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Two-Dimensional Cross-Flow Extraction

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Abstract

The separating power of two dimensional cross-flow (2DCF) cascades employing liquid–liquid extraction has been studied experimentally and theoretically. Toluene and ethylene glycol were used as solvents to separate a multicomponent feed consisting of nonane, methyl ethyl ketone, and 2-propanol. An efficient convergence scheme was developed for computer solution of the nonideal mass and equilibrium equations for each stage for either discrete transfer or continuous flow systems. Agreement between experimental results and theoretical predictions was good. It was clearly demonstrated that the 2DCF cascade is capable of separating a multicomponent feed into its individual components in continual operation.

INTRODUCTION

Various forms of cascades have long been used to increase the separation which can be obtained from a single equilibrium stage. In large-scale separations countercurrent cascades have been very popular, but they have two limitations when treating multicomponent feed streams. First, in continuous operation they can at best separate the multicomponent feed into two pure components and a mixture. Second, a series of processes may be required to separate two components whose distribution coefficients are close to each other.

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Both of these limitations can be overcome by two-dimensional separation techniques if one is willing to give up some of the advantages of countercurrent cascades such as reuse of the separating agent, use of reflux, and concentration of the desired solutes. Two-dimensional separation methods have been studied mainly for small-scale continuous contact systems instead of staged separation systems. Examples of continuous multicomponent separations are two-dimensional continuous chromatography (*1*), continuous surface chromatography (*2*), and various electrophoretic techniques (*3*). Two-dimensional development techniques have been employed in paper and thin-layer chromatography (*3–5*) in order to increase the separation. The application of all these techniques has been limited to small-scale systems.

The first investigation of two-dimensional staged systems was conducted by Meltzer (*6*) to study the structure and purity of the brain lipid, strandin. The experimental work employed batch operation of a three-phase system with one phase remaining stationary in the two-dimensional matrix of stages. An ideal theory was developed based on the binomial expansion. A completely automated device for discontinuous operation was later designed and constructed (*7*). Wankat (*8*) developed a binomial theory for two-dimensional cross-flow (2DCF) cascades using two phases applicable for pulse, continual,* or continuous feeding. Wankat (*9*) also presented ideal theories for sequential and simultaneous development with three-phase systems in two-dimensional cascades. Meltzer (*6*) utilized the two-dimensional cascade as a batch process for analysis of complex substances, whereas Wankat (*8*) emphasized using the cascade to separate a multicomponent feed of known composition into its individual components in continuous operation.

In this paper the theoretical and experimental aspects of a two-dimensional cross-flow cascade are investigated. A general nonideal calculational algorithm predicting the concentrations of the product streams leaving the cascade is presented. Experimental results with a five-component hydrocarbon system are in good agreement with the theory.

THEORETICAL CALCULATIONS

The two-dimensional cross-flow (2DCF) cascade can be arranged into various shapes to optimize a separation or reduce the number of stages

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* If the system is operated with discrete transfer and equilibrium steps and the feed stream is added to the feed stage at each transfer step, then the operation has continual feed.

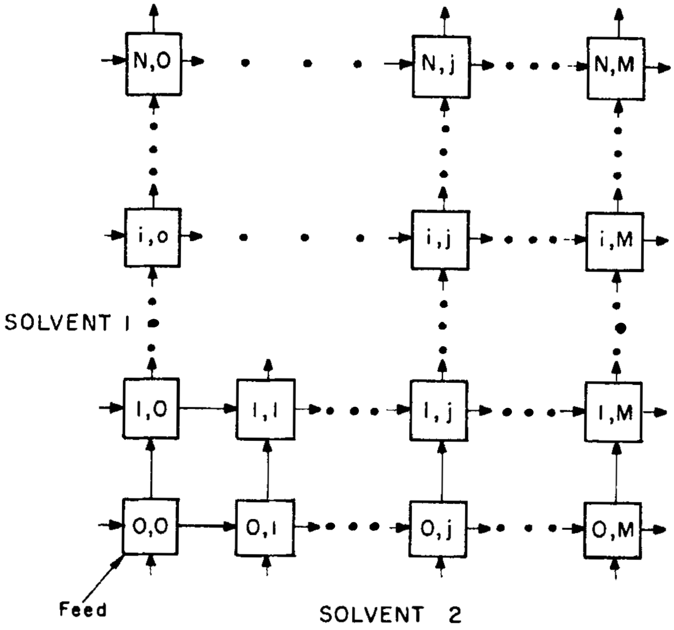

FIG. 1. Two-dimensional cross flow cascade.

