Journal of Metals, Materials and Minerals. Vol. 7 No. 2, pp.1-16, 1998.

An Equilibrium Theory on Separation Via Thermal Parametric Pump : Part II

Ura PANCHAROEN

Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University

Abstract

This work studied the removal of sodium chloride from its aqueous solution by utilizing the continuous parametric pump together with an amphoteric ion exchange resin. It is found that the separation is dependent on the half-cycle, time, the relative amounts of liquid fed to the adsorbent bed on the cold and hot half-cycles, and the permanence of the fluid and solid-phase concentration gradients imposed on the column by the coupled mass-transfer fluid-flow process. It is apparent for these pumps that the feed may be introduced to the column at either end. However, introducing the feed solution at the lean end of the column would enrich a stream already depleted in *A* with additional solute, thereby reducing the effect of the separation.

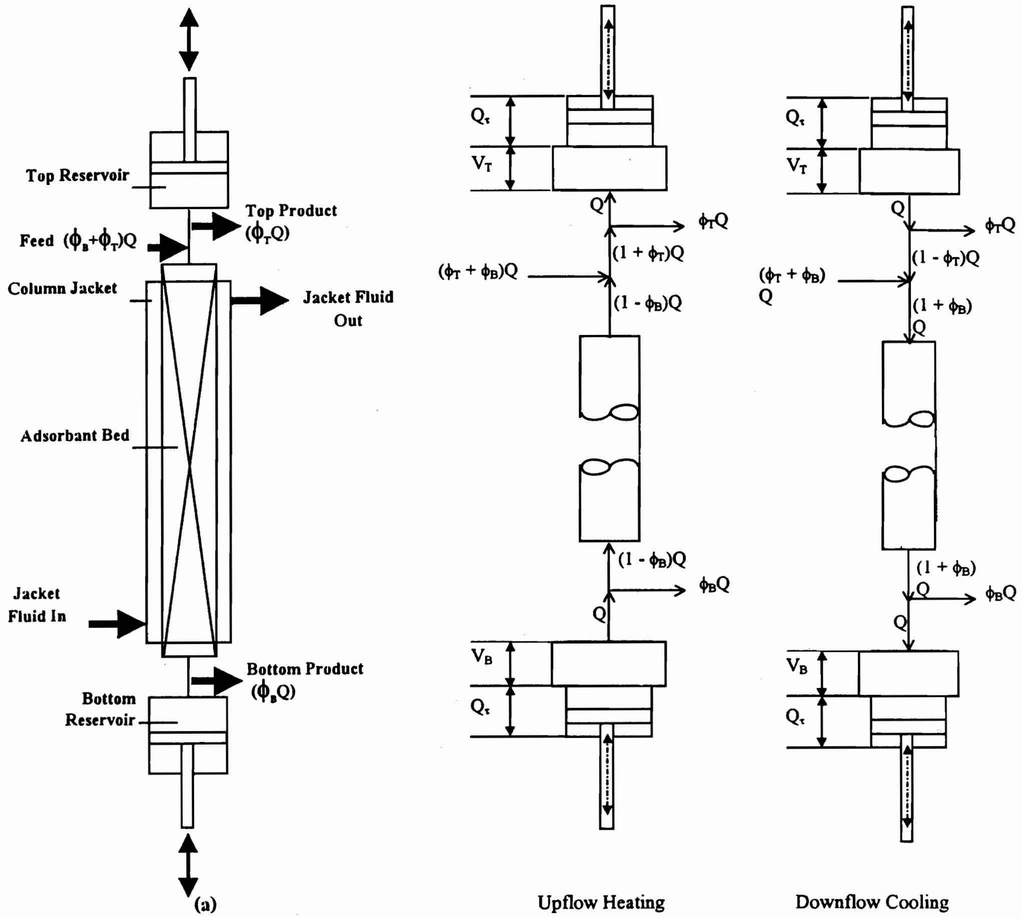
Introduction

In recent years, considerable attention has been paid to the field of parametric pumping in which the inherent ability of a particular two-phase system to achieve separation of the components in a fluid mixture is enhanced by synchronizing an oscillating direction of interphase mass transfer with an oscillation direction of fluid flow. As a result, a special separation of an initially homogeneous fluid mixture into two mixtures can be achieved,one is lean and the other is 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 position of physical equilibrium. This coupling of two direction physical phenomena becomes the uniqueness of the parametric pumping process.

