Separations via Continuous Parametric Pumping

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A continuous pump in which the feed and product streams flow steadily both in upflow and downflow is experimentally investigated in the model system toluene-n-heptane on silica gel adsorbent. The experimental data compare reasonably well with analytical results based on an equilibrium theory. The operating conditions necessary to achieve high separation factors are shown to be dependent on the relative magnitudes of penetration distances and the height of the column.

Wilhelm and Sweed (*1*) have shown that batch parametric pumping can yield very high separation factors in small equipment in a relatively short period of time. By extending the equilibrium theory of Pigford, Baker, and Blum (*2*), Chen and Hill (*3*) have derived mathematical expressions for the performance of batch, semicontinuous, and continuous parametric pumps. They have shown that under certain conditions the batch pump and continuous 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 a continuous pump in which the feed and product streams flow steadily both in upflow and downflow is experimentally investigated in the model system toluene-*n*-heptane on silica gel adsorbent. Comparison is made between the experimental data and the analytical results obtained by an equilibrium theory. Emphasis is placed on the operating conditions necessary to achieve high separation factors.

EXPERIMENTAL

The experimental apparatus is shown schematically in Figure 1. The equipment consists of a jacketed glass column (0.01 m. inside diameter) packed with 30 to 60 mesh chromatographic grade silica gel. The reservoirs at the two opposite ends of the column were two 50-cu.cm. glass syringes operated by a dual infusion-withdrawal pump manufactured by Harvard Apparatus Company. A micro-switch with stops was wired into the pump circuit to automatically reverse the action of the syringe plungers at the end of each half cycle. To fulfill the requirement of perfect mixing in the reservoirs, small magnetic stirrers were placed in the reservoir syringes.

The sources of hot and cold water supply were constant temperature hot and refrigerated baths. The baths were connected to the column and to recycle by solenoid valves wired to a dual timer so that hot water supply was always directed to the column jacket during upflow and cold water during downflow.

The feed was delivered to the top of the column by a second infusion-withdrawal pump with two 50 cu.cm. syringes operated in parallel. (Every three cycles, pump operation was interrupted and the feed syringes refilled). The product take-off valves were micrometer capillary valves used both to regulate flow and impose a small back pressure on the system. Rotameters were used in the feed and product lines.

Prior to each run the entire system, including the interstitial column volume, the bottom reservoir and the feed pump were filled with the feed mixture at ambient temperature. The reservoir syringes were set to deliver about 40 cu.cm. per half cycle with a dead volume of approximately 3 cu.cm. in each syringe.

At the beginning of the run the feed and reservoir pumps were started and the timer was activated. The bottom reservoir syringe pumped fluid into the bottom of the column and the timer switched the solenoids to supply hot water (343°K.) to the jacket. At the end of the cycle the microswitch reversed the action of the reservoir pump and simultaneously, the timer switched the solenoids to supply cold water (277°K.) to the jacket. This procedure was repeated for each cycle. The column temperature generally reached 90% of its final value 2 min.

Expansion and contraction flows were induced within t column by the periodic temperature changes, with correspondingly enhanced or diminished product flow rates. Therefore, the top and bottom product flow rates were adjusted so that their average values for the hot and cold cycles were the desired ones. Samples for analysis were taken from the product streams after each half cycle, and analyzed by ultraviolet spectrophotometer.

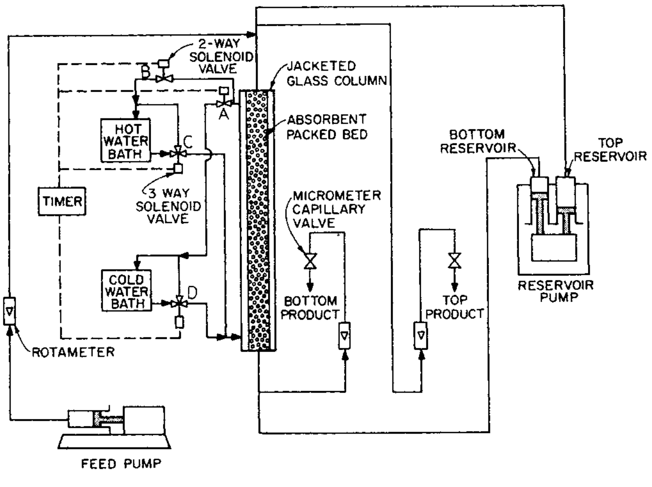

Fig. 1. Schematic diagram of experimental apparatus. (Upflow: valve A closed, valve B open, valve C open to the column and valve D open to recycle to the cold water bath; Downflow: valve A open, valve B closed, valve C open to recycle to the hot water bath and valve D open to the column).