required. Figure 1 is a rectangular matrix which illustrates the basic flow pattern of the 2DCF cascade. We can visualize from this figure how each row and column in the matrix functions as a cross-flow cascade.

The operational procedure for 2DCF was presented by Wankat (*8*) and will be repeated here for convenience. The procedure for continual operation begins with an addition of feed to stage (0,0). The feed is then mixed in stage (0,0) and is distributed between the two solvents. After equilibration the bottom phase in stage (0,0), consisting of solvent one and a portion of the feed, is transferred into stage (0,1). Likewise, the top phase from stage (0,0) is transferred into stage (1,0). At the same time a new addition of feed is added to stage (0,0) in such a manner that the new feed does *not* mix with the old feed added to stage (0,0). Fresh solvent is added to each stage in the left-hand column and bottom row of the cascade. Again, after equilibration, the top phases are transferred up the columns and the bottom phases are transferred across the rows. As was shown previously (*6–9*), the 2DCF cascade can also operate in a continuous or batch fashion.

The stage or stages where a particular component leaves the cascade depends on its distribution coefficient and the relative volumes of the solvents used. Components which have a high affinity for the bottom phase will exit in product streams in the lower right-hand corner of the cascade, and components with a high affinity for the top phase will depart from stages in the upper left-hand corner of the cascade. Components which have a distribution coefficient close to unity will migrate toward stage (N,M) and exit in that vicinity. As the numerical difference between the distribution coefficients of two components increases, the number of stages required for the separation decreases.

Ideal theories have been developed by Meltzer (*6*) and Wankat (*8*, *9*) for various two-dimensional cascades. In these theories it was assumed that: (a) The distribution coefficients were constant, (b) the two solvents were completely immiscible, and (c) the volumes of the phases were constant. A more general theory which eliminates these assumptions is presented below for 2DCF operated in continual fashion with two phases present.

Consider a system which contains p solutes and two solvents. For stage (i, j) the mass of top and bottom phases will be designated as $T_{i,j}$ and $B_{i,j}$ with their respective weight fractions being y and x. For a $p + 2$ component system there will be $2(p + 2) + 2$ unknowns: $B_{i,j}$, $T_{i,j}$, $y_{c,i,j}$, $x_{c,i,j}$ for $c = 1$ to $p + 2$, for each stage. The $T_{i,j}$ and $B_{i,j}$ can vary from stage to stage. The $p + 2$ component mass balances represented by Eq. (1) and the two summation equations represented by Eq. (2) are.

$$x_{c,i,j-1}B_{i,j-1} + y_{c,i-1,j}T_{i-1,j} = x_{c,i,j}B_{i,j} + y_{c,i,j}T_{i,j} \qquad c = 1, \ldots, p + 2 \tag{1}$$

$$\sum_{c=1}^{p+2} x_{c,i,j} = 1 \qquad \sum_{c+1}^{p+2} y_{c,i,j} = 1 \tag{2}$$

The solution must also satisfy the $p + 2$ equilibrium expressions where the distribution coefficients can be temperature, pressure, and concentration dependent.

$$K_{c,i,j}(T,P,conc) = y_{c,i,j}/x_{c,i,j} \qquad c = 1, \ldots, p + 2 \tag{3}$$

To solve this set of equations without any restrictive assumptions, a trial and error convergence procedure must be developed. Since the total cascade may be quite large, a linear convergence procedure would be desireable.