The simplest parametric pump illustrating the couple action is batch operated.. Suppose it is desired to remove the component *A* from a fluid mixture of *A* and *B*. *A* is preferentially adsorbed on solid *S* which is held firmly in the column.

Usually, *A* will be adsorbed on *S* when the system is cooled and desorbed when the system is heated. The column interstitial space and the two piston-operated fluid reservoirs at either end of the column are filled with the fluid mixture at some initial concentration of *A*, y_0. Assume that the position of interphase equilibrium is highly temperature dependent.

The temperature of the two-phase system is made to change periodically with time by alternately heating and cooling the system by applying some heat-transfer medium of appropiate temperature to the column jacket. Then the concentration of *A* in the liquid, y, and the concentration of *A* on the solid, x, will periodically adjust themselves to new values in response to the change in the thermodynamic state of the system which is induced by changing temperature.



Upflow Heating Half-cycle (b)

Downflow Cooling Half-cycle (c)

Figure 1 Diagram of column for batch parametric pumping in direct mode

Now let the direction of flow of the fluid be changed periodically with time by the piston arrangement shown in Figure 1 and the direction of flow be synchronized with the system temperature, e.g. flow only upward when heating and only downward when cooling. Then the fluid enclosed in the column interstitial space will be depleted in *A* by adsorption on *S* only when it moves downward and be enriched in *A* by desorption from *S* only when it moves upward. After successive application of the hot upflow and cold downflow intervals, the fluid depleted in *A* migrates to the bottom of the column while the fluid enriched in *A* migrates to the top. The result is a net displacement of component *A* to the top of the column after a number of synchronized temperature-flow cycles. Thus the separation of the system fluid into a fraction relatively lean in *A* at the bottom of column and a fraction relatively concentrated in *A* at the top of column has been achieved.

The feed flows to the column top at a constant rate, $(\phi_T+\phi_B)Q$; referring to Figure 1 (b); where Q is the reservoir displacement rate which is equal for both the top and the bottom of column, respectively. The product streams are located at the reservoirs themselves, so that reservoir discharge product flows only from the reservoir and not from the column discharge or feed streams. The column is heated during upflow for a period of time, *I*, and is cooled during downflow for an equal time interval so that a product lean in *A* can be taken from the column bottom and one enriched in *A* from the column top. During the hot upflow half-cycle, the concentration of the effluent from the column top varies with time and generally behaves as a desorption-breakthrough curve, while the concentration of the fluid entering the column bottom is constant. The effluent mixes with feed solution before a portion of the combined stream is taken off as the top product. The remainder of the stream enters the top reservoir, where it is mixed with the solution from the previous cold cycle that has remained in the top reservoir "dead volume." Meanwhile, from Figure 1 (c), during the ensuring cold half-cycle, a portion of the stream leaving the top reservoir is removed as the top product before the remainder mixes with feed solution to form the constant concentration influent to the top column. The concentration of the effluent from the column bottom varying with time behaves much like an adsorption-breakthrough curve. A portion of this stream is removed as the bottom product and the remainder enters the bottom reservoir where it is mixed with the solution that has remained in the bottom reservoir dead volume from the previous hot half-cycle. During the ensuring hot half-cycle, a portion of the effluent from the bottom reservoir is again removed as the bottom product while the remainder forms the constant concentration influent to the column bottom.

In 1968, Wilhelm and Sweed [Sweed and Rigaudeau, 1975] showed that the ability of a solid adsorbant to achieve separation of the components of a fluid mixture could be greatly enhanced by utilizing parametric pumping. Using silica gel adsorbent and the direct mode on a batch system, toluene was separated from n-heptane. The experimental results which showed the large separations were analyzed by the means of STOP-GO computer algorithm [Sabadell and Sweed, 1970]. In this method a numerical solution is derived from the model equations by dividing each half-cycle into a number of time increments. Each half-cycle was treated as a small flow displacement with no interphase mass transfer and followed by a period of mass transfer with no flow.

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 with 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.

When operating beyond the range of Gregory's work, however, 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 the regenerative action during the next hot half-cycle. In this case, a gradual buildup of solute in the adsorbant bed was noted and it is found that the active variables in changing the ability of the column to purge itself of adsorbed solute is the rate of lean product withdrawal. The effects of cycle time, reservoir displacement and column height on separation were examined.

