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ABSTRACT

Title of Thesis: An Equilibrium Theory of the pH Parametric Pump

Charles Omotayo Kerobo, Master of Science, 1979

Thesis directed by: Dr. H. T. Chen, Professor
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Parametric pumping, both batch and continuous, and cycling zone adsorption are theoretically scrutinized for various operating conditions by using the concept of equilibrium stages. The model system is Haemoglobin-Albumin-CM sepharose, a physical system in which a local equilibrium between liquid and sorbent in the layers of the separating medium in the column is characterized. For the batch process, the steady-state concentrations in both top and bottom reservoirs are found to be independent of the number of equilibrium stages, provided that $\alpha = 1$ (i.e., number of transfer steps/number of stages). For continuous parapump process, separation is enhanced with decreasing top feed ratio and/or decreasing bottom feed ratio. However, steadily degrading separation is found to exist when the top or bottom feed ratio exceeds the void volume of the column. The separation obtained for the cycling zone adsorption shows that an optimum number of stages is between 10 and 16. Below the lower limit, separation steadily decreases, and above the upper limit, the separation is found to be constant. Recycle ratio (β) is found to have an influence on the separation below the optimum number of stages and no influence above the optimum number of stages.

A computational algorithm for predicting equilibrium parametric pump performance (both batch and continuous) and cycling zone adsorption is developed. The algorithm is based on a set of exterior solute material balances and a linear adsorption isotherm for the solute-adsorbant system. The method of STOP-GO is combined with a finite difference approximation to solve the material balance equations.

AN EQUILIBRIUM THEORY OF THE
pH-PARAMETRIC PUMP

by
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Thesis submitted to the Faculty of the Graduate School of
the New Jersey Institute of Technology in partial fulfillment
of the requirements for the degree of
Master of Science in Chemical Engineering
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*I would like to dedicate this thesis
to my wife, Faye Lea Kerobo,
and our baby, who is
due within a
few months*

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Introduction

The initial theoretical analysis of parametric pumping was described by Wilhelm et al. in 1966. In this pioneering work, a recuperative mode of operation was applied; the fluid was heated in a heat exchanger before flowing up through the bed and cooled before flowing down. (See Figure 1(a).) This thermal recuperative mode was used for removing NaCl from water on a mixed bed of ion exchange resins. Wilhelm (1966) discussed the possibilities of applying the parapump idea to a variety of oscillating fields such as electrical, magnetic, or chemical potential. Wilhelm and Sweed (1968), and Wakao et al. (1968) independently developed the direct mode. (See Figure 1(b).) This direct mode of operation called for external application of heating and cooling source during up and down flow respectively (water jacket) on the stationary bed before upward flow of fluid, and then, the bed is cooled by an external source before downward flow of the fluid.

Sabadell and Sweed (1970) extended the parapump process to a recuperative pH mode to remove K^+ and Na^+ from water. In this recuperative mode of operation, the low pH end was closed, and the high pH end opened. To maintain the pH levels constant, HCl was added to the low end while fresh feed was introduced and product was withdrawn from the open end every half cycle. This setup was called a semibatch recuperative pH mode parapumping operation. The neutralization reaction which occurred in the

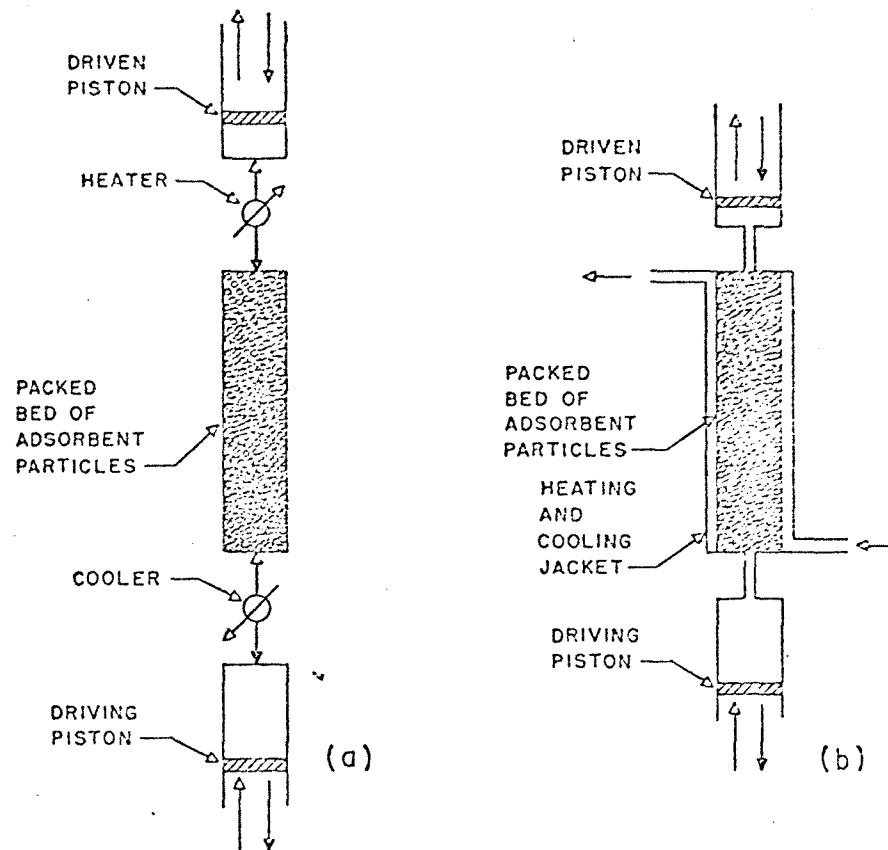


Fig. 1. Apparatus arrangement for thermal parametric pumping. (a) Recuperative mode. (b) Direct mode.

column was the source of energy used for the separation. Although this method of deriving energy source was not optimized, a separation factor of 1.84 was obtained. This value was better than that obtained by previous methods of parapumps.

The Batch Pump

Included in the parapump methods of separation is the batch process. Various forms of energy, such as pH and temperature, have been harnessed to effect parametric pumping separations. Since the basic concepts of pH parametric pumping were developed from the thermal system, thermal parapumping operation will be used in illustrating the principle behind the batch process. There are two different methods of imposing temperature fluctuations in thermal parapumping operation: the "recuperative" thermal mode and the "direct" thermal mode. (See Figure 1.)

In the recuperative mode, the fluid flows back and forth through the bed and carries thermal energy into and out of the bed. The solid particles within the column come in contact alternately with fluid coming from the hot end and with fluid from the cold end. Thus, each particle experiences an alternating temperature field. The adsorption-desorption cycle produced by this field causes the alternating mass flux between particle and liquid phases (Rolke and Wilhelm, 1969). The face angle between the temperature, which varies with axial position within the column, limits the separation obtainable from this mode

of operation.

The direct thermal mode was then developed to overcome the phase angle difficulty. Since the column is surrounded by heating and cooling jacket, temperatures can be changed uniformly throughout the bed. In both thermal modes, separation arises from the coupling of adsorption-desorption cycles with the reciprocating flow.

Many investigators have used different types of theoretical analysis in predicting the separations that can be obtained by batch process. Among these theories is the "equilibrium" theory promulgated by Pigford et al. (1969), and later generalized by Aris (1969). This equilibrium theory simplifies the transport equations by assuming that the solid and fluid are locally in equilibrium. Axial dispersion was neglected and the equilibrium relationship was assumed to be linear. The resulting equation after applying these assumptions is a hyperbolic partial differential equation solvable by method of characteristics. Pigford (1969) tested the validity of the analytical solution of the hyperbolic equation by applying a parameter curve fitting using Wilhelm and his co-worker's data (1968), but found no correlation. This lack of correlation, as one would suppose, is a result of the oversimplification of the transport equation obtained from the equilibrium theory. In any case, this paper (Pigford et al. 1969) served as the limelight behind the reason for separation. Pigford and his co-worker's paper (1969) raised considerable contro-

versy amongst active and prominent investigators in this field because of difference of opinions.

Originally, Pigford et al. (1969) and Aris (1969) assumed that there was no dead volume in the reservoirs and that the reservoirs are perfectly mixed. Gregory and Sweed (1970), and Chen and Hill (1971) extended the equilibrium theory by taking into account the reservoir dead volume. In their papers, both open and batch systems were considered. For the batch case, their results agreed very well with Aris (1969) in the limiting case where the reservoirs have no dead volume. In the study made by Thompson and Bowen (1972), in which a perfectly mixed reservoir was assumed, it was theoretically shown that, with no mixing in the reservoir, a much greater separation could be achieved. A two-column arrangement operated back-to-back (to minimize mixing) was also discussed in this paper.

Butts et al. (1972) extended the equilibrium theory to the separations of multicomponent mixtures. In their study, a linear and noncompetitive equilibria was assumed; it was a batch parapump process with unsymmetric cycles (higher flow to one of the reservoirs). With such arrangement, the penetration distance into the column during each half cycle was different. A theory for separating multicomponent mixtures and a two-column arrangement, which could be used for isolating nth number of components, was also discussed. A batch process was probably not very suitable for multicomponent systems, since a large reser-

voir dead volume that would allow sufficient cycles for separation before the fluid was pumped to the bottom reservoir would be needed. A single column would be best suitable to separate a binary mixture or make a split within a series of solutes. Another method of approach was used by Butts et al. (1973) to separate a binary mixture of K^+ and H^+ on a Dowex 50 x 8 resin. In this process, the binary mixture was adjusted to build up the concentration of K^+ in the top reservoir and H^+ in the bottom reservoir. A high separation factor in the neighborhood of thousands were obtained. Butts and his co-workers noticed that electro-neutrality must be preserved within the column so that separation of these ions would be possible, viz: when K^+ desorbs, H^+ must absorb. They also investigated the separation of ternary mixtures. In these experiments, K^+ ion was concentrated in the top reservoir, H^+ in the bottom reservoir, and Na^+ in the middle of the column. This paper brought to light the possibility of using a parametric pump to separate ionic mixtures.

Shortly after the promulgation of the equilibrium theory, Sweed and Wilhelm (1969) developed the STOP-GO algorithm. The STOP-GO method of solution is superior to that of characteristics in several respects. The number of ordinary differential equations to be solved are reduced by a factor of one-half. It also provided a very clear physical picture of what the calculations meant. The fluid is displaced a distance of one time step without interphase

transfer (no axial mixing occurs). When the flow (GO) ceases, transfer between the phases begins (STOP). The computational STOP-GO algorithm is more realistic than the equilibrium model. The STOP-GO model was used to show that separation increased as a result of the following: (1) increase in mass transfer coefficient, (2) decrease in fluid velocity, (3) increase in cycle time, and (4) decrease in reservoir dead volume. The most intriguing part of this STOP-GO model is that it predicts that separation first increases exponentially and then levels off to some limiting value as the number of cycles increases. Recently, Grevillot and Tondeur (1976) studied equilibrium staged parametric pump with non-linear isotherms. One single equilibration step and discrete transfer was regarded as one-half cycle. Suggestive analogies similar to that of total reflux distillation were given.

The Continuous Pump

Hung and Lee (1971) applied the equilibrium plate to parametric pumping. The model consisted of continuous contact columns in which the number of theoretical plates were adjusted to simulate experimental data. Unfortunately, this model did not agree with the equilibrium theory of Pigford et al. (1969). Wankat (1973) applied a two equilibrium stage theory for liquid-liquid extraction parapump (Figure 2) to test the hypothesis of Wilhelm et al. (1968), and Sweed and Wilhelm's (1969) (application of parapump to systems other than adsorption and ion exchange is possible).

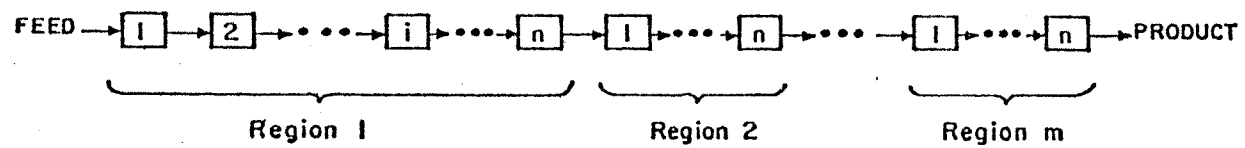


Fig. 2. Staged cycling zone extraction system (Wankat, 1973).

In this two equilibrium stage model, several methods for holding a liquid solvent stationary were presented. The system used was acetic acid and water using diethyl ether as the solvent in a horizontal helix and a test tube. This helical system consisted of a continuous-flow stage, the test modeled to fit a discrete transfer countercurrent distribution model similar to the process described in Craig and Craig's "Technique of Organic Chemistry," and the STOP-GO method (Sweed et al. in 1973). Comparatively, qualitative agreement was obtained, both experimentally and theoretically, but it was very poor. Hence, it was concluded that the application of the parapumping principle to extraction is inauspicious compared to adsorption and ion exchange.

In 1973, Gupta and Sweed used a mixing cell model to simulate non-equilibrium parapump. A "near equilibrium" approach to the analysis of parametric pumping, which is similar to the equilibrium staged model (Hung and Lee 1971, and Wankat 1973), was presented by the authors. The "near equilibrium" approach showed that significant deviations from equilibrium can exist and are, in fact, essential for improving conversion and concentration. In addition, the model requires considerably less computing time compared to other techniques, but it is rather very inaccurate. To obtain a good fit of experimental data by the mixing cell model, the number of cells has to be adjusted. A two-column paraphernalia for continuous separation of mixtures

containing two solutes were also presented.

Application of parametric pumping process to the separation of liquids in open systems have been studied extensively, both continuously and semicontinuously, in the direct thermal mode. Sweed (1971) was the first to do a considerable amount of experimental work, while Horn and Lin (1969) were pioneers in presenting a theoretical calculation for such an open system. The experimental arrangement of Horn and Lin (1969) consisted of a two-column arrangement with a center feed, a center reservoir, and reservoirs at both ends of the column where products were withdrawn. The mathematical description of the apparatus was rigorous. The theme of Horn and Lin (1969) was twofold. Firstly, a single solute system was used in which it was mathematically shown that the solute can be concentrated at one end of the reservoir (the "enrichment problem"). Secondly, the mathematical analysis of a two-component system (where these two components are to be separated from each other, by assuming that the components would be soluble in a suitable carrier liquid) was also presented (the "split problem").

Chen and Hill (1971), and Gregory and Sweed (1970) introduced the concept of "penetration distance," which was defined as the distance a concentration front will move into the column during a half cycle. Relative to this "penetration distance" concept, Chen and Hill (1971) used the equilibrium theory to study batch pump and open systems,

while Gregory and Sweed (1970) applied the equilibrium theory in the study of the semicontinuous system. The point of reversal of the cycles were determined in terms of this so-called penetration distance. In addition to the theoretical paper by Chen and Hill (1971), Chen and his co-workers (1972, 1973a, 1973b) made extensive investigations, both experimentally and theoretically, on open systems.

Chen, Rak, Stokes, and Hill (1972) studied the continuous parapump operation experimentally with feed introduced at the top. The system used for this continuous parapump was toluene-n-heptane on silica gel. For this system, transfer rates were very high and compared very well with the equilibrium theory. A separation factor of over 600 was obtained for only 14 cycles in the region predicted by the equilibrium theory. In 1972, Chen, Jaferi and Stokes studied the multicomponent separation of fructose and glucose from water using fullers earth, and equilibrium isotherms of Langmuir type was obtained. The transfer rates for this system were very slow, requiring more than 2 hours to reach equilibrium. A semicontinuous parametric pump with top feed was studied experimentally by Chen, Reiss, Stokes, and Hill (1973). The system was toluene-n-heptane-silica gel and the results were compared with the continuous pump with top feed (Chen, et al. 1972). The bottom product concentration did not agree so well as that obtained previously. In 1973, Chen, Stokes and Lin studied another continuous parapump operation with top

feed. This time the system was a mixture of toluene, aniline and n-heptane on silica gel. Equilibrium theory was applied by treating the multicomponent mixture as a series of pseudo-binary mixtures.

Thus far, the investigation of parapump operation by open, direct, and thermal mode has shown the possibility of obtaining continuous and semicontinuous separations. Large separation factors are readily obtainable when the shift of equilibrium with temperature is large and mass transfer is fast. Under these conditions, the equilibrium theory gives a good prediction, but if the mass transfer is slow, less separation is obtained and the equilibrium theory will not give a good prediction.

Shaffer and Hamrin (1975) combined affinity chromatography and pH parametric pumping to reduce trypsin concentration in an aqueous solution. Chen et al. (1977) experimentally investigated a semicontinuous pH parapump using haemoglobin and albumin on sephadex ion exchanger. The column had a center feed between an enriching column and a stripping column, and was operated batchwise during upflow and continuously during downflow. Chen et al. (1979) used a continuous pH parametric pumping for the separation of haemoglobin and albumin. The parapump had a feed, containing the protein mixture to be separated, introduced alternately to the column through the top and bottom of the column. The products were collected from the column during the top and bottom feed.

Stokes and Chen (1979) studied the design and scale-up of the separation of solutes from multicomponent systems on a commercial scale of a continuous thermal parapumping operation. The authors developed the design equations based on the analytical equations of dilute solution theory. Heat exchanger-type configuration to enable the authors to use direct thermal mode was adopted for the pilot plant and commercial systems. All the energy requirements for 0-100% solute separation were given, and auxiliary equipment was also included in this paper. It was shown that the energies required are of the same order of magnitude as that of distillation.

Cycling Zone Adsorption

Cycling zone adsorption, first developed by Pigford and his co-workers (1969), is similar to parametric pumping, except that the fluid to be separated flows in a single direction through a series of columns. (See Figures 2 and 3.) The "direct or standing wave" mode of operation utilizes a water jacket which changes the temperature cyclically between the cold temperature and the hot temperature. The temperature of adjacent columns are out of phase with each other. In the first half of each cycle, the column sequence is hot, cold, hot, cold, etc., and in the second half of the cycle the column sequence is cold, hot, cold, hot, etc. Each region of constant temperature was regarded as a "zone" by Pigford et al. (1969). Another mode of operation is the "traveling wave." The

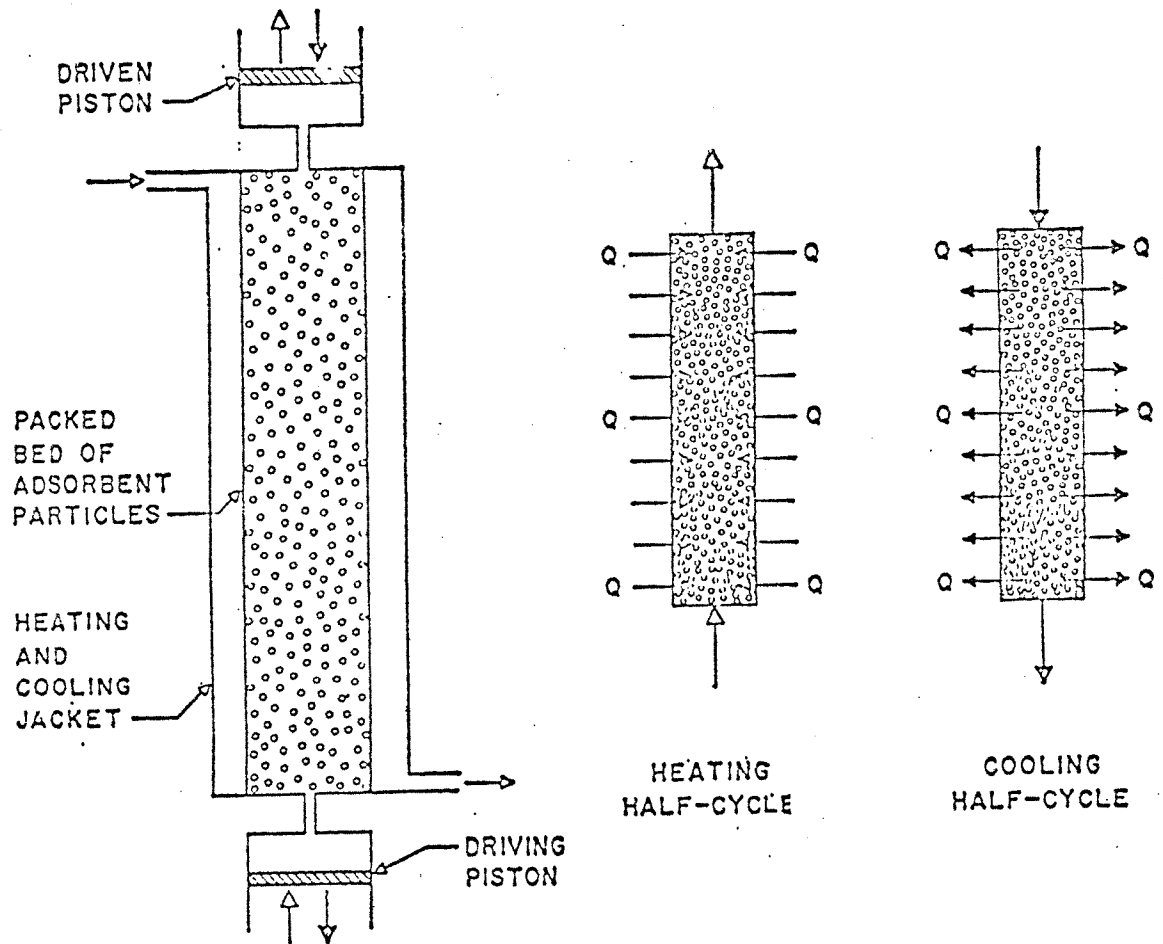


Fig. 3. Diagram of column for parametric pumping in direct mode (Pigford et al., 1969).

columns of the traveling wave are adiabatic and the fluid is alternately heated or cooled before entering the column. The temperatures are again out of phase in adjacent zones. In the standing wave mode of operation, experiment has shown that a two-zone system produced a larger separation than a single zone. It was also shown that a single-zone traveling wave separation was superior to the single-zone direct wave mode of separation. The reason for this difference in separation was attributed to the fact that the solid has better ability to remove solute from a fluid of low concentration by temporarily storing this solute and then give this solute up (when signal is given by increasing the temperature) to a fluid of high concentration. The author (Pigford et al. 1969) concluded that, since the use of several zones allow more opportunities to do this, the separation is enhanced when several zones are used.

Baker and Pigford (1969) did a detailed experimental and theoretical analysis on both the direct and traveling wave modes of operation. They also applied the local equilibrium theory by assuming that there is no axial dispersion and heat of adsorption as in parametric pumping. The solution of the resulting energy equation, after applying these assumptions, predicted that a temperature wave will pass through the column at a characteristic thermal wave velocity without changing shape or amplitude. The solution of the linear isotherm equation predicted that the separation factor would be infinite as the number of

zones becomes very large, but for nonlinear isotherms, the separation would not be infinite.

Gupta and Sweed (1971) utilized the method of characteristics to develop an equilibrium theory for the direct wave of operation. They emphasized that the fluid displacement must be correctly chosen to get an increasing separation. Van der Vlist (1971) used the cycling zone adsorption to separate oxygen and nitrogen from air. A two-zone direct mode system was used and obtained a maximum oxygen separation factor of 10.6. Ginde and Chu (1972) used a mixed bed of ion exchange resins in a single-zone cycling zone adsorber to separate NaCl from water. This process was essentially an unsteady state cycling zone with total recycle, since products from the column were recycled until the desired separation was obtained. The parameters which affected separations were the amount of liquid in the system, the flow rate, and the cycle time.

In 1972, Rieke extensively studied the standing wave mode of cycling zone adsorbers with and without partial recycle. Experimental results showed that, for a single zone without recycle separating toluene from n-heptane on silica gel, optimization of separation could be achieved by switching temperature at an optimum frequency. Results showed that partial recycle of a product can increase the separation, but longitudinal mixing limited the amount of separation.

Wankat (1973, 1974) extended the cycling zone adsorp-

tion to extraction. (See Figure 2.) In both the direction and the traveling wave modes of operation, he used the counter-current distribution type system similar to that in Craig and Craig's "Technique of Organic Chemistry," with discrete transfer and equilibrium steps which were applied to keep one liquid phase stationary. The theoretical result obtained for the direct mode (Wankat, 1973) showed that if the cycle time is optimized, there would be an increase in separation from zone to zone. A qualitative agreement of experiment with theory was obtained when diethylamine-water-toluene in the test-tube system was used, but quantitative agreement was not so good. The theory similar to the direct mode (Wankat, 1973) was also derived for traveling wave (Wankat, 1974), but this time energy balance was added. Theoretical calculations were made, and the results showed great dependency of separation on the optimized thermal wave velocity. The separations obtained for traveling mode was lower than that obtained for direct mode because the thermal wave velocity was too low. Cycling zone separation process seems to be better for the separation of liquids than for large separations of gases. It also has an advantage over parametric pumping since it is inherently an open system and does not require flow reversal, but disadvantageous because it has one less degree of freedom.

This work was focused mainly on theoretical and computer simulation of various versions of pH-driven parametric

pumps, viz: the batch parapump, the continuous parapump, and the cycling zone adsorption. A combination of STOP-GO algorithm and a simple equilibrium theory (Pigford et al., 1969; Jenczewski and Meyers, 1970; Wankat, 1974; Grevillot and Tondeur, 1976) and various performance characteristics were applied in predicting the protein separation.

Chapter I

PROCESS DESCRIPTION

Operational techniques were developed for continuous batch and cycling zone adsorption. In the simplest operational scheme, the separation was accomplished through dynamic adsorption of the mixture using a fixed bed. At all times, adsorption was followed by desorption of the mixture, provided the intensive variable (pH) is properly imposed on the column of ion exchange resins to effect the equilibrium distribution of the components being separated.

Batch and Continuous Parapumping System

The one-column parametric pumping system in this study applies the dynamic adsorption principles for separation of components from a mixture (see Figure 4). It consists of a column packed with an ion exchanger (cation or anion) and reservoirs attached to each end. Axial displacement of the fluid in the column imposes a pH difference within the column which can be adjusted periodically to high and low. The adsorption resin adsorbs solute when the pH is low and releases solute when the pH is high.

In this recuperative pH mode, the reservoirs are maintained at two different pH values. As the solution oscillates through the bed, the particles of the resin

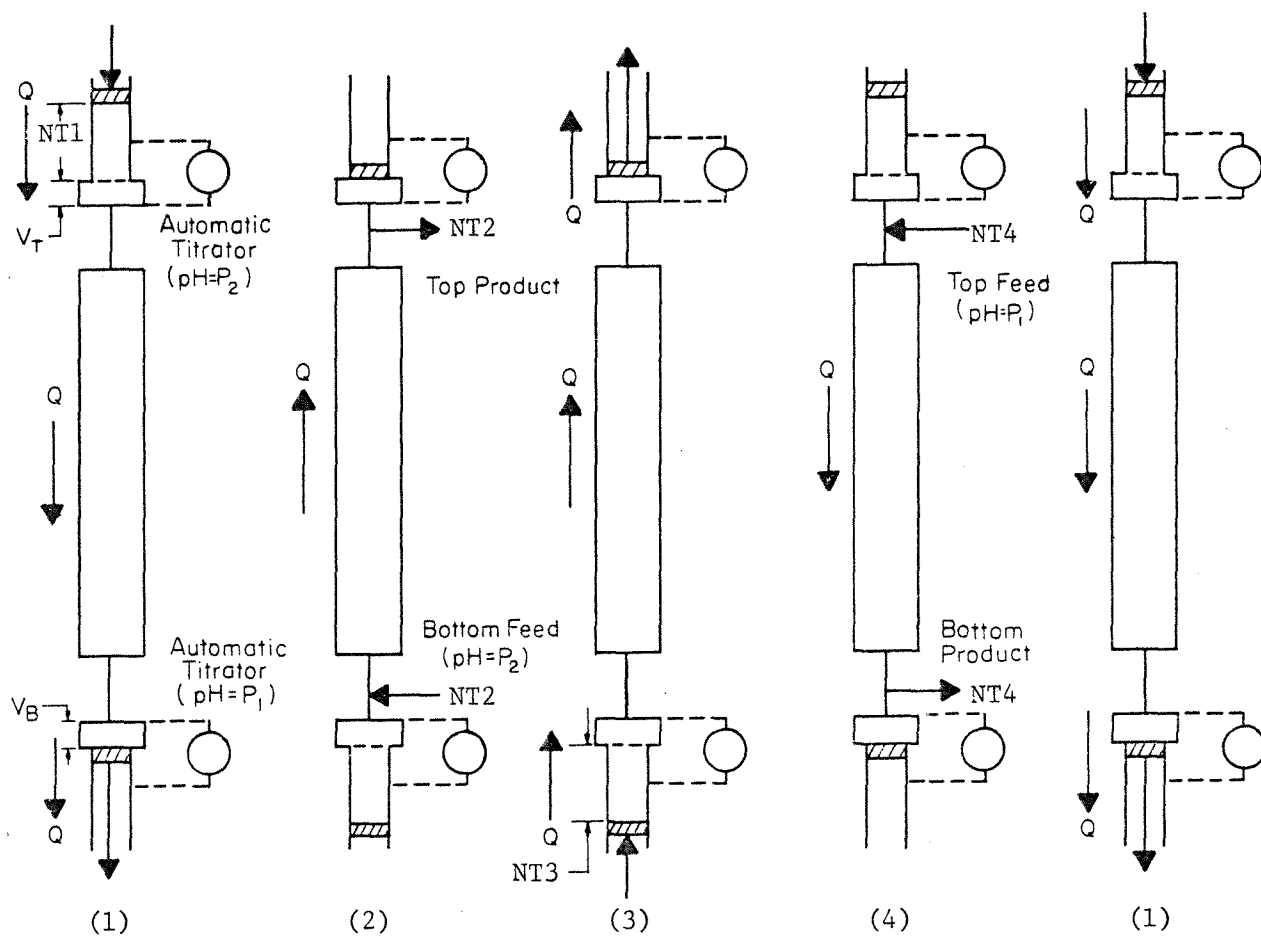


Fig. 4. Column diagram for continuous pH parametric pumping.

experience a periodic change in pH. During the first half-cycle, the fluid with low pH in the top reservoir is pumped into the top of the column. At the same time, the solution that emerges from the column fills the bottom reservoir. On the second half-cycle, the solution with high pH in the bottom reservoir flows back to the column. At the end of this half-cycle, the top reservoir is filled with a solution that comes forth from the top of the column, and one cycle is completed.

The top and bottom reservoirs of the parametric pumping system have dead volumes of V_T and V_B respectively. The top reservoir is maintained at a low pH level by an automatic titrator, while a second titrator is used to keep the bottom reservoir at a high pH level. The buffer ionic strengths for solutions in both top and bottom reservoirs are kept at IS_2 and IS_1 respectively, by means of two hollow fiber dialyzers manufactured by Amicon.

The mixture to be separated with concentration of $y_0 (=1)$ (normalized) fills the column voids, the top reservoir, and the bottom reservoir dead volume at the start of the process. Each cycle of operation consists of four steps for a continuous process and two steps for a batch process, and the sequence of operation is as follows:

1. Transfer down (push down): The fluid in the top reservoir is transferred to the column, and the fluid in the column is transferred to the bottom reservoir. Since the column was saturated with haemoglobin concentration of

$y_0(=1)$, the bottom reservoir concentration for the first cycle is $y_0(=1)$.

2. Equilibration at pH (=6): During this equilibration step, low pH feed is introduced from the bottom of the column, while the emergent fluid from the top of the column is collected as the lean product.

3. Transfer up (push up): The solution formerly adsorbed by the adsorbent is now desorbed and brought to the top reservoir, while the solution in the bottom reservoir is returned to the column.

4. Equilibration at pH (=8): High pH feed is introduced from the top of the column, and the emergent fluid from the bottom of the column is the rich product. This step ends the cycle of operation. For subsequent cycles, steps 1 to 4 are repeated until steady state product concentrations are achieved. (Note that for the batch process, steps 2 and 4 are omitted.)

The flow rate within the column is always identical to the reservoir displacement rate Q . The volumes of the bottom and top feeds (NT_2 and NT_4) are not necessarily equal to those of top and bottom products. For both the up and down flow, the reservoirs have the same displacement; that is, $NT_1 = NT_2$.

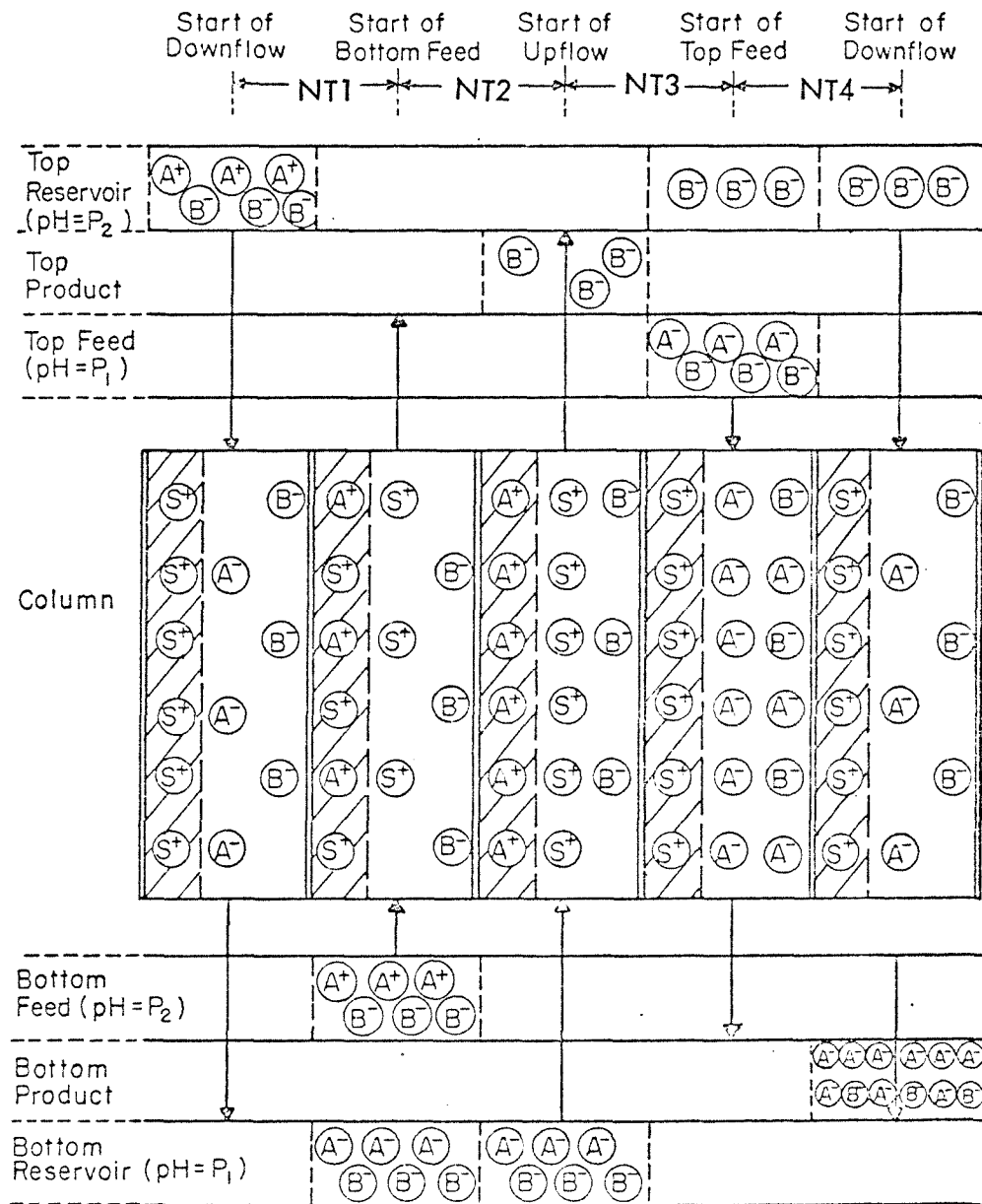
Since proteins carry both negatively and positively charged groups, which can normally bound to anionic or cationic exchangers, the net charge is dependent on the pH level. At low pH, the net charge is positive; at high pH,

it is negative. At the isoelectric point (no net charge), the proteins are not bound to any type of ion exchangers.

The schematic description of pH parametric pumping principle is shown in Figure 5. Suppose the protein mixtures to be separated contain species A and B with isoelectric points I_A and I_B , whereas $I_A > I_B$. Two constant pH fields (that is, high and low pH, P_1, P_2) are imposed periodically on the systems, and $P_1 > I_A > P_2 > I_B$. The ion exchanger is assumed to be cationic with counter ions S^+ . For illustrative purposes, assume the following (note that these assumptions are not necessarily true for the computational algorithm):

1. The displacement is equal to the void volume of the column V_e ; that is, $NT1 = NT3 = V_e$.
2. The volume of either the top or the bottom feed is identical to V_e ; that is, $NT2 = NT4 = V_e$.
3. The ionic exchange between the counter ions and the protein A is essentially complete at the end of each stage (Pharmacia Fine Chemicals, 1976).

At the start of the run, the void volume of the bed is filled with the high pH feed solution, and the top reservoir is filled with the solution containing a feed of pH = P_2 . The net charges for A and B in the column are negative, and in the top reservoir are positive and negative, respectively. During the first downflow stage NT1 the low pH (P_2) fluid coming from the top reservoir enters the top of the column, while the solution emerged from the other end



A, B = substances with isoelectric points, I_A and I_B respectively,
 $P_2 < I_A < P_1$; $I_B < P_2$; P_1 = high pH ; P_2 = low pH
 S⁺ = Counter ion
 ▨ = Cationic exchanger

Fig. 5. Schematic description of pH parametric pumping principle.

enters the bottom reservoir. The pH of the column is then changed from P_1 to P_2 . As a result, S^+ is exchanged for the A^+ originated from the top reservoir. During NT2, a feed with $pH = P_2$ is introduced through the bottom, and simultaneously a top product containing only pure B is removed from the column at the same rate. In addition, the A^+ initially present in the bottom feed is exchanged for S^+ . After this adsorption process, an upflow is followed, and the high pH enters the bottom of the column. The solution containing pure B flows out of the column to the top reservoir. Consequently, the pH in the column changes from P_2 to P_1 , and desorption of A occurs. S^+ shifts back to the bed, and the ion exchanger is then regenerated. During NT4, a feed with $pH = P_1$ enters the top, while a product rich in A is withdrawn from the bottom of the column. One whole cycle is thus completed. All the solute A entering from either the top or bottom always moves toward the bottom product stream. Complete removal of A from the top product stream is achieved with one single complete cycle. Note that this result is based on the assumptions made above. In practice, it may not be possible to implement the operating conditions that satisfy the required assumptions.

