in either fluid, or else by heterogeneous fluid continua when instantaneously straddling the interface. These diffusing particles were assumed to be subjected to either repulsive or attractive conservative forces exerted on them by the interface. Additionally their mobility was supposed to be affected by the proximity to the interface. Based on this theory, circumstances were found to exist under which the interface may offer significant resistances to interphase transport i.e. when the interface derived force exerted on the Brownian particle is repulsive in nature. However, conditions also exist where the force is attractive (i.e. adsorptive); the interfacial resistance is negative in this case and the interphase transport rate is actually enhanced rather than diminished.

2.4.3.1) Factors Affecting the Interface.

Any factor affecting the interface will naturally influence the rate of mass transfer. Indeed some of the anomalies observed on the application of the film theory may be due to specific conditions at the interface which were not considered in setting up the equation for "overall resistance"(19). Some of these conditions are:

2.4.3.1.1) Temperature Changes at the Interface.

Any difference in the heats of solution of a solute in the two liquids between which it is transferred, will lead to an evolution or absorption of heat, at the interface, that will alter its temperature. These temperature changes alter the distribution coefficient as well as altering the physical properties that influence the mass transfer coefficients.

Ordinarily, the heat of transfer, due to differences in heat of solution, is small. However, this phenomena is of particular importance when a chemical reaction, liberating or absorbing heat, is taking place simultaneously with the extraction process.

Blokker(30) and Lewis(25) have shown that interfacial turbulence caused by heat of solution or reaction may considerably increase the rate of mass transfer of solute between two liquids.

2.4.3.1.2) Interfacial Resistance Due to Adsorbed Trace Substances.

Certain "surface active" substances are strongly adsorbed at liquid-liquid interfaces thus introducing an additional resistance into the "resistance-additivity" equation. Thus Garner and Hale(32) showed that when 0.015% Teepol was added to water, the rate of extraction of diethylamine from tolouene droplets was reduced to 45% of its original value. Lindland and Terjesen(33) found that an addition of about 6×10^{-5} sodium oleyl-p-anisidinesulphonate per 100 mls of iodine in aqueous solution reduced the overall mass transfer coefficient of iodine by falling droplets of carbontetrachloride by 67 to 68%.

The presence of surface active agents reduces the terminal velocity of drops as well as affecting mass transfer rates(314).

There is no general agreement about the mechanism of the influence of adsorbed substances on mass transfer rates. Several forms have been suggested:

a) Retardation of internal circulation: The coefficient of mass transfer inside a droplet depends on the velocity of circulation of the liquid within(34). It is suggested in certain instances that surface active agents retard or even completely arrest internal circulation. Thus Levich and Frumkin(35) proposed that the surface active agents are adsorbed on the surface of the droplet and swept to its rear by the counter current flow of the liquids. This compressed film at the rear of the droplet will have a higher surface pressure. Therefore it tends to spread backwards opposing flow along the surface thereby impeding circulation as illustrated in figure (2.2).

b) Surface Rigidity: It has been demonstrated that surface active substances make droplet surfaces more rigid thus causing the droplets to approach the hydrodynamic behaviour of rigid spheres(32,33,36,37). This prevents the normal surface motion, thus reducing the k's to below expected values.

c) The above two mechanisms suggested for the influence of surface active agents are non-specific i.e. they should influence the transfer of different solutes to the same degree. However, it has been reported that some solutes are more retarded in their transfer, than others for a given surface active agent(38). This has been explained by Hutchinson(39) on the basis of a theory that the solute might be adsorbed on the adsorbed surface active agent. Further evidence for this is given by Boy-Christensen(40), Garner(32) and Lindland(33).

d) Blocking of the Surface. It is known that certain substances e.g. cetyl alcohol, when spread in a mono molecular film upon water, reduce the rate of evaporation, which has been attributed to a reduction of the area through which the water molecules must pass(19) i.e. a barrier effect.

Sawistowski and James(41,42) have studied the effect of surfactants on mass transfer coefficients for the transfer of acetic acid into water from a 0.98 M solution of benzene. For the case of teepol, Lissapol, dodecyl amine hydrochloride and sodium lauryl sulphate; they showed that the action of these surfactants was entirel hydrodynamic in nature, that is they suppressed interfacial convection. However, in the case of manoxol (sodium dioctyl sulphosuccinate), there was also some evidence for the presence of a barrier effect. This barrier effect has been confirmed by Kishinevskii and Kornienko(183) for the transfer of benzoic acid from water to non-polar solvents. At a low velocity, an adsorbed layer of benzoic acid was formed at the interface which acted as a barrier. At high Reynolds numbers, the barrier was destroyed.

2.4.3.1.3) Interfacial Phenomena:

The term "interfacial phenomena" is very general in nature and refers to any activity which either originates in the interface or is specific to it(43). While this definition covers many aspects of interfacial films, the influence of interfacial-tension-driven instabilities or disturbances is the important factor affecting mass transfer in liquid-liquid systems.

Thomson(44) was the first to observe the existence of spontaneous interfacial convection. The effect was explained in detail by Marangoni(45) and is generally known by his name.

Interfacial phenomena can affect the rate of mass transfer in two ways:

(1) By changing the mass transfer coefficient

(2) By changing the interfacial area.

In some cases the interfacial phenomena is strong with mass transfer in one direction but completely absent when the solute diffuses in the opposite direction(57). Sherwood and Wei(158) showed that the most pronounced interfacial turbulence is observed when a chemical reaction occurs simultaneously with mass transfer, as in the extraction of acetic acid from isobutyl alcohol by water containing ammonia.

Ellis and Biddulph(207) measured the amplitude of ripples on the surface of water as acetone was being absorbed from air and showed that the development of ripples was directly connected with the reduction in interfacial tension.

Sterling and Scriven(46) treated the instability in the interface mathematically through the equations of motion and diffusion. The analysis showed how some systems may be stable with solute transfer in one direction yet unstable with transfer in the opposite direction. Sterling and Scriven's analysis also suggests that interfacil turbulence is usually promoted by:

(1) Solute transfer out of the phase of higher viscosity;

(2) Solute transfer out of the phase in which its diffusivity is lower;

(3) large differences in kinematic viscosity and solute diffusivity between the two phases;

(4) steep concentration gradients near the interface;

(5) interfacial tension highly sensitive to solute concentration;

(6) low viscosities and diffusivities in both phases;

(7) absence of surface active agents;

(8) interfaces of large extent.

Orell and Westwater(75) have confirmed some of these conclusions.

Another model proposed by Bakker et al.(47,48) classified the solutes quantitatively according to their ability to impede or promote movement of a free interface. Furthermore, Bakker et al. divided interfacial movement, induced by differences in interfacial tension into two categories, "macro" scale and "micro" scale. The occurrence of the first depended on the geometry of the interface and the flow conditions, the latter on the physical properties of the phases.

2.4.4) Interfacial Area.

The interfacial area between the dispersed and the continuous phase in a liquid-liquid extractor depends on

(a) The dispersed phase hold-up

(b) The droplet size

2.4.4.1) Dispersed Phase Hold-Up.

The dispersed phase hold-up for batch extractors will change due to solute molecules transfer from one phase to the other. This can be significant in case of high mass transfer rates. In addition, the hold-up changes in case of a chemical reaction taking place when one or more of the phase constituents is consumed/created during the reaction. The instantaneous dispersed phase hold-up in batch extraction is found from the material balance on the system. The hold-up in continuous extractors e.g. rotating disc contactors depend on the dispersed phase superficial flow rate and the mean residence time of the droplets in the extractor. This is discussed in more detail in Chapter (4).

2.4.4.2) Droplet Size.

Droplet size in stirred tanks depends on physical properties of the system and the degree of agitation. Theoretical analysis of droplet break-up have resulted in prediction of maximum stable drop sizes(187;197;201). Further analysis took into consideration the effect of coalescence and redispersion which resulted in prediction of mean droplet diameters(199,202,203,204,205,215,218). These correlations have been mostly based of the theory of isotropic turbulence by Kolmogoroff(197) and the studies of Hinze(201) on deformation and break-up of globules in viscous and turbulent flows.

Kolmogoroff's theory is based on the fact that the velocity in a turbulent liquid stream varies from one point to another. This causes different dynamic pressures to be exerted at different points on the surface of the drop. Under certain conditions, this leads to deformation and break-up of the drop(187). Isotropic flow is difficult to realise in practice. Kolmogoroff overcame this difficulty by assuming isotropy if the volume under consideration is small enough compared to the scale of the main flow. This implies in practice that the width of the fluid ejected by the agitator is larger than the scale of the energy dissipating eddies. In addition, Kolmogoraff assumed a high Reynolds number. Both of these conditions apply frequently to processes in stirred tanks and liquid-liquid extractors(202). Hence Kolmogoroff derived a formula for the maximum stable drop diameter (187,197)

$$d_{max} = 2 \times \sqrt{2}\left(\frac{\sigma}{k_f \rho_c}\right)^{0.6}\left(\frac{d_a}{u^3}\right)^{0.4} \qquad (2.23)$$

where k_f is a constant = 0.5(187)

d_a is the diameter of the agitator which is approximately equal to L, the width of the fluid ejected by the agitator(202).

Rozen(187,200), found that the experimental data on the break up of the drops suspended in turbulent liquids, is correlated well with an empirical formula for mean drop diameter of

$$d_{mean} \sim \frac{\sigma^{0.5-0.6}}{u} \qquad (2.24)$$

On the other hand Hinze's study(201) resulted in an expression of the form

$$D_{max}\left(\frac{\rho_c}{\sigma}\right)^{3/5} \epsilon^{2/5} = C \qquad (2.25)$$

Hinze applied the above expression to the results obtained by Clay(206) and obtained the following expression

$$\frac{\rho_c \sigma D_{95}}{\mu_c^2} = 0.725\left[\frac{\mu_c^5 \epsilon}{\rho_c \sigma^4}\right]^{-2/5} \qquad (2.25)$$

where D_{95} is thevalue for which 95% by volume is contained in the drops with $D \leqslant D_{95}$.

2.5) LIQUID EQUILIBRIA.

Phase equilibria in liquid-liquid systems may be approached in two ways; these are based on (i) thermodynamics and the phase rule and (ii) the laws of distribution.

For the design or analysis of a solvent extraction process and other applications where data is required about the equilibrium states of a particular two phase liquid system the approach involving the laws of distribution only is of practical importance. These laws, as applied to liquid-liquid systems, include the various empirical correlations which attempt to systematize the relationship between the concentrations of the various components in different phases of the system.

2.5.1) THREE COMPONENT SYSTEMS:

Most frequently the equilibria of a three component partially miscible liquid system is represented on triangular coordinates, and the binodal curve is important in determining the solubilites. However, it is the tie-lie data which is of primary interest in determining the distribution of the various components between the two phases. This distribution may be presented in the following ways.

2.5.1.1) GEOMETRICAL TREATMENT OF TERNARY SYSTEMS TIE-LINES DATA:

Various geometrical methods for interpolation and extrapolation of tie-line data have been devised by Brancker,Hunter and Nash(323), Sherwood(324), Hand(106) and others. These methods are entirely graphical and are useful for extrapolation. They lack the flexibility of the mathematical formulations required for the analysis of solvent extraction processes particularly by computer.

2.5.1.2) EMPIRICAL TREATMENT OF TIE-LINE DATA:

The first empirical equation describing the distribution of components in a three component two phase liquid system was due to Bachman(107). He proposed that:-

$$x_{BB} = r + b(x_{BB}/x_{AA}) \qquad (2.26)$$

where r and b are constants.

Later Othmer and Tobias(104) showed that equation (2.26) is limited in application since it is based on ternary systems composed of practically immiscible nonconsolute components in the absence of the consolute component. They modified Bachman's equation so that a plot of the conjugate values of $\left(\frac{1-x_{AA}}{x_{AA}}\right)$ against $\left(\frac{1-x_{BB}}{x_{BB}}\right)$ on logarithmic coordinates produce straight lines. However, the Othmer and Tobias method also suffers from the fact that this formulation does not include the concentration of the distributed component. Hence it would appear that the most useful formula is that of Hand(106) which correlates the concentration of the solute in the two conjugate solutions. Hand's equation is represented by:

$$\frac{x_{CA}}{x_{AA}} = K\left(\frac{x_{CB}}{x_{BB}}\right)^{r} \qquad (2.27)$$

i.e. the logarithmic plot of $\left(\frac{x_{CA}}{x_{AA}}\right)$ against $\left(\frac{x_{CB}}{x_{BB}}\right)$ is rectilinear.

2.5.2) FOUR COMPONENT SYSTEMS:

Four dimensional geometrical models are necessary to represent four component systems and one method due to Brancker, Hunter and Nash(108,109) makes use of a regular tetrahedron.

Two types of quaternary two-phase liquid systems are possible. The first type is formed when one pair of components is partially miscible; i.e. when two solutes are distributed between two solvents. The other type is formed when one component is partially miscible with two of the others; i.e. when one solute is distributed between one of the solvents in one phase and with two "mixed" solvents in the other phase. These two types of quaternary system have been termed "Single binary quaternaries" and "Double binary quaternaries" respectively(110).

An example of a single binary quaternary, studied by Brancker et al.(108,109) and Hunter(325), is the system acetone-acetic acid-chloroform-water. Geometrical correlations were deduced for quaternary tie-lines and the saturation surface obtained from the different ternary data. A similar system, acetone-acetaldehyde-vinyl acetate-water, was studied by Pratt and Glover(111) who claimed that their results did not fit Brancker, Hunter and Nash's geometrical correlations.

Prince(110) studied a double binary quaternary system consisting of acetic acid-water-benzene-carbon tetrachloride. From the quaternary saturation surface and ternary data, two correlations were deduced, one algebraic and the other geometrical and he claimed that these two correlations could predict the equilibrium of the quaternary systems. Prince's model is a combination of a geometrical correlation of experimental data and an empirical relation which makes it complicated and possibly unreliable if applied to other systems. In addition it is not a complete prediction of quaternary data from the constituent ternaries since experimentation with the quaternary system is still required to determine the saturation surface.

Finally another double binary quaternary system, benzene-ethyl isovalerate-ethyl alcohol-water, was studied by Chang and Moulton(113). Results of the quaternary system were, again, expressed by geometrical correlations.

CHAPTER 3

MASS TRANSFER WITH SIMULTANEOUS CHEMICAL REACTION.

In any chemical reaction in a heterogeneous system, the reactants must diffuse from the bulk of one phase through the interface to arrive at the site of the reaction; and the reaction products must diffuse away to permit the reaction to continue. When these processes occur consecutively they may be treated separately and the series of resistances added together to express the resistance to the total driving force. An example of such a case, studied by Murdoch and Pratt(20) is the transfer of uranyl nitrate between water and organic solvents; where the mechanism is considered to be solvation of the uranyl nitrate with the organic solvent before entering that phase. In this case the reaction is considered to be heterogeneous, occurring at the interface and the rate of transfer was explained by Murdoch and Pratt in terms of three resistances in series.

However, often the diffusion and reaction occur in the same region of the system, and the diffusion and reaction rates are coupled so closely that they have to be treated simultaneously, in the analysis of the phenomenon, in the same differential equations.

3.1) The Theory of Simultaneous Diffusion and Chemical Reaction Near an Interface.

The possibilities of various reaction zones in mass transfer and simultaneous chemical reaction in a gas-liquid or liquid-liquid system, are illustrated in Fig.(3.1).

To account for the influence of the chemical reaction on the concentration of the diffusing species, in the reaction zone, the reaction rate expression is included in the unsteady-state diffusion equation (Ficks Second Law) obtaining an equation of the form,(57):

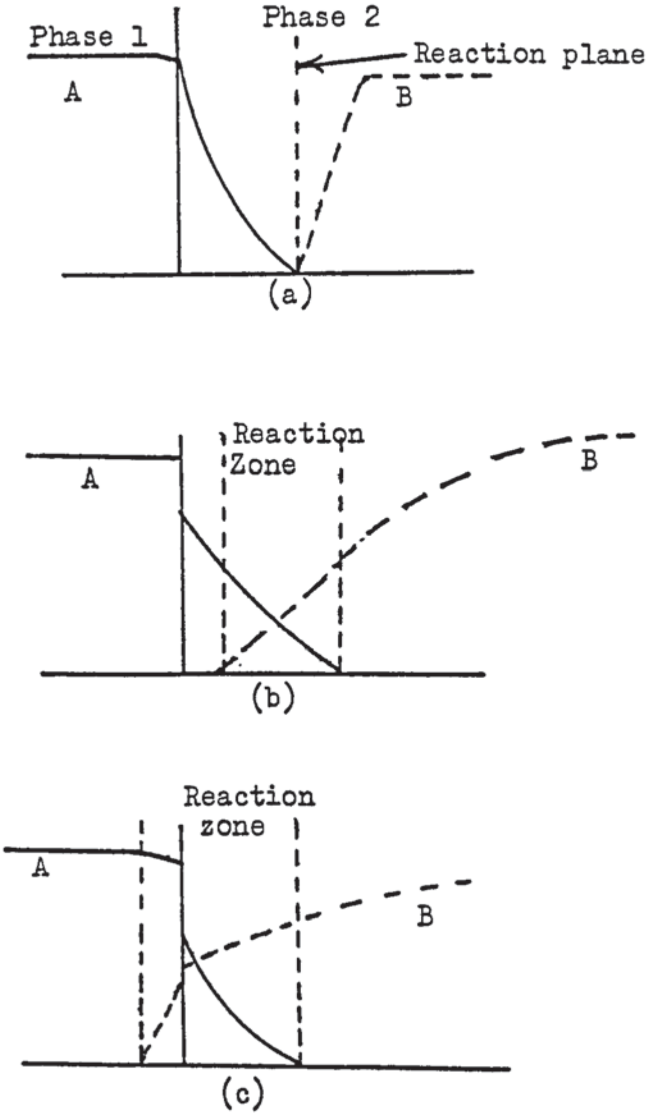


Fig.3.1 Concentration profiles for mass transfer with chemical reaction in a two-phase system. (a) instantaneous reaction; (b) reaction of finite rate, reaction zone limited to one phase; (c) reaction of finite rate, reaction zone extends into both phases(1),

$$D \frac{\partial^2 C_i}{\partial y^2} = \frac{\partial C_i}{\partial t} + u \frac{\partial C_i}{\partial x} + R_i(C) \qquad (3.1)$$

R_i represents the rate of loss of component i, owing to chemical reaction, per unit volume of the fluid.

In order to evaluate the change in rate of interphase molecular transport, owing to the reaction term, a "reaction factor" ϕ is used which is defined as the theoretical ratio of the mass transfer coefficient with the reaction, to the coefficient from the same theory without any reaction occurring.

Gas absorption with chemical reaction has been extensively studied because of its industrial importance and suitability for theoretical treatment. On the other hand, extractive reactions in liquid-liquid systems have received little attention(3). This is claimed to be justified because the hydrodynamic conditions in each phase are comparable with liquid or fluid phases in gas-liquid or fluid-solid systems. However, liquid-liquid systems possess some peculiar characteristics due to interactions between drops of the dispersed phase(4,5).

Due to the analogy drawn between reactions in liquid-liquid systems and other types of mass transfer with simultaneous chemical reaction, the hydrodynamic models of the gas-liquid interface have been applied with varying success to liquid-liquid extractive reactions. Therefore, a summary of these models is of relevance to this study.

The development of diffusion-effected reactions, in gas liquid systems, and the final form of the expression for the "reaction factor" will depend on which of the mass transfer models is applied.

3.1.1) First Order Irreversible Reactions.

Mass transfer accompanied by a first order irreversible chemical reaction has been extensively studied and equations have been developed for the reaction factor on the basis of all the major interface mass transfer models. Table 3.1 summarises these equations while figure (3.2) shows typical comparison between concentration distributions profiles of a gas in a liquid with and without an irreversible first order chemical reaction.

3.1.2) Second Order Irreversible Reactions.

An important type of gas-liquid reactions is represented by the chemical equation

$$A + \nu B \longrightarrow C \qquad (3.2)$$

B represents a non volatile reagent in the liquid phase. The reaction between A and B is second order of finite rate and can be represented by

$$R = k_2\, C_A C_B \qquad (3.3)$$

Van Krevlen and Hoftijzer(82,83), analysed the above type of reaction on the basis of Hatta's film theory. An implicit equation was obtained for the reaction factor,

$$\phi = \frac{M\sqrt{(1 - (\phi-1)/rS}}{\tanh[M\sqrt{1- (\phi-1)/rS}]} \qquad (3.4)$$

where the symbols are as given in the nomenclature.

Various other forms of equation (3.4) are found in the literature. One of the most convenient is obtained using ϕ_i which is defined as limiting value of ϕ for instantaneous reaction(84). Hence equation (3.4) is converted into the following form:-

Table 3.1

Relationships For Mass Transfer Accompanied by First Order Irreversible Chemical Reaction.

	Model	Equations	Reference
1)	Two film	$\phi = ay_o \operatorname{Coth} ay_o$	(76,79,315)
2)	Surface Replacement	$\phi = \left(1 + \frac{k_1}{s}\right)^{\frac{1}{2}}$ $s = \left(\frac{k_L^{o2}}{D}\right)^{\frac{1}{2}}$	(18,57)
3)	Penetration Model	$R = C_i\sqrt{Dk_1}\left[\operatorname{erf}\sqrt{(k_1t)} + \frac{e^{-k_1t}}{\sqrt{(\pi k_1 t}}\right]$ $Q = C_i\sqrt{\left(\frac{D}{k_1}\right)}\left[(k_1t+\tfrac{1}{2})\operatorname{erf}\sqrt{(k_1t} + \sqrt{\left(\frac{k_1t}{\pi}\right)}e^{-k_1t}\right.$	(79,89)
4)	Film Penetration Model	$R = \frac{D}{L}\left[1+2\sum_{n=1}^{\infty}\frac{1+\beta}{1+\beta+n^2\pi^2\alpha}\right](C_i - C_L)$ $\alpha = D/k_1L^2$ $\beta = s/k_1$	(77,78)

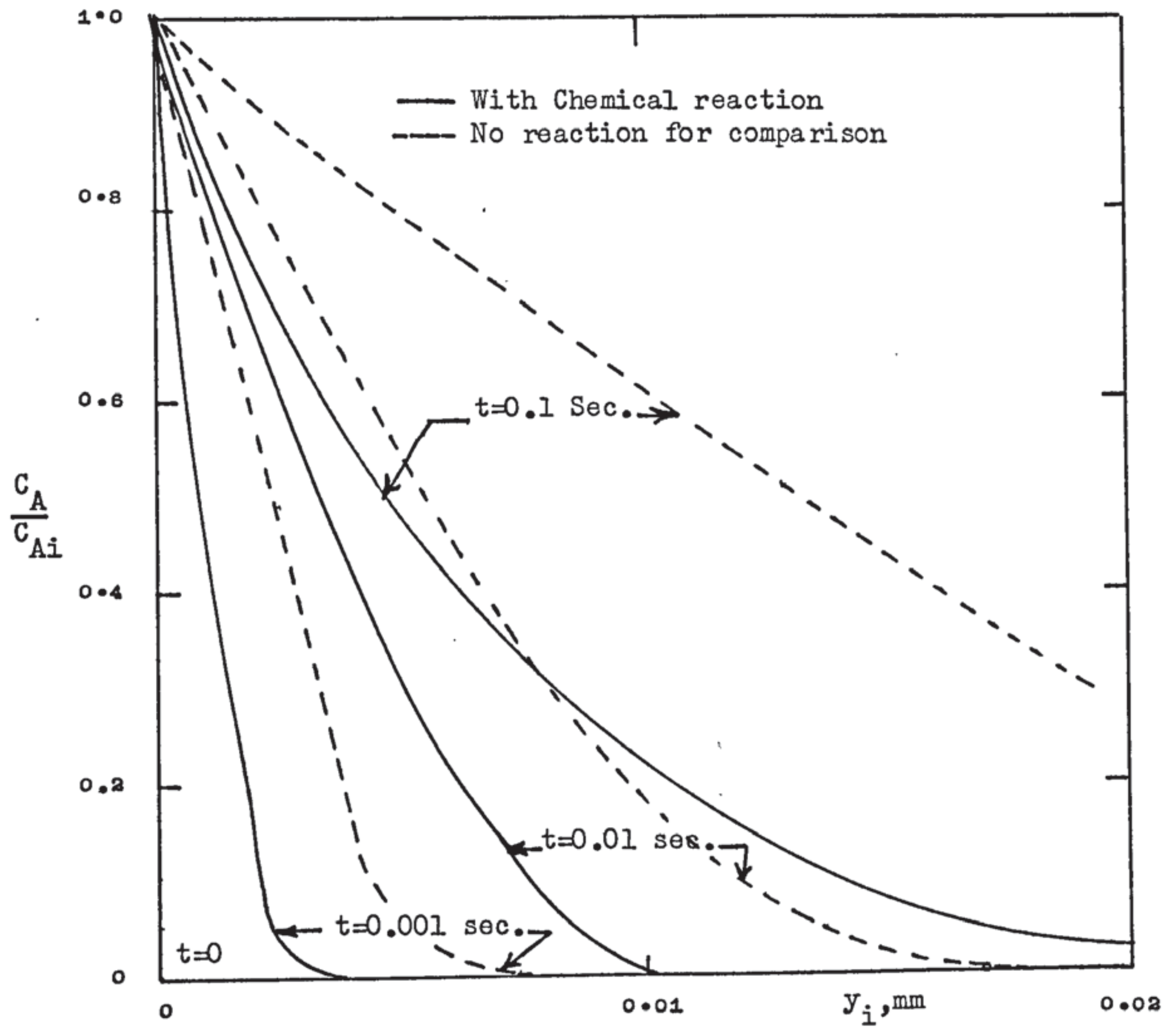


Fig.3.2 Calculated concentration profiles of diffusing and reacting molecules near an interface(57).

Numerical values in the figure represent a chemical reaction of rate constant equal to $0.1\ s^{-1}$ and $D = 2 \times 10^{-5}\ cm^2/s$

$$\phi = \frac{M\sqrt{\dfrac{\phi_i-\phi}{\phi_i-1}}}{\tanh M\sqrt{\dfrac{\phi_i-\phi}{\phi_i-1}}} \qquad (3.5)$$

Equation (3.5) is represented graphically by fig.(3.3). The following limiting types of behaviour are identifiable from fig. (3.3):

(1) When $M << 1$, $\phi \approx 1$; in these circumstances the time of contact between gas and liquid is very short, or the reaction is very slow, so that physical absorption predominates and the reaction has negligible effect.

(2) When $M << \phi_i$, the point representing ϕ lies on the line A-B-C forming the envelope of the family of curves on the figure; the reaction is then pseudo first order. Physically this means that the reactant diffuses towards the surface fast enough to prevent the reaction causing any significant depletion of B. Hence the concentration of reactants is everywhere B_o and the rate constant is

$$k_1 = k_o B_o$$

Provided $M < \frac{1}{2}\phi_i$, the rate of absorption follows the first order equation to within about 10%.

(3) When $1 \leqslant M \leqslant \phi_i$, the point representing ϕ lies on the straight part (B-C) of the envelope. This corresponds to a sufficiently long contact time or fast reaction; then the rate of absorption is independent of the time of contact.

(4) When $M >> \phi_i$, then $\phi = \phi_i$. This occurs when the reaction is fast, the contact time long, or the concentration of reactant small. The reactant is depleted in the neighbourhood of the surface to the extent that the rate of reaction is determined by diffusion alone. In practice ϕ is within few per cent of

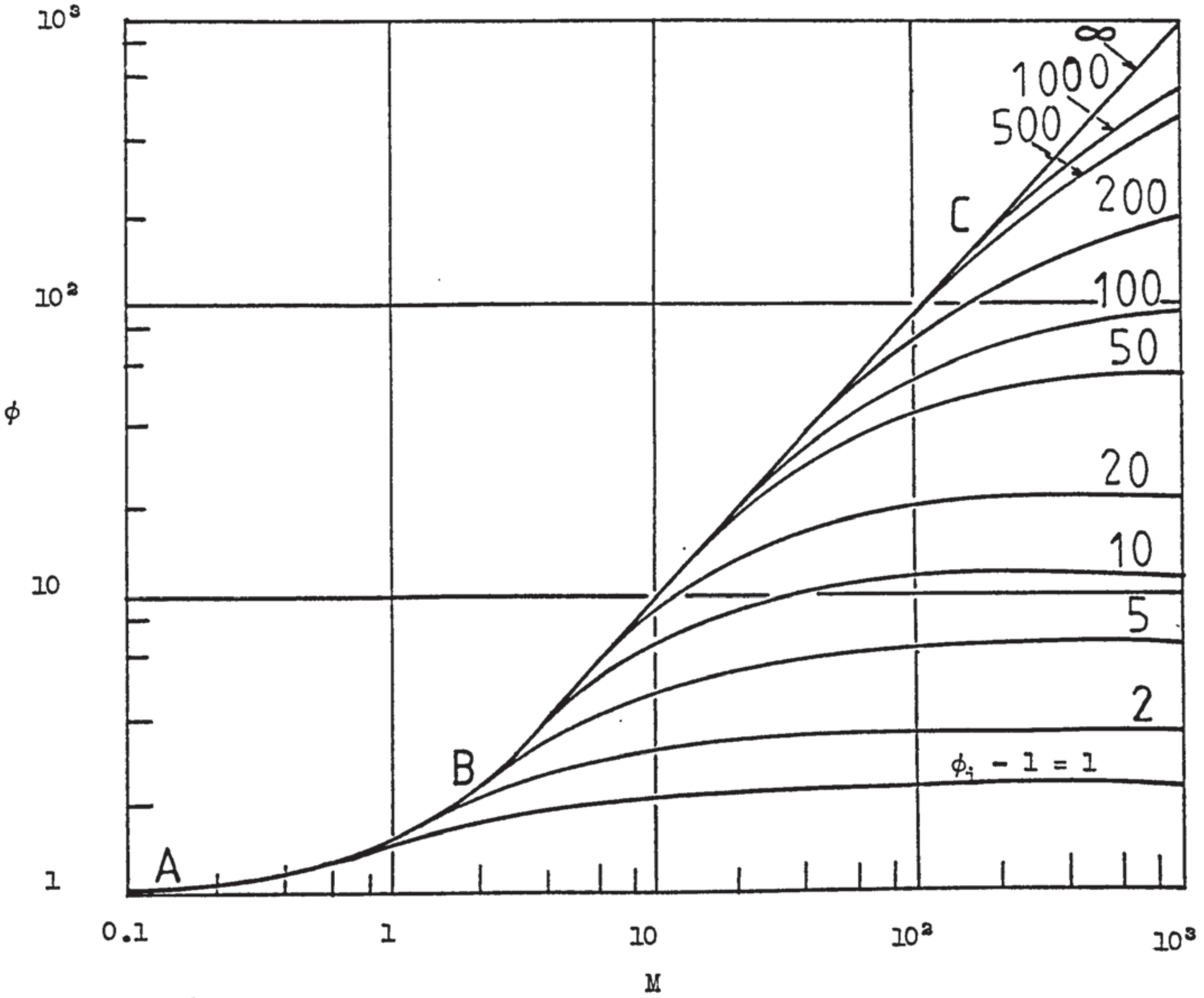


Fig.3.3 Reaction factors for second-order reaction (after van Krevlen and Hoftijzer(82))

(4) contd.

ϕ_i if $M > 10\phi_i$.

Other forms of equation (3.4), relating ϕ with the kinetics and physical parameters of the gas-liquid systems, have been developed by Yeramian et al.(91); and De Santiago and Farina(92). However, all these forms in common with equations (3.4) and (3.5) are explicit in ϕ. The first implicit expressions in ϕ are due to Kishinevskii(85,88) and Kishinevskii and Armash(86),

$$\phi = 1 + \frac{M}{\frac{M}{S} + e^{-0.35\frac{M}{S}}}\left[1 - \psi(0.85\sqrt{\frac{M^2}{S} + M}\right] \qquad (3.6)$$

The function ψ is determined by the expression

$$\psi(z) = \frac{e^{-z^2}}{z}\int_0^z ey^2\,dy \qquad (3.7)$$

Values of the function $\psi(z)$ are given in reference(88).

Equation (3.6) was developed for the case of equal diffusivities of A and B i.e. $r = 1$ and on the basis of the results of numerical solutions of Brian et al.(87).

Higbies penetration model has also been applied to second order irreversible gas-liquid reactions. The computed values of ϕ for the penetration and film models are almost equal for given values of M and ϕ_i, so that figure (3.3) can be used equally well for the penetration model(4).

Van Krevlen and Hoftijzer's method have been used successfully for gas-liquid systems by Onda et al.(213), and Hikita and Asai(98), while Merchuk and Farina(214) have extended the analysis to the case of simultaneous steady state diffusion and chemical reaction in a liquid-liquid system under such conditions that diffusion and chemical reaction are of the same order of magnitude in the two phases.

De Coursey(263) has performed an approximate analytical integration of the partial differential equations describing the unsteady state diffusion and reaction for Danckwert's surface renewal theory. A simple explicit relationship for the reaction factor was obtained

$$\phi = -\frac{M}{2(\phi_i - 1)} + \left(\frac{M^2}{4(\phi_i - 1)^2} + \frac{\phi_i M}{(\phi_i - 1)} + 1\right)^{\frac{1}{2}} \qquad (3.8)$$

Matheron and Sandall(262) solved the same equations numerically. The predicted reaction factors were found to differ only slightly from those calculated from Higbie's penetration theory, while they were in good agreement with the approximate analytical formula of De Coursey (eqn.3.8) over a wide range of parameters.

Recently Wellek and Co-workers(253) have developed another explicit mathematical expression for estimating the reaction factor for mass transfer accompanied by a second-order irreversible chemical reaction. Wellek et al. compared the different mathematical approximations as to their ability to duplicate the results of a precise numerical solution. It was concluded that the implicit equation by Van Krevelen and Hoftizer is the best approximation for the entire range of "M". Hence this equation was recommended for general use whenever an implicit equation can be used. Other equations were found to be accurate at particular ranges of "M"(253).

3.1.3) Instantaneous Irreversible Reactions.

A chemical reaction may be considered to be instantaneous whenever its rate is exceedingly large compared with the rate of diffusional processes.

Hatta(76) applied the film model to the analysis of instantaneous gas-liquid reactions. The mathematical derivation lead to an equation of the type

$$\begin{aligned} \bar{R} &= k_L A \left(1 + \frac{D_B B_o}{\nu D_A A}\right) \\ &= k_L A \ \phi_i \end{aligned} \qquad (3.9)$$

On the other hand, the mathematical formulations for both Higbie's penetration and Danckwert's surface replacement models are similar(90), and lead to the following expression for the reaction factor

$$\phi_i = \sqrt{\frac{D_A}{D_B}} + \frac{B_o}{\nu A} \sqrt{\frac{D_B}{D_A}} \qquad (3.10)$$

A number of workers(93-96) have verified equation (3.10) experimentally.

3.1.4) Zero-Order Reactions:

Zero-order reactions occur very infrequently in industrial processes. These reactions do occur in gas-liquid reactions; e.g. reactions of oxygen with a number of organic liquids are zero-order with respect to oxygen in certain circumstances, because the rate determining step is the production of free radicals by processes not involving oxygen(97).

The phenomena of absorption accompanied by a zero-order chemical reaction has been studied by Astrita and Marruci(80) for the case of gas absorption into a liquid moving in plug flow, and by Van de Vusse(81) for the case of liquid-phase oxidation of hydrocarbons.

3.1.5) (M,N)-th Order Irreversible Reactions.

The general case of an (m,n)-th order irreversible gas-liquid reaction, which is a reaction of an m-th order with respect to a dissolving gas and an n-th order with respect to a solute reactant, has been studied by Hikita and Asai(98), and Brian(99). Numerical solutions of the differential equations were obtained on the basis of both the film and penetration models.

3.1.6) The Effect of Reversability.

When the reaction is reversible, the differential equations for the forward and back reactions, with diffusion of reactants and products, have to be solved simultaneously. Thus Crank(100) considered the case of the first order reversible reaction. A rigorous mathematical solution was obtained on the basis of an assumption that the concentration of reacting species satisfy the mass action law, everywhere in the diffusion path.

Olander(102) applied the same assumption of local equilibrium to first and second order reversible chemical reactions. Equations were derived for both the film and surface-renewal models of mass transfer in conjunction with these reactions. The calculated mass transfer coefficients were found to be functions of the concentration driving force and the average concentration level over the diffusion path as well as of the magnitude of the equilibrium constant and the diffusivities of the reacting species.

Secor and Beutler(103) applied a finite-difference method to the generalised reversible reaction of the form

$$\nu_A A + \nu_B B \rightleftharpoons \nu_M M + \nu_N N$$

solutions, for different values of the parameters were obtained on the basis of Higbie's penetration model. These were presented in graphical form which have the general shape of figure (3.3).

3.2) Liquid-liquid Reactions.

A common liquid-liquid reaction occurs when a component A, which is highly soluble in phase a, reacts with component B, which is highly soluble in phase b. The two phases are of limited miscibility, and product C is highly soluble in phase a while product D is highly soluble in phase b(216).

For the general reaction $A+B \rightleftharpoons C+D$, the overall rate of the reaction is the sum of the reactions in the two phases. However, it frequently happens that the solubility relationships are such that the extent of chemical reaction in one of the phases is so small that it can be neglected in the analysis of the overall rate. In such a case the chemical reaction is assumed to occur in one phase only. This is called the reactive phase while the other is called the extractive phase(217).

3.2.1) General Theoretical Treatment of Liquid-liquid Reactions.

The position and depth of the reaction zone, in processes involving mass transfer and simultaneous chemical reaction, depends on the reaction velocity and the mass transfer rates. The latter depend on both the diffusivities of the various components and the degree of agitation imposed on the system(1). Hence the rate of conversion in such systems is controlled by both the kinetics of the chemical reaction and the diffusional characteristics of the system. However, a process may either be entirely diffusion or kinetic controlled.

A common example of a mass transfer controlled liquid-liquid reaction is the extraction of uranium as uranyl nitrate from aqueous solution into tri-n-butyl phosphate (TBP). This kind of extraction which has covered an increasing number of metals recovery from leach liquors has been the subject of continuing research(228-231). In most of these extraction processes, the rate of chemical reaction is extremely rapid compared with the rate of transfer between the two phases and so the reaction is neglected and the process is treated as a simple mass transfer operation.

On the other hand there are liquid-liquid reactions notably aromatic nitrations and alkylations for which the mass transfer rates are relatively much larger than chemical reaction rates. Hence these processes are usually treated as simple chemical reactions.

There is another group of reactions in liquid-liquid system usually referred to as "extractive reactions" for which neither the chemical reaction rate nor the mass transfer rate controls the overall rate of conversion.

3.2.2) Aromatic Nitrations and Alkylations Reactions:

The nitration of aromatic hydrocarbons has been the subject of numerous investigations(219,220,225). 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 is used either alone or mixed with sulphuric acid, depending on the ease of nitration.

Biggs and White(219) measured the rates of nitration of benzene by mixed nitric and sulphuric acids, in well emulsified reaction mixtures. The reaction rate based on the total volume of the reaction mixture was shown to be a function of the phase compositions, temperature and vol% of the acid phase.

Early theories attributed the influence of sulphuric acid in aromatic nitration to its dehydrating action in removing the water formed during the reaction. A more recent theory(221) on the mechanism of aromatic nitration, with mixed acids, consider the nitrating species to be the nitronium ion formed by dissociation of nitric acid. According to this theory the role of sulphuric acid is that of an ionizing medium for this dissociation. However, there are certain facts with which the nitronium ion mechanism is not compatible and there is still considerable uncertainty as to the mechanism of nitration processes(1).

In the alkylation of aromatics, it is generally agreed that the reaction proceeds through a carbonium ion mechanism(222,223,224) which is generated by addition of a proton to an olefin. The carbonium ion undergoes rapid isomerization, and finally attacks the aromatic to form a product. Komasawa et al.(224) studied the alkylation of benzene with straight-chain olefins in the presence of strong sulphuric acid at a carefully controlled low temperature. It was claimed that the mass transfer resistance could be eliminated completely by increased agitation of the reaction mixture. Under such conditions, the reaction was found to occur by a homogeneous mechanism in the acid phase only. Correlations were obtained for the reaction rate with sulphuric acid strength and reactants concentration.

3.2.3) Metal Extraction.

As stated earlier, the extraction of metals like uranium involves a chemical reaction which for a majority of cases is extremely rapid compared with the rate of transfer between the two phases and so it is justifiable to neglect the reaction and treat the process as a simple mass transfer operation. This generalisation is not strictly true, and the chemical reaction in certain metal extraction processes is known to be slow. This subject is adequately covered in references(232,233,313).

Interest in application of solvent extraction in extractive metallurgy has increased rapidly in recent years following the development of selective extractants for many metals, increased prices for metals and growing objections to pollution(228-231).

3.2.4) Extractive Reactions:

The label "extractive reaction" was used by Trambuze and Co-workers(235) to describe the reacting systems where an immiscible extractive component is delibertately added to increase the yield. Such processes encompass several unit operations and have been practiced for some time in liquid-liquid reacting systems as well as simultaneous reaction and distillation.

In extractive reactions, in liquid-liquid system, the reaction is carried out in the presence of a suitable solvent. Such a process was patented by Martin and Krchma(226), for the production of butyl acetate by the transesterification reaction,

$$C_4H_9OH+CH_3COOC_2H_5 \overset{H_2SO_4}{\rightleftharpoons} C_2H_5OH+CH_3COOC_4H_9$$

Equilibrium was displaced in favour of the product by carrying out the reaction in a two phase water-hydrocarbon system. The hydrocarbon preferentially dissolved the ester formed (butyl acetate) but not the other product (ethyl alcohol) which remained in the aqueous phase.

The term "extractive reaction" is used nowadays to describe any process involving simultaneous extraction and chemical reaction in liquid-liquid systems even though no "inert" solvent may be present.

Mhaskar and Sharma(227), considered the general case of extractive reactions. On the basis of the relative values of diffusion and chemical reaction, the situation where an A-rich phase (A-phase) is contacted with a B-rich phase (B-phase); was classified in the following manner:

A. Reaction occurs only in the bulk of the phases.
1.Diffusional resistance for the transfer of B in the A-phase and A in the B-phase are negligible. 2. Diffusional resistances are important in both the phase. The concentration of species B in the

bulk A-phase, and species A in the bulk B-phase are zero.

B. Reaction occurs in the films adjacent to the interface while the species are diffusing. 1. Concentration of A in the A-phase can be assumed to be uniform up to the interface. Similarly there is no depletion of B in the B-phase near the interface. 2. The reaction occurs on both the sides of the film while the species are diffusing and there is depletion of A at the interface in the A-phase and a similar situation exists for B in the B-phase. In other words the interface concentrations of A and B are very much different from their respective bulk concentrations. 3. If the reaction between A and B becomes instantaneous it can occur only in one of the two phases at a reaction plane. 4. The reaction between A and B is reversible and instantaneous. Under the circumstances reaction will occur in both the phases. 5. In some cases no reaction between A and B might occur in, say, the A-phase in spite of the fact that some B is transferred from the B-phase into the A-phase.

Mhaskar and Sharma derived rate equations for all the different situations described above.

Various other workers have analysed extractive reactions. Piret, Penny and Trambouze(234) considered two-phase extractive reactions occurring in batch or continuous stirred-tank reactor (CSTR) systems. Complete analytical solutions were obtained for cases where the concentration of the reactants were so low that the ratio of the two phases and the partition coefficients were constant. Trambouze and Piret(235), examined later the more complex problem of high concentrations and of reactions of any order. Homogeneity within each phase and physical equilibrium between the two phases was assmed as before. Thus rates of mass transfer were considered not to affect the overall rates of the reaction process. In addition, it was assumed that the reaction occurred in one phase only, no reaction occurred at the interface, and isothermal conditions prevailed. On this basis, graphical solutions of the rate equation were developed on the ternary equilibrium diagrams.

Other papers by Trambouze and Co-workers compared theoretical and experimental results for a slow chemical reaction(236); and evaluated the effect of phase ratio on the reaction rate(237).

A group of "extractive reactions" not involving an "inert" solvent is the hydrolysis of esters in alkaline solutions. These reactions have been studied by Sharma and Co-workers(238-240). Thus Sharma and Nanda(238) in a study of second order hydrolysis reactions in a stirred cell and a spray column claimed that the situation can be described by the theory of absorption with second order reaction and that a stirred cell could be used as a model for industrial columns. The same procedure was followed by Nanda and Sharma(239) in a study of the fast alkaline hydrolysis of an ester in the presence of an excess of one reactant i.e. a fast pseudo-first-order reaction.

Nanda and Sharma(240) claimed that the effective interfacial area, A, in a spray column can be measured by application of the theory of extraction accompanied by a fast-pseudo-first order reaction. This has become the basis of the "chemical method" for the measurement of A which has been adopted subsequently by many workers to obtain values of effective interfacial area in various types of liquid-liquid contactors(241-249).

Another type of extractive reaction in a two phase liquid-liquid system occurring without presence of an "inert" solvent is the hydrolysis of animal fats and vegetable oils. This process has been extensively studied, by Jeffreys and Co-workers(250-252,150), in a pilot scale batch reactor, a spray column and a full-scale plant. The continuous hydrolysis of fat was performed by feeding water at 220-280°C and 42-49 Kg/cm.sq. pressure through sprays into the top of a 22 m high tower. A simplified mathematical model of the hydrolyser, assuming constant mass flow rates and pseudo-first order reaction, was solved analytically by Jeffreys,Jenson and Miles(250). Subsequently, Jeffreys and Co-workers studied the process mechanism in greater detail in a pilot scale plant. A more rigorous mathematical model was proposed allowing for the presence of two phases, the extraction of glycerol from the fat phase into the water phase, the variation of the solubility of water in the fat phase as the reaction proceeds. Both batch and continuous hydrolysis were analysed by sets of equations which were solved by numerical computation techniques.

3.2.5) Segregation in Liquid-liquid Dispersions And its Effect on Chemical Reactions.

When an extraction, or an extraction combined with a chemical reaction, is carried out between two phases in a continuous stirred tank reactor in which there is no interaction occurring between the dispersed particles, the dispersed particles will have different concentrations because of the spread in residence time. Interaction between the dispersed particles by diffusion or coalescence and redispersion tends to eliminate these concentration differences. On the other hand, if such a process is carried out in a piston flow reactor (i.e. all particles have the same residence time distribution) in which the dispersed particles have different sizes and the chemical reaction is mass-transfer controlled, the smaller particles will sooner be converted than larger particles, unless the interaction is strong enough to equalize concentration differences between particles at the same spot in the reactor(254).

Poor interaction between dispersed phase droplets in liquid-liquid systems, have the same effect as segregation, due to incomplete mixing, on homogeneous reactions. Danckwerts(257) applied the term segregation to homogeneous reactions to indicate that there are clumps of fluid which have different concentrations.

The effect of segregation, in a liquid-liquid reacting system, is an increase in conversion for reactions of an order greater than 1 and a decrease in conversion when the order is less than 1 while the conversion is the same for an order equal to unity(256).

Rietema and Meyerink(255), have shown that segregation in the dispersed phase, of a liquid-liquid reacting system, can influence the chemical reaction in the following ways:

1) By changing the average reaction rate
2) By changing the apparent order of reaction
3) By changing selectivity in the case of complex reaction schemes.

The influence of segregation in liquid-liquid systems is relatively easy to evaluate for the two extreme cases of (a) no segregation (infinite interaction) and (b) complete segregation (no interaction). However, neither of these two extremes exist in real situations but segregation is partial. This has promoted the development of a number of theoretical models(258-261) to account for partial segregation. These models are difficult to confirm in actual reacting systems(254).

CHAPTER 4

LIQUID-LIQUID EXTRACTION EQUIPMENT.

4.1) Equipment Classification:

A wide variety of equipment has been developed for liquid-liquid extraction. This has been broadly divided into two main categories(152,264):

(i) Stage wise (discrete stage) contactors.

In this type of equipment, the liquids are mixed, extracted and separated in discrete stages. This class includes the mixer settler range of equipment and the different plate columns.

(ii) Continuous (differential contactors).

This equipment operates through continuous counter-current contact between the imiscible phases to give the equivalent of any desired number of stages. These may be further subdivided as follows:

A. Gravity Operated extractors
  (1) Non-mechanical dispersion
    a) Spray columns
    b) Baffle plate columns
    c) Packed Columns
  (2) Mechanically agitated extractors
    a) Pulsed Columns
    b) Rotary Agitated Columns
B. Centrifugal extractors.

4.2) Selection of Equipment

Various workers(114;152;209;264) have extensively reviewed the factors to be considered in choosing an extractor for a particular application. However, there are still no general rules for the choice of an extractor for any particular mass transfer application. The following factors are mainly considered; the final choice depends upon experience:

(i) The number of effective contact stages.

Mixer-settler equipment is commonly used where only a few contact stages are required. For a larger number of stages, column extractors are preferred. However, mixer settlers have to be used for processes requiring more than twenty stages because of practical limitations, and a compact alternating arrangement of mixers and settlers has been adopted in many of the "box-type" extractors developed particularly for processing radio active solutions(52).

(ii) Capacity:

For low and moderate throughputs, spray towers or packed columns could be used, while R.D.C's, pulsed plate columns or mixer-settlers could be used for intermediate and high throughputs.

(iii) Contact time.

Centrifugal extractors are superior to all others for processes requiring a low contact time. Gravity settling mixer settlers, have relatively the longest settling times. In differential contactors, the residence time is a function of the dispersed phase mean droplet velocity.

(iv) Phase flow-ratio.

Mixer-settlers are preferable to differential contactors at high phase ratios. Phase ratios of up to 10:1 are easily handled in most mixer settler designs, while phase ratios up to 100:1 may be accommodated by recycling the phase with the lower throughput to aid dispersion(152). The performance of differential contactors decreases as the phase ratio is decreased.

(v) Physical Properties:

Mechanically agitated extractors are preferred when the phases have higher viscosities or high $(\sigma/\Delta\rho)$ values.

(v) contd.

The drop size in non-agitated differential extractors is a function of the parameter $(\sigma/\Delta\rho)$; the larger the value of this parameter, the smaller the interfacial area and therefore the poorer the mass transfer performance.

The present investigation comprises the study of an extractive reaction. Unfortunately, apart from a study of the hydrolysis of esters(114) which is not a true extractive reaction, there is no data on the performance of continuous extractors as extractive reactors.

However, it was thought that for extractive reactions good mass transfer followed by quick and efficient separation is essential. In this study it was decided to use an R.D.C. in addition to an ordinary laboratory reactor. The latter was used for determining the reaction rate constants as well as the study of the extractive reaction under batch conditions.

4.3) The Rotating Disc Contactor.

The R.D.C. was proposed by Reman in 1951(265). The contactor consists of 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 in each compartment. A typical design is shown in Fig.(4.1). The vortices generated by the discs are constrained between the stators. Adjacent to the top and bottom compartments are feed inlets which are arranged tangentially in the direction of rotation. The dense phase is introduced into the top of the column and the light phase into the bottom; counter current flow is thus established by gravity. At the ends of the column are settling zones to allow the phases to separate. One of the phases is dispersed by the action of the rotating discs, which are flat to create uniform shearing conditions

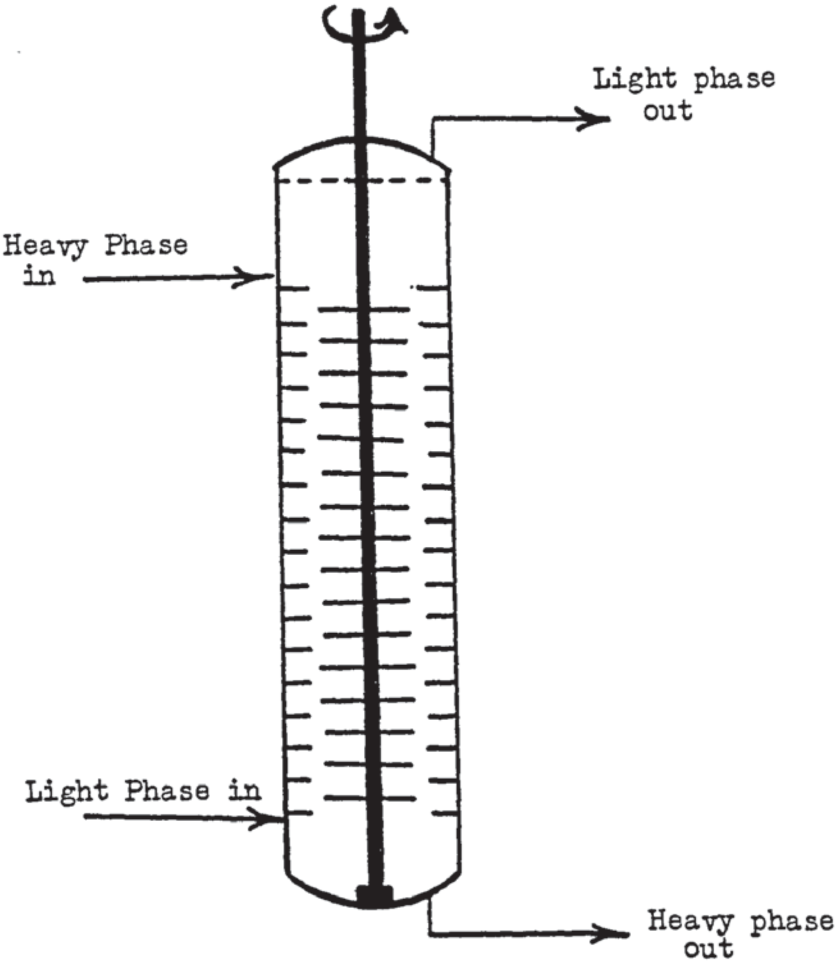


FIGURE 4.1 Rotating Disc Contactor

and hence obtain as small a spread in droplet sizes as possible. It is thought that the dispersed phase droplets spin at fairly high speeds and that this factor accounts for the high efficiencies obtainable with R.D.C's(266).

The R.D.C. was originally employed for the extraction of lubricating oils from crude oils using furfural as solvent; it has now found extensive use in various petroleum extraction processes(268), as well as in the food, metal separation, extraction of caprolactam(269) and in many other organic chemical industries(264).

In an attempt to improve the R.D.C's efficiency, or possibly to circumvent the Shell patent, many modified R.D.C's have been proposed. The Asymmetric Rotating Disc (A.R.D.) extractor is the most important modification of the R.D.C. and was developed by Misek and Co-workers(176,270). Its essential difference from the R.D.C. is that the shaft, carrying the rotating-disc agitators, is off-centre in the column. A transfer zone is located at the side of the column, providing a path to the mixing chambers above and below the one being considered. It is claimed that this arrangement reduces axial mixing considerably. Seidlova and Misek(271) published a detailed study giving data on the pattern of liquid movement over the cross section for the A.R.D.

Another modified R.D.C. is a multirotor extractor designed by Reman(272). This has two or more rotors in the column shell. This is claimed to minimise instability of the vortex flow pattern in large diameter columns. Other designs incorporate perforated disc rotors(273,274); and an R.D.C. in which the stator rings were omitted with the discs of two sizes, and the larger discs perforated(275) have also been considered.

Various other extractors are not simple modifications of one of the more common designs but a combination of more than one type. Perhaps the most important extractor of this kind is the Kuhni Column(276,277) which incorporates the principles of the Oldshue-Rushton, the sieve plate and the R.D.C. extractors. The Kuhni Column employs shrouded turbine impellers to promote radial discharge characteristics within the compartments. The column is divided into compartments by plates perforated only at the centre so that the flow from one compartment to the next is directed towards the agitator.

