

CHROM. 7036A

## THERMAL WAVE CYCLING ZONE SEPARATION

### A PREPARATIVE SEPARATION TECHNIQUE FOR COUNTER-CURRENT DISTRIBUTION AND CHROMATOGRAPHY

PHILLIP C. WANKAT

*School of Chemical Engineering, Purdue University, West Lafayette, Ind. (U.S.A.)*

(First received June 18th, 1973; revised manuscript received September 6th, 1973)

---

#### SUMMARY

Cycling zone separation is extended to counter-current distribution using the thermal traveling wave mode of operation. A counter-current distribution type theory was developed and used to explain and predict the separation. Experimental results with a diethylamine-water-toluene system were in qualitative agreement with the theoretical predictions. Use of the technique for preparative chromatographic separations is discussed.

---

#### INTRODUCTION

Recently, there has been considerable interest in cyclic separation processes which allow for continuous or semi-continuous feed to chromatographic apparatuses<sup>1-7</sup>. These processes such as parametric pumping and cycling zone adsorption utilize the periodic variation of a thermodynamic variable to force the separation while feed is added continuously instead of as a pulse as in standard elution development.

Cycling zone adsorption involves pumping the fluid to be separated in one direction through a series of columns. This technique can be operated in the "direct" mode, where the columns are heated and cooled periodically, or in the "traveling wave" mode, where the entering streams are heated and cooled periodically. This technique was developed by Pigford *et al.*<sup>1</sup> and has been considered in more detail by Pigford and his coworkers<sup>2-4</sup>. Investigations have also been done by Gupta and Sweed<sup>5</sup>, who developed an equilibrium theory for cycling zone adsorption, by Van der Vlist<sup>6</sup>, who separated oxygen and nitrogen, and by Wankat<sup>7</sup>, who investigated the application of cycling zone separation in the "direct" mode to extraction in counter-current distribution (CCD). The reason for separation in cycling zone adsorption has been discussed by all of the above authors. Briefly, when the column is cold, the stationary phase stores the solute so that the product stream leaving the column contains little solute. When the column is hot, the stationary phase now acts as a source for the solute

and the product stream contains more solute. The separation achieved can be increased by placing several columns in series<sup>1-5,7</sup> and by use of recycle from one column to another<sup>4</sup>.

Several separation schemes similar to cycling zone adsorption have been developed in the past. Parametric pumping also utilizes periodic changes in a thermodynamic variable, but the fluid to be separated flows back and forth through the column in sequence with the temperature changes. The work on parametric pumping has been reviewed by Sweed<sup>8</sup>, Skarstrom<sup>9</sup>, Alexis<sup>10</sup>, and Shendalman and Mitchell<sup>11</sup> all studied heatless adsorption systems which used pressure swings to achieve separation. Zhukhovitskii<sup>12</sup> developed chromathermography, which used a rotating heater on a chromatographic column. Thompson<sup>13</sup> developed a continuous chromatograph where the feed concentration in the carrier gas was varied sinusoidally instead of being fed as a pulse. Helfferich and Klein<sup>14</sup> discuss several chromatographic studies where various influent composition changes were made.

In this paper the cycling zone technique is extended to extraction using the thermal "traveling wave" mode of operation. Experimental and theoretical work was done for a staged system with discrete and separate transfer and equilibrium steps. This is essentially the conversion of CCD to a cycling zone separation. The use of CCD for cycling zone separation using the direct mode of operation has been reported previously<sup>7</sup>. Although this work was done for discrete transfer steps, the results should be qualitatively valid for staged continuous flow systems and for the standard column chromatographic techniques. A cycling zone extraction system has the advantage that no separate solvent removal step is required, and it provides a simple preparative method of obtaining continuous production from CCD.

### TRAVELING-WAVE CYCLING ZONE EXTRACTION

The basic apparatus for cycling zone extraction in the traveling wave mode of operation is shown schematically in Fig. 1. The apparatus consists of a series of equilibrium stages or test tubes arranged in regions. Each region or zone is a well insulated series of stages arranged so that the product from any stage is the feed to

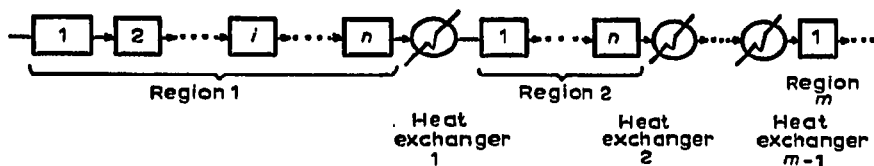


Fig. 1. Staged cycling zone extraction system for traveling wave mode.

the next stage. In the CCD mode of operation studied here, the entire mobile phase from each stage is transferred to the next stage at each transfer step. After a transfer step, the two phases in each stage are allowed to come to equilibrium. At each transfer step fresh feed is placed in stage 1 of region 1. The feed concentration is constant, but its temperature varies as a square wave starting at some hot temperature,  $T_H$ , for half of the cycle and then switching to the cold temperature,  $T_C$ , for the remainder of the cycle. The streams exiting from region 1 after each transfer step may be taken

as the products, or they may be fed to a heat exchanger and from there to a second region. The heat exchanger serves to reform the square temperature wave and to make the temperature of the feed to the second region  $180^\circ$  out of phase with the feed temperature for the first region. Thus during the first half cycle, while the feed to region 1 is hot, the feed to region 2 will be cold and vice versa. Additional regions and heat exchangers can be added to increase the desired separation. The bulk of this paper is concerned with the simple one-region process, but theoretical results will be presented to show the improved separation that can be achieved with several regions.

The product from the cycling zone system is time dependent in that the concentration of the product obtained at each transfer step will differ. However, the apparatus will eventually reach a repeating state where the product concentrations from cycle to cycle repeat themselves. Proper timing of a fraction collector or switching mechanism will result in continuous separation of the inlet feed.

The periodic alternation of the feed temperature will cause a temperature wave in the system. When a given stage is hot, the stationary phase will reject solute and the moving phase will become more concentrated\*. When a given stage is cooled, the equilibrium distribution coefficient changes and the stationary phase now stores the solute. The larger the temperature difference the more the distribution coefficient varies and the greater the separation. Thermodynamic variables other than temperature such as pH or ionic strength can be varied in the feed stream. If these variables affect the distribution coefficient a separation will be obtained. Since the staged system can also be considered as a model for continuous flow chromatography, the results to be presented later will also apply to chromatography.

## THEORY

The theoretical analysis of cycling zone extraction in the traveling wave mode of operation utilizes the long established theory for CCD machines<sup>15</sup> and is similar to the analysis previously reported for the direct mode<sup>7</sup>. The major assumption that will be made is that the solutes are present at low concentrations so that they do not interact with each other and the distribution coefficients are independent of concentration. With this assumption all equations and definitions can be written for a single solute.