Cycling Zone Adsorption

The cycling zone adsorption is similar to parametric pumping, except that the fluid to be separated does not flow back and forth through a single bed, but instead flows

in a single direction through a series of stages in the column. This process undertakes the pH recuperative mode of operation. The pH of the columns are changed cyclically between high pH (=8) and low pH (=6) (see Figure 6). In this figure, the column is represented as a series of equilibrium stages. Adjacent stages are out of phase with each other in that, when one stage has high pH (=8), the stages adjacent to it have low pH (=6).

During the first half of each cycle, the stage pH sequence is high, low, high, low, etc., and during the second half of the cycle, the stage pH sequence is low, high, low, high, etc. Each region of constant pH value is called a "zone;" hence, the name cycling zone adsorption. Various parameters such as number of stages and recycle ratios (B) were scrutinized in this study.

The product from the cycling zone adsorption is a function of time in that the pH and concentration of the product vary continually. However, a repeating state is reached where the product concentration repeats from cycle to cycle. The adsorption-desorption mechanism is similar to that of parametric pumping. When a zone is at high pH, the stationary phase rejects the solute and the moving phase becomes more concentrated. But, when a zone is at low pH, the equilibrium distribution coefficient changes and the stationary phase stores the solute. The separation is a function of the difference of the two pH levels. Therefore, for better separation, pH levels must be

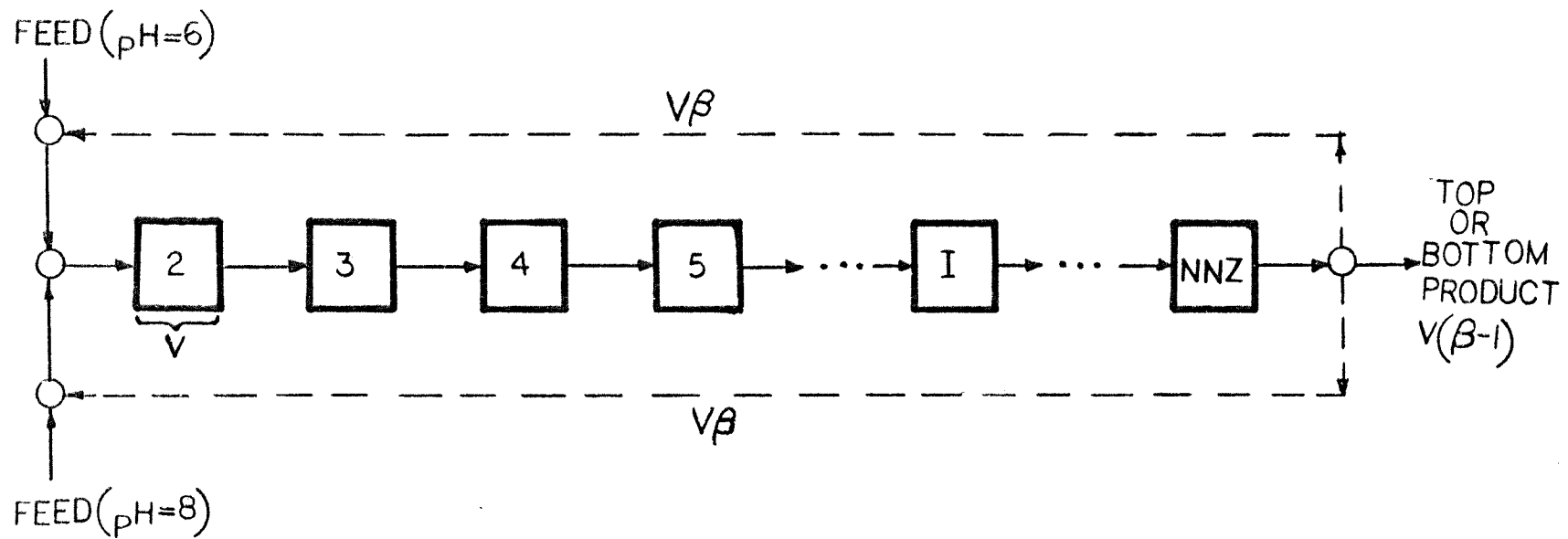


Fig. 6. Zone Diagram for pH Cycling Zone Adsorption with Recycle.

properly chosen to encompass the isoelectric points of the protein mixtures under consideration.

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Chapter II

DERIVATION OF THE WORKING EQUATION

The working equation used for the simulation of the computer programming was derived by using two different methods of approach. The first method was the simplification of the general transport equation for a dilute binary system, and the second method called for a simple material balance of the extensive variables of the column.

To illustrate the first method of solution, consider the ion-exchange column with the initial conditions as shown in Figure 7.

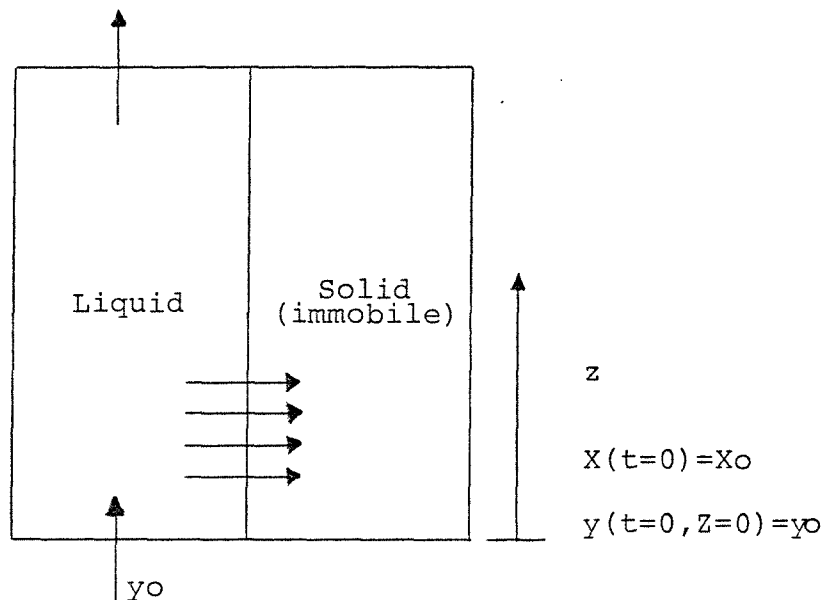


Fig. 7. Ion-exchange Column

Let y = moles of component A in the liquid phase per unit volume.

X = moles of component A in the solid phase (adsorbed on surfaces of course) per unit volume.

$X = ky$, the equilibrium relation for A between solid and liquid phases.

The transport equation for component A in the ion-exchange column (assuming dilute binary system) is:

$$\begin{aligned} \frac{\partial C_A}{\partial t} + V_x \frac{\partial C_A}{\partial x} + V_y \frac{\partial C_A}{\partial y} + V_z \frac{\partial C_A}{\partial z} \\ = D_{AB} \left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right) + R_A \end{aligned} \quad (1)$$

Under the stratum of physicochemical description, the principle of maximum gradient can be used for continuous flow system such as plug flow. This maximum gradient principle is a less detailed mode of description of flow equations, but it could be considered to be a simplified multiple-gradient model in which the dispersion terms are deleted, only one derivative retained in the bulk flow terms. Therefore, for a fixed bed adsorption column, only concentration gradients in the axial direction caused by the bulk flow are considered, and all radial gradients, dispersion, and the like are ignored. Applying the maximum gradient principle to equation 1, the following is obtained:

$$\frac{\partial C_A}{\partial t} + \frac{\partial (V_z C_A)}{\partial z} = R_A + m_A(t) \quad (2)$$

Since there is no chemical reaction, $R_A = 0$ and $V_z = \text{constant}$.

Therefore:

$$\frac{\partial C_A}{\partial t} + V_z \frac{\partial C_A}{\partial z} = m_A^{(t)} \quad (3)$$

The interphase mass transfer term, $m_A^{(t)}$, for the fluid phase is identical to the mass transferred from the solid phase, and due to the sign convention for $m_A^{(t)}$,

$$m_{A,l}^{(t)} = -m_{A,s}^{(t)} \quad (4)$$

The interfacial mass-transfer coefficient for the process is

$$m_{A,l}^{(t)} = -k_{A,l}(\text{pH})a(C_{A,l} - C_{Ai,s}) \quad (5)$$

where a = interfacial area per unit volume.

$C_{A,l}$ = bulk liquid phase concentration of A

C_{Ai} = interfacial concentration of A

Combination of equations 3 and 5 give

$$\frac{\partial C_A}{\partial t} + V_z \frac{\partial C_A}{\partial z} = -k(\text{pH})a(C_{A,l} - C_{Ai,s}) \quad (6)$$

Using the notations depicted in Figure 1, and rewriting equation 6 for both liquid and solid phase, we get

$$\text{Liquid:} \quad \frac{\partial y}{\partial t} + V_z \frac{\partial y}{\partial z} = -k(\text{pH})a(y - y_e^*) \quad (7)$$

$$\text{Solid:} \quad \frac{\partial x}{\partial t} = k(\text{pH})a(y - y_e^*) \quad (8)$$

Combination of equations 7 and 8 gives

$$\frac{\partial y}{\partial t} + \frac{\partial x}{\partial t} + \frac{q}{A} \frac{\partial y}{\partial z} = 0 \quad \text{where } V_z = \frac{q}{A} \quad (9)$$

Euler's single-step integration scheme written backward, but truncated before the first difference, is

$$\frac{dy}{dz} = f(y, z)$$

Therefore,

$$\text{if } \frac{dy}{dz} \text{ is replaced by } \frac{Y_i - Y_{i-1}}{Z_i - Z_{i-1}}$$

a difference equation of the first order is obtained,

$$\frac{Y_i - Y_{i-1}}{Z_i - Z_{i-1}} = f(Y_i, Z_i) \quad (10)$$

Rearranging equation 10.

$$y(i, j-1) = y(i-1, j-1) + f[y(i, j-1)] [z(i, j-1) - z(i-1, j-1)] \quad (11)$$

In general, difference equations does not require even spacing of the pivotal points, but assuming that equation 11 has evenly spaced pivot, $Z(i, j-1) - Z(i-1, j-1)$ is replaced by Δz and we get

$$y(i, j-1) = y(i-1, j-1) + \Delta z f[y(i, j-1)] \quad (12)$$

upon rearrangement,

$$\frac{y(i, j-1) - y(i-1, j-1)}{\Delta z} = f[y(i, j-1)] = \frac{dy}{dz} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \quad (13)$$

Similarly,

$$\frac{y(i, j) - y(i, j-1)}{\Delta t} = \frac{dy}{dt} \quad \text{and} \quad \frac{x(i, j) - x(i, j-1)}{\Delta t} = \frac{dx}{dt} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\}$$

Substituting equation 13 into equation 9, we get

$$\frac{y(i, j) - y(i, j-1)}{\Delta t} + \frac{x(i, j) - x(i, j-1)}{\Delta t} + \frac{q}{A} \frac{y(i, j-1) - y(i-1, j-1)}{\Delta z} \quad (14)$$

Multiply equation 14 by Δt and $A\Delta z$ to get

$$V[y(i, j) - y(i, j-1)] + \bar{V}[x(i, j) - x(i, j-1)] + V[y(i, j-1) - y(i-1, j-1)] = 0 \quad (15)$$

Where $V = \Delta t q = A\Delta z$,

V = Volume of component A in the fluid phase

and \bar{V} = Volume of component A in the solid phase

rearranging equation 15, we obtain

$$V_y(i,j) - V_y(i,j-1) + \bar{V}_x(i,j) - \bar{V}_x(i,j-1) = V_y(i-1,j-1) - V_y(i,j-1)$$

$$V_y(i,j) + V_x(i,j) = V_y(i-1,j-1) + V_x(i,j-1) \quad (16)$$

Let $x-ky$ be a linear equilibrium relation for A between solid and liquid phases.

Expressing this equilibrium relation in finite difference form, we get

$$x(i,j-1) = k(i,j-1)y(i,j-1) \text{ and } x(i,j) = k(i,j)y(i,j) \quad (17)$$

Substituting equation 17 into equation 16, we get

$$\begin{aligned} V_y(i,j) + \bar{V}k(i,j)y(i,j) &= V_y(i-1,j-1) + \bar{V}k(i,j-1)y(i,j-1) \\ y(i,j)[V + \bar{V}k(i,j)] &= V_y(i-1,j-1) + \bar{V}k(i,j-1)y(i,j-1) \end{aligned} \quad (18)$$

Upon rearrangement,

$$y(i,j) = \frac{V_y(i-1,j-1) + \bar{V}k(i,j-1)y(i,j-1)}{V + \bar{V}k(i,j)} \quad (19)$$

The second method of derivation which involves a simple mass balance of the extensive variables can be obtained from Figure 8.

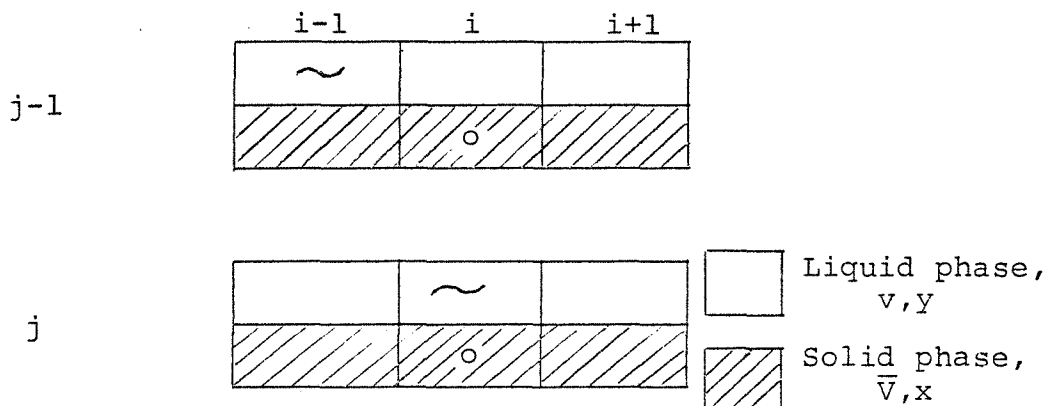


Fig. 8. Schematic of a One-Cell Model.

A mass balance for species A gives:

$$\frac{V[y(i,j)-y(i,j-1)]}{\Delta t} + \frac{\bar{V}[x(i,j)-x(i,j-1)]}{\Delta t} = q[y(i,j-1)-y(i-1,j-1)] \quad \dots(20)$$

Since $\Delta t q = V$, combination of equation 20 and 17 gives equation 19, which was previously obtained via the transport equation. This equation is so general that it is good for batch, continuous parapump and cycling zone adsorption simulation. The inputs of the computer program simulation depends on the desired process, viz: batch or continuous, as the case may be, but for the cycling zone, a different algorithm is needed. The standard fortran IV language was used for the simulation.

As can be readily seen from equation 19, the concentration for the next transfer step can be solved in terms of the concentrations in the previous transfer step. Since the linear isotherm constant, k , is a function of pH, and the pH varies with the transfer step, it then becomes necessary to use the appropriate $k(\text{pH})$ value that corresponds to the pH of the transfer step under consideration. The isotherm slope depends on pH; therefore, the concentration is different for the two half-cycles. Usually, it is larger at the higher pH since $k(\text{pH})$ is smaller there. At low pH, the solute wave moves slow and it is held up by the stationary (solid) phase during the first half-cycle. During the second half-cycle, i.e., at the high pH, the solute wave tends to become more concentrated, since it moves faster. These two effects cause a separation with

concentrated solute exiting when the pH is high.

Chapter III

EQUILIBRIUM THEORY OF LINEAR ION-EXCHANGE ISOTHERMS

In the equilibrium theory for the linear isotherms used in this study, it is assumed that local equilibrium between liquid and sorbent in the layers of the separating medium in the column is attained. Deviations from local equilibrium can be accounted for in a semiempirical way by introducing the concept of "effective plates." In this discontinuous model, the solution in an effective plate of the bed attains equilibrium with the ion exchanger (or sorbent) before it moves on into the next plate. The effluent thus consists of a sequence of finite solution volumes, each of which is so large as to fill an effective plate. On their way through the column, these volumes are subjected to a series of equilibrations, one in each effective plate. These equilibrium theories substitute mixing in the plates for non-equilibrium as the cause of boundary spreading.

Theoretical calculations were based on batch, continuous flow through the column, and finite rates of ion-exchange or sorption. These calculations brought out the effect of the operating variables such as the number of effective plates or cells (for batch, continuous and cycling zone adsorption); rate of displacement for the

batch process; rate of the feed from the bottom (or rate of the feed from the top); rate of product take-off for the continuous process; and the effect of recycle on the cycling zone adsorption. In any case, it has been shown both qualitatively and quantitatively that the column performance depends on these operating conditions.

The assumption of equilibrium theory is particularly very useful in simplifying the material balance made on the extensive variables of the column. The assumption of discrete transfer equilibrium stage model was used by Jenczewski and Meyer (1970); Wankat (1974); Grevillot and Tondeur (1976). The assumption of the equilibrium theory does enable us to have a clear insight of the pH-parametric pumping principle. The adsorbent bed is divided into N equal cells (plates or stages), each of length Z/NNZ , where Z is the length of the column, and each stage is represented as i, j . In this case, i will be the cell number and j , the transfer step. The schematic of this equilibrium theory is clearly depicted by Figure 9. Initially, the system is assumed to be in equilibrium at $j-1$, in which case each cell will have uniform concentrations in both the fluid and solid phases. If each fluid section is displaced exactly one step ahead in the transfer step, then the fluid $y(i, j-1)$ originally opposite the solid section i will now be opposite $i+1$. After each transfer step, the operation is stopped, and all stages are allowed to reach equilibrium. Thereafter, equilibrium is immediately re-established and

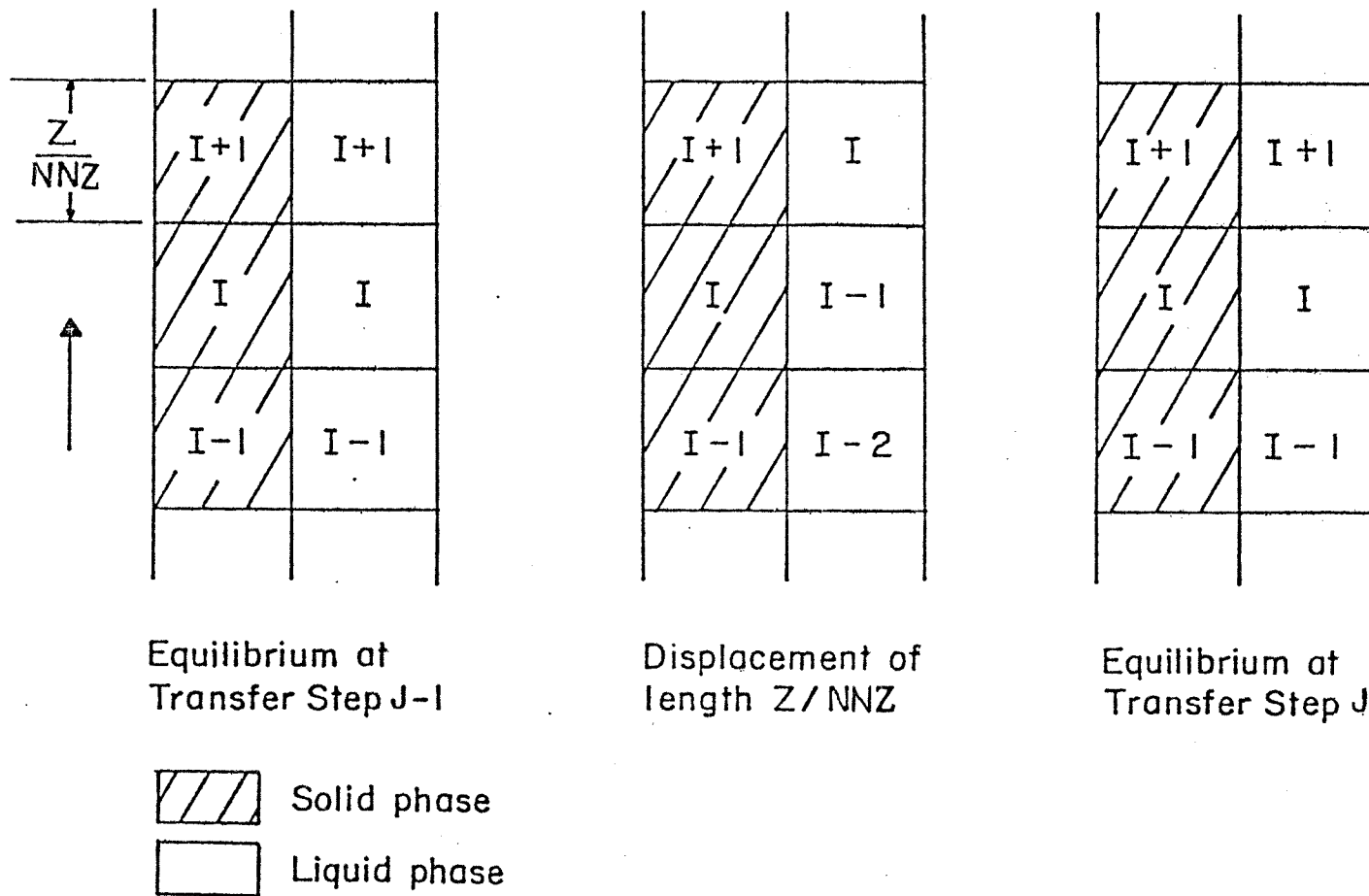


Fig. 9. Schematic of Equilibrium Theory.

and the next transfer step (j) begins.

Ion-Exchange Column

The framework of the ion-exchange is a positive or negative electric surplus charge, which is compensated by mobile counter ions of the opposite sign. Cation exchangers contain cations, and anion exchangers contain anions as counter ions. The counter ions can be exchanged for other ions of the same sign. Essentially, ion exchange is a diffusion process. The ion exchanger takes up certain counter ions in preference to others; i.e., it is selective. Ion-exchange equilibrium is attained when an ion exchanger is placed in an electrolyte solution containing a counter ion, which is different from that in the ion exchanger. Protein mixture is an amphoteric polyelectrolyte and can normally be bound to both anion and cation exchangers. Since they carry both negative (for example, carboxyl) and positive (for example, amino) groups, their net charge is dependent on pH. At low pH, the charge is positive; at high pH, it is negative. The point of zero charge is called the isoelectric point, and at this pH, the protein is not bound to either anion or cation exchangers.

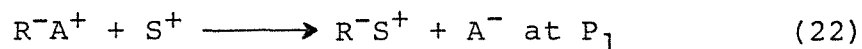
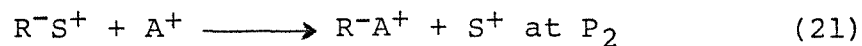
At pH below their isoelectric points, proteins are bound to cation exchangers, and at pH above their isoelectric points, they are bound to anion exchangers. The binding is also dependent on the amount of charge carried by the protein. The greater the charge, the greater is the binding. The ionic strength of the environment (i.e.,

buffer concentration) has a pronounced influence on the binding. An increase in ionic strength of the eluant means increased competition for the binding sites of the ion exchanger; the electrical properties of the eluant are also changed, decreasing the electrostatic interaction between the ion exchanger and the counter ions. These combine to produce binding strength with the ion exchanger. The porosity of the ion exchanger does not influence the binding mechanism, but it influences the capacity, since much of the ion exchanger may be unavailable to large molecules.

The parameters which can be varied to carry out the fractionation of bound protein mixture are buffer pH and ionic strength. Towards the isoelectric point, a change in pH renders the protein mixture neutral, thereby causing it to be desorbed and eluted from the ion exchange. If the ionic strength is low, a minimum competition for the charged groups on the ion exchanger exists, but an increase of the ionic strength will increase the competition, thus reducing the interaction between the ion exchanger and the protein mixture.

The practicality of the elution process described above can easily be understood if one considers the following: suppose a protein mixture contains species A and B and that the corresponding isoelectric points are I_A and I_B respectively. Protein A can be separated from the rest of the protein species if $P_2 < I_A < P_1$, where P_1 and P_2 are the two

constant pH fields ($P_1 = \text{pH}$ of the bottom reservoir and $P_2 = \text{pH}$ of the top reservoir). Species A will be negatively charged at P_1 , and at P_2 , it will be positively charged. Species A will be taken up by a cation exchanger, R^- (with the counter ion S^+) at P_2 and released at P_1 :



The parapump with these pH levels will then remove species A from the mixture at the pH end of the column and concentrating it at the high pH end (see Figure 5).

Chapter IV

COMPUTATIONAL ALGORITHM

Equilibrium Theory Cum STOP-GO Method

1. Divide the adsorbent bed into NNZ equal stages, each of length Z/NNZ and Z being the length of the bed.
2. Divide the time domain into NT increments. The time interval for introducing the feed from the bottom and product withdrawal from the top is NT2, and the time interval for introducing the feed from the top and product withdrawal from the bottom is NT4. The time interval for the downward fluid flow is NT1, and the time interval for the upward fluid flow is NT3. For continuous parapump process, NT2 and NT4 are greater than one; but for the batch parapump process, $NT2=NT4=1$ (i.e., no feed introduction or product withdrawal from either top or bottom of the column).
3. Initialize the fluid and solid compositions in the NNZ stages to some physically realizable values. Initial composition was assumed to be $YINT=1$ in this simulation. This initialization (equilibration) step is at $j=1$. (See Figure 10(a).)

The operational steps of the algorithm can now begin.

4. Push Down (Figure 10(b).): The time step NT1 for the downward flow of the fluid phase is divided into NNZ equal time increments of length $NT1/NNZ$. Each fluid section is now displaced one step ahead beginning at $j=2$ for

each time element $NT1/NNZ$. Equilibration is allowed to re-establish, the concentration profile Y in the column is determined and another displacement is made; this time at $j=3$. When $j=NT1$ time step is attained, the bottom reservoir concentration is calculated.

5. Feed from Bottom and Product from Top (Figure 10(c).): The time step $NT2$ for the bottom feed and top product withdrawal is divided into NNZ equal time increments of length $NT2/NNZ$. A predetermined volume of feed ($pH=6$) equal to volume element $NT2/NNZ$ is introduced beginning at $j=2$. Equilibration is re-established, the concentration profile YY in the column is determined, and the process is repeated until $j=NT2$, after which the top product concentration is calculated.

6. Push Up (Figure 10(d).): The time step $NT3$ for the upward flow of the fluid phase is divided into NNZ equal time increments of length $NT3/NNZ$. Each fluid section is displaced one step ahead beginning at $j=2$ for each time element $NT3/NNZ$. Successive equilibration is allowed, and concentration profile YYY determined until a final displacement at $j=NT3$ is attained, after which the top reservoir concentration is calculated.

7. Feed from Top and Product from Bottom (Figure 10(e).): The time step $NT4$ for the top feed and bottom product withdrawal is again divided into NNZ equal time increments of length $NT4/NNZ$. A predetermined volume of feed ($pH=8$) equal to volume element $NT4/NNZ$ is introduced,

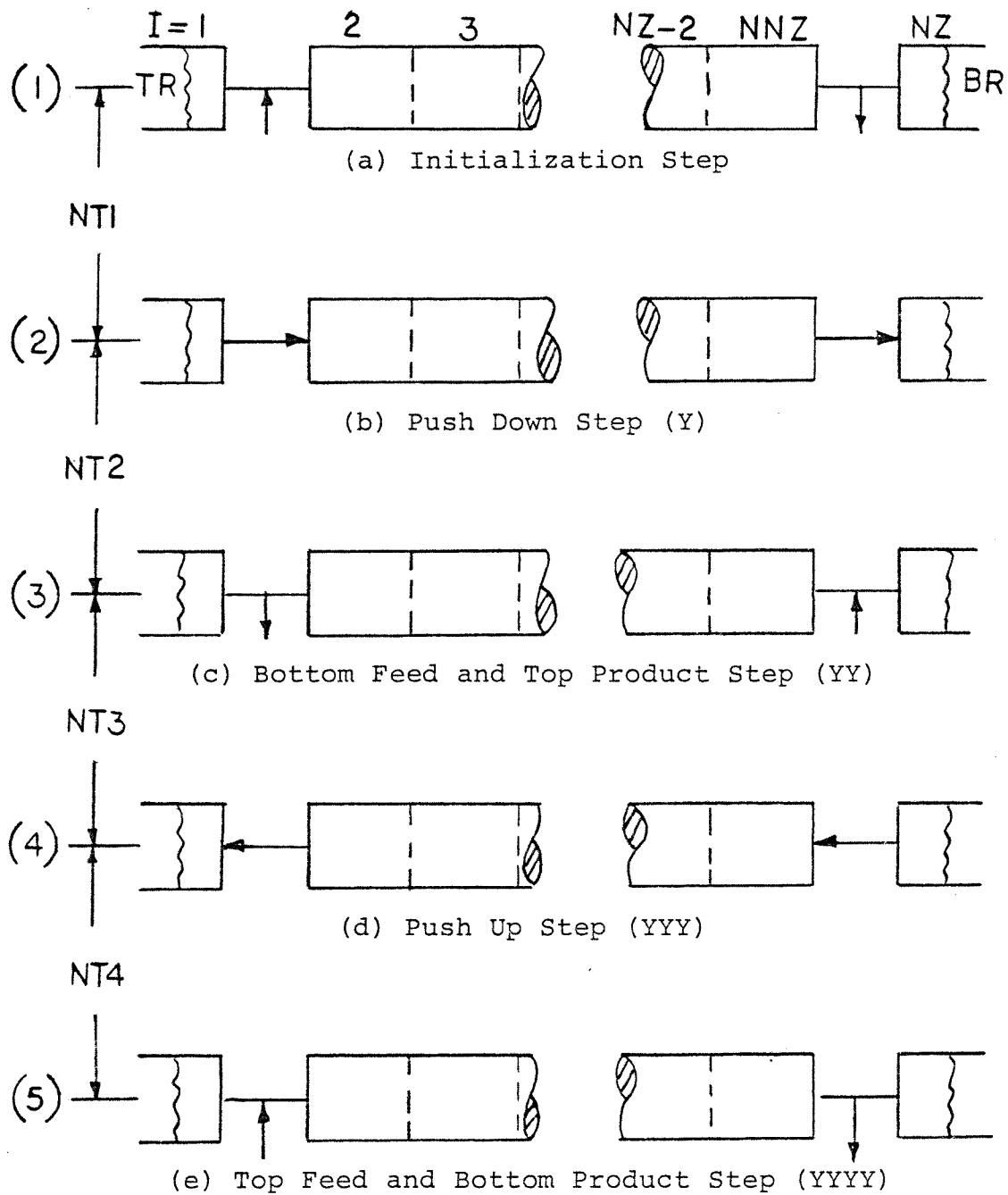


Fig. 10. Diagram of Operational Steps used in Computer Simulation (batch and continuous).

beginning at $j=2$. Equilibration is re-established, the concentration profile $YYYY$ determined, and the process repeated until $j=NT4$ is attained. The bottom product concentration is then calculated.

8. This sequence of operation ends the first cycle. For subsequent cycles, steps 4-7 have to be repeated.

Note that for batch parapumping calculation, steps 5 and 7 are omitted.

The simulation of this calculational algorithm assumes the following:

(a) That these NNZ increments (volume elements) are entirely independent of one another.

(b) That the volume elements represent batch reactors connected in series.

(c) That only partial equilibration between adjacent phases and full equilibration between opposite (solid and fluid) phases take place.

(d) That each volume element is treated individually for calculating concentrations.

Appendix A contains a listing of the FORTRAN IV digital computer program written to implement the EQUILIBRIUM THEORY CUM STOP-GO METHOD for the recuperative pH mode of parametric pumping.

pH Driven Cycling-Zone Adsorption

1. Divide the adsorbent bed into NNZ equal stages each of Z/NNZ , where Z is a length of the bed. (See Figure 11.)

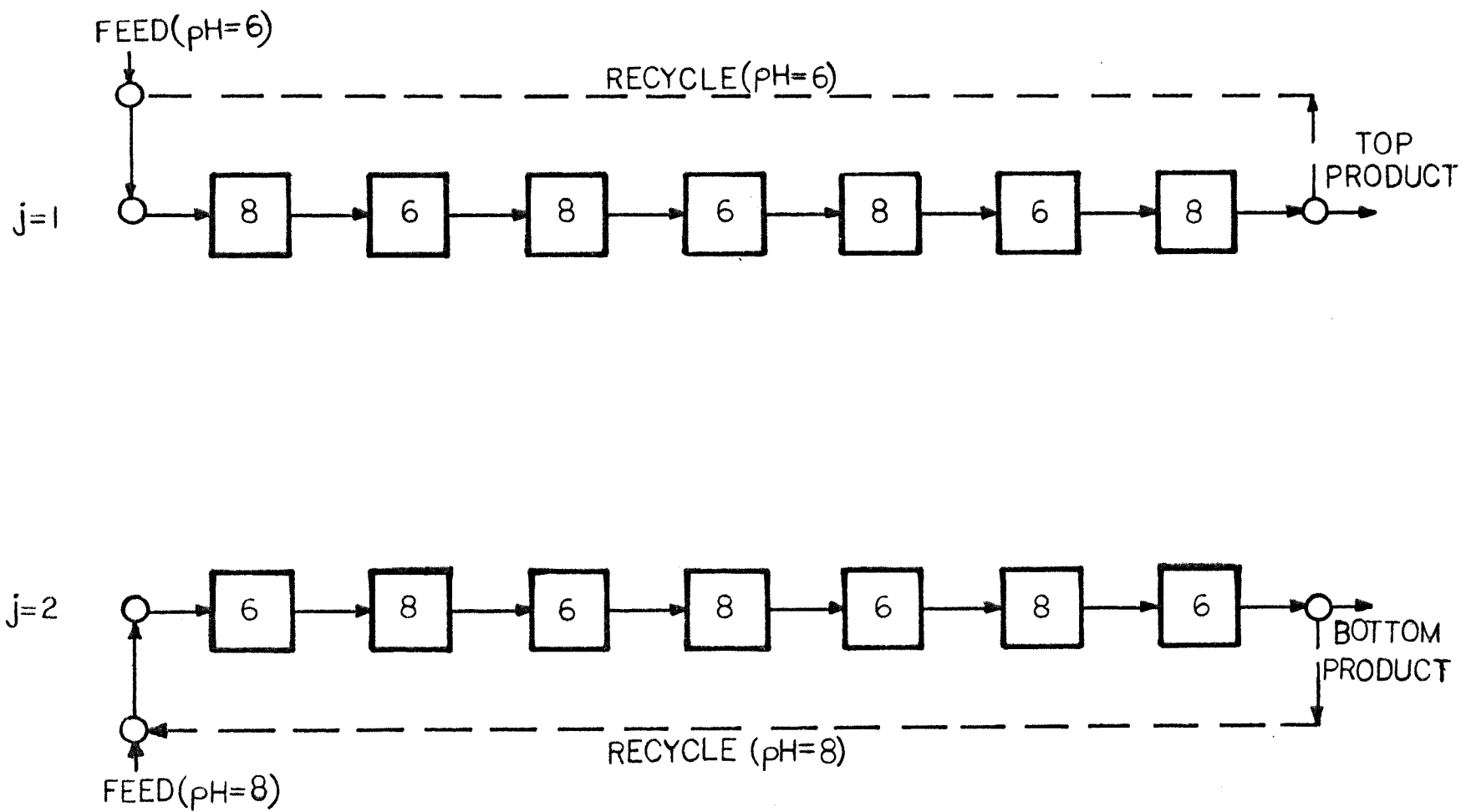


Fig.11. Schematic Description of pH Cycling Zone Adsorption Principle.

2. Initialize the fluid and solid compositions in some fashion so that the pH of the NNZ stages vary alternately as a square-wave between high pH (=8) and low pH (=6). Initial composition was assumed equal for both high and low pH feed (YINT=1), while the starting cycle was taken as $j=1$.

3. Each fluid section is now displaced one step ahead with a volume Z/NNZ . This would mean that a high pH feed has been transferred to a stage originally occupied by flow of low pH, and this constitutes the first half cycle ($j=2$). Allow the equilibrium distribution coefficient to change so that the stationary phase now releases the solute. Bottom reservoir concentration can now be calculated.

4. Displace each of the fluid sections one step with a volume Z/NNZ . This time, the fluid of low pH is transferred to a stage originally occupied by fluid of high pH and the system is in the second half cycle ($j=3$). Equilibrium is again allowed to occur and the stationary phase would now store the solute. The top reservoir concentration is then calculated.

For subsequent cycles, steps 3-4 are repeated. These calculational steps assume no recycle (BETA=0). If recycle is assumed, the fresh feed is now used as a makeup solute to obtain a total displaceable volume of Z/NNZ . This algorithm is good for continuous separation with no recycle (BETA=0), and partial recycle (BETA<1); and for batch separation; i.e., total recycle (BETA=1).

The following assumptions were made in the simulation of this algorithm:

(a) That the NNZ equal stages are independent of one another.

