AN EXPERIMENTAL STUDY OF EQUILIBRIUM PARAMETRIC PUMPS

BY

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ABSTRACT

Parametric pumping is a separation process characterized by periodic changes in axial displacement, coupled with synchronized changes in some variable affecting the position of the interphase equilibrium. Both continuous and semicontinuous pumps were investigated at various operating conditions using a model system of toluene-n-heptane on a 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 large interphase movement and hence by large values of the equilibrium parameter.

APPROVAL OF THESIS

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FOR

DEPARTMENT OF CHEMICAL ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________________

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NEWARK, NEW JERSEY

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INTRODUCTION

Thermal parametric pumping is a separation process characterized by periodic changes in axial displacement of a fluid coupled with synchronized changes in temperature. A jacketed column with top and bottom variable volume reservoirs is packed with a solid adsorbent (silica gel) and filled with a binary mixture (toluene-n-heptane). Reciprocal pumping action by the reservoirs causes either upflow or downflow of the fluid through the bed, while the column jacket and two temperature controlled baths provide the medium for the synchronized temperature changes.

This process has three modes of operation; batch, continuous, and semicontinuous. Batch operation is defined as a constant hot-upflow half cycle followed by a cold-downflow half cycle without feed input or product withdrawal. Continuous operation incorporates constant feed input and product withdrawal during the entire cycle. The semicontinuous mode is batch operation during the hot-upflow and continuous operation during the cold-downflow half cycle.

Previously, the semicontinuous and continuous pumps have been investigated by Chen and co-workers (1,2,3) and analyzed in terms of an equilibrium theory (4,5) describing pump performance. It has been shown that under certain conditions the parametric pump can completely remove solute from one product stream and give arbitrarily large enrichment of solute in the other product stream. The conditions which determine the separation are defined in terms of penetration distances and column height.

This project experimentally investigates the effect of various process parameters upon relatively high separations.

EXPERIMENTAL

A. Scope of Investigation

This project investigated the sensativity of the equilibrium parametric pump to various operating parameters, while obtaining high separation factors (the ratio of solute concentration in the two product streams). Thus, only region 1 operation of the pump will be considered. The operating parameters considered were product flow rate, feed flow rate, feed concentration, time, temperature, and mode of operation. Table 1 indicates the sequential details of this investigation.

B. Description of Apparatus

The thermal, liquid-solid phase, parametric pump shown in Figure 1 is similar to that used previously (2,3) and can be described as follows: (refer to Figure 1)

1. The adjustable length, jacketed, glass adsorption column was an Ace Glass Adjusta-Chrom Recycling Column (5819-06) with an inside diameter of .01 meters and a length of .90 meters.
2. Top and bottom reservoirs, located at either end of the column, along with the feed apparatus were 50 cc Becton and Dickinson, multifit, luer-lok tip, glass syringes. The syringes were automatically operated by variable speed infusion and withdrawal syringe pumps made by Harvard Apparatus

(series 940). The reservoir pump, which was set for reciprocal operation, was orientated in a vertical position which, along with a glycerin seal, minimized fluid losses. Also, small magnetic stirrers were placed in the reservoir syringes in order to meet the requirement of perfect mixing within the reservoir. The feed pump was orientated in a horizontal position and was set for parallel operation.

3. The reservoir, feed, and product lines were 0.063 inches OD X 0.031 inches ID teflon tubing (by Chromatronox Incorporated).
4. The sampling apparatus was two Micrometric Capillary Valves by Gilmont (M7100) and two 25 ml graduated cylinders.
5. Two Lauda Circulators, which are constant temperature, circulating baths, by Brinkmann Instruments Incorporated (models K-2 and K-2/R) provided hot and cold water mediums.
6. Standard $\frac{1}{2}$ inch rubber tubing and two 3 way universal operation ASCO solenoid valves (cat #8320A107) provided the means for switching the column temperature.
7. A recycling timer, type A-Tandem by Industrial Timer Corporation controlled the half cycle time and synchronized the column temperature with the

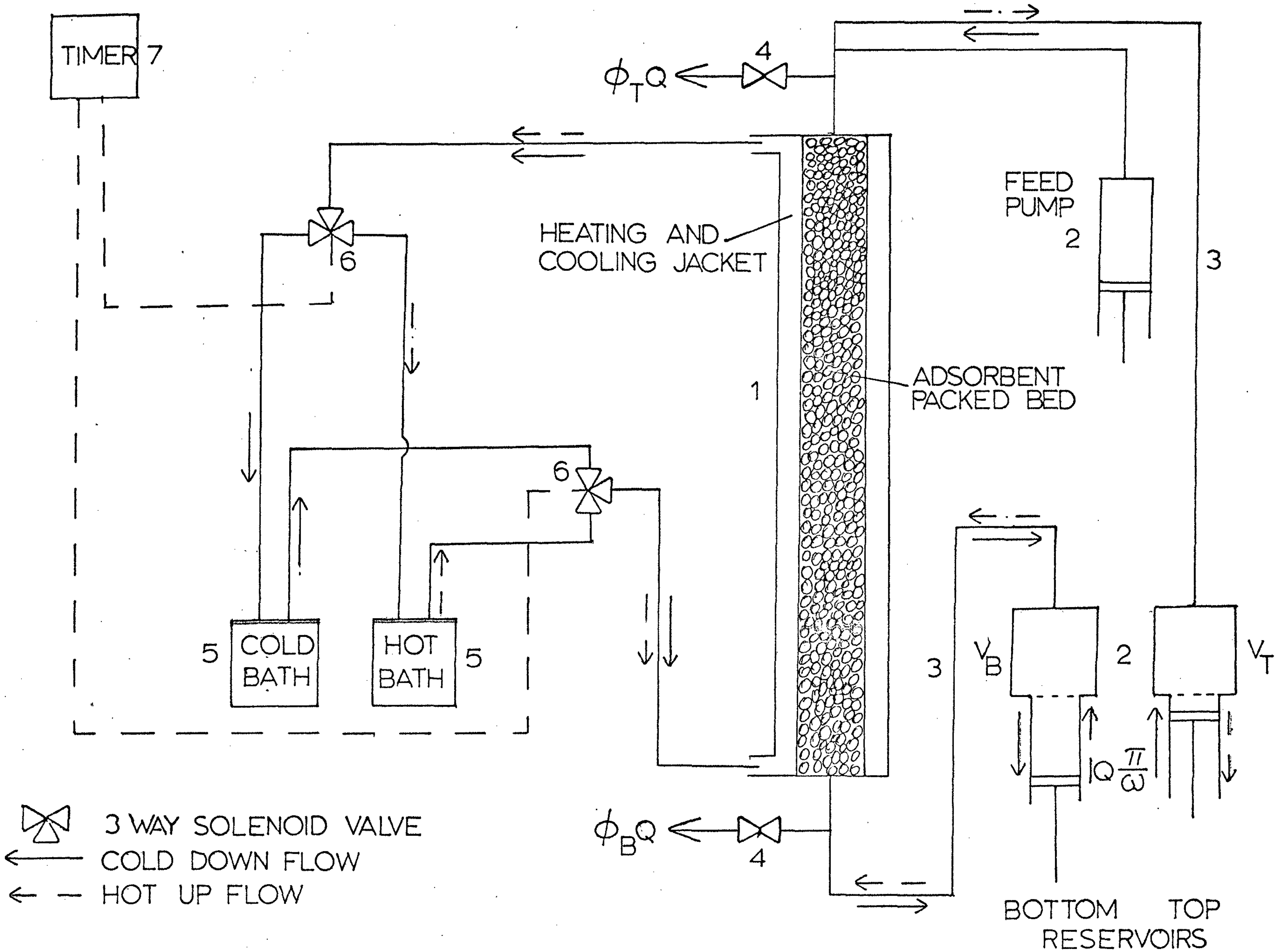

TIMER 7
$\phi_T Q$
4
FEED PUMP
2
3
HEATING AND COOLING JACKET
6
6
1
ADSORBENT PACKED BED
5
COLD BATH
HOT BATH
5
3
V_B
2
V_T
$Q \frac{\pi}{\omega}$
$\phi_B Q$
4
3 WAY SOLENOID VALVE
COLD DOWN FLOW
HOT UP FLOW
BOTTOM TOP
RESERVOIRS

FIGURE 1

direction of fluid flow.

8. Samples were analyzed for toluene content using a Beckmann DBG spectrophotometer operating in the ultraviolet spectrum region.

C. Experimental Procedure

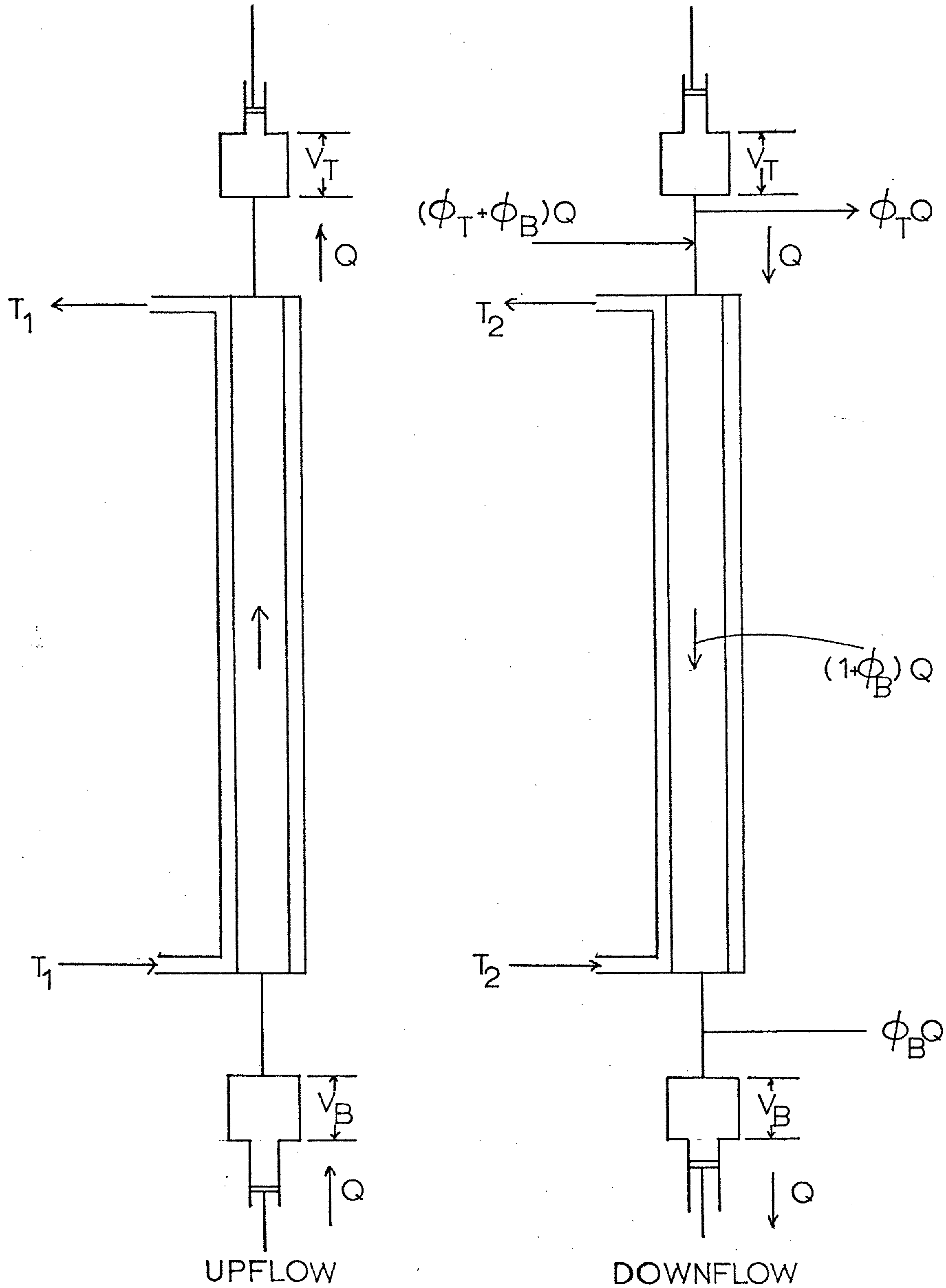
Preparation for an experimental run started with the lubricating of the reservoir and feed syringes with glycerin. Two cc of glycerin was left in the vertically orientated top and bottom reservoirs to provide a seal which prevented evaporation losses. Glycerin served the dual purpose of lubricant and seal because of its high viscosity (900 centipoises at 25°C), relatively high specific gravity (1.3 at room temperature), and low solubility in heptane-toluene solution ($<.03\%$ at room temperature).

The column was packed with dry 30-60 mesh, chromatographic grade silica gel and the interstitial volume in the column, along with the feed and reservoirs, was filled with feed solution of toluene and n-heptane at ambient temperature. To facilitate the removal of air from the system, the column was vibrated as the feed solution was introduced.

