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Phillip C. Wankat[a]
[a] SCHOOL OF CHEMICAL ENGINEERING PURDUE UNIVERSITY, WEST LAFAYETTE, INDIANA

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Cycling Zone Extraction

PHILLIP C. WANKAT

SCHOOL OF CHEMICAL ENGINEERING
PURDUE UNIVERSITY
WEST LAFAYETTE, INDIANA 47907

Abstract

Cycling zone separation techniques are extended to extraction systems using a system with discrete transfer and equilibrium steps. Experimentally, the direct thermal mode was used to separate diethylamine from water using toluene as the stationary solvent. A staged theory was developed and used to investigate the effects of the variables. The separation occurs in waves and requires proper spacing of the temperature changes to obtain optimum separation. Agreement between experiment and theory was fair.

INTRODUCTION

Recently, there has been considerable interest in separation processes which utilize the cyclic variation of a thermodynamic variable to achieve separation. These processes, such as parametric pumping and cycling zone adsorption, have been applied almost exclusively to adsorption or chromatographic separation systems, but there is no reason why this restriction must be adhered to. In addition, attention has been focused on continuous contact systems, but again there is no reason why staged or discrete contact systems cannot be employed.

Parametric pumping, which was first reported by Wilhelm et al. (*1*, *2*), consists of flowing the fluid to be separated back and forth through a stationary phase in sequence with changes of a thermodynamic variable such as temperature. The reason for the separation has been clearly explained using a simple analogy by Patrick et al. (*3*), and a simple equilibrium theory was developed by Pigford et al. (*4*). Considerable effort has been expended since 1966 in extending parametric pumping to gas separations, ion exchange separations, continuous and semicontinuous operation, traveling wave separations, and use of variables besides temperature as the forcing variable. Much of this work is discussed in the review article by Sweed (*5*).

Cycling zone adsorption is similar to parametric pumping, but involves pumping the fluid to be separated in only one direction through a series of beds containing a stationary adsorbent. The beds have some thermodynamic variable such as temperature varied periodically. This technique was invented by Pigford et al. (*6*) and was considered in more detail by Baker and Pigford (*7*). In addition, Gupta and Sweed (*8*) developed an equilibrium theory for cycling zone adsorption and Van der Vlist (*9*) separated oxygen and nitrogen using cycling zone adsorption.

Developments quite similar to parametric pumping and cycling zone adsorption have been reported in the past. Skarstrom (*10*), Alexis (*11*), and Shendalman and Mitchell (*12*) all studied heatless adsorption systems which used pressure swings to achieve separation. Zhukhovitskii (*13*) developed chromathermography which used a rotating heater on a chromatography column. Thompson (*14*) developed a continuous chromatograph where the feed concentration in the carrier gas was varied sinusoidally instead of being fed as a pulse.

All of the previously cited work has been concerned with separation of components of a mobile fluid phase using a stationary solid phase. The cyclic separation techniques can also be applied to separation of components in a mobile fluid phase using a stationary fluid phase. Wankat (*15*) studied liquid–liquid extraction parametric pumping in staged systems. Both continuous flow staged systems and discrete transfer staged systems (similar to a Craig countercurrent distribution apparatus) were used. That study proved that liquid–liquid extraction parametric pumping works and indicated that cycling zone extraction systems should be studied.

In this paper the cycling zone technique is extended to extraction using direct heating and cooling to force the separation. Experimental and theoretical work was done for a staged system with discrete and separate transfer and equilibrium steps. This is essentially the conversion of countercurrent distribution (CCD) to a cycling zone separation. Although this work was done for discrete transfer steps, the results should be qualitatively valid for staged continuous flow systems. A cycling zone extraction system has the advantage that no separate solvent removal step is required. It also provides a simple method of obtaining continuous production from CCD.

CYCLING ZONE EXTRACTION

A schematic diagram of the staged cycling zone extraction system is shown in Fig. 1. This system consists of $n \times m$ stages arranged into m regions with n stages per region. Operation was in the direct mode (*6*, *7*) where all stages in a region are held at the same temperature. After the desired number of transfer steps, the temperature of each region is switched from hot to cold or vice versa. For the first half of each cycle the temperatures of the regions would be hot, cold, hot, cold, hot, etc. and for the second half of each cycle the temperatures are cold, hot, cold, hot, cold, hot, cold, etc. This alternation of temperatures in time and in space causes a variation in the equilibrium distribution coefficient. This in turn causes the regions to alternately store and reject the solute and causes the solute to be concentrated in part of the cycle and depleted in the rest of the cycle. In order to acheive a maximum separation the period (number of transfer steps) for each cycle and the natural rate of movement of the solute must be synchronized. The addition of more regions causes an increase in separation.

Operation of the cycling zone extractor studied here was with a simultaneous transfer of the mobile phase from each stage followed by a separate equilibrium step. At the end of each half cycle the temperature of each region is changed and all stages are allowed to come to equilibrium. Feed is fed continually (at each transfer step) to the first stage. This method then constitutes a continual method for obtaining chromatographic separations.

An alternate method of operation called the traveling wave mode (*6*, *7*) involves heating and cooling the feed instead of the stages of each region. Heat exchangers are utilized between regions. Studies with adsorption systems (*6*, *7*) show that the traveling wave mode should have great promise. Use of the traveling wave mode for cycling zone extraction is not reported in this paper, but is currently being studied.

THEORY

The theory for cycling zone extraction in a staged system in the direct thermal mode with discrete and separate transfer and equilibrium steps relies heavily upon the long established theory for countercurrent distribution (16). Assume that the solutes are present in low enough con-

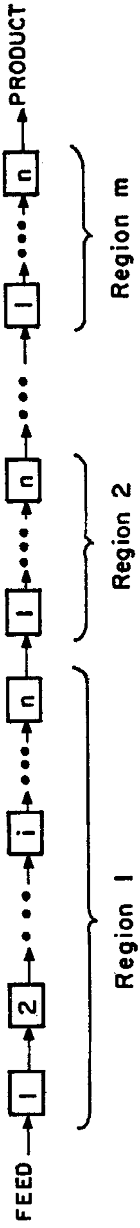

FIG. 1. Staged cycling zone extraction system.

centrations so that the solutes do not interact with each other and the distribution coefficients are independent of concentration. All equations and definitions will be written for a single solute.

The cycling zone extraction 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 the region number. When Region 1 is hot the system is in the first half of the cycle and when Region 1 is cold the system is in the second half of the cycle. The cycle "halves" are not necessarily equal. There are s_1 transfer steps in the first half cycle and s_2 transfer steps in the second half cycle. The total number of transfers per cycle is $s_T = s_1 + s_2$. Define V_M and V_S as the volume of moving phase and of stationary phase per stage, respectively. V_M and V_S will be assumed to be constant. C_M and C_S are the concentrations of moving and stationary phases, respectively. The distribution coefficient defined as $K(T) = C_M/C_S$ depends on temperature but is independent of concentration. Let $M_{i,j,s}$ be the mass of solute in Stage i of Region j after Transfer Step s. 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 (*16*) that the fraction of solute in the moving phase is given as

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

Unlike CCD, $f_{i,j,s}$ is not constant for all stages since the temperature varies from region to region and with time. $f_{i,j,s}$ is calculated after the Transfer Step s and *after* any temperature changes have been made. 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.

