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Separation of Multicomponent Mixtures via Thermal Parametric Pumping

A thermal continuous parametric pump for separating multicomponent mixtures was experimentally investigated using the model system toluene-aniline-*n*-heptane on silica gel adsorbent. A simple method for predicting separations is presented and is found to be in good agreement with the experimental results. The method, based on an equilibrium theory, invokes the assumption that a multicomponent mixture contains a series of pseudo binary systems. Each binary system consists of one of the solutes as one component and the common inert solvent as the other component.

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SCOPE

Thermal parametric pumping is a phase-change separation process which depends for its operation on the coupling of periodic changes in temperature affecting the position of interphase equilibrium with synchronous periodic changes in flow direction. In earlier papers (Chen et al., 1972, 1973), separations of binary systems (single solute and its solvent) were experimentally investigated via continuous and semicontinuous parametric pumping. It has been shown that under certain conditions the pumps with feed at the enriched end have the capacity for complete removal of solute from one product stream and, at the same time, give arbitrarily large enrichment of solute in the other product stream.

In this paper continuous parametric pumping is extended to the separations of multicomponent mixtures. The continuous pump is characterized by a steady flow of both feed and product streams during the hot upflow and cold downflow half-cycles. The system used is toluene-aniline-*n*-heptane on silica gel. A comparison is made between the experimental data and the calculated results based on the method proposed by Chen and Hill (1971). The prediction of multicomponent separations by this relatively simple method could eventually be applied to commercially important systems which are usually multicomponent in nature. It should be noted that a theoretical discussion of separations of multicomponent mixtures by other versions of parametric pumping has been given by Butts et al. (1972).

CONCLUSIONS AND SIGNIFICANCE

A simple means of predicting multicomponent separations in the continuous thermal parametric pump is presented. A multicomponent system is treated as a series of pseudo binary systems. Each binary system consists of one of the solutes as one component and the common inert solvent as the other component. This approach permits the use of existing transient and steady state equations for binary systems (Chen and Hill, 1971; Chen et al., 1972). Experimental data for the concentration transients agree reasonably well with the analytical predictions.

It is shown that the thermal parametric pump is capable of separating components in a multicomponent mixture and, as a theoretical limit, of attaining infinite separation factors. Also, the net movement of concentration fronts through the adsorption column is found to be important in determining the pump performance. Those solutes for which the net movement is upward would, at steady state, appear only in the top product. The remaining solutes would appear in both the top and bottom products. In the limiting case, it is possible for the bottom product to consist solely of pure solvent. This would result when all solutes in a mixture are very strongly adsorbed or desorbed in a given cycle or when the flow rate of the bottom product is very small.

MATHEMATICAL MODEL

Figure 1 shows the continuous parametric pump model considered here. Flow is upward during the hot half-cycle and downward during the cold half-cycle. Each half-cycle is π/ω time units in duration and the reservoir displacement volume is $Q(\pi/\omega)$, where Q is the reservoir displacement rate. The pump has dead volumes V_T and V_B for the top and bottom reservoirs respectively. The feed is directed to the top of the column at the flow rate $(\phi_T + \phi_B)Q$. The top product flow rate is $\phi_T Q$ and the bottom product flow rate is $\phi_B Q$, and ϕ_T and ϕ_B are the ratios of the top and bottom product rates to the reservoir displacement rate.

For processes inside the column we will assume, as did Pigford et al. (1969), that local interphase equilibrium exists with a linear distribution law having a temperature-dependent distribution coefficient. Also there is negligible axial diffusion, temperature changes between hot and cold cycles are instantaneous, plug flow exists, and the fluid density is constant. We will assume further that the multicomponent mixture may be treated as n pairs of pseudo binary systems. Each system includes one solute and the common inert solvent and could be characterized by a dimensionless equilibrium parameter b_i and corresponding values of the penetration distances of the hot and cold cycles L_{1i} and L_{2i}. L_{1i} and L_{2i} can be expressed in terms of ϕ_B and the equilibrium parameter b_i (Chen and Hill, 1971).