The system shown in Fig. 1 has  $n$  stages per region and  $m$  regions. Each stage will be represented as  $(i,j)$ , where  $i$  refers to the stage number and  $j$  to the region number. When the feed to region 1 is hot the system is in the first half of the cycle and when the feed to region 1 is cold the system is in the second half of the cycle. There are  $S_H$  transfer steps in the first half cycle and  $S_C$  transfer steps in the second half cycle. The cycle "halves" may be equal. The total number of transfers per cycle is  $S_T = S_H + S_C$ . We will assume that the volume of moving phase per stage,  $V_M$ , and the volume of stationary phase per stage,  $V_S$ , are constant.  $C_M$  and  $C_S$  are the concentrations of solute in the moving and stationary phases, respectively. Let  $T_{i,j,s}$  and  $M_{i,j,s}$

\* In this explanation we are assuming that the usual behavior of solid adsorbents is followed by the stationary liquid solvent. In actual practice more solute may be attracted to the stationary phase when the column is hot. If this occurs the explanation is reversed, but separation still occurs.

be the temperature of and the mass of solute in stage  $i$  of region  $j$  after transfer step  $s$ , respectively. The distribution coefficient defined as  $K(T_{i,j,s}) = C_M/C_S$  is temperature dependent, but is independent of concentration.  $\rho_M$ ,  $\rho_S$  and  $W_T$  are the densities of the moving and stationary phases and the weight of the tube or stage, respectively.  $C_{PM}$ ,  $C_{PS}$  and  $C_{PT}$  are the heat capacities of the moving phase, the stationary phase and the tube, respectively. It is assumed that the densities and heat capacities are constant. Finally, define  $f_{i,j,s}$  as the fraction of solute that is in the moving phase in stage  $i$  of region  $j$  after transfer step  $s$ .

It can easily be shown<sup>15</sup> that the fraction of solute in the moving phase is given as:

$$f_{i,j,s} = \frac{K(T_{i,j,s}) V_M/V_S}{1 + K(T_{i,j,s}) V_M/V_S} \quad (1)$$

Unlike CCD  $f_{i,j,s}$  is not constant for all stages since the temperature will vary from stage to stage.  $f_{i,j,s}$  is calculated after the transfer step  $s$  and after thermal equilibrium has been obtained. Since  $f_{i,j,s}$  is the fraction of solute in the moving phase,  $(1 - f_{i,j,s})$  is the fraction of solute in the stationary phase.

The mass balances used to calculate the mass of solute in stage  $i$  of region  $j$  after transfer step  $s$  are the same as those used for the direct mode<sup>7</sup>. If  $i \neq 1$  the mass balance is

$$M_{i,j,s} = f_{i-1,j,s-1} M_{i-1,j,s-1} + (1 - f_{i,j,s-1}) M_{i,j,s-1} \quad (2)$$

If  $i = 1$  but  $j \neq 1$

$$M_{1,j,s} = f_{n,j-1,s-1} M_{n,j-1,s-1} + (1 - f_{1,j,s-1}) M_{1,j,s-1} \quad (3)$$

If  $i = 1$  and  $j = 1$

$$M_{1,1,s} = C_{Feed} V_M + (1 - f_{1,1,s-1}) M_{1,1,s-1} \quad (4)$$

where  $C_{Feed}$  is the concentration of solute in the feed.

The  $f$  values in eqns. 2, 3 and 4 must be calculated for each stage from the temperature of that stage, which can be found from an energy balance. Assuming that the stages are well insulated, the energy balances can easily be developed by defining  $A$  as the fraction of energy that is in the moving phase for any stage. By an analysis similar to that used to find  $f_{i,j,s}$ ,  $A$  can be found as:

$$A = \frac{C_{PM} V_M \rho_M}{(C_{PM} V_M \rho_M + C_{PS} V_S \rho_S + C_{PT} W_T)} \quad (5)$$

With eqn. 5 defining  $A$ , the energy balance for  $i \neq 1$  is

$$T_{i,j,s} = A T_{i-1,j,s-1} + (1 - A) T_{i,j,s-1} \quad (6)$$

If  $i = 1$  but  $j \neq 1$

$$T_{1,j,s} = A T_{HE,j-1,s} + (1 - A) T_{1,j,s-1} \quad (7)$$

If  $i = 1$  and  $j = 1$

$$T_{1,1,s} = A T_{FS} + (1 - A)T_{1,1,s-1} \quad (8)$$

where  $T_{HE,j-1,s}$  is the temperature of material leaving heat exchanger  $j - 1$  for transfer step  $s$ , and  $T_{FS}$  is the temperature of the feed for transfer step  $s$ . Because of the restrictive assumptions made previously,  $A$  is independent of concentration or temperature, and the energy balance eqns. 6-8 are independent of the mass balances. Thus the energy balances can be solved to find any desired temperature, the  $f$  values can be calculated for each stage and transfer step, and then the mass balances can be solved. What we desire to find is the concentration of the product leaving stage  $(n,m)$  after each transfer step.

There are three ways of solving eqns. 2-4 and 6-8. In CCD similar equations have been solved as binomial distributions<sup>15,16</sup>. Eqns. 6-8 could be solved as summations of binomial distributions and then eqns. 2-4 would be more complicated functions of binomial distributions. This was not done since it was felt that direct iterative solutions would be simpler. A straightforward iterative solution can be obtained by using eqns. 6-8 and 2-4 as recursion relations with an appropriate set of initial conditions. When this is done, an additional subscript must be added in these equations to count the number of cycles. This cycle subscript was not used because the cycling zone system will eventually reach a limiting repeating state, where each cycle is an exact repeat of the cycle before it. This has been shown both experimentally and theoretically.

Since the major objective of this work was to study continuous separations in cycling zone extraction, the calculations and results are concerned with the limiting repeating state. For the periodically steady results the initial conditions are unimportant and a different solution technique can be used. The solution method employed uses the fact that  $M_{i,j,s}$ ,  $T_{i,j,s}$  and  $f_{i,j,s}$  are the same from cycle to cycle. First  $T_{1,1,1}$  is calculated by solving the  $S_T$  equations for a cycle represented by eqn. 8 for  $T_{1,1,1}$ . Then eqn. 8 is used to find  $T_{1,1,s}$  for all values of  $s$ :  $s = 2, 3, \dots S_T$ . With the temperature values known, eqn. 1 is used to find  $f_{1,1,s}$  for all values of  $s$ . Now  $M_{1,1,1}$  is found by solving the  $S_T$  equations for a cycle represented by eqn. 4, and then eqn. 4 is used to find  $M_{1,1,s}$  for all values of  $s$ . At this point we go to stage  $(2,1)$  and repeat the calculations using eqns. 6 and 2. This process is continued until the product concentrations leaving stage  $(n,m)$  are obtained for all transfer steps of a cycle. The equations and solution technique are very similar to the technique required for the direct mode of operation, and will not be presented here since the direct mode solution was presented in detail elsewhere<sup>7</sup>. This repeating state solution requires significantly less computer time than the iterative start-up solution which was also solved in this study.

