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Characteristics of Batch, Semicontinuous, and Continuous Equilibrium Parametric Pumps*

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Summary

Batch, semicontinuous, and continuous versions of the parametric pump are analyzed in terms of an equilibrium theory of pump performance. The batch pump and pumps with feed at the enriched end are shown under certain conditions to have the capacity for complete removal of solute from one product fraction and at the same time arbitrarily large enrichment of solute in the other product fraction. Under other conditions and for all conditions for pumps with feed at the depleted end separation factors and enrichment are modest.

INTRODUCTION

A recent experimental investigation by Wilhelm and Sweed (*1*) has shown that batch parametric pumping can yield very high separation factors in small equipment in a relatively short period of time. In this paper we investigate a number of batch, semicontinuous, and continuous versions of the parametric pump. We deduce their characteristics via extensions of the equilibrium theory of Pigford, Baker, and Blum (*2*). Emphasis is placed on the specification of operating conditions

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necessary to achieve high separation factors and at the same time arbitrarily large enrichment in the enriched fraction. A preliminary summary of this work has been reported elsewhere (3).

PARAMETRIC PUMP MODELS

We will consider the parametric pumps shown in Fig. 1 and certain variations of these pumps. Flow to and from the reservoirs of all pumps during each half-cycle is at the rate Q volume units per unit time. Each half-cycle is π/ω time units in duration so that the displacement volume is $Q\pi/\omega$. All pumps have dead volumes of size V_T and V_B volume units associated with the top and bottom reservoirs, respectively.

The pump in Fig. 1a is a batch pump while the others each have a feed stream and top and bottom product streams. The feed flow-rate is $(\varphi_T + \varphi_B)Q$ and the top and bottom product flow rates are $\varphi_T Q$ and $\varphi_B Q$, respectively, where φ_T and φ_B are the ratios of the top and bottom product flow rates to the reservoir displacement rate.

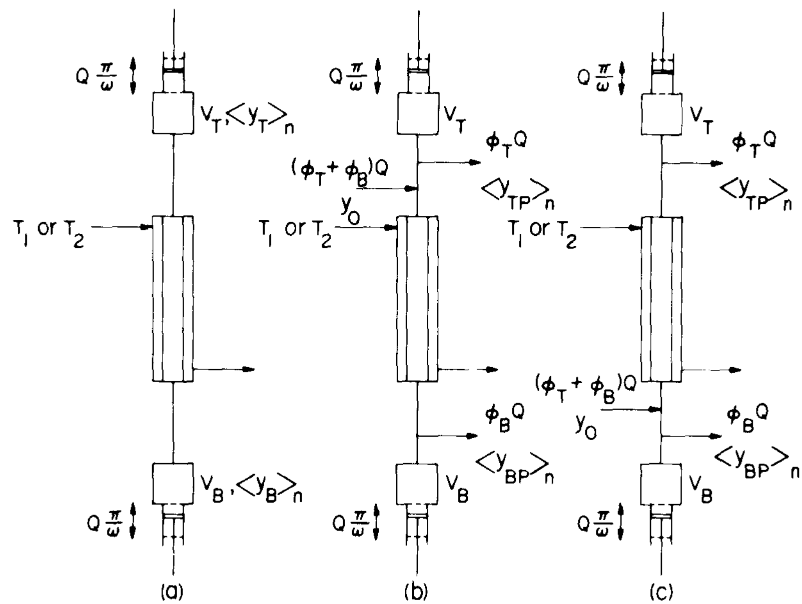

FIG. 1. Parametric pump models: (a) batch, (b) continuous with top feed, (c) continuous with bottom feed.

TABLE 1

Parametric Pump Characteristics

No.	Pump type	Column flowrate		Product flow rate limits	$\frac{L_1}{(u_0\pi/\omega)}$	$\frac{L_2}{(u_0\pi/\omega)}$	Penetration distance inequalities	Region of Fig. 3 where $\alpha_\infty \to \infty$	Regions of Fig. 3 where α_∞ is finite	Loci of switching points
		Upflow	Downflow							
1.	Batch	Q	Q	Not applicable	$\frac{1}{1-b}$	$\frac{1}{1+b}$	$L_1 > L_2$	1	3 ($L_1 > L_2$)	$L_2 = h; L_1 \geq n$
2.	Continuous top feed	$(1 - \varphi_B)Q$	$(1 + \varphi_B)Q$	$\varphi_T, \varphi_B < 1$	$\frac{1-\varphi_B}{1-b}$	$\frac{1+\varphi_B}{1+b}$	$L_1 \gtreqless L_2$	1	2, 3	$\begin{cases} L_2 = h; L_1 \geq h \\ L_1 = L_2; L_1, L_2 \leq h \end{cases}$
3.	Semicontinuous, continuous top feed during downflow, batch during upflow,	Q	$(1 + \varphi_B)Q$	$\varphi_T < 1$	$\frac{1}{1-b}$	$\frac{1+\varphi_B}{1+b}$	$L_1 \gtreqless L_2$	1	2, 3	
4.	Continuous bottom feed	$(1 + \varphi_T)Q$	$(1 - \varphi_T)Q$	$\varphi_T, \varphi_B < 1$	$\frac{1+\varphi_T}{1-b}$	$\frac{1-\varphi_T}{1+b}$	$L_1 > L_2$	None	1, 3 ($L_1 > L_2$)	None
5.	Semicontinuous, continuous bottom feed during upflow, batch during downflow	$(1 + \varphi_T)Q$	Q	$\varphi_B < 1$	$\frac{1+\varphi_T}{1-b}$	$\frac{1}{1+b}$	$L_1 > L_2$	None	1, 3 ($L_1 > L_2$)	None

The feed stream is located at the top of the column in Fig. 1b and at the bottom in Fig. 1c. Two modes of operation of these two pumps are treated. In one, the feed and product streams flow steadily both in upflow and downflow, resulting in truly continuous pumps. In the other, a semicontinuous form of operation results from batch operation during one half-cycle and continuous operation in the other. Thus we assume for the pump with feed at the top batch operation during upflow and continuous operation during downflow. The reverse arrangement is assumed for semicontinuous operation of the pump with feed at the bottom. The various pumps to be treated are listed in Table 1.

In the batch pump the flow rates within the column in upflow and downflow are identical and are equal to the reservoir displacement rate Q. The column flow rates in the pumps with feed and product streams may be determined by reference to flow diagrams such as those in Fig. 2 for the continuous pump with top feed. Material balances around the point of bottom product withdrawal show that the column flow rate in upflow must be $(1 - \varphi_B)Q$ and in downflow, $(1 + \varphi_B)Q$. Similarly, for the continuous pump with bottom feed the column flow rate is $(1 + \varphi_T)Q$ in upflow and $(1 - \varphi_T)Q$ in downflow. For the pumps with intermittent feed and product streams, the column flow rates are those of the corresponding continuous pumps during the half-cycle of continuous operation and those of the batch pump during the other half-cycle. The column flow rates in upflow and downflow in the various pumps are shown in Table 1.

