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SEPARATIONS BY CONTINUOUS COLUMN CRYSTALLISATION

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SUMMARY

A continuous column crystalliser has been designed and built using a Schildknecht-type Archimedean transportation screw within a stainless steel jacket. Problems concerned with the surface finish on the inner walls of the jacket which affect crystal transportation have been investigated, leading to effective operation of the apparatus.

The process of column crystallisation may be considered as a multistage separation and purification technique; it is applicable to both aqueous and organic systems. In the present work the examination has been undertaken by firstly continuously crystallising a flow of feed solution in the column. These crystals are transported along the screw, melted and some of the melt liquid allowed to flow countercurrently to the crystals thus washing them by reflux. The remainder of the melt liquid is removed as pure product, the impure product provided by the now impure reflux liquid being removed from the opposite extremity of the column.

Separations in aqueous solutions which have been investigated include the desalination of brine, concentration of metal salts, the extraction of deuterium oxide from a heavy water/water mixture and the concentration of ethanol in water. The purification of organic solvents included the removal of cyclohexane from benzene and the extraction of

para-xylene from o-, m-, p-xylene and ethylbenzene.

The unit operations involved in column crystallisation fall into the categories of heat transfer, mass transfer and mixing. In order to examine how dependent the efficient operation of the column is on these factors, the system has been optimised for organic, aqueous and mixed organic/aqueous cases. The variables studied including:-

(a) the speed of rotation of the transportation screw
(b) the length of the column
(c) the attitude of the column (ie crystals transported upwards or downwards).
(d) the position of the feed into the column
(e) the ratio of the products removal rates
(f) the rate of production of crystals

Since the scale-up of equipment is an ultimate aim of the present investigation it is necessary to study the results mathematically. Where possible, this examination has been undertaken thus establishing the major factors involved in the separation and purification scheme. It should also be possible to determine whether absolute optimisation of operation is attainable - i.e. does separation increase as the crystal rate increases to infinity or is an optimum separation eventually attained?

CONTENTS

INTRODUCTION

The separation and purification of components in mixtures has been of paramount importance to man during his evolution. During the last 10,000 years his advancement has depended upon agricultural pursuits, which have relied to a large extent upon the ion exchange capacity of the soil allowing fertilizing agents to be firmly held during leaching. This washing, needed to remove unwanted salts, was initially produced by rain, but as man's population and hence food requirements increased, the intensive farming needed relied more and more upon fresh water storage and irrigation.

As an important separation process, distillation has been in evidence since the formation of the oceans due to the evaporation of water and subsequent precipitation as rain. Crystallisation, however, is an even older fractionation process; the oldest example being the solidification of the earth's molten layer, the magma.

Ever since man has extensively sailed the oceans he has probably known that sea ice contains less salt than the surrounding water although the first report of this is attributed to the Danish physician Thomas Bartholinus(97) in the 17th century. However, it was not until 1786 that the Italian Anton Maria Lorgna(97) published results of his experiments in Venice to desalinate sea water by freezing.

Starting with 36,200 parts per million (ppm) he successively froze the liquid obtained from the melted ice five times and produced water with just a trace of salt.

The crystalline state belongs to the solid phase of matter; the purification which occurs upon freezing of a solution or melt is due to the inability of the rigid crystal lattice to tolerate the presence of other species.

Fractional crystallisation concerns the separation and purification of a mixture by the dissolution and formation of crystals. For the liquid/solid phases this process is possible by two mechanisms. The first is the purification of a solid by the addition of a solvent subsequently crystallising out the pure product (eg removal of trace impurities of potassium nitrate from sodium nitrate by solution in water) - known as fractional crystallisation (from a solution). The second technique, fractional solidification, utilises the solid/liquid phase transition without the addition of a solvent (eg the desalination of sea water).

Fractional solidification has many analogies with fractional distillation, [illegible] 'the former case purification being due to a liquid/solid phase transition is similar to the liquid/vapour transition which takes place during distillation. Both systems depend upon a concentration difference between two phases at equilibruim and separation of these phases from each other. The resemblance of a column crystalliser to a packed distillation column is obvious and the analogy is continued since both processes can be operated batchwise or continuously using countercurrent flow techniques.

However, differences between the two processes include the change in solubility when the liquid to solid phase change occurs - solid solubility usually being low whereas warm liquid mixtures are often completely miscible, the effect of pressure (there being little change for the solid/liquid phase whereas the liquid/vapour phase is very dependent) and the loss of convective mixing once the solid phase is formed causing large concentration differences within the crystal.

Distillation is a relatively well practised technology but suffers from several disadvantages when compared to crystallisation processes:-

(i) the need for a large capital outlay to construct the plant since the vapour phase is involved and larger volumes have to be contained at equivalent pressures.

(ii) the energy required to overcome the latent heat of evaporation - eg for sea water desalination the latent head of evaporation of water is approximatley seven times that for fusion.

(iii) The cost of separation of close boiling components is often prohibitively high (eg the separation of para and meta xylenes, boiling points 138° C and 139° C, respectively) whereas the fractional solidification process is simple (freezing points, +13.2° C for para and -54.8° C for the meta-xylene)

(iv) heat sensitive compounds (eg pharmaceuticals and flavours) cannot be purified by distillation due to decomposition.

(v) the increased fire risk involved by producing hot organic vapours, especially in the petroleum industry.

(vi) for the desalination process corrosion and scaling problems are readily apparent during operation of distillation plants; at low temperatures this problem is greatly reduced.

Crystallisation processes have been applied to both aqueous and organic systems. An application receiving increasing attention is the use of freezing techniques to desalinate sea water since the total energy requirement is almost half that for distillation.(129) The need for a comprehensive water recovery policy is becoming evident to most nations since even though the earth is the water-rich planet of this solar system, 99% of that total water is either salty or is locked up in the polar regions. The problem becomes even more critical when one considers the fact that 71% of the earth is covered by oceans and of the remainder 60% of the land area is arid or semi-arid. These arid areas, generally considered uninhabitable, could become fertile if a fresh water supply was available.

Obviously man's ability to survive is limited by the availability of potable water. Potable water is considered to be that containing no more than 500 ppm of dissolved salts, although, in some parts of the world, people are able to survive on water containing greater than 1000 ppm of salts(80).

Rain is the natural source of fresh water, 340 x 10^{12} US gallons per day being precipitated on the earths surface, averaging 50 inches per year overall. However, the spread is not uniform; some areas (eg the North Chilean desert) receive almost zero rain fall per year whereas in some tropical forests over 1000 inches/year are recorded.

Traditionally, water supply has been by means of storage in reservoirs and subsequent transportation by aqueducts, as necessary. However, the minimum total requirement to sustain human life assuming a diet of beef-protein, fat and vegetables is 2500 US gallons per day per person due to the needs of agriculture. Thus as the population increases, the supply of fresh water by means of traditional methods only may not be possible. If this situation should arise then a desalination process will be required in order to augment the traditional method. In fact, several large desalination plants producing a total of 50 million gallons per day world-wide (compared to the proposed 600 x 10^9 US gallons per day needed in the USA by 1980) have been built and as technology improves the operating costs of desalination plants is approaching those of new reservoirs and aqueduct systems.

Organic systems have also been separated and purified by crystallisation. The traditional method of producing pure laboratory samples is to dissolve them in a suitable warm solvent, filter the solution and cool the filtrate to recrystallise the product which is then dried by filtration and evaporation at a suitable temperature (lower than the melting or decomposition point of the product). This separation is based upon the differing solubility of the pure product and the impurity in the solvent, either may be the more soluble but it is preferable that all the impurity remains in solution on recrystallisation.

Solvents of ultrahigh purity have unique and unusual applications. One example is the extraction with benzene of carbonaceous materials from meteorites for analysis. These analyses, hampered by impurities in the benzene, help determine the possibilities of life forms existing outside those on earth. Both binary and multicomponent systems have been separated (90, 116, 119).

Organic mixtures with one component having a freezing point temperature between -10°C and +60°C can be economically and effectively purified by crystallisation techniques. Once the temperatures of freezing points decrease far below -10°C the cost of refrigeration increases and the separation becomes less economically viable. Crystallisation also allows the separation and purification of close freezing point components (eg benzene +5.5°C and cyclohexane +6.2°C) provided that one is considerably in excess (eg a benzene solution containing 3% cyclohexane) and the problem of constant boiling azeotropes experienced in some distillations (eg ethanol and water where further separation requires special techniques) can be overcome by crystallisation.

The industrial applications of organic crystallisation are not confined to the production of pure solid substances. The Phillips(92, 93) system for the purification of para-xylene from a mixture of its isomers has now been scaled-up to a plant capable of producing 60,000 metric tons per year of para-xylene and the petroleum industry, where distillation is extensively employed is considering low temperature crystallisation as a separation technique(96).

Thus the crystallisation process is becoming an economically viable and efficient separation method. Its potential applications are widespread with particular importance being stressed for its use where heat sensitive and highly inflammable compounds are involved. The desalination of sea water by the vacuum freeze-vapour compression method is already producing 250,000 US gallons per day at Eilat in Israel(129) and a comparative analysis of desalination processes has shown that freezing could be the most competitive process in the UK(141).

LITERATURE SURVEY

1. Crystallisation

Batch crystallistion requires the separation of mother liquor from the crystal and washing of the solid to remove the adhering liquid, this is most easily facilitated by use of centrifugation(110).

Briggs(28, 29, 30) working for the Coal Tar Research Association studied the purification of napthalene samples by centrifuging the crystals and washing with an aqueous detergent or methanol. He discovered that the contaminants of crystal naphthalene were caused by intra crystalline solid solutions and mother liquor adherence.

In 1971 Cutts(43) studied solvent crystallisation processes involving stirring a crystal slurry in a solvent before centrifuging, washing the crystals with a solvent while in the centrifuge or a combination of the two processes. He purified 73.5% benzene in toluene up to 99.85% benzene which is a purity better than for centrifuging only. However, although he explains the energy advantages of freezing over heating processes the proposed commercial plant involves two distillation columns as well as a centrifuge.

Another crystallisation technique developed from its inception in 1952 by Pfann(106) is known as zone-melting. This was developed to overcome the problem of batch progressive freezing where it is necessary to discard a portion of the solid after each crystallisation since remelting the solid restores homogeneity.

In zone melting only a thin zone of the solid is melted; this zone is caused to move slowly through the solid from one end to the other, either by moving the solid or by moving the heater. Many subsequent zones may easily be caused to follow the first, with each contributing to the separation of components. Zone-melting has proved very useful in the production of ultra-pure materials, especially semi-conductors (134, 148); Federova and Federova(56) and Cheng and Pigford(36) have both explained the mechanisms involved.

In 1962 Eldib (53) described a technique called zone precipitation which was similar to zone melting. In this case a solvent is added to the mixture to produce a gel-like liquid - the solvent itself does not have to solidify. On heating a zone the solid melts and as the zone moves the liquid behind solidifies, rejecting the most soluble components. Solids of greatest solubility are concentrated in the direction of movement, the fractionation being improved by use of solvents which reduce the liquid viscosity in the molten zone. He used the technique for separating petroleum waxes.

However, due to the difficulty of producing continuous zone-melting equipment the technique has never been extensively used.

2. Column Crystallisation

As recently as 1973 Knox(82) stated that multi-stage crystallisation could not be carried out; simultaneous production of crystals, melting of those crystals and the washing of the crystals was not yet possible. The method of zone-melting in which the processes occur sequentially was described but column crystallisation was never mentioned.

However, as early as 1951 Arnold(12) had performed several experimental runs on a column crystalliser. His crystalliser had no transportation mechanism for the crystals but he employed a pulsed countercurrent flow of melt liquid and small crystals. The significant suggestions made by Arnold were the use of a scraper if the crystals adhered to the cooling walls and some form of transportation (by buckets) if the crystals did not move freely along the column.

The next development was due to the Phillips Petroleum Co. USA. Hackmuth(68) developed the concept of Arnold; he combined pulsed flow and the suggestion of a scraped freezing section plus crystal transportation. Crystals are introduced to the column, compressed by a hydraulic piston which is porous to the mother liquor. The crystals are forced into a grid and onto a melting section where the pure product is withdrawn. This form of column crystalliser design was improved by McKay(90) who constructed a bench-scale purification column in 1960. He used a reciprocating porous piston to push the crystals down the column. The mother liquor was removed from the piston by means of a vacuum line and a heater at the base of the column melted the crystals. He raised a 77% p-xylene feed up to 98% but could only manage low flow rates of feed and product.

Schildknecht(117, 118) described a similar design of column crystalliser, but he used a helix rotating at 80 - 150 rpm to transport the crystals and scrape the freezing section. His initial designs were very small-scale, 13 - 15 cm long with a volume of approximately 15ml and operated batchwise. The inherent difference between this design and the crystallisers using a reciprocating piston was that the crystals were actually formed in the column and not in an external unit. Hence the problem of moving slurries from once piece of apparatus to the next was removed; crystallisation, melting, possible recrystallisation for solid solutions, and washing were carried out in one piece of equipment. The freezing section of the column could be at the top or base of the column, a melting section to melt the crystals being required at the opposite extremity of the column. The transportation helix was wound round a stationary central cylinder concentric to the containing walls of the crystalliser.

In 1962 Beattie and Gold(20) produced a type of column crystalliser operating in the horizontal plane. The column jacket is partially immersed in a cooling bath. Crystals form on the jacket and are carried to a heating element by rotating the jacket. By use of a helical thread along the column the melted liquid then progresses to the next crystallisation section where the process is repeated. Using several crystallisation sections suitable separations can be attained.

The design of crystallisation equipment was still largely an art by 1963 when Anikin(3) attempted to model the concentration profile produced in a column crystalliser. He considered a stage-wise operation as in distillation columns, but his model was only concerned with recrystallisation, the effects of washing being neglected.

Meanwhile, continued improvements to the established column crystallisers led to several patented designs. Phillips Petroleum of the USA took out a patent on McKay's(91) reciprocating piston crystalliser and McCarthy(89) further adapted this design by having a stationary porous section in approximately the mid-point of the column and producing a high pressure, low frequency pulse to move the crystals. The Sun Oil Co. of Philadelphia patented a design of Bohrer(24). This crystalliser was cooled by a concentric tube through the centre of the column and the crystals formed moved by applying a cylcic pressure pulse. The feed was centrally positioned and the products were distilled.

In 1967, McKay(92, 93) described the scale-up of operations of the p-xylene purification plant. In these plants feed of 65 - 72% p-xylene can be purified to 99 + wt% at 530 Kg/hr and the capacity of operating and announced plants at that time was 130,000 tons/yr. During the same year Schildknecht (119) demonstrated the suitability of continuous column crystallisers in the production of ultra-pure solvents. He produced 30 ml of benzene per hour in which no impurities could be detected by gas liquid chromatography.

The possibility of wide applications for column crystallisers was demonstrated by Betts etal (22). Using a continuous column crystalliser of Schildknecht design he purified or concentrated various organic or aqueous solutions. However, his flow rates were usually low; any attempts at feed rates above 1Kg/hr produced poor separations. Considering the experimental work undertaken the analysis of column operation should have been simple; however, this was not attempted.

Continued work on the analysis of the column crystalliser led to descriptions by Devyatykh (49) Arkenbout (8, 9) and Powers (2). The former developed a model of column crystallisation based upon diffusion in the solid phase being the rate determining stage in mass exchange between the liquid and the crystals. Arkenbout recognised that the column equation for exchange processes could be modified and introduced an expression for the inter facial mass transfer by extractive washing and recrystallisation whereas Powers having demonstrated the applicability of column crystallisers, developed a model dependent upon mass transfer between the adhering and free liquids and diffusion along the column. The solution of Powers was different for eutectic systems and systems forming solid solutions whereas Arkenbout produced a generally applicable equation.

Following much research into the design of column crystallisers(59, 60), the Coal Tar Research Corporation(41) patented a reflux crystalliser. The design incorporated a pulsed feed of crystal slurry to the centre of the column. Part of both the low and high melting point products are recycled to the column and crystal transport is facilitated by means of a polished helical conveyor. Armstrong(10) however, described the design of a scraped shell crystalliser and its possible applications to the dewaxing of petroleum oils, preparation of fatty acids and the separation of isomers.

In 1969 and 1970 mathematical modelling of column crystallisers was undertaken by several workers. Player(107) analysed the operation of both Phillips and Schildknecht type columns and explained the differences between the two designs. For the end-fed porous piston column refreezing is a dominant factor. If too pure a feed material is employed, little refreezing occurs and the crystal bed is then too porous to prevent channelling of the mother liquor into the melting zone. However, for centre fed columns of Schilknecht design, refreezing is minimal since the feed is only 1 - 5% impure hence the discontinuity in temperature and composition obtained in Phillips type columns is not demonstrated under centre bed column operation.

Bolsaitis(25) modelled a Schildknecht type column; he split the column into a stripping section where the crystals were formed and an enriching section where the washing occurred. The performance of the stripping section was described by a stripping efficiency, defined as the fraction or percentage of crystallisable material which is removed from the solution entering that section. Once the crystals form they are acted upon by gravitational, bouyant and viscous drag forces which lead to a minimum size of crystal above which transportation is allowed, the smaller crystals leaving with the stripped stream. Unfortunately, the enriching section equations only apply to cases where the volumes of desired product and impurity are approximately equal.

Powers continued the work on the analysis of column crystallisers. With Albertins(1) he developed a model for batch operation considering three distinct cases:

(a) Crystal was pure

(b) crystal impurity was constant along the length of the column but diffusion was negligible in determining the concentration profile.

(c) crystal impurity was constant along the length of the column but diffusion was the dominant factor in mass transfer.

Since the crystals were demonstrated to be impure, cases (b) and (c) were considered. If diffusion was dominant, as the crystal production rate was increased then the purity of the enriched product should increase whereas for mass transfer dominant the converse is true. The experimental results(1) proved diffusion to be the most important factor in determining the concentration profile in the column.

In an attempt to provide a better assessment of the column performance Gates and Powers(61) repeated the model of batch operation. The development of equations for systems with solid solubility and for eutectic systems allows a fuller analysis. By use of equations including diffusion coefficients and mass transfer coefficients, assuming that the crystal impurity was constant along the length of the column they obtained better results for the coefficients.

Continuous column crystallisation was modelled by Henry and Powers (72, 73) by studying the reduction of cyclohexane in benzene. The experimental work employed a column of 300 ml volume, maximum flow rate of 300g/hr for feed of 28000 ppm cyclohexane. For a ratio of enriched product to feed rate of 0.16 they obtained a pure product of 40 ppm impurity.

The model of the column performance, essentially based upon equations for extraction columns, is separated, as was Bolsaitis' model(25), into a stripping section profile and an enriching section profile. The important factors in determining the column concentration profile are the crystal rate, diffusion of impurity along the column and mass transfer between the free and adhering liquids. However, the model breaks down as the enriched product rate approaches the value of the crystal rate due to the flat composition profile obtained.

During 1970 a design of column crystalliser by Richmond and Exley was patented by Newton Chambers(111). The apparatus was essentially of Schildknecht design using a central feed point and a helical conveyor capable of driving the crystals downwards. The patent specification included a design where the crystal conveyor was a screw since the helix would often "sieze-up" in the column.

In the same year Schildknecht etal(120) described the operation of a column crystalliser with a pulsating spiral conveyor. The volume of the column used was 250 ml, the pulsations were employed to decrease the tendency of the column to block with crystals. The spiral was rotated at 70 - 80 rpm., driving the crystals downwards and oscillated 180 - 330 times per minute through a distance of 3 - 6 mm. For a feed rate up to 130g/hr the separations were acceptable but on attempting to increase the rates the purification was adversely affected.

A novel type of column crystalliser referred to as the Brodie-type design was announced in (4) and (31). The equipment was essentially an L shaped section with the horizontal arm at the top. This horizontal arm contained the recovery section where the feed is introduced. The recovery section joins to a refining section on the same arm. Crystals formed in the cold area of the recovery section are conveyed countercurrently to the feed towards the refining section. On entering the latter section the crystals are washed by a liquid reflux stream before entering the vertical arm of the apparatus - the purifying section. At the base of the purifying section the crystals are melted to form the desired product and reflux liquid. The product is removed at the base of the purifying section and the reflux liquid forced back along the column.

Matz(88) investigated the operation of a worm crystalliser in 1972. This type of crystalliser employs a helix driven in the opposite direction to a central cored shaft through which a heat transfer medium can pass. The outer jacket contains three heated sections, one above the centrally placed feed point and two below. The apparatus was suitable for coarse separation but not for ultra-purification.

Scale-up of operations using Schildknecht type column crystallisers was undertaken by Hobson and McGrath(74). Using data obtained from a 50mm internal diameter, 90cm in length column they built a column of 100mm diameter and 150 cm in length with an employable volume of 3.8 litres. However, this latter column was essentially filled with the Archimedean screw conveyor and the cooling apparatus available not sufficient to allow a complete analysis of the operation.

The recognition that column operation would probably be improved by cutting the volume occupied by the conveyor mechanism was employed by Moyers(95). The freezing section contained a wall scraper which was rotated and oscillated to keep the walls clear of crystals. The drive to the scraper causes a piston to be actuated which in turn drives the crystals into the purification section which is free of internal members. The crystalliser used a central feed point and the crystals were transported downwards. However, the apparatus described only allowed low flow rates of feed (up to 330ml/hr) and separations were not very efficient, any attempt to remove a significant fraction (0.4 - 0.5) of the feed as pure product increased the impurity content (in excess of, 1000ppm from a feed of 40,000 ppm acetamide in water.

Development of column crystallisation apparatus has also led to designs where the desired product is crystalline(135). Erbe(55) and Weech(145) describe equipment in 2 US Patents. The former apparatus consists of a horizontal jacket containing a spiral oscillating longitudually. Kneading teeth are attached to the jacket between the spirals which allow a conveying action. The melt is added at one end of the equipment and the crystalline product leaves from the other extremity. The design of Weech(145) is much more complex, being used to purify aluminium nitrate by alternate melting and crystallisation. The feed is introduced to the top of the column into a chilling section. The crystals produced move to a melting and recrystallising section. Finally the crystals are reformed in a second chilling section before removal of product. Wash liquid, in which the crystals are insoluble, enters below the lower chilling section and removed at the top chilling section.

3. Desalination

Desalted water has been available from the oceans ever since their formation. Evaporation and eventual precipitation as rain together with the freezing processes occurring at the North and South pole has provided sources of drinkable water.

Utilisation of the evaporation/precipitation process for purifying salt water has been utilised by man in the form of distillation apparatus. Distillation processes are basically those in which saline water is evaporated, pure water being obtained by condensation.

Several designs of distillation apparatus for desalination have been suggested.

Multi stage flash distillation has been extensively described by Frankel(57)and Silver(129). In this process heated brine enters a chamber maintained at a reduced pressure. Some of the water immediately evaporates (flashes) and then condenses on tubes cooled by the feed of sea water flowing to the steam heated input section. A series of such chambers (stages) at progessively reduced pressures forms the plant. The feed sea water increases in temperature as it is passed through the condenser tubes in the opposite direction to the flashing flow. The condensed steam is collected on trays below the condensers;product water emerging from the last stage.

The desalination of sea water by multiple effect evaporation(131, 141) has been shown to have certain advantages over multi-stage flash equipment by

Standiford(131). The process is basically one in which steam is used to evaporate some of the sea water in the first effect, the vapour condensing in the second, lower temperature effect, evaporating more water and so on. There may be as many as 20 effects in a commercial plant. A large plant has the following economical advantages over a multi-stage flash distillation rig:-
(1) heat transfer coefficients are generally higher; (2) more of the available temperature difference can be used for heat transfer and (3) less pumping energy is required for a multiple effect evaporater.

Silver(129) described a process known as vapour compression evaporation where steam generated from boiling brine is mechanically compressed to increase the vapour pressure and condensation temperature. The steam is fed to an evaporator tube bundle where it condenses forming product water and in doing so evaporates more brine. This equipment has a low energy consumption but the energy form is expensive (electrical) so the plants are often small.

All the above distillation processes suffer from several disadvantages:

(a) the high energy requirements to overcome the latent heat of evaporation.

(b) corrosion problems are high due to the elevated temperature employed.

(c) scale is easily formed at the temperatures required.

(d) the difference between operating temperatures and ambient is large. Hence insulation becomes a problem.

Some of these problems can be overcome by using the sun as a source of energy - solar distillation (141). The energy source for this equipment is free, if not always available and the scaling problem is removed. The principle of operation requires the placing of sea water in flat tanks with a roof of glass or tough transparent plastic. The solar heat vapourises the water which vapour condenses on the inside of the roof, draining off as fresh water. Its major disadvantage is the requirement of a large land area/unit of product.

Cheap readily available sources of energy are also provided by nuclear power stations leading to the proposal of nuclear distillation plants(48) and Barnea and Weyelin (17) suggested the use of geothermal fluids or geopressure reservoirs as a source of energy for multi-stage flash distillation. The main problem, however, was found to be the formation and removal of deposits contained in the fluids which affect heat transfer.

In order to alleviate the energy problem inherent in distillation equipment other separation techniques have been attempted to desalinate sea water. The theoretically most attractive of these systems is reverse osmosis(78, 85, 129). In this process a semi-permeable membrane is employed. By the application of a pressure in excess of the osmotic pressure of the solution fresh water is caused to pass from the brine to a fresh water compartment. Unfortunately, the pressure required is proportional to the salinity of the feed. For 5000 ppm dissolved salts the applied pressure employed is 40 atmospheres and for 35000 ppm, 100 atmospheres. Hence the system is usually only used for brackish waters.

Similarly, electrodialysis is used to desalinate brackish water due to the increasing costs as the salinity of the feed rises. Electrodialysis (127, 129) employs the transfer of ions through a membrane under the influence of an electrical potential difference. The positively charged metal ions and the anions move towards the electrodes through membranes permeable to either cations or anions - hence the gap between the membranes become depleted in ions. In theory the process is optimised for a high current density and a small membrane. However, a high current density causes concentration polarisation causing a wastage of power along with appreciable scaling.

Salt water has also been desalinated by use of ion exchange resins(7) and solvent extraction. Davison(44) described a solvent extraction plant which is dependent upon the solubility characteristics of certain secondary and tertiary amines with water and salt water. The solubility of water in the solvent which selectively dissolves water from salt water solutions is very sensitive to temperature. Unfortunately, the water content of the extract [illegible] decreases with increasing temperature and salinity and the selectivity decreases with increasing water content. Thus it is necessary to determine an optimum water content and the feed material used contains only 4000 to 9000 ppm salt.

Ion exchange processes(115, 141) usually employ a feed of only 1000 to 3000 ppm salinity. Scambary(115) describes an Australian process using resins which can be regenerated with hot water. The product water has 50 - 100 ppm dissolved salts and is used mainly as boiler water.

A novel method of desalination has been demonstrated by Avampto(6). This process is based upon the bending of the path of an ion by use of a magnet. Salt water is channelled through a pipe past an ultra-violet or X-ray source which further ionises the ions of dissolved salts. The water then passes a magnet which deflects the ions away from the centre of the pipe. The relatively purer water at the centre is removed via an internal pipe set concentrically within the original one and the less pure water goes to waste. Although claims of removing 92% of the ions have been made values of 15% removal are more usual for a 3.5% sodium chloride solution.

Gillam and McCoy(129) have postulated that by 1980 the energy cost of producing 1000 US gallons of potable water from sea water by distillation processes will be 180 Kw-hr compared to 35 Kw-hr for freezing processes (and 30 Kw-hr for reverse osmosis and 15 Kw-hr for electrodialysis - these two processes using brackish water as feed).

By 1975 Strobel(133) predicts that desalination water costs will be as low as 15 cents/1000 US gallons and Ennis(54) suggested that even in 1970 the costs of producing potable water by conventional storage methods (dams, reservoirs) and by desalination overlapped if a large plant was considered whereas by 1980 desalting will be at least as economically viable as conventional methods for plants producing 50×10^6 US gallons/day of product water.

With freezing processes appearing to be so economically acceptable much research into the type and design of various plants has been undertaken(64).

The early experiments in purifying sea water by freezing are described by Nebbia(97). The observation that water obtained by melting ice formed in sea water was fresh had been reported almost simultaneously by Bartholinus and Boyle in the 17th century but it was not until 1786 that Lorgna developed a working method for water desalination by freezing. By repeated freezing of the melt liquid obtained from the previous crystallisation he reduced water of 36,200 ppm to 800 ppm in three stages. On continuation to a 4th and 5th stage the melt water was essentially pure.

By 1908 Buchanan(32), after his Antartic cruise of 1874 in the Challenger and Petterssen on the Vega in 1878, had analysed sea ice and found it to be composed of frozen sea water, snow, salt spray, pieces of glaciers and occluded liquid brine. Buchanan had thus recorded that the freezing of a dilute solution can lead to purification of the solvent by rejection of the solutes into the melt.

The earliest extensive use of freezing as a method of desalting water was reported by Whitney in 1944(147). In this process ice was formed from impure water by causing a jet of water, at low temperature, to be forcibly projected against a surface maintained at a temperature low enough to allow the progressive accumulation of ice to occur on that surface. The velocity of the water is so great that the impurities rejected by the ice formation are washed away as fast as they appear.

By 1967 several experimental freeze-desalination plants had been designed and constructed. These were described by Barduhn(15).

Vacuum flash freezing process

This is also called vacuum freeze-vapour compression desalination. The process is further described by Bridge etal(27) Peck(103), Pachter(102), Barduhn(16), and Synder(129) whereas Schwatz(121) analysed the operation of the counterwashes used to wash the ice crystals.

Operation of the plant is based upon using water as a refrigerant. Sea water is introduced to a vacuum chamber maintained at a pressure equivalent to the vapour pressure of sea water at or below the freezing point. Some water flashes into vapour, the evaporation of water removes heat due to the requirements of latent beat for evaporation. Crystals form in the remaining water, the slurry is separated and the ice moved to a washing/melting unit where some of the melt water is used to wash the crystals. Schwartz(121) developed a model of the counterwasher in which brine is displaced by fresh water from the interstices of the ice plug. He discovered that output increased with an increase in the ice crystal size, the plug length above the screens in the washer, the concentration of ice in the slurry and the external mechanical restraining forces on the ice plug whereas the production increases with a decrease in the ice plug length below the screens.

Butane freezing process(5, 15, 16, 47, 83)

This system has been extensively studied by the United Kingdon Atomic Energy Authority (UKAEA). The secondary refrigerant freezing process uses a liquid hydrocarbon refrigerant (eg butane) which is immiscible with water. By direct contact with salt water the butane is vaporised due to the heat transfer. The salt water freezes producing an ice/brine slurry; the crystals are separated and washed to remove the brine. The ice is then melted to produce product water by contact with compressed butane vapour which has passed from the crystalliser to the melter for reuse. Crystal growth needs strict monitoring to allow for effective washing but still a butane taste remains in the product. This taste is disadvantageous for human use and it must be removed thus increasing the cost of the water. In 1970, the British Government revealed plans to build a butane freeze water treatment plant near Ipswich. This crystalliser was to be used to produce one million gallons of fresh water per day compared to the largest similar plant operating at present producing ten thousand gallons/day at Stockport. Unfortunately, by 1972 the decision to postpone the construction of the Ipswich Plant was taken by the Government.

Similarly in the USA the Office of Saline Water (OSW) have ceased to fund pilot plant work on secondary refrigerant freezing, stating that progress was too slow due to a high degree of coupling between components causing data evaluation and scale-up to be difficult.

Attempts to improve the secondary refrigerant process have been made. Fraser(58) used a non-toxic, non flammable fluorocarbon refrigerant and estimated a cost of 69 cents/1000 gallons for a 1 million gallon /day plant. The use of 80/20 mixtures of iso-and normal butane has also been tried(15, 16), Carrier(15) have employed octa fluoro cyclobutane and Johnson (76) in Avco's Crystalex process used Freon 114 which are both highly insoluble in water, non-toxic and non flammable.

The major drawback of all primary and secondary refrigerant crystallisation plants is the requirement of dividing the plant into three distinct parts, ie crystalliser, washer and melter which require the cost of elaborate piping systems, physical pumping of slurries and the extra insulation expense. The primary refrigerant system also suffers from a need to work under vacuum hence plant costs will be high since loss of the vacuum would be disadvantageous and in fact after several years running the plant at Eilat, Israel was shut down(65) in 1973.

Hydrates(15, 16, 129)

In order to alleviate the problems of low temperature running in crystallisers, several workers have employed hydrate formation. For this process the water solidifies and precipitates at a higher temperature and pressure than does pure ice. The ice formed contains no salt but has 5 - 15% hydrating agent incorporated in it. The hydrating agent (eg propane) is removed on melting since it is chosen to be insoluble in water. Otherwise, the system is similar to normal freezing units, i.e. it requires a reaction vessel (where hydrate forms), a separator, a melter and a washer. Unfortunately, the reaction of the hydrating agent with water to produce the solid hydrate occurs at an even slower rate than the freezing of ice and the separation of solid crystals and washing are more difficult than with ice.

In a novel paper, Wankat(143) described desalination by natural freezing. This process is applicable in relatively warm climates with ambient temperatures above freezing and the melted ice from a single freezing, without washing, was 3-6 times less salty than feed. The apparatus consists of a shallow, well insulated container with a shallow layer of water. The rig should be level and have a completely clear exposure to the night sky. During the night the energy balance over the rig shows that heat is lost from the water by radiation to the night sky and heat is gained by conduction from the ground and convection from the air. In addition if the humidity is low then heat is lost by evaporation or if the humidity is high then heat is gained by condensation. Under these conditions radiation will be the dominant factor and the water layer cools, possibly freezing.

The use of continuous column crystallisation in desalination was described by Hobson and McGrath(74) This process has the advantage over other freezing processes in that the crystallisation, washing and melting process occur in one piece of apparatus. The cystal size produced is dependent upon the rotational speed of the conveyor according to Bolsaitis(25) as well as the cooling rate. Thus control of washing by producing suitably sized crystals is more easily facilitated than in other types of crystalliser. Due to the problems of cooling in the larger crystalliser described (100mm diameter 1.5 metre long) they proposed using a butane freezer to produce the crystals. In fact this was unnecessary, redesigning the conveyor mechanism to markedly increase the annular volume of the crystalliser and reduction of the mass of the materials used in the construction producing very acceptable results.

Crystallisation processes obviously produce large amounts of concentrated brine. Some workers have proposed by-product recovery systems. Goto (67) etal considered potassium recovery and sodium, potassium and magnesium have been extracted by the Chemical and Technical Services of Kingston-upon-Thames.(35)

In an attempt to reduce the volume of waste brine from crystallisation processes Avco extended their Crystalex process to a Eutectic Freezing process(132) in which ice together with sodium chloride dihydrate are simultaneously formed. The operation of the apparatus requires crystallisation of the ice and salt hydrate, separation of the ice and hydrate crystals from a eutectic slurry, countercurrent washing of the eutectic ice and then drying of the hydrate crystals. The experiments so far have used feed of only 5000 ppm sodium chloride and the washing of the ice has been difficult due to the small crystals produced.

The crystallisation processes occuring upon freezing salt water solutions have been extensively studied(42, 45, 69, 70, 71). In 1967 Marriot(69) examined the growth of ice crystals in a stirred tank. The crystals were grown by direct contact with evaporating butane. For water subcooled 0.01 to 0.05°C, the particles grew about $\frac{1}{4}$ to $\frac{1}{2}$ as fast as predicted from heat transfer correlations. The growth rates in 2% salt solutions were about sevenfold lower than those for pure water because the concentration difference for salt diffusion lowered the interface temperature and the diffusion effect was shown to be much greater for disc shaped particles than for spheres.

Terwilliger(137) studied the salt redistribution process during the freezing of sodium chloride solutions. The process was found to depend upon:

(a) the liquid phase interface concentration which is controlled by the supercooling

(b) the thermal driving force imposed to initiate and maintain freezing.

His findings contradict other authors who believe that rejection is caused by a distribution coefficient dependent upon the freezing rate. This investigation showed that the distribution coefficient was only indirectly a function of the freezing rate.

The performance of a continuous well stirred ice crystalliser was described by Marjolis etal(86) in 1971. Photographs demonstrated that the ice particles were disc shaped and the permeability of the ice beds were found to depend upon the size and shape of the crystals and the method of forming the beds.

In two papers by Janzow and Chao(75) the crystallisation phenomena when ice is crystallised from brine were reported. The first paper provided a study of salt entrainment in ice crystallised from brine. They concluded that brine adhering to the thin plates of ice and retained in the interstices by capillary forces is responsible for the high salt concentration in melted ice. The other report studied crystallisation of brine solutions within a narrow range of subcooled brine temperatures. Large, plate-like free ice crystals up to several inches in length were formed in the bulk of a slowly traversing brine simultaneously with the growth of dendritic ice on the cold surface. Because the crystals are large the possibility of application to freeze desalting is noted.

The analysis of crystallisers has been much neglected but some workers have described models. In 1964 Godrey and Benham(66) provided an analogue simulation of a continuous counter current crystalliser using cascade from one unit to the next in order to decrease the cost of scale-up of operations.

Orcutt(99, 100) modelled both the operation of a well mixed crystallisation vessel and the nucleation and growth of ice crystals in secondary refrigerant freezing. The first paper(99) allows the vessel size required for crystallisation, the mean particle size, growth and nucleation rates to be calculated. The latter report(100) develops a mathematical model of the freezing/crystallisation step for secondary refrigerant freezing processes. He considered the influence of the refrigerant phase on the nucleation rate. The crystal size distribution was estimated assuming the crystal growth occurs by heat-transfer limited growth or by growth accompanied by agglomeration, of which the latter was considered more realistic.

Working with Carey, Orcutt(101) studied the mixing of liquid in a freezer/crystalliser vessel.

In order to simplify scale-up of crystallisation processes data obtained from transient dye tracer studies of a mixed freezer/crystalliser were analysed by use of an anolgue model. The deadwater region parameter was found to depend upon the specific power input with a parameter representing the exchange of material between the deadwater region and the remainder of the vessel contents being affected by the position of the agitator.

During 1973 Sarcona etal(114) derived a mathematical model describing the steady state operation of a continuous cooling-type crystalliser. The analysis was tested with various sets of hypothetical input data so as to determine crystalliser and heat exchanger design parameters and the study is purported to provide a means of solving the engineering problems associated with the process.

Continuous column crystallisation has been analysed by Powers etal(72, 73) by considering the effects of crystal rate, take off of products, diffusion of impurity along the column and mass transfer of impurity between the adhering and free liquid. The operation of the column can be effectively simulated by use of Powers' equations providing the take off of pure product does not approach the crystal rate.

4. Ethanol Concentration

Since the earliest times in many different places men have developed, quite independently of each other, the fermentation of sugar containing liquids to produce ethanol. However, the production of aqueous ethanol solutions of high alcohol content only became possible when distillation was invented during the 12th century. By the end of the Middle ages spirits were being produced and absolute ethanol was first obtained by distillation via potash and lime.

In Germany alcohol is produced almost exclusively by fermentation(112) although the production from ethylene by hydration(14) is now more widely employed.

Most table wines contain 9 - 12% by vol of ethanol although 18% by vol is possible(14). To obtain a spirit quality beverage from fermented liquour requires raising the alcohol content to 32 - 33% by wt. Distillation processes (38, 63, 149) have been used most extensively to obtain this concentration and since the boiling action undoubtedly produces the loss of flavours, Girard (63) worked under vacuum with a temperature of 30°C.

In 1909 Traube(139) proposed a solvent extraction process to recover a solution rich in ethanol. A concentrated solution of potassium carbonate or ammonum sulphate was added to the alcohol solution. Two phases separate, the lower being rich in the salt and poor in ethanol whereas the upper is poor in salt and rich in ethanol and fusel oils (a mixture of optically inactive isoamyl alcohol and active amyl alcohol which occur to a small extent in wines).

The Institute National dela Recherche Agronomique at Dijon(50) have concentrated wine by the fractional crystallisation of water. In an essentially batch process the ice/wine slurry is compressed in a perforated cylinder and packed, the ice being expelled by suction. The major disadvantages of the process are its batch-wise operation and the loss of 3% alcohol with the ice.

McKay(93) considered the possibility of concentrating beers using the Phillips type crystalliser in order to make storage and transportation possible. In the USA where beers sold are usually of the keg variety and sold at low temperature the consumer may allow the concentration and eventual dilution of beer whereas in this country much of the beer sold is still of draught quality and is still 'live' in the barrel (112) (fermentation to condition the beer is still occurring) and concentration may well kill the yeast present. However, the use of column crystallisation to concentrate wines etc. to spirit quality was not considered by McKay.

5. Deuterium Oxide

In 1927, Aston(13) measured the atomic wt of hydrogen by use of a mass spectrograph and found the value to be in good agreement with that obtained by chemical methods. Two years later when it was shown that naturally occurring oxygen consisted of a mixture of 3 isotopes, it was discovered that there was a discrepancy of the order of 2 parts in 10,000 between the two determinations of hydrogen atomic mass. This deviation could not be accounted for within the experimental errors and it was suggested that the difference may be due to the presence of 1 part in 5000 of a heavy hydrogen istope of mass 2 in the ordinary hydrogen.

The production of heavy water presents a difficult set of problems(122, 146). In natural water there is only about 0.015% of deuterium oxide and the method of concentration must depend upon the physical differences between hydrogen and deuterium containing materials such as H_2, HD, D_2. The methods will involve cascade operations with a large number of stages since the separation factors are likely to be low.

Distillation processes for producing heavy water concentrates was used by Pegram in 1938 and was patented by him in 1940(104). He also used his apparatus to concentrate water containing O^{18} and the only example of concentration given is that after 50 days operation, 20cc of water containing 2.5% H_2O^{18} was produced. By 1948, Dostrovsky had achieved a concentration to 5% HDO in the effluent from his distillation apparatus after 32 days' operation.

Due to the high costs and poor returns from distillation processes in concentrating heavy water, Gehrke(62) used a partial evaporation or condensation technique. In this process 10cc/min of water and 1l air were passed through a fritted glass filter at 20°C to produce a moist gas stream containing 1.1% D_2O. This stream was passed over granular basalt at 95°C for 100 minutes, then an inert gas was passed through the apparatus at 110°C, removing water containing 25% D_2O from the basalt.

Egi(52) and Smith(125) both concentrated deuterium oxide by use of zone melting. Egi used a horizontal ring type vessel with a U section equipped with movable heaters. The heaters were moved at 2mm/min and the solid was formed by using a cooling temperature of -10°C. The feed material was 56.4% D_2O/H_2O and after 26 hours the product was 98.4% D_2O. Smith used an approximately equimolar feed but found the separation to be much lower than predicted by the theoretical separation factor of 1.0211(108).

The electrolytic separation process has been widely used since it gives a good separation(87). By 1946 Tronstad(149) was using a series of stages and raised the concentration of natural water up to 0.07% D_2O. In his apparatus the product from each stage was distilled into the next stage before continuing the electrolysis. A similar process was used by Coles(39) and Bushell(33) where after electrolysis the deuterium was recovered by liquefying the deuterium/hydrogen mixture and fractionally distilling. The enriched deuterium was then burned in air to produce deuterium oxide.

In a report in 1941, Johnston(77) described the operation in 1934 of the Ohio State University Heavy Water Plant which operated in 3 main stages. He obtained 800 grams of heavy water from a feed of 1800 gallons of water in 16 weeks.

The enrichment of heavy hydrogen by isotope exchange has been studied by several workers(18, 23, 34, 109, 113, 128, 136, 142). An example of the process is given by the hydrogen/ammonia system. When two different hydrogen containing species such as hydrogen and ammonia are brought into equilibrium, the concentration of deuterium relative to hydrogen will be different. The ratio of the concentration of deuterium in the two species is known as the separation factor and depends upon the temperature.

eg at -40°C Separation factor 6) for H_2/NH_3
100°C " " 2.3) system

By use of a potassium amide catalyst (0.1 to 1% by wt), working at high pressures (255 Atmospheres) and with a temperature of -40°C the hydrogen (+nitrogen) stream is countercurrently washed with ammonia. In this apparatus 70% of the deuterium in the feed gas is transferred to the ammonia phase.

Barr(19) reviewed the most economically viable exchange reactions. These are:

(a) Hydrogen/water

(b) hydrogen/water using hydrazine as catalyst

(c) phosphine/water exchange where more hydrogen is available

(d) hydrogen iodide/water where equilibrium is quickly reached.