After the hot and cold baths had reached steady state at their specified temperatures, the run was initiated with upflow on the hot half cycle and continued for $\frac{\pi}{\omega}$ time units. Flow and temperature were then switched to downflow on a cold half cycle, $\frac{\pi}{\omega}$ time units in duration, to complete one cycle. The dead volumes V_T and V_B for top and bottom reservoirs respectively, were 4 cc (2 cc glycerin, 1 cc stirrer volume, and 1 cc solution). The reservoirs had a a displacement volume of $Q\frac{\pi}{\omega}$ where Q is the reservoir displacement rate and $\frac{\pi}{\omega}$ is the half cycle time. The feed rate was $(\phi_T+\phi_B)Q$, ϕ_T and ϕ_B being the ratio of product volumetric flow rate to the reservoir displacement rate for top and bottom reservoirs respectively.

Removing the top and bottom product while constantly introducing feed solution during both hot and cold half cycles is termed continuous operation. On the other hand, batch mode is operating the apparatus without feeding or sampling during the cycle. Semicontinuous is batch operation during the hot half cycle and continuous operation during the cold half cycle. Top and bottom products are withdrawn at $\phi_T Q$ and $\phi_B Q$ respectively.

After approximately 16 cycles, the run is terminated and the the samples analyzed for toluene content using the Beckmann DBG spectrophotometer operating in the ultraviolet region (see appendix B).



The Semicontinuous Parametric Pump

FIGURE 2

THEORY

Chen and Hill have extended the equilibrium theory of Pigford, Baker and Blum (5) and derived mathematical expressions describing pump performance (1). Three possible regions of pump operation were shown to depend upon the height of the column and the ratio of the penetration distances of the hot half cycle to that of the cold half cycle, i.e. L_1/L_2. Considering only pumps with the feed at the top, 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. The cold half cycle penetration distance, L_2, in both continuous and semicontinuous pump is express as:

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

while L_1 for the continuous and semicontinuous pump is:

$$L_1 = \frac{v_o\left(1-\phi_B\right)\frac{\pi}{\omega}}{(1-b)\left(1+\frac{1}{2}(m_1+m_2)\right)} \tag{4}$$

and

$$L_1 = \frac{v_o\,\frac{\pi}{\omega}}{(1-b)\left(1+\frac{1}{2}(m_1+m_2)\right)} \tag{5}$$

respectively. The equilibrium parameter is defined as follows:

$$b = \frac{\frac{1}{2}(m_1-m_2)}{1+\frac{1}{2}(m_1+m_2)} \tag{6}$$

where

$$m_i = \frac{\rho_S(1-\epsilon)M_i(T)}{\epsilon} \tag{7}$$

Mi(T) is the equilibrium distribution coefficient at temperature Ti. See appendix A for derivation of expressions for L_1, L_2, and b.

The three possible regions of pump operation are:

$$\begin{array}{lll} \text{Region 1:} & L_1/L_2 \geq 1 & L_2 \leq h \\ \text{Region 2:} & L_1/L_2 \leq 1 & L_2 \leq h \\ \text{Region 3:} & L_1 > h & L_2 > h \end{array} \tag{8}$$

It has been shown that only region 1 pump operation yields high separation factors. An indication of the separation is the ratio of the concentration of the bottom product on the cold half cycle to the concentration of the feed, i.e. y_{BP2}/y_0. For region 1 operation, the theoretical expression for $\langle y_{BP2}\rangle/y_0$ is (1)

$$\frac{\langle y_{BP2}\rangle_n}{y_0} = \left(\frac{1-b}{1+b}\right)\left(\frac{\frac{1-b}{1+b}+C_2}{1+C_2}\right)^{n-1} \tag{9}$$

furthermore, at $t=\infty$

$$\frac{\langle y_{BP2}\rangle_\infty}{y_0} = 0 \tag{10}$$

Equation 10 states that at steady state there is no solute in the bottom product and all the solute supplied by the feed is in the top product. The expression for the top product concentration is:

$$\langle y_{BP2}\rangle = y_0\left(1+\frac{\phi_B}{\phi_T}\right) \tag{11}$$

Equation (9) provides a relation from which b can be predicted. Taking the natural logs of equation (9) yields:

$$\ln\frac{\langle y_{BP2}\rangle_n}{y_0} = (n)\ln\left(\frac{\frac{1-b}{1+b}+C_2}{1+C_2}\right) + \ln\left(\frac{1-b}{1+b}\right) - \ln\left(\frac{\frac{1-b}{1+b}+C_2}{1+C_2}\right) \tag{12}$$

Since b and C_2, the ratio of the bottom reservoir dead volume to the displacement, are constants, equation (12) describes a straight line with a slope α of

$$\alpha = \ln\left(\frac{\frac{1-b}{1+b}+C_2}{1+C_2}\right) \tag{13}$$

and therefore

$$b = \frac{1-e^{\alpha}-C_2(e^{\alpha}-1)}{1+e^{\alpha}+C_2(e^{\alpha}-1)} \tag{14}$$

The equilibrium parameter can also be calculated from equilibrium data (see appendix A).

The quantity b is a measure of the extent of solute movement between phases due to column temperature change. b can be any value between zero and one, where b=0 indicates the equilibrium distribution is insensitive to temperature, and b=1 implies extreme temperature sensitivity.

RESULTS AND DISCUSSION

Eleven experimental runs were executed with conditions set so that region 1 operation of the pump would result, i.e. $L_1/L_2 \geq 1$ and $L_2 \leq h$. The process variables for the experimental runs are shown in table 1.

Experimental data was compared with calculations based on the transient equations (1,2,3) derived from the equilibrium theory. The primary assumptions of the theory are (see appendix A):

1. local interphase equilibrium exists with a linear distribution having a temperature dependent coefficient, i.e. $x = \bar{M}(T)y$
2. effects of axial diffusion are negligible
3. there are instantaneous temperature changes
4. there is plug flow displacement of fluid
5. the densities of the fluid and the solid are constant.

Figures 3 and 4 show the effect of feed concentration, product flow rate, and feed flow rate upon the bottom product concentration for the semicontinuous and continuous pumps. The agreement between experimental and calculated results is reasonably good. It is evident that y_0, ϕ_B, and $\phi_T + \phi_B$ have negligible effect upon the bottom product concentration, $\langle y_{BP2} \rangle_n / y_0$, provided that equilibrium of adsorbate between the two phases has been established ($\frac{\pi}{\omega} \geq$ 10 min.). These figures demonstrate that $\langle y_{BP2} \rangle_n / y_0$ and n are inversely proportional and as n becomes large, $y_{BP2\ n}/y_0$

approaches zero as predicted by equation (10). Equation (9) states that the bottom product concentration transient depends upon b and C_2, where $C_2 = V_B/(Q\frac{\pi}{\omega})$, and b is the dimensionless equilibrium parameter defined by equation (28). The values for b were calculated using equation (14) and were found to be 0.22 and 0.15 for $T_1 = 70°C$ $T_2 = 4°C$ and $T_1 = 60°C$ $T_2 = 25°C$ respectively. Pump performance is enhanced by large values of b and thus by large $|\alpha|$ (absolute value of α), where α defined in equation (13) is the slope of the plot $\ln(\langle y_{BP2}\rangle_n/y_0)$ vs n. For large values of b the transient time for depletion of solute from the bottom product would be very short and approach zero ($\alpha = -\infty$) as b approached one. Furthermore, as $b \rightarrow 0$, and $\alpha \rightarrow 0$ no separation can occur. Figure 3 and equation (11) indicate that an arbitrary high degree of enrichment of the top product may be obtained by adjusting ϕ_B provided steady state has been attained at a given $\phi_T + \phi_B$. This arbitrary degree of enrichment is not a function of b.

Figures 3 and 4 also show that the semicontinuous and continuous pumps are similar in nature. The principal difference between the two modes is the region switching points. For example, region 1 operation ($L_1/L_2 \geq 1$ and $L_2 \leq h$) of the semicontinuous pump can be defined as $\phi_B \leq 2b/(1-b)$ while for the continuous pump $\phi_B \leq b$ (3).

Figure 5 illustrates the effect of cycle time upon separation and gives some insight into the time required to reach local interphase equilibrium. If $\frac{\pi}{\omega} \geq 10$ minutes, complete solute removal is possible. When $\frac{\pi}{\omega} \leq 3$ minutes, only partial solute removal was obtained because the time was insufficient to reach equilibrium of the adsorbate between the solid and liquid phases.

Figure 6 together with the three previous graphs, gives experimental verification of assumption 1. A linear equilibrium relation with a temperature dependent coefficient is a good assumption. Furthermore, the degree of depletion of solute in the bottom product is solely a function of temperature (the value of b) and C_2 provided the pump is operated in region 1 with $\frac{\pi}{\omega} \geq 10$ minutes.

The remaining figures describe some of the experimental idiosyncrasies of the parametric pump. Consider figure 7 where $\langle y_{BP2} \rangle_n / y_0$ decreases as n increases up to a point where a drastic increase with n occurs. Run 3 was well within the criteria for region 1 ($L_1/L_2 = 1.13$ and $L_2 = 53$ cm), but yet the final separation was poor. During this run, no top product was removed ($\phi_T = 0$) which meant no toluene was removed from the system for the first 12 cycles. Eventually the toluene contained in the feed had to appear in the bottom product, i.e. the 13th cycle. The time at which the upward trend of the graph starts can be prolonged or partially eliminated by increasing the height of the column, decreasing y_0; but to eliminate it completely a sufficient quantity of top product must be withdrawn. Figures 7 and 8 demonstrate the observation that the upward trend can be eliminated or prolonged by varying y_0, ϕ_T and y_0 respectively at a specified h.

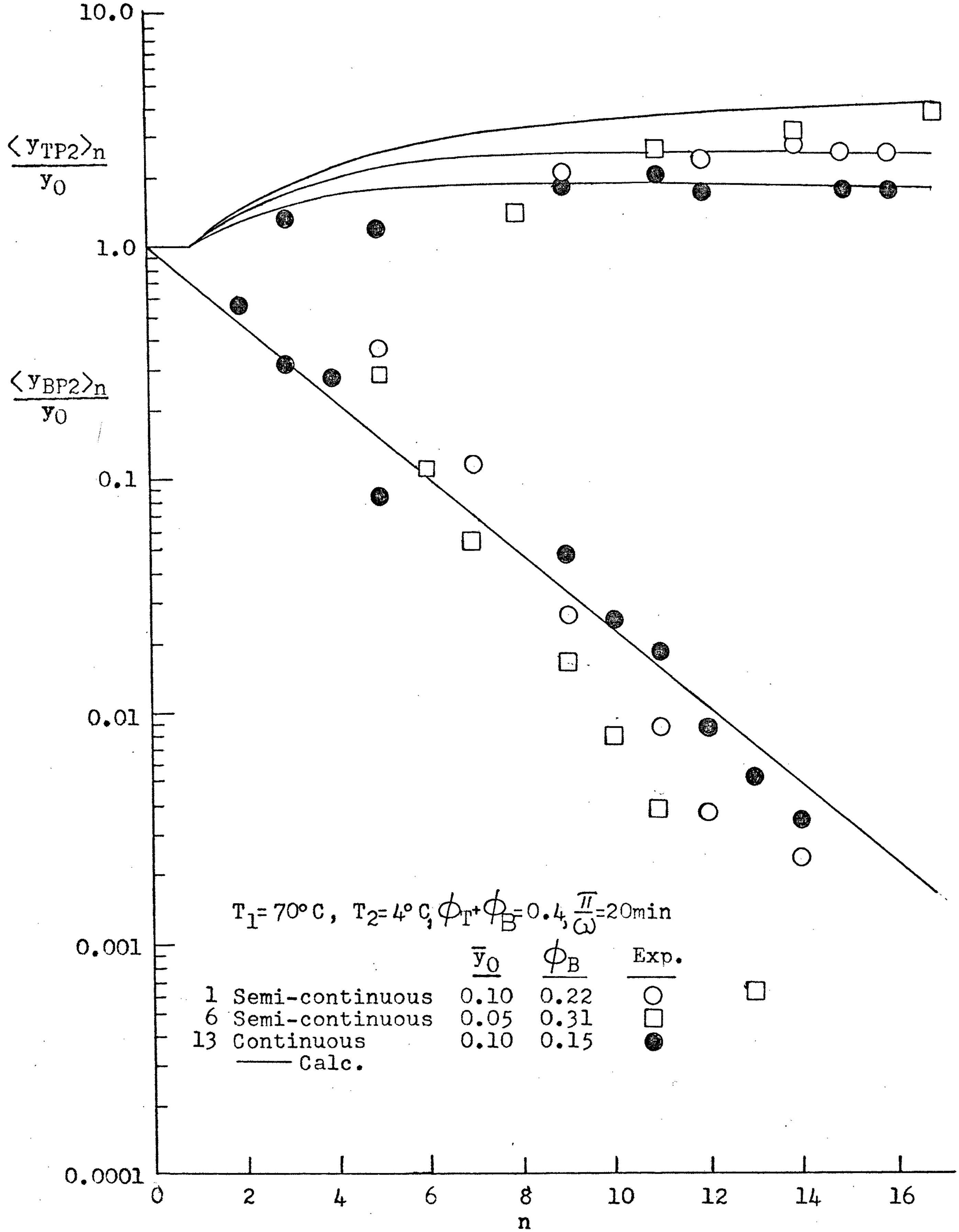
Figure 9 shows two runs which demonstrate region 2 operation. For run 9, $L_1 = 54$ cm and $L_2 = 54$ cm which by definition is a switching point or border between region 1 and region 2. It is highly likely that the process variables were such that region 2 operation resulted.

