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An Equilibrium Theory on Separation Via Thermal Parametric Pump : Part III. The Model Equations

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Abstract

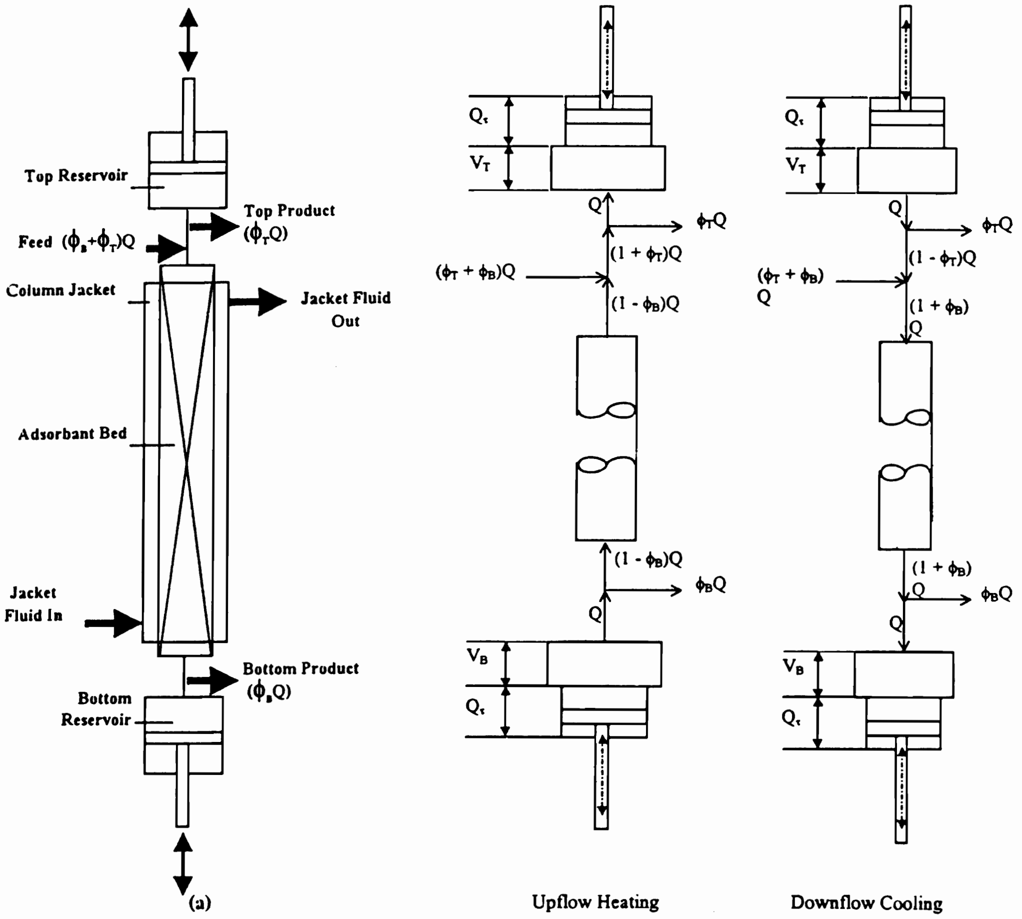
A research work in which a computational method developed for predicting continuous equilibrium parametric pump performance for proteins separation was carried out. The method was based on a set of exterior solute material balances, the equations of change for the two-phase system and a linear adsorption isotherm for the solute-solvent-adsorbant system. The method of characteristics was combined with a finite difference approximation to solve the equations of change. There was good agreement between predicted and experimental results.

Introduction

The field of parametric pumping process-a separation process where the inherent ability of a particular two-phase system is enhanced by synchronizing an oscillating direction of interphase mass transfer with an oscillating direction of fluid flow-has received considerable attentions in recent years. The result is a spatial separation of the components of an initially homogenous fluid mixture into two mixtures; one lean and the other concentrated in solute. The direction of interphase mass transfer can be made to oscillate by periodically changing the algebraic sign of the driving force, i.e. by periodically changing the positionb of physical equilibrium. This coupling of two directional physical phenomena is central to the uniqueness of the parametric pumping process.