Both Mercea(94) and Denton(46) have patented heavy water plants where the products of exchange reactions are distilled to further purify the deuterium oxide.

Other techniques of heavy water concentration have been proposed. Chapey(37) electrolysed natural water to produce hydrogen containing 0.15% HD. This was rectified at low temperature to separate HD from H_2 giving a product of 60% HD. This was oxidised and rectified to give 99.8% deuterium oxide. Brancker(26) suggested using solar energy for distilling heavy water in order to reduce the high cost whereas Cross(40) purported that light and heavy water should be separable by using centrifugal forces.

The difference in freezing points between heavy water(81) (3.8°C) and light water (0.0°C) suggests that separation by multi-stage crystallisation, especially if concentrates are used as feed material, should be possible. Thus the application of continuous column crystallisation to deuterium oxide purification should be considered.

THEORY

1. Mechanism of Crystallisation(96, 98, 150)

The production of crystals from a solution is governed by three basic steps:

(a) the attainment of supersaturation or supercooling

(b) the formation of crystal nuclei

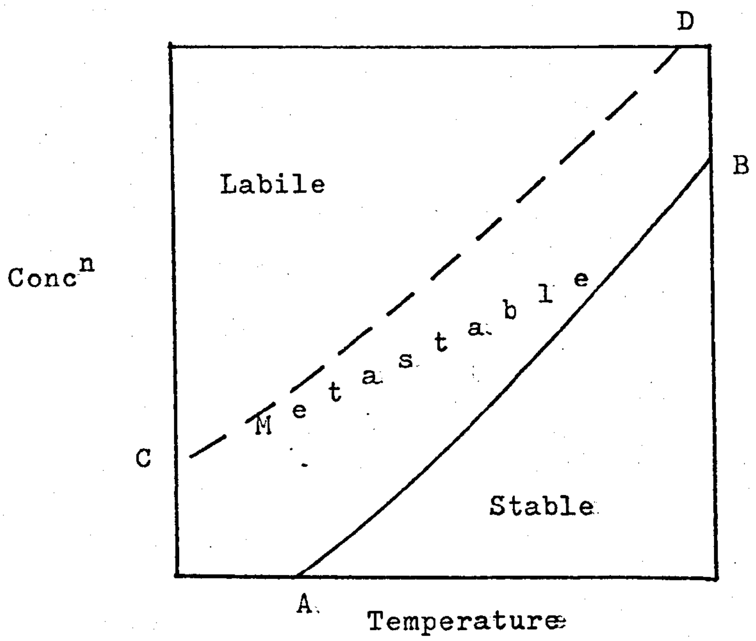
(c) the growth of the crystals

(a) Supersaturation

A saturated solution is one which is in equilibrium with the solid phase. If more solid is dissolved in the solution a supersaturated condition is obtained. This state of supersaturation is an essential feature of all crystallisation operations and can be achieved by cooling, evaporation, addition of precipitant (or diluent) or by chemical reaction.

Ostwald (1897) was the first to introduce the terms 'labile' and 'metastable' supersaturation. In the former case spontaneous deposition of crystals will occur from a superaturated solution, whereas in the latter spontaneous crystallisation is improbable.

Fig(10)



In Fig (10) line AB represents the normal solid solubility curve for the solid concerned. The line CD, referred to as the supersolubility curve, gives those temperatures and concentrations at which spontaneous crystallisation occurs. The supersolubility curve is not so well defined as the solubility curve and depends, among other things, on the degree of agitation of the solution.

The diagram represented by Fig (10) therefore consists of one well defined zone and two zones which exhibit some variation, viz:-

(i) the area below line AB where crystallisation is impossible due to unsaturation, the stable zone.

(ii) the metastable zone, between lines AB and CD where although the solution is supersaturated spontaneous crystallisation is unlikely. However, if a crystal seed is added growth would occur on it.

(iii) The unstable supersaturated solution in the labile zone above line CD where spontaneous crystallisation is most likely to occur.

(b) Nucleation

Once supersaturation has occurred the next essential step is the formation of solid sites at which crystallisation can commence. Nucleation may occur spontaneously (homogeneous) or can be caused by artificial inducement (heterogeneous).

For column crystallisation nucleation is usually induced by artificial means, eg seeding, stirring etc. However, in order to study the free energy changes associated with heterogeneous crystallisation it is necessary first to develop equations for the homogeneous case.

The free energy changes associated with nucleation may be represented by the equation(96).

$$\Delta G = \Delta G_s + \Delta G_v \qquad (1)$$

Where ΔG is the overall excess free energy between the particle of solute and the solute in solution.

ΔG_s (a positive quantity; proportional to r^2) is the surface excess free energy; ie the excess free energy between the surface of the particle and the bulk of the particle and ΔG_v (a negative quantity; proportional to r^3) is the volume excess free energy; ie the excess free energy between a very large particle ($r = \infty$) and the solute in solution.

As the size of the nucleus (r) increases from zero, G reaches a maximum value when the radius reaches its critical size (r_c)

ie $\Delta G_{crit} = \frac{4\pi\sigma r_c^{2}}{3}$ (2) where σ is the surface energy of the particle per unit area.

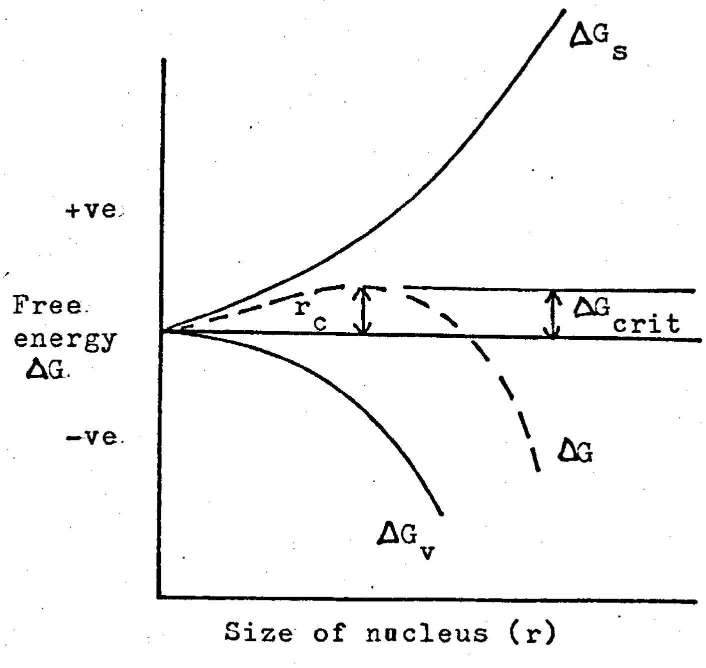


Fig (11)

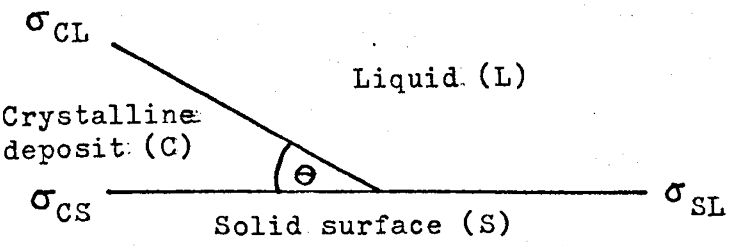
Fig (11) shows how the value ΔG_{crit} is attained. For values of r lower than r_c redissolution causes a reduction in free energy which is favourable and for $r > r_c$ growth is favoured.

For heterogeneous nucleation, the supercooling required is lower, thus the corresponding $\Delta G'_{crit}$ must be less than ΔG_{crit}

ie $\Delta G'_{crit} = \emptyset \, \Delta G_{crit}$ where $\emptyset$ is less than unity (3)

Now, the interfacial energy (σ) is one of the important factors involved in nucleation.

Fig (12)



In Fig (12) σ_{CL} is the interfacial energy between the crystalline phase and the liquid, σ_{SL} that between the foreign surface and the liquid, σ_{CS} between the crystalline phase the the foreign surface and θ is the angle of contact between the crystal and solid surface.

Resolving these forces (σ_{CL}, σ_{CS}, σ_{SL}) about the horizontal

$$\sigma_{SL} = \sigma_{cs} + \sigma_{cL} \cos \Theta \qquad (4)$$

whence
$$\cos \Theta = \frac{\sigma_{SL} - \sigma_{cs}}{\sigma_{cL}} \qquad (5)$$

According to Volmer$^{(96)}$ the value of ϕ in eq(3) is:

$$\phi = \frac{(2 + \cos \Theta)(1 + \cos \Theta)^2}{4} \qquad (6)$$

Thus when $\Theta = 180^\circ$, $\cos \Theta = -1$ and $\phi = 1$

Then $\Delta G'_{crit} = \Delta G_{crit}$, corresponding to non-affinity between the crystal and the solid surface. Hence the overall free energy is the same as for spontaneous nucleation.

when Θ is between 0° and 180° $\phi < 1$ and $\Delta G'crit < \Delta Gcrit$, now nucleation is easier than for spontaneous nucleation

but when $\Theta = 0$ $\phi = 0$

and $\Delta G'crit = 0$, corresponding to seeding of the solution (ie no nuclei have to be formed in the solution).

The rate of nucleation has been determined by Vanhook$^{(99)}$ who adapted the Eyring rate theory to nucleation data. The Eyring formula normally applies to homogeneous crystallisation but has been used in studies of heterogeneous mechanisms.

The formula may be stated as:

$$J = \frac{RT_L}{h} \exp \frac{AT_f^2}{T_L (T_f - T_L)^2} \text{ particles/mole-time} \qquad (7)$$

where A is an empirical constant, T_L the solution temperature, T_f the equilibrium transition temperature (freezing point), R is the gas constant and h is Planck's constant.

This equation predicts finite nucleation rates for all finite undercoolings whereas in many cases nucleation occurs only after a minimum undercooling has been reached. However, the equation allows the prediction of changes of nucleation of several orders of magnitude with a small charge of T_L due to its exponential form.

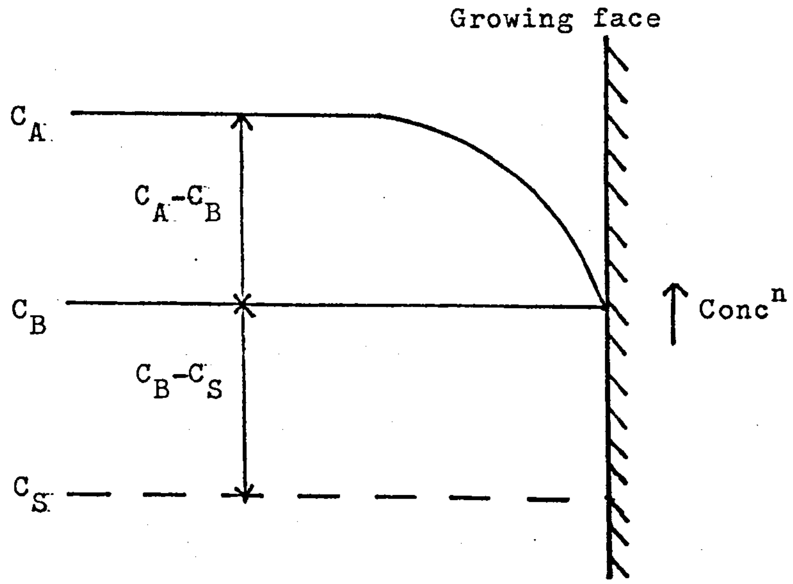
(c) Crystal Growth

The rate of growth of a crystal in a solution is dependent on the temperature and concentration of the liquid at the crystal face. These conditions are not generally the same as those in the bulk of the solution because a concentration gradient is necessary to allow transfer of solute to the face and a temperature gradient is necessary to remove the heat of crystallisation. As the resistance to heat and mass transfer is largely caused by the laminar sub-layer close to the surface of the crystal, stirring, which decreases the thickness of this sub-layer, is advantageous to crystal growth.

The rate of crystallisation is also a function of the degree of supersaturation, but for crystallisation from a solution, much less supercooling is possible than with melts (2 - 3 degrees for solutions compared with 50 - 100°C for melts) and the process becomes one of mass transfer rather than heat transfer.

Fig (13) shows the concentration gradient in the vicinity of the crystal face.

Fig(13)



(where C_S is the conc^n of the saturated sol^n and C_A is the conc^n in the bulk liquid)

The concentration falls from C_A to C_B through the liquid and the concentration difference $C_B - C_S$ is required to overcome the resistance at the interface. Thus the concentration difference responsible for mass transfer is only $C_A - C_B$ and not $C_A - C_S$.

By assuming that the diffusion of material to the crystal face is controlled by the resistance of the film near the face the following equation for growth rate over a period of time is obtained:

$$\frac{dm}{dt} = \frac{DA}{\delta_b}(C_A - C_B) \qquad (8)$$

where A is the area of the crystal surface D is the diffusivity of the solute in solution. δ_b is the thickness of the laminar layer and m the mass of solid deposited in time in t

Berthoud[1] assumed that the transfer was proportional to the supersaturation at the interface.

Thus $$\frac{dm}{dt} = KA(C_B - C_S) \qquad (9)$$

where K is the rate constant for the surface process

Eliminating C_B from these two equations ((8) and (9)) gives:

$$\frac{dm}{dt} = \frac{A}{\frac{1}{K} + \frac{\delta_b}{D}}(C_A - C_S)$$

This equation can be simplified by considering only .the linear growth rate (d l) and assuming $\frac{1}{K}$ and δ_b/D are constants.

Then $$\frac{dl}{dt} = K . \Delta C \qquad (10)$$ where $C = (C_A - C_S)$

Now the ratio of the volume, to the cube of the linear dimension, must remain constant since the crystal shape does not alter.

$$\text{let} \quad V = k^1 \, l^3 \qquad (11)$$

$$\text{then } dV = 3k^1.l^2.dl \qquad (12)$$

$$\therefore \frac{dV}{dt} = 3k^1.k.l.^2\Delta C \qquad (13)$$

$$\propto l^2.\Delta C \qquad (14)$$

Thus approximate calculations of growth rates may be made, but the results are often misleading due to the effect of small impurities on crystallisation.

Harriot(99) derived an expression for the growth rate applicable to crystals of diameter $>$0.002 inches in terms of the thermal driving force produced in a well mixed continuous crystalliser.

$$\text{ie Growth rate} = \frac{dD\,p}{dt} = \frac{G}{Dp}(T_i - T_{bl}) = \frac{G\Delta Ti}{Dp} \qquad (15)$$

where Dp is the crystal diameter, T_i is the temperature at the interface, T_{bl} the temperature of the bulk liquid and $\Delta Ti = T_i - T_{bi}$

The value of G, the growth rate parameter, is given by the equation: (16)

$$G = 2k_l \; (2 + 0.6(\mathrm{Re})^{\frac{1}{2}}(\mathrm{Pr})^{3/}2)/\rho_s(\Delta H_f[1+\Omega\,\omega_l/(1-\omega_l)]$$

where k_l is the thermal conductivity of the liquid

Re, Pr are the Reynolds and Prandtl nos, respectively

ρ_s is the density of the crystal

ΔH_f the latent heat of fusion

ω_l the mass fraction of solute in the liquid

and Ω is a parameter relating convective heat and mass transfer, given by the equation.

$$\Omega = \frac{mk_l}{\hat{\rho} D \Delta H_f}\left[\frac{2 + 0.6(Re)^{1/2}\,(Pr)^{3/2}}{2 + 0.6(Re)^{1/2}\,(Sc)^{3/2}}\right] \qquad (17)$$

where m is the slope of the equibilbrium freezing curve

$\hat{\rho}$ is average liquid density between interface and bulk liquid

D is diffusion coefficient of solute in liquid

and Sc is the Schmidt no.

Now the mean particle size ($\bar{r}$) may be calculated using the values of growth rate and holding time density function:

$$\text{ie} \quad 2\bar{r} = Dp = \int_0^\infty r.f(r)\,dr = \frac{\pi}{2} G \Delta T_i t_h \qquad (18)$$

where Δ isthe vessel size and t_h is the mean hold up time in the freezer.

2. Fractional Solidification

Although the separation which may be achieved in fractionalsolidification depends on several factors, the most important process is thermodynamic in nature. The phase diagram of the system under consideration is the expression of these thermodynamic processes and indicates the maximum change of concentration or degree of segregation that is theoretically possible by the freezing of the liquid.

Unfortunatley, phase diagrams refer to equilibrium conditions, whereas, in fractional solidification the system generally departs from equilibrium unless the freezing is very slow and/or the solid is finely divided and dispersed in the melt. Thus, althoughthe phase diagram describes the possibilities for separation the results will be modified by the departure from equilibruim.

For column crystallisation, most solid/liquid mixtures fall into the categories of eutectic or solid solution systems.

(a) Eutectic Systems

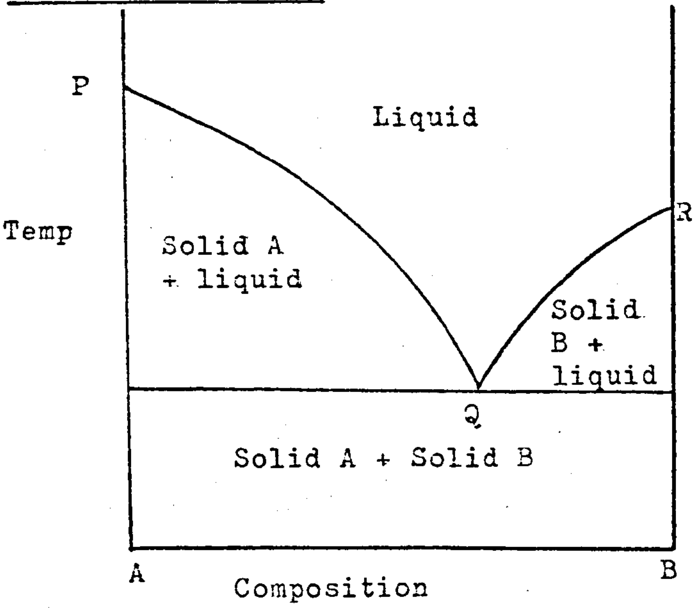


Fig (14)

In Fig (14) the lines PQR show the hypothetical freezing points of component A as B is added or the effect of adding A on the freezing point of B. Q represents the eutectic point, the lowest temperature at which solid appears. At the eutectic point solid A, solid B and liquid are in equilibrium.

The cooling of the liquid which forms a eutectic system on freezing is demonstrated by considering fig (15)

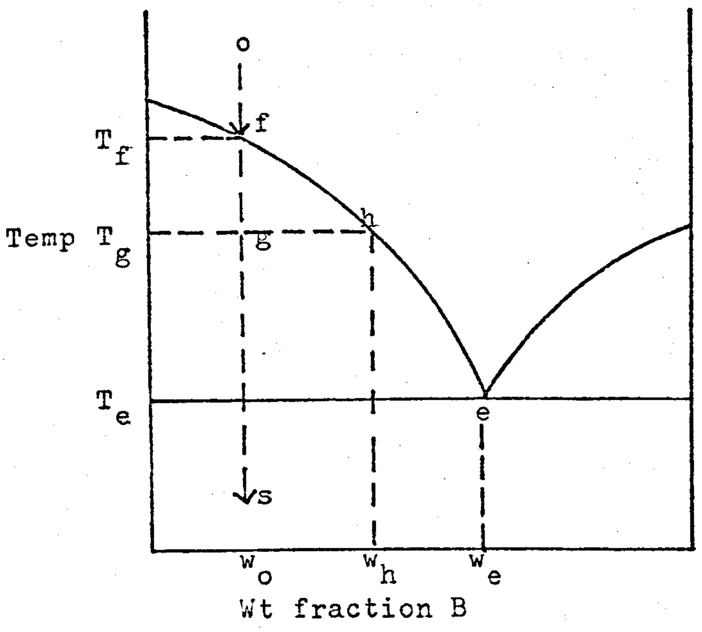


Fig (15)

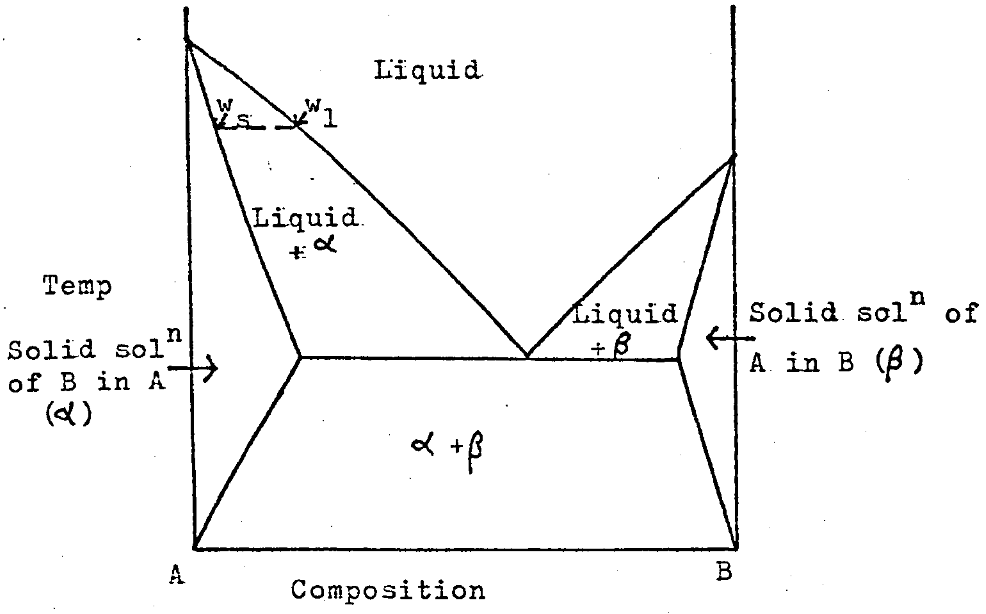
If liquid of composition Wo is slowly cooled from position o, when the temperature reaches T_f pure A begins to freeze out. Further lowering of temperature allows more A to crystallise, enriching the remaining liquid in B. When the temperature reaches Tg the melt is at h (composition W_h) and the fraction of the charge which is frozen is given by the lever rule

ie (W_h - W_o)/ W_h

Eventually, with continued cooling, the eutective point (e) is reached when B begins to freeze out. The temperature now remains constant until all the remaining liquid solidifies.

(b) Partial Solid Solubility

Fig (16)



Often the impurity is slightly soluble in the solid phase of the component to be purified. The phase diagram for this type of system is shown inFig (16).

The analogy with liquid-liquid extraction technology produces the definition of the term equilibrium distribution coefficient (k).

$$k = \frac{ws}{wl} \qquad (19)$$

where ws is the concentration of the solid and wl is the concentration of the liquid at equilibrium.

For the system described in Fig (16) $k < 1$ Unfortunately, k varies with composition but in fractional solidification processes the impurity content is usually low in the feed material (3 - 5 % by wt) and so the distribution coefficient may be assumed to be constant.

To understand the freezing of a limited solid solubility system consider fig (17) which is the upper left hand corner of Fig (16).

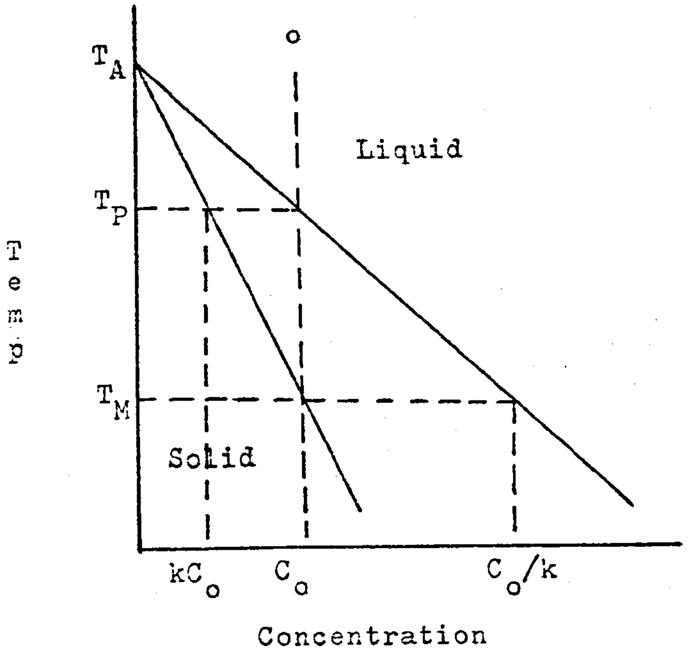


Fig (17)

Slow cooling of the liquid from point O allows solid of composition kC_o to freeze out. As cooling continues, the equilibrium conditions are rarely maintained since this requires diffusion of impurity B into the solid which is virtually non-existent in fractional solidification. The solid concentration therefore moves to the left of Co and the liquid to the right of Co/k.

(c) Complete solid solubility

This occurs when both species are very similar in size and nature and when the crystal structures of both can accommodate one another.

Fig (18)

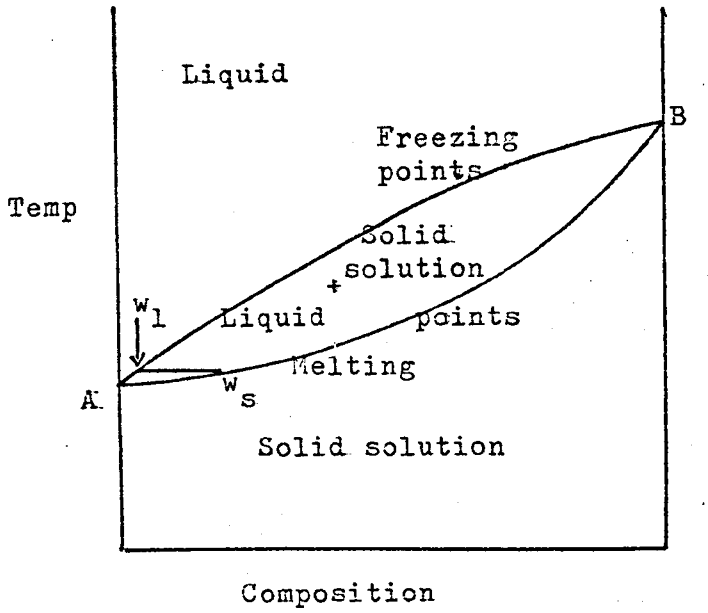
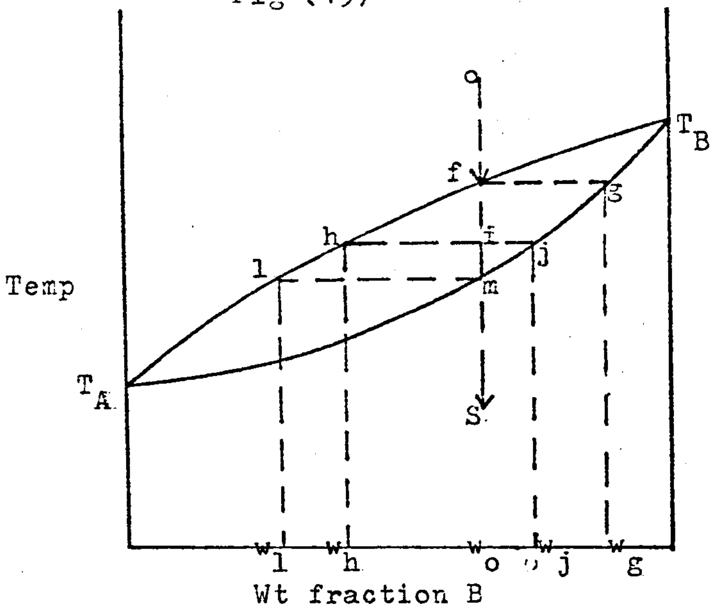


Fig (18) shows the form of the phase diagram for this type of system. If B is considered to be the impurity in A, then near pure A the distribution coefficient is constant and k ⟩ 1

The freezing operation of this type of system is represented by Fig (19)

Fig (19)



If the melt is cooled from point 0, assuming equilibrium is maintained, the liquid composition moves from f to l while the solid composition moves from g to m. At the intermediate point i, the lever rule gives the fraction of the original melt to have solidified

ie $(w_o - w_h)/(w_j - w_h)$.

At S the system is a homogeneous solid solution of composition w_o

3. The Freezing of a solution containing an impurity

The purification of a liquid by freezing rarely produces the predicted purity due to:

(i) the occlusions of mother liquor in crystal imperfections.

(ii) the trapping of mother liquor in crystal agglomerates

(iii) the mother liquor which adheres to the crystal mass by surface tension and capillary forces

(iv) the chemisorption of impurities onto the crystal face

(v) the possibility of solid solubility of impurity in the crystal phase.

Thus in order to obtain a product of high purity by crystallisation the impurity in the crystals and/or the amount of impurity in the adhering liquid must be reduced. Conventionally this may require several stages of crystallisation involving repeated handling of the solid phase. For column crystallisation, using a single piece of equipment, the impurity in the adhering liquid is reduced by washing with the reflux liquid produced by melting the crystals.

For eutectic systems the crystals themselves are fairly pure since the lattice cannot tolerate the impurity unless deformation occurs. For these systems washing is the dominant purification mechanism. The purification occurs since the concentration of impurity in the countercurrently flowing free liquid is less than that on the adhering liquid. However, since the crystals are thermally stable washing cannot remove the impurity in the solid.

When solid solubility occurs the crystal becomes unstable at the higher temperatures produced in the purification section and thus partial or total melting occurs. Simultaneously, the reflux liquid undergoes partial freezing. Thus as the crystals approach the warm end of the column their purity increases by the preferential melting of the less- pure crystal fraction and the formation of crystals of higher purity by the subsequent recrystallisation.

4. Continuous Column Crystallisation

Fig (20)

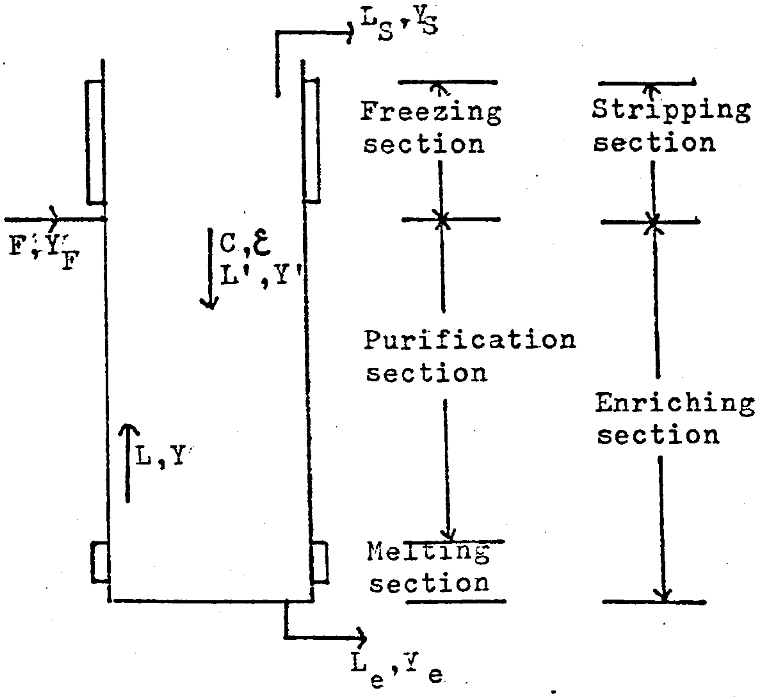


Fig (20) is a descriptive diagram of the liquid and solid flows in a column crystalliser under continuous operation, where:

F is the feed flow rate of impurity conc^n. Y_F

Ls is the impure product flow rate of impurity conc^n Y_S.

Le is the pure product flow rate of impurity concⁿ Y_e

C is the crystal flow rate of impurity concⁿ $\mathcal{E}$

L' is the adhering liq^d flow rate of impurity concⁿ Y'

L is the free liq^d flow rate of impurity concⁿ Y

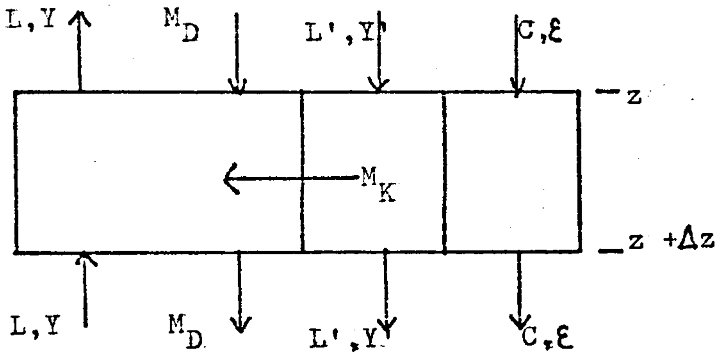


Fig (21)

An elemental description of the column crystalliser is afforded by fig (21) where z is the position in the column measured from the freezing jacket. Now, transport of impurity is achieved by bulk flow, axial dispersion and mass transfer. The bulk flow in the column is due to the movement of the crystals, adhering liquid and free liquid. The axial dispersion and mass transfer rates were described by Powers etal (72) who developed a model of the column operation derived from the comparison with packed bed extraction columns.

The rate of axial dispersion in the free liquid M_D, is defined as:

$$M_D = -D\rho A\eta_L(dY/dz) \qquad (20)$$

and the rate of mass transfer between the adhering and free liquids, M_k, is described by the equation:

$$M_k = KaA\rho(Y' - Y)\Delta z \qquad (21)$$

Powers$^{(72)}$ made several assumptions in order to develop his model.

(a) the internal flow rates, L, L' and C and the factors $KaA\rho$ and $D\eta A\rho$ are independent of the position in the column.

(b) the column is assumed to be at steady state

(c) the impurity associated with the crystal ε, is constant.

(d) radial variations in each phase are negligible

(e) all transport properties are constant

(f) the adhering liq^d rate is proportional to the crystal rate and the ratio is independent of position in column.

Taking a material balance on the differential element of free liq^d shown in fig (21) yields the general equation for all parts of the column:

$$L(dY/dz) + Ka\,A\rho\,(Y' - Y) + D\rho A\eta(d^2Y/dz^2) = 0 \qquad (22)$$

In order to solve the eq(22) another relationship between Y and Y' is required

Consider the envelope below

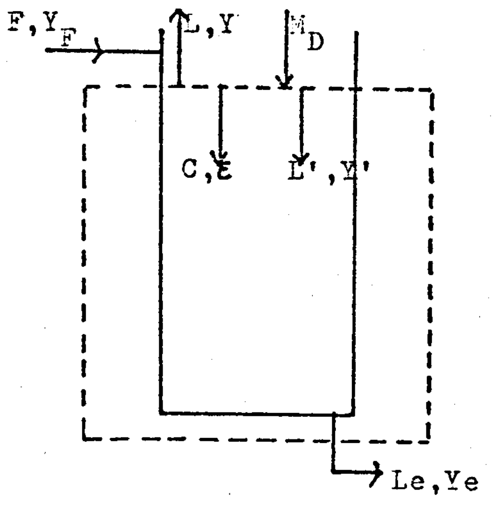


Fig (22)

A material balance gives

$$C\varepsilon + L'Y' - LY - D\eta A\rho\,(dY/dz) = Le\,Ye \qquad (23)$$

and an overall balance in the envelope yields:

$$L = L' + C - Le \qquad (24)$$

Powers$^{(72)}$ now introduced a simplification by neglecting the diffusion term in the free liquid balance.

Thus eq (22) becomes

$$L\,(dY/dz) + KaA\rho\,(Y' - Y) = 0 \qquad (25)$$

The solving of equation (23),(24) and (25) gives the differential equation describing the enriching section

$$\text{ie}\left[\frac{LL'}{KaA\rho} + D\eta A\rho\right]\frac{dY}{dz} + (C - Le)Y = C\varepsilon - Le\,Ye \qquad (26)$$

which can be solved for the boundary conditions

$$Z = Z_F \text{ for } Y = Y_0 \qquad (27)$$

where Y_0' is the free liq composition in the column at the feed point.

Solution of eq(26) to determine Y

Let $$\frac{C - Le}{\frac{LL'}{KaA\rho} + D\eta A\rho} = A \ (28) \quad \text{and} \quad \frac{C - LeYe}{\frac{LL'}{KaA\rho} + D\eta A\rho} = B \ (29)$$

Then eq (26) becomes $\frac{dY}{dz} + AY = B$ (30)

The solution to equation (30) is made up of two parts; one with $\frac{dY}{dz} = 0$ (ie a steady state solution, Yss) and the other part when B = 0 (Y_t, a transient solution).

for Steady state $AYss = B$ or $Yss = \frac{B}{A}$ (31)

for Transient $\frac{dYt}{dz} + AY = 0$ or $\frac{dYt}{dz} = -AY$ (32)

The solution of equation (32) is exponential in form

Let $Yt = Ce^{\phi Z}$ (33) where C and ϕ are constants

then $\frac{dYt}{d_Z} = C\phi e^{\phi Z}$ (34)

$\therefore$ Eq (32) becomes

$C\phi e^{\phi Z} = -ACe^{\phi Z}$ whence $\phi = -A$ (35)

$\therefore$ Equation (33) becomes $Yt = Ce^{-AZ}$

Now $Y = Yss + Yt$ (36)

$$\therefore \quad Y = \frac{B}{A} + Ce^{-AZ} \qquad (37)$$

But $Y = Y_0$ at $Z = Z_F$

or $Y_0 = \frac{B}{A} + Ce^{-AZ_F}$ whence $C = (Y_0 - \frac{B}{A})e^{+AZ_F}$ (38)

$$\therefore \quad Y = \frac{B}{A} + (Y_0 - \frac{B}{A}) \; e^{-A(Z - Z_F)} \qquad (39)$$

$$\text{Now } \frac{B}{A} = \frac{C\varepsilon - Le\,Ye}{C - Le} \qquad (40)$$

$$\text{Let } \frac{C\varepsilon - LeYe}{C - Le} = Yp \qquad (41)$$

$$\therefore \quad Y = Yp + (Y_0 - Y_p)\, e^{-A(Z - Z_F)} \qquad (42)$$

$$\text{or} \quad \frac{Y - Y_p}{Y_0 - Y_p} = e^{-A(Z - Z_F)} \qquad (43)$$

$$\text{Now, let } H = 1/A = \left[\frac{LL'}{KaA\rho} + D\eta A\rho\right]\frac{1}{(C-Le)} \qquad (44)$$

but $L = L' + C - Le$ (45) and $L^1 = \alpha C$ (46)

$$\therefore \quad \frac{Y - Y_p}{Y_0 - Y_p} = e^{\frac{-(Z - Z_F)}{H}} \qquad (47)$$

$$\text{Where } H = \frac{1}{(C-Le)}\left[D\eta A\rho + \frac{\alpha(1+\alpha)C^2 - \alpha LeC}{KaA\rho}\right]$$

For the total reflux (or batch) operation of the column Le is zero and the equations become:

$$\frac{Y - \varepsilon}{Y_{\emptyset} - \varepsilon} = \exp^{-Z/H} \quad (49) \text{ since } Yp = \varepsilon$$

where $Y_{\emptyset}$ is the conc^{n} of free liq^{d} at the base of the freezing section

$$\text{and } H = \frac{D\eta A\rho}{C} + \frac{\alpha(1+\alpha)C}{KaA\rho} \qquad (50)$$

For the stripping section a similar set of equations can be obtained

$$\text{ie } \frac{Y - \bar{Y}p}{Y_{\emptyset} - \bar{Y}_p} = \exp^{-\left(\frac{Z - Z_F}{\bar{H}}\right)} \qquad (51)$$

where $\bar{Y}p = (C\varepsilon + LsYs)/(C + Ls)$ (52)

$$\text{and } \bar{H} = \frac{1}{(C + Ls)}\left[D\eta A\rho + \frac{\alpha(1+\alpha)C^2 + \alpha LsC}{KaA\rho}\right]$$

which allow the conc^{n} profile of the stripping section to be determined. As above, for batch operation the equation may be simplified by reducing Ls to zero.

Bolsaitis$^{(25)}$, however disagreed with Powers' assumptions that crystal nucleation and growth can be described by a rate equation with a single mass transfer coefficient and that the action of the spiral is to transport the solid phase down the column. He did not confirm the effect of the spiral as the transporting mechanism and replaced the first order kinetics of nucleation with a stripping efficiency. This stripping efficiency (Es) is defined as the fraction of crystallisable material removed from the solution entering the stripping section; the fraction of crystallisable material is that amount which is in excess of saturation at the lowest temperature in the stripping section.

By analysing the action of gravity, buoyancy and viscous drag on the crystals he found that for spherical crystals there was a critical radius (r^*) required below which the crystal moves with the liquid phase and is not transported down the column.

The stripping efficiency was found to be reduced both when temperatures were lowered due to the increased viscosity and liquid density with a consequent increase in r^* and with an increase in spiral rotation since the size of the crystals is reduced. When, however, the column cross-section was increased or the liquid flow rate through the stripping section was decreased the efficiency was increased.

The stripping efficiency was defined by the equation:

$$Es = \frac{CY^*}{L(Y^*-Y_0) + F(Y^*-Y_F)} \qquad (54)$$

where Y^* is the concentration of impurity in the liquid in stripping section at zero stripping rate, Y_0 is the concentration of impurity in the free liquid at the feed point and Y_F is the feed composition.

Bolsaitis$^{(25)}$ also produced equations describing the enriching section but they can only be solved for special cases (eg for separation of isomers when the molar volumes of the crystallising and contaminating component in the liquid phase are approximately equal) which are not applicable to the present study.

GENERAL DISCUSSION

The design and operation of crystallisation apparatus is still largely empirical in nature. Although crystallisation is one of the oldest separation techniques,application in industry has been on a small scale compared to that of distillation. Subsequently, whereas distillation theory has been developed of necessity in order to decrease the capital cost of equipment, crystallisation processes have been governed by the art of the operator.

However, due to the increasing costs of power and materials it has become necessary to consider possible means of economising. Because of these considerations, crystallisation processes have become potentially more advantageous than distillation.

During the development of crystallisation apparatus the disadvantage had always been the inability of producing a continuous process. Batch operations become uneconomic due to the maintenance required, the decreased output of product compared to a continuous process and variation in product quality.

The inherent difficulty experienced in the design of continuous crystallisation apparatus is caused by the necessity of transporting solid material away from the freezing area, and then washing the crystals to remove the adhering liquid, making the operation multistage to increase the produce purity.

These problems were not really overcome until the continuous column crystalliser was developed.