We will restrict our interest in this paper to situations in which a given product stream during discharge of the adjacent reservoir comes only from that reservoir and not also from the column or from the feed stream. This restriction has the effect of limiting the values of φ_T and φ_B as shown in Table 1.

For all pumps we assume the column is filled with adsorbent particles, and the reservoirs and the voids in the column are filled with a two-component mixture, one component of which distributes between the two phases. Flow is upward during a hot half-cycle and downward during a cold half-cycle. The material in each reservoir is taken to be well mixed prior to flow reversal. The volume of material in the connecting lines is assumed to be included in the dead volume of the adjacent reservoir.

At pump startup the distributing solute fluid phase concentration is equal to the feed concentration y_0 throughout the apparatus and is in

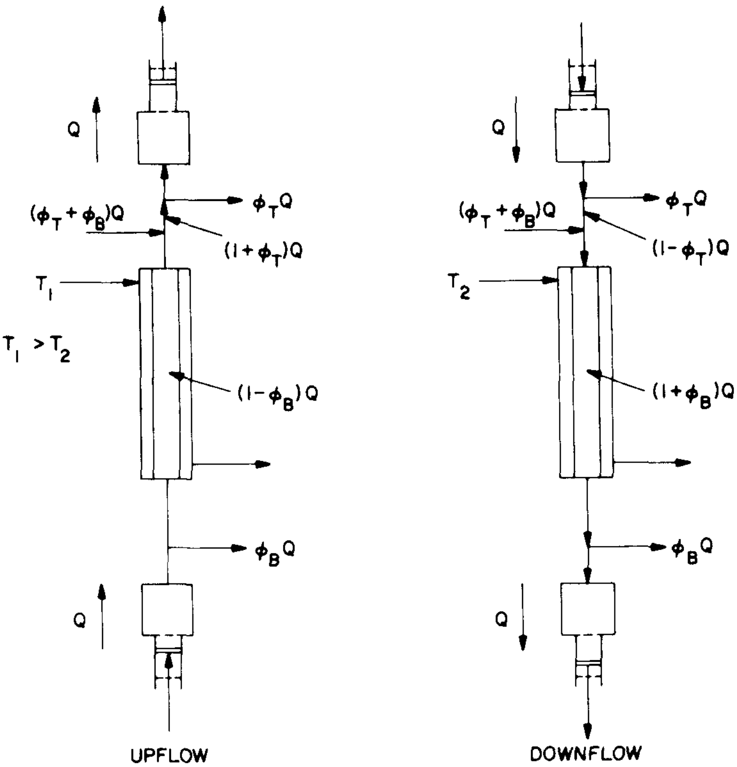

FIG. 2. Internal flow rates in continuous parametric pump with top feed.

equilibrium at the higher temperature with the solute concentration on the adsorbent particles. Flow in the first half cycle is upward.

MATERIAL BALANCES

Two types of equations are used in the calculation of the performance characteristics of the pumps just described: internal equations and external equations. An internal equation is a solute material balance reflecting events occurring within the adsorption column. An external equation is a solute material balance on streams flowing to and from a reservoir considering the presence of any adjacent feed and product streams. In general, solution of a system of two internal and two external equations is required in order to obtain expressions for the transients and steady-state concentrations in each pump.

Internal Equations

For processes inside the column we will assume as did Pigford, Baker, and Blum (*2*) that local interphase equilibrium exists with a linear distribution law having a temperature-dependent distribution coefficient, and that there is negligible axial diffusion. Based on these assumptions Pigford and co-workers derived a differential solute balance valid within the column which was solved by the method of characteristics. We will not repeat their derivation here but note that they found the slopes of the characteristic curves to be $u_0/(1-b)$ in upflow and $-u_0/(1+b)$ in downflow, where u_0 is the propagation velocity at the mean column temperature of the concentration fronts which enter the column at the start of each half-cycle, and b is a measure of the change in the amount of distributing solute found in the liquid phase as a result of a column temperature change, $0 \leq b \leq 1$.

In our application of this approach we allow for the possibility of different concentration front propagation velocities in upflow and downflow. The characteristic curves are again linear with slopes in our case $u_1/(1-b)$ in upflow and $-u_2/(1+b)$ in downflow, where now u_1 and u_2 are the propagation velocities at the mean column temperature in upflow and downflow, respectively. These velocities are equal to u_0 times the ratio of the column flow rate to the reservoir displacement rate.

The distance of penetration of the column by each new concentration front entering the column is equal to the product of the slope of the characteristic curve and the half-cycle duration and is

$$L_1 = \frac{u_1}{1-b}\frac{\pi}{\omega} \quad (1)$$

at the end of an upflow half-cycle, and

$$L_2 = \frac{u_2}{1+b}\frac{\pi}{\omega} \quad (2)$$

by the end of a downflow half-cycle.

The ratios $L_1/(u_0\pi/\omega)$ and $L_2/(u_0\pi/\omega)$ for each pump are given in Table 1.

The calculation of pump performance depends on the relative magnitudes of L_1, L_2, and h, the column height. Figure 3 indicates

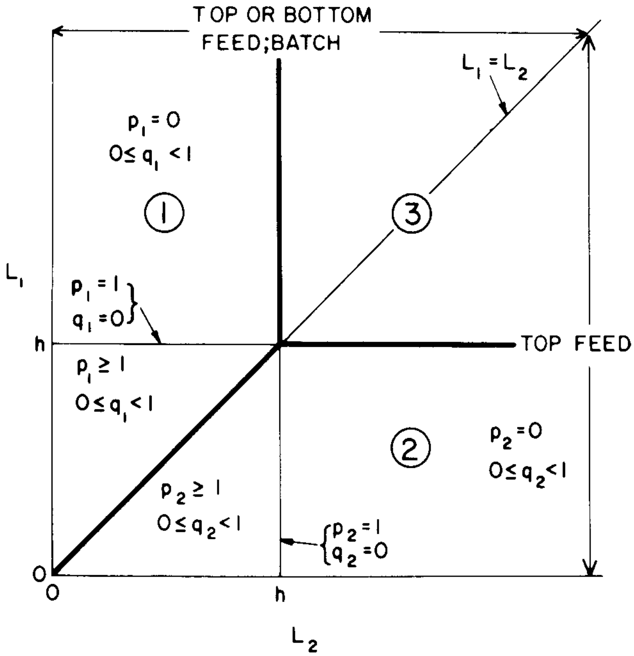

FIG. 3. Regions of parametric pump operation.

three regions in which, depending on these relative magnitudes, different internal equations apply.

We note by comparing the values of $L_1/(u_0\pi/\omega)$ and $L_2/(u_0\pi/\omega)$ given in Table 1 for the batch pump and the pump with feed at the bottom that for these pumps we will always have $L_1 > L_2$. Therefore in Fig. 3, only the region $L_1 > L_2$ is indicated as applying to these pumps. No such limitation exists for the pumps with feed at the top.

