SOLVENT EXTRACTION OF PHOSPHORIC ACID

by

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To

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SUMMARY

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This work investigated the purification of phosphoric acid using a suitable organic solvent, followed by re-extraction of the acid from the solvent using water. The work consisted of practical batch and continuous studies and the economics and design of a full scale plant, based on the experimental data.

A comprehensive literature survey on the purification of wet process phosphoric acid by organic solvents is presented and the literature describing the design and operation of mixer-settlers has also been reviewed.

In batch studies, the equilibrium and distribution curves for the systems water-phosphoric acid-solvent for Benzaldehyde, Cyclohexanol and Methylisobutylketone (MIBK) were determined together with hydrodynamic characteristics for both pure and impure systems. The settling time increased with acid concentration, but power input had no effect. Drop size was found to reduce with acid concentration and power input.

For the continuous studies a novel horizontal mixer-settler cascade was designed, constructed and operated using pure and impure acid with MIBK as the solvent. The cascade incorporates three air turbine agitated, cylindrical 900 ml mixers, and three cylindrical 200 ml settlers with air-lift solvent interstage transfer.

Mean drop size in the fully baffled mixer was correlated. Drop size distributions were log-normal and size decreased with acid concentration and power input and increased with dispersed phase hold-up.

Phase inversion studies showed that the width of the ambivalent region depended upon rotor speed, hold-up and acid concentration.

Settler characteristics were investigated by measuring wedge length.

Distribution coefficients of impurities and acid were also investigated. The following optimum extraction conditions were found: initial acid concentration 63%, phase ratio of solvent to acid 1:1 (v/v), impeller speed recommended 900 r.p.m. In the washing step the maximum phase ratio of solvent to water was 8:1 (v/v). Work on phosphoric acid concentration involved constructing distillation equipment consisting of a 10 ℓ spherical still.

A 100 T/d scale detailed process design including capital cost, operating cost and profitability was also completed. A profit model for phosphoric acid extraction was developed and maximised.

Recommendations are made for both the application of the results to a practical design and for extensions of the study.

KEY WORDS - Solvent extraction-Phosphoric Acid-Purification

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CHAPTER ONE

INTRODUCTION

The advance of the economic status of the developed countries of the world owes much to the discovery of phosphate ore and the development of the technologies required to transform it for the use of mankind. Phosphate rock has a limited use itself, chiefly because of the relatively low availability of the P_2O_5. Its main consumption however is as a raw material for the manufacture of phosphoric acid. It is well known in industries and used in manufacturing of both solid and liquid mixed fertilizers. It is also used in other areas of chemical technology, such as detergents, food and a number of feed additives for animal husbandary.

The end uses of phosphoric acid usually depend upon the purity of the acid, which in turn depends on the way in which the acid is produced, the origin and composition of the phosphate rock (50).

In principle there are two ways to make phosphoric acid, acidulation and thermal treatment (12). The thermal process gives a pure grade acid and therefore it is used mainly for food and water treatment. The second method (acidulation) produces impure acid known as wet process, which can be used in agriculture.

The difference between the manufacturing cost of the wet process and the thermal process phosphoric acid is substantial (27). This arises for both high energy consumption (about 11000 kw is used per ton of recovered phosphorus) which is too high considering the present energy crisis and more complex processing in the thermal route. This provides economic as well as technical incentives to use a purification technique to produce purer acid from the wet process route.

Numerous methods have been proposed for purifying wet process phosphoric acid, these include settling, precipitation and centrifugation with added flocculating agents under different operating conditions. None of the above methods have been completely effective. Although they improve the acid grade they do not solve the problem of additional sludge formation, and the uses of the produced acid are still limited to fertilizers. Chemical treatment of the acid is connected with excessive losses and waste disposal as well as being uneconomical (25, 138).

One of the successful attempts at purification is by solvent extraction which can lead to a range of specifications up to food stuff quality as well as being cheap with good yield, and with virtually no pollution (25). The solvents used are organic, and the technique is based on the ability of that solvent or solvents to extract the acid and to reject to some extent the impurities.

Different ideas are reported in the literature for using solvent extraction techniques for purification purposes (19,20,39,144,215,239,240,271) and many solvents were reported (7,41,44,281,282). However, only a few papers have been published or even describe the type and the design of the equipment used for the purification processes in a continuous manner. From studies of the solubility systems, it will be seen that in order to effectively remove the major portion of the phosphoric acid, inordinately large amounts of organic reagent must be employed. Therefore it is essential that the continuous extraction can be carried out in a counter-current fashion whereby the material containing the lowest concentration of phosphoric acid is subjected to the relatively pure organic solvent and thus, complete recoveries are possible with a considerably smaller amount of organic solvent.

The object of this work is to provide pilot plant equipment to study the purification and extraction of phosphoric acid, which comprises contacting an impure and/or pure aqueous phosphoric acid in a multistage counter extraction (mixer-settlers) with organic solvent. Another object of this work is to confirm the work which has been reported in literature (282). Still another object of this work is to evaluate and optimize the profit function by choosing a reasonable solvent and process parameters.

Taking into account the outlook for the use of organic solvents for wet process acid, it was decided to investigate the process using methyl-isobutylketone. Some batch work has also been studied using cyclohexanol and benzaldehyde as solvents.

Hydrodynamic studies for both batch and continuous work were also considered. Batch work was carried out first in a small scale mixer to assist in the prediction of the theoretical design of continuous equipment.

The mixer-settler unit, consisting of mixing and settling chambers, has a number of unique features, these include: (a) inter-stage pumping, carried out by the use of air lift pumps, and (b) mixing was carried out by air driven motors for safety. In general the equipment needs no source of electricity.

CHAPTER
TWO

PRODUCTION OF PHOSPHORIC ACID

Although the main objective of this work is not to study the production of the phosphoric acid, brief descriptions of the principle methods of production are included.

Two types of phosphoric acid are marketed - a purified acid made by the electric furnace method and a less pure dark acid by the "wet" process method.

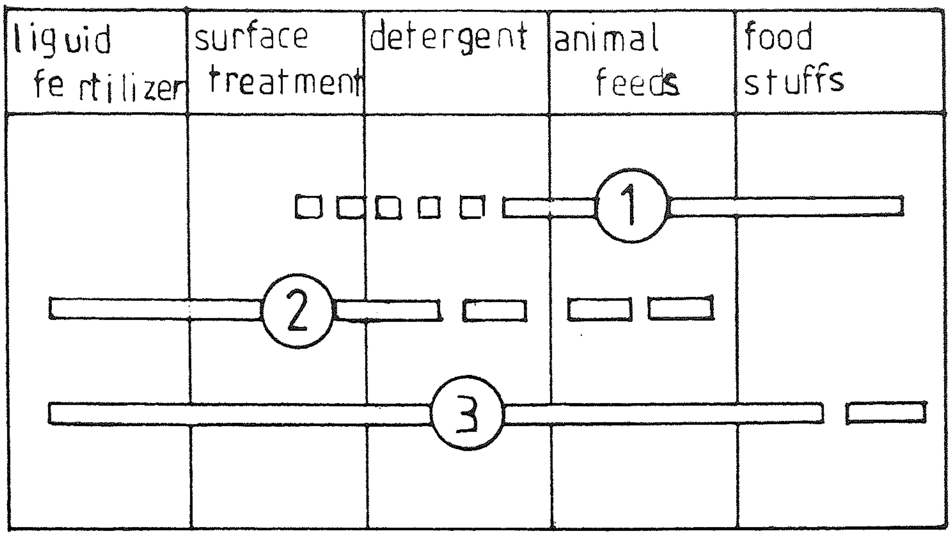
Both acids are widely used in industry, see Fig. 2.1. However, wet process acid can not be used directly for some products, such as foodstuffs, unless it has first been purified, see Fig. 2.2. Production/capacity of both acids in the U.S.A. is shown in Fig. 2.3.

2.1 FURNACE PROCESS

Furnace grade phosphoric acid is produced from elemental phosphorus, therefore the production of the acid is closely related to the production of phosphorus. Phosphorus is first produced by the electric reduction of phosphate rock. This is then followed by oxidation and hydration to give phosphoric acid:

FIG. 2.1.

Uses of phosphoric acid [18]



region: ▭ normal; ▭ ▭ limited by quality

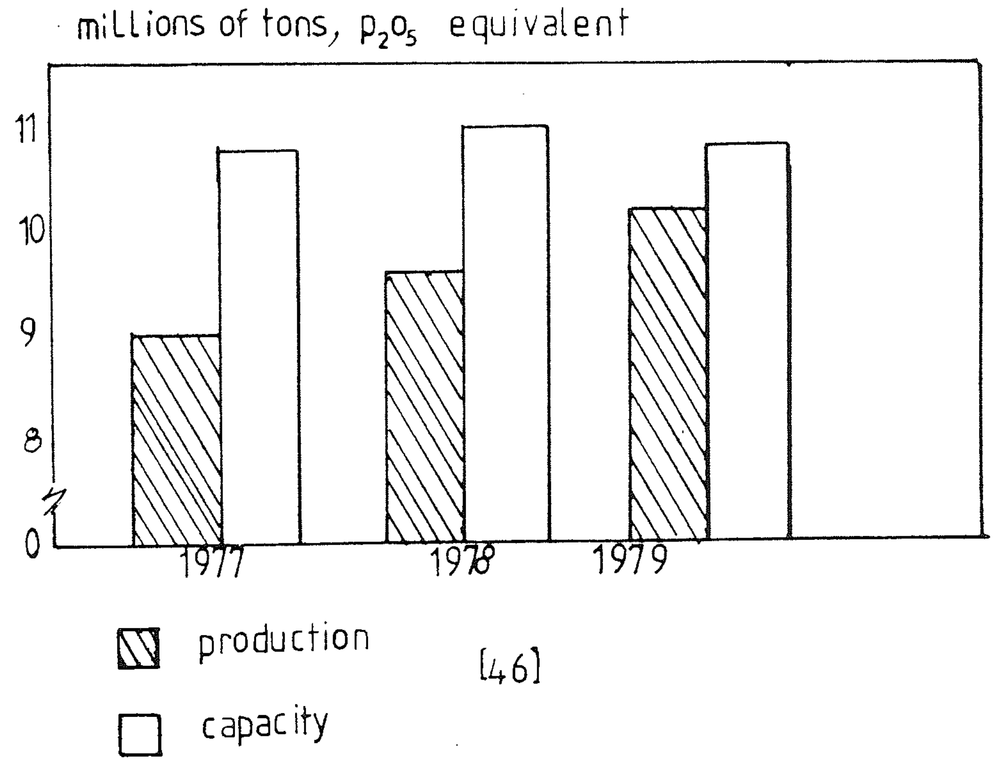
□ □ □ limited by price

1 – furnace grade acid .

2 – wet process acid , chemical treatment .

3 – wet process acid , solvent extraction .

FIG 2.2, REGIONS OF APPLICATION OF ACID



[46]

FIG 2.3, PRODUCTION/CAPACITY
INCLUDES BOTH WET AND FURNACE ACID

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

The oxidation and hydration takes place in furnaces either similar to normal blast furnaces (in this case, dust separation and phosphorus condensation from the gas is required), or electric furnaces to produce phosphorus vapour which can be burned directly to P_2O_5, and the latter reacted with water to form phosphoric acid. However, in the electric furnace, the total cost of electrodes, power, coke, and phosphorus condensation is lower than the cost of coke plus the expense of removing dust and condensing phosphorus from the rather large quantities of gas in the blast-furnace process.

The final acid is diluted to 75 to 85% H_3PO_4 for commercial application (178).

2.2 WET PROCESS ACID

The world requirement for fertilizer is increasing as shown in Table 2.1, and wet process phosphoric acid plays an important part in its production. The acid was first produced commercially, by this method, in Germany between 1870 and 1872 (277), and in the United States, at Baltimore. In general the process involved the acidulation of phosphate rock (which generally contains phosphorus in the form of fluorapatite ($Ca_{10}F_2(PO_4)_2$), with a mineral acid, normally sulphuric acid, to precipitate the calcium salt. The phosphoric acid which is in solution can be removed by filtering it from the mixture.

Table 2.1

Fertilizer Supply, metric tons [245]

The quantity of mineral acid consumed is a function of the rock composition only; it is therefore advantageous to use a rock of high P_2O_5 content and low CaO/P_2O_5 ratio (105); however, to convert all the calcium present into an insoluble salt (gypsum) an excess of the mineral acid is required.

It is not normally possible to use sulphuric acid of strength greater than that which will yield a phosphoric acid containing about 30% by weight of P_2O_5, since with more concentrated acid the precipitated calcium sulphate becomes more difficult to filter.

Different concentrations and compositions of the final product acid can be obtained if different mineral acids are used. When sulphuric acid is used (133,201,221), the byproduct of the reaction is calcium sulphate which is a waste product as reported by Gattikek (81). I.M.I. and others (8,17,28,104,227) used hydrochloric acid where the byproduct of the reaction is calcium chloride, and the advantage of the process lies in the fact that it can accommodate waste or byproduct hydrochloric acid from any source.

Gattiker (81) used nitric acid in which calcium nitrate is produced as a byproduct which can be used as fertilizer or may be further treated to recover the nitrate radical in the form of ammonium nitrate. Other recent processes for production of phosphoric are reported in (66,67,68).

Whatever route is used to produce the acid, a loss of P_2O_5 value occurs and the final acid contains impurities.

2.3 NATURE AND EFFECT OF IMPURITIES

A typical analysis of wet process phosphoric acid after filtering it from insoluble matter such as calcium (in the form of gypsum) shows it contains dissolved and suspended materials both inorganic and organic. Since the phosphate rock is a natural product, it is the primary source of these impurities. On the other hand, the impurities may be introduced as chemical additives, during the beneficiation, in the mineral acid and by the corrosion and erosion of the equipment.

Different raw materials from different origins and different production methods have a considerable effect on the relative amount of the impurities.

More than 50 chemical elements have been identified in phosphate rock, the key constituents of these impurities are iron, aluminium, calcium, magnesium and sulphate which are present in appreciable amounts. Others are present in very small amounts (e.g. barium, strontium, vanadium, uranium and fluoride).

Fox (78) suggested that the origin of the organic matter was from vegetable rather than animal sources. His conclusion is supported by the observation of plant residues in rock samples from the Idaho and Wyoming deposits (115).

All the dissolved and suspended impurities adversely affect the quality of the acid, produce undesirable colour or turbidity, and change physical properties such as viscosity, density and conductivity; other impurities are toxic, e.g fluorine which limits the use of acid in food industries.

Waggaman (274) states that the organic matter reduces sulphuric acid to sulphur dioxides and hydrogen sulphide. This means greater consumption of acid. Toyo Soda Co. (263) report the following observations on the organic impurities:

(a) The organic materials in the wet process phosphoric acid can be classified into those which cause colour and those which do not.

(b) The non-colouring organic material can be converted into colouring materials by heating.

(c) The colouring organic materials can be removed but the non-colouring organic materials cannot be removed by conventional decolouring methods.

(d) A portion of the colouring material can be removed but the non-colouring organic materials are not substantially removed by extraction methods.

Hiromi (95) claims that phosphoric acid can be decolourized by heating the wet process acid in an autoclave at 100-300°C to carbonize the organic substances, then cooling to settle the carbon before removal.

Impurities in wet process acid become more troublesome when they crystallise from the acid as solids (275) or during prolonged storage. The major difficulties encountered in the production of wet process acid are those in obtaining a readily filterable calcium sulphate and in preventing the formation of sludge in the acid, especially when it is concentrated.

The instability of dissolved impurities and their tendency towards precipitation are very common, giving problems (72) in the filtration stages, where they interfere with the recovery of acid from the filter cake.

The chemical process by which solid continues to separate from wet process acid over long periods of time have not been clearly defined, but in general most precipitation of the dissolved impurities take place during the evaporation (concentration) step and continues for days or weeks during storage (77).

The presence of the settled solid impurities therefore causes difficulties in handling the acid because these solids tend to plug the lines, valves and acid spraying nozzles and this often results in the shut down of the plant to clean the equipment (219). The precipitated impurities can be removed by filtration, decantation, etc., however this results in prohibitive losses of valuable P_2O_5.

Different sources of phosphate ores have different compositions (see Table 2.2) and these affect process parameters, including the form of the calcium sulphate crystals, slurry filtration rate, viscosity, density, colour of the acid and the rate at which the sludge impurities are precipitated (35). These are affected in roughly the same relative proportions, but the minerlogical form in which the impurities occur vary widely from one deposit to another. The minerals differ considerably in their solubility in the acid, thus the extent to which the impurities dissolve in the acid is controlled by

Source	Composition %										ref.
	P_2O_5	CaO	F	CO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SiO_2	SO_3	
Florida and Pebble Hard Rock	30-36 33-36	46-50 49-51	3.3-4.0 3.4-3.9	1.5-4.4 1.8-2.8	.71-2.6 0.5-1.4	0.7-2.6 0.7-1.3	0.04-0.5 0.03-0.2	0.09-0.5 0.06-0.3	.07-0.6 0.1-0.4	7.3-9.8 4.5-6.4	0.5-1.5 0.1-0.6	18
Tennessee Blue Rock Brown Rock	28.3-33 32.8-37	43-49 45.5-50.8	3.3-3.8 3.4-4.0	0.9-2.6 1.1-3.7	0.6-1.2 1.2-2.7	1.8-3.5 0.9-3.4	0.07-0.4 0.01-0.2	0.04-0.6 0.2-0.4	0.1-0.3 0.1-0.3	4.9-12.4 1.9-8.1	4.0-7.1 0.4-0.8	18
Wyoming	30.2	46.2	3.54	4.13	1.2	0.87	0.1	0.35	0.64	7.2	1.35	18
North Carolina	30.2-30.3	48.6-49	3.5-3.8	5.4-5	0.5-0.6	0.6-0.7	0.5	0.11	0.9-1.0	2.3-3.6	0.98	18
Morocco	32-37.2	51.1-54.2	3.5-4.2	2.6-4.6	0.3-0.4	0.1-0.5	0.09-0.1	0.1-0.11	0.3-0.8	1.07-2.4	0.6-1.6	18
Algeria	30.1	50.1	2.65	6.7	0.2	0.35	0.9	0.8	1.53	2.13	2.4	18
Togo	3.7	51.7	3.32	1.27	0.67	1.60	0.1	0.03	0.12	3.35	0.24	18
Quebec	40-40.5	52.4-55	3.3-3.4	0.3-1.5	0.6	-	0.5	-	-	0.5-3.1	-	18
Kala	39.6	52.2	3.20	0.2	0.79	0.68	0.1	0.28	0.77	2.4	nil	18

TABLE 2.2
COMPOSITION OF SOME COMMERCIAL PHOSPHATE ROCK

the chemical composition and solubilities of the individual minerals in which the impurities occur. The resultant acid will therefore have a different composition of impurities as shown in Table 2.3A and 2.3B.

Although fertilizer production does not require acid of high purity, there is a limit to the impurities content of the acid. Impurities have the following effects on production and application in fertilizers:

(1) They reduce the concentration of finished fertilizer made from the acid.

(2) When wet process acid is used in making liquid fertilizers, iron and aluminium compounds precipitate as voluminuous sludge that interfere with the application of the liquid through spray equipment. Magnesium compounds also form solids that interefere with applications of liquid fertilizer.

On considering the effect of impurities on the distribution coefficient of the acid, Yacu (282) reported the following:

(1) They reduce the distribution coefficient of the acid.

(2) They also increase the hetrogeneous area of ternary phase equilibrium diagram, acid-water-solvent.

Yoichi (284) reported that the organic impurities can be removed by solvent extraction and then treatment of solvent with active carbon. The organic impurity causes the following disadvantages on the operation of phosphoric acid plant:

Table 2.3A Composition of Concentrated Wet - Process Phosphoric Acid (18)

Table 2.3B Composition of Filtrate Wet Process Phosphoric Acid (18)

(1) The phosphoric acid extraction efficiency and the impurity separation efficiency are lowered.

(2) The speed of phase separation of the two liquid phases in the extraction process is very low.

(3) Sometimes a stable emulsion is formed whereby the separation of the two liquid phases is impossible.

CHAPTER
THREE

SCOPE OF SOLVENT EXTRACTION FOR THE PURIFICATION OF WET PROCESS PHOSPHORIC ACID

The disadvantages of the thermal methods for the production of phosphoric acid are the requirements for relatively expensive capital equipment, larger amounts of electrical energy and pollution control. In fact, because of the wide gap between the price of wet process phosphoric acid and the price of electrothermal acid, the purification of wet process phosphoric has received increasing attention.

Several attempts have been made to purify wet process phosphoric acid such as chemical treatment and settling (82,111,110), however most progress has been made in the application of solvent extraction technology. This turned out to be one of the more successful methods. It is based on the ability of some organic solvents to extract the acid and reject, to a large extent, the impurities present.

The selectivity of a solvent is usually indicated by the ratio of the concentration of the acid and/or acids and their simple salts in one layer, on a solvent free basis, to the corresponding concentration in the other layer (249).

Solvent extraction entered the inorganic chemical process industry (as opposed to the petrochemical and pharmaceutical industries) with the implementation of an extraction process for the recovery of uranium. In the case of phosphoric acid solvent extraction falls into two main categories, one having reference to the basic separation between the complementary components of phosphate rock, e.g. phosphoric pentoxide and calcium oxide, the other being concerned with upgrading the phosphorus pentoxide values by eliminating impurities (29). It is not the purpose of the present work to consider the first category, a comprehensive discussion of this has been given by Slack (18).

3.1 THEORIES OF EXTRACTION

It is not the purpose of this work to study in detail the theories behind the extraction process. Diamond (64) published a very good survey of this topic.

There are a number of different ways in which the experimental data on the solvent extraction of inorganic compounds can be organised for review. Any scheme is an arbitrary one, and nature provides examples which seem to fit simultaneously into more than one category.

Browning (36) divided solvents into three types:

(i) non-hydrogen bonding solvents

(ii) solvents forming hydrogen bonds preferentially with other molecules, e.g. ether and

(iii) solvents which form a hydrogen bonded structure, e.g. CH_3OH.

Diamond (64) organised the extractable compounds into the following six classes.

1. Simple molecules - Involves the partition of a simple covalent molecule between an aqueous solution - organic solvent pair. The simplest system involves the distribution of a relatively inert molecule between two immiscible solvents. Under such circumstances the activity coefficient ratio will be close to unity.

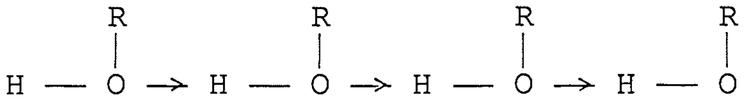
2. Pseudo molecular systems - On general principles, ionic compounds would not be expected to extract into organic solvents from aqueous solution because of the large loss in electrostatic solvation energy which would occur. However, the most obvious way to make an aqueous ionic species extractable is to destroy its charge. This can be done by combining the ion of interest with an ion or ions of opposite charge to form a neutral molecular species.

3. Mineral acids - The extraction of a covalent molecule from aqueous acid solution is possible with essentially any organic solvent which is immiscible with water. Small ionic species are strongly solvated in aqueous solution by the highly polar water molecules, to an extent depending on their charge density and chemical properties. There is consequently little tendency for them to extract into non polar, non coordinating solvents which cannot compensate for the resulting loss of hydrogen energy. When the molecules of a substance are polar, they exhibit a dipole moment caused by unequal sharing

of the electrons of the covalent bonds of the molecule. Oxygenated solvents such as ether, ketone, alcohol and ester have such properties. In the case of an alcohol (265), the electron pair that makes up the bond between oxygen and hydrogen lies closer to the oxygen.

$$R \text{———} \overset{\delta-}{O:} \quad \overset{\delta+}{H}$$

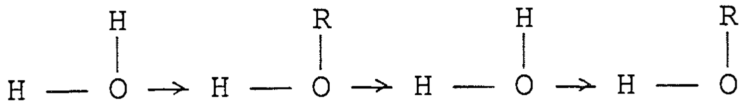
Consequently, the hydrogen portion of the molecule is relatively positively charged and the remainder is negatively charged, and the dipole moment is used as a measure of this phenomenon. Polar molecules tend to associate with coordination hydrogen atoms between the negative parts of adjacent molecules:



$$H - \overset{R}{\overset{|}{O}} \rightarrow H - \overset{R}{\overset{|}{O}} \rightarrow H - \overset{R}{\overset{|}{O}} \rightarrow H - \overset{R}{\overset{|}{O}}$$

Hydrogen can also coordinate between other donor atoms such as nitrogen or fluorine as well as oxygen.

Solution of solute into a solvent which takes place through hydrogen bonding may involve either breaking the hydrogen bonds or forming new ones (64). Thus, for example, if an alcohol dissolves in water, the hydrogen bonds between the water molecules and between the alcohol molecules may be broken and new bonds formed between alcohol and water molecules as shown below:



$$H - \overset{H}{\overset{|}{O}} \rightarrow H - \overset{R}{\overset{|}{O}} \rightarrow H - \overset{H}{\overset{|}{O}} \rightarrow H - \overset{R}{\overset{|}{O}}$$

The evidence for the formation of hydrogen bonded complex between solvent and nitric acid molecules was explained by Sutton (251). He used diethylether as solvent and the equilibrium can be represented by:

$$HNO_3 + (CH_3CH_2)_2.O \rightleftharpoons (CH_2CH_2)_2.O.HNO_3$$

Baronov (22) studied the behaviour of phosphoric acid and plutonium (IV) during extraction with trioctylamine and reported the formation of a salt. Krupatkin's (163) study of binary systems formed by phosphoric acid with benzophenone, ethylmethylketone and cyclohexanone shows the existence of a compound of composition 1:1. In addition a compound with a 2:1 ratio of acid to ketone is formed.

Ewell-Harrison and Berg (72) classified liquids into five groups based on their potentialities for forming hydrogen bonds and these are:

Class I : Liquids capable of forming three-dimensional networks of strong hydrogen bonds, e.g. water, glycol, glycerol and amino alcohols.

Class II : Liquids composed of molecules containing both active hydrogen atoms and donor atoms (oxygen, nitrogen and fluorine), e.g. alcohols, acids and phenols.

Class III: Liquids composed of molecules containing donor atoms but not active hydrogen atoms, e.g. ethers, ketones and aldehydes.

Class IV : Liquids composed of molecules containing active hydrogen atoms but no donor atoms, e.g. $CHCl_3$, CH_2Cl_2.

Class V : All other liquids, e.g. liquid having no hydrogen bond forming capabilities, e.g. hydrocarbons.

It is worth noting the effect of basicity on the solubility of water in organic solvents. The solubility of hydrocarbons in water is typically equivalent to a mole fraction of $10^{-3} \rightarrow 10^{-4}$ in ethers. On the other hand, the solubility is an order of magnitude higher than this and in the case of strongly basic phosphoryl compounds, the solubility of water corresponds to complete formation of a 1:1 complex such as tri-n-butylphosphate (TBP) : H_2O. In the presence of concentrated nitric acid and a diluent in TBP this system becomes more complicated (4) due to the formation of a ($TBP:HNO_3$) complex as a third phase. The appearance of this third phase was not obtained when phosphoric acid was used, instead of nitric acid, but a third phase was observed when di-isopropyl ether was used as solvent (282). This was confirmed in earlier work by Schallert (240) on the purification of phosphoric acid using di-isopropyl ether and diethylether. The phosphoric acid-ether complex formed in both cases was claimed to be accompanied by a molecule of water as expressed by the chemical formula:

$H_3PO_4.H_2O(CH_3)_2.CHOCH(CH_3)_2$; with di-isopropyl ether

and $H_3PO_4.H_2O(CH_3CH_2)_2O$; with diethylether

Both complexes are insoluble in dilute phosphoric acid solutions or in excess ether.

The binary systems formed by phosphoric acid with cyclohexanone, furfural, salicyldehyde and benzaldehyde have been investigated (162,150) and it was concluded that a 1:1 complex compound is formed between the acid and the solvent, and in some cases a compound with 2:1 ratio of acid to solvent was also formed.

Grinberg and Lazhkiha (85) suggested that extraction of acid with organic solvent involves two main procedures. The use of salting out agents and complex compound formation known as oxonium compounds. The former consists of adding a salt to the aqueous phase to act mainly as a binding agent for water and thus reducing its concentration as available solvent. Different salting out agents result in different effects on the distribution coefficient.

Seaton and Geankoplis (243) studied the effect of pH, activity coefficient and internal pressure of the aqueous solution on the extraction of phosphoric acid. They concluded that pH should play an important part in the extraction of a partly ionized acid like phosphoric acid. When the pH value was increased from 0 to 10 the distribution coefficient of the phosphate ion dropped by a factor of 1:100. However, in changing the pH (by adding HCl and NaOH) new chemicals (phosphate salts) are formed which behave completely differently from the acid in their solubility in the organic phase. The distribution coefficient of phosphoric acid increased when HCl was added, this was explained by the theory that since HCl lowers the internal pressure of water it diminishes the activity of water towards the acid and hence the organic phase is able to share a greater amount of the acid. The addition of sulphuric acid was claimed (111) to have a similar effect on the distribution coefficient of phosphoric acid.

4. Complex metal acids - They are formed by some of the transition metals with halide and pseudo halide (CN^-, SCN^-, etc) ions. They show all the properties of the simple strong acids, with the added complication that the extractable complex has to be formed by reaction of the metal cation with the appropriate number of halide ions. One of the earliest examples is the ferric chloride - hydrochloric acid - diethylether system.

5. Coordinately unsolvated salts - These include the extraction of large ions such as Ph_4AS^+, Ph_4P^+. The size and structure of these ions are such that they do not have a primary hydration shell, i.e. no coordinate bonding to the nearest water . With the exception of hydroxylated solvents such as the alcohols, organic solvents do not possess a hydrogen-bonded structure, and the attractive interactions of the solvent molecules which must be displaced are Van der Waals' interactions of the same order of magnitude as those between the ion itself and the nearest solvent molecule.

6. Coordinately solvated salts - In order to transfer a hydrated ionic species from aqueous solution into an organic solvent, a loss in solvation energy must be compensated for in the organic phase. For the hydrogen

ion there is a unique mechanism for this solvation, but with other cations there is no such specific concentration of charge at any point on the surface of the hydrated ion. The solvation forces are therefore correspondingly weaker. This comparatively poor primary solvation which weakly basic solvents offer small ionic species is reflected in the low solubility of the latter in such solvents.

3.2 PURIFICATION METHODS OF WET PROCESS PHOSPHORIC ACID BY ORGANIC SOLVENTS

Solvent extraction processes for phosphoric acid purification did not reach industrial implementation until nearly 30 years ago. In the early 1960's there was a very sharp intensification of effort in this direction, as measured by the increasing number of patents and other scientific papers. In 1932 Milligan (183,184,185) was probably the first to attempt to use a polar immiscible solvent for purifying wet process phosphoric acid, the organic solvents which give favourable results are water immiscible monohydroxyl alcohols of not exceeding 8 carbon atoms in the chain carrying a hydroxyl group, preferably n-butylalcohol or amyl-alcohol. Ketones, aldehydes and esters are also claimed to be successful (14,41).

The extracted phosphoric acid can be recovered from the organic solvent in many ways for example by distillation, or back extraction with water, and the purer acid thus transferred from the solvent phase to the water phase (108, 215).

In selecting a purification system, one must consider how the impurities are to be rejected. One approach that is simple in concept is based on separating a fraction of the phosphoric acid in pure form leaving the remainder of the acid to carry the impurities. Another approach depends on full extraction of phosphorus pentoxide values, still a third exploits the characteristics of specific impurities in order to separate them more or less completely from the phosphorus pentoxide, as in the case of removing iron impurities (142,228,213), silica (262), vanadium and titanum (129), fluorine (215), potassium and fluosilicate (144), fluoride (71) and uranium (1,49,50,53,118,217). A fourth approach is based on extraction of impurities instead of the acid as stated by Borisov (31).

All these approaches have been made the basis of processes to be described below and summarised in Fig.(3.1). However they have not necessarily yet been commercialized.

3.2.1 PURIFICATION BY PARTIAL EXTRACTION OF THE WET PROCESS ACID

This can be further subdivided into two methods based on the solvents used:

(A) Conceptually the most straight-forward method is to extract the acid from the aqueous phase with a

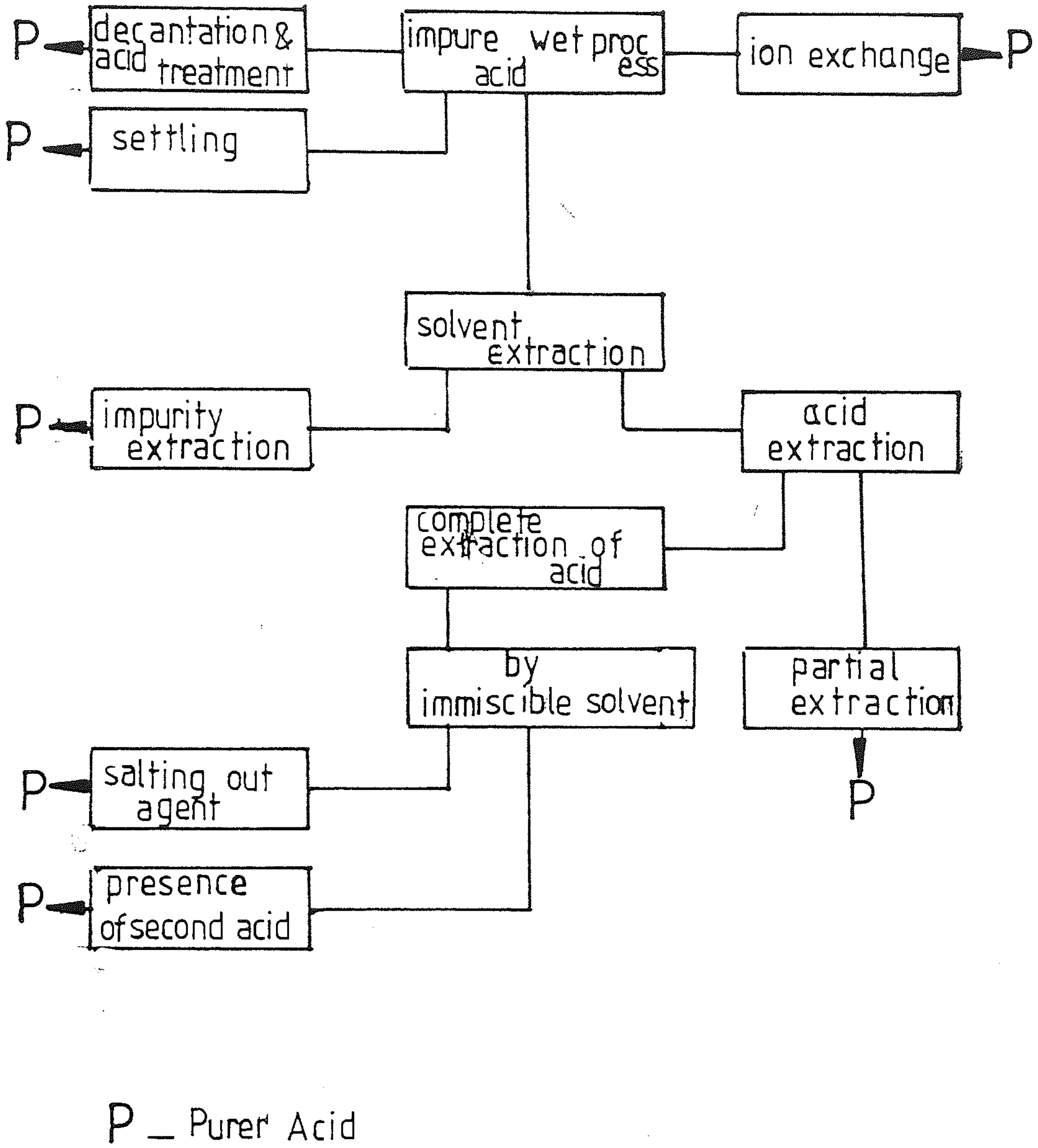


FIG 3.1 Summary OF The Purification Processes

solvent that will extract phosphoric acid at any concentration. For the solvents selected phosphoric acid should show a reasonably constant distribution coefficient down to fairly low concentration and with acceptable selectivity over impurities up to the highest concentration built up in the reject acid. Suitable solvents that may be classified in this group are mainly alcohols (26,29,30,41,55,60,271).

Vana (271) in 1934 was the first to attempt to purify wet process acid, using oxygenated cyclo-paraffins such as cyclohexanol. Other processes based on aliphatic alcohols were described by Toyo Soda Manufacturing Company in the preliminary economic estimate published by them (261). They claimed that it is possible to produce high purity acid at a cost below that provided by the thermal methods.

Solvents such as benzaldehyde and ethylacetate are also claimed by Vana (271). A mixture of a minor proportion (5-20%) of a water insoluble amine e.g. octadecylamine, dinonylamine and a major proportion of an aliphatic alcohol having 4 to 12 carbon atoms per molecule is also claimed by Archambault (9) and Milligan (185).

Alkyl phosphates and arylphosphates (e.g. tri-n-butyl phosphate) have been claimed by Bunin, Champ and Martin respectively (39,44,174) for partial extraction of acid, the method of extraction in these patents uses the same principle except in the way the acid is treated prior to its extraction. Champ and Martin suggested the addition of anions of boron, such as boric acid, and fluoride to the impure phosphoric acid to enable purified phosphoric acid to be separated by a water immiscible organic solvent without the formation of undesirable silicagel or other interfering species.

Phosphate rock addition to the acid to increase the acid concentration was reported by Bunin (39), addition of sodium carbonate as insoluble sodium fluosilicate was also claimed in the same patent.

The addition of benzene, xylene and toluene to the alkyl or arylphosphate can improve the phase separation, these solvents dilute the alkyl or arylphosphate and facilitate extraction by lowering the viscosity and density of the organic phase.

A process for purifying phosphoric acid with respect to iron impurities has been claimed by Koerner (142), it involves reducing the trivalent iron (Fe^{3+}) impurities contained in the phosphoric acid to the divalent iron (Fe^{2+}) oxidation state and contacting the phosphoric acid containing the reduced iron impurities with a water insoluble amine extractant.

Long chain alkylamines and/or amine salts preferably dissolved in an organic diluent, may be used first to remove certain impurities and then to extract the phosphoric acid from the partially purified aqueous phase using the same solvent (142,230).

A process using an ester as solvent such as butyl-acetate, amyl acetate and a mixture thereof, has been claimed by Kamaradhya (215). In this process the

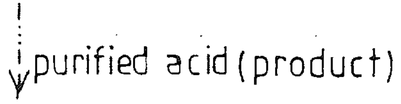


FIG 3.2 Basic Flow-Sheet For Wet-Process Phosphoric Acid Purification by ,Partial Purification, methods [261]

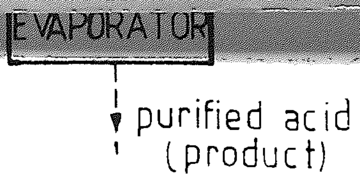


FIG. 3.3 Basic Flow-Sheet For Wet-Process Phosphoric Acid Purification by „Partial Purification„ Methods with Purification step [112]

addition of a defluorination stage was introduced to remove the chloride ion, the defluorination of the acid was carried out by adding sodium carbonate and silicic acid in order to precipitate sodium fluosilicate. However, the ester may hydrolyse in the process which is a factor of economic significance against their choice as solvents.

The above processes have a common basic flow sheet for the partial extraction of the acid as shown in Fig.(3.2) or purification step may be introduced as shown in Fig.(3.3). As a consequence they are all multistage, usually counter-current operations and the product acid is always more dilute than the impure feed acid. The higher the mutual miscibility of solvent and water, the greater will be the dilution effect but very likely the smaller will be the volume of solvent to be handled, but is not possible to predetermine whether a longer or a shorter chain alcohol will give a better overall water balance (29).

On considering Fig.3.2 and 3.3, the extraction step is to extract the phosphoric acid using any of the solvents described above; the purification step where most of the impurities (as claimed by IMI (112)) are transferred to the aqueous phase leaving pure extract saturated with acid; and the washing step which achieves its purpose when the purified acid product at acceptable concentration has been fully separated from the solvent. The final pure acid is then concentrated by removing water uisng either evaporation or distillation.

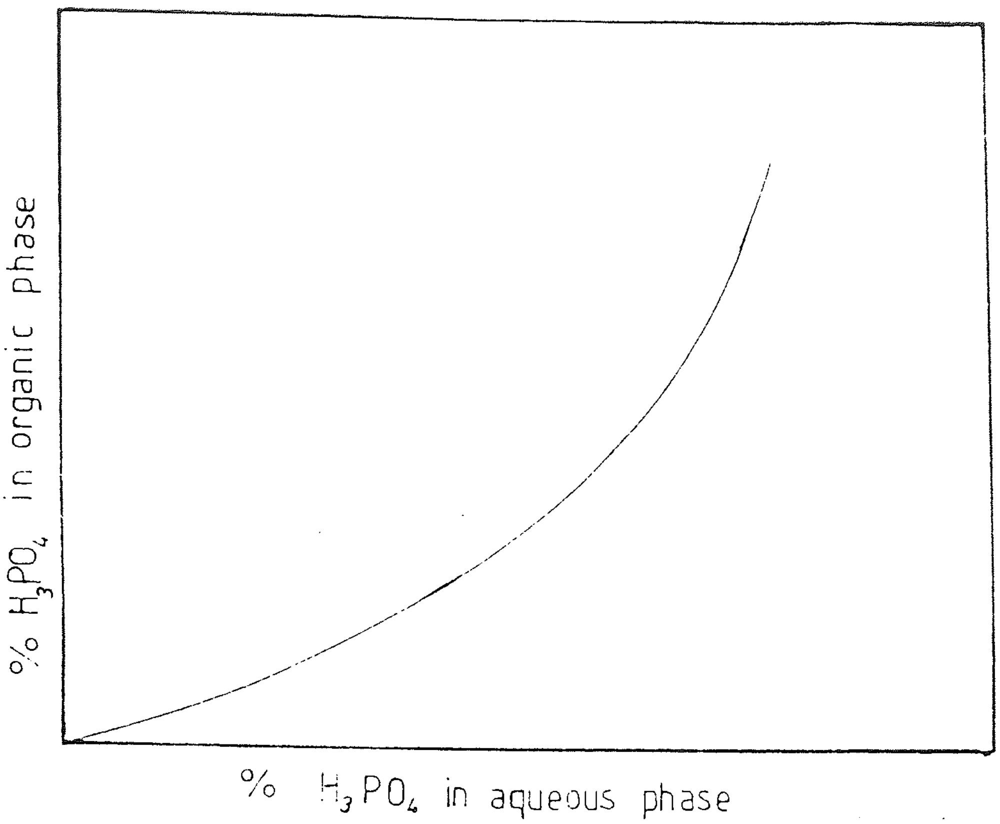


FIG 3.4 Representative Distribution Curve For Method (1)

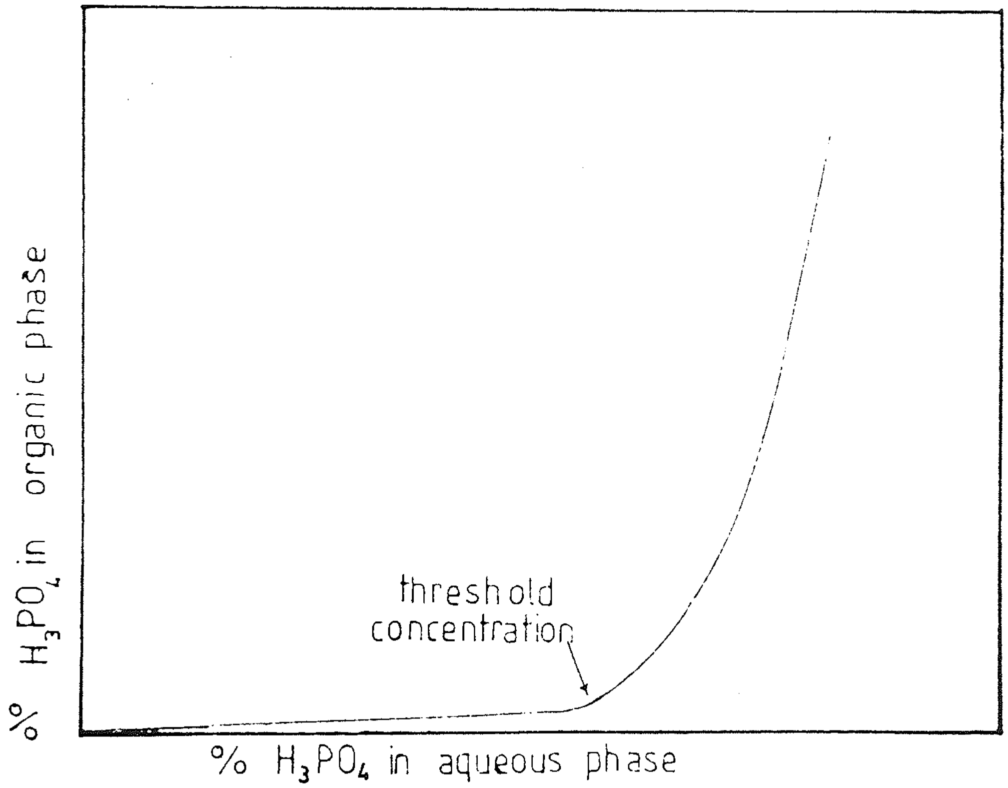


FIG 3.5 Representative Distribution Curve For Method (2)

(B) A different approach to the processes mentioned so far is based on the utilisation of solvents which show very little extraction capacity for phosphoric acid below a specific threshold concentration, in other words, the distribution coefficient of the acid is very sharply concentration dependent as shown in Fig.3.5. compared with the first type of solvent shown in Fig.3.4. However, this method will have limited potential compared with the solvent types used for method A, since no increase in extraction stages can now increase the yield. On the other hand compared with the solvents of method (A) the operation may be simplified since the extraction can be performed in fewer contact steps. Ethers, glycol ethers, esters and selected ketones were included in this group (29) and their threshold concentration was found to be temperature dependent.

Based on the above method IMI (109) claimed that some of these solvents when added in a sufficient amount to an aqueous H_3PO_4 solution at temperatures within a range depending on the solvent, three phases can form and co-exist, a bottom phase comprising predominantly an aqueous H_3PO_4 solution, an intermediate phase comprising predominantly an H_3PO_4 solution in the solvent and a top phase comprising predominantly the solvent.

Schallert (293,240) and Yacu (282) claimed that on using di-iso-propylether (IPE) and diethyl ether (EE) to extract phosphoric acid a three phase region was formed. Schallert's conclusion was that a complex was formed under critical conditions, of the form

$H_3PO_4 \cdot H_2O(C_3H_7)_2O$ with a composition 45% H_3PO_4, 8% H_2O and 47% IPE, in the case of diethyl ether EE the complex was $H_3PO_4 \cdot H_2O(CH_3 \cdot CH_2)_2O$. The three-phase region is a moderately thin liquid which was not appreciably soluble in either aqueous H_3PO_4 solution of lower than a certain threshold concentration (68% H_3PO_4 with IPE and 53.8% H_3PO_4 with EE) or in excess solvent. The total amount of phosphoric acid complexed with the solvent was found to be linearly proportional to the acid concentration for aqueous solutions having H_3PO_4 concentrations higher than the threshold values. The effect of temperature on the system H_2O-H_3PO_4-solvent (e.g. H_2O-H_3PO_4-n-butyl ether) was reported by Baniel and Blumberg (18) who showed that in some cases the capacity of solvent to extract phosphoric acid from water varies inversely with temperature. Therefore, advantages have been claimed by extracting the acid from the aqueous phase in the extraction step at low temperature (0-5°C) so as to give a homogeneous mixture, and then to release the acid from the extract in the washing step at a high temperature (40-60°C) with or without addition of water. By this treatment the purified portion of the acid could be recovered at relatively high acid concentration. Other solvents included in this category and reported in references (20,21,107,110) are di-ethylether, di-n-amylether, glycol ethers such as di-ethylene glycol, esters such as butyl acetate and ketones such as cyclohexanone.

Blumberg and Simon (20) claimed an improved process for extracting phosphoric acid with a mixture of at least two extracting solvents each of which was capable of extracting phosphoric acid from aqueous solution which has threshold values of acid concentration of 35%.

Yacu (282) selected four different solvents (n-amyl alcohol; tri-butyl phosphate; di-siopropyl-ehter and methyl-iso-butyl ketone. His experimental results were based on a small scale batch mixer and his conclusion was that solvent extraction can be successfully applied for purification of phosphoric acid, and isopropylether was the most suitable solvent among those studied. However the possibility of peroxide formation may constitute a potential hazard. Although the three layer formation may cause operational difficulties, this could be overcome by precise flow rate control.

Albright and Wilson Ltd (2), claimed a process based on a solvent chosen from saturated cyclic ketones containing five or six carbon atoms. Of these methyl-iso butyl-ketone (MIBK) was preferred when extracting a concentrated phosphoric acid (70%) because it has a high flash point (24°C) and is therefore not unduly hazardous. If less concentrated acid is to be used (40-42%) a pentanone such as diethyl ketone or methyl-n-butyl ketone can be used.

Other plants and processes based on partial purification of phosphoric acid were reported in references (26,67,66).

3.2.2 PURIFICATION BY COMPLETE EXTRACTION OF PHOSPHORIC ACID

All the purification processes referred to above have the advantages of leaving a residual acid to carry the impurities. The lowering of the quality of the residual acid thus bears a direct relation to the quantity of the purified acid produced, so even though the impure residual acid can often be accommodated in a wet phosphoric acid fertilizer, complex processes which permit essentially full purification of the phosphorus pentoxide values may sometimes be preferred.

The purification by complete extraction of the acid can be explained using two possible procedures.

I. Complete Extraction with Immiscible Solvent

Two types of process have been described.

(A) Purification in the presence of salts

Salts such as calcium chloride or calcium nitrate may be added to the impure phosphoric acid. The degree of extraction and the purity of the produced phosphoric acid is enhanced by controlling the calcium chloride content with respect to the P_2O_5 concentration in the aqueous medium prior to the extraction with organic solvent (18). The processes are based on the same principle as that used in production of phosphoric acid by acidulation of phosphate rock with hydrochloric acid as reported in (60,169,241) or by treating the phosphate rock with an approximately stoichiometric amount

FIG 3.6

Purification of Wet_Process
Phosphoric Acid With $CaCl_2$
In Cycle [19]

FIG 3.7

Purification of Wet_process
Phosphoric Acid With External
Sourse of HCL(18)

(45 to 65%) of concentrated nitric acid (81,270).

Cationic impurities remain with the $CaCl_2$ in the form of chlorides and the calcium salt used to promote phosphoric acid extraction may be recycled after precipitation of accumulated impurities and reconcentration (19), or it may be generated in each cycle by dissolving a part of the phosphate rock with the appropriate acid (HCl) (17). The basic flow-sheets for both methods are shown in Figs.(3.6) and (3.7). The hydrochloric acid may be added to the organic solvent or it may be added to the wet process acid along with the calcium chloride. The concentration of calcium chloride needed to produce greatest extraction of phosphoric acid depends on the acid concentration itself. When the initial acid concentration is low the Ca^{2+} content must be relatively high, and vice versa. The effect of Ca^{2+} on the distribution coefficient of phosphoric acid at various concentration and $CaCl_2$ concentrations was studied by Baniell (19) and his experimental results are shown in Table (3.1) where the effect of calcium chloride on extractability of H_3PO_4 is not always positive. The contact time has to be selected so that substantially all of the phosphoric acid is extracted from the aqueous reaction mixture without simultaneous coextraction of appreciable amounts of the more slowly extractable calcium chloride. Hydrochloric acid is added to prevent the formation of calcium phosphate and to increase the distribution coefficient of phosphoric acid (243).

Table 3.1

Influence of $CaCl_2$ on the extractabilty of H_3PO_4 in the system H_3PO_4 – $CaCl_2$ – H_2O – i-AmOH(17,19)

The solvent extracted containing phosphoric acid and a quantity of hydrochloric acid, is washed with water, and phosphoric acid and hydrochloric acid are transferred to the aqueous medium, thus freeing the solvent for recycle.

Alcohols such as butanol or amylalcohol and trialkyl phosphates, such as tri-n-butyl phosphate which show reasonably constant distribution coefficients down to fairly low H_3PO_4 concentrations are suggested to be suitable organic solvents. The above procedure can be equally applied to fresh wet phosphoric acid and to residual acid (29). Although the method has the advantage of extracting all the H_3PO_4 value, the process is relatively complicated and can be rather costly if HCl and $CaCl_2$ can not be cheaply provided. However, a plant based on this approach using isoamyl alcohol as the extracting solvent was constructed by IMI (16) in 1961. Another was constructed by Foret S.A. Spain in 1969 (66,67).

Ishibashi (113)described a process based on the same principle. However wet process phosphoric acid was treated with 10-1000% of methanol, ethanol, isopropane, dimethyl butane and 1% of aqueous sodium, potassium, or ammonium hydroxides, sulphates, nitrates, halides or phosphates at 0.05-0.4% per mol P_2O_5 at 0-60°C. The precipitate was separated by filtration or centrifugation, the solvent was then distilled and extracted with 10-1000% of 2-ethyl hexanol.

Mills (187) treated wet process phosphoric acid with a precipitate containing Ca^{2+} and F^- ions at a Ca^{2+}/F^- mole ratio of 1:2 for the removal of Mg^{2+} and Al^{3+}, the precipitation was accelerated by adding polyacrylamide.

Masaki (176) and Takahashi used H_2SO_4 and Ba compounds instead of hydrochloric acid and calcium compounds.

(B) <u>Purification in the presence of a second acid</u>

A different approach is to add a second acid to the phosphoric acid to boost the hydrogen ion level, thus permitting the continual extraction of phosphoric acid (111). The addition of the second acid (e.g. H_2SO_4) to the wet process phosphoric acid can improve the distribution coefficient of H_3PO_4. Although sulphuric acid for instance is also extracted by the solvent, its proportion is normally less than that in the feed, the basic flow sheet of the process is similar to those for partial purification and any suitable immiscible solvent may be used.

The method has been recommended for extracting phosphoric acid from aqueous raffinate solution resulting from the partial purification method (247). The amount of other acid to be added is from 30 to 100% by weight of the H_3PO_4 and the mixture is then subjected to a further extraction with an organic solvent of the same kind as that employed in the primary extraction stage.

Although most of the H_3PO_4 values may be recovered the method still has the disadvantages that the final aqueous phase is rich in sulphuric acid together with the impurities, which might not have an end use, therefore extra cost could be involved in disposal.

Impure wet process phosphoric acid can also be treated with an acid that has an anion which forms a precipitate with an impurity. The resulting mixture is then treated with water miscible solvent to precipitate the impurity. The liquid phase is recovered and distilled to remove the solvent for recycle.

Ammonia may be added to the acid along with the second acid as claimed by Burova (40). Toyo Soda (262) described a process to remove organic impurities, based on treating phosphoric acid with HCl and chlorate at a temperature of 100°C. James (117) claimed the use of water immiscible organic acid phosphate in conjunction with water immiscible organic sulfonic acid, which results in an improvement in the purification of phosphoric acid. Winand (281) described a process where SO_4^{2-} ions are continuously removed from an organic phase, immiscible with H_2O, containing the H_3PO_4 and H_2SO_4, and the liquid-liquid extraction is carried out in three zones, each including one or several mixer-decanters, the throughput ratio of organic to aqueous phase is 5:1 in zone 1, 2:1 to 20:1 in zone 2, and 20:1 in zone 3.

Occidental petroleum corporation (198) described a process using immiscible solvent without addition of acid or a salt. The process comprised extracting the impurities from phosphoric acid using primary amine in an amount of up to 50% by volume and a water immiscible organic solvent for the primary amine. The resultant acid was observed to be water-white and non-turbid.

II. Complete Extraction with Miscible Solvent

It has been found that the impure acid (the raffinate acid generated by partial extraction of phosphate from wet process phosphoric acid as well as the original phosphoric acid product) can be purified by precipitation of the impurities (82), the precipitate could be separated by filtration and the solvent by distillation before it is recycled to the process. The precipitation of impurities results from the mixing of two immiscible solvents, preferably a mixture of 1:3 methanol to isopropanol (82), gives a better result than that achieved with either alcohol individually. The weight ratio of alcohol blend to the impure wet process phosphoric acid normally ranged from 1:1 to 2:1. A disadvantage is the greater amount of alcohol which has to be distilled out.

Schroeder (242) treated the wet process acid with methanol to precipitate ammonium sulphate, ammonium phosphate, and inorganic impurities and the precipitate was then separated by filtration. Other organic solvents such as methyl and ethyl alcohol or acetone are also claimed especially when applied in conjunction with the addition of ammonia (226) or the addition of the crude acid of a soluble inorganic salt, particularly a salt of an alkali metal where it facilitates the precipitation of impurities, particularly fluosilicate. The addition of these compounds although it improves the quality of the acid, also decreases the amount of recovered H_3PO_4. This approach has other limitations, the product although of improved quality, is still far from pure acid and contains a considerable amount of impurities. Subsequent purification using a strongly acid cation exchange was suggested (79).

Chern (50) described a process for the purification of acid from organic material using kerosene.

Kohayagawa (145) described a process where the impure H_3PO_4 solution was mixed with an organic solvent and aqueous solution of sulphide. The solution was then filtered, and the organic solvent removed from the filtrate to produce pure H_3PO_4.

3.2.3 ADVANTAGES AND LIMITATIONS OF PARTIAL PURIFICATION METHODS

Partial purification methods have the following advantages (18):

1. Practical extraction usually necessitates operating with high acid concentration. Although this is a limitation, it provides high throughput per unit equipment volume.
2. A small number of operations and no additional materials are needed.

3. Distillation or evaporation are only used for stripping solvent from the aqueous phase and not for the main solvent recovery.
4. The product can be recovered with relatively little reduction in its concentration compared with the feed.

The method has the following limitations:

1. Feed acid concentration should normally be high to make the process economically attractive, but the feasible concentration will depend on the solvent used.
2. The residual acid containing the feed impurities must be used in the production of solid phosphate fertilizers, or in some other processes where purity is not a critical property.
3. Some impurities are only partially removed.

In general the following results can be achieved from partial purification.

1. The fraction of purified acid may be increased up to 90% depending on the solvent phase ratio and the number of extraction stages.
2. Colour should be greatly improved.
3. Total cations, excluding H^+, can be reduced to 0.1-0.2%.

3.2.4 OTHER PURIFICATION METHODS USING SOLVENT EXTRACTION

The purification of phosphoric acid using solvents such as alcohols has, along with its positive aspects, a number of shortcomings which hinder its industrial realization - the use of large volume of flammable organic compounds, incomplete extraction of P_2O_5, losses of extractant during, e.g. distillation.

A method suggested by Borisov V.M. (31) is based on extraction of impurities in the acid from the aqueous solution rather than extracting the acid from the aqueous solution. Organophophoric, carboxylic and sulfonic acids may be used as solvents. The latter, for example, consisting of a mixture of isomers of alkylbenzensulfonic acid having the general formula $R\ SO_3H$ with from 14 to 30 carbon atoms and a molecular weight of from 360 to 400. It is a brown, oily, viscous liquid which is insoluble in water; however it can be extracted with kerosene.

3.3 THE RECOVERY OF SOLVENT FROM AQUEOUS ACID

Various methods are available for the recovery of phosphoric acid or conversion products from the extraction liquid, for example it can be separated by distillation and a normal column with a suitable number of plates can be used. This method has the disadvantage that part of the organic material in the extraction liquid may be broken down due to the dehydrating effect of the orthophosphoric acid. Where the extraction liquid contains alcohol, for example, it may be in part broken down during the distillation with the resultant conversion of part of the solvent into olefines; ethers may also be present (18).

It is also feasible to either completely neutralize the acid, employing, for example, sodium carbonate and/or hydroxide, or to carry the neutralization to the point at which little or no free orthophosphoric acid is left.

Crystallisation may alternatively be employed to separate the dissolved phosphoric acid compound, and in this case the orthophosphoric acid in the extraction liquid may be neutralized with ammonia.

It is also feasible to neutralize the acid with a base producing a salt, which separates from the extraction liquid by precipitation, and then to recover the extraction liquid by decantation or filtration.

Another method of recovering the phosphoric acid compounds from the extraction liquid consists in adding to the extraction liquid a second substance or substances, preferably liquids, which are soluble therein, but which are not perse solvents for orthophosphoric acid, or which dissolve orthophosphoric acid to a much lesser extent than the extraction liquid. Hydrocarbons and particularly the light hydrocarbons less than 15 carbon atom to the molecule are suitable for this purpose.

Finally Milligan (185) in 1933 described a simple and economical method of separation of the phosphoric acid from the extraction liquid. On contacting the water with the extracting solvent the phosphoric acid passed into the water layer. With certain extraction liquids the phosphoric acid would pass almost completely into the water phase, the final acid concentration could be adjusted by limiting the volume of water. The extraction of acid by water was improved by increasing the temperature above that where primary extraction takes place (110).

After contacting the extraction liquid with water it may ordinarily be recycled without further treatment, and utilized directly for the extraction of further batches of phosphoric acid. The phosphoric acid separated in the water phase may either be utilized as such, or converted by suitable treatment into any other form required by the market.

3.4 ACID CONCENTRATION

There are two stages where phosphoric acid needs to be concentrated. The first is after phosphate rock is reacted with a mineral acid and the resulting slurry is filtered to obtain a relatively dilute phosphoric acid. This acid needs to be concentrated for subsequent treatment, for example, in purification by extraction. The second occurs after back extraction of solvent with water in the purification plant. The resulting acid is diluted and needs to be concentrated for shipping.

Phosphoric acid may be concentrated by using high-temperature heating methods, consisting essentially of producing from a generator or an immersed burner hot gases at 1000°C or more, which are brought into contact with the acid to be concentrated. These methods suffer from several serious drawbacks because gases have to be handled which are extremely hot and which entrain large volumes of fumes loaded with acid droplets. These mists tend to form aerosols which cannot be collected completely under practical conditions, thus leading to losses of acid and to atmospheric pollution (11).

Phosphoric acid may also be concentrated by steam-heated vacuum evaporators. Although efforts have been made to heat the acid under such conditions as to assure a relatively uniform heating, the acid is close to, or in contact with the heat-transfer medium which makes it advisable in some cases to apply some form of agitation to prevent localised overheating. Wet process phosphoric acid contains impurities which tend to form metal phosphate solids on the surface, and thus constitute a substantial loss (216).

Another method of concentrating dilute acid is by electrolysis in which a direct current is applied to electrodes placed in the acid with the evolution of hydrogen and oxygen. The obvious drawback of this process is the evolution of hydrogen and oxygen in the proportions as obtained from the electrolysis of water.

If not separated, the gases in these proportions are highly explosive. Also on using this method fluorine containing compounds may contaminate the hydrogen and oxygen which will impair their usefulness as raw materials.

Peter (210) described a process for concentration of phosphoric acid which comprises contacting it with hot combustion gases to heat it to a temperature of between 120°C and about 180°C at atmospheric pressure so as to evaporate volatile impurities and water. After this step, the acid is subjected to a sub-atmospheric pressure (about 50 mm Hg) in the absence of any further heating to effect molecular dehydration of the acid and remove additional water vapour. Other methods to concentrate phosphoric acid are described in references (18,101), and a typical process based on sludge circulation is shown in Fig.(3.8). Fig.(3.9) shows typical evaporating unit.

The materials of construction for the equipment have to be carefully selected (see Appendix D due to the nature of the process and the chemical compounds handled. Materials suitable for construction of the vessel include those that are corrosion resistant, have low or no electrical conductivity and can withstand prolonged operation at high temperature. The choice of material is dependent on the concentration of the acid being sought. Among the suitable materials for the vessel are fibre reinforced polyester, polytetrafluoro ethylene , polypropylene, or acid resistant brick. Polypropylene was successfully used in the

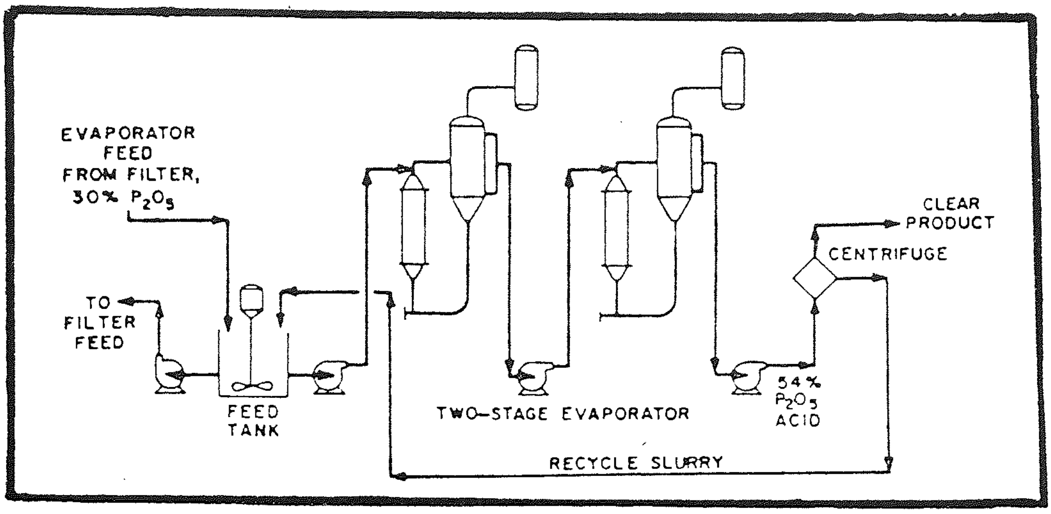


FIG 3.8

Typical process for phosphoric acid concentration based on sludge recirculation

FIG 3.9

Typical phosphoric acid evaporator (18)

continuous concentration of dilute wet-process phosphoric acid to concentrated acid containing 50-60% P_2O_5 content. For the concentration of acids containing the polyphosphoric acids, acid resistant brick can be used (10).

3.5 BEHAVIOUR OF SOLVENTS IN TERNARY SYSTEMS AND SELECTION OF SOLVENT

If the principle purpose of extraction is to remove the impurities present in the wet process phosphoric acid by extraction of the acid, a wide choice of solvents is possible. In fact many widely different solvents have been stated to be suitable for the extraction of acid, apparently without preference for any particular type of solvent. In choosing a solvent, there are several principles that can be used as a guide, bearing in mind that no single substance would ordinarily possess every desirable characteristic.

1. Selectivity

This refers to the ability of a solvent to extract one component of a solution in preference to another. Therefore, the solvent should be as selective as possible for the phosphoric acid over the water and impurities. In other words the most suitable solvent from this point of view would dissolve a maximum of phosphoric acid and a minimum of impurities and water.

The selectivity β of a solvent (B) for solute (C) is defined as the ratio of concentration of non-consolute (A) in the solvent-rich phase divided by the ratio in the aqueous rich phase; therefore it can be written mathematically as:

$$\text{(selectivity)} \qquad \beta_{CA} = \frac{X_{CB}}{X_{AB}} \cdot \frac{X_{AA}}{X_{CA}} \quad \text{------} \quad 3.1$$

The numerical value of β_{CA} will be the same whether weight or mole fraction units are used for concentration, but in most cases β varies with concentration (265); and is too low in the case of phosphoric acid (21).

Practical processes require that β exceeds unity; the more so the better, if $\beta=1$ separation is impossible. Therefore, if selectivity is close to unity it will result in large plant equipment, large numbers of extraction contacts or stages, and in general, costly investment and operation.

The above equation can be arranged as:

$$\beta_{CA} = \frac{X_{CB}}{X_{CA}} \cdot \frac{X_{AA}}{X_{AB}} \quad \text{------} \quad 3.2$$

$$= D_C \cdot \frac{X_{AA}}{X_{AB}}$$

A system with an unfavourable distribution coefficient ($D_C < 1$) will not necessarily give values of β less than unity except if the mutual solubility of A and B is considerable .

2. Distribution Coefficient (D_C)

High values of distribution coefficient are desirable since it influences selectivity, and in turn the number of contact stages required. This will effect the capital and operating costs.

3. Capacity

Large solvent capacities to dissolve the preferentially extracted solute are required to minimise the amount of circulated solvent. High values of X_{CB} are therefore required in addition to high values of distribution coefficient. In some cases (not in the case of phosphoric acid since the non-consolute is always water), a compromise between high selectivity and high solvent capacity must be made (265).

4. Solvency (Solvent Solubility)

The solvent should have minimum solubility in the raffinate acid phase, to reduce or eliminate the cost of recovery. Substantial improvement in solvent solubility characteristics may sometimes be brought about by even moderate changes in temperature.

5. Reversibility (Recoverability)

It must be possible to reverse the extraction process, i.e. to remove the solvent from the product for reuse. This parameter dominates the economics of many processes.

6. Cost

Ideally, the solvent should be cheap, but cost alone is rarely critical in comparison with other parameters.

7. Availability

The solvent should be readily available from more than one supplier. Otherwise the supply may be too easily interrupted.

8. Physical Properties

Reasonably high values of interfacial tension, and density difference from phosphoric acid solution, help promote rapid phase separation. Similarly, a low viscosity promotes both mass transfer and phase separation, potentially reducing plant size, power input requirements, or both.

9. Safety

Toxicity (effects caused directly to operators or effects caused by losses to the phosphoric acid stream) and flammability are important parameters.

To understand the behaviour of different solvents for extraction of phosphoric acid, a knowledge of the phase equilibrium of the system is vital. The shape of the ternary diagrams and the relative size of the heterogeneous area is different from one solvent to another. It is also different for impure phosphoric acid compared with pure phosphoric acid as reported by Yacu (282). Therefore the whole extraction pattern will be affected. At a particular concentration of phosphoric acid one solvent may appear to be suitable, while at a different concentration this solvent may be unsuitable, because the phases might become completely miscible.

Several workers have studied the phase equilibrium diagram for phosphoric acid-water-solvent. In 1959 Seaton and Geankoph (243) studied the theory of solvent extraction by organic solvents for both HCl and H_3PO_4. They selected four solvents n-butanol, 2-hydroxethyl, n-hexylether, cyclohexanol and i-amylalcohol. They studied the effect of concentration and temperature on the distribution coefficient of both acids, and the effect of concentration on the mutual solubility of water and solvent. Their conclusion was that alcohols were the best solvents for the extraction of both HCl and H_3PO_4. However, ketone and ether show some ability to extract them. Those solvents which are best for hydrochloric acid are also best for phosphoric acid. However KHCl is greater than KH_3PO_4 for the same solvent.

The following can be concluded from the study of the various phase diagrams. Binodal curves were determined by the cloud point method (273).

1. The binodal curve of most alcohol systems is not affected when the temperature changes from 25°C to 35°C (147).

2. For those ethers studied, it was found that the tie lines diverge fanwise from the ether corner towards the phosphoric acid-water-binary system and that a solvent with a given number of carbon atoms is more effective for the extraction of acid if it has an iso rather than a normal structure.

3. For those ketones studied (160), it was found that straight chain aliphatic ketones with assymmetrical molecules such as methyl hexyl ketone are better than symmetrical ketones, such as di-iso-butyl ketone, for which all the tie lines almost converge at the solvent corner and the partitition coefficients are close to zero.

4. The heterogeneous region within each group of solvents increases with increasing length of carbon chain of the solvent molecules, and therefore the mutual miscibility between the aqueous and solvent phases decreases accordingly. Hence the longer the solvent molecule chain, the higher should be the feed acid concentration to achieve practical extraction.

5. The higher the mutual miscibility, the greater will be the dilution effect; however, conversely the smaller will be the amount of solvent to be handled.

6. The maximum of the binodal curve with most solvents is shifted towards the phosphoric acid-water binary system.

7. The partition coefficients of phosphoric acid between the aqueous and organic phases may increase if two solvents are used rather than one solvent.

8. The presence of amine salts as a fourth component effect the system H_2O-H_3PO_4-n-butanol in different ways. N-butylamine reduces the heterogeneous area as its concentration is increased (158). However triethylamine increases the heterogeneous region. The same effect, but to a lesser extent, is demonstrated in the presence of 10% diethylamine, and both amines were found to increase the distribution coefficient of the acid. When the diethylamine content was increased to 40% the whole binodal curve could not be investigated owing to crystallization of the amine salt with increasing acid concentration.

9. Layer inversion was observed in the investigation of phase equilibrium of the system furfural-water phosphoric acid at 25°C (150).

It can be concluded from the work of Walter et al (275), on their study on eight solvents that:

10. The higher the initial H_3PO_4 concentration, the better the extraction.

11. The addition of ammonia increases the separation of the impurities but decreases the amount of H_3PO_4 extracted.

12. Increase in the anion impurities (SO_3,F) increased the extraction of the impurities but also increased the extraction of metallic impurities.

    Yacu (282) on his studies on four solvents concluded the following:

13. As the concentration of the acid increases, the density and viscosity of the phases is increased.

14. The formation of a three layer region when iso-propyl-ether was used as solvent, although it is the most suitable solvent among the four solvents selected; the possibility of peroxide formation may constitute a potential hazard.

15. As acid concentration increases, the interfacial tension also increases which results in smaller drops and longer settling times of the dispersed phase.

16. The presence of cationic impurities results in a larger heterogeneous area, smaller distribution coefficient and longer settling time for a mixture containing low acid concentration. As acid concentration increases, settling time decreases.

Table (3.2) summarises some of the systems with remarks on their suitability as solvents, while Fig.(3.10) represents the shape of the ternary phase diagrams of the systems water-phosphoric acid-solvent using:

A - Solubility of solvent (wt %) in water in the binary system.

B - Solubility of water (wt %) in solvent in the binary system.

C - Maximum point of the binodal curve in wt %.

D - Critical isothermal solubility point (plait point).

3.6 CLASSIFICATION OF LIQUID-LIQUID EXTRACTION EQUIPMENT FOR PHOSPHORIC ACID EXTRACTION

The intimate contacting of the two liquid phases is bought about by various devices which produce localised turbulence. This turbulence produces a dispersion of one phase in the other and provides a large surface area for mass transfer at the phase boundary. The contacting of wet process phosphoric acid solution with the solvent is no different, and can be effected in many ways. However, it is possible to make an immediate division of the equipment into two main categories (39). Although not directly relevant to this work, these are:

(A) Batchwise (Stage Contactors)

This is done by stirring the two materials (phosphoric acid solution and solvent) together in a vessel. The solvent phase can then be separated by decantation or in a simple separating funnel, this

Solvent	Temp. °C	A	B	C		D		Ref.	Remarks
				Acid	Water	Acid	Water		
N-BUTYL ALCOHOL	25/35	7.5	20	42.7	50.0	35.5	37.7	147	Good solvent but expensive
ISO-BUTYL ALCOHOL	20/30	9.5	14.5	47.0	45.0	33.0	26.0	146	Good solvent but expensive
N-AMYL ALCOHOL	20	2.6	10.0	67.5	27.7	61.5	21.5	156	Good solvent but expensive
ISO-AMYL ALCOHOL	25/35	3.5	9.5	65.8	33.0	61.2	27.7	147	Good solvent but expensive
CYCLOHEXANOL	25/35	3.6	11.4	61.3	35.5	56.0	29.7	152,205	Good solvent, freezing point is 24°C, very viscous
PHENOL	25	8.6	29	-	-	-	-		Poisonous, must be avoided
DIETHYL ETHER	25	6.53	1.2	48.5	40.0	-	-	12	Boiling point is 34°C, dangerous
DIPROPYL ETHER	25	0.17	0.23	81.4	14.0	53.1	5.8	157	Partion coefficient is nearly equal to zero
DI-ISOPROPYL ETHER	25	1.37	0.38	61.0	29.0	44.0	12.0	159	Formation of three layers and peroxide
DI-BUTYL ETHER	25	0.18	0.66	90.0	8.0	57.0	4.0	159	FOrmation of three layers and peroxide
DI-ISOAMYLETHER	25	0.24	0.64	96.9	3.7	67.0	2.0	159	Expensive, makes it uneconomical for industrial use
METHYL ETHYL KETONE	25	23.5	11.5	14.8	53.0	11.0	34.0	154	Can only extract acid at low concentration
CYCLOHEXANONE	25	8.6	5.4	31.9	50.8	27.4	38.0	154	Can only extract acid at low concentration
ACETO PHENONE	25	0.71	1.37	CRYSTAL FORM AT HIGH CONC				154	Crystal formation
METHYLHEXYL KETONE	25	0.19	1.12	79	18	69	18	160	Promising solvent, but it is very expensive
DI-ISOBUTYL KETONE	25	0.19	1.41	90.3	7.0	48.4	4.0	160	Partion coefficient is nearly zero
BUTYL ACETATE	25	0.76	1.46	72.4	26	48.5	13.8	161	Good solvent and cheap
ETHYL ACETATE	25	7.47	3.58	45.6	42	27.8	18.8	161	
AMYL ACETATE	25	0.22	1.2	78.8	20.0	44.3	8.6	161	
METHYL ISO BUTYLKETONE	35							206	Good solvent
FURFURAL	20							150	Maximum phosphoric acid in the extract reached 51%
BENZALDEHYDE	25	0.33	0.3	77.1	20.8	58.1	12.1	151	On oxidation benzoic acid is formed
SAUCYLADEHYDE	25	0.58	0.98	78.5	16.6	40.7	5.65	151	
N-BUTANOL + 10% TRI-ETHYLAMINE	25	0	1.0	48.0	42.0	38.0	22.0	158	Maximum acid in the extract reached 52%
N-BUTANOL + 10% N-BUTYLAMINE	25	11.0	23.0	4.8	60.0			158	Maximum acid in the extract is only 4.9%
N-BUTANOL + 10% DI-ETHYLAMINE	25	10.0	19.0	48.0	42.0	41.0	25.0	158	Maximum acid in the extract reached 48%
N-BUTANOL + 40% DI-ETHYLAMINE	25			CRYSTALLIZATION				158	Salt Crystallization

TABLE 3.2 SUMMARY OF SOME EXTRACTING SYSTEMS

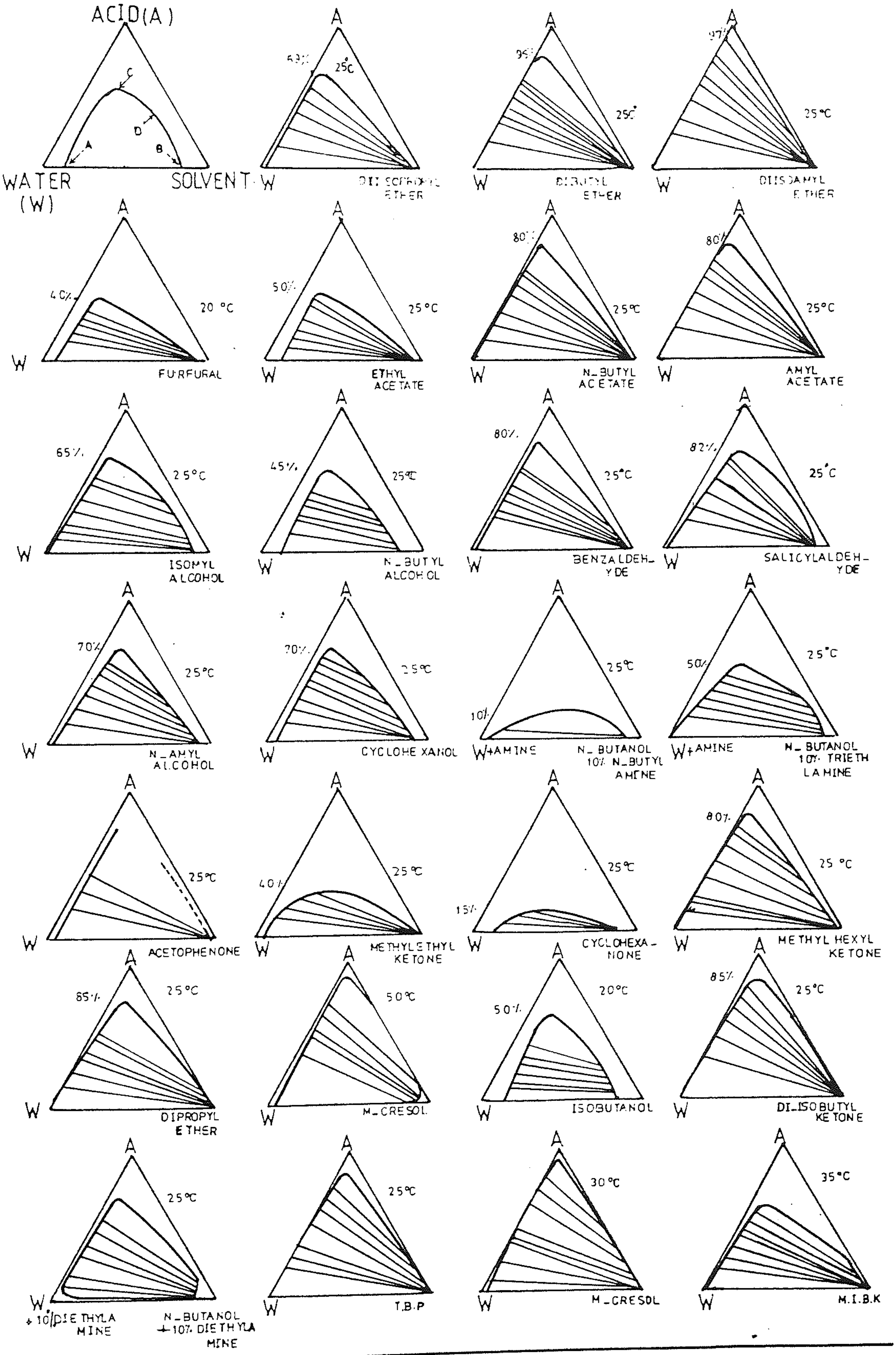


FIG 3.10 TERNARY PHASE DIAGRAMS OF SOME OF THE SYSTEMS WATER_SOLVENT_PHOSPHORIC ACID

class includes mixer-settler types of equipment and perforated plate columns.

Yacu (282) carried out his experimental work on phosphoric acid purification in a jacketted batchwise mixer as shown in Fig. 3.11.

(B) Continuous (Differential Contact) Extractors

Here the contact of the solvent and phosphoric acid solution is brought about by continuous counter current extraction where equipment of many stages may be incorporated into a single apparatus, these can be categorised as follows:

1. Gravity operated extractors which include:
   (a) non-mechanical dispersion (Fig. 3.12)
   (b) mechanically agitated extractors (Fig. 3.13)
2. Centrifugal extractors

A typical classification of the above equipment is shown in Fig. (3.14).

Liquid-liquid extraction equipment could also be classified into vertical column type and horizontal extractors. The former are further divided, according to the mode of agitation provided for the inter-dispersion of liquids as unagitated rotor-agitated and pulse-agitated columns. The principal types of contactors are classified according to this method in Table 3.3.

In batch processes, the volume of the vessel is that of the batch plus that corresponding to the fireboard above the top of the liquid. For continuous processes, the volume of the contained liquid assuming

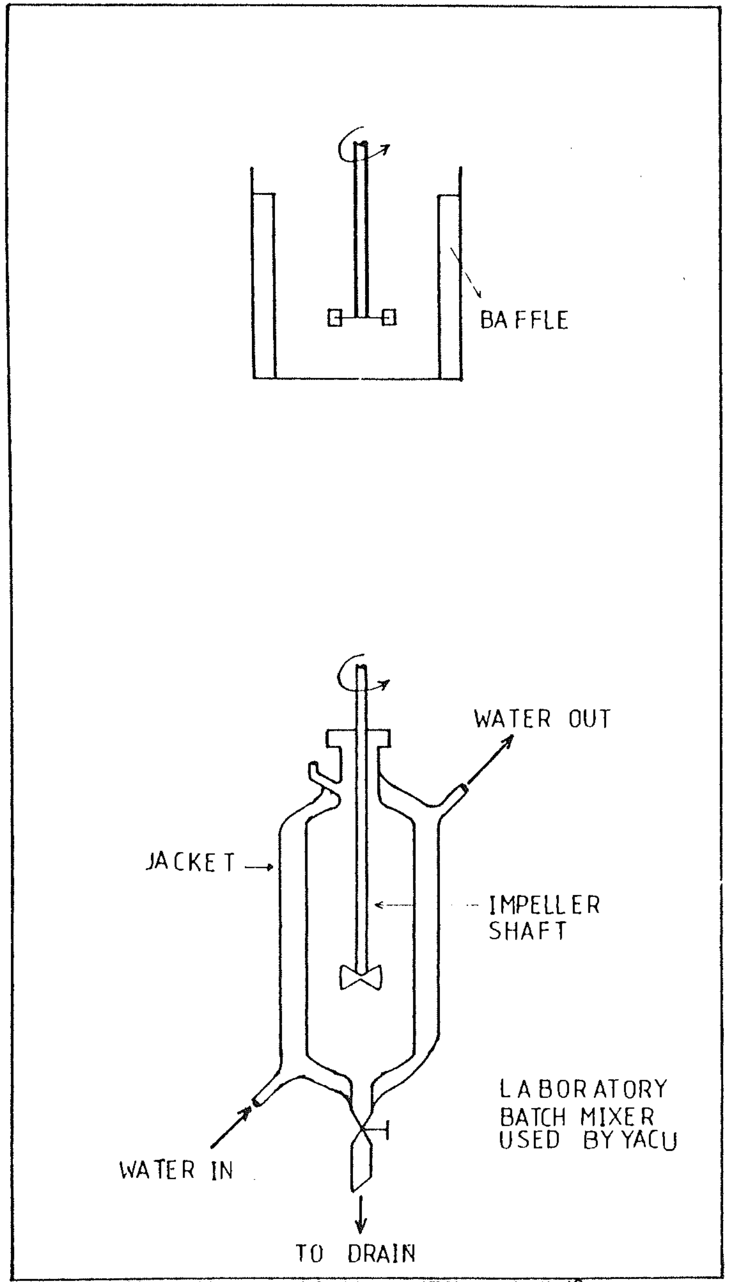
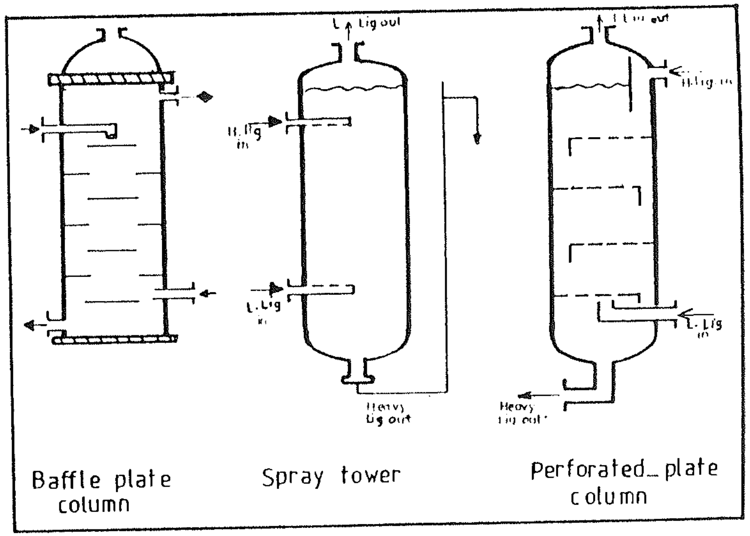


FIG 3.11 TYPICAL BATCH MIXER'S

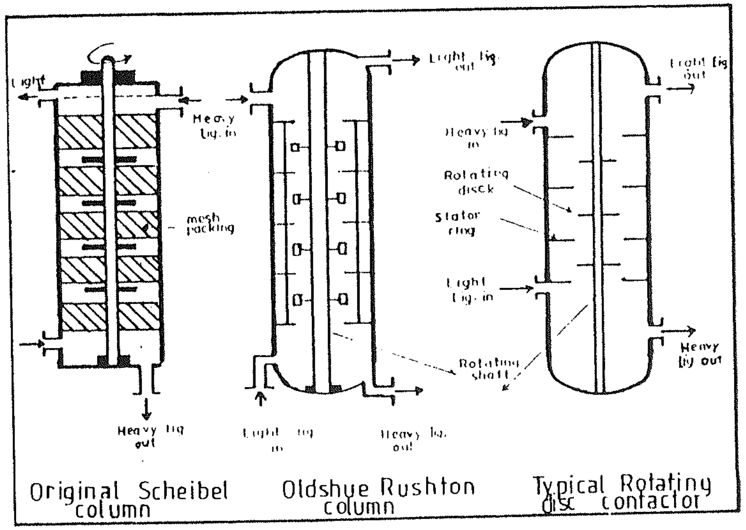


Baffle plate column

Spray tower

Perforated_plate column

FIG 3.12 Non mechanical extractor's



Original Scheibel column

Oldshue Rushton column

Typical Rotating disc contactor

FIG 3.13 Mechanical agitated extractors

FIG 3_14 A Typical Classification of Industrial Liquid-Liquid Extraction Equipment (90)

I. VERTICAL COLUMN TYPE EXTRACORS

- A. Unagitated
  - 1. Spray column
  - 2. Packed column
  - 3. Plate column
- B. Rotor agitated
  - 1. Rotary Disc Contactor(RDC)
  - 2. Asymmetric Rotating Disc COntactor (ARD)
  - 3. OLdshue-Rushton Contactor
  - 4. Scheibel extractor
  - 5. Rotary annular column
- C. Pulse_agitated
  - 1. Pulsed spray column
  - 2. Pulsed packed column
  - 3. Pulsed packed column

II. HORIZONTAL EXTRACTORS

- A. Mixer settlers
- B. Centrifugal extractor
- C. Horizontal rotating disc contactor
- D. Raining bucket extractor

Table 3.3 Classiffication of Liquid_Liquid Extractors plug flow is $\nu = Q\theta$, where θ = holding time, Q = flow rate of both materials.

3.6.1 NON MECHANICAL (GRAVITY) EXTRACTORS

3.6.1.1 BAFFLE PLATE COLUMNS

Baffle towers are cylindrical shells containing baffles to direct the flow of the liquids. However, the purpose of the baffles is principally to reduce the vertical circulation to which the empty tower is subject and to provide somewhat longer residence time.

Baffle towers have been used for many years, particularly for the extraction of acetic acid from pyroligneous acid.

3.6.1.2 WETTED-WALL COLUMNS

In a wetted wall-column, a thin film of one liquid (usually the heavier) is allowed to flow along the inside surface of a narrow vertical circular tube, and a countercurrent flow of the other is maintained in a central core.

3.6.1.3 SPRAY TOWERS

Spray towers are merely empty shells with provision for introducing and removing the liquids. They can be used for handling liquids containing suspended solids.

3.6.1.4 PACKED TOWERS

The shell of the extraction tower may be filled with packing which serves principally to reduce axial mixing and also to jostle and distort the droplets of dispersed liquids, thus promoting high mass transfer rates.

3.6.1.5 PERFORATED-PLATE (SIEVE-TRAY) COLUMNS

In the perforated plate column, one of the liquids is repeatedly dispersed and coalesced by causing it to flow through a series of trays in which a large number of small holes have been drilled or punched.

3.6.2 MECHANICAL (GRAVITY) EXTRACTORS

These include:

3.6.2.1 THE OLDSHUE-RUSHTON COLUMN

No literature has been found on the use of the Rushton column for phosphoric acid purification, since it was only introduced 30 years ago and has only recently achieved commercial use. The extractor consists of a vertical column divided into compartments. Each compartment is agitated by a turbine.

3.6.2.2 THE SCHEIBEL COLUMN

The Scheibel column consists of an alternate sequence of mixing and packed sections in a vertical column. Each mixing section is agitated by a turbine impeller supported on a central shaft. Open knitted mesh is used in the packed compartments.

3.6.2.3 ROTATING DISC CONTACTOR

The rotating disc contactor was first introduced by Reman in 1951 (218). It consists of a vertical cylindrical shell divided into a number of compartments by a series of stator rings.

One type of rotating disc contactor has been used for the purification of wet process phosphoric acid. That is in the phorex acid plant, which was developed by Azote et produits chimiques S.A., France (25,26). The plant uses isobutanol as solvent for the purification, the raw acid is introduced into the extractor and counter-currently extracted with isobutanol. Residual acid is fed to a distillation column for recovery of dissolved isobutanol. The extract is washed in the top part of the same type for stripping in counter-current contact with water. The acid is extracted back into the aqueous phase.

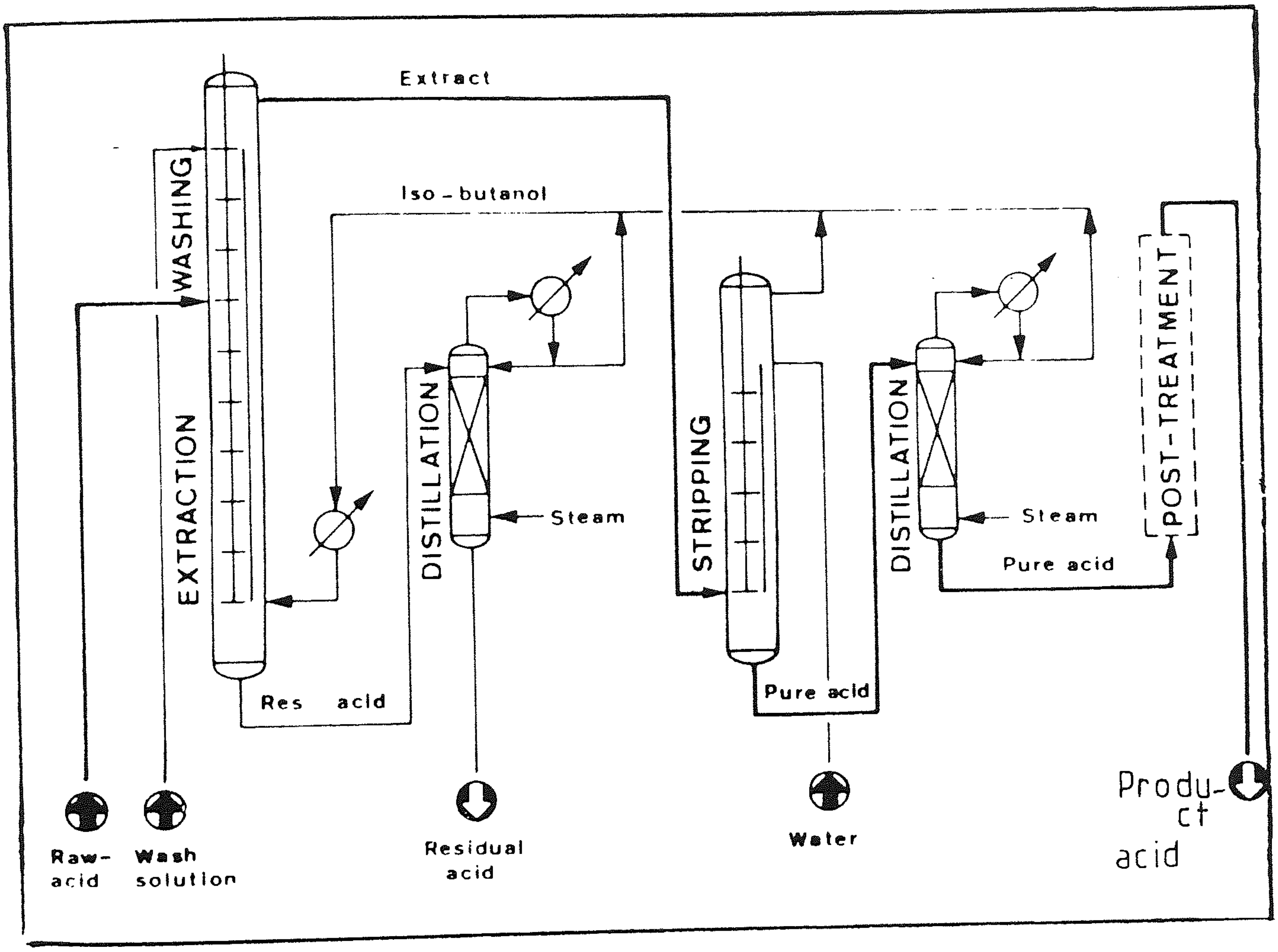


FIG 3.15 Flowsheet of the Phorex acid plant

3.6.2.4 MIXER-SETTLERS

Because the basic mixer-settler design is one of the objects of this work, it was considered appropriate to discuss it in detail in the next chapter. However it is essential here to consider the use of mixer settlers and their types in phosphoric acid extraction.

A mixer settler (shown in Fig.3.16) was developed by I.M.I. They claimed that it has the following important features:

1. Complete hydraulic independence of mixer and settlers.
2. Complete separation of the mixing and pumping function.
3. Minimum turbulence in settler.
4. Simplicity of design and scale up.

Ramaradhya (215) used the same design principle, but a completely different shaped mixer settler (Fig.3.17) for the purification of phosphoric acid, and his experiments were based on three extraction stages.

Libhaber and Blumberg (166) developed a dynamic simulation model for the extraction and purification stages of the IMI phosphoric acid process; the validity of the model was confirmed by simulating experimental runs of a small scale mixer-settler shown in Fig.3.18.

It should be noted that all the above contactors of the mixer-settler type use the same principle of operation, that is to mix two liquids in a mixer and separate the resultant two phases in a settler.

Aston University

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FIG 3.18 Schematic drawing of an experimental mixer-settler used by IMI for phosphoric acid and Uranium extraction. (166)

3.7 SELECTION OF EXTRACTION EQUIPMENT

The technical advantages and disadvantages of the two basic types of extractors (continuous, batch) are summarised in Table (3.4), but the selection of a particular extractor for a desired separation process is dictated also by economics and is still based largely upon experience. In general, it is necessary to establish the desired solute recovery for specific flow rates and also to know the physical and chemical properties of the system to be extracted. Any special requirements such as complications arising from the presence of solids, emulsion formation and easily degradable materials, must be taken into account. The location of extractors in terms of floor area or head room available, is also important.

The following criteria together with Fig. (3.19) can provide broad guidance and a quick method of selection:

1. The number of effective contact stages

All types of extractors can be used satisfactorily for the purification of phosphoric acid. Few stages are needed when solvents of type 2 (described in Section 3.2) are used for the extraction of phosphoric acid. Column extractors are preferred for processes involving a large number of stages. However mixer-settlers may have to be used for processes requiring more than twenty stages because of practical limitations.

	CONTINUOUS DIFFERENTIAL CONTACTOR	DISCRETE STAGE CONTACTOR
ADVANTAGES		
	I. LOW Initial cost	I. Good contacting
	II. LOw operating cost	II. Handles wide flow ratio
	III. Simple in construction	III. High efficiency
		IV. Handles large number of stages
		V. Low headroom
		VI. Reliable to scale-up
		VII. Flexibility in operation
DISADVANTAGES		
	I. Limited throughput	I. Large holdup
	II. Can not handle wide flow ratio	II. High power cost
	III. Some times Low efficiency	III. Large floor space
	IV. High headroom	IV. High investment
	V. Difficult to scale-up due to back mixing	

TABLE 3.4 Advantages and Disadvantages of the two basic types of contactors

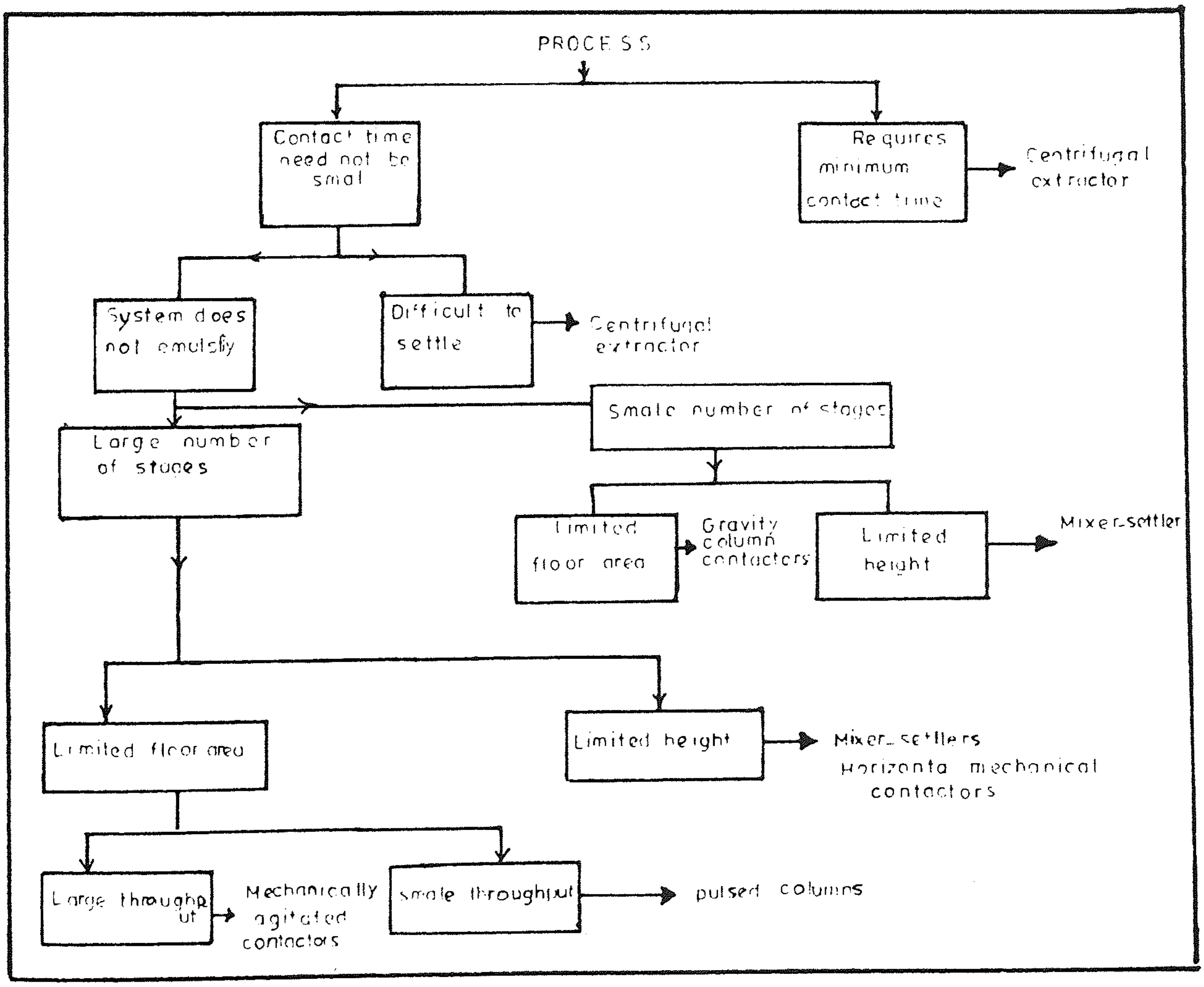


FIG 3.19 Liquid extraction equipment selection.

