ADVANCED LIQUID-LIQUID EXTRACTION STUDIES IN A LABORATORY MIXER-SETTLER

by

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

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July 1975

SUMMARY

A ten stage laboratory mixer-settler has been designed, constructed and operated with efficiencies up to 90%. The phase equilibrium data of the system acetic acid-toluene-water at different temperatures has been determined and correlated. Trials for prediction of these data have been investigated and a good agreement between the experimental data and the predictions obtained by the NRTL equation have been found. Extraction processes have been analysed. A model for determination of the time needed for a countercurrent stage-wise process to come to steady state has been derived. The experimental data was in reasonable agreement with this model. The discrete maximum principle has been applied to optimize the countercurrent extraction process and proved to be highly successful in predicting the optimum operating conditions which were confirmed by the experimental results.

The temperature has proved to be a prosolvent for mass transfer in both directions but the temperature profile functioned as an anti solvent.

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Professor G.V. Jeffreys, the Head of the Department of Chemical Engineering for providing the facilities for this research, for his invaluable supervision, for his patience, encouragement and clear vision, and for his continual help and constructive criticism.

The author wishes also to thank

The technical staff of the Department of Chemical Engineering for their assistance.

The typists who participated in typing the thesis.

The University of Aston in Birmingham, for financial support.

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1. Introduction

Liquid extraction is the mass transfer operation in which a solute is distributed between two immiscible phases (74) . The process may be carried out in a number of ways . In most instances , the solution to be treated is contacted intimately with a suitable immiscible solvent which preferentially extracts the desired components. Separations of this sort are essentially physical transfer operations in character , and all the components remain unchanged chemically . Nevertheless , the chemical nature of the liquids strongly influences the extent of separation possible , since the distribution of a solute depends on the extent of nonideality of the solutions involved (47) . Furthermore , the nonideality may be altered to influence the distribution more favorably , for example , by changing the temperature , by addition of salt to "salt out" an organic solute from a water solution , or by adjusting the pH of the solution (47) .

Liquid extraction is an indirect mass transfer operation because it utilizes a solvent , where-as distillation , for example , is a direct mass transfer operation (74) , but because liquid extraction results in a new solution which must in turn be separated , distillation is usually considered initially as the separation process . However , liquid extraction separates primarily according to chemical type , and is therefore capable of separations which are impossible by ordinary distillation . Even solutions which can be separated by distillation , but which are expensive to deal with in this manner may frequently be separated better by liquid extraction (47) .

1.1. Fields of application

Liquid extraction is widely used in many fields as extractive metallurgy , heavy inorganic chemical industry as phosphoric acid and bromine , water desalination , petroleum and petrochemical industries , coal tar industries , and pharmaceutical industries . Review of these processes is found elsewhere (48 , 74 , 75) and this thesis will be devoted to the principles which are common to all the examples quoted .

1.2. Extraction equipment :

Many types of contacting equipment have been developed . They can be broadly divided into two categories:

i) Stage-wise (discrete stage) contactors .
ii) Continuous (differential) contactors , as listed in Table 1.1.

1.3. Choice of contactors :

Generally in selecting the best unit for a particular application one must consider three main criteria ;

i) The number of effective contact stages required.
ii) The throughput .
iii) The residence time .

TABLE 1.1. CLASSIFICATION OF CONTACTING EQUIPMENT

Type of agitation	Stage wise contactors	Continuous contactors
None		1. Wetted-wall towers (74). 2. Spray columns (41,74). 3. Baffle plate columns (74). 4. Packed towers (74).
Rotary devices	1. Simple mixer-settler (50,74). 2. Pump-mix mixer settler (67). 3. Stacked-stage mixer settler (41). 4. Individual stage centrifuges (41,74)	1. Scheibel column (44). 2. Old shue-Rushton column (16). 3. Multistage mixer columns (41,74). 4. Podbielniak extractor (41). 5. Luwesta (41) 6. Rotating dis-contactor (41,74).
Pulsed	Pulsed mixer settler (41).	1. Pulsed columns (41,74).

Each contactor has certain desirable features which may meet a special need . Some of these are : high efficiency , high capacity , low hold-up or low residence time , and the ability to handle extractions where one phase has a very different flow from the other or where emulsification occurs .

A problem occasionally encountered is that the rate of flow of one of the liquid phases is much greater than that of the other . This is a serious limitation in many of the extractors , particularly when the ratio of flows is 10 to 1 or greater . This is a less important problem in mixer-settlers since they can handle such wide flow ratios without difficulty , although in some it is practicable to recycle the phase with the lowest throughput to reduce the disparity between the flow rates . Furthermore mixer-settlers are inherently simple in design and construction and are easy to operate . Because of these features mixer-settlers have found widespread use . However there are some disadvantages to their use in some applications ; the most important of which is that they require large floor space .

In Table 1.2 is summarized the most important design considerations and the process parameters which should be borne in mind before making a final choice of a contactor.

TABLE 1.2. FACTORS DETERMINING THE CHOICE OF A CONTACTOR

Factor	Contactor
1. Number of stages required :	
i) Few (2-3) stages	all types
ii) (10-20) stages	Spray towers (100 ft. height) mixer-settlers
2. Capacity (through-put)	
i) Low or moderate	Spray or packed columns
ii) Intermediate and high	RDC, pulsed columns, or mixer-settlers
3. Solvent residence time	
i) Short	Centrifugal types
ii) Longer	1. Mixer-settlers (settling and phase separation depend on the rate of coalescence of the dispersed phase) 2. Differential contactors (the residence time is a function of the meandroplet velocity and not on the coalescence rate).
4. Phase flow ratio	
i) ϕ_d less than 0.1 of the flow	Mixer-settlers (30)
ii) ϕ_d greater	Other types
5. Physical properties	
i) Small $\left(\frac{\sigma}{\Delta \rho}\right)$	Non-agitated contactors

Contd. TABLE 1.2

ii) Large $\left(\frac{\sigma}{\Delta \ell} \right)$	Mechanically agitated contactors
iii) High viscosities	Mechanically agitated contactors
6. Direction of mass transfer	
i) From solvent to aqueous phase	Mechanically agitated contactors
ii) From the aqueous phase to the solvent	Little information is available
7. Phase dispersion and hold up	
i) If the phase of the highest throughput is to be dispersed	Difficulties may be encountered in column contactors due to irregular shape of the dispersed phase
ii) If a low hold up of one phase is required	Centrifugal contactors
8. Slow reactions	Mixer-settlers
9. Presence of solids in one or both feeds	Pulsed plate column, Luwesta centrifugal extractor, and Graesser contactor
10. Overall performance	
i) Performance index = $\frac{\text{mass of superfacial flow rates at flooding}}{\text{HTU}}$	For continuous differential contactors
ii) Performance index = $\frac{\text{Sum of the volumetric phase flow rates at flooding}}{\text{Total volume of one stage}}$	For stage-wise contactors

1.4. Process optimization :

Before a process can be optimised it is necessary to specify a single variable which must be a maximum (or , in some cases , a minimum) when the process is operating . This optimised quantity may be , for example the production rate or the profit . When a chemical process is to be optimised there are almost certain to be limiting conditions which cannot be changed to any great extent . In liquid extraction processes for example the optimum number of stages and solvent to feed ratio , are dependent on the selectivity of the solvent as well as the costs of the materials and equipment .

1.4.1. Solvent selectivity :

Two important parameters for the comparison of solvents in liquid-liquid extraction processes are the solvent power and selectivity (2 , 74 , 187) . The solvent power (or capacity) is the solubility of the solute in the extract phase in equilibrium with the feed and is determined by the tie line going through the feed composition (189) . Somekh (188) stated that the solvent capacity increases generally as the molecular weight of the solvent increases . This causes the extract ends of the tie lines to be stretched out resulting in a higher solute content in the extract , Weimer and Prausnitz (192) determined the selectivity of a solvent by the ratio of the coefficients of the hydrocarbons dissolved in the solvent and feed . Good selectivity is obtained when this ratio is much greater than unity . Somekh (190) stated that the deviation of the equilibrium curve from the y = x line is a measure of the solvent selectivity . As the deviation of the curve from that line increases selectivity increases . Woodle (187) inter-related both the selectivity and the solvent power in the following way . Thus if s is the volume fraction of oil in solvent phase and R is the solvent to oil volumetric ratio then

$$S = \frac{a}{R^n} \qquad 1.1$$

Where $1 > n > 0$

He stated that the larger the value of a , the greater the solvent power ; the larger the value of n , the greater the selectivity . He also stated that the value of the constant "a" should be mainly a function of temperature , increasing as the temperature is increased until it reaches a maximum value . Fenske et al (2) stated that unless the solvent has relatively large solubility under the conditions of good selectivity the solvent suitability is limited because excessive solvent treatments may be necessary .

Many workers (2 , 3 , 187 _ 193) have studied the factors that can improve selectivity . Somekh (188 -191) discussed the effect of the molecular weight of the solvent , temperature , anti solvents and solvent power on selectivity . He stated (190) that the aromatic selectivity of the glycols decreases with increasing temperature and that there is probably an optimum temperature range within which it is desirable to operate ; probably near the lower limit of this range . Reeves (12) derived two equations for the calculation of the raffinate and extract outlet temperature in a column contactor . He claimed that both outlet temperatures should be below zero but gave no information about the temperature of the intermediate stages . He also stated that a temperature gradient between extraction stages is necessary only when the number of stages is small . When a large number of stages is required the extraction may be conducted at constant temperature without product loss , but his mathematical treatment did not consider the second derivative which would have confirmed the optimum . Also there was no experimental work to support the hypothesis . Fenske et al (2) stated that if the solute is completely miscible with both solvents it cannot be obtained pure by liquid extraction unless some way is found to change the solubility behaviour as the concentration of the solute increases in the extractor . He suggested three ways to produce a purer component ;

i) Lower the temperature successively in the extractor as the solvent phase becomes progressively richer in the extractable component .

ii) Inject an anti-solvent along the main solvent flow path to gradually reduce the dissolving power of the solvent as it flows towards the extract end of the extractor .

iii) Introduce another solvent , incompletely miscible with the main solvent but having a good solubility for the material being extracted , at the extract end of the extractor flowing counter currently to the main solvent . The disadvantage of this double-solvent system is that two solvents , instead of one , must be circulated through the process and separated at appropriate points in the system . Fenske et al (2) recomended the use of liquid ammonia as a pro-solvent in hydrocarbon processing because of its good solvency and selectivity for separating several hydrocarbon types . Furthermore they stated that a three - component system comprised of water , liquid ammonia and monomethylamine enable a great variety of hydrocarbons to be separated . Hutton (193) recommended using water as a second solvent with dimethyl formamide to over come some of its disadvantages in aromatic extraction . Somekh (191) reported that , although the addition of the anti-solvent water improves solvent selectivity , it drastically reduces capacity . Therefore only small proportions of water should be added . Other anti-solvent material could be added which increase the area of immiscibility so that feeds of higher aromaticity can be extracted and higher purity aromatics can be obtained (191) .

2. Stage-wise Contactors (Mixer-Settlers)

2.1. Introduction

Mixer-Settlers are the oldest form of multiple contact equipment and although most tower-type extractors were devised to improve upon this type of equipment , mixer-settlers offer certain advantages .

1) In contrast with countercurrent continuous-contact extractors , in mixer-settlers the degree of dispersion or intensity of turbulence may be established at any desired level through mechanical agitation without fear of "flooding" or reducing the capacity of the equipment . However unsettlable emulsions resulting from excessively fine dispersions must be avoided .
2) Any proportion of the two liquids may be handled easily with either phase dispersed . Also the ratio of the two liquids in the mixer may be controlled independently of the ratio of the flow through the cascades as a whole .
3) It is claimed (74) that suspended solids are more successfully handled by mixer-settlers than by most other extractors but these should have special arrangements for interstage pumping .
4) The common horizontal arrangement of multistage cascade is especially useful when the available headroom is low .
5) The horizontal arrangement makes it possible to

add additional stages at any time should that be necessary .

6) Continuously operated mixer-settlers may easily be shut down for relatively long periods of time without very much affecting the steady state concentration which is useful in case of power cut.
7) A high degree of approach to equilibrium (stage efficiency) is almost always possible and this makes for reliable design .
8) Reasonably reliable scale-up from small to industrial size is possible for at least the simpler designs .

Mixer-Settlers also have some disadvantages such as:

1) Large floor space .
2) High investment .
3) High power costs .
4) Large holdup .
5) Inter stage pumping may be required .

2.2. Mixer-Settler Equipment

The function of a stage is to contact the liquids for mass transfer to occur and for equilibrium to be approached , and to accomplish separation of the phases. The operations may be carried out batch-wise or with continuous flow .

1. Mixers :

These are either :

a. Flow or line mixers with or without mechanical agitation .

b. Agitated vessels with mechanical or gas agitation .

2. Settlers :

These are either :

a. Non-mechanical settlers :

 i) Gravity

 ii) Centrifugal (cyclones)

b. Mechanical settlers (centrifuges)

Settlers are sometimes provided with settler auxiliaries such as :

i) Coalescers or baffles are most frequently used.

ii) Separation membranes . Those should be open meshed and wetted by the dispersed phase .Their disadvantage is that they retard the operation and limit the throughput .

iii) Electrostatic equipment . These are seldom used due to explosive hazards ; also since water must be one of the phases this limits the application .

2.3. Mixers :

In the design of mixers for liquid extraction , the object is to establish the best size and shape of vessel, method of agitation , internal construction and power application to bring about the best rate of extraction at the lowest cost . Full details of the various impellers and their design are given in references (66) and (74). The mixing tank is usually a vertical cylinder with a smooth internal surface but baffles may be fitted . Mixing in a vessel is influenced by :

i) Degree of turbulence .

ii) Rate of circulation , which can be expressed as the time required for passage of the entire contents through a given area-usually the peripheral area swepted out the agitator blades or the orifice of a jet (66) .

The degree of turbulence in an agitated vessel can be correlated with an impeller Reynolds number . Provided that the fluid behaviour in a mixing tank is isotropic the flow is turbulent when the Reynolds number is greater than 10000 . Between Reynolds numbers of 10000 and approximately 300 is a transition range in which flow is turbulent at the impeller and laminar in remote parts of the vessel . When the Reynolds number is less than 300 the flow is laminar (47 , 66) .

2.3.1. The effect of the agitator :

In general the agitator has the following effects :

i) Promotion of mass and heat transfer between phases (74) .

ii) Reduction of concentration and temperature differences (47) .

iii) Production of large interfacial area and small droplets (66) .

The degree of dispersion is a measure of the ability of the mixer to achieve a homogeneous dispersion . The term complete dispersion as defined by Van Heuven and Beek (164) describes a situation in which no large drops are found in any parts of the vessel . A homogeneous dispersion is one in which the concentration of droplets is uniform throughout the whole vessel . The degree of dispersion can be measured by the drop size distribution (55).

2.3.2. Drop size distribution :

Generally in countercurrent flow equipment in liquid-liquid extraction studies the dispersed phase exists as discrete drops (77) and in order to achieve a useful analysis of the extraction data the assumption is often made that the drops are of uniform size . This permits one to estimate the interfacial area and the mass transfer coefficient on the basis of the average drop size from which is obtained the mass transfer rate

$$N = K.A.\Delta C \qquad 2.1$$

However , it is well known that the distributors commonly used in extraction contactors generally deliver a rather wide distribution of drop sizes . Moreover , beyond the inlet there are the competing effects of the generation of new drops due to shear through turbulence in the bulk flow and droplet coalescence due to drop interaction effects . Depending upon the characteristics of the particular contactor there will be a balance of these processes so that at a distance considerably removed from the feed inlet two limiting situations may arise; a distribution of drop sizes and drop residence times (little drop interaction) , or a size distribution of drops all essentially of the same age (equal probability of repeated coalescence and redispersion among drops of all sizes) . This size distribution may be considered to be bounded by an upper limit or maximum stable size (77) and a lower limit or minimum size depending upon the break-up processes prevailing .

The maximum drop size in a turbulent liquid is governe by the Weber number which is the ratio of the dynamic pressure of the liquid which tends to break up the drop and the interfacial tension forces that tend to resist rupture . Thus , when two immiscible liquids are agitated a dispersion is formed in which continuous break-up and coalescence of droplets occur until , after a short time, a dynamic equilibrium is established between the break-up and coalescence processes . This results in a distribution of drop sizes which , together with the mean drop size , depends on the type and extent of agitation and the physical properties of the liquids . If the extent of agitation is sufficient to maintain a uniform level of turbulence throughout the vessel the mean drop size and drop size distribution will be the same throughout . Otherwise clusters of drops of different size will exist in different parts of the vessel . However , for every physical system and set of conditions there must be a stable drop size . Drops larger than this will tend to break-up whereas smaller drops will tend to coalesce (75) .

2.3.3. Prediction of droplet size :

Droplet sizes in fully baffled stirred tanks have been studied extensively . Theoretical analysis of droplet break-up have resulted in predictions of minimum , mean and maximum droplet diameters (56 , 58 , 78 , 141 , 149) . Caution is needed in using these correlations since they do not generally agree with each other due to the different systems and equipment used . These correlations have been mostly based on the theory of local isotropy by Kolmogoroff (58) and by Hinze (141) . Turbulence in stirred tanks is definitely not isotropic but isotropy of the main flow is not necessary for local isotropy to exist . Kolmogoroff makes only two assumptions for local isotropy :

i) A high Reynolds number of the main flow .

ii) The width of the fluid ejected by the agitator should be larger than the scale of the energy dissipating eddies .

Both conditions apply frequently in stirred vessels . In the dispersion of two liquids by turbulent agitation break-up is not the only mechanism taking place but coalescence of droplets might also occur (17 , 58 , 140) .

Methods of measuring coalescence rates in agitated tanks have relied mainly upon following the rate of spread of a tracer due to coalescence and mixing in the drops of the dispersed phase . Madden and Damerell (56) followed the spread of Sodium thiosulfate among water drops dispersed in toluene by measuring the rate of reaction with iodine in solution in the continuous phase . Miller et al (17) followed the spread of a dye in an organic phase dispersed in water . On the other hand Groothuis and Zuiderweg (57) measured coalescence rates by feeding two organic liquids with densities greater or less than the continuous water phase continuously fed to an agitated tank , and measuring the amount of the light phase converted to heavy phase as a result of coalescence . Howarth (143) stated that the tracer may modify coalescence behavior to an unknown extent .

In the absence of specific factors preventing coalescence (protective colloids , surface active agents) , it is assumed that coalescence and break-up of drops proceed simultaneously but independently . Eventually a mean drop size is established which remains constant and is determined by the two opposing processes coalescence and break-up . If the impeller speed is changed , the mean drop size will also change until it reaches the new steady state value associated with the new impeller speed. The addition of small quantities of simple ectrolytes- which are considered to be surface inactive - to the continuous phase was found to cause a marked reduction in coalescence frequency (143) . Increasing temperature aids coalescence by promoting film and reducing inter-facial tension (143 , 197) .

Madden and Damerell (56) derived a model considering coalescence and break-up and stated that the mean droplet diameter in a dispersion was 70 % of the maximum size predicted by Hinze (141) .

$$d_{max} = C\left(\frac{\sigma}{\rho_c}\right)^{0.6} . E^{-0.4} \qquad 2.2$$

Where C = a const. = 0.25 for a propeller or a turbine agitator .

Sprow (54) found that considering coalescence and break-up .

$$d_{mean} = 0.38 \quad d_{max}. \qquad 2.3$$

2.3.4. Measurement of droplet diameter

Several methods have been used for measuring drop size . These are :-

1) Light transmittance (24 , 25) . While ideal for the determination of average drop surface area does not yield satisfactory size distribution data and must be

largely restricted to dispersions having drop diameter greater than 50 microns (24) .

2) Light scattering technique (55) . Light passing through a dispersion is scattered and there is a relationship between the intensity of light scattered at any angle from the incident beam and the size of the particles that causes scattering (55) .

3) Photomicrographic methods (55) . These require the preparation of slides and necessitate the addition of drop-stabilizing agents to the dispersions . Dynamic photomicrographic methods pose a serious problem of field depth through windows on the sides or bottom of the tanks.

4) Electronic particle Counter (54) : Sprow (54) used a coulter Counter to measure the drop size distribution. This instrument determines both the number and size of emulsion particles suspended in an electrically conductive continuous phase by forcing the emulsion through a small aperture between two electrodes . The resistance between the elctrodes changes as a particle passes through the aperature and this change is converted to a voltage pulse in the instrument . These pulses are approximately proportional to particle volume and therefore the diameter corresponding to a particle count can be determined . Coincidence corrections must be applied to account for the probability of two or more particles traversing the aperture simultaneously . The instrument must be calibrated with particles of known size and the continuous

medium must be moderately conductive . The use of electronic counting provides a rapid and accurate (54) method for determination of drop size distribution but necessitate the addition of undesirable conductive materials to the dispersion (55) .

2.3.5. Effect of temperature on droplet size distribution:

The droplet size distribution is very sensitive to temperature changes . Valentas and Amundson (140) found that for a temperature change from 30° to 70°C there was a decrease in interfacial area by 18 % . Maximum drop size varied with temperature . Over the temperature range considered the coalescence efficiency increased two fold with a corresponding increase of 50 % maximum drop size .

2.3.6. Power for agitation

The power for agitation is dependent upon the following factors :

1) Type of impeller .
2) Speed of rotation .
3) Physical characteristics of the fluids .
4) Shape of the container .
5) Relative location of all component parts of the systems such as baffles , coils and supports .

White et al (79) stated that it is possible and advantageous to correlate the performance of mixing impellers by the use of dimensional analysis . Rushton et al (69) stated that the most useful correlations of impeller performance and its effect on mixing can be made by plotting N_p Vs. N_{Re} to give a characteristic curve of the impeller . For example See Fig 2.1 .

Physical properties of the system , the impeller dimensions , its speed of rotation , the vessel diameter , the liquid depth , and the number of baffles influence the power required for agitation . A detailed account of these factors and their effect on power requirements is to be found in Reference (70) .

2.3.7. Mixer Efficiency :

A decisive factor for evaluating the efficiency of a mixer is the drop-size distribution attained after a certain time . A measure of the homogenizing effect of the mixer is either the standard deviation of the composition of samples withdrawn after the specified time or the so called degree of mixing . Fox and Gex (83) define the degree of mixing as the uniformity of composition which is desired in the finishing mix .

Sleicher (21) calculated the mixer efficiency in terms of Murphree efficiency and extraction factor . Chapman and Holland (84) determined the mixing efficiency from the time to disperse a given quantity of dye solution throughout a vessel containing a given volume of liquid . Davis and Colven (101) determined the mixing

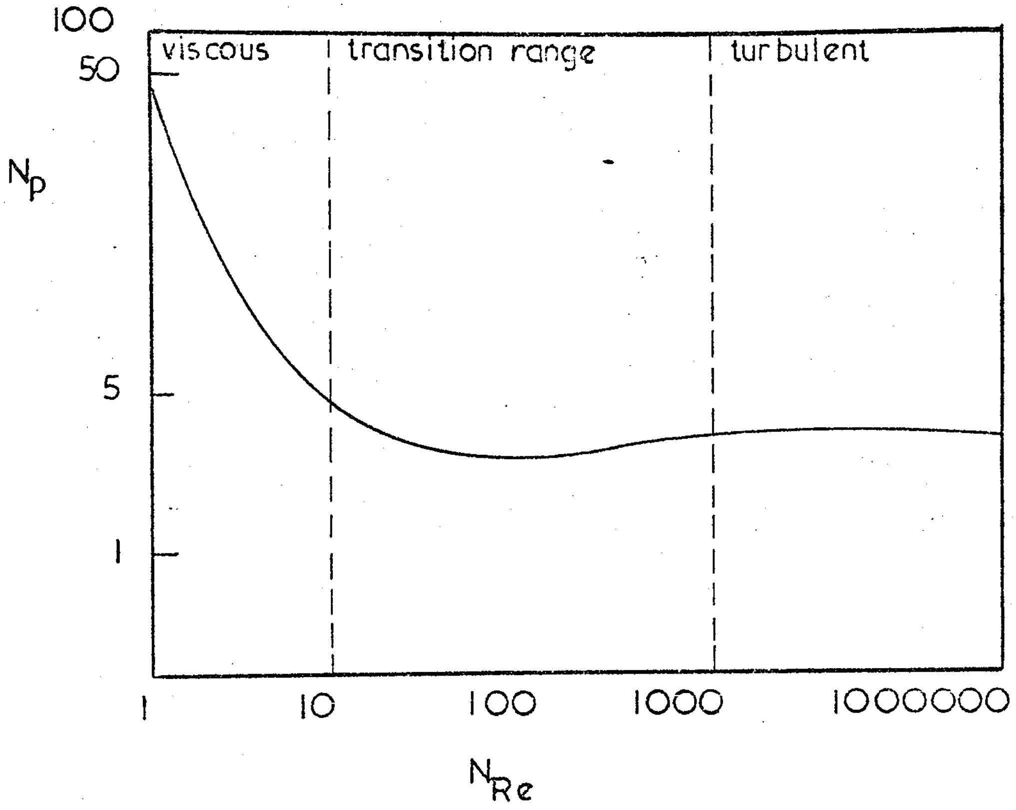


Fig. 2.1. Power number, Reynolds number plot

efficiency by a heat transfer technique . The difference in temperature of the two phases after mixing compared with the temperature difference before mixing was used as a measure of how efficiently the two phases had been contacted . Danckwerts (85) developed the idea of hold-back and segregation based on the residence times distribution function and from which the mixing efficiency can be calculated . Cerro and Parera (102) used the residence time distribution function as a criterion to measure the degree of mixing .

2.3.8. Mass transfer rates :

In general it is assumed that the process of mass transfer in liquid-liquid systems consists of three relatively simple steps ;
diffusion of solute molecules from the bulk of the raffinate phase to the interface , passage across the interface and diffusion into the bulk of the extracting solvent . Accordingly , calculation of the mass transfer rate in extraction requires a knowledge of the resistance to transfer in each phase .

2.3.8.1. Mass-transfer Coefficients

The rate of mass transfer in any process depends on the coefficient of mass transfer , the interfacial area and the driving force and is expressed by the general rate equation 2.1 .

The mass transfer coefficient K embodies the characteristics of the laminar-and turbulent-flow regions of the flows of each phase and the molecular and eddy diffusivities in whatever proportions they may occur . Two major theories are applied to explain mass-transfer coefficients : viz the film theory and the penetration or surface-renewal theory (74) . In practice neither the film nor the penetration theory provide an entirely satisfactory description . Mass transfer of solute occurs across the interface separating the immiscible liquids and will continue until the chemical potential , or activity of the solute is the same in both phases and equilibrium is established . The concentrations of the solute in the two phases are not the same although the concentrations in each phase could be uniform . Generally there will be a concentration discontinuity at the interface . In an actual extraction the two phases are not in equilibrium although equilibrium will exist at the interface . That is , it is generally accepted that there is no resistance to mass transfer across the interface but there will be resistance to mass transfer in each of the phases so that at steady state there will be a rate expression for each phase . Thus :

$$N_A = k_R\,(C_R - C_{Ri}) = k_E\,(C_{Ei} - C_E) \qquad 2.4$$

The relation between the individual coefficients of mass transfer is given by

$$\frac{1}{K_R} = \frac{1}{k_R} + \frac{1}{mk_E} \qquad 2.5$$

In terms of the overall mass transfer coefficient , the rate of mass transfer of the solute between the liquid phases , N_A , is described by equation 2.1.

Mass transfer of a solute between a dispersed phase and a continuous phase can be considered as a transfer between systems of spheres and surrounding liquid . A promising start towards a theory for mass transfer in such systems is the study of mass transfer between a single sphere and surrounding liquid ; since the rate expression for mass transfer from an isolated sphere occasionally will approximate the rate for a sphere in a multisphere system (135) .

Mass transfer between a single drop and surrounding fluid is usually divided into three parts :

1) Mass transfer inside the droplet .
2) Mass transfer through the interface .
3) Mass transfer outside the droplet through the surrounding fluid .

2.3.8.2. Mass transfer inside the droplet :
Dispersed phase coefficient :

There are three distinct stages that must be considered in the study of the mechanism of solute transfer to or from a drop in solvent extraction processes . These are:

i) Drop formation at the nozzle or spray tip

ii) Drop movement through the continuous phase

iii) Drop coalescence at the interface

Numerous investigations (43 , 80 , 81 , 96 , 122) have been undertaken in the constant velocity region . Stages (i) and (iii) , often termed end effects are sometimes neglected in practical extraction . In fact end effects may sometimes effect the transfer to a considerable degree and should be taken into consideration .

2.3.8.3. Mass transfer during drop formation :

Attempts to measure the amount of solute extracted as the drop is formed before its release from the nozzle was first made by Sherwood , Evans , and Longcore (133 , 195) . They reported that 40 - 45 percent of the solute is extracted before the drop leaves the nozzle . West and Robinson (130) used similar equipment and similar procedures to those used by Sherwood et al (195) and reported that only 14-20 % extraction occured during drop formation . Nandi and Viswanathan (144) reported that 45 % extraction in spray columns takes place during drop formation . A comprehensive study about the end effects in an extraction column have been done by Johnson and Hamielec (96) .

The conditions under which solute transfer is occuring during the formation of a single drop from a submerged nozzle in a stationary solvent phase are probably as follows (80) . While the drop is in the process of being formed the interior must be in rapid motion and of relatively uniform concentration . The surrounding continuous phase undergoes viscous displacement due to the expansion of the drop . Hence , there is no film in the drop , or rather a "film" of infinite extent surrounds the drop . Mathematical analyses of this mechanism is given in references (80 , 96) .

Heertjes et al (94) by assuming Higbie's equation (134) for transient diffusion into the surface of a drop as it is formed developed the following equation for mass transfer during formation :

$$\frac{C_0 - C_1}{C - C^*} = \frac{20.6 \, (Dt)^{\frac{1}{2}}}{d} \qquad 2.6$$

While Licht and Pansing (80) proposed the following expression

$$\frac{C_0 - C_1}{C_0 - C^*} = \frac{2.9 \, (Dt)^{\frac{1}{2}}}{md} \qquad 2.7$$

While these two models indicate that the extraction during drop formation depends on the drop size and time of formation , Licht and Conway (43) and Licht and Pansing (80) found that the percent solute extracted in their column was independent of drop size and drop formation time . They concluded (130) that the amount of extraction occuring during drop formation is sufficiently small so that the experimental results do not detect the variation of this extraction with drop formation time and drop size . Finally experiments carried out in these laboratories indicated that about 10 % of the mass transfer occurs during drop formation under extraction conditions .

2.3.8.4. Mass-transfer during passage through the continuous phase :

Many workers (43 , 80 , 81 , 96 , 122 , 136) have studied extraction mechanisms during the flow of the drop through the continuous phase . The mass transfer process depends on whether the liquid inside the drop has

I . no internal motion .

II. internal circulation .

or

III. The drops oscillate .

Each will be discussed .

I. Rigid drops . Solution of the unsteady - state diffusion equation (80 , 81 , 122 , 136) for a quiescent, homogeneous , spherical drop of diameter d and constant diffusivity D is

$$\frac{C_o - C_1}{C_o - C^*} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} . \exp\left(- \frac{4\pi^2 n^2 D t}{d^2}\right) \qquad 2.8$$

from which

$$k_d = - \frac{d}{6t} . \ln \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left\{ \frac{1}{n^2} . \exp\left(-\frac{4\pi^2 n^2 D . t}{d^2}\right) \right\} \qquad 2.9$$

II. Drop with internal circulation : The liquid inside a drop moving in a viscous continuous phase tends to circulate due to the shear stresses at its interface

(18 , 126) . As a result of this circulation the transfer rate is increased by a factor proportional to Prandtl number compared with the rigid drop (136) . Circulation increases with drop size and the viscosity ratio of the two fluids . The Reynolds number at which circulation begins within the drop decreases with increasing viscosity of the continuous phase (19) . Garner and Skelland (22) suggested a correlation for the critical Reynolds number for determining the onset of circulation , but it is rather unreliable since circulation is highly dependent on the purity of the fluid and on the presence of surface-active impurities (126 , 135) . The lower the interfacial tension , the lower the transition Reynolds number (23) , and the higher the overall coefficient . For a drop with a high surface tension and appreciable surface tension gradient at the interface circulation is greatly retarded . For a given system , the effect of surface tension gradient increases with decreasing drop diameter , and below a certain size circulation is reduced or arrested with the transfer coefficients approaching the "rigid drop" regime . According to Savic (160) - in the presence of surface active agents an immobile cap forms at the rear of the drop and circulation is confined to the front part , since velocities in the vicinity of the rear stagnation point are relatively small .

An interesting point regarding the aging of circulating drops was also observed by Deindoefer and Humphrey (161) . Experiments showed that the transfer coefficients of drops 1-2 sec. old were in agreement with those obtained from the theories of Higbie (134) and Boussinesq (18) whereas coefficients of drops 6 sec. old were close to those predicted by the rigid drop theories . This could be due to the accumulation of surface active material on the surface of the drop .

Internal circulation is believed to also reduce the thickness of the outside boundary layer thereby appreciably increasing the transfer coefficient of the continuous phase .

The equations of fluid motion inside and outside a drop with circulation under viscous flow regime have been solved by Hadamard (136) . Kronig and Brink (127) employed these functions and derived equations for temperature distribution and heat transfer inside a drop with internal circulation . Their equations were similar to equation 2.8 and based on the assumption that the time required for a liquid particle to pass around a stream line within the drop and return to its starting point is very much smaller than the time constant for diffusion . Disregarding outside film resistance they obtained the following equation for the transfer efficiency

$$\frac{C_o - C_1}{C_o - C^*} = 1 - \frac{3}{8} \sum_{n=1}^{\infty} A_n^2 \exp \left(- \frac{\lambda n . 64 \, D . t}{d^2} \right) \qquad 2.10$$

from which the mass transfer coefficient becomes

$$k_d = -\frac{d}{6t} \ln \frac{3}{8} \sum_{n=1}^{\infty} A_n^2 \exp\left(-\frac{\lambda n.64.D.t}{d^2}\right) \qquad 2.11$$

West (130) derived a simplified correlation , which is :

$$k_d = 1.13 \ \rho_c \left(\frac{D}{t_e}\right)^{\frac{1}{2}} \qquad 2.12$$

III. Oscillating Drops . Handlos and Baron (129) super imposed a turbulence due to random radial motion upon a circulatory pattern . They derived an expression which they assumed would represent an oscillating drop . Although Stagnant droplet data gave good agreement with the Newman relationship 2.8 and fully circulating droplets agree with the Kronig and Brink expression 2.10 mass transfer coefficients for oscillating drops deviate signifficantly from the prediction of the Handlos and Baron model (129) . Rose and Kintner (122) studied five organic-water systems at Reynolds numbers greater than 200 where oscillations of droplets would most likely occur . They reported that oscillatory motion causes interfacial stretch and its accompanying variation in the driving force results in a very large increase in the rate of mass transfer . They found a satisfactory agreement between their data and their model (122) . Angelo , Lightfoot and Howard (1) developed a model which they claimed to be a generalization of the penetration theory which gave slightly lower predictions of mass transfer rates than that of Rose and Kintner (122) which they considered a special case from their general model . They claim that their model is much simpler than that of Rose and Kintner . HOwever , this model (1) needs the calculation of an amplitude factor which is very difficult to assess and limits its application .

Rose and Kintner's correlation is :

$$k_d = 0.45\ (Dw)^{\frac{1}{2}} \qquad 2.13$$

where

$$w = \left(\frac{\sigma b}{r^2}\right)\ \left(\frac{1}{3\rho_d + 2\rho_c}\right) \qquad 2.14$$

and $b = 0.805\ d^{0.225}$ 2.15

A summary of the correlations derived for the dispersed phase is given in Table 2.1 .

2.3.8.5. Resistance to transfer at interface :

Interfacial resistance mechanism (80) assumes that there is undefined resistance to solute transfer at the interface between the continuous and dispersed phase . This resistance may be in the form of a chemical or physical barrier to the transfer of solute molecules . The resistance offered by the interface to mass-transfer could be due to a reduction in the circulation by the formation of an absorbed film of impurities , dirt or surface active material . The interfacial resistance might be influenced by temperature changes at the interface owing to differences in the heats of solution of the solute in the two phases (74) . This can alter the local

TABLE 2.1

INSIDE TRANSFER EQUATIONS

Ref.	$\frac{C - Co}{C^x - Co}$	Description	Derivation
(122)	$1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-\pi^2 n^2 Dt}{R^2}\right)$	rigid sphere $hc = \infty$ $Tc = const.$	Conduction equation
(150)	$\left(1 - \exp\left(-\frac{\pi^2 D t}{R^2}\right)\right)^{0.5}$	ditto	Empirical derived from that of (122)
(88)	$1 - 6 \sum_{n=1}^{\infty} A_n \exp\left(-\frac{\lambda^2 n Dt}{R^2}\right)$	rigid sphere $hc \neq \infty$ $Tc = const.$	Conduction equation
(90, 94 and 95)	$1 - \frac{3}{8} \sum_{n=1}^{\infty} A_n^2 \exp\left(-\frac{\lambda n 16Dt}{R^2}\right)$	drop circulation $hc = \infty$ & $hc \neq \infty$ $Tc = const.$ $\sigma = o$ and $Rc < 1$	Hadamard stream function
(137)	$\left(1 - \exp\left(-\frac{2.25 \pi^2 Dt}{R^2}\right)\right)^{0.5}$	drop circulation $hc = \infty$ $Tc = const.$ $10 < Re < 200$ and $6 < Pr < 3000$	Empirical, derived from that of (250 and 255)
(86)	$1 - 2 \sum_{n=1}^{\infty} A_n^2 \exp\left(-\frac{\lambda n D \, Pe d t}{512R^2}\right)$	drop circulation allowed with a radial motion $hc = \infty$ $Tc = const.$ $Re = 1000$	Einstein equation

CONTD. TABLE 2.1 INSIDE TRANSFER EQUATIONS

Ref.	$\frac{C - Co}{C^x - Co}$	Description	Derivation
(142)	$1 - 6 \sum_{n=1}^{\infty} An \exp \left(- \frac{\lambda n^2 \bar{R} D t}{R^2} \right)$	drop circulation or oscillation 10<Re<120 315<Re<620	Emperical derived from that of (88)
(142)	$0.905 \sqrt{\frac{R\pi^2 D t}{R^2}} + 0.0189$ $1 - 6A_1 \exp \left(- \frac{\lambda^2 \bar{R} D t}{R^2} \right)$	drop circulation or oscillation E < 0.5 E > 0.5	Derived from the previous equation of (142)

distribution coefficient and the physical properties affecting the coefficient .
Kintner (151) stated that if a chemical or thermal difference along an interface causes an interfacial tension gradient violent flow in the direction of low interfacial tension will result . This is termed the Maragonic effect and such an effect can increase the mass transfer rate by 10 times or decrease it by 50% according to the system and this could be interpreted to be an interfacial resistance (151) .

2.3.8.6. Mass-transfer outside the droplet - Continuous phase Coefficient .

Hanson (75) stated that , although the various factors during the different stages of drop life have been recognized for the dispersed phase , it is less true for the continuous phase . Transfer from the bulk of the continuous phase to the drop interface can be considered to take place across a laminar film moving over the drop surface . Outside this film the continuous phase is well mixed and at the bulk concentration and temperature . West (80) suggested the following model to predict the continuous phase coefficient :

$$N_u = 1.13 (Pe)^{0.5} \qquad 2.16$$

Treybal (118) also developed a correlation to estimate the continuous phase coefficient but it does predict values that were inconsistent with experimental

measurements of overall coefficients .
The continuous phase mass transfer coefficient has been studied by many workers (92 , 94 , 126 , 131 , 137) for drops in which the liquid inside is circulating . Some correlations obtained were empirical (92 , 126) while others have some theoretical basis . A summary of these correlations is given in Table 2.2. The most widely accepeted formula is that of Garner , Foord and Tayeban (137) which is :-

$$\frac{K_c \cdot d}{D_c} = 126 + 1.8\ Re^{0.5}\ Sc^{0.42} \qquad 2.17$$

This model was based on the postulation that internal circulation thins the boundary layer around the droplet to a thickness between that for a solid sphere and a sphere in potential flow as implied by the penetration theory .

Some of the factors affecting the continuous phase mass-transfer are summarized in Table 2.3 (40 , 97 , 100).

2.3.8.7. The distribution Coefficient :

The Nernst distribution law (82) is limited to cases in which the molecular weight of the solute is the same in each phase and that the two solvents must remain immiscible even after the addition of the common solute . Then Nernst expanded his distribution law to include cases of association or dissociation . One of the first systems investigated by Nernst was the distribution of

TABLE 2.2 EQUATIONS FOR OUTSIDE NUSSELT NUMBER

Reference	Nu_c	Re_c	Pr_c	Pe_c	Description	Derivation
(87)	$2(1 + \frac{Pe}{4} + \frac{Pe^2}{12} + \ldots)$	< 1		< 1	rigid, laminar flow, thick thermal boundary layer	Boundary layer theor Stokes stream function
(87)	$0.89\ (Pe)^{\frac{1}{3}}$	< 1		$> 10^3$	rigid, laminar flow thin thermal boundary layer	" "
(89)	$0.978(Pe)^{\frac{1}{3}}$	< 1		$> 10^4$	"	"
(98)	$2(1 + 0.16\ Pe^2)$	< 1		< 1	rigid, laminar flow	Perturbation method
(91)	$2(1 + 0.25\ Pe + 0.15\ Pe^2$	< 1		< 1	"	"
(131)	$0.89\ Pe^{\frac{1}{3}} \left(\frac{\mu_d + 1.33\mu_c}{\mu_d + \mu_c}\right)^{\frac{1}{3}}$	< 1		$>> 1$ $<< 24(3\frac{\mu_d}{\mu_c} + 4)^2 (\frac{\mu_d}{\mu_c} + 1)$	rigid, laminar flow thin thermal layer	Hadamard stream function
(136)	$1.075(Pe)^{\frac{1}{3}}$	< 1		-	rigid	Boundary layer theory and Empiricism

CONTD. TABLE 2.2 EQUATIONS FOR OUTSIDE NUSSELT NUMBER

Reference	Nu_c	Re_c	Pr_c	Pe_c	Description	Derivation
(136)	$2 + 0.55(Re)^{\frac{1}{2}}(Pr)^{\frac{1}{3}}$	2 - 1000	1		rigid	Boundary layer theory and Empiricism
(103)	$2 + 0.54(Re)^{\frac{1}{2}}(Pr)^{\frac{1}{3}}$	50 - 350	1		"	"
(104)	$2.1 + 0.42(Re)^{\frac{1}{2}}(Pr)^{\frac{1}{3}}$	50 - 1000	1		"	"
(123)	$2.83 + 0.6(Re)^{\frac{1}{2}}(Pr)^{\frac{1}{3}}$	50 - 1000	1		"	"
(136)	$2 + 0.57(Re)^{\frac{1}{2}}(Pr)^{\frac{1}{3}}$	0 - 2500	1		"	"
(124)	$2 + 0.95(Re)^{\frac{1}{2}}(Pr)^{\frac{1}{3}}$	60 - 660	1100-2200		"	"
(136)	$44 + 0.59(Re)^{\frac{1}{2}}(Pr)^{\frac{1}{3}}$	0 - 20	1100-2200		"	"
(136)	$0.8(Re)^{\frac{1}{2}}(Pr)^{\frac{1}{3}}$	$1 << - < 10^4$	-		"	"
(136)	$2 + 1.31(Pr)^{0.15} + 0.66(Re)^{\frac{1}{2}}(Pr)^{\frac{1}{3}}$	90 - 1500	0.4 - 1000		"	"

CONTD. TABLE 2.2 EQUATIONS FOR OUTSIDE NUSSELT NUMBER

Reference	Nu_c	Re_c	Pr_c	Pe_c	Description	Derivation
(136)	$0.43(Re)^{0.56}(Pr)^{\frac{1}{3}}$	$440 - 10^5$	1		rigid	Boundary layer and Empiricism
(137)	$0.43(Re)^{0.56}(Pr)^{\frac{1}{3}}$	1 - 200	3000		"	"
(125)	$0.43(Re)^{0.56}(Pr)^{\frac{1}{3}}$	$800 - 10^4$	1000-3000		"	"
(136)	$1.5(Re)^{0.35}(Pr)^{\frac{1}{3}}$	4 - 400	1		"	"
(136)	$(1.2+0.53\,Re^{0.54})$ $(Pr)^{\frac{1}{3}}(\frac{\mu d}{\mu c})^{\frac{1}{4}}$	1-300000	2 - 380		"	"
(136)	$1.13(Pe)^{\frac{1}{2}}$			large	Irrational flow	Potential flow theory
(94)	$(12/\pi)^{0.5}(Pe)^{0.5}$			"	drop circulation	Simplified boundary layer theory
(131)	$0.67(Pe)^{0.5}(\frac{\mu c}{\mu c+\mu d})^{0.5}$	< 1		$>> 2.4(3\frac{d}{c}+4)^2$ $(\frac{\mu d}{\mu c}+1) >> 1$	"	Hadamard stream function

CONTD. TABLE 2.2 EQUATIONS FOR OUTSIDE NUSSELT NUMBER

Reference	Nu_c	Re_c	Pr_c	Pe_c	Description	Derivation
(126)	$-126 + 1.8(Re)^{0.5}(Pr)^{0.42}$			large	drop circulation	Empirical
(92)	$-178 + 3.62(Re)^{0.5}(Pr)^{\frac{1}{3}}$	50-800		"	drop, with and without circulation	Empirical

TABLE 2.3 FACTORS AFFECTING Kc BY THREE DIFFERENT AUTHORS

Factor	(40)	(97)	(100)
Re. of the impeller	$Kc\ av = m(Re.10^{-4})^n$	Kc increases as Re increases	-
Diameter d	Kc increases as d increases	-	-
Coalescence	Kc increases with coalescence	-	-
Baffles	Decrease KC	-	-
Drop size d_p	-	no effect	For small particles Kc is inversely proportional with d_p. For larger particles $> 200\mu$, Kc is independent on d_p.
Density difference	-	no effect	No effect below 0.4 gm/c.c. but at higher values : $Kc = f(\Delta \ell)^{0.3-0.4}$
D/T	-	negligible	Kc increases as this ratio increases
Vessel size	-	Kc increases as the vessel size decreases.	-

CONTD. TABLE 2.3 FACTORS AFFECTING Kc BY THREE DIFFERENT AUTHORS.

Factor	(40)	(97)	(100)
Diffusivity D	-	no effect	Kc is proportional to D.
Fluctuation on velocity	-	Kc is proportional to it.	-
Impeller speed N	-	$Kc=f(N)^{0.87}$	(i) For $d_p < 100\mu$, $Kc = f(N)^{0.5}$ (ii) For $d_p > 100\mu$, $Kc = f(N)^{0.3}$
Stirrer location	-	-	no effect
Viscosity	-	no effect	small effect (i) For large particles $Kc = f(\mu)^{-0.22}$ (ii) For small particles $Kc = f(\mu)^{0.06}$

acetic acid between water and benzene . The expression , (C_1^2 / C_2) was found to be much more constant than (C_1 / C_2) in concentrated solutions .Neither ratio was found to be constant for the low concentrations studied. The distribution of acetic acid in different solvents was studied by many workers (80 , 147, 148 , 175 , 181, 182) . There is a general agreement that the distribution of acetic acid in a solvent varies with concentration due to association and splitting up of the acid molecules . According to Farmer (178) the degree of association or dissociation of the acid differs from one solvent to the other .

The distribution coefficient can be determined from an accurate knowledge of phase-equilibrium relationships. These data can serve also for the determination of the quantities of solvent required and the driving forces determining the rates of mass transfer .
If the activities can be correctly expressed as functions of concentration , the equilibrium can be predicted . With the present state of knowledge (47) , it is not generally possible to do this well enough to rely upon the predicted equilibrium for extractor design but for purposes of choosing possible solvents and in the absence of data it is possible to make useful predictions of the general trend of the equilibrium and to check the reliability of an available data .

Generally it should not be expected that very good agreement is obtained between the thermodynamic and the experimental data for every system . Joy and Kyle (132) stated that reasonable predictions of liquid-liquid equilibria for type 1 ternary systems from binary data alone cannot be expected when the ordinary two-parameter activity coefficient equations are used . Kenny (99) also found his calculated results were not in agreement with experimental data . Some other workers (162 ,163 , 166) reported poor agreement between calculated and experimental results for type 1 while for type II systems the data may be in good agreement .

The activity coefficients can be determined by using an equation derived by integration of the Gibbs-Duhem equation (74) . The recomended equations for liquid-liquid systems are Wilson's equation and NRTL equation (167 , 185) .

Distribution coefficients for a given system can be expected to change with temperature because of the change in the solubility and tie lines compositions . For some systems the effect of temperature on distribution may be slight (38) . Treybal (74) tried to regularize the change in distribution coefficient with temperature by assuming that the change in mutual solubility of the solvents is negligible but his correlation is difficult to apply .

2.3.8.8. Interfacial area

The interfacial area , a factor which greatly affects the rate of mass transfer in liquid extraction is very much related to the drop size discussed above . Most of the work (24 , 49 , 61 , 62 , 63 , 64 , 65 , 68 , 72 , 73 , 77) reported in the literature regarding interfacial area has been obtained under conditions where no mass - transfer occurs and a summary of the results published on interfacial area , with the pertinent details of the equipment used and the range of variables investigated , is given in Tables 2.4 , 2.5 . There it will be seen that there is a considerable discrepancy concerning the effect of variables such as speed of the agitator , dimensions of the agitator , Weber number and dispersed phase hold-up.

The interfacial area has been estimated by a number of different techniques . These may be summarised as :

1) By light transmittance (24 , 25 , 63) .
2) By measuring the light produced by scintillators activated by transfer across the interface of the alpha and beta particles from radioactive disintegration .
3) By photography(76) .
4) By electronic counting (60) .
5) By using a sedimentometer (64) .
6) By liquid extraction accompanied by fast pseudo-first order reaction (52) .

TABLE 2.4

SOME LITERATURE DATA ON INTERFACIAL AREA

Ref.	Range of variables				Method of Measuring A	Type	No. of blades	N	D	Ø	Weber No.	σ
	N (rev/min)	D/T	T (cm)	Ø								
(63)	100-500	-	25-50	0.1-0.4	Light transmission	Paddle	4	1.2	0.8	0.5	0.6	-0.6
(24)	60-1200	-	15-50	0.5	Photography and Light transmission	Turbine	6	0.72	1.0	-	0.36	-
(77)	-	0.33-0.66	17-38	0-0.2	Light transmission	Paddle	4	1.2	0.8	1	0.6	-0.6
(65)	-	0.1-0.7	20-30	0.075-0.4	Photography	Propeller	3	1.0	1.65	0.32	0.56	0.56
(64)	-	0.33	20-40	0.05-0.35	Sedimentation and Photography	Turbine Paddle Propeller	6 6 3	1.11	0.7	0.84	0.5	-0.5
(61)	-	-	-	-	Local isotropy	-	-	0.75	0.5	-	-	-
(72)	400-1200	0.27-0.67	15-40	0.4	Light transmission	Turbine and Propeller	-	1.2	2	-	-	-
(49)	-	-	18	0.1-0.5	Photography	-	-	-	-	1	-	-
(62)	100-900	0.5	10-30	.004-0.5	Photography	Turbine	6	1.9	0.95	-	0.75	-0.75
(68)	-	0.5	12-30	-	Light transmission	Paddle	2	-	-	-	-	-
(73)	300-700	0.3-0.5	15	0.082	Conductivity	Turbine	6	2.1	-	-	-	-

TABLE 2.5 A COMPARISON BETWEEN STUDIES TO SHOW THE EFFECT OF VARIOUS FACTORS ON THE INTERFACIAL AREA.

Factor	Verm. (63)	Kavarov (64)	Rodger (24)
ϕd	d decreases as ϕd decreases	$A=K\ \phi\ d^{0.84}$	-
N	$d_p = K.N^{-1.2}$	$A=K_2\ .N^{1.11}$	$A=K.N^{0.72}$
d_s	-	$A=K_3\ .d_s^{0.7}$	$A=d_s^{(K+0.08)}$
μ	Little effect	Little effect	Increases slowly
σ	smaller d at lower σ	$A=K_4\cdot\ \sigma^{-0.5}$	$A=K\ \sigma^{-0.38}$
ℓ	-	$A=K_5\cdot\ \ell^{0.6}$	-
$\Delta\ell$	no effect	$A=K_6\cdot\ell\ mx^{0.6}$	increases exponentially with $(\Delta\ell/\ell_c)$
settling time	-	-	$A=K\left(\frac{t}{to}\right)^{\frac{1}{6}}$
concentration of dispersed phase C	-	$A=K\ \overset{0}{c}{}^{.84}$	-
mixer diameter T	-	-	$A=f\ \left(\frac{1}{T}\right)$

Trice and Rodger (25) measured the interfacial area using a light transmittance technique . The light transmitted through a polydisperse system of transparent isotropic spherical particles provides a measure of the interfacial area since light transmission is a function of the total projected area . Conversely a correlation is not possible if the scattered light energy is sensitive to the particle size distribution . For a poly disperse system consisting of N_i particles of diameter d_i given size interval ,

$$d_{sv} = \frac{\sum N_i . d_i^3}{\sum N_i . d_i^2} \qquad 2.18$$

For a volume fraction of dispersed phase ϕd , the volumetric area

$$A = \frac{6\phi_d}{d_{sv}} \qquad 2.19$$

This correlation is based on the assumption that the droplets are spherical and are essentially of uniform size .

Rodger , Trice and Rushton (24) measured the interfacial area in two ways : photographically and by a correlation developed between interfacial area and light transmission . The interfacial area was determined from photographs taken through the base of the mixing vessel . This technique is tedious , while the other techniques also have limitations (24 , 25 , 60 , 63 , 64 , 76) .

The correlations for estimating the interfacial area, have been derived by dimensional analysis ; the most important dimensionless number being the Weber number . These methods have many disadvantages . Calderbank (73) pointed out that the correlations of Vermeulen , Williams and Langlois (63) and Rodger , Trice and Rushton (42) depend on the particular geometry of the system and the refractive indices of the two phases . In the methods based on optical instruments the introduction of the probe into the system might disturb the hydrodynamics and if the dispersion is non-isotropic , the measurement of local value may not be representative . Vermeulen , Williams and Langolois (63) showed how the interfacial area differs with position in the vessel , indicating that the effect of coalescence and redispersion is not clear . Fernandes and Sharma (52) stated that the coalescence frequency affects the final estimate of the interfacial area . They (52) suggested that the value of the interfacial area could be obtained by small scale experiments by liquid extraction accompanied by fast pseudo-first-order reaction but their method needs some other experimental confirmations .

The available data in the literature indicates that values of the interfacial area in agitated liquid-liquid contractors are in the range of 30 to 800 cm^2 / cm^3 . By contrast in a spray extraction column and rotating disc contactor (52) the values are in the range of 1 to 10 Cm^2 / Cm^3 . Equation 2.19 indicates that the interfacial area can be calculated from the mean droplet size and dispersed phase hold-up .

The dispersed phase hold-up is defined as the volume fraction of the total liquid in the vessel which is dispersed phase . In the case of a batch operation this will be the same as the volume fraction of the dispersed liquid in the batch . In a continuously operated vessel the ratio of the dispersed phase hold-up to volume fraction of dispersed liquid in the feed mixture is probably influenced by such physical properties of the liquids as density , viscosity , and interfacial tension , rate of flow , shape and size of vessel , extent of baffling , type and position of impeller . The dispersed phase hold-up can be predicted from the dispersed phase superfacial flow rate and the mean residence time of the droplets in the extractor .

$$\phi_d = v_d \cdot \frac{t}{V} \qquad 2.20$$

The residence time of the droplets in the equipment is a function of the droplet size , the difference in density between the phases , the viscosity and density of the continuous phase and the length of travel between consecutive coalescences (139) . In column type extractors ϕ_d may be predicted from an equation of the form :

$$\frac{v_d}{\phi_d} - \frac{v_c}{(1-\phi_d)} = V_s^* \qquad 2.21$$

Where the slip velocity , V_s^* , is characteristic of the equipment .

The interfacial area can also be calculated by knowledge of :

a - drop diameter

b - drop volume

c - number of drops .

The drop diameter has been discussed above . The drop volume and number of drops are considered here .

Many investigators have tried to predict the drop volumes for various flow rates of a dispersed phase in a static continuous phase (93 , 119 , 120 , 121 , 179 , 180) . Most of these studies have been based on the assumption of spherical droplets . The volume of spherical droplet was best correlated by Scheele and Meister (119) based on a two stage drop formation process . In the static stage the drop is assumed to expand until the buoyancy force balance the interfacial tension force . During the second stage , when the drop is detaching from the nozzle it continues to grow . It was assumed that there are four major forces acting on a drop during formation at a nozzle . The buoyancy force due to the density difference between the two fluids and the Kinetic force associated with fluid flowing out of the nozzle act to separate the drop from the nozzle , while the interfacial tension force at the nozzle tip and the drag exerted by the continuous phase act to keep the drop on the nozzle . When the lifting force exceeds the restraining force , the drop begins to break away from the nozzle .

At equilibrium :

$$F_B + F_K = F_S + F_D \qquad 2.22$$

This equation gives the volume of liquid on the nozzle tip at equilibrium . If the drop broke off instaneously at the nozzle multiplication of equation 2.22 by the Harkins-Brown coefficient would give the volume of the separated drop . That is

The drop volume after break off is given by :

$$V = F\left(\frac{\pi\sigma D_N}{g\ \Delta\rho} + \frac{20\mu_C Q D_N}{D_F^2 g\ \Delta\rho} - \frac{4\rho Q U_N}{3g\ \Delta\rho} + \frac{4.5(Q^2 . D_N^2 . \rho . \sigma)^{1/3}}{(g . \Delta\rho)^2}\right) \qquad 2.23$$

Where

F = Harkins and Brown correction factor , which can be obtained from Fig. 2.2 . The quantity $D_N\ (F / V_F^{1/3})$ can be calculated directly from equation 2.23 when the drag term is negligible . For continuous phase viscosities greater than 10 centipoises the drag term is not negligible and the solution necessitates a trial-and-error procedure .

The drop volume obtained by four workers (119 , 120 , 121 , 93) is plotted in Fig . 2.3 .

Wellek , Agrawl and Skelland (138) stated that at low droplet Reynolds numbers droplet shape will approximate a sphere ; however , at high Reynolds numbers drops will be distorted and eventually drop break-up will occur . The change in shape effects not only interfacial area but also , as indicated by recent experimental and theoretical

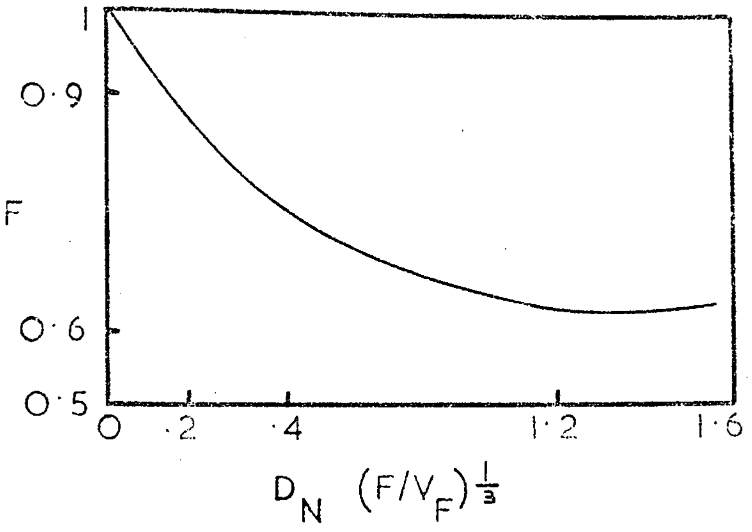


Fig. 2.2 Harkins - Brown factor F

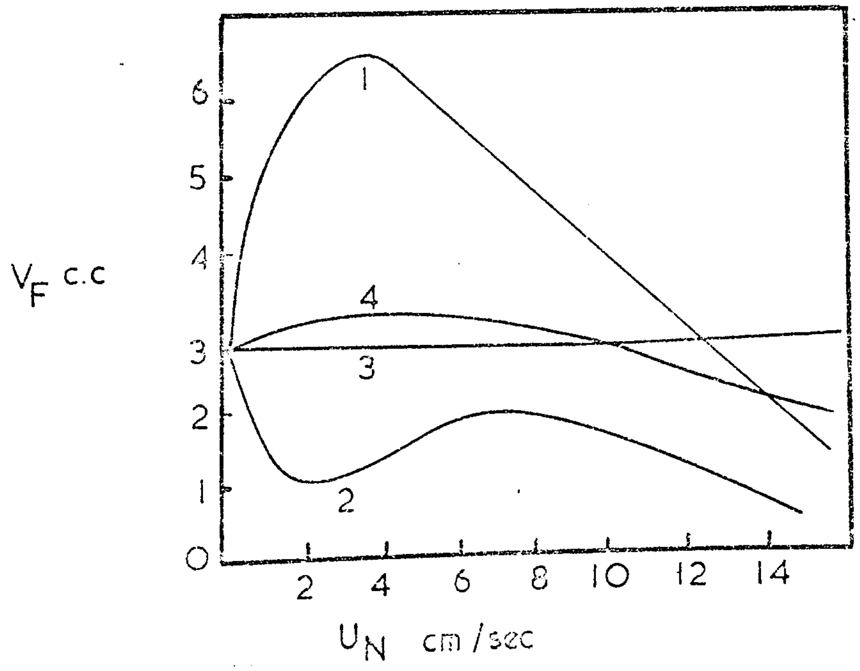


Fig. 2.3 Correlation of droplet volume

1. Howorth - Trybal (121)
2. Null - Johnson (120)
3. Harkins - Brown (93)
4. Scheele - Meister (119)

studies (26 , 27 , 28) , the continuous phase mass transfer coefficient . Drops moving in low viscosity liquids are first distorted to approximately an oblate spherical shape . As the drop increases the eccentricity E of the drop increases . The ratio of the area of an oblate spheroid A_{os} to that of a sphere of equal volume A_s is given by (29)

$$\frac{A_{os}}{A_s} = \frac{1}{2} E^{2/3} + E^{-1/3} (E^2 - 1)^{\frac{1}{2}} \ln (E + (E^2 - 1)^{\frac{1}{2}}) \qquad 2.24$$

$$\text{Where } E = \frac{\text{horizontal diameter of the droplet}}{\text{Vertical diameter of the droplet}}$$

$$E = 1.0 + 0.093 \, (N_{we})^{0.98} \left(\frac{\mu_c}{\mu_d} \right)^{0.07} \qquad 2.25$$

To calculate the interfacial area , it is necessary to get the volume of the corresponding spherical droplet by equation 2.23 .

$A_s = \dfrac{\text{Volume}}{\text{diameter}}$, then to find A_{os} from equation 2.24 .

The number of the droplets can be calculated from the dispersed phase hold-up ϕ_d and the drop volume V

$$n = \frac{\phi_d . v_d}{V} \qquad 2.26$$

Then the total interfacial area can be estimated from :

$$A = n . A_{os} \qquad 2.27$$

2.3.8.9. The driving force :

Most theoretical interpretations of interphase mass transfer presume that the process can be adequately described by an Ohm's law type of rate expression in which the transfer resistance is independent of both the concentration level and the direction and magnitude of the concentration driving force (36) . This assumption is not valid at very large driving forces when the effects of property variations and interfacial velocity begin to affect the mass transfer coefficient .

Some investigators (31 , 32 , 37) suggested that activities rather than concentrations should be used as measure of the driving force . Nevertheless , since activities are difficult to evaluate accurately in extraction equipment , concentration is usually used to estimate the driving force .