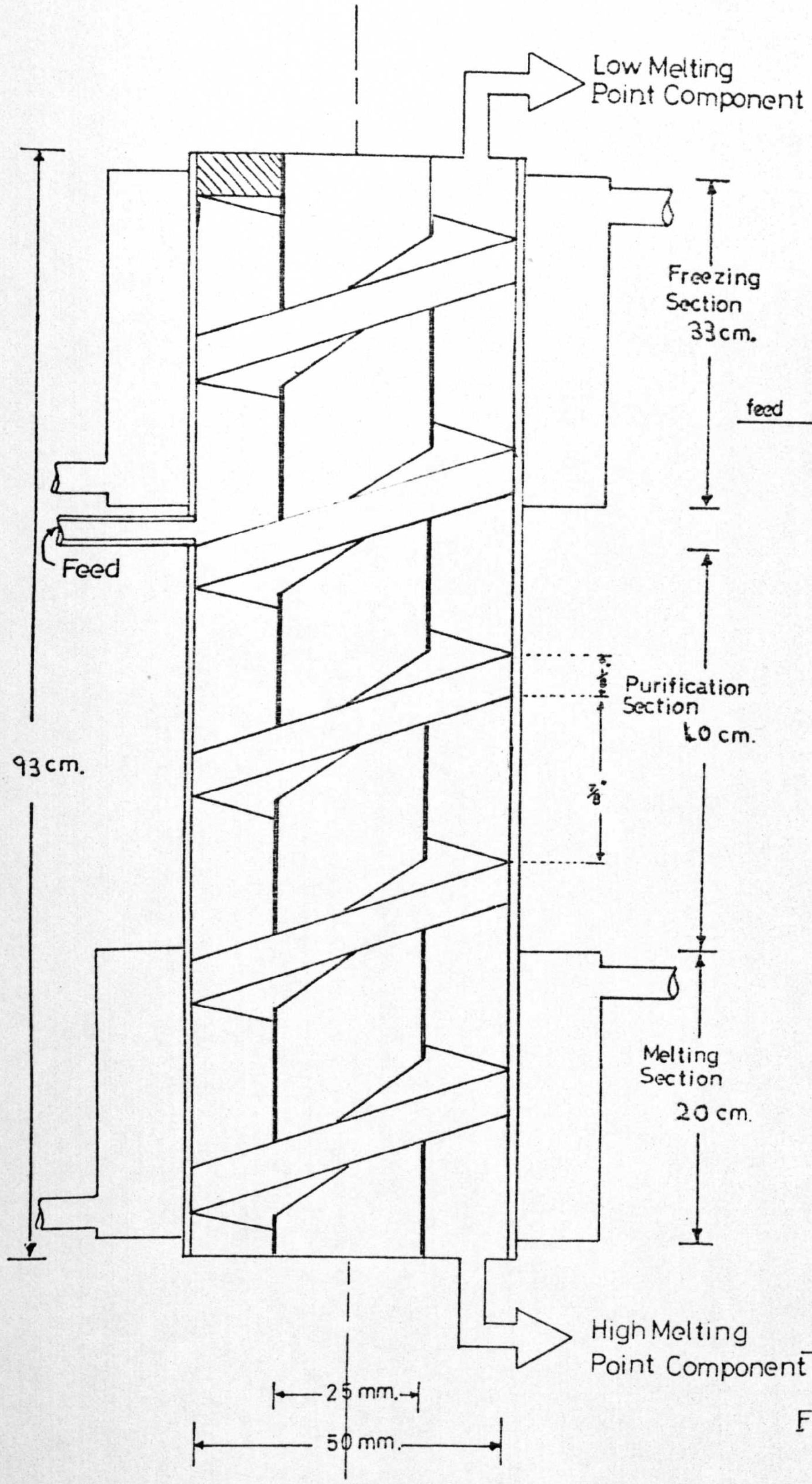


FIG.1 COLUMN CRYSTALLIZER

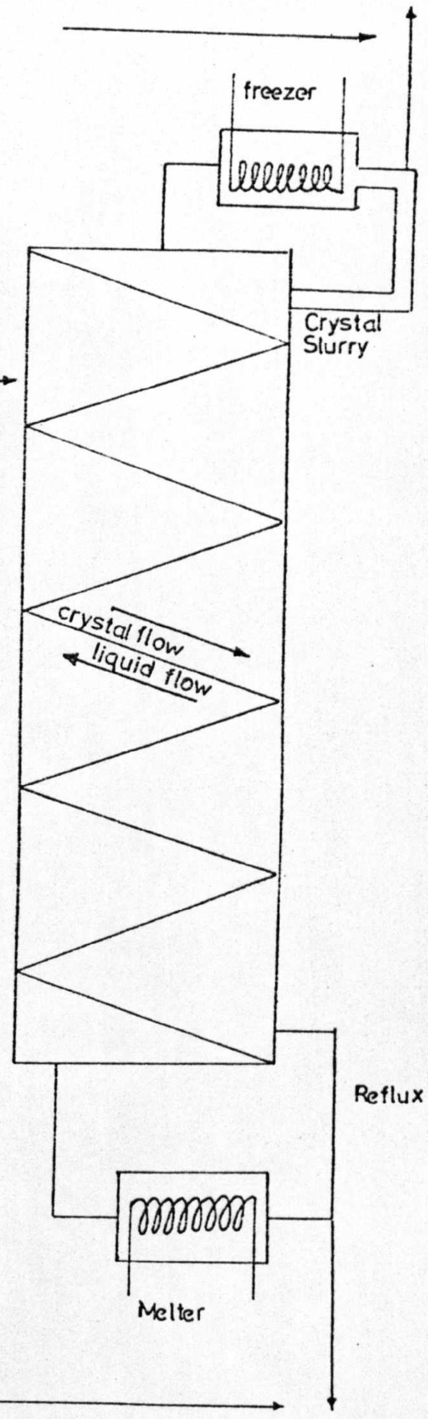


FIG.2 FLOW DIAGRAM

THE CITY UNIVERSITY
LONDON

SUBJECT
TITLE
SCALE
DATE
PASSED
COURSE & YEAR
NAME

The operation of a continuous column crystalliser requires consideration of the following principles:

(i) nucleation and growth of the crystals

The system chosen for separation must have one component with a freezing point reasonably close to ambient temperatures for the separation achieved to be economical. It is not usual to attempt purification of a system where a component freezes below -20°C or above 70°C.

Having chosen a suitable system, it is necessary to nucleate the crystals which may require seeding since sometimes undercooling is not sufficient to allow the occurence of nucleation. By controlling factors such as cooling rate, rate of agitation etc. the crystals which form in the freezing section may be suitable for efficient washing and subsequent melting.

(ii) transportation of crystals

A method of removing the crystals from the freezing section must be used to allow more to be formed. Arnold(12) utilised an oscillating piston whereas Schildknecht(116) developed an Archimedean screw conveyor for this purpose.

(iii) washing of the crystals

In order to obtain effective washing of the crystals it is necessary to allow some pure product to reflux countercurrently to the crystal flow. This washing is facilitated if the crystals are large and separate.

(iv) recrystallisation of the crystals for systems exhibiting solid solubility

For these cases it is necessary to produce a temperature gradient down the column which causes the impure crystals to melt allowing more pure liquid to recrystallise.

(v) melting the crystals in the melting section

This poses a problem which has to be compromised with the washing procedure. In contrast to that process, melting requires a small crystal which allows heat transfer to be more quickly achieved.

(vi) heat transfer through the freezing and melting section walls

In order to attain high crystal production rates in the freezer and efficient melting in the melting section it is necessary to use a coolant with good heat transfer properties. In addition, the wall thickness should be as low as possible and in order to decrease the build-up of stationary films on the outer wall the coolant (or heating fluid) flow rate should be high. The heat transfer is also increased by the presence of the crystal transporter which both scrapes the inner wall and stirs the liquid thus decreasing the possibility of stagnant films.

(vii) the production of constant flow rates of crystals, feed liquid and products.

If these flow rates are allowed to vary the column operation is upset and equilibrium will not be attained.

(viii) stirring

This is required to facilitate crystal nucleation, decrease film formation at the heat transfer walls and to ensure a constant bulk liquid concentration. The stirring is effected by the use of the crystal conveyer.

(ix) optimisation of the column's operation

An incorrect choice of the conditions of operation can produce poor results. Some variables may be of more importance than others, but as yet coherence between results reported has not been achieved. The comparison between continuous multistage distillation and crystallisation has led to some problems; eg, normal operation of distillation columns requires feed at or near the mid-point of the column whereas for crystallisation columns feed near to the freezing section is normal.

(x) Mathematical modelling

Correlation of the experimental results obtained with a theoretical analysis. Thus, principles of column design can be determined and scale-up problems can be minimised.

EXPERIMENTAL

1. Materials

(a) Chemicals

(i) Benzene - analar grade for standard solutions

Benzene - technical grade for experimental use

Cyclohexane - spectroscopic grade for standard solutions

Cyclohexane - technical grade for experimental use

(ii) Sodium chloride - 56lb bags, technical grade from ICI

(iii) Para-xylene - 99.9% pure; 5 gallons donated by BP Sunbury

Mother liquor - mixture of o ,m and p-xylene + ethylbenzene 5 gallons donated by BP Sunbury.

Analar grade o, m and p xylene for standard p-xylene solutions.

(iv) Industrial Methylated spirits - approximately 95% ethanol and 5% methanol for experiments Absolute ethanol for standard solutions.

(v) Deuterium oxide (99.8% pure) from AERE, Winfrith, Dorset

(vi) Copper sulphate - technical grade ($CuSO_4 .5 H_2O$) from BDH, Poole Dorset

(vii) Concentrated sulpuric acid (used to acidify copper sulphate).

(b) Analytical

Gas liquid chromatography (GLC)

(i) Polyethylene glycol 20M (PEG 20M) for analysis of benzene/cyclohexane mixtures. 20% PEG 20M by wt added to Celite 60 - 80 mesh as solid support.

(ii) Bentone 34 + di-iso decyl phthalate for analysis of xylene isomers. 5% by wt of each added to Chromosorb W 100 - 120 mesh as solid support.

(iii) PEG 400M for analysis of ethanol/water system. 20% by wt added to Chromosorb W 100 - 120 mesh as solid support.

Infra-red spectroscopy

Analar grade methyl orthoformate and carbon tetrachloride (both dried with molecular sieve 5A) + phosphorus pentoxide.

2. Analytical apparatus

(a) Pye 104, flame ionisation detector (FID) GLC - Nitrogen used as carrier gas; hydrogen burnt in air to produce flame.

(b) Pye E7566/4 conductivity bridge with 1ml micro-cell type E7598/B used to measure conductivity of sodium chloride solutions and neutral copper sulphate solutions.

(c) Perkin Elmer infra-red apparatus for analysis of deuterium oxide, water mixtures.

(d) EEL portable colorimeter

3. Sampling apparatus

(a) 1μl syringe with stop at $\frac{1}{2}\mu$l for GLC analysis

(b) 5ml syringe for conductivity samples

(c) 10ml sample bottles for conductivity samples.

4. Existing Apparatus - October 1972

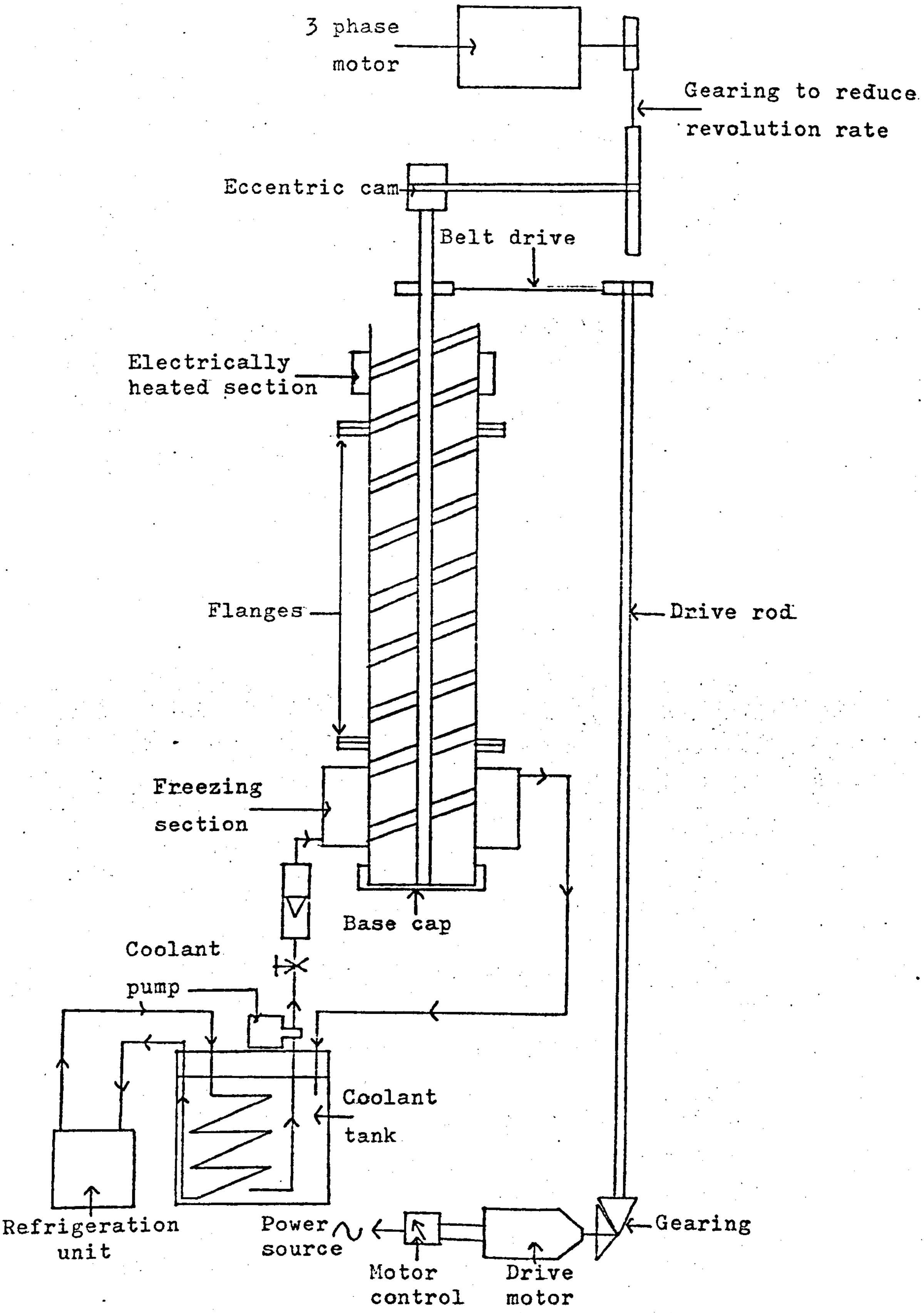
The column consisted of a polytetraflouroethylene (PTFE) Archimedean screw with a mild steel support shaft. The outer screw dimension was a nominal 2" and the support shaft had a diameter of 1". A jacket comprising a freezing section, purification section and melting section, partially fabricated in mild steel, fitted over the length of the screw with a clearance of $^1/_{25}$th" on a radius. The transportation screw was rotated by using a single phase $\frac{1}{4}$ HP voltage controlled motor, power being transferred via a belt; the possibility of oscillation drive to the screw was provided by a 3 phase geared-down motor connected to an eccentric cam resting on the top of the support shaft.

Temperatures along the length of the column and at various points on the refrigeration line were measured by using iron-constantan thermocouples connected to a 6 point Honeywell temperature recorder.

Refrigeration to the column was provided from a 20 gallon galvanised tank containing a 50/50 by wt anti-freeze/water solution cooled by a $\frac{1}{2}$ HP refrigeration unit to -15°C.

Diagram of apparatus in Oct 1972

Fig (3)



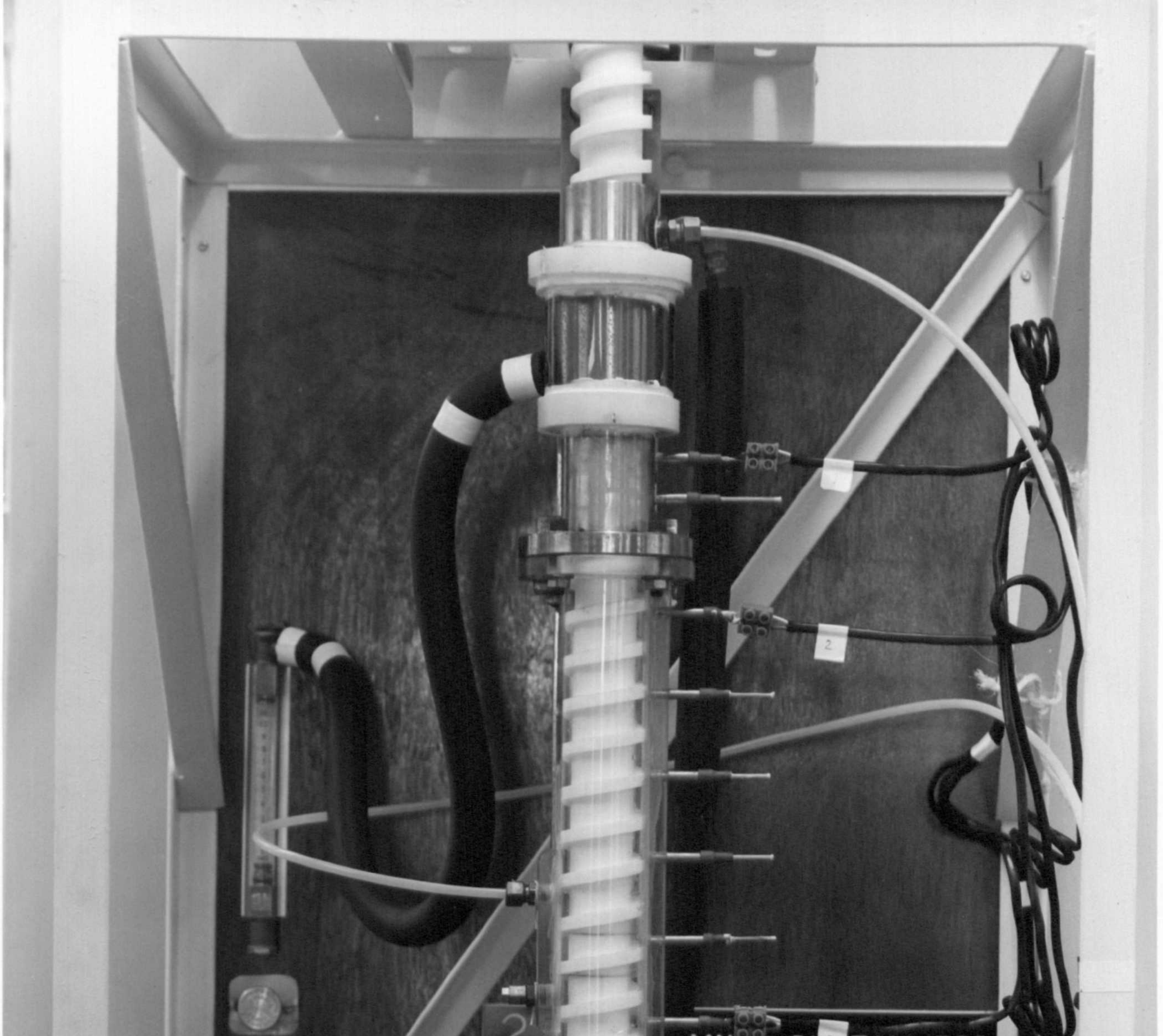


Fig (4) Column assembly October 1972

5. Improvements to the System

A stainless steel jacket with a freezing and melting section + 4 purification sections of differing lengths was designed and constructed.

The drive to the transportation screw was not sufficiently powerful to allow rotation once crystals formed in the column and the screw would sieze up even at the maximum voltage (and torque) available. In order to overcome this problem a 3 phase $\frac{1}{3}$ HP Kopp variator motor was attained and installed. This motor worked at constant torque and voltage providing sufficient power to drive the screw even at low rotational speeds. Transmission of power was attained via gear cogs and a chain allowing rotational speeds from 50 rpm to 300 rpm.

In order to cool the column before a run it was necessary to pass cold feed liquid round the system. A centrifugal immersion pump, all immersed parts constructed in PTFE or stainless steel, was obtained. Since the pump was of very high throughput, the voltage imput to the motor was controlled by a 2 amp Variac controller to give an acceptable flow rate. Once the whole system had been sufficiently cooled, circulation was terminated and the same pump used as a feed pump.

For continuous operation of the column it was necessary to measure and regulate both the flow rate of the feed to the column and of the base product from the column (the top product overflowing via the port provided and being the difference between the other two flow rates). Two rotameters were used for this purpose, the range of flows measurable being from 100 to 1500ml/hr of water.

The first set of benzene/cyclohexane runs were undertaken with the apparatus as now constructed. Once this set of runs had been completed, desalination of brine solutions was the next problem to be investigated.

With salt water solutions being present in the column corrosion effects would have to be minimised. The mild steel support shaft of the screw would be inadequate for the requirements, thus it was necessary to design and build a new PTFE screw with a stainless steel shaft and a larger annular space giving a large volume in the column.

The home-made thermocouples, allowing contact between the salt water and the iron of the metal junction, would soon prove insufficient. J-type iron/constantan thermocouples were obtained. These were sheathed in stainless steel thus decreasing any corrosion effects and were easier to manimpulate due to their robust construction. The 6 point facility of the temp recorder was increased to 12 points since accurate temperature control of the column necessitated further measurements.

For the analysis of the brine solutions in the column a conductivity bridge and 1ml sampling cell were obtained and commissioned.

The control of product quality from the column depends upon constant flow rates of both the feed and the base product. The circulation/feed centrifugal pump was variable in its output and the constant manipulation of the base product valve needed to control that flow led to poor operation of the column. Two metering peri-staltic pumps were bought from Watson-Marlow (type MHRE 100); these effectively controlled the flow rates and allowed for repeatable product quality.

In order to increase the efficiency of the column in its ability to desalinate sea water a longer freezing section was designed and constructed. This was polished on its inner wall and used with a previously constructed perspex purification section to examine the transportation of ice crystals.

The equipment was now operating satisfactorily and was employed to investigate the sodium chloride/water, mixed xylenes, deuterium oxide/water, ethanol/water and copper sulphate/water systems.

Freezing section

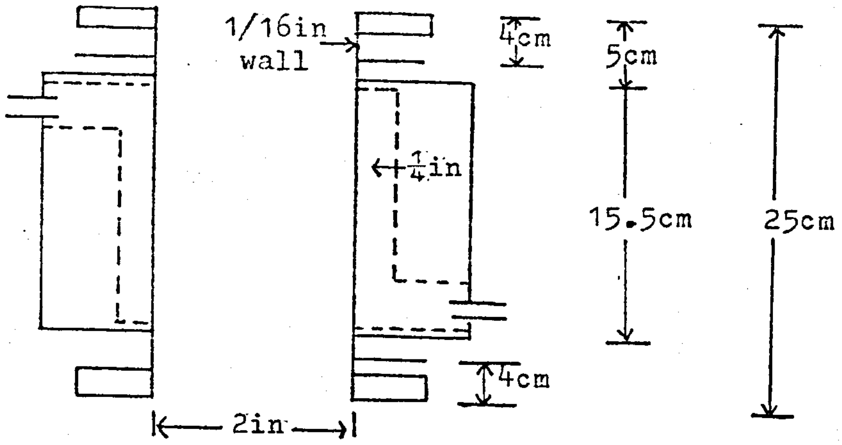
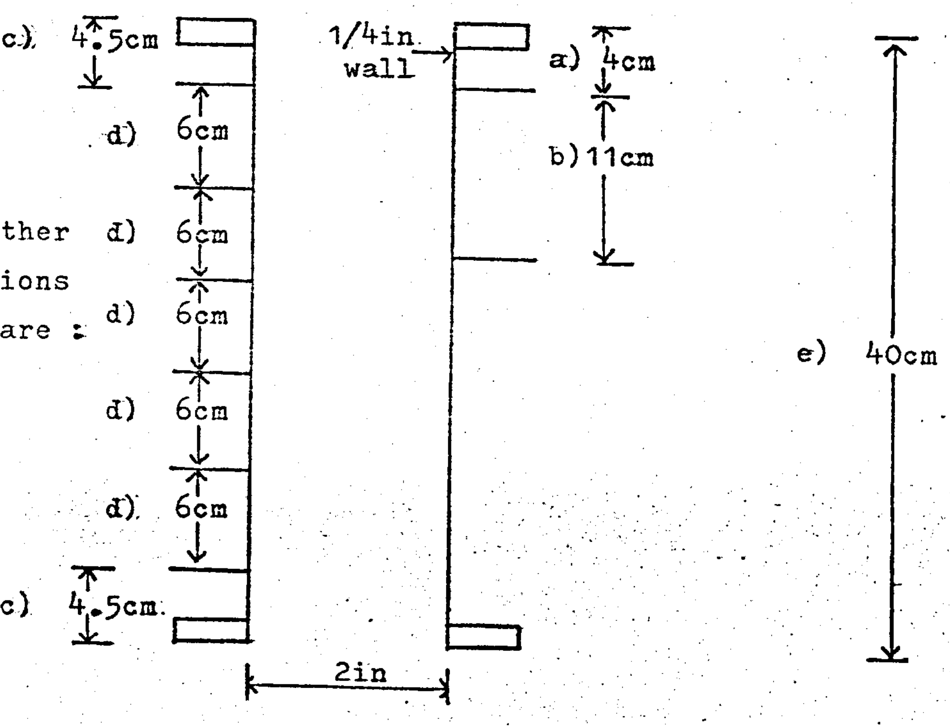


Fig (5)

Column assembly with unpolished freezing section + melting & purification sections

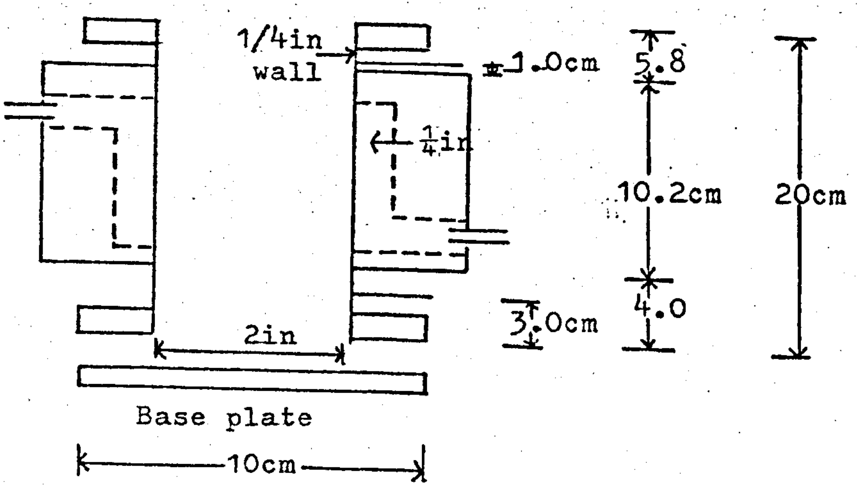
Purification section



There are three other purification sections whose dimensions are :

	1	2	3
a)	2.0	4.0	4.0
b)	5.0	6.5	9.5
c)	2.0	4.0	4.0
d)	2.5	3.3	4.8
e)	19.0	26.0	33.0

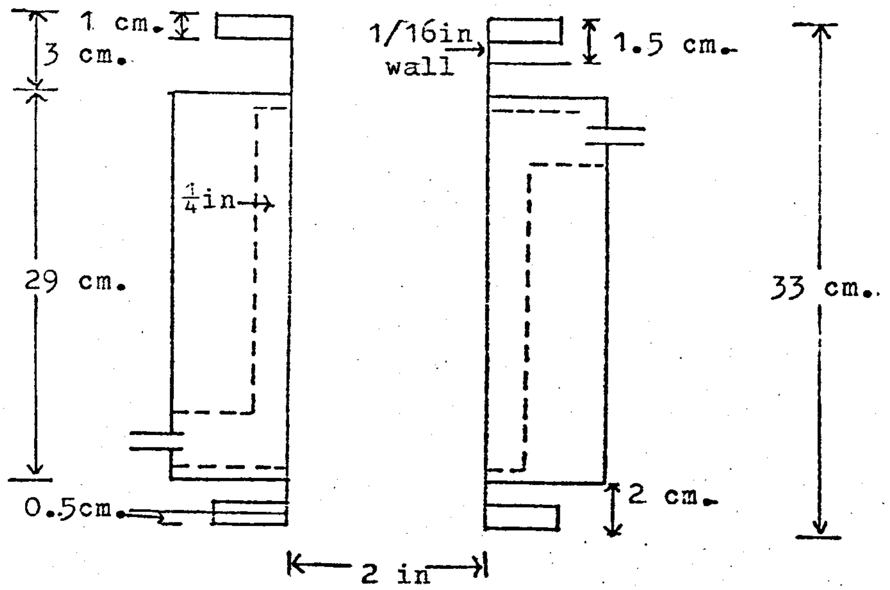
Melting section



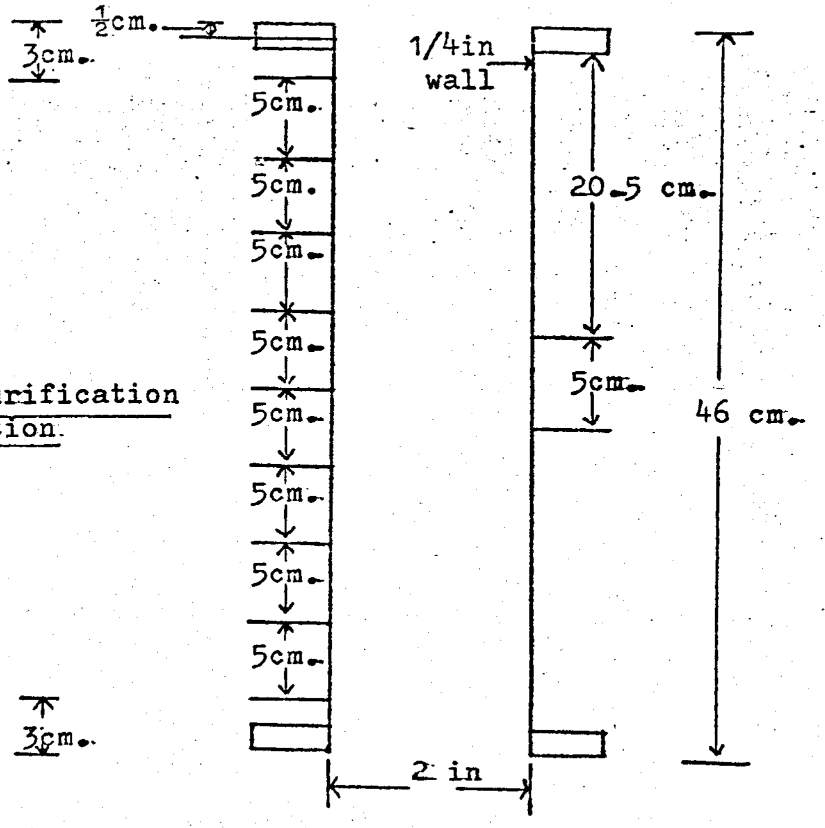
Design of polished freezing section and perspex section

Fig (6)

Freezing section

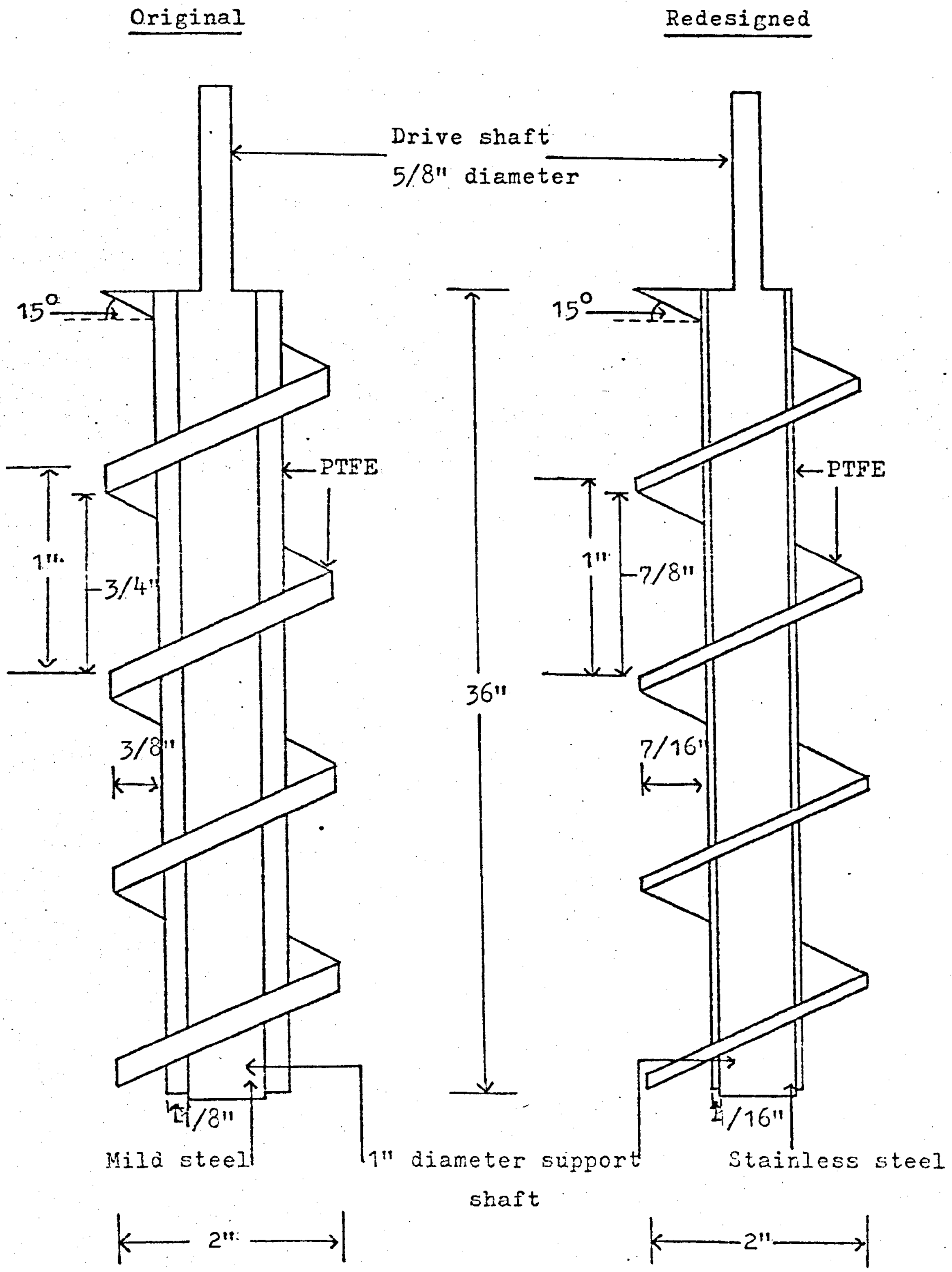


Perspex purification section



Original and redesigned P.T.F.E transportation screws

Fig (7)



6. Method of operation

The column jacket was cleaned, then assembled, placed over the transporation screw and secured to the frame. The connections to and from the refrigeration and heating jackets were made allowing flow of coolant and hot water to those sections, respectively. The feed and products lines were connected and pressure gauge line joined to the base of the column. Since the column operates at below ambient temperatures the jacket except the heating section was insulated by pre-formed expanded polystyrene or mineral wool pipe sections and the refrigeration piping by expanded neoprene tubing.

Feed solution of known concentration was now pumped round the system using a peristaltic pump, overflowing back to the feed tank via a port at the top of the column. Once the jacket was full the transporation screw was turned on and its rotational speed checked with a stop-watch, adjusting as was necessary. Cooling to the column was now commenced; the refrigeration pump was turned on and coolant introduced to the freezing jacket via a valve and rotameter. The feed solution was allowed to continue circulating until the whole of the system was down to a temperature about $1^{o}C$ above the crystallisation point of the mixture concerned, monitored by observing the temperatures along the column, which were logged by the 12 point temperature recorder.

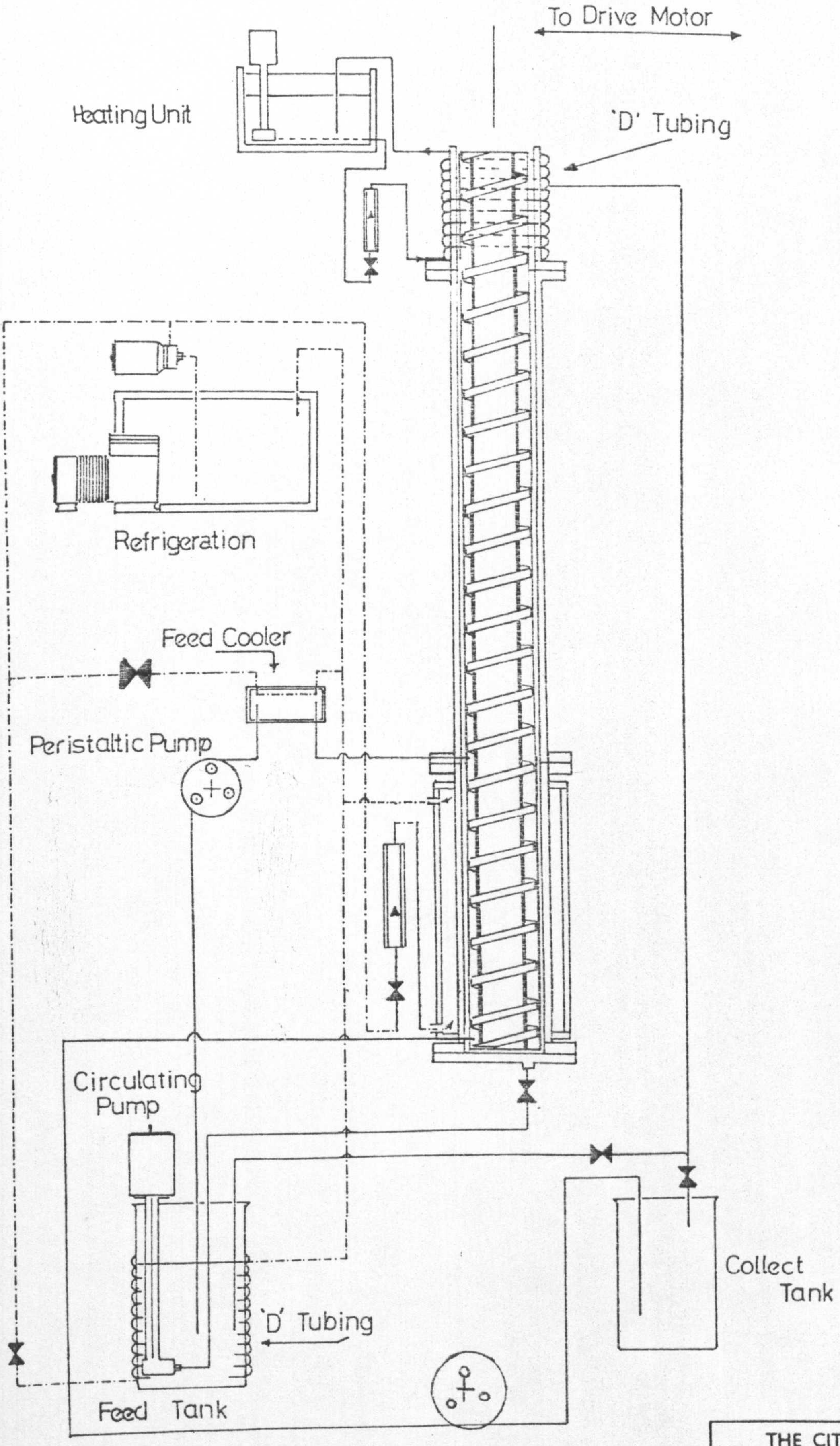
Circulation was terminated and feed solution was passed at the proposed flow rate via a second peristaltic pump, through a pre-cooler unit then into the column at the designated feed point. Base product was removed from the column by using the circulating peristaltic pump set at the required flow rate, the top product cascading from the port at the top of the column. The products were collected in separate containers and their volume rates measured.

For efficient column operation, the refrigerant flow rate had to be maintained at a constant value and the temperatures of refrigerant into and from the freezing section had to be constant. In order to prevent blockage of the feed line due to the solution crystallising in the pre-cooler it was necessary to monitor both the feed temperature and the temperature of the coolant in the feed pre-cooler unit. Observations of the load on the screw's rotation due to crystals in the column was possible by means of ammeters connected to each phase of the drive motor. If the current drawn increased above the norm for the column operation this was indicative of a blockage in the column and the run was terminated. A blockage in the freezing section was also indicated if the pressure in the column, measured by the pressure gauge connected to the base of the jacket, becomes greater than usual. For crystals transported downwards this increase in pressure could also be due to crystal build-up developed by insufficient heat input to the heating jacket but under continuous operation with removal of liquid from the base of the column this possibility was rare. If crystals were transported upwards a blockage in the column was also indicated by a stationary needle on the pressure gauge which was usually oscillating slightly. It was also necessary to check whether crystals were leaving the column when transport was upwards since this decreased the efficiency of the separation. Under normal operation most of the crystals were melted by natural heat inputs (friction, heat transfer across the walls of the heating section) but provision was made for passing hot water through the heating jacket if necessary.

Due to the toxic nature of benzene/cyclohexane and xylenes, curtains were placed round three sides of the support frame and an extraction fan was used to help remove the vapours.

Sampling and analysis at points along the column was undertaken after each hour of operation, temperatures were noted and the product volumes measured (the products were then remixed and analysed to check the constitution before adjusting the concentration if necessary and replacing them in the feed tank). Once equilibrium had been reached, determined by plotting the log of concentration against position in the column on semi-log paper to obtain a straight line graph, the run was terminated.

Fig (8)



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TITLE 2" Column Crystalliser

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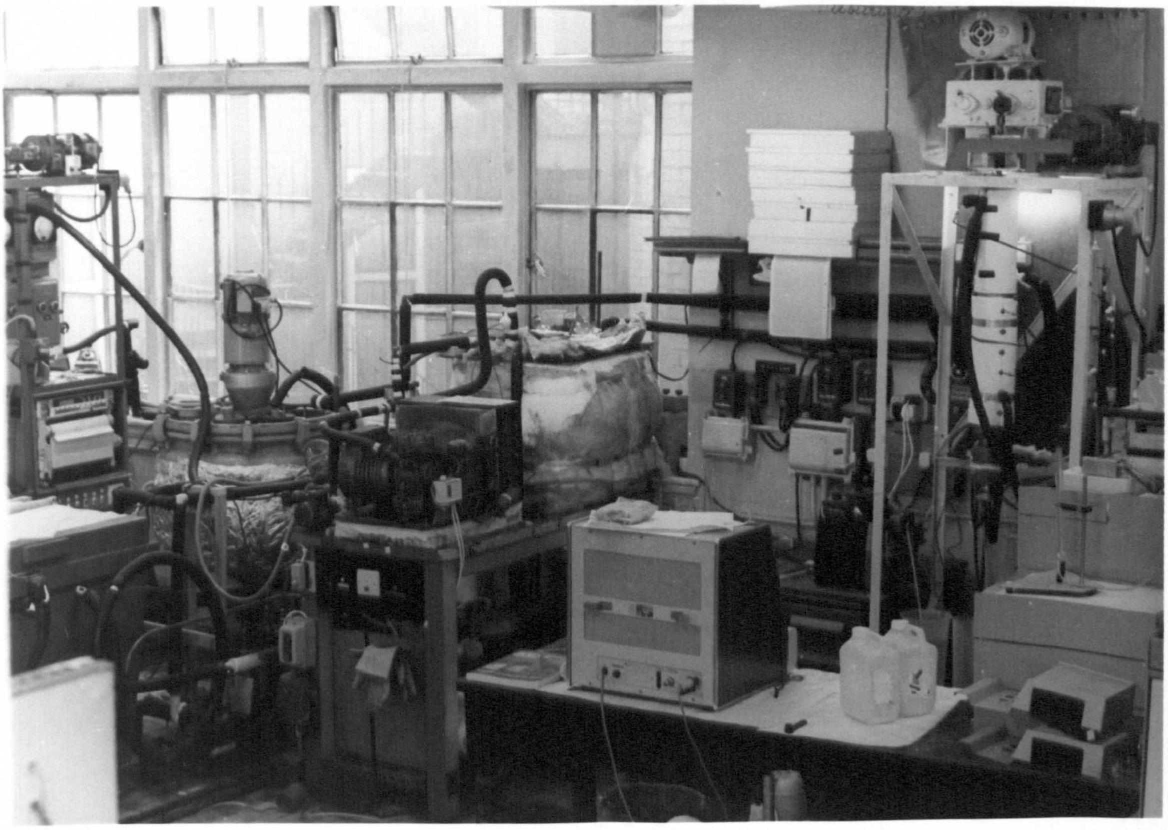
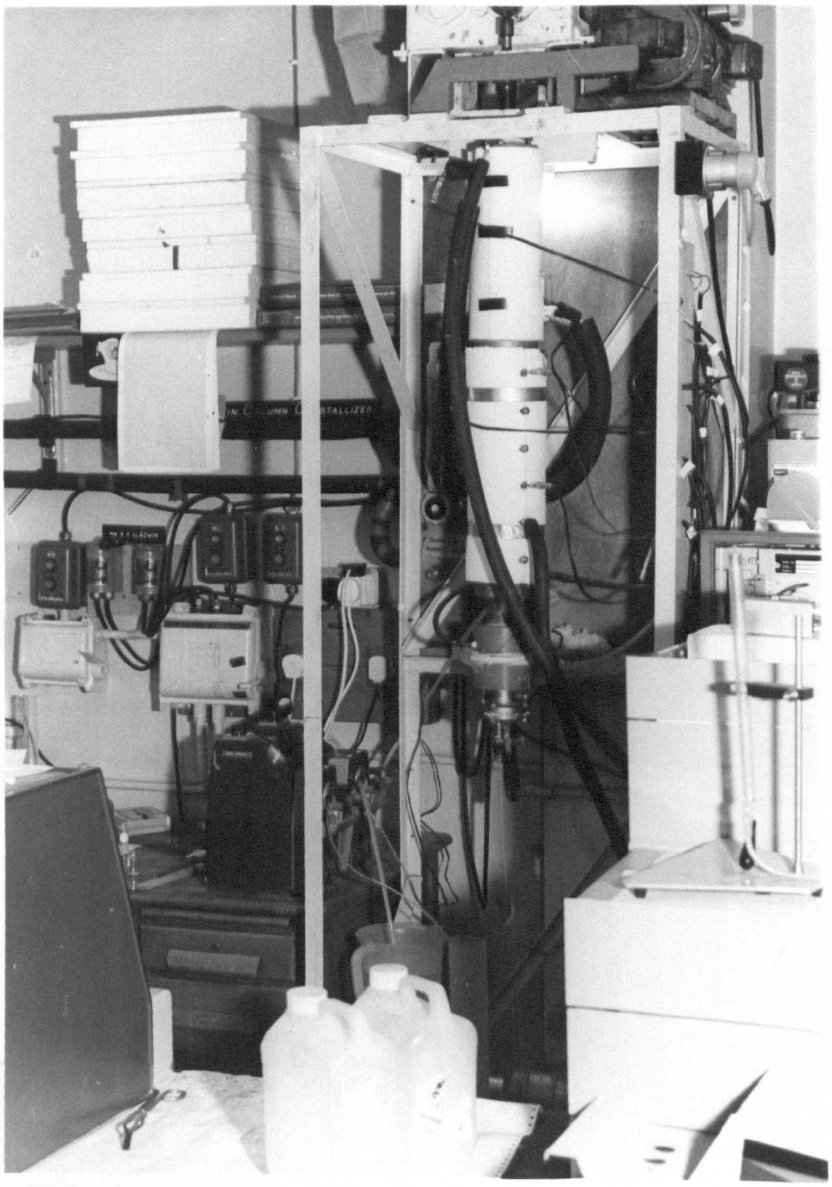


Fig (9)
Photographs of equipment once improved.
Above – general layout.
Right – column assembly with polished freezing section + 40 cm. purification section + melting section.