When the batch pump and the pumps with feed at the top are operated in Region 1 we will find that at steady-state solute removal from the lower reservoirs and lower product streams will be complete and the separation factors, defined as the ratio of the top and bottom product or reservoir concentrations, will approach infinity. When these pumps are operated outside Region 1 solute removal from the lower reservoirs and lower product streams will be incomplete and the steady-state separation factors will be modest in size by comparison. No region of infinite separation factor will be found for pumps with feed at the bottom.

The boundaries between Regions 1 and 3 and between Regions 1 and 2 are the loci of so-called "switching points." If in a pump originally operating in Region 1, L_2 is increased until it exceeds h, or L_1 becomes less than L_2, corresponding switching points are encountered and the steady-state behavior of the pump abruptly switches from a mode in which solute is completely removed from the lower reservoir to one in which solute removal is incomplete. One may visualize the crossing of the boundary $L_2 = h$ as resulting from increasing L_2 by increasing the reservoir displacement volume. Crossing of the boundary $L_1 = L_2$ may be thought of as resulting from increasing the rate of bottom product withdrawal, i.e., increasing φ_B so that L_1 becomes less than L_2. The regions of infinite and finite steady-state separation factor and the loci of switching points are shown in Table 1.

We now discuss the internal equations corresponding to Regions 1, 2, and 3 of Fig. 3.

Region 1. $L_2 \leq L_1$ and h

If in this region one traces the progress of concentration fronts entering the bottom and the top of the column in successive half-cycles after startup, one finds after a certain number of complete cycles of operation a constant pattern of characteristics separating regions of constant concentrations. This pattern is shown in Fig. 4 for the subregion $L_2 < L_1 < h$. The equations given below apply to all of Region 1. The pattern is established $p_1 + 1$ cycles after startup where

$$p_1 + q_1 = (h - L_2)/(L_1 - L_2) \tag{3}$$

where p_1 is zero or a positive integer, and $0 \leq q_1 < 1$. The values assumed by p_1 and q_1 in different parts of Region 1 are indicated in Fig. 3. Note that when $q_1 = 0$, just two concentrations emerge from the top of the column. When $q_1 > 0$ three concentrations emerge. It can be shown that three is the maximum number of concentrations which can emerge (*4*).

We take Fig. 4 to represent the nth cycle of operation where $n > p_1$. If we base derivations similar to those of Aris (*5*) on Fig. 4, we can obtain the following equations for the average concentrations leaving the top and bottom of the column

$$\langle y_{T1}\rangle = \frac{L_2}{L_1}\frac{1+b}{1-b}\langle y_{T2}\rangle_{n-1} + \left(1 - \frac{L_2}{L_1}\right)[q_1\langle y_{B1}\rangle_{n-p_1-1} + (1 - q_1)\langle y_{B1}\rangle_{n-p_1}] \tag{4}$$

$$\langle y_{B2}\rangle_n = \frac{1-b}{1+b}\langle y_{B1}\rangle_n \tag{5}$$

Equation (4) is valid when $n \leq p_1$ if the bottom concentrations are set equal to y_0 whenever the indices of these terms are zero or negative.

Region 2. $L_1 < L_2$ and $L_1 \leq h$

In a manner opposite to that of Region 1, the constant pattern of characteristics developed in this region results in three concentrations emerging from the *bottom* of the column during downflow and one from the top during upflow. The internal equations are

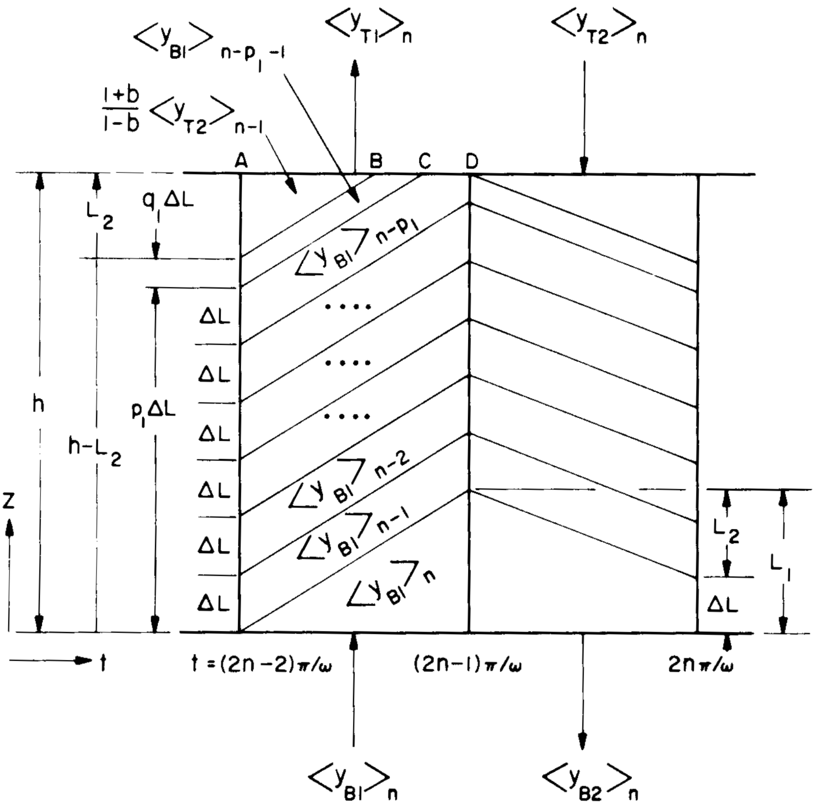

FIG. 4. Steady pattern of characteristics separating zones of constant concentrations as found in Region 1 of Fig. 3.

$$\langle y_{T1}\rangle_n = \frac{1+b}{1-b}\langle y_{T2}\rangle_{n-1} \tag{6}$$

and

$$\langle y_{B2}\rangle_n = \frac{L_1}{L_2}\frac{1-b}{1+b}\langle y_{B1}\rangle_n + \left(1 - \frac{L_1}{L_2}\right)[q_2\langle y_{T2}\rangle_{n-p_2-1} + (1-q_2)\langle y_{T2}\rangle_{n-p_2}] \tag{7}$$

where p_2 is zero or a positive integer defined by

$$p_2 + q_2 = \frac{h - L_1}{L_2 - L_1} \tag{8}$$

and $0 \leq q_2 < 1$. In Eq. (7) the top concentrations are set equal to y_0 when their indices are zero or negative, and the quantities p_2 and q_2 vary over Region 2 as indicated in Fig. 3.

Region 3. $h < L_1$ and L_2

The constant pattern is established by the end of the second upflow half-cycle. Two concentrations emerge from both the top and bottom of the column in this region, and the internal equations are

$$\langle y_{T1}\rangle_n = \frac{h}{L_1}\frac{1+b}{1-b}\langle y_{T2}\rangle_{n-1} + \left(1 - \frac{h}{L_1}\right)\langle y_{B1}\rangle_n \qquad n \geq 2 \tag{9}$$

and

$$\langle y_{B2}\rangle_n = \frac{h}{L_2}\frac{1-b}{1+b}\langle y_{B1}\rangle_n + \left(1 - \frac{h}{L_2}\right)\langle y_{T2}\rangle_n \qquad n \geq 1 \tag{10}$$

External Equations

Whereas there are three regions in the L_1–L_2 plane in each of which one pair of internal equations applies, the external equations are not affected by the magnitudes of L_1 and L_2. Therefore for a given pump model there is just one set of external equations—one for the top and one for the bottom column externals. For purposes of illustration we will derive the top external equation for the pump with continuous feed at the top.