Experimental method

THE EXPERIMENT SYSTEM

Sodium Chloride could be removed from its aqueous solution by attachment of the ionic species to a suitable solid phase, such as BioRad AG11A8 Ion Retardation Resin. The resin is an "amphoteric ion exchange resin" which contains an equal number of positively and negatively charged sites within the resin matrix. Ionic species are attracted to sites of opposite charge (rather than exchanged for another ion of like charge) in such a way that ionic neutrality is maintained in both liquid and solid phases. The ionic species, then, diffuse through a liquid film surrounding the resin particle and react electro-chemically with the ionic fragment of opposite charge connected to the resin matrix. The diffusion is a slow step while the reaction is the rapid step. The desorption reaction follows the reverse sequence. The rapid electrochemically dissociation is followed by a relatively slow diffusion through the liquid film to the bulk of the surrounding liquid.

Uncomplicated, therefore, by counter-diffusion of the exchanged ionic species or by the presence of fluid-phase reactions involving the exchanged species (H^+ and OH^-, for example); the interphase mass transfer can be viewed as one of which the diffusion across the liquid film surrounding the solid particle is the controlling resistance, and of which the concentration difference between bulk liquid and the liquid corresponding to the existing local solid concentration is the driving force.

DESCRIPTION OF APPARATUS

The laboratory continuous parametric pump was shown in Figure 2. A 1.0 × 90.0 cm adjustable length jacketed glass column (A) was packed to a specified height with 40 — 80 mesh BioRad AG11A8 Ion Retardation Resin in equilibrium at room temperature with aqueous sodium chloride solution of feed concentration. The reservoirs at either end of the column (B and C for top and bottom, respectively) creating the axial flow displacement were 50 cm^3 Becton-Dickenson Multi-Fit glass syringes driven by a Harvard Apparatus variable speed infusion-withdrawal pump set (D) for reciprocal operation. While the plunger at C ran in the forward direction, emptying C, the plunger at B withdraw, filling B, and vice versa. The reservoir displacement rate was set by adjusting the speed of the drive mechanism. The syringe plungers were lightly greased with Dow-Corning flouro-silicone stopcock grease. To ensure that both reservoirs were well mixed, the small teflon-coated magnetic stirring bars were placed in the syringes and driven by water-activated magnetic stirrers.

The synchronous temperature changes within the column were achieved by supplying the column jacket with 70°C water during upflow and 5°C water during downflow. The hot and cold water sources were constant temperature baths (E and F for hot and cold baths, respectively). The hot-bath temperature was maintained by a George Ulanit Co. Heetgrid electric immersion heater (G) and the cold-bath temperature by a Neslab Instrument U-Cool refrigerated cooling coil (H). Both temperatures were regulated by HB Insturment Co. Quickset temperature controllers (I). Little Giant submerged centrifugal pumps (J) circulated the water to and from the baths. Two check valves (K) at the column jacket entrance prevented the baths from mixing while the stopcock valves (L) at the column jacket exit insured the return of jacket fluid to the proper bath.

The fluid feed was delivered to the column top by a Chemical Apparatus Co. Vibrostaltic laboratory pump (M) whose pumping rate was regulated by a Variac motor control (N). The feed tank was a calibrated burette (O) and the feed rate was monitored by a calibrated Manaostat rotameter (P). The top and bottom products whose flow rates are controlled by the glass and teflon capillary valves (S) exited continuously to the calibrated receivers (Q and R, respectively). Air pockets and flow disruptions due to expansion and contraction effects in the interstitial column fluid induced by rapid temperature change between half-cycle were relieved by a 10-cm^3 expansion-contraction reservoir (T) and valve (U) at the column top. The expansion-contraction reservoir was initially filled with 2.0-cm^3 feed solution. The connecting tubing (1/32" ID), joints and adapters were constructed of teflon and/or glass and manufactured by Rainin Instrument Corporation.

EXPERIMENTAL PROCEDURE

Before each run, fresh resin in the self-adsorbed form was equilibrated with feed solution at room temperature for 24 hours. Fresh feed solution was prepared for each run by weighing an exact amount of USP·Grade NaCl into distilled water and adjusting the solution to an exact volume. The concentration was checked by electrical conductivity, the conductiving apparatus having been pre-checked with a standard 0.1000M NaCl solution.