7. Sampling

A strict routine was used in obtaining samples. The syringe (1μl for organic systems, 5ml for inorganic systems) was pushed through a septum at the sampling point and flushed twice before taking a sample. Samples were collected in order of increasing impurity (ie purest sample taken first) to decrease the effects of sample contamination. After each sample the syringe was flushed three times with air to remove traces of that sample.

(i) Benzene/cyclohexane

0.5μl samples were analysed on the GLC. Peak heights were compared with a graph of peak heights for standard cyclohexane solutions (1000 ppm up to 50,000 ppm) in benzene to determine the cyclohexane content. The GLC conditions were:

Column oven temperature	100°C	
Detector oven temperature	105°C	
Nitrogen flow rate	40ml/min	
Hydrogen pressure and flow rate	20psi	45ml/min
Air pressure and flow rate	13psi	600ml/min
Attenuation of detector amplifier	50×10^4	
Column length/internal diameter	5ft x 4mm	

(ii) Sodium chloride/water

2ml samples were removed from the column, placed in 10ml sample bottles and the lids positioned. The samples were then left for 2½ hours to equilibrate with room temperature before a measurement of conductivity was made. The measurement was compared with a calibration curve of known sodium chloride solutions in water to determine the concentration in the test solutions. Measurements were made thus:

Each day of operation the state of the calibration curve was checked by using the calibrate function of the conductivity bridge; ie connections to the sampling cell were broken, the range switch was moved to 'calibrate' and the sweeper rotated until a maximum deflection of the meter was observed - this should occur at 1.0 on the scale. Cell connections were re-made. The cell was flushed twice with distilled water, emptied and the tube to the electrodes dried with Kleenex Medical Wipes. The sample was sucked into the cell and flushed out to waste, then a second 1 ml of the sample was pulled into electrode area and flushed up and down twice to ensure any bubbles in the cell were removed before the measurement was made. After reading the value of conductivity for maximum deflection of the meter the sample was flushed to waste. The tube to the cell was now dried as before, the cell washed twice with distilled water, dried and the next sample measured as above.

Xylenes

As with benzene/cyclohexane system except for a different column. The GLC conditions were:

Column oven temperature	70°C
Detect oven temperature	75°C
Nitrogen flow rate	40ml/min
Hydrogen pressure and flow rate	20psi 45ml/min
Air pressure and flow rate	13psi 600ml/min
Attenuation of detector amplifier	50×10^4
Column length/internal diameter	5ft x 4mm

Ethanol/water

As with benzene/cyclohexane system except for a different column. Only the ethanol peak was recorded since a flame ionisation detector was in use. The GLC conditions were:

Column oven temperature	80°C
Detector oven temperature	100°C
Nitrogen flow rate	40ml/min
Hydrogen pressure and flow rate	20psi 45ml/min
Air pressure and flow rate	13psi 600ml/min
Attenuation of detector amplifier	50×10^4
Column length/internal diameter	5ft x 4mm

Deuterium oxide/water

Initially analysed by infra-red technique as used by Kimbrough and Askins(79), but the accuracy was less than 4% in the range under examination. Specific gravity was used later. A 10ml sample was weighed to 4 decimal places at 20°C ± 1°C but the measurement was complicated due to the presence of the ethanol as a crystal habit modifier. The ethanol was determined by GLC as for the ethanol/water system. Using the densities for the three liquids present and knowing the ethanol concentration the heavy water content was calculated to within ±2%. Later work used sodium chloride solutions as habit modifier since this had less effect upon the density of aqueous solutions.

Copper sulphate/water

For the initial work with neutral solutions the measurements were by conductivity - see sodium chloride /water system. When the solutions were acidified a portable colorimeter was employed. Using the green filter the values of optical density for the unknown solutions were compared with standard copper sulphate solutions. Measurement:-

For each run the standards were checked and a graph was drawn. For each sample the cell was washed twice with distilled water, filled with distilled water (ensuring no air bubbles were present) and the outside surface wiped clean with Kleenex Medical Wipes. Zero on the meter scale was now determined for absence of copper in solution, the cell emptied and washed twice with distilled water. After drying the cell, both inside and outside, the sample was introduced to the cell and the measurement made. The samplewas now emptied to waste, the cell washed twice with distilled water, dried and the next sample chosen. Once all the samples for one hour's running had been measured the clean cellwas filled with distilled water and placed in the photometer until samplingwas next required.

8. Optimisation of column operation

Possible variables

(i) Crystal transportation

- (a) Screw speed
- (b) Oscillation of screw or feed to column
- (c) Geometry of screw (eg annular space, angle of flights)
- (d) Column attitude (ie crystal transport upwards or downwards)
- (e) Nature of the surface of the inner walls of the jacket (ie polished or rough).
- (f) Length of purification section.
- (g) Size and shape of crystal.

(ii) Crystal production rate

- (a) Length of freezing section
- (b) Flow of coolant to freezing jacket
- (c) Temperature of coolant to freezing jacket

(iii) Heat input to column

- (a) Frictional effects due to movement of screw
- (b) Heat transfer from the room
- (c) Hot water supplied to the heating jacket (flow rate and temperature)

(iv) Effect of continuous operation

- (a) Feed rate
- (b) Feed position
- (c) Feed temperature
- (d) Products removal ratio

(v) Effect of pressure in the column

(vi) Effect of oscillations on the separations

Optimisation procedure

(i) Benzene/cyclohexane

A feed solution of benzene containing 3% of cyclohexane was column crystallised to remove the cyclohexane component from the benzene. Although cyclohexane has a freezing point similar to benzene (cyclohexane +6.2°C, benzene +5.5°C) the benzene crystals are the only type to form due to its high concentration. Cyclohexane and benzene exhibit no solid solubility thus the crystal lattice is relatively pure, the impurity being mainly found in the liquid adhering to the crystal.

Since benzene crystals are heavier than the mother liquor (density of crystals 1.02g/ml, density of benzene 0.88g/ml) the column was mounted with the freezing section at the top and crystals were transported downwards. Operation of the column was initially investigated under batch or total reflux conditions with no feed or products removal.

The first five runs were unsuccessful due to the low torque drive motor employed. As soon as a significant amount of crystals had been formed the screw would seize-up in the stainless steel jacket and the column operation would have to be aborted.

With a higher power, higher torque drive motor commissioned runs 6-10 were used to determine the optimum speed of revolution of the transportation screw. All the runs were successful, no sieze-up of the screw occurred.

The column jacket had been constructed with a fixed length for the freezing and melting sections but with four different lengths for the purification section. Six runs were undertaken to determine which length of column would give the best separation of cyclohexane from benzene at the previously determined optimum screw speed.

It had been noted in the above runs that although crystals had reached the base of the column, determined by an increase of pressure measured on a 20psig pressure gauge no heating was required to melt the crystals - base pressure rarely rose above 5psig, normal being 1.5 to 2.0 psig with a full column but no crystals. In fact in the last six runs the separation was enhanced by allowing a low flow rate of coolant through the melting jacket.

Several unsuccessful runs were now undertaken. It appeared that the drive motor, mounted to the right hand side of the column, was creating a sideways movement of the screw during rotation. This movement would be accentuated due to the length of the screw and would cause excess friction by rubbing on the jacket walls thus melting the crystals. In order to overcome this problem two things were tried; (a) cooling the base of the column by pumping refrigerant round the melting section and (b) seating a ball be aring at the centre of the base plate of the screw to ensure the screw ran centrally. However, little improvement occurred and it was decided to reverse the attitude of the column placing the freezing section at the base and transporting the crystals upwards. This way the frictional effects would be minimised by increasing the refrigeration to the freezing section.

The optimum speed of rotation of the screw was now determined and then an assessment of the effect of cooling the purification section was undertaken. Under these conditions the product at the top of the column was adequate and continuous operation was attempted.

The feed tank was cooled by passing refrigerant through Calorex D-section heat exchange tubing wrapped round the outside of the vessel. Under continuous operation some trouble with blockages in the freezing section occurred; thus causing the base product flow rate to drop to zero. The problem was removed by decreasing the cooling to the freezing section and some successful continuous runs were undertaken.

After these runs had been completed a critical examination of the whole apparatus was made. During this survey plumb-lines were employed to check the verticality of the screw and support frame. It was discovered that the support frame was not vertical and a movement of $\frac{3}{8}$" was necessary at the base to position the column jacket vertically over the screw.

(ii) Salt Water (1st attempt)

The feed consisted of a 3.5% sodium chloride solution in tap water. Ice crystals formed on freezing and these are lighter than the mother liquor (density ice 0.92g/ml, density 1.0254g/ml for 3.5% by wt sodium chloride sol^{n}); thus the apparatus was constructed such that crystals were transported upwards. The sodium chloride/water system is a eutectic type and the crystal lattice excludes any ions unless imperfections are present; thus the majority of the impurity remains in the adhering liquid and must be washed for removal.

Seventeen runs were undertaken, the first two were under batch operation and the others with continuous feed and products removal. Most of the experiments were of an investigatory nature since it was found that although at start-up crystals were formed in plenty and were easily transported, crystal transport eventually decreased towards zero and the freezing section be came blocked, detected by: an increase in oscillation in the current drawn by the drive motor, a cracking noise emitted from the column and immediate stoppage of the screw once the drive motor was switched off.

Investigation of the crystal types in the column gave an indication of the nature of the problem. Initial crystals leaving the column were small and easily melted - the crystal mass was in fact a mush. Once the freezing section had blocked the column jacket was removed (with some difficulty) and a glass-like, very hard ice mass was found on the screw in the freezing section area.

To try to prevent this glass-like ice forming:

(a) the salt water feed solution was saturated with phloroglucinol (an aid to ice nucleation) but no improvement was observed.

(b) PTFE swarf from the screw was added (it having been considered that in the more successful early runs the PTFE had been rubbed from the screw by contact with the jacket and may have acted as favourable sites for ice nucleation); this caused a slight improvement.

(c) the effect of the temperature of coolant into the freezing section was noted. -15°C causing glass-like ice to form; the optimum was between -12 and -13°C.

(d) the temperature of the coolant in the refrigerant tank must be above -16.5°C, even for low flow rates of refrigerant to the freezing section.

(e) the area of refrigeration to the column was investigated. Calorex D-section heat exchange tubing was used to extend the freezing section 15cm up the purification section but the results were inconclusive.

(f) the attitude of the column was reversed, crystals now being driven downwards, but no improvement occurred.

(g) the effect of the feed position was determined. Feed was introduced at three points above the freezing section and through the base of the column. The optimum position was found to be just above the freezing section.

(h) the temperature of the feed input to the column should be as low as possible subject to prevention of nucleation in the feed-line. This decreases the possibility of remelting of crystals in the freezing section due to a warm input and increases the resistance of the crystals to caking.

(i) oscillations (amplitude of 6.0mm 120 per minute) of the screw in the jacket as well as revolutionary drive were undertaken. Glass-like ice formed at temperatures required to overcome the extra friction caused.

(j) the optimum speed of rotation of the screw was determined as 80 rpm.

Finally, it was decided that a larger freezing jacket was required to produce the quality of crystals needed for increased feed throughput. This was designed and constructed.

(iii) Xylenes

While the new freezing section was being fabricated, work with the existing freezing jacket was continued by investigating the purification of p-xylene from a mixture of o, m and p-xylene and ethylbenzene.

Although the isomers have very close boiling points (ortho 144.6°C, meta 138.8 to 139.2, para 137.8 - 138.1) making distillation prohibitively expensive, their freezing points are markedly separated (ortho -27.1, meta -54.8, para +13.2). The purification of p-xylene should be possible by column crystallisation. However the separation was never successfully accomplished due to the difficulty of transporting the needle-like p-xylene crystals formed from the solution.

(ii) Salt Water (2nd attempt)

The new freezing section being ready the column was reconstructed. This time the purification section consisted of a 46cm perspex tube thus allowing a visual observation of the crystal transportation.

Column operation was again hindered by lack of crystal transport after the initially good transportation had terminated. The reason for this was now thought to be due to the nature of the surface of the inner wall of the stainless steel part of the freezing section. This surface had been left as bought (unpolished) to aid nucleation of ice crystals by presenting a relatively rough surface. Unfortunately, the ice had formed a continuous collar round the screw and the friction at the wall allowed the ice to move backwards along the screw as the transportation tried to remove them. The longer the ice remained in the cold area of the freezing jacket the greater the tendency to form glass-like ice. The column was dissembled and the freezing section given a mirror-finish polish on its inner wall. Crystal transport was markedly improved and nucleation was not impaired.

The system was now ready for optimisation of operation.

(a) the screw speed was varied from 53 to 140 rpm to determine its effect on product quality and the time required to reach equilibrium conditions

(b) using the best speed of transportation of crystals the position of entry of feed into the column was investigated to determine its effect on column operation.

(c) it is assumed that a longer column produces purer products provided that heat inputs from the surroundings can be minimised. The effect of column length was investigated to test this assumption.

(d) product ratios were varied. The possibilities are low flow rate with high purity or vice versa; in practice a compromise is necessary.

(e) as the crystal rate is increased it would be expected that separation would be enhanced. This is true up to a certain rate when a limiting separation occurs, any further increase in crystal production will not increase the separation.

(f) the direction of transportation of the crystals was changed from downwards to upwards. At all but the highest crystal rates the former was the better.

(g) attempts at varying the crystal pressure at the base of the column were futile. As the pressure increased above 5psig the ice packed together and could not be easily melted thus causing shut-down of operation.

(h) effect of oscillations upon the separation achieved. Two types of oscillation were tried. In the first, the screw was mechanically moved up and down by an eccentric cam driven by a 3-phase motor. The other method was to attach a displacement pump to the column; joining the input and output parts of a pump together caused a liquid pulse in the column when the pump was turned on. In both cases the extent of oscillation was variable but for each these fluctuations were kept to a minimum.

(v) Deuterium oxide/water

The problem with this system is not so much with the actual separation but more in the analysis of the samples.

The perspex section used in the desalination experiments could not be used for this system since it had developed leaks - the heavy water being very expensive, loss by leakage could not be tolerated. Thus, the column consisted of a 40cm stainless steel purification section, 33cm freezing section and 20cm melting section.

Water, heavy water and their mixtures form needle-like crystals which readily form into glass-like ice. The problem with systems that form needle-like crystals (as discovered with p-xylene) is that the crystal transport becomes impossible. In order to facilitate the transport of heavy ice it was necessary to use a habit modifier. A 3% ethanol solution caused mushy crystals of heavy ice to form thus allowing the transport of the solid.

The need for a habit modifier caused the problem with the analysis. Density measurements are affected due to the low density (0.7893g/ml) of ethanol, thus a correction is necessary to obtain the density of the sample. The ethanol would of course be less in the pure product than in the feed or impure product due to its very low freezing point (-118°C) and its concentration would be determined by GLC analysis. To overcome this problem an infra-red technique was tried but in the range of concentration concerned (70 - 85% heavy water) the accuracy was approximately 3-4%. Eventually the accuracy of the density measurements was determined as 1-2% and this method was used to analyse the samples in the runs undertaken.

Although heavy ice is lighter than the mother liquor it was decided to transport crystals downwards since the desalination work had demonstrated that this method was to be preferred at all but the highest crystal rates and due to the expense of purchasing deuteruim oxide the loss of any material due to crystals leaving the column could not be tolerated.

The feed solution was made up as a 75% by wt heavy water, 25% by wt distilled water with 3% ethanol by wt added to the resultant mixture.

The effect of screw rotation speed was investigated over the region 50 to 120rpm to determine the optimum value.

More deuterium oxide was attained to allow for longer running times and it was decided to use 3% sodium chloride as habit modifier since this had less effect upon the density of aqueous solutions.

(vi) Ethanol concentration

The use of column crystallisation to raise the concentration of ethanol in water from fermentation levels (usually 9-12% by vol, but 18% by vol is possible) to spirit strength of 70° proof (32-33% by wt) or to fortified wine strength of 20-22% by vol for sherries, ports, etc. was investigated.

Absolute Ethanol, present to the extent of 3% by wt, was used as a crystal habit modifier in the deuterium oxide work. These runs had shown that concentration of the ethanol was possible and that a column assembly such that crystals were transported downwards was better than the converse - this being due to the low specific gravity of ethanol (0.7893g/ml) and its very low freezing point (-118°C) which causes the ethanol to remain liquid at the top of the column.

The concentration of industrial methylated spirits (IMS) in the initial runs undertaken was 20% by wt. Unfortunately, due to the anti-freeze affect of ethanol on water it was impossible to attain any significant concentration with the present refrigeration unit. Eventually 10% by wt IMS solutions in water were used for the investigations.

For this sytem the column was running in an opposite sense to usual. The concentrated ethanol product from the freezing section (top) end of the column would usually be the impure product due to its lower freezing point.

The form of ice crystals from ethanol/water solutions is the mushy, easily transportable type; the system was optimised for screw speed (50 - 100 rpm), effect of feed position, product removal ratio and crystal production rates.

(vii) Copper sulphate concentration from aqueous solution

This system can be considered from two points of view: the first is the environmentalists. If trade effluent high in metal salts is allowed to enter the water table, at some time it is likely to reach catchment areas and pollute drinking water. For this viewpoint it is necessary to column crystallise and produce large quantities of purer water the waste being of low volume and easily treatable. The other viewpoint is that of metal recovery. For this it is necessary to produce a high concentration of metal in solution. to allow for efficient removal from water (by high current density solid/liquid fluidised bed electrolysis for example). This means the product required would be that from the freezing section end of the column (top) and the waste would be a volume of water containing a concentration of metal salt at too low a concentration to allow for economic recovery.

Copper sulphate was chosen as the metal salt since it was cheap and readily available but application to other systems is possible.

Using optimisation data for aqueous systems already available the concentration of approximately 3% by wt copper sulphate (as $CuSO_4$ from $CuSO_4.5H_2O$) solutions in tap water was undertaken.

The first run was hindered by hard ice forming in the freezing section. However it was possible to concentrate the solution up to 11.5% $CuSO_4$ from

2.85% $CuSO_4$ collected at 200ml/hr from a feed rate of 860 ml/hr. Due to the transportation problem the crystallisation of copper sulphate solutions in water was investigated for the column system.

The first indication of blocking in the column was observed when the high copper product had a concentration of approximately 8% $CuSO_4$ by wt. A test solution of 8% $CuSO_4$ in tap water was rapidly frozen in a well stirred stainless steel beaker placed in the refrigerant tank. Hard ice formed round the sides of the beaker but none appeared in the bulk of the solution. This hard ice was difficult to move or break up.

Another solution of 5%$CuSO_4$ by wt was similarly treated. This time the ice formed mainly in the bulk solution and the ice on the walls was readily removed.

A 7% by wt sol^n was now similarly cooled. This time less ice formed in the bulk of the solution and the ice at the walls was more difficult to remove. This appears to be the limit of easily transportable crystals.

Next a 15% solution similarly treated formed crystals as in the 5% case but copper sulphate (as $CuSO_4 \cdot 5H_2O$) was present amongst the ice crystals but for a 10% solution the crystallisation was as for the 7% case.

The solubility limit of copper sulphate in aqueous solution at 0°C is 13.41% by wt. Thus for a 10% + solution of copper sulphate by wt freezing at approximately -1°C the $CuSO_4.5H_2O$ crystals may leave solution on cooling and present good nucleation sites for ice crystallisation. Up to 7% the ice from solution is also easily transportable but in the 8-9% region the crystals form as a hard mass on the walls of the containing vessel.

Using this nucleation data, further runs were attempted. However, blockages in the freezing section still occurred. After running the column jacket was removed. Under the freezing section the crystals were mushy and easily transportable, having a decreasing concentration of copper sulphate as the base of the column was approached. At the base of the freezing section hard ice was found but above this the ice was mushy, $CuSO_4.5H_2O$ crystals being present.

Attempts were made at solving this problem:

(a) the solutions in tap water allowed the precipitation of copper carbonate; perhaps this was fouling the ice lattice causing the blockages. Solutions were made up in distilled water to remove this problem but no improvement was observed.

(b) the solutions were made up in acid solution (pH1) since this had shown promise when crystallised in the stainless steel jug immersed in the refrigerant tank. However, no improvement occurred.

This problem of ice nucleation from copper sulphate solutions had not been solved but the possibility of significant concentrations was shown, allowing for economic recovery.

Benzene/cyclohexane (2nd set of runs)

Now that the column's operation had been significantly improved, the removal of cyclohexane from benzene/cyclohexane solutions was again undertaken. Optimisation of screw speed, feed position and products removal rates were varied using a 22300ppm cyclohexane in benzene solution. The effect of crystal rate and feed rate was investigated by using a 33000ppm cyclohexane in benzene solution.

All runs were undertaken with crystals trasnported downwards, under continuous operation with a column 93cm in length.

DISCUSSION (Note : Figs (23) to (43) may be found in appendix)

Analysis of results

Using Powers$^{(72, 73)}$ method of predicting concentration profiles for continuous column crystallisation, the effect of diffusion along the column and mass transfer between the adhering liquid and free liquid on the separation achieved was determined

Powers solution for the enriching section is given by eq$^{(47)}$

ie
$$\frac{Y-Yp}{Y_{\emptyset}-Yp} = \exp\frac{-(Z - Z_F)}{H} \qquad (47)$$

(Z being measured from the freezing jacket)

$$\text{where } H = \frac{1}{(C-Le)}\left[D\eta A\rho + \frac{\alpha(1+\alpha)\,C^2 - \alpha L_e C}{KaA\rho}\right] \qquad (48)$$

$$\text{and } Yp = \frac{C\varepsilon - LeYe}{C - Le} \qquad (41)$$

Now eq (47) may be rewritten:

$$\ln(Y - Yp) = \frac{-(Z - Z_F)}{H} + \ln(Y_{\emptyset} - Y_p)$$

which is the equation to a straight line on semi-log paper; the slope of which is -1/H

The values of H are determined along with a determination of the constants η , α , ρ and A. Several simultaneous equations can now be formed by fitting the values of crystal rate and base product rate into eq (48). By solving these simultaneous equations, values of D and Ka can be determined.

Alternatively eq (48) may be rewritten:

$$H(C - Le) = D\eta A\rho + \frac{\alpha(1 + \alpha)C^2 - \alpha LeC}{KaA\rho} \qquad (48)$$

By plotting H(C -Le) values against $\left(\frac{\alpha(1+\alpha)C^2 - \alpha LeC}{A\rho}\right)$ a straight line graph is obtained whose slope is $^1/_{Ka}$ and whose intercept is $D\eta A\rho$ which allows a determination of Ka and D.

Having established the values of D and Ka the theoretical values of H for different crystal rates and/or base product rates can be evaluated and fitted into equation (47). Now, theoretical plots of free liquid impurity concentration vs position in the column can be compared with the experimental values.

As an extension to Power's study if the value of H in eq (48) is differentiated with respect to C the theoretical optimum value of crystal rate for a constant base product take-off can be evaluated.

$$\text{ie}\quad \frac{dH}{dC} = \frac{1}{(C-Le)^2}\left[-D\eta A\rho + \frac{\alpha(1+\alpha)}{KaA\rho}(C^2 - 2CLe) + \frac{\alpha(Le)^2}{KaA\rho}\right] \quad (55)$$

But for a maximum or minimum value $\frac{dH}{dC} = 0$

$$\therefore\quad D\eta A\rho = \frac{\alpha(1+\alpha)\left[C^2 - 2C\,Le\right]}{KaA\rho} + \frac{\alpha(Le)^2}{KaA\rho} \quad (56)$$

which may be solved for C using the values of the constants determined and for the particular value of Le chosen ($Le \neq C$).

The double differential of eq (48) determines which value of crystal rate produces a minimum value of H (maximum separation) or a maximum value of H (minimum separation)

$$\text{Now}\quad \frac{d^2H}{dC^2} = \frac{1}{(C-Le)^3}\left[2D\eta A\rho + \frac{\alpha(1+\alpha)(2Le)^2}{KaA\rho} - \frac{2\alpha(Le)^2}{KaA\rho}\right] \quad (57)$$

and for a minimum value $\frac{d^2H}{dC^2}$ is positive and vice versa.

Most of the work involved in this project has been to maximise the potential of an existing column crystalliser. This optimisation procedure has led to the discovery and solution of unforseen problems. The systems investigated were:

(1) <u>Benzene/cyclohexane</u>

Benzene is commercially prepared by catalytically dehydrogenating cyclohexane using a platinum or palladium catalyst. Consequently the product contains some cyclohexane which must be removed if analar grade benzene is required. Pure benzene is required by the polymer industry as a solvent; it is also used as a raw material for the synthesis of dyes, explosives, medicinal and photographic chemicals and ultra-pure benzene is used in the analysis of meteorites, moon-rock etc. to determine the possibility of life outside the earth. Benzene has a melting point (5.5°C) very near to those of ambient temperatures so the power required for freezing is low and, moreover, the benzene crystals are easily nucleated in a form which facilitates transportation in a column crystalliser.

The disadvantages of investigating the purification of benzene are due to its toxic and inflammable nature. The former problem was largely overcome by placing curtains around three sides of the apparatus and employing an extractor fan to cause an updraught of air over the column length. The fire hazard is reduced since apart from the feed and products tanks which are covered the benzene exists as crystals or low temperature liquid.

The investigation of the reduction of cyclohexane in benzene was divided into two sections.

(i) These were the first experiments undertaken and most employed batchwise operation. Once optimisation of the column had been investigated under total reflux several continuous operation runs were attempted.

The major problem which had to be overcome was a constructional fault, ie the column support had not been vertically positioned, thus the jacket did not fit correctly over the screw. The resulting friction caused the results obtained to be poorer than expected, especially under continuous conditions. The other difficulty concerned the control of the cooling rate. If it was too high the column's freezing section would block with a plug of crystals but if high crystal rates were not attained the friction problem mentioned above caused poor separation in the column.

Although the difficulty in attaining and maintaining equilibrium in this set of experiments means that the results are unreliable they are included since they give a direct comparison with the second set of benzene/cyclohexane runs showing the improvement in the column operation during the course of the project.

Optimisation

(a) Screw speed

For both column attitudes (crystals

transported downwards and upwards), the screw speed was varied from 60 to 100 rpm in 20 rpm steps. The concentration of cyclohexane at the melting section extremity of the column was determined. For both cases 80 rpm produced the purest benzene after transportation along the column.

(b) Column length

For crystals transported downwards the purification section length was varied (17, 24, 31, and 40 cm) with a constant length for the freezing and melting sections and screw speed of 80 rpm. It was determined that the longer the purification section length the better the separation achieved although as the length increased the returns became less (ie an asymptotic value of concentration would be reached as the length is increased towards infinity).

(ii) For the second set of runs the column's operation had been fully maximised and a complete analysis of the enriching section was undertaken. For crystals transported downwards under continuous operation.

Using equations (47) and (48) and a graphical solution of D and Ka the value of the diffusion coefficient was determined as 0.56 $cm^2\ sec^{-1}$ and the overall mass transfer coefficient as 1.67 x $10^{-3}\ sec^{-1}$. For the values of crystal production rates investigated these values are such that the diffusion term is approximately twice as important as the overall mass transfer factor in determining the concentration of the free liquid in the column. This means that successful operation of the column requires the minimising of cyclohexane diffusion down the column while maintaining the mass transfer of cyclohexane from the adhering liquid to the free liquid by washing.

Optimisation

(a) Screw speed (see fig (23))

From the values of D and Ka above it is seen that a compromise will be required. Diffusion is decreased if agitation (and hence screw speed) is lower but this adversely affects the mass transfer coefficient. The optimimum speed of rotation of the screw was determined as 60 rpm which gives a crystal transportation rate of one inch per sec assuming negligible frictional, drag or bouyancy forces.

(b) Feed position

The effect of the feed position on the base product purity is shown in fig (24). This is optimal for a position closest to the freezing jacket. As the freezing jacket is reached the separation achieved reaches an asymptotic value and feed into the freezing jacket would be unlikely to improve the purity of the base product. This is explained by consideration of equation (47). Ye depends upon $e^{-(Z - Z_F)}$ for constant value of H. Therefore as Z_F

increases Ye increases but the exponential form of the equation ensures that Ye will not reach zero.

(c) Products removal ratio

Consideration of equation (48) shows that as the value of C-Le is decreased then H increases and therefore if the pure (base) product removal rate is increased the product purity is decreased. However, as seen in fig (25) for a feed rate of 1200ml/hr, base product rates of 500-600 ml/hr give purities which are only marginally improved upon decreasing the pure product flows even further. This can be explained by examination of equation (47). Here the product purity is dependent upon the exponent of $^1/H$ and as H decreases the value of Ye may not decrease correspondingly.

(d) Crystal rate (see fig 26)

The theoretical optimum value of crystal rate may be determined upon differentiation of equation (48). For a value of base product removal rate (Le) of 0.268g/sec the optimal value of C is 0.695g/sec. Attempts to reach this value experimentally were unsuccessful since the freezing section blocked at a crystal rate of 0.542g/sec.

(e) Feed rate

After optimisation of the column the feed rate was increased to 3.08 litres/hr to study the effect of higher flow rates on the product purity. The residence time of any liquid in the feed line was now less than 20 minutes. Providing the Le/C rates can be maintained column operation should not be adversely affected. It was found in fact that a slight decrease in separation occurred probably due to some crystals being carried out of the column in the stripped product stream due to the high flow rate.

2. Desalination

The need for a desalination programme in all industrial and developing countries is becoming increasingly important. Research to find the most economical method of potable water production has shown that for sea water strength brine solutions freezing techniques are the most viable. Sea water contains 3.5 to 3.6% solids by wt for the most part of which sodium chloride makes up approximately 85% of the TDS, however, since a readily available supply of sea water was not available a 3.5% sodium chloride solution in tap water was used as a substitute.

The concentrated sea-water removed as waste product from a crystalliser can in fact be a useful side product. The extraction of bromine and iodine is possible, electrolysis to form sodium hydroxide can be undertaken and the extraction of metals is made more economically viable.

The examination of this system presented a major problem and on solution an important design factor. The difficulty lay in the facilitation of crystal transport. Although, at start-up of continuous running, sufficient, easily transportable crystals were formed, as operation continued the movement of crystals subsided and eventually the freezing section blocked. On removal of the column jacket hard, glass-like ice would be found on the screw at the position of the freezing section. This was found to be due to the nature of the inner wall of the freezing section. This had been left unpolished to aid nucleation but the friction thus caused allowed the crystals to remain in the freezing section by moving back along the screw as the rotation tended to remove them. The crystals eventually formed a hard, glass-like ice collar round the annular space and blocked the column. By polishing the inner wall of the freezing section to a mirror finish the problem was overcome and crystal transport was easily facilitated.

The operation of the column for desalination is conveniently separated into two sections

(i) <u>Before the freezing section was polished</u>

For these runs it was difficult to operate the column for long enough to reach equilibrium. Optimisation was not possible but the problems encountered allowed the subsequent marked improvement in column operation.

(ii) <u>After polishing the inner wall of the freezing section</u>

The values of the diffusion coefficient (D) and the overall mass transfer coefficient (Ka) were determined by solving the simultaneous equations obtained from the experimental plots of ln (Y-Yp) VS $(Z - Z_F)$ and an estimation of the constants η, A, ρ and α

The values of the diffusion and overall mass transfer coefficients obtained at screw speeds of 60 and 100 rpm are tabulated below:

<u>Table 1</u>

Crystal Transport	Screw Speed (rpm)	$D(cm^2 sec^{-1})$	$Ka(sec^{-1})$
Down	60	0.16	5.56×10^{-4}
Down	100	1.63×10^{-2}	5.93×10^{-5}
Up	100	1.96×10^{-2}	7.16×10^{-5}

At 60rpm the values of the diffusion and overall mass transfer coefficients are such that for the crystal rates measured, D is two to four times more important than Ka. This implies that diffusion down the column will be more noticeable than mass transfer upon separation achieved but it is not dominant in controlling the column operation.

Both coefficients are seen to be lower at 100rpm than at 60 rpm whereas the opposite should be true. However, increasing the screw speed decreases the size of the crystals, allowing poor resistance to crystal caking. This effect was, in fact, observed several times during column operation when using a perspex purification section. If the crystals agglomerate they will not allow easy washing of the adhering liquid (hence a low value of Ka) and diffusion along the column will be come diminished (hence a low value of D)

As can be seen the diffusion and overall mass transfer coefficients at 100 rpm (especially D, the diffusion coefficient) are similar. Now, for the crystal rates measured the column's operation was more efficient for crystals transported downwards whereas the value of the overall mass transfer coefficient is lower in this case. However, the value of Ka is so low for both modes of operation that this effect will be negligible.

The theoretical value of the maximum crystal rate for optimum separation was determined by differentiation of eq (48).

Values of these crystal rates are tabulated below:

Table 2

Crystal Transport	Screw Speed(rpm)	C.(g/sec)
Down	60	0.330
Down	100	0.202
Up	100	0.205

Now, the value of the theoretical optimum crystal rate is larger for a 60 rpm than for a 100 rpm screw speed. This is caused by the greater effect of diffusion on the separation achieved for the lower speed. The form of eq (48) shows that in determining the value of H, the effects of raising the value of C on $\frac{D\eta A\rho}{(C-Le)}$ and $\frac{\alpha(1+\alpha)C^2 - \alpha LeC}{(C-Le)KaA\rho}$ must be considered. For the diffusion term, if D is large then C must increase a considerable amount until the effect of C^2 increases the value of the mass transfer function of the equation to produce the minimum value of H.

The higher value of C obtained for 60 rpm means that the value of H obtained will be lower than for 100 rpm and hence the separation achieved will be superior.

At 100 rpm the values of optimum crystal rates are similar, suggesting that both modes of operation become equally efficient when this value of crystal rate is approached.

Optimisation

(a) Screw Speed

The first set of desalination runs had

suggested that 80 rpm was the optimum speed of rotation of the transportation screw but for the set of runs with a mirror finish polish on the inner wall of the freezing section the maximum separation was achieved at 60 rpm. This difference is possibly due to the poor crystal transport afforded by the rough surface of the freezing section. An increased speed allowed more crystals to be removed from that section thus allowinga better separation.

Bolsaitis(25) has said that as screw speed is decreased, column efficiency increases due to the larger crystals produced. However, as the screw speed is decreased the washing of the adhering liquid by the free liquid is adversely affected due to the lower agitation. The separation achieved is also dependent on the diffusion of sodium chloride down the column; this will be lower for decreased agitation thus improving the separation. However, for desalination the value of the diffusion coefficient is so low that the diffusion effect can be neglected.

The effects of screw speed need to be balanced in order to achieve the optimal separation. Fig (29) shows the effect of screw speed on the purity of the enriched product.

(b) Attitude of the column

This has already been discussed with regard to the mathematical treatment (page 130). From a physical point of view the increase in separation achieved with crystals transported downwards can be described by considering the washing action of the free liquid. For crystals transported upwards the melt water simply percolates back down the column under the action of gravity and the crystals due to their low relative density position themselves at the top of the screw's flights whereas the wash liquid runs down the bottom of the flight. However, for crystals transported downwards it is possible to build up a pressure (3 - 5 p sig) due to the head of liquid and the crystals reaching the base of the column. This forces the melted liquid back up the column causing a more searching washing action.

(c) Feed Position

The best position found for introducing the feed to the column was determined as being as close to the freezing jacket as possible. It is even possible that feed into the freezing jacket would improve the separation further but this effect could not be evaluated by using the present apparatus. From equation (47)

$$\text{ie } \frac{Y - Yp}{Y\phi - Yp} = \exp \frac{-(Z - Z_F)}{H}$$

it is seen that as Z_F is increased the value of the exponential factor $(Z - Z_F)$ decreases, hence the exponent increases and Y increases. If Z_F becomes negative, corresponding to feed into the freezing section, $Z - Z_F$ increases and Y becomes smaller. However, it is assumed that a sharp change in parameters is experienced at the intersection of the enriching and stripping section thus the improvement in separation by feeding into freezing section may not occur experimentally.

More simply, the amount of washing is decreased due to the shortening of the purification section as the feed is moved away from the freezing jacket and thus the separation is adversely affected. The effect of feed position on the pure product is shown by fig (30).

(d) Ratio of products removal - see fig (31)

Since the concentration of sodium chloride in the pure product is largely dependent on the impure liquid associated with the crystal, a decrease in the impurity concentration in that liquid should increase the separation achieved. Now, the crystals are formed in the freezing section and the concentration of impurity in that area is determined by flow rate and impurity content of the feed and reflux liquid entering. Since the feed concentration and rate are fixed for any run and for good separation the reflux liquid concentration should be low (it then removes much of the impurity from the adhering liquid), the impurity in the freezing section must be decreased by increasing the flow rate of the reflux liquid. This means that the flow rate of the enriched product will be low but due to the high reflux ratio and the decreased sodium chloride content in the adhering liquid the impurity concentration of this pure product should be low. However, this approach leads to the condition where very pure base product is obtained but at such a low flow rate that returns are minimal. It is, therefore, necessary to compromise on the requirements and obtain a reasonable flow rate of fairly pure water.

(e) Crystal rate - see fig (32)

Optimisation of this variable has already been discussed but the effect of crystal rate for all normal values can be examined by consideration of equation (48)

ie $$H = \frac{1}{(C-Le)}\left[D\eta A\rho + \frac{\alpha(1+\alpha)C^2 - \alpha LeC}{KaA\rho} \right]$$

For a constant value of Le, as C is increased the value of $^1/(C-Le)$ decreases whereas the mass transfer function $(\alpha(1+\alpha)C^2 - \alpha LeC)/KaA\rho$ increases. Thus at low crystal rates diffusion may be important in determining the separation obtained but as C is increased mass transfer becomes more and more dominant. Therefore, an increase in crystal rate will improve the purification although experimentally, the theoretical optimum crystal rate was not attained due to blockages in the freezing section.

(f) Column Length

As seen in fig (33) decreasing the length of the purification section produces a less pure enriched product. This effect is similar to that of moving the feed position away from the freezing section when the washing action of the free liquid is decreased. Consideration of equation (47) explains this effect:

$$\text{ie } \frac{Y - Yp}{Y\emptyset - Yp} = \exp^{-\frac{(Z - Z_F)}{H}} \qquad (47)$$

Now a decrease in the column length decreases the value of Z. Therefore, $(Z - Z_F)$ is decreased and Y increases.

(g) Effect of oscillations

Attempts to improve the washing action of the free liquid by oscillating the screw or by pulsing the liquid in the column proved fruitless. The mechanical oscillation of the screw through 6mm, 104 times per minute (the lowest amount possible) adversely affected the column equilibrium to such an extent that the separation achieved was negated by the increase in the diffusion of sodium chloride down the column. Oscillating the liquid in the column by using a displacement pump afforded an improvement over mechanical oscillation of the screw but the diffusional effect was still so greatly increased that any improvement in washing was masked. Concentration profiles for operation with and without oscillations for a 60 rpm screw speed are shown in fig (34).

(3) Ethanol Concentration

Except in Germany, only a small amount of pure ethanol is produced by concentrating the alcohol formed in the fermentation process; production from ethylene is more economic. However, the distillation of fermented liquours to produce spirits is a thriving industry.

Distillation is the common method of producing these alcoholic spirits but freezing processes should produce more economic products. Since 9-12% by vol ethanol is normal for fermented liquours, the freezing point will be close to ambient (-3 to -5°C). Freezing processes also have the advantage that flavours which are often destroyed by boiling can be retained.

Communication with M Dupuy at the Institut National de la Recherche Agronomique shows us that they in fact use a batch freezing process where the concentrated wine/ice slurry is placed on a perforated disc filter, the concentrated wine being drawn off the other side by vacuum.

Since industrial methylated spirits are a cheap readily available, source of ethanol, solutions were made up in water and used as test liquids.

Experimental work on the concentration of ethanol required. an analysis of the stripping section since the ethanol-rich product would be that from the top of the column for crystals transported downwards. Unfortunately, due to the design of the freezing section, the only concentrations measurable were the top product and the concentration of liquid entering the stripping section. However, since the theoretical analysis is derived from four different crystal rates, this is equivalent to eight experimental readings.

The form of the concentration profile for the stripping section is given by:

$$\frac{Y - \bar{Y}_p}{Y_\phi - \bar{Y}_p} = e^{\frac{-(Z - Z_F)}{\bar{H}}} \qquad (51)$$

which suggests that $\bar{H}$ should be large for a corresponding large value of Y.

$$\text{Where } \bar{H} = \frac{1}{(C+L_s)} \left[D\eta A\rho + \frac{\alpha(1+\alpha)C^2 + \alpha L_s C}{K_a A\rho} \right] \qquad (53)$$

As differentiation of this equation shows, $\bar{H}$ only reaches a minimum as C is increased. Therefore the separation never reaches a maximum as the cooling rate is increased. The values of D and Ka were determined by solving the simultaneous equations produced by the four different crystal rates for a constant stripping section product rate.

The value of Ka was determined as 0.74×10^{-3} sec^{-1}

and D was determined as 1.24 cm^2 sec^{-1}

This means that the diffusion along the column and mass transfer between the adhering and free liquids are both important in determining the value of the separation factor $\bar{H}$ for all the crystal rates measured. Provided that $Y_\emptyset$ is known, the values of the diffusion coefficient and overall mass transfer coefficients can be used to predict the concentration of ethanol in the top product for crystals transported downwards.

Optimisation

(a) Screwspeed

As seen in fig (39) the best screw speed for maximum separation was 60 rpm. For the crystal rates measured, the diffusion coefficient was approximately as important as the mass transfer coefficient in determining the separation achieved. Since a high concentration of ethanol in the stripped stream depends upon the concentration of the liquid entering the stripping section a low screw speed is required to diminish the diffusion effects in the enriching section although too low a speed will decrease washing to such an extent that no removal of ethanol from the adhering liquid by the free liquid will occur. fig (33) shows that 60 rpm is the optimal balance between these two opposing effects.

(b) Feed position

Fig (40) shows the effect of feed position on the concentration of ethanol in the top product. It can be readily observed that a position closest to the freezing section is favoured and that feed actually in the freezing section may further enhance the separation. Although, this may appear contradictory (ie a shorter length of stripping section providing an improved concentration of ethanol), it should be remembered that the concentration of the ethanol in the freezing section can only effectively be improved by removing the ethanol in the adhering liquid, which requires a long washing section.

