

**THE EFFECTS OF FREQUENCY AND AMPLITUDE IN A PULSED
EXTRACTION COLUMN EMPLOYING THE SYSTEM
CARBON TETRACHLORIDE-ACETIC ACID-WATER**

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INTRODUCTION

Liquid-liquid extraction, often referred to as solvent extraction, is an important unit operation involving two basic steps: (a) the intimate mixing of an insoluble or slightly soluble liquid solvent with a solution containing a solute which is to be extracted into the solvent, and (b) the separation of the liquid solvent phase from the liquid solution phase. Liquid-liquid extraction processes have been used industrially as a means of chemical separation and purification when other unit operations such as adsorption or distillation are less economical or impossible. Such processes have become particularly important during recent years in the vital field of nuclear research and development. Separation of radiochemical solutions requires that extraction equipment have the characteristics of efficiency, mechanical simplicity, and flexibility. Work in this field has led to the development of many improved types of liquid-liquid extractors.

Liquid-liquid extraction equipment may be divided into two major categories: (a) single-stage extractors, and (b) multistage extractors. In single-stage extractors, the two liquid phases are mixed, extraction occurs,

and the insoluble liquids are settled and separated. A series of such single-stage extractors may be arranged to obtain greater overall extraction efficiency. The mixer-settler is the most important type of extractor in this category at present. In multistage extractors the equivalent of many stages may be incorporated into a single unit. Some extractors in this category are: (a) centrifugal extractors, (b) vertical flow columns such as packed, perforated-plate, spray columns, etc., and (c) oscillary flow vertical columns, including the perforated-plate pulse column. Each of the four types of extractors cited has distinct advantages and disadvantages. The best type for a given extraction operation depends on the nature of the application. A complete comparison of the relative advantages of these four types of extractors for applications in the important radiochemical field has been published by the Atomic Energy Commission (8, p. 1-12). In general, extractors in the multistage category have wider industrial applications.

The perforated-plate pulse column was first suggested in a patent granted to Van Dijck (19) in 1935. This type of extractor was little known, though, until studies at the Hanford Atomic Products Operation in 1949 showed that it possessed several distinct advantages over other types of extractors for radiochemical separations. A

perforated-plate pulse column is a vertical extraction column containing a series of perforated plates through which the light and heavy liquid phases pass counter-currently. The normal countercurrent flow is aided by a pulsation of the liquids, which is produced by an external device. This pulsation increases the intimacy of contact and permits a shorter column to achieve a given separation when compared with other vertical extractors. Operating variables peculiar to the pulse column include: (a) pulse amplitude, (b) pulse frequency, (c) pulse wave form, (d) plate spacing, (e) plate perforation size, and (f) percent free area or open area through a plate. The major operating variables, pulse amplitude and frequency, can be controlled externally in most cases, giving the pulse column a high degree of flexibility.

The proposed study of this thesis was to investigate the effects of frequency and amplitude of pulsation on the efficiency of a perforated-plate pulse column liquid-liquid extractor. Data were taken on the change in extraction efficiency with pulse frequency at a given pulse amplitude. Other variables affecting efficiency were held constant. The chemical system employed was carbon tetrachloride-acetic acid-water.

EVOLUTION OF THE PULSE COLUMN

While liquid-liquid extraction is often competitive with other unit operations as a means for making chemical separations, it possesses two inherent disadvantages: (a) the additional component which is introduced to carry out the desired separation must be recovered by succeeding operations, and (b) conventional extraction equipment often yields relatively low efficiencies. Though little can be done about the former disadvantage, much attention has been given to the latter in recent years.

The primary difference between the performance of an extraction column and that of other mass transfer equipment such as a distillation tower, would appear to be due to the degree of turbulence obtained. While considerable external energy is furnished in a distillation tower, the conventional extraction column derives its mixing energy solely from the difference in density of the two liquid phases (20, p. 183). The intimate contact brought about by the high degree of turbulence in mixer-settlers has made them a popular extractor for many years in the applications where a single-stage-type extractor is suitable. A number of improved extraction columns have made use of baffles, packing, and sieve-plates to obtain

a higher degree of contact during countercurrent flow of the liquid phases.

In a sieve-plate column new droplets of the dispersed phase are formed while passing through each plate. This fact was of particular interest in light of the work by Sherwood, Evans and Longcor (13, p. 1144) which indicated that as much as 40 to 50 percent of the total extraction takes place during drop formation. As the hole size in the plates is decreased, inter-phase contact is improved, but column capacity drops until a point is reached when countercurrent flow due to density difference alone will cease. Supplying additional energy by mechanical pulsation permits the greater contact associated with smaller perforations at much higher flow rates than in an unpulsed column. Also contributing to higher efficiencies is such a unit is the fact that the liquid may pass through a single plate more than once, giving additional coalescence and forming of new drops.

The liquid-liquid extractor patented by Van Dijck was a column in which the perforated plates were oscillated up and down to disperse the two liquid phases. In the same patent, however, he mentioned the possibility of dispersing the liquid phases by pulsing the liquids instead of moving the plates. This latter method of agitation is the basis for what is referred to as a pulse column (2, p. 1).

BASIC DESIGN OF A PULSE COLUMN

Nearly all reported studies of pulse columns have dealt with experimental rather than commercial-type units. Equipment descriptions and operating characteristics cited are based on experimental studies of pulse columns.

Most pulse columns are constructed of precision-bore glass tubing into which is placed the perforated-plate cartridge. The cartridge consists of perforated plates and spacers strung alternately on a central rod and secured by a nut on each end (14, p. 1005). An alternate style of construction consists of short sections of glass tubing stacked between perforated plates and held in compression (9, p. 56). The plates are made of stainless steel in most cases. Sege and Woodfield (12, p. 400-401) report using fluorothene plates and plates made of stainless steel faced with plastic on one side. Such plates were found to be useful when the plate-wetting characteristics of the chemical system employed were unfavorable to the use of ordinary stainless steel plates. Phase disengaging sections approximately 30 percent larger in diameter than the column proper usually are placed on each end of the column.

Pulsation of the liquid within the column may be

accomplished in several ways. One common method employs metal or teflon bellows driven by an electric motor through a cam on the motor shaft or through an adjustable eccentric. The latter is a convenient means for adjusting pulse amplitude. A variable-speed drive arrangement usually is included in the power train to permit a range of pulse frequencies. A reciprocating metering pump is sometimes used to provide pulsation. In reported experimental studies, frequencies as high as 510 cycles per minute and as low as 10 cycles per minute were used (14, p. 1006). Operating pulse amplitudes of from 0.11 inches (14, p. 1006) to 2 inches (1, p. 4) have been reported. In his fine review on pulse column technique, Thornton (17, p. 39-52) describes a method of pulsation in which the continuous phase liquid in a tube within the column is pulsed by air from above, causing the pulsation to be transmitted to the column proper. Some pulse units are arranged so as to pulse the light or heavy phase feed streams into the column; others pulse the column contents as a whole.

The heights of pulse columns reported ranged from a single plate in a study by Goldberger and Benenati (6, p. 641) to a plate section 16 feet high (15, p. 8). Column diameters have been as low as $\frac{1}{2}$ inch and as great as 12 inches (14, p. 1006). Plate spacings ranging from

$\frac{1}{2}$ inch (14, p. 1006) to 4 inches (12, p. 397) have been used. Perforation diameters are usually small enough that countercurrent flow of the liquid phases will not take place in the absence of pulsation. Reported values were as small as 0.025 inches (14, p. 1006) and as large as 0.1875 inches (12, p. 397). The percent free area of a plate varied from about 2 percent (3, p. 1154) to 62 percent (14, p. 1006).

