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Equilibrium Parametric Pumps

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Abstract

Semicontinuous and continuous pumps were experimentally investigated at various operating conditions. The model system used was toluene–*n*–heptane on silica gel adsorbent. It has been shown that when the penetration distance for the cold cycle is less than or equal to that for the hot cycle and the height of the column, the pump has the capacity of complete removal of solute from one product stream. A quantity which is important in determining pump performance is the equilibrium parameter, *b*. Pump performance is enhanced by a large value of *b*.

INTRODUCTION

Parametric pumping is a phase change separation process which depends for its operation on the coupling of periodic changes in some variables affecting the position of interphase equilibrium with synchronous periodic changes in flow direction. In an earlier paper (*1*), semicontinuous and continuous parametric pumps were analyzed in terms of an equilibrium theory (*2*, *3*) of pump performance. It has been shown that under certain condition the pumps with feed at the enriched end have the capacity for complete removal of solute from one product stream and at the same time give arbitrarily large enrichment of solute in the other product stream. The conditions necessary for accomplishing this are defined by the relative magnitudes of penetration distances and the height of the column.

In this paper we experimentally examine the sensitivity of the equilib-

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rium parametric pumps to various operating parameters while obtaining high separation factors (defined as the ratio of solute concentrations in two product streams). The system used was toluene–*n*–heptane on silica gel. Two modes of pump operation were considered, continuous and semicontinuous. The continuous pump is characterized by a steady flow for both feed and product streams during both upflow and downflow cycles, while the semicontinuous pump is operated batch-wise during upflow and continuously during downflow.

EXPERIMENTAL

The experimental apparatus shown in Fig. 1 is similar to that used previously (*4*, *5*). A syringe pump delivered the feed. An infusion-withdrawal syringe pump was operated in reciprocal fashion to act as the top and bottom reservoirs. The jacketed glass column (length = 90 cm, i.d. = 1 cm) was packed with 30 to 60 mesh chromatographic-grade silica gel.

Flow is upward during the hot half-cycle and downward during the cold half-cycle. Each half-cycle is π/ω time units in duration, and the reservoir

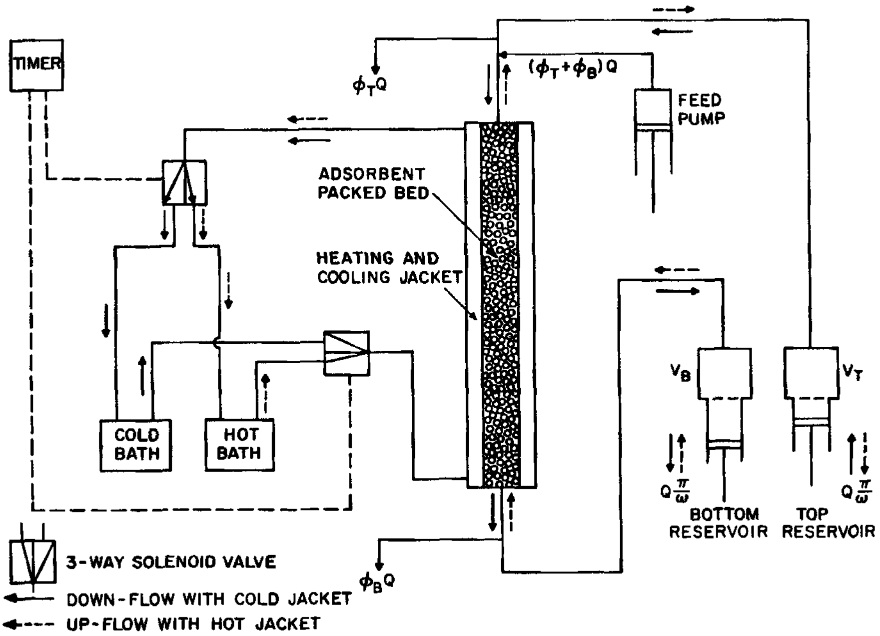

FIG. 1. Schematic diagram of experimental apparatus.

displacement volume is $Q(\pi/\omega)$. The pump has dead volumes V_T and V_B for the top and bottom reservoirs, respectively. The feed is directed to the top of the column at a flow rate $(\phi_T + \phi_B)Q$. The top and bottom product flows are $\phi_T Q$ and $\phi_B Q$, respectively, where Q is the reservoir displacement rate, and ϕ_T and ϕ_B are the ratios of the top and bottom product rates to the reservoir displacement rate, respectively. For the continuous pump, ϕ_T and ϕ_B have given magnitudes between zero and one ($0 < \phi_T$ or $\phi_B < 1$) during both upflow and downflow. Semicontinuous operation results when $\phi_T = \phi_B = 0$ during upflow and $0 < \phi_T$ or $\phi_B < 1$ during downflow.