The simplest parametric pump is batch operated and will illustrate the coupling action. From a fluid mixture of two components, A and B, suppose it is desired to remove component A which is preferentially adsorbed on solid S held fixed in the column as pictured in Figure 1. Suppose that the position of interphase equilibrium is highly temperature dependent. Let the temperature of the two-phase system be made to change periodically with time by alternately heating or cooling the system by applying some heat transfer media of appropriate temperature to the column jacket. Then the concentrations of A in the liquid, y, and on the solid, x, will periodically adjust themselves to new values in response to the change in the thermodynamic state of the system induced by temperature changing. Usually, A will be adsorbed on S when the system is cooled and desorbed when the system is heated.

Theoretical treatment of parametric pumping processes in system where interphase mass transfer is rapid has largely been based on the work of Pigford, Baker, and Blum (Gregory and Sweed, 1972). They applied a theory of operation to the batch parametric pump based on the assumption that interphase mass transfer was so rapid that local fluid-solid equilibrium existed every where in the bed at all times. They showed that the solute traveled through the adsorbant bed in sharply defined wave fronts whose distance of penetration into the column could be theoretically established. Chen and Hill (1971) then extended the analysis to semi-continuous and continuous parametric pumps. In the former case, portions of the lean and



Upflow Heating Half-cycle (b)

Downflow Cooling Half-cycle (c)

Figure 1 Diagram of column for batch parametric pumping in direct mode concentrated products are removed intermittently from the lower and upper reservoirs, respectively, during one or both half-cycles of operation. Also, a feed stream of constant composition is introduced intermittently during a portion of one or both half-cycle. In the continuous case, a fluid of composition Y_O is continuously fed into the dynamically coupled thermodynamic changer fluid flow field. The product streams are then removed continuously from the top and bottom of column at compositions Y_{TP} and Y_{BP}, respectively. The feed is introduced and the products are removed at such a rate that the fluid volume contained in the system remains constant.

Attempts to theoretically treat the non-equilibrium case have all been based on reducing the model equations (partial differential equations) to linear ordinary form and solving them numerically. Sweed and Gupta (Chen, *et al.* 1980) had developed a mixing cell algorithm and a near-equilibrium model as alternates to the STOP-GO algorithm. In the present work, the method of characteristics is combined with a numerical solution based on Euler's method to predict parametric pump behavior for a non-equilibrium system.

In the present work, completely continuous parametric pumping was applied to the same physical-chemical system. Whereas in Gregory's study, no product flow or intermittent product flow was obtained during certain portions of each half-cycle of operation, this work treated the case where lean and concentrated products existed from opposite ends of the adsorbent bed in a continuous manner. Using the method described above to solve the model equations, it is shown that, under non-equilibrium operation the solute moved through the bed in a diffuse manner; no sharply defined wave fronts were found to exist. Limited but steadily decreasing separations were achieved where loading of the adsorbent bed by solute during a cold half-cycle was exceeded by the capacity for removal of solute from the bed during the next hot half-cycle, in agreement with the general trend of Gregory's results. However, when operating outside the range of Gregory's work, a limited separation of steadily decreasing magnitude was found to exist. This result was related to the situation where column loading during the cold half-cycle exceeded regenerative action during the next hot half-cycle. A gradual buildup of solute in the adsorbant bed was noted in these cases and it is found that the active variables in changing the ability of the column to purge itself of adsorbed solute was the rate of lean product withdrawal. The effects of cycle time, reservoir displacement, and column height on separation were examined and comparisons with the equilibrium theory were made.