Some investigators (16 , 33 , 36 , 37) have noted change in mass transfer rate with a change of solute concentration and have attributed this to a change in the interfacial tension . Olander and Redd (36) reported that the over-all mass transfer coefficient for the three systems studied increased sharply by factors of 1.5-4 as the driving force was increased . In addition to high solute concentrations causing greater interfacial turbulence and hence higher rates of mass transfer (34 , 39) , Licht and Conway (43) reported that , for equal concentration driving forces , the rate of mass transfer of a common solute , such as acetic acid , depends upon whether the solute is going from the organic phase to the water phase or in the opposite direction . This phenomenon is presumed to be the result of hydrogen bonding forces being more intense when acetic acid is being extracted from water than when it is being extracted from an organic phase . OverCashier , Kingsley , JR. and Olney (132) found that the average mass transfer driving force itself was affected by the degree of baffling in the mixer . They stated that when baffles are present , axial flow is increased , especially with the propellers , and the entering feed streams are diluted with solutions closer to equilibrium , thus reducing the average mass transfer driving force . In the absence of baffles , end-to-end mixing is diminishing and a swirling plug-type flow results which better utilizes the driving force and permits mass transfer at lower agitation level .

The driving force in an extraction process is measured (200) , as with any diffusion process , by the distance the system is from equilibrium . The difference between the actual concentration of solute in one phase and the concentration which should be in equilibrium with that of the other phase is the force tending to dissolve (or release from solution) the solute . The algebraic sum of these differences of concentrations causes the process to proceed . Jeffreys (149) used Simpson's rule to estimate the mean concentration driving force over the whole process but if both the equilibrium curve and the operating line are straight lines the mean driving force is best determined by the logarithmic mean .

2.4. Settlers

A settler is a device in which phase separation is accomplished . Before discussing the analysis of the settler performance and design it is beneficial to consider the behavior of emulsions and dispersions .

2.4.1. Emulsions and dispersions :

The mixture of immiscible liquids resulting from mixing is an emulsion or dispersion of one liquid in the other . Emulsions and dispersions are usually characterized by the terms water-in-oil and oil-in-water dispersions. Dispersions are generally considered to be unstable or temporary emulsions , the dispersed phase droplets of which are relatively coarse .

2.4.2. The phase dispersed :

The rate of extraction , the equipment size , and power requirements may be affected by which phase is the continuous one in the resulting dispersion (9) . Either type of dispersion can be made and maintained by starting the agitator in the phase present and then adding the phase to be dispersed . Ryon et al (10) reported that either type can be formed and maintained even when the ratio of dispersed to continuous phase is greater than 3:1 . Quinn and Sigloh (7) stated that the type of dispersion depends on the volume concentration of the two liquids , their physical properties , and the dynamic characteristics of the mixing process . They stirred liquid pairs in a closed vessel . They found that the phase which became continuous depended strongly upon the impeller position and , at low stirring rates , the stirring rate itself . They also observed that for the cyclohexane-water dispersion , both phases were subdivided throughout the tank and there was no continuous phase. Selker and Sleicher , Jr (9) concluded from a more comprehensive study of the factors affecting which phase will disperse when immiscible liquids are agitated together that the range of volume fraction within which either of two immiscible liquids may be continuous , which they called the range of ambivalance , is primarily a function of viscosity ratio . It is not strongly dependent upon vessel characteristics and stirring speed and that within the ambivalent range the phase which will be continuous depends upon the starting procedure .

Quinn and Sigloh (7) used a conductivity probe for measuring the value for the resistance of the dispersion. For water continuous dispersion the resistance was relatively small and for organic continuous dispersion the resistance was effectively infinite . This method was used also by Selker and Sleicher , Jr (9) . The continuous phase could also be detected by the manner in which the dispersion settled . It is possible also to identify the phases with dyes that are either oil or water-soluble (9) but most dyes are surface active and so their addition may affect the behaviour of the dispersion .

Rodger , Trice and Rushton (24) in a study of interfacial area in concentrated dispersions reported some qualitative observations on phase inversion . Their observations are contrary to the findings of Selker and Sleicher, Jr (9) . Quinn and Sigloh (7) stated that at a fixed volume concentration the dispersed and continuous phases can be inverted by changing the impeller geometry and by changing the rate of energy input . However Yeh et al (8) reported that the phase-volume ratio at the point of inversion is equal to the square root of the ratio of the viscosities of the respective phases at the interface . It could be concluded that phase inversion , which probably reduces the efficiency , may occur due to the change in the flow rates , or sometimes to the addition of surface active agents which may influence the viscosity ratio.

2.4.3. Stability of Dispersions :

The stability of a dispersion represents the resistance offered by the dispersion to coalesce (74) . In order for a dispersion to separate into its phases in bulk the droplets of the dispersed phase will first collide with other droplets which then flocculate or agglomerate ; eventually two or more flocculated drops merge with each other by puncturing of the surrounding film . Not every collision is effective in bringing about separation of the dispersion and if the collisions are completely ineffective the emulsion is said to be stable

(74) . A stable emulsion is characterized by small drop sizes of less than about 100 microns which is called secondary dispersion . The presence of surface-active agents , solid particles , or electrolytes may increase the stability of the dispersion and hinder flocculation and separation .

Meissner and Chertow (75) described the appearance of an unstable dispersion during the time immediately following cessation of agitation . As soon as agitation is stopped the mixture separated by sedimentation and coalescence into two liquid layers (primary break) fairly rapidly unless the viscosity of the continuous phase is large . Both liquid layers may then be clear , but one of them , and sometimes both , are cloudy owing to a fog-like dispersion of a relatively small quantity of the other phase . The cloud eventually settles out , leaving both layers (secondary break) clear .

Secondary dispersions are made up of droplets of maximum size of about 100 microns and these may require a long time to separate into two clear liquid layers by simple settling . Fibrous beds are frequently used to facilitate separation . The basic requirement is to promote inter-drop coalescence until the resulting drops can be separated as a primary dispersion under gravity . High separation efficiency can only be achieved if droplets can approach and adhere to a packing surface and reside there long enough for coalescence with an adjacent or approaching drop to take place .

2.4.4. The design features of gravity settler :

Primary break of a dispersion is ordinarily so rapid that merely providing a period of some minutes without agitation is sufficient to permit phase separation . In batch process the mixture may be settled in the agitation vessel . In continuous processes the mixture is usually allowed to flow through a separation vessel which is called a settler . Different types of gravity settlers with different designs have been reported in literature (47, 74) . Ryon et al (10) reported that the stage efficiency of a mixer-settler unit is greater than that measured in the mixer only depending on the residence time of the dispersion in the settler . Phase separation in gravity settlers is characterized by a uniform dispersion band at the interface . Ryon et al (10) suggested that the thickness of the dispersion band could serve as an index to flow capacity for various systems . They reported that the thickness of the band increases exponentially with increasing flow until the settler is flooded . They arbitrarily selected the nominal flow capacity of the settler for design purposes as one half of the flow rate causing flooding of the settler and reported that the depth of the settler is primarily determined by the sensitivity of the interface control system . Jeffreys , Davis and Pitt (75) studied separation of dispersions in a single mixer-settler . They reported that dispersion was wedge shaped , the length of which increased with increasing dispersed phase flow and decreasing inlet drop diameter . However , it is more likely that in continuous counter-current mixer-settlers where the settlers are horizontal the dispersion band is of a uniform thickness and its thickness depends on the interface control system . The settler capacity may be greatly related to the mixer capacity , the rate of agitation , entrainment and the economic factors .

2.4.5. Entrainment :

If settling of a dispersion is incomplete , a portion of one of the liquids is entrained in the other and if the stage in question is one of a counter current cascade the entrained or unsettled liquid is carried opposite to its normal direction of flow . The net result is a lowering of the overall efficiency (21 , 74) . Rowden , Scuffham and Warwick (201) reported that the phase ratio in the mixer has a major effect on the separation rate and entrainment . They observed that a phase ratio of oil / aqueous 1 : 2 was the optimum ratio at which organic entrainment was minimum but this phase ratio may not be an optimum ratio in the economic sense .

2.5. The stage and stage efficiency :

A stage consists of any unit or group of units wherein mixing of the immiscible phases takes place , where mass transfer occurs and the resulting dispersion separated and withdrawn . If the effluents from a stage are in equilibrium , the stage is said to be ideal or theoretical . The fractional approach to equilibrium that may be actually realized is the stage efficiency (47 , 74) . The Murphree stage efficiency may be expressed in terms of extract or raffinate compositions . The overall stage efficiency of a cascade is defined as the ratio of the number of ideal stages to the number of real stages required to bring about a given concentration change . Overcashier et al (132) used the following relationship for the counter-current stage efficiency .

$$E = \frac{\log\left(\frac{my_2 - x_2 + b}{my_1 - x_1 + b}\right)}{\log \frac{m(y_2 - y_1)}{(x_2 - x_1)}} \qquad 2.28$$

Macmulin and Weber (5) derived an equation which relates the stage efficiency to the rate of extraction

$$E = \frac{1}{1 + k.a.t.\phi_w} \qquad 2.29$$

Effect of agitator speed and power , vessel size , rate of flow , and phase ratio on the stage efficiency of agitated extractors has been studied by Flynn and Treybal (53) . They concluded that the agitator power per unit volume of total liquid flowing may be the most important factor that influence the stage efficiency . The stage efficiency increased expontentially with the agitation speed for the systems they studied . Coplan et al (71) reported the same conclusion using a pump-mix mixer - settler . However , Overcashier et al (132) correlated the stage efficiency as follows

$$E = 1 - \frac{3.18 \times 10^{5}}{Re^{3.2} . C^{137}} \left(\frac{D_a}{T}\right)^{n} \qquad 2.30$$

Coplan et al (71) observed that increasing the speed of agitation over its optimum value not only does not increase the efficiency but does increase the dispersion so that settling is more difficult and capacity decreased . Scheibel and Karr (194) stated that the efficiency of Scheibel extraction column increased with increasing the agitator speed to a maximum value and then decreases. They attributed this decrease in the efficiency with the further increase of the agitator speed to that under these conditions the dispersion produced was so fine that phase separation was incomplete in the packing .However the decrease in the efficiency with increase in the agitation speed suggests that the drop size may be reduced, probably from an oscillating to a circulating drop and then to a stagnant drop which would largely reduce the rate of mass transfer and hence the efficiency :

2.6. Mixer-settlers arrangements :

A mixer-settler unit consists of several stages arranged for counter current operation , each stage consisting of a combination of a mixer and a settler . Additional equipment , such as coalescing aids may be included and variations in design are possible . A possible special arrangement may be a common shaft for all stirrers . Davis , Hicks , and Vermeulen (44) discussed the advantages and disadvantages of each arrangement and a summary of the main design features for twelve types of mixer-settler is given in Table 2.6 . Hanson and Kaye (6) stated that the Horizontal mixer-settlers are more versatile and have as high as 93 % efficiency. The advantages of this type of equipment compared with columns have been discussed in some detail by Coplan (71).

The characteristics of some of the Horizontal mixer-settlers which have been described in the literature are summarized in Table 2.7 .

2.7. Laboratory mixer-settlers :

Bench-scale laboratory extractions are frequently made in glass to evaluate solvents for separating complex mixtures and for assessing settling conditions to be used in a commercial process prior to pilot-plant study In addition , to devise the special extraction techniques for analyzing complex natural and synthetic products .

Laboratory extractions may be done in equipment resembling that used in a full-sized plant , specially on a continuous or semi-continuous basis . The conditions to be used industrially should resemble in every case the flow-sheet solvent to feed ratios and number of stages since stage calculations may not be possible .

As a preliminary study , on occasion it may be advantageous to carry out small scale laboratory experiments and either of the following procedures may be followed

a) A batch simulation of the continuous counter-current multistage process may be carried out , or

b) A continuous extraction in a miniature extractor of known number of stages may be used .

The principal experimental problem in these systems will be the maintenance of steady-state flow rates for the feed and solvents (71 , 74) .

TABLE 2.6 COMPARISON OF MIXER-SETTLER DESIGN

Inventor	Type of stirring	Type of settling	Arrangement	Driving force for flow	Relation of phase ratio to overall flow ratio.
Mckittrick (1939), (111)	Common shaft	Cocurrent	Vertical	Gravity	Independent
Schoneborn (1934), (112)	Common shaft	Cocurrent	Vertical	Gravity	Dependent
Mcconnell (1937), (113)	Common shaft	Cocurrent	Vertical	Heavy phase by gravity	Independent
Scheibel (1946), (114)	Common shaft	Counter current	Vertical	Gravity	Dependent
Bottaro (1940), (115)	Common shaft	Counter current	Near Vertical	Gravity	Dependent
Othmer (1935), (116)	Common shaft	Counter current	Vertical	Gravity	Independent
Van Dijck (1941), (117)	Common shaft or individual stirrers	Counter current	Near Horizontal	Gravity	Either dependent or independent
Holley (1934), (107)	Individual stirrers	Counter current	Near Horizontal	Gravity	Independent
Mensing (1947), (106)	Individual stirrers	Counter current	Horizontal	Both phase pumped by mixer	Independent

CONTD. TABLE 2.6 COMPARISON OF MIXER-SETTLER DESIGN

Inventor	Type of stirring	Type of settling	Arrangement	Driving force for flow	Relation of phase ratio to overall flow ratio.
Edeleanu (1927),(106)	Individual stirrers	Cocurrent	Horizontal	Light phase pumped, heavy phase pumped by gravity	Dependent
Standard oil development (1949),(44)	Individual stirrers	Cocurrent	Near Horizontal	Gravity	Independent
Gordon (1939),(108)	Individual stirrers	Cocurrent	Horizontal	Both phase pumped by mixer	Dependent

TABLE 2.7

DESIGN CHARACTERISTICS OF SOME HORIZONTAL MIXER-SETTLERS WITH MECHANICAL AGITATION AND GRAVITY SETTLING.

Title	Type	Recirculation	Type of Impellor	Interface Control	Mixing section design
Barstow (1904) (105)	Simple, early box contactor	Not designed for recirculation but probably occurred to an unknown extent	Simple double paddles	Probably automatic between stages, with one variable heavy phase off-take weir.	Simple box compartment feeds in and out via slots in walls
Argonne Laboratory (1948) (44)	Box contactor	Not designed for recirculation, but this probably occurred to a slight degree from settler back to mixer	Simple, vertical paddles	Ditto	Feeds in and out via slots in walls but interposition of ante-chamber before mixer compartment.
Standard Oil Co.Ltd. (1949) (44)	Ditto	Similar to Argonne contactor	Ditto	Automatic between stages, but heavy phase off-take control on last stage.	Ditto.

CONTD. TABLE 2.7 DESIGN CHARACTERISTICS OF SOME HORIZONTAL MIXER-SETTLERS WITH MECHANICAL AGITATION AND GRAVITY SETTLING

Title	Type	Recirculation	Type of Impeller	Interface Control	Mixing section design
Knolls Atomic power laboratory, or "KAPL" (1953) (71)	Box contactor	Recirculation within mixing stage, and also circulation of light phase from settler to mixer	Special pump-mix-impeller	By impellers but variable heavy phase weir on last stage	Similar to Standard Oil Co. and Argonne types but antechamber situated underneath mixing chamber proper
University of California (1954) (44)	Ditto	Similar to Argonne and Standard Oil Development Co. contactors.	Simple vertical paddles 1½ in. dia.	Similar to Argonne and Standard Oil Co. Type	Similar to Argonne and Standard Oil Co. contactors.
Edeleanu (1927) (106)	Separate mixers, settlers and pumps not a true horizontal type, as in cascade.	No recirculation	Simple stirrers (pumps for light phase)	Probably controlled by final heavy phase weir	Simple tanks, ports in walls.

CONTD. TABLE 2.7

DESIGN CHARACTERISTICS OF SOME HORIZONTAL MIXER-SETTLERS WITH MECHANICAL AGITATION AND GRAVITY SETTLING

Title	Type	Recirculation	Type of impeller	Interface Control	Mixing Section Design
Holley-Mott (1934) (107)	Separate mixers and settlers	Both phases can be re-recycled from settler to mixer, via pipes, valve control	Simple, vertical, diamond shaped paddles	Probably automatic between stages and final heavy phase weir adjustable	Simple tanks, ports in walls
Gordon-Zeigler (1939/41) (108)	Separate stages but mixers inside	Designed for no recirculation whatsoever	Turbine wheel type	Could control aqueous weir on each stage by pressurised vents	Mixing section small and within settler. Two phases enter impeller at centre to promote maximum development of pumping head.
Mensing (1946) (109)	Ditto	Recirculation from settler to mixer via adjustable leg	Up thrust prop. type stirrer	Could pressurise vent on heavy phase weir on each stage	Ditto

CONTD. TABLE 2.7

DESIGN CHARACTERISTICS OF SOME HORIZONTAL MIXER-SETTLERS WITH MECHANICAL AGITATION AND GRAVITY SETTLING

Title	Type	Recirculation	Type of impeller	Interface Control	Mixing Section Design
Pump-settler contact (1954) (110)	Separate stages; pumps used as mixers	Not designed for recirculation	Centrifugal pumps as mixing section	Pumps control	The mixing section is in fact a centrifugal pump in a conventional casing. The combination produces excellent mixing (turbulence)
A.E.R.E. Cylindrical type (1954)	Separate stages; mixers inside settlers	Recirculation only within the mixers	Up thrust type. Stirrer.	Stirrer automatically controls each inter-phase except final one	Phases feed into chamber in similar fashion to Mensing.

3. Optimization

3.1 Introduction

The act of optimization frequently presents a mathematical problem of such a nature that a certain function of several variables is to be maximised or minimized with some constraints imposed on the variables. Himsworth (196) considered that optimization in the chemical field can be divided into:

(a) Static optimization; in which the most suitable state operation conditions of the process is to be established without taking into account the fluctuations in the process about the nominal conditions.

(b) Dynamic optimization; in which the best procedure for correcting the fluctuations in the process about the nominal conditions is established. This could be considered as an extension of the automatic control analysis of the process.

Many techniques of searching for the extremal of a function have been discussed in detail in relevant references (15, 169, 170, 172, 173, 176, 196). Among the numerous attempts to find new powerful optimization techniques, dynamic programming developed by Bellman (176) and themaximum principle derived by Pontryagin (202) are probably the two most successful. Doust (173) reported that Lee stated that the use of dynamic programming is limited by the small number of variables it can conveniently handle.

3.2 The Maximum Principle

This was based on the method of Lagrangian multipliers of finding the maximum and minimum of a function under constrained conditions in the field of the calculus of variation (169, 170, 176, 202). A clear and concise derivation of the Maximum principle was given by Rozonoer (203).

Many successful applications of the Maximum principle to chemical engineering processes have been reported (169, 173, 176). However, Coward and Jackson (204) in studying the optimum temperature profiles in tubular reactors have found cases in which there were several profiles, all satisfying Pontryagin's conditions, only one of which is the required, and cases in which there were an infinite number of profiles, all satisfying the conditions of the principle and all providing valid solutions of the problem.

3.3 The Discrete Maximum Principle

Rozonoer (203) made the initial progress in extending the Maximum principle for linear stagewise processes. Katz (170) next extended it for non-linear simple processes. Fan and Wang (169, 172) generalized Katz's algorithm for complex cyclic and branched processes and applied the result successfully to several examples (176). However, studying these examples show that they have a very simple nature which are not really practical, for example, in liquid extraction processes they only tried (170, 172), to solve the cross-current processes usually assuming a linear distribution relationship. They have never discussed the counter-current extraction process which is widely used and never tried the non-linear distribution relationship. Also in their derivation of the discrete maximum principle (169, 170, 172) they neglected to check that the nature of the stationary point of the Hamiltonian is the same as that of the objective function. They usually assume that both stationary points are the same which is not true in all cases.

3.4 Statement of the Algorithm of the Discrete Maximum Principle

Fan and Wang (169) derived an algorithm which they claimed could be applied to any multistage process. The problem is to maximize

$$y = \sum_{i=1}^{S} C_i x_i^N \qquad 3.1$$

of a multistage decision process described by the performance equations

$$x_i^n = T_i^n (x_i^{n-1}, \theta^n), \quad \begin{matrix} i=1, \dots, S \\ n=1, \dots, N \end{matrix} \qquad 3.2$$

where $x_i^o = a_i^f$ 3.3

The sequence of decision vectors θ^n, $n=1,2, \dots, N$ to maximise the objective function 3.1 is to be found. The procedure for solving such an optimization problem by the discrete maximum principle is to introduce an n dimensional covariant vector Z^n and a Hamiltonian function H^n satisfying

$$H^n = \sum_{i=1}^{S} Z_i^n \cdot T_i^n (x_i^{n-1}, \theta^n) \qquad n=1,2,\ldots,N \tag{3.4}$$

$$Z_i^{n-1} = \frac{\partial H^n}{\partial x_i^{n-1}} \quad i = 1,2,\ldots, S; \; n=1,2, \ldots,N \tag{3.5}$$

and $$Z_i^N = C_i, \; i=1,2, \ldots, S \tag{3.6}$$

The optimal sequence of the decisions θ^n can then be determined from the conditions for H^n to be maximum

$$\frac{\partial H^n}{\partial \theta^n} = 0, \; n=1,2, \ldots, N \tag{3.7}$$

Both x and Z are considered as fixed in maximizing the Hamiltonian.

Assuming a value for x_i^N both θ^N and x_i^{N-1} can be obtained by solving equations 3.7 and 3.2 simultaneously. Using equations 3.5, 3.7 and 3.2 θ^{N-1} and x_i^{N-2} can be obtained. By iterative processes x_i^o can be obtained which is compared with x_i^f. The whole procedure is repeated until the calculated value of x_i^o is equal to the given x_i^f. It is worth noting that, for each assigned value of x_i^N, the corresponding values of θ_1^n, n=1,2,..,N calculated are the optimal decisions corresponding to the initial condition of x_i^f computed in each run of trial calculations (169).

4. Analysis of Extraction Processes

In this section counter-current extraction processes have been analysed to estimate the time required for the process to come to steady state and to assess the optimum operating variables ; for example the number of stages, the solvent/feed ratio and the optimum temperature profile.

4.1. Time to reach steady state :

Very little work has been published to determine the time needed for an extraction process to come to steady state . Coplan , Davidson and Zebroski (71) in operating 8-stage pump mixer-settler withdrew samples for analysis after approximately four times the holdup volume was fed to the apparatus . They considered that such time would be sufficient to reach steady state . Fenske and Long (13) reported that it took about 5 hrs to make a 20 - stage extraction with a lube -phenol system and about 1 hr. for a similar run on the n-heptane-methylcyclohexane-aniline system to obtain a reasonable size product sample . Over cashier et al (132) used a single stage continuous flow contactor for the system water-kerosene-n-butylamine. Their efficiency-time plot shows sinosoidal oscillation around 90 % efficiency starting at a time of 10 min . The only mathematical analysis of a counter current mixer-settler has been presented by Jenson and Jeffreys (196) for an 8-stage contactor . Their analysis concentrated on the mathematical techniques . They did not discuss the implications of the different parameters . Therefore it was decided to extend the investigation in this study assuming the extractor is to operate with efficiencies less than 100 % to find out whether the efficiency has an effect on the time required to steady state .

Fig 4.1 shows the stagewise counter-flow process . A solute balance over the n^{th} stage gives :

$$Fx_{n-1} + Sy_{n+1} = Fx_n + Sy_n + \phi_1 \frac{dx_n}{dt} + \phi_2 \frac{dy_n}{dt} \qquad 4.1$$

Introducing the Murphree efficiency for the raffinate phase (47 , 74)

$$E = \frac{x_{n-1} - x_n}{x_{n-1} - x_n^*} \qquad 4.2$$

where

$$y_n = m\, x_n^* \qquad 4.3$$

Introducing equation 4.2 and 4.3 in 4.1 , taking the Laplace transform , and collecting the similar terms gives a second order finite difference equation (Appendix 1) . Its general solution is

$$\bar{x}_n = C_1 r_1^{\,n} + C_2\, r_2^{\,n} \qquad 4.4$$

The constant C_1 and C_2 are the constants determined by the boundary conditions .

The method of residues (196) have been used to invert equation 4.4 to get :

$$x_n = x_o \left(\left(\frac{A^{N+1} - A^n}{A^{N+1} - 1}\right) + \sum_{n=1}^{N} (-1)^n \frac{2.r^{n+2}.\sin\theta.\sin(N-1-n)\theta}{S(N+1)\ (C.\cos\theta - B.r)}\, e^{st} \right) \qquad 4.5$$

where

$$S = \frac{1}{2}\left(-\frac{2B(1+A) - 4C\,\mathrm{Cos}^2\theta}{B^2} - \sqrt{\frac{\{2B(1+A)-4C\,\mathrm{Cos}^2\theta\}^2}{B^4} + \frac{4\{4A\,\mathrm{Cos}^2\theta - C(1+A)^2\}}{B^2}}\right) \qquad 4.6$$

$$\gamma = \sqrt{A + CS} \qquad 4.7$$

$$\theta = \left(\frac{n\pi}{N+1}\right) \qquad 4.8$$

$$A = 1 - E\left(1 - \left(\frac{F}{Sm}\right)\right. \qquad 4.9$$

$$B = \frac{\phi_1 E + \phi_2 m}{Sm} \qquad 4.9$$

$$C = \frac{\phi_2 (1 - E)}{S} \qquad 4.11$$

4.2. Results and discussion

4.2.1. Effect of the efficiency of an extractor on the time to reach steady state :

The following data were used to test the analysis

$F = 62.5$ gm /min.

$S = 10.962$ gm /min.

$\phi_1 = 0.75 \times 0.877 \times 175 = 114.1$ gm

$\phi_2 = 0.25 \times 1 \times 175 = 43.75$ gm

Mixer volume = 175 c.c.

$m = 6$, $n = 8$

$x_o = 0.14$ gm of solute per gm of feed .

Equation 4.5 was programmed on a Honeywell 316 computer using Basic 16 language . The program is presented in Appendix 1 . The results are given in Table 4.1.
The values of the 8 th stage were not produced because the computer gave a signal of numerical underflow , but the values of the concentrations at that time suggests

that the value for the 8th stage would be between 6.5-7.5 hrs. It will be seen from Table 4.1 that the stage efficiency of an extractor has no effect on the time required to reach steady state in the internal stages. It can also be seen that stages 1 , 7 and 8 are affected by efficiency. The results for stage 1 shows that , at lower efficiencies, the time is longer .

The following studies were carried out using a 100 % efficiency .

4.2.2. Effect of the number of stages on the time to steady state :

Equation 4.5 was used to estimate the effect of the number of stages on the time to reach steady state . Different values of N were used with the other data constant and the results obtained are presented in Fig 4.2. The results show that : As N increases , the time to reach steady state increases , but the relationship is difficult to predict whether it is exponential or otherwise . When the time was correlated against all the independent variables by multiple regression analysis the linear relationship between t and N gave better results .

The results were also used to find out the relationship between the time to reach steady state and the time of filling the extractor . These results are presented in Table 4.3 .

Finally the actual time to reach 95 % of the steady state concentrations is shown in Fig 4.3 . There it will be seen that 95 % of steady state conditions are reached in 2.5 hrs which is 35.7 % of the time needed to reach full steady state .

4.2.3. Effect of the phase Ratio on the time to steady state .

Equation 4.5 was also used with the same data and different phase ratios to assess the effect of the phase ratio on the time to reach steady state . The results are plotted on Fig 4.4. The curve shows that as the feed to solvent ratio increases the time increases exponentially until a constant value is obtained at a phase ratio of 8.

4.2.4. Effect of the dispersed phase holdup on the time to steady state :

Equation 4.5 was used with the same data but with different values for the dispersed phase holdup and the results are plotted on Fig 4.5 . The figure shows an approximately linear relationship between the time to steady state and the dispersed phase holdup .

4.2.5. Effect of the capacity of mixer on the time to steady state :

Equation 4.5 was used , with the same data and different mixer volumes , to find out the effect of the volume of the mixer on the time to reach steady state . The results are plotted on Fig 4.6 . The figure shows that the time increases linearly with the mixer capacity as would be expected .

4.2.6. Effect of the equilibrium constant on the time to steady state :

Equation 4.5 was used , with the same data but with different distribution coefficients and the results obtained are plotted on Fig 4.7. The results show an exponential increase of the time with the distribution coefficient m until a certain value is attained . This value is characteristic of the other parameters of the process .

4.2.7. Effect of the feed concentration on the time to steady state :

Different values of the feed concentration were inserted into equation 4.5 with the data remaining the same and the results are given in Table 4.2 , and the time for the final stage to reach steady state is plotted on Fig 4.8 . The curve shows that as the feed concentration increases the time to reach steady state increases exponentially then levels out at a certain value of x_0 . The actual value depends on the physical and hydrodynamic properties of the system and the design of the equipment. The curve shows no substantial effect of the feed concentration on the time to reach steady state when the distribution coefficient is constant over the whole range of concentration for extract to final raffinate .

4.2.8. Effect of the position of the stage on its time to steady state :

It will be seen in Tables 4.1 and 4.2 that not all the stages reach steady state at the same time . Therefore equation 4.5 was applied with the same data , using different values for the number of stages in the process, and the results are shown in Table 4.4 . These show that at $N \geqslant 4$ the pattern of the time to reach steady state is the same . It will be seen that the stages reach steady state in the following order :

i) Stages N/2 and (N+2)/2 generally reach steady state in the same time with possibly (N+2)/2 sometimes attaining steady state first .

ii) Then stages (N-2)/2 and (N+4)/2 reach steady state in the same time with the $\frac{N-2}{2}$ sometimes faster .

iii) Then stages (N-4)/2 and (N+6)/2 reach steady state in the same time with the $\frac{N-4}{2}$ sometimes faster .

iv) Stage 1 ; at which the feed is introduced reaches steady state after all the internal stages .

v) The last to reach steady state is stage N where the solvent is introduced .

The above pattern indicates that steady state is first achieved as far as possible from the points where the liquids are fed to the system . These are the positions of minimum disturbance in the middle of the extractor . The steady state then propagates in the form of a wave in both directions through the extractor ; somewhat faster in the direction of the feed stage ; which attains steady state before the solvent stage .

For a feed concentration $x_o = 0.133$ in an 8 stage extractor , the times to reach steady state in stages 1 , 2 , 3 , and 4 are plotted on Fig 4.9 and for stage 8 on Fig 4.3 .

The curves show that the curvature of the plots of the middle stages is very sharp and increases as the stage approaches the feed or the solvent inlet stages .

4.2.9. Regression Analysis :

Attempts were made to find a correlation by which the time to reach steady state could be calculated directly . The data previously obtained using equation 4.5, was fed to ICL 1900 statistical analysis package XDS3/22 using Fortran IV language . The results obtained are shown in Table 4.5 . The package was also processed using the smoothed data obtained from the previous plots between t and the different independent variable . The results , as shown in Table 4.6 were insignificantly better . Initially the relation between t and N was considered to increase exponentially but this was not very satisfactory . Following this the relation was considered to be linear and the results are shown in Table 4.7 , where it can be seen that they are significantly improved .

Thus , it could be concluded that the time to reach steady state can be estimated from the expression

$$t = 2.35 \times 10^{-4} . V^{0.95} . \phi^{0.66} . R^{1.19} . m^{0.83} . N^{1.31} . x_o^{0.1} \qquad 4.12$$

and for practical purposes the time to reach steady state is approximately

$$t_p = 0.4t \qquad 4.13$$

Where t_p is the time to reach 95 % steady state conditions .

4.3. Optimum number of stages :

Although some work has been done in optimization of cross-current liquid extraction processes (169 , 170, 172 , 173 , 176) very little have been published on counter-current liquid extraction . Mitten and Nemhauser (14) applied dynamic programming for the optimization of a multistage counter-current mass transfer process while Jeffreys et al (15) used the Hooke and Jeeves search technique for the optimization of a solvent extraction process in which solvent is recovered by distillation . Jenson and Jeffreys (196) gave a detailed cost analysis of counter-current extraction processes to maximize the profit function with respect to the number of stages and flow-rate of extracting solvent .

The analysis undertaken here follows the basic equations proposed by Jenson and Jeffreys (196) without using the contour charts in their analysis . The profit function to be maximized is the difference between the cost price of the solute extracted and the total cost of the feed , solvent losses and recovery costs and the cost of the equipment (stages) . The profit function is expressed mathematically as

$$P = \lambda C(x_o - x_N) - (\alpha N + \beta B + \gamma C\, x_o) \qquad 4.14$$

X_N is related to x_o by the Kremser-Brown equation :

$$x_N = x_o \left(\frac{S^{N+1} - S^N}{S^{N+1} - 1}\right) \qquad 4.15$$

Substitution of equation 4.15 into 4.14 gives

$$P = \lambda C x_o \left(\frac{S^N - 1}{S^{N+1} - 1}\right) - (\gamma C x_o + \alpha N + \beta B) \qquad 4.16$$

For P to be maximum :

$$\frac{\partial P}{\partial N} = 0 \quad \text{and} \quad \frac{\partial P}{\partial B} = 0 \qquad 4.17$$

$$\therefore \quad \frac{\alpha}{\lambda C x_o} = \frac{S^N (S-1) \ln S}{(S^{N+1}-1)^2} \qquad 4.18$$

and

$$\frac{\beta}{\lambda m x_o} = S^{N+1} \left(\frac{S^{N+1} + N(1-S) - S}{(S^{N+1}-1)^2} \right) \qquad 4.19$$

Dividing 4.19 by 4.18 gives

$$\frac{\beta}{\alpha} \cdot \frac{C}{m} = \frac{S(S^{N+1} + N(1-S) - S)}{(S-1)\ \ln S} \qquad 4.20$$

But $$S = \frac{C}{mB} \qquad 4.21$$

$$\therefore \quad \frac{C}{m} = BS \qquad 4.22$$

Substitution of 4.22 into 4.20 gives

$$B = \frac{S^{N+1} + N(1-S) - S}{(\frac{\beta}{\alpha})\ (S-1)\ \ln S} \qquad 4.23$$

and rearrangement of equation 4.22 gives

$$B = \frac{C}{mS} \qquad 4.24$$

The right hand side of equation 4.23 was evaluated for any pair of values of S and N and the right hand side of equation 4.24 was evaluated for the corresponding values of S . The number of stages corresponding to this amount of solvent approximately equals that given by equation 4.24 was considered to be the optimum number of stages . This number N was used in equation 4.15 to obtain the corresponding extractability x_N / x_o .

A computer program was developed for this algorithm and the data obtained was fed into a regression analysis package which gave the following correlation for the optimum number of stages .

$$N = 38.6\ (\frac{x_N}{x_o})^{-0.24} \cdot (\frac{\beta}{\alpha})^{0.41} \cdot (m)^{-0.08} \cdot (R)^{-0.36} \qquad 4.25$$

The correlation coefficient was 0.978
Checking the second derivative with respect to both independent variables, they were negative for all values of N.

The effect of the various factors on the optimum value of N have then been investigated and the results obtained are reported below.

4.3.1 Effect of the phase ratio on the optimum number of stages:

Fig. 4.10 shows that as the phase ratio increases the optimum number of stages decreases. This is the reverse of what is normally known in the Mc Cabe-Thiele diagram; but from the economic point of view, it can be seen that as the phase ratio decreases, implying that a larger amount of solvent will be required, it is more economical to use this amount of solvent in a greater number of stages to get a higher extractability and vice versa; which means that a larger consideration of the extractability should be taken into account in terms of the phase ratio.

4.3.2. Effect of the extractability on the optimum number of stages :

Fig 4.11 shows that the extractability increases (i.e. $\frac{X_N}{X_O}$ decreases) as the number of stages increases , which would be expected .

4.3.3. Effect of the ratio of solvent cost to the equipment cost per stage on the optimum number of stages :

Fig 4.12 shows that the effect is very pronounced and is increasing exponentially . The curve indicates that as the cost of solvent increases relative to the equipment cost per stage it is more economical to use a large number of stages especially when the phase ratio is small .

4.3.4. Effect of the distribution coefficient on the optimum number of stages :

Fig 4.13 shows that the optimum number of stages decreases exponentially as the distribution coefficient increases . It also shows that this effect is most pronounced at m less than 3 .

The effects of the different factors on the optimum number of stages required show only the general trends which would assess the local optimum . For more rigorous analysis constraints should have been applied which would imply the use of Largangian method or Pontrayagin's maximum principle .

4.4 Optimum Temperature Profile:

Denbign (205) and Aris (206) have independently studied the optimum temperature profile in sequences of reactors. They concluded that large increases in yield may be obtained by use of an optimum sequence of temperatures in cases of competing side reactions. However, it appears that the optimum temperature profile in a multistage countercurrent mixer-settler has not been considered hitherto and in this investigation use will be made of the discrete maximum principle initially proposed by Katz (170) and developed by Fan and Wong (172).

4.4.1 Derivation of the Algorithm

The problem is to maximize an objective function described by the performance equations which are derived from a steady state mass balance over the nth stage in Fig. 4.1. Thus:-

$$Fx_{n-1} + Sy_{n+1} = Fx_n + Sy_n \tag{4.26}$$

Since

$$y_n = m_n x_n \tag{4.27}$$

where m_n is the distribution ratio for the nth stage and can be expressed as a function of concentration and temperature as follows:

$$m_n = k\, x_n^a \cdot T_n^b \tag{4.28}$$

Using equation 4.28 and 4.27 in equation 4.26, then

$$x_{n-1} = x_n + \frac{k}{R}\left(x_n^{1+a} \cdot T_n^b - x_{n+1}^{1+a} \cdot T_{n+1}^b\right) \qquad 4.29$$

$$n=1,2, \ldots, N$$

at n=N, equation 4.29 is reduced to

$$x_{N-1} = x_N + \frac{k}{R}\, x_N^{1+a} \cdot T_N^b \qquad 4.30$$

since $x_{N+1} = 0$.

By recurrence operation using equation 4.30 in 4.29 for n = N-1, ..., 1, the solution of equation 4.29 is:

$$x_n = \left(\frac{R}{kT_n^b}\,(x_{n-1} - x_N)\right)^{\frac{1}{1+a}} \qquad 4.31$$

$$n=1,\ 2,\ \ldots,\ N$$

The profit function which has to be maximised can be expressed as follows:

P = value of extracted solute - (cost of equipment (stages + heating/cooling units) + cost of solvent + cost of feed + cost of heat supplied) or,

$$P = \lambda F(x_o - x_n) - (\alpha N + \beta S + \gamma F\, x_o + z\, f(T_n)) \qquad 4.32$$

where the symbols are as given in the nomenclature.

The terms of the right hand side of equation 4.32 can be written as

$$x_o - x_N = \sum_{1}^{N} x_{n-1} - x_n$$

$$\alpha N + \beta S + \gamma F x_o = \sum_{1}^{N} B_n$$

where $B_n = \dfrac{\alpha N + \beta S + \gamma F x_o}{N}$, n=1, 2, ..., N

and $F(Tn) = k_1(T \ - k_2)^2$, n=1,2, ..., N

The 'heat cost' function was considered to have a minimum value at normal temperatures where the least amount of energy would be consumed. The 'heat parameter cost', k_1, was considered to acquire values in case of heating different than those of cooling.

Equation 4.32 can then be written as

$$P = \sum_{n=1}^{N} (\lambda F(x_{n-1} - x_n) - (B_n + k_1(T_n - k_2)^2)) \qquad 4.33$$

By defining a new state variable P_n satisfying

$$P_n = P_{n-1} + \lambda F(x_{n-1} - x_n) - (B_n + k_1(T_n - k_2)^2) \qquad 4.34$$

$$n=1, 2, \ldots, N$$

and $P_o = 0$.

the problem was then transferred into one in which P_N is to be maximized by the proper choice of T_n, n=1, 2, ..., N for a process described by equations 4.31 and 4.34 with x_o given.

According to the discrete maximum principle (169, 170) the sequence of decision variable T_n, n=1, 2, ..., N must be chosen so that the following conditions are satisfied:

$$H^n = Z_1{}^n \, x_n + Z_2{}^n \, P_n = \text{maximum} \qquad 4.35$$

$$n=1,2, \ldots, N$$

$$\therefore H^n = Z_1{}^n \left(\frac{R(x_{n-1} - x_N)}{kT_n^b} \right)^{\frac{1}{1+a}} + Z_2{}^n \, (P_{n-1} +$$

$$\lambda F(x_{n-1} \left(\frac{R(x_{n-1} - x_N)}{kT_n{}^b} \right)^{\frac{1}{1+a}}) - (B_n + k_1(T_n - k_2)^2) \qquad 4.36$$

$$n=1, 2, \ldots, N$$

where the Z functions are defined as follows:

$$Z_1^{n-1} = \frac{\partial H^n}{\partial x_{n-1}} \quad \text{and} \quad Z_2^{n-1} = \frac{\partial H^n}{\partial P_{n-1}} \qquad 4.37$$

subject to the final conditions

$$Z_1^N = 0 \quad \text{and} \quad Z_2^N = 1 \qquad 4.38$$

Thus

$$Z_2^{n-1} = Z_2^n = 1 \qquad 4.39$$

and

$$Z_1^{n-1} = \frac{R(Z_1^n - \lambda F)}{k(1+a)x_n^a \cdot T_n^b} + \lambda F \qquad 4.40$$

From equation 4.36, for maximum H^n, $\frac{\partial H^n}{\partial T_n} = 0$

This gave the sequence of temperatures T_n as

$$T_n = \frac{1}{2}\left(k_2 \pm \left(k_2^2 + \frac{2b\, x_n(\lambda F - Z_1^n)}{k_1(1+a)}\right)^{\frac{1}{2}}\right) \qquad 4.41$$

$$n = 1, 2, \ldots, N$$

A complete derivation of this algorithm is given in Appendix III.

4.4.2 Results:

The algorithm was programmed in basic 16 language and processed on a Honeywell 316 computer. The program is presented in Appendix I and the data used in the program was:

$F = 1260$, S = different values, N = different values,

$\alpha = 5.25$ p/h, $\beta = 0.01$ p/gm, $\gamma = 0.2$ p/gm, k_1 = different values, $k_2 = 20$, 30 and 60° C.

$k = 5.19$, $a = -0.4535$, $b = -0.2856$

The results showed that using the positive sign of the square rooted term in equation 4.41 would lead to a temperature profile with the higher temperature, usually less than k_2, at the raffinate discharge and vice versa if the negative sign in equation 4.41 was used. However, since the negative value leads to solutions most of which were unstable the positive sign was only considered to give the solution of the problem. The results are presented in Table 4.8. This table shows that many factors are interacting to give the optimum results and changing any one would drastically alter the optimum. Some of these factors are distinguished as follows:

4.4.2.1 Effect of the Feed Concentration:

Table 4.8 shows each feed concentration has an optimum solution with optimum profit for a fixed value of phase ratio. However, at fixed values of the heat parameter cost k_1 and number of stages N there was a maximum profit at a particular feed concentration.

4.4.2.2 Effect of the Number of Stages:

The results in table 4.8 also show that the number of stages may be the one of the most important factors. Thus for this system a process containing a larger number of stages than 5 is most likely to be unprofitable if a temperature gradient is to be applied. That is such a process should best be operated isothermally.

4.4.2.3 Effect of the Heat Cost Parameter k_1:

Experiments have been carried out to assess approximately the effects of differences in the value of the heat cost parameter k_1. A Churchill Chiller thermo-circulator with a control range of -5 to 60° C was connected to the jackets of a 7-stage mixer-settler, (described in Section 5), which were filled with distilled water and agitated. A wattmeter was connected to the mains to determine the quantity of electricity consumed under heating or cooling conditions over a range of 12° C below or above ambient. It was found that when heat was supplied to the contactor it required 20 minutes for the distilled water to reach the temperature required while 60 minutes were required for cooling. The wattmeter showed that the quantity of electricity consumed in cooling was double that required for heating. Although simulation of this batch experiment may not be representing the actual continuous mixer-settler process nevertheless it may give an idea about the order of magnitude of the cost of cooling relative to that of heating the contactor.

According to this experiment k_1 was considered to be = 1 at temperatures below 30°C and 0.5 above 30° C. Analysis of the results in table 4.8 shows that a profit of 124.843 units would be performed at temperatures below 30°C , while only a profit of 122.5 units could be performed above 30°C with a 1.84% decrease in profit. This suggests that although the cooling costs may be higher than the heating costs, it would be more profitable for such system to operate at a temperature lower than 30° C.

4.4.2.4 Effect of the Phase Ratio:

Different phase ratios with different heat cost parameters were fed to the program and the results are shown in Table 4.9. The table clearly indicates that when operating such system in a 4 stage mixer-settler the phase ratio of 1:3 would give the maximum profit if a temperature gradient was applied. Operating this system with a larger number of stages is not profitable unless the contactor is operated at ambient temperature. For a feed concentration of 0.17 it is seen in Table 4.10 that for 6 stages the optimum phase ratio is 4, for 8 stages the optimum phase ratio is 5, and for 9 stages it could be between 5 and 6. However, comparing the profits achieved in all these cases, the most profitable is operating only 4 stages with 1:3 phase ratio either with or without a temperature gradient.

TABLE 4.1 EFFECT OF MURPHREE EFFICIENCY ON THE TIME TO STEADY STATE.

E	Time to steady state in hrs. for each stage							
	1	2	3	4	5	6	7	8
0.5	5	1.5	1	0.5	0.5	1	1.5	
0.6	5	1.5	1	0.5	0.5	1	2	
0.7	4.5	1.5	1	0.5	0.5	1	1.5	
0.8	4.5	1.5	1	0.5	0.5	1	1.5	
0.9	4.5	1.5	1	0.5	0.5	1	2	
1	4.5	1.5	1	0.5	0.5	1	2	

TABLE 4.2 EFFECT OF FEED CONCENTRATION ON THE TIME TO STEADY STATE.

x_o	Time to steady state in hrs. for each stage					
	1	2	3	4	5	6
0.01	4.0	1.5	0.5	0.5	1.0	4.0
0.05	3.5	1.0	0.5	0.5	1.0	5.0
0.10	4.0	1.5	0.5	0.5	1.0	4.0
0.14	3.5	1.5	1.0	0.5	1.5	4.0
0.20	4.0	1.0	0.5	0.5	1.5	4.5
0.30	3.0	1.5	0.5	0.5	1.5	4.5
0.50	3.5	1.0	0.5	0.5	1.0	5.0
0.70	5.0	1.0	0.5	0.5	1.0	5.0

TABLE 4. 3 RELATION BETWEEN TIME TO STEADY STATE AND THE FILLING TIME

Number of stages N	Time of filling t_1 min.	Time to steady state t_2 hrs.	t_2/t_1
2	13.70	1	4.38
4	27.40	2	4.38
6	41.10	4	5.84
8	54.80	7	7.66

TABLE 4. 4 PATTERN OF STEADY STATE

No. of Stages	Time to steady state in hrs.											
N	1	2	3	4	5	6	7	8	9	10	11	12
2	1	1										
4	1.25	1	1	2								
6	3.5	1.5	1	0.5	1.5	4						
8	4.5	1.5	1	0.5	0.5	1	1.5	7				
10	x	2	1.5	1	0.5	0.5	1	1.5	3	x		
12	x	3	1.5	1	1	0.5	0.5	1	1	1.5	x	x

TABLE 4.5 REGRESSION ANALYSIS FOR THE DATA PRODUCED FROM EQUATION 4.5 - CASE (i)

Variable	Regression Coeff.	Partial Correlation	Multiple Correlation	Standard Error	Remarks
V	0.954301	0.96	0.646	0.0599856	Multiple correlation = 0.974 Intercept term = Exp(-8.2426672) E.S.S.= 1.21029 Residual error= 0.224564
Ø	0.6414865	0.71	0.948	0.129414	
R	1.1997742	0.81	0.922	0.175285	
M	0.6355532	0.77	0.935	0.106242	
N	1.3885674	0.83	0.915	0.190706	
X_o	0.0417706	0.14	0.974	0.0621473	

TABLE 4.6 REGRESSION ANALYSIS FOR THE SMOOTHED DATA - CASE (ii)

Variable	Regression Coeff.	Partial Correlation	Multiple Correlation	Standard Error	Remarks
V	0.9437589	0.96	0.646	0.0591046	Multiple correlation = 0.975 Intercept term = Exp(-8.1127529) E.S.S.= 1.17501 Residual error= 0.221266
Ø	0.6379756	0.71	0.947	0.127514	
R	1.2009027	0.82	0.921	0.172711	
M	0.6383645	0.78	0.934	0.104681	
N	1.3425672	0.82	0.918	0.187906	
X_o	0.0417718	0.14	0.974	0.0612346	

TABLE 4.7 REGRESSION ANALYSIS FOR CASE (iii)

Variable	Regression Coeff.	Partial Correlation	Multiple Correlation	Standard Error	Remarks
V	0.9567142	0.97	0.666	0.0515905	Multiple correlation = 0.982 Intercept term = Exp(-8.353137) E.S.S.= 0.896261 Residual error= 0.193247
Ø	0.6666497	0.77	0.954	0.111301	
R	1.1918152	0.85	0.932	0.150835	
M	0.838443	0.87	0.924	0.0982951	
N	1.3174521	0.85	0.931	0.164076	
X_o	0.0999960	0.36	0.979	0.0534803	

Table 4.8 Results of Optimization by the Discrete Maximum Principle

K_2 °C	K_1	x_0	N	Temp. grad. $T_N - T_1$	Profit
30	1	0.1935	4	2.1	175.973
30	1	0.1665	4	1.4	144.652
30	1	0.15008	4	1.1	124.843
30	0	0.284	4	0	288.856
60	1	0.257	4	0	233.699
60	1	0.15	3	0.9	123.176
60	1	0.304	3	5.2	230.145
60	1	0.348	3	7.1	235.184
60	1	0.351	3	7.3	234.87
60	1	0.3716	3	8.3	230.773
60	1	0.396	3	9.7	219.376
60	1	0.2349	5	6.9	165.866
60	1	0.249	5	8.7	146.341
60	1	0.293	5	16.3	-26.557
60	1	0.332	5	25.4	-396.925
60	1	0.2751	6	18.3	-123.553
60	0.5	0.15	4	2.0	122.5
30	1.5	0.15	4	0.7	120.0
30	1.5	0.3	4	5.6	262.238
30	1.5	0.355	4	9.3	248.055
30	1.5	0.387	4	12.4	160.00
60	1.5	0.197	4	1.8	173.552
60	1.5	0.254	4	4.0	205.00
60	1.5	0.2627	4	4.5	205.955
60	1.5	0.302	4	6.7	193.526
60	1.5	0.15015	3	1.6	144.243
60	1.5	0.2538	3	2.2	212.195
60	1.5	0.379	3	5.6	257.558
60	1.5	0.394	3	6.1	256.794
60	1.5	0.2549	5	6.5	164.62
60	1.5	0.3049	5	12.7	2.7329
60	1.5	0.2595	6	10.2	58.8459
60	1.5	0.273	6	12.2	-38.1718
30	0	0.363	4	0	366.766
30	2	0.2978	4	4.0	271.00
30	2	0.352	4	6.7	264.3
30	2	0.38	4	7.7	230
30	2	0.415	4	10.6	144
30	2	0.434	4	13.7	50.66
30	5	0.304	4	1.6	295.34
30	5	0.384	4	3.5	319.459
30	5	0.404	4	4.1	311.676
30	5	0.455	4	5.9	254.657
30	5	0.5	4	7.9	143.01
30	5	0.305	3	1.1	290.157
30	5	0.35	3	1.6	324.649
30	5	0.384	3	2.0	345.63
30	5	0.404	3	2.2	355.612
30	5	0.4518	3	2.9	372.291

Contd:

Contd. Table 4.8

K ^{o}C	K_1	x	N	Temp. grad. $T_N - T'$	Profit
30	5	0.36	5	4.0	280.965
30	5	0.384	5	5.2	240.252
30	5	0.402	5	6.3	188.874
30	5	0.431	5	8.2	65.061
30	5	0.443	5	9.0	-4.29173
30	5	0.418	6	10.0	-121.563
30	5	0.446	6	12.8	-442.589
60	5	0.1498	3	0.2	123.229
60	5	0.252	3	0.6	216.257
60	5	0.303	3	1.0	252.539
60	5	0.3507	3	1.4	278.121
60	5	0.2563	6	3.2	176.426
60	5	0.303	6	6.9	-21.0112
60	5	0.2805	8	12.0	-650.468
60	0	0.2584	8	0	240.385
60	0	0.27	8	0	249.305
60	0	0.2428	6	0	228.643
60	0	0.302	6	0	274.858
60	0	0.361	6	0	313.173
20	0	0.351	4	0	373.869
20	0	0.3014	4	0	315.266
20	0	0.2502	3	0	250.736
20	0	0.4003	5	0	434.434
20	0	0.41	6	0	450.955

Table 4.9 Optimum phase ratio in a 4-stage mixer settler

R	K_1	K_2	x_o	ΔT	profit
1	unstable solution				
2	2	30	0.48605	2.8	530.33
	5	30	0.4558	1.9	504.4
3	1	30	0.3005	8.1	240.672
	1	30	0.176	1.6	156.174
	1	30	0.158	1.2	134.425
	2	30	0.173	0.7	153.965
	2	30	0.157	0.6	133.808
	5	30	0.178	0.3	161.081
	5	30	0.1507	0.23	126.654
4	1	30	0.175	5.8	115.376
	2	30	0.17	2.6	130.301
	5	30	0.167	1.0	136.446
6	1	30	0.109	8.8	-27.0327
	2	30	0.109	4.2	16.5617
	5	30	0.109	1.6	40.5221

Table 4.10 Optimum phase ratio - for different number of stages operating at ordinary temperature

N	R	x_o	profit
6	1	unstable	solution
	2	unstable	solution
	3	below	$x_o = 0.35$
	4	0.17	144.720
	4	0.18	156.355
	4	0.2	176.712
	5	0.1305	88.53
	6	0.1308	56.785
		0.0931	41.183
8	3	unstable solution below $x_o = 0.37$	
	4	0.195	156.0
	4	0.2	174.105
	5	0.1358	87.54
	5	0.1486	96.414
	5	0.1717	111.159
	6	0.0952	36.4737
		0.1016	40.7816
		0.129	57.68
		0.149	69.07
		0.169	79.18
	8	0.093	-8.34
9	4	0.202	173.026
	5	0.157	98.831
		0.195	121.396
		0.213	131.236
	6	0.095	32.8687
		0.1338	56.453
		0.15	66.0129
		0.184	82.771
		0.2	90.305
	8	0.107	10.97
		0.152	30.22
	12	0.101	-20.715
		0.152	-5.93

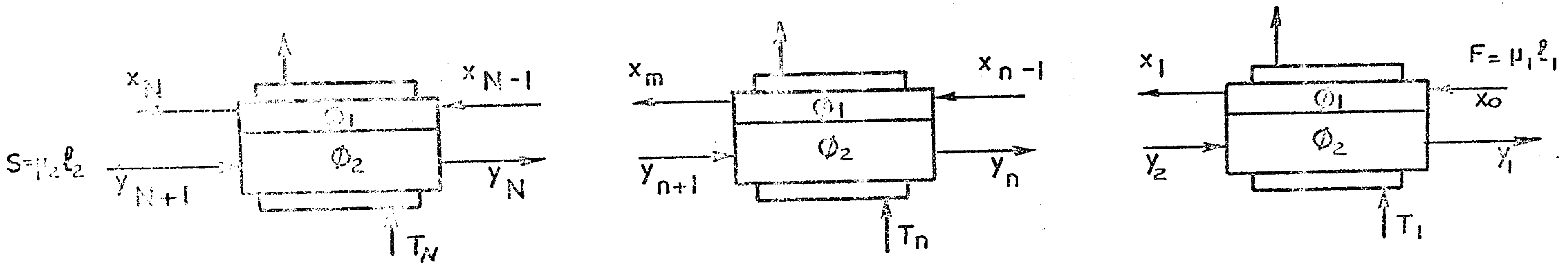


Fig. 4.1. Stagewise counterflow system.

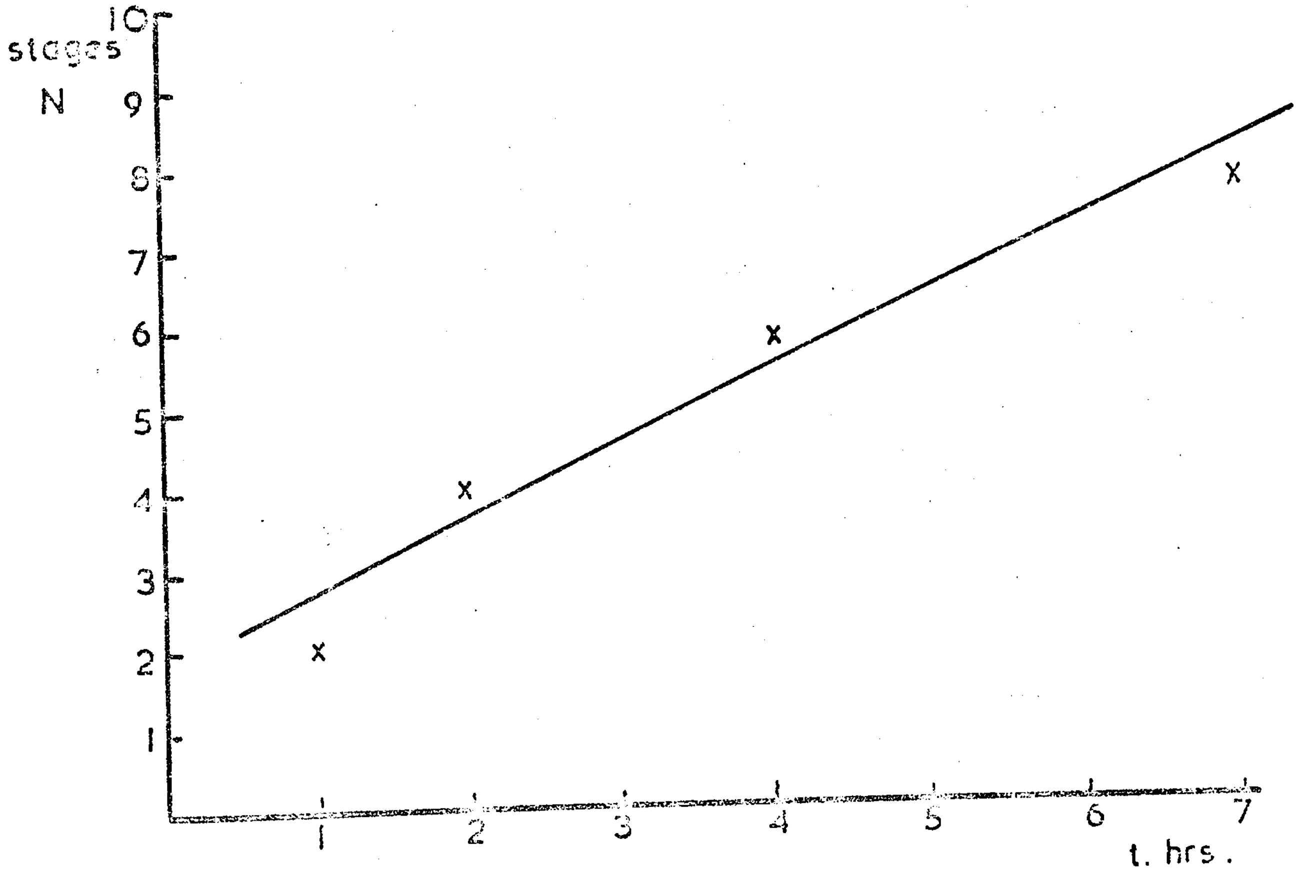


Fig. 4.2 Number of stages vs time to steady state

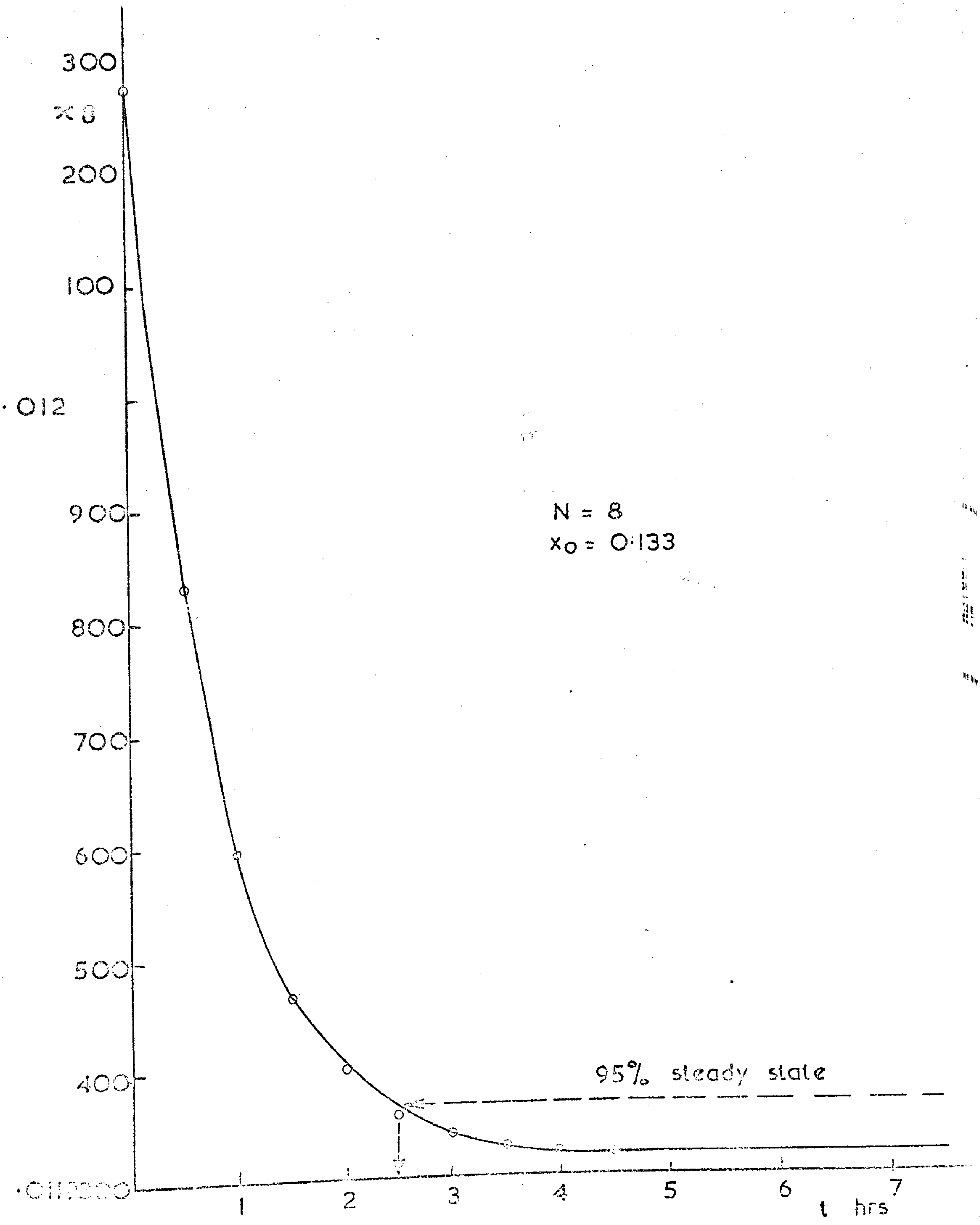


Fig. 4.3 Time to steady state and 95 % steady state of stage 8

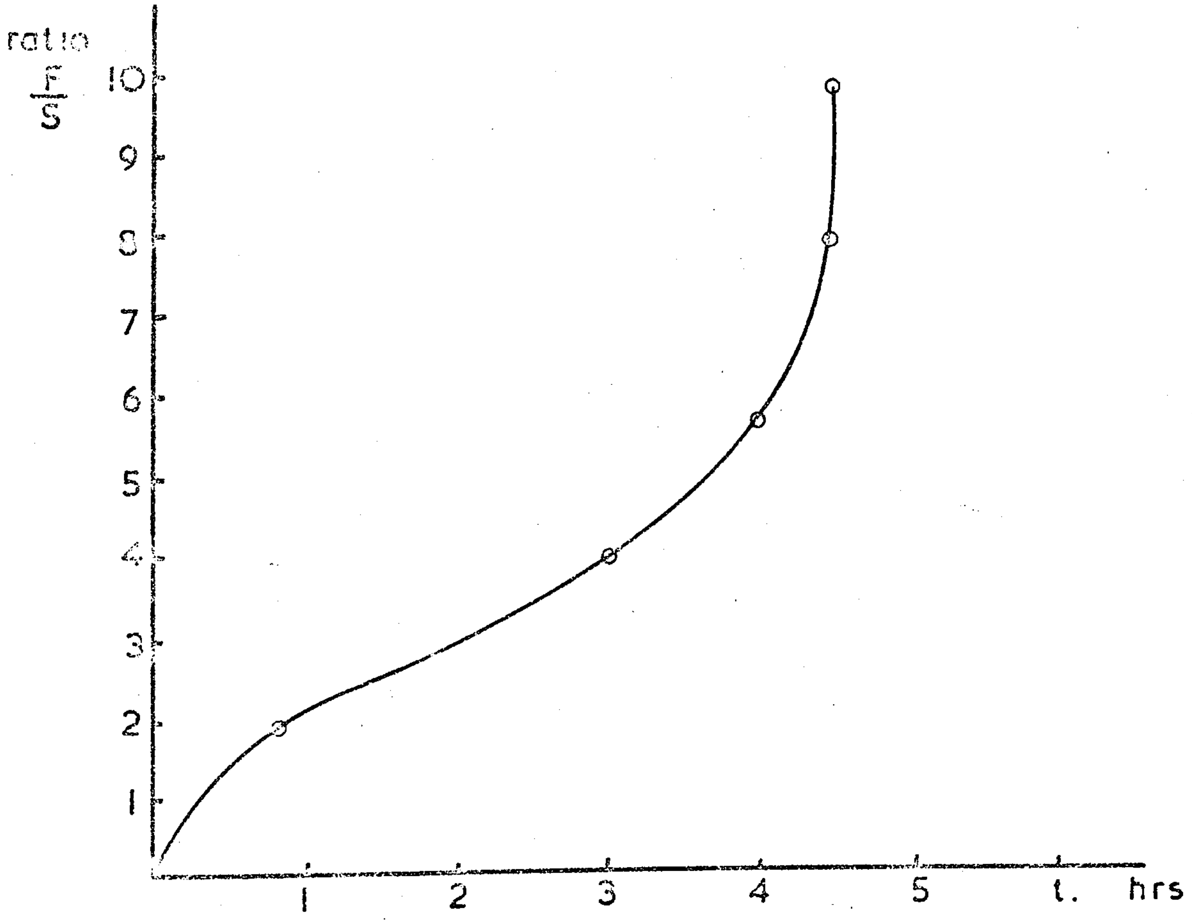


Fig. 4.4 Effect of the phase ratio on the time to steady state.