Prior to each run the interstitial column volume and the bottom reservoir were filled with feed mixture at ambient temperature. The hot and cold baths were connected to the column jacket. Two three-way solenoid valves were wired to a dual timer so that hot water was always directed to the column jacket during upflow and cold water during downflow. The product take-off valves were micrometer capillary valves used both to regulate flow and impose a small back-pressure on the system. Samples for analysis were taken from the product streams at the end of each cycle and analyzed by UV spectrophotometer.

THEORY

The performance characteristics of semicontinuous and continuous pumps have been derived in terms of an equilibrium theory of pump operation (*1*). It has been shown that pump performance depends on the column height, and the ratio of the penetration distance of the hot cycle to that of the cold cycle, L_1/L_2. With the feed at the top of the column, L_1/L_2 can be expressed in terms of ϕ_B and the equilibrium parameter, b, as

$$\frac{L_1}{L_2} = \left(\frac{1 + b}{1 - b}\right)\left(\frac{1 - \phi_B}{1 + \phi_B}\right) \tag{1}$$

for the continuous pump, and

$$\frac{L_1}{L_2} = \left(\frac{1 + b}{1 - b}\right)\left(\frac{1}{1 + \phi_B}\right) \tag{2}$$

for the semicontinuous pump. In either case, L_2 is defined as

$$L_2 = \frac{v_0(1 + \phi_B)}{(1 + b)[1 + \frac{1}{2}(m_1 + m_2)]}\left(\frac{\pi}{\omega}\right) \tag{3}$$

There are three possible regions of pump operation:

Region 1: $L_1/L_2 \geqq 1,\ L_2 \leqq h$

Region 2: $L_1/L_2 < 1,\ L_1 \leqq h$

Region 3: $L_1 > h,\ L_2 > h$

When the pumps are operated in Region 1, the bottom product concentrations is

$$\frac{\langle y_{\mathrm{BP2}}\rangle_n}{y_0} = \frac{1-b}{1+b}\left[\frac{\dfrac{1-b}{1+b} + C_2}{1 + C_2}\right]^{n-1} \tag{4}$$

At steady state ($n \to \infty$)

$$\frac{\langle y_{\mathrm{BP2}}\rangle_\infty}{y_0} = 0 \tag{5}$$

Thus, in this region, at the steady state, complete removal of solute from the bottom reservoir or bottom product stream occurs, and the top product stream must contain all of the solute supplied by the feed stream, i.e.,

$$\frac{\langle y_{\mathrm{TP}}\rangle_\infty}{y_0} = 1 + \frac{\phi_B}{\phi_T} \tag{6}$$

When the pumps are operated outside Region 1 (i.e., Region 2 or 3), complete removal of solute from the product stream cannot be obtained.

The quantity b shown in Eqs. (1)–(4) is expressed as

$$b = \frac{\frac{1}{2}(m_2 - m_1)}{1 + \frac{1}{2}(m_1 + m_2)} \tag{7}$$

where

$$m_i = \frac{\rho_s M_i(1 - \varepsilon)}{\rho_f \varepsilon} \tag{8}$$

and $M_i(= x/Y)$ is the equilibrium distribution coefficient at temperature T_i.

Based on Eq. (7), b is associated with a given two-phase system when operated at two specific temperatures. The value may be as small as zero for a system in which the equilibrium distribution is insensitive to temperature or as large as 1 for a system in which distribution is highly temperature sensitive. The quantity b is a measure of the extent of movement of solute between phases as the result of a change in column temperature. Pump performance is enhanced by large movement and hence by large b.

RESULTS AND DISCUSSIONS

Seven experimental runs were made with conditions set so that pumps were operated in Region 1 where $L_1/L_2 \geqq 1$ and $L_2 \leqq h$. The experimental parameters are shown in Table 1.

Comparisons were made between the data and the calculated results based on the transient equations (*4*, *5*) derived from the equilibrium theory. Primary assumptions of the equilibrium theory are: local interphase equilibrium exists with a linear distribution law having a temperature-dependent distribution coefficient, there is negligible axial diffusion, temperature changes between hot and cold cycles are instantaneous, plug flow exists, and the fluid density is constant.

