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Nonequilibrium Parametric Pumps

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Abstract

A nonequilibrium continuous pump was experimentally investigated using the model system NaCl–H_2O on an ion exchanger. A simple method for predicting separation is presented and is found to be in good agreement with experimental results. The criterion for approach to equilibrium operation, where large separations are possible, is also established.

The process known as parametric pumping represents a new development in separation science. It has attracted considerable attention both because of its novelty and because it permits continuous operation in small equipment with very high separation factors. As first investigated by Wilhelm and Sweed (*1*), the variable, temperature, was used to change the equilibrium distribution of toluene between a toluene–*n*-heptane solution and a bed of silica gel adsorbent particles. Separation factors (defined as the ratio of toluene concentrations in two reservoirs attached to the ends of the bed) as high as 10^5 were attained. This high separation capability provided an incentive for studies by many authors. A comprehensive literature review has been made by Wankat (*2*).

Pigford et al. (*3*) originated an important and simple equilibrium theory and, using this theory, derived expressions for the performance of batch parametric pumps. By extending the equilibrium theory, Chen and Hill (*4*) derived mathematical expressions for the performance of

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continuous and semicontinuous pumps. They have shown that under certain conditions pumps with feed at the enriched end of the bed have the capacity for complete removal of solute for one product stream and, at the same time, give arbitrarily large enrichment of solute in the other product stream. Experimental verification of the models has subsequently been presented by Chen et al. (*5–10*).

In this paper a continuous thermal parametric pump is experimentally investigated using the model system NaCl–H_2O on ion-retardation resin adsorbent, and the experimental results are compared with a nonequilibrium model. Emphasis is placed on the operating conditions necessary to achieve high separations. It should be pointed out that separations of NaCl from aqueous solutions by open parapump systems have also been studied by Sweed and Gregory (*11*). However, Sweed's open systems are semicontinuous in the sense that feed is introduced and products are withdrawn only during a portion of each half-cycle, whereas the continuous pump considered here is characterized by a steady flow for both feed and product streams during the upflow and downflow half-cycles.

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MATHEMATICAL DESCRIPTION

The continuous pump we have studied is shown in Fig. 1. Flow is upward during the hot-half cycle and downward during the cold-half cycle. Temperature for upflow and downflow are T_1 and T_2, respectively. Each half-cycle is (π/ω) time units in duration, and the reservoir displacement volume is $Q(\pi/\omega)$, where Q is the reservoir displacement rate. The pump has dead volume V_T and V_B for the top and bottom reservoirs, respectively. The feed is directed to the top of the column at the flow rate $(\phi_T + \phi_B)Q$. The top product flow rate is $\phi_T Q$ and bottom product flow rate is $\phi_B Q$, where ϕ_T and ϕ_B are the ratios of the top and bottom product rates to the displacement rate.

Two types of equations are needed in the calculation of the performance characteristics of the pump, i.e., internal and external equations. External equations are solute material balances on streams flowing to and from a reservoir, considering the presence of any adjacent feed and product streams. During the nth upflow half-cycle a solute balance at the feed point is

$$(\phi_T + \phi_B)y_0 + (1 - \phi_B)\langle y_{T1}\rangle_n = (1 + \phi_T)\langle y_{TP1}\rangle_n \qquad (1)$$

and the balance on the top reservoir yields

$$Q\left(\frac{\pi}{\omega}\right)\langle y_{TP1}\rangle_n + V_T\langle y_{TP2}\rangle_{n-1} = \left(V_T + Q\frac{\pi}{\omega}\right)\langle y_{TP2}\rangle_n \qquad (2)$$

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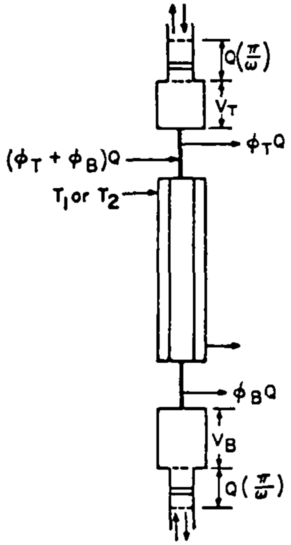

FIG. 1. Column diagram for continuous parametric pumping.