$$\frac{L_{1i}}{L_{2i}} = \left(\frac{1-\phi_B}{1+\phi_B}\right)\left(\frac{1+b_i}{1-b_i}\right) \qquad (1)$$

$$L_{2i} = \frac{v_0\,(1+\phi_B)}{(1+b_i)\,[1+0.5(m_{1i}+m_{2i})]}\left(\frac{\pi}{\omega}\right) \qquad (2)$$

where

$$m_i = \frac{\rho_s(1-\epsilon)\,M_i}{\epsilon} \qquad (3)$$

and $M_i(= x_i/y_i)$ is the equilibrium distribution coefficient at temperature T. The quantity b_i is associated with a given two-phase system when operated at two specific temperatures and may be expressed as

$$b_i = \frac{0.5(m_{2i}-m_{1i})}{1+0.5(m_{1i}+m_{2i})} \qquad (4)$$

The pump performance depends on the relative magnitudes of L_{1i}/L_{2i} and the height of the column h. There are three possible regions of pump operations depending on L_{1i}/L_{2i} and h,

$$\text{Region 1,}\quad \frac{L_{1i}}{L_{2i}} \geqq 1 \quad (\text{or } \phi_B \leqq b_i) \quad \text{and} \quad L_{2i} \leqq h \qquad (5)$$

$$\text{Region 2,}\quad \frac{L_{1i}}{L_{2i}} < 1 \quad (\text{or } \phi_B > b_i) \quad \text{and} \quad L_{1i} \leqq h$$

$$\text{Region 3,}\quad L_{1i} \text{ and } L_{2i} > h$$

By treating the multicomponent mixture as a series of pseudo binary systems, the multicomponent separation could be predicted by the existing mathematical expression for binary systems (Chen and Hill, 1971; Chen et al., 1972, 1973). We will not repeat their derivations here but note that it has been found that at steady state ($n \to \infty$) solute removal from the bottom product stream $\phi_B Q$ is complete in Region 1 and only partial in Regions 2 and 3.

Now let us consider a mixture containing s solutes, each with its own b_i and

$$b_1 > b_2 > --- \; b_k \geqq \phi_B > b_{k+1} --- > b_s \qquad (6)$$

where subscripts 1, 2, etc., refer to solutes 1, 2, etc. Furthermore

$$\begin{aligned} L_{2i} &\leqq h \quad \text{when} \quad i = 1, 2, --- \; k \\ L_{1i} &\leqq h \quad \text{when} \quad i = k+1, --- \; s \end{aligned} \qquad (7)$$

At steady state the components, $i = 1, 2, --- k$ for which the operations are indicated in Region 1, would appear only in the top product stream, and the remaining components ($k+1, --- s$) would appear in both the top and bottom product streams. In the extreme case where $k = s$ the bottom product stream would consist only of pure sol-

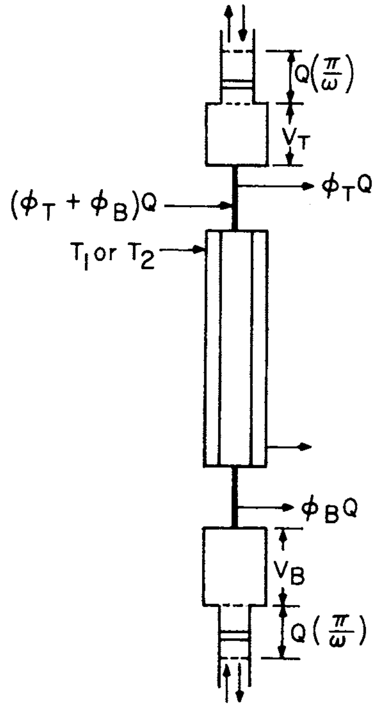

Fig. 1. Column diagram for thermal parametric pumping.