At the repeating state the solution depends upon the variables  $n, m, S_H, S_C, A, T_C, T_H, V_M/V_S$ , and the functional dependence of  $K$  upon  $T$ . Thus, before considering the numerical results, it would be a good idea to obtain a qualitative feel for the separation that will be achieved. The average distance that solute will move is  $f \times$  (number of transfer steps)<sup>7,15</sup>. If we compare eqns. 2 and 6 and look at the meaning of parameter  $A$ , we see that  $A$  is a measure of the speed of the thermal wave. The distance the thermal wave travels is then  $A \times$  (number of transfer steps).

Unless  $A = 1.0$ , the thermal wave will be spread by the same band-spreading phenomena that occur in CCD. If  $A$  is near 1.0, the thermal waves will remain sharp and will travel faster than the concentration waves. When the hot portion of the thermal wave passes through the bed, the  $f$  value increases rapidly since less solute is held by the stationary solvent. Thus, behind the hot front of the thermal wave is a slower moving concentration wave of concentrated solute. Behind the cold front of the thermal wave will be a slowly moving region (low  $f$  value) of low concentration solute. Thus a considerable separation can be achieved by collecting the material in the two concentration waves separately. For low values of  $A$  the thermal wave moves slowly and is spread out considerably. As a result the temperatures within the column vary little and little separation is achieved. For reasons that will be discussed in Results, there is often an optimum value of  $A$  less than 1.0 which gives a maximum separation. Before considering the theoretical results the experimental work will be discussed.

## EXPERIMENTAL

A very simple experimental system was used to check the theoretical predictions and to look for unexpected results. This system consisted of a set of three 15-ml centrifuge test tubes held in a styrofoam holder. The moving phase was transferred with a 10-ml B-D syringe. Since the moving phase was heavier than the stationary phase, accurate phase separation could be obtained at the conical bottom of the test tube. Runs were made with glass test tubes with glass stoppers, with round-bottomed plastic test tubes with plastic caps, and with glass test tubes with plastic caps. Changing the test-tube type changes the value of  $A$ .

The separation attempted was the removal of diethylamine from water using toluene as the stationary solvent. This chemical system was chosen since it was used previously for the direct mode study<sup>7</sup>, has a significant change in the distribution coefficient with temperature<sup>7,17</sup>, and the concentration of amine can easily be determined by titration using methyl red as the indicator.

Three runs were made, one for each of the three types of test tube. In all runs the hot feed temperature was 28°, the cold feed temperature was 0°, the volumes of moving and stationary phases were 5 ml each, and the system consisted of 1 region with 3 stages with 4 transfers per half cycle. Feed concentrations of 0.301  $N$  and 0.325  $N$  diethylamine in water were used. Initially there was no amine in each stage and each stage was at 15°. For the all-glass and all-plastic systems 10 min were allowed for settling between each transfer step and a total of three cycles were run before the results were analyzed. This settling time was felt to be too long and allowed for too much heat transfer with the surroundings. For the last run, using the glass test tubes with plastic caps, 5 min were allowed after each transfer step and the products were analyzed in the fourth cycle. Theoretical calculations predicted that the repeating state will be reached in two cycles.

The distribution coefficients are both temperature and concentration dependent. An average concentration was used and the distribution coefficient was fitted approximately to the equation

$$K = 4.59 - 0.163T + 1.70 \times 10^{-3} T^2 \quad (9)$$

where  $T$  is in  $^{\circ}\text{C}$ . The  $A$  values were calculated by weighing the tubes and using literature values for heat capacities. For the Pyrex test tubes with Pyrex stoppers  $A = 0.466$ . This value was relatively low, so an attempt was made to use other materials which would give higher values for  $A$ . Polyethylene tubes with polyethylene caps were tried next, but their  $A = 0.428$ . Polyethylene is lighter, but has a much higher heat capacity than glass. By switching to Pyrex tubes with polyethylene caps the value of  $A$  was raised to 0.516. As will be shown later, the best separation was obtained with this system.

The main experimental problem was the loss of a sharp temperature wave. This occurred because of the relatively low  $A$  values and because of unavoidable energy gains and losses. The tubes were well insulated, but the moving phase was heated or cooled by the syringe every time a transfer step was made. There were also some unavoidable losses of toluene and amine due to evaporation when the tubes were opened for the transfer step. At  $28^{\circ}$  emulsions were easily formed and required a long settling time. This problem was particularly severe in the plastic tubes. The experimentation was slow and tedious, and it had to be completed in one sitting so that the temperature profiles would not be lost. The repeating state was probably not reached completely in any of the three runs since input of solute exceeded output. The percent error in the mass balance for the eight transfer steps in the last cycle was 0.67%, 2.6%, and 1.6% for the all-glass, all-plastic, and glass tube with plastic cap systems, respectively. This error could also represent evaporation losses and other experimental errors. For practical use or further experimentation an automated device would be very convenient.

## RESULTS

The theoretical results will be presented first in Figs. 2–10 and then the experimental results will be compared with the theoretical predictions in Figs. 11 and 12. The basic temperature and concentration product curves are shown in Fig. 2 for a system with 1 region and 40 stages per region. The inlet temperature was a square wave with 40 transfer steps at  $50^{\circ}$  and 40 transfer steps at  $0^{\circ}$ . The outlet temperature had a maximum of  $49.87^{\circ}$  and a minimum of  $0.13^{\circ}$ . The temperature wave is no longer square and it is delayed behind the square wave. The outlet concentration profile is delayed behind the thermal wave and shows a maximum separation,  $\alpha_{\text{max}}$ . (= maximum concentration/minimum concentration), of 9.99. The  $K$  dependence on temperature corresponds to a maximum of  $f_{50} = 0.667$  and minimum of  $f_0 = 0.50$  and is represented by the equation  $K = 1.0 + 0.02T$  with  $T$  in  $^{\circ}\text{C}$ . The maximum separation achieved for this system is greater than the separation that can be achieved with the comparable direct mode system for the same parameter values<sup>7</sup>. For the direct mode system  $\alpha_{\text{max}} = 1.78$  with 1 region and  $\alpha_{\text{max}} = 6.62$  for 4 regions with 10 stages per region and 19 transfers per half cycle. Thus the travelling wave mode can give larger separations than the direct mode. Shortly, we will see that the separation can be increased by increasing the number of stages, optimizing  $A$ , and by use of several regions with heat exchangers between the regions.