(b) That the volume element represent batch reactors connected in series.

(c) That partial equilibration between adjacent phases and full equilibration between moving and stationary phases take place.

(d) That each volume element is treated individually for calculating concentration values.

(e) That the pH wave is not affected by the solute concentration in the column.

(f) That the pH wave is time dependent.

(g) That the distribution between the stationary (solid) and mobile (fluid) phases obey linear equilibrium theory locally in each zone.

(h) That the cycle "halves" are equal (unequal halves could also be assumed).

Appendix B contains a listing of the FORTRAN IV digital computer program written to implement the calculational algorithm for the pH DRIVEN CYCLING ZONE ADSORPTION.

Chapter V

RESULTS AND DISCUSSION

General

Computer solution of the mass balance equation (equation 19) was used to generate concentration curves for batch and continuous parametric pumps and cycling zone adsorption at various values of the operating parameters of interest in this study. These concentration curves give the variation in solute separation, i.e., top and bottom product concentrations for parametric pumping and cycling zone adsorption with number of cycles.

The major variables affecting the shape of the batch parametric pump concentration curves is α , defined as the quotient of the reservoir displacement and the column void volume, while the concentration curves for the continuous was mostly affected by volume of top feed (NT_4), and volume of bottom feed (NT_2). It is also interesting to note that for large reservoir displacements, a large number of cycles (n) is needed to attain steady state. The cycling zone has a limited functional dependency on the number of stages (N_z) and recycle ratio (β). Above this limit, separation can no longer be improved upon, and below this limit, degrading separation is found to exist.

Cycling Zone Adsorption

The conditions used for the simulation of the mass balance equation are summarized in Table 1. The theoretical results obtained for various number of stages and for different recycle ratio are shown in Tables 2 to 5. From these data, Figures 12 to 15, which show the average product concentration divided by the feed concentration for haemoglobin ($\langle Y_B \rangle_n / \langle Y_T \rangle_n$) are plotted against the number of cycles (n). Symmetric cycles have been used with 1, 4, 8 or 16 transfers per half cycle (stages). For the different stages used, a recycle ratio (β) of 0.0, 0.5, and 1.0 ($\beta = 0.0$ means no recycle; $\beta = 0.5$ partial recycle; and $\beta = 1.0$, total recycle) were used. The results showed that recycle ratio only have some effect on the separation when the number of stages is small. But, when the number of stages becomes large, the effect of β become negligibly small (see Figure 16).

Figure 12, which is the result of 16 stages, shows that recycle ratio has virtually no effect on the separation; and Figure 13, which is a plot for 8 stages, shows that the separation is equally as good as the separation obtained with 16 stages, but the top product has a small dependency on β . Figure 14 exhibits a plot for 4 stages, and it is found that separation is functionally dependent on β ; the maximum separation obtained when $\beta = 1.0$, and the minimum separation when $\beta = 0.0$. Shown in Figure 15, is a plot of 1 stage versus n which gave inverse separation. This

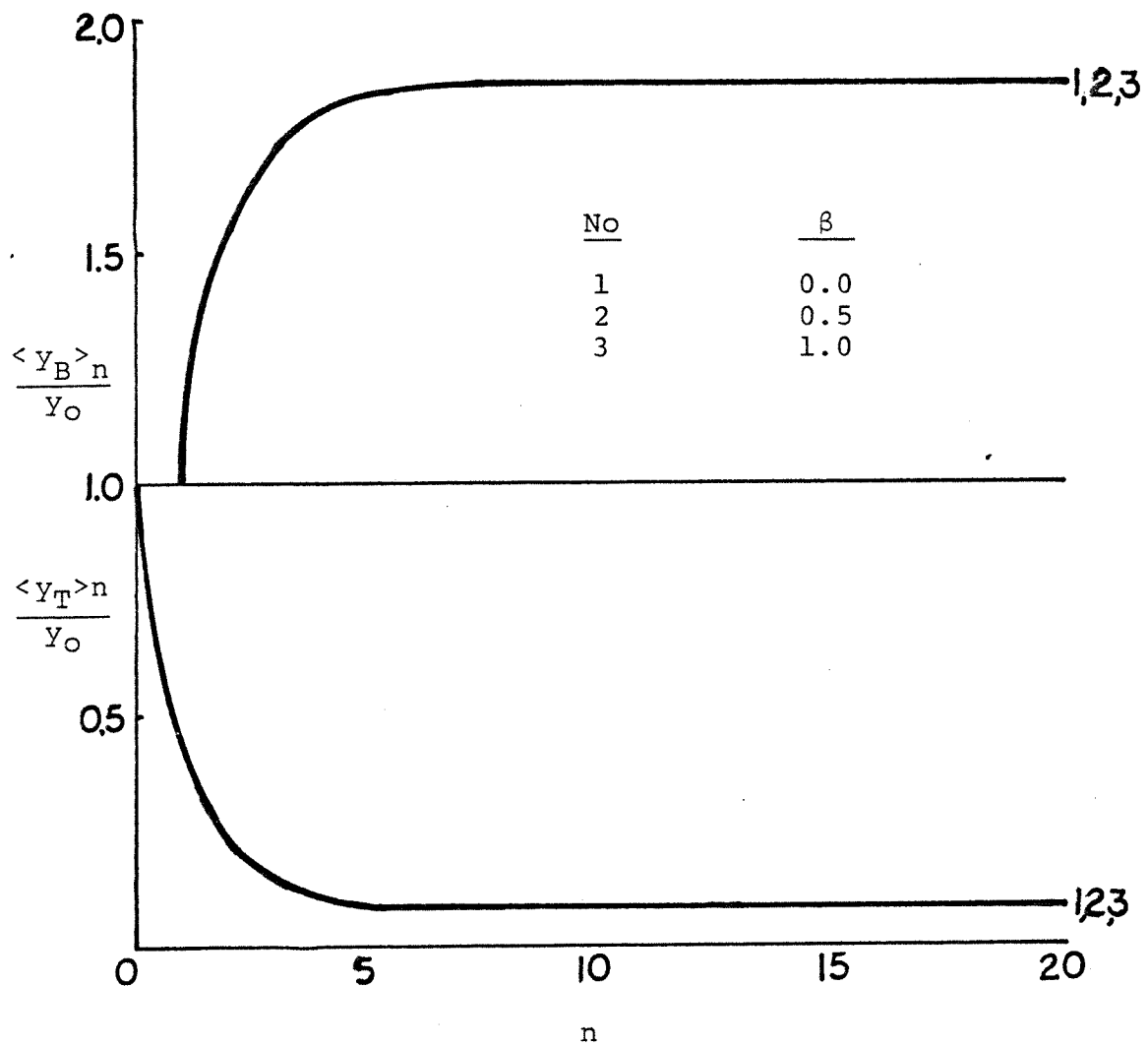


Fig. 12. Sixteen Stage Cycling Zone with Recycle.

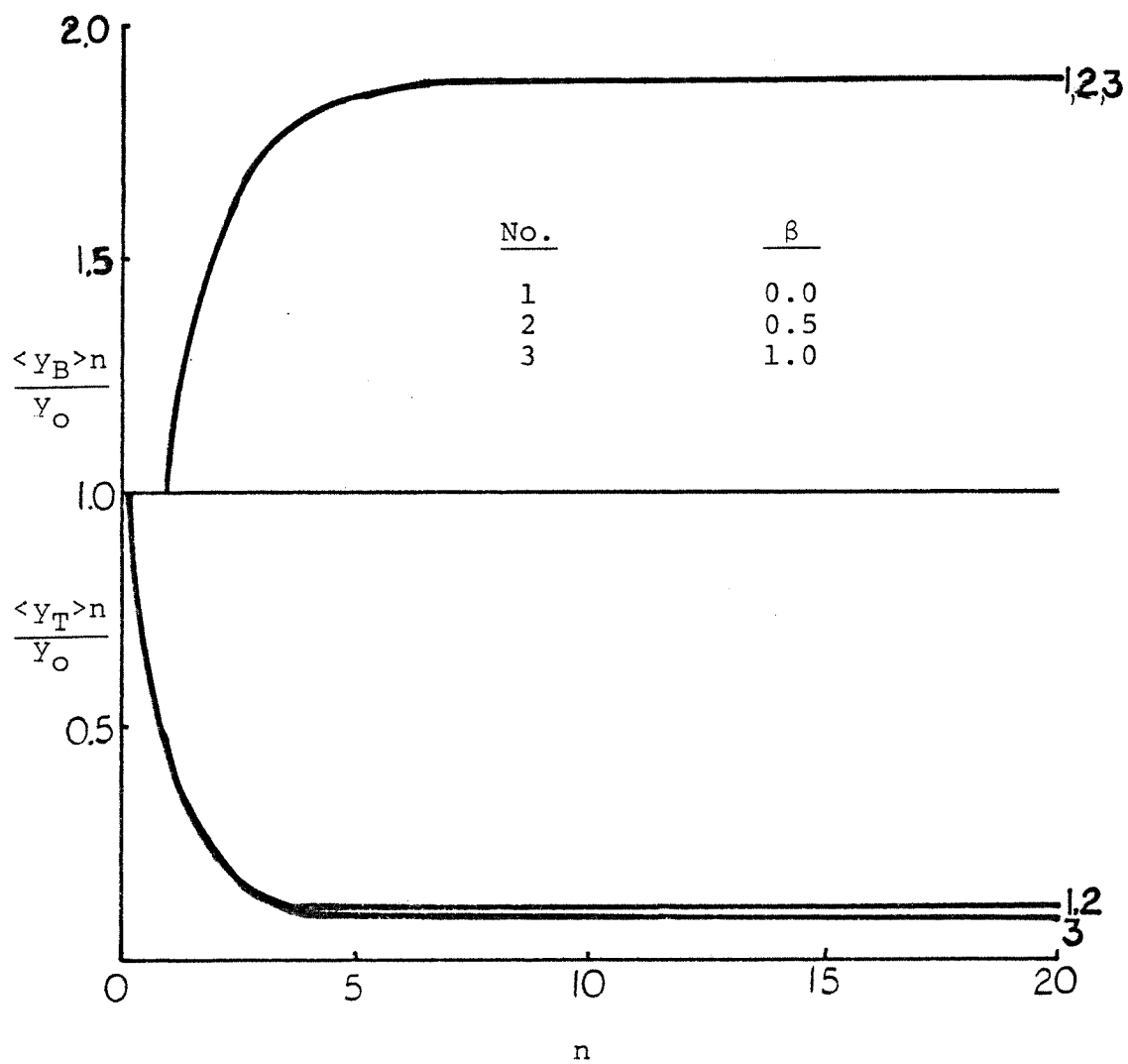


Fig. 13. Eight Stage Cycling Zone with Recycle.

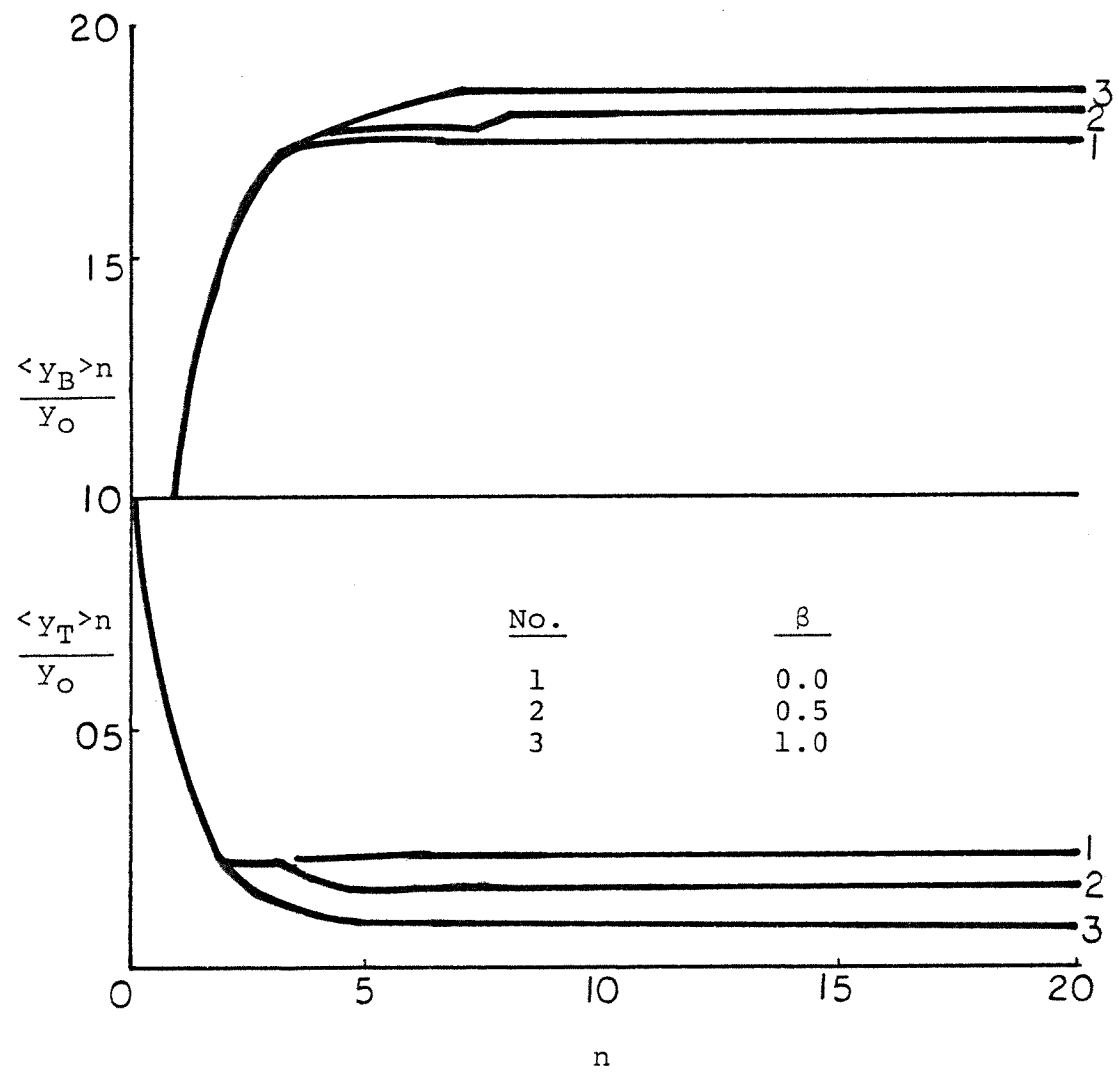


Fig. 14. Four Stage Cycling with Recycle.

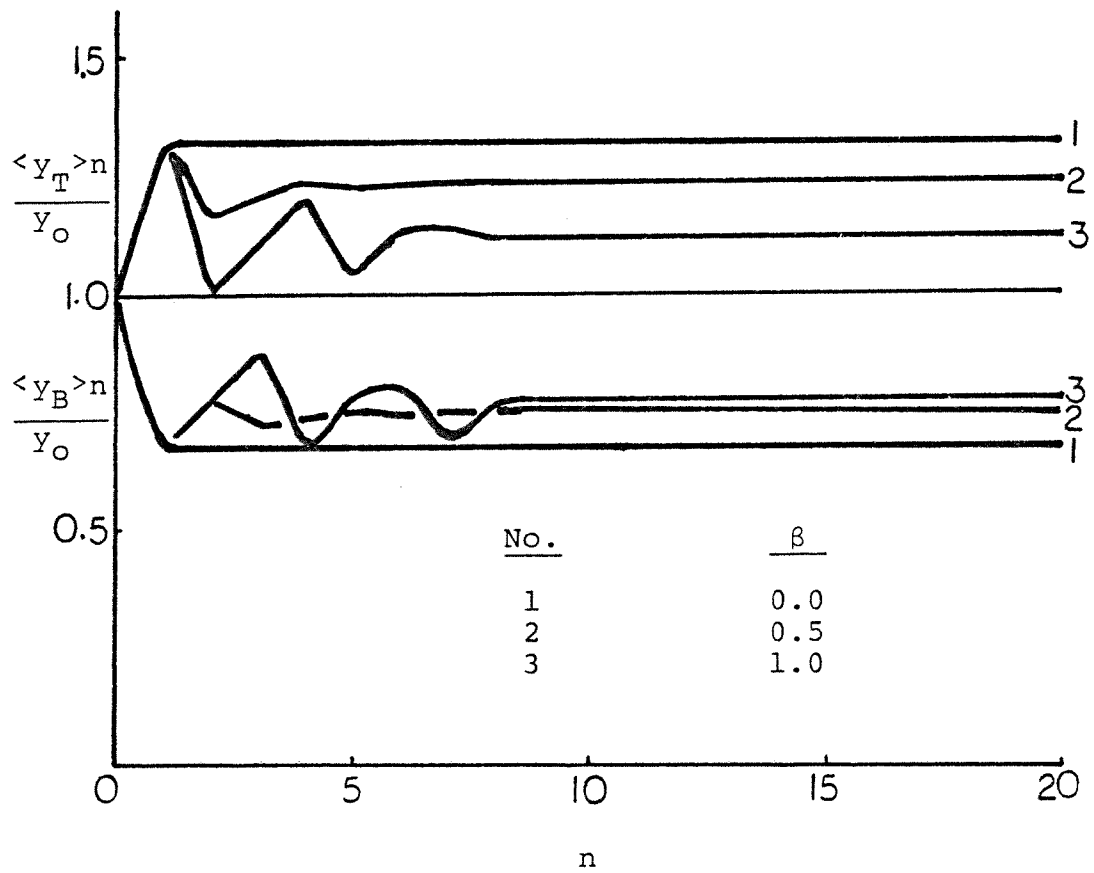


Fig. 15. One Stage Cycling Zone with Recycle.

phenomenon is consistent with previous reports by Wilhelm et al. (1966, 1968), Sweed and Rigaudeau (1975), and Chen et al. (1977) for small displacements. One can also see that separation is functionally dependent on β . Figure 16 is a plot of the separation factors ($\langle Y_B \rangle_\infty / \langle Y_T \rangle_\infty$) versus β (Table 6). β has the greatest effect on separation when the column is divided into 4 stages as the separation increases exponentially from $\beta = 0.0$ to $\beta = 1.0$. From this figure, the relative separation factors for all the simulated transfers per half cycle are easily discernable.

From the ongoing analysis, it can be seen that more separation would be obtained with a smaller number of theoretical stages if the adsorbent was operating near its saturation limit. With more stages, there is more adsorption between stages and more opportunities for equilibrium between the solid phase and the fluid phase. From the transient concentration plots, the values of the product concentrations approach a limit after few cycles. An increase in separation and decrease in the effect of β can be seen as the number of stages increases. However, as the number of stages becomes large, the effect of β on separation and the improvement on transient concentrations becomes non-existent.

The Batch Parapump

The conditions for the simulation of the batch parametric pumping are given on Table 7, and calculated results obtained to demonstrate the effect of α on the transient

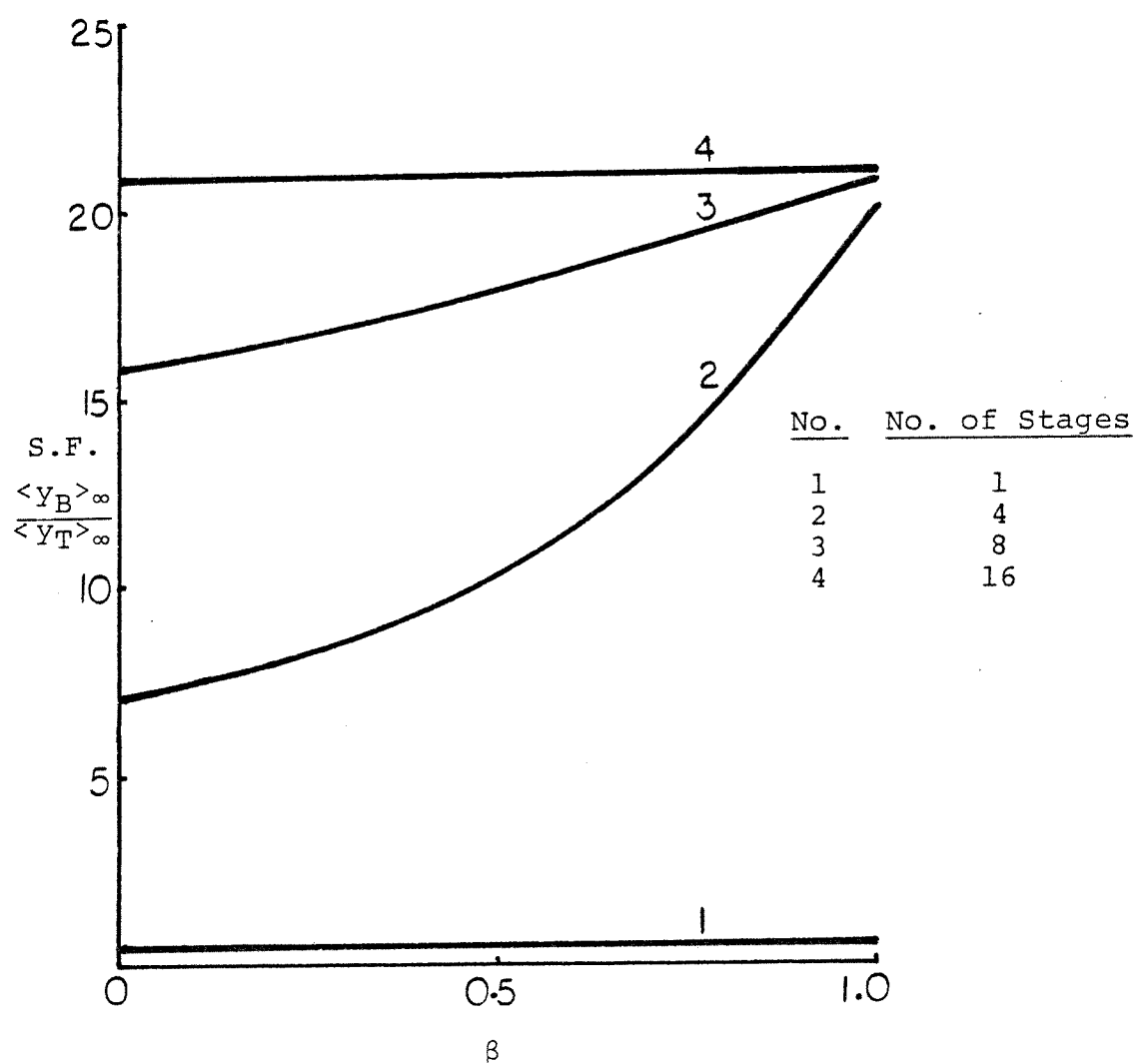


Fig. 16. Separation as a Function of Recycle Ratio (β).

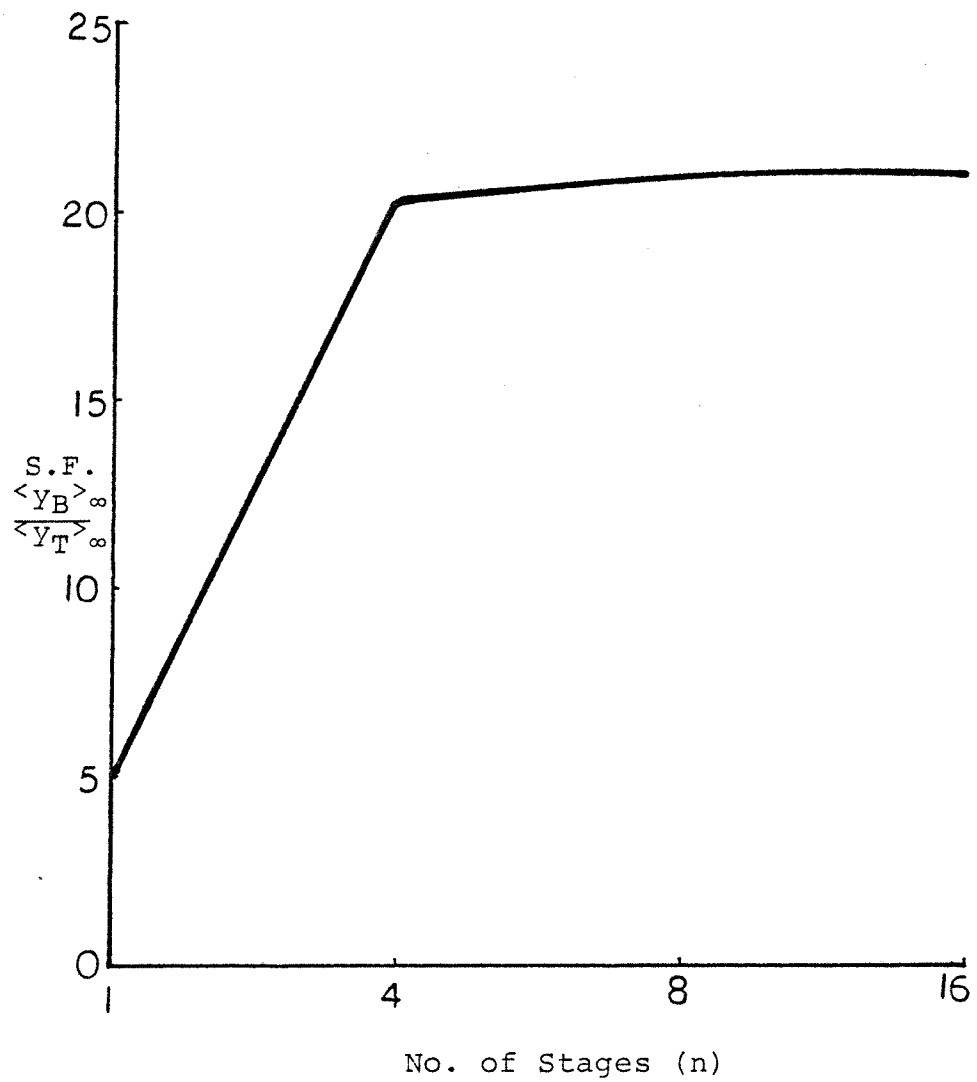


Fig. 17. Effect of Number of Stages on Separation for $\beta=1$.

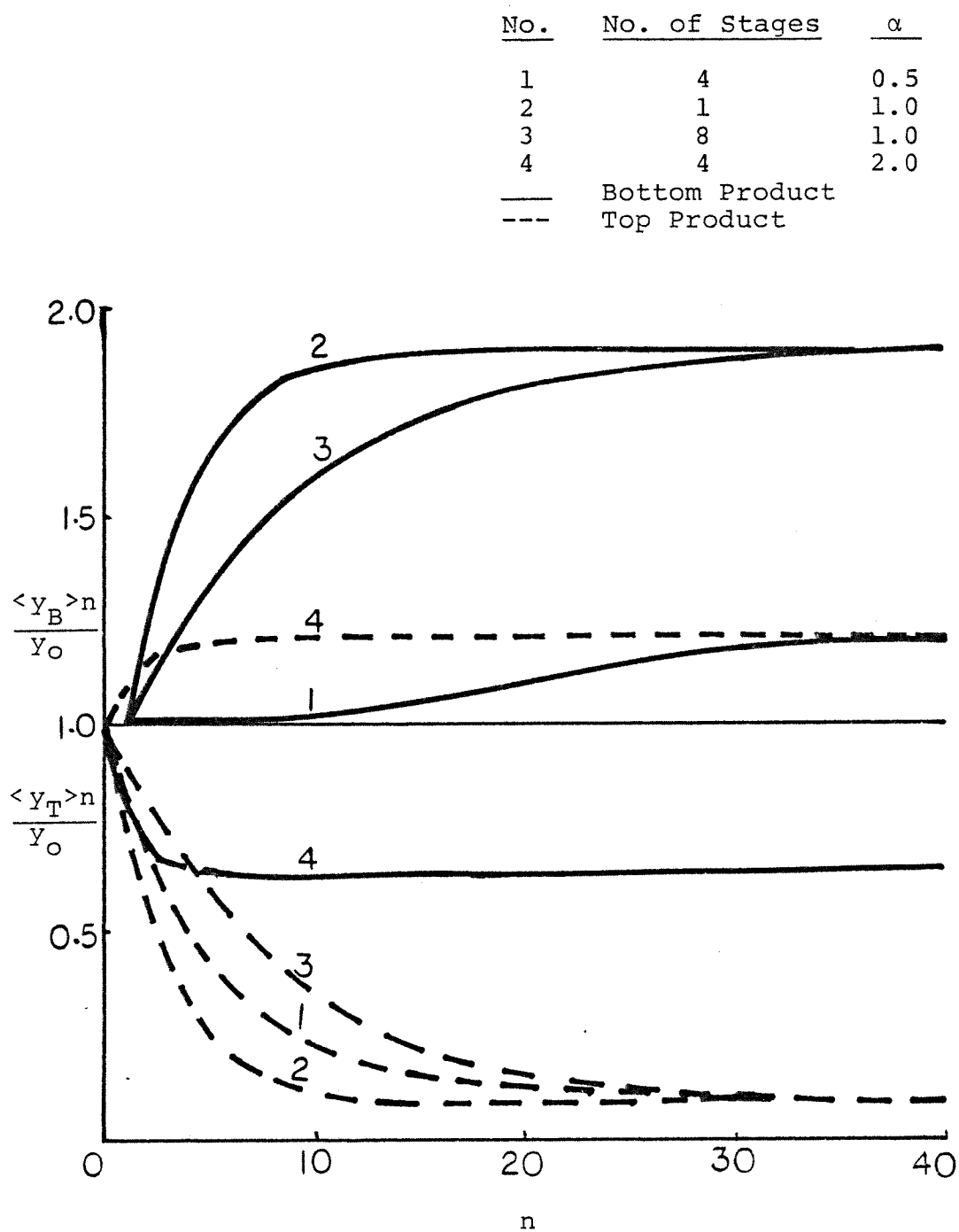


Fig. 18. Effect of α on Concentration Transients.

concentrations are shown on Tables 8 to 17. Following these data, the effect of α on concentration transients is shown in Figure 18. The ordinate is the average reservoir concentrations divided by the initial liquid phase concentration, while the abscissa is the number of cycles. For $\alpha = 1$, the separation first increases exponentially and then levels off to some limiting value as the number of cycles increases. α is defined as the quotient of the reservoir displacement and the column void volume (i.e., number of transfer steps/number of stages). This limiting value is the steady state concentration. The value is independent of N chosen. For $\alpha \leq 1$, the steady state concentrations in both top and bottom reservoirs are functionally dependent on N chosen.

Figure 18 reveals three phenomenon, viz: Case I: $\alpha=1$ and $N = Q(\frac{H}{w})V$. In this case, the upward and downward flow fluid displacements corresponded to the column void volume, and maximum separation factor was obtained. The results obtained showed that the number of hypothetical cells or stages (N) chosen for the computational algorithm has no effect on the steady state average concentration values of the top and bottom reservoirs. In Case II: $\alpha < 1$ (the upward or downward fluid displacement is less than the column void volume), the number of cells (N) was found to have a marked influence on the separation. The steady state average concentration values of the top and bottom reservoirs were much less than those obtained with $\alpha = 1$.

The reason for this behavior is very clear, since the penetration distance is less than the column void volume, some of the solute are attached to the upper part of the column in upflow displacement and to the lower part of the column in the downflow displacement, thus resulting in a permanent loss of solute at steady state. Case III: $\alpha > 1$ (the upward or downward fluid displacement is greater than the column void volume), some of the solute from the bottom reservoir is pushed to the top reservoir and vice versa. This resulted in inverse separation, which is consistent with the view that interface mass transfer is very slow, a basis on which equilibrium theory is based.

On Table 18, a summary of the effect of α on separation is given and plotted in Figure 19. The plot indicates that an increase in α will result in higher values of $\langle y_B \rangle_\infty / \langle y_T \rangle_\infty$ reaching 22:1 for $\alpha = 1$. Beyond that, the separation dropped sharply and becomes nonexistent because of intermixing between reservoirs. From this figure, it is obvious that the condition for maximum separation is $\alpha = 1$.

Figure 20 shows a one equilibrium stage recuperative pH batch parapumping system. From Figure 19, it is concluded that at $\alpha = 1$, the steady state separation is optimum and independent of the number of stages (N). Hence $N=1$ has been chosen to give a clearly describable diagram. In order to construct Figure 20, which is based on the mass balance equation (equation 19), two linear equilibrium isotherms with slopes $k_6=1.58$ and $k_8=0.07$ are drawn. These

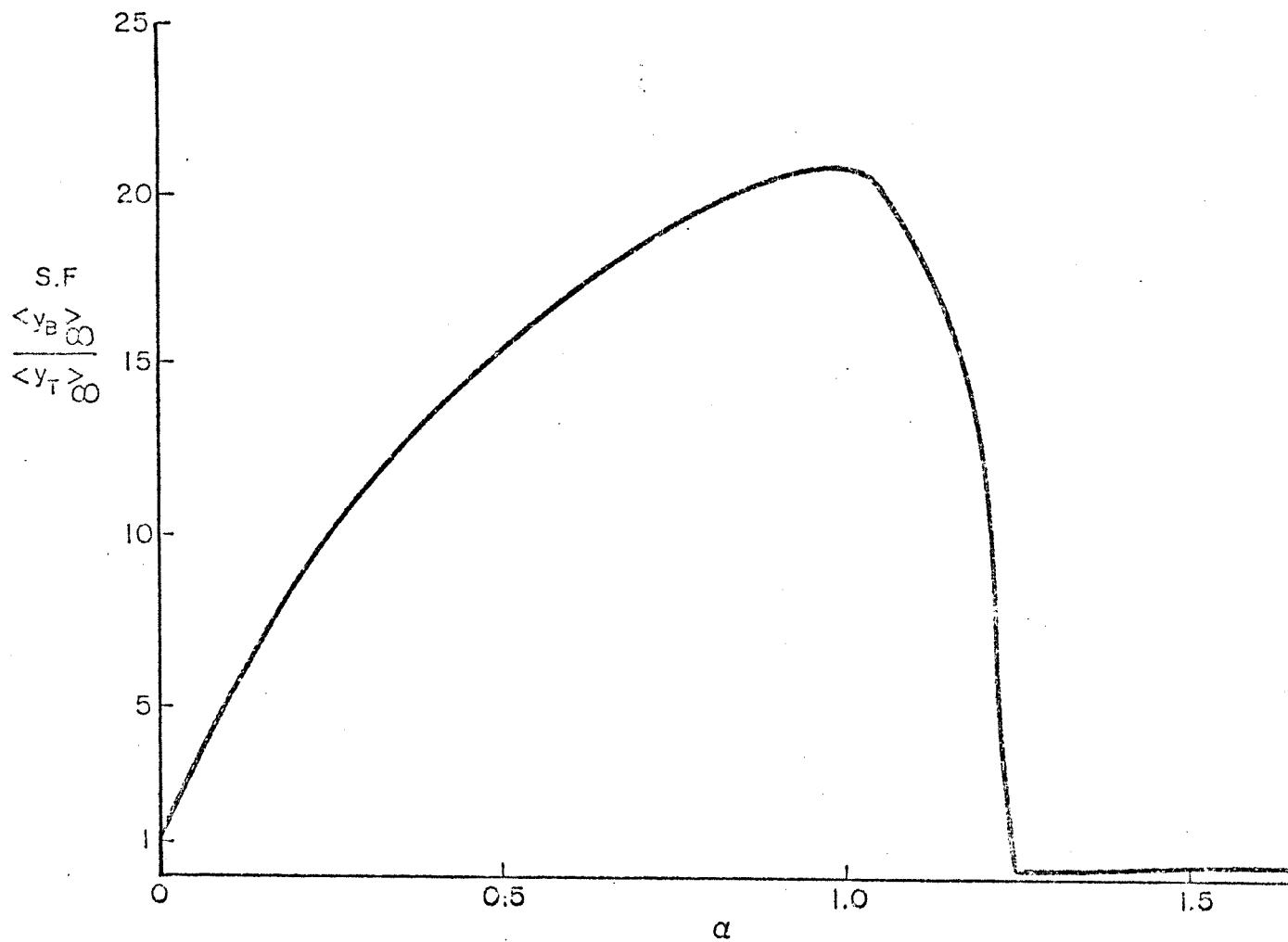


Fig. 19. Effect of α on Separation.