OPERATING CHARACTERISTICS OF A PULSE COLUMN

In a study of pulse columns, as with any other mass transfer device, two characteristics are of primary interest: (a) flow capacity or throughput, and (b) efficiency. Since most studies report results in terms of one or both of these characteristics, it will be beneficial to discuss them briefly at this point. The condition that limits throughput is commonly known as flooding. This occurs when flow conditions are such that all the dispersed phase entering the column cannot leave at the opposite end (16, p. 8). Since the two liquid phases must move countercurrently past each other, increasing the feed rates will bring about a situation in which the dispersed phase becomes entrained in and exits with the continuous phase. Capacities are usually described in terms of superficial velocity, i.e. volume flow of liquid per square foot of column cross-section per unit time. Correlations generally are in terms of the sum of the superficial velocities of the continuous and dispersed phases. Efficiencies for multistage extractors such as the pulse column may be defined in several ways. Probably the most common measure of efficiency for such units is the over-all height of a transfer unit, H.T.U., based on the phase in which the

principal resistance to mass transfer occurs. A similar measure of efficiency is the height equivalent to a theoretical stage, H.E.T.S. (18, p. 427). The third measure of efficiency used is the over-all mass transfer coefficient, K , based again on the phase furnishing the principal resistance to mass transfer. There is an inverse relationship between H.T.U. and K . It is desirable to have low values of the former or high values of the latter.

In observing pulse column operation, three distinct types of behavior have been noted as a function of total flow rates and pulse frequency at a given pulse amplitude. This is shown graphically in Figure 1. The figure shows only general trends and has no numerical values along the axes. This figure and the discussion based on it were presented originally by Sege and Woodfield (12, p. 397).

The straight line designated pulse volume velocity represents the volume flow due to the product of frequency and amplitude, a measure of "pulse energy", which has the same units as the superficial velocity. This assumes a column in which no flow may occur without pulsation. Region A represents a condition of flooding due to insufficient pulsation.

As pulse frequency increases, a mixer-settler-type

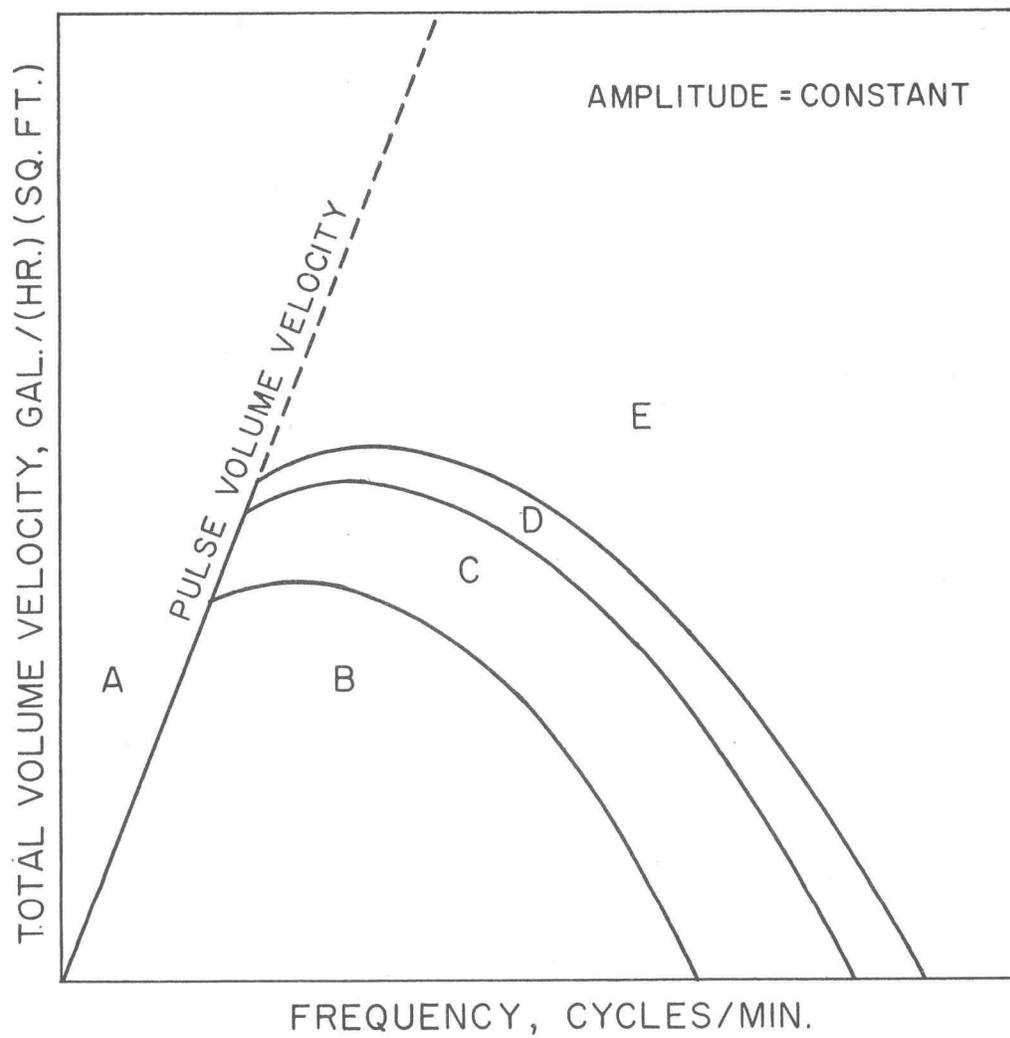


FIGURE 1 OPERATING CHARACTERISTICS OF A PULSE COLUMN

of operation is observed as in region B. This type of operation is characterized by a dispersed jetting of one phase into the other during alternate upward and downward pulsations. Complete phase separation occurs between each set of plates during the quiescent portions of the pulse cycle. During mixer-settler pulse conditions the operation of a pulse column is quite stable, but the efficiency of the unit is relatively low when compared with emulsion-type operation. Wiegandt and Von Berg (20, p. 186) felt that the mixer-settler-type of operation was the most efficient, but most other investigators agree with the conclusions of Sege and Woodfield.

Emulsion-type operation, region C, occurs at higher frequencies and increased flow rates. This form of operation is characterized by smaller drop sizes and uniform dispersion of the dispersed phase. There is little change in phase dispersion during a pulse cycle. Such operation gives a high degree of interphase contact, and is probably the most efficient type of operation.

At still higher frequencies and flow rates unstable operation, represented by region D, occurs. Mixtures of both fine and coarse droplets of the dispersed phase liquid characterize this form of operation. Large, irregular globules of the dispersed phase liquid and periodic phase reversal, or local flooding, also are

noted. The efficiency of the column in this region of operation is generally lower and often irregular.

A further increase in frequency and flow rates beyond the unstable region brings about total flooding due to emulsification, region E. Thus there are two types of flooding in a pulse column, and the line bounding regions B, C, and D is a typical flooding curve.

The operation of a pulse column is viewed by some (5, p. 285) as countercurrent flow superimposed on cocurrent mixing. As the degree of pulsation increases, the efficiency of the column is seen to reflect the sum of the opposing effects of increased efficiency due to greater interphase contact and decreased efficiency due to back-mixing or recycle. Mar and Babb (10, p. 1011-1014) have studied the possible means of predicting and reducing such back-mixing.

Li and Newton (9, p. 58-62) studied pulse column operation in terms of the Reynolds number through the plate perforations. They viewed the pulse column as having two distinct types of operation: (a) streamline operation, and (b) turbulent operation. The transition from streamline to turbulent operation occurred at a Reynolds number of about 1100. A sharp difference in the effect of Reynolds number on efficiency in the two regions was noted.

OPERATING VARIABLES OF A PULSE COLUMN

One of the primary problems in a complete study of pulse column operation is the number of variables present. The effects produced by each of these variables will be discussed briefly.

The most important operating variables are frequency f and amplitude a . Since the product of these two variables is a measure of pulse energy, it is beneficial to view them together. At any point in operation a given increase in frequency will produce essentially the same effect as a similar relative increase in amplitude would have produced. Thus a plot of H.T.U. versus amplitude at constant frequency will look very much like a plot of H.T.U. versus frequency at constant amplitude. The values of H.T.U. will first decrease due to improved interphase contact, pass through a minimum, and finally increase due to back-mixing. In many cases a plot of H.T.U. versus the product $f \times a$ will yield a good single curve for a given chemical system. Some investigators (12, p. 399) (20, p. 187) feel that a correlator such as $f^n a$, where n has a value between 1 and 2, will yield a better representation of their data.

Since the plates within the column are the means by which the energy input of pulsation is transformed into

useful turbulence, it is seen that at infinite plate spacing the effects of pulsation would be small. At zero pulse input essentially no flow would be possible and the effects of plate spacing would be negligible. Thus it is concluded that the effects of plate spacing become greater with increasing pulsation (16, p. 12). An increase in plate spacing generally will give higher values of H.T.U. and flooding capacity. While the latter is desirable, the former is undesirable. A decrease in plate spacing generally will give the reverse effects (12, p. 401).