The results obtained when the number of stages is increased to 160 are shown in Fig. 3. For this case  $\alpha_{\text{max}} = 108.9$  because of the low minimum concentration. The minimum concentration was decreased by a factor of 5 compared to Fig. 2,

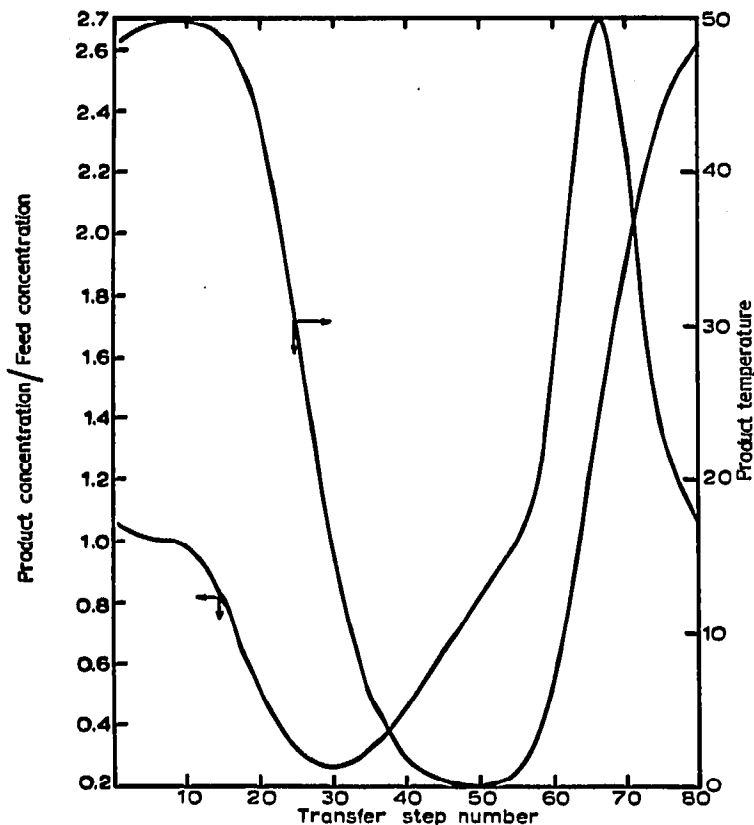


Fig. 2. Product concentrations and temperatures for a complete cycle: 40 stages/region, 1 region,  $T_c = 0$ ,  $T_H = 50$ ,  $S_c = S_H = 40$ ,  $K = 1.0 + 0.02T$ ,  $A = 0.6$ .

while the maximum concentration was approximately doubled. Both Figs. 2 and 3 show a region of little separation where the product concentration is approximately the same as the feed concentration. These products could be recycled. The number of transfer steps per half cycle was increased when the number of stages was increased. For single region systems a low number of transfers per half cycle compared to the number of stages decreases the separation while increasing the number of transfers per half cycle has little effect after a certain point. The behavior with more than one region is significantly different since then there is an optimum number of transfers per half cycle.

The effect of the thermal wave velocity, parameter  $A$ , is shown in Fig. 4, where  $\alpha_{max.}$  is plotted *versus*  $A$  for a 40-stage system. There is an optimum value of  $A$  of approximately 0.67, for which  $\alpha_{max.} = 10.8$ . Low values of  $A$  are extremely detrimental to the separation and should be avoided. High values of  $A$  are also detrimental, but do not have as large an effect as low values.  $A$  can be varied to optimize the separation by changing the tube weight or heat capacity.

The reasons for the maximum separation at an  $A$  value approximately equal to  $f_H$  are relatively complex. The cause of low separations at low  $A$  values is evident



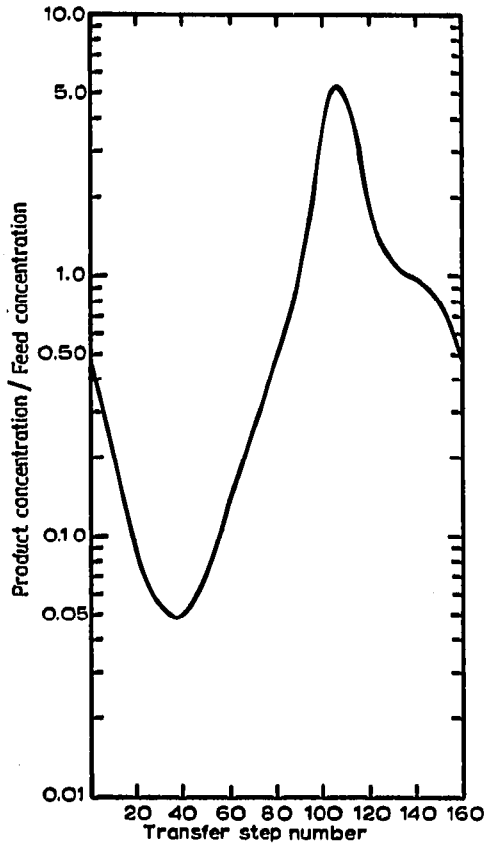


Fig. 3. Product concentrations for a complete cycle: 160 stages/region, 1 region,  $T_c = 0$ ,  $T_H = 50$ ,  $S_c = S_H = 80$ ,  $K = 1.0 + 0.02T$ ,  $A = 0.6$ .

when the temperature profiles shown in Fig. 5 for a series of  $A$  values are studied. As the thermal wave velocity is decreased, the thermal wave becomes more diffuse and the temperature differences in the column decrease. When this occurs, the variation of the distribution coefficient is minimized and there is less driving force for separation. As  $A$  approaches 1.0 the thermal wave approaches a square wave with very sharp temperature differences and correspondingly large differences in the distribution coefficient. To explain the decrease in separation which occurs as  $A$  approaches 1.0 the relative velocities of the thermal and concentration waves must be considered. This explanation will be given for thermal waves that are assumed to be square. This simplifies the calculation of the concentration waves since  $f$  is either  $f_c$  or  $f_H$ .

The thermal and concentration waves for a 40-stage system with  $A = 1.0$  are shown in Fig. 6. The thermal waves have a slope of 1.0, since this is the rate of travel of the thermal waves. The thermal wave lines allow one to determine the temperature of any stage for any transfer step number. The temperature is  $50^\circ$  in the hot regions and  $0^\circ$  in the cold regions. Material in stage 41 is the product whose temperature was shown in Fig. 5. In the hot regions the concentration waves have a velocity of  $f_H = 2/3$  while in the cold regions the velocity is  $f_c = 1/2$ . Thus the concentration waves