2. Throughput

If the throughput is very low, a spray tower could be used from the economic point of view, while R.D.C., pulsed plate columns or mixer-settlers could be used for intermediate and high throughput.

3. Solvent residence time

This is important when handling materials of low stability. Centrifugal extractors are normally preferable since they can provide fast settling rates, if the interfacial tension of the system processed is suitable.

The residence time in mixer-settler extractors will depend on the number of stages and the rate of coalescence of the dispersed phase at each stage; thirty seconds is reported normally to be sufficient (215).

4. Phase flow ratio

Mixer-settlers are preferable to differential contactors at high phase ratio, since the dispersed phase hold-up in differential contactors is a fraction of the phase ratio and hence, the performance decreases as this ratio decreases.

5. Presence of solids

Mixer-settlers are usually more flexible in handling liquids with solids, since it is required to shut down the plant for cleaning out the solid deposited in the piping and valves.

6. Economics

The overall economics of the process should be worked out before a final decision is taken.

On considering the above criteria regarding equipment suitable for phosphoric acid purification, the most suitable equipment is a mixer-settler since:

1. Wet process phosphoric acid solution may contain some solids and frequent shut down may be necessary during running. Mixer settlers maintain the distribution profile and no off-specification streams form on restart.
2. The number of equilibrium stages required is small, so concentration gradients are steep from stage to stage; this imposes the necessity for high individual stage efficiencies.
3. High stage efficiencies can be controlled by the level of agitation of the mixer.
4. As the solvents considered are partly miscible with water, there may be large volume changes from stage to stage; so operation of each stage as a separate entity is desirable.
5. Volumes flowing per unit of product are large.
6. The limited selection of suitable materials of construction resistant to the corrosive system of the phosphoric acid process excludes the choice of centrifugal machines.

7. Uncertainty of scaling up other extractors like columns whereas mixer settlers can be constructed for any desired number of stages.
8. In mixer-settler equipment, the flow of the two phases can be easily adjusted.
9. Should the solvent change, additional stages may easily be introduced.

Mixer settlers, however, have the following disadvantages.

1. Unsettleable emulsions may be formed owing to high mixing efficiencies.
2. Interstage pumping of either or both of the liquids is required for most designs.
3. Independent agitation equipment for each stage involves additional capital.
4. The horizontal arrangement occupies valuable floor space.
5. High holdup of the liquids in the settlers increases the investment on solvent and also on the initial equipment due to large settling volumes required.

3.8 HAZARDS AND SAFETY IN HANDLING PHOSPHORIC ACID SOLUTIONS AND SOLVENTS

3.8.1 PHOSPHORIC ACID

(a) Acid Hazards

Phosphoric acid does not classify as a dangerous chemical. However it is a corrosive liquid that may cause burns on contact with any part of the body.

Phosphoric acid is not explosive, or flammable, however certain impurities e.g. fluorine can cause dangerous poisoning if enough acid is swallowed to give about 1g of fluorine. The most effective treatment for eye or skin contact is by washing with large amounts of water. However mineral oil, olive oil, may be applied to relieve pain from hot acid.

(b) Corrosivity

Corrosivity of the acid is too high for satisfactory use of carbon steel and cast iron as materials of construction. Acidic solutions (pH less than 5) are highly corrosive to carbon steel, and wet process phosphoric acid is observed to have a corrosion rate of over 300-mil penetration per year under laboratory conditions (275).

Type 304 and 316 stainless steel is sometimes used (see Appendix (I)), and in concentrations of phosphoric acid over about 80 to 95 percent the corrosiveness towards stainless steel decreases. However, hydrogen gas can accumulate at hazardous rates in tanks made of the material.

Rubber-lined steel is widely used for shipping phosphoric acid, e.g. butyl rubber is very good up to 180-200°F. Certain plastics, such as pvc may be used to line steel for shipping of the acid.

Malowan (172) and Kiselev (139) improved the resistanceof stainless steel by adding a corrosion inhibitor to the solution of phosphoric acid. Examples of corrosion inhibitors are given in Table (3.5) and the criteria of the test was based on the amount of gas evolved as a result of the acid corrosion.

(c) Storage

Wet-process phosphoric acid is most commonly stored in rubber lined steel tanks, some wet acid tanks are equipped with agitators.

More comprehensive detail is given in Slack (18).

3.8.2 SOLVENTS

Solvents are liquids which exhibit the power of dissolving other substances and thereby converting them into a fluid state. Flury and Wirth (76) in their study of the toxity of organic solvents have found that some solvents, e.g. methyl alcohol, acetone, ethylene glycol cause irritation of the mucus of the eye. Their report also disrupts the general belief that esters are not very harmful.

INHIBITOR	DAYS	GAS HEIGHT
NO INHIBITOR	3(hrs)	500
O-AMINO DICYCLOHEXYL	55	0.9
HEXADOCYL AMINE	55	2.0
DODECYCLAMINE	30	Bubble
DECYLAMINE	55	1.9
α-NAPHTHONITRILE	212	2.5
β-NAPHTHONITRILE	70	11.0
ρ-TOLUNITRILE	45	2.4
BENZONITRILE	45	2.4
PHENYLACETONITRILE	240	3.5
DODECANENITRILE	96	4.0
TETRADECANENITRILE	332	0.3
OCTADECANENITRILE	648	2.3
MELAMINE	2	500
MORPHOLINE	4	500
ACETONITRILE	23	500
FUMARONITRILE	23	500
CHLORACETOAMIDE	25	500
PYRIDINE	2	500
2-AMINO-PYRIDINE	4	500
STEARAMIDE	2	500
AZOBENZENE	2	500

TABLE 3.5 - PHOSPHORIC ACID INHIBITORS TO
REDUCE CORROSION OF
BASED ON 75% PHOSPHORIC ACID

N.B. The height of the gas evolved is measure of the extent of dissolution of metal

Toxicity goes hand in hand with the volatility of solvents. A volatile substance when exposed will escape and find free access to human olfactory systems should men be within the vicinity of its vapour. Broadly, solvent vapours are more or less toxic and their physiological action can be equally varied. A volatile solvent will find its way into the blood-stream by mixing with the inhaled oxygen, and thus ultimately it comes into contact with every body tissue upon which it exerts toxic action.

Specific toxicities of solvents tested will be considered in Chapter 6.

CHAPTER
FOUR

STAGE-WISE CONTACTORS MIXER-SETTLERS

4.1 ARRANGEMENT

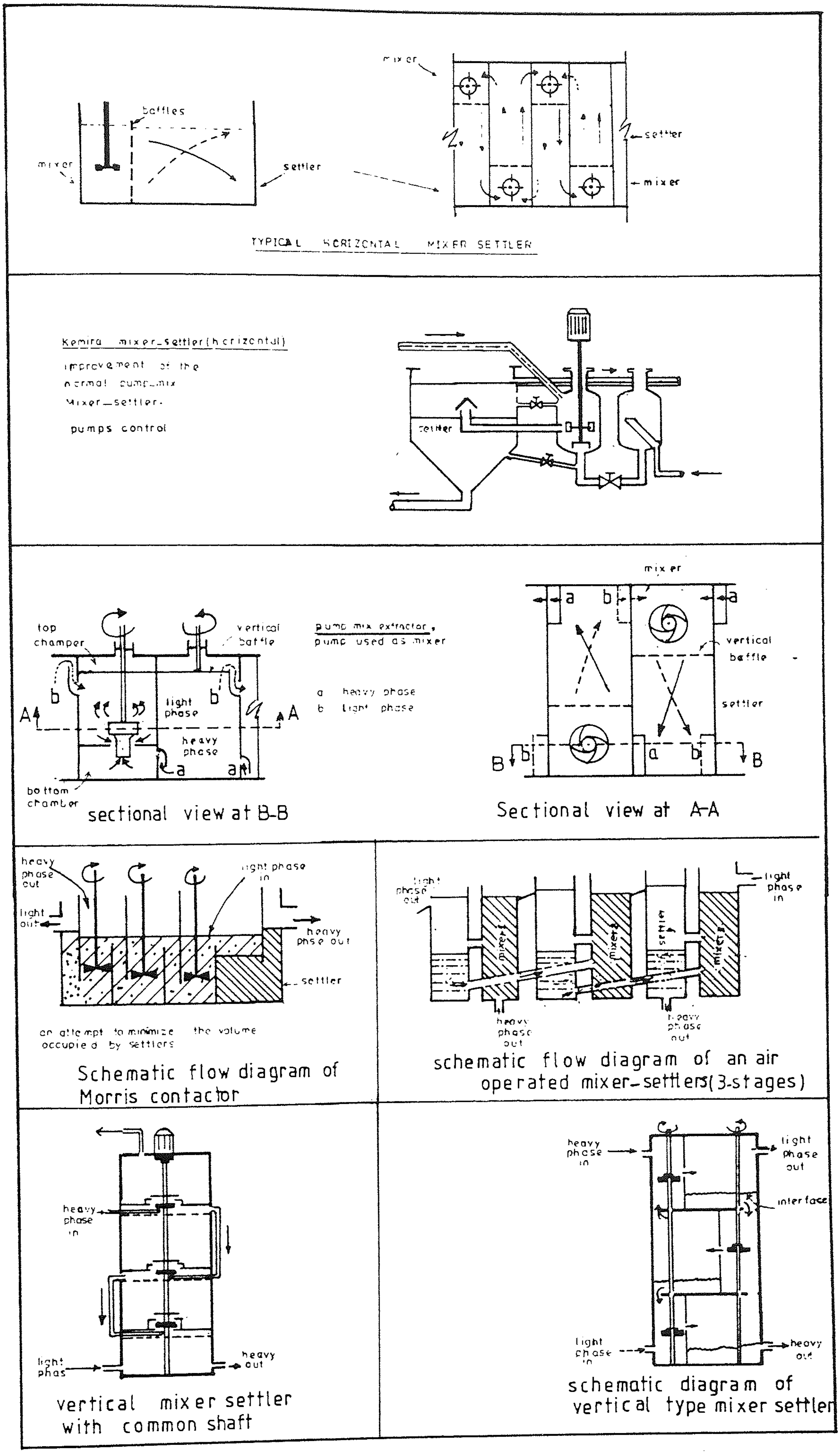
Mixer-settler types of liquid/liquid extractors have been in use since 1904 (54). They comprise one or more stages incorporating a mixer and a settler. The simplest form of mixer-settler is the batch extractor consisting of a cylindrical tank with or without baffles on the inner walls, provided with a centrally located paddle agitator. In order to obtain continuous operation two tanks in series are used. One for mixing and the other for settling the mixed phase (dispersion).

Other forms of mixer-settler have been proposed having varying degrees of complexity, both in the horizontal and vertical planes. A wide range of geometric possibilities between horizontal and vertical mixer settlers is summarised in Table 4.1. Figure 4.1 summarises some types of extractors.

A simple classification of mixer-settlers is given in Fig.4.2. However mixer-settlers may be classified according to the manner by which the flow of liquid through the unit is brought about.

Inventor	Type of Stirring	Type of contacting	Arrangement	Driving Force for Flow	Ref.
Schoneborn 1934	Common Shaft	Co-Current	Vertical	Gravity	238
Othmer 1935	Common Shaft	Counter-Current	Vertical	Gravity	204
McConnel 1937	Common Shaft	Co-Current	Vertical	Gravity+Pump	65
Mensing 1947	Individual Stirrers	Counter-Current	Horizontal	Pump	
Bottaro 1940	Common Shaft		Vertical	Gravity	23
Standard Oil Development 1949	Individual Stirrers	Co-Current	Horizontal	Gravity	235
Hanson et al 1965	Common Shaft	Counter-Current	Vertical	Gravity	89

TABLE 4.1 COMPARISON OF MIXER SETTLER DESIGNS



sectional view at B-B

Sectional view at A-A

Schematic flow diagram of Morris contactor

schematic flow diagram of an air operated mixer-settlers(3-stages)

vertical mixer settler with common shaft

schematic diagram of vertical type mixer settler

FIG 4.1 SOME TYPES OF HORIZONTAL AND VERTICAL MIXER SETTLERS

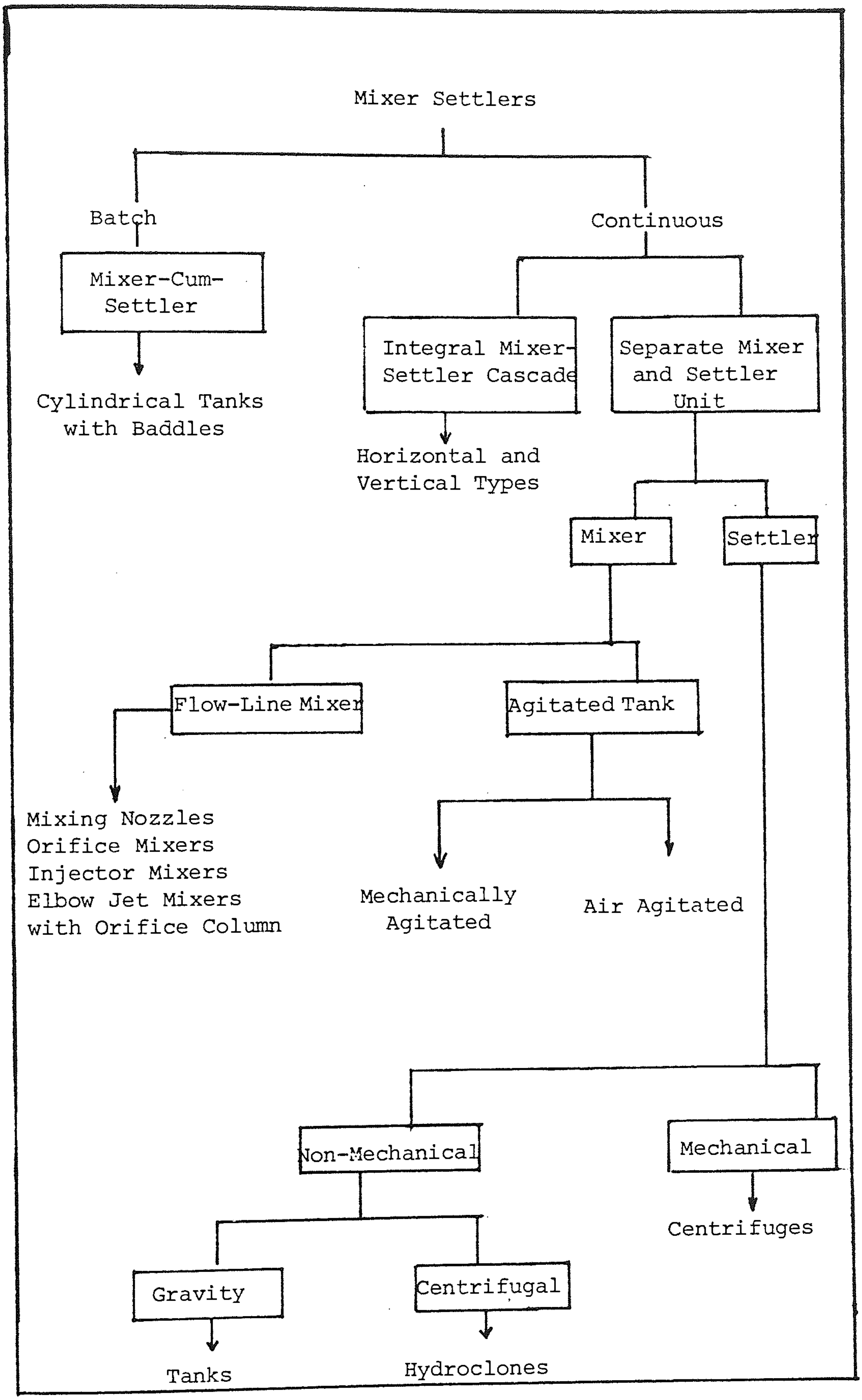


FIG.4.2 - Broad Glassification of Mixer-Settler

I Gravity Flow Type In which the driving force for the liquid flow in each phase is the head between the inlet and outlet.

II Interstage Pumping In which pumping is used between stages, this may include air operated mixer-settlers (177).

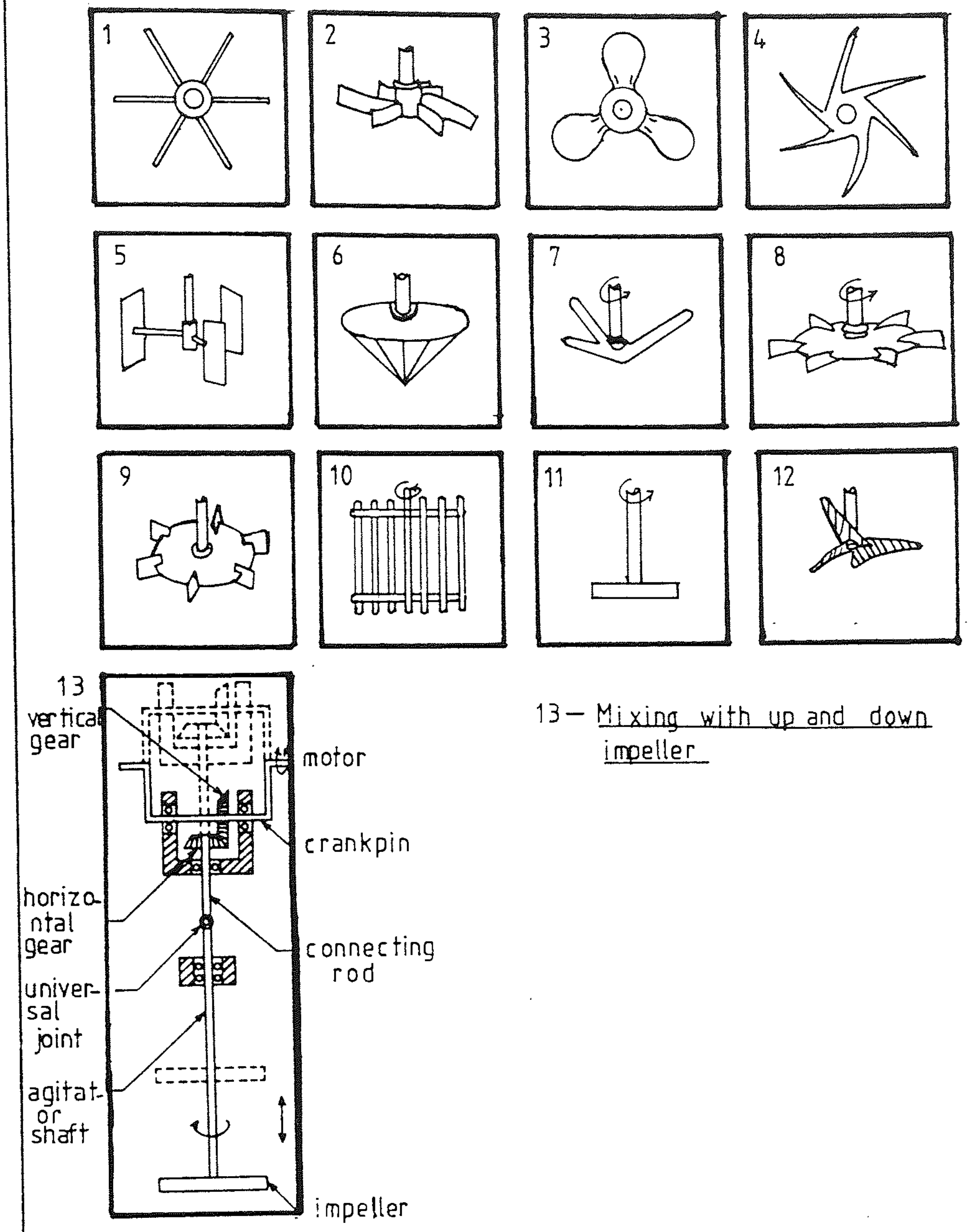
III Pump-Mixing Type In which the mixing intensity and hydraulic head for heavy phase flow rate is provided by the impeller.

4.2 MIXER-SETTLER EQUIPMENT

4.2.1 AGITATED MIXING TANK

The mixer is usually a baffled tank with a turbine or propeller agitator, jet mixer, injector or orifice mixer. Nozzles and pumps are also used but are less satisfactory in many cases because contact time is insufficient to permit a reasonable approach to equilibrium.

The internal surface of the mixing tank is smooth, however baffles are introduced to prevent vortexing and to direct the circulating current. The number of baffles and the ratio of baffle width to tank diameter is more or less arbitrary (229), but there are normally four baffles each having a width of 1/10 to 1/12 tank diameter. For good mixing, and constant interchange of the agitated material in all parts of the tank a mixing element is mounted on a vertical, horizontal or inclined shaft driven mechanically. They are distinguished



13— Mixing with up and down impeller

1- flat plate paddle, handle low viscosity liquids or suspensions

2,8,9- Turbines, the turbine has high pumping capacity, handles the majority of fluids

3- Marine-type propeller

4- Centrifugal turbine

5- Special type of turbines

6- Cone shape mixer

7,12- Sabre blade for low viscosity liquids, has low power consumption

10 - Gate type, for viscous liquids and suspensions

11- Flat/ pitched, low viscosity liquids

FIG 4.3 Mixing impellers

according to their shape or the flow pattern which they produce as paddles, propellers, turbines and special mixers (see Fig.(4.3)). They can be sub-divided into low speed impellers including paddles with a maximum speed of 60 r.p.m., which has limited use with liquids of viscosity <1.0 kg/m sec as shown in Fig.4.4. High speed impellers includes turbines and propellers. The main advantages of turbines are their adaptability for liquids of high viscosity and density. Propellers are of two basic types, the first is similar to an aircraft propeller, and the second similar to marine propellers.

Murakami (194) used a new technique for mixing high viscosity liquid by introducing up and down impeller as shown in Fig.4.3 (13).

Mixing equipment may also be distinguished according to the type of flow pattern produced, i.e. tangential, radial, axial or compound flow. Different impellers give different flow patterns see Fig.(4.5) . Propellers produce axial flow while turbines and paddles produced radial flow (230). In general the design of the mixer mainly depends on:

(a) Dispersed phase hold-up

(b) Uniformity of mixing and impeller power, i.e. shape, impeller HP, speed and diameter

(c) Interfacial area of drops and drop size

(d) shape and size of the vessel

(e) position of the mixer

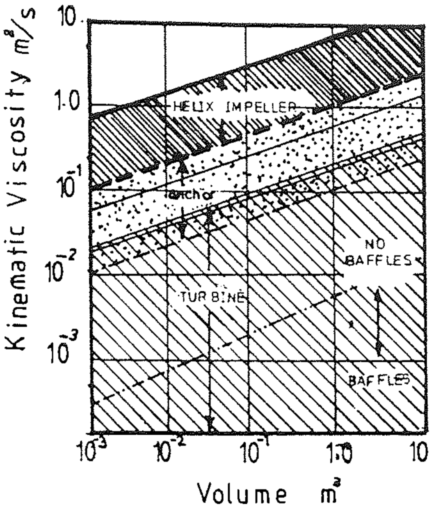
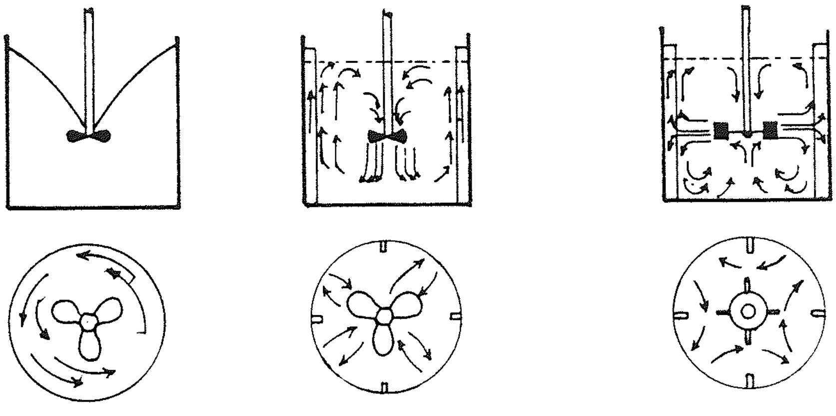


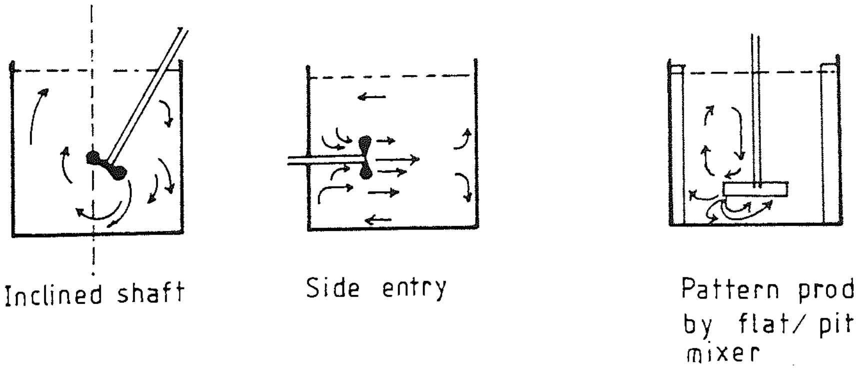
FIG 4.4 Operating range for different impeller types



vortex and rotary flow pattern in tank without baffles.

Propeller in tank with baffles, Axial flow pattern.

Blade turbine with baffles, Radial flow pattern



Inclined shaft

Side entry

Pattern produced by flat/ pitched mixer

FIG 4.5 classiffcation of mixing equipment according to the type of pattern produce.

Factor Involved in Mixing

Perfect mixing can easily be obtained in a batch process, however in a continuous flow system perfect mixing may never be obtained since stagnant regions may arise and part of the feed may pass directly to the outlet. Piston or plug flow may also occur.

Three factors generally affect practical mixing:

(a) Effective Volume - Part of the tank contents may not be mixed and stationary or stagnant zones may occur. That part of the total volume where mixing is complete is known as the "effective volume" of mixing.

(b) Short Circuit - Part of the feed may pass directly between the inlet and outlet without being mixed, causing channelling or short circuit.

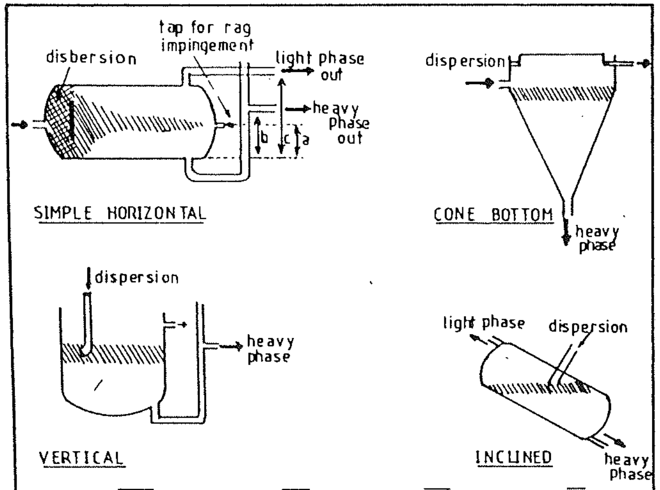
(c) Piston Flow - Part of the feed may undergo piston or plug flow. Liquid in the stagnant zone may be replaced by some from the well agitated zone or from part of the feed, this type of circulation may go on steadily in the form of piston or plug flow. Very good mixing occurs in the region of the impeller.

4.2.2 SETTLERS

The settler or separator is usually a tank designed to minimise turbulence caused by the entering liquid, and to separate the emulsion generated from the mixer into two phases. Settlers may be divided into mechanical types or non-mechanical types, e.g. gravity settlers and centrifugal settlers or cyclones. Only gravity settlers will be considered here.

Gravity settlers can be subdivided into horizontal and vertical settlers (Fig.4.6). Cylinders are used in some cases, and advantages have been claimed when they are put at an angle to the horizontal. In the present work horizontal settlers were selected as being most typical of industrial units. Therefore vertical settlers will not be considered. There is no general accepted design procedure to determine the size of the settler needed for a specific application. However, there have been three approaches to the design: (1) provision of sufficient residence time based on laboratory observation of settling, (2) estimation of the rate of flow to produce a suitable dispersion-band thickness, and (3) calculation of the time to settle individual drops through a clear liquid above and below the dispersion band, this is related to the physical properties of the system, and operating characteristics of the mixer (121). None of these methods is very reliable in the absence of any experience with the specific dispersion. A first estimate of settler size can be made from an empirical expression given by Treybal (266).

$$T_S = 8.4(q_C + q_D)^{0.5} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.1)$$



The heavy phase outlet is provided with a syphon break to prevent emptying of the tank and to maintain the interface at level given by;

$$b\rho_H + \Delta p_H = a\rho_H + (c-a)\rho_L + \Delta p_L$$

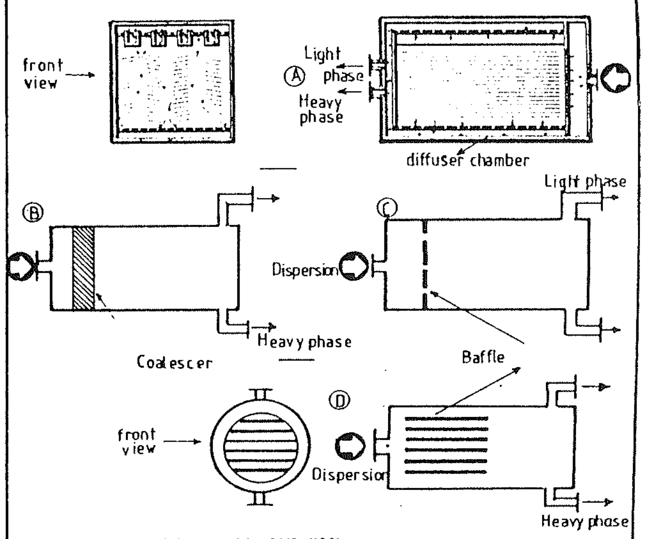
Δp's pressure drops for flow through the piping, g/g_c being taken as=1

FIG 4.6 Gravity settlers

A, Location of coalescence wedge when heavy phase dispersed

B, Shape of actual and idealised coalescence

FIG 4.7 The behavior of the wedge in the settler



A-Compact settler used by I.M.I (190)
B-Simple settler with coalescer
C-Simple settler with one vertical baffle
D-Simple settler with horizontal baffles

FIG.4.8 Settlers and settler auxiliaries

FIG 4.9 Performance comparison for settling equipment (190)

This was developed on the basis of typical settling rates from droplets of dispersed phase and length/diameter ratio for the vessel equal to 4.

Mizrahi (190) has proposed a practical design of a compact settler in which dispersion bands of practically constant thickness 0.5 to 2m are claimed to occur. Under these conditions, and with all other parameters held constant, the relationship between dispersion band thickness and settler loading can be expressed approximately as:

$$\Delta H = K(Q/A)^{Y} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.2)$$

where ΔH is dispersion band thickness, K is a constant, Q is dispersion feed throughput, A is the horizontal cross-sectional area of the settler, and Y is an exponent. The values of K and Y depend on the dispersion characteristics, liquid system, temperature, phase ratio and mixing conditions, Y varying within the range 2.5 to 7 for different systems. Equation 4.2 can be modified as follows:

$$Q/(A\Delta H) = Q/V = 1/(K^{1/Y}\ \Delta H^{1-1/Y}) \quad \ldots\ldots\ldots\ldots \quad (4.3)$$

where $Y > 2.5$

Equation 4.3 shows that the settler capacity per unit volume of dispersion band (working volume) decreases with increase in the dispersion band thickness.

Practical settler designs should also be based on the worst settling conditions. However, it was considered necessary to design a settler with such a large area (i.e. low flow rate/unit area) that the wedge-shaped dispersion band reduced to zero before the solution reached the outlet weir.

The heterogeneous zone at the phase boundary between the two liquids may exist above the interface if the more dense liquid is dispersed as shown in Fig. 4.7A. The depth of this dispersion band is determined by the difference between the input rate of the emulsion and the rate of coalescence of droplets in the wedge interface. Fig. 4.7B shows the shape of an actual and an idealised coalescence wedge.

Jeffreys et al (121) were the first to attempt to take account of the effect of the physical properties of the system on separation and coalescence of drops, and a mathematical model was developed to predict the dimensions of the hetrogeneous wedge in the settler. The main assumptions were:

(1) The droplets within the wedge form a hexagonal close packing or face-centred cubic configuration.

(2) The inclined edge of the coalescence wedge approximates to a straight line.

(3) There is no distribution of coalescence time irrespective of whether coalescence is drop to drop or drop to interface.

(4) The coalescence process takes place step-wise.

(5) Inlet drops to the settler are all of equal size.

4.2.2.1 SETTLER AUXILIARIES

In practice the dispersion band should not cover the whole length of the settlers, but extend over only about 70% of the length of the settler, therefore the capacity of the unit is determined by the separation in the dispersion band. In this case the coalescence of the drops may be enhanced by adding coalescers as shown in Fig.(4.8), which include separating membranes, electrical devices, packings or baffles.

(i) Baffles

Vertical baffles are often used to reduce turbulence introduced from the mixer. Horizontal baffles are also used to reduce the depth through which droplets must settle and to ensure laminar flow. The position and dimension of the baffles is critical. Hossiain(100) suggested optimum design of the settler, in that the position and diameter of the vertical baffle is related to the settler diameter and equal to 1/10 of settler length and 0.75 ds, where ds = settler diameter. Baffles produce no significant improvement with secondary dispersions.

(ii) Packing

It is important to distinguish at this point between two types of dispersion which may be generated in the mixer, (a) primary dispersions generally characterised by droplets of mean diameter greater than

100 microns and (b) secondary dispersions or haze made up of much smaller droplets, often less than 1 micron diameter. The primary dispersions settle and coalesce rapidly after agitation is stopped, (primary break), while the settling and separation of secondary dispersions is very slow and may take days or even weeks.

Packing can be used to separate primary dispersions only. Knitted mesh packings are often used (257), and for maximum efficiency the coalescer should be preferentially wetted by the dispersed phase, and possess a large surface to volume ratio (100). Jeffreys et al (124) studied the behaviour of drops in primary dispersions flowing through a bed packed with glass ballotini and his conclusion was that the depth of packing in the bed, the superficial velocity of the dispersed phase, preferential surface treatment, and inlet drop size had only minor effects on the drop size in the effluent dispersion which emerged from the packing.

A mixed metal/plastic knitted mesh packing has been used recently which may give some advantages both in economy and flexibility.

I.M.I. (190) developed a low pressure drop coalescer, which increased the capacity of either a normal or compact settler of the type already described by 50-100% (see Fig.4.9). A potential disadvantage of using packing in wet process acid is that it may be prone to blockage by solid.

(iii) Other Coalescers

(a) Effect of electric fields - very little was found in the literature concerning electrically induced coalescence. However, Brown (37) reported that an electrostatic field promotes coalescence.

(b) Effect of ultrasonic vibrations - as reported by Chen (48).

4.2.2.2 SETTLER FUNDAMENTALS

In a coalescence process droplets first approach each other to form a close packed, heterogeneous zone between the two bulk liquid phases. In so doing the droplets velocity is reduced and they move towards the interface in a close packed arrangement. Thus the process involves two modes of coalescence: interdroplet and drop-interface coalescence. Only the latter reduces the volume of the wedge (12). Not every collision between droplets results in coalescence and if the collisions are totally ineffective the emulsion is stable. Surface active agents, which are particularly effective in lowering the surface tension and increasing the stability, may hinder separation.

Ryon (233) demonstrated the tendency of colloidal silica and clay to produce stable emulsions in aqueous continuous systems. Under some conditions however, the presence of solid in the dispersion might be beneficial in that the rate of coalescence can be increased.

The rate of coalescence of drops on a surface (e.g. settler surface) depends mainly on the surface properties of the solid such as surface wettability and surface roughness since it affects the contact angle between the drops and the surface.

4.2.3 DESIGN CONSIDERATIONS

The design of each type of mixer-settler must include the following:

1. A reasonably high stage efficiency which mainly depends on the operating characteristics of the mixer; this includes impeller design and speed of rotation.
2. A simple interface control.
3. The ability of the settler to separate a certain volume flow of feed dispersion, under a particular set of a process conditions. This depends on the fundamental physical properties of the system such as density between the phases, the interfacial tension.
4. Continuous movement of the two phases through the equipment.
5. Minimum horizontal area.
6. Minimum operational attention and maintenance costs.

4.3 STAGES AND STAGE EFFICIENCY

A single stage is formed when two tanks in series are used, one for mixing and theother for settling the mixed phase. If the effluent liquids from a stage are in chemical equilibrium, the stage is an ideal or theoretical stage. The fractional approach to equilibrium attained by the effluent from an actual stage is then stage efficiency which is not necessarily 100%.

A single stage is shown in Fig.(4.10), and the stage efficiency can be derived from:

$$\zeta_s = \frac{X_1 - X_2}{X_1 - X_e} = \frac{Y_2 - Y_1}{Y_e - Y_1} = \frac{AB}{AC} \quad \text{----------} \quad 4.4$$

The stage efficiency can be expressed in many ways. The Murphree stage efficiency is frequently used; it measures the fractional approach to equilibrium of the two effluent streams, thus if it is based on extract, then it is defined as

$$\zeta_{M_E} = \frac{Y_2 - Y_1}{Y_2^* - Y_1} = \frac{BE}{DF} \quad \text{------------} \quad 4.5$$

and if it is based on raffinate, then

$$\zeta_{M_R} = \frac{X_1 - X_2}{X_1 - X_2^*} = \frac{FA}{GA} \quad \text{----------} \quad 4.6$$

Treybal (265) has recommended the following equation for estimation of Murphree stage efficiency for baffled or well-stirred vessels which show complete mixing in the continuous phase:

$$\zeta_{M_C} = \zeta_{M_D} = 1 - \exp\{-K_{od}\, a \frac{t_a}{V\phi_2}\} \qquad 4.7$$

where

t_a = average residence time

$V\phi_2$ = volume fraction of dispersed phase

The overall efficiency of a cascade of stages is the ratio of the number of ideal to actual stages required for a given concentration change.

$$\zeta_o = \frac{n}{n_r}$$

and ζ_o can range from 0.75 to 1.0.

Felix (73) measured the efficiency in terms of the physical properties by using the refractive index (RI), and the ratio was called "co-current" efficiency defined as

$$\zeta = \frac{(RI)_F - (RI)_R}{(RI)_F - (RI)_R^*} \qquad 4.8$$

Flynn and Treybal (77) indicate that agitated vessels could be used for obtaining high extraction efficiencies, depending on the system properties and the dispersion characteristics of the phases. The overall stage efficiency ζ_o shows a steep increase with an increase in power input initially, and after an optimum value is reached, the increase in efficiency is not appreciable (see Fig.4.12). Flynn and Treybal also concluded that factors such as vessel size, rate of flow, and phase ratio have only a small effect on the efficiency.

Overchasheir et al (204) used the relation

$$\zeta_o = \log\left(\frac{mY_{A_2} - X_{A_2} + b}{mY_{A_1} - X_{A_1} + b}\right) / \log\left(\frac{mY_{A_2} - Y_{A_1}}{X_{A_2} - X_{A_1}}\right)$$

where m = slope of the equilibrium line of the countercurrent stage efficiency.

Brown (36) applied the following restrictions for the above expression which deal with low efficiency due to the poor settling resulting from high power supply to the fluid.

1. The degree of entrainment of one phase in the other is constant for all stages, except that the effluent from the end stage of the cascade is completely settled and free of entrainment.
2. The complete backmixing of each phase in the mixer.
3. The same mass transfer coefficient for each stage.
4. Essentially all the mass transfer occurs in the mixer.

4.4 ENTRAINMENT AND ITS EFFECT ON THE EFFICIENCY OF MIXER-SETTLERS

If settling of a dispersion is incomplete, then a portion of one of the liquids is entrained in the other, and if the stage in question is one of a countercurrent cascade, the entrained or unsettled liquid is carried opposite to its normal direction of flow. In several cases, entrainment of each liquid in the other is a possibility, i.e. organic entrainment in the aqueous phase and aqueous entrainment in the organic phase. The net result is a lowering of the overall efficiency of the cascade.

The effect of entrainment on efficiency of extractors has been analysed by Felix (73) for the type of mixer which operates at 100% efficiency. However their equation:

$$\frac{(R_I)_F - (R_I)_N}{(R_I)_F} = \frac{1 - \{1 + \frac{1}{E_f}(\frac{s}{m} - 1)\}^N}{1 - (\frac{s}{m})\{1 + \frac{1}{E_f}(\frac{s}{m} - 1)\}^N}$$

where

E_f = entrainment factor

m = equilibrium line slope

s = operating line slope

yields zero extraction for infinite internal entrainment rate.

Sleicher (248) proposed two models, model (1) for high entrainment rate, and model (2) for low entrainment, his conclusions were that entrainment rates as high as 10% are rarely consequential, and that high entrainment rates have relatively little effect on the efficiency of a mixer-settler extractor. When such extractors have poor efficiency, it is therefore more likely to be caused by low mass transfer rate than by entrainment from the settler.

4.5 MIXER-SETTLER CONTROL

Chemical engineers by tradition have designed automatic control systems to keep constant those variables in a chemical process which are considered to be of primary importance, e.g. pressure, temperature, composition and flowrate of all input, output and internal material streams. Therefore if the operating conditions have been established it should be possible to operate mixer-settlers with virtually no supervision and at near 100% efficiency, see fig.(4.13).

Using the SIMTEX and QUANTEX systems of computer programs Mills and Bell (186) described the operation of a small multistage mixer-settler under optimum conditions using simple in-line control techniques for forward extraction and back extraction. The method of control was shown to be suitable for both long and short term input transients.

In the case of phosphoric acid plant, a knowledge of end conditions is not sufficient for controlling the operation of the mixer settler. It is essential to know, for each set of operating conditions, the intra-battery situation. This information can be obtained by taking profile samples of conjugate phases from the individual transfer stages. The profile samples will immediately indicate how the operation of a battery can be optimised and also provide a basis of comparison to be used after a change in operating conditions. A typical profile extraction using mixer-settlers is shown in Fig.(4.14).

Entrainment in mixer-settler equipment must be avoided. If entrainment in one stage is permitted to continue unchecked, it may eventually reach such proportions as to overload the mixer-settler pump. The gravity flow principle will then be nullified, and the final result will be back-up of both solvent and aqueous phases around the flooded unit, leading to spillage and low efficiency.

4.6 SCALE UP OF MIXER SETTLERS

Although mixer-settlers are one of the oldest types of contactors used for liquid-liquid extraction, there are few published methods of scale up. Rarely has there been any attempt to verify the methods from the operational data of full-scale plants.

Miller and Mann (182) suggested scale up by use of a constant power input per unit mixer volume. Karr and Scheibel (132) demonstrated scale-up as a function of power of agitator, speed and diameter. The main difficulty in using energy input is lack of theoretical derivation to explain its limited applicability when dispersion of small drops or particles are involved and only pilot plant data are available. Early work by Rushton (231) suggested the use of heat transfer coefficient for scaling-up a mixer, it was based on making $h_2 = h_1$. Although Shinnar (246) reported that a dimensional analysis presents difficulties on scaling up a mixer, Royon and Daley (233,234) conclude that the mixer can be scaled-up by geometric similitude at constant power input per unit mixer volume as shown in Table 4.2.

TABLE 4.2 SCALE UP OF MIXER

	Small Scale	Large Scale
Flow Rate	Q_1	Q_2
Specific Power Input	P_1/V_1	$P_2/V_2 = P_1/V_1$
Residence Time	t_1	$t_2 = t_1$
Mixer Volume	$V_1 = t_1 Q_1$	$V_2 = t_1 Q_1$
Total Power	$P_1 = (P_1/V_1)^* V_1$	$P_2 = P_1/V_1{}^* V_2$
Mixer Diameter	$T_1 = (\frac{4}{\Pi V_1})^{1/3}$	$T_2 = (\frac{4}{\Pi V_2})^{1/3}$
Turbine - Mixer Diameter	$\frac{D_1}{T_1}$	$\frac{D_2}{T_2} = \frac{D_1}{T_1}$
Turbine Speed	$N_1 \sim (\frac{P_1}{D_1 S})^{1/3}$	$N \sim (\frac{P_2}{D_2 S})^{1/3}$

For scaling up the settler, the suggested methods have often been based on residence time (265). Ryon and Daley (233,234), based the scale up of the settler on flow rate per unit cross-sectional area, while Mizrahi (190) used the relation between dispersion band thickness and settler loading for scaling up the settler.

Houssin (100) developed a similar model by introducing the system properties such as density.

$$t = 1250.5 * (\frac{1}{n}) * (m)^{0.36} * (R)^{0.28} *$$

$$* (\frac{DV\rho_m}{\mu_m})^{0.33} * (\frac{X_F - X_E}{\rho F})^{0.21}$$

where $R = \frac{F}{S}$, n = number of stages

The model was based on the system kerosene/water and toluene/water using 5-stage mixer-settlers. Both Salem and Houssan concluded that the time to reach steady state decreases with the power input as shown in Fig.4.15.

To establish experimentally whether the steady state has been reached closely enough, an appropriate physical constant of the final extraction product can be measured, refractive index, density, or concentration may be used. The steady state is assumed to be reached as soon as the physical properties of both extraction products become constant.

4.7 CAPACITY AND FLOODING

The quantities of feed and solvent that can be passed per unit of time through extraction equipment (throughput) determine its capacity. Obviously, increasing the rate of feed intake will affect stage efficiency, as this reduces the contact time. In general, it may be concluded that the value of efficiency decreases as throughput is increased. To

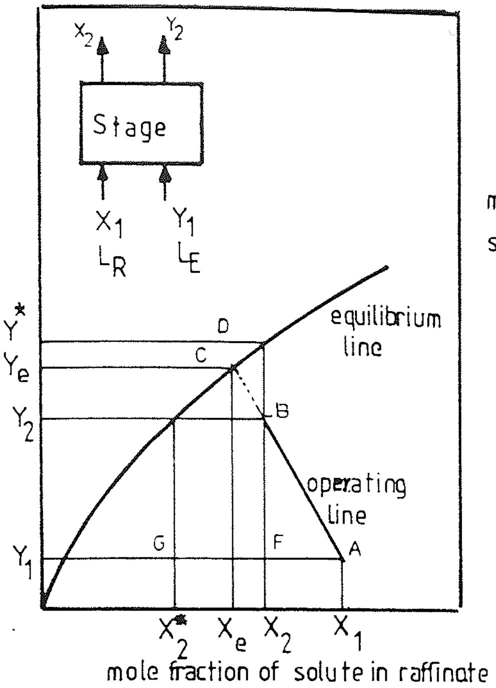


FIG 4.10 Stage efficiencies of one stage

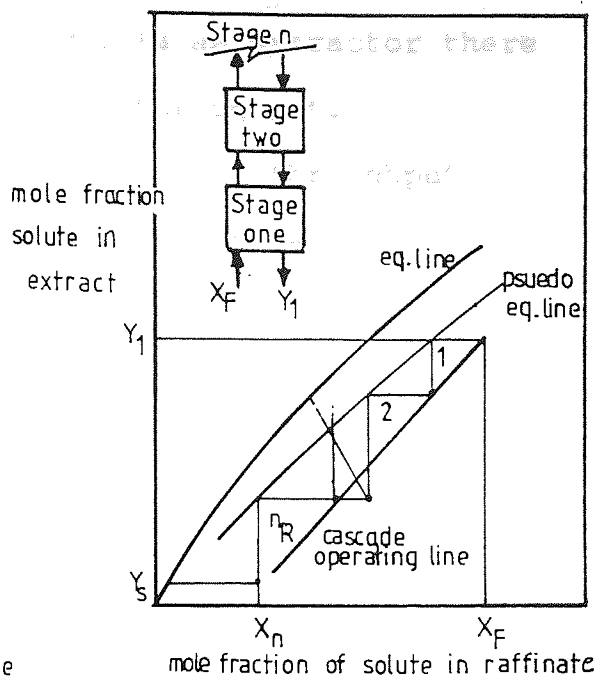


FIG 4.11 Stage efficiencies in a coutercurrent cascade

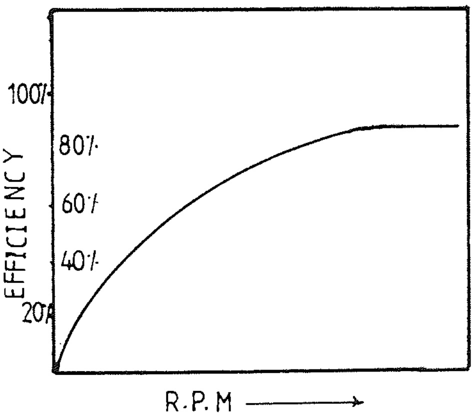


FIG 4.12 effect of power input on stage efficiency

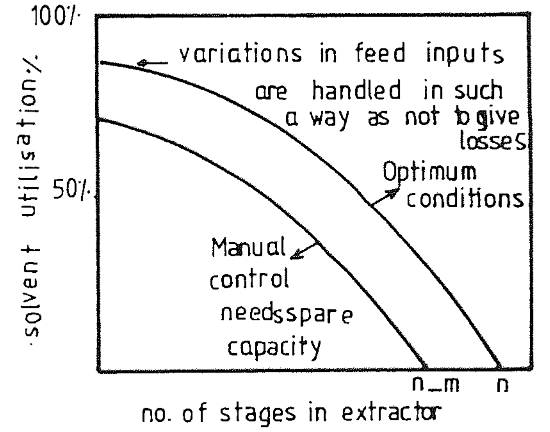


FIG 4.13 Solvent utilisation profile for an extraction system

FIG 4.14 Typical extraction profile in I.M.I mixer settlers(112)

FIG 4.15 Time to reach steady state versus impeller speed (100) maintain a given number of stages in an extractor there is therefore a (maximum) limit to throughput.

Besides the fact that an increasing throughput reduces the number of (ideal) stages, it may also cause "flooding". With some systems it is difficult to recognise flooding; instead of flooding in the usual way the phase will invert and make it impossible to operate the extractor.

CHAPTER
FIVE

MASS TRANSFER THEORY AND DROPLET PHENOMENA

This Chapter is a basic review of mass transfer and droplet phenomena.

5.1 MASS TRANSFER FUNDAMENTALS

Mass transfer occurs by droplet phenomena and it depends on: (a) Rate of formation of the drops, (b) Turbulence within the drops and their rate of passage through the equipment, (c) Resistance and back mixing in the continuous phase, and (d) Rate of coalescence of the drops.

The rate of mass transfer is normally described by an equation of the form

$$Na = K.A.\Delta C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5.1)$$

$\Delta C = C^* - C$, where C^* represents the composition of the solute in phase 1 in equilibrium with the solute concentration in the bulk of phase 2.

K embraces three fundamental resistances which are the dispersed and continuous phase film coefficients, K_d, K_c, and the interfacial resistance which is very small and can usually be neglected

$$\therefore \quad \frac{1}{K_d} = \frac{1}{k_d} + \frac{1}{mk_c} \quad \text{or} \quad \frac{1}{K_c} = \frac{1}{k_c} + \frac{m}{k_d} \quad \ldots\ldots \quad (5.2)$$

where m = distribution coefficient of the solute, the
choice of k_d, k_c depends on the driving
force chosen in equation 5.1.

5.1.1 MASS TRANSFER IN THE DISPERSED PHASE (INSIDE DROP)

The following models can be used to describe the phenomena.

(a) Rigid Drops

This is a limited case, and holds for small drops. Newman (197) has proposed a relationship for the prediction of mass transfer for such cases:

$$E = \frac{C_o - C_F}{C_o - C^*} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-n^2\pi^2 . 4D_d t}{d^2}\right) \quad (5.3)$$

for which

$$k_d = \frac{d}{6t} \ln \frac{5}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-4\pi^2 n^2 D_d t}{d^2}\right) \quad \ldots\ldots\ldots \quad (5.4)$$

where the symbols have their usual meaning as given in the nomenclature.

(b) Non-Rigid Drops

These may exhibit either circulation or oscillation. Drop oscillations are expected when the drop size in a low viscosity liquid is increased above the laminar flow region. Rose and Kinter (225) developed a correlation for the mass transfer coefficient for an oscillating drop:

$$K_d = 0.45(D_D W)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5.5)$$

where $W = (\frac{\sigma b}{r^2})(\frac{1}{3\rho_d + \rho_c^2})$

$b = 0.805d$

For the regions of laminar circulation, the relation of Kroning and Brink (149) with no continuous phase resistance is generally accepted:

$$\frac{C_o - C_F}{C_o - C^*} = 1 - \frac{3}{8}\sum_{n=1}^{\infty} B_n^2 \exp\{-\lambda_n \frac{64 D_d t}{d^2}\} \quad \ldots \quad (5.6)$$

from which the mass transfer coefficient:

$$K_d = -\frac{d}{6t} \ln \frac{3}{8}\sum_{n=1}^{\infty} B_n^2 \exp\left(\frac{-64\ \lambda_n D_d t}{d^2}\right) \quad \ldots\ldots (5.7)$$

Table 5.1 summarises values of B_n and λ_n as given by Jonson et al (131).

n	1	2	3	4	5	6	7
B_n	1.29	0.596	0.386	0.35	0.28	0.22	0.16
λ_n	1.656	9.08	22.2	38.5	63.0	89.8	123.8

Table 5.1 - Summary of Values of B_n and λn for Equation (5.3) with Zero Continuous-Phase Resistance.

Handlos and Baron (86) proposed a similar expression for turbulent circulation.

$$E = 1 - 2\sum_{n=1}^{\infty} (B_n)^2 \exp\left\{-\frac{\lambda_{ut}}{128(1 + \frac{U_D}{U_C})d}\right\} \quad \ldots\ldots\ldots \quad (5.8)$$

from which Olander (199) correlates:

$$K_d = 0.92 \text{ KHB} + 0.075 \frac{d}{t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5.9)$$

K_d = actual transfer coefficient

KHB = coefficient calculated from Handlos and Baron's model.

(c) Mass Transfer During the Period of Development or Movement of Drops

Extraction during drop formation before detachment of a drop from the dispersing nozzle is reported to form a major fraction of the total extraction. (10% to 50% of total solute transfer) as observed in many investigations (132,236,279).

Heerjijes et al (93) developed the following equation for the formation efficiency.

$$E_{f_f} = \frac{20.6}{d} \sqrt{\frac{D\phi}{\pi}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5.10)$$

D = molecule diffusivity

ϕ = drop formation time

5.1.2 MASS TRANSFER AT THE INTERFACE

According to the Whitman theory (280) (the two film theory) that the interfacial concentrations are equilibrium concentrations, and that the resistance to mass transfer in the two phases, as measured by reciprocal K's, are additive.

Equilibrium at the interface means equal values of chemical potential in the liquids at the interface and, consequently, no resistance to transfer across the interface. However, there are some conditions under which the two film theory does not appear to apply, because the observed overall resistance $\frac{1}{K}$ is either larger or smaller than might be estimated from the expected individual K's. Some of these conditions might have a considerable affect on the interface mass transfer, e.g. interface turbulence, rigidity at the surface, blocking of the surface and temperature change at the interface.

Sternling and Scriven (252) noted the Marangoni effect in mass transfer operations. They observed that some systems may be stable with solute transfer in one direction yet unstable with transfer in the opposite direction. Peker et al (208) introduced a dimensionless quantity such as the ratio of interfacial stresses to the kinetic energies of the eddies, to explain the hydrodynamics at the interface.

5.1.3 MASS TRANSFER IN THE CONTINUOUS PHASE

There are two different conditions for mass transfer in the continuous phase:

(a) From and to Rigid Drops

For this case Lintion and Sutherland (168) have proposed:

$$Sh = 0.582(Re)^{\frac{1}{2}}(Sc)^{\frac{1}{3}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5.11)$$

while Manning and Manning (173) considered the effect of the Wake and proposed:

$$Sh = 2.0 + (Sh)_n + 0.450\ Re^{\frac{1}{2}}\ Sc^{\frac{1}{3}} + 0.0484\ (Re)(Sc)^{\frac{1}{3}} \quad \ldots\ldots\ldots\ldots\ldots \quad (5.12)$$

(b) From and to Non-Rigid Drops

Heertiges Denie (93) recommended the following correlation for circulating drops:

$$Sh = 1.13\ (Re)^{\frac{1}{2}}\ (Sc)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5.13)$$

Because of the existence of the Wake, Garner and Tayeban (256,80) suggest

$$Sh = 0.6(Re)^{\frac{1}{2}}\ (Sc)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5.14)$$

and for oscillating drops

$$Sh = 50 + 0.0085\ (Re)(Sc)^{0.7} \quad \ldots\ldots\ldots\ldots\ldots \quad (5.15)$$

Mass transfer during drop coalescence has also been investigated, and it is concluded that mass transfer during drop coalescence could be described by the same equation as that for drop formation (265).

5.2 DROPLET PHENOMENA

5.2.1 DROP FORMATION

During formation of drops it is necessary to know: (a) volume of drop as a function of the time of formation, (b) surface area of drop as a function of the solid volume. However, it is not the object of this work to give details of drop formation, a good survey can be found in "Recent Advance in Liquid-Liquid Extraction" (91) and Treybal (265).

5.2.2 BREAK UP MECHANISM

Break up of a droplet occurs if it undergoes sufficient deformation, the forces causing deformation are viscous stress and/or dynamic pressure in the surrounding continuous phase.

Hinze (94) selected the dimensionless groups

$$N\nu_i = \frac{U_D/d}{(\rho_D \frac{\sigma}{d})^{\frac{1}{2}}} \qquad \text{viscous group}$$

$$N_{We} = \frac{P}{\sigma/d} \qquad \text{weber number}$$

An expression for the maximum drop size may be derived from

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

where u = mean square fluctuating velocity

Hinze also considered the case of isotropic turbulence in a batch system and suggested the following expression

$$d_{max} = \left(\frac{\rho_c}{\sigma}\right)^{-\frac{3}{5}} E^{-\frac{2}{5}} C_1$$

where C_1 is a coefficient of the power number reported by Clay (52) to be 0.72 and

$$E = \frac{4}{\pi} C_2 \frac{N^3 D^5}{H D_T^2}$$

This presupposes a high Reynolds number (Re>50,000) and the macroscale of turbulence based upon the agitator characteristic.

For fully baffled conditions Rushton et al (232) derived the following

$$We = \frac{K_1 N^2 R^{\frac{3}{4}} d^{\frac{5}{3}} \rho}{\sigma} \quad \text{for } d \gg y$$

y = microscale of turbulence

Shinar and Church proposed to relate drop size to the energy input as $E/\sigma d^2 = 0.26$ where E = total energy associated in breaking drops.

5.2.3 DROP SIZE DISTRIBUTION

A drop size distribution is created in any agitated liquid-liquid contacting device, where the smaller drops are near the impeller in the zone of high turbulence intensity (see Fig. 5.1) and larger drops away from the impeller where coalescence takes place. The most common distribution of drop size is the normal which is characterized by two parameters, mean and standard deviation, and the log normal distribution.

Chen et al (47) correlate the average drop size in a mixing vessel as

$\frac{d32}{L} = 0.053\, N_{We}^{-0.60}$ and their conclusion is that the distribution function for volume fraction is normal and depends only upon d32.

Sprow (250,251) suggested a skewed distribution. A log-normal distribution can also be used.

Oulaloglou and Tavlarides (56) used the normal distribution to correlate the Sauter mean diameter as

$$\frac{d_{32}}{D} = 0.081\ (1 + 4.47\phi)\,(\mathrm{We})_T^{-0.6}$$

where ϕ = hold up, D = impeller diameter
Other correlations may be found in Table (5.2).

The drop size distribution in a mixer-settler arrangement may follow a similar trend to that in stirred vessels, but would be expected to be affected by the outlet restriction caused by the settler.

5.2.4 COALESCENCE OF DROPS

After mixing or agitating two liquids, the resulting dispersion has to be coalesced in a settler where the two phases are separated for further processing.

The mechanism of coalescence depends mainly on the type of dispersion. Unstable primary emulsions (i.e. where droplet sizes are greater than 10 micron) can be settled by gravity to form heterogeneous layers. However secondary emulsions, frequently called "secondary haze" consisting of large numbers of very small drops (less than 1 micron) cannot be settled by gravity. Thus the problem of coalescence and clarification of such systems is much more difficult. For this reason the two types of emulsions will be treated separately.

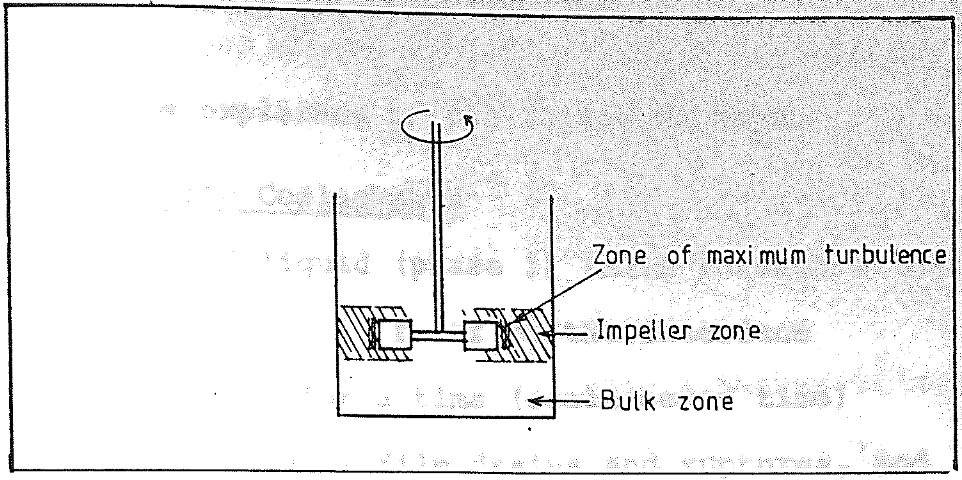
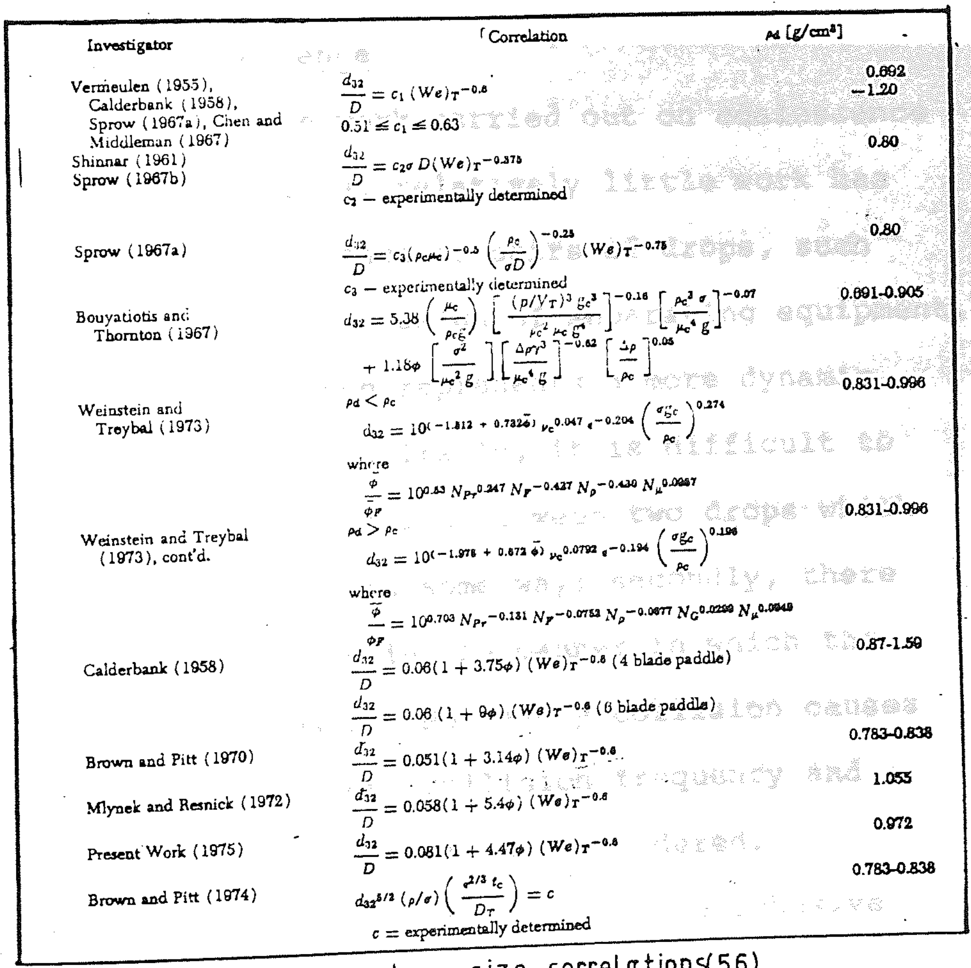


FIG 5.1 Zones of turbulence



Investigator	Correlation	ρ_d [g/cm³]
Vermeulen (1955), Calderbank (1958), Sprow (1967a), Chen and Middleman (1967)	$\frac{d_{32}}{D} = c_1 (We)_T^{-0.6}$ $0.51 \leq c_1 \leq 0.63$	0.692 –1.20
Shinnar (1961) Sprow (1967b)	$\frac{d_{32}}{D} = c_{2\sigma} D (We)_T^{-0.375}$ c_2 — experimentally determined	0.80
Sprow (1967a)	$\frac{d_{32}}{D} = c_3(\rho_c \mu_c)^{-0.5} \left(\frac{\rho_c}{\sigma D}\right)^{-0.25} (We)_T^{-0.75}$ c_3 — experimentally determined	0.80
Bouyatiotis and Thornton (1967)	$d_{32} = 5.38 \left(\frac{\mu_c}{\rho_c g}\right) \left[\frac{(p/V_T)^3 g_c^3}{\mu_c^2 \mu_c g^4}\right]^{-0.16} \left[\frac{\rho_c^3 \sigma}{\mu_c^4 g}\right]^{-0.07}$ $+ 1.18\phi \left[\frac{\sigma^2}{\mu_c^2 g}\right] \left[\frac{\Delta\rho\gamma^3}{\mu_c^4 g}\right]^{-0.62} \left[\frac{\Delta\rho}{\rho_c}\right]^{0.05}$	0.691-0.905
Weinstein and Treybal (1973)	$\rho_d < \rho_c$ $d_{32} = 10^{(-1.812 + 0.732\bar{\phi})} \nu_c^{0.047} \epsilon^{-0.204} \left(\frac{\sigma g_c}{\rho_c}\right)^{0.274}$ where $\frac{\bar{\phi}}{\phi_F} = 10^{0.53} N_{P_T}^{0.247} N_F^{-0.427} N_\rho^{-0.430} N_\mu^{0.0987}$	0.831-0.996
Weinstein and Treybal (1973), cont'd.	$\rho_d > \rho_c$ $d_{32} = 10^{(-1.978 + 0.872\bar{\phi})} \nu_c^{0.0792} \epsilon^{-0.194} \left(\frac{\sigma g_c}{\rho_c}\right)^{0.196}$ where $\frac{\bar{\phi}}{\phi_F} = 10^{0.703} N_{P_T}^{-0.131} N_F^{-0.0752} N_\rho^{-0.0677} N_G^{0.0299} N_\mu^{0.0949}$	0.831-0.996
Calderbank (1958)	$\frac{d_{32}}{D} = 0.06(1 + 3.75\phi) (We)_T^{-0.6}$ (4 blade paddle) $\frac{d_{32}}{D} = 0.06(1 + 9\phi) (We)_T^{-0.6}$ (6 blade paddle)	0.87-1.59
Brown and Pitt (1970)	$\frac{d_{32}}{D} = 0.051(1 + 3.14\phi) (We)_T^{-0.6}$	0.783-0.838
Mlynek and Resnick (1972)	$\frac{d_{32}}{D} = 0.058(1 + 5.4\phi) (We)_T^{-0.6}$	1.055
Present Work (1975)	$\frac{d_{32}}{D} = 0.081(1 + 4.47\phi) (We)_T^{-0.6}$	0.972
Brown and Pitt (1974)	$d_{32}^{5/2} (\rho/\sigma) \left(\frac{\epsilon^{2/3} t_c}{D_T}\right) = c$ c = experimentally determined	0.783-0.838

Table 5.2 average drop size correlations(56)

5.2.4.1 COALESCENCE OF PRIMARY DISPERSIONS

This can be explained in the following ways.

(A) Drop-Interface Coalescence

When a drop of liquid (phase 1) falls through a less dense liquid (phase 2), it rests on the interface separating the phases for a time (coalescence time) until the trapped phase 2 film drains and ruptures, and the contents of the drop are deposited into the bulk phase 1. This process has been termed step-wise or partial coalescence.

The effect of changing variables on the system characteristics has been summarised in Table (5.3)(165).

(B) Drop-Drop Coalescence

In contrast to the work carried out on coalescence of drops at the interface, relatively little work has been reported on coalescence of pairs of drops, such data are important to the design of separating equipment.

Drop-drop coalescence represents a more dynamic situation on two counts. Firstly, it is difficult to produce a controlled collision between two drops which have not been restrained in some way; secondly, there is an inherent randomness in the manner in which the drops rebound or coalesce. Not every collision causes coalescence, therefore both collision frequency and coalescence probability have to be considered.

Shiner (246) postulated that since the cohesive force holding any two drops together is independent of drop diameter, there should be a minimum size of separable drop at a given turbulence level. Drops below this size should coalesce rapidly. Support for this is claimed from the fact that a critical agitator speed exists below which coalescence will not occur.

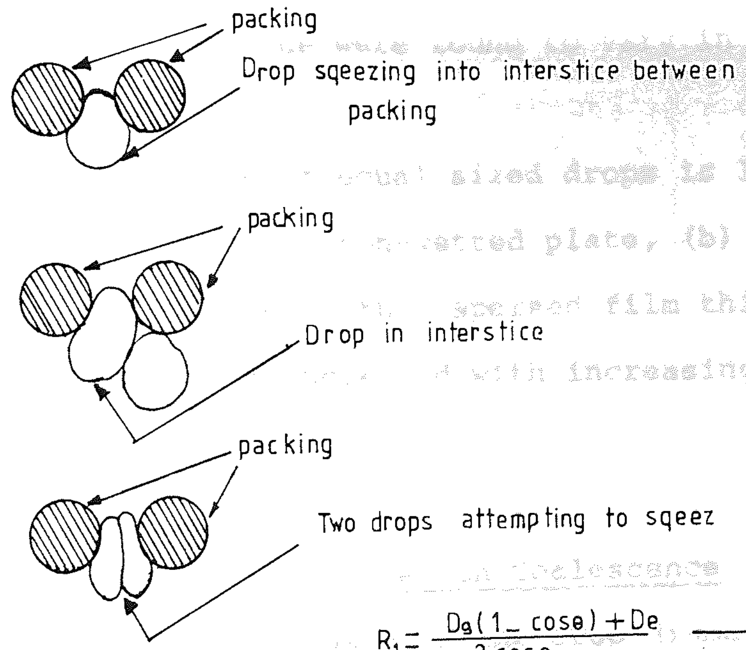
Jeffreys and Mumford (124) developed a mathematical model to describe drop behaviour in a bed packed with glass ballotini (Fig.5.2). More details about drop-drop coalescence can be obtained from (114,121,165,120).

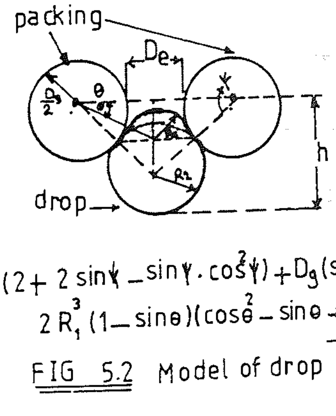
(C) Coalescence of Swarms in Settlers

In mixer-settlers the emulsion generated in the mixer passes into the settling chamber and is distributed in the form of a wedge between the two phases in the settler. The dispersion wedge may exist above the interface if the more dense liquid is the dispersed phase, or below the interface if the less dense liquid is dispersed as illustrated in Fig. (4.7). The volume of the heterogeneous wedge between the phases is determined by the equilibrium between the rate of input of emulsion and the rate at which droplets of the dispersed phase coalescence at the surface of the emulsion. The emulsion settling rates are a function of both the surface area of the emulsion and the volume it occupies. It is evident that drop-to-drop coalescence occurs within the wedge, and droplets having a larger diameter than the mean exist at the emulsion surface. Coalescence of

Variable (increasing)	Effect on coalescence time	Explanation in terms of effect on phase-2 film drainage rate
1. Drop size	Longer	More phase 2 in film
2. Length of fall	Longer	Drop 'bounces' and film is replaced
3. Curvature of interface towards drop (a) Concave (b) Convex	Longer Shorter	More phase 2 in film Less phase 2 in film
4. Interfacial tension	Shorter	Less phase 2 in film (More rigid drop)
5. Phase μ ratio $\left(\frac{\mu \text{ drop}}{\mu \text{ continuous}}\right)$	Shorter	Either less phase-2 film or increase in drainage rate
6. Phase $\Delta\rho$	Longer	More deformation of drop more phase-2 film
7. Temperature	Shorter	Increases phase μ ratio
8. Temperature gradients	Shorter	Thermal gradients 'weaken' film
9. Vibrational effects	Shorter	Assist drainage rupture
10. Electrostatic effects	Shorter	Increase effective gravitational force
11. Applied electric field	Shorter	Increases effective gravitational force
12. Presence of a third component (a) stabiliser (b) mass transfer into drop (c) mass transfer out of drop	 Longer Longer Shorter	 (a) Forms 'skin' around drop (b) Sets up interfacial tension gradients which oppose flow of film (c) Sets up interfacial tension gradients which assist flow of film

Table 5.3 The effect of changing certain variables on the system characteristic(165)





$$R_1 = \frac{D_g(1-\cos\theta)+De}{2\cos\theta} \qquad \text{——— 1}$$

$$R_2 = \frac{D_g(1-\cos\psi)+De}{2\cos\psi} \qquad \text{——— 2}$$

$$h = \frac{2R+(D_g+De)\tan\psi}{2} - \frac{1}{2}[(D_g+De)(\tan\theta-\sec\theta)-D_g] \qquad \text{——— 3}$$

$$D_b = R_2^3(2+2\sin\psi-\sin\psi\cdot\cos^2\psi)+D_g(\sin\psi-\sin\theta)(R_1^2\cos^2\theta+R_1R_2\cos\theta\cos\psi+R_2^2\cos^2\psi+2R_1^3(1-\sin\theta)(\cos^2\theta-\sin\theta+1) \qquad \text{——— 4}$$

FIG 5.2 Model of drop residing in packing interstice see(124) these droplets greatly affects the volume of the wedge and thus the capacity of the mixer-settler extraction unit.

(D) Coalescence Time

The time period between the arrival of a drop at the interface and its disappearance is termed coalescence time. Several idealised models exist to describe the process of coalescence (96). However only few have been proposed for coalescence time as a function of physical properties of the system (125).

The presence of impurities can increase or decrease coalescence time. It is of some relevance to the selection of settlers to note that the coalescence times of drops on a solid surface were found to vary in the following manner (100).

(a) The coalescence time of equal sized drops is less on a wetted plate than on a non-wetted plate, (b) The coalescence time increased with dispersed film thickness, (c) The coalescence time increased with increasing drop size.

(E) Effect of Surface Properties on Coalescence

Coalescence time increases as the drop diameter d, density difference between the phases D_ρ and continuous phase viscosity μ_c increase, and as the interfacial tension decreases. Therefore separation of primary dispersions in packing will be more easily carried out in systems of high interfacial tension and low continuous phase viscosity. The most efficient arrangement for separating the primary dispersion is when the dispersed phase wets the packing. A measure of the wettability can be obtained from determination of the contact angle (120). "Knit Mesh" packings made up of stainless steel (high surface energy material), polypropylene (low surface energy material), and stainless steel and P.T.F.E. meshes have been used by Jeffreys and Davies (122). Their results are shown in Table (5.4) where the maximum flow rates of dispersed phase pass through a mixed packing.

Packing	Dispersed Phase	Flooding Velocity ml/cm^2.sec
Stainless Steel	Kerosene Water	0.069 0.993
Polypropylene	Kerosene	1.117 0.0475
Composite Packing Stainless Steel Polypropylene	Kerosene Water	1.45 1.45

Table 5.4 (122)

5.2.4.2 COALESCENCE OF SECONDARY DISPERSIONS

Here the droplet sizes are so very much smaller and the separation mechanisms different from primary dispersions that the previous discussion cannot be directly applied. The basic requirement is to promote interdrop coalescence until the resulting drops can be separated as a primary dispersion or settle under gravity. In this region the wetting properties of the packing are less important since the droplet sizes are very much less than the equilibrium drop size. Secondary dispersions must be distinguished from double-multiple emulsions, which are composed of a number of minute drops of one liquid within a containing phase of another (136), Fig. (5.3).

The phenomena of the secondary dispersion may be explained in the following ways.

(a) Formation of Secondary Dispersion

In the operation of any extraction plant secondary drops are formed in the mixer if the agitation is intense, and in the settler by step-wise coalescence of droplet as shown in Fig. (5.4). The film separating the drop and interface ruptures (B on Fig.5.4) and the drop begins to deflate, as a result of drainage a cylindrical shape is formed (C), the latter then detaches and forms secondary drops (D)(E).

Spontaneous emulsification which may occur when two phases are very gently brought into contact may sometimes be responsible for the formation of troublesome fine dispersions or "haze" (114).

(b) Coalescence and Prevention of Secondary Dispersion

Secondary dispersion may be reduced by lowering the agitation intensity in the mixer, and the spontaneous

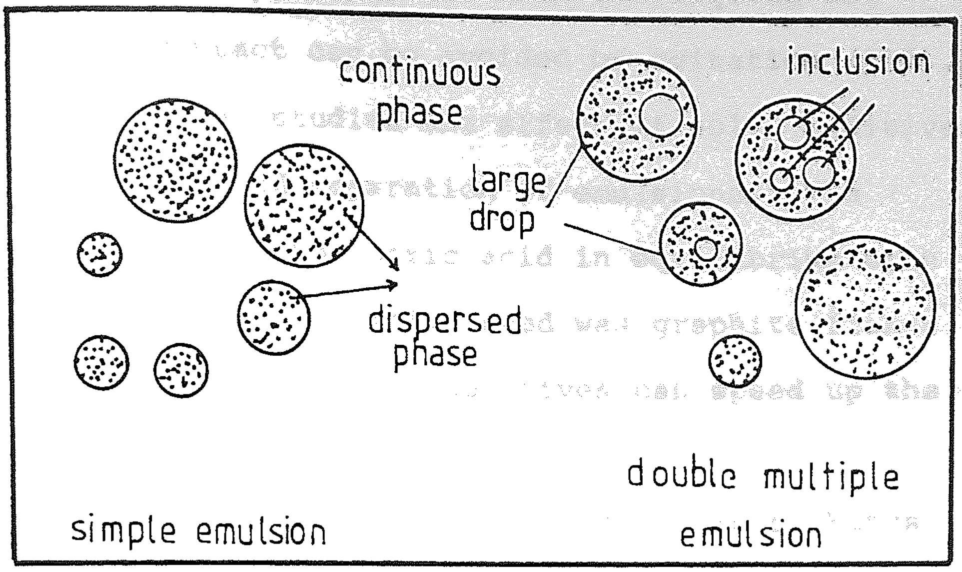


FIG 5.3 Simple and multiple emulsion

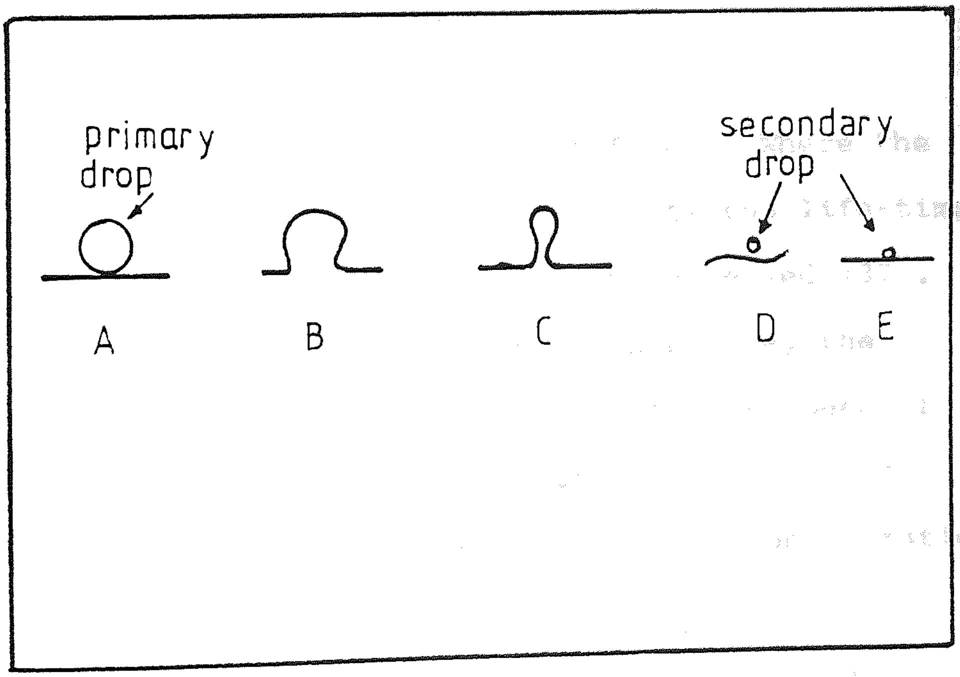


FIG 5.4 Step wise coalescence (165)

emulsification which may occur when two liquids are brought into contact can be avoided by agitation (116).

Mizrahi (189) studied the effect of solid additives on the formation and separation of emulsions. The solution used was phosphoric acid in equilibrium with a solvent phase; the additive used was graphite flakes. The results show that solid additives can speed up the coalescence processes.

Coalescence of secondary dispersions in packings is more efficient in systems of high interfacial tension and high density difference. The proper selection of the packing is of vital importance. Packings made up from fine fibres with high surface roughness appear most efficient.

5.2.4.3 EFFECT OF IMPURITIES AND SURFACE ACTIVE AGENTS ON COALESCENCE OF DROPS

Impurities may take a number of forms. Where the impurity is of an inert nature (e.g. dirt) the life-times of drops at the interface are markedly decreased (37). Where the impurity is surface active in nature, the result is invariably a marked decrease in the speed of coalescence. It has been found that the life time of drops depends roughly upon the cube root of concentration of surfactant.

Drop-soluble surfactant lowers the interfacial tension and causes smaller drops and longer time for coalescence.

5.2.4.4 EFFECT OF MASS TRANSFER ON COALESCENCE OF DROPS

The explanation of this phenomenon is beyond the scope of this work. However Jeffreys and Lawson (126) using a ternary system of benzene-acetone-water, found experimentally that coalescence time changes with the direction of transfer, and the most desirable direction of mass transfer is from the dispersed phase to the continuous phase - although, if the physical properties of the phases are such that step-wise coalescence might be expected, a large hold-up of stabilised secondary drops might occur. The action in this case is to apply some external agent such as temperature or electric field to remove the step-wise condition of the process.

5.2.5 DROP SIZE PREDICTION

Frequently, workers concerned with dispersion of immiscible liquids desire knowledge of the drop size of the system. These have been estimated by different experimental techniques including:

(1) Light transmittance (267,223,272)
(2) Light scattering (253)
(3) Photography (99)
(4) Electronic particle counting (193)
(5) Sedimentometry
(6) Liquid-liquid extraction by fast pseudo-first order reaction

5.3 MASS TRANSFER IN AN AGITATED TANK

This may be sub-divided into two general categories, the first is to study the power consumption and the second is the observation of the rate of mass transfer and quality of mixing. The former area has been investigated for a number of years, with both Newtonian and non-Newtonian fluids. However little has been done in regard to quantitative determination of mixing rates or to provide an understanding of flow patterns and the factors controlling them.

The term short-circuit, or mathematically by-passing (described in Chapter 4) has been used by Denbigh (63) and Weber (278) to denote the conditons involving probability considerations applicable to well-agitated tanks in which the contents are substantially homogeneous and some of the molecules in the feed appear almost immediately in the effluent as a result of good agitation.

MacMulline (171) later agreed that shortcut or channellised flow between inlet and outlet would indeed alter conditions in a tank and suggested that the efficiency of a stirred tank could be evaluated by studying the conversion rate of a reacting system of known kinetics.

5.3.1 MASS TRANSFER COEFFICIENT AND INTERFACIAL AREA

It has been mentioned in the previous sections that mass transfer coefficient embraces three fundamental

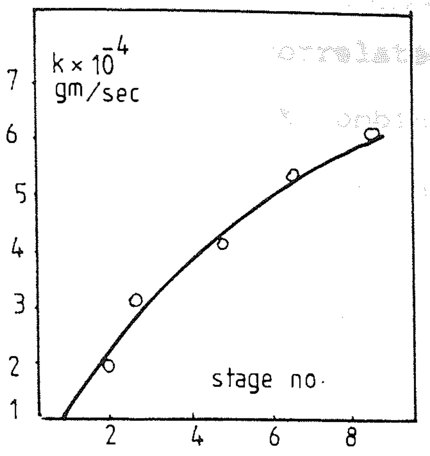


FIG 5.5 Effect of the number of stages on mass transfer coefficient

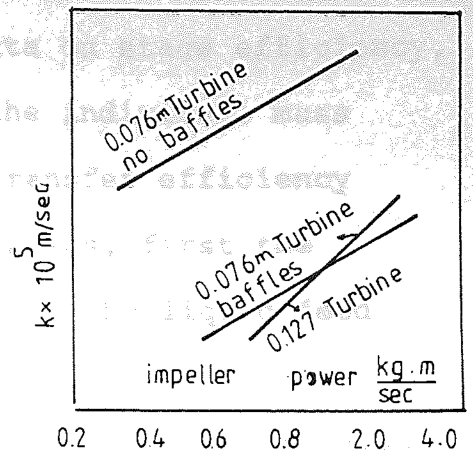


FIG 5.6 Influence of baffles and impeller power on k, flow rate 0.185 to 0.249 kg/s. and 0.065 kg org/kg aq.

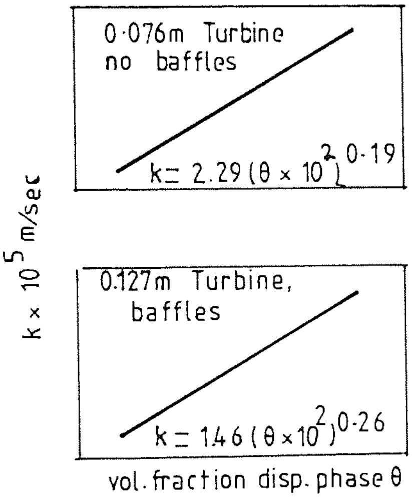


FIG 5.7 Influence of disperse phase hold up on k. flow rate .249 kg/s NRe 28,500-32200

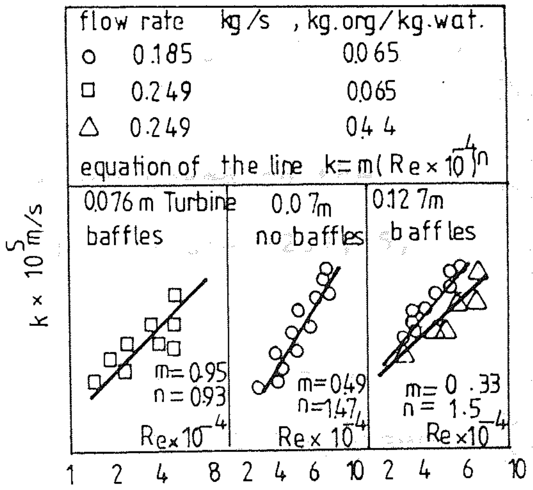


FIG 5.8 Continuous phase mass transfer coefficients

resistances. However, much of the literature on the extraction characteristics of mixing vessel provides only scattered and uncorrelated data on stage efficiency, and using K in which K combines the individual mass transfer coefficients. The mass transfer efficiency is affected by two classes of variables, first the impeller and its operation and second the liquid feed rate and phase ratio.

The individual mass transfer coefficients are also different with the above variables as confirmed by Negate (196).

Salem (237) in his studies on mass transfer in a laboratory scale mixer-settler using the system acetic acid-toluene-water shows that the overall mass transfer coefficient increased as the number of stages increased, as shown in Fig. 5.5.

Figs. 5.6-5.8 are self explanatory based on the experimental data reported in the literature (237,75, 86,264).

The interfacial area can be calculated from a knowledge of average drop diameter (d_{32}) and dispersed phase ratio as given by Sprow (172).

$$A = \frac{\sigma \phi d}{d_{32}}$$

ϕ_d = volume fraction of dispersed phase

$d_{32} = 0.38 d_{max}$

d_{max} = maximum stable size

$$= K_1 E^{-0.4} \left(\frac{\rho c}{\sigma}\right)^{-0.6}$$

where $$E = \frac{4K_2}{\pi} - \frac{N^3 D^5}{1+D_T^2}$$

Some of the important correlations for estimation of interfacial area are presented in Table 5.5.

5.3.2 PHASE RATIO AND PHASE INVERSION

In an agitated tank the application of external energy sub-divides one of the phases into droplets, the dispersed phase, while the other liquid forms the continuous phase.

If more and more dispersed phase is added to a fixed volume of continuous phase the most significant change is an increase in interfacial area.

Correlation for 'a' ft^2/ft^3	
$a = \frac{25.4(x)^{0.5}(N_{We})^{0.6}}{D}$	Vermeulen (1955): for 4-bladed, flat paddles
$a = \frac{100(x)(N_{We})^{0.6}}{C.D.}$	Calderbank (1958) $C = 1+7.75(x)$ for 4-bladed paddles $C = 1+9.0(x)$ for 6-bladed paddles where x = hold up of dispersed phase
$a = \frac{C(N_{We})^{0.5}(N_{Re})^{0.1}(x)}{D}$	Kafarov (1959) $C = 25.9$ for 6-bladed turbines $C = 18.65$ for 2-bladed vertical turbines $C = 13.85$ for propellers

Table 5.5 Transport Phenomena in Liquid Extraction by Laddha, G.S. and Degaleesan, T.E., Tata McGraw Hill Publishing Co. Ltd (1976)

However, a point is eventually reached at which the addition of more dispersed phase causes inversion to take place. The continuous phase suddenly becomes dispersed and the original dispersed phase becomes continuous.

The most important factor in determining which phase will be dispersed in a binary mixture of immiscible liquids is the phase ratio, which reported by Ostwald, and became known as Ostwald's ratio. Clarke (51) claimed that the introduction of a small quantity of solute under non-equilibrium conditions has an effect on Ostwald's ratio, and makes inversion easier.

Other factors that control which of the two immiscible liquids will be continuous in a stirred tank have been studied by many other authors. Equipment size, power input, and mass and heat transfer may be affected by which of the phases is the continuous one in the resulting dispersion.

Quinn and Sighoh (214) found that the phase which becomes continuous depended strongly upon the impeller position and stirring rate, Fig. (5.9).

Selker and Sleicher (244) included in their study the variables viscosity, density, speed of mixing, manner of initiating the dispersion, and the material and construction of the mixing apparatus. Their first step in developing a means of predicting which phase would be the continuous one was to determine the upper limit of hold-up (volume fraction of dispersed phase) of each component under a given set of conditions. There is always a range of volume fractions throughout

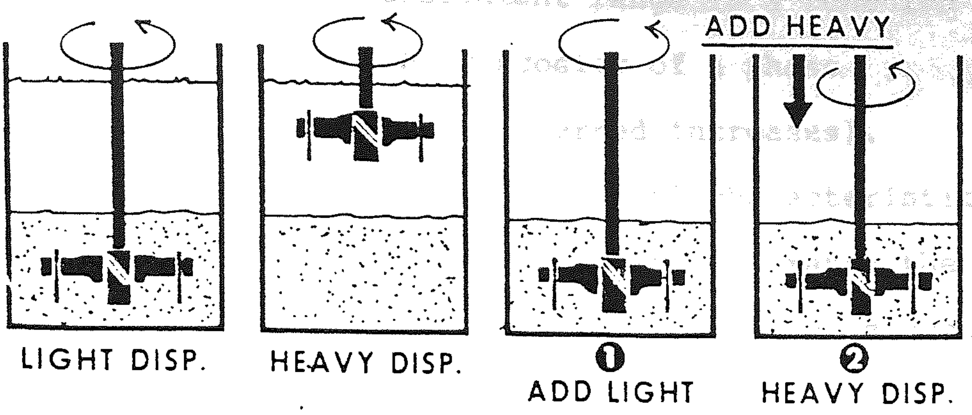


FIGURE 5.9

METHOD OF CONTROLLING WHICH PHASE IS DISPERSED IN BATCH EXTRACTIONS

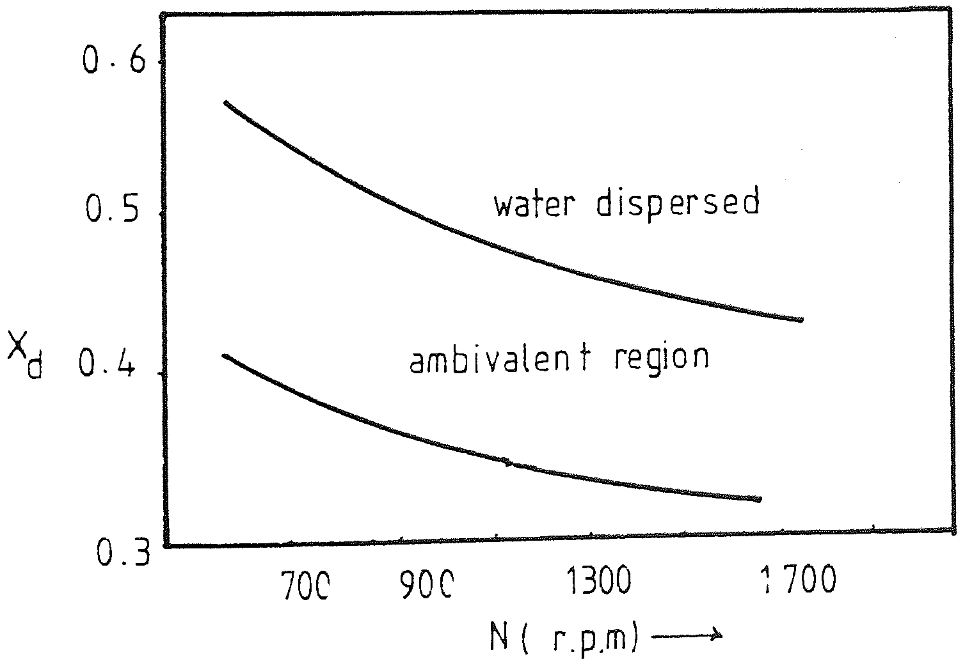


FIGURE 5.10 INVERSION CHARACTERISTICS FOR HEXANE – WATER SYSTEM DATA FROM HOSSAIN (100)

which either component would remain stably dispersed, and this range was termed ambivalent range. Their conclusion was that the ambivalent range is a function of the viscosity ratio (as the viscosity of a phase increases its tendency to be dispersed increases). It is not strongly dependent upon vessel characteristics or stirring speed, and within the ambivalent range the phase which will become the continuous one depends upon the starting procedure.

Phase inversion is best presented graphically by plotting the volume fraction at inversion of one phase against stirring speed as illustrated in Fig. (5.10). Volume fraction of the organic phase is used as the ordinate valve, and in water dispersed organic continuous (W/O) systems, the dispersion lies above the upper curve and as organic dispersed/water continuous (O/W) the dispersion lies below the lower curve. In between the two curves either configuration is possible.

Batch studies on phase inversion were performed in an agitated baffled tank by Quin et al (214), and they concluded that at a fixed impeller speed the inversion concentration C_1 expressed as volume fraction in the organic phase is given by

$$C_1 = C_o + \frac{b}{p}$$

P = energy input

C_o = asymptotic valves for high energy input

b = constant proportional to $\frac{\sigma}{\rho_c}$

Houssain (100) carried out his investigation of phase inversion in a continuous system using mixer-settler equipment, and concluded that phase inversion occurs at high ratio of the dispersed to the continuous phase, and hold-up value in the mixer at the point of the inversion is correlated by

$$\frac{V_c}{V_d} = 1 - \frac{4}{3x} + \frac{1}{9x^2} + \frac{2}{27x^3} + \frac{4}{81x^4}$$

with the initial condition

$V_c = 0, \quad X = 1$

$V_d = 0, \quad X = 0$

more data on phase inversion can be obtained in literature (10).

Which phase is dispersed in an industrial mixer-settler is clearly of importance since

(a) Mass transfer efficiency is dependent on the direction of transfer of solute

(b) Wedge length is dependent on which phase is dispersed.

CHAPTER
SIX

EXPERIMENTAL INVESTIGATION

6.1 PURPOSE OF INVESTIGATION

On the basis of the literature reviewed in Chapter 3, the purification of phosphoric acid using solvent extraction methods appeared to be of practical and economical significance. This study set out to investigate the effect of variables such as solvent/feed ratio, number of stages, feed (acid) concentration composition and power input on the operation of a pilot scale continuous contactor to extract phosphoric acid from pure and impure aqueous solutions. Another object of this work was to confirm the work reported in the literature (282) which was based on a small scale (250 ml) batch extractor. Still another object of this work was to choose a reasonable solvent for extraction of phosphoric acid. It was also an object of this work to design and evaluate economically a full scale process based on the data obtained from the pilot plant experiments.

The investigation was based on a continuous counter-current extractor. A horizontal mixer-settler cascade was chosen since this is the most common in industry, and for the small number of stages involved in the extraction, mixer-settlers seemed to be the most adaptable, simplest and least costly (16,105). Therefore a novel horizontal, air-operated, gravity mixer-settler cascade of the type described in Section 4.2 was designed to meet this requirement. In the case of impure phosphoric acid, the investigation was conducted with artificially prepared mixtures.

6.2 EQUIPMENT DESIGN AND CONSTRUCTION

6.2.1 LABORATORY SCALE EQUIPMENT

6.2.1.1 EQUIPMENT USED FOR BATCH STUDIES AND TIE LINE DETERMINATION

This equipment used by Yacu (282) consisted of jacketed cylinders each having the dimensions shown in Fig. (3.11) and photographed in Fig. (6.1). A thermo-circulator supplied by Churchill Co. Ltd. was used to supply water at a constant temperature (25^{o} ± 0.5) through the jacket of each cylinder. The cylinders acted as mixer-settlers and were fitted with a Gallen Kamp stirrer of maximum speed 1300 r.p.m.

6.2.1.2 EQUIPMENT USED FOR ANALYSIS AND BINODAL CURVE DETERMINATION

These include:

(a) Large temperature controlled bath provided with a circulator motor.

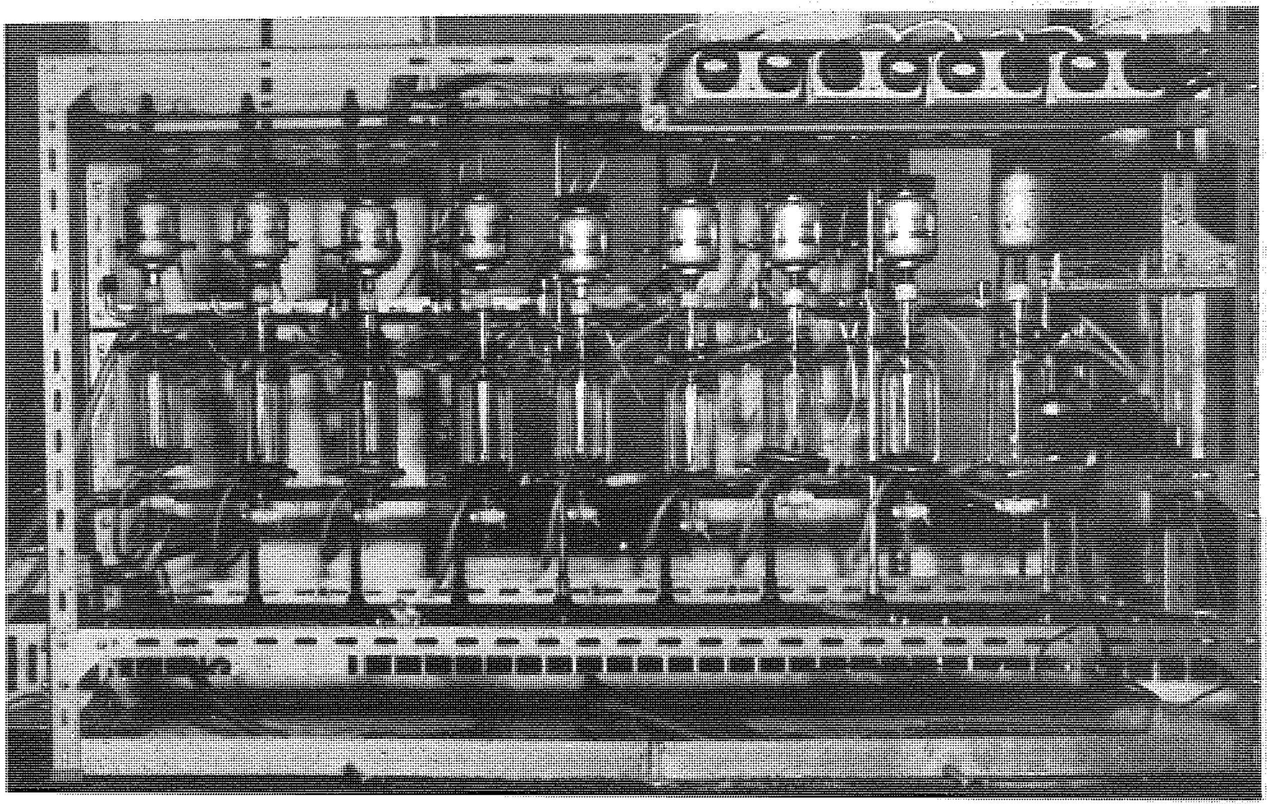


FIG. 6.1 JACKETED CYLINDERS ASSEMBLY

(b) Clear glass measuring cylinders fitted with cock and having capacities ranging from 50 to 100 c.c.

