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Separation of Nonlinearly Sorbing Solutes by Parametric Pumping

A rigorous mathematical analysis shows that parametric pumps can separate, concentrate, and recover in pure form all components of a multisolute mixture. The obtained separation cannot be predicted by existing linear models. Criteria for determining steady periodic separations of binary mixtures are discussed in detail for batch and continuous systems.

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SCOPE

Parametric pumping is a cyclic fixed-bed sorption process for separating and purifying fluid mixtures. Previously, experiments with hydrocarbon mixtures, aqueous solutions of inorganic salts, and other mixtures have shown that parametric pumping can produce very large separations. These separations have been modeled mathematically in two ways. In one method computer solutions of a set of partial differential equations are obtained. This is not easy to implement, and the results apply only to the specific system studied. The other method for modeling is easy to use and is more general, but it is restricted to systems where sorption isotherms are linear, that is, where sorbed phase concentration is directly proportional to fluid phase concentration.

However, in real systems, linear isotherms usually occur only at low concentrations. More likely, the sorption process will follow a Langmuir type of isotherm. In the case of ion-exchange, where sorbing species compete for ion-exchange sites, the isotherms are not linear. Also, when nonionic species compete for sites, sorption is nonlinear. The linear theory cannot adequately treat these cases. A case in point where the linear theory fails is the separation of $K^+ - Na^+ - H^+$ by Butts, et al. (1973), where K^+ and H^+ accumulated at opposite ends of a bed, while Na^+ accumulated in the middle.

In this paper, the theory of nonlinear, multisolute, equilibrium chromatography developed by Rhee, et al. (1970) is used to analyze parametric pumping systems. Using this theory, one can obtain convenient to use algebraic relations for understanding and predicting parametric pumping behavior. The experimental results of Butts, et al. (1973), are predictable from this theory with little effort. The analytical, nonlinear theory also makes the exploration of continuous (that is, not batch) separations much easier.

CONCLUSIONS AND SIGNIFICANCE

A mathematical analysis of parametric pumping separations is presented which rigorously takes into account for the first time realistic nonlinear sorption equilibria.

First, for batch, binary separation, the criteria in Table 2 were developed to determine which type of separation will occur at steady periodic state. The criteria depend on initial loading of the system, sorption isotherm constants, and amount of fluid displaced per half cycle. Transient analysis of this case is also examined.

Second, it was shown how a batch, multisolute parametric pump can separate, concentrate, and recover in pure form all components of a multicomponent mixture. When complete separation occurs, the components will be arranged in the bed in order of their affinity for the sorbent. Criteria for this separation are shown in Equations (21) to (29). The linear theory cannot predict this separation, since the separation is due to nonlinear interactions.

Third, the nonlinear theory applies easily to the two continuous binary separation schemes in Figures 5 and 6, and to a combination of these.

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Parametric pumping is a cyclic separation process which experiments have shown can produce very large separations of fluid mixtures. Sweed (1971, 1972) and Wankat (1974) have reviewed the subject.

One process arrangement, called the direct thermal mode, employs a jacketed, fixed bed of adsorbent or ion-exchange particles through which the fluid being separated is caused to flow. The direction of flow is changed periodically, and the temperature of the bed is cycled synchronously between two temperatures.

As a result of this process, certain solute species migrate toward one end of the bed and accumulate in a reservoir there, while other species migrate toward the other end of the bed. With a strong cationic exchange resin and an aqueous solution of K^+-Na^+-H^+ chlorides, Butts, et al. (1973), found that K^+ accumulates at the end toward which fluid flows when the bed is hot, H^+ accumulates at the other end, and Na^+ migrates away from both ends and accumulates in the middle of the bed. The extent of separation increases with the number of cycles, approaching a steady periodic state after many cycles.

Several mathematical models of the process have been developed. These fall into one of two categories: complete or ideal. If complete, they include mass transfer resistances, axial dispersion, and realistic nonlinear sorption isotherms. If ideal, they neglect mass transfer resistances and axial dispersion, and require linear isotherms. The complete models simulate experiments well (Sweed and Gregory, 1971) but require extensive computer solution of partial differential equations. The ideal models set limits on the separation (Chen and Hill, 1971; Pigford, et al. (1969), and are algebraic rather than differential equations. However, they do not handle realistically nonlinear isotherms, where solutes compete for sites on the sorbent. Linearization of the isotherm is necessary when the ideal models are used, yet this linearization removes much of the realism for high concentration solutions and for ion exchange where competition for sites exists. Indeed, the separation found by Butts, et al. (1973), cannot be predicted by any linear model.

In this paper, the rigorous mathematical analysis of parametric pumping systems is extended to nonlinear sorption and ion exchange, although the effects of axial dispersion and mass transfer resistances are still neglected. Transient and steady periodic states are examined, as well as the simultaneous separation of several sorbing species. Continuous fractionation of such multisolute mixtures is also discussed.

The equations which describe each half cycle of parametric pumping are exactly those of chromatography. Our approach to solving these equations draws on the work of Rhee (1968) and Rhee, et al. (1970). The results are applicable to systems in which the sorption isotherms are of the favorable type, including adsorption characterized by Langmuir isotherms and ion exchange with constant binary selectivities.