However, the "standard" R.D.C. remains by far the most common and probably versatile extractor of its type. A pilot plant R.D.C. of 0.101 m diameter, 0.92 m long column was employed in this study.

4.3.1) R.D.C's Hydrodynamics:

In the R.D.C., the motion of drop swarms depends on the tortuosity of the path offered by the stator compartments. The rotor, in addition, introduces a complex nature to the movement of both phases due to the rotating action of the rotor discs.

The hydrodynamics of the R.D.C. fall into two regions defined by a critical rotor speed(267). Kung and Beckmann(116) observed that the characteristic droplet velocity $\bar{u}_o$ (defined as the mean velocity of droplets in the multiparticle system) remained constant below a rotor peripheral speed of about 152 cm/s but decreased with peripheral speeds above this value. The two hydrodynamic regions of the R.D.C. may be considered to represent the following:

Region I:

This region covers the low rotor speeds at which the characteristic velocity $\bar{u}_o$ is very nearly constant. Here the dispersed drops are merely deflected by the rotating discs without any breakup of liquid drops. Hence the drop terminal velocities are affected only slightly due to the deflection caused by the rotor discs.

Region II:

This region covers high rotor speeds. As the rotor speed increases, the path of the dispersed phase droplets becomes increasingly torturous and there is increasing drop breakdup. Thus the characteristic velocity shows a marked decrease with rotor speed.

The R.D.C.is generally operated in region II to achieve high mass transfer rates. The two flow patterns are shown in Figs.4.2 and 4.3

4.3.1.1) Hold-Up:

Hold-up is the fraction of the column volume occupied by the dispersed phase. Hold-up values in agitated contactors are needed for the estimation of interfacial area. The interfacial area is expressed in terms of hold-up by:

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

It is generally agreed that the hold-up increases with increasing rotor speed and dispersed phase flow rates$^{(114,115,118,131)}$. Logsdail and Co-workers$^{(278)}$, showed that for a given system, column geometry and rotor speed; hold-up and the phase flow rates are related by the equation

$$\frac{u_d}{x} + \frac{u_c}{1-x} = \bar{u}_o(1-x) \qquad (4.2)$$

Kung and Beckmann$^{(116)}$ took into consideration the effect of column geometry and operating flow rates on hold-up. Equation (4.2) was found to be applicable to a wide range of column geometries in the form,

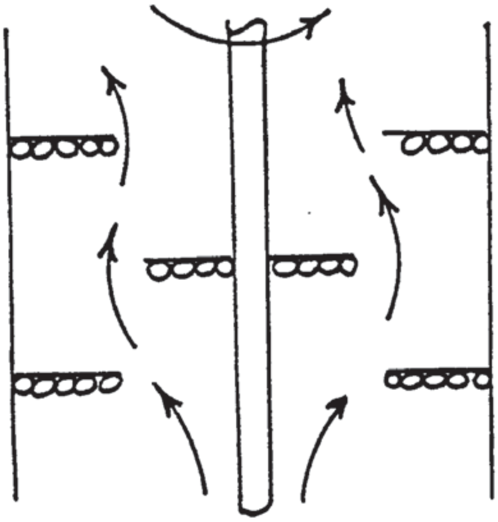


FIGURE 4.2 Dispersed phase flow pattern in a Rotating Disc Contactor. Peripheral Speed < 152 cm/s system: Toluene-Water(116)

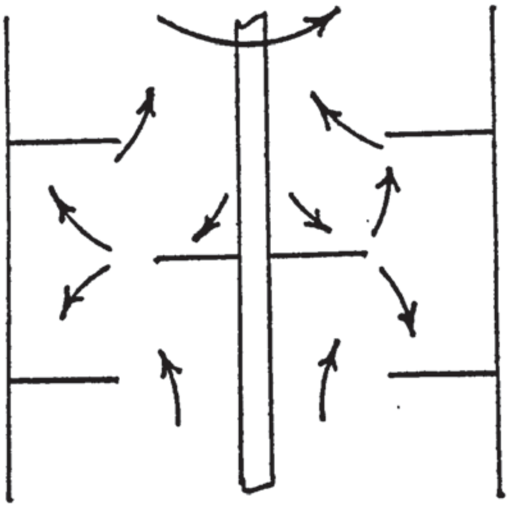


FIGURE 4.3 Dispersed phase flow pattern peripheral speed > 152 cm/s(116)

$$\frac{u_d}{x} + \frac{k_1 u_c}{1-x} = \bar{u}_o(1-x) \qquad (4.3)$$

A similar result was obtained by Strand et al.(203),

$$\frac{u_d}{x} + \frac{u_c}{1-x} = C_R\,\bar{u}_o(1-x) \qquad (4.4)$$

where C_R = minimum constriction factor, dependent on the column geometry.

Equations (4.2)-(4.4) make no allowance for coalescence and break-up or backmixing in the column. Misek(279) therefore proposed a modified form of equation (4.2),

$$\frac{u_d}{x} + \frac{u_c}{1-x} = \bar{u}_o(1-x)\,\exp\left[\left(\frac{z}{\alpha'} - 4.1\right)x\right] \qquad (4.5)$$

where z is coalescence correction factor which depends on the system properties as well as the column geometry.

α' is a backmixing correction factor

$\alpha' = f(d_o, \bar{u}_o, \rho_c/\mu_c)$

To verify equation (4.5), Misek investigated different systems in a 250 mm diameter R.D.C. The results were plotted graphically as,

$$\log \frac{u_d}{x(1-x)} + \frac{u_c}{(1-x)^2} = f(x) \qquad (4.6)$$

The results showed good agreement for systems of low interfacial tensions, whereas high interfacial tension systems showed poor agreement.

In all the above studies, only the average value of hold-up has been determined. Some workers have reported the variation of hold-up along the radial and axial directions. Strand and Co-workers(203) determined radial and axial point values of hold-up in 15 cm and 110 cm colum diameter R.D.C's. Results for the smaller column were erratic presumably due to small dimensions. However, in the larger diameter column, the radial hold-up was found to remain substantially constant except in the vicinity of the rotor shaft. In the axial direction, the hold-up was found to increase up the column. Towards, the end of the column, the hold-up decreased. Other workers(115,114) have reported similar results for axial hold-up profiles. These, generally, show a maximum value at a point about midway up the column.

Mumford and Al-Hemeri(282) proposed an empirical correlation for point hold-up x', at a dimensionless height h,

$$x' = \left[0.0013\,N + 0.38\left[(V_d-1)-1\right](h-h^2) + 0.076\left(1 - \frac{1}{V_d}\right)\right. \quad (4.7)$$

More recently, Murakami and Co-workers(286) derived a correlation, based on dimensional analysis, for the dispersed phase hold up over the whole length of the column. This was claimed to give good agreement with their own as well as other workers'(116,287,288) experimental results.

4.3.1.2) Drop Size:

In all liquid-liquid extractors, the dispersed phase exists predominantly as discrete drops. Hence, in order to analyse the performance of an extractor, the assumption is made that these drops are spherical and of uniform size. The mean drop size is normally calculated from the sauter, or volume-surface mean,

$$d_{32} = \sum i\ n_i\ d_i^{3} \Big/ \sum i\ n_i\ d_i^{2} \quad (4.8)$$

Research workers(282-290) who have made drop size measurements in R.D.C's, have used 300 drop samples as the basis for representing the dispersons. All of these workers with the exception of Misek(283), have presumed that d_{32} is the appropriate mean drop diameter to represent dispersion behaviour. Misek considered that a higher order of mean size,

$d_{43} = \sum i\ n_i d_i^{\,4} \Big/ \sum i\ d_i d_i^{\,3}$, represented the hydrodynamic and mass transfer processes better.

Various workers(285,291,292) have concluded that it is not sufficient to evaluate a mean size, but the distribution of drop sizes must be considered in predicting column performance.

Chartres and Korchinsky(177), measured drop size distributions in a 23 cm diameter, 135 cm high R.D.C. column. Inlet drop sizes were found to have a strong influence on measured column drop sizes with a large inlet drop size, the column drop size was influenced by the break-up rate of drops which was dependent on the presence of solute and on the direction of mass transfer.

By analogy with droplet break-up mechanism in packings, Misek(279) considered the vertical velocity of the drops leading to successive impacts on the stators and discs. From limited experimental work, Misek proposed the following expression for the mean diameter,

$$d_{\text{mean}} = 0.38\left(\frac{\sigma}{\Delta\rho g}\right)^{0.5} \tag{4.9}$$

Mumford(118), found that in the region of $Re \simeq 10^4$, the mean drop sizes were independent of hold-up and in agreement with the correlation proposed by Misek, equation (4.9). At increased speeds, the overall tendency was for drop sizes to increase, over the whole spectrum, with hold-up.

Jeffreys and Mumford(293); and Thomas and Mumford(294) have shown the droplet break-up by impact on stators or discs was not the predominant mechanism, influencing drop sizes. However, drops may rupture by impact on the edge of the stators or discs as shown by Thornton(295).

Jeffreys and Mumford(293), investigated the droplet break-up mechanism photographically in a 7.5 cm R.D.C. with (a) a non-wetted disc below Re $\simeq 1.75 \times 10^4$, when discrete drops persisted beneath the disc and (b) with a wetted disc, when the dispersed phase coalesced into a layer beneath the disc and re-dispersed from the periphery. For non-wetted discs, a criterion was expressed for droplet break-up due to dynamic pressure based on the stable drop size after Kolmogoroff, viz,

$$r_{s.d} \simeq \sqrt{2}\left[\frac{\sigma}{K_f \rho}\right]^{3/5}\left(\frac{L^{2/5}}{V^{6/5}}\right) \qquad (4.10)$$

Good agreement was found between equation (4.10) and maximum observed drop sizes. For the case of wetted discs, the value of the drop measured mean diameter formed from ligament disintegration was found to be consistently less than the value of d predicted from atomization equations for centrifugal discs. The disparity increased as the ratio $(\sigma/\Delta\rho.g)$ increased.

Mumford and Al-Hemiri(282) derived an empirical formula for the Sauter-mean diameter in terms of the system properties and the column height. d_{32}, decreased with column height and the results were correlated by,

$$d_{32}/R = 4.7\times10^{17}\left(\frac{NR^2\rho_c}{\mu_c}\right)^{-3.33}\left(\frac{\mu_d}{\mu_c}\right)^{0.23}\left(\frac{NR\mu_c}{\sigma}\right)^{2.0}(x)^{0.225}\left(\exp 0.4\left(\frac{n}{z}\right)\right) \qquad (4.11)$$

4.3.1.3) Flooding.

A characteristic of all counter current contactors, unlike parallel flow mixers, is that for each flow rate for one of the liquids, there is a maximum possible flow rate for the other, governed by the liquid properties, the design of the device, and the motivating force, whether gravitational or centrifugal. If an attempt is made to exceed the maximum flowrate for the second liquid, one of the liquids will be rejected by the equipment, which is said to be"flooded"(19). With some systems, it is difficult to recognise flooding(114). Instead of flooding in the usual way, the phases invert.

Reman(300), showed that the capacity of the RDC was contolled by the size of dispersed phase droplets which depend on the power dissipated by the rotor discs per unit mass. The latter was shown to be proportional to the following combination of R.D.C's geometric variables

$$\text{power input} \sim \frac{N^3R^5}{HD^2}$$

Reman determined a rough guide for power input operating range as shown in figure (4.4).

Logsdail et al.(278), determined the flood point for a 7.5 cm diameter RDC using a number of solvent-water systems. The variables studied were the rotor speed, compartment height, and the disc and stator diameters. In the absence of solute, data was interpreted in terms of the characteristic droplet velocities which were correlated with column geometry and the physical properties of the system. In the presence of mass transfer, the total throughput increased by 100-200% when solute transfer took place from the solvent (dispersed phase) to the aqueous phase, whereas in the reverse direction the throughput was reduced by approximately 10% compared with the solute-free system.

4.3.1.4) 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. When phase inversion in a stirred tank is presented graphically by plotting the volume fraction at inversion of one phase against stirring speed, a hysteresis effect is clearly

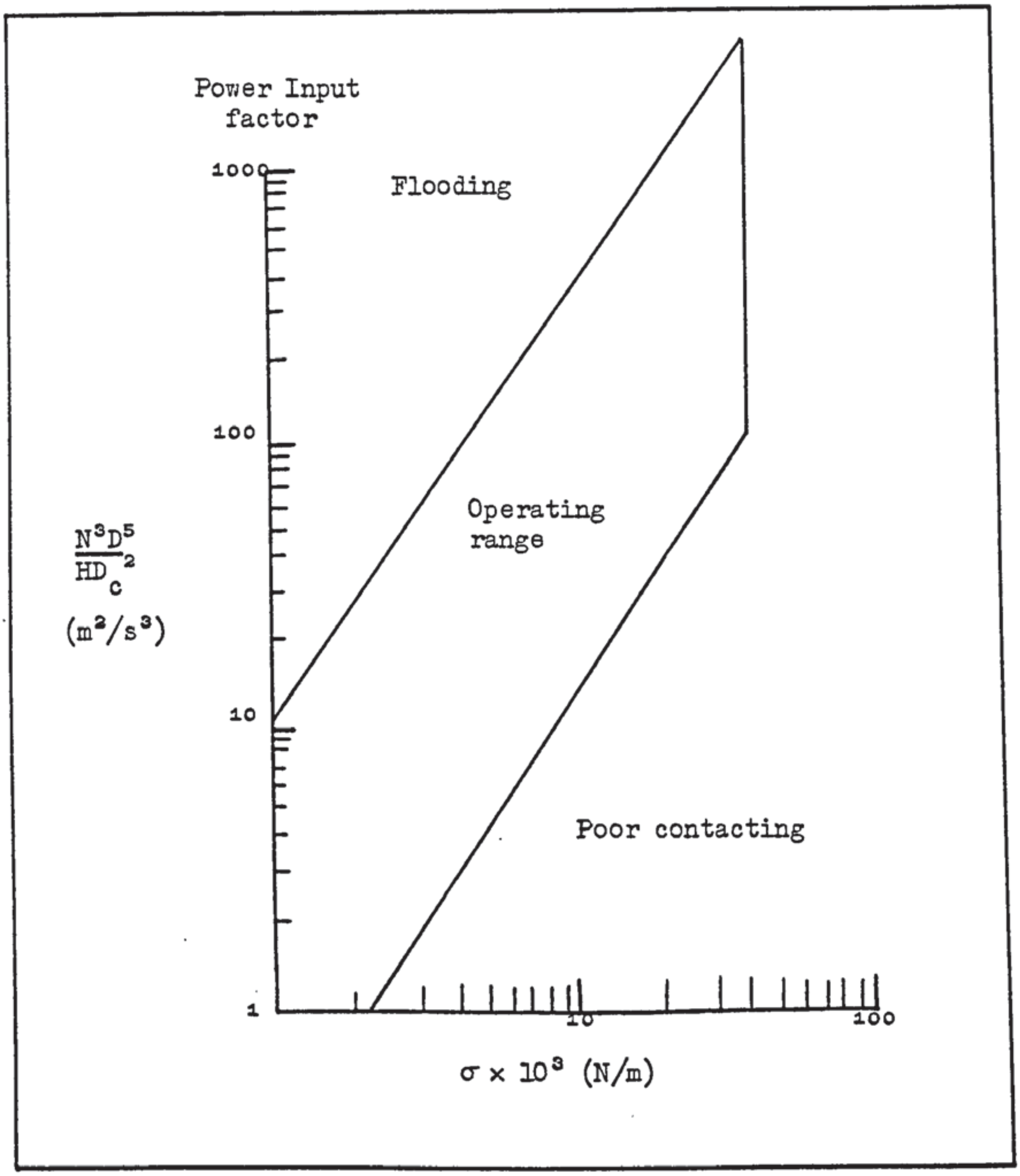


FIGURE 4.4: R.D.C. power input operating range(300)

defined by two curves defining a meta stable or ambivalent region. Figure (4.5) represents inversion characteristics for the tolune/water system(301). In this figure, the system can only exist as water dispersed/organic continuous (W/O) dispersion above the upper curve and as organic dispersed/water continuous (O/W) dispersion below the lower curve. In between the two curves either configuration is possible depending on the system's past history. If at constant speed the organic liquid is added to the O/W dispersion, inversion takes place on reaching the upper curve. Conversely, on adding water to the W/O dispersion, inversion is indicated by the lower line.

Selker and Sleicher(304) found that the ambivalent range was a function of the viscosity ratio and not strongly dependent upon vessel characteristics or stirring speed. This was confirmed by Yeh and Hayne(303) who found that the phase-volume ratio at the point of inversion was equal to the square root of the viscosities ratio of the respective phases.

In a study using an agitated tank, 2.3L in volume, Quin and Sigloh(302) found that for a fixed impeller speed, the inversion concentration ϕ expressed as volume fraction of the organic phase was given by,

$$\phi = \phi_0 + a/p \qquad (4.12)$$

where ϕ_0 was the asymptotic value for high energy input, p the energy input and a approximately proportional to σ/ρ_{mean}.

Luhning and Sawistowski(305) by investigating the inversion characteristics of a number of different systems showed that the width of the hysterisis gap was critically affected by the interfacial tension; the lower the interfacial tension, the wider was the hysteresis gap, i.e. the greater was the resistance of the system to inversion.

Clarke and Sawistowski(301) investigated the effect

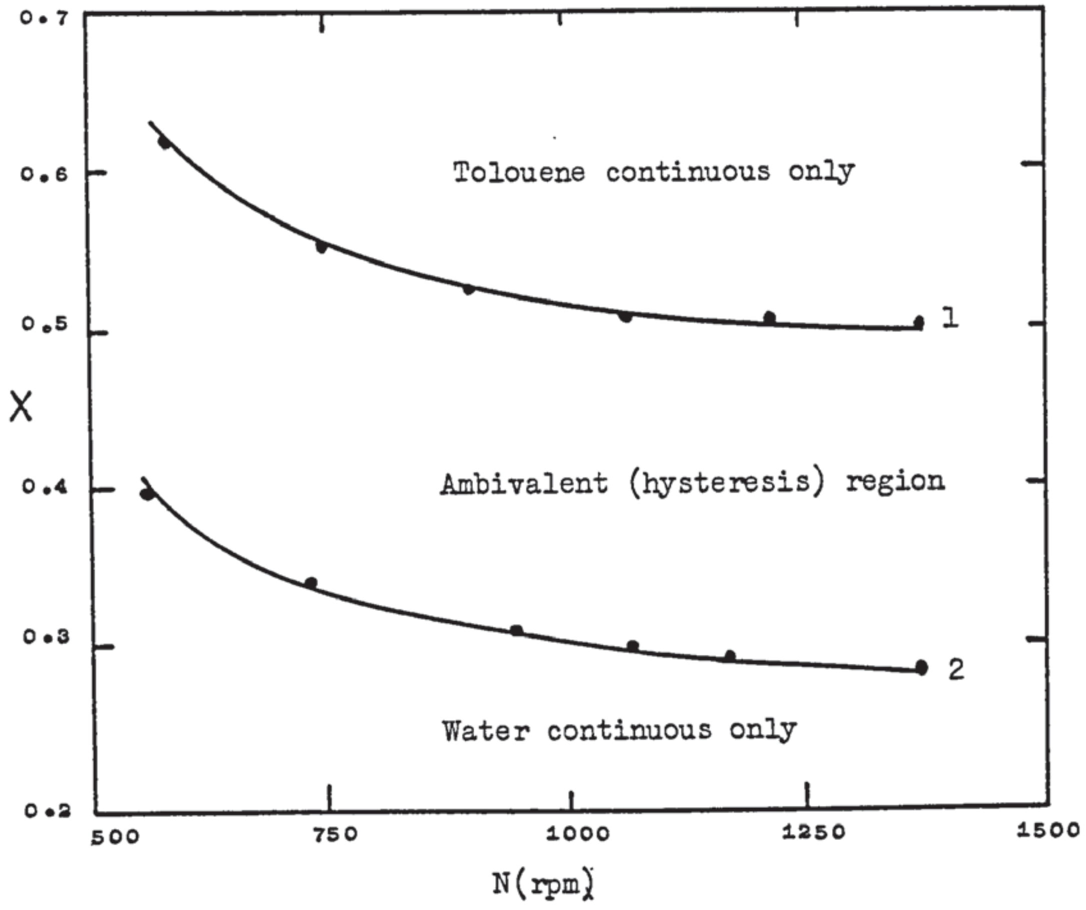


FIGURE 4.5: Inversion characteristics for the toluene/water system(301)

1 - Inversion from O/W to W/O
2 - Inversion from W/O to O/W
X is volume fraction of toluene

on inversion characteristics of the presence of a solute. It was found that the presence of a solute in equilibrium between the phases increased the resistance of the dispersion to phase inversion. This was attributed to the lowering of interfacial tension causing a widening of the hysteresis gap.

Any factor affecting coalescence is likely to influence phase inversion characteristics of a system. Such a factor, of overriding importance, is the effect of a third diffusing component(320). Jeffreys and Lawson(316) and Others(317-319), have shown that the transfer of a third component into a drop stabilizes the drop, whereas diffusion out of the drop accelerate coalescence. Jeffreys and Davies(321) suggested that promotion of coalesence when solute was being transferred from the drop is a result of interfacial tension gradients developed in the region of the approaching drops. For most pairs of immissible liquids the addition of a third component soluble in each phase lowers the interfacial tension. Thus when mass transfer takes place from the drop the concentration of solute in the contact zone between the two approaching drops rapidly reaches equilibrium with the drop. This results in a decrease in the interfacial tension locally which causes the interface in the contact zone to dilate drawing with it part of the intervening film which promotes coalescence. When solute is transferred into the drop the situation is reversed and material from the bulk continuous phase is drawn towards the contact area, which retards film drainage and hence stabilizes the drops.

Al-Hemeri(115) investigated phase inversion phenomenon in a 0.10 m RDC. The onset of phase inversion occurred in the bottom compartment giving rise to a very large "slug", possessing a high terminal velocity which travelled up the column and eventually dispersed in higher compartments. With further increase in dispersed phase flow the same effect was repeated at an increased frequency until other compartments reached their phase inversion hold-ups, i.e. complete inversion obtained in the mixing section.

Sarkar(114), reported a different phase inversion mechanism in the same RDC. According to Sarkar phase inversion was a cyclic phonomenon with inversion normally commencing at the bottom compartment and moving up gradually. As soon as the 'slug' 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. The whole process was repeated indefinitely. The same mechanism was reported by Arnold(119) for phase inversion in an Oldshue Rushton column.

4.3.1.5) Backmixing.

Longitudinal or backmixing is an important parameter in the design of continuous differential contactors. Backmixing in the R.D.C. occurs due to non-ideal flow in which a random movement of fluid is superimposed on the main flow. This phenomenon destroys the true counter current flow pattern and tends to decrease the concentration driving force.

Strand et al.(203) observed that there are several phenomena that may affect the spread of residence times of a droplet phase in the presence of a counterflowing continuous phase. Among these are:

1. Coalesence and break-up of drops
2. Droplet velocity distribution across the column radius due to vessel geometry and rotor speed.
3. Droplet velocity distribution due to different settling velocities of the various size fractions

4. Axial spreading of small drops due to turbulent velocity fluctuations in the continuous phase.

The extent of longitudinal mixing in an extractor can be evaluated by several methods. The most common is to measure the concentration of a tracer substance along the extraction column length during steady state mass transfer. Such a technique was followed by Westerterp and Landsman(299) in backmixing studies in two small R.D.C's of 4.1 and 5.0 cm diameter. Results were interpreted by means of a diffusion model. The axial diffusivity was considered as the sum of a flow contribution and a rotational contribution. Results were correlated by,

$$\mathrm{Pe} = \frac{2n}{1+13\times10^{-3}(NR/U)} \qquad (4.13)$$

Most of the studies on backmixing have concentrated on the continuous phase. Determinations of the dispersed phase axial mixing are much more difficult to make(306). Values of the dispersed phase axial diffusivities obtained by Stemerding and Co-workers(307) in 6.4 and 64 cm diameter columns were much higher than those of the continuous phase. The ratio of dispersed to continuous phase axial dispersion coefficient varied from about 100 to 1, with the ratio approaching unity at decreasing velocities of the dispersed phase. Stainthorp and Sudall(308) determined backmixing in both phases using a 3.5 cm diameter RDC, under conditions of actual mass transfer, for the system water, O-cresol,kerosene. A dye impulse technique was used to arrive at an estimate for backmixing of both phases. The extent of backmixing was expressed as the ratio of the backflow between stages to the feed-rate. The measurements for the dispersed phase did not agree with the models proposed by previous workers. A backmixing factor for the dispersed phase about twice that, predicted theoretically, was recommended(308).

Recently, Murakami and Misonou(309) have derived a correlation on the bais, of dimensional analysis, for the back-mix ratio; and operating conditions and geometry of the RDC. This was claimed to give good agreement with experimental results.

4.3.2) Mass Transfer.

Mass transfer studies in the RDC have been carried out by various research workers and the effect of different parameters on the overall efficiency assessed. The factors affecting mass transfer are generally recognised as the specific load, peripherial speed, the ratio of dispersed to continuous phase flow rate, column geometry and the extent of backmixing(310). On the other hand mass transfer affects the hold-up of the dispersed phase, and the characteristic velocity of the droplet swarm(278). This was attributed to the change in interfacial tension resulting in interfacial turbulence, inhibition or enhancement of drop circulation and change of drop size depending on the direction of solute transfer(267).

The importance of allowing for backmixing in all mass transfer calculations involving the RDC has been realised for sometime. However, it has been reported that the effect of back-mixing on mass transfer rate coefficients obtained in laboratory RDC units is considerably lower as compared to that in industrial size RDC units(203,308,311,312).

Various research workers have derived correlations for the mass transfer in the RDC. Table 4.1 represents the most common of these correlations.

Table 4.1
Correlations for Mass Transfer in RDC

AUTHOR AND REFERENCE	CORRELATION	REMARKS
Vermijs and Kramers (298)	$K_{od}a = f(x)$	f(x)-function of hold-up dependent on rpm and system variables, - reporte data is for water as dispersed phase; graphical.
Reman and Olney (310)	$\eta = f\left(\frac{N^3 N_R^5}{Z_c D_t^2}\right)$	η - Efficiency; empirical
Logsdail et al (278)	$(HTU)_{oc}(x)\left(\frac{g^2\rho_c}{\mu_c}\right)^{1/3} = K'\left(\frac{\mu_c\, g}{\bar{u}_o^3(1-x)^3\rho_c}\right)^{\frac{2m'}{3}}\left(\frac{\Delta\rho}{\rho_c}{}^{2/3}\right)^{(m'-1)}$	K' and m' are constants varying with direction of mass transfer and systems employed.
Olney (285)	$\xi_c \frac{d^2y}{dz^2} + \frac{V_c}{1-h}\frac{dy}{dz} = -\frac{6h}{1-h}\int_{d_o}^{d_m}\frac{K_D(d)}{d} f(d)\,[x(d)-my]\,\delta(d)$	similar expression is given for dispersed phase. No analytical solutic is available. f(d) represents drop size distribution
Al-Hemeri (115)	$\sum_{n=1}^{n}\left[\sum_{i=1}^{i}\int\left[\left[\frac{dc}{(c-c^*)}\right]_i\right]\right]_n = \sum_{n=1}^{n}\left[\sum_{i=1}^{i} A_i/V_i \int K_i\, dt\right]_n$	n is total number of compartments and i refers to the particular period, viz formation, free rise, etc.

CHAPTER 5

EXPERIMENTAL INVESTIGATIONS

It is apparent from the literature reviewed in Chapter (3), that coordinated experimental work and mathematical modelling of extractive reactions, in which one of the reactants is dissolved in an organic solvent and a second reactant resides in an aqueous phase, is lacking. Therefore it was decided to study this process under batch conditions as well as under continuous counter current conditions. For the second case a rotating disc contactor was chosen because of its versatility and suitability for use with systems of low interfacial tension(131,132,152).

5.1) Selection of a System.

A review of the factors necessary for the study of an extractive reaction in a two phase liquid-liquid system revealed that the following considerations have to be taken into account:

1) It is desirable that the reaction takes place in one phase only; e.g. the aqueous phase, and be fast enough to be studied at room temperature if possible.
2) The equilibrium distribution of the different components should be such that the product favours the non-reactive phase so that it will be extracted as it is formed. On the other hand the reactants themselves should favour the aqueous phase in order to increase the reaction rate.
3) The components should be available in a reasonably pure form and be relatively inexpensive, non-toxic and free of other hazards as much as possible.
4) The physical properties be conducive to good phase separation.
5) All the components should be amenable to simple chemical analysis independently.
6) In the selection of the reactive system it would be preferable if the kinetics were simple and no solid deposition or side reactions occurred.

7) Data required for the system should either be readily available and/or easily determined and correlated.

An appraisal of the possible two phase liquid-liquid systems for kinetics(135), solubilities and physical properties(136,139), hazards and toxicity(137,138) and other considerations set out above led to the conclusion that an esterification reaction in the presence of an organic solvent might be suitable. Further investigations and experiments with different alcohols(51) and solvents(134,148) led to the selection of the esterification of n-butyl alcohol in the presence of sulphuric acid as catalyst and n-heptane as solvent.

$$CH_3COOH+C_4H_9\,OH \xrightleftharpoons{H_2SO_4} CH_3COOC_4H_9+H_2O$$

5.2) Description of Equipment.

5.2.1) Batch Reaction

The equipment used for determining the reaction kinetics and performing the batch reaction in the presence of the solvent, is shown in figure (5.1). It essentially consisted of a one litre flask with three openings. An electric stirrer was passed through a glass gland of the middle opening. The other two openings were used for inserting a thermometer and withdrawing samples respectively.

Samples were withdrawn from the sampling point using a syringe. The reactants were fed into the reactor through a funnel placed in the sampling port.

The reactor was kept in a Townson and Mercer constant temperature water bath to within ∓ 0.1°C.

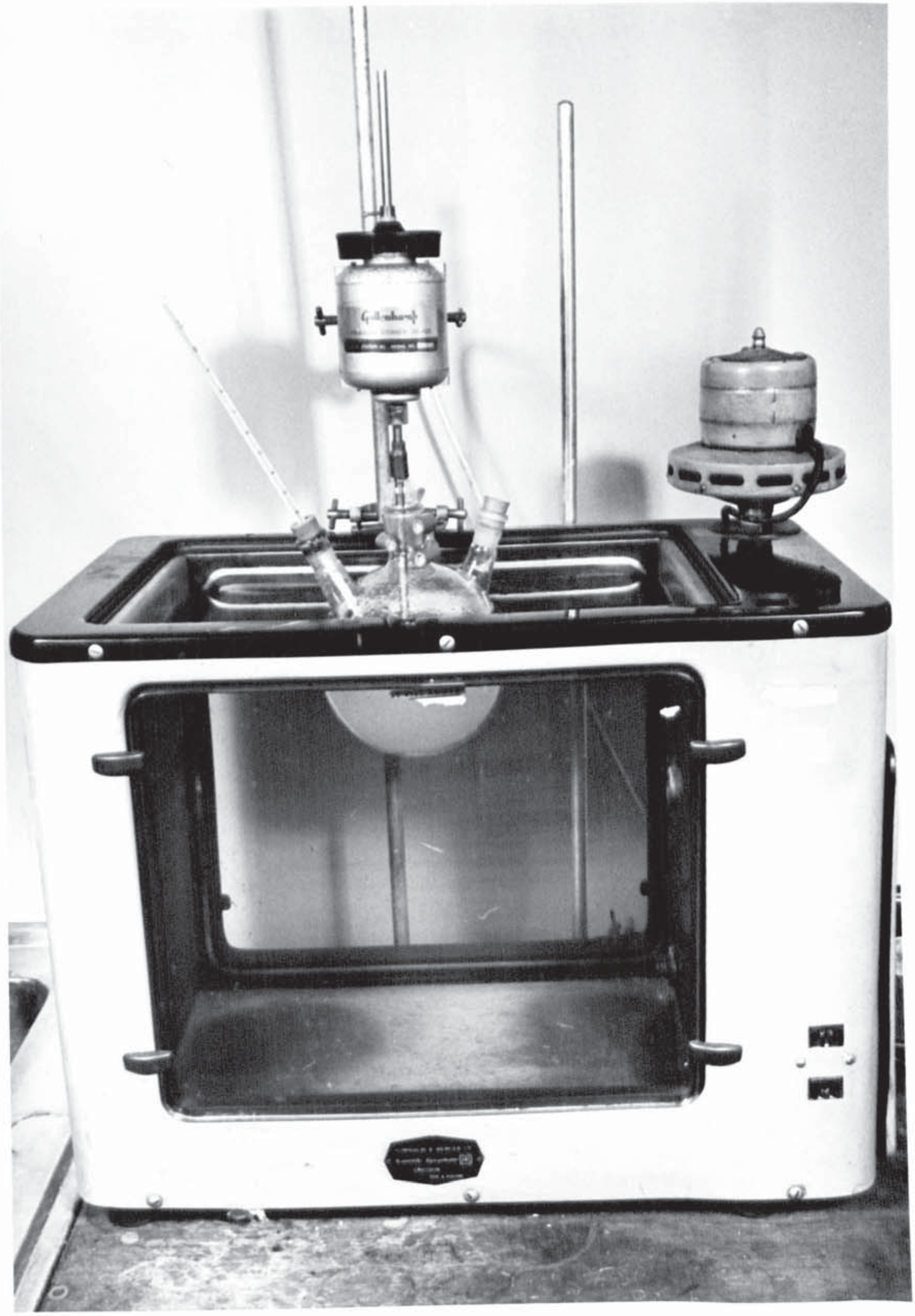


FIGURE 5.1 Batch Reactor

5.2.2) Equipment for Solubilities Data of Two Phase Liquid-Liquid Systems.

The equipment used for the determination of solubilities data of two phase liquid-liquid systems were:

A. Equipment used for binodal curves determination by the cloud point. These were:

1. large temperature controlled water bath
2. Clear glass measuring cylinders of capacities ranging from 50 to 100 cc
3. Precise 25 ml and 50 ml burettes fitted with PTFE stop-cocks.

B. Equipment used for tie line determination. This consisted of a 1 litre capacity separating funnel, fitted with PTFE stop-cock. This acted as a mixer-settler and was placed in the constant temperature bath. Agitation was by means of a Gallenkamp stirrer of fixed rotation speed at 1200 rpm.

5.2.3) Equipment for Continuous Extraction Reaction-The Rotating Disc Contactor.

The rotating disc contactor designed by Al-Hemeri(115) and modified by Sarkar(114) was used as continuous extractor reactor. Only minor modifications were necessary e.g. drain-lines for each phase were added which could be used for either draining or flushing the pumps and the column with water after each run to minimise corrosion. Some process lines were also altered and new Q.V.F. control valves installed as appropriate. However, the main equipment remained essentially that of Al-Hemeri.

A flow diagram is shown in figure (5.2) and a general arrangement in figure (5.3). The column shown in figure (5.4) 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. Five

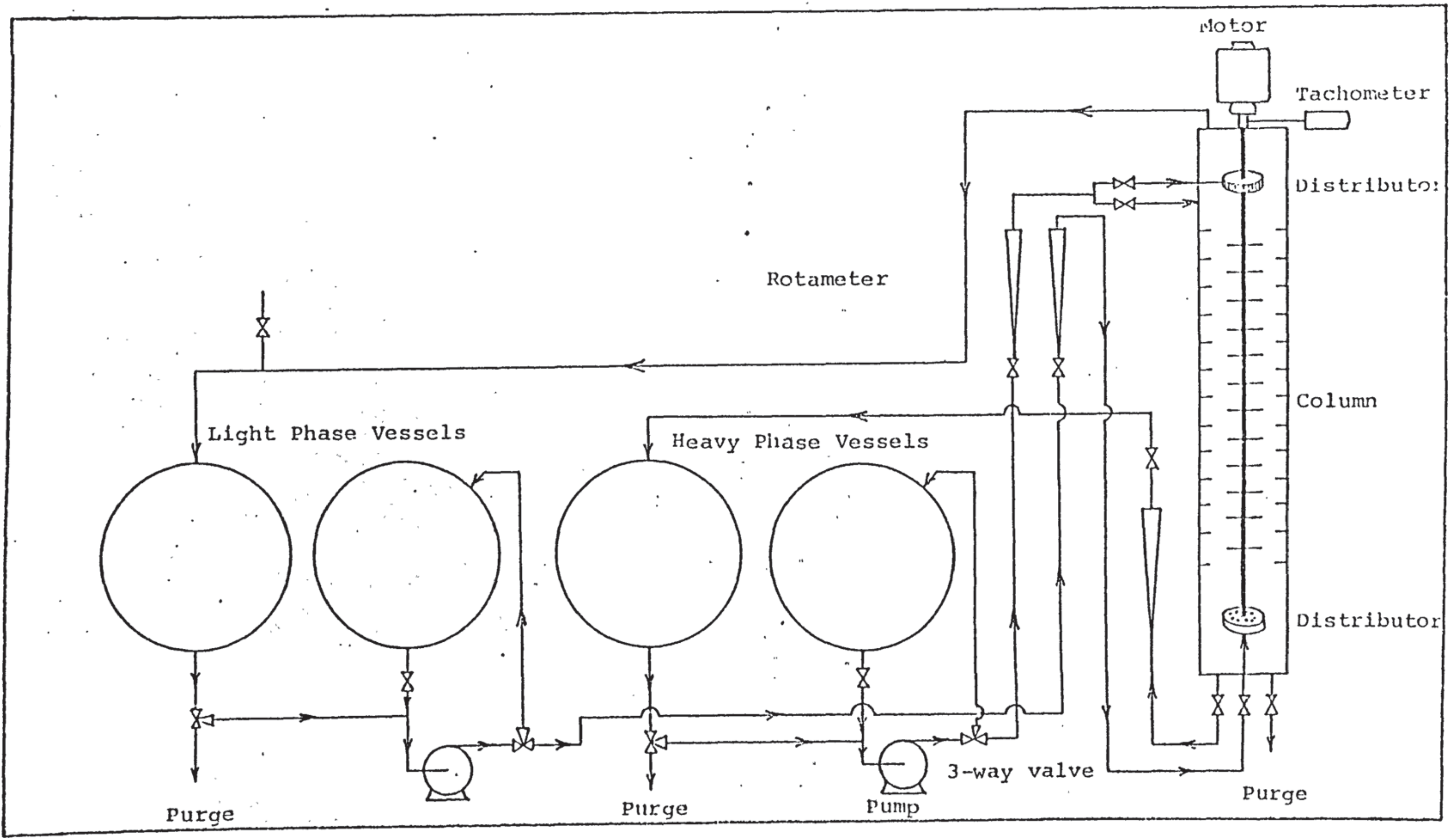


FIG. 5.2 Flow Diagram

FIGURE 5.3 General Arrangement

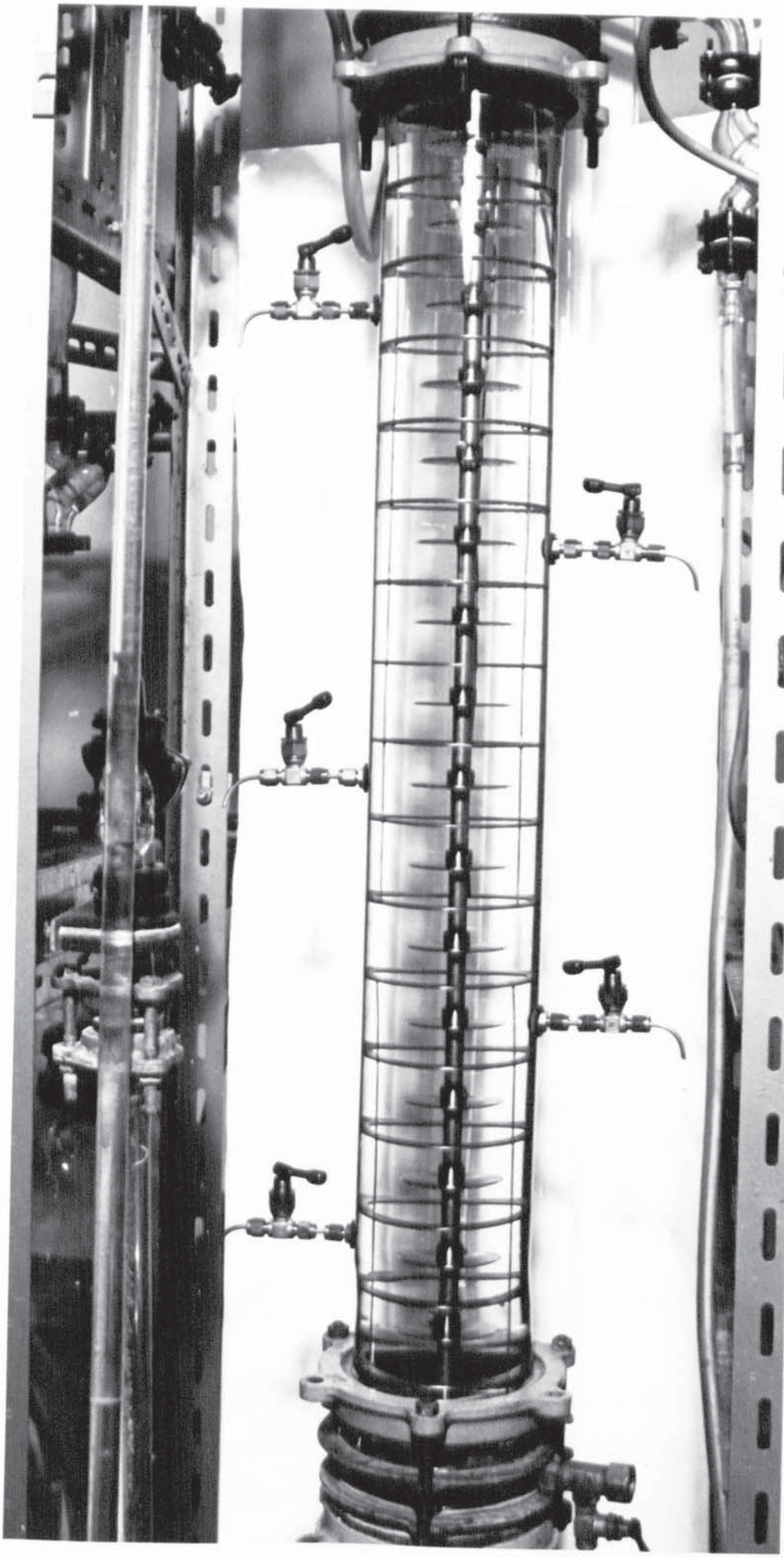


FIGURE 5.4   R.D.C.

sampling points were present at 0.15 m intervals along the column length. Each point comprised a 10 mm diameter hole fitted with a quick-acting toggle valve. Additional sampling points were provided at the respective phase inlets and outlets.

The column internals were fabricated from 18/8 stainless steel which were fitted closely at the column walls. The stators were supported by means of three equispaced lengths of 1 mm stainless steel wire. The thickness of the discs and stators was 2 mm. 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.

The heavy phase was introduced into the column at a point just above the top compartment, through a stainless steel distributor plate, and left via a pipe at the bottom of the column. The heavy phase inlet was such that, if desired, the stream could pass through the stainless steel disperser illustrated in figure (5.5) and hence constitute the dispersed phase. The lighter phase was similarly introduced via a distributor plate. Each distributor consisted of 46,2 mm dia holes arranged on 6 mm triangular pitch inside a 0.10 m dia circle. There was a small upward projection around the periphery of each hole.

The column end plates were made 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. The necessary inlet and outlet pipes were integral with the end plates.

The agitator shaft was driven by a $\frac{1}{4}$ h.p A.C.Voss motor, controlled by a 'Torovolt' variable voltage mains transformer. The drive shaft of the motor was coupled to the column shaft via a flexible rubber joint. The other end was attached to a high pre-

FIGURE 5.5 Top Distributor and Bearing Assembly

cision Comrack Type 2101 electronic tachometer of 0-3000 rpm. 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 reservoir and receiver for the light phase and the other two as reservoir and receiver for the heavy phase. Pipe work was mainly of 16 mm i.d. borosilicate glass but P.T.F.E tubing was used in certain sections. Flowrates were measured by rotameters with stainless steel floats. Provision was available for the circulation of the liquids in the reservoirs, or between two vessels containing the same liquid.

Fluids were transferred by means of two Stuart-Turner centrifugal pumps, type No 10 and 12 capable of handling 1.25/0.45 ℓ/s 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. The speed of each pump could be varied by means of a 'Torovolt' variable voltage unit.

The equipment was located in an isolated pilot plant room provided with flameproof switchgear and lighting and an efficient air extraction system. No provision was made for temperature control of the equipment, but environment temperature was always within 20 ∓ 1°C.

5.3) Materials used.

The following materials were used: glacial acetic acid, G.P.R.'A' grade of density 1.048-1.051 gm/c.c.; n butyl alcohol, G.P.R.Grade of density 0.809-0.811 gm/c.c.; n-heptane conforming to IP specifications for 'Normal heptane', density 0.682-0.684 gm/cc; n butyl acetate, GPR grade of density 0.878-0.880 gm/cc; sulphuric acid G.P.R grade of density 1.84 gm/cc and filtered water.

N-heptane used in the extraction-reaction process was first washed thoroughly with water and then distilled and reused.

Interfacial tension and gas-liquid chromotographic analysis were used as tests of purity. During distillation, it was observed that an azeotrope of acetic acid-water was obtained at 76.6°C, and another azeotrope of n-heptane-water was obtained at 79.2°C. Above this point still bottoms were rejected.

5.4) Measurement Techniques

5.4.1) Chemical Analysis

Simple acid base titrations were used for determining the concentration of sulphuric and acetic acids. For percentage esterification in the batch process, samples of the reaction mixture were diluted with cold water to 'quench' the reaction and the free acid quickly titrated. This method has been followed in esterification studies rate measurements and is reported to give good results(104,140).

A number of methods are available for analysing mixtures of alcohols and esters,

1) A fractionation technique developed by Fehlandt and Adkins(122) To remove the lower boiling alcohol and determine the ester in the residue by saponification.
2) A turbidity technique developed by Bogin(121) has been employed by several workers(122,123).
3) Baker and White(124) used infra red spectrophotometry.
4) Furnas and Leighton(125) analysed samples by density determinations at 25°C with 10 cm^3 pycnometers.
5) The most common method employed nowadays is gas liquid chromotographic techniques(120,128-130) and it was decided to adopt this method for the quantitative determination of the alcohol and ester on account of its simplicity and versatility. A standard Pye analytical column (PEG 400) was used. Stationary phase was polythylene gylcoal MW400 and detection was made by a flame ionisation detector, together with an integrator.

5.4.2) Interfacial Area.

Droplet size distributions were measured by photography and the drops were counted using the Zeiss TG3 particle counter.

5.4.3) Solubility Data.

5.4.3.1) Saturation Composition.

Data for the binodal curves of the ternary systems was determined, using the cloud point method described in references(18,14,142).

5.4.3.2) Tie Line Data.

Tie line data of the different systems were determined by vigorously agitating known amounts of the constituents for at least three hours in a one litre separating funnel placed in a constant temperature water bath. The phases were then allowed to settle and separate analytical determination of the different constituents was performed according to the procedure described above in (5.4.1).

5.4.4) Photographic Techniques.

5.4.4.1) Still Photography.

Photographs of the dispersions were taken on Kodak Tri-X panchromatic 35 mm film, 400 ASA using an Asahi Pentax Spotmatic Still Camera with a 100 mm Macro-Takomat lens at a shutter speeed of 1×10^{-3}S. Lighting was from the rear of the column using 2 × 650 watt bulbs. Two to three photographs were taken for each event.

5.4.4.2) Cine Photography.

Cine films were taken to record the phenomena of phase inversion. Kodak 16 mm Tri-X Reversa-roll film, type 7278 was used in a Beaulieu R16 cine camera. Lighting was provided by 2 × 650 watt bulbs. The films were taken at 64 f.p.s.

5.4.5) Viscosities.

Viscosities were determined by timing the passage of the fluid through a capillary immersed in a constant temperature bath (20 ∓ 0.1°C), i.e. by Cannon Fenske Viscometer.

5.4.6) Interfacial Tension.

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

5.5) Cleaning Procedure.

Great care was taken to ensure that the equipment was always free of any dirt and other impurities. Cleaning was initiated with a solution of Decon-90 which is a phosphate-free surface active agent of high pH value. However, it is widely accepted that surface active agents affect the mass transfer rates(19,34,144-146), therefore extra care was taken to make sure all the surface active agent was rinsed out of the equipment. The procedure was as follows:

The whole system was filled with 1-2% solution of Decon and this was then circulated throughout the system with the agitator on for about an hour. The system was then left for at least 12 hours after which the Decon was circulated again and then the solution was drained. Following this the equipment was filled with filtered water which was circulated for at least one hour with agitator operating and when this was complete the contents were drained. This was repeated until the system was free of the surface active agent which was checked by measuring the surface tension of the water. Care was taken to ensure that all sampling ports were well flushed.

CHAPTER 6

EXPERIMENTAL PROCEDURES AND RESULTS.

6.1) Esterification Kinetics and Batch Extraction Reaction.

The simple batch reactor shown in figure 5.1 was used for esterification kinetics as well as batch extraction-reaction studies.

The following operating procedure was adhered to: The water bath was set to the temperature required (20 °C). The reactants, catalyst and solvent were weighed separately and the acetic acid, water and sulphuric acid were mixed in the reactor while the butanol and solvent (in the case of extraction-reaction studies) were mixed in a flask which was also kept in the water bath. When all the liquid mixtures had reached the required temperature, the alcohol or solvent-alcohol solution was poured into the reactor and the stirrer started. This was considered the start of the reaction and a stop watch was started. After one minute, a sample of the reaction mixture was taken and put immediately into a preweighed flask containing 25 c.c. of chilled water to quench the reaction. The flask was weighed again to determine the exact weight of the sample and the contents were then titrated with 0.1N NaOH solution. As the reaction proceeded, further samples were taken in the same way, at definite time intervals. The length of an experiment was usually 60 minutes and the sampling frequency between one sample per minute at the beginning and one sample per 15 minutes at the end.

Finally the mixture was kept overnight and stirred again for several hours the next day and a sample taken as before and titrated to determine the equilibrium concentration. Results are shown in Appendix I.

6.2) Solubility Data.

Extensive studies were carried out to determine the various solubility data for all the different combinations of ternary and quaternary systems constituting the extractive-reactive system. The procedure set out in 5.4.3 was followed. These data are recorded in appendix II.

6.3) Studies in the Rotating Disc Contactor.

6.3.1) Hydrodynamic and Mass Transfer Studies.

Hydrodynamic and mass transfer studies were restricted to gaining useful information in support of the main study. Earlier workers(114,115) have undertaken extensive hydrodynamic and mass transfer studies in the same column.

6.3.1.1) Hold-Up.

To measure the hold-up, the column was operated under the desired conditions until steady state was reached; then the inlet and outlet valves were rapidly closed. After stopping the agitator and allowing time for complete phase separation, the height of the dispersed phase from a previously marked interface and the overall operating height of the column were measured by reference to a fixed graticule. This method gave satisfactory results for the total column hold-up. However, the method employed by other workers(115,116) for determining the variation of hold-up along the column axis, viz point hold-up was found to be completely unreliable and no attempt was made to devise a better method for point hold-up measurements.

Results of variation of average hold-up against dispersed phase flow rates at various rotor speeds are shown in appendix III.

6.3.1.2) Drop Size Distributions.

Numerous workers(115-118) have reported that drop size distributions are not directly affected by continuous phase flow rates. Therefore observations and photographs of droplets phenomena for non-mass transfer studies were mostly carried out with a stationary continuous phase. Photographs were taken after hydrodynamic equilibrium was attained which was conditional on attainment of a steady interface level.

Drop size measurements were taken from prints with (2-3) X magnitification. A Carlzeiss particle analyser was used to count and measure droplets. Irregular size droplets were recorded as spheres of equivalent diameters. Normally at least 300 drops were measured.

Sauter mean diameter was evaluated from

$$d_{32} = \sum in_i \ d_i^3 \Big/ \sum in_i \ d_i^2$$

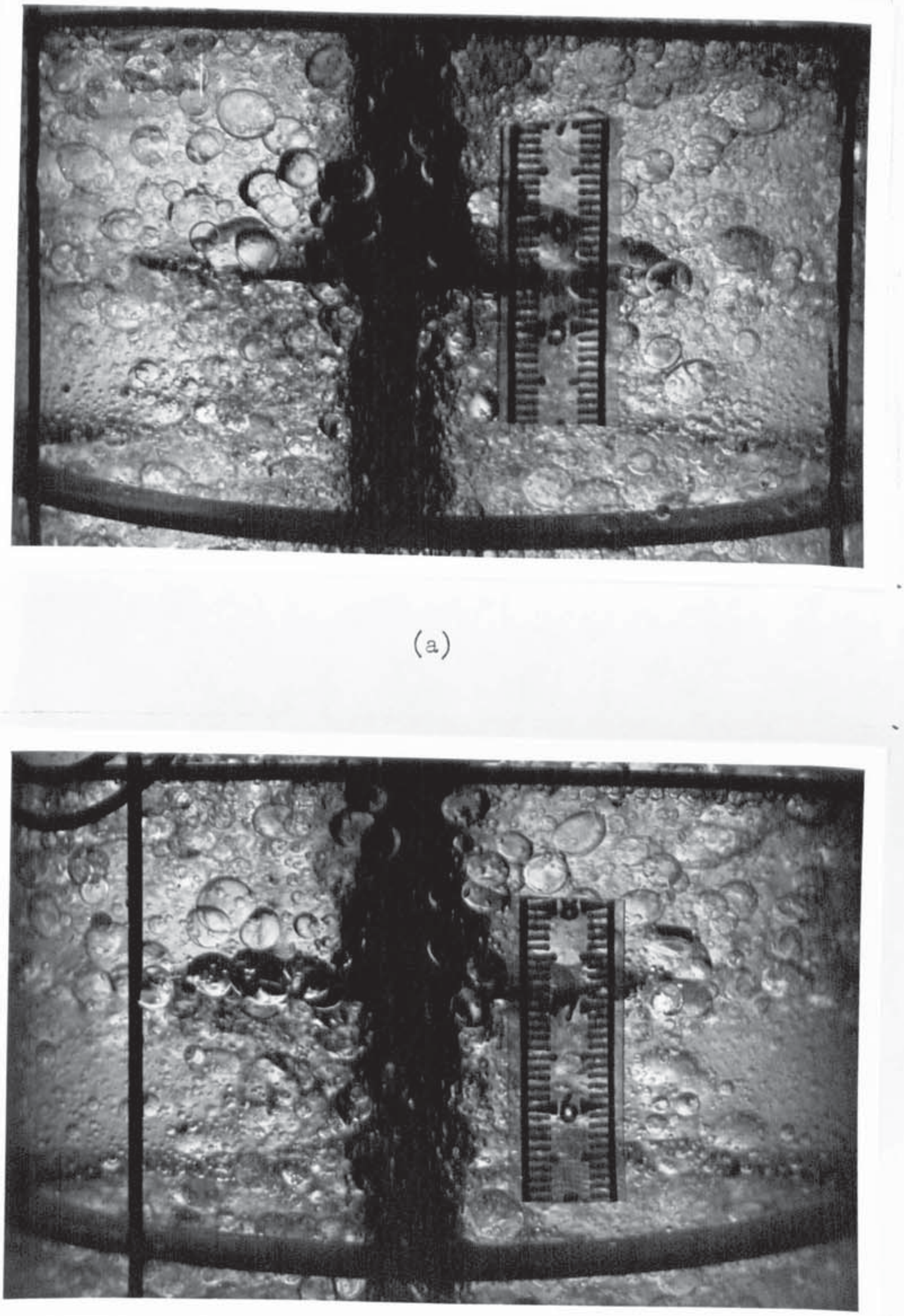
A computer program was written to evaluate d_{32}. This program is shown in appendix IV.