Rachford and Rice (*10*) have developed the following relatively linear convergence function for multicomponent flash distillation

$$f(V/F) = \sum_{c=1}^{p+2} \frac{z_c(K_c - 1)}{(K_c - 1)(V/F) + 1} = 0 \tag{4}$$

where V/F is the fraction vaporized and z_c is the feed concentration. Equation (4) rapidly converges to the correct value of V/F to solve the material and energy balance. The equations for flash distillation are quite similar to the equations for a 2DCF cascade with two differences. There are two feed streams entering each stage in 2DCF instead of one as in flash distillation, and the top phase is a liquid in 2DCF instead of a vapor. These differences can be eliminated if streams $B_{i,j-1}$ and $T_{i-1,j}$ are combined into one feed stream and the V in Eq. (4) is replaced with $T_{i,j}$. Defining the feed to stage (i, j) so that

$$F_{i,j} = B_{i,j-1} + T_{i-1,j} \tag{5}$$

and

$$z_{c,i,j}F_{i,j} = B_{i,j-1}x_{c,i,j-1} + T_{i-1,j}y_{c,i-1,j} \tag{6}$$

then the equation equivalent to the Rachford and Rice equation is

$$f(T_{i,j}/F_{i,j}) = \sum_{c=1}^{p+2} \frac{z_c(K_c - 1)}{(K_c - 1)(T_{i,j}/F_{i,j}) + 1} = 0 \tag{7}$$

The Newton convergence method (*11*) requires only a few iterations for the convergence of Eq. (7) to find the correct $T_{i,j}$ to solve Eqs. (1)–(3).

A computer program has been written (*12*) which calculates the concentrations in each stage. Assuming the composition and mass of the feed stream are known, the calculation is started by guessing the values of $T_{i,j}/F_{i,j}$ and the weight fractions in the bottom phase. These weight fractions and the known temperature and pressure are then used to calculate the distribution coefficients. The Newton convergence scheme is then applied to Eq. (7) and a value of $T_{i,j}/F_{i,j}$ which satisfied Eq. (7) is obtained. To calculate the new weight fractions in the bottom phase, the mass balance Eqs. (1) and (6) and equilibrium Eq. (3) for stage (i, j) are combined and then solved for the desired weight fractions:

$$x_{c,i,j} = z_{c,i,j}/[(T_{i,j}/F_{i,j})K_{c,i,j} + 1 - (T_{i,j}/F_{i,j})] \tag{8}$$

These weight fractions are used to calculate new K values, and the iteration scheme is continued until the weight fractions calculated in Eq. (8) are equal to the weight fractions calculated in the previous iteration. Once

$T_{i,j}/F_{i,j}$ and the $x_{c,i,j}$'s are known, a mass balance around stage (i,j) is used to find $B_{i,j}$ and either Eq. (1) or Eq. (3) is used to find the $y_{c,i,j}$.

This completes the calculation for stage (i,j). Next we would proceed to stage $(i+1,j)$ and repeat the trial-and-error calculation. Once stage (N,j) has been solved for, the calculations for the next column are started with stage $(0,j+1)$. When stage (N, M) is reached, the complete steady-state flow and compositions for every stage have been obtained. If this calculational procedure is started at the feed stage (0,0), then both feed streams to a given stage will be known when the calculations are done for that stage.

This calculational procedure is much faster than calculations for multicomponent countercurrent systems because trial and error is required for each stage but not for the entire cascade. For a countercurrent system starting conditions must be assumed at one end of the column and a trial-and-error calculation is required for each stage and for the entire cascade (*11*).

The calculations have been presented for operation with continual feed and discrete transfer and equilibrium steps. These calculations can also be interpreted for steady-state continuous flow operation. In this case $B_{i,j}$, $T_{i,j}$, and $F_{i,j}$ now represent flow rates instead of masses. Equations (1) to (8) are valid and the results presented later can be interpreted as steady-state continuous flow results.

This calculational procedure could also be extended to two- or three-dimensional systems with three phases. Ideal theories for these systems were developed by Meltzer (*6*) and Wankat (*9*). With a third phase present the mass balances would require an additional term on each side. An additional summation equation would be needed for the third phase. Additional equilibrium expressions would be required to supplement Eq. (3). With three phases the present Eq. (4) is not applicable. Instead the flash distillation equations developed by Henley and Rosen (*13*) for systems with three phases could be adapted to 2DCF. For batch operation the computer time would increase significantly.

