ρ_{app} = apparent density, kg/cm^3
ρ_L = density in liquid state, kg/cm^3
σ = surface tension, N/m
ϕ = horizontal angle

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An Efficient, General Method for Computation of Countercurrent Separation Processes with Axial Dispersion

A calculational method is proposed for the simulation of steady-state, multisolute, countercurrent extraction with axial dispersion. The method provides for complex chemical-equilibrium and phase-equilibrium relationships, and accounts for the individual resistances of the liquid phases in the calculation of mass-transfer rates. The solution procedure follows that developed by Newman (1967, 1968) for systems of simultaneous, second-order difference equations.

Three example problems are solved to demonstrate the efficiency and flexibility of the method. These include (1) an example from McSwain and Durbin (1966), (2) calculation of axial-dispersion and mass-transfer parameters from experimental data for the extraction of acetic acid from water by a tertiary amine in an RDC extractor, and (3) simultaneous extraction of solutes that interact in an acid-base complexing reaction at the liquid-liquid interface. The examples all assume that extraction is governed by interphase mass-transfer rates and cell-wise backmixing; however, the method is also applicable to equilibrium-stage separators, separators described by the diffusional model of axial dispersion, and other countercurrent separation processes.

N. L. RICKER
FUMIYUKI NAKASHIO
and
C. J. KING

Department of Chemical Engineering
University of California
Berkeley, California 94720

SCOPE

It is well established that axial dispersion can have a large, adverse impact on the performance of separation devices. While many previous workers have proposed calculational methods that allow prediction of the effects of axial dispersion (Mecklenburgh and Hartland, 1975; etc.), these methods are generally limited to simple situations, as when one can assume a constant degree of axial dispersion throughout the device, linear or quadratic phase-equilibrium relationships, constant overall mass-transfer coefficients, and the interphase transfer of either a single solute, or multiple dilute, non-interacting solutes. The goal of the present work was to develop a calculational method that could be applied to more general problems. This was motivated by the need to analyze experimental mass-transfer data obtained in a small-scale liquid-liquid extraction column for systems exhibiting complex phase-equilibrium behavior. The performance of the column appeared to be dominated by axial dispersion.

The laboratory column was a rotating disk contactor (RDC). In the proposed calculational method, the RDC was represented by a series of well-mixed cells connected by forward and

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Correspondence concerning this paper should be addressed to N. L. Ricker, who is presently with the Department of Chemical Engineering, BF-10, University of Washington, Seattle, WA 98195. F. Nakashio is with the Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan.

back-flowing portions of each of the two liquid phases, a model used previously by several authors (McSwain and Durbin, 1966; etc.). Equations were derived for the case of multicomponent extraction; the rate of mass transfer was assumed to be governed by the addition-of-resistances concept, i.e., by the individual resistance of each phase and the prevailing bulk and interfacial concentrations. The equations were solved by a multidimensional Newton-Raphson procedure.

CONCLUSIONS AND SIGNIFICANCE

The proposed calculational method was successfully applied to the analysis of data from the RDC extraction column. In this and in other tests, a converged solution of the governing equations required only 3-5 Newton-Raphson iterations. Convergence was stable, even in regions well removed from the final solution; no special convergence-promotion techniques were required.

The calculational method was used to determine continuous-phase Peclet numbers and transfer units from the RDC data. These parameters would generally be needed to scale up a pilot extraction column. Calculated Peclet numbers varied from 0.55 to 1.15, and were 15-60% lower than values predicted by established correlations. Although no direct measurements of axial dispersion were performed, these results suggest that RDC columns are subject to severe axial dispersion, as noted by previous investigators (e.g., Laddha and Degaleesan, 1978).

A second application of the calculational method involved the simultaneous extraction of two dicarboxylic acids by a liquid-ion-exchange reagent, a process sometimes called dissociation extraction. The calculational method appears to be especially suited to such difficult problems. The results of the simulation showed that under certain conditions, the concentration of the weaker acid could build up within the extraction column. This concentration peak is analogous to the formation of a temperature peak in a gas-absorption column.

The proposed calculational method has been presented in the context of continuous, countercurrent extraction with cell-wise backmixing; the method can, however, be applied to other countercurrent separation processes, and the cell-backmixing model can be replaced by a diffusional model of axial dispersion, if necessary.

INTRODUCTION

Axial dispersion can greatly reduce the efficiency of countercurrent separations, especially when separation devices lack discrete stages. For example, in column type liquid-liquid extractors, such as spray columns, axial dispersion can dominate the degree of separation obtained (Vermeulen, et al., 1966; etc.). Other examples of strong axial dispersion are found in the continuous phase of bubble columns (Deckwer, et al., 1974; Valdes-Krieg, et al., 1977), and in certain packed-column absorbers (Dunn, et al., 1977).

Mecklenburgh and Hartland (1975) summarize calculational methods for the simulation of axial dispersion in separation devices. In general, such methods use either a diffusional or a cell-backmixing model of axial dispersion. If the radial concentration gradients are neglected, the use of a diffusional model requires the solution of a set of non-linear, ordinary differential equations; a cell-backmixing model results in a set of non-linear difference equations. In either case, in order to obtain an analytical solution, one must assume a constant degree of axial dispersion throughout the device, simple linear or quadratic equilibrium relationships, constant phase flow rates, and constant overall volumetric mass transfer coefficients, e.g., K_La. Analytical solutions are also restricted to a single transferring solute, or to multiple dilute solutes that do not interact with one another through the equilibrium relationships or in other ways. For situations in which these assumptions are invalid, solutions must be obtained numerically.

Numerical solutions of the diffusional model generally begin with the substitution of standard finite-difference approximations for the differential terms. The resulting *difference* equations are very similar to those for the cell-backmixing model; hence, a solution method that works well for the diffusional model can usually be used with the cell-backmixing model, and vice versa.

One common numerical technique is boundary-value iteration, wherein the values of the dependent variables (e.g., compositions) at one end of a contactor are assumed, and the equations are then solved step-by-step for the variables at each point along the length of the contactor. The calculated values at the far end of the contactor are compared to specified boundary conditions, e.g., the composition of a feed stream. If there is a mismatch, new values of the assumed variables are obtained through a convergence procedure, and additional iterations are performed until the boundary conditions are satisfied.

