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NOTATION

A, B = transferred components
C = total concentration, moles/cm^3
C_j = concentration of j (A or B) moles j/cm^3 (or 1)
C^*_j = equilibrium value of C_j
C_{jk} = concentration of component j in phase k
C^*_{jk} = equilibrium value of C_{jk}
$\overline{C}_{jk}$ = mean concentration of j in phase k
C_{jo} = concentration of j at cell top
D_{AB} = molecular diffusivity of A in B, cm^2/s
D^{id}_{AB} = value of D_{AB} for an ideal solution
$\overline{D}^{id}_{AB}$ = mean value of D^{id}_{AB}, defined by Equation (12)
D_{int} = corrected integral diffusivity, defined by Equation (8)
N_i = interfacial molar flux, moles/cm^2, s
N_j = molar flux of j (A or B)
N_{jk} = molar flux of j in phase k
P = total pressure, atm
P^*_A = vapor pressure of A
P_{Ao} = partial pressure of A at $z = 0$
R = universal gas constant
S_i = interfacial transport area, cm^2
t = time, s
T = temperature, °K
$\tilde{V}_{jk}$ = partial molal volume of component j in phase k, cm^3/mole
X_j = mole fraction of j
X^*_j = equilibrium value of X_j
z = diffusion depth (in phase 2), measured from cell top, cm
z_i = interface depth
z_1 = initial interface depth

Greek Letters

α = integral defined by Equation (8), moles/cm, s
β^* = equilibrium distribution coefficient, defined by Equation (6)
ρ_j = molar density of component j, moles j/cm^3 of j
λ, ξ = dummy variables of integration
∇ = gradient, cm^{-1}

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Steady State Predictions for Nonequilibrium Parametric Pumps

S. C. FOO and R. G. RICE

University of Queensland
St. Lucia, Qld., Australia

Recently, Foo and Rice (1975) presented an analysis of the ultimate separation obtainable in closed parapumps using linear adsorption equilibria along with the dissipative forces associated with axial dispersion, film resistance, and pore diffusion. The general theory was based on the experimental observation that the time-average flux (solute pumping rate) tends to zero for large times. In closed parapump systems, there is an additional constraint associated with the fact that total solute in the system is constant. In the present report, it is shown under what conditions the zero flux condition provide admissible solutions to the quasi steady (ultimate separation) transport equations.

Particular attention is focused on the value of initial feed composition which admits physically realizable separation factors using the previous (Foo and Rice, 1975) zero-flux theory. The previous work is extended to include a more general temperature dependence in the linear isotherm. Finally, the effects of reservoir dead volume are accounted for in the coupling of the zero-flux and constant mass equations.

ANALYSIS

The analysis proceeds exactly as given previously for the simple binary system except for the introduction of an isotherm of the form

$$q = k(T)\, C^* + a(T) \tag{1}$$

which allows for a temperature dependent intercept. The isotherm parameters are taken to depend on temperature in a linear way:

$$k(T) = k_0 + k_1 T \tag{2}$$

$$a(T) = a_0 + a_1 T \tag{3}$$

The introduction of $a(T)$ into the analysis adds an additional pumping term to the previous work.

The transport equations and nomenclature are unchanged from the previous work (Foo and Rice, 1975), and when perturbation variables of the form

$$C^*(x, r_s, t) = \overline{C}^*(x, r_s) + C^*{}_{+1}(x, r_s)\, e^{i\,\omega t} + C^*{}_{-1}(x, r_s)\, e^{-i\,\omega t} \tag{4}$$

$$C(x, t) = \overline{C}(x) + C_{+1}(x)\, e^{i\,\omega t} + C_{-1}(x)\, e^{-i\,\omega t} \tag{5}$$

$$V(t) = \frac{A\omega}{2}\, e^{i\,\omega t} + \frac{A\omega}{2}\, e^{-i\,\omega t} \tag{6}$$

$$T(t) = \overline{T} - \frac{1}{2} T_b\, e^{i(\omega t + \gamma)} - \frac{1}{2} T_b\, e^{-i(\omega t + \gamma)} \tag{7}$$

are inserted, with products of perturbations neglected as before, the following perturbation function is obtained:

$$C_{+1}(x) = \psi_0 - \psi_1\, \overline{C}(x) - \psi_2 \left(\frac{A\omega}{2}\, \frac{R^2}{\mathfrak{D}} \right) \frac{d\overline{C}(x)}{dx} \tag{8}$$