(c) Burette fitted with a P.T.F.E. stop cock.

(d) Liquid droppers.

(e) Four decimals (mgm) electrical balance.

(g) Automatic pipette.

(h) Separating funnels.

(i) Glass bottles of 100-300 ml capacity.

(j) Magnetic stirrer.

(k) Atomic absorption spectrometer.

(l) Specific gravity bottles.

(m) "Cannon-Fensky" u-tube.

(n) "White" torsion balance.

(o) "Abbey" A60 refractometer.

(p) Conductivity device.

6.3 PILOT PLANT EQUIPMENT DESIGN

6.3.1 MATERIALS OF CONSTRUCTION

Three main materials of construction were employed.

(i) Industrial glass Q.V.F., for mixing and settling tanks, valves, air lift pumps and storage and feed vessels.

(ii) Stainless steel, for impellers, rotor shafts, settler and feed tank end plates, some pipe connections, feed tank coils, parts of the air lift pumps and baffles.

(iii) Rubber ("Siliscol" acid resistant) and polytetrafluoroethylene, (Teflon) for pipe connections, gaskets and alternative discs.

6.3.2 EQUIPMENT FOR EXTRACTION AND SOLVENT WASHING

This includes the construction of a three stage horizontal mixer-settler cascade to extract phosphoric acid countercurrently from the aqueous solution using organic solvent. The same equipment was to be used for washing the solvent with water. The flow diagram of the cascade (three stages) is shown schematically in Fig. (6.2) and photographically in Fig. (6.3). Each stage in the process scheme incorporated one mixer and one horizontal settler as shown in Fig. (6.4). The mixers are 10cm diameter cylindrical vessels, made of Q.V.F. industrial glass, fitted with dished bottoms, each mixer was provided with a four-bladed turbine and four vertical baffles.

The agitation was carried out by means of an air driven motor. The mixer speed was variable in the range 400 to 4000 r.p.m., and was measured by means of a high precision comark type 2101, electronic tachometer. Each agitation shaft was provided with a photoelectric probe connected via a three-way switch box to the tachometer as shown in photograph (6.4).

The phase separation occurred in 3, 10 cm diameter and 30 cm long, horizontal cylindrical settlers with their ends fitted with rectangular stainless steel plates.

The equipment was operated countercurrently at 25°C, both solvent and aqueous phase (phosphoric acid solution) being heated by means of water at 25°C passing

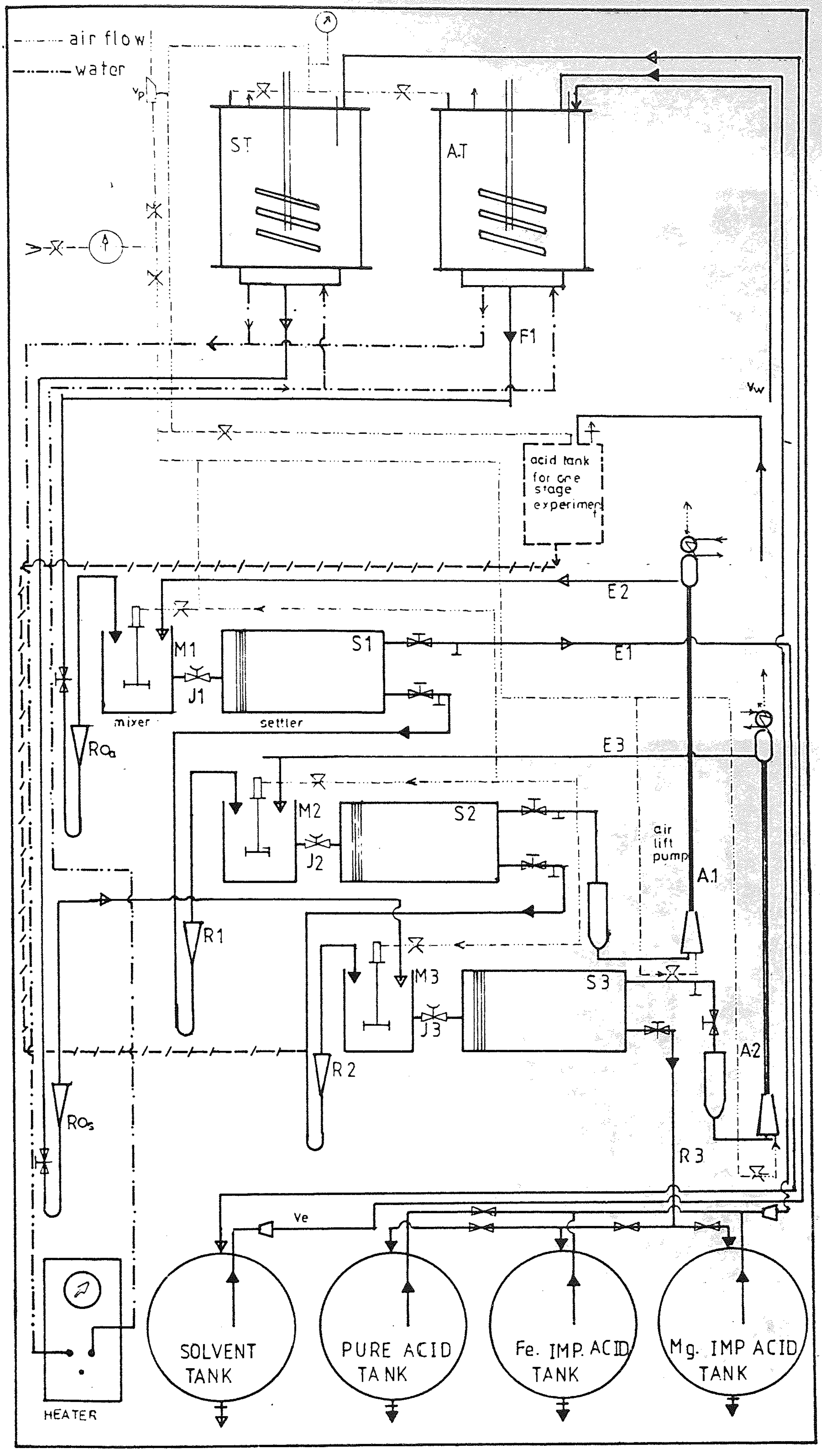
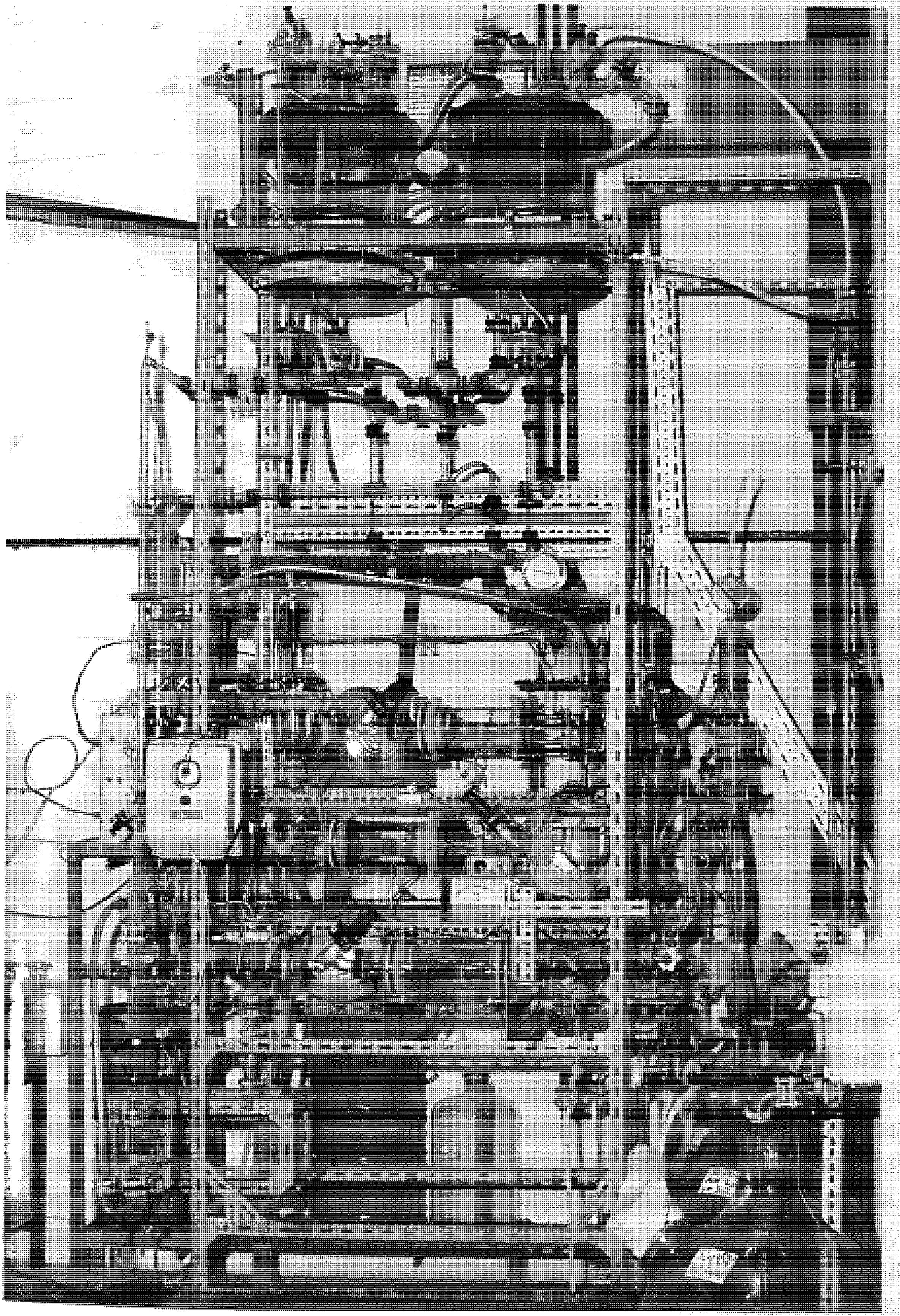


FIG 6.2 FLOW DIAGRAM



through a coil and a jacketted dish fitted to the feed tanks as explained in the next Section. The temperature of the water was raised to 25^{o}C by means of a thermo-circulator supplied by Churchill Instrument Co. Ltd. The thermo-circulator could circulate water ranging from -5^{o}C to 60^{o}C in temperature.

Referring to Fig.(6.2), the aqueous phosphoric acid phase was fed from feed tanks (A.T.) via line (F1) through a rotameter (RO_a) to mixer (M1). Here it was caused to mix with the solvent or the extract from the settler of the second stage (S2) which flowed via line (E2), using air-lift pump (A.1). Emulsion from the mixing vessel flowed through (J1) to settler S1, from which the heavy phase, the raffinate was transferred by gravity to the second mixer (M2) of the second extraction stage through a rotameter and line (R1). At the second extraction stage the raffinate was contacted with the extract from the settler (S3) of the third extraction stage. The extract from the third extraction step was transferred from the settler (S3) to the mixer (M2) by means of air-lift pump (A2) and line E3. The emulsion from the second mixer flowed via line (J2) to the settler (S2) of the second stage, where a second stage of separation took place. The extract, solvent phase, passed to the air-lift pump (A.1) via line (E2) and then to the first mixer (M1), while the aqueous phase acid, raffinate, entered the mixer of the third extracting stage (M3) by gravity through a rotameter and line (R2) and was contacted with the solvent entering the third mixer via line (F2), after passing through rotameter (RO extract) from the feed storage tank (ST). The emulsion from the mixer (M3) was passed through (J3) to the final settler (S3) where a third separation stage took place. The extract (E3) was lifted by air-lift pump (A2) via line (E3) to the mixer (M2) of the second stage, while the final raffinate left the third extraction stage through a rotameter and line (R3) to the storage tank, while the final extract left the first stage via line (E1) to the extract storage tank.

For washing the solvent, the same equipment was used and the rich solvent was lifted from the solvent tank via line (V_p) using vacuum to the feed tanks (ST), while the tank (A.T) was filled with water via line (V_w). The flow of phases was carried out similarly to the above procedure, but in this case the acid was transferred from the solvent phase to the aqueous phase.

6.3.2.1 MIXER DESIGN

Extraction efficiency or the percentage approach to equilibrium achieved in a mixer depends mainly on mixer design. The mixing vessel, Fig. (6.5) and (6.6) was of Q.V.F. industrial glassware, 10 cm I.D. and 15 cm high, and covered with circular stainless steel plates of 3.1 mm thickness. There are two inlet ports (feed pipes), arranged as recommended by Rushton (229)

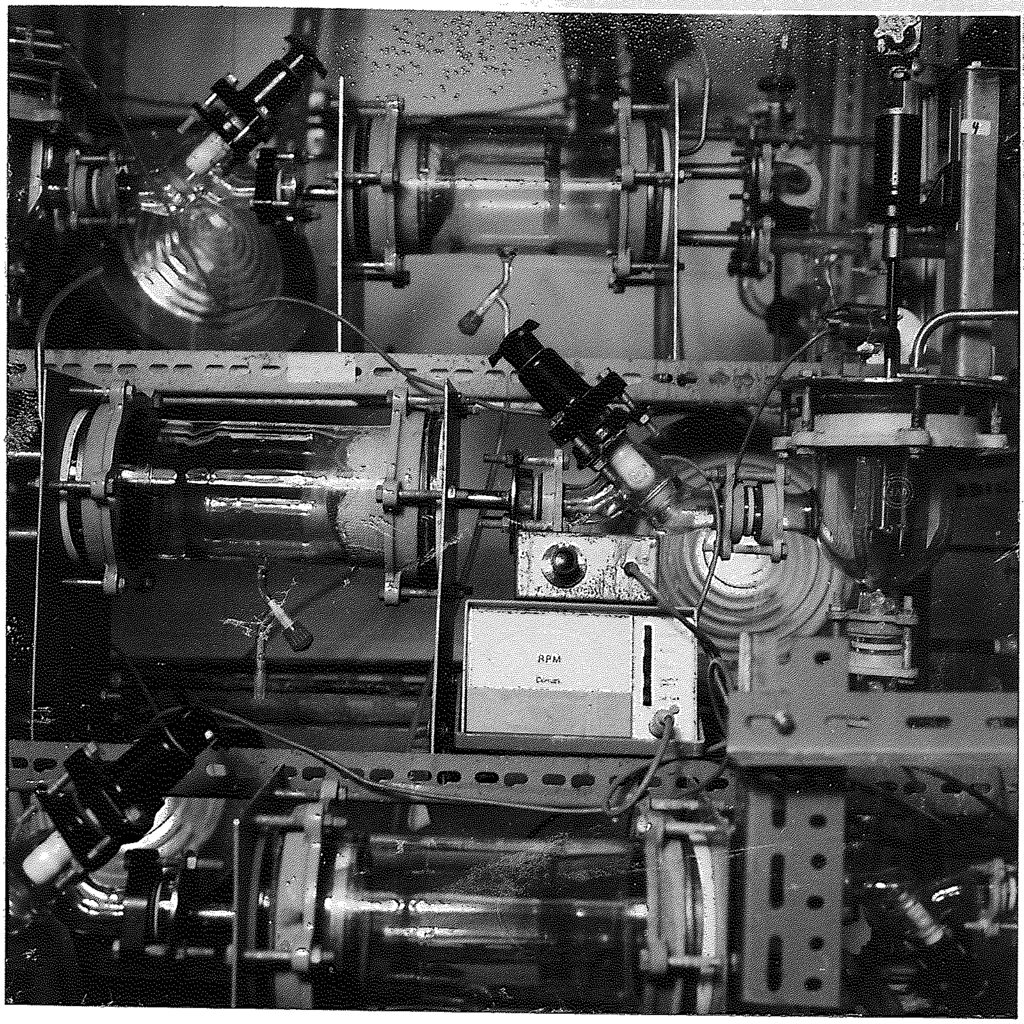


FIG. 6.4

THREE STAGES MIXER-SETTLER

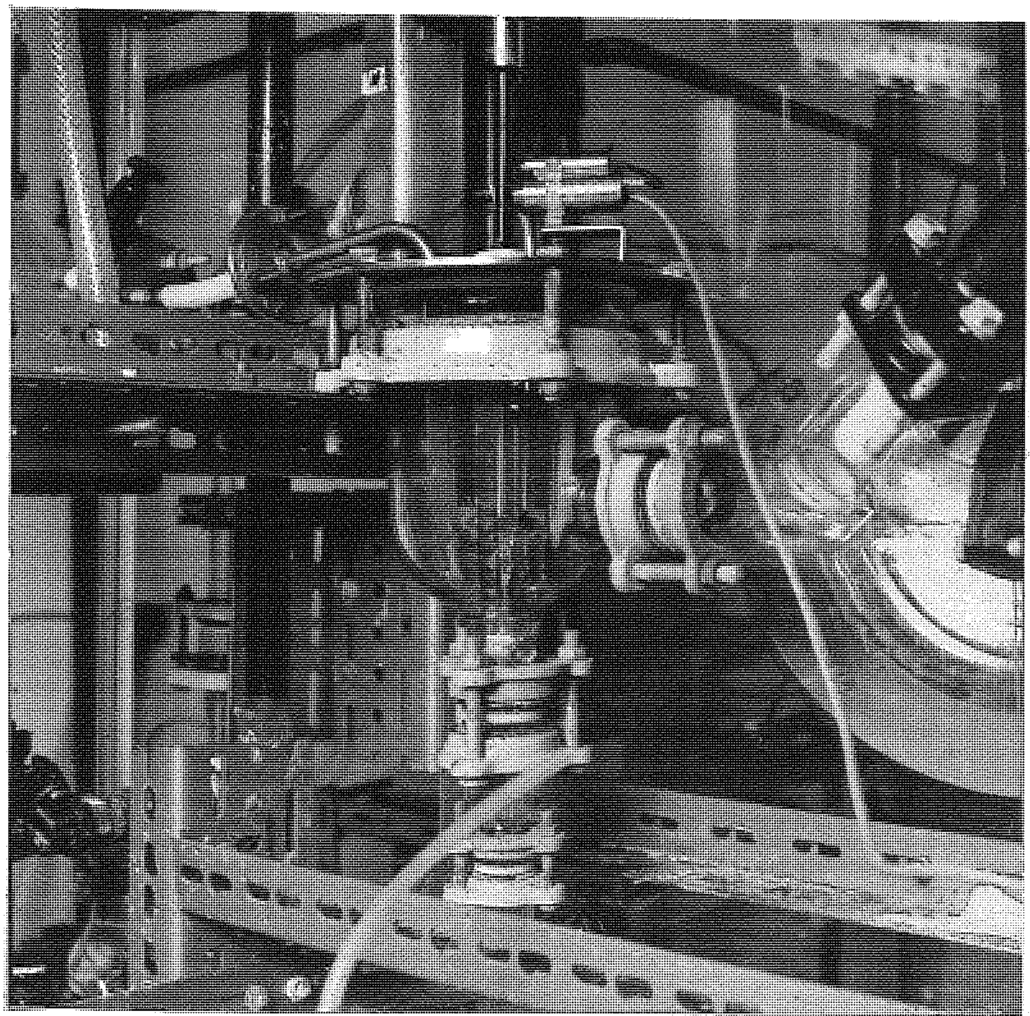


FIG. 6.5

SINGLE MIXING UNIT

as close as possible to the centre of the impeller for the light phase, while the heavy phase (aqueous acid phase) is fed directly above the impeller. The inside diameter of each feed pipe was 1.0 cm.

Agitation was provided by a central high efficiency turbine type agitator having a shaft made of stainless steel, 1 cm diameter and 30 cm long, and was supported in the cover plate by a P.T.F.E. bush. The turbine was driven in a clockwise direction by an air-operated motor supported by a bracket. Each motor was automatically lubricated by means of a special lubricator/ filter arrangement, Fig. (6.7).

The agitator had the flexibility of moving up and down. Each propeller and shaft was welded to provide resistance to the attack of both MIBK and acid. The design of the mixing vessels was dimensionally similar to those recommended by Rushton and Oldshue (232) based on the standard tank configuration.

Each mixing vessel was provided with four equally-spaced stainless steel baffles welded to the cover-plate, the width of each baffle was one-tenth of that of the vessel diameter and of thickness 1.5 mm. Each baffle was cut off at the bottom end at 45° to conform with the shape of the vessel wall. The baffles were fixed at right angles to the wall and 5 mm away from it. To reduce the dead zone in the mixer, small spheres made of glass each 1 cm in diameter were placed at the bottom of the dished shape (see Fig. (6.8)). The mixing vessel also contained a 2 cm

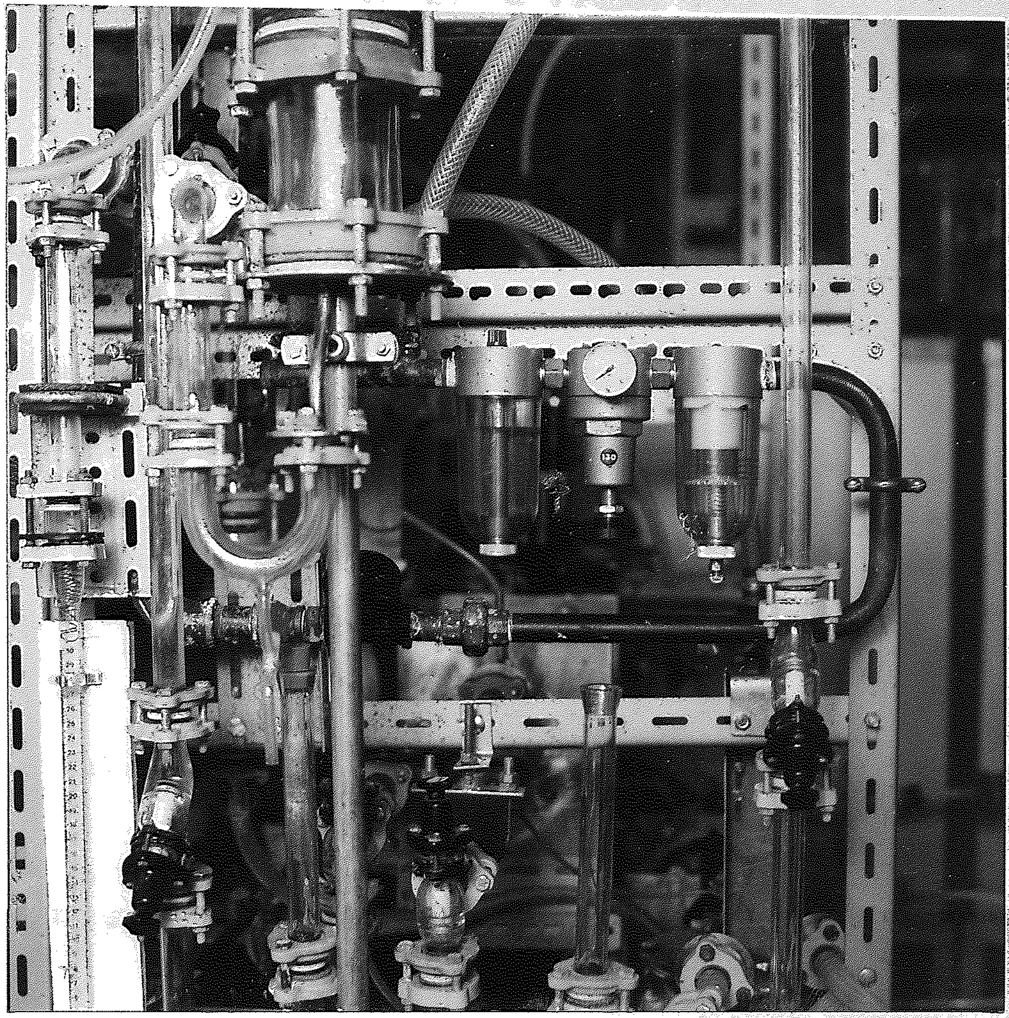
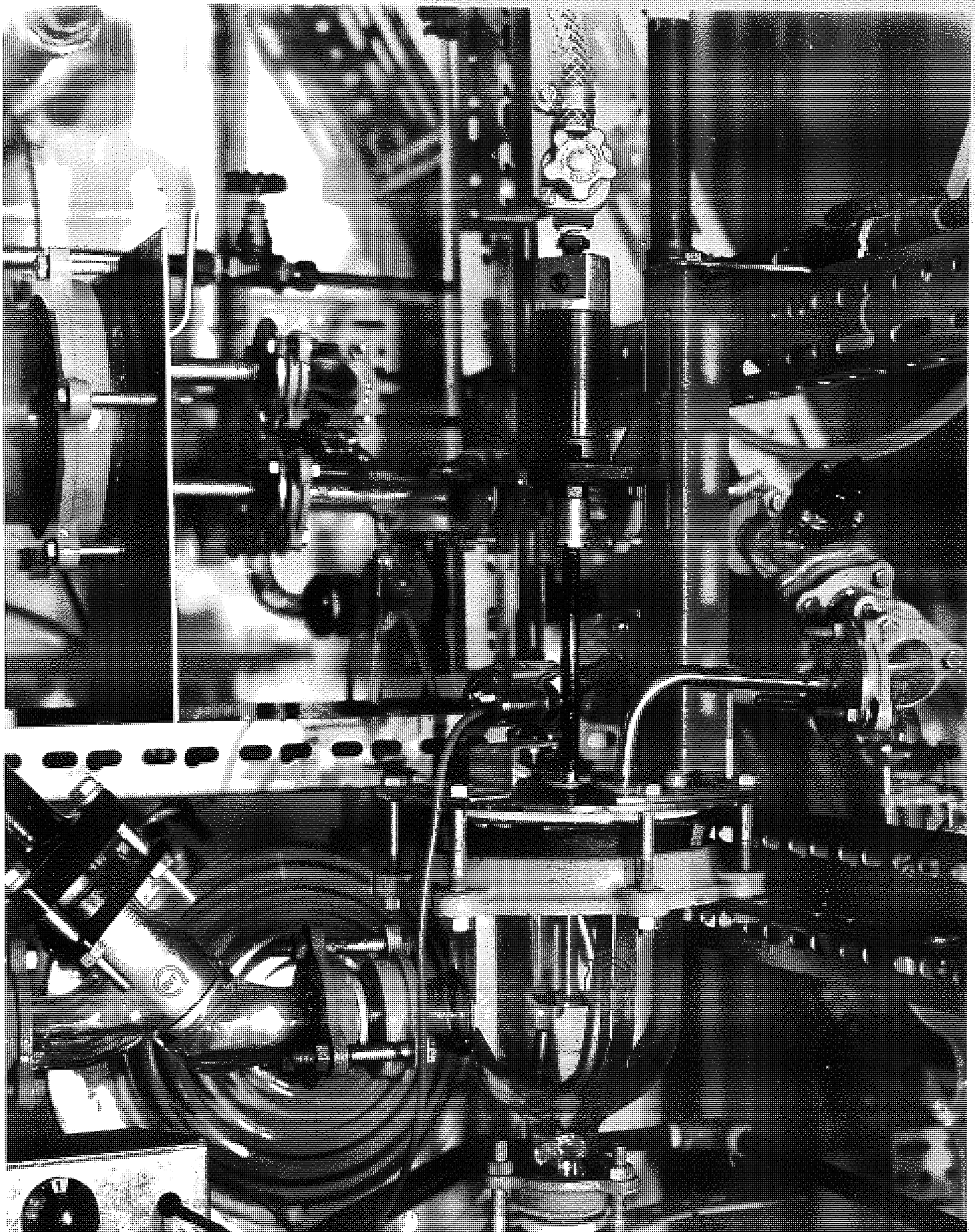


FIG. 6.7 AIR TREATMENT EQUIPMENTS

1. Lubricator
2. Regulator
3. Filter


RPM

opening for the dispersion to pass from the mixer to the settler, and a small vent 1.0 cm diameter, so that the mixer was under atmospheric pressure.

The designed impeller (having dimensions given in Fig. (6.6)) produced a radial flow pattern. Bales et al (13) showed that the space beneath a disc turbine impeller has an effect on the power consumption, there being a reduction in power as the clearance is reduced, the clearance size may change the type of flow from one pattern into another.

6.3.2.2 HORIZONTAL SETTLER-DESIGN

The settler design is dependent to some extent on the operating characteristics of the mixer, and in particular on the impeller design and its speed of rotation. The density difference between the solvent and the aqueous acid phase, the interfacial tension and fluid viscosities are the fundamental physical properties which affect the rate of coalescence, and even within one system these will vary with the different acid and solvent concentrations in the aqueous and organic phases in each stage of the cascade.

The horizontal settler is a cylindrical shape 10 cm diameter and 30 cm long, made of Q.V.F. industrial glass. Two rectangular stainless steel plates 3.1 mm thick were fixed at each end of the settler. The size of the settler was estimated approximately by measuring the settling time in the batch process.

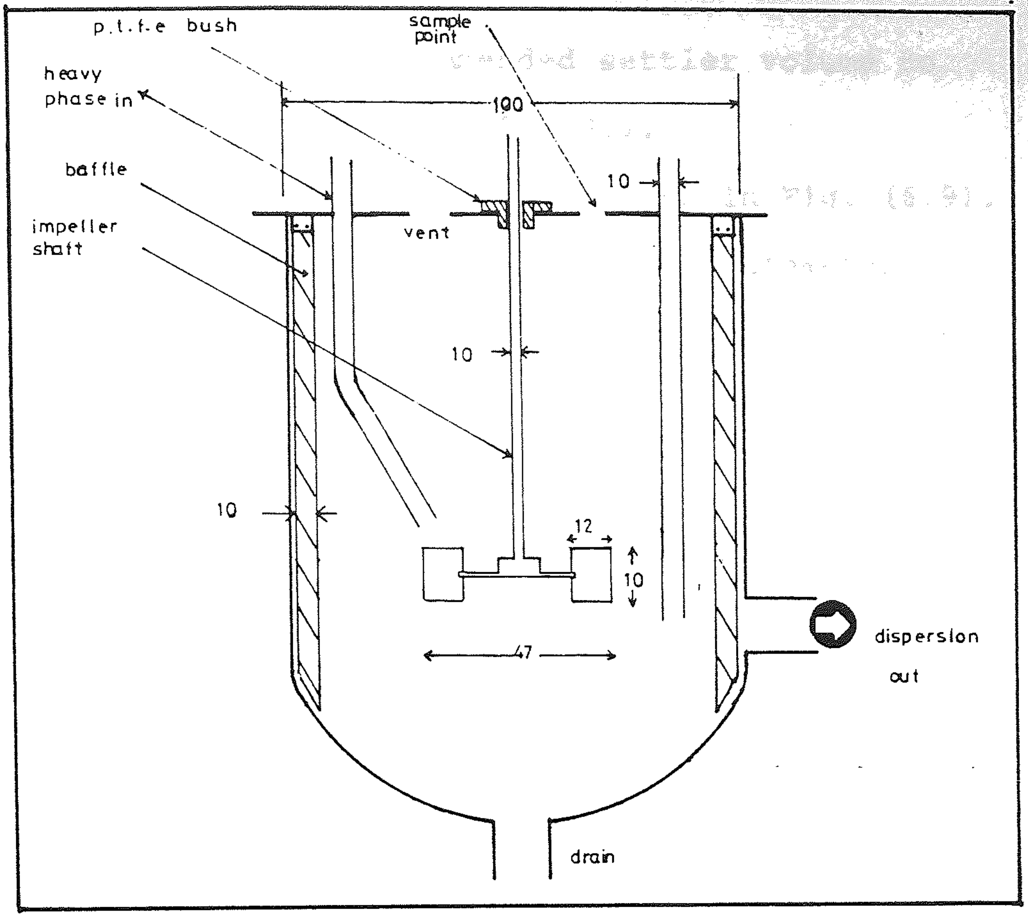


FIG 6.6 Diagram of mixer unit

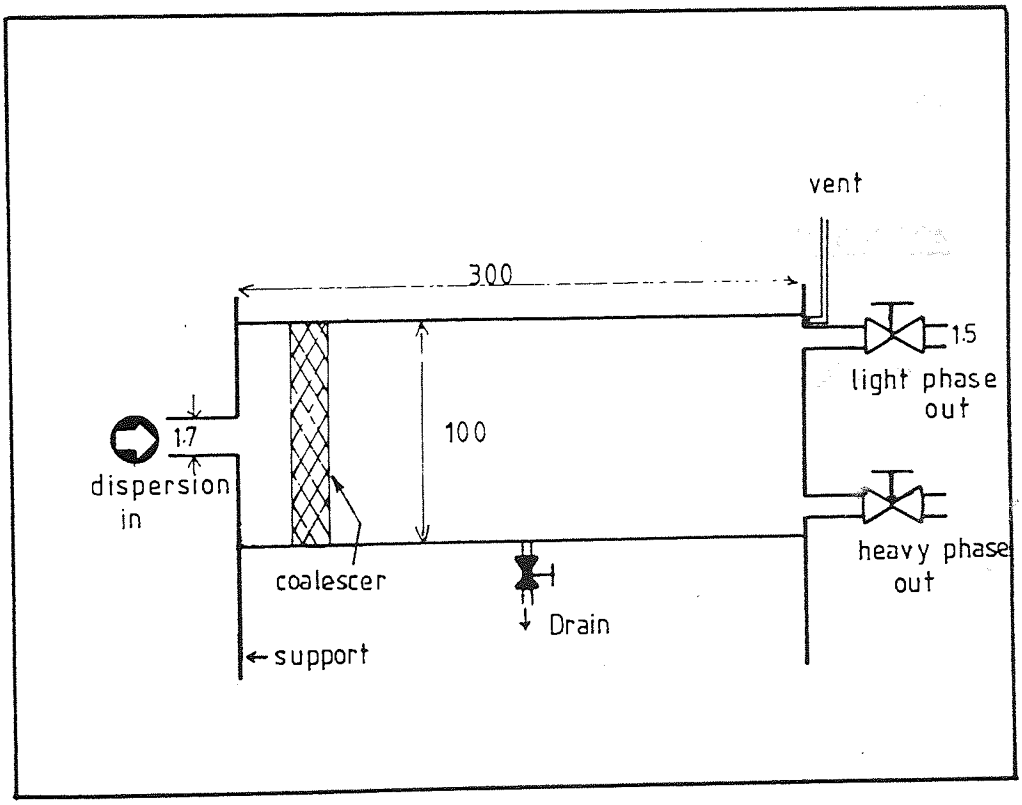


FIG 6.9 Diagram of gravity-settler

However Houssain (100) recommended settler volume to mixer volume to be around 2.5-3:1.

Other settler dimensions are given in Fig. (6.9). The inlet port of the settler was 1.7 cm diameter and located centrally in one end plate, the other end section containing the light (solvent) and heavy (aqueous acid) phase discharge ports each of 1.5 cm I.D., both phases were controlled via valves made of industrial Q.V.F. glassware.

In order to improve coalescence in the settler and to eliminate turbulence a baffle and coalescers were tried. The types of baffle and coalescers used are shown in Appendix (2), Fig. (1). Houssain (100) suggested that the optimum baffle position is one-third settler diameter from the inlet port. A drain valve was fitted centrally at the bottom of the settler and a vent at the top through the end plate.

The flow from the mixer to the settler was controlled by 2.54 cm Q.V.F. glass industrial valve.

6.3.2.3 FEED AND STORAGE TANKS DESIGN AND OPERATION

The feed tanks shown in Fig. (6.10) and photographically in Fig. (6.11) were construced from Q.V.F. industrial glass pipe section each 30 cm diameter and 45 cm high. Both ends of the section were fitted with a stainless steel plate of 0.3 cm thickness. The plates were specially fabricated, with a lower plate designed for heat transfer and fitted with a dished bottom 2.54 cm high and 25 cm in diameter. Four baffles were fitted and equally spaced inside the dish to give a turbulent flow of water. The dish was also connected to a coil, the latter immersed in the liquid inside the vessels. Water was passed from the heater at a temperature of 25°C ± 0.5 to the dish bottom and then passed through the coil.

The upper plate had six inlets A,B,C,D,E and F with the following functions:

A - Thermometer inlet, the thermometer calibrated from 0-40°C.

B - This has an off/on valve to the atmosphere.

C - Feed inlet, fitted with a Q.V.F. valve, and connected to the ground level storage tank via a pipe.

D - Connected to an outside pneumatic vacuum filter pump.

E - This inlet is to give a constant pressure inside the tank in order to give a constant flow - cocurrent lead device.

F - Connected to a vacuum gauge.

The technique for filling the tank was as follows:

(i) A,B and E closed.

(ii) C and D opened, with C connected to the ground level storage tank, and D to a vacuum filter pump.

(iii) On passing air through the vacuum pump the feed tanks will be evacuated, and when the vacuum is sufficient $\sim$(0.4 bar) the liquid from the ground storage tank is then sucked and lifted by atmospheric pressure through inlet C to the upper feed tank.

When full;

(iv) Inlet (C) and (D) are closed.

(v) Stop the action of vacuum pump by closing (v).

(vi) Open (B) for a few seconds in order to return to atmospheric pressure.

(vii) Inlet E opened leaving the tank ready for discharging

The storage tanks are four 50-litre spherical vessels made of Q.V.F. industrial glass as shown in Fig. (6.12). They are for

(1) solvent storage
(2) pure phosphoric acid storage
(3) impure phosphoric acid with Fe^{3+} impurities.
(4) impure phosphoric acid with Mg^{2+} impurities

The storage tanks are also used to prepare the required concentration of solution.

6.3.2.4 DESIGN AND OPERATION OF AIR LIFT PUMPS

This kind of pump is very easily made, is cheap, and needs little supervision (211). Fig. (6.13) is a schematic drawing of the pump design to be used in this work, Fig. (6.14) shows a photograph of the top part of the pump. The pump is designed to conform to the safety regulations as will be explained in the

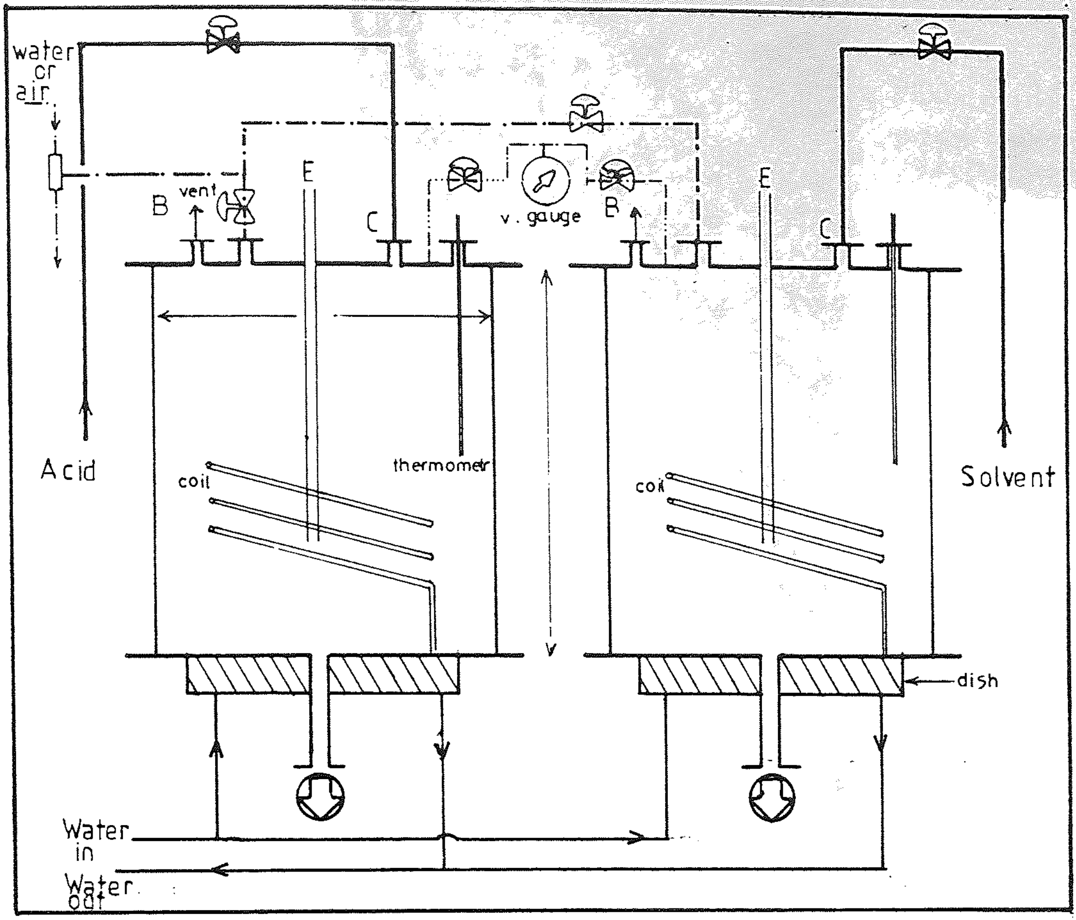


FIG 6.10 Feed tanks design

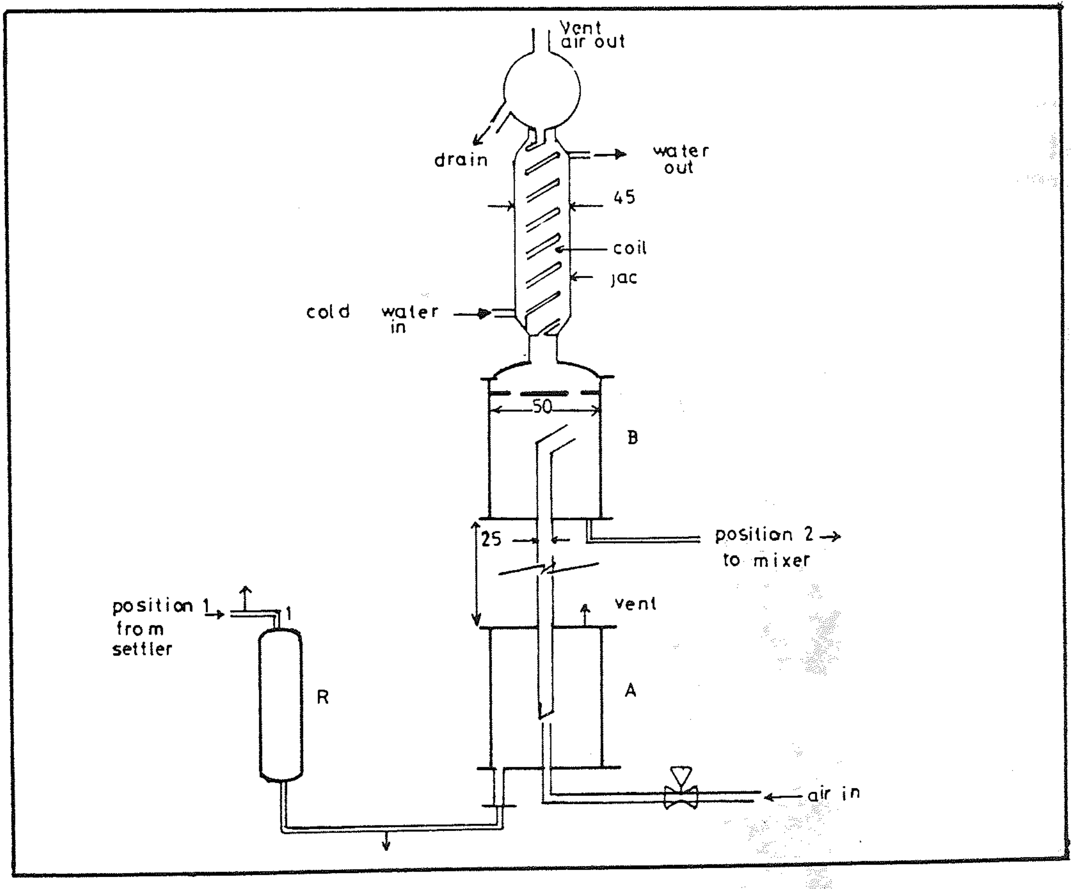


FIG 6.13 Air lift pump

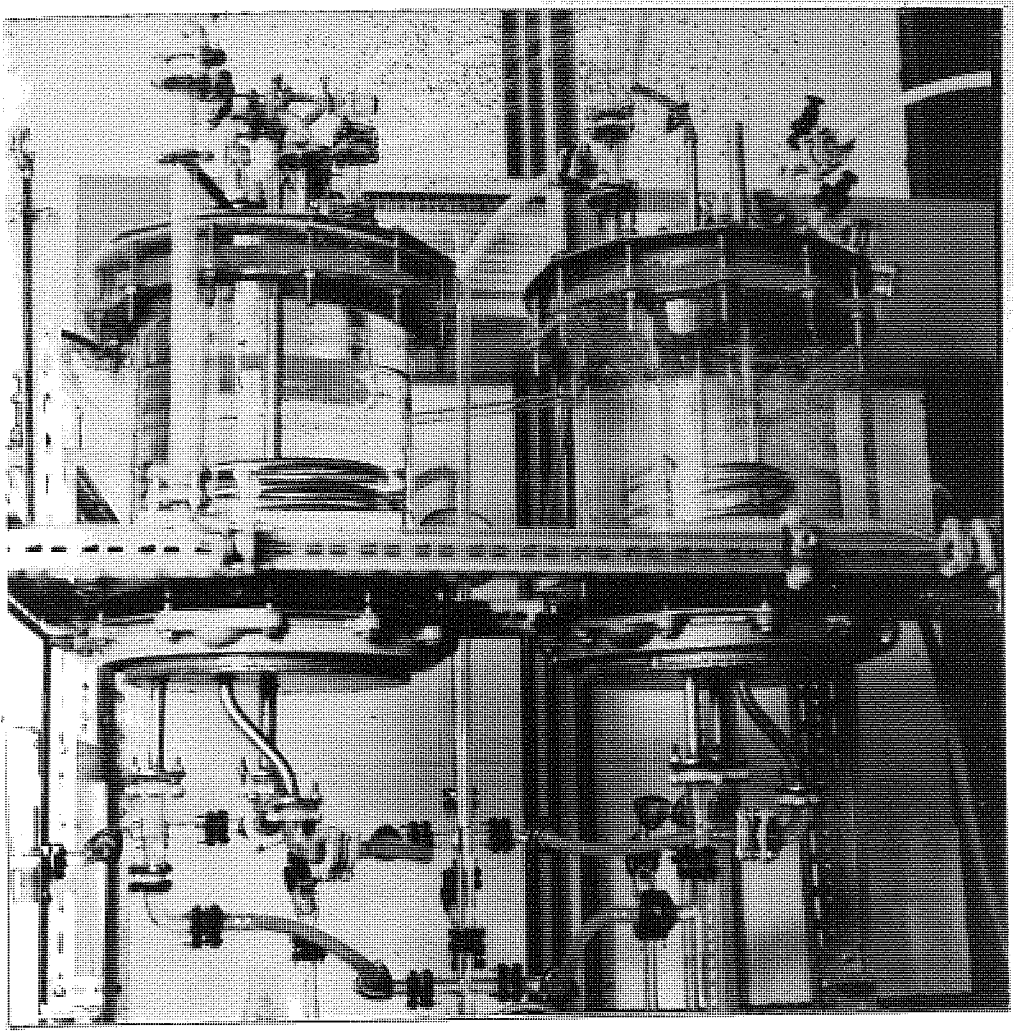


FIG. 6.11
FEED TANKS
ARRANGEMENT

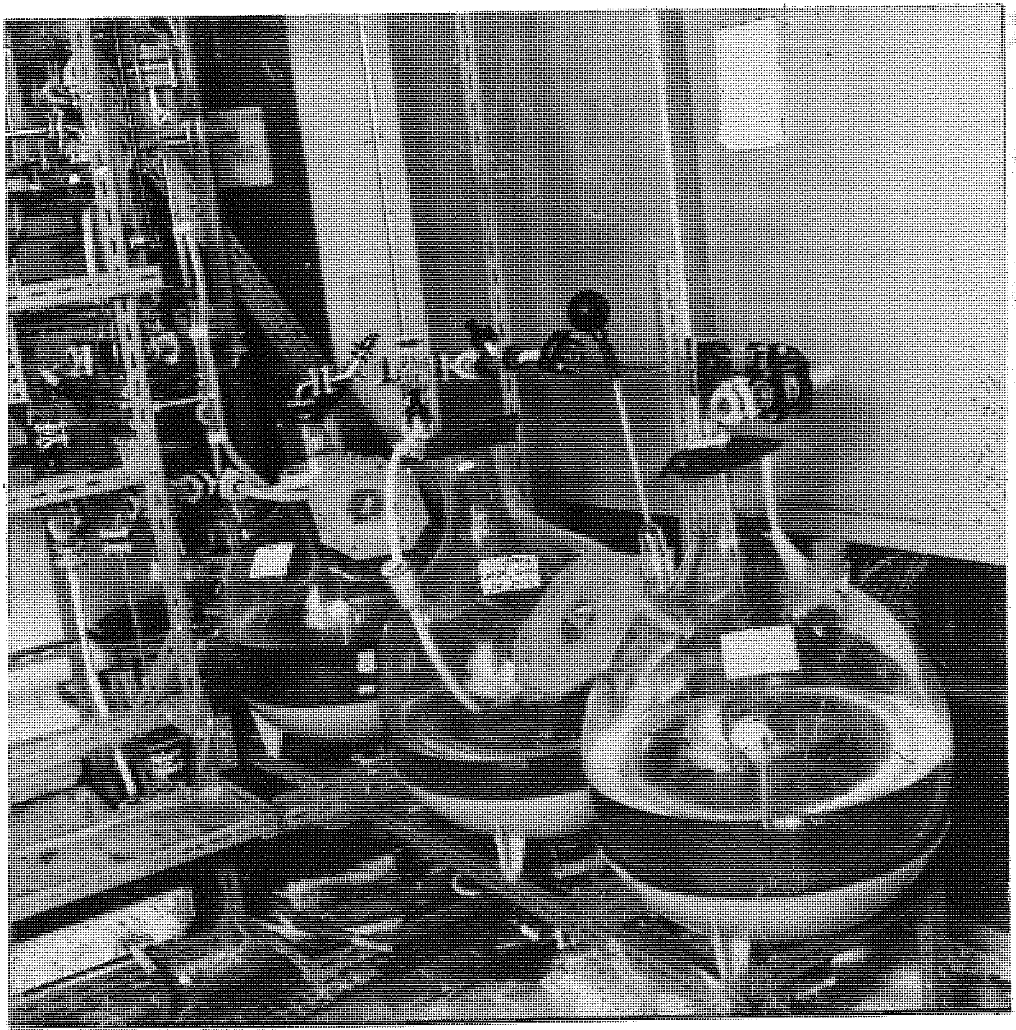


FIG. 6.12
STORAGE TANKS
ARRANGEMENT

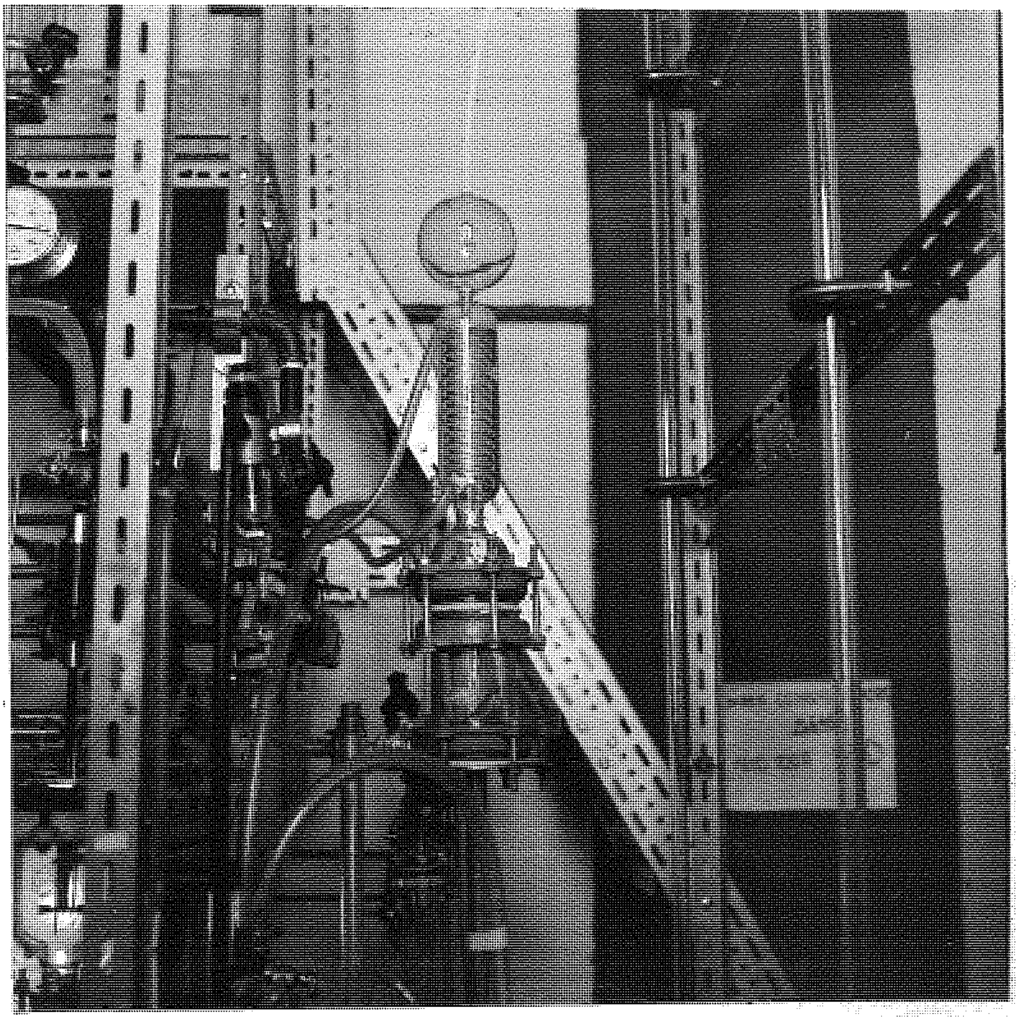


FIG. 6.14 UPPER PART OF THE AIR LIFT PUMP WITH A CONDENSER

next section. The principle behind the operation of the pump is as follows: the liquid extract flows from the settler through line (1), position (1), into a small reservoir (R) which communicates with a vessel (A) constructed from a 5 cm internal diameter by 15 cm length of Q.V.F. industrial glass with stainless steel end plates (3 mm thickness). Compressed air, controlled by a valve (v) is introduced into vessel (A) through a stainless steel pipe (p) 1 cm I.D., the resultant mixture of air and liquid extract rise through a stainless steel tube (3) (2.54 cm oudside diameter and 2 mm thickness) to a vessel (B) similar to A. The connection of tube (3) and p is designed as shown in Fig. (6.13) to raise the maximum amount of liquid to vessel (B). Tube (3) acts as a transport line and a support line for vessel (B). To prevent the escape of the extract with the air, tube (3) is bent 45^{o} to the horizontal and a baffle (b) is fitted to prevent liquid rising into the condenser. In vessel (B) liquid and air are separated, and the air escapes through a condenser and vent (4) while liquid solvent is transferred to a mixer through line (2) on position (2). The condenser is fitted at the top of vessel (B) to condense solvent vapour for return back to vessel (B). The liquid is thus pumped from position 1 to position 2.

The reservoir (R) is fitted to make the operation of the pump independent of the level in the settler and to provide enough head to pump the liquid to a higher position.

6.3.2.5 EQUIPMENT CONTROL, RELIABILITY AND LAYOUT

The equipment is manually controlled. The type of control which is based on liquid flow and interface level in the settler and mixer is not sufficient by itself to judge steady state. A knowledge of end streams and conditions is also not sufficient for controlling the operation, therefore the intra-stage situation is controlled by taking profile samples of the conjugate phases from the individual stage.

Samples from each stage can easily be taken from a sampling point on each line of the heavy and light phases.

The variable part in the equipment was the head between each stage, which was found by trial and error, and the impeller position, which was integral with the driving shaft of the air-motor. The shutting of a single impeller did not stop the operation of the contactor, and had a slight effect on the speed of agitation of the other two impellers since they are driven by a common air line.

The equipment was erected inside a steel frame structure, 3.1 meters in height, and the equipment occupied a surface area of 1.3 m^2.

6.3.2.6 OPERATING PROCEDURE

Before the start of the operation, the two rotameters had to be calibrated for each particular acid concentration so that the flow of the two phases could be controlled. After ensuring that the equipment was thoroughly clean, (as explained in 6.6), the mixer, settler and the raffinate line were filled with the aqueous phase to the required operating level. Agitators were then started at the selected speed for the particular experiment for each individual mixer. Solvent phase was then introduced into the final stage and then flow up to the other stages through the air lift pump was initiated.

The reason for starting the impeller before introducing the solvent was to avoid the inversion of the system to w/o and to reduce the formation of secondary haze.

6.3.3 EQUIPMENT USED FOR PHOSPHORIC ACID CONCENTRATION

The equipment is shown photographically in Fig. (6.15). The still (s) was a 10 litre spherical vessel made of Q.V.F. industrial glass, fitted with a condenser (H) on the top and surrounded by an isomantle for heat supply. The latter was controlled by changing the input voltage through a controller (c). Phosphoric acid was charged into the still and the temperature was read using a thermometer.

The condenser and the overhead product tank were connected to a vacuum filter (f), and the vacuum inside the system could be measured using a vacuum gauge and was automatically controlled using a control

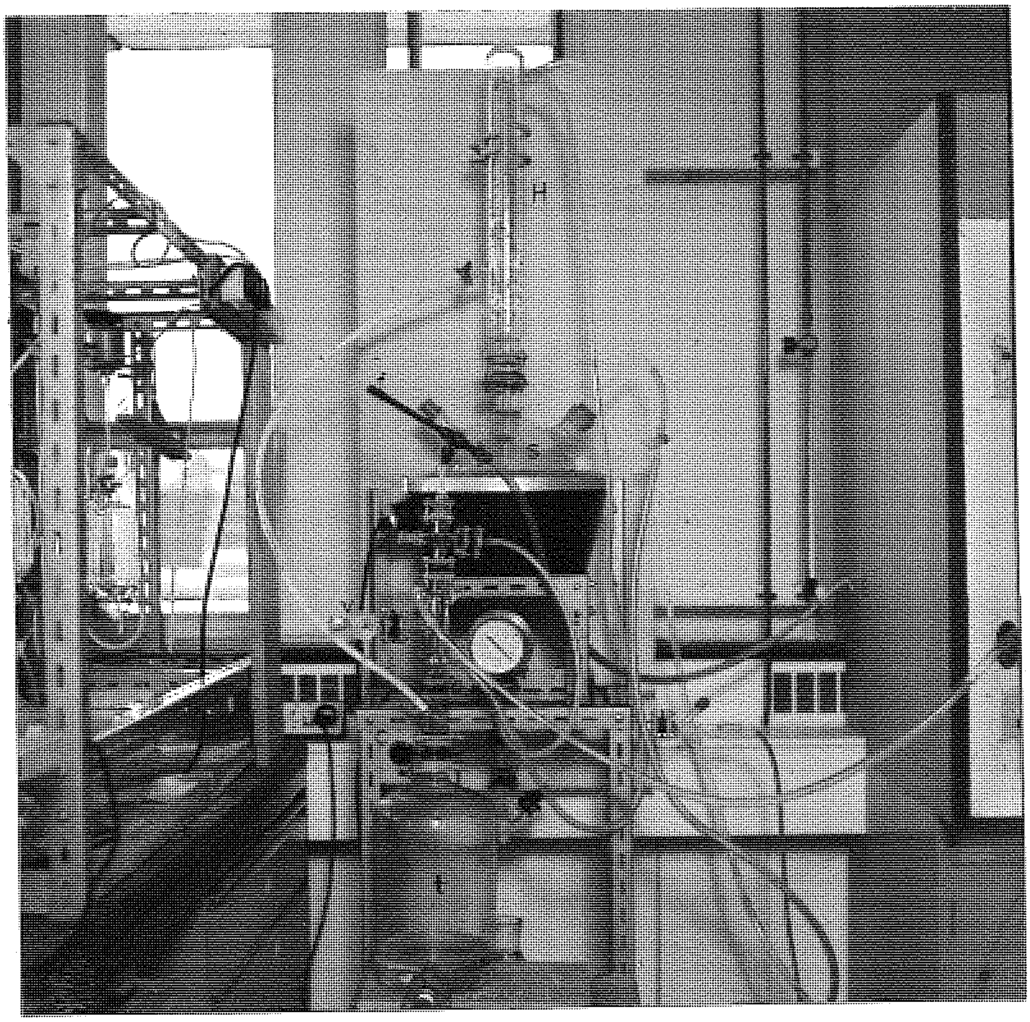


FIG. 6.15 VACUUM DISTILLATION EQUIPMENT

valve (V) fabricated in the Chemical Engineering Department. A small condenser was fitted on top of the collecting tank (t) to condense and reflux back any solvent which might be evaporated under vacuum.

The equipment could be made to work continuously by introducing an additional vessel (10 litres) in which case a valve controlling the feed to the still was used.

6.4 SOLVENT SELECTION AND MATERIAL USED

While the number of solvents, immiscible or partly miscible with water is large, the number of commercially available solvents for inorganic compounds is distinctly limited. When referring to extraction of phosphoric acid, and back extraction of acid from solvent into water, the choice is still more restricted.

A number of solvents are listed in Fig. (3.10) and table (3.2). With reference to Section 3.6 the solvents selected for extensive examination were cyclohexanol, benzaldehyde and methyl iso-butyl ketone (MIBK). They were selected and chosen according to

(1) Availability at low cost.

(2) Acid-water-ketone system stability (200).

(3) Covering most suitable chemicals types of solvent and to cover a wide range of phosphoric acid concentrations, i.e. cyclohexanol has gradual increase in its distribution coefficient while MIBK, benzaldehyde have a step change.

(4) Availability of phase equilibrium information Fig. (3.10) so that the experimental work could be compared (151,152,281).

(5) Low toxicity.

(6) Extraction capacity at high acid concentration. (This can be estimated from the tie line data)

(7) MIBK and cyclohexanol have high boiling points (115.9 and 161°C), therefore evaporation error on analysis can be neglected.

(8) These solvents have been claimed in patent acid literature to be reasonably successful to extract.

Both benzaldehyde and cyclohexanol were rejected because benzaldehyde oxidizes into benzoic acid on contact with air. The latter can not be readily dissolved in water, it can only be dissolved using alcohol or it may be removed by physical means, therefore presenting practical difficulties as well as solvent losses. It was also observed that on extraction of high acid concentrations the solvent (benzaldehyde) layer became yellow, turning to red with higher concentration.

Cyclohexanol was rejected because:

(1) It required a long time for phase separation especially at high acid concentration. This is due to the fact that the interfacial tension between acid and solvent is very low $\approx$(4 dyn/cm).

(2) High viscosity and low interfacial tension make secondary haze formation easy.

(3) A cyclohexanol layer saturated with acid will have a density equal to or greater than 1, therefore making it difficult to operate the contactor for back extracting the acid into water.

(4) Although the freezing point of cyclohexanol is 24°C, phosphoric acid and cyclohexanol solution can not be separated on cooling below 5°C.

(5) On distillation, cyclohexanol and water form an azeotrope at 98°C, 20% by volume cyclohexanol and 80% water and since solubility of cyclohexanol in water is around 20%, the solvent losses will be very high.

(6) The solubility of water in cyclohexanol saturated with water is very much temperature dependent, so any variation in temperature will effect the solubility and make the solvent layer cloudy.

The list of materials used and their suppliers are presented in Table (6.1). Their physical and chemical properties, and composition are listed in Appendix (1).

TABLE 6.1

	Material Used	Supplier
1.	Methyl isobutyl ketone	B.D.H.
2.	Cyclohexanol	B.D.H.
3.	Benzaldehyde	B.D.H.
4.	Sodium hydroxide (standard volumetric solution)	Hopkin & Williams
5.	Phosphoric acid	Fisons
6.	Magnesium nitrate (standard solution)	B.D.H.
7.	Ferric chloride (standard solution)	B.D.H.
8.	Methyl orange solution pH indicator	B.D.H.
9.	Phenolphthalein pH indicator (1% solution in propane 2-Ol)	B.D.H.
10.	Ferric orthosphate (impurity)	B.D.H.
11.	Magnesium hydrogen ortho phosphate (impurity)	B.D.H.
12.	Water (distilled)	Departmental still water
13.	Acetone	B.D.H.
14.	Decon	B.D.H.

6.5 SAFETY

6.5.1 EQUIPMENT LOCATION AND HAZARDS

The equipment was located in a flame proof laboratory in the Chemical Engineering Building. Fire hazards due to the presence of solvent vapours are reduced in this area in which all the electrical equipment was designed to be spark free. Some flame proof equipment is far too expensive, therefore two methods were used to satisfy the regulations.

(a) In general, the use of the electrical equipment such as motors and starters has been avoided. The plant was largely operated without the use of the electricity. Air motors were used for mixing the phases, air lift pumps were designed to transfer between stages.

(b) Other equipment such as the thermo circulator for heat supply was placed in a box made of aluminium as shown in the photograph and Fig. (6.16).

Air was introduced to the box through an opening at one side of the box and leaves from a small flap on the top. The air supply was regulated by using an air reducer (r) as shown in Fig. (6.18). When the pressure inside the box is high enough the flap will be opened to balance the pressure. This method prevents the contamination of heater atmosphere with solvent, so reducing the spark hazard.

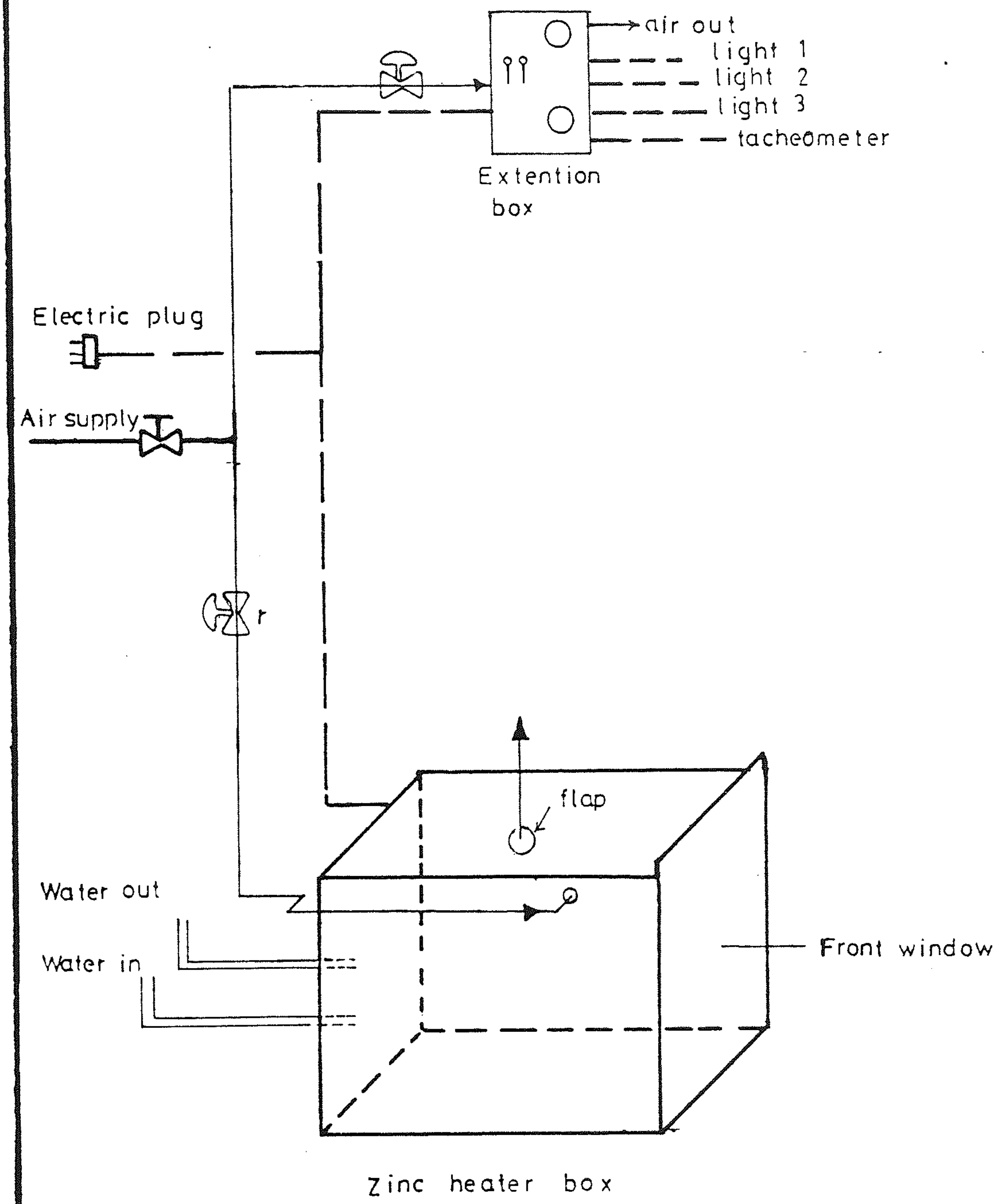


FIG 6.18 Air and electricity supply in the flame proof area

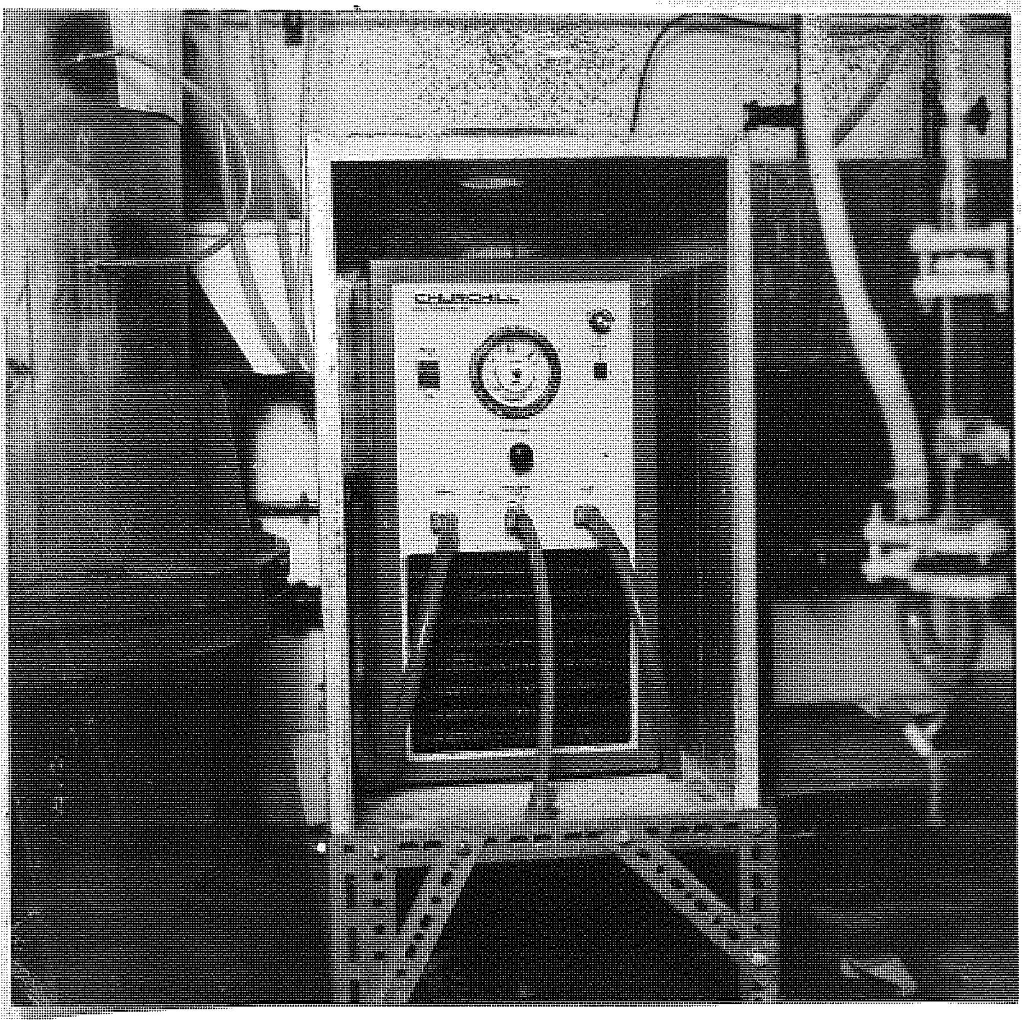


FIG. 6.16

CHURCHILL THERMOCIRCULATOR INSIDE A BOX

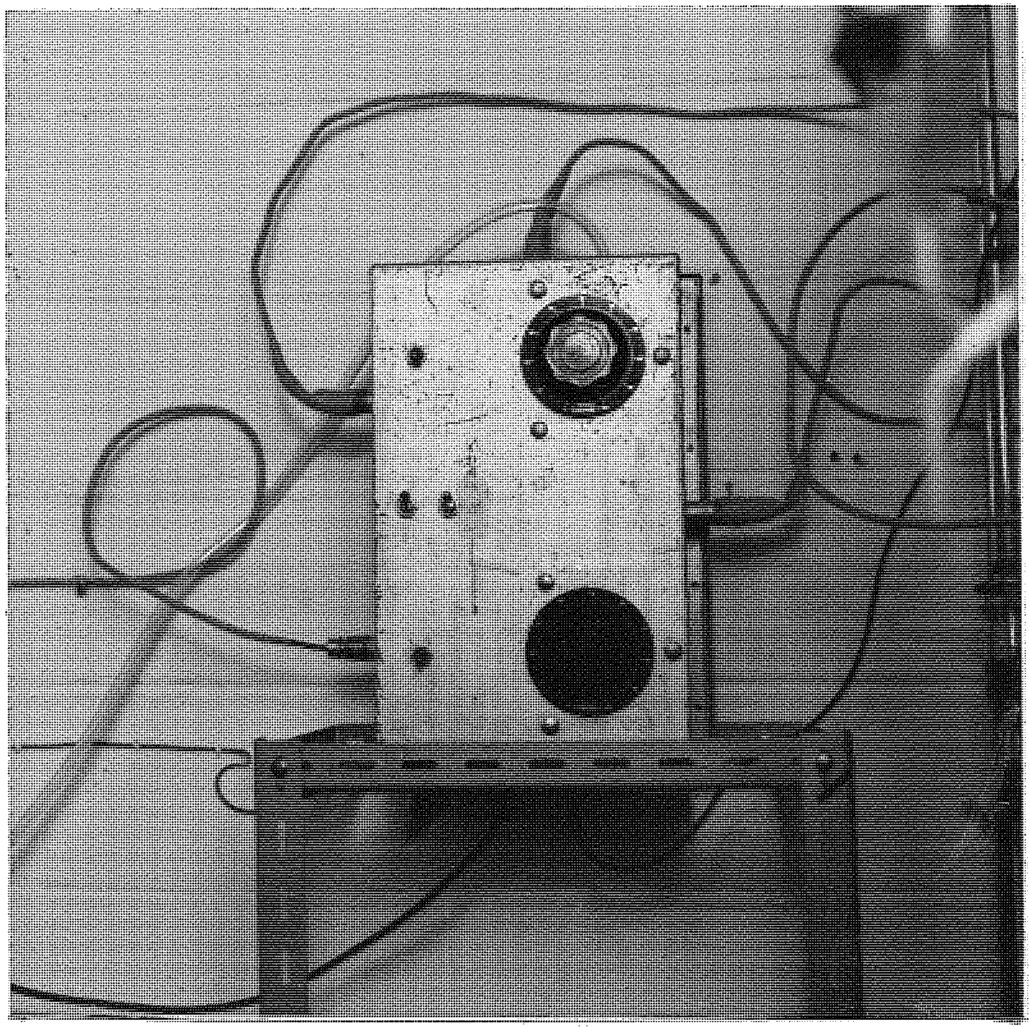


FIG. 6.17

ELECTRICITY SUPPLY FOR LIGHTING AND HEATING

Three extensions and two regulators were connected to a single supply to provide electricity to the flame proof lights and thermocirculator. The connections were made inside an iron box (as shown in the photograph and Fig. 6.18) and air was introduced and regulated in the same manner as above.

The lights used for photography and the conductivity meter were of flame proof design.

6.5.2 VACUUM DISTILLATION

No serious hazards in the distillation equipment can arise except when vacuum is applied in which case a small safety valve was fabricated in the Chemical Engineering Department which opened should the vacuum be reduced to a dangerous point.

6.5.3 SOLVENT HAZARDS AND TOXICITY

(i) Cyclohexanol. Low volatility of this alcohol precludes any serious danger from inhalation of air mixtures. It tends to cause nausea and has some slight action on the blood and central nervous system, but otherwise it appears to be non-toxic.

(ii) MIBK. This is not corrosive to metal when dry. Iron, mild steel, or aluminium being suitable for plant and containers. It is flammable and when transported must be consigned as flammable. It forms an explosive mixture with air with upper limit at 100°C of 8 vol percent, lower limit at 5°C, 1.34 vol percent. Flash point open cup 24°C, closed cup 15.6°C (170).

Because of its relatively low vapour pressure there is no serious industrial hazard at ordinary temperature. The TLV in air is 100 ppm, and the odor threshold is 0.4 ppm. Even at the threshold limit value MIBK may irritate the eyes of the more sensitive person. At 200 ppm this compound strongly irritates the respiratory tract and eyes and produces headaches, dizziness and nausea.*

6.5.4 PHOSPHORIC ACID HAZARDS

Details of phosphoric acid hazards have been explained in Section (3.3).

6.5.5 HAZARDS OF STORAGE VESSELS AND CONTAINERS

Care was taken when opening solvent containers, by using a wooden tool to open the top, or by taking the containers into the open air. Using metals such as hammers may cause sparks. When the containers were empty they were washed with water to eliminate the possibility of solvent vapour.

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* Clinical Toxicology Clinton, H. Thieness and Thomass, J. Haley., fifth edition, Philadelphia, 1972, Henry Kimpton publish, London.

6.6 EQUIPMENT CLEANING AND SYSTEM PURITY CHECKS

All mixers, settlers, transfer lines, pumps and rotameters were first cleaned thoroughly by using hot tap water with agitation. The whole equipment was then cleaned twice again with distilled water making sure that all the sample points were well flushed and free from any trace of chemicals. Periodically there was a tendency for dirt and other impurities to be deposited on the internal surfaces of the mixer and settlers. In this case the equipment was cleaned with a low concentration of 'Decon', followed by leaving water standing in it overnight. The water was then discharged and the equipment dried using compressed air.

All cylinders, sampling bottles and pipettes were cleaned after each run, first with hot tap water then with decon, followed by washing twice with distilled water. They were then dried in an oven before use.

To reduce the dirt and other impurities which have a significant effect on the system under study, particularly the settling time, a stainless steel filter and layer of carbon cloth were fitted on the feed line of both the acid phase and the solvent phase. These filters collect contaminate in the liquids before they are fed to the equipment.

The purity and the identity of the systems were checked at regular intervals, by measuring the physical properties, e.g. refractive indices and density so that they satisfy the properties given in Appendix (I).

6.7 ANALYSIS AND MEASUREMENT TECHNIQUES

6.7.1 DETERMINATION OF PHOSPHORIC ACID CONCENTRATION

At first the concentration of phosphoric acid in both layers (extract and aqueous raffinate phases) was determined by titrating with standard sodium hydroxide solution using both a pH meter and phenolphthalein and methyl orange as indicators. Both methods gave identical results so the use of the pH meter was stopped.

It has been reported by Huhti and Gartagonis (102) that when the concentration of phosphoric acid is less than 68.8% P_2O_5 (i.e. 95% H_3PO_4, see Appendix (2)) then only orthophosphoric acid is present. Acid with higher P_2O_5 acid concentration would contain condensed phosphoric acid components (pyro, tri-, tetra, etc). The solution dealt with in this work was, therefore, assumed to contain only orthophosphate. This contains two different acidic strengths, one strong acid function and two weak acid functions. Therefore, on titration of phosphoric acid a series of salts are formed. This can be observed by studying the pH-titration curve reported in literature (69,281) which has inflection points near pH 4.5 and 9. Accordingly two different indicators must be used to detect the points of inflection.

The amount of alkali required to titrate phosphate solution from its original pH to a pH 4.5 is a measure of its strong acid function. Titration from the end point at pH 4.5 to the end point at pH 9 measures the first weak acid function.

The amount of alkali required to reach these two points is always the same for a given sample, except in the case of an aqueous phase raffinate containing magnesium phosphate impurities. This was explained by Yacu (282) as it is due to the interference of these impurities with the strong acid hydrogen.

Two samples of each phase were weighed using a 4 decimal point balance, and they were titrated for their strong and weak acid functions. There was no difficulty in titrating the extract phase samples, because the samples were diluted in a large amount of water, which extracts the H_3PO_4 completely from the solvent.

6.7.2 DETERMINATION OF IMPURITY CONCENTRATION

Atomic absorption spectroscopy was used for the measurement of iron and magnesium in both aqueous and solvent phases. This method was recommended by Yacu (282) and Edward (69) as being reliable, accurate and able to detect very small amounts of the elements. The instrument is simple, straightforward, and relatively inexpensive, it is of type IL 151. A nitrous oxide-acetylene flame, burning at a temperature near 3000°C was used throughout to break the elemental PO_4 bonding and produce enough neutral and excited atom population for detection.

The theory behind absorption is that when a solution of the sample to be analysed is introduced into a chemical flame as a fine aerosol or mist the solution of droplets first undergoes desolvation, then the resulting particles are dissociated into atoms. These atoms are in their normal electronic configuration, the zero energy state. An external light source, which emits the atomic line spectrum of the atom to be analysed is employed. This is a sealed device containing a low pressure inert gas as an anode, and a hollow cathode made of the desired element. An electrical glow discharge concentrated in the cathode cavity sputters the element from the surface and excites the atom by collision with ions and electrons. Thus the spectrum of the cathode element is emitted from the hollow cathode, and the radiation exits through a suitable window.

Light from the source passes through the flame containing the sample and is absorbed by ground state atoms in the flame cell. The amount of light absorbed is a function of:

(a) Absorbtivity constant for the element of the wave length measured.

(b) Length of the light path through the flame.

(c) Concentration of the element being measured.

By making the first two factors constant, the amount of light absorbed is a measure of the concentration of the element.

In addition to neutral atoms other species may also absorb light in the flame. Ionic species may also absorb their respective line, however the ratio of the ionic species to the neutral is so small that at the temperature used neutral atoms are primarily measured. A known volume of each sample (aqueous and extract phases) was measured and diluted to lie within the sensitivity and recommended concentration region of the element. This region is 10 ppm for Fe and 1 ppm for Mg. The range of dilution was between 500 to 800 times in the case of aqueous phase and 10 to 50 times for extract phase. Each extract phase was back-extracted with water and separation of the organic phase was performed in a series of funnels. The operating procedure of the equipment is explained in Appendix 2. The equipment was calibrated before each set of samples since different conditions (e.g. temperature, fuel flow rate) will give different calibration curves. The standard solution for calibration was obtained from B.D.H. ($FeCl_2$, $Mg(NO_3)_2$). A typical calibration curve is given in Appendix (2). It is not recommended to prepare the standard solution from solid orthophosphate using a titration method since the result will not be accurate as the end point is difficult to detect due to the fact that it is a titration of weak acid and weak base.

6.7.3 PHYSICAL ANALYSIS

Physical properties of both aqueous and extract phases are important and have to be determined for safety and design reasons. Also impurities have an influence on viscosity and density as reported by Danbigh (63). The physical properties measured were viscosity, density, interfacial tension, surface tension and sometimes refractive index.

(i) Specific Gravity

Relative density was measured by using a density bottle. A sample calculation is presented in Appendix 3. The samples were stored in a bath operating at 25°C for at least 4 hours before measurement.

(ii) Interfacial Tension

Interfacial tension was determined for each system using the standard DuNouy method on a White torsion balance. The samples were placed in a bath operating at 25°C for at least one hour. The ring (platinum 2 cm in diameter) was thoroughly cleaned by rinsing in acetone then distilled water followed by drying after each sample.

(iii) Surface Tension

The same method was used for measuring the surface tension of each phase, i.e. using White torsion balance.

(iv) Viscosity

The viscosity was measured using a Cannon Fensky U-tube viscometer. Samples were placed inside a controlled temperature bath at 25°C, and each tube was calibrated with distilled water as shown in Appendix II .

(v) Refractive Index

An Abbey A60 refractometer was used for refractive index measurement. Measurements were made at constant temperature 20 ± 0.2°C, which was kept constant by means of Townson and Mercer temperature control circulating unit.

6.7.4 DROP SIZE AND PHOTOGRAPHIC TECHNIQUE

Since all the equipment was made from transparent Q.V.F. industrial glass, the behaviour of the phases under mixing inside the mixer could be clearly observed and studied using photographic techniques. Pentax and Praktica LTL3 35 mm cameras were employed. Extension tubes and close-up lens was used to give magnified photographs. Photographs were also enlarged to give a magnification 9 to 10 times of the object. An adhesive tape was placed on the mixer for calibration. The film employed was Ilford HP5 400 ASA, the lens aperture and shutter speed were adjusted according to the light meter reading inside the camera. In most cases a shutter speed of 1/1000 sec was possible. Appropriate lighting was provided by 500 watt flame proof lights. For each experiment two or three photographs were taken for each set of conditions. A typical photograph is reproduced in Fig. (II.1) (Appendix 2)

Drop size measurements were made from photographic prints with approximately a 2X magnification using a Carl-Zeiss particle size analyser TG.Z-3. 100 to 150 drops were counted in each photograph, this number was quite enough for accuracy because of the homogeneity of the dispersions. The curvature of the glass was reported to have no effect on the size of the drops (100).

6.7.5 WEDGE LENGTH MEASUREMENT

The wedge produced in the settler was measured using a calibrated tape placed on the outside wall of the settler, this was measured in cm.

6.8. SOLVENT STABILITY

The identity of the system was checked periodically by measuring the physical properties and by analysing the solvent using gas liquid chromatography. Small amounts of sample are injected into the column which was operating under controlled conditions. The analytical output was in the form of a chromatograph, the number of peaks on which is equal to the number of components desorbed by the carrier gas. The position of each chromatograph peak is representative of a certain component and its area to the concentration. The operating conditions and a sample of the results are presented in Appendix 3. Solvent recovered from the distillation on concentration of the acid was discarded since it had been subjected to a temperature of 100°C.

CHAPTER
SEVEN

EXPERIMENTAL PROCEDURES AND RESULTS

7.1 BATCH STUDIES

7.1.1 DETERMINATION OF EQUILIBRIUM DATA AND MASS TRANSFER STUDIES

(I) Binodal Curve Determination

Ternary solubility curves were determined by the cloud point titration method (87,174). In this a homogeneous mixture of phosphoric acid in water was prepared on a weight basis in a measuring cylinder (50 and 100 cc). The cylinders were fitted with stoppers to reduce or avoid the volumetric error due to evaporation of the liquid. The mixture was then shaken repeatedly and stored separately together with pure solvent containers in a water bath whose temperature was maintained constant at 25°C ± 0.1 with the aid of a temperature controller.

A cylinder containing acid solution was placed on the weighing balance, then the mixture was titrated with solvent using a burette and a dropper. Loss by evaporation due to opening the measuring cylinder was neglected.

The cylinder was then vigorously agitated to bring the mixture to equilibrium and allowed to stand in the temperature bath. The procedure was repeated until the single phase system was no longer clear, but had become cloudy. The cloud can be seen with the aid of a small torch placed behind the cylinder. This is the "cloud point" representing the boundary between the single and two-phase systems. Further addition of a very small amount of solvent would result in the appearance of a second phase after equilibration. Finally the agitation of the cylinder was continued for about 15 minutes after the cloud point has been detected to ensure permanency of the turbidity.

By determining the different cloud points, the water rich side of the binodal curve was determined. The same procedure was repeated to determine the solvent rich side of the binodal curve in which phosphoric acid-solvent solution were titrated against pure water, taking into consideration the amount of water already present with the phosphoric acid.

Only pure acid solutions were studied for binodal curve determinations since Yacu (282) showed that pure and impure systems differed slightly in their equilibrium curve.

(II) Determination of Equilibrium Distribution Curve

The experimental work was carried out in cylindrical jacketed vessels as shown in Fig. (3.11). The procedure was to fill the vessel with the two phases for either a pure or an impure system (aqueous acid solution and solvent were prepared in such proportions as to produce 1:1 water to solvent by weight). The solutions were mixed for 4-6 hours and the phases were allowed to settle, after which the two were collected separately for analysis.

The binodal curve data and the tie line data for the three systems (pure and impure), phosphoric acid-water MIBK, phosphoric acid-water-cyclohexanol, phosphoric acid-water-benzaldehyde are presented in Appendix (3) and plotted in the form of triangular diagrams in Fig. 7.1. The tie line data are also presented in the form of distribution diagrams by Hands method coordinates, Othmer-Tobias coordinates, and selectivity diagrams in Fig. 7.2 to 7.11. The composition of the phases at the plait point was not found. However, the plait point was determined using Hands coordinates based on plotting and extrapolting both the tie line and the binodal curve data, see Fig. 7.8. The results obtained were:

Plait Points for Three Systems Studied:

	Benzaldehyde	Cyclohexanol	MIBK
Phosphoric Acid	43%	55.16%	53.5%
Water	11.8%	25.14%	20.5%
Solvent	45.2%	19.7%	26.0%

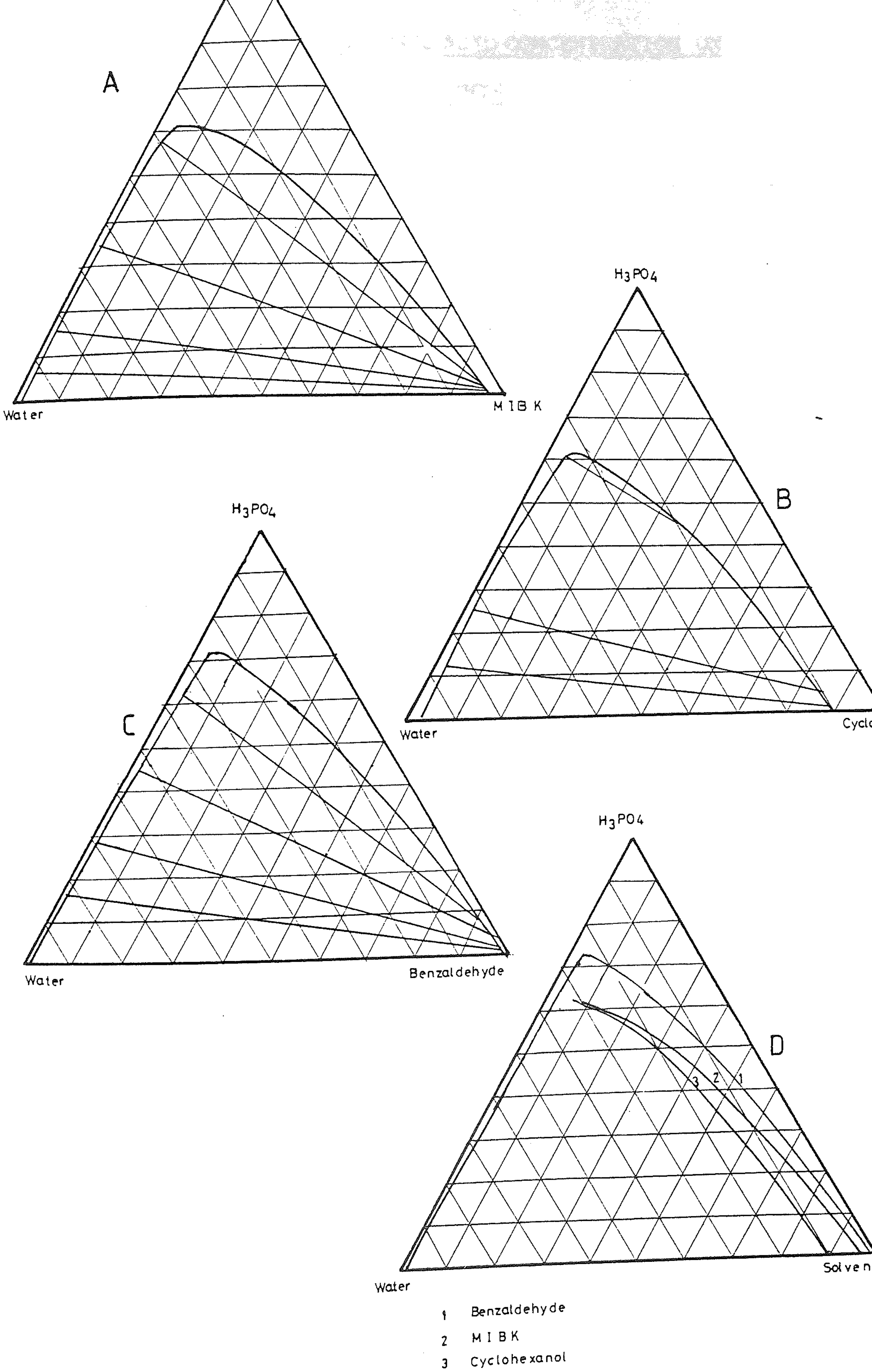


Fig 7.1 liguid phase equilibrium in the system phosphoric acid – water – solvent at 25 °C ± 0.1

A for M I B K
B for cyclohexanol
C Benzaldehyde
D Comparison of the three systems

7.1.1.1 EFFECT OF PHOSPHORIC ACID CONCENTRATION ON DISTRIBUTION COEFFICIENTS

The results show that the distribution coefficient of phosphoric acid in all systems studied increased with the acid concentration as shown in Figs. (7.2 to 7.5). With cyclohexanol the increase was gradual, while it was more likely to be step with MIBK and benzaldehyde.

7.1.1.2 THE EFFECT OF CATION IMPURITIES ON THE DISTRIBUTION COEFFICIENT OF PHOSPHORIC ACID

The impurities (Fe^{3+}, Mg^{2+}) increased the size of the heterogeneous area of the phase equilibrium diagram as reported by Yacu (282). The presence of impurities also decreased the solubility of phosphoric acid in the extract phase especially at high acid concentration and therefore lowered the slope of the distribution curve of phosphoric acid.