Visual inspection did not detect any significant variation in mean drop size with column height. Therefore the measurements were done mostly on the middle compartment.

Figure (6.1) shows heptane in water dispersions while Fig.(6.2) is a typical water in heptane dispersion.

6.3.1.3) Phase Inversion.

Phase inversion was studied for the system n heptane-water in the absence of mass transfer. The procedure was similar to that described by Arnold(119). 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. This procedure,



(a)

(b)

FIGURE 6.1: The system n heptane in water dispersions in the RDC. Typical drop size distributions at 750 RPM rotor speed (a) for top and (b) for bottom of the column. There is considerable droplet size distribution but little overall change between top and bottom of the column.

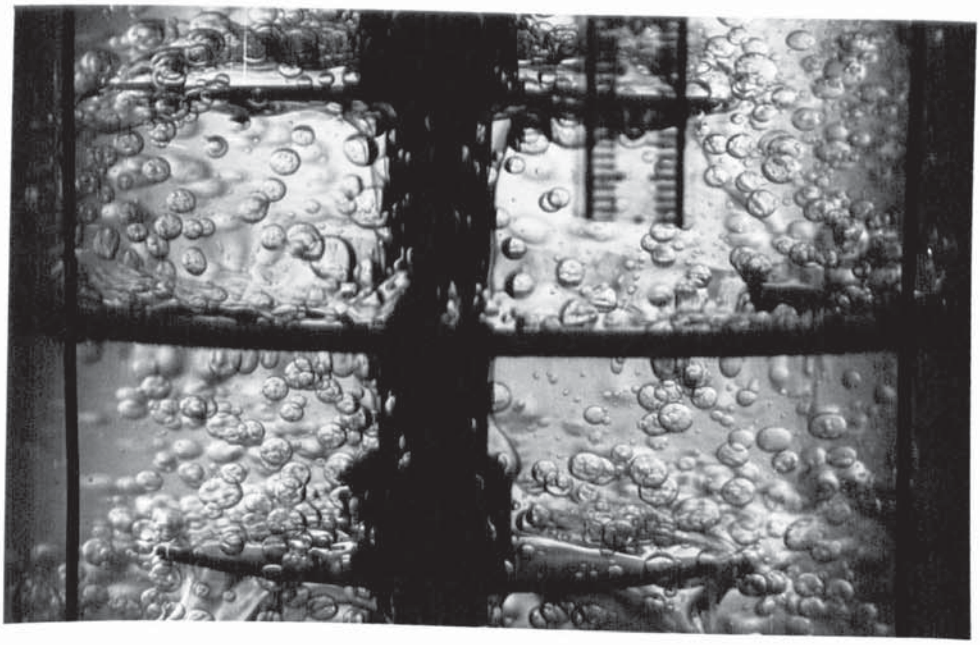


FIGURE 6.2. Typical water in n heptane dispersion showing coalescence on the column internals due to "wetting"

when adopted to water in heptane dispersions led to the phase inversion starting from the bottom of the column immediately above the lower distributor. No flooding occurred prior to phase inversion i.e. the dispersed phase droplets were not rejected. Instead an oil in water dispersion was directly formed. This consisted of very well packed droplets, accompanied by intense mixing, which gradually moved up the column until the whole section between the upper and lower distributors was full of regular polygonal shaped drops similar in appearance to that of a gas-liquid foam. The droplets were of the same size as those ensuing from the distributor i.e. there seemed to be no coalescence or break-up. When the flows were continued at the same rate, the droplets at the bottom started coalescing so that a 'normal' O/W dispersion was formed starting from the bottom and gradually moving up until the whole column was a 'normal' O/W dispersion instead of the well packed dispersion formed initially as a result of phase inversion. The process was generally very slow and took from 30-45 minutes for the column to invert from a W/O dispersion to 'normal' O/W dispersion.

It was observed that the rotor speed had no noticeable effect on phase inversion characteristics and surprisingly it was possible to obtain phase inversion with the same droplet sizes with the rotor stationary.

Phase inversion also occurred when initiating from heptane in water dispersions. Droplet build up in this case started from the top and moved down until the whole column was filled with W/O dispersion which coalesced very slowly reverting to a 'normal' W/O dispersion starting from the top and moving downwards.

A characteristic feature observed with all the phase inversion runs was the very wide hysteresis gap i.e. once inversion occurred, very high changes in phase flows were required to reinvert the dispersion. Typical results are shown in appendix III while figure (6.3) shows W/O dispersion inverting.

A cine film was taken at 64 f.p.s. This film has been deposited in the Departmental Library

6.3.1.4) Mass Transfer.

6.3.1.4.1) One Way Mass Transfer.

The term "one way" mass transfer is used here to refer to the conventional mass transfer operation whereby solute is transferred from a raffinate to an extract. Another type of mass transfer operation which does not seem to have been studied before, was performed in this study. This was the case of "two way" mass transfer whereby a solute A was transferred from water to the organic phase simultaneously with the transfer of a solute B from the organic to the aqueous phase.

One way mass transfer runs were done for acetic acid and butanal. In both cases the investigations were limited to mass transfer from n heptane dispersed phase to the water continuous phase.

The procedure followed during these runs was as follows; first the raffinate solution was made up to the required concentration. The column was filled with the continuous phase and the agitator adjusted to the required speed. The dispersed phase was introduced into the columnand its flow rate adjusted to a set value. Then the continuous phase flow was adjusted to the required value.

After steady state conditions were reached, normally after 10 minutes; samples were taken from the raffinate and extract. For the case of acetic acid mass transfer, it was also possible to get samples of the continuous phase from sampling points along the column. However, in the case of butanol mass transfer, a dispersion was obtained from these sampling ports. Photographs were taken for drop size measurements. Finally the samples were analysed by

FIGURE 6.3 Phase inversion in the water-n heptane system. The system was water/heptane dispersion originally. Inversion occurred at the bottom and slowly moved up until the whole column was filled with a well packed dispersion of heptane/water. This dispersion cleared very slowly from the bottom upwards reverting to a "normal" heptane/water dispersion.

FIGURE 6.3

titration with 0.1 N NaOH in the case of acetic acid and by gas liquid chromotography in the case of butanol. Results were recorded in appendix III.

In general mass transfer resulted in violent interfacial agitation as the dispersed phase was discharged from the distributor. Coalescence occurred as the dispersed phase moved up the column. In the case of butanol mass transfer, the dispersed phase droplets were of very irregular shape with some rivulets appearing. At high rpm's, it appeared that a double dispersion was formed. Under these circumstances no meaningful drop size count could be done for butanol-heptane/water dispersions.

Figures (6.4) and (6.5) show typical.droplets characteristics for acetic acid and butanol transfer respectively.

6.3.1.4.2) Two Way Mass Transfer.

In "two way" mass transfer, the heavy phase was a solution of acetic acid in water, while the light phase was a butanol-heptane solution.

The column was filled with the aqueous phase (Heavy phase) and the flow rate adjusted to the required value. The agitator was also set to the required speed and the light phase introduced through the distributor. As the O/W dispersion filled the column, it was noticed that phase inversion commenced at the bottom of the column and gradually moved up until it reached about half way whereby it stabilised and the column continued operating with the upper part of the column an O/W dispersion, the lower part W/O dispersion; and about 20 cms in the middle an inversion band. This is illustrated in figure (6.6).

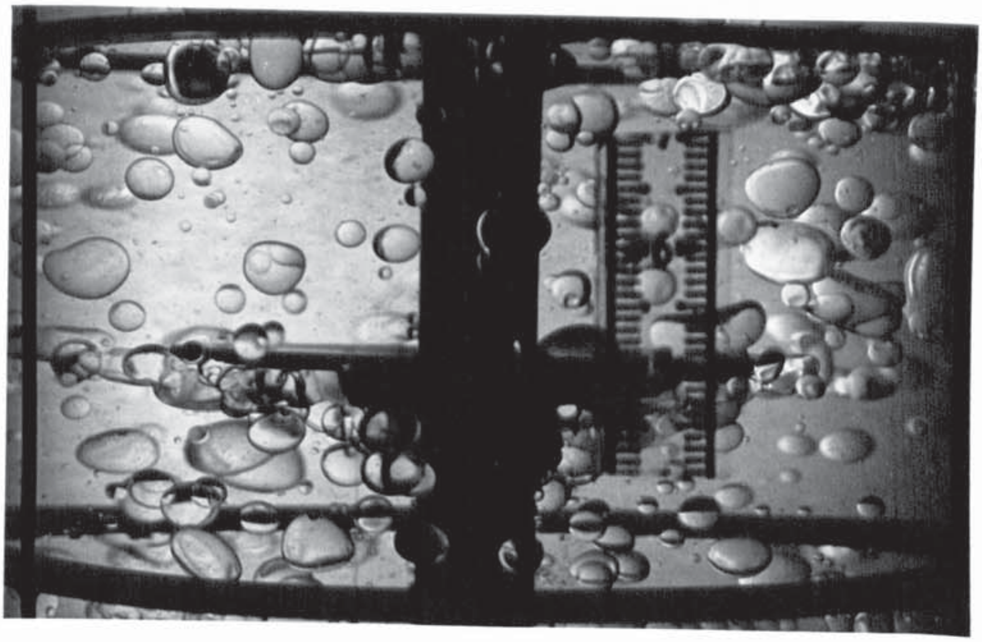
A cine film was taken which is also deposited in the Departmental Library.

FIGURE 64 Mass transfer characteristics for the system

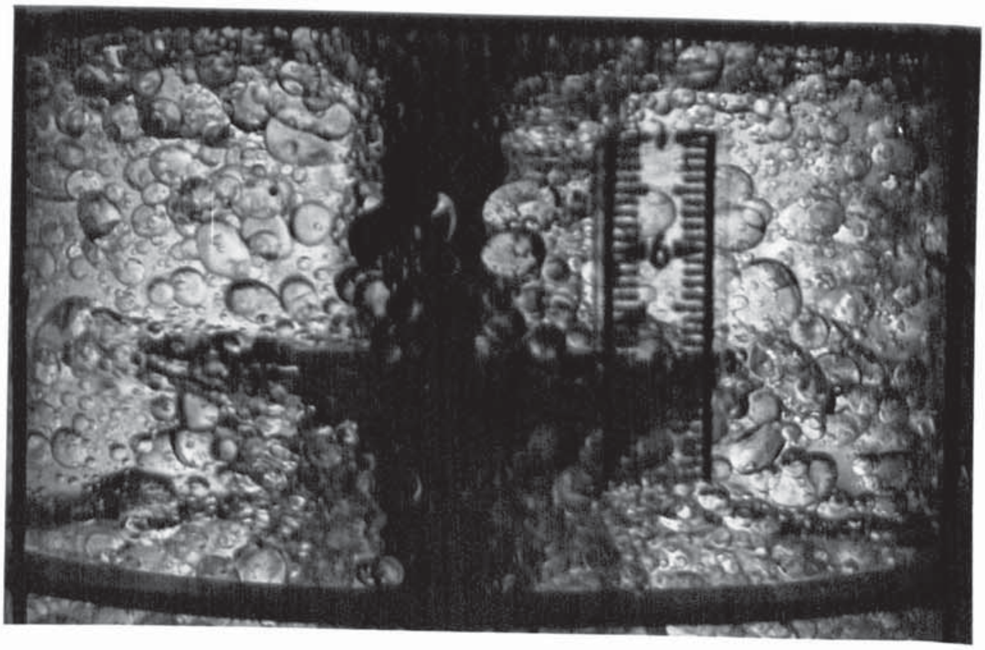
acetic acid/n heptane → water
(dispersed) (continuous)

Rotor speed = 500 RPM
Feed concentration = 27.47% acetic acid

Figure shows (a) formation of a fine dispersion due to violent interfacial phenomenon as the ruffinate ensues from the distributor, (b) shows the dispersion in the middle of the column where much of the fine droplets have coalesced while (c) shows the top of the column where practically all the secondary dispersion has disappeared and a clear O/W dispersion is formed.



(c)



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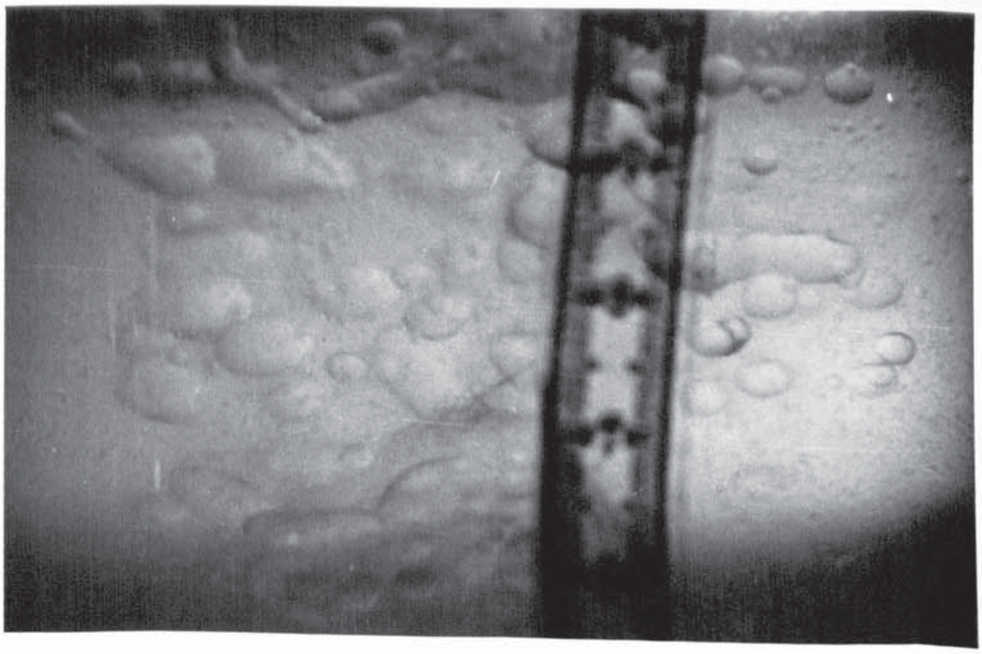
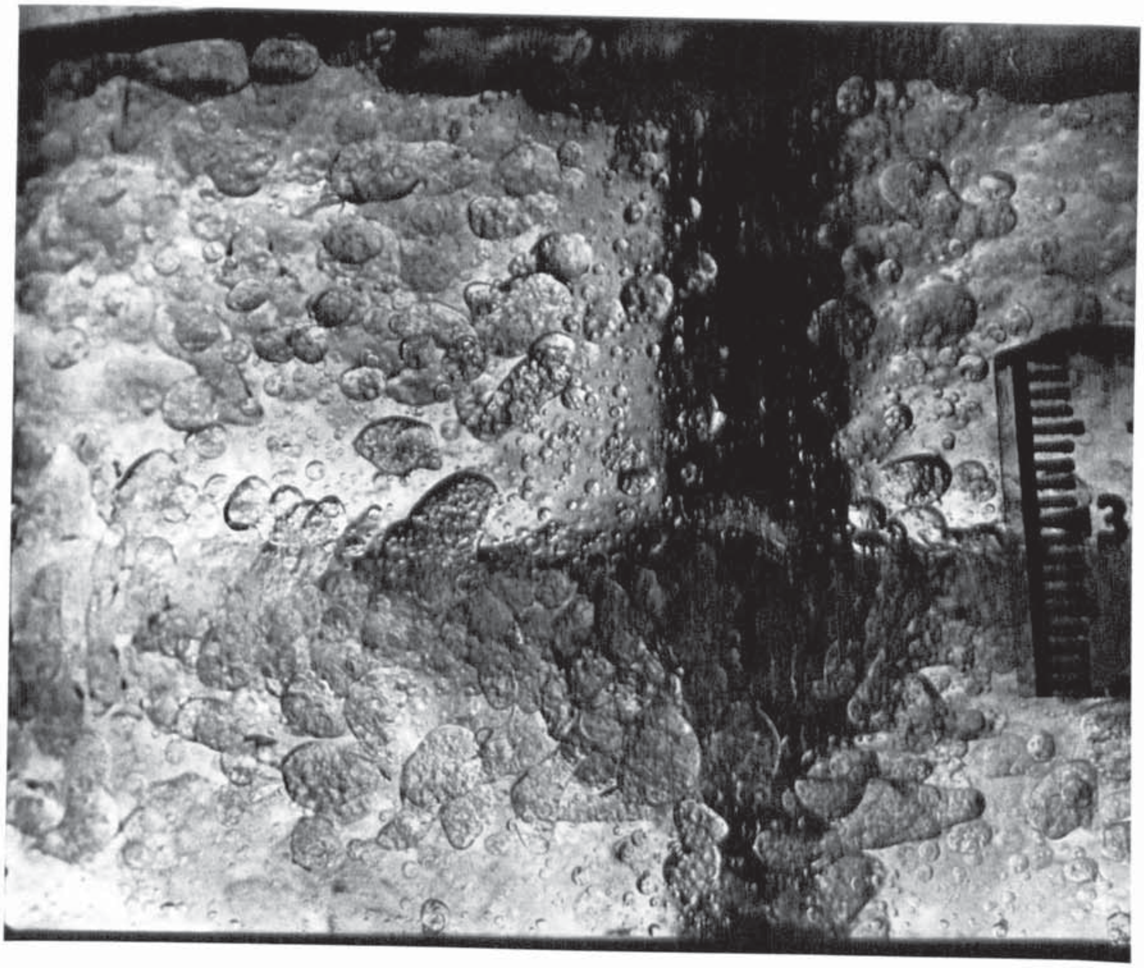


(a)

FIGURE 6.5: Mass transfer characteristics for the
system n butanol/n heptane ⟶ water
(dispersed) (continuous)

Feed concentration = 26.0% butanol

Figure (a) shows middle compartment at 500 RPM. Rivulets of the dispersed phase are formed. Figure (b) shows same compartment at 1000 RPM where a double dispersion is formed.



(b)

(a)

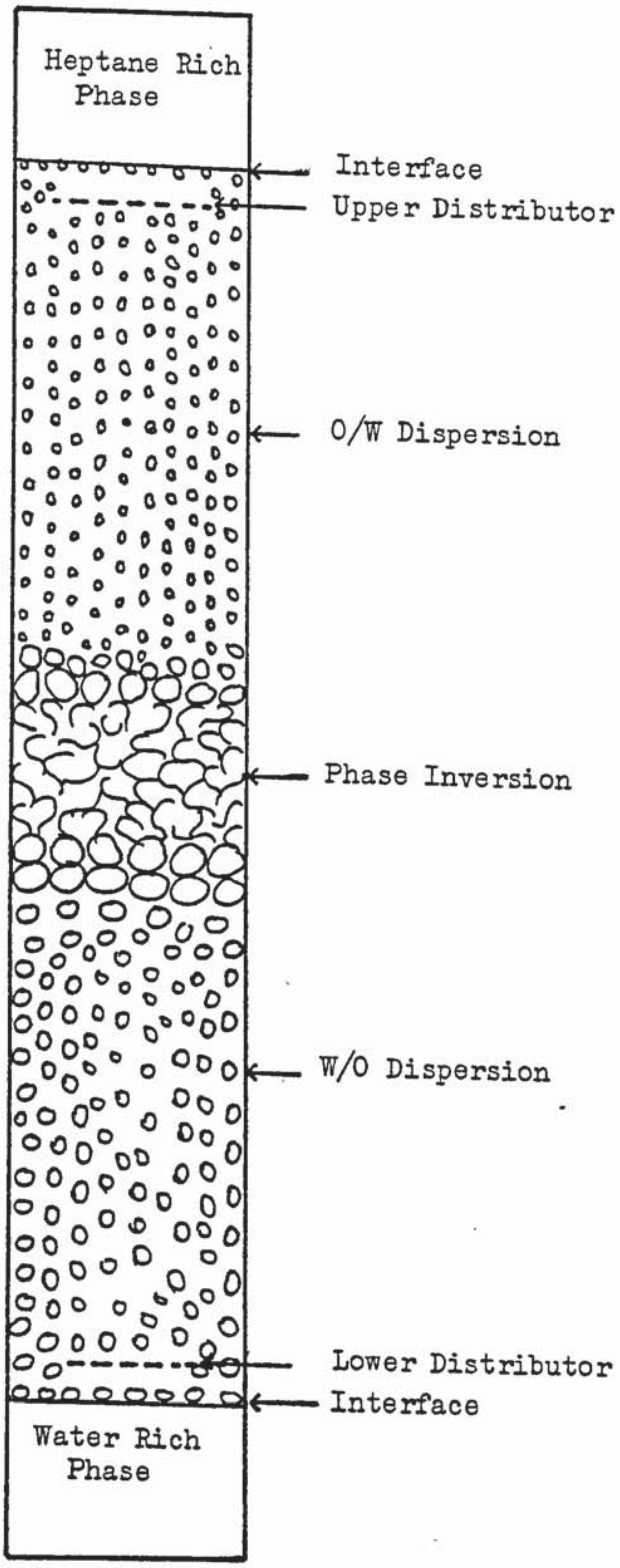


FIGURE 6.6: Illustration of Phase Inversion Phenomenon in an R.D.C. Column due to "Two Way" Mass Transfer.

6.3.2) Mass Transfer With Chemical Reaction.

Mass transfer with chemical reaction was done for the aqueous phase feed consisting of a solution of acetic and sulphuric acids in water and the organic phase a solution of butanol in heptane. The aqueous (reactive) phase was continuous while the organic (extractive) phase was dispersed. Measurement of the quantity of ester formed (hence determination of % conversion) was performed by gas liquid chromotographic analysis of the light phase.

Initial investigations were carried out to determine the approximate time taken for the column to reach steady state conditions. This was done by taking samples of the light phase extract at 3 minutes time intervals until identical values of the ester per cent were obtained. Subsequently measurements were taken only after the approximate minimum time had elapsed.

The concentration range of acetic acid was 60-80% while that of the sulphuric acid catalyst was 4-10%. The concentration of butanol was much less than that of acetic acid (20-25%) since this was found to increase conversion due to salting effects.

Although the concentration of the reactants was extremely high, separation was found to be complete with practically no entrainment of the outflowing phases.

The results are recorded in appendix V, while Figure (6.7) shows a typical view of the dispersion in the column during the extraction-reaction process.

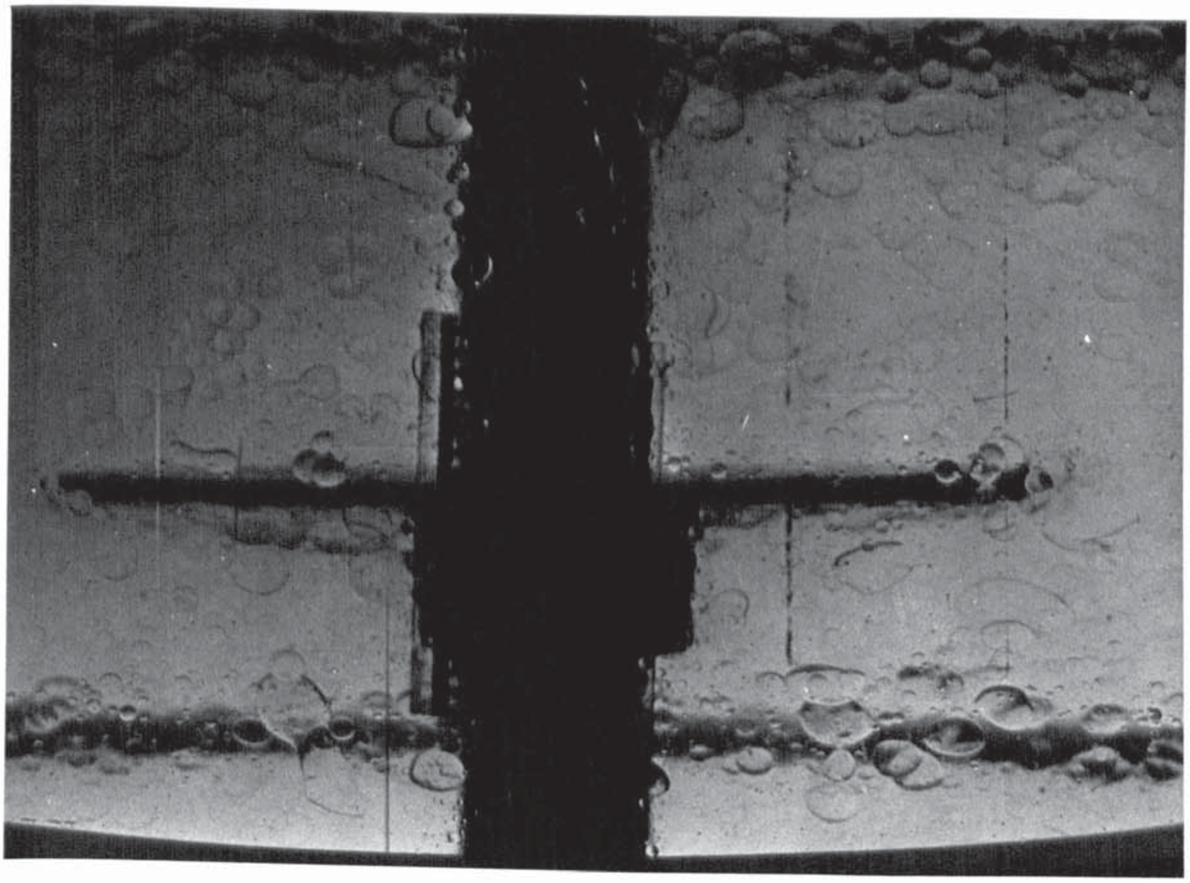


FIGURE 6.7 Typical view of the dispersion in the R.D.C. column during the extraction-reaction process.

CHAPTER 7

DISCUSSION OF RESULTS

7.1) Kinetic Data.

7.1.1) Kinetics of Esterification Reaction

Stoichiometrically, the esterification of n-butyl alcohol can be written as:

$$CH_3COOH + C_4H_9OH \overset{H_2SO_4}{\rightleftharpoons} CH_3COOC_4H_9 + H_2O \tag{7.1}$$

$$B \;+\; C \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} E \;+\; A$$

The rate equation is$^{(105)}$,

$$\frac{d[E]}{dt} = -\frac{d[B]}{dt} = k_2[C][B] - k_2'[A][E] \tag{7.2}$$

If [X] is the amount of B which has reacted, expressed as a concentration; the concentration of B at any time will be,

$$[B] = [B]_o - [X] \tag{.7.3}$$

Rewriting Eqn.(7.2) in terms of [X] and replacing k_2' with $k_2|K$ gives

$$\frac{d[X]}{dt} = k_2\left\{([B]_o-[X])([C]_o-[X])-\frac{1}{K}([E]_o+[X])([A]_o+[X])\right\}.$$

$$= \quad \alpha + \beta[X] + \gamma[X]^2 \tag{7.4}$$

where

$$\alpha = k_2\left\{[B]_o[C]_o - \frac{1}{K}[E]_o[A]_o\right\} \tag{7.5}$$

$$\beta = -k_2\left\{([B]_o+[C]_o+\frac{1}{K}([E]_o+[A]_o)\right\} \tag{7.6}$$

$$\gamma = k_2 - \frac{k_2}{K} \tag{7.7}$$

Integration of eqn.(7.4) with initial conditions, $[B] = [B]_o, [C] = [C]_o, [E] = [E]_o, [A] = [A]_o$, gives

$$\ln \frac{\{2\gamma[X]/(\beta-q^{\frac{1}{2}})\}+1}{\{2\gamma[X]/(\beta+q^{\frac{1}{2}})\}+1} = q^{\frac{1}{2}}t \tag{7.8}$$

where

$$q = \beta^2 - 4\,\alpha\,\gamma \tag{7.9}$$

Equation (7.8) is difficult to use with concentration-time data to determine k_2. The solution is a trial-and-error one, requiring successive choices of k_2 and comparison of the data with equation (7.8) for each choice to establish the best value. However, if the initial concentration of the product is zero and the reactants are equimolar, equation (7.8) is simplified as follows:

$$\frac{2k_2[M]_o}{K^{\frac{1}{2}}} t = \ell n \frac{[M]_o+[X](K^{-\frac{1}{2}}-1)}{[M]_o-[X](K^{-\frac{1}{2}}+1)} \qquad (7.10)$$

$$k_2 = \frac{K^{\frac{1}{2}}}{2[M]_o t} \quad \ell n \frac{1+x[K^{-\frac{1}{2}}-1)}{1-x[K^{-\frac{1}{2}}+1)} \qquad (7.11)$$

where $[M]_o$ is the initial concentration of either reactant and x is the fraction reacted.

k_2 can be evaluated directly from either equation (7.10) or (7.11).

On the other hand if k_2 is known, [X] can be evaluated from a rearranged form of equation (7.8)

$$[X] = \frac{e^{q^{\frac{1}{2}}t} - 1}{\frac{2\gamma}{\beta-q^{\frac{1}{2}}} - \frac{2\gamma e^{q^{\frac{1}{2}}t}}{\beta + q^{\frac{1}{2}}}} \qquad (7.12)$$

7.1.2) <u>Side Reaction</u>.

There is a reaction between butanol and sulphuric acid to form butyl mono sulphate(146,147) (alkyl sulphuric acid). The rate of this reaction varies greatly with temperature. At 0 °C and 13°C, the rate is scarcely measurable up to 8 hours; at 25-30 °C the reaction proceeds over a period of days; and at 100 °C and 115°C, the reaction is complete in 15 to 30 minutes(146).

To confirm that this side reaction does not occur to any great extent at the reaction temperature in this study (20 °C), mixtures of butanol and sulphuric acid were tested at the concentration of the acid used in the esterification studies.

The change in the acid concentration over a period of 24 hours was scarcely measurable. Therefore it was concluded that the effect of the side reaction was insignificant.

7.2) A correlation for Esterification Rate in Presence of High Concentration of Reactants and Catalyst.

Table (I.1) shows the results of esterification for two runs initiated with 9.8% and 4.55% sulphuric acid and stoichiometric quantities of acetic acid and butanol.

The equilibrium constant K was calculated from the concentrations of products and reactants at 24 hours and k_2 was calculated from equation (7.11). The average concentration of water generated was also evaluated. The initial reaction rate was rapid but this decreased as the water formed diluted the catalyst. The results are shown in figure (7.1) and table (I.1), while Fig.7.2 shows the experimental results for 4 runs.

Regression analysis was made on the data of table (I.1) and the following correlation for k_2 was evaluated:

$$k_2 = (0.0112)[H_2SO_4]^{1.18}[H_2O]^{-0.324} \qquad (7.13)$$

where k_2 is in litre/(g mole)(Min).

In figure 7.3 experimental values of k_2 were plotted against k_2 values obtained from equation 7.13. Good agreement was obtained, the maximum deviation being about 13%, and the average deviation about 5%.

To calculate the conversion starting with any amounts of A,B,C,E and catalyst, equation (7.12) together with equation (7.13) are used. In equation (7.12), [X] is implicit since α,β and γ are functions of k_2 which is a function of [X]. Therefore a computer program was written to calculate [X] by iteration process whereby an initial value is given to [X]; k_2 and the RHS of equation (7.12) evaluated and compared with the previous value of [X] until

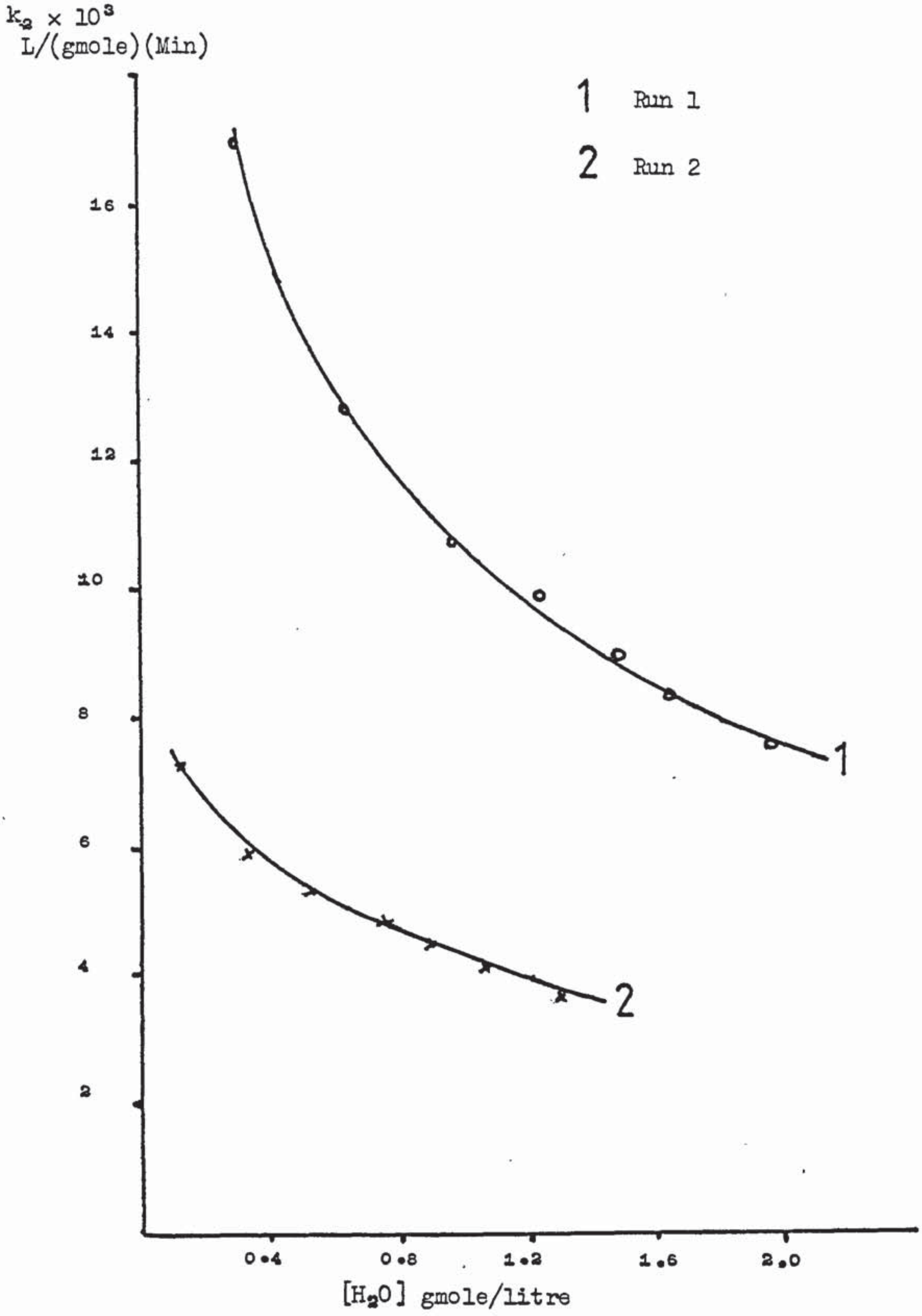


Fig.7.1 Esterification of Butanol
k_2 vs. $[H_2O]$

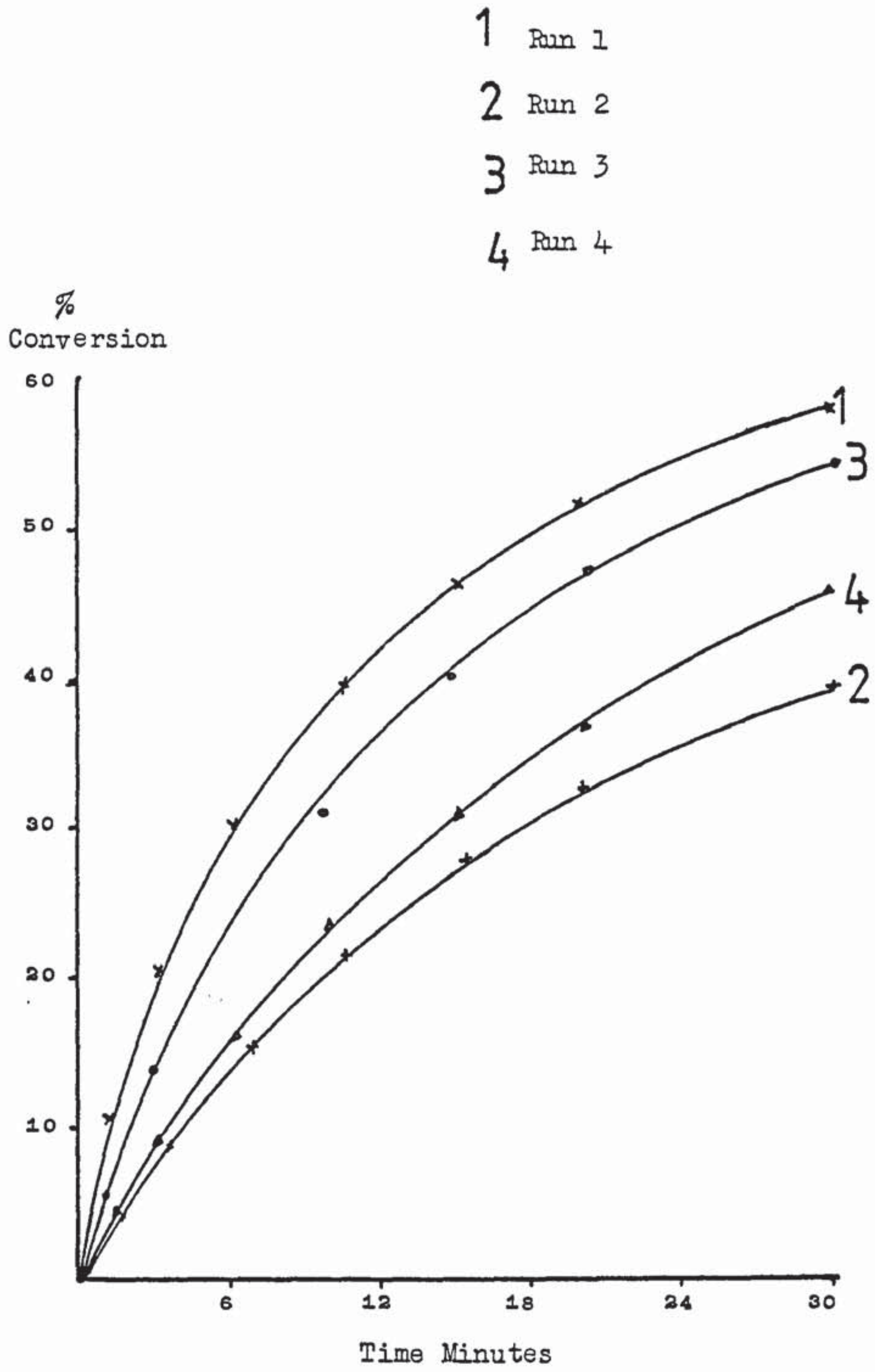


Fig.7.2 Esterification of Butanol
Conversion vs. Time

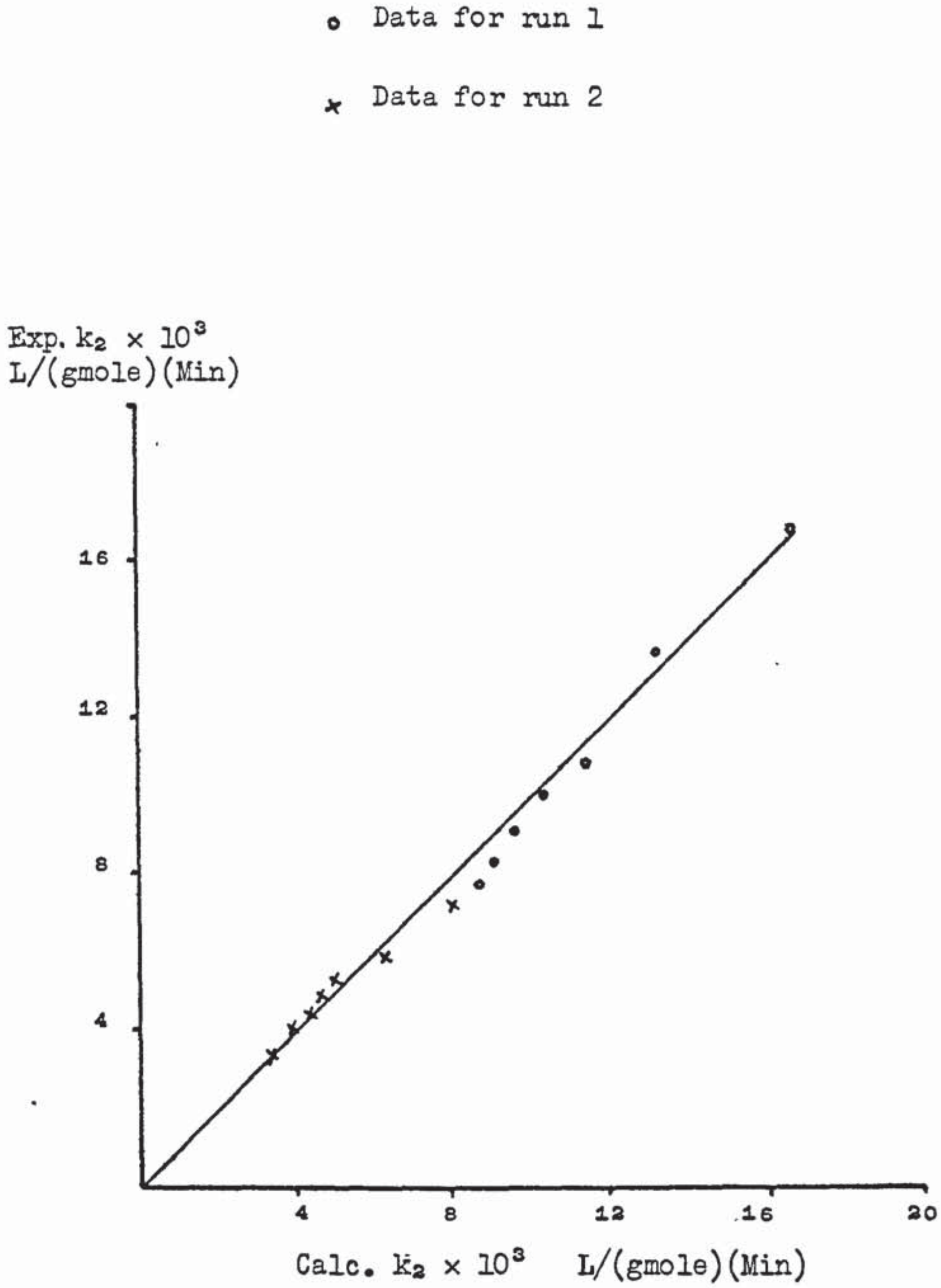


Fig.7.3 Batch Esterification
Experimental vs. calculated k_2

convergence criteria is met. This program is shown in appendix (VI). It is designed to read in the initial values of the reaction components and an index (NT) which is used for calculating any number of runs.

Results of the computer calculations for two runs together with the actual experimental values are shown in figure (7.3a) and table (I.2). Good agreement was achieved between the experimental and computed values, the maximum deviation was about 8%.

The reactions carried out in this study were initiated with high reactants and catalyst concentrations in order to make the reaction reasonably fast at room temperature. The conventional method for n butyl acetate manufacture depends on high temperatures and distillation(149). Therefore the reaction is fast enough with relatively low catalyst concentration and removal of water by distillation ensures high yields. Hence previous studies of esterification kinetics has been concentrated on determining the reaction rate at elevated temperatures and low catalyst concentration. None of the published data on the esterification of butanol(135,140,146,151) gave rate constants for concentrations comparable to the concentrations employed in this study. The nearest is a value of 0.0002969 moles/(litre)(sec) for k_2 at 30°C and catalyst concentration of 0.0322%(146). This value is of the same order of magnitude as that found in this study for concentrated reactants and catalyst at 20°C.

The values of the equilibrium constant K shown in table (I.3), indicate that K increases as the catalyst concentration is increased or the initial concentration of water is decreased. These values are considerably larger than the average of 2.35 reported by Leyes and Othmer(146). The variation is thought to be due to the very much higher catalyst concentration

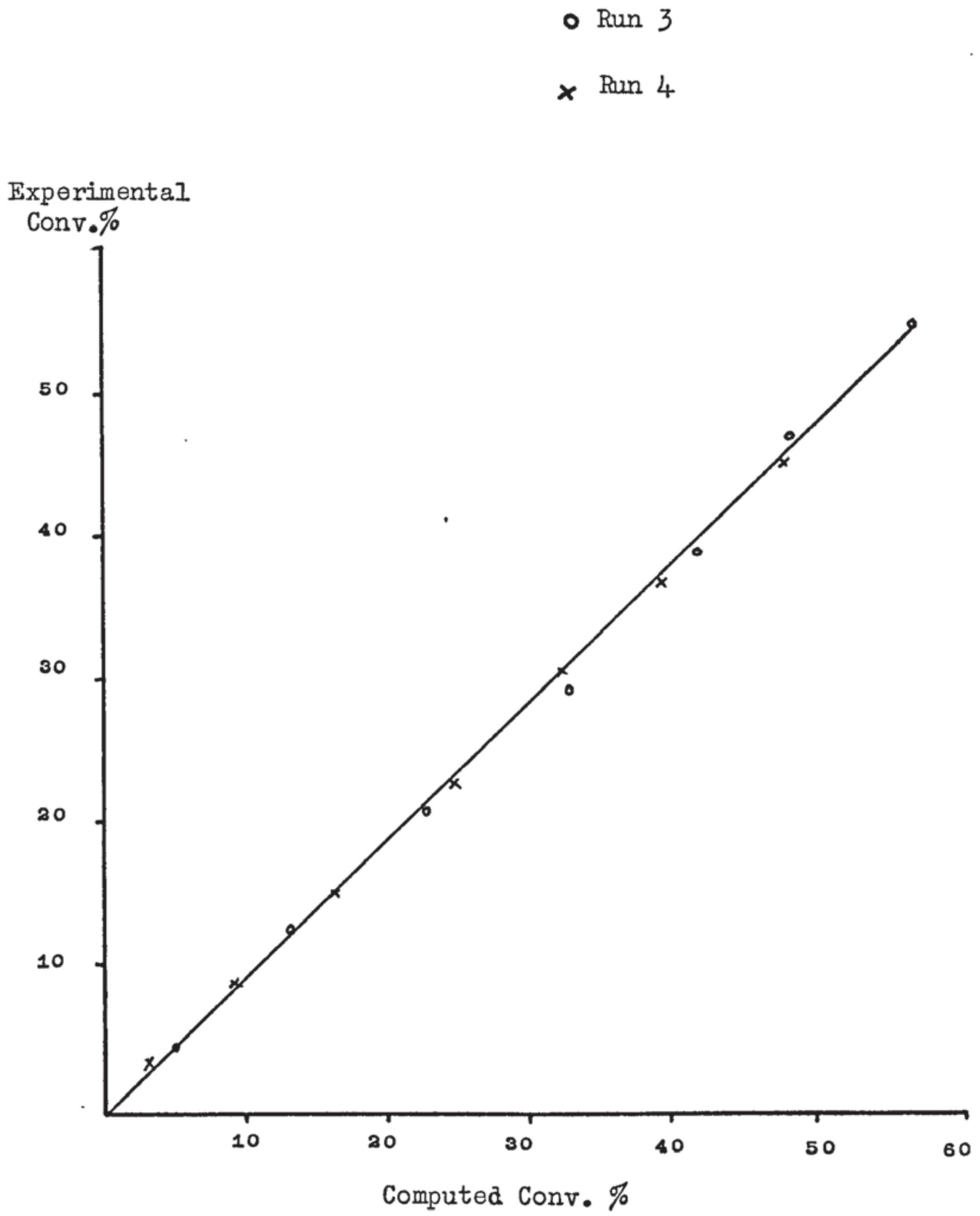


Fig.7.3a Batch Esterification
Experimental vs. computed conversion

employed in this study.

Recently, Dhanuka, Malshe and Chandalia(151) have re-interpreted the published data on kinetics of liquid phase esterification of carboxylic acids with alcohols in the presence of sulphuric acid catalyst. According to Dhanuka et al., both sulphuric acid and butyl monosulphate act as catalysts and the reaction rate is considerably different for the two. Hence the variations in the reaction rate during the progress of the esterification reaction, starting with sulphuric acid catalyst, were attributed to the change in the ratio of the two catalysts as more sulphuric acid was converted to the monosulphate. In order to avoid this complication Dhanuka et al. reacted the usual amount of sulphuric acid and alcohol for sufficient time at 100°C so that the entire amount of sulphuric acid was converted to monosulphate before the carboxylic acid was added. It was claimed that the results of esterification thus obtained gave the reaction rate constant for the monosulphate catalyst. Data thus obtained was correlated by a second order reversible kinetics equation.

If Dhanuka et al 's interpretation of esterification kinetics is correct, then it can be stated that the rate constant values found in this study refer exclusively to sulphuric acid catalyst since no butyl monosulphate was formed during the relatively short time of the reaction at the low operation temperature of 20°C.

7.3) MATHEMATICAL MODEL FOR A MULTI-COMPONENT TWO PHASE SYSTEM.

A mathematical model was required to describe the course of a chemical reaction taking place in one of two phases of a multicomponent system. To do this it was thought necessary first to predict the concentration of the reactants in the reactive phase i.e. determine the distributions of the reacting species in the two phase multicomponent system. Geometrical representation which is normally applied to four or more component systems was inadequate and therefore a model was constructed to systematize the relationships between concentrations of the various components in the two phases. The system under investigation consisted originally of two reactants; acetic acid and n-butyl alcohol with water and the solvent as well as a limited amount of sulphuric acid catalyst. As the reaction proceeded, ester was formed which increased the total number of components to six. Therefore the mathematical model was required to take into consideration the interaction between all these components.

Since the sulphuric acid concentration did not exceed about 10%. it was thought that this might not have a significant effect. Therefore the effect of sulphuric acid on acetic acid and butanol distribution, within the concentration ranges encountered in the reaction, was tested. It was found that sulphuric acid "salting" effect was indeed insignificant. Therefore the problem was reduced to modelling the distribution of the other five components.

The problem was approached on the basis of the experimental data for the different combinations which could be built-up into an overall model for all the components. Apart from the different ternaries, the system consisted of two kinds of quaternaries viz the double binary quaternary and the single binary quaternary. Hence it was necessary to model both of these types. Combination of the two models gave a model for the five component system.

7.3.1) TERNARY SYSTEMS:

Hands formula (equation 2.27) was found to be adequate for predicting the concentration of a solute B in the water phase (A) for any combinations of A,B and D, where D is a solvent, provided the concentration of A in phase D and D in phase A was negligible. Parameters k and r were determined from a regression analysis of the experimental data, hence:

$$\frac{B_1}{A} = k\left(\frac{B-B_1}{D}\right)^r \qquad 7.14$$

where B_1 is the fraction of B in phase A.

Equation (7.14) is easiy solved for B_1 by any iteration process, e.g. the reguli-falsi or Newton-Raphson methods.

Tables II.1 and II.2 show the data for the different saturation compositions of the different ternaries, found by the cloud point method. These are plotted on triangular diagrams figures (7.4-7.8). Tables II.3-II.6 show the tie lines solubilities data evaluated on the basis of Hand's method. Figures 7.9-7.12 show the plotting of the data on double logarithmic coordinates, while figures 7.13-7.16 show the same data on linear coordinates. It is clear from these figures that all the experimental ternary data could be represented by Hand's formula.

Regression analysis was carried out on the ternary data to evaluate the constants in Hand's formula (equation 2.27). As a result the following equations were obtained for the different ternary systems investigated:

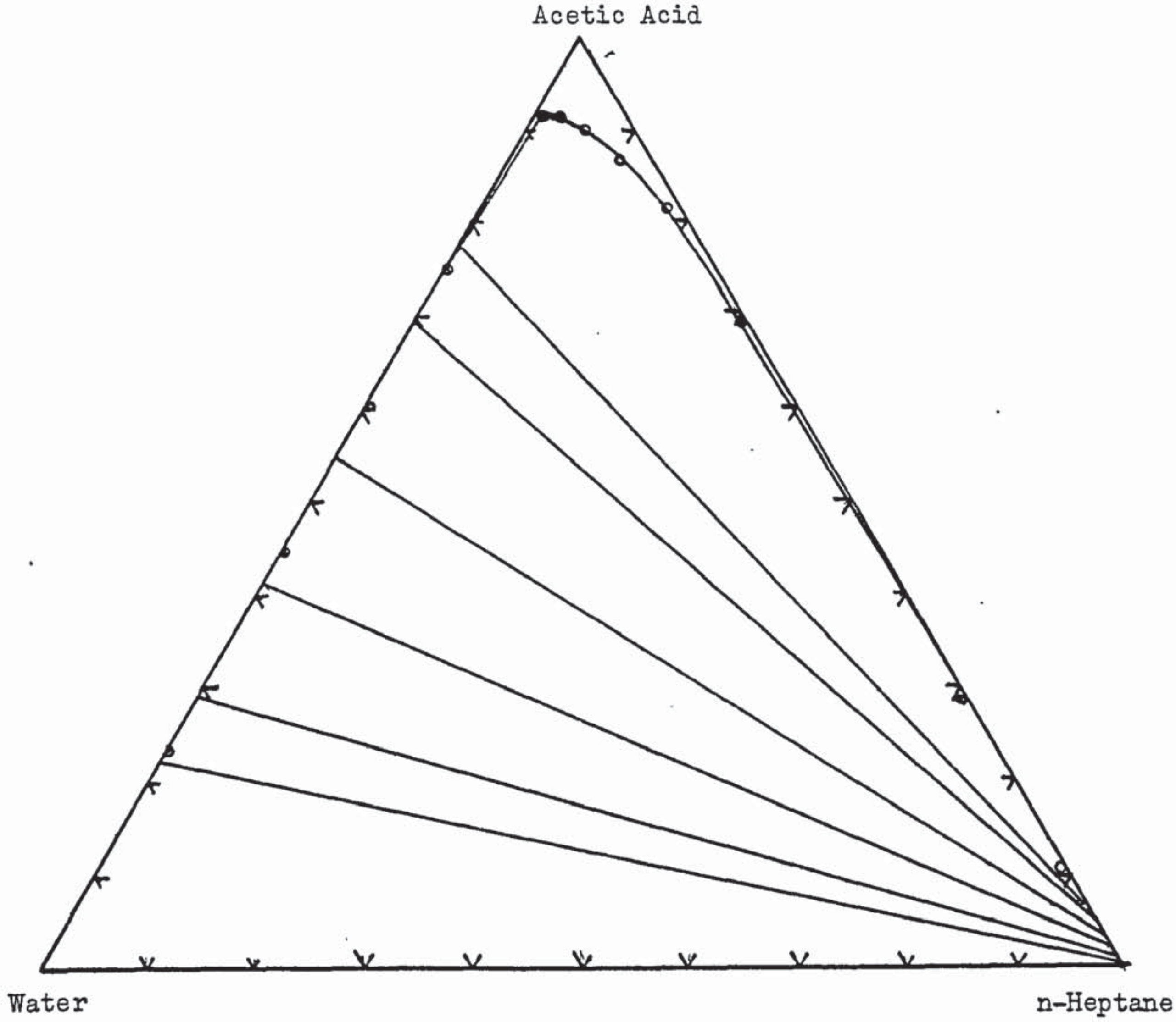


Figure 7.4 Ternary Phase Equilibrium Diagram at 20°C for Water-Acetic Acid-n Heptane System.