Figures 2 and 3 show the results at various operating conditions for two modes of pump operation, continuous and semicontinuous. The agreement between experiment and theory is reasonably good. One can see that Y_0, ϕ_B, and $(\phi_T + \phi_B)$ and the mode of pump operation have negligible effects on the bottom product concentration $\langle y_{\text{BP2}}\rangle_n/y_0$, provided that the cycle time is long enough to permit the establishment of the equilibrium distribution of adsorbate between the solid and fluid phases, i.e., $\pi/\omega = 10$ min or longer. In every case $\langle y_{\text{BP2}}\rangle_n/y_0$ decreases as n increases, and will approach zero as n becomes large, as theory predicts. From Eq. (4), if the operating conditions are in Region 1, the concentration transient for the bottom product stream depends on the values of C_2 and b, where C_2 is defined as the ratio of the dead volume of the bottom reservoir to the displacement [i.e., $C_2 = V_B/Q(\pi/\omega)$], and b is the dimensionless equilibrium parameter. The quantity b as defined by Eq. (7) is a function of T_2 and T_1 only. It 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. The values of b for Run 1, 2, or 3 (Fig. 2, $T_1 = 70°\text{C}$, $T_2 = 4°\text{C}$) and Run 4, 5, or 6 (Fig. 3, $T_1 = 60°\text{C}$, $T_2 = 25°\text{C}$) are 0.22 and 0.15, respectively. They were calculated by using the rearranged form of Eq. (4):

$$b = \frac{1 - 10^\alpha + C_2(1 - 10^\alpha)}{1 + 10^\alpha - C_2(1 - 10^\alpha)} \tag{9}$$

where α is the slope of the plot of $\log[\langle y_{\text{BP2}}\rangle_n/y_0]$ vs n, and is always nega-

TABLE 1

Experimental and Model Parameters ($h = 90$ cm)

Run	Mode	T_1 (°C)	T_2 (°C)	π/ω (min)	Y_0	Q (cc)	$\phi_T + \phi_B$	ϕ_B	C_1	C_2	L_1 (cm)	L_2 (cm)	b
1	Semicontinuous	70	4	20	0.10	40	0.4	0.22	0.10	0.15	59	46	0.22
2	Semicontinuous	70	4	20	0.05	40	0.4	0.31	0.11	0.15	60	50	0.22
3	Continuous	70	4	20	0.10	40	0.4	0.15	0.14	0.15	51	44	0.22
4	Semicontinuous	60	25	10	0.05	40	0.4	0.17	0.12	0.13	54	47	0.15
5	Semicontinuous	60	25	10	0.05	40	0.5	0.17	0.12	0.13	54	47	0.15
6	Continuous	60	25	20	0.035	40	0.4	0.07	0.12	0.13	51	43	0.15
7[a]	Semicontinuous	60	25	3	0.05	15	1.02	0.23	0.35	0.43	22	19	—