Theory

From figure 1 (a) at the feed point, during the up-flow half-cycle

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

and for a successive upflow-downflow sequence, at the top reservoir,

$$Q\tau\langle y_{TP1}\rangle_n+V_T\langle y_{TP2}\rangle_{n-1}=(Q\tau+V_T)\langle y_{TP2}\rangle_n \quad ....(2)$$

Dividing (2) through by $Q\tau$ and letting C_T=V_T, equation (2) can be rearranged to obtain

$$\langle y_{TP2}\rangle_n=(\frac{1}{1+C_T})\left[(\frac{1-\phi_B}{1+\phi_T})\langle y_{T1}\rangle_n+(\frac{\phi_B+\phi_T}{1+\phi_T})y_0\right]+(\frac{C_T}{1+C_T})\langle y_{TP2}\rangle_{n-1} \quad ....(3)$$

Where, for n = 1, $\langle y_{T1}\rangle_1=\langle y_{TP2}\rangle_0=y_0$, equation (3) gives the cold half-cycle top product for cycles 1 through n. To obtain the column top boundary condition for the n-th cold half-cycle, we make a downflow material balance at the feed point,

$$(1-\phi_T)\langle y_{TP2}\rangle_n+(\phi_T+\phi_B)y_0=(1+\phi_B)\langle y_{T2}\rangle_n \quad ...(4)$$

From Figure 1(b) for the downflow cold cycle, we see that

$$\langle y_{BP2}\rangle_n=\langle y_{B2}\rangle_n \quad ....(5)$$

and a material balance on the bottom reservoir for a successive downflow-upflow sequence gives

$$Q\tau\langle y_{BP2}\rangle_n+V_B\langle y_{BP2}\rangle_{n-1}=(V_B+Q\tau)\langle y_{B1}\rangle_{n+1} \quad ....(6)$$

Rearranging by letting $C_B = V_B/Q_\tau$ to obtain the hot halt-cycle boundary condition,

$$\langle y_{B1}\rangle_n=(\frac{1}{1+C_B})\langle y_{BP2}\rangle_{n-1}+(\frac{C_B}{1+C_B})\langle y_{BP2}\rangle_{n-2} \quad ....(7)$$

where for n = 1, $\langle y_{BP2}\rangle_0=\langle y_{BP2}\rangle_0=y_0$

Equations (3) and (5) are used to calculate the cold half-cycle product concentrations. The equation of continuity for the two-phase solution-adsorbant system – neglecting axial diffusion, radial concentration gradients, and variation of fluid density with concentration-is

$$\varepsilon v\frac{\partial y}{\partial z}+\varepsilon\frac{\partial y}{\partial t}+(1-\varepsilon)\rho_s\frac{\partial x}{\partial t}=0 \quad ....(8)$$

For adsorption process where liquid film resistance to mass transfer is rate controlling, the interphase transport of the adsorbed component of the fluid mixture is said to be driven by departure of the actual liquid concentration from the equilibrium liquid concentration for the existing solid concentration. Thus,

$$\frac{\partial x}{\partial t}=\lambda(y-y^*) \quad ....(9)$$

In general, the mass transfer coefficient, λ, is a function of liquid phase physical properties, solid geometry, and liquid velocity. The principal parameters of interest in the case of parametric pumping are temperature effects on fluid properties and fluid velocity since they will be markedly different for the hot and cold temperature half-cycles.Concentration effects on fluid properties can be ignored for dilute solutions and moderate ranges of concentration.

The equation relation the existing solid concentration to an equilibrium liquid concentration is given by the adsorption isotherm for the liquid-solid system at the temperature of interest. It the form of adsorption isotherm is linear, $y^* = x/m$, by substituting y^* in equation (9) and combining with (8), then

$$v\frac{\partial y}{\partial z}+\frac{\partial y}{\partial t}+(\frac{1-\varepsilon}{\varepsilon})\rho_s\lambda(y-\frac{x}{M})=0 \qquad ....(10)$$

Equations (9) and (10) can be reduced to a more manageable form by introducing a new variable, z defined by (Butts *et al.* 1972; and Chen, *et al.* 1976)

$$\bar{z} = z/v \qquad ....(11)$$

Then, by the chain rule

$$\frac{\partial y}{\partial z}=\frac{\partial y}{\partial \bar{z}}\frac{\partial \bar{z}}{\partial z}=\frac{1}{v}\frac{\partial y}{\partial \bar{z}} \qquad ....(12)$$