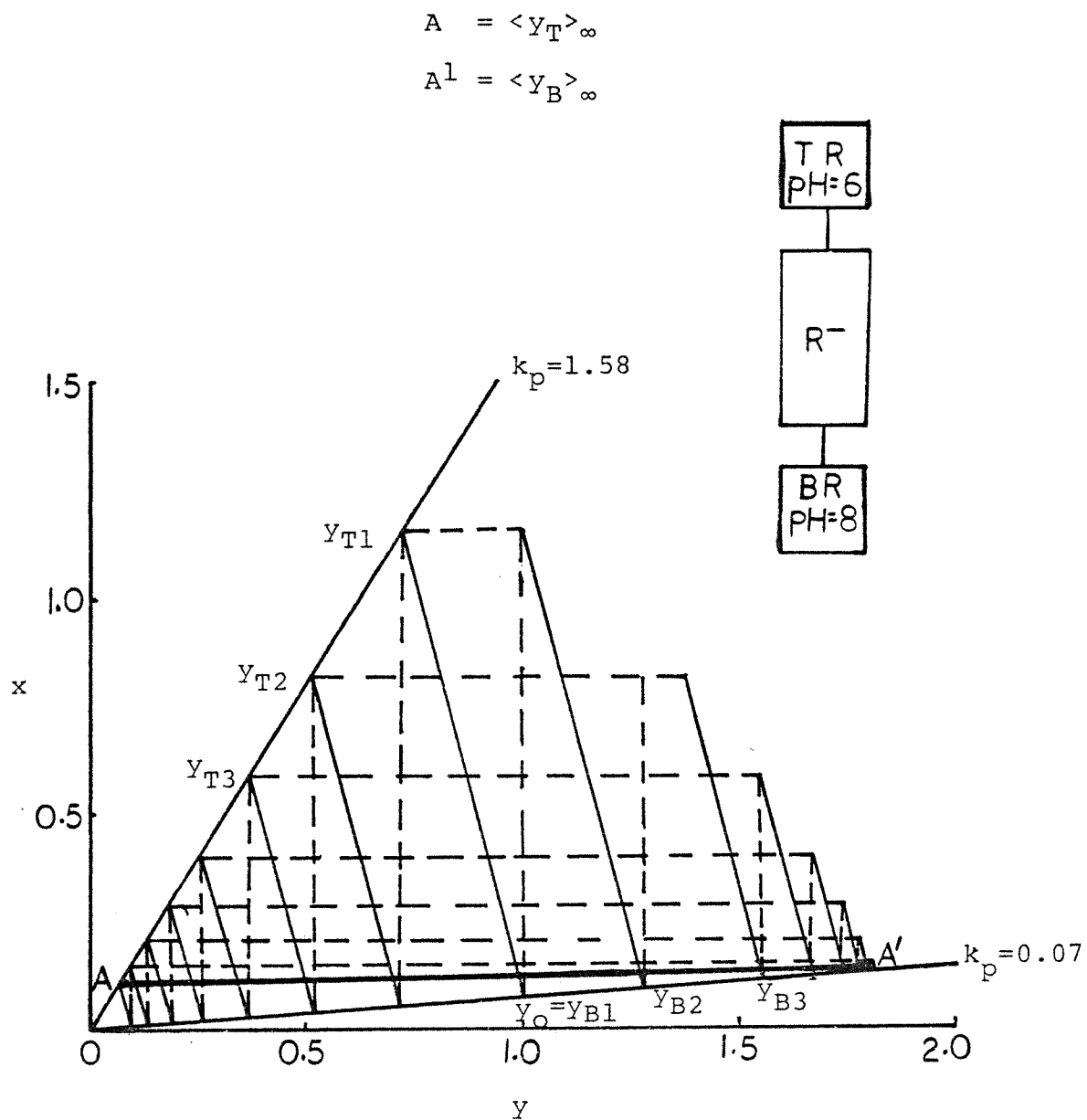


Fig. 20. One Equilibrium Stage of pH Batch Parapumping System.

equilibrium isotherms were obtained by trial and error procedure by correlating the experimental data obtained by Chen et al. (1978) semi-empirically.

The batch parapump apparatus consists of a column packed with cation exchanger and two reservoirs attached to each end. The pH values of the top and bottom reservoir were maintained at given levels $P_2 (=6)$ and $P_1 (=8)$ respectively. The operation began with column filled with mixture of concentration $y_0 (=1)$ and $P_1 (=8)$, and was allowed to equilibrate with the solid. The bottom reservoir had a concentration of $y_0 (=1)$ and a pH of $P_2 (=6)$.

The first fluid motion was downward, with $V_T = V_B = 0$. x and y here represent the concentrations of solute in the solid and fluid phases respectively (see equation 17). Based on the results of the simulation given in Table 12, an x - y diagram was constructed. The initial concentration in the column ($y_0; x_0$) is represented by the $y_0 (=1)$. A complete cycle of the operation included four steps. The procedure started as follows:

1. Transfer down: The fluid in the top reservoir is transferred to the column, while the fluid in the column is transferred to the bottom reservoir. The concentration of the bottom reservoir for the first cycle is $y_0 (=1)$.

2. Equilibrium at $P_2 (=6)$: The column pH is changed from $P_1 (=8)$ to $P_2 (=6)$. The two phases (solid and liquid) are then allowed to equilibrate at P_2 . A new composition in the column ($y_{T1}; x_{T1}$) is now the equilibrium line k_6 and

of the operating line passing through $(y_0; x_0)$. The slope of the operating line is $(-V/\bar{V})$ (see equation 16).

3. Transfer up: The solution in the bottom reservoir is returned to the column, while the solution in the column is brought to the top reservoir. The composition in the column is now $(y_{B1}; x_{B1})$.

4. Equilibration at $P_1 (=8)$: The column pH is shifted back to P_1 and a phase equilibrium is re-established. The new equilibrium point $(y_{B1}; x_{B2})$, represented by y_{B2} , is located at the intersection of the equilibrium line k_8 and the operating line passing through $(y_{B1}; x_{T1})$ and having a slope of $(-V/\bar{V})$. The first cycle is thus ended.

The second cycle is then started by transferring the fraction y_{T1} from the top reservoir to the column and the fraction y_{B2} to the bottom reservoir. To complete this cycle, steps 1 and 4 described above are repeated. Subsequent cycles are then constructed on the diagram using the results in Table 12. It can be seen that as the number of cycles (n) becomes large, the top and bottom reservoir concentration approach steady state values, $\langle y_T \rangle_\infty$ and $\langle y_B \rangle_\infty$ respectively. At steady state, the solid phase has a constant composition which is in equilibrium with both and $\langle y_B \rangle_\infty$, i.e., $x = k_8 \langle y_B \rangle_\infty = k_6 \langle y_T \rangle_\infty$, thereby leading to a line $\overline{\langle y_T \rangle_\infty \langle y_B \rangle_\infty}$ which is parallel to the y axis.

The Continuous Parametric Pump

Presented on Table 19, is a summary of the conditions for runs with variable volume of bottom feed, and Tables 20

to 23 show the results obtained. Shown in Figures 21 to 29 are typical concentration transients and separation factors following the simulation of continuous parapumping operations for variable volume of bottom feed (NT2). For each value of top feed (NT4) used, four runs of NT2 were made, viz: 6, 11, 16 and 21. In Figures 21, 23, 25, and 27 plots of the average product concentrations divided by the initial liquid phase concentrations vs. the number of cycles (n) of operations are shown.

Figure 21 shows the concentration transients using different values of NT2 (=6, 11, 16, and 21) and a constant value of NT4 (=6). The results show that if a high separation is desired, NT4=6 and NT2=6 would be more preferable. For this condition, a separation factor of 28.167 was obtained for 20 cycles. On the other hand, if higher separation can be sacrificed for bottom product enrichment, NT4=6 and NT2=21 would give the best results. The plot of the separation factors ($\langle y_B \rangle_\infty / \langle y_T \rangle_\infty$) versus NT2 is shown in Figure 22. From this figure, one can see that, as NT2 increases, the separation factor decreases.

In Figure 23, a constant value of NT4 (=11) and NT2=6, 11, 16, and 21 were used. Each run consisted of NT2 and a constant NT4, NT2 being varied each time a run was made. The separation factors obtained for these set of runs are not as good as that obtained with NT4=6. Since NT4 is a high pH feed introduced from the top and bottom products withdrawn, one would expect that an increase in NT4 would result in

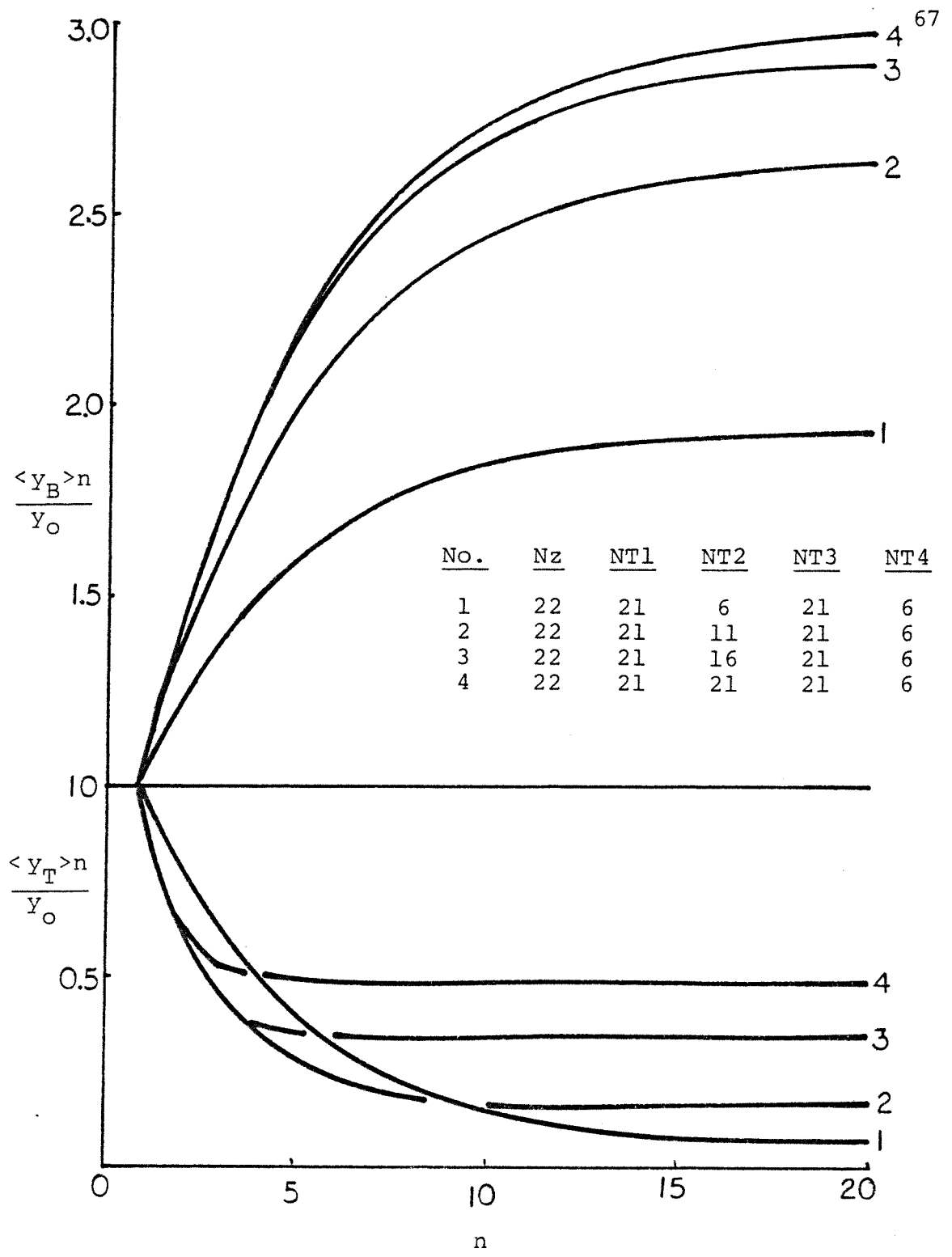


Fig. 21. Effect of NT2 on Transient Concentrations for NT4=6.

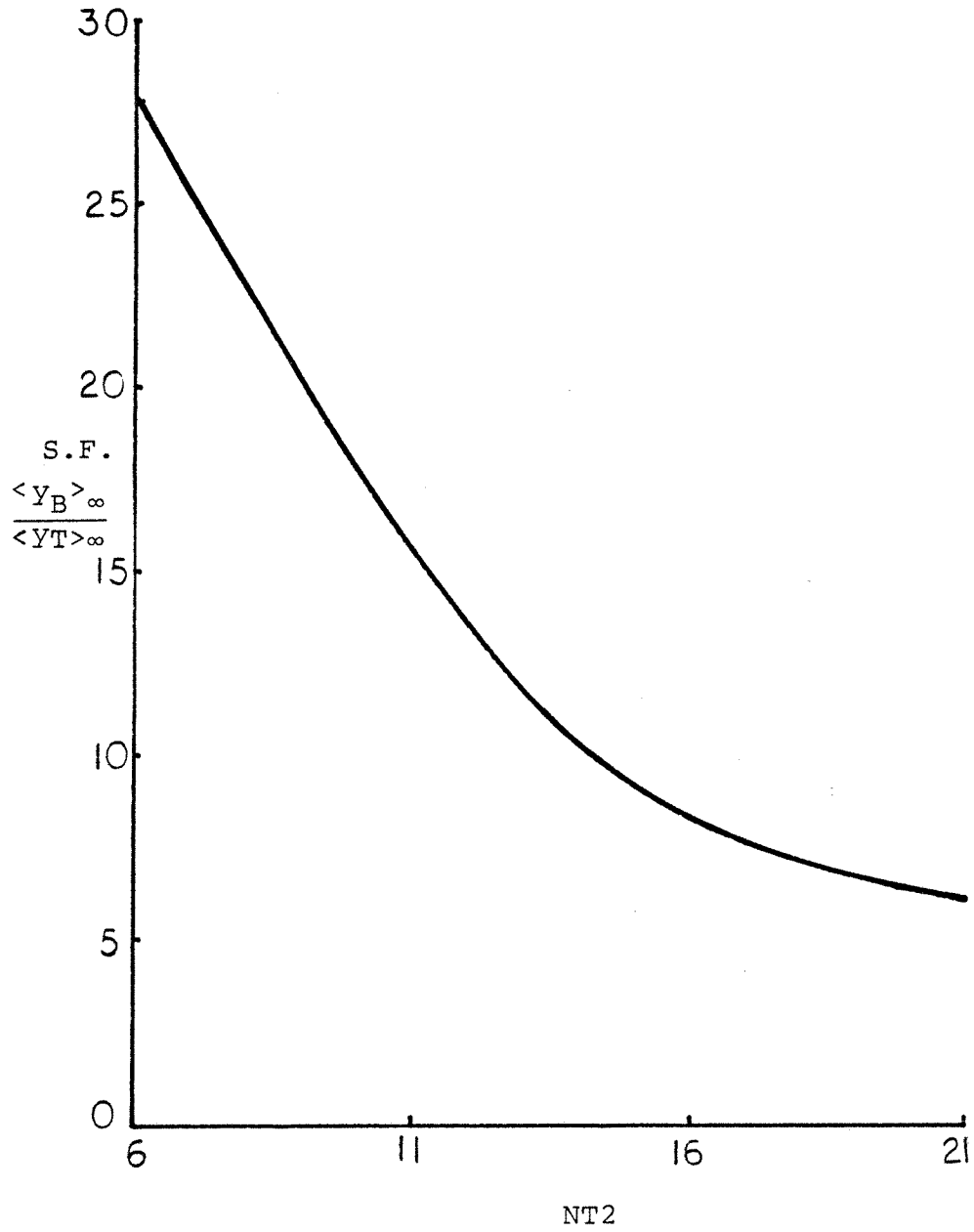


Fig. 22. Effect of NT2 on Separation Factor for NT4=6.

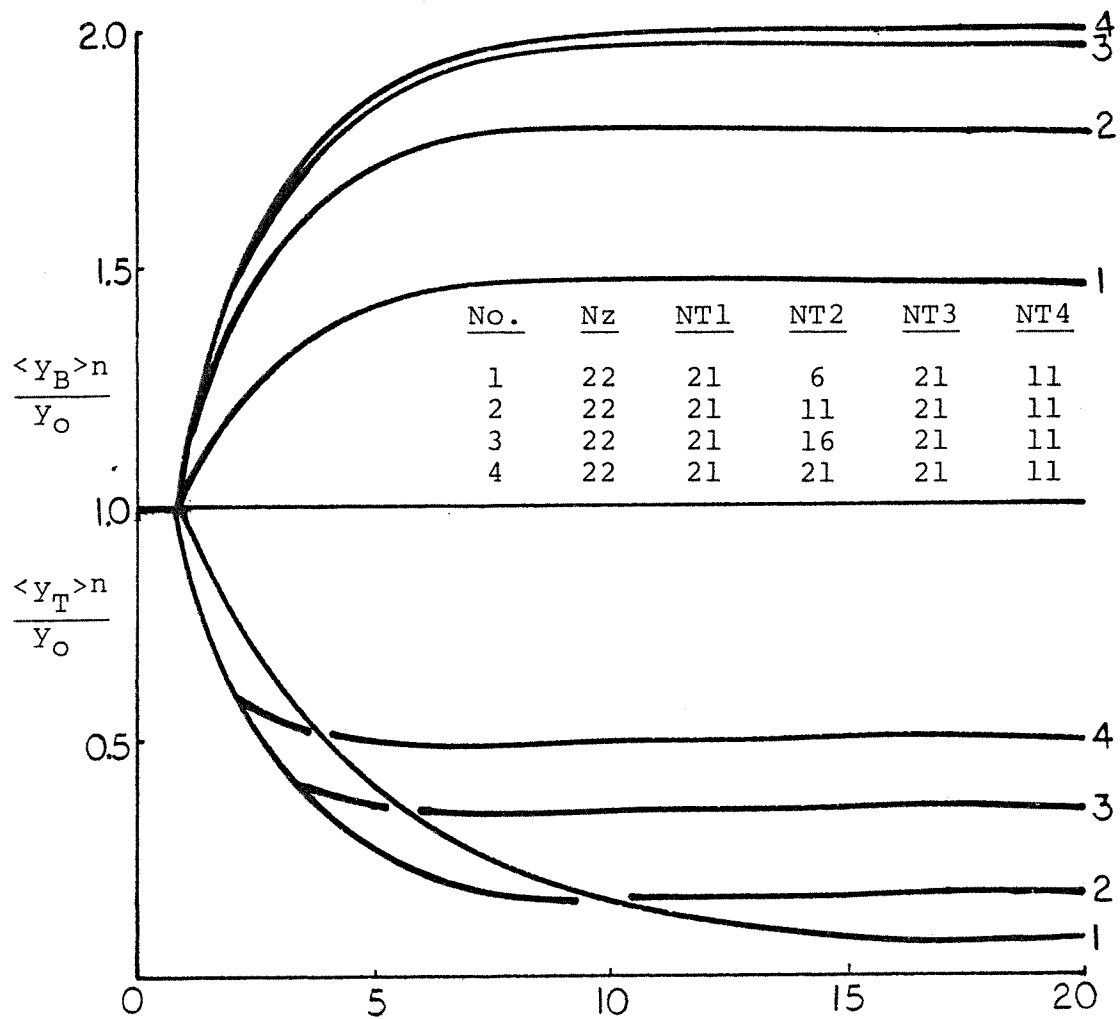


Fig. 23. Effect of NT2 on Transient Concentration for NT4=11.

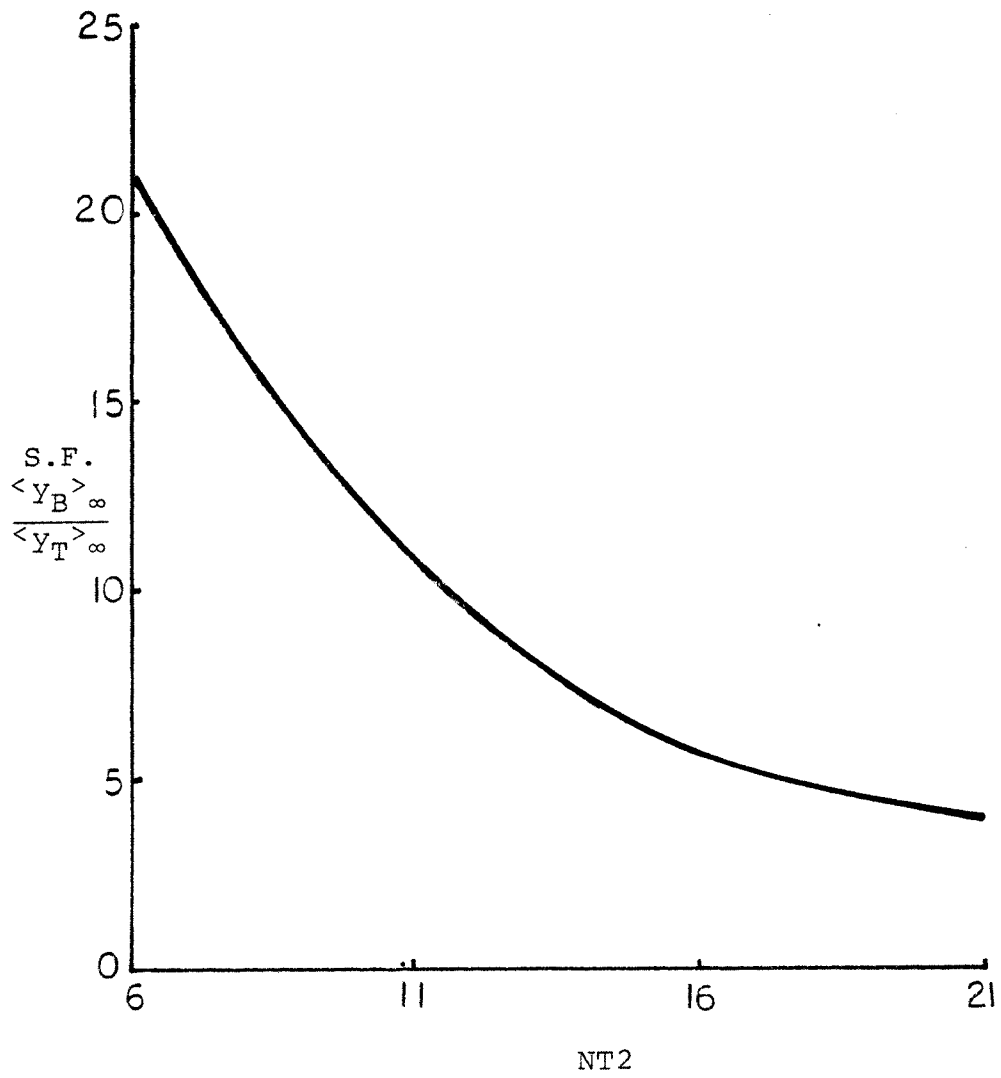


Fig. 24. Effect of NT2 on Separation Factor for NT4=11.

increased desorption of already adsorbed protein, and hence result in better separation. But, on the contrary, the separation was decreasing with increasing value of NT_4 . From this phenomenon, one would conclude that high pH feed is not the controlling factor in the separation. Comparing Figure 24 to Figure 22, the marked decrease in the separation factor can be seen.

Figure 25 is the plot for constant NT_4 (=16) and various values of NT_2 (=6, 11, 16, 21). The trend of decreasing separation factor for increasing values of NT_4 can also be seen from this figure. Comparing the bottom product concentration ratios for $NT_2=16$ and $NT_2=21$, one can see that the difference in the separation is not very significant. The separation factors plotted against NT_2 shown in Figure 26 decreases sharply as NT_2 increases and tends to level off between $NT_2=16$ and $NT_2=21$. It seems obvious that NT_2 greater than 16 for $NT_4=16$ is of no practical value, since the separation factor is the lowest and does not give any appreciable improvement for enrichment purposes.

In Figure 27, a plot for $NT_4=21$ and different values of NT_2 (=6, 11, 16, and 21) is shown. During the first cycle, the top product concentration ratios remain essentially the same as the feed concentration ratio before decaying exponentially. As one can see, NT_4 has the same value as NT_1 and NT_3 (downflow and upflow reservoir displacement). This seems to suggest that, when NT_1 , NT_3 and

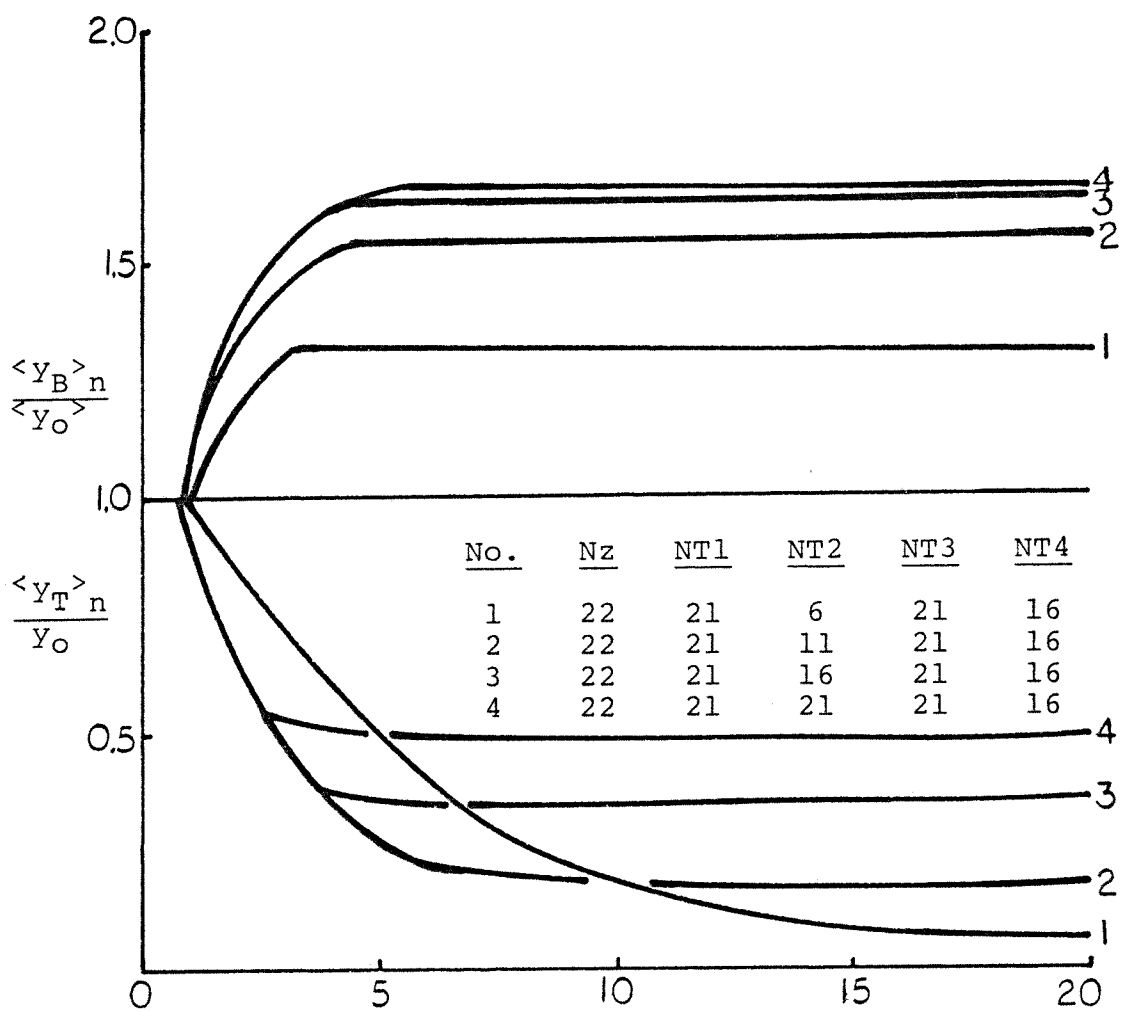


Fig. 25. Effect of NT2 on Transient Concentrations for NT4=16.

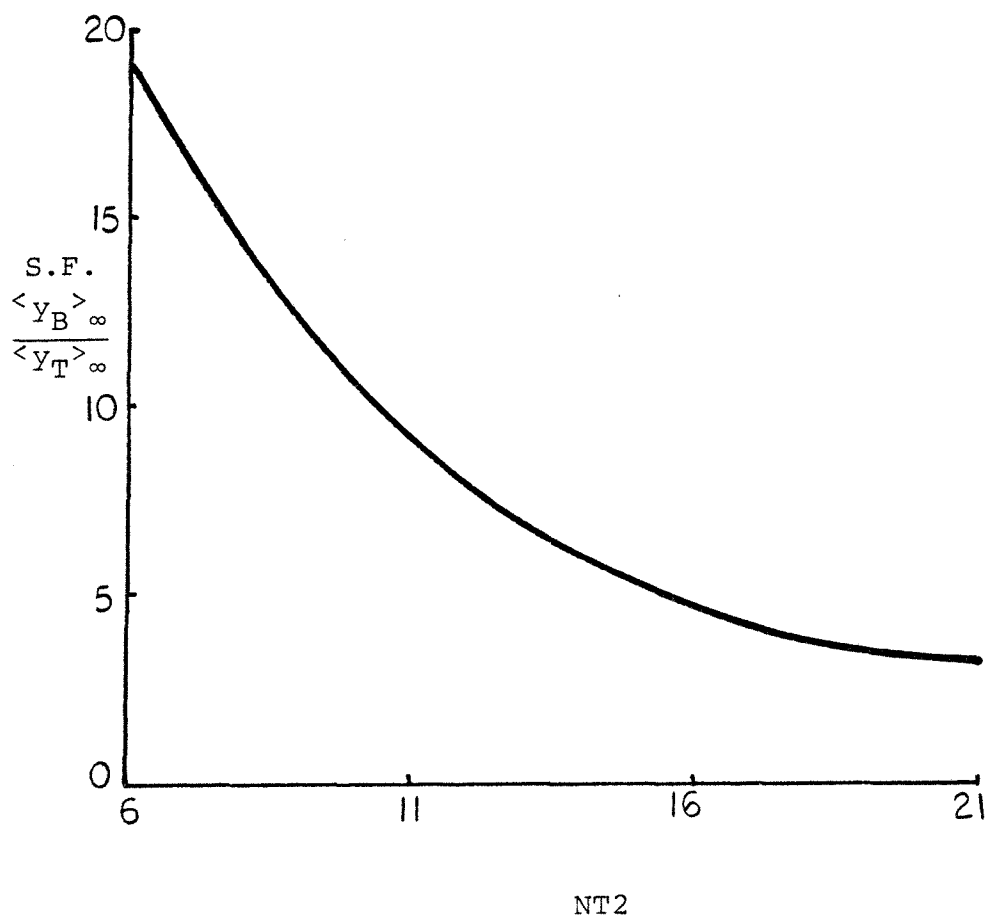


Fig. 26. Effect of NT2 on Separation Factor for NT4=16.

NT4 are equal, the concentration of the top product is essentially the same as the concentration of the fluid phase in the column for approximately the first cycle, since the fluid phase in the column is literally pushed out of the column and taken as sample, due to complete saturation of the column before the start of run. The separation factors for this set of runs is shown in Figure 28.

In Figure 29, a plot of the steady state separation factors vs. NT2 (Table 24) is shown for constant values of NT4. At NT4=6, the highest separation factors were obtained in both the high region (NT2=6) and low region (NT2=21), while at NT4=21, the lowest separation factors in both regions were obtained. The characteristic behavior of the separation factors with increasing values of NT4 in all four cases are the same. From the above results, it was evident that if a high degree of separation is desired, low values of NT2 and NT4 must be used, preferably NT1=6 and NT4=6. If, on the other hand, enrichment of the rich section is desirable, then NT2=21 and NT4=6 would yield best results.

Since we have seen the effect variable NT2 for constant NT4 had on the separation, one is now in a position to scrutinize the effect of variable NT4 for constant value of NT2 has on transient concentrations. The theoretical results shown on Table 26-29 for this case using the operating conditions on Table 25 have been presented in Figures 30, 32, 34, and 36, while the corresponding

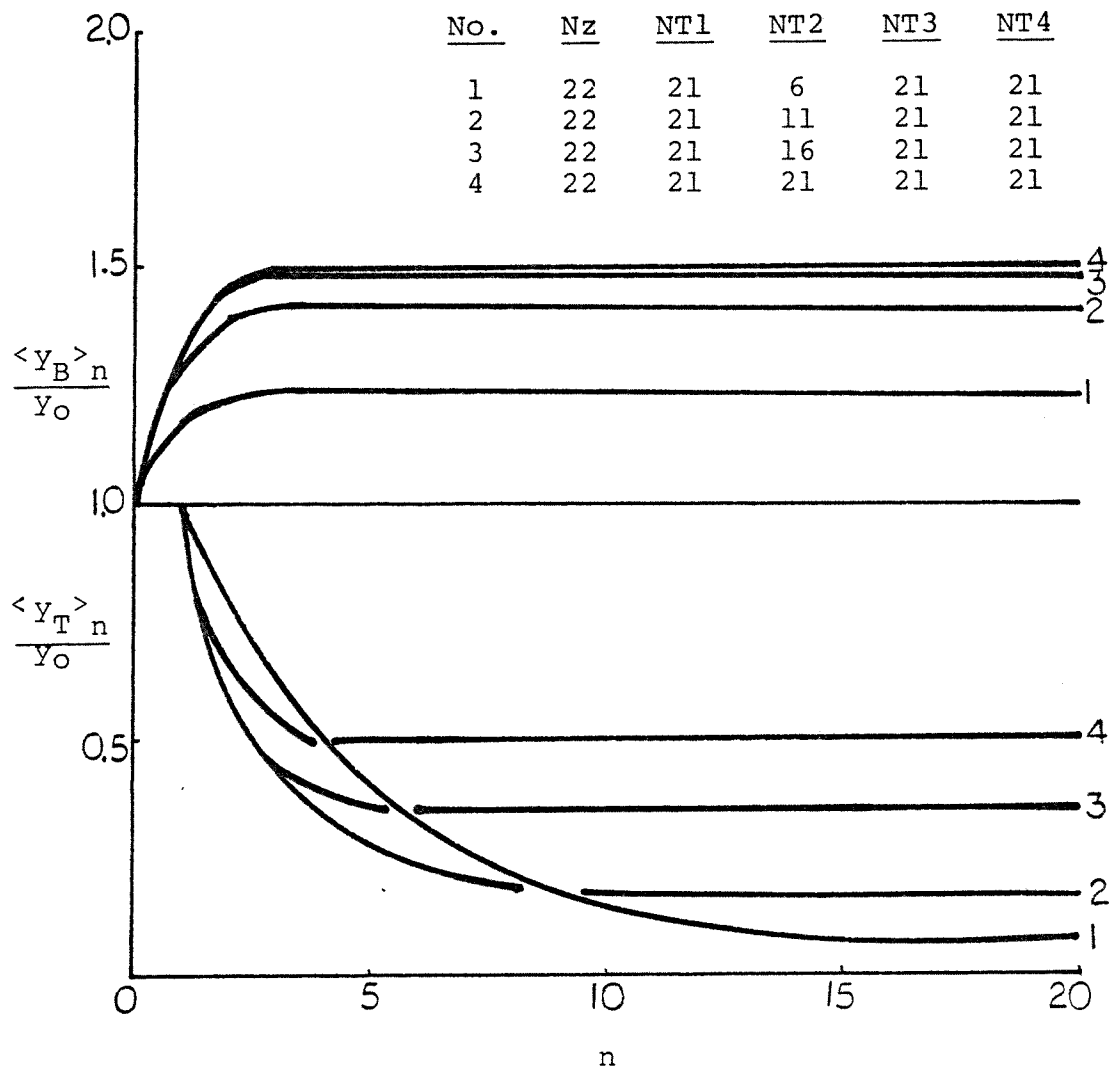


Fig. 27. Effect of NT2 on Transient Concentrations for NT4=21.

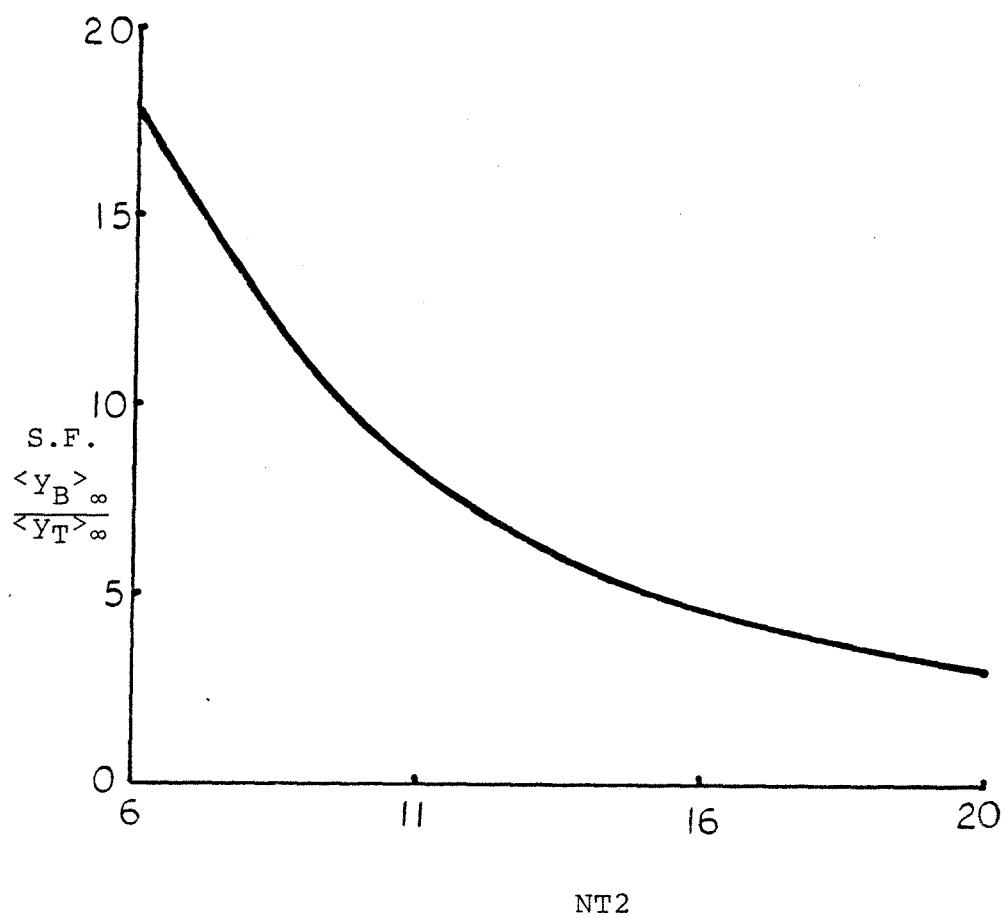


Fig. 28. Effect of NT2 on Separation Factor for NT4=21.