EXPERIMENTAL

The equipment used for the experimental work was quite simple. Pyrex centrifuge test tubes (15 ml) were used for the stages of the cascade, and 10 ml hypodermic syringes were employed for transferring the phases. The taper at the bottom of the test tubes allowed for highly accurate physical separation of the phases.

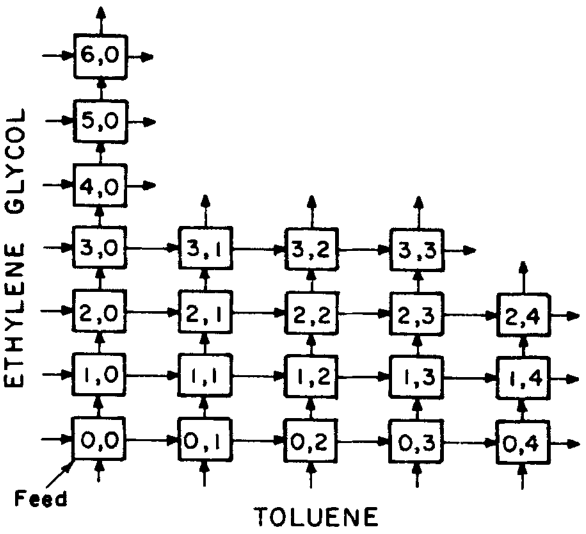

FIG. 2. Nonrectangular cascade for Run 2.

Ethylene glycol and toluene were the solvents used for this work while the multicomponent feed consisted of nonane, methyl ethyl ketone, and 2-propanol. All the experimental work was conducted at atmospheric pressure and room temperature. The fluctuations in ambient temperature were not large enough to produce any noticeable change in the distribution coefficient for this particular system. The quantitative analysis was conducted with a Perkin-Elmer Model 154 Gas Chromatograph. Some difficulties were experienced with reproducibility of the analysis, and standard deviations as large as 18.8% were observed in determining the K values.

Two experimental runs were performed. In the first run a cascade with four rows and six columns was used. In the second run the irregular shaped cascade shown in Fig. 2 was employed in an attempt to optimize the separation. The three-component feed was mixed with the toluene phase going to stage (0,0). Aliquots of 5 ml were used for solvent flows in Run 1. In Run 2, 8-ml aliquots of ethylene glycol were added to stages (0,0) and (1,0) in an attempt to extract the ketone from Column 1 into Column 2. The remaining stages in Row 0 and Column 0 received 5 ml aliquots of solvent. The feed composition was 6.93% ketone, 6.13% 2-propanol, 2.03% nonane, and 84.90% toluene. Complete details of the experiments are available elsewhere (*12*).

RESULTS

The distribution coefficients for the five components were determined as functions of concentration (*12*). Within the detection capabilities of the gas chromatograph it was found that nonane was completely immiscible in the ethylene glycol phase and ethylene glycol was completely immiscible in the toluene phase. The 2-propanol had a high affinity for the ethylene glycol phase, whereas the ketone favored the toluene phase. The theoretical and experimental results of Runs 1 and 2 are presented in graphical form in Fig. 3 to 6.

In Run 1 the ketone and nonane concentrated in the toluene phase while the 2-propanol concentrated in the ethylene glycol products. Some toluene was also recovered in the ethylene glycol phase products. The concentrations of ketone and nonane in the toluene products are shown in Fig. 3. No ethylene glycol was recovered in the toluene products and the highest 2-propanol concentration in the toluene products was less than