Figure 5 shows the feed point, top product exit, and upper reservoir during the nth cycle of operation. The top external equation for this case may be obtained from material balances based on Figure 5.

By means of a solute balance in combination with a total mass balance, both at the feed point, one may obtain the following relation for the nth upflow half-cycle:

$$(\varphi_T + \varphi_B)y_0 + (1 - \varphi_B)\langle y_{T1}\rangle_n = (1 + \varphi_T)\langle y_{TP1}\rangle_n \tag{11}$$

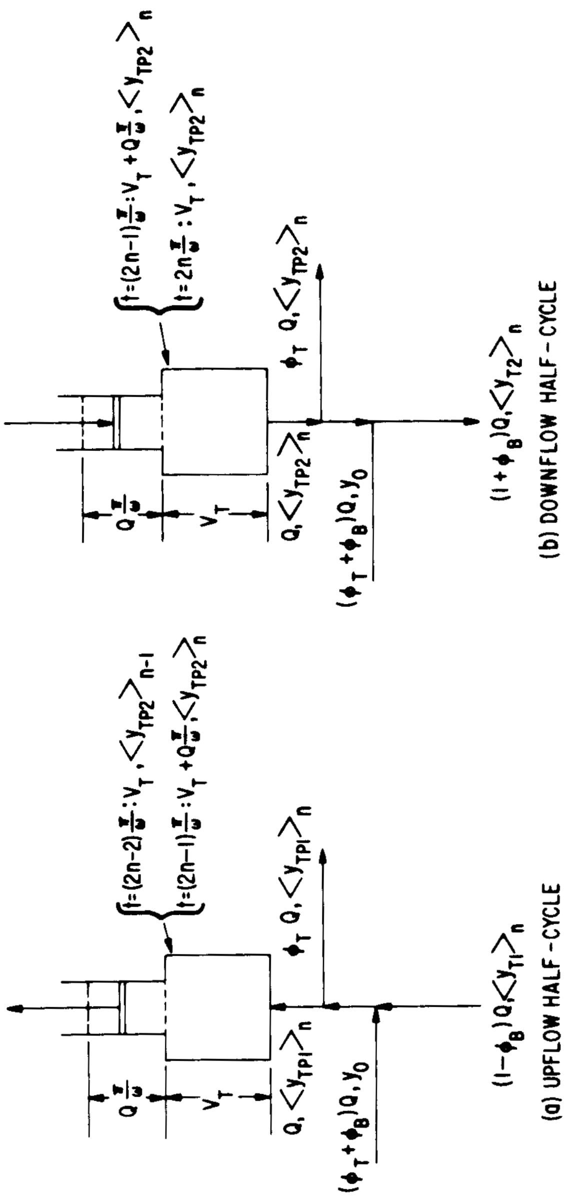

FIG. 5. Top column externals for parametric pump with continuous top feed.

TABLE

Steady-State

No.	Pump type	Region 1 (Fig. 3)	Region 2 (Fig. 3)
1.	Batch	$\frac{\langle y_{BP}\rangle_\infty}{y_0} = 0$	
		$\frac{\langle y_{TP}\rangle_\infty}{y_0} = 1 + \frac{2b}{1+b}\frac{1}{1+V_T/(Q\pi/\omega)} \times \left(p_1 + q_1 + \frac{1-b}{2b} + \frac{1+b}{2b}\frac{V_B}{Q\pi/\omega}\right)$	
2.	Continuous top feed	$\frac{\langle y_{BP}\rangle_\infty}{y_0} = 0$	$\frac{\langle y_{BP}\rangle_\infty}{y_0} = \frac{(\varphi_B - b)(\varphi_T + \varphi_B)}{\varphi_B[(\varphi_T + \varphi_B) - b(1 + \varphi_T\varphi_B)]}$
		$\frac{\langle y_{TP}\rangle_\infty}{y_0} = 1 + \frac{\varphi_B}{\varphi_T}$	$\frac{\langle y_{TP}\rangle_\infty}{y_0} = \frac{(\varphi_T + \varphi_B)(1 - b\varphi_B)}{\varphi_T + \varphi_B - b(1 + \varphi_T\varphi_B)}$
3.	Semicontinuous, continuous top feed during downflow, batch during upflow	$\frac{\langle y_{BP}\rangle_\infty}{y_0} = 0$	$\frac{\langle y_{BP}\rangle_\infty}{y_0} = \frac{(\varphi_T + \varphi_B)[\varphi_B - b(2 + \varphi_B)]}{\varphi_B[(\varphi_T + \varphi_B) - b(2 + \varphi_B - \varphi_T)]}$
		$\frac{\langle y_{TP}\rangle_\infty}{y_0} = 1 + \frac{\varphi_B}{\varphi_T}$	$\frac{\langle y_{TP}\rangle_\infty}{y_0} = \frac{(\varphi_T + \varphi_B)(1 + b)}{\varphi_T + \varphi_B - b(2 + \varphi_B - \varphi_T)}$
4.	Continuous bottom feed	$\frac{\langle y_{BP}\rangle_\infty}{y_0} = \frac{(\varphi_T + \varphi_B)(1 + b\varphi_T)}{\varphi_T + \varphi_B + b(1 + \varphi_T\varphi_B)}$	
		$\frac{\langle y_{TP}\rangle_\infty}{y_0} = \frac{(\varphi_T + \varphi_B)(b + \varphi_T)}{\varphi_T[\varphi_T + \varphi_B + b(1 + \varphi_T\varphi_B)]}$	
5.	Semicontinuous, continuous bottom feed during upflow, batch during downflow	$\frac{\langle y_{BP}\rangle_\infty}{y_0} = \frac{(\varphi_T + \varphi_B)(1 - b)}{\varphi_T + \varphi_B + b(2 + \varphi_T - \varphi_B)}$	
		$\frac{\langle y_{TP}\rangle_\infty}{y_0} = \frac{(\varphi_T + \varphi_B)[\varphi_T + b(2 + \varphi_T)]}{\varphi_T[\varphi_T + \varphi_B + b(2 + \varphi_T - \varphi_B)]}$	

[a] $C_1 = V_T(Q\pi/\omega)$; $C_2 = V_B/(Q\pi/\omega)$.