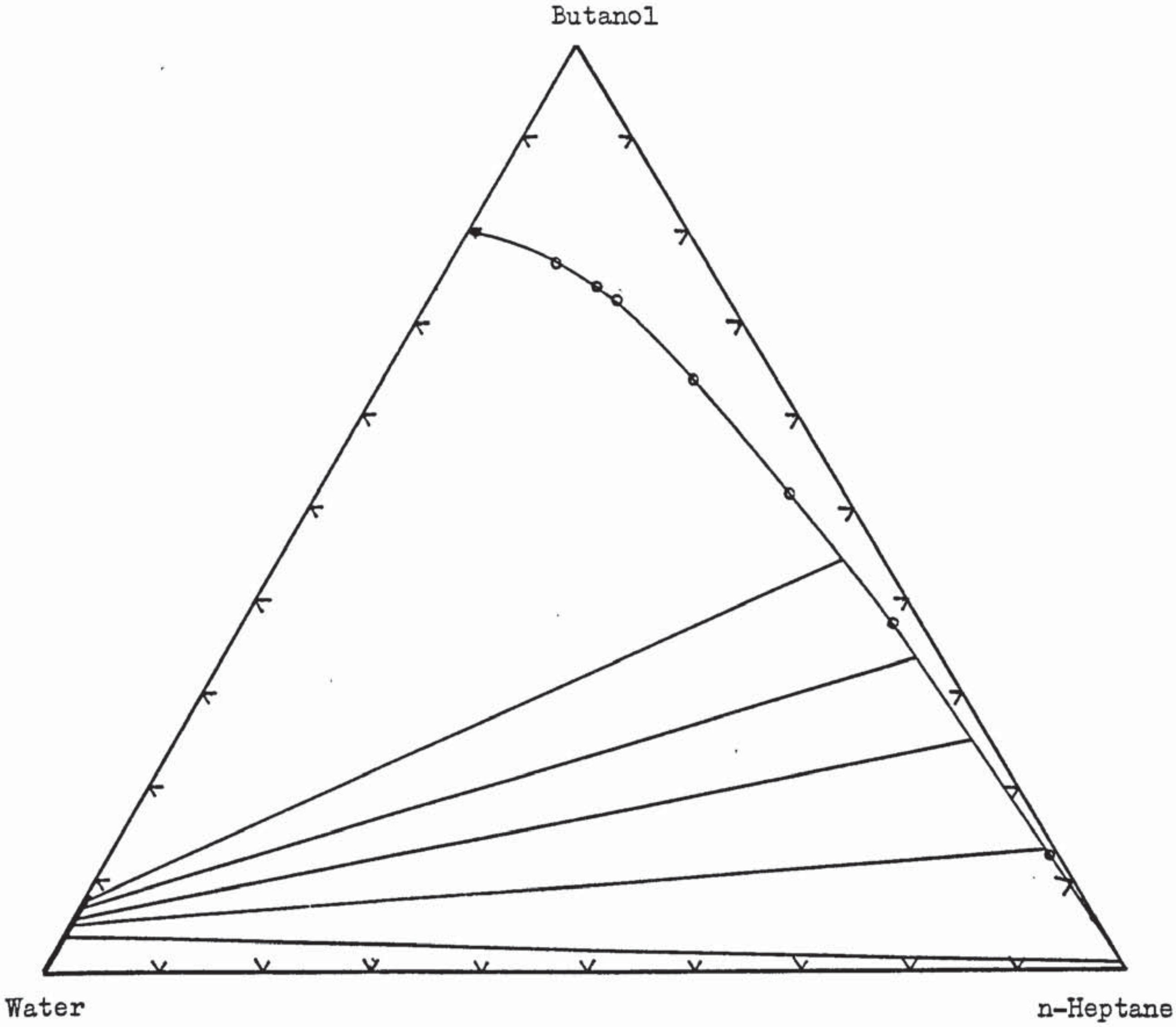


Figure 7.5 Ternary Phase Equilibrium Diagram at 20°C for Water-Butanol-n-Heptane System.

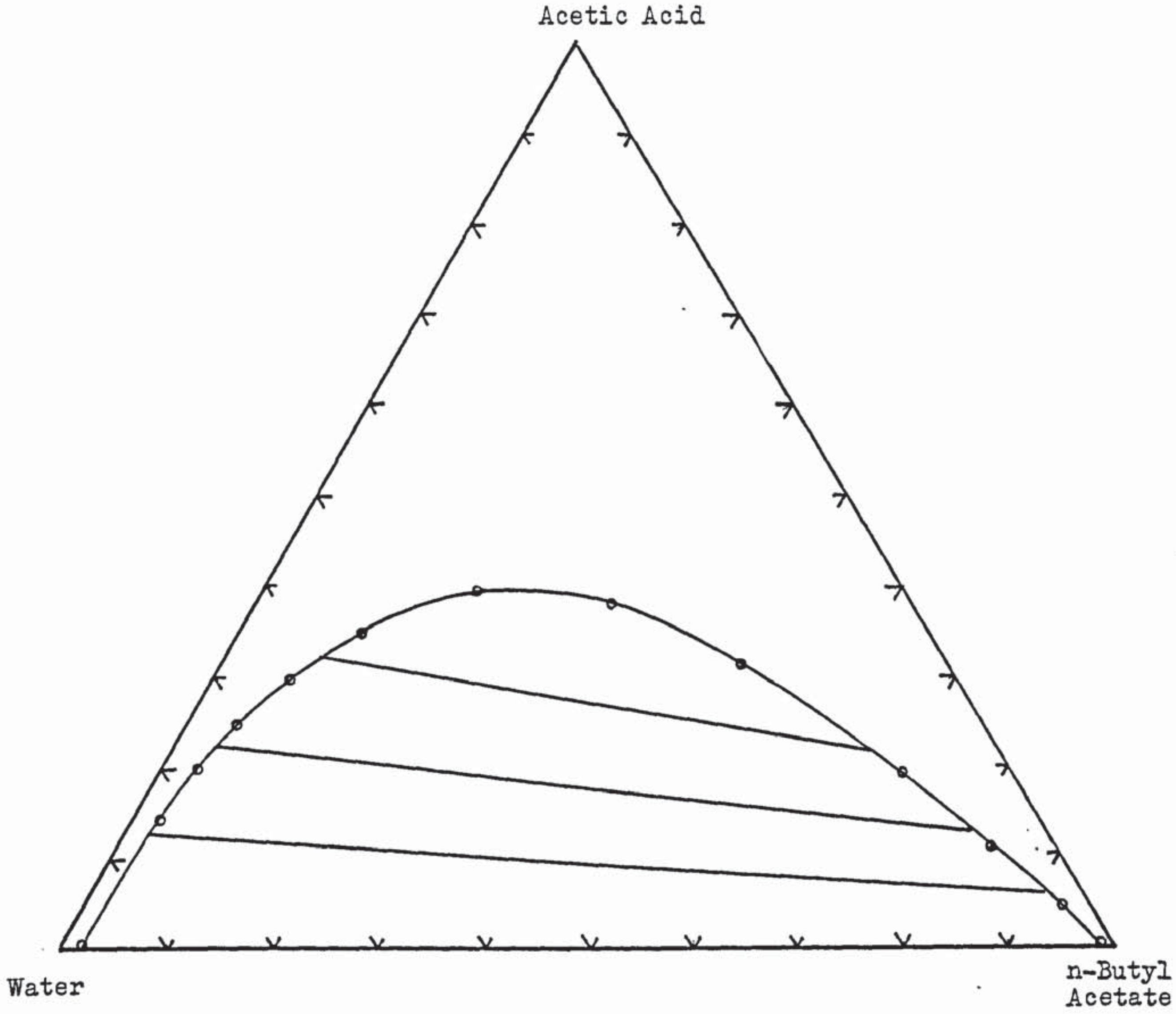


Figure 7.6 Ternary phase Equilibrium Diagram at 20°C
for Water-Acetic Acid-n Butyl Acetate System.

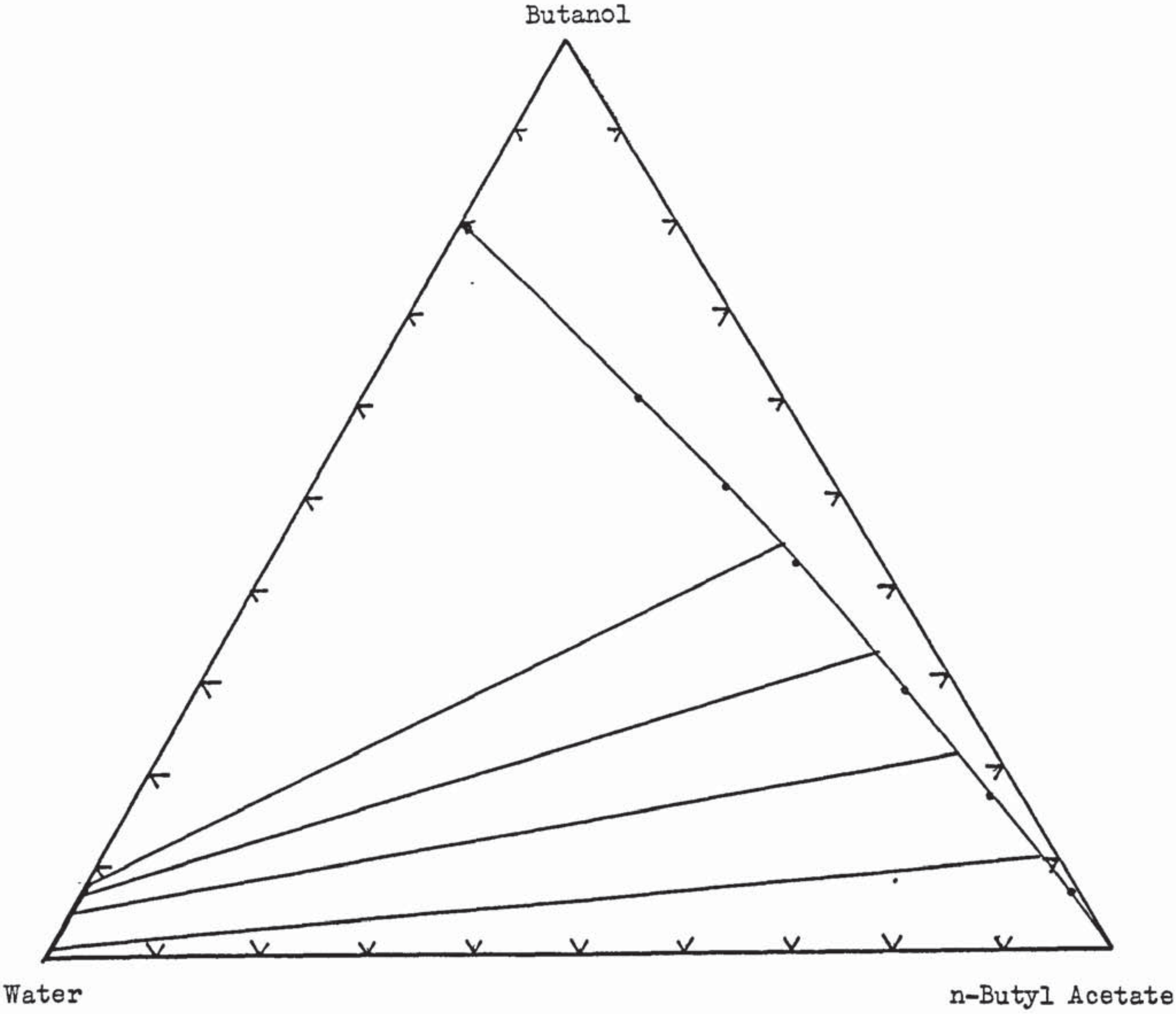


Figure 7.7 Ternary Phase Equilibrium Diagram at 20°C for Water-Butanol-n Butyl Acetate System.

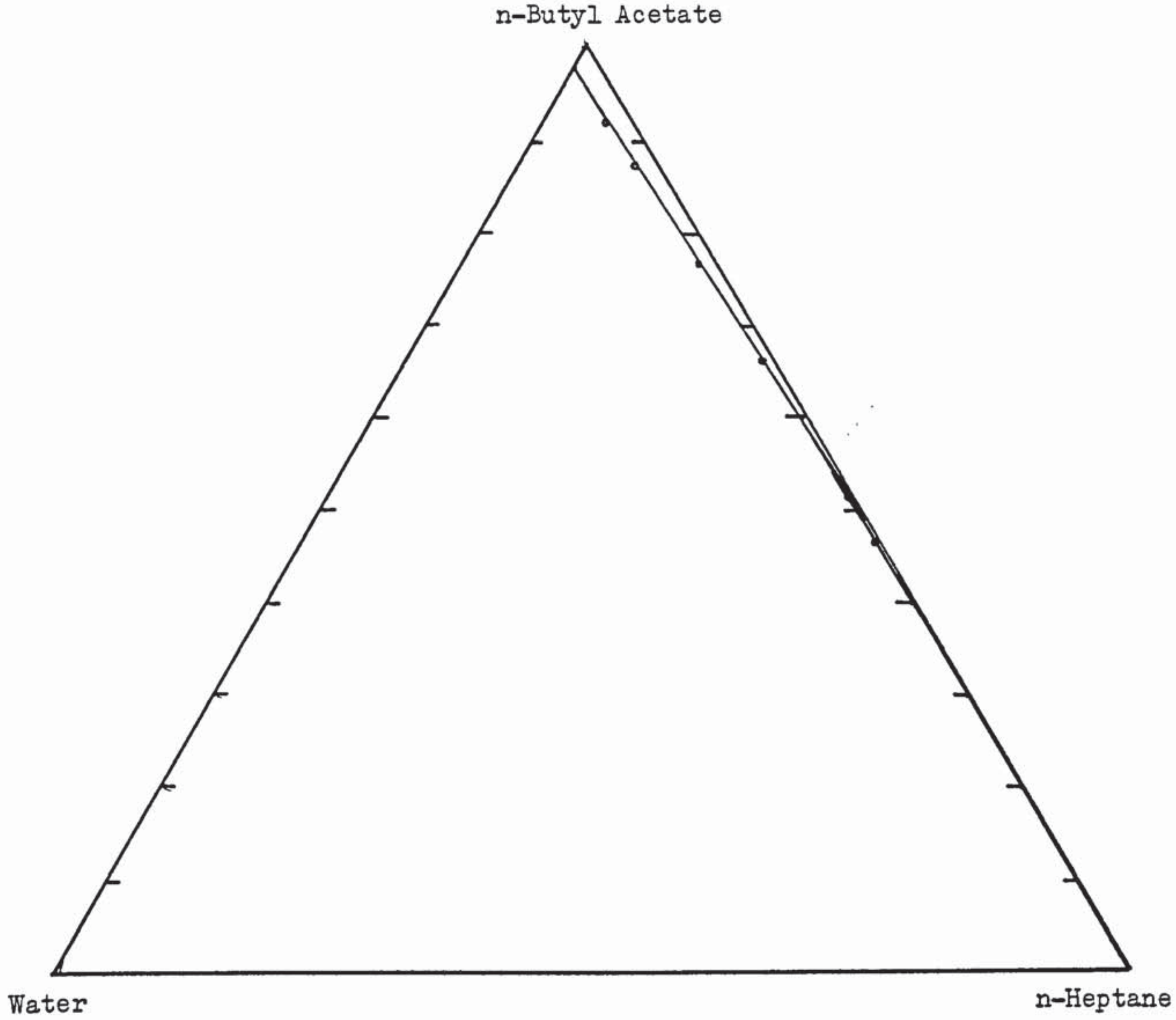


Figure 7.8 Ternary phase Equilibrium Diagram at 20°C for Water-n Butyl Acetate-n Heptane System.

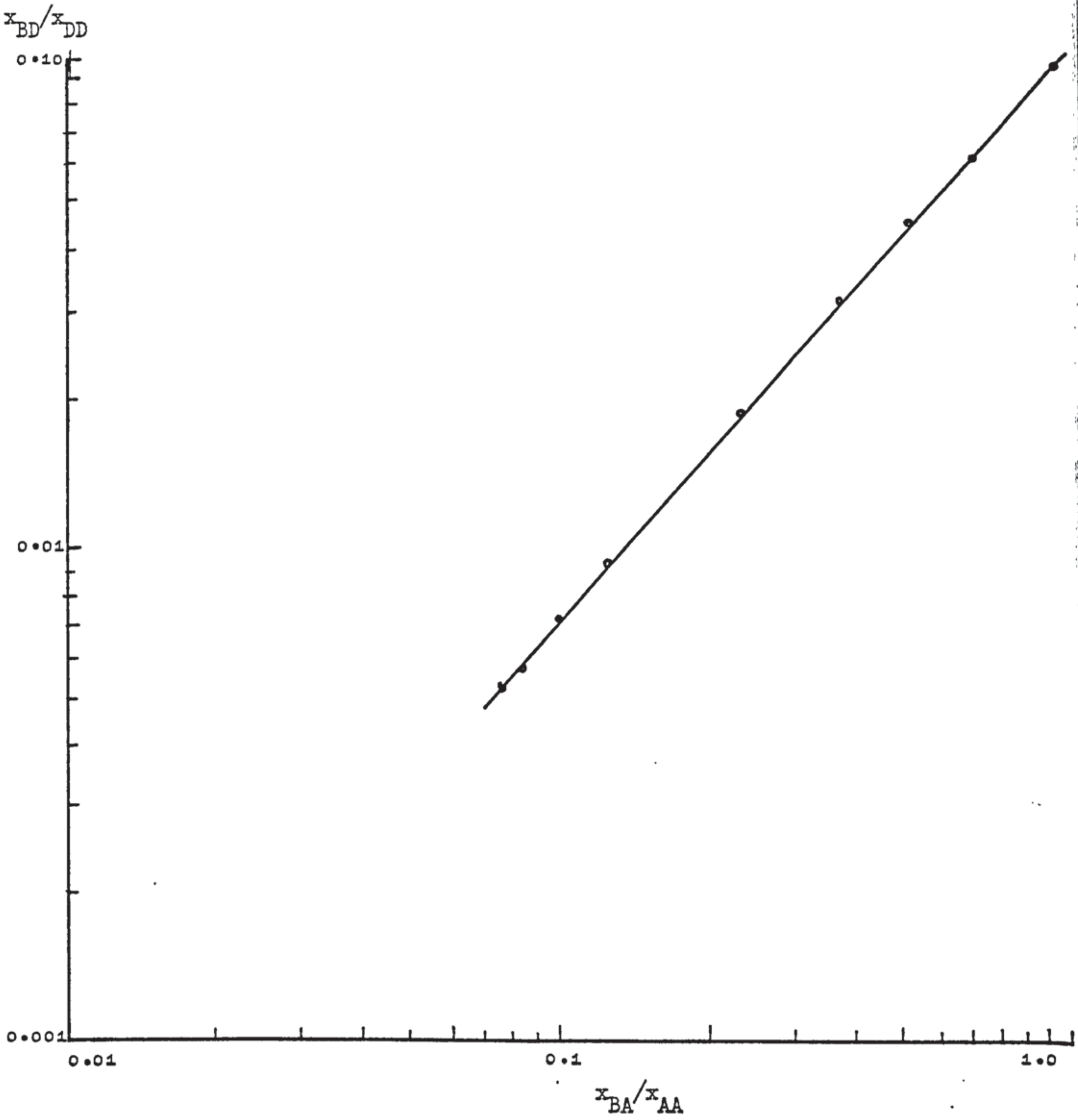


Fig.7.9 Hand Coordinates for the Water-Acetic Acid-n Heptane System

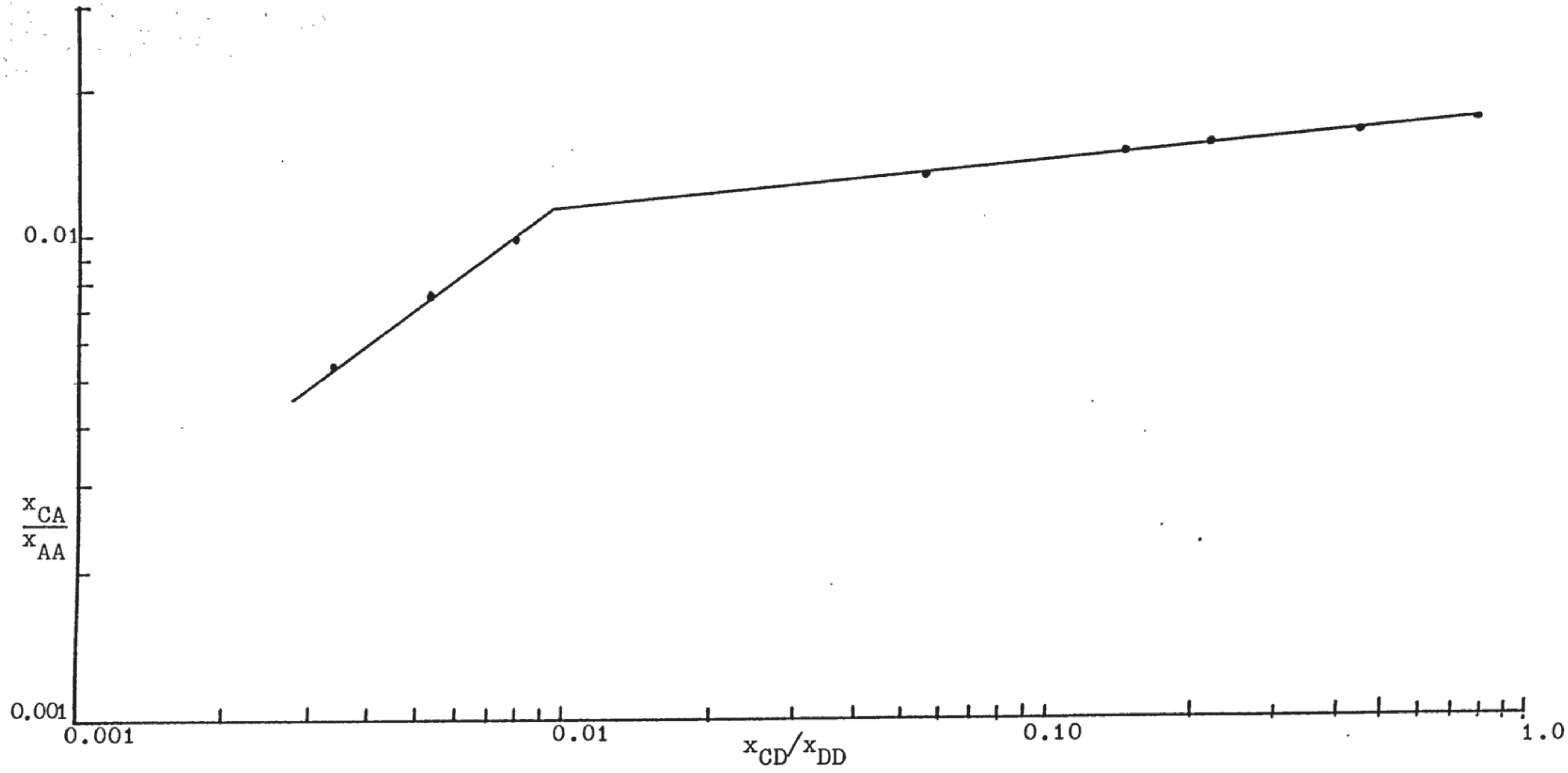


Figure 7.10 Hand Cordinates for the Water - Butanol - Heptane System.

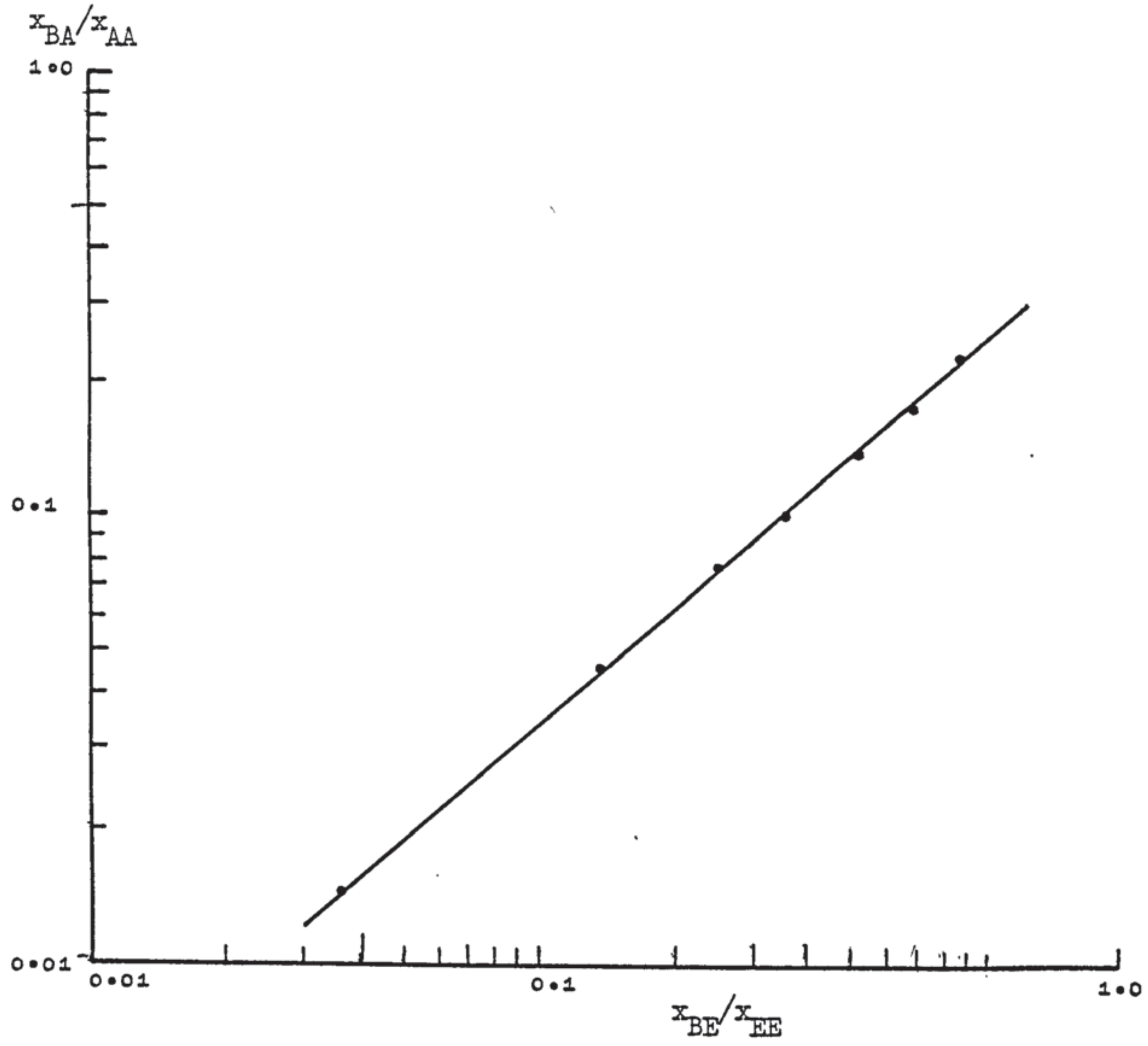


Figure 7.11 Hand Coordinates for the System Water-Acetic Acid-n Butyl Acetate

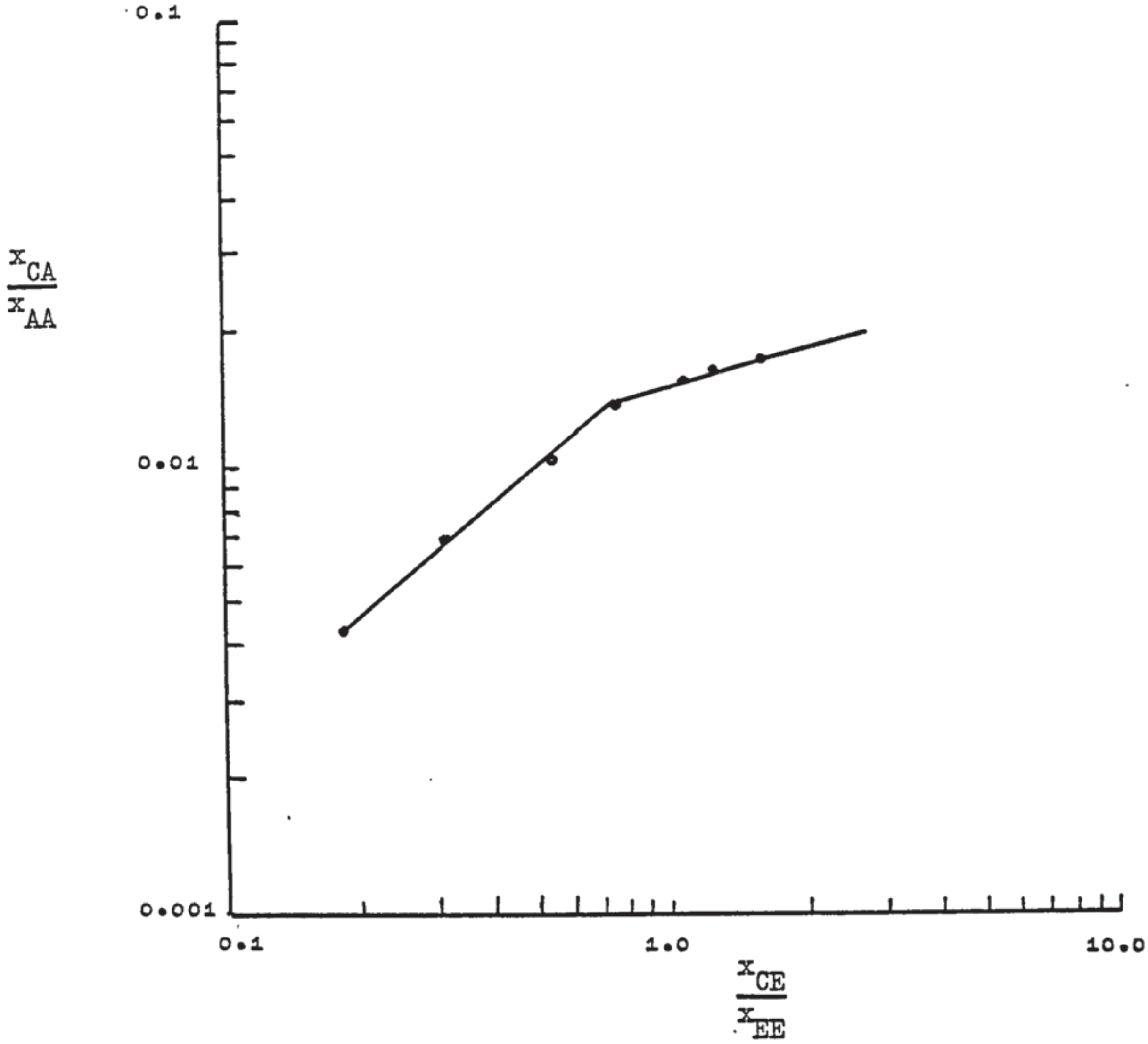


Figure 7.12 Hand Coordinates for the Water-Butanol-n Butyl Acetate System.

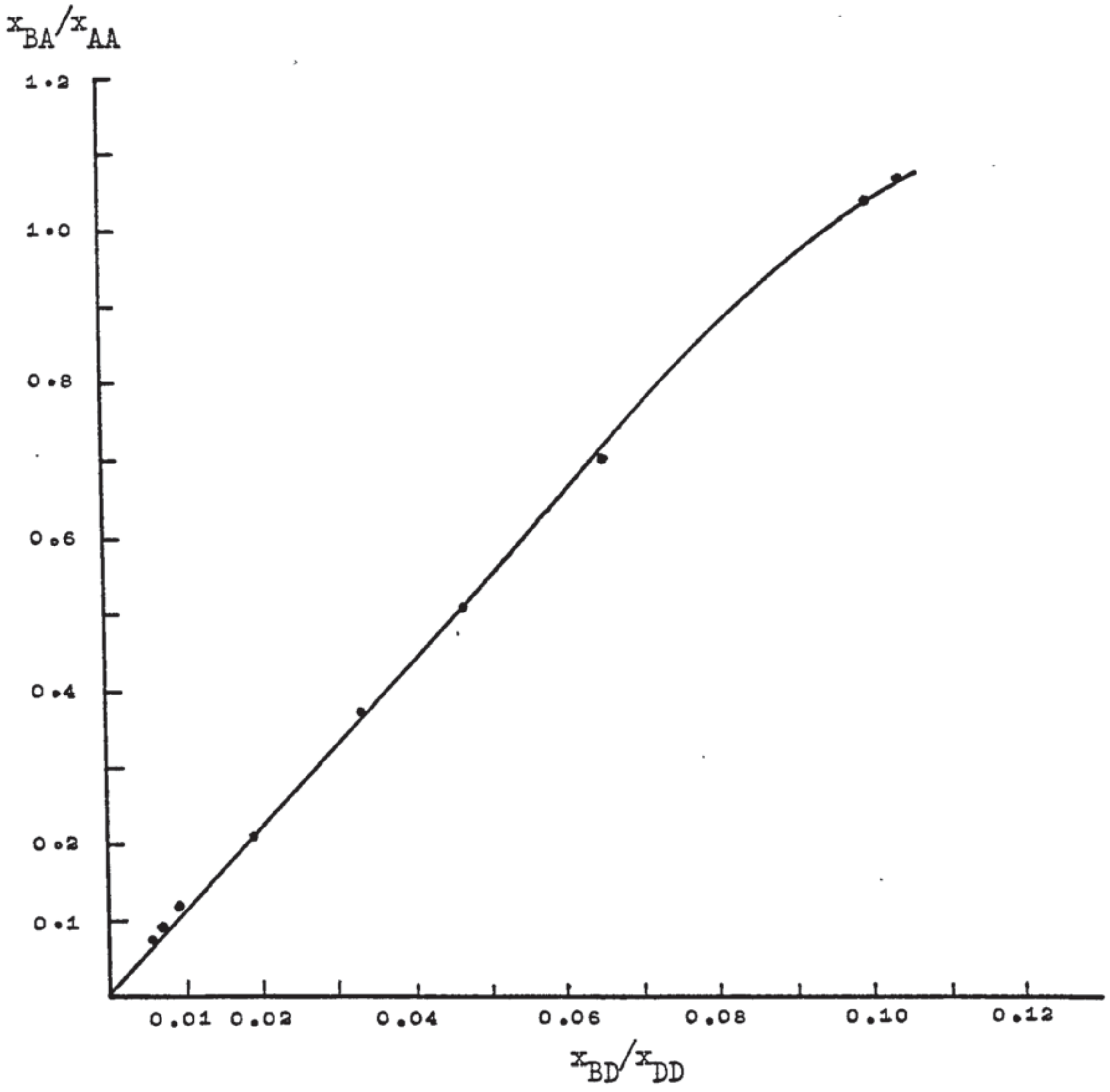


Figure 7.13 Distribution of Acetic Acid Between Water-Heptane

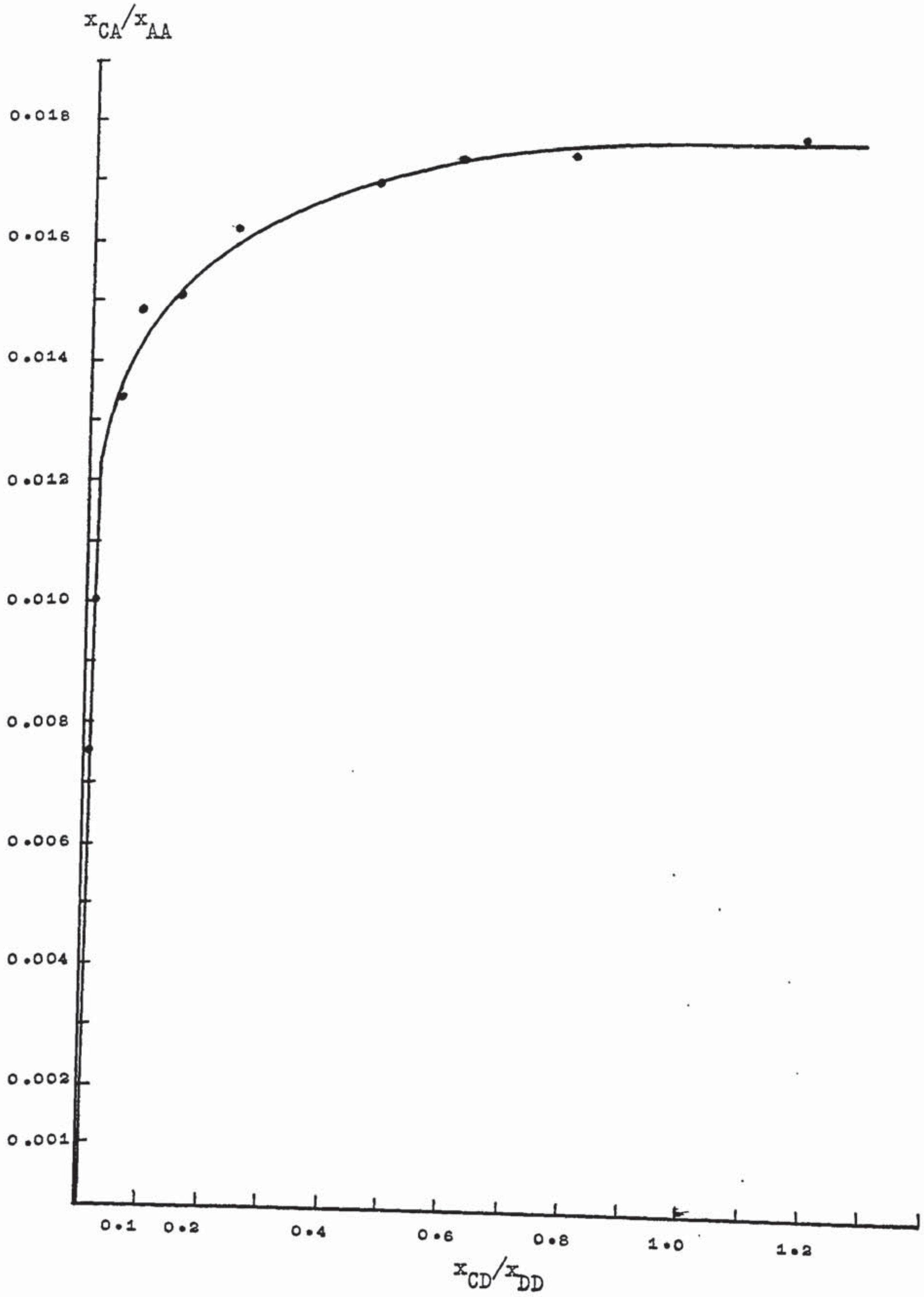


Figure 7.14 Distribution of Butanol Between Water-Heptane

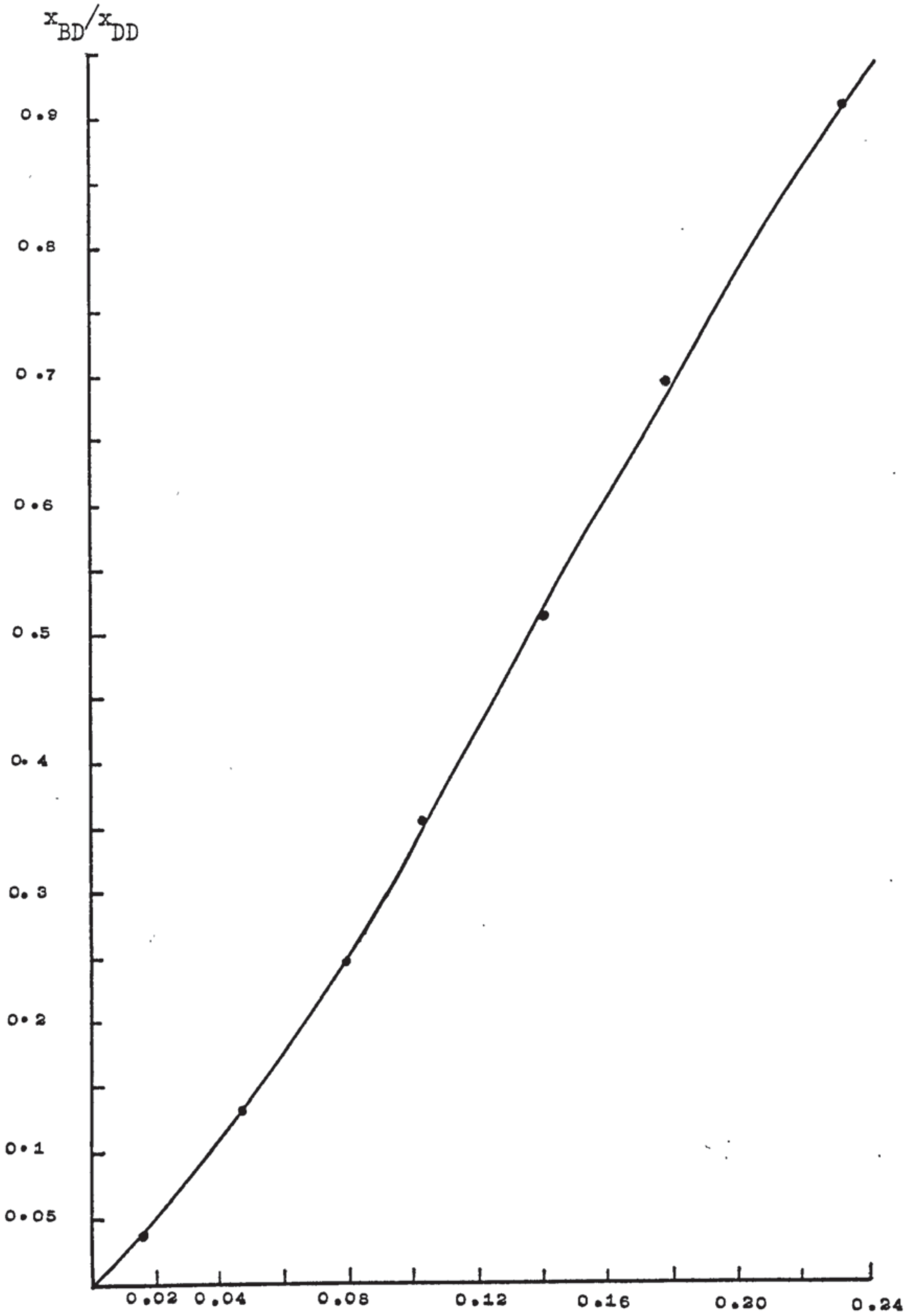


Figure 7.15 Distribution of Acetic Acid Between Water-Ester

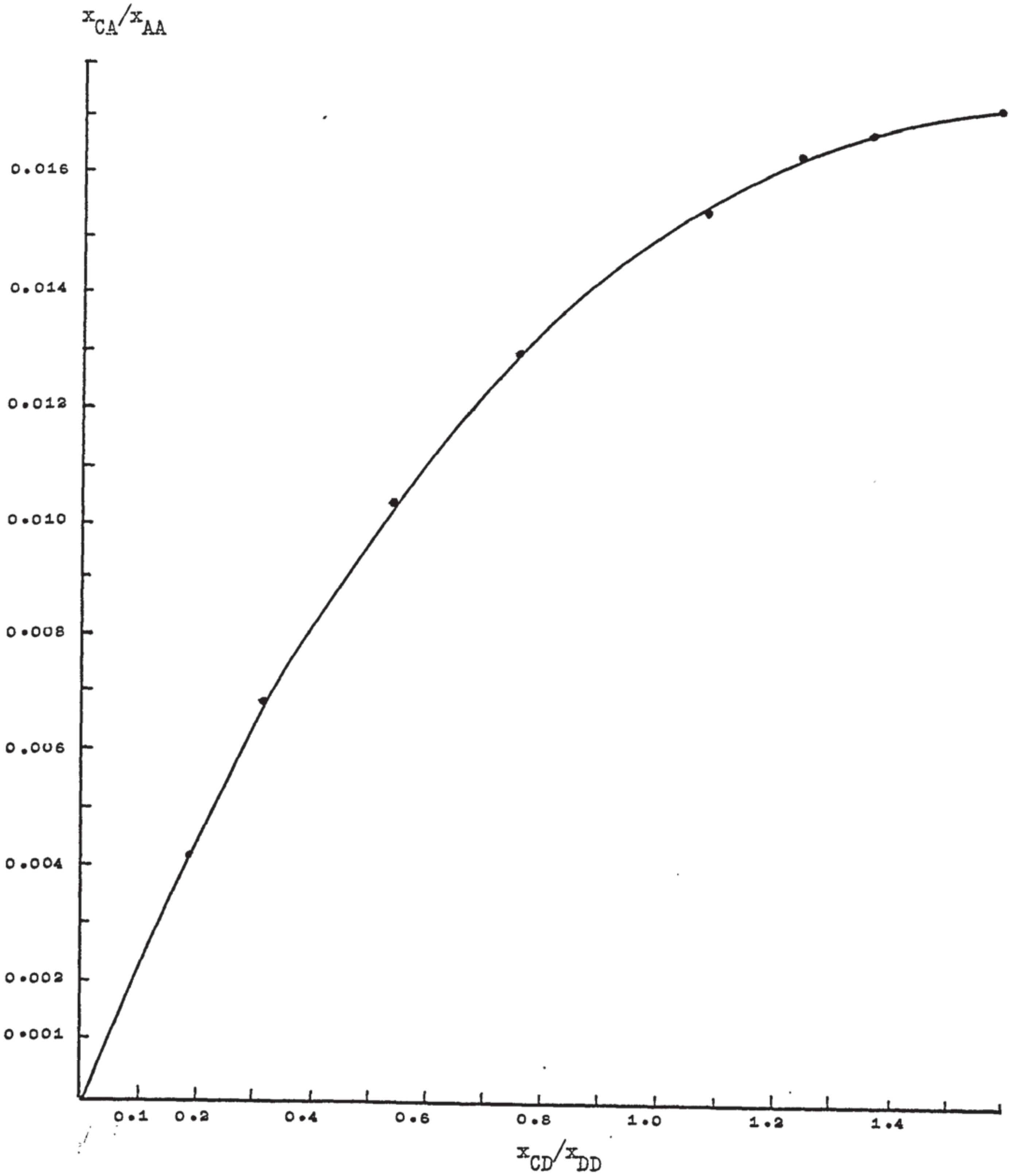


Figure 7.16 Distribution of Butanol Between Water-Ester.

(i) Water-Acetic Acid-n heptane System:

$$\frac{x_{BA}}{x_{AA}} = 7.82\left(\frac{x_{BD}}{x_{DD}}\right)^{0.89} \tag{7.15}$$

(ii) Water-butanol-n heptane System:

$$\frac{x_{CA}}{x_{AA}} = 0.02\left(\frac{x_{CD}}{x_{DD}}\right)^{0.18} \tag{7.16}$$

(iii) Water-acetic acid-n butyl acetate System:

$$\frac{x_{BA}}{x_{AA}} = 0.25\left(\frac{x_{BE}}{x_{EE}}\right)^{0.85} \tag{7.17}$$

(iv) Water-butanol-n butyl acetate System:

$$\frac{x_{CA}}{x_{AA}} = 0.014\left(\frac{x_{CE}}{x_{EE}}\right)^{0.65} \tag{7.18}$$

The ICL 1900 computer of the University of Aston in Birmingham was used with Fortran IV programming for all the computation work in this study. For regression analysis, the data was fed to the ICL 1900 statistical analysis package XDS3.

7.3.2) QUATERNARY SYSTEMS:

Two types of quaternaries were present in the system; i.e. the "single binaries quaternaries" of water-acetic acid-n butyl alcohol and n heptane (or n butyl acetate) and the "double binaries quaternaries" of water, acetic acid (or n butyl alcohol), n butyl acetate and n heptane. Each type was modelled differently.

7.3.2.1) MODELLING A SINGLE BINARY QUATERNARY SYSTEM:

In a four component system of two solutes B and C in two solvents A and D; the components B and C will influence each other's distribution; i.e. there is likely to be a mutual "salting" effect and this effect will be proportional to the total amount of each component present. A measure of the distribution of any solute, e.g. solute B between A and D is the ratio of its concentration in the phase rich in A to its concentration in the phase rich in D and this ratio will be affected by the total amount of B as well as the salting effect of C. For the purpose of mathematical formulation, the "total amount" can be represented by the sum of the concentrations in the two phases. However, in order to take into account the distribution of B in the absence of C, a term must be included which will account for ternary distribution. Hence the equation to describe the single binary quaternary distribution will be of the form;

$$\frac{X_{BA}/X_{AA}}{X_{BD}/X_{DD}} = \frac{x_{BA}/x_{AA}}{x_{BD}/x_{DD}} + K\left(\frac{X_{BA}}{X_{AA}} + \frac{X_{BD}}{X_{DD}}\right)^{m}\left(\frac{X_{CA}}{X_{AA}} + \frac{X_{CD}}{X_{DD}}\right)^{n} \qquad (7.19)$$

where X denotes the concentration of the species in the quaternary case and x the concentration in the binary i.e. in the absence of C. K,m and n are constants. The last term of this equation represents the salting effect. K will be positive if C salts out B from phase D into A and negative if it salts it out of A into D.

Similarly for solute component C,

$$\frac{X_{CA}/X_{AA}}{X_{CD}/X_{DD}} = \frac{x_{CA}/x_{AA}}{x_{CD}/x_{DD}} + K'\left(\frac{X_{BA}}{X_{AA}} + \frac{X_{BD}}{X_{DD}}\right)^{m'}\left(\frac{X_{CA}}{X_{AA}} + \frac{X_{CD}}{X_{DD}}\right)^{n'} \qquad (7.20)$$

K,K',m,m',n and n' can be found from regression analysis of experimental data. Hence two simultaneous non-linear algebraic equations for X_{BA} and X_{CA} are obtained which can be solved by a suitable iteration procedure.

As for the case of ternary systems, this method is suitable for the case of negligible mutual solubilities of A in phase D and D in phase A, since in the iteration process, it is assumed that all A remains in phase A while all D remains in phase D.

7.3.2.1.1) WATER-ACETIC ACID-BUTANOL-HEPTANE SYSTEM:

Experimental results of the above binary quaternary system are shown in table (II.7). Regression analysis of the variables based on equations (7.19) and (7.20) led to the following correlations:

$$\frac{X_{BA}/X_{AA}}{X_{BD}/X_{DD}} = \frac{x_{BA}/x_{AA}}{x_{BD}/x_{DD}} - 10.85\left(\frac{X_{BA}}{X_{AA}} + \frac{X_{BD}}{X_{DD}}\right)^{-0.21}\left(\frac{X_{CA}}{X_{AA}} + \frac{X_{CD}}{X_{DD}}\right)^{0.16} \qquad (7.21)$$

$$\frac{X_{CA}/X_{AA}}{X_{CD}/X_{DD}} = \frac{x_{CA}/x_{AA}}{x_{CD}/x_{DD}} + 0.20\left(\frac{X_{BA}}{X_{AA}} + \frac{X_{BD}}{X_{DD}}\right)^{2.00}\left(\frac{X_{CA}}{X_{AA}} + \frac{X_{CD}}{X_{DD}}\right)^{-2.20} \qquad (7.22)$$

Equations (7.21) and (7.22) demonstrate the salting effect between acetic acid and butanol in water-heptane systems. Distribution of acetic acid relative to the aqueous phase is depressed in accordance with equation (7.21), while enhancement of the alcohol distribution in the aqueous phase is indicated by equation (7.22).

A computer program was written for solving equations (7.21) and (7.22). This program was subsequently used as a subprogram in the batch-extraction-reaction model and is shown in Appendix (VII). The program was initiated with given amounts of A,B,C,D in moles. Ternary distribution values were calculated first according to equations (7.15) and (7.16). Then the simultaneous equations (7.21) and (7.22) were solved by an iteration process using Newton-Raphson method with partial derivatives. The assumption was made that no intermixing between water and heptane occurred. Table II.7 shows that this assumption was justified since the maximum amount of water in the heptane rich phase was 7.0%, while the maximum amount of heptane in the water rich phase was 4.4% only.

Results of the computer calculations of the acid and alcohol concentrations relative to water together with the experimental values and per cent deviation between experimental and calculated values are shown in table II.7a. These results are plotted in figures (7.17) and (7.18). Fair agreement was achieved between the experimental and computed results. The deviation in case of acetic acid was always less than 20%, the average being about 10%. The agreement between experimental and computed values, for butanol distribution, was slightly less satisfactory, there being two values out of 8 showing deviations of 20.8 and 23.9%. The average deviation was about 11%. The reason for the larger deviations in butanol distribution values is thought to be due to the method followed in butanol analysis viz gas liquid chromotographic analysis which was less accurate than the acid-base titration adopted for acetic acid analysis.