Figure 10 illustrates an interesting experimental error and its results. On the 8th cycle of run 10A, the temperature of the column did not change and two hot half cycles were run instead of the alternate hot and cold half cycles. Notice this resulted in a horizontal shift of two cycles. Furthermore, subsequent data continued with the same slope, α, as run 10B which did not contain a temperature switching error.

Table 1 Experimental and Model Parameters

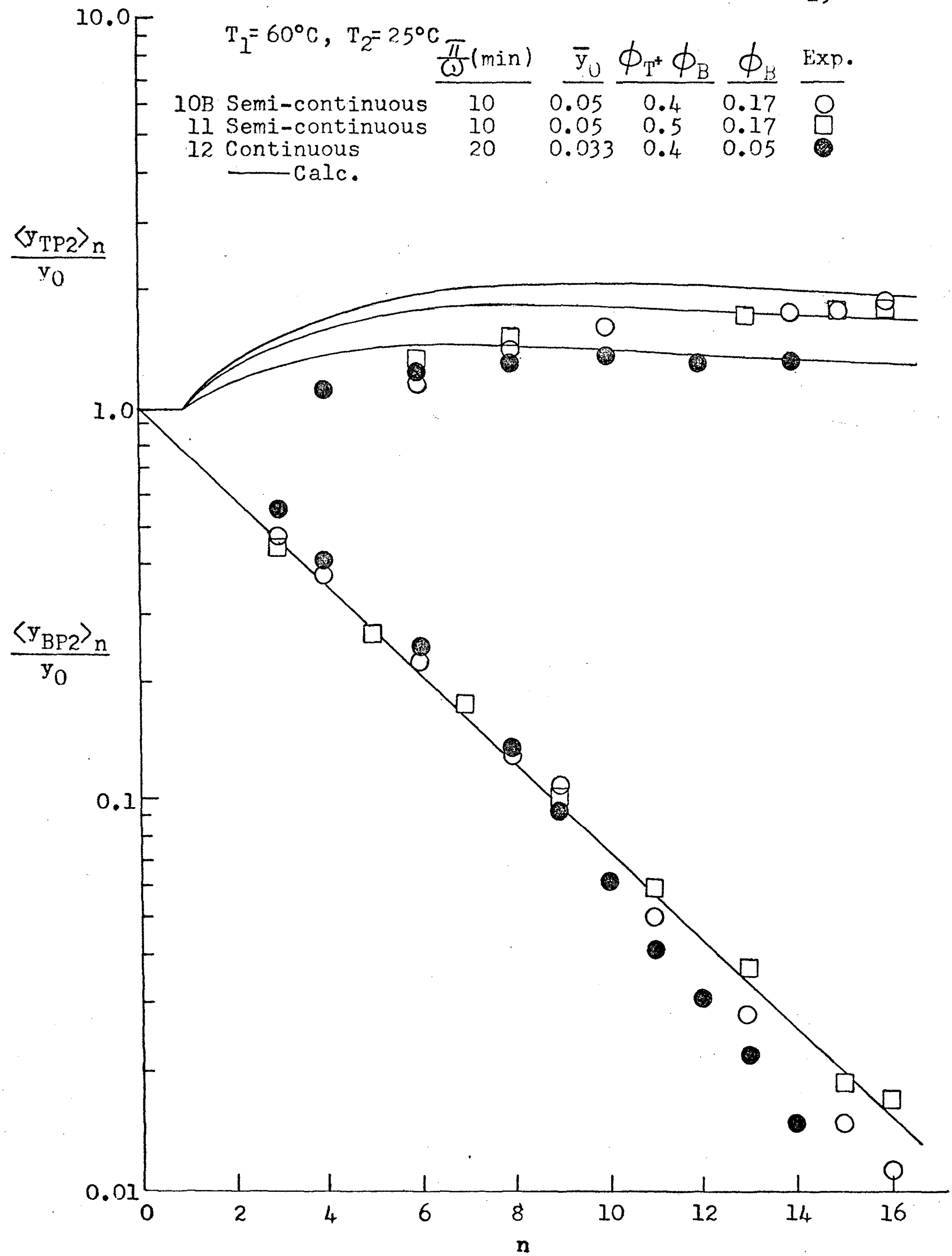
Run Number	Mode	T_1 (°C)	T_2 (°C)	$\frac{\pi}{\omega}$ (min)	$\bar{y}_0$ mole frac	Q (cc)	$\phi_T + \phi_B$	ϕ_B	C_1	C_2	L_1 (cm)	L_2 (cm)	b
1	Semi	70	4	20	0.10	40	0.4	0.22	0.10	0.15	60	46	0.22
2	Semi	70	4	20	0.10	40	0.4	0.25	0.14	0.15	60	48	0.22
3	Semi	70	4	20	0.10	40	0.4	0.4	0.12	0.15	60	53	0.22
4	Semi	70	4	20	0.10	40	0.5	0.4	0.13	0.14	60	53	0.22
5	Semi	70	4	20	0.10	40	0.4	0.32	0.12	0.13	60	50	0.22
6	Semi	70	4	20	0.05	40	0.4	0.31	0.11	0.15	60	50	0.22
7	Semi	70	4	10	0.05	40	0.4	0.32	0.13	0.15	60	50	0.22
8	Semi	70	4	10	0.10	40	0.4	0.31	0.13	0.16	60	50	0.22
9	Semi	60	25	10	0.05	40	0.4	0.34	0.13	0.13	54	54	0.15
10A	Semi	60	25	10	0.05	40	0.4	0.17	0.12	0.13	54	47	0.15
10B	Semi	60	25	10	0.05	40	0.4	0.17	0.12	0.13	54	47	0.15
11	Semi	60	25	10	0.05	40	0.5	0.17	0.12	0.13	54	47	0.15
12	Cont	60	25	20	0.034	40	0.4	0.07	0.12	0.13	51	43	0.15
13	Cont	70	4	20	0.10	40	0.4	0.15	0.14	0.15	51	44	0.22
14*	Semi	60	25	3	0.05	15	1.02	0.23	0.35	0.43	22	19	----

* Equilibrium theory can not be applied.



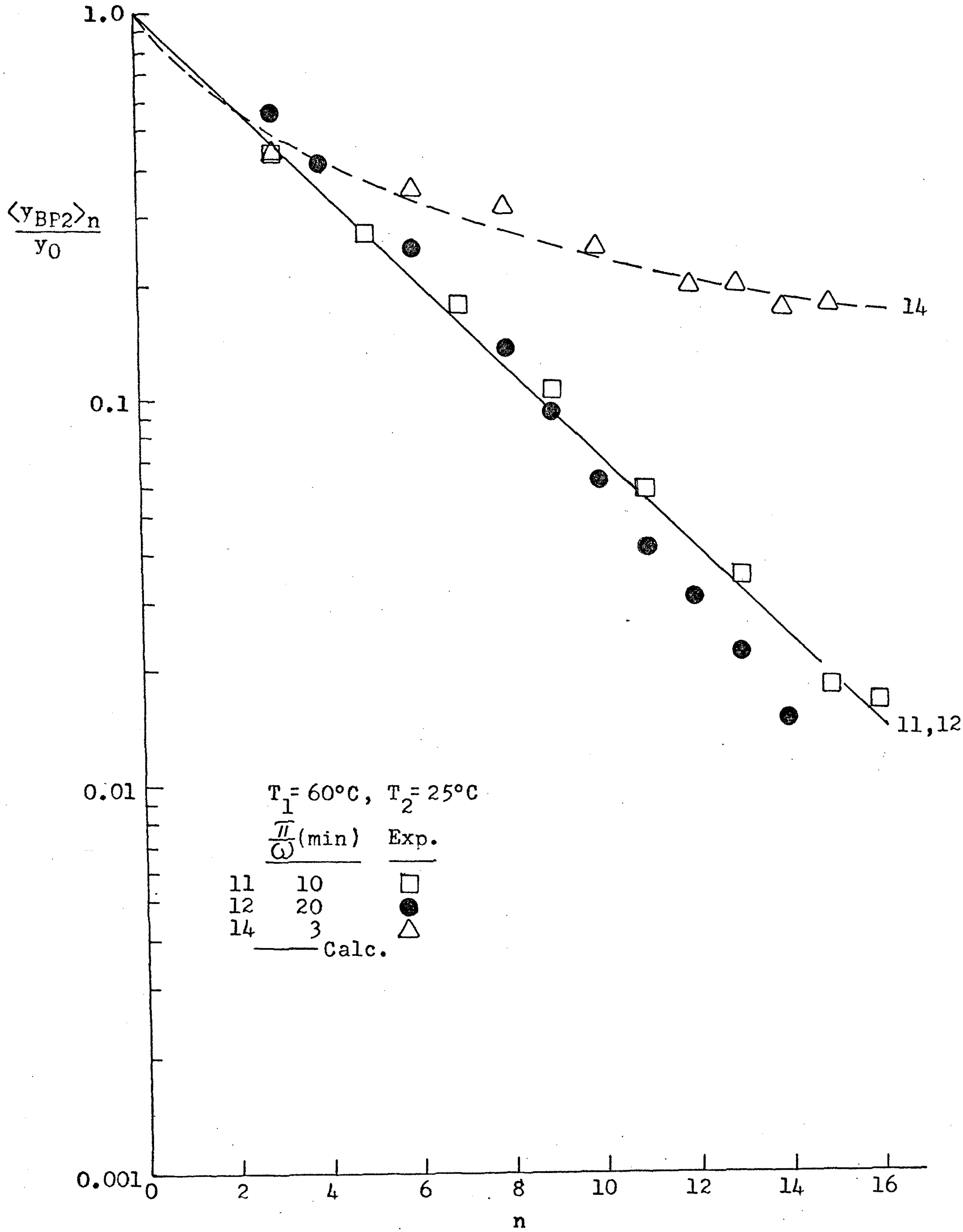
Effect of $\bar{y}_0$ and ϕ_B Upon Separation For Semicontinuous And Continuous Pumps

Figure 3



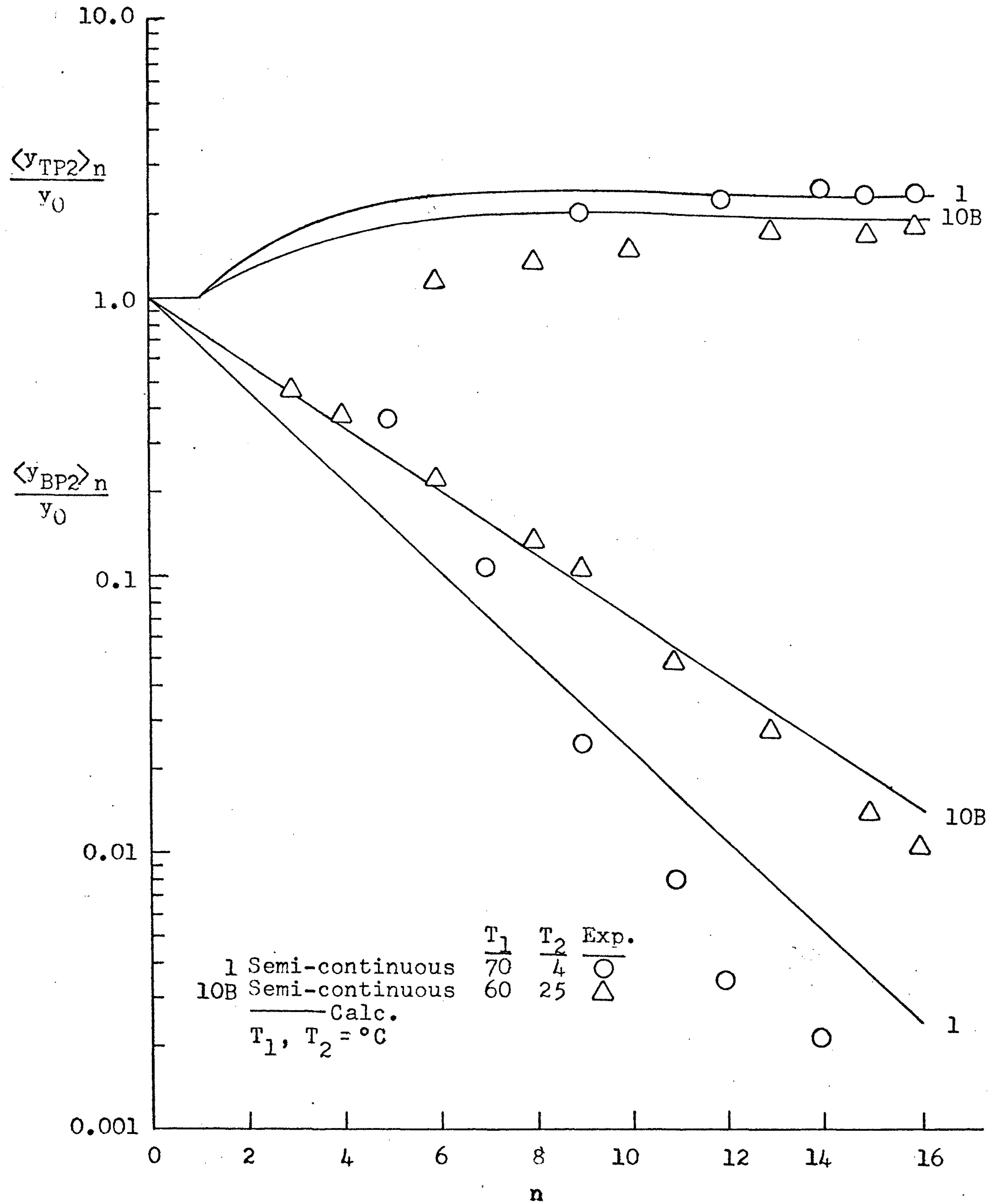
Effect of $\phi_T + \phi_B$ Upon Separation