So

$$\frac{\partial y}{\partial \bar{z}}+\frac{\partial y}{\partial t}=-(\frac{1-\varepsilon}{\varepsilon})\rho_s\lambda(y-\frac{x}{M}) \qquad ....(13)$$

Now consider two families of curves, $\partial t/\partial\bar{z} = 1$ and $\partial\bar{z}/\partial t = 0$, in the $\bar{z} - t$ plane in which along any direction,

$$\frac{dy}{dz}=\frac{\partial y}{\partial z}+\frac{\partial y}{\partial t}\frac{\partial t}{\partial z} \qquad ....(14)$$

and

$$\frac{dx}{dt}=\frac{\partial x}{\partial t}+\frac{\partial x}{\partial z}\frac{\partial z}{\partial t} \qquad ....(15)$$

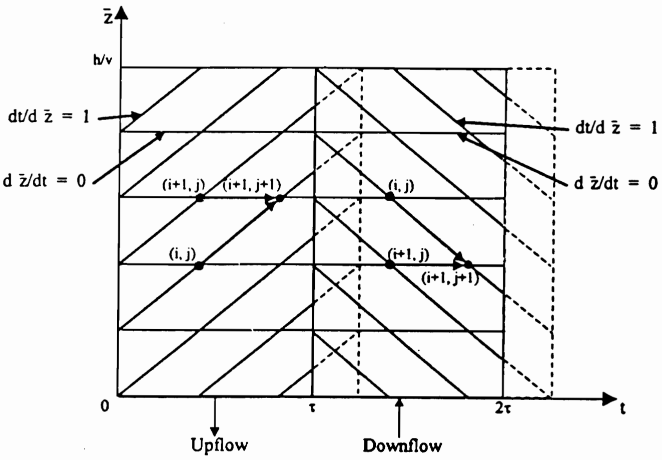


Figure 2 Upflow and downflow characteristics

Therefore

....(16)

and

$$\frac{dy}{dz}=-(\frac{1-\varepsilon}{\varepsilon})\rho_s\lambda(y-\frac{x}{M})$$

....(17)

$$\frac{dx}{dt}=\lambda(y-\frac{x}{M})$$

Equations (16) and (17) now form a set of ordinary differential equations which can be solved numerically to obtain x and y as functions of $\bar{z}$ and t. The boundary and initial conditions are revised to reflect the new independent variables as follows:

a) initial conditions,

$$@t = 0,\quad \bar{z} \geq 0, y = y(\bar{z}) \qquad ....(18)$$

$$@t = 0,\quad \bar{z} \geq 0, x = x(\bar{z}) \qquad ....(19)$$

b) upflow boundary conditions,

$$@\ \bar{z} = 0,\ t \geq 0, y = \langle y_{B1} \rangle \qquad ....(20)$$

c) downflow boundary conditions,

$$\left.\frac{dx}{dt}\right|_{\bar{z}=0} = \lambda_1 (\langle y_{B1} \rangle - \frac{x}{M_1}) \qquad ....(21)$$

$$@\bar{z} = h/v_2, t \geq 0, y = \langle y_{T2} \rangle \qquad ....(22)$$

$$\left.\frac{dx}{dt}\right|_{\bar{z}=h/v_2} = \lambda_2 (\langle y_{T2} \rangle - \frac{x}{M2}) \qquad ....(23)$$

APPLYING THE MODEL

Initial Condition

At time zero the system is at equilibrium at the high temperature with the liquid concentration everywhere equal to the feed composition. The process is initiated by a hot upflow half-cycle to further insure establishment of the equilibrium condition. No mass transfer takes place; the system remains at equilibrium at the higher temperature and the concentration of the effluent from the column top remains constant at y_o.