For the following downflow half-cycle, solute balances around the feed point and on the bottom reservoir are, respectively,

$$(\phi_T + \phi_B)y_0 + (1 - \phi_T)\langle y_{TP2}\rangle_n = (1 + \phi_B)\langle y_{T2}\rangle_n \tag{3}$$

and

$$Q\left(\frac{\pi}{\omega}\right)\langle y_{BP2}\rangle_{n-1} + V_B\langle y_{B1}\rangle_{n-1} = \left(Q\frac{\pi}{\omega} + V_B\right)\langle y_{B1}\rangle_n \tag{4}$$

Internal equations are solute material balances reflecting events occurring within the adsorption column. By assuming plug flow, linear equilibrium adsorption, and dilute solution, and neglecting diffusion along the Z-axis, one may obtain the following expressions:

$$\varepsilon v\frac{\partial y}{\partial z} + \varepsilon\frac{\partial y}{\partial t} = -(1 - \varepsilon)\rho_s\frac{\partial x}{\partial t} \tag{5}$$

$$\partial x/\partial t = \lambda(y - y^*) \tag{6}$$

$$y^* = x/M(T) \tag{7}$$

The first term of Eq. (5) represents axial fluid phase convective mass transfer, the second is the fluid phase transient, and the third is the solid phase transient. Equation (6) is a simplified rate equation for transfer of a solute to and from the adsorbent. Equation (7) is an equilibrium relationship.

Let

$$\bar{z} = z/v \tag{8}$$

and by the method of characteristics, Eqs. (5)–(7) may be expressed as follows.

For Characteristic I:

$$d\bar{z}/dt = 1 \tag{9a}$$

$$\frac{dy}{d\bar{z}} = -\frac{1-\varepsilon}{\varepsilon}\rho_s\lambda\left(y - \frac{x}{M}\right) \tag{9b}$$

For Characteristic II:

$$d\bar{z}/dt = 0 \tag{10a}$$

$$\frac{dx}{dt} = \lambda\left(y - \frac{x}{M}\right) \tag{10b}$$

Applying a modified Euler method (*12*), one can transform Eqs. (9 and 10) into

$$y^{k+1}(I+1, J+1) = y(I, J) - \left(\frac{1-\varepsilon}{\varepsilon}\right)\rho_s\lambda\frac{\Delta t}{2}[y^k(I+1, J+1) - x^k(I+1, J+1)/M + y(I, J) - x(I, J)/M] \tag{11}$$

and

$$x^{k+1}(I+1, J+1) = x(I+1, J) + \frac{\lambda\Delta t}{2}[y^k(I+1, J+1) - x^k(I+1, J+1)/M + y(I+1, J) - x(I+1, J)/M] \tag{12}$$

where $y^k(I, J)$ and $x^k(I, J)$ are the kth approximations of y and x at the position $\bar{Z}$ ($= I\Delta t$) and time t ($= J\Delta t$). The value of M is set equal to M_1 and M_2 for upflow and downflow, respectively.

By combining Eqs. (1)–(4), (11), and (12) along initial and boundary conditions, one may calculate concentration transients (i.e., $\langle y_{TP2}\rangle_n$ and

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$\langle y_{BP2}\rangle_n$ vs n) as follows:

1. Divide the column into NZ equal axial position increments, and the half-cycle time into NT increments, such that $\Delta\bar{Z} = \Delta t = h/(NZv) = (\pi/\omega)/NT$.
2. The system is initially assumed to be in equilibrium with the feed concentration at T_1, i.e., $\langle y_{T1}\rangle_1 = \langle y_{TP1}\rangle_1 = \langle y_{B1}\rangle_1 = y_0$, so that, at the end of the first upflow half cycle (or $n = 1/2$), $y(\bar{Z}) = y_0$ and $x(\bar{Z}) = M_1 y_0$.
3. Set $\bar{Z} = 0$ at the top of the column during downflow, and at the bottom of the column during upflow.
4. Calculate $y(I, J)$ and $x(I, J)$ by Eqs. (11) and (12) with the initial ($J = 1$) and boundary ($I = 1$) condition shown below:

Initial. Conditions:

For downflow, $y(I, 1)|_n = y(I, NT + 1)|_{n-1/2}$ = concentration of y at the end of nth upflow half-cycle.

For upflow, $y(I, 1)|_n = y(I, NT + 1)|_{n-1}$ = concentration of y at the end of $(n - 1)$th downflow half-cycle.