The adsorbent column was packed to specified height for each run by introducing a slurry of fresh resin in equilibrium with feed solution at room temperature to the column top. The feed tank and the connecting tubing were filled with the feed solution. The bottom reservoir was filled with a predetermined amount of feed solution and the top reservoir, except for its dead volume was empty. Hot water was directed to the column jacket with the expansion-contraction reservoir valve open and, as the column contents approached the thermal equilibrium with the jacket fluid, the expansion-contraction reservoir rose to 5.0 cm^3. After 2.5 minutes at 70°C, the expansion-contraction reservoir valve was closed and the feed solution was delivered to the column top at the feed rate set for the particular run. Two column volumes of feed solution were delivered to the column top and removed at the bottom product take-off valve to bring the column contents to the same initial condition for each run, i.e., resin in equilibrium with feed solution at 70°C .

Each run began with a hot upflow half-cycle, the flow pattern actuated by simultaneous filling of the top reservoir and emptying of the bottom reservoir. Top and bottom products were continuously withdrawn at a uniform rate by adjusting the top and bottom product valve positions and observing the volume in the calibrated receivers. The feed solution of which rate was observed at the rotameter was continously delivered to the column top. When the required reservoir volume was displaced from column bottom to column top, the reservoir pump was shut off, the feed stopped and the product valves closed. The expansion-contraction reservoir valve was opened, the hot water pump shut off, and the cold water pump activated. The expansion-contraction reservoir volume dropped to 2.0 cm^3 in 2.5 minutes and its valve was shut. Meanwhile, the feed volume, half-cycle time, and product volume were observed. Reservoir pump action was reversed and the cold downflow half-cycle was initiated. Again, both top and bottom products were continuously removed and the feed solution was continuously delivered as in the previous half-cycle. At the completion of the cold half-cycle the next hot half-cycle was begun after relieving expansion effects as before. This procedure was repeated for the desired number of full cycles.

The top and bottom products were analyzed for sodium-chloride content by electrical conductivity at each cold half-cycle. When necessary, the sample was diluted to 8.0 cm^3 with distilled water to fill the conductivity cell. Then the product concentration in mmoles/ml were determined by

$$\text{Product molarity} = \frac{\text{Sample molarity} \times \text{Sample volume}}{\text{Product volume}}$$

Table 1 summarizes the experimental conditions for three runs at 24, 36, and 48 minute half-cycle duration, respectively. Column height, reservoir volume and lean-product discharge rate were chosen such that, if equilibrium conditions were obtained, Region I operation was assured.

Results and discussion

EFFECT 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 was operated at equilibrium. Under those conditions, the maximum quantity of solute was removed from the liquid to phase the solid phase at the cold temperature, ensuring the minimum possible solute concentration in the lean product. Similarly, under equilibrium conditions, the maximum quantity of solute was discharged from the solid to the liquid phase at the hot temperature; ensuring, in turn, the maximum possible solute concentration in the enriched product. Therefore if leaner bottom product concentrations and richer top product concentrations, i.e. better separations, were obtained with longer half-cycle times; it is apparent that equilibrium operation had not been attained at the shorter half-cycle time.

From the graphical representation of the data on Figure 2, 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.

Table 1 Experimental conditions for runs with variable cycle time

Operation Variable	**Value**
Hot Temperature	343 K
Cold Temperature	278 K
Reservoir Displacement	25 cm^3
Bottom Product Withdrawal Ratio	0.04
Top Product Withdrawal Ratio	0.36
Dead Volume	4.5 cm^3
Feed Composition	0.100 mole NaCl/liter
Feed Rate	0.4167 cm^3/min
Column Height	90 cm

EFFECT OF BOTTOM PROCUCT WITHDRAWAL RATE, ϕ_B

In equilibrium parametric pump operation, increasing bottom product withdrawal rate, ϕ_B, to the point that ϕ_B = b marked the transition from Region I to Region II. In Region I, bottom product concentration was independent of ϕ_B and was seen to be a monotonically decreasing function with cycle number. In Region II, however, the bottom product concentration was minimized after a number of cycles before a steadily increasing concentration characterized the lean-product concentration performance curve. In essence, if hot half-cycle concentration front penetration was exceeded by cold half-cycle concentration front penetration, solute tends to migrate toward the lean end of the column, disrupting the separation and producing the degenerating separation characterizing equilibrium Region II.