MATHEMATICAL MODEL

In order to obtain the transient equations for $<y_{BP2}>_{n/y_0}$ and $<y_{TP2}>_{n/y_0}$, solution of a system of two internal and two external equations is required. An internal equation is a solute material balance reflecting events occurring within the adsorption column, and 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. Internal and external equations and their steady state solutions for the pump described in this paper and for other pumps have been discussed by Chen and Hill (3).

For the continuous pump with feed at the top there are three possible regions of operation (see Figure 2), depending on relative magnitudes of the penetration distances L_1 and L_2 and the column height h (3). 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

$$L_1 = \frac{v_0\,(1-\phi_B)}{(1-b)(1+m_0)}\,\frac{\pi}{\omega} \tag{1}$$

at the end of an upflow half cycle, and

$$L_2 = \frac{v_0\,(1+\phi_B)}{(1+b)(1+m_0)}\,\frac{\pi}{\omega} \tag{2}$$

by the end of a downflow half-cycle. We have solved the system of internal and external equations for all 3 regions by the use of the method of characteristics. We have assumed

1. Instantaneous equilibrium between adsorbate in the solid and liquid phases
2. A linear model of equilibrium adsorption, that is, $\chi = M(T)y$
3. One dimensional system with no axial dispersion
4. Plug flow
5. Instantaneous temperature changes
6. Fluid with constant density

We present below the concentration transients, corresponding to Regions 1, 2, and 3. We restrict our interest to the situation in which a given product stream during discharge of the adjacent reservoir comes only from that reservoir and not from the column or from the feed stream, that is, ϕ_T, $\phi_B < 1$. The detailed derivations are available elsewhere (4).

In Region 1 expressions for the concentration transients in the two product streams are

$$\frac{<y_{BP2}>_n}{y_0} = \frac{1-b}{1+b}\left[\frac{\frac{1-b}{1+b}+C_2}{1+C_2}\right]^{n-1}, \quad n \geqq 1 \tag{3}$$

$$\frac{<y_{TP2}>_n}{y_0} = -\frac{\phi_T+\phi_B}{1-\phi_T}+\frac{1+\phi_B}{1-\phi_T}\left[\frac{C_1+\frac{1-\phi_T}{1+\phi_T}}{1+C_1}\right]^{n-1}$$

$$+\frac{1+\phi_B}{1-\phi_T}\left(\frac{1+\phi_T}{2\phi_T}\right)\left[1-\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-b}{1+b}\right)\right]$$

$$\left[1-\left[\frac{C_1+\frac{1-\phi_T}{1+\phi_T}}{1+C_1}\right]^{n-1}\right], \quad n \leqq p_1+1 \tag{4}$$

$$\frac{<y_{TP2}>_n}{y_0} =$$

$$-\frac{\phi_T+\phi_B}{1-\phi_T}+\frac{1+\phi_B}{1-\phi_T}\left\{\left[\frac{C_1+\frac{1-\phi_T}{1+\phi_T}}{1+C_1}\right]^{n-1}\right.$$

$$+\frac{1+\phi_T}{2\phi_T}\left[1-\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-b}{1+b}\right)\right]$$

$$\left[1-\left[\frac{C_1+\frac{1-\phi_T}{1+\phi_T}}{1+C_1}\right]^{p_1}\right]\left[\frac{C_1+\frac{1-\phi_T}{1+\phi_T}}{1+C_1}\right]^{n-p_1-1}$$

$$+\frac{1}{1+C_1}\left[\frac{C_1+\frac{1-\phi_T}{1+\phi_T}}{1+C_1}\right]^{n-p_1-2}$$

$$\left[1-\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)+\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)\right.$$

$$\left(1-\frac{L_2}{L_1}\right)q_1+\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)$$

$$\left.\left.\left(1-\frac{L_2}{L_1}\right)(1-q_1)\left[\frac{\frac{1-b}{1+b}+C_2}{1+C_2}\right]\right]\right]$$

$$+\frac{1+\phi_T}{2\phi_T}\left[1-\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)\right]$$

$$\left[1-\left[\frac{C_1+\frac{1-\phi_T}{1+\phi_T}}{1+C_1}\right]^{n-p_1-2}\right]$$

$$+\left[\frac{\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)}{\frac{1+C_1}{1+C_2}\left(\frac{1-b}{1+b}+C_2\right)-C_1-\frac{1-\phi_T}{1+\phi_T}}\right]$$

$$\left[\frac{\frac{1-b}{1+b}+C_2}{1+C_2}\right]\left[\left(1-\frac{L_2}{L_1}\right)q_1\right.$$