A solute balance on the reservoir over the same half-cycle yields

$$Q\frac{\pi}{\omega}\langle y_{TP1}\rangle_n + V_T\langle y_{TP2}\rangle_{n-1} = \left(V_T + Q\frac{\pi}{\omega}\right)\langle y_{TP2}\rangle_n \qquad (12)$$

We may eliminate $\langle y_{TP1}\rangle$ between Eqs. (11) and (12) to obtain

2

Solutions

Region 3 (Fig. 3)

$$\frac{\langle y_{BP}\rangle_\infty}{y_0} = 1 - \frac{h\left(1 - \frac{L_2}{L_1}\right)}{L_2(1 + C_2)} + (1 + C_1)(L_1 - L_2)\left(\frac{h}{L_1L_2}\right)^2\left[\frac{L_1 + \frac{h - L_1}{1 + C_2}}{\left(C_1 + \frac{h}{L_2}\right)\left(C_2 + \frac{h}{L_1}\right) - (1 + C_1)(1 + C_2)}\right]^a$$

$$\frac{\langle y_{TP}\rangle_\infty}{y_0} = 1 + \frac{h\left(\frac{1}{L_2} - \frac{1}{L_1}\right)\left(C_2 + \frac{h}{L_1}\right)}{(1 + C_1)(1 + C_2) - \left(C_1 + \frac{h}{L_2}\right)\left(C_2 + \frac{h}{L_1}\right)}^{\,a}$$

$L_1 > L_2$

$$\frac{\langle y_{BP}\rangle_\infty}{y_0} = \frac{(\varphi_T + \varphi_B)\left(1 - \frac{h}{L_2}\right)}{\varphi_T\left[1 - \frac{h}{L_1}(1 - \varphi_B)\right] + \varphi_B\left[1 - \frac{h}{L_2}(1 - \varphi_T)\right]}$$

$$\frac{\langle y_{TP}\rangle_\infty}{y_0} = \frac{\varphi_T + \varphi_B}{1 - \varphi_T}\left\{\frac{1 + \varphi_B - \frac{h}{L_1}(1 - \varphi_B)}{\varphi_T\left[1 - \frac{h}{L_1}(1 - \varphi_B)\right] + \varphi_B\left[1 - \frac{h}{L_2}(1 - \varphi_T)\right]} - 1\right\}$$

$$\frac{\langle y_{BP}\rangle_\infty}{y_0} = \frac{(\varphi_T + \varphi_B)\left(1 - \frac{h}{L_2}\right)}{\varphi_T\left(1 - \frac{h}{L_1}\right) + \varphi_B\left[1 - \frac{h}{L_2}(1 - \varphi_T)\right]}$$

$$\frac{\langle y_{TP}\rangle_\infty}{y_0} = \frac{\varphi_T + \varphi_B}{1 - \varphi_T}\left\{\frac{1 + \varphi_B - \frac{h}{L_1}}{\varphi_T\left(1 - \frac{h}{L_1}\right) + \varphi_B\left[1 - \frac{h}{L_2}(1 - \varphi_T)\right]} - 1\right\}$$

$$\frac{\langle y_{BP}\rangle_\infty}{y_0} = \frac{\varphi_T + \varphi_B}{1 - \varphi_B}\left\{\frac{(1 + \varphi_T)\left[1 - \left(\frac{1 - \varphi_T}{1 + \varphi_T}\right)\left(\frac{h}{L_2}\right)\right]}{\varphi_T\left[1 - \frac{h}{L_1}(1 - \varphi_B)\right] + \varphi_B\left[1 - \frac{h}{L_2}(1 - \varphi_T)\right]} - 1\right\}$$

$$\frac{\langle y_{TP}\rangle_\infty}{y_0} = \frac{(\varphi_T + \varphi_B)\left(1 - \frac{h}{L_1}\right)}{\varphi_T\left[1 - \frac{h}{L_1}(1 - \varphi_B)\right] + \varphi_B\left[1 - \frac{h}{L_2}(1 - \varphi_T)\right]}$$

$L_1 > L_2$

$$\frac{\langle y_{BP}\rangle_\infty}{y_0} = \frac{\varphi_T + \varphi_B}{1 - \varphi_B}\left\{\frac{(1 + \varphi_T)\left[1 - \left(\frac{1 - \varphi_T}{1 + \varphi_T}\right)\left(\frac{h}{L_2}\right)\right]}{\varphi_T\left[1 - \frac{h}{L_1}(1 - \varphi_B)\right] + \varphi_B\left(1 - \frac{h}{L_2}\right)} - 1\right\}$$

$$\frac{\langle y_{TP}\rangle_\infty}{y_0} = \frac{(\varphi_T + \varphi_B)\left(1 - \frac{h}{L_1}\right)}{\varphi_T\left[1 - \frac{h}{L_1}(1 - \varphi_B)\right] + \varphi_B\left(1 - \frac{h}{L_2}\right)}$$

$L_1 > L_2$

$$(\varphi_T + \varphi_B)y_0 + (1 - \varphi_B)\langle y_{T1}\rangle_n = (1 + \varphi_T)\left[\left(1 + \frac{V_T}{Q\frac{\pi}{\omega}}\right)\langle y_{TP2}\rangle_n - \frac{V_T}{Q\frac{\pi}{\omega}}\langle y_{TP2}\rangle_{n-1}\right] \quad (13)$$

From the combination of a solute balance and total mass balance around the feed point during the nth downflow half-cycle we can derive an expression for $\langle y_{TP2} \rangle_n$:

$$\langle y_{TP2} \rangle_n = \frac{1 + \varphi_B}{1 - \varphi_T} \langle y_{T2} \rangle_n - \frac{\varphi_T + \varphi_B}{1 - \varphi_T} y_0 \tag{14}$$

Finally we may evaluate $\langle y_{TP2} \rangle_n$ and $\langle y_{TP2} \rangle_{n-1}$ in Eq. (13) using Eq. (14) and obtain the top external equation

$$\langle y_{T1} \rangle_n = \left(\frac{1 + \varphi_B}{1 - \varphi_B}\right)\left(\frac{1 + \varphi_T}{1 - \varphi_T}\right)\left[\left(1 + \frac{V_T}{Q\frac{\pi}{\omega}}\right)\langle y_{T2} \rangle_n - \frac{V_T}{\varphi\frac{\pi}{\omega}}\langle y_{T2} \rangle_{n-1}\right] - \left(\frac{\varphi_T + \varphi_B}{1 - \varphi_B}\right)\left(\frac{2}{1 - \varphi_T}\right) y_0 \tag{15}$$

The derivation of the top external difference equation for the pump with intermittent top feed proceeds in the same manner except that there is no feed or product during the upflow half-cycle. The bottom external equation is derived for a given pump in a similar manner, with cognizance taken of the presence or absence of continuous or intermittent bottom feed. The bottom external difference equation corresponding to Eq. (15), i.e., for a pump with continuous top feed, is

$$\langle y_{B2} \rangle_{n-1} = \left(1 + \frac{V_B}{Q\frac{\pi}{\omega}}\right)\langle y_{B1} \rangle_n - \frac{V_B}{Q\frac{\pi}{\omega}}\langle y_{B1} \rangle_{n-1} \tag{16}$$

To calculate the performance of that pump, Eqs. (15) and (16) must be solved simultaneously with the internal equations for each region in Fig. 3.

We have solved the system of difference equations for all regions of Fig. 3 for each of the five pumps. The steady-state solutions are given in Table 2. Certain transient solutions are given below. Expressions for all concentration transients are available elsewhere (*4*). We present in the following section a sampling of the significant characteristics of the five pump models.