7.1.1.3 EFFECT OF PHOSPHORIC ACID CONCENTRATION ON THE DISTRIBUTION OF IMPURITIES

Only MIBK and cyclohexanol systems were studied and the results show that the distribution coefficient of impurities in both systems increased with the acid concentration in the extract phase as shown in Figs. (7.13-7.16). The distribution coefficients of the Fe^{3+} ion is higher than that of the Mg^{2+} ion at the same

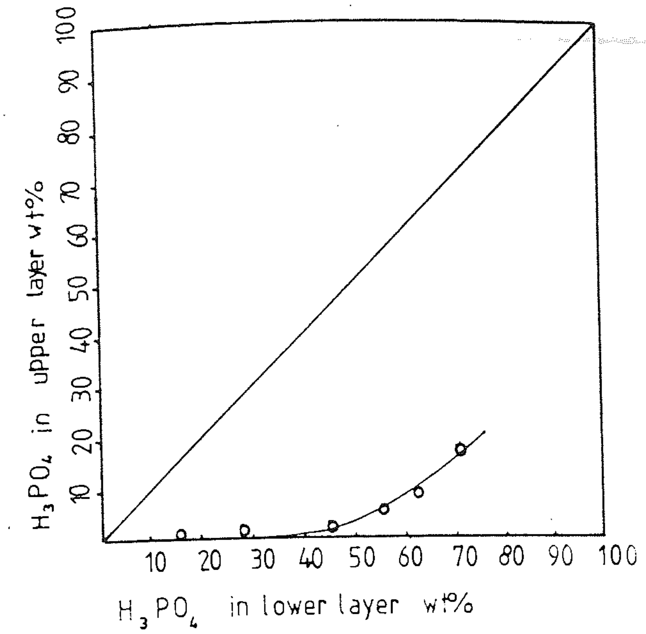


Fig 7.2 Distribution curve for phosphoric acid in the system water–phosphoric acid – Benzaldehyde at 25°C

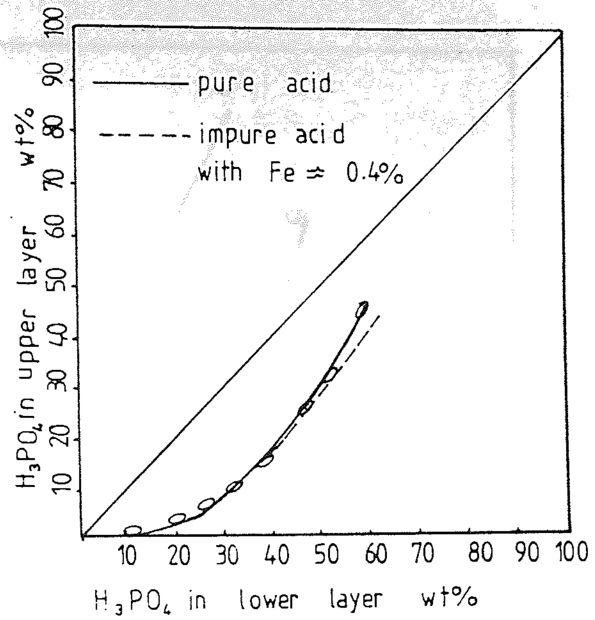


Fig 7.3 Distribution curve for phosphoric acid in the system water–phosphoric acid – cyclohexanol at 25°C

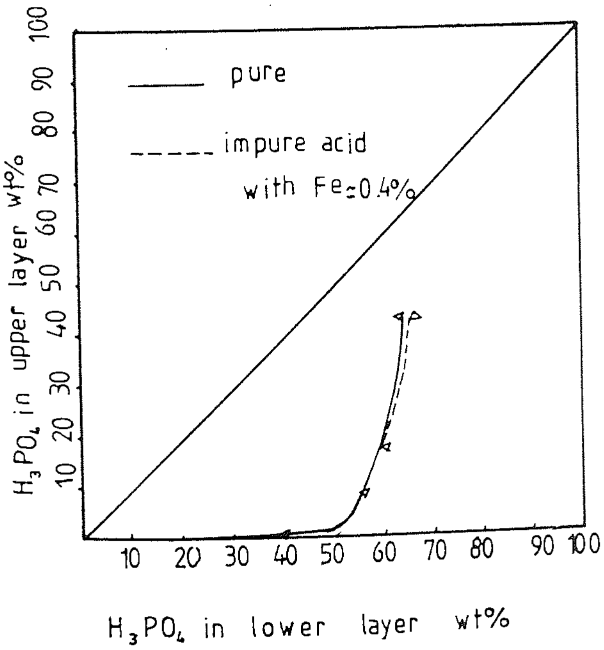


Fig 7.4 Distribution curve for phosphoric acid in the system water–phosphoric acid – methyl iso butyl ketone at 25°C

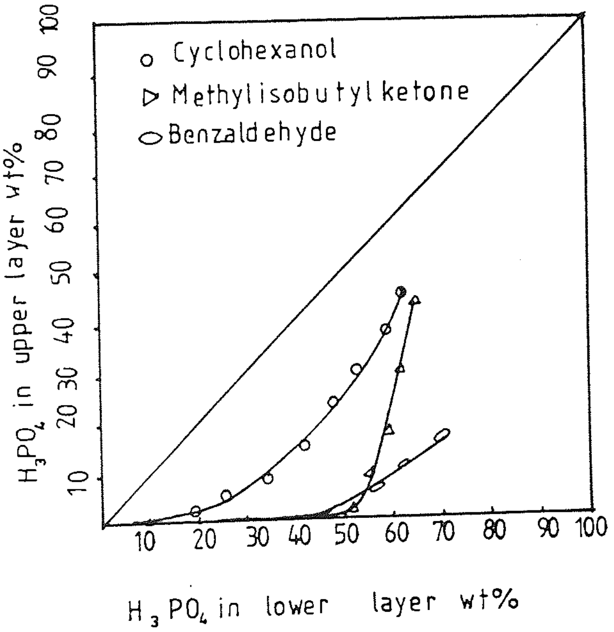


Fig 7.5 Distribution curves for phosphoric acid in the system water– phosphoric acid– solvent at 25°C

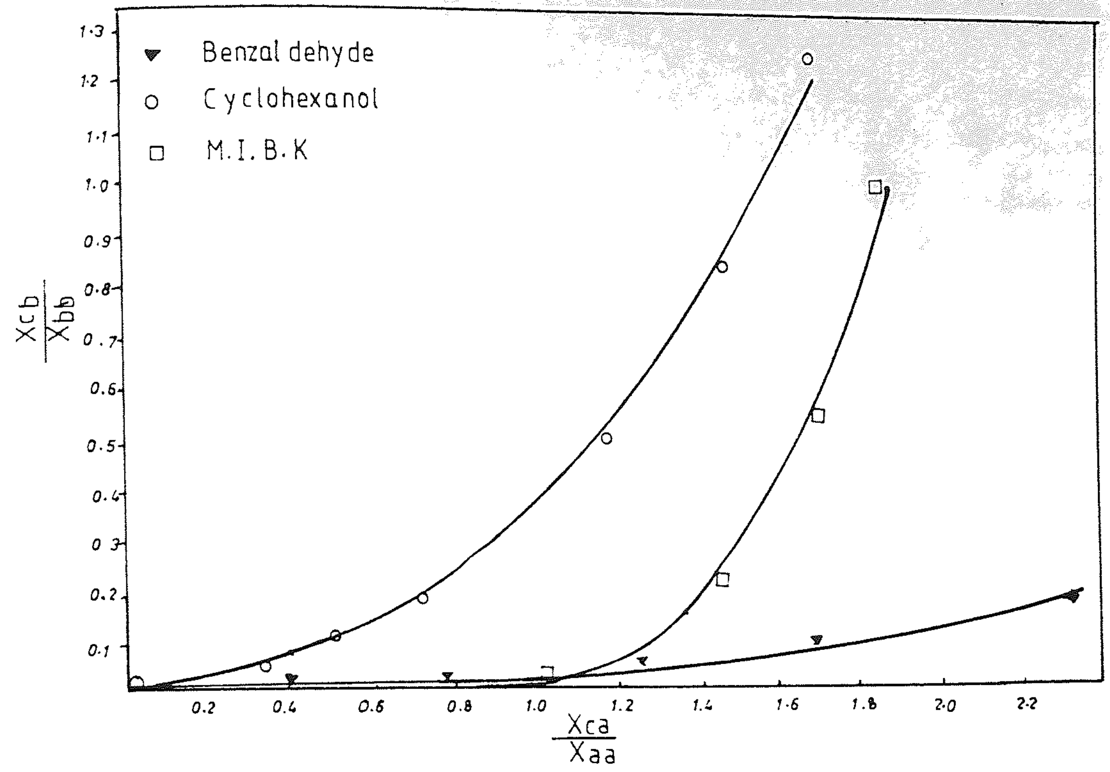


Fig7.6 Distribution curve of H_3PO_4 on solute free basis at 25°C for water – phosphoric acid – solvent

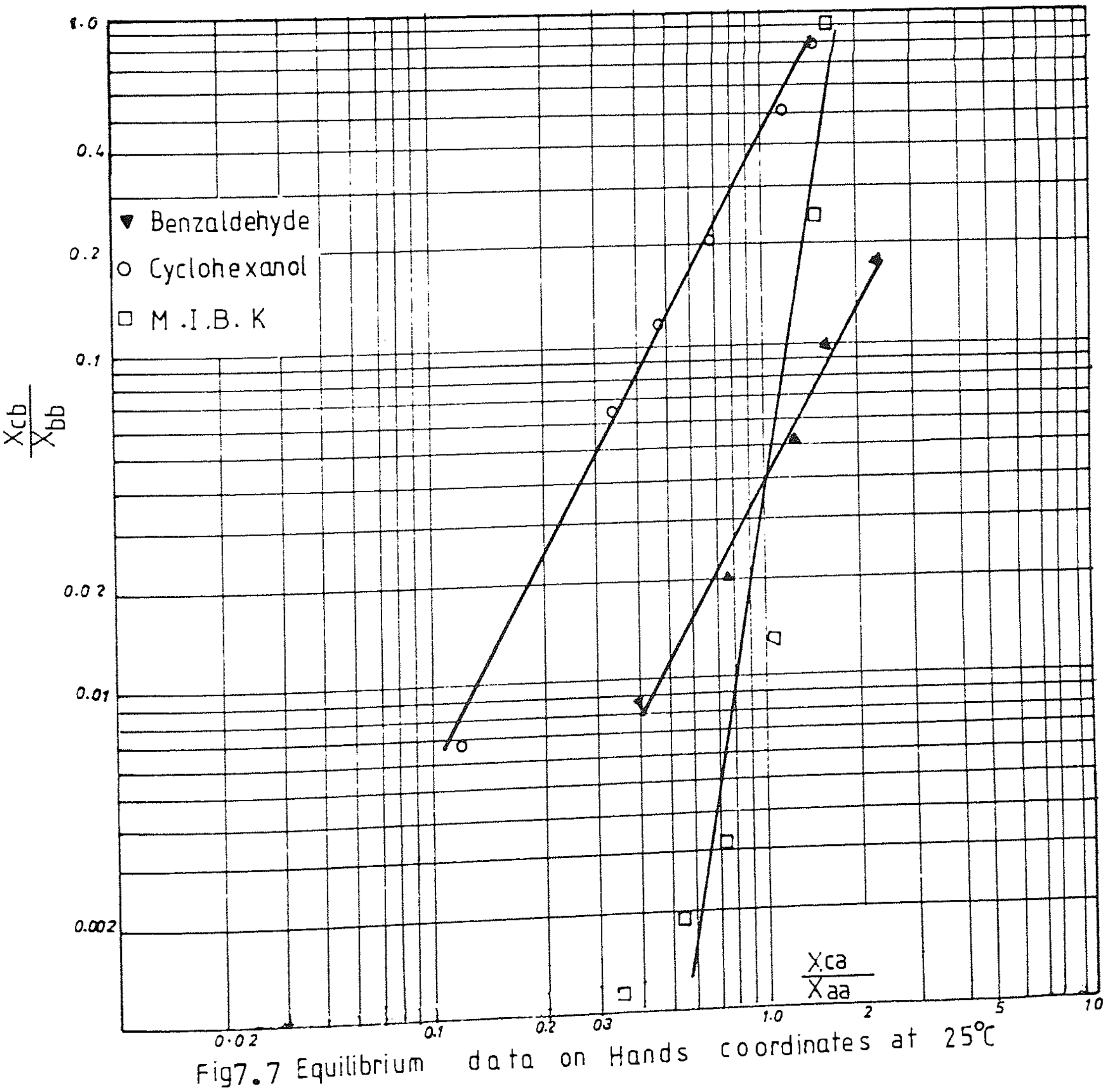


Fig7.7 Equilibrium data on Hands coordinates at 25°C

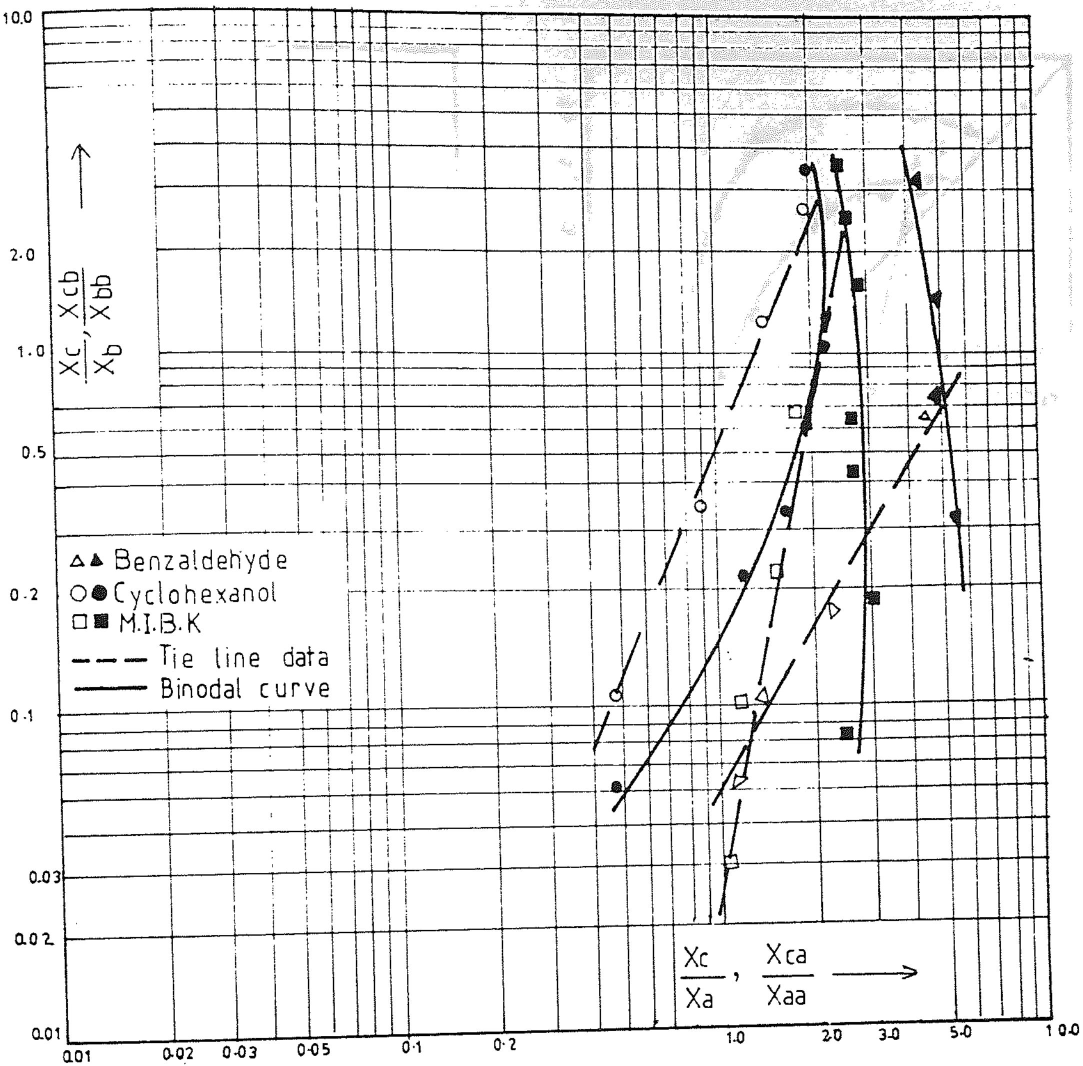


Fig7.8 Plait point determination using Hand's coordinates for the systems phosphoric acid – water – solvent.

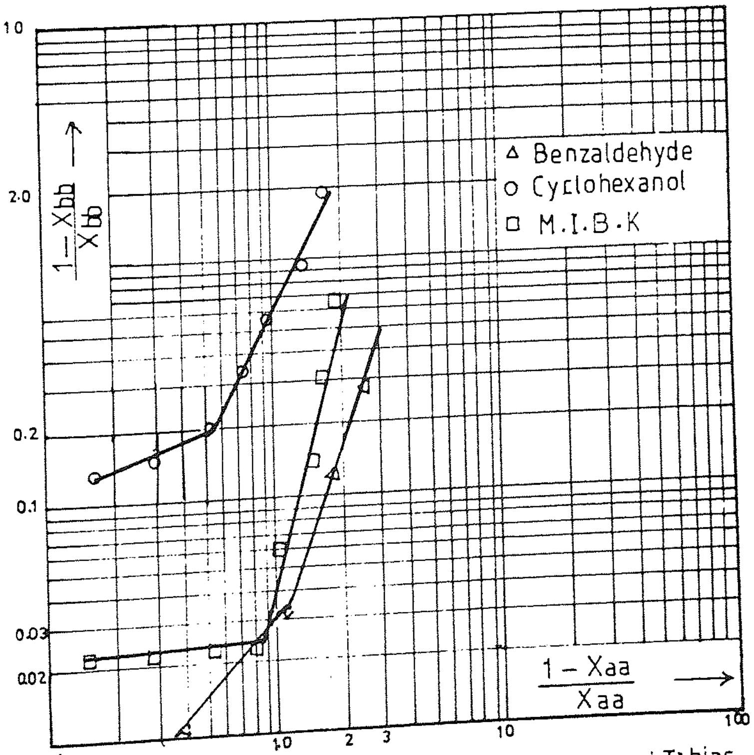


Fig7.9 Tie line data using Othmer and Tobias coordinates at 25 °C

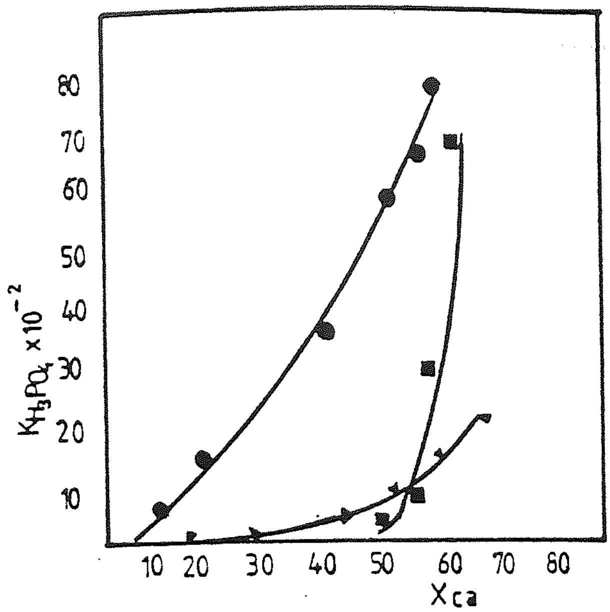


FIG 7.10 $K_{H_3PO_4}$ VS. ACID CONC. IN WATER LAYER

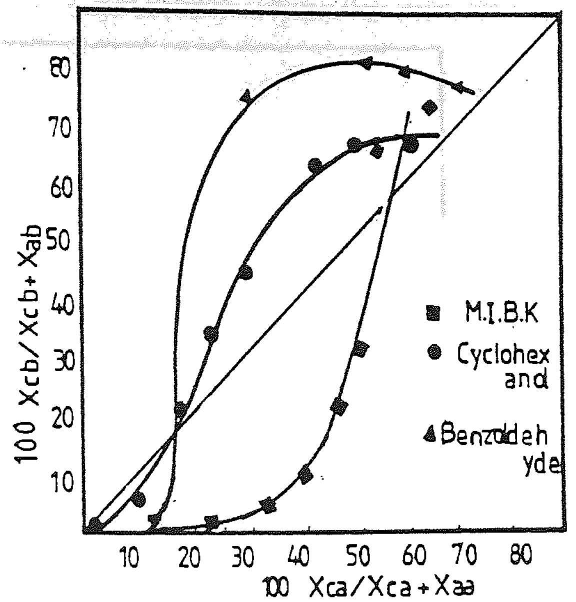


FIG7.11 Selectivity diagrams for phosphoric acid – water–solvent

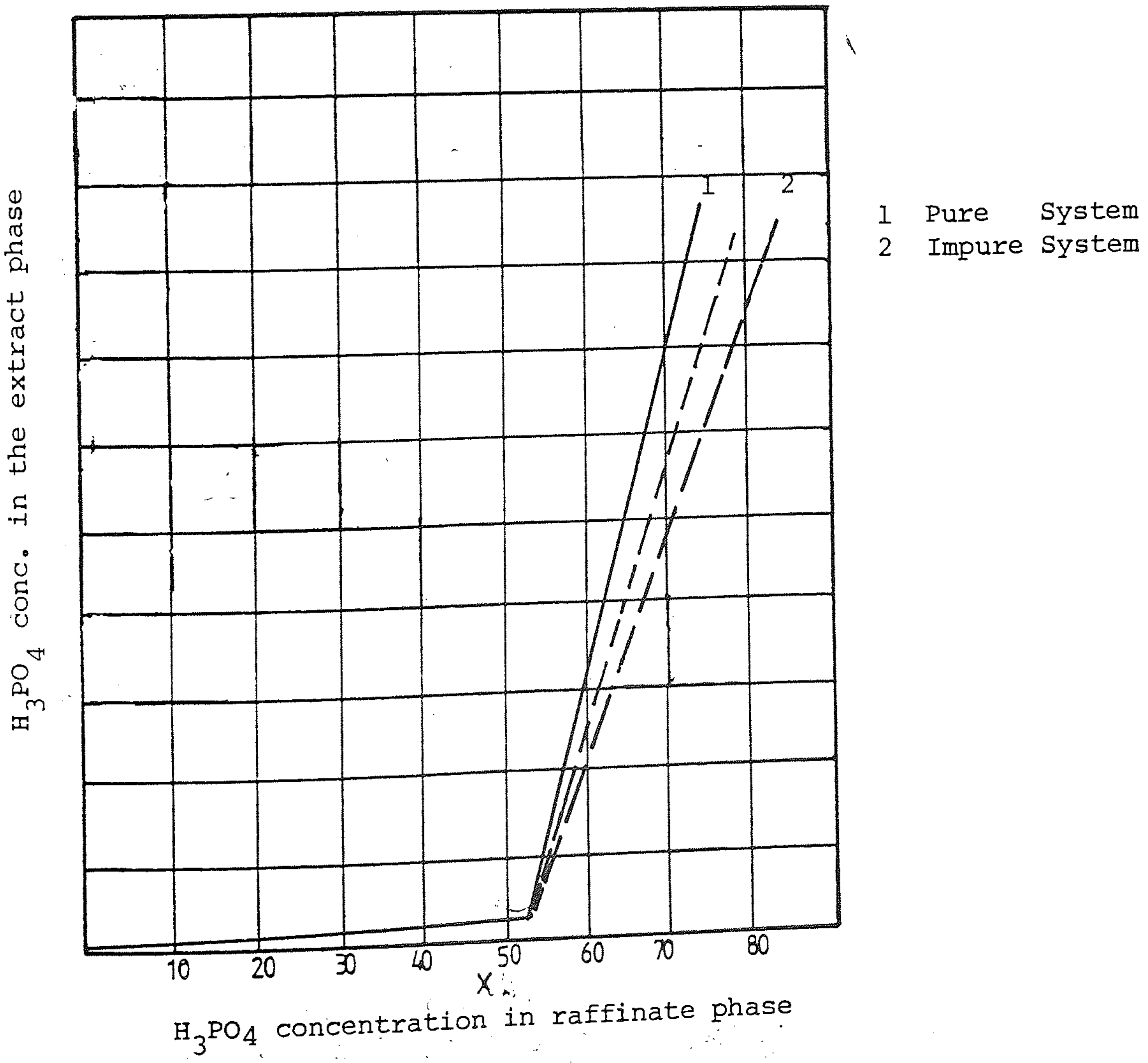


Fig. 7.12 - Effect of impurity presence on the slope of the distribution curve for phosphoric acid

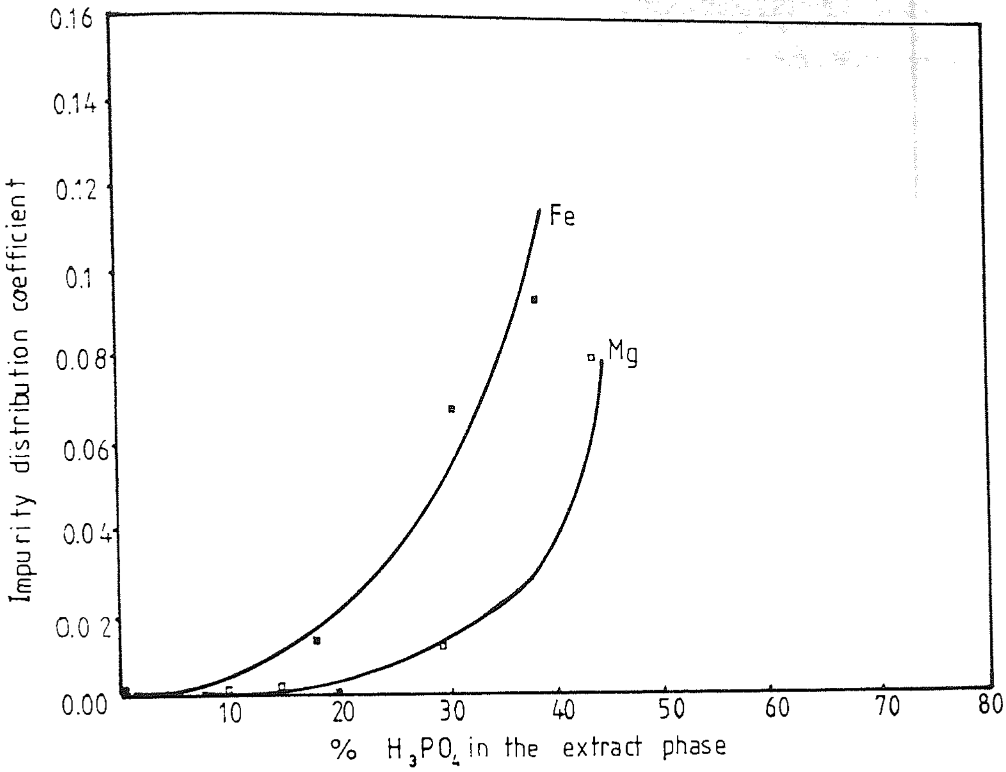


Fig 7.13 Effect of H_3PO_4 concentration on the impurity distribution coefficient at 0.4_0.5% impurity concentration in the feed aqueous acid for the system water_ H_3PO_4 Methyl_iso butyl ketone

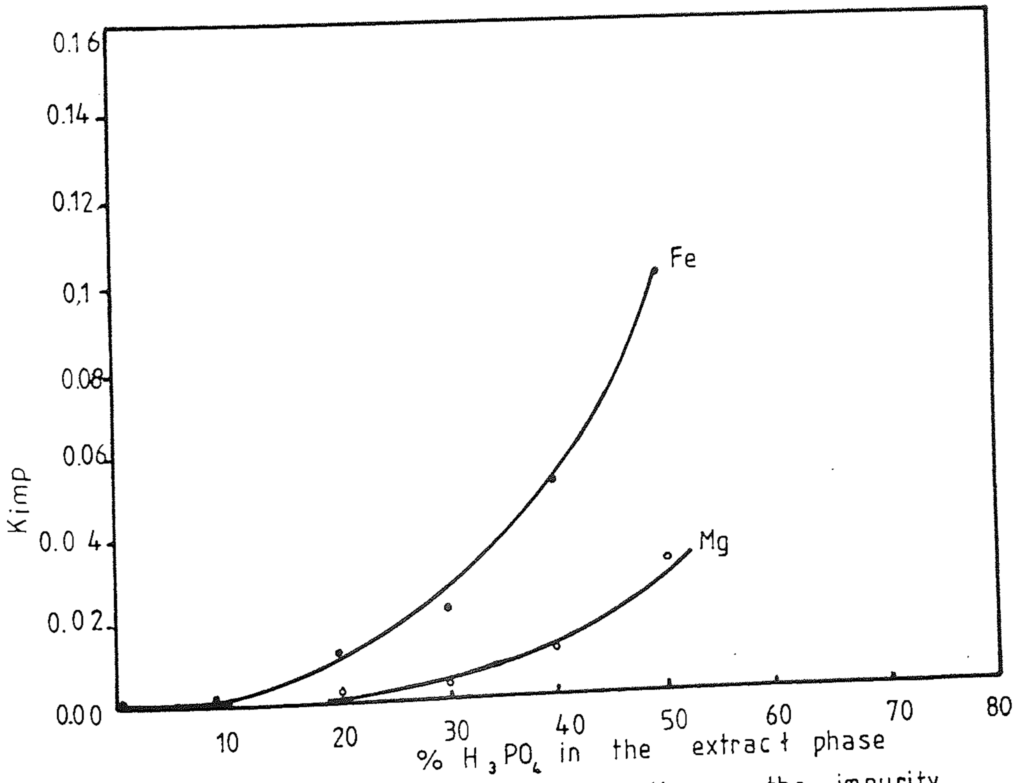


Fig. 7.14. Eeffect of H_3PO_4 concentration on the impurity distribution coefficient at 0.4 0.5% impurity concentration in the feed aqueous acid for the system water_ H_3PO_4_ Cyclohexanol

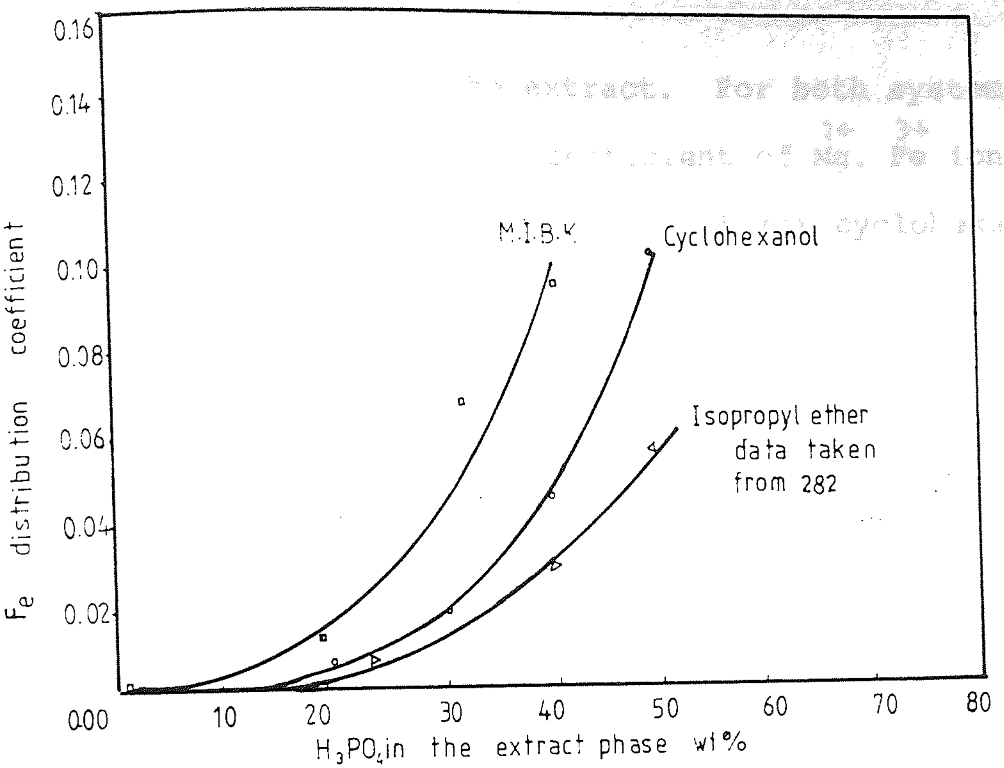


Fig 7.15 Comparison of the effect of H_3PO_4 concentration in the extract phase on the distribution coefficient of Fe^{3+} at ≈0.5 % concentration in the aqueous feed at temperature 25°C

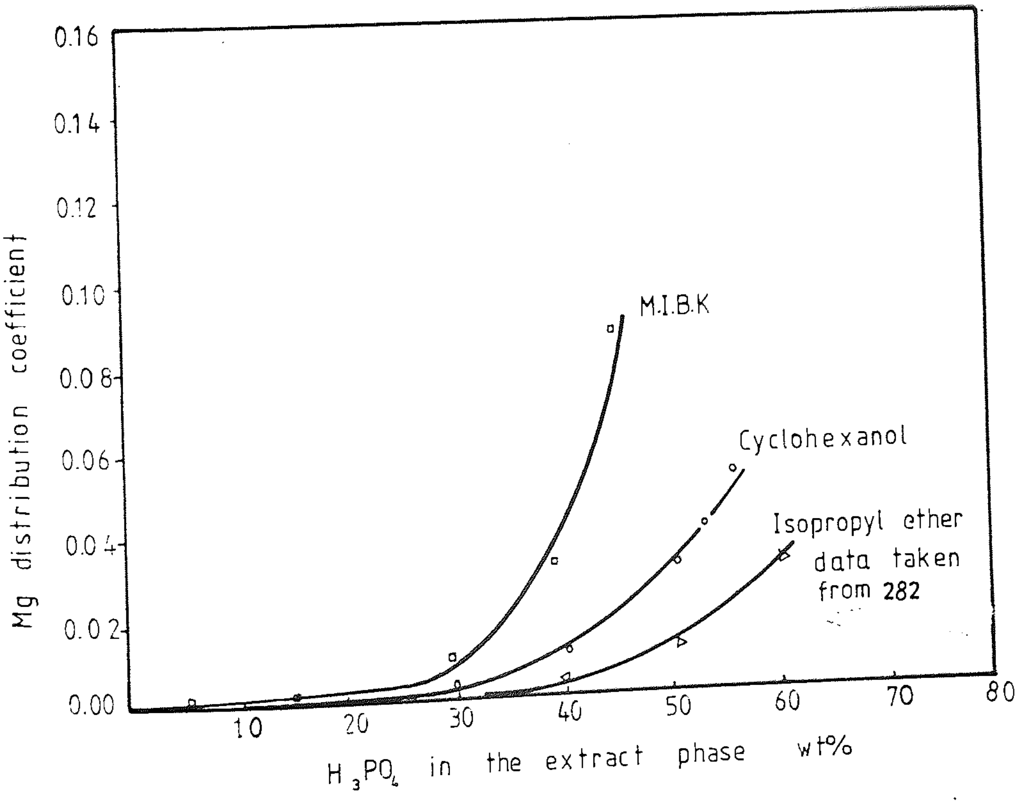


Fig 7.16 Comparison of the effect of H_3PO_4 concentration in the extract phase on the distribution coefficient of Mg^{2+} at ≈ 0.5 % concentration in the aqueous feed acid at temperature 25°C

acid concentration in the extract. For both systems, however, the distribution coefficient of Mg^{2+}. Fe^{3+} ions in the MIBK phase is higher than that for cyclohexanol as shown in Figs. (7.15 and 7.16).

7.1.1.4 EFFECT OF INITIAL IMPURITY CONCENTRATIONS ON THE DISTRIBUTION COEFFICIENT OF IMPURITIES

Only MIBK as solvent was studied, the data area presented in Appendix (3) and plotted in Fig. 7.17. The results show that as the initial impurity concentration in the acid increases, the distribution coefficient of the impurity decreases, however the concentration of impurities in the extract layer increases.

7.1.1.5 EFFECT OF MIXING TWO SOLVENTS ON THE DISTRIBUTION COEFFICIENT OF ACID

MIBK and cyclohexanol were mixed together to improve the physical properties of cyclohexanol, such as its freezing point and viscosity as shown in Appendix (3). This should also improve its extractive property as shown in Fig. 7.18.

7.1.2 HYDRODYNAMIC STUDIES

Experiments on settling time and the effect of agitation power were carried out in a jacketted

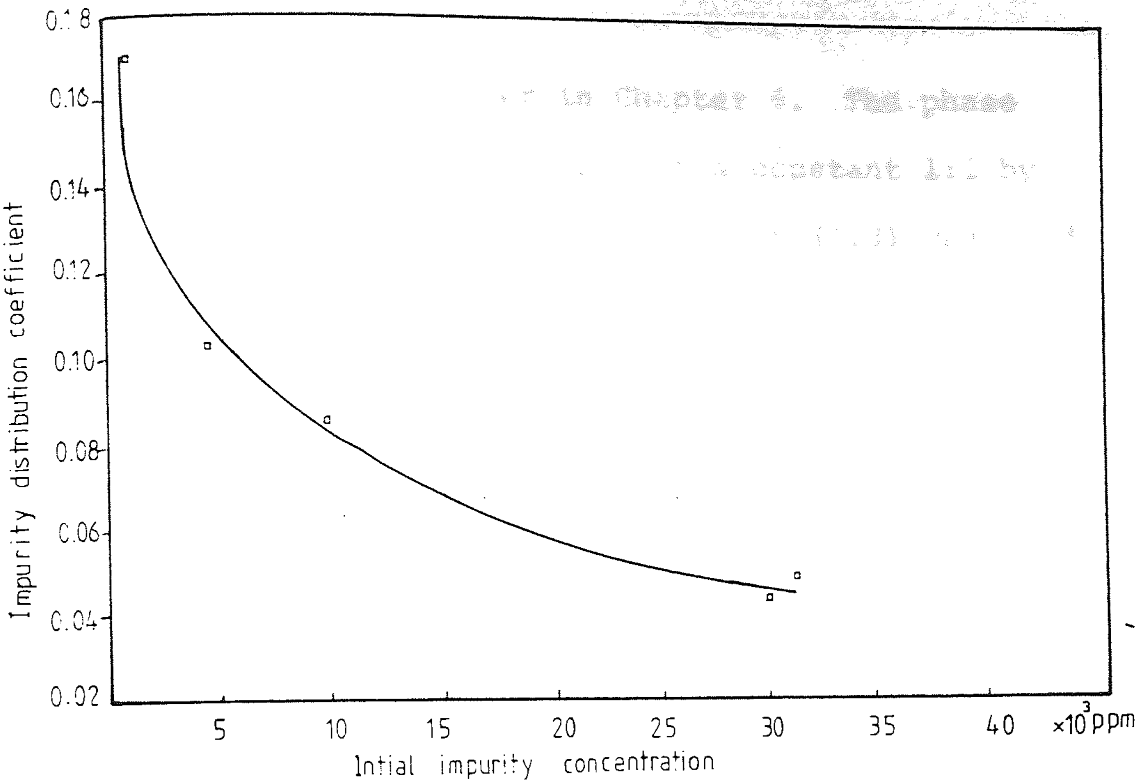


Fig 7.17 Effect of intial impurity concentration on the distribution coefficient of impurity for the system water – H_3PO_4 – M.I.B.K at intial acid concentration 70%

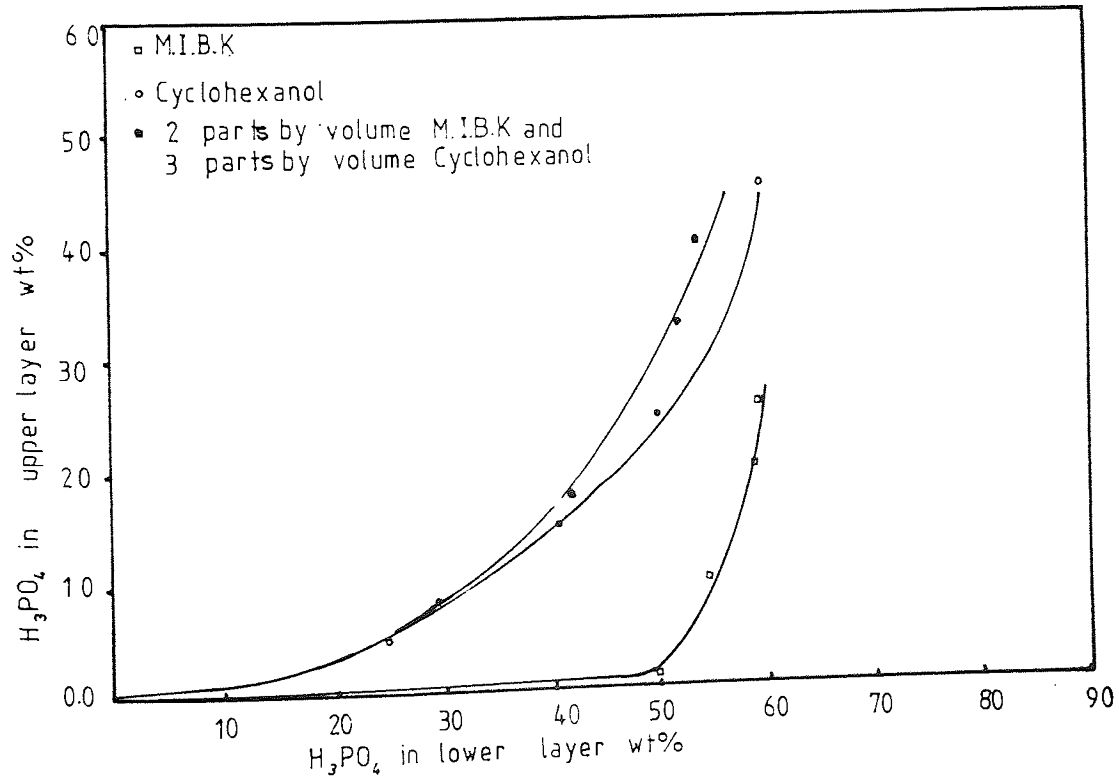


Fig 7.18 Effect of mixing two solvents on the distribution of phosphoric acid

cylinder described earlier in Chapter 6. The phase ratio of water to solvent was kept a constant 1:1 by weight. The mixer described in Section (6.3) was used to study drop size and phase inversion.

Both solvent and aqueous phases were saturated before any experiment was started. The procedure was to fill the vessel with the two phases then to start agitation and allow equilibrium to be reached (10-15 minutes). All the systems studied were O/W, and the position of the impeller was always in the lower aqueous phase to maintain the O/W system.

7.1.2.1 EFFECT OF ACID CONCENTRATION ON THE SETTLING TIME OF THE TWO PHASES

After equilibrium was achieved by agitation, the impeller was switched off and the time required for the two phases to separate was measured using a stop watch. Different acid concentrations and different solvents were used. The settling time of dispersion increased with the phosphoric acid concentration for all solvents studied. The curves (Figs. 7.19, 7.20) are similar to those of the distribution coefficient of the system in that there is a gradual change with cyclohexanol and a step change with MIBK and benzaldehyde.

7.1.2.2 EFFECT OF IMPURITY ON SETTLING TIME

Only Fe^{3+} ion as the introduced impurity was studied since Yacu (282) reported that all the ionic impurities have the same effect on settling time.

In general the presence of impurity lengthened the settling time for mixtures containing relatively low acid concentrations while it shortened it for mixtures containing high acid concentrations as shown in FIg. 7.19, 7.20, and 7.21. Fig. 7.23 compares the three solvents studied.

7.1.2.3 EFFECT OF MIXING TWO SOLVENTS ON SETTLING TIME

As mentioned in Section 7.1.1.5 two solvents may be mixed together to improve certain properties of the system. Cyclohexanol was mixed with MIBK to improve the system settling time. Fig. 7.25 shows that mixture of cyclohexanol and MIBK settles in less time than pure cyclohexanol at any concentration of acid.

7.1.2.4 EFFECT OF AGITATION ON SETTLING TIME

The potential range of agitator speeds was determined by varying the impeller speed from 200 r.p.m. to 1400 r.p.m. At low r.p.m. (200) the dispersion was not homogeneous, while at high speed a secondary haze was formed.

The effect of agitation was, therefore, studied between 450 and 1150 r.p.m. Within this range the

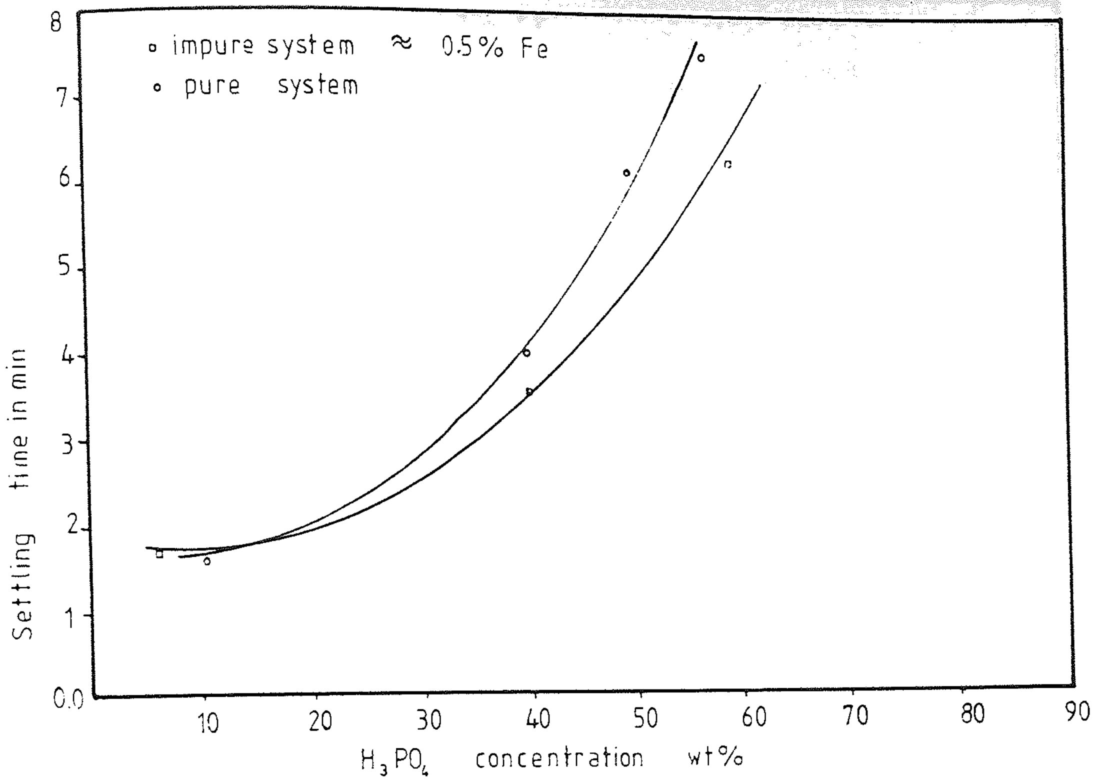


Fig 7.19 Settling time vs phosphoric acid concentration at 25°C for the system H_3PO_4- water- cyclohexanol at 1100 R.P.M. with (O/W)

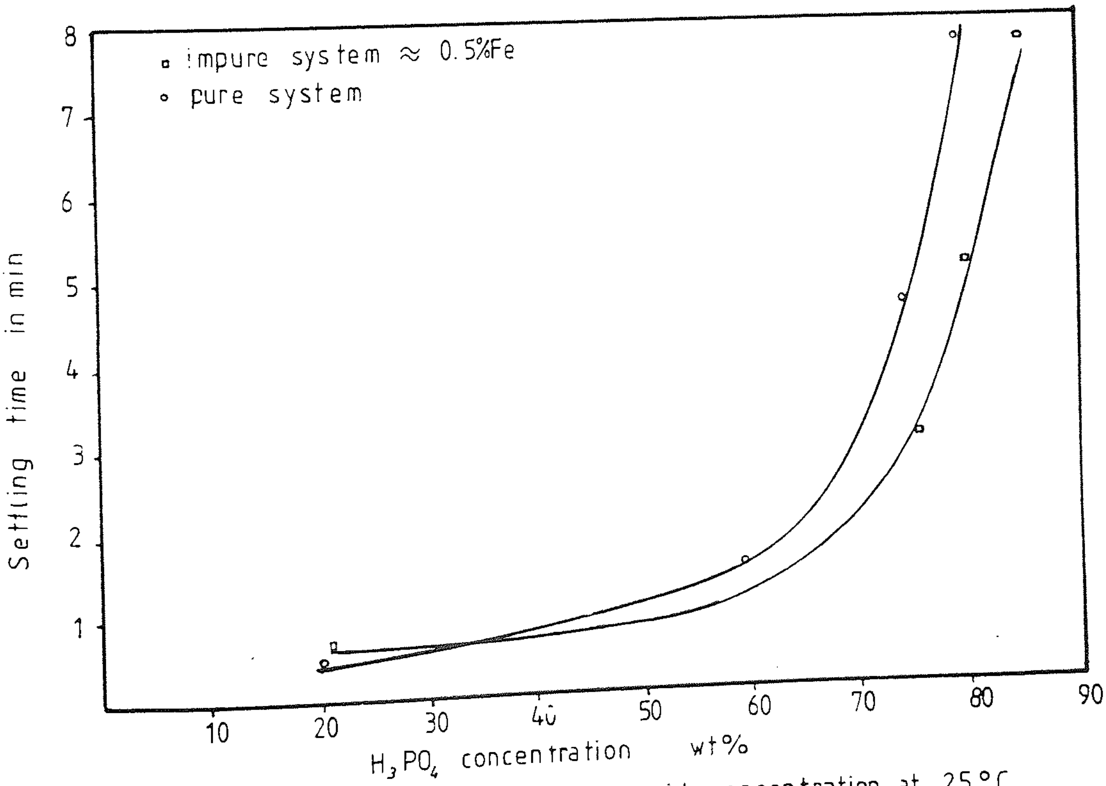


Fig 7.20 Settling time vs phosphoric acid concentration at 25°C for the system H_3PO_4 - Water- Benzaldehyde - at 1100 R.P.M with (O/W).

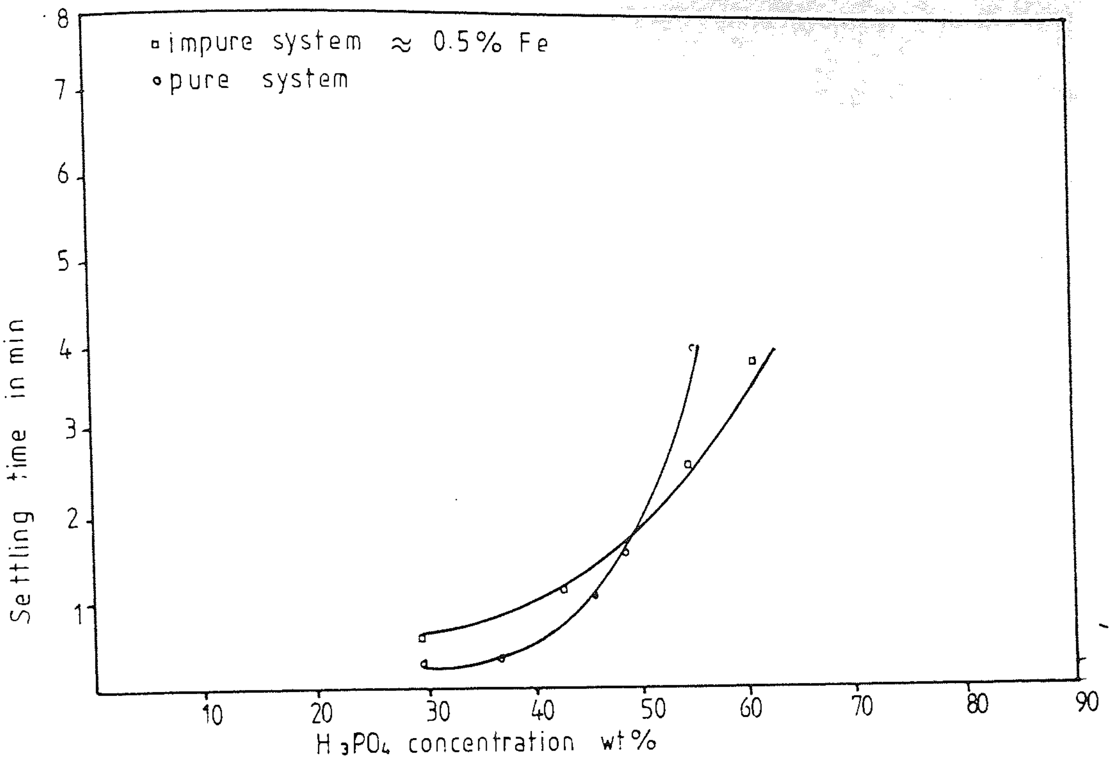


Fig 7.21 Settling time vs phosphoric acid concentration at 25°C for the system H_3PO_4–Water–M.I.B.K at 1100 RPM, with (O/W)

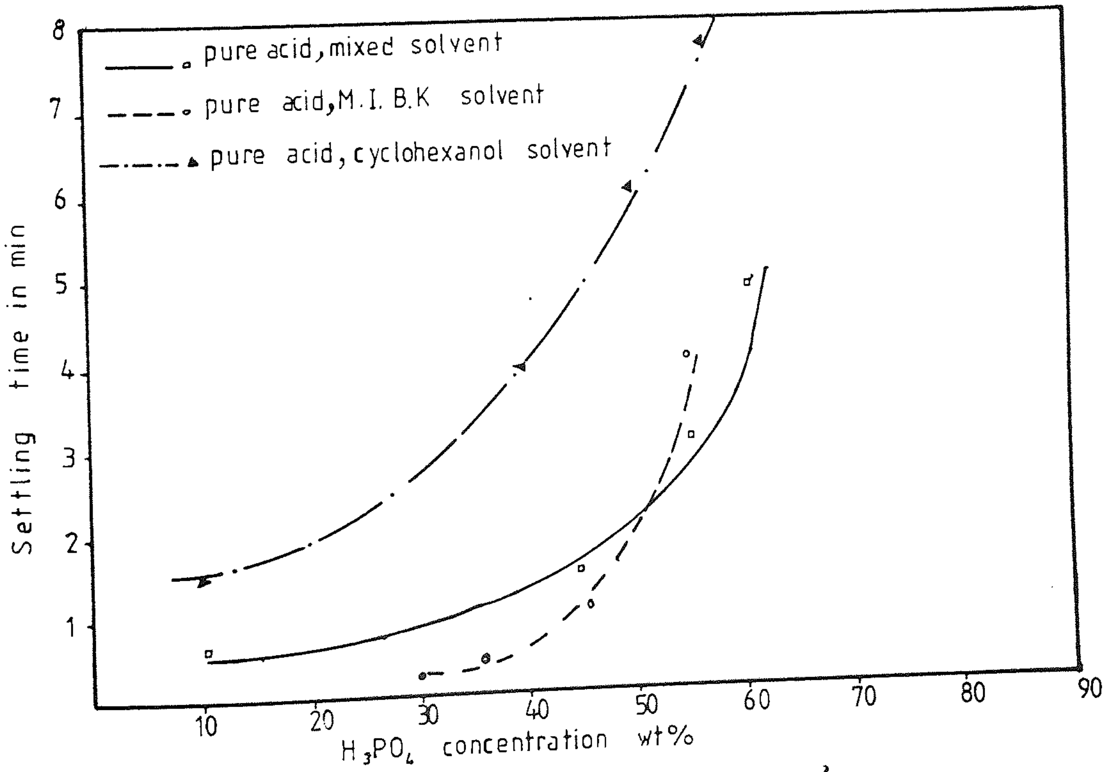


Fig 7.22 Effect of mixing the two solvent 'M.I.B.K and Cyclohexanol [2:3] by volume' on settling time, at 1100 R.P.M and 25 °C

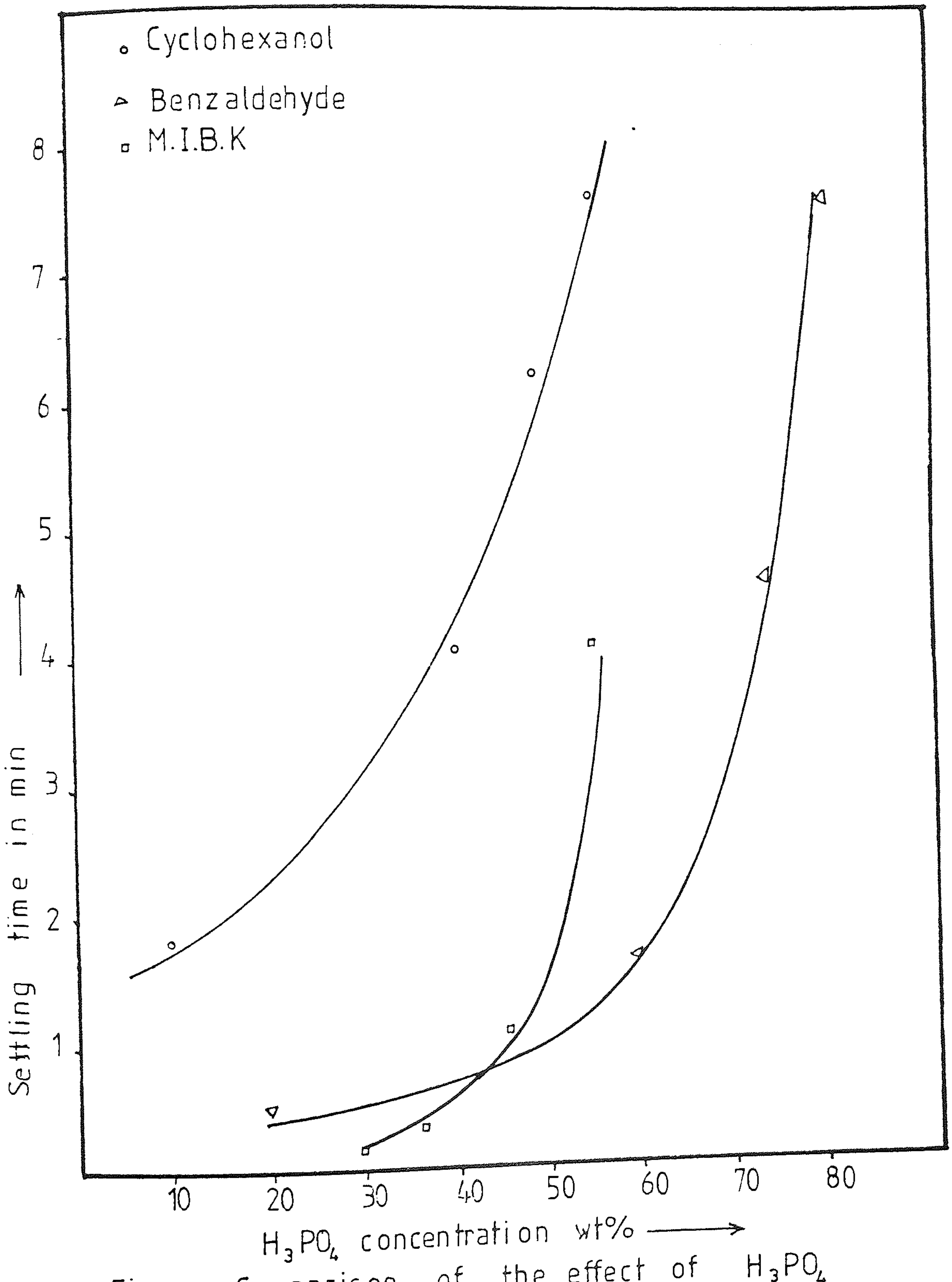


Fig 7.23 Comparison of the effect of H_3PO_4 concentration on settling time for the system H_3PO_4–Water–Solvent at 25 °C and 1100 RPM, (O/W)

primary break (settling time) was generally not affected with the speed of agitation as shown in Figs. (7.24 and 7.26). The dotted line in Fig. 7.24 is due to incomplete mixing at the speed required due to the high viscosity of cyclohexanol.

7.1.2.5 EFFECT OF TIME OF MIXING ON SETTLING TIME

Time of mixing has no significant effect on settling time as shown in Fig. (7.37).

7.1.2.6 EFFECT OF ACID CONCENTRATION AND AGITATOR SPEED ON DROP SIZE

After mixing the two phases until equilibrium was achieved two or three photographs were taken. Even with low energy input and low acid concentration it was difficult to photograph and measure the drop size. Therefore the impeller was stopped and photographs were then taken immediately. The results are reproduced in Figs. (7.28, 7.29). The drop size of the dispersed phase (solvent phase) decreased with an increase of phosphoric acid concentration and increasing agitator speed.

7.1.2.7 DROP SIZE VERSUS DISPERSED PHASE HOLD-UP

In these studies the rotor speed was kept constant at the required value and photographs were taken at different hold-up values. The results are presented in Fig. (7.30).

7.1.2.8 PHASE INVERSION CHARACTERISTICS

In this experiment, the mixer was filled so that the impeller was immersed with the continuous phase (aqueous phosphoric acid phase) about 350 cm^3. The impeller was switched on and the speed was set at the required rate. Solvent (dispersed phase) was added until the total volume of the two phases in the mixer became around 650 cm^3. 50 ml of the dispersion were then slowly withdrawn using a pipette. About 10 minutes were allowed to reach steady state, then dispersed phase was again added until the total volume again became 650 cm^3. This process was then repeated until the phase inversion point was reached. The inversion points of the system from o/w - w/o were detected by a conductivity meter, when the system is o/w the conductivity is high and when it is w/o the conductivity is low. Approach to phase inversion can be detected by erratic movement of the meter in the conductivity equipment. Growth of the drops was also noted near phase inversion. After inversion the impeller was switched off and the dispersed phase holdup was measured and plotted against the rotor speed. The results are presented in Fig. (7.31).

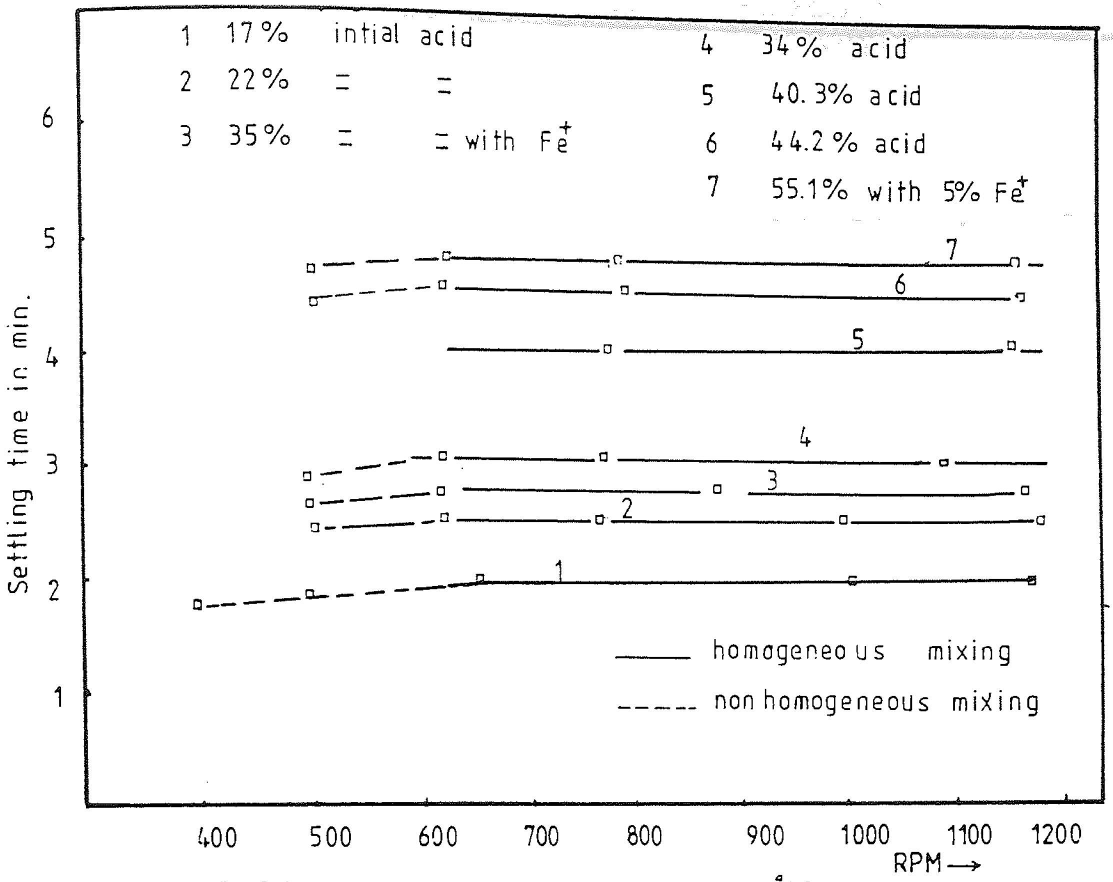


FIG 7.24 Primary break vi r.p.m at 25°C for system phosphoric acid-water- cyclohexanol (O/W)

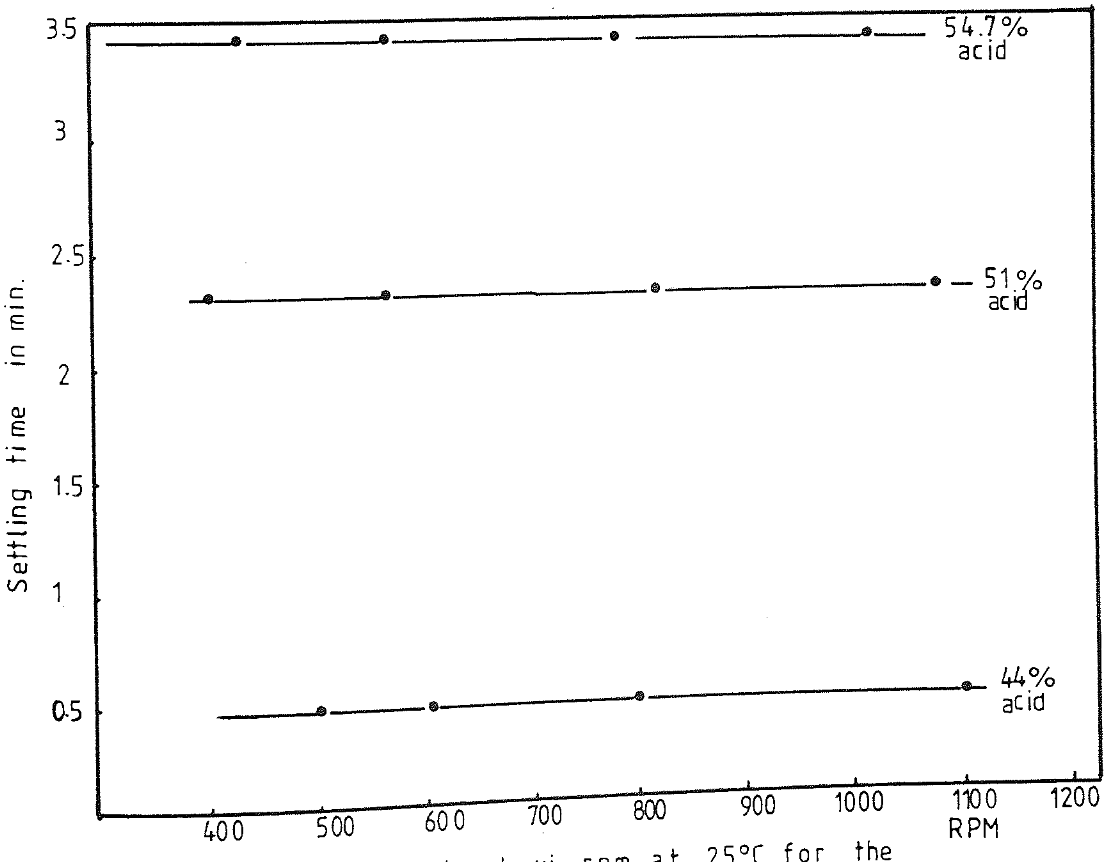


FIG 7.25 Primary break vi r.p.m at 25°C for the system phosphoric acid - water - M.I.B.K. (O/W)

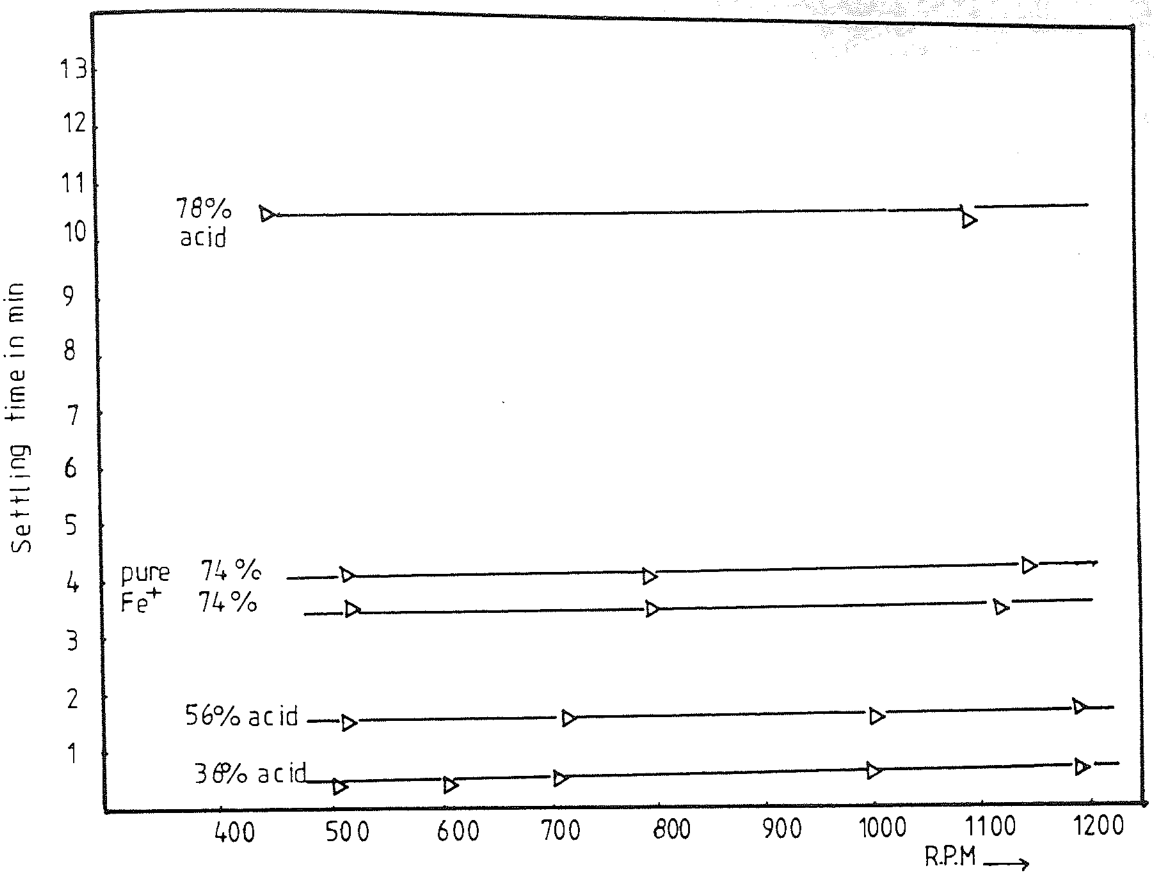


FIG 7.26 Primary break vi r.p.m at 25°C for the system phosphoric _ acid _ water Benzaldehyde

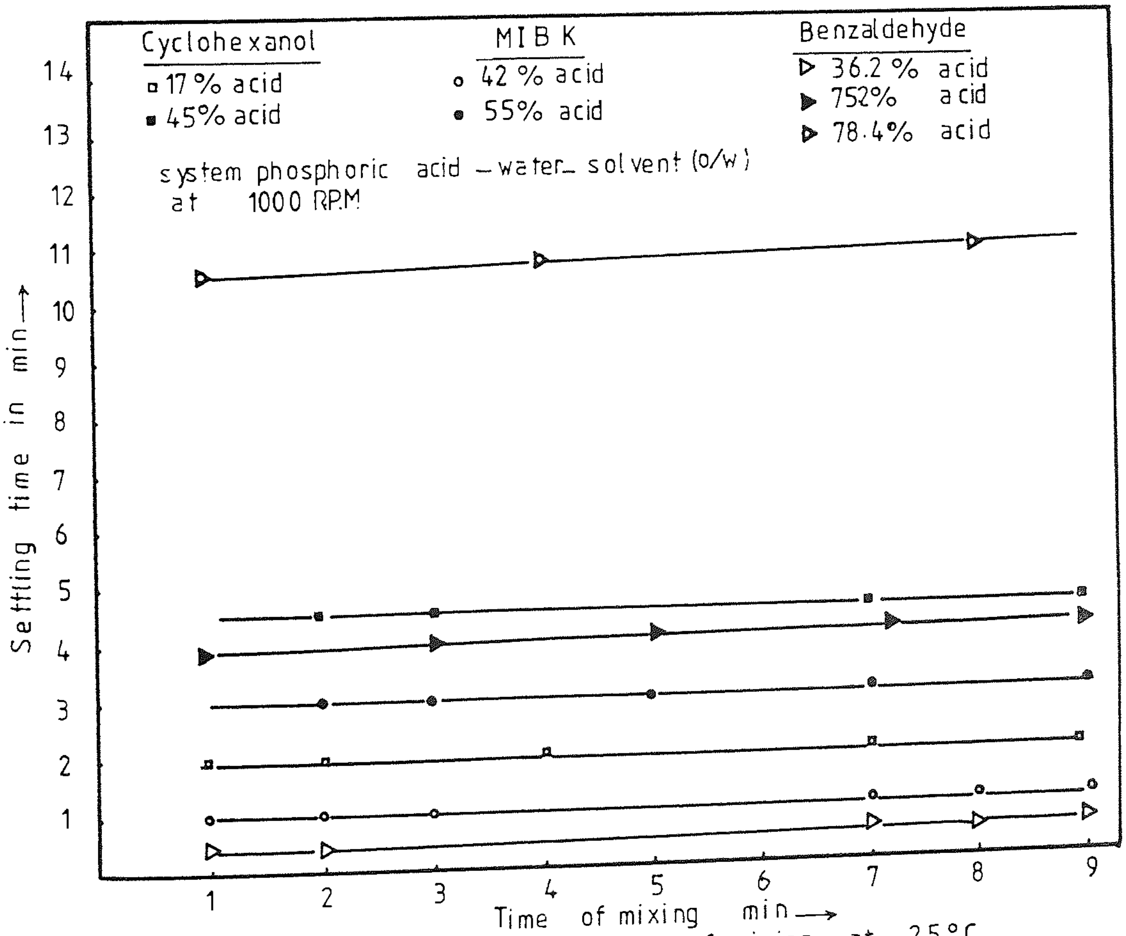


FIG 727 Break time as afunction of time of mixing at 25°C

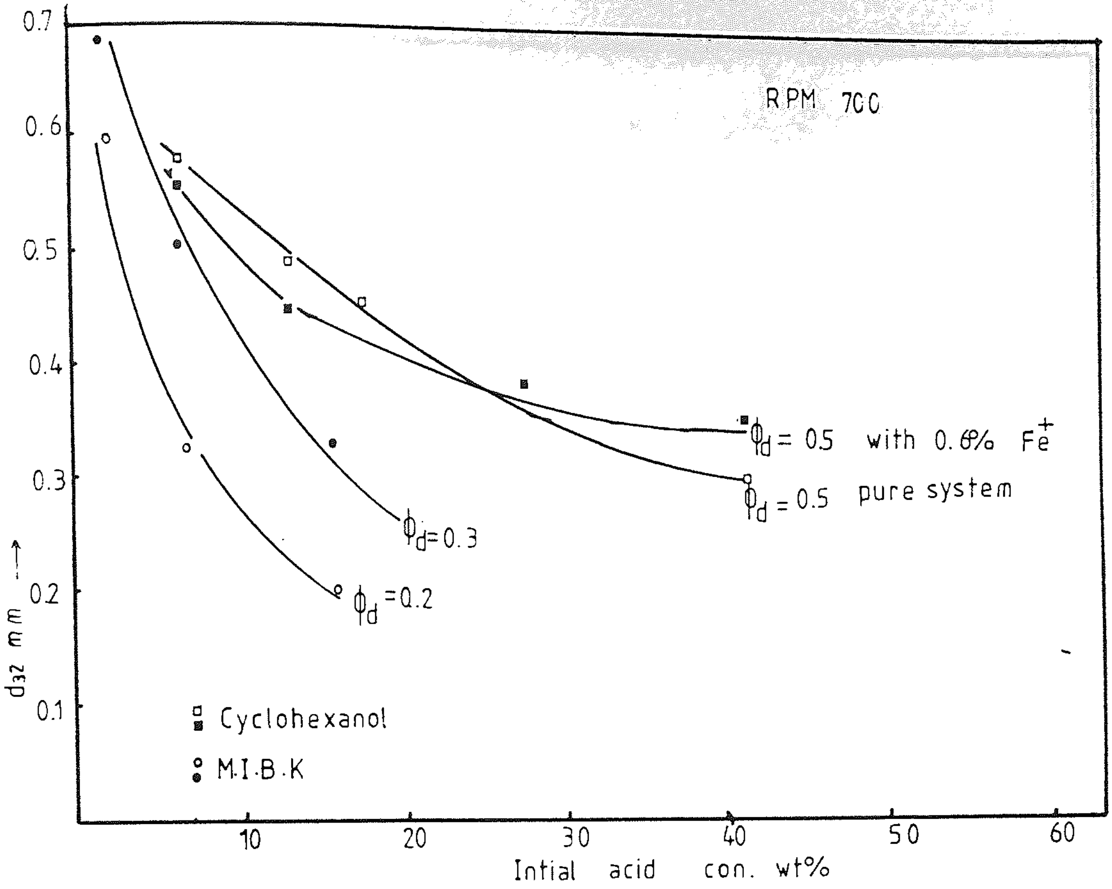


FIG 7.28 Drop size vs phosphoric acid concentration system phosphoric acid – water – solvent o/w.

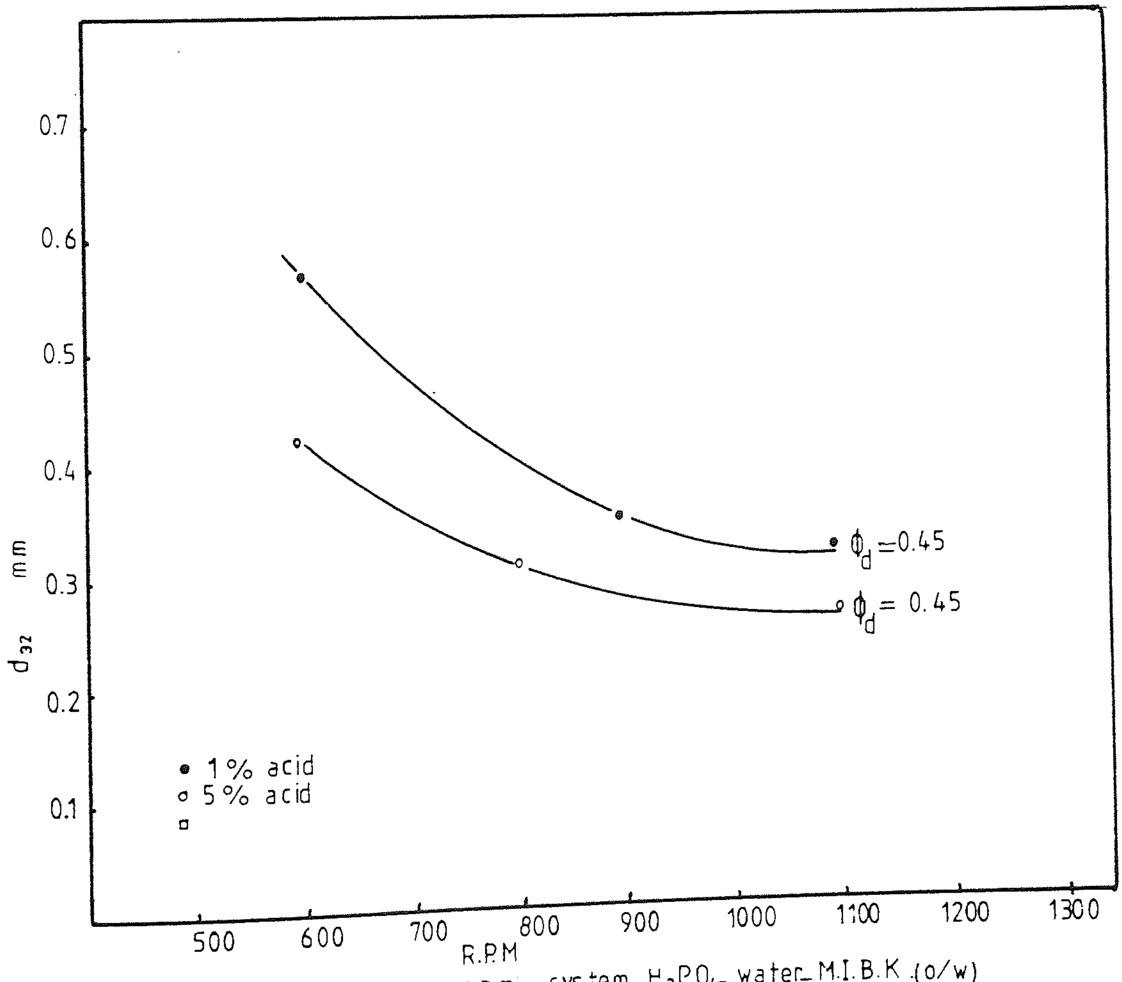


FIG 7.30 Drop size vs r.p.m system H_3PO_4 – water – M.I.B.K (o/w)

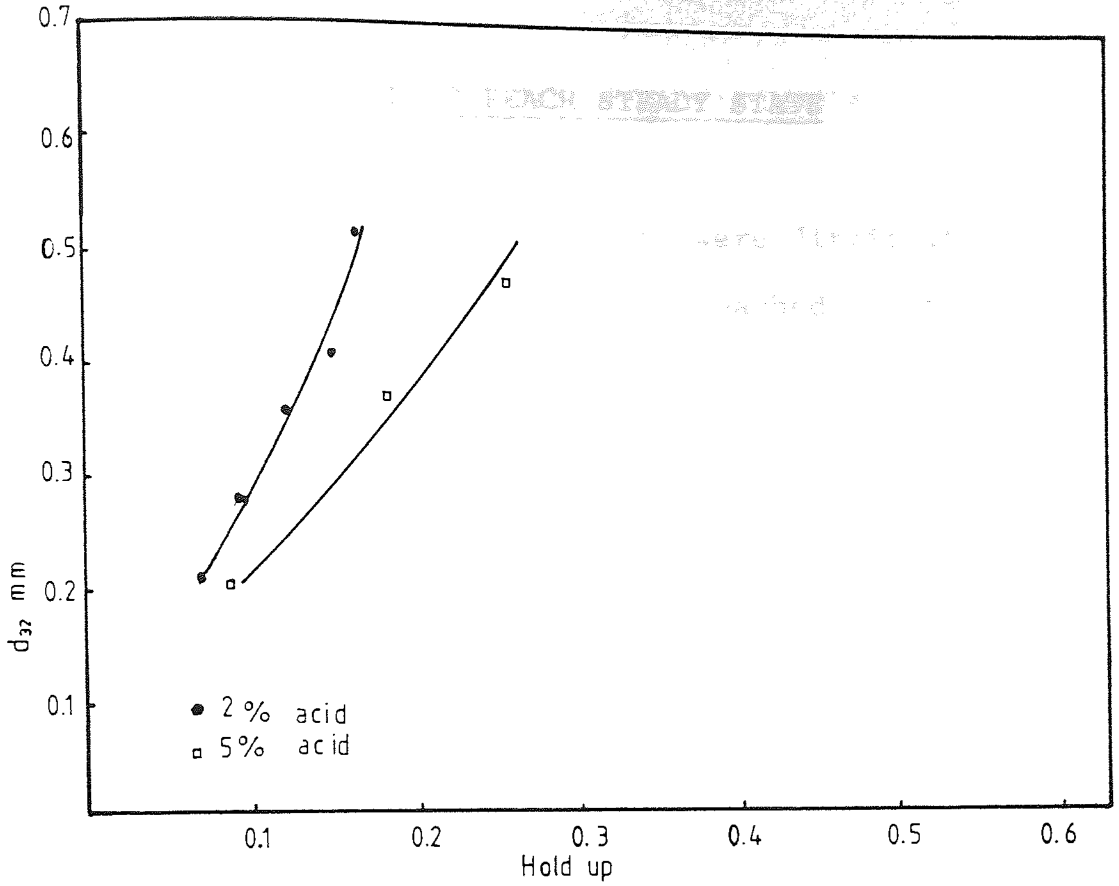


FIG 7.30 Variation of drop size with hold up for the system phosphoric acid – water – solvent (M.I.B.K)

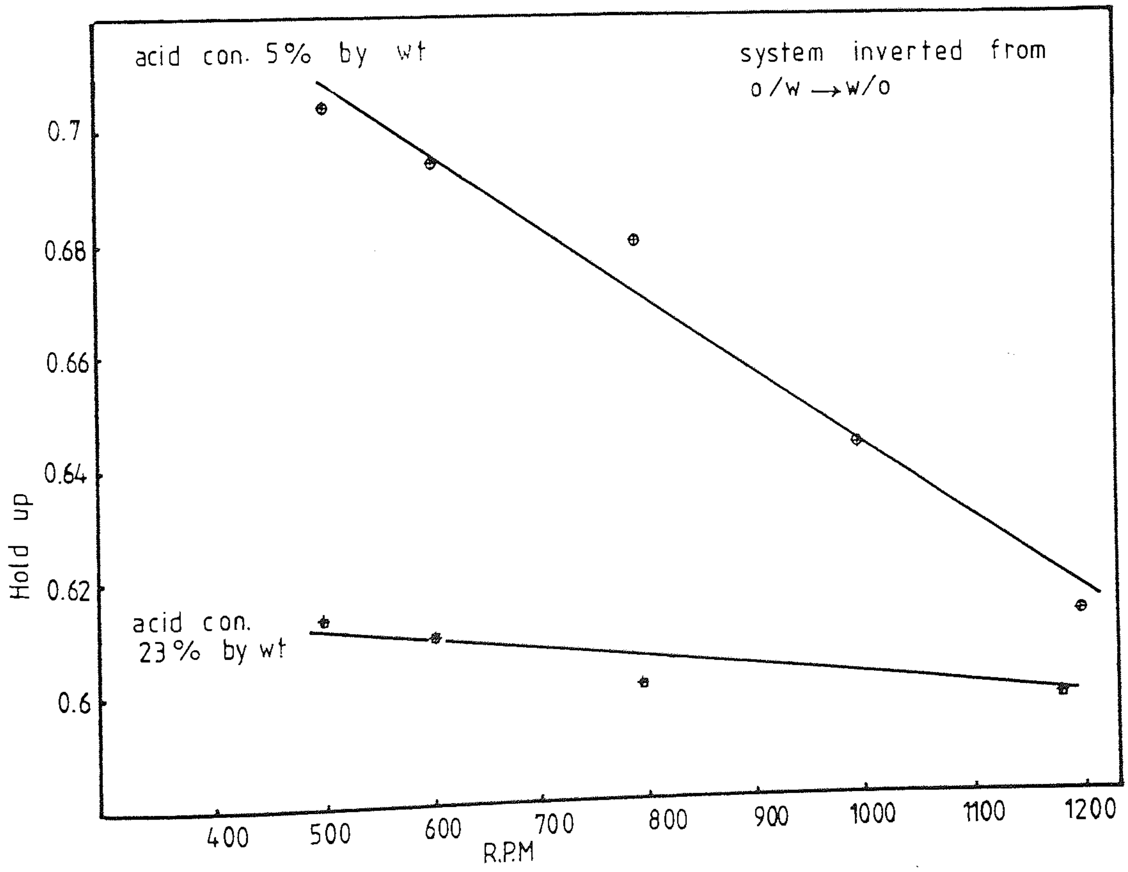


FIG 7.31. positions of phase inversion for the system phosphoric acid – water – M.I.B.K at different r.p.m

7.1.2.9 TIME REQUIRED TO REACH STEADY STATE

Batch mass transfer experiments were difficult to carry out before steady state was reached due to the rapid approach to equilibrium, and since the two phases were in intimate contact. This increased the sampling and measurement problems considerably. In this set of experiments two equal volumes of acid and solvent were mixed (at 1000r.p.m.), the impeller was switched off at 30 seconds intervals and samples were then taken at the first appearance of the extract layer. The results of the analysis are presented in Fig. (7.32). The time to reach equilibrium was no longer than 6 minutes in either case.

7.1.3 HYDRODYNAMIC STUDIES ON BACK EXTRACTION OF PHOSPHORIC ACID

After extracting the acid using solvent, experiments were done to recover the acid, by back extracting the saturated solvent with water. On extracting the acid a milky layer (upper layer) was observed, which required about 3 hours to clear. However the time for disappearance of this layer can be made shorter by increasing the power input as shown in Fig. (7.33). Although this is advantageous for reducing equipment cost, secondary drops were formed at speeds higher than 1050 r.p.m.

After the milky layer had disappeared, neither the power input nor the time of mixing have any significant effect as shown in Figs. (7.34 and 7.35).

7.1.4 EFFECT OF PHOSPHORIC ACID CONCENTRATION ON THE PHYSICAL PROPERTIES OF THE PHASES

7.1.4.1 INTERFACIAL TENSION

The effect of phosphoric acid concentration on the interfacial tension is shown in Fig. 7.36. For both systems studied as acid concentration increased the interfacial tension decreased and at very high acid concentrations, and nearer to the plait point the interfacial tension was always close to zero. In the case of cyclohexanol, decrease in interfacial tension caused finer dispersion and formation of a secondary haze. Considering Fig. 7.36, the rate of decrease of the interfacial tension with H_3PO_4 concentration varied with the solvent and was greater with MIBK. By comparison of Fig. 7.36 and 7.23, the higher the surface tension, the faster the settling of the two phases.

7.1.4.2 SPECIFIC GRAVITY

The results for the two systems cyclohexanol and MIBK are summarised in Fig. (7.37). The results show that specific gravity of all the systems (aqueous and organic phase) increased almost linearly with the acid concentration. The average density of a mixture was taken as $\rho_{av} = \phi_D \rho_d + \phi_C \rho_C$

7.1.4.3 SURFACE TENSION

The effect of phosphoric acid concentration in both aqueous and raffinate phases for both systems (cyclohexanol and MIBK) is shown in Fig. 7.38.

The surface tension of the aqueous phase is constant with phosphoric acid concentration within the experimental error, but the surface tension of the solvent phase increases with phosphoric acid concentration.

7.1.4.4 VISCOSITY

Fig. (7.39) shows that the viscosity of both aqueous and raffinate phases for both systems increases almost linearly with increase in phosphoric acid concentration.

The effective viscosity of a mixture as a geometric mean can be taken as

$$\mu_m = (\mu_d)^{\phi_D} + (\mu_C)^{\phi_C}$$

$$\phi_C = 1 - \phi_D$$

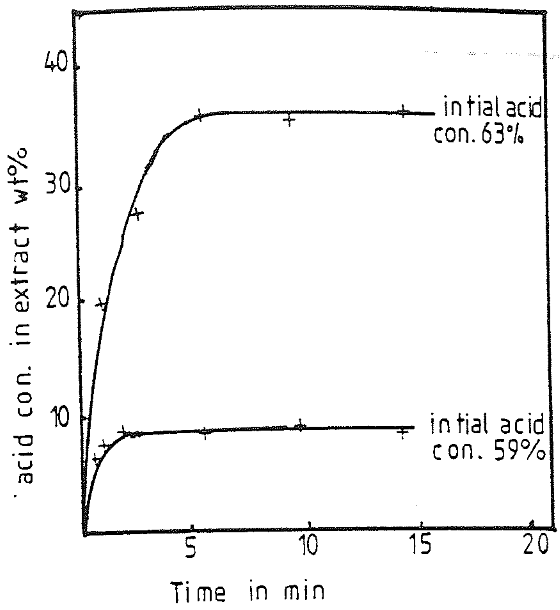


FIG 7.32 Time to reach steady state vs concentration of acid in the extract. Volume of acid 300ml and volume of solvent is 300ml, temp. 25°C r.p.m 1000, solvent M.I.B.K.

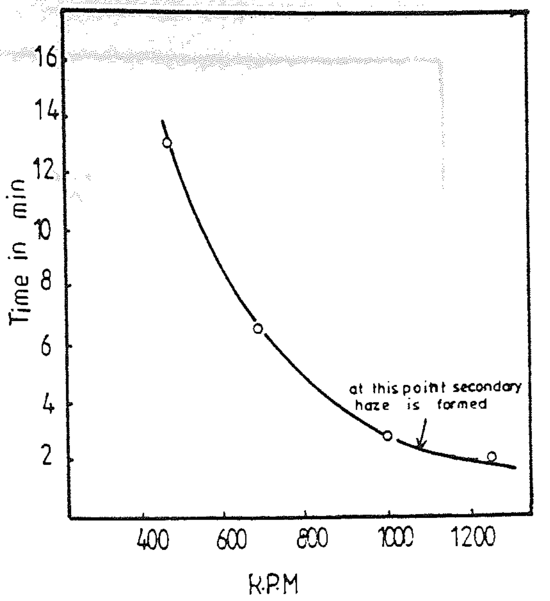


FIG 7.33 Time of disappearance of the milky layer vs power imput. system phosphoric acid – water – M.I.B.K. volume of saturated solvent is 120ml, contain 15% wt/wt phosphoric acid, and volume of extracting water is 60ml.

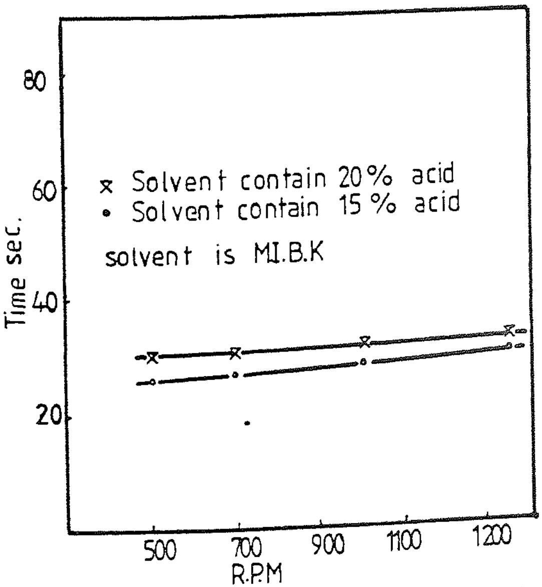


FIG7.34 Time of settling vs power input for back extraction stage

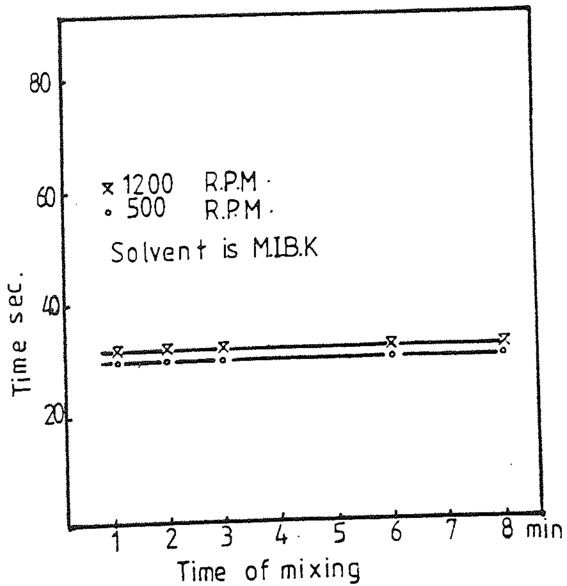


FIG7.35 Time of agitation vs settling time for back extraction stage

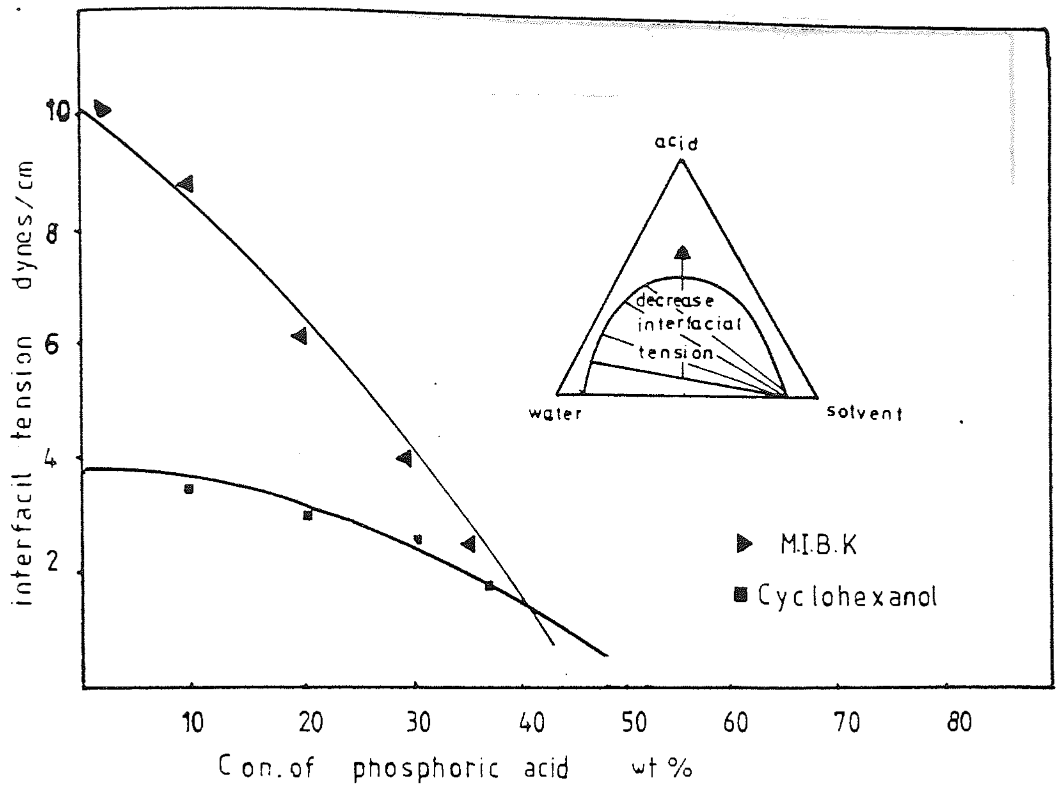


FIG 7.36 Interfacial tension for co-existing phases at equilibrium at 25°C for water-phosphoric acid solvent

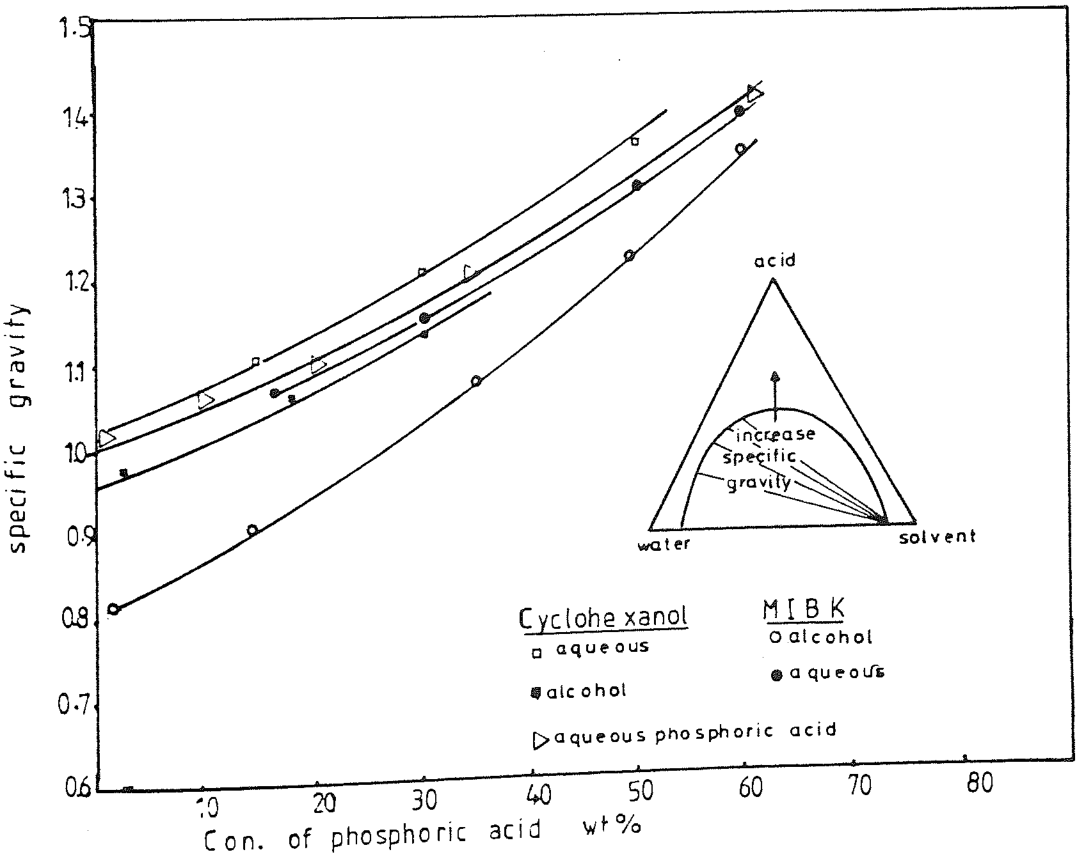


FIG 7.37 Specific gravity of the coexisting phases at 25°C

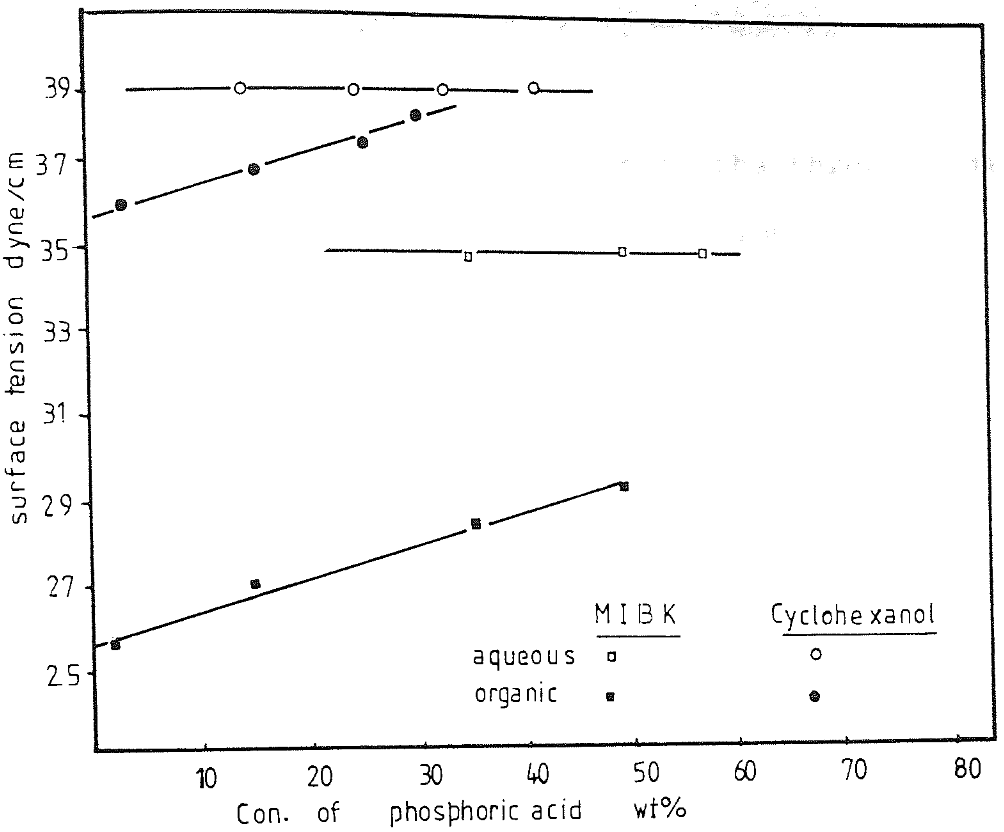


FIG 7.38 Surface tension of the co-existing phases of the system phosphoric acid-solvent-water at 25°C

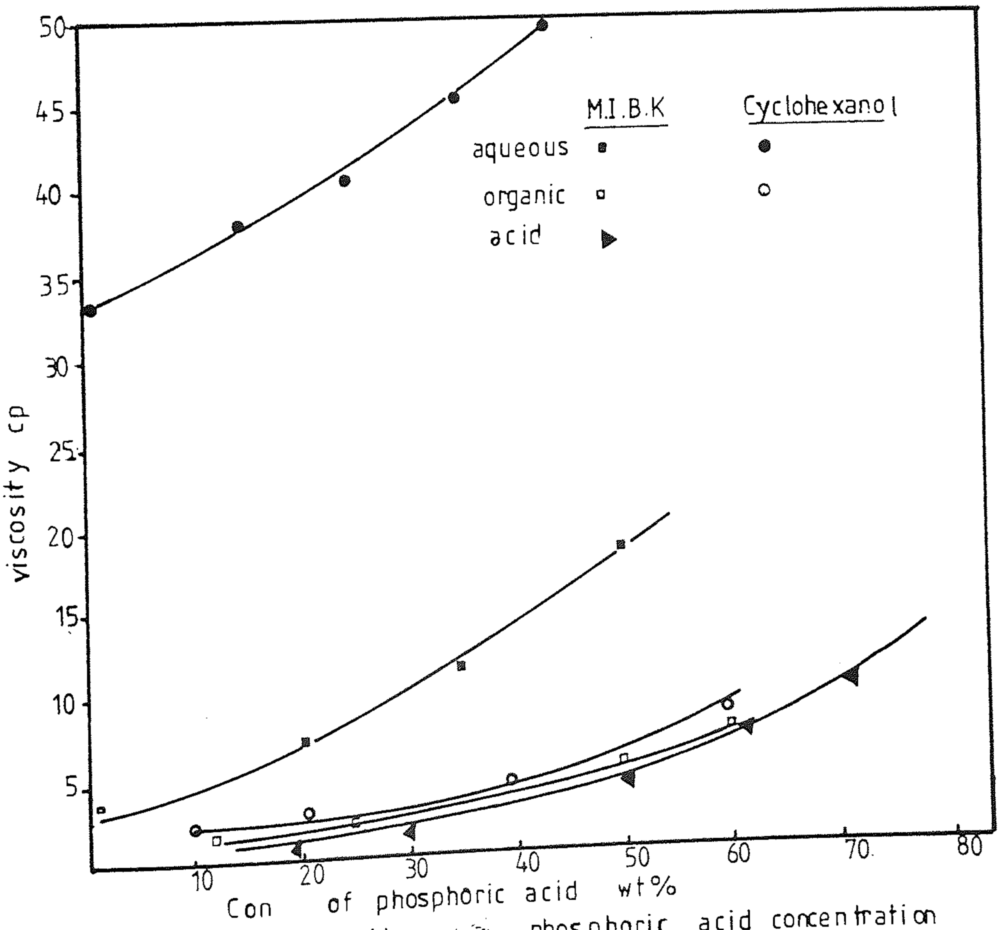


FIG 7.39 Viscosity vs. phosphoric acid concentration

7.2 CONTINUOUS STUDIES

These studies were carried out in the three stage mixer-settlers described earlier in Section 6.2. One stage was used for hydrodynamic studies, in this case a new feed tank (20 litres) was introduced for the continuous phase. Baffles and coalescers were removed to measure the wedge length under worst operating conditions.