Variations in perforation diameter and percent free area of a plate have essentially the same effect on values of H.T.U. and flooding capacity as does plate spacing. That is, an increase in either brings about an increase in both H.T.U. and flooding capacity (12, p. 401). An increase in either of these two variables also was found to decrease the sensitivity of flooding capacity to variations in pulsation (16, p. 13). Sege and Woodfield (12, p. 396) simplified their investigation by selecting what they felt was an optimum "standard cartridge", composed of stainless steel plates spaced 2 inches apart, with 1/8 inch holes drilled to give 23 percent free area.

The effects of total flow rate V_T and the ratio of continuous to dispersed flow rates V_C/V_D are not too consistent and probably depend somewhat on the chemical system employed. In general the values of H.T.U. are relatively insensitive to changes in V_T . Several investigators (5, p. 282) (9, p. 60) (12, p. 400) (14, p. 1008) found that an increase in V_C/V_D gave higher values of H.T.U. based on the continuous phase. Cohen and Beyer (5, p. 282) found the converse to be true with H.T.U. based on the dispersed phase. Choffé and Gladel (4, p. 584) found that an increase in V_C/V_D caused an increase in H.T.U. at low frequencies and a decrease at high frequencies. The flooding capacity of a pulse column will usually increase with an increase of V_C/V_D (16, p. 11).

The effects of pulse wave form have not received much attention. Most standard pulse units generate a sine wave. It is thought that a pulse unit generating a wave with a sharp front might be helpful when the density difference between the liquid phases is small. The effect of wave form probably would be noticeable only at low frequencies (20, p. 188).

A number of other variables that may be studied are functions of the chemical system employed. One of these

is the choice of the phase that is to be continuous. In general, the continuous phase should: (a) have the lower flow rate, (b) have the faster solute diffusion rate, (c) be the phase that wets the plates, (d) have the lower viscosity, and (e) have the lower surface tension. In most cases it is impossible to satisfy all of these conditions. The choice usually will be based on the factor that is felt to be most important. Solute concentration in the feed stream also may affect efficiency, but concentrations usually are not considered as a variable.

The properties of the particular chemical system employed, particularly the interphase density difference, are often important. Several attempts have been made to obtain general correlations between H.T.U. or flooding capacity and the many variables that have been mentioned. Smoot and Babb (14, p. 1005-1010) have made such general correlations by applying dimensional analysis and multiple regression techniques to nearly all the published data on pulse columns. Much work remains to be done in this area, particularly with regard to the properties of the chemical system employed.

DESCRIPTION OF THE APPARATUS

An overall flow diagram of the apparatus is shown in Figure 2. The basic design and construction of the apparatus was done by Mr. Walter Meyer. Modifications necessary for this study were worked out and constructed by the author. Owing to the corrosive nature of the chemical system employed, all construction materials in contact with the liquids were stainless steel, teflon, or glass.

The column proper was constructed of a 36 inch section of 3 inch inside diameter Pyrex Double Tough glass pipe. Connecting the column to the base was a 10 inch glass tee of the same material. An identical tee and a 6 inch pipe section were attached to the top of the column. The 6 inch section was used to prevent overflow at high pulse rates.

Seven plates, constructed of 0.064 gauge, type 310 stainless steel sheet, were spaced 1 inch apart on a 3/8 inch, type 316 stainless steel rod, which was threaded into the base. The spacers were cut from 5/8 inch, type 304 stainless steel tubing. Each plate contained 114 holes which were 1/8 inch in diameter. These holes were arranged so that their centers formed a pattern of equilateral triangles. This arrangement

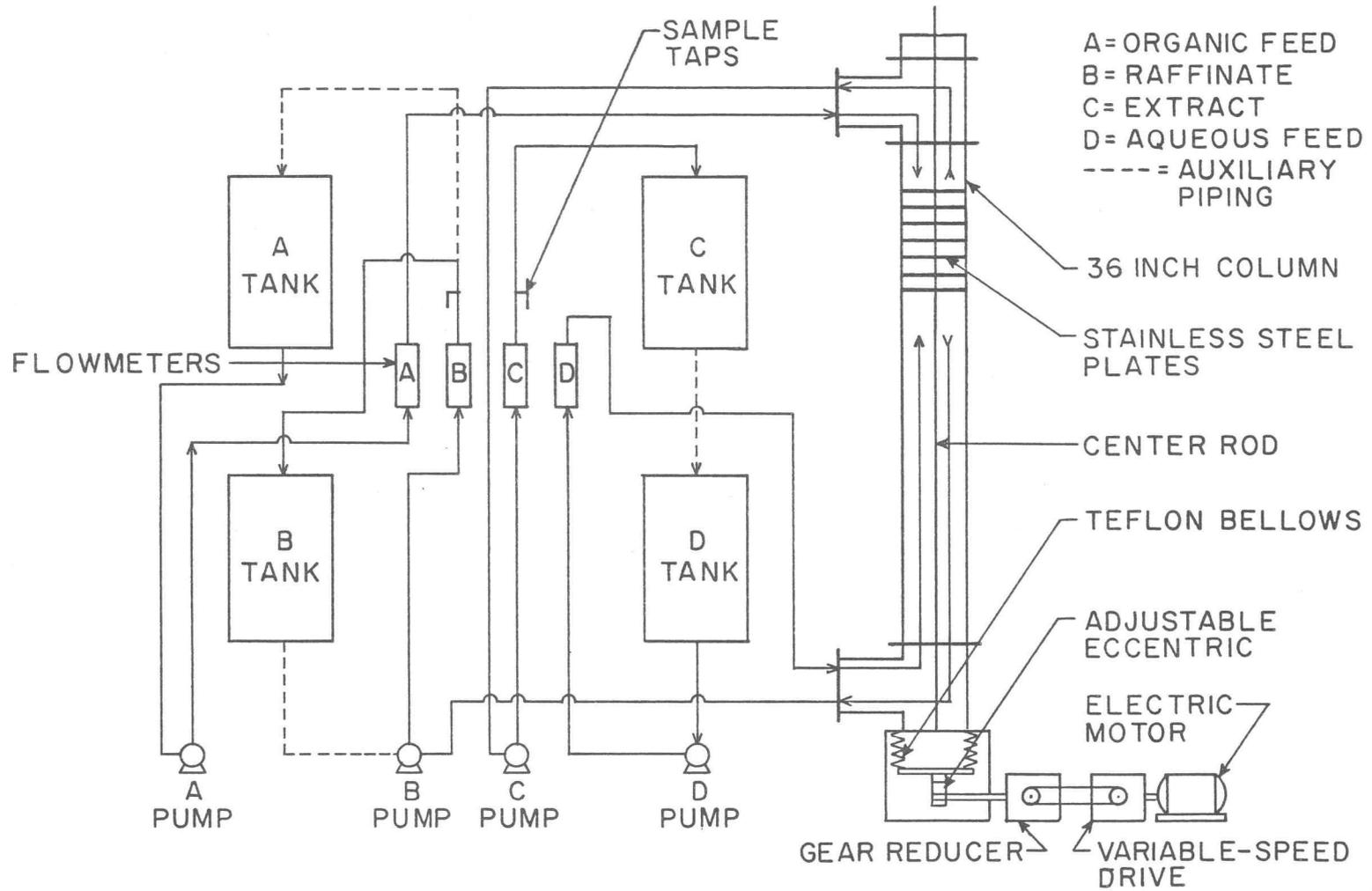


FIGURE 2 DIAGRAM OF THE APPARATUS

yielded a free area of 22.6 percent. The plates were sealed against the wall of the column by means of gaskets which were made by splitting a length of small diameter teflon tubing. The height of the plate section was 7.54 inches.

The feed and receiving tanks were made from stainless steel low-pressure oxygen tanks by threading one end to accept $\frac{1}{2}$ inch pipe and by cutting a hole approximately 3 inches in diameter in the other end. Each tank had an approximate volume of 9.1 gallons.