The transendental functions ψ_0, ψ_1, ψ_2 are given in the Appendix. The new term ψ_0 arises from the temperature coefficient of $a(T)$ [see Equation (22), Foo and Rice, 1975]. Similar to the previous work, the average steady column profile of composition is easily found to be

$$\overline{C}(x) = C_B - \frac{(C_B - C_T)}{1 - e^{uL}}\,(1 - e^{ux}) \tag{9}$$

which is unchanged from the original paper.

ZERO-FLUX CONDITION

As before, the steady $[C(x)]$ and perturbation $[C_{+1}(x)]$ functions are used to compute the time average flux using

$$<J> = \left\langle -\mathfrak{D}^* \frac{\partial C}{\partial x} \right\rangle + <V \cdot C> \rightarrow 0 \tag{10}$$

which, of course, is set equal to zero at the ultimate separation ($t \rightarrow \infty$). When the indicated operations are performed, there results

$$C_B = (e^{-uL} - 1)\, \frac{\text{Real}\,[\psi_0]}{\text{Real}\,[-\psi_1]} + C_T\, e^{-uL} \tag{11}$$

where C_B is average bottoms reservoir composition (rich) and C_T is top reservoir composition (lean).

Previously, $\psi_0 = 0$, and the separation factor $\alpha_\infty = C_B/C_T$ was immediately obtainable from Equation (11). However, an important discovery will result from this lack of simplicity in the current analysis. The dissipation function u is unchanged from the previous work:

$$u = \frac{A\omega\, \text{Real}\,[\psi_1]}{\mathfrak{D}^* + \dfrac{(A\omega)^2}{2}\, \dfrac{R^2}{\mathfrak{D}}\, \text{Real}\,[\psi_2]} \tag{12}$$

In passing, we note that enhancement is built into the numerator of u via ψ_1, while dissipation is reflected in the denominator via $\mathfrak{D}^*$ and ψ_2.

CONSTANT MASS CONDITION

Since we are dealing with a batch parapump system, the total solute in the system (including reservoirs) is constant. As a consequence of the parapumping action, the initial solute in the system is redistributed.

The total mass of solute in the system (including reservoirs) at the completion of separation ($t \rightarrow \infty$) is calculated from

$$M = V_T C_T + V_B C_B + \epsilon_b A_b \int_0^L \overline{C}(x)\,dx + (1 - \epsilon_b) A_b \int_0^L Q(x)\,dx \tag{13}$$

where Q is the solute held in the solid phase (adsorbed plus pore fluid) and is computed from

$$Q = \rho_s (1 - \epsilon_p) [a_0 + a_1 \overline{T} + (k_0 + k_1 \overline{T})\, \overline{C}(x)] + \epsilon_p\, \overline{C}(x) \tag{14}$$

The total solute contents M can also be calculated from the initial feed to the system, taking as the starting point an equilibrium column at temperature $\overline{T}$; hence

$$M = V_T\, C_0 + V_B\, C_0 + \epsilon_b\, A_b\, L\, C_0 + (1 - \epsilon_b) A_b L [\rho_s (1 - \epsilon_p) ((a_0 + a_1 \overline{T}) + (k_0 + k_1 \overline{T}) C_0) + \epsilon_p\, C_0] \tag{15}$$