A mass balance can be written to calculate the mass of solute in Stage i of Region j after Transfer Step s. If $i \neq 1$, the mass balance is

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

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

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

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

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

where C_{Feed} is the concentration of solute in the feed. The f values in Eqs. (2), (3) and (4) will be either f_H corresponding to a stage at the hot temperature T_H, or f_C corresponding to a stage at the cold temperature T_C. We would like to find the concentration of the product leaving stage (n,m) after each transfer step. In order to do this, the initial conditions must be specified. If all stages initially contain no solute, the initial conditions are

$$M_{i,j,0} = 0 \qquad \text{for } i,j \geqq 1, \text{ Cycle } \# = 0 \tag{5}$$

A straightforward solution can be obtained by using Eqs. (2) to (4) as recurrsion relations with initial conditions given by Eq. (5). When this is done, an additional subscript must be added to M in order to count the number of cycles. This was not done in Eqs. (2) to (5) because the cycling zone extractor will eventually reach a limiting condition where each cycle is an exact repeat of the cycle before it. This was proven both theoretically and experimentally, and is reasonable since with a periodic input into the system a periodic output would be expected eventually. For adsorption systems the occurrence of this limiting condition has been proved by Lavie and Rielly (*17*).

Since the major objective of this work was to study continuous separations in cycling zone extraction, most of the calculations and results are concerned with the limiting periodic conditions. The start-up behavior will be discussed when the theoretical and experimental results are compared. For the periodically steady results an alternate solution method can be employed that uses the fact that $M_{i,j,s}$, $T_{i,j,s}$, and $f_{i,j,s}$ are the same from cycle to cycle. For one cycle the mass balances for stage (i,j) can be written as

$$\begin{aligned}
f_{i-1,j,s_T}M_{i-1,j,s_T} + (1 - f_{i,j,s_T})M_{i,j,s_T} &= M_{i,j,1} \\
f_{i-1,j,1}M_{i-1,j,1} + (1 - f_{i,j,1})M_{i,j,1} &= M_{i,j,2} \\
&\vdots \\
f_{i-1,j,s_T-1}M_{i-1,j,s_T-1} + (1 - f_{i,j,s_T-1})M_{i,j,s_T-1} &= M_{i,j,s_T}
\end{aligned} \tag{6}$$

where we have assumed that $i \neq 1$.

If $i = j = 1$, then the first term on the left-hand side of Eqs. (6) is $V_M C_{\text{Feed}}$. For i or $j \neq 1$, the first term on the left-hand side of Eqs. (6) will be known if we start our calculations at Stage (1, 1) in Fig. 1 and work to the right. Since these terms are known, we can define them as the feed to Stage (i,j) for the transfer step being calculated. Thus

$$\begin{aligned}
\text{Feed}_1 &= f_{i-1,j,s_T}M_{i-1,j,s_T} \\
\text{Feed}_s &= f_{i-1,j,s-1}M_{i-1,j,s-1} \qquad s = 2, \ldots, s_T - 1 \\
\text{Feed}_{s_T} &= f_{i-1,j,s_T-1}M_{i-1,j,s_T-1}
\end{aligned} \tag{7}$$

If $i = 1$, then the obvious changes in Eqs. (6) and (7) should be made. With the definition of the term Feed_s, Eqs. (6) are now

$$\begin{aligned}\text{Feed}_1 + (1 - f_{i,j,s_T})M_{i,j,s_T} &= M_{i,j,1}\\ \text{Feed}_s + (1 - f_{i,j,s-1})M_{i,j,s-1} &= M_{i,j,s} \qquad s = 2,\cdots, s_T - 1 \quad (8)\\ \text{Feed}_{s_T} + (1 - f_{i,j,s_T-1})M_{i,j,s_T-1} &= M_{i,j,s_T}\end{aligned}$$

In Eq. (8) there are s_T variables $M_{i,j,s}$ for $s = 1, ..., s_T$ and s_T equations. We can develop a solution for $M_{i,j,1}$ and then use Eqs. (8) to solve for $M_{i,j,2}$, $M_{i,j,3}$, etc. To solve for $M_{i,j,1}$ we first remove M_{i,j,s_T}, then M_{i,j,s_T-1}, then M_{i,j,s_T-2}, etc. from Eqs. (8) by direct substitution. After some rearrangement, the solution is found as

$$\begin{aligned}M_{i,j,1} = {} & [\text{Feed}_1 + (1 - f_{i,j,1})\text{Feed}_{s_T} + (1 - f_{i,j,1})(1 - f_{i,j,s_T})\text{Feed}_{s_T-1}\\ & + (1 - f_{i,j,1})(1 - f_{i,j,s_T})(1 - f_{i,j,s_T-1})\text{Feed}_{s_T-2} + \cdots\\ & + (1 - f_{i,j,1})(1 - f_{i,j,s_T})(1 - f_{i,j,s_T-1}) \cdots (1 - f_{i,j,3})\text{Feed}_2]\\ & /[1 - (1 - f_{i,j,1})(1 - f_{i,j,2}) \cdots (1 - f_{i,j,s_T})] \qquad (9)\end{aligned}$$

Once Eq. (9) has been solved, it gives the mass of solute in Stage (i,j) after the first transfer step of every cycle after the repeating state was obtained.

Unfortunately, even at the repeating state the solution depends upon the six variables n, m, s_1, s_2, f_H, and f_C. Thus before considering the complex results it would be a good idea to obtain a qualitative feel for what the results will look like. This qualitative picture can be achieved by considering the rate of movement of the solute through the system. Since f is the fraction of solute in the moving phase, the average distance that solute will move is $f \times$ (number of transfer steps). This result is also found in CCD theory (*16*). The separation is forced when the temperature within a region is changed and solute is either rejected or stored by the stationary solvent. To get the best separation each solute molecule should, on the average, go through one temperature change in each region. If it goes through two temperature changes, they will tend to cancel each other out and the separation achieved will be a minimum. With three changes of temperature the separation should then increase above the minimum and so on. If there is less than one change per region, then some solute molecules miss the temperature changes and the separation is decreased. In order for each solute molecule to experience one and only one temperature change per region we want

$$\frac{f(\text{number of transfers/half cycle})}{(\text{number of stages/region})} = 1 \qquad (10)$$

Since f varies, Eq. (10) cannot be used for an exact calculation of the optimum number of transfers/half cycle, but limits can be put on the optimum. Assuming that $f_H > f_C$, these limits are

$$\frac{\text{(number of stages/region)}}{f_C} \geqq \begin{array}{l}\text{(optimum number of}\\ \text{transfers/half cycle)}\end{array} \geqq \frac{\text{(number of stages/region)}}{f_H} \tag{11}$$

If $f_C > f_H$, the inequalities in Eq. (11) will be reversed. For the separation minimum and subsequent maxima and minima the limits given in Eq. (11) can be multiplied by 2, 3, 4, etc. Also, the narrower the limits in Eq. (11), the sharper we would expect the optimum to be.