7.3.2.1.2) WATER-ACETIC ACID-BUTANOL-n BUTYL ACETATE SYSTEM:

Experimental results for the binary quaternary, formed by water-acetic acid-butanol-n butyl acetate, are shown in table II.8. Regression analysis led to the following correlations:

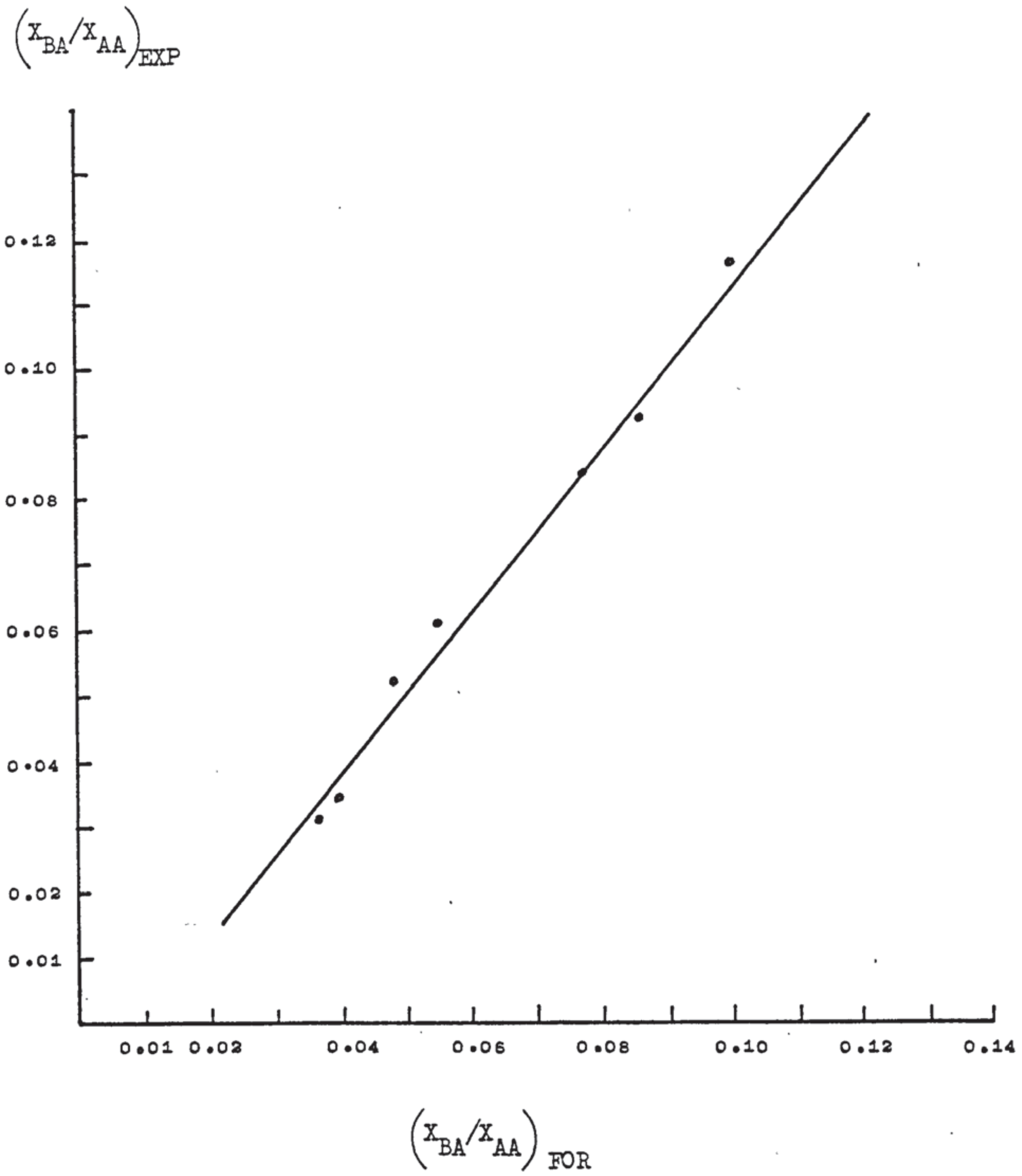


Figure 7.17 Distribution of Acetic Acid in Water-Acetic Acid-Butanol-n Heptane Quaternary

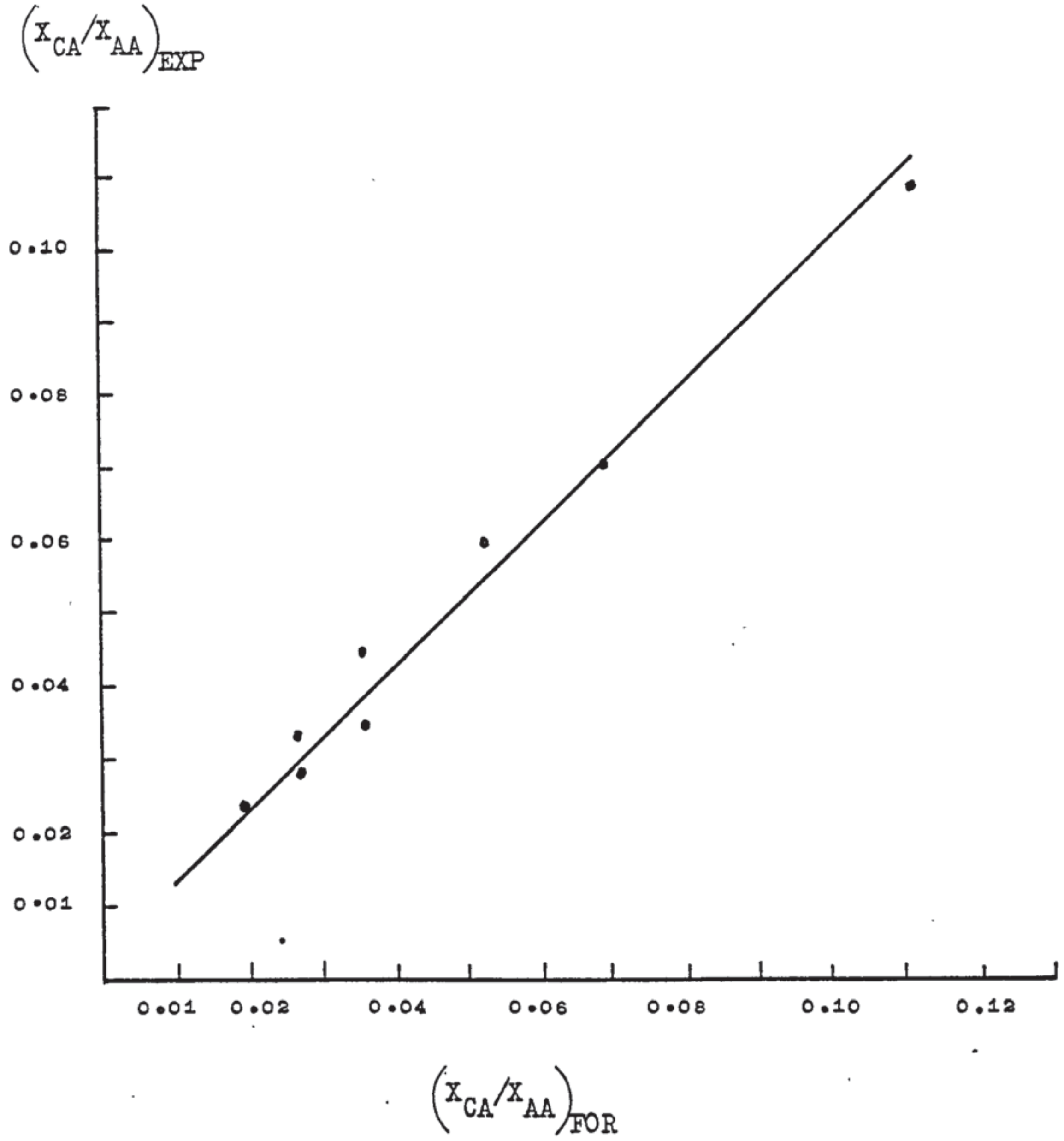


Figure 7.18 Distribution of Butanol in Water-Acetic Acid-Butanol-n Heptane quaternary

$$\frac{X_{BA}/X_{AA}}{X_{BE}/X_{EE}} = \frac{x_{BA}/x_{AA}}{x_{BE}/x_{EE}} - 0.20\left(\frac{X_{BA}}{X_{AA}} + \frac{X_{BE}}{X_{EE}}\right)^{-0.20}\left(\frac{X_{CA}}{X_{AA}} + \frac{X_{CE}}{X_{EE}}\right)^{0.35} \tag{7.23}$$

$$\frac{X_{CA}/X_{AA}}{X_{CE}/X_{EE}} = \frac{x_{CA}/x_{AA}}{x_{CE}/x_{EE}} + 0.0021\left(\frac{X_{BA}}{X_{AA}} + \frac{X_{BE}}{X_{EE}}\right)^{2.06}\left(\frac{X_{CA}}{X_{AA}} + \frac{X_{CE}}{X_{EE}}\right)^{-2.02} \tag{7.24}$$

The last term of equation (7.24) is very small indicating that the salting effect of acetic acid on butanol in water-n butyl acetate systems is very small and can in practice be neglected. Hence in programming, equations (7.23) and (7.24), the last term of equation (7.24) was ignored. Thus,

$$x_{CA} = X_{CA}$$

$$x_{CE} = X_{CE}$$

and the concentration of butanol was calculated directly from the ternary correlation (equation (7.18)). In this case equation (7.23) was reduced to a single unknown which was easily solved by Newton-Raphson iteration procedure.

The computed values together with the experimental and per cent deviation are shown in table II.8a and plotted in figures 7.19 and 7.20. Good agreement was achieved between the experimental and calculated values. All deviations were less than 20%, the average being 7.7% for acetic acid and 4.0% for butanol.

7.3.2.13) CONCLUDING REMARKS ON THE SINGLE BINARY QUATERNARY MODEL

The mathematical model for a binary quaternary system developed in this study, represented by equations (7.19) and (7.20), describes the distribution of two solutes between two immiscible solvents (e.g. water and an organic solvent). Application of this method to two systems, studied experimentally, showed good agreement between experimental and predicted distri-

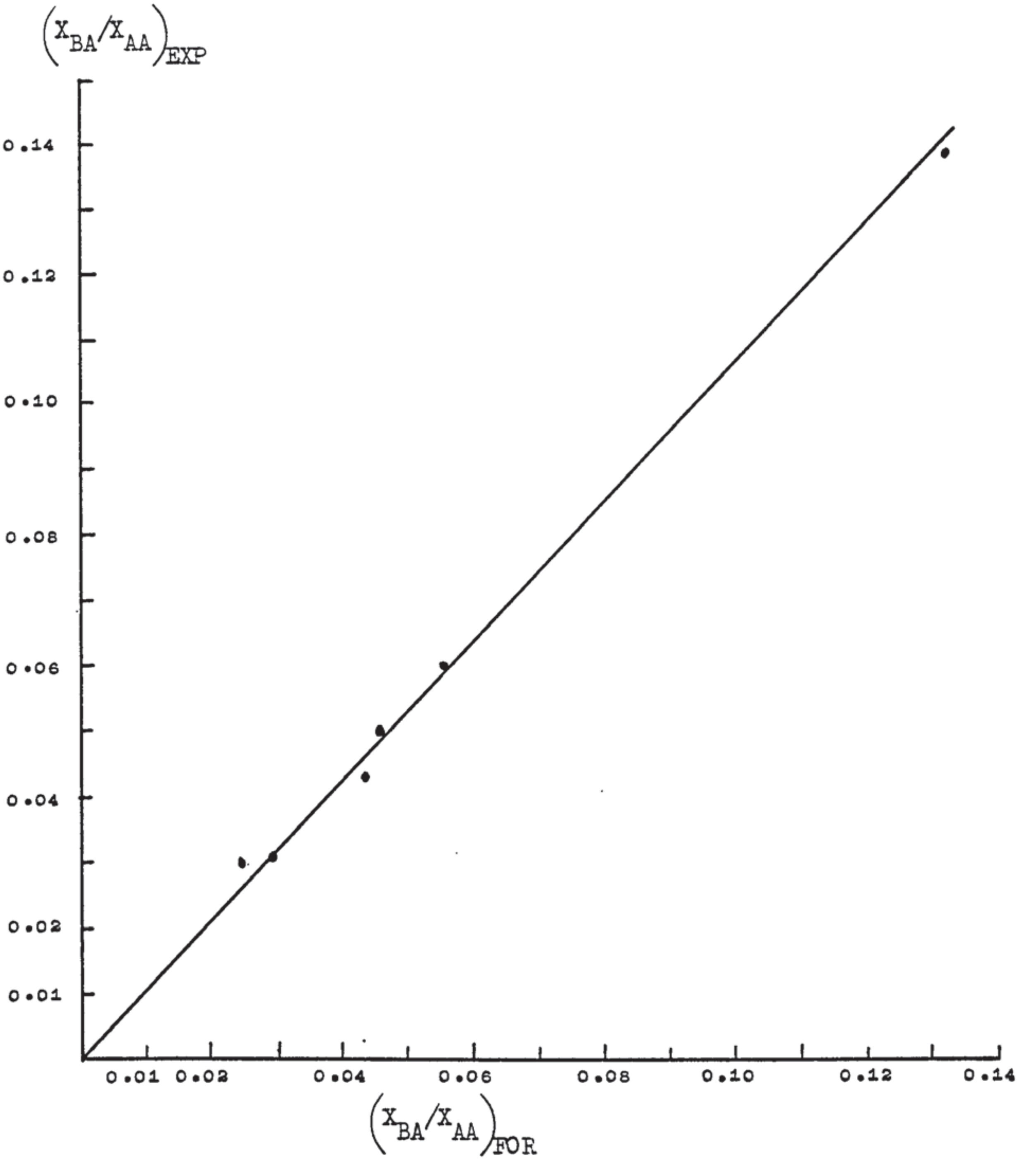


Figure 7.19 Distribution of Acetic Acid in Water-Acetic Acid-Butanol-Ester quaternary system.

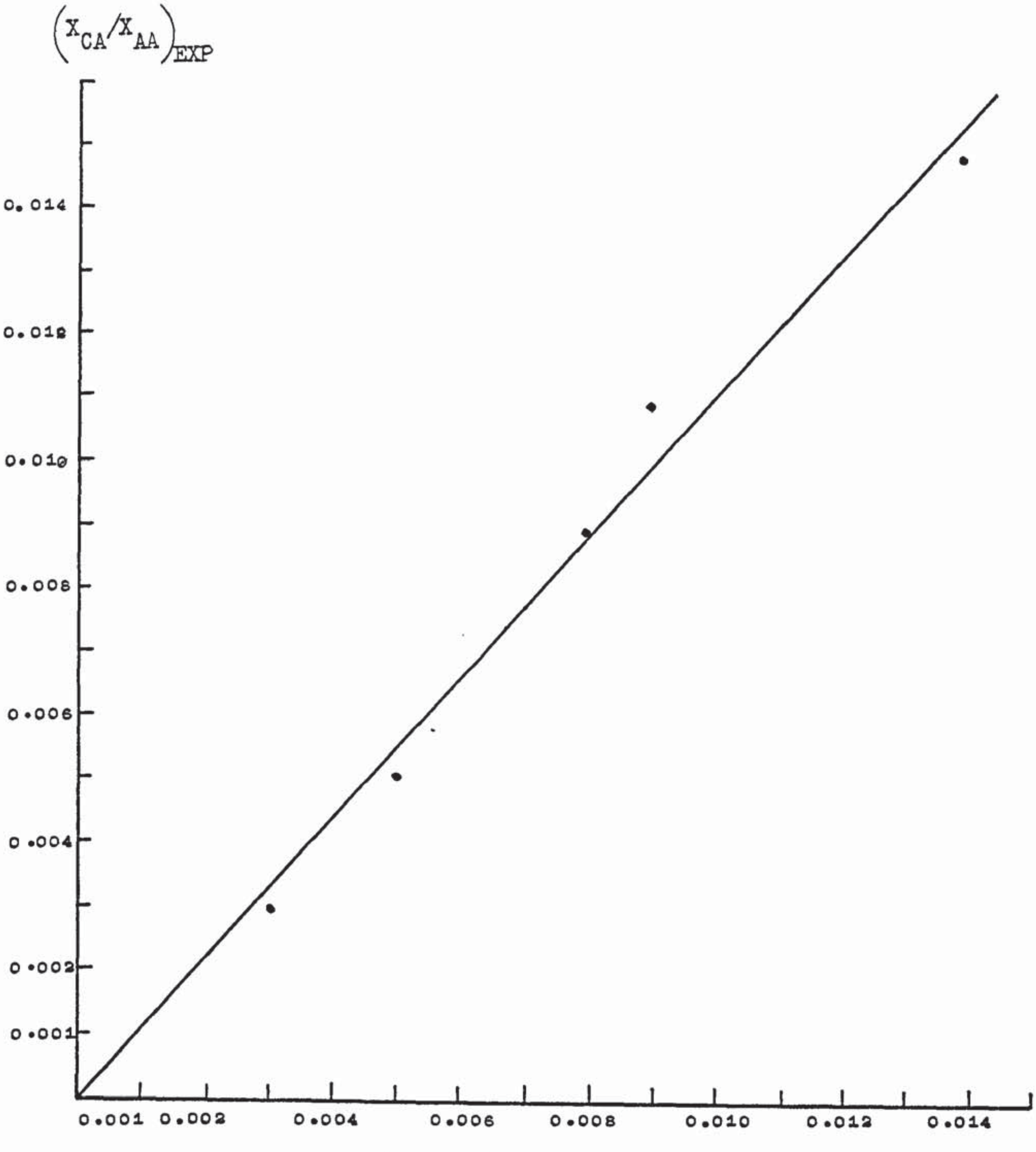


Figure 7.20 Distribution of Butanol in Water-Acetic Acid-Butanol-Ester quaternary System.

bution values for the two solutes.

The model thus developed is the first published algebraic correlation for a single binary quaternary system. It is believed to be superior to the conventional geometrical methods for the analysis of solvent extraction processes.

In order to demonstrate the applicability of the model to other systems, the data of Brancker, Hunter and Nash(109) was analysed. In this case the agreement between the experimental and predicted values, for one of the solutes, was good; while the deviations between experimental and calculated values, for the second solute, were unacceptably large. The reasons for these are explained in Appendix II.

7.3.2.2) MODELLING A DOUBLE BINARY QUATERNARY SYSTEM

In this case a solute B or C is distributed between phase A which consists of water, with negligible amounts of D and E and an organic phase of (D+E) with negligible amounts of water.

The concentration of B in phase A represented by $\frac{B_1}{A}$ is likely to change as the ratio of D to E is changed. At one extreme, when E is zero, $\left(\frac{B_1}{A}\right)$ is the ternary concentration for the system A,B,D. On the other hand if D is zero $\left(\frac{B_1}{A}\right)$ is the concentration for the ternary system A,B,E. If D-E solution is ideal, each component of its mixture can be expected to "contribute" a share to the distribution proportional to its mole fraction.

Hence it would be expected that the distribution of a solute in a double binary quaternary could be described by the equation

$$\frac{X_{BA}}{X_{AA}} = \left(\frac{D}{D+E}\right)\left(\frac{x_{BA}}{x_{AA}}\right)_D + \left(\frac{E}{D+E}\right)\left(\frac{x_{BA}}{x_{AA}}\right)_E \qquad (7.25)$$

where:

$\left(\frac{x_{BA}}{x_{AA}}\right)_D$ is found from experimental data for the ternary system A,B,D and corrected for the quaternary composition by multiplying by the ratio $\left(\frac{\text{moles of D}}{\text{moles of (D+E)}}\right)$; and

$\left(\frac{x_{BA}}{x_{AA}}\right)_E$ is found from experimental data for the ternary system A,B,E and corrected for the quaternary composition by multiplying by the ratio $\left(\frac{\text{moles of E}}{\text{moles of (D+E)}}\right)$.

7.3.2.2.1) WATER-ACETIC ACID-n HEPTANE-n BUTYL ACETATE SYSTEM

The data for the water-acetic acid-n heptane-n butyl acetate system is shown in table II.9. In this table, the experimental concentration of the solute in the aqueous phase was calculated directly from the aqueous phase per cent composition. The predicted composition was computed from equation (7.25). The two factors $\left(\frac{x_{BA}}{x_{AA}}\right)_D$ and $\left(\frac{x_{BA}}{x_{AA}}\right)_E$ were found from the respective ternary correlations (equations (7.15) and (7.17)), while the mole fractions $\frac{D}{D+E}$ and $\frac{E}{D+E}$ were found from weight fractions of the two mixed solvents (n heptane and n butyl acetate). Finally % deviation was found between the experimental and computed values. Experimental vs predicted values were plotted in figure 7.21.

It is clear from table II.9 and figure 7.21 that very good agreement had been achieved between the experimental and predicted distribution values. The deviations for all the points were less than 10%, the average being about 5%. This is

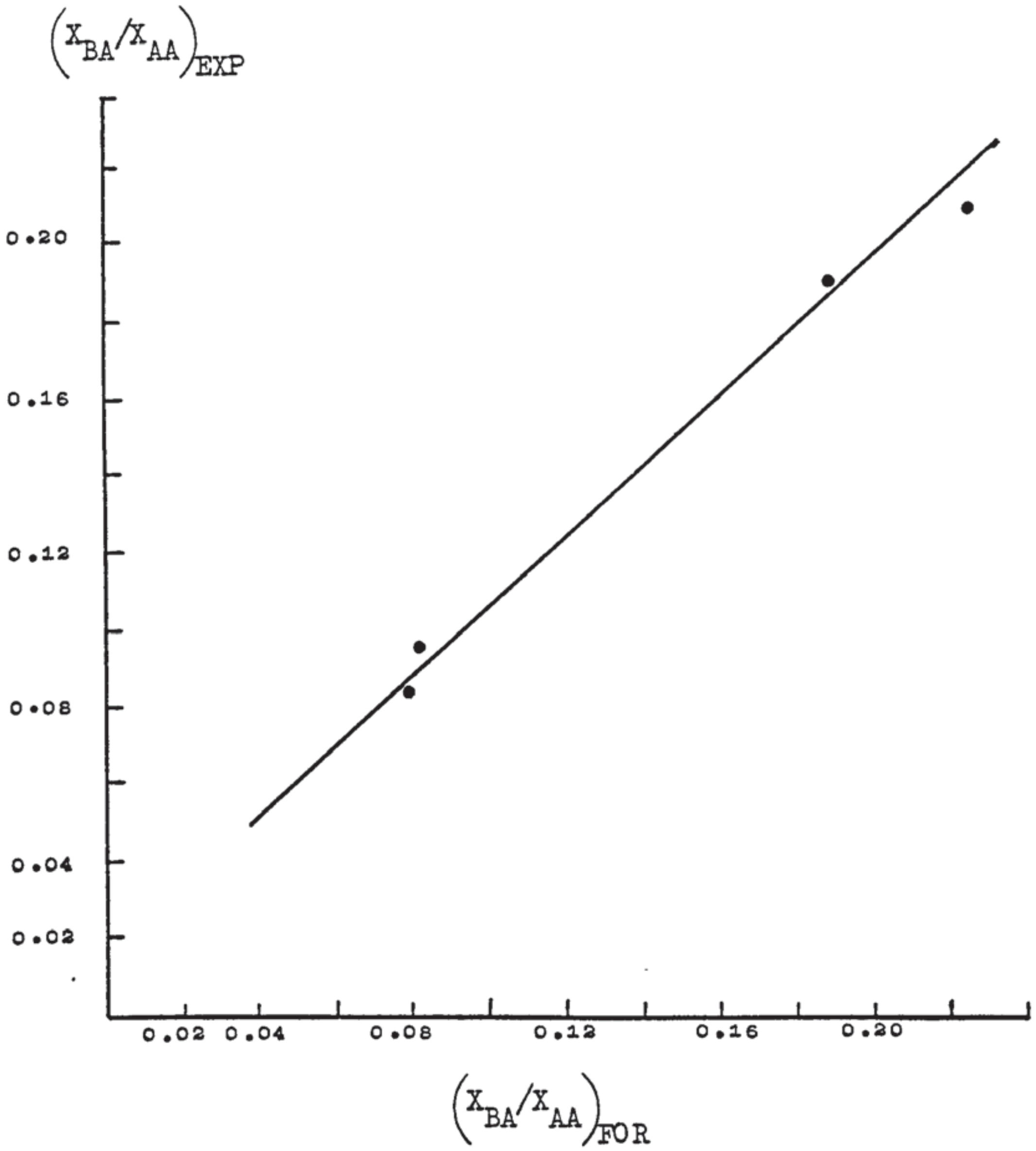


Figure 7.21 Distribution of Acetic Acid in the Water-Acetic Acid-n Heptane-Ester quaternary System.

thought to be within the experimental errors.

7.3.2.2.2) WATER-BUTANOL-n HEPTANE-n BUTYL ACETATE SYSTEM

The data for this system is shown in table II.10 and figure 7.22. Again good agreement was achieved between the experimental and predicted distribution values. The deviation for all the points were less than 10%, the average being about 7.5%.

7.3.2.2.3) CONCLUDING REMARKS ON THE DOUBLE BINARY QUATERNARY MODEL

The mathematical model for a double binary quaternary system represented by equation (7.25) predicts algebraically the distribution of a solute between one solvent in one phase and two "mixed" solvents in the other phase. Equation (7.25) is similar in form to Raoults Law and is indeed based on the same principle.

The agreement between the predicted and experimental values, for the two cases investigated experimentally, was very good. Equation (7.25) appears to be an exact representation of the physical forces prevailing in double binary quaternary systems.

Equation (7.25) was tested on Prince's data(110), for the water-acetic acid-benzene-carbon tetrachloride system. Again the agreement between experimental and predicted distribution values was also very good. In this case the average deviation for 23 points was about 3%. These evluations are shown in Appendix (II).

Determinations of solubilities in four component systems is a time consuming operation and prone to experimental errors. Hence equation (7.25), which does not required any quaternary experimental values, may find application in predicting

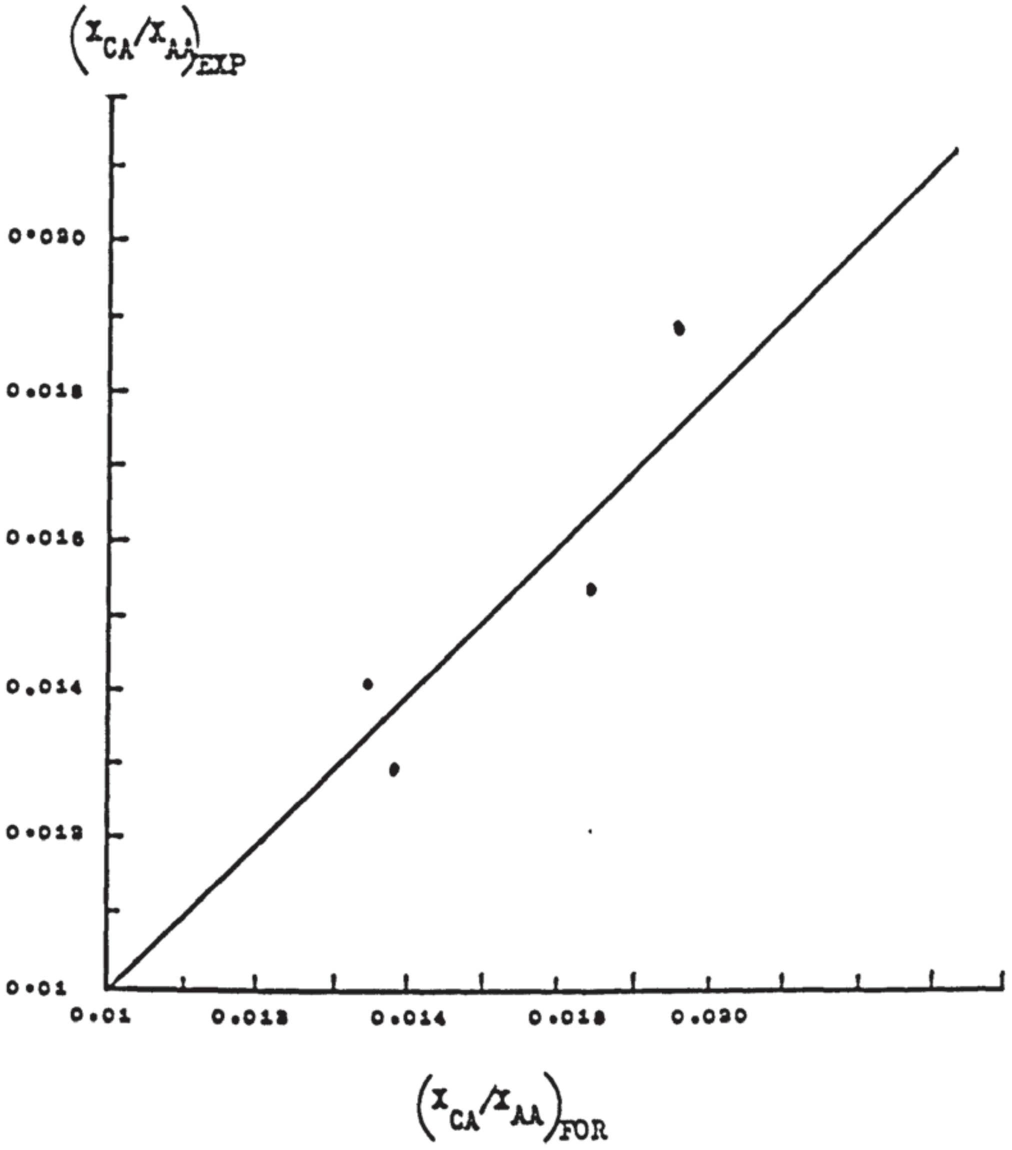


Figure 7.22 Distribution of Butanol in Water-Butanol-n Heptane-Ester quaternary System.

the composition of double binary quaternary systems without resort to experimentation on the quaternary. It is very likely that the same equation can be used for systems of more than two "mixed solvents" by including a term for each solvent.

7.3.3) FIVE COMPONENT SYSTEM.

The original reaction mixture contained one binary quaternary system. Generation of the ester increased the number of components to five in addition to the sulphuric acid catalyst which was found to have negligible effect on the distributions. The solubility of the ester generated was negligible in the aqueous phase. Hence the ester was considered as a second organic solvent and the distribution of acetic acid and butanol, as a result of ester addition, was expected to change in a manner similar to the change in distribution of a solute in a double binary quaternary, as the ratio of the two organic solvents is changed, i.e. the distribution was expected to be described by a system of equations consisting of equations (7.21-7.24) plus one equation of the double binary quaternary form (equation (7.25)) for each component.

Table (II.11) shows the experimental and computed distribution values in the five component system. Good agreement was achieved between the experimental and calculated distribution values. The maximum deviation was 14.1%.

7.4) BATCH EXTRACTION-REACTION

Tables (I.4) and (I.5) show the results of 14 runs for the esterification reaction initiated with various amounts of reactants, catalyst and solvent. Figures (7.23), (7.24) and (7.25) indicate the influence of the catalyst concentration on reaction mixtures of the same composition. Figure (7.23) includes

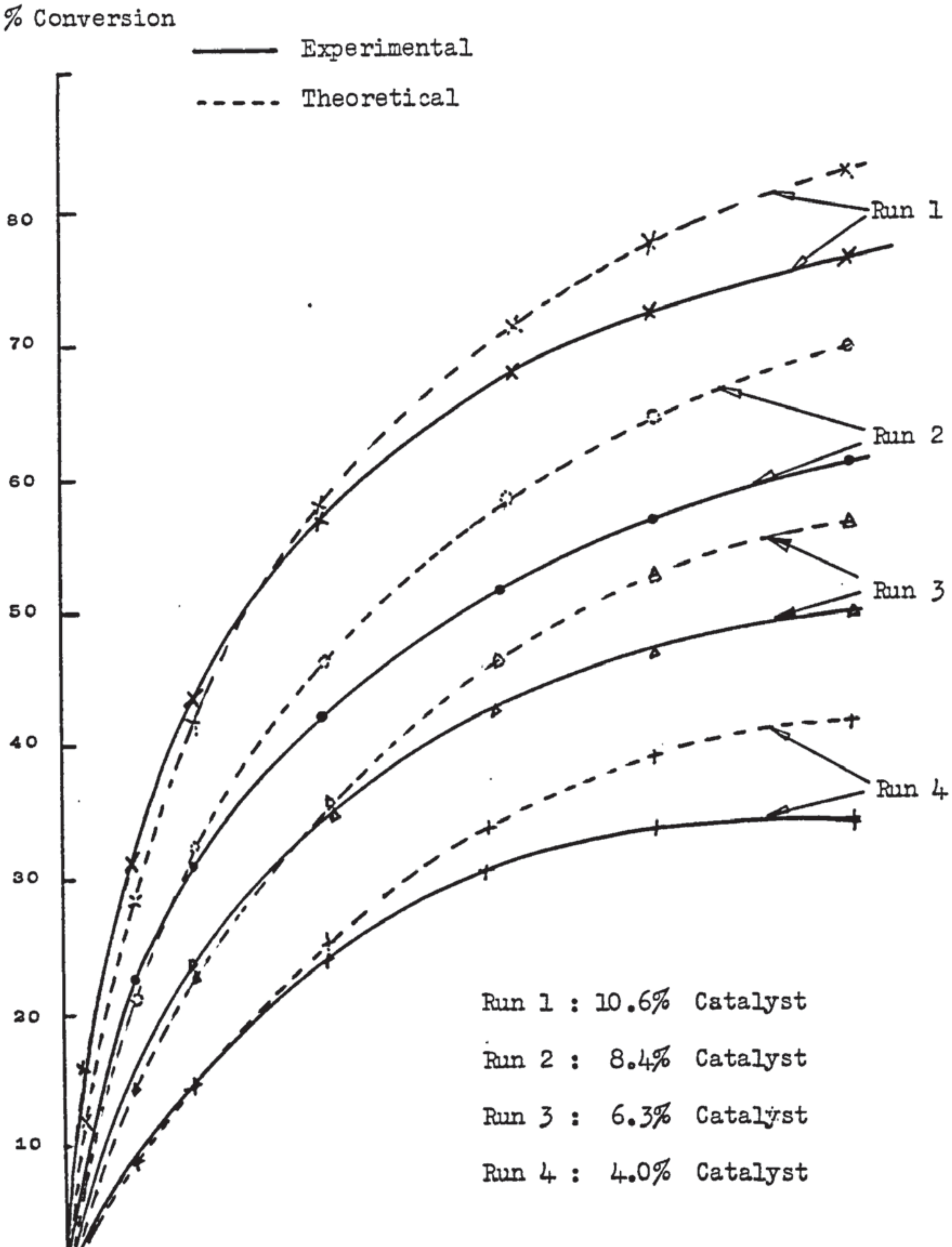


Figure 7.23 Batch extraction reaction
Theoretical and experimental
conversion at various Catalyst concentrations.

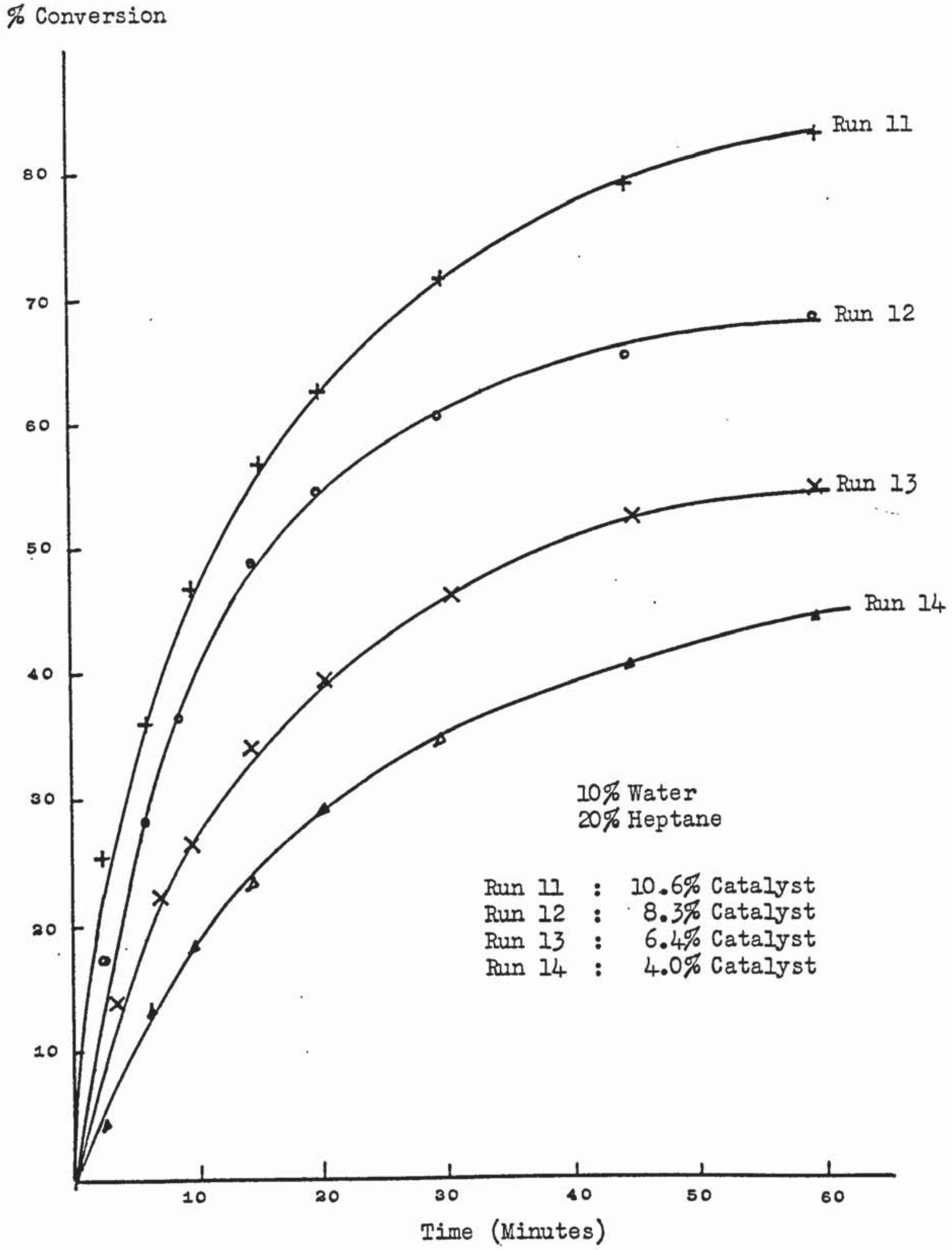


Figure 7.24 Batch extraction reaction experimental conversion at various catalyst concentrations.

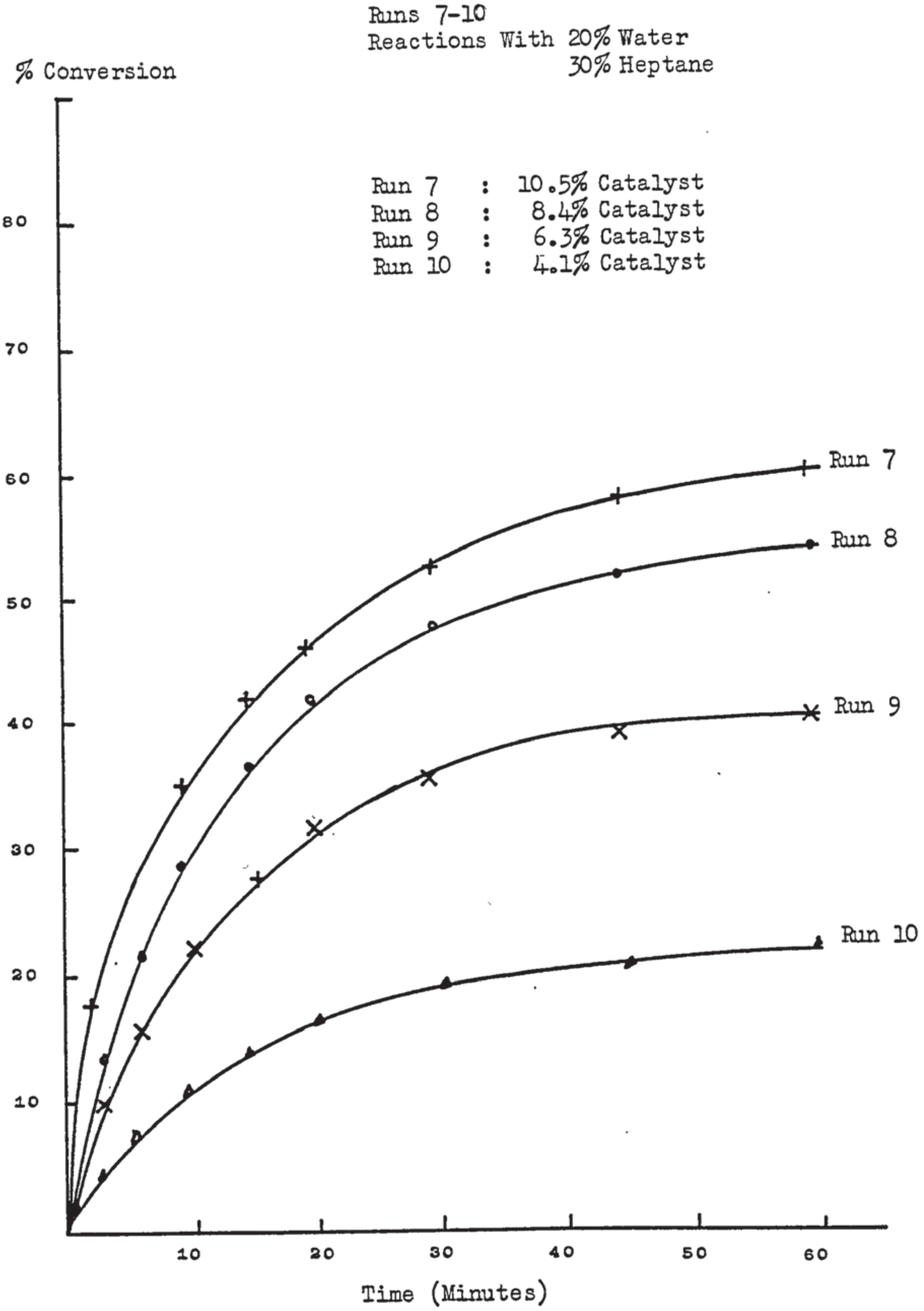


Figure 7.25 Batch extraction reaction experimental conversion at various catalyst concentrations.

the results of the mathematical model developed in Section (7.4.1). These figures show the increased catalyst concentration influence in enhancing the reaction rate.

Figure (7.26) shows the conversion rates for the same amounts of catalyst, water and heptane concentration but different ratios of acetic acid to butanol. Conversion is improved as the acid:alcohol ratio is increased. This is in accordance with the distribution studies done in Section (7.3). Excess acetic acid salts the butanol into the aqueous phase where the reaction can proceed, whereas excess butanol salts the acid out into the organic phase thus depleting the aqueous (reactive) phase of both reactants.

Figure (7.27) indicates conversion for the same catalyst and reactants concentration but differing heptane and water amounts. Conversion is improved when the water:heptane ratio is increased. However, this is of limited importance since very low or high phase ratios are likely to cause appreciable intermixing.

7.4.1) MATHEMATICAL MODEL

The basic approach of Jenson and Jeffreys in modelling hydrolysis of fats$^{(150)}$ was adopted in modelling the esterification reaction in the presence of heptane. However, the "pecularities" of this system necessitated modifying this model. First consideration had to be given to the reactants distributions which were not directly related to the equilibrium distribution ratios of the two components measured independently, but were interdependent according to the model developed in Section (7.3.2.1). Secondly, as ester was generated it changed the distributions according to equations (7.23-7.25). Therefore new distribution values had to be calculated after each numerical

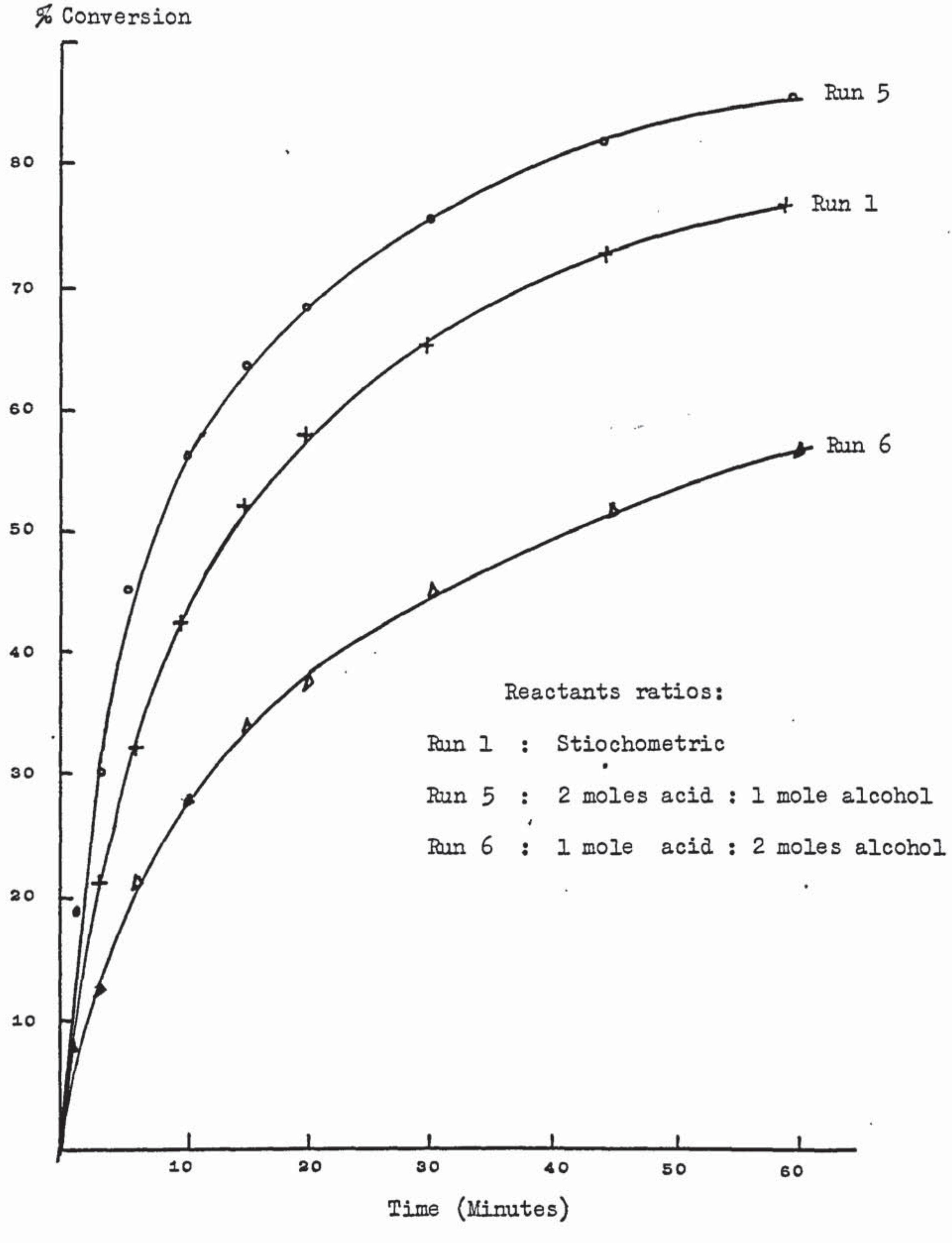


Figure 7.26 Batch extraction reaction influence of reactants ratio on conversion.

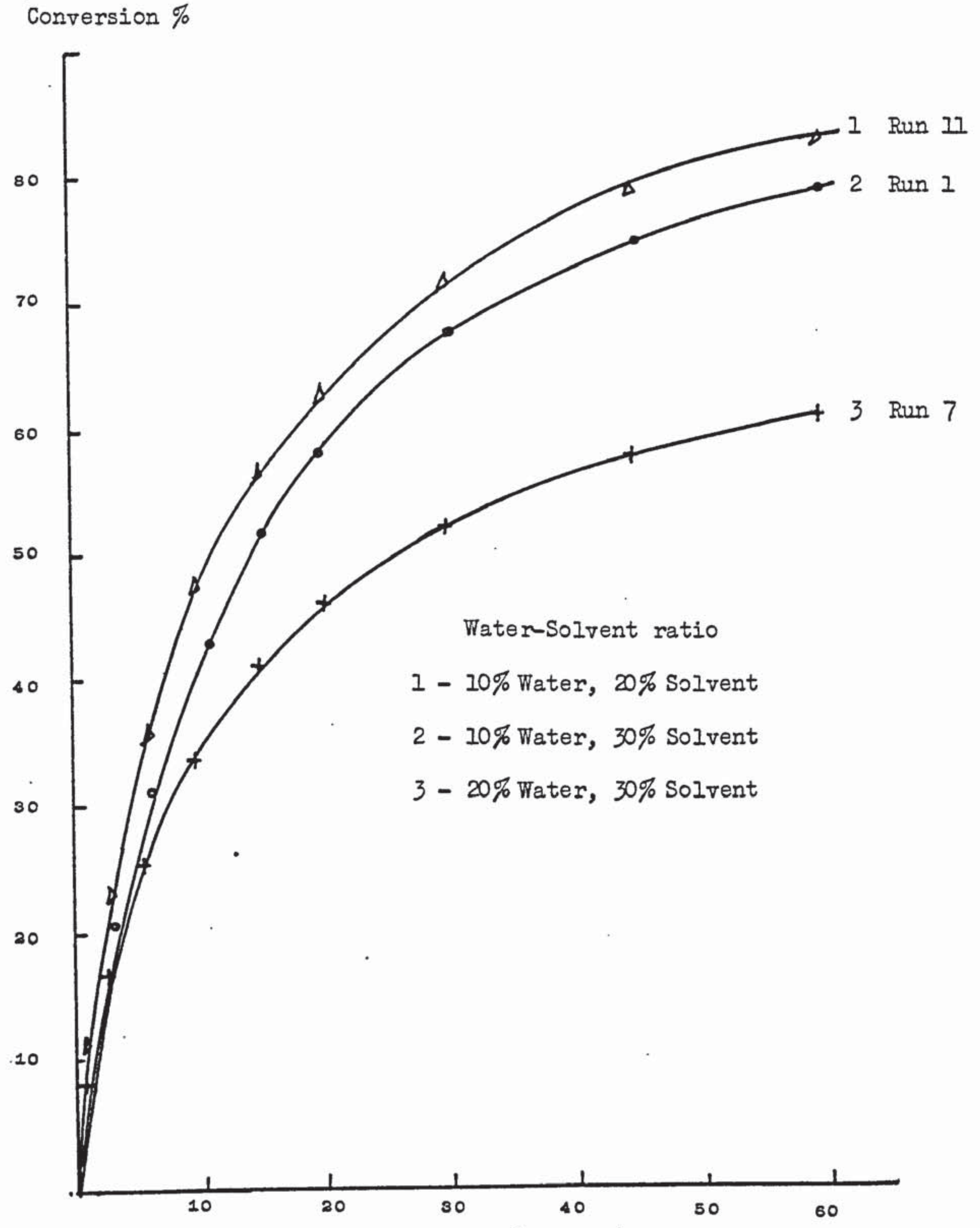


Figure 7.27 Batch extraction reaction influence of Water: Solvent ratio on conversion.

integration step of the rate equation. The same procedure was applied to the reaction rate k_2 which had to be freshly calculated after each integration step and subsequent incremental increase of the water content.

Basically, the following sequence of calculations was followed:

(1) From the initial reactants and solvent feed, the concentration of acid and alcohol in the aqueous phase was determined by application of the distribution model developed in Section 7.3.

(2) The reaction rate was calculated from equation (7.13).

(3) The rate equation (equation (7.2)) was to be solved numerically for E. Therefore the derivative had to be evaluated, in terms of reactants and products concentration,

$$DE = k_2[A][B] - k_2'[E][C] \qquad (7.26)$$

[A],[B] and [C] having been determined in (1) above. However, according to the distribution studies done in Section 7.3, concentration of the ester in the aqueous phase is zero in case of phase equilibrium. If this condition is satisfied, the reaction will behave irreversibly and the last term of equation (7.26) will be zero. However, during the computer program development, as explained in Section (7.4.2), it was found that the mass transfer was not fast enough to maintain the aqueous phase free of the ester molecules particularly in the early stages of the reaction when the reaction rate was relatively fast. A unique procedure was found for accounting for this mass transfer effect.

(4) A step was introduced into the numerical integration of equation (7.2) using the derivative value just calculated

(4) contd.

from equation (7.26).

(5) The variables were tested for a print interval and whether the computation has reached a termination value.

(6) All the variables were updated according to the stoichiometry of the reaction and new values of [A], [B], [C] and [E] evaluated according to the distribution model, i.e. the computation was recycled to the beginning.

The following assumptions were made in this treatment:

(1) No reaction takes place in the heptane rich phase. This assumption is valid as long as no H_2SO_4 is present in that phase. The distribution of H_2SO_4 in water-heptane mixtures was tested and no H_2SO_4 could be detected in the heptane phase. Addition of acetic acid did not cause any H_2SO_4 to salt out into the organic phase. However, the presence of butanol did cause "salting in" of H_2SO_4 into the heptane-butanol phase. Table (II.18) shows H_2SO_4 to be present at a concentration of 3.0% (corresponding to 18.5% in the heavy phase) when the concentration of butanol was 47.5%. This 3.0% H_2SO_4 will cause a reaction in the organic phase.

The presence of acetic acid causes "salting in" of the butanol into the aqueous phase, consequently the concentration of butanol in the organic phase is not high enough for reaction mixtures considered to cause appreciable salting of sulphuric acid into organic phase. This situation is always true for AcH :BuoH mole ratios of ≥ 1. If the mole ratio is $\ll 1$, the acetic acid-alcohol mutual salting effects cause appreciable

(6) contd.

(1) contd.

alcohol as well as acetic acid concentration in the organic phase with the consequence of sulphuric acid being "salted out" into the organic phase and the reaction occurring in both phases.

(2) The solubility of water in the heptane rich phase; and heptane as well as ester in the aqueous phase are negligible throughout the course of the reaction.

(3) All components attain equilibrium between the two phases instantaneously throughout the course of the reaction. This assumption was modified, during computer program development and the effect of ester on the reverse reaction accounted for.

(4) No volume changes on mixing or during the course of the reaction.

7.4.2) PROGRAMMING DEVELOPMENT AND DETAILS

The main program arrangement for computing the yield or per cent conversion in batch esterification in presence of the heptane solvent is shown in general form in figure (7.28). The program consists of a preliminary housekeeping section and six subroutines.

The housekeeping section contains common statements, specifications of the problem parameter and coefficients, initial conditions and new data for repetitive runs which are introduced via a READ statement. The algebraic equation specifying the derivative of the integrated variable is also included in this section. Then follow the CALLS to the different subprogrms. These are:

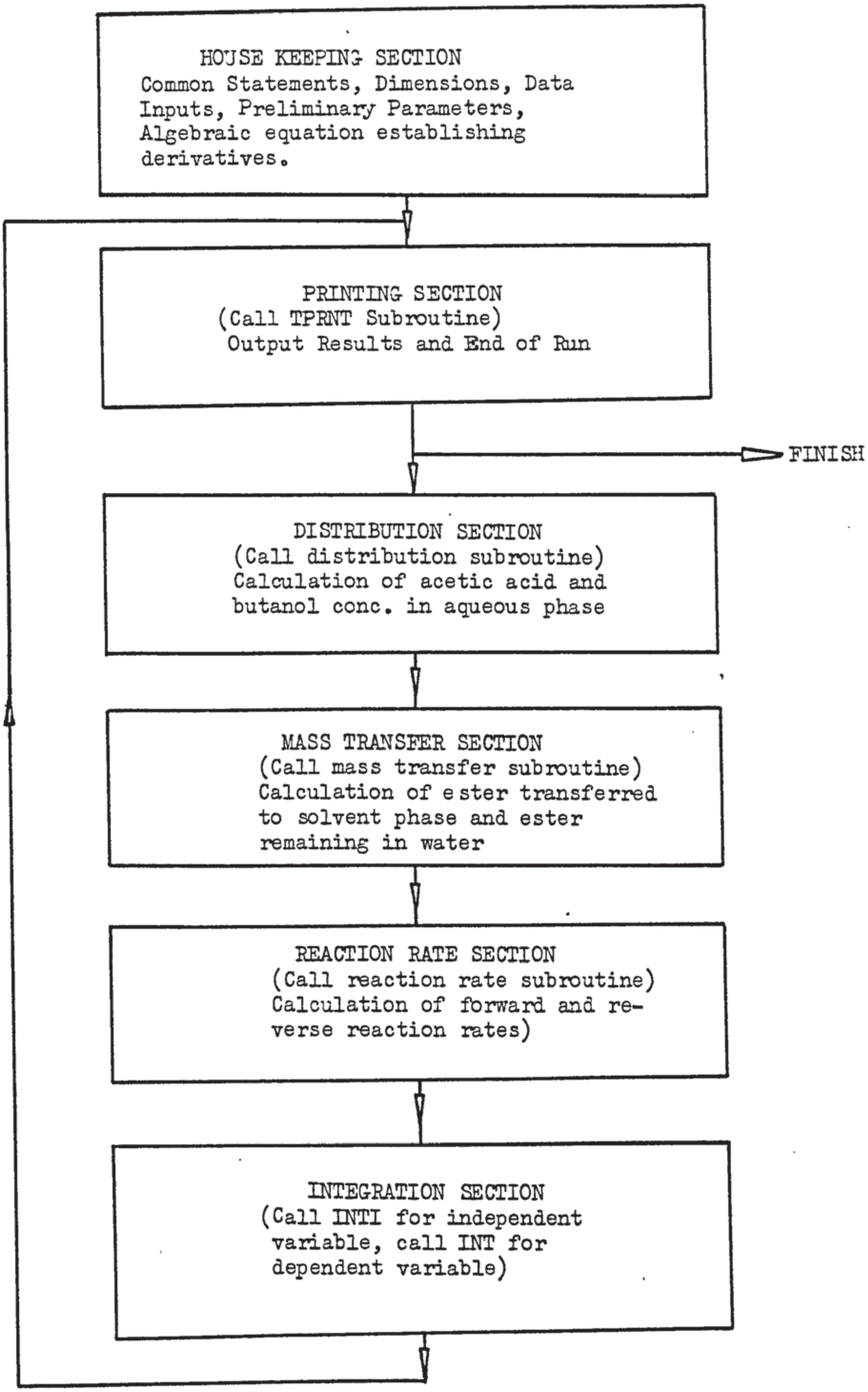


Figure 7.28 General Arrangement of Program for calculating conversion in Esterification Reaction in the Presence of Solvent.