When the integral is performed in Equation (13), a linear relationship connecting C_T and C_B is obtained:

$$C_B = \Theta_0(u) - \Theta_1(u)\, C_T \tag{16}$$

where

$$\Theta_0(u) = \frac{M - n_0}{V_B - d_0 \left(\dfrac{e^{uL}}{1 - e^{uL}} \right) + d_1/uL} \tag{17}$$

$$\Theta_1(u) = \frac{V_T + d_0 \left(\dfrac{1}{1 - e^{uL}} \right) + d_1/uL}{V_B - d_0 \left(\dfrac{e^{uL}}{1 - e^{uL}} \right) + d_1/uL} \tag{18}$$

and the parameter groups n_0, d_0, d_1 are defined in the Appendix.

Thus, Equation (11) (zero-flux condition) and Equation (16) (constant mass condition) completely define the possible steady state reservoir compositions for the system. Feed composition C_0 enters through the calculation of M from Equation (15).

The admissible solutions to the linear Equations (11) and (16) can be conveniently studied in graphical form as shown in Figure 1. Admissible solutions are defined such that

$$0 \leq y_T \leq 1 \quad \text{and} \quad 0 \leq y_B \leq 1 \tag{19}$$

and intersections of Equations (11) and (16) outside this region are taken to be inadmissible. The definitions of y_T and y_B are somewhat arbitrary and depend on the specific system. For the Sweed-Gregory (1971) system using sodium chloride in water, one would naturally define $y_T = C_T/C_{\text{sat}}$ and $y_B = C_B/C_{\text{sat}}$ where C_{sat} is saturation value for salt solution and, under normal circumstances, is the maximum possible value of composition. For a system which is miscible in all proportions, y_T and y_B would be taken as mass or mole function. The calculation of the dissipation function u proceeds from the specification of fluid displacement (A), frequency (ω), column length (L), and suitable correlations for axial dispersion ($\mathfrak{D}^*$) and transfer coefficient (k_C). The correlations used for ex-

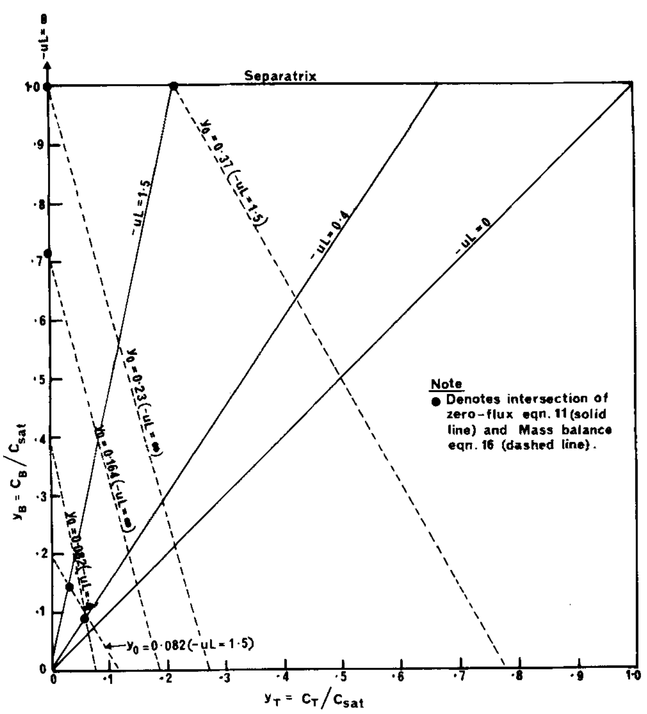

Fig. 1. Illustration of the intersection of the zero-flux and mass balance equations; $y_0 = C_{feed}/C_{sat}$.