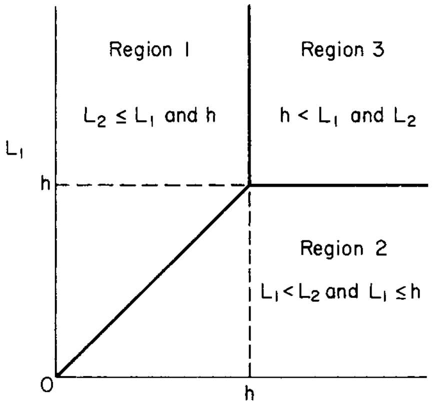

Fig. 2. Regions of continuous parametric pump with top feed.

$$+\left[\frac{\frac{1-b}{1+b}+C_2}{1+C_2}\right]\left(1-\frac{L_2}{L_1}\right)(1-q_1)\Bigg]$$

$$\Bigg[\left[\frac{\frac{1-b}{1+b}+C_2}{1+C_2}\right]^{n-p_1-2}$$

$$-\left[\frac{C_1+\frac{1-\phi_T}{1+\phi_T}}{1+C_1}\right]^{n-p_1-2}\Bigg]\Bigg\},$$

$$n \geqq p_1+2 \quad (5)$$

where

$$p_1+q_1=\frac{h-L_2}{L_1-L_2} \quad (6)$$

$p_1 =$ zero or a positive integer and

$0 \leqq q_1 < 1$

Region 2 expressions are

$$\frac{<y_{TP2}>_n}{y_0}=-\frac{\phi_T+\phi_B}{1-\phi_T}$$

$$+\frac{1+\phi_B}{1-\phi_T}\left[\frac{C_1+\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)\left(\frac{1+b}{1-b}\right)}{1+C_1}\right]^{n-1}$$

$$+\frac{\phi_T+\phi_B}{1-\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)\left(\frac{1+b}{1-b}\right)}$$

$$\left[\frac{2}{(1+\phi_T)(1-\phi_T)}\right]$$

$$\left\{1-\left[\frac{C_1+\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)\left(\frac{1+b}{1-b}\right)}{1+C_1}\right]^{n-1}\right\},$$

$$n \geqq 1 \quad (7)$$

$$\frac{<y_{BP2}>_n}{y_0}=(1+C_2)\frac{<y_{B1}>_{n-1}}{y_0}-C_2\frac{<y_{B1}>_n}{y_0}$$

where

$$\frac{<y_{B1}>_n}{y_0}=\left[\frac{C_2+\frac{1-\phi_B}{1+\phi_B}}{1+C_2}\right]^{n-1}$$

$$+\left[\frac{1-b-\frac{1-\phi_B}{1+\phi_B}(1+b)}{\left(1-\frac{1-\phi_B}{1+\phi_B}\right)(1+b)}\right]$$

$$\left[1-\left[\frac{C_2+\frac{1-\phi_B}{1+\phi_B}}{1+C_2}\right]^{n-1}\right],$$

$$n \leqq p_2+1 \quad (8)$$

$$\frac{<y_{B1}>_n}{y_0}=\left[\frac{C_2+\frac{1-\phi_B}{1+\phi_B}}{1+C_2}\right]^{n-1}$$

$$+\left[\frac{1-b-\frac{1-\phi_B}{1+\phi_B}(1+b)}{\left(1-\frac{1-\phi_B}{1+\phi_B}\right)(1+b)}\right]$$

$$\left[\frac{C_2+\frac{1-\phi_B}{1+\phi_B}}{1+C_2}\right]^{n-p_2-1}\left[1-\left[\frac{C_2+\frac{1-\phi_B}{1+\phi_B}}{1+C_2}\right]^{p_2}\right]$$