PUMP CHARACTERISTICS

Batch Pump

In Region 1 expressions for the concentrations transients in the two reservoirs are

$$\frac{\langle y_{B2}\rangle_n}{y_0} = \frac{1-b}{1+b}\left[\frac{Q\pi/\omega}{V_B + Q\pi/\omega}\frac{1-b}{1+b} + \frac{V_B}{V_B + Q\pi/\omega}\right]^{n-1} \qquad n \geq 1 \quad (17)$$

$$\frac{\langle y_{T2}\rangle_n}{y_0} = 1 + \frac{2b}{1+b}\frac{Q\pi/\omega}{V_T + Q\pi/\omega}(n-1) \qquad 1 \leq n \leq p_1 + 1 \quad (18)$$

$$\frac{\langle y_{T2}\rangle_n}{y_0} = 1 + \frac{2b}{1+b}\frac{Q\pi/\omega}{V_T + Q\pi/\omega}\left\{p_1 + \left[q_1 + (1-q_1)\frac{1}{V_B + Q\pi/\omega}\right.\right.$$

$$\left.\left.\times\left(\frac{Q\pi}{\omega}\frac{1-b}{1+b} + V_B\right)\right]\frac{1 - \left\{\frac{1}{V_B + Q\pi/\omega}\left[(Q\pi/\omega)\frac{1-b}{1+b} + V_B\right]\right\}^{n-p_1-1}}{1 - \frac{1}{V_B + Q\pi/\omega}\left[(Q\pi/\omega)\frac{1-b}{1+b} + V_B\right]}\right\}$$

$$n \geq p_1 + 1 \quad (19)$$

In the applicable portion of Region 3 ($L_1 > L_2$) the expressions are

$$\frac{\langle y_{B2}\rangle_n}{y_0} = (C_2 + 1)\left(\frac{g_3}{y_0}\xi_1^n + \frac{g_4}{y_0}\xi_2^n\right) - C_2\left(\frac{g_3}{y_0}\xi_1^{n-1} + \frac{g_4}{y_0}\xi_2^{n-1}\right) \quad n \geq 1 \quad (20)$$

$$\frac{\langle y_{T2}\rangle_n}{y_0} = \frac{g_1}{y_0}\xi_1^n + \frac{g_2}{y_0}\xi_2^n \qquad n \geq 1 \qquad (21)$$

where

$$\frac{g_1}{y_0} = \frac{1}{\xi_1}\left[1 - \frac{1}{\xi_2 - \xi_1}(W_4 - \xi_1)\right]$$

$$\frac{g_2}{y_0} = \frac{1}{\xi_2(\xi_2 - \xi_1)}(W_4 - \xi_1)$$

$$\frac{g_3}{y_0} = \frac{1}{\xi_1}\left[W_5 - \frac{1}{\xi_2 - \xi_1}(W_6 - \xi_1 W_5)\right]$$

$$\frac{g_4}{y_0} = \frac{1}{\xi_2(\xi_2 - \xi_1)}(W_6 - \xi_1 W_5)$$

$$\xi_1 = \tfrac{1}{2}[W_1 + (W_1^2 - 4W_2)^{1/2}]$$

$$\xi_2 = \tfrac{1}{2}[W_1 - (W_1^2 - 4W_2)^{1/2}]$$

$$W_1 = \frac{1}{1+C_1}(a_1 + a_2 a_3) + a_4 + \frac{C_1}{1+C_1}$$

$$W_2 = \frac{1}{1+C_1}a_1 a_4 + a_4\frac{C_1}{1+C_1}$$

$$W_5 = a_3 + a_4$$

$$W_6 = a_3\frac{1}{1+C_1}(C_1 + a_1 + a_2 a_3 + a_2 a_4) + a_4(a_3 + a_4)$$

$$a_1 = \frac{1+b}{1-b}\frac{h}{L_1}$$
$$a_2 = 1 - \frac{h}{L_1}$$
$$a_3 = \frac{1}{1+C_2}\left(1 - \frac{h}{L_2}\right)$$
$$a_4 = \frac{1}{1+C_2}\left[C_2 + \left(\frac{1-b}{1+b}\right)\left(\frac{h}{L_2}\right)\right]$$
$$C_1 = V_T/(Q\pi/\omega)$$
$$C_2 = V_B/(Q\pi/\omega) \qquad (22)$$

We see from Eqs. (17) and (20) that at steady-state, solute removal from the lower reservoir is complete in Region 1 but only partial in Region 3.

Concentration transients calculated by means of the above expressions are shown as a function of number of cycles of operation in Figs. 6 and 7. The ordinate is the average reservoir concentration during the downflow half-cycle divided by initial liquid phase concentration. (The upflow and downflow concentrations are identical in pumps with no reservoir dead volume. In pumps which have reservoir dead volume they are identical at steady-state.) Dimensionless concentrations greater than one are top reservoir concentrations, while those less than one are bottom reservoir concentrations. In the cases considered $b = 0.1$ and $h = 100$ units of length. Figure 6 shows the effect of varying reservoir displacement volume on the transients in a pump with no dead volume in either reservoir. As long as the penetration distance L_2 is less than or equal to h (Cases 1 and 2), the separation factor, defined as the quotient of the top and bottom concentrations, approaches infinity as n becomes large. However, as L_2 is increased to the point where it exceeds h, the steady-state concentration in the lower reservoir abruptly switches to a finite value and the steady-state separation factor becomes finite. In Case 3, $L_2 = 120$ and $\alpha_\infty = 1.97$.

One can see from Fig. 6 and the expressions in Table 2 for the steady-state concentrations in the batch pump with no reservoir dead volume ($C_1 = C_2 = 0$) that not only can one obtain complete removal of solute from the lower reservoir—by making L_2 less than h—but at the same time one may obtain an arbitrarily high concentration in the upper reservoir by making $L_2 \ll h$, i.e., by making the column very long relative to the reservoir displacement volume.