[a] Equilibrium theory cannot be applied

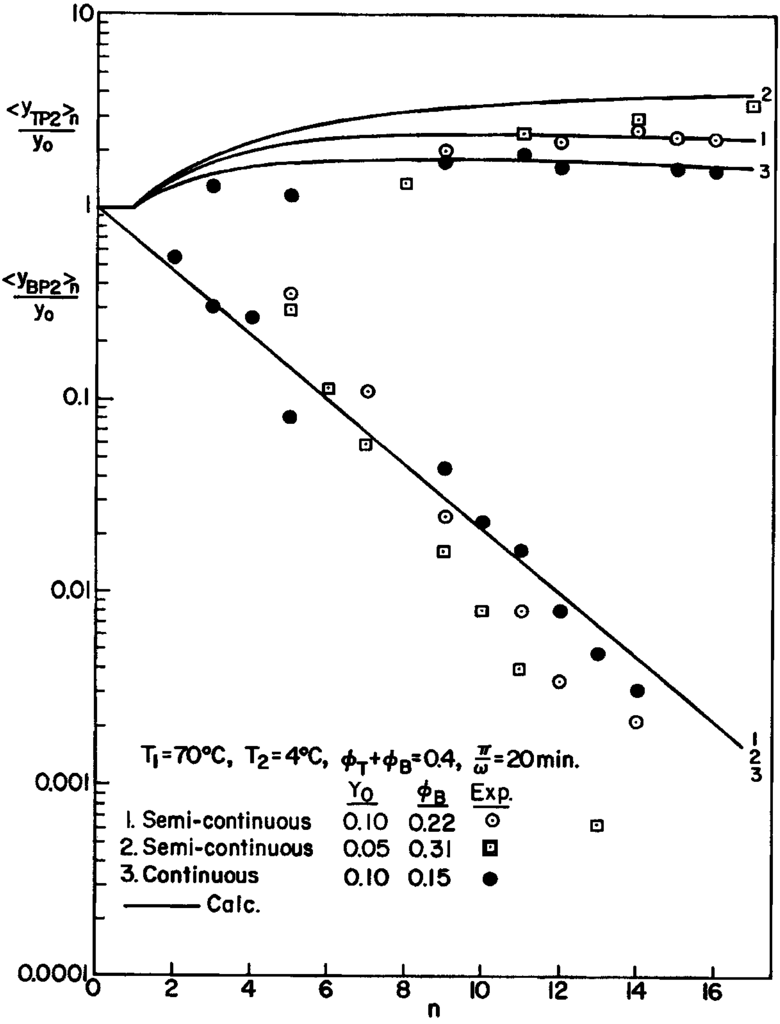

FIG. 2. Concentration transients at $T_1 = 70$ °C and $T_2 = 4$ °C.

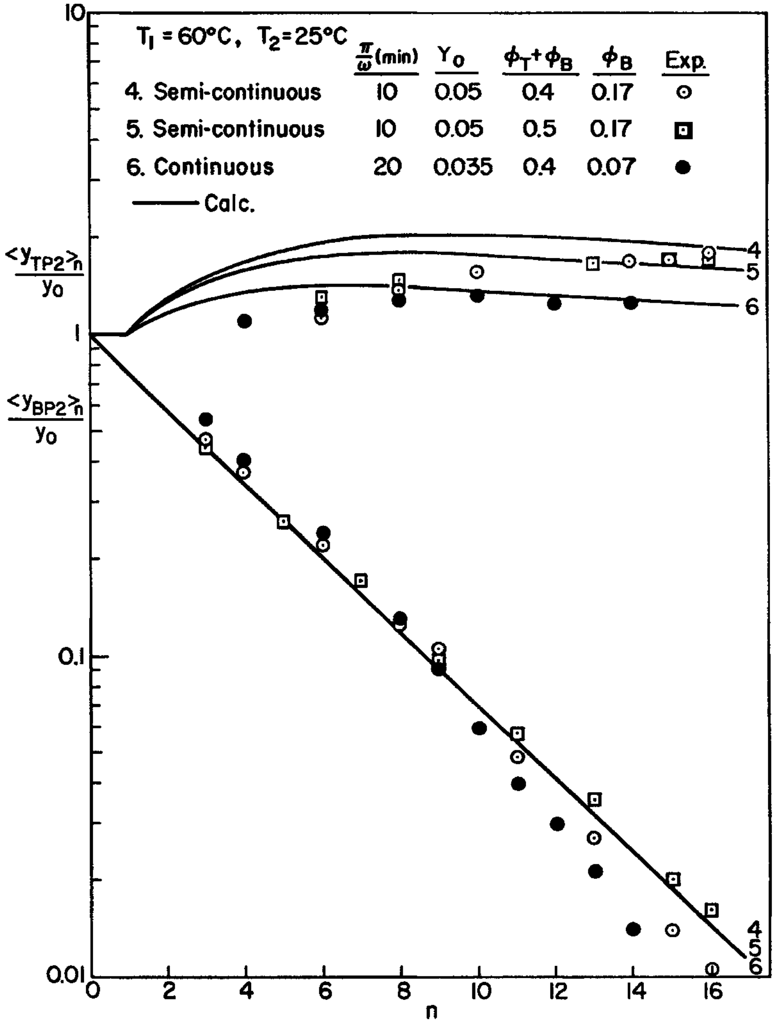

FIG. 3. Concentration transients at $T_1 = 60\,°C$ and $T_2 = 25\,°C$.