Mecklenburgh and Hartland (1969, 1975) have found that this end-to-end approach works well for cocurrent contactors. For countercurrent devices, however, they report that the boundary-value iterations can be very difficult to converge. This is not surprising, since the boundary-value method is analogous to the use of stage-to-stage calculational methods for multicomponent distillation (King, 1980). Such methods can be difficult or impossible to converge; the product compositions must be assumed, and small errors in the assumed amounts of dilute components tend to build up as the calculation proceeds along the column.

More reliable convergence can be achieved through the use of relaxation or successive-approximation methods. Relaxation methods simulate the dynamic approach of a physical process to its steady state; as long as the process is inherently stable, relaxation can be made convergent. Examples of the application of relaxation methods to complex extraction processes are given by Mecklenburgh and Hartland (1969), who describe a relaxation method for the use of a single-transferring solute, and by Boyadzhiev and Angelov (1976), who use a form of relaxation in the context of equilibrium-stage extraction with multiple, interacting solutes and with backmixing.

A potential disadvantage of the conventional relaxation methods is that the approach to the steady-state solution is asymptotic, and the rate of convergence tends to decrease as the solution is approached. Successive-approximation methods, on the other hand, converge more rapidly in the region of the steady state solution. Convergence is especially rapid when the method is based on a multi-dimensional Newton-Raphson or other high-order convergence scheme. McSwain and Durbin (1966) describe a Newton-Raphson solution of the cell-backmixing model. The method exhibits rapid convergence, but is limited to a single transferring solute (or to no interactions between multiple solutes), linear or quadratic equilibrium, constant phase flow rates, and constant K_La values.

Our calculational method is similar to that of McSwain and Durbin, but is more general in that it allows for solute interactions through complex phase equilibrium relationships and/or transport phenomena. The rate of mass transfer is assumed to be governed by the addition-of-resistances concept, through which the rate of mass transfer at any point depends on the resistances of the individual phases and the prevailing bulk and interfacial concentrations. The general approach is applicable to both the cell-backmixing and diffusional models of axial dispersion, although we develop the equations for the cell-backmixing model only. Further, the equations are developed for a liquid-liquid extraction column with two feeds and with phase-separation zones at each end of the column; other separation devices can be handled in an analogous manner. Since our application of the method involves dilute solutes and relatively insoluble phases, we assume constant net phase flow rates; the method could be extended to handle the more general problem. Finally, we assume constant temperature. If necessary, one could easily incorporate energy balances in the model and treat the cell temperature as an additional dependent variable.

OUTLINE OF THE CALCULATIONAL METHOD

Figure 1 is a schematic of a cell-backmixed, two-feed extractor composed of N cells. Cells 1 to $m-1$ represent the y-phase settling zone, cell m is the x-phase feed zone, cells $m+1$ to $n-1$ are the primary mass transfer zone, cell n is the y-phase feed zone, and cells $n+1$ to N are the x-phase settling zone. The volume of the feed zones is assumed to be negligible; no mass transfer occurs at the feed points. Otherwise, mass transfer occurs between each pair of x and y-phase cells. The x and y phases within a given cell are each fully mixed. F_x and F_y are the constant net phase flow rates; f_{xj} and f_{yj} are variable backmix flow rates leaving cell j.

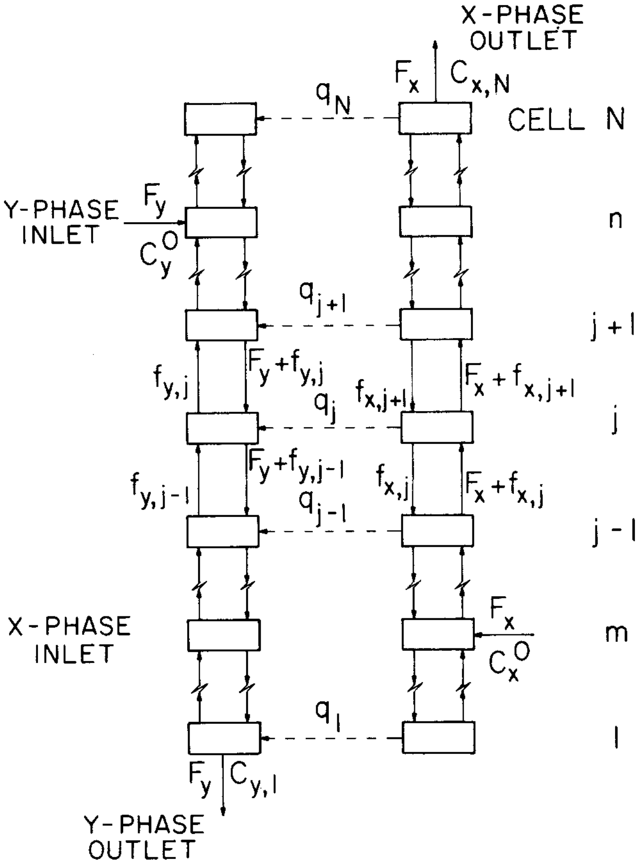

Figure 1. Schematic of cell-backmixed extraction column.

An x-phase mass balance for solute i at cell j gives:

$$(F_x + f_{xj})C_{xi,j-1} - (F_x + f_{xj} + f_{x,j+1})C_{xij} + f_{x,j+1}\, C_{xi,j+1} - q_{ij} = 0 \tag{1}$$

Similarly, a y-phase balance gives:

$$f_{y,j-1}\, C_{yi,j-1} - (F_y + f_{y,j-1} + f_{yj})C_{yij} + (F_y + f_{yj})C_{yi,j+1} + q_{ij} = 0 \tag{2}$$

The steady-state interphase flux of component i is defined in terms of the individual mass transfer coefficients in each phase and the interfacial concentrations, C_x^i and C_y^i:

$$q_{ij} = V_j a_j k_{xij}\,(C_{xij} - C^i_{xij}) = V_j a_j k_{yij}(C^i_{yij} - C_{yij}) \tag{3}$$

Finally, the interfacial concentrations are assumed to be at equilibrium:

$$C^i_{yij} = K_{ij}\, C^i_{xij} \tag{4}$$

where K_{ij} is, in general, a complicated, nonlinear function of all the interfacial concentrations and the temperature.