When the results are presented, we will see that this simple argument based on the velocity of solute movement through the system does a good job of predicting the separation behavior. Before presenting the results, the experimental work will be discussed.

EXPERIMENTAL

In the experiments diethylamine in water was separated using toluene at the stationary solvent. The objective was to concentrate most of the diethylamine in half the water and purify the remaining water. This particular chemical system was chosen since there is a significant change in the distribution coefficient with temperature (*18*) and the concentration of amine can easily be determined by titration.

The apparatus used consisted of stoppered 15 ml centrifuge test tubes suspended in a constant temperature bath. The test tubes were initially stoppered with corks, but these reacted with the amine so glass stoppers were used for the later work. The cold bath was at 0 °C while the hot bath was at 28 °C. The moving water phase was transferred from stage to stage with a 10-ml B-D syringe. With the conical bottom of the tubes a very accurate separation of phases was obtained. The product concentrations were analyzed by titration with HCl using Methyl Red as the indicator. Additional equilibrium data was taken to supplement the data available in the literature (*18*). The distribution coefficients were found to be both temperature and concentration dependent. The volumes of the moving and stationary phase were equal to 5 ml each.

Five runs were made starting with the initial condition of no amine in each stage and continuing until the repeating solution was approximately reached. The systems tried had 3 stages/region, 3 transfers/half cycle and 2 regions; 3 stages/region, 3 transfers/half cycle and 1 region; and 6 stages/region, 6 transfers/half cycle and 1 region. The results for the last two systems are more accurate since they were obtained in the all glass systems instead of with the cork stoppers. For the experimental conditions used, $f_C = 0.824$ and $f_H = 0.582$ at the feed concentration of 0.4226 g mole/liter. Variation of f_C and f_H over the entire concentration range was a few percent.

Some loss of the toluene phase occurred due to evaporation. At 28 °C settling of the phases was hindered by the formation of a white emulsion at the interface. In addition, experimentation was very slow and tedious due to the many individual transfer steps that had to be made, and the long time required to reach the repeating state. A properly modified CCD apparatus would decrease the error and greatly reduce the drudgery of the experimental work.

RESULTS

Figures 2 through 11 show the theoretical results while Figs. 12 to 15 compare the experimental results to the theoretical predictions. This large number of figures is necessary to show the effect of all the variables. All of the theoretical results shown were obtained from the unsteady solution of Eqs. (2) to (5). Many more theoretical results were obtained than are shown here.

Figures 2, 3, and 4 show the product concentrations over an entire cycle for a system with 5 stages/region, 4 regions, $f_C = 0.5$ and $f_H = 0.6$. Symmetric cycles have been used with 10, 17, or 28 transfers per half cycle. By comparing these figures we see that 10 transfers/half cycle gives the best separation and 17 transfers/half cycle the worst. With 17 transfers/half cycle there is considerable cancellation of the separation effect. Figure 4 is interesting since it shows approximately one and one-half complete separation waves exiting from the system for each half cycle. Since $f_H > f_C$, we would expect the solute to be released when a region was hot. This is clearly the case in Fig. 2 where the maximum concentration occurs in the portion of the cycle where the product is leaving a hot region. In Figs. 3 and 4 the more complex interactions tend to obscure this point. Figure 5 shows the maximum and minimum product concentrations plotted versus the number of transfers/half cycle. This shows a maximum separation at approximately 10 transfers/half cycle and a minimum separation at 18 which agrees with Figs. 2 and 3. The predicted optimum separation from Eq. (11) is between 8-1/2 and 10 stages. Thus Figs. 2, 3,

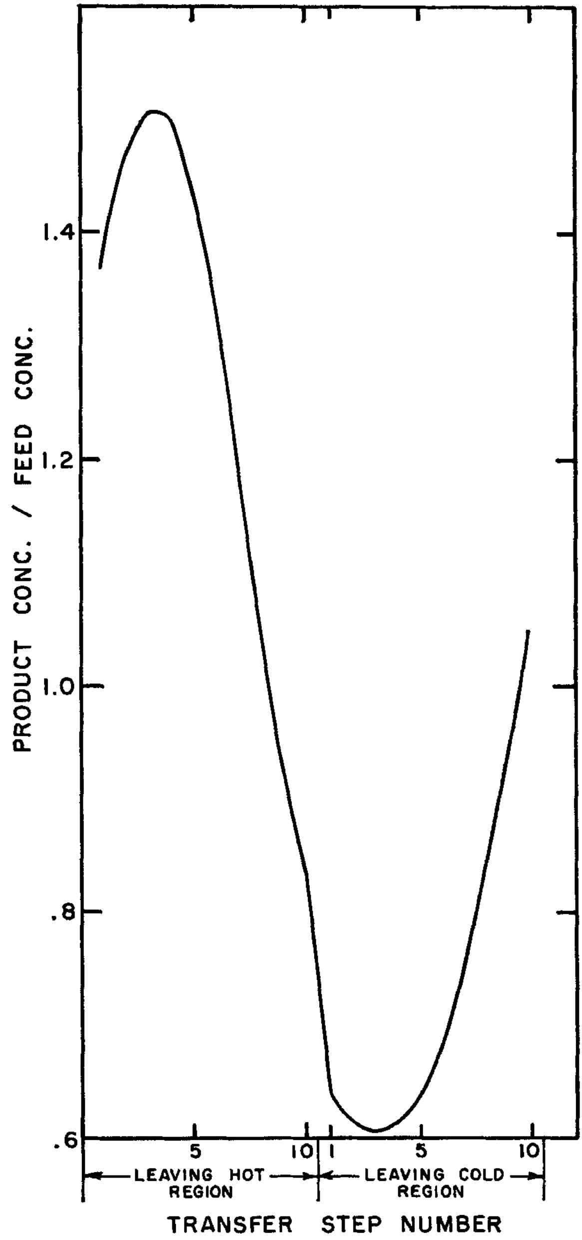

FIG. 2. Product concentrations for a complete cycle: 5 stages/region, 4 regions, $f_C = 0.5$, $f_H = 0.6$, 10 transfers/half cycle.