There were no sharply defined wave fronts along the axis of a non-equilibrium adsorption column. Axial concentration gradients were continuous, smooth, and their shape is time-dependent as well. However, penetration theory may also be applied, in a qualitative sense, to the non-equilibrium case. If, on the average, downward movement of solute along the axial length of column was greater during the cold half-cycle than upward movement of solute on the hot half-cycle, solute would tend to migrate toward the bottom of the column, having the same disruptive effect on separation as in the Region II equilibrium case. Movement of solute was affected by the rate of interphase mass transfer as well as the fluid velocity (bulk flow).The bottom product withdrawal rate, ϕ_B, was the principal variable affecting the relative movement of liquid along the column axis between the hot and the cold half-cycles since the velocities of the cold and the hot flowing fluid, respectively, were given by

$$v_1 = (1-\phi_B) \qquad (1)$$

and

$$v_2 = (1+\phi_B) \qquad (2)$$

The next series of experimental runs were designed to examine this effect. Table 2 shows the experimental conditions for a series of experimental runs where, for a given column height and reservoir displacement, the bottom product rate was varied across a wide range ($0.04 \leq \phi_B \leq 0.28$).

Table 2 Experimental conditions for runs with variable bottom product withdrawal rate (long column)

Operating Variable	**Value**
Hot temperature	343 K
Cold temperature	278 K
Reservoir Displacement	25 cm^3
Feed Rate Ratio ($\phi_B + \phi_T$)	0.400
Dead volume	4.5 cm^3
Feed composition	0.100 moles NaCl/liter
Column height	90 cm
Half-cycle time	24 min

For the first group of runs, at 90-cm. column height, operating parameters were chosen such that column operation matched the requirements for equilibrirm Region I and II, that is $L1 < h$ and $L2 < h$, if equilibrium operation could be obtained. In addition, for these runs, fluid breakthrough from one of the column to the other was precluded by the length of the column

The experimental conditions for the medium (60 cm.) and the short (30 cm.) column height were similar to the long column. From the graphical representation of the experimental data in Figure 3, it is apparent that the same qualitative behavior existed in the non-equilibrium case. For low bottom-product withdrawal rates ($\phi_B = 0.04$), the bottom product concentration curve had a monotonically decreasing character. For high bottom-product withdrawal rates ($\phi_B = 0.28$), the characteristic degenerating separation was the case both theoretically and experimentally.

The next series of experimental runs were designed to demonstrate the effect of column length on the separation of solute into lean and concentrated products. The results showed that it was the relative fluid displacement between cold and hot half-cycles, rather than total displacement relative to column length, that made the transition between steadily increasing separation and steadily degrading separation. The experimental results for medium and short column are shown in the following Figures.

The experimental results for the short column showed the same qualitative behaviour indicated at the longer column length. For $\phi_B = 0.08$, the lean-product concentration was decreased with the increasing number of cycles. At $\phi_B = 0.24$, a minimum in lean-product concentration appeared early and the degenerating level of separation continued thereafter. Here, the lean-product concentration was shown as a function of cycle number and column height for $\phi_B = 0.08$ and $\phi_B = 0.24$. The characteristic shape of the curve was not changed by decreasing column length but was strongly affected by bottom product withdrawal rate.