(1) SUBROUTINE PRNTF: This subroutine controls the frequency of printing the variables of interest and tests for the end of the run. The print interval is designated as PRI. The printing is done after the previous legitimate step had been completed and the new derivative had been calculated. The pass index for the first and second order integration method JS is 2. For the fourth order method, the pass index JS4 is 4. The print interval PRI is referred to the independent variable T through the COMMON/CINT. The next item FNR specifies when the run is complete. This is followed by the index NF that indicates whether the run is not finished (NF = 1) or is complete (NF = 2). This index is used in the main program to direct the computation to continue (NF = 1) on the same set of data or terminate the integration and start with new data (NF = 2).

(2) DISTRIBUTION SUBROUTINE: This subroutine calculates the moles of acetic acid and butanol in the aqueous phase on the basis of the mathematical model developed for the two types of quaternary systems. In this procedure the values of A,B,C and S (total quantity of organic solvent) are updated after each integration step, then the distribution is computed assuming all S is heptane on the basis of equations (7.21) and (7.22). For the solution of these equations, Newton-Raphson method was applied with partial derivatives and the Jacobian of the system(112). Next the distribution was computed on the basis of S being all ester. Finally equation (7.25) was applied to both B and Ccomponents to arrive at the distribution values of the two reactants in the five component system.

During the program development, it was found

(2) contd.

that the reguli-falsi iteration method can be used instead of the Newton-Raphson method for the calculation of ternary coefficients. However , Newton-Raphson method, while in general required a smaller number of iterations to locate a root, was more likely to locate imaginary roots. To avoid this a constraint was placed on the value of the computed variable so that if it went outside the physical limits, the correction factor was halved. This procedure always ensured location of the correct root.

Another program development concerned the initialisation values for the different variables to start the iteration loops. It was found that the calculation of distribution values at the beginning often required a considerable number of iterations. However, each subsequent integration step changed the quantities of reactants and products by a small amount. Insertion of the new values did not lead to any significant changes in the distribution values. Hence by utilising the previous values for each subsequent use of the DISTRIBUTION subroutine, it was found that one iteration only was always sufficient. This was achieved by having an index IN which was initialised in the main program at 1 and connected to the DISTRIBUTION subroutine through the COMMON statement. When IN was 1, i.e. for the very first utilisation of the subroutine, a guess value was used for every variable in iteration loops. However at the end of the subroutine, IN became 2 and each fresh application started with the variables calculated from the previous application.

(3) REACTION RATE SUBROUTINE.

This subroutine calculates a fresh value for the forward reaction rate after each application of the DISTRIBUTION subroutine, on the basis of equation (7.13); and a value for the reverse reaction on the basis of an average value of the equilibrium constant calculated from table (I.3).

(4) SUBROUTINE INTI AND INT

These subroutines are used together and share information through a COMMON statement. They are together capable of performing any one of the three orders of integration, that is first, second or fourth.

Subroutine INTI is always called first. The three items in the argument list are; TD, the name of the independent variable, DTD, the integration increment, and IOD, the integration order required. Subroutine INT follows. In this subroutine, X is the name of the integrated variable (i.e. the quantity of ester formed,E) and DX is the derivative calculated in the main program.

Subroutines PRNTF, INTI and INT were adopted from Franks(132).

(5) SUBROUTINE MASSTRANSFER

This subroutine was designed to take care of the effect of slow transfer of the ester out of the aqueous phase. This slow transfer means effectively that the ester is present in the aqueous phase and effects partial reversal of the reaction.

The need for mass transfer considerations arose during programming development. At first the program was tested on the assumption that all the ester was transferred instantaneously to the solvent phase as it was

(5) contd.

formed i.e. the reaction was completely irreversible. This was in accordance with the equilibrium distribution of the ester between heptane and water where practically all the ester distributes to the heptane phase. However, when the program was run on the assumption of irreversability, the computed values were exceptionally high. Next the assumption was made that a certain proportion of the ester was always present in the aqueous phase. The program was tested on the assumption of 10, 20 and 30% of the total ester remaining in the aqueous phase. The different conversion curves thus obtained were compared. Figure (7.29) shows that while the assumption of partial reversability, with a proportion of the ester, brought the computed values nearer to the experimental values; yet this assumption was too rigid and resulted in an equilibrium conversion while in actual fact 100% conversion was obtained i.e. the reaction did eventually become completely irreversible. This was thought to be due to the fact that at the beginning, the reaction rate was faster than mass transfer rate, therefore the ester builds up in the aqueous phase. However, as the reaction slows down, the ester concentration in the aqueous phase recedes allowing complete conversion to occur at the conclusion.

To overcome the above difficulty, it was decided to use the computer to infer hypothetical values for the amount of ester present in the aqueous phase due to slow mass transfer rates. The computer program was modified so that a factor [E'], representing the hypothetical ester concentration, in the aqueous phase, was included in equation (7.26) i.e. the equation was modified to:

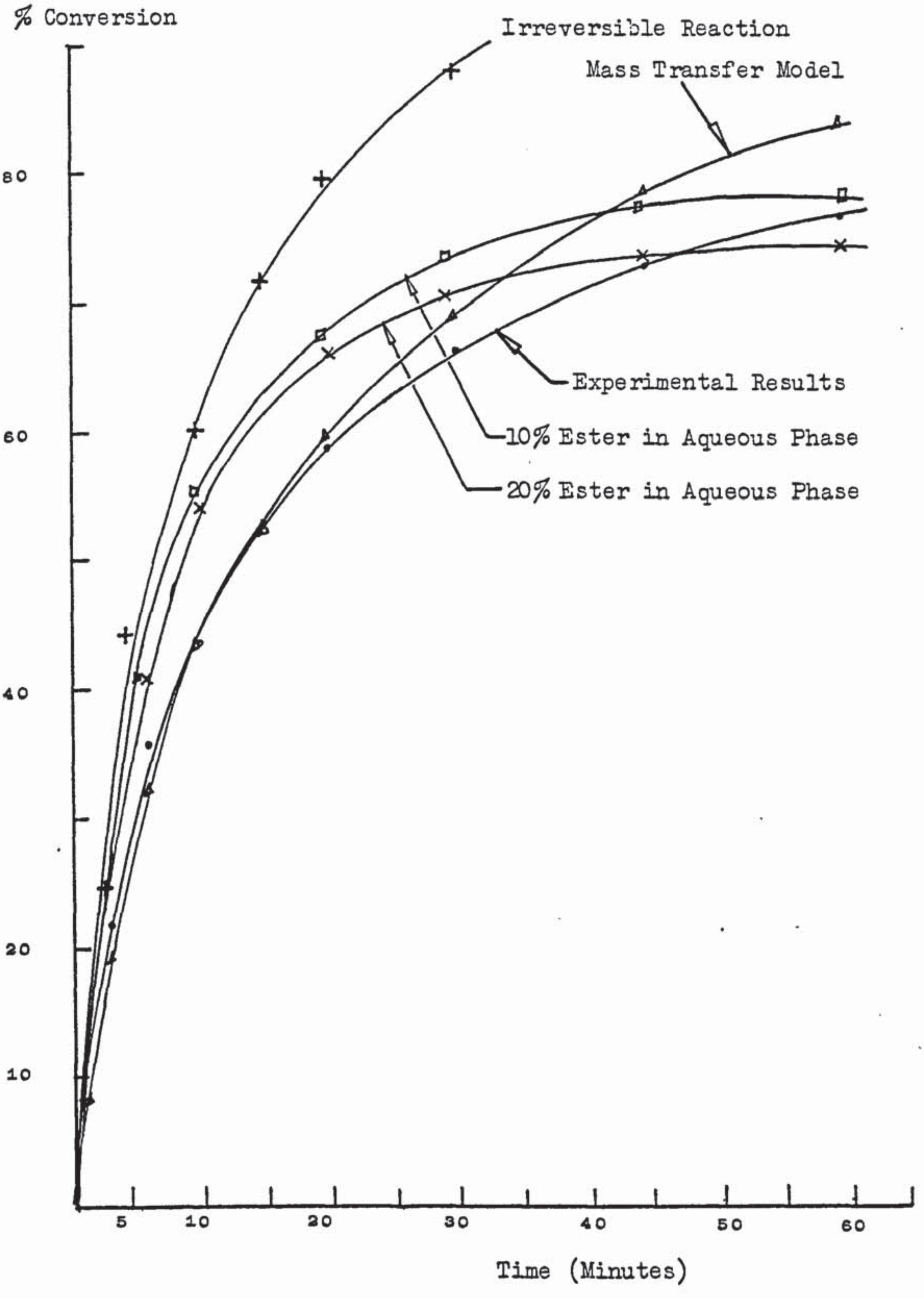


Figure 7.29 Modelling Esterification Reaction in Presence of n-Heptane Results for Run 1.

(5) contd.

$$DE = k_2[A][B] - k_2'[E'][C] \qquad (7.27)$$

The program was run and [E'] was incremented until the experimental conversion values were achieved at each stage. As a result a table of [E'] values, corresponding to the time intervals used in sampling the reaction mixture, was obtained. Figure (7.30) shows the build up and decay of E' as the reaction proceeds. From material balance on [E'] ,

$$\frac{\delta[E']}{\delta t} = \frac{\delta E}{\delta t} - \left(K_G\ a\right)\left(E'-E^*\right)$$

where (E'-E*) is the driving force.

E* is the equilibrium concentration of E' in the reactive phase. However, E* is always approximately zero. Hence,

$$K_G\ a = \frac{\frac{\delta[E]}{\delta t} - \frac{\delta[E']}{\delta t}}{E'} \qquad (7.28)$$

The experimental values of E' calculated by computer and $K_G a$ values calculated from equation (7.28) are shown in table (I.6). No $K_G a$ values could be estimated for the first minute of the reaction time. In all the batch extraction-reaction runs, it was found that conversion was unusually high at the beginning of the reaction. This is the reverse of an inhibition period to be expected in a two phase reaction process. This may be due to the high concentration gradients present when the two phases are first contacted. This was found to result in violent interfacial activity which is known to result in extremely rapid mass transfer so much so that mass transfer appears to be 'infinitely' fast and no inhibition period is exhibited.

It is apparent from table (I.6) that $K_G a$ values are

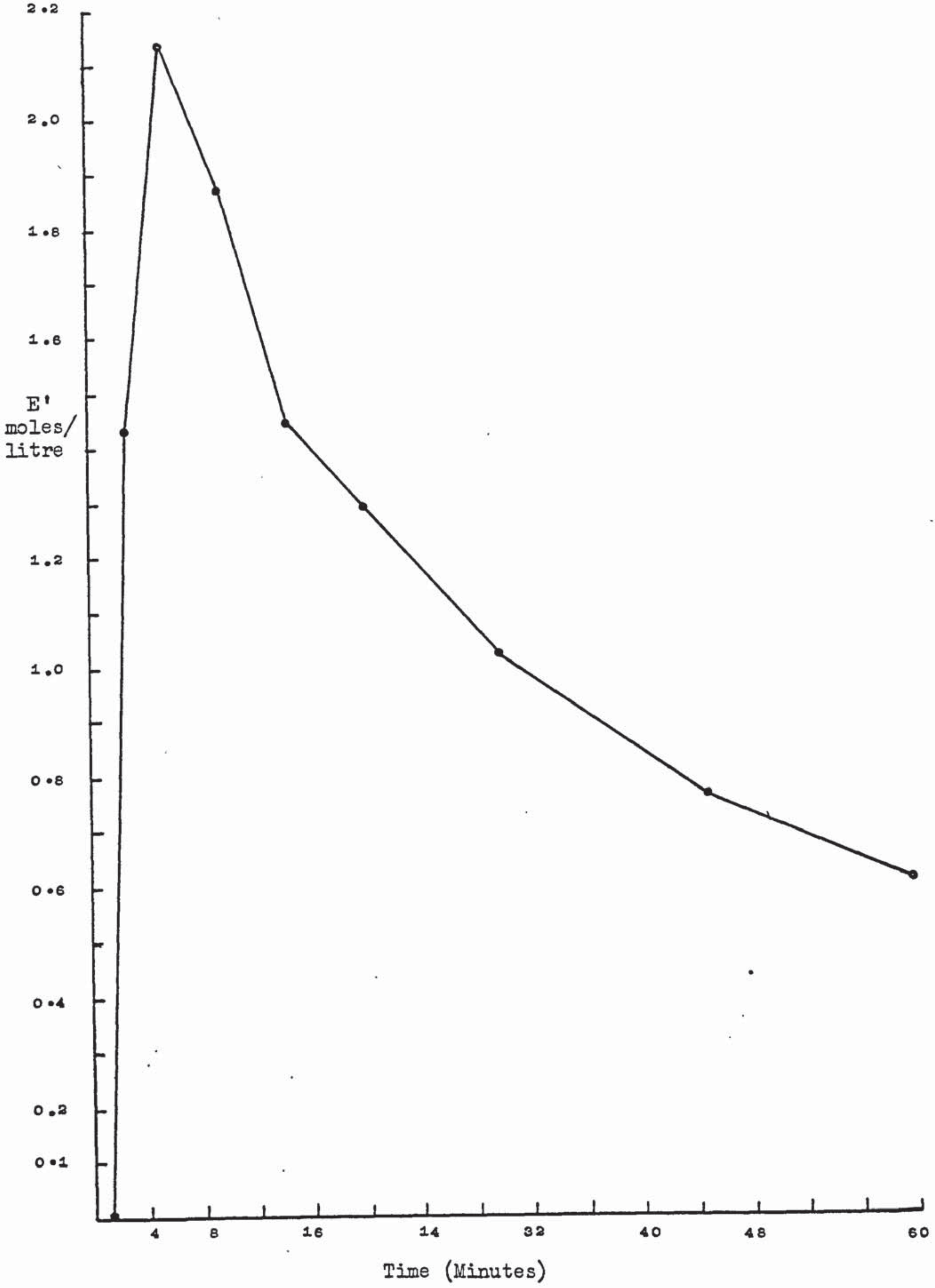


Figure 7.30 Ester concentration in the Aqueous Phase vs Reaction Time (Data based on Run 1).

(5) contd.

not constant but decrease steadily as the concentration of the ester in the aqueous phase is decreased.

In order to evaluate the mass coefficient and incorporate it in the general model, the drop size was evaluated by application of Kolmogoroff's law(187,197) and a theoretical formula used to determine the mass transfer coefficient. A sample of these calculations is shown in Appendix (IX).

The physical properties, density ρ_c, viscosity μ_c and interfacial tension σ used in the mass transfer calculations were determined experimentally. ρ_c was found to change slightly with composition as the reaction proceeded. An average value of 0.75 was taken. The change in μ_c was also insignificant. However σ was found to change significantly as the reaction proceeded. The maximum σ value was 21.0 dynes/cm at completion with a minimum of 6.0 dynes at the initiation of the reaction. The change was approximately linear as shown in figure (7.31). Therefore a correlation of the form,

$$\sigma = 21 - 15 \times \frac{\text{Total Weight of remaining reactants}}{\text{Total Weight of initial reactants}}$$

was assumed.

Considering the formula for the overall mass transfer coefficient,

$$\frac{1}{K_G} = \frac{1}{k_c} + \frac{1}{mk_d} \qquad (7.29)$$

However, the value of m was found to be very large as shown in table (II.11).

Therefore from equation (7.29) it would appear that

$$K_G \simeq k_c$$

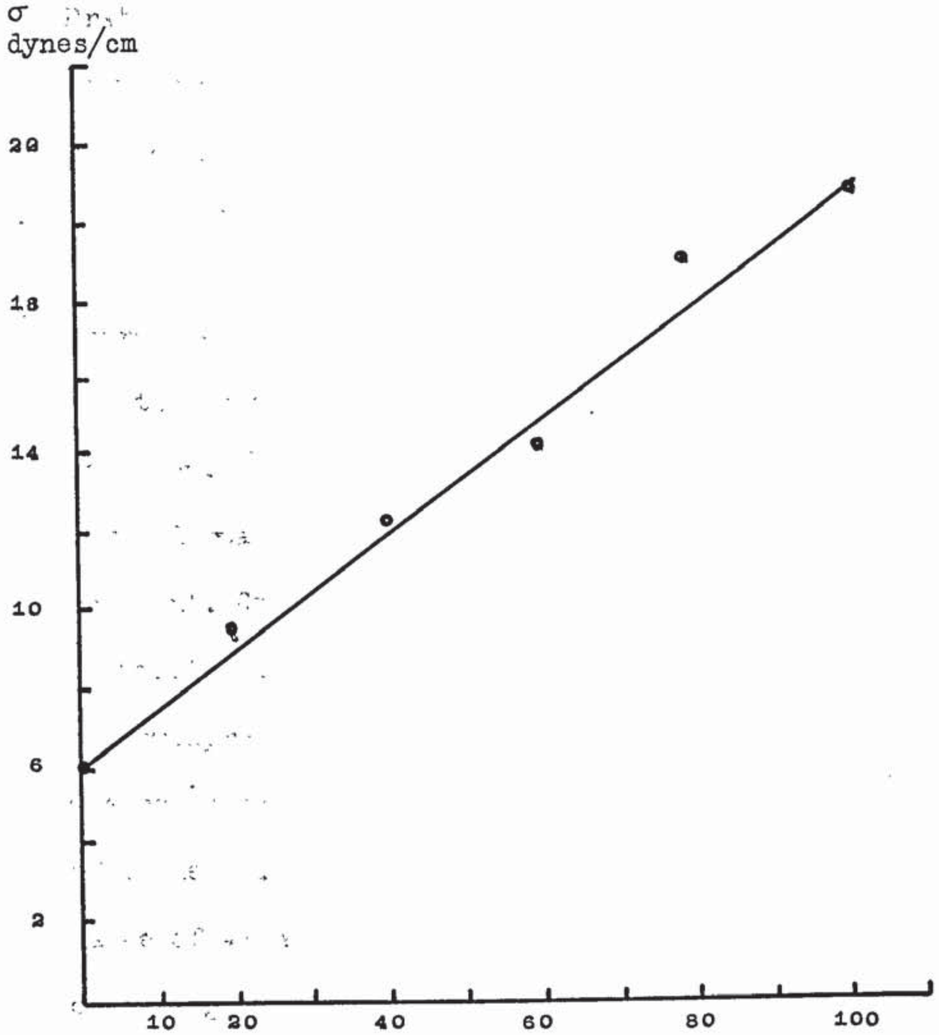


Figure 7.31 Variation of interfacial tension with Composition. (Data based on run 1)

(5) contd.

When k_c was evaluated theoretically, it was found to be consistently larger than $\left(K_G\right)_{EXP}$ as shown in table (I.7). This indicated the existence of an additional resistance. This could be attributed to the effects of the reverse reaction causing hydrolysis of the ester as it is transferred to the organic phase. Murdoch and Pratt(20) and Lewis(25,26) have reported similar findings. They proposed that the total resistance to mass transfer in such a case is given by:

$$\frac{1}{K_G} = \frac{1}{k_c} + \frac{1}{mk_d} + r_i \qquad (7.30)$$

where the value of r_i is $\frac{1}{\overline{k_1}}$ and $\overline{k_1}$ is the reverse reaction rate evaluated on the basis of pseudo first order reaction. $\overline{k_1}$ was calculated from the expression for the forward reaction rate (equation (7.13)) and the equilibrium constant. Combination of the continuous phase mass transfer coefficient, k_c and a reaction resistance effect, given by the reciprocal of $\overline{k_1}$ gave the theoretical value of K_G.This was compared with the experimental K_G values. Examination of table (I.7) show that these results agree within the range of +16% to -24%; with the positive deviations occurring at the lower conversion range.

In order to incorporate the mass transfer effect in the overall batch-extraction-reaction model, K_Ga was calculated on the basis of K_G from equation (7.30) and a from application of Kolmogoroff's law. As each step was taken, in the numerical integration of the reaction rate equation, the mass transfer subroutine was called. This subroutine incremented the value of [E'] by the following quantity,

(5) contd.

$[EXQ - (K_Ga)(E)(DTD)]$

where EXQ is the increment of E, calculated from the previous integration step; and DTD the time increment. When this procedure was applied to the reaction run used in deriving the experimental mass transfer coefficients shown in table (I.7), close agreement was obtained as shown in figure (7.29). It is noticeable that, at the beginning, the computed values are slightly less than the experimental values, however, the two curves cross at a point corresponding to a reaction time of about 10 minutes after which the computed values become higher, the maximum deviation being about 8% at a reaction time of 60 minutes. The same feature was observed on the application of the program to other runs. Figure (7.23) indicates the experimental and computed results for 4 runs with catalyst concentration ranging from 4.0-10.6%. In all the 4 cases, the computed values were higher at the completion of the reaction. This deviation becomes progressively larger for smaller reaction rates, the maximum deviation being 24% for the run with 4.0% catalyst. This indicates that the resistance to mass transfer is higher than accounted for by equation (7.30). This resistance is particularly effective at low values of the driving force. This "additional" resistance is believed to be counterbalanced at high values of the driving force. The increase in mass transfer rate, at high values of the driving force, has been confirmed by numerous investigators(153,160). The effect is attributed mostly to increasing interfacial turbulence as solute concentration is increased. However, Olander and Reddy's results(157) show that out of the three

(5) contd.

cases they investigated, the concentration level had no effect in two cases; the driving force alone being the cause of increased mass transfer. In the third case, the mass transfer coefficient was a function of concentration level as well as driving force. These results showed increases of overall mass transfer coefficient by factors of 1.5-4 as the driving force was increased.

7.5) STUDIES IN THE ROTATING DISC CONTACTOR

7.5.1) NON-MASS TRANSFER STUDIES

7.5.1.1) HOLD-UP:

The variation of hold-up with dispersed phase flowrate is illustrated in Fig.(7.32). The quantitative values of hold-up are generally lower than the results of others(114,115,118) by as much as 50%. The shape of the curves are also different. Whereas others have reported slow hold-up increases at low dispersed flow rates to be followed by a sharper increase beyond a point corresponding to about 40-50% of the flooding point; the hold-up increase with the heptane/water system investigated in this study was sharp even at low dispersed phase flow rates.

The heptane/water system seems to possess some other 'pecularities' e.g. no flooding could be detected; instead phase inversion, of a unique type, occurred when the flows passed certain values. This will be discussed later.

7.5.1.2) DROP SIZE:-

Drop size increased with increasing hold-up and decreased with increasing rotor speed as shown in Fig.(7.33). The range of d_{32} was between 3-5 mm. Sarkar(114) have reported a range of 1-5 mm for the toluene-water system in the same R.D.C. However,

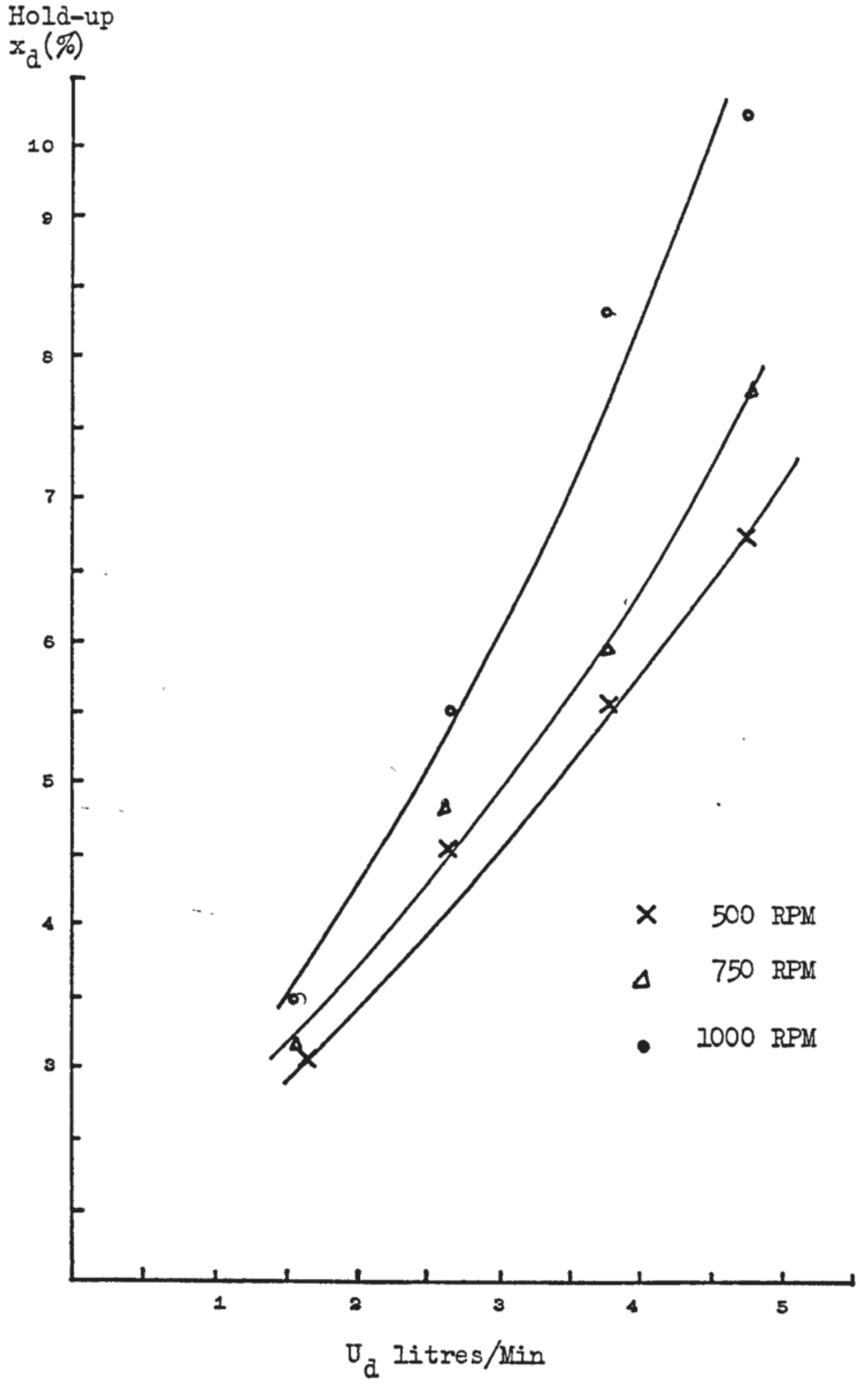


Figure 7.32 Hold-up vs. dispersed phase flow rate for n heptane-water system.

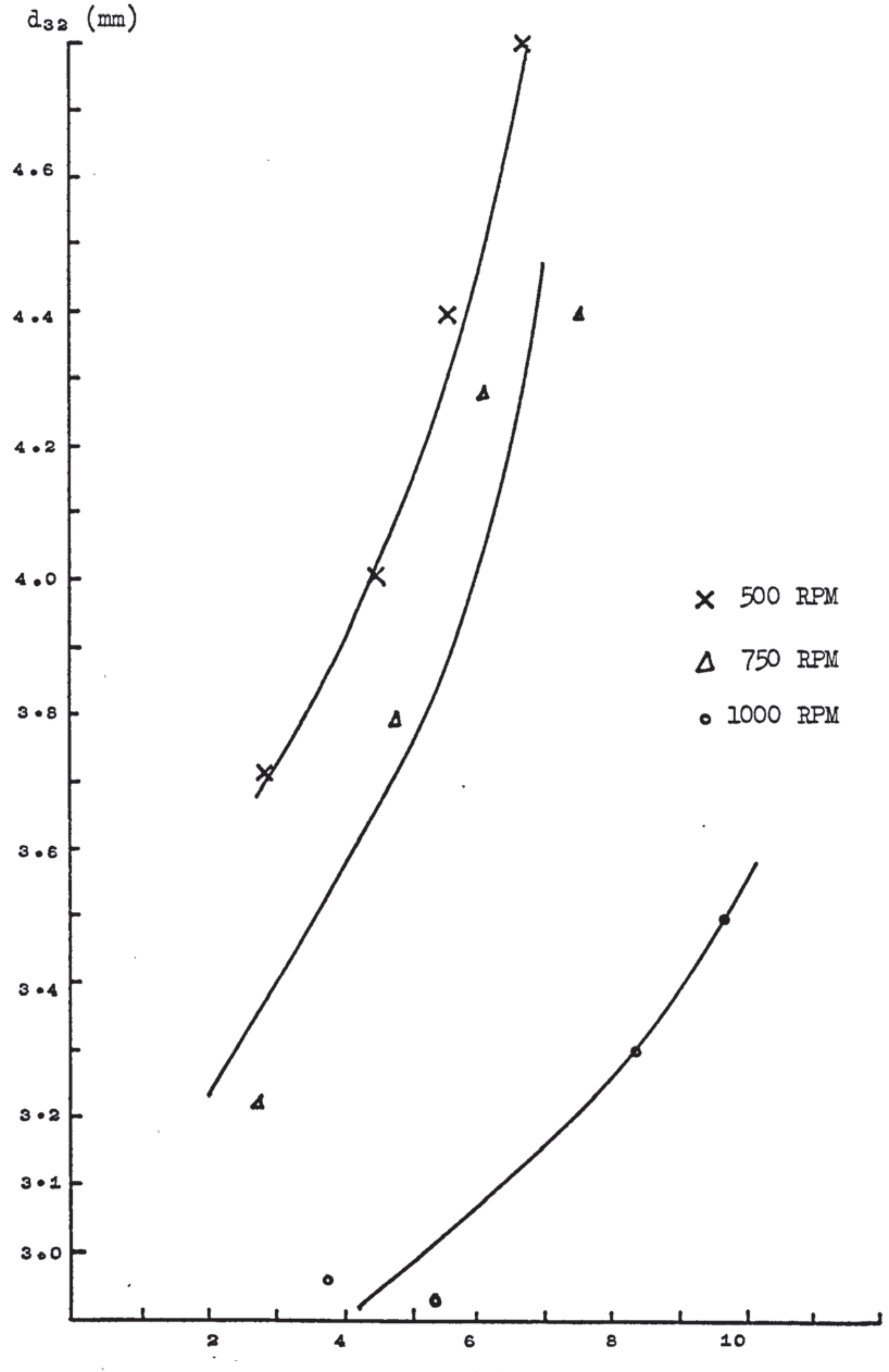


Figure 7.33 Variation of d_{32} vs. hold-up n heptane-water system.

the shape of the curves for d_{32} vs. hold-up obtained by Sarkar are such that, the d_{32} seems to approach a limiting value whereas the heptane-water system showed much sharper increases in the d_{32} values with no tendency to level off to a limiting value.

7.5.1.3) PHASE INVERSION:

The phase inversion phenomenon observed in this study for the heptane-water system had some "peculiar" characteristics,

(1) No "proper" flooding preceded phase inversion. Instead droplets of the hitherto continuous phase started building up from the distributor onwards until the whole column was filled with well packed polygonal droplets. Coalescence of these droplets was slow taking from 15-30 minutes before the column reverted to normal operation. One explanation for this phenomenon may be that instead of flooding "proper" whereby one or both phases is rejected, the hitherto continuous phase is "rejected" but the high agitation caused by the onset of flooding spins the droplets thus preventing them from coalescing, and in this case it seems flooding is characterised by formation of a dense droplet layer rather than a dense monophase of coalesced droplets which is a characteristic feature of "flooding proper".

Similar shaped drops have been reported by Robinson and Hartland(322) in a study of the effect of adjacent drops on the drop shape approaching a liquid-liquid interface, when the coalescence rate of droplets was slow so that an array of droplets was built up on the interface.

(1) contd.

The hold-up when all the column was full of the well packed drops was considered as the inversion hold-up. This varied from 60-80%. However, as mentioned earlier, the well packed droplets cleared gradually until the hold-up was back to the 'normal' values of 3-10% range.

(2) Once inversion set in by way of the well packed drops, it was not possible to reverse the process and very large changes in phase ratios were needed to reinvert. Other workers(114,115) have reported that 2-3% change in phase flow rate was sufficient to disturb the inversion and revert to the original dispersion.

7.5.2) MASS TRANSFER

7.5.2.1) ONE WAY MASS TRANSFER

Values of the area based overall mass transfer coefficient $K_G a$ were calculated for both the acetic acid and butanol transfer from the organic to the aqueous phase. For acetic acid mass transfer, the interfacial area per unit volume of the column, a, was also evaluated and hence K_G values were obtained. A sample calculation is shown in Appendix (III). It was not possible to evaluate the interfacial area for butanol mass transfer due to the very irregular nature of the heptane/butanol drops.

The $K_G a$ values for acetic acid lie between $(1.23-1.78) \times 10^{-2}$ cm/sec; while the values for butanol were $(2.16-2.68) \times 10^{-3}$ cm/sec. From the limited experimental values obtained for acetic acid (table III.3), it is observed that K_G is not constant but tends to increase with solute feed concentration i.e. the driving force. This is in accordance with observations of many research workers(153-160).

7.5.2.2) TWO WAY MASS TRANSFER

The interesting phase inversion phenomena observed when mass transfer was occurring in both directions simultaneously i.e. when there were two solutes one being transferred from the organic into the aqueous phase while the other one was being transferred in the opposite direction can be explained as follows:

It is generally agreed that transfer of a third component from the continuous phase to the dispersed phase stabilizes the droplets, whereas diffusion out of the drops accelerates coalescence(316-319). This has been attributed to formation of interfacial gradients, a phenomenon elegantly described by Davies and Jeffreys(321) as stated in Section (4.3.1.4). The phase inversion phenomenon encountered when two-way mass transfer was taking place fit in with Davies and Jeffreys postulation.

Considering the top of the column, mass transfer is predominantly from the aqueous to the organic phase since the driving force for the transfer of acetic acid is high, whereas the organic phase is lean in the second solute (butanol) and the driving force is much less. Hence the flux of molecules is much greater in the aqueous → organic direction. This stabilizes the O/W dispersion. However, as the aqueous phase descends down the column, acetic acid molar flux from the aqueous to the organic phase decreases while the butanol flux increases in the reverse direction. Eventually the latter flux predominates a process which leads to enhanced coalescence of the organic phase droplets and eventual phase inversion. The aqueous phase droplets thus formed continue to receive an increasing flux of butanol molecules while the reverse flux is decreased further. Thus from the inversion point downwards, conditions are more and more conducive to formation of a stable W/O dispersion.

7.5.3) Mass Transfer With Chemical Reaction

7.5.3.1) Analysis of Continuous Countercurrent Extraction - Reaction Process

Consider an extraction-reaction column which operates continuously under steady state conditions as shown in figure (7.34), where L_o Kg/Min of butanol/n heptane solution is fed into the base of the column to ascend as the dispersed phase. The ascending organic phase will be termed the extractive phase. This is contacted with a counter current aqueous stream consisting of water, acetic and sulphuric acids; which is the reactive phase, entering the top of the column where the flow is V_H Kg/Min. Butanol is transferred from the extractive phase to the reactive phase where it reacts with acetic acid to form the ester which is extracted back into the extractive phase.

The following assumptions were made in the analysis presented below:

(1) No reaction takes place in the extractive phase.

(2) The solubility of water in the extractive phase and heptane in the reactive phase are negligible throughout the column.

(3) All components attain equilibrium between the two phases instantaneously.

(4) No volume changes on mixing or during the course of the reaction.

(5) Dispersed phase hold-up is constant and independent of position in the column.

Taking an element of the column of height δh as

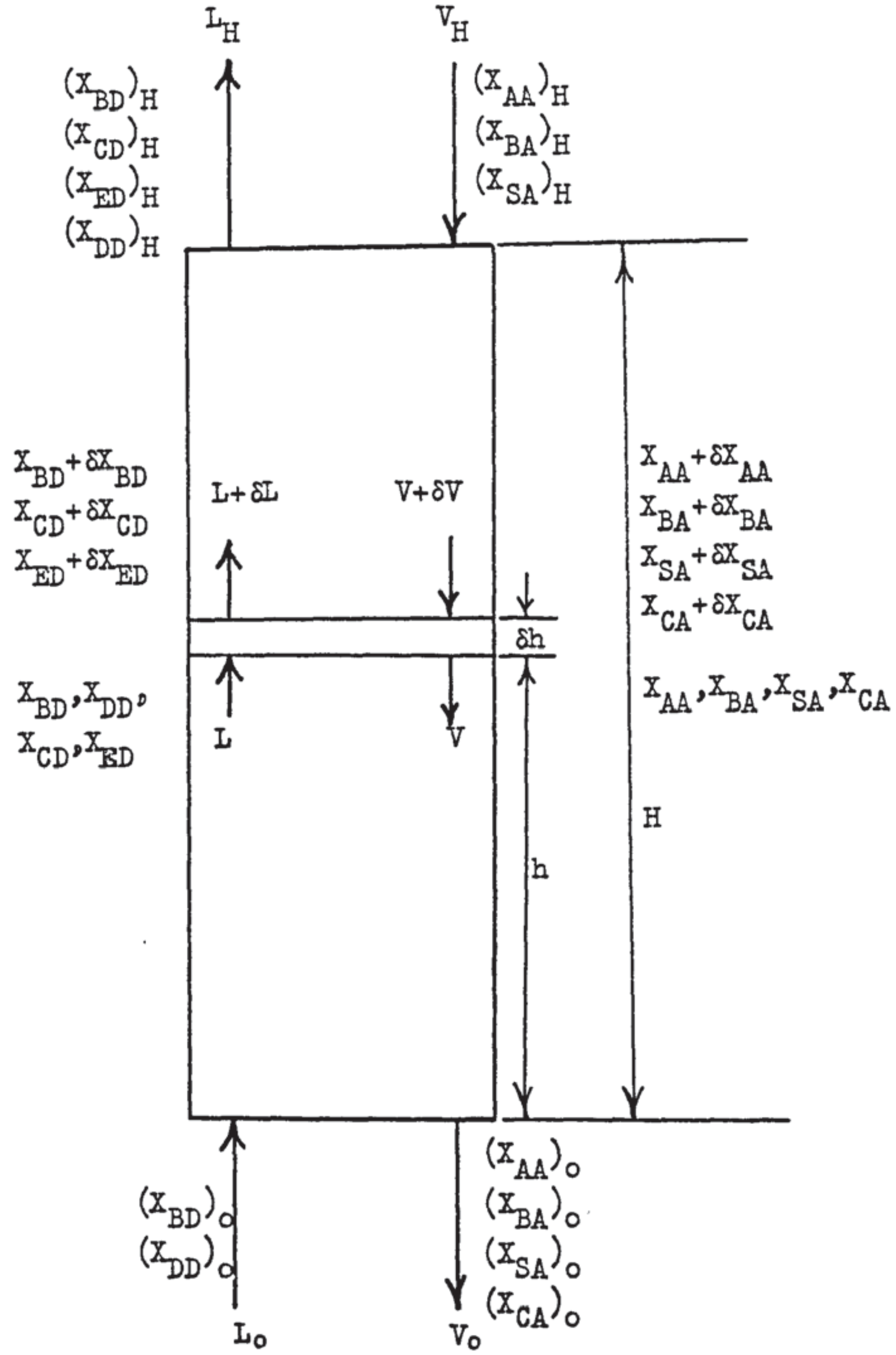


FIGURE 7.34 Continuously Operating Extraction-Reaction Column Under Steady State Conditions

shown in figure (7.34), the rate of ester formation is:

$$\frac{dE}{dh} = k_2\ S\rho_c\ \phi_c X_{BA} X_{CA}\ \frac{\delta h}{U_c} - k_2' S\rho_c X_{AA} X_{EA}\ \frac{\delta h}{U_c} \qquad (7.31)$$

where S is the cross sectional area of the column. ϕ_c is the fractional hold-up volume of the continuous phase. X_{EA} is the mole fraction of the ester assumed to be momentarily present in the aqueous phase causing the reverse reaction to occur. In a short column where conversion is not high, the quantity of the ester in the system is small and since most of this will be extracted into the extractive phase, hence the concentration of the ester remaining in the reactive phase will be very small. Thus the last term of equation (7.31) can be ignored and the equation is reduced to

$$\frac{dE}{dh} = k_2 S\rho_c \phi_c X_{BA} X_{CA}\ \frac{\delta h}{U_c} \qquad (7.32)$$

An ester balance over the element is:

$$(L)(X_{ED}) + (L)(X_{CD})/\nu + (V+\delta V)\left(X_{CA} + \frac{dX_{CA}}{dh}\ \delta h\right)\Big/\nu$$

$$= \left(X_{ED} + \frac{dX_{ED}}{dh}\ \delta h\right)\left(L+\delta L\right) + \left(X_{CD} \pm \frac{dX_{CD}}{dh}\right)\left(L+\delta L\right)\Big/\nu \qquad (7.33)$$

An equivalent ester balance between the element and the base of the column is:

$$(Lo)(X_{BD})_o/\nu + V(X_{EA})/\nu = (L)(X_{ED})+L(X_{CD})/\nu \qquad (7.34)$$

The relationships between water, acetic acid, butanol, n-heptane and ester entering and leaving the element is governed by the distribution equations developed in Section (7.3) i.e. equations (7.21) to (7.25). Equations (7.32) to (7.34) are sufficient for numerical integration starting from the bottom of the column provided the concentration of B and C i.e. $(X_{BA})_o$ and $(X_{CA})_o$ are known for the initiation of the integration. To do this a certain conversion from the bottom to the top of the column was assumed and values for $(X_{BA})_o$ and $(X_{CA})_o$

computed. Then the numerical integration was started. The ester produced was calculated on the basis of equation (7.32). Equilibrium was assumed inside each integration element i.e. local extractive/reactive phases equilibrium. Hence application of equations (7.21) to (7.25) determined fresh values of X_{BA} and X_{CA}. Conversion was calculated, after each integration step up the column, until the total height of the column was reached. Finally the conversion value attained at the top was compared with the value assumed for starting the iteration procedure. If convergence criteria were not met, the conversion value was incremented and the computation recycled to the beginning.

The general form of the computer program, used in calculating conversion in continuous countercurrent extraction reaction, is shown in figure (7.35). It consisted of a main program and four subroutines. The subroutines were similar to the corresponding subroutines developed for the batch extraction. The main program together with typical results is shown in Appendix (VIII).

7.5.3.2) Comparison of Computed and Experimental Conversion Values

Experimental and computed conversion values are tabulated in Appendix V. Figure (7.36) shows typical calculations of conversion up the column for the first four runs done with about 10% water and 3.8-9.9% catalyst. The figure shows how conversion is increased with increasing catalyst concentration and column height. Due to sampling difficulties it was not possible to measure conversion except at the top of the column i.e. after phase separation was complete. The experimental conversion values at the top of the column are also indicated in figure (7.36).

Good agreement was achieved between experimental

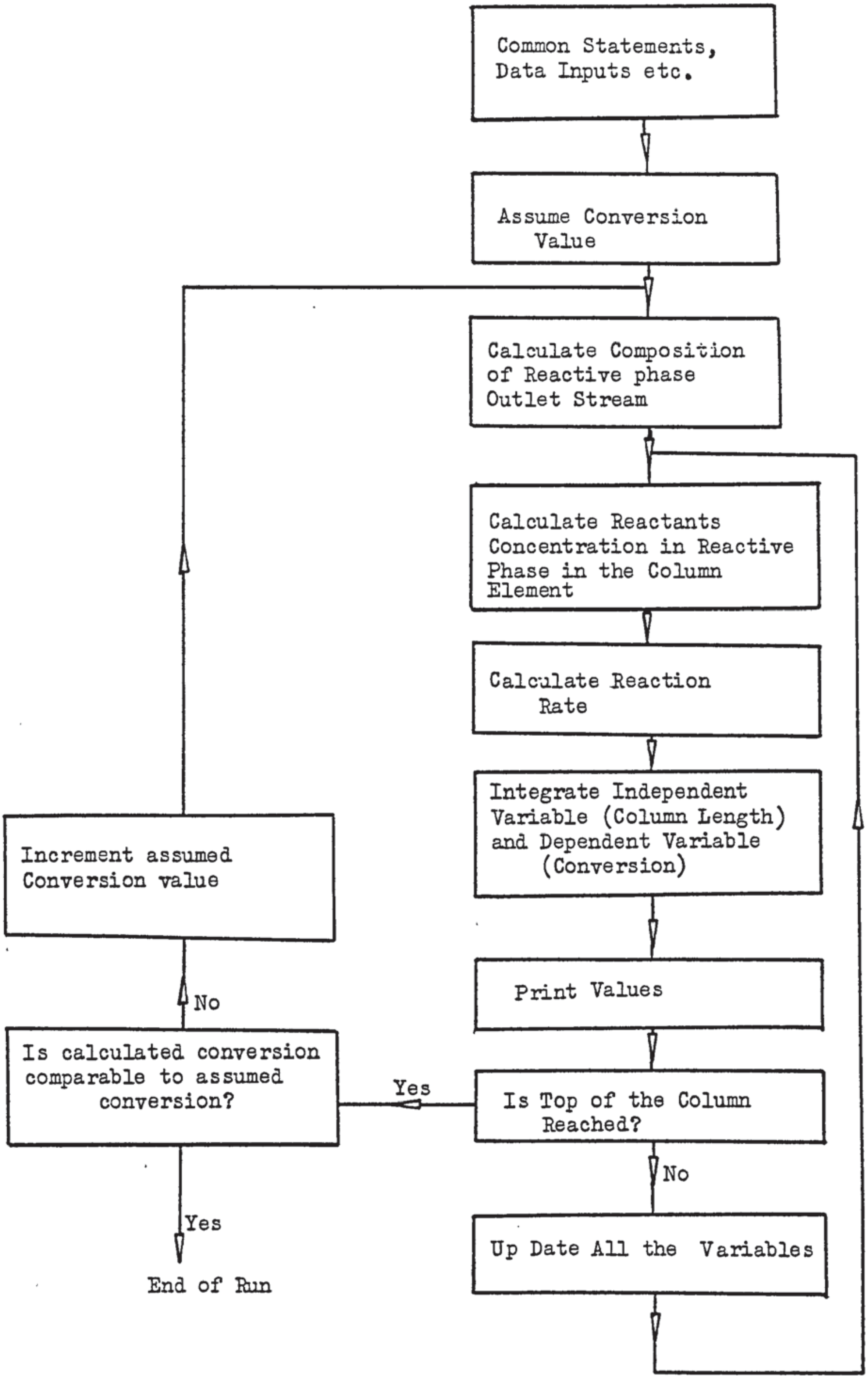


FIGURE 7.35 General Arrangement of Computer Program for Calculating Conversion in the R.D.C.

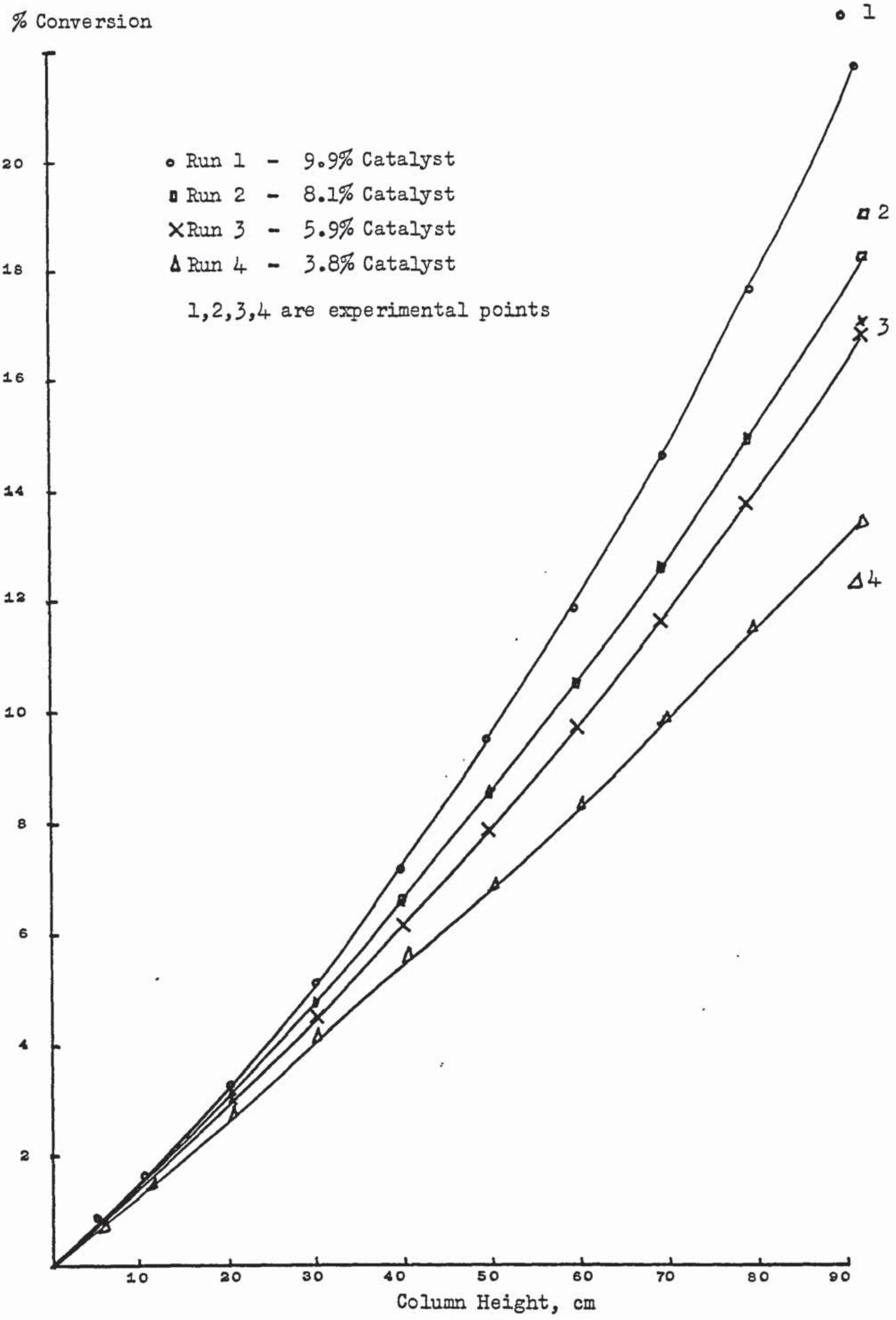


FIGURE 7.36 Esterification Reaction in the R.D.C.
Computed Conversion vs Column Height

conversion and values computed according to the procedure set out in (7.5.3.1) above. The maximum deviation for all runs was about 22% while the average was about 14%.

CHAPTER 8

CONCLUSIONS

The main conclusions arising from this work are as follows:

A) Esterification of n-Butyl Alcohol at Room Temperature.

n-Butyl alcohol can be esterified at room temperature using concentrated solutions of acetic acid, n-butyl alcohol and sulphuric acid catalyst. The reaction rate constant was found to be a function of catalyst concentration and the water concentration.

Computer predictions of conversion, on the basis of reaction rate constant correlation, were in excellent agreement with the experimental results.

B) Phase Equilibria in Multi-Component Liquid-Liquid Systems.

(1) Hand's formula (equation (2.27)) is a reliable method for correlating the concentration of a solute in the two conjugate solutions of a two-phase liquid-liquid system.

(2) Distribution of two solutes between two solvents i.e. in the single binary quaternary system can be correlated algebraically by a system of equations based on the difference between distribution ratios (i.e. salting effect) of the two solutes in the binary and quaternary cases.

(3) Distribution of one solute between one solvent in one phase and two "mixed" solvents in the other phase i.e. in the double binary quaternary system can be predicted by an equation similar to Raoult's Law. Binaries data only is needed for predicting the distribution in the quaternary.

B) contd.

(4) In certain cases it is possible to combine the two systems of equations for the single and double binary quaternary systems to correlate the distributions in five component systems.

C) Batch Esterification of n-Butanol in the presence of n-Heptane Solvent.

(1) n-heptane is a good solvent for the extractive reaction of butanol esterification. The reaction goes to completion through continuous extraction of the ester as it is formed.

(2) The mechanism of the extraction-reaction process can be modelled by assuming the reaction rate constant for the solvent free system applies to the reactive phase of the extraction-reaction system, computing the instantaneous concentrations of the reactants in this phase on the basis of the distribution equations developed in this study, allowing for slow mass transfer of the ester out of the reactive phase and applying the reverse reaction rate to the net quantity of the ester remaining in this phase.

D) Studies in the Rotating Disc Contactor.

(1) The hydrodynamic studies on the n-heptane/water system confirmed earlier observations with regard to hold-up and mean drop size variations with the column operating conditions that is the mean drop size increased with increasing dispersed flow rate but decreased with increasing rotor speed. However, the unique phase inversion phenomenon for the n-heptane/water system, where the "flooding" point was characterised by formation of a dense droplet layer of the hitherto continuous phase which continued to build-up until the whole column was filled with well packed polygonal

D) contd.

(1) contd.

shaped droplets, showed that flooding and phase inversion characteristics can be different from the conventional mechanism so far described in literature.

(2) Mass transfer with high solute fluxes can lead to considerable droplet deformation and formation of rivultes of the dispersed phase or double dispersions in certain systems like the n-heptane/butanol (dispersed) → water system.

(3) The interfacial gradients set up due to mass transfer in both directions can create a situation whereby part of a counter current column, operating under steady state conditions, is an O/W dispersion separated by a phase inversion band from the second part of W/O dispersion.

(4) The R.D.C. is a good contactor for carrying out extraction-reaction processes. The analysis of these processes can be done on the basis of the distribution equations and the reaction rate in the reactive phase.

CHAPTER 9.

RECOMMENDATIONS FOR FURTHER WORK.

(1) Study further extractive-reaction systems at room temperature as well as higher temperatures.

(2) Apply the algebraic equations developed in this study to other quaternary two phase liquid-liquid systems.

(3) The extraction-reaction runs done in the R.D.C. confirmed the suitability of this type of equipment for extractive-reactions. However, the conversion was rather low due to the short column employed. It is recommended that the extractive reaction performed in this study or similar ones be carried out in longer columns to arrive at more precise quantitative results for the effect of column length on conversion.

(4) The computer program developed for the prediction of conversion in batch extraction reaction showed how a model can be built up on the basis of reaction kinetics and distribution correlations. The effect of slow mass transfer needs further investigation to improve prediction accuracy.

(5) Carry out quantitative investigations of the phase inversion phenomena occurring due to "two-way" mass transfer.