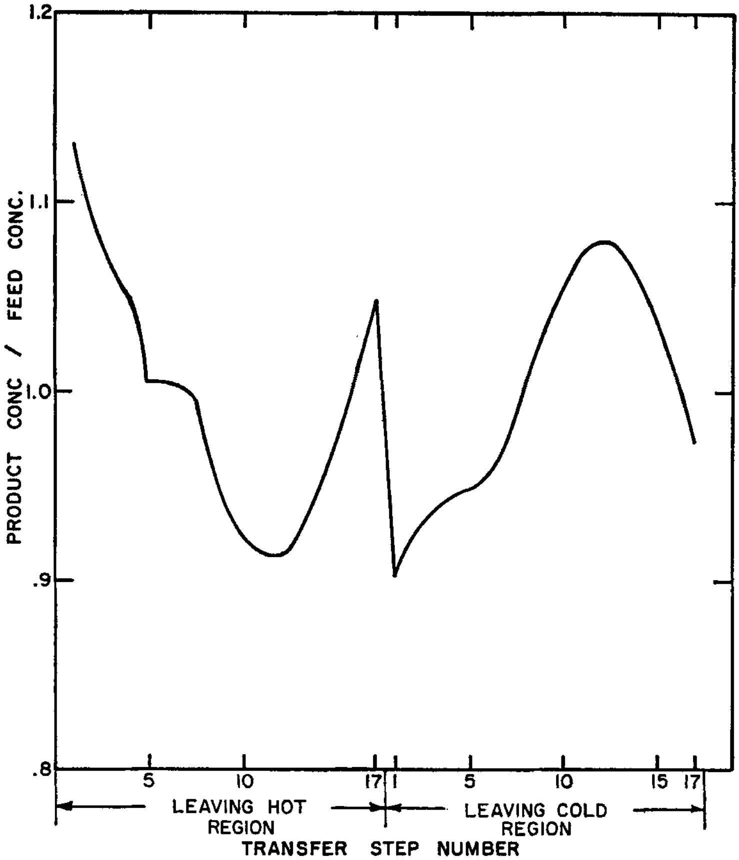

FIG. 3. Product concentrations for a complete cycle: 5 stages/region, 4 regions, $f_C = 0.5$, $f_H = 0.6$, 17 transfers/half cycle.

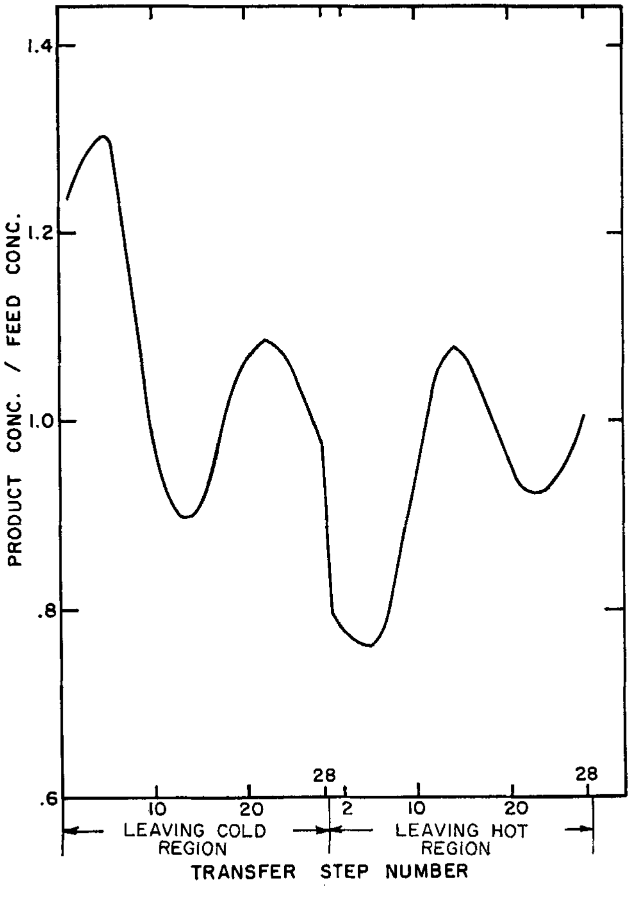

FIG. 4. Product concentrations for a complete cycle: 5 stages/region, 4 regions, $f_C = 0.5$, $f_H = 0.6$, 28 transfers/half cycle.

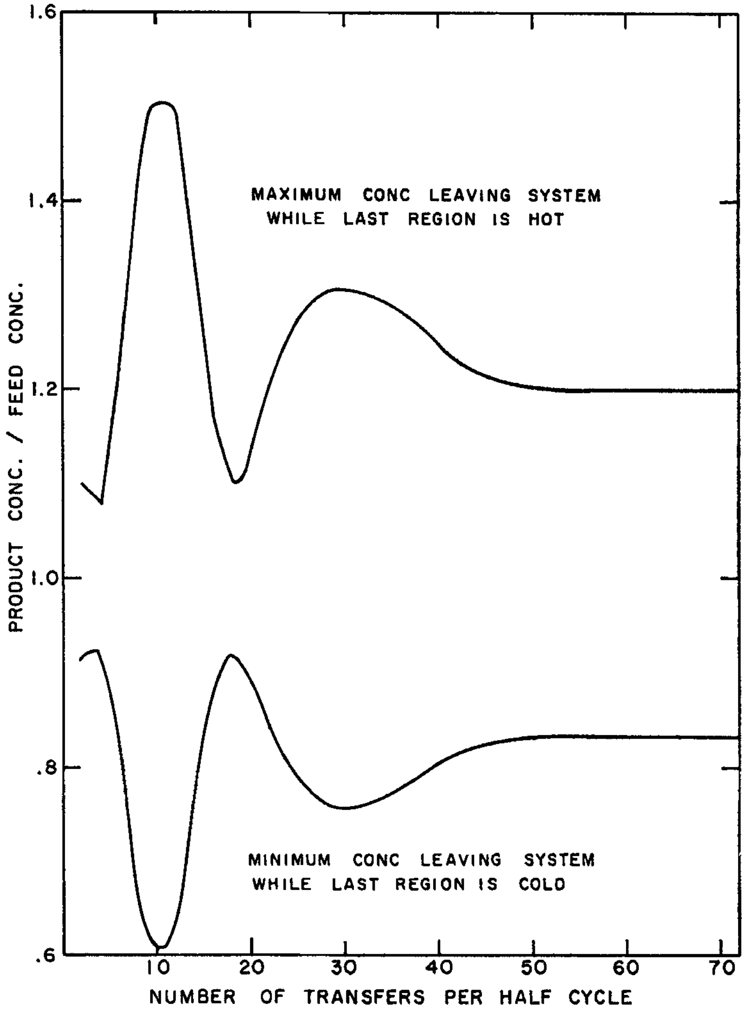

FIG. 5. Maxima and minima product concentrations as a function of the number transfers per half cycle: 5 stages/region, 4 regions, $f_C = 0.5$, $f_H = 0.6$.