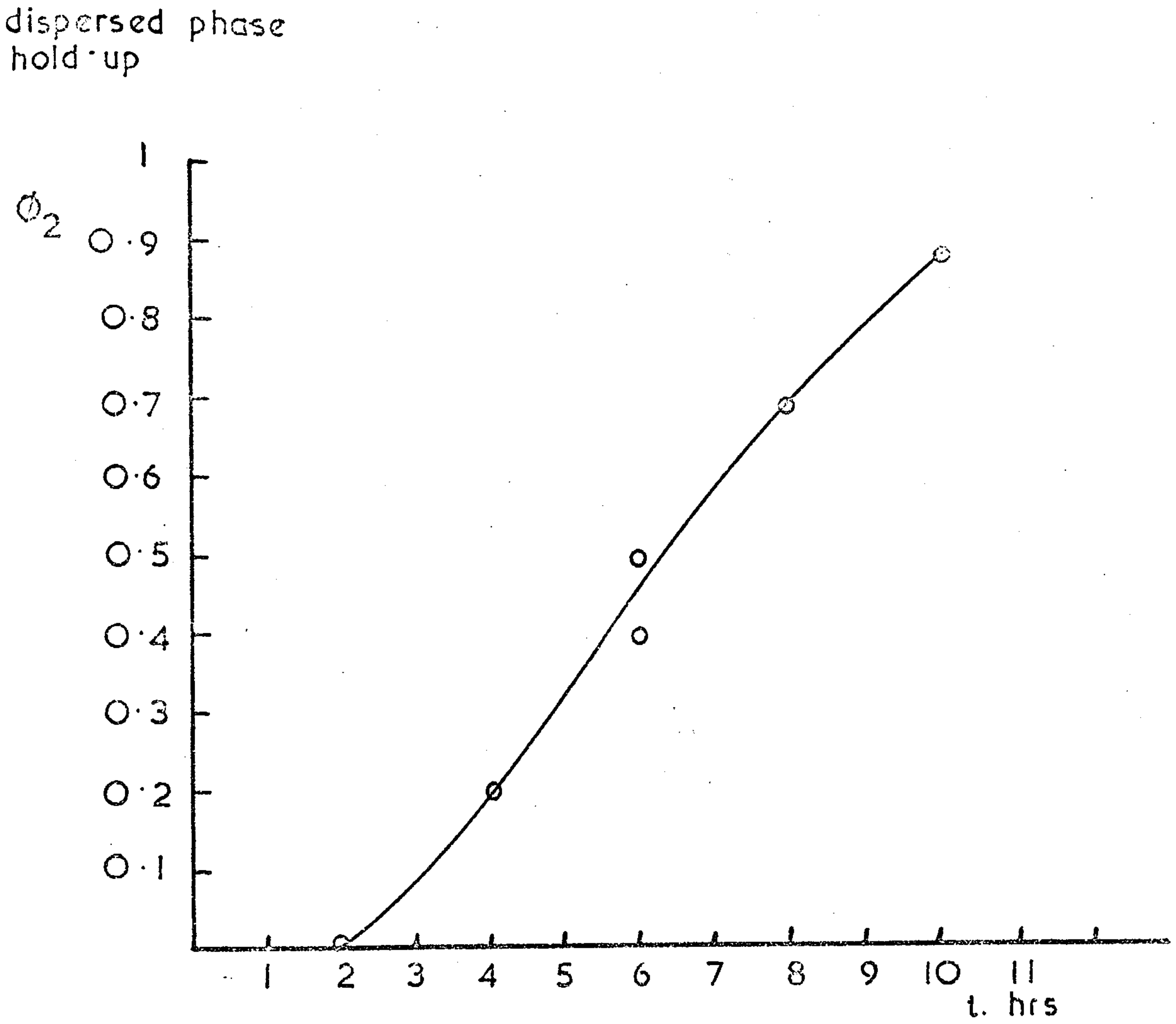


Fig. 4.5 Effect of the dispersed phase hold-up on the time to steady state

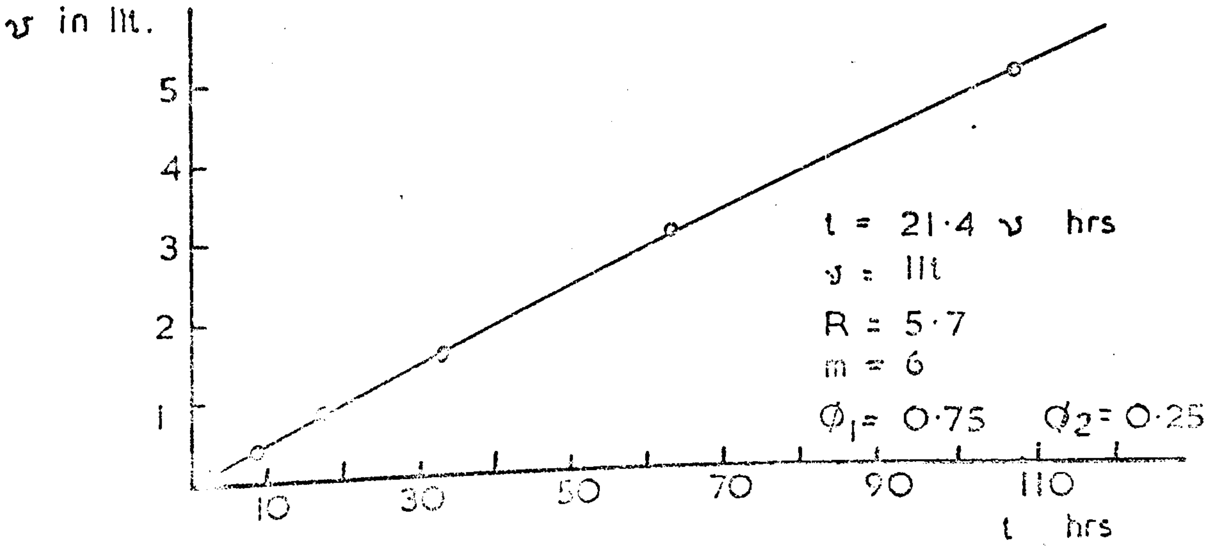


Fig. 4.6 Effect of the volume of mixer on the time to steady state.

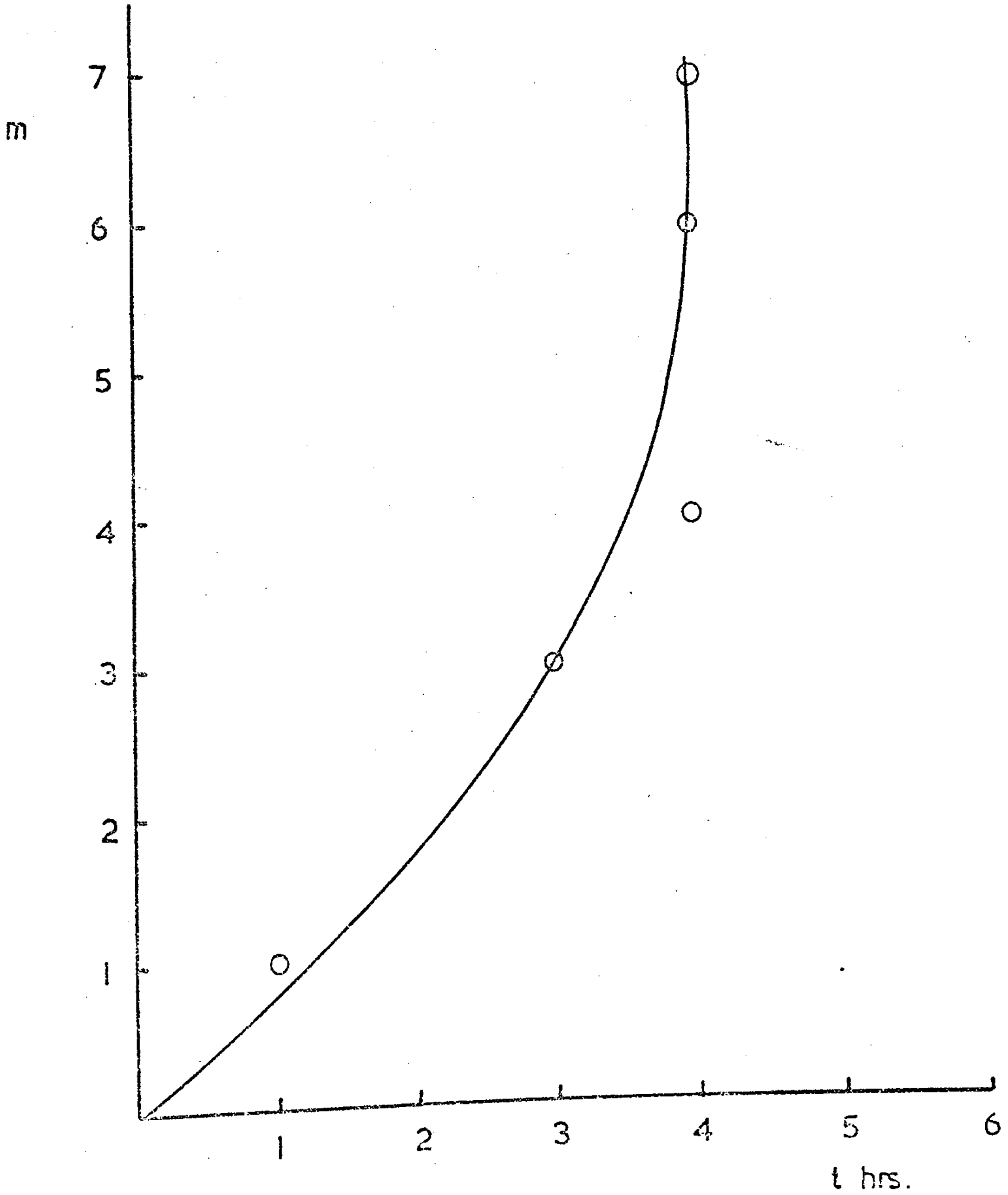


Fig. 4.7 Effect of the distribution coefficient on the time to steady state.

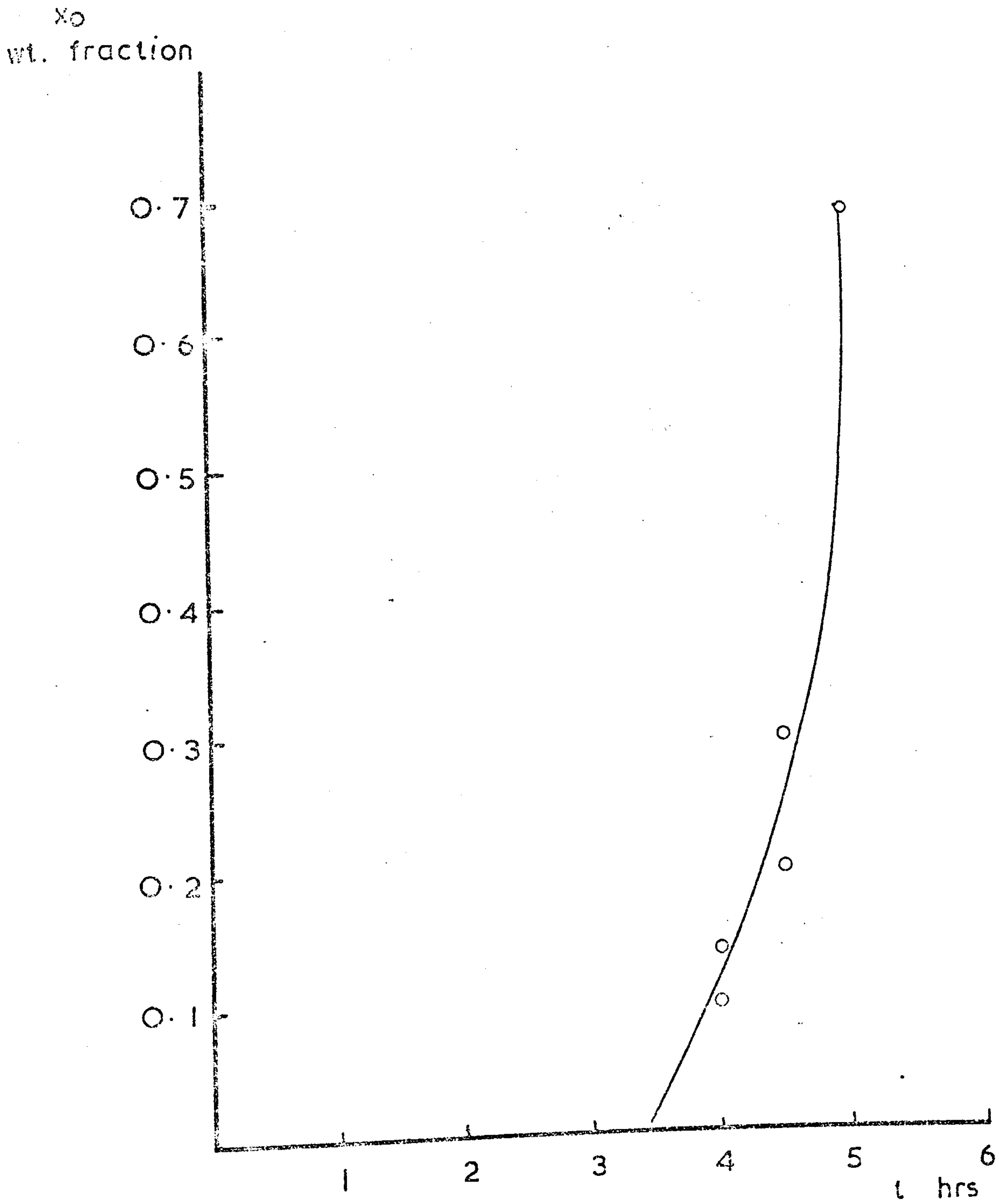


Fig. 4.8 Feed concentration vs. time to steady state

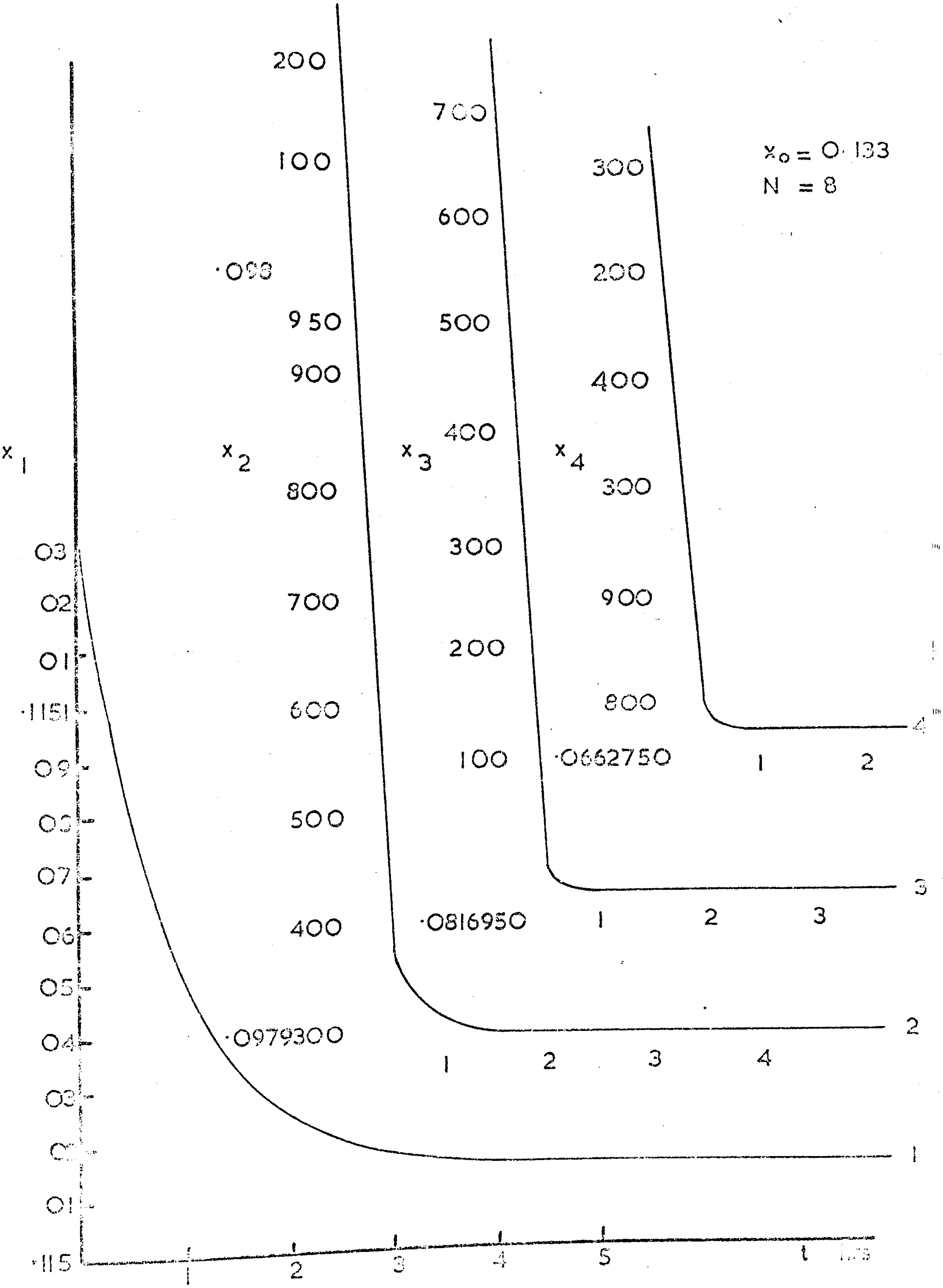


Fig 4.9 Effect of the position of the stage on its time to steady state

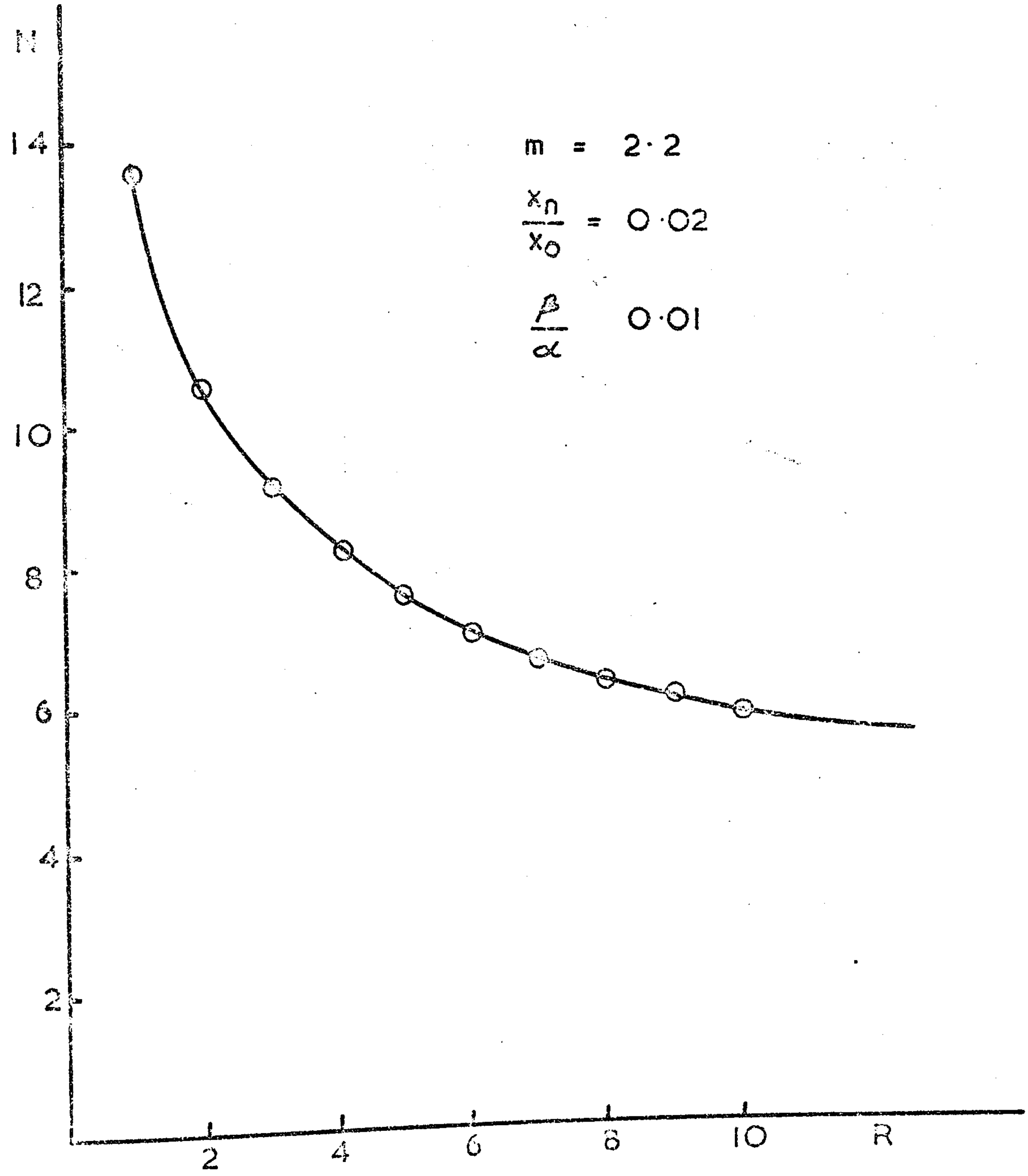


Fig. 4. 10 Effect of the phase ratio on optimum number of stages

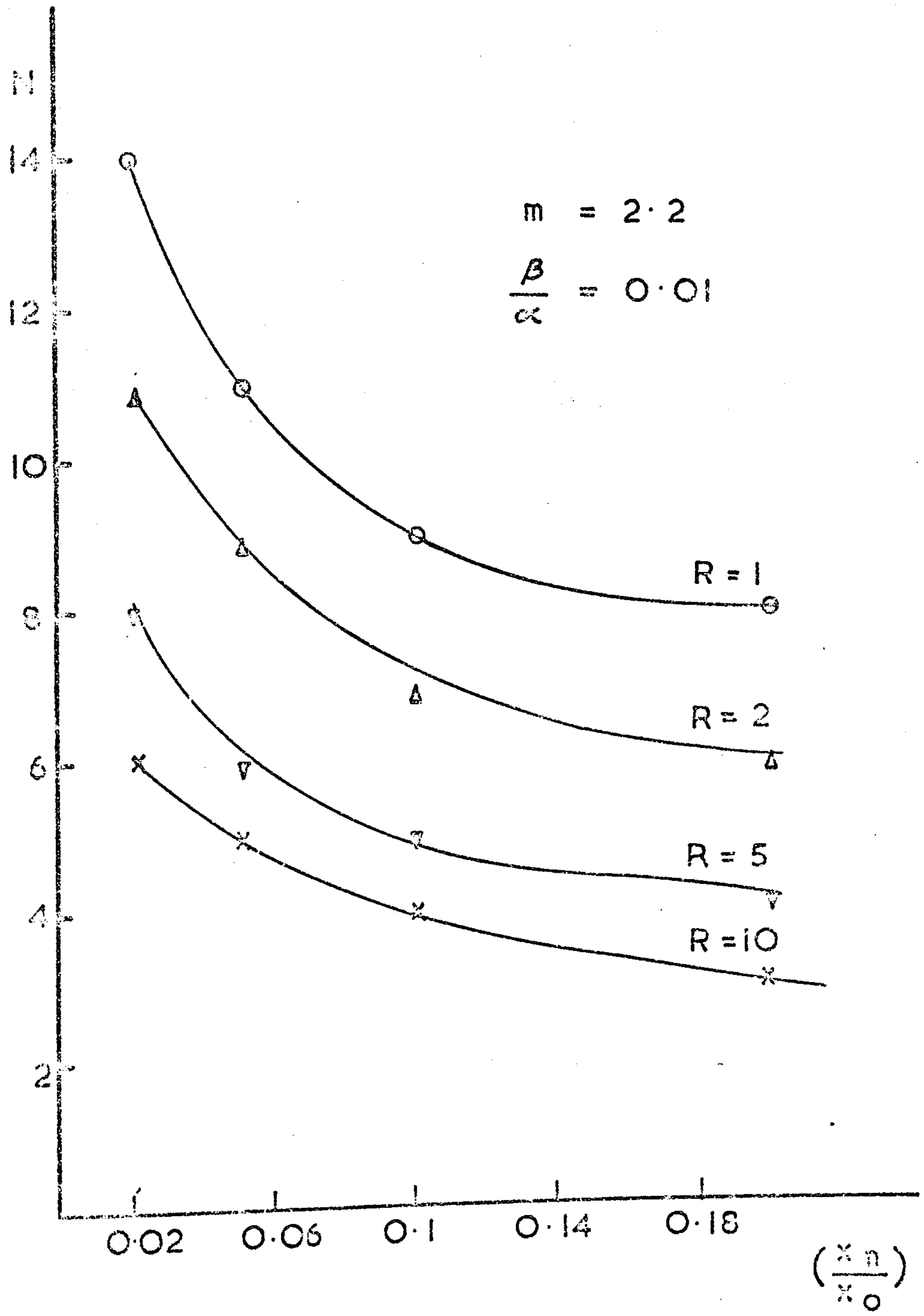


Fig. 4. 11 Optimum number of stages vs. extractability

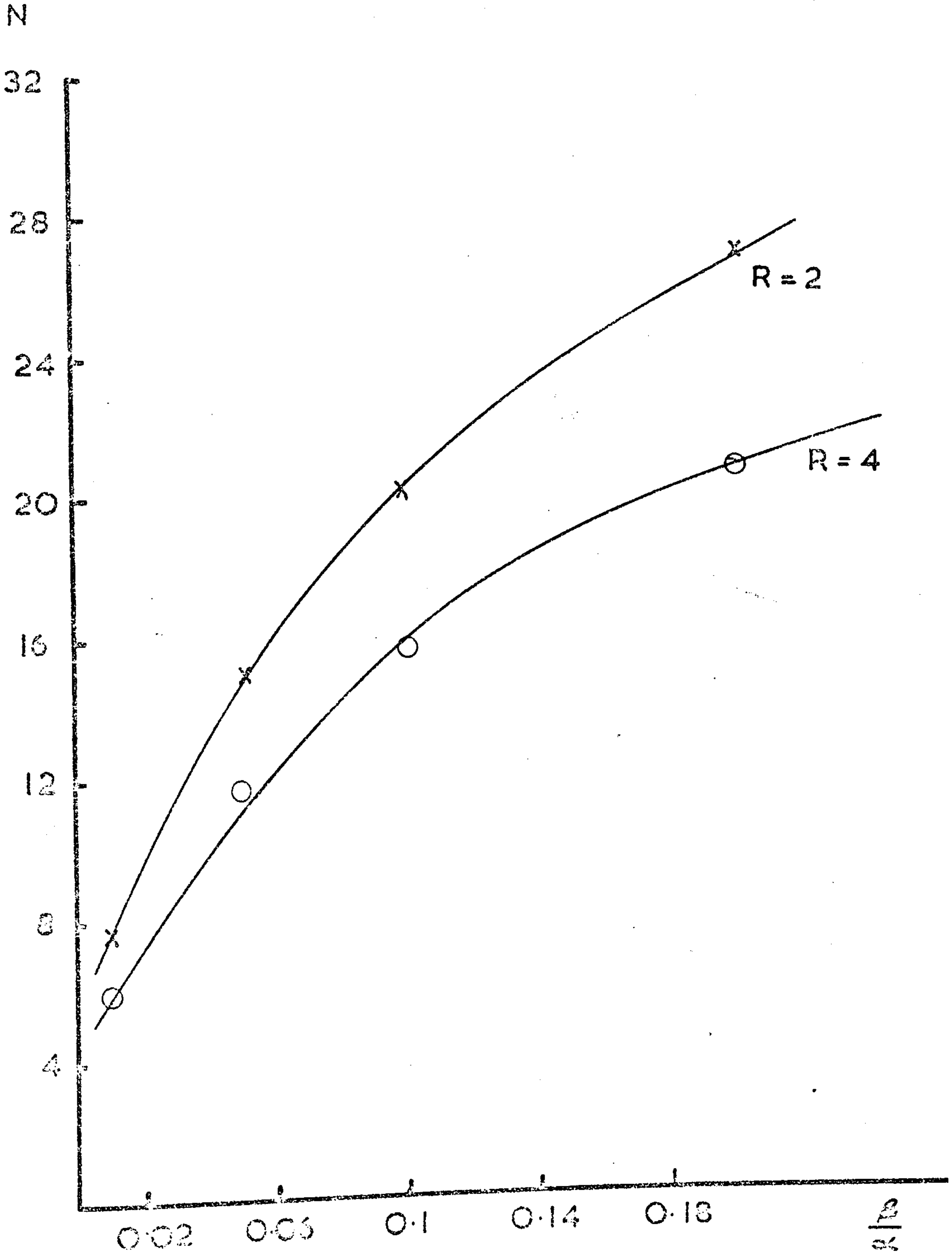


Fig. 4.12 Effect of the economic factor on optimum number of stages

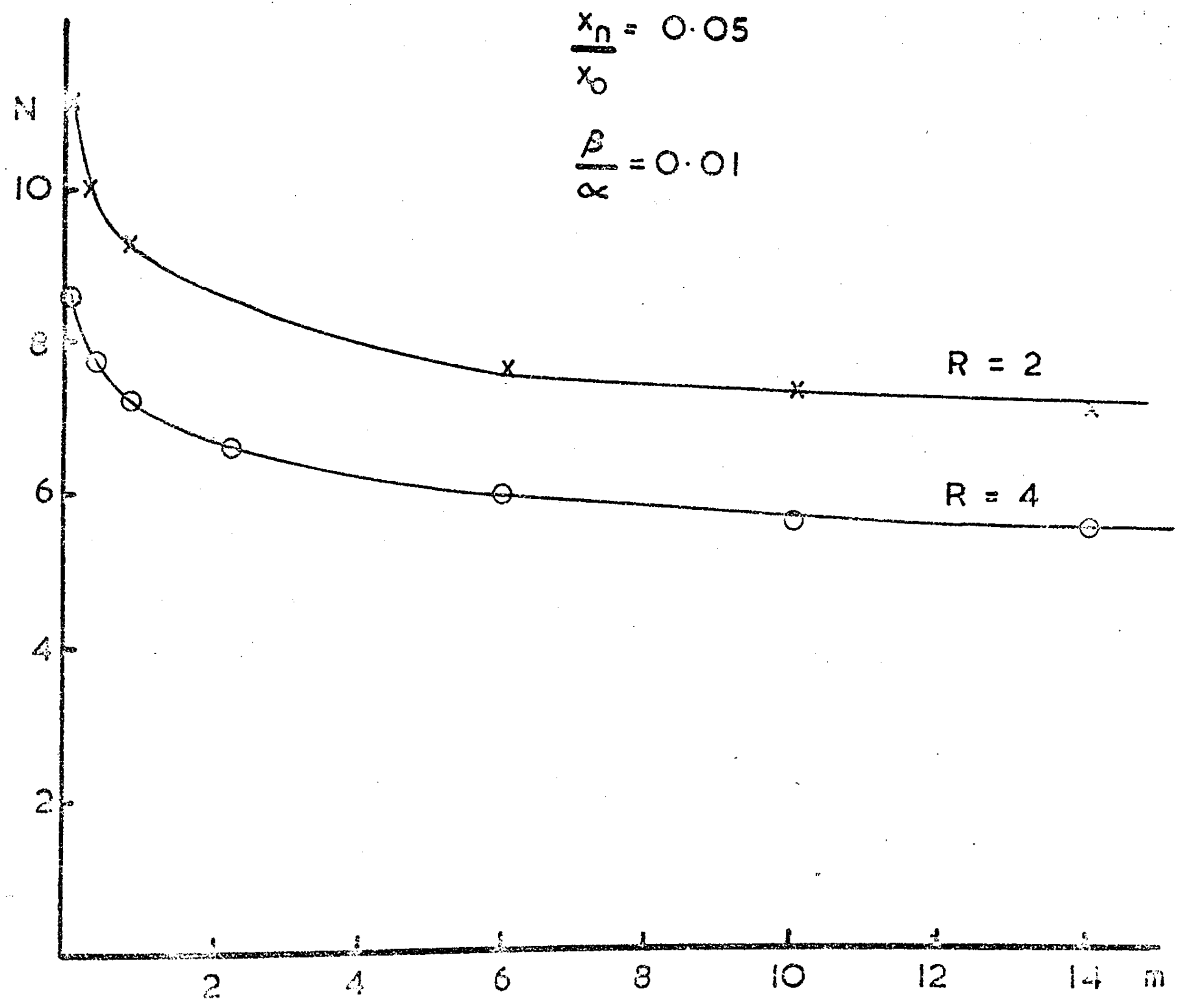


Fig. 4.13 Effect of the distribution coefficient on optimum number of stages

5 . Experimental Investigation

The object of the experimental work is to develop a laboratory mixer-settler suitable for advanced studies of liquid-liquid extraction . The apparatus should be simple to operate and inexpensive to construct and yet be suitable for the treatment of corrosive organic liquids . In addition the temperature of each stage must be easily controlled and changed and each agitator should rotate at substantially uniform speed so that the phases under-going treatment are intimately contacted .

The essential requirements were :

a) That the apparatus should be easily and rigorously cleaned .

b) That wide range of operating parameters , vis flow rate and agitator speeds , should be attainable .

c) That individual temperature control could be provided on both mixers and settlers .

5.1. Apparatus Design :

The apparatus consisted of ten stages connected as shown in Fig 5.1 . The phases within each stage were completely mixed whilst the flow through the system as a whole was countercurrent . Two aspirators , each of 20 lit. capacity served as feed and solvent reservoirs and were located at a height of about 65 cm above the cells as shown in Fig 5.2 to provide sufficient head for flow via two flowmeters (Flowbits GS /$\frac{1}{4}$'S 0 - 300 c.c.per min.) . Two similar flowmeters were included to determine the flow rates of the outlet streams from the apparatus as shown in Fig 5.3. The extract and raffinate were collected in two aspirators of 10 lit.each located at the ground level .

The general arrangement of the ten stages is shown in Figs 5.4 and 5.6 .

5.1.1. The mixer

Each mixer consisted of a glass-jacketed cylinder of 4.57 cm internal diameter and 11 cm height and was provided with two inlet nozzles of about 1.8 cm diameter for the two phases . A 18.5 cm long and 2 cm diameter central glass tube surrounded the agitator and served to transfer the dispersion to the settler as illustrated in Fig 5.5 . A small hole was drilled in the side of the draught tube just below the neck of the mixer to balance the pressure and enable the mixer to be filled . Initially the draught tube was connected directly to the horizontal settler through a SVL joint with a P.T.F.E. sealing ring but this junction restricted the flow from the mixer to the settler . Therefore the settler was lowered 6 cm and connected directly to the draught tube through a P.T.F.E. tube . The draught tube was provided with a vertical vent as shown in Fig 5.6. The agitator was constructed from a rod of stainless steel 10 cm long , 6mm diameter and

An Archimedean screw made of P.T.F.E. 18 cm long and 10 mm diameter fitted tightly over the rod as shown in Fig 5.4 . The grooves in the screw were 4.75 mm in height . Since mixing in the lower regions of the vessel was not efficient two paddles were included at the lower end of the agitator . Overcashier et al (132) stated that the best agitator design is any impeller that has a diameter about 40% of the vessel diameter and is centred in the unbaffled vessel . Therefore the paddles were made of stainless steel 1.9 cm long and 1.4 cm wide which is about 40% of the vessel diameter . This was found to yield a good emulsion and micromixing at speeds higher than 1000 r.p.m. . The agitator was located as low as possible to the bottom of the vessel to increase the pumping capacity of the agitator from the mixer to the settler via the draught tube . The ten agitators were driven by five Voss Instruments Ltd S/8 motors of 1/8 H.P. which were capable of speeds as high as 3000 R.P.M. . Each motor rotated two agitators ; one directly connected to the motor and the other through a flexible drive connected to the top side of the motor shaft . The motors were held on one side of the frame as shown in Fig 5.7. The agitators' speeds were measured by an electric tachometer with a photoelectric probe for each motor connected to a five-key point box to indicate the speed of each motor at a time as shown in Fig 5.8. Each agitator speed was controlled by a variac transformer directly linked in series with the mains and the motor . This was found to be not satisfactory and therefore a gear box was designed. It consisted of two brass plates containing 6 steel pinions . Each pinion had 15 teeth . The dimensions of the pinions are given in Fig 5.9. The pinions are connected together by a simpler roller steel chain as shown in Fig 5.9. A pinion and the chain are presented in Fig 5.10 . Each pinion rotated a mild steel spindle which is supported by 2 stainless steel bearings . Each motor connected to the spindle via a flexible drive while another five flexible drives transmitted the movement from the gear box to the agitators on the other side of the frame as shown in Fig 5.11 .

The speed of each agitator was tested and the maximum difference between the speeds of each was about 6 % at 1800 r.p.m. and lower as the speed increases . At a later stage , it was found more economical to use only a $\frac{1}{4}$ HP series motor instead of the five motors .

Each mixer possessed a glass-jacket for cooling water or heating fluid . Dimensions of the mixer are given in Table 5.1 .

Four Townson and Mercer thermostatic circulating units equipped with contact thermometers (0 - 100^{o}c) provided water at a constant temperature to the mixer-settler jackets . Each unit had a capacity of 5.8 litres . The connections of the circulating units to the different stages are shown in Fig 5.12 . Copper distributors of

1.5 cm diameter provided with a number of smaller tubes of 6.3 mm diameter were used to supply the stages with water from the circulators . Similar copper distributors, provided with vertical vents , were used for the outlet water from the stages to the circulators .

5.1.2. The Settler

Each settler was a glass cylinder of 6.42 cm internal diameter and 13 cm long , and was provided with a glass-jacket . The settler was supported horizontally and connected to the draught tube of the mixer via a P.T.F.E. tube . The settler contained two outlets of the same dimensions as the inlets of the mixer . Two P.T.F.E. valves were connected to each outlet ; one for sampling purposes and the other for separating the stages and for adjusting the interface in the settler . The connections between the settlers and mixers were made of glass and P.T.F.E. tubes of 6 mm diameter .

The settler capacity and other dimensions are given in Table 5.1 .

5.2. Equipment for preparation of feed and solvent :

Two 50 lit. Q.V.F. spherical glass vessels were mounted on a frame of 60 cm high and served as feed and solvent preparation and storage vessels . A stainless steel , Stuart Turner No. 10 pump , packed with P.T.F.E. was used to circulate the liquids from and to each vessel for homogenization and to pump the liquids to the 20 litres overhead reservoir as shown in Fig 5.2 and 5.13 .

Table 5.1 Dimensions of the mixer-settler

Item	Mixer	Settler
Inside diameter	4.57 cm	5.42 cm
Outside diameter	6.60 cm	8.00 cm
Capacity	175 cc	300 cc
Jacket capacity	130 cc	175 cc
Length	11.0 cm	13.0 cm
Heat-transfer area	158 sq cm	221 sq cm

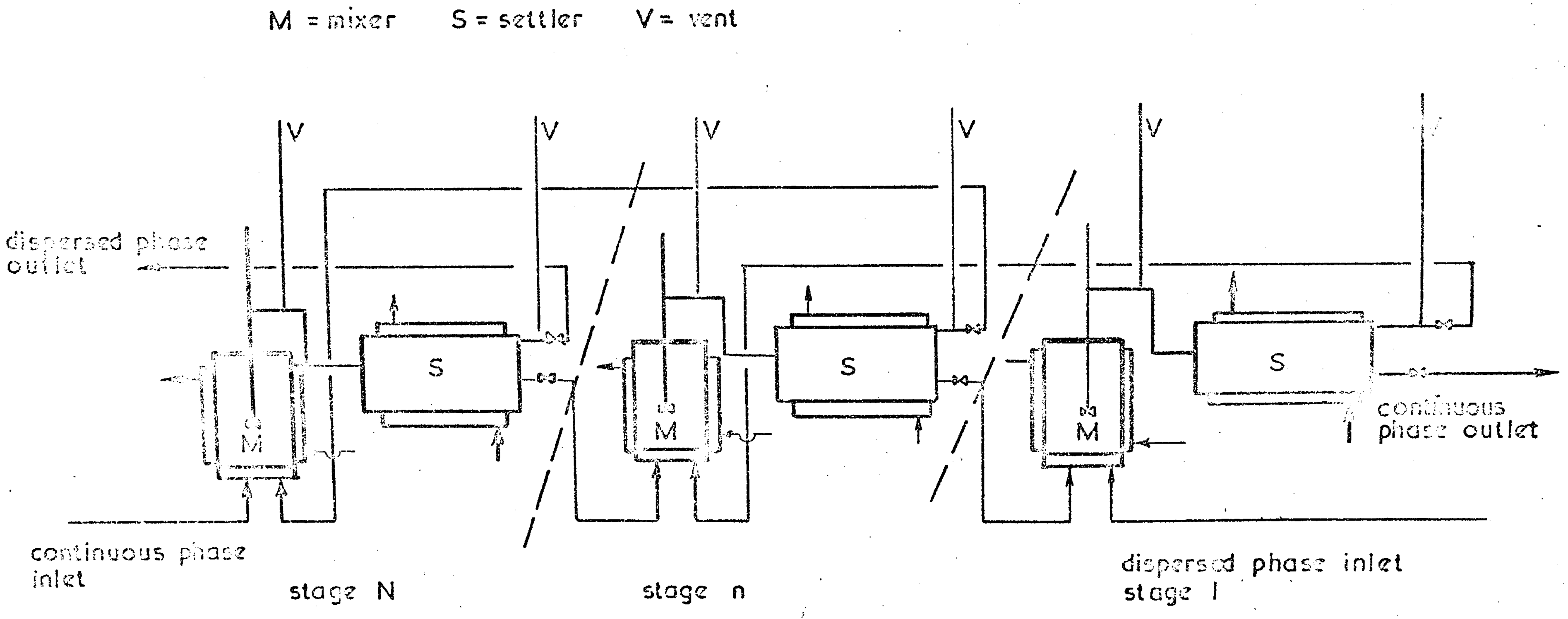


Fig. 5.1 Diagramatic representation for the mixer - settler arrangement

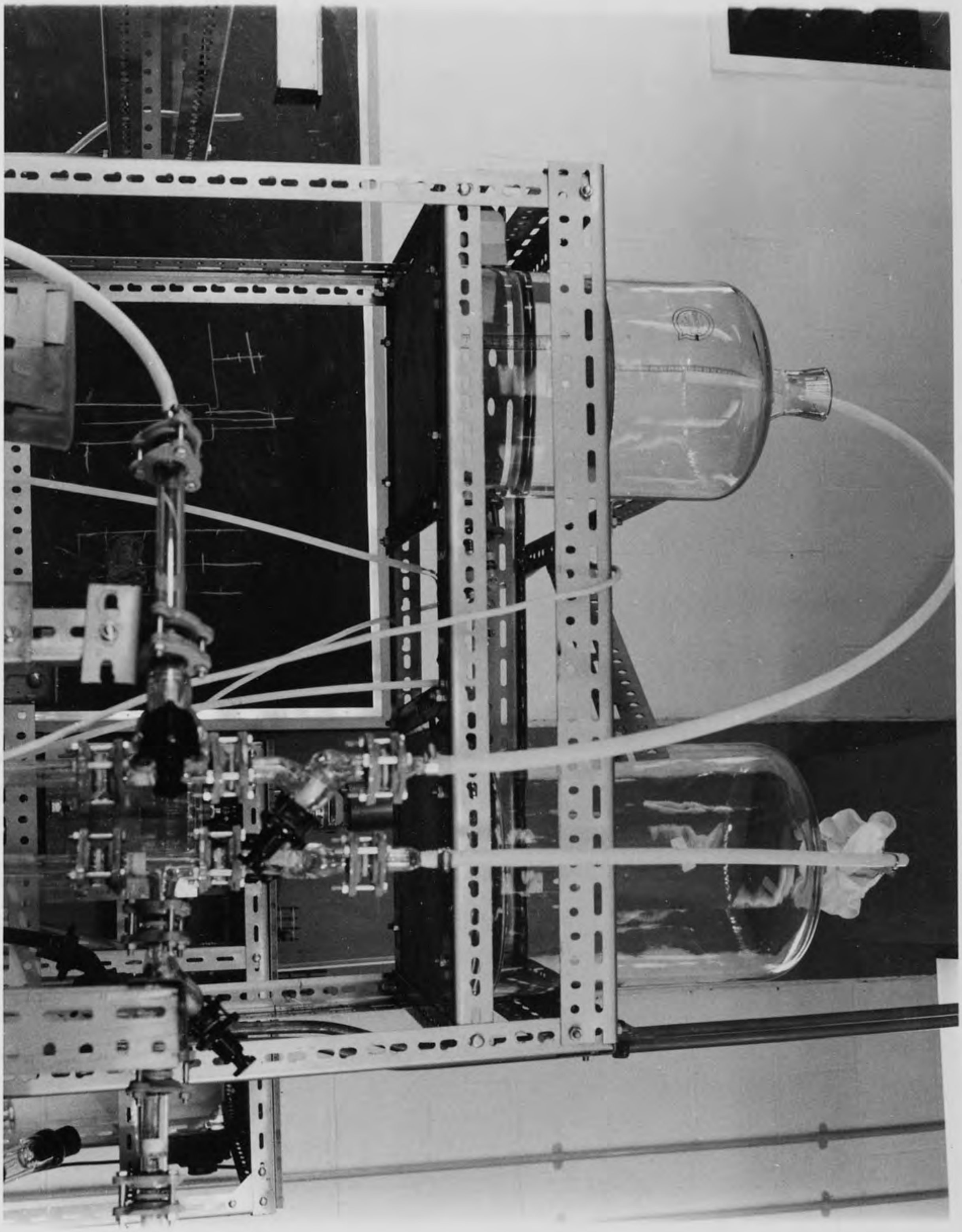


Fig. 5.2 Overhead reservoirs for liquid feed

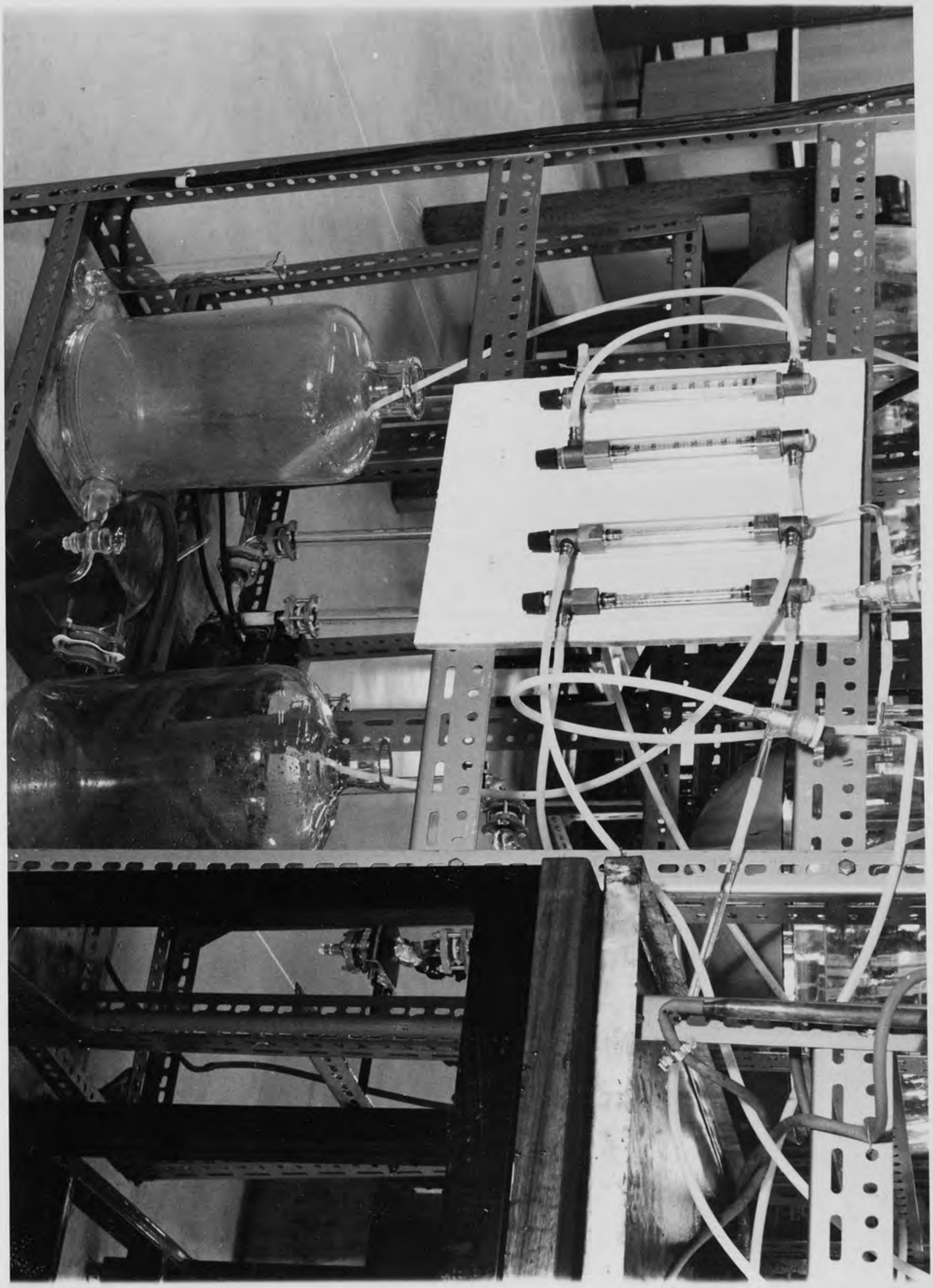


Fig. 5.3 Resorvoirs for the exit liquids

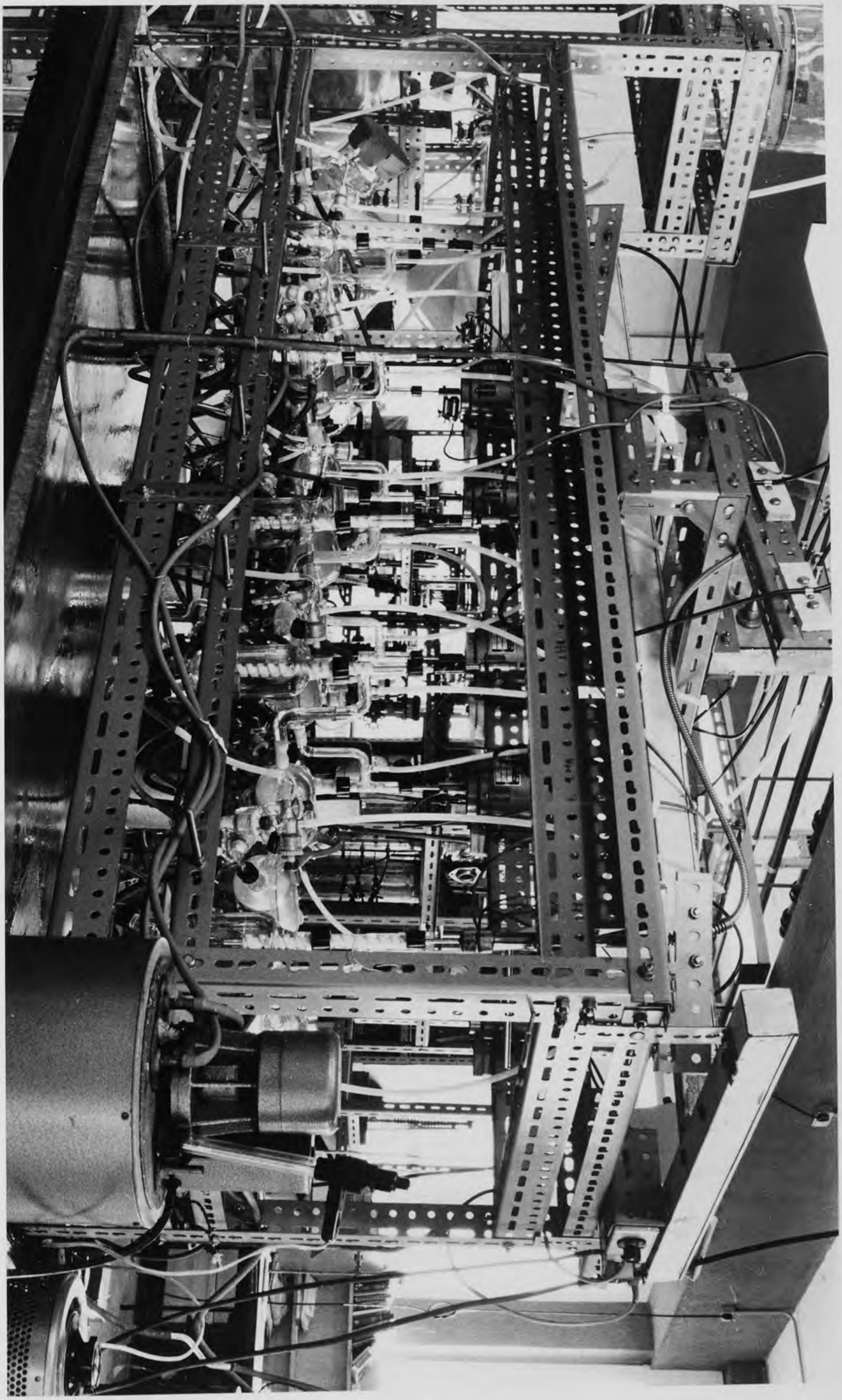


Fig. 5.4 A 10 stage mixer - settler

Fig.5.5 The agitator and draught tube

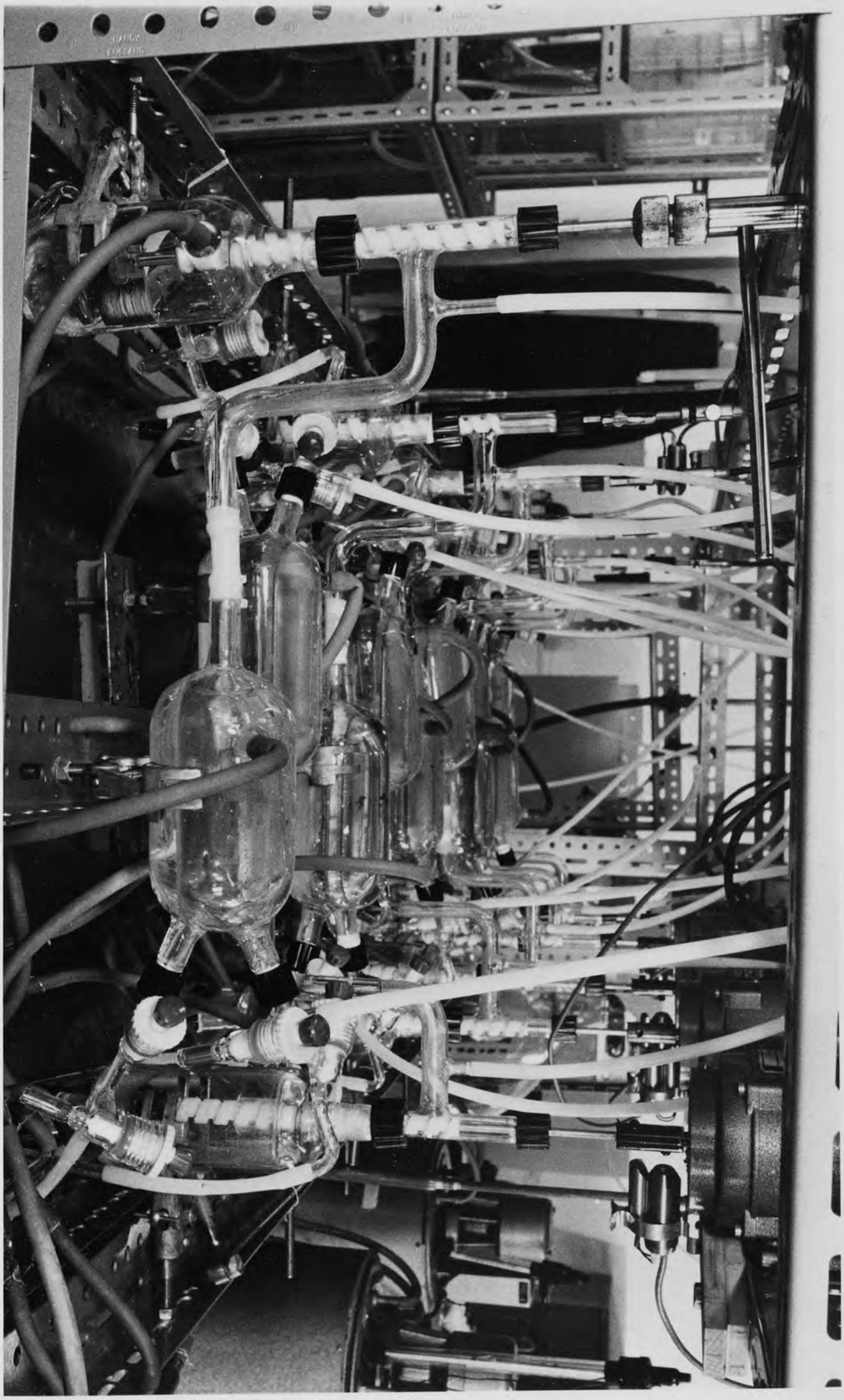


Fig 5.6 The mixer settlers arrangement

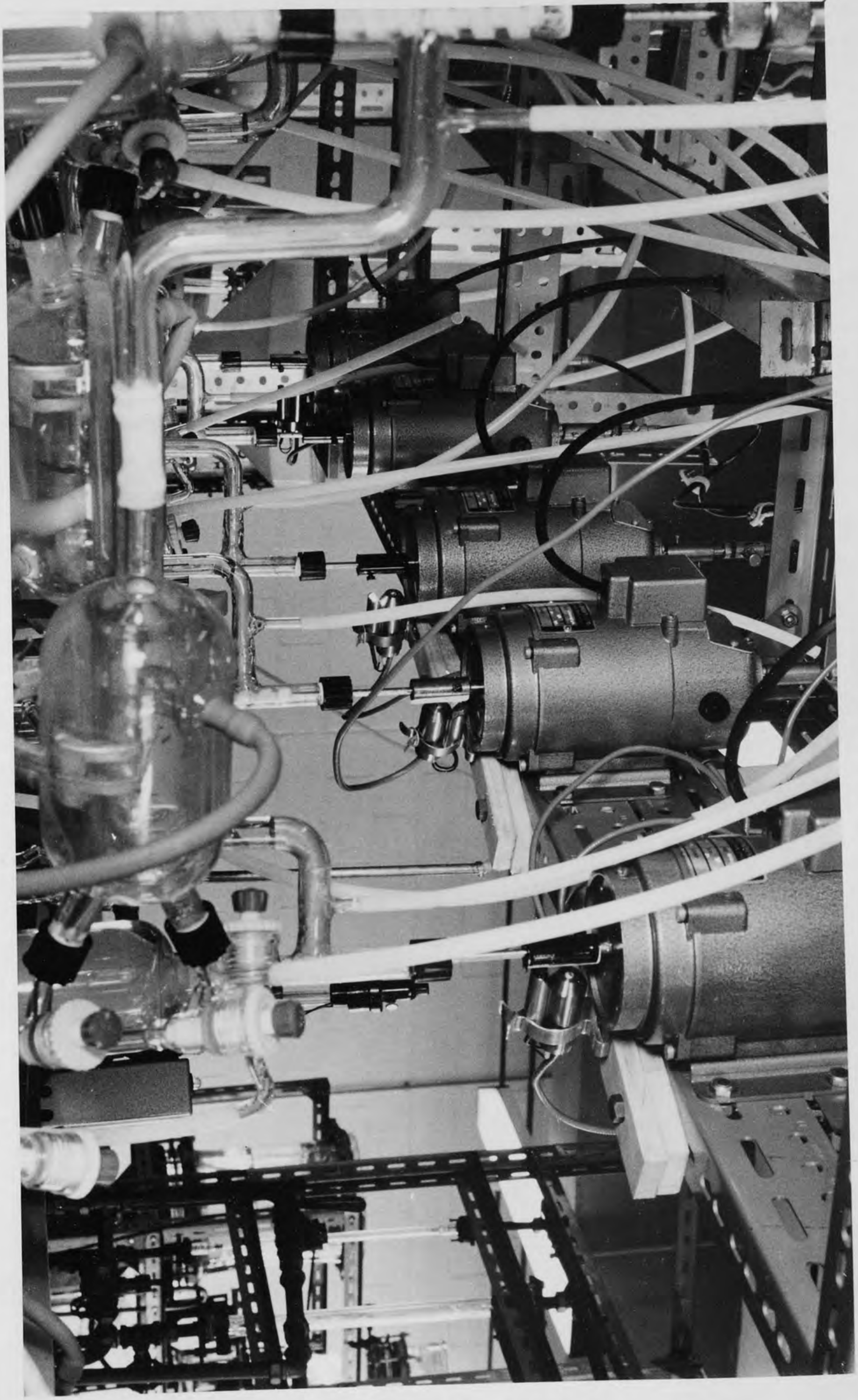


Fig . 5 . 7 Motors arrangement

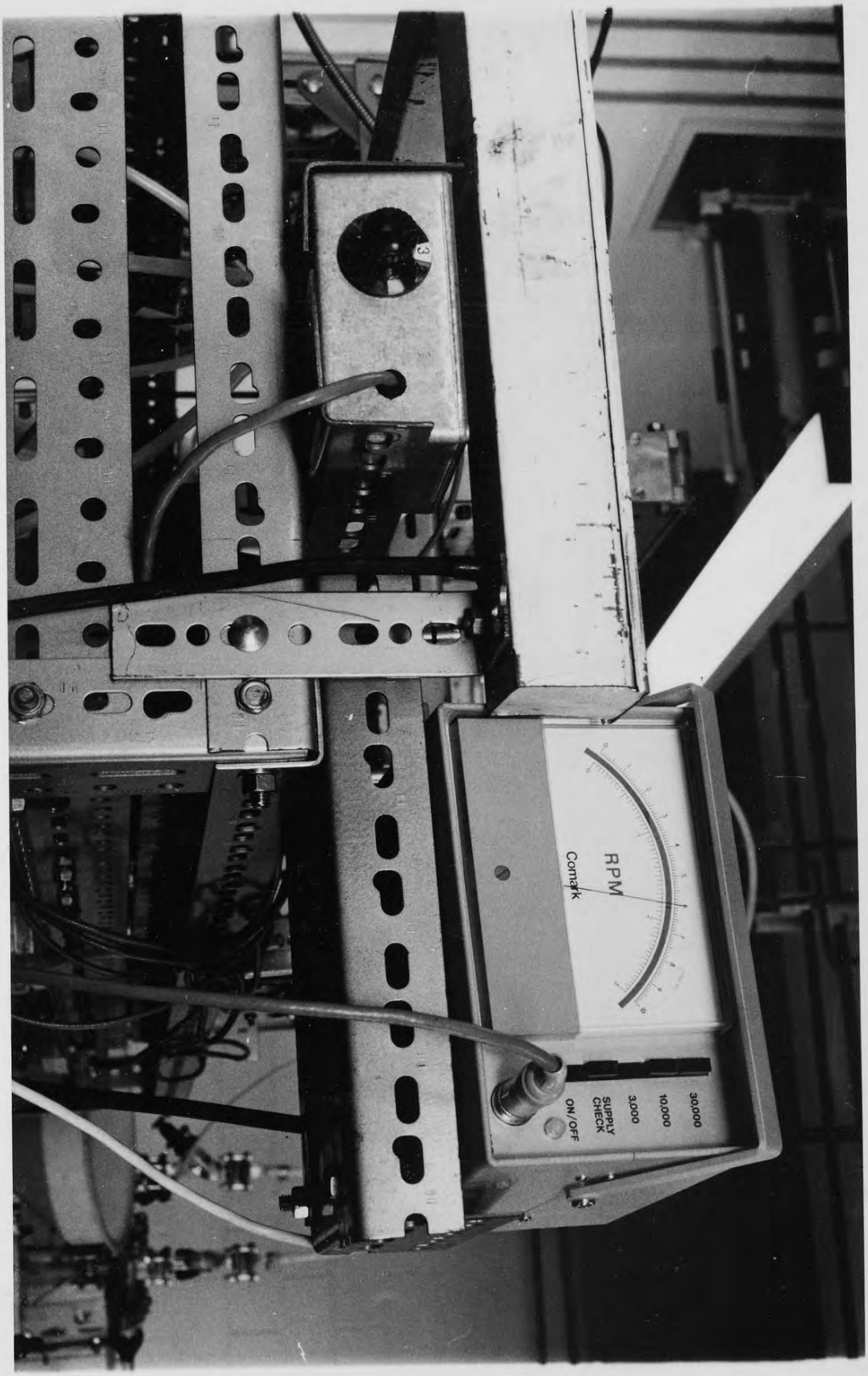


Fig. 5.8 Tachometer for measuring the speed of agitation with a 5 key box

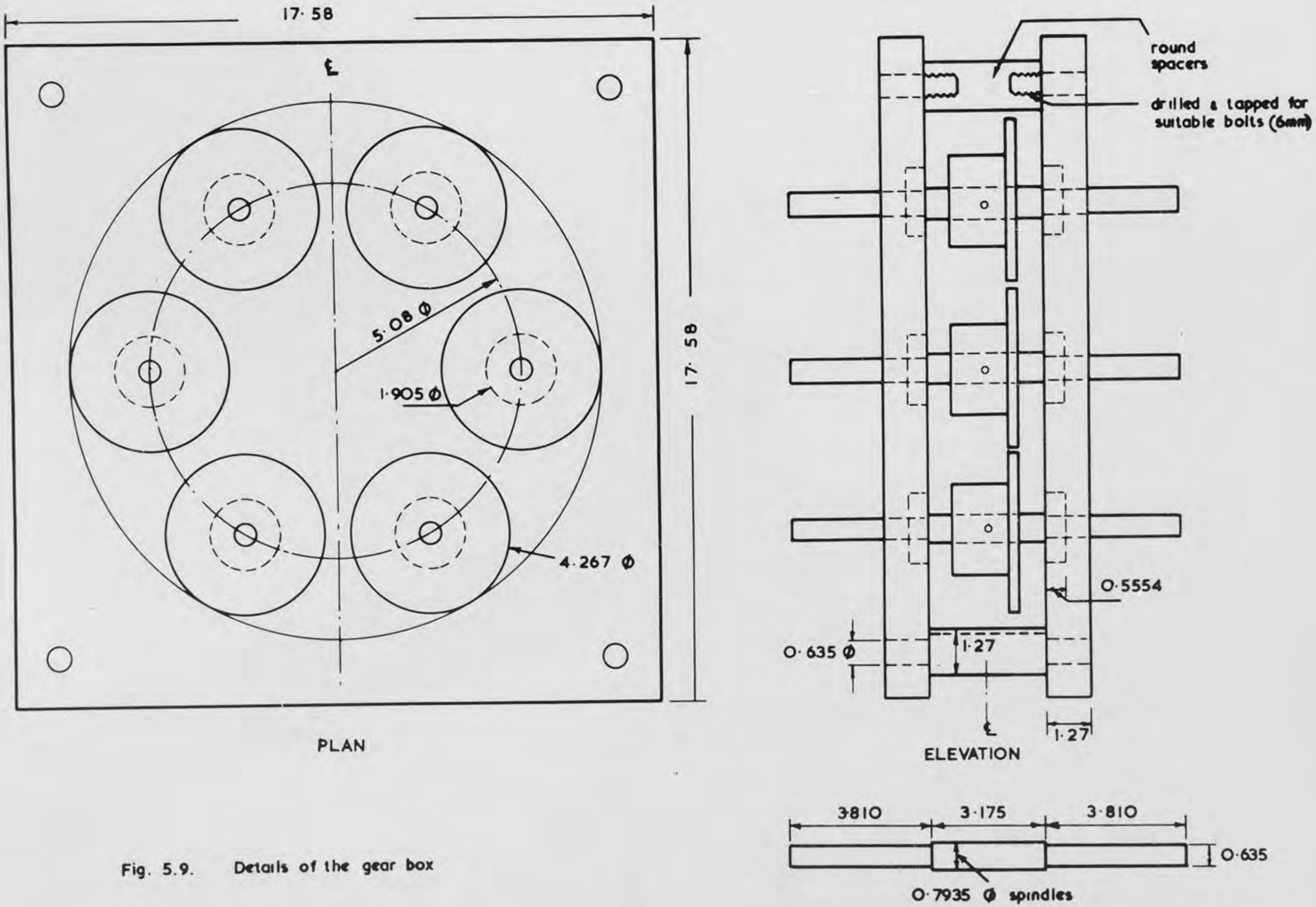
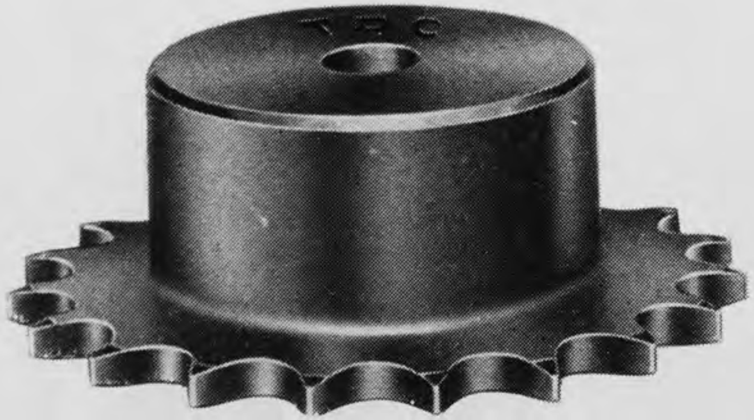