Figure 4

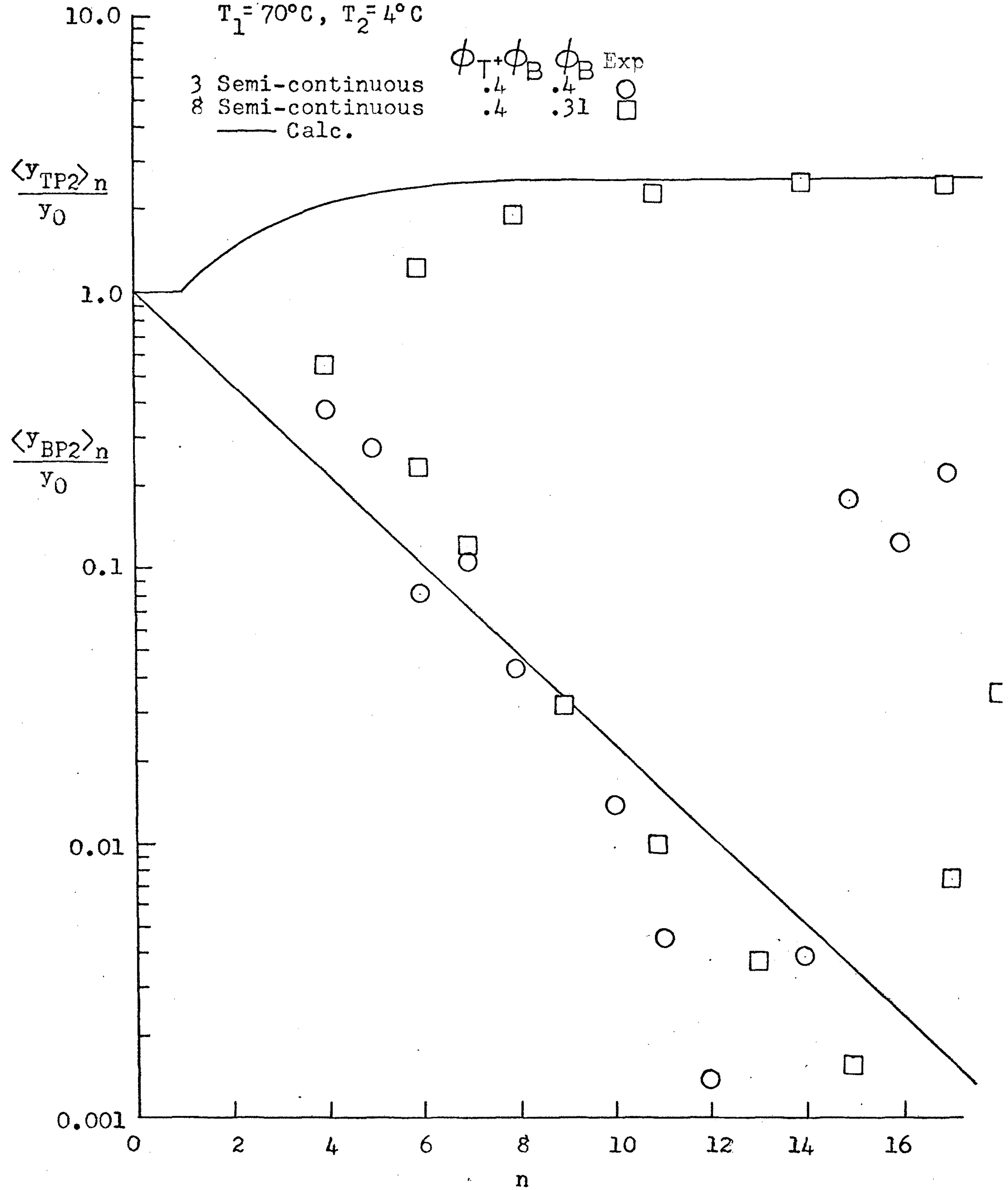


Effect of $\frac{\pi}{\omega}$ Upon Separation

Figure 5

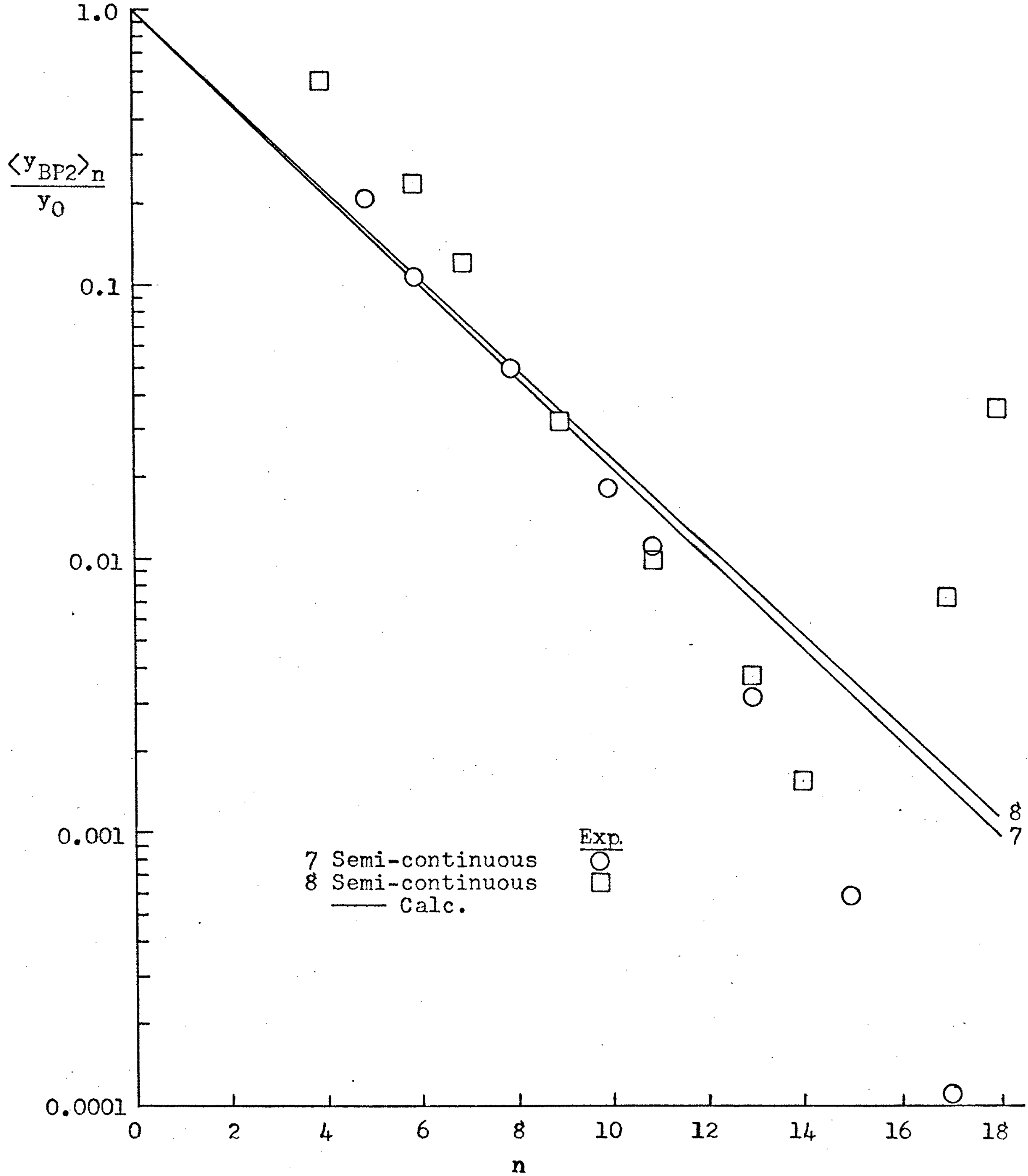


Comparison of Different Operating Temperatures
Figure 6



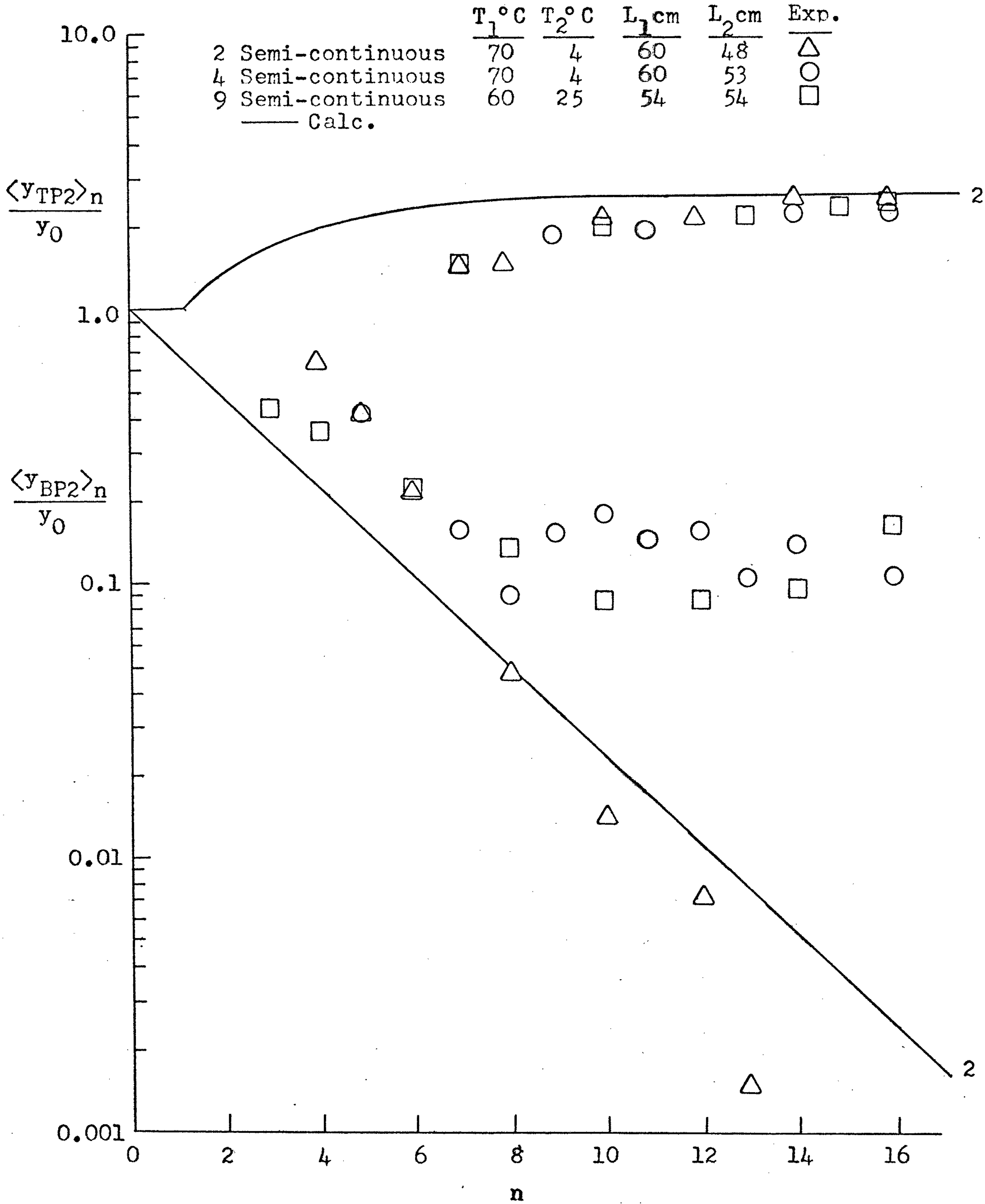
Region 1 Operation With Small ϕ_T

Figure 7



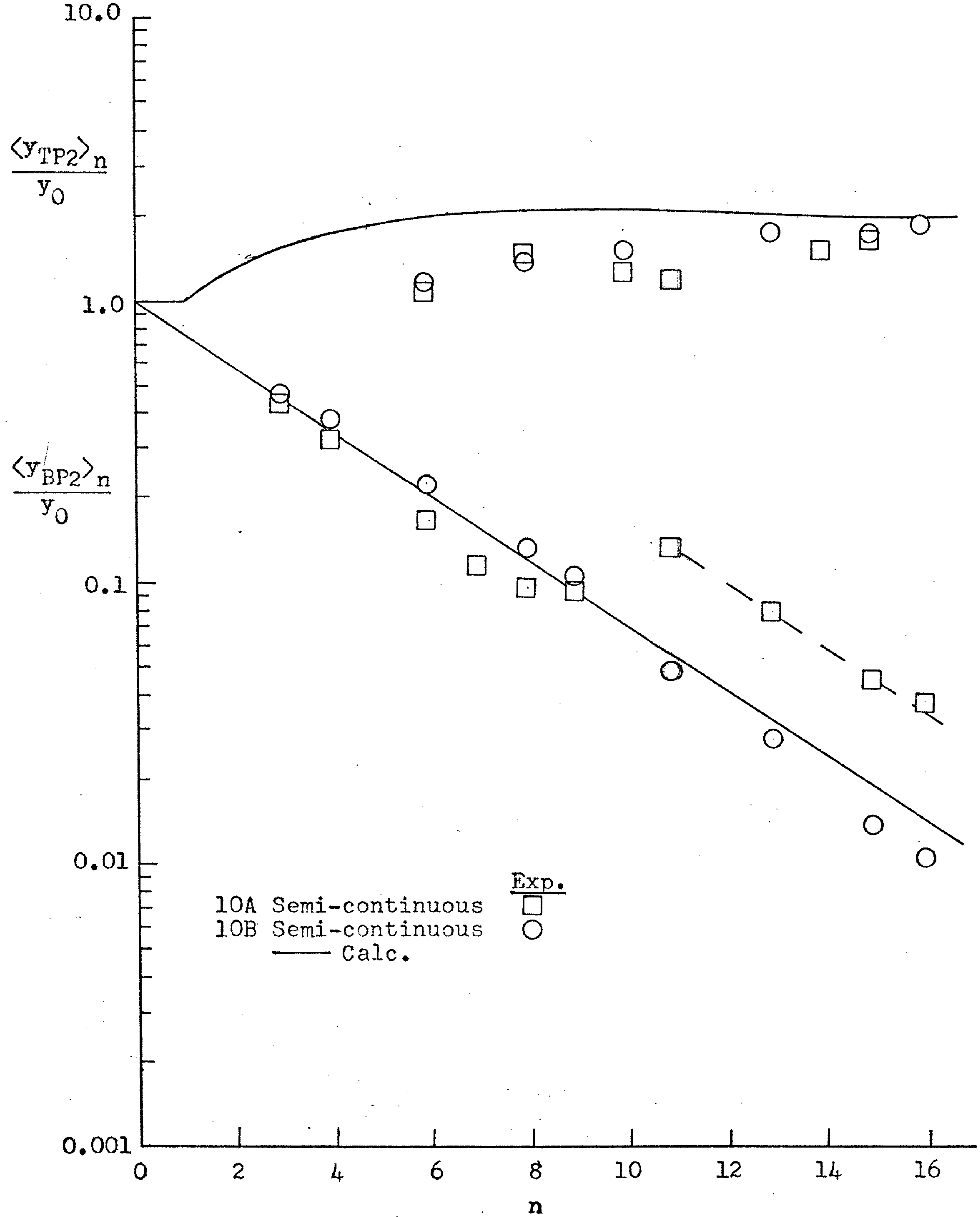
Sufficient ϕ_T Contrasted With Insufficient ϕ_T

Figure 8



Comparison Of Region 1 With Region 2

Figure 9



Experimental Shift of Bottom Product Concentration

Figure 10

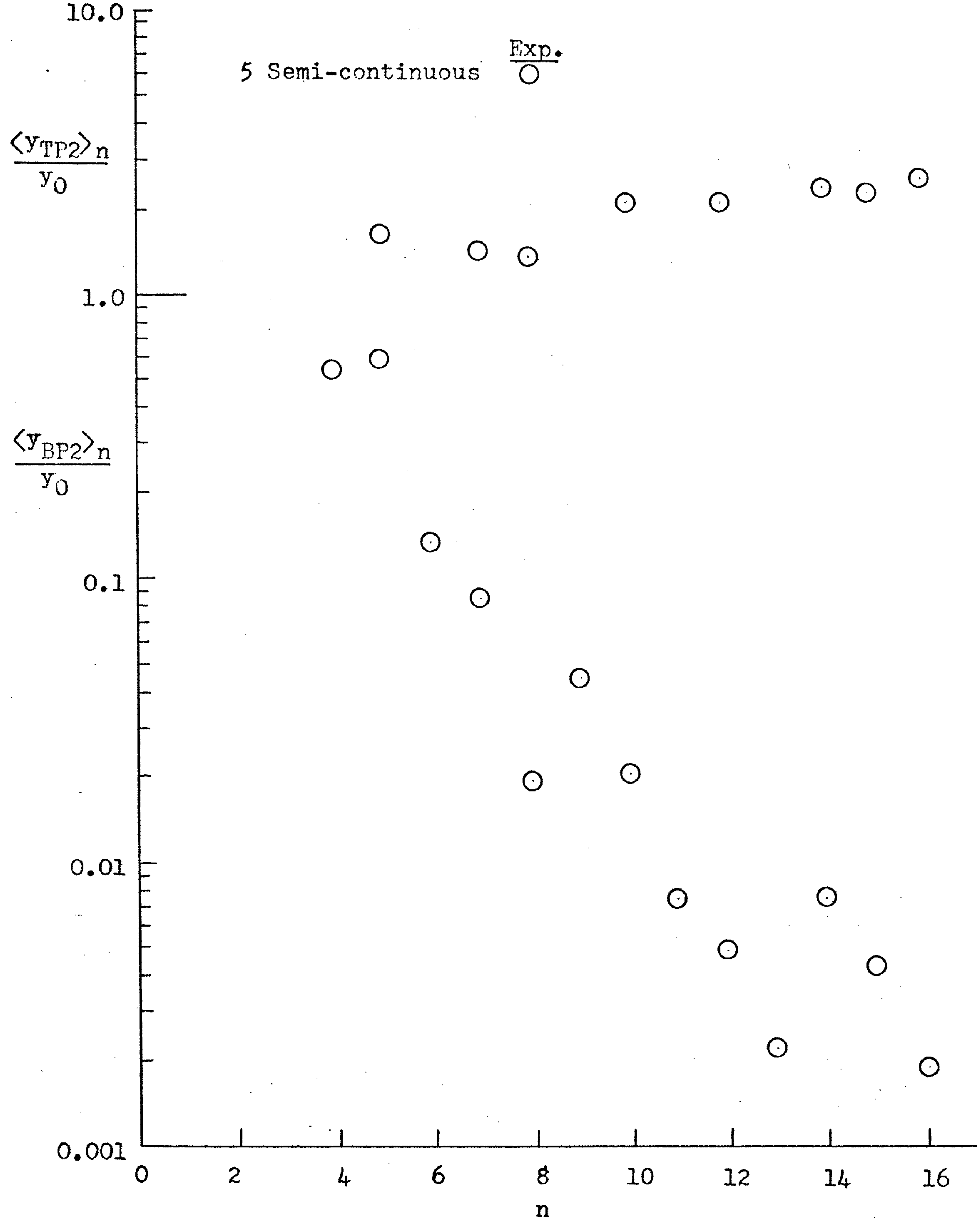

10.0
5 Semi-continuous
Exp.
$\frac{\langle y_{TP2}\rangle_n}{y_0}$
1.0
$\frac{\langle y_{BP2}\rangle_n}{y_0}$
0.1
0.01
0.001
0
2
4
6
8
10
12
14
16
n

Figure 11

CONCLUSION

Region 1 operation of continuous and semicontinuous pumps were investigated to determine the effect of certain process variables upon the separation of the binary components. The variables investigated were temperature, time, feed concentration, feed flow rate, mode of operation, and the product flow rate. Conclusions of this research are as follows:

1. Both pumps have the capability to completely remove solute from one product stream and give an arbitrary enrichment in the other stream provided interphase equilibrium has been attained, i.e. $\frac{\pi}{\omega} > 10$ minutes.
2. The degree of depletion of solute in the bottom product stream is a function of reservoir dead volume, temperature, and temperature changes which cause the interphase solute movement.
3. As the temperature difference between T_1 and T_2 increases, the value of the equilibrium parameter increases and pump performance is enhanced.
4. y_0, ϕ_B, and $\phi_T \cdot \phi_B$ have negligible effect upon the bottom product concentration.
5. At steady state and a given feed rate, the adjustment of ϕ_B gives an arbitrary degree of enrichment in the top product stream.
6. The semicontinuous and continuous pumps are

similar in nature. The degree of separation is not a function of the mode of operation.

7. The primary assumptions of the equilibrium theory are valid since the agreement between theory and experiment is relatively good.

NOMENCLATURE

b = dimensionless equilibrium parameter defined by equation (28).

C_1 = $V_T/(Q\frac{\pi}{\omega})$, ratio of dead volume of the top reservoir to displacement, dimensionless.

C_2 = $V_B/(Q\frac{\pi}{\omega})$, ratio of dead volume of the bottom reservoir to displacement, dimensionless.

F = volumetric flow rate/reservoir displacement rate entering or leaving the column, dimensionless.

h = column height, cm.

L = penetration distance defined by equations (3), (4), and (5).

M = $x/\bar{y}$ $\quad\quad$ $\bar{M} = x/y$

m = equilibrium constant parameter defined by equation (17), dimensionless.

N = final cycle of pump operation.

n = cycle number

Q = reservoir displacement, cc/sec.

T = temperature, ^{o}C.

v = interstial velocity, cm/sec.

V_T = top reservoir dead volume, cc.

V_B = bottom reservoir dead volume, cc.

x = concentration of solute in the solid phase, g mole/g.

y = concentration of solute in the liquid phase, g mole/cc.

$\bar{y}$ = concentration of solute in the liquid phase, g mole/g.