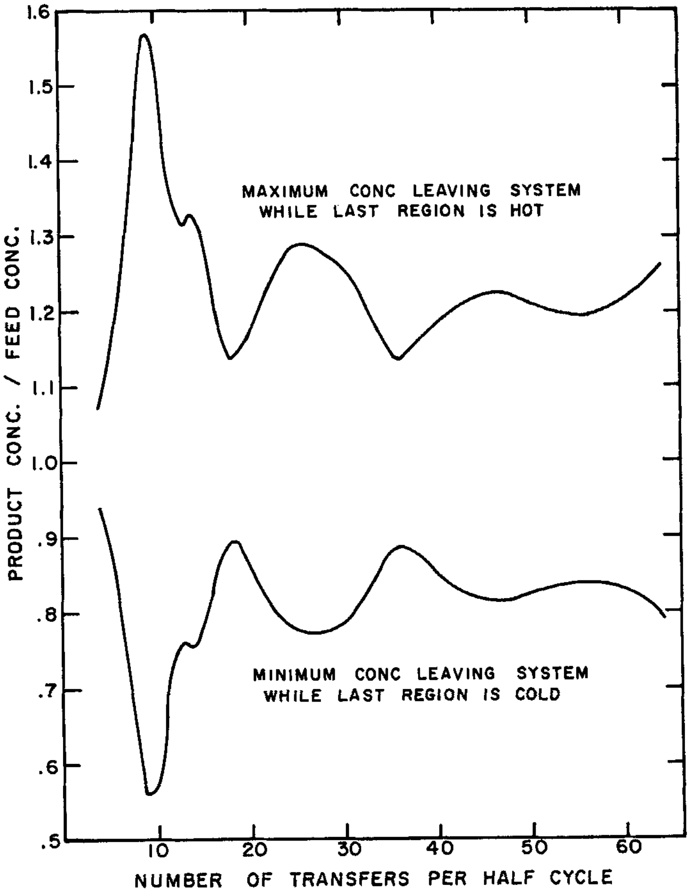

FIG. 6. Maxima and minima product concentrations as a function of the number of transfers per half cycle: 5 stages/region, 8 regions, $f_C = 0.5, f_H = 0.6$.

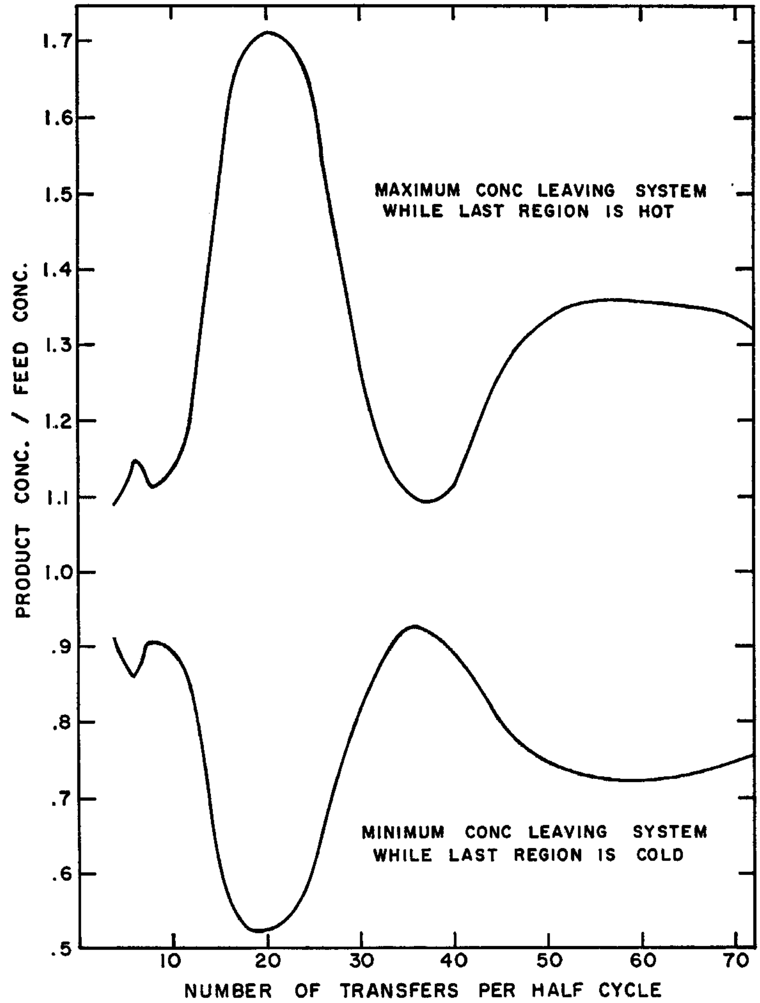

FIG. 7. Maxima and minima product concentrations as a function of the number of transfers per half cycle: 10 stages/region, 4 regions, $f_C = 0.5$, $f_H = 0.6$.

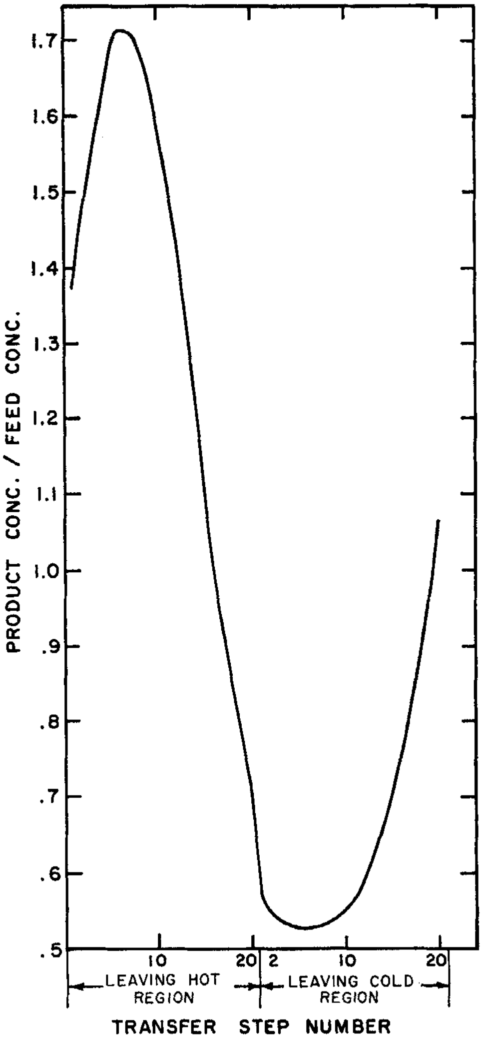

FIG. 8. Product concentrations for a complete cycle: 10 stages/region, 4 regions, $f_C = 0.5$, $f_H = 0.6$, 20 transfers/half cycle.