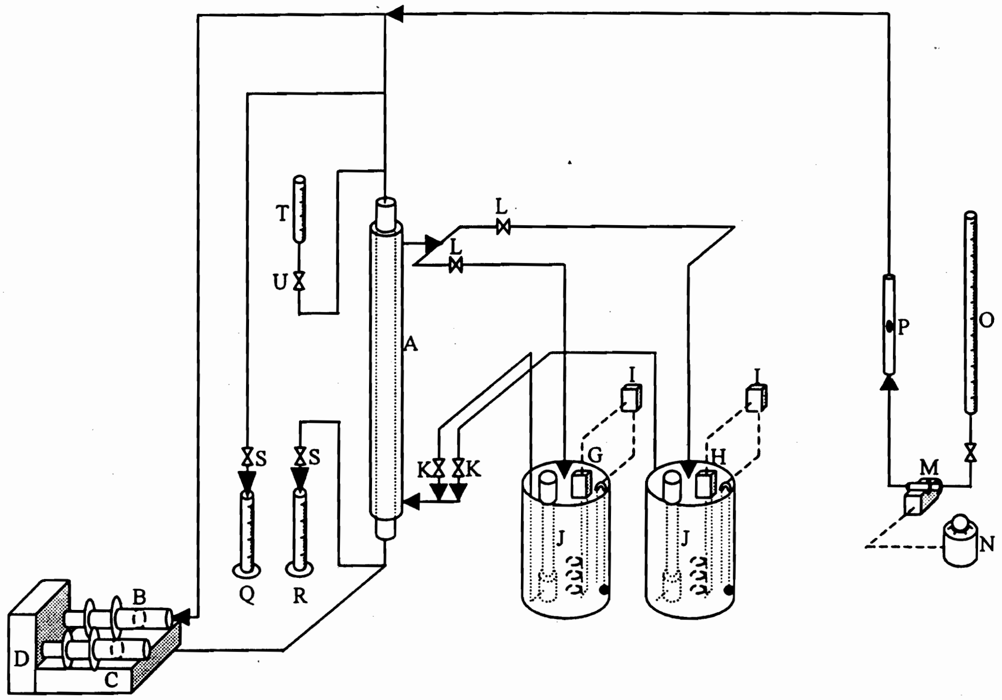


Figure 2 Experimental Continuous Parametric Pump

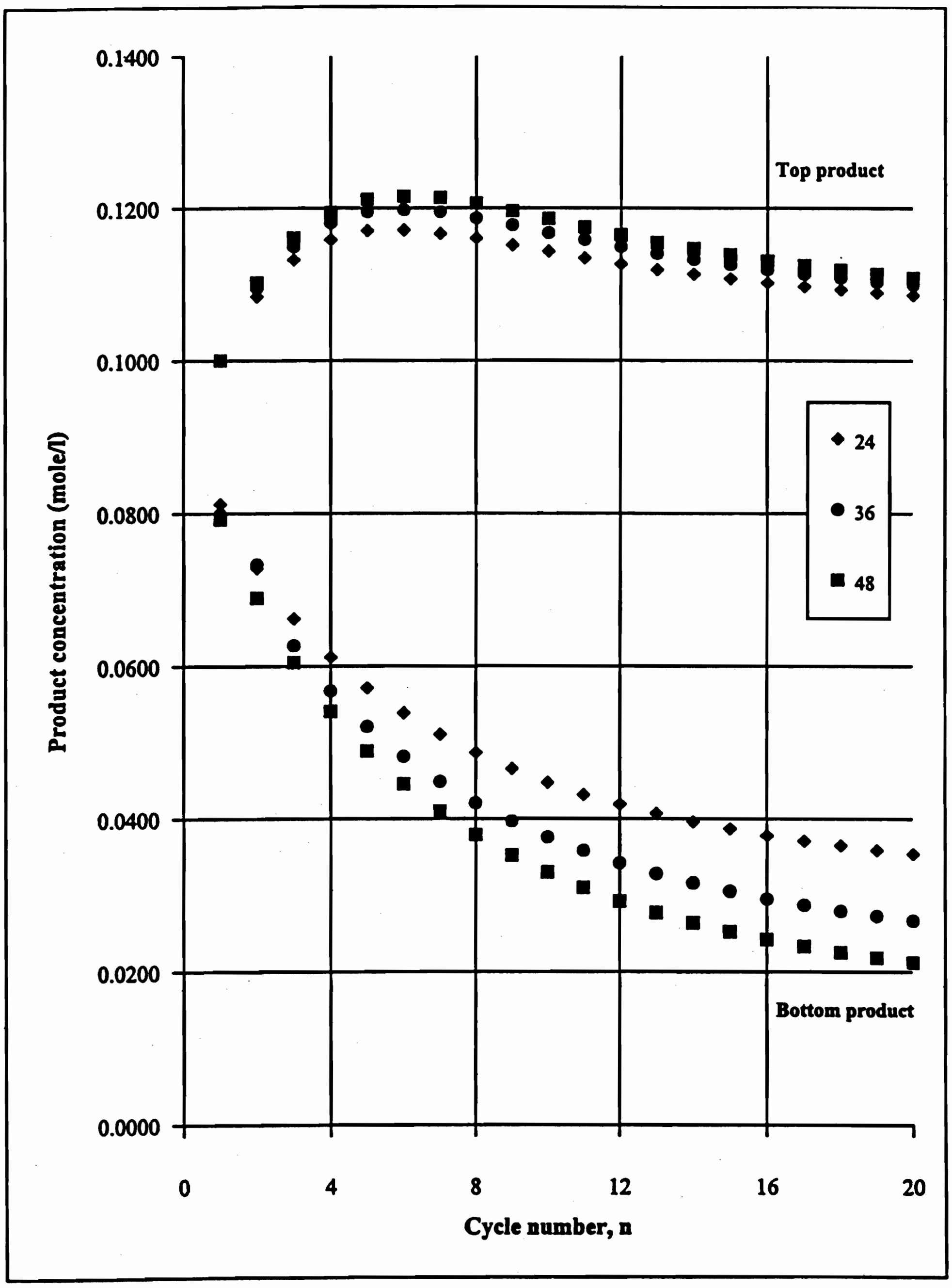