THEORY OF NONLINEAR CHROMATOGRAPHY

Chromatographic theory will be reviewed briefly. Details can be found elsewhere (Camero, 1974).

The following ideal conditions are assumed:

1. The system is one dimensional in the direction of flow with uniform cross-sectional area.
2. The volumetric flow rate of fluid and the void fraction of the bed are constant.
3. Axial diffusion is negligible, and plug flow exists.
4. Local equilibrium between the fluid and solid phases exists everywhere in the column.
5. The sorption process, that is, either conventional adsorption or ion exchange, is isothermal and isochoric.
6. Heating and cooling of the bed are instantaneous.

Consider a system in which only one independent component or solute is distributed between the phases. Binary ion exchange and two-component mixtures with constant molar density are examples of systems with a single independent component.

Assume that the sorption isotherm (in dimensionless form)

$$\bar{y}_1 = g_1(y_1, \theta) \tag{1}$$

is of the favorable type; that is

$$\frac{\partial g_1}{\partial y_1} > 0 \quad \text{and} \quad \frac{\partial^2 g_1}{\partial y_1^2} < 0$$

The solute material balance for constant temperature operation is

$$\frac{\partial y_1}{\partial x} + \frac{\partial y_1}{\partial \tau} + \nu \frac{\partial \bar{y}_1}{\partial \tau} = 0 \tag{2}$$

Differentiating Equation (1) with respect to τ at constant temperature and substituting into Equation (2), we get

$$\frac{\partial y_1}{\partial x} + \left[1 + \nu \frac{\partial g_1}{\partial y_1}\right] \frac{\partial y_1}{\partial \tau} = 0 \tag{3}$$

This quasilinear, first-order, hyperbolic partial differential equation has the solution that y_1 is constant along characteristic curves given by

$$\sigma_1(y_1, \theta) \equiv \left(\frac{d\tau}{dx}\right)_{y_1,\theta} = 1 + \nu \left.\frac{\partial g_1}{\partial y_1}\right|_{y_1,\theta} \tag{4}$$

Since y_1 is constant, the right side of Equation (4) is also constant along a characteristic. Therefore, the characteristics are straight lines with slope σ_1^{-1} when plotted in the $x - \tau$ plane.

Physically, σ_1^{-1} is the speed that a wave of constant concentration moves through an isothermal bed. For the favorable isotherm considered here, σ_1 decreases with increasing concentration. Equivalently, waves of high concentration move faster than waves of lower concentration. In the dimensionless notation used here, the bulk or carrier fluid has a speed of $\sigma^{-1} = 1.0$, and no waves can move more rapidly.

One can use these characteristic lines and the $x - \tau$ plane to obtain concentration profiles and histories for a chromatographic process, provided that the characteristics do not intersect one another.

If they do intersect, a discontinuity in concentration, or a shock, will begin to form at the first point of intersection. Once a shock forms, Equation (2) no longer applies in the neighborhood of the shock, and it must be replaced by a macroscopic (that is, nondifferential) conservation equation. This leads to the following equation for the characteristic direction of a shock in the $x - \tau$ plane:

$$\sigma^s \equiv \left(\frac{d\tau}{dx}\right)^s = 1 + \nu \frac{\{\bar{y}_1\}}{\{y_1\}} \tag{5}$$

where $\{\ \}$ is the difference between the quantity in the braces evaluated upstream of the shock and downstream. The shock moves with speed $(\sigma^s)^{-1}$. Note that σ^s need not be constant; hence its characteristic curve in the $x - \tau$ plane may not be straight.

At the end of each half cycle, the bed temperature changes instantaneously with a simultaneous redistribution of solute between the solid and fluid phases. If the two temperatures are denoted by θ_U and θ_D (for upflow and downflow, respectively), then the concentrations before and after the temperature change are related by

$$y_{1D} + \nu g_1\,(y_{1D}, \theta_D) = y_{1U} + \nu g_1\,(y_{1U}, \theta_U) \qquad (6)$$

at each point within the bed. Since to this point g_1 has not been specified, Equation (6) cannot be solved explicitly for y_{1U} as a function as y_{1D}. However, let us denote this solute redistribution function as

$$y_{1U} = h(y_{1D}) \qquad (7)$$

TRANSIENT PARAMETRIC PUMPING WITH A SINGLE INDEPENDENT SOLUTE

The transient analysis of a parametric pumping separation applies the concepts discussed above one half cycle at a time. The interaction patterns that arise depend on the sorption isotherm, initial conditions in the bed and reservoirs, and the amount of fluid displaced per half cycle.

To illustrate the transient method, consider the batch separation of a binary ionic mixture with a strong cation exchange resin as the sorbent. Parameters are shown in Table 1. The equilibrium isotherm is

$$g(y, \theta) = \frac{K_2{}^1(\theta) y}{[K_2{}^1(\theta) - 1]y + 1} \qquad (8)$$

where y and g refer to component 1, and $K_2{}^1$, the binary selectivity constant, depends only on temperature. The components are numbered so that $K_2{}^1 > 1$, making Equation (8) a favorable isotherm.