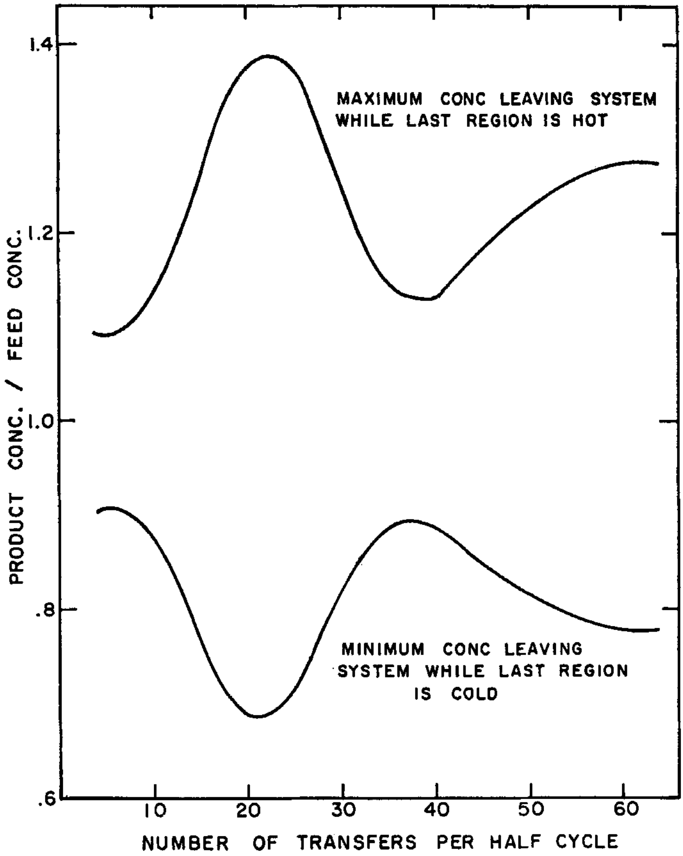

FIG. 9. Maxima and minima product concentrations as a function of the number of transfers per half cycle: 5 stages/region, 4 regions, $f_C = 0.25$, $f_H = 0.3$.

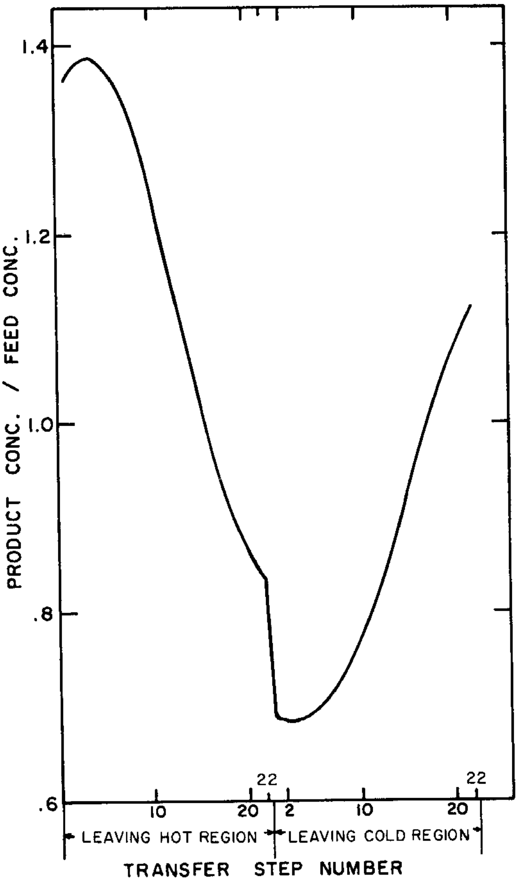

FIG. 10. Product concentrations for a complete cycle: 5 stages/region, 4 regions, $f_C = 0.25$, $f_H = 0.3$, 22 transfers/half cycle.

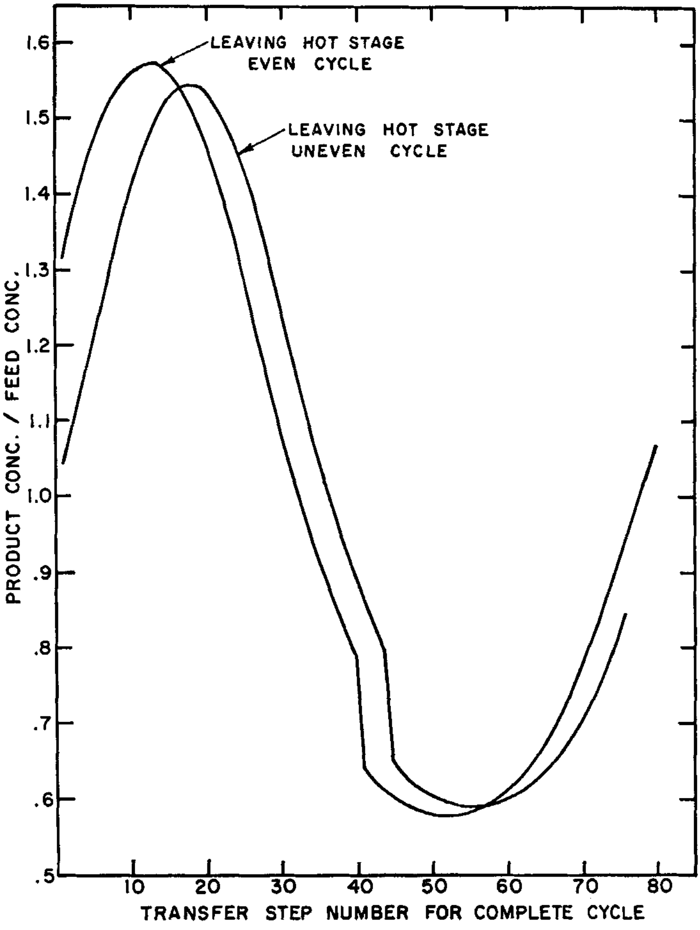

FIG. 11. Comparison of even and uneven half cycles: 10 stages/region, 4 regions, $f_C = 0.25$, $f_H = 0.3$. Even half cycles: 40 transfers/half cycle. Uneven: hot, 44 transfers; cold, 32 transfers.

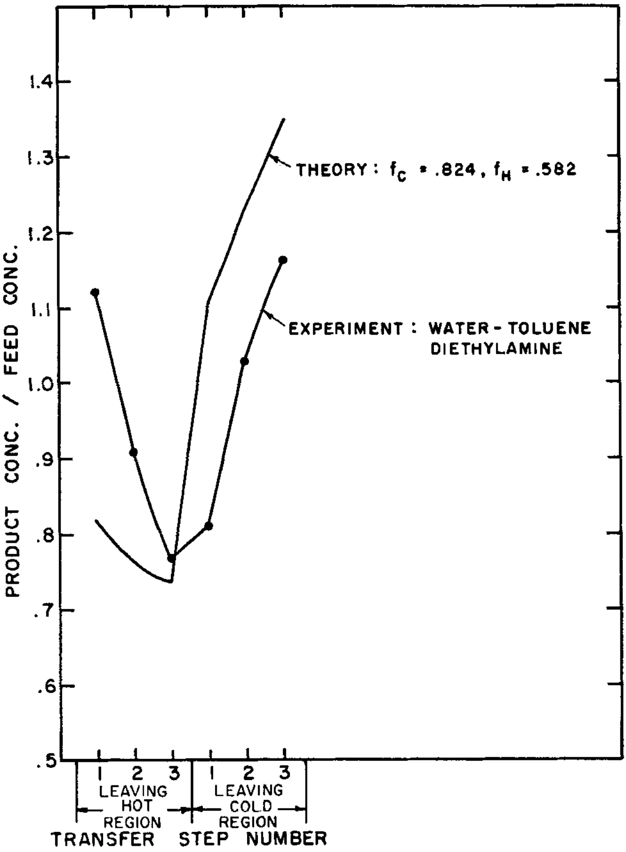

FIG. 12. Comparison between theory and experiment for diethylamine–water–toluene system: 3 stages/region, 1 region, 3 transfers/half cycle.