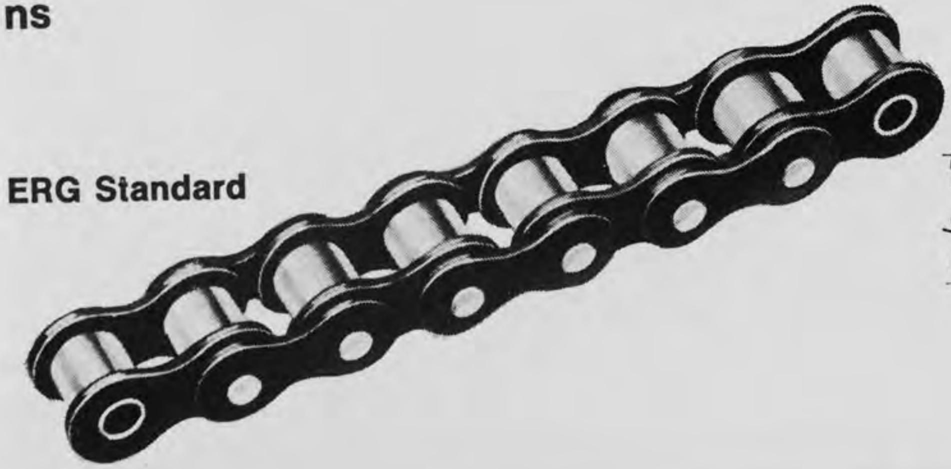
Fig. 5.9. Details of the gear box

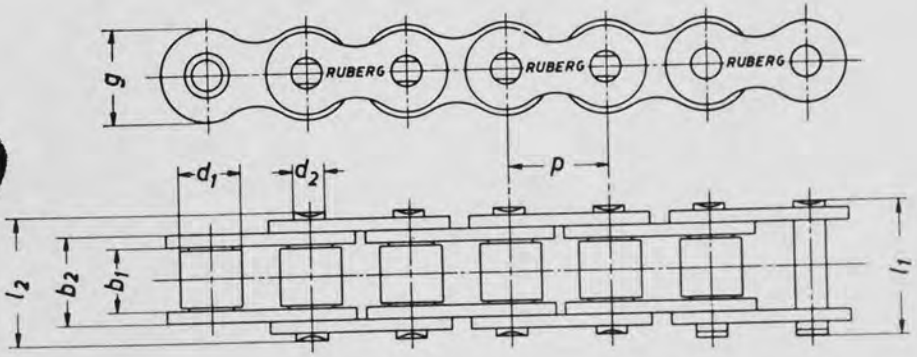


STANDARD DIMENSIONS
Pitch 8 mm Roller Diameter 0·197 in (5·00 mm)
Tooth Width ·100/·106 in (2·54/2·69 mm)

ns

ERG Standard





Connecting link

Fig. 5.10 A pinion and the connecting chain used in the gear box

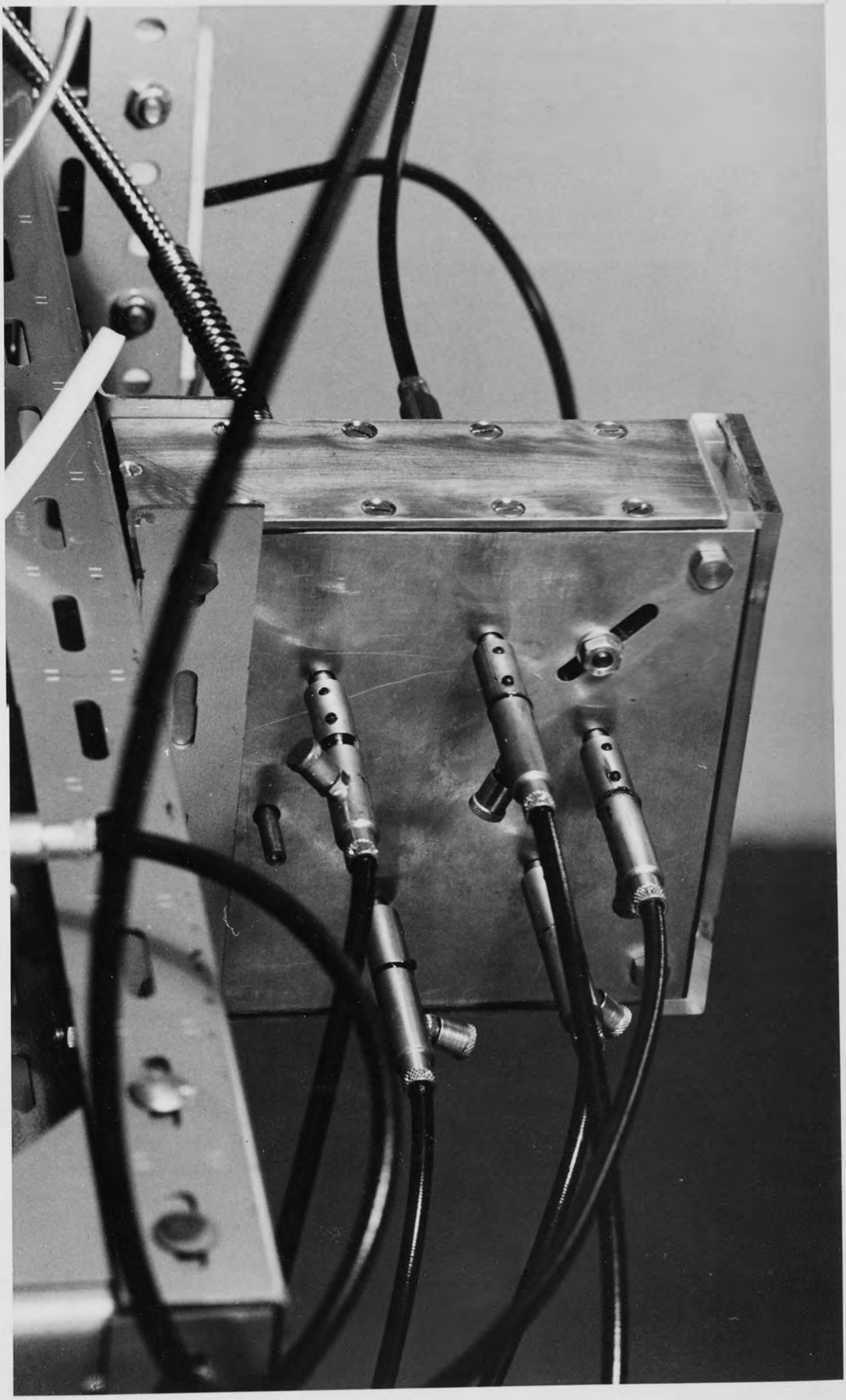


Fig 5.11 Gear box

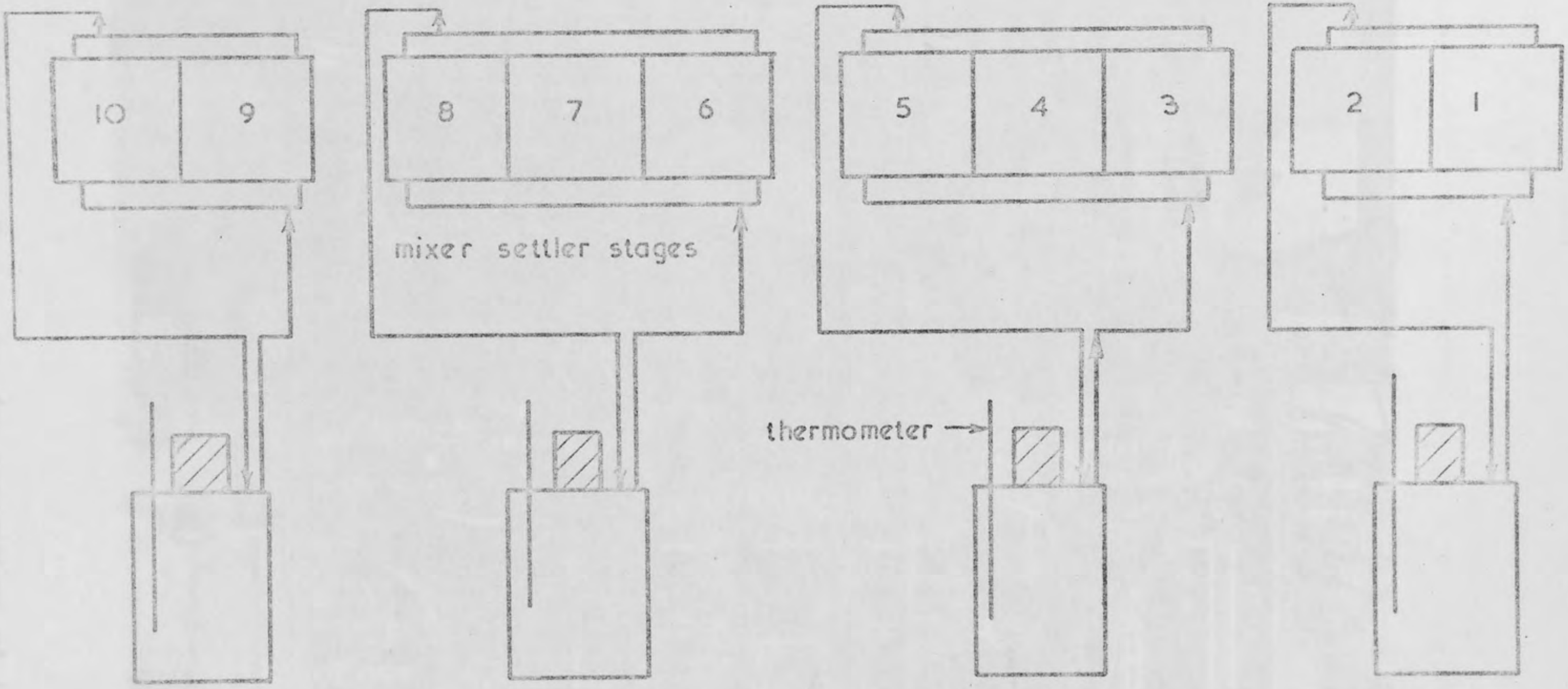


Fig. 5.12 Schematic diagram for the circulating units

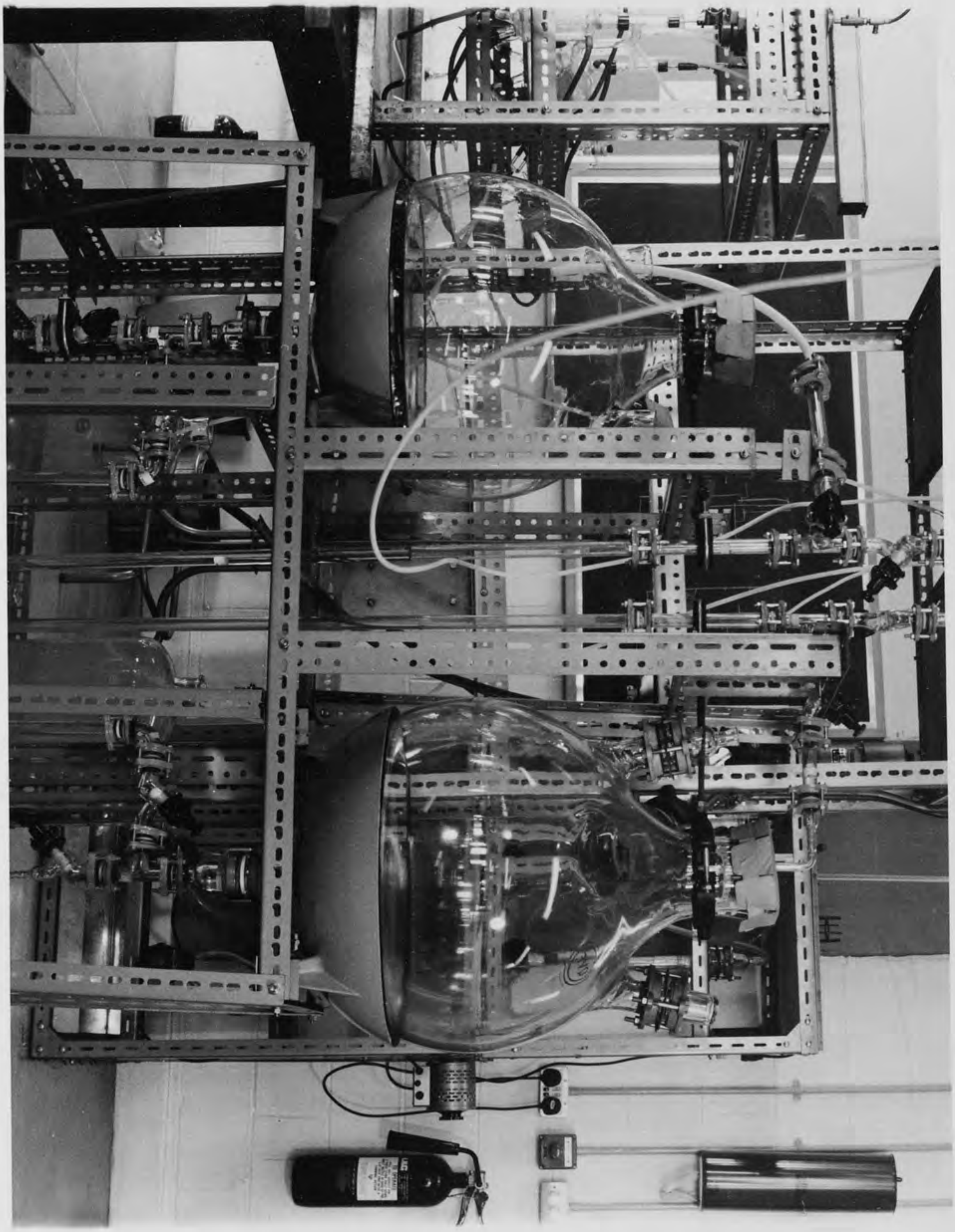


Fig. 5.13 Reservoirs for preperation of liquids

6. Experimental procedures and Measurement Techniques :

6.1. Selection of the liquid-liquid system :

The system acetic acid-toluene-distilled water was chosen for the investigation due to the following advantages :

i) The solubility data is available (46 , 146) for the system at different temperatures .

ii) The equilibrium constant varies appreciably with temperature (46)which is a requirement in this study .

iii) The interfacial tension of the system is reasonably high at moderate concentrations of the acid (152) which facilitates for fast settling.

6.1.1. Materials used :

Glacial acetic acid , analar grade (Hopkin and Williams) of density 1.048 - 1.05 gm/c.c ; analar grade toluene (Hopkin and Williams) of density 0.864-0.866 gm/c.c. and distilled water produced in the laboratory from an all-glass still , were used . No attempt have been made for further purification of the materials . The toluene used in extraction runs was separated from water using a one-litre separating funnel . It was then distilled and reused . It was observed that an azeotrope of toluene-water was obtained at 84^{o} and another azeotrope acetic acid-toluene was collected at 105-108^{o} c . These fractions were then mixed with some distilled water and agitated in a mixer specially designed for the purpose to extract the acid from toluene . The toluene was then separated and redistilled . The fraction of toluene boiling at 110-110.5°c was collected and reused for subsequent experiments .

6.1.2. Densities :

Distilled water densities at different temperatures were taken from Perry (47) . Acetic acid and toluene densities at different temperatures were calculated by the correlation recommended by Perry (47) .

$$D_2 = D_1 \left(\frac{T_C - T_2}{T_C - T_1}\right)^{0.29} \qquad 6.1$$

Mixture densities were calculated by the correlation (47 , 74) :

$$\rho_m = \rho_1 \phi_1 + \rho_2 \phi_2 \qquad 6.2$$

The densities used are given in Table 6.1 .

6.1.3. Solubility data :

The ternary data for the system ecetic acid-toluene-water was determined , using the cloud point method described in references (47 , 59 ,74) , at 30 , 45 and 60°c . The data determined and some of the published data (46 , 146) are presented in Figs. 6.1 , 6.2 and 6.3 . The solubility data of this work together with Woodman's data at 25°c (146) were correlated with a correlation similar to that of Hlavaty (198 , 199) .

$$w_c = C + A\, x_1 \ln x_1 + A_2\, x_2 \ln x_2 + x_1\, x_2 \sum_{i=3}^{n} A_i (x_2 - x_1)^{i-3} \qquad 6.3$$

where

$$x_1 = \frac{w_B + k.w_c - w^o_{BA}}{w^o_{BB} - w^o_{BA}} \qquad 6.4$$

and

$$x_2 = \frac{w^o_{BB} - w_B - k.w_c}{w^o_{BB} - w^o_{BA}} \qquad 6.5$$

The K is an empirical constant from interval (0.1) , the value of which was determined by trial and error to give the best multiple correlation coefficient and the lowest residual error . The value of n was 5 . The same statistical package used for the correlation of the time to reach steady state and the optimum number of stages was used to correlate the solubility data . The coefficients of the correlation 6.3 at different temperatures are given in Table 6.2. Another correlation was derived to correlate the solubility data at different temperatures.

$$w_c = C + A_1 x_1 \ln x_1 + A_2 x_2 \ln x_2 + x_1\, x_2 \sum_{i=3}^{n} A_i (x_2 - x_1)^{i-3} + Bt \qquad 6.6$$

The coefficients of this correlation 6.6 are given in Table 6.2 .

The distribution coefficient was correlated with the following correlations using the same statistical package.

$$m = 5.19\, (x_{CT})^{-0.45} \;.\; (t)^{-0.28} \qquad 6.7$$

$$m = 20.2\, (x_{CW})^{-0.78} \;.\; (t)^{-0.51} \qquad 6.8$$

The multiple correlation coefficients were 0.985 and 0.951 and the residual errors were 0.0645418 and 0.113771 respectively.

The agreement between correlation 6.7 and all the available experimental data are presented in Figs. 6.5 to 6.9. These correlations gave accurate values at x_{cT} greater than 1%.

Tie lines were determined, using a Smith-Bonner Cell, and correlated by Othmer and Tobias relationship (45). The tie lines are given in Tables 6.3, 6.4 and 6.5 and presented in Fig. 6.4, and the constants of Othmer and Tobias correlation are given in Fig. 6.4.

The six parameter NRTL equation (185) was used to predict the solubility data. The values of these parameters are given in table 6.10 . These parameters were calculated by the method proposed by Robinson and Jenkins (207) at 30° C. Vapour phase association was analysed using a special subroutine following the procedure of Null (185). No account was taken of liquid phase association as it was assumed that this could be accounted for by the activity coefficients. The agreement between the experimental and predicted data is shown in Figure 6.23. The figure shows a very good agreement in both phases up to the range of 55% acid concentration. The disagreement in the higher ranges may be attributed to association in the liquid phase which was not considered but which becomes significant at these concentrations where the mutual solubility of all components is appreciable.

Tests have been made to assess the degree of association of acetic acid in both phases using the proton magnetic resonance and the infra red absorption spectrum. These results are presented in figures 6.10 - 6.18 and the degree of association of acetic acid was correlated by Marek's correlation (175, 181)

$$Z = \frac{1 + \sqrt{1 + 4k}}{1 + \sqrt{1 + 4kx(2-x)}} \qquad 6.9$$

where k is a fictitious liquid phase association constant expressed by the relation

$$\log k = 3.8326 - \frac{1030}{T} \qquad 6.10$$

The relation 6.10 was determined from experimental data (181). The results are presented in figure 6.19. The other symbols are given in the nomenclature.

The proton magnetic resonance was used to examine the molecular constitution of the acid in pure toluene. The spectrum obtained for the samples of 1 and 3 and 10 and 30% acid in toluene was checked against the infra red absorption spectrum. Both results were compatible and figures 6.10 to 6.18 show that the position, shape and concentration dependence of thepeak ascribed to the carboxylic acid proton strongly suggest the presence of a dimer-hydrogen bonded. The strength of the hydrogen bond appears to be greater at lower concentrations.

Thus, it could be concluded that at ordinary temperature, in an acid range of 1-30%, acetic acid occurs virtually as a dimer in pure toluene. Unfortunately it was not possible to use these methods at higher temperatures. The spectrum for acetic acid in toluene saturated with water shows a small shift of the hydroxy proton most likely due to the presence of water. The shift was approximately 0.75% and 1.9% in a 10% and 30% samples respectively. (No allowances have been made for losses due to extraction in the water phase).

Hence, the presence of water has a negligible effect in the constitution of the acid in toluene and it could also be considered as a dimer in the toluene phase.

The spectrum for acetic acid in water saturated with toluene shows only two peaks (toluene was not detected under these conditions). One peak may be clearly ascribed to methyl ($\tau = 7.5 - 7.8$). The other is in a likely position for, and may be sensibly ascribed to hydroxyl proton. This means that there is only one type of hydroxyl proton present, i.e. the protons of the acid and water are indistinguishable implying a rapid interchange by hydrogen bonding. The position of this peak changes with concentration, indicating a change in the mean strength of this bonding. It is likely then, that an extended structure in rapid equilibrium of the form $CH_3COOH \cdot (H_2O)_n$ is formed and dissociated with a further inter-association and dissociation where n decreases as the concentration of the acid increases. Toluene appears to have very little effect on this structure, probably slightly weakening it.

Marek's correlation 6.16 indicated that the liquid phase association k, depends only on temperature and that k increases as T increases. It indicated also that at constant temperature, k is constant irrespective of the concentration of the acid. It follows that the association factor Z in equation 4.9 is dependent only on concentration at constant temperature. As the concentration increases, the association factor Z decreases which supports the trend shown above. Using the results obtained from the proton magnetic resonance and from Marek's correlation a possible association factor for acetic acid in water phase at 30° C is presented in figure 6.24, which may be used in the NRTL equation for better prediction of the solubility data. However, construction of a model taking into account liquid phase association is being under consideration of Robinson and Jenkins (207) and will hopefully give better prediction in the future.

6.1.4. Viscosities :

Acetic acid and toluene viscosities at different temperatures were taken from Reid and Sherwood (157) . Water viscosity was taken from Handbook of chemistry and physics (184) .

Water phase and toluene phase viscosities were determined experimentally , at three concentrations and two temperatures , using a U - tube capillary viscometer. This data was then used to correlate the viscosities of both phases over the required range of concentration using Tamura's correlation (165) :

$$\mu_m = x_1\phi_1\mu_1 + x_2\phi_2\mu_2 + 2\mu_{12}(x_1x_2\phi_1\phi_2)^{0.5} \qquad 6.11$$

The mutual viscosity coefficient μ_{12} was determined experimentally using a number of known values of μ_m and the average of μ_{12} was obtained at the temperature of the experiment as required by Tamura (165) , μ_{12} is constant at constant temperature , but varies with temperature . The viscosities of these mixtures were then calculated over the desired range of temperatures using Archenius correlation (47) , and the values obtained are given in Tables 6.6 and 6.7 and Fig 6.20 .

6.1.5. Interfacial Tension :

The interfacial tension of the acetic acid-toluene-water system was measured by DuNoy's method at 25°, 45° and 50°c . Samples of different concentrations of acid were thoroughly mixed in a Smith-Bonner cell for 4 hours at an agitator rate of 1430 r.p.m. , at constant temperature , until equilibrium was attained . The system was then allowed to settle until the phases were clear and then the interfacial tension was determined .

The results are presented in Fig 6.21 .

The interfacial tension data was then correlated using the same statistical package used above and the correlation obtained was :

$$\sigma = 3.95\, x_o^{-0.70} \, . t^{-0.05} \qquad 6.12$$

The concentration used in the correlation 6.12 is the total acid concentration in the system . If only the concentration of the acid in a phase was known , the total acid concentration x_o could be calculated from the following correlation .

$$x_o = 0.4 x_{CT}(1 + 1.3247m) \qquad 6.13$$

This correlation has been derived from material balance relationships .

6.1.6. Diffusivities :

Diffusivities of acetic acid in water and in toluene at infinite dilution were taken from Perry (47) . Wilke's equation (47 , 174) was used to calculate the diffusivities of the acid in both phases at different concentrations and temperatures .

The diffusivities obtained are presented in Fig 6.22 and Tables 6.8 and 6.9 .

A computer program in basic 16 language for calculating the diffusivities is given in Appendix 1 .

6.2. Calibration techniques :

6.2.1. Calibration graphs for measurement of the concentration :

The acetic acid concentration in each phase was estimated by two methods .

Titration of the acid using standard solutions of sodium hydroxide in methanol . Thymol blue was used as an indicator . This method necessitated the use of either large quantities of low normality sodium hydroxide solutions or alternatively a strong solution , preferably more than 1.0 normal . This was impractical because the presence of the methanol inhibited the dissolution of the sodium hydroxide in the titration mixture .

The refractive index method using Abbe refractometer was preferred because samples of small size were required .

A graph of concentrations Vs refractive index was constructed for each phase . These graphs are presented in Appendix 1 .

6.2.2. Calibration graphs for measurement of the flow rates :

The flow meter for the inlet water-phase was calibrated over the range 20 - 300 c.c./m . But since in some experiments the water-phase flow rate was less than 20 c.c./m. The lower part of the tube was calibrated for flow rates of 0-20 c.c./m. using water saturated with toluene .

Since the outlet water phase contained different acid concentrations in different experiments and sometimes during the same experiment , the outlet water-phase was measured frequently during each run and the average was recorded .

The flowmeter for the inlet toluene phase was calibrated using a 15 % acetic-toluene phase . The outlet toluene phase flow rate was also measured during each run . The calibration graphs for the inlet fluids are given in Appendix 1 .

6.3. Cleaning Procedure

Since it is widely accepted that surface active agents affect the mass-transfer rates (47 , 74 , 80 , 139 , 151 , 155 , 158) no detergents were used in cleaning the mixer settler or other equipment used in this investigation .

The mixer-settlers were filled with distilled water after each run and the heating/ cooling units were set at 60°c. The agitators were started and the distilled water was allowed to flow through the extractor , until the water discharged was free from any impurities . The equipment was then emptied and dried by compressed air .

The sampling bottles were washed three times with hot tap water , then rinsed with distilled water and dried in an oven .

6.4. Preparation of liquid phases :

The toluene phase was selected as raffinate and the feed containing about 15% W/w of acetic acid was extracted by the water phase . The acid concentration was restricted to about 15 % W/W for the following reasons :

i) With a solvent to feed ratio of the order of 1:6 water phase concentration approaches 50 % acid-at which the interfacial tension is low as shown in Fig 6.21 . If higher concentrations of acid in the feed were introduced the concentrations of acid in the water phase would be very high and the interfacial tension would be correspondingly very low so that it would be more difficult to settle .

ii) The 15 % feed concentration is a practical concentration which gives a reasonable mass transfer driving force .

iii) With such a feed concentration , there would be a reasonable difference in outlet raffinate and extract concentrations from the different stages , which would be easier to determine with a small error .

The feed was prepared by mixing the requisite amounts of toluene , acid and water for saturation at the required temperature in the feed reservoir using the pump for circulation . A sample was withdrawn every 10 minutes to check the concentration using the refractive index method . It was found that 30 minutes was sufficient for homogenization of the feed mixture after which a certain amount was then pumped to the overhead feed reservoir .

The required amount of toluene for saturation was added to the distilled water and mixed by a circulating pump and then pumped to the overhead tank to be used as the solvent .

6.5. Operating procedure

The mixer-settlers were first filled with the continuous phase after which the flow was stopped . The heating / cooling medium was circulated from the thermostat-baths which had been set at the desired temperature and when the temperature of the liquid inside the mixer-settlers reached the required temperature and the speed of agitation had been set the feed and solvent were pumped in at the required ratio . The interface in the feed settler was adjusted by controlling the valves of the outflow rotameters . The interface in the other settlers was adjusted by the valves on the outlet water-phase to the mixers . No other means of interface control was necessary . Samples from each phase were withdrawn periodically for measurement of the concentration .
At the end of each run the liquids flowing were stopped , the stages were separated by closing the interconnecting valves and the agitators were stopped . After allowing sometimes for settling in the mixers , the hold-up was measured . Sometimes the mixers were emptied immediately for measuring the interfacial tension .

Table 6.1 Densities of the materials used in gm/c.c.

Temp C	Water	Acetic	Toluene	Acetic - Toluene system		
				10%	20%	30%
10	0.999728	1.05897	0.873248	0.89091	0.909592	0.928268
15	0.999126	1.05401	0.869148	0.88673	0.905321	0.92391
20	0.998234	1.049	0.865	0.8825	0.901	0.9195
25	0.997077	1.04393	0.860803	0.878218	0.896628	0.915038
30	0.995678	1.03879	0.856555	0.873884	0.892203	0.910523
35	0.994061	1.0336	0.852254	0.869497	0.887724	0.905951
40	0.992249	1.02833	0.8479	0.865054	0.883189	0.901323
45	0.99025	1.023	0.843491	0.860556	0.878596	0.896636
50	0.98807	1.01761	0.839024	0.855999	0.873943	0.891888
55	0.98573	1.01214	0.834498	0.851381	0.869229	0.887077
60	0.98324	1.0066	0.829912	0.846702	0.864451	0.882201
65	0.98059	1.00098	0.825262	0.841958	0.859608	0.877259
70	0.97781	0.99528	0.820548	0.837149	0.854698	0.872247
75	0.97489	0.98950	0.815766	0.83227	0.849717	0.867164
80	0.97183	0.98364	0.810914	0.82732	0.844664	0.862007

Table 6.2 Coefficients of the correlations of the solubility data

Coefficient	Correlation 6.3				Correlation 6.6
	25°c	30°c	45°c	60°c	
K	0.4	0.7	0.7	0.3	same values
C	-.1556159	-.0126067	-.0167605	-.0919986	-0.0062238
A_1	1.2458249	-1.679265	-1.5752294	-.1235035	0.3192657
A_2	-2.2222352	-.2313011	-.2931241	-1.8785505	-1.4897911
A_3	1.9374113	0.0	0.0	0.0	1.2338204
A_4	-3.6135834	2.3929681	2.1054487	-2.8475605	-1.0119546
A_5	-.0050982	-1.4184949	-1.1887854	-.019909	-0.6161356
B	-	-	-	-	-0.0011975
Multiple correlation coefficient	0.999	0.999	1.000	0.998	0.924
Residual error	.0100015	.0115516	.00452372	.014306	0.0756873

Table 6.3 Tie Line Data - Composition on Wt.% basis

Date of DAKS At 30 (46)			Data of this work At 30 C		
Solute	Water	Toluene	Solute	Water	Toluene
Water Phase					
16.50	83.50	0.0	23.013	76.7	0.287
24.25	75.45	0.30	29.152	70.5	0.348
31.50	67.80	0.70	34.302	65.1	0.598
40.9	58.25	0.85	38.186	60.9	0.914
46.00	53.05	0.95	41.476	57.4	1.124
55.10	43.60	1.30	44.64	54.0	1.356
63.50	33.50	3.00	47.218	51.3	1.482
66.20	29.20	4.60	49.469	48.7	1.832
			51.45	46.6	1.95
			55.7	41.7	2.6
			59.8	37.0	3.2
			62.45	33.9	3.62
			64.00	31.85	4.15
			67.85	27.4	4.75
			69.85	25	5.15
Toluene Phase					
1.25	0.15	98.60	1.845	0.155	98
2.20	0.18	97.62	2.81	2.81	97
3.10	0.2	96.7	3.489	0.211	96.3
5.20	0.38	84.42	4.365	0.235	95.4
6.50	0.45	93.05	5.335	0.265	94.4
12.20	0.75	87.05	6.205	0.295	93.5
16.50	0.90	82.60	7.08	0.32	92.6
18.00	0.95	81.05	7.954	0.346	91.7
			8.603	0.397	91.0
			10.200	0.4	89.4
			12.530	0.47	87.0
			14.63	0.57	84.8
			16.09	0.61	83.3
			19.29	0.71	80.0
			22.19	0.81	77.0

Table 6.4 Tie Line Data - Composition on Wt. % basis

Daks. Data at 40 (46)			Data of this work at 45°C		
Acetic	Water	Toluene	Acetic	Water	Toluene
Water phase					
13.75	86.00	0.25	18.1023	81.55	0.3477
24.60	74.90	0.50	23.9690	75.5	0.5310
29.00	70.40	0.60	28.8665	70.40	0.7335
34.90	64.40	0.70	33.1042	66.0	0.8958
41.10	58.10	0.80	36.5926	62.35	1.0574
45.80	53.20	1.00	39.0190	59.80	1.181
53.75	44.30	1.95	42.7150	55.85	1.435
62.50	33.1	4.40	45.202	53.2	1.597
65.50	29.0	5.50	47.377	51.0	1.663
			55.992	40.5	3.508
			59.70	35.75	4.55
			64.618	27.95	7.432
Toluene phase					
0.90	0.10	99.00	1.5424	0.3076	98.15
2.30	0.15	97.55	2.5589	0.3411	97.1
3.25	0.20	96.55	3.3200	0.38	96.3
5.20	0.25	95.55	4.1918	0.4082	95.4
6.00	0.30	93.70	5.0636	0.4364	94.5
8.80	0.35	90.85	6.0311	0.4689	93.5
11.75	0.45	87.80	6.9986	0.5014	92.5
15.2	0.60	84.20	7.7726	0.5274	91.7
17.80	0.9	81.30	8.5950	0.555	90.85
			12.9985	0.7015	86.3
			15.7808	0.8192	83.4
			21.7298	1.2702	77.0

Table 6.5 Tie Line Data - Composition on Wt.% basis

Daks. Data at 60 C (46)			Data of this work at 60^{o}C		
Acetic	Water	Toluene	Acetic	Water	Toluene
Water phase					
13.00	86.45	0.55	12.194	87.45	0.356
22.00	77.30	0.70	17.8645	81.7	0.4355
28.60	70.55	0.85	22.399	77.0	0.601
36.2	62.8	1.00	26.6996	72.5	0.8004
43.90	54.80	1.30	30.3791	68.65	0.9709
50.50	47.90	1.60	33.7241	65.15	1.1259
61.80	33.4	4.80	4.80	61.95	1.2679
64.0	29.1	6.90	39.605	59.00	1.395
			42.219	56.25	1.531
			53.9006	44.32	1.7794
			56.87	38.50	4.63
			63.1762	29.4	7.4238
Toluene phase					
0.9	0.40	98.70	1.4183	0.4317	98.15
4.0	0.45	95.55	2.4324	0.4676	97.1
5.0	0.50	94.50	3.1914	0.5086	96.3
6.60	0.60	92.80	4.0606	0.5394	95.4
8.80	0.75	90.45	4.9298	0.5702	94.5
9.75	0.80	89.45	5.8973	0.6027	93.5
17.30	1.00	81.70	6.8648	0.6352	92.5
19.00	1.10	79.90	7.6474	0.6526	91.7
			8.4683	0.6817	90.85
			12.8628	0.8372	86.3
			15.6103	0.9897	83.4
			21.5103	1.4897	77.0

Table 6.6 Viscosities (in Centi poise) of acetic acid in Toluene phase at different temperatures

Wt.%	5	10	15	20	25	30	35	40	45	50
t°C										
5	0.735	0.79	0.845	0.925	1.00	1.07	1.11	1.15	1.2	1.27
13	0.66	0.7	0.74	0.8	0.85	0.91	0.94	0.97	1.01	1.06
21	0.59	0.621	0.65	0.69	0.725	0.77	0.79	0.818	0.845	0.88
30	0.53	0.552	0.574	0.595	0.62	0.64	0.66	0.69	0.715	0.74
39	0.475	0.49	0.5	0.518	0.53	0.545	0.56	0.58	0.6	0.61
49	0.425	0.435	0.44	0.442	0.45	0.46	0.475	0.485	0.5	0.505
60	0.38	0.385	0.385	0.38	0.382	0.385	0.4	0.41	0.42	0.42
72	0.34	0.345	0.338	0.33	0.328	0.328	0.34	0.345	0.355	0.35

Table 6.7 Viscosities (in centipoise) of acetic acid in water - phase at different temperatures

Wt.%	5	10	15	20	25	30	35	40	45	50
t°C										
5	1.41	1.46	1.495	1.55	1.56	1.64	1.70	1.82	1.9	1.93
13	1.2	1.26	1.3	1.37	1.41	1.48	1.55	1.67	1.75	1.82
21	1.01	1.08	1.19	1.21	1.22	1.34	1.425	1.55	1.63	1.71
30	0.856	0.93	1.00	1.07	1.145	1.215	1.3	1.43	1.5	1.61
39	0.723	0.8	0.872	0.945	1.035	1.10	1.19	1.33	1.37	1.53
49	0.61	0.69	0.762	0.84	0.93	1.00	1.09	1.23	1.27	1.44
60	0.52	0.59	0.67	0.74	0.84	0.9	0.998	1.13	1.17	1.35
72	0.44	0.51	0.585	0.657	0.758	0.82	0.91	1.05	1.08	1.28

TABLE 6.8 DIFFUSIVITIES OF ACETIC ACID IN TOLVENE AT DIFFERENT CONCENTRATIONS AND TEMPERATURES $DX10^{-5}$, in $cm.^2/sec.$

	% wt.									
t^{o} c	5	10	15	20	25	30	35	40	45	50
5	.998206	.945064	.892385	.820271	.776315	.740482	.731462	.720564	.710621	.687115
13	1.14363	1.09727	1.04833	.975732	.939595	.895732	.88604	.87886	0.868598	0.846932
21	1.3151	1.27145	1.22687	1.1629	1.13241	1.0882	1.0869	1.07132	1.06725	1.0487
30	1.50879	1.47417	1.43184	1.38989	1.36472	1.34932	1.32874	1.30894	1.2999	1.28528
39	1.7335	1.71002	1.69258	1.64391	1.64389	1.63159	1.62718	1.60344	1.59506	1.6055
49	1.99954	1.98797	1.98503	2.08256	1.99819	1.99504	1.97985	1.97897	1.97542	2.00149
60	2.31272	2.32288	2.34611	2.39175	2.4343	2.46511	2.43139	2.4209	2.43203	2.48285
72	2.67795	2.68561	2.76864	2.85338	2.93724	2.99777	2.96354	2.98075	2.98102	3.09414

TABLE 6.9 DIFFUSIVITIES OF ACETIC ACID IN WATER AT DIFFERENT CONCENTRATIONS AND TEMPERATURES. $D \times 10^{-5}$, in cm.^{2}/sec.

% wt. t°C	5	10	15	20	25	30	35	40	45	50
5	.775403	.767689	.770688	.768918	.794451	.783286	.775905	.771445	.776055	.83503
13	.937317	.915143	.911796	.894978	.904262	.892943	.875482	.864931	.866821	.910981
21	1.1448	1.09753	1.02394	1.04167	1.07432	1.01382	.982362	.95796	.956668	.996703
30	1.3921	1.31357	1.25579	1.21402	1.17973	1.15235	1.10589	1.07013	1.0714	1.09102
39	1.69714	1.57238	1.4829	1.41543	1.34388	1.31063	1.244	1.18477	1.20791	1.18216
49	2.076	1.88148	1.75136	1.6434	1.54355	1.48791	1.40166	1.32216	1.34479	1.29631
60	2.51851	2.27555	2.05989	1.92921	1.76731	1.7097	1.58317	1.48832	1.50959	1.42996
72	3.08367	2.72736	2.44421	2.25123	2.02907	1.94413	1.79883	1.65944	1.69433	1.56251

Table 6.10 The parameters of the NRTL equation for the system acetic acid - toluene water at 30°C

System	T_{12}	T_{21}	x
Acetic acid-water	-1.2348	2.1523	0.2
Toluene-water	3.554	6.460	0.198
Acetic acid-toluene	0.9169	0.7131	-1.5747

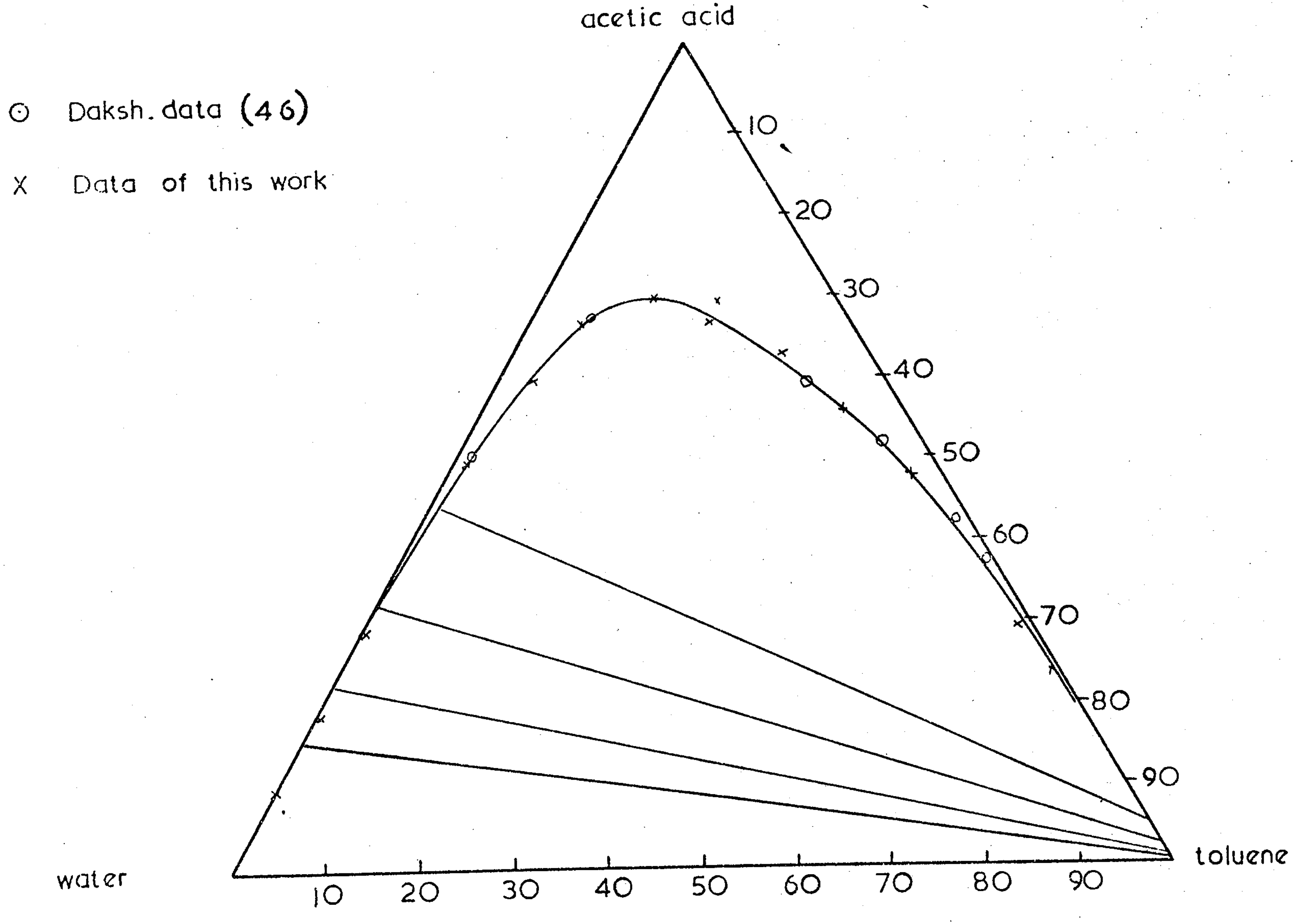


Fig. 6.1 Solubility data at 30° C

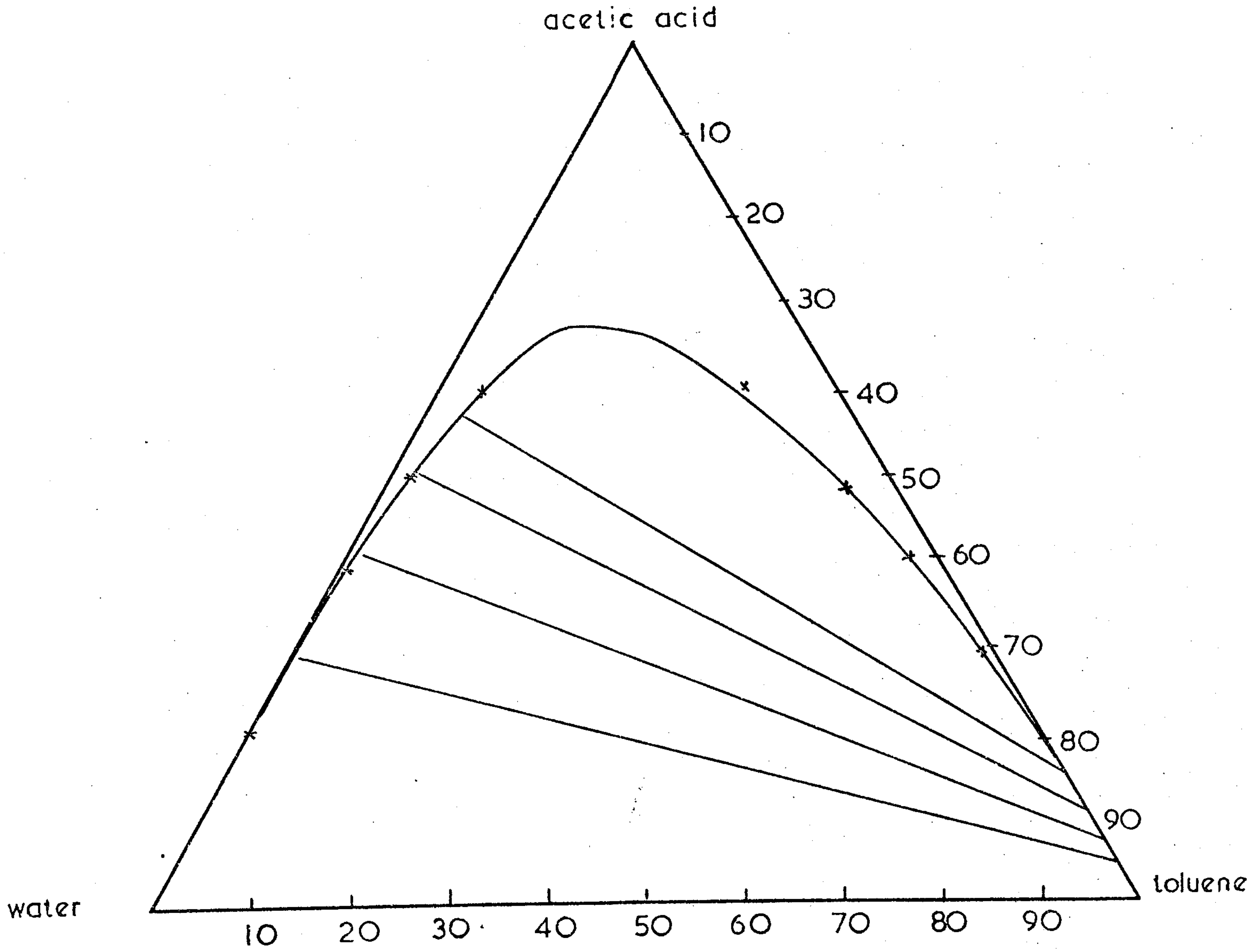


Fig 6.2. Solubility data at 45° C

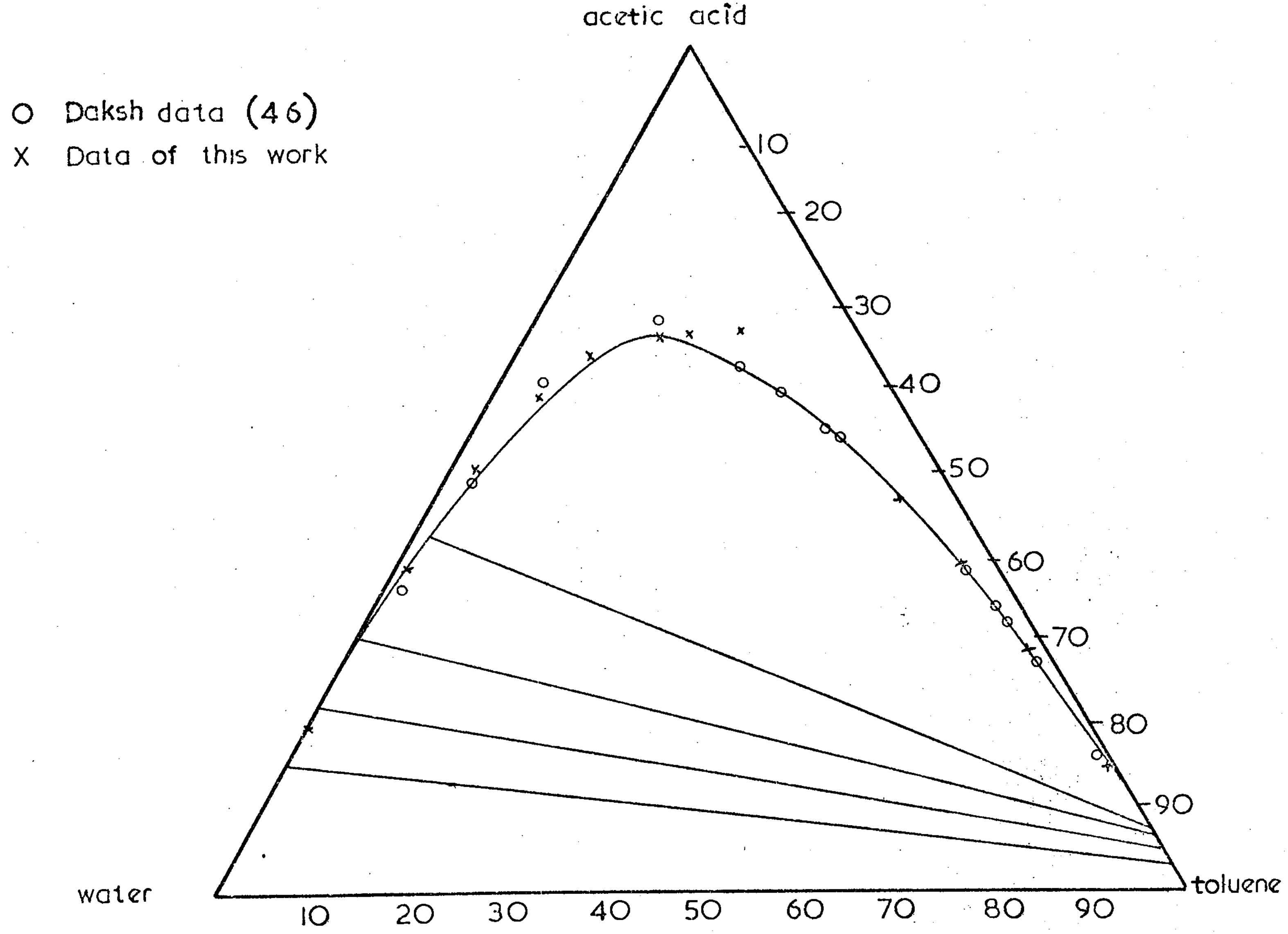


Fig. 6.3 Solubility curve at 60° C

1) at 25°C , m=1.24 , k=0.075 (Woodman)
2) at 30°C , m=1.195 , k=0.081 (Data of this work)
3) at 40°C , m=1.125 , k=0.105 (Data of this work)
4) at 60°C , m=0.961 , k=0.1285 (Data of this work)

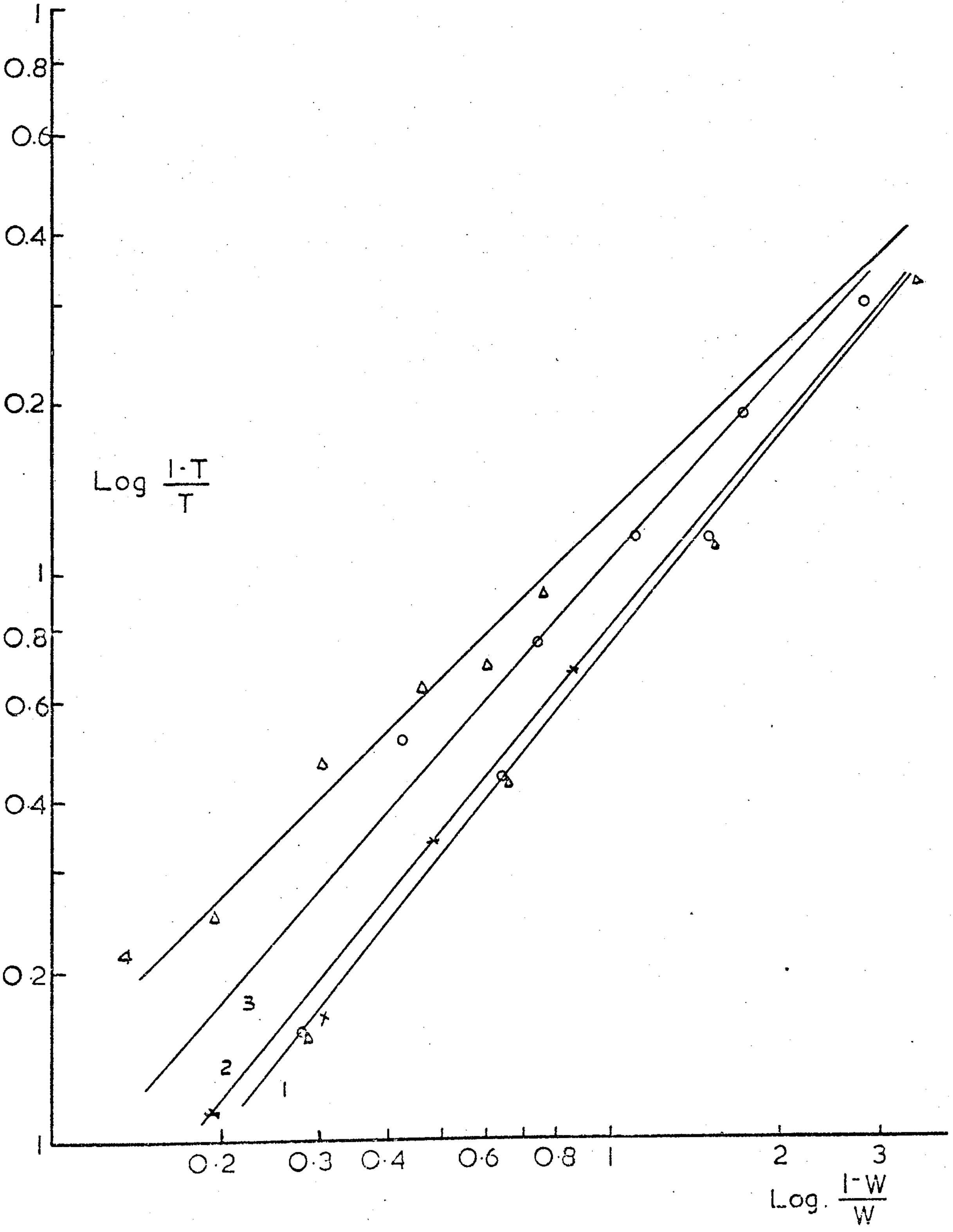


Fig. 6.4 Othmer - tobias correlations for the tie lines of the system acetic - toluene - water