Boundary Conditions:

For downflow,

$$x(1, J)|_n = \langle Y_{T2}\rangle_n M_2 - [\langle y_{T2}\rangle_n M_2 - x(1, 1)] \exp[-(\lambda/M_2)\Delta t(J - 1)]$$

$$y(1, J)|_n = \langle y_{T2}\rangle_n$$

For upflow,

$$x(1, J)|_n = \langle y_{B1}\rangle_n M_1 - [\langle y_{B1}\rangle_n M_1 - x(1, 1)] \exp[-(\lambda/M_1)\Delta t(J - 1)]$$

$$y(1, J)|_n = \langle y_{B1}\rangle_n$$

where $\langle y_{T2}\rangle_n$ and $\langle y_{B1}\rangle_n$ can be calculated from Eqs. (1)–(4). The first approximations for Eqs. (11) and (12) can be obtained by the aid of the Euler forward integration method:

$$y^1(I + 1, J + 1) = y(I, J) - \left(\frac{1 - \varepsilon}{\varepsilon}\right)\rho_s\lambda\Delta t[y(I, J) - x(I, J)/M] \quad (11a)$$

$$x^1(I + 1, J + 1) = x(I + 1, J) + \lambda\Delta t[y(I + 1, J) - x(I + 1, J)/M] \quad (12a)$$

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RESULTS AND DISCUSSION

The performance of nonequilibrium continuous pumps was studied for the case of NaCl separation from H_2O using an ion retardation resin (Bio-Rad AG11A8) as adsorbent. The experimental apparatus is identical to that used previously (*5*). The experimental parameters are shown in Table 1, and the data are plotted in Fig. 2 to 6. The equations derived were used to calculate the concentration transients, and computed results corresponding to the experimental runs are also presented in Figs. 2 to 6. These results compare reasonably well with the observed values. The equilibrium parameter M and the rate constant λ used in the calculations were experimentally determined by a method described by Sweed and Gregory (*11*).

Figure 2 shows the effect of cycle time on the bottom product concentration. Separation is poor at short cycle times because there is little time for interphase mass transfer to take place. The separation improves with increasing π/ω and, as π/ω becomes very large, will approach equilibrium operation (curve 8). The concentration transient, $\langle y_{BP2}\rangle_n$ for equilibrium pumps can be expressed as (*4*)

$$\frac{\langle y_{BP2}\rangle_n}{y_0} = \frac{1-b}{1+b}\left[\frac{(1-b)/(1+b)+C_2}{1+C_2}\right]^{n-1} \qquad (n \geq 1) \qquad (13)$$

and at steady state ($n \rightarrow \infty$)

$$\langle y_{BP2}\rangle_\infty / y_0 = 0 \qquad (14)$$

Thus, for an equilibrium pump at the steady state, complete removal of solute from the bottom product stream can occur.

TABLE 1

Experimental and Model Parameters

$T_1 = 278\,°K$, $T_2 = 343\,°K$, $h = 90$ cm, $\varepsilon = 0.38$
$\lambda_1 = 0.328v^{0.3}$ cc/g-min, $\lambda_2 = 0.0736v^{0.3}$ cc/g-min
$M_1 = 4.6347$ cc/g, $M_2 = 0.00993$ cc/g
$\phi_T + \phi_B = 0.4$, $V_T = V_B = 5$ cc

	$C_0 = y_0$ (g moles/cc)	π/ω (min)	$Q(\pi/\omega)$ (cc)	ϕ_B
1	0.05	35	25	0.04
2	0.1	35	25	0.04
3	0.1	35	25	0.16
4	0.1	35	35	0.04
5	0.1	25	25	0.04