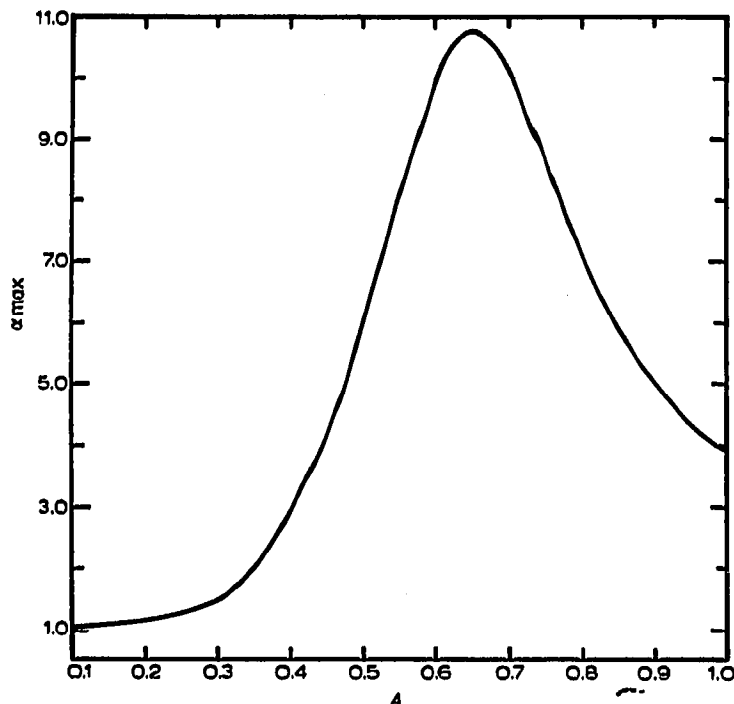


Fig. 4. Effect of thermal wave velocity,  $A$ , on maximum separation: 40 stages/region, 1 region,  $T_c = 0$ ,  $T_H = 50$ ,  $S_c = S_H = 40$ ,  $K = 1.0 + 0.02T$ .

are shown with slopes of  $2/3$  or  $1/2$ . The concentration wave lines represent the location of the "average" molecule of solute a given number of transfer steps after it has been fed to the system. Thus by following the concentration wave lines, we can calculate when material will leave the system and compare this with the product concentrations shown in Fig. 7. Comparison of Figs. 6 and 7 can be used to determine the history of a particular product stream. For instance, the product of maximum concentration leaves the system at transfer step 50 while the product streams are hot but the feed to the column is cold. By following the concentration wave for this product we find that the average molecule entered the column in transfer step 56 of the previous cycle while the feed was cold. This average molecule underwent one temperature change when the hot thermal wave overtook the concentration wave at transfer step 25. Also, the concentration waves are closer together (and hence the product is more concentrated) in the product than in the feed. This concentration occurs because of the increased speed of the concentration wave when it is overtaken by the thermal wave. The dilute product stream histories can also be traced. Here we find that the dilute product concentration waves are further apart than they were in the feed because of the decrease in wave speed when the temperature is decreased. The increase in dilute product concentration after transfer step 25 is the result of the familiar breakthrough phenomena. Since products 63 to 81 undergo no temperature changes in the bed, their concentrations rapidly approach the feed concentration.

The optimum value of  $A$  shown in Fig. 4 can be explained by use of Fig. 6.

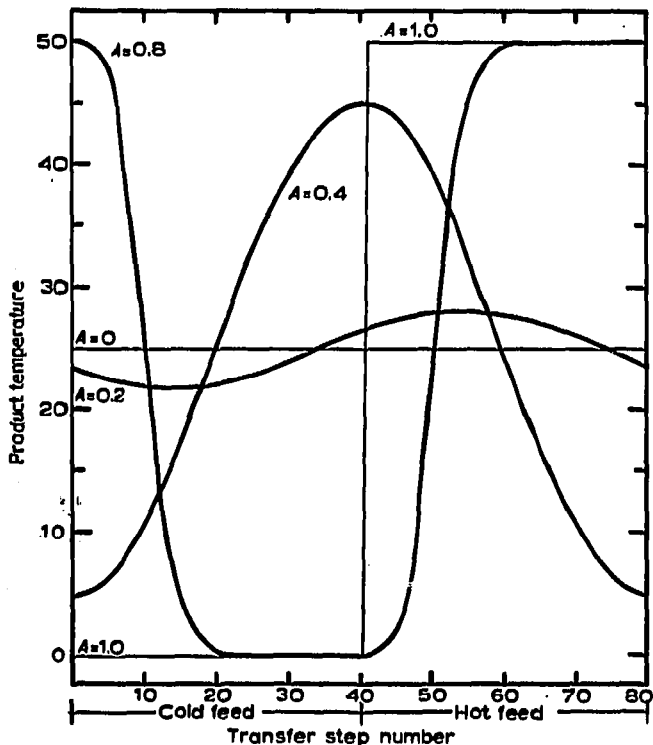


Fig. 5. Product temperature profiles for several values of thermal wave velocity: 40 stages/region, 1 region,  $T_c = 0$ ,  $T_H = 50$ ,  $S_c = S_H = 40$ ,  $K = 1.0 + 0.02T$ .

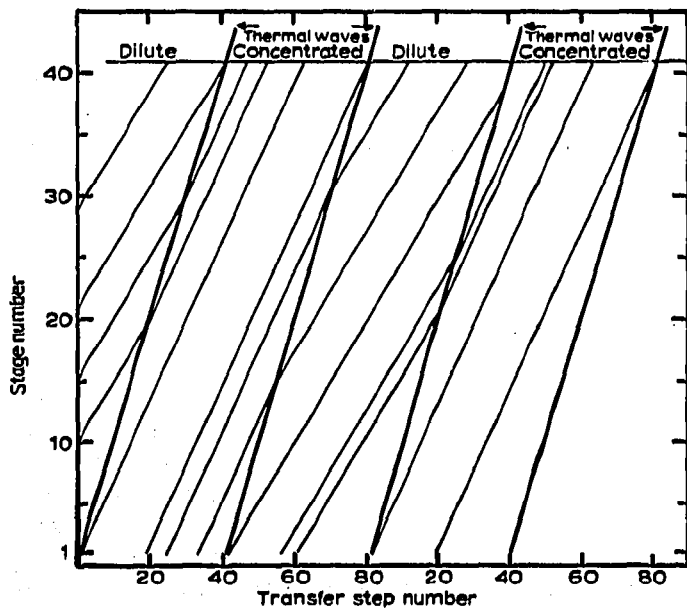


Fig. 6. Concentration and thermal waves: 40 stages/region, 1 region,  $T_c = 0$ ,  $T_H = 50$ ,  $S_c = S_H = 40$ ,  $K = 1.0 + 0.02T$ ,  $A = 1.0$ .