Cold Downflow Half-Cycle

The initial axial concentration profiles for this first cold half-cycle are

$$y = y_0 \quad \text{and} \quad x = y_0/M_1$$

and the liquid concentration at the column top, the downflow boundary condition is

$$\langle y_{T2} \rangle = y_0$$

Starting at the column top (z = h), equation (23) is solved analytically giving the solid-phase concentration , x, as function of time, to yield

$$x = M_2 \langle y_{T2} \rangle \left[1 - (1 - \frac{M_1}{M_2}) \exp(-\frac{\lambda_2 t}{M_2}) \right] \qquad ....(24)$$

Hot Upflow Half-Cycle

Once the cold half-cycle is completed, the initial axial concentration profiles for both the liquid and solid phases are then established for the succeeding hot half-cycle. In a manner similar to that employed for the previous cold half-cycle, Solution of (21) establishes the solid phase boundary condition at the column bottom for each time interval. The solution is

$$x=M_1\left\langle y_{B1}\right\rangle\left[1-\left(1-\frac{M_2}{M_1}\right)\exp\left(-\frac{\lambda_1 t}{M_1}\right)\right] \qquad ....(25)$$

Product Concentration

The estimation of the cold half-cycle product concentrations requires knowledge of the average concentration of the column effluent for each half-cycle. This average is easily computed for r finite difference time intervals for the column top by

$$\left\langle y_{T1}\right\rangle = \left(\sum_{i=1}^{r_1} y_{Ti}\right)/r_1 \qquad ....(26)$$

$$\left\langle y_{B2}\right\rangle = \left(\sum_{i=1}^{r_2} y_{Bi}\right)/r_2 \qquad ....(27)$$

Computer Solution

The computer program was devised to carry out the calculations. Values for the relevant physical parameters are read initially into the program, these being hot and cold temperatures, column height, reservoir displacement, half-cycle time, product withdrawal ratios for top and bottom, and feed composition. The equilibrium parameters were calculated as a function of temperature. Using the bed cross-section, solids void fraction, reservoir displacement rate and half-cycle time, fluid velocities for both half-cycles were calculated via the relations

$$V_1 = Q(1-\phi_B)/A \qquad ....(28)$$

and

$$V_2 = Q(1+\phi_B)/A \qquad ....(29)$$

Results and Discussion

Computer solution of the model equations was used to generate performance curve for the continuous parametric pump at various values of the operating parameters of interest in this study. These performance curve gave the variation in solute separation, i.e., top and bottom product concentrations for the cold-and half-cycle, with number of cycles and were then compared with the results of experimental runs to establish the efficiency of the model equations in predicting parametric pump performance.

EFFECTS OF HALF-CYCLE DURATION

It is apparent that maximum separation of solute between the lean and concentrated product streams was achieved when the adsorbant column is operated at equilibrium. From the graphical representation of the data on Figure 3, it is apparent that longer half-cycle times gave markedly better separations and that assuming non-equilibrium operation for the 24-minute half-cycle time was justified. Figure 3 also compared the separation predicted by the model equations with the experimental data, showing a reasonable fit to the data and indicating that the model equations, do, in fact predict the same trend as do the experimental results.

From the graphical representation of the experimental data on Figure 3, for low bottom product withdrawal rates (ϕ_B = 0.04), the bottom product concentration curve had a monotonically decreasing character, matched – within reason – by the behavior predicted by the computational model. For high bottom product withdrawal rated (ϕ_B = 0.28), the characteristic degenerating separation was the case both theoretically and experimentally.

EFFECTS OF BOTTOM PRODUCT WITHDRAWAL RATE, ϕ_B

There are no sharply defined wave fronts along the axis of a non-equilibrium adsorption column. Axial concentration gradients are continuous and smooth, and their shape is time-dependents as well. However, penetration theory may also apply, in a qualitative sense, to the non-equilibrium case. If, on the average, downward movement of solute along the column's axial length is greater during the cold half-cycle than upward movement of solute on the hot half-cycle; solute will tend to migrate toward the bottom of the column, having the same disruptive effect on separation as in the equilibrium case. The bottom product withdrawal rate, ϕ_B, is the principal variable affecting the relative movement of liquid along the column axis between the hot and cold half-cycles since the velocities of the cold and the hot flowing fluid, respectively, are given by

$$V_1 = \frac{Q}{\varepsilon A}(1 - \phi_B) \qquad \text{....(30)}$$

and

$$V_2 = \frac{Q}{\varepsilon A}(1 + \phi_B) \qquad \text{...(31)}$$

Movement of solute is affected by the rate of interphase mass transfer as well as fluid velocity (bulk flow), but it will be shown that the bottom product withdrawal rate has the above described effect on separation.