Equation (8) has the same form as the Langmuir isotherm; hence this analysis applies to it, too. At time $\tau < 0$, the bed is at temperature θ_D, the fluid in the bed and in the bottom reservoir has concentration $y = 0.500$, the sorbent is in equilibrium with this fluid, and the top reservoir is empty. The volume of the bottom reservoir is equal to the volume of fluid α to be displaced each half cycle; hence there is no dead volume in either reservoir. For this example $\alpha = 50$. In the notation used here α is also the time needed to complete one half cycle. The bottom of the bed is located at $x = 0.0$; the top is at $x = 1.0$.

To begin the first cycle, the bed temperature is switched from θ_D to θ_U. Equation (7), evaluated for these isotherms, is used to calculate the new fluid concentrations in the bed at $\tau = 0^+$. As Figure 1 shows, the fluid increased to concentration $y = 0.598$ in the bed, while the bottom reservoir, which has no sorbent, is unchanged. Fluid from the bottom reservoir flows upward through the bed until $\tau = 50$. Since the concentration of the incoming fluid $y = 0.500$ is less than that ahead of it in the bed, a fan of characteristics, that is, an expansive wave, forms at the bed inlet. The top reservoir fills with fluid of concentration $y = 0.598$ through the entire half cycle; hence the top reservoir at $\tau = 50$ has concentration $y_T = 0.598$.

At $\tau = 50^+$, the bed temperature changes to θ_D for the second half cycle, and the solute redistributes itself between the solution and sorbent. Downward flow continues till $\tau = 100$. Since the concentration now decreases in the flow direction, a shock wave will tend to form at each concentration boundary. The discontinuity between the bed and reservoir at $x = 1.0$ moves downward as a shock with constant velocity, since the concentration on both sides of it remain constant. The shock speed is computed from Equation (5).

The expansive wave which formed during upflow now becomes a compressive wave and eventually becomes a complete shock. Fluid of concentration $y = 0.401$ fills the bottom reservoir; hence $y_B = 0.401$.

Figure 1 shows that at the end of cycle 1, $\tau = 100$, the bed has three concentration plateaus, $y = 0.598$, 0.500, and 0.401, with sharp boundaries between them. The procedure can be repeated cycle after cycle to give bed profiles and reservoir concentrations.

Table 1. Parameters Used in Transient Analysis of Single Independent Component Separation

$\nu = 75$
$K_2{}^1\,(\theta_U) = 2.0$
$K_2{}^1\,(\theta_D) = 3.0$
$\alpha = 50$
$\gamma = 0$
$TM = 81.75$

Uniform initial conditions: temperature $= \theta_D$
$y_1 = 0.5$
$g_1 = 0.75$

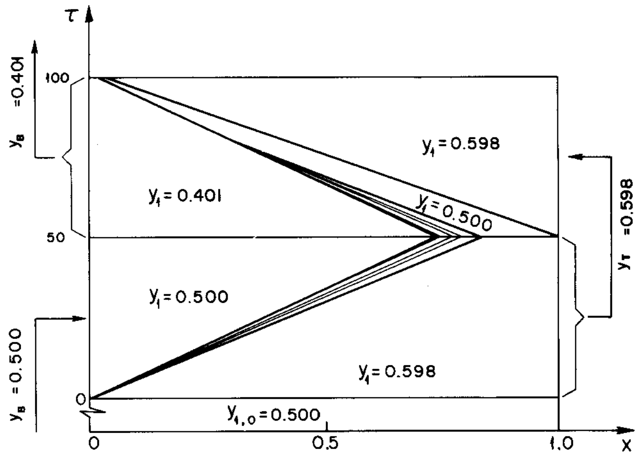


Fig. 1. Characteristics for batch separation of a binary mixture. System parameters taken from Table 1. Cycle 1.

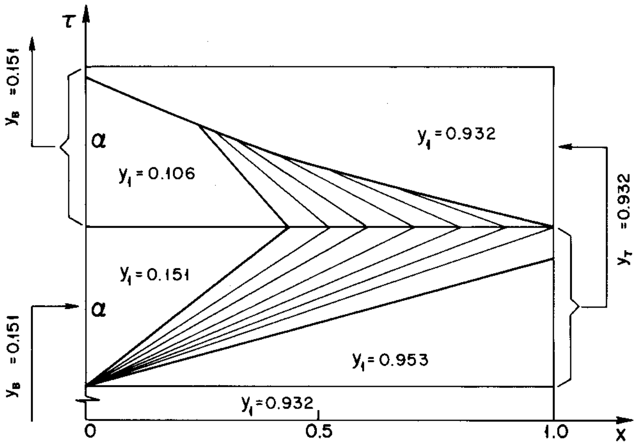
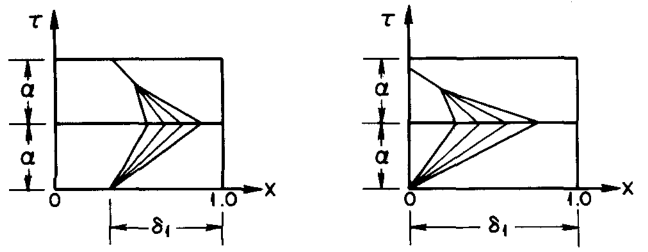


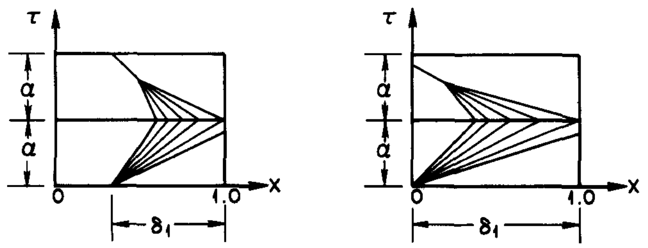
Fig. 2. Characteristics for batch separation of a binary mixture. System parameters taken from Table 1. Steady periodic state.