$$+\frac{1}{1+C_2}\left[\frac{C_2+\frac{1-\phi_B}{1+\phi_B}}{1+C_2}\right]^{n-p_2-2}$$

$$\left[\left(\frac{1-b}{1+b}\right)q_2\left(1-\frac{L_1}{L_2}\right)+\left(1-\frac{L_1}{L_2}\right)(1-q_2)\right]$$

$$+\frac{1}{1+C_2}\left[\frac{C_2+\frac{1-\phi_B}{1+\phi_B}}{1+C_2}\right]^{n-p_2-3}$$

$$\Bigg\{q_2\left(1-\frac{L_1}{L_2}\right)$$

$$+\left[\frac{C_1+\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)\left(\frac{1+b}{1-b}\right)}{1+C_1}\right]$$

$$(1-q_2)\left(1-\frac{L_1}{L_2}\right)+(1-q_2)\left(1-\frac{L_1}{L_2}\right)$$

$$\left[\frac{2(\phi_T+\phi_B)}{(1+\phi_T)(1+\phi_B)(1+C_1)}\right]\Bigg\}+\frac{1}{1+C_2}$$

$$\left[\frac{1}{\frac{C_1+\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)\left(\frac{1+b}{1-b}\right)}{1+C_1}-\frac{C_2+\frac{1-\phi_B}{1+\phi_B}}{1+C_2}}\right]$$

$$\Bigg\{q_2\left(1-\frac{L_1}{L_2}\right)+(1-q_2)\left(1-\frac{L_1}{L_2}\right)$$

$$\left[\frac{C_1+\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1-\phi_B}\right)\left(\frac{1+b}{1-b}\right)}{1+C_1}\right]\Bigg]\Bigg\}$$

$$\left[\frac{C_1+\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)\left(\frac{1+b}{1-b}\right)}{1+C_1}\right]$$

$$\Bigg\{\left[\frac{C_1+\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)\left(\frac{1+b}{1-b}\right)}{1+C_1}\right]^{n-p_2-3}$$

$$-\left[\frac{C_2+\frac{1-\phi_B}{1+\phi_B}}{1+C_2}\right]^{n-p_2-3}\Bigg\}$$

$$+\left[\frac{\phi_T+\phi_B}{\phi_B(1+\phi_T)}\right]\left(1-\frac{L_1}{L_2}\right)$$

$$\left[\frac{1}{1-\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)\left(\frac{1+b}{1-b}\right)}\right]$$

$$\left[1 - \left[\frac{C_1 + \frac{1-\phi_B}{1+\phi_B}}{1+C_2}\right]^{n-p_2-3}\right]$$

$$- \frac{2(\phi_T + \phi_B)}{(1+\phi_T)\,(1+\phi_B)\,(1+C_2)}$$

$$\left[\frac{1}{\dfrac{C_1 + \frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)\left(\frac{1+b}{1-b}\right)}{1+C_1} - \dfrac{C_2 + \frac{1-\phi_B}{1+\phi_B}}{1+C_2}}\right]$$

$$\left[q_2\left(1 - \frac{L_1}{L_2}\right) + (1-q_2)\left(1 - \frac{L_1}{L_2}\right)\right.$$

$$\left.\frac{C_1 + \frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)\left(\frac{1+b}{1-b}\right)}{1+C_1}\right]$$

$$\left[\frac{1}{1 - \frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)\left(\frac{1+b}{1-b}\right)}\right]$$

$$\left[\frac{C_1 + \frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)\left(\frac{1+b}{1-b}\right)}{1+C_1}\right]$$

$$\left\{\left[\frac{C_1 + \frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)\left(\frac{1+b}{1-b}\right)}{1+C_1}\right]^{n-p_2-3}\right.$$

$$\left. - \left[\frac{C_2 + \frac{1-\phi_B}{1+\phi_B}}{1+C_2}\right]^{n-p_2-3}\right\},$$

$$n \geqq p_2 + 2 \qquad (9)$$

where

$$p_2 + q_2 = \frac{h - L_1}{L_2 - L_1} \qquad (10)$$

$$p_2 = \text{zero or a positive integer and } 0 \leqq q_2 < 1$$

The expressions for Region 3 are

$$\frac{<y_{TP2}>_n}{y_0} = -\frac{\phi_T + \phi_B}{1 - \phi_T} + \frac{1+\phi_B}{1-\phi_T}\left[\frac{g_1}{y_0}\zeta_1{}^n + \frac{g_2}{y_0}\zeta_2{}^n + (1-a_4)\,\eta\right]$$