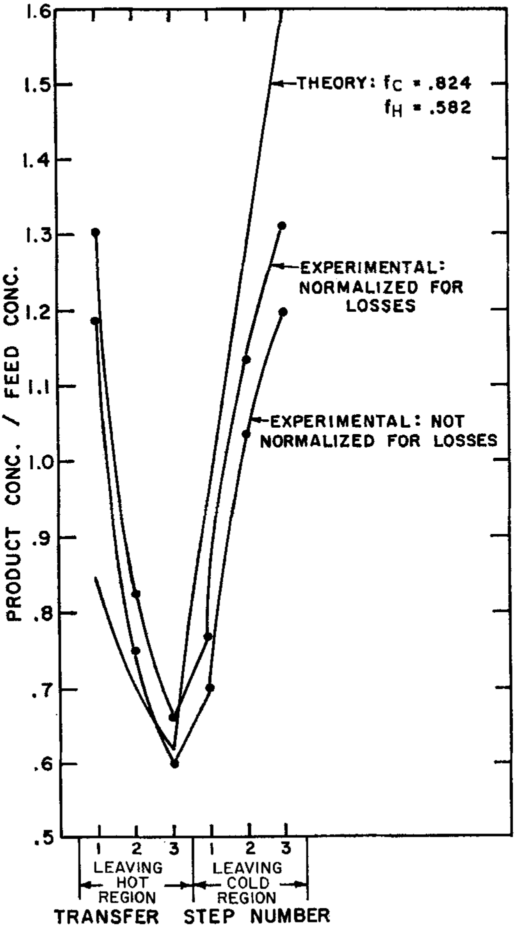

FIG. 13. Comparison between theory and experiment for diethylamine–water–toluene system: 3 stages/region, 2 regions, 3 transfers/half cycle.

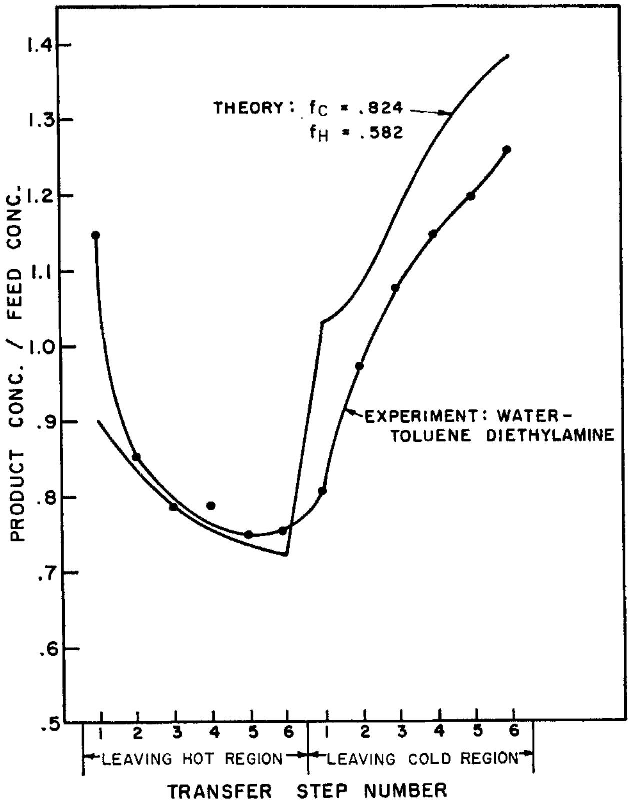

FIG. 14. Comparison between theory and experiment for diethylamine–water–toluene system: 6 stages/region, 1 region, 6 transfers/half cycle.

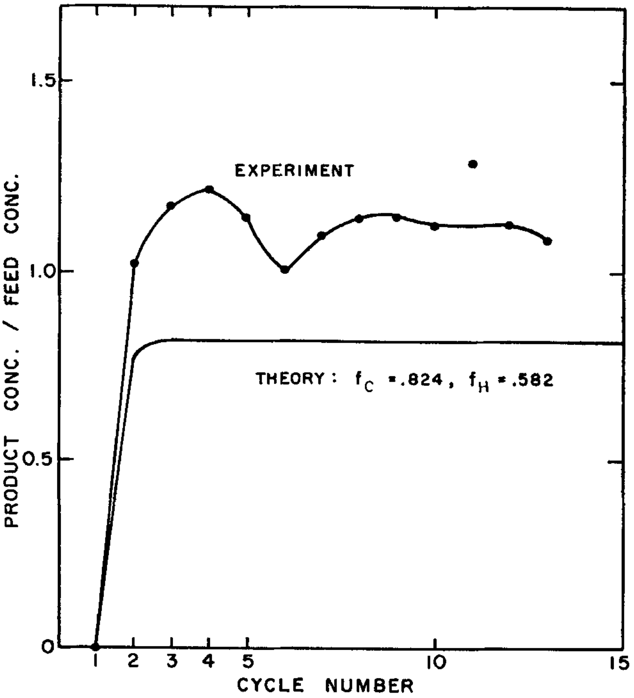

FIG. 15. Comparison between theory and experiment for unsteady development with diethylamine–water–toluene system. Product is from the first transfer step of each cycle: 3 stages/region, 1 region, 3 transfers/half cycle.

and 4 can be interpreted as having one, two, or three complete waves exiting from the system for each full cycle. With one wave there is maximum separation, with two waves maximum interference, and with three waves some interference and some separation. With only one region the results are somewhat different in that there is no optimum number of transfers per half cycle. This is reasonable since the waves passing through the single region do not have to be timed to enter the second region in sequence with heating and cooling.