Figure 3 Effects of half-cycle time on separation

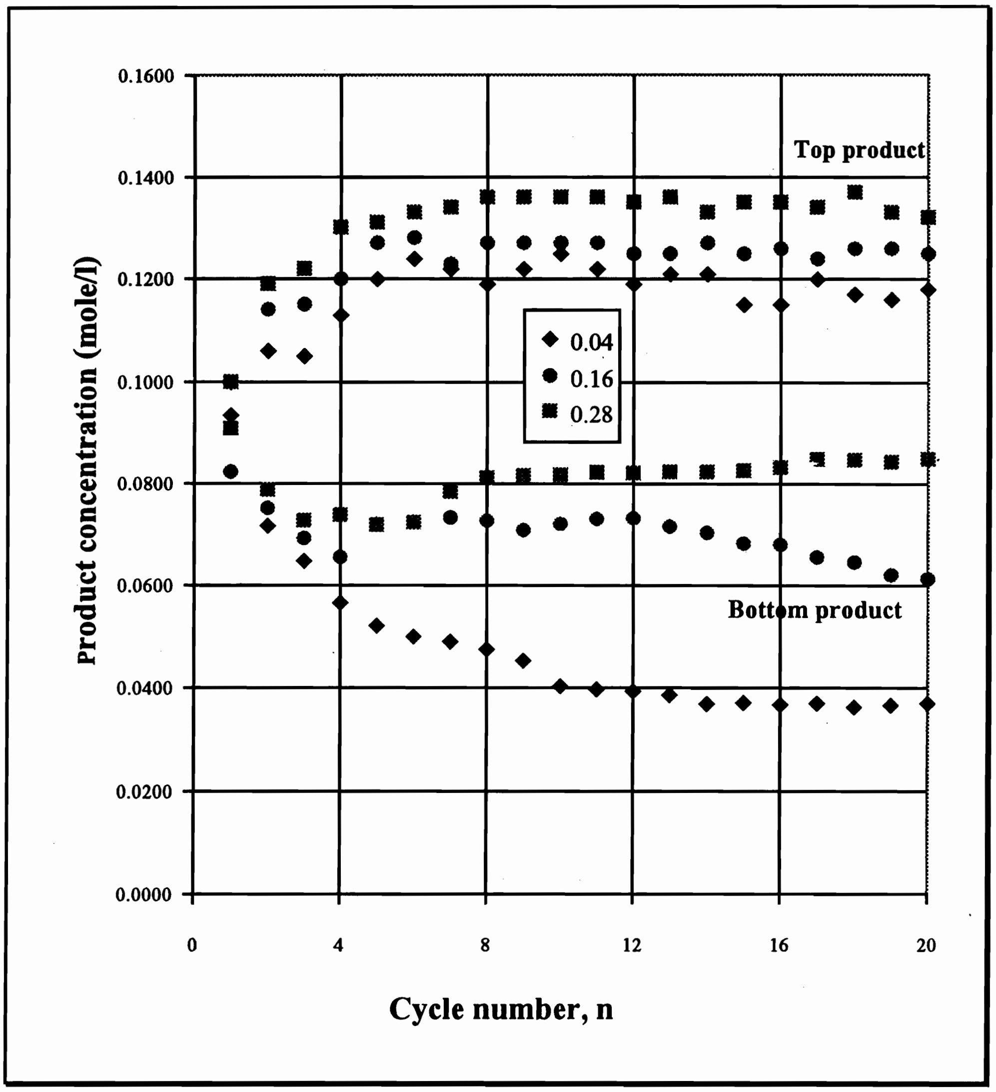


Figure 4 Effects of bottom-product withdrawal rate on separation, 90-cm column