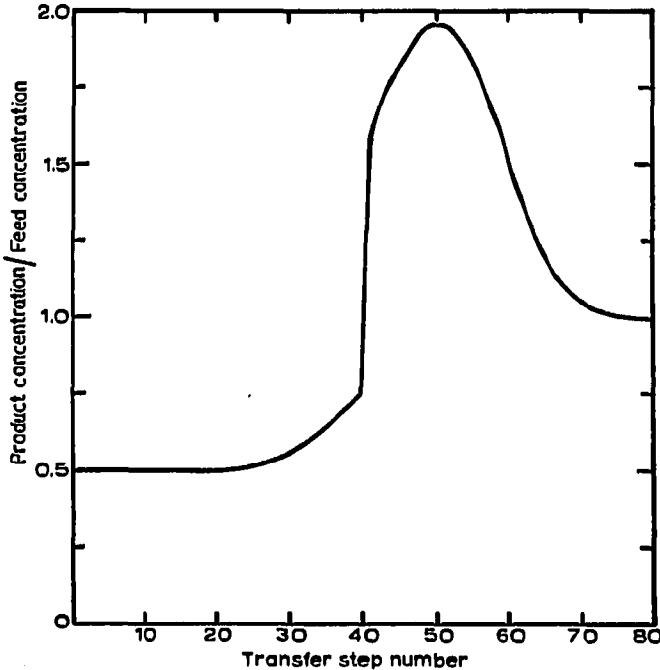


Fig. 7. Product concentrations for a complete cycle: 40 stages/region, 1 region,  $T_c = 0$ ,  $T_H = 50$ ,  $S_c = S_H = 40$ ,  $K = 1.0 + 0.02T$ ,  $A = 1.0$ .

We will first assume that the thermal wave remains square and then include the effect of the actual non-square thermal wave shape that was shown in Fig. 5. If  $A$  is decreased then the velocity of the thermal wave decreases, and the slope of the thermal waves in Fig. 6 approaches the slope of the concentration waves. Fewer of the cold waves fed to the column during transfer steps 41 to 80 will intersect the thermal wave. However, those that do intersect a thermal wave will be bunched closer together in the product since their velocity is close to that of the thermal wave velocity. This effect can be seen in Fig. 6 by drawing a thermal wave with a slope less than one. As the angle between the thermal wave and the cold concentration wave decreases, the hot concentration waves become closer together, causing a more concentrated product. Since one product is more concentrated, a mass balance shows that the dilute product must be less concentrated and the separation is increased. When the thermal wave velocity is between the two concentration wave velocities,  $f_c < A < f_H$ , a maximum separation occurs. Any solute in a cold concentration wave that is overtaken by a thermal wave must follow the thermal wave. If it drops behind the thermal wave, it will be in a hot stage and will have a velocity greater than the thermal wave and will catch up. Any solute that gets ahead of the thermal wave will be in a cold region and must thus slow down until it is again overtaken by the thermal wave. As a result the solute concentrates immediately behind the thermal wave. The closer  $A$  is to  $f_H$  the more cold concentration waves are overtaken by the thermal wave and the greater the separation achieved. When the thermal wave moves slower than the cold concentration wave,  $A < f_c$ , this concentration effect does not occur.

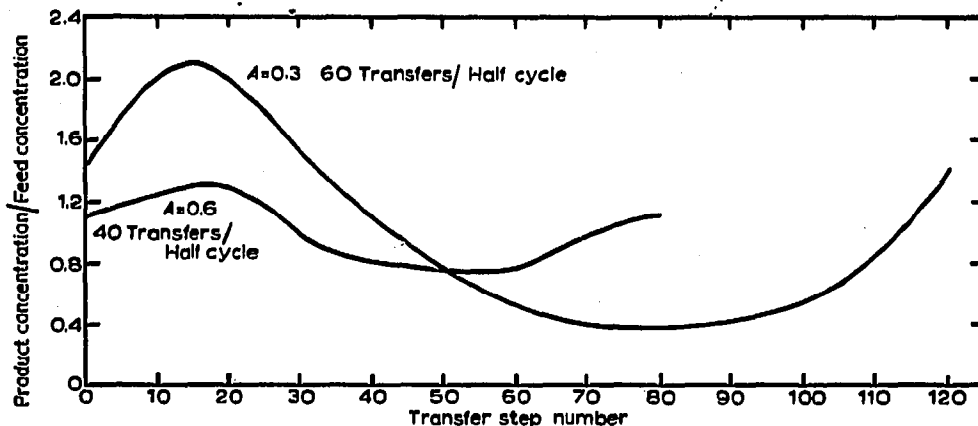


Fig. 8. Product concentrations for a complete cycle: 40 stages/region, 1 region,  $T_c = 0$ ,  $T_H = 50$ ,  $K = 0.3333 + 0.003337$ .

This explanation is modified in practice because the thermal waves are not square if  $A < 1.0$ . This prevents a shock front from occurring and causes a lag between the product maximum and the thermal wave. In addition, at low  $A$  values the separation is further decreased because the maximum temperature change is decreased and the change in  $f$  values is decreased.

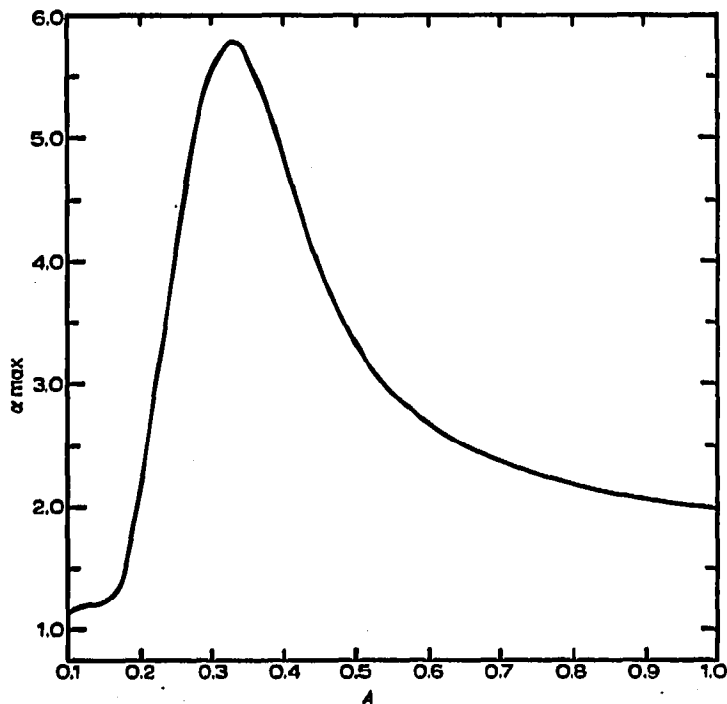


Fig. 9. Effect of thermal wave velocity,  $A$ , on maximum separation: 40 stages/region, 1 region,  $T_c = 0$ ,  $T_H = 50$ ,  $S_c = S_H = 60$ ,  $K = 0.3333 + 0.003337$ .

Enough stages must be present for these waves to develop in order to obtain these effects. For the 3-stage systems used in the experiments the separation is highest for  $A = 1.0$  since this gives the best thermal distribution. Fig. 6 and the discussion presented here are similar to the figures used by Baker and Pigford<sup>3</sup> to explain their theoretical results obtained using the method of characteristics.