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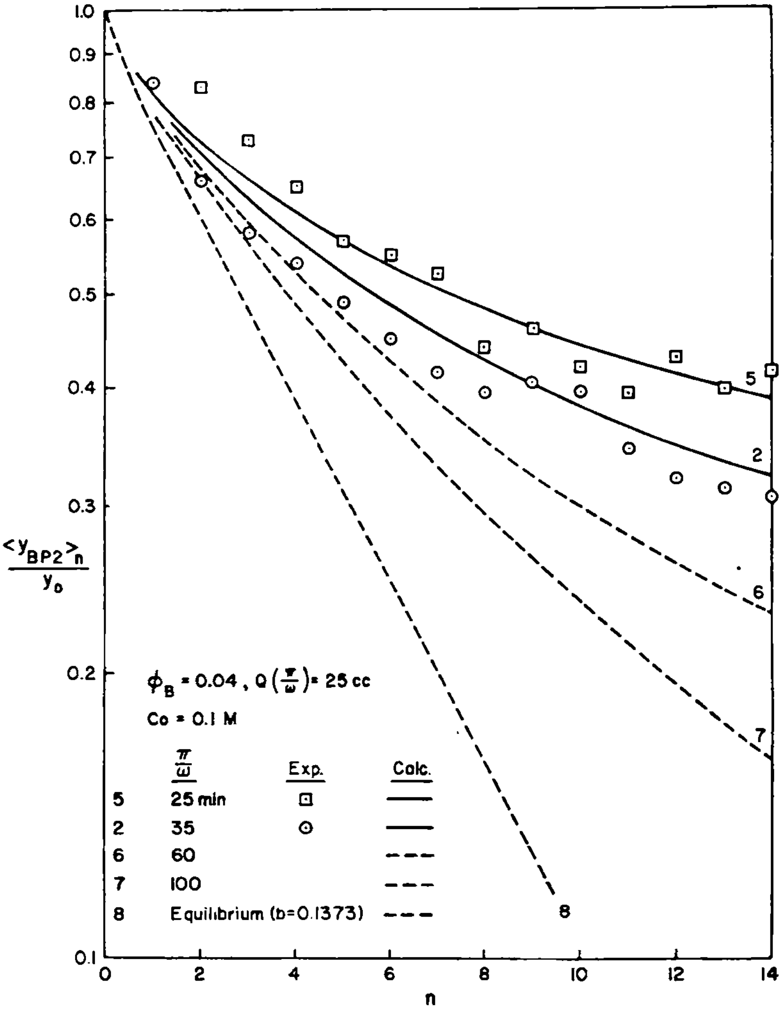

FIG. 2. Effect of cycle time on bottom product concentrations.

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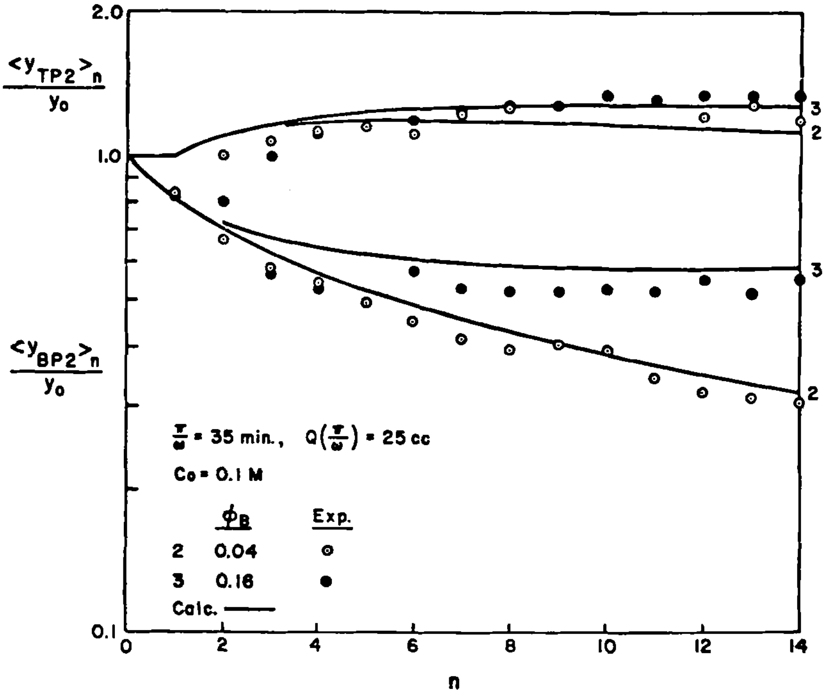

FIG. 3. Effect of bottom product flow rate on concentration transients.

One can see from Fig. 3 that the decrease of ϕ_B produces a decrease in steady-state bottom product concentration, and at the same time the transient time for depletion of the solute from the lower reservoir or the bottom product stream would become long. Note that at the steady state the top product concentration is

$$\frac{\langle y_{TP2}\rangle_\infty}{y_0} = 1 + \frac{\phi_B}{\phi_T}\left[1 - \frac{\langle y_{BP2}\rangle_\infty}{y_0}\right] \tag{15}$$

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. Therefore, a pump with top feed can continuously separate a two-component system into one fraction with low solute and another fraction enriched in solute to any desired degree.