Table 1. Experimental and Model Parameters

$$\frac{\pi}{\omega} = 1{,}200\text{ s},\quad T_1 = 333°\text{K}, T_2 = 298°\text{K}, h = 0.9\text{ m}, \phi_T + \phi_B = 0.4$$

	Feed (vol. fraction)		ϕ_B	C_1	C_2	b_i	L_{1i} (m)	L_{2i} (m)	Region
	Toluene	Aniline							
1. Toluene-*n*-heptane	0.025	0	0.07	0.12	0.13	0.15	0.51	0.43	1
2. Aniline-*n*-heptane	0	0.025	0.10	0.11	0.13	0.31	0.70	0.45	1
3. *Aniline-toluene-*n*-heptane	0.025	0.025	0.09	0.12	0.13				
a. Toluene-*n*-heptane						0.15	0.49	0.44	1
b. Aniline-*n*-heptane						0.31	0.71	0.45	1
4. *Aniline-toluene-*n*-heptane	0.025	0.025	0.22	0.12	0.13				
a. Toluene-*n*-heptane						0.15	0.42	0.49	2
b. Aniline-*n*-heptane						0.31	0.62	0.51	1

* Assume that a ternary system contains two pseudo binaries.

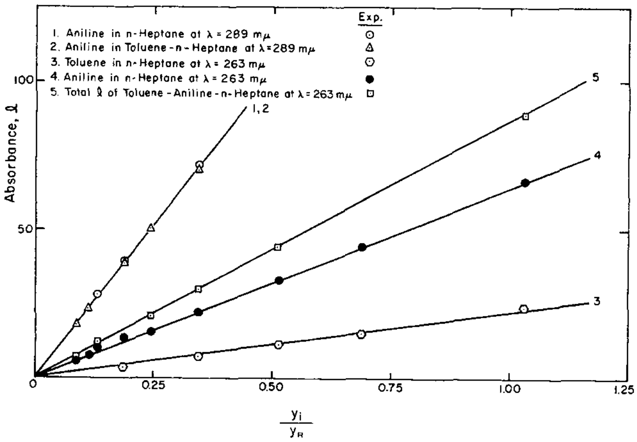

Fig. 2. Relation of absorbance to concentration. ($y_R = 1.097 \times 10^{-9}$ k gmoles/cm^3, when i = aniline; $y_R = 0.941 \times 10^{-9}$ k gmoles/cm^3, when i = toluene).

vent. By proper adjustment of ϕ_B in Equation (6) a solute split could be made which is analogous to that obtained by a multicomponent distillation column.

EXPERIMENT

The experimental apparatus was the same as that used previously (Chen et al., 1972) and included two dual infusion-withdrawal syringe pumps manufactured by the Harvard Apparatus Company, one for the feed and one for the reservoirs. The jacketed column (length = 0.9 m and inside diameter = 0.01 m) was packed with 30 to 60 mesh chromatographic-grade silica gel. Prior to each run the column and the bottom reservoir were filled with the feed mixture of concentrations y_{0i}. The reservoir syringes were set to deliver about 40 cm^3 per half-cycle. Hot and cold water baths were connected to the column jacket, and solenoid valves were wired to a dual timer to ensure that hot water (333°K) was directed to the column during upflow and cold water (298°K) during downflow. The total cycle time was 2,400 s (1,200 s of upflow followed by 1,200 s of downflow). A feed flow rate of 16 cm^3 per half-cycle was delivered to the top of the column. The top and bottom product micrometer capillary valves were used both to regulate flow and impose a small back pressure on the system.