(c) Products ratio - see Fig (41)

The enrichment of ethanol in the stripping section requires a high concentration of ethanol as feed to that section. Feed rate and concentration to the column are constant for any run therefore a low flow rate of highly concentrated reflux liquid into the freezing section will markedly improve the column performance. Thus a high enriched product flow rate with a moderate concentration of ethanol will yield optimal stripped product. However, if the requirement is to remove most of the ethanol from the enriched product, that product rate must be decreased causing the concentration of ethanol in the stripped product to be adversely affected.

(d) Effect of crystal rate

From equation (53) $\left[\overline{H} = \frac{D\eta A\rho}{(C+Ls)} + \frac{\alpha(1+\alpha)C^2+\alpha L_s C}{KaA\rho(C+Ls)}\right]$ it can be seen that as C is increased for a constant value of Ls, the factor (C+Ls) increases and thus $D\eta A\rho/(C + Ls)$ decreases whereas $(C^2(1+\alpha)\alpha + \alpha CLs)/KaA\rho(C+Ls)$ increases - these two effects being in opposition. Now, for a high concentration of ethanol in the stripped stream, $\overline{H}$ must be large since then the value of the exponent in equation (51) is small and negative which produces a high value of Y. Therefore, as a maximum separation is never reached as the crystal rate rises so the mass transfer effect must be raised to a greater extent and the diffusion effect is decreased for all crystal production rates.

Since the maximum crystal rate attained experimentally was 0.239g/sec, due to the inability of the present refrigerator to maintain higher values, a full assessment of the effect of increasing the crystal rate could not be made. However, considering fig (42) which shows the effect of crystal rate on the stripped product ethanol concentration, it can be seen that increasing the crystal rate up to 0.239g/sec does improve the separation although the curve begins to level off at higher production rates.

(e) Effect of column attitude

Since ethanol was used as a crystal habit modifier for the deuteruim oxide experiments, an assessment of ethanol concentration with crystals transported downwards or upwards was possible. Ethanol is less dense than water, thus it would be expected to migrate to the top of the column when the water fraction freezes. This suggests that ethanol concentration should be easier for crystals transported downwards than for the converse, as was discovered in practice.

(4) Deuterium oxide Concentration

Power requirements in the industrialised countries increase rapidly with population increase. Traditionally man has produced power by burning, in ancient times wood and dried grass but with dawning of the Industrial Revolution, coal and oil were discovered. These provided a greatly improved source of energy and allowed the massive industrialisation to continue. However, these resources took millions of years to develop and man is rapidly consuming them in hundreds of years. This fact, plus the economic blow to the industrial nations of the oil-crisis in 1974, gave new life to the processes of nuclear fission and fusion as energy sources.

The use of deuterium oxide as a moderator in nuclear fission reactors will greatly increase the requirements for pure heavy water when the British government's plans to build the next generation of stations are realised.

Deuterium oxide is also a source of deuterium which is required in fusion research. At present the only economical process requires the fusion of a deuterium ion with a tritium ion, this reaction being some one hundred times faster than the deuterium ion - deuterium ion fusion reaction.

The experimental work on concentration of deuterium oxide was hindered by two major problems. The first difficulty concerned the analysis of samples obtained (discussed in the experimental section).

The other problem is caused by the form of the crystals obtained. Pure water and heavy water nucleate as needle-like crystals and in order to produce transportable ice it was necessary to use a habit modifier. This difficulty of transporting needle-like crystals is discussed more fully in the conclusions.

Using a solution of heavy water/water containing 3% by wt ethanol satisfactory nucleation occurred and the system was optimised for screw speed. Attempts to continue the optimisation were not successful due to the very small volume of deuterium oxide available; earlier, infra-red sampling had not allowed re-use of the samples and on one occasion due to excessive cooling the freezing section blocked causing the feed-line to break with the subsequent loss of feed solution. With small volumes of feed material available the stripped product would return to the feed tank in a diluted state before the crystals reached the base of the column (for crystals transported downwards) and thus the feed solution would be diluted.

A mathematical analysis of the system was not possible since sampling was confined to the enriched and stripped product in order to conserve the feed material but the optimum screw speed was determined as being 60 rpm (see fig 43). Although the results obtained are not conclusive they had demonstrated the possibility of using continuous column crystallisation in the concentration of deuterium oxide.

(5) Separation of p-xylene from its isomers

Ortho, meta and para xylene plus ethyl benzene distill together from the light oil fraction of coal tar. Thus, the xylene isomers are an obvious choice for separation by freezing, since their boiling points are so close together making distillation prohibitively expensive. However, their freezing points are markedly separate, p-xylene freezing at +13.2°C, thus continuous column crystallisation to produce an enriched p-xylene product is an economically viable proposition. Para-xylene on oxidation yields p-toluic acid, then terephthalic acid is formed, the latter being employed in the production of such synthetic fibres as 'Terylene'.

Unfortunately, the investigation of this system produced no results but confirmed the inability of transporting needle-like crystals. McKay(93) has also found that p-xylene crystallises in the form of needles for pilot-plant apparatus although for commercial sized equipment the crystal shape is markedly different. The effect of crystal shape on transportation by Archimedean screw conveyors is more fully discussed in the conclusion.

(6) Concentration of metal salts in aqueous solution

As resources are rapidly being consumed by our technological society, eventually a point is reached where recovery of metals be comes an economical consideration.

In the electrical and electronic industry copper is etched from laminates to form printed circuits. This process often removed 60% or more of the original copper, thus any process facilitating the recovery would be useful.

Now, the extraction of metals from solution becomes more economical with increasing concentration, the use of continuous column crystallisation was applied to the concentration of copper sulphate in aqueous solution.

Using the optimisation data available from previous work, 3% $CuSO_4$ (from $CuSO_4\ 5H_2O$) by wt solutions in water were column crystallised.

At first the solutions were made up in tap water. The column ran successfully for one hour but then blocked. This was thought to be due to the precipitation of copper carbonate which had affected the previously good crystal nucleation. Subsequently solutions were made up in distilled water but again operation became impossible after one hours running. On removal of the column jacket, samples of the ice were removed for analysis at known points up the column. Hard, glass-like ice was found in the lower half of the freezing section (concentration of copper sulphate 8%). Above this was 'mushy' ice containing $CuSO_4 \cdot 5H_2O$ crystals. Experiments were continued outside the column, cooling test solutions in a stainless steel beaker with constant agitation. The concentration of copper sulphate at which hard-ice formed was found to be 8 - 9 % and at this point nucleation was in the form of needle-like crystals which very quickly agglomerated to form a glass-like mass. The effect of needle-like crystals had by now become well documented but attempts to overcome the problem were not successful. However, the results obtained after one hours operation show the considerable concentration of copper sulphate in the aqueous solution that can be obtained and give a pointer to the application of column crystallisation to concentration of metal salts in solution. With more time available a suitable crystal habit modifier could be discovered to overcome any problems. Further discussion of the difficulty encountered with needle-like crystals is to be found in the conclusions.

CONCLUSIONS

The experimental work undertaken in this study has demonstrated the characteristic operating conditions for optimisation of the column employed. For the various systems investigated, including aqueous solutions, organic mixtures and combined organic/aqueous liquids and both for stripped and/or enriched stream as the desired product, the operating conditions are similar for the attainment of maximum separation.

An analysis of the separation in the column using a mathematical model affords a basis for confirming the experimental conditions required for efficient operation.

The conditions, for a column with an available volume of 1020ml, total volume of 1830 ml and a length to diameter ratio of 18.6 are:

1. Screw Speed

For every system studied, variation of the speed of the transportation screw from 53 to 100 or 140 rpm demonstrated that 60 rpm allowed for maximum purification in this column.

According to the model of the column, back diffusion of impurity along the column and mass transfer of impurity from the adhering liquid to the wash liquid are the important factors governing the separation. For every system, with a 60 rpm screw speed the diffusional effect was more important than, though not dominant over, mass transfer in determining the separation achieved until the crystal rate is increased to approach its theoretical maximum. This indicates that for normal crystal rates the washing of the adhering liquid is efficient but this affect will be reduced, by decreasing the agitation in the column. However, the diffusion factor is adversely affected by increasing the agitation in the column, therefore the separation achieved will be decreased by raising the screw speed. Bolsaitis(25) has also demonstrated that better separations are achieved by producing larger crystals. These large crystals can be formed by lowering the screw speed, the improved column efficiency being caused by a decrease in the number of crystals removed from the freezing section by the stripped product. The removal of crystals by the stripped product was observed in this study only when high flow rates were employed.

At 60 rpm a compromise between diffusional, mass transfer and crystal size considerations is attained and the column operation is optimised. The variation of separation power of the column is most easily explained by considering the changes in the dominance of diffusional and mass transfer effects in determining the value of the separation factor (H or $\overline{H}$).

A study of fig (29) demonstrates the mechanisms at work. For areas where the slope is negative increasing the screw speed enhances the washing action more than it raises the diffusion of impurity along the column. At zero slope the two effects are balanced and for positive slope diffusional effects are most important.

2. Feed Position

A position close to the freezing jacket produces a better separation for both enriched and/or stripped streams as the required product. For ethanol concentration and desalination, feeding into the freezing section may further improve the efficiency, though for benzene purification the separation reaches an asymptotic value at the freezing jacket.

Consideration of equations (47) and (51) demonstrate the effect of this parameter mathematically:

ie $$\frac{Y - Yp}{Y_0 - Yp} = \exp\frac{-(Z-Z_F)}{H} \qquad (47)$$

and $$\frac{Y - \overline{Y}p}{Y_0 - \overline{Y}p} = \exp\frac{-(Z-Z_F)}{\overline{H}} \qquad (51)$$

For a constant value of Z and H or $\overline{H}$ on the RHS of these equations, increasing Z_F (measured from the freezing jacket along the column) affects $(Z - Z_F)$. For the enriching section Z and Z_F are positive values. Now, a large negative value of the exponent produces a small value of Y; thus Z_F should be as small as possible to produce an optimal separation. In equation (51) the value of Z is positive but Z_F since it is positioned in the enriching section is negative. For efficient concentration of the desired substance we require a large value of Y. Therefore a smaller negative value of the exponent is required, this being achieved by placing the feed point as close to the freezing section as possible. It may appear contradictory that a shorter stripping section is more efficient but it must be remembered that effective stripping can only occur when the washing in the enriching section is optimal, thus requiring a long purification section.

3. Ratio of Products Removal

Since an overall balance over the column gives:

$$F = Le + Ls \qquad (58)$$

For a constant feed flow rate if Le is decreased Ls must increase.

Now, if Le is decreased the ratio Le/C is lowered ie the amount of melted crystals returned to the column as reflux is enlarged. The presence in the column of increasing amounts of free liquid improves the washing of the adhering liquid and hence the separation achieved in the enriching section.

If, however, the stripped stream is the product required, as in the case of ethanol concentration, the purpose of the reflux liquid is to present as high as possible a concentration of ethanol in the liquid entering the freezing section. To achieve this, the wash liquid should be allowed to exchange with the adhering liquid for as long a time as possible, ie a low flow rate of free liquid along the column is required. This aim may be achieved if the value of Le/C is high; ie most of the melted crystals are removed as the enriched section product.

Generally, it can be stated that decreasing the stream rate of the desired product will increase its purity (for enriched product) or concentration (for stripped product). Mathematically, this concept is most easily explained by examination of equations (48) and (53).

$$\text{ie} \quad H = \frac{1}{(C-Le)}\left[D\eta A\rho + \frac{\alpha(1+\alpha)C^2 - \alpha LeC}{KaA\rho} \right] \quad (48)$$

$$\text{and} \quad \overline{H} = \frac{1}{(C+Ls)}\left[D\eta A\rho + \frac{\alpha(1+\alpha)C^2 + \alpha LsC}{KaA\rho} \right] \quad (53)$$

In equation (48) if Le is decreased for all other factors on the RHS constant, the function 1/(C-Le) is decreased and H becomes smaller which improves the purity in the enriched product. However, decreasing Le increases the mass transfer function which enlarges the value of H. These two effects are in opposition to each other but the value of H is more dependent upon the former. The presence of the group LeC does however, demonstrate the possibility that decreasing the removal rate of the enriched product will eventually lead to little increase in the purity of that stream.

Similarly, in eq (53) if Ls is decreased $^1/(C+Ls)$ increases and the mass transfer factor is decreased, the former effect being dominant. Now, a larger value of $\overline{H}$ produces a higher concentration of the desired substance in the stripped stream and, hence a more effective separation.

For total reflux (batchwise) operation, the values of Ls and Le are zero. For a zero value of Ls then, the concentration of impurity in the stripping section will be a maximum. This implies that the adhering liquid will have a high concentration of impurity and the separating power of the column will be reduced compared to continuous flow operation.

(4) Effect of Crystal Rate

Increasing the rate at which crystals are produced in the freezing section should increase the possible separation and purification in the column.

Consideration of equations (48) and (53) demonstrates the effect of raising the crystal production rate which is similar to reducing the product stream rate concerned.

(i) For the enriching section

The separation factor, H, is decreased if C is increased since $^1/(C-Le)$ becomes smaller; however, the mass transfer function $(\alpha(1+\alpha)C^2 - \alpha LeC)$ increases as C becomes larger due to the squaring of the crystal rate. Thus, as the crystal rate becomes larger separation increases until a maximum purification is attained when the two opposing effects mentioned above cancel each other out. The optimum crystal rate is determined by differentiation of equation (48) and solving for C

ie
$$\left[-D\eta A\rho + \frac{\alpha(Le)^2}{KaA\rho}\right] - \frac{2\alpha(1+\alpha)LeC}{KaA\rho} + \frac{\alpha(1+\alpha)C^2}{KaA\rho} = 0 \qquad (56)$$

For all the systems investigated, increasing the crystal rate in fact increased the separation since the theoretical maximum value was not surpassed. For most cases the freezing section would block with crystals at values below the optima.

The physical reason for an optimum crystal rate above which separation is decreased can be explained by considering the crystal slurry. Efficient operation of the column requires effective washing of the adhering liquid by the reflux liquid. As increasing amounts of crystals are transported down the column any free spaces are consumed and the reflux liquid can no longer penetrate the crystal mass. The adhering liquid within the slurry can no longer be washed and thus separation will be decreased.

(ii) For the stripping section

If C increases $1/(C + Ls)$ decreases and the separation is adversely affected whereas the factor $(\alpha(1 + \alpha)C^2 + \alpha LsC)$ increases causing a subsequent increase in $\overline{H}$. As the crystal production rate is increased these two effects act in opposition to each other but for all rates, increased crystal production raises the value of $\overline{H}$ and hence the concentration of the desired substance in the stripped stream is raised. An examination of eq (53) allows an explanation of this phenomenon. Differentiation of $\overline{H}$ with respect of C allows a determination of the minimum value of $\overline{H}$ only (the other root being negative) which suggests that the slope of the separation factor ($\overline{H}$) against crystal rate never becomes negative as the cooling to the column is increased.

5. The effect of the length of the purification section

As would be expected, increasing the length of the purification section will increase the purity in the enriched product and the concentration in the stripped product, providing that the effects of increased heat input due to friction of the screw on the column jacket and from the column's environment can be neglected.

The greater amount of washing which can occur with a longer purification section and the increased length over which diffusion of impurity must travel suggest that column efficiency should be further enhanced by continuing to lengthen the column.

Examination of the equations$^{(47)}$ and $^{(51)}$ predicting the concentration profile over the length of the column show, however, that due to the exponential nature of the profiles, increasing the column length over a certain value will produce diminished returns. The present study shows that, for most cases, increasing the enriching section length from 50 to 60 cm produces only a marginally increased purity and further lengthening of the column would only produce a more expensive product.

6. Effect of oscillation

Mass transfer between the adhering liquid and free liquid is poor for desalination, especially at a 100 rpm screw speed. The effect of oscillations is purported to prevent the coalescence of adhering liquid films, thus presenting an increased interfacial mass transfer surface, furthering the analogy between column crystallisation and packed extraction columns.

However, these oscillations increase the mixing of the liquid in the column to such an extent that any increase in the washing action is negated by the facilitation of diffusion of impurity along the column.

Powers and co-workers(1, 61, 72) pulsed their column in experiments to reduce the concentration of cyclohexane in benzene. They obtained larger values of the diffusion coefficient than the present study (1.3 - 1.7(61), cf 0.56) although their mass transfer factor (Ka) was increased to 3.0 $(x\ 10^{-3})^{*}$(61) for 67 oscillations/minute through 1mm of travel (cf 1.67). Since Powers etal(1, 61, 72) report that the diffusion of cyclohexane along the column is dominant in deciding the separation attained whereas mass transfer occurs with little difficulty, it would seem reasonable to suggest that increasing the oscillations either in their number/minute or their amplitude would adversely affect the column's operation. This was in fact demonstrated in references (1) and (61).

Where an annular cross section of the column is small, the adhering liquid can be adequately washed by the reflux liquid simply by the agitation produced by rotating the conveyor. However, as shown by preliminary experiments with a column having an annular cross section 7 to 8 times larger than for this study, liquid oscillations (caused by displacement pump with its output and input connected to a T-piece which enters the base of the column) may well enhance column efficiency.

*Estimated using the value of 'a' given by Albertins(1).

7. Effect of column attitude

Even for systems where the crystals formed were less dense then the mother liquor, eg desalination, operating the column with crystals transported downwards is a marked improvement over the reverse process.

Fig (30) shows that for desalination until high crystal rates are attained, the separation achieved by transporting crystals upwards is poorer than for the downwards mode of operation. The ability to concentrate ethanol in aqueous solution is seen by reference to table (8) page (220) to be suitably enhanced when ice crystals are transported downwards.

This effect cannot be explained by consideration of the mathematical model unless one accepts the premise that washing of the adhering liquid by the free liquid is more effective when crystals are trasnported downwards. The pressure built up by crystals reaching the base of the column allows a more searching washing action and the fact that less heating is required to ensure that crystals do not leave the column (which is possible if crystals are transported upwards) present better conditions for separation and purification.

8. Effect of crystal shape

The shape of crystals produced in the freezing section is of paramount importance.

The needle-like crystals produced when

(i) p-xylene freezes from a mixture of its isomers

(ii) deuterium oxide ice freezes from a mixture of heavy and light water

(iii) paraffin wax crystals separate from a mixture of paraffin waxes(13)

cannot be easily transported by using an Archimedean screw conveyor. This is caused by the tendency of this type of crystal to agglomerate into one fixed mass of glass-like consistency which forms a collar round the conveyor in the freezing section eventually causing blockage of that section. This presents a limitation upon column crystallisers of the Schildknecht type which can only be overcome by finding convenient crystal habit modifiers (eg ethanol or sodium chloride added to heavy water).

The small irregular crystals formed by high screw speeds (eg desalination at 100 rpm) also have a greater chance of agglomerating. For this case the freezing section will block only at very high crystal rates when a glass-like collar of crystals forms in the freezing section but at lower crystal rates, although transportation is possible, the crystals still agglomerate, preventing the effective washing of the adhering liquid and decreasing diffusion along the column.

The crystal 'mushes' produced when

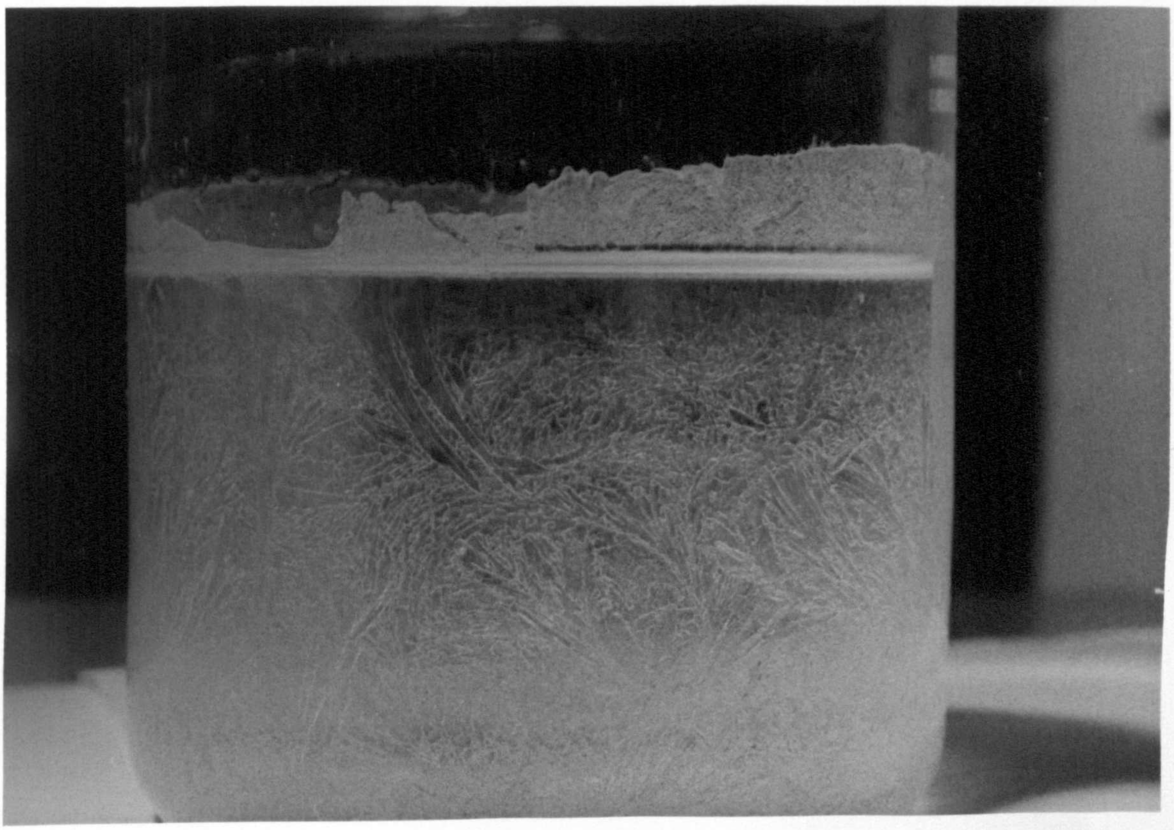
(i) Brine solutions were frozen at 60 rpm screw speed

(ii) Ethanol/water and Ethanol/heavy water solutions were frozen.

(iii) 3% cyclohexane by wt in Benzene solutions were frozen.

were easily transportable and allowed good separation and purification to be obtained. Obviously then, this is the type of crystal slurry to form if efficient column operation is to be achieved.

a) Non-transportable crystals.

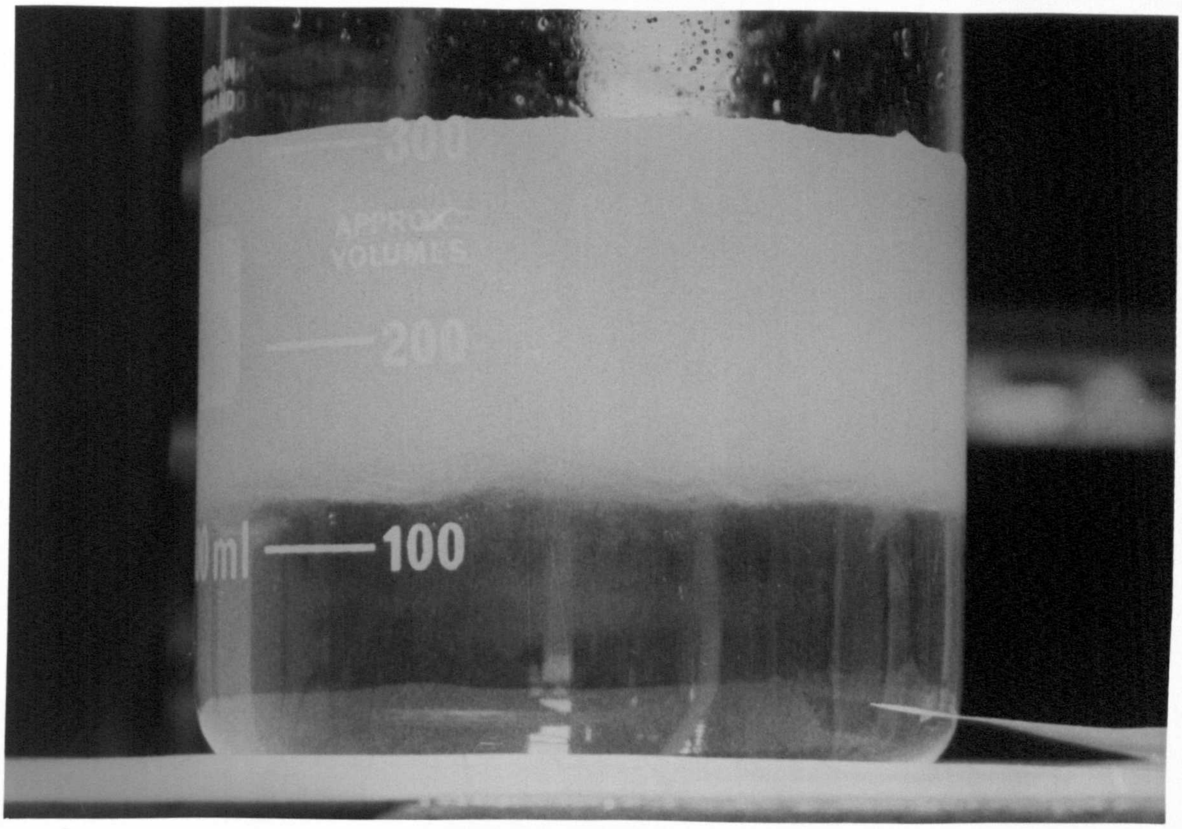


i) p-xylene crystals which adhere to the containing vessel.

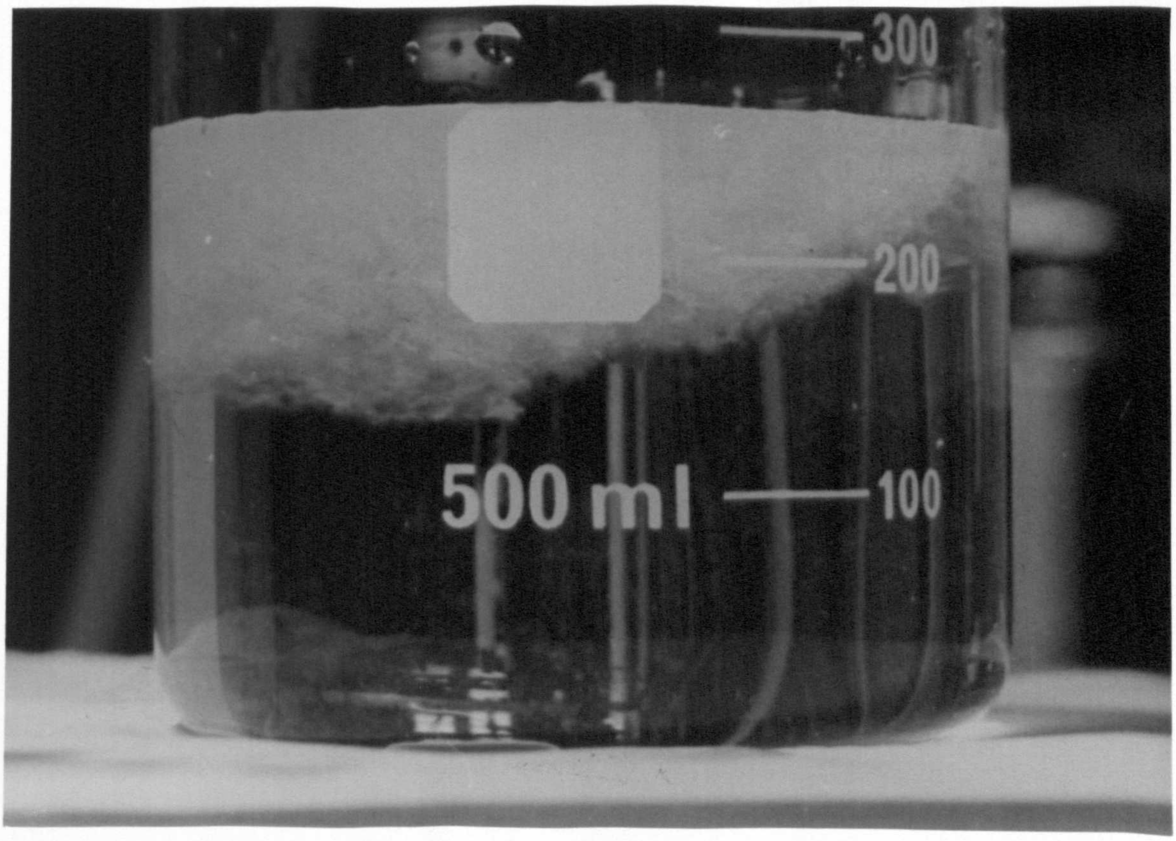
ii) heavy water crystals showing needle-like formation.

iii) paraffin wax crystals formed from a mixture of waxes (x 450).

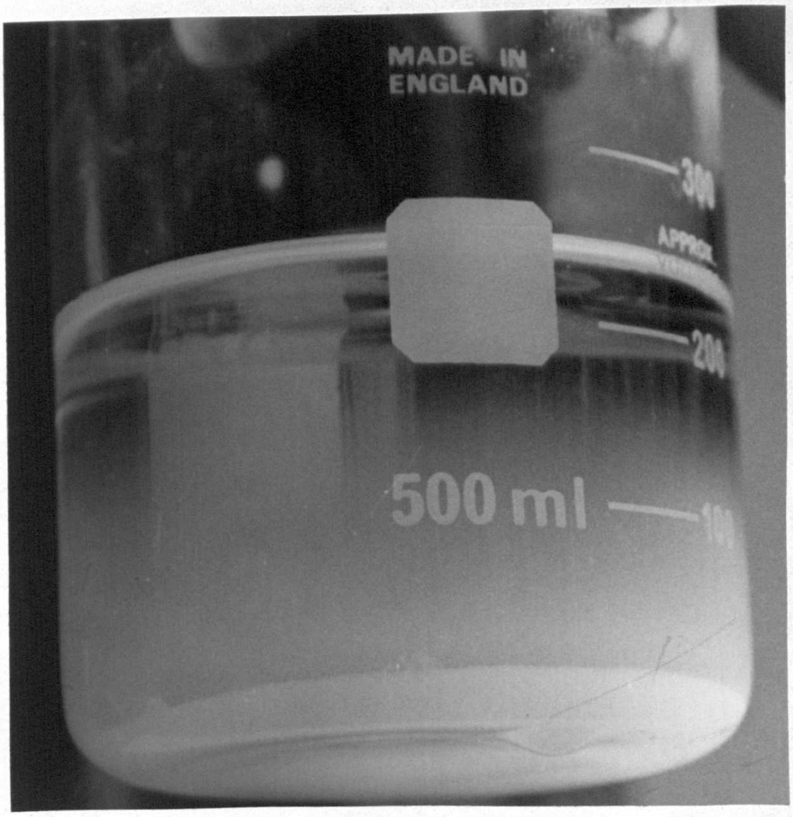
b) Transportable crystals.



i) ice mush formed from a solution of brine.



ii) type of crystals formed when ethanol/water solutions freeze.



iii) benzene cystals from a 3% cyclohexane +benzene solution.

9. Effect of the surface finish on the inner wall of the column jacket

Early work with benzene/cyclohexane as well as brine solutions had demonstrated that 80 rpm and not 60 rpm was the optimum value of screw speed for the column. These early runs, especially for desalination, had been affected by "sieze-up" of operation due to crystals blocking up the freezing section. After various attempts to overcome this problem for desalination experiments (as described in the experimental section) it was decided to polish the inner surface of the freezing section to a mirror finish. The reasoning governing this decision was that the unpolished walls allowed the crystals to remain in the freezing section by frictional effects. The trapped crystals now became over-cooled, forming glass-like ice which eventually formed a collar round the conveyor with the resultant blockage of the freezing section.

Mirror-finish polishing of the freezing section inner-wall completely removed this problem. The ease with which crystals could now be transported meant that lower screw speeds could be used hence improving the separating power of the column.

After continued experiments on desalination the crystal transportation again became difficult. The column was dismantled and the polish was found to be less than desired. The section was repolished and the column reassembled when crystal transportation was again facilitated.

The problem of losing the surface polish, especially in the freezing section, may require that chromium plating of the walls may be necessary or a different material may be required in fabrication of the column jacket.

Since polishing the freezing section greatly improved the column operation, before the ethanol concentration work was started, the polish was extended to cover the entire length of the column.

10. Effect of diffusion and mass transfer

Several workers (11, 51, 124, 144) have measured the coefficients of diffusion and mass transfer in extraction columns and the analogy with crystallisation columns indicates the need for a similar analysis.

For optimum column operation in the enriching section, the diffusion of impurity along the column should be as low as possible and the mass transfer between the adhering and reflux liquids should be as large as possible. Although, for concentrating material in the stripped stream the converse is true, the coefficients apply along the whole column length and the requirements for the enriching section must be met in order to raise the concentration of the desired substance in the free liquid entering the stripping section.

The values of the coefficients obtained were:

Table 3

System	Screw Speed (rpm)	Crystal Direction	D $cm^2 sec^{-1}$	Ka sec^{-1}
Benzene/ cyclohexane	60	↓	0.56	1.67×10^{-3}
Ethanol/ concentration	60	↓	1.24	0.74×10^{-3}
Desalination	60	↓	0.16	0.56×10^{-3}
	100	↓	0.02	0.06×10^{-3}
	100	↑	0.02	0.07×10^{-3}

The values obtained by Gates and Powers (61) for column operation employing 67 oscillations/minute with an amplitude of 1mm for crystals transported upwards with a screw speed of 59rpm, for the reduction of the cyclohexane content of benzene solutions were:

$D = 1.3 \text{ cm}^2 \text{ sec}^{-1}$ and $Ka = 3.0\times10^{-3} \text{ sec}^{-1*}$

these values comparing favourably with literature values for pulsed extraction columns(84, 126, 138).

Now, diffusional and mass transfer effects are increased by oscillating the liquid in the column; thus the values obtained in the present study should be less than those in the literature(61). For benzene purification the diffusion coefficient obtained is just less than half of Powers' value whereas the overall mass transfer factor is just greater than half.

The ethanol concentration values, obtained from an analysis of the stripping section show a diffusion coefficient comparable with that for a pulsed column. This is most likely caused by the low flow rate of free liquid through the column which normally decreases the rate of diffusion. The overall mass transfer coefficient is lower than for benzene purification, possibly due to the decreased amount of washing action caused by a high value of enriched product take-off rate.

For desalination, the diffusional effects at 100 rpm are negligible due to the agglomeration of the crystals which also results in a poor mass transfer between the adhering and free liquids. At 60 rpm the caking of the crystals is reduced since the crystals produced are larger, however, the diffusion of sodium chloride along the column is still very low whereas the mass transfer is almost ten times larger, now being comparable with that for ethanol concentration.

At 60 rpm the effects of mass transfer are lower but of comparable importance to diffusion in determining the value of H or ($\overline{H}$) and hence the separation achieved for all the systems investigated.

*Estimated using the values of 'a' obtained by Albertins(1).

11. Effect of scale-up of operation

The high feed rate run during the purification of benzene experiments shows that fairly high flow rates of products could be attained considering the size of the apparatus (volume of 93cm column, 1020ml). Residence times could be reduced to below 10 minutes with some loss of product purity, though acceptable values will depend upon the use for which the product is intended.

For laboratory use, the output from a crystalliser of this size would be more than sufficient for producing ultra-pure solvents in situ, however, for desalination or ethanol concentration outputs required are considerably higher and larger apparatus would be required.

There are many problems involved in scaling-up the design of a crystalliser. McKay(93) found that crystal shapes in pilot plant apparatus was markedly different to those for commercial size equipment. However, of the different conditions which are required to be simulated in progressing from a small to a large crystalliser the four most important are:

(i) identical flow characteristics of liquid and solid particles

(ii) identical degrees of supersaturation in all equivalent regions of the crystalliser.

(iii) identical initial seed sizes and magma densities

(iv) identical contact times between growing crystals and supersaturated liquor.

FINAL CONCLUSIONS

The aim of the project, ie to redesign an existing column crystalliser and optimise its performance has been accomplished. The optimisation data fits aqueous, organic and mixed aqueous/organic mixtures such that the characteristic operating conditions may be applied to all systems. The mathematical analysis, where undertaken, has confirmed the experimental findings and theoretical calculations have shown that there is an optimum crystal production rate for each system. This analysis affords much economy since fruitless attempts to surpass the theoretical values on commercial equipment can be avoided.

The apparatus, in its present form, is a valuable analytical tool, allowing a determination of the dominant factors affecting the column's operation. The effects upon column crystalliser design caused by the surface finish on the inner wall of the jacket and the problem that the shape of the crystal formed may produce have been demonstrated.

Continuous column crystallisation has clearly been shown to be a powerful technique useful in the separation and purification of various materials.

SUGGESTIONS FOR FURTHER WORK

(1) Already information from the enriching section for desalination experiments is being used to develop a dynamic model of the 2" column crystalliser. There is a need, however, to observe the nucleation and growth of the crystals in the freezing section. The design and construction of a glass freezing section, using a transparent coolant is proposed in order to facilitate this requirement.

(2) Continuation of operation of the 4" diameter column crystalliser designed and built from data obtained by experiments with the 2" crystalliser. The data from both sets of experiments, together with the dynamic model of the system should alleviate much of the difficulty associated with scale-up.

(3) The application of the 2" column crystalliser to purification of heat sensitive compounds (eg pharmaceuticals, flavourings); to the separation of micro crystalline waxes by use of suitable crystal habit modifier and the treatment of trade effluent (removing metals and possibly toxic waste before disposal).