The mass balance equations (Eqs. 1 and 2) are slightly different for feed and settling-zone cells. For the feed cells, Eqs. 1 and 2 must include feed terms, and Eqs. 3 and 4 are replaced by the requirement that:

$$C^i_{yij} = C_{yij} \tag{3-a}$$

and

$$C^i_{xij} = C_{xij}\,, \tag{4-a}$$

i.e., $q_{ij} = 0$ for these cells. The mass-balance equations for the end cells must reflect the requirement that there be no entrainment of x-phase in the y-phase product, and vice versa, as shown in Figure 1.

For a general cell ($j \neq 1$, m, n, or N), Eqs. 1-4 are made dimensionless to yield:

$$F_{1ij} = (p_{xj} + \beta_{xj})X_{i,j-1} - (p_{xj} + \beta_{xj} + \beta_{x,j+1})X_{ij} + \beta_{x,j+1}\, X_{i,j+1} - Q_{xij} = 0 \tag{5}$$

$$F_{2ij} = \beta_{y,j-1}Y_{i,j-1} - (p_{yj} + \beta_{yj} + \beta_{y,j-1})Y_{ij} + (p_{yj} + \beta_{yj})Y_{i,j+1} + \lambda\, Q_{yij} = 0 \tag{6}$$

$$F_{3ij} = Q_{xij} - Q_{yij} = 0 \tag{7}$$

$$F_{4ij} = Y^i_{ij} - K_{ij}\, X^i_{ij} = 0 \tag{8}$$

where

$$Q_{xij} = \alpha_{xij}\,(X_{ij} - X^i_{ij}) \tag{9}$$

$$\lambda Q_{yij} = \alpha_{yij}\,(Y^i_{ij} - Y_{ij}) \tag{10}$$

For certain cells, Eqs. 5-8 take on a special form, as follows:

$$\left.\begin{aligned} F_{1i1} &= \beta_{x2}(X_{i2} - X_{i1}) - Q_{xi1} = 0 && \text{(5-a)}\\ F_{2i1} &= (1 + \beta_{y1})\,(Y_{i2} - Y_{i1}) + \lambda\, Q_{yi1} = 0 && \text{(6-a)} \end{aligned}\right\} j = 1$$

$$\left.\begin{aligned} F_{1im} &= \beta_{xm}X_{i,m-1} - (1 + \beta_{xm} + \beta_{x,m+1})\, X_{im} + \\ &\quad \beta_{x,m+1}\, X_{i,m+1} - Q_{xim} + 1 = 0 && \text{(5-b)}\\ F_{2im} &= \beta_{y,m-1}\, Y_{i,m-1} - (1 + \beta_{ym} + \beta_{y,m-1})\, Y_{im} + \\ &\quad (1 + \beta_{ym})Y_{i,m+1} + \lambda\, Q_{yim} = 0 && \text{(6-b)} \end{aligned}\right\} j = m$$

$$\left.\begin{aligned} F_{1in} &= (1 + \beta_{xn})X_{i,n-1} - (1 + \beta_{xn} + \beta_{x,n+1})X_{in} \\ &\quad + \beta_{x,n+1}\, X_{i,n+1} - Q_{xin} = 0 && \text{(5-c)}\\ F_{2in} &= \beta_{y,n-1}\, Y_{i,n-1} - (1 + \beta_{yn} + \beta_{y,n-1})\, Y_{in} \\ &\quad + \beta_{yn}\, Y_{i,n+1} + Y_i^\circ + \lambda\, Q_{yin} = 0 && \text{(6-c)} \end{aligned}\right\} j = n$$

$$\left.\begin{aligned} F_{1iN} &= (1 + \beta_{xN})X_{i,N-1} - (1 + \beta_{xN})X_{iN} \\ &\quad - Q_{xiN} = 0 && \text{(5-d)}\\ F_{2iN} &= \beta_{y,N-1}(Y_{i,N-1} - Y_{iN}) + \lambda\, Q_{yiN} = 0 && \text{(6-d)} \end{aligned}\right\} j = N$$

$$\left.\begin{aligned} F_{3ij} &= X^i_{ij} - X_{ij} = 0 && \text{(7-a)}\\ F_{4ij} &= Y^i_{ij} - Y_{ij} = 0 && \text{(8-a)} \end{aligned}\right\} j = m \text{ and } j = n$$

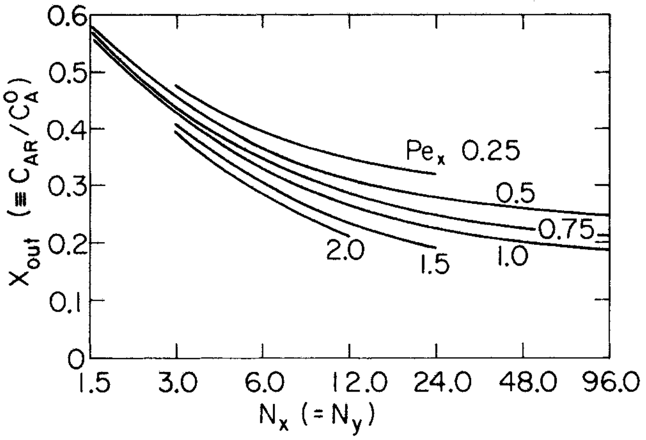

Figure 2. Fractional removal vs. number of X and Y-phase transfer units for example 2.

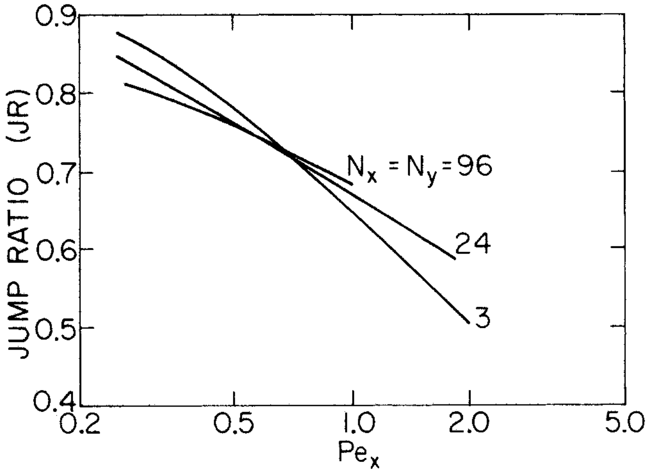

Figure 3. Jump ratio vs. X-phase peclet number for Example 2.