Samples for analysis were taken from the product streams at the end of each cycle and analyzed by ultraviolet spectrophotometry using the procedure illustrated in Figure 2. For the runs involving binary systems (toluene or aniline in *n*-heptane) the analysis was straightforward and the concentration of solute was linearly proportional to the absorbance l at λ (wavelength) = 263 mμ for toluene and at λ = 289 mμ for aniline. This is clearly shown in curves 3 and 1 of Figure 2. In the case of the ternary system, aniline-toluene-*n*-heptane, the analysis was somewhat complicated. As shown in Figure 2, l for aniline at λ = 289 mμ in toluene-*n*-heptane coincided with that in *n*-heptane alone and was found to be independent of the presence of toluene (curves 1 and 2). This is because toluene has negligible absorbance at λ = 289 mμ. The l at λ = 263 mμ in toluene-aniline-*n*-heptane (curve 5) was the sum of that in toluene-*n*-heptane (curve 3) and in aniline-*n*-heptane (curve 4). Therefore, for an unknown ternary mixture the aniline concentration was determined directly from l at λ = 289 mμ regardless of the toluene concentration. Knowing the aniline concentration, l for aniline at λ = 263 mμ was determined from curve 4. Subtraction of this l from the total l obtained at λ = 263 mμ in toluene-aniline-*n*-heptane gave the contribution of l by toluene alone and hence its concentration from curve 3.

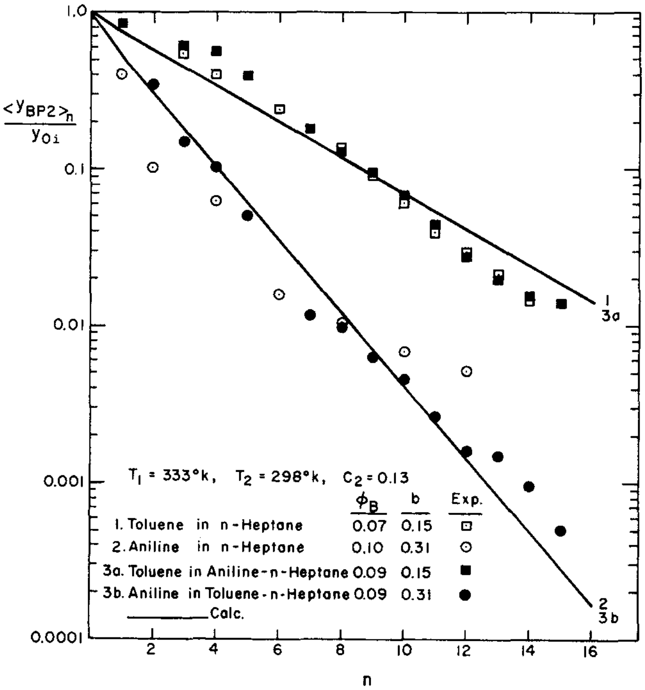

Fig. 3. Concentration transients for the bottom product.

RESULTS AND DISCUSSION

Four experimental runs were made, including 2 binary and 2 ternary systems. The experimental parameters are shown in Table 1 and the data are plotted in Figures 3 and 4. The equations previously derived (Chen et al.,

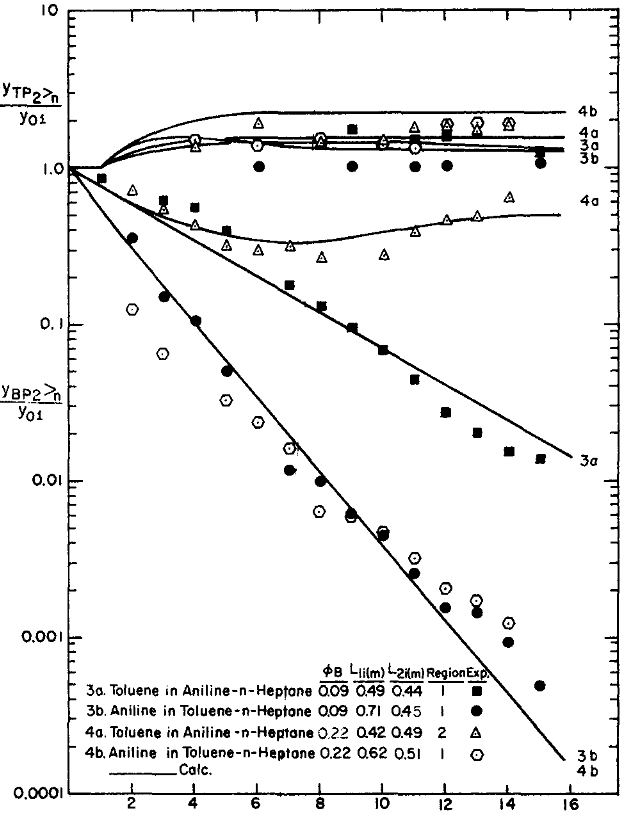

Fig. 4. Effects of operating conditions on product concentrations.