$\langle\ \rangle$ = average value.

Greek letters:

α = slope of line on plot of $\ln(\langle y_{BP2}\rangle_n/y_0)$ vs n.

ρ_s = density of the solid, g/cc.

ρ_f = density of the fluid, g/cc

ϵ = void fraction in packing, dimensionless.

ϕ = product volumetric flow rate/reservoir displacement rate, dimensionless.

$\frac{\pi}{\omega}$ = duration of half cycle, time units.

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.

APPENDICES

Appendix A

Theory

THEORY (References 1,2,3)

Expression for L_1, L_2, and b have been developed from the so called internal equations of the parametric pump. Assuming no axial diffusion, the equation of transport, obtained from a material balance around a differential volume of the liquid and solid phase in the column, is:

$$\cancel{\epsilon D\frac{\partial^2 y}{\partial z^2}}_{\;0} + \epsilon v\frac{\partial y}{\partial z} + \epsilon\frac{\partial y}{\partial t} + (1-\epsilon)\rho_s\frac{\partial x}{\partial t} = 0 \qquad (15)$$

net flow by axial diffusion + net flow by bulk movement + rate of accumulation on liq. + rate of accumulation on solid = 0

We can eliminate x in equation (15) if an instantaneous linear equilibrium relationship is assumed, i.e. $x = M(T)\bar{y}$ or $x = M(T)y/\rho_f = \bar{M}(T)y$. Differentiation yields

$$\frac{dx}{dt} = y\frac{\partial \bar{M}(T)}{\partial t} + \bar{M}(T)\frac{\partial y}{\partial t} \qquad (16)$$

and substituting equation (16) into (15) we find

$$\epsilon v\frac{\partial y}{\partial z} + \epsilon\frac{\partial y}{\partial t} + (1-\epsilon)\rho_s\left(\bar{M}(T)\frac{\partial y}{\partial t} + y\,\frac{\partial \bar{M}(T)}{\partial T}\,\frac{\partial T}{\partial t}\right) = 0$$

Rearranging gives

$$\left(1 + \frac{(1-\epsilon)\rho_s\bar{M}(T)}{\epsilon}\right)\frac{\partial y}{\partial t} + v\,\frac{\partial y}{\partial z} + \frac{(1-\epsilon)\rho_s}{\epsilon}\frac{\partial \bar{M}(T)}{\partial T}\frac{\partial T}{\partial t} = 0$$

By assuming constant fluid and solid densities and letting

$$m = \frac{(1-\epsilon)\rho_s \overline{M}(T)}{\epsilon} \tag{17}$$

we have

$$(1+m)\frac{\partial y}{\partial t} + v\frac{\partial y}{\partial z} = -\frac{\partial m}{\partial T}\frac{\partial T}{\partial t}y \tag{18}$$

This hyperbolic partial differential equation can be solved by the method of Lagrange-Charpit. Within the method of solution lies the mathematical definitions of L_1, L_2, and b. Taking the right hand terms of equation (18), we let

$$-\frac{\partial m}{\partial T}\frac{\partial T}{\partial t}y = \left(\frac{\partial y}{\partial s}\right)_\theta \tag{19}$$

where

$$y = y(z,t) = y(s,\theta) \quad z = z(s,\theta) \quad t = t(s,\theta)$$

Obviously

$$\left(\frac{\partial y}{\partial s}\right)_\theta = \left(\frac{\partial t}{\partial s}\right)_\theta \frac{\partial y}{\partial t} + \left(\frac{\partial z}{\partial s}\right)_\theta \frac{\partial y}{\partial z} \tag{20}$$

and comparing equation (20) with (19) while holding constant we see

$$\frac{dt}{ds} = 1 + m \quad \text{and} \quad \frac{dz}{ds} = v$$

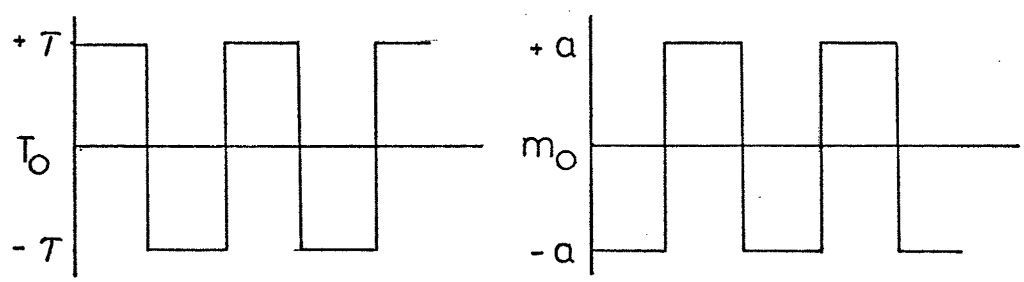
then

$$\frac{dz}{v} = \frac{dt}{1+m} = \frac{-dy}{\frac{\partial m}{\partial T}\frac{\partial T}{\partial t}y} \tag{21}$$