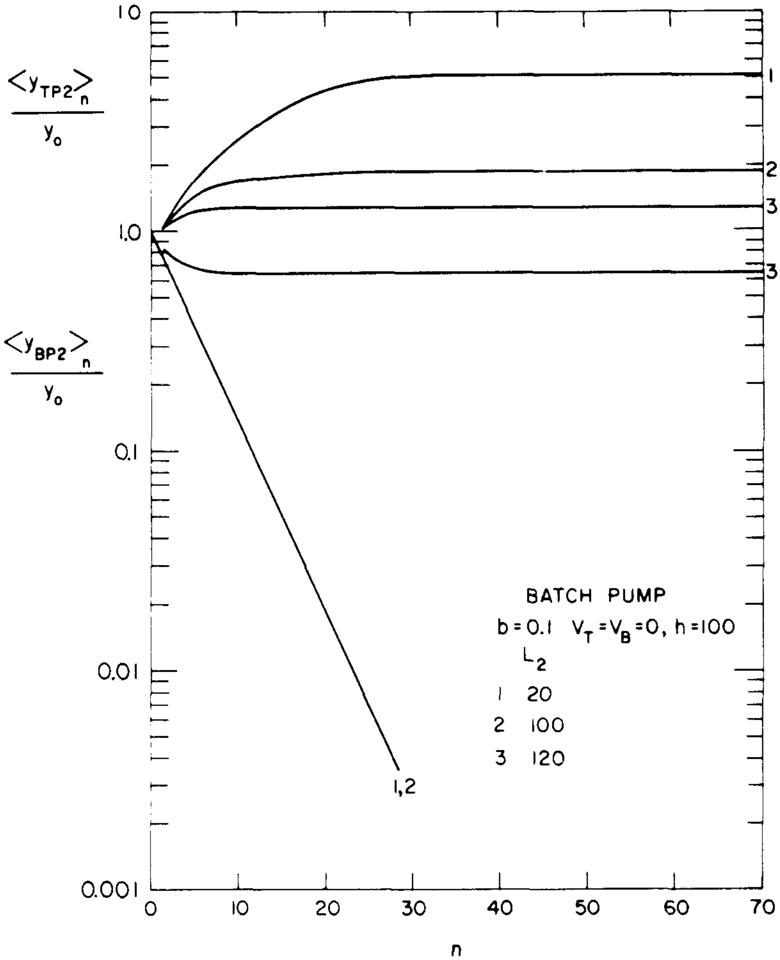

FIG. 6. Effect of reservoir displacement volume on concentration transients in batch parametric pump with no reservoir dead volume.

Another way of achieving an infinite separation factor with arbitrarily high enrichment in the upper reservoir is with a pump with dead volume in the lower reservoir and no dead volume or less dead volume in the upper reservoir. Figure 7 shows concentration transients illustrating this point for a pump with $h = 100$ and a reservoir displacement volume corresponding to a downflow penetration distance of 100. Thus this pump is operating at the switching point where transients in the upper reservoir are shortest. In Case 1 there is no

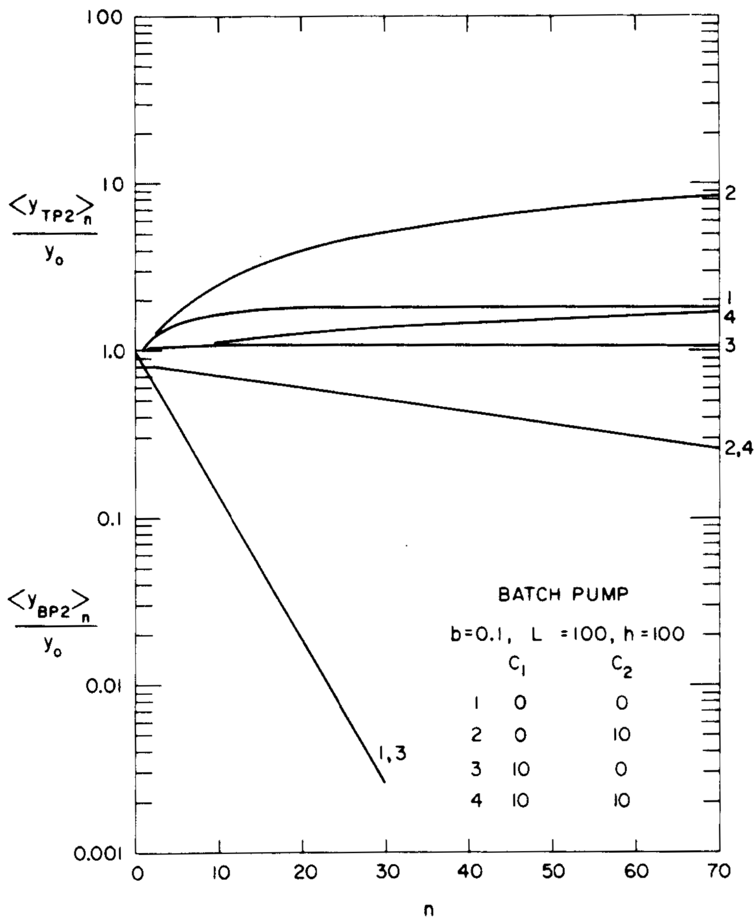

FIG. 7. Effect of reservoir dead volume on concentration transients in batch parametric pump operating at the switching point.

dead volume in either reservoir. This case is identical to Case 2, Fig. 6. The addition of dead volume to the lower reservoir (Case 2, Fig. 7) equal to 10 times the displacement volume produces an increase in steady-state top reservoir concentration roughly consistent with the ratio of the reservoir volumes. Addition of dead volume to the upper reservoir alone (Case 3) has the opposite effect. A bottom reservoir arbitrarily large with respect to the top reservoir would lead to an arbitrarily large enrichment in the upper reservoir but at the same time the transient time for depletion of the solute from the lower reservoir would become very long.

Transients in the continuous and semicontinuous pumps are in general similar to those shown in Figs. 6 and 7 for the batch pump except that for small bottom product flow rates ($\varphi_B < b$) there is an overshoot in the top product transient, and for large bottom product flow rates ($\varphi_B > b$) there is an undershoot in the bottom product transient.

Pumps with Feed at the Top

In Region 1 the solution for the concentration transients in downflow in the bottom product streams in these pumps is identically Eq. (17). Thus in this region at steady-state complete removal of solute from the bottom reservoir and bottom product stream occurs.

Also in this region at steady-state the top product concentration is

$$\frac{\langle y_{TP}\rangle_\infty}{y_0} = \frac{\varphi_T + \varphi_B}{\varphi_T} \tag{23}$$

While this expression is the steady-state limit of the solution of the set of difference equations for these pumps, it is also obtained from a simple material balance which states that in Region 1 the top product stream must carry away all of the solute supplied by the feed stream. Note that in this region the value of b does not affect the steady-state product concentration.

We see from Eq. (23) that for a given value of φ_B by adjustment of φ_T to an arbitrarily low value we may obtain an arbitrarily high degree of enrichment in the top product stream. The pumps with top feed thus are ideal separation devices in the sense that they can continuously or semicontinuously separate a two-component system into one fraction completely free of solute and another fraction enriched in solute to any desired degree.