Feed and exit streams were pumped through $\frac{1}{2}$ inch, type 304 stainless steel pipe by four Eastern Industries pumps. Relative flow rates were indicated by a Manostat Predictability Flowmeter, model FM1048T, inserted in each of the four lines. Flow was controlled by $\frac{1}{4}$ inch stainless steel needle valves. Sample taps were provided on both effluent streams. Auxiliary piping was included to allow pumping from one tank to another and to permit easy draining of the liquids from the apparatus. Polyethylene extensions were sealed to the feed and exit pipe nipples within the column to reduce the effective height of the column, thus hastening the achievement of steady-state operation. Distributors were fashioned on each of the feed tubes by sealing the end of the tube and drilling a series of eight, $\frac{1}{8}$ inch holes around

its circumference.

A teflon bellows of 3 inch inside diameter was driven by a $\frac{1}{2}$ HP Smithway electric motor through a Reeves Flexi-Speed Drive, a Boston 40:1 gear reducer, and an adjustable eccentric. This pulse unit permitted a frequency range of from 20 to 150 cycles per minute and an amplitude within the column of from 0 to 3 inches.

The flowmeters and major control valves were mounted in appropriate locations on a control panel on which had been painted a flow diagram. This "graphic panel" made operation of the unit a great deal easier.

DESCRIPTION OF THE CHEMICAL SYSTEM

The carbon tetrachloride-acetic acid-water system was used in this investigation. This system was chosen for several reasons: (a) good equilibrium data were available, (b) the needed chemicals were easily obtainable, and (c) the two solvents, carbon tetrachloride and water, are nearly immiscible. Since past work had dealt almost entirely with systems employing water and a lighter organic solvent having a relatively small difference in density, it was thought desirable to investigate a system in which the solvent was heavier than water and in which the density difference was relatively large. The chemicals used were carbon tetrachloride U.S.P., glacial acetic acid, and distilled water.

The equilibrium data of Prince and Hunter (11, p. 253-257) were used. The data, which were taken at 25°C, are listed in Table 2 of the appendix. The tie line data are listed in Table 3 of the appendix. Prince and Hunter tested the tie line data by the method of Hand, and found them to be quite acceptable. Figure 3 represents the equilibrium data of Prince and Hunter on a conventional triangular diagram. Figure 4 shows the tie line data as they actually were used. For the operating range that was involved in the investigation,

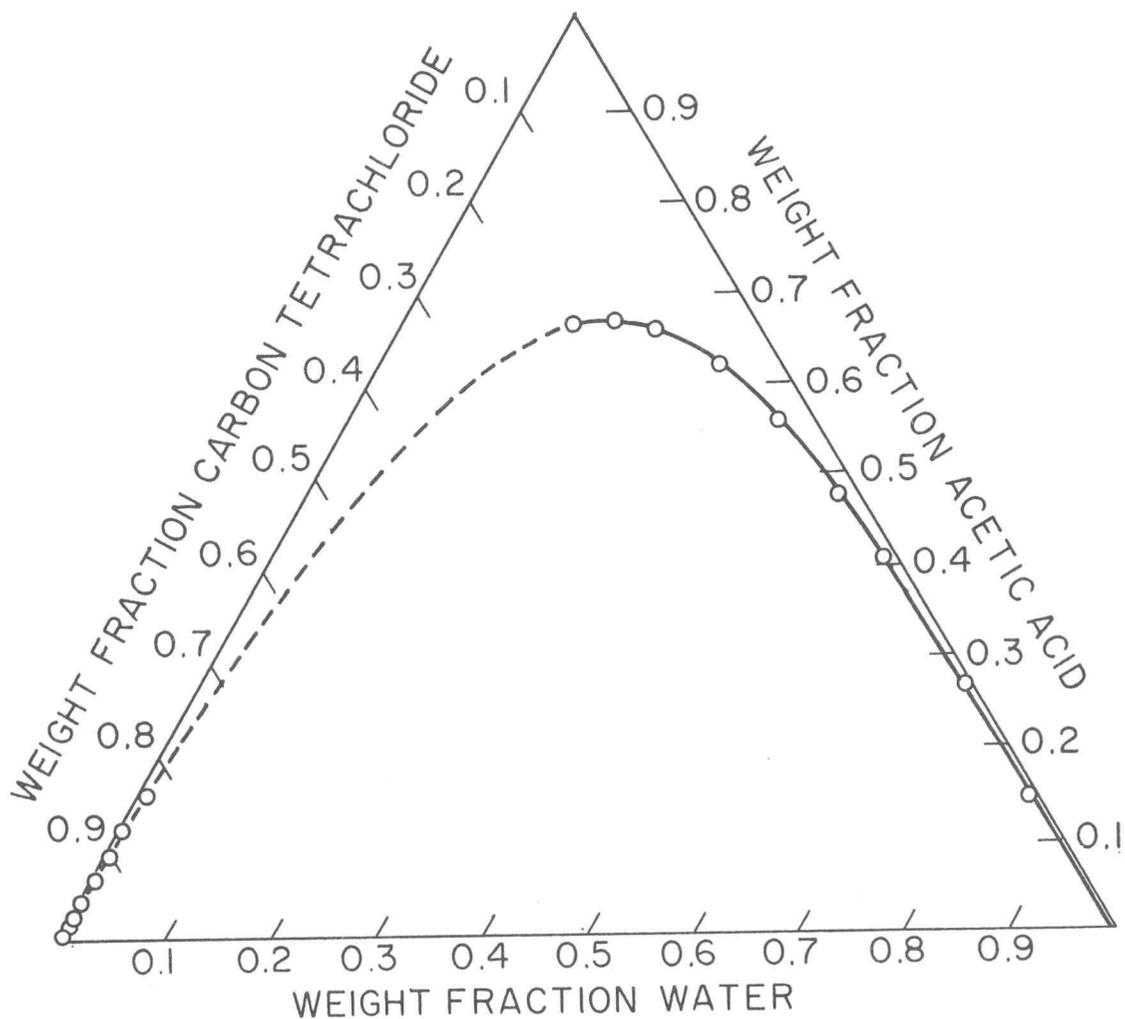


FIGURE 3 EQUILIBRIUM DIAGRAM FOR CARBON TETRACHLORIDE-ACETIC ACID-WATER AT 25° C.