Solution Procedure

The bulk and interfacial concentrations, X_{ij}, X_{ij}^i, Y_{ij} and Y_{ij}^i, are taken as the dependent, unknown variables. The remaining variables (β_{kj}, α_{kij} and K_{ij}) are assumed to be specified *a priori* or to be known functions of the dependent variables. For a system with M solutes, there are thus $4M$-dependent variables per cell; these can be determined through the solution of Eqs. 5-8. As noted by Newman (1967, 1968) and others (e.g., Naphtali and Sandholm, 1971; Fredenslund, et al., 1977; King, 1980, etc.), if the equations are grouped by stage, they can be solved by an efficient multidimensional Newton-Raphson algorithm.

The procedure is iterative; for each iteration, the equations are linearized about the current values of the dependent variables. Since the equations for a given cell, j, are functions of the variables for cells $j - 1$, j and $j + 1$ only, the matrix of coefficients for the linearized equations is block-tridiagonal;

$$\begin{bmatrix} \underline{\underline{B}}_1 & \underline{\underline{C}}_1 & & & & \\ \underline{\underline{A}}_2 & \underline{\underline{B}}_2 & \underline{\underline{C}}_2 & & & \\ & \underline{\underline{A}}_3 & \underline{\underline{B}}_3 & \underline{\underline{C}}_3 & & \\ & & \ddots & \ddots & \ddots & \\ & & & \underline{\underline{A}}_{N-1} & \underline{\underline{B}}_{N-1} & \underline{\underline{C}}_{N-1} \\ & & & & \underline{\underline{A}}_N & \underline{\underline{B}}_N \end{bmatrix} \begin{bmatrix} \Delta\underline{X}_1 \\ \Delta\underline{X}_2 \\ \Delta\underline{X}_3 \\ \vdots \\ \Delta\underline{X}_{N-1} \\ \Delta\underline{X}_N \end{bmatrix} + \begin{bmatrix} \underline{F}_1 \\ \underline{F}_2 \\ \underline{F}_3 \\ \vdots \\ \underline{F}_{N-1} \\ \underline{F}_N \end{bmatrix} = \underline{0}$$

where

$\underline{F}_j$ = current values of the $4M$ functions for cell j (see Appendix)

$\Delta\underline{X}_j$ = predicted change in the values of the dependent variables for cell j (see Appendix)

$\underline{\underline{A}}_j$, $\underline{\underline{B}}_j$ and $\underline{\underline{C}}_j$ = $4M \times 4M$ coefficient matrices for the linearized equations: i.e., $\underline{\underline{A}}_j$ contains the coefficients of the equations for cell j with respect to the variables for cell $j-1$; $\underline{\underline{B}}_j$ contains the coefficients of the equations for cell j with respect to the variables for cell j; and so on. The elements of $\underline{\underline{A}}$, $\underline{\underline{B}}$ and $\underline{\underline{C}}$ are given in an appendix.

The linearized equations are solved for the $\Delta\underline{X}_j$ values. These are used to generate new estimates of the dependent variables, and the corresponding $4\,MN$ function values, F_{kij} are calculated. The above procedure is repeated until

$$\sum_{j=1}^{N}\sum_{i=1}^{M}\sum_{k=1}^{4}(F_{kij}^2) < \epsilon$$

where ϵ is an error tolerance. A value of $\epsilon = 10^{-8}$ was used in the present work. It should be noted that the above criterion weights the F_{kij} values equally. In the present work, the equations were normalized so that the F_{kij} values were of the same order of magnitude. In general, weighting functions should be used to insure an accurate solution.

The first iteration of the procedure requires initial estimates of the dependent variables. In the present work, the following initial estimates were used:

$$X_{ij} = X_{ij}^i = X_{if} \qquad (11)$$

$$Y_{ij} = Y_{ij}^i = Y_{if} \qquad (12)$$

i.e., as if the column were operating with no interphase solute fluxes. These relatively poor initial estimates were intended to test the convergence properties of the solution procedure.

The major computational requirements of the method are in the calculation of the $\underline{\underline{B}}_j$ coefficients, which generally involve partial derivatives of the equilibrium distribution coefficient, K_{ij}, with respect to X_{ij}^i and Y_{ij}^i, and in the solution of the linearized equations. The examples described below all converged smoothly within five iterations. No special damping or convergence-promotion schemes were needed. CPU time requirements ranged between 1 and 5 seconds on a CDC 6400, depending on the number of solutes and cells in the example problems.

EXAMPLES

Solutions of several example problems are described below to demonstrate the flexibility and efficiency of the computational method and to illustrate ways in which it can be used.

Example 1

McSwain and Durbin's (1966) Case I (24 cells, 1 transferring component) was solved for linear and quadratic equilibrium relationships (their Figure 3, curves B, D and E). The resulting concentration profiles matched those reported by McSwain and Durbin. The solution of case B, linear equilibrium, required only a single iteration, as would be expected, and the others required three to four iterations. McSwain and Durbin assume that the X-phase resistance controls the rate of mass transfer. Hence, in order to match their results, it was necessary to set the dimensionless Y-phase mass transfer coefficient, α_{yij}, to a large value, taken as 10^6.