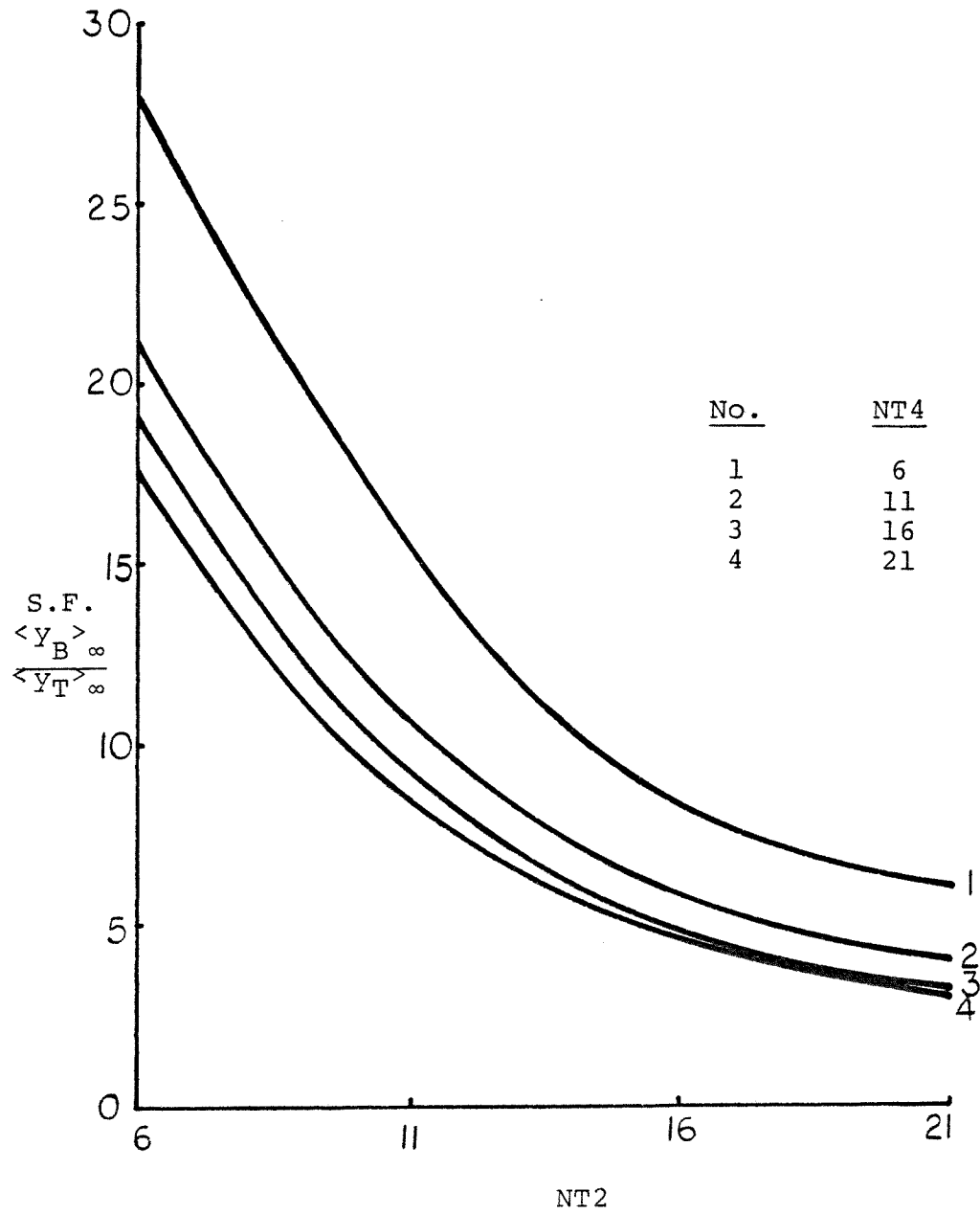


Fig. 29. Separation Factor vs. NT2.

separation factors have been respectively plotted against NT4 and are presented in Figures 31, 33, 35, and 37. For the purpose of comparison, the separation factors have been combined and presented in Figure 38. The results showed that when the volume of top products, NT2, is held constant, and the volume of bottom products varied, the lean product concentrations were found to be constant. In other words, if NT2 is held constant, and NT4 varied, the lean product concentrations are constant for the specific NT2 used. It should be emphasized that the amount of sample withdrawn as product (both top and bottom) must also be introduced as feed, and for a top product to be sampled, fresh feed must be introduced from the bottom and vice versa.

Figure 30 shows the plot for NT2(=6) and NT4(=6, 11, 16, and 21). The top product transient concentration ratio (lean product) for all values of NT4 have constant concentration value while the bottom product transient concentration ratio decreases as NT4 increases. In Figure 32, the plot for NT2(=11) for various values of NT4 (6, 11, 16 and 21) is shown, and NT2 (=16) for various values of NT4 (6, 11, 16 and 21) is shown in Figure 34. Figure 36 shows the plot for NT2 (=21) for various values of NT4 (6, 11, 16 and 21). The characteristic behavior of the separation for all of these three cases are the same, viz: constant top product concentration ratio is constant for specific value of NT2, while the bottom product transient concentration ratio decreases as NT4 increases. It is worth noticing that for constant

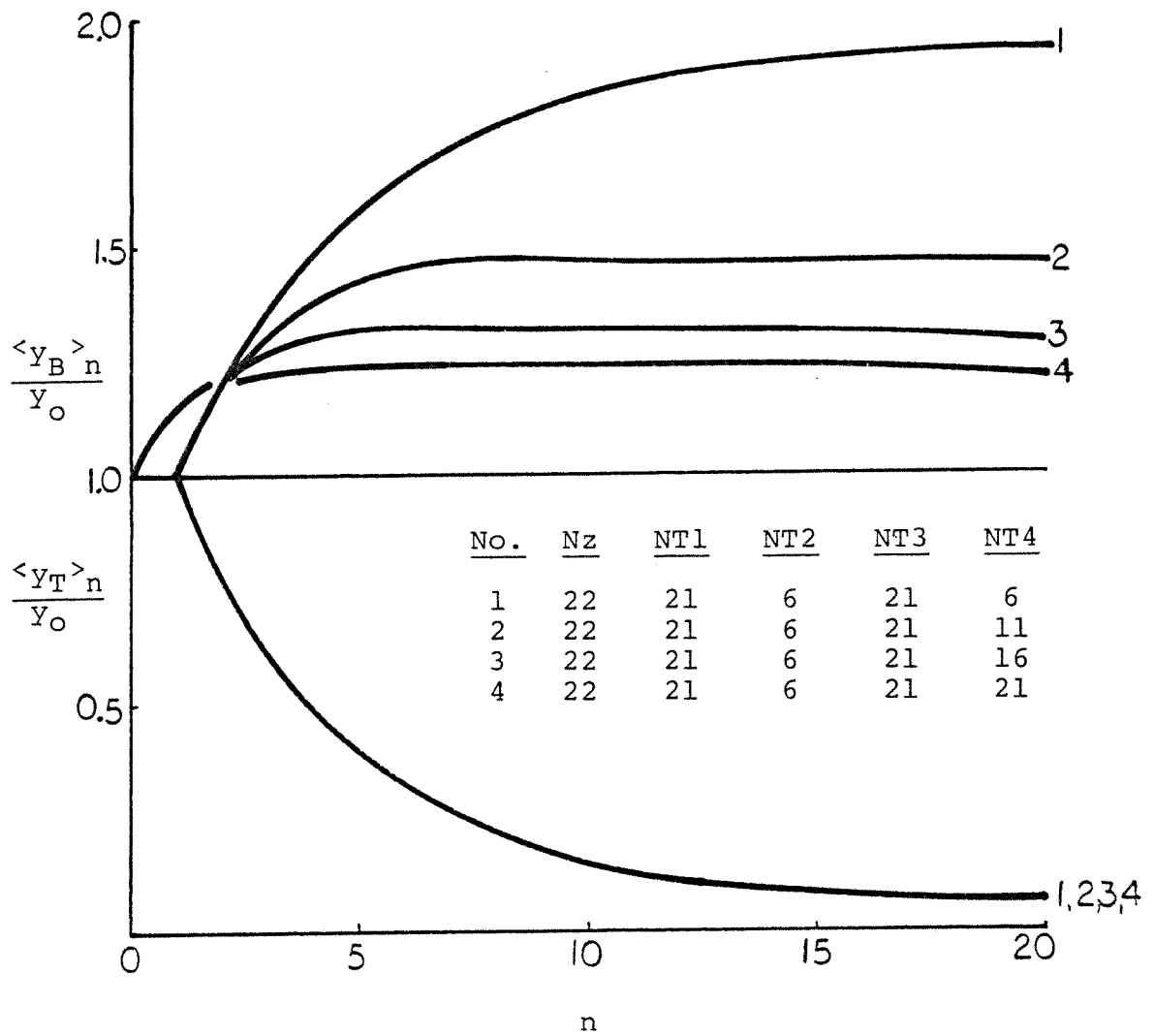


Fig. 30. Effect of NT4 on Transient Concentrations for NT2=6.

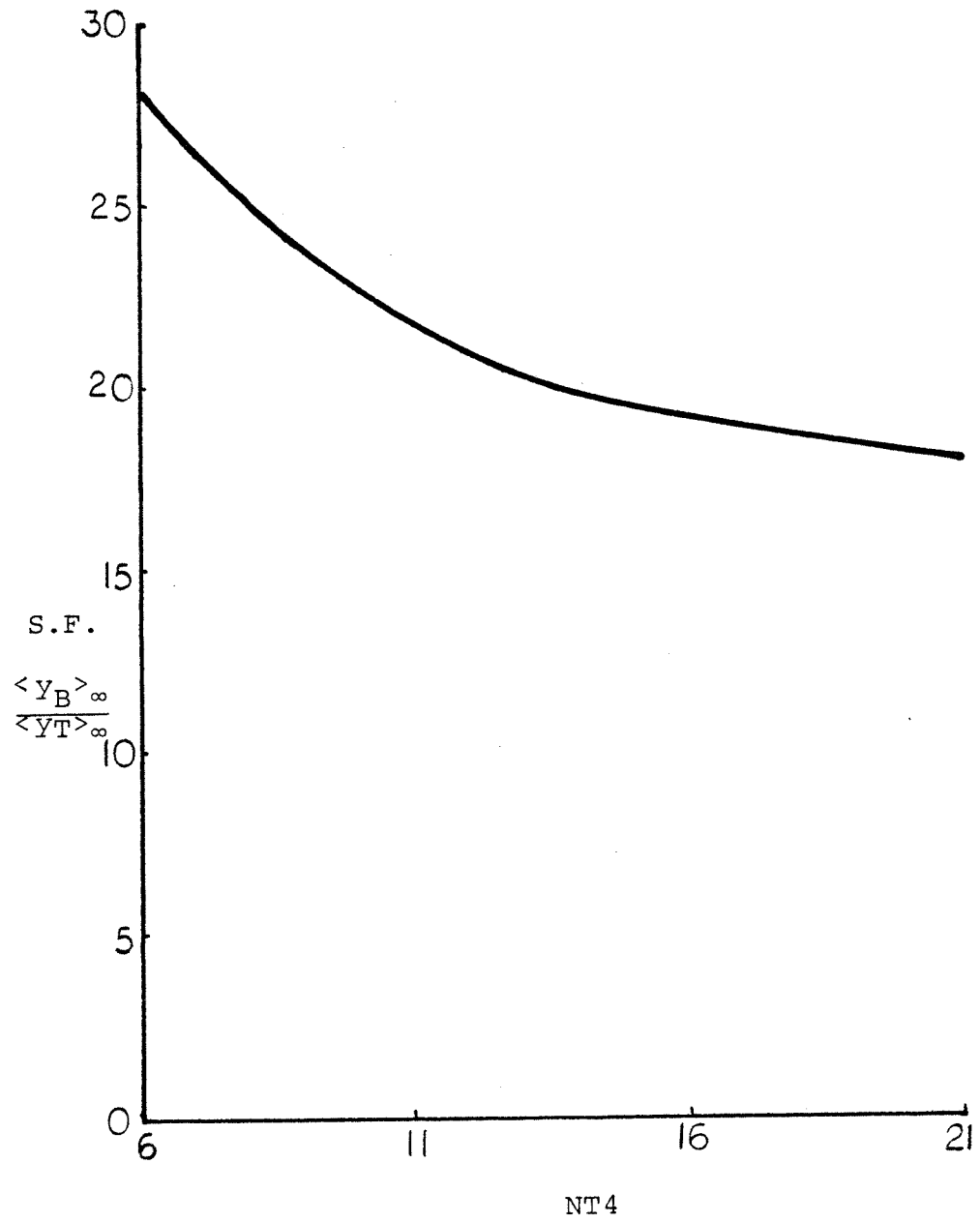


Fig. 31. Effect of $NT4$ on Separation for $NT4=6$.

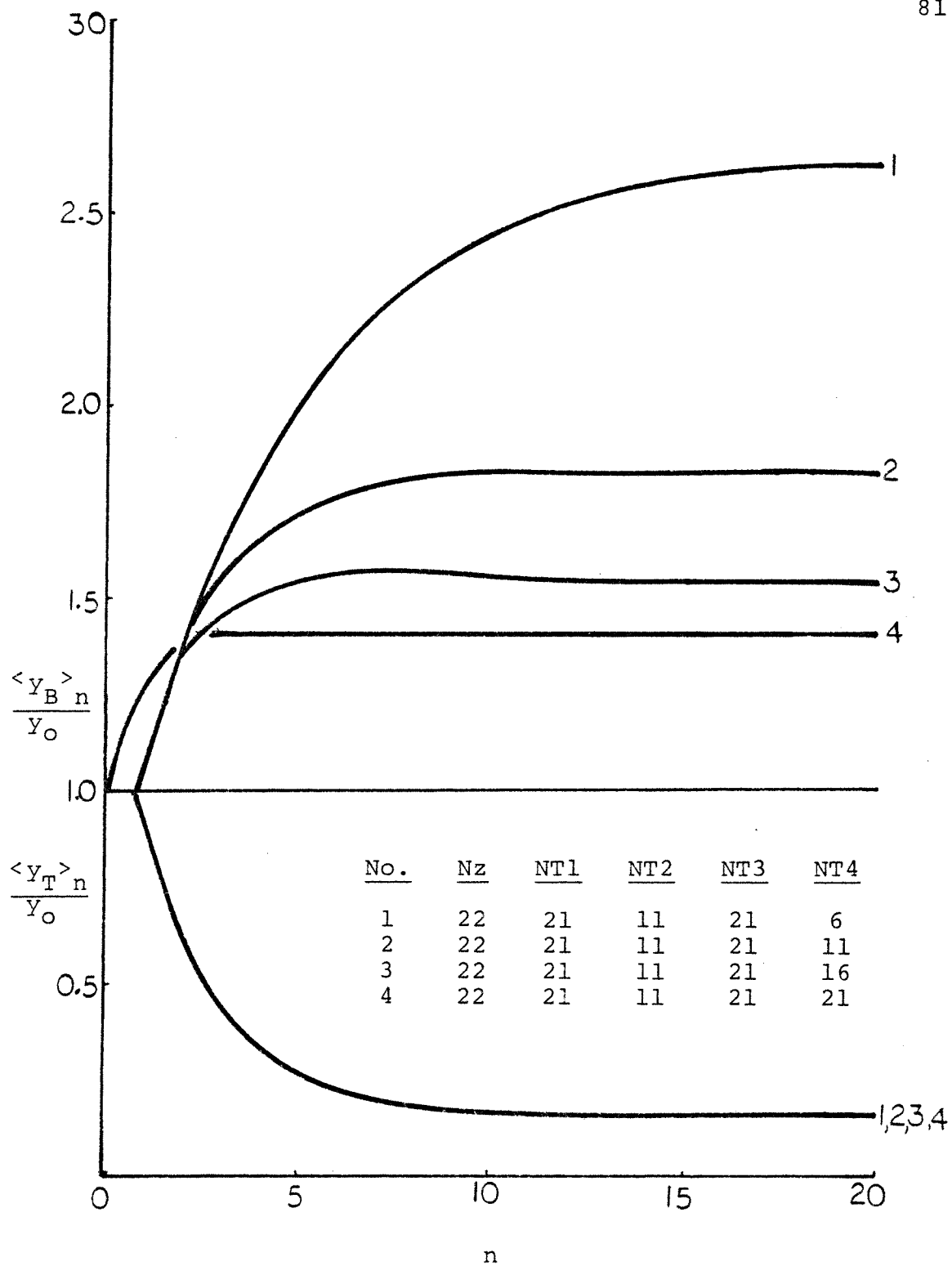


Fig. 32. Effect of $NT4$ on Transient Concentrations for $NT2=11$.

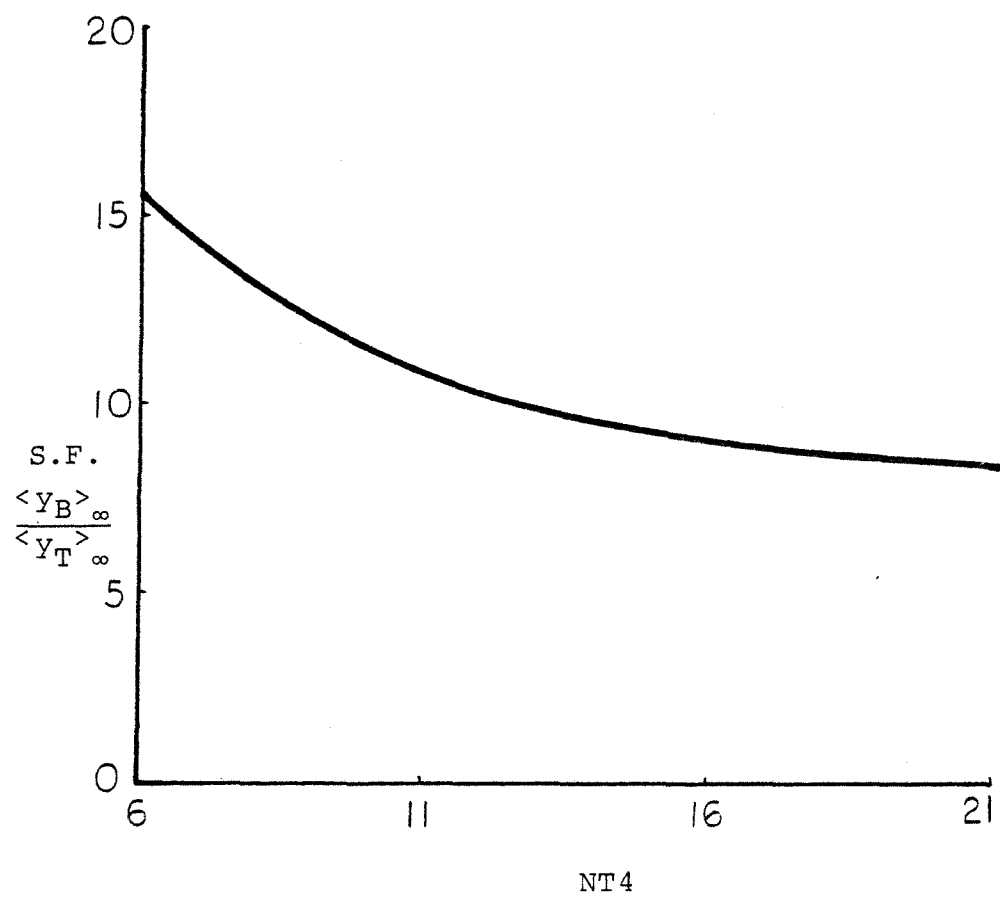


Fig. 33. Effect of NT4 on Separation Factors for NT2=11.

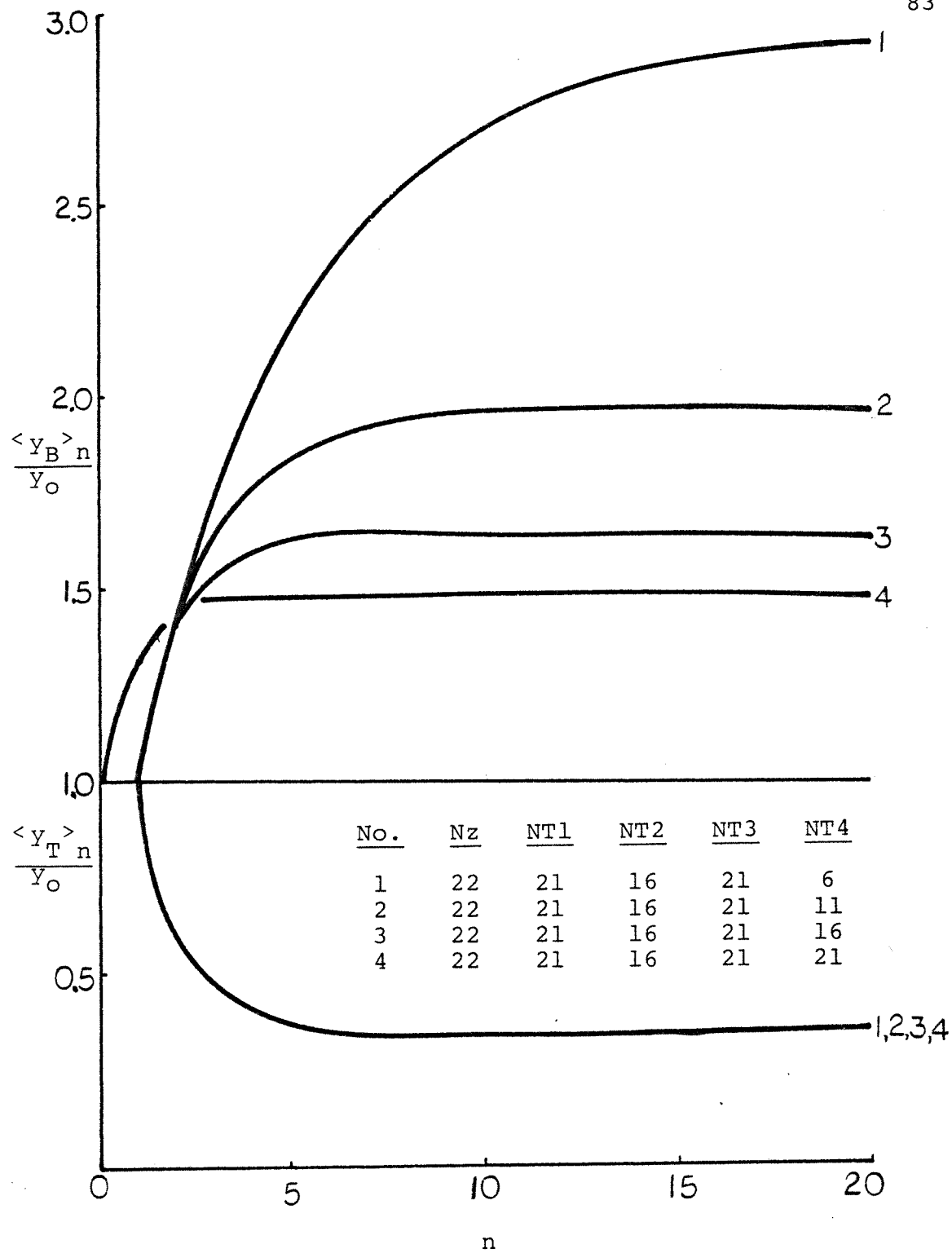


Fig. 34. Effect of NT4 on Transient Concentrations for NT2=16.

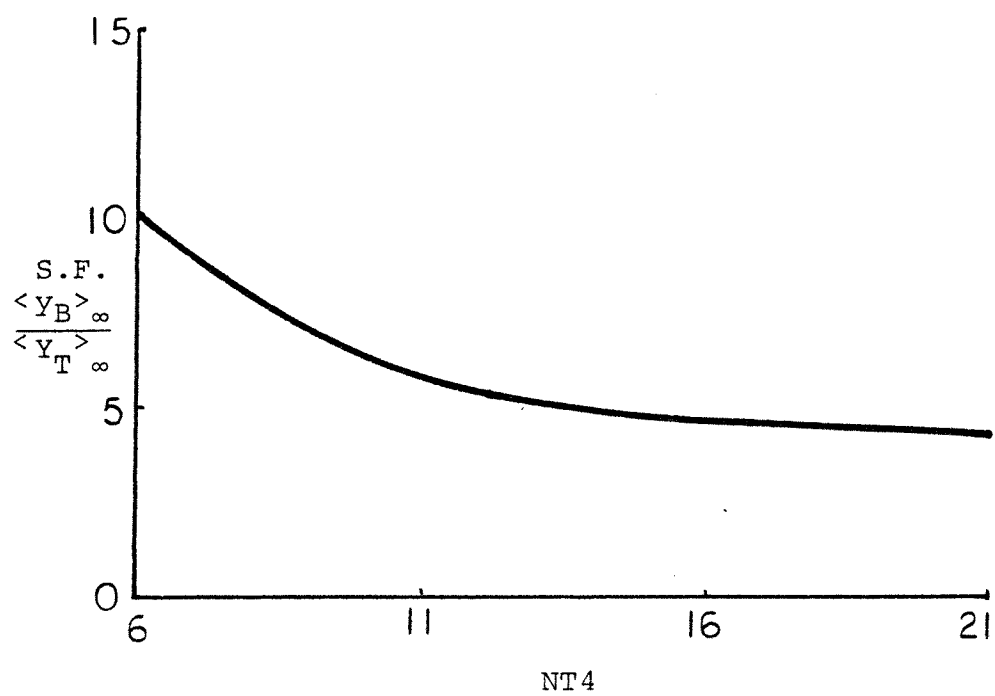


Fig. 35. Effect of NT4 on Separation Factor for NT2=16.

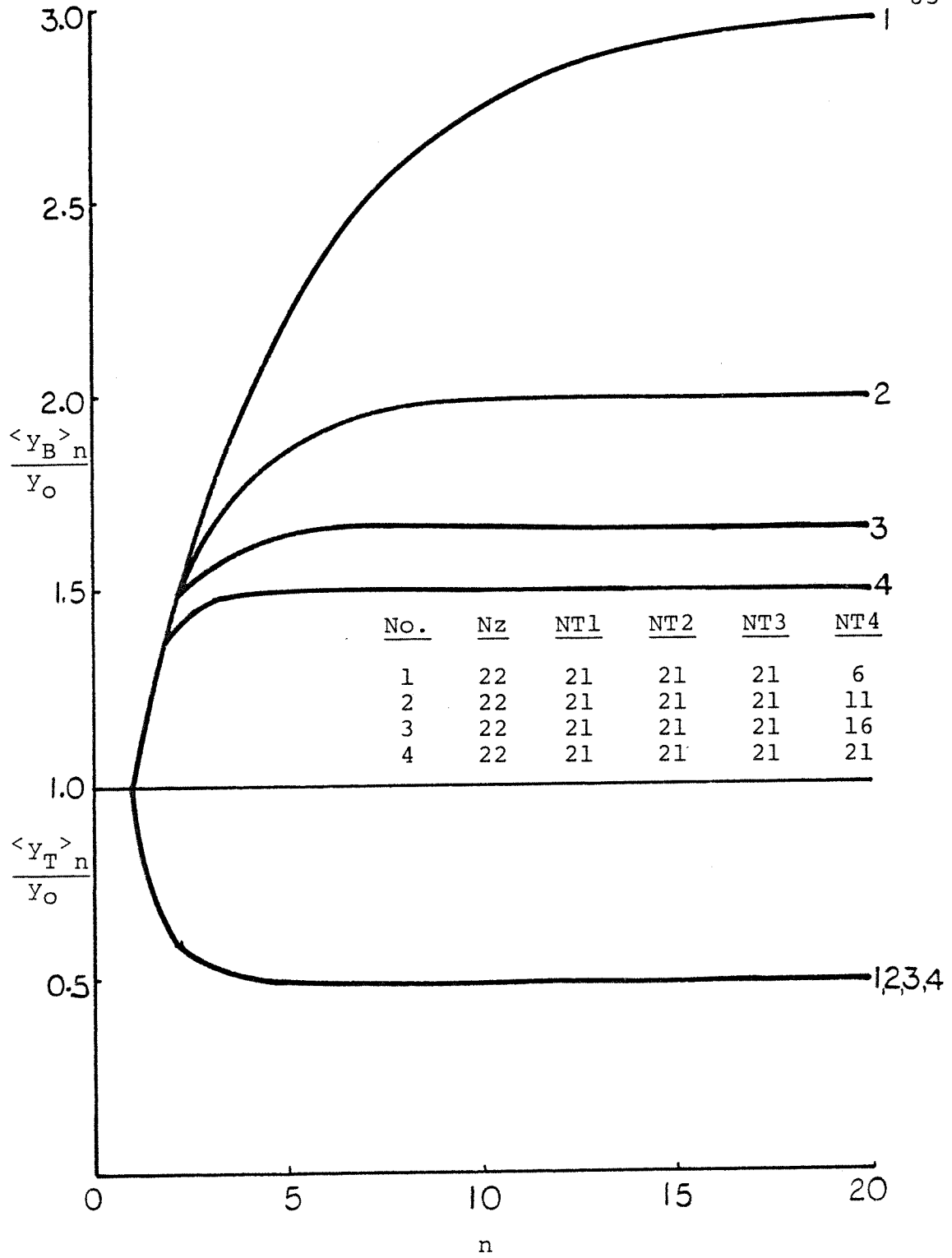


Fig. 36. Effect of NT4 on Transient Concentrations for NT2=21.

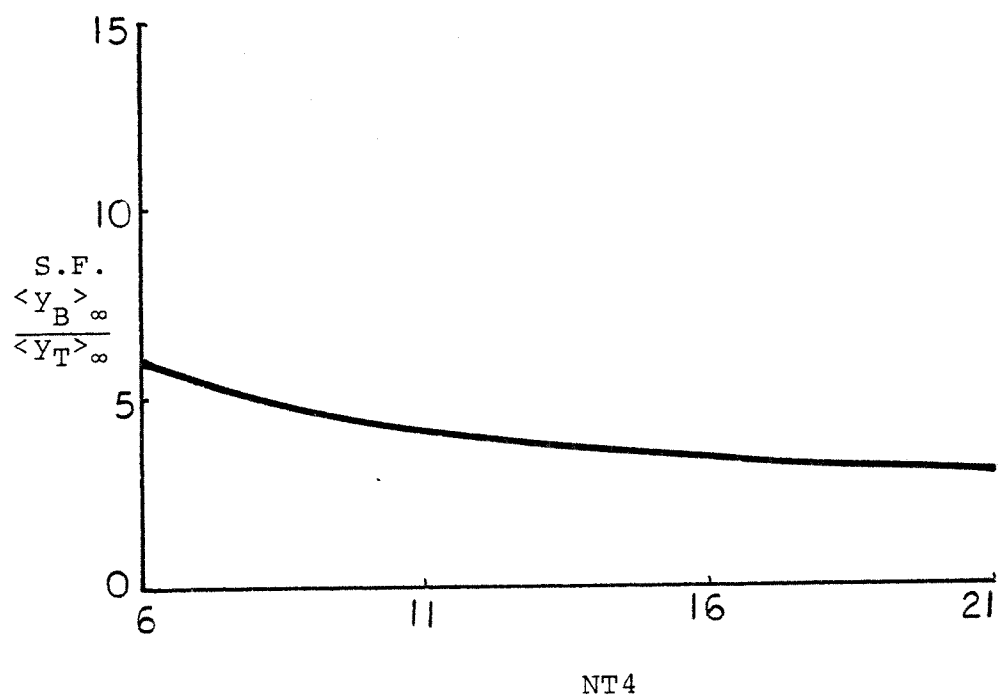


Fig. 37. Effect of NT4 on Separation Factors for NT2=21.

NT2, though the top product concentration ratio remain constant for various NT4 used, an increase of NT2 shifts the top product concentration ratio upward. Since we have seen from the ongoing analysis that increase in NT4 for constant value of NT2 decreases the separation factor (see Figures 31, 33 and 35), it is evident that, when NT4 becomes too excessive, haemoglobin from the top feed passes through the column and out as the bottom product. If NT4 is made even larger than the values used here (note that this also means large top feed), the top and bottom product will eventually have the same concentrations as the feed. NT4 and NT2 are not found to have the same effect on separation. However, constant NT4 for various values of NT2 described earlier do have a very good agreement with the experimental findings of Chen et al. (1979).

The steady state separation factors for the four values of NT2 used are shown on Table 30 and plotted against NT4 is presented in Figure 38. The slopes as can be seen from this graph for the four cases are somehow steeper between NT4=6 and NT4=11 as compared to the slopes between NT4=11 and NT4=21. These phenomenon seem to suggest that as NT4 increases, the separation decreases drastically after NT4=11 for the same reason discussed above.

The effect of NT2 and NT4 on the concentration transients is shown in Figure 39. The ordinate is the average product concentration (grams per cubic centi-

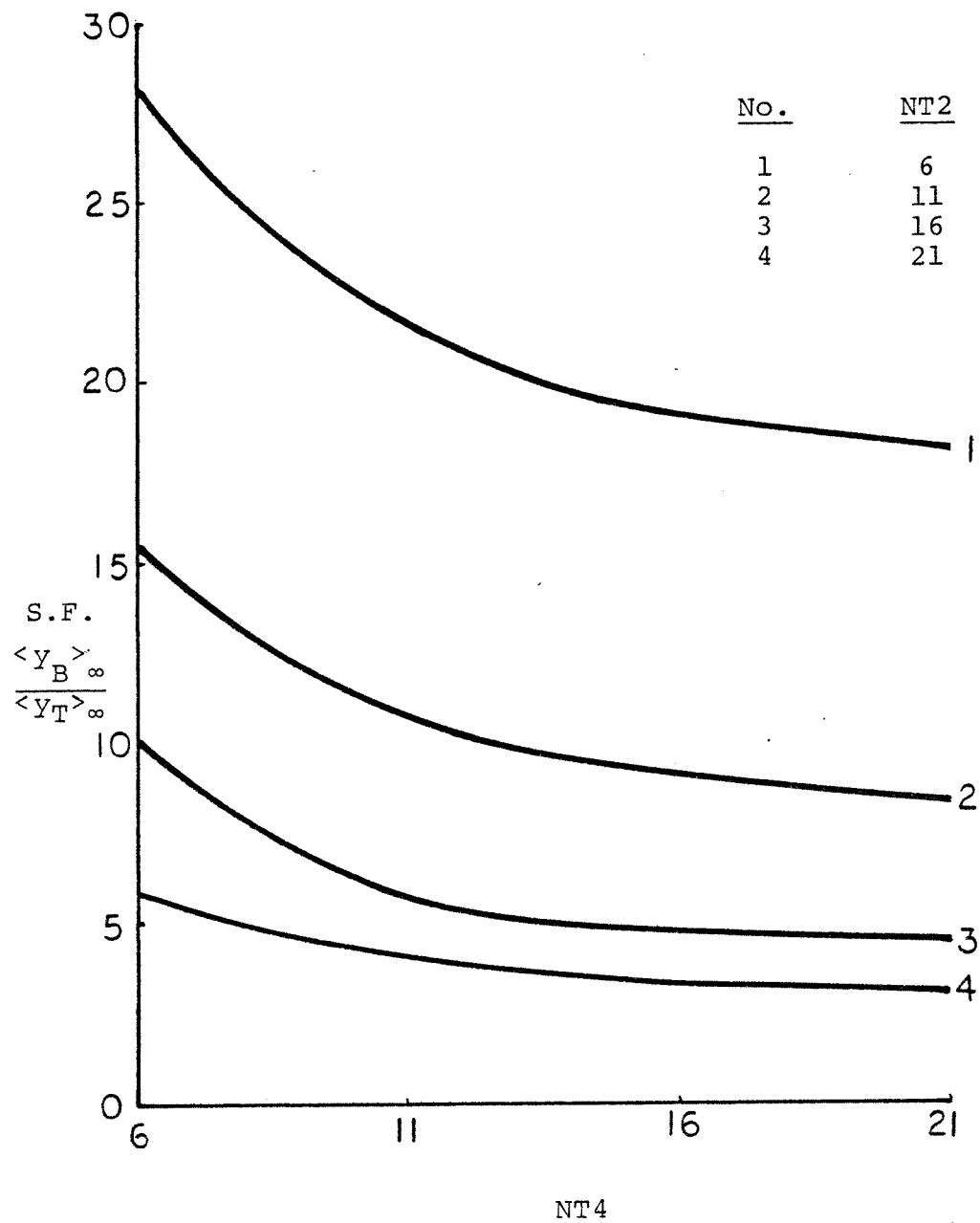


Fig. 38. Separation Factors vs. NT4.