$$\frac{<y_{BP2}>}{y_0} = (1+C_2)\left(\frac{g_3}{y_0}\zeta_1{}^n + \frac{g_4}{y_0}\zeta_2{}^n + a_3\eta\right) - C_2\left(\frac{g_3}{y_0}\zeta_1{}^{n-1} + \frac{g_4}{y_0}\zeta_2{}^{n-1} + a_3\eta\right) \qquad (11)$$

where

$$\zeta_1 = \frac{1}{2}\,[W_1 + (W_1{}^2 - 4W_2)^{1/2}]$$

$$\zeta_2 = \frac{1}{2}\,[W_1 - (W_1{}^2 - 4W_2)^{1/2}]$$

$$\frac{g_1}{y_0} = \frac{1}{\zeta_1}\left[1 - \frac{g_2}{y_0}\zeta_2 - (1-a_4)\ \eta\right]$$

$$\frac{g_2}{y_0} = \frac{1}{\zeta_2\,(\zeta_2 - \zeta_1)}\,[W_4 - \zeta_1 + (1-a_4)(\zeta_1 - 1)\,\eta]$$

$$\frac{g_3}{y_0} = \frac{1}{\zeta_1}\left(W_5 - \frac{g_4}{y_0}\zeta_2 - a_3\eta\right)$$

$$\frac{g_4}{y_0} = \frac{1}{\zeta_2\,(\zeta_2 - \zeta_1)}\,[W_6 - \zeta_1\,W_5 + a_3\,(\zeta_1 - 1)\,\eta]$$

$$\eta = \begin{cases} 0 & \text{if } \phi_T = \phi_B = 0 \\ \dfrac{W_3}{1 - W_1 + W_2} & \text{otherwise} \end{cases}$$

$$W_1 = (a_1 + a_2\,a_3)\,\frac{\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)}{1+C_1} + a_4 + \frac{C_1}{1+C_1}$$

$$W_2 = a_1 a_4\,\frac{\frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)}{1+C_1} + \frac{a_4\,C_1}{1+C_1}$$

$$W_3 = \frac{1}{1+C_1}\left[1 - \frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)\right]$$

TABLE 1. EXPERIMENTAL AND MODEL PARAMETERS

$\pi/\omega = 1200$ sec., $T_c = 277$°K., $T_h = 343$°K.,
$b = 0.22$, $m_o = 1.88$

Region	h, m	$\phi_T + \phi_B$	ϕ_B	C_1	C_2	L_1, m.	L_2, m.
1	0.90	0.4	0.15	0.137	0.15	0.51	0.44
2	0.90	0.4	0.30	0.15	0.25	0.47	0.56
3	0.31	0.4	0.10	0.10	0.10	0.51	0.40

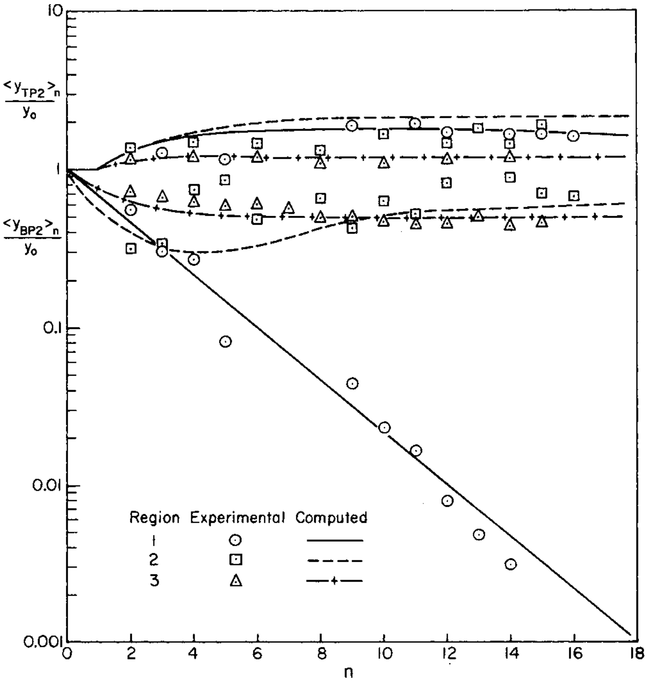

Fig. 3. Effects of L_1, and L_2, and h on product concentrations.