The steady-state performance of a continuous pump with top feed is illustrated in Fig. 8. For this figure $b = 0.1$ and $F/Q = 0.3$. The product concentrations divided by the feed concentration are plotted against P_B/F, the fraction of the feed removed as bottom product. For the interval $0 < P_B/Q \leq 0.1$ corresponding to the interval $0 < P_B/F \leq 0.33$, no solute appears in the bottom product stream. Over the same interval the top product concentration increases in accordance with Eq. (23). Beyond the switching point, i.e., beyond $P_B/F = 0.33$, solute appears in the bottom product and the top concentration

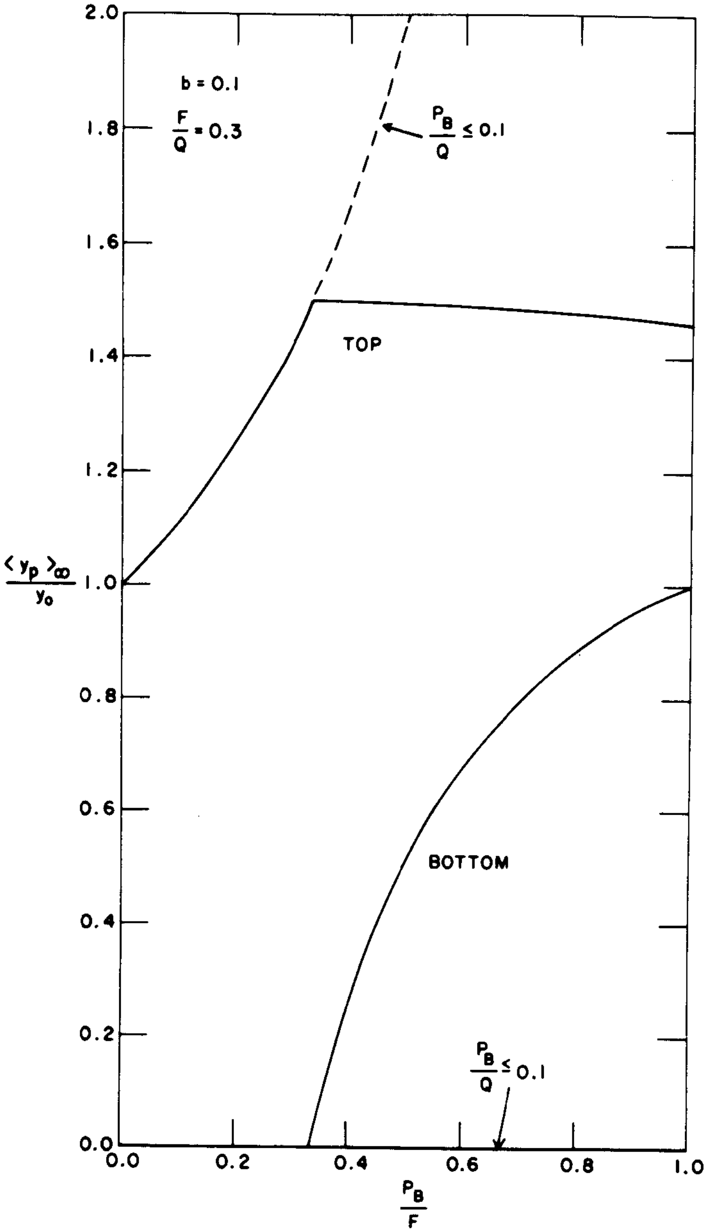

FIG. 8. Steady-state concentrations in continuous parametric pump with continuous top feed.

decreases correspondingly and according to the appropriate expression in Table 2. Note that if the feed rate is reduced so that $F/Q \leq 0.1$, then P_B/Q could never exceed $b = 0.1$ and no solute would be found in the bottom product stream over the entire allowed range of bottom product flow rates, $0 < P_B/F < 1$. Eq. (23) would then be valid for the top product concentration over the same range.

As indicated above, the performance characteristics of both pumps with top feed are similar in nature. Infinite steady-state separation factors are found in Region 1 for both pumps and finite separation factors are found outside this region. The principal difference between the two pumps is the difference in switching points resulting from bottom product flow rate variation. For the continuous pump this point corresponds to the condition $P_B/Q = b$, whereas for the semicontinuous pump the condition is $P_B/Q = 2b/(1 - b)$ (see Table 1). For semicontinuous operation the average bottom flow rate during a cycle is $P_B/2$. Thus in terms of the average flow rate the switching condition is $(P_B/2)/Q = b/(1 - b)$. For small values of b, complete separation may be obtained at little greater bottom flow rate than in the continuous pump. However, for large b, the rate of production of pure solvent in the semicontinuous pump may become quite large relative to that in the continuous pump. In the extreme case where $b \rightarrow 1$ the intermittent pump will permit complete separation with arbitrarily great enrichment and a throughput approaching infinity.

Pumps with Feed at the Bottom

For these pumps, even though we always have $L_1 > L_2$, there is no region of infinite separation factor. Because of the introduction of feed at the bottom, complete depletion of solute from the bottom product stream is not attainable. The separation factor can, however, be large in Region 1 if φ_T is made small. It can be very large in the semicontinuous pump with large throughput if $b \rightarrow 1$. Modest separation factors are found in Region 3.

CONCLUDING REMARKS

We have seen that the net direction of movement of concentration fronts through the adsorption column is important in determining the nature of pump performance. If the net direction is upward, then complete removal of solute from the bottom fraction may be obtained in all pumps except those with feed streams located at the bottom of the column. However, even though the net direction is upward, as is inherently the case in the batch pump, modest separation will result if the reservoir displacement volume is excessive. If the net direction is downward, then solute removal from the bottom fraction will be incomplete. In continuous or semicontinuous pumps with top feed, a net downward direction will result if the bottom product flow rate becomes too large.

At the same time that removal of solute from the bottom fraction is complete, arbitrarily large enrichment may be obtained in the top fraction of a batch pump by the use of a sufficiently long column or by the use of sufficient dead volume in the bottom reservoir. The same result may be achieved in the pumps with top feed by adequate restriction of the top product flow rate.

Many versions of parametric pumps other than those examined here are conceivable. Those with feed streams located at the enriched end of the column will evidently be capable of achieving infinite steady-state separation factors. We have investigated a continuous model with center feed between an enriching column and a stripping column and have found this model also capable of complete removal of solute from one product fraction and of arbitrarily large enrichment in the other (*4*).

The picture of parametric pump operation developed in the present paper with reference to the separation of two-component systems may as a first approximation be extended to multicomponent separations as follows. Let us assume that a dilute solution of n independently adsorbable components in an inert solvent is to be treated. Let us assume further that for each component adsorption decreases with increasing temperature and that there is a different value of the parameter b, say b_i, for each component, and corresponding values of the penetration distances L_{1_i} and L_{2_i}. For those components for which the relative values of L_{1_i}, L_{2_i}, and h indicate operation in Region 1 of Fig. 3, infinite steady-state separation factors will be obtained. For the remaining components the steady-state separation factors found will be finite.

List of Symbols

b dimensionless equilibrium parameter (see Ref. *2*)

C $\frac{V}{Q(\pi/\omega)}$, dimensionless

F	feed volumetric flow rate
h	column height
L	penetration distance defined by Eq. (1) or (2)
n	number of cycles of pump operation
P	product volumetric flow rate
p_1, p_2	defined by Eqs. (3) and (8)
Q	reservoir displacement rate
q_1, q_2	defined by Eqs. (3) and (8)
u	velocity of concentration fronts
V	reservoir volume
y	concentration of fluid
$\langle\ \rangle$	average value

Greek Letters

α_∞	steady-state separation factor
φ	P/Q
ω	frequency of cyclic operation

Subscripts

0	initial condition or mean column temperature
1	upflow
2	downflow
B	stream from or to bottom of the column
P	product stream
T	stream from or to top of the column
BP	bottom product
TP	top product

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