Separation will continue with succeeding cycles, and a steady period state (SPS) will be approached asymptotically. Figure 2 shows the $x - \tau$ plot for one cycle at SPS, $y_T = 0.932$, $y_B = 0.151$. Note that an infinite number of cycles are needed to reach the SPS.

Based on this example, two observations should be made. First, since the system was operated so that the more strongly sorbed component, solute 1, desorbed during upflow and migrated to the top, the concentration increased from bottom to top. Thus, during upflow, expansion waves developed, and during downflow compressive waves developed. At SPS there is only one wave front in the bed; it is expansive on upflow, compressive on downflow, and ends downflow as a complete shock. Camero (1974) showed that the isotherm used here, Equation (8), always leads to this pattern of behavior. For batch parametric pumping, note that in cycle 1 there were two waves on downflow. By the time the SPS is reached, only one wave exists in the column.



(a) Type I: $y_T = 1$, $y_B = 0$ (b) Type II: $y_T = 1$, $y_B > 0$



(c) Type III: $y_T < 1$, $y_B = 0$ (d) Type IV: $y_T < 1$, $y_B > 0$

Fig. 3. Steady periodic wave patterns for binary separations.

Second, if α had been much less than 50, there would have been no breakthrough of solute into the bottom reservoir, and the bottom reservoir's concentration would have approached zero.

The use of the characteristic method for situations more complex than this batch, binary case follows the same method: the characteristics are determined for each portion of the cycle from the conditions at the start of that portion, and the characteristics are followed until that portion ends. Between portions of the cycle the solute is redistributed according to the change in equilibrium due to temperature.

The transient method is directly applicable to continuous processes, where feed and product streams are involved. It is also applicable to multisolute systems, where solutes compete for sorption sites. However, the method becomes quite complicated for these cases, since several wavefronts can exist in the bed simultaneously, and these fronts can merge or interact with one another.

Frequently one is interested more in the steady periodic state which results after start-up transients have died away than in the transients themselves. The next section shows how SPS can be calculated directly without going through the transients. This is done first for the batch binary case, and then is extended to continuous binary, and batch, multisolute cases.

DIRECT CALCULATION OF STEADY, PERIODIC, BATCH SEPARATION OF BINARY MIXTURES

As mentioned above, the steady periodic state for the isotherm in Equation (8) must contain only one wave. Additional waves from start-up transients eventually disappear. Further, at the start of upflow there must be one concentration discontinuity in the bed. Figure 3 shows qualitatively the $x - \tau$ plots for the only possible steady periodic states. If both reservoirs contain components in pure form ($y_T = 1.0$, $y_B = 0.0$), the separation is called type I. All types are shown on Figure 3.

The factors that determine which separation type will occur are initial solute loading, the sorption isotherms at the temperatures involved, and the displacement α. One additional variable is the dead volume in the reservoir, γ. Since only the steady periodic state is desired, the initial concentration profile is not important.

In all four types the distance δ of the discontinuity from the top of the bed at the end of downflow depends on the solute loading in the system and the top concentration y_T. The total moles of component 1 in the system per bed void volume TM at the end of the downflow is given by

$$\text{TM} = y_T(\gamma + \delta) + (1 + \gamma + \alpha - \delta)y_B + g(y_T, \theta_D)\nu\delta + g(y_B, \theta_D)\,\nu(1 - \delta) \qquad (9)$$

where $0 \leq \delta \leq 1$.

Another useful quantity is the slope $\sigma^*(y_T)$ of the leading edge of the expansive wave on upflow. Since the concentration at that edge is [from Equation (7)]

$$y_U = h(y_T) \qquad (10)$$

the characteristic has slope

$$\sigma^*(y_T) = 1 + \nu \frac{\partial g}{\partial y}\bigg|_{h(y_T)} \qquad (11)$$

Type I ($y_T = 1.0$, $y_B = 0.0$)

From Figure 3*a*, δ is seen to lie within the column; that is, $0 < \delta < 1$. Also, to insure that the leading edge of the expansive wave does not enter the top reservoir on upflow and lower y_T, δ must be greater than $\alpha/\sigma^*(1.0)$.

From Equation (9), for this case

$$\delta = \frac{\text{TM} - \gamma}{1 + \nu} \qquad (12)$$

Therefore, for type I separation

$$\frac{\alpha}{\sigma^*(1.0)} < \frac{\text{TM} - \gamma}{1 + \nu} < 1 \qquad (13)$$

The left inequality keeps $y_T = 1$, while the right one insures that $y_B = 0$.