Rearrangement of the first equality in equation (21) yields

$$\frac{dz}{dt} = \frac{v}{1+m} \tag{22}$$

Assuming instantaneous temperature changes and instantaneous equilibrium between adsorbate in the liquid and solid phases, it is evident both T(t) and m(t) are periodic square waves. Graphically

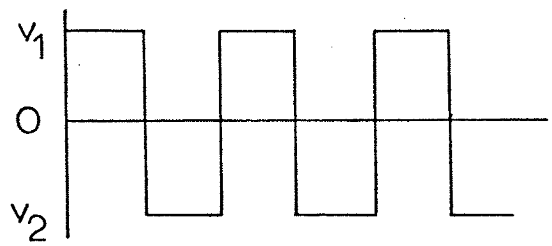


and mathematically

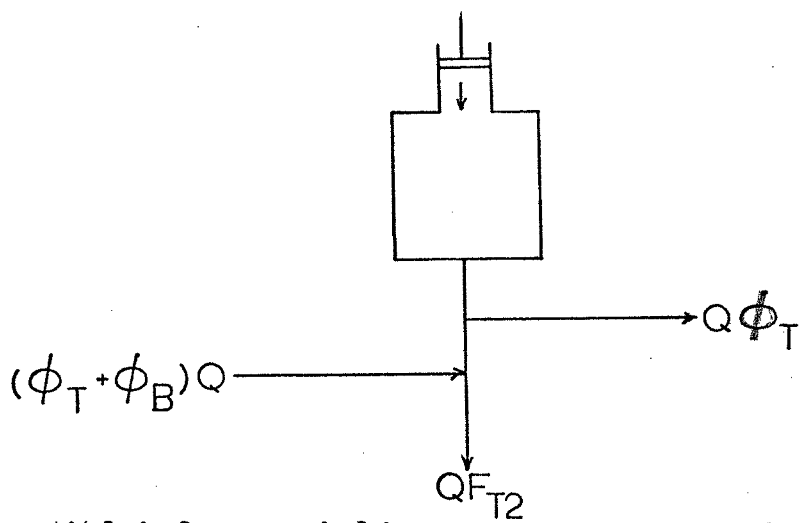
$$T = T_o + \mathcal{T}\,Sq(\omega t) \qquad\qquad m = m_o - a\,Sq(\omega t)$$

In other words, $m = m_o - a$ for hot upflow and $m = m_o + a$ for cold downflow.

Furthermore, the velocity of the concentration front within the column, dz/dt, is also a periodic square wave, represented by



Expressions for v_1 and v_2 are found by material balances. Consider a semicontinuous pump's top reservoir, feed, and product lines on the cold downflow half cycle.

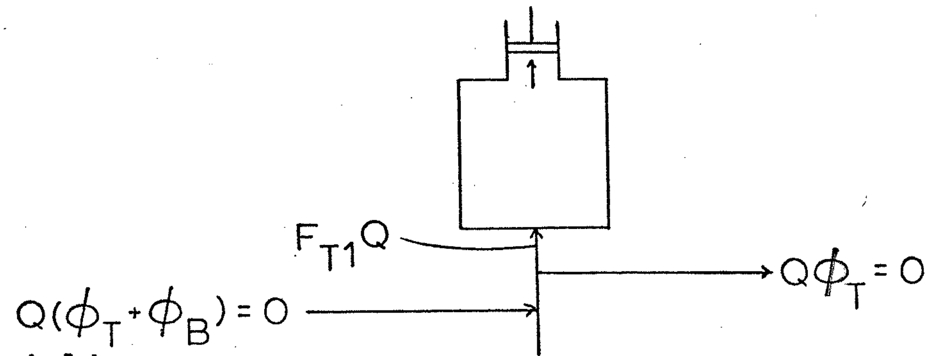


A material balance yields

$$Q + Q(\phi_T + \phi_B) = Q\phi_T + QF_{T2}$$

$$F_{T2} = 1 + \phi_B$$

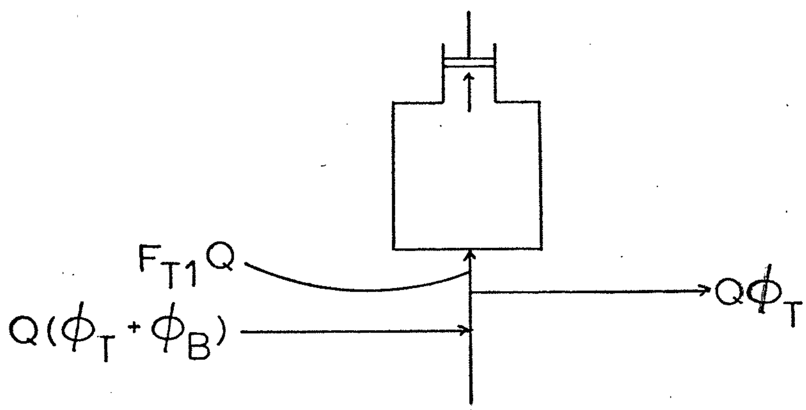
Since Q cc/sec = (v_o cm/sec)(A cm^2); the downflow velocity is expressed as $v_2 = v_o(1+\phi_B)$. Similarly, a material balance around the top reservoir of a semicontinuous pump in a hot upflow half cycle,



yields

$$Q = QF_{T1}$$

It follows that $v_1 = v_o$. For a continuous pump in a hot upflow half cycle we find



$$F_{T1}Q + Q(\phi_T+\phi_B) = Q + Q\phi_T$$

$$F_{T1} = 1-\phi_B$$

and therefore $v_1 = v_o(1-\phi_B)$. It is obvious that semicontinuous and continuous pumps have the same downflow velocity expression.

For the semicontinuous pump, substitution of v_1 and v_2 into equation (22) yields

$$\frac{dz}{dt} = \frac{v_o(1+\phi_B)}{1+m_o+a} = \frac{v_o(1+\phi_B)}{(1+m_o)(1+b)} \tag{23}$$

for downflow, and

$$\frac{dz}{dt} = \frac{v_o}{1+m_o-a} = \frac{v_o}{(1+m_o)(1-b)} \tag{24}$$

for upflow, where

$$b = \frac{a}{1+m_o} \tag{25}$$

Knowing that

$$m_o = \frac{m_1+m_2}{2} \tag{26}$$

and

$$a = m_2 - m_o = m_o - m_1 \tag{27}$$

we find from equation (25) that

$$b = \frac{\frac{1}{2}(m_2-m_1)}{1+\frac{1}{2}(m_1+m_2)} \tag{28}$$

Equations (23) and (24) represent the slope of the y constant characteristic lines on a z vs t plot (see Figure 11). These two equations can be integrated to yield expression for L_1 and L_2 (see equations (3), (4), and (5)).

Rearranging the second equality in equation (21), we obtain

$$-\frac{dy}{y} = \frac{\frac{\partial m}{\partial T}\frac{\partial T}{\partial t}\,dt}{1+m}$$

which upon integration yields

$$\ln y = -\ln(1+m) + K = -\ln\left(1+m_o - aSq(\omega t)\right) + K$$

It follows that

$$\ln y = -\ln\left(1-bSq(\omega t)\right) + K$$

and

$$\frac{d\ln y}{dt} = \frac{d\ln\left(1-bSq(\omega t)\right)}{dt} \qquad (29)$$

Furthermore

$$y\left(1-bSq(\omega t)\right) = \bar{K} \qquad (30)$$

which implies y constant characteristics. Equation (29) represents the change in y along the characteristic directions.

Pump performance relations are derived by combining equation (30) with certain external relations obtained by material balances. See Reference (1) for the method to and solutions of pump performance.

Calculation of b from equilibrium data (Ref 2)

On a linear x-y diagram, $x = \overline{M}(T)y$, the area beneath the line can be expressed as an integral or the area of a triangle, i.e.

$$\int_0^y x_1 \, dy_1 = \frac{1}{2}xy = \frac{1}{2}\overline{M}(T)y^2$$

It follows that

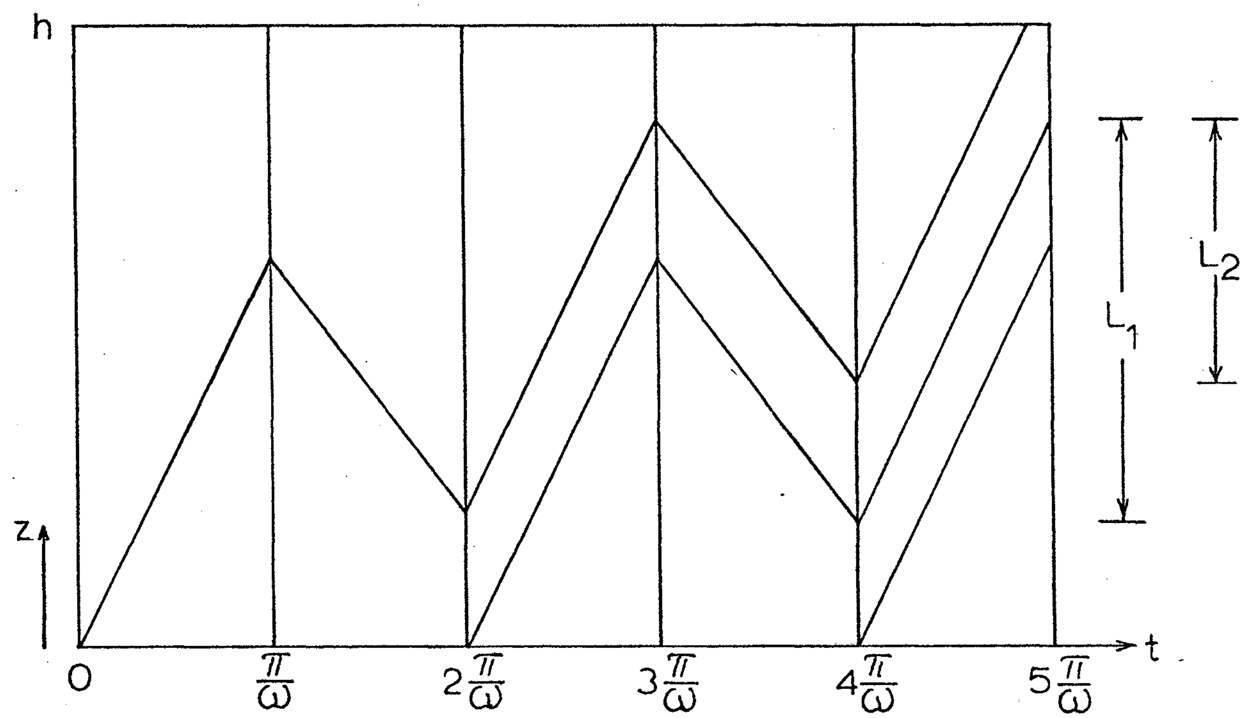
$$\overline{M}(T) = \frac{2}{y^2}\int_0^y x_1 dy_1$$

where x_1 and y_1 are observed values.

Equation (17) can now be expressed as

$$m_i = \left[\frac{(1+\epsilon)\rho_s}{\epsilon}\right]\frac{2}{y^2}\int_0^y x_1 dy_1 \qquad (31)$$

It is now possible to obtain m_1 and m_2 at T_1 and T_2 respectively. b can be calculated from equation (28).



z-t Characteristics For Region 1

Figure 12

Appendix B

Sample Analysis

SAMPLE ANALYSIS

Beer's law states: for absorbing solutes, the decrease in the radiant power of a beam of parallel monochromatic radiation with b, the path length, is proportional to I, the intensity, and the concentration, y, of the solution. Mathematically this is:

$$\frac{dI}{db} = -aIy$$

Separating the variables and integration between the limits of Io to I and 0 to b yields:

$$\ln\frac{I}{I_o} = -aby$$

$$A = \ln\left(\frac{1}{T}\right) = \ln\frac{I_o}{I} = aby$$

where

A = absorbance

T = transmittance

I = intensity or radiant power

Io = intensity of incident light

a = absortivity, a constant

b = path length or sample cell's thickness

y = concentration

Pure n-heptane does not absorb over the range of 150mu to 300mu while toluene does and has a maxium peak at 262mu. The concentration of the samples can be calculated using Beer's Law.