Figure 4 illustrates a comparision of steady-state concentrations for equilibrium and nonequilibrium pumps. For the equilibrium pump in the interval $[\phi_B/(\phi_T + \phi_B)] \leq 0.35$, corresponding to $\phi_B \leq b$, no solute

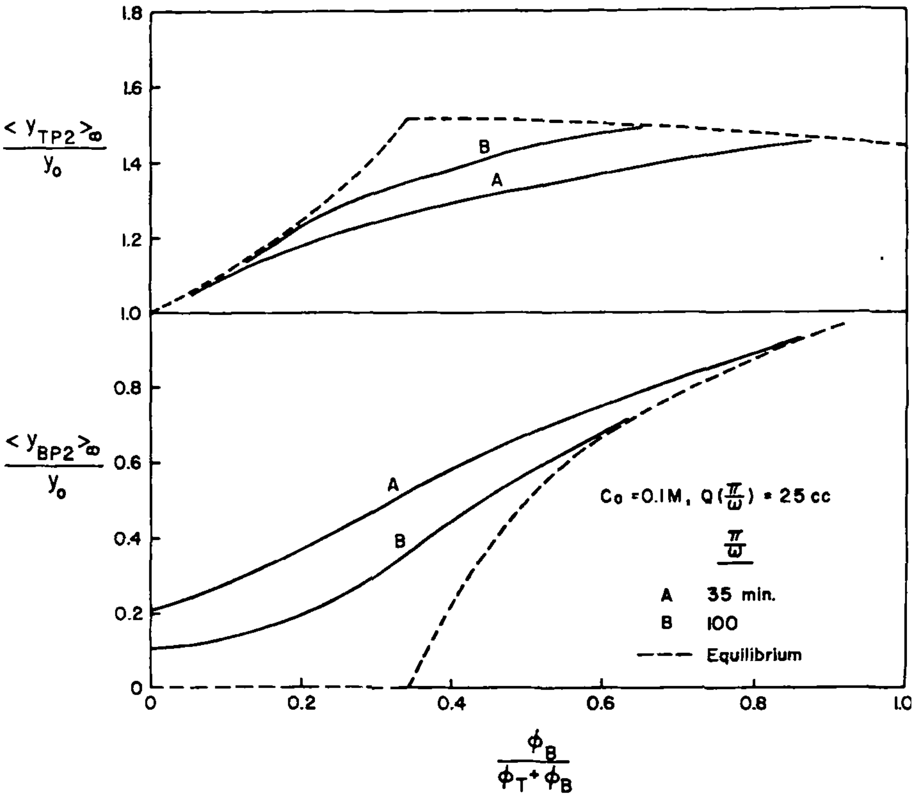

FIG. 4. Steady-state concentrations for equilibrium and nonequilibrium pumps.

appears in the bottom stream. However, beyond $\phi_B = b$, $\langle y_{BP2}\rangle_\infty/y_0$ increases with increasing $\phi_B/(\phi_T + \phi_B)$ and will equal unity when all the feed emerges from the bottom of the column ($\phi_T = 0$). In the case of the nonequilibrium pump, solute always appears in the bottom product. At lower $\phi_B/(\phi_T + \phi_B)$ separation improves as π/ω increases, and at higher $\phi_B/(\phi_T + \phi_B)$ separation is independent of π/ω, i.e., separation for the equilibrium pump is identical to that for the nonequilibrium pump.

In Fig. 5, $\langle y_{BP2}\rangle_\infty/y_0$ is plotted against the displacement, $Q(\pi/\omega)$. As long as $Q(\pi/\omega)$ is greater than V_B, $\langle y_{BP2}\rangle/y_0$ decreases as $Q(\pi/\omega)$ decreases. However, when $Q(\pi/\omega) < V_B$, $\langle y_{BP2}\rangle_\infty/y_0$ increases with the decrease of $Q(\pi/\omega)$, and will approach 1 (or $\langle y_{BP2}\rangle_\infty = y_0$) as $Q(\pi/\omega)$ becomes small.