The apparatus was used for both forward extraction and back-extraction of acid. In the case of forward extraction, the phosphoric acid solution was prepared in a 50 litre storage tank. Impurities were then added in phosphate form in an amount so that saturation or near saturation was achieved. This was around 0.5 to 0.6%. It was observed that when Fe^{3+} impurities are added, the solution at first became milky, and it required 30 minutes before becoming colourless. When more and more Fe^{3+} was added the solution turned pink/brown. When Mg^{2+} ions were added the solution became greenish.

The flow meters for the inlet flow were calibrated over the range 30-800 ml/min for phosphoric acid solutions, and 100 to 900 for MIBK.

When the equipment was used for back-extracting the acid from the solvent, the flow meters for both aqueous (water) and organic phase (MIBK saturated with acid) were also calibrated. The calibration graphs at different acid concentration are given in

Appendix 2. Since the outlet water and solvent phases contained different acid concentrations in different experiments and some times during the same experiment, the outlet flow of both was measured frequently during each run.

7.2.1 CONTINUOUS HYDRODYNAMIC STUDIES (FORWARD EXTRACTION)

Before using the solvent in these studies, it was passed twice through carbon cloth to pick up impurities. One stage was used for these studies, the flowrates of both phases were adjusted to set values, and following steady level being reached throughout the equipment, samples of the emulsion were taken from the middle part of the mixer using a long pipette. These samples were then allowed to separate in a 50 cc measuring cylinder. If the average hold-up values did not agree with the value of the hold up of the charge as a whole, the impeller speed was increased. Above a certain limit the increase in speed had no effect on the hold-up, (see Fig. 7.40). That is to say it depended mainly on the phase flowrate as shown in Figs. 7.41 and 7.42.

7.2.1.1 MIXER CHARACTERISTICS

After steady state and homogeneous dispersion was achieved a photograph of the dispersion was taken and analysed. All the photographs were taken above the critical speed (700 r.p.m.). The Sauter mean diameter was calculated from the usual expression:

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

Typical results are presented in Appendix (4).

In most cases, the droplet size exhibited a consistent log normal distribution as shown in Fig. 7.43. Results for MIBK as solvent is shown in Figs. (7.44 and 7.45).

The impeller was always in the lower layer, and all the runs were carried out for the system organic dispersed water continuous (o/w).

7.2.1.2 SETTLER CHARACTERISTICS

After removing the baffle and the coalescer from the settler, wedge dimensions were measured over a range of phase flow rates and energy inputs to the mixer.

No deposition of interfacial scum occurred in about 98% of the runs. Although scum is common in mixer-settler units in industry, it was reduced in this case by keeping the system clean. Alternatively it may be absent due to the system being acidic. Scum in industrial mixer-settlers can be removed by introducing a tapping off device in the settler.

The variation of wedge dimensions with dispersed, continuous phase flow rates and power input at different acid concentrations are shown in Figs. 7.46-7.51.

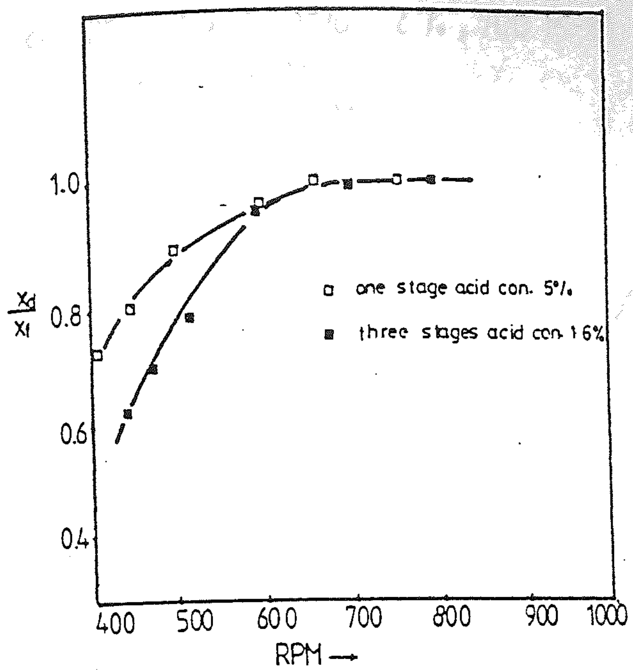


FIG 7.40 Xd / Xf VS R.P.M

System phosphoric acid – M.I.B.K

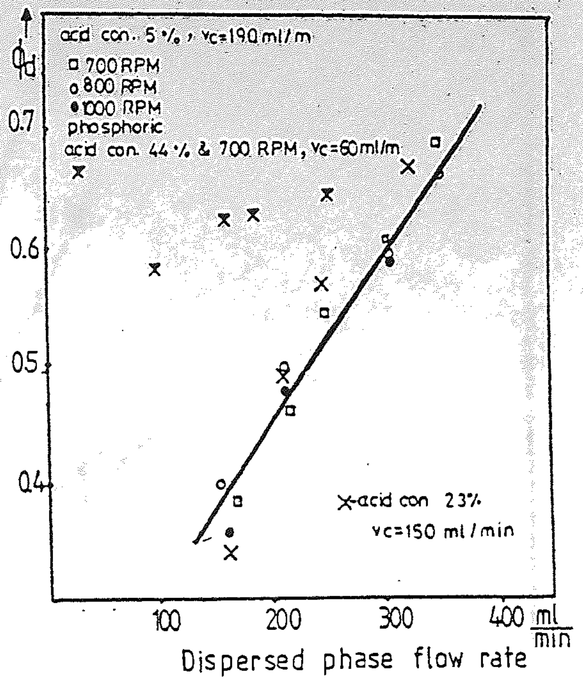


FIG 7.41 Hold up vs dispersed phase flow rate at above critical speed 700 r.p.m.

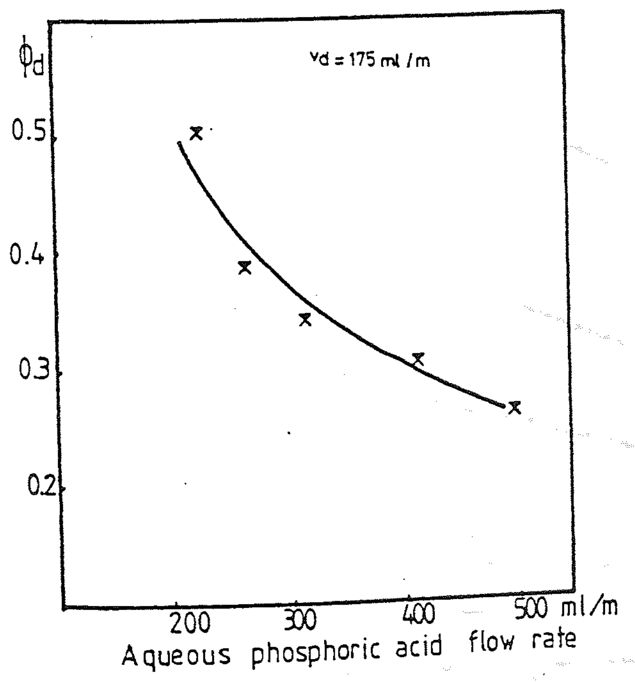


FIG 7.42 Hold up vs phosphoric acid flow rate at 700 R.P.M,

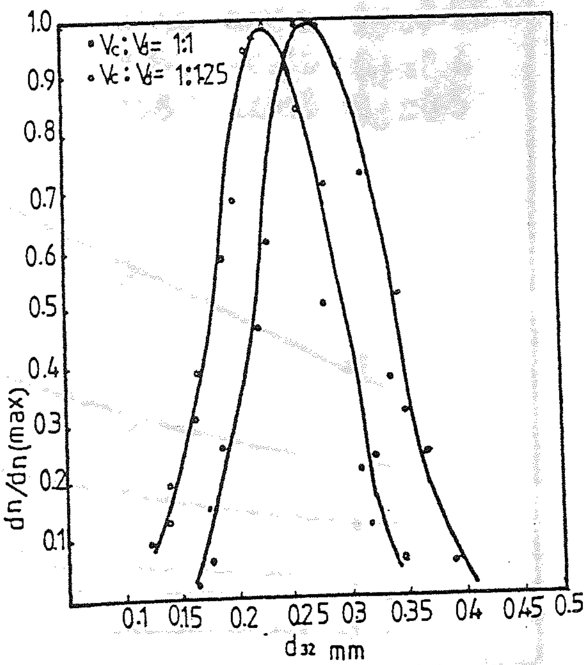


FIG 7.43 Typical drop size distribution for the system phosphoric acid-water-M.I.B.K at 900 R.P.M 5%.

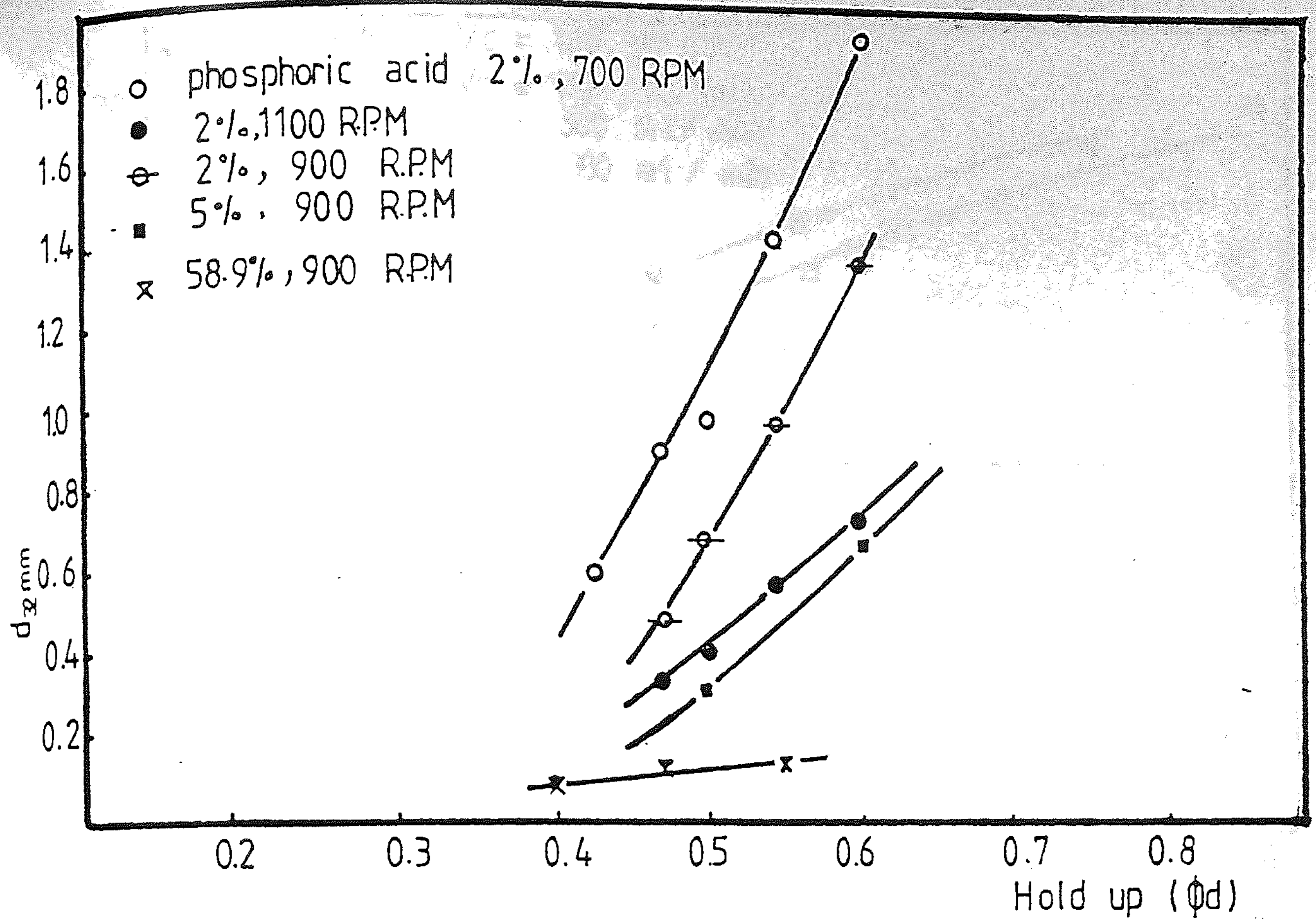


FIG 7.44 Drop size vs hold up for the system phosphoric acid _ water_ M.I.B.K

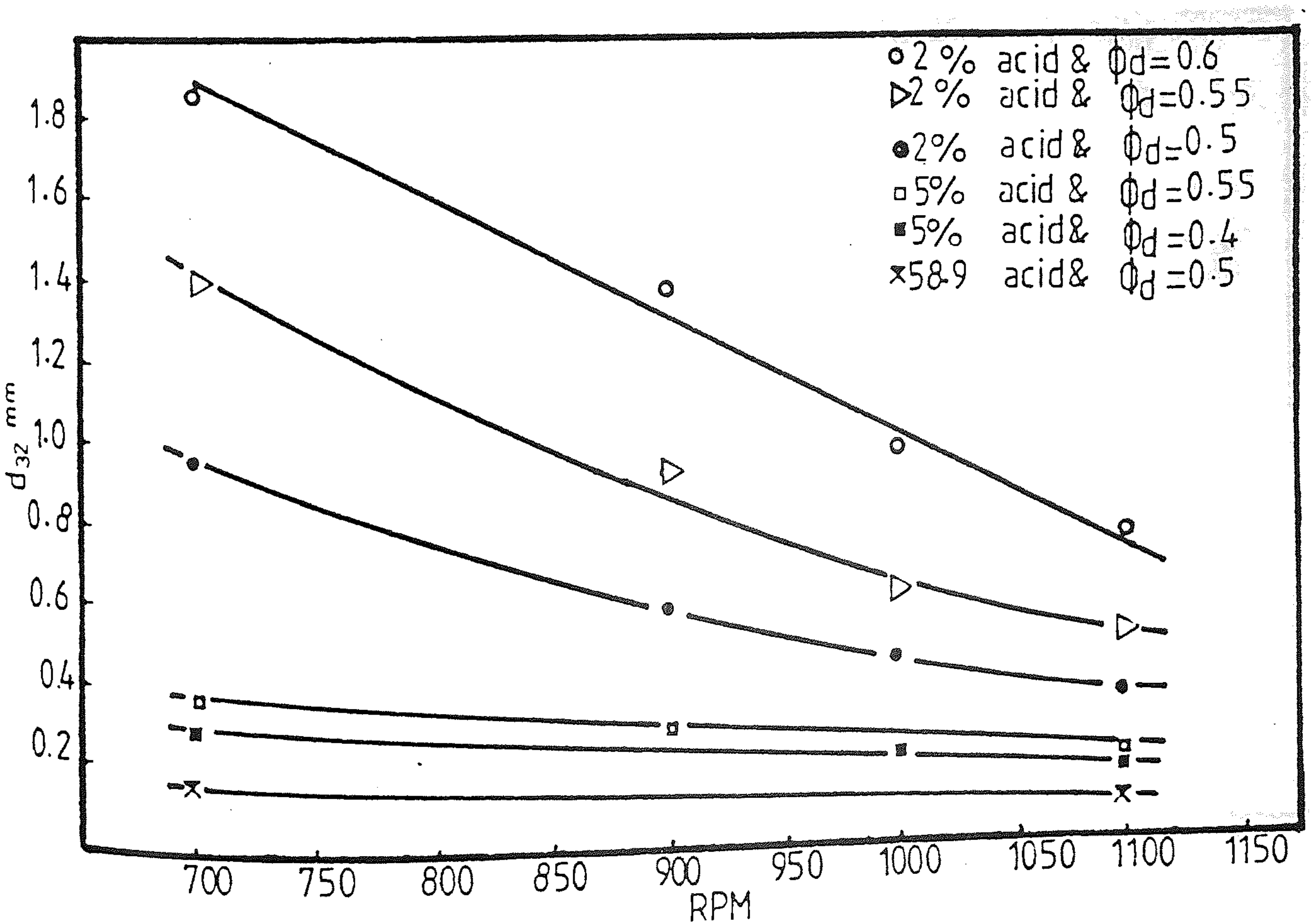


FIG _ Drop size vs power input

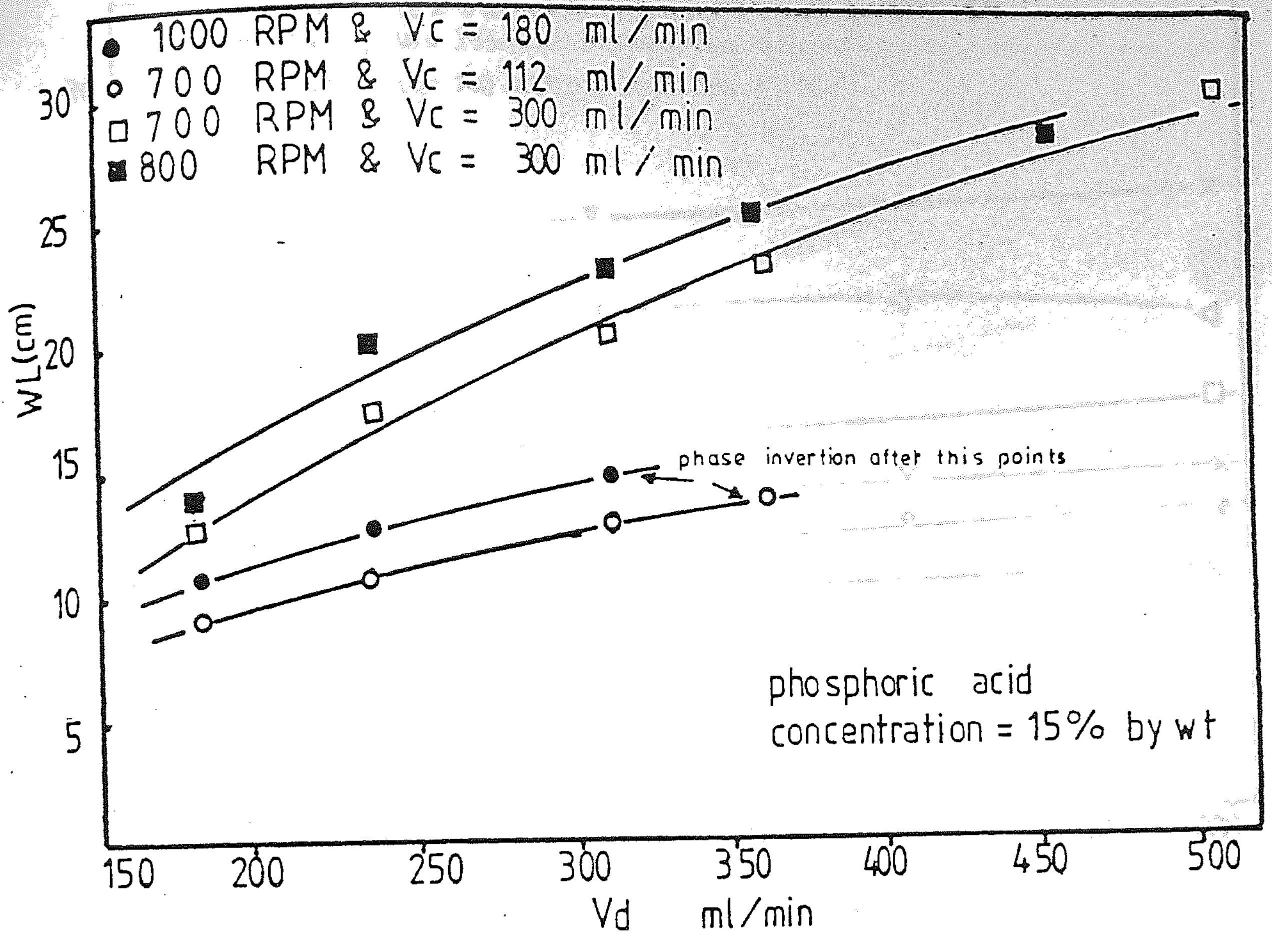
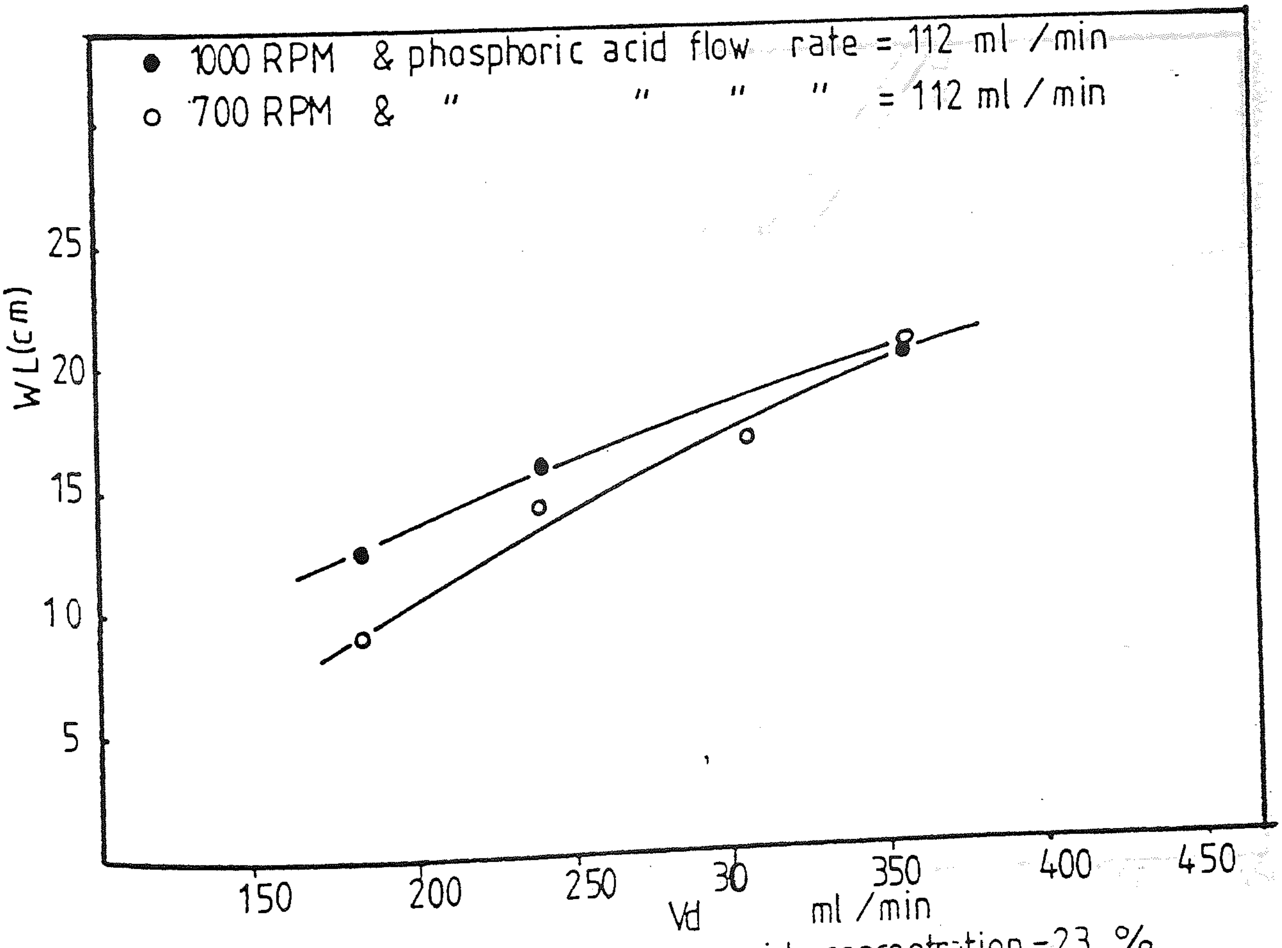


FIG 7.46

Wedge length vs dispersed phase flow rate
acid concentration = 15%



length vs Vd ; acid concentration =23 %

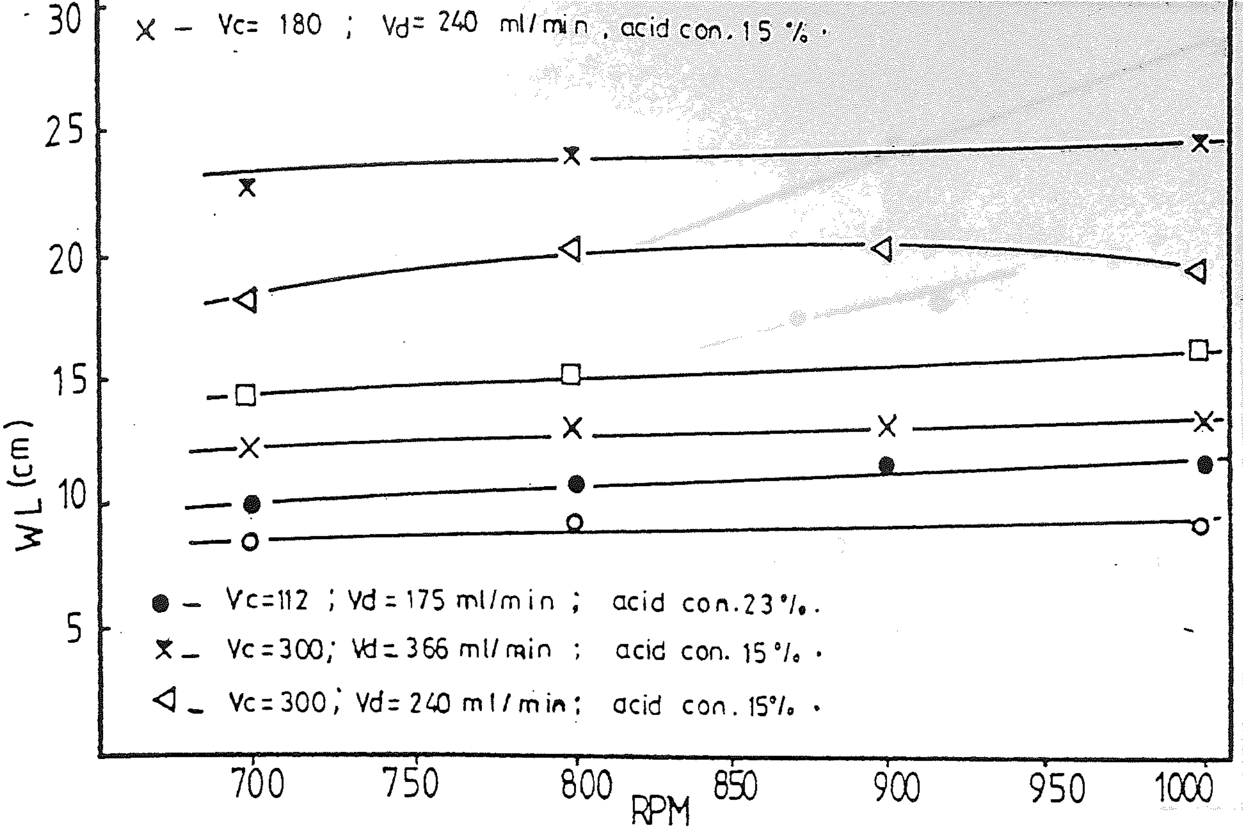


Fig 7.50 Wedge length vs power input.

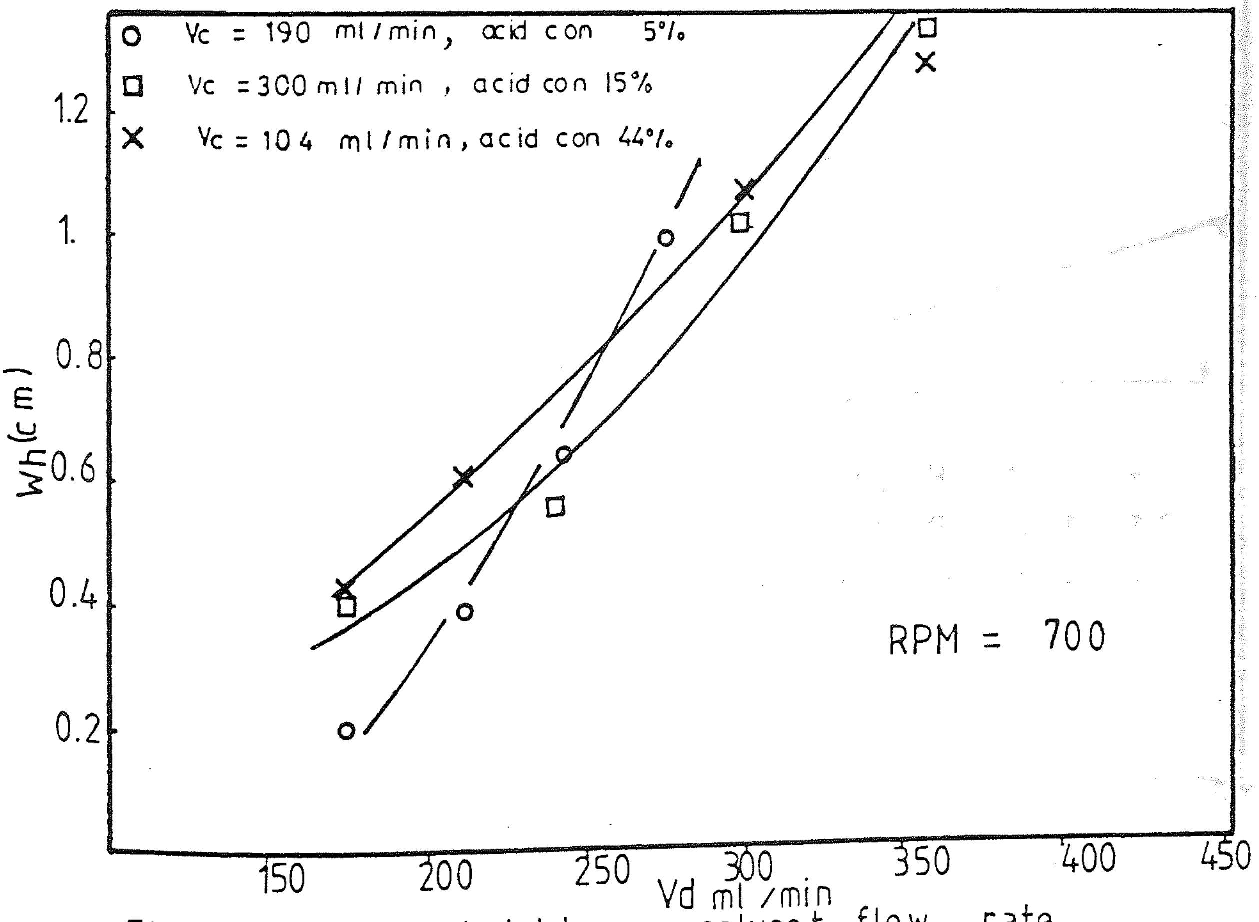


Fig 7.51 Wedge height vs solvent flow rate.

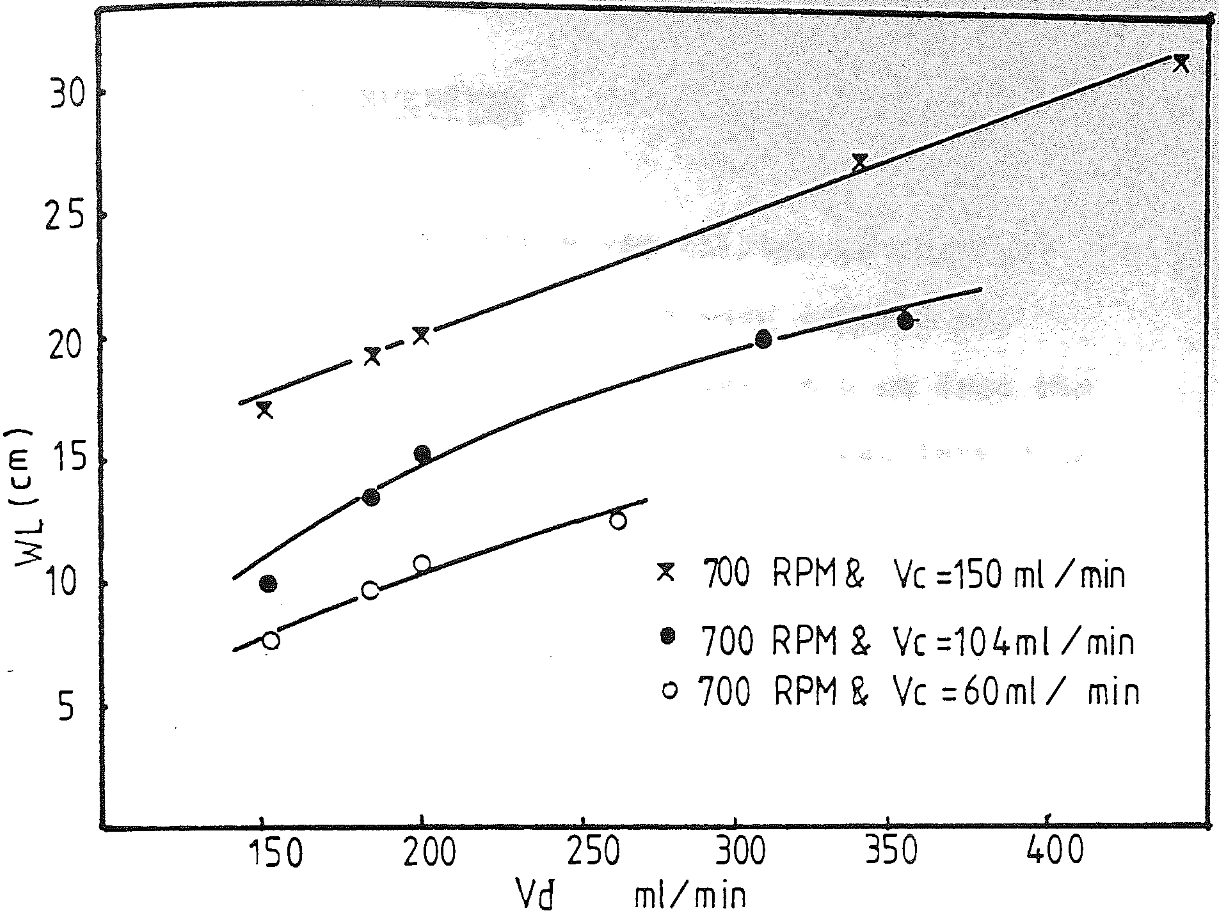


FIG 7.48 Wedge length vs dispersed flow rate at acid concentration = 44%

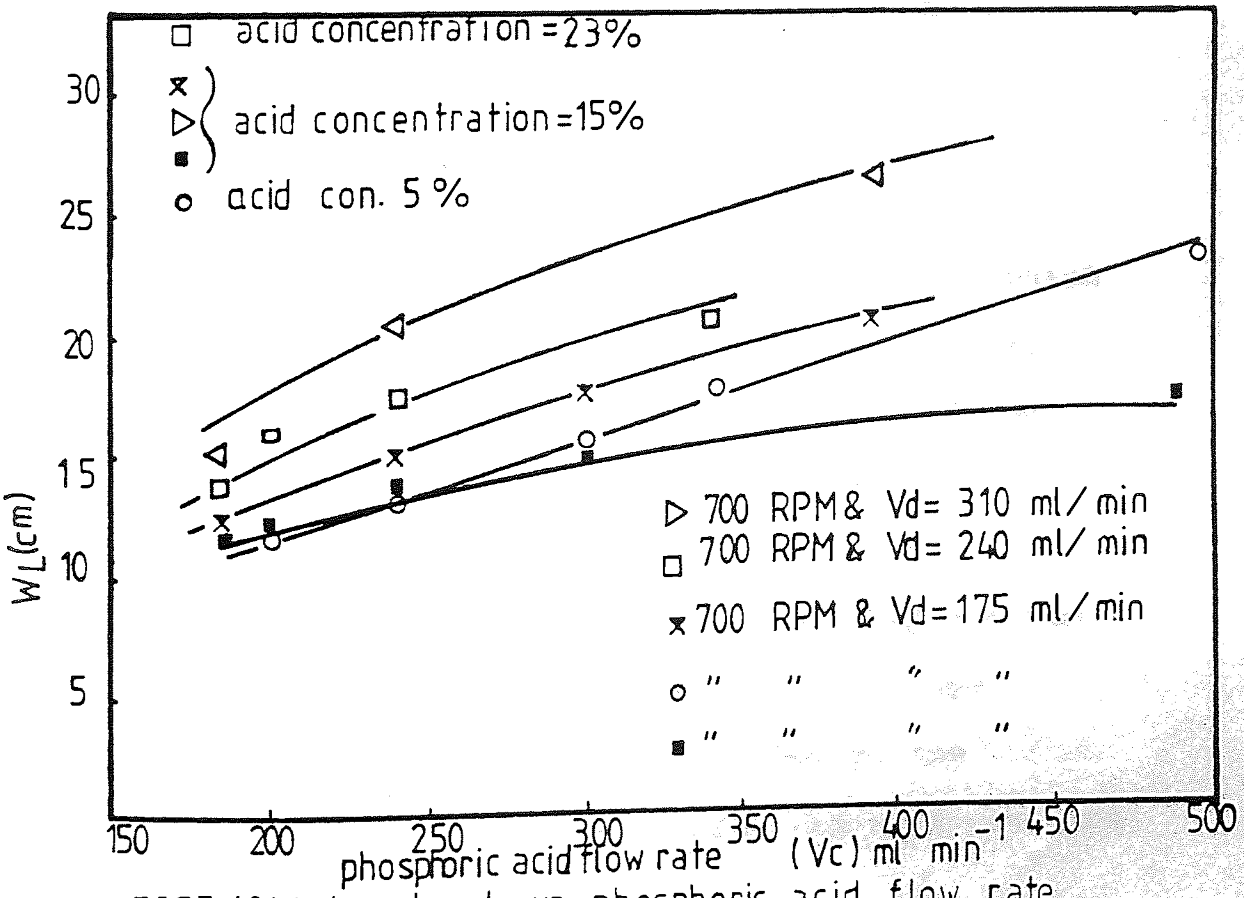


FIG7.49 Wedge lengt vs phosphoric acid flow rate

7.2.1.3 PHASE INVERSION

The start up procedure was similar to that of Section (6.3). Most of the runs were carried out with the impeller in the lower layer (4.5 cm from the bottom of the mixer). Continuous phase was introduced first, then the dispersed phase. System w/o can be obtained by introducing the organic phase first. Agitator speed and continuous phase flow rate were kept constant and the dispersed phase flow rate was then increased incrementally by 3-5% until phase inversion occurred. The onset of inversion was detected as will be described later. Studies were carried out with different acid concentrations and within the range of impeller speeds 700 to 1200 r.p.m.

This limitation was necessary since below 700 r.p.m. dispersion was not uniform and above 1200 r.p.m. secondary hazes were formed.

Onset of Phase Inversion

There are several methods and observations which can be used to detect the inversion of the system. Considering the mixer, a visual observation of the type of settling in a glass mixer is sufficient to find out which phase is dispersed. After the cessation of the agitation, a region of droplets can be seen between the two coalesced regions. One surface of this region is irregular due to the coalescence occurring near it, while the other surface is flat. The phase in which coalescence takes place is the dispersed phase and the phase with the flat surface is the continuous phase. Furthermore the total settling time was lower for 'water continuous' than for 'organic continuous' dispersions. Water continuous dispersions exhibited a 'sparkle' due to the reflection of light from the droplets; in contrast, droplets in an 'organic continuous' dispersion appeared relatively dull and opaque.

After settling the two phases for the system w/o, the upper layer contained a secondary haze. In contrast the system o/w was clear after settling. Secondary droplets were also observed in the line connecting the mixer and the settler and in the settler itself.

A conductivity device with platinum cell was introduced into the mixing vessel. When the system was o/w the conductivity was high, however the conductivity was lower when the system was w/o.

The observation on the settler shows that when 'organic dispersed' droplets moved freely through the phosphoric acid phase they coalesce with each other and with the bulk phase. When organic was dispersed the wedge was above the interface, however it was below the interface when water was dispersed.

Finally, measurements were made of changes in wedge length in the settler at or near phase inversion. Fig. 7.53 shows wedge length versus dispersed phase flow rate near phase inversion. The lines all have maxima which represent the transfer from the system O/W to W/O.

At a point just before phase inversion, very large drops were observed in the line between the mixer and the settler.

Other methods can be used to observe inversion. These are the injection of organic soluble dye, e.g. methyl red or photography of the dispersion when organic drops are larger than aqueous phosphoric acid drops under similar hydrodynamic conditions. The onset of inversion was not restricted to any particular volume within the mixer. It was spontaneous and unlike that in an agitated column it extended throughout the vessel volume and within a few seconds changed the conditions in the settler, such as the formation of spontaneous secondary haze.

Hussain (100) reported in his observations on phase inversion in a multistage operation that there was a well defined time lag between successive stages. This time lag was found to be approximately 55-60 seconds which was due to the time taken by each down stream stage to reach the point of inversion.

With the system w/o the wedge could not be defined, since the upper layer was so cloudy and sometimes did not exist, therefore no measurements were taken.

Figs. 7.54-7.58 show the variation of holdup at inversion with agitator speed at different dispersed and continuous phosphoric acid concentrations.

Fig. 7.59 shows the variation of inversion point with agitator speed for different dispersed and phosphoric acid phase flow rates.

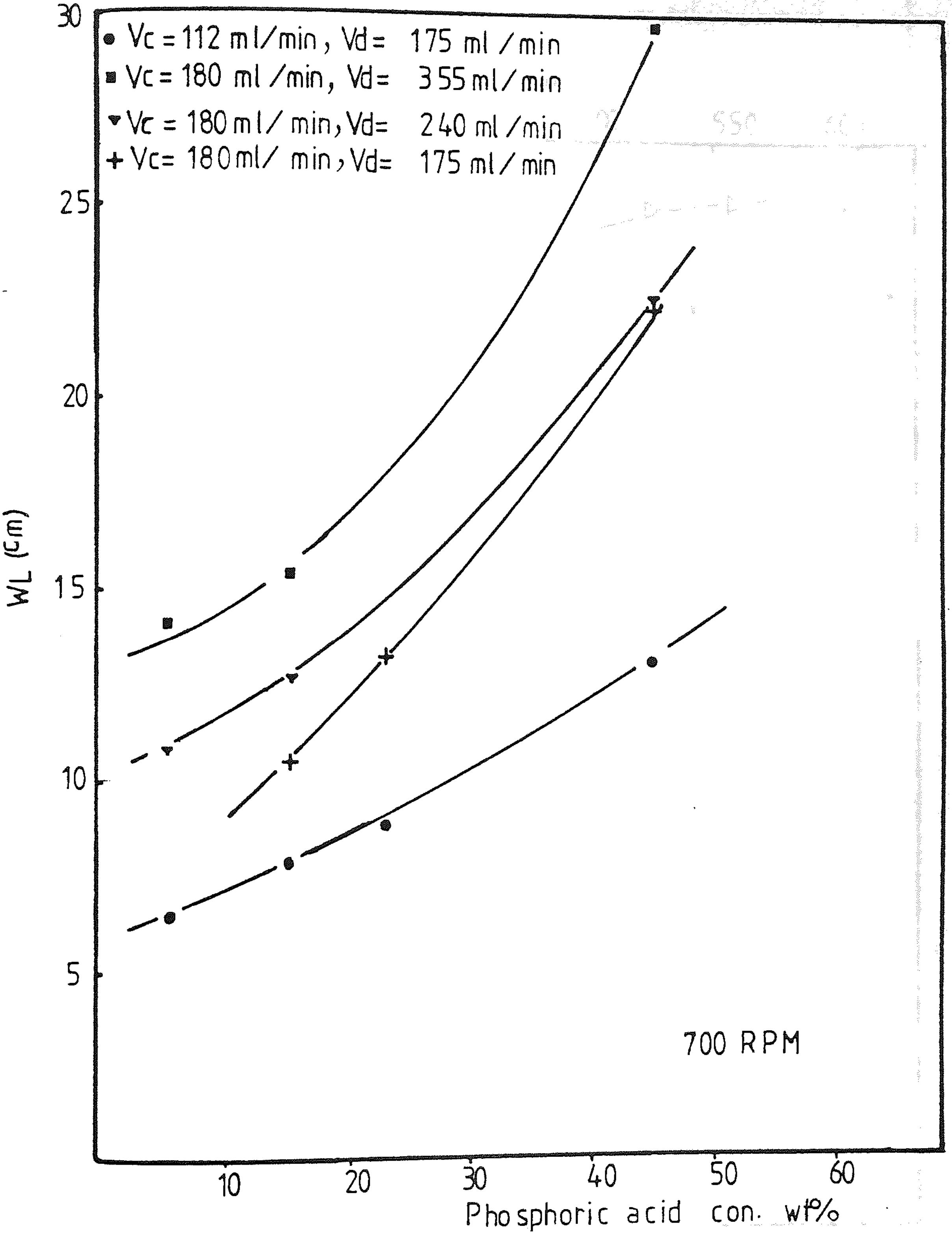


Fig 7.52 Variation of wedge length with acid con.

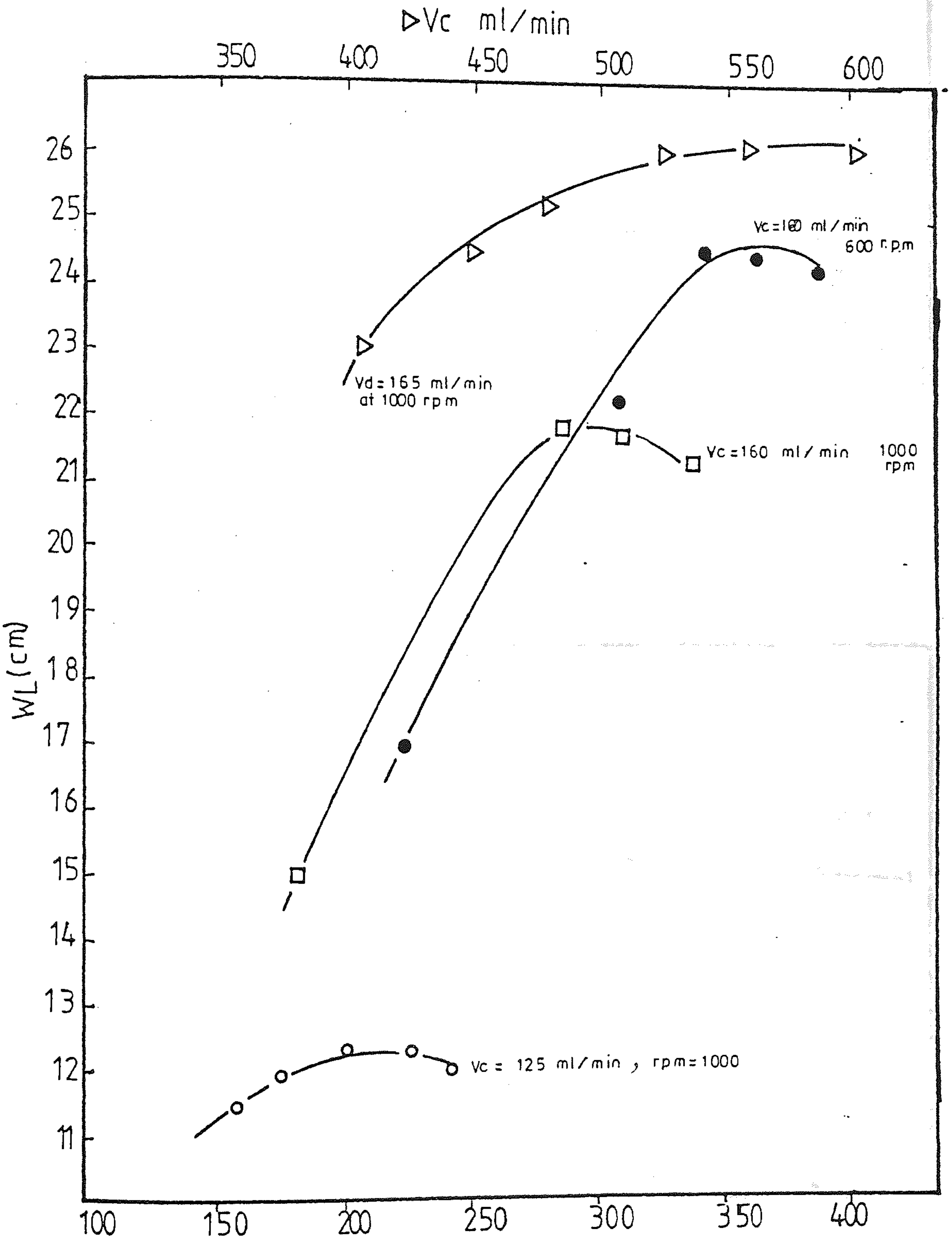


Fig 7.53 Wedge length near point of phase inversion
(44% acid)

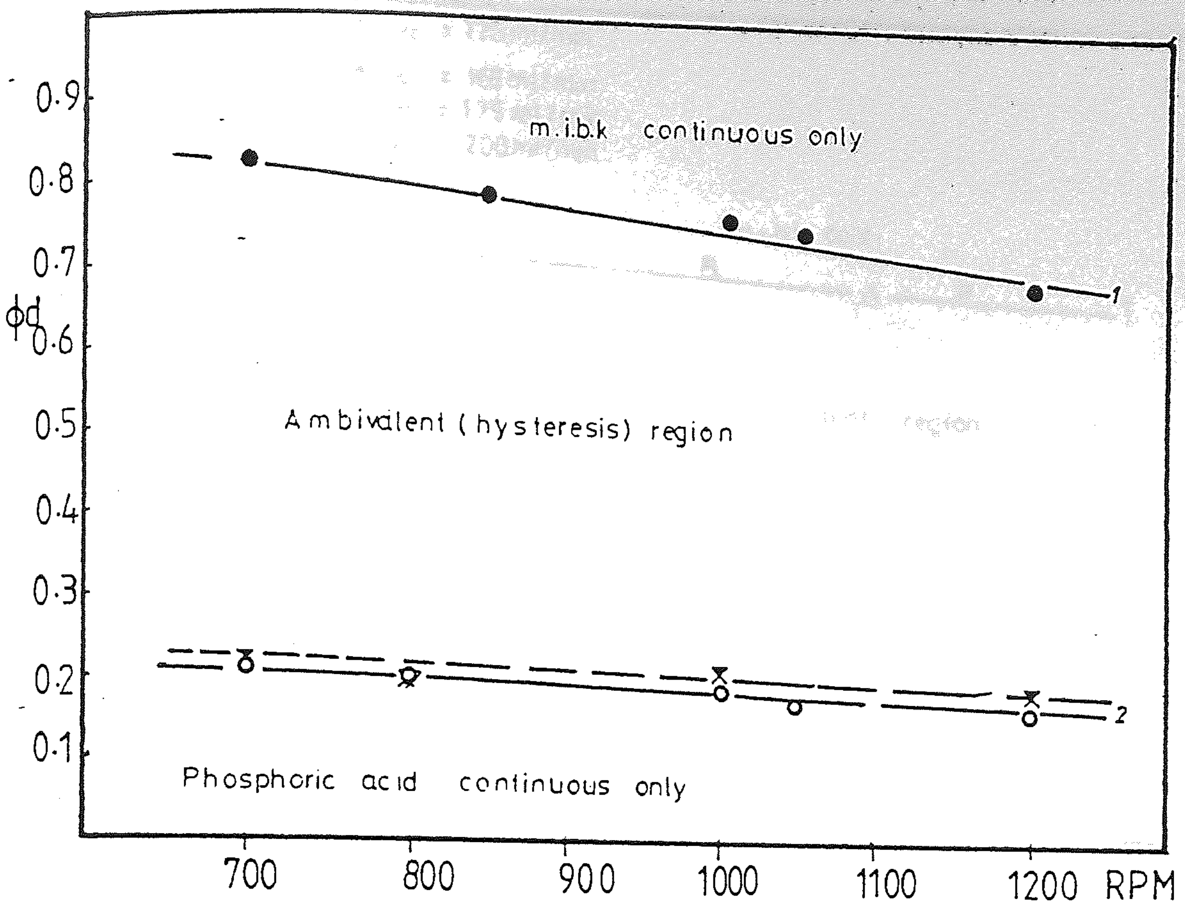


Fig 7.54 Inversion characteristics for the system aq. phosphoric acid (5% wt) - m·i·b·k. 1- inversion from o/w to w/o. 2- inversion from w/o to o/w. x- impeller in organic phase

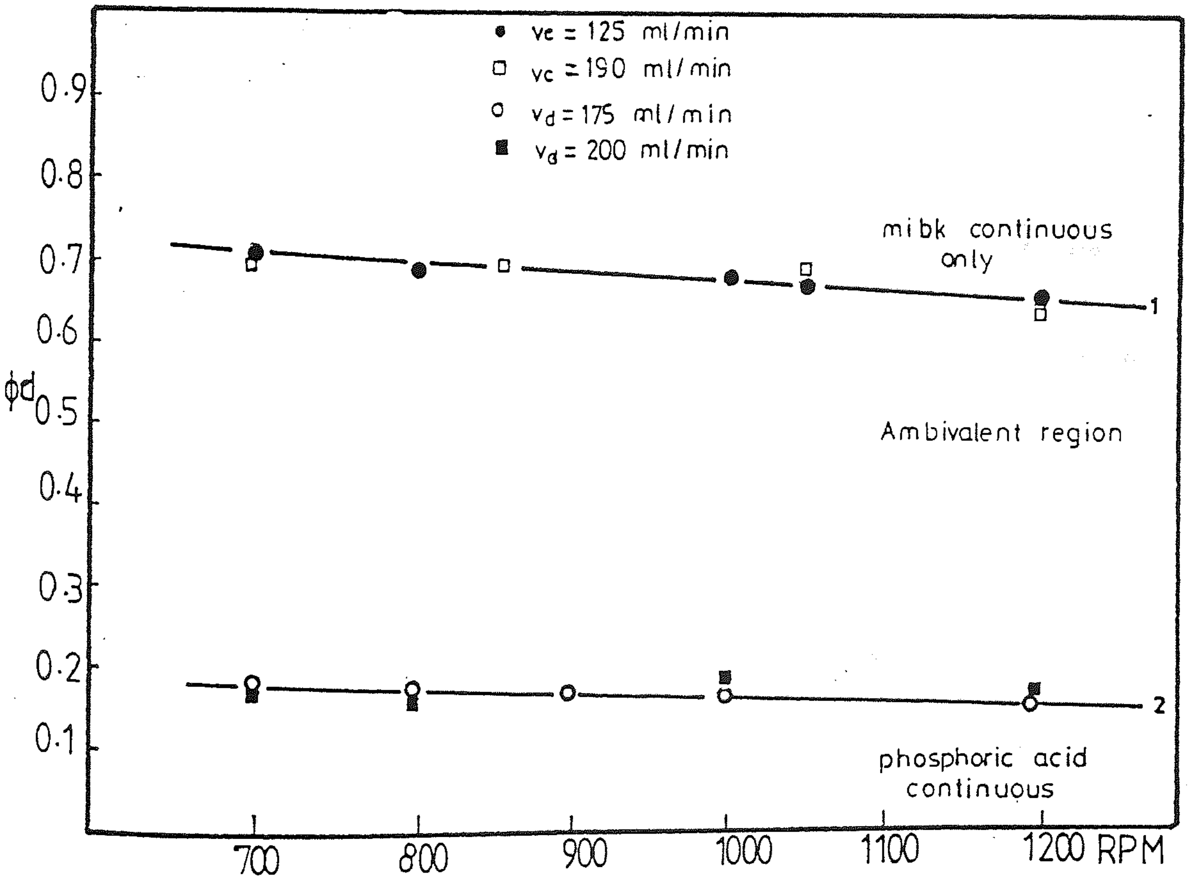


Fig 7.55 Inversion characteristics for the system phosphoric acid (15%)_ mibk

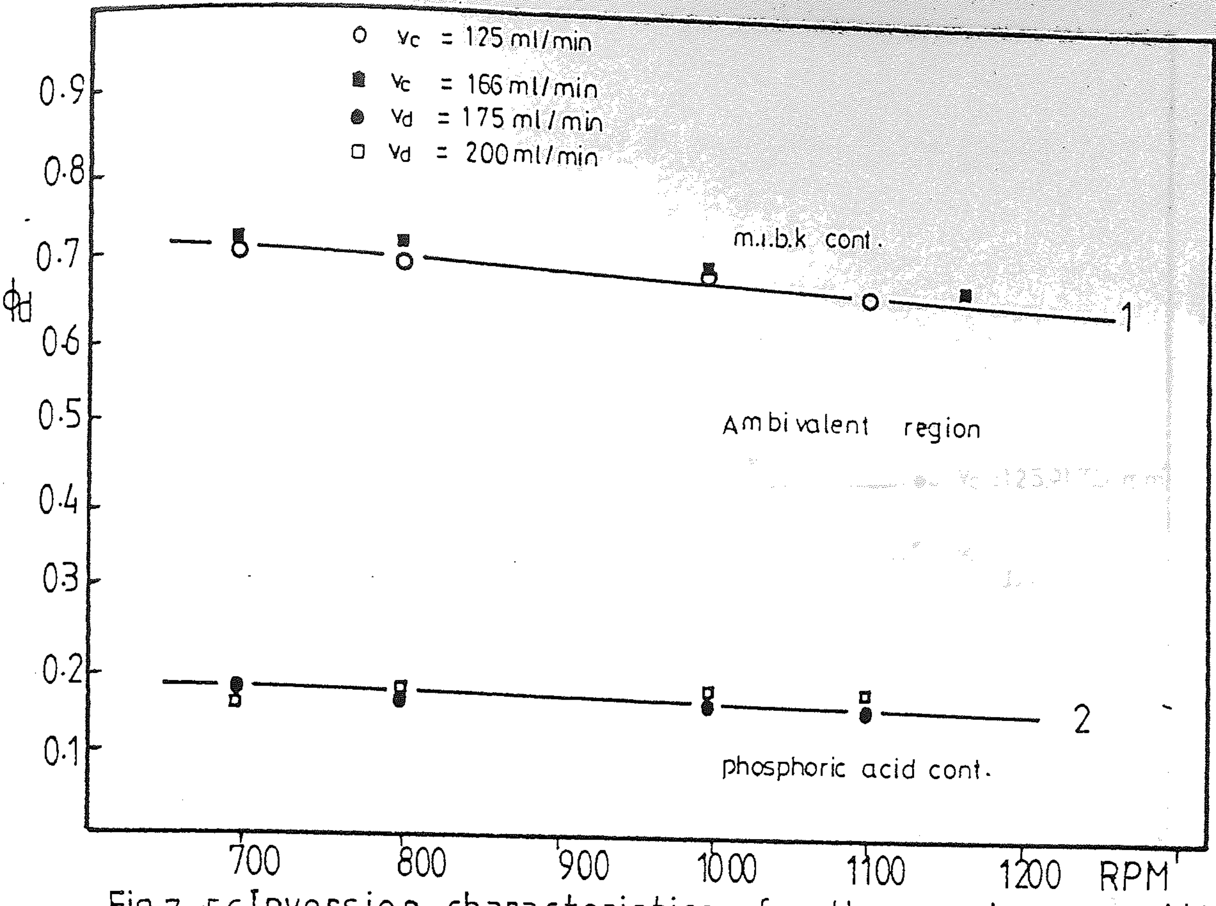


Fig 7.56 Inversion characteristics for the system aq. acid (23%) mibk. 1-inversion from o/w to w/o. 2- inversion from w/o to o/w

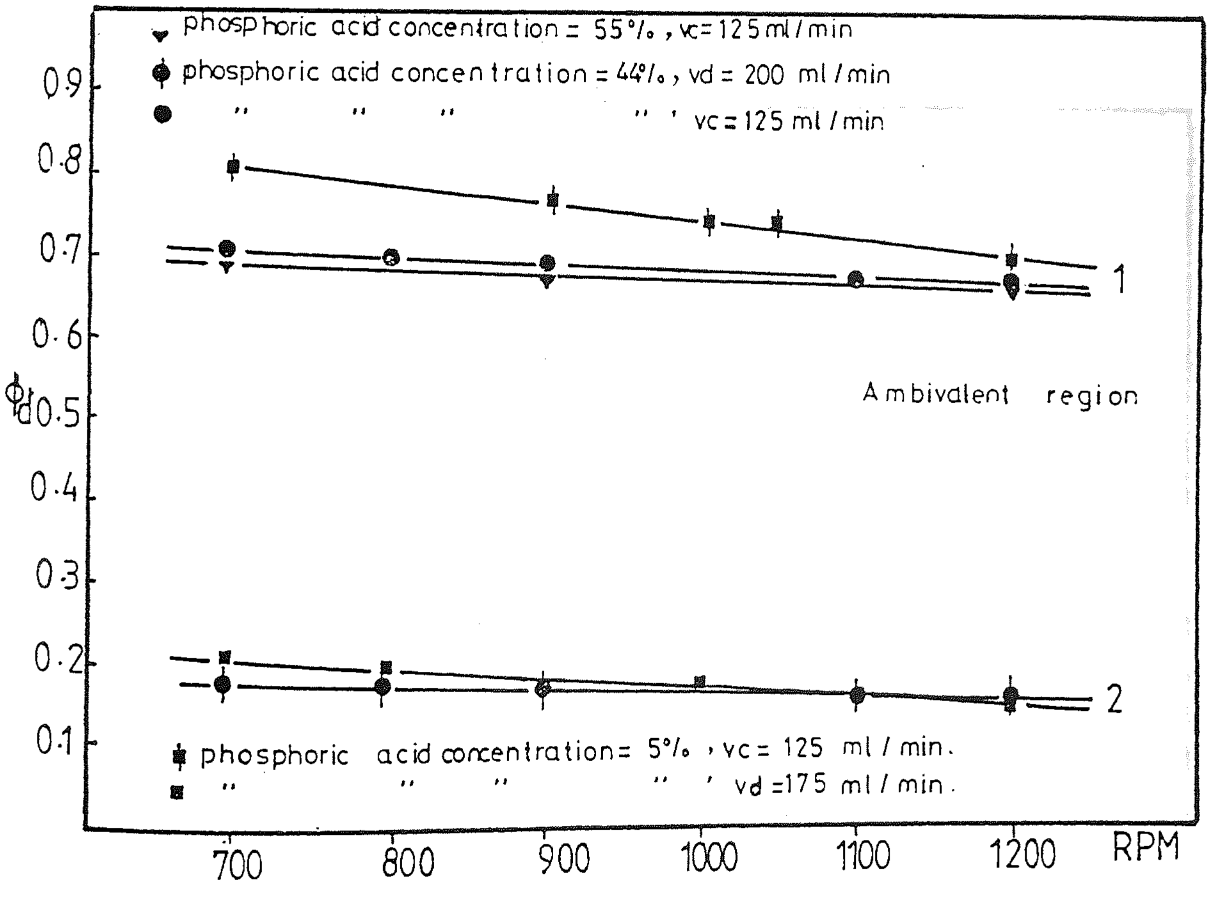


Fig 7.57 Inversion characteristics at differnt acid concentration
1- inversion from o/w to w/o.

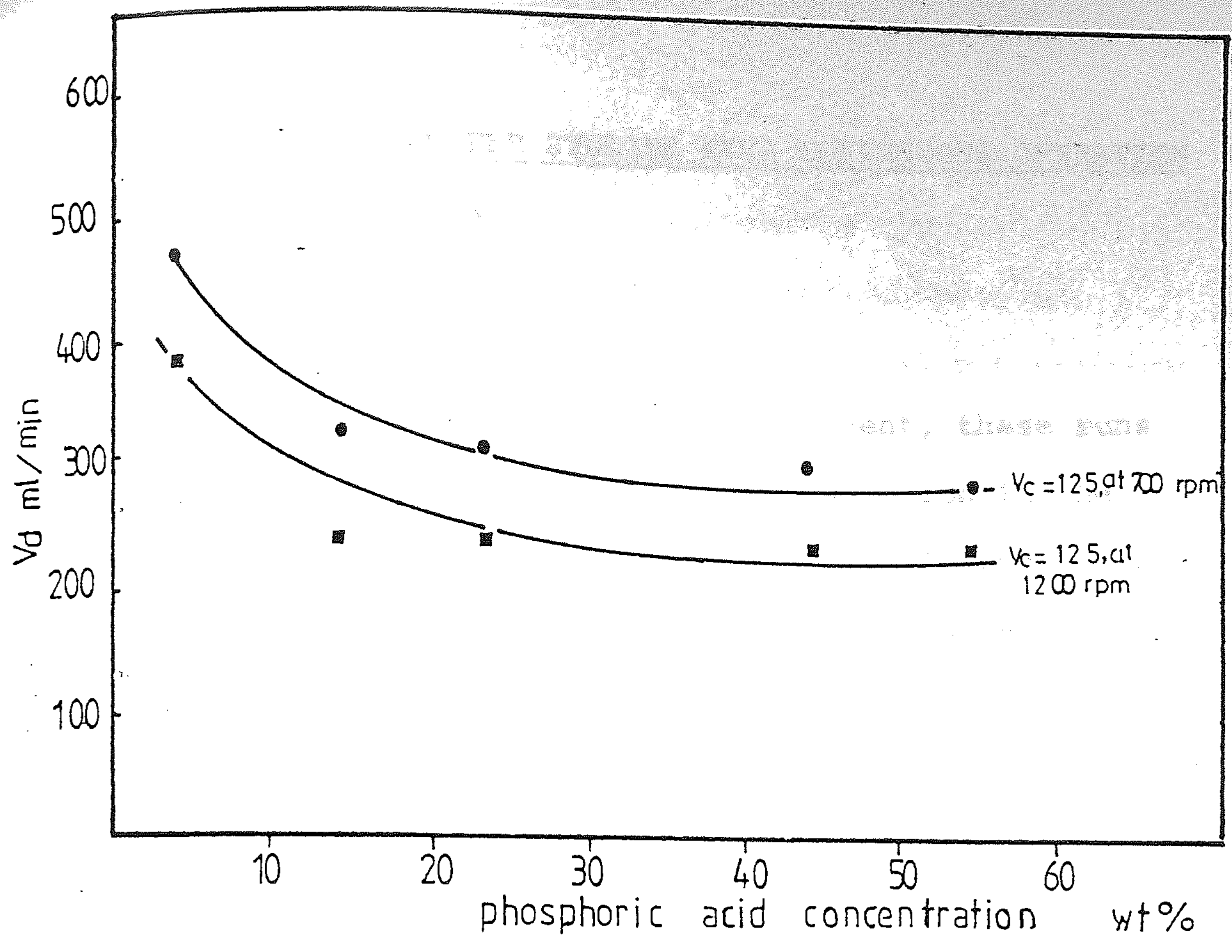
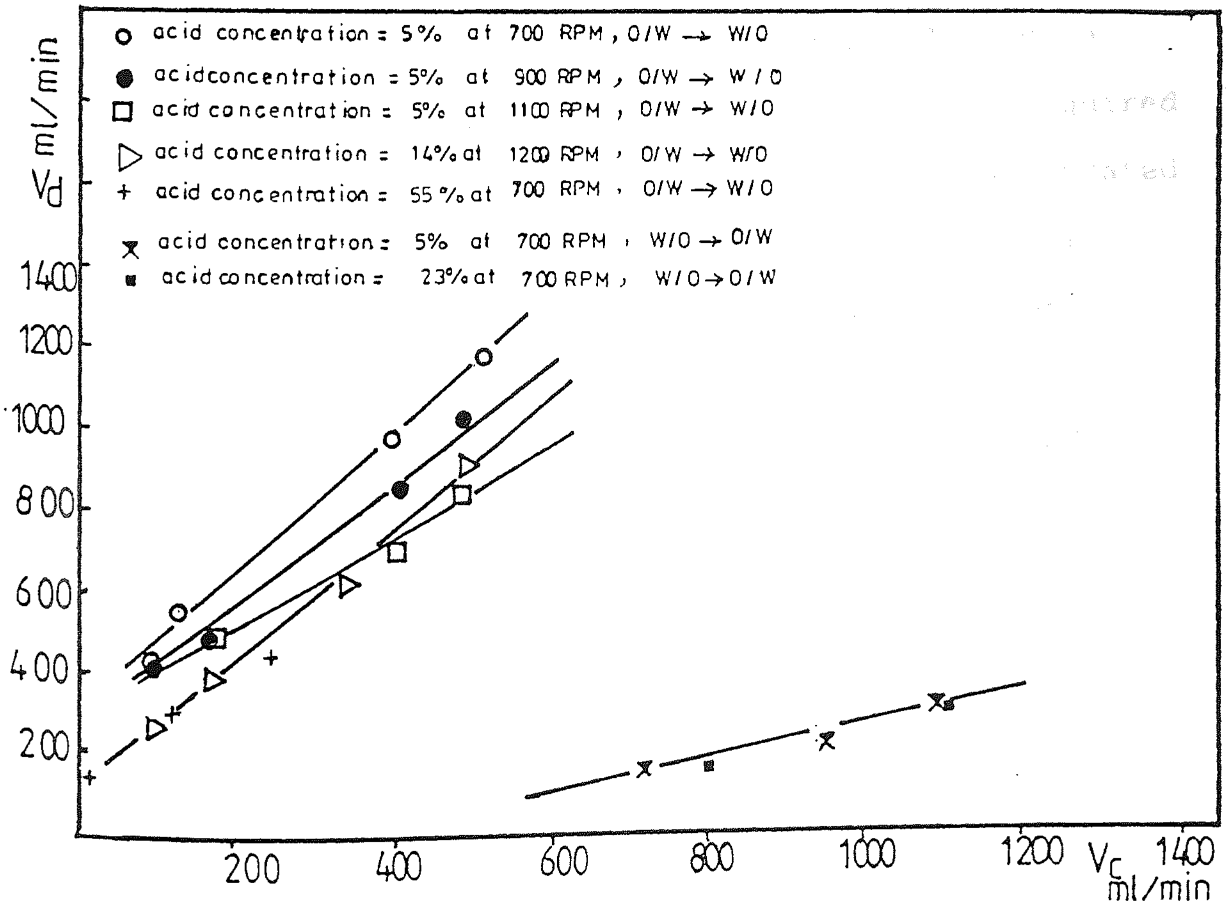


Fig 7.58 effect of acid concentration on dispersed phase flow rate (mibk) at the point of phase inversion.



7.2.2 MASS TRANSFER STUDIES WITH CONTINUOUS OPERATION (SYSTEM O/W)

Forward Extraction of Acid

With MIBK as the extracting solvent, these runs were carried out at high acid concentration in the range 54% to 63%. Below 54% only a small proportion of phosphoric acid was extracted, and at above 63% the settling time of the phases was too high.

In these runs also the initial phosphoric acid concentration in the solvent was reduced to a negligible level by back extracting the acid with water (as will be explained in the following sections). The initial feed phosphoric acid concentration was checked by measuring the physical properties (density and refractive index) as well as by titration with 0.1N NaOH solution. If the initial acid concentration was less than the required value, concentrated acid was added. This procedure was repeated until the required value was obtained. Both phases were pre-equilibrated i.e. MIBK was saturated with water, and phosphoric acid was saturated with fresh solvent. Therefore the system could be treated as two immiscible liquids. Acid was then the only material to be transferred from the aqueous to the organic phase.

Back Extraction of Acid

The same equipment was used to recover the phosphoric acid from the solvent (washing step), leaving the solvent to be recycled. Fresh distilled water was used as a second solvent to recover the acid.

At first three stages were used, however one stage was found to be sufficient for complete recovery. To establish experimentally whether the steady state had been reached closely enough, samples of 20-30cc were taken at 10 minute intervals from the extract and the raffinate of each stage until virtually identical values of acid concentration were obtained. Properties such as the refractive index and pH value were used. However, these were abandoned since the refractive index method gave identical results compared with titration for acid concentration. The pH method was not efficient especially when the extract phase was used. Each sampling point was opened in turn starting from the solvent introduction stage. 5-8 samples were found to be sufficient so a total volume of 100 ml from each stage was taken in each run. At the end of each run, the phase flow was stopped, the stage isolated by closing the interconnecting valves and the agitator switched off. After allowing sufficient time for settling in the mixer, the hold-up was measured by measuring cylinder (1000 ml). Average hold-up of the three stages was taken as the dispersed phase holdup ϕ_d. See Figs. (7.60-7.63) for sample holdup per stage and average holdup versus the speed of agitation.

Sample graphs for the concentration of phosphoric acid and impurities in both extract and raffinate layers from each stage for pure and impure systems are shown in Figs. (7.64-7.65) and Appendix (5). Fig. 7.66 shows impurity concentration profiles along the contactor, Fig. 7.67 shows impurity concentration as a function of acid concentration.

7.2.2.1 EFFICIENCY OF THE EQUIPMENT

The overall efficiency ζ_o was calculated as the number of ideal to real stages required to accomplish the concentration change. The ideal number of stages was obtained using a McCabe-Thiele diagram. Fig. (7.68) shows that the efficiency of the cascade increased with the power input for both pure and impure systems and decreased at high acid concentration as shown in Fig. (7.69).

7.2.2.2 TIME TO REACH STEADY STATE

The effect of impeller speed, stage position, feed to solvent flow ratio and acid concentration, on time to reach steady state are shown in Figs. (7.70-7.73) respectively. The figures show that the time required for the cascade to reach steady state decreased with the power input and increased with phase ratio of phosphoric acid to solvent (F/S). Fig. 7.71 shows that the solvent inlet stage reached steady state before the phosphoric acid inlet stage.

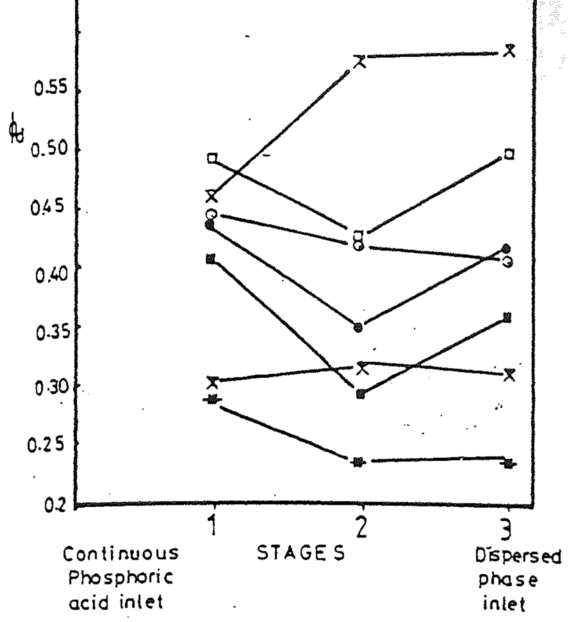


Fig7.60 Hold-up profiles along contactor for pure system

- ○ 500 rpm,v.phase ratio = 1:1
- ● 700 rpm,v.phase ratio = 1:1
- ■ 900 rpm,v.phase ratio = 1:1
- □ 500 rpm,v.phase ratio = 1:2
- X 900 rpm,v.phase ratio = 1:2
- X 900 rpm,v.phase ratio = 2:1
- -■- 900 rpm,v.phase ratio = 3:1

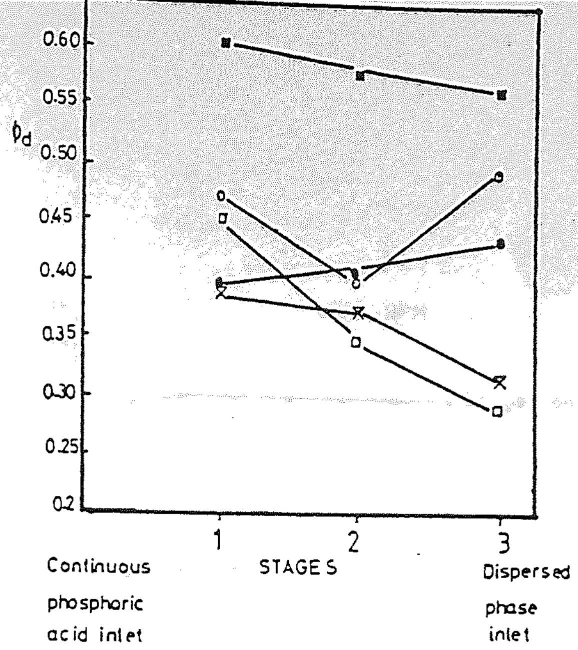


Fig7.61 Hold_up profiles along contactor for impure system (Fe^{+})

- ○ 500 rpm,v.phase ratio = 1:1
- ● 700 rpm,v.phase ratio = 1:1
- ■ 500 rpm,v.phase ratio = 1:2
- □ 900 rpm,v.phase ratio = 2:1
- X 900 rpm,v.phase ratio = 3:1

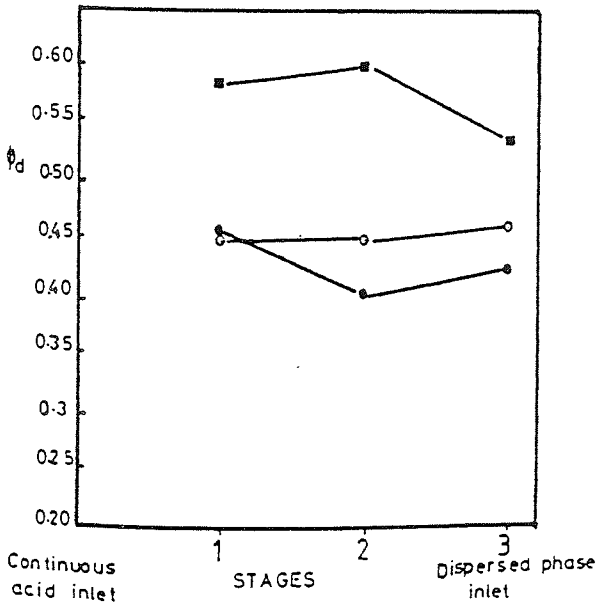


Fig 7.62 Hold-up profiles along contactor for impure(Mg) system

- ○ 500 rpm, v.phase ratio = 1:1
- ● 700 " " " "
- ■ 500 " " " ~ 1:2

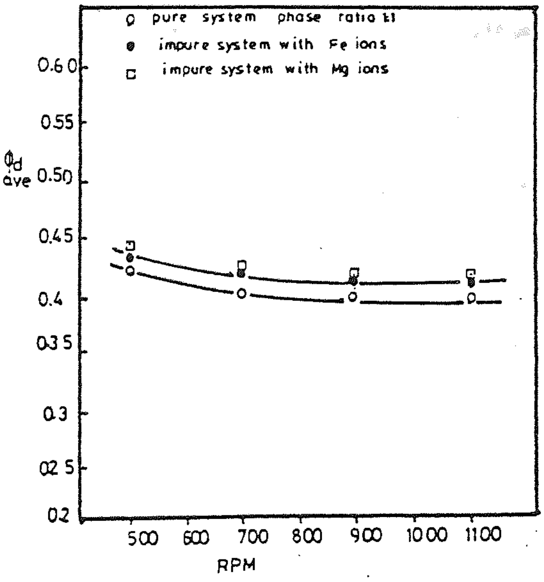


Fig7.63 average hold_up of contactor vs powe input

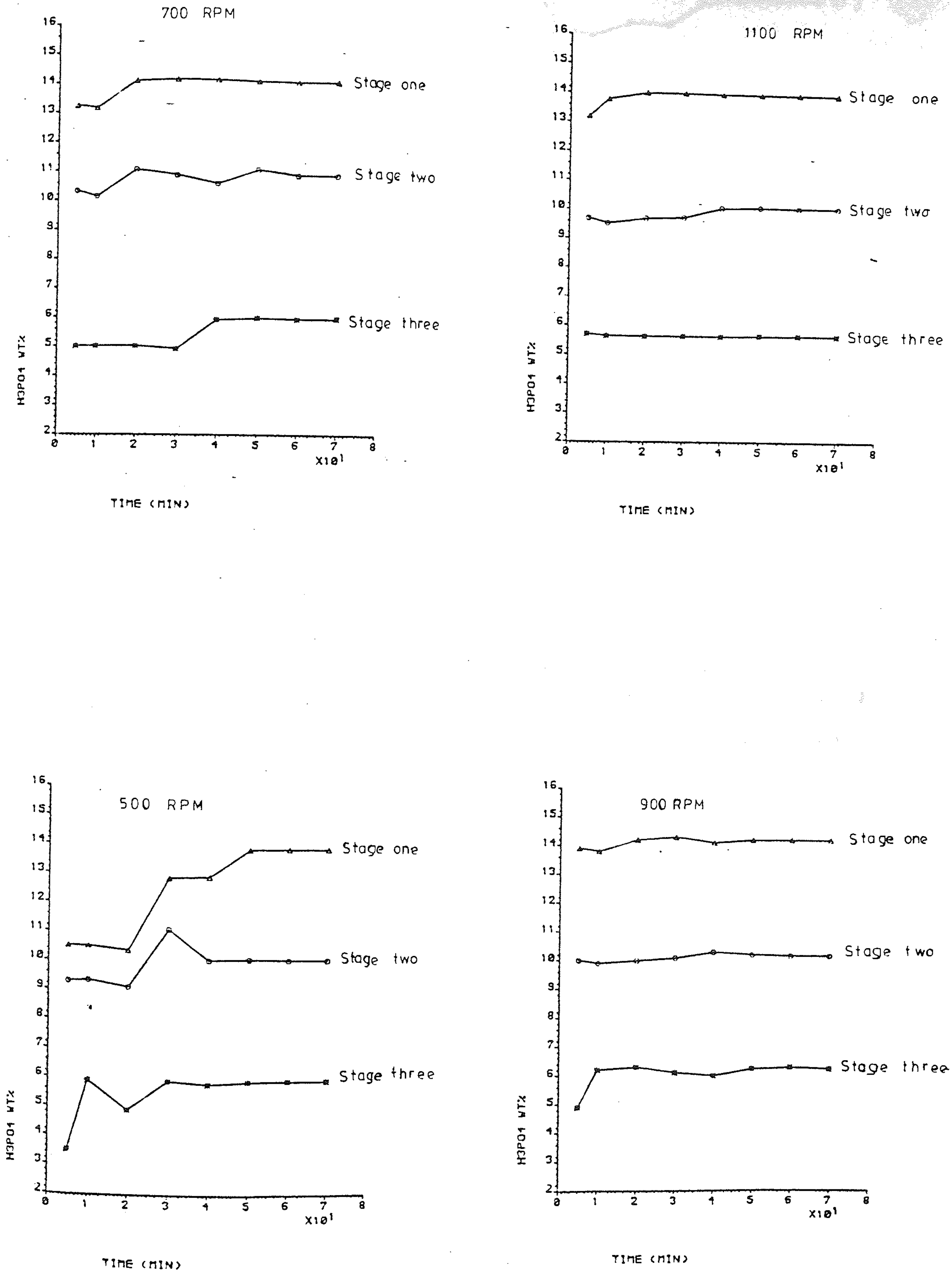
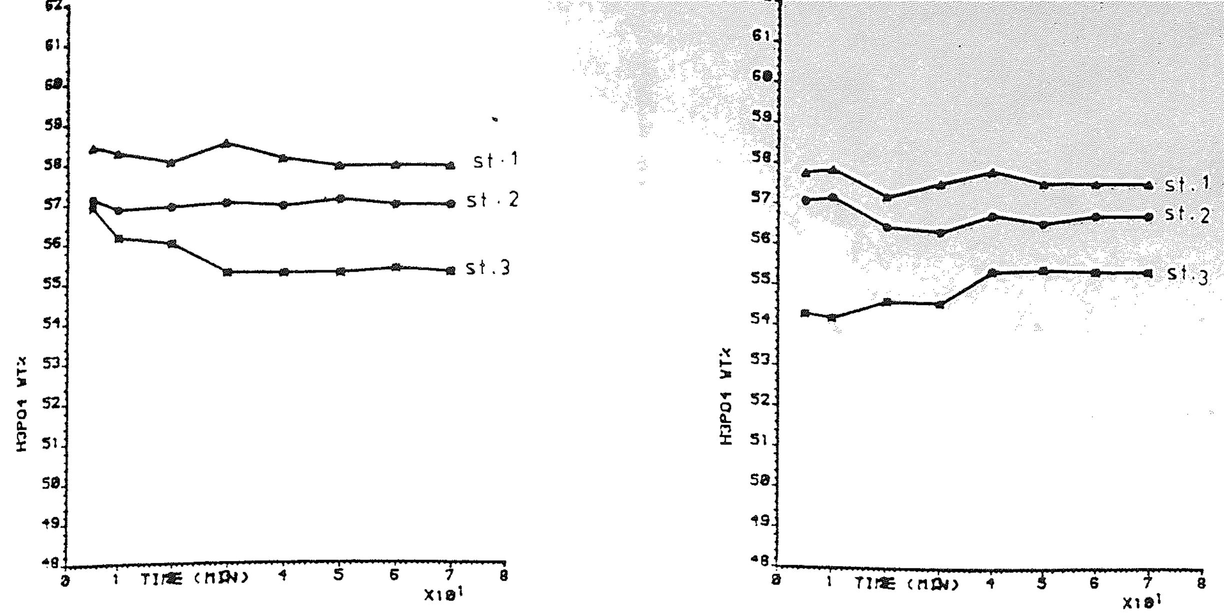


Fig 7.64 Steady state of extract at a differnt rotor speeds



700 RPM

1100 RPM

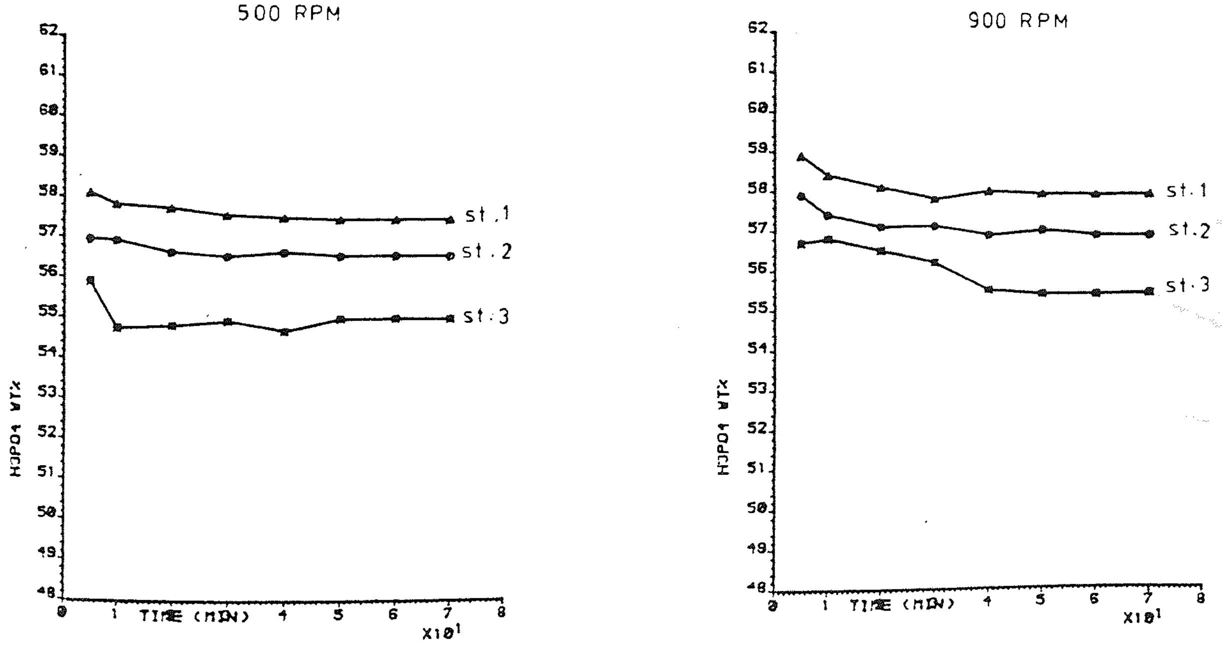


Fig 7.65 Concentration time curves for impure (Fe) system of the raffinate phase, phase ratio = 1:1

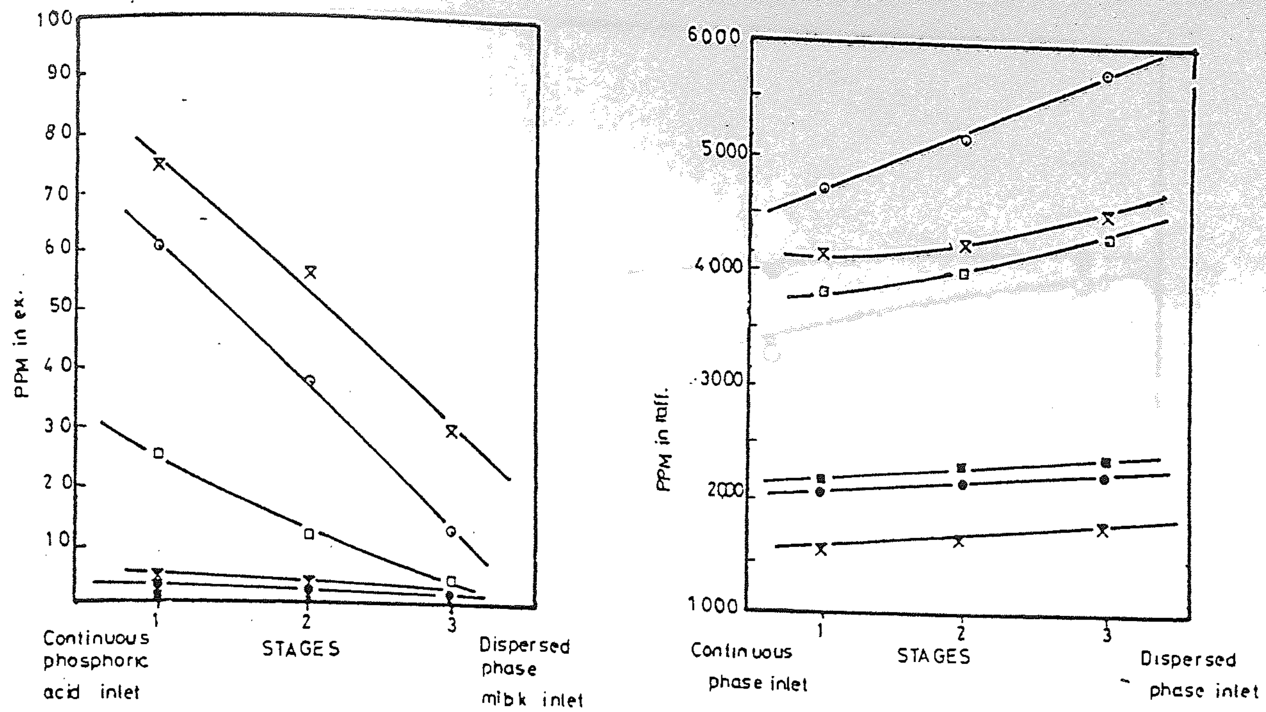


Fig 7.66 impurities concentration profiles along the contactor . 900 rpm

○ phase ratio 1:1 acid con. 589 (Fe).
● phase ratio 1:1 acid con. 58.9 (Mg).
□ phase ratio 1:2 acid con. 58.9 (Fe).
■ " " " " " " (Mg)
⧖ phase ratio 2:1 " " " (Fe)
✕

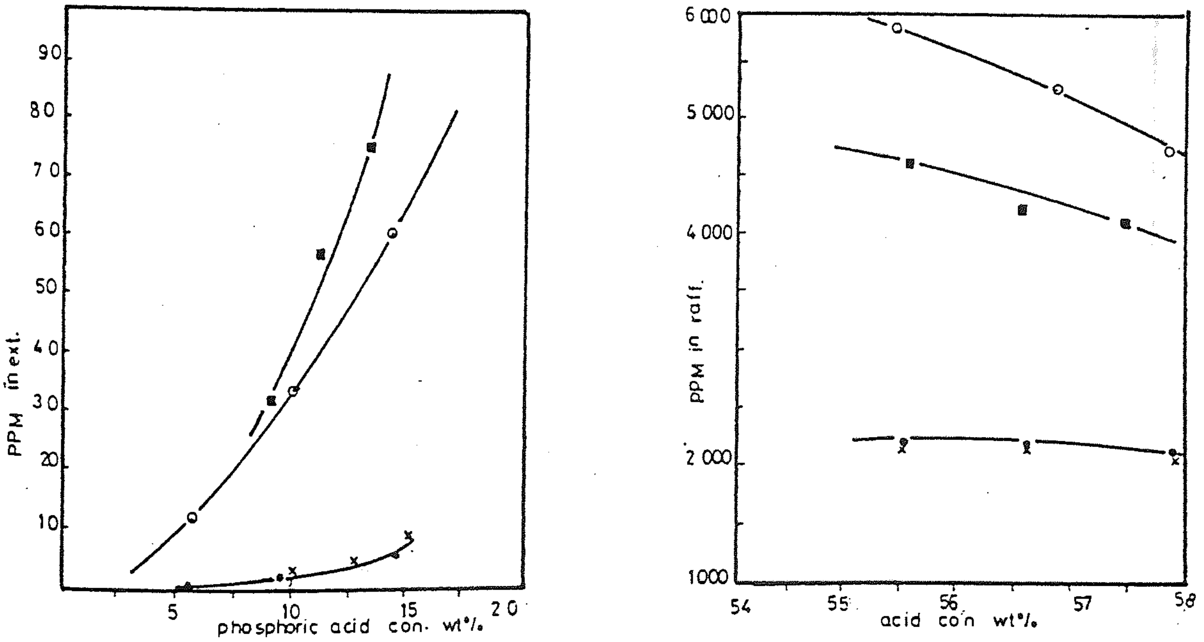


Fig 7.67 Impurities concentration vs phosphoric acid con. along the contactor at 900 rpm, I_o = 589%.

○ Fe phase ratio 1:1
• Mg " " "
■ Fe phase ratio 2:1
× Mg " " 3:1

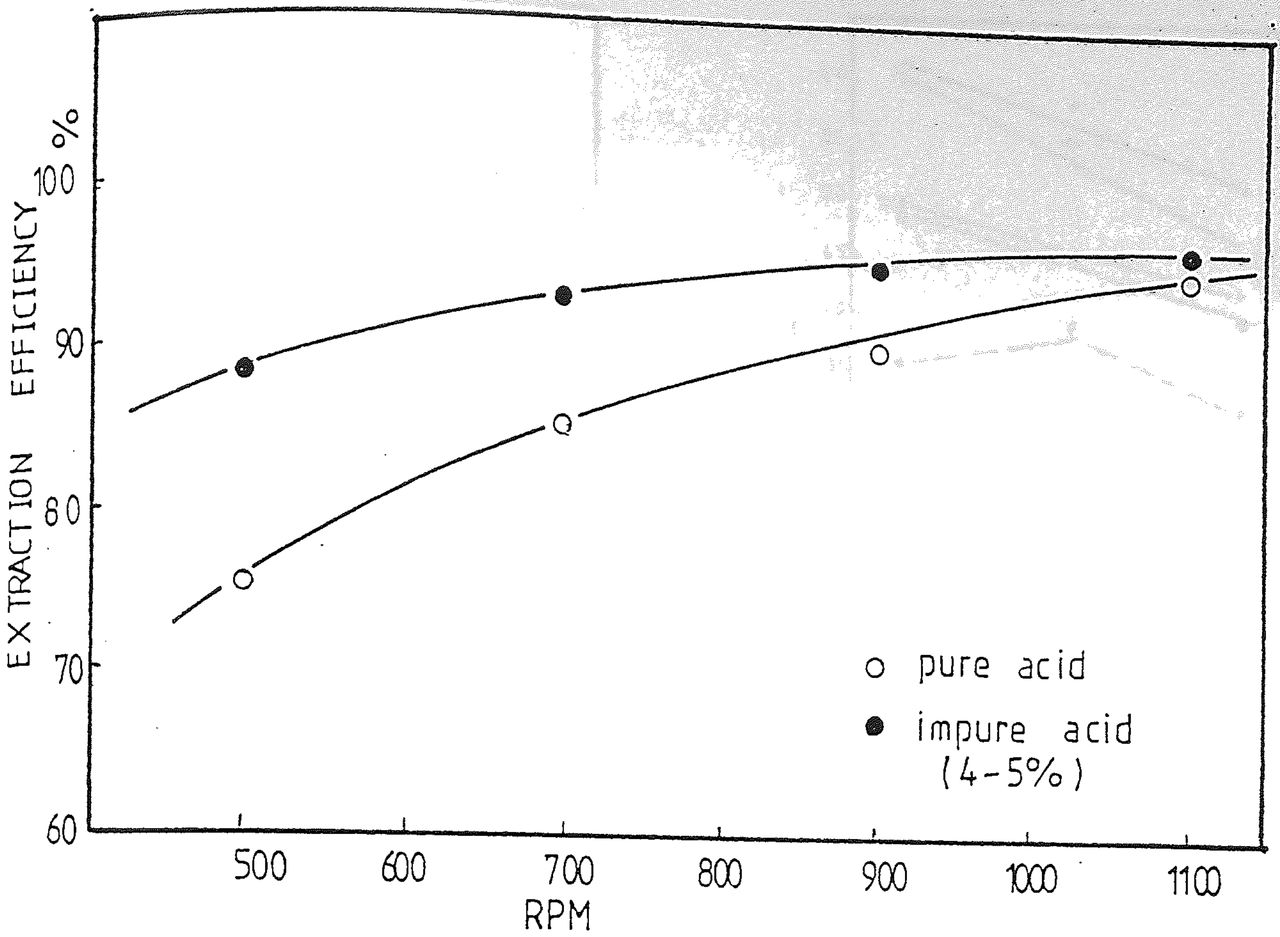
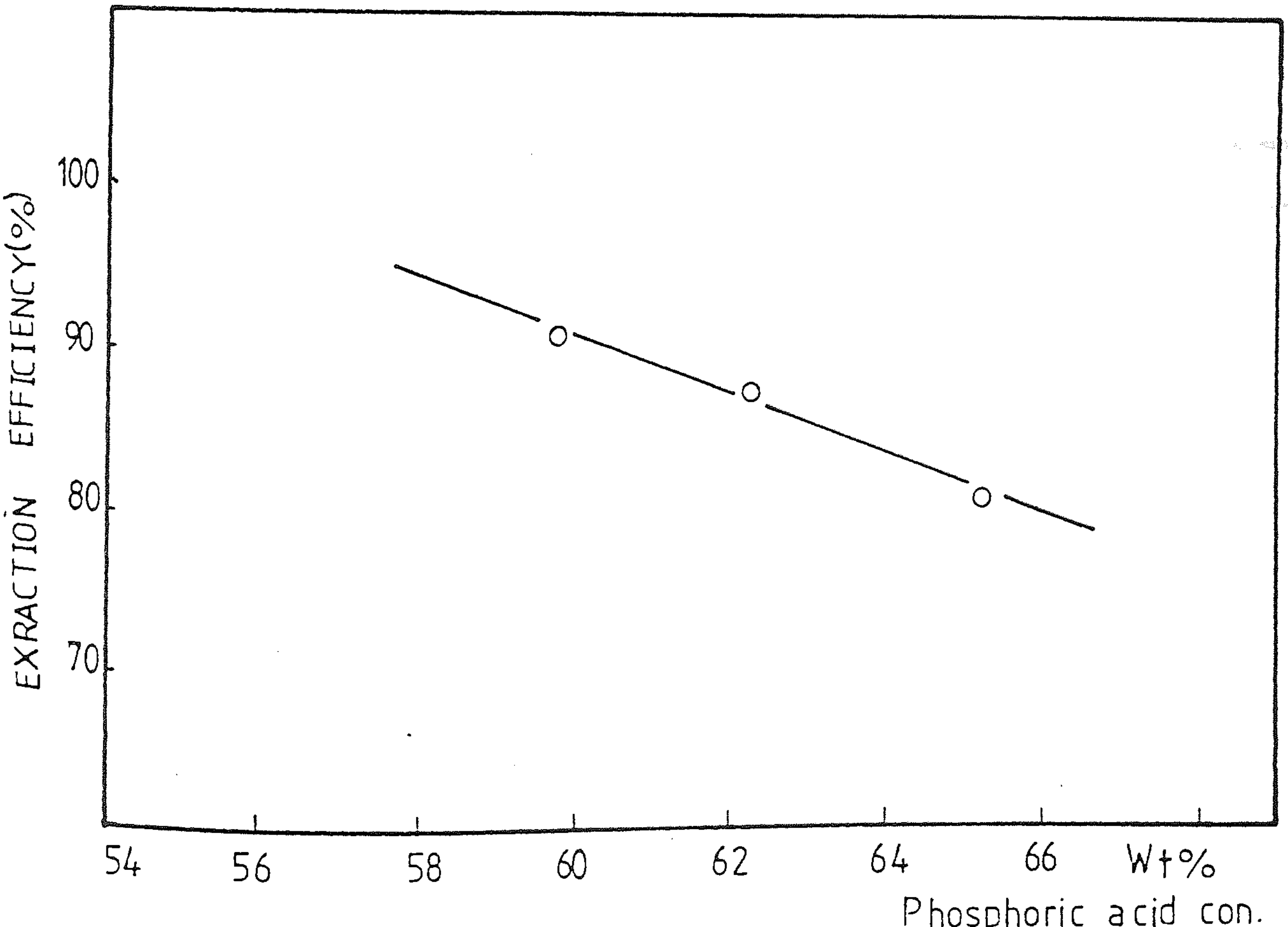


Fig 7.68 Extraction efficiency versus impeller speed system phosphoric acid (58.9) – water – mibk. (o/w) Vd = Vc 177 ml/min



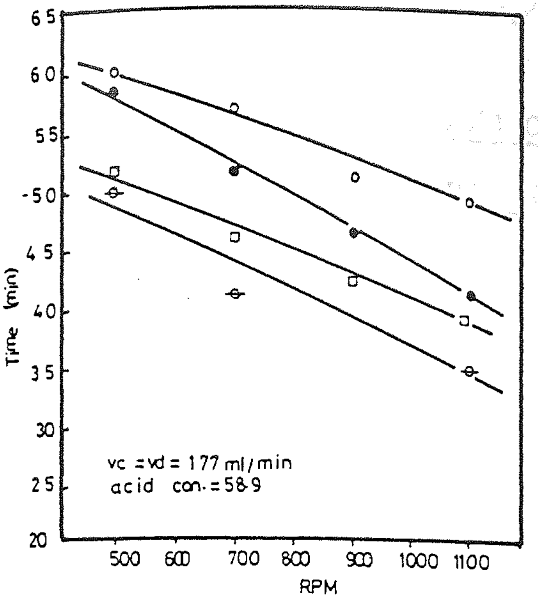


Fig 7.70 Time to reach steady state vs RPM

○ pure system stage 1, v.phase ratio 1:1
● pure system stage 2, v.phase ratio 1:1
□ pure system stage 3, v.phase ratio 1:1
-o- impure system stage 1, v phase ratio 1:1

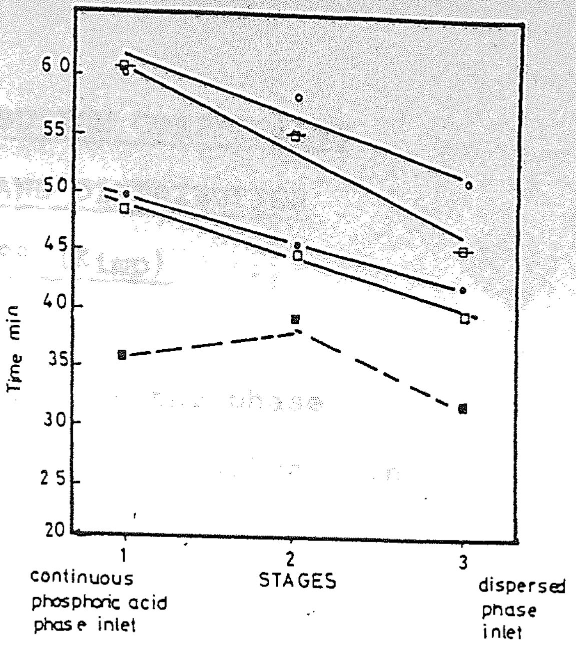


Fig 7.71 Time to reach steady state vs stage no.