Example 2

The computational method was used to determine values of dispersion coefficients and volumetric mass-transfer coefficients from experimental data taken with a laboratory RDC extractor. Such information is important for scale-up of pilot extraction columns. The laboratory extraction process was designed to recover acetic acid from an aqueous industrial process stream (Ricker, et al., 1980); the solvent was a mixture of 50 volume % Alamine 336 (General Mills, Inc.) in diisobutyl ketone. Alamine

TABLE 1. CONDITIONS AND RESULTS OF EXPERIMENTS WITH RDC EXTRACTOR AND FITTED MODEL PARAMETERS

Conditions	Run 12	Run 13	Run 17	Run 18
Stator hole diameter (cm)	5.71	5.71	5.08	5.08
Disc diameter (cm)	3.81	3.81	4.45	4.45
Shaft Rotation Speed (rev./min)	580	720	530	460
Aqueous Feed Flow Rate (L/h)	1.25	1.26	3.53	2.93
Solvent/Feed (vol/vol)	1.00	0.98	0.98	0.98
Predicted Pe_x^1	0.86	0.69	2.79	2.69
Experimental Results				
Removal of Acetic Acid (%)	67.7	69.2	77.7	74.2
Jump Ratio (see text)	0.757	0.748	0.667	0.649
Fitted Parameters				
Pe_x	0.55	0.59	1.10	1.15
$N_x(=N_y)$	(9)	(11)	(22)	(12)

[1] From the correlation of Strand, et al. (1962).

336 is an isomeric mixture of > 95% tertiary alkyl amines derived from C_8-C_{10} alcohols. Acetic acid is extracted as an acid-base complex. The experimental data were taken by Pittman (1979), using the RDC extractor described by Earhart et al. (1977). Although 12 solutes were detected in the aqueous process stream, acetic acid was by far the most concentrated—about 5 weight %. Possible effects of the other solutes were neglected.

Pittman (1979) found that the following equation gave an adequate representation of the extraction equilibrium:

$$K' = 0.7803 + 0.0779\, C_A + 6.392\, C_A^2 \tag{13}$$

where K' is the ratio of the concentration of acetic acid in the extractant phase to that in the aqueous phase at equilibrium, and C_A is the concentration of acetic acid in the aqueous phase (mol/L).

Conditions for several of the extraction runs are shown in Table 1. The major experimental measurements were the fractional removal of acetic acid ($\equiv 1-C_{AR}/C_A^\circ$), and the concentration of acetic acid in the bulk aqueous phase at the aqueous feed point. The latter is expressed in Table 1 as a jump ratio, defined as

$$JR = \frac{C_A^\circ - C'_{AF}}{C_A^\circ - C_{AR}} \tag{14}$$

where C_A°, C'_{AF} and C_{AR} are the aqueous feed, aqueous feed point and raffinate concentrations, respectively. A jump ratio close to 1.0 indicates a high degree of aqueous-phase axial dispersion; a zero value indicates no axial dispersion.

Predictions of the correlation of Strand, et al. (1962) indicated that axial dispersion in the dispersed (extractant) phase should be negligible compared with that in the continuous (aqueous) phase. Consequently, in subsequent calculations the dispersion coefficient for the dispersed phase, β_{yj}, was set to zero. We also assumed that the dispersion coefficient for the continuous phase, β_{xj}, was the same for all cells, and N_{xij} and N_{yij} were constant and equal. The latter assumption implies that the individual mass transfer coefficients were constant and the effective interfacial area was the same in each cell. The lack of detailed experimental concentration profiles prevented a more rigorous analysis. Finally, in the calculations the RDC was represented by a total of 30 cells—one for each of the 26 compartments between stators, plus two for each phase-settling zone. The extractant-to-aqueous volumetric flow ratio was fixed at 1.0.

The above assumptions allowed the use of a single mass transfer parameter, $N_x(=N_y;\ N_x \equiv \sum_j N_{xij})$ and a single dispersion coefficient, β_{xj}, to characterize the operation of the RDC. As noted by McSwain and Durbin (1966), in a region, R, of constant axial dispersion, the dispersion coefficient and Peclet Number, Pe_x, are related, as follows:

$$\beta_{xj} = (Pe_x h)_R^{-1} - \frac{1}{2}\, p_x \tag{15}$$

where h is the dimensionless length of a cell in region R and p_x is either one or zero, as noted previously. We used the proposed calculational method to determine how variations in N_x and Pe_x should affect the experimentally measured values of C_{AR}/C_A° and the jump ratio. The results are summarized in Figures 2 and 3.

To determine estimates of N_x and Pe_x from the experimental data, we made use of the fact that the jump ratio is primarily dependent upon Pe_x (see Figure 3). The procedure was then to choose a trial value of N_x, determine Pe_x from the data in Figure 3, and then determine a new value of N_x from the data in Figure 2. Additional iterations were performed until successive N_x and Pe_x values agreed within 1%. Convergence was rapid. The results are shown in Table 1. In most cases, these agreed with our prior expectations of the behavior of the RDC. For example, runs 17 and 18 used narrower constrictions between the discs and stators and greater phase flow rates resulting in higher Pe_x values, as shown.

In general, the experimentally determined Pe_x values were very low, indicating severe axial dispersion. In all cases, our Pe_x values were substantially below the predictions of the correlation of Strand, et al. (1962). If this separation were to be scaled up, it would be important for the designer to realize that the degree of separation achieved in the RDC would be increased more readily through a reduction in the continuous-phase axial dispersion than through an increase in the number of transfer units.

We should add, however, that the above method for the determination of N_x and Pe_x is subject to significant experimental error. The N_x values shown in Table 1 are uncertain because of the sensitivity of N_x to C_{AR}/C_A° at high N_x values (see Figure 2). Measurement of one or more points in the internal concentration profile would have reduced this uncertainty. The Pe_x values are sensitive to the jump ratio, which is difficult to measure accurately; we estimate an experimental error of 10-20% in Pe_x. A more accurate value could perhaps be determined by tracer-injection techniques.

Example 3

The final example involves multiple solutes that compete for a common extractant. Vieux, et al. (1974) give equilibrium data for the extraction of oxalic, succinic and malonic acids by tri-isooctylamine in an o-dichlorobenzene diluent. As in the previous example, extraction occurs through an acid-base complexing reaction. For a given acid species, A_i, base B, and complex C_i, the complexing reaction is represented by:

$$A_i(aq) + B(org) \overset{K_i''}{\rightleftharpoons} C_i(org),\ K_i'' = \frac{[C_i]}{[A_i][B]}. \tag{16}$$

The B and C_i species are assumed to be insoluble in the aqueous phase, and the free acid species, A_i, are assumed to be insoluble in the extractant phase. Values of K_i'', the equilibrium constant for the complexing reactions, are 244.0 for malonic acid and 6.14 for succinic acid. When two or more acids are extracted simultaneously, each competes for the available base, and the stronger acids (having the higher K_i'' values) extract preferentially. This separation technique has been termed dissociation extraction.