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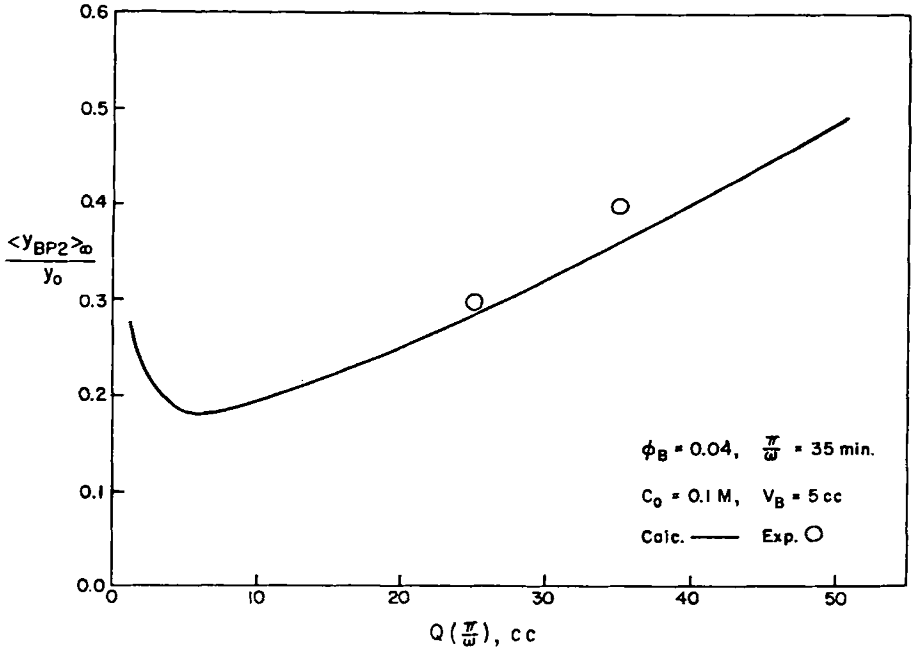

FIG. 5. Effect of reservoir displacement on separations.

We present here a method for predicting separations by nonequilibrium parametric pumping. The method invokes the assumption that the molar density of the fluid, ρ_f, is constant (or the feed concentration C_0 is low), and the concentration transients are independent of C_0. This is clearly shown in Fig. 6. However, the calculation becomes somewhat more complicated if ρ_f varies with y, i.e., when the value of C_0 is high. Experimental verification of the effect of C_0 on separation will be presented in subsequent papers.

SYMBOLS

b	dimensionless equilibrium parameter (see Ref. 3)
C	$\frac{V}{Q(\pi/\omega)}$
C_0	feed concentration
h	column height

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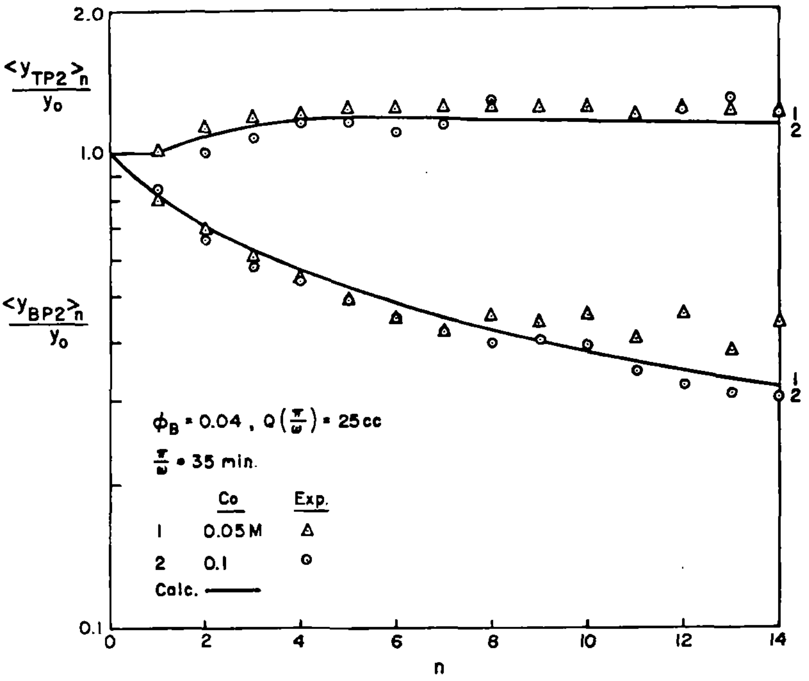

FIG. 6. Effect of feed concentration on contraction transients.

M	x/y
n	number of cycles of pump operation
Q	reservoir displacement rate
T	temperature
t	time
V	reservoir volume
v	interstitial velocity
x	concentration of solute in the solid phase
y	concentration of solute in the liquid phase
z	position
$\langle\ \rangle$	average value

Greek Symbols

ρ_s	density of the solid
ρ_f	density of the fluid

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λ	rate constant for mass transfer as defined by Eq. (6)
ε	void fraction in packing
ϕ	product volumetric flow rate/reservoir displacement rate
π/ω	duration of half-cycle

Subscripts

0	initial condition
1	upflow or hot-half cycle
2	downflow or cold-half cycle
BP	bottom product
TP	top product

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