$$W_4 = \frac{1}{1+C_1}\left[C_1 + \frac{1-\phi_T}{1+\phi_T}\left(\frac{1-\phi_B}{1+\phi_B}\right)(a_1 + a_2a_3 + a_2a_4)\right] + W_3$$

$$W_5 = a_3 + a_4$$

$$W_6 = a_3W_4 + a_4\,(a_3 + a_4)$$

$$a_1 = \left(\frac{1+b}{1-b}\right)\frac{h}{L_1}$$

$$a_2 = 1 - \frac{h}{L_1}$$

$$a_3 = \frac{1}{1+C_2}\left(1 - \frac{h}{L_2}\right)$$

$$a_4 = \frac{1}{1+C_2}\left[C_2 + \left(\frac{1-b}{1+b}\right)\frac{h}{L_2}\right] \tag{12}$$

We find from the above equations that at steady state ($n \to \infty$) solute removal from the lower stream is complete in Region 1 but only partial in Regions 2 and 3.

RESULTS AND DISCUSSION

Three runs corresponding to Regions 1, 2, and 3 were carried out. The experimental parameters are shown in Table 1. In all cases the feed had a concentration of 10 volume % of toluene in n-heptane, and the total cycle time was 2,400 sec. (1,200 sec. of upflow followed by 1,200 sec. of downflow). Figure 3 shows the experimental verification of the effects of L_1, L_2, and h on the product concentrations. The ordinate is the ratio of the average product concentration to the feed concentration during the downflow half-cycle. Dimensionless concentrations greater than one are top product concentrations, while those less than one are bottom product concentrations. One can see that in Region I the separation factor (defined as $\langle y_{TP2}\rangle_n / \langle y_{BP2}\rangle_n$) increases as n increases. It evidently will increase without limit as n becomes large, as theory predicts. On the other hand, the separation factors become finite in Regions 2 and 3.

The equations derived were used to calculate the concentration transients. The data needed in the calculations are h, ϕ_T, ϕ_B, C_1, C_2, b and L_2, where L_2 is defined in terms of ϕ_B, π/ω, b and m_0 [see Equation (2)]. The computations corresponding to the three experimental runs are presented in Figure 3. One can see that the calculated results compare reasonably well with the observed values. The relatively high deviations in Region 2 could have been due to the use of practical grade n-heptane for the experiment, rather than the reagent grade used in the other two cases.

The values of b and m_0 used in the computations were 0.22 and 1.88 respectively. These values were obtained from the model equations along with the experimental data of the concentration transients of Region 1, and applied to the other two regions. The procedure used for calculating the values of b and m_0 is as follows

1. Plot the experimental values of log $\langle y_{BP2}\rangle_n / y_0$ versus n (as in Figure 3), and obtain the slope, α by a linear least square fit.
2. Calculate b using the rearranged form of Equation (3)

$$b = \frac{1 - 10^{\alpha} + C_2\,(1 - 10^{\alpha})}{1 + 10^{\alpha} - C_2\,(1 - 10^{\alpha})} \tag{13}$$

3. Using Equations (4) and (5) calculate $\langle y_{TP2}\rangle / y_0$ versus n for several arbitrary values of L_2. Choose the value of L_2 which gives the minimum sum of square deviations of $\langle y_{TP2}\rangle / y_0$ from the experimentally determined values.
4. Using the value of L_2 calculate m_0 by Equation (2).

Pigford, Baker, and Blum (*2*) used the data of Wilhelm et al. (*6*) and showed that $b = 0.125$ at the same hot and cold temperatures we have used here. Their b value, however, was based on the assumption that the reservoir dead volume (or C_2) was zero. It seems reasonable to say that the condition with $C_2 = 0$ is practically impossible to achieve especially in laboratory apparatus. In fact, Sweed has reported that the dead volume was about 9 cu.cm. for his batch parametric pump (*5*). In the present case the effect of the dead volume can be seen from Equation (13) in which C_2 contributes considerably to the value of b. For a given α, the value of b calculated from the assumption that $C_2 = 0$ will be lower than the value obtained by taking the dead volume into account.