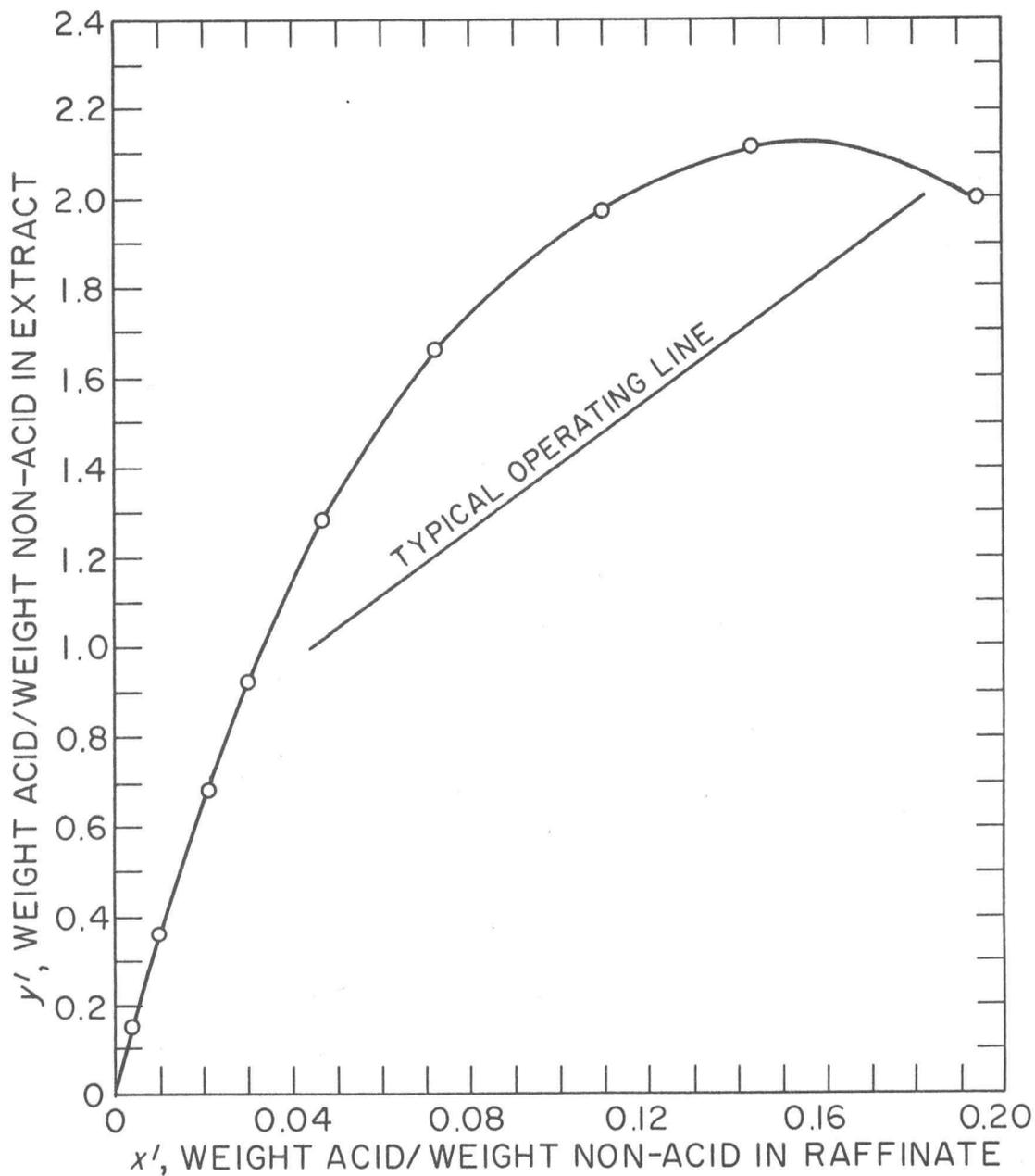


FIGURE 4 TIE LINE DIAGRAM FOR CARBON
TETRACHLORIDE-ACETIC ACID-
WATER AT 25° C.

it was necessary to plot the data on an x' - y' diagram, x' and y' being the weight fraction of solute in the raffinate and extract phases, respectively, on a solute-free basis. The raffinate phase is defined as the phase from which the solute is removed. The extract phase is the phase into which the solute is extracted. This approach was necessary to obtain a straight operating line in the range in which the work was carried out. This method is discussed by Treybal (18, p. 410-412). The x' - y' data are shown also in Table 3 of the appendix.

The system chosen was desirable in that it permitted the use of water as the extract phase. This eliminated the problem of solvent recovery since the aqueous phase could be discarded. It had been hoped that pure water saturated with carbon tetrachloride could be used as the aqueous feed. Examination of the tie line data and a verifying trial run showed this to be impractical. The solute distribution so heavily favored the aqueous phase that equilibrium results were approached very rapidly. This would make the calculation of efficiencies very difficult. Steffanson, Higbie, and Walton (15, p. 14-17) encountered this problem in their investigation. The use of pure water also necessitated very high organic to aqueous flow ratios which were undesirable. It was decided to use feed concentrations of 50.00 weight

percent acid in the aqueous feed and 15.50 weight percent acid in the organic feed. These feed concentrations gave an operating line with a slope of 6.5, as seen in Figure 4. The phase flow ratio was then 3.85 grams organic phase per gram aqueous phase, or 2.68 milliliters organic phase per milliliter aqueous phase. Absolute feed rates were approximately 707 milliliters per minute and 264 milliliters per minute of the organic and aqueous phases, respectively.

Since the organic phase had the higher flow rate, and since the aqueous phase preferentially wets the plates, it would seem desirable to disperse the organic phase. However, in view of the low aqueous phase flow rate and the desire to achieve rapid steady-state operations, it was decided to disperse the aqueous phase. Actual check runs proved this to be the more practical selection.

OPERATIONAL PROCEDURE

At the beginning of each series of runs the pulse amplitude was set by means of the adjustable eccentric. The amplitude was measured by determining the high and low points of the phase interface while manipulating the drive belts by hand. Amplitudes of 0.857, 1.35, and 1.90 inches were used.

In preparing for each run, the volumes of chemicals necessary for each feed tank were calculated. The calculated amounts of chemicals were measured into each tank and mixed thoroughly. The aqueous and organic feeds were saturated with carbon tetrachloride and water, respectively. Samples from each feed tank were taken and exact concentrations determined. When corrections were necessary, the additional amounts of chemicals required were calculated and mixed into the feed tanks. A second set of samples then were taken to verify the concentrations. Since the extract and raffinate solutions both were reused, make-up essentially consisted of adding acid and a small amount of carbon tetrachloride to the organic feed tank and discarding part of the aqueous phase prior to diluting the balance to the required concentration.

The frequency for each run was set by counting the number of pulse cycles over a period of several minutes

and adjusting the variable-speed drive until the frequency desired was maintained exactly for about five minutes. Pulse frequencies of from 20 to 140 cycles per minute were used. One run was made with no pulsation in order to determine H.T.U. for an unpulsed column.

A run was begun by starting the organic feed pump and setting the desired organic feed rate, bringing the interface to a mark that had been made near the top of the 36 inch section. The column usually contained some organic phase and aqueous phase liquids from the previous run. Once the mark had been reached, the organic effluent pump was started and the flow rate adjusted to maintain the interface level. The aqueous feed pump was started next and the desired flow rate was set. The aqueous effluent pump then was started and the flow rate adjusted to bring the aqueous surface to a mark on the upper tee. These adjustments were carried out essentially simultaneously, usually taking less than a minute. Once these levels were established the pulse unit was started. As the concentration gradient through the column became established in the early minutes of the run, the effluent flow rates had to be adjusted to maintain the two levels that had been set. Since the interface and aqueous surface levels had been set with the bellows in the lowest position, the levels could be

maintained by ascertaining that they came even with their respective marks at the bottom of each cycle. The flow rates had little tendency to fluctuate and were easily controlled. A run usually lasted about 53 minutes, its duration being limited by the capacity of the organic feed tank.

Samples were taken by means of sample taps in the effluent lines of each phase. Before taking a pair of samples, the taps were opened and the liquids allowed to run into beakers for nearly a minute in order to clear the short tap lines. The sample flasks then were placed under the taps and about 75 milliliters of liquid were drawn off into each. The flasks were stoppered immediately to prevent any evaporation.

During the initial runs, five sets of samples were taken 3 to 5 minutes apart in order to verify that steady-state operation had been achieved. In later runs two sets of samples were taken 3 minutes apart during the last 5 minutes of the run.

When the organic feed tank ran dry, the pulse unit and all pumps were stopped immediately. The proper valves then were set and the raffinate was pumped back into the organic feed tank. Some of the extract was drained from the receiving tank and discarded so that it would not overflow during the next run. The aqueous flow

rate was enough slower than the organic flow rate that one tank of aqueous feed would last for two runs.

The experimental runs and analyses of this thesis were carried out at room temperature, which varies from 22 to 25°C over the period of time in which the study was made.

The main difficulties encountered with this apparatus were due to the corrosive nature of the chemical system used. Leaks in the pipe joints had to be corrected on numerous occasions until a more suitable pipe compound was found. Two of the pumps leaked on occasion and each had to be repacked once. Each flow-meter developed a leak at some time during the study and had to be resealed. Except for these leaks, the equipment functioned very well.

ANALYTICAL PROCEDURE

All samples were analyzed as soon as possible after each run. The analysis was performed with diluted Acculate sodium hydroxide solution which was standardized against a sodium hydroxide solution of known concentration. An ascarite tube was used to maintain the base free of carbon dioxide. The samples from the first nine runs were titrated with 0.9920 normal sodium hydroxide. A solution of 1.0031 normal sodium hydroxide was used in the analyses of the balance of the runs.

The sample size of the aqueous phase was 2 milliliters. The organic phase samples were 10 milliliters. The latter samples were diluted with about 50 milliliters of distilled water and agitated throughout the titration in order to extract the acid from the organic phase. The volume of base required was in the range of 12 to 25 milliliters. The titrations were done to a phenolphthalein end point. All samples were titrated twice or until the difference between two titrations was 0.05 milliliters or less. The maximum error thus induced was 0.3 percent.

The same pipets were used in each analysis to avoid any variation in sample size. This was a potential problem in view of the relatively small samples. The titrations were made with a 10 milliliter micro-buret.

After the titrations of each set of samples were completed, the density of each sample was determined by the use of a standard Westphal balance. With the normality and density of each sample known, the weight fraction of acetic acid in each could be calculated.