In order to solve this problem, the governing Eqs. 5-8 are modified as follows:

1) For the acid species, X_{ij} represents the concentration of free acid in the aqueous phase, and Y_{ij} represents the concentration of complexed acid in the extractant phase. The acid material balances and flux equations are then the same as in Eqs. 5-7. The interfacial equilibrium equation (Eq. 8) is changed to agree with the form of Eq. 16.

2) For the amine, Y_{ij} represents the concentration of free base in the organic phase, and X_{ij} represents an imaginary concentration of complexed base in the aqueous phase. Eqs. 5-7 are normalized by the concentration of base in the *extractant* feed, but are otherwise unchanged. Eq. 8 is replaced with a flux equation that forces the imaginary transfer of a mole of base to the X phase for each mole of acid transferred to the extractant

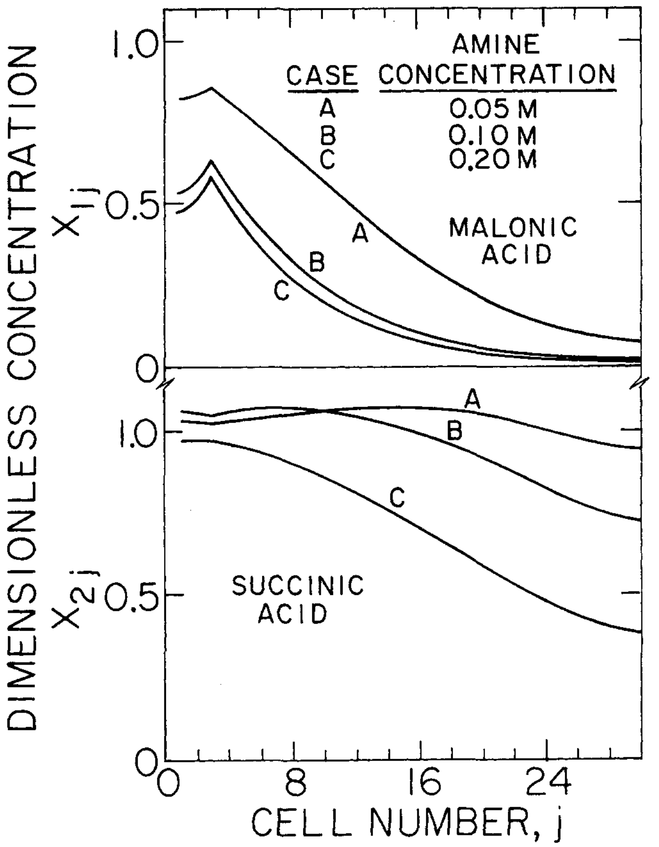

Figure 4. X-phase concentration profiles for simultaneous extraction of malonic and succinic acids.

phase to account for the disappearance of free base according to the stoichiometry of the complexing reactions.

The above modifications required only minor changes in the computer program used to solve Examples 1 and 2. Calculational results for the simultaneous extraction of succinic and malonic acids are shown in Figure 4 for three different cases. In each case, the number and distribution of extractor cells was the same as Example 2, the X and Y phase flow rates were equal, $Pe_x = Pe_y = 8.0$, $N_{xi} = N_{yi} = 4.0$ for all solutes, and the feed concentrations of malonic and succinic acids were $0.04M$ and $0.06M$, respectively. The feed concentrations of amine in cases A, B and C were $0.05M$, $0.1M$, and $0.2M$, respectively.

For case A, in which the acids are in excess, 92% of the malonic acid is extracted from the aqueous phase, whereas only about 6% of the weaker succinic acid is extracted. The relative amount of succinic acid extracted increases as the feed concentration of amine increases in cases B and C. The calculations indicate that a good separation of the acids can be achieved by proper selection of the feed concentration of the amine.

For cases A and B, the calculations predict that the X-phase concentration of succinic acid will exceed its feed concentration at some intermediate point in the column (Figure 4). This concentration peak is not caused by axial dispersion; it is the result of the interaction of the two acids with the basic extractant. At the Y-inlet end of the extractor, the X-phase is more depleted of malonic acid than of succinic acid, and the Y-phase therefore contains significant amounts of both acids. As the Y-phase rises toward the X-inlet end of the extractor, it begins to encounter high X-phase concentrations of malonic acid, which displaces some of the weaker succinic acid back into the X-phase. The resulting concentration peak is analogous to the temperature peak often found in gas absorption columns and the build-up of a component of intermediate volatility in multicomponent distillation.

DISCUSSION

The method and the examples have been presented in terms of solvent extraction with a cell-backmixing model of axial dispersion and a mass-transfer-limited rate of equilibration in each cell. The method can readily be extended to other countercurrent separation processes. The individual cells can be treated as equilibrium stages, if appropriate, by exchanging the rate equations for a single set of equilibrium relationships. In that case the interfacial concentrations should not be included as dependent variables. Furthermore, the cell-backmixing model of axial dispersion can be replaced by the axial-diffusion model. The diffusion-model equations should then be used instead of Eqs. 5-8, with central-difference numerical approximations used for the derivatives. The equations are different, but still assume the block-tridiagonal form so that the remaining solution procedure is the same as presented for the cell-backmixing model.

There are, of course, alternative formulations for the Newton-Raphson solution of Eqs. 5-8. In particular, we have chosen to treat both the bulk and the interfacial concentrations as state variables, but one could also designate the bulk concentrations alone as state variables and eliminate a corresponding number of equations from the simultaneous Newton-Raphson solution procedure. This was the approach taken by McSwain and Durbin (1966); it appears to work well for relatively simple problems. For multicomponent extraction problems, however, when K_{ij} is an implicit function of all the interfacial concentrations for a particular cell (see, e.g., Boyadzhiev and Angelov, 1976), the McSwain and Durbin formulation would require an additional "inner loop" to converge the K_{ij} values, and the overall performance could differ considerably from that of the method proposed here.