APPENDIX (I)

ESTERIFICATION KINETICS AND BATCH EXTRACTION - REACTION RESULTS

Table I.1 : Esterification of Butanol at 20°C

Run No.1. Feed Composition
Acetic Acid 40.67%, Butanol 49.53%
H_2SO_4 9.8%

TIME Minutes	% Free Acetic Acid	% Conversion	k_2 L/(gmole)(Min)	Mean Water Conc. g.mole/L
1	36.65	9.88	0.0170	0.319
3	32.5	20.01	0.0129	0.646
6	28.7	29.43	0.0108	0.950
10	24.65	39.39	0.0101	1.272
15	21.85	46.27	0.0090	1.494
20	19.8	51.30	0.0083	1.656
30	17.05	58.08	0.0076	1.875
24 Hours	6.4	84.26	-	-

Run No.2 Feed Composition:
Acetic Acid 43.1%, Butanol 52.35%
H_2SO_4 4.55%

TIME Minutes	% Free Acetic Acid	% Conversion	k_2 L/(gmole)(Min)	Mean Water Conc. g.mole/L
1	41.3	4.18	0.0073	0.136
3	39.0	9.51	0.0058	0.309
6	36.15	16.13	0.0053	0.524
10	33.3	22.74	0.0049	0.739
15	30.8	28.54	0.0045	0.928
20	28.85	33.06	0.0041	1.074
30	25.92	39.86	0.0037	1.295
24 Hours	8.5	80.28	-	-

Table I.2 : Esterification of Butanol at 20 °C

Run No.3		Run No.4	
Feed Composition:		Feed Compositions:	
Acetic Acid	38.2%	Acetic Acid	36.0%
Butanol	46.95%	Butanol	44.3%
H_2SO_4	9.89%	H_2SO_4	9.66%
H_2O	4.96%	H_2O	10.04%

TIME MIN.	Exp.Conv. %	Computed Conv. %	Expt.Conv. %	Computed Conv.%
1	4.92	4.74	3.61	3.17
3	12.95	12.87	8.72	8.90
6	21.05	22.56	15.96	16.26
10	29.64	32.33	23.87	24.30
15	38.73	41.31	30.51	32.29
20	47.25	47.98	36.90	38.64
30	55.01	57.16	46.17	48.06
24 hrs.	76.04	-	75.1	-

Table I.3: Esterification Reaction Equilibrium Constant

RUN NO.	H_2SO_4 Wt.%	H_2O Wt.%	K
1	9.8	0.0	28.7
2	4.55	0.0	16.0
3	9.89	4.96	22.4
4	9.60	10.04	18.2

TABLE I.4: Batch extraction reaction results

Runs 1-4: Water 10%, n heptane 30%
Acetic acid and butanol in Stoichometric ratios

Run No.	% Catalyst
1	10.6
2	8.4
3	6.3
4	4.0

Runs 5 and 6: 10.6% Catalyst
10.0% Water
30.0% Heptane

Acid/Alcohol Mole ratio:

Run No.5: 2

Run No.6: 0.5

Note: A total of 400 grms reaction mixture was taken in each run

TIME MINS	% CONVERSION					
	RUN NO.					
	1	2	3	4	5	6
1	8.7	7.1	6.7	4.0	20.1	4.9
3	21.5	16.8	12.4	7.5	30.9	13.2
6	33.2	27.4	19.8	12.1	46.2	21.5
10	43.8	34.8	27.2	16.1	56.8	27.4
15	53.8	42.2	33.0	19.9	64.7	34.6
20	59.0	47.1	37.1	22.5	68.3	39.2
30	66.5	53.0	42.8	25.9	77.1	46.3
45	73.0	57.0	47.5	29.3	83.0	54.1
60	77.2	60.2	50.1	30.8	86.1	58.2

TABLE I.5: Batch extraction reaction results.

Runs 7-10: Water 20%, heptane 30%

Run No.	% Catalyst
7	10.5
8	8.4
9	6.3
10	4.1

Acetic acid and butanol
in Stiochometric ratios

Runs 11-14: Water 10%, heptane 20%

Run No.	% Catalyst
11	10.6
12	8.3
13	6.4
14	4.0

Acetic acid and butanol
in Stoichometric ratios

TIME MINS	% CONVERSION							
	RUN NO.							
	7	8	9	10	11	12	13	14
1	8.4	6.5	5.9	2.8	9.4	7.5	7.1	4.6
3	17.6	15.4	11.0	5.25	23.1	17.1	12.8	8.6
6	26.5	25.3	17.1	8.47	36.1	29.0	21.3	14.0
10	34.9	32.1	24.5	11.7	47.0	36.2	27.8	19.5
15	42.6	37.6	30.1	14.6	57.3	44.3	35.1	24.1
20	46.6	42.5	33.0	15.9	63.6	53.4	41.6	29.8
30	52.7	48.0	34.8	18.9	71.9	60.7	48.2	37.0
45	57.9	51.6	38.6	21.2	77.8	64.8	53.5	40.8
60	61.2	54.5	40.7	22.4	83.4	68.7	56.3	44.2

Note In all extraction reaction runs, conversion was approximately complete after 24 hours.

TABLE I.6

Distribution of Ester during the course of the Batch Extraction-Reaction

Results for Run 1 (10.6% Catalyst)

Time (Minutes)	E Formed Moles/Litre	$\delta E/\delta T$ M/(L)(Min)	E' M/L	$\delta E'/\delta T$ M/(L)(Min)	$K_G a$ L/Min
0-1	1.13	1.13	0.0	-	-
1-3	1.78	0.89	1.43	+0.355	0.374
3-6	1.70	0.567	2.14	-0.09	0.307
6-10	1.58	0.395	1.87	-0.105	0.267
10-15	1.47	0.294	1.45	-0.032	0.225
15-20	0.91	0.182	1.29	-0.054	0.183
20-30	1.19	0.119	1.02	-0.025	0.141
30-45	1.16	0.077	0.77	-0.011	0.114
45-60	0.86	0.057	0.61	-	-

TABLE I.7

Experimental and Theoretical Mass Transfer Coefficients
For Run 1 - Batch Extraction - Reaction with 10.6% Catalyst

$\left(K_G a\right)_{EXP}$ litres/Min	a cm^2/cm^3	$\left(K_G\right)_{EXP}$ cm/sec	k_c cm/sec	$\bar{k}_1 = \frac{1}{r_i}$ cm/sec	$\left(K_G\right)_{Theo}$ cm/sec
0.374	146	0.0427	0.060	0.0894	0.0358
0.307	131	0.0390	0.057	0.0784	0.0330
0.267	120	0.0370	0.055	0.0761	0.0321
0.225	108	0.0347	0.053	0.0753	0.0311
0.183	103	0.0296	0.052	0.0720	0.0302
0.141	98	0.0240	0.051	0.0651	0.0286
0.114	93	0.0204	0.050	0.0573	0.0267

APPENDIX II

Data Pertaining to Solubility for two phase Multicomponent Systems.

TABLE II.1 Saturation Composition of Ternary Systems at 20°C Wt.%

Water	Acetic Acid	n-Heptane
99.97	-	0.63
0.03	-	99.97
89.5	10.4	0.1
28.3	71.5	0.2
27.5	72.0	0.5
15.9	83.8	0.3
11.2	88.6	0.2
7.1	92.7	0.2
0.6	60.2	39.2
0.9	69.1	30.0
1.3	81.1	17.6
1.7	84.5	13.8
2.1	86.2	11.7
4.3	89.2	6.5

Water	n-Butyl Alcohol	n-Heptane
92.3	7.7	-
20.0	80.0	-
93.9	6.1	0.1 >
0.4	11.6	88.0
2.8	38.6	58.6
4.8	51.6	43.6
6.8	60.0	33.2
8.1	64.9	27.0
9.8	70.4	19.8
11.1	73.5	15.4
12.5	74.8	12.7

Water	Acetic Acid	n-Butyl Acetate
99.0	-	1.0
1.37	-	98.63
35.2	40.6	24.1
31.6	40.0	28.4
28.7	39.1	32.2
25.9	38.1	36.0
23.5	37.1	39.4
20.5	35.2	44.3
17.6	33.3	49.1
14.5	30.5	55.0
87.2	11.8	1.0
79.7	18.9	1.4
73.5	24.9	1.7

TABLE II.2 Saturation Composition of Ternary Systems
At 20°C WT %

Water	n-Butyl Alcohol	n-Butyl Acetate	Water	n-Butyl Acetate	n-Heptane
2.0	8.3	89.7	99.0	1.0	-
3.8	18.0	78.2	1.37	98.63	-
6.2	29.6	64.2	1.0	94.5	4.5
9.4	43.4	47.2	0.7	87.2	12.1
11.2	51.5	37.3	0.5	65.5	33.5
13.3	58.5	28.2	0.2	52.5	47.3
15.3	64.4	20.3	0.1>	40.0	6.0

Table II.3 Solubility Data For The System
Water - Acetic Acid - n Heptane
at 20^{o}C.

AQUEOUS PHASE COMPOSITION WT. % BASIS			ORGANIC PHASE COMPOSITION WT. % BASIS			x_{BA}	x_{AA}	x_{BD}	x_{DD}	$\frac{x_{BA}}{x_{AA}}$	$\frac{x_{BD}}{x_{DD}}$
ACID	WATER	HEPTANE	ACID	WATER	HEPTANE						
78.1	21.9	0.1>	5.93	0.1>	94.07	1.3006	1.2167	0.0988	0.9387	1.069	0.105
77.7	22.3	0.1>	5.66	0.1>	94.34	1.2940	1.2389	0.0943	0.9414	1.044	0.100
70.0	30.0	0.1>	3.80	0.1>	96.20	1.1657	1.6667	0.0633	0.9600	0.699	0.066
62.6	37.4	0.1>	2.74	0.1>	97.26	1.0425	2.0778	0.0456	0.9706	0.502	0.047
55.4	44.6	0.1>	1.95	0.1>	98.05	0.9226	2.4778	0.0325	0.9784	0.372	0.033
42.6	57.4	0.1>	1.16	0.1>	98.84	0.7094	3.1889	0.0193	0.9863	0.222	0.0196
29.3	70.7	0.1>	0.57	0.1>	99.43	0.4879	3.9278	0.0095	0.9922	0.124	0.0096
23.2	76.8	0.1>	0.39	0.1>	99.61	0.3863	4.2667	0.0065	0.9940	0.091	0.0065
21.5	78.5	0.1>	0.35	0.1>	99.65	0.3580	4.3611	0.0058	0.9944	0.082	0.0058

Table II.4 Solubility Data For The System
Water - n-Butyl Alcohol - n-Heptane
at 20°C

AQUEOUS PHASE COMPOSITION WT. % BASIS			ORGANIC PHASE COMPOSITION WT. % BASIS			x_{CA}	x_{AA}	x_{CD}	x_{DD}	$\frac{x_{CA}}{x_{AA}}$	$\frac{x_{CD}}{x_{DD}}$
ALCOHOL	WATER	HEPTANE	ALCOHOL	WATER	HEPTANE						
6.9	93.1	0.1>	45.1	3.2	51.7	0.0931	5.1722	0.6085	0.5159	0.0180	1.1795
6.8	93.2	0.1>	36.0	2.5	61.5	0.0917	5.1788	0.4857	0.6137	0.0177	0.7914
6.6	93.4	0.1>	25.5	2.0	72.5	0.0890	5.1889	0.3440	0.7235	0.0171	0.4755
6.3	93.7	0.1>	14.6	1.1	84.3	0.0850	5.2056	0.1970	0.8422	0.0163	0.2339
5.9	94.1	0.1>	9.8	0.7	89.5	0.0796	5.2278	0.1322	0.8901	0.0152	0.1485
5.8	94.2	0.1>	5.6	0.4	94.0	0.0783	5.2333	0.0756	0.9380	0.0150	0.0806
5.25	94.75	0.1>	4.0	0.3	95.7	0.0708	5.2639	0.0540	0.9560	0.0134	0.0565
4.0	96.0	0.1>	0.6	0.1>	99.4	0.0540	5.3333	0.0081	0.9919	0.0101	0.0082
3.0	97.0	0.1>	0.4	0.1>	99.6	0.0405	5.3889	0.0054	0.9939	0.0075	0.0054
2.2	97.8	0.1>	0.25	0.1>	99.75	0.0297	5.4333	0.0034	0.9954	0.0055	0.0034

Table II.5 Solubility Data For The System Water - Acetic Acid - n Butyl Acetate at 20^{o}C.

AQUEOUS PHASE COMPOSITION WT. % BASIS			ORGANIC PHASE COMPOSITION WT. % BASIS			x_{BA}	x_{AA}	x_{BE}	x_{EE}	$\frac{x_{BA}}{x_{AA}}$	$\frac{x_{BE}}{x_{EE}}$
ACID	WATER	ESTER	ACID	WATER	ESTER						
4.8	94.2	1.0	1.8	1.5	96.7	0.0800	5.2333	0.0300	0.8336	0.015	0.036
13.1	85.1	1.8	6.4	2.1	91.5	0.2182	4.7278	0.1066	0.7888	0.046	0.135
20.1	78.0	1.9	11.0	3.2	85.8	0.3347	4.333	0.1832	0.7397	0.077	0.248
24.7	73.2	2.1	14.9	4.6	80.5	0.4113	4.0667	0.2481	0.6940	0.101	0.357
30.4	65.1	4.5	19.9	6.8	73.3	0.5062	3.6167	0.3314	0.6319	0.140	0.524
34.6	57.9	7.5	24.0	9.0	67.0	0.5762	3.2167	0.4000	0.5776	0.179	0.693
38.4	49.1	12.5	28.2	12.0	59.8	0.6395	2.728	0.4696	0.5155	0.234	0.911

Table II.6 Solubility Data For The System Water - n Butyl Alcohol - n Butyl Acetate at 20°C.

AQUEOUS PHASE COMPOSITION WT. % BASIS			ORGANIC PHASE COMPOSITION WT. % BASIS			x_{CA}	x_{AA}	x_{CE}	x_{EE}	$\frac{x_{CA}}{x_{AA}}$	$\frac{x_{CE}}{x_{EE}}$
ALCOHOL	WATER	ESTER	ALCOHOL	WATER	ESTER						
1.75	98.25	0.1>	10.3	2.1	87.6	0.0236	5.4583	0.1390	0.7552	0.0043	0.184
2.8	97.2	0.1>	16.0	3.2	80.8	0.0378	5.4000	0.2159	0.6966	0.0070	0.310
4.1	95.9	0.1>	24.2	5.0	70.8	0.0553	5.3278	0.3265	0.6103	0.0104	0.535
5.1	94.9	0.1>	30.5	6.2	63.3	0.0688	5.2722	0.4115	0.5457	0.0130	0.754
6.05	93.95	0.1>	37.8	7.8	54.4	0.0816	5.2194	0.5100	0.4690	0.0156	1.087
6.4	93.6	0.1>	40.7	8.2	51.1	0.0863	5.2000	0.5491	0.4405	0.0166	1.247
6.7	93.3	0.1>	45.8	9.1	45.1	0.0904	5.1833	0.6180	0.3888	0.0174	1.590

Table II.7 Solubility Data For The System
Water - Acetic Acid - n Butyl Alcohol - n Heptane
at 20°C

AQUEOUS PHASE COMPOSITION WT. %				ORGANIC PHASE COMPOSITION WT. %			
WATER	ACID	ALCOHOL	HEPTANE	WATER	ACID	ALCOHOL	HEPTANE
79.4	9.3	11.3	0.1>	5.3	7.1	39.3	48.3
59.2	23.1	17.2	0.5	6.1	10.4	30.8	52.6
45.2	29.9	20.5	4.4	1.2	15.3	28.3	55.2
83.2	8.6	8.2	0.1>	6.8	1.5	9.6	82.1
75.5	5.4	9.1	0.1>	6.9	2.3	6.9	83.9
68.7	21.4	9.9	0.1>	7.0	2.25	3.3	87.45
73.4	12.8	13.8	0.1>	5.1	7.4	31.4	56.1
65.2	18.3	16.5	0.1>	5.5	9.9	25.2	59.4

continued/

Table II.7 continued.

R1= $\frac{X_{BA}/X_{AA}}{X_{BD}/X_{DD}}$	R2= $\frac{X_{CA}/X_{AA}}{X_{CD}/X_{DD}}$	$\frac{X_{BA}}{X_{AA}}+\frac{X_{BD}}{X_{DD}}$	$\frac{X_{CA}}{X_{AA}}+\frac{X_{CD}}{X_{DD}}$	R3= $\frac{x_{BA}/x_{AA}}{x_{BD}/x_{DD}}$	R4= $\frac{x_{CA}/x_{AA}}{x_{CD}/x_{DD}}$	R3-R1	R2-R4
0.142	0.031	0.281	1.131	15.67	0.018	15.53	0.013
0.355	0.089	0.447	0.863	12.46	0.020	12.10	0.069
0.428	0.159	0.661	0.803	11.76	0.020	11.33	0.139
1.069	0.160	0.060	0.174	15.21	0.098	14.14	0.062
1.419	0.276	0.104	0.134	13.68	0.082	12.26	0.194
2.172	0.686	0.136	0.086	13.64	0.102	11.47	0.584
0.236	0.061	0.272	0.803	14.1	0.031	13.86	0.030
0.302	0.106	0.362	0.635	12.86	0.024	12.56	0.082

Table II.8 Solubility Data For The System
Water - Acetic Acid - n Butyl
Alcohol - n Butyl Acetate.

AQUEOUS PHASE COMPOSITION WT. % BASIS				ORGANIC PHASE COMPOSITION WT. % BASIS			
WATER	ACID	ALCOHOL	ESTER	WATER	ACID	ALCOHOL	ESTER
90.6	7.5	1.9	0.1>	3.1	5.6	11.0	80.3
86.2	7.3	5.9	0.6	12.9	9.7	36.2	41.2
79.7	15.9	3.1	1.3	8.6	13.8	15.2	62.4
63.4	31.6	3.3	1.7	20.6	29.2	11.8	38.4
80.2	13.4	5.8	0.6	18.5	12.5	26.9	42.1
86.6	12.3	1.1	0.1>	3.2	9.8	5.0	82.0

continued/

Table II.8 continued.

R1= $\frac{X_{BA}/X_{AA}}{X_{BE}/X_{EE}}$	R2= $\frac{X_{CA}/X_{AA}}{X_{CE}/X_{EE}}$	$\frac{X_{BA}}{X_{AA}}+\frac{X_{BE}}{X_{EE}}$	$\frac{X_{CA}}{X_{AA}}+\frac{X_{CE}}{X_{EE}}$	R3= $\frac{x_{BA}/x_{AA}}{x_{BE}/x_{EE}}$	R4= $\frac{x_{CA}/x_{AA}}{x_{CE}/x_{EE}}$	R3-R1	R2-R4
0.1840	0.0237	0.1596	0.2195	0.3607	0.0226	0.1767	0.0011
0.0558	0.0120	0.4806	1.3916	0.3196	0.0116	0.2638	0.0004
0.1396	0.02476	0.4872	0.3906	0.3070	0.0209	0.1674	0.0038
0.1017	0.0262	1.6196	0.4935	0.2630	0.0169	0.1613	0.0093
0.0874	0.0174	0.6242	1.0191	0.2844	0.0129	0.1970	0.0450
0.1986	0.0327	0.2571	0.0979	0.3305	0.0259	0.1319	0.0068

TABLE II.7a. Solubility Data for the Water-Acetic Acid Butanol-n Heptane System at 20°C

x_{BA}/x_{AA} Experi-mental	x_{BA}/x_{AA} Calcu-lated	Deviation %	x_{CA}/x_{AA} Experi-mental	x_{CA}/x_{AA} Calcu-lated	Deviation %
0.035	0.040	14.3	0.034	0.027	17.6
0.117	0.097	17.1	0.071	0.069	5.6
0.198	0.188	5.0	0.110	0.113	2.6
0.031	0.027	12.9	0.024	0.019	20.8
0.061	0.055	10.9	0.029	0.028	3.4
0.093	0.087	6.4	0.035	0.036	2.8
0.052	0.048	7.7	0.046	0.035	23.9
0.084	0.078	7.1	0.061	0.053	13.1

TABLE II.8a. Solubility Data for the System Water-Acetic Acid-n Butyl Alcohol-n Butyl Acetate

X_{BA}/X_{AA} Experi-mental	X_{BA}/X_{AA} Calcu-lated	Deviation %	X_{CA}/X_{AA} Experi-mental	X_{CA}/X_{AA} Calcu-lated	Deviation %
0.025	0.024	4	0.0051	0.005	2
0.025	0.028	12	0.017	0.017	0
0.060	0.055	8.3	0.009	0.008	1.1
0.150	0.132	12.0	0.013	0.009	3.1
0.050	0.045	10	0.017	0.014	17.6
0.043	0.043	0	0.003	0.003	0

TABLE II.9 Solubility Data for the Quaternary System, Water-Acetic Acid-n Heptan-n Butyl Acetate at 20°C

Aqueous Phase Composition Wt % Basis				Organic Phase Composition Wt % Basis				$\left(\frac{X_{BA}}{X_{AA}}\right)_{EXP}$	$\left(\frac{X_{BA}}{X_{AA}}\right)_{FOR}$	% DEVIATION
Water	Acid	Heptane	Ester	Water	Acid	Heptane	Ester			
76.5	22.6	0.1>	0.9	0.5	3.5	46.7	49.3	0.089	0.083	7.2
58.3	41.5	0.1>	0.2	0.4	3.1	76.2	20.3	0.214	0.206	3.9
60.5	39.0	0.1>	0.5	1.0	6.7	50.9	41.7	0.193	0.188	2.6
77.4	22.0	0.1>	0.6	0.6	5.8	33.1	62.4	0.085	0.080	6.2

TABLE II.10 Solubility Data for the Quaternary System Water-n Butyl Alcohol-n Heptane-n Butyl Acetate at 20°C

Aqueous Phase Composition Wt % Basis				Ogranic Phase Composition Wt % Basis				$\left(\frac{X_{CA}}{X_{AA}}\right)_{EXP}$	$\left(\frac{X_{CA}}{X_{AA}}\right)_{FOR}$	% DEVIATION
Water	Alcohol	Heptane	Ester	Water	Alcohol	Heptane	Ester			
94.95	5.05	0.1>	0.1>	2.0	20.4	46.0	31.6	0.0129	0.0138	7.0
94.5	5.5	0.1>	0.1>	1.2	24.5	44.0	30.3	0.0141	0.0135	4.4
92.7	7.3	0.1>	0.1>	1.6	34.6	44.6	19.2	0.0191	0.0174	9.8
94.1	5.9	0.1>	1.1>	1.7	40.5	20.2	37.5	0.0152	0.0165	8.5

Table II.11 Distribution of Acetic Acid and Butanol in a 5 Component System.

HEAVY PHASE COMPOSITION WT. % BASIS					LIGHT PHASE COMPOSITION WT. % BASIS				
ACETIC ACID	BUTANOL	WATER	HEPTANE	ESTER	ACETIC ACID	BUTANOL	WATER	HEPTANE	ESTER
30.8	21.1	45.4	2.2	0.5	19.7	28.6	2.6	35.6	13.5
20.8	8.4	70.8	0.1>	0.1>	9.2	15.0	3.9	36.0	35.9
20.5	15.6	61.5	1.0	1.4	16.0	21.1	1.9	37.2	23.8

continued/

Table (II.11) continued.

ACETIC ACID IN HEAVY PHASE			BUTANOL IN HEAVY PHASE		
X_{BA}/X_{AA} EXP	X_{BA}/X_{AA} CALC	% DEV	X_{CA}/X_{AA} EXP	X_{CA}/X_{AA} CAL	% DEV
0.203	0.185	8.9	0.113	0.097	14.1
0.088	0.081	8.0	0.029	0.032	10.3
0.100	0.112	12.0	0.062	0.057	8.1

TABLE II.12 Solubility Data for the Water-Acetic Acid-Chloroform System(109)

Aqueous Phase Composition Wt. % Basis			Organic Phase Composition Wt. % Basis			$\frac{x_{BA}}{x_{AA}}$	$\frac{x_{BJ}}{x_{JJ}}$	$\left(\frac{x_{BA}}{x_{AA}}\right)_{FOR}$	Dev %
Water	Acid	Chloroform	Water	Acetic Acid	Chloroform				
81.5	17.4	1.1	0.9	4.1	95.0	0.0640	0.0858	0.0632	1.2
63.3	34.1	2.6	1.4	10.8	87.8	0.1615	0.2445	0.1644	1.8
48.5	44.5	7.0	2.1	17.9	80.0	0.2750	0.4448	0.2840	3.3
38.1	49.5	12.4	3.0	22.6	74.4	0.3894	0.6039	0.375	3.7

TABLE II.13 Solubility Data for the Ternary System Water-Acetone-Chloroform(109)

Aqueous Phase Composition Wt. % Basis			Organic Phase Composition Wt. % Basis			$\frac{x_{IA}}{x_{AA}}$	$\frac{x_{IJ}}{x_{JJ}}$	$\left(\frac{x_{IA}}{x_{AA}}\right)_{FOR}$	Dev %
Water	Acetone	Chloroform	Water	Acetone	Chloroform				
96.0	3.0	1.0	1.0	9.0	90.0	0.0097	0.2055	0.0083	14.4
90.5	8.3	1.2	1.3	23.7	75.0	0.0284	0.6495	0.0328	15.5
85.0	13.5	1.5	1.6	32.0	66.4	0.0492	0.9906	0.054	9.8
81.0	17.4	1.6	2.0	38.0	60.0	0.0666	1.3018	0.075	12.7
76.1	22.1	1.8	2.5	42.5	55.0	0.0900	1.5883	0.0955	6.1
73.0	25.5	1.5	2.4	42.6	55.0	0.1082	1.5920	0.0958	11.5
66.0	31.9	2.1	4.5	50.5	45.0	0.1498	2.3067	0.149	0.5
51.0	44.5	4.5	8.0	57.0	35.0	0.2704	3.3474	0.233	13.8

Table II.14 Solubility Data For The Quaternary System
Water - Acetic Acid - Acetone - Chloroform
(Brancker, Hunter and Nash's Data)

AQUEOUS PHASE COMPOSITION WT. % BASIS				ORGANIC PHASE COMPOSITION WT. % BASIS			
WATER	ACID	ACETONE	CHLOROFORM	WATER	ACID	ACETONE	CHLOROFORM
71.7	15.3	11.2	1.8	1.6	3.3	31.6	63.5
57.1	29.9	9.3	3.7	3.3	8.7	29.2	58.8
41.2	38.2	10.8	9.8	6.2	16.2	25.8	51.8
28.3	39.0	13.6	19.1	10.6	24.1	22.8	42.5
59.5	32.8	4.6	3.1	1.8	9.6	11.8	76.8
57.4	31.6	7.5	3.5	2.8	9.6	20.3	67.3
54.8	30.4	10.9	3.9	4.0	9.2	28.9	57.8
51.4	28.8	15.4	4.4	6.3	9.6	36.8	47.3
44.5	24.2	24.4	6.9	13.7	11.2	44.3	30.8

continued/

Table II.14 continued.

R1= $\frac{X_{BA}/X_{AA}}{X_{BJ}/X_{JJ}}$	R2= $\frac{X_{IA}/X_{AA}}{X_{IJ}/X_{JJ}}$	$\frac{X_{BA}}{X_{AA}}+\frac{X_{BJ}}{X_{JJ}}$	$\frac{X_{IA}}{X_{AA}}+\frac{X_{BJ}}{X_{JJ}}$	R3= $\frac{x_{BA}/x_{AA}}{x_{BJ}/x_{JJ}}$	R4= $\frac{x_{IA}/x_{AA}}{x_{IJ}/x_{JJ}}$	R3-R1	R2-R4
0.621	0.047	0.167	1.071	0.744	0.055	0.123	-0.008
0.534	0.049	0.451	1.071	0.680	0.055	0.146	-0.006
0.447	0.079	0.900	1.105	0.644	0.055	0.197	0.024
0.366	0.135	1.540	1.252	0.626	0.055	0.260	0.080
0.665	0.076	0.413	0.340	0.675	0.045	0.010	0.031
0.581	0.065	0.449	0.660	0.672	0.050	0.091	0.015
0.523	0.060	0.482	1.088	0.673	0.055	0.150	0.005
0.417	0.223	0.571	1.692	0.676	0.059	0.259	0.164
0.225	0.756	0.886	3.126	0.680	0.064	0.455	0.692

TABLE II.14a
Solubility Data for the Water-Acetic Acid-Acetone-Chloroform System(109)

$\left(\frac{X_{BA}}{X_{AA}}\right)_{EXP}$	$\left(\frac{X_{BA}}{X_{AA}}\right)_{FOR}$	DEV %	$\left(\frac{X_{IA}}{X_{AA}}\right)_{EXP}$	$\left(\frac{X_{IA}}{X_{AA}}\right)_{FOR}$	DEV %
0.064	0.064	0	0.048	0.064	33.3
0.157	0.149	5.1	0.050	0.070	40
0.278	0.247	11.1	0.081	0.083	2.5
0.413	0.332	19.6	0.149	0.086	42.3
0.165	0.153	7.3	0.024	0.017	29.2
0.165	0.161	2.4	0.040	0.040	0
0.166	0.154	7.2	0.062	0.075	21.0
0.168	0.148	11.9	0.093	0.127	36.5
0.163	0.139	14.7	0.170	0.238	40

TABLE II.15 Solubility Data for the Benzene-Acetic Acid-Water System(110)

Aqueous Phase Composition Wt.% Basis			Organic Phase Composition Wt.% Basis			$\frac{x_{BA}}{x_{AA}}$	$\frac{x_{BF}}{x_{FF}}$
Benzene	Acetic Acid	Water	Benzene	Acetic Acid	Water		
0.57	25.56	73.87	97.22	2.66	0.12	0.1037	0.0355
0.57	25.62	73.81	97.20	2.68	0.12	0.1040	0.0358
0.98	36.49	62.58	94.84	4.99	0.17	0.1748	0.0683
1.04	38.31	60.65	94.20	5.61	0.19	0.1893	0.0774
10.00	65.35	24.65	74.77	24.05	1.18	0.7947	0.4178
11.24	65.73	23.03	72.67	25.95	1.38	0.8555	0.4638

TABLE II.16 Solubility Data for the System Carbon Tetrachloride-Acetic Acid-Water (Prince's Data)

AQUEOUS PHASE COMPOSITION Wt. % Basis			ORGANIC PHASE COMPOSITION Wt. % Basis			$\frac{x_{BA}}{x_{AA}}$	$\frac{x_{BG}}{x_{GG}}$
CCl_4	Acetic Acid	Water	CCl_4	Acetic Acid	Water		
0.30	15.12	84.58	99.62	0.36	0.02	0.0536	0.0092
0.51	26.97	72.52	99.02	0.96	0.02	0.1115	0.0248
1.07	40.91	58.02	97.93	2.04	0.03	0.2114	0.0553
1.80	48.02	50.18	97.02	2.94	0.04	0.2868	0.0776
3.24	56.22	40.54	95.44	4.49	0.07	0.4157	0.1205
5.60	62.53	31.87	93.14	6.76	0.10	0.5881	0.1859
9.50	66.39	24.11	89.90	9.92	0.18	0.8254	0.2826
12.77	67.27	19.96	87.21	12.54	0.25	0.9351	0.3683
17.41	66.70	15.89	83.32	16.26	0.42	1.2582	0.4998

TABLE II.17 Solubility Data for the Benzene-Carbon Tetrachloride-Acetic Acid-Water System(110)

INITIAL MIXTURE MOLES				ACID CONCENTRATION IN AQUEOUS PHASE		%
Benzene	CCl_4	Acetic Acid	Water	$\left(\frac{x_{BA}}{x_{AA}}\right)$ EXP	$\left(\frac{x_{BA}}{x_{AA}}\right)$ FOR	DEVIATION
0.922	0.156	0.723	3.367	0.191	0.194	1.5
0.834	0.143	1.512	1.230	0.947	0.860	9.2
0.945	0.159	0.475	4.078	0.107	0.108	1>
0.925	0.155	0.727	3.348	0.194	0.196	1
0.850	0.142	1.441	1.412	0.801	0.755	5.7
0.632	0.320	0.466	4.080	0.107	0.108	1>
0.622	0.316	0.712	3.390	0.195	0.196	1>
0.607	0.306	1.068	2.300	0.404	0.416	3
0.580	0.302	1.388	1.386	0.809	0.791	2.2
0.573	0.300	1.483	1.111	1.044	0.930	1
0.633	0.320	0.471	4.064	0.108	0.110	2
0.623	0.315	0.719	3.323	0.197	0.202	2.5
0.587	0.298	1.396	1.369	0.820	0.797	2.8
0.580	0.295	1.500	1.071	1.089	0.954	1.4
0.318	0.481	0.534	3.841	0.131	0.135	3
0.316	0.477	0.709	3.303	0.200	0.207	3.5
0.310	0.469	1.055	2.234	0.422	0.446	5.7
0.302	0.467	1.347	1.319	0.848	0.880	3.8
0.299	0.469	1.431	1.031	1.111	0.991	1.2
0.319	0.482	0.474	4.028	0.112	0.115	2.7
0.316	0.478	0.717	3.279	0.203	0.211	3.9
0.307	0.464	1.366	1.259	0.895	0.899	1>
0.313	0.461	1.442	1.002	1.146	1.000	14.6

TABLE II.18 Distribution of Sulphuric Acid in Water-butanol-n heptane System

Aqueous Phase Composition Wt. %				Organic Phase Composition Wt.%			
Water	Acid	Alcohol	Heptane	Water	Acid	Alcohol	Heptane
85.5	8.0	6.5	-	0.25	0.15	20.5	79.1
75.7	18.2	6.1	-	0.35	0.7	20.2	78.75
86.2	7.0	6.8	-	1.9	0.35	47.0	50.75
74.8	18.5	6.7	-	2.3	3.0	47.5	47.2

APPLICATIONS OF QUATERNARIES SYSTEMS MATHEMATICAL MODELS TO OTHER WORKERS DATA.

The mathematical models developed in sections (7.3.2.1) and (7.3.2.2) for single and double binaries quaternaries were applied to data published by other workers. The following results were obtained.

(A) Single binary quaternary:

The data of Brancker,Hunter and Nash(109) for the water-acetic acid-acetone-chloroform system were tested in the manner described in section (7.3.2.1):

(i) The two ternaries: The experimental results for the two ternaries systems viz the water-acetic acid-chloroform and water-acetone-chloroform are shown in tables (II.12) and (II.13) respectively. Figures (II.1-II.4) show the plots of the concentration variables, according to Hand's formula, on double logarithmic and linear coordinates. Regression analysis led to the following correlations:

For the water-acetic acid-chloroform ternary,

$$\frac{x_{BA}}{x_{AA}} = 0.595 \left(\frac{x_{BJ}}{x_{JJ}}\right)^{0.913} \qquad (1)$$

For the water-acetone-chloroform ternary,

$$\frac{x_{IA}}{x_{AA}} = 0.055 \left(\frac{x_{IJ}}{x_{JJ}}\right)^{1.194} \qquad (2)$$

From the above correlations, the values of $\frac{x_{BA}}{x_{AA}}$ and $\frac{x_{IA}}{x_{AA}}$ were calculated to test the deviation between experimental and calculated results. These are also shown in tables (II.12) and (II.13).

(ii) The Quaternary System.

The water-acetic acid-acetone-chloroform

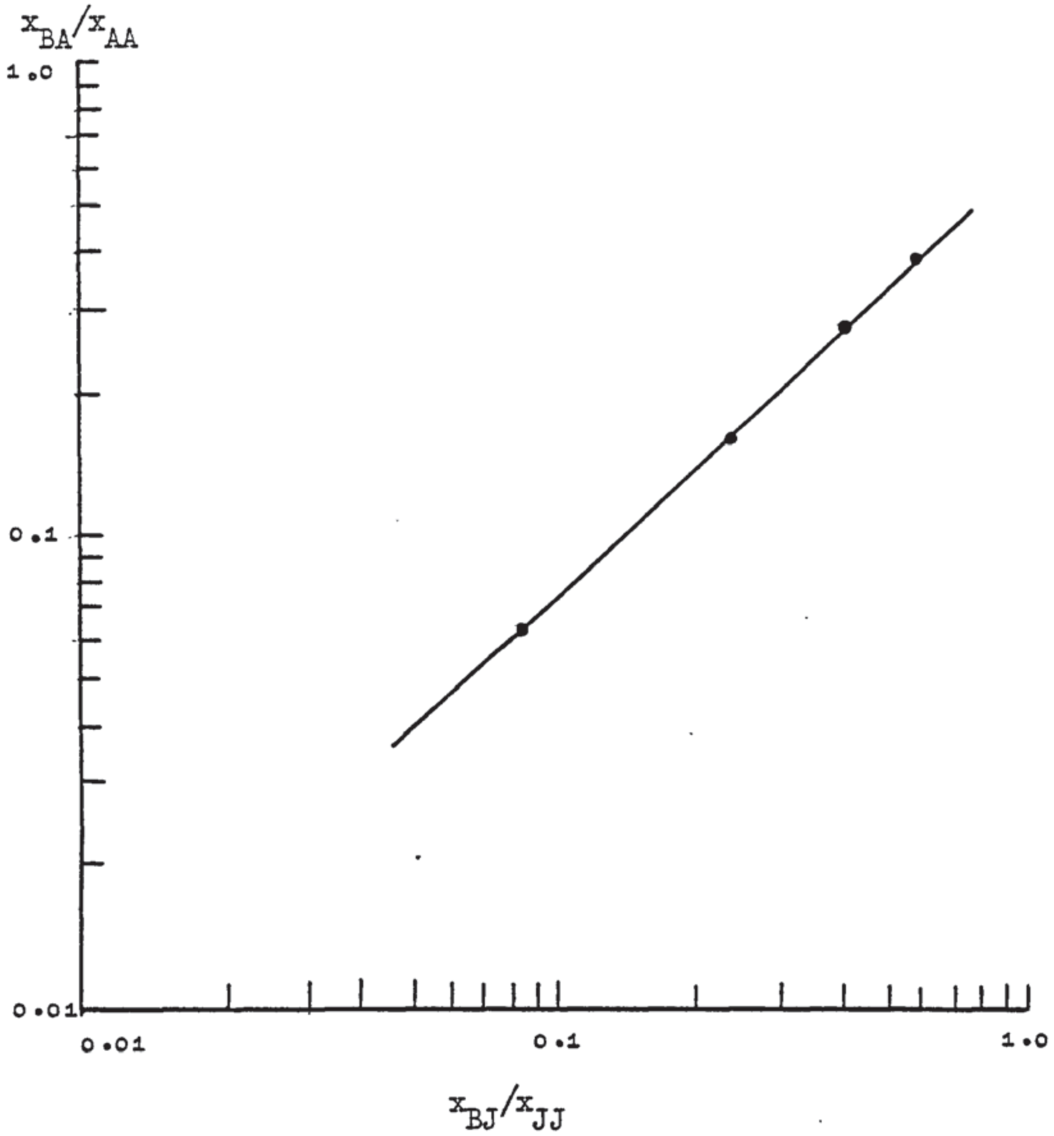
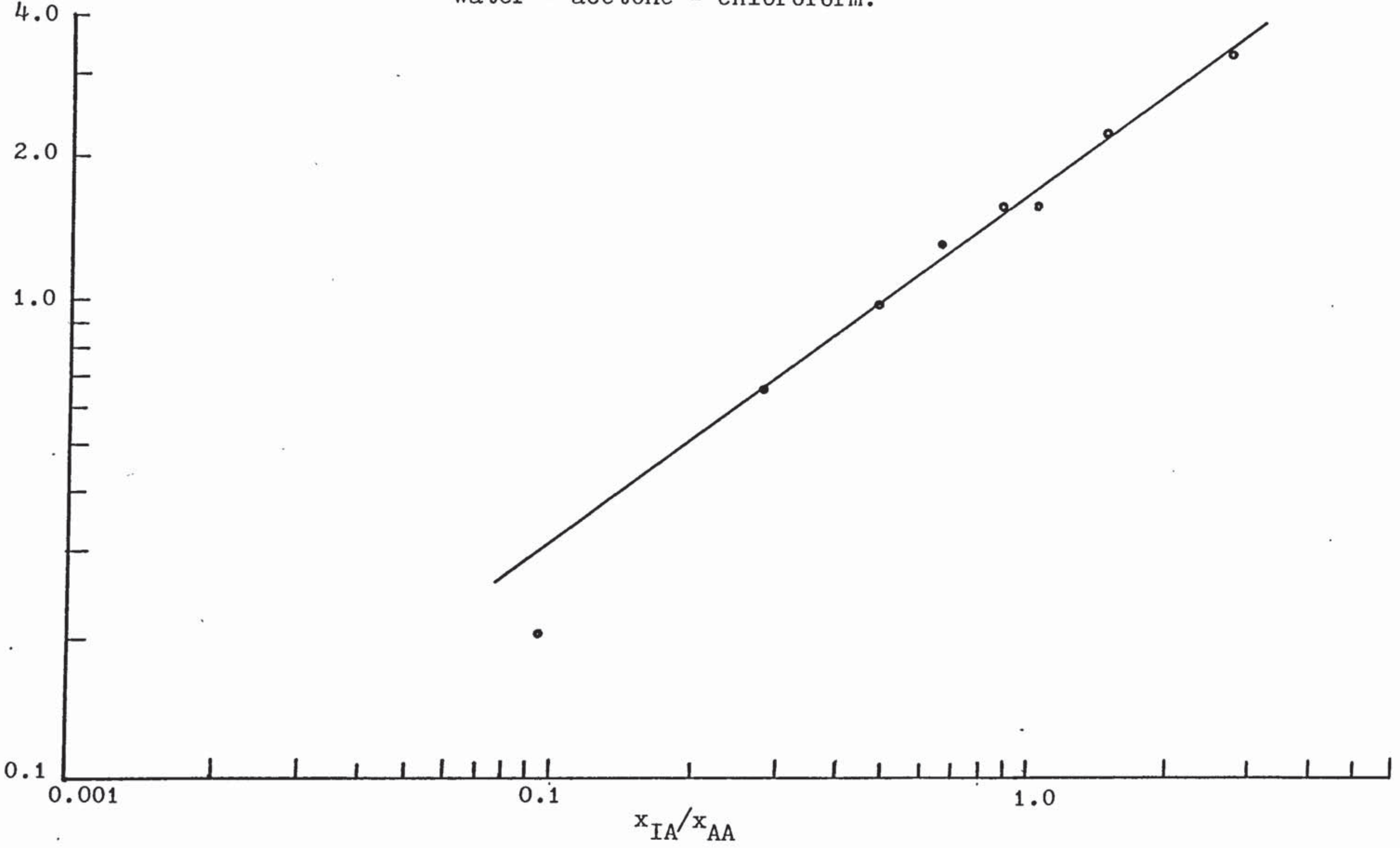


Figure II.1 Hand Coordinates for the Ternary System Water-Acetic Acid-Chloroform.

Figure II.2 Hand Coordinates for the ternary system water - acetone - chloroform.



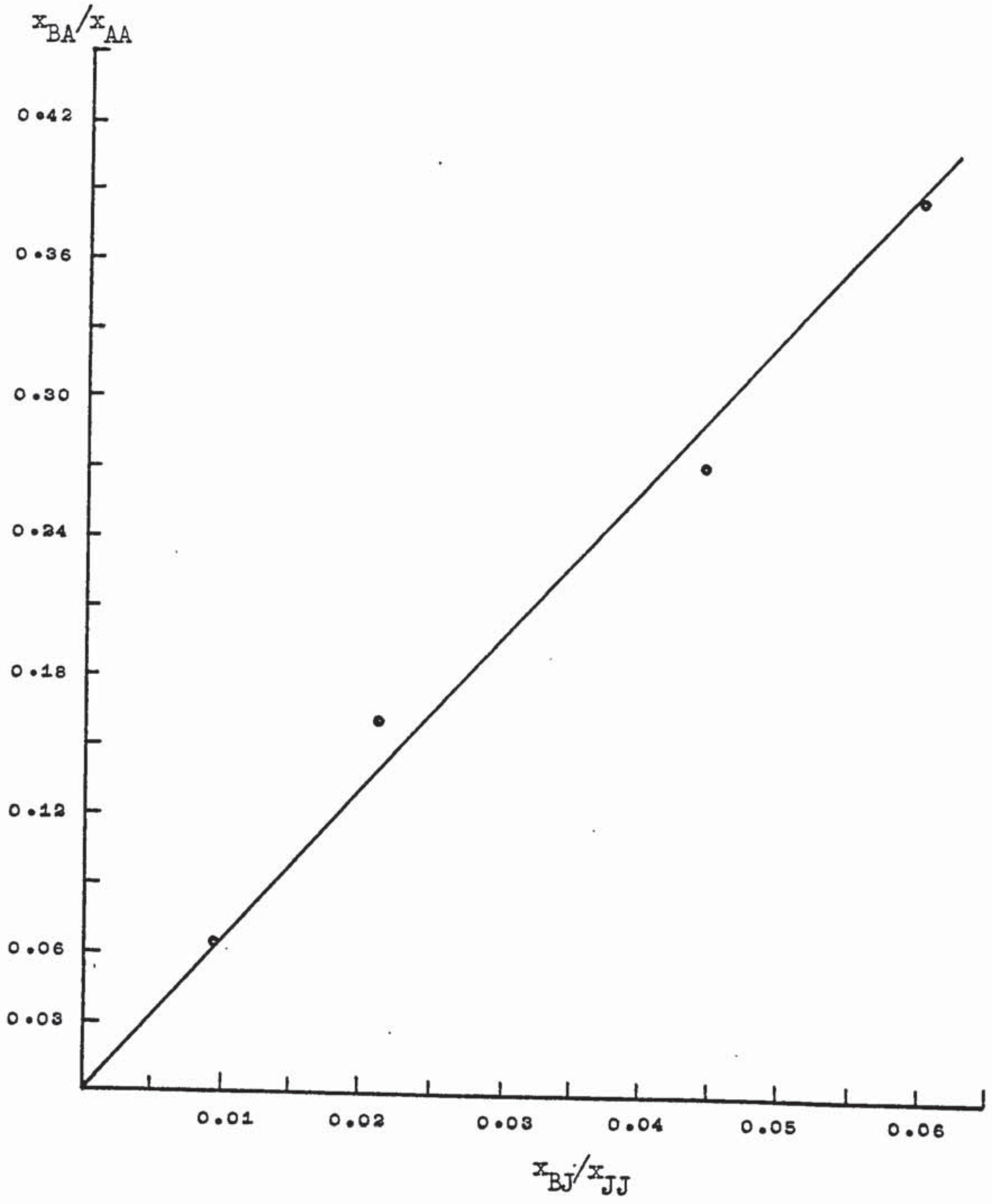


Figure II.3 Solubility Data for the ternary system Water-Acetic Acid-Chloroform.

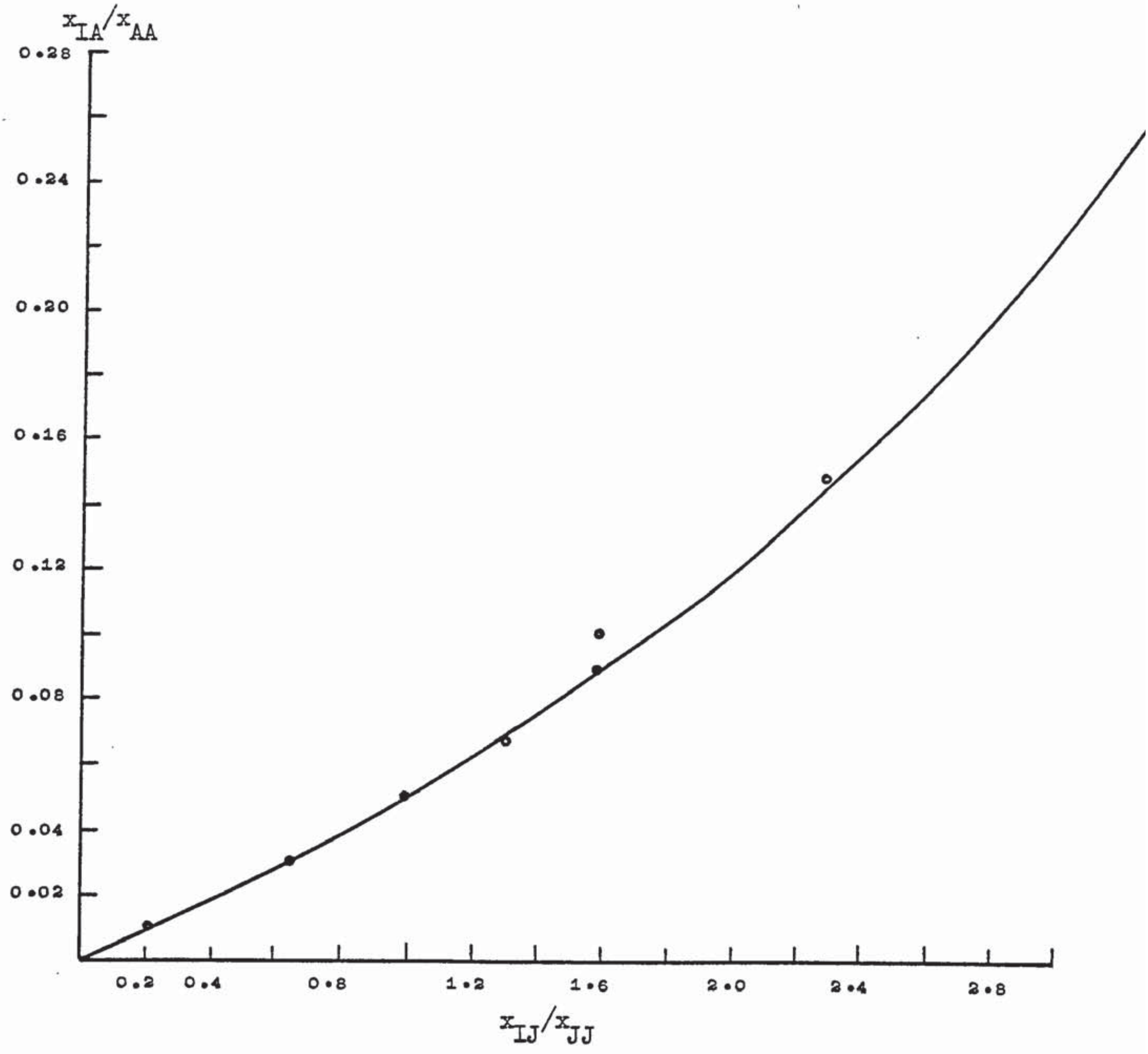


Figure II.4 Solubility Data for the Ternary System Water-Acetone-Chloroform.

(A) contd.

(ii) contd.

quaternary data were evaluated and tabulated in table (II.14). Regression analysis led to the following correlations for acetic acid and acetone concentrations:

$$\frac{X_{BA}/X_{AA}}{X_{BJ}/X_{JJ}} = \frac{x_{BA}/x_{AA}}{x_{BJ}/x_{JJ}} - 0.132\left(\frac{X_{BA}}{X_{AA}} + \frac{X_{BJ}}{X_{JJ}}\right)^{0.181}\left(\frac{X_{IA}}{X_{AA}} + \frac{X_{IJ}}{X_{JJ}}\right)^{1.600} \quad (3)$$

$$\frac{X_{IA}/X_{AA}}{X_{IJ}/X_{JJ}} = \frac{x_{IA}/x_{AA}}{x_{IJ}/x_{JJ}} + 0.051\left(\frac{X_{BA}}{X_{AA}} + \frac{X_{BJ}}{X_{JJ}}\right)^{0.504}\left(\frac{X_{IA}}{X_{AA}} + \frac{X_{IJ}}{X_{JJ}}\right)^{1.348} \quad (4)$$

Equations (3) and (4) indicate the change in acetic acid and acetone distributions for the quaternary relative to the binaries. The concentration of acetic acid in the aqueous phase is depressed, while that of acetone is enhanced. A computer program was written for solving the two simultaneous equations (3) and (4). This program was similar to that developed for the water-acetic acid-butanol-n heptane system. Results of the computer calculations are compared with experimental values in table (II.14a) and figures (II.5) and (II.6).

Discussion.

Application of the single binary quaternary model, developed in this study, to Brancker, Hunter and Nash's data(109) achieved good agreement for acetic acid concentration values. The maximum deviation between experimental and computed values was below 20% and the average was about 8.8%. However, in the case of acetone, the agreement was poor, there being deviations of over 40% and an overall average of about 27%. This was thought to be due to the pecularities shown by the experimental values for acetone:

(1) Out of all the ternaries studied, the data for the water-

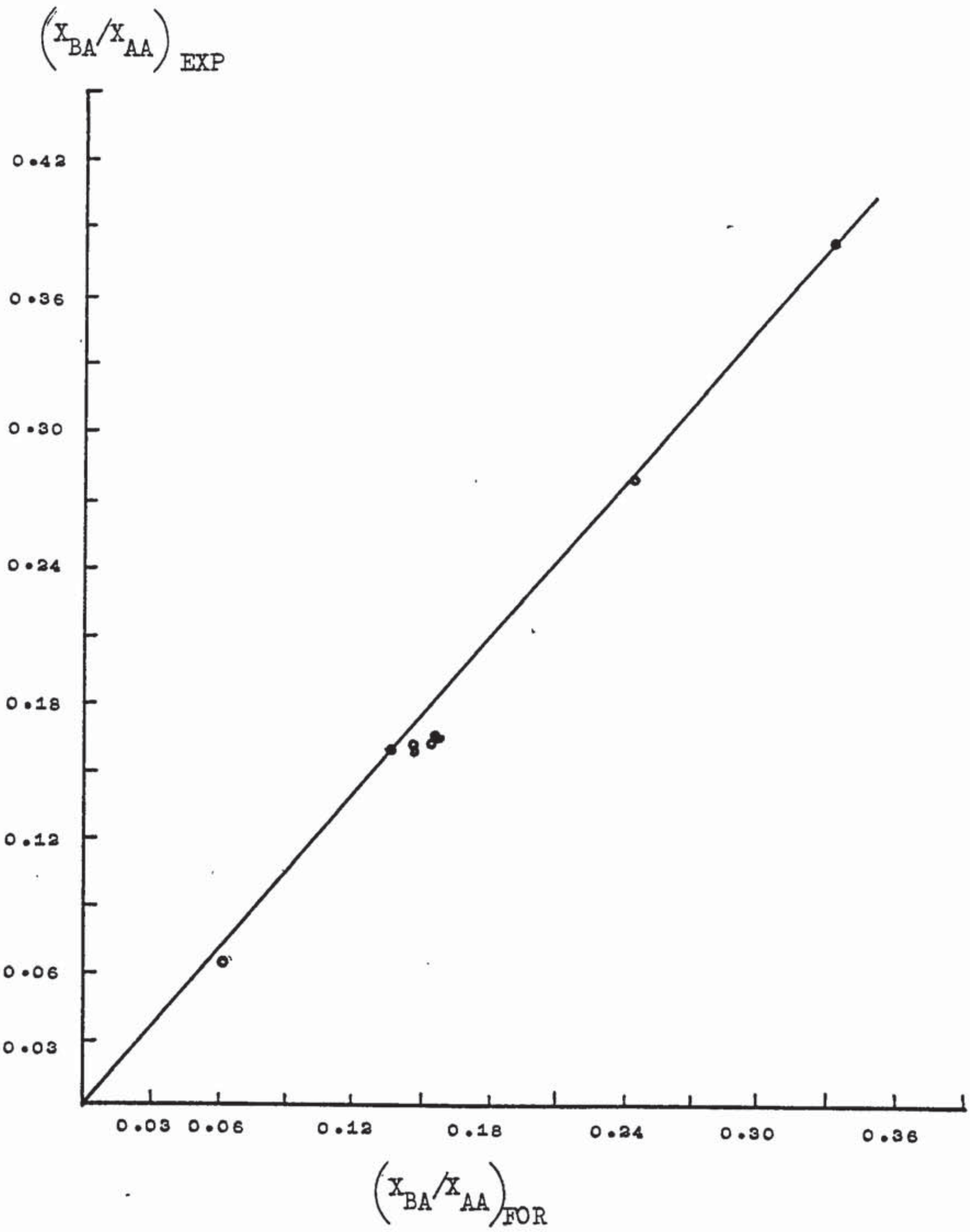


Figure II.5 Distribution of Acetic Acid in the Water-Acetic Acid-Acetone-Chloroform quaternary System.