CALCULATION OF H.T.U._{OE}

The over-all height of a transfer unit H.T.U. was determined by first calculating the over-all number of transfer units N.T.U. H.T.U. and N.T.U. are related by the equation

$$\text{H.T.U.} = \frac{Z}{\text{N.T.U.}} \quad (1)$$

where Z is the height of the plate section in the column. The method described by Treybal (18, p. 428-431) was used in determining N.T.U.

Since the solute distribution in this chemical system heavily favored the extract phase, it was believed that the major resistance to mass transfer would be in the raffinate phase. H.T.U. based on the raffinate phase H.T.U._{OR} and H.T.U. based on the extract phase H.T.U._{OE} both were calculated for several runs. It was found that the values of H.T.U._{OE} were the higher. This would indicate that the major resistance was in the extract phase. In view of this the calculations were all based on the extract phase.

The basic equation that was used to determine N.T.U._{OE} for each run is given below.

$$\text{N.T.U.}_{\text{OE}} = \int_{y_2}^{y_1} \frac{(1-y)_m dy}{(1-y)(y^*-y)} \quad (2)$$

This equation was simplified by inserting the expansion

of $(1-y)_m$ and rearranging. The conversion factor 0.4343 was inserted since it was more convenient to use common logarithms rather than natural logarithms. The equation actually used was

$$\text{N.T.U.}_{\text{OE}} = \int_{y_2}^{y_1} \frac{0.4343 \, dy}{(1-y) \log \left(\frac{1-y}{1-y^*} \right)} \quad (3)$$

The term y is the weight fraction of acetic acid in the extract phase. The subscripts 1 and 2 refer to concentrations at the top and bottom of the column, respectively, for either phase. The term y^* is the equilibrium value of y obtained as described below.

It was necessary to graphically integrate Equation (3). The procedure for run number 13 will be described. The values of terms mentioned and a complete tabulation of the calculations involved are shown in Table 4 of the appendix.

The initial and final concentrations of each phase were determined by analysis. These weight fractions then were converted to weight fractions on a solute-free basis by the following relationships: (a) $x' = \frac{x}{1-x}$, and (b) $y' = \frac{y}{1-y}$. The points x'_1 , y'_1 , and x'_2 , y'_2 then were plotted on an expanded tie line diagram similar to Figure 4. A straight line drawn between these two points represented the operating line for this run. A series

of ten values of y' between y'_2 and y'_1 were arbitrarily selected as shown in column two of Table 4. Each of the twelve values of y' was located in turn on the tie line curve and a horizontal line drawn through it to the operating line. Through the point of intersection on the operating line a vertical line was drawn to the tie line curve. This last point of intersection is the equilibrium value of y' , or y'^* . These values are shown in column three of Table 4. The values of y' and y'^* then were converted to values of y and y^* , as shown in columns one and four of Table 4, by the equation $y = \frac{y'}{1+y'}$. Successive calculations were made to determine the value of the term within the integral of Equation (3) for each value of y . The values of this term then were plotted versus the corresponding values of y as shown in Figure 7. The area under this curve from y_1 to y_2 then was determined. The area thus obtained is the value of the integral in Equation (3) and is equal to the number of transfer units $N.T.U._{OE}$. The height of a transfer unit was obtained by dividing the height of the plate section, 7.54 inches, by $N.T.U._{OE}$ as shown in Equation (1).