When necessary, the samples were diluted with n-heptane to reduce the height of the absorption peak so that the concentration would fall within the scale of the instrument. This introduced a dilution factor into the calculation for the unknown concentration. For example, 1 ml of sample diluted with 5 ml of n-heptane gave a dilution factor of 6. If 1 ml of this solution was diluted with another 5 ml of solvent, the dilution factor would be 36. Since the concentration and absorption of the feed are known (y_0 and A_0 at 262mu), the concentration of sample n can be calculated.

$$y_n = y_o \left[\frac{A_n (\text{dil. fac.})_n}{A_o (\text{dil. fac.})_o} \right] \tag{32}$$

The tabulated experimental analysis results follow.

Data Sheet

Analysis Run 1

Bottom Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
Feed	396	34.0	-----
5	216	23.0	0.368
7	36	40.5	0.108
9	6	56.0	0.0249
11	6	18.0	0.00802
12	1	46.0	0.00341
14	1	29.0	0.00215
15	1	0*	-----
16	1	0*	-----

Top Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
9	576	57.5	1.97
12	576	66.0	2.26
14	576	73.0	2.49
15	396	79.0	2.32
16	306	80.0	2.35

* 0 indicates that the sample was of higher purity than the reference which was Spectro-quality n-heptane (MC&B).

Data Sheet

Analysis Run 2

Bottom Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
Feed	216	78.1	-----
4	396	26.8	0.629
5	216	32.5	0.416
6	36	100	0.2134
8	36	22.3	0.0476
10	6	32.0	0.014
12	6	20.0	0.00711
13	1	24.5	0.00145
15	1	<0	-----
16	1	<0	-----

Top Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
7	1296	18.5	1.42
8	1296	19.2	1.48
10	1296	27.9	2.15
12	1296	28.0	2.15
14	1296	33.1	2.54
16	1296	32.8	2.52

Data Sheet

Analysis Run 3

Bottom
Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
Feed	216	74.0	-----
4	216	27.5	0.372
5	216	20.0	0.270
6	216	6.0	0.0812
7	36	46.5	0.105
8	36	19.0	0.0428
10	6	37.0	0.0139
11	6	12.0	0.00450
12	1	22.0	0.00138
14	1	62.0	0.00387
15	36	78.0	0.176
16	216	9.0	0.122
17	216	15.7	0.212

Top
Product

No top product was taken during this run.

Data Sheet

Analysis Run 4

Bottom Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
Feed	216	95.0	-----
5	216	39.5	0.416
7	36	88.0	0.154
8	36	52.0	0.0912
9	36	86.0	0.151
10	36	102.	0.179
11	216	15.0	0.144
12	36	88.0	0.154
13	36	59.0	0.104
14	36	79.0	0.139
16	36	61.0	0.107

Top Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
8	1331	29.0	1.88
11	1331	30.0	1.95
14	1331	36.0	2.34
16	1331	34.0	2.21

Data Sheet

Analysis Run 5

Bottom
Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
Feed	216	82.0	-----
4	216	45.0	0.549
5	216	49.0	0.598
6	216	11.0	0.134
7	216	7.0	0.0854
8	216	16.0	0.0195
9	36	22.0	0.0447
10	6	61.0	0.0207
11	6	22.0	0.00745
12	1	83.0	0.00469
13	6	3.0	0.00226
14	6	22.0	0.00745
15	1	76.0	0.00430
16	1	34.0	0.00192

Top
Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
5	1296	13.0	1.61
7	2197	11.5	1.43
10	2197	17.0	2.11
12	2197	17.0	2.11

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
14	2197	19.0	2.36
15	2197	18.0	2.23
16	1331	18.0	2.55

Data Sheet

Analysis Run 6

Bottom Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
Feed	121	67.0	-----
5	121	20.0	0.296
6	36	27.0	0.119
7	6	80.5	0.0590
9	2	66.5	0.0163
10	1	64.0	0.00784
11	1	33.0	0.00400
13	1	5.0	0.000610
14	1	<0	-----
16	1	<0	-----

Top Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
8	1296	8.5	1.35
11	1296	15.5	2.46
14	1296	18.0	2.86
17	1296	23.0	3.65

Data Sheet

Analysis Run 7

Bottom Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
Feed	121	70.0	-----
5	36	48.5	0.206
6	36	25.0	0.106
8	36	11.5	0.0489
10	6	25.5	0.0181
11	1	97.0	0.0115
13	1	26.5	0.00313
15*	1	5.0	0.000590
17*	1	1.0	0.000118

Top Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
6	121	loo	1.43
8	1331	13.5	2.12
11	1331	17.5	2.75
14	1331	22.0	3.46
17	1331	24.5	3.85

*Chromo-qualiey n-heptane used as the reference.

Data Sheet

Analysis Run 8

Bottom Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
Feed	216	80.0	-----
4	126	75.0	0.547
6	231	17.0	0.227
7	231	9.0	0.120
9	36	15.0	0.0313
11	6	28.0	0.00972
13	1	65.0	0.00376
15	1	27.0	0.00156
17	21	6.0	0.00729
18	36	17.0	0.0354

Top Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
6	1331	16.0	1.23
8	1331	24.5	1.89
11	1331	30.0	2.31
14	1331	32.5	2.50
17	1331	34.0	2.62

Data Sheet

Analysis Run 9

Bottom Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
Feed	121	75.0	-----
1	121	61.0	0.813
3	121	33.0	0.440
4	121	27.0	0.360
6	121	17.0	0.227
8	121	10.0	0.133
10	121	6.5	0.0867
12	121	6.5	0.0867
14	36	24.0	0.0952
16	36	41.0	0.0163

Top Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
7	1331	10.0	1.47
10	1331	13.5	1.98
13	1331	15.0	2.20
15	1331	16.0	2.35
16	1331	16.5	2.42

Data Sheet

Analysis Run 10A

Bottom Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
Feed	121	75.0	-----
3	121	32.0	0.427
4	36	81.5	0.323
6	36	41.0	0.163
7	36	29.0	0.115
8	36	24.0	0.0952
9	36	23.5	0.932
11	36	33.5	0.133
13	36	20.0	0.0793
15	6	69.0	0.0456
16	6	55.0	0.0377

Top Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
6	396	24.0	1.05
8	726	18.0	1.44
10	726	16.0	1.28
11	1331	8.0	1.17
14	1331	10.0	1.47
15	1331	11.0	1.61

Data Sheet

Analysis Run 10B

Bottom Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
Feed	121	77.3	-----
3	121	36.5	0.473
4	36	99.0	0.381
6	36	57.5	0.222
8	36	34.0	0.131
9	11	88.5	0.104
11	6	75.5	0.0485
13	6	43.0	0.0276
15	6	21.5	0.0138
16	6	16.5	0.0106

Top Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
6	216	50.5	1.17
8	216	59.0	1.36
10	216	65.3	1.51
13	396	41.0	1.74
15	726	22.0	1.71
16	726	23.5	1.83

Data Sheet

Analysis Run 11

Bottom
Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
Feed	121	69.0	-----
3	121	29.5	0.428
5	36	61.0	0.263
7	21	68.0	0.171
9	11	78.5	0.103
11	6	79.5	0.0571
13	6	48.0	0.0345
15	6	27.5	0.0198
16	6	22.0	0.0158

Top
Product

Cycle	Dilution Factor	Absorbance A	$\frac{y_{BP2}}{y_0}$
6	216	49.5	1.28
8	216	55.0	1.42
10	216	58.0	1.50
13	396	35.0	1.66
15	726	19.5	1.70
16	726	19.5	1.70

Data Sheet

Analysis Runs 12-13-14

This data was obtained from other sources, see page 81.

Appendix C

Flow Data

Data Sheet

Run 1 Semicontinuous

Cycle	Feed cc Left	Feed cc Right	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
Initial	46	45	44	4	---	---
1	--	--	7	44	---	---
	39	38	45	4	2.3	7.4
2	--	--	7	44	---	---
	32	31	44	4	8.6	6.5
3	--	--	6	44	---	---
	24	23	42	4	8.4	6.6
4	--	--	4	44	---	---
	16	15	44	4	3.5	6.5
Feed	50		44	4	---	---
5	--		8	44	---	---
	35		44	4	11.0	6.8
6	--		7	44	---	---
	19		44	7	9.4	6.5
7	--		7	44	---	---
	3		44	7	9.2	6.7
Feed	50		44	4	---	---
8	--		5	44	---	---
	35		41	4	1.2	6.6
9	--		4	44	---	---
	20		44	4	8.2	6.7

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
10	--	7	44	---	---
	5	43	4	1.8	6.3
Feed	50	43	4	---	---
11	--	7	44	---	---
	35	44	4	13.2	6.5
12	--	5	44	---	---
	19	44	4	5.0	6.5
13	--	6	44	---	---
	---	45	4	---	---
Feed	50	45	4	---	---
14	--	5	44	---	---
	35	44	4	---	6.3
15	--	7.5	44	---	---
	20	44	4	14.8	6.6
16	--	6	44	---	---
	4	44	4	4.1	6.6

Data Sheet

Run 2 Semicontinuous

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
Initial	50	45	5	---	---
1	--	10	44	---	---
	37.5	45	5	9.0	---
2	--	7	46	---	---
	20	45	5	7.5	2.5
Feed	28	45	5	---	---
3	--	4	42	---	---
	13	45	4	7.1	1.8
Feed	51	45	4	---	---
4	--	4	44	---	---
	31	45	5	7.9	9.5
5	--	5	46	---	---
	14	45	5	8.0	1.0
Feed	41.5	45	5	---	---
6	--	4	44	---	---
	26.5	44	4	7.0	---
Feed	45	44	4	---	---
7	--	5	45	---	---
	28	45	5	8.0	10.0
8	--	5	45	---	---
	12	45	5	7.5	2.0

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
Feed	41	45	5	---	---
9	--	7	46	---	---
	23	45	5	7.8	11
10	--	7	46	---	---
	8	45	5	8.1	---
Feed	40	45	5	---	---
11	--	7	43	---	---
	20	44	4	8.15	7.8
Feed	46	44	4	---	---
12	--	5	46	---	---
	28	45	4	8.0	---
13	--	5	46	---	---
	12.5	45	4	7.7	10.0
Feed	45	45	4	---	---
14	--	5	45	---	---
	24	45	5	8.0	7.2
Feed	46	45	5	---	---
15	--	6	45	---	---
	32.5	45	5	8.8	---
16	--	7	46	---	---
	--	45	5	7.8	9.0

Data Sheet

Run 3 Semicontinuous

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
Initial	40	45	5	---	---
1	--	5	46	---	---
	26	47	5	12.4	---
2	--	7	45	---	---
	11	47	5	13.4	---
Feed	45	47	5	---	---
3	--	7	46	---	---
	33	45	5	9.0	---
4	--	6	46	---	---
	20	46	5	15	---
5	--	6	45	---	---
	5	45	5	11.0	
Feed	45	45	5	---	---
6	--	6	44	---	---
	30	44	5	12.6	---
7	--	5	45	---	---
	17	43	5	13.8	---
Feed	45	43	5	---	---
8	--	5	41	---	---
	33	41	5	9.4	---
9	--	4	44	---	---
	18	44	4	13.8	---

Cycle	Feed cc	Reservoir cc Bottom	Top	Product cc Bottom	Top
Feed	40	44	4	---	---
10	--	4	43	---	---
	25	45	5	10.2	---
11	--	10	45	---	---
	10	45	4	16.5	---
Feed	45	45	4	---	---
12	--	6	46	---	---
	29	47	5	11.8	---
13	--	7	45	---	---
	13	48	5	13.4	---
Feed	45	48	5	---	---
14	--	7	45	---	---
	29	45	5	14.6	---
15	--	7	46	---	---
	12	46	5	16.0	---
Feed	25	46	5	---	---
16	--	5	45	---	---
	10	45	5	15.4	---

Data Sheet

Run 4 Semicontinuous

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
Initial	40	45	4	---	---
1	--	6	45	---	---
	25	45	5	11.7	2.8
Feed	45	45	5	---	---
2	--	5	47	---	---
	23	45	6	15.8	3.6
Feed	47	45	6	---	---
3	--	6	46	---	---
	25	45	5	15.8	4.2
4	--	5	46	---	---
	4	44	7	13.6	3.6
Feed	45	44	7	---	---
5	--	5	45	---	---
	25	44	5	13.8	4.0
6	--	5	45	---	---
	5	45	5	11.8	3.9
Feed	46	45	5	---	---
7	--	5	45	---	---
	26	45	5	13.0	2.4
8	--	6	46	---	---
	7	45	5	12.8	3.8

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
Feed	47	45	5	---	---
9	--	5	46	---	---
	27	45	5	11.0	2.6
10	--	5	46	---	---
	7	45	5	13	13.2
Feed	45	45	5	---	---
11	--	5	45	---	---
	24	44	5	14.6	3.7
Feed	45	44	5	---	---
12	--	5	45	---	---
	26	45	5	9.8	4.3
13	--	6	46	---	---
	7	45	5	13.8	3.6
Feed	45	45	5	---	---
14	--	6	46	---	---
	25	45	5	11.8	3.8
15	--	6	46	---	---
	5	45	5	16.5	3.8
Feed	30	45	5	---	---
16	--	5	45	---	---
	10	44	5	14.2	3.5