<u>No.</u>	<u>Nz</u>	<u>NT1</u>	<u>NT2</u>	<u>NT3</u>	<u>NT4</u>
1	6	5	5	5	5
2	12	5	11	5	11

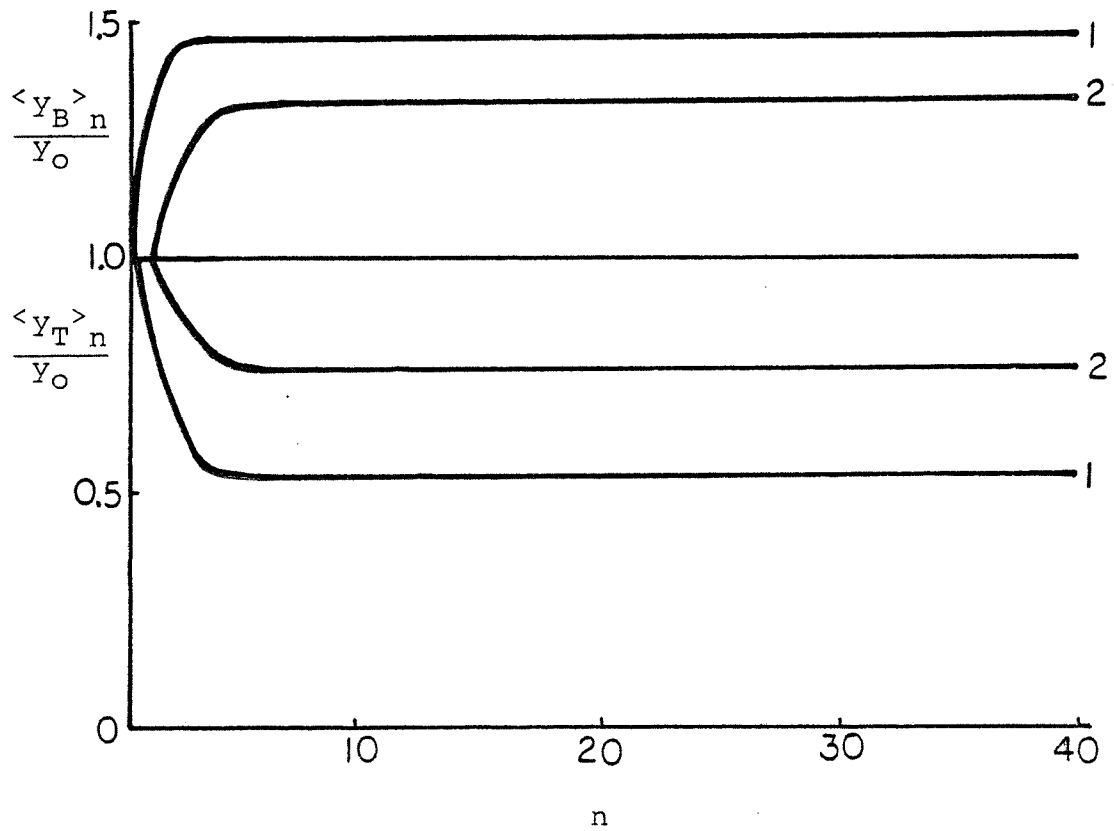


Fig. 39. Transient Concentrations as a Function of Number of Stages, Top and Bottom Feed.

meters) divided by the feed concentration for haemoglobin. The dimensionless concentration ratios for the bottom products are always greater than one, while those for the top product are always less than one. It can be seen from the graph that so long as the NT_2 and NT_4 , which is the volume of top product and volume of bottom product respectively (volume of feed from bottom and volume of feed from the top), are equal or less than NT_1 and NT_3 , upflow displacement and downflow displacement, that a reasonable separation can be obtained. The moment NT_2 and NT_4 are doubled, the top and bottom product concentration ratios both approach the dimensionless concentration ratio (i.e., $y_0=1$). From Figure 40, one can see that, if all the initial conditions are doubled including the number of theoretical plates, there is virtually no improvement in the separation obtained (see Tables 31 to 33). Since the time of operations are also doubled, it is probably not worthwhile doubling the initial conditions.

Table 34 gives the summary of the initial conditions for runs in which the volume of the top and bottom feed are varied simultaneously, and on Tables 35 to 39, the calculated results are given. On Table 40, and in Figure 41, it has been demonstrated that a considerable improvement in separation can be obtained if $NT_2 \ll NT_1$ and $NT_4 \ll NT_3$. The separation can be seen to increase for $NT_2=NT_4=1$ (batch) to a maximum when $NT_2=NT_4=3$ (approximately one-third the value of NT_1 and NT_3), and rapidly decreases exponentially. (See

<u>No.</u>	<u>Nz</u>	<u>NT1</u>	<u>NT2</u>	<u>NT3</u>	<u>NT4</u>
1	6	5	5	5	5
2	12	11	11	11	11

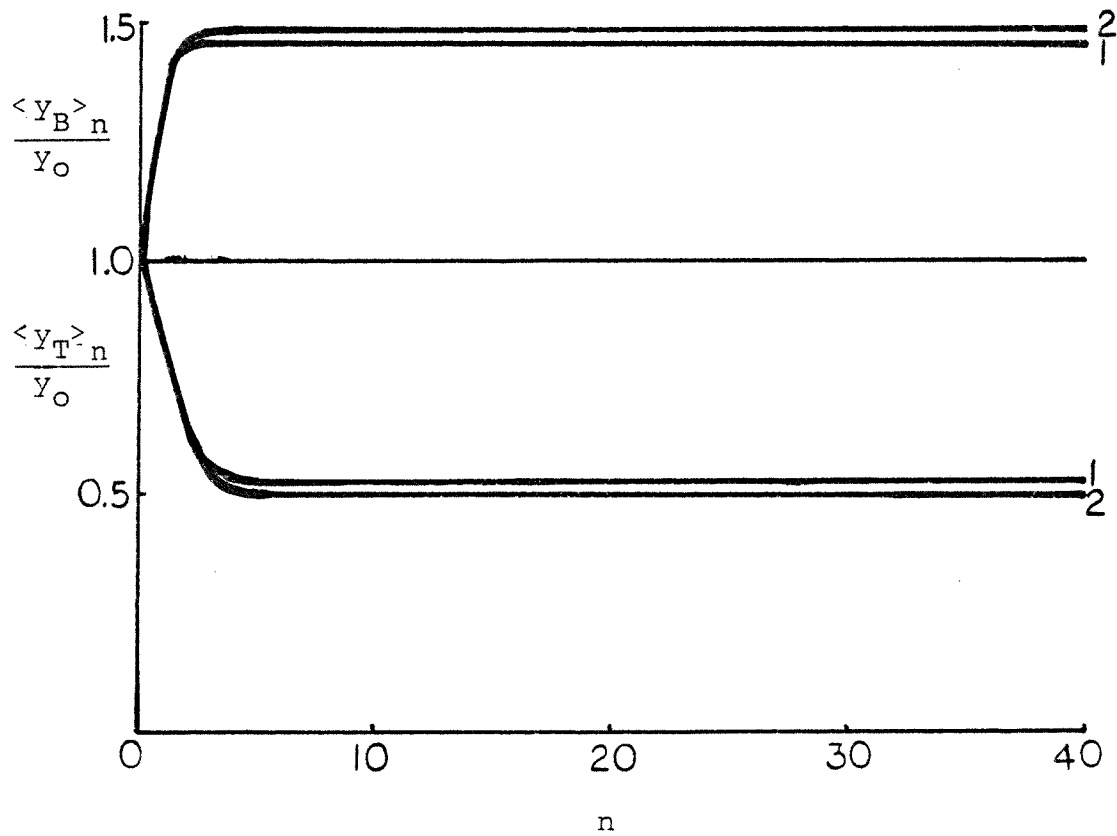


Fig. 40. Effect of Doubling Column Parameters.

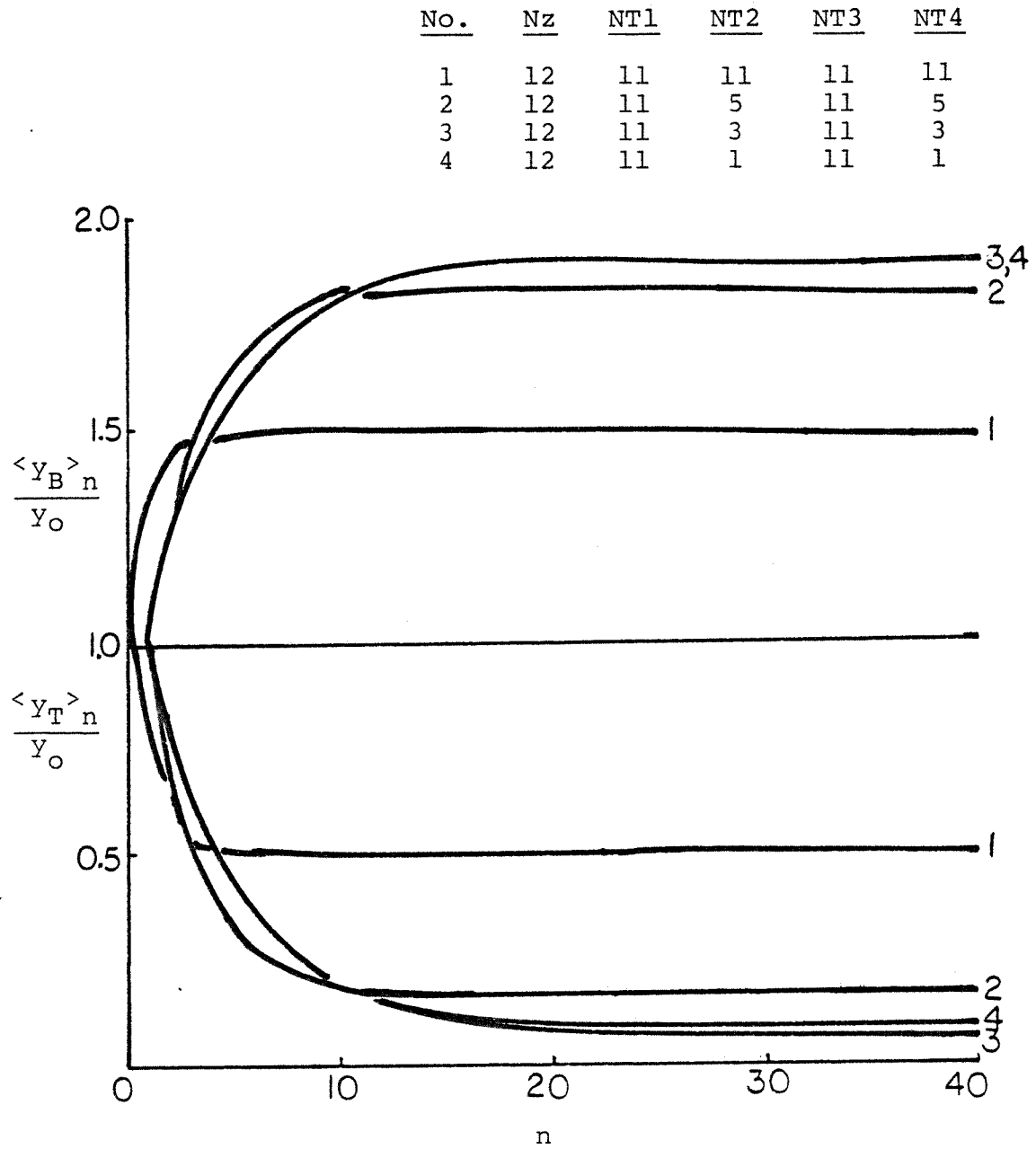


Fig. 41. Transient Concentrations as a Function of NT2 and NT4.

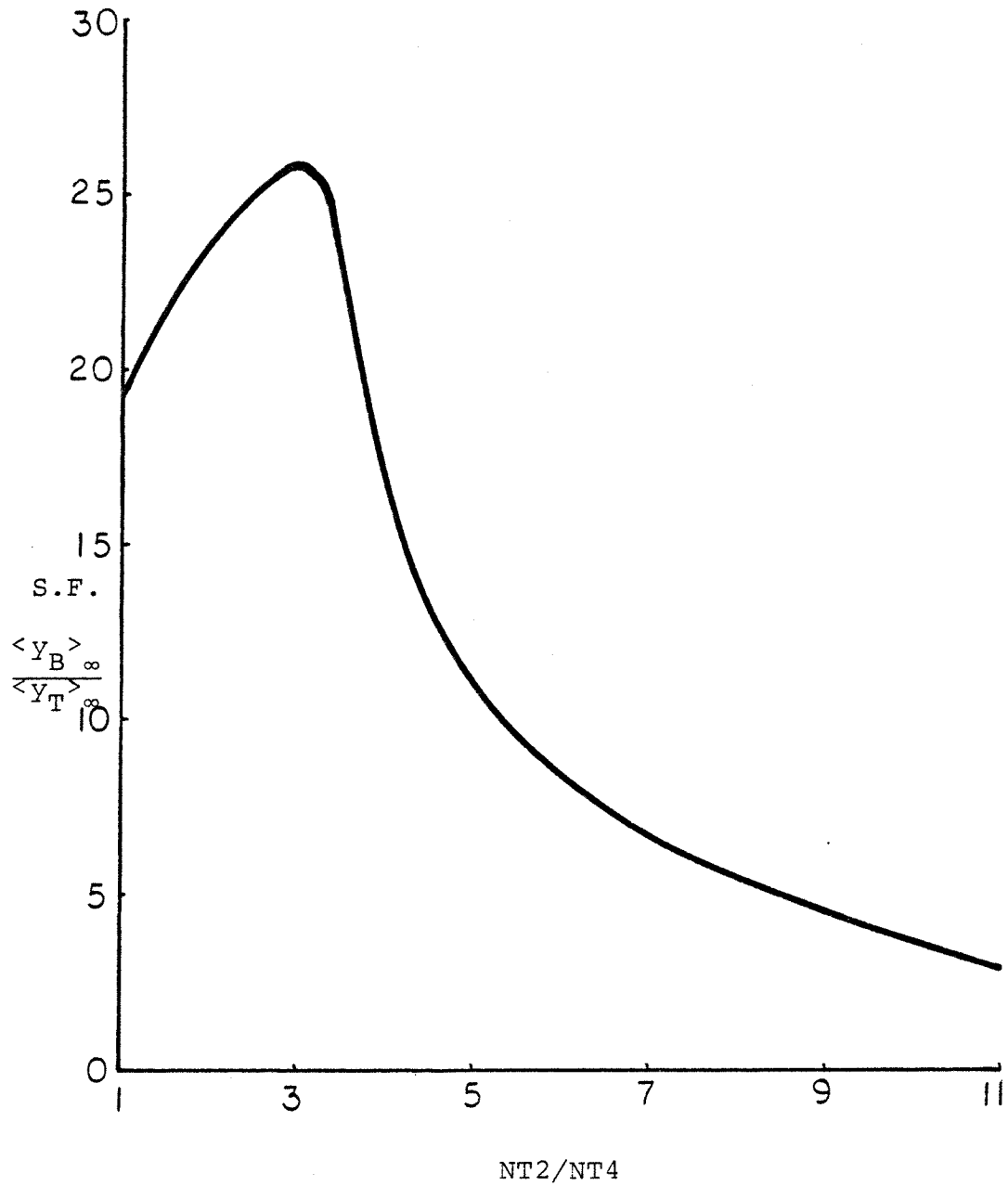


Fig. 42. Separation Factors as a Function of NT2 and NT4

Figure 42.) From the previous work in this area, batch process is known to offer the best separation. The reason for this behavior is yet to be substantiated theoretically and experimentally.

Chapter VI

SUMMARY OF CONCLUSIONS

This study further establishes the reliability of predicting column performance in terms of equilibrium theory. The simulated equation is based on the equations of change for the liquid-solid system with the diffusion term of negligible importance, and a linear equilibrium relation between the liquid and solid phases. The results show that a combination of equilibrium and STOP-GO algorithm give a good prediction of the concentration transients compared to previous methods of solution of the material balance relations of the extensive variables.

The results of the cycling zone adsorption simulation show very good agreement with results obtained by previous investigators, viz: limiting separation with increasing number of theoretical stages. This study, which extends the simulation to recycling of the product shows that increase in separation and decrease in the effect of β can be seen as the number of stages increases.

The concentration transients obtained for the batch parapump system shows that the steady state concentrations in both top and bottom reservoirs are independent of the number of theoretical stages chosen provided $\alpha = 1$. For

$\alpha < 1$, both top and bottom reservoir concentrations are less than that obtained for $\alpha = 1$, and for $\alpha > 1$, an inverse separation is obtained. The optimum separation is also obtained when α is unity.

For the continuous parapump operation, the following were noted:

1. If high separation factor is desired, volume of top and bottom feed should be as small as possible, preferably approximately one-third the volume of top and bottom reservoir displacements.

2. If enrichment of rich product is desired, volume of bottom feed should be made as large as possible.

3. Literally, scaling up column parameters results in no improved separation.

Nomenclature

i	=	stage number
I_i	=	isoelectric point of i
IS_1	=	ionic strength in the bottom reservoir
IS_2	=	ionic strength in the top reservoir
J	=	transfer step
k	=	x/y , equilibrium constant
k_{P_1}	=	equilibrium constant at $pH = P_1$
k_{P_2}	=	equilibrium constant at $pH = P_2$
n	=	number of cycles of pump operation
$m_A^{(t)}$	=	interface mass transfer
NNZ	=	number of stages or cells
NZ	=	number of stages or cells including top and bottom reservoir
P_1	=	high pH level
P_2	=	low pH level
Q	=	reservoir displacement rate, cm^3/s
V	=	volume of fluid phase per stage, cm^3
\bar{V}	=	volume of solid phase per stage, cm^3
V_B	=	bottom reservoir dead volume, cm^3
V_T	=	top reservoir dead volume, cm^3
x	=	concentration of solute in the solid phase, kg moles/ cm^3
y	=	concentration of solute in the fluid phase, kg moles/ cm^3
y_o	=	concentration of solute in the feed, kg moles/ cm^3
$\langle y_B \rangle_n$	=	average concentration of solute in the bottom reservoir at n^{th} cycle, kg moles/ cm^3

$\langle y_T \rangle_n$ = average concentration of solute in the top reservoir at n^{th} cycle, gm moles/cm³

$\langle y_B \rangle_\infty$ = steady state concentration of solute in the bottom reservoir, gm moles/cm³

$\langle y_T \rangle_\infty$ = steady state concentration of solute in the top reservoir, gm moles/cm³

Greek Letters

α = (reservoir displacement)/(column void volume)

β = recycle ratio

Other Symbols and Subscripts

$\langle \rangle$ = average value

n = cycle number

N = number of cells (used for analysis of batch para-pump)

T = top

B = bottom

o = initial condition

Nomenclature for Computer Program Input and Output Redefined

$NT1$ = Upflow displacement, cc.

$NT2$ = Volume of bottom feed

$NT3$ = Downflow displacement, cc.

$NT4$ = Volume of top feed, cc.

See Appendix A for other definitions.

Appendix A

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EQUILIBRIUM THEORY CUM STOP-GO COMPUTER ALGORITHM FOR PH PARAMETER
SYSTEM WRITTEN IN FORTRAN IV FOR THE IBM 360 COMPUTER

DEPARTMENT OF CHEMICAL ENGINEERING
M. J. I. T.
NEWARK, NEW JERSEY

PROGRAM WRITTEN BY CHARLES O. KERDOO AND H. T. CHEN

THIS PROGRAM CALCULATES THE SEPARATIONS ARISING FROM THE PH
RECUPERATIVE MODE OF PARAMETRIC PUMPING

N O M E N C L A T U R E

NT1 =DOWNFLOW TIME INTERVAL
NT2 =BOTTOMFEED AND TOP PRODUCT WITHDRAWAL TIME INTERVAL
NT3 =UPFLOW TIME INTERVAL
NT4 =TOPFEED AND BOTTOM PRODUCT WITHDRAWAL TIME INTERVAL
Y =CONCENTRATION PROFILE DURING DOWNFLOW
YY =CONCENTRATION PROFILE DURING BOTTOMFEED AND TOP PRODUCT
YYY =CONCENTRATION PROFILE DURING UPFLOW
YYYY =CONCENTRATION PROFILE DURING TOPFEED AND BOTTOM PRODUCT
TP =TOP PRODUCT
BP =BOTTOM PRODUCT
BRES =BOTTOM RESERVOIR CONCENTRATION
TRES =TOP RESERVOIR CONCENTRATION
Q =VOLUMETRIC FLOWRATE ,CC/SEC
AK8 =SPECIFIC RATE CONSTANT FOR PH=8
AK6 =SPECIFIC RATE CONSTANT FOR PH=6
YINT =INITIAL SOLUTE CONCENTRATION
TVOL =TOTAL VOLUME OF COLUMN
VOID =COLUMN VOID VOLUME
HPH =HIGH PH
LPH =LOW PH
VDEAD=DEAD VOLUME OF TOP RESERVOIR
VBEAD=DEAD VOLUME BOTTOM RESERVOIR
NFNL =NUMBER OF CYCLES

MAIN PROGRAM

```

1      REAL LPH
2      DIMENSION Y(30,30),BP(50),PRES(50),YY(30,30),YYY(30,30),
3      1YYYY(30,30),TP(50),TRES(50),PH(30,30),PPH(30,30)
4      READ(5,65)O,AK8,AK6,YINT,TVOL,VOID,HPH,LPH,VTDEAD,VBDEAD
5      READ(5,1001)NI
6      DO 1000 IK=1,NI
7      1001 FORMAT(I3)
8      READ(5,66)NZ,NT1,NT2,NT3,NT4,NFINL
9      65  FORMAT(12F5.2)
10     66  FORMAT(12I5)
11     NNZ=NZ-1
12     AANZ=ANZ-2
13     V=(TVOL/AANZ)*VOID
14     VB=(TVOL/AANZ)*(1.-VOID)
15     PH(1,1)=LPH
16     DO 560 I=2,NNZ
17     560 PH(I,1)=HPH
18     BRES(1)=YINT
19     TRES(1)=YINT
20     N=2
21     YT=YINT
22     J=1
23     DO 10 I=1,NNZ
24     10  Y(I,J)=YINT
25     WRITE(6,102)
26     102 FORMAT('1')
27     550 WRITE(6,35)N
28     35  FORMAT( // 5X, 'CYCLE=' I20)
29     DO 30 J=2,NT1
30     Y(I,J)=YT
31     PH(1,J)=LPH
32     PH(2,J)=LPH
33     DO 800 I=3,NNZ
34     800 PH(I,J)=PH(I-1,J-1)
35     DO 32 I=2,NNZ
36     32  Y(I,J)=ALPHA(V,VB,AK6,AK8,Y(I,J-1),Y(I-1,J-1),
37     *PH(I,J),PH(I,J-1),LPH)
38     30  CONTINUE
39     SUM=0.
40     NNT1=NT1-1
41     ANNT1=NNT1
42     DO 31 J=1,NNT1
43     31  SUM=SUM+Y(NNZ,J)
44     BRES(N)=((SUM/ANNT1)*(V*ANNT1)+VBDEAD*BRES(N-1))/(V*ANNT1+VBDEAD)
45     WRITE(6,37)BRES(N)
46     37  FORMAT( / 5X, 'BOTTOM RESERVIOR CONCENTRATI(ON)=' E20.5)
47     MM=1
48     DO 50 I=2,NNZ
49     M=NNZ-MM+1
50     YY(I,1)=Y(M,NT1)
51     PPH(I,1)=PH(M,NT1)
52     MM=MM+1
53     50  CONTINUE
54     IF (NT2-1)552,552,562
55     552 YY(1,1)=BRES(N)
56     PPH(1,1)=HPH
57     GO TO 570
58     562 YY(1,1)=YINT

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57      PPH(1,1)=LPH
58      DO 52 J=2,NT2
59      PPH(1,J)=LPH
60      52  YY(I,J)=YINT
61      DO 43 J=2,NT2
62      PPH(2,J)=LPH
63      DO 810 I=2,NNZ
64      810 PPH(I,J)=PPH(I-1,J-1)
65      DO 42 I=2,NNZ
66      42  YY(I,J)=ALPHA(V,VB,AK6,AK8,YY(I,J-1),YY(I-1,J-1),
1PPH(I,J),PPH(I,J-1),LPH)
67      43  CONTINUE
68      SUM=0.
69      NNT2=NT2-1
70      ANNT2=NNT2
71      DO 150 J=1,NNT2
72      150 SUM=SUM+YY(NNZ,J)
73      TP(N)=SUM/ANNT2
74      WRITE(6,101)TP(N)
75      101 FORMAT( // 5X,'TOP PRODUCT=',E20.5)
76      570 DO 110 I=2,NNZ
77      PPH(I,1)=PPH(I,NT2)
78      110 YYY(I,1)=YY(I,NT2)
79      DO 111 J=1,NT3
80      111 YYY(1,J)=BRES(N)
81      DO 120 J=2,NT3
82      PPH(1,J)=HPPH
83      PPH(2,J)=HPPH
84      DO 820 I=3,NNZ
85      820 PPH(I,J)=PPH(I-1,J-1)
86      DO 122 I=2,NNZ
87      122 YYY(I,J)=ALPHA(V,VB,AK6,AK8,YYY(I,J-1),YYY(I-1,J-1),
*PPH(I,J),PPH(I,J-1),LPH)
88      120 CONTINUE
89      SUM=0.
90      NNT3=NT3-1
91      ANNT3=NNT3
92      DO 431 J=1,NNT3
93      431 SUM=SUM+YYY(NNZ,J)
94      TRES(N)=((SUM/ANNT3)*(V*ANNT3)+VTDEAD*TRES(N-1))/(V*ANNT3+VTDEAD)
95      WRITE(6,805)TRES(N)
96      805 FORMAT( / 5X,'TOP RESERVIOR CONCENTRATION=',E20.5)
97      MM=1
98      DO 250 I=2,NNZ
99      M=NNZ-MM+1
100     YYYY(I,1)=YYY(M,NT3)
101     PH(I,1)=PPH(M,NT3)
102     MM=MM+1
103     250 CONTINUE
104     IF (NT4-1)580,580,590
105     580 YYYY(1,1)=TRES(N)
106     PPH(1,1)=LPH
107     GO TO 595
108     590 DO 252 J=1,NT4
109     252 YYYY(1,J)=YINT
110     DO 243 J=2,NT4
111     PH(1,J)=HPPH
112     PH(2,J)=HPPH

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113      DO 860 I=3,NNZ
114      860 PH(I,J)=PH(I-1,J-1)
115      DO 242 I=2,NNZ
116      242 YYY(I,J)=ALPHA(V,VB,AK6,AK8,YYY(I,J-1),YYY(I-1,J-1),
      *PH(I,J),PH(I,J-1),LPH)-
117      243 CONTINUE
118      SUM=0.
119      NNT4=NT4-1
120      ANNT4=NNT4
121      DO 300 J=1,NNT4
122      300 SUM=SUM+YYY(NNZ,J)
123      BP(N)=SUM/ANNT4
124      WRITE(6,301)BP(N)
125      301 FORMAT( // 5X,'BOTTOM PRODUCT=',E20.5)
126      595 YT=TRES(N)
127      IF(N-NFINL)600,700,700
128      600 N=N+1
129      DO 520 I=2,NNZ
130      Y(I,1)=YYY(I,NT4)
131      520 PH(I,1)=PH(I,NT4)
132      PH(1,1)=LPH
133      Y(1,1)=YT
134      GO TO 550
135      700 WRITE(6,5)
136      5   FORMAT( 1H1,10X,'PH PARAMETRIC PUMPING- BATCH PROCESS')
137      WRITE(6,710)O,AK8,AK6,YINT,TVOL,VOID,HPH,LPH,VTDEAD,VBDEAD
138      WRITE(6,711)KZ,NT1,NT2,NT3,NT4,NFINL
139      710 FORMAT('O', 'Q=',F5.2,5X,'AK8=',F5.2,5X,'AK6=',F5.2,/,/,
      11X,'YINT=',F5.2,5X,'TOTAL VOLUME=',F5.2,5X,'VOID VOLUME=',F5.2,
      2//,1X,'HIGH PH=',F5.2,5X,'LOW PH=',F5.2,/,/,
      31X,'DEAD VOLUME OF TOP RESERVOIR=',F5.2,5X,/,/,
      41X,'DEAD VOLUME OF BOTTOM RESERVOIR=',F5.2)
140      711 FORMAT('O', 'NZ=',I5,2X,'NT1=',I5,2X,'NT2=',I5,
      12X,'NT3=',I5,2X,'NT4=',I5,2X,/,/, 'NFINL=',I5)
141      WRITE(6,740)
142      DO 720 N=2,NFINL
143      SF=BPRES(N)/TRES(N)
144      WRITE(6,730)N,TRES(N),BPRES(N),SF
145      740 FORMAT( // 4X,1H1,10X,4HTRES,11X,4HBPRES,11X,2HSF)
146      730 FORMAT( / I5,3F15.5)
147      720 CONTINUE
148      WRITE(6,1)
149      1000 CONTINUE
150      1   FORMAT('1')
151      STOP
152      END

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C   FUNCTION FOR CALCULATING THE CONCENTRATION PROFILE IN THE COLUMN
C
153      FUNCTION ALPHA(V,VB,AK6,AK8,YTP,YZP,PH,PHP,PBL)
154      IF(PH-PHP)10,15,20
155      10  A6=AK6
156      A8=AK8

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157          GO TO 30
158      20    A6=AK8
159          A8=AK6
160          GO TO 30
161      15    IF.(PH-PHL)40,40,50
162      40    A6=AK6
163          A8=AK6
164          GO TO 30
165      50    A6=AK8
166          A8=AK8
167      30    ALPHA=(1./(V+A6*VB))*(Y1P*A8*VR+V*YZP)
168          RETURN
169          END
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Appendix B

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CYCLING ZONE ADSORPTION COMPUTER ALGORITHM FOR PH PARAMETRIC
SYSTEM WRITTEN IN FORTRAN IV FOR THE IBM 360 COMPUTER

DEPARTMENT OF CHEMICAL ENGINEERING

N. J. I. T.

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PROGRAM WRITTEN BY CHARLES D. KEROPO AND H. T. CHEN

THIS PROGRAM CALCULATES THE SEPARATIONS ARISING FROM THE PH
RECUPERATIVE MODE OF CYCLING ZONE ADSORPTION

N O M E N C L A T U R E

TP =TOP PRODUCT
BP =BOTTOM PRODUCT
BRES =BOTTOM RESERVOIR CONCENTRATION
TRES =TOP RESERVOIR CONCENTRATION
Q =VOLUMETRIC FLOWRATE ,CC/SEC
AK8 =SPECIFIC RATE CONSTANT FOR PH=8
AK6 =SPECIFIC RATE CONSTANT FOR PH=6
YINT =INITIAL SOLUTE CONCENTRATION
TVOL =TOTAL VOLUME OF COLUMN
VOID =COLUMN VOID VOLUME
HPH =HIGH PH
LPH =LOW PH
VTDEAD=DEAD VOLUME OF TOP RESERVOIR
VRDEAD=DEAD VOLUME BOTTOM RESERVOIR
NFINL =NUMBER OF CYCLES

MAIN PROGRAM

```

1 REAL LPH
2 DIMENSION Y(61,61),BP(20),BRES(61),YY(20,20),YYY(20,20),
1YYYY(20,20),TP(20),TRES(61),PH(61,61),PPH(20,20)
3 READ(5,65)Q,AK8,AK6,YINT,TVOL,VOID,HPH,LPH,VTDEAD,VRDEAD,BETA
4 READ(5,66)NZ,NT1,NT2,NT3,NT4,NFINL
5 WRITE(6,5)
6 5 FORMAT(/// 10X,'*** PH PARAMETRIC PUMPING -BATCH PROCESS ***' ///)
7 WRITE(6,711)NZ,NT1,NT2,NT3,NT4,NFINL

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```

8      WRITE(6,710)Q,AK8,AK6,YINT,TVOL,VOID,HPH,LPH,VTDEAD,VBDEAD,BETA
9      65  FORMAT(12F5.2)
10     66  FORMAT(12I5)
11     710  FORMAT( // 5X,'Q=',F5.2,5X,'AK8=',F5.2,5X,'AK6=',F5.2,/,
12         15X,'YINT=',F5.2,5X,'TOTAL VOLUME=',F5.2,5X,'VOID VOLUME=',F5.2,/,
13         25X,'HIGH PH=',F5.2,5X,'LOW PH=',F5.2,/,
14         35X,'DEAD VOLUME OF THE FLUID PHASE=',F5.2,5X,
15         4'DEAD VOLUME OF THE SOLID PHASE=',F5.2,
16         55X,'RECYCLE RATIO=',F5.2)
17     711  FORMAT( // 5X,'NZ=',I5,5X,'NT1=',I5,5X,'NT2=',I5,/,
18         15X,'NT3=',I5,5X,'NT4=',I5,5X,'NFINAL=',I5)
19     NNZ=NZ-1
20     AANZ=NZ-2
21     V=(TVOL/AANZ)*VOID
22     VB=(TVOL/AANZ)*(1.-VOID)
23     BRES(1)=YINT
24     TRES(1)=YINT
25     PH(1,1)=HPH
26     Y(1,1)=YINT
27     DO 1000 I=2,NNZ
28     M=(-1)**I
29     IF(M)1010,1020,1020
30     1010 PH(I,1)=HPH
31     Y(I,1)=YINT
32     GO TO 1000
33     1020 PH(I,1)=LPH
34     Y(I,1)=YINT*(V+VB*AK8)/(V+VB*AK6)
35     1000 CONTINUE
36     PH(1,2)=LPH
37     PH(1,3)=HPH
38     Y(1,2)=YINT
39     Y(1,3)=YINT
40     J=2
41     1070 DO 1800 I=2,NNZ
42     1800 PH(I,J)=PH(I-1,J-1)
43     350  WRITE(6,35)J
44     35  FORMAT( // 5X,'CYCLE='I20)
45     DO 32 I=2,NNZ
46     32  Y(I,J)=ALPHA(V,VB,AK6,AK8,Y(I,J-1),Y(I-1,J-1),
47         *PH(I,J),PH(I,J-1),LPH)
48     Y(1,J)=Y(1,J-1)
49     PH(1,J)=LPH
50     210  WRITE(6,36)J,(I,PH(I,J),Y(I,J),I=1,NNZ)
51     36  FORMAT( // 5X,'J=',I20/19X,'I',16X,'PH',16X,'Y'/(I20,2F20.5))
52     BRES(J)=Y(NNZ,J-1)
53     WRITE(6,37)BRES(J)
54     37  FORMAT( // 5X,'BOTTOM RESERVOIR CONCENTRATION=',E20.5)
55     PH(1,J)=LPH
56     J=J+1
57     1100 DO 1900 I=2,NNZ
58     1900 PH(I,J)=PH(I-1,J-1)
59     Y(1,J-1)=YINT*(1.-BETA)+BETA*TRES(J-2)
60     DO 1032 I=2,NNZ
61     1032 Y(I,J)=ALPHA(V,VB,AK6,AK8,Y(I,J-1),Y(I-1,J-1),
62         *PH(I,J),PH(I,J-1),LPH)
63     Y(1,J)=Y(1,J-1)
64     PH(1,J)=HPH
65     WRITE(6,36)J,(I,PH(I,J),Y(I,J),I=1,NNZ)

```