1972) were used to calculate the concentration transients and the computed results corresponding to the experimental runs are also presented in Figures 3 and 4. These results compare reasonably well with the observed values. In the computations for the ternary system (toluene-aniline-n-heptane), it was assumed that there are no interactions between solutes, and the system contains two pseudo binaries, each binary consisting of one solute as one component and the common solvent as the other component, that is, toluene-n-heptane and aniline-n-heptane.

When the pumps are operated in Region 1, (that is, $(L_{1i}/L_{2i}) \geqq 1$ (or $\phi_B \leqq b_i$) and $L_{2i} \leqq h$), the bottom concentration transient is (Chen et al., 1972).

$$\frac{\langle y_{BP2}\rangle_n}{y_{0i}} = \frac{1-b_i}{1+b_i}\left[\frac{\dfrac{1-b_i}{1+b_i}+C_2}{1+C_2}\right]^{n-1}, \quad n \geqq 1 \tag{8}$$

and at steady state ($n \to \infty$),

$$\frac{\langle y_{BP2}\rangle_\infty}{y_{0i}} = 0 \tag{9}$$

Figure 3 illustrates $\langle y_{BP2}\rangle_n/y_{0i}$ versus n for both toluene and aniline in both binary and ternary systems. One can see that $\langle y_{BP2}\rangle_n/y_{0i}$ decreases as n increases and, as the theory predicts, approaches zero as n becomes large. The slope α (of log $\langle y_{BP2}\rangle_n/y_{0i}$ versus n) of the solute i (toluene or aniline) in the binary mixture (toluene-n-heptane or aniline-n-heptane) is coincident with that in the ternary system (toluene-aniline-n-heptane). In other words, for a given C_2, T_1, and T_2, the value of b_i which can be calculated from α by Equation (8) is essentially the same for both the binary and ternary systems. It should be emphasized that the quantity b_i is a measure of the extent of movement of solute i between phases as the result of a change in column temperature. Pump performance is enhanced by a large b_i. The particular b_i values considered here were determined to be 0.15 and 0.31 for toluene and aniline, respectively.

Figure 4 shows the effects of L_{1i}, L_{2i}, and h on the product concentrations. As long as L_{2i} is less than or equal to L_{1i} and h (Region 1), the separation factor, defined as the quotient of the top and bottom concentrations, approaches infinity as n becomes large. If, in a pump originally operated in Region 1, L_{2i} is increased until it exceeds h or if L_{1i} becomes less than L_{2i}, switching points are encountered which cause the steady state behavior of the pump to abruptly switch from a mode in which solute is completely removed from the bottom product stream to one in which solute removal is incomplete. One may visualize crossing the boundary $L_{2i} = h$ as a result of increasing L_{2i} by increasing the reservoir displacement volume $Q\dfrac{\pi}{\omega}$. Crossing of the boundary $L_{1i} = L_{2i}$ may be viewed as resulting from an increase of ϕ_B so that $\phi_B > b_i$, or $L_{2i} > L_{1i}$. At $T_1 = 333°K$ and $T_2 = 298°K$ the switching point for toluene corresponds to the condition $\phi_B = b_{\text{toluene}} = 0.15$. In the case of aniline, the condition is $\phi_B = b_{\text{aniline}} = 0.31$. Thus, when $\phi_B \leqq 0.15$ (curves 3a and 3b), the operation is in Region 1 for both toluene and aniline, and solute removal from the bottom product stream may be complete at $n \to \infty$. If ϕ_B is increased to the interval range, $0.15 < \phi_B \leqq 0.31$ (curves 4a and 4b), the operation switches to Region 2 for toluene and, remains in Region 1 for aniline and the bottom product could eventually contain only toluene. If ϕ_B is further increased $\phi_B > 0.31 = b_{\text{aniline}}$ the operation is now in Region 2 for both toluene and aniline, and both toluene and aniline would appear in the bottom product stream at $n \to \infty$. Note that over the interval $\phi_B \leqq b_i$ = switching point of solute i, the top concentration of i at $n \to \infty$ would be $\langle y_{TP2}\rangle_\infty/y_{0i} = 1 + \phi_B/\phi_T$. Beyond the switching point, $\langle y_{TP2}\rangle_\infty/y_{0i}$ can be expressed according to the equations by Chen and Hill (1971).