○ pure system, 500 rpm, acid con. = 58.9%
● impure system, 500 rpm, acid con. = 58.9%
□ Pure system, 1100 rpm, acid con. = 58.9%
■ impure system 1100 rpm, acid con. = 58.9%
-□- impure system 900 rpm, acid con. = 66.5%

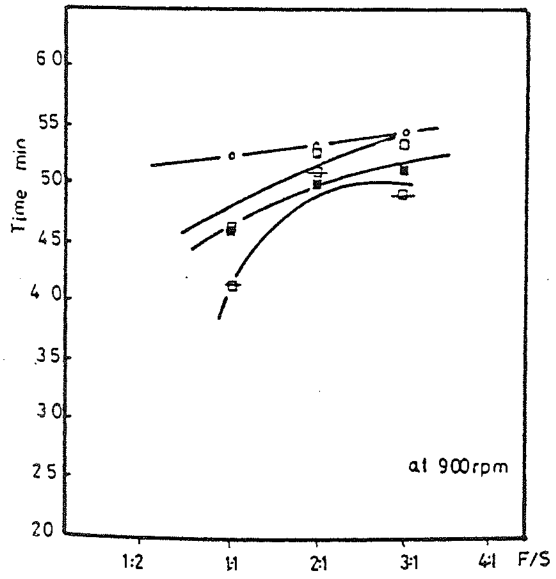


Fig 7.72 Time to reach steady state vs F/S

○ stage one pure system.
□ stage two pure system.
□ stage one impure system.
□ stage three impure system.

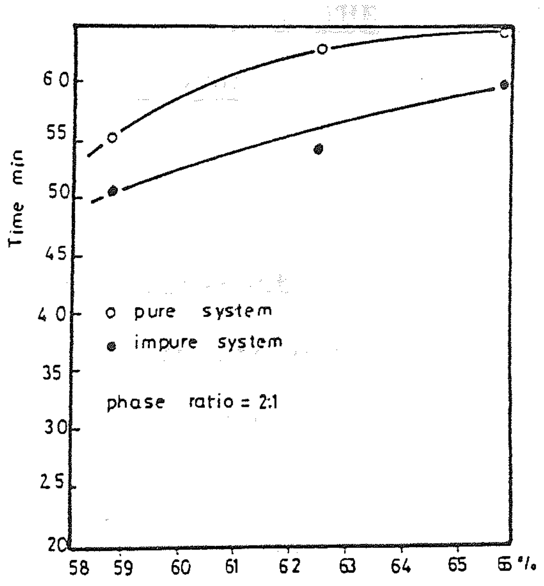


Fig 7.73 Time to reach steady state vs phosphoric acid conc. at 900 rpm

7.2.2.3 EFFECT OF F/S ON DISTRIBUTION COEFFICIENT OF PHOSPHORIC ($K_{H_3PO_4}$) AND DISTRIBUTION COEFFICIENT OF IMPURITIES (K_{imp})

Figs. (7.74 and 7.75) show that as the phase ratio of phosphoric acid to the extracting solvent in the extraction step (F/S) increased, the distribution coefficient of phosphoric acid and impurities (Fe and Mg) increased. This indicates that the K_{imp} is function of $K_{H_3PO_4}$.

7.2.2.4 EFFECT OF AGITATOR SPEED ON $K_{H_3PO_4}$ AND K_{imp}

Figs. (7.76 and 7.77) show that agitator speed had little effect on the distribution coefficient of acid and impurities for both pure and impure systems.

7.2.2.5 EFFECT OF INITIAL ACID CONCENTRATION ON THE DISTRIBUTION COEFFICIENT OF ACID AND IMPURITIES

Experiments were carried out with different initial concentrations, and the results are presented in Figs. 7.78 and 7.79. As initial acid concentration increased, the impurity distribution coefficients (K_{imp}) and phosphoric acid distribution coefficient ($K_{H_3PO_4}$) increased.

7.2.2.6 EFFECT OF FLOWRATE ON K_{imp} AND $K_{H_3PO_4}$

In these sets of experiments, acid (59.9%) containing both impurities (Fe^{+++} and Mg^{++} ions) was used. Experiments were carried out with different flow rates; the results are presented in Figs. 7.80 and 7.81.

7.2.2.7 EFFECT OF PHOSPHORIC ACID CONCENTRATION IN THE SOLVENT, ON THE CONCENTRATION OF THE FINAL PRODUCT IN THE WASHING STEP

Fig. 7.82 shows that as acid concentration in the feed solvent for the washing step increased the final acid concentration in the aqueous phase also increased.

7.2.2.8 EFFECT OF SOLVENT/WATER RATIO ON THE CONCENTRATION OF THE FINAL PRODUCT

Fig. 7.83 shows that the final acid concentration in the washing step increased with the solvent/water ratio.

The impurity concentration in the product also increased with solvent/water ratio as shown in Fig. 7.85 and with the initial impurity concentration in the feed solvent as shown in Fig. 7.86.

The effect of recovering the solvent with different acid concentrations on the final purity of the product is shown in Fig. 7.87. Within the acid concentration range studied the recovering aqueous phase has little effect on the purity of the final product.

Fig. 7.84 shows that the extraction factor increased as feed to solvent ratio in the extraction step increased.

7.3 CONCENTRATION OF ACID

Acid concentration was carried out in the equipment described in Section (6.3.2). An electric immersion heater was first used but it caused uneven heating. Samples were collected in time intervals ranging from 0 to 13 hours. The maximum acid concentration was 88 wt %.. The results of the concentration step are shown in Figs. 7.88 and 7.89.

Figs. 7.88-7.89 show, as expected, that the boiling temperature of the acid in the boiler increased with the time and with the concentration of the acid. Impurities concentration will also be expected to increase with acid concentration and time.

7.4 CONTINUOUS STUDIES (FORWARD EXTRACTION SYSTEM W/O)

Only a few experiments were carried out for the system W/O. The system was characterised by the formation of secondary haze which normally caused flooding due to the high percentage of entrainment. During the experiments it was observed that almost all of the feed acid was entrained by the solvent.

A trial was made to reduce the entrainment of secondary drops by including coalescence aids. Different meshes with different sizes were tried. Table 7.1 shows the observed results. The mesh used in this study was treated before it was used. It was cleaned with hot water and left overnight in Decon solution.

The speed of agitation had little effect on the entrainment of phosphoric acid in the organic phase. For instance the entrainment was 14.6% at 600 r.p.m. while it was 16% at 800 r.p.m. No more experiments or investigations were carried out under different rotor speeds. It was also observed that the first and middle stage entrained more acid than the final stage where the solvent was introduced.

	Mesh Size	Material	Pressure Drop	Average Entrainment and Observations
in the line connected the mixer settler	3 mm	fibre glass	very small	very high, approx.30% with very little improvement
	2 mm	stainless steel	very small	very high, approx.30% with very little improvement
	three layers of 1mm size	stainless steel and polypropylene	medium	high about 25%
	0.25 mm	fibre glass	very high	20% entrainment
	packing made of stainless steel and polypropylene mesh placed inside the settler about 3 cm away from inlet. Thickness of layer = 3 cm		almost no pressure drop	average entrainment is 15% (improved)
	thickness of packing = 7cm which occupied ¼ of the settler length		almost no pressure drop	average entrainment = 13% improved

TABLE 7.1 - SIZE AND MATERIAL OF MESH USED TO IMPROVE COALESCENCE OF THE SYSTEM (W/O)

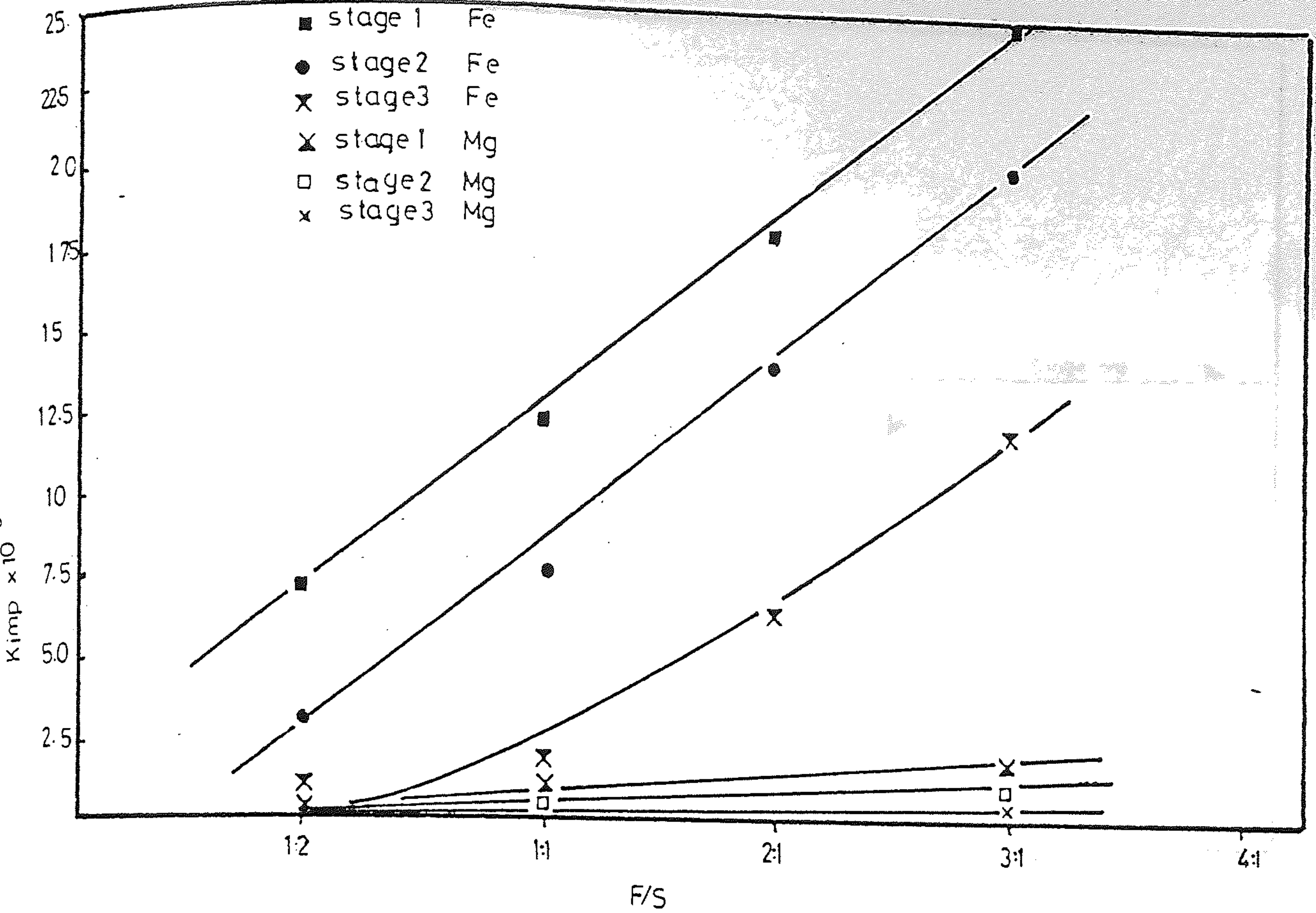


Fig 7.74 phase ratio (phosphoric acid / mibk) vs impurities distribution coeff. at intial acid con. = 58.9% Intial impuities con. = 4 _ 6%

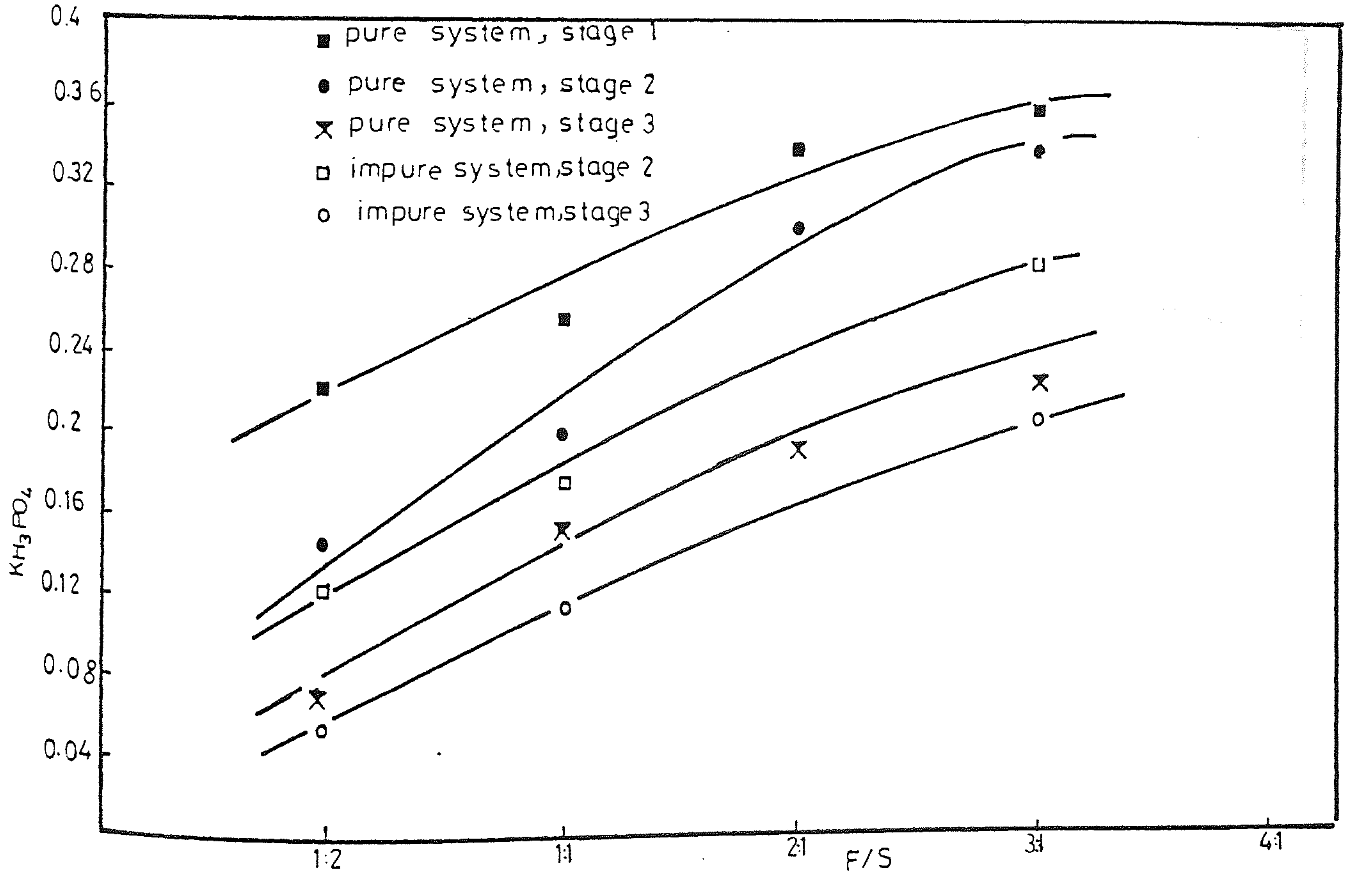


Fig 7.75 phase ratio vs phosphoric acid distribution coeff, with intial

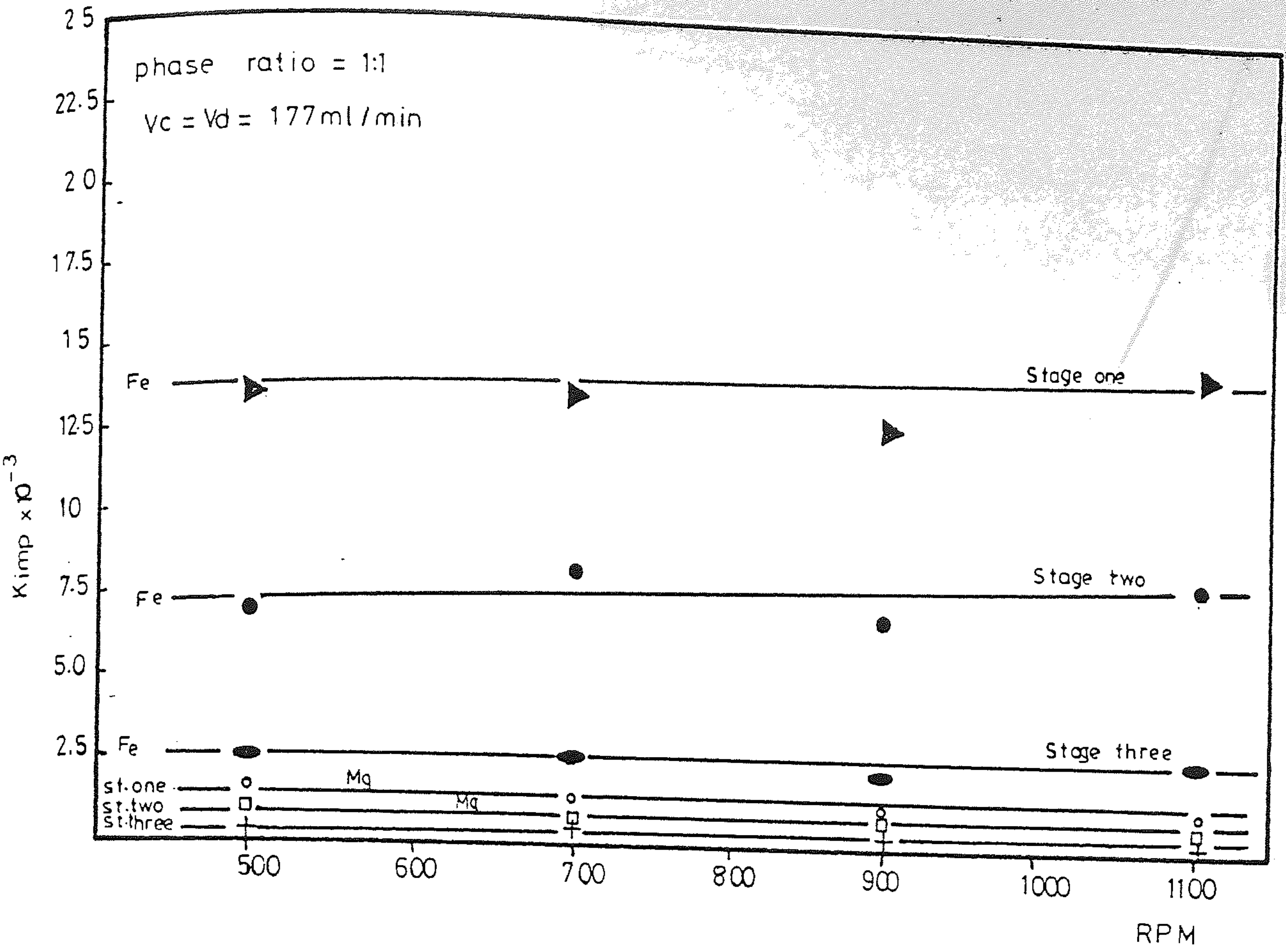


Fig 7.76 impurities distribution coeff. vs rpm
system mibk-water- phosphoric acid 58.9%

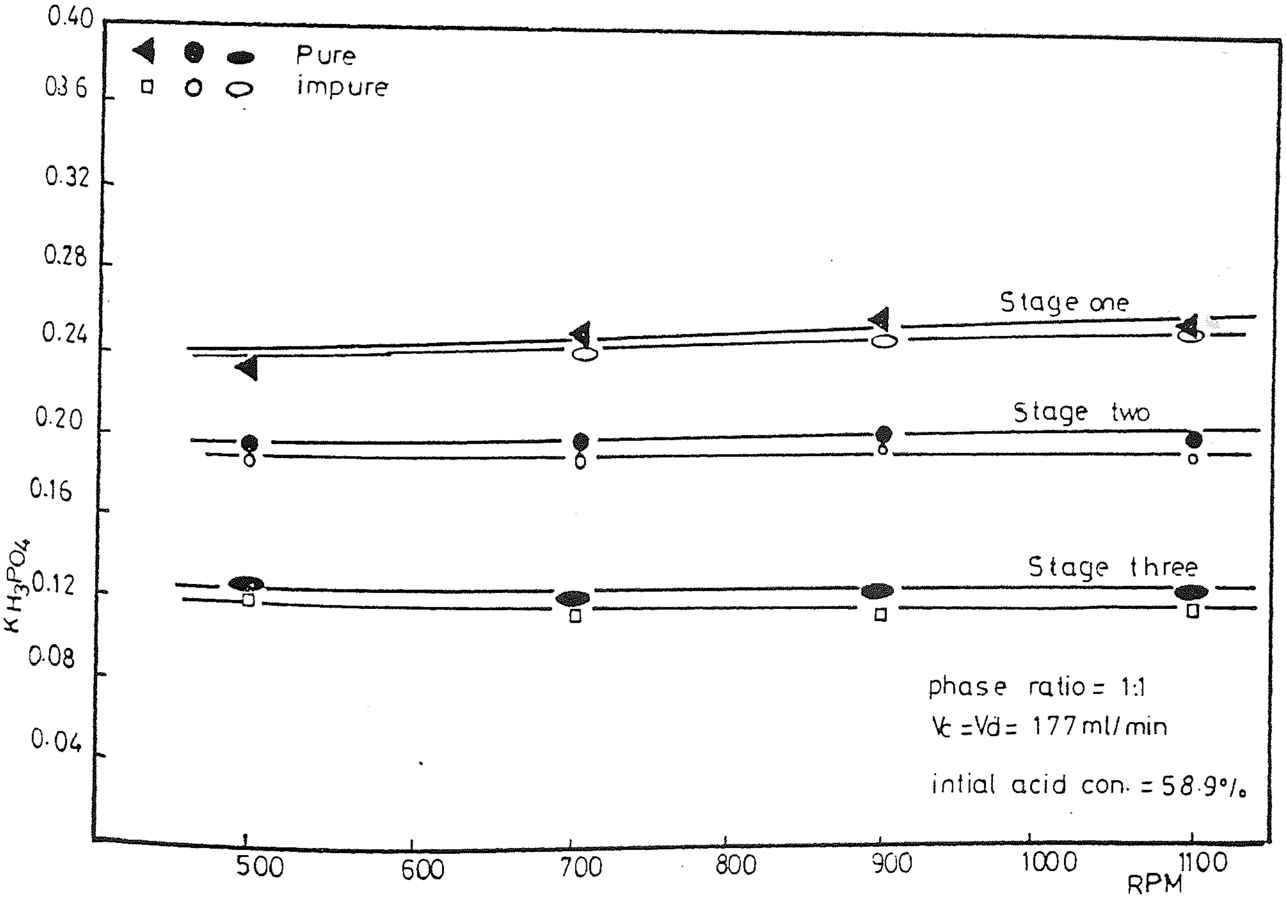


Fig 7.77 distribution coeff. of phosphoric acid vs rpm.

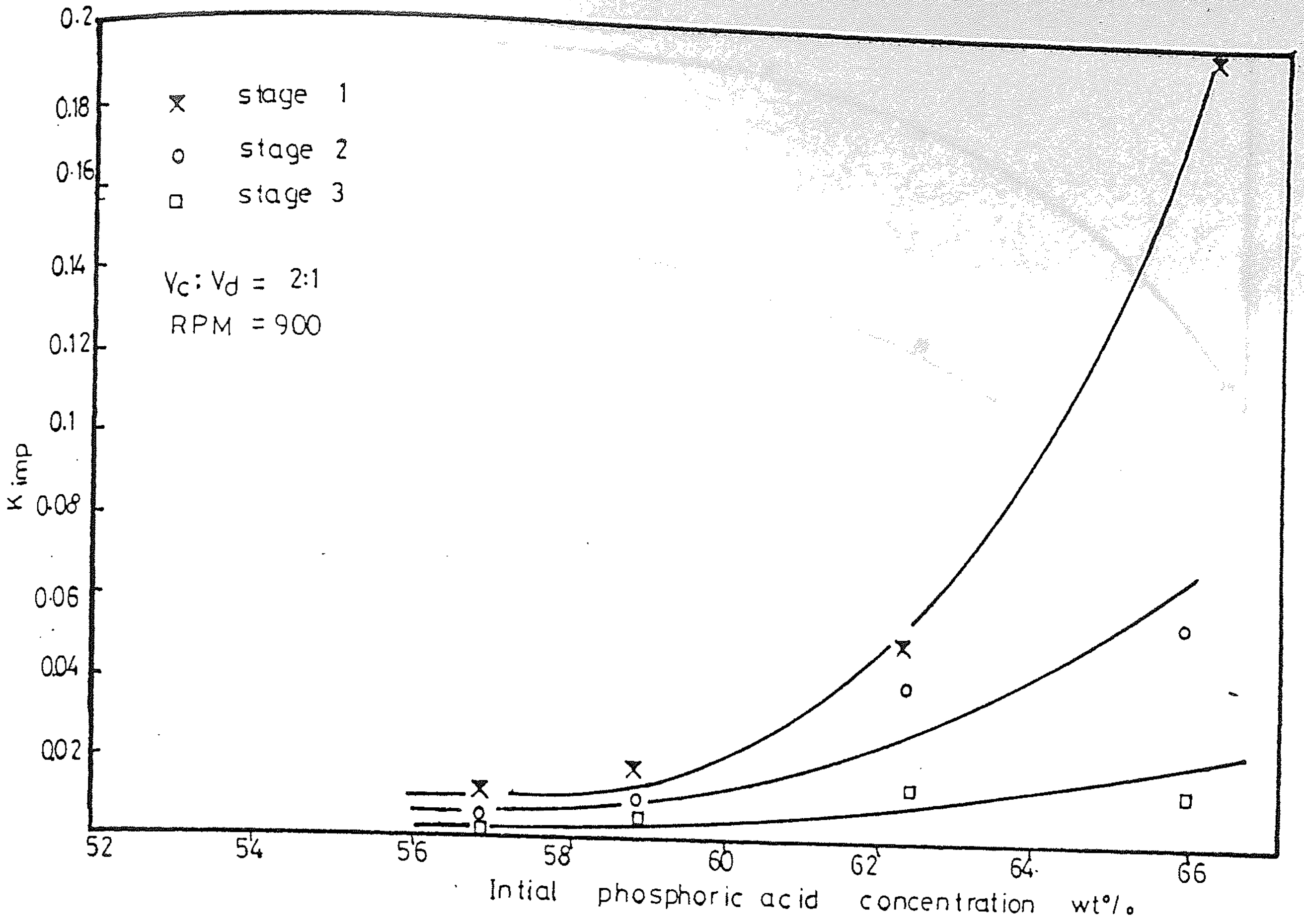


Fig 7.78 Effect of intial acid concentration on distribution coeff. of impurities solvent is mibk, Fe impurities

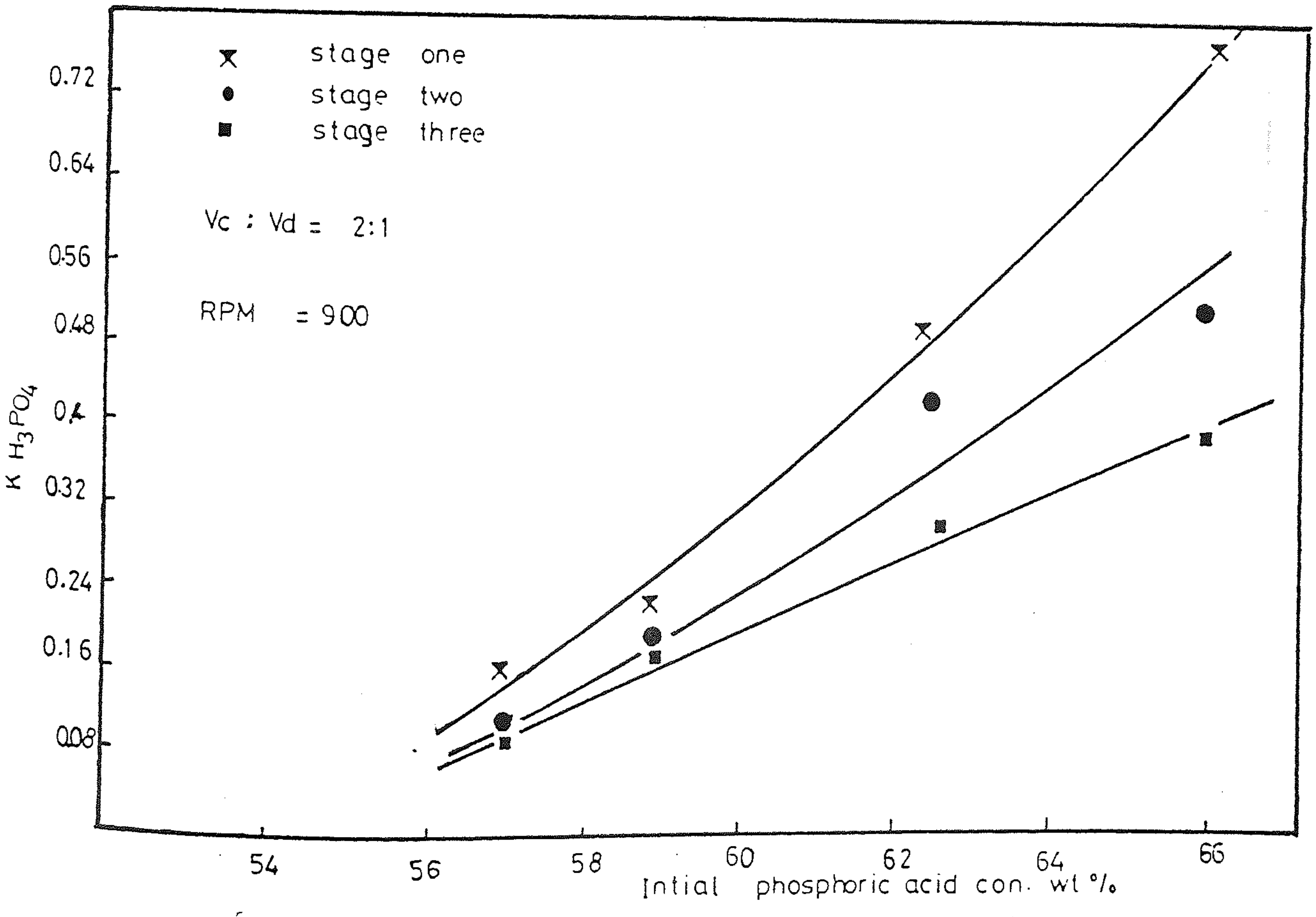


Fig 7.79 Effect of intial acid concentration on its distribution coeff.

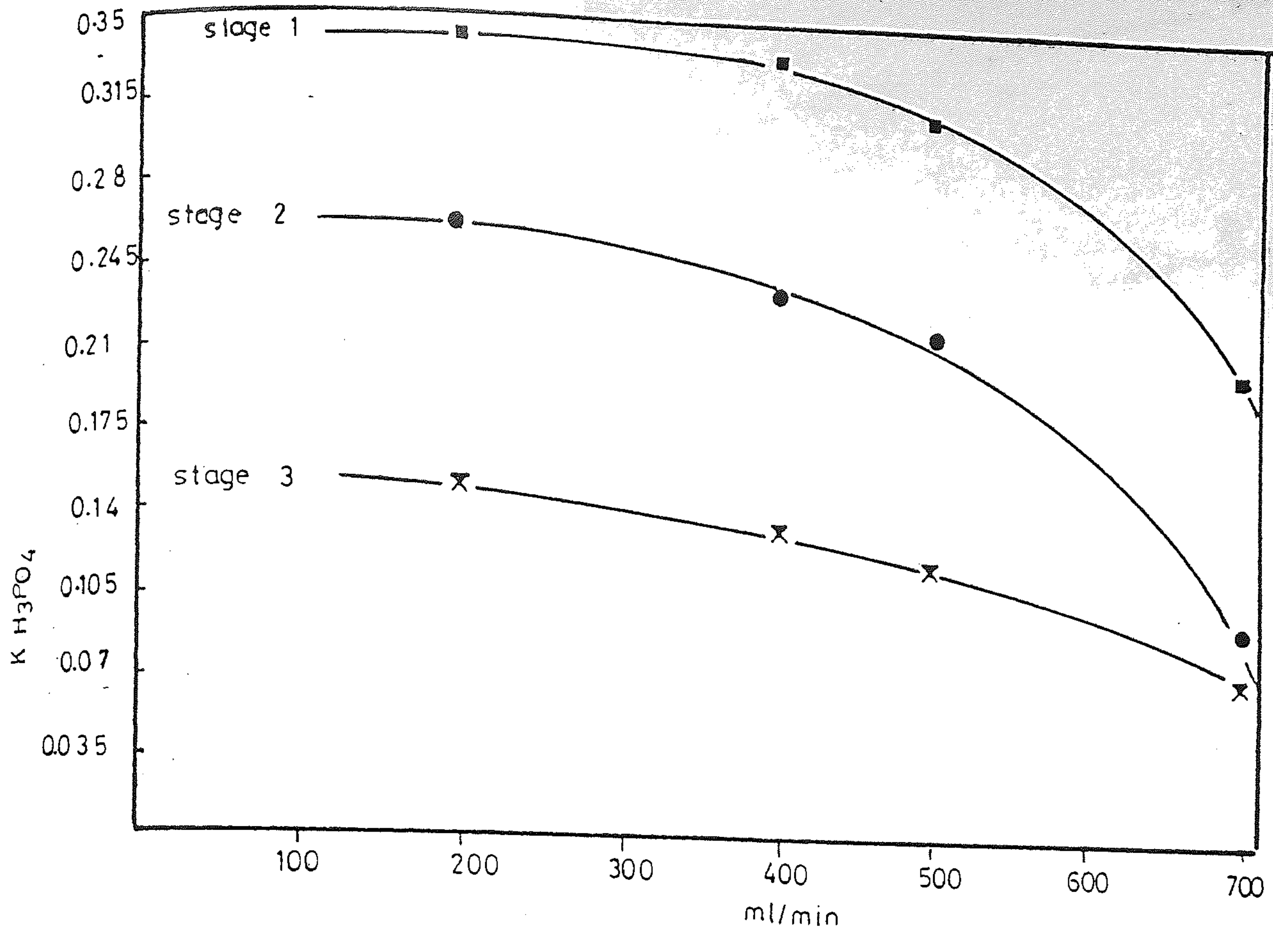
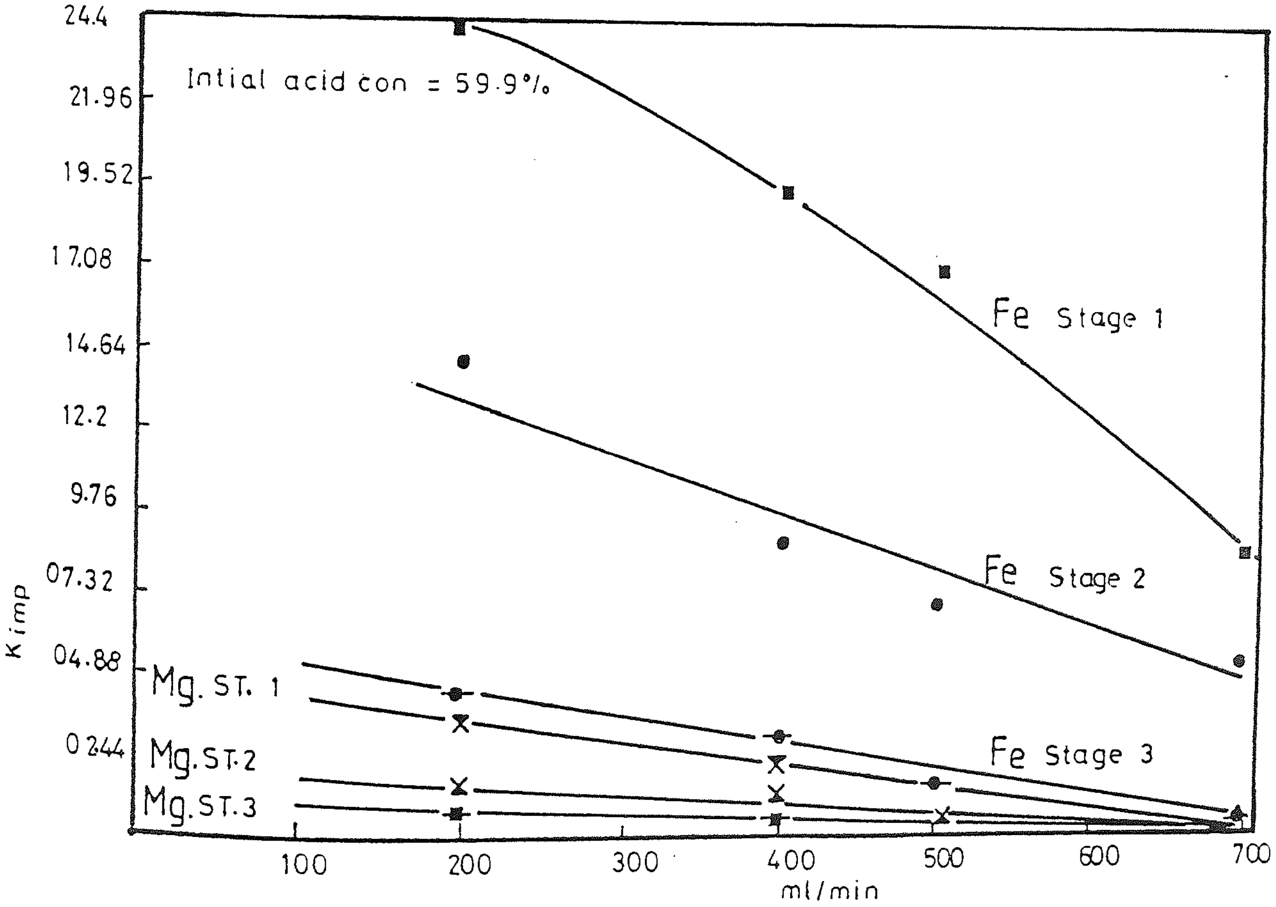


Fig 7.80 acid (H_3PO_4) distribution coeff vs total flow rate
Intial acid con.= 59.9% RPM = 900



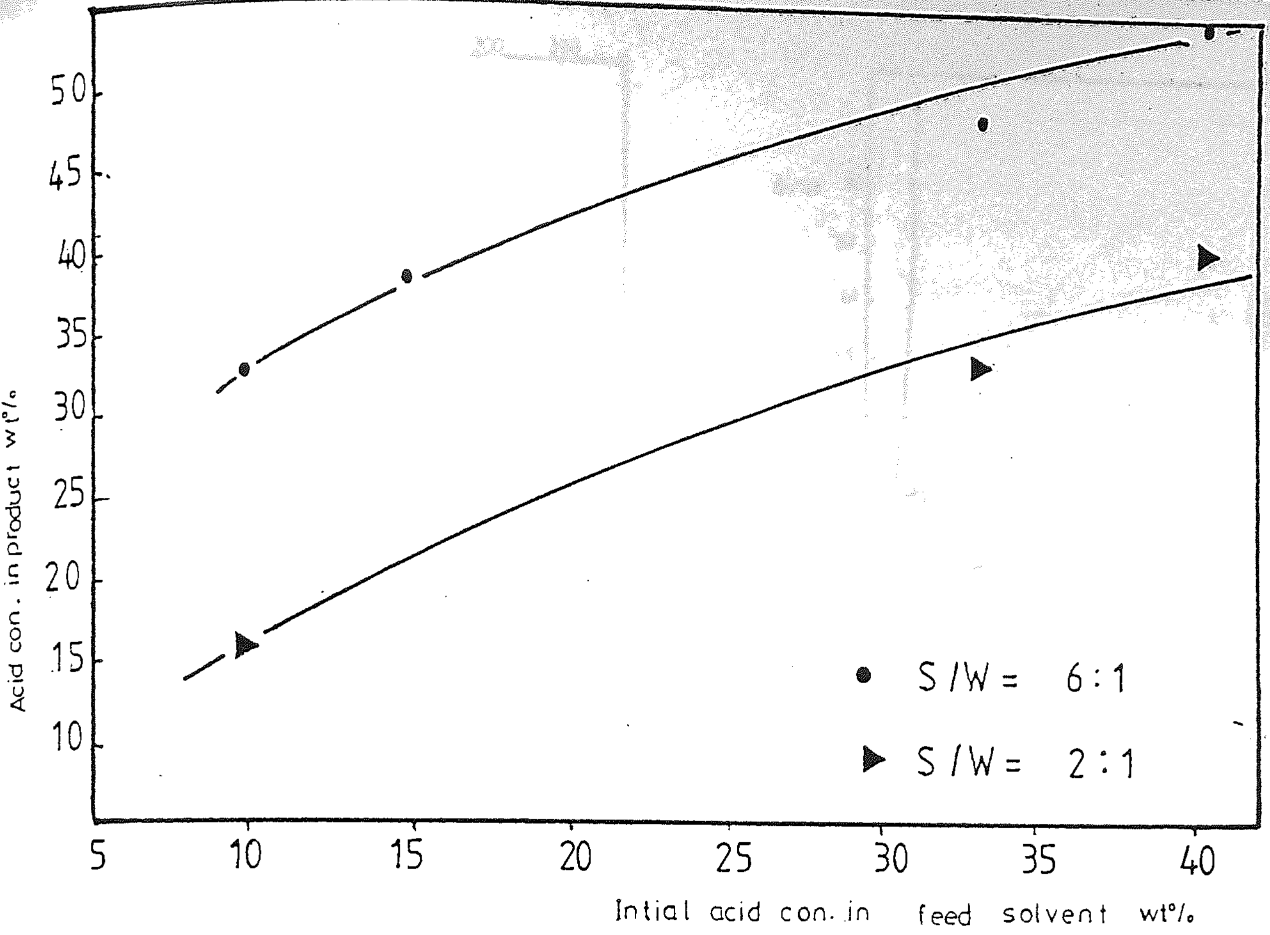
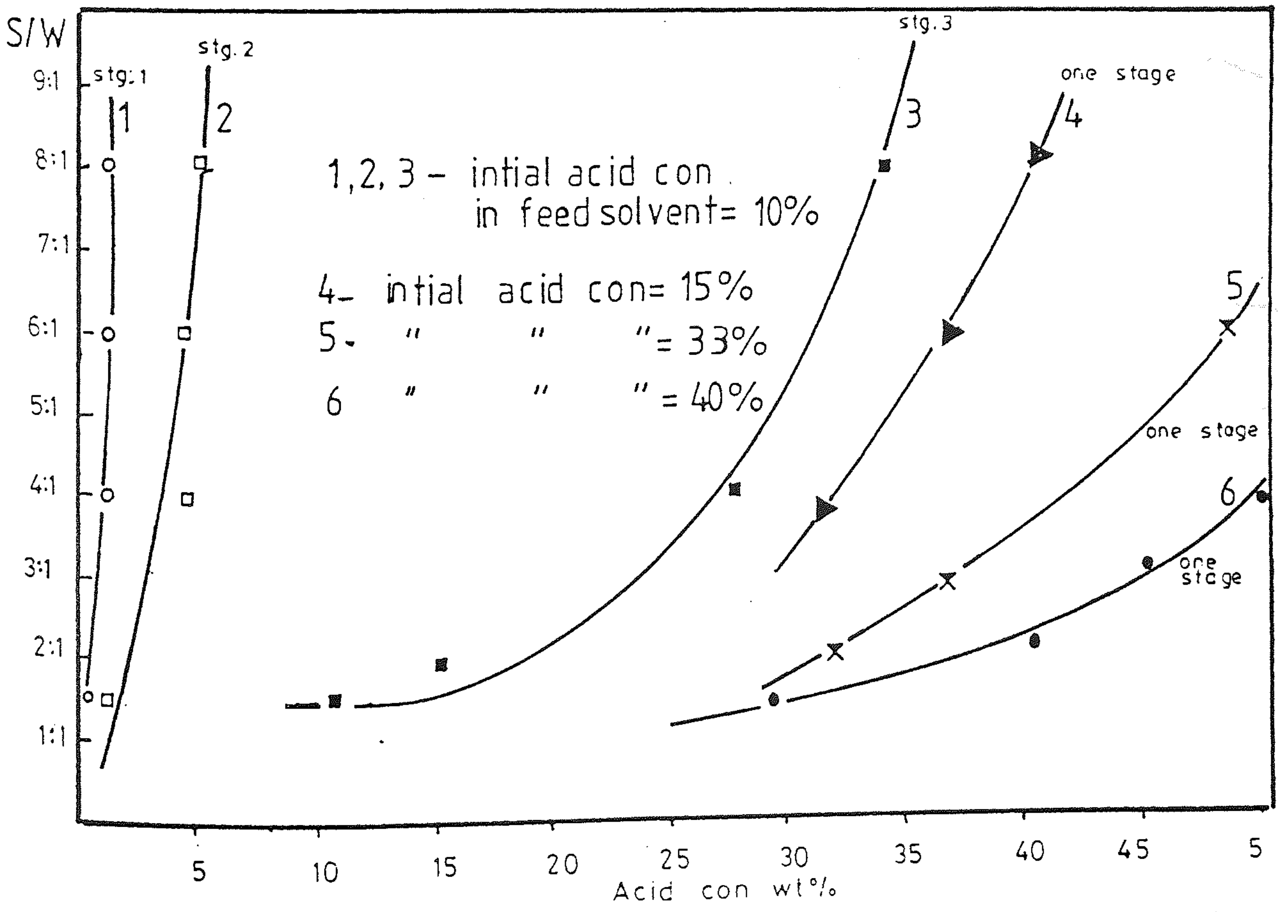


Fig 7.82 Effect of phosphoric acid con. in the solvent on the con. of the final product (back extraction step)



Fi Solvent/water ratio vs. concentration of acid in

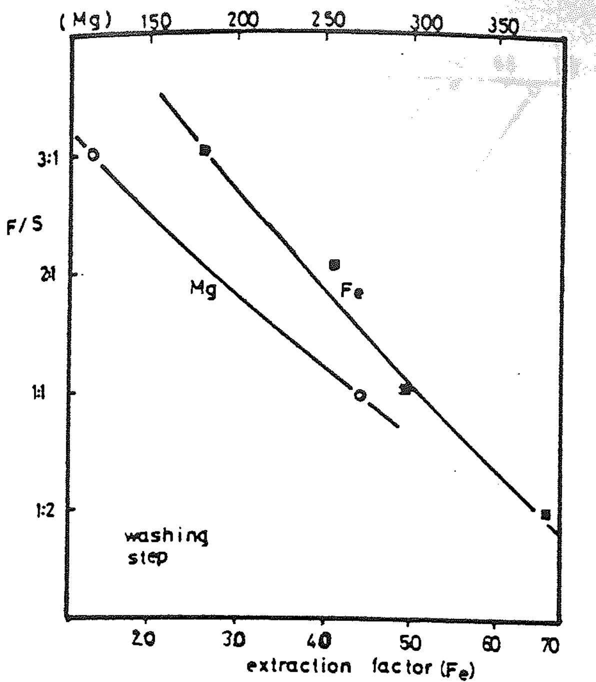


Fig 7.84 extraction factor vs intial Feed/Solvent.
rpm = 900 . Intial acid con. in
the extraction step = 58.9 %

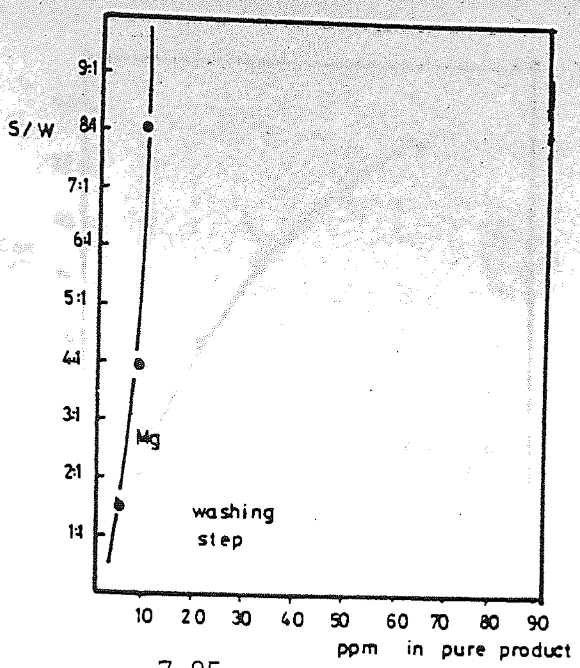


Fig 7.85 effect of Solvent/Water
ratio on the purity of
the final product.
rpm = 900
" " " Mg = 2 ppm.

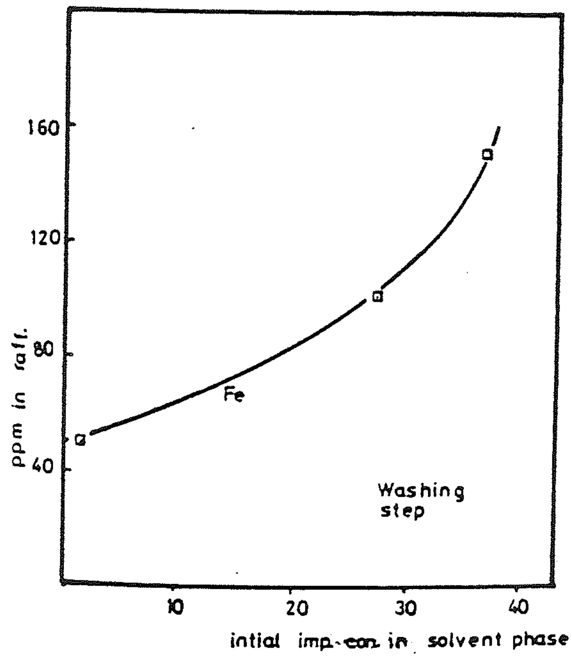


Fig 7.86 effect of intial imp. con. in the
feed solvent on purity of the
final product

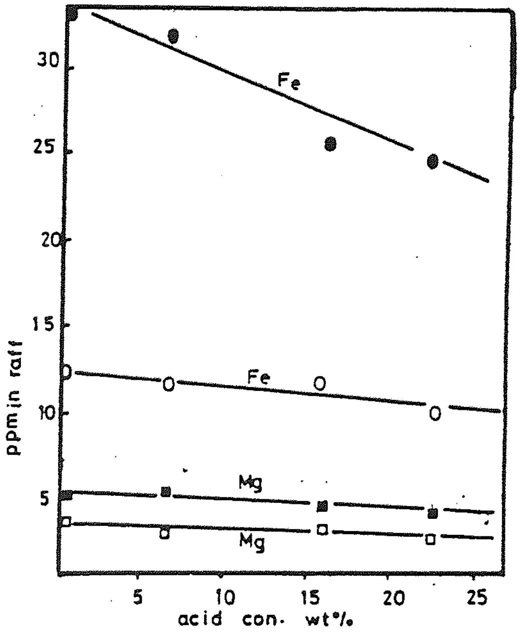


Fig 7.87 effect of back extracting
the solvent with different
acid con. on purity of the
final product
intial acid con, in solvent = 18%

■ ● s/w = 7.5:1
□ ○ s/w = 2:1

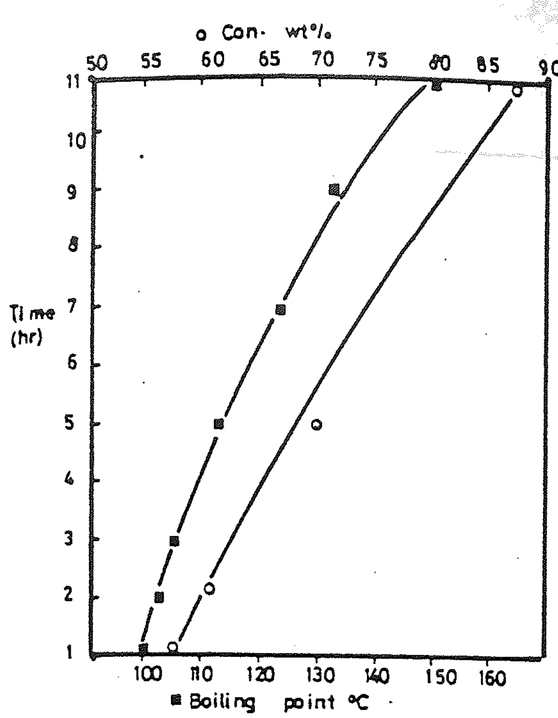


Fig 7.88 {Boiling point / and acid con.} vs time of heating

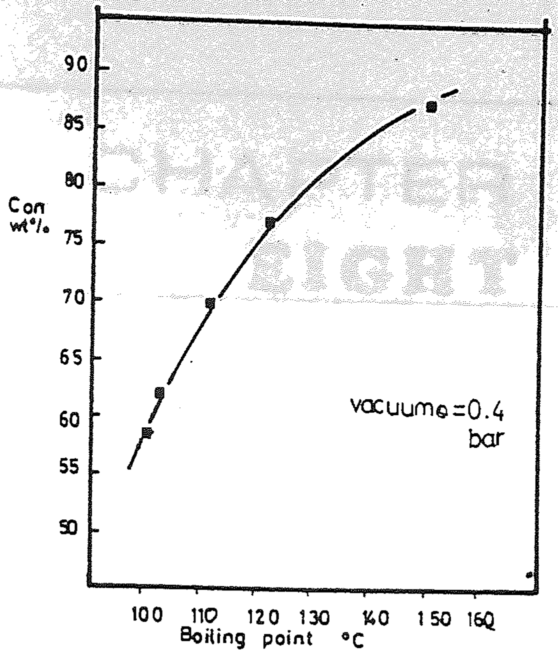


Fig 7.89 Boiling point vs acid con.

CHAPTER
EIGHT

DISCUSSION OF EXPERIMENTAL RESULTS

8.1 LIQUID-LIQUID PHASE EQUILIBRIUM AND IMPURITY DISTRIBUTION COEFFICIENTS

The binodal curves and tie lines for the three systems phosphoric acid-water-solvent for cyclohexanol, benzaldehyde and MIBK are shown in Fig. 7.1A to 7.1C. All three systems have heterogeneous regions occupying large areas in the triangular diagrams with the maxima of the binodal curves near the phosphoric acid corner. The sizes of the hetergeneous areas increase in the order cyclohexanol > MIBK > Benzaldehyde. The tie lines run almost from the solvent corner towards the binary system phosphoric acid-water.

Figs. (7.2-5) show that the distribution coefficients of phosphoric acid between the water and solvent layers increases with phosphoric acid concentration, and at low acid concentration cyclohexanol has the highest distribution coefficient followed by benzaldehyde and MIBK. This does not mean that cyclohexanol is the recommended solvent among the three chosen solvents, since other factors such as density, viscosity and settling time have to be considered as will be explained later.

Impurities (Fe^{3+} and Mg^{2+}) lower the slope of the distribution curve as shown by the dotted lines of Figs. 7.3-4. Yacu (282) observed the same effect and he also found that the impurities increased the mutual immiscibility of the acqueous and organic phases. This may increase the possibility of operating the equipment with higher initial acid concentration for the continuous process.

The sharp decrease in the distribution coefficient of phosphoric acid at concentrations below a certain value (52% for MIBK and 50% for benzaldehyde) placed a limit on the amount of phosphoric acid extractable from the feed. This phenomenon must be allowed for during design of the contactor since no further extraction of acid is possible even by increasing the number of stages.

Tie-line correlation was also carried out by Hand's method. The correlation curve (Fig. 7.7) represents the dependence of X_{ca}/X_{aa} on X_{cb}/X_{bb} logarithmic coordinates. Except in the case of MIBK, excellent straight lines were obtained. The tie lines when plotted using the Othmer and Tobias method (Fig. 7.9) give a point at which a sudden change of slope of the line occurs. Fig. 7.11 shows that although the selectivity of MIBK is low in comparison with cyclohexanol and benzaldehyde at low acid concentration, it has approximately the same value at high acid concentration. Considering physical properties (viscosity, freezing point, interfacial tension), MIBK was found to be a good solvent for extracting phosphoric acid. Comparison between the results achieved in this work and published data on the phase equilibrium diagram of water-phosphoric acid-solvent shows that the sizes of the heterogeneous areas in all systems are slightly smaller. Similar results were obtained by Yacu (282). This might be due to the use of different grades of acid and solvent by different workers. Yacu (282) approximated the distribution curve as a straight line, with an intercept of the x-coordinate at a point b representing a particular acid concentration. The slope of the equilibrium line is lower with increasing concentration of impurities as shown in Fig. 7.12. Based on this approximation a relationship to express the effect of the impurities on the slope of the distribution coefficient curve and hence on the extraction operation can be made as will be explained in the next chapters.

Figs. 7.13 and 7.14 show that the distribution coefficients of iron and magnesium increase sharply at high acid concentrations. This is rather discouraging since practical and economical extraction operations need to be performed at high acid concentration. Iron (Fe^{3+}) has a higher distribution coefficient than magnesium (Mg^{2+}). This explains why the choice of phosphate rock (origin and composition) is very important in the phosphoric acid industry.

Cyclohexanol was found to be less selective of impurities than MIBK. This phenomenon must also be considered in choosing a suitable solvent for phosphoric acid purification based on solvent extraction.

The higher the initial impurity concentration in the acid, the lower the distribution coefficient of impurity as shown in Fig. 7.17. This does not mean that the concentration of impurity in the organic layer is lower, in fact the higher the concentration of impurities in the initial acid the less pure the product acid.

Organic and anionic impurities were not tested in this work, however they tend to increase the distribution coefficient of the acid and would be expected to have a similar distribution coefficient themselves to cationic impurities since they are present in the form of saturated cationic salts (111,235).

Two solvents (cyclohexanol and MIBK) were mixed together in a ratio of 3:2 by volume. This was an attempt to improve the physical properties of the cyclohexanol, e.g. interfacial tension and specific gravity as shown in Appendix 2, and hence to improve the settling time as will be explained later.

The blending of the two solvents does not only improve the physical properties of the solvent, but also the new solvent will have more power to extract phosphoric acid than either solvent (see Fig. 7.18). This results in advantages, which could be used in industry to improve other solvents. However this is beyond the scope of this investigation and will be recommended for future work.

8.2 BATCH HYDRODYNAMIC STUDIES

As can be seen from Figs. (7.19, 7.23) the settling time of the two phases increases with the acid concentration. This can be explained by considering the physical properties of the two phases. The higher the acid concentration in the extract phase, the more viscous the phases, and therefore the slower the coalescence of the drops due to slow film drainage. Interfacial tension between the phases decreases with higher acid concentration and results in a longer settling time. This phenomenon means an increase in the size of the equipment, so cyclohexanol cannot be recommended for phosphoric acid extraction. The time required for phase separation at acid concentration of 60% is around 8 minutes as shown in Fig. 7.19. However, it is equal to 1.5 and 4.5 minutes for benzaldehyde and MIBK as shown in Figs. 7.20 and 7.21 respectively. Fig. 7.22 shows how cyclohexanol may be modified by mixing with MIBK, so reducing the settling time of the phases from 8 minutes to around 5 minutes. Since the rate of primary break is the controlling factor for design and operation of mixer-settler contactors, benzaldehyde would be the recommended solvent regarding the primary break, followed by MIBK and cyclohexanol as shown in Fig. 7.23.

Neither mixing power for 500 to 1200 r.p.m. nor mixing time from 1 to 9 minutes had any effect on primary break time for all three systems studied, see Figs. 7.24-7.29. This simplifies the design of the mixer settler unit because the mixing can be selected to optimize stage efficiency without changing settler capacity.

8.2.2 DROP SIZE DISTRIBUTION

The drop size distribution at various impeller speeds, hold-ups and different acid concentrations are shown in Figs. 7.28-31. As phosphoric acid concentration increases, the interfacial tension and density difference between the two phases decreases, resulting in a smaller drop size. The data shows a sharp reduction in drop size upto a certain acid concentration and impeller speed. This is an indication that the drops are near stagnant conditions.

Drop size also increases with the dispersed phase holdup. This phenomenon was observed until the point of phase inversion. Detailed investigations regarding holdup with respect to drop size, mixer geometry and economic factors have to be made to give the optimum design. No attempt was made to fit the data in the Hinze equation (94) since Yacu (282) using the same system (MIBK) showed that the drop size data can be fitted to a Hinze equation only by modifying the constant to account for the turbulence and physical properties of the system. Furthermore Hinze did not consider the effect of hold-up in his correlation of drop size. An attempt was made to fit the experimental results of this work in a more recent correlation given by Gnansundaram*, where the hold-up was considered. The proposed correlation for prediction of mean drop size in an agitated batch vessel under a wide range of hold-ups from 0.01 to 0.5 and impeller Weber number from 35-200,000 is

$$d_{32} = \text{Impeller diameter} * C_1 * (We)^{-0.6} * e^{\lambda x} \quad \ldots \quad (8.5)$$

where

$e^{\lambda x}$ = the exponential series (see 8.6)

x = fractional hold-up of dispersed phase

For $W_e < 10{,}000$ $C_1 = 0.052$

$\lambda = 4.0$

For $W_e > 10{,}000$ $C_1 = 0.39$

$\lambda = 0.0$

$$e^{\lambda x} = 1 + \lambda x + \frac{(\lambda x)^2}{2!} + \frac{(\lambda x)^3}{3!} + \ldots\ldots + \ldots \quad \ldots \quad (8.6)$$

Some of the results obtained from equation 8.5 were compared with the experimental values. These are shown in Appendix 2. The deviation between the calculated and experimental results ranges from 10% to around 40%, and decreases with the acid concentration. This might be because coalescence of drops at low acid concentration is faster after stopping the impeller, therefore the photographs of the dispersion do not give the actual size. However at high acid concentration, coalescence of the drops was slow,

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* S. Gnansundaram, T.E. Degalessan and Laddha G.S., Canadian Journal of Chemical Eng., Vol.57, April 1979, p.141.

and there was a time during which the dispersion could be photographed. At high acid concentration (above 50%) the refractive indeces of the two phases become nearly equal and the interfacial tension becomes smaller. This resulted in smaller drops and difficulty in focussing the camera.

8.2.3 PHASE INVERSION

Phase inversion is described as a phenomenon in which the dispersed phase becomes continuous and vice versa. Which phase is to be continuous and which is going to be dispersed depends on the starting procedure, system properties and impeller position. The organic phase was dispersed by agitating the phosphoric acid then introducing the solvent MIBK.

It was observed that by starting the impeller at high speed with the two phases in the mixer, the system was w/o. The approach of phase inversion is characterised by the formation of large droplets of the solvent (dispersed phase).

Considering Fig. 7.31, an increase in rotor speed decreases phase inversion hold-up for the organic phase while it increases phase inversion hold-up for the phosphoric acid phase.

Arashmid (10) reports that globules usually appear from the discharge region of the impeller and the rate of appearance of these globules fluctuates, leading to variations of drop size. At higher impeller speeds this becomes more regular leading to less fluctuation of drop size. The appearance of globules indicates that at phase inversion the bulk of coalescence occurs in the discharge region of the impeller and every impact will lead to coalescence.

As acid concentration increases, the dispersed phase hold-up is smaller at the same rotor speed as shown in Fig. 7.31. This is a disadvantage since in practice it is required to operate at high acid concentrations with high dispersed phase hold-up, as will be explained for continuous operation. Yacu (282) divided phosphoric acid concentration into three regions, low, medium and high. At low acid concentration where the organic phase was continuous in most cases, the volume of organic phase and the viscosity and density as well as density difference were relatively low. With increasing acid concentration (medium range), the volumes of the phases were similar, and viscosities, densities as well as density difference increases accordingly.

The organic phase was continuous only when starting the impeller at high speed. Otherwise, the aqueous phosphoric acid phase became continuous and remained so if no organic was added. With further increase of phosphoric acid concentration, the densities and viscosities increases further, and the stable continuous phase was in most cases the phosphoric acid. The phase inversion time from o/w to w/o was short compared with the time taken for inversion from w/o to o/w. A typical time for inversion of the system o/w was around 10 seconds compared with the 40 seconds it took for the system w/o. The high resistance of a viscous phosphoric acid phase will resist its coalescence.

Which phase is to be dispersed at production scale is very important. The primary break time for the system o/w at 50% acid concentration is around 2 minutes, while it took an hour for the system w/o. Based on this phenomenon it was decided to operate the continuous contactor for the system o/w rather than w/o.

8.3 CONTINUOUS STUDIES

8.3.1 HYDRODYNAMIC STUDIES

8.3.1.1 HOLD UP

In general the hold-up increased with increasing dispersed flowrate (solvent MIBK) at a constant rotor speed. However hold-up was independent of rotor speed provided this was above a critical value (700 r.p.m.) as shown in Figs. 7.40 and 7.41. This is in agreement with the observation reported by Houssain (100). The dispersed phase hold-up approached the volume fraction of the dispersed phase in the feed with increasing power input. Hold-up of the dispersed phase also decreased with the aqueous phosphoric acid flowrate. This is demonstrated in Fig. 7.42.

8.3.1.2 DROP SIZE

It is desirable to obtain the drop size of the dispersion since a knowledge of this and the dispersed phase hold-up will give the interfacial area of contact. In this work Sauter mean drop size was used and it was found to vary with rotor speed, hold-up, system physical properties and acid concentration in the range of 0.15 to 1.2 mm, which is characteristic of agitated aqueous/organic systems (compared with 0.25 to 5 mm in various columns). For mass transfer studies the use of Sauter mean diameter is preferred since solute transfer across the interface is an area dependent process. In this study, Sauter mean diameters were found to be log-normally distributed as shown in Fig. 7.43. No attempt was made to measure any variation in drop size with position in the vessel since the drops were too small, and the mixture was homogeneous once the critical speed was exceeded. The Sauter mean diameter (d_{32}) at a constant phosphoric acid concentration and rotor speed increases almost linearly with hold-up due to coalescence effects. As hold-up increases the probability of drop collisions followed by coalescence increases. Hence drop-drop coalescence is enhanced by an increase in hold-up.

Experimental values of d_{32} were compared with the correlation given by Houssain (100):

$$d_{32} = 0.43D \times (We)^{-0.58} \times \left(\frac{r}{r+1}\right)^{1.02} \left(\frac{\mu d}{\mu c}\right)^{-0.21} \quad .. \quad (8.7)$$

where $r = \frac{V_C}{V_D}$ and D = impeller diameter values differed by 30 to 40%. This may be due to the differences in the physical and chemical properties of the system studied as well as system acidity.

No other correlation has previously been published for drop size and hold-up at different phosphoric acid concentrations in the mixer of a mixer-setter chain. Such a correlation can be derived by consideration of d_{32} as a function of the physical properties of the system, operating conditions, impeller geometry and phosphoric acid concentration.

$$d_{32} = f(N, \phi_d, \mu_d, \mu_c, \sigma_i, \rho_m, D, X_F) \quad \ldots\ldots\ldots\ldots \quad (8.8)$$

where the notation are as given in the nomenclature. Equation 8.8 can be arranged in terms of dimensional analysis as:

$$\frac{d_{32}}{D} = k(We)^{a} \; (We)^{-b} \; \left(\frac{\rho_m}{X_F}\right)^{c} (\phi_d)^{d} \left(\frac{\mu_d}{\mu_c}\right)^{e}$$

The exponents a, b, c, d, e and values of k were calculated from the experimental results.

The correlation applies only for hold-up ranging between 0.38 and 0.6, since at low hold-up the drops were difficult to measure and at hold-up higher than 0.6, the phase will be inverted from o/w to w/o.

$$\frac{d_{32}}{D} = 0.632 \; (\phi_d)^{3.62} \; \left(\frac{\mu_d}{\mu_c}\right)^{-3.02} (We)^{-1.071} \; \left(\frac{\rho_m}{X_F}\right)^{1.08} \quad \ldots\ldots\ldots\ldots\ldots \quad (8.10)$$

The data has a correlation coefficient of 0.97. Fig. 8.1 shows that the experimental values lie within ±9.5% of those predicted by equation 8.10.

The change in drop size with stage number is not considered in the above correlation. However, since

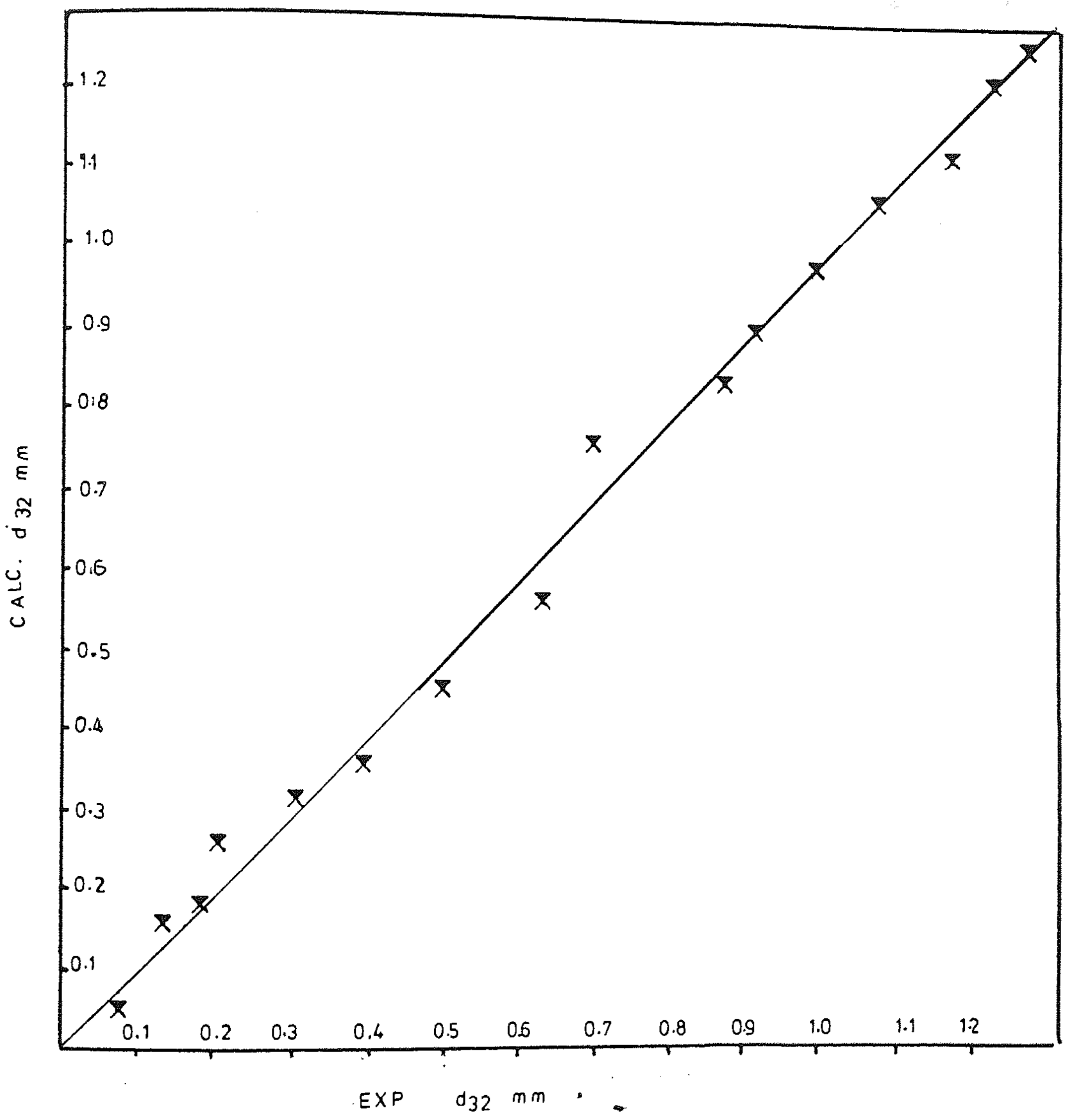


Fig 8.1 Calculated versus experimental mean drop size

phosphoric acid concentration decreases and interfacial tension increases from stage one to stage three, it will be expected that the mixer of stage one has smaller drops than that of the second and third stages. This may also explain why wedge length in the first stage is longer, resulting in a longer or larger settler being required for first stage.

8.3.1.3 SETTLER CHARACTERISTICS

Within the experimental work studied wedge length in the settler increased with increasing dispersed phase flowrate, continuous phase flow, acid concentration and to a certain extent the power input in the mixing tank, as shown in Figs. 7.46 to 7.52.

All these parameters affect the hold-up and drop size in the mixer, and therefore coalescence and flow conditions in the settler. When the dispersed phase throughput (MIBK) was increased at a fixed agitator speed the wedge length in the settler increases to a certain value, after which it became almost constant near phase inversion (Fig. 7.53).

Fig. 7.50 shows that the power input has less effect on wedge length compared with the effect of flow rate, this result is not surprising, since in the batch studies (Section 8.2) the power input did not affect the primary break of the two phases.
Fig. 7.52 as expected from the batch studies shows the higher the acid concentration the longer the wedge

length. This means that with the high acid concentration a larger settler is required for phase separation. Settler capacity was improved for mass transfer studies by introducing a baffle and coalescing aid (knitted mesh packing).

No correlation has previously been proposed to predict wedge length in a cylindrical settler without baffles and for phosphoric acid as the transfer solute. A correlation for W_L (wedge length) has therefore been determined in the range of phosphoric acid concentration from 5 to 55 wt % by taking wedge length as a function of the physical properties of the system, operating conditions and phosphoric acid concentration.

$$W_L = f(V_D, V_C, N, D_s, \rho_m, \sigma_i, \mu_m, X_F) \quad \ldots\ldots\ldots\ldots (8.11)$$

where the notation are given in the nomenclature. The above equation can be expressed in terms of dimensionless groups:

$$\frac{W_L}{D_s} = K'\left(\frac{V_D}{ND_s^3}\right)^{a'}\left(\frac{V_C}{ND_s^3}\right)^{b'}\left(\frac{\sigma}{N^2 D_s^3 \rho_m}\right)^{c'}\left(\frac{\mu_m}{ND_s^2\rho_m}\right)^{d'}\left(\frac{X_F}{\rho_m}\right)^{e'} \quad \ldots\ldots\ldots\ldots (8.12)$$

The exponents of a', b', c', d', e' and value of k' were determined experimentally. The final equation can be written as:

$$\frac{W_L}{D_s} = 5.524\text{x}10^{-5}\left(\frac{V_C}{V_D}\right)^{0.433}\left(\frac{\sigma}{N^2 D_s^3 \rho_m}\right)^{0.098}\left(\frac{\mu_m}{ND_s^2\rho_m}\right)^{-0.81}\left(\frac{X_F}{\rho_m}\right)^{0.550} \quad \ldots\ldots\ldots\ldots (8.13)$$

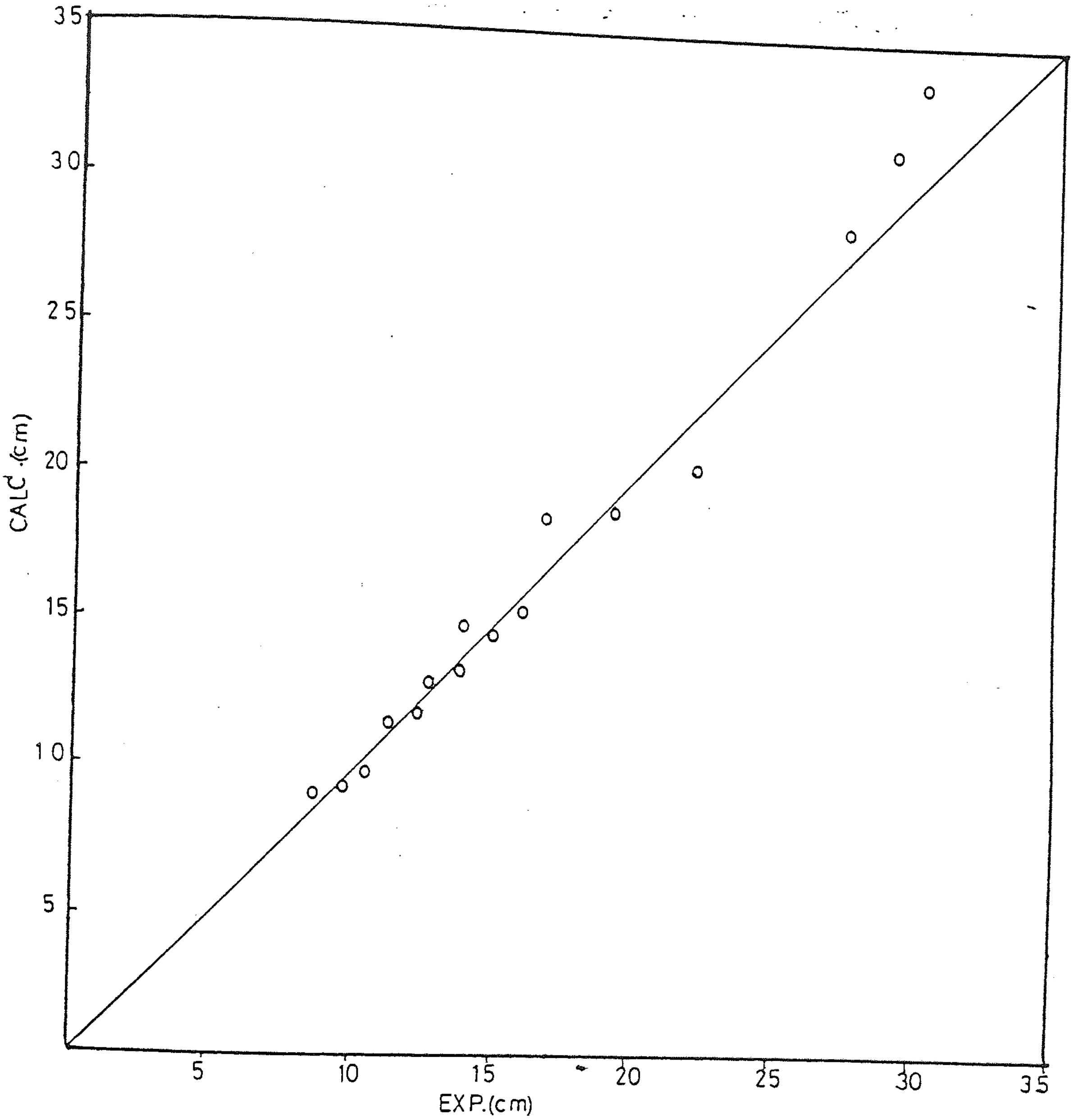


Fig 8.2 Calculated vs experimental wedge length for the system phosphoric acid – water – mibk

Fig. 8.2 shows that the experimental values at low wedge length lie within ±10% of those predicted by the above equation, while at higher values of W_L, the deivation is about 25%.

Clearly from the equation, wedge length was more influenced by throughput and acid concentration than by energy input. The same observation was made by another worker (100) using the system kerosene-water, and acetone-water. When all three stages were used with mesh (occupying ¼ of settler length) in each settler, it was observed that the wedge length was zero in the middle and solvent introductory stages and about 10 cm long in the acid introductory stage. This observation can be explained since the density difference between the two phases as well as interfacial tension, are reduced in the first stage, resulting in a smaller mean inlet drop size, and a lower coalescence efficiency. The behaviour is of economic importance and must be considered in the design of the mixer-settler units. A larger and a longer settler is therefore required for the first stage (acid introductory stage) and a smaller settler is required for the solvent introductory stage. Other stages will require a settler size between those of the first and last stages.

8.3.1.4 PHASE INVERSION

Phase inversion in a batch operated stirred mixer was reviewed in Section 8.2. For continuous operation the conditions are different. Figs. 7.54 to 7.57 illustrate that hold-up at inversion varied inversely with rotor speed . This is because at high energy input smaller drops will exist and, therefore the rate of coalescence will increase. The width of the ambivalence zone was found to increase with decreasing Weber number in all cases, which is in agreement with Lunning and Sawistowski, Arashmid and Houssain (170, 100, 10).

Apart from the difference in drop sizes and settling rates for different acid concentrations, a difference in the rate of coalescence and physical properties, e.g. interfacial tension, would be expected to cause a change in the width of the ambivalent zone. The zone also becomes smaller with increase of phosphoric acid concentration. This result is caused by a large downward shift of the upper inversion curve. The corresponding shift of the lower line was much less pronounced. The shifts were much more obvious in the o/w than w/o dispersion. Since interfacial tension is the same in both cases, the shorter time required for phase inversion from o/w to w/o could be attributed to the fact that the system organic dispersed water continuous always coalesces more rapidly than the corresponding water dispersed organic continuous system.

On considering Figs. 7.54 to 7.57, continuous operations for phosphoric acid extraction using MIBK as the extracting solvent is not recommended above line (1) since the system is w/o and this required a long settling time as explained above. It is economically important to extract as much phosphoric acid as possible from the aqueous solution but this requires a large quantity of solvent. However large solvent acid ratios lead to phase inversion which makes settling difficult. Therefore it is best to operate the equipment with case as near as possible to line (2) which keeps the system at o/w.

Impeller position plays an important part in determining the identity of the dispersion as claimed by Arashmid and Quinn (10,24). They attempted to use a double paddled impeller. The two paddles were spaced on the shaft so that they were centred in the upper and lower halves of the mixer. This impeller swept out the same liquid volume as a single paddle impeller, however their results with the double impeller were completely different from those with a single impeller.

8.3.2 MASS TRANSFER CHARACTERISTICS

8.3.2.1 EQUIPMENT PERFORMANCE

Since the equilibrium data was obtained at $25^{\circ}C \pm 0.1$, the cascade was also operated at this temperature. As mentioned in Chapter 6, the hold-up value of each stage was measured using a measuring cylinder, and since average hold-up values do not differ greatly from the stage hold-up values as shown in Figs. 7.60-7.63 it is convenient to consider the average rather than the stage hold-up in calculating mass transfer coefficients. The steady state conditions were obtained by measuring the concentration of acid and impurities from each stage with time as shown in Figs. 7.64 and 7.65. Only two experiments are presented in this section, the times required to reach steady state for other experiments are presented in Appendix IV.

The impurity concentration profiles along the contactor are presented in Fig. 7.66. The organic phase of stage one is saturated with the impurities (Fe^{3+}, Mg^{2+}) followed by stages two and three, while the raffinate of stage 3 is saturated with impurities. The conclusion from this phenomenon is that each stage of the cascade can give a different grade phosphoric acid. It can also be concluded that impurity concentration in a given layer goes hand in hand with the concentration of acid in that layer as shown in Fig. 7.67.

The average equipment efficiency achieved was around 80% and stage efficiencies as high as 95% were reached. Efficiency of the equipment increased with impeller speed as shown in Fig.7.68 for both pure and impure systems. The figure also shows that the impure system has a higher efficiency than the pure system; this may be because the slope of the equilibrium line for the impure system is lower than that of the pure system. When the impeller speed was increased at a fixed phase ratio, the drop size was found to decrease with a consequent increase in the interfacial area and hence efficiency.

The time required for the equipment to reach steady state is a function of many factors. Generally it decreases with the power input as shown in Fig. 7.70 and increases with phosphoric acid concentration. This time is an approximate time, since the equipment was manually controlled and the instantaneous values of the concentration fluctuate about the average. For impure phosphoric acid, the time required to reach steady state is shorter than in the case of the pure system. This may contribute to the fact that at high acid concentration, the impure system settles faster than the pure system.

As reported by Yacu (282), three stages were sufficient to extract phosphoric acid using MIBK as the extracting solvent. At initial acid concentrations below 55% the process is not profitable. The partition coefficient at initial acid concentrations below 55% is low. At high acid concentrations above 64% the two phases required a long time for settling. Similarly it is found that one stage is sufficient to wash the solvent with water to extract the acid.

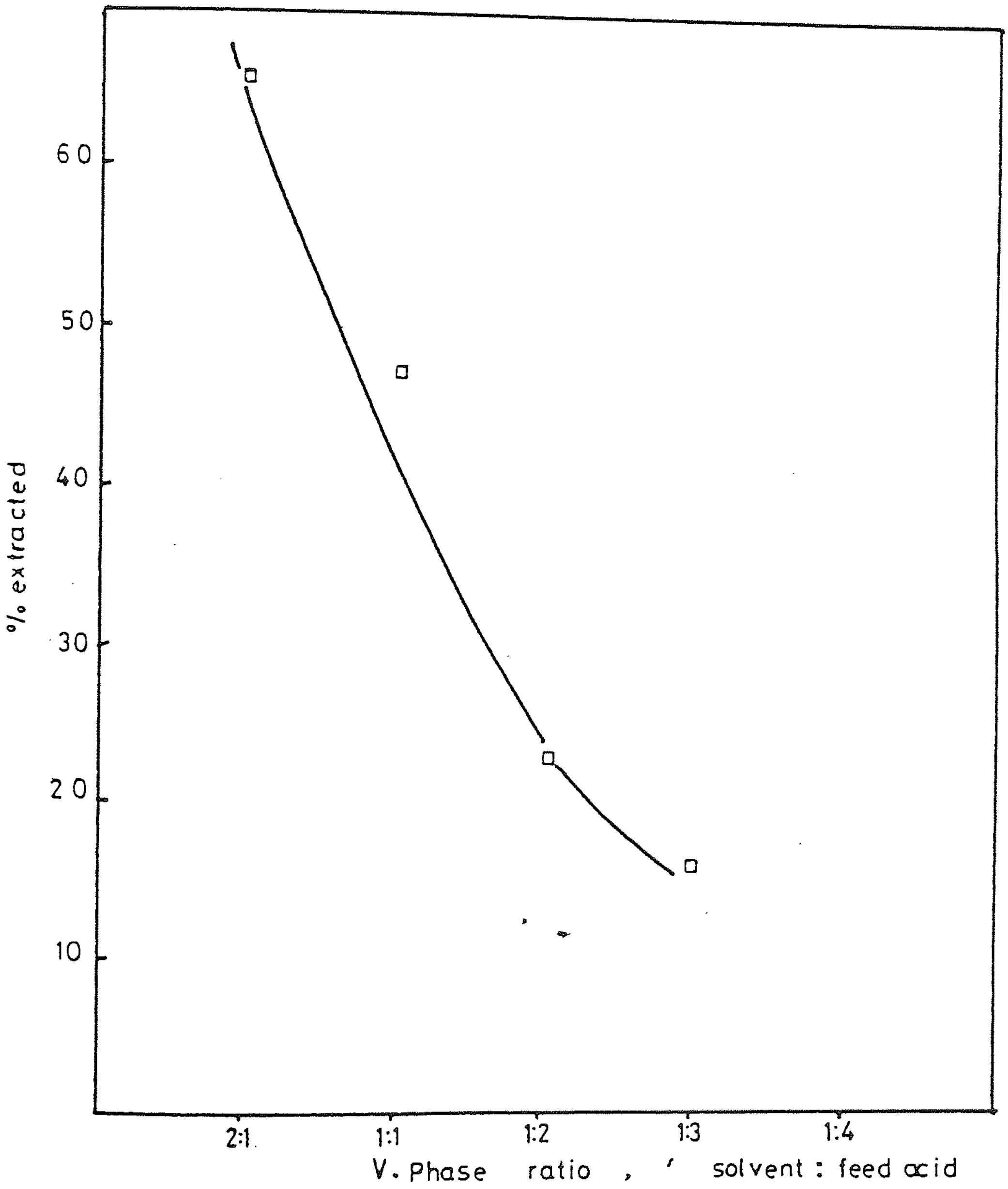


Fig 8.3 effect of phosphoric : solvent phase ratio on % acid extracted acid con.= 58.9%

8.3.2.2 EFFECT OF OPERATING PARAMETERS ON DISTRIBUTION COEFFICIENT OF ACID AND IMPURITY

In the process for phosphoric acid purification using solvent extraction, there are so many variables to be considered that it is not possible to model and optimise the process theoretically, therefore practical optimization is recommended.

(A) Extraction Step

Impurity concentration profiles along the contactor varied from stage to stage and, as mentioned earlier, each stage gives a different grade of acid. The influence of the volume ratio of the phases (F/S) on the distribution coefficient of impurity and acid is shown in Figs. 7.74 and 7.75. The higher the phase ratio the lower the grade of final product phosphoric acid. The increase in phase ratio of solvent : feed acid increased the degree of extraction of phosphoric acid as shown in Fig. 8.3 (in the case of MIBK), however the following factors may be barriers to a commercial process.

(1) Phase inversion may occur at high solvent : acid ratios, as in the case of these studies where the optimum phase ratio before phase inversion was 1:1.

(2) More solvent needs to be distilled or back extracted, which has to be considered in the design and economic evaluation of the process.

Rotor speed has no significant effect on the distribution coefficient of both the impurities and the acid, however, as expected from the batch studies, coefficients are increased with initial acid concentration as shon in Figs. 7.78 and 7.79. This is a disadvantage as it may require a compromise to be made between the grade of final product acid and the yield of acid, considering the settling capacity and the settling time of the two phases at high acid concentration. The optimum value of acid therefore can be taken as 63%. The value was recommended in the theoretical model used by Yacu (282). The effect of total flowrate of the two phases on distribution coefficient of impurities and acid is shown in Figs. 7.80 and 7.81. Again both K_{imp} and $K_{H_3PO_4}$ decrease with flow rate. In industry the total flowrate can be made the optimum by considering settler capacity, grade of acid, yield and initial acid concentration. The optimum experimental condition was between 300 and 400 ml/min.

Overall mass transfer coefficient increases with increasing impeller speed and to a maximum limit with feed:solvent phase ratio, as shown in Figs. 8.4 and 8.5. When the impeller power was increased at a fixed phase ratio, the drop size decreased with a consequent increase in the interfacial area. With further increase of agitation beyond an optimum energy level, no further increase in mass transfer rate results due to the formation of stagnant drops (265).

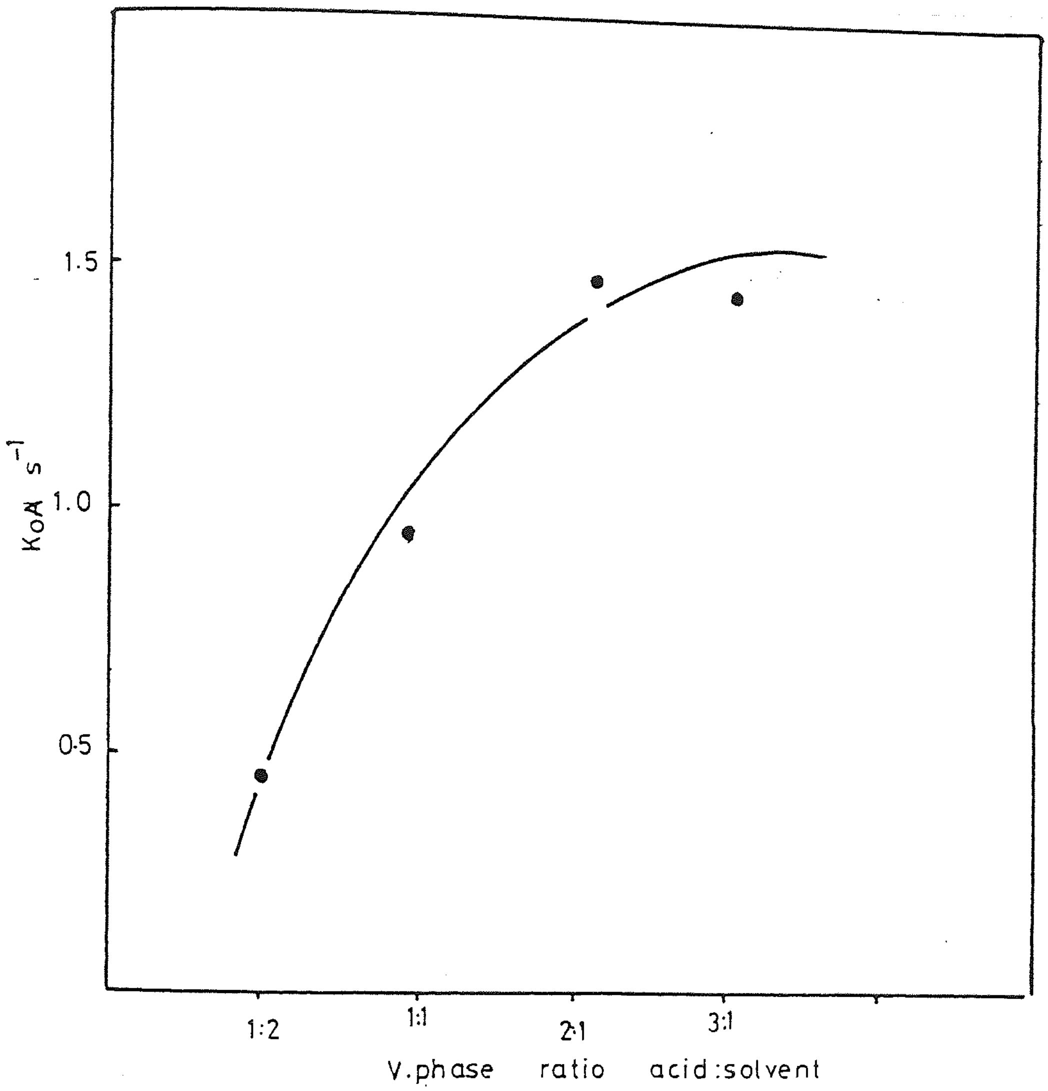


Fig 8.4 Overall mass transfer coefficient versus phase ratio

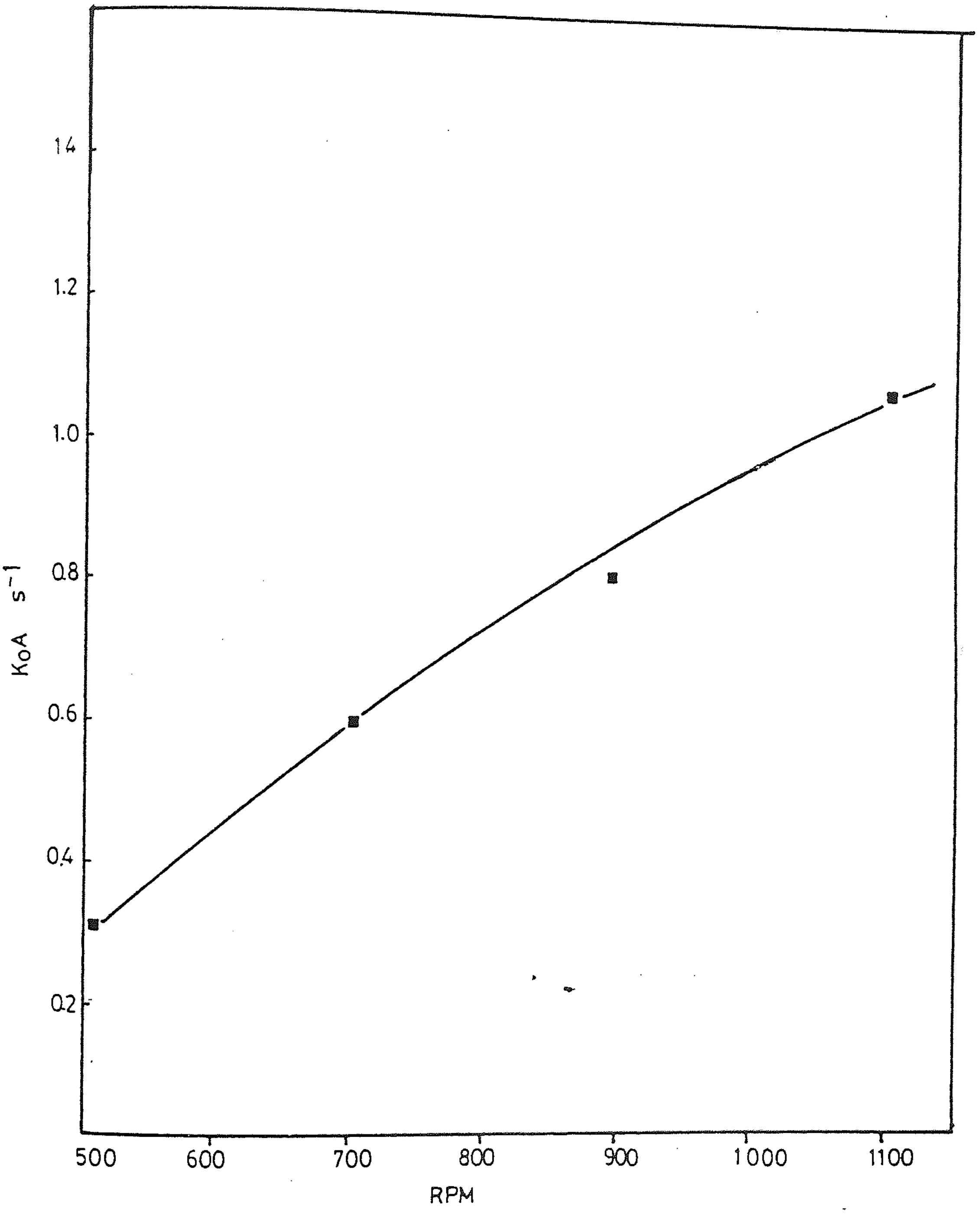


Fig 8.5 Overall mass transfer coefficient versus impeller speed for the system phosphoric acid - water - mibk. with intial acid con. = 58.9 . at . 25°C .

However, the formation of stagnant drops was not reached in this work. When phosphoric acid flow rate increases, at a fixed rotor speed (900 r.p.m.), mean drop size decreases thus increasing interfacial area. Hence the dispersed phase mass transfer coefficient might have been expected to increase. However, the continuous phase mass transfer coefficient was almost constant, since it is not a function of drop size. In fact the overall mass transfer coefficient increased.

(B) Washing Step

Washing also represents an important step in the purification process. The effect of phosphoric acid concentration in the feed solvent on the concentration of the final product is shown in Fig. 7.82. This indicates that the design and operation of the washing step is connected to those of the extraction step. The higher the initial acid concentration in the feed acid, the higher the concentration of pure product acid and therefore the less energy required for acid concentration by evaporation. Fig. 7.83 shows that the solvent:water ratio also has a considerable influence on the concentration of the final product acid. Concentration up to 55% was achieved at a phase ratio of solvent:water equal to 6:1. There was a limit above which the equipment could not be operated since solvent saturated with phosphoric acid has a density equal to or more than the density of water. At high phase ratio solvent:water and high flow rate, there was incomplete mixing in the mixer with a results that most of the organic (heavy phase) settled in the lower part of the settler.

It can also be concluded from Fig. 7.83 that one stage is sufficient to extract the acid as reported by Yacu. Curves 1, 2, 3 represent the three stage extraction in which stages 1 and 2 have no significant effect in comparison with stage 3. The higher the impurity concentration in the feed solvent the less pure the final product acid as shown in Fig. 7.86. An attempt was made to find the effect of washing the saturated solvent with acid as shown in Fig. 7.87. The idea was to find whether or not the purification step is profitable. Yacu (282) reported that six stages are required for this step, however within the experimental range studied (0 to 25% acid) the purification step is not profitable particularly if the cost of the six stages is considered, since the advantage is only marginal with reasonable phase ratios.