```

58      TRES(J)=Y(NMZ,J-1)
59      WRITE(6,805)TRES(J)
60      IF(J-NFINL)1061,1065,1065
61  1061 PH(1,J)=HPP
62      J=J+1
63  1060 Y(1,J-1)=YINT*(1.-BETA)+BETA*8RES(J-2)
64      GO TO 1070
65  805  FORMAT( / 5X, 'TOP RESERVIOR CONCENTRATION=',F20.5)
66  1065 STOP
67      END

```

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68      FUNCTION ALPHA(V,VB,AK6,AK8,YTP,YZP,PH,PHP,PHL)
69      IF(PH-PHP)10,15,20
70  10   A6=AK6
71      A8=AK8
72      GO TO 30
73  20   A6=AK8
74      A8=AK6
75      GO TO 30
76  15   IF(PH-PHL)40,40,50
77  40   A6=AK6
78      A8=AK6
79      GO TO 30
80  50   A6=AK8
81      A8=AK8
82  30   ALPHA=(1./(V+A6*VB))*(YTP*A8*VB+V*YZP)
83      RETURN
84      END

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Appendix CTable 1CYCLING ZONE ADSORPTION

Conditions for Computational Algorithm with
Variable Number of Stages and Recycle Ratio

<u>Operating Variable</u>	<u>Value</u>
Volumetric Flow Rate	0.5 cc.
Specific Rate Constant for High pH	0.07
Specific Rate Constant for Low pH	1.58
Initial Feed Concentration (Normalized)	1.00 gm. mole/cc.
Dead Volume of Top Reservoir	5.00 cc.
Dead Volume of Bottom Reservoir	5.00 cc.
Number of Cycles	20

Table 2
Recycle Ratio (β)
No. of Stages =16

β n	0.00		0.50		1.00	
	Top Res.Conc	Bottom Res.Conc	Top Res.Conc	Bottom Res.Conc	Top Res.Conc	Bottom Res.Conc
1	0.4561	1.0000	0.4561	1.0000	0.4561	1.0000
2	0.2348	1.5228	0.2348	1.5228	0.2348	1.5228
3	0.1467	1.7307	0.1467	1.7307	0.1467	1.7307
4	0.1117	1.8133	0.1117	1.8133	0.1117	1.8133
5	0.0978	1.8462	0.0978	1.8462	0.0978	1.8462
6	0.0923	1.8593	0.0923	1.8593	0.0923	1.8593
7	0.0912	1.8645	0.0912	1.8645	0.0901	1.8645
8	0.0892	1.8645	0.0895	1.8666	0.0892	1.8666
9	0.0895	1.8666	0.0907	1.8674	0.0895	1.8674
10	0.0910	1.8674	0.0907	1.8995	0.0904	1.8995
11	0.0110	1.8995	0.0907	1.8995	0.0904	1.8995
12	0.0110	1.8995	0.0907	1.8995	0.0904	1.8995
13	0.0110	1.8995	0.0907	1.8995	0.0904	1.8995
14	0.0110	1.8995	0.0907	1.8995	0.0904	1.8995
15	0.0110	1.8995	0.0907	1.8995	0.0904	1.8995
16	0.0110	1.8995	0.0907	1.8995	0.0904	1.8995
17	0.0110	1.8995	0.0907	1.8995	0.0904	1.8995
18	0.0110	1.8995	0.0907	1.8995	0.0904	1.8995
19	0.0110	1.8995	0.0907	1.8995	0.0904	1.8995
20	0.0110	1.8995	0.0907	1.8995	0.0904	1.8995

Table 3
 Recycle Ratio (β)
 No. of Stages = 8

β n	0.00		0.50		1.00	
	Top Res.Conc	Bottom Res.Conc	Top Res.Conc	Bottom Res.Conc	Top Res.Conc	Bottom Res.Conc
1	0.4561	1.0000	0.4561	1.0000	0.4561	1.0000
2	0.2348	1.5228	0.2348	1.5228	0.2348	1.5228
3	0.1467	1.7307	0.1467	1.7307	0.1467	1.7307
4	0.1117	1.8133	0.1179	1.8133	0.1117	1.8133
5	0.1162	1.8462	0.1083	1.8462	0.1162	1.8462
6	0.1176	1.8795	0.1050	1.8795	0.0991	1.8795
7	0.1176	1.8822	0.1039	1.8721	0.0924	1.8620
8	0.1177	1.8823	0.1034	1.8735	0.0901	1.8646
9	0.1170	1.8823	0.1036	1.8744	0.0892	1.8666
10	0.1170	1.8823	0.1036	1.8748	0.0895	1.8674
11	0.1170	1.8823	0.1036	1.8748	0.0895	1.8674
12	0.1170	1.8823	0.1036	1.8748	0.0895	1.8674
13	0.1170	1.8823	0.1036	1.8748	0.0895	1.8674
14	0.1170	1.8823	0.1036	1.8748	0.0895	1.8674
15	0.1170	1.8823	0.1036	1.8748	0.0895	1.8674
16	0.1170	1.8823	0.1036	1.8748	0.0895	1.8674
17	0.1170	1.8823	0.1036	1.8748	0.0895	1.8674
18	0.1170	1.8823	0.1036	1.8748	0.0895	1.8674
19	0.1170	1.8823	0.1036	1.8748	0.0895	1.8674
20	0.1170	1.8823	0.1036	1.8748	0.0895	1.8674

Table 4
 Recycle Ratio (β)
 No. of Stages = 4

β n	0.00		0.50		1.00	
	Top Res. Conc	Bottom Res. Conc	Top Res. Conc	Bottom Res. Conc	Top Res. Conc	Bottom Res. Conc
1	0.4561	1.0000	0.4516	1.0000	0.4516	1.0000
2	0.2348	1.5228	0.2348	1.5228	0.2348	1.5228
3	0.2469	1.7307	0.2469	1.7307	0.2469	1.7307
4	0.2474	1.7519	0.1974	1.7519	0.1473	1.7519
5	0.2475	1.7525	1.1796	1.7832	0.1118	1.8139
6	0.2475	1.7525	0.1819	1.7994	0.1162	1.8462
7	0.2475	1.7525	0.1779	1.8160	0.0991	1.8795
8	0.2475	1.7525	0.1762	1.8123	0.0924	1.8620
9	0.2475	1.7525	0.1765	1.8130	0.0935	1.8646
10	0.2475	1.7525	0.1765	1.8215	0.0916	1.8646
11	0.2475	1.7525	0.1765	1.8215	0.0916	1.8646
12	0.2475	1.7525	0.1765	1.8215	0.0916	1.8646
13	0.2475	1.7525	0.1765	1.8215	0.0916	1.8646
14	0.2475	1.7525	0.1765	1.8215	0.0916	1.8646
15	0.2475	1.7525	0.1765	1.8215	0.0916	1.8646
16	0.2475	1.7525	0.1765	1.8215	0.0916	1.8646
17	0.2475	1.7525	0.1765	1.8215	0.0916	1.8646
18	0.2475	1.7525	0.1765	1.8215	0.0916	1.8646
19	0.2475	1.7525	0.1765	1.8215	0.0916	1.8646
20	0.2475	1.7525	0.1765	1.8215	0.0916	1.8646

Table 5
Recycle Ratio (β)
No. of Stages = 1

β n	0.00		0.50		1.00	
	Top Res. Conc	Bottom Res. Conc	Top Res. Conc	Bottom Res. Conc	Top Res. Conc	Bottom Res. Conc
1	1.3206	0.6714	1.3206	0.6714	1.3206	0.6714
2	1.3233	0.6766	1.1630	0.6766	1.0027	0.6766
3	1.3233	0.6766	1.2182	0.7790	1.1130	0.8814
4	1.3233	0.6766	1.2421	0.7283	1.2068	0.6750
5	1.3233	0.6766	1.2268	0.7468	1.0433	0.7488
6	1.3233	0.6766	1.2397	0.7543	1.1455	0.8075
7	1.3233	0.6766	1.2410	0.7496	1.1486	0.7021
8	1.3233	0.6766	1.2408	0.7538	1.0802	0.7691
9	1.3233	0.6766	1.2431	0.7542	1.1461	0.7900
10	1.3233	0.6766	1.2433	0.7542	1.1245	0.7263
11	1.3233	0.6766	1.2422	0.7542	1.1245	0.7263
12	1.3233	0.6766	1.2422	0.7542	1.1245	0.7263
13	1.3233	0.6766	1.2422	0.7542	1.1245	0.7263
14	1.3233	0.6766	1.2422	0.7542	1.1245	0.7263
15	1.3233	0.6766	1.2422	0.7542	1.1245	0.7263
16	1.3233	0.6766	1.2422	0.7542	1.1245	0.7263
17	1.3233	0.6766	1.2422	0.7542	1.1245	0.7263
18	1.3233	0.6766	1.2422	0.7542	1.1245	0.7263
19	1.3233	0.6766	1.2422	0.7542	1.1245	0.7263
20	1.3233	0.6766	1.2422	0.7542	1.1245	0.7263

Table 6

CYCLING ZONESeparation as a Function of Recycle Ratio (β)

<u>Number of Stages (n)</u>	<u>Recycle Ratio (β)</u>	<u>Steady State Product Concentration moles/cc.</u>		<u>Separation Factor ($\langle y_B \rangle_\infty / \langle y_T \rangle_\infty$)</u>
		<u>Top</u>	<u>Bottom</u>	
16	0.00	0.09108	1.8995	20.8552
	0.50	0.09076	1.8995	20.9288
	1.00	0.0904	1.8995	21.0005
8	0.00	0.1170	1.8823	15.9923
	0.50	0.10361	1.8948	18.0947
	1.00	0.0895	1.8674	20.8648
4	0.00	0.24751	1.7525	7.0805
	0.50	0.17652	1.8215	10.3189
	1.00	0.09169	1.8988	20.3359
1	0.00	1.3233	0.6766	0.5112
	0.50	1.2433	0.7542	0.6066
	1.00	1.1245	0.7263	0.5833

Table 7
 CONDITIONS FOR
BATCH PARAMETRIC PUMPING

Effect of Reservoir Displacement/Number of
 Stages (α) on Separation

<u>Operating Variable</u>	<u>Value</u>
Volumetric Flow Rate	0.5 cc.
Specific Rate Constant for High pH	0.7
Specific Rate Constant for Low pH	1.58
Feed Concentration (Normalized)	1.00 gm. mole/cc.
Total Volume of Column	30.00 cc.
Void Volume of Column	0.75
Dead Volume of Top Reservoir	5.00 cc.
Dead Volume of Bottom Reservoir	5.00 cc.
Volume of Bottom Feed (NT2)	0.00
Volume of Top Feed (NT4)	0.00
Numbers of Cycles	40.

Table 8
 $\alpha = 0.25$
 Number of Stages=4

I	TRES	BRES	SF
2	0.82546	1.00000	1.21145
3	0.68540	1.00000	1.45901
4	0.57295	1.00000	1.74535
5	0.48262	1.00000	2.07203
6	0.41000	1.00000	2.43903
7	0.35157	1.00001	2.84443
8	0.30450	1.00002	3.28411
9	0.26655	1.00005	3.75183
10	0.23590	1.00010	4.23951
11	0.21110	1.00017	4.73778
12	0.19101	1.00026	5.23630
13	0.17468	1.00039	5.72707
14	0.16138	1.00055	6.20013
15	0.15050	1.00076	6.64939
16	0.14159	1.00100	7.06989
17	0.13424	1.00129	7.45885
18	0.12816	1.00163	7.81523
19	0.12311	1.00202	8.13944
20	0.11887	1.00246	8.43298
21	0.11531	1.00295	8.69808

Table 8 (cont'd)

22	0.11228	1.00350	8.93740
23	0.10969	1.00410	9.15373
24	0.10746	1.00476	9.35000
25	0.10552	1.00548	9.52871
26	0.10382	1.00624	9.69237
27	0.10231	1.00707	9.84315
28	0.10097	1.00795	9.98300
29	0.09976	1.00888	10.11357
30	0.09866	1.00987	10.23632
31	0.09765	1.01091	10.35245
32	0.09672	1.01200	10.46301
33	0.09586	1.01314	10.56885
34	0.09506	1.01434	10.67069
35	0.09430	1.01558	10.76916
36	0.09359	1.01686	10.86472
37	0.09292	1.01820	10.95783
38	0.09228	1.01957	11.04882
39	0.09167	1.02099	11.13797
40	0.09108	1.02245	11.22552

Table 9

$\alpha = 0.5$

No. of stages = 4

I	TRES	BRFS	SF
2	0.82333	1.00000	1.21458
3	0.68332	1.00000	1.46344
4	0.57220	1.00015	1.74790
5	0.48385	1.00072	2.06824
6	0.41346	1.00188	2.42315
7	0.35725	1.00372	2.80958
8	0.31224	1.00629	3.22278
9	0.27610	1.00959	3.65666
10	0.24697	1.01361	4.10422
11	0.22340	1.01829	4.55817
12	0.20425	1.02360	5.01152
13	0.18861	1.02948	5.45815
14	0.17578	1.03587	5.89311
15	0.16517	1.04271	6.31276
16	0.15636	1.04993	6.71478
17	0.14898	1.05750	7.09803
18	0.14276	1.06534	7.46230
19	0.13747	1.07342	7.80812
20	0.13294	1.08169	8.13645
21	0.12903	1.09010	8.44862

Table 9 (cont'd)

22	0.12561	1.09861	8.74603
23	0.12261	1.10721	9.03015
24	0.11995	1.11584	9.30237
25	0.11758	1.12450	9.56399
26	0.11544	1.13314	9.81620
27	0.11349	1.14175	10.06007
28	0.11172	1.15032	10.29650
29	0.11009	1.15882	10.52629
30	0.10858	1.16724	10.75014
31	0.10718	1.17557	10.96862
32	0.10586	1.18380	11.18222
33	0.10463	1.19192	11.39136
34	0.10347	1.19992	11.59639
35	0.10238	1.20780	11.79758
36	0.10134	1.21555	11.99520
37	0.10035	1.22317	12.18944
38	0.09940	1.23065	12.38049
39	0.09850	1.23798	12.56846
40	0.09763	1.24518	12.75350

Table 10

$$\alpha = 0.75$$

No. of stages = 4

I	TRES	BRES	SF
2	0.83463	1.00000	1.19813
3	0.70253	1.00272	1.42730
4	0.59671	1.01456	1.70026
5	0.51169	1.03296	2.01871
6	0.44315	1.05592	2.38278
7	0.38766	1.08193	2.79090
8	0.34256	1.10963	3.23983
9	0.30571	1.13873	3.72490
10	0.27544	1.16798	4.24042
11	0.25043	1.19709	4.78009
12	0.22964	1.22569	5.33747
13	0.21223	1.25352	5.90641
14	0.19755	1.28041	6.48131
15	0.18509	1.30623	7.05733
16	0.17442	1.33092	7.63045
17	0.16523	1.35444	8.19746
18	0.15724	1.37677	8.75590
19	0.15025	1.39791	9.30396
20	0.14409	1.41790	9.84036
21	0.13863	1.43677	10.36419

Table 10 (cont'd)

22	0.13375	1.45455	10.87490
23	0.12938	1.47128	11.37211
24	0.12543	1.48701	11.85566
25	0.12185	1.50180	12.32542
26	0.11858	1.51568	12.78139
27	0.11560	1.52871	13.22357
28	0.11287	1.54093	13.65200
29	0.11036	1.55239	14.06677
30	0.10804	1.56313	14.46793
31	0.10590	1.57320	14.85555
32	0.10392	1.58263	15.22974
33	0.10208	1.59147	15.59059
34	0.10037	1.59974	15.93821
35	0.09878	1.60749	16.27275
36	0.09731	1.61475	16.59436
37	0.09593	1.62154	16.90321
38	0.09465	1.62790	17.19949
39	0.09345	1.63385	17.48337
40	0.09234	1.63942	17.75511

Table 11

$$\alpha = 1$$

No. of stages = 8

I	TPES	BRES	SF
2	0.88896	1.00000	1.12491
3	0.79580	1.09311	1.37361
4	0.71384	1.18484	1.65981
5	0.64136	1.26690	1.97532
6	0.57723	1.33959	2.32072
7	0.52048	1.40393	2.69736
8	0.47026	1.46086	3.10648
9	0.42582	1.51124	3.54899
10	0.38649	1.55582	4.02545
11	0.35169	1.59527	4.53594
12	0.32090	1.63018	5.08001
13	0.29365	1.66107	5.65664
14	0.26953	1.68840	6.26414
15	0.24819	1.71259	6.90018
16	0.22931	1.73399	7.56174
17	0.21260	1.75293	8.24517
18	0.19781	1.76969	8.94624
19	0.18473	1.78452	9.66024
20	0.17315	1.79764	10.38206
21	0.16290	1.80925	11.10640

Table 11 (cont'd)

22	0.15383	1.81953	11.82785
23	0.14581	1.82862	12.54111
24	0.13871	1.83667	13.24111
25	0.13243	1.84378	13.92314
26	0.12687	1.85008	14.58302
27	0.12194	1.85566	15.21717
28	0.11759	1.86059	15.82259
29	0.11374	1.86495	16.39700
30	0.11033	1.86881	16.93877
31	0.10731	1.87222	17.44687
32	0.10464	1.87525	17.92097
33	0.10228	1.87792	18.36118
34	0.10019	1.88029	18.76801
35	0.09834	1.88238	19.14243
36	0.09670	1.88423	19.48570
37	0.09525	1.88587	19.79935
38	0.09397	1.88732	20.08495
39	0.09283	1.88860	20.34425
40	0.09183	1.88973	20.57910

Table 12

$$\alpha = 1$$

No. of stages = 1

I	TRES	RRFS	SF
2	0.73025	1.00000	1.36939
3	0.54067	1.26360	2.33711
4	0.40671	1.44995	3.56507
5	0.31206	1.58162	5.06836
6	0.24518	1.67466	6.83037
7	0.19792	1.74040	8.79337
8	0.16453	1.78685	10.86026
9	0.14094	1.81967	12.91120
10	0.12427	1.84286	14.82992
11	0.11249	1.85924	16.52856
12	0.10416	1.87082	17.96043
13	0.09828	1.87900	19.11841
14	0.09413	1.88478	20.02385
15	0.09119	1.88886	20.71339
16	0.08912	1.89175	21.22801
17	0.08765	1.89379	21.60634
18	0.08661	1.89522	21.88136
19	0.08588	1.89624	22.07970
20	0.08536	1.89696	22.22188
21	0.08500	1.89747	22.32339

Table 12 (cont'd)

22	0.08474	1.89782	22.59563
23	0.08456	1.89808	22.44696
24	0.08443	1.89825	22.48337
25	0.08434	1.89838	22.50916
26	0.08427	1.89847	22.52739
27	0.08423	1.89853	22.54030
28	0.08420	1.89857	22.54944
29	0.08417	1.89860	22.55589
30	0.08416	1.89862	22.56046
31	0.08415	1.89864	22.56369
32	0.08414	1.89865	22.56596
33	0.08413	1.89865	22.56758
34	0.08413	1.89866	22.56871
35	0.08412	1.89866	22.56952
36	0.08412	1.89866	22.57010
37	0.08412	1.89866	22.57050
38	0.08412	1.89866	22.57080
39	0.08412	1.89866	22.57100
40	0.08412	1.89866	22.57112

Table 13

$\alpha = 1.25$

No. of stages = 4

I	TRES	BRES	SF
2	1.10152	0.86759	0.78763
3	1.18294	0.76996	0.65089
4	1.24801	0.69196	0.55445
5	1.30001	0.62963	0.48433
6	1.34155	0.57982	0.43220
7	1.37476	0.54001	0.39281
8	1.40129	0.50820	0.36267
9	1.42248	0.48278	0.33939
10	1.43942	0.46247	0.32129
11	1.45296	0.44624	0.30712
12	1.46377	0.43327	0.29509
13	1.47241	0.42290	0.28722
14	1.47932	0.41462	0.28027
15	1.48483	0.40800	0.27478
16	1.48924	0.40270	0.27041
17	1.49276	0.39848	0.26694
18	1.49557	0.39510	0.26418
19	1.49782	0.39240	0.26198
20	1.49961	0.39024	0.26023
21	1.50104	0.38851	0.25883

Table 13 (cont'd)

22	1.50219	0.38713	0.25771
23	1.50310	0.38603	0.25682
24	1.50383	0.38515	0.25611
25	1.50441	0.38445	0.25555
26	1.50487	0.38388	0.25509
27	1.50524	0.38343	0.25473
28	1.50553	0.38307	0.25444
29	1.50576	0.38279	0.25421
30	1.50595	0.38255	0.25403
31	1.50609	0.38237	0.25388
32	1.50621	0.38222	0.25376
33	1.50630	0.38210	0.25367
34	1.50637	0.38201	0.25359
35	1.50643	0.38193	0.25354
36	1.50647	0.38187	0.25349
37	1.50651	0.38182	0.25345
38	1.50653	0.38178	0.25342
39	1.50655	0.38175	0.25339
40	1.50657	0.38172	0.25337

Table 14

$$\alpha = 1.5$$

No. of stages = 4

I	TRES	BRFS	SF
2	1.13770	0.80886	0.71096
3	1.22758	0.68446	0.55757
4	1.28624	0.60327	0.46902
5	1.32452	0.55028	0.41546
6	1.34951	0.51570	0.38214
7	1.36581	0.49313	0.36105
8	1.37645	0.47839	0.34755
9	1.38339	0.46877	0.33886
10	1.38792	0.46250	0.33323
11	1.39087	0.45840	0.32958
12	1.39280	0.45572	0.32720
13	1.39405	0.45398	0.32565
14	1.39487	0.45284	0.32465
15	1.39540	0.45209	0.32399
16	1.39574	0.45160	0.32356
17	1.39596	0.45129	0.32328
18	1.39610	0.45108	0.32310
19	1.39620	0.45094	0.32298
20	1.39625	0.45085	0.32290
21	1.39629	0.45079	0.32285

Table 14 (cont'd)

22	1.39631	0.45075	0.32282
23	1.39632	0.45072	0.32279
24	1.39633	0.45071	0.32278
25	1.39633	0.45069	0.32277
26	1.39632	0.45068	0.32277
27	1.39632	0.45068	0.32276
28	1.39632	0.45067	0.32276
29	1.39631	0.45067	0.32276
30	1.39631	0.45067	0.32276
31	1.39630	0.45066	0.32275
32	1.39629	0.45066	0.32275
33	1.39629	0.45066	0.32275
34	1.39628	0.45065	0.32275
35	1.39627	0.45065	0.32275
36	1.39627	0.45065	0.32275
37	1.39626	0.45065	0.32275
38	1.39625	0.45065	0.32275
39	1.39625	0.45064	0.32275
40	1.39624	0.45064	0.32275

Table 15

$$\alpha = 1.75$$

No. of stages = 4

I	TRES	BRES	SF
2	1.13161	0.79156	0.69949
3	1.20096	0.68173	0.56765
4	1.23750	0.62386	0.50413
5	1.25675	0.59336	0.47214
6	1.26689	0.57729	0.45567
7	1.27223	0.56882	0.44710
8	1.27505	0.56436	0.44262
9	1.27652	0.56200	0.44026
10	1.27730	0.56076	0.43902
11	1.27771	0.56011	0.43837
12	1.27792	0.55976	0.43802
13	1.27802	0.55957	0.43784
14	1.27808	0.55948	0.43775
15	1.27810	0.55942	0.43770
16	1.27811	0.55939	0.43767
17	1.27812	0.55938	0.43766
18	1.27811	0.55937	0.43765
19	1.27811	0.55936	0.43765
20	1.27811	0.55936	0.43764
21	1.27810	0.55935	0.43764

Table 15 (cont'd)

22	1.27809	0.55935	0.43764
23	1.27809	0.55935	0.43764
24	1.27808	0.55934	0.43764
25	1.27807	0.55934	0.43764
26	1.27807	0.55934	0.43764
27	1.27806	0.55933	0.43764
28	1.27805	0.55933	0.43764
29	1.27805	0.55933	0.43764
30	1.27804	0.55932	0.43764
31	1.27803	0.55932	0.43764
32	1.27803	0.55932	0.43764
33	1.27802	0.55932	0.43764
34	1.27801	0.55931	0.43764
35	1.27801	0.55931	0.43764
36	1.27800	0.55931	0.43764
37	1.27799	0.55930	0.43764
38	1.27799	0.55930	0.43764
39	1.27798	0.55930	0.43764
40	1.27797	0.55930	0.43764

Table 16

$$\alpha = 2$$

No. of stages = 4

I	TRES	BRES	SF
2	1.11523	0.79440	0.71232
3	1.16453	0.70643	0.60662
4	1.18563	0.66878	0.56407
5	1.19465	0.65267	0.54633
6	1.19850	0.64578	0.53882
7	1.20015	0.64282	0.53562
8	1.20085	0.64156	0.53425
9	1.20115	0.64101	0.53367
10	1.20127	0.64078	0.53342
11	1.20132	0.64068	0.53331
12	1.20133	0.64063	0.53327
13	1.20134	0.64061	0.53325
14	1.20134	0.64060	0.53324
15	1.20133	0.64059	0.53324
16	1.20133	0.64059	0.53323
17	1.20132	0.64058	0.53323
18	1.20131	0.64058	0.53323
19	1.20131	0.64058	0.53323
20	1.20130	0.64057	0.53323
21	1.20129	0.64057	0.53323

Table 16 (cont'd)

22	1.20129	0.64057	0.53323
23	1.20128	0.64056	0.53323
24	1.20127	0.64056	0.53323
25	1.20127	0.64055	0.53323
26	1.20126	0.64055	0.53323
27	1.20125	0.64055	0.53323
28	1.20125	0.64054	0.53323
29	1.20124	0.64054	0.53323
30	1.20123	0.64054	0.53323
31	1.20123	0.64053	0.53323
32	1.20122	0.64053	0.53323
33	1.20121	0.64053	0.53323
34	1.20121	0.64052	0.53323
35	1.20120	0.64052	0.53323
36	1.20119	0.64052	0.53323
37	1.20119	0.64051	0.53323
38	1.20118	0.64051	0.53323
39	1.20117	0.64050	0.53323
40	1.20116	0.64050	0.53323

Table 17

$$\alpha = 3$$

No. of stages = 4

I	TRES	BRES	SF
2	1.06012	0.84445	0.79656
3	1.07271	0.81186	0.75683
4	1.07534	0.80503	0.74862
5	1.07589	0.80359	0.74691
6	1.07600	0.80329	0.74655
7	1.07602	0.80322	0.74647
8	1.07602	0.80320	0.74646
9	1.07601	0.80319	0.74646
10	1.07600	0.80319	0.74645
11	1.07600	0.80318	0.74645
12	1.07599	0.80318	0.74645
13	1.07598	0.80317	0.74645
14	1.07598	0.80317	0.74645
15	1.07597	0.80316	0.74645
16	1.07596	0.80316	0.74645
17	1.07596	0.80315	0.74645
18	1.07595	0.80315	0.74645
19	1.07594	0.80314	0.74645
20	1.07594	0.80314	0.74645
21	1.07593	0.80313	0.74645

Table 17 (cont'd)

22	1.07592	0.80313	0.74645
23	1.07592	0.80312	0.74645
24	1.07591	0.80312	0.74645
25	1.07590	0.80311	0.74645
26	1.07590	0.80311	0.74645
27	1.07589	0.80310	0.74645
28	1.07588	0.80310	0.74645
29	1.07588	0.80309	0.74645
30	1.07587	0.80309	0.74645
31	1.07587	0.80308	0.74645
32	1.07586	0.80308	0.74645
33	1.07585	0.80308	0.74645
34	1.07585	0.80307	0.74645
35	1.07584	0.80307	0.74645
36	1.07583	0.80306	0.74645
37	1.07583	0.80306	0.74645
38	1.07582	0.80305	0.74645
39	1.07581	0.80305	0.74645
40	1.07581	0.80304	0.74645

Table 18

Effect of Reservoir Displacement/Column
Void Volume (α) on Separation

<u>α</u>	<u>$(\langle Y_B \rangle_\infty / \langle Y_T \rangle_\infty)$</u>
0.25	10.6730
0.50	12.2700
1.00	20.8500
1.25	0.2580
1.50	0.3237
1.75	0.4384
2.00	0.5340
2.50	0.6670
3.00	0.7470

Table 19CONTINUOUS PARAMETRIC PUMPING

Conditions for Runs with Variable Volume
of Bottom Feed (NT2)

<u>Operating Variable</u>	<u>Value</u>
Volumetric Flow Rate	0.5 cc.
Specific Rate Constant for High pH	0.07
Specific Rate Constant for Low pH	1.58
Feed Concentration (Normalized)	1.00 gm. mole/cc.
Total Volume of Column	30.00 cc.
Void Volume of Column	0.75
High pH	8
Low pH	6
Dead Volume of Top Reservoir	5.00 cc.
Dead Volume of Bottom Reservoir	5.00 cc.
Total Number of Stages (Nz)	22
Upflow Displacement (NT1)	21 cc.
Downflow Displacement (NT3)	21 cc.
Number of Cycles	20

Table 20

Constant Volume of Top Feed (NT4 = 6 cc.)

Volume of Bottom = 6 cc.

I	YT	YB	SF
2	0.99999	0.99999	0.99999
3	0.79271	1.20725	1.52294
4	0.63102	1.36891	2.16934
5	0.50492	1.49500	2.96090
6	0.40655	1.59335	3.91920
7	0.32983	1.67007	5.06347
8	0.26998	1.72990	6.40747
9	0.22330	1.77658	7.95590
10	0.18689	1.81298	9.70063
11	0.15849	1.84138	11.61802
12	0.13634	1.86352	13.66806
13	0.11906	1.88080	15.79667
14	0.10559	1.89428	17.94060
15	0.09507	1.90479	20.03487
16	0.08687	1.91299	22.02016
17	0.08048	1.91938	23.84953
18	0.07549	1.92437	25.49158
19	0.07160	1.92826	26.93120
20	0.06856	1.93130	28.16760

Table 20 (cont'd)

Volume of Bottom Feed = 11 cc.

I	YT	YB	SF
2	0.99932	0.99999	1.00067
3	0.65835	1.34144	2.03759
4	0.45745	1.61238	3.52471
5	0.33908	1.82750	5.38962
6	0.26933	1.99838	7.41983
7	0.22823	2.13417	9.35086
8	0.20402	2.24211	10.98977
9	0.18975	2.32792	12.26634
10	0.18134	2.39615	13.21334
11	0.17639	2.45040	13.89201
12	0.17347	2.49355	14.37448
13	0.17175	2.52788	14.71826
14	0.17074	2.55517	14.96549
15	0.17014	2.57688	15.14557
16	0.16979	2.59415	15.27864
17	0.16958	2.60788	15.37830
18	0.16946	2.61880	15.45385
19	0.16939	2.62749	15.51169
20	0.16935	2.63441	15.55640

Table 20 (cont'd)

Volume of Bottom Feed = 16 cc.

I	YT	YB	SF
2	0.98395	0.99999	1.01631
3	0.60162	1.39866	2.52483
4	0.45003	1.71572	3.81243
5	0.38993	1.96790	5.04680
6	0.36610	2.16848	5.92322
7	0.35665	2.32804	6.52751
8	0.35290	2.45495	6.95644
9	0.35142	2.55590	7.27311
10	0.35083	2.63621	7.51422
11	0.35060	2.70009	7.70143
12	0.35050	2.75091	7.84845
13	0.35047	2.79133	7.96461
14	0.35045	2.82348	8.05667
15	0.35045	2.84905	8.12978
16	0.35044	2.86939	8.18788
17	0.35044	2.88558	8.23410
18	0.35044	2.89846	8.27084
19	0.35044	2.90870	8.30006
20	0.35044	2.91684	8.32330

Table 20 (cont'd)

Volume of Bottom Feed = 21 cc.

I	YT	YB	SF
2	0.91316	0.99999	1.09509
3	0.60466	1.41033	2.33242
4	0.52565	1.73673	3.30396
5	0.50541	1.99636	3.94998
6	0.50023	2.20289	4.40379
7	0.49890	2.36717	4.74479
8	0.49856	2.49785	5.01015
9	0.49847	2.60181	5.21957
10	0.49845	2.68450	5.38570
11	0.49844	2.75027	5.51772
12	0.49844	2.80259	5.62269
13	0.49844	2.84421	5.70619
14	0.49844	2.87732	5.77262
15	0.49844	2.90365	5.82545
16	0.49844	2.92460	5.86747
17	0.49844	2.94126	5.90090
18	0.49844	2.95451	5.92749
19	0.49844	2.96506	5.94864
20	0.49844	2.97344	5.96547

Table 21

Constant Volume of Top Feed (NT4 = 11 cc.)

Volume of Bottom Feed = 6 cc.

J	YT	YB	SF
2	0.99999	0.99999	0.99999
3	0.79271	1.20724	1.52294
4	0.63102	1.32651	2.10216
5	0.50491	1.39449	2.76183
6	0.40655	1.43271	3.52406
7	0.32983	1.45377	4.40770
8	0.26998	1.46503	5.42645
9	0.22330	1.47076	6.58647
10	0.18689	1.47343	7.88388
11	0.15849	1.47444	9.30297
12	0.13634	1.47460	10.81563
13	0.11906	1.47435	12.38313
14	0.10558	1.47393	13.95987
15	0.09507	1.47348	15.49863
16	0.08687	1.47305	16.95654
17	0.08048	1.47267	18.29939
18	0.07549	1.47234	19.50441
19	0.07160	1.47208	20.56068
20	0.06856	1.47186	21.46761

Table 21 (cont'd)

Volume of Bottom Feed = 11 cc.

I	YT	YR	SF
2	0.99932	0.99999	1.00067
3	0.65835	1.34144	2.03759
4	0.45745	1.54254	3.37205
5	0.33907	1.66097	4.89855
6	0.26932	1.73072	6.42616
7	0.22823	1.77179	7.76331
8	0.20401	1.79598	8.80336
9	0.18974	1.81023	9.54045
10	0.18134	1.81861	10.02902
11	0.17638	1.82356	10.33871
12	0.17346	1.82647	10.52944
13	0.17174	1.82819	10.64489
14	0.17073	1.82919	10.71396
15	0.17013	1.82979	10.75507
16	0.16978	1.83014	10.77939
17	0.16957	1.83034	10.79379
18	0.16945	1.83047	10.80236
19	0.16938	1.83054	10.80733
20	0.16934	1.83058	10.81027

Table 21 (cont'd)

Volume of Bottom Feed = 16 cc.

I	YT	YB	SF
2	0.98395	0.99999	1.01630
3	0.60162	1.39866	2.32483
4	0.45003	1.63417	3.63127
5	0.38992	1.77332	4.54786
6	0.36609	1.85553	5.06848
7	0.35664	1.90410	5.33897
8	0.35289	1.93280	5.47699
9	0.35141	1.94976	5.54841
10	0.35082	1.95978	5.58629
11	0.35059	1.96571	5.60691
12	0.35049	1.96920	5.61837
13	0.35046	1.97127	5.62486
14	0.35044	1.97250	5.62859
15	0.35044	1.97322	5.63075
16	0.35043	1.97365	5.63202
17	0.35043	1.97391	5.63276
18	0.35043	1.97405	5.63318
19	0.35043	1.97414	5.63342
20	0.35043	1.97420	5.63360

Table 21 (cont'd)

Volume of Bottom Feed = 21 cc.

I	YT	YB	SF
2	0.91316	0.99999	1.09509
3	0.60466	1.41033	2.33242
4	0.52565	1.65280	3.14432
5	0.50540	1.79608	3.55374
6	0.50022	1.88074	3.75982
7	0.49889	1.93077	3.87011
8	0.49855	1.96033	3.93205
9	0.49846	1.97780	3.96778
10	0.49844	1.98812	3.98867
11	0.49844	1.99422	4.00096
12	0.49843	1.99783	4.00820
13	0.49843	1.99996	4.01247
14	0.49843	2.00121	4.01499
15	0.49843	2.00196	4.01650
16	0.49843	2.00240	4.01737
17	0.49843	2.00266	4.01789
18	0.49843	2.00281	4.01820
19	0.49843	2.00290	4.01839
20	0.49843	2.00296	4.01849

Table 22

Constant Volume of Top Feed (NT4 =16 cc.)

Volume of Bottom = 6 cc.

I	YT	YB	SF
2	0.99999	0.99999	0.99999
3	0.79271	1.20724	1.52293
4	0.63102	1.28411	2.03497
5	0.50491	1.31132	2.59711
6	0.40655	1.31988	3.20654
7	0.32983	1.32167	4.00717
8	0.26998	1.32117	4.89359
9	0.22330	1.32007	5.91162
10	0.18689	1.31890	7.05706
11	0.15849	1.31789	8.31524
12	0.13634	1.31707	9.66020
13	0.11906	1.31641	11.05659
14	0.10558	1.31588	12.46292
15	0.09507	1.31547	13.83666
16	0.08687	1.31515	15.13897
17	0.08048	1.31491	16.33914
18	0.07549	1.31470	17.41612
19	0.07160	1.31455	18.36044
20	0.06856	1.31444	19.17157

Table 22 (cont'd)

Volume of Bottom Feed = 11 cc.

I	YT	YB	SF
2	0.99932	0.99999	1.00067
3	0.65835	1.34144	2.03758
4	0.45745	1.47270	3.21938
5	0.33907	1.52301	4.49170
6	0.26932	1.54221	5.72623
7	0.22823	1.54949	6.78928
8	0.20401	1.55222	7.60854
9	0.18974	1.55324	8.18605
10	0.18134	1.55359	8.56751
11	0.17638	1.55372	8.80884
12	0.17346	1.55375	8.95726
13	0.17174	1.55376	9.04700
14	0.17073	1.55376	9.10070
15	0.17013	1.55376	9.13262
16	0.16978	1.55375	9.15152
17	0.16957	1.55375	9.16272
18	0.16945	1.55375	9.16932
19	0.16938	1.55375	9.17321
20	0.16934	1.55375	9.17550

Table 22 (cont'd)

Volume of Bottom Feed = 16 cc.

I	YT	YB	SF
2	0.98395	0.99999	1.01630
3	0.60162	1.39866	2.32483
4	0.45003	1.55263	3.45006
5	0.38992	1.61209	4.13433
6	0.36609	1.63506	4.46627
7	0.35664	1.64392	4.60946
8	0.35289	1.64734	4.66809
9	0.35141	1.64867	4.69159
10	0.35082	1.64919	4.70095
11	0.35059	1.64938	4.70462
12	0.35049	1.64945	4.70607
13	0.35046	1.64948	4.70665
14	0.35044	1.64949	4.70688
15	0.35044	1.64949	4.70697
16	0.35043	1.64949	4.70700
17	0.35043	1.64949	4.70701
18	0.35043	1.64949	4.70702
19	0.35043	1.64949	4.70702
20	0.35043	1.64949	4.70702

Table 22 (cont'd)

Volume of Bottom Feed = 21 cc.

I	YI	YB	SF
2	0.91316	0.99999	1.09509
3	0.60466	1.41033	2.33242
4	0.52565	1.56887	2.98465
5	0.50540	1.63012	3.22538
6	0.50022	1.65378	3.30611
7	0.49889	1.66293	3.33324
8	0.49855	1.66646	3.34260
9	0.49846	1.66763	3.34593
10	0.49844	1.66835	3.34713
11	0.49844	1.66855	3.34758
12	0.49843	1.66863	3.34775
13	0.49843	1.66866	3.34781
14	0.49843	1.66867	3.34783
15	0.49843	1.66867	3.34783
16	0.49843	1.66868	3.34784