Figures 5 and 6 show the net direction of concentration fronts moving through the adsorption column as n increases (or a function of time). The average top and bottom product concentrations relative to the feed concentration are also given. In Figure 5 the operation for both toluene and aniline is in Region 1 and, since in this case

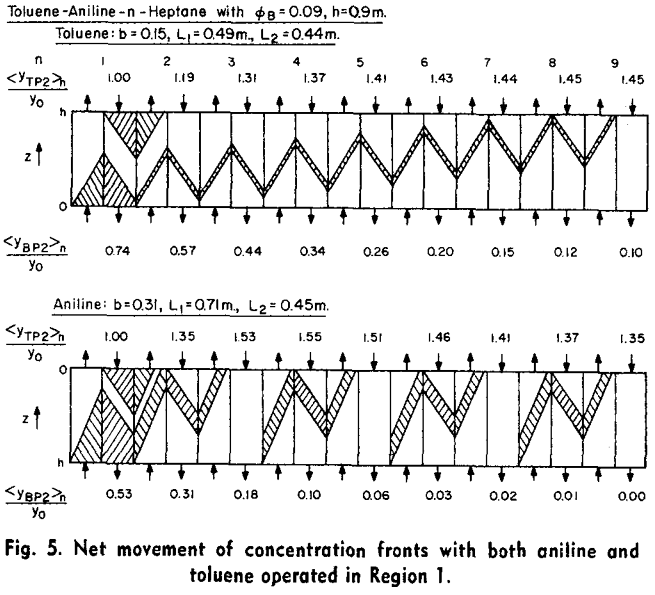

Fig. 5. Net movement of concentration fronts with both aniline and toluene operated in Region 1.

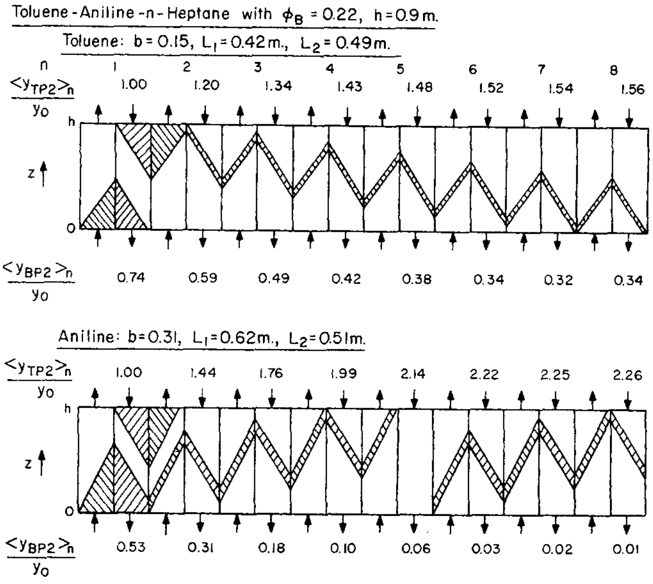

Fig. 6. Net movement of concentration fronts with aniline and toluene operated in Regions 1 and 2, respectively.