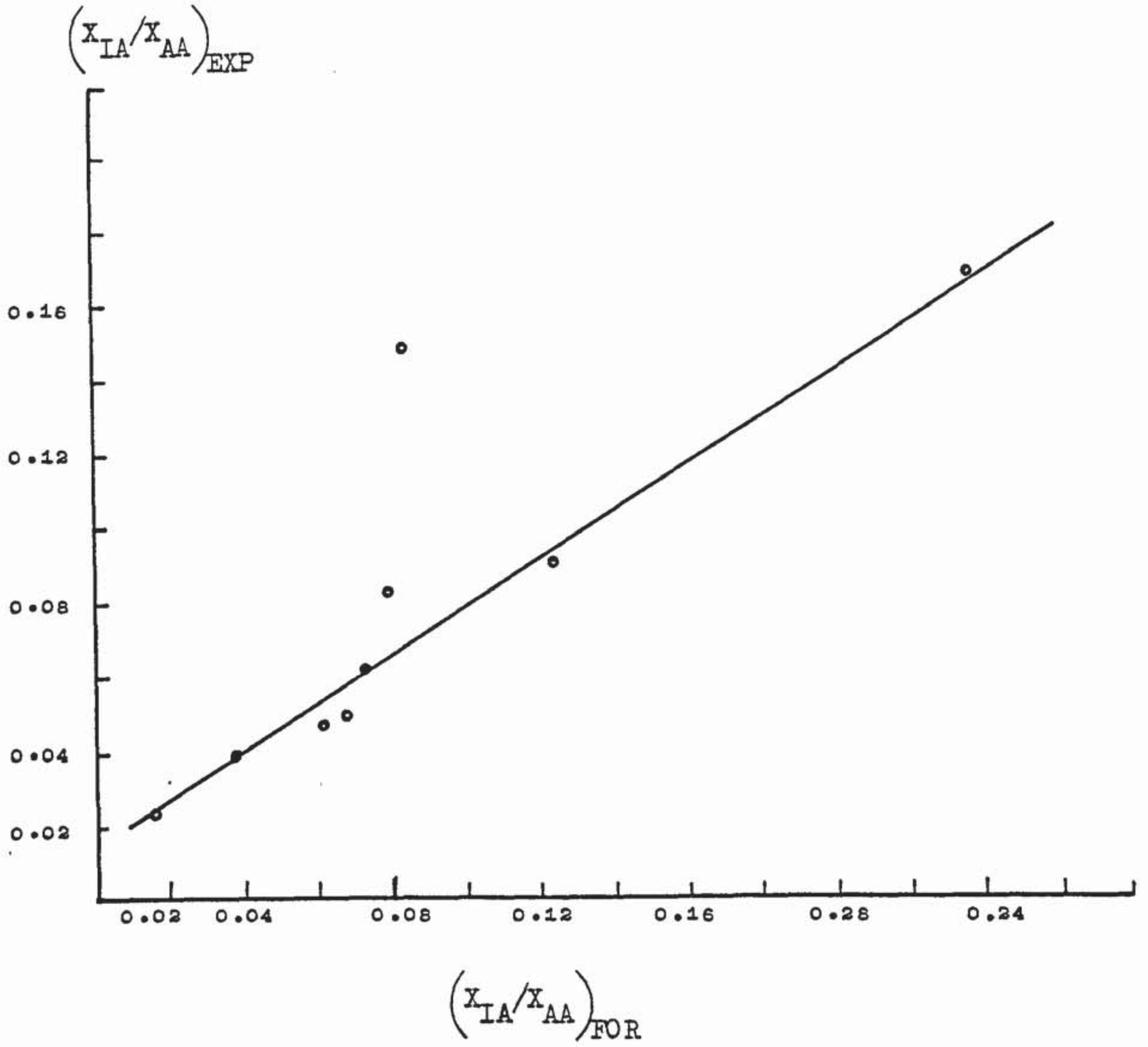


Figure II.6 Solubility of Acetone in the Water-Acetic Acid-Acetone-Chloroform quaternary system.

(A) contd.

(1) contd.

acetone-chloroform ternary only did not fit Hand's coordinates well. Fig.(II.2) shows considerable scattering of the points on the double logarithmic coordinates whereas figure (II.1) for the data of the same workers show that the other ternary viz the water-acetic acid-chloroform was much more "well behaved". When regression analysis was carried out on the water-acetone-chloroform ternary data, and the resulting correlation tested back, again above normal deviations were observed as shown in table (II.13). The average deviation was over 10% whereas for the case of water-acetic acid-chloroform ternary (table II.12) it was 2.5% only.

(2) Pecularities were also shown in the acetone concentration values for the quaternary system data shown in table (II.14). This is evident from the difference between $\frac{X_{IA}/X_{AA}}{X_{IJ}/X_{JJ}}$ and $\frac{x_{IA}/x_{AA}}{x_{IJ}/x_{JJ}}$ terms which is a measure of enhancement or depression of the I component (acetone) concentration in the quaternary aqueous phase relative to the ternary aqueous phase due to influence of the other solute (acetic acid). This difference is negative for two values indicating that acetic acid depresses acetone solubility in the aqueous phase. For the other seven values, the difference is positive indicating enhancement.

(B) Double Binary Quaternary.

The data of Prince(110) for the water-acetic acid-benzene-carbontetrachloride system were tested.

(i) The Two Ternaries.

Prince's data for the water-acetic acid-benzene

(B) contd.

(i) contd.

and water-acetic acid-carbontetrachloride ternaries, evaluated according to Hand's method are shown in tables (II.15) and (II.16). Regression analysis led to the following correlations:

For water-acetic acid-benzene system,

$$\frac{x_{BA}}{x_{AA}} = 1.616 \left(\frac{x_{BF}}{x_{FF}}\right)^{0.827}$$

For water-acetic acid-carbontetrachloride system,

$$\frac{x_{BA}}{x_{AA}} = 2.18 \left(\frac{x_{BG}}{x_{GG}}\right)^{0.794}$$

(ii) The Double Binary Quaternary System.

Distribution values for the water-acetic acid-carbontetrachloride double binary quaternary system, were calculated according to equation (7.25). The computed values and Prince's experimental results are shown in table (II.17) and figure (II.7). Very good agreement was obtained. Only one deviation out of 23 values was above 10% and a further 3 values were between 5 and 10%, while the great majority were under 3%. The average deviation for all values was about 3%, which is believed to be well within the experimental error, considering that any errors in either the ternary data or the quaternary experimental values will reflect on the deviation. The only relatively high deviation which was 14.6% can easily be understood when the composition of the quaternary is scrutinized. The acetic acid content was extremely high for this run resulting in appreciable intermixing between water and the organic solvents.

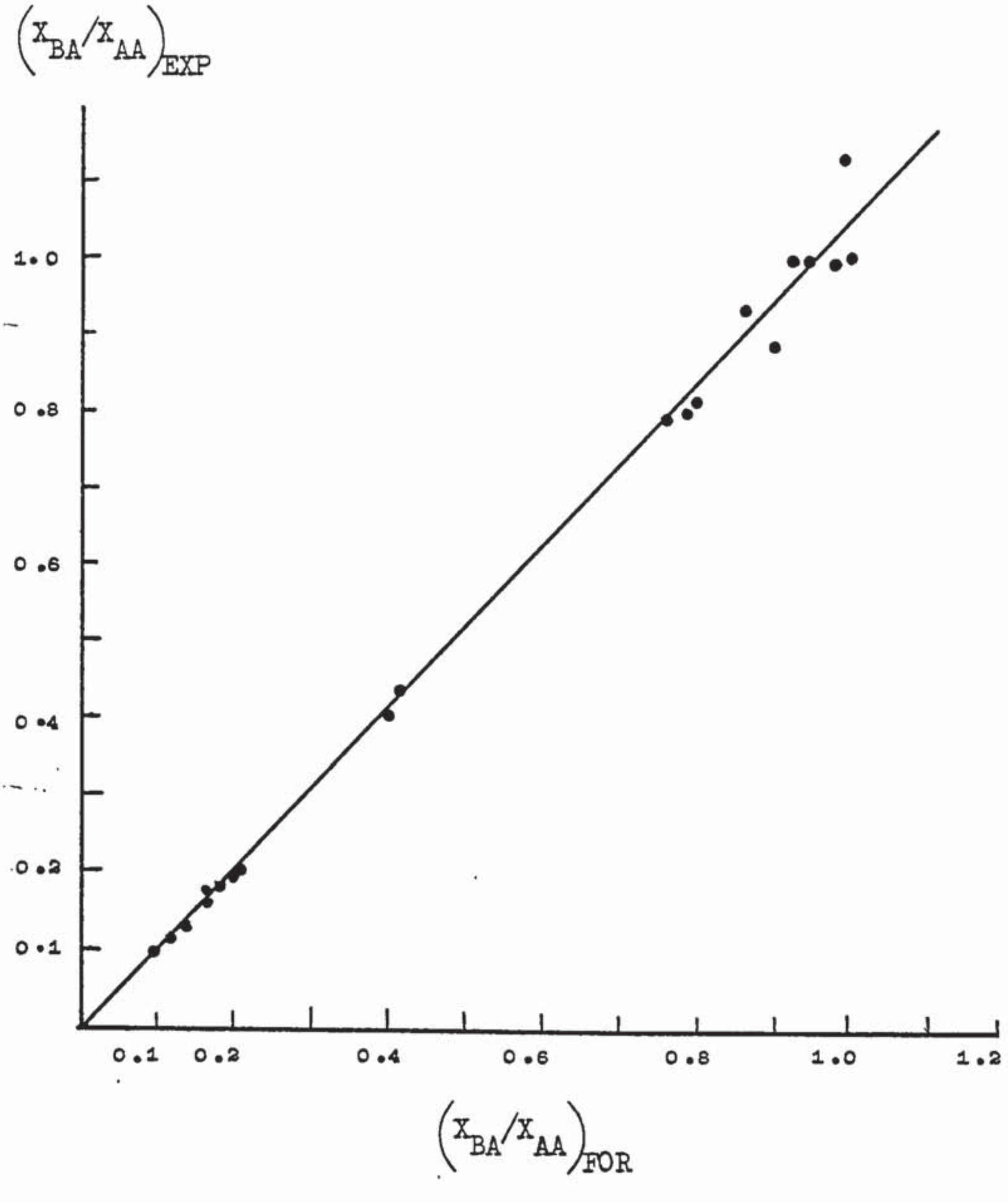


Figure II.7 Distribution of Acetic Acid in Water-Acetic Acid-Benzene-Carbon Tetrachloride System.

APPENDIX III

Results of Hydrodynamic and Mass Transfer Studies in the R.D.C.

TABLE III.1 R.D.C.Column Hydrodynamics

U_d ℓ/Min	RPM	X_d %	d_{32} cm
1.6	500	3.1	0.37
2.7	500	4.5	0.40
3.8	500	5.6	0.44
4.8	500	6.8	0.48
1.6	750	3.2	0.32
2.7	750	4.8	0.38
3.8	750	5.9	0.43
4.8	750	7.8	0.44
1.6	1000	3.5	0.30
2.7	1000	5.5	0.29
3.8	1000	8.4	0.33
4.8	1000	9.8	0.35

TABLE III.2 Phase inversion characteristics.
The system n heptane (initially continuous)-water

U_c ℓ/Min	U_d ℓ/Min	RPM	d_{32} cm
1.6	5.8	0	0.40
1.6	4.1	500	0.39
1.6	4.2	750	0.43
1.6	4.0	1000	0.38

U_d is the dispersed phase (water) flow at inversion point.

Typical Calculations for Mass transfer Studies.

System: n heptane/acetic acid ⟶ water
(dispersed phase) (continous phase)

Feed Concentration = 27.47%

Raffinate concentration = 0.56%

Extract concentration = 9.6%

Feed flow = 1.70 litres/Min = 1.31 Kgs/Min

Solvent (water) flow = 3.05 L/Min = 3.05 Kgs/Min

RPM = 500

Hold-up = 5.0%

Drop Count

Magnification = 2.50

d mm	n	d mm	n	d mm	n
2.59	3	11.42	5	19.7	10
4.25	2	11.98	1	20.26	8
4.80	3	12.53	5	20.81	1
5.35	3	13.08	2	21.36	2
5.90	1	13.63	1	21.91	2
6.46	1	14.18	1	22.46	4
7.01	2	14.74	3	23.02	1
7.56	2	15.29	2	24.12	4
8.11	5	15.84	5	24.67	6
8.66	7	16.39	6	25.22	1
9.22	6	16.94	1	26.88	1
9.77	1	17.50	1		
10.32	1	18.05	1	TOTAL	121
10.87	8	18.60	2		

Calculation of Overall Mass Transfer Coefficient.

$$N = K_G \ A \ \Delta C$$

$$N = 0.36 \text{ Kg/Min} = 6.0 \text{ grm/sec}$$

$$d_{32} = 0.76 \text{ cm}$$

Surface area per unit volume:

$$a = \frac{(6)(0.05)}{0.76} = 0.395 \text{ cm}^2/\text{cm}^3$$

Effective volume of the column

$$= 5.0^2 \times \pi \times 120 = 942 \text{ cm}^3$$

Hence $A = 0.395 \times 9425 = 3723 \text{ cm}^2$

ΔC is the log mean concentration driving force

$$\Delta C_1 = (27.47-0.1) \times 10 \times 0.77$$

$$= 210.7 \text{ grms/litre} = 0.2107 \text{ grms/cm}^3$$

where 0.1 is the concentrate of acetic acid in organic phase corresponding to 9.6% concentration in aqueous phase

0.77 is the density

similarly $\Delta C_2 = 0.0039 \text{ grm/cm}^3$

$$\text{LMC} = \frac{0.2107-0.0039}{\ell n \dfrac{0.2107}{0.0039}} = 0.0518 \text{ cm/sec}$$

Hence $K_G = 3.11 \times 10^{-2}$ cm/sec

Table III.3: Mass Transfer Characteristics of RDC
System: n-heptane/acetic acid→water
(dispersed phase) (continous phase)

U_d 1/min	U_c 1/min	X 90	C_F Wt. %	C_R Wt. %	C_E Wt. %	RPM	d_{32} cm	$K_G a$ cm/sec	K_G sec^{-1}
1.70	3.05	5.0	27.47	0.56	9.60	500	0.76	1.23×10^{-2}	3.11×10^{-2}
1.70	3.05	5.9	27.47	0.54	9.65	1000	0.57	1.24×10^{-2}	2.00×10^{-2}
2.50	2.00	8.0	20.20	0.25	15.20	750	0.52	1.40×10^{-2}	1.52×10^{-2}
2.50	2.00	7.1	32.30	1.51	23.70	750	0.79	1.42×10^{-2}	2.64×10^{-2}
2.75	2.00	8.2	16.80	0.24	13.90	750	0.63	1.78×10^{-2}	2.28×10^{-2}
2.85	2.55	8.8	10.00	0.13	8.20	750	0.55	1.80×10^{-2}	1.88×10^{-2}

Table III.4: Mass Transfer Characteristics of R.D.C.
System: n heptane/n butyl alcohol⟶water
(dispersed phase) (continous phase)

U_d 1/min	U_c 1/min	X %	C_F Wt. %	C_R Wt. %	C_E Wt. %	RPM	K_Ga cm/sec
2.70	2.00	16.6	26.0	20.5	5.25	500	2.16×10^{-3}
2.70	2.00	16.2	26.0	20.0	5.36	1000	2.20×10^{-3}
2.70	2.00	15.3	20.2	15.1	5.28	500	2.64×10^{-3}
2.70	2.00	14.4	20.2	15.2	5.30	1000	2.68×10^{-3}

TABLE III.5: Typical results for "two way" mass transfer

Light phase feed (Butanol in heptane solution)

Composition: 22.8% Butanol by weight

Flow : 1.80 litres/Min

Heavy Phase feed: (Acetic acid in water solution)

Composition : 25.9% Acetic acid by weight

Flow : 0.78 L/Min

Extract Composition:

Acetic Acid	17.8%
Butanol	12.8%
Water	69.4%

Ruffinate Composition:

Acetic acid	4.5%
Butanol	15.0%

Hold-Up Values

H = Volumetric ratio of light: Heavy phase

H at the middle of phase inversion band = 1:0343

H about 10 cm below the middle = 1:0.343

H about 10 cms above the middle = 1:1.455

H for the whole column = 1:0.753

APPENDIX IV

Computer Program for Calculating the Sauter Mean Diameter of Droplets (d_{32}).

```
      MASTER SAUTER
      REAL MF, ND1, ND2, ND3
      INTEGER K, I
C     MAGNEFING FACTER, MF
    5 READ(1,200)I,B,K,MF
  200 FORMAT(I5,F5.0,I5,F10.3)
      WRITE(2,201)I,B
  201 FORMAT(1H1,5X,'SERIALNO= ',I5,5X,'PHOT.NO= ',F5.0)
      WRITE(2,111)
  111 FORMAT(1H0,36X,'SAUTER MEAN DIAMETER AND ST.DEVIATION CALCULATION'
     1)
      WRITE(2,112)
  112 FORMAT(24X,'DM',8X,'D',0X,'N',9X,'D2',8X,'D3',7X,'ND1',7X,'ND2',
     17X,'ND3')
      SUMD=0
      SUMN=0
      SUMND1=0
      SUMND2=0
      SUMND3=0
C     DROP MEAN DIAMETER,DM
C     NUMBER OF DROP,N
      DO 20J=1,K
      READ(1,114)DM,F
  114 FORMAT(2F0.0)
      D=DM/MF
      D2=D**2
      D3=D**3
      ND1=F*D
      ND2=F*D2
      ND3=F*D3
      SUMD=SUMD+D
      SUMN=SUMN+F
      SUMND1=SUMND1+ND1
      SUMND2=SUMND2+ND2
      SUMND3=SUMND3+ND3
   20 WRITE(2,115)DM,D,F,D2,D3,ND1,ND2,ND3
  115 FORMAT(22X,F5.2,3X,F9.5,4X,F3.0,4X,F9.5,1X,F8.4,2X,F9.4,2X,F9.4,
     11X,F9.4)
   21 WRITE(2,116)
  116 FORMAT(30X,'----------',4X,'----',24X,'----------',1X,'---------',2X
     1,'----------')
      WRITE(2,117)SUMD,SUMN,SUMND1,SUMND2,SUMND3
  117 FORMAT(30X,F9.5,3X,F4.0,22X,F9.4,2X,F9.4,1X,F9.4)
      WRITE(2,116)
C     ARITHMETIC MEAN DIAMETER,AMD
C     SAUTER MEAN DIAMETER ,SMD
C     ST.DEVIATION ,SD
      AMD=SUMND1/SUMN
      SMD=SUMND3/SUMND2
      SD=SQRT((SUMND2-(SUMN*AMD**2))/(SUMN-1))
      WRITE(2,118)AMD
  118 FORMAT(20X,'ARITHMETIC MEAN DIA= ',F10.5)
      WRITE(2,119)SMD
  119 FORMAT(20X,'SAUTER MEAN DIA= ',F10.5)
      WRITE(2,120)SD
  120 FORMAT(20X,'STD.DEV= ',F10.6)
      STOP
      END
      FINISH
****
```

APPENDIX V

RESULTS OF CONTINUOUS EXTRACTION REACTION IN THE R.D.C

TABLE V.1

Run	Heavy Phase Composition Wt. % Basis			Light Phase Composition Wt. % Basis		Conversion %	
No.	Water	Acetic Acid	Catalyst	Butanol	Heptane	EXP.	CALC
1	10.0	80.1	9.9	25.0	75.0	22.9	21.8
2	10.9	81.0	8.1	25.1	74.9	19.8	18.4
3	11.5	82.6	5.9	24.9	75.1	17.4	17.0
4	10.2	86.0	3.8	25.3	74.7	12.2	13.2
5	23.0	67.0	10.0	22.0	78.0	19.9	21.5
6	22.0	70.1	7.9	24.8	75.2	16.3	19.6
7	24.1	69.8	6.1	25.0	75.0	13.7	17.6
8	26.1	69.9	4.0	24.9	75.1	9.7	12.5
9	39.9	50.1	10.0	25.2	74.8	5.7	6.7
10	9.9	80.1	10.0	20.2	79.8	38.6	33.0
11	9.8	82.2	8.0	21.3	78.7	28.7	24.5
12	10.0	83.9	6.1	20.0	80.0	23.6	20.2

Flows:

Light Phase = 0.700 Kgs/Min

Heavy Phase = 0.680 Kgs/Min

APPENDIX VI

Computer Program for Calculating Conversion in Batch Esterification of n-Butyl Alcohol With High Reactants and Sulphuric Acid Catalyst Concentrations.

TEXT BOUND INTO

THE SPINE

```
####   #####    ##    #####      FFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFF
   #   #   #     #    #   #      FFFF                      FFFFFFFFFFFF
  #    #   #     #    #   #      FFFF                      FFFFFFFFFFFF
 #     #   #     #    #####      FFFF         MOP          FFFFFFFFFFFF    :ECF
#      #   #     #    #   #      FFFF                      FFFFFFFFFFFF
#      #   #     #    #   #      FFFF                      FFFFFFFFFFFF
#      #####   #####  #####      FFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFF

ISTING OF :ECP7018,CONV(2/)   PRODUCED ON  3APR78 AT 13.36.23

8,62S AT ASTON    IN ':ECP7018,MOP' ON 21SEP78 AT 12.01.49 USING  U14

CUMENT    CONV


      MASTER SAADI
C BATCH ESTERIFICATION OF BUTANOL
C CALCULATION OF CONVERSION
      DIMENSION T(10)
      REAL K2
C K2 IS THE FORWARD REACTION RATE CONSTANT
      READ(1,50)NT
 50   FORMAT(I3)
C NT IS THE NUMBER OF RUNS
      N=1
 400  READ(1,100)AI,BI,CI,DI,RK,CS,NC
C AI,BI,CI,DI ARE INITIAL CONC. OF ACID,ALCOHOL,ESTER AND WATER
C RK IS THE EQUILIBRUM CONSTANT
C CS IS THE CATALYST CONCENTRATION
C ALL CONCENTRATIONS ARE IN MOLES PER LITER
C NC IS THE NUMBER OF MEASUREMENTS REQUIRED FOR THE RUN
 100  FORMAT(6F0,0,I2)
      WRITE(2,500)AI,BI,CI,DI,RK,CS,NC
 500  FORMAT (1H ,' RESULTS FOR: AI= ',F6.3,' ,BI= ',F6.2,' ,CI= ',F6.2
     1,' ,DI= ',F6,2,' ,RK= ',F6.2,' ,CS= ',F6.2,' NC=',I4)
      WRITE (2,150)
 150  FORMAT (1X,'TIME',4X,'% CONVERSION')
      DO 20 I=1,NC
      READ(1,200)T(I)
 200  FORMAT(1F0.0)
      X=0.1*T(I)
 10   CD=(2*DI+X*18/60)/2
      K2=0,0112*(CD**(-0,345))*(CS**1.18)
      ALPHA=K2*(AI*BI-CI*DI/RK)
      BETA=-K2*(AI+BI+(CI+DI)/RK)
      GAMMA=K2-K2/RK
      Q=BETA**2-4*ALPHA*GAMMA
      Z1=EXP ((SQRT (Q))*T(I))
      Z2=(2*GAMMA)/(BETA-(SQRT (Q)))-2*GAMMA*Z1/(BETA+SQRT(Q))
      XN=(Z1-1)/Z2
      IF(ABS(X-XN).LE.0,01) GO TO 21
      X=XN
      GO TO 10
 21   CON=100*XN/AI
      WRITE (2,300)T(I),CON
 300  FORMAT(1X,F5.2,F10,4)
   20 CONTINUE
      IF (N.EQ.NT) GO TO 30
      N=N+1
      GO TO 400
 30   STOP
      END
      FINISH
 ****
```

APPENDIX VII

Computer Program for Calculating Conversion in Batch Esterification of n-Butyl Alcohol in presence of n-Heptane.

```
      TRACE 1
      MASTER BATCH ESTERIFICATION
      COMMON/CINT/T,DT,JS,JN,DXA(500),XA(500),IO,JS4,TPRNT,BI,CI
      COMMON/MED/AI,D,E,BQ,CQ,IN,A,B,C
      J=6
      DO 4 I=1,J
      READ(1,100)AI,BI,CI,D,SU
C AI,BI,CI,D,SU ARE INITIAL QUANTITIES OF
C     WATER,ACID,ALCOHOL,HEPTANE,CATALYST IN REACTION MIXTURE
  100 FORMAT (5F0.0)
      WRITE(2,102)AI,BI,CI,D,SU
 102  FORMAT(1X,'BATCH ESTERIFICATION FOR AI = ',F6.3,2X,'BI= ',F6.3,2X,
     1'CI= ',F6.3,2X,'D= ',F6.3,2X,'SU= ',F6.3)
      EAQ=0.0
      EXQ=0.0
      E=0.0
      RAWA=1.00
      RAWB=1.05
      RAWC=0.81
      RAWSU=1.84
      RAWD=0.68
      RAWE=0.88
      TPRNT=0.0
      T=0.0
      JS4=0
      JS=0
      IN=1
      MN=1
      NF=1
      WRITE(2,101)
 101  FORMAT(4X,'TIME',4X,'%CONVERSION')
C TEST FOR PRINT AND FINISH
 2    CALL PRNTF(1.0,60.0,NF,E)
      GO TO (3,4),NF
 3    CALL DISTRIBUTION(BI,CI)
C V1 IS THE VOLUME OF THE WATER RICH PHASE IN LITERS
      V1=(A*18.0/RAWA+BQ*60.05/RAWB+CQ*74.12/RAWC+SU*98.08/RAWSU)/1000.0
C BQ IS MOLES OF B IN AQUEOUS PHASE (CALCULATED BY DISTRIBUTION SUB)
C CQ IS MOLES OF C IN AQUEOUS PHASE (CALCULATED BY DISTRIBUTION SUB)
C V2 IS THE VOLUME OF THE HEPTANE RICH PHASE IN CC
      V2=(B-BQ)*60.05/RAWB+(C-CQ)*74.12/RAWC+E*116.16/RAWE+D*100.2/RAWD
C DETERMINATION OF REACTION RATE CONSTANT
      CALL REACTIONRATE(V1,A,SU,RK,RK2,COA)
C MASS TRANSFER CALCULATIONS
      CALL MASSTRANSFER(EXQ,0.1,V1,V2,EAQ,B,BI,MN,C,CI,RK2,COA)
C DERIVATIVE
      DE=RK*BQ*CQ/(V1**2.0)-RK2*EAQ*A/(V1**2.0)
C INTEGRATION
      CALL INTI(T,0.1,1)
      CALL INT(E,DE,EXQ)
      GO TO 2
 4    CONTINUE
      STOP
      END

 , LENGTH   199, NAME  BATCHESTERIFICATION
```

```
      SUBROUTINE DISTRIBUTION(BI,CI)
      COMMON/MED/AI,D,E,BQ,CQ,IN,A,B,C
      REAL JC
      A=AI+E
C E IS MOLES OF ESTER FORMED
      B=BI-E
      C=CI-E
      S=E+D
C CALCULATION OF DISTRIBUTION COEFFS. FOR HEPTANE SOLVENT
C CALCULATION OF TERNARY DISRIBUTION COEFFICIENT FOR ACETIC ACID
C REGULI FALSI ITERATION
      BA=0.9*B
      F1=BA/A-7.82*(((B-BA)/S)**0.89)
      IF (IN.EQ.2) GO TO 7
      BB=0.99*B
 7    F2=BB/A-7.82*(((B-BB)/S)**0.89)
      DELBB=F2*(BB-BA)/(F2-F1)
 22   BAN=BB-DELBB
      IF((BAN.LE.0.0).OR.(BAN.GE.B)) GO TO 23
      IF(ABS(BAN-BB).LE.0.001) GO TO 6
      BB=BAN
      GO TO 7
 23   BAN=BAN+DELBB
      DELBB=DELBB/2.0
      GO TO 22
  6   R1=(BAN*S)/(A*(B-BAN))
C CALCULATION OF TERNARY COEFF FOR BUTANOL
C NEWTON-RAPHSON METHOD
      IF (IN.EQ.2) GO TO 9
      CA=0.5*C
  9   F3=CA/A-0.02*(((C-CA)/S)**0.18)
      F4=1.0/A+0.0036*(((C-CA)/S)**(-0.82))/S
      DELCAN=F3/F4
 20   CAN=CA-DELCAN
      IF((CAN.LE.0.0).OR.(CAN.GE.C)) GO TO 21
      IF(ABS(CAN-CA).LE.0.001) GO TO 11
      CA=CAN
      GO TO 9
 21   CAN=CAN+DELCAN
      DELCAN=DELCAN/2.0
      GO TO 20
 11   R2=(CAN*S)/(A*(C-CAN))
C CALCULATION OF QUTARNARY DISTRIBUTION COEFFICIENTS
C NEWTON-RAPHSON METHOD
      N=1
      IF (IN.EQ.2) GO TO 16
      B1=BAN
      C1=CAN
C B1,C1 ARE MOLES OF B,C ASSUMED IN AQUEOUS PHASE
 16   TERM1=(B1*S)/(A*(B-B1))
      TERM2=B1/A+(B-B1)/S
      TERM3=C1/A+(C-C1)/S
      TERM4=C1*S/(A*(C-C1))
      TERM5=TERM2**(-0.21)
      TERM6=TERM3**0.16
      TERM7=TERM2**2.0
      TERM8=TERM3**(-2.2)
      TERM9=TERM2**(-1.21)
      TERM10=TERM3**(-0.84)
      TERM11=TERM3**(-3.2)
      TERM12=S*B/(A*((B-B1)**2.0))
      TERM13=S*C/(A*((C-C1)**2.0))
```

```
      TERM14=1.0/A-1.0/S
      F=TERM1+10.85*TERM5*TERM6-R1
      G=TERM4-0.20*TERM7*TERM8-R2
      PD1=TERM12-2.2785*TERM14*TERM9*TERM6
      PD2=TERM13+0.44*TERM14*TERM7*TERM11
      PD3=1.736*TERM14*TERM5*TERM10
      PD4=-0.4*TERM14*TERM2*TERM8
C JC IS THE JACOBIAN OF THE SYSTEM
      JC=PD1*PD2-PD3*PD4
      IF(N.EQ.2)GO TO 12
      DELB=(F*PD2-G*PD3)/JC
   14 BN=B1-DELB
      IF((BN.LE.0.0).OR.(BN.GE.B)) GO TO 5
      IF(ABS(BN-B1).LE.0.01) GO TO 31
      B1=BN
      GO TO 16
    5 BN=BN+DELB
      DELB=DELB/2.0
      GO TO 14
   31 M=1
   12 DELC=(F*PD4-G*PD1)/JC
   15 CN=C1+DELC
      IF((CN.LE.0.0).OR.(CN.GE.C)) GO TO 17
      GO TO 19
   17 CN=CN-DELC
      DELC=DELC/2.0
      IF(ABS(DELC).LE.0.001) GO TO 32
      GO TO 15
   19 IF(ABS(CN-C1).LE.0.001) GO TO 32
      C1=CN
      B1=BN
      M=M+1
      N=2
      GO TO 16
   32 IF (M.EQ.1) GO TO 18
      N=1
      GO TO 16
   18 XBH=BN/A
      XCH=CN/A
C CALCULATION OF DISTRIBUTION COEFFS. FOR ESTER SOLVENT
C CALCULATION OF TERNARY DISRIBUTION COEFFICIENT FOR ACETIC ACID
C REGULI FALSI ITERATION
      BA=0.2*B
      F1=BA/A-0.25*(((B-BA)/S)**0.85)
      IF (IN.EQ.2) GO TO 117
      BE=0.6*B
  117 F2=BE/A-0.25*(((B-BE)/S)**0.85)
      DELBE=F2*(BE-BA)/(F2-F1)
   24 BAN=BE-DELBE
      IF((BAN.LE.0.0).OR.(BAN.GE.B)) GO TO 25
      IF(ABS(BAN-BE).LE.0.001) GO TO 216
      BE=BAN
      GO TO 117
   25 BAN=BAN+DELBE
      DELBE=DELBE/2.0
      GO TO 24
  216 R1=(BAN*S)/(A*(B-BAN))
C CALCULATION OF TERNARY COEFF FOR BUTANOL
      IF (IN.EQ.2) GO TO 119
      CE=0.3*C
  119 F3=CE/A-0.014*(((C-CE)/S)**0.65)
      F4=1.0/A+0.0091*(((C-CE)/S)**(-0.35))/S
```

```
      DELCE=F3/F4
 27   CAN=CE-DELCE
      IF((CAN.LE.0.0).OR.(CAN.GE.C)) GO TO 26
      IF(ABS(CAN-CE).LE.0.001) GO TO 111
      CE=CAN
      GO TO 119
 26   CAN=CAN+DELCE
      DELCE=DELCE/2.0
      GO TO 27
 111  R2=(CAN*S)/(A*(C-CAN))
C CALCULATION OF QUATERNARY DISTRIBUTION FOR WATER,ACID,ALCOHOL,ESTER
      CON=(CAN/A+(C-CAN)/S)**0.31
      IF (IN.EQ.2) GO TO 116
      B2=BAN
 116  TERM1=(B2*S)/(A*(B-B2))
      TERM2=B2/A+(B-B2)/S
      TERM3=S*B/(A*((B-B2)**2.0))
      TERM4=1.0/A-1.0/S
      F1=TERM1+0.2*CON*(TERM2**(-0.2))-R1
      F2=TERM3-0.04*CON*TERM4*(TERM2**(-1.2))
      DELB=F1/F2
 126  BN=B2-DELB
      IF((BN.LE.0.0).OR.(BN.GE.B)) GO TO 127
      GO TO 128
 127  BN=BN+DELB
      DELB=DELB/2.0
      GO TO 126
 128  IF(ABS(BN-B2).LE.0.001) GO TO 131
      B2=BN
      GO TO 116
 131  XBE=BN/A
      XCE=CAN/A
      XBEH=XBH*D/S+XBE*F/S
      XCEH=XCH*D/S+XCE*E/S
      BQ=XBEH*A
      CQ=XCEH*A
      IN=2
      RETURN
      END

MENT, LENGTH   851, NAME  DISTRIBUTION

      SUBROUTINE REACTIONRATE(V1,A,SU,RK,RK2,COA)
      COA=A/V1
      CS=SU/V1
      RK=0.0112*(COA**(-0.345))*(CS**1.18)
C RK IS THE FORWARD REACTION RATE CONSTANT
      RK2=RK/21.3
C RK2 IS THE REVERSE REACTION RATE CONSTANT
      RETURN
      END

MENT, LENGTH    62, NAME  REACTIONRATE

      SUBROUTINE PRNTF(PRI,FNR,NF,E)
      COMMON/CINT/T,DT,JS,JN,DXA(500),XA(500),IO,JS4,TPRNT,BI,CI
      IF(TPRNT.LT.PRI) GO TO 4
      IF((T.GE.FNR-DT/2.).AND.((JS.EQ.2).OR.(JS4.EQ.4))) GO TO 6
```

```
        IF((T.GE.TPRNT-DT/2.).AND.((JS.EQ.2).OR.(JS4.EQ.4))) GO TO
        NF=1
        RETURN
      4 NF=1
      5 TPRNT=TPRNT+PRI
 8      IF(BI.LE.CI) GO TO 9
        CONV=E*100.0/CI
        GO TO 10
 9      CONV=E*100.0/BI
 10     WRITE(2,200)T,CONV
 200    FORMAT(1X,1F8.1,1F10.3)
        IF(NF.EQ.2)T=0.0
        RETURN
 6      TPRNT=0.
        NF=2
        DO 7 J=1,500
      7 XA(J)=0.
        GO TO 8
        END

OF SEGMENT, LENGTH   151, NAME  PRNTF

        SUBROUTINE INT(X,DX,EXQ)
        COMMON/CINT/T,DT,JS,JN,DXA(500),XA(500),IO,JS4,TPRNT,BI,CI
        JN=JN+1
        GO TO (9,8,3,3),IO
      9 X=X+DX*DT
        EXQ=DX*DT
        RETURN
      8 GO TO (1,2);JS
      1 DXA(JN)=DX
        X=X+DX*DT
        RETURN
      2 X=X+(DX-DXA(JN))*DT/2.
        RETURN
      3 GO TO(4,5,6,7),JS4
      4 XA(JN)=X
        DXA(JN)=DX
        X=X+DX*DT
        RETURN
      5 DXA(JN)=DXA(JN)+2.*DX
        X=XA(JN)+DX*DT
        RETURN
      6 DXA(JN)=DXA(JN)+2.*DX
        X=XA(JN)+DX*DT
        RETURN
      7 DXA(JN)=(DXA(JN)+DX)/6.0
        X=XA(JN)+DXA(JN)*DT
        RETURN
        END

OF SEGMENT, LENGTH   169, NAME  INT

        SUBROUTINE INTI(TD,DTD,IOD)
        COMMON/CINT/T,DT,JS,JN,DXA(500),XA(500),IO,JS4,TPRNT,BI,CI
        IO=IOD
        JN=0
        GO TO (6,5,1,1),IO
```

```
    6 JS=2
      GO TO 7
    5 JS=JS+1
      IF(JS.EQ.3)JS=1
      IF(JS.EQ.2)RETURN
    7 DT=DTD
    3 TD=TD+DT
      T=TD
      RETURN
    1 JS4=JS4+1
      IF(JS4.EQ.5)JS4=1
      IF(JS4.EQ.1) GO TO 2
      IF(JS4.EQ.3) GO TO 4
      RETURN
    2 DT=DTD/2.0
      GO TO 3
    4 TD=TD+DT
      DT=2.*DT
      T=TD
      RETURN
      END
```

```
T, LENGTH   120, NAME INTI
```

```
      SUBROUTINE MASSTRANSFER(EXQ,DTD,V1,V2,EAQ,B,BI,MN,C,CI,RK2,COA)
      REAL KC,KGA
C CALCULATION OF DROPLET DIAMETER USING KOLMOGOROFF LAW
      IF (MN.EQ.2) GO TO 1
      C1=2.0*(2.0**0.5)
      C2=(0.5*0.75)**(-0.6)
      C3=(3.0/((3.1416*3.0*20.0)**3.0))**0.4
C SEGMA IS THE INTERFACIAL TENSION
 1    SIGMA=21.0-15.0*((BI+CI-B-C)/(BI+CI))
      DMEAN=0.7*C1*C2*C3*(SIGMA**0.6)
C CALCULATION OF INTERFACIAL AREA
      DROPNO=6.0*V1*1000.0/(3.1416*(DMEAN**3.0))
C THE AREA IS IN SQUARE CENTIMETER PER CC
      A=DROPNO*4.0*3.1416*(DMEAN**2.0)/(V1*1000.0+V2)
C CALCULATION OF MASS TRANSFER COEFFICIENT
C DROPLETS ARE ASSUMED STAGNANT
      RENO=0.75*DMEAN*60.0*3.1416/0.006
      SCNO=0.006*100000.0/(0.75*1.70)
C LINTON AND SUTHERLANDS FORMULA IS USED FOR CONTINOUS PHASE COEFFICIENT
      KC=0.582*(RENO**0.5)*(SCNO**0.333)*1.70/(DMEAN*100000.0)
      RI=60.0/(RK2*A*COA)
C RI IS THE INTERFACIAL RESISTANCE IN SECONDS PER CM
      KGA=KC*A*60.0/((RI*KC+1.0)*1000.0)
C KGA IS IN LITERS PER MINUTE
C EAQ IS THE INSTANTANEOUS AMOUNT OF ESTER IN THE AQUEOUS PHASE
C EXQ IS THE AMOUNT OF ESTER FORMED IN TIME DTD
      CEAQ=EAQ/V1
      CEXQ=EXQ/V1
C DELTA IS THE CHANGE IN AQUEOUS PHASE CONCENTRATION IN TIME DTD
      DELTA=CEXQ-KGA*CEAQ*DTD
      CEAQ=CEAQ+DELTA
      EAQ=CEAQ*V1
      IF(EAQ.LE.0.0) EAQ=0.0
      MN=2
      RETURN
      END
```

APPENDIX VIII

Computer Program for Calculating Conversion in Continuous Extraction-Reaction in R.D.C.

```
      TRACE 1
      MASTER CONTINOUS ESTERIFICATION
      COMMON/CINT/T,DT,JS,JN,DXA(500),XA(500),IO,JS4,TPRNT,WI,CI
      COMMON/MED/AI,D,E,XBEH,XCEH,IN,A,B,C
      READ(1,100)FC,W,ACH,S
C FC IS CONTINOUS PHASE FLOW IN GRAMS PER MINUTE
C W,ACH,S ARE WEIGHT FRACTIONS OF WATER,ACETIC ACID AND CATALYST
  100 FORMAT (4F0.0)
      READ(1,100)FD,ALC,HEPT,XD
C FD IS THE DISPERSED PHASE FLOW IN GRAMS PER MINUTE
C ALC,HEPT,XD ARE WEIGHT FRACTIONS OF ALCOHOL,HEPTANE AND DISPERSED
C PHASE HOLD-UP
      READ(1,105)CONVI
C CONVI IS AN ARBITRARY CONVERSION VALUE ASSUMED TO START ITERATION
  105 FORMAT(1F0.0)
      WRITE(2,102)
  102 FORMAT(5X,'MODELLING CONTINOUS EXTRACTION REACTION IN THE R.D.C
     1,/)
      WRITE(2,106)
  106 FORMAT(5X,'RESULTS FOR RUN NO 1',/)
      WRITE(2,103)FC,W,ACH,S
  103 FORMAT(1X,'FC= ',F6.1,3X,'W= ',F6.3,3X,'ACH= ',F6.3,3X,'S= ',F6
     1,/)
      WRITE(2,107)FD,ALC,HEPT,XD
  107 FORMAT(5X,'FD= ',F6.1,3X,'ALC= ',F6.3,2X,'HEPT= ',F6.3,2X,'XD=
     1,F6.3,/)
      WRITE(2,104)CONVI
  104 FORMAT(1X,'CONVI= ',F6.2,/)
      WRITE(2,101)
  101 FORMAT(4X,'HEIGHT',2X,'XCONVERSION')
      XSECT=25.0*3.142
    1 CI=ALC*FD/74.12
      E=CI*CONVI/100.0
      AI=W*FC/18.0+E
      BI=ACH*FC/60.05-E
      SU=S*FC/98.08
      Y=SU/AI
      CI=CI-E
      D=HEPT*FD/100.21
      VEL=FC/(XSECT*(1.0-XD))
C VEL IS CONTINUOUS PHASE VELOCITY IN THE COLUMN IN CMS PER MINUTE
      TM=1.0/VEL
      T=0.0
      JS4=0
      JS=0
      NF=1
      A=AI
      B=BI
      C=CI
      IN=1
      CALL DISTRIBUTION(BI,CI)
      IN=1
      E=0.0
      AI=XSECT*(1.0-XD)/(18.0+Y*98.08/1.84+XBEH*60.05+XCEH*74.12/0.81
      BI=XBEH*AI
      CI=TM*FD*ALC/74.12+XCEH*AI
      D=TM*FD*HEPT/100.21
    2 CALL PRNTF(5.0,92.0,NF,E,CONV,A,B,C,RK,XBEH,XCEH)
```

```
  3     A=AI-E
        C=CI-E
        B=BI+E
        CALL DISTRIBUTION(BI,CI)
        BQ=XBEH*A
        CQ=XCEH*A
        V=XSECT*(1.0-XD)/1000.0
C V IS VOLUME OF CONTINOUS PHASE IN THE ELEMENT IN LITERS
        COA=A/V
        SU=S*XSECT*(1.0-XD)/98.08
        CS=SU/V
        RK=0.0112*(COA**(-0.345))*(CS**1.18)
        DE=RK*BQ*CQ*TM/(V**2.0)
C IN THIS PROG THE INDEPENDENT VAR IS WEIGHT OF COLUMN REPRESENTED B
        CALL INTI(T,0.1,1)
        CALL INT(E,DE)
        GO TO 2




  4     IF(ABS(CONVI-CONV).LE.1.0) GO TO 5
        IF((CONVI-CONV).LE.0.0) GO TO 6
        CONVI=CONVI+0.1
        GO TO 1
  6     CONVI=CONVI-0.1
        GO TO 1
  5     STOP
        END

SEGMENT, LENGTH   331, NAME  CONTINOUSESTERIFICATION
```

```
#####  ####    ##    #####      DDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDD
    #  #   #    #    #   #      DDDD                     DDDDDDDDD
   #   #   #    #    #   #      DDDD                     DDDDDDDDD
  #    #   #    #    #####      DDDD                     DDDDDDDDD
 #     #   #    #    #   #      DDDD                     DDDDDDDDD
 #     #   #    #    #   #      DDDD                     DDDDDDDDD
 #     #####  #####  #####      DDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDD

#LISTING OF :WORKFILE.AAAE0UU11U42(1/)  PRODUCED ON 16NOV78 AT 22.48.

#G8.02S AT ASTON    IN ':ECP/018.CESTER' ON 16NOV78 AT 22.50.27 USING

DOCUMENT     !


    MODELLING CONTINOUS EXTRACTION REACTION IN THE R.D.C

    RESULTS FOR RUN NO 1

FC=  680.0   U=  0.100   ACH=  0.801   S=  0.099

    FD=  700.0   ALC=  0.250  HEPT=  0.750  XD=  0.120

CONVI=  21.70

   HEIGHT  %CONVERSION
     1.0        0.5
     5.0        1.1
    10.0        1.8
    15.0        2.6
    20.0        3.4
    25.0        4.3
    30.0        5.2
    35.0        6.2
    40.0        7.2
    45.0        8.3
    50.0        9.5
    55.0       10.7
    60.0       11.9
    65.0       13.3
    70.0       14.7
    75.0       16.2
    80.0       17.7
    85.0       19.4
    90.0       21.1
    92.0       21.8
```

APPENDIX IX

Sample Calculation of overall mass transfer coefficient of n-butyl acetate in water at 20°C (Batch esterification reaction)

(1) Calculation of the Mean Droplet Diameter:

(a) Using Kolmogoroff's law(187,197)

$$d_{max} = 2 \times \sqrt{2} \left(\frac{\sigma}{k_f \rho_c} \right)^{0.6} \left(\frac{d_a}{u^3} \right)^{0.4} \qquad (1)$$

where

σ = interfacial tension = 9.2 dynes/cm at 21.5% conversion

k_f = constant = 0.5(187)

ρ_c = continuous phase density = 0.75 gm/cc

d_a = diameter of agitator = 3.0 cm

u = agitator tip velocity = $\pi d_a N$ cm/s

N = agitator speed = 1200 r.p.m.

$\therefore\ d_{max} = 0.056$ cm

taking $d_{mean} = 0.7\ d_{max}$(199)

$d_{mean} = 0.039$ cm

(b) Using Rozen's empirical formula (equation 2.24), assuming $n = 0.6$

$$d_{mean} = 2 \times \frac{\sigma^{0.6}}{u} = 0.040 \text{ cm}$$

The mean drop diameter calculated from Kolmogoroff's law and Rozen's formula are in close agreement.

(2) Calculation of the Interfacial Area:

Since the mean droplet diameter was very small, the droplets were considered spherical, hence

$$\text{Interfacial area} = n.4\pi\, d_{mean}^2$$

where n = number of droplets

$$n = \frac{\text{Total volume of dispersed phase in the batch}}{\text{drop volume}}$$

$$= \frac{111}{\frac{\pi}{6} d_m^3} = 3.57 \times 10^6$$

The total volume of the reaction mixture was 466 cc (for a total reaction mixture of 400 grms)

Hence $a = 146\ \text{cm}^2/\text{cm}^3$

(3) Calculation of the Continuous Phase Mass-Transfer Coefficient.

Due to the small diameter of droplets, they are likely to behave like rigid spheres, hence the formula for rigid spheres was applied i.e. Linton and Sutherlands formula(182):

$$Sh = 0.582\,(Re)^{0.5}(Sc)^{\frac{1}{3}} \qquad (2)$$

$$= \frac{k_c d_{mean}}{D_{EC}}$$

where D_{EC} is the diffusion coefficient of ester in the continuous phase (heptane rich phase)

μ_c = 0.006 p.

ρ_c = 0.75 gm/cc

d_{mean} = 0.039 cm

u = 60π cm/sec

Hence

$$(Re)_{drop} = 919$$

$$Sc = \frac{\mu_c}{\rho_c\, D_{EC}}$$

D_{EC} is calculated from Wilke and Chang's formula(56)

$$D_{EC} = 7.4 \times 10^{-8}\left[(\phi M_H)^{0.5}\,\frac{T}{\mu_c V_E^{\,0.6}}\right] \qquad (3)$$

where D_{EC} = diffusion coefficient of solute (ester) in heptane solvent

ϕ = association parameter = 1.0 for heptane(56)

M_H = Heptane molecular weight = 100.2

T = Temperature °K = 293°K

μ_c = viscosity of the heptane solution in cp = 0.60 cp

V_E = molecular volume of the ester at its normal boiling point

V_E is obtained by addition of the Le Bas atomic and group volumes listed in reference(198)

Hence $V_E = 162.8$ cc

$$D_{EC} = 7.4 \times 10^{-8} \left[100.2^{0.5} \times \frac{293}{0.6 \times 162.8^{0.6}} \right]$$

$$= 1.7 \times 10^{-5} \text{ cm}^2/\text{sec}$$

Hence $Sc = \dfrac{0.006}{0.75 \times 1.7 \times 10^{-5}} = 470$

Hence from equation (2)

$$\frac{k_c \, d_{mean}}{D_{EC}} = 0.582(919)^{0.5}(470)^{\frac{1}{3}}$$

$$k_c = 0.060 \text{ cm/s}$$

According to the computer evaluation of the reaction rate constant at 21.5% conversion $a\bar{k}_1\left(\text{i.e } \frac{a}{r_i}\right) = 0.0894$ cm/s

Hence $(K_G)_{THEO} = 0.0358$ cm/s

This compares with a value of $(0.0427)_{EXP}$ cm/s.

NOMENCLATURE

The symbols have the following meanings unless otherwise stated in the text:-

A	Total area of interface, cm^2
a	Interfacial area per unit packed volume cm^{-1}
a =	$(k_1/D)^{\frac{1}{2}}$ in equation (1) of table 3.1
a'	Interfacial area per unit volume of liquid, cm^{-1}
$[A]$	Concentration of component A, moles/litre
B_o	Concentration of B in bulk of liquid, g mole/cm^3
C	Concentration, g mole/cm^3
C	Concentration at depth x and time t in equation (2.5)
C	Constant in equation 2.25
c	Dimensionless concentration
C_o	Bulk concentration, g mole/cm^3
c_o	Initial concentration of the solution in equation 2.5
C_i	Interfacial concentration, g mole/cm^3
C_e	Concentration of the solution corresponding to partial pressure of solute gas in equation 2.5
D	Molecular diffusivity, cm^2/s
d	Diameter of drop, cm
d_a	Diameter of agitator, cm
d_{32}	Sauter mean diameter = $\Sigma i n_i d_i^3 / i \Sigma n_i d_i^2$, cm
d_p	Diameter of a sphere of volume equal to that of a drop, cm.
D_A	Diffusivity of dissolved gas, cm^2/s
D_B	Diffusivity of liquid phase reactant, cm^2/s
D_R	Diameter of rotor disc, cm
D_s	Diameter of stator opening, cm
D_T	Inside diameter of column, cm
D_{ev}	Deviation

$\mathrm{erf}(y)$	$= \frac{2}{\sqrt{\pi}} \int_0^y e^{-z^2} \, dz$
$\mathrm{erfc}(y)$	$= 1 - \mathrm{erf}(y)$
E'	Hypothetical concentration of E in the reactive phase, moles/litre
E^*	Equilibrium concentration of E in the reactive phase, moles/litre
f	Gas absorbed in time t_e, g mole/cm^2
F_r	Froude number = $\frac{u^2}{Lg}$
g	Acceleration due to gravity, cm/s^2
H	Compartment height, cm
H_T	Column height, cm
h	Distance, cm
HTU	Height of transfer unit, cm
J	Molecular diffusion flux, g moles/(S)(cm^2)
k	Mass transfer coefficient, cm/sec
K	Equilibrium constant for a chemical reaction
k_f	Kolmogoroff's constant $\simeq 0.5$
k_1	First-order reaction-rate constant, sec^{-1}
$\bar{k}_1$	Pseudo first-order reaction-rate constant, sec^{-1}
k_2	Second-order forward reaction-rate constant, ℓ/(g mole)(sec)
k_2'	Second-order reverse reaction-rate constant, ℓ/(g mole)(sec)
K_G	Overall mass transfer coefficient, cm/s
k_L	Mass-Transfer Coefficient for liquid phase, including effect of Chemical reaction, cm/s
k_L°	Mass Transfer Coefficient without Chemical reaction effect, cm/s
k_g	Diffusion Coefficient through gas film, cm/s
k_ℓ	Diffusion Coefficient through liquid film, cm/s
L	Average thickness of a surface element, cm Characteristic dimension of turbulence, cm Characteristic distance, cm
m	Distribution coefficient

M	Dimensionless number = $\sqrt{\frac{k_2 B_o D_A}{k_L^{o2}}}$
N	Molecular flux, g moles/s
N	Rotor speed, r/s
n	Number of compartments
n	Mode of oscillation in equation 2.15
O/W	Oil in water
P_e	Peclet number = $\frac{Lu}{D}$
Q	Quantity of gas absorbed by unit area in time of contact t, g mole/cm^2
$\bar{R}$	Average rate of absorption over contact time t, g mole/(cm^2)(s)
R	Rate of mass transfer per unit area of surface, g mole/(cm^2)(sec)
R	Disc diameter, cm
r_i	Interfacial resistance, S/cm
Re	Reynolds number = $\frac{uL}{\nu}$
r	Radius of half-axis length in equation (2.15), cm
r	Ratio of diffusion coefficients = D_B/D_A
$r_{s.d}$	Stable drop diameter, cm
S_c	Schmidt number = $\mu/\rho_D = v/D$
s	Fractional rate of surface replacement, s^{-1}
S	Stoichiometric ratio = B_o/vC_{ai}
S_h	Sherwood number = $k_c d/D$
t	Time, s
T	Temperature, °K
t_e	Time of exposure, s
u	Droplet axial velocity, cm/s
U	Velocity of fluid, cm/s
U	Flow of fluid, ℓ/Min
$\bar{u}_o$	Characteristic velocity, cm/s
u_s	Surface velocity of liquid film, cm/s

u_t	Droplet terminal velocity, cm/s
V	Velocity component in the vicinity of a rotating disc, cm/s
V	Superfacial velocity, cm/s
V_d	Volumetric flow rate of the dispersed phase, ℓ/Min
We	Weber number = $\frac{\rho u^2 L}{\sigma}$
W/O	Water in oil
x	Direction perpendicular to the film surface
x	Raffinate phase concentration, moles/ℓ
x, x_d	Dispersed phase hold-up
y	Distance into liquid film, dimensionless
Y	Extract Concentration, moles/ℓ
y_o	Film thickness, cm
y_i	Distance from interface, mm
z	Dimensionless parameter involving distance in the direction of flow
Z	Height of column, cm
Z	Total number of Compartments
Z_C	Compartment height, cm

GREEK LETTERS

Δ	Film thickness, cm
μ	Viscosity, g/(s)(cm); poises
ν	Stoichiometric coefficient in chemical reaction
ν	Kinematic viscosity, cm^2/s
ρ	Density, g/cm^3
σ	Interfacial tension, dyne/cm
ϕ	Reaction factor, equal to rate of mass transfer in the presence of a reaction to rate without reaction
ϕ_i	Reaction factor for instantaneous reaction
ϵ	Eddy diffusivity, cm^2/s
ϵ	Energy input per unit mass and time
ϵ_c	Effective diffusivity, cm^2/s
ω	Frequency of oscillations, radians/s
ψ	Age distribution function, s^{-1}

SUBSCRIPTS,

A,B,C	Components A,B,C ... respectively; X_{AB} = mole fraction of A in Brich solution
A	Water
B	Acetic Acid
C	n-Butyl alcohol
D	n-Heptane
E	n-Butyl acetate
F	Benzene
G	Carbon tetrachloride
I	Acetone
J	Chloroform
S	Sulphuric acid

SUBSCRIPTS (contd)

c	Continuous
Calc	Calculated
d	Dispersed
E	Extract
EXP	Experimental
F	Feed
FOR	Formula
g,G	Gas
i	Interface, interfacial
ℓ,L	Liquid
max	Maximum
min	Minimum
o	Overall
od	Overall based on dispersed phase
R	Raffinate
THEO	Theoretical
*	Equilibrium condition

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