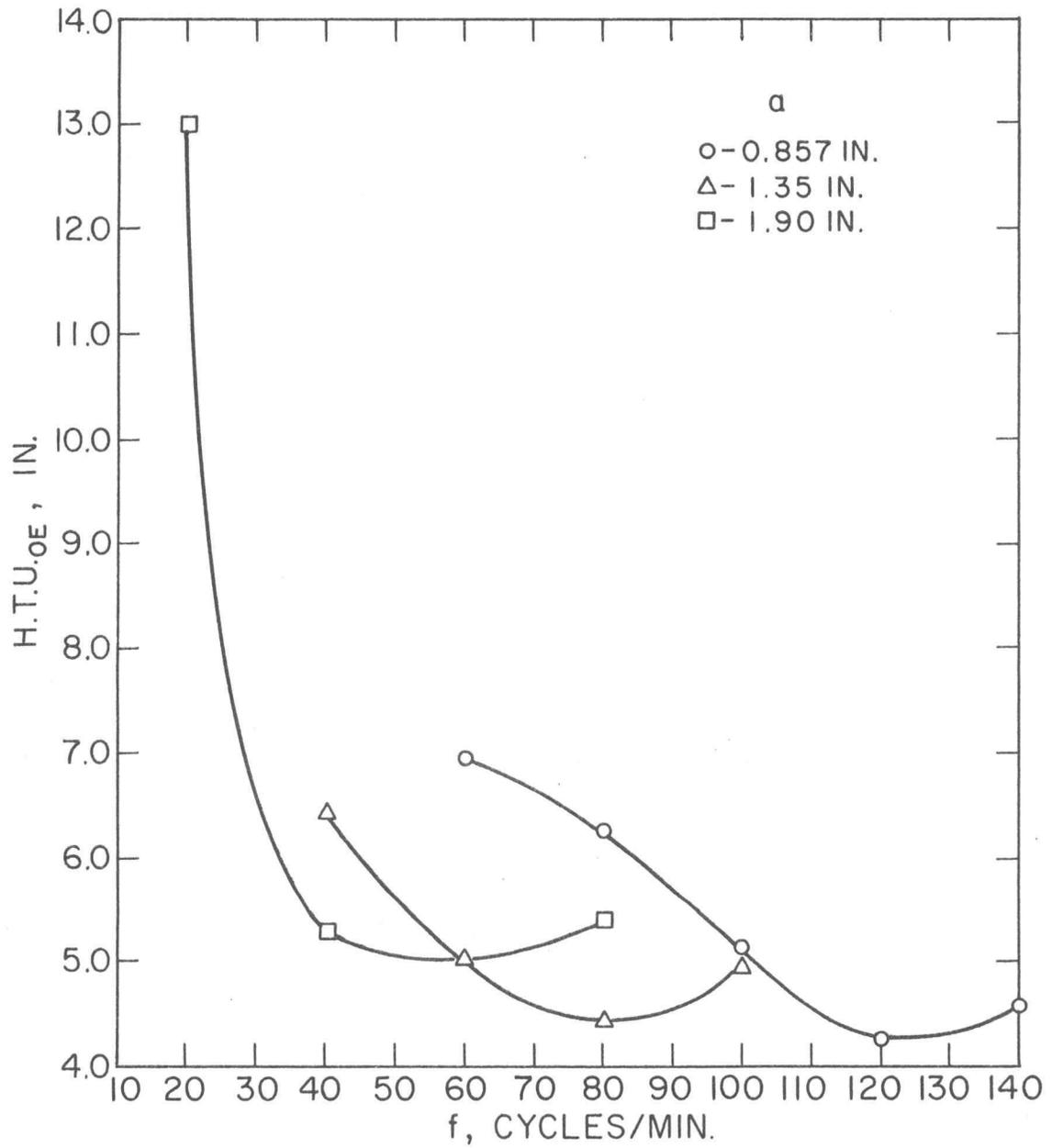
PRESENTATION OF RESULTS

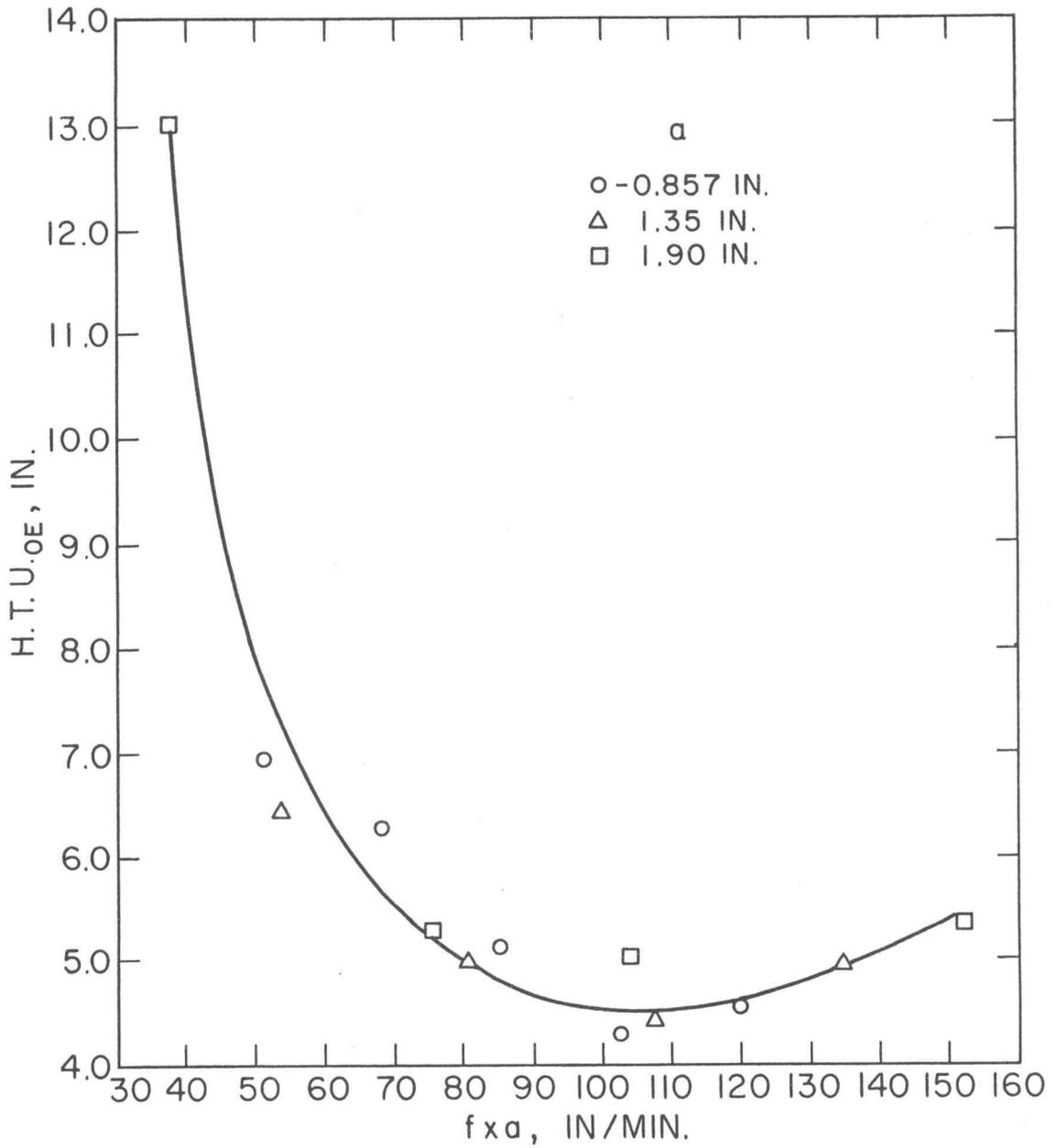
The results obtained from this study are given in Table 1. Values also are shown for what is termed as the "improvement factor". These values were obtained by dividing $H.T.U._{OE}$ for an unpulsed column by $H.T.U._{OE}$ obtained in each pulsed run. Two graphs were made using the data of Table 1 as shown in Figures 5 and 6. Figure 5 is a plot of $H.T.U._{OE}$ versus frequency at each of the three amplitudes that were used. Figure 6 is a plot of $H.T.U._{OE}$ versus the product of frequency and amplitude which is thought to be significant by many investigators. A graph involving the improvement factor was not made since this would merely show inversions of the curves in Figure 5.

The results shown in Figures 5 and 6 seem to agree with the general results obtained by other investigators. Since there is no reported investigation of pulse column performance using the same chemical system, direct comparison of absolute values of $H.T.U._{OE}$ would be meaningless. In the area of improvement over an unpulsed column, however, a comparison can be made. Most investigators reported approximately a three-fold reduction in $H.T.U.$ at optimum pulsation. The reduction in $H.T.U._{OE}$ factors at optimum pulsation in this

Table 1
Experimental Data

Run Number	a (in.)	f (cycles/min.)	f x a (in./min.)	H.T.U. _{OE} (in.)	Improvement factor
1	0	0	0	14.8279	1.00
2	0.857	60	51.4	6.9583	2.13
3	0.857	80	68.5	6.2755	2.37
4	0.857	100	85.7	5.1475	2.88
5	0.857	120	102.8	4.2544	3.49
6	0.857	140	120.0	4.4597	3.24
7	1.900	20	38.0	13.0022	1.14
8	1.900	40	76.0	5.2987	2.80
9	1.900	60	104.0	5.0435	2.94
10	1.900	80	152.0	5.3876	2.75
11	1.350	40	54.0	6.4516	2.30
12	1.350	60	81.0	5.0020	2.97
13	1.350	80	108.0	4.4639	3.33
14	1.350	100	135.0	4.9648	2.99

FIGURE 5 H. T. U._{0E} VS. f

FIGURE 6 $H.T.U._{0E}$ VS. $f x \alpha$

investigation were 3.50, 3.33, and 2.96 for the three amplitudes studied.

It is noted that lower optimum values of $H.T.U._{OE}$ were obtained for the smaller pulse amplitudes. This is in line with the findings of Chantry, Von Berg, and Wiegandt (3, p. 1156), who concluded that the use of high frequencies and low amplitudes yielded the best results. Since the three curves do not have the same minimum value of $H.T.U._{OE}$, the points on the plot of $H.T.U._{OE}$ versus $f \times a$, as shown in Figure 6, are a little scattered. It is interesting to note, though, that the minimum value of each $H.T.U._{OE}$ versus frequency curve occurred at nearly the same value of $f \times a$. The minimum occurred at 104.5 inches per minute in two cases and 108.0 inches per minute in the third. This would seem to bear out the belief that the efficiency of a pulse column is related to a function of both frequency and amplitude.

The unique aspect of this study was the use of a chemical system in which the difference in density between the two phases was very large. This created some problems during the work, but it is felt that the results are very much in line with previous studies.

RECOMMENDATIONS FOR FUTURE WORK

Much work remains to be done before it will be possible to predict the efficiency of a pulse column employing a given chemical system without actual experimental runs. One interesting study might be to run a series of chemical systems in a pulse column with fixed operating variables to study the effects on efficiency of a range of liquid properties such as density, viscosity, and surface tension. Another possible investigation would be a closer study of the effects of pulse amplitude to determine whether it is the value of amplitude per se, or its relationship to plate spacing that is the important thing to consider in over-all correlations.

As far as the apparatus used in this study is concerned, two improvements would be beneficial. The feed tanks were somewhat small in relation to the capacity of the column. While steady-state operation was achieved in all runs reported in this study, nearly the full length of the run was required to reach steady-state. In some preliminary runs it was evident that steady-state operation was not achieved.

A second gear reducer that could be interchanged with the existing reducer would allow a greater range of

frequencies. It had been desired to use an amplitude of less than 0.857 inches, but it was found that at the frequencies this would require the gear speeds in the reducer were much too high. A more powerful electric motor probably would be required with a lower ratio gear reducer.

NOMENCLATURE

- a - pulse amplitude, in.
- f - pulse frequency, cycles/min.
- H.E.T.S. - height equivalent to a theoretical stage, in.
- H.T.U._{OE} - over-all height of a transfer unit based on the extract phase, in.
- H.T.U._{OR} - over-all height of a transfer unit based on the raffinate phase, in.
- K - over-all mass transfer coefficient, lb. moles/(hr.)(sq.ft.)(driving force)
- log - common logarithm
- ln - natural logarithm
- N.T.U._{OE} - over-all number of transfer units based on the extract phase, dimensionless
- V - superficial volume velocity, cu.ft./(hr.)(sq.ft.)
- x - concentration of acid in the raffinate phase, weight fraction
- x' - concentration of acid in the raffinate phase, lb. acid/lb. non-acid
- y - concentration of acid in the extract phase, weight fraction
- y' - concentration of acid in the extract phase, lb. acid/lb. non-acid
- Z - height of plate section, in.
- Subscripts:**
- C - continuous phase
- D - dispersed phase

m - logarithmic average, i.e. $(1-y)_m = \frac{(1-y) - (1-y^*)}{\ln \left(\frac{1-y}{1-y^*} \right)}$

n - a constant

T - sum of continuous and dispersed phases

1 - that end of column where raffinate enters

2 - that end of column where extract enters

Superscript:

* - equilibrium concentration

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1. The first part of the report discusses the background of the project and the objectives of the study. It also outlines the methodology used for data collection and analysis.