While we have not made a detailed comparison of the convergence properties of the two methods, experience with multicomponent distillation calculations suggests that a simultaneous solution of the mass balance and equilibrium equations is generally the more successful approach (King, 1980). It is also very flexible, as shown in the third example problem. The increased dimensionality of our formulation may be a significant disadvantage for problems involving many cells and/or components, but for problems in which $4 \times M \times N < 400$, the computer storage and CPU time requirements are minimal, as already noted.

Our test problems have included nonlinear phase-equilibrium behavior for a single transferring component (first and second examples) and extraction of multiple components that interact through a non-linear phase equilibrium relationship (third example). We feel that these constitute a good test of the method. In all cases, the Jacobian matrix formed in the solution procedure was well-conditioned; in the region of the solution, the error criterion decreased quadratically and all the state variables converged to stable values. In the initial iterations, where a poor initial estimate might be expected to cause problems, no special convergence-promotion schemes were needed. In general, however, extremely difficult problems might require the use of more sophisticated methods. A combined relaxation/Newton-Raphson method (e.g., Ketchum, 1979; King, 1980), for example, would have the advantage of stability in the initial iterations and a high overall rate of convergence.

The model, as presented, is suitable for an operating problem, where the values of Pe_x, Pe_y, N_x and N_y are specified in the problem statement. Design problems, where separation parameters are specified rather than N_x and N_y, may be handled by interpolation among results of a number of operating problems, as in Example 2. A more efficient computational method would adjust these parameters systematically between iterations in the successive-approximation solution, as is outlined by Ricker and Grens (1974) for distillation. This would accomplish simultaneous convergence of the composition profiles and of the contactor-length parameters.

A listing of a computer program for the model presented here is available from any of the authors.

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APPENDIX: DETAILS OF BLOCK-TRIDIAGONAL MATRICES

The equations and dependent variables are arranged so that:

$$\underline{F}_j = \begin{bmatrix} F_{11j} \\ \cdot \\ \cdot \\ \cdot \\ F_{1Mj} \\ F_{21j} \\ \cdot \\ \cdot \\ \cdot \\ F_{2Mj} \\ F_{31j} \\ \cdot \\ \cdot \\ \cdot \\ F_{3Mj} \\ F_{41j} \\ \cdot \\ \cdot \\ \cdot \\ F_{4Mj} \end{bmatrix} \quad \text{and} \quad \Delta\underline{X}_j = \begin{bmatrix} \Delta X_{1j} \\ \cdot \\ \cdot \\ \cdot \\ \Delta X_{Mj} \\ \Delta Y_{1j} \\ \cdot \\ \cdot \\ \cdot \\ \Delta Y_{Mj} \\ \Delta X^i_{lj} \\ \cdot \\ \cdot \\ \cdot \\ \Delta X^i_{Mj} \\ \Delta Y^i_{lj} \\ \cdot \\ \cdot \\ \cdot \\ \Delta Y^i_{Mj} \end{bmatrix}$$

Equations are linearized in the manner of Naphtali and Sandholm (1971). We assume that the β_{xj} and β_{yj} ratios are independent of composition. The $\underline{\underline{A}}_j$ and $\underline{\underline{C}}_j$ coefficient matrices are then diagonal, which can be exploited to speed up the calculations and reduce computer storage requirements. Non-zero, diagonal elements of the $\underline{\underline{A}}$ and $\underline{\underline{C}}$ matrices:

$$\begin{array}{lll}
a_{ii} = \beta_{xj} + p_{xj}; & i = 1,M & ; j \neq m \neq 1 \\
a_{ii} = \beta_{xj} & ; \ i = 1,M & ; j = m \\
a_{ii} = \beta_{y,j-1} & ; \ i = M+1,2M & ; j \neq 1 \\
c_{ii} = \beta_{x,j+1} & ; \ i = 1,M & ; j \neq N \\
c_{ii} = \beta_{yj} + p_{yj}; & i = M+1,2M & ; j \neq n \neq N \\
c_{ii} = \beta_{yj} & ; \ i = M+1,2M & ; j = n
\end{array}$$

All remaining diagonal elements are zero.
The $\underline{\underline{B}}_j$ *matrix has a higher fraction of nonzero elements than the* $\underline{\underline{A}}_j$ and $\underline{\underline{C}}_j$ matrices and must be treated as a general 4M × 4M matrix. Its nonzero elements are the following:

$$\begin{array}{ll}
b_{ii} = -\ (\beta_{x,j+1} + \alpha_{xij}) & ; i = 1,M; j=1 \\
b_{ii} = -\ (p_x + \beta_{xj} + \alpha_{xij}) & ; i = 1,M; j=N \\
b_{ii} = -\ (p_x + \beta_{xj} + \beta_{x,j+1} + \alpha_{xij}) & ; i = 1,M; j \neq 1,N \\
b_{ii} = -\ (p_y + \beta_{yj} + \alpha_{yij}) & ; i = M+1,2M; j=1 \\
b_{ii} = -\ (\beta_{y,j-1} + \alpha_{yij}) & ; i = M+1,2M; j=N \\
b_{ii} = -\ (p_y + \beta_{yj} + \beta_{y,j-1} + \alpha_{yij}) & ; i = M+1,2M; j \neq 1,N \\
b_{i,i+2M} = \alpha_{xij} & ; i = 1,M \\
b_{i+M,i+3M} = \alpha_{yij} & ; i = 1,M
\end{array}$$