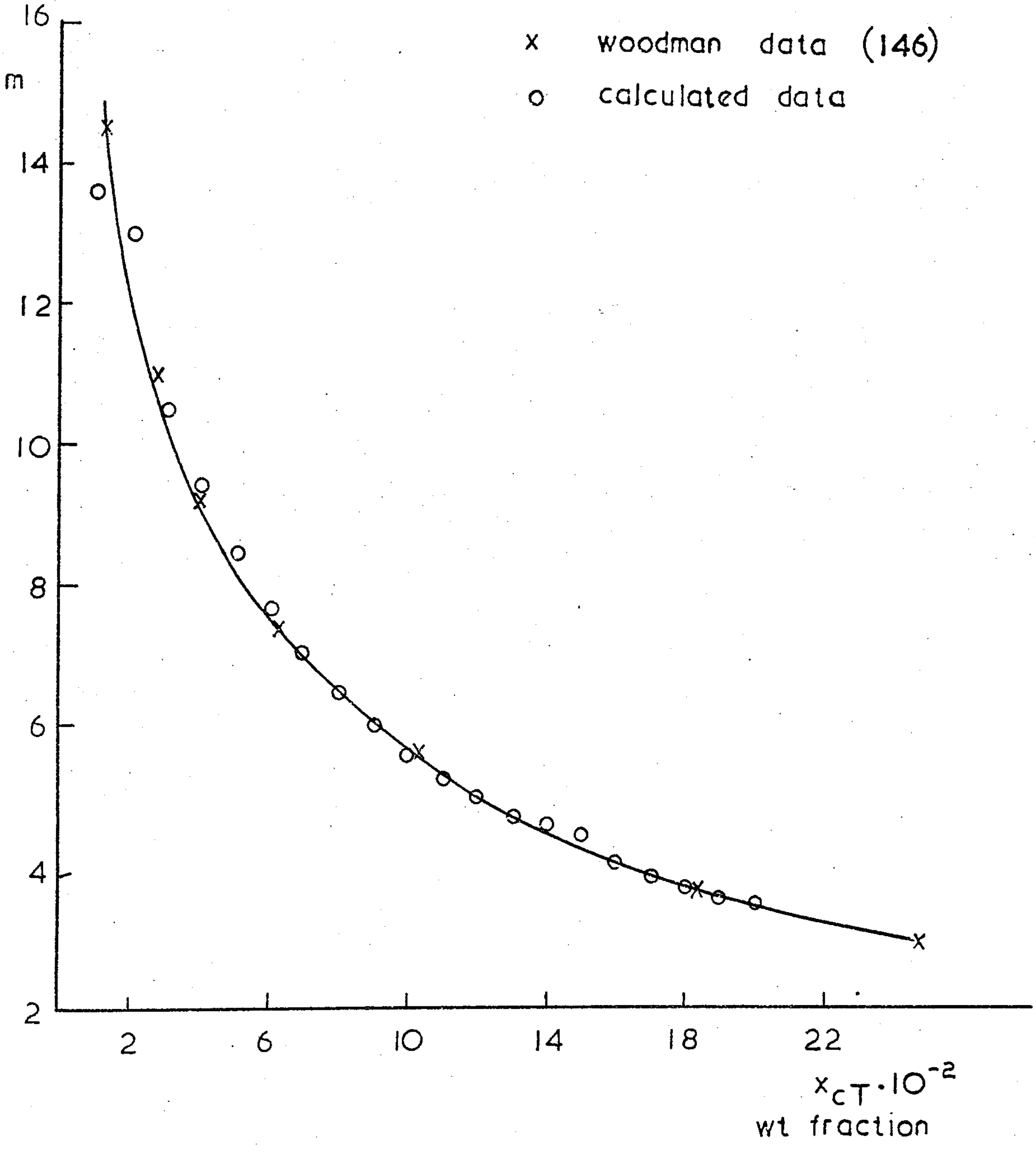


Fig. 6.5 Equilibrium distribution constant at 25°C

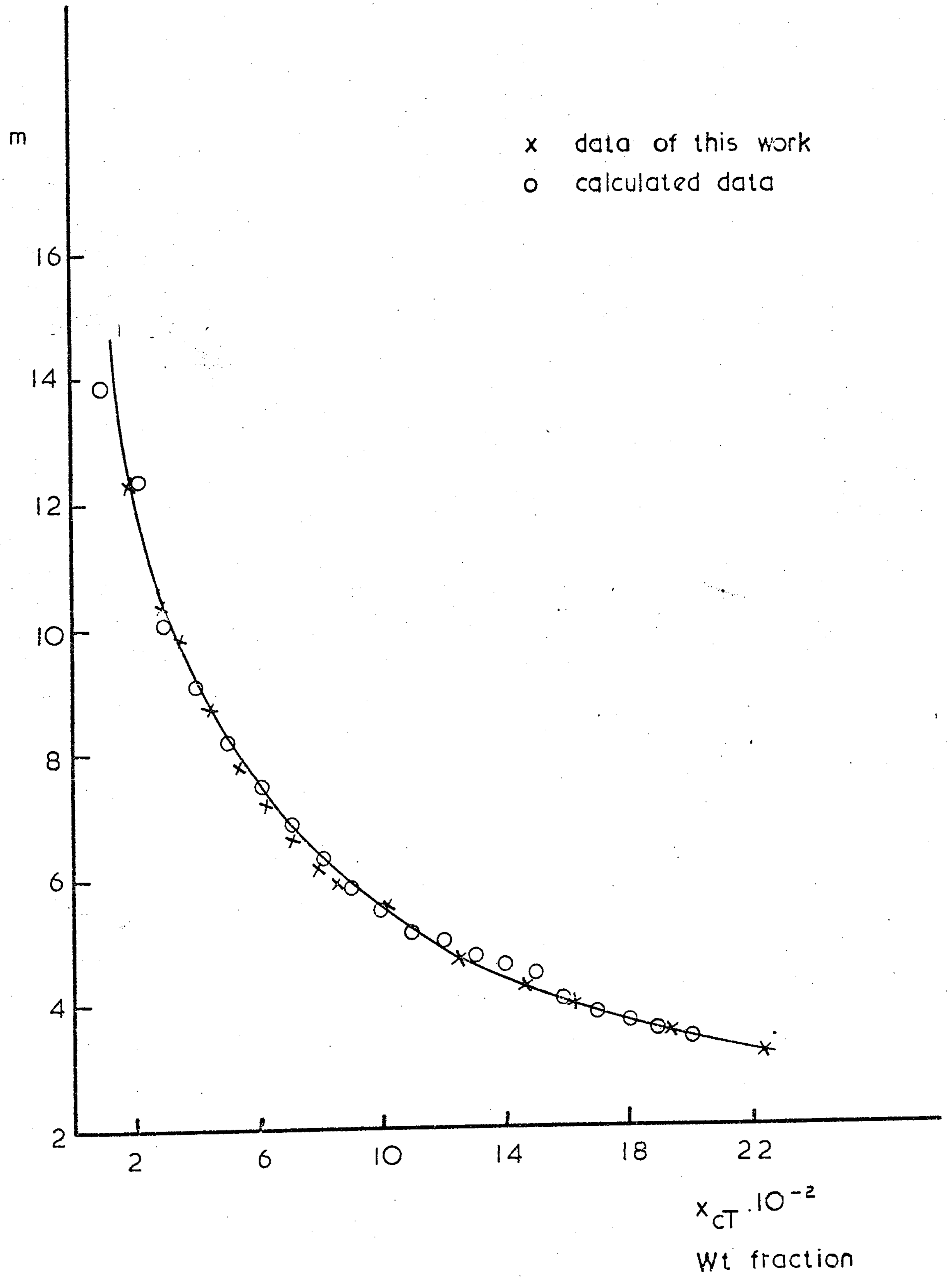


Fig 6.6 Equilibrium distribution constant at 30° C

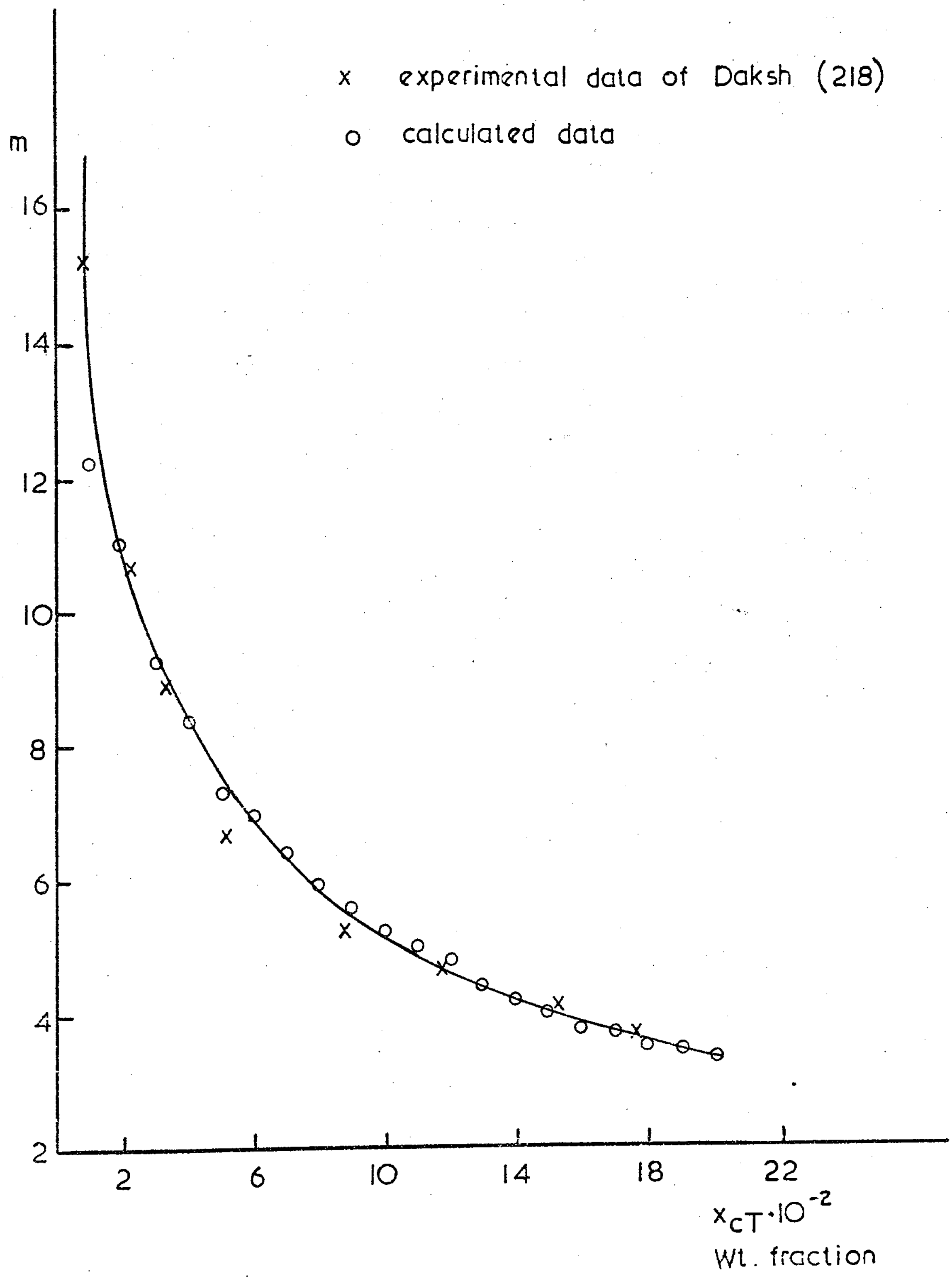


Fig. 6.7 Equilibrium distribution constant at 40°C

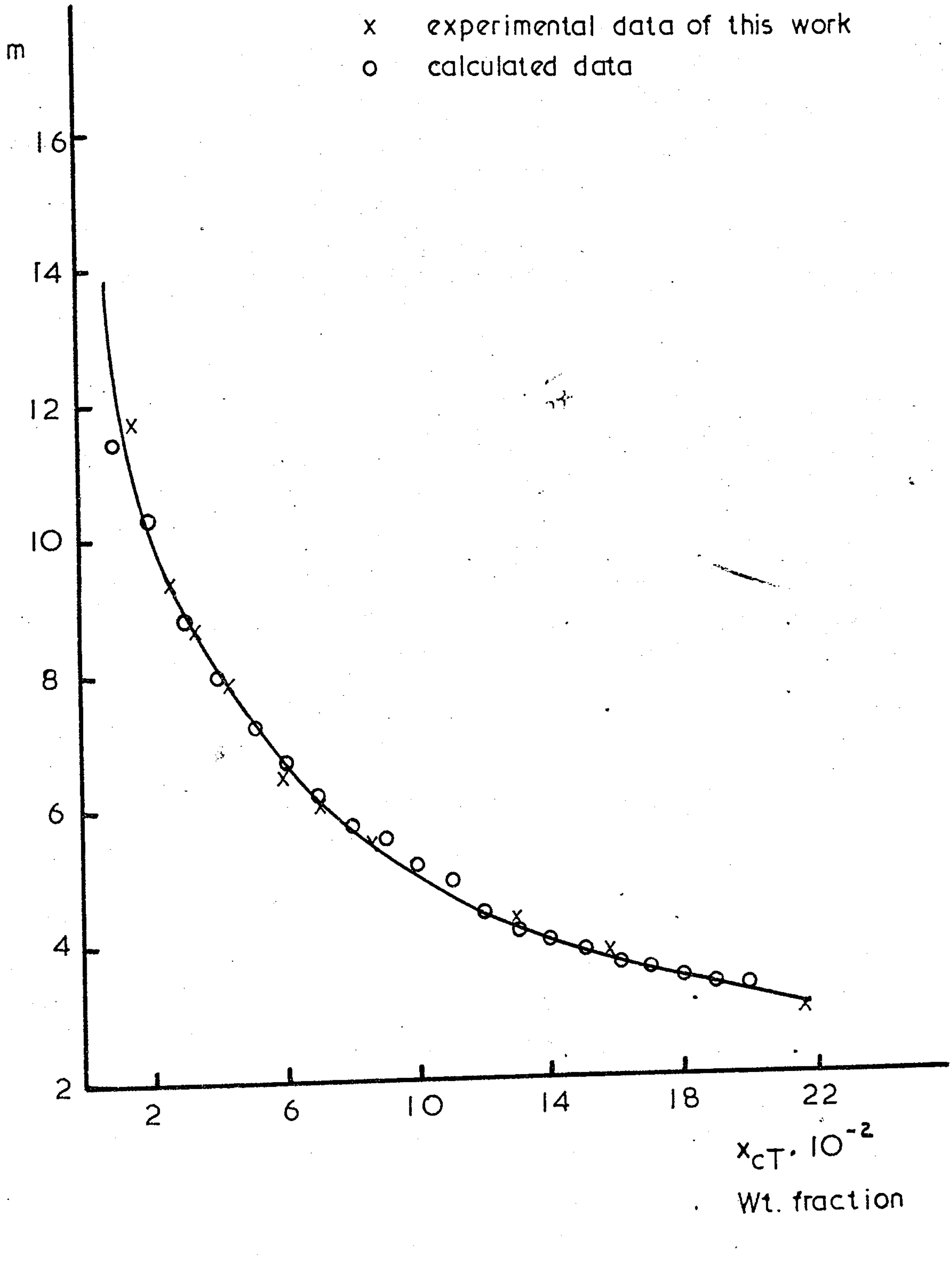


Fig. 6.8 Equilibrium distribution constant at 45° C

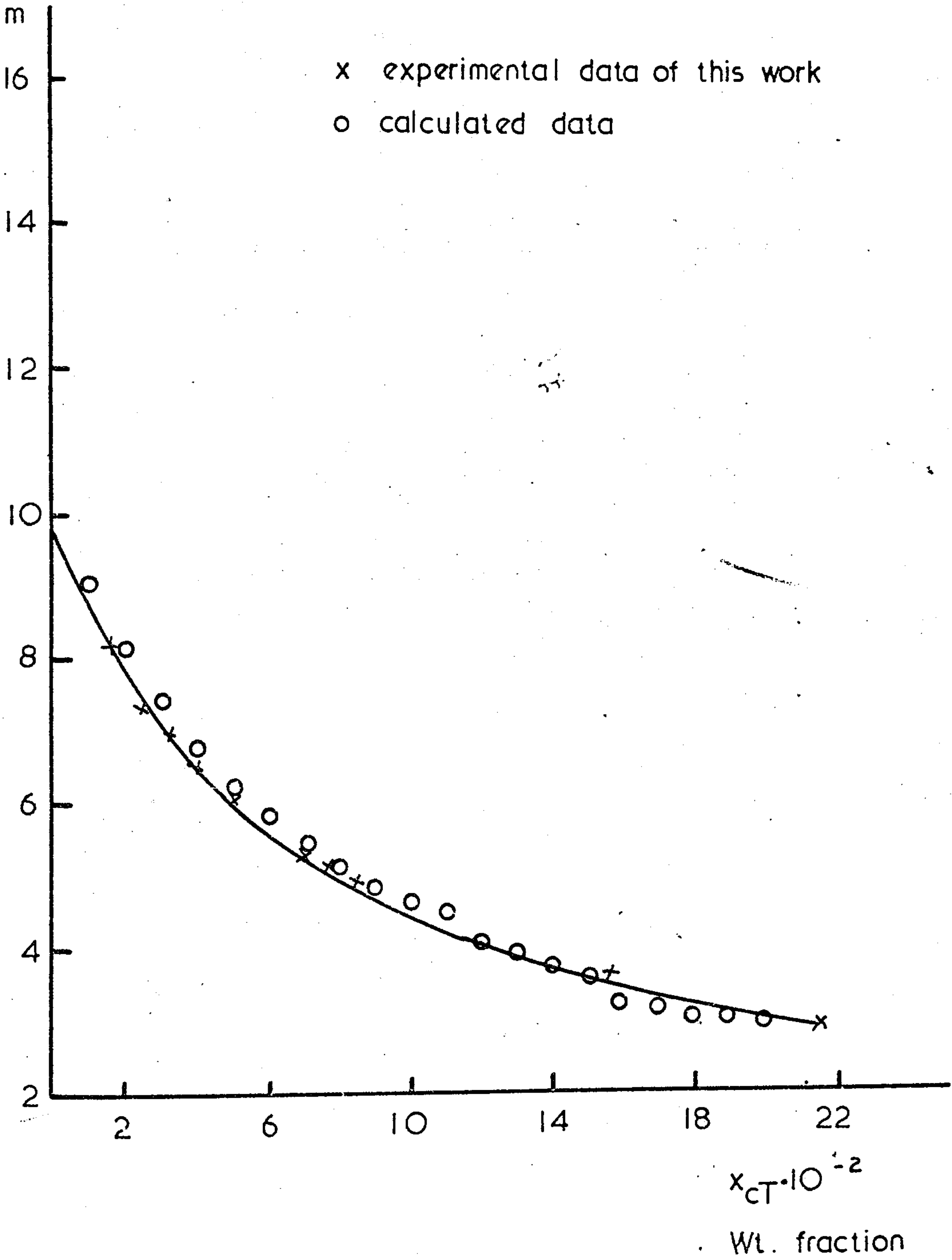


Fig. 6.9 Equilibrium distribution constant at 60° C

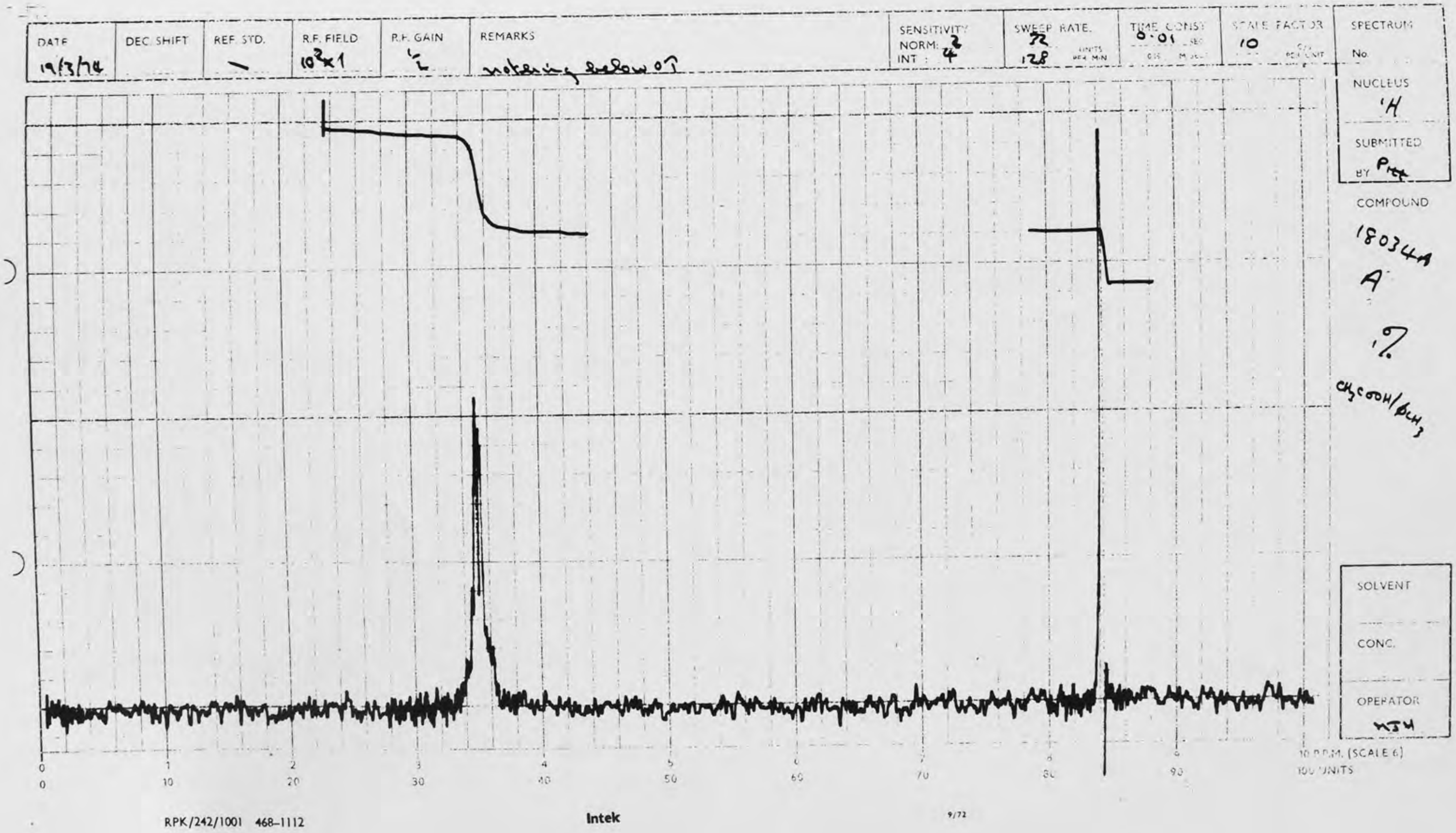
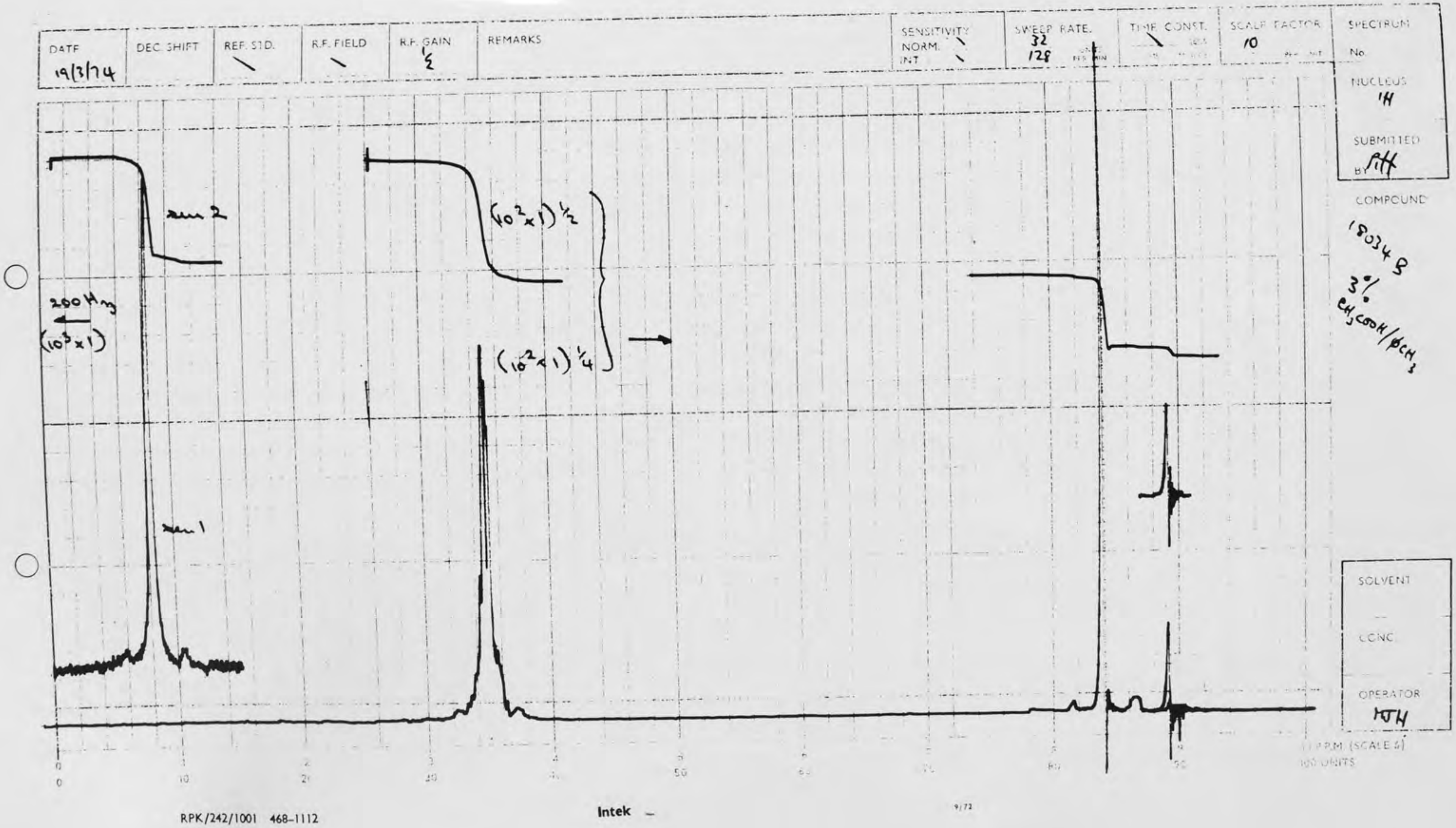


Fig. 6.10 Analysis of a 1% acetic acid in pure toluene using the proton magnetic resonance



DATE 19/3/74
DEC. SHIFT
REF. STD. \
R.F. FIELD \
R.F. GAIN ½
REMARKS
SENSITIVITY NORM. \ INT. \
SWEEP RATE 32 128
TIME CONST. \
SCALE FACTOR 10
SPECTRUM No.
NUCLEUS ^1H
SUBMITTED BY PH
COMPOUND 18034 B 3% $CH_3COOH/\phi CH_3$
SOLVENT
CONC.
OPERATOR MJH

Fig. 6.11 Analysis of a 3% acetic in pure toluene using the proton magnetic resonance

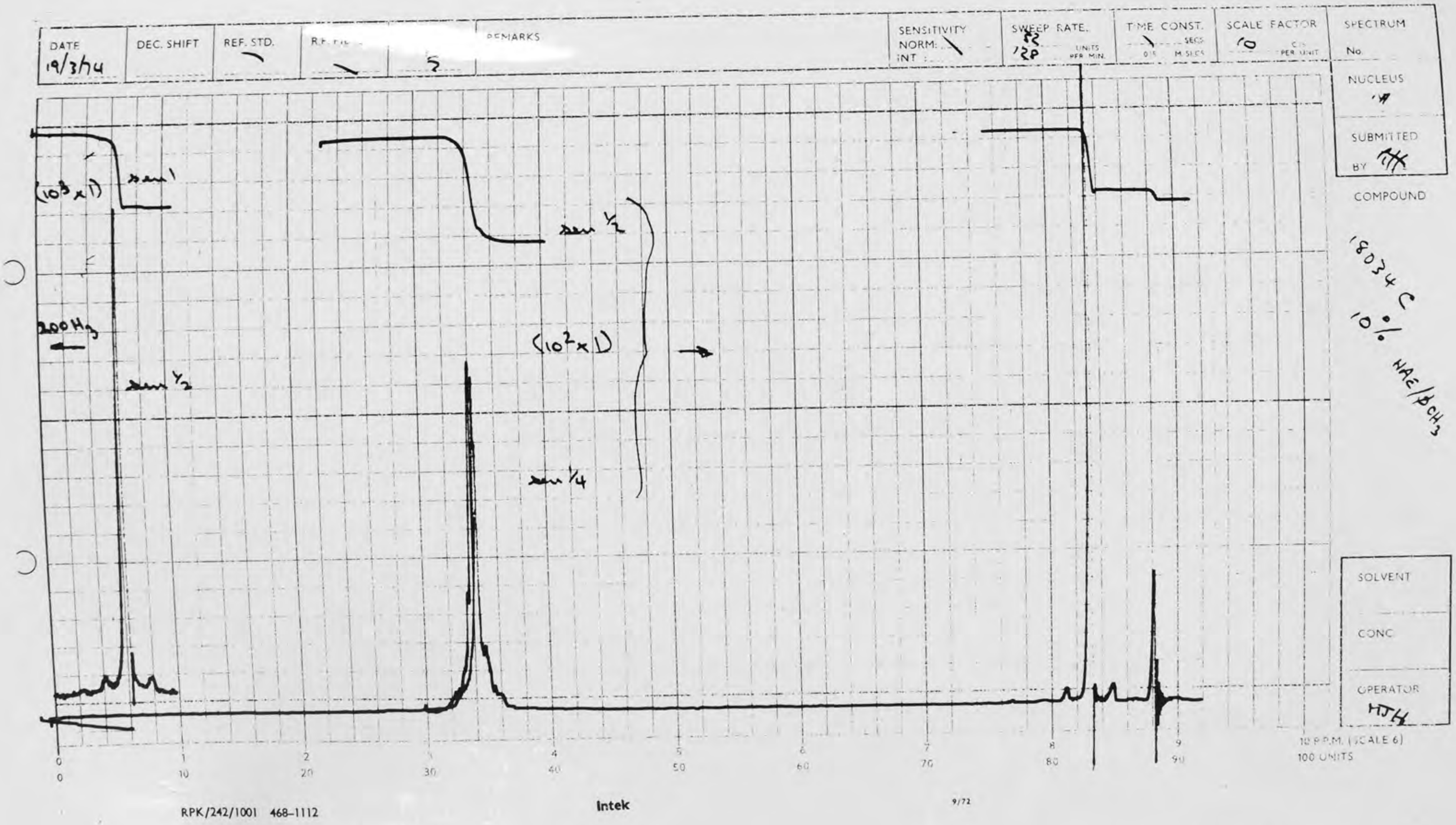


Fig. 6.12 Analysis [illegible] a 10% acetic acid in pure toluene using the proton magnetic resonance

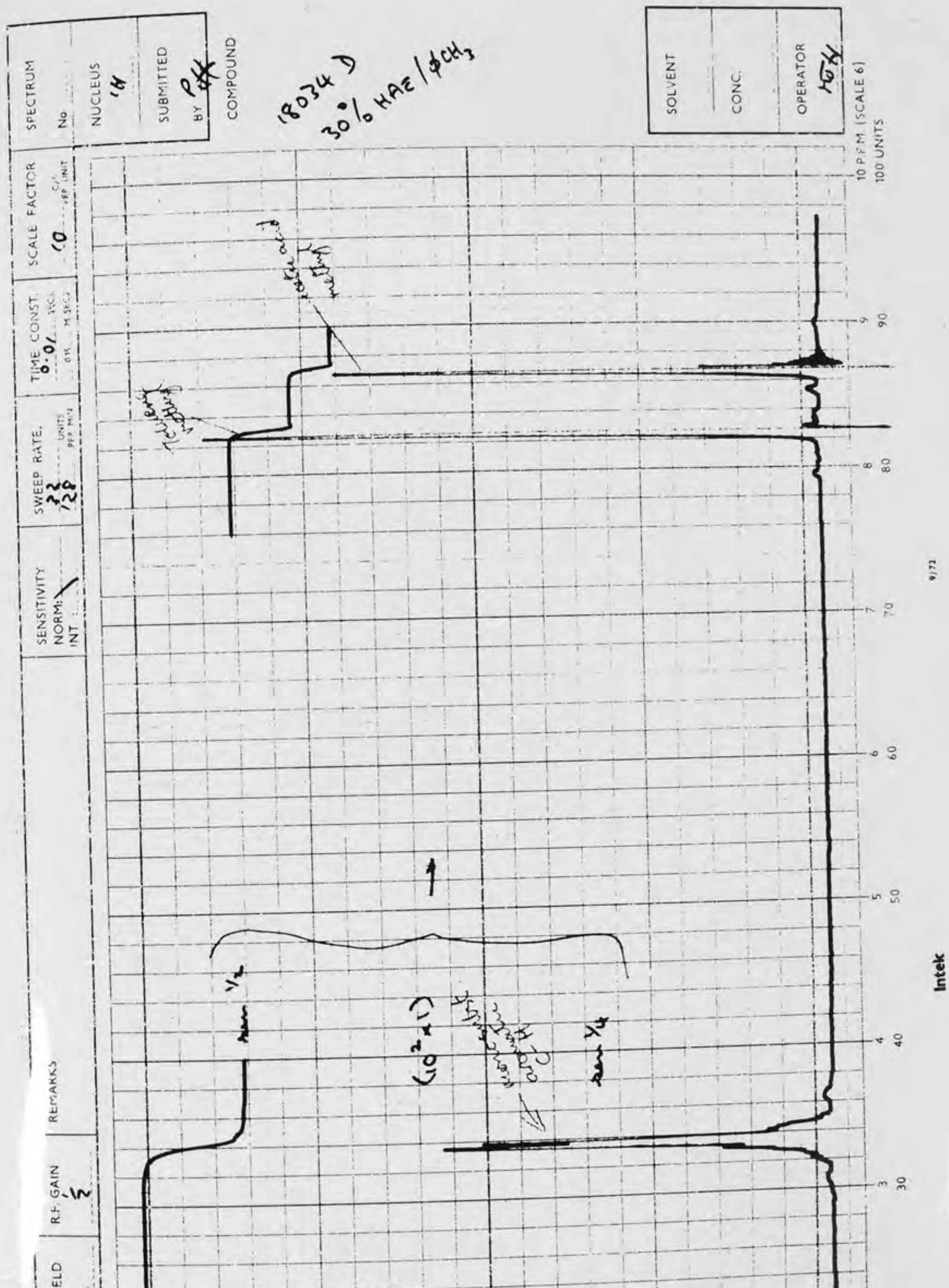
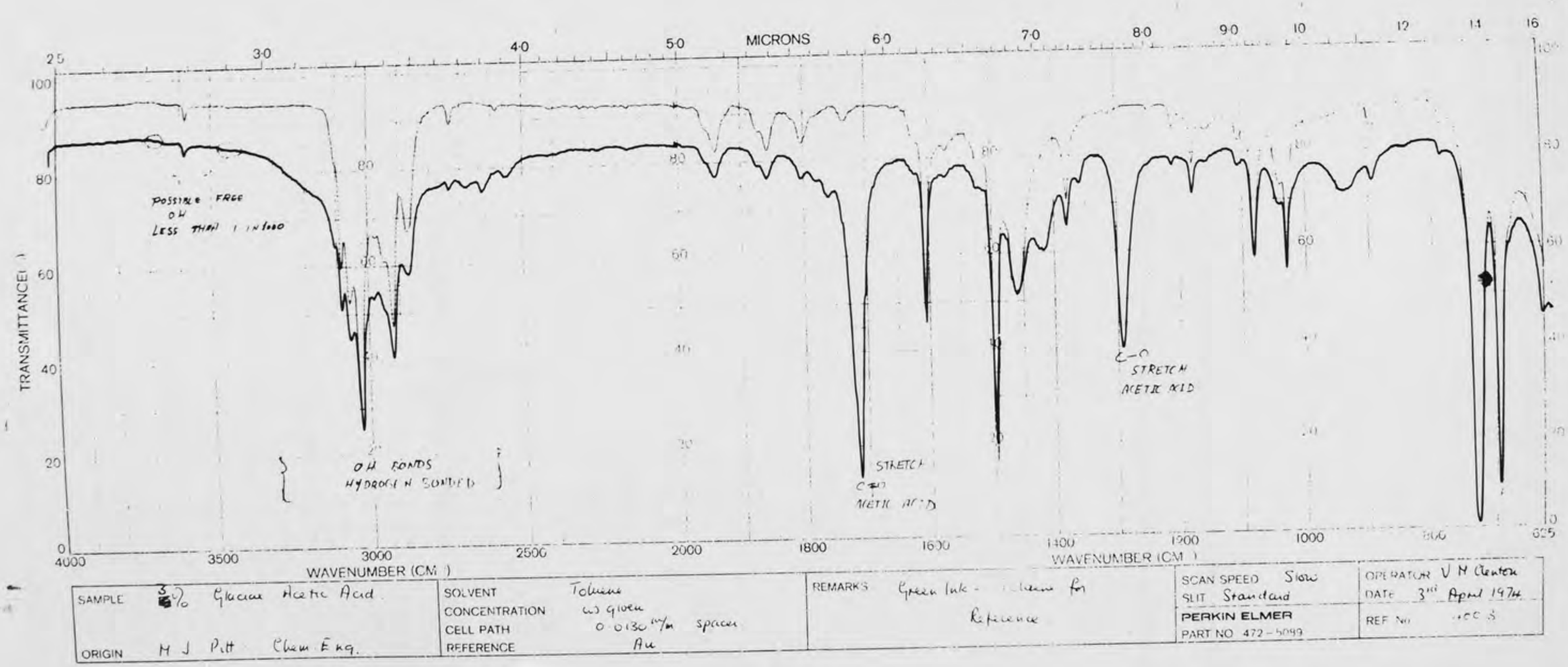


Fig. 6.13 Anc of a 30 % acetic acid in pure toluene using the proton magnetic resonance



SAMPLE 3% Glacial Acetic Acid

ORIGIN H J Pitt Chem Eng.

SOLVENT Toluene

CONCENTRATION as given

CELL PATH 0·0130 m/m spacer

REFERENCE Air

REMARKS Green Ink - toluene for Reference

SCAN SPEED Slow

SLIT Standard

PERKIN ELMER

PART NO 472-5099

OPERATOR V M Clenton

DATE 3rd April 1974

REF No [illegible]

Fig. 6.14 Analysis of a 3% acetic acid in pure toluene using the infra-red absorption spectrum

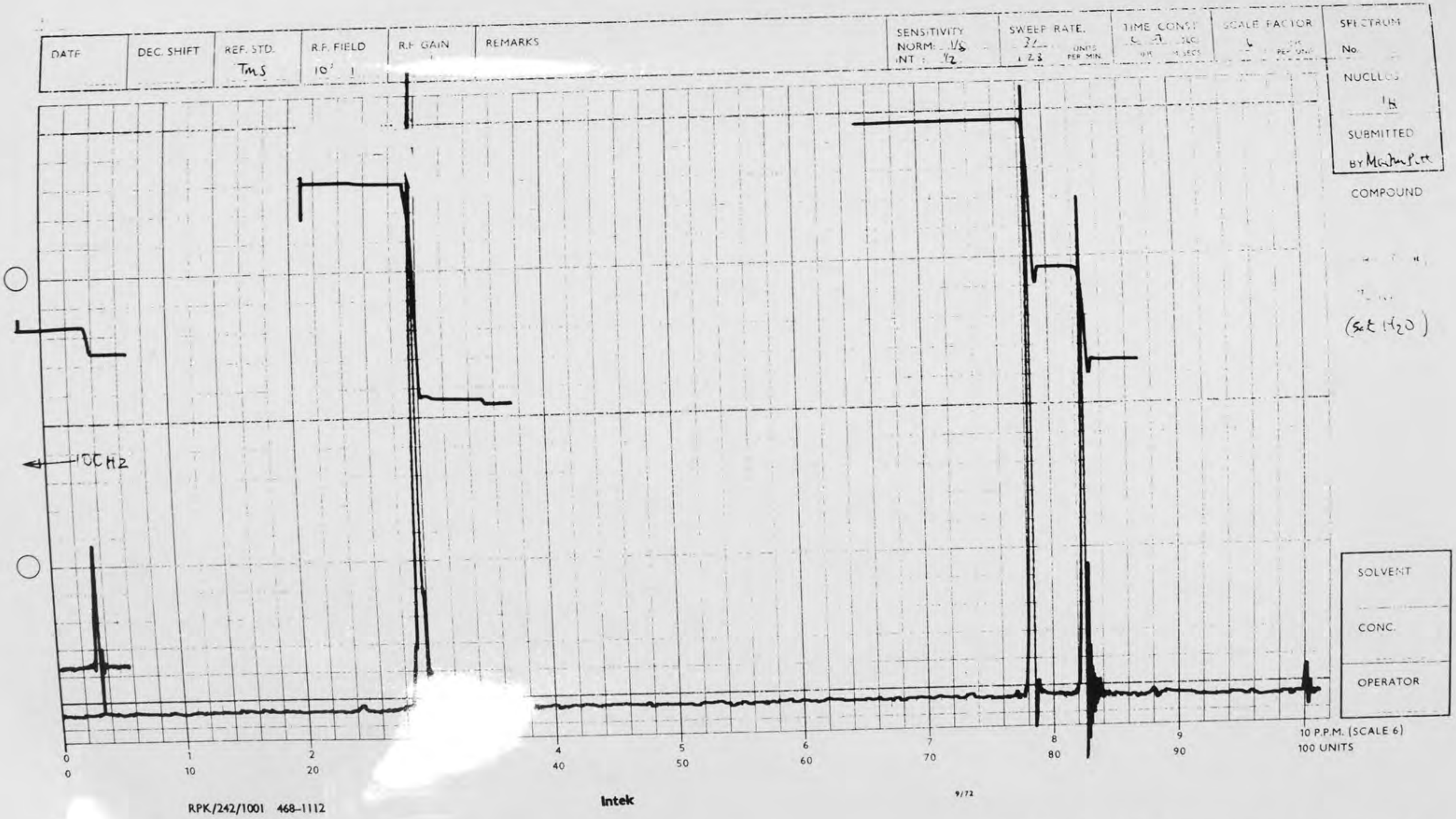


Fig. 6.15 Analysis of a 10 % acetic acid in toluene saturated with water using the proton magnetic resonance

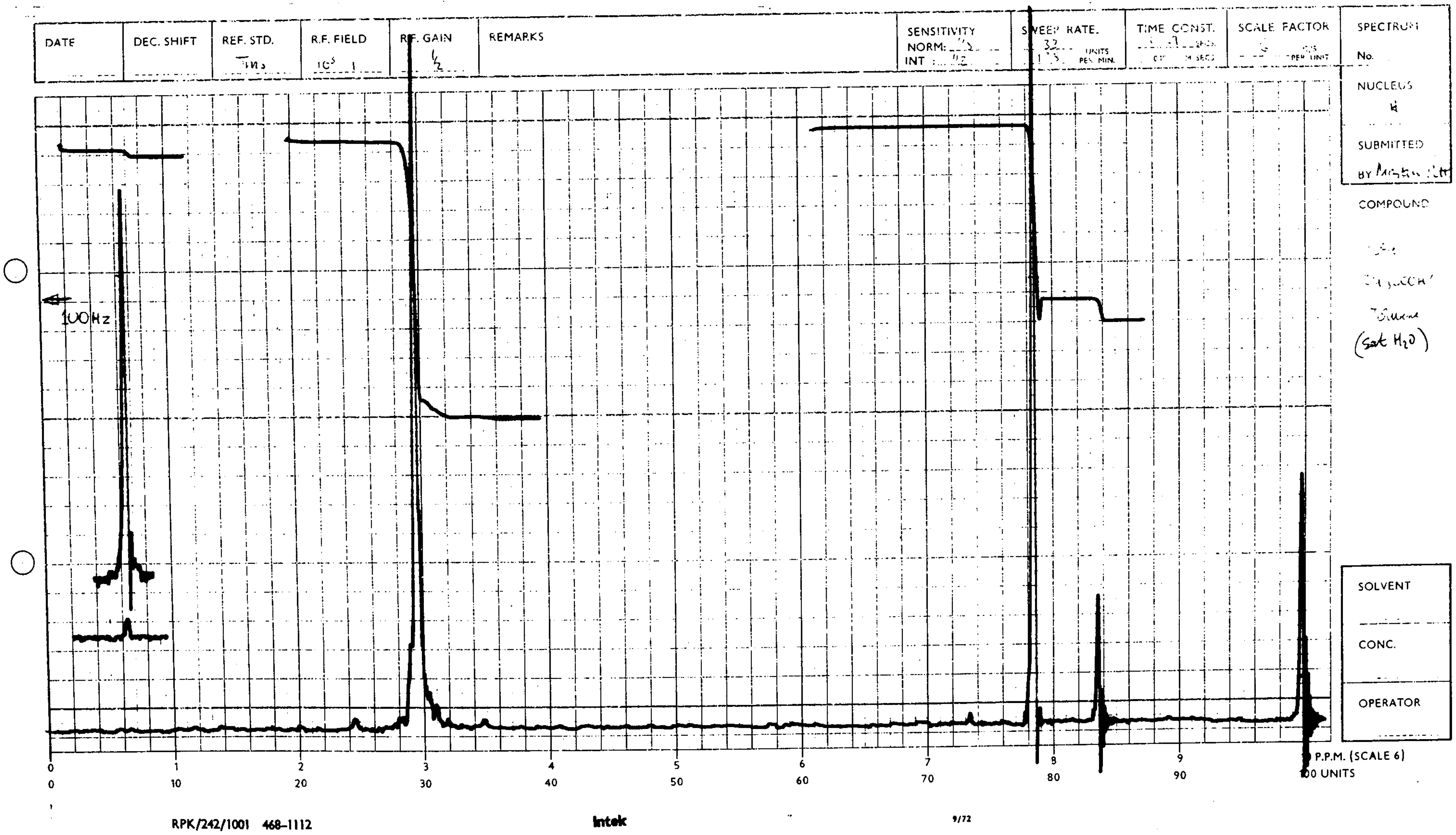


Fig. 6.16 Analysis of a 30% acetic acid in toluene saturated with water using the proton magnetic resonance

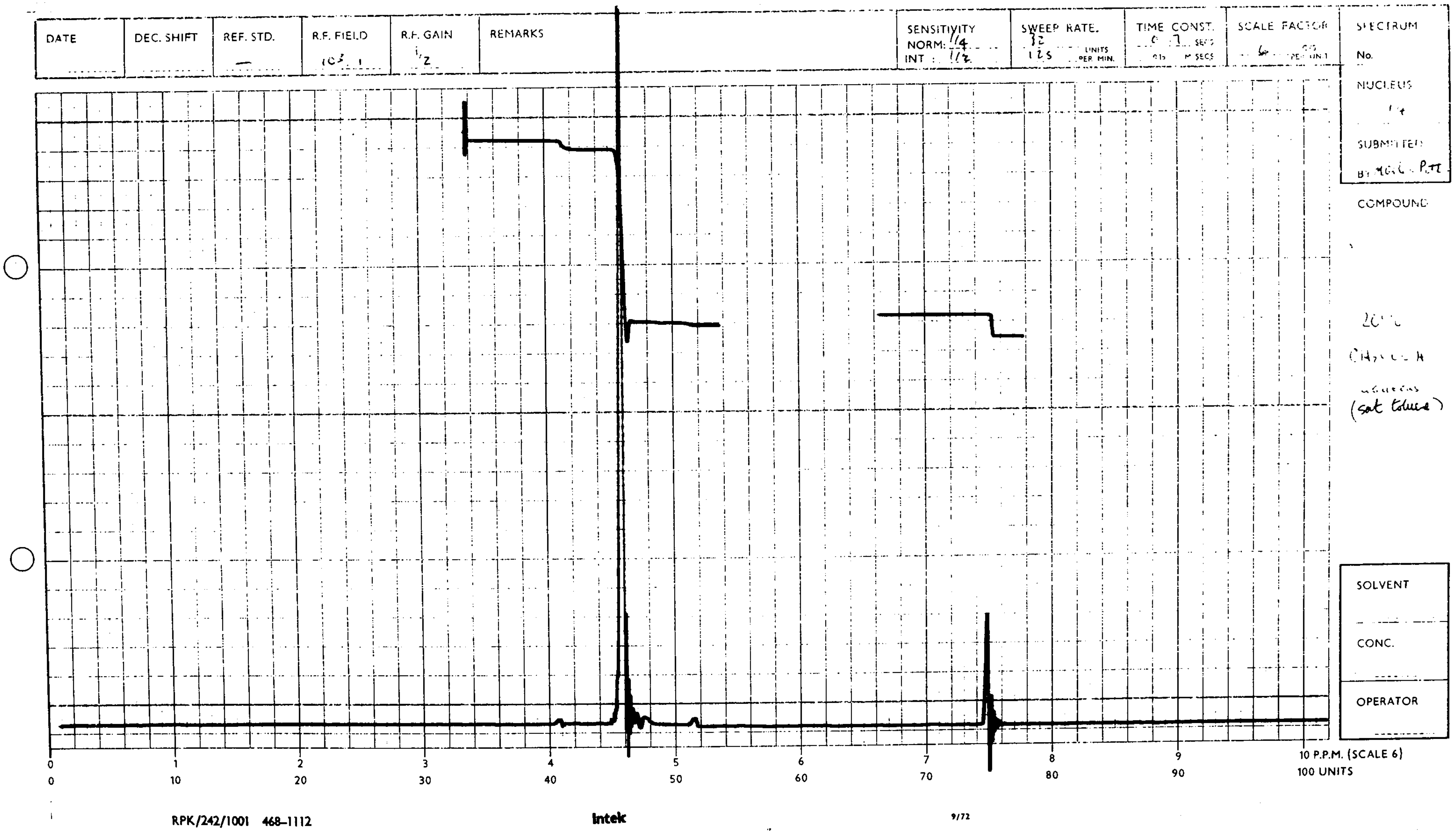


Fig. 6.17. Analysis of a 20% acetic acid in water saturated with toluene using the proton magnetic resonance

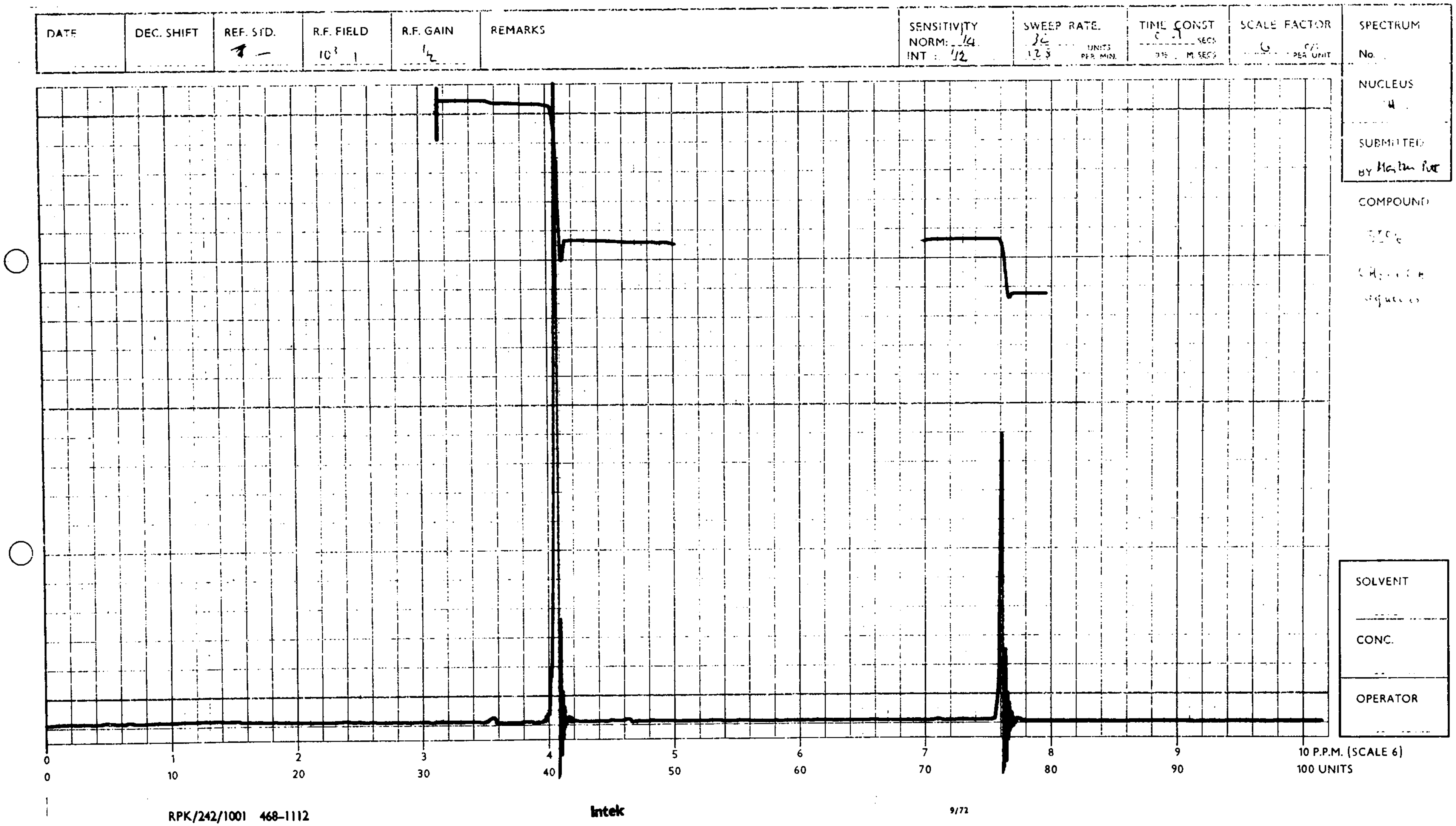


Fig. 6.18 Analysis of a 50% acetic acid in water saturated with toluene using the proton magnetic resonance

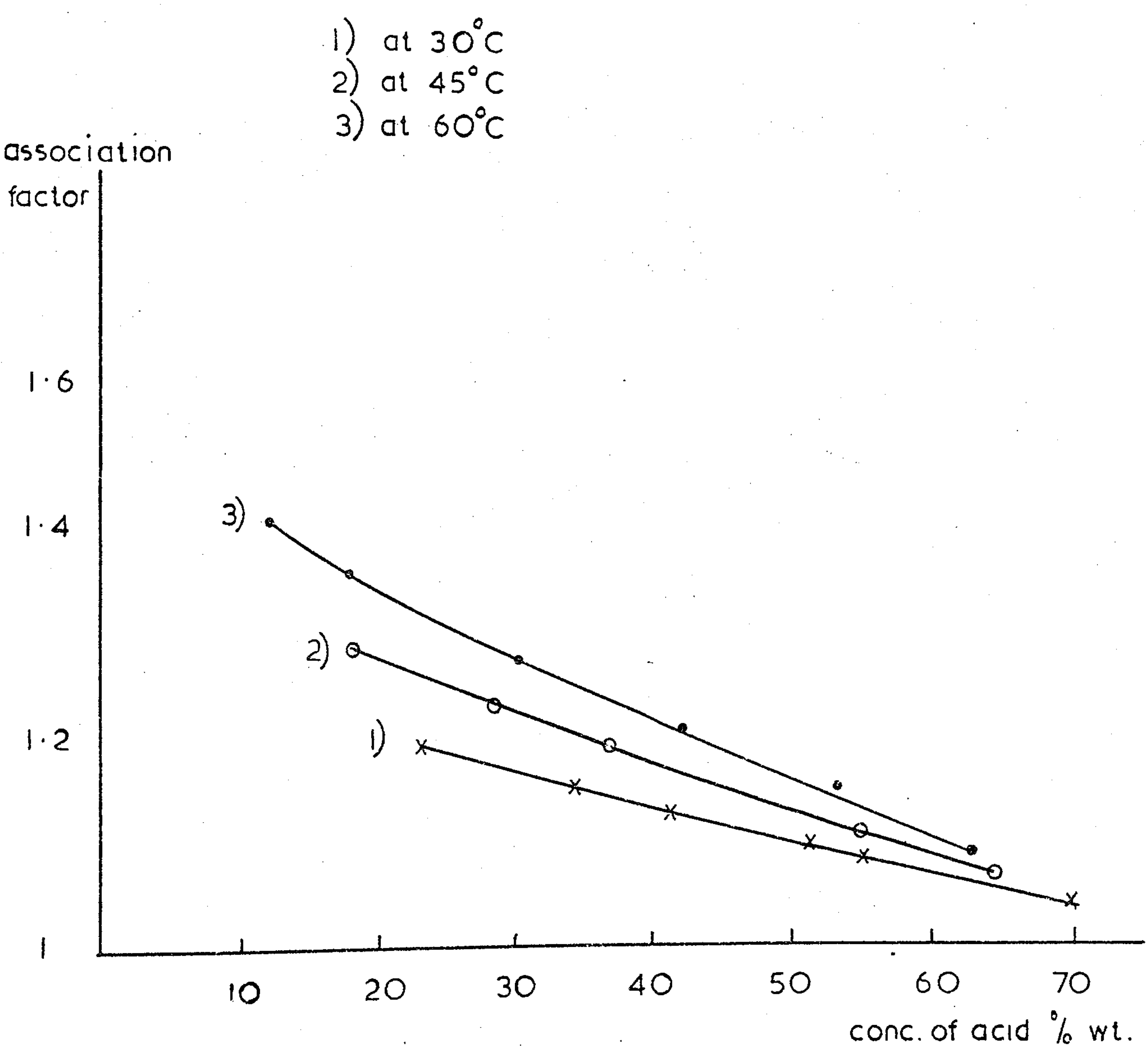


Fig. 6.19. Association factor of acetic acid in the water phase determined by Marek's correlation (175,181)

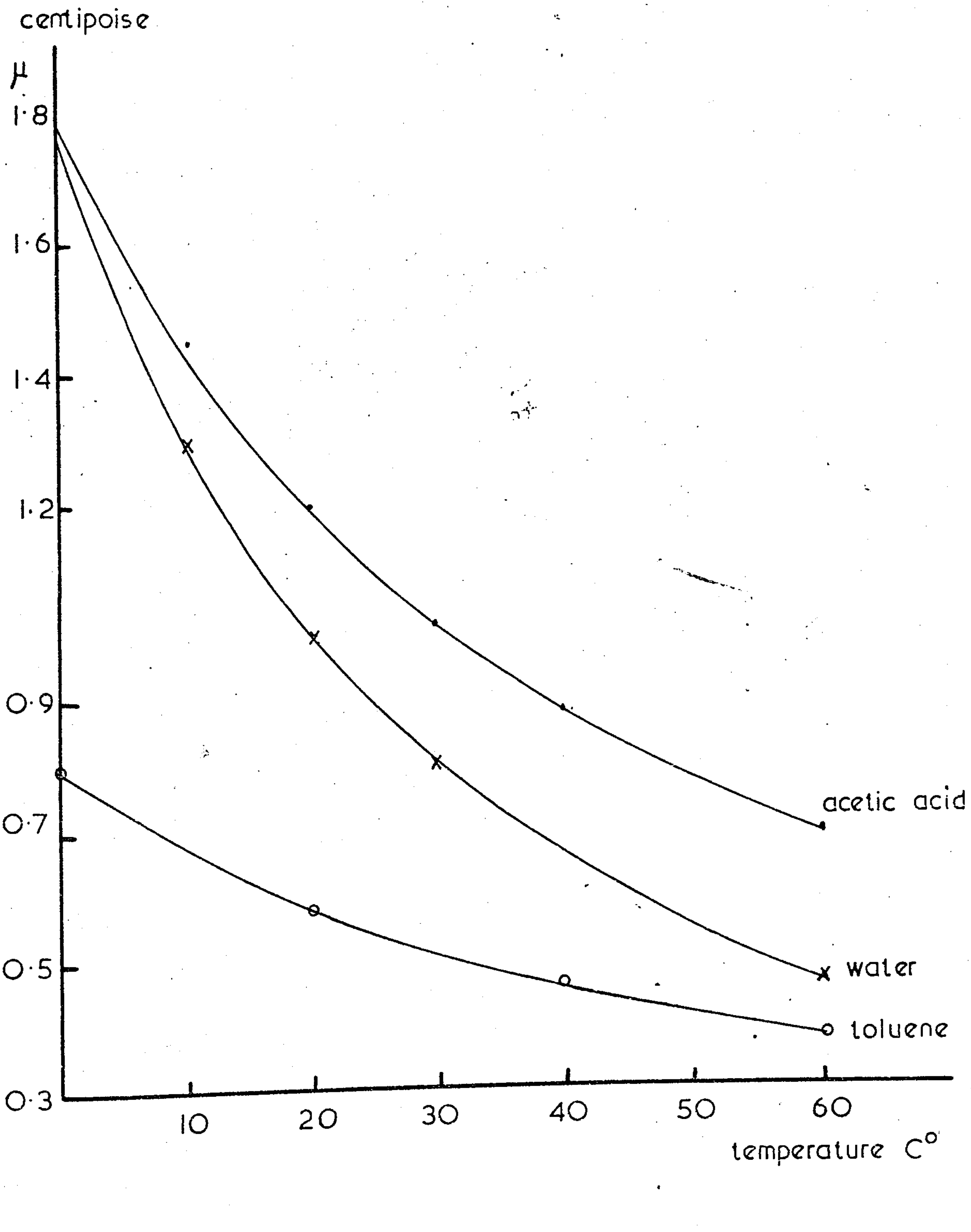


Fig. 6.20 Viscosities at different temperatures

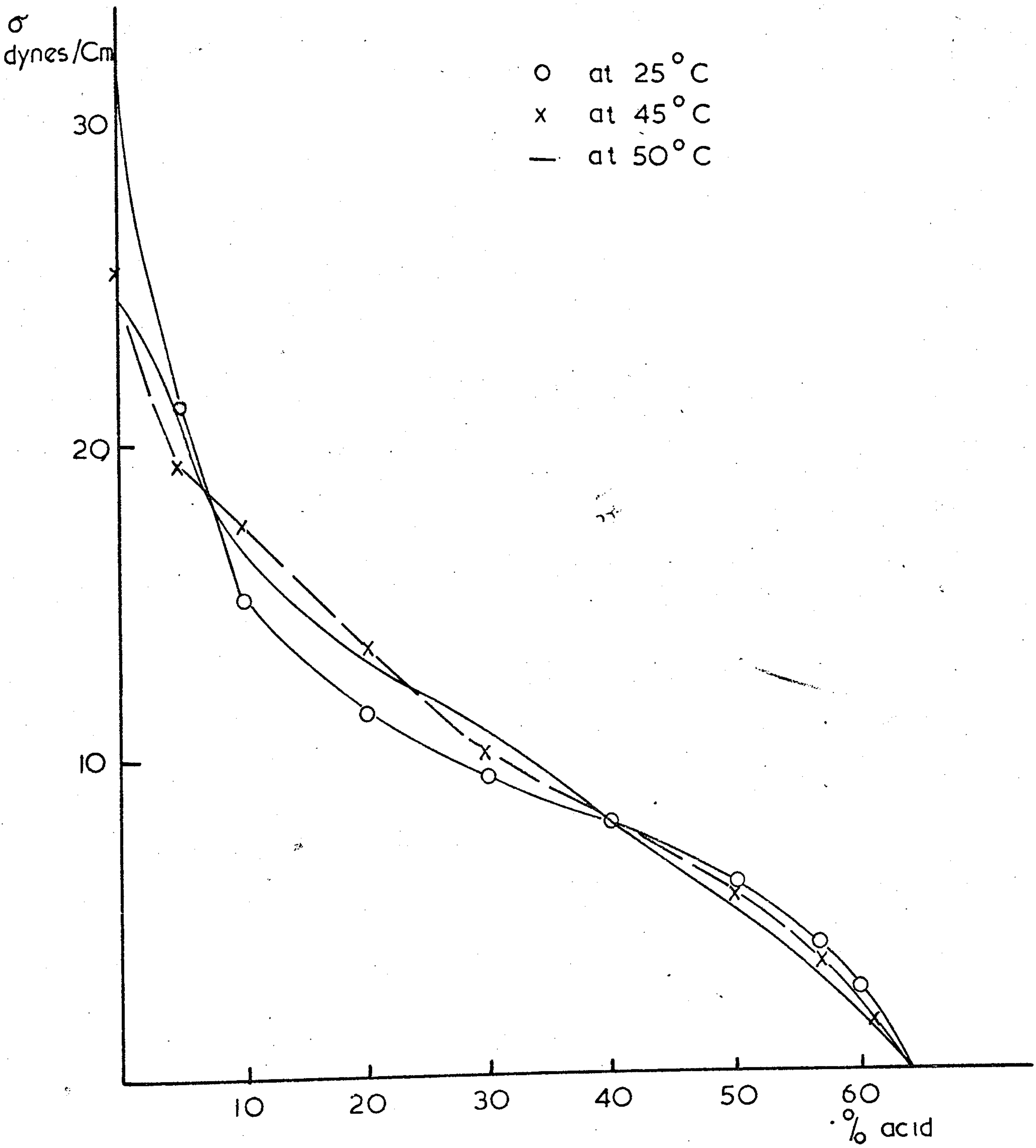


Fig. 6.21 Interfacial tension of the system acetic-acid-toluene-water at different temperatures