LIST OF SYMBOLS

a	Area available for mass transfer between the adhering and free liquids per unit volume of the column (L^1)
A	cross-sectional area of the column (L^2)
C	crystal production rate ($M.T^{-1}$)
D	coefficient of diffusion ($L^2.T^{-1}$)
E_S	stripping efficiency defined by eq (54)
F	feed flow rate ($M.T^{-1}$)
H	separation factor for enriching section; defined by equation (48) (L)
$\overline{H}$	separation factor for stripping section, defined by equation (53) (L)
K	mass transfer coefficient ($L.T^{-1}$)
L	free liquid stream rate ($M.T^{-1}$)
L^1	adhering liquid stream rate ($M.T^{-1}$)
Le	enriched stream rate ($L^3.T^{-1}$)
Ls	stripped stream rate ($L^3.T^{-1}$)
M_D	mass transfer rate of impurity due to axial dispersion ($M.T^{-1}$)
M_K	mass transfer rate of impurity from adhering liquid to free liquid ($M.T^{-1}$)
S^o	stream rate of liquid into the stripping section ($M.T^{-1}$)
Y	impurity content of free liquid ($M.M^{-1}$)
Y^1	impurity content of adhering liquid ($M.M^{-1}$)
Ye	impurity content of enriched stream ($M.M^{-1}$)
Y_F	impurity content of feed stream ($M.M^{-1}$)
Y_p	defined by equation (41) ($M.M^{-1}$)

$\bar{Y}_p$	defined by equation (52) ($M.M^{-1}$)
Y_s	impurity content of stripped stream ($M.M^{-1}$)
Y^{so}	impurity content of liquid entering the stripping section ($M.M^{-1}$)
Y_{ϕ}	impurity content of free liquid at the feed point ($M.M^{-1}$)
Y^*	impurity content of stripped stream at zero stream rate ($M.M^{-1}$)
Z	position in the column measured from freezing section (L)
Z_F	feed point measured from freezing section (L)

Greek symbols

α	ratio of adhering liquid stream rate to crystal rate
ε	impurity content of solid phase ($M.M^{-1}$)
η	volume fraction of free liquid
ρ	density of liquid phase ($M.L^{-3}$)

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APPENDIX

APPENDIX CONTENTS

Table (4)

Benzene/cyclohexane Experimental results

Run no.	Feed rate (g/hr)	Feed composition (ppm)	Feed point, distance from freezing jacket (cm)	Crystal rate(g/sec)	Enriched product rate (g/hr)	Enriched product composition (ppm)	Screw speed
BC1	1220	23000	0.5	0.393	360	38	60
BC2	1220	23000	0.5	0.393	360	91	80
BC3	1220	23000	0.5	0.393	360	41	53
BC4	1050	33000	0.5	/	280	119	60
BC5	1050	33000	0.5	/	530	398	60
BC6	1050	33000	0.5	/	845	4800	60
BC7	1420	33000	7.0	/	460	439	60
BC8	1420	33000	18.0	/	460	972	60
BC9	1240	33000	0.5	0.457	485	37*	60
BC10	1240	33000	0.5	0.393	485	145	60
BC11	1240	33000	0.5	0.272	485	6958**	60
BC12	1240	33000	0.5	0.541	485	77***	60
BC13	2710	33000	0.5	0.541	1200	245****	60

Notes

* Crystal rate such that impurity in crystals only appears once base product samples taken. Sample 3cm above base had only 27ppm cyclohexane in the free liquid. This allows a direct estimation of the impurity content of the crystals, the value being 10ppm which agrees well with the calculated result of 10.6ppm

** Feed runs cocurrently with crystals due to low crystal rate, hence base product purity low

*** Attempt to reach very high crystal rate. Freezing section blocked

**** Continuation of Run BC12 at high feed rate

Table (5)

Benzene/cyclohexane   Experimental results-conc^n profile

Run no.	Cyclohexane concentration (ppm) Distance from feed point $(z-z_F)$ in cm.							
	-31.5	5.5	11.5	17.5	29.5	35.5	57.5	60.5
B/C1	44688	4524	4088	1736	487	354	/	38
B/C2	44000	7800	5000	3100	/	1000	44	91
B/C3	44500	5000	1700	1000	190	/	36	41
B/C4	/	/	/	/	/	/	/	119
B/C5	/	/	/	/	/	/	/	398
B/C6	/	/	/	/	/	/	/	4800
B/C7	/	/	/	/	/	/	/	439
B/C8	52000	/	/	/	/	/	/	972
B/C9	56563	4878	2208	1343	/	282	27	37
B/C10	55000	8985	5969	3828	1225	1074	173	145
B/C11	54500	22219	19131	17211	11919	10451	7137	6958
B/C12	64000	3752	/	705	/	265	/	77
B/C13	60500	8583	3569	2855	/	750	324	245

Fig (23)

Effect of screw speed on conc of cyclohexane in pure product

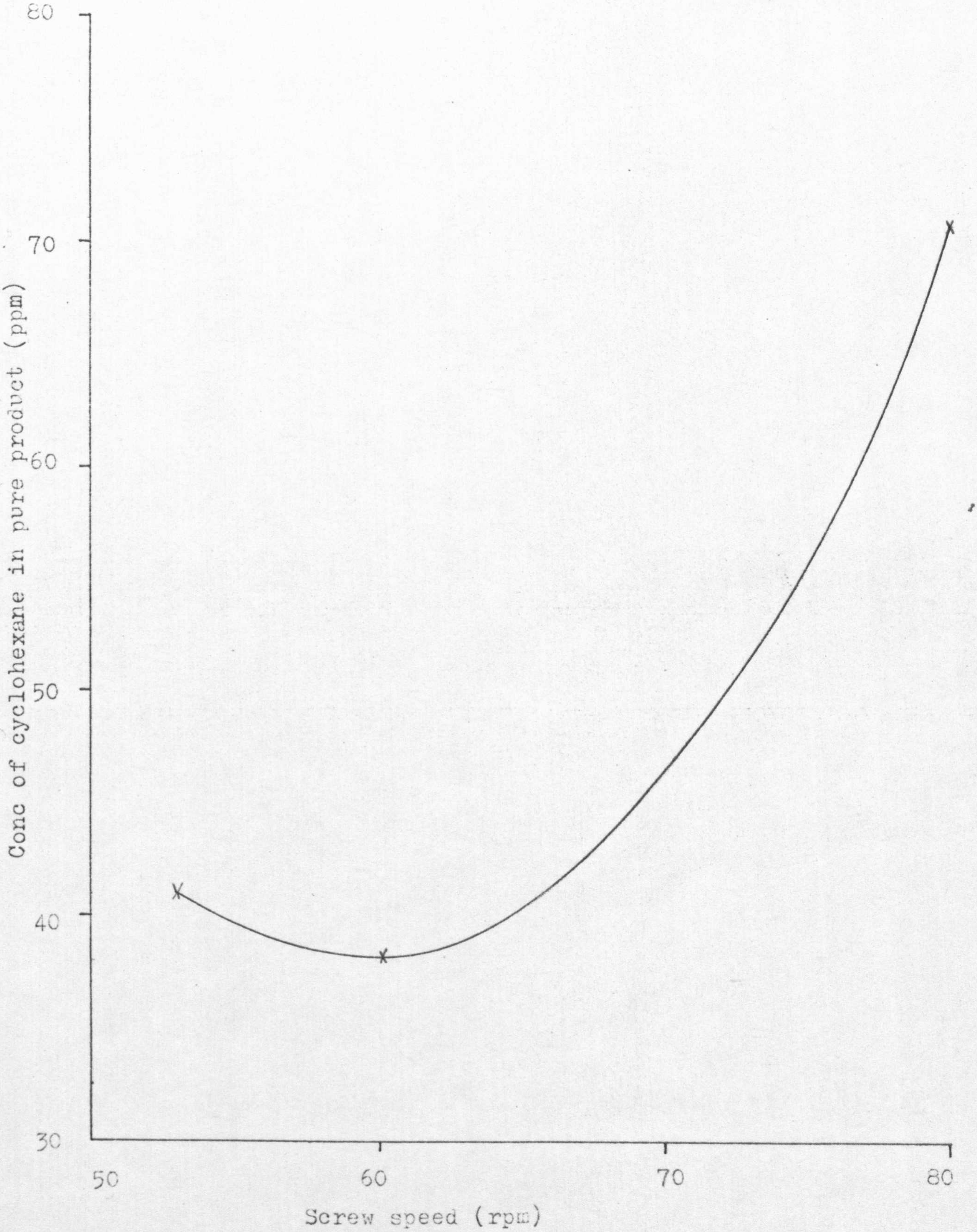
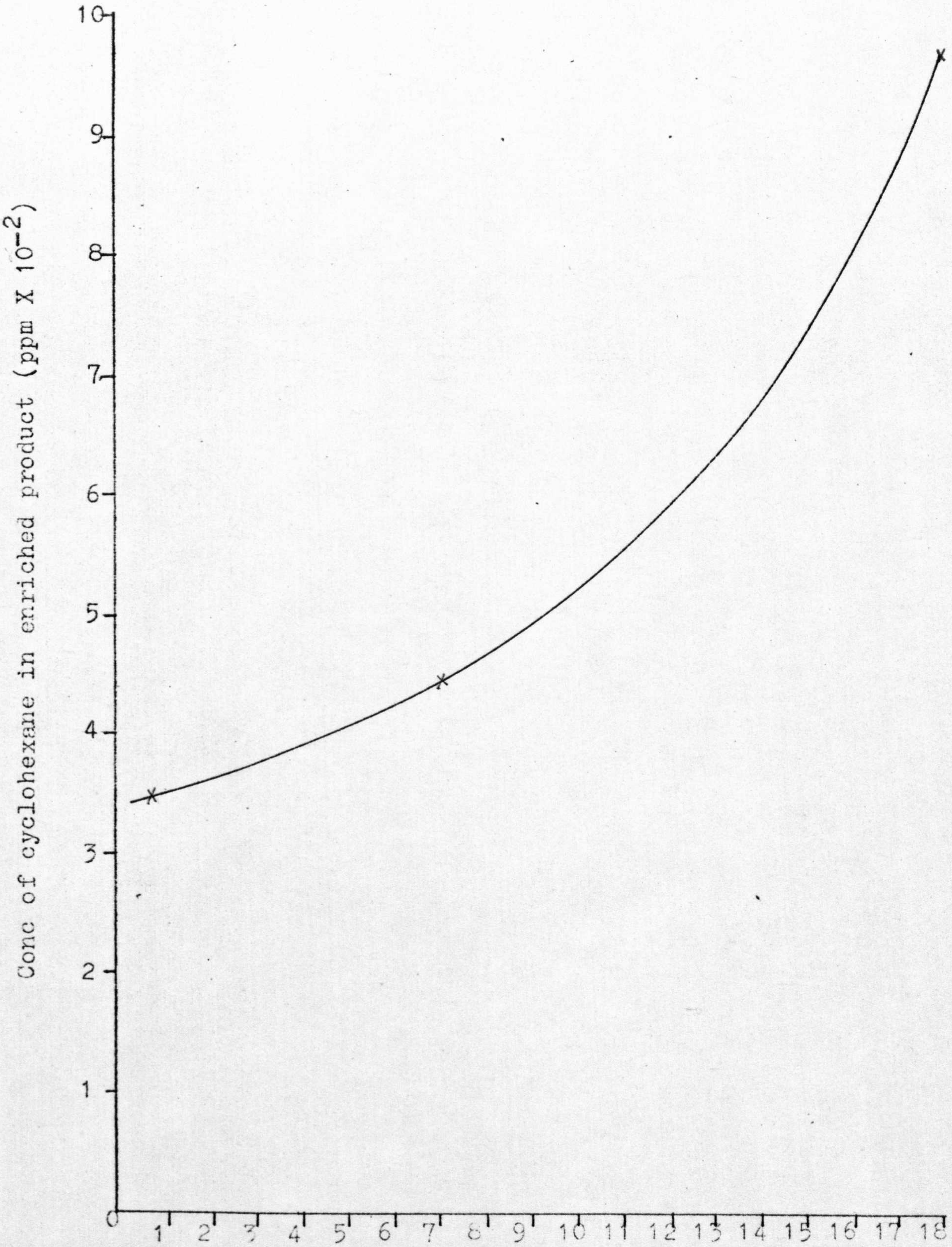


Fig (24)

Effect of feed position on enriched product purity



Distance of feed point from freezing jacket (cm)

Fig (25)

Effect of removal rate on impurity content of the enriched stream

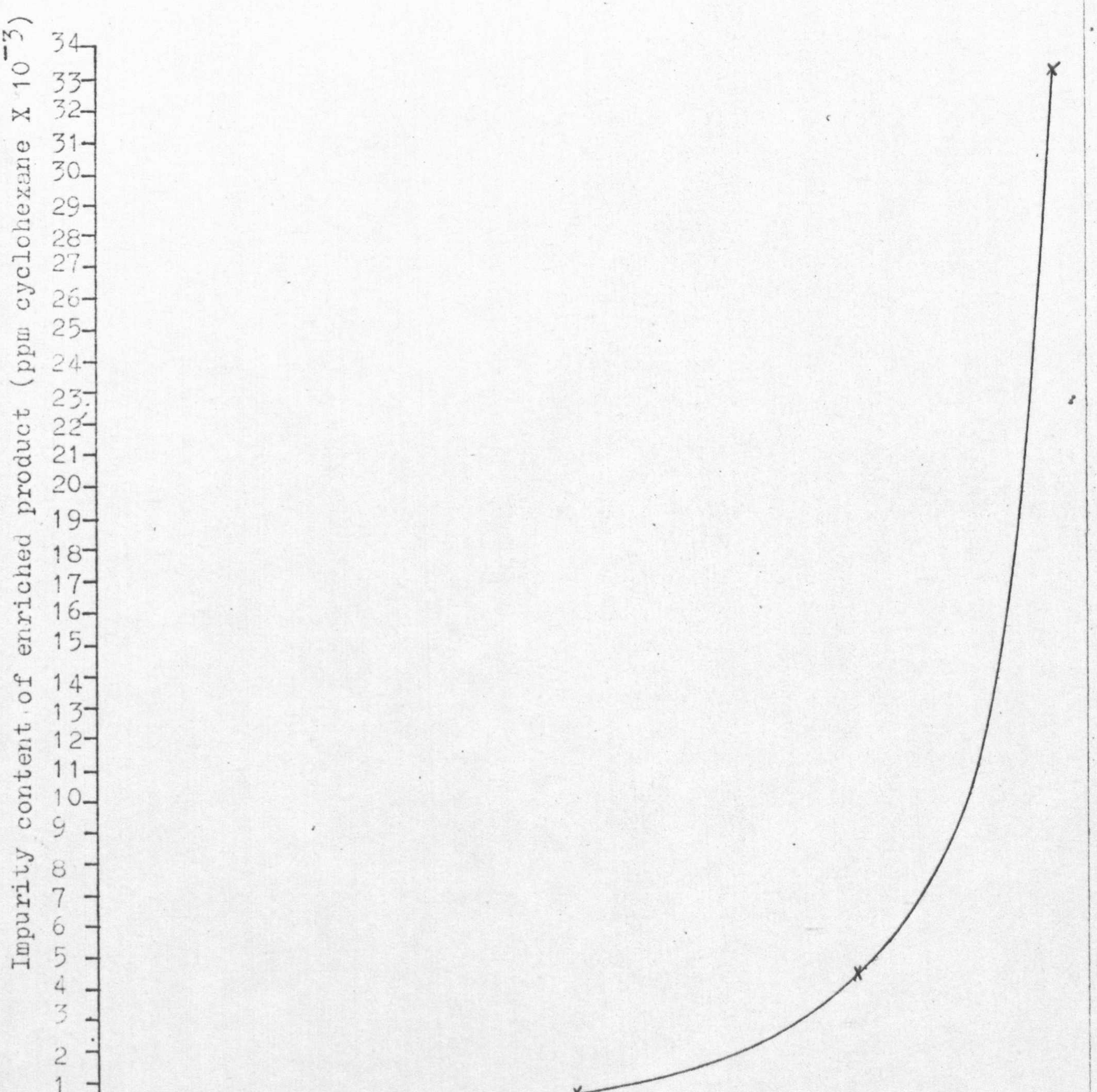
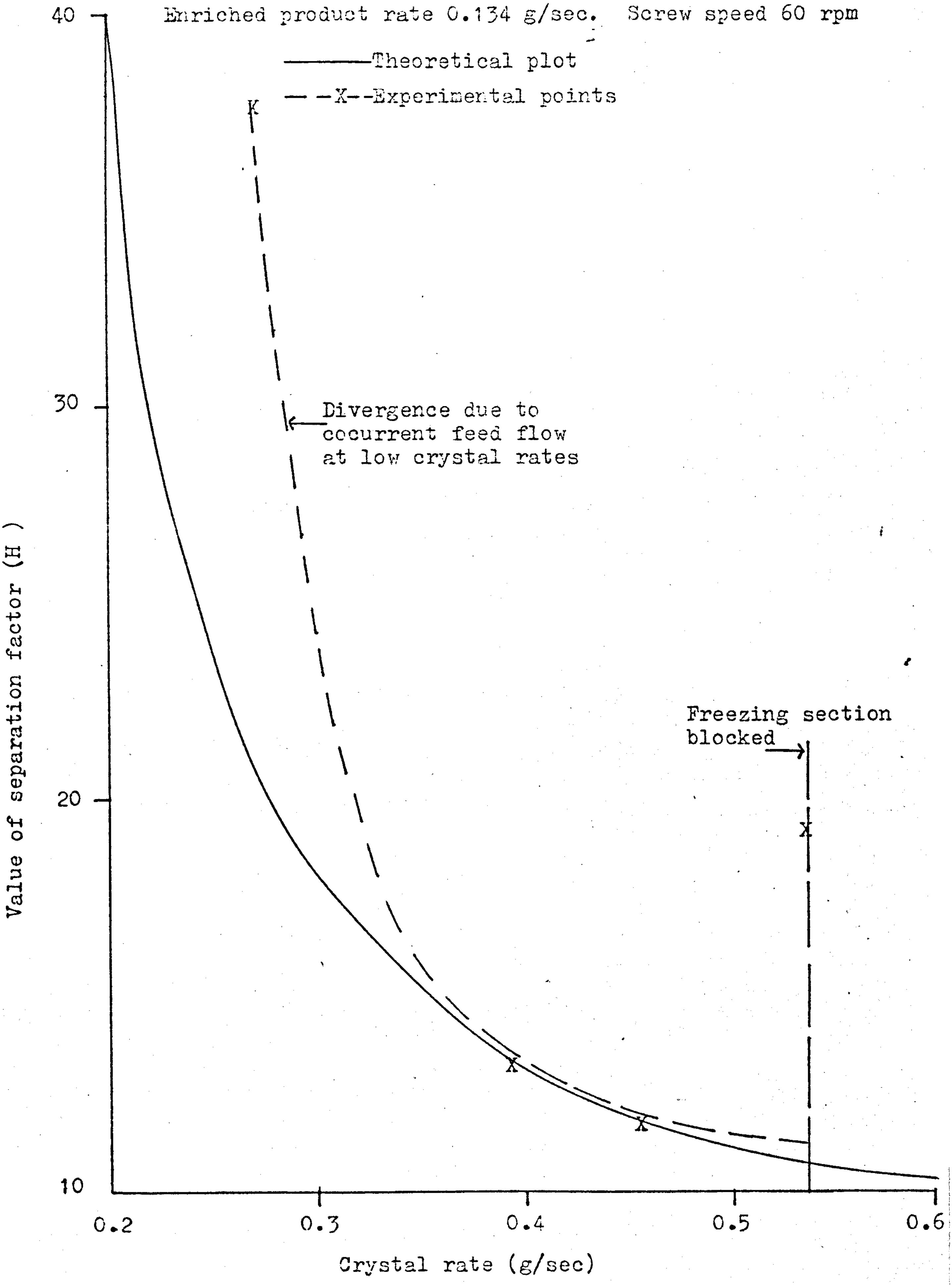


Fig (26) p190

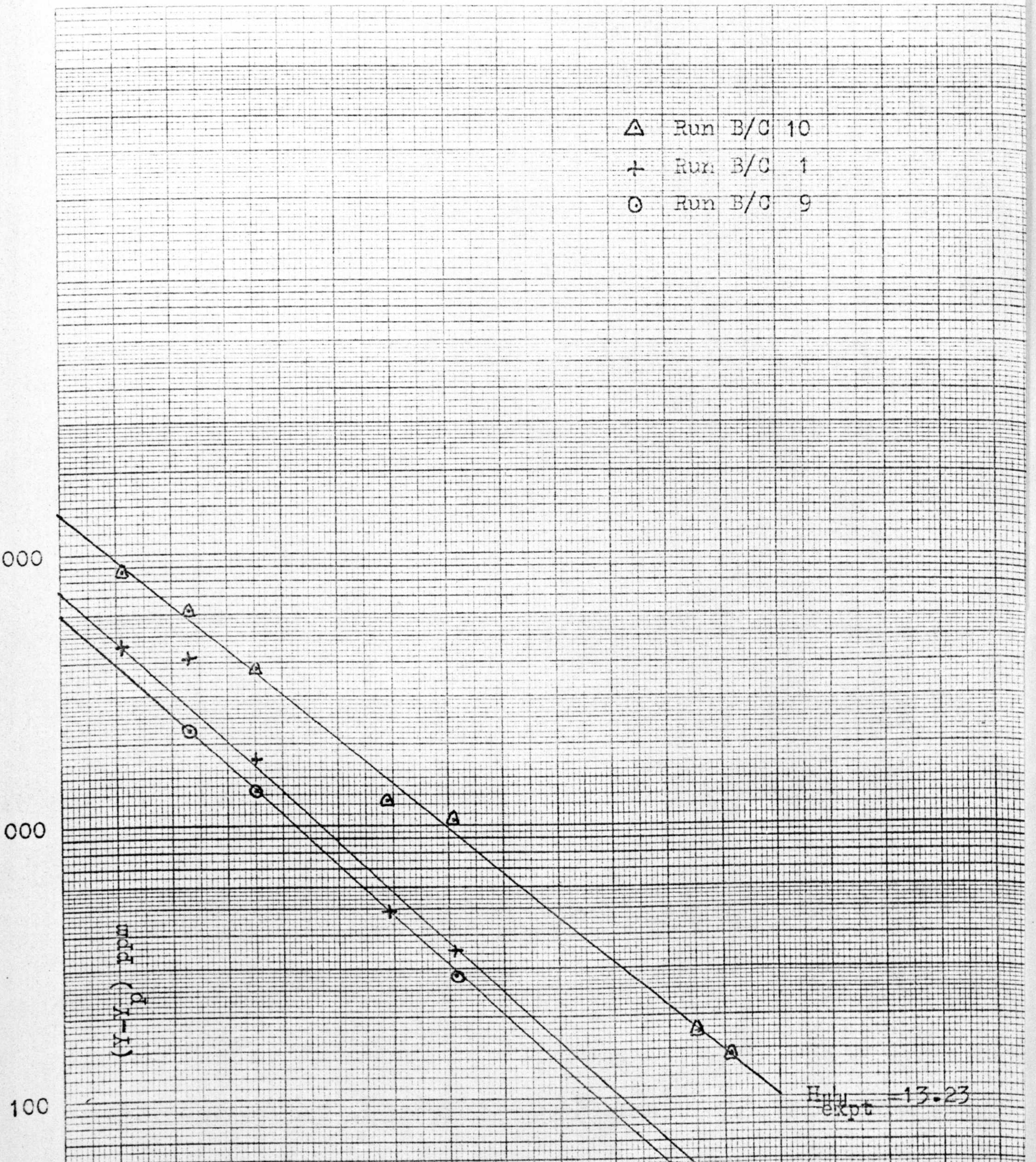
Effect of crystal rate on the separation factor (H) for a feed of 33000 ppm cyclohexane in benzene

Enriched product rate 0.134 g/sec. Screw speed 60 rpm



Graph of $(Y-Y_p)$ vs $(z-z_F)$ for the benzene / cyclohexane system

Fig (27)   p191



Calculation of diffusion and mass transfer coefficients for the benzene/cyclohexane system.

Now, from Powers(72):

$$H=\frac{1}{C-L_e}\left[D\eta A\rho+\frac{\alpha(1+\alpha)C^2-\alpha L_eC}{KaA\rho}\right] \qquad (48)$$

where D and Ka are the coefficients required and H is determined from the plots of $(Y-Y_p)$ vs $(z-z_F)$ on semi-log graph paper.

In order to evaluate D and Ka it is necessary to determine the crystal rate (C) by taking a heat balance over the freezing section of the column, measure the rate of removal of enriched product from the column and estimate the constants ρ, A, η, α.

The value of both η and α can be determined by consideration of the following equations:-

$$S^oY^{so}=FY_F+LY_\emptyset \qquad (58)^{(25)}$$

$$S^o=FY_F-L_eY_e+L'Y^* \qquad (59)^{(25)}$$

whence $$LY_\emptyset=L'Y^*-L_eY_e \qquad (60)$$

also $$C+L'=L_e+L \qquad (24)^{(72)}$$

which may be derived by considering mass balances over the column.

Solutions to equations (60) and (24) allow the evaluation of free liquid (L) and adhering liquid (L') stream rates and hence the constants η and α can be determined.

The cross-sectional area of the column (A) and the density of the liquid phase (ρ) are easily evaluated.

Using the values of (H) determined for different crystal rates with a known value of L_e several simultaneous equations can be derived by substitution in equation (48).

Values of constants :-

$A = 12.43$; $\rho = 0.88$; $\alpha = 0.13$; $\eta = 0.41$

For Run B/C1 $C = 0.393$ and $L_e = 0.098$

For Run B/C9 $C = 0.457$ and $L_e = 0.134$

For Run B/C10 $C = 0.393$ and $L_e = 0.134$

Thus equation (48) becomes :-

$$\text{B/C1} \quad 3.50 = 4.49D + \frac{1.62 \times 10^{-3}}{Ka}$$

$$\text{B/C9} \quad 3.86 = 4.49D + \frac{2.08 \times 10^{-3}}{Ka}$$

$$\text{B/C10} \quad 3.43 = 4.49D + \frac{1.45 \times 10^{-3}}{Ka}$$

These three equations were solved graphically in order to evaluate the diffusion coefficient(from the intercept) and the overall mass transfer coefficient(from the slope).

Whence $\underline{D = 0.56 \pm 0.07 \ \text{cm}^2 \text{sec}^{-1}}$
and $\underline{Ka = (1.67 \pm 0.39) \times 10^{-3} \ \text{sec}^{-1}}$

Substitution of these values of D and Ka into equation(48) allows the theoretical values of the separation factor(H) to be determined.

Thus :-

Run no.	$H_{\text{experimental}}$	$H_{\text{theoretical}}$	Error
B/C1	11.84	11.83	0.1%
B/C9	11.98	11.64	2.9%
B/C10	13.23	13.05	1.4%

Now,for a maximum separation H should be a minimum.Therefore differentiation of equation (48) using the values of D and Ka as determined above affords a determination of the crystal rate required to produce this optimum separation.

Whence C is 0.695 g/sec for an enriched stream rate of 0.134 g/sec.

In practice this theoretical optimum crystal rate could not be reached since the freezing section blocked at a crystal rate of 0.542 g/sec.

By substitution of the theoretical values of H in equation(47)

i.e. $$\frac{Y - Y_p}{Y_\phi - Y_p} = \exp -\frac{(z - z_F)}{H}$$

a comparison of the experimental and theoretical concentration profiles can be made.

Values of Y_p and Y can be estimated from the experimental concentration profiles and thus the free liquid impurity content (Y) can be evaluated for different positions in the column (z).

Now, for Run B/C1 $Y'_p=0$; $Y_{\phi}=$ 7200 ppm

for Run B/C9 $Y_p=0$; $Y_{\phi}=$ 5900 ppm

for Run B/C10 $Y'_p=0$; $Y_{\phi}=$ 14000 ppm

Thus :-

Position in column $(z-z_F)$ cm.	Theoretical impurity content (Y)ppm		
	Run B/C1	Run B/C9	Run B/C10
0	7200	5900	14000
10	3092	2499	6506
20	1328	1058	3024
30	570	448	1405
40	245	190	653
50	105	80	304
60	45	34	141
70	19	14	66

Reference to fig.28(a),(b),(c) affords a comparison between these values and the experimental concentration profiles.

Fig (28,a)

Effect of position in column on conc^n of cyclohexane in the free liquid

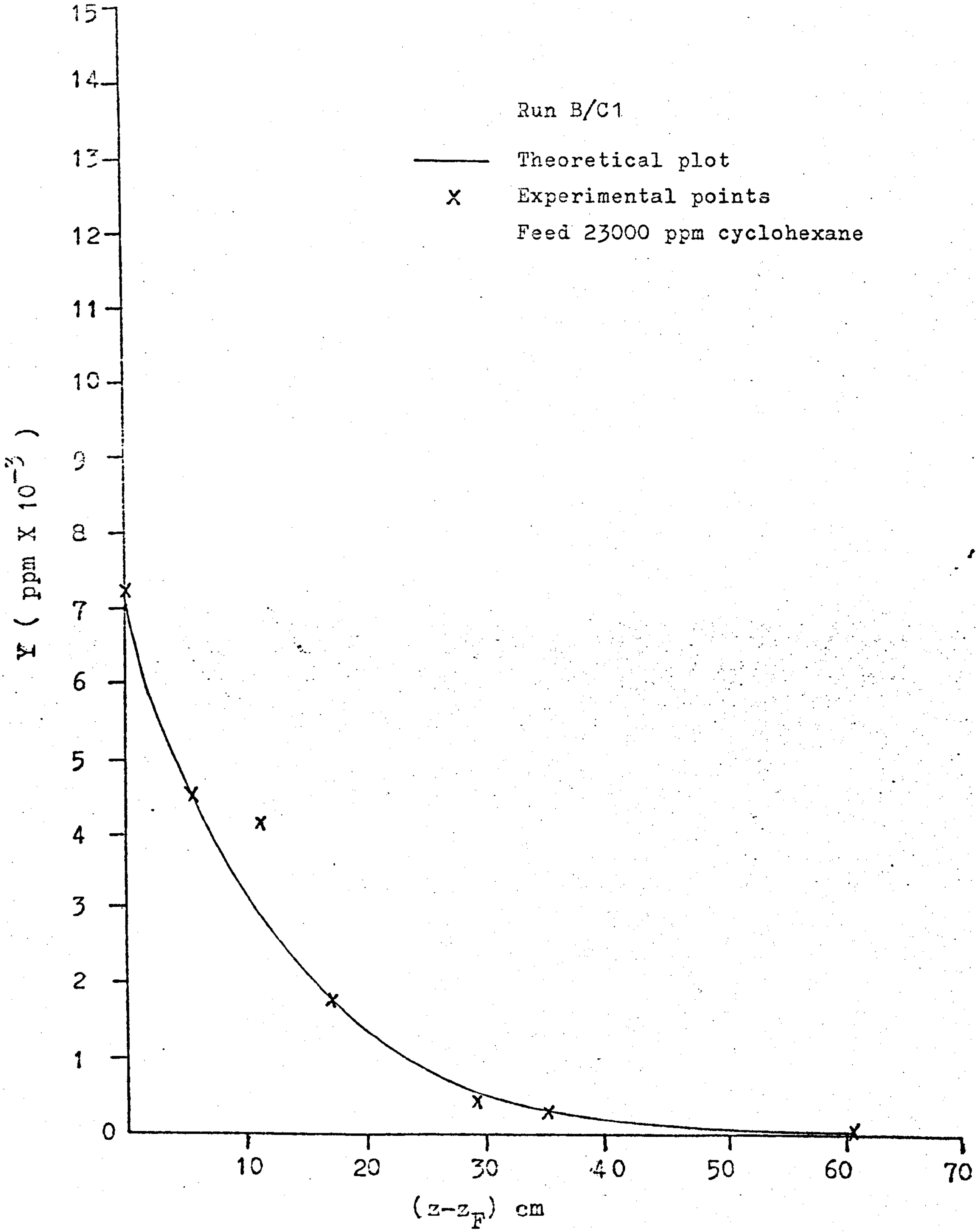


Fig (28,b)

Effect of position in column on conc^n of cyclohexane in the free liquid

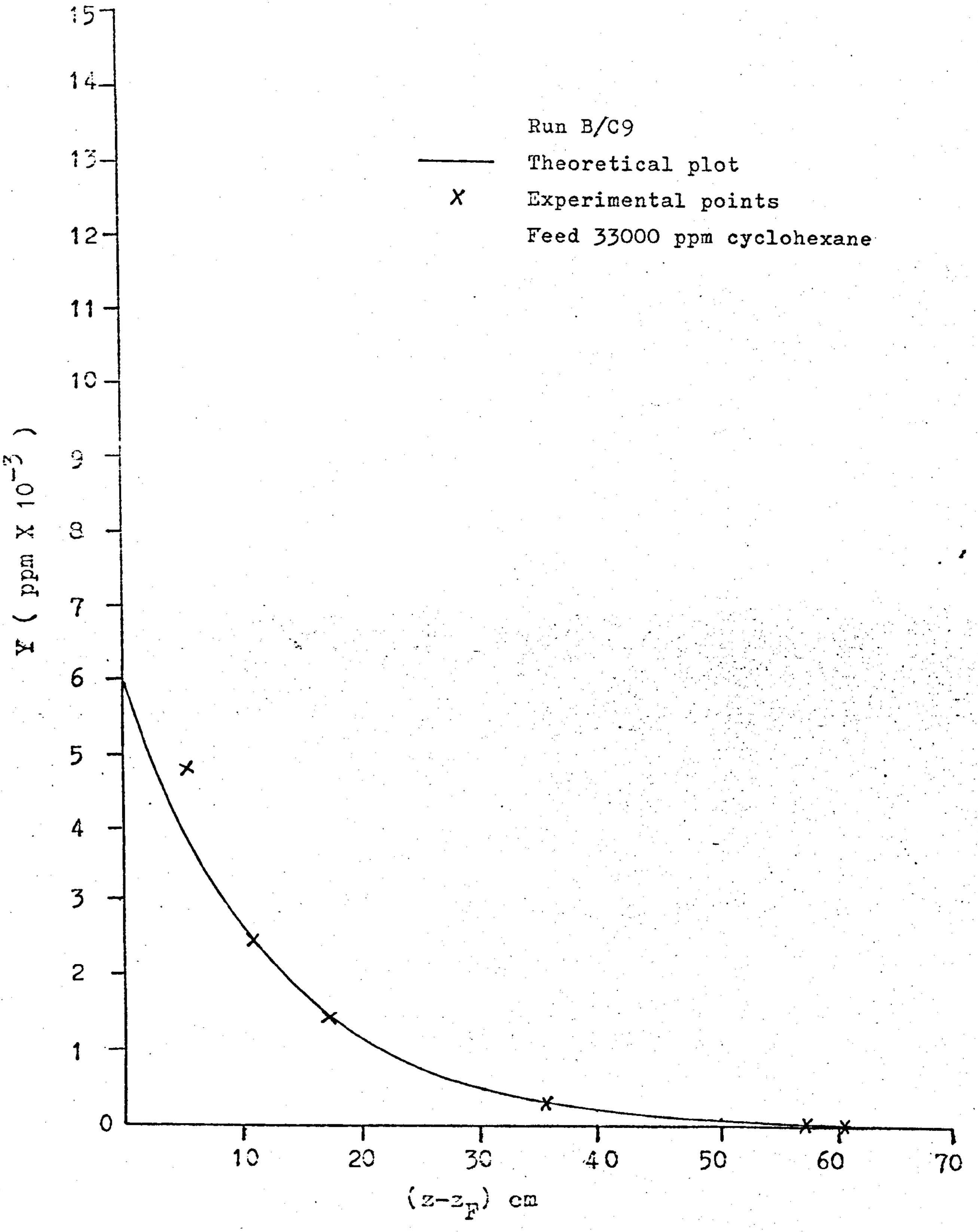
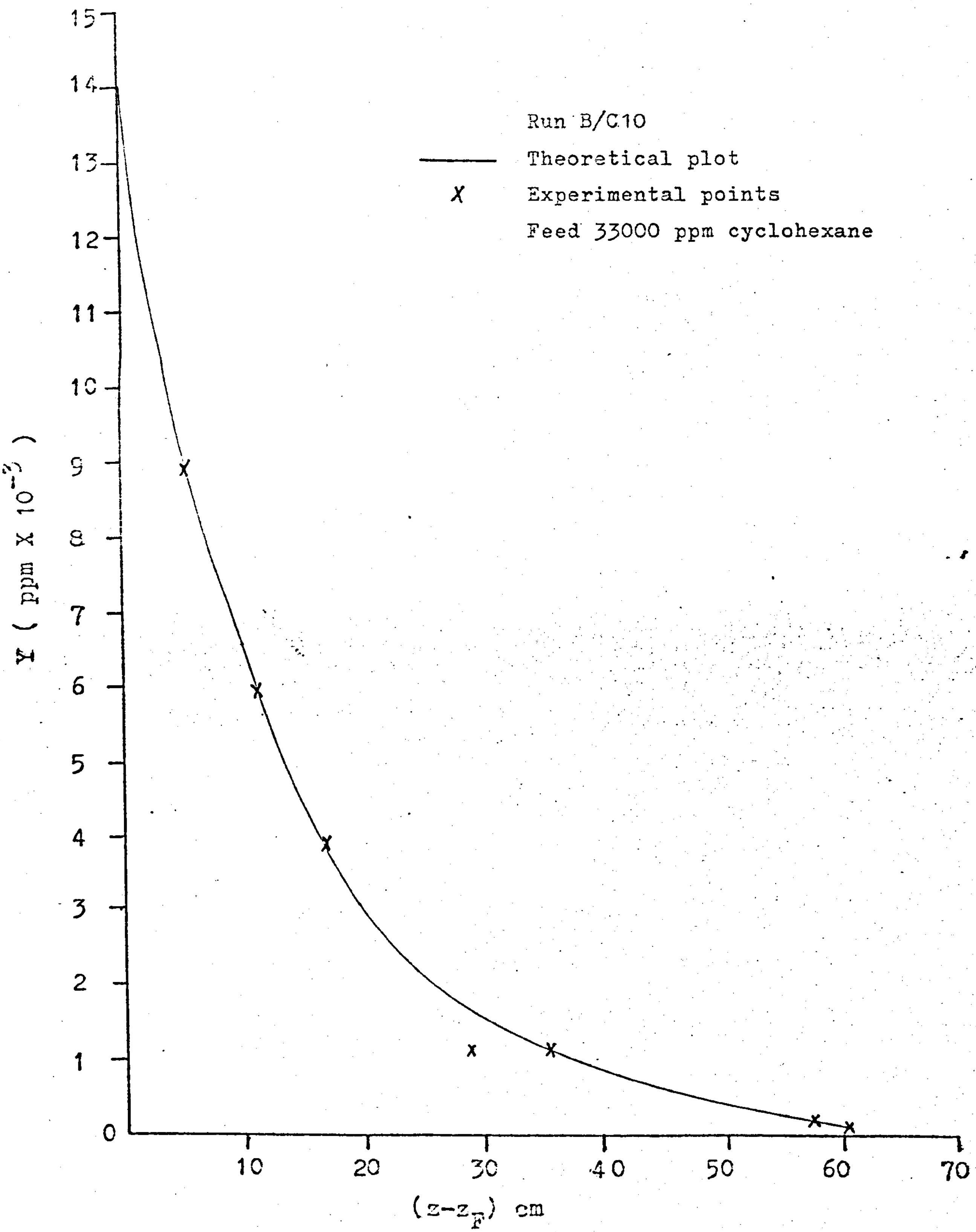


Fig (28,c)

Effect of position in column on conc^n of cyclohexane in the free liquid



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Desalination Experimental results

Run no.	Feed rate (g/hr)	Feed composition (ppm NaCl)	Feed point, distance from freezing jacket (cm)	Enriched product rate (g/hr)	Enriched product composition (ppm NaCl)	Crystal rate (g/sec)	Crystal direction	Screw speed	Column length (cm)
S1	1200	34000	0.5	540	12800	0.173	Down	60	93
S2	1200	34000	0.5	540	8500	0.173	"	60	93
S3	1200	34000	0.5	540	750	0.173	"	60	93
S4	1200	34000	0.5	500	800	0.180	"	60	93
S5	1200	34000	0.5	500	510	0.200	"	60	93
S6	1200	34000	0.5	500	143	0.210	"	60	93
S7	1210	37000	2.5	480	6100	/	Up	100	91
S8	1210	37000	2.5	480	9250	/	"	120	91
S9	1210	37000	2.5	480	6400	/	"	80	91
S10	1210	37000	2.5	480	6400	/	"	60	91
S11	1240	37000	15.5	490	13900	/	"	100	91
S12	1240	37000	22.5	490	18000	/	"	100	91
S13	1700	37000	2.5	1030	13550	/	"	100	91
S14	1800	37000	2.5	680	8900	/	"	100	91
S15	1820	37000	2.5	440	3790	/	"	100	91
S16	1830	37000	2.5	1400	19700	/	"	100	91
S17	1800	38500	2.5	930	15600	/	"	100	66
S18	1800	37500	2.5	950	14600	/	"	100	77
S19	1840	37000	2.5	900	17000	/	"	100	56
S20	1250	35500	2.5	500	14700	0.110	"	100	91
S21	1250	35500	2.5	510	7000	0.151	"	100	91
S22	1250	35500	2.5	580	2750	0.184	"	100	91
S23	1200	34000	0.5	540	1250	0.173	Down	53	93
S24	1200	34000	0.5	540	7000	0.173	"	80	93
S25	1200	34000	0.5	540	4800	0.173	"	120	93
S26	1200	34000	0.5	540	4700	0.173	"	100	93
S27	1250	35500	2.5	580	2450	0.190	"	100	91
S28	1250	35500	2.5	500	4700	0.148	"	100	91
S29	1250	35500	2.5	500	6500	0.142	"	100	91
S30	1250	35500	2.5	510	13500	0.105	"	100	91

Notes

During run S1 the screw was oscillated 104 times/min through 6mm

During run S2 the liquid in the column was pulsed 95 times/min through 2mm

Table (7)

Desalination Experimental results

Concentration profile

Run no.	Concentration NaCl in the free liquid Distance from feed point ($z-z_F$) in cm.							
	-31.5	5.5	11.5	17.5	29.5	35.5	57.5	60.5
S1	54000	25100	21800	17750	14600	13800	13750	12800
S2	57000	24300	20750	18800	/	12800	9600	8500
S3	77000	24200	/	14750	/	6000	1800	750
S4	77000	18800	10600	8000	2750	2100	800	/
S5	77000	12000	8200	2800	1100	1300	510	/
S6	85000	9900	4100	2725	498	568	143	/
S23	/	/	/	/	/	/	/	1250
S24	/	/	/	/	/	/	/	7000
S25	/	/	/	/	/	/	/	4800
S26	/	/	/	/	/	/	/	4700

	Concentration NaCl in the free liquid Distance from feed point ($z-z_F$) in cm.							
	-31.5	1.0	11.0	21.0	31.0	41.0	47.0	52.0
S7	72500	24600	15400	11800	9250	7280	7000	6100
S8	73000	29750	18800	13750	12800	11600	/	9250
S9	73000	26600	18000	12750	9300	7800	/	6400
S10	73000	/	/	/	/	/	/	6400
S11	70000	26150	/	19700	17800	15500	/	13900
S12	69000	28000	/	21800	20750	19900	/	18000
S13	85000	/	/	/	/	/	/	13550
S14	64500	/	/	/	/	/	/	8900
S15	57000	/	/	/	/	/	/	3790
S16	106000	/	/	/	/	/	/	19700
S17	/	/	/	/	/	/	/	15600
S18	/	/	/	/	/	/	/	14600
S19	/	/	/	/	/	/	/	17000

Table (7) cont^{d}

Desalination Experimental results

Concentration profile

Run no.	Concentration NaCl in the free liquid Distance from feed point ($z-z_F$) in cm.							
	-31.5	2.0	12.0	21.0	31.0	41.0	49.5	62.0
S20	55000	33100	28000	25200	24600	18300	/	14700
S21	73000	29750	23000	16900	15400	11250	/	7000
S22	81000	23000	14500	10100	7000	5750	/	2750
S27	86000	20750	/	10000	/	4550	3750	2450
S28	67000	24500	/	14000	/	8700	/	4700
S29	71000	27500	/	15000	/	10100	8900	6500
S30	55000	30700	/	22750	/	20200	15600	13500

Fig(29) Effect of screw speed on enriched product purity for crystals transported downwards

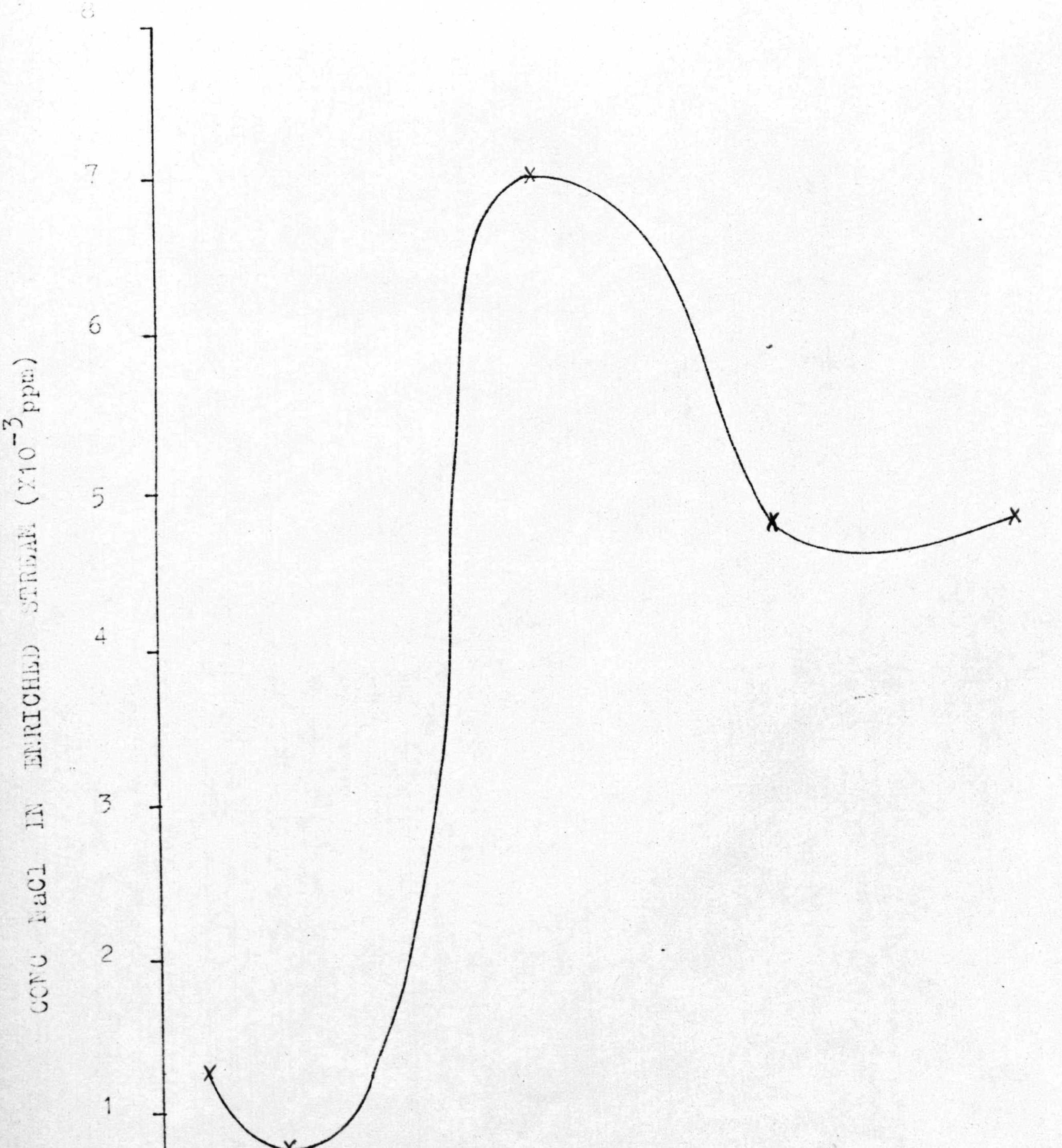


Fig (30) p202

Effect of feed position on enriched product purity
Crystals transported upwards
Screw speed 100 rpm

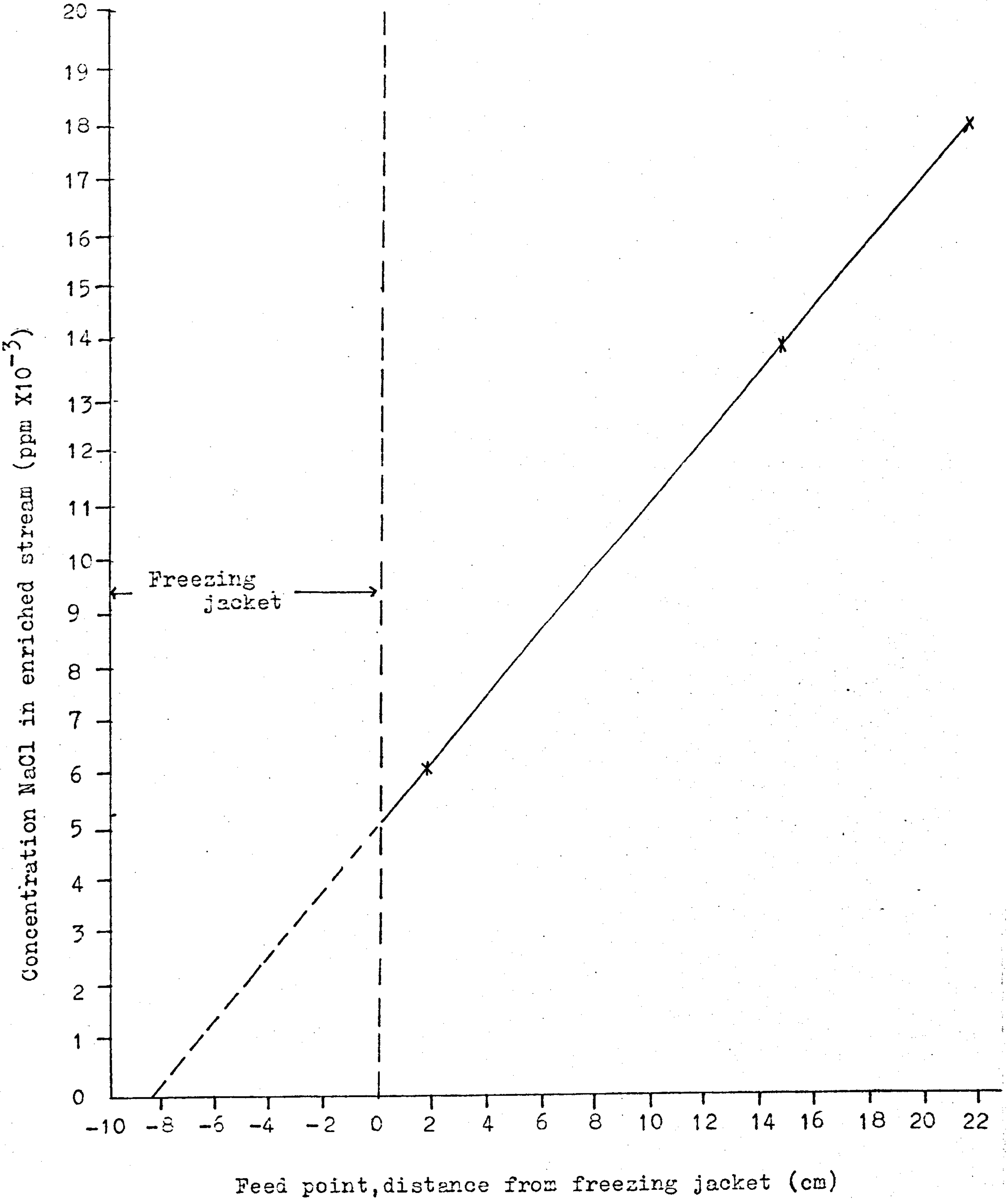


Fig (31) p203

Effect of reflux ratio on the separation obtained in the column at 100 rpm screw speed with crystals transported downwards