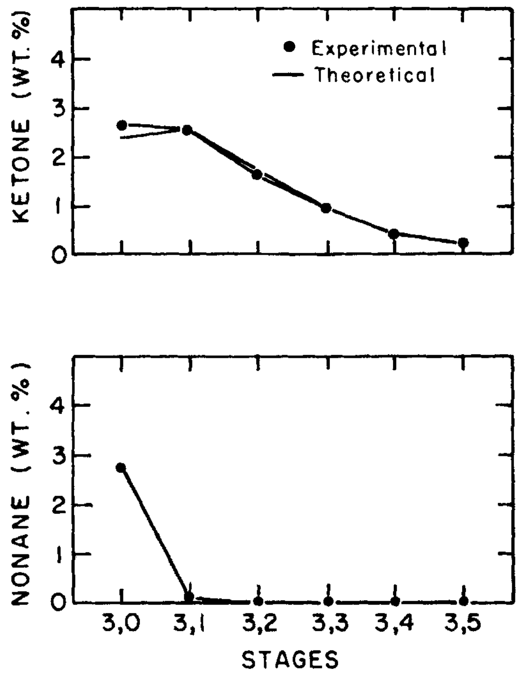

FIG. 3. Toluene phase products for Run 1.

0.05 wt%. The product concentrations for 2-propanol and toluene in the ethylene glycol products are shown in Fig. 4. No nonane was found in the ethylene glycol products, and the highest ketone concentration in the ethylene glycol products was less than 0.10 wt%. The agreement between experiment and theory was generally excellent. The small amount of nonane recovered in the toluene product from stage (3, 1) is probably due to carry over of nonane caused by phase transfer error. The ketone concentrations decrease as the column number is increased since ketone prefers the toluene phase. Similarly, most of the 2-propanol leaves in the first few rows of the ethylene glycol product since the 2-propanol is not attracted to the toluene. The toluene concentrations in the ethylene glycol phase products remain fairly constant since toluene enters every stage in column zero. Toluene is attracted to the ethylene glycol phase by 2-propanol. Therefore, toluene has its highest concentration in the stage where the 2-propanol is at its highest concentration.

Comparison of the ketone and nonane concentrations in the toluene

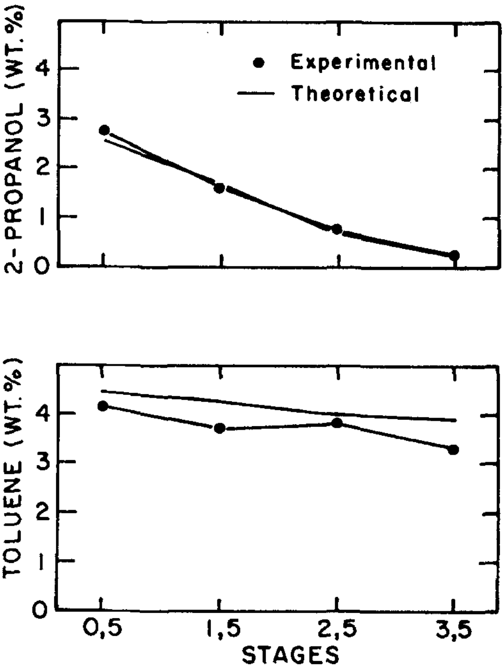

FIG. 4. Ethylene glycol phase products for Run 1.

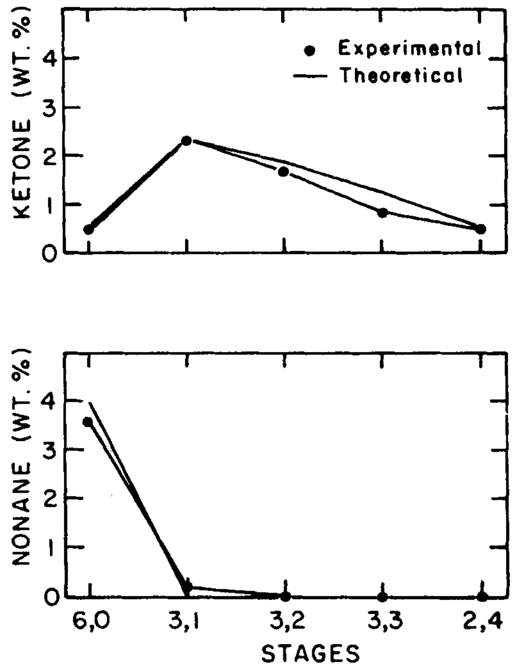

FIG. 5. Toluene phase products for Run 2.