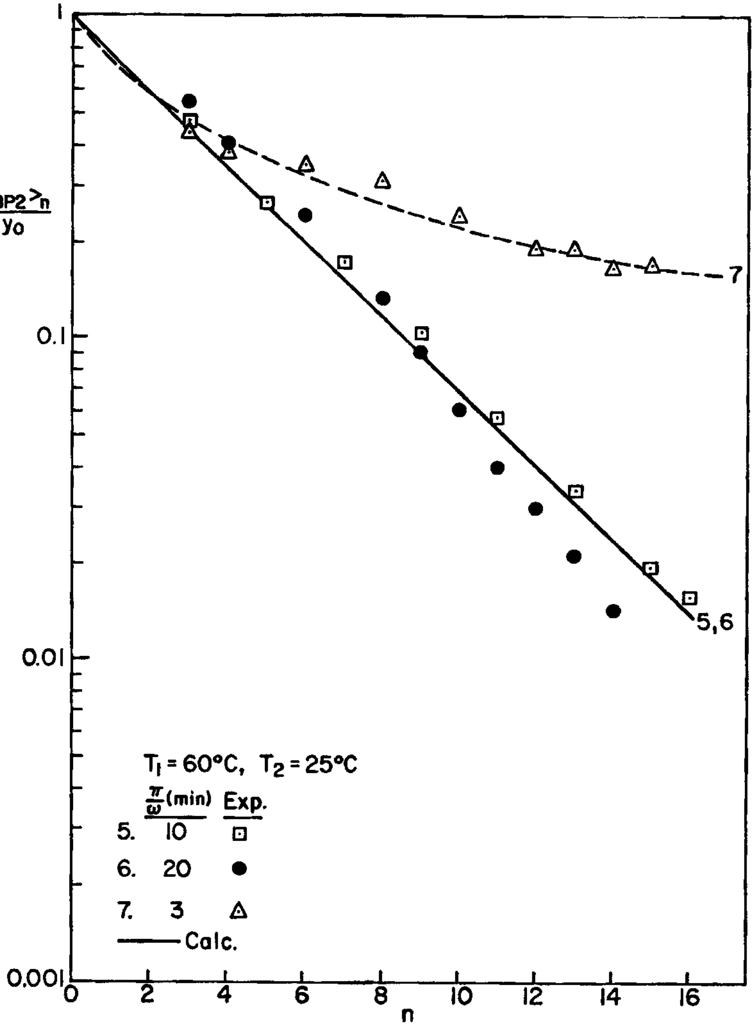

FIG. 4. Effect of cycle time on separation.

tive. For a given C_2 a larger $|\alpha|$ (absolute value of α) provides a greater b. It follows that, for large values of b, the transient time for depletion of the solute from the lower reservoir or the bottom product stream would become very short. In the extreme case where $b \to 1$, the pump will have a zero transient time (i.e., $\alpha = -\infty$). On the other hand, when $b \to 0$, α becomes zero and thus no separation can occur. Also, one can see from Fig. 2 that for a given value of $(\phi_T + \phi_B)$ at steady state one may obtain an arbitrarily high degree of enrichment in the top product stream by adjusting ϕ_B to an arbitrary high value as shown in Eq. (6). Note that b does not affect this steady-state product concentration.

As shown in Figs. 2 and 3, the performance characteristics of both continuous and semicontinuous pumps are similar in nature. If the pumps are operated in Region 1, the bottom product concentration decreases as n increases and the separation factor becomes large as n becomes large. The principal difference between the two pumps is the difference in switching points resulting from bottom product flow rate variation, i.e., for large b the rate of production of pure solvent by the semicontinuous pump may become quite large relative to that by the continuous pump. A more detailed explanation of the switching points and their effects on the product flow rate is given by Chen et al. (*5*).

Figure 4 illustrates the effect of cycle time on the separation. As n becomes large, solute removal in the bottom product stream is essentially complete for longer cycle times ($\pi/\omega = 10$ and 20 min), but only partial for the shorter cycle time ($\pi/\omega = 3$ min). Clearly, the shorter time may not be long enough to permit the establishment of the equilibrium distribution of adsorbate between the solid and fluid phases, and the maximum separation may never be obtained.

SYMBOLS

b	dimensionless equilibrium parameter defined by Eq. (7)
C_1	$V_T/Q(\pi/\omega)$, fraction of dead volume of the top reservoir to displacement, dimensionless
C_2	$V_B/Q(\pi/\omega)$, fraction of dead volume of the bottom reservoir to displacement, dimensionless
h	column height, cm
L	penetration distances defined by Eqs. (1), (2), and (3), cm
M	x/Y, (g mole/g)/(g mole/g mole)
m	equilibrium constant parameter defined by Eq. (8), dimensionless
n	number of cycles of pump operation

Q	reservoir displacement, cm^3/sec
T	temperature, °C
V_0	interstial velocity, cm/sec
V_T	top reservoir dead volume, cm^3
V_B	bottom reservoir dead volume, cm^3
x	concentration of solute in the solid phase g mole/g
y	concentration of solute in the liquid phase, g $mole/cm^3$
Y	mole fraction, g mole/g mole
$\langle\,\rangle$	average value

Greek Letters

ρ_s	density of the solid, g/cm^3
ρ_f	density of the fluid, g $mole/cm^3$
ε	void fraction in packing, dimensionless
ϕ	product volumetric flow rate/reservoir displacement rate, dimensionless
π/ω	duration of half cycle, sec

Subscripts

0	initial condition
1	upflow or hot-half cycle
2	downflow or cold-half cycle
BP	bottom product
TP	top product
B	stream from or to bottom of the column
T	stream from or to top of the column
∞	steady-state

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