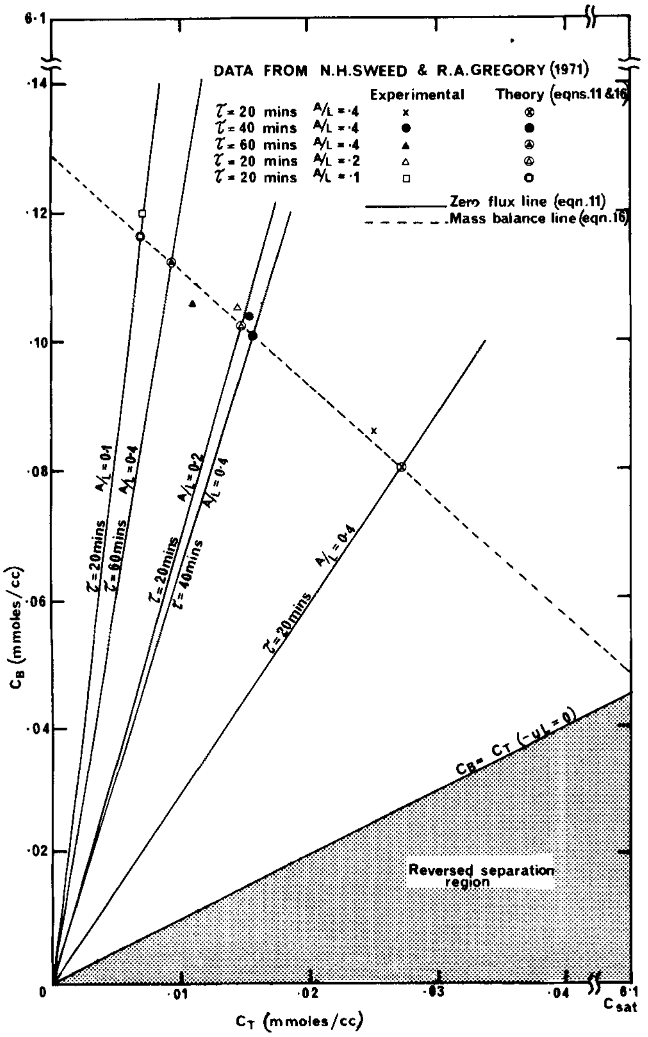

Fig. 2. Comparison of theory and experiment using mass balance constraint; τ is cycle time = 2π/ω.

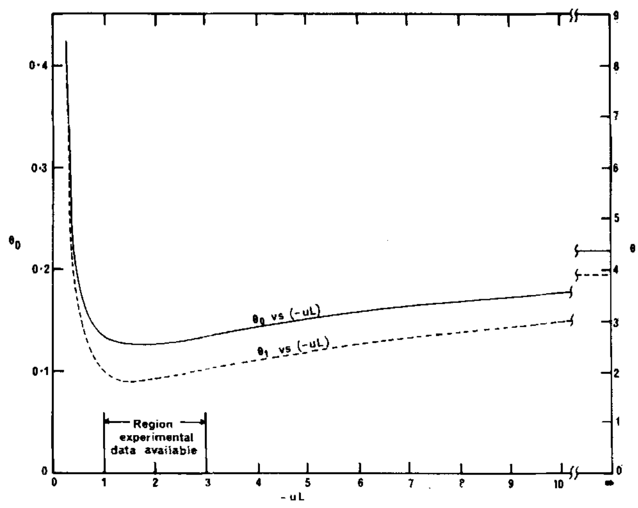

Fig. 3. Relationship of mass balance slope ($-\theta_1$) and intercept (θ_0) to dimensionless dissipation function (*—uL*); note constancy of θ_0, θ_1 in region of experimental data.

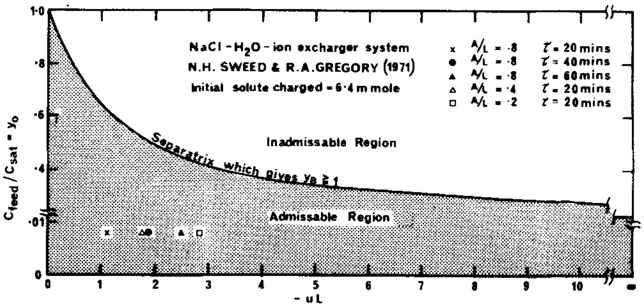

Fig. 4. Admissable feed composition as related to dimensionless dissipation function (*—uL*).