The effect of changing the number of stages/region and the number of regions is shown in Figs. 6, 7 and 8. Figures 6 and 7 show the maxima and minima product concentrations as a function of number of transfers/half cycle and should be compared with Fig. 5. Increasing the number of regions will increase the separation but has little effect on the location of the maxima and minimum. Increasing the number of stages/region also increases the separation and changes the locations of minima and maxima. With a given total number of stages the tradeoff between stages/region and number of regions is not clearcut. Comparison of Figs. 6 and 7 indicates that in this case more stages/region is desirable. However, results with 20 stages/region and 2 regions showed less separation than in either Fig. 6 or 7. Thus a balance between the number of stages/region and the number of regions must be achieved. Figure 8 shows the product concentrations for a complete cycle for a system with 10 stages/region, 4 regions, $f_C = 0.5$, $f_H = 0.6$, and 20 transfers/half cycle. Comparison with Fig. 2 shows that the shapes of the curves are quite similar except more separation was obtained in Fig. 8.

Next the effect of variation of the equilibrium parameters f_C and f_H was studied. For the previous results with $f_H > f_C$ the distribution coefficient must increase as the temperature is increased, $K_H > K_C$. For this case we found that the solute was concentrated when product was withdrawn from a hot region. If $K_C > K_H$, we would expect that the solute would be concentrated when product was withdrawn from a cold region. This was tried for $f_C = 0.6$ and $f_H = 0.5$ with other conditions the same as in Fig. 2. The resulting product concentrations were exactly like those in Fig. 2 except that they were shifted half a cycle and the solute was more concentrated when leaving a cold region. This result indicates that separation of two solutes should be easy if their distribution coefficients shift in opposite directions with temperature.

The effect of varying f_C and f_H with $f_H > f_C$ is shown in Figs. 9 and 10. Comparison of Figs. 9 and 5 show that as predicted by Eq. (11) the maxima and minima are shifted. Also less separation is achieved for the lower f

values even though the ratio of f_C/f_H was kept constant. Figure 10 shows the best separation that can be achieved over an entire cycle with $f_C = 0.25$ and $f_H = 0.3$. Complete separation of this solute from a solute with $f_C = 0.5$ and $f_H = 0.6$ would be difficult since the curves are roughly in phase with each other.

In Fig. 11 the separation achieved with symmetric and unsymmetric cycles is compared for a system with $f_C = 0.25$ and $f_H = 0.30$. There does not appear to be any advantage to use unsymmetric cycles in this case.

The comparison between the experimental results and theoretical predictions are shown in Figs. 12 to 15. In all runs the experimental results agreed qualitatively with the theoretical predictions, except that the concentration jump for temperature changes was much smaller than predicted. The theoretical results predicted more separation than was achieved. In all experimental runs there was some loss of amine due to evaporation, spillage, or reaction with the corks. In Figs. 12 and 15 this loss (measured by a mass balance) was 3.3%, in Fig. 13 the loss was 8.8%, and in Fig. 14 the loss was 4.0%. The large loss in Fig. 13 was due to reaction of the amine with the corks while the other results were obtained in all-glass systems. An attempt to correct for the reaction loss was made by normalizing the experimental data to correct for the losses. This normalized curve satisfies the mass balance and will be used for comparison with the other figures. For the results shown in Fig. 14, Stage (2, 1) was broken and its contents were replaced by feed mixture. As expected from CCD experience (*16*), this did not appear to affect the final results.

A comparison of the experimental results shows that increasing the number of stages also increases the separation. A system with 3 stages/region and 2 regions gives somewhat better separation than the system with 6 stages/region and only 1 region. This illustrates the increased separation achievable due to the multiplying effect of regions.

In Fig. 15 a comparison of the experimental and theoretical results is shown for the unsteady buildup to the limiting repeating state. The product concentration for the first transfer step of each cycle is shown for the same conditions shown in Fig. 12. The oscillation observed experimentally occurred in all of the experimental runs. This oscillation was unexpected and is not predicted by the theoretical calculations.

DISCUSSION

The work presented here certainly does not exhaust the subject of cycling zone extraction. The systems studied both theoretically and experimentally were quite small. Experimentally, small systems were necessitated by the lack of a CCD apparatus. As it was, a run could take several days using the syringe and test-tube equipment. Modification of CCD equipment for cycling zone studies would be relatively simple, requiring jackets around the tubes. In the theoretical calculations the cascade size and number of transfers per half cycle was limited by computer time. This problem could be greatly reduced by use of the limiting repeating solution presented previously, but unfortunately this solution was not developed until after the theoretical work was completed.

Perfect agreement between theory and experiment was not expected since the theory did not model the nonconstant distribution coefficients or the evaporation which occurred in the experimental system. However, agreement between theory and experiment could have been better. In particular, the experimentally observed oscillations and the small jump upon changing temperature need to be studied further. The theory and the probability explanation for rate of movement of solute do appear to explain the major effects that occurred.

Use of cycling zone extraction with continual feed for separation of two or more solutes does not appear to be too promising except when the distribution coefficients shift in opposite directions with temperature. When the shift is in the same direction, it does not appear to be possible to concentrate one solute in one product stream and to concentrate the other solute in the other product stream. Possibly this could be accomplished using unequal cycle times and variable heating of each region. The cycling zone system can remove one solute from one product stream while the second solute concentration is essentially unchanged. However, the other product stream would be a mixture of both solutes. In any case, future work is needed to study multicomponent separations.

All of the work presented here involved direct heating and cooling of each region. The "traveling wave" mode of operation (*6*, *7*) is currently being studied. This mode of operation would also require very little modification in a CCD apparatus. In the traveling wave mode it is possible to use thermodynamic variables other than temperature, such as pH, to force the separation. In this mode of operation unequal cycle times are probably beneficial (*7*).

Another area of interest is continuous flow instead of discrete transfer and equilibrium steps. This could be done in a sieve or valve tray column without downcomers. Although the theoretical calculations are quite different, the separations would be expected to be quite similar to those reported here.

The extraction results reported here and the adsorption results reported elsewhere (*6*, *7*, *9*) can be extended by analogy to various chromatographic systems. Chromatographic separations of gases should be sensitive to cycling zone operation using temperature variations to force the separation. Chromatographic separations of liquids would be less temperature sensitive, but would be sensitive to pH changes. Thus a cycling zone system may allow preparative chromatographic separations for simple mixtures.

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SYMBOLS

C_{Feed}	concentration of solute in feed, moles/liter
C_M	concentration of solute in mobile phase, moles/liter
C_S	concentration of solute in stationary phase, moles/liter
f_C	fraction of solute in mobile phase when temperature is cold
f_H	fraction of solute in mobile phase when temperature is hot
$f_{i,j,s}$	fraction of solute in mobile phase in stage (i,j) after transfer step s
Feed_s	defined in Eq. (7), moles
i	location of stage within a region
j	location of region
$K(T)$	distribution coefficient $= C_M/C_S$
$M_{i,j,s}$	moles of solute in stage (i,j) after transfer step s
m	total number of regions
n	number of stages/region
s	transfer step number within a cycle
s_1, s_2, s_T	number of transfer steps in hot half, cold half and entire cycle, respectively
T, T_C, T_H	temperature, cold bath temperature, hot bath temperature, respectively, °C
V_M, V_S	volume per stage of mobile and stationary phases, liters

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