2. The second part of the report presents the results of the study, including a detailed description of the data and the statistical analysis performed. The results show a significant correlation between the variables studied.

3. The third part of the report discusses the implications of the findings and provides recommendations for future research. It also highlights the limitations of the study and the need for further investigation.

APPENDIX

The appendix contains the raw data used in the study, as well as the statistical tables and charts. It is organized into several sections, each corresponding to a different aspect of the data analysis.

1. The first section of the appendix contains the raw data for the first variable, including the names of the subjects and their corresponding values.

2. The second section contains the raw data for the second variable, including the names of the subjects and their corresponding values.

3. The third section contains the statistical tables, including the mean, standard deviation, and correlation coefficient for each variable.

4. The fourth section contains the charts, including a scatter plot showing the relationship between the two variables and a bar chart showing the distribution of the data.

Table 2
Equilibrium Data by Prince and Hunter

a - weight fraction carbon tetrachloride

b - weight fraction acetic acid

c - weight fraction water

a	b	c
0.9962	0.0036	0.0002
0.9902	0.0096	0.0002
0.9793	0.0204	0.0003
0.9702	0.0294	0.0004
0.9544	0.0449	0.0007
0.9314	0.0676	0.0010
0.8990	0.0992	0.0018
0.8721	0.1254	0.0025
0.8332	0.1626	0.0042
0.1741	0.6670	0.1589
0.1277	0.6727	0.1996
0.0950	0.6639	0.2411
0.0560	0.6253	0.3187
0.0324	0.5622	0.4054
0.0180	0.4802	0.5018
0.0107	0.4091	0.5802
0.0051	0.2697	0.7252
0.0030	0.1512	0.8458

Table 3

Tie Line Data by Prince and Hunter

Organic Phase		Aqueous Phase	
x	x'	y	y'
0.0036	0.0036	0.1512	0.1781
0.0096	0.0097	0.2697	0.3690
0.0204	0.0208	0.4091	0.6920
0.0294	0.0303	0.4802	0.9340
0.0449	0.0470	0.5622	1.2840
0.0676	0.0725	0.6253	1.6690
0.0992	0.1101	0.6639	1.9770
0.1254	0.1434	0.6727	2.0570
0.1626	0.1942	0.6670	2.0020

Table 4

Calculations for Run Number 13

y	y'	y'*	y*	(a) 1-y	1-y*	$\frac{1-y}{1-y^*}$	(b) $\log\left(\frac{1-y}{1-y^*}\right)$	$\frac{0.4343}{(a)(b)}$
0.5000	1.0000	1.3290	0.5706	0.5000	0.4294	1.1644	0.0661	13.1407
0.5146	1.0600	1.4980	0.5997	0.4854	0.4003	1.2126	0.0837	10.6865
0.5327	1.1400	1.6910	0.6284	0.4673	0.3716	1.2575	0.0995	9.3398
0.5495	1.2200	1.8300	0.6466	0.4505	0.3534	1.2748	0.1054	9.1432
0.5652	1.3000	1.9360	0.6594	0.4348	0.3406	1.2766	0.1061	9.4188
0.5781	1.3700	1.9980	0.6664	0.4219	0.3336	1.2647	0.1020	10.0930
0.5902	1.4400	2.0370	0.6707	0.4098	0.3293	1.2445	0.0950	11.1559
0.6000	1.5000	2.0510	0.6722	0.4000	0.3278	1.2203	0.0865	12.5557
0.6098	1.5630	2.0570	0.6729	0.3902	0.3271	1.1929	0.0766	14.5299
0.6183	1.6200	2.0520	0.6723	0.3817	0.3277	1.1648	0.0663	17.1728
0.6283	1.6900	2.0390	0.6709	0.3717	0.3291	1.1294	0.0529	22.1130
0.6366	1.7518	2.0230	0.6692	0.3634	0.3308	1.0985	0.0408	29.2852

$$x_1 = 0.1550$$

$$y_1 = 0.6366$$

$$x_2 = 0.0473$$

$$y_2 = 0.5000$$

$$\text{Area under curve} = \text{N.T.U.}_{\text{OE}} = 1.6891$$

$$\text{H.T.U.}_{\text{OE}} = 4.4639 \text{ inches}$$

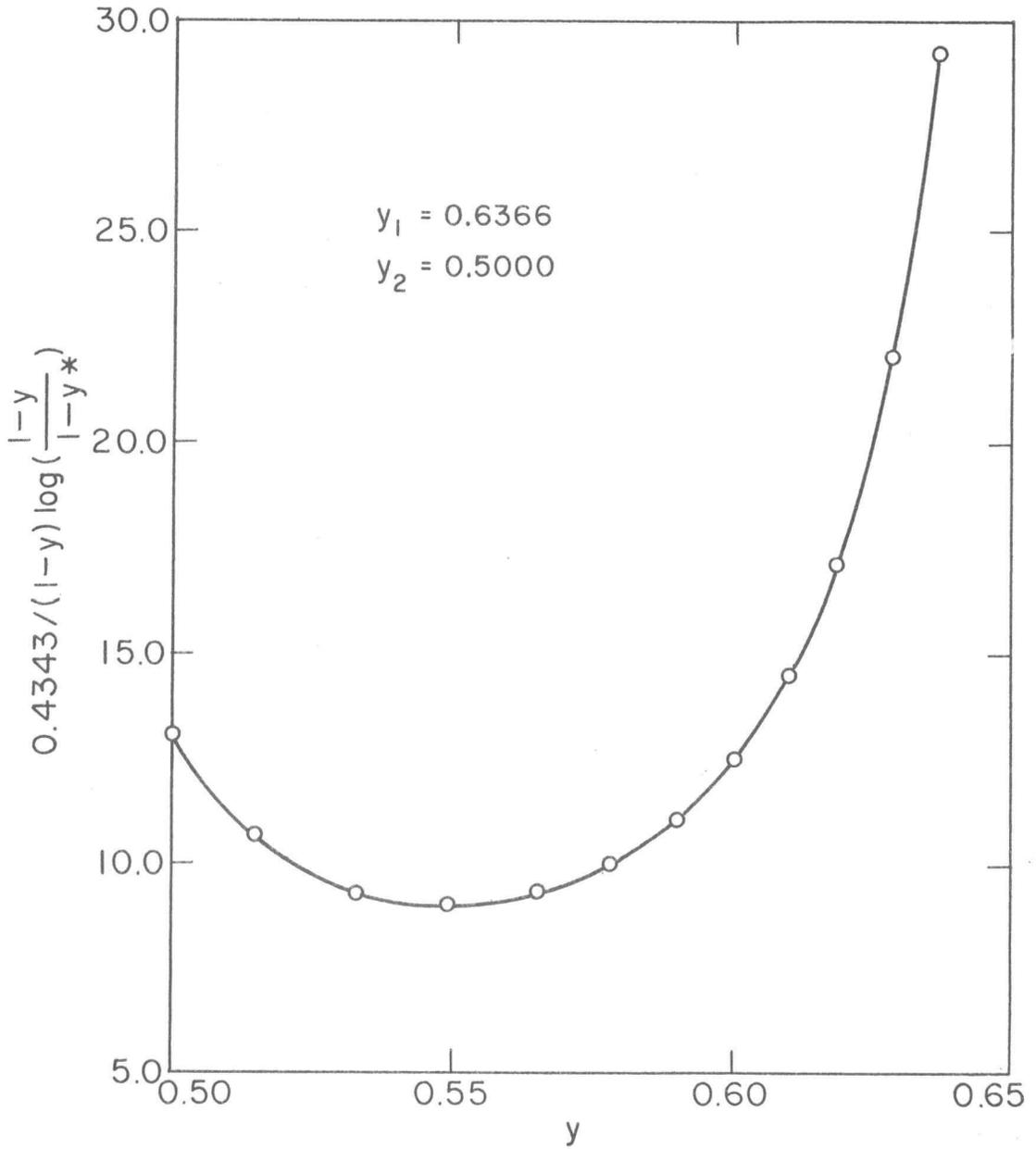


FIGURE 7 GRAPHICAL INTEGRATION FOR
RUN NUMBER 13