TABLE 1. PHYSICAL PROPERTIES AND ESTIMATED PARAMETERS FOR THE SWEED-GREGORY SYSTEM (1971)

ρ_s	= 1.1 g/ml	L/R	= 109.1
ϵ_b	= 0.36	R/R_s	= 11
ϵ_p	= 0.5	S_c	= 483
k_0	= 1.02 ml/g	V_B	= 25 ml
k_1	= −0.0066 ml/g-°C	V_T	= 25 ml
$\mathfrak{D}/\mathfrak{D}_p$	= 3.44	V_{bed}	= 56.5 ml
τ_b	= 39.2 s	Sc	= 6.1 mmoles/ml

ample calculations in the present study are the same as used previously.

EXAMPLE CALCULATION

To illustrate our findings, we again analyze the experiments of Sweed and Gregory (1971) which appeared to have been successfully accounted for by using the zero-flux theory (Foo and Rice, 1975). In particular, we wish to find under what conditions (if any) the zero-flux relationship produces inadmissible solutions, especially with regard to initial feed composition. Such an analysis is crucial to the design of a parapump system, since intuitively one suspects that feed composition should affect the final separation. As we shall see, for a given separation (specified as a separation factor α_∞), there is the possibility of certain inadmissible feed compositions (reflected as inadmissible values M of total solute mass in the system).

The zero-flux lines [Equation (11)] are drawn in Figure 2 for the conditions corresponding to the Sweed-Gregory (1971) experiments with physical parameters presented in Table 1. For this particular case (see Foo and Rice, 1975), the equilibrium data is such that $\psi_0 = 0$. Each frequency-amplitude combination gives a specific value of u, hence a different slope in the C_T, C_B plane according to Equation (11) [similarly, for Equation (16)]. In the present case, however, the change in Θ_0 and Θ_1 (see Figure 3) for the changing values of u corresponding to experiments is only slight; hence a single constant mass line results as drawn in Figure 2. It is seen that all predictions from the zero-flux relation, Equation (11), are admissible for these experiments. Figure 1 is based on the Sweed-Gregory parameters also and covers a wider frequency spectrum than actually studied by Sweed and Gregory. The changing slope of the mass balance lines is clearly illustrated. Here, also, we see that for the feed composition specified by Sweed and Gregory, the predictions of the zero-flux theory are all admissible.

In Figure 4, the effect of changing feed composition is highlighted. When we use physical parameters corresponding to the Sweed-Gregory system, the regions corresponding to admissible and inadmissible feed composition are seen to depend on uL, the dimensionless dissipation function given by Equation (12). For comparison, the experimental feed composition used by Sweed and Gregory is also presented. The physical interpretation of this important illustration is as follows. If the feed composition [or more generally, total solute mass computed from Equation (15)] is within the admissible region, then the theoretical zero-flux expression, Equation (11), can be used to estimate the maximum possible separation factor, which, for the present data, is

$$C_B/C_T = \alpha_\infty = e^{-uL} \qquad (20)$$

For this particular system, then, the predictions computed by Foo and Rice (1975) using the above Equation (20) are all admissible and do not defy the mass balance constraint, Equation (16).

LIMITING CASES

We have so far considered the special case covered in the previous work (Foo and Rice, 1976), where $\psi_0 = 0$. Hence, effects arising from the temperature dependent isotherm intercept $a(T)$ have not been considered.