Type II ($y_T = 1.0$, $y_B > 0$)

From Figure 3*b*, it is seen that the shock on downflow appears to intersect the $\tau = 2\alpha$ line at $\delta > 1$. On upflow $\alpha/\sigma^*(1.0)$ must be less than 1 to keep $y_T = 1.0$. Therefore, for type II separation

$$\frac{\alpha}{\sigma^*(1.0)} < 1 < \frac{\text{TM} - \gamma}{1 + \nu} \qquad (14)$$

In this case there is so much solute present that even if the top reservoir and column are filled to concentration $y = g(y, \theta_D) = 1.0$, enough solute is left over to keep $y_B > 0$.

Type III ($y_T < 1.0$, $y_B = 0$)

From Figure 3*c*, it is seen that $\delta < 1$, but now δ is calculated from Equation (9), not (12), since $y_T < 1$.

Thus

$$\delta = \frac{\text{TM} - \gamma y_T}{y_T + \nu g(y_T, \theta_D)} \qquad (15)$$

On upflow $\alpha/\sigma^*(y_T)$ must be greater than δ, thus keeping $y_T < 1$. Therefore, for type III separations

$$\frac{\text{TM} - \gamma y_T}{y_T + \nu g(y_T, \theta_D)} < \frac{\alpha}{\sigma^*(y_T)} \qquad (16a)$$

and

$$\frac{\text{TM} - \gamma y_T}{y_T + \nu g(y_T, \theta_D)} < 1.0 \qquad (16b)$$

Note that y_T is the average concentration to enter the reservoir on upflow; that is

$$y_T = \frac{1}{\alpha} \int_0^\alpha y|_{x=1}\, d\tau \qquad (17)$$

From $\tau = 0$ to $\tau = \sigma^*(y_T)\delta$, the concentration entering the reservoir is $h(y_T)$. From $\tau = \sigma^*(y_T)\delta$ to $\tau = \alpha$, a fan of characteristics enters. Since the concentration and slope of a characteristic are related through Equation (4), one can solve that equation for $y(\tau)|_{x=1}$, the concentrations at $x = 1$. This gives

$$y(\tau)|_{x=1} = \frac{\sqrt{\dfrac{\delta\nu K_U}{\tau - \delta}} - 1}{K_U - 1}, \quad \sigma^*(y_T)\delta < \tau < \alpha \qquad (18)$$

Integrating according to Equation (17), we get

$$y_T = \frac{\tau_A}{\alpha} h(y_T) + \frac{1}{\alpha(K_U - 1)} \{(2\sqrt{\nu\delta K_U})$$
$$([\alpha - \delta]^{1/2} - [\tau_A - \delta]^{1/2}) - [\alpha - \tau_A]\} \qquad (19)$$

where $\tau_A = \sigma^*(y_T)\delta$ is the time when the leading characteristic first reaches the top of the bed. A combination of (15) and (19) gives y_T in implicit form.

Therefore, for type III separations, Equations (16*a*) and (16*b*) apply where y_T is given by the solution of (15) and (19).

Type III occurs when there is not enough solute in the system to fill the top reservoir with concentration $y_T = 1.0$, yet α is small enough to prevent contamination of the bottom.

If in solving (15) and (19) for y_T it turns out that $\tau_A > \alpha$, or $\delta > 1$, or y_T lies outside the allowable range (0, 1), then type III separation does not exist, and one of the other types occurs for the value of α selected.

Type IV ($y_T < 1.0$, $y_B > 0.0$)

Figure 3*d* shows this type to occur when $\delta > 1$ as calculated from (15) and $\alpha/\sigma^*(y_T) > 1$. Here y_T is calculated as for type III with $\delta = 1$. Therefore, for type IV

$$\frac{\alpha}{\sigma^*(y_T)} > 1 \qquad (20a)$$

and

$$\frac{\text{TM} - \gamma y_T}{y_T + \nu g(y_T, \theta_D)} > 1 \qquad (20b)$$

Note too that

$$\frac{\text{TM} - \gamma}{1 + \nu} < \frac{\text{TM} - \gamma y_T}{y_T + \nu g(y_T, \theta_D)}$$

Thus, if the left-hand side is greater than 1.0, so is the right-hand side.

Let us consider again the binary batch example used in the transient analysis. From the initial conditions and the isotherm, TM = 81.75. Also, $\sigma^*(1.0) = 38.5$. Thus, by using data from Table 1

$$\frac{\text{TM} - \gamma}{1 + \nu} = 1.0756$$

$$\frac{\alpha}{\sigma^*(1.0)} = 1.2987$$

The top concentration can be calculated from Equations (15) and (19), and then the bottom concentration can be calculated from Equation (9). Referring to Table 2 which summarizes the criteria for each separation type, one sees that type IV separation is predicted. This agrees with results obtained above.

Table 2. Criteria for Each Type of Separation

Type	y_T	y_B	Criteria
I	1.0	0.0	$\frac{\alpha}{\sigma^*} < \delta < 1.0$
II	1.0	>0.0	$\frac{\alpha}{\sigma^*} < 1 < \delta$
III	<1.0	0.0	$\frac{\alpha}{\sigma^*} > \delta; \delta < 1$
IV	<1.0	>0.0	$\frac{\alpha}{\sigma^*} > 1; \delta > 1$

Notes: δ is given by equation (15).
σ^* is given by Equation (11).