An attempt was also made to observe whether the colour of phosphoric acid is improved using solvent extraction. Acid was concentrated using the distillation equipment, and it became dark. The acid was then extracted using the three stage mixer settler. It was observed that the colour of the solvent layers of the three stages ranged from yellow-brown to light yellow, the first stage being darker than the second and last stages. The colour in the solvent layer did not transfer from the extract to the aqueous layer in the washing step and the solvent remained yellowish.

8.4 PHOSPHORIC ACID CONCENTRATION

Phosphoric acid was concentrated by evaporation, the usual concentration range was from 10% to about 88% by weight. Colouring of phosphoric acid during concentration only started to be noticeable at high temperature and acid concentration (120°-130°C and ∿70% acid). If the heating was continued, the colour became more obvious and at a temperature of 150°C with acid concentration around 88%, the finished product was dark brown. The first group of samples from the still were colourless, on the other hand later samples were coloured. In industry various decolouring methods are used such as adsorption treatments with active carbon and ion-exchange resins. Toyo Soda (263) described this phenomenon of colouring the acid caused by heating (see Chapter Two). MIBK, an organic solvent, under high temperature may react with the acid in the presence of oxygen and this may contribute to acid colour. The boiling point of the acid at a given pressure is a function of its concentration, the degree of concentration of the product acid can therefore be controlled by monitoring the boiling point of the bulk of the acid in the vessel as shon in Fig. 7.88 and Fig. 7.89. Impurity concentration will also increase with time and acid concentration.

The concentration step may not be necessary in the process of phosphoric acid extraction. However, its design and capacity depends directly on the phase ratio of solvent to water in the washing step.

CHAPTER NINE

PROCESS DESIGN AND SPECIFICATION

9.1 GENERAL CONSIDERATIONS

The object of this chapter is to develop a process design for phosphoric acid purification based on solvent extraction using MIBK as the extracting solvent. The equipment selected for the design is a mixer-settler chain for the reasons described in Chapter 3. Solvent extraction operations constitute only part of the plant. However, the interaction between sections of the plant affects engineering design, construction and overall economics. Thus the industrial success of a solvent extraction process may critically depend on its mode of integration into the complete plant.

9.2 GENERAL OUTLINE OF THE PROCESS

The process entails two main liquid-liquid contacting operations. The extraction of phosphoric acid together with its separation from the impurities present, and the washing of the solvent extract to transfer the phosphoric acid back into an aquoues medium and thus free the solvent for recycle as shown in Fig. 9.1. In addition the process may have a subsidiary purification, operation as proposed by Yacu (282), but this will not be considered in this process design for the reasons described in Chapter 8.

9.3 BASIS AND SUGGESTED OPERATING SCHEDULE

The process was designed to be continuous, hence it would be highly desirable to operate with few shutdowns (127), say 24 hours per day, 5 days per week (start up and shut down times are neglected).
Therefore:

Annual required output of P_2O_5 = 2.5×10^4 tonnes
Operating three shift (8 hours each) per day
Operating days per annum = 250 days
Hourly production = 4.16 tonnes P_2O_5
Final acid concentration = 90% H_3PO_4 (65% P_2O_5)

9.4 LABORATORY AND PILOT PLANT DATA

Physical solubility data and chemical specifications are presented in the appendices. Distribution coefficients and the shape of the equilibrium curve is such that a high degree of extraction can be obtained at high initial acid concentration with only a small number of theoretical stages. The mass transfer is rapid since the phases are partially miscible. Separation of the phases is fast in the solvent introductory stage, however a bigger settler is required for the acid introductory stage.

Initial impurity concentration in the feed acid is assumed to be 0.5% and with initial acid concentration recommended from the pilot plant experiments to be optimum at 63%. The optimization is related to the volume ratios of the two phases which affect the ultimate concentration of both acid and impurity, and also phase separation indirectly in both extraction and washing steps. The optimum volumetric ratio in the extraction step is 1:1, since hydrodynamic studies indicated that inversion from O/W to W/O is likely to occur during earlier start, and back inversion of the system to O/W is very difficult. It was decided to design the process at phase ratio of 2:1 feed/solvent. The phosphoric acid separated and recovered in the solvent extraction operation forms the feed to the evaporator where the dissolved solvent is to be recovered for recycle, and the product acid containing less impurity is concentrated to 90% H_3PO_4. The process entails a second distillation operation for stripping dissolved solvent from the aqueous acid. The acid leaving this unit is assumed to have a concentration equal to 63%.

9.5 PROPOSED BLOCK DIAGRAM AND MATERIAL BALANCE

The block diagram is shown in Fig. (9.1).

1. Overall Material Balance

Considering the block diagram, assume no solvent losses.

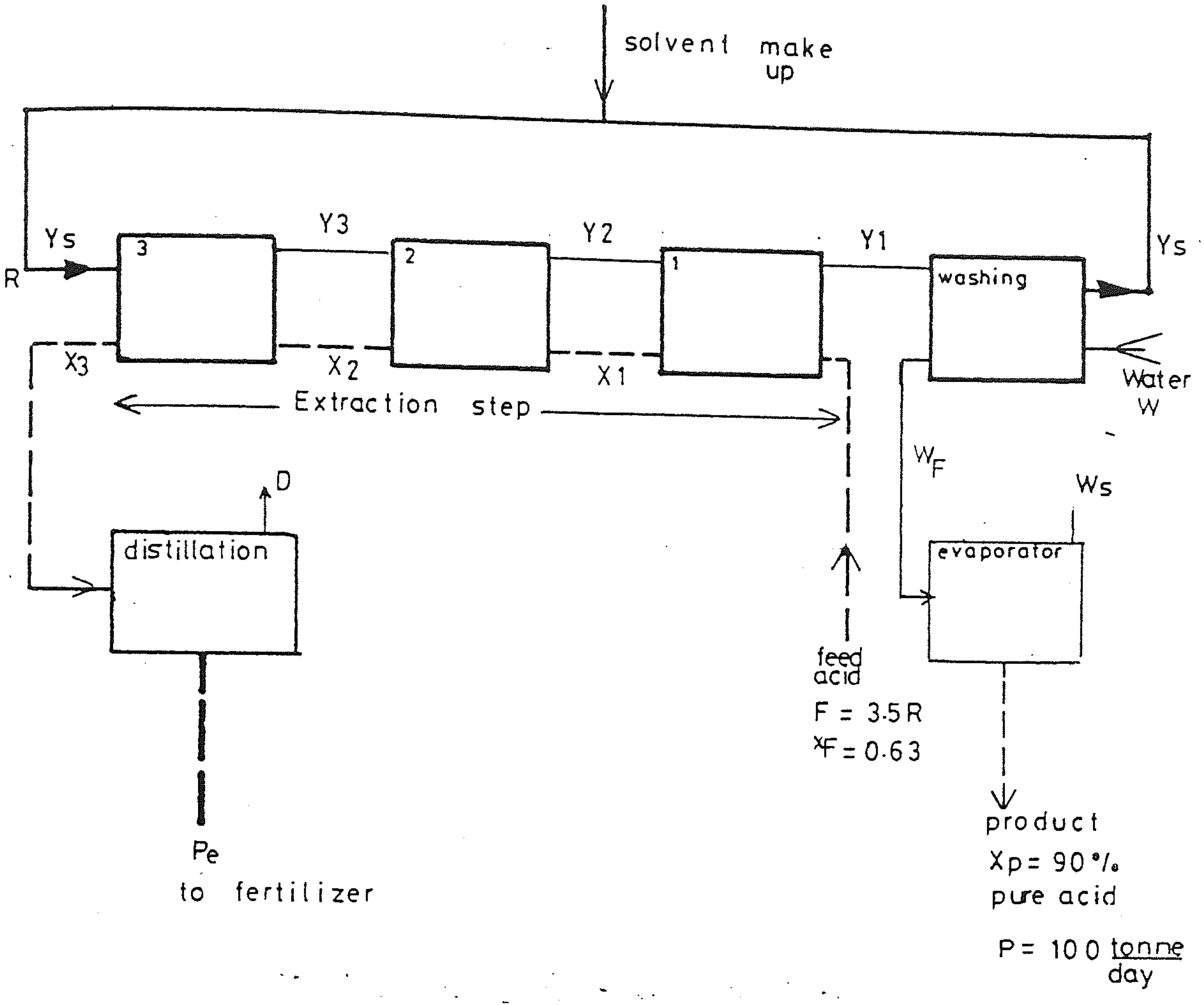


Fig 9.1 flowsheet of the solvent extraction steps in the purification of phosphoric acid.

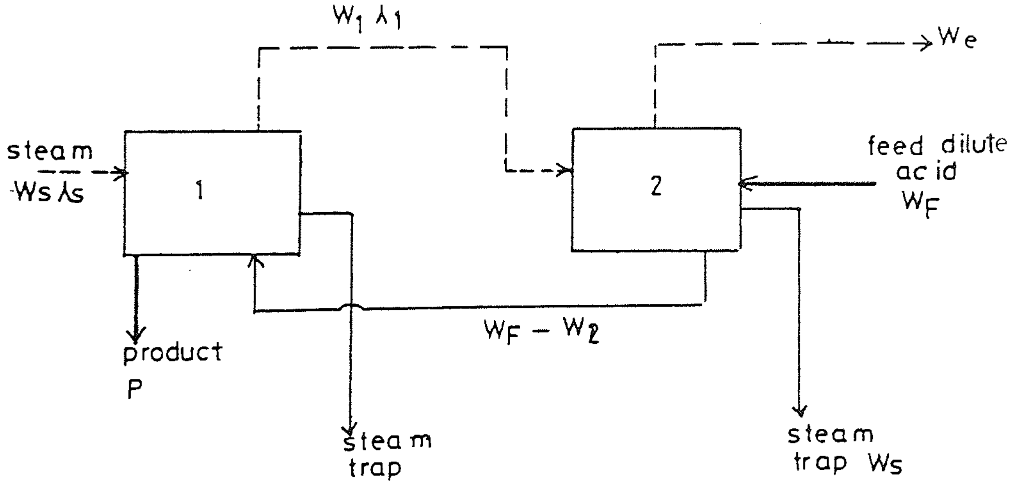


Fig 9.2 evaporation section flowsheet

(i) Total material balance

$$F + W = W_s + P + P_c + D \quad \ldots\ldots\ldots\ldots\ (9.1)$$

(ii) H_3PO_4 balance

$$(3.5R)0.63 + 0 = 0 + 0.9P + 0.63P_c + 0$$

$$2.205R = 0.9P + 0.63P_c \quad \ldots\ldots\ldots\ldots\ (9.2)$$

2. <u>Material Balance Excluding Distillation</u>

(i) Total material balance

$$F + W = W_s + P + F \quad \ldots\ldots\ldots\ldots\ldots\ (9.3)$$

(ii) H_3PO_4 balance

No water losses

$$0.63^*(3.5R) = 0.9P + (3.5R)X_3 \quad \ldots\ldots\ (9.4)$$

3. <u>Material Balance on Extraction Step</u>

(i) H_3PO_4 balance

$$(3.5R)0.63 + R.Y_s = 3.5R\ X_3 + RY_1 \quad \ldots\ (9.5)$$

(ii) H_3PO_4 balance on stage 1

$$3.5R(X_F-X_1) = R(Y_1-Y_2)$$

or $$X_F = X_1(1+\varepsilon) - \frac{Y2}{m}\,\varepsilon \quad \ldots\ldots\ldots\ldots\ldots\ (9.6)$$

where $\varepsilon = \frac{Rm}{3.5R}$

(iii) H_3PO_4 balance on stage 2

$$3.5R(X_1-X_2) = R(Y_2-Y_3)$$

or $$X_F = X_2(1+\varepsilon+\varepsilon^2) - \frac{Y3}{m}(\varepsilon+\varepsilon^2) \quad \ldots\ldots\ldots\ (9.7)$$

(iv) H_3PO_4 balance on stage 3

$$3.5R(X_2-X_3) = R(Y_3-Y_s)$$

or $$X_F-X_3 = (X_3 - \frac{Y_s}{m})(\varepsilon+\varepsilon^2+\varepsilon^3) \quad \ldots\ldots\ldots\ (9.8)$$

$$x_F - \frac{Y_s}{m} = (X_3 - \frac{Y_s}{m})(1+\varepsilon+\varepsilon^2+\varepsilon^3) \quad \ldots\ldots \quad (9.9)$$

Divide equation 9.8 by 9.9

$$\frac{X_F - X_3}{X_F - \frac{Y_s}{m}} = \frac{\varepsilon^4 - \varepsilon}{\varepsilon^4 - 1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9.10)$$

$\therefore$ with $Y_s = 0$

$X_3 = 55\%$

and from equation 9.5, $Y_1 = 29\%$

and from equation 9.4, R = 478.9 tonne/day

and volumetric flow rate of solvent = 0.4 m^3/min

required acid flow rate = 0.8 m^3/min

4. Material Balance on Washing Step

(i) Total material balance

assume no change in volume

$$R + W = W + R \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9.11)$$

(ii) H_3PO_4 balance

$$R.Y_s + W*0 = W*0.63+0 \quad \ldots\ldots\ldots\ldots\ldots \quad (9.12)$$

$W = 221 - 84$ tonne/day

$= 0.14\ m^3/min$

5. Evaporator Balance

Consider Fig. 9.2

(i) Overall mass balance

$$W_F = W_e + P \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9.13)$$

(ii) Heat balance

$$P = W_F - W_2 - W_1$$

(a) Second effect balance

$$W_2\lambda_2 = W_F(T_F-T_2)C_F+W_1\lambda_1 \quad \ldots\ldots\ldots\ldots\ldots \quad (9.14)$$

(b) First effect balance

$W_1\lambda_1 = (W_F-W_2)\ C_{av}(T_1-T_2) + W_s\lambda_s$ ..... (9.15)

from which W_F = 212.84 tonne/day

or (1955.1 lb/hr)

Total material evaporated = 63.84 tonne/day

$W_e = W_1 + W_2$ .... (9.16)

W_e = 63.84 tonne/day

= (5864.2 lb/hr)

If C_F = specific heat of feed and assumed to be (0.5 cal/G/deg°C)

= (0.5 Btu/lb/°F) by definition

∴ C_{av} = 0.45 (Btu/lb/°F)

λ = latent heat of vaporization (Btu/lb)

equations 9.14, 9.15 and 9.16 can be solved for the three unknowns.

Assumption

1. Assume feed temperature = 25°C = (77°F)
2. Steam temperature = 180°C = (356°F)
3. Assuming at first that heating areas A_1 and A_2 in both effects are equal.

The complete solution is shown in appendix 5. The results are presented here.

$A_1 = 13\ m^2 = (139\ ft^2)$

$A_2 = 13.2\ m^2 = (143\ ft^2)$

steam required = 35.07 tonne/day

= (3222.2 lb/hr)

heat of condenser = 521, 396 watts

= (1779,086 Btu/hr)

Mass of water evaporated = 20419 m^3/hr

Condenser area = 4.2 m^2

9.6 DISTILLATION COLUMN

The duty of the distillation column is to flash the solvent and concentrate the raffinate acid before it goes to fertilizer use. Yacu (281) suggests the following assumption:

(i) Reflux ratio = 1.5

(ii) Vapour speed at the top of the column
= 0.762 m/sec
= (2.5 ft/sec)

(iii) Perfect gas law is applicable

Total flow rate of the acid leaving the extraction step is equal to 69.83 tonne/hr, with acid concentration = 55%.

∴ total acid flow rate to the column = 38.406 tonne/hr

Let the final acid concentration leaving the column = 63% and assume no acid is evaporated.

∴ product = 60.96 tonne/day

It will be assumed that MIBK vapour has the same physical properties of water vapour in the calculation of column diameter, since it is very small proportion compared with the amount of water present.

Water evaporated = 69.83 - 60.96 = 8.87 tonne/hr

8.8*1000*2.205/18 = 1078 lb mol/hr

Since reflux ratio = 1.5

∴ lb moles vapour per hour at top of the column

= 1078 * (1+1.5) = 2695 lb/mol

$$\text{Vapour velocity} = 2.5 = \frac{2695 * 359 * (460+212) * 4}{3600 * 392 * \pi * d^2}$$

d = 4.5 m = (15 ft)

9.7 PROPOSED FLOWSHEET

Equipment layout and specifications are shown in Fig. (9.3).

9.8 EQUIPMENT DESIGN AND SIZING

1. Storage Tank

(i) MIBK storage tank

a. Sizing

Assume one day capacity

Assuming cylindrical tank with diameter = 10 m

Volume of MIBK per day = 593.28 m^3/day

$\therefore$ with the tank 90% full, volume of tank = 659 m^3

using two equal tanks each = 329.5 m^3

b. Duty

To provide MIBK as extracting solvent for one day's capacity, and to act as a feed tank.

c. Material of construction

Stainless steel supported by a concrete saddle

(ii) Phosphoric acid feed/storage tank

a. Sizing

Assume three days capacity distributed in three tanks. Again 90% full.

Capacity of each tank = $\frac{3467}{0.9} \times \frac{1}{3}$ = 1284 m^3

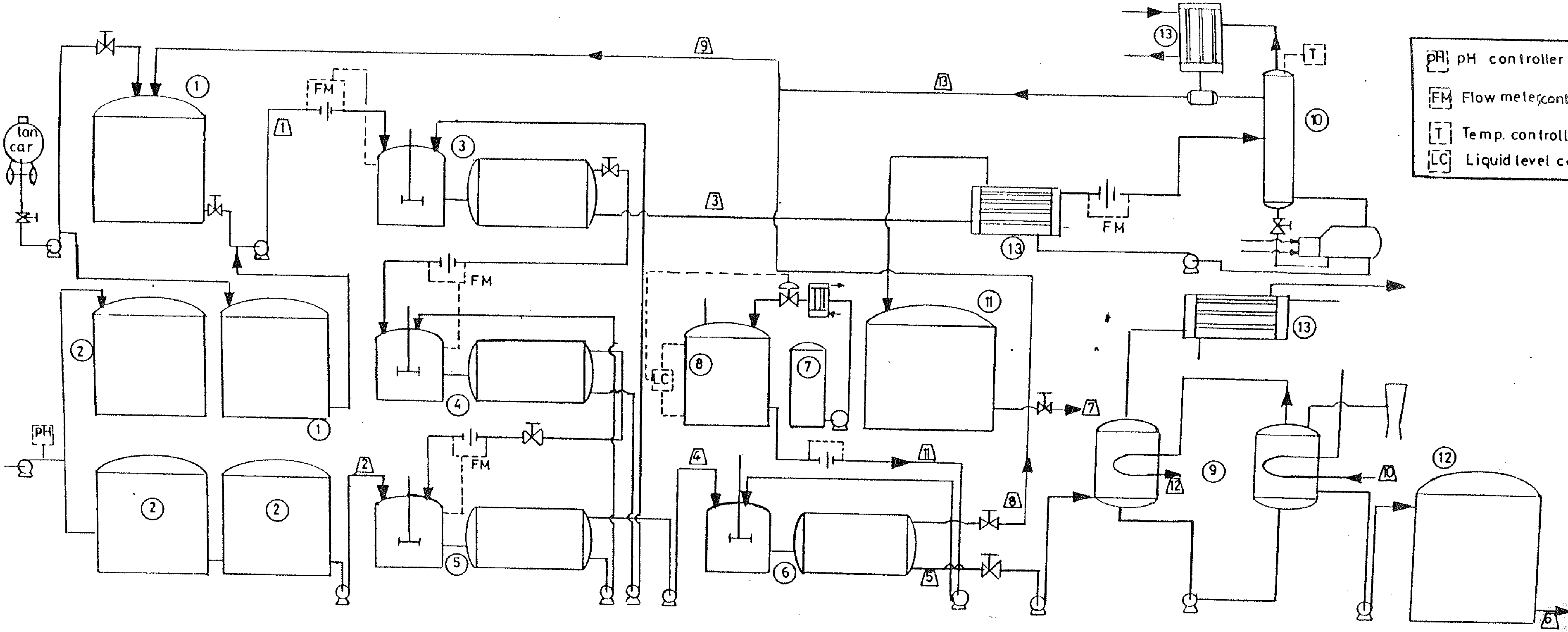
with D = 12.7 m and L = 10 m.

b. Duty

To provide three days capacity for the process.

c. Material of Construction

Stainless steel(316) supported with 4 concrete saddles.



ITEM NO.	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩	⑪	⑫	⑬
DESCRTPTION	MIBK Transfer tank	phosphoric acid transfer tank	Extraction stage one mixer-settlers	Extraction stage two mixer-settlers	Extraction stage three mixer-settler	Washing step mixer-settler	Water still	Water stoarge tank	Evaporator-steam operated	Distillation col.	product raff. imp. acid stoarge tank	Pure acid product tank	Heat exch.
SIZE or Area	each has vo. 329.5 m^3	each has vo 1284 m^3	each 7 m^3, 28 m^3	7 m^3 + 21 m^3	7 m^3 + 14 m^3	3.5 + 10.5	—	1182.4 m^3	each 13 m^2	15 m diameter	no. required 3 each 1284	413.8 m^3	—
MATERIAL OF CONST.	st. steel	st. steel	st. steel	st. steel	st steel	st steel	tinned copper	tinned copper	carbon/graph	—	st. steel	st steel	—
COST IN £	41560	133 685	92688 4585	92688 3847	92688 3000	9368	—				133685	41 700	17236
LINE NO.	1	2	3	4	5	6	7	8	9	10	11	12	13
LIQUID	mibk feed line the pump has 0.7 hp	acid feed line, pump has 2.5 hp	final raff. acid from ext. step	final ext from ex. st. 28% acid	final pure acid to con. step. 63%	product pure acid 90% acid	to fertilizer, sat. with impurities	recycle solvent	total recycle solvent	steam at 180°C	water supp. to the washing st.	steam trap	recovered solvent

Fig 9.3 Equipment flow sheet phosphoric acid purification plant.

(iii) Product tank

a. Sizing

Total product = 74.5 m^3/day [illegible] in Table 9.1

Assume one week capacity and 90% full.

$\therefore$ the tank will have capacity = 413.8 m^3

and dimensions D = 8 m

L = 8 m

b. Duty

To store the feed acid on site after purification.

c. Material of Construction

Stainless steel, supported with 4 concrete saddles.

(iv) Raffinate and feed to the fertilizer plant

a. Size

Water required for washing = 212.8 tonne/day

Assume one week capacity, 90% full

The size required = 1182.45 m^3

With D = 11.4 m and L = 11.4 m.

b. Duty

To store and provide water for washing step.

c. Material of construction

Stainless steel suported with 4 concrete saddles.

2. Pump Design

The size and duty of each pump is shown in Table 9.1 and their sizes are calculated in the appendix.

TABLE 9.1

	Type and Duty	No. Required	Capacity and Horse Power
i)	MIBK transfer pump centrifugal explosion proof pump	1	0.45 m^3/min (100 gal/min) with 1.49 kw (2 hp) motor
ii)	Acid transfer pump, to transfer acid from tank car to storage tank (centrifugal pump)	2	0.45 m^3/min (100 gal/min) 2.60 kw (3.5 hp)
iii)	Water pump to transfer water from still to storage tank. (centrifugal pump)	1	0.159 m^3/min (35 gal/min) 1.86 kw (2.5 hp)
iv)	(MIBK) feed pump to transfer solvent to the extraction battery (centrifugal pump)	1	0.494 m^3/min (08.8 gal/min) 0.521 kw (0.7 hp)
v)	(H_3PO_4) feed pump to transfer phosphoric acid of 63% concentration to the extraction battery (centrifugal pump)	2	0.961 m^3/min (211.3 gal/min) 1.86 kw (2.5 hp)
vi)	Interstage pumps, explosion proof to transfer the acid between stages	3	0.961 m^3/min (211.3 gal/min) 1.49 kw (2 hp)
vii)	Water feed pump to transfer water to the washing step (centrifugal pump)	1	0.176 m^3/min (38.85 gal/min) 0.372 kw (0.5 hp)
viii)	Other pumps for evaporator	3	Assumed to be 0.7455 kw (1 hp)

3. Design of Mixer-Settler Units (EXTRACTION SECTION)

(a) Mixer

It will be assumed that the level of the liquid in the mixer is equal to the tank diameter.

Flow rate in ton/day of acid = 1676.15

= 1.163 ton/min

If Q = flow rate in m^3/min = $\frac{1.163}{1.45}$ = 0.8 m^3/min

MIBK flowrate = 0.41 m^3/min

Assume 5 min residence time and the mixer 90% full

$\therefore$ total capacity of mixer = 7 m^3

The number of mixers required for three stages are 3 units made of stainless steel.

(b) Settler capacity

The process requires three different size settlers for phase separation, the size of each settling tank can be related to the corresponding mixer. Therefore (i) acid introductory stage, where the density difference between phases is very small and the phases require longer time for settling, the settler capacity will be assumed to be 4 x mixer capacity = 28 m^3; (ii) Intermediate stage will be assumed to have a settler = 3 x mixer capacity = 21 m^3, while (iii) the settler for the solvent introductory stage will be assumed to have a volume = 2 x mixer capacity = 14 m^3.

4. Design of Mixer-Settler Unit (Washing Step)

Only one single stage has been found to be required for back extracting the acid from solvent.

Mixer Size

Water flow required = 212.84 ton/day

= 0.147 m^3/min

Solvent leaving the extraction unit = 0.412 m^3/min

Total flow rate = 0.559 m^3/min

Assume 5 mins contact time

$\therefore$ volume of mixer = 5 x 0.559 = 2.795 m^3

Assume the mixer is 80% full with D=L

$\therefore$ total capacity of mixer = 3.5 m^3

with D=L=1.64 m

Settler Capacity

From the pilot plant equipment design it was found that one mixer volume was sufficient for phase separation at the design flow rate.

$\therefore$ settler volume will be made equal to 3 x mixer volume

= 10.5 m^3

5. Impeller Design

For extraction step.

Assume that mixer diameter = $D_T = 3 \times D_A$

$\therefore D_A = 0.69$ m

Since pilot plant results have been satisfactory and gave an optimum at about 900 r.p.m., it is necessary how to predict the agitator speed in a geometrically similar production size unit using a suitable rule for scale up. The two liquids will have the same properties in both pilot plant equipment and full scale equipment. The following equation can be used

$$N_1^3 D_{A_1}^2 = N_2^3 D_{A_2}^2$$

$$(900)^3 * (0.035)^2 = N_2^3 (0.69)^2$$

$$N_2^3 = \frac{(900)^3 (0.035)^2}{(0.69)^2} \sim 123 \text{ r.p.m.}$$

$$\sim 2.05 \text{ r.p.s.}$$

$$Re = \frac{D^2 N \rho}{\mu} = \frac{(2.26)^2 (2) * 87.44}{0.00537}$$

$$\sim 167770$$

The power consumption = $P = (\frac{K}{gc}) \rho N^3 D^5$

where K = constant = 6.3 for turbines

$$P = (\frac{6.3}{32.2}) (87.44) (2)^3 (2.26)^5$$

$$P = (8069.13 \text{ ft-lb/sec})$$

$$P = (15 \text{ hp})$$

$$\sim 11.17 \text{ kw}$$

The power required to drive the turbine in the washing section can also be calculated by scaling up the pilot plant mixer. Assuming water properties

$$(900)^3 (0.035)^2 = N_2^3 (0.54)^2$$

$$N_2^3 = \frac{(900)^3 (0.035)^2}{(0.54)^2}$$

$$N_2 = 1.6 \text{ r.p.s.}$$

$$P = (\frac{6.3}{32.2}) (62.4) (1.6)^3 (1.62)^5 = (1.1 \text{ hp}) = 0.82 \text{ kw}$$

9.9 INSTRUMENTATION AND CONTROL

The phosphoric acid purification flowsheet is a typical solvent extraction process with recycle streams which require the maximum number of primary automatic control loops (on flow level and in some instances temperature). Free flow by gravity between stages is needed, however since the solvent circulates in a closed cycle, a solvent metering point is required. A metering device is also required between the extraction and washing batteries of the process. Electromagnetic flow meters may be used in a pipe of a large diameter, with low pressure head available and under corrosive conditions. Alarms or controlling transmitters may be used for liquid level control. Most of the instrumentation and control points are shown in the proposed flow chart.

CHAPTER
TEN

ECONOMIC EVALUATION OF THE PROCESS

10.1 INTRODUCTION

The design study has been concerned with the extraction of phosphoric acid, however the proposed design cannot be justified if the process is not profitable. The economic evaluation of the proposed process involves the acquisition of capital and operating cost data. Many techniques of cost estimation are available (260). Since the sum of the percentage costs for process equipment and process piping shows relatively little variation with the size of the plant and the type of process, the technique suggested by Lang for arriving at a quick approximation of cost of a plant was chosen. This was compared with the functional unit cost approach. Many cost indices exist, but the international EPE plant cost index is recommended for use with the chemical industry (34,260).

10.2 EQUIPMENT CAPITAL COST

10.2.1. COST OF STORAGE TANK

A. Solvent feed tank

There are two tanks each has the capacity of $329\ m^3$. Bridgwater and Mumford (34) propose general equations relating the cost of the equipment to its volume. The equation for a tank is

$$C = K.632\ (V_m)^{0.44} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10.1)$$

Based on January 1978 costs

where V_m = volume in m^3

K = factor relating to the material of construction of the tank = 2 for stainless steel

Up date to 1981

$$C = 2 \times 632 \times (329)^{0.44}\ \frac{(385)}{(300)}\ \frac{(1981)}{(1978)}$$

$$= £20,780$$

Cost of two tanks = £41,560

B. Phosphoric acid feed tanks

There are three tanks each of volume = $1284\ m^3$

Using the equation

$$C = 65.3\ (V_m)^{0.78} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10.2)$$

Up dated to 1981

$$C = 2 \times 65.3\ (1284)^{0.78} * \frac{(385)}{(300)}$$

$$= £44561.8$$

For three tanks = £133,685

C. Final raffinate storage tanks

These are taken to be the same as the phosphoric acid feed tanks and therefore they have equal cost

= £133,685

D. Product Tank

One tank made of stainless steel of capacity

$= 413.8 \text{ m}^3$

Cost $= 2 \times 632 \times (413.8)^{0.44} (\frac{385}{300})$

= £22,986

E. Water storage tank

Cost $= 2 \times 65.3 \times (1182.45)^{0.78} (\frac{385}{300})$

= £41,700

Total cost of storage tanks = 41,560 + 133,685 + 22,986 + 41,700

= £373,616

10.2.2 COST OF MIXER-SETTLERS (EXTRACTION STEP)

A. Cost of stage one including mixer, settler, motor agitator exclusing pump. Bridgwater and Mumford correlation can be used:

$C_{M1} = 2 \times (1522)(6.05)^{0.4} (\frac{385}{300})$

= £9269

Cost of the settler, assumed to be a normal stainless steel tank of capacity $= 28 \text{ m}^3$

$C_{S1} = 2 * 234 (28)^{0.61} (\frac{385}{300})$

= £4585

Total cost of stage 1 = £9269 + £4585 = £13,854

B. Cost of stage two

The mixer has the same dimension and capacity, therefore its cost = C_{M2} = £9269

Cost of settler $C_{S2} = 2 \times 234\ (21)^{0.61}\ \frac{(385)}{(300)}$

= £3847

Cost of stage 2 = £3847 + £9269 = £13,116

C. Cost of stage 3

$C_{M3} = 9269$

$C_{S3} = 2 \times 234\ (14)^{0.61}\ \frac{(385)}{(300)}$

= £3004

Cost of stage 3 = £3004.16 + £9269

= £12,273

10.2.3 COST OF A MIXER-SETTLER (WASHING STEP)

Volume of mixer = 3.5 m^3

Bridgwater correlation is not available for mixer size less than 5 m^3. The cost of the mixer can be found by using both the 2/3 rule and Bridgwater correlation. Cost of 5 m^3 mixer = $1 \times 1522 \times (5)^{0.48} \times \frac{(385)}{(300)}$

= £4229

By 2/3 rule (260)

$$\frac{\text{Cost of A}}{\text{Cost of B}} = \left(\frac{\text{Size of A}}{\text{Size of B}}\right)^{0.67} \quad \ldots\ldots\ldots\ldots\ldots\ (10.3)$$

Cost of 3.5 m^3 mixer = $4229 \left(\frac{3.5}{5}\right)^{0.67}$

= £3330

Settler volume = 10.5 m^3

cost = £6038

Cost of mixer-settler = £9368

10.2.4 PUMPS

Bridgwater and Mumford recommended the following equation for costing the pumps.

$$\text{Cost} = 266.7(V_m)^{0.4} \times \text{cost index}$$

$$= 266.7(V_m)^{0.4} \times \frac{385}{300}$$

A. Cost of interstage pump in extraction section.

Five pumps each capable of delivering 47.9 m^3/hr.

$$\text{Cost of each pump} = 266.7(47.9)^{0.4} \times \frac{385}{300}$$

$$= £1609 \text{ each}$$

Cost of five pumps = £8045

B. Cost of solvent transfer pump

$$C = 266.7(22.71)^{0.4} \left(\frac{385}{300}\right)$$

$$= £1193$$

C. Cost of solvent feed pump

$$C = (266.7)(24.70)^{0.4} \times \frac{385}{300} = £1234$$

D. Pump to water storage tank, its cost

= £1190.

E. Water feed pump to washing section

$$\text{Cost} = 266.7(8.8)^{0.4} \left(\frac{385}{300}\right)$$

$$= £817$$

F. Cost of solvent recycle pump

$$\text{Cost} = 266.7(24.7)^{0.4} \left(\frac{385}{300}\right)$$

$$= £1234$$

G. Other pumps (6) including evaporator pumps

these are assumed to have a cost of £6000 (total)

Total cost of pumps = £8045 + £1193 + £1234 + £1190

+ £817 + £1234

= £13713

10.2.5 HEAT EXCHANGERS

Assume there are six heat exchangers in the plant. Their respective costs were determined by the correlation presented by Bridgwater.

Cost of 15 m^2 $C = 2 \times 561(15)^{0.57} (\frac{385}{300})$

$= £6740.6$

$\therefore$ cost of 4.2 m^2 exchanger using the 2/3 rule

$= 6740.6 \times (\frac{4.2}{15})^{0.67}$

$= £2873$

Cost of six heat exchangers = £17,238

10.2.6 EVAPORATOR COST

Two-effect evaporator, each has an average area

13.19 m^2

Cost $= 2 \times 561(13.19)^{0.57} (\frac{385}{300})$

$= £6265$

Cost of the two units $= 2 \times 6264.8 = £12,530$

10.2.7 DISTILLATION EQUIPMENT

The diameter of the column = 15 ft

Yacu (281) estimated the cost of 19.6 ft column to be £70,000, using 2/3 rule:

$$\text{Cost of 15 ft column} = 58515 \times \left(\frac{385}{300}\right)$$

$$= £75,094$$

10.2.8 TOTAL EQUIPMENT COST

Table 10.1 summarises the total equipment cost.

Plant Equipment	No.	Remarks	Cost in £
Storage and Feed Tanks	10	Capacity varies from one day to three days. Made of stainless steel	373,616
Mixer-Settler (Extraction Step)	3	Including motor (explosion proof), mixer volume for all stages = 6.05 m^3. Capacity of settler stage 1 = 28 m^3, stage 2 = 21 m^3, stage 3 = 14 m^3	39,242
Mixer-Settler (Washing Step)	1	Mixer has volume = 3.5 m^2, settler capacity = 10.5. Provided with motor (explosion proof)	9,368
Pumps	16	Their prices vary with capacity	13,714
Heat Exchangers	5	Assumed to have the same price, their price was based on their heat transfer area	17,236
Evaporator	2	Capable of concentrating phosphoric acid from 63% to 95%	12,529
Distillation Column	1	Used for recovering the solvent from the raffinate and concentrate the acid to its original concentration of 63%	75,094

Total Equipment Cost = £540,800

10.3 TOTAL FIXED INVESTMENT

10.3.1 LANG FACTOR APPROACH

This factor expresses the remaining direct and indirect costs as a function of equipment cost. The values used for fluid processing plant are given in Table 10.2 and the Lang factor was found to be 3.65.

Total fixed investment = 3.65 × 540,800 = £1,973,920

say £2m

Table 10.2 Derivation of Lang Factor for Phosphoric Acid Extraction Plant

	Range E	Typical Value for Fluid Processing Plant	Percentage of E
Direct Costs			
Delivered equipment, E	E	100	100
Equipment installation	0.18-1.0E	46	40
Instrumentation and Control	0.06-0.2E	18	15
Piping (installed)	0.09-0.6E	66	35
Electrical (installed)	0.06-0.35E	11	11
Buildings	0.15-1.2E	18	20
Site improvement	0.04-0.25E	10	10
Service facilities	0.1-1.0E	70	15
Land	0.02-0.1E	6	4
Total Direct Plant Cost	0.7-4.7E	345	250
Indirect Costs			
Engineering and supervision	0.15-0.6E	33	30
Construction expenses	0.15-0.6E	41	40
Total Direct and Indirect Cost		419	320
Contractors fee		21	15
Contingency		42	30
Fixed capital investment		482	365
Lang factor		4.82	3.65

10.3.2 FUNCTIONAL UNIT OR STEP-COUNTING APPROACH

A functional unit is a significant step in a process and includes all equipment and ancillaries necessary for operation of that unit. Bridgwater and Mumford (34) define the functional unit as a unit operation, unit process or separation method that has energy transfer, moving parts and/or high level of internals. All process streams are considered including side and recycle. For this process four functional units are proposed, namely extraction of acid, washing the solvent, solvent recovery column and acid concentration evaporator.

A number of correlations and procedures have been devised. One correlation is recommended by Bridgwater:

$$C = K.N\left(\frac{Q}{S^{0.5}}\right)^{0.85}\left(\frac{T.n_1}{N}\right)^{-0.17}\left(\frac{P.n_2}{N}\right)^{0.14} F_m \; \frac{\text{EPE Cost Index}}{100} \quad \ldots\ldots\ldots\ldots\ldots \; (10.4)$$

(where the symbols are presented in nomenclature)

$$C = 5.5\times4\times\left(\frac{25,000}{(0.086)^{0.5}}\right)^{0.85} (1.1) \; \left(\frac{385}{100}\right)$$

$$C = 5.5\times4\times(15527)(1.1)(3.85) = £1,446,650$$

The values of £2M will be used since it is more analytical.

10.4 OPERATING COSTS

Variable or operating costs comprise all recurrent costs directly or indirectly incurred in purification of the acid. It is common practice to express the total operating cost in terms of the raw material, direct labour, energy (or utilities) and fixed capital cost.

10.4.1 RAW MATERIAL COST

The process for the extraction of the wet process phosphoric acid may be considered to be part of a large chemical plant complex for production of wet process phosphoric acid from phosphate rock. However in this work it is assumed to be a separate unit, requiring wet process acid as the main raw material.

Solvent make-up can be reduced by minimising:

1. Solvent losses by evaporation, through imperfections of the venting system
2. Solvent in stability - MIBK found to be stable solvent
3. Solvent losses due to imperfections of the solvent recovery operation
4. Mechanical losses, due to faulty operation, e.g. spillage, vessels left open, etc.

For practical costing purpose a certain quantity of solvent make up must be assumed. This is taken as 1% for MIBK. Based on a solvent cost of £320/tonne this loss becomes £382400/year.

The cost of agricultural grade phosphoric acid 52-54% P_2O_5 is £200* per tonne. From the material

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* Process Economics International, Vol.11, No.3, Spring 1981

balance the total feed acid required is 41825 tonne/year, which costs £83.65 x 10^6, to this must be added the cost of methyl iso butyl ketone (solvent) makeup.

$\therefore$ total raw material cost = £84.03x10^6 per year

10.4.2 LABOUR COST

The direct operating labour costs for a chemical process may be expressed as given by Bridgwater as $L = 2.600.N.Q^{-0.87}$ per year, where N is the number of functional units and Q is the plant capacity (tonne p.a.).

$$L = 2600 \times 4\ (2.5\times10^4)^{0.13} \times (\frac{385}{248})$$

$$= £60,224$$

This would allow for three men per shift with one spare man.

10.4.3 ENERGY (UTILITIES) COTS

For a continuous chemical process, energy cost can be assessed roughly by a short cut method using the correlation suggested by Bridgwater:

$$E = 0.39\ I^{0.75} \times (Q)^{0.25}\ (N)^{0.77} \ldots\ldots\ldots\ldots \quad (10.5)$$

where E = total energy cost (£ per year)

$$I = \frac{\text{Capital Cost (£)}}{\text{EPE index based on 100 in 1970}}$$

up dating the data

$$E = 0.39(\frac{2\text{x}10^6}{385})^{0.75}\ (4)^{0.77}\ (2.5\times10^4)^{0.25}$$

$$E = £8725 \text{ per year}$$

10.4.4 TOTAL OPERATING CHARGES

In addition to the three principal direct costs as calculated above, the remaining constituent elements of the operating cost including fixed costs (rates, rent, taxes) indirect costs (safety, general overheads, research and development, etc.) and administration and distribution costs may be expressed as a function of raw material, direct labour, energy and the fixed investment costs. Evaluation of the total operating cost is shown in Table (10.3) using the method described by Bridgwater.

Table 10.3 OPERATING COST ESTIMATION

	Range	R	L	E	CI
Direct Cost					
1. Raw materials		1.0			
2. Energy				1.0	
3. Labour			1.0		
4. Supervision	0.1L-0.25L		0.15		
5. Pay roll charges	0.15-0.5(3+5)		0.575		
6. Maintenance	$0.02C_1$-$0.15C_1$				0.04
7. Operating supplies	$0.005C_1$-$0.01C_1$				0.005
8. Laboratory	0.03L-0.2L		0.05		
9. Royalty	0-0.65* = zero assumed own process				
sub total		1.0	1.775	1.0	0.085
10. Contingency	0.01-0.1(1→9)	0.01	0.08	0.05	0.002
Indirect Costs					
11. Rates	$0.02C_1$-$0.04C_1$				0.025
12. Insurance	$0.004C_1$-$0.02C_1$				0.008
13. Administration	0.01-$0.04C_1$				0.03
14. Research	$0.015s^*$-$0.055s^*$			0.045	
15. Distribution and selling	$0.021s^*$-$0.2s^*$				
sub total	0.01→0.05(11→15)				0.063
16. Contingency	0.01→0.05(11→15)				0.0031
Total		1.01R	1.855L	1.05E	0.113

s^* is the selling price of the product which may be approximated as 1.3 (O_p) where O_p is the total operating cost.

Fixed operating cost = $1.355L + 0.108C_1 + 0.04(1.3(0))$

$$\ldots\ldots\ldots\ldots \quad (10.6)$$

$$O_{fix} = 1.956L + 0.113C_1$$

$$O_{fix} = 117798.14 + 223052.2$$

$$O_{fix} = £340\ 850/\text{year}$$

The variable operating costs include raw materials services and solvent make-up.

Total variable cost = $1.01R + 1.05E + 0.005C_1 + 382400$

$$\ldots\ldots\ldots\ldots \quad (10.7)$$

$$= £85\text{x}10^6/\text{year}$$

10.4.5 DEPRECIATION AND TAXATION

Depreciation and taxation are interrelated and affect costs and profitability of the venture. The assessment of each is financially complex and left to the accountants of the company to minimise overall tax. The following values can be assumed.

(a) 50% corporation tax is imposed on gross profit payable in three years following the time of imposition.

(b) A linear rate of depreciation of capital equipment is assumed over an operating life of 8 years with a sum of 5% of the initial investment being recoverable as scrap value at the end of this period. Inflation may affect the above assumptions.

10.5 PROCESS EVALUATION

An economic evaluation of the phosphoric acid purification plant is essential to ensure that adequate returns are obtained from the capital employed. The level or degree of return may be assessed as a percentage rate of return, in money or cash terms, or in time units.

10.5.1 RETURN ON INVESTMENT (ROI)

This can be represented approximately as

$$\frac{\text{profit (before tax)}}{\text{tangible assets (fixed + variable)}} \times 100$$

Taking the manufacturing cost as the sum of (fixed + variable) costs. The net income for a given year is the difference between the income and expenditures at that year. The following assumptions or conditions were used in the calculation of ROI.

1. Estimated life time = 8 years
2. 5% of initial investment being recovered as scrap = £100,000
3. The plant operates at 80% capacity in the first year and at full capacity for the remainder of its life
4. The variable operating cost and the fixed cost was taken as constant for 8 years
5. Capital investment = £2M
6. Selling price of pure product = £280 per tonne

7. Selling price of impure product (raffinate) phase saturated with impurity = £190 per tonne

From Table 10.4

$$\frac{\frac{10^6}{8} \times (-0.34+1.06+1.06+1.06+1.06+1.06+1.06+1.06)}{2000000}$$

ROI = 44%

and ROI after tax = 26%

The project seems attractive if this value is compared to a minimum acceptable rate of return of 20%. However it requires re-examination of the cash flow data using other profitability criteria. Also from Table 10.4 the NPW = £1.5M.

10.5.2 PAY BACK TIME

The time to recover the total investment is known as pay back time. This is found to be 3.9 years after tax.

Year	Capital Cost	Fixed Op. Cost £	Variable Op. Cost £	Annual Output tonne	Income from Pure Acid £	Income from Impure Acid £	N.C.F. before Tax £	Tax Allowance	Taxable Profit	50% Tax	N.C.F. after Tax	Discount Factor at 25%	Present W'th £M
0	2000,000						-2M	0	-		-2M		
1		$-0.34x10^6$	$-85x10^6$	20,000	$5.6x10^6$	$79.4x10^6$	-.34M	0.24M	-0.1	0	-0.34M	0.8	-0.272
2		$-0.34x10^6$	$-85x10^6$	25,000	$7.0x10^6$	$79.4x10^6$	+1.06M	0.24M	+0.82M	0	+1.06M	0.64	+0.6784
3		$-0.34x10^6$	$-85x10^6$	25,000	$7.0x10^6$	$79.4x10^6$	+1.06M	0.24M	+0.82M	-0.41M	+0.651M	0.512	+0.334
4		$-0.34x10^6$	$-85x10^6$	25,000	$7.0x10^6$	$79.4x10^6$	+1.06M	0.24M	+0.82M	-0.41M	+0.651M	0.409	+0.2658
5		$-0.34x10^6$	$-85x10^6$	25,000	$7.0x10^6$	$79.4x10^6$	+1.06M	0.24M	+0.82M	-0.41M	+0.651M	0.327	+0.212
6		$-0.34x10^6$	$-85x10^6$	25,000	$7.0x10^6$	$79.4x10^6$	+1.06M	0.24M	+0.88M	-0.41M	+0.651M	0.262	+0.1703
7		$-0.34x10^6$	$-85x10^6$	25,000	$7.0x10^6$	$79.4x10^6$	+1.06M	0.24M	+0.82M	-0.41M	+0.65M	0.209	+0.135
8		$-0.34x10^6$	$-85x10^6$	25,000	$7.0x10^6$	$79.4x10^6$	+1.06M	0.24M	0.82M	-0.41M	+0.65M	0.167	+0.108
9							+0.1M	0	0.1M	-0.41M	-0.31M	0.134	-0.041
10										-0.05M	-0.05M	0.107	-0.0053

TABLE 10.4 EVALUATION OF NET CASH FLOW

10.6 BASIC EQUATIONS FOR PROCESS OPTIMIZATION AND MODELLING

10.6.1 PROCESS OPTIMIZATION

The total annual manufacturing cost for extraction of phosphoric acid processes can be taken as the sum of all step costs.

$$\beta_T = \beta_e + \beta_D + \beta_W + \beta_S + \beta_L + \beta_C + \beta_V \quad \ldots\ldots \quad (10.8)$$

β_T = Annual cost of the process
β_e = Annual cost of the extraction unit
β_D = Annual cost of the distillation unit
β_W = Annual cost of solvent recovery (washing step)
β_S = Annual cost of the cost solvent
β_L = Annual cost of labour
β_C = Annual cost of product concentration
β_V = Annual value of unextracted, unrecovered acid as a function of feed acid cost

The mathematical equation and the quantity to be optimised of each of these factors is presented in Table (10.5 and 10.6)

The cost of a distillation operation is made up of three items:

1. The annual fixed charges agains the installed cost of the distillation column and its internal (sieve trays, bubble cup trays, packing or both).
2. Annual fixed charges against the cost of the heat exchange surface in the condenser and reboiler.

3. Annual cost of the heat needed to produce the steam in the column plus the cost of the water needed to condense the stream at the top of the column.

For a mixer-settler the quantity of solvent lost is proportional both to the solvent circulation rate and the number of stages. For tower-type extractors, the loss is more likely to be proportional only to the circulation rate.

Table (10.5) - SUMMARY OF THE BASIC MATHEMATICAL EQUATIONS FOR PROCESS OPTIMISATION

Cost Factor	Equation
β_e	$= n_E c_E / Mo_E$ where

$$\frac{Y_S}{M_E}\left(1 - \frac{1}{M_E R_E}\right) \qquad n_E = \frac{\log\left(X_A - \left(\frac{Y_S}{M_E}\right)\left(1 - \frac{1}{M_E R_E}\right) + \frac{1}{M_E R_E}\right)}{\log M_E R_E}$$

and

C_E = Annual cost per stage (£/year)

$C_E = CV_E\left(\frac{P}{Y} + b\right) + (P_A + P_p)WH$

P = 1.0 + cost of instruments, piping and installation as a function of CV_E

CV_E = purchase cost of main equipment in £

W = cost of power (£/kw)

H = hours of operation/year

Y = pay out time/year

$P_A + P_p$ = power requirement for pump and agitator (kw)

b = Annual maintenance costs as function of equipment costs

$CV_E = f(Q)$

TABLE (10.5) - continued

Q = is the total volume rate of the phases, and this is proportional to the area of a settler (m^3/h)

$CV_E = K.a^x$

in terms of solvent/feed ratio

$CV_E = K.(q_F(R_E+1)/V_C+V_D)^X$

$C_E = K.(q_1=(R_EH)V_C+V_D)^X + (P_A+P_P)W.H.$

where X = constant

Q_F = feed flow rate (m^3/h)

β_D

$$= \frac{C_1N(1+R)}{EYGa} + \frac{C_2(1+R)}{YG_b} + C_3(1+R)$$

where

C_1 = annual incremental unit investment cost

N = number of plates

E = fractional plate efficiency

R = reflux ratio

Y = hours/year operation

Ga = allowable vapour velocity

C_2 = annual incremental unit investment cost in condenser and reboiler

Gb = vapour handling capacity of the condenser and reboiler equipment combined

Gb = $UDT/2L_V$
where L_V = latent heat of vaporisation of MIBK

C_3 = cost of steam and coolant to vaporise and condense respectively (£/year)

β_W

As in the case of the extraction section

$$= n_sC_s/\zeta_{os}$$

where

$$n_s = \frac{\log(\frac{Y_c}{Y_s}(1-\frac{1}{M_wR_w})+\frac{1}{M_sR_s})}{\log M_sR_s}$$

and

$$C_s=Cv_s(\frac{P}{Y}+b)_w + P_A+P_p)_wW.H$$

TABLE (10.5) - continued

β_s $= (\frac{n_E}{\zeta o_E} + \frac{n_p}{\zeta o_w})$. solvent rate $X\ell XsXHXR$

where ℓ = fraction losses

s = value of solvent (£/tonne)

β_c $= P(1+X_p).(X_F-X_p)C_p$

where
C_p = cost of concentrating one g. of accid by 1% in £

β_v $= RX_n*F*H$

where
F is unit cost per (g.mole)

10.6.2 MODELLING EQUATION

A dynamic mass balance on the cascade can be written by considering Fig. (10.1) with each mixer-settler stage as one unit with a volume equal to the volume of the mixer and the settler.

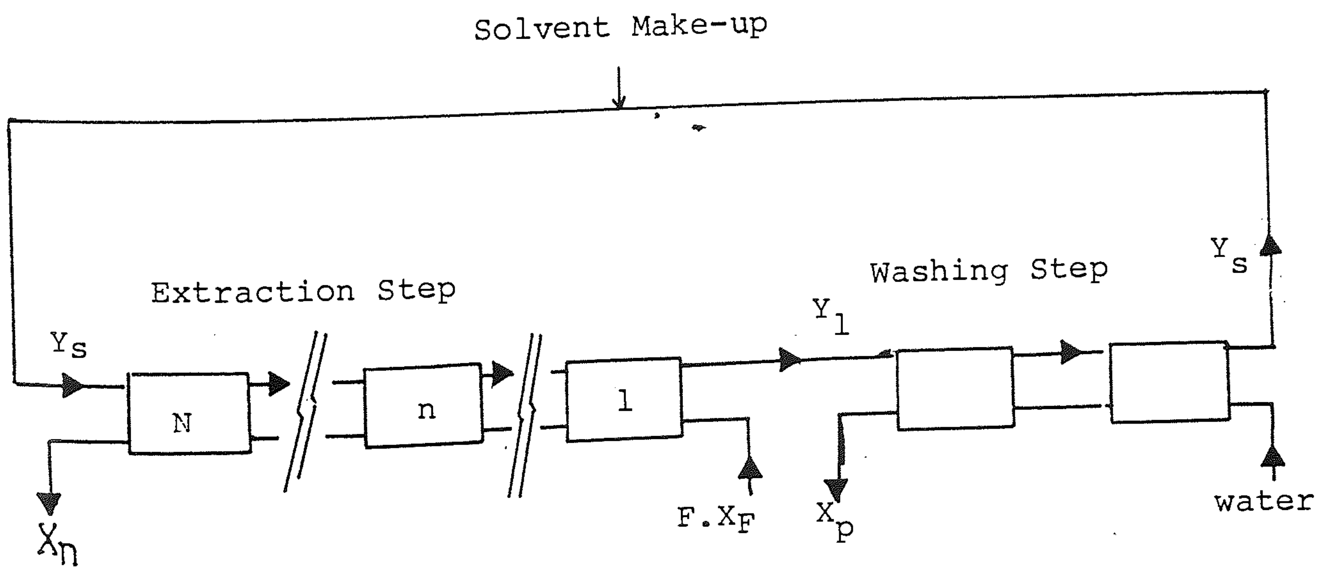

Fig. 10.1 Flow Diagram for Phosphoric Acid Extraction

TABLE 10.6 - QUANTITY TO BE OPTIMIZED

	Cost of Item Effected	Equation
1. Design of extraction	β_e, β_w	
2. Design of distillation column or solvent recovery	β_D	
3. Concentration of H_3PO_4 in the raffinate	$\beta_e, \beta_w, \beta_v$	$\frac{\partial C_T}{\partial X_n} = \frac{\partial \beta_e}{\partial X_n} + \frac{\partial \beta_w}{\partial X_n} + \frac{\partial \beta_v}{\partial X_n}$
4. Concentration of solute in the recycle solved	β_e, β_w	$\frac{\partial C_T}{\partial Y_s} = \frac{\partial \beta_e}{\partial Y_s} + \frac{\partial \beta_w}{\partial Y_s} = 0$
5. Solvent to feed ratio in two extraction step	$\beta_e, \beta_w, \beta_s$	$\frac{\partial C_T}{\partial R_E} = \frac{\partial \beta_e}{\partial R_E} + \frac{\partial \beta_w}{\partial R_E}$
6. Concentration of impurities in the finished product	β_e	
7. Concentration of solvent in the product	β_v, β_s	$\frac{\partial C_T}{\partial S_p} = \frac{\partial \beta_v}{\partial S_p} + \frac{\partial \beta_s}{\partial S_p}$
8. Concentration of solvent in the finished raffinate	β_s, β_d	$\frac{\partial C_T}{\partial S_R} = \frac{\partial \beta_s}{\partial S_R} + \frac{\partial \beta_D}{\partial S_R}$
9. Concentration of H_3PO_4 in final product	β_w, β_c	$\frac{\partial C_T}{\partial X_p} = \frac{\partial \beta_w}{\partial X_p} + \frac{\partial \beta_c}{\partial X_p}$
10. Solvent feed ratio in washing step	β_w, β_c	$\frac{\partial C_T}{\partial R_W} = \frac{\partial \beta_w}{\partial R_W} + \frac{\partial \beta_c}{\partial R_W}$

Extraction Section

Under non-steady state conditions mass balance on nth stage

$$F\,X_{n-1} + B\,Y_{n+1} = F\,X_n + B\,Y_n + \phi_1 \frac{dX_n}{dt} + \phi_2 \frac{dy_n}{dt} \;\ldots\ldots\; 10.9$$

since

$$\zeta = \frac{X_{n-1} - X_n}{X_{n-1} - X_n^*}, \text{ also } Y_n = mX_n + b \;\ldots\ldots\ldots\ldots\; (10.10)$$

$$\therefore\; Y_n = \frac{M}{\zeta}(X_n - (1-\zeta)X_{n-1}) + b \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\; (10.11)$$

and

$$Y_{n+1} = \frac{M}{\zeta}(X_{n+1} - (1-\zeta)X_n) + b \;\ldots\ldots\ldots\ldots\ldots\; (10.12)$$

∴ by substitution, rearranging and taking Laplace transform, the equation can be reduced to:

$$\bar{X}_{n+1} - (1+A+\bar{B}S)\bar{X}_n + (A+CS)\,\bar{X}_{n-1} = (C-\bar{B})X_o \;\ldots\; (10.13)$$

where

$$A = (1-\zeta)\frac{M}{\zeta}, \quad C = \frac{\phi 2}{B}(1-\zeta)$$

$$\bar{B} = \frac{\phi 2}{B} + \frac{\phi_1 \zeta}{mB} \quad \text{and} \quad \zeta = \frac{mB}{F}$$

Equation 10.13 is a second order finite difference equation whose solution is the sum of the complementary solution and the particular solution.

Complementary solution is:

$$\bar{X}_{n+1} - (1+A+\bar{B}S)\bar{X}_n + (A+CS)\bar{X}_{n-1} = 0 \;\ldots\ldots\ldots\ldots\; (10.14)$$

and has a general solution of

$$\bar{X}_n = C_1\, r_1^2 + C_2\, r_2^n \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\; (10.15)$$

where

$$r_1, r_2 = \frac{1+A+\bar{B}S+\sqrt{(1+A+BS)^2 - 4(A+CS)}}{2} \quad \ldots\ldots\ldots \quad (10.16)$$

$$r_1 + r_2 = 1+A+BS \quad \ldots\ldots\ldots \quad (10.17)$$

$$r_1 r_2 = A+CS \quad \ldots\ldots\ldots \quad (10.18)$$

and C_1, C_2 are constants to be determined by B conditions. A similar equation can be obtained for the washing step.

$$\bar{X}_{n+1} - (1+A_w+\bar{B}_w S)\bar{X}_n + (A_w+C_w S)\bar{X}_{n-1} = 0 \quad \ldots\ldots\ldots \quad (10.19)$$

with $A_w = (1-\zeta_w)(\frac{\zeta_w}{\varepsilon_w})$, $\bar{B}_w = \frac{\phi_4}{B} + \frac{\phi_3 \zeta_w}{MB}$

$$C_w = \frac{\phi_4}{B}(1-\zeta_w) = C_w$$

Different B. conditions and therefore different solutions will be obtained:

$$\bar{X}_{nw} = C_3 r_3^n + C_4 r_4^n$$

Yacu (282) approximated the equilibrium curve for MIBK solvent as a straight line with a slope equal to m.

A relationship to express the effect of the impurities on the slope of operation was also presented by Yacu (282) as follows.

From Figure 7.12

$$Y_p = mX + b \quad \ldots\ldots\ldots \quad (10.20)$$

where m is the slope of the distribution lines and b is its intercept for the pure case.

$$Y_i = m_{ei} X_{ni}^* + b' \quad \ldots\ldots\ldots \quad (10.21)$$

where m_{ei} and b' are the slope and intercept for the impure case.

$$\text{But } m_{ei} = (m - kC_i) \quad \ldots\ldots\ldots \quad (10.22)$$

where C_i is the impurity concentration and k is a constant characteristic of the impurities.

$$\therefore\ Y_i = (m - kC_i)X^*_{ni} + b' \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (10.23)$$

The above equation can be used to develop an equation similar to equation 10.13 for impure system with

$$A = (1-\zeta_i)\left(\frac{\zeta_i}{\varepsilon_i}\right), \quad C = \frac{\phi_{2i}}{B}(1-\zeta_i)$$

$$\bar{B} = \frac{\phi_{2i}}{B} + \frac{\phi_{1i}\zeta_i}{(m-kC_i)}$$

$$\varepsilon_i = \frac{(m-kC_i)B}{F}$$

No attempt was made to solve the above equations since this is beyond the scope of this work.

10.7 OPTIMIZATION OF PROFIT FUNCTION

Considering the basic block diagram for a phosphoric acid purification process operating for a given feed rate there is an optimum amount of solvent and number of stages which will give the most economical operating conditions. These conditions depend on the cost of feed (impure wet process phosphoric acid) cost of solvent (MIBK) recovery and make-up, and operating cost of the process. Other workers did not consider the value of the final impurity saturated raffinate. However it is important in this work, and it has a significant economic effect.

If X_o = concentration of feed (impure wet process phosphoric acid), i.e. kg solute/kg of solute free basis.

F = flow rate of acid in kg/hr

N = number of stages

B = solvent flow rate kg/hr

X_n= concentration of final impurity rich raffinate, which is recommended usually for fertilizer use.

Let the unit cost of wet process phosphoric acid = γ per kg, and let α = total hourly cost of each stage. Let cost of solvent including recovery by washing and make up of spillage be β per kg.

Let the value of final raffinate richer with impurities including stripping by distillation = π unit cost per kg.

Basis One hour's operation

Cost of feed = $\gamma F X_o$ .... (10.24)

Cost of solvent = βB .... (10.25)

Cost of final acid = $F.X_n.\pi$ .... (10.26)

Similarly, if λ is the value of 1.0 kg of extracted product, then the total value of the product

$= \lambda F(X_o - X_n)$ .... (10.27)

Assume π fraction of λ

or $\pi = Z.\lambda$

The hourly profit p can be given as

$p = \lambda F(X_o - X_n) + F X_n \pi - \{\alpha N + \beta B + \gamma C X_o\}$ ...... (10.28)

equation 5 must be solved so that p is maximum and since the different unit costs will be known. N, B and Xn are the variables. Of these Xn is related to X_o by the equation given by Mickley* et al.

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* H.S. Sherwood, T.K. and Reed C.E. Applied Mathematics in Chemical Engineering, McGraw Hill 1957.

$$X_n = X_o\{\frac{S^{N+1} - S^n}{S^{N+1} - 1}\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10.29)$$

where $S = \frac{F}{mB}$ and m is the distribution ratio, assumed to be constant at high acid concentration and over a small concentration change.

Substitution of equation 10.29 into 10.28 gives:

$$p = \lambda_F(X_o - X_o(\frac{S^{N+1} - S}{S^{N+1} - 1}) + F(X_o(\frac{S^{N+1} - S^N}{S^{N+1} - 1}))\pi - (\alpha N + \beta B + \gamma F X_o)$$

or

$$p = \lambda F X_o\{\frac{S^N - 1}{S^{N+1} - 1}\} + \pi F X_o\{\frac{S^{N+1} - S^N}{S^{N+1} - 1}\} - \{\alpha N + \beta B + \gamma F X_o\} \ldots . \quad (10.30)$$

If the wet process phosphoric acid feed is from part of a complete complex then cost of feed, $\gamma F X_o$, will not be subject to optimization. The profit function will be defined as

$$p = \lambda_F X_o\{\frac{S^N - 1}{S^{N+1} - 1}\} + \pi F X_o\{\frac{S^{N+1} - S^N}{S^{N+1} - 1}\} - \{\alpha N + \beta B) \quad \ldots (10.31)$$

The variables in equation 10.30 are N and B. It is necessary to find the values of these variables which will make p a maximum, this can be obtained by using the maximal and minimal surface.

Differentiating equation 10.30 with respect to N

$$\frac{\partial P}{\partial N} = S^N X_o F\{\frac{\lambda(S-1) + \pi(1-S)}{(S^{n+1} - 1)^2}\} \ln S$$

equating $\frac{\partial P}{\partial N} = 0$ at maximum and minimum

$$\frac{\alpha}{FX_o} = S^N \{\frac{\lambda(S-1) + \pi(1-S)}{(S^{N+1} - 1)^2}\} \ln S$$

Since $\pi = Z\lambda$

$$\frac{\alpha}{\lambda_F X_o} = S^N\{\frac{(S-1) + Z(1-S)}{(S^{N+1} - 1)^2}\} \ln S \quad \ldots\ldots\ldots\ldots\ldots\ldots (10.32)$$

If Z = 0, in which case final impurities saturated raffinate has no value, the equation will reduce to:

$$\frac{\alpha}{\lambda F X_o} = S^N\{\frac{(S-1)}{(S^{N+1}-1)^2}\} \ln S \dots\dots\dots\dots\dots\dots \quad (10.33)$$

Similarly differentiating equation 7 with respect to B

$$\frac{\partial P}{\partial B} = \frac{m\lambda X_o\ S^{N+1}(S^{N+1}+N-NS-S)\ +\ m\pi X_o S^{N+1}(-S^{N+1}-N+NS+S)}{(S^{N+1}-1)^2}$$

with $\pi = Z\lambda$ and setting $\frac{\partial P}{\partial B} = >0$

$$\frac{\beta}{m\lambda X_o} = \frac{S^{N+1}(S^{N+1}+N-NS-S+Z(-S^{N+1}-N+NS+S)}{(S^{N+1}-1)^2} \dots\dots\dots \quad (10.34)$$

Equation 10.34 can also be reduced to equation 9.1

$$\frac{\beta}{m\lambda X_o} = S^{N+1}(\frac{S^{N+1}+N-NS-S}{(S^{N+1}-1)^2})\dots\dots\dots\dots\dots\dots \quad (10.35)$$

if the final raffinate has no value

$$B = \frac{S^{N+1}\ +\ N(1-S)-S}{(\frac{B}{\alpha})\ (S-1)\ \ln S} \dots\dots\dots\dots\dots\dots \quad (10.36)$$

equations 10.32 and 10.34 are two complex simultaneous equations that will be difficult to solve analytically, however a sufficiently accurate solution can be obtained graphically.

Dividing equation 10.32 by 10.34

$$\frac{\beta}{\alpha} \cdot \frac{F}{m} = S\{\frac{S^{N+1}+N-NS-S+Z(-S^{N+1}-N+NS+S)\}}{\{(S-1)+Z(1-S)\}\ln S}$$

since $S = \frac{F}{mB}$ $\quad\therefore \frac{F}{m} = B.S.$

$$B = \frac{S^{N+1}+N-NS-S+Z(-S^{N+1}-N+NS+S)}{(\frac{\beta}{\alpha})\{(S-1)+Z(1-S)\}\ln S} \dots\dots\dots\dots \quad (10.37)$$

$$\text{Put } B_1 = \frac{F}{mS} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (10.38)$$

Given a pair of values of S and N the right hand side of equation 10.37 and the right hand side of equation 10.38 can be evaluated for the corresponding values of S. The number of stages corresponding to this amount of solvent approximately equals that given by equation 10.38 is considered to be the maximum.

Only equation 10.37 will be considered since this is the more general form which is representing the process and the solution in case of MIBK as extracting agent.

With β = £0.004/kg

α = £2/hr

λ = £0.28/kg H_3PO_4

Z = 0.67

π = £0.19/kg H_3PO_4

γ = £0.2/kg H_3PO_4

F = 69510 kg/hr

is shown graphically in Fig. D.2 to give N = 3, S = 3.8 and B = 25500 kg/hr. The hourly profit from equation 10.30 is equal to £348. This will give a difference of +50% over the profit calculated based on net cash flow of the process shown in Table. 10.4. This may contribute to the difference of solvent flow rate. Operating the system at solvent flow rate near 25500 kg/hr will be near the critical point of phase inversion from o/w to w/o as shown experimentally. It should be noted that different values of p will be obtained by using different values of $\alpha,\beta,\gamma,\lambda,\pi$ and Z.

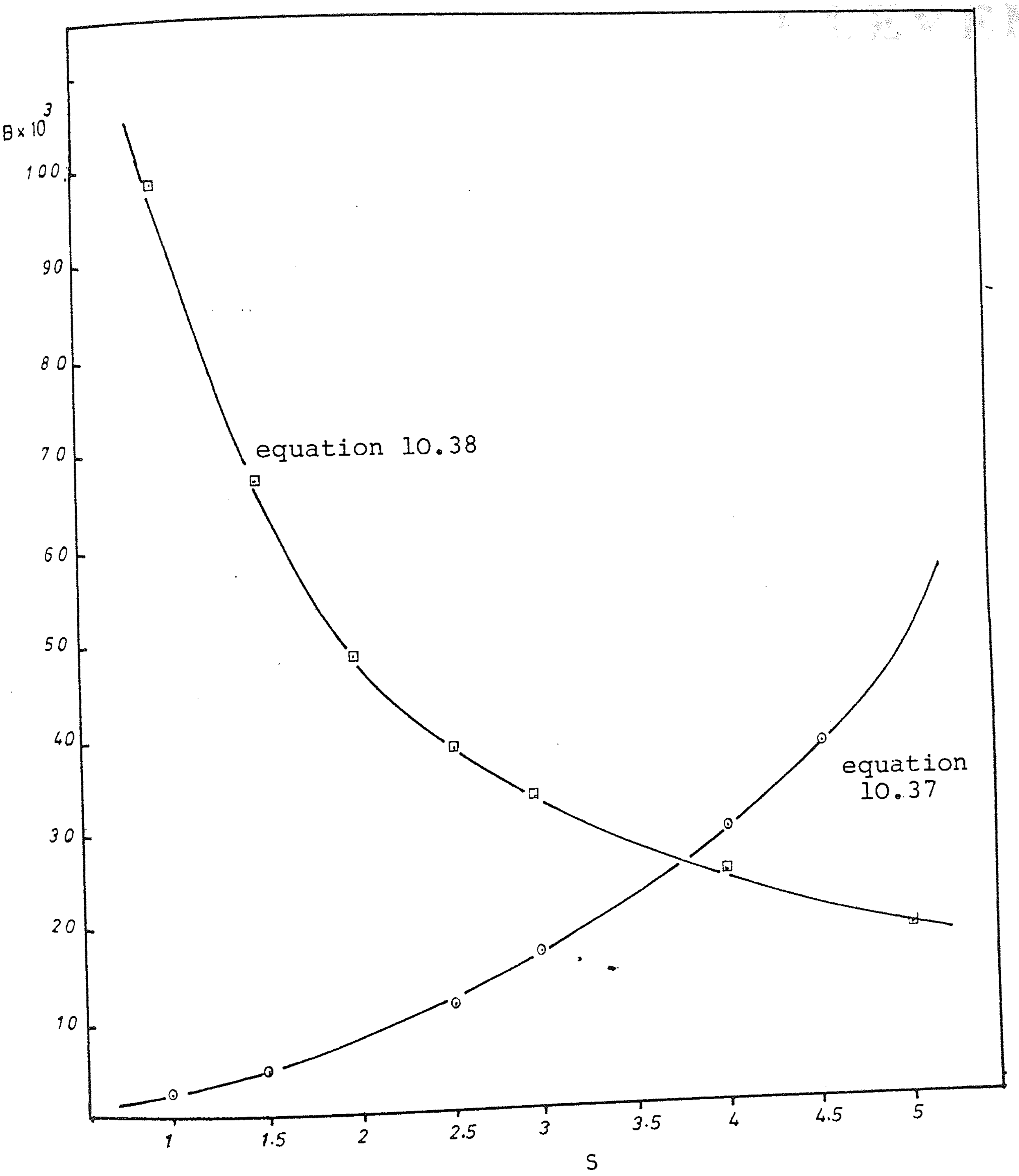


Fig 10.2 Graphical solution of equations 10.37 and 10.38

CHAPTER ELEVEN

CONCLUSIONS AND PROPOSAL FOR FUTURE WORK

The distribution of phosphoric acid between two layers (organic solvent and aqueous) can be utilised as a powerful separation method which can be used for purification of the acid because impurities tend not to pass to the organic phase. Theoretically many solvents appear to be promising for phosphoric acid extraction, however practical difficulties often arise which make them difficult to use. In this work a novel pilot plant containing three mixer-settlers was designed, constructed and developed for phosphoric acid extraction. This study offers a practical and fundamental understanding of the mixer-settler extraction of phosphoric acid. The main conclusions from the work may be summarised.

1. Phase equilibrium data are not alone enough to predict the operating conditions of a contactor, since many other factors affect performance.
2. Mixer-settlers are more practical for phosphoric acid extraction than towers and columns.
3. Methylisobutylketone was found to be the most practical solvent among the solvents studied.

4. A purification step (reported by Yacu (282)) is not necessary. However, his theoretical model for forward and back extraction of acid give the optimum conditions.

5. The effect of process variables on distribution coefficients of impurities and phosphoric acid are as follows:
    (a) Both phosphoric acid and impurities distribution coefficients decreases with solvent/feed ratio.
    (b) Power of agitation has little effect on the distribution coefficient of both acid and impurities.
    (c) As initial acid concentration increases in the feed acid, the impurity concentrations in the final product acid increases.
    (d) Distribution coefficients of impurities and acid decrease with the total flowrate of the phases.

6. The concentration of impurities in the extract along the cascade increases from the solvent introductory stage and reaches a maximum at the phosphoric acid introductory stage. Similarly the impurity concentrations in the raffinate increase from the acid introductory stage and reaches a maximum at the solvent introductory stage.

7. Solvent extraction can also be successfully applied for the solvent washing step. As reported theoretecally by Yacu (282), one stage

was sufficient to recover the acid from the solvent. The following conclusions can be drawn from the solvent-washing experiments.

(a) As the phase ratio of solvent:water increases, the concentration of acid and impurities in the final pure product increases. However, there is a maximum flow of solvent after which incomplete settling was observed.

(b) A milky extract layer is formed in the settler containing a small entrainment of phosphoric acid. It was observed in the batch studies that this milky layer disappears with increased power of agitation, however at high speed secondary drops in the raffinate are obtained.

(c) As initial acid and impurity concentration in the extract layer increase, the final acid and impurity increases.

8. Drop-size distributions in the fully baffled mixer were log-normal. Drop size increases with the dispersed phase hold-up. and decreases with the phosphoric acid concentration and impeller speed. Drop size can be predicted by the correlation developed in this work as

$$\frac{d32}{D} = 0.632(\phi_d)^{3.62} \left(\frac{\mu_d}{\mu_c}\right)^{-3.02} (We)^{-1.071} \left(\frac{\rho m}{X_p}\right)^{1.08}$$

9. Hold-up values were dependent only on phase flow rates above a critical impeller speed of 700 r.p.m.

10. Wedge length increases with the solvent (MIBK) flow-rate and with phosphoric acid concentration. The wedge length can be predicted by the correlation developed in this work as

$$\frac{W_L}{D_S} = 5.524\times10^{-5}\left(\frac{V_C}{V_D}\right)^{0.433}\left(\frac{6}{N^2 D_s \rho_m}\right)^{-0.098}\left(\frac{\mu_m}{N D_s^2 \rho_m}\right)\left(\frac{X_F}{\rho_m}\right)^{0.55}$$

11. The first stage (acid introductory stage) required a larger settler than other stages.

12. Phase inversion in the mixer was observed to be a steady state phenomenon and occurred easily from o/w to w/o at high ratio of the dispersed to continuous phases, high rotor speed and high phosphoric acid concentration. Phase inversion was characterised by the existence of an ambivalence range which becomes smaller with increasing acid concentration. The stable system at high acid concentration is o/w and at low acid concentration w/o.

13. The time to reach steady state increased with initial acid concentration and decreased with power of agitation. In most runs the solvent introductory stage reached steady state before the middle and phosphoric acid introductory stages.

14. During the phosphoric acid concentration the following conclusions can be drawn.
    (a) Phosphoric acid starts to colourise at a still temperature of 120°C and at acid concentration of 70%.
    (b) Impurity concentration increases with acid concentration.

(c) No deposition of impurities was observed.

15. The optimum conditions at which to run the process are: initial acid concentration 63% by weight, impeller speed 900 r.p.m. and phase ratio 1:1 to 2:1. For the washing step the optimum phase ratio is 7:1 solvent:water.

16. The installed capital cost of the full scale process (100 T/d) is approximately £2M. The profitability of the process was evaluated and found to be 44% before tax and 26% after tax, with pay back time = 3.9 years

17. The profit function was found to be

$$P = \lambda_F(X_o - X_n) + FX_n\pi - (\alpha N + \beta B + \gamma C X_o)$$

which was then optimized to give two general equations in terms of dimensionless quantities.

$$\frac{\alpha}{\lambda C X_o} = S^N\left\{\frac{(S-1) + Z(1-S)}{(S^{N+1}-1)^2}\right\}\ln S$$

$$\frac{\beta}{m\lambda X_o} = S^{N+1}\left\{\frac{S^{N+1}+N-NS-S+Z(-S^{N+1}-N+NS+S)}{(S^{N+1}-1)^2}\right)$$

The two equations were solved and the hourly profit was found to be £348

18. Batch Studies

(a) An increase in phosphoric acid concentration in the system water-phosphoric acid-solvent results in: i) increase of densities and and viscosities of the phases, (ii) decrease of the interfacial area and surface tension which results in smaller drops and longer settling time, (iii) increase of the distribution coefficients of cationic impurities.

(b) The presence of cationic impurities in the system results: (i) reduces the distribution coefficients of acid, (ii) lengthens the settling time for mixtures containing low acid concentration and vice versa.

(c) Rotor speed and time of mixing has no significant effect on the separation of the two phases.

(d) Mixing two solvents (cyclohexanol and MIBK) improved the physical properties of cyclohexanol and selectivity of acid was improved.

During the course of this research several areas for further research become apparent. Only the basic design variable and factors were studied in the present work, and more detailed studies would be worthwhile, therefore the following further work is recommended.

1. Study other solvent systems on the continuous pilot equipment that might produce purer product acid or a more economical process.
2. Study other impurities in wet-process phosphoric acid, with special emphasis on the anionic and organic impurities which have not been given high priority in the present work.
   Anions such as F^- and $SO_4^=$ affect the corrosive properties and organic materials give rise to colour.
3. Study the extraction process at other temperature because at lower temperature the extraction is

reported to be more effective and at higher temperature the washing is more effective.

4. Some organic solvents have extraction power greater than or nearly equal to unity. However they are solid at room temperature or they might have high viscosity. These solvents may be improved by mixing them with other solvents or by adding other components, e.g. H^+ ion might be added to the solvent to improve its extrability (20).

5. Determine the effect of geometric variations of baffle size, impeller size and vessel size as well as settler design to provide more information for scale-up.

6. Study in detail the hydrodynamics of the system such as drop size with impurity concentration. Also use other methods for drop size analysis, e.g. the newly introduced Laser equipment.

7. The pilot plant equipment described in Chapter 6 could be modified by adding a washing step and a concentration step, in which case the complete continuous process could be studied.

8. Impurities in the final product acid reduced as solvent/feed ratio reduced, however the system would eventually be inverted from o/w to w/o. The latter required a long time for settling and contained a large percentage of entrainment due to secondary haze. A method of either improving the settling of the secondary haze in the settler for the system w/o or of keeping the system o/w at high solvent/feed ratio may be worth seeking.

APPENDIX I

CONTENTS OF THIS APPENDIX

1. Material of construction for acid.
2. Physical and chemical properties of the material used in this work.
3. Baffles and settler auxiliaries used in this work.
4. A graph of H_3PO4 VS P_2O5.

APPENDIX I

I.1 MATERIAL OF CONSTRUCTION FOR ACID

Table (I) ., shows the material reported to be used in phosphoric acid service. The austenitic stainless steel of chromium nickel-molybdenum (and to a lesser extent chromium-nickel) compositions are commonly used for handling phosphoric acid solutions within limits of concentration.

Carbon and graphite as the only materials proven and reported to be satisfactory for use in boiling phosphoric acid.

Table I Nominal compositions of nickel alloys in use or corrosion-tested in phosphoric acid solutions

Composition, per cent	Ni	Fe	Cr	Mo	Cu	C	Si	Mn	Other
Stainless steels									
AISI Type 304	9·5	70	18	—	—	0·08 max	0·5	1·3	—
AISI Type 304L	10	69	18	—	—	0·03 max	0·5	1·3	—
AISI Type 310	21	52	25	—	—	0·25 max	0·75	1·3	—
AISI Type 316	13	65	17	2·0 min	—	0·08 max	0·5	1·7	—
AISI Type 316L	13	63	17	2·0 min	—	0·03 max	0·5	1·8	—
AISI Type 317	14	61	19	3·0 min	—	0·08 max	0·4	1·6	—
AISI Type 329	4·5	67	27	1·5	—	0·20 max	—	—	—
AISI Type 347	11	68	18	—	—	0·08 max	0·5	1·3	Nb(+Ta) 0·6
ACI Type CD-4MCu (c)	5·4	62	26	2·0	3·0	0·04 max	1·0 max	1·0 max	—
ACI Type CF-3 (c)	10	68	19	—	—	0·03 max	2·0 max	1·5 max	—
ACI Type CF-8 (c)	9·5	68	19·5	—	—	0·08 max	2·0 max	1·5 max	—
ACI Type CF-3M (c)	11	65	19	2·5	—	0·03 max	1·5 max	1·5 max	—
ACI Type CF-8M (c)	10·5	55	19·5	2·5	—	0·08 max	1·5 max	1·5 max	—
ACI Type CG-8M (c)	11	64	19·5	3·5		0·08 max	1·5 max	1·5 max	—
Illium* alloy P (c)	8	57	28	2·25	3·25	0·20	0·75 max	1·0 max	—
Iron-base nickel-chromium-copper-molybdenum alloys									
Worthite* stainless (d)	24	48	20	3	1·75	0·07 max	1·25	0·6	
Carpenter* Stainless No. 20Cb	29	44	20	2·5	3·3	0·07 max	0·6	0·75	Nb(+Ta) 0·6
ACI Type CN-7M (a)	29	44	20	2·2	3·3	0·07 max	1·5 max	1·5 max	—
Carpenter* Stainless No. 20Cb-3	34	39	20	2·5	3·3	0·07 max	0·6	0·75	Nb(+Ta) 0·6
Nickel-base iron-chromium-molybdenum alloys									
Incoloy* alloy 825	41·8	30	21·5	3·0	1·80	0·03	0·35	0·65	Al 0·15; Ti 0·90
Hastelloy* alloy G (b)	45	19·5	22·2	6·5	2·0	0·03	0·35	1·3	W 0·5; Nb – Ta 2·12
Hastelloy* alloy F (b)	47	17	22	6·5	—	0·05 max	—	—	Co 2·5 max; W 0·6; Other 5·5
Nickel-base chromium-molybdenum alloys									
Illium* alloy 98 (c)	55	1·0	28	8·5	5·5	0·05	0·7	1·25	—
Illium* alloy G (c)	56	6·5	22·5	6·4	6·5	0·20	0·65	1·25	—
Inconel* alloy 625	61	3	22	9·0	0·1	0·05	0·3	0·15	Nb 4
Illium* alloy R	68	1	21	5	3	0·05	0·7	1·25	—
Nickel-base molybdenum-chromium alloy									
Hastelloy* alloy C (b)	54	5	15·5	16	—	0·08 max	1·0 max	1·0 max	Co 2·5 max; W 4; V 0·4 max
Nickel-base molybdenum alloy									
Hastelloy* alloy B (b)	61	5	1 max	28	—	0·05 max	—	—	Co 2·5 max; Other 3
Nickel-base silicon alloy									
Hastelloy* alloy D (c)	82	2 max	1 max	—	3·0	0·12 max	9	—	Co 1·5 max; Other 2
Nickel-alloyed cast irons									
Ni-Resist Type 1 (c)	15·5	69	2·5	—	6·5	2·8	2·0	1·2	—
Ni-Resist Type 2 (c)	20	72	2·5	—	—	2·8	2·0	1·0	—
SG Ni-Resist Type D-2 (c)	20	72	2	—	—	3·0 max	2	0·85	P0.08 max
Nickel-copper alloys									
Monel* alloy 400	66	1·35	—	—	31·5	0·12	0·15	0·90	—
Copper-nickel alloy CA 715	31	0·55	—	—	67	—	—	1·0 max	Pb 0·05 max; Zn 1·0 max
Nickel									
Nickel 200	99·5	0·15	—	—	0·05	0·06	0·05	0·25	—
Nickel-base chromium alloys									
Corronel* alloy 230	55 min	5·0 max	36	—	1·0 max	0·08 max	0·6 max	1·0 max	Ti 1·0 max; Al 0·5 max
Inconel* alloy 600	76	7·2	15·8		0·10	0·04	0·20	0·20	—
Iron-nickel-chromium alloy									
Incoloy* alloy 800	32	46	20·5	—	0·30	0·04	0·35	0·75	—

(a) Cast '20' alloys, such as ***Durimet**** *20,* ***Aloyco**** *20, etc* *(b) Composition of wrought alloy; available also in cast form*

(c) Available in cast form only *(d) Composition of cast alloy*

**Trade mark*

I.2 PHYSICAL AND CHEMICAL PROPERTIES OF MATERIAL

1. Ortho phosphoric acid

The phosphoric acid is supplied in liquid form by Fisons at concentration 88% by wt, it has the following physical properties.

Molecular formula	H_3PO4
Molecular weight	98
Density at 20°C	1.75
Minimum assay	88 %

Maximum limit of impuritiesat 20% P_2O5 = 0.8 ppm

Specific heat at 40% P_2O5 = 0.6 Cl/g/degree

at 70% P_2O5 = 0.4 Cl/g/degree

2. 4-Methylpentan 2-one (MIBK)

Molecular formula = $(CH_3)_2$-CH-CH_2-CO-CH_3

Molecular weight = 100.16

Density at 20°C = 0.809

Minimum assay = 97.5 %

Maximum limit of impurities = 0.01

Solubility at 25°C

MIBK in water = 1.7 per cent w/w

Water in Ketone = 1.9 per cent w/w

Viscosity at 25°C = 0.546 cp

Surface tension at 25°C = 25.4 dyn/cm.

Azeotropes with water

75.7 w/w MIBK to 24.3 w/w water at 87.9°C

Flash point

open cup = 24°C

closed cup = 15.6°C

Boiling point at 760 mm Hg = 15.90

3. Cyclohexanol

Molecular formula $CH_2(CH_2)$ 4.CH.OH

Molecular weight 100.16

Density at 20°C 0.95

Minimum assay 98%

Maximum limit of impurities - water 0.2%.

Cyclohexanone 1.0%

Freezing point 19 - 24°C

Refractive index 1.465 - 1.467

4. Benzaldehyde

Molecular formula = C_6H_5 CH_O

Molecular weight = 106.12

Density at 20°C = 1.044 - 1.047

Boiling range (95%) = 176 - 180°C

Maximum limits of impurities

Acidity (C_6H_5COOH) 0.3%

Chlorine 0.2%

Refractive index 1.544 - 1.546

5. Ferric orthophosphate

Formula = $FePO_4 + H_2O$

m.wt = 186.85

Density = 2.74

6. Magnesium phosphate

Formula = $Mg_3(PO4)_2$

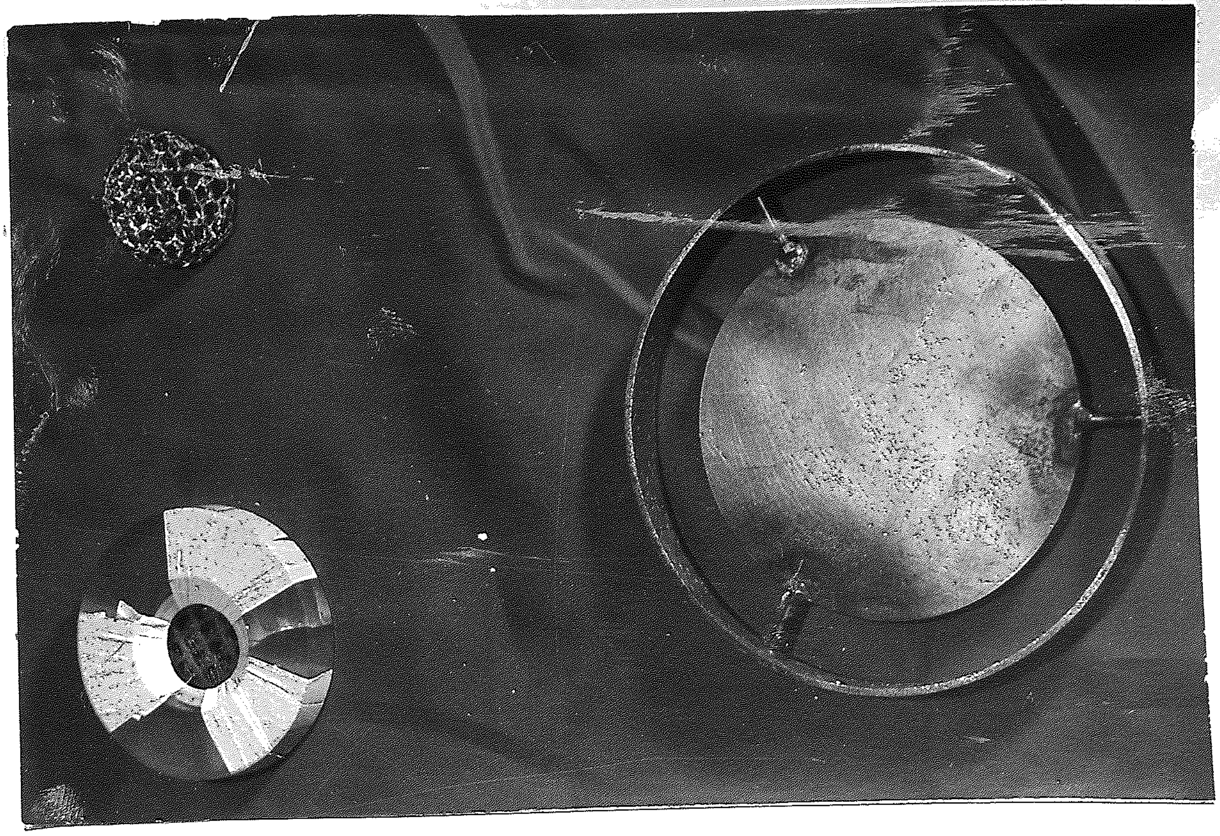
m.wt = 370.96

7. Distilled water

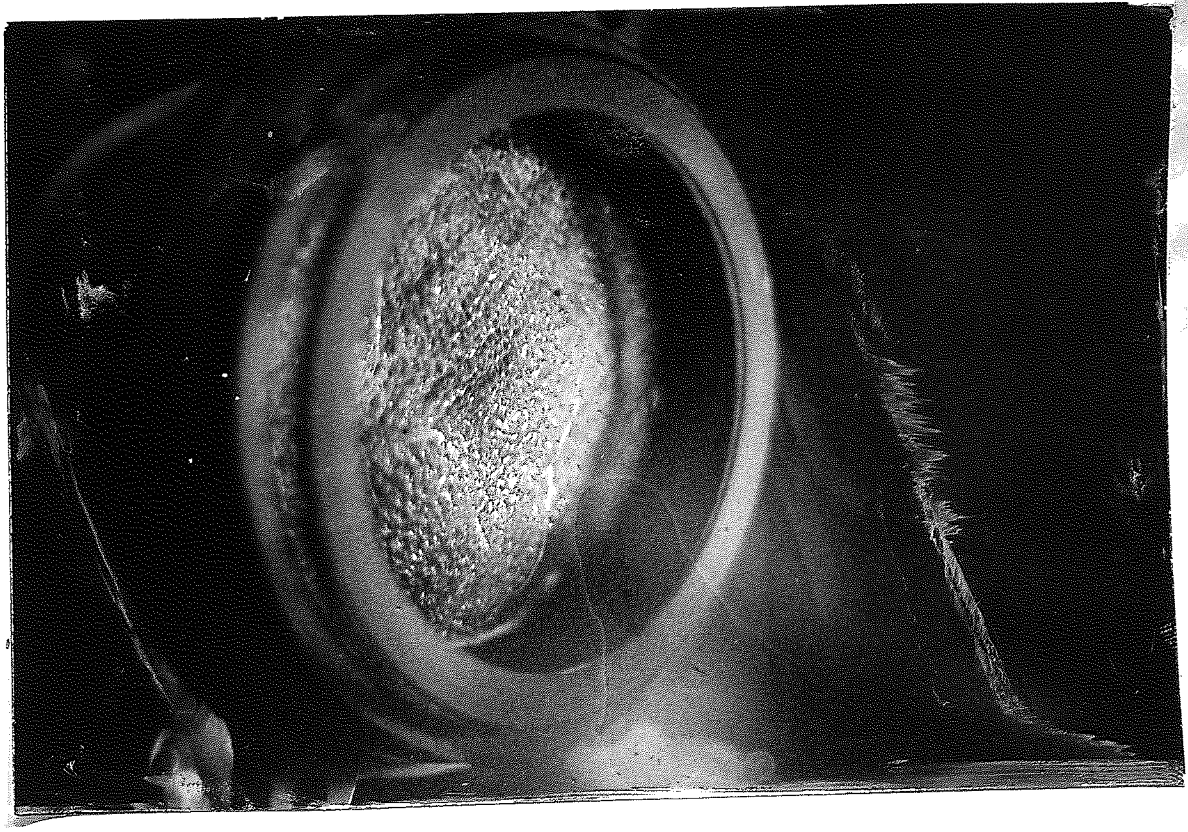
Formula = H_2O

m.wt = 18

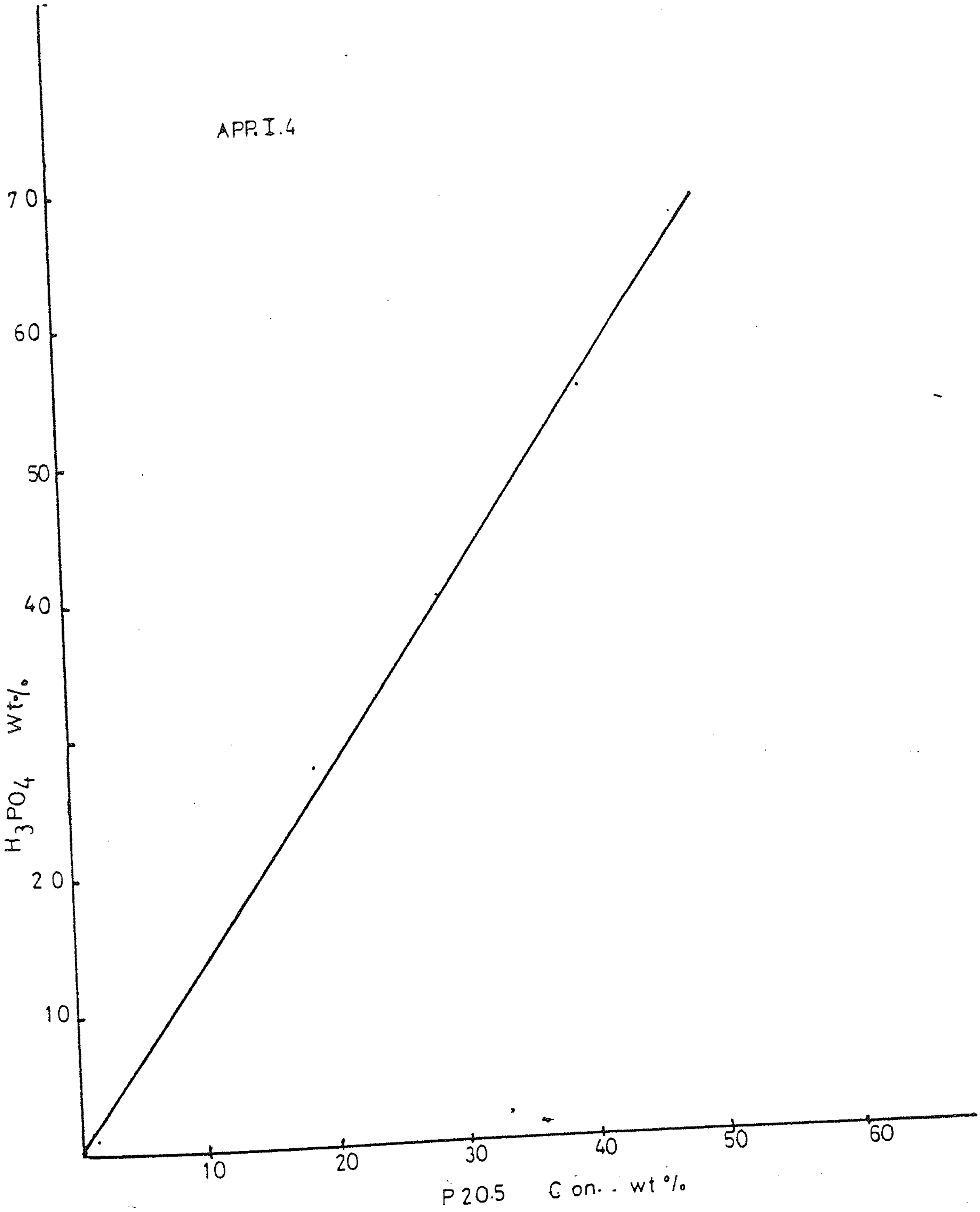
Density = 0.99



APPENDIX I.3 BAFFLES AND SETTLER AUXILIARIES USED IN THIS WORK



APP. I.4



H_3PO_4 VS P_3O_4 Concentration in phosphoric acid solution.

APPENDIX II

CONTENTS OF THIS APPENDIX

APPENDIX II

II.1 TYPICAL DROP-SIZE ANALYSIS COUNT AND PHOTOGRAPH

System: water-phosphoric acid (5%) - MIBK, continuous studies at 700 r.p.m.

Diameter of Drop	N	Nxd_{32}	Nd_{32}/d_{max}
0.164	1	0.161	0.025
0.174	2	0.358	0.056
0.194	5	0.975	0.155
0.2116	8	1.696	0.269
0.228	12	2.748	0.437
0.244	15	3.675	0.584
0.762	24	6.288	1.00
0.279	14	3.906	0.621
0.298	13	3.848	0.611
0.313	6	1.872	0.2977
0.33	4	1.316	0.209
0.345	6	2.076	0.330
0.36	5	1.81	0.287
0.379	4	1.52	0.241
0.397	1	6.396	0.061

$$d_{32} = \frac{Nd^3}{Nd^2}$$

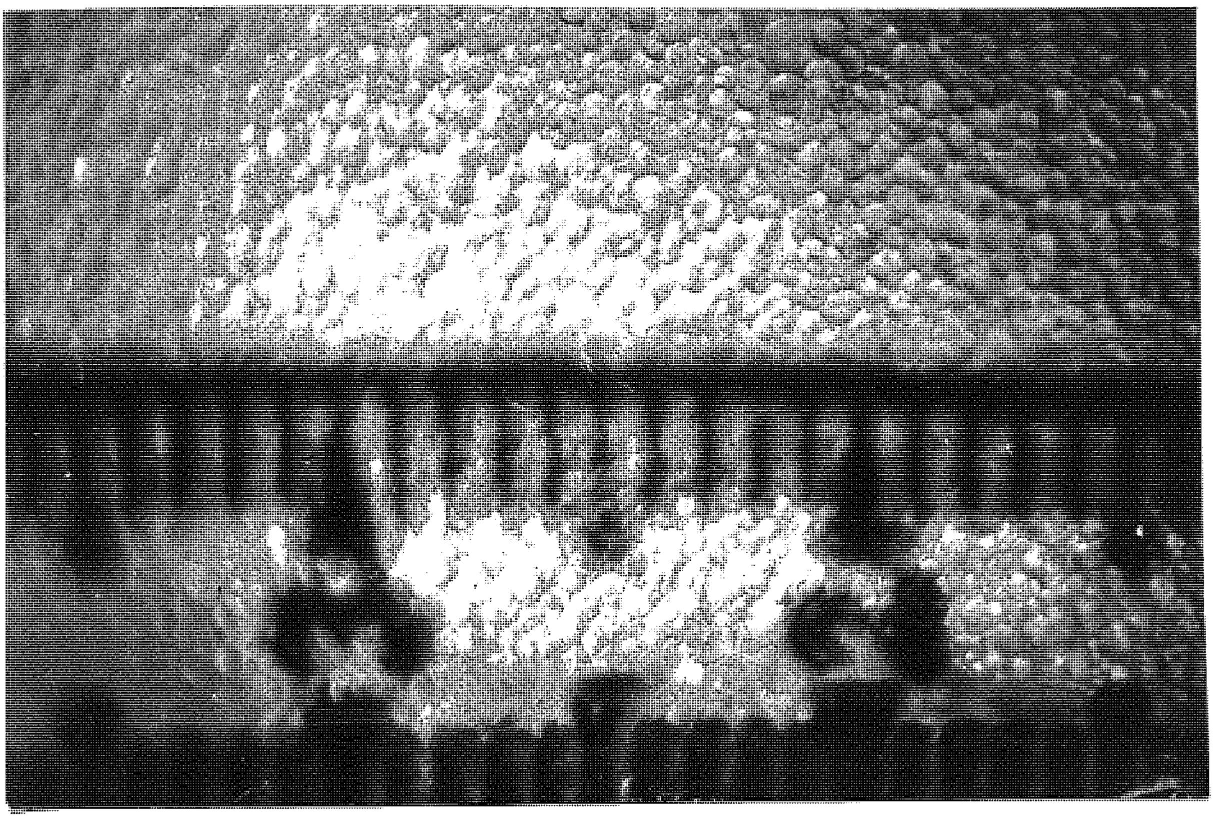


FIG. TYPICAL PHASE DISPERSION IN THE MIXER (O/W) SYSTEM
PHOSPHORIC ACID - WATER - MIBK

II.2

TABLE II.1

R.P.S.	We.	Hold-up	Acid conc.	System	C_1	λ	$e^{\lambda X}$	cal.d_{32}	exp.d_{32}	% diff.
10	430.89	0.45	1%	MIBK	0.052	4	6.2	0.3	0.5	- 40%
13.3	762.0	0.45	1%	MIBK	0.052	4	6.2	0.2	0.35	- 42.8%
18.3	1447.9	0.45	1%	MIBK	0.052	4	6.2	0.15	0.25	- 40%
10	435	0.45	5%	MIBK	0.052	4	6.2	0.29	0.4	- 27.5%
13.3	769.47	0.45	5%	MIBK	0.052	4	6.2	0.2	0.28	- 28.5
18.3	1456.7	0.45	5%	MIBK	0.052	4	6.2	0.14	0.2	- 30%
11.6	634	0.2	15%	MIBK	0.052	4	6.2	0.23	0.2	+ 13%

where

$$We = \frac{d^3_R \times N^2 \times \rho_c}{\sigma_i}$$

$$e^{\lambda x} = 1 + \lambda x + \frac{(\lambda x)^2}{2!} + \frac{(\lambda x)^3}{3!} + ---- + \infty$$

COMPARISON BETWEEN DROP-SIZE OBTAINED IN THIS WORK WITH THE EQUATION PRESENTED BY GNANASUNDARAM

II.3 CALIBRATION AND ATOMIC ABSORPTION EQUIPMENT (ILI S1).