Theoretical calculations were also made to study the effect of separating different solutes which have a different  $K$  dependence on  $T$  and have different values of  $f_C$  and  $f_H$ . First the effect of having  $K_C > K_H$  instead of  $K_H > K_C$ , as in Figs. 2-6, was studied. This was done by using a temperature dependence for  $K$  of  $K = 2.0 - 0.02T$  with  $T$  in  $^{\circ}\text{C}$ . This equation gives  $f_C = 0.66667$  and  $f_H = 0.5$ . All other parameters were the same as in Fig. 2. The resulting product concentrations were exactly similar to those in Fig. 2 except they were shifted by half a cycle. This result shows that separation of two solutes should be easy if their distribution coefficients shift in opposite directions with temperature.

The effects of variation of the  $K$  values with  $f_H > f_C$ , but with smaller  $f$  values are shown in Figs. 8 and 9. The equation for  $K$  was  $K = 0.3333 + 0.003337T$ , which results in  $f_C = 0.25$  and  $f_H = 0.3333$ . Product concentrations are shown for  $A = 0.3$  and 60 transfers per half cycle and for  $A = 0.6$  with 40 transfers per half cycle. The latter result is non-optimum, but allows for direct comparison with Fig. 2. The separation achieved for this solute is considerably less than that obtained for the solute in Fig. 2. Also note that the concentration waves for the two solutes are out of

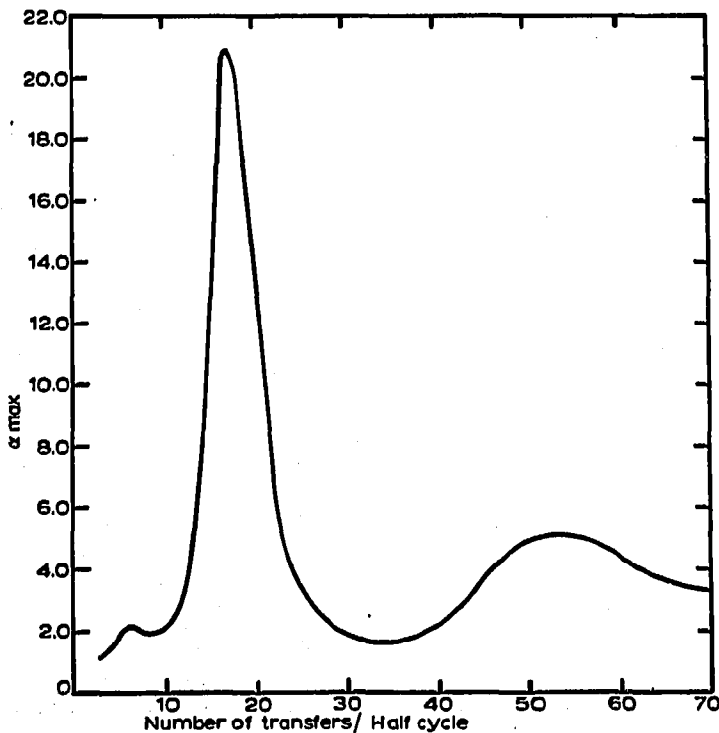


Fig. 10. Effect of number of transfers/half cycle for a four region system: 10 stages/region, 4 regions,  $T_C = 0$ ,  $T_H = 50$ ,  $K = 1.0 + 0.02T$ ,  $A = 0.6$ .

phase with each other. Thus some separation can be achieved between these two solutes even though one of them must be separated at a non-optimum value of  $A$ . In Fig. 9 the effect of  $A$  is shown for this system. As expected the optimum  $A$  is slightly less than  $f_H$  and the maximum separation is less than that shown in Fig. 4 because the maximum temperature variation has been decreased.

The effect of uneven cycles was also studied for the 160-stage system shown in Fig. 3. The total number of transfers per cycle was unchanged, but  $S_H = 50$  and  $S_C = 110$  were used. This resulted in a very slight increase in  $\alpha_{\max}$  from 108.9 to 110.0 and changed the shape of the outlet concentration curve.

In the direct mode calculations<sup>7</sup> it was shown that the separation could be increased by having several regions. Pigford *et al.*<sup>1</sup> and Baker and Pigford<sup>3</sup> also found this to be true for both direct and traveling wave modes. In Fig. 10 the effect of increasing the number of regions for the CCD traveling wave mode is shown. There is an optimum number of transfers per half cycle to get reinforcement from zone to zone. This phenomenon also occurs in the direct mode of operation. For the same total number of stages the separation achieved is greater than that obtainable for a 1-region system even though a non-optimum value of  $A$  was used. For a given total number of stages there is an optimum number of regions. For this system with 40 stages the optimum separation is obtained with 4 regions and 10 stages per region as shown in Fig. 10.

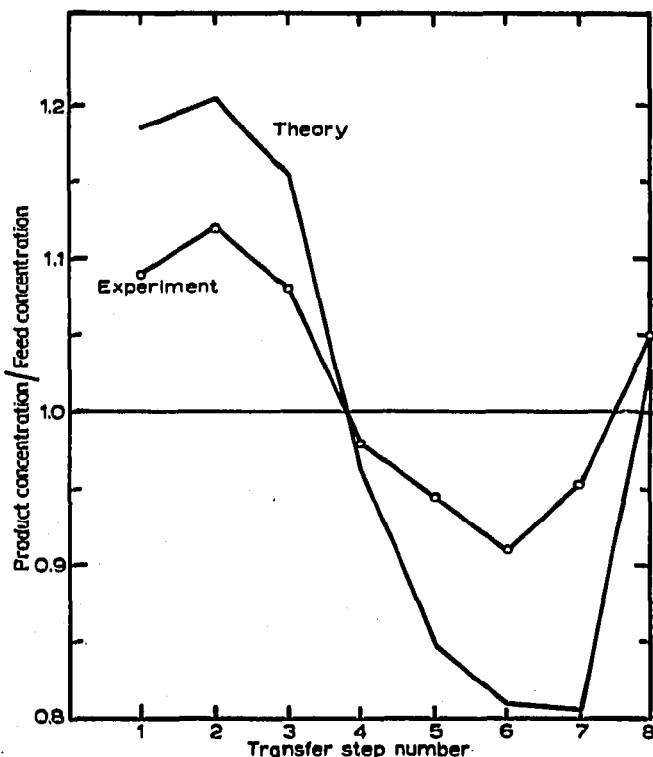


Fig. 11. Comparison of experimental and theoretical results for an all-glass system. Experiment: diethylamine-water-toluene,  $T_c = 0$ ,  $T_H = 28$ , 3 stages/region, 1 region,  $S_c = S_H = 4$ , Theory:  $K = 4.63 - 0.163T + 0.001707T^2$ ,  $A = 0.466$ .