17	0.49843	1.66868	3.34784
18	0.49843	1.66868	3.34784
19	0.49843	1.66868	3.34784
20	0.49843	1.66868	3.34784

Table 23

Constant Volume of Top Feed (NT4 = 21 cc.)

Volume of Bottom Feed = 6 cc.

J	YT	YB	SF
2	0.99999	1.17898	1.17899
3	0.79271	1.23628	1.55956
4	0.63102	1.24485	1.97275
5	0.50491	1.24450	2.46478
6	0.40655	1.24286	3.05708
7	0.32983	1.24130	3.76350
8	0.26998	1.24004	4.59308
9	0.22330	1.23905	5.54877
10	0.18689	1.23827	6.62561
11	0.15849	1.23766	7.80901
12	0.13634	1.23719	9.07431
13	0.11906	1.23682	10.38811
14	0.10558	1.23653	11.71138
15	0.09507	1.23630	13.00396
16	0.08687	1.23613	14.22935
17	0.08048	1.23599	15.35847
18	0.07549	1.23589	16.37201
19	0.07160	1.23580	17.26057
20	0.06856	1.23574	18.02365

Table 23 (cont'd)

Volume of Bottom Feed = 11 cc.

I	YT	YB	SF
2	0.99932	1.28995	1.29083
3	0.65835	1.39196	2.11432
4	0.45745	1.41141	3.08541
5	0.33907	1.41493	4.17294
6	0.26932	1.41546	5.25562
7	0.22823	1.41547	6.20207
8	0.20401	1.41542	6.93800
9	0.18974	1.41538	7.45949
10	0.18134	1.41536	7.80519
11	0.17638	1.41534	8.02432
12	0.17346	1.41534	8.15930
13	0.17174	1.41533	8.24098
14	0.17073	1.41533	8.28988
15	0.17013	1.41533	8.31895
16	0.16978	1.41533	8.33618
17	0.16957	1.41533	8.34638
18	0.16945	1.41533	8.35239
19	0.16938	1.41533	8.35595
20	0.16934	1.41533	8.35803

Table 23 (cont'd)

Volume of Bottom Feed = 16 cc.

I	YT	YB	SF
2	0.98395	1.33564	1.35763
3	0.60162	1.45768	2.42294
4	0.45003	1.48141	3.29181
5	0.38992	1.48602	3.81107
6	0.36609	1.48691	4.06160
7	0.35664	1.48709	4.16970
8	0.35289	1.48712	4.21406
9	0.35141	1.48712	4.23189
10	0.35082	1.48713	4.23900
11	0.35059	1.48713	4.24182
12	0.35049	1.48713	4.24294
13	0.35046	1.48713	4.24339
14	0.35044	1.48713	4.24357
15	0.35044	1.48713	4.24364
16	0.35043	1.48713	4.24366
17	0.35043	1.48713	4.24367
18	0.35043	1.48713	4.24368
19	0.35043	1.48713	4.24368
20	0.35043	1.48713	4.24368

Table 23 (cont'd)

Volume of Bottom Feed = 21 cc.

I	YT	YB	SF
2	0.91316	1.34506	1.47298
3	0.60466	1.47102	2.43279
4	0.52565	1.49557	2.84520
5	0.50540	1.50035	2.96862
6	0.50022	1.50129	3.00125
7	0.49889	1.50147	3.00962
8	0.49855	1.50150	3.01173
9	0.49846	1.50151	3.01227
10	0.49844	1.50151	3.01241
11	0.49844	1.50151	3.01245
12	0.49843	1.50151	3.01246
13	0.49843	1.50151	3.01246
14	0.49843	1.50151	3.01246
15	0.49843	1.50151	3.01246
16	0.49843	1.50151	3.01246
17	0.49843	1.50151	3.01246
18	0.49843	1.50151	3.01246
19	0.49843	1.50151	3.01246
20	0.49843	1.50151	3.01246

Table 24CONTINUOUS PARAPUMP

Separation as a Function of NT2

<u>NT4</u> (cc)	<u>NT2</u> (cc)	Steady State Product Concentration moles/cc.		Separation Factor ($\langle y_B \rangle_\infty / \langle y_T \rangle_\infty$)
		<u>Top</u>	<u>Bottom</u>	
6	6	0.06856	1.9313	28.1676
	11	0.1693	2.6344	15.5564
	16	0.3504	2.9168	8.3233
	21	0.4984	2.9734	5.9654
11	6	0.0685	1.4718	21.4676
	11	0.1693	1.8305	10.8102
	16	0.3504	1.9742	5.6336
	21	0.4984	2.0029	4.0184
16	6	0.0685	1.3144	19.1715
	11	0.1693	1.5537	9.1755
	16	0.3504	1.6494	4.7070
	21	0.4984	1.6686	3.3478
21	6	0.0685	1.2357	18.0236
	11	0.1693	1.4153	8.3580
	16	0.3504	1.4871	4.2436
	21	0.4984	1.5015	3.0124

Table 25CONTINUOUS PARAMETRIC PUMPING

Conditions for Runs with Variable Volume
of Top Feed (NT4)

<u>Operating Variable</u>	<u>Value</u>
Volumetric Flow Rate	0.5 cc/s
Specific Rate Constant for High pH	0.07
Specific Rate Constant for Low pH	1.58
Feed Concentration (Normalized)	1.00 gm. mole/cc.
Total Volume of Column	30.00 cc.
Void Volume of Column	0.75
High pH	8
Low pH	6
Dead Volume of Top Reservoir	5.00 cc.
Dead Volume of Bottom Reservoir	5.00 cc.
Total Number of Stages (Nz)	22
Upflow displacement (NT1)	21 cc.
Downflow Displacement (NT3)	21 cc.
Number of Cycles	20

Table 26

Constant Volume of Bottom Feed (NT2 = 6 cc.)

Volume of Top Feed = 6 cc.

I	YT	YB	SF
2	0.99999	0.99999	0.99999
3	0.79271	1.20725	1.52294
4	0.63102	1.36891	2.16934
5	0.50492	1.49500	2.96090
6	0.40655	1.59335	3.91920
7	0.32983	1.67007	5.06347
8	0.26998	1.72990	6.40747
9	0.22330	1.77658	7.95590
10	0.18689	1.81298	9.70063
11	0.15849	1.84138	11.61802
12	0.13634	1.86352	13.66806
13	0.11906	1.88080	15.79667
14	0.10559	1.89428	17.94060
15	0.09507	1.90479	20.03467
16	0.08667	1.91299	22.02016
17	0.08048	1.91938	23.84953
18	0.07549	1.92437	25.49158
19	0.07160	1.92826	26.93120
20	0.06856	1.93130	28.16760

Table 26 (cont'd)

Volume of Top Feed = 11 cc.

T	YT	YB	SF
2	0.99999	0.99999	0.99999
3	0.79271	1.20724	1.52294
4	0.63102	1.32651	2.10216
5	0.50491	1.39449	2.76183
6	0.40655	1.43271	3.52406
7	0.32983	1.45377	4.40770
8	0.26998	1.46503	5.42645
9	0.22330	1.47076	6.58647
10	0.18689	1.47343	7.88388
11	0.15849	1.47444	9.30297
12	0.13634	1.47460	10.81563
13	0.11906	1.47435	12.38313
14	0.10558	1.47393	13.95987
15	0.09507	1.47348	15.49863
16	0.08687	1.47305	16.95654
17	0.08048	1.47267	18.29939
18	0.07549	1.47234	19.50441
19	0.07160	1.47208	20.56068
20	0.06856	1.47186	21.46761

Table 26 (cont'd)

Volume of Top Feed = 16 cc.

I	YT	YB	SF
2	0.99999	0.99999	0.99999
3	0.79271	1.20724	1.52293
4	0.63102	1.28411	2.03497
5	0.50491	1.31132	2.59711
6	0.40655	1.31988	3.24654
7	0.32983	1.32167	4.00717
8	0.26998	1.32117	4.89359
9	0.22330	1.32007	5.91162
10	0.18689	1.31890	7.05706
11	0.15849	1.31789	8.31524
12	0.13634	1.31707	9.66020
13	0.11906	1.31641	11.05659
14	0.10558	1.31588	12.46292
15	0.09507	1.31547	13.83666
16	0.08687	1.31515	15.13897
17	0.08048	1.31491	16.33914
18	0.07549	1.31470	17.41612
19	0.07160	1.31455	18.36044
20	0.06856	1.31444	19.17157

Table 26 (cont'd)

Volume of Top Feed = 21 cc.

I	YT	YB	SF
2	0.99999	1.17898	1.17899
3	0.79271	1.23628	1.55956
4	0.63102	1.24485	1.97275
5	0.50491	1.24450	2.46478
6	0.40655	1.24266	3.05708
7	0.32983	1.24130	3.76350
8	0.26998	1.24004	4.59308
9	0.22330	1.23905	5.54877
10	0.18689	1.23827	6.62561
11	0.15849	1.23766	7.80901
12	0.13634	1.23719	9.07431
13	0.11906	1.23682	10.38811
14	0.10558	1.23653	11.71133
15	0.09507	1.23630	13.00396
16	0.08687	1.23613	14.22935
17	0.08048	1.23599	15.35847
18	0.07549	1.23589	16.37201
19	0.07160	1.23580	17.26057
20	0.06856	1.23574	18.02365

Table 27

Constant Volume of Bottom Feed (NT2 = 11 cc.)

Volume of Top Feed = 6 cc.

I	YT	YB	SF
2	0.99932	0.99999	1.00067
3	0.65835	1.34144	2.03759
4	0.45745	1.61238	3.52471
5	0.33408	1.82750	5.38962
6	0.26933	1.99838	7.41983
7	0.22823	2.13417	9.35086
8	0.20402	2.24211	10.98977
9	0.18975	2.32792	12.26834
10	0.18134	2.39615	13.21334
11	0.17639	2.45040	13.89201
12	0.17347	2.49355	14.37443
13	0.17175	2.52768	14.71826
14	0.17074	2.55517	14.96549
15	0.17014	2.57688	15.14557
16	0.16979	2.59415	15.27864
17	0.16958	2.60788	15.37830
18	0.16946	2.61880	15.45385
19	0.16939	2.62749	15.51169
20	0.16935	2.63441	15.55640

Table 27 (cont'd)

Volume of Top Feed = 11 cc.

I	YT	YB	SF
2	0.99932	0.99999	1.00067
3	0.65835	1.34144	2.03759
4	0.45745	1.54254	3.37205
5	0.33907	1.66097	4.89855
6	0.26932	1.73072	6.42616
7	0.22823	1.77179	7.76331
8	0.20401	1.79598	8.80336
9	0.18974	1.81023	9.54045
10	0.18134	1.81861	10.02902
11	0.17636	1.82356	10.33871
12	0.17346	1.82647	10.52944
13	0.17174	1.82819	10.64489
14	0.17073	1.82919	10.71396
15	0.17013	1.82979	10.75507
16	0.16976	1.83014	10.77939
17	0.16957	1.83034	10.79379
18	0.16945	1.83047	10.80236
19	0.16938	1.83054	10.80733
20	0.16934	1.83058	10.81027

Table 27 (cont'd)

Volume of Top Feed = 16 cc.

I	YT	YB	SF
2	0.99932	0.99999	1.00067
3	0.65835	1.34144	2.03753
4	0.45745	1.47270	3.21938
5	0.33907	1.52301	4.49170
6	0.26932	1.54221	5.72623
7	0.22823	1.54949	6.78923
8	0.20401	1.55222	7.60854
9	0.18974	1.55324	8.18605
10	0.18134	1.55359	8.56751
11	0.17638	1.55372	8.80884
12	0.17346	1.55375	8.95726
13	0.17174	1.55376	9.04700
14	0.17073	1.55376	9.10070
15	0.17013	1.55376	9.13262
16	0.16978	1.55375	9.15152
17	0.16957	1.55375	9.16272
18	0.16945	1.55375	9.16932
19	0.16938	1.55375	9.17321
20	0.16934	1.55375	9.17550

Table 27 (cont'd)

Volume of Top Feed = 21 cc.

I	YT	YB	SF
2	0.99932	1.28995	1.29003
3	0.65835	1.39196	2.11432
4	0.45745	1.41141	3.08541
5	0.33907	1.41493	4.17294
6	0.26932	1.41546	5.25562
7	0.22823	1.41547	6.20207
8	0.20401	1.41542	6.93800
9	0.18974	1.41538	7.45949
10	0.18134	1.41536	7.80519
11	0.17638	1.41534	8.02432
12	0.17346	1.41534	8.15930
13	0.17174	1.41533	8.24098
14	0.17073	1.41533	8.28923
15	0.17013	1.41533	8.31895
16	0.16978	1.41533	8.33618
17	0.16957	1.41533	8.34633
18	0.16945	1.41533	8.35239
19	0.16938	1.41533	8.35595
20	0.16934	1.41533	8.35803

Table 28

CONSTANT VOLUME OF BOTTOM FEED (NT2 = 16 cc.)

Volume of Top Feed = 6 cc.

I	YT	YB	SF
2	0.98395	0.99999	1.01631
3	0.60162	1.39866	2.32483
4	0.45003	1.71572	3.81243
5	0.38993	1.96790	5.04680
6	0.36610	2.16848	5.92322
7	0.35665	2.32804	6.52751
8	0.35290	2.45495	6.95644
9	0.35142	2.55590	7.27311
10	0.35083	2.63621	7.51422
11	0.35060	2.70009	7.70143
12	0.35050	2.75091	7.84845
13	0.35047	2.79133	7.96461
14	0.35045	2.82348	8.05667
15	0.35045	2.84905	8.12978
16	0.35044	2.86939	8.18788
17	0.35044	2.88558	8.23410
18	0.35044	2.89846	8.27084
19	0.35044	2.90870	8.30006
20	0.35044	2.91664	8.32330

Table 28 (cont'd)

Volume of Top Feed = 11 cc.

I	YT	YB	SF
2	0.98395	0.99999	1.01630
3	0.60162	1.39866	2.32483
4	0.45003	1.63417	3.63127
5	0.38992	1.77332	4.54786
6	0.36609	1.85553	5.06848
7	0.35664	1.90410	5.33897
8	0.35289	1.93280	5.47699
9	0.35141	1.94976	5.54841
10	0.35082	1.95978	5.58629
11	0.35059	1.96571	5.60691
12	0.35049	1.96920	5.61837
13	0.35046	1.97127	5.62486
14	0.35044	1.97250	5.62859
15	0.35044	1.97322	5.63075
16	0.35043	1.97365	5.63202
17	0.35043	1.97391	5.63276
18	0.35043	1.97405	5.63313
19	0.35043	1.97414	5.63342
20	0.35043	1.97420	5.63360

Table 28 (cont'd)

Volume of Top Feed = 16 cc.

I	YT	YB	SF
2	0.98395	0.99999	1.01630
3	0.60162	1.39866	2.32483
4	0.45003	1.55263	3.45006
5	0.38992	1.61209	4.13438
6	0.36609	1.63506	4.46627
7	0.35664	1.64392	4.60946
8	0.35289	1.64734	4.66809
9	0.35141	1.64867	4.69159
10	0.35082	1.64919	4.70095
11	0.35059	1.64938	4.70462
12	0.35049	1.64945	4.70607
13	0.35046	1.64948	4.70665
14	0.35044	1.64949	4.70688
15	0.35044	1.64949	4.70697
16	0.35043	1.64949	4.70700
17	0.35043	1.64949	4.70701
18	0.35043	1.64949	4.70702
19	0.35043	1.64949	4.70702
20	0.35043	1.64949	4.70702

Table 28 (cont'd)

Volume of Top Feed = 22 cc.

I	YT	YB	SF
2	0.98395	1.33584	1.35763
3	0.60162	1.45768	2.42294
4	0.45003	1.48141	3.29181
5	0.38992	1.48602	3.81107
6	0.36609	1.48691	4.06160
7	0.35664	1.48709	4.16970
8	0.35289	1.48712	4.21406
9	0.35141	1.48712	4.23189
10	0.35082	1.48713	4.23900
11	0.35059	1.48713	4.24182
12	0.35049	1.48713	4.24294
13	0.35046	1.48713	4.24339
14	0.35044	1.48713	4.24357
15	0.35044	1.48713	4.24364
16	0.35043	1.48713	4.24366
17	0.35043	1.48713	4.24367
18	0.35043	1.48713	4.24368
19	0.35043	1.48713	4.24368
20	0.35043	1.48713	4.24368

Table 29

CONSTANT VOLUME OF BOTTOM FEED (NT2 = 21 cc.)

Volume of Top Feed = 6 cc.

I	YT	YB	SF
2	0.91316	0.99999	1.09509
3	0.60466	1.41033	2.33242
4	0.52565	1.73673	3.30396
5	0.50541	1.99636	3.94998
6	0.50023	2.20289	4.40379
7	0.49890	2.36717	4.74479
8	0.49856	2.49785	5.01015
9	0.49847	2.60181	5.21957
10	0.49845	2.68450	5.38570
11	0.49844	2.75027	5.51772
12	0.49844	2.80259	5.62269
13	0.49844	2.84421	5.70619
14	0.49844	2.87732	5.77262
15	0.49844	2.90365	5.82545
16	0.49844	2.92460	5.86747
17	0.49844	2.94126	5.90090
18	0.49844	2.95451	5.92749
19	0.49844	2.96506	5.94864
20	0.49844	2.97344	5.96547

Table 29 (cont'd)

Volume of Top Feed = 11 cc.

T	YT	YB	SF
2	0.91316	0.99999	1.09509
3	0.60466	1.41033	2.33242
4	0.52565	1.65280	3.14432
5	0.50540	1.79608	3.55374
6	0.50022	1.88074	3.75982
7	0.49889	1.93077	3.87011
8	0.49855	1.96033	3.93205
9	0.49846	1.97780	3.96778
10	0.49844	1.98812	3.98867
11	0.49844	1.99422	4.00096
12	0.49843	1.99783	4.00820
13	0.49843	1.99996	4.01247
14	0.49843	2.00121	4.01499
15	0.49843	2.00196	4.01650
16	0.49843	2.00240	4.01737
17	0.49843	2.00266	4.01789
18	0.49843	2.00281	4.01820
19	0.49843	2.00290	4.01839
20	0.49843	2.00296	4.01849

Table 29 (cont'd)

Volume of Top Feed = 16 cc.

I	YT	YB	SF
2	0.91316	0.99999	1.09509
3	0.60466	1.41033	2.33242
4	0.52565	1.56887	2.98465
5	0.50540	1.63012	3.22538
6	0.50022	1.65378	3.30611
7	0.49889	1.66293	3.33324
8	0.49855	1.66646	3.34260
9	0.49846	1.66783	3.34593
10	0.49844	1.66835	3.34713
11	0.49844	1.66855	3.34758
12	0.49843	1.66863	3.34775
13	0.49843	1.66866	3.34781
14	0.49843	1.66867	3.34783
15	0.49843	1.66867	3.34783
16	0.49843	1.66868	3.34784
17	0.49843	1.66868	3.34784
18	0.49843	1.66868	3.34784
19	0.49843	1.66868	3.34784
20	0.49843	1.66868	3.34784

Table 29 (cont'd)

Volume of Top Feed = 21 cc.

I	YT	YR	SF
2	0.91316	1.34506	1.47298
3	0.60466	1.47102	2.43279
4	0.52565	1.49557	2.84520
5	0.50540	1.50035	2.96862
6	0.50022	1.50129	3.00125
7	0.49889	1.50147	3.00962
8	0.49855	1.50150	3.01173
9	0.49846	1.50151	3.01227
10	0.49844	1.50151	3.01241
11	0.49844	1.50151	3.01245
12	0.49843	1.50151	3.01246
13	0.49843	1.50151	3.01246
14	0.49843	1.50151	3.01246
15	0.49843	1.50151	3.01246
16	0.49843	1.50151	3.01246
17	0.49843	1.50151	3.01246
18	0.49843	1.50151	3.01246
19	0.49843	1.50151	3.01246
20	0.49843	1.50151	3.01246

Table 30

CONTINUOUS PARAPUMP

Separation as a Function of NT4

<u>NT2</u> (cc)	<u>NT4</u> (cc)	Steady State Product Concentration moles/cc.		Separation Factor ($\langle y_B \rangle_\infty / \langle y_T \rangle_\infty$)
		<u>Top</u>	<u>Bottom</u>	
6	6	0.0685	1.9313	28.1676
	11	0.0685	1.4718	21.4676
	16	0.0685	1.3144	19.1715
	21	0.0685	1.2357	18.0236
11	6	0.1693	2.6344	15.5564
	11	0.1693	1.8305	10.8102
	16	0.1693	1.5537	9.1755
	21	0.1693	1.4153	8.3580
16	6	0.3504	2.9168	8.3233
	11	0.3504	1.9742	5.6336
	16	0.3504	1.6494	4.7070
	21	0.3504	1.4871	4.2436
21	6	0.4984	2.9734	5.9654
	11	0.4984	2.0029	4.0184
	16	0.4984	1.6686	3.3478
	21	0.4984	1.5015	3.0124

Table 31CONTINUOUS PARAMETRIC PUMPING

Conditions for Runs to Show the Effect
of Doubling Column Conditions

<u>Operating Variable</u>	<u>Value</u>
Volumetric Flow Rate	0.5 cc/sec
Specific Rate Constant for High pH	0.07
Specific Rate Constant for Low pH	1.58
Feed Concentration (Normalized)	1.00 gm. mole/cc.
Total Volume of Column	30.00 cc.
Void Volume of Column	0.75
Dead Volume of Top Reservoir	5.00 cc.
Dead Volume of Bottom Reservoir	5.00 cc.
Number of Cycles	40

Table 32

Upflow Displacement (NT1) = 11 cc.
 Downflow Displacement (NT3) = 11 cc.
 Volume of Top Feed (NT4) = 11 cc.
 Volume of Bottom Feed (NT2) = 11 cc.
 Number of Stages-12

I	YT	YB	SF
2	0.87814	1.40032	1.59522
3	0.61286	1.47500	2.40676
4	0.53710	1.48959	2.77337
5	0.51547	1.49246	2.89532
6	0.50929	1.49302	2.93154
7	0.50753	1.49312	2.94194
8	0.50703	1.49315	2.94491
9	0.50688	1.49315	2.94575
10	0.50684	1.49315	2.94599
11	0.50683	1.49315	2.94606
12	0.50683	1.49315	2.94608
13	0.50683	1.49315	2.94609
14	0.50683	1.49315	2.94609
15	0.50682	1.49315	2.94609
16	0.50682	1.49315	2.94609
17	0.50682	1.49315	2.94609
18	0.50682	1.49315	2.94609
19	0.50682	1.49315	2.94609
20	0.50682	1.49315	2.94609
21	0.50682	1.49315	2.94609

Table 32 (cont'd)

22	0.50682	1.49315	2.94609
<u>23</u>	<u>0.50682</u>	<u>1.49315</u>	<u>2.94609</u>
24	0.50682	1.49315	2.94609
25	0.50682	1.49315	2.94609
26	0.50682	1.49315	2.94609
27	0.50682	1.49315	2.94609
28	0.50682	1.49315	2.94609
29	0.50682	1.49315	2.94609
30	0.50682	1.49315	2.94609
31	0.50682	1.49315	2.94609
32	0.50682	1.49315	2.94609
33	0.50682	1.49315	2.94609
34	0.50682	1.49315	2.94609
35	0.50682	1.49315	2.94609
36	0.50682	1.49315	2.94609
37	0.50682	1.49315	2.94609
38	0.50682	1.49315	2.94609
39	0.50682	1.49315	2.94609
40	0.50682	1.49315	2.94609

Table 33

Upflow Displacement (NT1) = 5 cc.
 Downflow Displacement (NT3) = 5 cc.
 Volume of Top Feed (NT4) = 5 cc.
 Volume of Bottom Feed (NT2) = 5 cc.
 Number of Stages - 6

I	YT	YB	SF
2	0.81182	1.42964	1.76104
3	0.62687	1.45285	2.32719
4	0.56547	1.46409	2.58914
5	0.54509	1.46494	2.68752
6	0.53832	1.46504	2.72151
7	0.53607	1.46504	2.73291
8	0.53533	1.46503	2.73671
9	0.53508	1.46503	2.73797
10	0.53500	1.46503	2.73833
11	0.53497	1.46503	2.73852
12	0.53496	1.46503	2.73857
13	0.53496	1.46503	2.73858
14	0.53496	1.46503	2.73859
15	0.53496	1.46503	2.73859
16	0.53496	1.46503	2.73859
17	0.53496	1.46503	2.73859
18	0.53496	1.46503	2.73859
19	0.53496	1.46503	2.73859
20	0.53496	1.46503	2.73859
21	0.53496	1.46503	2.73859

Table 33 (cont'd)

22	0.53496	1.46503	2.73859
<u>23</u>	<u>0.53496</u>	<u>1.46503</u>	<u>2.73859</u>
24	0.53496	1.46503	2.73859
<u>25</u>	<u>0.53496</u>	<u>1.46503</u>	<u>2.73859</u>
<u>26</u>	<u>0.53496</u>	<u>1.46503</u>	<u>2.73859</u>
<u>27</u>	<u>0.53496</u>	<u>1.46503</u>	<u>2.73859</u>
<u>28</u>	<u>0.53496</u>	<u>1.46503</u>	<u>2.73859</u>
<u>29</u>	<u>0.53496</u>	<u>1.46503</u>	<u>2.73859</u>
30	0.53496	1.46503	2.73859
<u>31</u>	<u>0.53496</u>	<u>1.46503</u>	<u>2.73859</u>
<u>32</u>	<u>0.53496</u>	<u>1.46503</u>	<u>2.73859</u>
33	0.53496	1.46503	2.73859
<u>34</u>	<u>0.53496</u>	<u>1.46503</u>	<u>2.73859</u>
<u>35</u>	<u>0.53496</u>	<u>1.46503</u>	<u>2.73859</u>
36	0.53496	1.46503	2.73859
<u>37</u>	<u>0.53496</u>	<u>1.46503</u>	<u>2.73859</u>
<u>38</u>	<u>0.53496</u>	<u>1.46503</u>	<u>2.73859</u>
39	0.53496	1.46503	2.73859
<u>40</u>	<u>0.53496</u>	<u>1.46503</u>	<u>2.73859</u>

Table 34CONTINUOUS PARAMETRIC PUMPING

Conditions for Runs to Show the Effect of Simultaneously
Varying Volume of Top and Bottom Feed (NT2 and NT4)

<u>Operating Variable</u>	<u>Value</u>
Volumetric Flow Rate	0.5 cc/sec
Specific Rate Constant for High pH	0.07
Specific Rate Constant for Low pH	1.58
Feed Concentration (Normalized)	1.00 gm. mole/cc.
Total Volume of Column	30.00 cc.
Void Volume of Column	0.75
Deat Volume of Top Reservoir	5.00 cc.
Dead Volume of Bottom Reservoir	5.00 cc.
Upflow Displacement (NT1)	11
Downflow Displacement (NT3)	11
Number of Cycles	40

Table 35

Volume of Top Feed (NT4) = 11 cc.

Volume of Bottom Feed (NT2) = 11 cc.

I	YT	YB	SF
2	0.99732	1.00000	1.00264
3	0.71024	1.28874	1.81451
4	0.52210	1.47773	2.83039
5	0.39879	1.60143	4.01572
6	0.31798	1.68238	5.29087
7	0.26502	1.73536	6.54815
8	0.23031	1.77003	7.68553
9	0.20756	1.79272	8.63725
10	0.19265	1.80757	9.38277
11	0.18288	1.81728	9.93720
12	0.17647	1.82364	10.33382
13	0.17228	1.82780	10.60971
14	0.16953	1.83052	10.79790
15	0.16772	1.83230	10.92457
16	0.16654	1.83346	11.00905
17	0.16577	1.83422	11.06507
18	0.16526	1.83472	11.10207
19	0.16493	1.83505	11.12643
20	0.16471	1.83526	11.14254
21	0.16457	1.83540	11.15295

Table 35 (cont'd)

22	0.16447	1.83549	11.15967
<u>23</u>	<u>0.16441</u>	<u>1.83555</u>	<u>11.16439</u>
24	0.16437	1.83559	11.16736
<u>25</u>	<u>0.16434</u>	<u>1.83562</u>	<u>11.16932</u>
<u>26</u>	<u>0.16433</u>	<u>1.83563</u>	<u>11.17058</u>
<u>27</u>	<u>0.16432</u>	<u>1.83564</u>	<u>11.17141</u>
<u>28</u>	<u>0.16431</u>	<u>1.83565</u>	<u>11.17197</u>
<u>29</u>	<u>0.16430</u>	<u>1.83565</u>	<u>11.17232</u>
30	0.16430	1.83566	11.17255
<u>31</u>	<u>0.16430</u>	<u>1.83566</u>	<u>11.17271</u>
<u>32</u>	<u>0.16430</u>	<u>1.83566</u>	<u>11.17281</u>
<u>33</u>	<u>0.16430</u>	<u>1.83566</u>	<u>11.17288</u>
<u>34</u>	<u>0.16430</u>	<u>1.83566</u>	<u>11.17292</u>
<u>35</u>	<u>0.16430</u>	<u>1.83566</u>	<u>11.17295</u>
36	0.16429	1.83566	11.17296
<u>37</u>	<u>0.16429</u>	<u>1.83566</u>	<u>11.17297</u>
<u>38</u>	<u>0.16429</u>	<u>1.83566</u>	<u>11.17298</u>
<u>39</u>	<u>0.16429</u>	<u>1.83566</u>	<u>11.17298</u>
<u>40</u>	<u>0.16429</u>	<u>1.83566</u>	<u>11.17298</u>

Table 36

Volume of Top Feed (NT4) = 5 cc.

Volume of Bottom Feed (NT2) = 5 cc.

I	YF	YB	SF
2	1.00000	0.98250	0.98250
3	0.78684	1.20680	1.53374
4	0.71070	1.28698	1.81085
5	0.68352	1.31563	1.92481
6	0.67380	1.32588	1.96775
7	0.67034	1.32954	1.98339
8	0.66910	1.33085	1.98902
9	0.66866	1.33131	1.99103
10	0.66850	1.33148	1.99175
11	0.66844	1.33154	1.99201
12	0.66842	1.33156	1.99210
13	0.66841	1.33157	1.99214
14	0.66841	1.33157	1.99215
15	0.66841	1.33157	1.99215
16	0.66841	1.33157	1.99215
17	0.66841	1.33157	1.99215
18	0.66841	1.33157	1.99215
19	0.66841	1.33157	1.99215
20	0.66841	1.33157	1.99215
21	0.66841	1.33157	1.99215

Table 36 (cont'd)

22	0.66841	1.33157	1.99215
<u>23</u>	<u>0.66841</u>	<u>1.33157</u>	<u>1.99215</u>
24	0.66841	1.33157	1.99215
<u>25</u>	<u>0.66841</u>	<u>1.33157</u>	<u>1.99215</u>
<u>26</u>	<u>0.66841</u>	<u>1.33157</u>	<u>1.99215</u>
27	0.66841	1.33157	1.99215
<u>28</u>	<u>0.66841</u>	<u>1.33157</u>	<u>1.99215</u>
<u>29</u>	<u>0.66841</u>	<u>1.33157</u>	<u>1.99215</u>
30	0.66841	1.33157	1.99215
<u>31</u>	<u>0.66841</u>	<u>1.33157</u>	<u>1.99215</u>
<u>32</u>	<u>0.66841</u>	<u>1.33157</u>	<u>1.99215</u>
33	0.66841	1.33157	1.99215
<u>34</u>	<u>0.66841</u>	<u>1.33157</u>	<u>1.99215</u>
<u>35</u>	<u>0.66841</u>	<u>1.33157</u>	<u>1.99215</u>
36	0.66841	1.33157	1.99215
<u>37</u>	<u>0.66841</u>	<u>1.33157</u>	<u>1.99215</u>
<u>38</u>	<u>0.66841</u>	<u>1.33157</u>	<u>1.99215</u>
39	0.66841	1.33157	1.99215
<u>40</u>	<u>0.66841</u>	<u>1.33157</u>	<u>1.99215</u>

Table 37

Volume of Top Feed (NT4) = 4 cc.

Volume of Bottom Feed (NT2) = 4 cc.

I	YT	YB	SF
2	0.99922	1.00000	1.00077
3	0.75538	1.24418	1.60708
4	0.57859	1.42120	2.45630
5	0.45041	1.54953	3.44029
6	0.35746	1.64255	4.59505
7	0.29007	1.70998	5.89511
8	0.24126	1.75886	7.29205
9	0.20577	1.79429	8.71985
10	0.18008	1.81998	10.16650
11	0.16145	1.83860	11.38790
12	0.14794	1.85209	12.51879
13	0.13815	1.86187	13.47704
14	0.13105	1.86896	14.26168
15	0.12590	1.87410	14.88549
16	0.12217	1.87782	15.37089
17	0.11946	1.88052	15.74179
18	0.11750	1.88248	16.02141
19	0.11607	1.88390	16.23010
20	0.11504	1.88492	16.38853
21	0.11429	1.88567	16.49837

Table 37 (cont'd)

22	0.11375	1.88621	16.58179
<u>23</u>	<u>0.11336</u>	<u>1.88660</u>	<u>16.64278</u>
24	0.11307	1.88688	16.68727
<u>25</u>	<u>0.11287</u>	<u>1.88709</u>	<u>16.71968</u>
<u>26</u>	<u>0.11272</u>	<u>1.88723</u>	<u>16.74324</u>
<u>27</u>	<u>0.11261</u>	<u>1.88734</u>	<u>16.76036</u>
<u>28</u>	<u>0.11253</u>	<u>1.88742</u>	<u>16.77281</u>
<u>29</u>	<u>0.11247</u>	<u>1.88748</u>	<u>16.78166</u>
<u>30</u>	<u>0.11243</u>	<u>1.88752</u>	<u>16.78841</u>
<u>31</u>	<u>0.11240</u>	<u>1.88755</u>	<u>16.79317</u>
<u>32</u>	<u>0.11238</u>	<u>1.88757</u>	<u>16.79662</u>
<u>33</u>	<u>0.11236</u>	<u>1.88759</u>	<u>16.79913</u>
<u>34</u>	<u>0.11235</u>	<u>1.88760</u>	<u>16.80099</u>
<u>35</u>	<u>0.11234</u>	<u>1.88761</u>	<u>16.80229</u>
<u>36</u>	<u>0.11234</u>	<u>1.88762</u>	<u>16.80322</u>
<u>37</u>	<u>0.11233</u>	<u>1.88762</u>	<u>16.80395</u>
<u>38</u>	<u>0.11233</u>	<u>1.88762</u>	<u>16.80444</u>
<u>39</u>	<u>0.11233</u>	<u>1.88763</u>	<u>16.80478</u>
<u>40</u>	<u>0.11233</u>	<u>1.88763</u>	<u>16.80505</u>

Table 38

Volume of Top Feed (NT4) = 3 cc.

Volume of Bottom Feed (NT2) = 3 cc.

I	YT	YB	SF
2	0.99983	1.00000	1.00016
3	0.80510	1.19439	1.48353
4	0.65144	1.34814	2.06946
5	0.53010	1.46955	2.77222
6	0.43427	1.56543	3.60471
7	0.35860	1.64115	4.57652
8	0.29884	1.70094	5.69176
9	0.25165	1.74816	6.94674
10	0.21439	1.78545	8.32821
11	0.18496	1.81490	9.81256
12	0.16172	1.83815	11.36654
13	0.14336	1.85652	12.94975
14	0.12887	1.87102	14.51867
15	0.11742	1.88247	16.03130
16	0.10839	1.89152	17.45158
17	0.10125	1.89866	18.75235
18	0.09561	1.90430	19.91682
19	0.09116	1.90875	20.93816
20	0.08765	1.91227	21.81799
21	0.08487	1.91505	22.56433

Table 38 (cont'd)

22	0.08268	1.91724	23.18913
<u>23</u>	<u>0.08095</u>	<u>1.91898</u>	<u>23.70684</u>
24	0.07956	1.92035	24.13087
<u>25</u>	<u>0.07850</u>	<u>1.92143</u>	<u>24.47647</u>
<u>26</u>	<u>0.07765</u>	<u>1.92228</u>	<u>24.75620</u>
<u>27</u>	<u>0.07698</u>	<u>1.92295</u>	<u>24.98146</u>
<u>28</u>	<u>0.07644</u>	<u>1.92348</u>	<u>25.16217</u>
<u>29</u>	<u>0.07602</u>	<u>1.92390</u>	<u>25.30667</u>
<u>30</u>	<u>0.07569</u>	<u>1.92424</u>	<u>25.42189</u>
<u>31</u>	<u>0.07543</u>	<u>1.92450</u>	<u>25.51364</u>
<u>32</u>	<u>0.07522</u>	<u>1.92471</u>	<u>25.58649</u>
<u>33</u>	<u>0.07506</u>	<u>1.92487</u>	<u>25.64433</u>
<u>34</u>	<u>0.07493</u>	<u>1.92500</u>	<u>25.69017</u>
<u>35</u>	<u>0.07483</u>	<u>1.92510</u>	<u>25.72650</u>
<u>36</u>	<u>0.07475</u>	<u>1.92518</u>	<u>25.75529</u>
<u>37</u>	<u>0.07469</u>	<u>1.92525</u>	<u>25.77802</u>
<u>38</u>	<u>0.07464</u>	<u>1.92530</u>	<u>25.79601</u>
<u>39</u>	<u>0.07460</u>	<u>1.92534</u>	<u>25.81024</u>
<u>40</u>	<u>0.07456</u>	<u>1.92537</u>	<u>25.82153</u>

Table 39

Volume of Top Feed (NT4) = 1 cc.

Volume of Bottom Feed (NT2) = 1 cc.

I	TRES	BRES	SF
2	0.90029	1.00000	1.11075
3	0.81592	1.08016	1.32385
4	0.74083	1.16260	1.58934
5	0.67350	1.23787	1.83797
6	0.61308	1.30557	2.12952
7	0.55886	1.36636	2.44489
8	0.51020	1.42091	2.78502
9	0.46652	1.46987	3.15070
10	0.42732	1.51381	3.54255
11	0.39214	1.55325	3.96093
12	0.36057	1.58864	4.40594
13	0.33223	1.62040	4.87735
14	0.30680	1.64891	5.37459
15	0.28397	1.67449	5.89671
16	0.26348	1.69746	6.44233
17	0.24510	1.71806	7.00969
18	0.22860	1.73656	7.59659
19	0.21379	1.75315	8.20049
20	0.20049	1.76805	8.81845
21	0.18855	1.78142	9.44725

Table 39 (cont'd)

22	0.17786	1.79341	10.08363
23	0.16825	1.80418	10.72333
24	0.15962	1.81384	11.36325
25	0.15188	1.82251	11.99947
26	0.14494	1.83029	12.62832
27	0.13870	1.83727	13.24636
28	0.13310	1.84354	13.85037
29	0.12808	1.84916	14.43741
30	0.12357	1.85421	15.00467
31	0.11953	1.85873	15.55862
32	0.11590	1.86279	16.07286
33	0.11264	1.86644	16.57027
34	0.10971	1.86971	17.04184
35	0.10709	1.87264	17.48697
36	0.10473	1.87528	17.90552
37	0.10262	1.87764	18.29752
38	0.10072	1.87976	18.66333
39	0.09902	1.88166	19.00365
40	0.09749	1.88337	19.31914

Table 40

Separation Factors as a Function of
Top and Bottom Feed (NT2 and NT4)

<u>NT2 and or NT4 (cc)</u>	<u>Type of Parapump</u>	<u>Steady State Product Concentration moles/cc.</u>		<u>Separation Factor ($\langle Y_B \rangle_\infty / \langle Y_T \rangle_\infty$)</u>
		<u>Top</u>	<u>Bottom</u>	
1	Batch	0.0975	1.8834	19.3169
3	Continuous	0.0746	1.9254	25.8215
4	Continuous	0.1123	1.8876	16.8050
5	Continuous	1.1643	1.8357	11.1730
11	Continuous	0.5068	1.4932	2.9461

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