It is also possible to compute b from the equilibrium data (x-y data). Values at 273°K. and 338°K. are available from (*5*). With this limited information, we have estimated b as shown below

1. Calculate M for $T = 273$°K. and 338°K. by

$$M = \frac{2}{y^2}\int_0^y X_1\,dy_1$$

(where X_1, y_1 = observed values)

2. Obtain M for $T = 277$°K. and 343°K. by linear interpolation and extrapolation, and then calculate b.

In spite of the fact that the procedure described above is only an approximation, the estimate of $b = 0.19$ (for $y = 0$ to $y = 0.2$) is in reasonable agreement with the value obtained from the concentration transients. This lends support to the applicability of the local linear adsorption equilibrium assumed here.

In this paper we have shown the effects of L_1, L_2, and h on the performance of a continuous pump, both experimentally and theoretically. When the pump with feed at the top was operated in Region 1 we found that at the steady state solute removal in the lower product stream was essentially complete. When the pump was operated outside Region 1, solute removal in the lower product stream was incomplete.

In practice it would be desirable to have a short cycle time $2\pi/\omega$. The shorter time, however, 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 factors may never be obtained. Experimental verification of the effects of $2\pi/\omega$ on the approach to equilibrium and on the separation will be presented in subsequent papers.

NOTATION

b = dimensionless equilibrium parameter (*2*)

C_1 = $\dfrac{V_T}{Q\frac{\pi}{\omega}}$, fraction of dead volume of the top reservoir to displacement, dimensionless

C_2 = $\dfrac{V_B}{Q\frac{\pi}{\omega}}$, fraction of dead volume of the bottom reservoir to displacement, dimensionless

h = column height, m.

L = penetration distances defined by Equation (1) or (2), m.

M = equilibrium constant
m_0 = equilibrium constant parameter, dimensionless (2)
n = number of cycles of pump operation
p_1, p_2 = defined by Equations (6) and (10)
Q = reservoir displacement rate, cu.cm./sec.
q_1, q_2 = defined by Equations (6) and (10)
v_0 = interstitial velocity, m./sec.
V_T = top dead reservoir volume, cu.cm.
V_B = bottom dead reservoir volume, cu.cm.
y = concentration of solute in the liquid phase, kg.-mole/cu.cm.
$< >$ = average value

Greek Letters

χ = concentration of solute in the solid phase, kg.-mole/Kg.
ϕ = product volumetric flow rate/reservoir displacement rate, dimensionless
$\frac{\pi}{\omega}$ = duration of half cycle, sec.

Subscripts

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

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Manuscript received July 27, 1971; revision received September 3, 1971; paper accepted October 26, 1971.

Forced Convection Heat Transfer Correlations for Flow in Pipes, Past Flat Plates, Single Cylinders, Single Spheres, and for Flow in Packed Beds and Tube Bundles

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Previously obtained experimental heat transfer data have been collected and are illustrated along with minor variations of the standard correlations. Analysis of data for heat transfer in randomly packed beds and compact (void fraction less than 0.65) staggered tube bundles indicates that the Nusselt number for a wide range of packing materials and tube arrangements is given by

$$N_{Nu} = (0.5\, N_{Re}^{1/2} + 0.2\, N_{Re}^{2/3})\, N_{Pr}^{1/3}\, (\mu_b/\mu_0)^{0.14}$$

provided $N_{Re} \geqq 50$. The correlations presented in this paper are not necessarily the most accurate available; however, they have wide application, are easy to use, and are quite satisfactory for most design calculations.

For the past forty years there has been a steady effort to improve our knowledge of forced convection heat transfer rates for a variety of important process configurations. It is of value to periodically review the experimental data and construct new correlations on the basis of new data and theoretical advances. McAdams (23) contributed much along these lines in 1954; however, enough new data have been obtained so that these correlations deserve a second look.

All the experimental data that we wish to consider in this paper can be satisfactorily described in terms of the following equations:
equations of motion

$$\rho\left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v}\cdot\nabla\mathbf{v}\right) = -\nabla p + \rho\mathbf{g} + \nabla\cdot\boldsymbol{\tau} \qquad (1)$$

constitutive equation for a Newtonian fluid

$$\boldsymbol{\tau} = \mu\,(\nabla\mathbf{v} + \nabla\mathbf{v}^{+}) \qquad (2)$$

continuity equation

$$\nabla\cdot\mathbf{v} = 0 \qquad (3)$$