SWITCHING ON

1. Electricity on / compressed air on / fan on.
2. Gases - N_2O 30 psi, Acetylene 12 psi /Air - 40 psi
3. Insert appropriate lamp
4. Insert correct burner. Press in firmly.
5. Switch on equipment, allowing ½ hour to warm up.
6. Adjust lamp current A to that recommended in manual.

   Lamp current for Fe is = 9 am.

   Lamp current for Mg is = 4 am.
7. Set recommended values of slit width/H.V/ at a given wavelength.

   248.2 nm for Fe.

   320.0 nm for Mg.
8. Optimizing focal length of beam from lamp, using white card.
9. Adjust wavelength to obtain highest intensity reading.
10. Turn on air and acetylene or air/acetylene/N_2O.
11. Check flowrate through aspirator with oxidant control knob off, i.e. fully screwed out, as rate should be 4-6 ml/mint.
12. Turn oxidant to 4 units more than in above.
13. Turn fuel up to about 6 on gauge.
14. Press flame on - acetylene flame.
15. If flame fails to ignite or gases are not coming through, is probably because pressure on acetylene cylinder is not quite high enough.
16. Regulate flame, by changing both oxidant and fuel.

SWITCHING-OFF

1. Turn on the original flame position (smokey).
2. Press oxidant button.
3. Air and acetylene off.
4. Press fuel/oxidant off, until no flow through the system is observed.

GENERAL NOTES

1. Use only de-ionised water.
2. Use plastic bottle only.
3. Make stock solution up to 1000 PPM ; dilute as required.
4. Use the pipettes that have been soaked in de-ionised water.

STANDARD CONDITIONS AND INSTRUMENTAL PARAMETERS

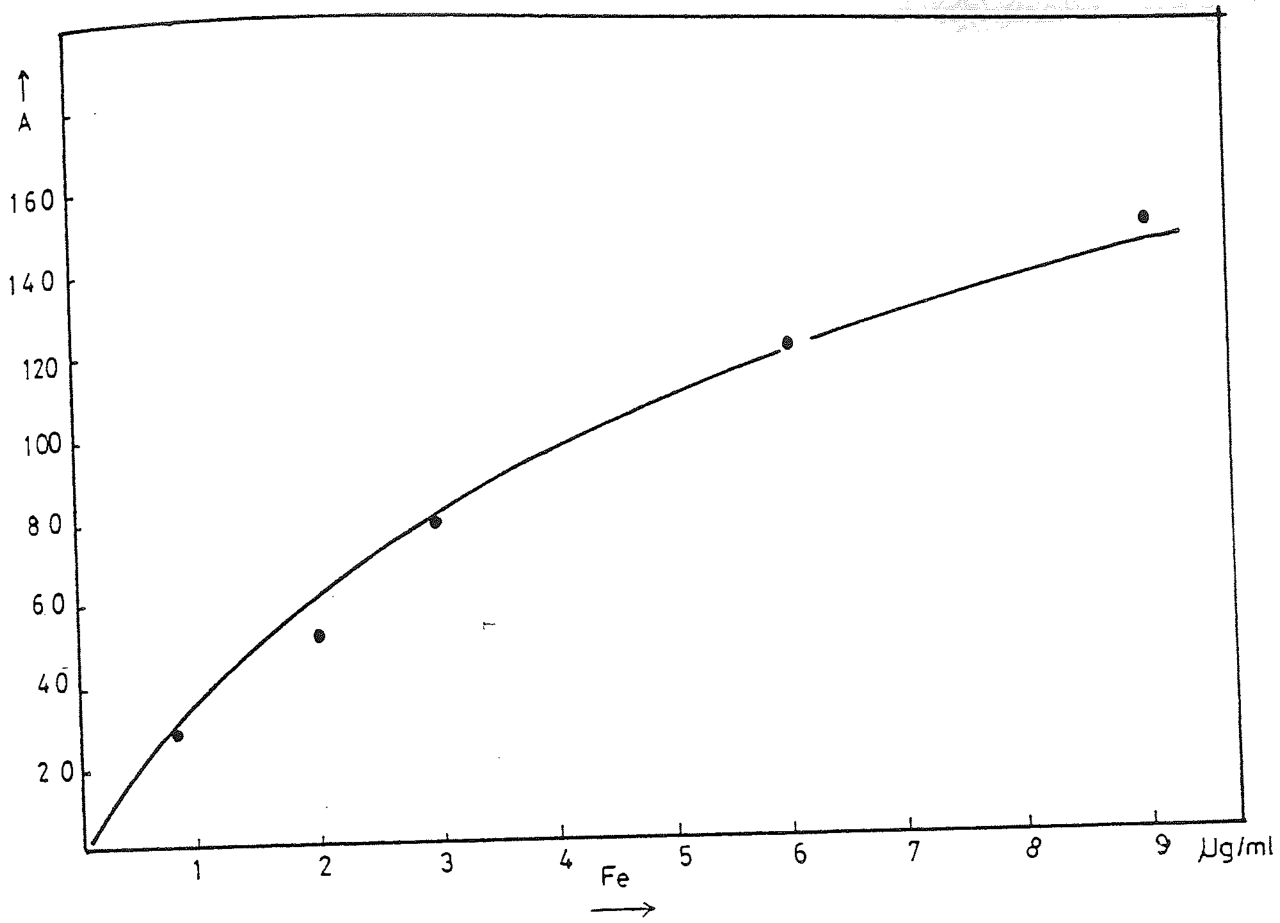
	Fe	Mg
Optimal range:	0.1 - 11 μg/ml	0.003 - 1 μg/ml
Detection limit:	0.003 μg/ml.	0.001 μg/ml
Sensitivity:	0.05 μg/ml.	0.004 μg/ml.
Lamp current:	9 mA	4 mA
p.m voltage:	620V	530V
slit width :	160 μm	320 μm
Wavelength:	248.3 nn.	285.2 nn
Burner :	27019 boiling	27019
Fuel:	Acetylene	Acetylene
Fuel Pressure:	5.0 - 5.3 psig	5.4 - 5.5 psig
Oxidant:	Air	Air
Oxidant pressure:	5.0 psig	5.0 psig

Flame:	Fuel lean	Starchiometric
Burner height	11 mm	8 mm.

TYPICAL DILUTION OF SAMPLES

	Fe	Mg
Extract (extraction step)	x 10	x 20
Raffinate (extraction step)	x 500	x 4000
Extract (Washing step)	x 2.5	x 2.5
Raffinate (Washing step)	x 50	x 100

Typical calibration curves are shown in Fig.II.31 It should be noted that once the equipment is switched off, the same curve cannot be used, since different conditions must be set up. Fig.II.3.2 shows that AA will give different calibration curves for the same stock solution.



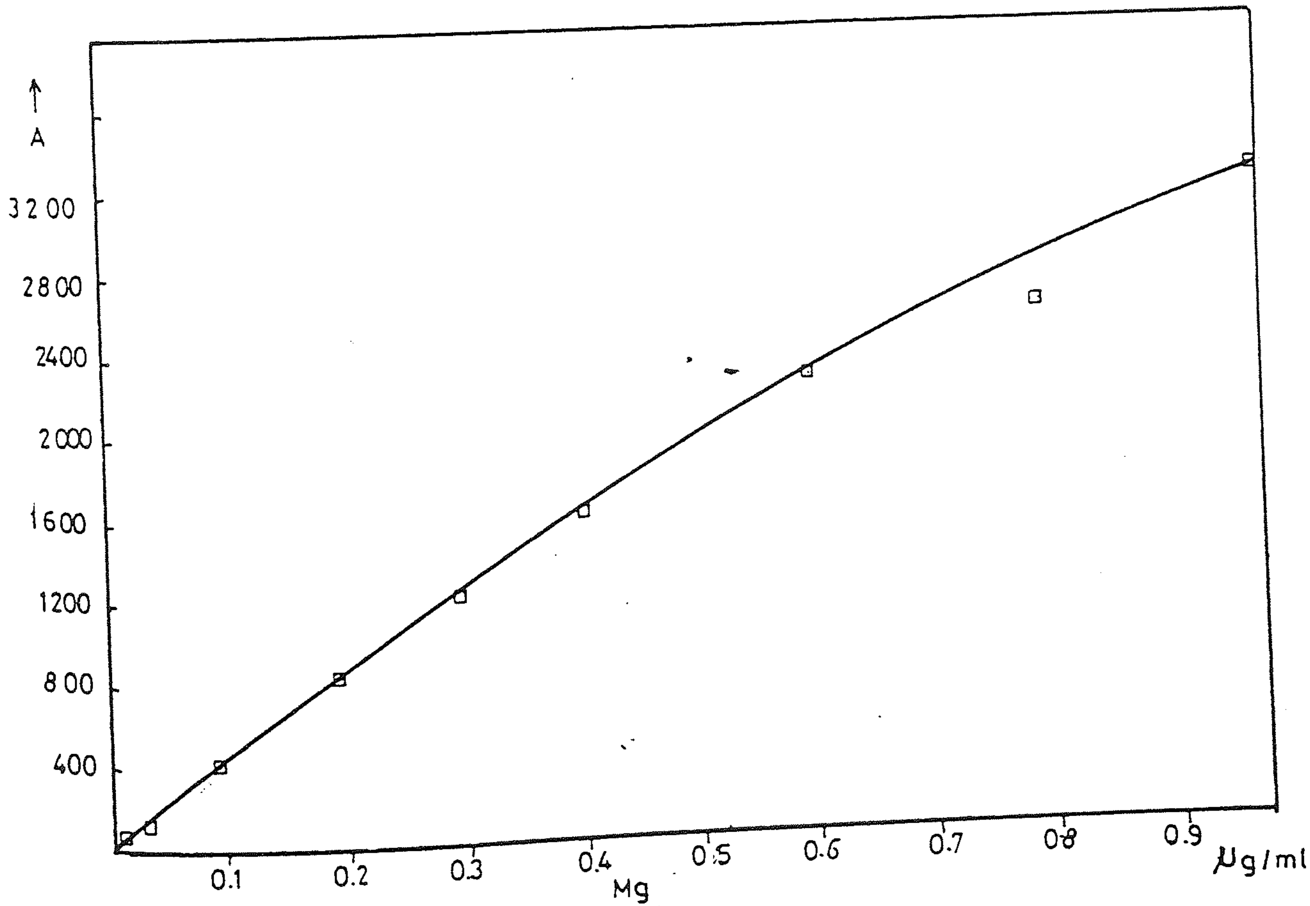


Fig II.3.1 Typical calibration curves for Fe & Mg of the AA equipment

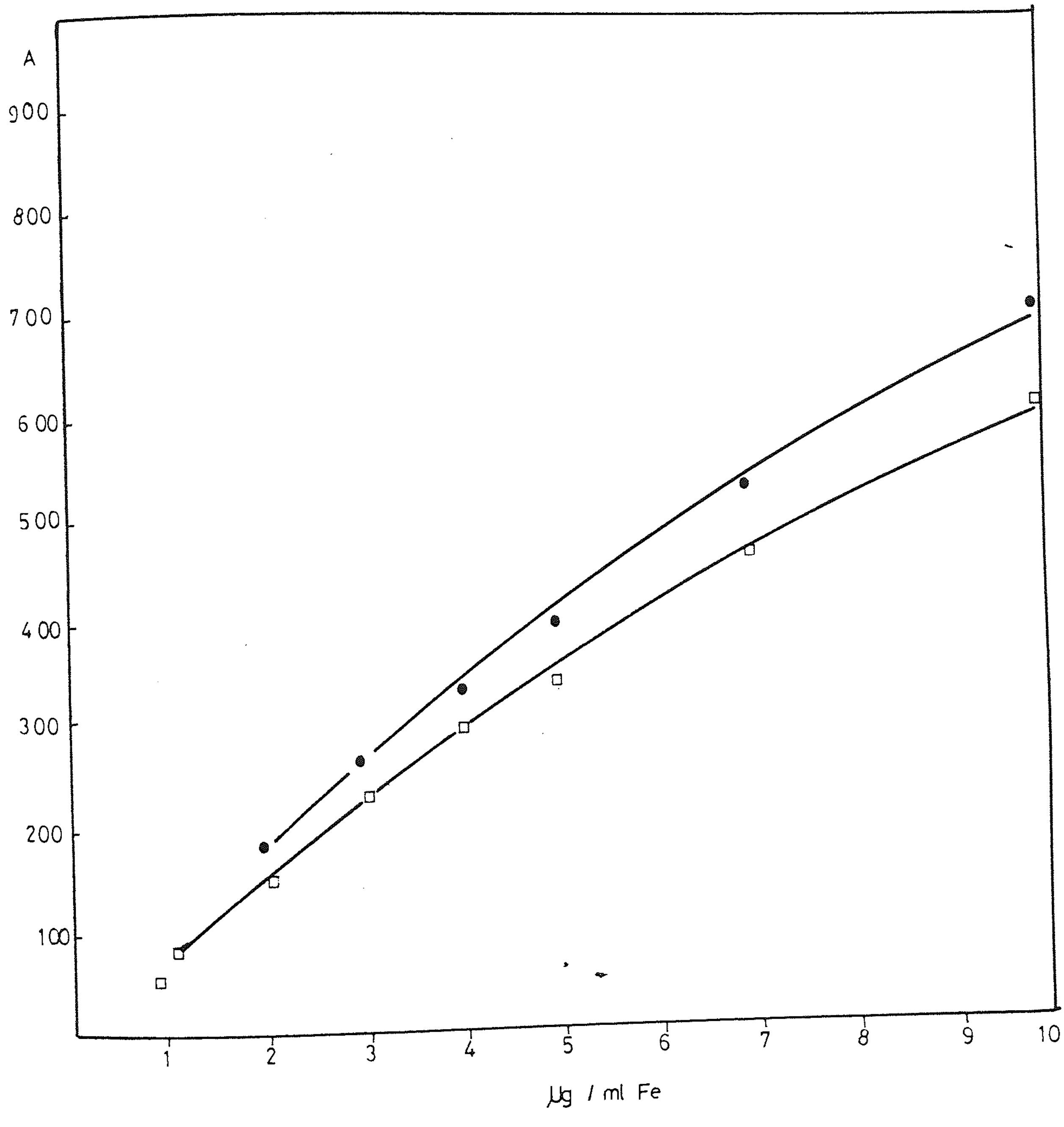


Fig.II.3.2 Two different calibration curves are obtained after switching the AA off, under the same condtions,

APPENDIX II.4

FLOWRATE CALIBRATION CURVES

For phosphoric acid flow.

This is presented in Fig. II.4.1 for different acid concentration.

For solvent flow.

This is presented in Fig. II.4.2 for different content of phosphoric acid.

APPENDIX II.5

Let W = mass of density bottle = 12.1731g.

W_1= mass of bottle and water = 21.93o7g.

W_2= mass of bottle and solution.

$\therefore$ mass of water = W_1-W = 9.75768

mass of solution 2 W_2-W = 13.6109g

Relative density = specific gravity = $\frac{\text{mass of wg}}{\text{mass of water}}$

Density = sp.gravity * density of water at temp. t.

APPENDIX II.6

Viscosity of water at 23°C = 0.8904 Cst

Using the equation $C = \frac{v}{t}$

where t = time in seconds for passage of fluid

v = viscosity of water

C = constant. depends on the size of the U-tube

using size 100 tube

$$C = \frac{0.8904}{64.75} = 0.01474$$

using size 150 tube

$C = 0.0383$

For all viscosity determination, the volume of water for calibration must equal the volume of each liquid, and it was 10 cc of liquid solution.

$1 \text{ cst} = 10^{-2} \text{ st.}$

Dynamic viscosity in Cp = kinematic viscosity in stock X density.

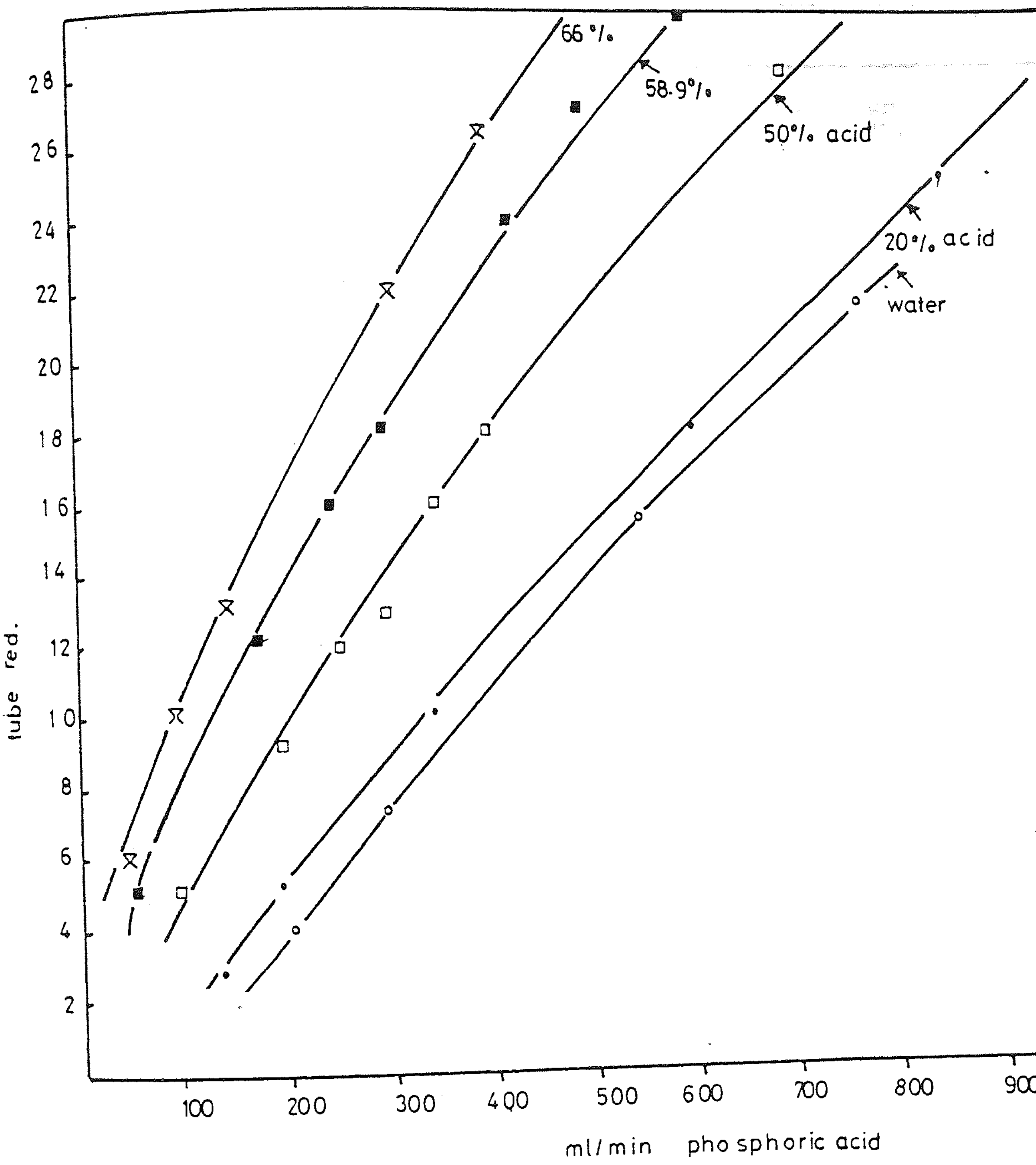


Fig. II.4.1 Calibration chart for water and phosphoric acid at different con. Metric series tube size 7. Stainless steel float type s d= 7.6 mm w= 2.48gm.

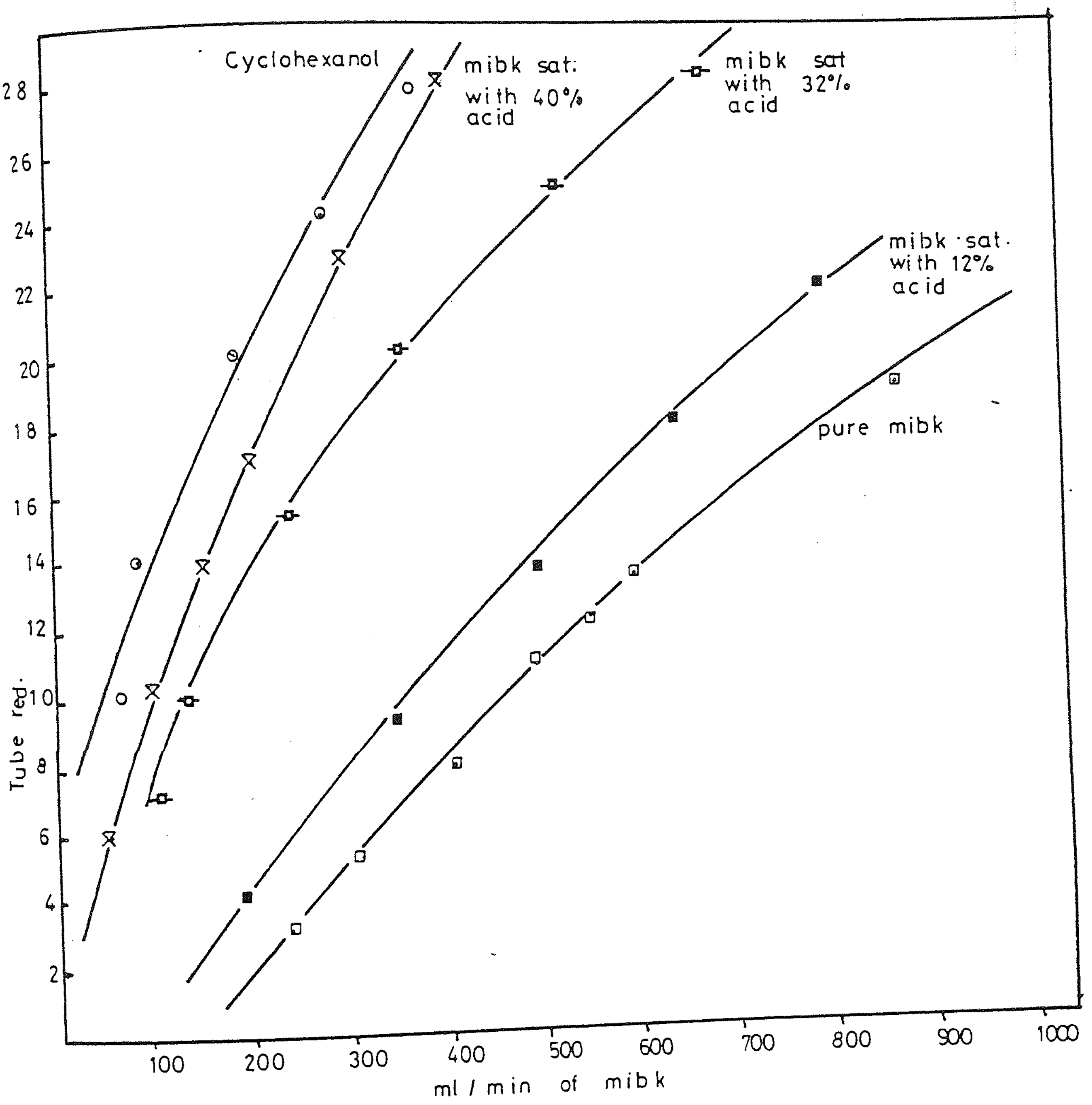
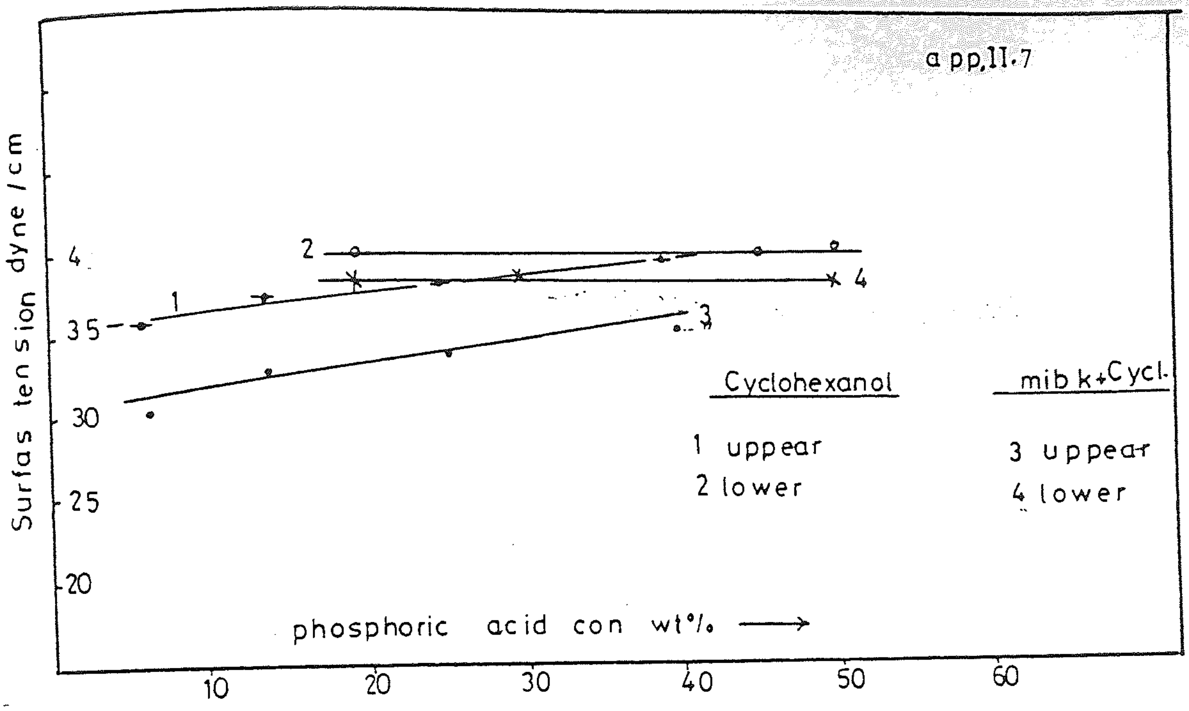
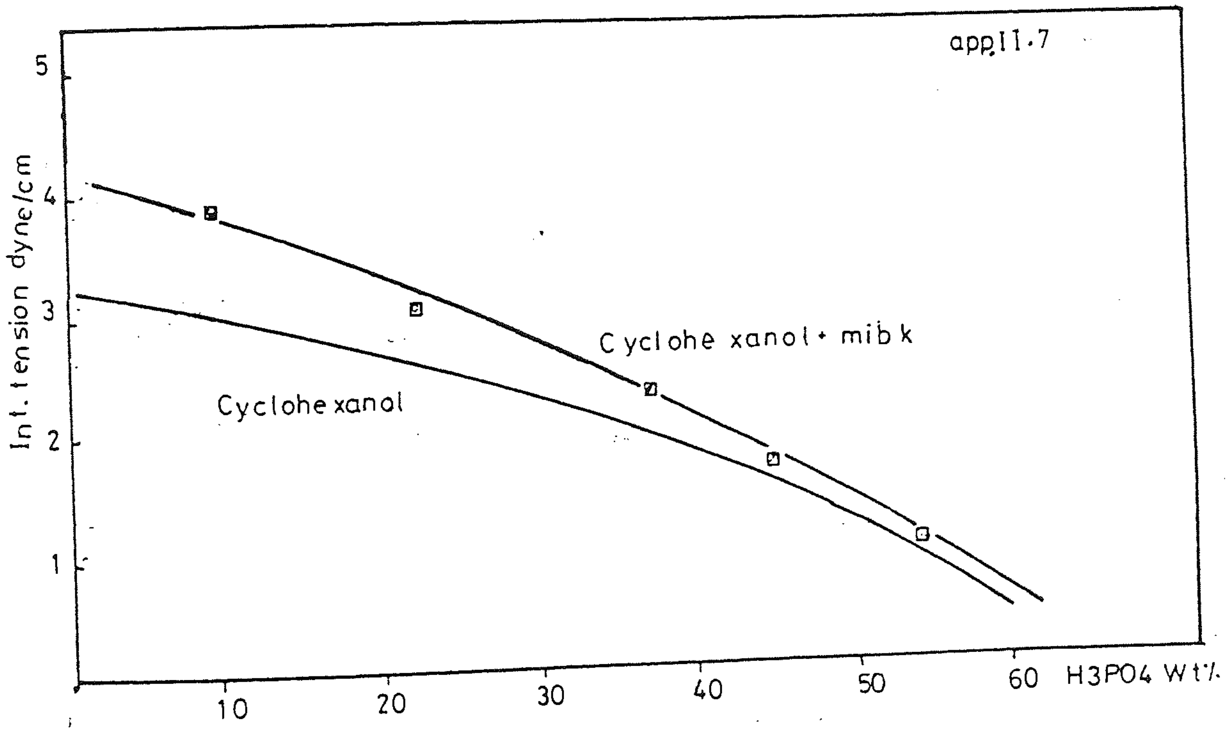
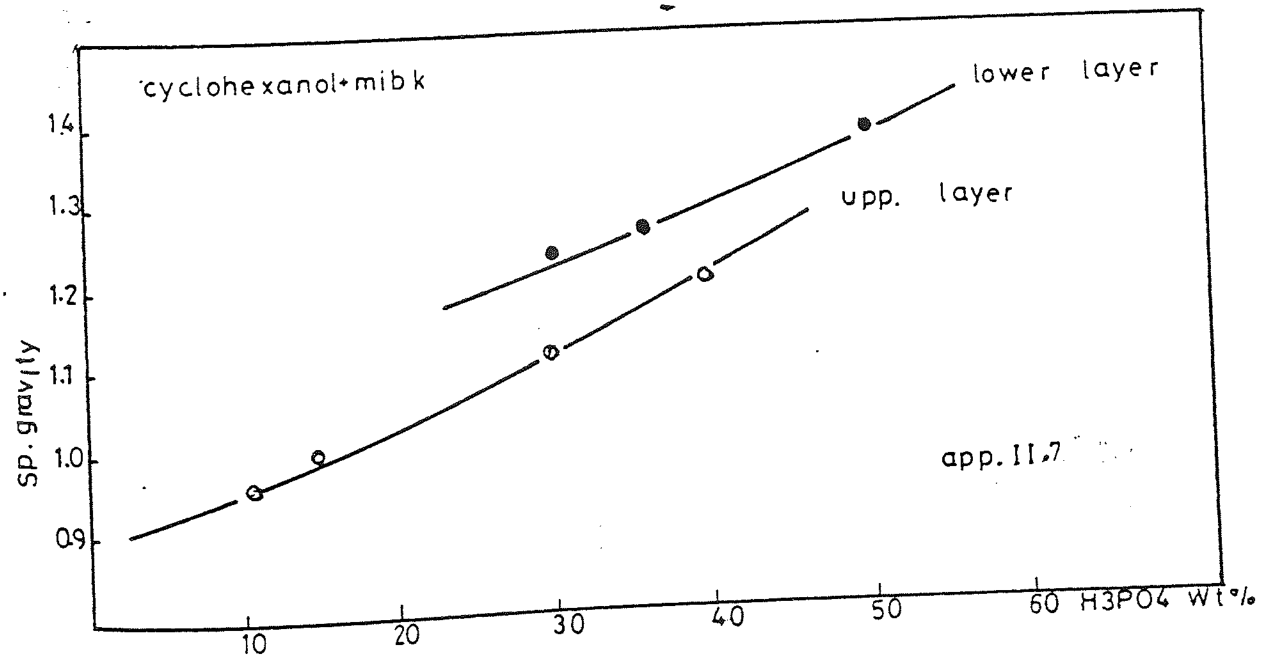


Fig II.4.2 Calibration chart for mibk at different con. of acid Metric series tube size 7. Stainless steel float type S d= 7.6 mm ω = 2.48 gm.


a pp.II.7
Surfas tension dyne /cm
4
35
30
25
20
1
2
3
4
Cyclohexanol
1 uppear
2 lower
mib k+Cycl.
3 uppear
4 lower
phosphoric acid con wt% →
10
20
30
40
50
60


app.II.7
Int. tension dyne/cm
5
4
3
2
1
Cyclohe xanol+ mibk
Cyclohe xanol
10
20
30
40
50
60
H3PO4 Wt%


cyclohexanol+mibk
lower layer
upp. layer
app. II.7
sp. gravity
1.4
1.3
1.2
1.1
1.0
0.9
10
20
30
40
50
60
H3PO4 Wt%

APPENDIX III

CONTENTS OF THIS APPENDIX

1. Equilibrium data, Tables III.1 to III.6.
2. Impurities distribution data. Table III.7 and Table III.8.
3. Solvent stability for checking solvent identity using gas liquid chromatography method.

APPENDIX III

EQUILIBRIUM DATA

Table III.1

Compositions corresponding to points on the binodal curve and the co-ordinate of hands method, for Benzaldehyde system.

X_c = weight fraction of solute (phosphoric acid)

X_b = weight fraction of solvent

X_a = weight fraction of water

X_{ca} = weight fraction of solute (phosphoric acid) in water-rich phase.

X_{cb} = weight fraction of acid in solvent-rich phase

X_{bb} = weight fraction of solvent in solvent-rich phase

X_{aa} = weight fraction of water in water-rich phase

Composition wt%

Phosphoric acid X_c wt %	Water X_a wt%	solvent X_b wt%	Hands coordinate $X = \frac{X_c}{X_a}$	$Y = \frac{X_c}{X_b}$
0.0	99.6	0.35	0.0	0.0
9.52	90.04	0.46	0.105	20.69
15.26	84.26	0.48	0.181	31.79
33.2	66.31	0.49	0.5008	67.75
45.7	53.78	0.52	0.849	61.01
55.43	52.94	0.71	1.065	79.4
66.6	31.7	1.70	2.100	39.17
64.25	15.25	20.5	4.21	3.13
52.5	11.38	36.1	4.61	1.454
37.8	7.99	54.2	5.74	0.69
23.5	4.00	72.5	5.875	0.324
0.0	0.39	99.6	0.0	0.0

Table III.2

COMPOSITION OF CO-EXISTING PHASES IN THE SYSTEM PHOSPHORIC ACID-WATER-BENZALDEHYDE at 25°C

Composition of Aqueous phase wt. %			Composition of Solvent phase wt. %									
Acid	Water	Solvent	Acid	Water	Solvent	KH_3PO_4	$\frac{X_{ca}}{X_{aa}}$	$\frac{X_{cb}}{X_{bb}}$	$\frac{1-X_{aa}}{X_{aa}}$	$\frac{1-X_{bb}}{X_{bb}}$	$\frac{X_{ca}}{X_{ca}+X_{aa}}$	$\frac{X_{cb}}{X_{cb}+X_{ab}}$
0.00	99.3	0.7	0.00	0.27	99.73	0.0	0	0	0.01	2.7×10^{-3}	0	0
16.00	83.28	0.72	0.01	0.29	99.7	0.0006	0.19	1.0×10^{-4}	0.201	$3.\ \times10^{-3}$	16.1	3.3
28.61	70.48	0.91	0.85	0.24	98.91	0.029	0.40	8.5×10^{-3}	0.4188	0.01	28.8	77.9
44.2	55.00	0.8	4.0	1.00	9 .85		0.80	0.020	0.818	0.032	44.55	
55.1	43.91	0.99	4.8	1.23	93.97	0.087	1.25	0.051	1.277	0.064	55.6	79.6
62.3	36.7	1.00	8.9	2.3	88.8	0.14	1.69	0.100	1.724	0.126	62.9	79.46
70.1	28.87	1.03	15.01	4.89	80.1	0.21	2.42	0.187	2.463	0.248	70.8	75.4

Table III.3

COMPOSITIONS CORRESPONDING TO POINTS ON THE BINODAL CURVE, AND THE CO-ORDINATE OF HAND METHODS FOR THE SYSTEM PHOSPHORIC ACID-WATER-CYCLOHEXANOL

Composition Wt. %

Phosphoric Acid	Water	Solvent	Hands Methods Co-ordinate	
			$X = \frac{X_c}{X_a}$	$Y = \frac{X_c}{X_b}$
0.0	97.0	3.0	0.0	0.0
8.50	89.	2.5	0.095	3.4
35.75	62.0	2.25	0.576	15.88
50.0	47.89	2.11	1.044	23.69
57.01	41.00	1.99	1.390	28.64
62.25	34.25	3.5	1.8175	17.78
40.5	19.25	40.25	2.1	1.00
31.5	16.11	52.39	1.955	0.60
22.5	13.5	64.0	1.66	0.351
15.6	12.1	64.0	1.66	0.215
5.0	11.10	84.0	0.45	0.059
0.0	10.9	89.1		

Table III.4

COMPOSITION OF CO-EXISTING PHASES IN THE SYSTEM PHOSPHORIC ACID-WATER-CYCLOHEXANOL IN TERMS OF OTHMER-TOBAS CO-ORDINATE

Composition of Aqueous phase wt. %			Composition of Solvent phase wt. %									
Phosph. acid X_{ca}	Water X_{aa}	Solvent X_{ba}	Acid X_{cb}	Water X_{ab}	Solvent X_{bb}	KH_3PO_4	$\frac{X_{ca}}{X_{aa}}$	$\frac{X_{cb}}{X_{bb}}$	$\frac{1-X_{aa}}{X_{bb}}$	$\frac{1-X_{bb}}{X_{bb}}$	$\frac{X_{ca}}{X_{ca}+X_{aa}}$	$\frac{X_{cb}}{(X_{cb}+X_{ab})}$
11	86.52	2.48	0.6	10.4	89.	0.054	0.127	$6.7x10^{-3}$	0.15	0.123	11.27	5.45
20	77.55	2.45	3.0	11.	86.	0.15	0.257	0.03	0.289	0.162	20.5	21.4
25.5	72.1	2.4	5.5	11.1	83.4	0.215	0.353	0.065	0.386	0.199	26.12	33.3
32.5	65.15	2.35	9.5	11.25	79.25	0.29	0.498	0.119	0.533	0.261	33.2	45.89
40.0	57.7	2.3	15	12.1	72.9	0.37	0.693	0.205	0.733	0.371	40.94	55.3
47.5	50.3	2.21	23.	14.0	63.	0.48	0.944	0.365	0.98	0.58	48.5	62.1
53.5	44.25	2.25	31.0	16.0	53.	0.579	1.209	0.58	1.259	0.88	54.73	65.9
57.5	40.51	1.99	37.5	18.1	44.4	0.65	1.419	0.849	1.676	1.25	58.66	67.4
60.5	37.40	2.1	45.	21.5	33.5	0.75	1.617	1.34	1.673	1.98	61.79	67.66

Table III.5

COMPOSITIONS CORRESPONDING TO PARTS ON THE BINODAL CURVE AND THE CO-ORDINATE OF HANDS METHODS CORRELATIONS FOR THE SYSTEM PHOSPHORIC ACID-WATER-MIBK

Compositions Wt. %

PHOSPORIC ACID X_c Wt. %	WATER X_a Wt.%	SOLVENT X_b Wt.%	HANDS CO-ORDINATE $X = \frac{X_c}{X_a}$	$Y = \frac{X_c}{X_b}$
0.0	98.5	1.5	0.0	0.0
10.34	88.15	1.51	0.117	6.89
40.5	57.9	1.60	0.699	25.31
49.15	49.06	1.69	1.003	29.14
55.20	42.55	2.45	1.297	22.53
60.00	37.0	3.0	1.621	20.
61.5	35.5	3.2	1.732	19.21
62.8	31.19	6.01	2.013	10.44
58.0	-25	17.	2.32	3.411
55.0	-23.9	21.1	2.30	2.60
50.09	20.66	29.25	2.42	1.712
34.0	12.01	54.0	2.83	0.629
27.25	9.79	62.96	2.78	0.432
15.2	4.9	79.9	3.10	0.1902
7.2	2.9	89.9	2.48	0.080
0.00	2.25	97.8	0.00	0.00

Table III.6

COMPOSITION OF CO-EXISTING PHASES IN THE SYSTEM PHOSPHORIC ACID-WATER-MIBK, IN TERMS OF HANDS METHODS, OTHMER-TOBAS CO-ORDINATES

Composition of aqueous Phase Wt. %			Composition of upper solvent. Phase Wt. %									
Acid X_{ca}	Water X_{aa}	Solvent X_{ba}	Acid X_{cb}	Water X_{ab}	Solvent X_{bb}	KH_3PO_4	$\frac{X_{ca}}{X_{aa}}$	$\frac{X_{cb}}{X_{bb}}$	$\frac{1-X_{aa}}{X_{aa}}$	$\frac{1-X_{bb}}{X_{bb}}$	$\frac{X_{ca}}{X_{ca}+X_{aa}}$	$\frac{X_{bb}}{X_{cb}+X_{ab}}$
1. 6.5	92.3	1.200	0.02	2.19	97.9	0.003	0.07	0.0003	0.083	0.022	6.57	0.90
2.13.3	85.3	1.5	0.04	2.2	97.78	0.003	0.154	0.0004	0.172	0.022	13.40	1.78
3.16.5	81.99	1.51	0.05	2.248	97.7	0.00303	0.201	0.0005	0.219	0.023	16.75	2.17
4.36 2	62.25	1.55	0.188	2.249	97.57	0.00519	0.581	0.0019	0.606	0.0249	36.76	7.714
5.43.2	55.14	1.66	0.3	2.26	97.44	0.0069	0.78	0.003	0.813	0.026	43.92	11.71
6.47	50.96	2.01	0.7	2.28	97.02	0.0146	0.937	0.007	0.962	0.0307	48.3	23.48
7.50	47.91	2.09	1.25	2.72	96.03	0.025	1.043	0.03	1.08	0.0413	51.0	31.48
8.56	41.5	2.5	9.01	4.5	86.49	0.0803	1.349	0.104	1.409	0.156	57.4	66.69
9.59	37.99	3.01	18.00	6.9	75.1	0.305	1.55	0.739	1.632	0.331	60.83	72.28
10.62	32.79	5.01	42.00	15.5	62.20	0.675	1.89	0.675	2.079	0.607	65.48	73.00

TABLE III.7

CONCENTRATION OF H_3PO_4 AND IMPURITIES IN THE CO-EXISTING PHASES AT EQUILIBRIUM FOR WATER-IMPURE PHOSPHORIC ACID-MIBK

NAME OF IMPURITIES AND CONCENTRATION	UPPER LAYER		LOWER LAYER		DIST. COEFFS.	
	H_3PO_4 Wt.%	PPM	H_3PO_4	PPM	IMP.	H_3PO_4
Fe 4000	0.3	0	43.0	4010	0	0.0069
Fe 5000	19.	177.	59.5	5980	0.013	0.31
Fe 5070	30.	418.6	60.	6300	0.07	0.5
Fe 5050	40.	594.15	61.5	6990	0.085	0.65
Mg 3090	0.9	0	48.1	3099	0	0.01
Mg 4000	6.0	3	52.1	4100	0.007	0.11
Mg 4105	15.1	10.9	56.1	4399	0.0025	0.261
Mg 3600	30.	5.0	60.	4600	0.011	0.5
Mg 3800	39.	186.2	60.8	4900	0.038	0.64
Mg 3000	43.	330.	62.4	3800	0.086	0.68

TABLE III.8

EFFECT OF INITIAL IMPURITIES CONCENTRATION ON THE DISTRIBUTION COEFFICIENT OF IMPURITIES. INITIAL ACID CONCENTRATION = 70% by wt.

INITIAL IMPURITIES	CONCENTRATION OF IMPURITIES IN UPPER LAYER	CONC. IN RAFFINETE	KIMP
2416.5	270.6	1583.2	0.170
4374.8	792.	7499.7	0.105
9624.6	1320.	16250.	0.0812
31362.	2475.	52000	0.048
35000.	2640	45000	0.058

APPENDIX III.3

SOLVENT STABILITY - USING G.L.C.

Instrument	Pye 204, FID Detector
Carrier gas	Nitrogen
Flow rate	50 ml/minute
H_2/air ratio on flow controller (if FID)	11½/6½
Column	PEG 400 (polyethylene glycol, mw 400
Max. operating temperature (°C)	100°C
Its application	Alcohols, Esters, Ketones
Sample(s) and Size(s) and bp	- 0.3 µl MIBK standard - 0.3 µl sample
Column temp/inj/det/°C	150°/150°
Attenuation	8×10^3
Recorder chart speed	10 mm/min
Voltage output/Min PK width/ Noise FIlter	5 mV/3/6
Temperature Programme -	Initial - Isotherma (°C/min) Rate increase - Final

Results (see Fig. III.3)

Sample	Retention Time/min	Area
Pure (MIBK)	3.20	88195
From washing step	3.19	87191
From concentration equipment	3.21	87399

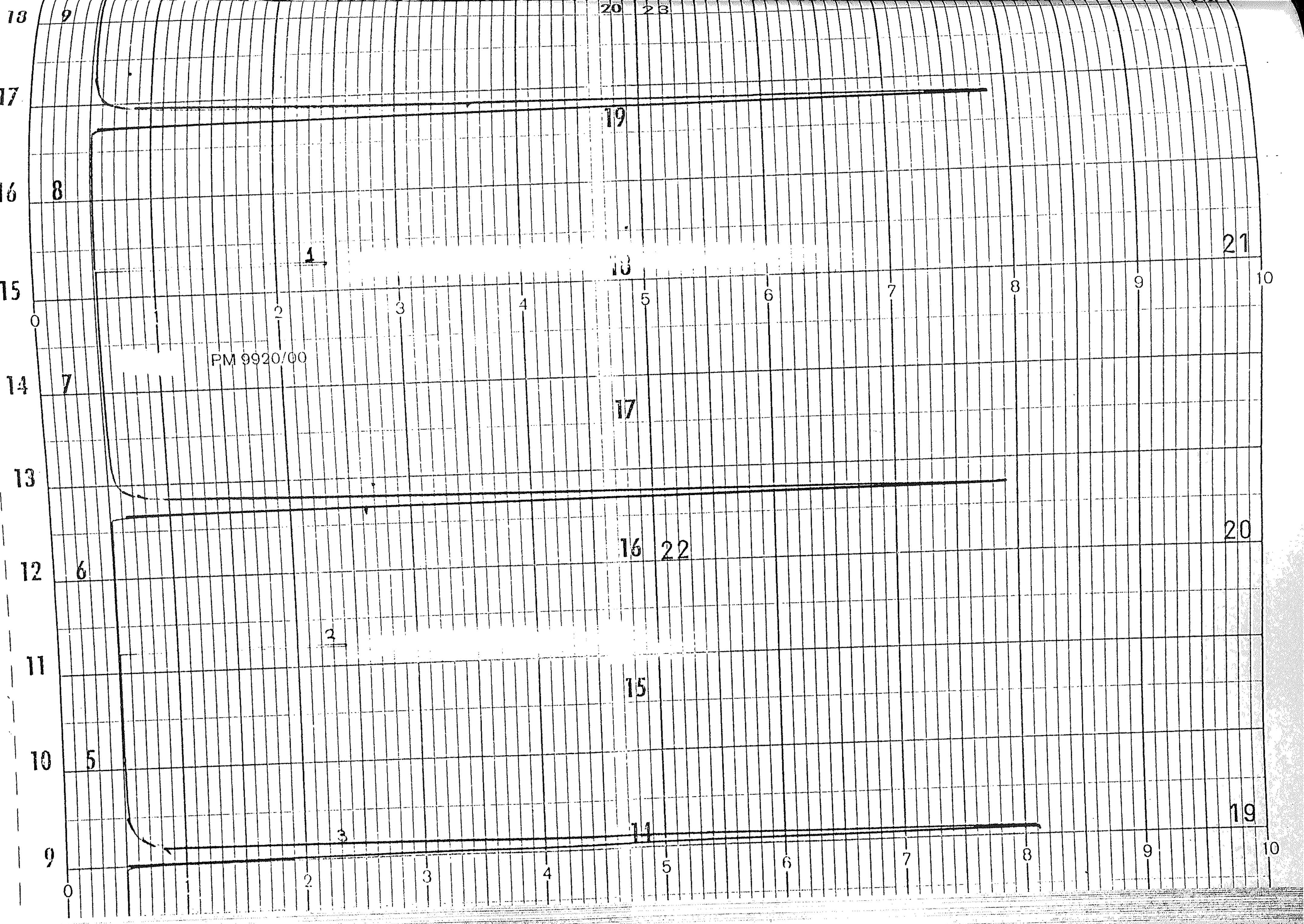

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Fig. III.3

APPENDIX IV

CONTENTS OF THIS APPENDIX

IV.1 DETERMINATION OF CRITICAL SPEED

Phases flow. Aqueous phase = 225ml/mint.

MIBK = 180 ml/mint.

X_F = 5%

R.P.M.	Average total liq. in 50 cc cylinder	Average acid	Average MIBK	X_d	$\frac{X_d}{X_F}$
400	50	34	16	0.32	0.727
450	50	32	18	0.36	0.81
500	50	30	20	0.4	0.9
600	50	28.5	21.5	0.43	0.96
650	50	27.9	22.1	0.44	1.00
700	50	27.2	22.8	0.44	1.00

Three stage with X_F = 16%

R.P.M.	Stage No.	Org.	Aqueous	Total	X_d	$\frac{X_d}{X_F}$
500	1	10	36	46	0.21	
	2	20	30	50	0.4	
	3	15.5	17.5	33	0.46	
ϕ_{ave}					0.35 →	0.7

R.P.M.	Stage No.	Org.	Aqueous	Total	X_d	$\frac{X_d}{X_F}$
500	1	10	32.5	42.5	0.235	
	2	23.5	29.	52.5	0.44	
	3	20.5	24.5	45	0.45	
					0.37 →	0.75

R.P.M.	Stage No.	Org.	Aqueous	Total	X_d	$\frac{X_d}{X_F}$
500	1	16.	19.5	35.5	0.45	
	2	22	23	45	0.45	
	3	20	22.7	42.7	0.46	
					0.46	0.93

R.P.M.	Stage No.	Org.	Aqueous	Total	X_d	
700	1	25.5	25.5	51	0.5	
	2	24.5	20	44.5	0.55	
	3	20	22	42	0.47	
					0.50 →	1.0

IV.2 PHASE INVERSION CHARACTERISTICS

RUN 1 X_F = 5%

R.P.M.	R. READING	V_c	V_d	ϕ_d	SYSTEM CHANGE
500	1	125	605	0.828	O/W → W/O
700	1	125	525	0.807	O/W → W/O
850	1	125	475	0.791	O/W → W/O
1000	1	125	425	0.773	O/W → W/O
1050	1	125	400	0.76	O/W → W/O
1200	1	125	389	0.68	O/W → W/O

RUN 2 X_F= 15%

R.P.M.	V_c	V_d	ϕ_d	SYSTEM CHANGE
500	650	175	0.212	W/O → O/W
700	700	175	0.20	W/O → O/W
850	710	175	0.197	W/O → O/W
1000	720	175	0.195	W/O → O/W
1050	750	175	0.189	W/O → O/W
1200	900	175	0.162	W/O → O/W

RUN 3 x_F = 14%

R.P.M.	R.READING	V_c	R.READING	V_d	ϕ_d	SYSTEM CHANGE
500	1.1	125	5.7	315	0.716	O/W → W/O
700	1.1	125	5.2	300	0.705	O/W → W/O
800	1.1	125	4.5	280	0.686	O/W → W/O
1000	1.1	125	4.1	260	0.675	O/W → W/O
1050	1.1	125	3.7	240	0.64	O/W → W/O
1200	1.1	125	3.5	235	0.65	O/W → W/O

RUN 4 X_F = 14%

R.P.M.	R.READING	V_c	R.READING	V_d	ϕ_d	SYSTEM CHANGE
700	3	190	9.6	445	0.7	O/W → W/O
800	3	190	8.4	440	0.698	O/W → W/O
1000	3	190	7.4	360	0.65	O/W → W/O
1200	3	190	6.5	330	0.63	O/W → W/O

RUN 5 X_F = 14%

R.P.M.	R.READING	V_c	R.READING	V_d	ϕ_d	SYSTEM CHANGE
700	9	340	16.8	725	0.690	O/W → W/O
800	9	340	15.3	656	0.658	O/W → W/O
1000	9	340	15.	640	0.653	O/W → W/O
1200	9	340	14.5	625	0.641	O/W → W/O

RUN 6 X_F = 14%

R.P.M.	R.READING	V_c	R.READING	V_d	ϕ_d	SYSTEM CHANGE
700	13	515	21	900	0.636	O/W → W/O
800	13	515	21	870	0.628	O/W → W/O
1000	13	515	21	830	0.617	O/W → W/O
1200	13	515	21	835	0.618	O/W → W/O

RUN 7 X_F = 14%

R.P.M.	R.READING	V_c	R.READING	V_d	ϕ_d	SYSTEM CHANGE
700	20	769	1.1	175	0.185	W/O → O/W
800	20.1	770	1.1	175	0.185	W/O → O/W
1000	20.2	775	1.1	175	0.184	W/O → O/W
1200	20.2	775	1.1	175	0.184	W/O → O/W

RUN 8 X_F = 14%

R.P.M.	R.READING	V_c	R.READING	V_d	ϕ_d	SYSTEM CHANGE
600	20.2	775	1.7	200	0.2	W/O → O/W
700	23.2	930	1.7	200	0.176	W/O → O/W
800	23.2	930	1.7	200	0.176	W/O → O/W
1000	23.2	930	1.7	200	0.176	W/O → O/W
1200	23.2	930	1.7	200	0.176	W/O → O/W

RUN 9 $X_F = 14\%$

R.P.M.	R.READING	V_c	R.READING	V_d	ϕ_d	SYSTEM CHANGE
700	30	1100	5	310	0.217	W/O → O/W
900	30	1100	5	310	0.217	W/O → O/W
1000	30	1100	5	310	0.217	W/O → O/W
1200	30	1100	5	310	0.217	W/O → O/W

RUN 10 $X_F = 23\%$

R.P.M.	R.READING	V_c	R.READING	V_d	ϕ_d	SYSTEM CHANGE
700	1.1	125	4.9	295	0.7	O/W → W/O
800	1.1	125	4.4	275	0.68	O/W → W/O
1000	1.1	125	3.9	260	0.67	O/W → W/O
1050	1.1	125	3.3	240	0.65	O/W → W/O

RUN 11 $X_F = 23\%$

R.P.M.	R.READING	V_c	R.READING	V_d	ϕ_d	SYSTEM CHANGE
700	3.10	166	8.6	415	0.71	O/W → W/O
800	3.10	166	6.5	342	0.67	O/W → W/O
1000	3.10	166	6.5	342	0.67	O/W → W/O
1150	3.10	160	6.0	325	0.66	O/W → W/O

RUN 12 $X_F = 23\%$

R.P.M.	R.READING	V_c	R.READING	V_d	ϕ_d	SYSTEM CHANGE
700	9.1	280	16.3	710	0.717	O/W → W/O
800	9.1	280	16.2	700	0.714	O/W → W/O
1000	9.1	280	14.5	650	0.697	O/W → W/O
1150	9.1	280	13.8	615	0.687	O/W → W/O

RUN 13 $X_F = 23\%$

R.P.M.	R.READING	V_c	R.READING	V_d	ϕ_d	SYSTEM CHANGE
700	24.5	810	1	175	0.178	W/O → O/W
800	24.6	820	1	175	0.176	W/O → O/W
1000	24.7	835	1	175	0.173	W/O → O/W
1150	25	850	1	175	0.170	W/O → O/W

RUN 14 $X_F = 23\%$

R.P.M.	R.READING	V_c	R.READING	V_d	ϕ_d	SYSTEM CHANGE
700	26.2	9.20	1.8	200	0.178	W/O → O/W
800	26	900	1.8	200	0.181	W/O → O/W
1000	25.6	890	1.8	200	0.182	W/O → O/W
1150	25.6	890	1.8	200	0.183	W/O → O/W

RUN 15 X_F = 45%

R.P.M.	R.READING	V_c	R.READING	V_d	ϕ_d	SYSTEM CHANGE
700	2	125	4.9	292	0.70	O/W → W/O
800	2	125	4.2	270	0.68	O/W → W/O
1000	2	125	3.0	255	0.67	O/W → W/O
1200	2	125	2.9	235	0.65	O/W → W/O

RUN 16 X_F = 45%

R.P.M.	R.READING	V_c	R.READING	V_d	ϕ_d	SYSTEM CHANGE
700	29	1100	1.8	200	0.15	W/O → O/W
800	30	1150	1.8	200	0.14	W/O → O/W
1200	30.5	1200	1.8	200	0.14	W/O → O/W

FLOW RATE OF PHOSPHORIC ACID AND SOLVENT AT THE POINT OF PHASE INVERSION

X_F = 5%

700 R.P.M.		900 R.P.M.		1100 R.P.M.	
V_c	V_d	V_c	V_d	V_c	V_d
110	345	110	345	110	345
145	500	180	490	400	630
400	900	400	780	490	820
500	1180	490	1050	---	---

$x_F = 14\%$

700 R.P.M.		800 R.P.M.		1000 R.P.M.		1200 R.P.M.	
V_c	V_d	V_c	V_d	V_c	V_d	V_c	V_d
125	300	125	280	125	260	125	210
190	445	190	440	190	360	190	330
340	725	340	656	340	640	340	625
515	900	515	870	515	840	515	835

$x_F = 23\%$

700 R.P.M.		800 R.P.M.		1000 R.P.M.		1200 R.P.M.	
V_c	V_d	V_c	V_d	V_c	V_d	V_c	V_d
95	300	95	280	95	270	95	250
135	415	135	355	135	342	135	325
280	710	280	700	280	650	280	615
430	1050	430	1000	430	920	430	880

$x_F = 45\%$

700 R.P.M.		800 R.P.M.		1000 R.P.M.		1200 R.P.M.	
V_c	V_d	V_c	V_d	V_c	V_d	V_c	V_d
60	280	60	260	60	225	60	210
100	360	100	350	100	345	100	350
125	431	125	425	175	415	125	400

IV.3 WEDGE LENGTH

RUN 1 X_F = 5% SYSTEM O/W

R.P.M.	R.READING	V_c	R.READING	V_d	WL in cm	WH in cm
700	3	190	1	175	8.2	0.2
700	3	190	2	210	10.	0.4
700	3	190	3	240	11.	0.6
700	3	190	4	270	12.	1.0
700	3	190	6	355	14.	1.1
1000	3	190	1	175	9.5	0.6
1000	3	190	3	240	12.2	0.8
1000	3	190	5	310	14.5	1.0
1000	3	190	6	355	16.	1.3
700	4	200	1	175	11.5	0.4
700	5	240	1	175	13.	0.4
700	7	300	1	175	15.5	0.3
700	9	340	1	175	17.	0.2
700	15	520	1	175	22.	0.2

RUN 2 $X_F = 15\%$ SYSTEM O/W

R.P.M.	R.READING	V_c	R.READING	V_d	WL in cm.	WH in cm.
700	1	112	1	175	8.3	0.1
700	1	112	3	240	10.1	0.4
700	1	112	5	310	12.1	0.5
700	1	112	7	366	14.3	0.7
700	3	180	1	175	9.5	0.2
700	3	180	3	240	12.	0.5
700	3	180	5	310	14.1	0.7
700	3	180	7	366	16.1	0.9
800	3	180	1	175	10.	0.3
800	3	180	3	240	12.2	0.5
800	3	180	5	310	14.2	0.7
800	3	180	7	366	16.5	0.9
800	3	180	9	← Phase inversion →		
1000	3	180	1	175	10.1	0.3
1000	3	180	3	240	12.2	0.5
1000	3	180	5	310	14.5	0.7
1000	3	180	7	366	← Phase inversion →	
700	7	300	1	175	13.1	0.4
700	7	300	3	240	16.8	0.7
700	7	300	5	310	20.9	1.
700	7	300	7	366	22.6	1.5
700	7	300	9.5	455	26.5	1.6
700	7	300	11.	512	← All length of settle →	

IV.4 A SAMPLE OF EXPERIMENTAL LOG SHEET IMPURE SYSTEM

Date: 6.6.1980

Experiment No: 2

Solvent Used: MIBK

Acid and Solvent Property:

	Acid		Solvent	
Concentration	input	58.9	input	0.1
	output	55.1	output	13.95
Density	input	1.423	input	0.807
	output	1.3837	output	0.8925

Position of Impeller = 4.5 cm from bottom of mixer

R.P.M. = 700

Height of liquid in Mixer = 9 cm.

The Continuous Phase is: O/W organic dispersed in water

Flow Rates:

	Votometer Reading	Input		Output	
		ml/min	g/min	ml/min	g/min
Acid	12	177	251.8	140	195
Solvent	1	177	142.92	208	185.64
Total Flow		354	394.72	348	380.64

∴ Phase Ratio = 1:1

Initial Acid Composition (Impurities)

Length of the wedge in the settler = 0.0 cm

Width of the wedge in the settler = 0.0 cm

Residence time in the settler = 6 min $= \frac{\text{volume of settler}}{\text{total flow rate}}$

Residence time in the mixture = 2.96 min $= \frac{\text{volume of mixer}}{\text{total flow rate}}$

Hold-up Value (cm /cm)

Sample taking	Stage 1			Stage 2			Stage 3		
	Solv	Acid	Hold-up	Solv	Acid	Hold-up	Solv	Acid	Hold-up
By stopping system	240	360	0.4	270	410	0.397	255	315	0.447

Average Hold-up = 0.422 ∴ $\phi_c = 0.578$

Time Experiment Finished =

Temperature of operation = 25 ± 0.5 °C

Entrainment

mix(1) = 0

mix(2) = 0

mix(3) = 0

RESULT

		R. Index	Time		R. Index
Stage 1	E1.1	1.39909	10	R1.1	1.39799
	E1.2	1.40024	20	R1.2	1.39755
	E1.3	1.39944	30	R1.3	1.39775
	E1.4	1.3998	40	R1.4	1.39762
	E1.5	1.3999	50	R1.5	1.3974
	E1e	1.3999	60	R1e	1.3974
Stage 2	E2.1	1.39905	10	R2.1	1.39719
	E2.2	1.40001	20	R2.2	1.39658
	E2.3	1.39969	30	R2.3	1.39658
	E2.4	1.39978	40	R2.4	1.39646
	E2.5	1.39977	50	R2.5	1.39648
	E2e	1.39977	60	R2e	1.39646
Stage 3	E3.1	1.39797	10	R3.1	1.39370
	E3.2	1.39773	20	R3.2	1.39532
	E3.3	1.39758	30	Rw.3	1.3949
	E3.4	1.39768	40	R3.4	1.3948
	E3.5	1.39768	50	R3.5	1.3948
	E3e	1.39768	60	R3e	1.3948

	Min.	Acid Conc.Wt%	Impurities conc.PPM	AA Reading	Acid Conc.Wt%	Impurities conc.PPM	AA Reading	KH_3PO_4	K imp
Stage 1	10	E1.1 13.1	33.0	62	R1.1 58.2	4392	277	0.225	0.0075
	20	E1.2 14.01	48.0	96	R1.2 57.9	4125	262	0.241	0.0116
	30	E1.3 14.04	56.0	111	R1.3 58.0	4275	270	0.242	0.0130
	40	E1.4 14.01	55.7	110.5	R1.4 57.9	4125	260	0.241	0.0135
	50	E1.5 13.96	55.0	110	R1.5 57.7	4175	266	0.241	0.0131
	60	E1e 13.95	55.0	110	R1e 57.7	4175	265	0.241	0.0131
Stage 2	10	E2.1 10.1	37	75	R2.1 56.8	4425	277	0.177	0.0080
	20	E2.2 10.99	38	78	R2.2 56.7	4427	278	0.193	0.0085
	30	E2.3 10.51	35	52	R2.3 56.8	4625	285	0.185	0.0075
	40	E2.4 10.98	36	68	R2.4 56.85	4625	285	0.193	0.0077
	50	E2.5 10.80	38	76	R2.5 56.75	4700	290	0.190	0.008
	60	E2e 10.80	38	76	R2e 56.75	4750	292	0.190	0.008
Stage 3	10	E3.1 5.01	11	21	R3.1 55.1	4140	264	0.0909	0.0026
	20	E3.2 5.00	10	16	R3.2 55.9	4900	299	0.894	0.0020
	30	E3.3 4.99	10	16	R3.3 55.14	4950	309	0.090	0.0020
	40	E3.4 5.93	13	21	R3.4 55.11	5000	310	0.1076	0.0026
	50	E3.5 5.95	14	30	R3.5 55.1	4955	301	0.1079	0.0028
	60	E3e 5.95	14	30	R3e 55.1	4955	302	0.1079	0.0028

IV.4B SAMPLE OF EXPERIMENTAL ARRANGEMENT (PURE SYSTEM)

Date: 16.4.1980

Experiment No.3

Solvent Used: MIBF

Acid and Solvent Property:

	Acid		Solvent	
Concentration	input	58.9	input	0.05
	output	55.5	output	14.6
Density	input	1.423	input	0.807
	output	1.384	output	0.892

Position of Impeller: = 4.5 cm from bottom of mixer

R.P.M. = 900

Height of Liquid in Mixer

The Continuous Phase is:

Flow Rates:

	Input		Output	
Votometer Reading	ml/min	g/min	ml/min	g/min
Acid 12	177	251.5	140	196
Solvent 1.1 – 1.2	177	143.0	210	168
Total Flow	354	394.5	350	364

∴ Phase Ratio cm^3/cm^3

Initial Acid Composition (Impurities) = 0.0

Length of the wedge in the settler = 0.0 cm

Width of the wedge in the settler = 0.0 cm

Residence time in the settler = 6 min = $\frac{\text{volume of settler}}{\text{Total flow rate}}$

Residence time in the mixture = 2.96 min = $\frac{\text{volume of mixer}}{\text{total flow rate}}$

Hold-Up Value (cm^3/cm^3)

	Mix 1			Mix 2			Mix 3		
Sample Taking	Solv	Acid	Hold-up	Solv	Acid	Hold-up	Solv	Acid	Hold-up
By stopping system	25.2	370	0.403	188	480	0.282	211	351	0.36

Average Hold-up ϕ_d = 0.388 ϕ_c = 0.645

Temperature of Operation = 25°C

Entrainment

Mix 1 =)
)
Mix 2 =) zero
)
Mix 3 =)

RESULTS

		R.Index	Time	wt% Conc.		R.Index	wt% Conc.	KH$_3$PO$_4$
Stage 1	E1.1	1.40278	10	15.0	R1.1	1.39654	58	0.256
	E1.2	1.4029	20	15.1	R1.2	1.39709	58.1	0.255
	E1.3	1.4029	30	14.9	R1.3	1.39683	58.9	0.256
	E1.4	1.4028	40	14.7	R1.4	1.39644	57.89	0.254
	E1.5	1.4028	50	14.6	R1.5	1.39620	57.99	0.251
	E1..6	1.4028	60	14.6	R1.6	1.39620	57.99	0.251
Stage 2	E2.1	1.39941	10	11.99	R2.1	1.39649	57.43	0.2072
	E2.2	1.39940	20	11.88	R2.2	1.39617	57.2	0.2076
	E2.3	1.49918	30	11.34	R2.3	1.39600	56.99	0.1989
	E2.4	1.39918	40	11.13	R2.4	1.34606	57.18	0.1944
	E2.5	1.39916	50	11.1	R2.5	1.39606	57.99	0.194
	E2.6	1.39916	60	11.1	R2.6	1.29606	56.90	0.195
Stage 3	E3.1	1.39938	10	7.68	R3.1	1.39386	55.9	0.1373
	E3.2	1.39889	20	7.07	R3.2	1.39375	55.6	0.127
	E3.3	1.39877	30	6.65	R3.3	1.39375	55.6	0.119
	E3.4	1.39867	40	6.73	R3.4	1.39375	55.6	0.121
	E3.5	1.39867	50	6.71	R3.5	1.39380	55.5	0.120
	Ew.6	1.39867	60	6.71	R3.6	1.39380	55.55	0.120

IV.4C SAMPLE OF EXPERIMENTAL DATA ON WASHING STEP

Initial acid conc. in solvent ≃ 40% - one stage was used

	R.READING	FLOW RATE IN m/l mint	PHASE RATIO	CONC. OF FINAL PRODUCT
Water	1.0	120	3.79	51
Solvent	30	455		
Water	1.0	120	2.83	46
Solvent	25	340		
Water	1.0	120	2.08	41.6
Solvent	20	250		
Water	1.0	120	0.68	35.8
Solvent	15	175		
Water	1.0	120	0.25	20
Solvent	5	30		

IV.5 MASS TRANSFER EXPERIMENTAL RESULTS

TABLE IV.5 SUMMARY OF EXPERIMENTAL DATA

RPM	R.Reading		%	Feed Solvent	da	System Purity	Init. Acid Conc.	Acid Con. Wt.%				Init. Imp. Conc.	Imp. Conc. p.p.m.			Time to reach Steady state			Residence Time
	Vs	Va							St.1	St.2	St.3		St.1	St.2	St.3	St.1	St.2	St.3	
500	1:1 (177)	12 (177)	75	1:1	0,470	P	58.9	Raf.	57.48	56.3	55.6	Zero	Zero			60	58	52	8.96
								Ex.	13.5	10.3	6.7								
								KH_3PO_4	0.234	0.190	0.120								
700	1:1 (177)	12 (177)	85	1:1	0.398	P	58.9	Raf.	57.8	56.9	55.4	Zero	Zero			57	52	42	8.96
								Ex.	14.1	11.11	6.6								
								KH_3PO_4	0.243	0.195	0.119								
900	1.1 (177)	12 (177)	90	1:1	0.38	P	58.9	Raf.	57.9	56.9	55.5	Zero	Zero			51	46	42	8.96
								Ex.	14.6	11.1	6.71								
								KH_3PO_4	0.252	0.195	0.120								
1100	1:1 (177)	12 (177)	96.53	1:1	0.35	P	58.9	Raf.	57.5	56.4	55.6	Zero	Zero			48	44	38	8.96
								Ex.	14.2	10.4	6.61								
								KH_3PO_4	0.246	0.184	0.118								
500	6.5 (354)	12 (177)	70	1:2*	0.52	P	59.7	Raf.	57.6	56.1	55.7	Zero	Zero			57	55	50	5.97
								Ex.	12.83	7.7	4.12								
								KH_3PO_4	0.222	0.137	0.073								
900	6.5 (354)	12 (177)	75	1:2*	0.5	P	59.2	Raf.	57.2	56.4	55.0	Zero	Zero			———			5.97
								Ex.											
								KH_3PO_4											

* Phase inversion

( ) = Rotameter Reading ( ) = Atomic Absorption Reading

TABLE IV.5 (cont...)

RPM	R.Reading		%	Feed Solvent	da	System Purity	Init. Acid Conc.	Acid Conc. Wt.%				Init. Imp. ppm	Imp. Conc. ppm				Time to reach steady state			Residence time
	Vs	Va												St.1	St.2	St.3	St.1	St.2	St.3	
900	1:1 (177)	20.8 (354)	86	2:–	0.316	P	58.9	Raf.	58.8	57.8	57.3			—	—	—	53	53	45	6.58
								Ex.	20.7	17.7	11.									
								KH_3PO_4	0.352	0.306	0.191									
900	1.2 (177)	27.5 (522)	78	3:1	0.24	P	59.2	Raf.	59.	58.	57.8	Zero		Zero			54	54	47	4.5
								Ex.	20.9	18.9	12.9									
								KH_3PO_4	0.354	0.325	0.223									
900	1.0 (177)	25. (354)	95	2:1	0.5	P	63.	Raf.	61.7	50.1	58.2	Zero		Zero			63.5	60.	59.	6.58
								Ex.	36.25	29.2	18.3									
								KH_3PO_4	0.587	0.485	0.314									
500	1.1 (177)	12 (177)	88	1:1	0.435	Pe	58.9	Raf.	57.6	56.5	54.9	4060	Raf.	4000	4210	4390	48	44	42	8.96
								Ex.	13.65	10.0.	5.89		Ex.	54	30	11				
								KH_3PO_4	0.236	0.176	0.10		Kimp	0.013	0.007	0.0025				
700	1.1 (177)	12 (177)	93.3	1:1	0.42	Pe	58.9	Raf.	57.7	56.5	55.1	4300	Raf.	4175 (265)	4750 (292)	4955 (302)	42	39	37	8.96
								Ex.	13.95	10.8	5.95	4300	Ex.	55 (110)	38 (75)	14 (303)				
								KH_3PO_4	0.241	0.190	0.107		Kimp	0.013	0.008	(0.0025				

TABLE IV.5 (cont....

RPM	R.Reading		%	Feed Solvent	da	System Purity	Init. Acid Conc.	Acid Conc. Wt.%				Init. Imp. Conc. ppm	Imn. Conc. ppm.				Time to reach Steady State			Residence Time
	Vs	Va							St.1	St.2	St.3			St.1	St.2	St.3	St.1	St.2	St.3	
900	1.1	12	96	1:1	0.41	Fe	59.1	Raf.	57.0	56.3	55.4	4600	Raf.	4690	5200	5700	44	42	40	8.96
	(177)	(177)						Ex.	14.2	10.17	6.23		Ex.	60	37	11.5				
														(740)	(460	(189)				
								KH_3PO_4	0.242	0.179	0.112		Kimp	0.012	0.007	0.002				
600	1.1	12	-	1:1	0.43	Fe	59.1	Raf.	58.7	57.7	56.3	4600	Raf.	4790	4870	5420	—	—	—	8.96
	(177)	(177)												(978)	(1058)	(1088)				
								Ex.	14.3	11.01	6.4		Ex.	63	35	13				
														(743)	(459)	(181)				
								KH_3PO_4	0.243	0.190	0.113		Kimp	0.013	0.007	0.0023				
1100	1.1	12	99	1:1	0.41	Fe	58.9	Raf.	52.6	56.8	55.4	4550	Raf.	4375	4925	5075	35	40	30	8.96
	(177)	(177)						Ex.	14.01	10.15	5.67		Ex.	62	44	13				
								KH_3PO_4	0.243	0.178	0.102		Kimp	0.014	0.008	0.0025				
500	6.5	12	78	1:2*	0.55	Fe	58.7	Raf.	57.25	55.9	54.2	4000	Raf.	3650	3995	4225	55	50	42	
	(350)	(177)												(202)	(211)	(223)				
								Ex.	12.	7.25	3.39		Ex.	25	10	3				
														(89)	(38)	(12)				
								KH_3PO_4	0.209	0.129	0.62		Kimp	0.008	0.0025	0.0007				

TABE IV.5 (Cont....)

RPN	R. Reading		%	Feed Solvent	da	System Purity	Init. Acid Conc.	Acid Conc. Wt. %				Init. Imp. Conc.	Imp. Conc. ppm				Time to reach steady State			Residence Time
	Vs	Va							St.1	St.2	St.3			St.1	St.2	St.3	St.1	St.2	St.3	
900	6.5	12	50	1:2*	0.45	Fe	58.9	Raf	57.02	56.3	54.3	3800	Raf	3425	3735	3860	—	—	—	5.97
	(354)	(177)												(988.2)	(1022)	(1044)				
								Ex.	10.2	7.0	4.0		Ex.	25	10	4				
														(280)	(189)	(55)				
								KH_3PO_4	0.178	0.124	0.073		Kimp	0.007	0.0026	0.001				
900	1.1	20.8	70	2:1	0.33	Fe	58.9	Raf.	57.47	56.76	55.3	4000	Raf	4110	4111	4660	50	48	45	6.58
	(177)	(354)												(59.5)	(60)	(65)				
								Ex.	13.25	11.8	10.8	Ex.	74	86	30					
													(55)	(44)	(25)					
								KH_3PO_4	0.230	0.707	0.193	Kimp	0.018	0.0136	0.0064					
900	1.1	27.8	92	3:1	0.36	Fe	60	Raf	59.4	38.3	56.6	4178	Raf	4150 (59)	4050 (57)	4250 (61)	50	49	48	4.56
	(177)	(522)						Ex.	20.07	17.01	11.1		Ex.	105	85	53				
														(70)	(60	(43)				
								KH_3PO_4	0.337	0.291	0.196		Kimp	0.025	0.02	0.0124				
500	1.1	12	95	1:1	0.44	Mg	58.9	Raf	57.1	36.7	55.23	1600	Raf	1428	1500	1680	45	40	40	8.96
	(177)	(177)						Ex.	13.6	10.2	6:01		Ex.	1.88	1.1	0.33				
								KH_3PO_4	0.237	0.178	0.108		Kimp							

TABLE IV.5 (Contd....)

RPM	R.READING Vs	Va	%	Feed Solvent	da	System Purity	Init. Acid Conc.	Acid Conc. Wt. %	St.1	St.2	St.3	Init. Imp. Conc.	Imp. Conc. ppm	St.1	St.2	St.3	Time to reach steady state St.1	St.2	St.3	Residence Time
700	1.1 (177)	12 (177)	93	1:1	0.423	Mg	58.9	Raf	57.2	53.5	5.5	1900	Raf	1900 (160)	1950 (162)	2125 (166	42	40	36	8.96
								Ex.	13.7	10.2	5.9			2.1 (57)	0.9 (35)	0.45 (75)				
								KH_3PO_4	0.239	0.180	0.107		Kimp	0.0011	0.00046	0.0002				
900	1.1 (177)	12 (177)	96	1:1	0.42	Mg	58.9	Raf	57.8	56.5	55.5	2000	Raf	2030 (2580)	2109 (2635)	2119 (2682)	41	35	25	8.96
								Ex.	14.1	9.99	6.46		Ex.	2.1 (480)	1.0 (313.6)	0.63 (153)				
								KH_3PO_4	0.243	0.176	0.116		Kimp	0.00103	0.00047	0.00029				
1100	1.1	12	90	1:1	0.41	Mg	58.9	Raf	52.62	56.5	55.34	1900	Raf	1800 (150)	1970 (154)	2135 (166)	40	37	30	8.96
								Ex.	14	10.1	6.20			1.8 (50)	0.8 (40)	0.38 (29)				
								KH_3PO_4	0.242	0.178	0.112		Kimp	0.001	0.0004	0.00017				
500	6.5	12	—	1:2*	0.55	Mg	59	Raf	56.7	54.9	53.99	1550	Raf	1655 (1529.5)	1565 (1580)	1709 (1578)	—	—	—	5.87
								Ex.	10.64	6.1	3.41		Ex.	0.93 (198)	0.4 (72)	0.11 (25)				
								KH_3PO_4	0.137	0.111	0.063		Kimp	0.00059	0.00025)	0.000064				

TABLE IV.5 (Cont)

RPM	R.Reading Va	Vs	%	Feed Solvent	da	System Purity	Init. Acid Conc.	Acid Conc. Wt. %	St.1	St.2	St.3	Init. Imp.	Impurities Conc. ppm	St.1	St.2	St.3	Time to reach steady state St.1	St.2	St.3	Residence Time
900	6.5 (354)	12 (177)	—	1:2*	0.4	Ng	58.9	Raf	56.4	56.1	54.21	2150	Raf	2121 (2715)	2238 (2835)	2240 (2840)	—	—	—	5.97
								Ex.	10.1	6.8	3.2		Ex.	0.99 (245)	0.58 (145)	0.45 (108)				
								KH_3PO_4	0.179	0.121	0.059		Kimp	0.0047	0.00075	0.0002				
900	1.1 (177)	27.5 (522)	—	3:1	0.3	Mg	58.9	Raf	57.8	56.8	56.4	1760	Raf	1620 (420)	1720 (440)	1830 465)	—	—	—	4.5
								Ex.	15.2	13.1	11.45		Ex.	3.6 (199)	2.66 (163)	0.85 (403)				
								KH_3PO_4	0.262	0.232	0.203		Kimp	0.0021	0.0015	0.00046				
900	1.1 (177)	20 (354)	83	2:1	0,4	Fe	62.5	Raf	60.4	59.1	58.3	3040	Raf	3030 (377)	3090 (388)	3350 (420)	52	48	40	6.58
								Ex.	29.8	25.78	18.2		Ex.	1778 (203)	132 (155)	46 (60)				
								KH_3PO_4	0.493	0.436	0.812		Kimp	0.0589	0.0427	0.0115				
900	1:1 (177)	24 (354)	80	2:1	0.42	Fe	66.2	Raf.	63.67	63.1	59.78	3100	Raf	3158 (62)	3198 (66)	3820 (73)	60	55	44	6.58
								Ex.	48.2	29.5	21.6			660 (53)	190 (18)	35 (6)				
								KH_3PO_4	0.75	0.46	0.361		Kimp	0.2089	0.059	0.009				

TABLE IV.5 (Cont...)

RPM	R.Reading		%	Feed Solvent	da	System Purity	Init. Acid Conc.	Acid Conc. Wt. %				Init. Imp.	Impurity Conc. ppm				Time to reach steady state			Residence time
	Vs	Va							St.1	St.2	St.3			St.1	St.2	St.3	St.1	St.2	St.3	
900	1.1 (177)	18 (354)	—	2:1	0.41	Fe	56.6	Raf	55.7	55.5	54.7	3500	Raf	3700 (276)	4115 (302)	4120 (305)	—			6.58
								Ex.	9	8.2	62		Ex.	50 (30)	38 (20)	13 (12)				
								KH_3PO_4	0.161	0.147	0.11		Kimp	0.013	0.0092	0.003				
900	0.8 (100)	8.5 (100)	—	1:1	0.4	Fe and Mg	59.9	Raf	58.7	57.8	55.5	Fe 892	Raf	899 (230)	930 (235)	982 (255)	40	38	40	~6
								Ex.	19.8	14.6	8.3		Ex	22 (200)	13.5 (122)	4 (55)				
								KH_3PO_4	0.337	0.252	0.149		Kimp	0.0244	0.0145	0.0040				
												Mg 890	Raf	877 (89)	9166 (93)	980 (100)				
													Ex.	3.2 (135)	1.6 (73)	0.4 (25)				
													Kimp	P.0036	0.0017	0.0004				
900	2 (200)	12 (200)	—	1:1	—	Fe and Mg	59.9	Raf	57.75	56.7	54.7	Fe 892	Raf	940 (238)	983 (256)	1000 (267)	35	32	30	8.24
								Ex.	18.36	12.11	6.09		Ex.	17.5 (170)	9 (86)	2.3 (42)				
								KH_3PO_4	0.317	0.213	0.111		Kimp	0.0186	0.009	0.0025				
												Mg 890	Raf	895 (90)	1085 (111)	1145.8 (116)				
													Ex.	2.42	0.66 (103)	0.39 (36)	(24) —			
													Kimp	0.0027	0.000059	0.00034				

TABLE Iv.5 (Cont....)

RPM	R.Reading		%	Feed Solvent	da	System Purity	Init. Acid Conc.	Acid Conc. Wt.%				Init. Imp. Conc.	Impurity Conc. ppm				Time to reach steady state			Residence Time
	Vs	Va							St.1	St.2	St.3			St.1	St.2	St.3	St.1	St.2	St.3	
900	4 (250	13.5 (250)	—	1:1	0.4	Fe and Mg	59.9	Raf	57.1	56.	54.9	Fe 892	Raf	9999 (46)	1107 (50)	1178 (54)	30	30	30	6.47
								Ex.	17.85	11.5	5.7		Ex.	17 (30	0.75 (16)	0.43 (10)				
									0.312	0.212	0.107		Kimp	0.017	0.0006	0.0004				
												Mg 890	Raf	917 (72)	1083.3 (88)	1166.7 (95)				
													Ex.	1.3 (40)	0.5 (18)	0.27 (9)				
													Kimp	0.0014	0.00046	0.00023				
900	6 (350)	23.8 (350)	—	1:1	—	Fe and Mg	59.9	Raf	56.4	54.89	54.29	Fe 892	Raf	874.9 (40)	911 (42)	960 (45)				4.2
								Ex.	10.76	8.91	5.01		Ex.	0.7 (15)	0.5 (10)	0.25 (5)				
									0.191	0.16	0.09		Kimp	0.0008	0.000054	0.00025				
												Mg 890	Raf	977 (75)	965 (81)	967 (81)				
													Ex.	1.	0.32	0.2				
													Kimp	0.0001	0.00003	0.000020				

APPENDIX V

CONTENTS OF THIS APPENDIX

APPENDIX V

V.1 SAMPLE PUMP DESIGN AND SIZING

(i) MIBK Transfer Pump

Calculation of horsepower required to drive the pump.

Total mechanical energy balance on pump.

$$w_o = z_2 - z_1 + \frac{v_2^2}{2\alpha g_c} - \frac{v_1^2}{2\alpha g_c} + p_2v_2 - p_1v_1 + \varepsilon F$$

$p_1 = p_2 =$ atmospheric pressure.

Assume the tank car is open to atmosphere and so is the storage tank.

$$\frac{v_2^2}{2\alpha g_c} = 0 \quad \text{and} \quad \frac{v_1^2}{2\alpha g_c} = 0$$

$$v_1 = v_2 \qquad p_2v_2 - p_1v_1 = 0$$

The head $= z_2 - z_1 = (30 \text{ ft}) = 9.14\text{m}$

assuming $g = g_c$

Determination of Friction

Assume the flow rate per minute = 100 gallon

Average velocity in 3" pipe = Vft/sec.

$$\text{Average Velocity} = \frac{100\times144}{60*7.48*(3)^2*0.785} = (4.5 \text{ ft/sec}) = 1.37 \text{ m/sec}$$

Viscosity of MIBK = 0.546 cp

$= 0.546*0.000672$ (lb/ft.sec)

$= 3.669*10^{-4}$ (lb/ft.sec.)

Specific gravity of MIBK = 0.8041

Density $= 0.8041 * 62.5$

$= (50.25 \text{ lb/ft}^3)$

$$Re = \frac{3*4.5*50.25}{12\times(3.669\times10^{-4})} = 154456.$$

$$\frac{\varepsilon}{D} = \frac{0.00015*12}{3.000} \quad 6\times10^{-4} = 0.0006$$

f = Friction factor from the well-known chart

= 0.0055

$$\text{Total } L_e \text{ for fitting and valves} = \frac{2*7*3}{12} + \frac{3*3*32}{12}$$

$= 27.5$

$$\text{Friction due to flow} = \frac{2fv^2(L+L_o)}{g_c D}$$

$$= \frac{2*0.005*(4.5)^2(.100+27.5)^{12}}{(32.17)(3)}$$

$= 3.19$

Friction due to contraction and enlargement

$$= \frac{0.5*(4.5)^2}{3\times1\times3^{2.17}} + \frac{(4.5-0)}{3\times1\times32.17}$$

$= 0.3$

$f = 3.19+0.3 + 3.49$ (ft.lb.f/lbm.)

w_o from mechanical Energy Balance.

$30 + 3.49 = 33.49$ ft.lbf/lbm

hp of Motor required to drive the pump

$$= \frac{33.49 \times 100 \times 50.25}{0.4 * 60 * 7.48 * 5.50}$$

$= (1.7$ hp or $= 2$ hp.) $= 1.49$ KW

Short Cut Method

$$hp = \frac{Q*H*SG}{3960}$$

$$= \frac{100*0.8014*30}{3960*0.4}$$

$= (1.5$ hp or 2 hp.) $= 1.49$ KW

V.II EVAPORATOR BALANCE

(i) Mass Balance

$W_F = W_e + P$

$212.84 = W_e + 149$

$W_e = 63.84$ tonne/day Water leaving evaporator.

(ii) Heat Balance on Evaporator

$$P = W_F - W_2 - W_1 \qquad (V.1)$$

Second affect Balance

$$W_2 * \lambda_2 = W_F(T_F - T_2)C_F + W_1\lambda_1 \qquad (V.2)$$

First affect Balance

$$W_1\lambda_1 = (W_F - W_2)(T_1 - T_2)C_2 + W_S\lambda_S \qquad (V.3)$$

Since

$W_1 = 212.84$ ton/day

$= 218840$ Kg/day

$= 212840 * 2.2046 = (469227.0$ lb/day)

($W_F = 19,551$ lb/hr)

($W_e = 63.84$ ton/day)

$= 63840$ Kg/day

$= 140741.6$ lb/day

if λ = latent heat of vapourization BTU/lb

solving the (V.3) equation for 3 unknown.

Assume

C_F = specific heat of feed in BTU/(lb)(°F)

From Slack page 937, or page 140.

C_F = 0.53 (Call/G/Degree C)

C_F = (0.5 BTU/lb/°F)

by definition. See unit operation of Chemical Engineering (Appendix III)

$W_e = W_1 + W_2$ = (5864 lb/hr)

Assumption

(1) Assume feed temperature = 25°C = (77°F).

(2) Steam temperature = 180°C = (356°F)

(3) Assuming at first that the heating area A_1 & A_2 in both affects are equal.

$$q_1 = A_1 U_1 \Delta T_1 = q_2 = A_2 U_2 \Delta T_2$$

$$U_1 \Delta T_1 = U_2 \Delta T_2 = \frac{q}{A}$$

Experiment shows that acid at 63% H_3PO_4 Boil at about 110°C = 230°F. Therefore the temperature in the last affect must be equal to 230°F.

(4) Since the viscosity of liquid changed from 10 C_P in the second affect where the feed is introduced

to about 40 C_p in the first affect $\therefore$ The assumption of U_2, U_1 from unit operations of Chemical Engineering by WARREN C. McCABE page 140 is between 400 in the first affect to 250 BTU/ft^2.h.$^\circ$F in the second affect.

Let $U_1 = 400$ (BTU/ft^2.h.$^\circ$F)

$U_2 = 280$ (BTU/ft^2.h.$^\circ$F)

Temperature drop = 356 - 230°F = (126°F.) = 52.2°C

$$\Delta T_1 = 126 * \frac{\frac{1}{400}}{\frac{1}{400} + \frac{1}{280}} = \frac{0.0025}{0.0025+0.0035}$$

$$\Delta T_1 = 51.8$$

Similarly

$$\Delta T_2 = 126 * \frac{\frac{1}{280}}{\frac{1}{400} + \frac{1}{280}}$$

$$= \frac{0.0035}{0.0025+0.0035} \quad 126$$

$$\Delta T_2 = (73^\circ F) = 22.7^\circ C$$

Consequently Boiling Point in first effect

Temperature of Steam - ΔT_1

$= 356-51.8 = 304.2^\circ$F

$= 151^\circ$C

and that in the Second and Last stage will be

$= 304.2^\circ$F $- 73^\circ$F

$= 231.2^\circ$F

$= 110^\circ$C as assumed.

i.e. $T_{sec} = 356^{o}F = 180^{o}C \quad \lambda_s \simeq 780$

$T_{feed} = 77^{o}F = 25^{o}C$

$T_1 = 304.2^{o}F = 151^{o}C \quad \lambda_1 \simeq 845$

$T_2 = 231^{o}F = 110^{o}C \quad \lambda_2 \simeq 900$

$$W_1 + W_2 = (5864 \text{ lb/hr}) \tag{V.4}$$

$$W_2 * 900 = 19551\ (77-231) \times 0.5 + W_1 * 845$$

$$900\ W_2 = 845\ W_1 - 15\ 05427 \tag{V.5}$$

also

$$W_1 845 = (19551-W_2) \times 0.5(3042-231) + W_s \times 780$$

$$845\ W_1 = 36 \times (19551-W_2) + 780\ W_s \tag{V.6}$$

$$W_1 = (5864-W_2) \quad \text{From Equation (V.4)}$$

$$900W_2 = 845\ (5864-W_2) - 1505427$$

$$900W_2 = 4955080 - 845W_2 - 1505427$$

$$W_2 = \frac{34496153}{1745}$$

$$W_2 = (1976.8 \text{ lb/hr})$$

$$W_1 = (3887.2 \text{ lb/hr})$$

Into equation (V.6)

$$845(3887.2) = 36(19551-1976.8) + 780\ W_s$$

$$W_s = (3400.0 \text{ lb/hr}).$$

$$A_1 = \frac{W_s \quad \lambda_s}{U_1(T_s-T_1)} = \frac{3400*780}{400(356-304)}$$

$$=(127 \text{ ft}^2) = 11.79 \text{ m}^2$$

$$A_2 = \frac{W_1 \lambda_1}{U_2(t_1-t_2)} = \frac{3887.2*845}{270(304-231)}$$

$$=(166 \text{ ft}^2) = 15.4 \text{ m}^2$$

For the First trial average surface area was

$$\frac{127+166}{2} = 146.5 \text{ ft}^2$$

Assume an average area, and repeat the calculation.

$$T_s-t_1 = \frac{3400\times780}{400*146.5}$$

$$T_s-T_1 = 45.$$

$$T_1 \quad = 356-45 = 310.75$$

$$T_1-T_2 = \frac{388712\times845}{270 \ (146.5)}$$

$$T_1-T_2 = 83$$

$$T_2 \quad = 226.9$$

Re-calculate with $\lambda_2 = 910$, $\lambda_1 = 830$.

$$W_2 910 = 19551(77-226.9)0.5+(5864-W_2) \times 830$$

$$W_2 910 = 830(5864-W_2)-1465347.45$$

$$1740W_2 = 4867120-1465347.45$$

$$W_2 \quad = 1955.04 \text{ New}$$

$W_1 = 5864-1955.0$ New Value

$= (3908.9s\ lb/hr)$

Since

$$W_1\lambda_1 = (W_F-W_2)(T_1-T_2)C_2+W_s\lambda_s$$

$$3908.95*830 = (19551-1955.04)(310-226.9)*0.5+W_s*780$$

$$W_s = 3222.2\ lb/hr.$$

$$A_1 = \frac{3222.2\times780}{400(356-310.74)} = (139\ ft^2) = 13\ m^2$$

$$A_2 = \frac{3908.9\times830}{270(310.74-226.9)} = (143\ ft^2) = 13.2\ m^2$$

Heat of condenser $= W_2\ \lambda_2$

$$Q = 1955.04\times910 = 1,779,086\ Btu/hr$$

$$Q = 521,396\ watts$$

$$\Delta T_m = \frac{(T_2-t_1)-(T_2-t_2)}{m\,\frac{T_2-t_1}{T_2-t_2}} = \frac{(226-85)-(226-100)}{\frac{226-85}{226-100}} = 98$$

$$\Delta T_m = 98$$

$$\text{Mass of Water} = m = \frac{Q}{C_P\Delta T_m} = \frac{1779086}{0.4*98}$$

$$m = 45017\ lb/hr$$

$$= 20,419\ KG/hr$$

$$= 20419\ m^3/hr$$

Take U_D over all mass transfer couple.

(400 BTU/ft^2.h.^oF)

$$A = \frac{Q}{U_D \Delta T_m}$$

$$A = \frac{1779086}{2100*9.8}$$

$$=(45.3\ ft^2)$$

$$= 4.2\ m^2$$

NOMENCLATURE

A	Interfacial area: cm^2 Horizontal cross sectional area of settler. Component A
A_1, A_2	Area of heat transfer, cm^3,m^2
B	Component B Flowrate of B, unit mass/unit time
B_n	Factor in equation 5.6
b	Intercept of equilibrium line
b	Annual maintenance cost as a fraction of equipment cost
c	Constant interfacial concentration in equation 5.3
C	Component C Total installed operating capital cost (£) in equation 10.1 Solute concentration, molar volume: g moles/cm^3
C_E	Annual cost of a real extraction stage including equipment and operating cost, £/year
C_F	Specific heat capacity of feed in BTU/lb ^{o}F
C_i	Concentration of impurities, Wt/wt
C_3	Cost of steam and coolant in Table 10.5
ΔC	Concentration driving force, molar volume, gm.moles/cm^3
D	Component D Impeller diameter (cm)
D_T	Tank (vessel) diameter (cm)
D_D	Molecular diffusivity, cm^2/cm
D_s	Settler diameter
d	Drop diameter, (mm)
d_{max}	Maximum stable drop size
d_i	Individual drop diameter (mm)
d_{32}	Souter mean droplet diameter, mm
d_B	Baffle diameter (cm)

E	Energy input per unit mass and time $N^3D^5\frac{p}{M}$ Energy (utilities) cost in £/year
EPE	Plant cost index (1970=100)
F	Feed Flow rate of aqueous solution, mass/time
F_m	Material of construction factor = 1.1 for corrosive/inorganic/acid system
G_a	Vapour velocity (table 10.5)
G_b	Vapour handling capacity of the condenser and reboiler equipment (Table 10.5)
H	Time of operation, hr/year Liquid height in the mixer
IPE	Isopropylether
K	Overall mass transfer coefficient Correlation constant in equation 10.4 = 5.5
k	Mass transfer coefficient
K	Constant in equation 4.2
L	Direct labour cost in £/year Cost factor £/tonne
L_s	Settler length
ℓ	Fraction losses in Table 10.5
ℓ_v	Latent heat of vaporization
M	Mass of fluid in mixer, gm
MIBK	Methylisobutyl ketone (solvent)
M	Molecular weight
m	Equilibrium constant
N	Agitator speed, r.p.m. Number of functional unit
N_A	Mass transfer rate, g moles/sec (cm^2)
N(Re)	Reynolds number $\frac{d_p u_t \rho_c}{\mu_c}$ dimensionless
N(Sh)	Sherwood number $\frac{k_c d_p}{D_c}$

N(Vi)	Viscosity group
n	Number of stages Number
nr	Net sales
O_p	Operating cost Maximum pressure of any functional unit in equation 10.1 Profit function Product, product flow rate wt/day Cost of instruments, piping and installation as function of equipment cost
P_A	Power requirement for agitation
P_p	Power requirement for pump, h_p
ΔP	Pressure drop
P_r	Gross profit
Q	Volumetric flow rate, Cu.m/hr
q	Plant capacity, tonne p.a.
R	Raw material cost, £/tonne Reflux ratio in table 10.5
ROI	Return on investment
RI	Refractive index in equation 4.8
r	Droplet radius, cm
	Phase ratio $\frac{V_c}{V_d}$
Sc	Schmidt number $\frac{d_p u_t \rho_c}{\mu_c}$ dimensionless
Sch	Sherwood number $\frac{k_c d_p}{D_c}$
TBP	Tri-n-butyl phosphate (solvent)
T	Temperature of any functional unit in the main process stream °C in equation 10.1
T_s	Settler size in equation 4.1
t	Time in hr
t_a	Average residence time in min.
U	Velocity, cm/sec

U_t	Terminal velocity
V	Velocity, cm/sec
V_c	Continuous phase flow rate, cm^3/min
V_d	Disperse phase flow rate
W	Water component Water flow rate, tons/day
We	Power cost Mass flow rate to evaporator in tons/day
We	Weber number $\frac{D^3N^2p}{\mu i}$
W_F	Mass flow rate in ton/day
W_h	Wedge height in cm
W_L	Wedge length in cm
X	Solute concentration in an aqueous phase, wt/wt
Y	Constant in equation 4.2
	Solute concentration in solvent phase, wt/wt
y	Pay out time as a function of annual cost per stage
Z	Fraction

GREEK LETTERS

α	Total hourly cost of each stage
β	Selectivity in equation 3.1 Cost of solvent make up, kg
β_T	Total annual cost of the process
β_e	Annual cost of the extraction unit
β_D	Annual cost of the distillation unit
β_w	Annual cost of washing step
β_s	Annual cost of the lost solvent
β_L	Annual cost of labour

β_c	Annual cost of product concentration
γ	Unit cost of wet process phosphoric acid
ϕ_d	Volume fraction
ϕ_d	Average volume fraction of the cascade
ζ	Efficiency of stage
ζ_o	Overall cascade efficiency
ζ_{ME}	Murphree stage efficiency based on extract phase
ζ_{MR}	Murphree stage efficiency based on raffinate
ζ_W	Efficiency of washing section
ρ	Density, g/cm^3.
ρ_m	Mean density of two phases
μ	Viscosity, poise = g/cm sec
μ_m	Mean viscosity
ν	Kinematic viscosity stoke = cm^2/sec
σ_i	Interfacial tension, dynes/cm
Δ	Difference
π	Cost of final fertilizer grade acid, £/kg
ξ	$\frac{mB}{F}$ = constant
λ	Value of 1 kg of extracted product in equation 10.28 Constant in equation 8.5
λ_1	Latent heat of vaporization, Btu/lb

SUBSCRIPTS

A,B,C,D	Components A,B,C, and D
a	Average value
C,c	Continuous phase
D,d	Dispersed phase

E	Extract
E,f	Feed
H	Heavy phase
i	Impurity for impure system
	Initial values
L	Light phase
m	Mean
max	Maximum
min	Minimum
o	Oil
	Output
O	Initial conditions
P	Product
R	Recycle stream Raffinate
S	Solvent
	Equilibrium valve
1	In phase one
2	In phase two

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