The next series of experimental runs were designed to examine this effect of total liquid displacement and column length on separation of solute into lean and concentrated products. Figure4-6 showed the experimental and calculated results for a given column height and reservoir displacement, the bottom product withdrawal rate was varied across a wide range (0.04 $\leq \phi_B \leq$ 0.28). The column heights were 90, 60, and 30 cm, respectively.

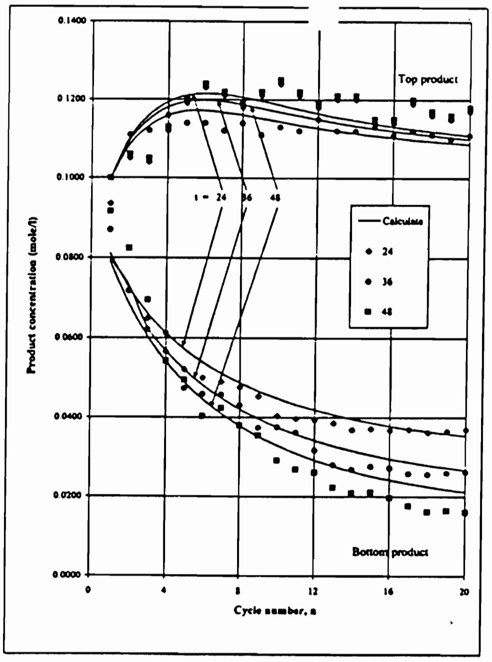


Figure 3 Effects of Half-Cycle Time on Separation

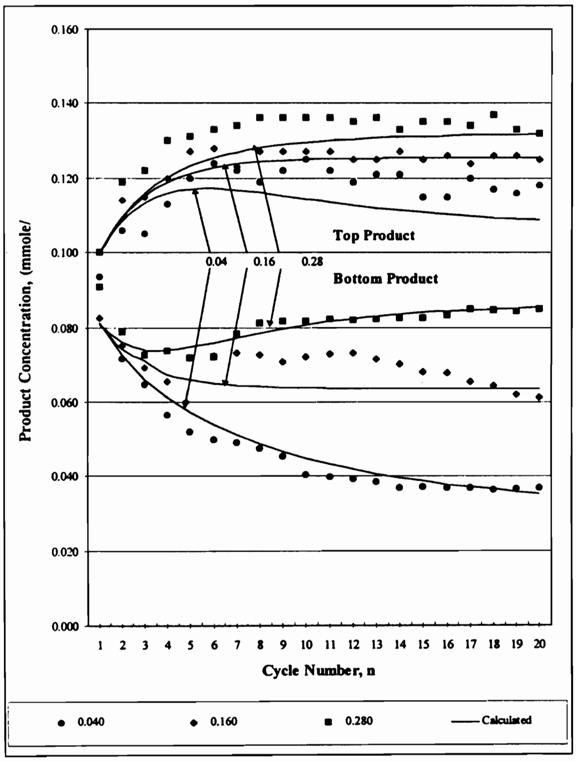


Figure 4 Effects of Bottom Product Withdrawal Rate on Separation, 90-Cm Column

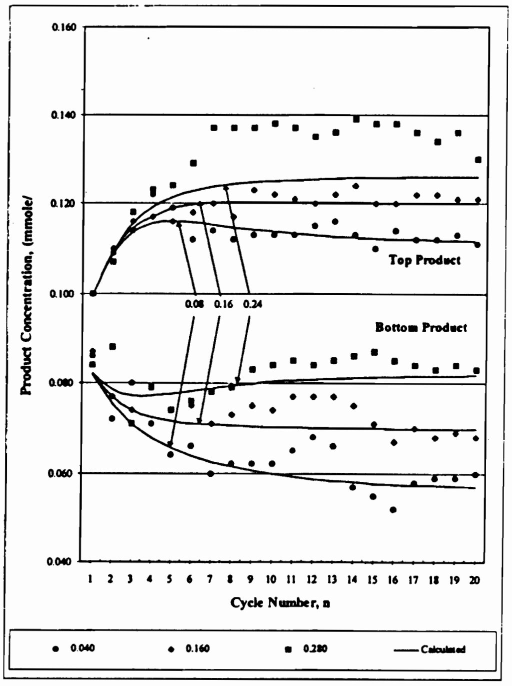


Figure 5 Effects of Bottom Product Withdrawal Rate on Separation, 60-Cm Column

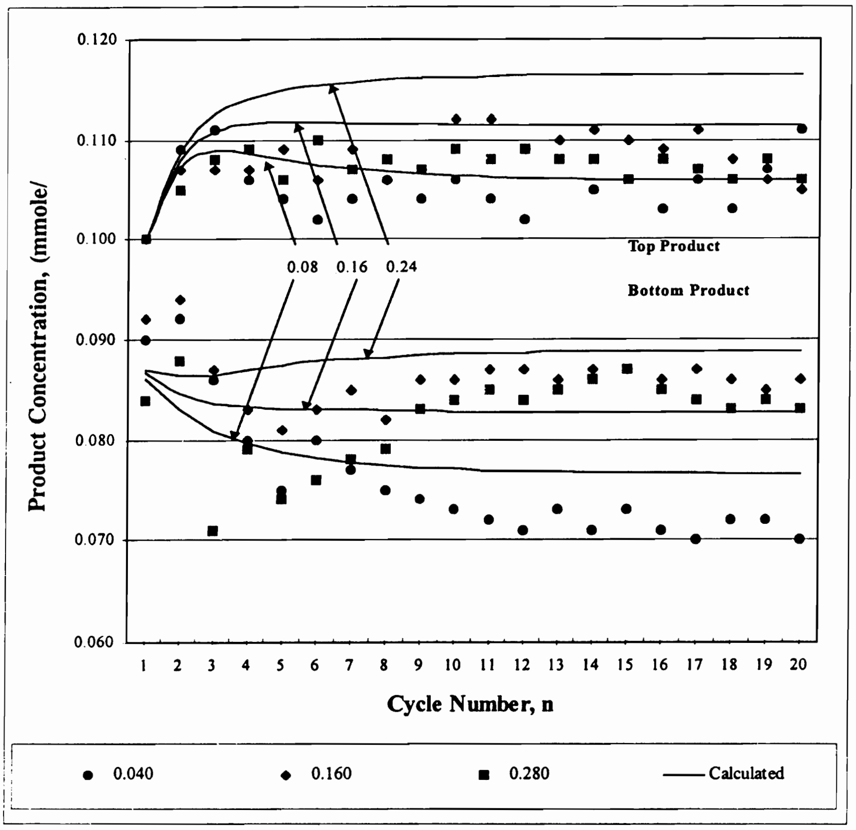


Figure 6 Effects of Bottom Product Withdrawal Rate on Separation, 30-Cm Column

The results show that a reasonable fit of the model to the experimental data was obtained and the same qualitative behavior showed up. For low bottom product withdrawal rates ($\phi_B = 0.08$), a steadily decreasing bottom product concentration was shown to exist; in other words, the lean product concentration decreased with increasing number of cycles. But for a high bottom product withdrawal rates ($\phi_B = 0.24$), a minimum in bottom product concentration existed and separation was seen to degrade thereafter with increasing number of cycles.

EFFECTS OF RESERVOIR DISPLACEMENT, Q

A final series of experiments was conducted at $\phi_B = 0.04$ for various reservoir displacements holding the column length constant at 90 cm. Figure 7 compared the experimental results with the model equations and showed a good agreement between experimental and predicted results.

Sweed had reported an interesting aspect of batch non-equilibrium parametric pump operation. He had shown that the ultimate separation factor, defined as the ratio of top product solute concentration to bottom product solute concentration after many cycles of separation was maximized at a particular value of reservoir displacement. For bis-direction mode batch parametric pumps, the maximum separation appeared to occur where the reservoir displacement equaled the column void volume. At reservoir displacement greater than the column void volume, separation diminished because fluid breakthrough occurs from one end of the column to the other. The poorer separations at reservoir displacements less than the column void space were not explained.