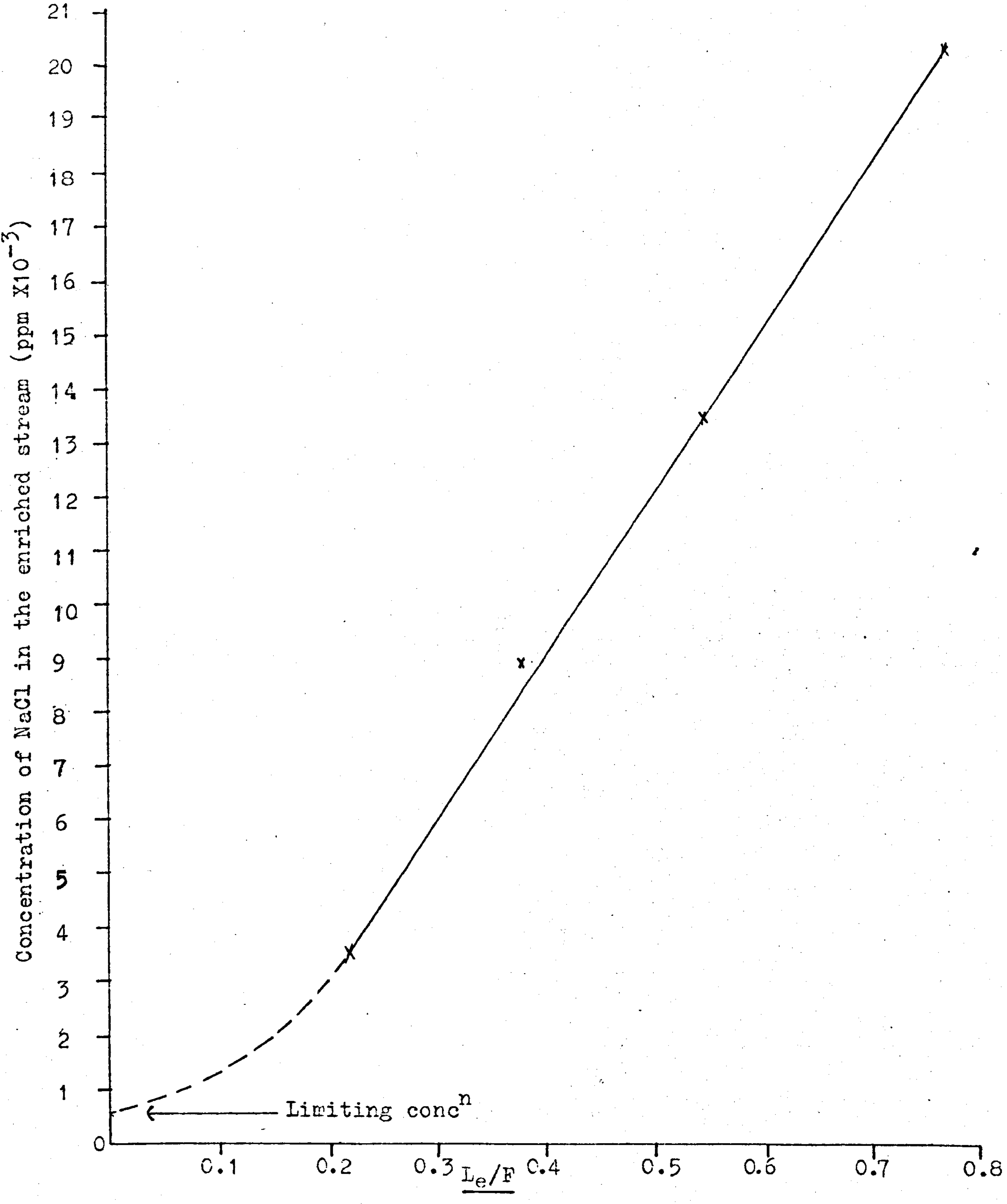


Fig (32)   p204

Effect of crystal production rate on enriched product purity for a screw speed of 100 rpm

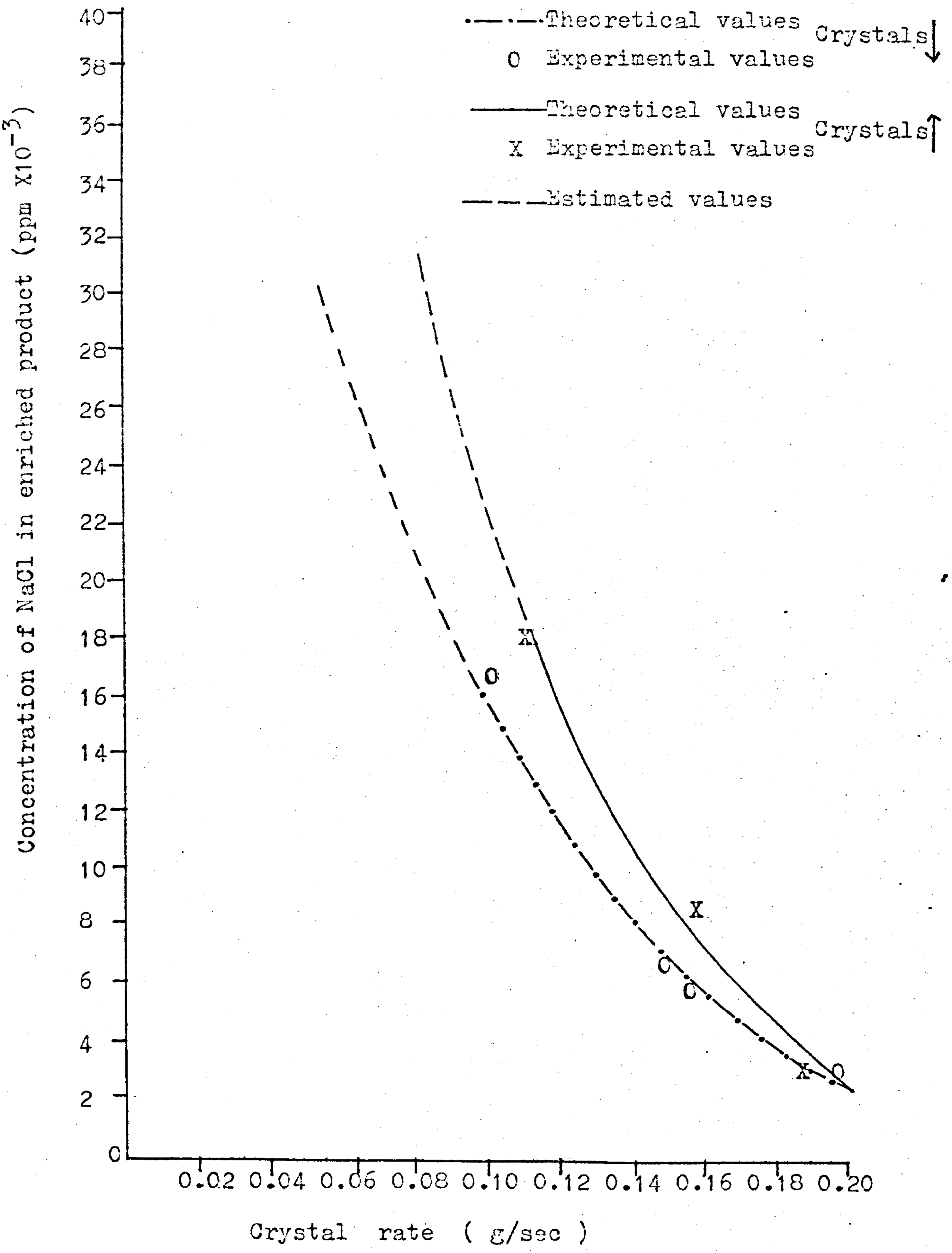


Fig (33) p205

Effect of column length on enriched product purity
Crystals transported upwards
Screw speed 100 rpm

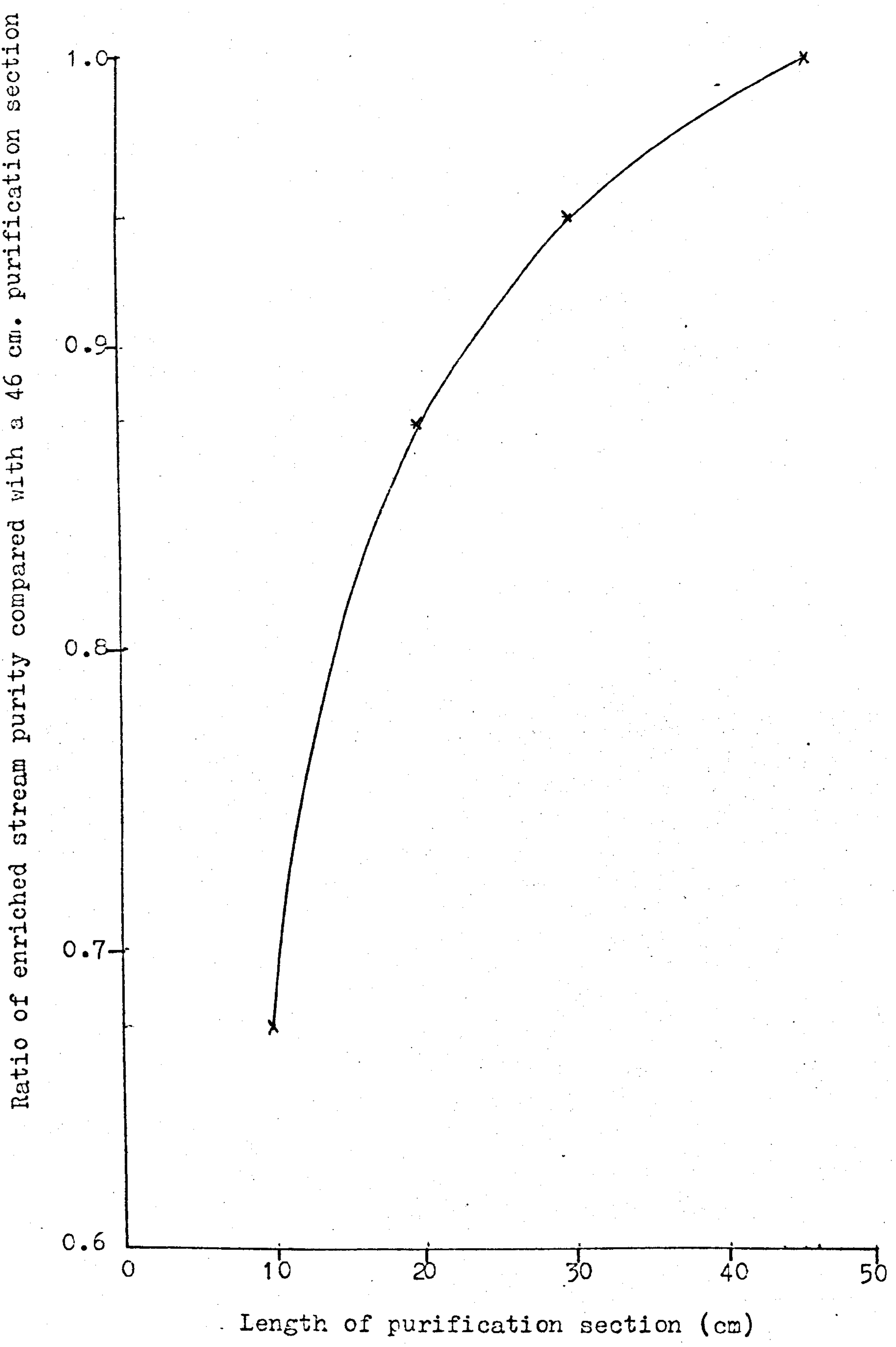
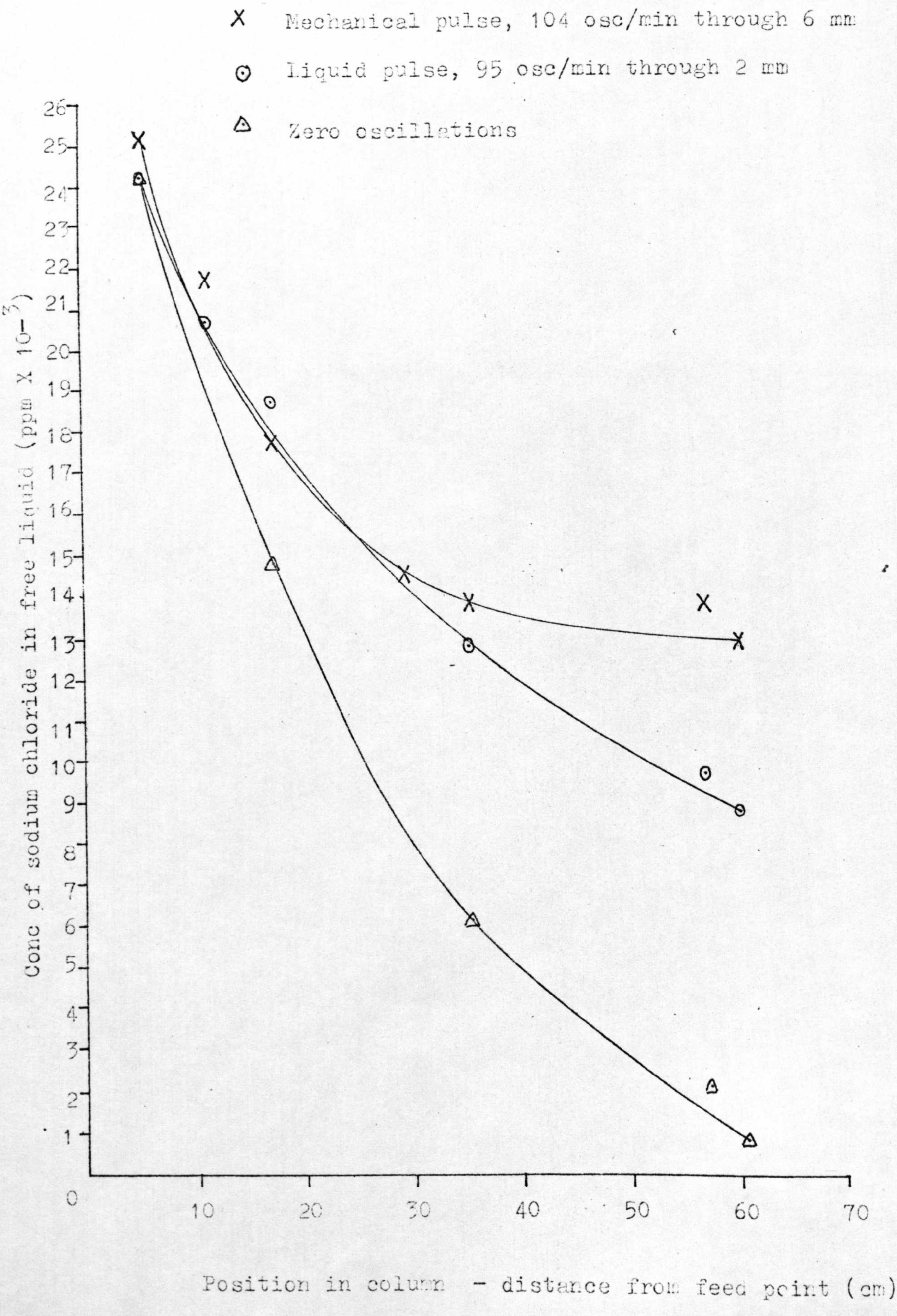


Fig (34) p206

Effect of oscillations on conc profile of impurity in column



Graph of $(Y-Y_p)$ vs $(z-z_F)$ for desalination with a screw speed of 60 rpm and for crystals transported downwards

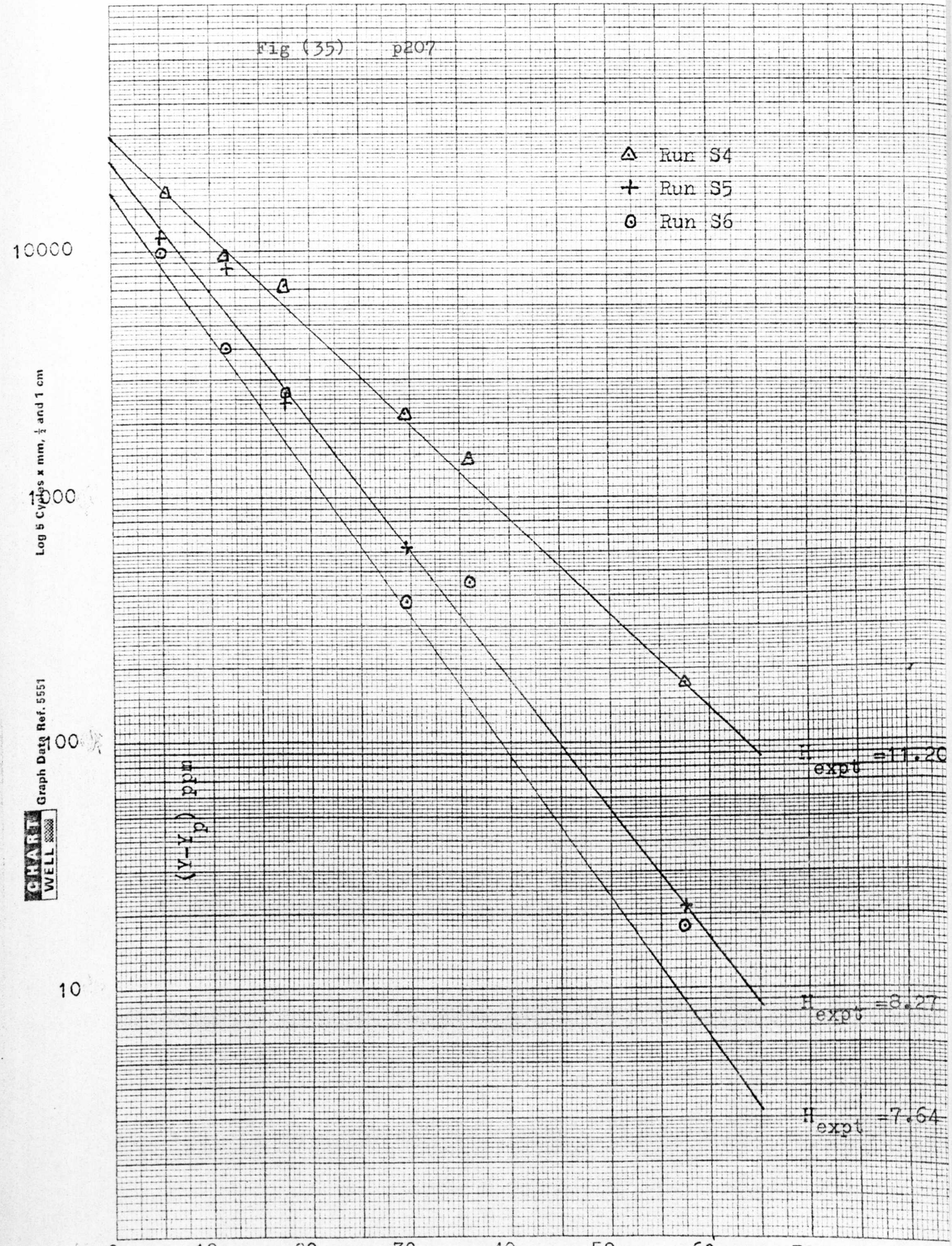


Fig (35) p207

Graph of $(Y-Y_p)$ vs $(z-z_F)$ for desalination with a screw speed of 100 rpm

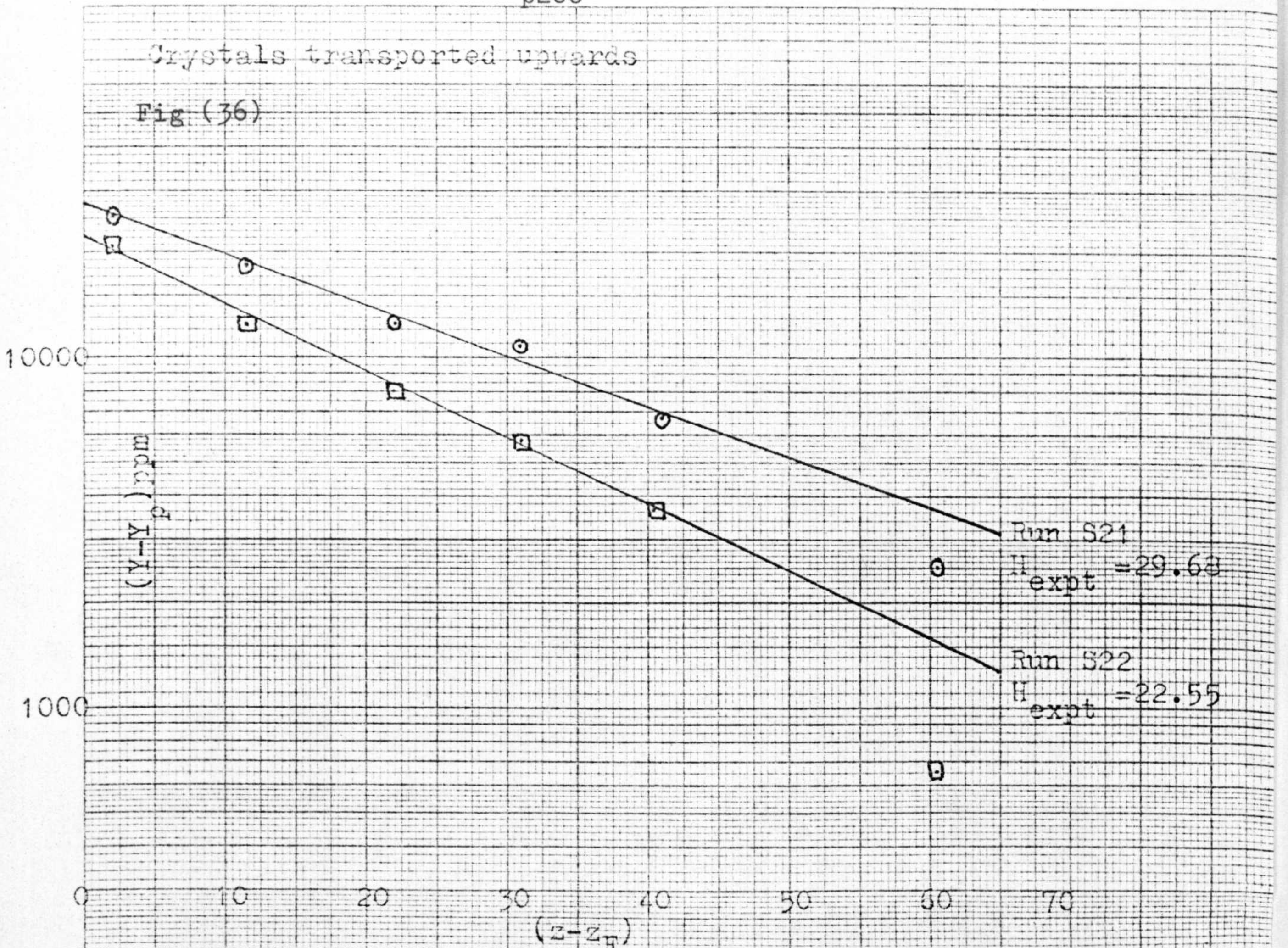


Fig (36)

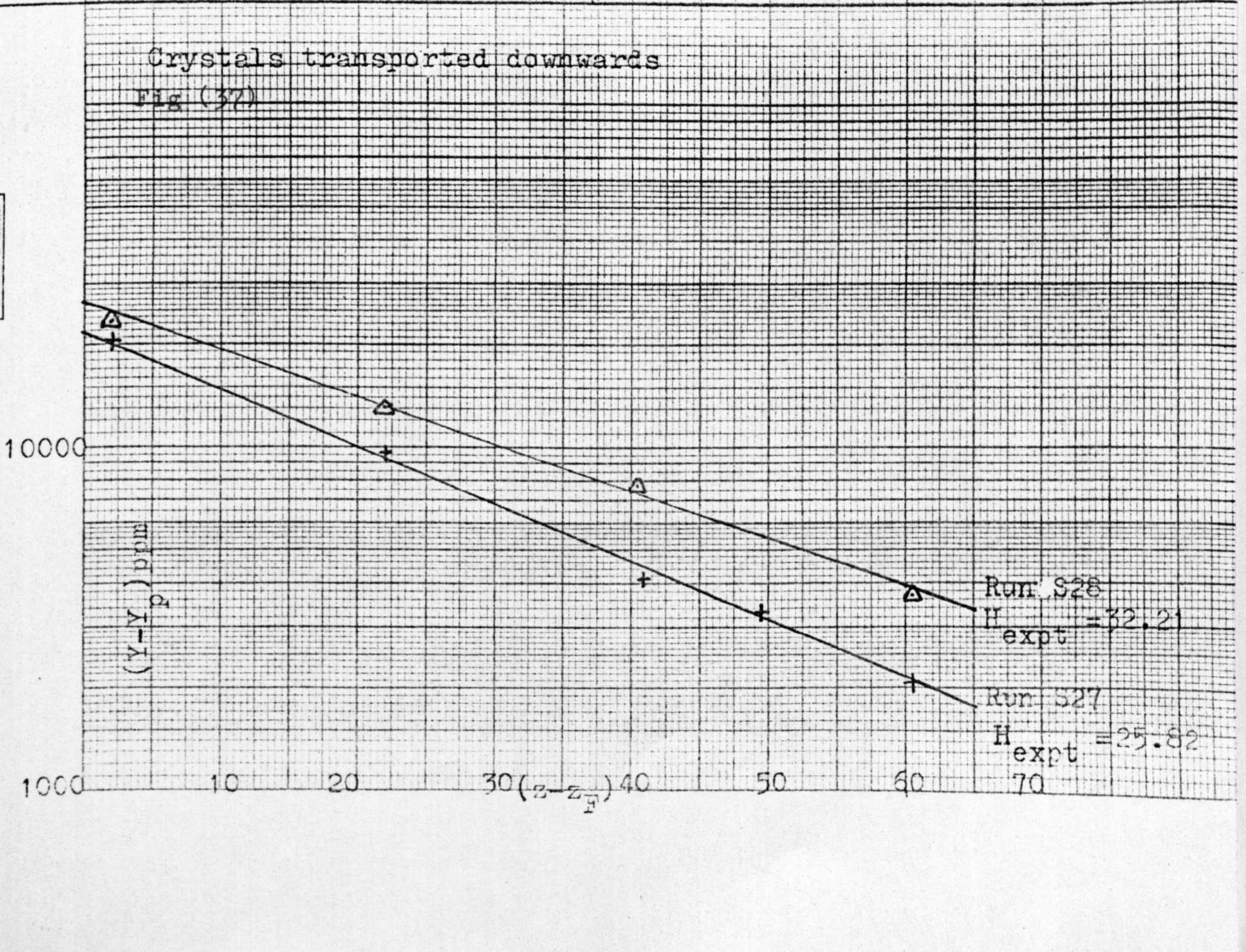


Fig (37)

Calculation of diffusion and mass transfer coefficients for desalination.

As with the benzene/cyclohexane system the constants in equation (48) ;

$$\text{i.e.}\quad H = \frac{1}{C-L_e}\left[D\eta A\rho \quad + \alpha\frac{(1+\alpha)C^2}{KaA\rho} - \alpha L_e C\right]$$

can be evaluated, L_e can be measured experimentally and H and C may be calculated.

Values of constants :-

a) For a 60 rpm screw speed and with crystals ↓
   $A = 12.43$; $\rho = 1.03$; $\alpha = 0.07$; $\eta = 0.18$

b) For a 100rpm screw speed and with crystals ↑
   $A = 12.43$; $\rho = 1.03$; $\alpha = 0.07$; $\eta = 0.16$

c) For a 100rpm screw speed and with crystals ↓
   $A = 12.43$; $\rho = 1.03$; $\alpha = 0.07$; $\eta = 0.18$

a) Run S4 $L_e = 0.139$ g/sec ; $C = 0.180$; $H_{expt} = 11.20$
   Run S5 $L_e = 0.139$ g/sec ; $C = 0.200$; $H_{expt} = 8.27$
   Run S6 $L_e = 0.139$ g/sec ; $C = 0.210$; $H_{expt} = 7.64$

Equation 48) may now be written as a set of simultaneous equations which may be used to solve for D and Ka.

Thus :-

Run S4 $$0.459 = 2.31D + \frac{5.28 \times 10^{-5}}{Ka}$$

Run S5 $$0.505 = 2.31D + \frac{8.20 \times 10^{-5}}{Ka}$$

Run S6 $$0.542 = 2.31D + \frac{9.84 \times 10^{-5}}{Ka}$$

Using a graphical solution to the above equations where D is determined from the intercept and Ka from the slope;

$$\underline{D = 0.16\ \text{cm}^2\text{sec}^{-1}}$$
$$\underline{Ka = 5.56 \times 10^{-4}}\ \text{sec}^{-1}$$

Using these values of D and Ka , theoretical values of H may be determined and compared with those obtained experimentally.

Thus :-

Run no.	$H_{experimental}$	$H_{theoretical}$	Error
S4	11.20	11.34	1.3%
S5	8.27	8.49	2.8%
S6	7.64	7.71	1.0%

These theoretical values of H can now be substituted in equation (47)

i.e. $$\frac{Y - Y_p}{Y_0 - Y_p} = \exp -\left(\frac{z - z_F}{H}\right)$$

in order to compare theoretical concentration profiles with those obtained by experiment.

For Run S4 Y_0 =30600ppm ; Y_p =627ppm

For Run S5 Y_0 =22500ppm ; Y_p =489ppm

For Run S6 Y_0 =17125ppm ; Y_p =125ppm

Thus :-

Position in column $(z-z_F)$ cm.	Theoretical impurity content (Y)ppm Run S4	Run S5	Run S6
0	30600	22500	17125
10	13048	6648	4772
20	5770	2386	1395
30	2756	1073	472
40	1509	669	220
50	992	544	151
60	778	508	132
70	690	494	127

Reference to fig38(a),(b),(c) allows a comparison between these theoretical profiles and the experimentally obtained results.

In the analysis of the enriching section of the column it is possible to determine a theoretical optimum crystal rate by differentiating equation (48) with respect to C. This value was calculated to be 0.330 g/sec for a screw speed of 60 rpm and with crystals transported downwards.

b) Run S21 L_e =0.142 g/sec ; C =0.151 ; H_{expt} =29.68
Run S22 L_e =0.158 g/sec ; C =0.184 ; H_{expt} =22.55

Thus the simultaneous equations obtained are :-

Run S21 $$0.27 = 2.05D + \frac{1.62 \times 10^{-5}}{Ka}$$

Run S22 $$0.59 = 2.05D + \frac{3.91 \times 10^{-5}}{Ka}$$

Whence $\underline{D = 1.96 \times 10^{-2} \ cm^2 sec^{-1}}$

and $\underline{Ka = 7.16 \times 10^{-5} \ sec^{-1}}$

These values can now be used to calculate H.

Thus :-

Run no.	$H_{experimental}$	$H_{theoretical}$	Error
S21	29.68	29.60	0.3%
S22	22.55	22.55	0

By using the calculated values of H the theoretical and experimental concentration profiles may be compared.

For Run S21 Y_{ϕ} =32000ppm ; Y_p =4500ppm
For Run S22 Y_{ϕ} =24600ppm ; Y_p =2100ppm

Thus :-

Position in column ($z-z_F$) cm	Theoretical impurity content (Y)ppm	
	Run S21	Run S22
0	32000	24600
10	24116	16541
20	18492	11368
30	14481	8049
40	11620	5918
50	9578	4550
60	8123	3672
70	7084	3109

Reference to fig38(d)and (e) allows a comparison between these values and those obtained experimentally.
By differentiation of equation (48) with respect to C the theoretical optimum crystal rate was determined as 0.205 g/sec.

c) Run S27 $L_e = 0.158$ g/sec ; $C = 0.190$; $H_{expt} = 25.82$
Run S28 $L_e = 0.139$ g/sec ; $C = 0.148$; $H_{expt} = 32.21$

Thus the simultaneous equations obtained are :-

Run S27 $0.83 = 2.30D + \frac{0.47 \times 10^{-4}}{Ka}$

Run S28 $0.29 = 2.30D + \frac{0.15 \times 10^{-4}}{Ka}$

Whence $\underline{D = 1.63 \times 10^{-2} \ cm^2 sec^{-1}}$

and $\underline{Ka = 5.93 \times 10^{-5} \ sec^{-1}}$

These values can now be used to calculate H.

Thus :-

Run no.	$H_{experimental}$	$H_{theoretical}$	Error
S27	25.82	25.94	0.5%
S28	32.21	32.27	0.2%

By using the calculated values of H the theoretical and experimental concentration profiles may be compared.

For Run S27 $Y_{\phi} = 21900$ppm ; $Y_p = 401$ppm
For Run S28 $Y_{\phi} = 26500$ppm ; $Y_p = 1000$ppm

Thus :-

Position in column $(z-z_F)$ cm	Theoretical impurity content (Y)ppm Run S27	Run S28
0	21900	26500
10	15023	19705
20	10346	14720
30	7165	11065
40	5001	8383
50	3529	6415
60	2529	4972
70	1848	3914

Reference to fig38(f) and (g) allows a comparison between these values and those obtained experimentally.
By differentiation of equation (48) with respect to C the theoretical optimum crystal rate was determined as 0.202 g/sec.

Fig (38,a)

Effect of position in column on conc^{n} of sodium chloride in free liquid

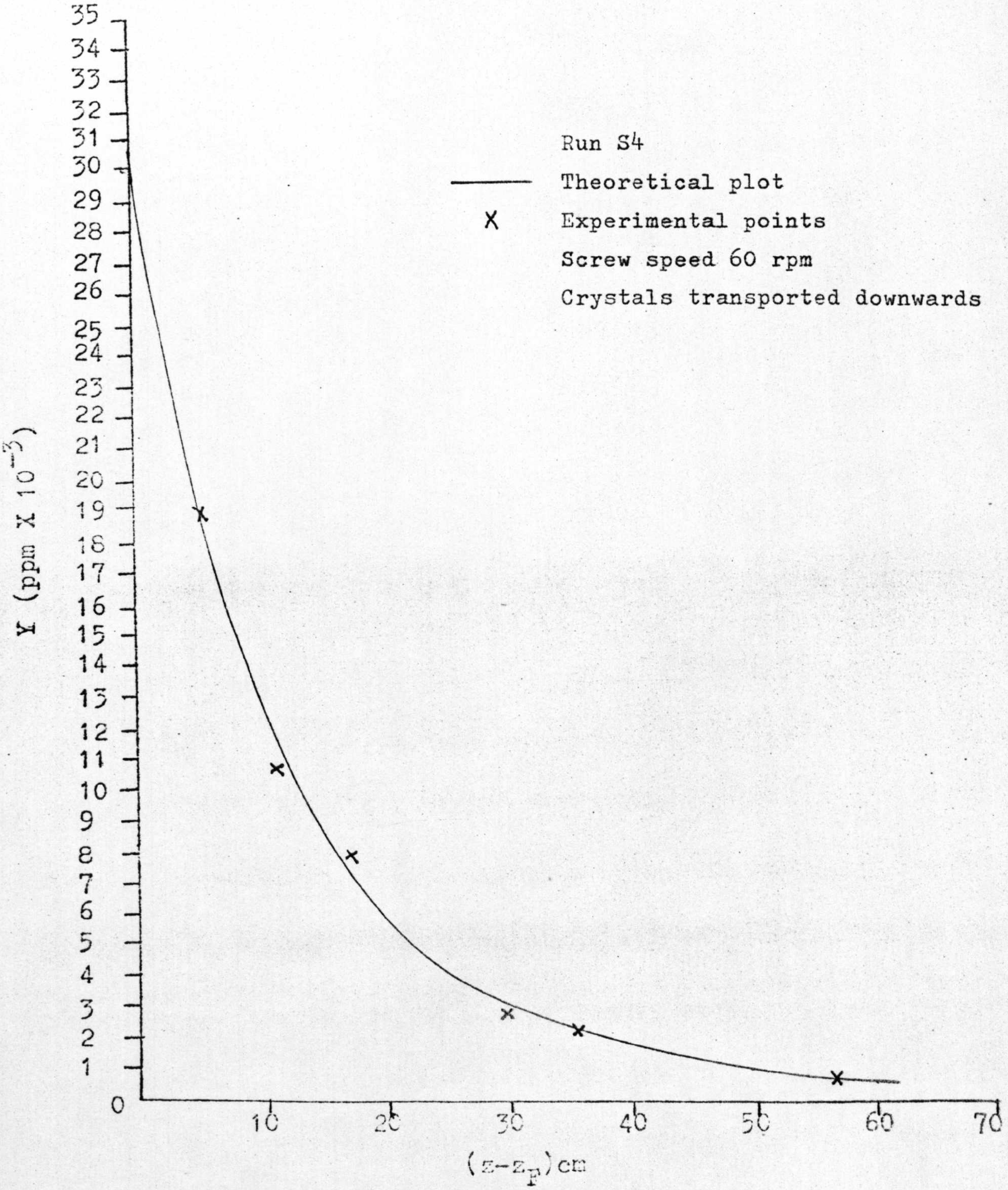


Fig (38,b)

Effect of position in column on conc^n of sodium chloride in free liquid

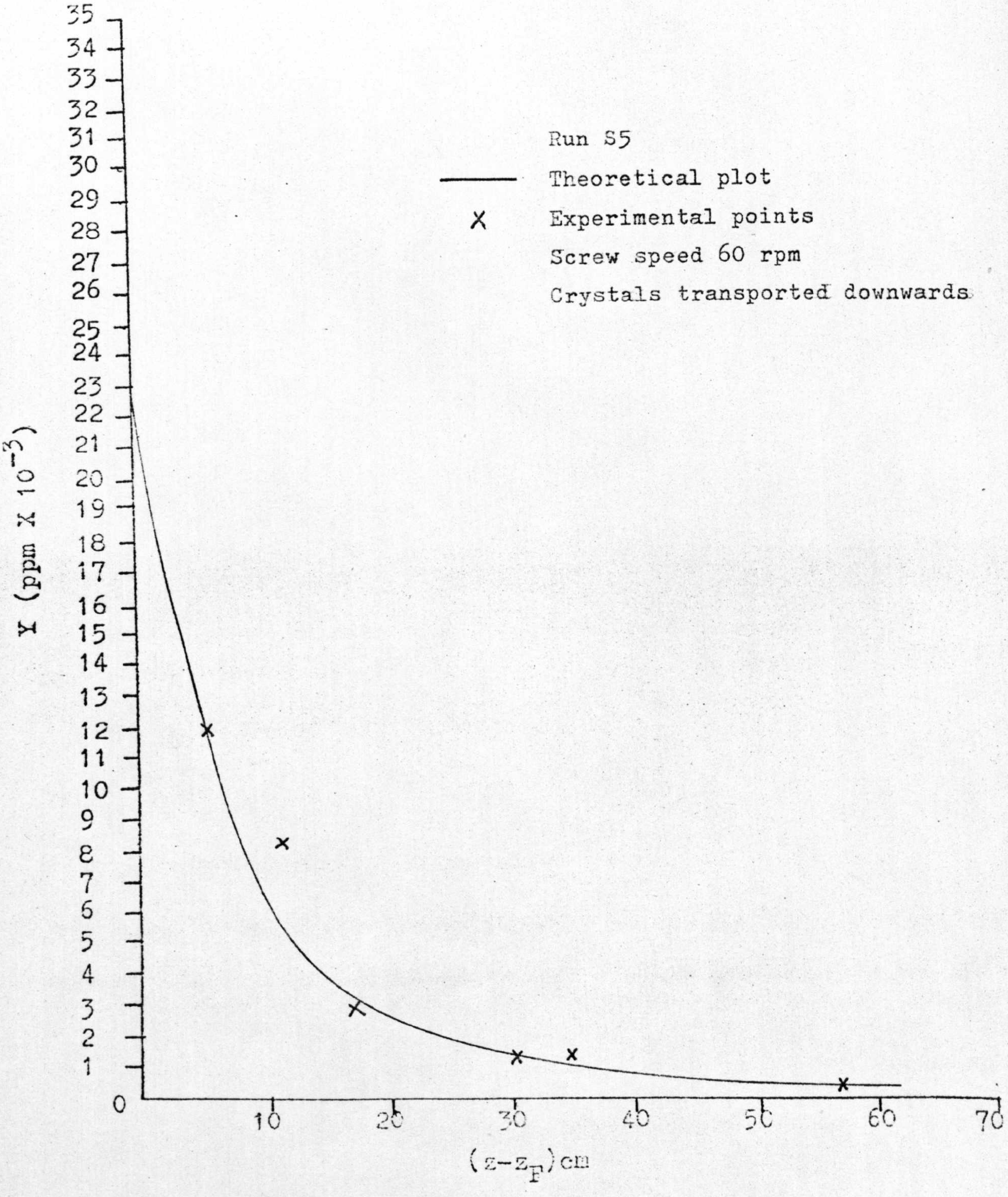


Fig (38,c)