products in Fig. 3 shows that these two components are not well separated. The nonrectangular cascade arrangement shown in Fig. 2 was used to try and improve the separation between ketone and nonane. The concentrations of ketone and nonane in the toluene products are shown in Fig. 5. Again, no ethylene glycol was found in the toluene products and very little 2-propanol was found. This cascade did have the desired characteristic of increasing the separation between ketone and nonane since sufficient stages are available to extract the ketone into the ethylene glycol solvent. The concentrations of ketone, 2-propanol, and toluene in the ethylene glycol products are shown in Fig. 6. Note that the abscissa representing the product stages is an unusual combination of stages because of the nonrectangular shape of the cascade. More ketone is found in the ethylene glycol products for Run 2 than for Run 1 because more stages are available to extract the ketone from the toluene into the ethylene glycol. The results for 2-propanol and toluene concentrations are similar to those obtained

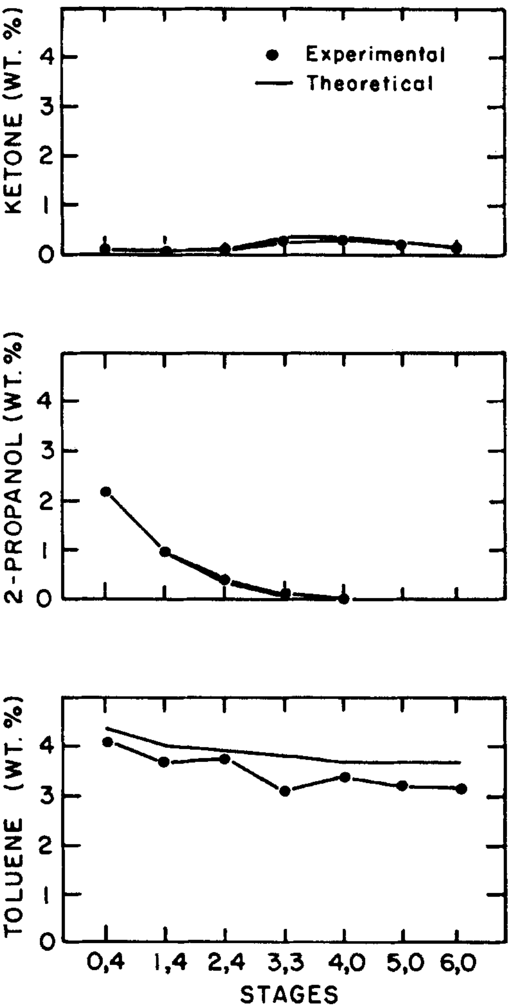

FIG. 6. Ethylene glycol phase products for Run 2.

for Run 1. These results show that a 2DCF cascade can be designed to facilitate the separation of two components.

DISCUSSION

Agreement of the experimental results with the theoretical predictions was quite good as all of the results were within experimental error. Sources of experimental error were the determination of weight factors and hence distribution coefficients, measurement of peak areas, evaporation losses, and transfer of the liquid phases.

This paper has illustrated that two-dimensional cross-flow extraction can continuously separate a multicomponent feed into all its components. The major disadvantages of 2DCF are that it requires a large solvent-to-feed ratio and a large number of stages may be required to attain an adequate separation of components whose K values differ only by a small amount. It would probably be desireable to decrease the fresh solvent requirements by recycling dilute product streams.

In practice a device for automatic operation of the equilibrium and transfer steps would be very desireable. Meltzer et al. (*7*) developed an automatic discrete transfer laboratory apparatus for two-dimensional batch development in a three-phase system. This apparatus could easily be modified for continual operation with a two-phase system. Hudson (*12*) presented a mixer–settler design for continuous operation of the 2DCF cascade. This mixer–settler design could be adapted to either laboratory or commercial scale operation. Additional work is necessary to determine the economics of large-scale operation.

SYMBOLS

B	mass of liquid in the bottom phase (grams)
F	mass of feed to a stage (grams) (Eq. 5)
K	distribution coefficient (Eq. 3)
T	mass of liquid in the top phase (grams)
x	weight fraction in bottom phase
y	weight fraction in top phase
z	weight fraction in feed (Eq. 6)

Subscripts

c	component
i	row number in cascade
j	column number in cascade

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