The following are for nonfeed cells only, i.e., $j \neq M,n$

$$\begin{array}{ll}
b_{i+2M,i} = \alpha_{xij} & ; i = 1,M \\
b_{i+2M,i+M} = \alpha_{yij}/\lambda & ; i = 1,M \\
b_{i+2M,i+2M} = -\alpha_{xij} & ; i = 1,M \\
b_{i+2M,i+3M} = -\alpha_{yij}/\lambda & ; i = 1,M \\
b_{i+3M,k+2M} = X^i_{ij}\partial K_{ij}/\partial X^i_{kj} & ; i = 1,M\ ; k = 1,M; k \neq i \\
b_{i+3M,\ i+2M} = b_{i+3M,\ k+2M} + K_{ij} & ; i = 1,M; k=1 \\
b_{i+3M,k+3M} = X^i_{ij}\ \partial K_{ij}/\partial Y^i_{kj} & ; i = 1,M; k=1,M; k \neq i \\
b_{i+3M,i+3M} = b_{i+3M,k+3M} - 1 & ; i = 1,M; k=1
\end{array}$$

The following are for feed cells only, i.e., $j=m$ or $j=n$:

$$\left.\begin{array}{l}
b_{i+2M,i} = -1 \\
b_{i+2M,i+2M} = 1 \\
b_{i+3M,i+M} = -1 \\
b_{i+3M,i+3M} = 1
\end{array}\right\} \quad i = 1,M$$

NOTATION

a_j = interfacial area per unit volume in cell j (m^{-1})
$\bar{a}$ = average interfacial area per unit volume (m^{-1})
$\underline{\underline{A}}, \underline{\underline{B}}, \underline{\underline{C}}$ = coefficient matrices in the tridiagonal formulation of the linearized governing equations (see Appendix)
C°_{ki} = concentration of solute i in feed of phase k
C_{kij} = bulk concentration of solute i in phase k in cell j (mol/m^3)
C^i_{kij} = concentration of solute i at x-y interface in phase k, cell j (mol/m^3)
C°_A = concentration of acetic acid in the aqueous feed, mol/L
C'_{AF} = bulk concentration of acetic acid in the aqueous phase at the aqueous-phase feed point, i.e., in cell m (mol/L).
C_{AR} = concentration of acetic acid in the raffinate (mol/L).
f_{kj} = volumetric back-flow of phase k leaving cell j, Figure 1, (m^3/s)
$\underline{F}_j$ = vector of function values of governing equations for cell j (see Appendix)
F_k = net volumetric flowrate of phase k, see Figure 1, (m^3/s)
F_{kij} = elements of $\underline{F}_j$, as defined by Eqs. 5-8
JR = jump ratio, defined in Eq. 14
K' = equilibrium distribution ratio for acetic acid, defined by Eq. 13
K''_i = equilibrium constant for complexing reaction between acidic species i and tri-isooctylamine (Eq. 16), Units are (mol/L)$^{-1}$
K_{ij} = ratio of interfacial concentrations of solute i in cell j at equilibrium
K_La = overall volumetric mass-transfer coefficient, based on one liquid phase
k_{kij} = individual mass transfer coefficient for solute i in phase k, cell j (m/s)
M = number of transferring solutes
N = number of cells in extraction column
N_{kij} = number of individual k-phase transfer units for solute i, ($\equiv V\bar{a}k_{kij}/F_x$)
N_{ox} = overall number of transfer units based on the x phase
Pe_k = Peclet number in phase k, related to back-flow ratio in Eq. 15
p_{xj} = 0 for cells $1 \leq j < m$; = 1 for cells $m \leq j \leq N$
p_{yj} = 1 for cells $1 \leq j \leq n$; = 0 for cells $n < j \leq N$
Q_{kij} = dimensionless flux of solute i in cell j referred to phase k ($= q_{kij}/F_xC^\circ_{xi}$)
q_{ij} = interphase flux of solute i in cell j, defined by Eq. 3 (mol/s)
V = total volume of extractor (m^3)
V_j = volume of cell j (m^3)
X_{ij} = dimensionless x-phase concentration of solute i in cell j ($= C_{xij}/C^\circ_{xi}$)
Y°_i = $C^\circ_{yi}/C^\circ_{xi}$
Y_{ij} = dimensionless y-phase concentration of solute i in cell j ($= C_{yij}/C^\circ_{xi}$)
$\Delta\underline{X}_j$ = vector of predicted changes in dependent variables calculated by the multivariate-Newton procedure

Subscripts

m = position of x-phase feed cell
n = position of y-phase feed cell
i = index of solute species
j = cell index
x = refers to x-phase property
y = refers to y-phase property

Superscripts

i = interfacial property
o = initial (feed) property

Greek Symbols

α_{kij} = dimensionless mass-transfer coefficient for phase k, solute i, cell j,

$$\left[= N_{kij}\left(\frac{V_j a_j}{V\bar{a}}\right)\right]$$

β_{kj} = back-flow ratio of phase k for cell j, $(= f_{kj}/F_k)$
λ = ratio of feed flowrates, F_x/F_y
ϵ = error tolerance, used to determine convergence of solution

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An Experimental Investigation of Stability and Multiplicity of Steady States in a Biological Reactor

DAVID DIBIASIO
H. C. LIM
and
W. A. WEIGAND
School of Chemical Engineering
Purdue University
West Lafayette, Indiana 47907

The existence of multiple stable and unstable steady states in a continuous stirred tank biological reactor (CSTBR) was demonstrated experimentally for the first time. These experiments resulted in the determination of growth rate, yield and intermediate metabolite concentration data entirely from continuous culture. This information was used to qualitatively interpret the stability behavior in terms of the biochemistry and bioenergetics of substrate metabolism.

SCOPE

For several decades microorganisms have been considered as potential sources of protein for human and animal consumption. Methanol-utilizing organisms are of particular interest. These organisms, which exhibit nonmonotonic specific growth rates, are predicted to show multiple stable and unstable steady states in continuous culture.

The objective of this paper is to present the results of an experimental demonstration of the existence of multiple stable and unstable steady states in a CSTBR. The demonstration of the existence of these multiple steady states is of fundamental, theoretical and practical interest. In addition to supplying an experimental comparison to theoretical predictions, information desirable for the design of single cell protein (SCP) processes with inhibitory substrates is also obtained. This information includes knowledge of the type and degree of feedback control necessary for stabilization, but more importantly a better understanding of the biochemical regulatory mechanisms which result in the observed stability behavior.

The correspondence concerning this paper should be addressed to H. C. Lim.

David DiBiasio is with the Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, MA 01609. W. A. Weigand is with the National Science Foundation, Washington, D.C. 20550

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