Some generalizations can be made in the trends of separation by inspection of the transendental functions ψ_0, ψ_1, ψ_2 (see Appendix) appearing in the general zero-flux expression, Equation (11) (note ψ_2 appears only in u). Normally, the temperature coefficients k_1 and a_1 [see Equations (2) and (3)] are negative; hence Equation (11) shows that increasing ψ_0 (by increasing $|a_1|$) enhances the enriched reservoir composition C_B. Similarly, enhancement occurs when $|k_1|$ increases; however, the increase is more dramatic since, according to Equation (11), the increase proceeds of order $e^{|k_1|}/|k_1|$ Separation increases as k_0 decreases (via H_0), since $-u$ increases conversely as $k_0 \rightarrow \infty$. From this, one concludes that a favorable type of isotherm enhances separation in the high composition region, and the unfavorable type is preferred in the low composition region.

Finally, reverse separation (see Foo and Rice, 1975) can be analyzed from the technique outlined herein; however, intersections of the zero-flux and constant mass equations occur below the line $C_B = C_T$ (see Figure 2), since for reverse separation $[-u]$ takes a negative value.

NOTATION

A_b = cross-sectional area of bed

a_0 = adsorption parameter, defined by Equation (3)

a_1 = adsorption parameter, defined by Equation (3)

C_{sat} = saturation composition of solute

d_0 = group of terms, defined by Equation (A5)

d_1 = group of terms, defined by Equation (A6)

M = total solute mass in system, defined by Equations (13) and (15)

n_0 = group of terms, defined by Equation (A4)

T_b = average bed temperature amplitude = $(T_H - T_C)/2$ if thermal response is instantaneous

V_B = volume bottom reservoir (time average)

V_T = volume top reservoir (time average)

V_{bed} = fluid interstitial volume in bed (excluding solid pore volume)

Greek Letters

α_∞ = C_B/C_T, ultimate separation factor

ψ_0 = transendental function defined by Equation (A1)

ψ_1 = transendental function defined by Equation (A2)

ψ_2 = transendental function defined by Equation (A3)

Θ_0 = defined by Equation (17)

Θ_1 = defined by Equation (18)

A complete detailed description of all other symbols is given in the original paper (Foo and Rice, 1975).

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APPENDIX

$$\psi_0 = \frac{1}{2}\left[\frac{\rho_s(1-\epsilon_p)a_1}{\epsilon_p(1+H_0)}\right] \frac{Sh\, T_b\, e^{i\gamma}\,[z_{+1}\cot(z_{+1}) + Nu_p - 1]}{[z_{+1}\cot(z_{+1}) - 1](Sh + i\,Pe_M) + i\,Nu_p\,Pe_M} \qquad \text{(A1)}$$

$$\psi_1 = -\frac{1}{2}\left(\frac{H_1}{1+H_0}\right) \frac{Sh\, T_b\, e^{i\gamma}\,[z_{+1}\cot(z_{+1}) - 1]}{[z_{+1}\cot(z_{+1}) - 1](Sh + i\,Pe_M) + i\,Nu_p\,Pe_M} \qquad \text{(A2)}$$

$$\psi_2 = \frac{z_{+1}\cot(z_{+1}) - 1 + Nu_p}{[z_{+1}\cot(z_{+1}) - 1](Sh + i\,Pe_M) + i\,Nu_p\,Pe_M} \qquad \text{(A3)}$$

$$n_0 = \rho_s(1-\epsilon_b)(1-\epsilon_p)\,V_{\text{bed}}\,(a_0 + a_1\overline{T}) \qquad \text{(A4)}$$

$$d_0 = V_{\text{bed}}\,[\epsilon_b + \rho_s(1-\epsilon_b)(1-\epsilon_p)(k_0 + k_1\overline{T}) + \epsilon_p(1-\epsilon_b)] \qquad \text{(A5)}$$

$$d_1 = \epsilon_b + \rho_s(1-\epsilon_b)(1-\epsilon_p) + \epsilon_p(1-\epsilon_b) \qquad \text{(A6)}$$

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