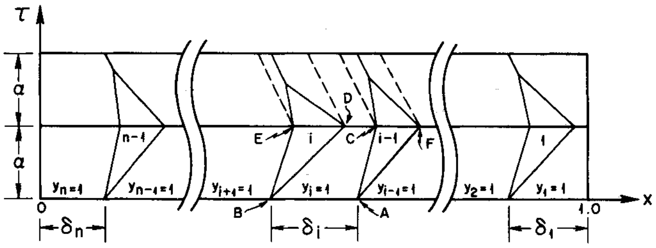


Fig. 4. Steady periodic wave pattern for complete separation of an *n*-component mixture.

Camero (1974) has shown that the criteria in Table 2 unambiguously determine which type of separation will result for any initial, equilibrium, and operating conditions.

BATCH SEPARATION OF MULTICOMPONENT MIXTURES

Multicomponent systems behave in a manner similar to those of binary systems; that is, separation proceeds until a steady periodic state is reached. In this section, the complete separation of an n component mixture will be considered. First, the steady periodic wave pattern will be examined (the transient behavior becomes quite complex and is not treated here), and then the criteria for complete separation will be developed.

Steady Periodic Wave Pattern

If complete separation occurs among n components, the concentration profile in the bed will involve $(n - 1)$ sharp discontinuities between regions containing only one component each. The wave pattern in the immediate vicinity of each discontinuity is influenced, therefore, only by the components present on the sides of the discontinuity. As a result, interactions between only two components need to be considered at each discontinuity, and the approach presented above for binary mixtures is applicable.

The results of the previous section indicate that a complete separation between two components can be obtained at the end of the downflow half cycle as long as the wave formed in the region between the components does not break through either end of the column. The wave pattern then repeats itself cycle after cycle. For the complete separation among n components, therefore, there must be $(n - 1)$ waves in the column at the steady periodic state, and the steady periodic wave pattern must be of the form shown in Figure 4. If this pattern does not develop, then complete separation is not possible. Note that there is no interaction between adjacent waves. If this occurred, it would lead to additional interaction in some of the waves, and the concentration profile at the end of the cycle would not be the same as that at the beginning.

Let the components be numbered from 1 to n in their order from the top of the bed at the SPS, as shown in

Figure 4. As discussed in the previous section, complete separation between any pair of components i and $(i + 1)$ requires that

$$K^i_{i+1}(\theta_D) > K^i_{i+1}(\theta_U) > 1, \quad i = 1, 2, \dots n - 1 \tag{21}$$

Another way of expressing the same information is

$$K_i^1 > K_i^2 > \dots > K_i^{n-1} > K_i^n, \quad i = 1, 2, \dots, n \tag{22}$$

at each temperature. Thus, if complete separation does occur, then the components will arrange themselves in the bed in decreasing order of their selectivity coefficients or their affinities for the solid phase.

Separation Criteria

The criteria for complete separation of an n component mixture can be obtained by analyzing the steady periodic wave pattern shown in Figure 4. The wave formed between components i and $(i + 1)$ will be referred to as wave i, and the slope of the characteristics in the expansion part of wave i will be denoted by

$$\sigma_i(y_i, \theta_U) = 1 + \nu \frac{\partial g_i}{\partial y_i}(y_i, \theta_U) \tag{23}$$

The solid phase concentration of each component is formally a function of the fluid concentration of the $(n - 1)$ independent components in the system, but since only one independent component is present in each wave i at the steady periodic state, the derivative in Equation (23) is a function of only one component.

At the end of downflow, the total moles of component 1 are divided between the top reservoir and a fraction of δ_1 of the bed (see Figure 4); that is

$$TM_1 = \gamma + \delta_1 (1 + \nu) \tag{24}$$

Components 2 through $(n - 1)$ are contained entirely in the bed, and thus

$$TM_i = \delta_i (1 + \nu), \quad i = 2, 3, \dots (n - 1) \tag{25}$$

Component n exists both in the bottom reservoir and in the bed. Since the volume of the bottom reservoir at the end of downflow is $(\alpha + \gamma)$, one may write

$$TM_n = (\alpha + \gamma) + \delta_n (1 + \nu) \tag{26}$$

Equations (24) through (26) define the δ_i's. A necessary condition for complete separation is that

$$\delta_i > 0 \quad i = 1, 2, \dots n \tag{27a}$$

and

$$\sum_{i=1}^{n} \delta_i = 1.0 \tag{27b}$$

Also, the leading characteristic in wave 1 must not break through the top of the bed on upflow or else the fluid in the top reservoir won't be pure component 1; thus

$$\delta_1 > \frac{\alpha}{\sigma_1^*(1.0)} \tag{28}$$

To prevent the leading characteristic of wave i (line BD in Figure 4) from intersecting the trailing characteristic of wave $i - 1$ (line AC) requires that

$$\delta_i > \alpha \left[\frac{1}{\sigma_i(1.0, \theta_U)} - \frac{1}{\sigma_{i-1}(0.0, \theta_U)} \right] \tag{29}$$

Camero (1974) has proved that if the waves do not intersect on upflow, they will not intersect on downflow.