$(L_{1i}/L_{2i}) \geqq 1$, the net movements of the concentration fronts for both components are upward and, as a result, the bottom product concentrations show a steady decrease. Note that (L_{1i}/L_{2i}) for aniline is greater than that for toluene and, consequently, aniline moves up the column faster than does toluene.

In Figure 6 the operations for aniline and toluene are in Regions 1 and 2, respectively, that is, $(L_{1i}/L_{2i})_{\text{aniline}} \geqq 1$ and $(L_{1i}/L_{2i})_{\text{toluene}} < 1$. The net movements of the concentration fronts of the two components are clearly in opposite directions. The net direction of aniline is upward and the bottom product concentration, $<y_{BP2}>_n/y_{0i}$ decreases as n increases. The net direction of toluene is downward and $<y_{BP2}>_n/y_{0i}$ approaches a limiting value (see also 4a in Figure 4). The net downawrd direction occurs due to an excessive bottom product flow rate, that is, $\phi_B > b_{\text{toluene}}$. However, it must be noted that even though the net direction is upward, a modest separation will also occur if the reservoir displacement volume is excessive, that is, $L_{2i} > h$ (Region 3).

When the operation for toluene is in Region 2 (Curve 4a in Figure 4 or Figure 6), $<y_{BP2}>_n/y_{0i}$ decreases up to the $(p_2 + 1)$th cycle, increases again, and then approaches a limiting value. This is also shown by the equations previously presented (Chen et al., 1972). Here, $(p_2 + 1)$ is the number of cycles required for concentration fronts to emerge from the bottom of the column. By examining Figure 6 one can see that, up to the seventh cycle (or $n = p_2 + 1$), the bottom product concentration has dropped due to the net adsorption of toluene in the fluid initially present in the column. When $n > 7$ the concentration front moving down the column breaks through, bringing into play the streams from the enriched end of the column. This results in an increase of $<y_{BP2}>_n/y_{0i}$ for a certain number of cycles and then a leveling out to a steady state value.

The method presented here is a means of predicting multicomponent separations by assuming that solutes do not interact with one another. In practice, the concentrations of solutes may be quite high and the high solute concentrations may cause competition for the adsorption sites. Therefore, the maximum separation factors may never be obtained. Experimental verification of the effect of solute concentrations on the separation will be presented in subsequent papers.

NOTATION

b = dimensionless equilibrium parameter defined by Equation (4)
C_1 = $\dfrac{V_T}{Q\dfrac{\pi}{\omega}}$, dimensionless
C_2 = $\dfrac{V_B}{Q\dfrac{\pi}{\omega}}$, dimensionless
h = column height, m
L = penetration distances defined by Equation (1) or (2), m
M = $\dfrac{x}{y}$, cm^3/kg
m = dimensionless equilibrium parameter defined by Equation (3)
n = number of cycles of pump operation
Q = reservoir displacement rate, cm^3/s
p_2 = integer $\left(\dfrac{h - L_{1i}}{L_{2i} - L_{1i}}\right)$ as defined by Chen et al. (1972)
v_0 = interstitial velocity based on the reservoir displacement rate, m/s
V_T = top reservoir dead volume, cm^3
V_B = bottom reservoir dead volume, cm^3
x = concentration of solute in the solid phase, kg moles/kg of adsorbent
y = concentration of solute in the liquid phase, kg moles/cm^3
$< >$ = average value

Greek Letters

ϕ = product volumetric flow rate/reservoir displacement rate, dimensionless
$\dfrac{\pi}{\omega}$ = duration of half cycle, s
ϵ = void fraction in packing, dimensionless
ρ_s = density of adsorbent, kg/cm^3

Subscripts

0 = initial condition
1 = upflow
2 = downflow
B = stream from or to bottom of the column
i = solute i
P = product stream
T = stream from or to top of the column
BP = bottom product
TP = top product
∞ = steady state

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