Data Sheet

Run 5 Semicontinuous

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
Initial	45	45	5	---	---
1	--	6	44	---	---
	28	45	5	10.3	1.3
2	--	7	43	---	---
	12	46	5	11.4	3.1
Feed	46	46	5	---	---
3	--	6	45	---	---
	26	45	5	10.2	2.2
4	--	25	45	---	---
	10	45	6	13.0	2.7
Feed	45	45	6	---	---
5	--	8	45	---	---
	31	45	5	14.2	2.2
6	--	6	44	---	---
	16	43	5	13.4	2.0
Feed	45	43	5	---	---
7	--	5	44	---	---
	31	39	5	13.6	2.2
8	--	4	41	---	---
	12	41	4	10.0	1.0
Feed	50	41	4	---	---

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
9	--	5	43	---	---
	36	40	5	10.0	2.1
10	--	5	45	---	---
	21	42	5	12.2	1.7
11	--	4	42	---	---
	6	42	4	6.6	2.1
Feed	51	42	4	---	---
12	--	4	43	---	---
	35	44	4	13.6	2.4
13	--	4	43	---	---
	20	43	4	8.6	1.9
14	--	4	44	---	---
	4	43	4	12.6	2.0
Feed	42	43	4	---	---
15	--	4	44	---	---
	26	44	4	8.2	2.1
16	--	4	44	---	---
	10	44	4	14.6	2.3

Data Sheet

Run 6 Semicontinuous

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
Initial	40	44	4	---	---
1	--	5	44	---	---
	25	44	5	9.0	2.1
2	--	6	45	---	---
	12	45	5	10.8	2.0
Feed	45	45	5	---	---
3	--	6	44	---	---
	30	45	5	11.4	2.4
4	--	6	45	---	---
	15	45	5	12.6	2.5
Feed	46	45	5	---	---
5	--	6	44	---	---
	30	45	4	11.4	2.0
6	--	7	45	---	---
	14	45	5	10.6	2.7
Feed	43	45	5	---	---
7	--	6	45	---	---
	28	45	4	11.0	2.1
8	--	4	45	---	---
	13	44	4	10.6	2.1
Feed	50	44	4	---	---

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
9	--	4	44	---	---
	35	44	4	7.0	1.9
10	--	6	45	---	---
	19	45	4	11.2	3.0
11	--	5	46	---	---
	4	45	5	12.1	2.0
Feed	50	45	5	---	---
12	--	5	45	---	---
	34	44	4	9.8	1.9
13	--	4	44	---	---
	19	45	5	11.0	2.0
14	--	7	44	---	---
	4	45	4	10.6	2.0
Feed	43	45	4	---	---
15	--	5	45	---	---
	27	44	4	9.6	2.1
16	--	5	45	---	---
	12	45	4	12.7	2.2

Data Sheet

Run 7 Semicontinuous

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
Initial	45	45	5	---	---
1	--	6	45	---	---
	30	45	5	2.0	9.4
2	--	7	45	---	---
	15	46	5	2.4	9.8
Feed	48	46	5	---	---
3	--	6	46	---	---
	32	45	5	2.2	11.4
4	--	6	45	---	---
	17	46	5	2.2	10.6
Feed	45	46	5	---	---
5	--	6	46	---	---
	30	46	5	1.7	10.8
6	--	7	45	---	---
	15	45	5	2.2	11.4
Feed	50	45	5	---	---
7	--	7	45	---	---
	34	46	5	2.4	11.4
8	--	6	46	---	---
	18	47	5	2.3	11.4
9	--	8	46	---	---
	2	46	6	2.3	13.0

Cycle	Feed cc	Reservoir cc Bottom	Top	Product cc Bottom	Top
Feed	50	46	6	---	---
10	--	5	46	---	---
	34	45	5	2.2	11.3
11	--	5	46	---	---
	18	45	5	1.8	11.6
Feed	52	45	5	---	---
12	--	4	45	---	---
	36	44	5	1.7	9.0
13	--	5	45	---	---
	20	45	5	2.2	11.8
14	--	5	46	---	---
	4	45	5	2.3	13.4
Feed	40	45	5	---	---
15	--	5	46	---	---
	24	44	5	2.0	10.4
16	--	6	46	---	---
	8	46	5	2.2	11.6

Data Sheet

Run 8 Semicontinuous

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
Initial	42	44	4	---	---
1	--	5	45	---	---
	26	45	5	8.2	1.4
2	--	5	45	---	---
	10	45	5	8.4	1.2
Feed	45	45	5	---	---
3	--	5	46	---	---
	29	45	5	9.2	1.8
4	--	9	45	---	---
	14	45	5	13.4	2.3
Feed	45	45	5	---	---
5	--	6	46	---	---
	30	46	5	11.4	2.3
6	--	7	46	---	---
	14	46	5	12.6	1.8
Feed	44	46	5	---	---
7	--	5	45	---	---
	28	45	5	9.8	2.0
8	--	5	45	---	---
	12	45	5	11.0	1.8
Feed	45	45	5	---	---

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
9	--	6	46	---	---
	29	46	5	9.0	3.5
10	--	6	46	---	---
	13	46	5	11.2	1.8
Feed	45	46	5	---	---
11	--	5	46	---	---
	30	45	5	10.2	2.0
12	--	6	47	---	---
	14	46	5	11.0	2.0
Feed	45	46	5	---	---
13	--	7	45	---	---
	29	47	5	10.6	2.0
14	--	9	46	---	---
	13	47	5	11.6	2.0
Feed	44	47	5	---	---
15	--	7	45	---	---
	29	46	5	11.2	1.8
16	--	8	46	---	---
	13	47	6	10.4	2.2

Data Sheet

Run 9 Semicontinuous

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
Initial	45	44	4	---	---
1	--	5	45	---	---
	27	45	5	13.2	2.0
2	--	6	45	---	---
	11	44	6	13.2	2.1
Feed	45	44	6	---	---
3	--	6	45	---	---
	29	45	5	12.8	2.0
4	--	6	45	---	---
	13	45	5	13.6	2.0
Feed	50	45	5	---	---
5	--	6	45	---	---
	34	45	5	13.6	2.0
6	--	6	45	---	---
	18	45	5	13.3	2.1
Feed	45	45	5	---	---
7	--	5	45	---	---
	28	44	5	13.1	2.1
8	--	5	45	---	---
	12	44	6	13.2	2.0
Feed	45	44	6	---	---

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
9	--	4	45	---	---
	29	43	6	13.6	2.1
10	--	4	44	---	---
	13	43	6	13.4	2.0
Feed	42	43	6	---	---
11	--	4	45	---	---
	27	44	5	12.6	2.1
12	--	5	45	---	---
	12	44	5	13.4	1.6
Feed	45	44	5	---	---
13	--	5	45	---	---
	30	44	5	11.4	2.0
14	--	5	45	---	---
	15	44	5	13.0	2.0
Feed	43	44	5	---	---
15	--	4	44	---	---
	28	44	5	12.4	2.0
16	--	5	44	---	---
	12	44	5	13.8	2.0

Data Sheet

Run 10A Semicontinuous

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
Initial	45	45	5	---	---
1	--	6	45	---	---
	30	44	5	7.3	8.2
2	--	5	45	---	---
	15	45	5	6.0	7.9
Feed	45	45	5	---	---
3	--	5	46	---	---
	29	45	5	7.9	7.9
4	--	5	45	---	---
	13	45	5	6.7	7.8
Feed	32	45	5	---	---
5	--	5	45	---	---
	26	45	5	5.9	2.8
6	--	5	44	---	---
	10	44	5	7.5	7.2
Feed	46	44	5	---	---
7	--	5	44	---	---
	30	44	5	7.5	8.0
8	--	5	44	---	---
	12.5	44	5	7.6	7.9
Feed	43	44	5	---	---

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
9	--	5	45	---	---
	28	44	5	8.1	8.0
10	--	4	43	---	---
	12	43	4	7.4	8.0
Feed	45	43	4	---	---
11	--	4	44	---	---
	28	45	5	4.8	8.1
12	--	5	45	---	---
	12	45	5	6.8	8.0
Feed	46	45	5	---	---
13	--	5	46	---	---
	30	45	5	7.4	8.0
14	--	5	46	---	---
	14	45	5	7.6	7.9
Feed	45	45	5	---	---
15	--	6	46	---	---
	29	45	5	7.8	7.9
16	--	5	45	---	---
	12.5	45	5	7.0	8.1

Data Sheet

Run 10B Semicontinuous

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
Initial	45	45	5	---	---
1	--	5	45	---	---
	30	45	5	6.4	8.0
2	--	6	46	---	---
	14	45	5	7.6	8.1
Feed	45	45	5	---	---
3	--	6	46	---	---
	30	46	5	7.0	8.1
4	--	6	46	---	---
	14	46	5	7.8	8.0
Feed	45	46	5	---	---
5	--	6	46	---	---
	30	45	5	7.6	8.0
6	--	6	46	---	---
	14	45	5	8.1	8.0
Feed	45	45	5	---	---
7	--	4	44	---	---
	30	43	4	5.2	5.3
8	--	4	44	---	---
	14	44	5	5.2	7.8
Feed	45	44	5	---	---

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
9	--	5	44	---	---
	30	44	4	6.4	7.7
10	--	5	45	---	---
	14	45	5	6.8	8.0
Feed	45	45	5	---	---
11	--	5	45	---	---
	30	45	5	7.6	7.4
12	--	5	46	---	---
	14	45	5	8.0	8.0
Feed	45	45	5	---	---
13	--	5	46	---	---
	30	45	5	8.2	7.7
14	--	5	45	---	---
	14	45	5	7.5	8.1
Feed	45	45	5	---	---
15	--	5	45	---	---
	30	45	5	7.8	8.1
16	--	5	45	---	---
	14	45	5	8.5	8.0

Data Sheet

Run 11 Semicontinuous

Cycle	Feed cc	Reservoir cc Bottom	Reservoir cc Top	Product cc Bottom	Product cc Top
Initial	43	45	5	---	---
1	--	5	45	---	---
	23	45	5	8.0	8.0
2	--	5	45	---	---
	3	45	5	7.0	9.8
Feed	46	45	5	---	---
3	--	5	45	---	---
	26	42	4	10.2	9.0
4	--	4	43	---	---
	7	42	4	8.0	9.0
Feed	46	42	4	---	---
5	--	4	44	---	---
	27	44	4	7.8	9.3
6	--	5	45	---	---
	6.5	44	5	8.8	10.0
Feed	46	44	5	---	---
7	--	5	45	---	---
	26	45	5	8.8	10.0
8	--	5	45	---	---
	6	45	4	9.0	9.5
Feed	46	45	4	---	---

Cycle	Feed cc	Reservoir cc Bottom	Top	Product cc Bottom	Top
9	--	5	45	---	---
	26	45	5	8.6	10.0
10	--	5	45	---	---
	6	45	5	8.5	10.0
Feed	46	45	5	---	---
11	--	5	45	---	---
	26	45	5	9.0	9.5
12	--	5	46	---	---
	6	45	5	10.0	9.5
Feed	46	45	5	---	---
13	--	5	45	---	---
	27	45	5	9.0	9.3
14	--	5	45	---	---
	7	45	5	9.4	9.5
Feed	46	45	5	---	---
15	--	5	45	---	---
	26	45	5	9.1	9.3
16	--	5	45	---	---
	6	46	5	10.2	9.0

Data Sheet

Runs 12-13-14

These runs were obtained from other sources.

Run 12 Continuous--Executed by W. Lin on 6/7/73.

Run 13 Continuous--Taken from a thesis by Rak, L. *An Experimental Study of Continuous Parametric Pumping*. Newark College of Engineering (1972).

Run 14 Semicontinuous--Executed by J. Gudzer.

Appendix D

Calculations

CALCULATIONS

The method to calculate the theoretical results is given below.

1. A least square analysis was performed on the bottom product sample analysis data (see appendix B for sample analysis calculations). This computation yielded a value of α.
2. C_1 and C_2 were calculated from the flow data given in appendix C.

$$C_1 = \frac{\sum_{n=1}^{N}\left(V_T/Q\frac{\pi}{\omega}\right)_n}{N} \quad \text{and} \quad C_2 = \frac{\sum_{n=1}^{N}\left(V_B/Q\frac{\pi}{\omega}\right)_n}{N}$$

where N is the final cycle of pump operation.

3. The experimental value of b could now be found using equation (14).
4. ϕ_B was obtained from the experimental flow data.

$$\phi_B = \frac{\sum_{n=1}^{N}\left(V_{BP}/Q\frac{\pi}{\omega}\right)_n}{N}$$

5. L_2 was calculated using equation (3) for the semi-continuous pump.

$$L_2 = \frac{V_0(1+\phi_B)\frac{\pi}{\omega}}{(1+b)(1+\frac{1}{2}(m_1+m_2))}$$

where

$$m_o = \tfrac{1}{2}(m_1 + m_2) = 1.88$$

$$\epsilon = 0.38$$

$$v_o = Q/(\pi r^2 \epsilon)$$

6. The variables calculated above along with $\phi_T + \phi_B$ and h serve as data for computer programs written by Dr. H.T. Chen. These programs solve for the transient concentration ratio. They have the flexibility to solve for all possible combinations of the parameters read in, provided the number of each parameter to be considered is specified on the data cards. A listing of the programs can be found in a thesis by E.H. Reiss, <u>Separations Via Semicontinuous Parametric Pumping</u>, Newark College of Engineering, 1972.

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