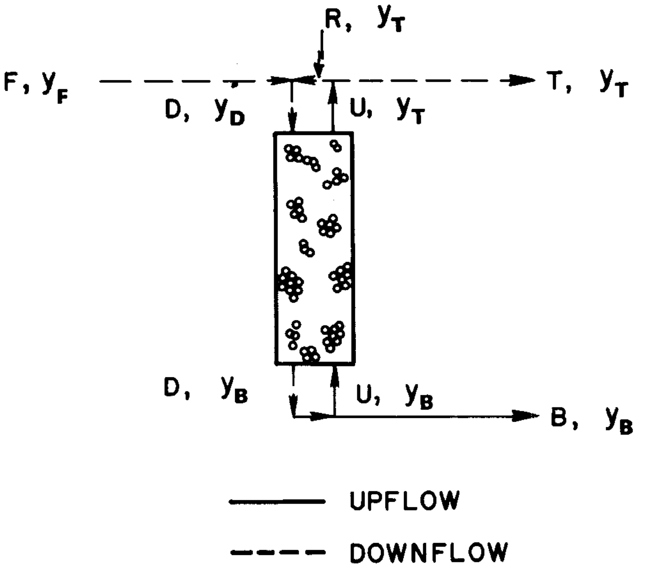


Fig. 5. Schematic of mode I.

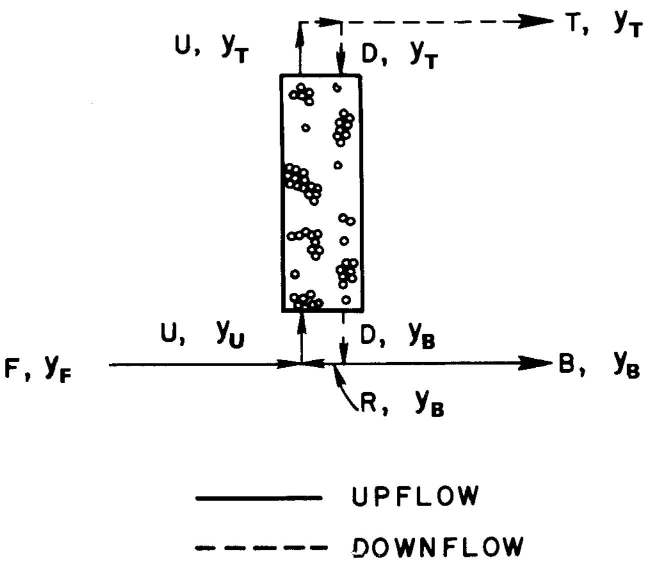


Fig. 6. Schematic of mode II.

Thus, complete separation among n solutes requires that the solute selectivities be ordered as in Equation (22), and that the order not change with temperature; that all $\delta_i > 0$ as given by Equations (24) through (26); that there be no breakthrough of solute 2 at the top of the bed [Equation (28)]; and that the waves of adjacent solutes not intersect [Equation (29)].

If complete separation is achieved for ion-exchange systems, the final fluid concentration of each ion will be equal to the total ionic concentration of the original fluid mixture. As discussed previously, the required isotherm shapes for complete separation in binary systems can be satisfied by ion-exchange systems with constant separation factors, as well as by Langmuir adsorption systems.

These separation criteria have been applied (Camero, 1974) to the experimental system used by Butts, et al. (1973). All the criteria for complete separation are satisfied for their K^+-Na^+-H^+ system. Experiments of Butts, et al. (1973), did indeed approach complete separation as predicted, with the most strongly sorbed species K^+ going to the top of the bed, the next most strongly sorbed species Na^+ going to the middle of the bed, and H^+ going to the bottom.

Recovery of Components

If complete separation is achieved among n components, then at the end of downflow, the components are separated from each other by sharp discontinuities. They may be recovered in pure form by elution in the downward direction at temperature θ_D by using any component r such that $K_1^r \geqq 1$. The total concentration (or molar density) of the elutant must be the same as the total concentration of the fluid already in the system.

As downflow occurs, the boundary between each component will remain sharp, since $K^i_{i+1} > 1$ across every shock. Each boundary moves through the bed at a dimensionless velocity of $(\sigma^s)^{-1}$, where

$$\sigma^s = 1 + \nu \tag{30}$$

The solutes will leave the bottom of the column in the order $n, n-1, n-2, \ldots, 2, 1$. Complete elution requires that $(1+\nu)$ column void volumes of elutant be passed through the bed.

CONTINUOUS SEPARATION OF BINARY MIXTURES

The batch system discussed in the previous sections is well suited to processing small volumes of material. Batch processing becomes impractical for large scale operations, and some type of continuous operation must be considered.

Many continuous parametric pumping systems have been considered in the literature (Chen and Hill, 1971; Gregory and Sweed, 1972). These systems usually differ from each other according to how and when the feed is introduced. In the systems examined here, it is assumed that the feed is introduced only at the ends of the column, and that the concentration of the column influent is constant during each half cycle. These systems are amenable to direct analysis of the steady periodic state.

In the discussion which follows, two one-column configurations or modes are presented, each of which is capable of producing large separations. One mode is analogous to a stripping column in distillation, and the other is analogous to an enriching column. The two modes can be combined to form a continuous system which can separate a binary mixture into two rather pure streams, in analogy with a combined stripping and enriching column in distillation.