Effect of position in column on conc^n
of sodium chloride in free liquid

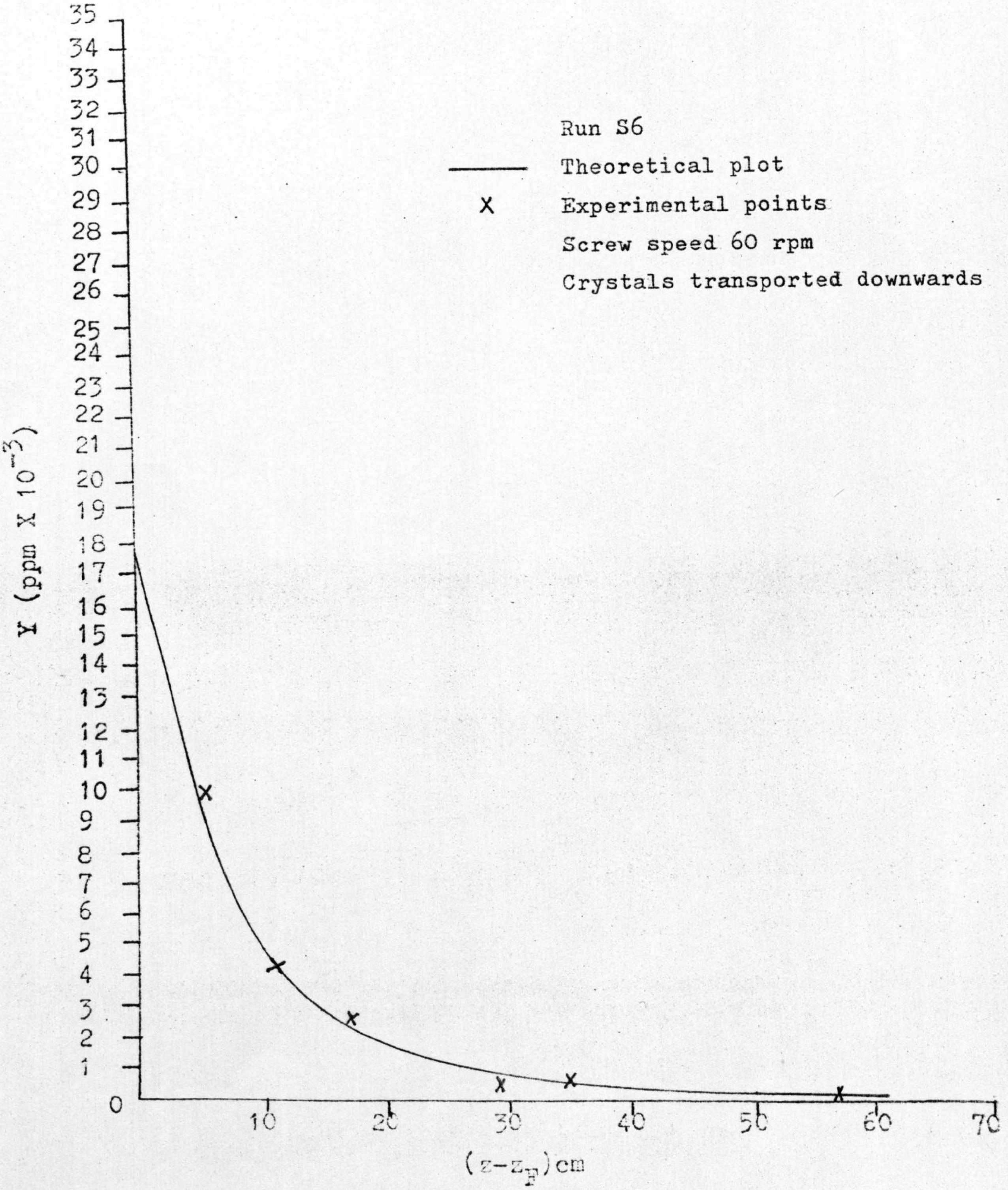


Fig 38,d)

Effect of position in column on conc^n of sodium chloride in free liquid

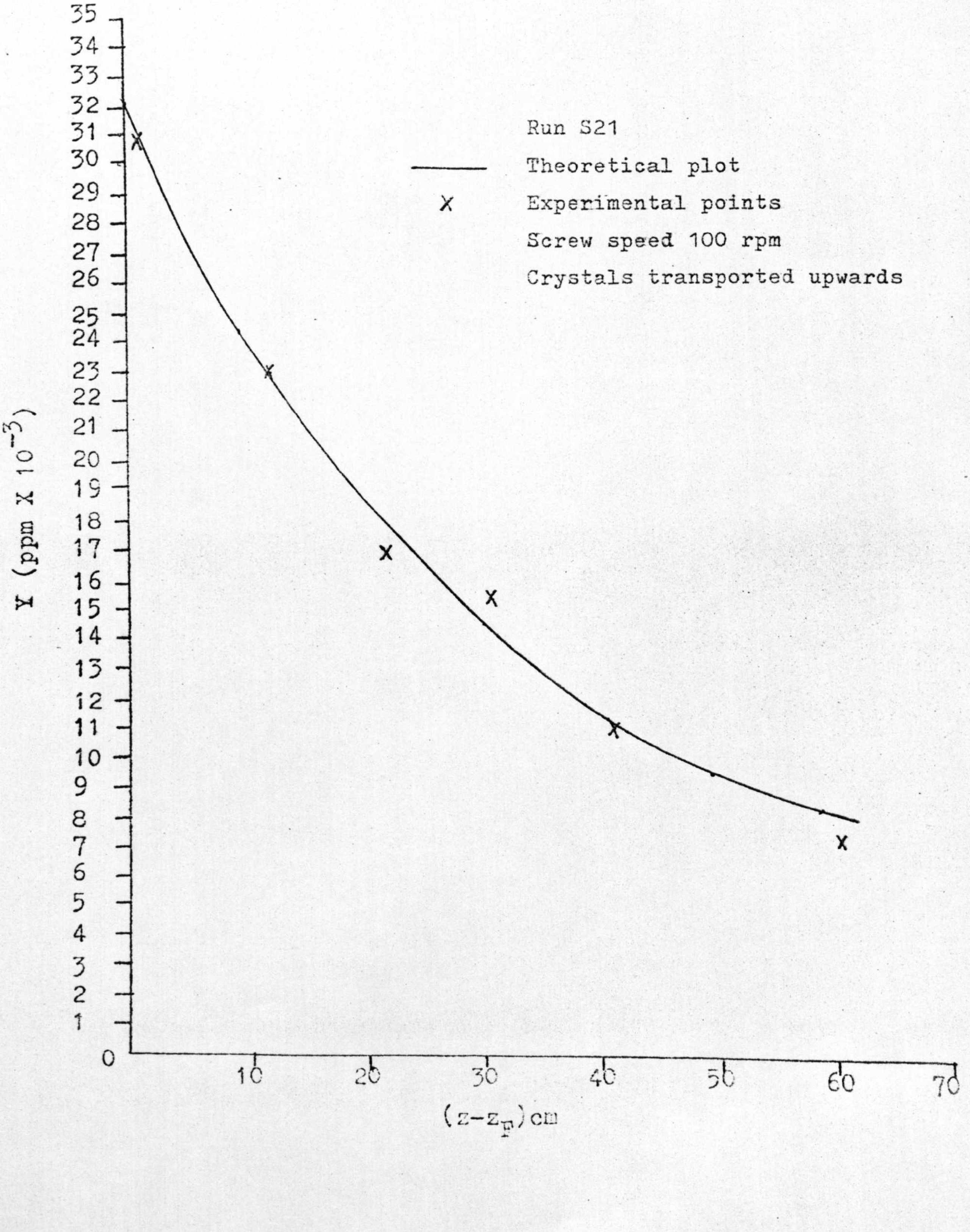


Fig (38,e)

Effect of position in column on conc^n of sodium chloride in free liquid

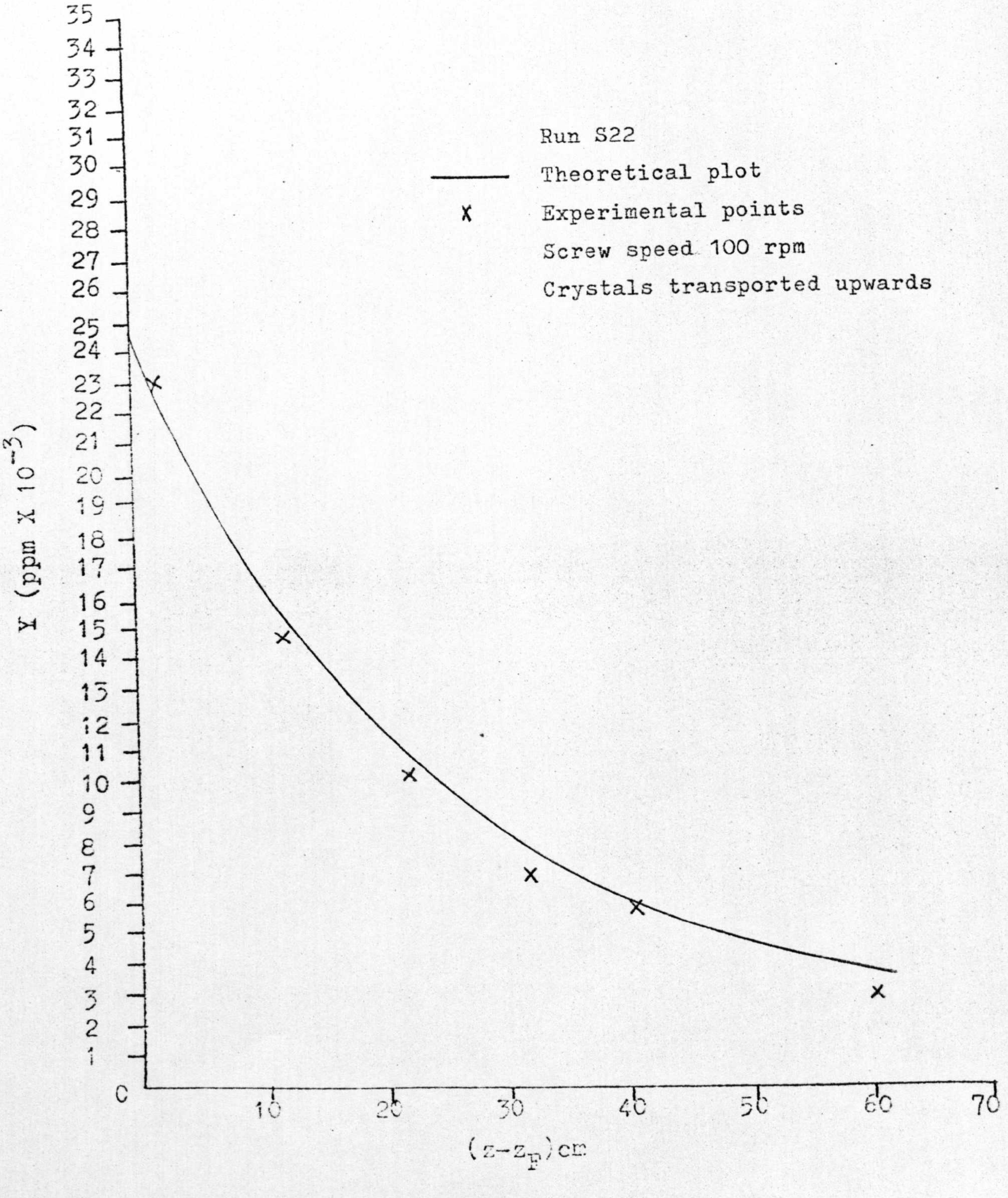


Fig (38,f)

Effect of position in column on conc^n of sodium chloride in free liquid

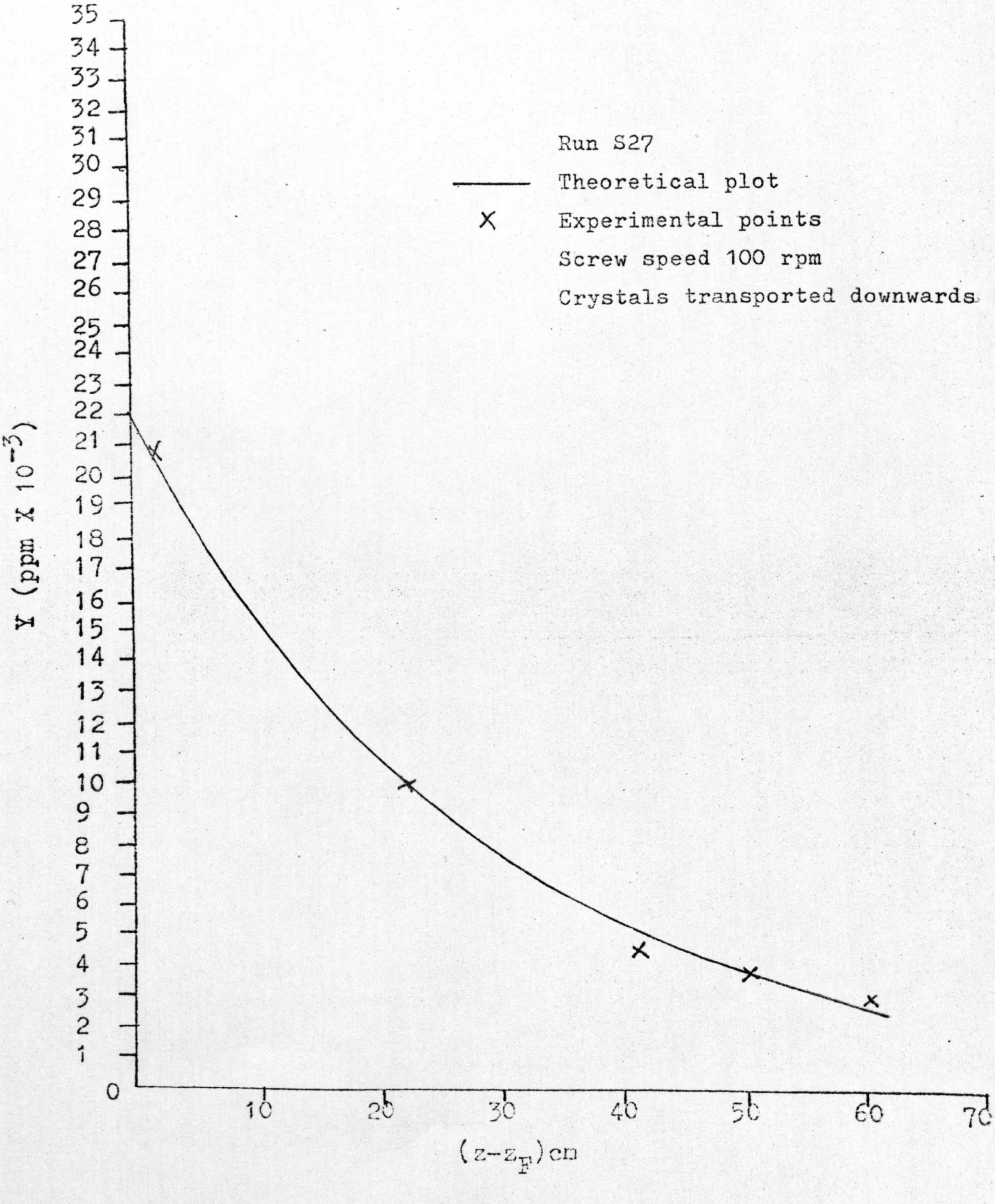
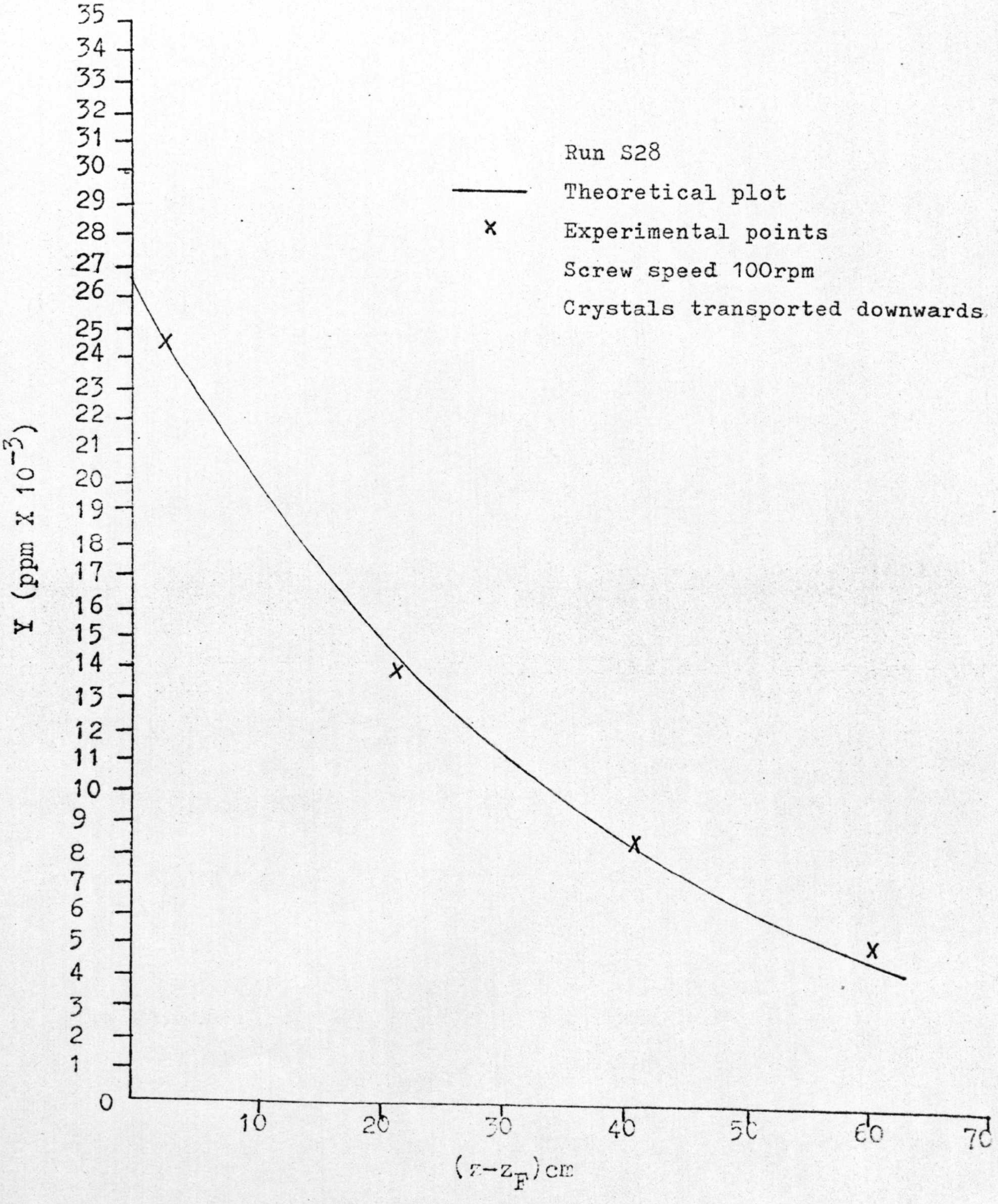


Fig (38,g)

Effect of position in column on conc^n of sodium chloride in free liquid



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Ethanol concentration   Experimental results

Column length 93 cm.   Column volume 1020 ml.   Crystal direction downwards

Run no.	Feed rate (g/hr)	Feed composition %EtOH by wt	Feed point, distance from freezing jacket (cm)	Top product rate (ml/hr)	Top product composition %EtOH by wt	Base product rate (ml/hr)	Base product composition %EtOH by wt	Crystal rate (g/sec)	Screw speed (rpm)
1	1080	20.0	1.0	/	/	/	/	/	100
2	1080	20.0	1.0	320	/	775	/	/	100
3	1080	10.9	1.0	320	19.0	775	2.8	/	100
4	1080	9.9	1.0	320	18.6	780	5.6	/	100
5	1070	9.9	1.0	300	18.7	800	6.0	/	80
6	1100	9.8	1.0	300	20.2	780	5.7	0.198	60
7	1100	9.8	1.0	290	19.1	800	5.8	/	53
8	1080	9.8	19.0	310	19.0	780	6.1	/	60
9	1080	9.8	7.0	300	19.4	780	5.4	/	60
10	1080	10.0	30.0	290	18.9	780	6.0	/	60
11	1070	9.9	1.0	290	16.5	790	7.2	0.153	60
12	1070	9.9	1.0	300	18.5	790	6.4	0.173	60
13	1070	9.9	1.0	300	21.4	780	4.5	0.239	60
14	1070	9.9	1.0	640	16.0	400	0.2	/	60
15	1070	9.8	1.0	500	18.5	600	2.3	/	60
16	1550	3.3	1.0	1280	6.3	270	0.2	/	60
17	1550	3.3	1.0	270	4.6	1280	0.3	/	60
18	1080	14.0	1.0	290	25.8	800	10.0	/	60

Notes

Run no.	
1,2	Failures since the ethanol conc was too high for the refrigeration equipment, no crystals formed
3	Insufficient cooling to feed line
4	Improved feed pre-cooler installed
16	Top and base product rates in g/hr
17	As 16 + crystal direction - upwards (Thus 4.6% EtOH refers to enriched stream and 0.3% EtOH to stripped stream)

Table (9)

Ethanol concentration   Experimental results

Concentration profile

Run no.	% Ethanol by wt in free liquid Distance from feed point ($z-z_F$) in cm.							
	-31.5	5.5	11.5	17.5	29.5	35.5	57.5	60.5
3	19.0	/	10.0	9.8	8.2	8.4	3.0	2.8
4	18.6	/	9.7	9.0	6.1	6.8	5.8	5.6
5	18.7	10.1	9.6	9.0	7.3	7.1	/	6.0
6	20.2	10.2	9.5	9.1	7.8	7.5	/	5.7
7	19.1	10.5	9.9	8.6	7.2	6.6	6.6	5.8
8	19.0	10.9	9.8	9.6	8.2	7.8	/	6.1
9	19.4	11.2	9.3	8.7	7.7	7.4	/	5.4
10	18.9	8.7	8.1	7.4	7.2	6.6	6.3	6.0
11	16.5	10.3	9.5	8.9	7.4	7.0	/	7.2
12	18.5	9.7	8.7	8.6	6.5	6.3	/	6.4
13	21.4	9.8	9.2	7.9	/	/	4.8	4.5
14	16.0	2.7	1.2	0.7	0.3	0.3	0.2	0.2
15	18 5	10.3	10.2	10.2	9.1	5.0	2.9	2.3
16	6.3	/	/	/	/	/	/	0.2
17*	0.3	/	/	/	/	/	/	4.6
18	25.8	15.0	13.7	/	13.1	12.1	/	10.0

Notes

* Crystals transported upwards

Fig (39) p222

Effect of screw speed on ethanol concentration in the top product for crystals transported downwards

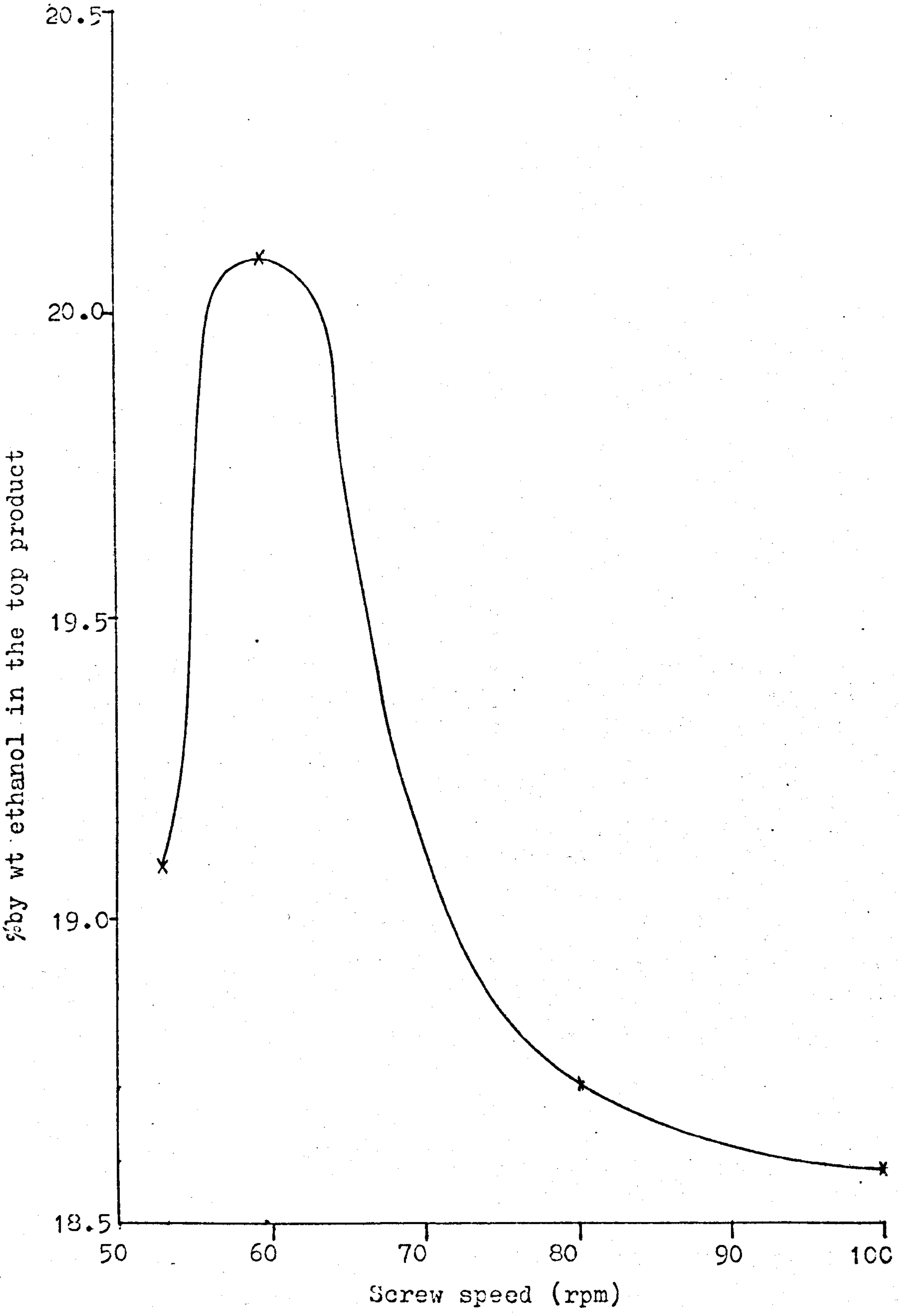


Fig (40).   p223

Effect of feed position on the concentration of ethanol in the top product for crystals transported downwards and a screw speed of 60 rpm

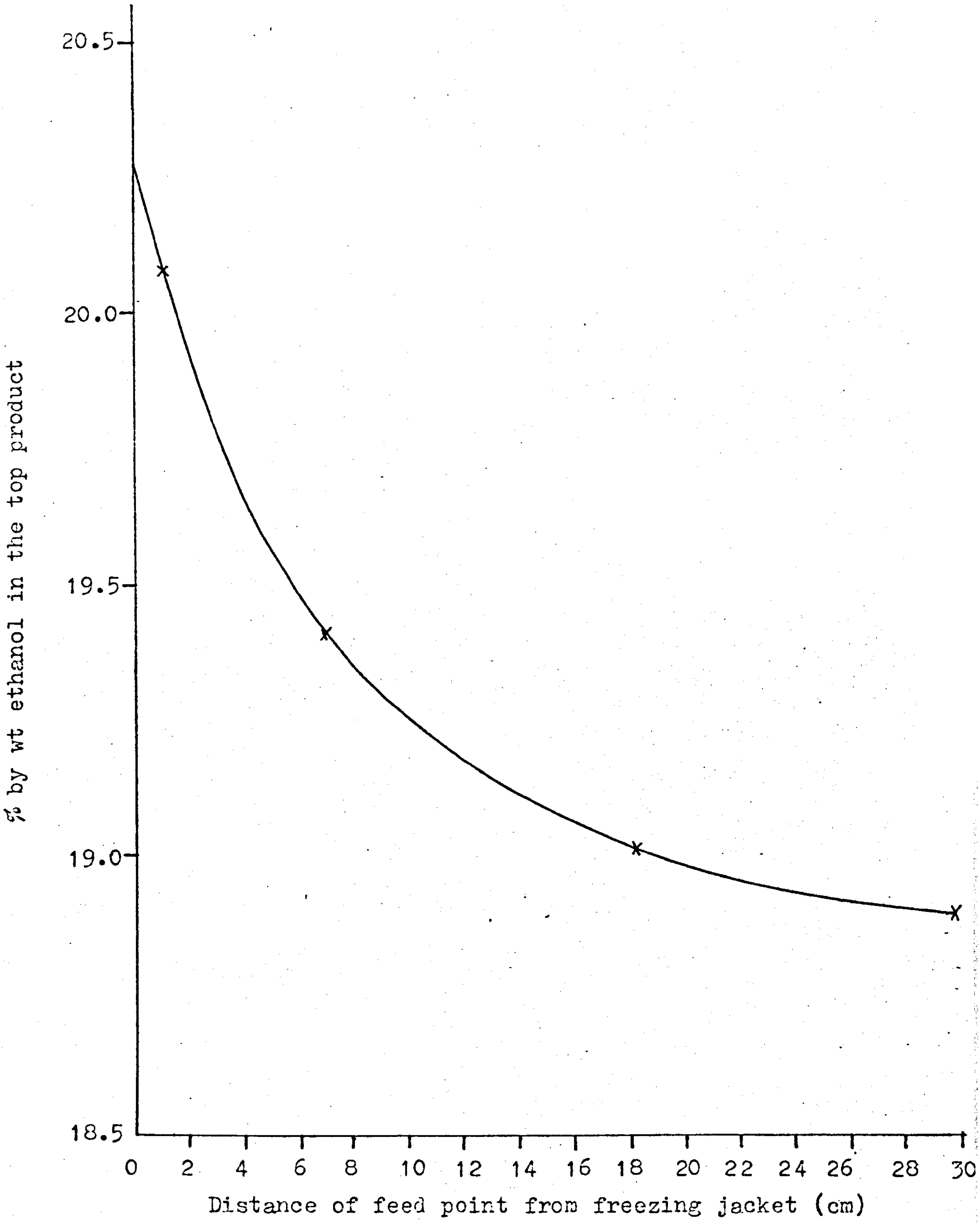


Fig (41)

Effect of removal rate on ethanol content of the top product for crystals transported downwards and 60 rpm screw speed

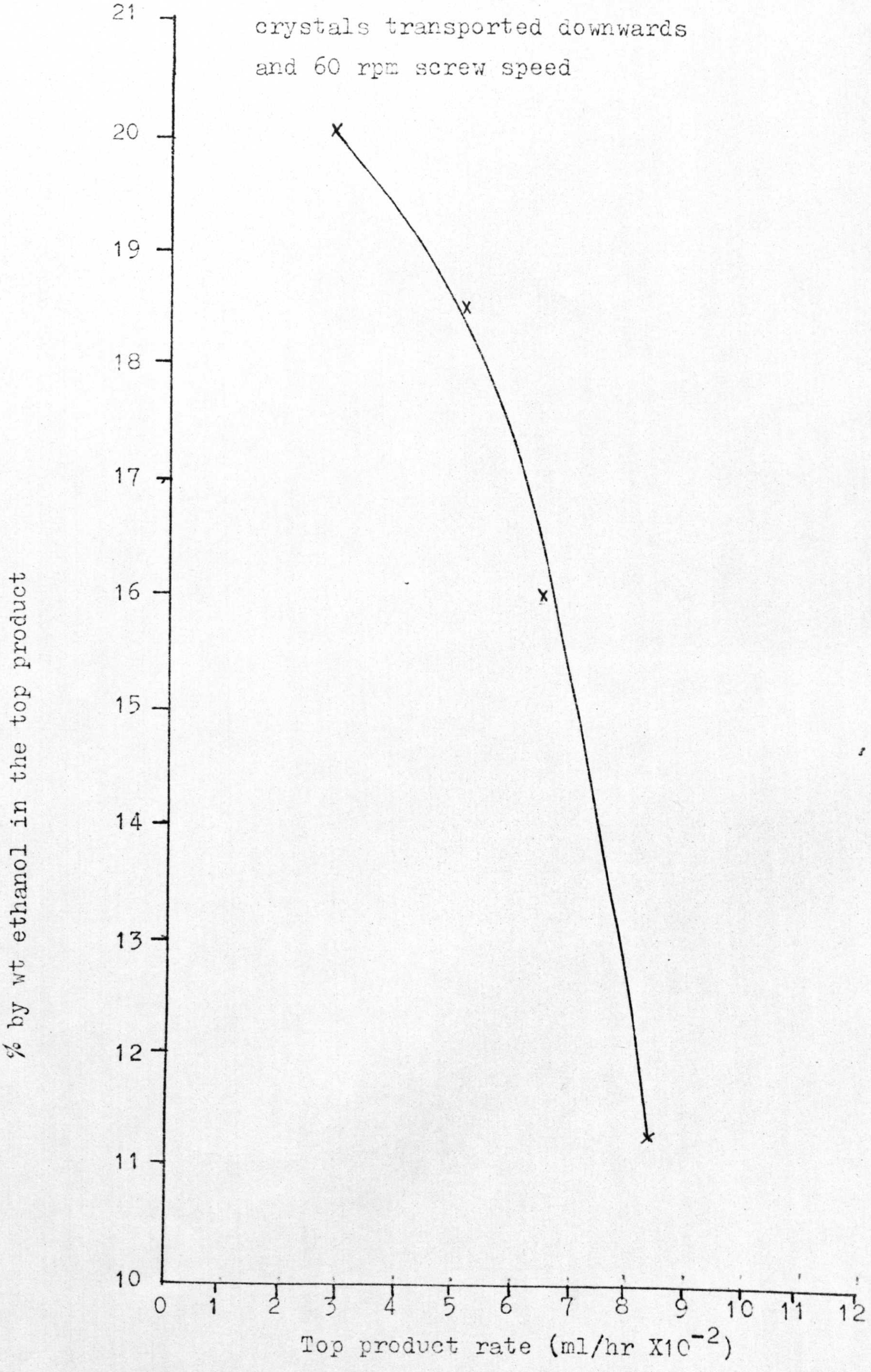
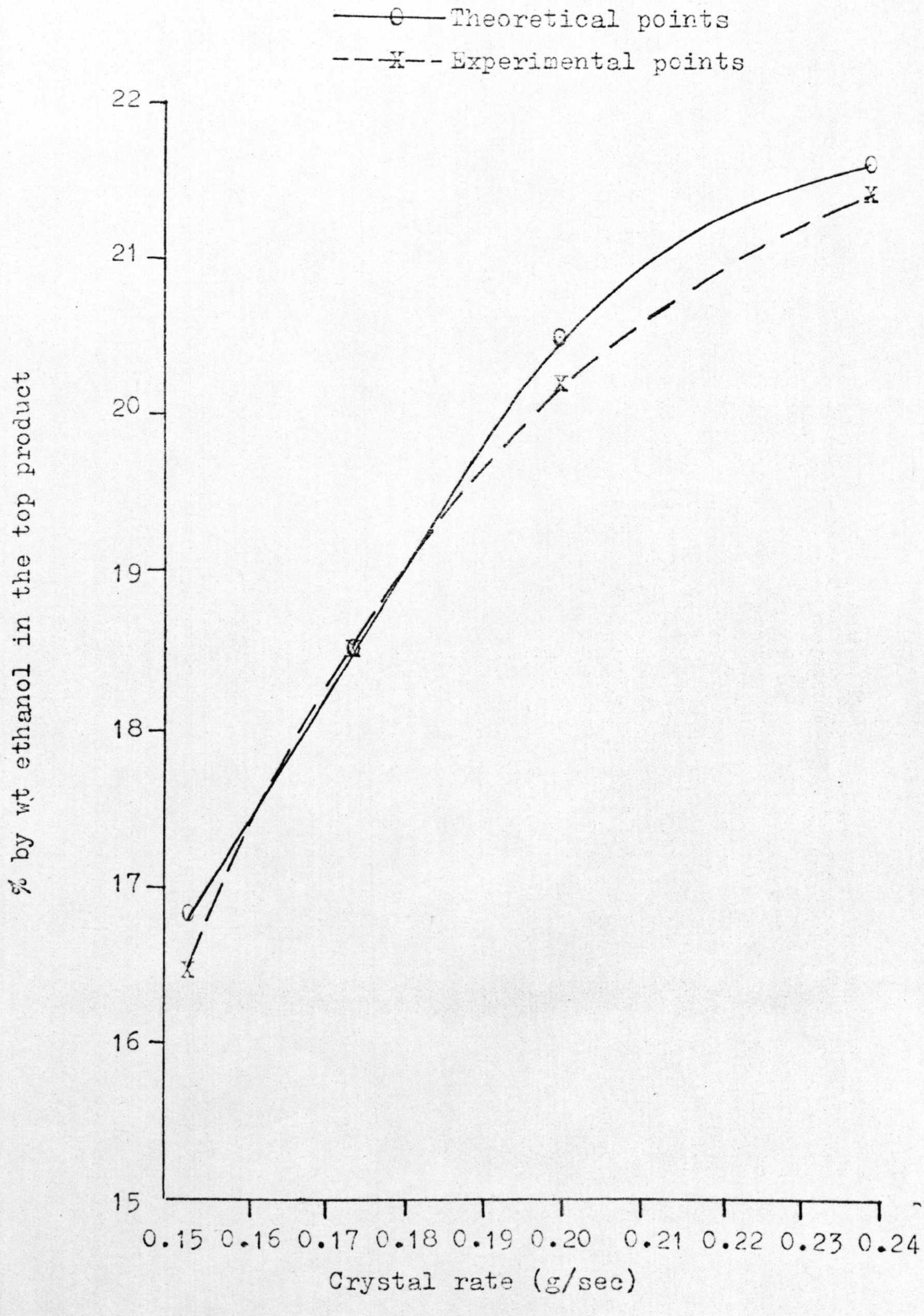


Fig (42) p225

Effect of crystal rate on the concentration of ethanol in the top product for crystals transported downwards and a screw speed of 60 rpm



Calculation of diffusion and mass transfer coefficients for the concentration of ethanol in aqueous solution.

Now, from Powers(72)

$$\overline{H} = \frac{1}{C+L_s}\left[D\eta A\rho + \frac{\alpha(1+\alpha)C^2 + \alpha L_s C}{KaA\rho}\right] \quad (53)$$

for the stripping section of the column.

By evaluating the constants η, A, ρ, α, and by measuring the value of L_s for different crystal production rates, the diffusion and mass transfer coefficients may be determined.

Values of constants :-

$A\rho = 12.16$; $\alpha = 0.34$; $\eta = 0.24$; $L_s = 0.081$ g/sec

For Run 13 $C = 0.239$ g/sec ; $\overline{H}_{expt} = 22.85$

For Run 6 $C = 0.198$ g/sec ; $\overline{H}_{expt} = 22.64$

For Run 12 $C = 0.173$ g/sec ; $\overline{H}_{expt} = 22.36$

For Run 11 $C = 0.153$ g/sec ; $\overline{H}_{expt} = 22.57$

Substitution of these values into equation (53) produces simultaneous equations which may be solved to determine the diffusion and overall mass transfer coefficients.

i.e.

Run 13 $7.25 = 2.92D + \frac{2.68 \times 10^{-3}}{Ka}$

Run 6 $6.30 = 2.92D + \frac{1.91 \times 10^{-3}}{Ka}$

Run 12 $5.68 = 2.92D + \frac{1.52 \times 10^{-3}}{Ka}$

Run 11 $4.89 = 2.92D + \frac{0.93 \times 10^{-3}}{Ka}$

whence $\underline{D = 1.24 \pm 0.02 \text{ cm}^2\text{sec}^{-1}}$

and $\underline{Ka = (0.74 \pm 0.02) \times 10^{-3} \text{ sec}^{-1}}$

Now the theoretical values of $\overline{H}$ may be determined if the diffusion and overall mass transfer coefficients are substituted in equation (53).

Thus:-

Run no.	$\bar{H}$ experimental	$\bar{H}$ theoretical	Error
13	22.85	22.66	0.9%
6	22.64	22.23	1.9%
12	22.36	22.34	0.1%
11	22.57	22.50	0.4%

Using the theoretical values of $\bar{H}$ in equation (51)

i.e.

$$\frac{Y-\bar{Y}_p}{Y_\phi-\bar{Y}_p} = \exp -\frac{(z-z_F)}{\bar{H}}$$

the concentration of ethanol in the stripped stream can be calculated and compared with the experimental values.

For Run 13 $Y_\phi=11.6$; $\bar{Y}_p=8.2$

For Run 6 $Y_\phi=11.4$; $\bar{Y}_p=8.4$

For Run 12 $Y_\phi=11.0$; $\bar{Y}_p=8.5$

For Run 11 $Y_\phi=10.6$; $\bar{Y}_p=8.6$

Thus:-

Run no.	Experimental Y_s	Theoretical Y_s	Error
13	21.4%	21.6%	1.0%
6	20.2%	20.5%	1.5%
12	18.5%	18.5%	0
11	16.5%	16.8%	1.8%

For the analysis of the stripping section of the column, differentiation of equation (53) using the values of the diffusion and overall mass transfer coefficients will only allow a determination of a minimum value of $\bar{H}$, whereas, for a high concentratio of ethanol in the stripped stream $\bar{H}$ should be large. Therefore there is no theoretical optimal crystal rate and the ethanol content of the stripped stream should continue rising as the crystal rate is increased.

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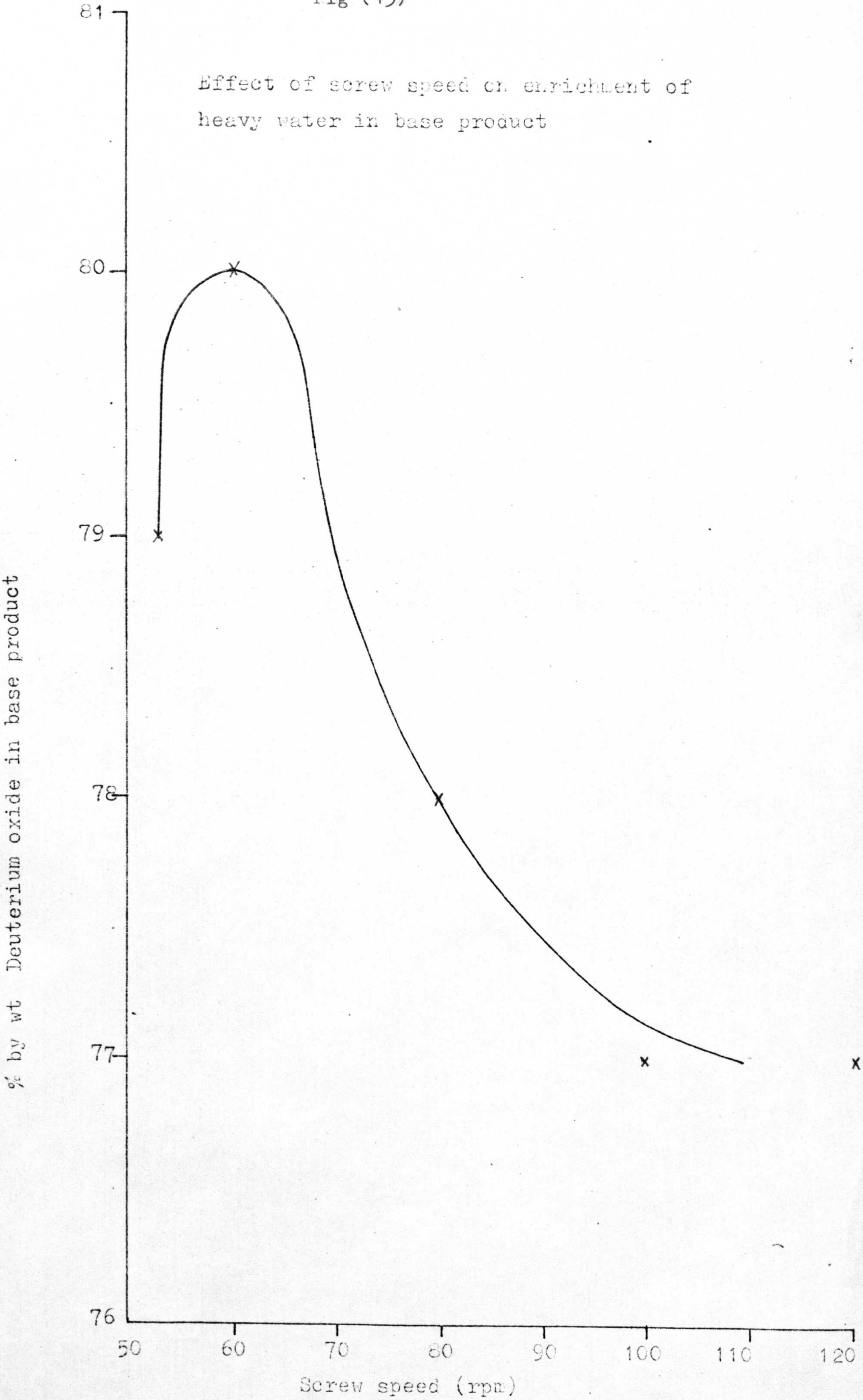
Table (10)

Deuterium oxide Experimental results

Feed 75% by wt deuterium oxide in distilled water
+3% by wt ethanol
Feed point 0.5 cm from freezing jacket
Feed rate 1000 g/hr
Enriched product rate 240 g/hr
Stripped product rate 760 g/hr
Crystal rate 0.142 g/sec (using latent heat of fusion of 75.8 cal/g ( )
Crystal direction ↓
Column length 93 cm
Oscillations Zero

Run no.	SCREW SPEED (RPM)	Conc of deuterium oxide in enriched product (% by wt)
D1	80	78
D2	100	77
D3	120	77
D4	60	80
D5	53	79

Fig (43)



Effect of screw speed on enrichment of heavy water in base product