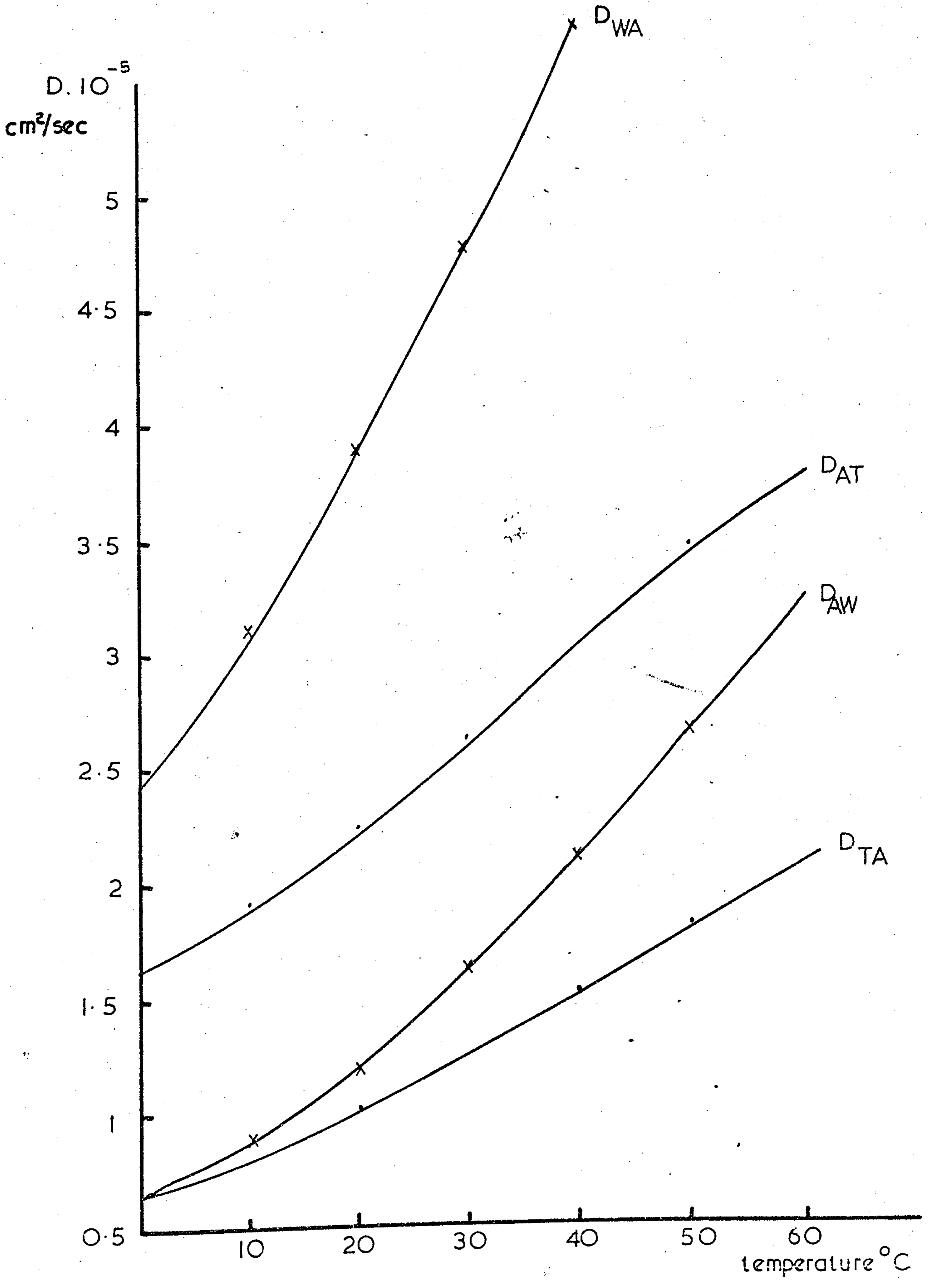


Fig. 6. 22 Diffusivities at infinite dilution

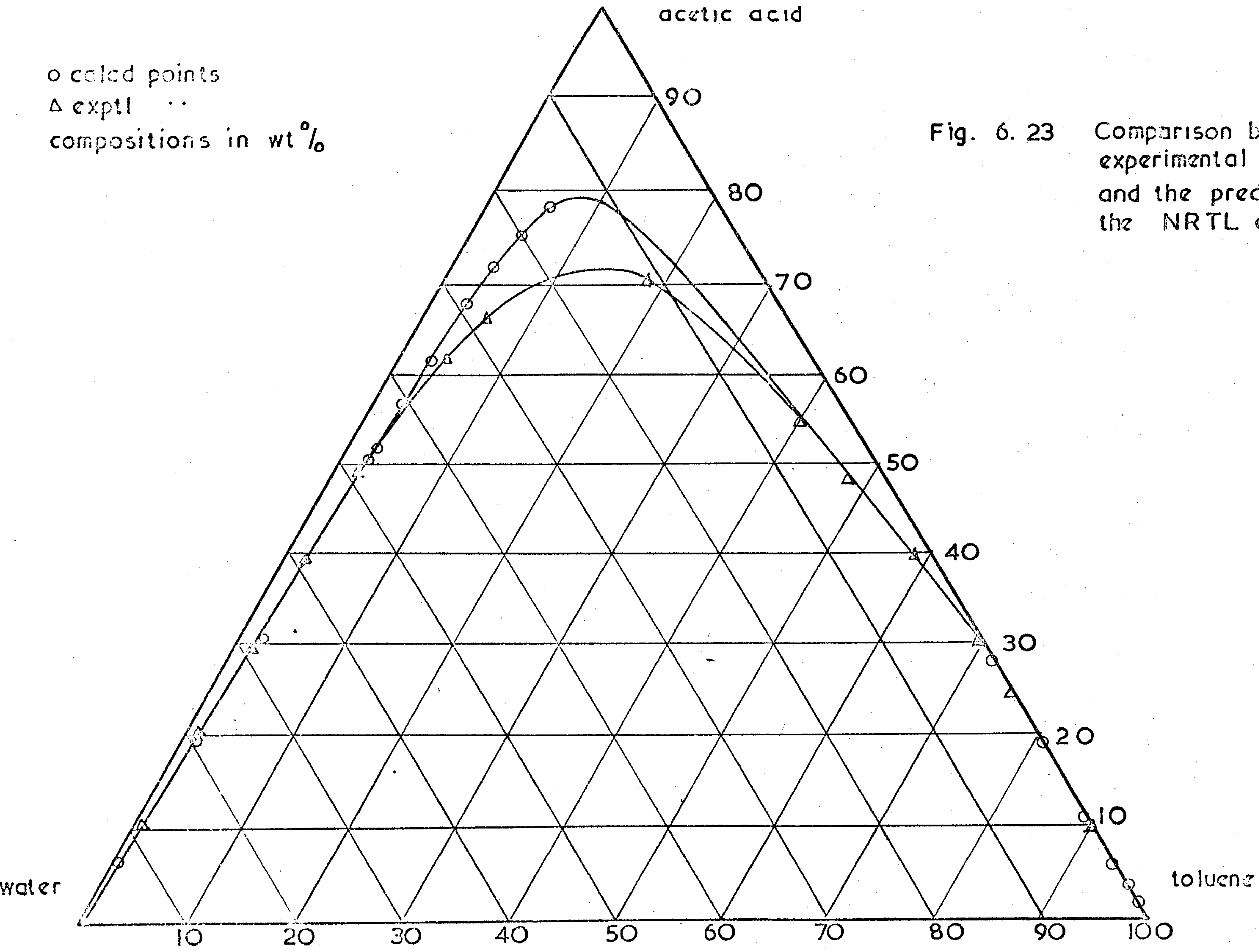


Fig. 6. 23 Comparison between the experimental solubility data and the predicted data by the NRTL equation

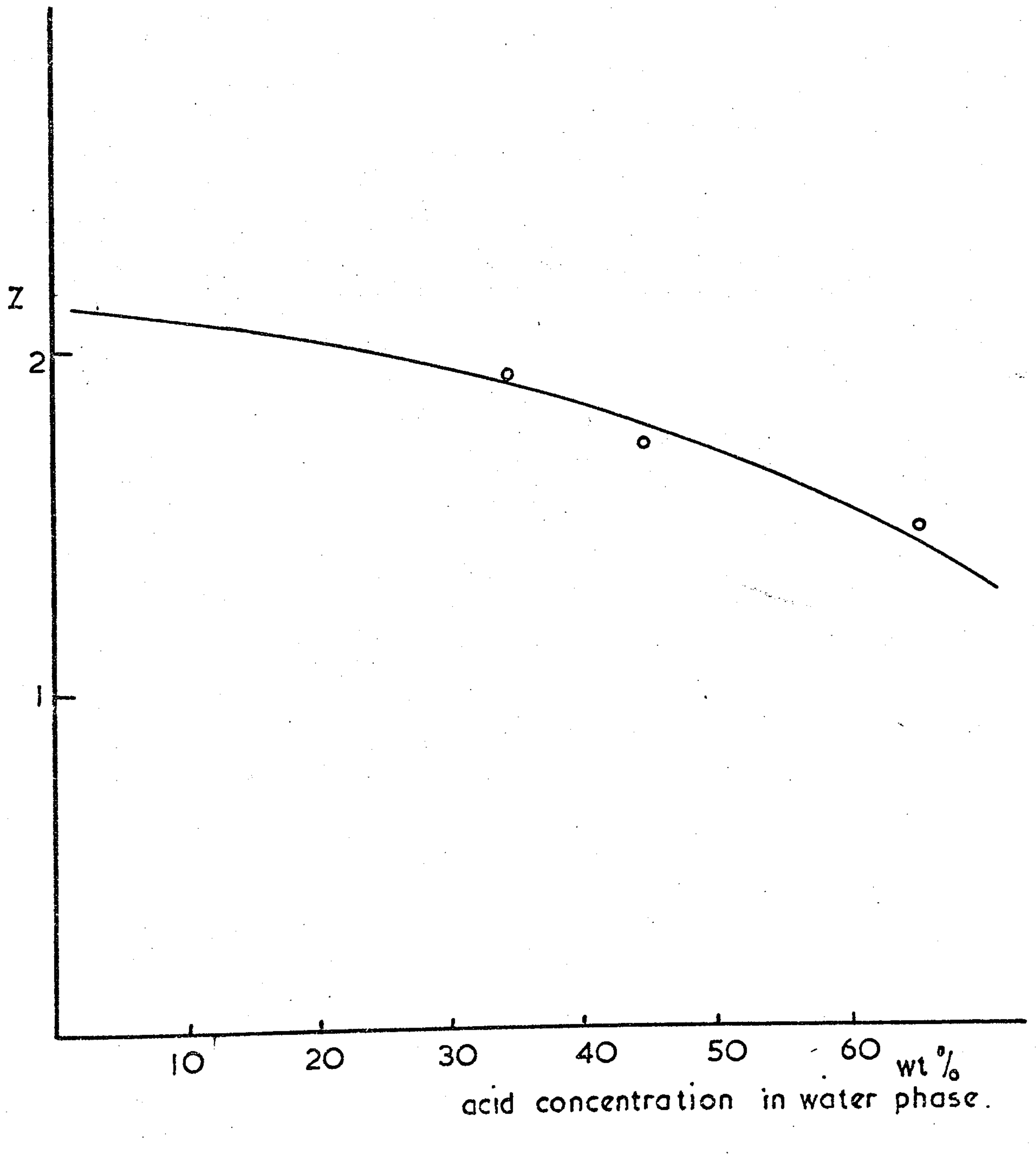


Fig. 6.2.4 Association factor of acetic acid in water phase at 30 °C

7. Experimental Results

The mixer-settler has been operated to investigate the following:-

(a) Confirmation of the correlation of the time required for the counter-current contactor to reach steady state.

(b) Effect of the impeller speed on the efficiency.

(c) Effect of the direction of mass transfer on the efficiency.

(d) Effect of temperature gradient on the extraction efficiency.

7.1 Time Required for the Mixer-settler to Reach Steady State:

Effect of the number of stages, position of the stage, impeller speed, direction of mass transfer, efficiency and temperature on the time required for the contactor to reach steady state has been studied.

7.1.1 Effect of the Number of Stages on Time To Reach Steady State:

The results of operating the equipment with 2,4,6 and 10 stages are presented in figures 7.1 to 7.7. The phase ratio of 1:3 was adhered to in most cases, since it was appropriate up to 6 stages, but higher phase ratios were used in order to assess the maximum possible flow rate. Acetic acid in toluene was extracted by water with the agitators speed maintained at about 1800 rpm. The temperature of each stage of the process was maintained at 30°C ± 0.5°C. It can be seen in figures 7.1 to 7.7 that the time required to reach steady state, for the extract phase, is not in all cases the same as that for the raffinate phase. Fig. 7.8 indicates that the time for the extract phase to reach steady state is longer, irrespective of the direction of mass transfer. Fig. 7.8 also shows that there is a linear relationship between the time required to reach steady state and the number of stages; confirming that predicted by the model in section 4.1.

7.1.2 Effect of the Direction of Mass Transfer on the Time Required to Reach Steady State:

Equation 4.12 shows that the time required for a counter current contactor to reach steady state increases as the distribution coefficient increases. This has been confirmed experimentally. Acetic acid in water was extracted with toluene with 4, 5 and 7 stages operating. The phase ratios were chosen to give higher efficiencies and to decrease back mixing and prevent flooding of the apparatus. The results obtained are given in figures 7.9 to 7.14. Fig. 7.8 indicates that extraction of acetic by water from toluene, where the distribution coefficient is large, requires a longer time than that required if extraction was performed in the other direction confirming that predicted by the model in section 4.1.

7.1.3 Effect of the Agitation Speed on the Time Required to Reach Steady State:

The pilot plant was operated with 4 stages to extract acetic acid from toluene by water at 30° C and at agitation speeds of 2100, 2550 and 2850 rpm, and the results obtained are presented in figures 7.15 to 7.20. In these figures it can be seen that at lower agitation speeds, disturbances in the system are more pronounced so that this delayed the system acquiring steady state conditions.

7.1.4 Effect of Temperature on Time Required to Reach Steady State:

Figures 7.21 to 7.28 summarize the results of operating the equipment with 4 stages at 45 and 60° C and at agitation speeds of 2400 and 2550 rpm. These figures together with the results at 30° C show that as the temperature increases the time to reach steady state is reduced.

7.1.5 Effect of the Position of a Stage on its Time Needed to Reach State:

The time required for each stage, in an N stage process, to reach steady state at different temperatures and agitation speeds for extraction of acetic acid by water from toluene is given in table 7.1. This table shows that the intermediate stages reach steady state conditions faster. The solvent stage is the last to reach steady state. Some discrepancies to this conclusion were observed when the process contained only 4 stages and was operated at 2850 rpm. However, the trend shown by the model in section 4.1 is substantiated in table 7.1.

7.1.6 Effect of the Efficiency on Time Required to Reach Steady State:

Fig. 7.29 shows that as the mixer-settler operates with a lower efficiency, the time required for acquiring steady state is longer. Fig. 7.30 also confirms this trend. This figure shows that the percentage extracted is most likely to be the best test of attainment of steady state conditions and not the concentration or the stage efficiency. The concentration, as shown in figures 7.1 to 7.29, was greatly affected by any disturbance to the system; for example, sudden changes in the speed of agitation or changes in the flow to or from the equipment. For this reason the percentage extracted will be taken in most of the following analyses as the measure of the efficiency of the contactor.

7.2 Effect of the Impeller Speed on the Efficiency of the Mixer-settler:

Fig. 7.31 shows that the percentage extracted increased experimentally with the impeller speeds when acetic acid was extracted from toluene by water at 30° C using 4 stages and 6 stages in the mixer-settler under similar operating conditions. The data were correlated with the same statistical package as before, and the correlation obtained was

$$E = 0.5515N^{0.02} \cdot S^{0.06} \qquad 7.1$$

The correlation coefficient was 0.977 and the residual error was 0.00270528.

7.3 Effect of the Direction of Mass Transfer on the Efficiency:

Figure 7.32 shows that although 6 stages can bring about 97% extraction of acetic acid from toluene when water was used as a solvent, the same number of stages could hardly achieve 7% of the extraction if toluene was used to extract the acid from water.

7.4 Effect of Temperature on the Extraction Efficiency:

The results of studying the effect of changing the temperature of the extraction process with mass transfer in both directions are given in Table 7.2 and Fig. 7.33. A comparison has been given between data derived from phase equilibria and data obtained from a 4-stage mixer-settler. The trend in the solubility data indicates a decrease in efficiency with rising temperature. In the mixer-settler the reverse trend occurred, especially when extracting acetic acid from water by toluene Table 7.2 shows that, according to the phase equilibria the best operating conditions which would result in the highest possible extraction efficiency would be to apply a temperature gradient on the stages at 30° C at the solvent end rising to 60° C at the feed stage. Operating a 4 stage mixer-settler with the solvent stage and the neighbouring one at 30°C and the other two stages at 60^{o} C actually gave the lowest extraction efficiency. This is discussed in section 8.

7.5 Effect of the Number of Stages on Mass Transfer Coefficient:

The mass transfer coefficient has been calculated for extraction, performed with 4, 6, 8 and 10 stages, of acetic acid from toluene by water. The results are presented in Fig. 5.34. Average values for interfacial tension, dispersed phase hold up and droplet diameter was considered. It was tried to determine the droplet diameter photographically but the emulsion was so fine at the speeds of agitation used that no satisfactory prints have been developed. The mean droplet diameter was then calculated by Kolmogoroff's law (148) and by Hinze's equation (149). The droplet diameter calculated by Hinze's equation was 3 times that calculated by Kolmogoroff's law. The latter was considered to be more satisfactory since it was more likely representative of the actual droplet diameter in the contactor. A detailed calculation of the droplet diameter and mass transfer coefficients is presented in Appendix IV. The average mass transfer coefficient in 6 stages was found to be higher than that calculated by the stagnant drop model and just below that calculated by the circulating drop model.

Table 7.1 Time to reach steady state in each stage in the mixer settler

N	temp. °C	speed r.p.m.	Direct. of mass transfer	Phase	Time to reach steady state in stage (in hours)									
					1	2	3	4	5	6	7	8	9	10
10	30	1800	A → W	Extract	9	8	7	-	-	6	-	8	-	10
				Raffinate	8.5	7.5	7	-	-	6	-	7.5	-	9.5
7	30	2550	A → T	Extract	3	3	4	-	-	-	4.5			
				Raffinate	2.5	2	2	-	-	-	4			
6	30	1800	A → W	Extract	4	3.5	3	2	3	5				
				Raffinate	3	3	2	1	3	5				
6	30	2100	A → W	Raffinate	2.5	2	2	1	2.5	4.5				
5	30	2550	A → T	Extract	1.75	1.5	1.5	2	2					
				Raffinate	2	2	2	2	2.5					
4	30	1800	A → W	Extract	3	2.5	2.5	3.5						
				Raffinate	2.5	2.5	1.5	2.5						
4	30	2100	A → W	Extract	3	3	3	3						
				Raffinate	2.5	2	2	3						
4	30	2550	A → W	Extract	2	2	1	2.5						
				Raffinate	2	2	2	2.5						
4	30	2850	A → W	Extract	4	4	3	3.5						
				Raffinate	4	4.5	3	3						
4	45	2400	A → W	Extract	2.5	2.5	2.5	2.5						
				Raffinate	2.5	2.5	2.5	2.5						
4	45	2550	A → W	Extract	2.5	1.5	1.5	2.5						
				Raffinate	2.5	2.5	1.5	2.5						
4	60	2400	A → W	Extract	1.5	1.5	1.5	2.5						
				Raffinate	2.5	2.5	2.5	2.5						
4	60	2550	A → W	Extract	2	2	2	2						
				Raffinate	2.5	2.5	1.5	2.5						
4	60	2550	A → T	Extract	2	2	2	2						
				Raffinate	2	2	2	2						
2	30	1800	A → W	Extract	1.5	1.5								

Table 7.2 Percentage extracted in both directions of mass-transfer at different temperatures

Temperature ^{o}C	Percentage Extracted			
	Acetic → water		Acetic → Toluene	
	From Solubility data	Mixer-settler data	From Solubility data	Mixer-settler data
30	96.148	93.8	11.96	4.00
45	92.0	94.20	11.8	11.00
60	89.045	99.07	11.667	22.19
30- 60 atS atF	96.55	91.97	12.248	-
60- 30 atS atF	94.4	90.20	11.32	-

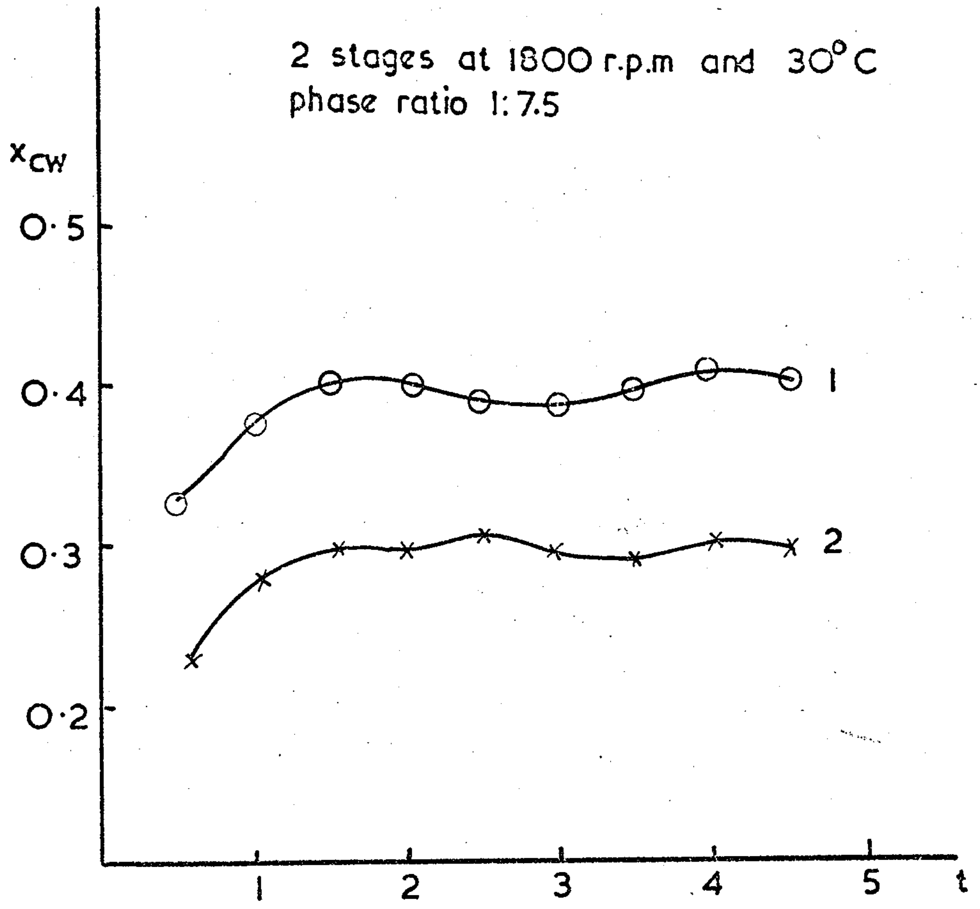


Fig. 7.1. Steady state in the raffinate phase

4 stages at 1800 r.p.m and 30°C
phase ratio 1:3

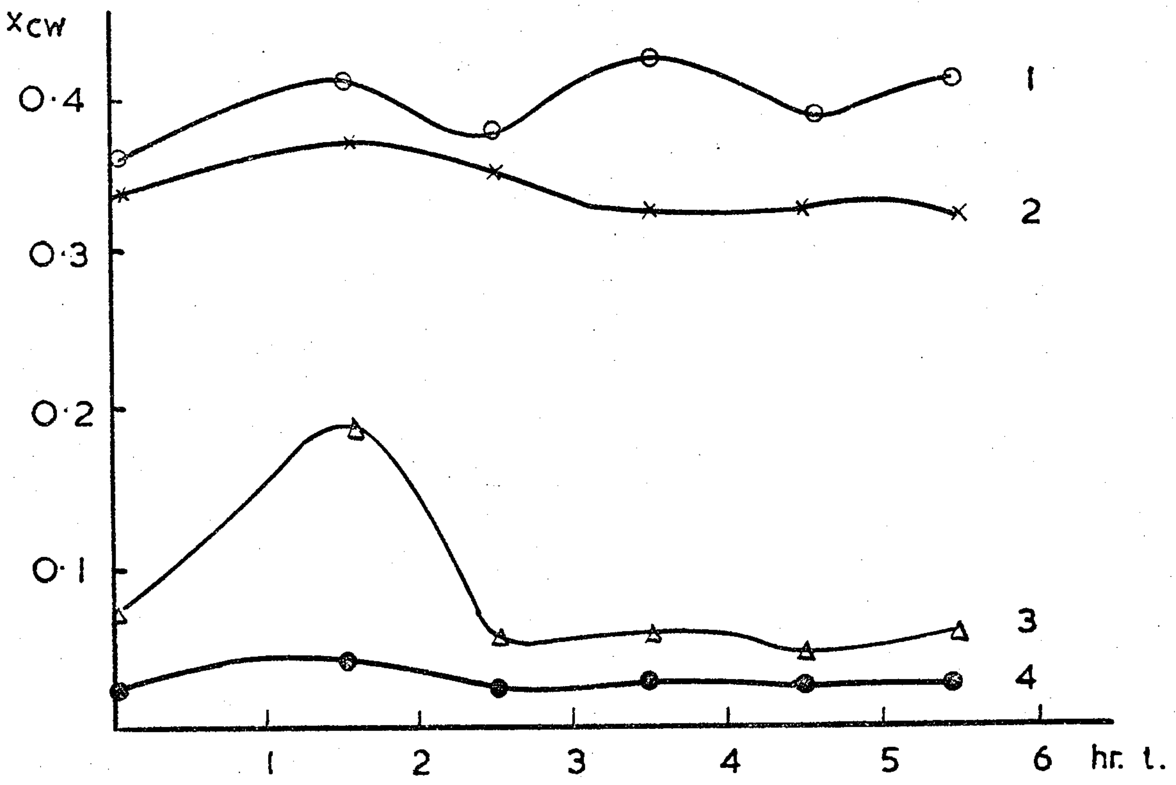


Fig. 7.2 Steady state in the extract phase.

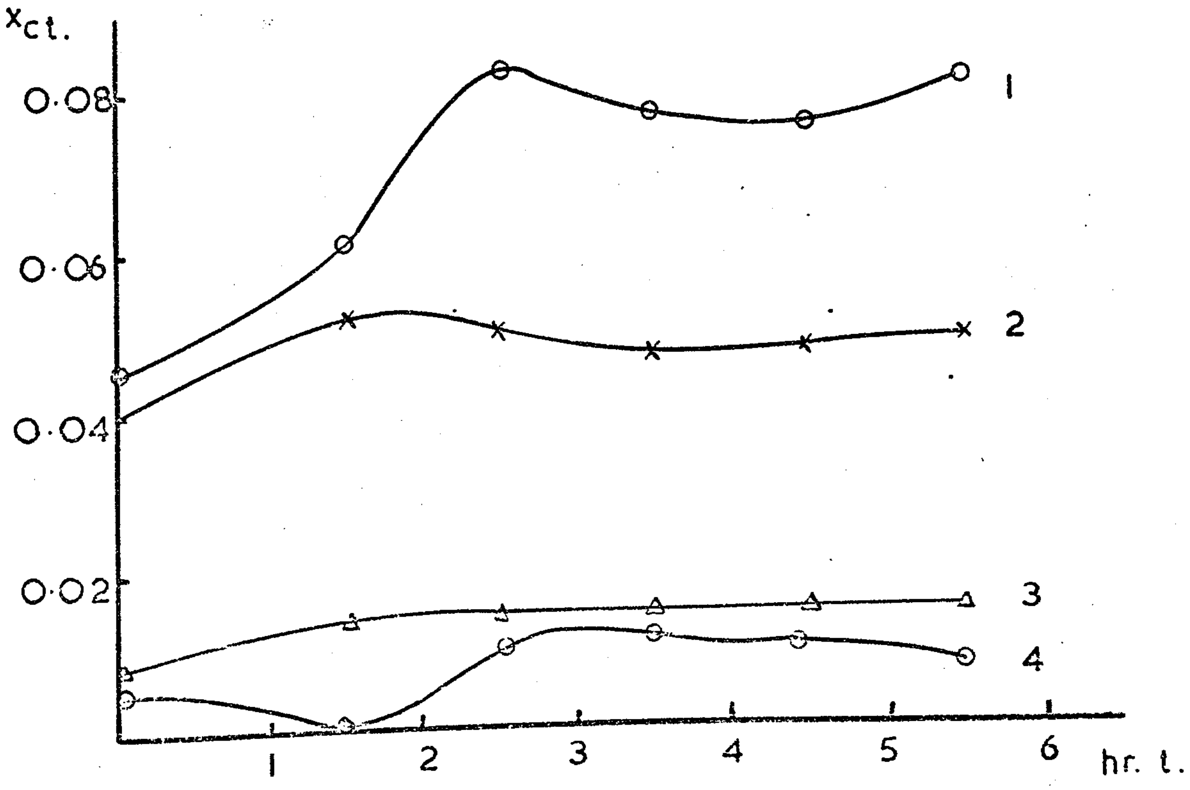


Fig. 7.3. Steady state in the raffinate phase.

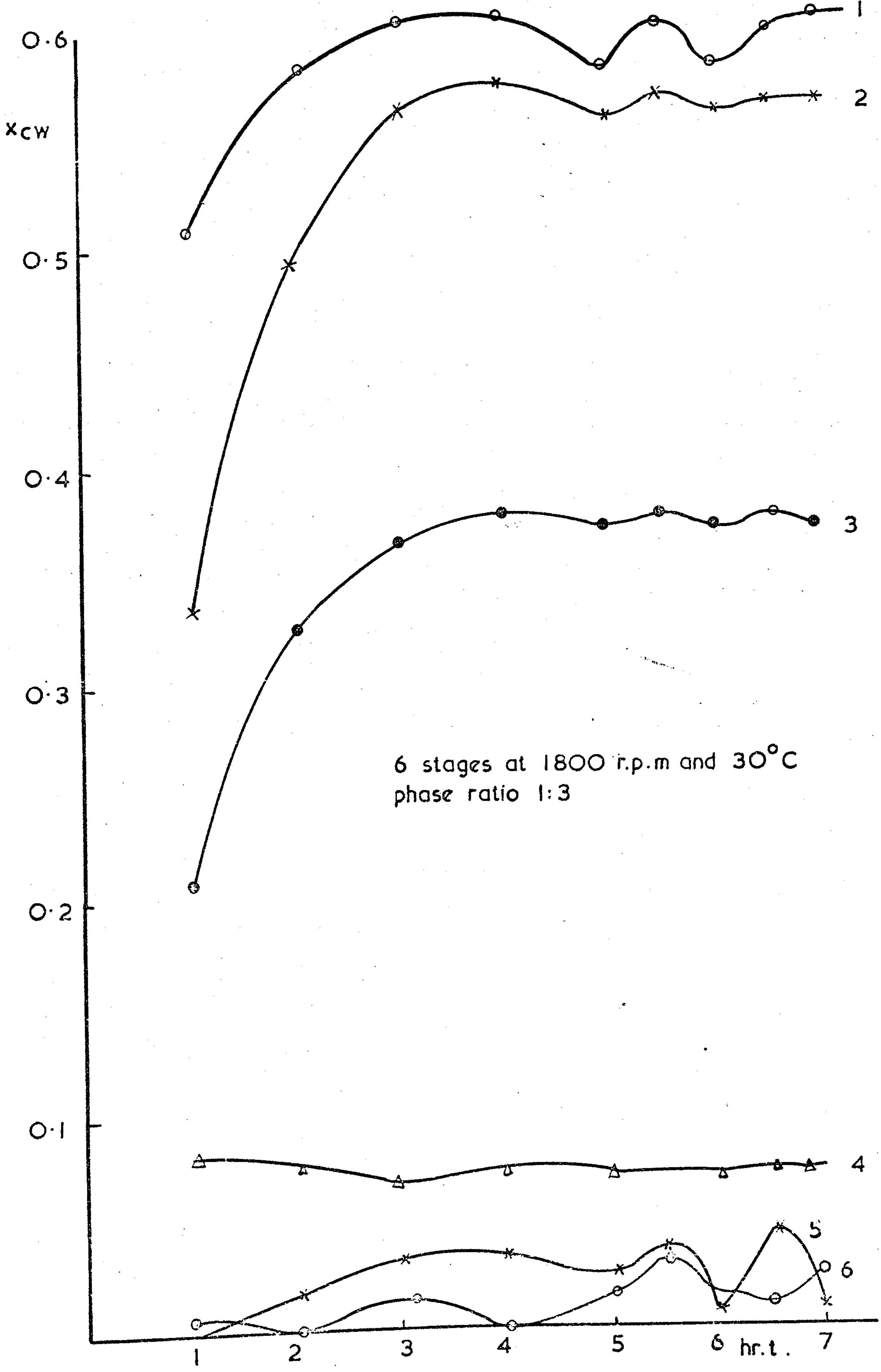


Fig. 7.4. Steady state of the extract phase

6 stages at 1800 r.p.m and 30°C
phase ratio 1:3

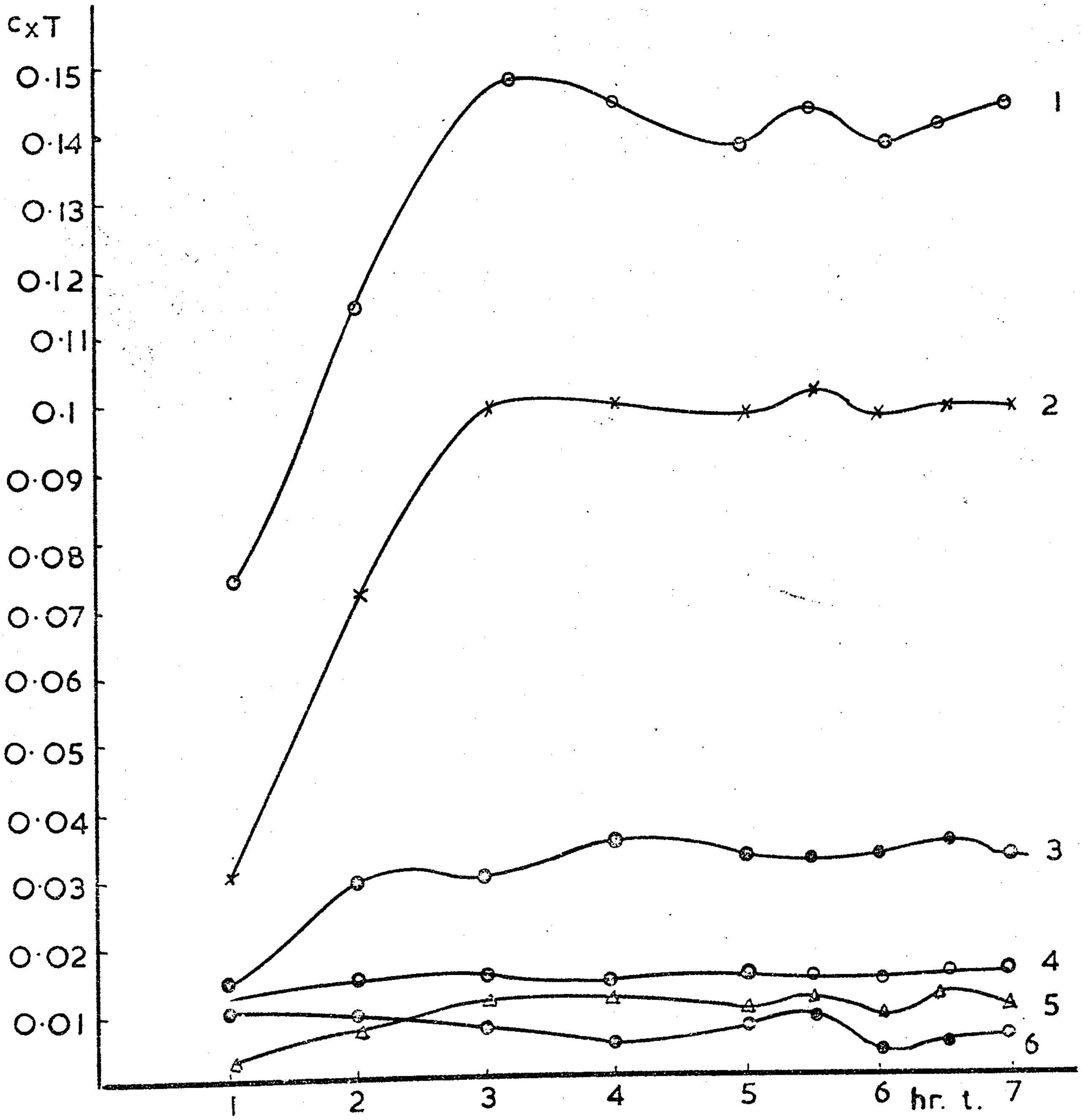


Fig. 7.5. Steady state in the raffinate phase

10 stages at 1800 r.p.m and 30° C
phase ratio 1: 7.5

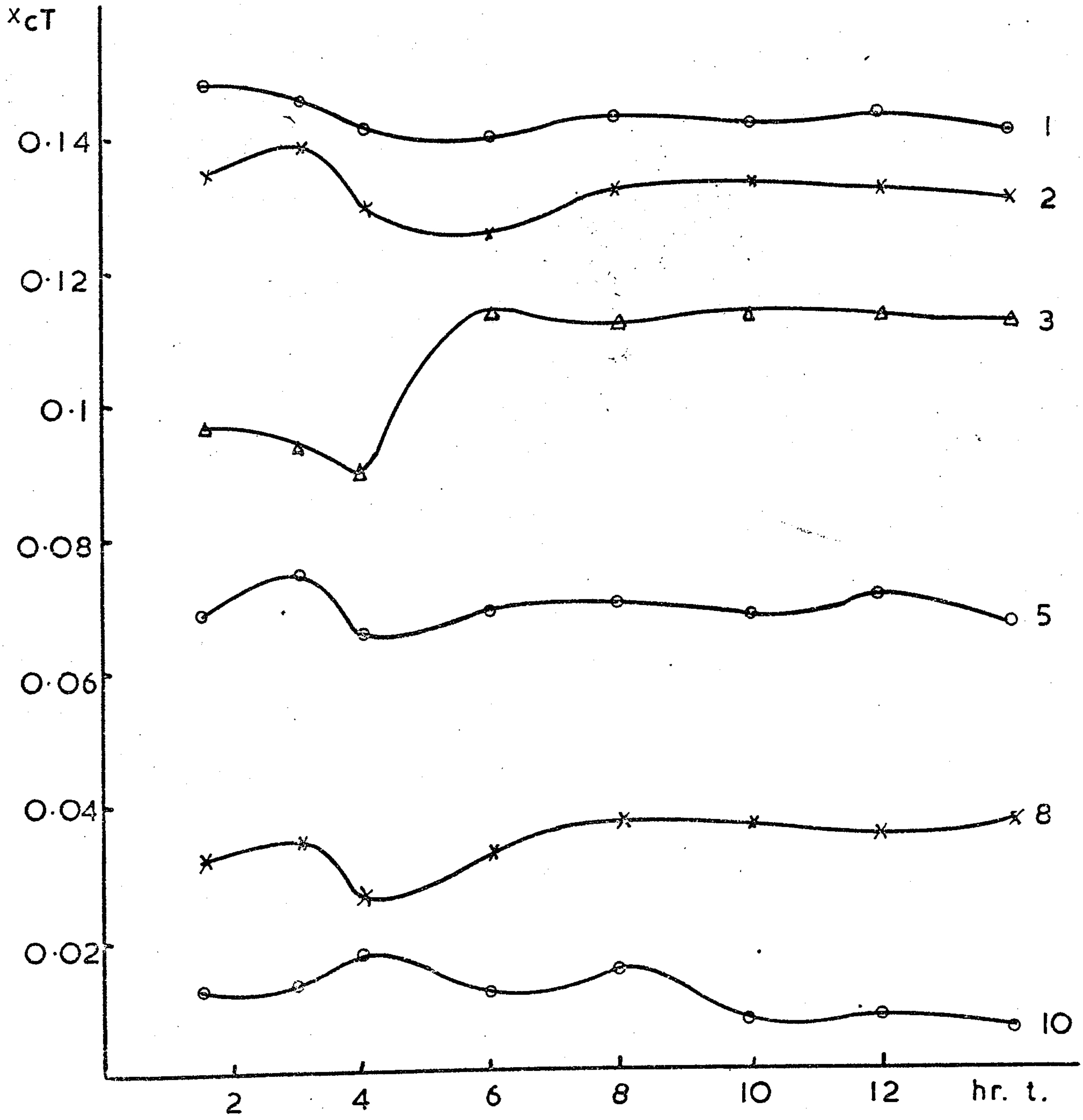


Fig 7.6 Steady state in the raffinate phase

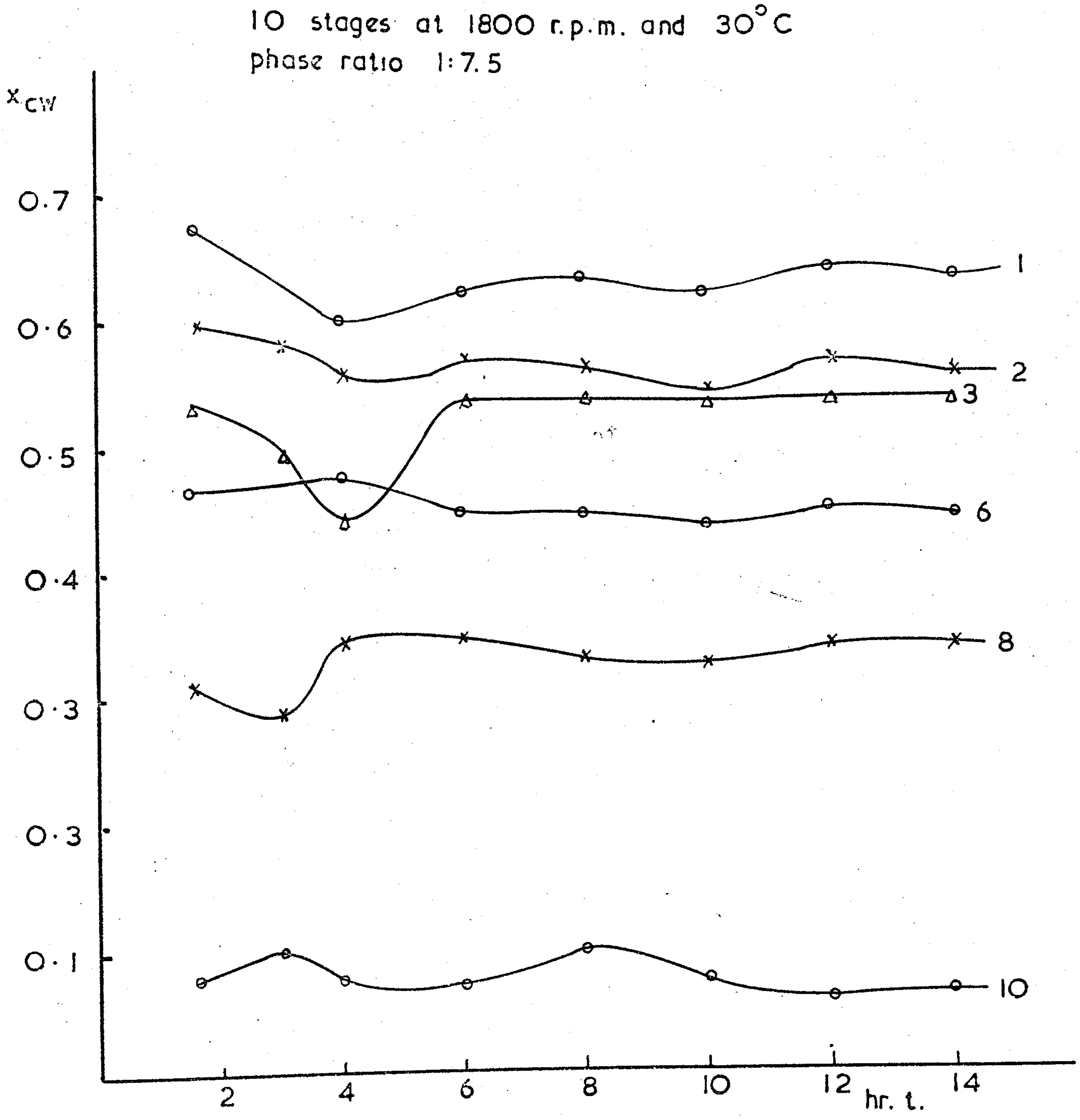


Fig. 7.7. Steady state in the extract phase

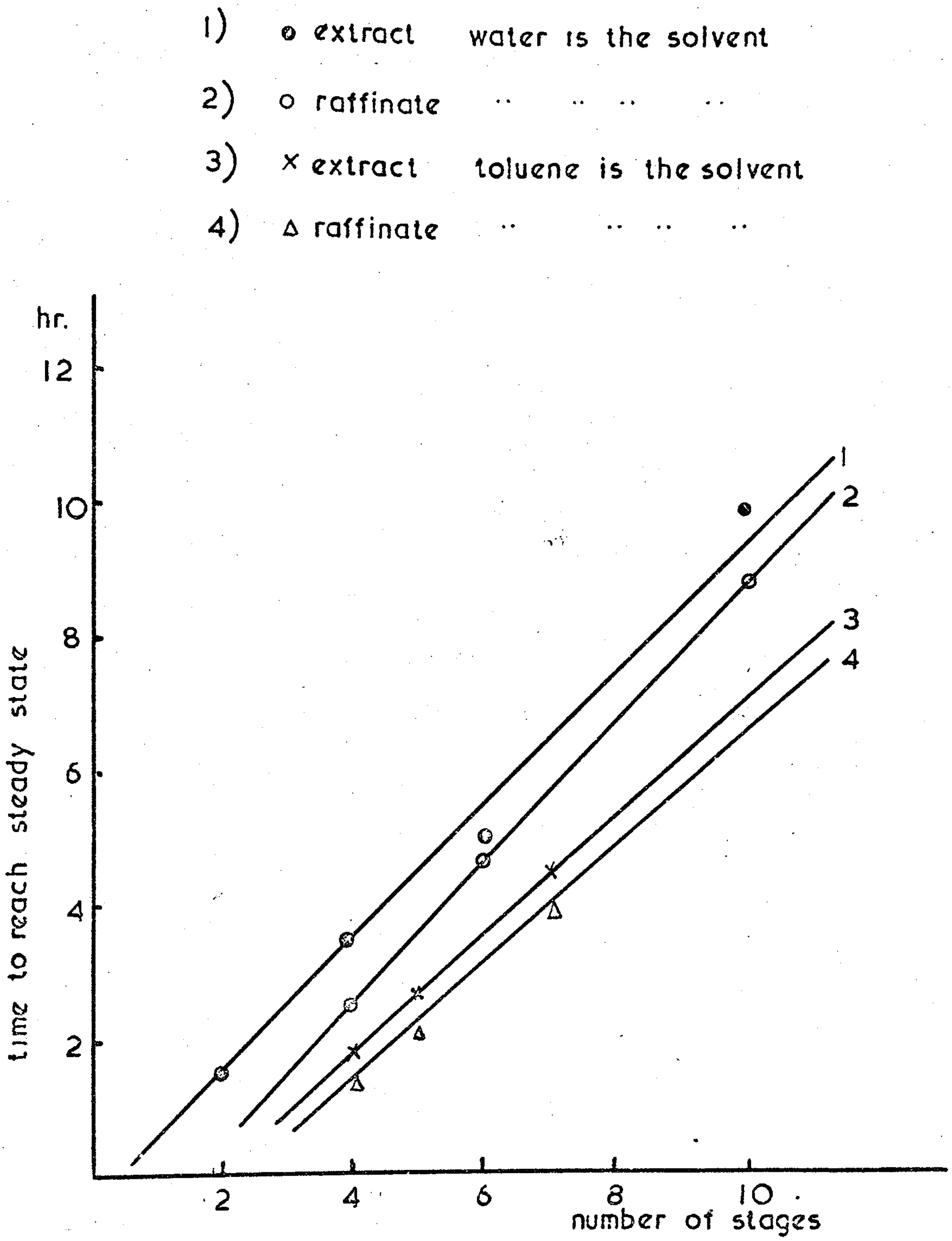


Fig. 7.8. Effect of the direction of mass transfer on time to steady state

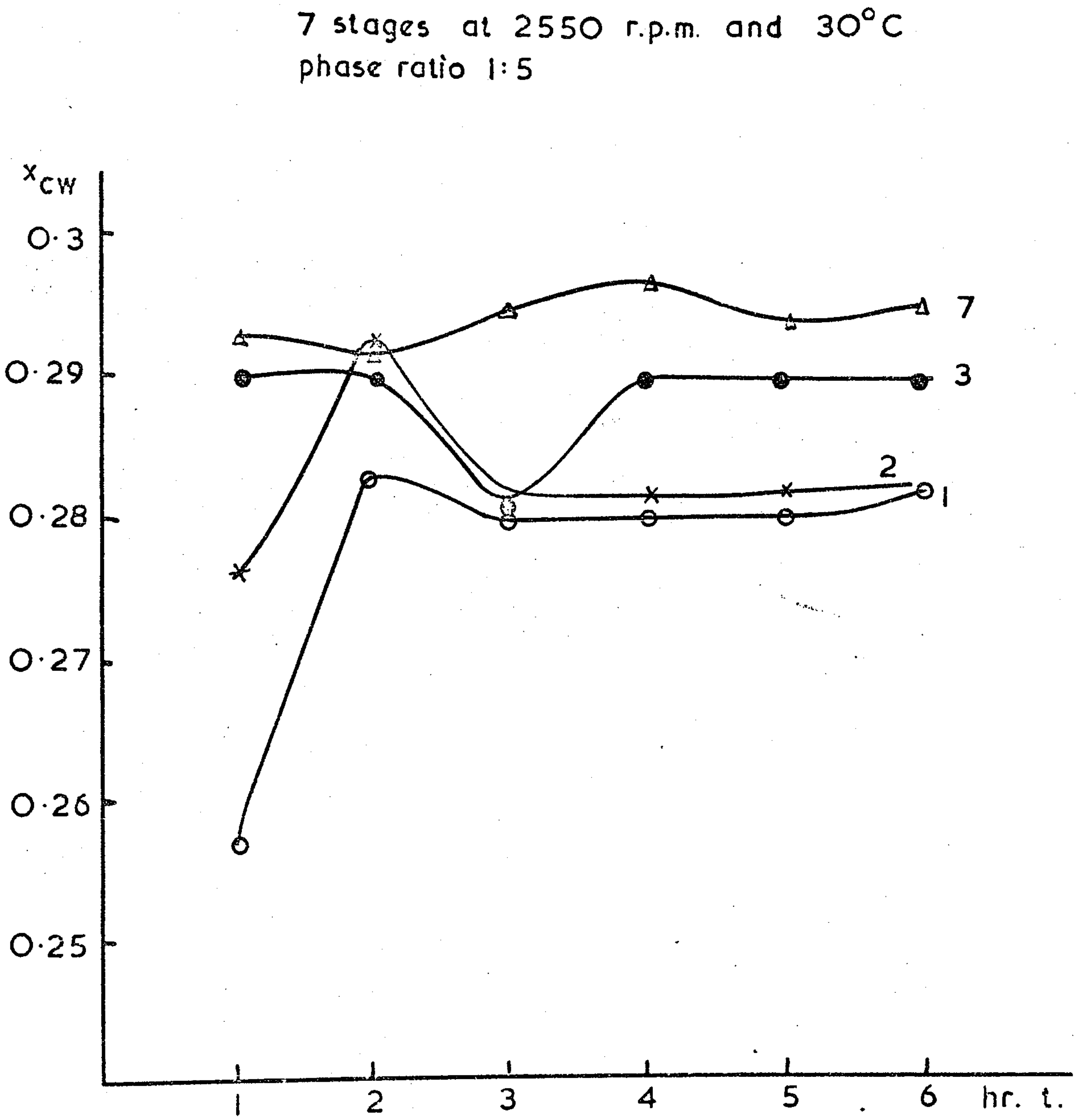
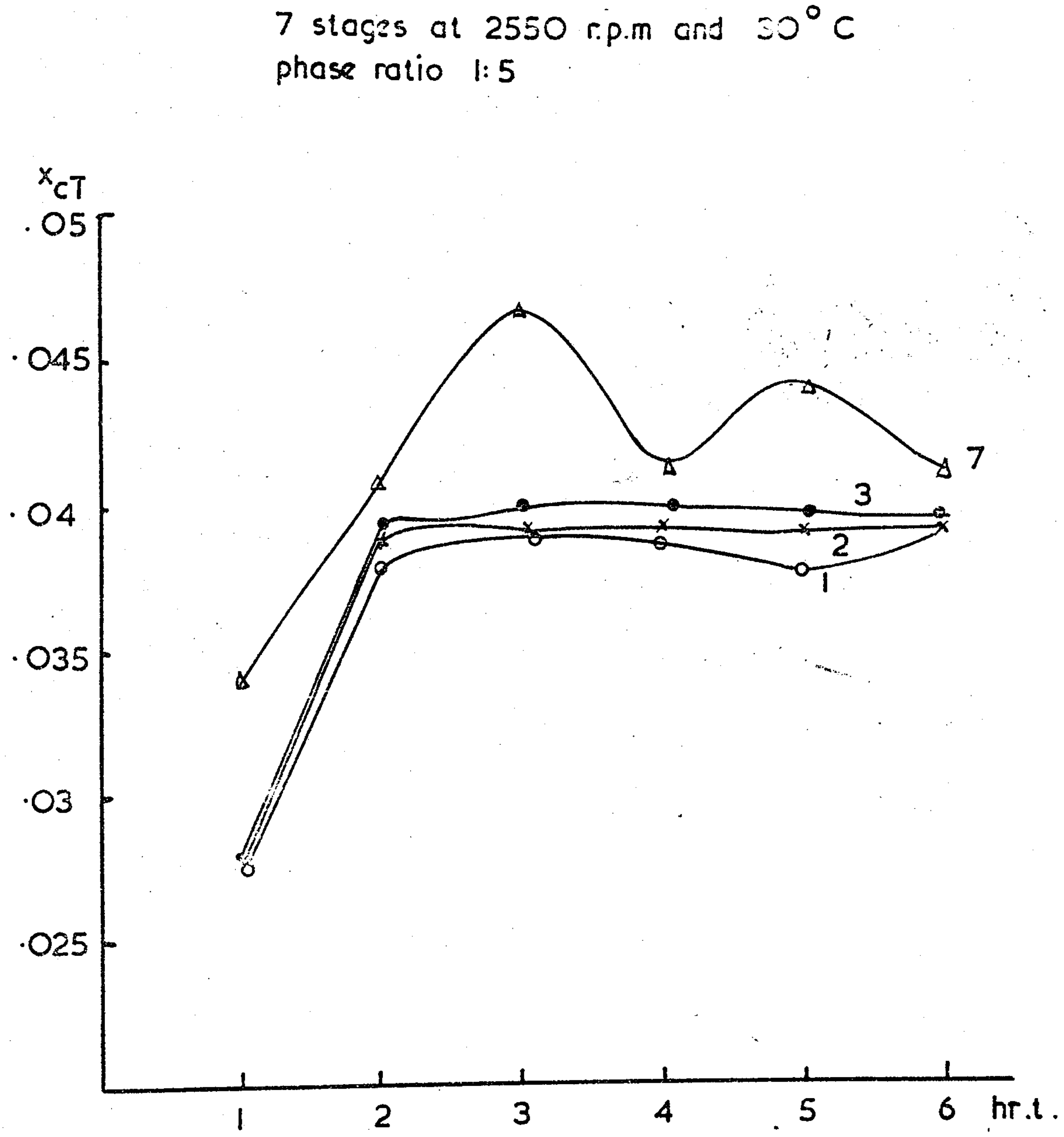
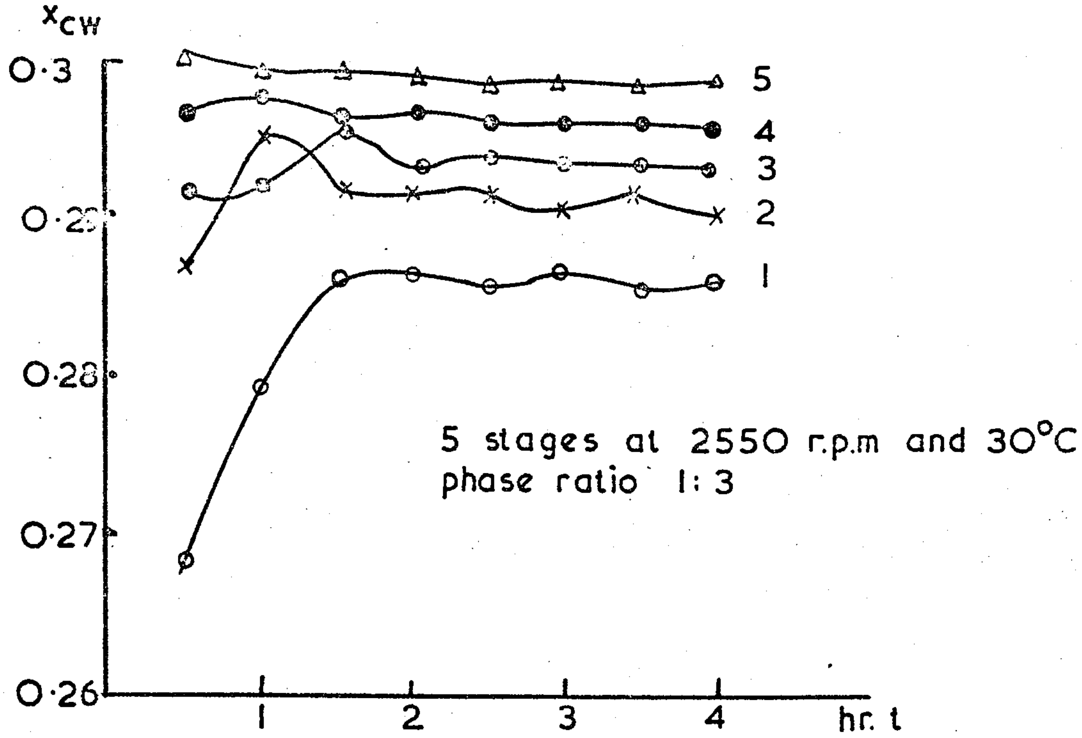


Fig 7.9. Steady state in the extract phase.



7 stages at 2550 r.p.m and 30° C
phase ratio 1:5

Fig. 7.10 Steady state in the raffinate phase.