The theoretical and experimental results for the all-glass system are shown in Fig. 11 and for the system with glass tubes and plastic caps in Fig. 12. Since very little separation was obtained in the all-plastic system, these results will not be shown. In Fig. 11 there is good qualitative agreement between theory and experiment although less separation was achieved than was predicted. Qualitative agreement in Fig. 12 is

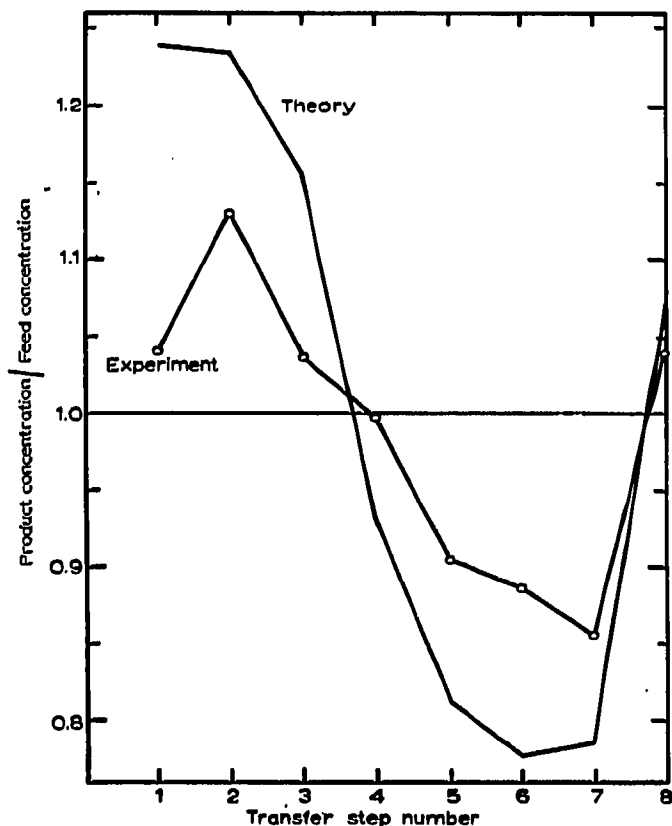


Fig. 12. Comparison of experimental and theoretical results for a system with glass tubes and polyethylene caps. Experiment: diethylamine-water-toluene,  $T_C = 0$ ,  $T_H = 28$ , 3 stages/region, 1 region,  $S_C = S_H = 4$ . Theory:  $K = 4.63 - 0.163T + 0.001707T^2$ ,  $A = 0.516$ .

not as good possibly because of increased experimental errors. Both the theoretical and experimental separations shown in Fig. 12 are greater than those in Fig. 11. This is due to the increased value of  $A$  although  $A$  is less than  $f_H$  in both cases. Note that this chemical system has  $K_C > K_H$ . The separations obtained here were less than the direct mode separations<sup>7</sup> because the value of  $A$  was too small to be optimum.

## DISCUSSION

Perfect agreement between theory and experiment was not expected because the theory did not include the concentration dependence of the distribution coefficient.



cient. However, better agreement could be achieved by better control of heat losses and gains and by controlling evaporation. This could be done in a closed, automated CCD apparatus, but the resulting  $A$  values might be small due to the large amount of glass involved.

Comparison with the direct mode results shows that if the thermal wave velocity,  $A$ , can be adjusted to be close to optimum, the traveling wave mode will result in larger separations. Even larger separations can be obtained by using heat exchangers between several regions. Recycle of some of the streams to different heat exchangers can also increase the separation<sup>4</sup>. This would be particularly applicable to those streams whose concentrations are close to the feed concentration.

The separations studied here involved a single solute contained in an immiscible diluent. Two solutes could be separated from each other if their distribution coefficients shifted in opposite directions with temperature changes. If the shift of the distribution coefficient was in the same direction for both solutes, a partial separation could be achieved. Continuous multicomponent separations might be achieved by superimposing one or more waves of pH, ionic strength or other thermodynamic variable on top of the thermal wave. This might give a multiple solvent elution effect and needs to be investigated further.

Although a CCD apparatus was used in these studies, cycling zone separation techniques are also applicable in column chromatographic systems. Pigford and his coworkers<sup>1-4</sup> have studied adsorption systems extensively. Extension to gas-liquid and liquid-liquid chromatography should be relatively straightforward. The theoretical results developed here for CCD should be applicable to chromatographic systems if the number of theoretical plates is relatively large. One question that needs to be answered is what effect, if any, does use of this cycling technique have on the HETP. Cycling zone techniques may represent an alternative chromatographic preparative technique for relatively easy separations.

#### ACKNOWLEDGEMENTS

The experimental assistance of Mr. Walter Mueller is gratefully acknowledged. This work was partially supported by NSF Grant No. GK-32681.

#### REFERENCES

- 1 R. L. Pigford, B. Baker and D. E. Blum, *Ind. Eng. Chem., Fundam.*, 8 (1969) 848.
- 2 B. Baker, *Ph.D. Thesis*, University of California, Berkeley, 1969.
- 3 B. Baker and R. L. Pigford, *Ind. Eng. Chem., Fundam.*, 10 (1971) 283.
- 4 R. D. Rieke, *Ph.D. Thesis*, University of California, Berkeley, 1972.
- 5 R. Gupta and N. H. Sweed, *Ind. Eng. Chem., Fundam.*, 10 (1971) 280.
- 6 E. van der Vlist, *Separ. Sci.*, 6 (1971) 727.
- 7 P. C. Wankat, *Separ. Sci.*, 8 (1973) 473.
- 8 N. H. Sweed, in E. S. Perry and C. J. van Oss (Editors), *Progress in Separation and Purification*, Vol. 4, Wiley, New York, 1971, pp. 171-240.
- 9 C. W. Skarstrom, *Ann. N.Y. Acad. Sci.*, 72 (1959) 751.
- 10 R. W. Alexis, *Chem. Eng. Prog.*, 63 (1967) 5, 69.
- 11 L. H. Shendalman and J. E. Mitchell, *Chem. Eng. Sci.*, 27 (1972) 1449.
- 12 A. A. Zhukovitskii, in R. P. W. Scott (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, pp. 293-300.
- 13 D. W. Thompson, *Trans. Inst. Chem. Eng.*, 39 (1961) 289.

- 14 F. Helfferich and G. Klein, *Multicomponent Chromatography: Theory of Interference*, Marcel Dekker, New York, 1970, pp. 210-219.
- 15 L. C. Craig and D. Craig, in A. Weissberger (Editor), *Technique of Organic Chemistry*, Vol. 3. Interscience, New York, 1956, pp. 149-332.
- 16 C. N. Reilley, G. P. Hildebrand and J. W. Ashley, *Anal. Chem.*, 34 (1962) 1198.
- 17 K. C. Williams and S. R. M. Ellis, *J. Appl. Chem.*, 11 (1961) 492.