The same results had obtained in the continuous case by using the model equations to calculate product concentrations at various reservoir displacements. The conditions chosen for the calculations were the reservoir displacement changed over the range 45 cm^3 to 5.0 cm^3 for a 1.0 cm diameter by 90 cm long column (void volume = 27 cm^3).

The steadily decreasing separation factor for $Q>25\ cm^3$ is apparently due to the breakthrough of solute from the concentrated to the lean end of the column during the cold half-cycle. Obviously, where the reservoir displacement is less than the column void space, the fluid contained in the column has more than one "pass" across the adsorbant surface, which it undergoes on successive cold half-cycles. Due to it has been shown earlier that a steadily decreasing solid and liquid phase concentration gradient exists in the column at the chosen value of bottom product withdrawal, it is clearly that proportionately more solute can be transferred from the liquid to the solid as it is subjected to more extensive contact with the liquid phase.

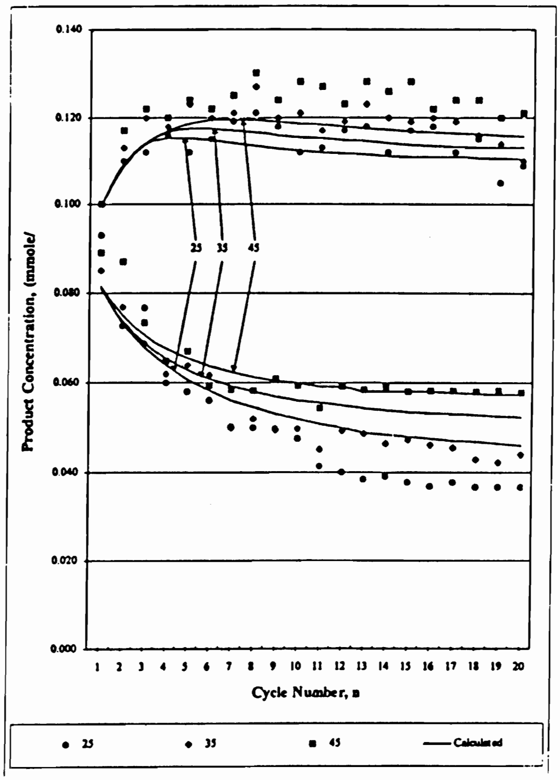


Figure 7 Effect of reservoir displacement on separation : h = 90 cm., ι = 24 min,ϕ_B = 0.04, and ϕ_T=0.36

Summary of Conclusions

THE THEORETICAL MODEL

This work establishes the reliability of the model equations for predicting the behavior of continuous non-equilibrium parametric pumps. The model is based on the equations of change for the liquid-solid system with the diffusion term of negligible importance, a liquid-film controlling mass transfer rate expression, and a linear equilibrium relation between the liquid and solid phases. Gregory had previously established the reliability of the same model equations for batch and semi-continuous parametric pumps.

This work further establishes the reliability of the method of characteristics for resolving the model equations into a set of four algebraic relations governing liquid boundary conditions and a set of two finite-difference expressions governing internal column operation. Gregory's study of batch and semi-continuous parametric pumps made use of a STOP-GO algorithm for solution of the internal equations and a set of material balance relations for the external equations, which were particular to his experimental set-up.

The agreement between the experimental results and the behavior predicted by the model equations is good. The qualitative differences between separations achieved under varying operating conditions are correctly predicted by the model expressions. The investigation of internal pump operation using the model equations leads to meaningful interpretation of the behavioral differences noted from experiment to experiment.

Better separation, i.e. leaner bottom product and more concentrated top product, is achieved at longer half-cycle times. Whereas poorer separation is achieved when the reservoir liquid displacement per half-cycle exceeds the liquid volume in the adsorbent bed. This conclusion matches that of Gregory for his batch and semi-continuous operations.

Acknowledgment

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