5 stages at 2550 r.p.m and 30°C
phase ratio 1:3

Fig. 7.11 Steady state in the extract phase

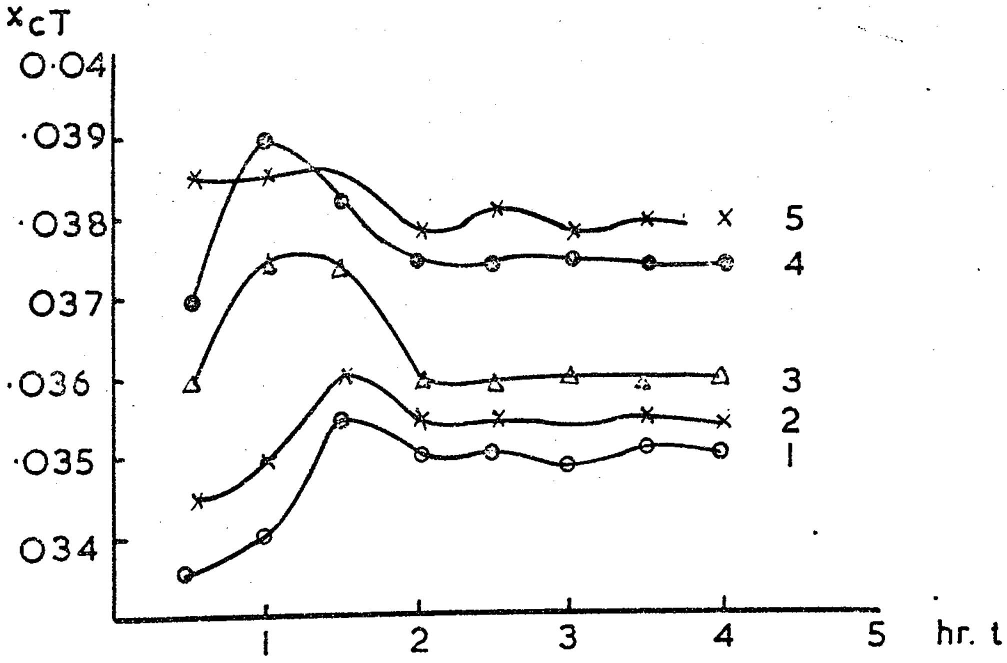


Fig. 7.12 Steady state in the raffinate phase

4 stages at 2550 r.p.m and 60°C
phase ratio 1:3

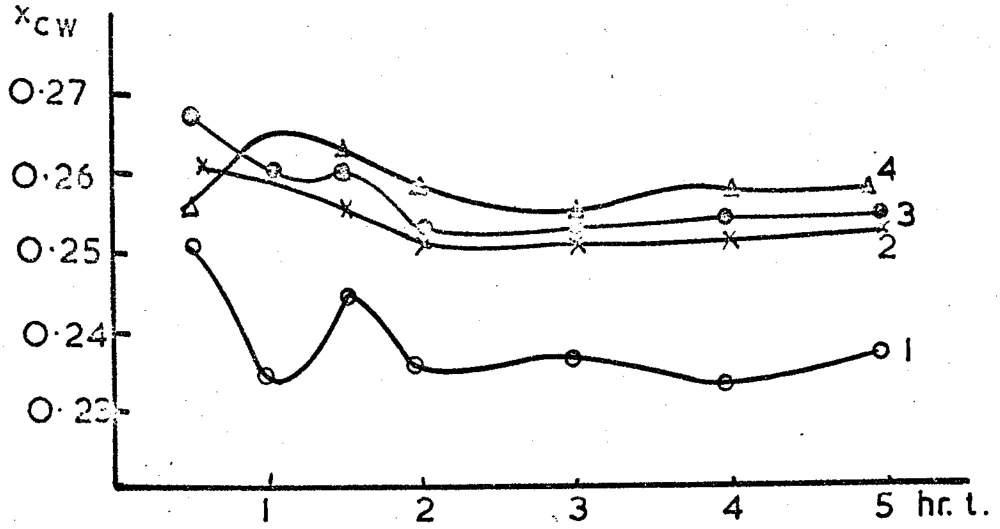


Fig. 7.13. Steady state in the extract phase

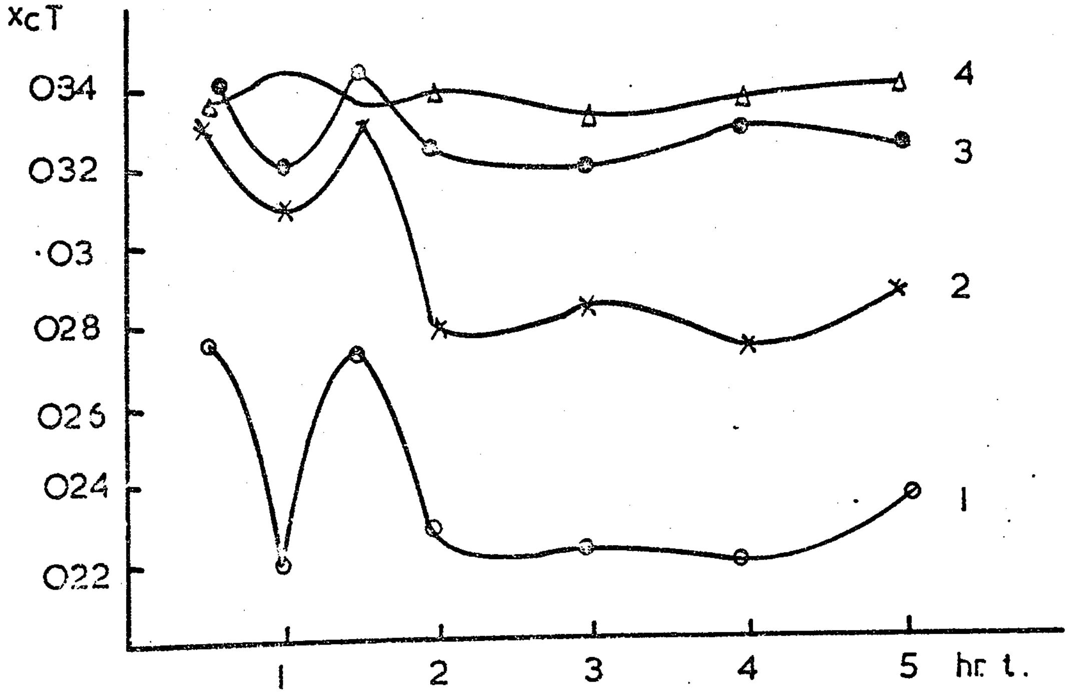


Fig. 7.14. Steady state in the raffinate phase

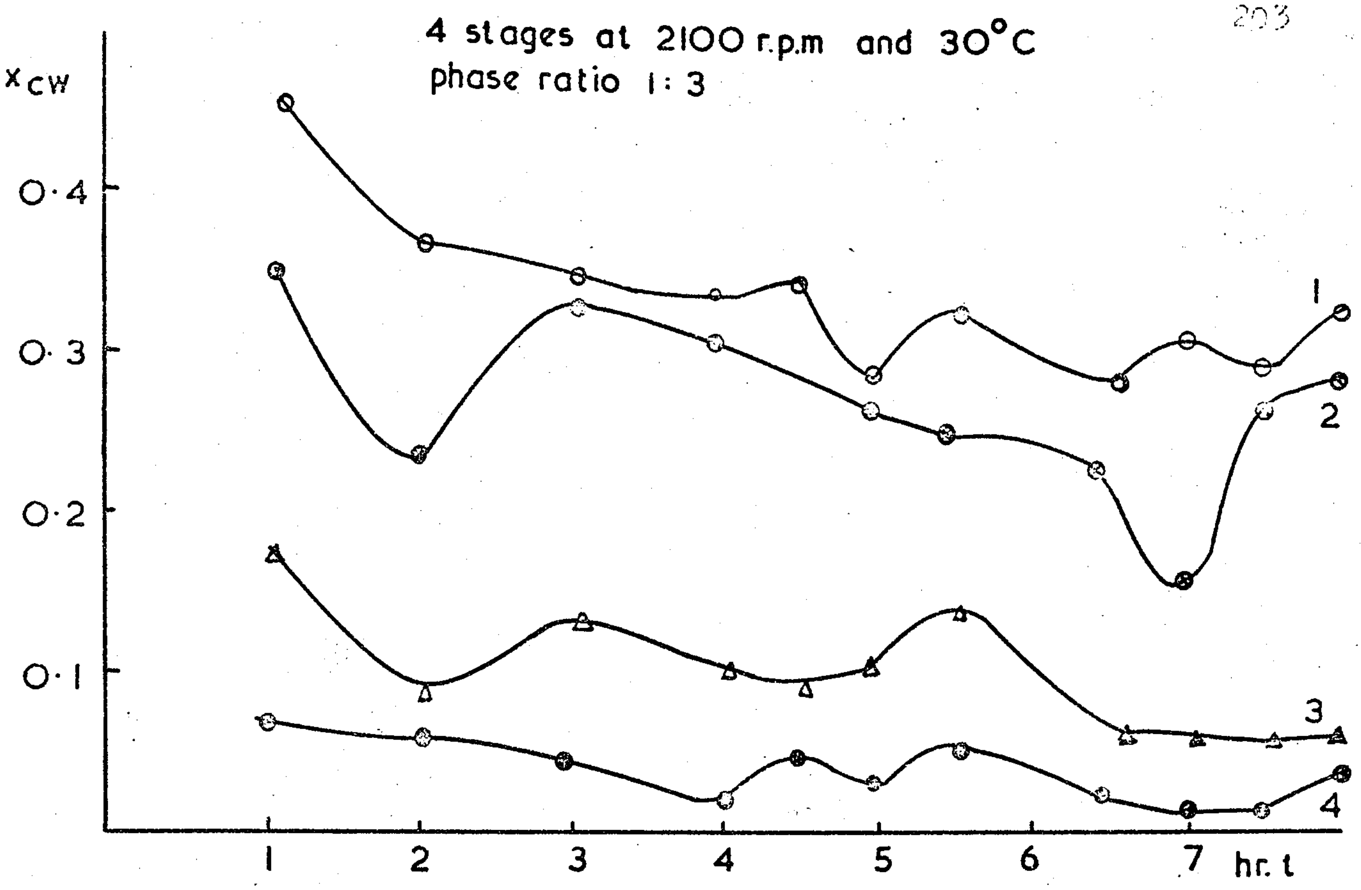


Fig. 7.15 Steady state in the extract phase

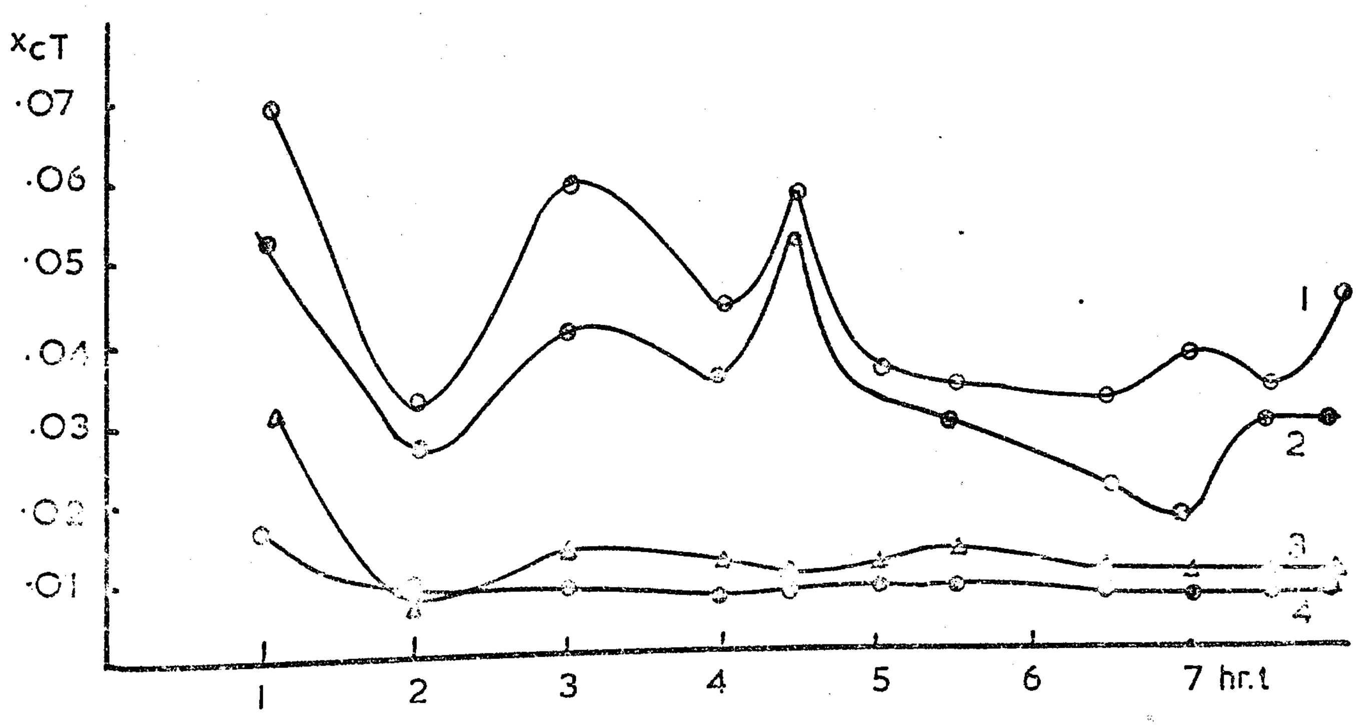


Fig. 7.16 Steady state in the raffinate phase

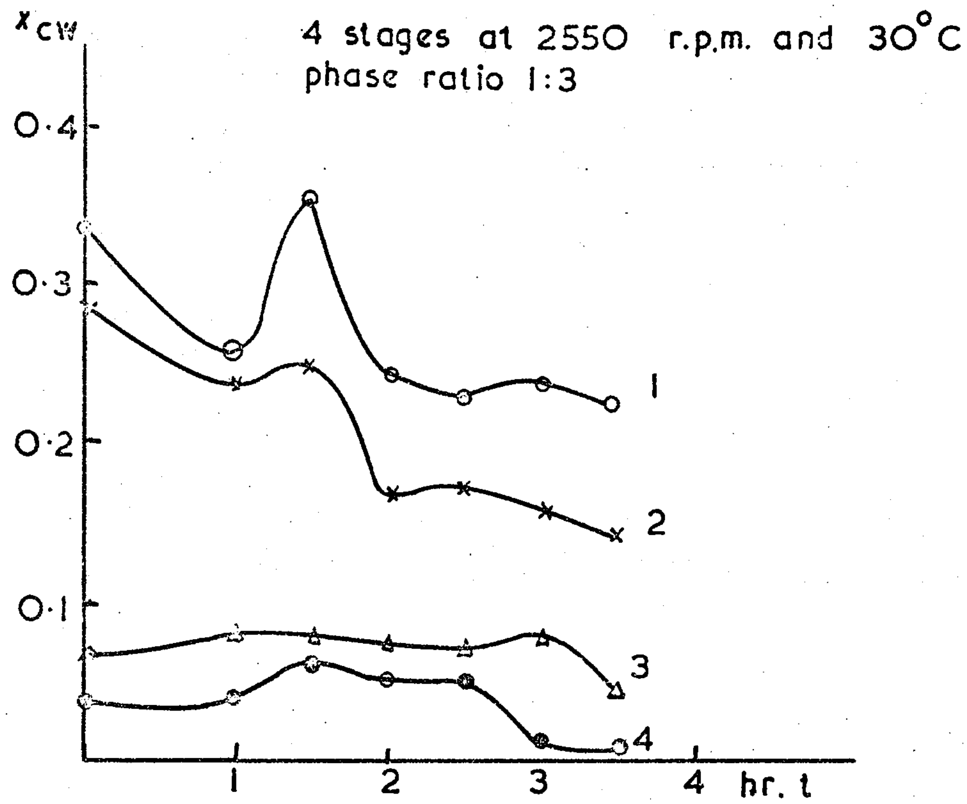


Fig. 7.17. Steady state in the extract phase

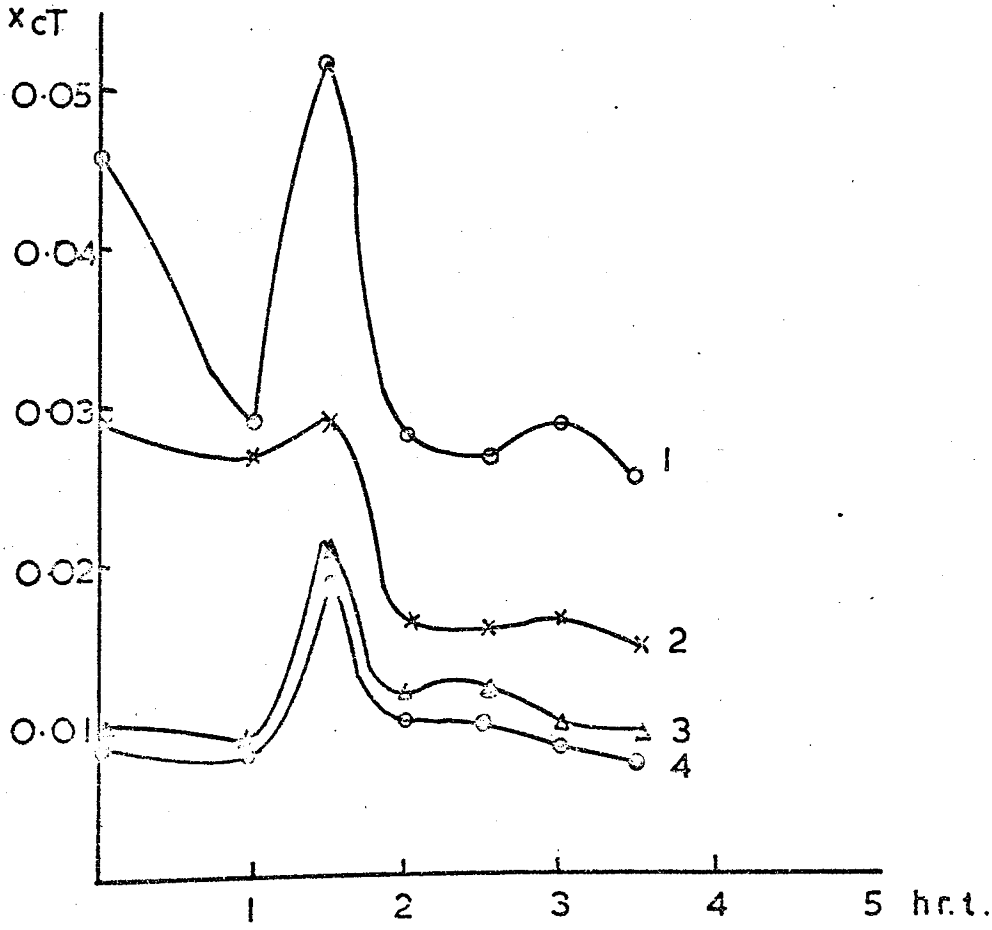


Fig. 7.18 Steady state in the raffinate phase

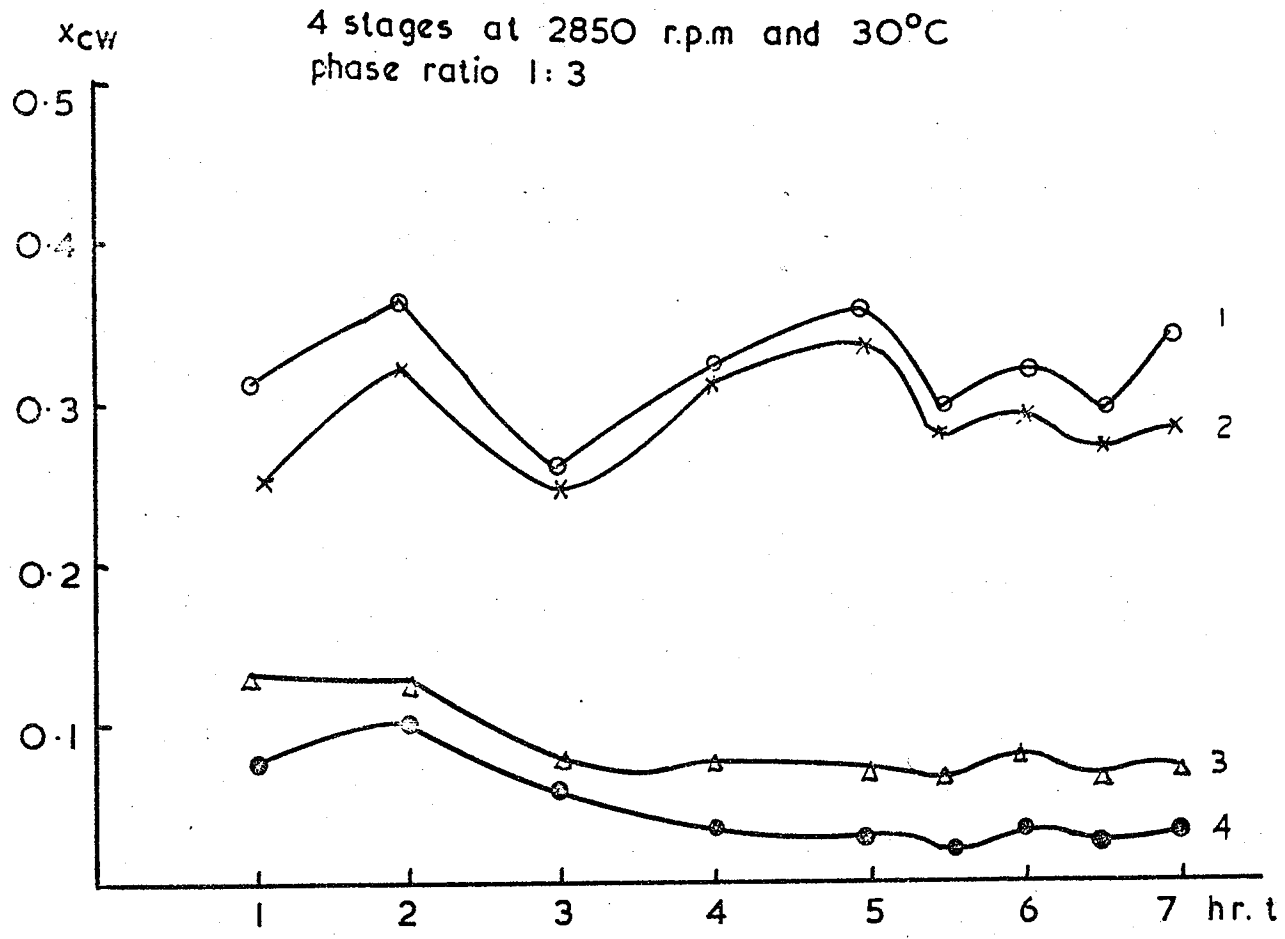


Fig. 7.19 Steady state in the extract phase

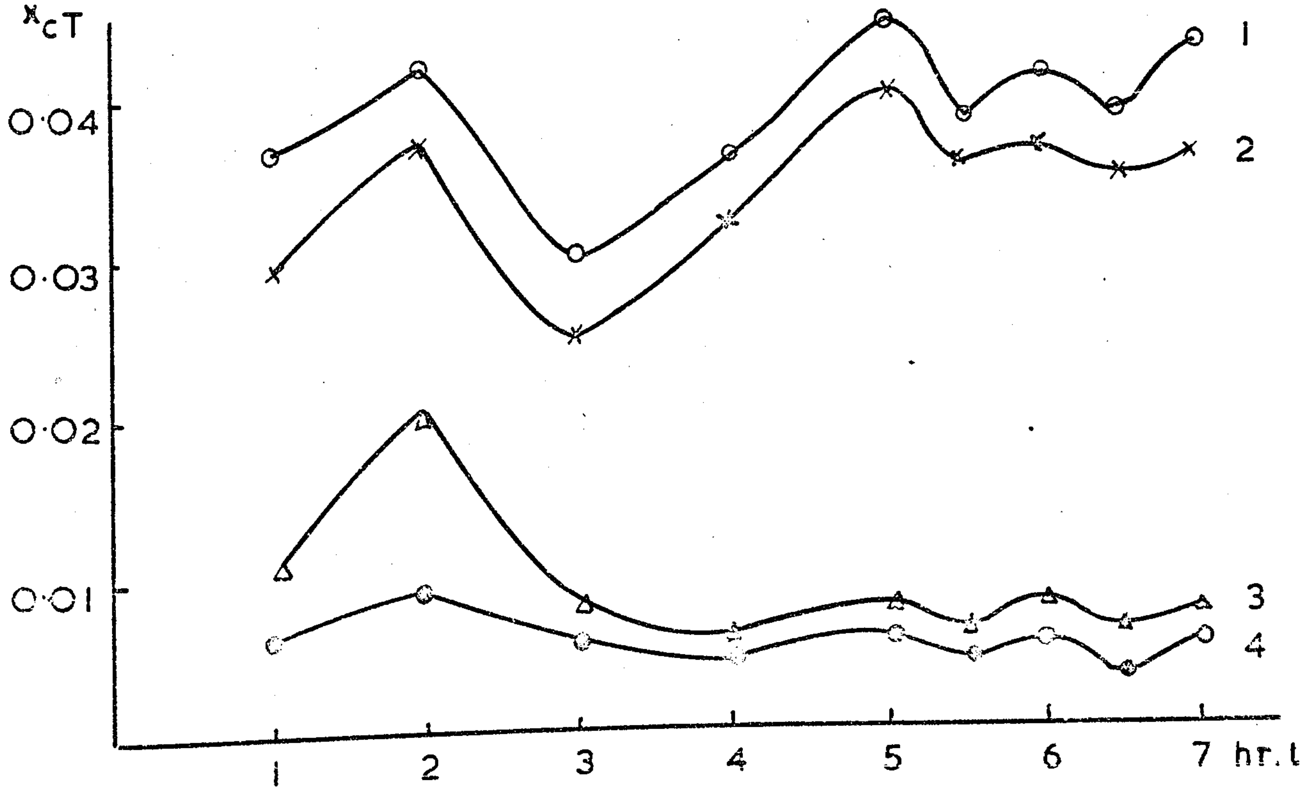


Fig. 7.20 Steady state in the raffinate phase

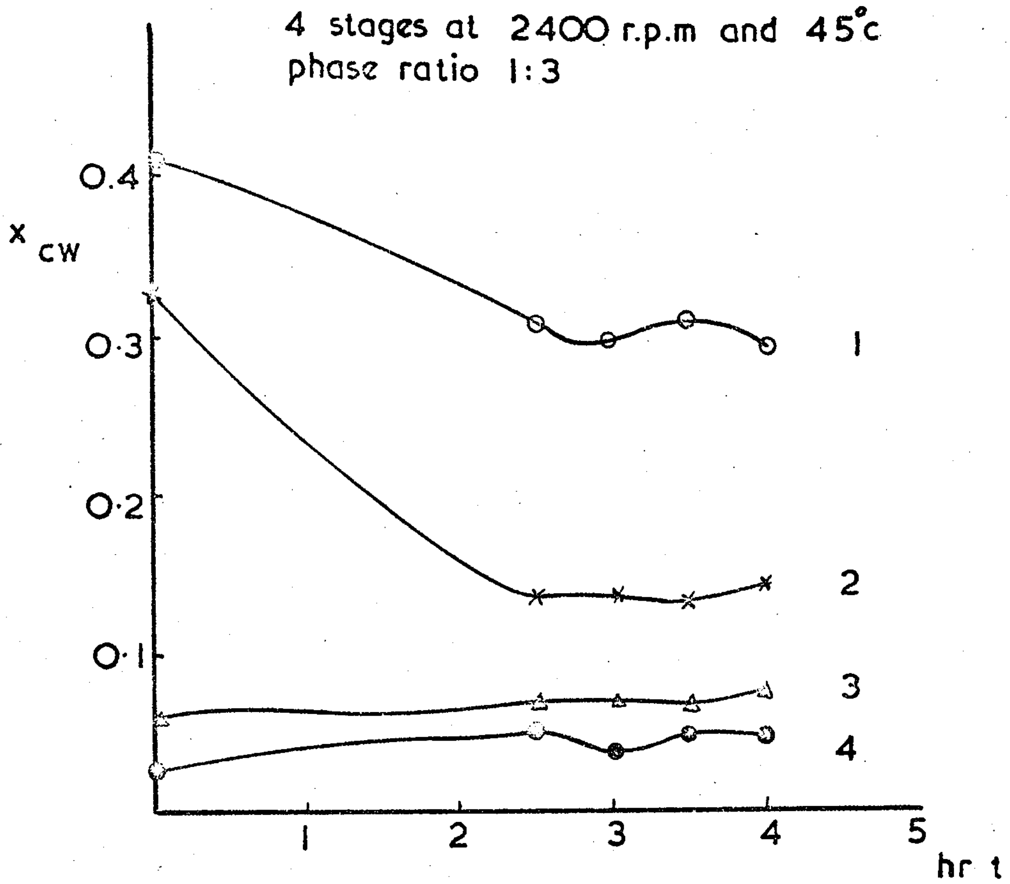


Fig. 7.21 Steady state in the extract phase

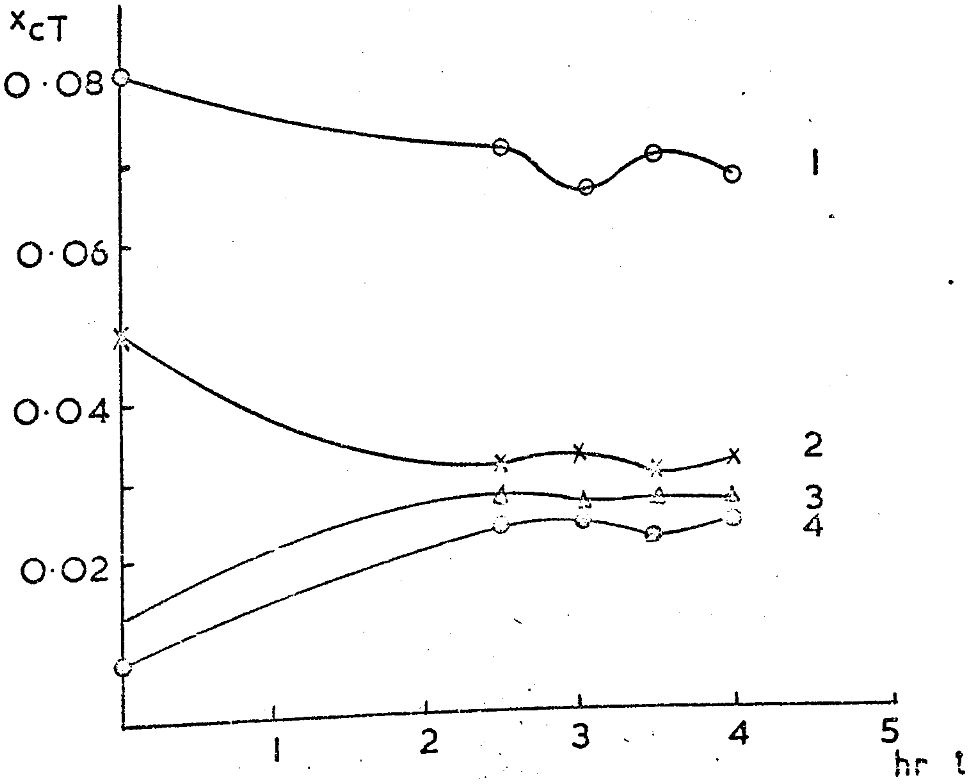


Fig. 7.22 Steady state in the raffinate phase

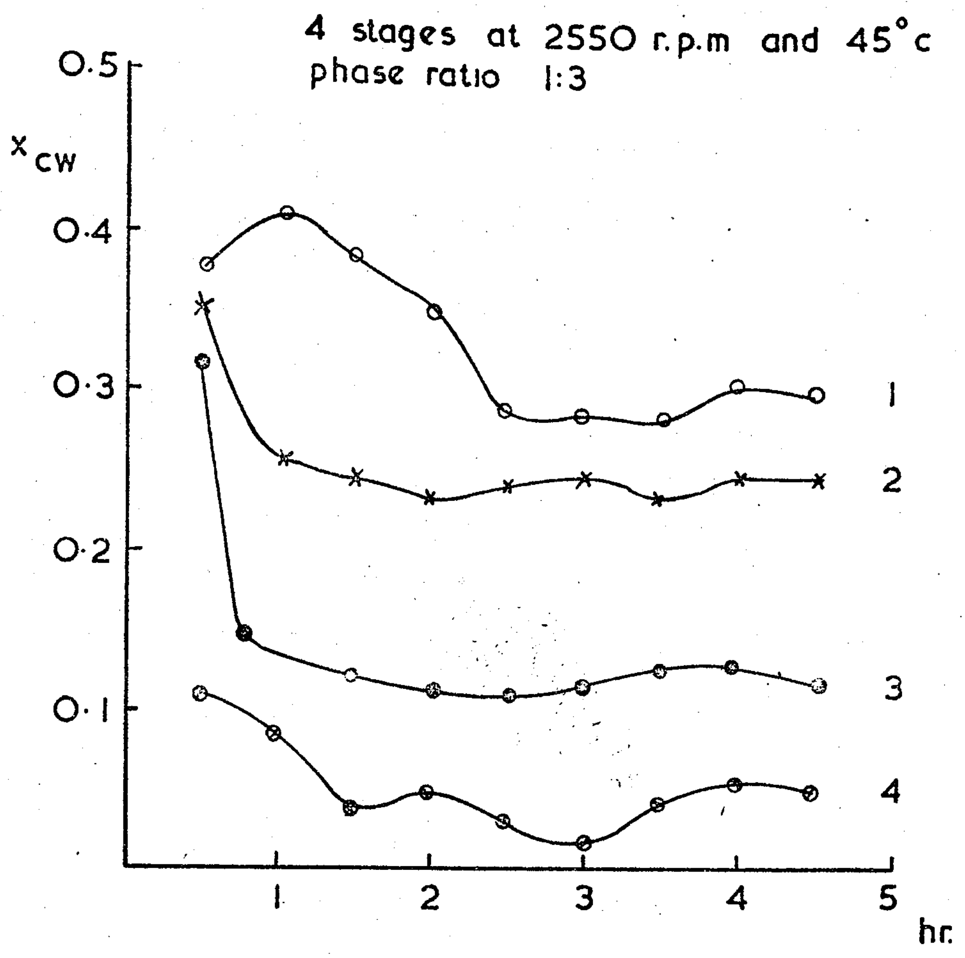


Fig. 7.23 Steady state in the extract phase

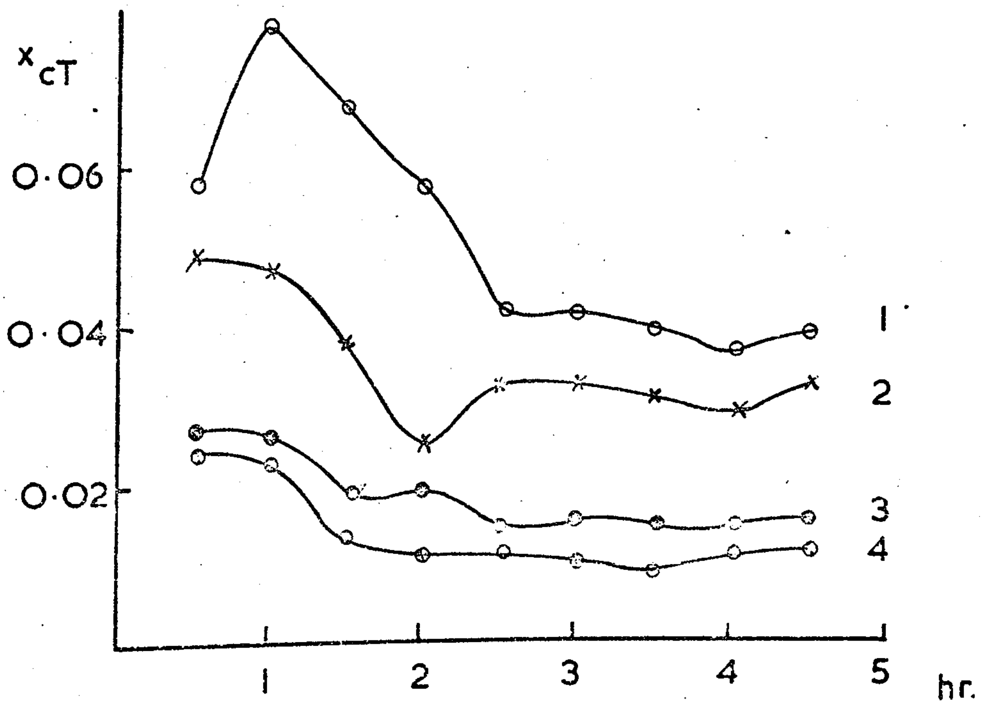


Fig. 7.24. Steady state in the raffinate phase

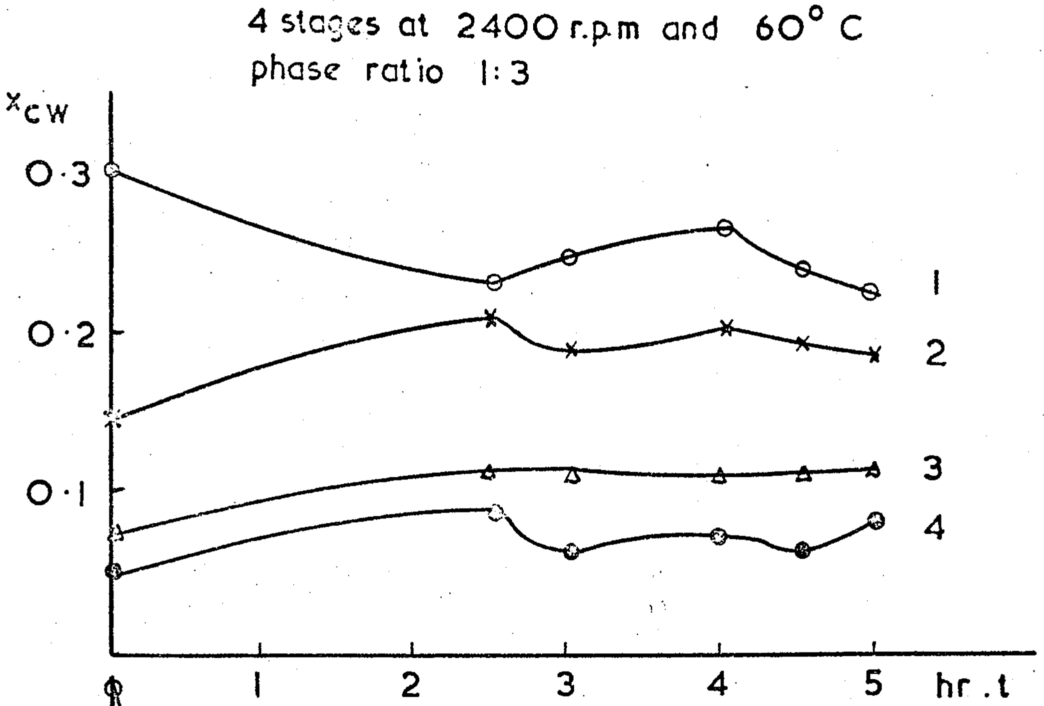


Fig. 7.25 Steady state in extract phase

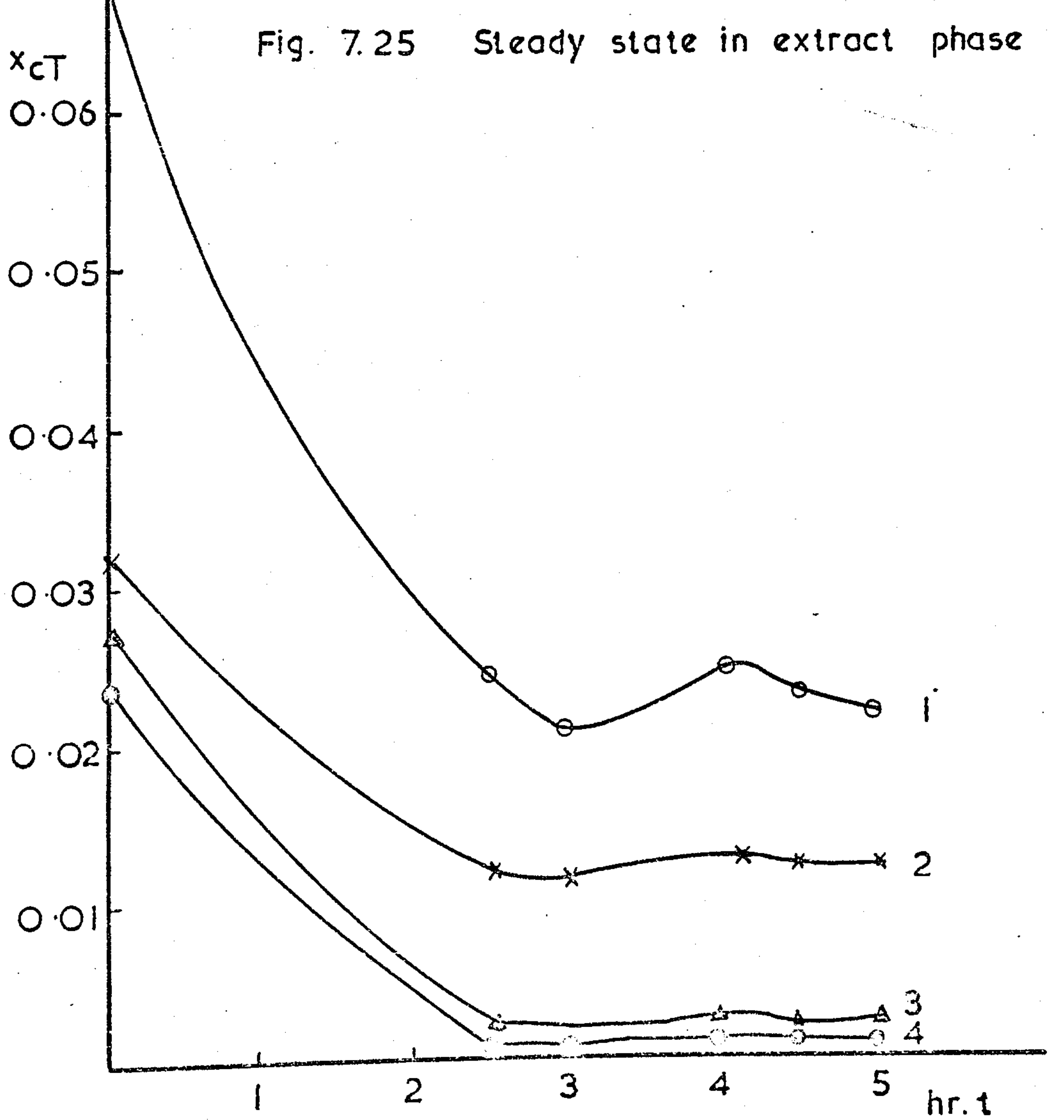


Fig. 7.26 Steady state in the raffinate phase

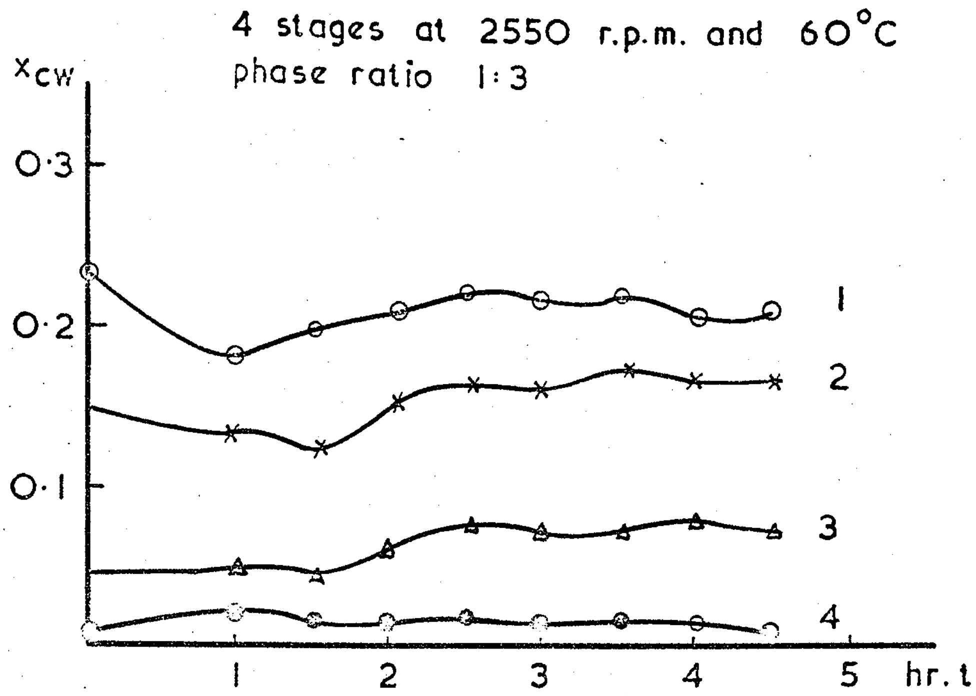


Fig. 7.27. Steady state in the extract phase

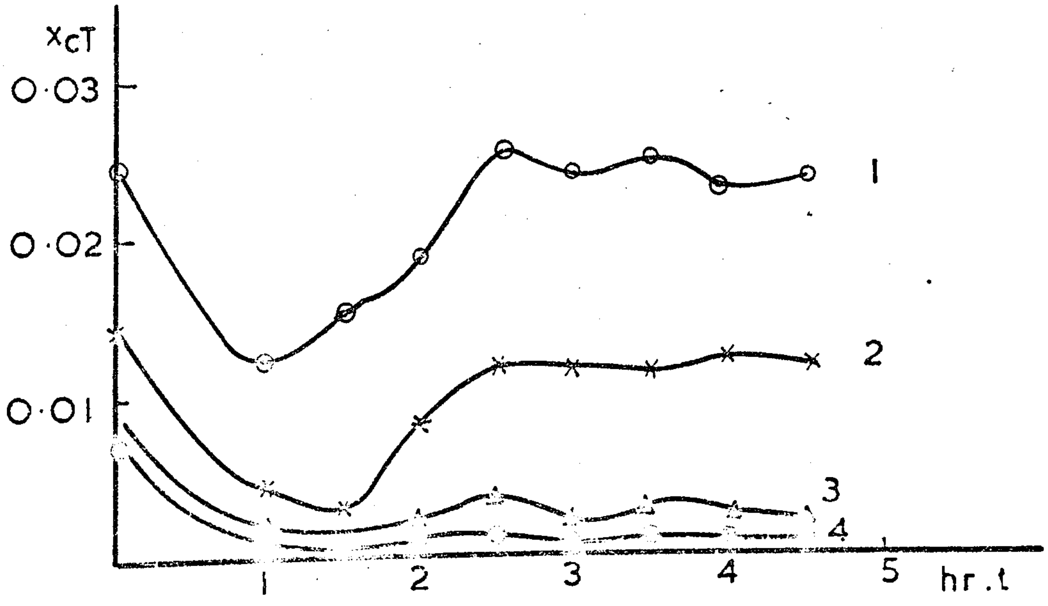


Fig. 7.28 Steady state in the raffinate phase

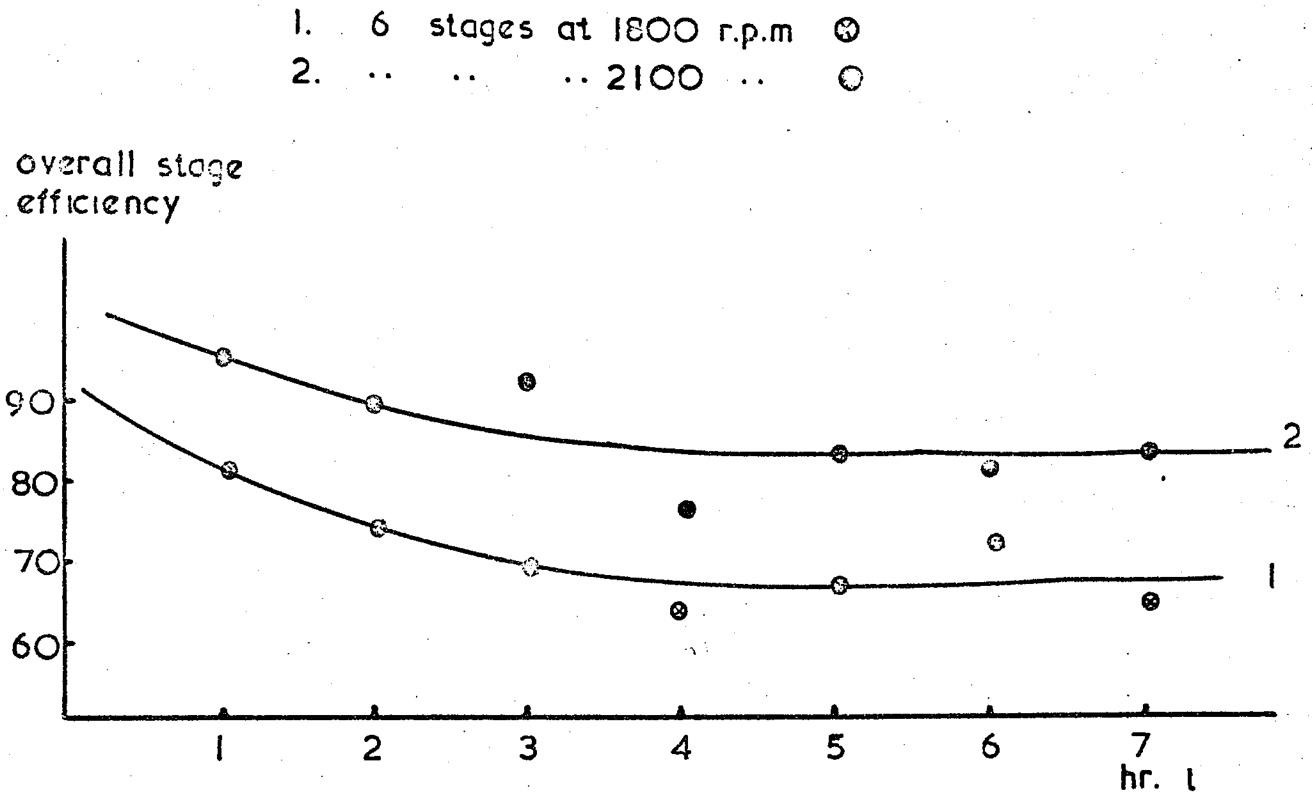


Fig. 7.29. Effect of stage efficiency on time to reach steady state

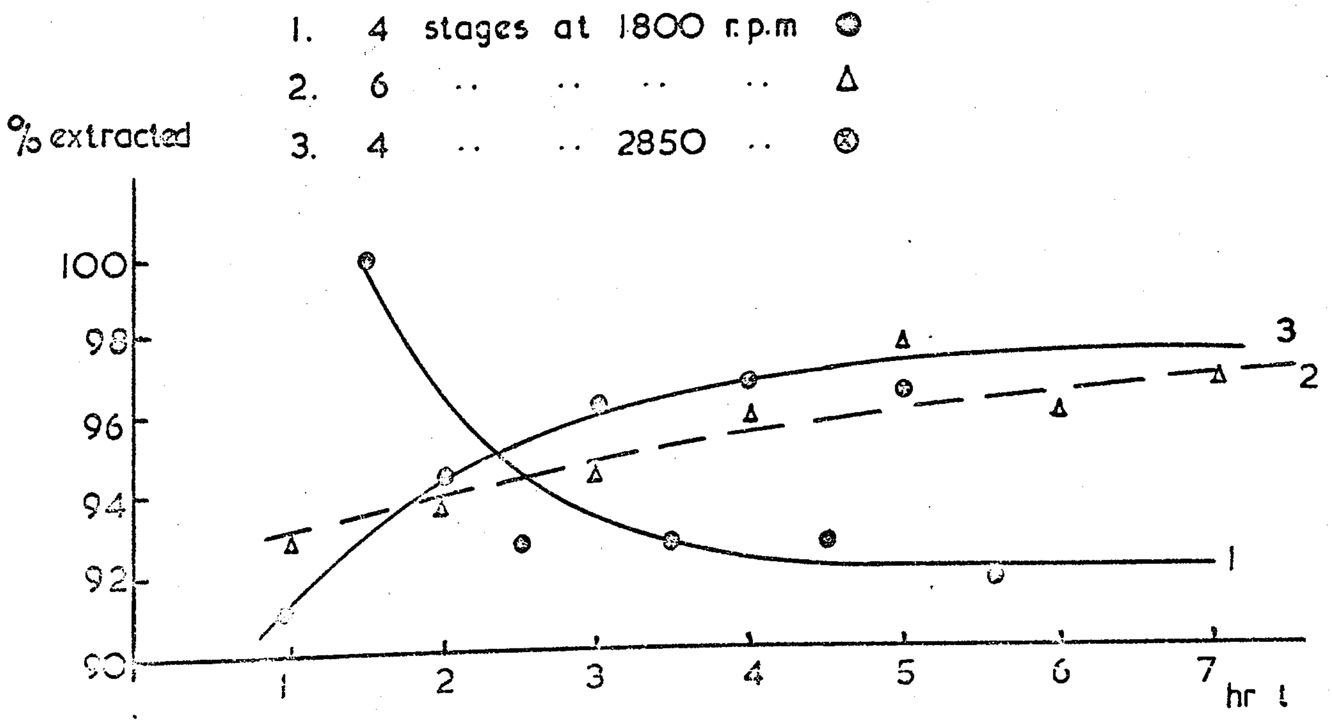


Fig. 7. 30. Effect of percentage extracted on time to steady state

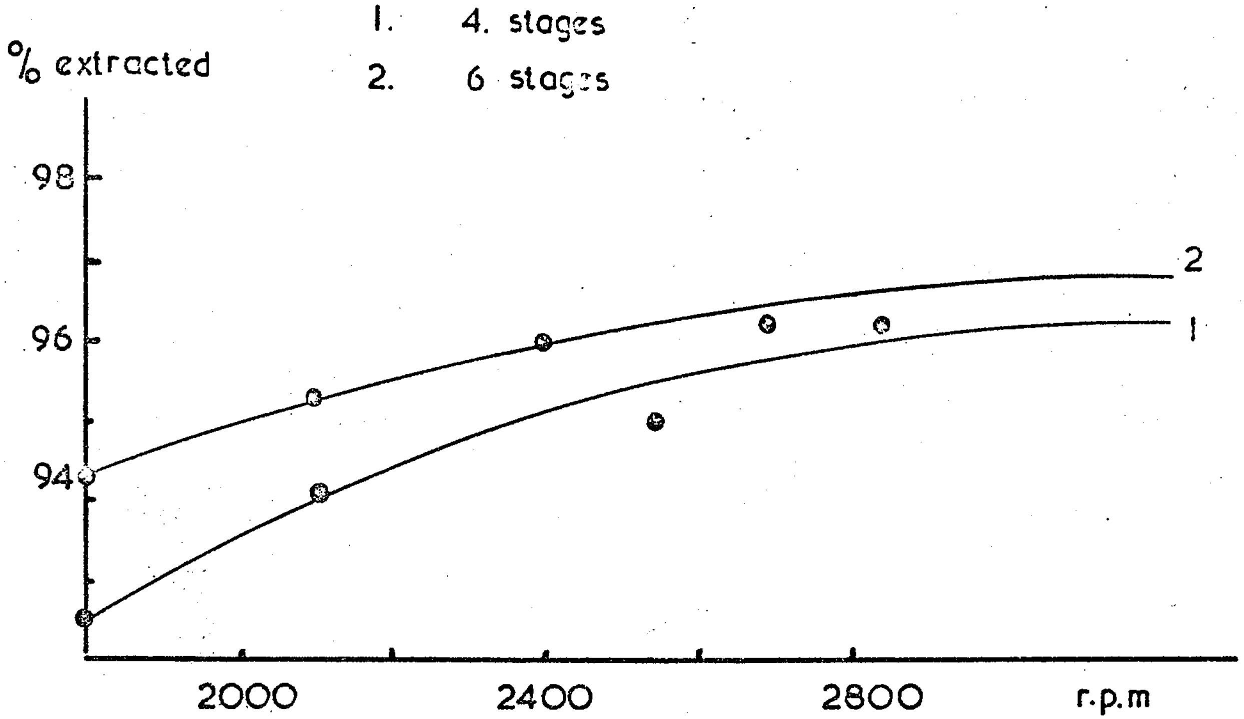


Fig. 7.31 Effect of the impeller speed on the efficiency

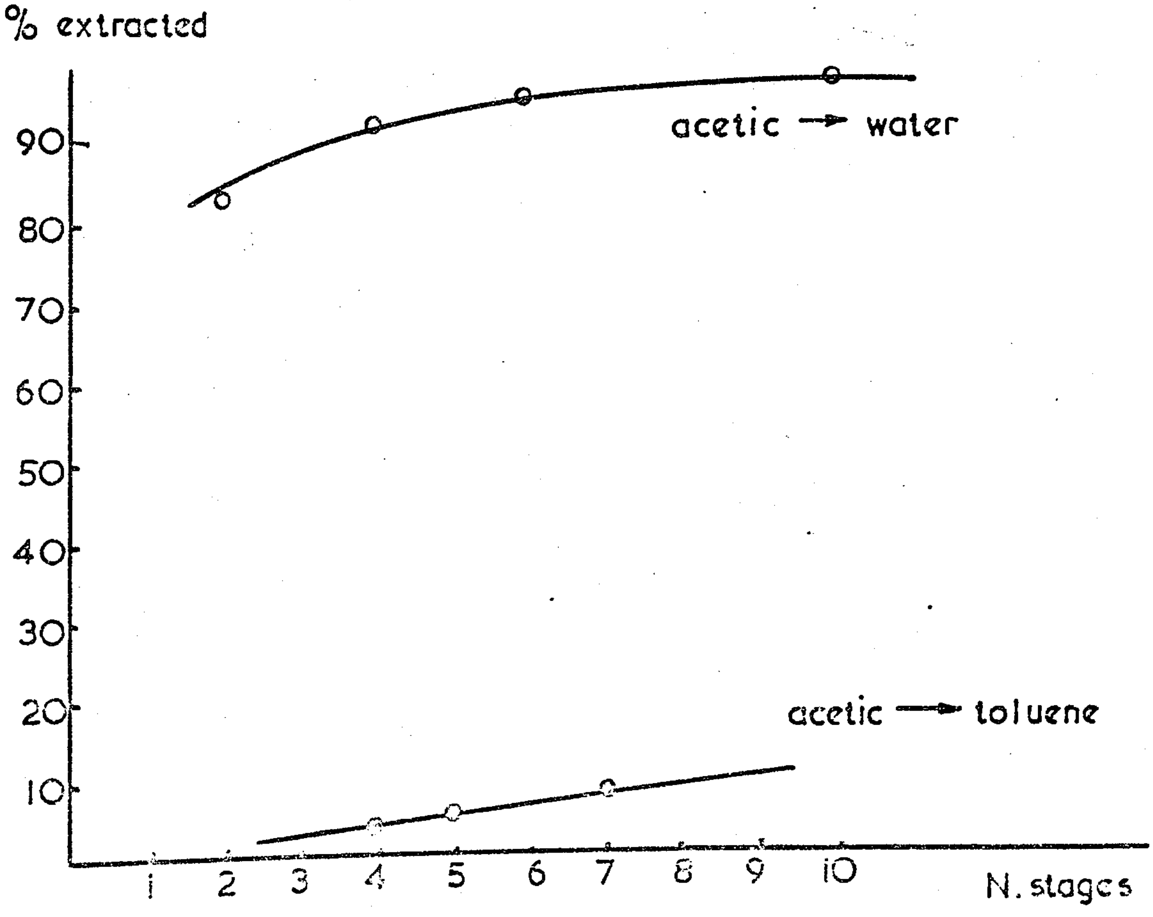
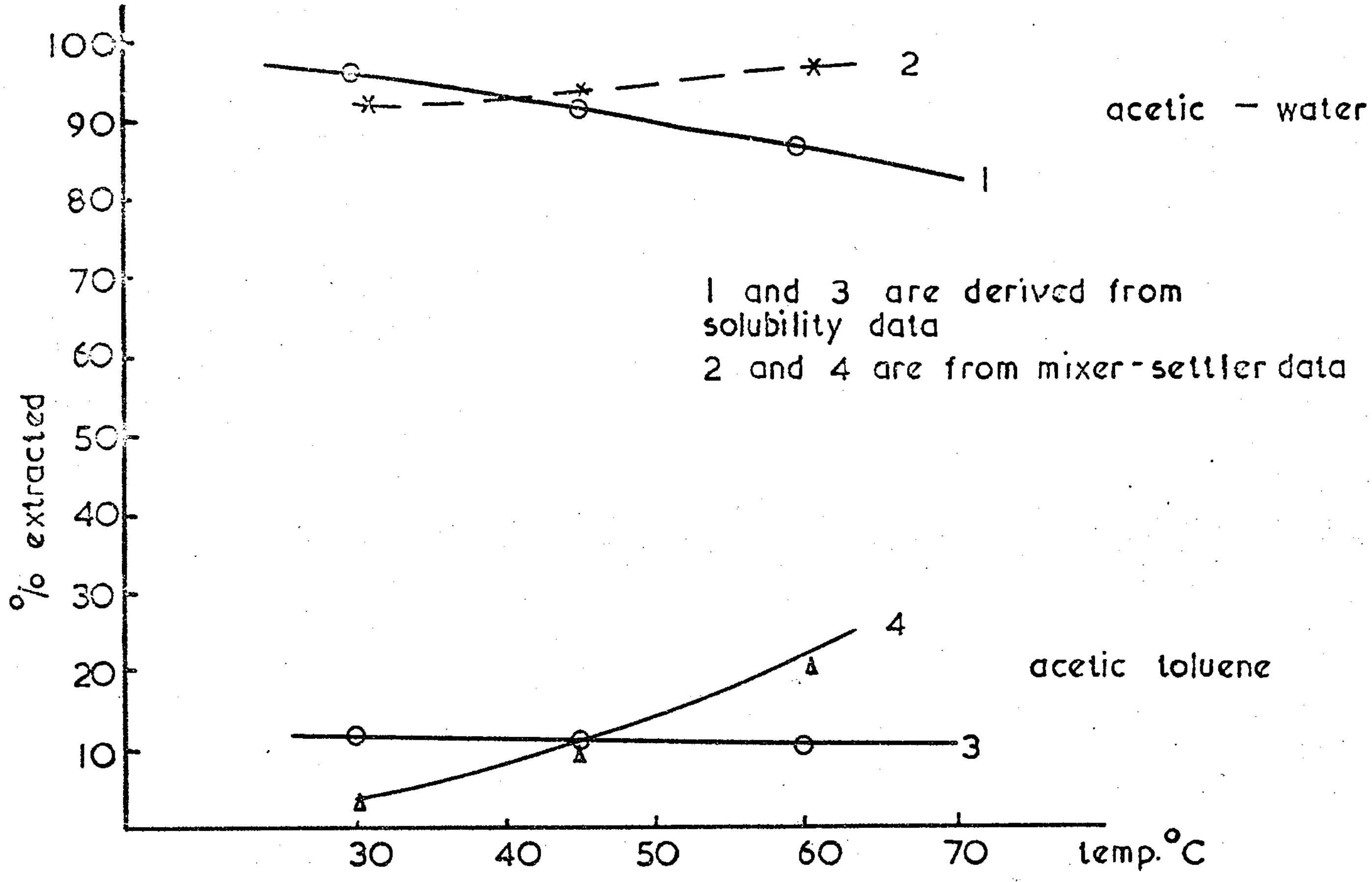


Fig 7.32 Effect of the direction of mass transfer on the efficiency.



1 and 3 are derived from solubility data
2 and 4 are from mixer-settler data

Fig. 7.33 Effect of temperature on the extraction efficiency.

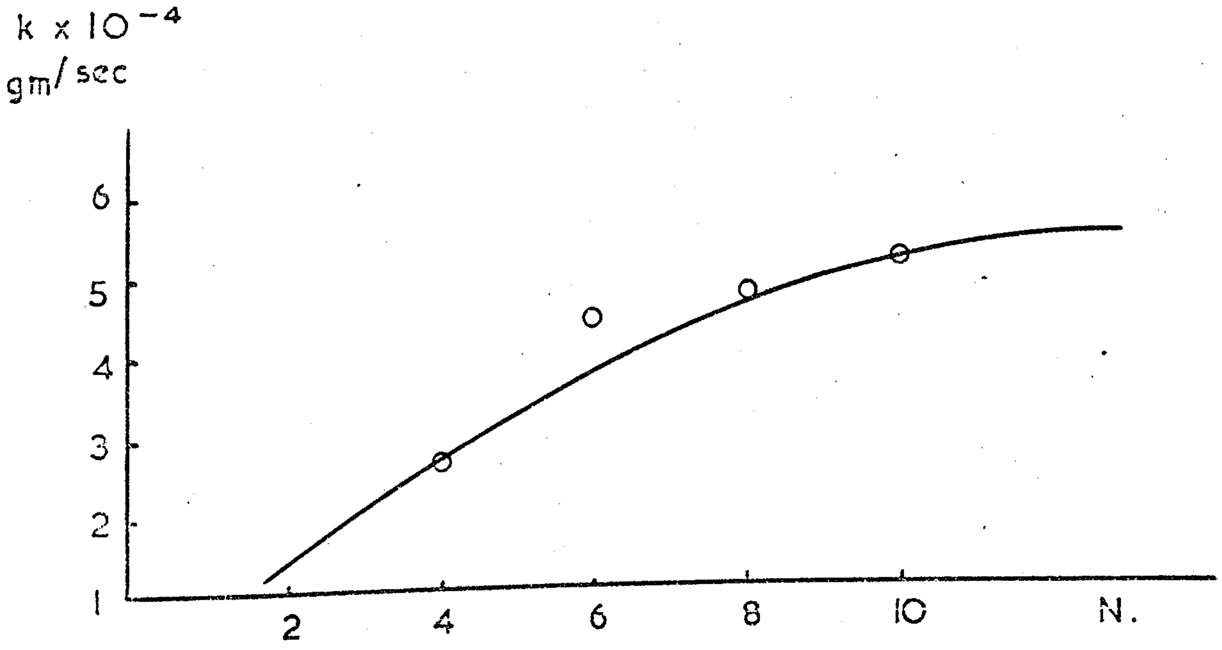


Fig. 7.34 Effect of the number of stages on mass transfer coefficient.

8. Discussion

8.1 The System Acetic Acid-water-toulene

The solubility data of this system was available in literature (46, 146) at different temperatures. However, Dakshinamurty et al (146) introduced two analytical expressions to calculate the binodal curves at any temperature in the range of 10 to 60° C. They claimed good agreement between their experimental and calculated data. Unfortunately on checking their expressions negative values were obtained. Therefore it was decided to determine experimentally the ternary data for this system at different temperatures and to correlate and check these data thermodynamically. Hlavaty's (198) correlation fitted the data extremely well. However, a computer program using trial and error technique, should be developed for calculation of the binodal curve at any temperature (199). Association of the acid introduced pecularities in the physical properties of the system especially the interfacial tension as is shown in figure 6.21. Smyth and Roger (148) observed a similar behaviour in the dielectric constant of acetic acid. They found that the dielectric constant increases with temperature instead of decreasing. They attributed that to the strong molecular association, known to occur in acetic acid. The degree of association of the acid in a liquid or a vapour phase most likely change with concentration and temperature. Many workers (150, 175, 181, 185) reported that correlations for the molecular weight of the acid should be introduced in predicting the solubility data in order to take account of the acid association in the phase under consideration. Marek (181) stated that the failure of the usual correlation methods for such systems may be explained by the use of a constant molecular weight of the associating substance throughout the whole composition range. The use of the NRTL equation to predict the solubility data proved to be extremely good up to concentrations of 55% acid using only association parameters in the vapour phase. The disagreement between the experimental and predicted data at higher concentrations necessitates the use of a suitable association factor for the liquid phase. As a possible start an association factor of 2 in the toluene phase and an association factor given by figure 6.24 may lead to a better agreement in the higher concentrations between the predicted and experimental data. However this is beyond the scope of this investigation and will be recommended for future work.

8.2 The Mixer-settler Performance:

As high as 90% stage efficiency has been achieved by the equipment. However, on the average only about 80% stage efficiency was obtained under the different operating conditions. This may be attributed to the following factors:

(1) Mixing was extremely vigorous so that the mean drop size was of the order of 400 microns (see Appendix IV). Therefore in all probability on a number of occasions the mass transfer was to stagnant drops so that equilibrium was not achieved in spite of the large interfacial area. Furthermore, the small drop size required a considerable time to settle and separate in the settler and it is likely that there was some entrainment of the very small drops, thereby reducing the efficiency. It could be assumed that a settler capacity 2.5 - 3 times that of the mixer would provide sufficient time for such dispersion to separate more efficiently and this would lead to higher stage efficiency.