One-Column Configurations

Consider the two modes shown in Figures 5 and 6. Each takes a feed stream F and separates it into a top product stream T and a bottom product stream B. In mode I, a portion of the fluid from the top reservoir is withdrawn as product during downflow. The remainder is combined with the feed, and the resulting stream is sent down the column and into the bottom reservoir. During upflow, a portion of the fluid from the bottom reservoir is withdrawn as product, and the remainder is sent up the column and into the top reservoir. Operation of mode II is similar to that of mode I. The assumptions and isotherms used above will be used here, too.

Modes I and II are both characterized by unequal fluid displacements in each direction. It is thus necessary to define two values of α, that is, α_U and α_D, corresponding to the number of column void volumes displaced during upflow and downflow, respectively. In spite of these unequal fluid displacements, the steady periodic wave pattern in these continuous systems is the same as in the batch system; that is, only one concentration wave can exist in the column at the steady periodic state, and the wave must originate from a sharp discontinuity at the beginning of upflow and must completely coalesce into a shock by the end of downflow.

The method of calculation is identical to that used for the batch binary case with the following exceptions.

First, α_U does not equal α_D, so the separation criteria involving $\alpha/\sigma^*(y_T)$ must use α_U. The calculation of δ is unaffected.

Second, in mode I, y_D is not simply the integral of what exits the top of the column as it was for the batch case. Here y_D is the weighted average of the refluxed top product y_T and the feed of concentration y_F. In mode II, y_U is the weighted average of feed and reflux.

Third, mode I cannot produce a pure top product ($y_T = 1.0$) unless the feed is already pure. Hence mode I is like a stripping column, and only separation types III and IV are possible. Mode II cannot produce a pure bottom product ($y_B = 0.0$), and so it is like an enriching column with only types II and IV possible.

If a mode II column is placed above mode I so that feed enters between the two, then this same analytical approach can calculate the behavior of a complete rectification column. Details of this can be found in Camero (1974).

CONTINUOUS SEPARATION OF MULTICOMPONENT MIXTURES

Analysis of continuous multicomponent parametric pumps is much more difficult than any of the systems discussed above. For the case of n independent sorbing components, where all species compete for sorption sites, every concentration discontinuity will usually generate n different waves. Thus, on the first half cycle of operation of a multisolute parapump, the discontinuity between the reservoir and the bed will cause n waves to enter the bed. If α is insufficient to push any waves out of the bed, then on the next half cycle each of the n waves will generate n waves. These waves will interact with one another in one of several ways if they intersect. Clearly, the number of waves and wave-wave interactions increases rapidly with cycle number.

Even at steady periodic state, the column will contain many waves, since the feed-column discontinuity will generate them. So a rigorous analysis of the multicomponent system certainly will be complex. Also, any criteria for separation ability which might evolve from such an analysis are likely to be so complex that their use would be limited.

If a parametric pump used to separate multicomponent mixtures continuously were like modes I or II above, then only two product stream would be involved, and a separation based on key components could be used. (The use of key components in multicomponent distillation is well known.) This approach to multicomponent separation reduces it to a binary case which has already been discussed.

CONCLUSION

The ability of a batch parametric pump to separate completely a multicomponent mixture is based on the nonlinear nature of the isotherms, and indeed on the interference of each species with all others in the sorption equilibrium.

Usual chromatographic practice for multicomponent separation is most effective when concentrations are low so that sorption isotherms are linear and solutes don't interact. Parametric pumping is just the opposite, since it takes advantage of the interaction and higher concentration to bring about the separation.

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NOTATION

B = bottom product volume
D = downflow internal stream volume in continuous systems
F = feed stream volume
g_i = solid phase concentration of species i in equilibrium with fluid; if not subscripted, then it refers to species 1
$h(y_D)$ = function, Equation (7), relating concentrations before and after temperature change
i, j = names of solutes
$K_j^i(\theta)$ = binary selectivity coefficient between species i and j at temperature θ, see Equation (8)
n = number of components in a multicomponent system
R = reflux stream volume in continuous system
T = top product volume
TM_i = total moles of species i in a batch system; if not subscripted, it refers to species 1
U = upflow stream volume in continuous system
x = axial position in sorbent bed with $x = 0$ at the bottom and $x = 1.0$ at the top
y_i = fluid phase concentration of species i; if not subscripted, it refers to species 1
$\bar{y}_i$ = solid phase concentration of species i; if not subscripted, it refers to species 1

Greek Letters

α = number of column void volumes displaced per half cycle
γ = number of column void volumes in reservoirs not displaced
δ_i = fraction of sorbent bed length; if not subscripted, it refers to species 1
θ = temperature
ν = ratio of molar capacity of sorbent to molar capacity of fluid on an equal basis, for example, per unit volume of bed
σ = slope of a characteristic in $x - \tau$ plane
τ = time

Subscripts and Superscripts

B = bottom reservoir or product
D = downflow or stream D
F = feed stream
R = reflux stream
s = shock
T = top reservoir or product
U = upflow or stream U
1,2,... = component number
$*$ = leading edge of expansive wave

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Solid Phase Reactions Under Nonadiabatic Conditions

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The kinetics of solid phase reactions proceeding through nucleation and subsequent nucleus growth is treated by taking into account heat losses by convection and radiation from the reacting solid. A critical initial reaction temperature dependent upon particle size is identified below which the reaction decays and above which explosion can occur.

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