(2) Back mixing from the mixer to the preceding settler was pronounced, especially when large phase ratios were used. It is recommended here that, in future the optimization technique using the discrete maximum principle developed in section 4 be applied before operating the equipment in order to ascertain the optimum number of stages with the associating optimum phase ratio. It has been confirmed experimentally in this study that at such phase

ratios, back mixing was minimum.

(3) Although agitation rate in each stage was the same, the control of the speed was not very good, especially at speeds lower than 2000 rpm. The variations in the speed of agitation brought about surges in the flow to and from the system and also in the flow rates between the stages. This can be detected in the concentration profiles in figures 7.1 to 7.28. In addition deviations of the speed of agitation from the preset value also led to entrainment and back mixing. Since speeds higher than the controlled value caused more heavy phase to be drawn in to the mixer bringing about entrainment of the toluene phase in the water phase. Variation in the speed of agitation may be reduced considerably by using a feed back control system.

In conclusion it may be stated that if the above modifications were introduced this mixer-settler equipment could prove to be a very highly efficient and suitable laboratory extractor, since it contains a temperature control facility which is very desirable in most liquid-extraction studies.

8.3 Time for the Mixer-settler to Reach Steady State:

In spite of the difficulties described in Section 8.2 it is clear from the concentration profiles in figures 7.1 to 7.28 that the pattern of the approach to steady state has been confirmed experimentally. The intermediate stages reach steady state in a shorter time than the end stages thereby confirming the model which predicted that the solvent entry stage is the last to acquire steady state. Some abnormalities may be shown in Table 7.1. This table shows that in some cases the solvent entry stage is not the last to reach steady state. However, since the solute concentration in this stage is usually smaller than that in the other stages, changes of the concentration with time in the solvent entry stage may not be pronounced. Accordingly, for practical determination of time to reach steady state, it is recommended that samples are taken from the feed stage to assess this time.

Not all the factors affecting the time for the countercurrent contactor to reach steady state, which were referred to in section 4, were tested experimentally. The factors tested ; the distribution coefficient; the number of stages, the position of the stage in an N-stage contactor and the efficiency as a function of the speed of agitation showed that the model is fairly representative to the behaviour of such equipment. However, the liquid system used may offer some difficulties in applying this model when the distribution coefficient cannot be easily linearized. This was the case for the acetic acid-toluene-water system where the time for the contactor to reach steady state only agreed with the following relation

$$t_p = 2.5\ t \qquad 8.1$$

and not with the relationship 4.13. Additional study must be done with other systems to confirm relation 4.13 or 8.1. However, since this mixer-settler is relatively very small and the disturbances were many, as discussed above, it could be assumed that the steady state conditions might have been reached faster in the absence of these disturbances. This could only be confirmed if these disturbances are removed or if other types of mixer-settlers are tried to check whether relation 4.13 or 8.1 is actually determining the time for a countercurrent extractor to reach steady state conditions.

8.4 Effect of the Speed of Agitation on the Efficiency:

The extraction efficiency increased exponentially with the speed of agitation as shown in Fig. 7.31. Taking into consideration the relationship between agitation speed and drop size it follows from Kolmogoroff's law (148) that since as, the speed of agitation increases the drop size decreases with a consequent increase in the interfacial area but the mass transfer coefficient may still remain in the circulating and oscillating drop model range. In addition the increase in the speed of agitation may also increase the driving force so that the net result will be an overall increase in the mass transfer rate and therefore an increase in the efficiency. Continued increase in agitation speed results in a certain speed being attained at which the driving force becomes constant but the drop size will decrease to that of the smallest spherical drop bringing about a constant mass transfer coefficient determined by the stagnant drop model. Increasing the agitation speed beyond these limits may not have any effect on these values of mass transfer coefficient, interfacial area and driving force, and hence the efficiency remains constant. Fig. 7.31 shows that contactors with different number of stages have different maximum agitation speed at which the maximum efficiency is attained. This value, however, depends on the contactor and the physical properties of the liquid systems.

8.5 Effect of Temperature on the Extraction Efficiency:

The solubility data determined in section 6 for the water-acetic acid-toluene system indicated that as the temperature increases, solubility of the acetic acid in both phases increases, but the distribution coefficient decreases. This suggests that carrying out the extraction of this system at low temperatures would give higher efficiencies, but figure 7.33 shows that extraction efficiency increases appreciably by rising temperature. Valentas and Amundson (140) reported an increase of 50% in the drop size due to a twofold increase in the coalescence efficiency over a range of temperature from 30 to 70° C for the system they used. The acetic acid-toluene-water system is known to be abnormal and undergoes association and dissociation to different degrees at certain concentrations and temperatures, and since figure 6.21 shows that in the acetic acid concentration range between 0.1 and 0.4 raising the temperature from 25 to 50° C leads to an increase in the interfacial tension of about 8.8%. Therefore the coalescence rate would be expected to increase with rising temperature. It follows that the mass transfer rate could also increase through increase in the drop size and inception of circulation and oscillation.

The actual performance of the mixer-settler showed also that the higher the temperature the better the liquid flow and consequently the lower the back mixing and entrainment.

8.6 Effect of Temperature Profile on the Extraction Efficiency:

The phase equilibrium data predicted an increase in extraction efficiency if a temperature gradient was applied in which the feed end should be at the higher temperature. Table 7.2 shows that application of a temperature gradient on the mixer-settler equipment would not give a better efficiency and that isothermal conditions, especially at high temperature are preferable. This may be attributed to the pecularities in the water-acetic acid-toluene system. Since, as discussed above, the interfacial tension is relatively sensitive to changes in temperatures, instituting different temperatures in different stages in the process may lead to different drop sizes and coalescence rates which may lead to lower efficiencies.

Optimization of the mixer-settler process by the discrete maximum principle showed that application of a temperature profile may be profitable for a small number of stages (less than 5) but that generally it was more profitable to operate isothermally at low temperature conditions. It should be borne in mind that this optimization technique used the data produced from the solubility data. Accordingly, the distribution coefficient correlation 6.7 suggests that the distribution coefficient increases as the temperature decreases and hence higher extraction efficiencies will be attained at lower temperatures. The optimization technique did not take into account the effects of temperature on the drop size and mass transfer coefficient and hence on the efficiency. However, an increase of 7% in extraction efficiency when the process was operated at 60° C may be offset by the costs of heating/cooling units, consumption of electricity and by the necessity of providing the mixer-settler with jackets. Therefore it is possible that this optimization technique has given the appropriate answer of operating the mixer-settler at ambient. However, for more accurate results the optimization program would have been provided with the additional information of the effect of temperature on drop size and mass transfer coefficient which would be associated with the distribution coefficient in the form

$$m_n = f(x_n, T_n, k_n) \qquad 8.2$$

8.7 The Discrete Maximum Principle Technique:

Beveridge and Schechter (206) stated that it is important to note that the modified objective function (the Hamiltonian in the maximum principle) cannot be tested in the usual way to determine if the stationary point is a maximum or a minimum. This, incidentally, is a point missed in most applications of the discrete maximum principle, where it is falsely asserted that sufficiency conditions can be used to test the Hamiltonian function. The success of the method of Lagrangian multipliers is, basically, attributable to the fact that Δx_n vanishes for all displacements of interest. However, there is no reason to suppose that $\Delta^2 x_n$ will vanish even if Δx_n does. Therefore, while ΔH is entirely equivalent to ΔP, it is not possible to assert that $\Delta^2 H$ equal $\Delta^2 P$. Since $\Delta^2 P$ is to be investigated in the region of the stationary point, the original objective function P, and not the fictitious one, H, must be considered in determining the character of the restricted objective function. It is generally true that the modified function H can be used only to determine possible locations of any optimum, and the task remains to ensure that it is an optimum. The technique used here took this point into consideration by feeding the data obtained for the location of a possible optimum into the original objective, and then taking the values which gave the maximum profit to be the optimum values.

It is also a usual practice to linearize the distribution coefficient function in order to avoid difficulties arising in the computation process (170). However, in this work, the distribution coefficient correlation 6.7 has been used in the optimization technique without linearization.

Considering the previous points, together with the fact that the results obtained experimentally, largely confirmed the data predicted by applying this technique while totally rejecting the data predicted by the classical optimization technique presented in section 4.3, it could be said that the discrete maximum principle offers a very powerful technique for optimizing a counter current extraction process giving in advance an accurate prediction about the optimum operating conditions.

8.8 Optimum Operating Conditions:

The classical optimizing technique presented in section 4.3 would give an optimum number of stages of 7 if the phase ratio was 1:3 as calculated by the correlation 4.25. If the number of stages used was 4 the optimum phase ratio would be 1:1. The discrete maximum principle showed that for a maximum profit to be obtained only 4 stages of the mixer-settler are required with a phase ratio of 1:3 under the optimum operating conditions. The technique also provided the feed and solvent rates to be used under such conditions. Experimentation confirmed that operating 4 stages with a phase ratio of 1:3 was the most suitable while higher phase ratios brought about flooding of the contactor, back mixing and entrainment also took place with a substantial loss in the efficiency of the extractor. Alternatively, operation at lower phase ratios would be uneconomical. Experiments with 7 stages were undertaken with different phase ratios and the experimental optimum was found to be 1:5. For 10 stages it was 1:6.5 as had been predicted by the discrete maximum principle technique.

9. Conclusion

This work is an attempt to construct a laboratory mixer-settler suitable for advanced studies in liquid-liquid extraction. The main conclusions are summarized as follows:

(1) Different design and physical properties factors affect the time required for a mixer-settler to come to steady state. Further studies on the same mixer-settler and other types of mixer-settlers with different systems should be carried out to draw a more general conclusion whether the correlation proposed suitably fits most countercurrent extraction processes.

(2) Association and dissociation of acetic acid highly influence the physical properties and the solubility data of the system. It was found to be a function of concentration and temperature in the water phase but was approximately constant in the toluene phase.

(3) Extraction of acetic acid by water from toluene is highly efficient. As high as 99% of acetic acid could be extracted from toluene by water. However, extraction of the acid by toluene from water may need a large number of stages and high temperature to get a reasonable extraction efficiency.

(4) Phase equilibrium data is not reliable to predict the

operating conditions of a contactor since many other factors affect performance, vis: speed of agitation, mass transfer coefficient, interfacial tension, ... etc., which can only be provided by the actual experiment on the extraction equipment.

(5) Temperature is a prosolvent in extraction of acetic acid from water or toluene but a temperature profile appeared to be an anti solvent in the same process. Therefore isothermal extraction of acetic acid is recommended.

(6) The discrete maximum principle proved to be a very powerful technique in optimizing a countercurrent extraction process. It is capable of providing the optimum operating conditions required in the feasibility study stage.

10. Recommendations for Further Work

(1) Studies were initiated to confirm the model to predict the time required to reach steady state by studying the effect of relevant factors on that time. Some other factors remain to be studied; such as: the mixer capacity and the dispersed phase holdup using other types of systems.

(2) The settlers could be replaced by larger settlers of 2.5 - 3 times the mixer capacity to allow for better settling, thereby attaining higher efficiencies.

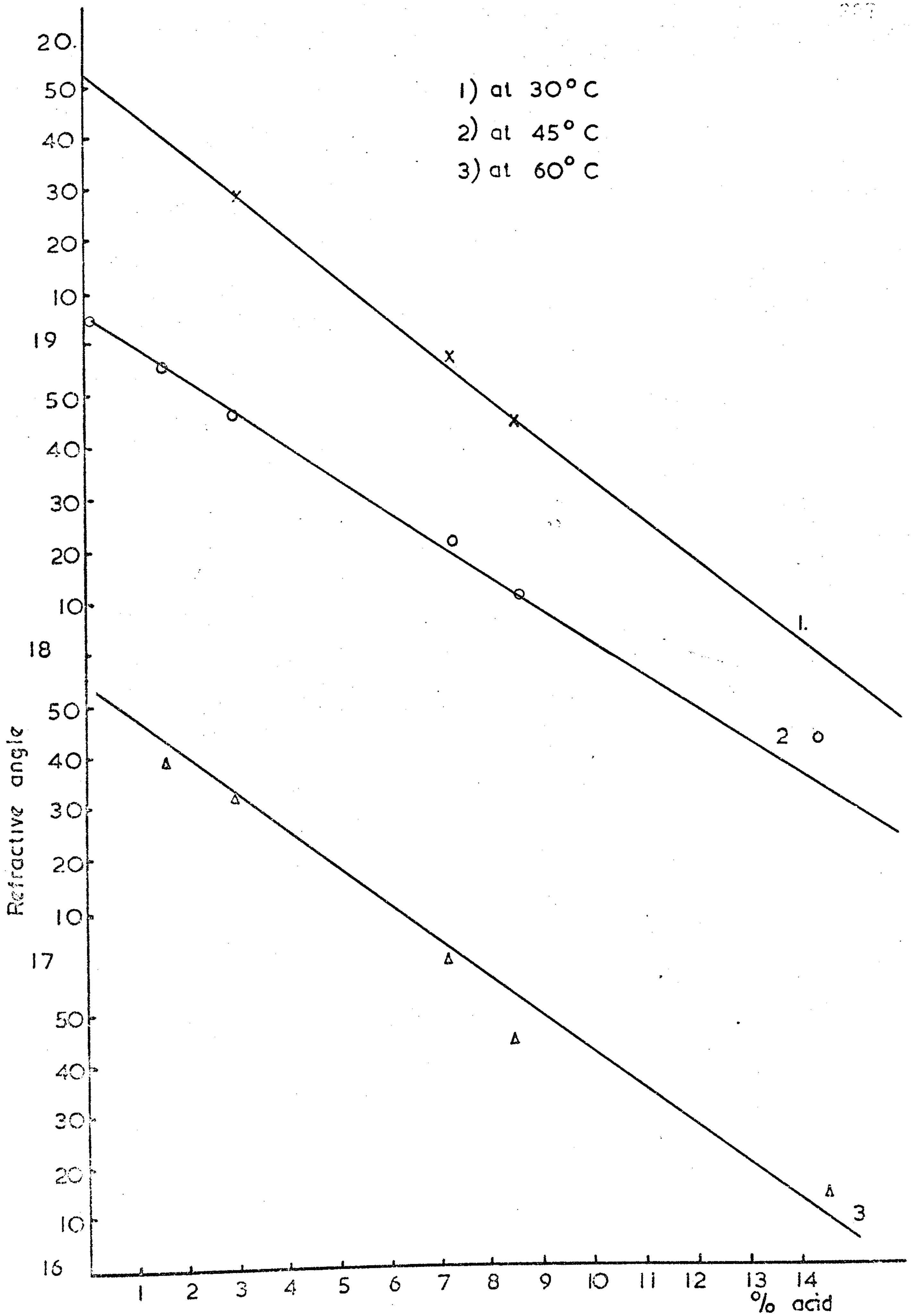
(3) Association and dissociation of acetic acid in liquid phases should be further studied at different concentrations and temperatures. Such study would provide for better prediction of acetic acid solubility data.

(4) The discrete maximum principle optimization technique should be used for other systems where the distribution coefficient can be correlated as

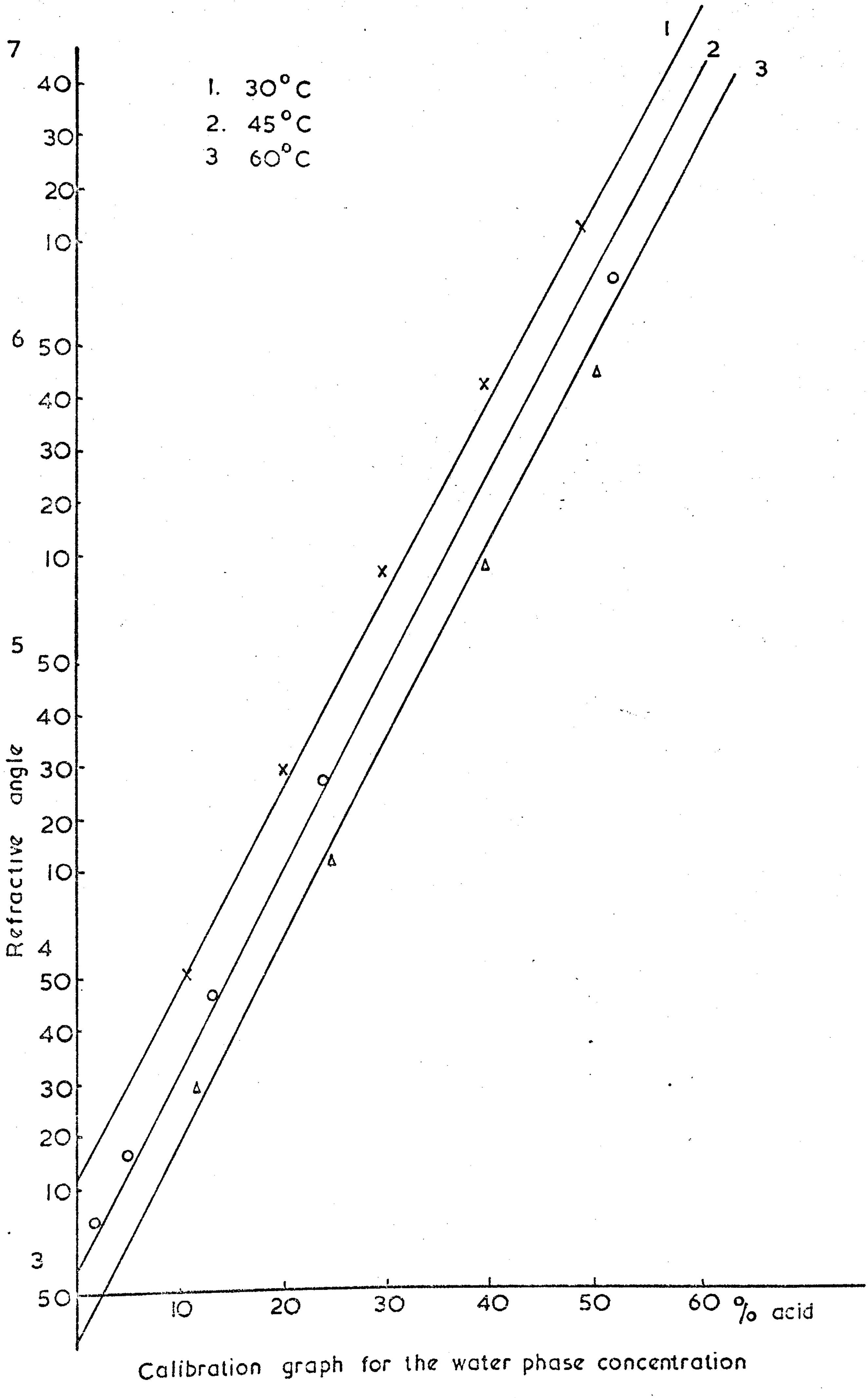
$$m = k . x^a . T^b$$

in order to investigate the effect of the physical properties parameter; k and exponents a and b on the optimum operating conditions.

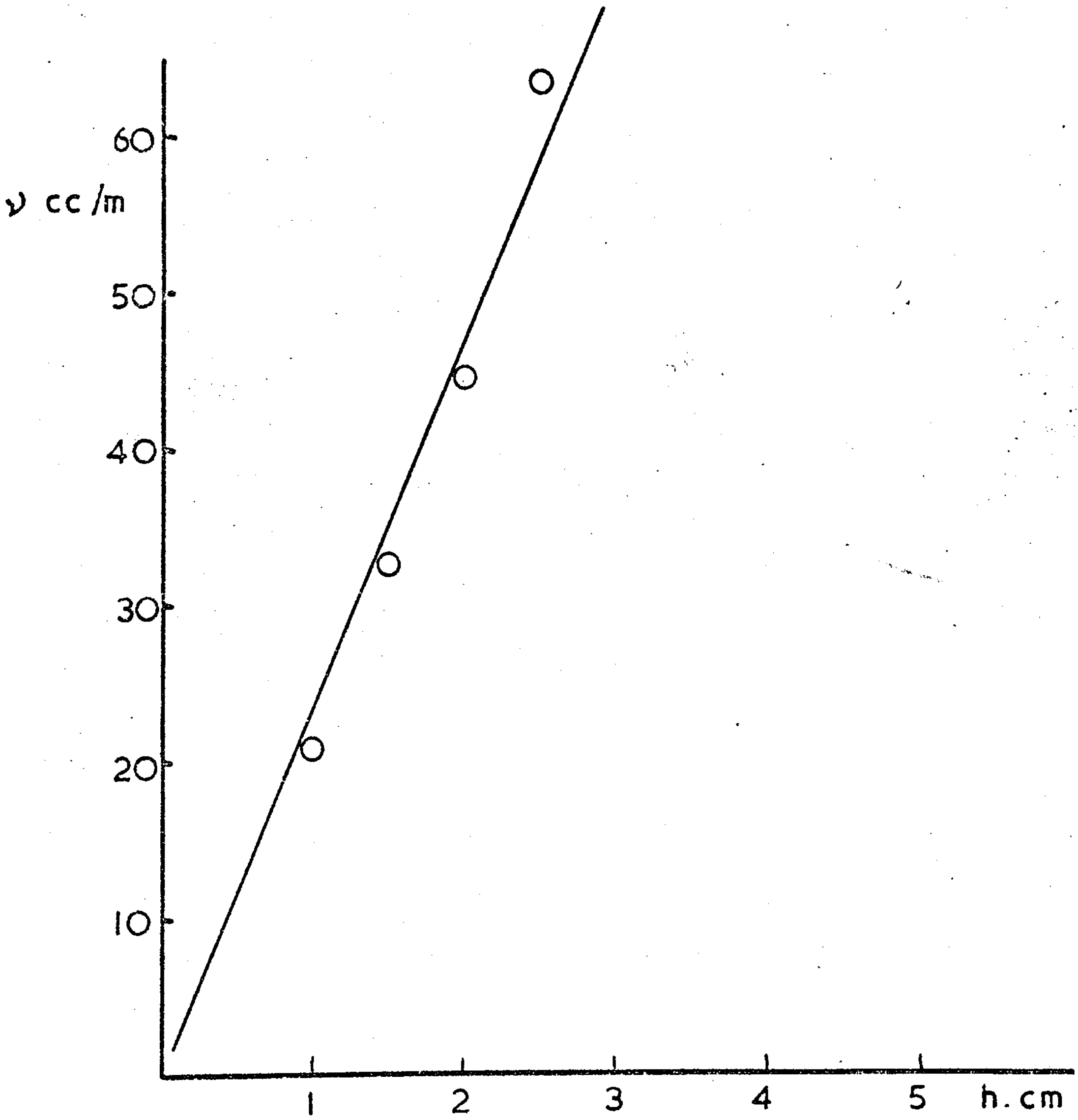
APPENDIX I



Calibration graph for the toluene phase concentration.



Calibration graph for the water phase concentration



Calibration graph for the toluene phase flowmeter at 15% acid concentration

```
5  PRINT " DIFF.OF A.-W.AT DIFF.CONC."
10  DIM A(20),G(20),S(20),T(20),U(20)
15  FOR I=1,14
20  READ A(I),G(I)
30  S(I)=G(I)*((.16094E-06)*A(I)+(.431672E-07)*(1-A(I)))
50  PRINT I;A(I);S(I)
55  NEXT I
60  I=1
70  FOR J=1,8
80  READ T(J),U(J)
90  D(J)=S(I)*T(J)/U(J)
100  PRINT I;J;T(J),U(J),D(J)
110  NEXT J
120  STOP
130  DATA .78329E-02,.892,.163934E-01,.894,.25738E-01,.897
140  DATA .361446E-01,.904,.476191E-01,.914,.604027E-01,.919
150  DATA .747331E-01,.913,.104714,.91,.123368,.91
160  DATA .171429,.915,.201835,.911,.236842,.91
170  DATA .27758,.913,.325581,.908
180  DATA 278,1.41,286,1.2,294,1.01,303,.856,312,.723,322,.61
185  DATA 333,.52,345,.44
190  DATA 278,1.46,286,1.26,294,1.08,303,.93,312,.8,322,.69
195  DATA 333,.59,345,.51
200  DATA 278,1.495,286,1.3,294,1.19,303,1,312,.872
205  DATA 322,.762,333,.67,345,.585
210  DATA 278,1.55,286,1.37,294,1.21,303,1.07,312,.945,322,.84
215  DATA 333,.74,345,.657
220  DATA 278,1.56,286,1.41,294,1.22,303,1.145,312,1.035
225  DATA 322,.93,333,.84,345,.758
230  DATA 278,1.64,286,1.48,294,1.34,303,1.215,312,1.1
335  DATA 322,1,333,.9,345,.82
340  DATA 278,1.7,286,1.55,294,1.42,303,1.3,312,1.19
345  DATA 322,1.09,333,.998,345,.91
350  DATA 278,1.82,286,1.67,294,1.55,303,1.43,312,1.33
355  DATA 322,1.23,333,1.13,345,1.05
360  DATA 278,1.9,286,1.75,294,1.63,303,1.5,312,1.37
365  DATA 322,1.27,333,1.17,345,1.08
370  DATA 278,1.93,286,1.82,294,1.71,303,1.61,312,1.53
375  DATA 322,1.44,333,1.35,345,1.28
```

```
5  PRINT " DIFFUSIVITIES OF ACETIC ACID IN TOLUENE AT DIFFERENT CONC."
16  DIM X(20),G(20),A(20),S(20),T(20),U(20)
18  FOR I=1,14
20  READ X(I),G(I)
30  A(I)=(X(I)/120)/((X(I)/120)+((100-X(I))/92))
40  S(I)=G(I)*((.430645E-07)*A(I)+(.473225E-07)*(1-A(I)))
50  PRINT I,X(I),A(I),S(I)
55  NEXT I
60  I=1
70  FOR J=1,8
80  READ T(J),U(J)
90  D(J)=S(I)*T(J)/U(J)
100  PRINT I;J;T(J),U(J),D(J)
110  NEXT J
120  STOP
130  DATA 5,.554,10,.566,15,.574,20,.58,25,.596,30,.611,35,.629
140  DATA 40,.645,45,.667,50,.686,55,.713,60,.75,65,.804,70,.75
150  DATA 273,.735,286,.66,294,.59,303,.53
160  DATA 312,.475,322,.425,333,.38,345,.34
170  DATA 273,.79,286,.7,294,.621,303,.552
180  DATA 312,.49,322,.435,333,.385,345,.345
190  DATA 273,.845,286,.74,294,.65,303,.574
200  DATA 312,.5,322,.44,333,.385,345,.333
210  DATA 273,.925,286,.8,294,.69,303,.595
220  DATA 312,.518,322,.422,333,.38,345,.33
230  DATA 273,1,286,.85,294,.725,303,.62
240  DATA 312,.53,322,.45,333,.382,345,.328
250  DATA 273,1.07,286,.91,294,.77,303,.64
260  DATA 312,.545,322,.46,333,.335,345,.328
270  DATA 273,1.11,286,.94,294,.79,303,.666
280  DATA 312,.56,322,.475,333,.4,345,.34
290  DATA 273,1.15,286,.97,294,.818,303,.69
300  DATA 312,.58,322,.485,333,.41,345,.345
310  DATA 273,1.2,286,1.01,294,.845,303,.715
320  DATA 312,.6,322,.5,333,.42,345,.355
330  DATA 273,1.27,286,1.06,294,.88,303,.74
340  DATA 312,.61,322,.505,333,.421,345,.35
```

```
?LIST

5   PRINT " OPTIM. OF A COUNTER CURR. EXTR. BY THE MAX. PRINC."
20   READ F,S,X,A,B,D
21   N=4
25   R=F/S
27   K1=.3
28   K2=60
30   X(N)=.5E-02
40   Z(N)=4
45   A(N)=(K2)↑2+(2*B*X(N)*F)/(K1*(1+A))
50   T(N)=.5*(K2+(A(N)↑.5))
60   N=N+1
70   X(N)=0:T(N)=0
80   N=N-1
90   FOR I=N,1,-1
100   L=I+1:K=I+2
105   IF I=N THEN  GOTO 114
110   U(I)=(X(K)↑(1+A))*(T(K)↑B)
112   X(I)=X(L)+(D/R)*((X(L)↑(1+A))*(T(L)↑B)-U(I))
113   GOTO 120
114   X(I)=X(L)+(D/R)*((X(L)↑(1+A))*(T(L)↑B))
120   Z(I)=R*(Z(L)-F)/(D*(1+A)*(X(L)↑A)*(T(L)↑B))
122   A(I)=(K2)↑2+(2*B*X(I)*(F-Z(I))/(K1*(1+A)))
125   T(I)=.5*(K2+(A(I))↑.5)
130   NEXT I
131   I=1:K=I-1:L=I+1
132   G(I)=(X(L)↑(1+A))*(T(L)↑B)
133   X(K)=X(I)+(D/R)*((X(I)↑(1+A))*(T(I)↑B)-G(I))
134   Y=X-X(K)
135   PRINT X(K)
136   FOR I=1,N
137   E(I)=(4*N+.1E-01*S+.3E-01*F+5)/N
139   H(I)=K1*(T(I)-K2)↑2
140   K=I-1
142   IF I>1 THEN  GOTO 150
145   P(K)=0
146   P(I)=P(K)+F*(X(K)-X(I))-(E(I)+H(I))
147   GOTO 160
150   P(I)=P(K)+F*(X(K)-X(I))-(E(I)+H(I))
160   PRINT I;X(I),Z(I),T(I),P(I)
165   NEXT I
200   IF ABS(Y)<.1E-03 THEN  GOTO 230
220   X(N)=X(N)+Y/1000
225   GOTO 40
230   STOP
240   DATA 1260,420,.15,-.4935,-.2356,5.19

?
```

```
LIST

5   PRINT "EXIT CONC. USING MURPHREE EFFICIENCES"
7   DIM X(50),M(50),Z(50),Q(50),F(50),G(50),H(50),J(50)
8   DIM L(50),P(50),R(50),U(50),V(50),W(50),S(50),Y(50)
9   DIM A(20),B(20),C(20),D(50),E(50),N(50)
10   B=10
11   C=B+1
15   FOR K=1,B
20   X(K)=K*3.14/C
30   M(K)=COS(X(K))
40   Z(K)=SIN(X(K))
45   Q(K)=SIN((C-K)*3.14)/C
55   NEXT K
[illegible]   I=10
[illegible]5   E=I/10
90   A(I)=1-.5E-01*E
91   B(I)=(1.733*E+3.995)/60
92   C(I)=3.995*(1-E)/60
95   I=10
100   FOR K=1,B
110   F(K)=(2*B(I)*(1+A(I))-4*((M(K))↑2)*C(I))/((B(I))↑2)
120   G(K)=(4*(4*((M(K))↑2)*A(I)-(1+A(I))↑2))/((B(I))↑2)
140   H(K)=((F(K))↑2+G(K))↑.5
150   J(K)=(-F(K)+H(K))/2
170   P(K)=(A(I)+C(I)*J(K))↑.5
200   NEXT K
210   FOR M=0,12
215   T=M/2
220   PRINT T
230   I=10
235   PRINT I
240   FOR K=1,B
245   S(K)=0
250   FOR N=1,K
260   W(N)=2*((P(K))↑(K+2))*Q(K)*Z(K)*(EXP(J(K)*T))
270   U(N)=C*J(K)*(C(I)*H(K)-B(I)*P(K))
280   V(N)=((-1)↑K)*(U(N)/W(N))
290   S(K)=S(K)+V(N)
300   NEXT N
310   D(K)=((A(I))↑C)-((A(I))↑K)
311   E(K)=((A(I))↑C)-1
312   R(K)=.95*.14*(D(K)/E(K))
315   Y(K)=R(K)+.95*.14*S(K)
320   PRINT K,R(K),Y(K)
330   NEXT K
350   NEXT M
360   STOP

?
```

```
5  PRINT " MUTUAL VISC.COEFF. OF ACITIC ACID -WATER AT 25 C."
7  S=0
10  FOR I=1,4
15  READ X(I),V(I)
20  Y(I)=1-X(I)
25  M(I)=68.4*X(I)+14.8*Y(I)
30  F(I)=68.4*X(I)/M(I)
35  G(I)=1-F(I)
45  L(I)=2*(X(I)*Y(I)*F(I)*G(I))↑.5
50  U(I)=(V(I)-((X(I)*F(I)*1.1)+(Y(I)*G(I)*.89)))/L(I)
60  PRINT I;X(I);V(I),U(I)
65  S=S+U(I)
70  NEXT I
75  S1=S/4
77  PRINT S,S1
80  STOP
90  DATA .361446E-01,1.114,.64027E-01,1.334
100  DATA .128368,1.599,.27758,1.904
```

```
5   PRINT " VISC.OF ACETIC ACID -WATER AT 25 C."
6   DIM A(20),T(20),V(20),F(20),L(20),S(20),U(20)
7   Y=3.21049
10   FOR I=1,14
15   READ A(I)
50   T(I)=1-A(I)
70   V(I)=63.4*A(I)+14.8*T(I)
80   F(I)=63.4*A(I)/V(I)
90   L(I)=1-F(I)
95   S(I)=(A(I)*T(I)*F(I)*L(I))↑.5
100   U(I)=1.1*A(I)*F(I)+.89*T(I)*L(I)+2*Y*S(I)
105  PRINT I;A(I),U(I)
110   NEXT I
120   STOP
130 DATA .78329E-02,.163934E-01,.25788E-01,.361446E-01,.476191E-01,
140   DATA .747331E-01,.107143,.128368,.171429,.201835,.236842
150   DATA .27758,.325581
```

```
5  PRINT " DIFF.OF A.-W.AT DIFF.CONC."
10  DIM A(20),G(20),S(20),T(20),U(20)
15  FOR I=1,14
20  READ A(I),G(I)
30  S(I)=G(I)*((.16094E-06)*A(I)+(.431672E-07)*(1-A(I)))
50  PRINT I;A(I),S(I)
55  NEXT I
60  I=1
70  FOR J=1,8
80  READ T(J),U(J)
90  D(J)=S(I)*T(J)/U(J)
100  PRINT I;J;T(J),U(J),D(J)
110  NEXT J
120  STOP
130  DATA .78329E-02,.892,.163934E-01,.894,.25788E-01,.897
140  DATA .361446E-01,.904,.476191E-01,.914,.604027E-01,.919
150  DATA .747331E-01,.913,.104714,.91,.128363,.91
160  DATA .171429,.915,.201835,.911,.236842,.91
170  DATA .27758,.913,.325581,.908
```

APPENDIX II

Determination of the time to steady state of a stagewise countercurrent extraction process at different efficiencies:

A solute balance over the nth stage in Fig. 4.1 gives

$$u_1\rho_1 x_{n-1} + u_2\rho_2 y_{n+1} = u_1\rho_1 x_n + u_2\rho_2 y_n + \phi_1 \frac{dx_n}{dt} + \phi_2 \frac{dy_n}{dt} \qquad 1$$

The Murphree efficiency for the raffinate phase is given by:

$$E = \frac{x_{n-1} - x_n}{x_{n-1} - x_n^*} \qquad 2$$

since

$$y_n = m\, x_n^* \qquad 3$$

from equations 2 and 3

$$x_n^* = \frac{x_n - x_{n-1}(1-E)}{E} \qquad 4$$

$$\therefore \quad y_n = \frac{m(x_n - x_{n-1}(1-E)\ )}{E} \qquad 5$$

and

$$y_{n+1} = \frac{m(x_{n+1}) - x_n(1-E)\ )}{E} \qquad 6$$

Dividing equation 1 by $u_2\rho_2$ and taking its Laplace Transform we get,

$$\bar{y}_{n+1} - \frac{u_1\rho_1}{u_2\rho_2}\bar{x}_n - \bar{y}_n - \frac{\phi_1}{u_2\rho_2}\frac{d\bar{x}_n}{dt} - \frac{\phi_2}{u_2\rho_2}\frac{d\bar{y}_n}{dt} + \frac{u_1\rho_1}{u_2\rho_2}\bar{x}_{n-1} = 0 \qquad 7$$

Using 5 and 6 in 7:

$$\frac{m}{E}(\bar{x}_{n+1} - \bar{x}_n(1-E)) - \frac{u_1\rho_1}{u_2\rho_2}\bar{x}_n - \frac{m}{E}(\bar{x}_n - \bar{x}_{n-1}(1-E)$$

$$-\frac{\phi_1 S}{u_2\rho_2}\bar{x}_n - \frac{\phi_2}{u_2\rho_2}(\frac{ms}{E}(\bar{x}_n - \bar{x}_{n-1}(1-E))) + \frac{u_1\rho_1}{u_2\rho_2}\bar{x}_{n-1} = 0$$

Collecting the similar terms and dividing by $(\frac{m}{E})$:

$$\bar{x}_{n+1} - ((2-E+\frac{u_1\rho_1 E}{u_2\rho_2 m}) + (\frac{\phi_1 E}{u_2\rho_2 m} + \frac{\phi_2}{u_2\rho_2})S)\bar{x}_n$$

$$+ ((1-E+\frac{u_1\rho_1 E}{u_2\rho_2 m}) + (\frac{\phi_2(1-E)}{u_2\rho_2})S)\bar{x}_{n-1} = 0 \qquad 8$$

putting:

$$(1-E+\frac{u_1\rho_1 E}{u_2\rho_2 m}) = A,$$

$$(\frac{\phi_1 E}{u_2\rho_2 m} + \frac{\phi_2}{u_2\rho_2}) = B \qquad \&$$

$$\frac{\phi_2(1-E)}{u_2\rho_2} = C$$

Equation 8 becomes

$$\bar{x}_{n+1} - (1+A+BS)\bar{x}_n + (A+CS)\bar{x}_{n-1} = 0 \qquad 9$$

This is a 2nd order finite difference equation, its general solution is:

$$\bar{x}_n = C_1 r_1^{\,n} + C_2 r_2^{\,n} \qquad 10$$

where:

$$r_1, r_2 = \frac{(1+A+BS) \pm \sqrt{(1+A+BS)^2 - 4(A+CS)}}{2} \qquad 11$$

$$r_1 + r_2 = 1 + A + BS \qquad 12$$

$$r_1 \, r_2 = A + cS \qquad 13$$

c_1 and c_2 are constants determined by the boundary conditions:

$$\text{at } n = 0 \quad \bar{x}_n = \frac{x_o}{s} = c_1 + c_2$$

$$\text{at } n = N + 1 \quad \bar{y}_{n+1} = m\, \bar{x}_{n+1} = 0 = c_1 r_1^{N+1} + c_2 r_2^{N+1}$$

Hence

$$c_1 = \frac{x_o}{S\left(1 - \left(\frac{r_1}{r_2}\right)^{N+1}\right)} \qquad 14$$

$$c_2 = - \frac{x_o \left(\frac{r_1}{r_2}\right)^{N+1}}{S\left(1 - \left(\frac{r_1}{r_2}\right)^{N+1}\right)} \qquad 15$$

∴ Equation 10 becomes

$$\bar{x}_n = \frac{x_o \quad (r_1^{\,n} . r_2^{\,N+1} - r_2^{\,n} . r_1^{\,N+1})}{S(r_2^{\,N+1} - r_1^{\,N+1})} \qquad 16$$

In order to invert equation 16 to the time domain, keeping in mind that r_1 and r_2 are functions of S, the method of residues must be used.

To simplify the nomenclature, put

$$\bar{f}(s) = \frac{r_2^{\,N+1} . r_1^{\,n} - r_1^{\,N+1} . r_2^{\,n}}{S(r_2^{\,N+1} - r_1^{\,N+1})} \qquad 17$$

Since equation 13 ensures that if $|r_2|$ is large, then $|r_1|$ is small. Hence it is clear that as $|r_2| \to \infty$, $\bar{f}(s) \to 0$; and the only singularities of $\bar{f}(s)$ arise from the poles of the denominator (since the numerator could become infinite if $|r_2|$ became infinite). These zeros occur at:

(i) $S = 0$

(ii) when $r_1^{N+1} = r_2^{N+1}$

Now, to find the residues at these poles, the following formula is used:

$$f(t) = \int^{-1} e^{st}\,\bar{f}(s) = \sum \text{(residues of } e^{st}.\bar{f}(s)\text{)} \qquad 18$$

Equation 17 is multiplied by e^{st}

$$e^{st}\bar{f}(s) = \frac{r_2^{N+1}.r_1^{n} - r_1^{N+1}.r_2^{n}}{S(r_2^{N+1} - r_1^{N+1})}.e^{st} \qquad 19$$

The residues of equation 19 have to be found at the different poles:

(i) The residue at $S = 0$

The residue is determined by L'Hopital's rule (196)

$$R(a) = \frac{F(a)}{g'(a)} \qquad 20$$

where $R(a)$ residue at $S = a$

$F(a)$ numerator of $\bar{f}(s)$ evaluated at $s = a$

$g'(a)$ differential coefficient of the denominator of $\bar{f}(s)$ evaluated at $s=a$

Now,

$$F(a) = (r_2^{N+1}.r_1^{n} - r_1^{N+1}.r_2^{n})\ e^{st}\Big|_{s=0}$$

$$g'(a) = (r_2^{N+1} - r_1^{N+1}).1 + S\frac{d}{ds}(r_2^{N+1} - r_1^{N+1})\Big|_{s=o}$$

But from 11

$$(r_1, r_2)_{s=o} = \frac{1 + A + 0 \pm \sqrt{(1 + A + 0)^2 - 4(A + 0)}}{2}$$

$$\therefore \quad r_1 = 1$$

$$r_2 = A$$

$$\therefore \quad F(a)_{s=o} = A^{N+1} - A^n$$

$$g'(a)_{s=o} = A^{N+1} - 1$$

$$\therefore \quad R(o) = \frac{A^{N+1} - A^n}{A^{N+1} - 1} \qquad 21$$

(ii) To find the residues at $r_1^{N+1} = r_2^{N+1}$:

Since r_1 and r_2 are the roots of a quadratic equation with real coefficients, they must be equal, or mutual complex conjugates.

Therefore, putting:

$$r_1 = r\,e^{-i\theta} \quad , \quad r_2 = re^{i\theta} \qquad 22$$

and since

$$\frac{e^{iy} - e^{-iy}}{2i} = \sin\theta \;\&\; \frac{e^{iy} + e^{-iy}}{2} = \operatorname{Cos}\theta$$

$$\therefore \quad r_2 - r_1 = 2\,i\,r\sin\theta$$

$$r_2 + r_1 = 2\,r\operatorname{Cos}\theta \qquad 23$$

$$r_1\,r_2 = r^2$$

$$\therefore \quad r_2^{N+1} - r_1^{N+1} = 2\,i\,r^{N+1}.\,\sin(N+1)\theta \qquad 24$$

for r_1^{N+1} to be equal to r_2^{N+1}, $\sin (N+1) \quad \theta = 0$

$\therefore \quad (N+1) \quad \theta = k \pi$, K is an integer

$$\therefore \quad \theta = (\frac{k \pi}{N+1}) , \; k = 0, 1, \ldots\ldots, N+1 \qquad 25$$

From 13 and 23, we get

$$r = \sqrt{A + CS} \qquad 26$$

and from 12 and 23, we get:

$$1 + A + BS = 2r \operatorname{Cos} \theta \qquad 27$$

$$\therefore \frac{(1 + A + BS)^2}{2 \operatorname{Cos} \theta} - CS = A$$

Solving this equation gives:

$$S = \frac{1}{2} \Big(- \frac{2B(1 + A) - 4C. \operatorname{Cos}^2\theta}{B^2} \pm \sqrt{\frac{(2B(1+A)-4C.\operatorname{Cos}^2\theta)^2}{B^4} \pm \frac{4(4A\operatorname{Cos}^2\theta - (1+A)^2}{B^2}} \qquad 28$$

Now, the residue of $\overline{f}(s)$ is to be found at a value of s determined by equation 28.

Putting $\overline{f}(s)$ as a function of r and θ :

$$\overline{f}(s) = \frac{r.^{N+1}e^{i(N+1)\theta}.r^{n}.^{-in\theta} - r^{N+1}.e^{-i(N+1)\theta}r^{n}.e^{in\theta}}{S(r^{N+1}e^{i(N+1)\theta} - r^{N+1}.e^{-i(N+1)\theta})}$$

$$= \frac{r^{N+1+n}.2i \sin(N+1 -n)\theta}{S.r^{N+1}.2i \sin(N+1)\theta}$$

$$\therefore \quad e^{st}.\bar{f}(s) = \frac{r^n \sin (N+1 - n)_\theta}{S.\sin (N+1)_\theta} \, . \, e^{st} \qquad 29$$

$$F(a) = r^n . \sin (N+1)\ _\theta . e^{st}$$

when s is defined by equation 28 and r by equation 26.

$$g'(a) = s(N+1) \operatorname{Cos}(N+1)_\theta \, . \, \frac{d\theta}{ds} + \sin (N+1)_\theta$$

$\frac{d\theta}{ds}$ could be found from equation 27 as follows:

$$2r \operatorname{Cos} \theta = 1 + A + BS$$

$$2\sqrt{A + CS} \operatorname{Cos}\theta = 1 + A + BS$$

$$\therefore \quad 2\sqrt{A + CS} \, . \, (- \sin \theta) \frac{d\theta}{ds} + 2 \operatorname{Cos} \theta . \frac{+ C}{2\sqrt{A + CS}} = B$$

Hence

$$\frac{d\theta}{ds} = \frac{(C.\operatorname{Cos}\theta - B.r)}{2 r^2 \operatorname{Sin} \theta} \qquad 30$$

$$\therefore \quad g'(a) = s(N+1) \times (-1)^K . \frac{(C \operatorname{Cos}\theta - B.r)}{2r^2 \sin \theta} + 0$$

$$R(a) = \frac{(-1)^K.2.r^{n+2}.\sin(N+1 - n)\theta \sin \theta}{s(N+1) (C.\operatorname{Cos} \theta - B.r)} e^{st} \qquad 31$$

putting 21 and 31 into 18 gives the inversion of $\bar{x}_n$ as

$$x_n = x_o \left(\frac{A^{N+1} - A^n}{A^{N+1} - 1}\right) + x_o \sum_{K=1}^{N} \frac{(-1)^K.2.r^{n+2}.\sin_\theta \sin(N+1-n)\theta}{S \ (N+1)C.\operatorname{Cos} \theta - B.r)} . e^{st} \qquad 32$$

It should be noted that for each value of K = 0, ..., N there are two values of s and that the values of K > N+1 will give repeated values of S.

Equation 32 is the complete solution to the problem.

APPENDIX III

Optimization of a Countercurrent Extraction Process by the Discrete Maximum Principle

(a) Using Fig. 4.1, a steady state balance on the nth stage gives:

$$Fx_{n-1} + sy_{n+1} = Fx_n + sy_n \qquad 1$$

Since $y_n = m_n x_n$ 2

and $m_n = k\, x_n^a \cdot T_n^b$ 3

Using equations 2 and 3 in 1

$$x_{n-1} = x_n + \frac{k}{R}\,(x_n^{1+a} . T_n^{\,b} - x_{n+1}^{\;1+a} . T^b_{\;n+1}) \qquad 4$$

at n = N, equation 4 is reduced to the form

$$x_{N-1} = x_N + \frac{k}{R}\;\; x_N^{1+a} .\; T_N^{\,b} \qquad 5$$

By recurrence operation using equation 5 in equation 4 for n = N-1, ..., 1

$$x_n = (\frac{R}{kT_n^{\,b}}(x_{n-1} - x_N)\ )^{\frac{1}{1+a}} \qquad 6$$

(b) The objective function which should be maximized is the profit function

P = value of extracted solute- (cost of equipment + cost of solvent + cost of feed + cost of heat supplied)

$$P = \lambda F\ (x_o - x_N) - (\alpha N + \beta S + \gamma F x_o + k_1\ f(T_n)\ ) \qquad 7$$

The terms of the right hand side of equation 7 could be written as follows:

$$x_o - x_N = \sum_{1}^{N} x_{n-1} - x_n$$

$$(\alpha N + \beta S + \gamma F x_o) = \sum_{1}^{N} B_n$$

where

$$B_n = \frac{\alpha N + \beta S + \gamma F x_o}{N}$$

and

$$\text{cost of heat} = k_1 (T_n - k_2)^2$$

Equation 7 can be written in the form

$$P = \sum_{1}^{N} \lambda F(x_{n-1} - x_n) - (B_n + k_1 (T_n - k_2)^2) \qquad 8$$

Since the summation of the right hand side of equation 8 for n = 1, 2, ..., N gives P_N, equation 8 could be written as follows

$$P_n = P_{n-1} + \lambda F(x_{n-1} - x_n) - (B_n + k_1(T_n - k_2)^2) \qquad 9$$

with $P_o = 0$

(c) Now it is required to maximize P_N by the choice of the optional sequence of temperatures T_n, for n = 1, 2, ..., N.

According the discrete maximum principle; the Hamiltonian which should be maximised is

$$H^n = Z_1^{\,n} x_n + Z_2^{\,n} P_n \qquad 10$$

$$H^n = Z_1^{\,n}\left(\frac{R}{kT_n^{\,b}}(x_{n-1} - x_N)\right)^{\frac{1}{1+a}} + Z_2^{\,n}\left(P_{n-1} + \lambda F\left(x_{n-1} - \left(\frac{R}{kT_n^{\,b}}(x_{n-1} - x_N)\right)^{\frac{1}{1+a}} - (B_n + k_1(T_n - k_2)^2)\right)\right) \qquad 11$$

The adjoint functions Z's are given by

$$\text{(i)}\quad Z_1^{n-1} = \frac{\partial H^n}{\partial x_{n-1}} = \frac{Z_1^n}{1+a} \left(\frac{R}{kT_n^{\,b}}(x_{n-1}-x_N)\right)^{\frac{1}{1+a}-1} \cdot \frac{R}{kT_n^{\,b}}$$

$$+ Z_2^n(\lambda F(1 - \frac{1}{1+a} \left(\frac{R}{kT_n^{\,b}}(x_{n-1}- x_N)\right)^{\frac{1}{1+a}-1} \cdot \frac{R}{kT_n^{\,b}} \qquad 12$$

Using equation 6 reduces equation 12 to the form

$$Z_1^{n-1} = \frac{R\ Z_1^n}{k(1+a)\ x_n^a . T_n^{\,b}} + Z_2^n(\lambda F(1- \frac{R}{k(1+a)\ x_n^a .\ T_n^{\,b}}) \qquad 13$$

$$\text{(ii)}\quad Z_2^{n-1} = \frac{\partial H^n}{\partial P_{n-1}} = Z_2^n \qquad 14$$

Equations 13 and 14 are subject to the final conditions of the process and since P_N is to be maximised the final conditions could be defined as:

$$Z_1^N = 0 \quad \text{and} \quad Z_2^N = 1 \qquad 15$$

Using equation 15 in equation 14 gives

$$Z_2^{n-1} = Z_2^n = 1 \qquad 16$$

Using equations 15 and 16 in equation 13 gives

$$Z_1^{n-1} = \frac{R(Z_1^n - \lambda F)}{k(1+a)x_n^a . T^b_n} + \lambda F \qquad . \qquad 17$$

(d) For maximum H^n, $\frac{\partial H^n}{\partial T_n} = 0$

From equation 11

$$\frac{\partial H^n}{\partial T_n} = \frac{Z_1^n}{1+a} \left(\frac{R}{kT_n^b}(x_{n-1}- x_N) \right)^{\frac{1}{1+a}-1} \cdot \frac{-Rb\ T_n^{\,b-1}(x_{n-1}-x_N)}{kT_n^{\,2b}} -$$

$$\frac{\lambda F}{1+a}\left(\frac{R}{kT_n^{\,b}}\,(x_{n-1}-x_N)\right)^{\frac{1}{1+a}-1}\cdot\frac{-Rb\,T_n^{\,b-1}(x_{n-1}-x_N)}{kT_n^{\,2b}}-2k_1(T_n-k_2)=0 \qquad 18$$

Using equation 6 in equation 18 gives

$$\frac{b\,x_n^{-a}}{(1+a)T_n}\cdot\frac{R(x_{n-1}-x_N)}{kT_n^{\,b}}\cdot(\lambda F-Z_1^{\,n})=2\,k_1(T_n-k_2) \qquad 19$$

further reduction of equation 19 by use of equation 6 gives

$$\frac{b\,x_n^{-a}}{(1+a)T_n}\cdot x_n^{\,1+a}\cdot(\lambda F-Z_1^{\,n})=2\,k_1(T_n-k_2)$$

$$\therefore\quad \frac{b(\lambda F-Z_1^{\,n})\,x_n}{(1+a)\,T_n}=2\,k_1(T_n-k_2) \qquad 20$$

$$\therefore\quad T_n^{\,2}-k_2T_n-\frac{b(\lambda F-Z_1^{\,n})\,x_n}{2\,k_1(1+a)}=0 \qquad 21$$

$$\therefore\quad T_n=\frac{1}{2}\left(k_2\pm\left(k_2^2+\frac{2b(\lambda F-Z_1^{\,n})\cdot x_n}{k_1(1+a)}\right)^{\frac{1}{2}}\right) \qquad 22$$

(e) The algorithm of the solution was set as follows:

1 - x_N was assumed and T_N was calculated from equation 22 by knowledge of equation 15

2 - x_{N-1} was then calculated from equation 5

3 - $Z_1^{\,N-1}$ was then calculated from equation 17

4 - T_{N-1} was to be calculated from equation 22, then x_{N-2} from equation 4.

5 - The process was iterated until x_o was obtained from equation 4.

6 - x_o was compared with x_f and the process was iterated until $x_o = x_f$. Then the sequence of T_n obtained for n = 1, 2, ..., N was the optimum temperature profile.

APPENDIX IV

Calculation of the overall mass-transfer coefficient at 30^{o} C :

(1) Calculation of the mean droplet diameter.

(a) Using Kolmogoroff's law (148)

$$d_{max} = 2(d_p)^{0.4} . \frac{\sigma^{0.6}}{k.\rho_c} . \frac{\sqrt{2}}{V^{1.2}} \qquad 1$$

where

d_p = paddle diameter cm = 1.9 cm

k = constant = 0.5

σ = interfacial tension = 15 dyne/sec.

ρ_c = continuous phase density = 0.87 gm/c.c.

V = tip speed velocity = $\pi . d_p . N$ cm/sec.

N = agitator speed = 2550 r.p.m.

$\therefore \quad d_{max} = 0.0556237$ cm

taking $d_{mean} = 0.7\ d_{max}$.

$\therefore \quad d_m = 0.0389$ cm

(b) Using Hinze's formula (149)

$$d_{max} = C\ (\frac{\sigma^{0.6}}{\rho_c}).\ E^{-0.4} \qquad 2$$

where

C = constant = 0.25 for propellers

E = power per unit mass

$P = C_2\ N^3\ (d_p)^5$

C_2= constant = 1 for propellers

$$E = \frac{C_2 N^3 d_p^{\ 5}}{\frac{\pi}{4} d^2_{mixer} \cdot \rho_c \cdot N \cdot H} \qquad 3$$

where

d_{mixer} = mixer diameter = 4.57 cm

H = mixer height = 11 cm

$\therefore$ E = 285.0771

$\therefore$ d_{max} = 0.1614676 cm

$\therefore$ d_m = 0.113027 cm

Since the value obtained by Hinze's formula was considered unsatisfactory, a value of d_m = 0.04 cm was considered in the following calculation as calculated by using Kolmogoroff's correlation.

(2) Calculation of the interfacial area

Since the droplet diameter was very small, the droplets were considered spherical and distortion from the spheriod shape was negligible.

$$\text{Interfacial area} = n \cdot 4\pi d^2_{mean} \qquad 4$$

where n = number of droplets

$$n = \frac{\text{Total volume of dispersed phase in the mixer}}{\text{drop volume}} \qquad 5$$

$$n = \frac{\phi_d \cdot V_{mixer}}{\frac{\pi}{6} \cdot d_m^{\ 3}} = \frac{0.01 \times 175}{\frac{\pi}{6} (0.04)^3} = 5.222 \times 10^4$$

$\therefore$ Interfacial area = 1050 cm^2

(3) Calculation of the Driving Force ΔC:

The driving force was calculated by Simpson's rule as used by Jeffreys (149).

For 6 stages at 30° C and 2100 rpm

$$\Delta C = \frac{1}{18}\left(\Delta C_1+4\Delta C_2+2\Delta C_3+\Delta C_4+2\Delta C_5+4\Delta C_6+\Delta C_7\right) \qquad 6$$

$$= \frac{1}{18}(2.3 + 4x1.5 + 2x2.1 + 4.26 + 2x3 + 4x3.7 + 4.9) \text{ x } 0.04$$

$$= 0.0948$$

(4) Calculation of the Overall Mass Transfer Coefficient:

The rate of mass transfer $N = K.A.\Delta C$ 7

considering the continuous phase

$$N_c = V_c.\rho_c(x_o - x_N) \qquad 8$$

$$= \frac{22 \text{ x } 0.87}{60}(0.15 - 0.008)$$

$$= 0.045298 \text{ gm/sec.}$$

$\therefore$ From equations 7 and 8

$$0.045298 = K_c \text{ x } 1050 \text{ x } 0.0948$$

$$\therefore \quad K_c = 4.546 \text{ x } 10^{-4} \text{ cm/sec.}$$

(5) Calculation of the continuous phase coefficient using Garner, Ford and Tayeban's relation (149)

$$\frac{k_c.d_m}{D_c} = -126 + 1.8\,(Re)^{0.5}.Sc^{0.42} \qquad 9$$

$$(Re)_{drop} = \frac{\rho_c d_m.U}{\mu_c} = \frac{0.87 \text{ x } 0.04 \text{ x } \quad \text{ x } 1.9 \text{ x } 2550}{60 \text{ x } 0.0055} \qquad 10$$

$$Sc = \frac{\mu_c}{\rho_c D_c} = \frac{0.0055}{0.87 \text{ x } 1.441 \text{ x } 10^{-5}} \qquad 11$$

$\therefore$ $k_c = 4.6834 \times 10^{-4}$ cm/sec.

(6) Calculation of the overall mass transfer coefficient using the rigid drop model

$$\frac{1}{K_c} = \frac{1}{k_c} + \frac{m_{cd}}{k_d} \qquad 12$$

$$k_d = -\frac{d_m}{6t} \ln \frac{6}{\pi^2} \exp(-\frac{4\pi^2 . D_D . t}{d_m^2}) \qquad 13$$

$$t = \text{holding time} = \frac{\phi\, d . V_{mixer}}{v_d} \qquad 14$$

$$= \frac{0.01 \times 175 \times 60}{7.5} = 14 \text{ sec.}$$

D_D = diffusivity of acetic acid in the dispersed phase (water) at 30°C and 0.25 concentration

$D_D = 1.17973 \times 10^{-5}$

$\therefore$ $k_d = 2.177095 \times 10^{-3}$ cm/sec.

$\therefore$ From equation 12

$K_c = 4.469687 \times 10^{-4}$ cm/sec.

(7) Calculation of the overall mass-transfer coefficient using the circulating drop model

$$k_d = -\frac{d_m}{6t} \ln \frac{3}{8} \sum_{n=1}^{\infty} A_n^2 \exp(\lambda_n . \frac{64Dt}{d_m^2}) \qquad 15$$

taking $n = 1$, $A_1 = 1.32$, $\lambda_1 = 1.678$

$\therefore$ $k_d = 5.481549 \times 10^{-3}$ cm/sec.

From equation 12

$K_C = 4.596094 \times 10^{-3}$ cm/sec.

(8) Calculation of the overall mass-transfer coefficient using the oscillating drop model:

$$k_d = 0.45\, (D_D w)^{0.5} \qquad 16$$

$$w^2 = \frac{24\sigma b}{a^3(3\rho d + 2\rho_c)} \qquad 17$$

$$b = \frac{{d_m}^{0.225}}{1.242} = 0.390249 \qquad 18$$

$$V = \frac{4}{3}\pi a^2 b = \frac{\pi}{6} d_m^3 \qquad 19$$

$$\therefore \quad a^2 = \frac{{d_m}^3}{8b}$$

$$\therefore \quad a = 4.527663 \times 10^{-3} \text{ cm}$$

$$\rho_d = 1.04, \quad \rho_c = 0.87$$

from 17, $w = 1.176479 \times 10^{-4}$ sec.$^{-1}$

from 16, $K_d = 20.532896 \times 10^{-3}$ cm/sec.

from equation 12, $K_C = 4.6597 \times 10^{-4}$ cm/sec.

NOMENCLATURE

A	Coefficient in equations 2.10 and 6.3, surface area, Interfacial area, cm^2.
a	Constant in equation 1.1
B	Coefficient in equation 6.6 Solvent in Section 4.
C	Concentration, gm/gm. Feed in equation 4.14. Power number in equation 2.30, $\frac{Pg_c}{\rho N^3 d_i^5}$, dimensionless
D	Density in equation 6.1, gm/c.c. Diffusivity, cm^2/sec.
D_F	Drop diameter in equation 2.23, cm.
D_N	Nozzle diameter, cm.
d	diameter, cm
E	Extraction efficiency power per unit mass, $\frac{C\rho N^3 \, d_i}{\frac{\pi d^2}{4} \, T.N.H_T}$ Droplet eccentricity in equation 2.24.
F	Feed
H	Height, cm.
h	Heat transfer coefficient, gm. cal/sec. cm^2 .^oC.
K	constant overall mass transfer coefficient, cm/sec.
k	Individual mass transfer coefficient, cm/sec. Thermal conductivity in Nussult number ,g-cal/sec.cm^2.^oC.

N	Mass transfer rate, gm/sec.
	Number of stages
	Speed of agitation, r.p.m.
Nu	Nussult number, $\frac{hD}{k}$, dimensionless.
P	Profit
Pe	Peclet number, $\frac{\rho_c vd}{k}$, dimensionless.
Pr	Prandtl number, $\frac{C_p \mu}{k}$, dimensionless.
Q	Rate of flow in equation 2.23.
R	Phase ratio, $\frac{F}{S}$
Re	Reynolds number, $\frac{\rho_c vd}{\mu}$, dimensionless.
r	Droplet radius in equation 2.14.
	Root of equation 4.4.
S	Solvent
	Extraction factor in equation 4.15.
Sc	Schmidt number, $\frac{\mu}{\rho D}$, dimensionless.
T	Tank diameter, cm
	Temperature in equation 6.10, ^{o}K.
t	Time of contact, sec.
	Temperature in equations 6.6 to 6.8, ^{o}C.
te	Time for a drop to rise a distance equal to its t_e diameter, sec.
u	Rate of flow, cc./m.
V	Total volume, c.c.
	Drop volume, c.c.
v	Flow rate, c.c./m.
	Velocity, c.c./m.
Vs	Slip velocity, c.c./m.
w	Weight, gm/gm.

w^o	Weight at zero solute concentration, gm/gm.
We	Weber number, $\frac{\rho N^2 d^3}{\sigma}$, dimensionless.
x	Concentration in the raffinate phase, gm/gm.
y	Concentration in the extract phase, gm/gm.
Z	Association factor.
α	Cost per stage per hr, pence.
β	Cost of solvent per gm, pence.
γ	Cost of feed per gm, pence.
λ	Cost of extracted solute per gm, pence.
	Eigen value in equation 2.10.
μ	Viscosity, centipoise.
ν	Kinematic viscosity, μ/ρ
π	3.14
ρ	Density, gm/c.c.
$\sum$	Summation.
σ	Interfacial tension, dynes/cm.
ϕ	Volume fraction of a liquid in a vessel.
ω	Frequency of oscillation of a drop, 1/sec.

SUBSCRIPTS

A	Water
B	Organic solvent
C	Continuous phase
	Critical in equation 6.1.
CT	Solute in toluene
Cw	Solute in water
d	Dispersed
E	Extract
i	Interface
	Impeller

m	mean mixture in equations 6.2 and 6.11
max.	Maximum
O	Initial
OS	Oblate spheriod
S	Sphere
Sv	Sauter mean diameter.
R	Raffinate
T	Mixing tank
*	Equilibrium value
1,2	Phases.

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