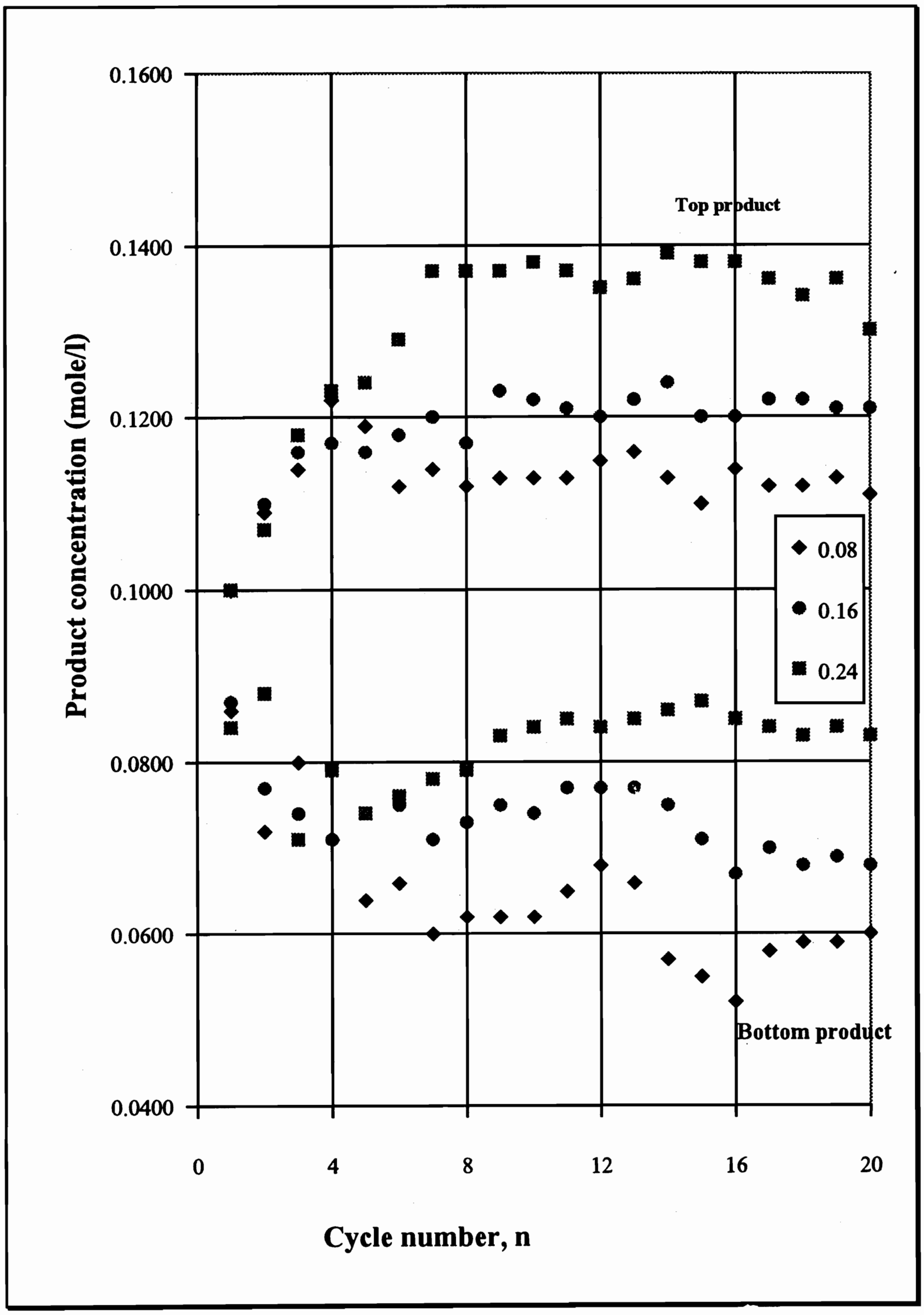


Figure 5 Effects of bottom-product withdrawal rate on separation, 60-cm column

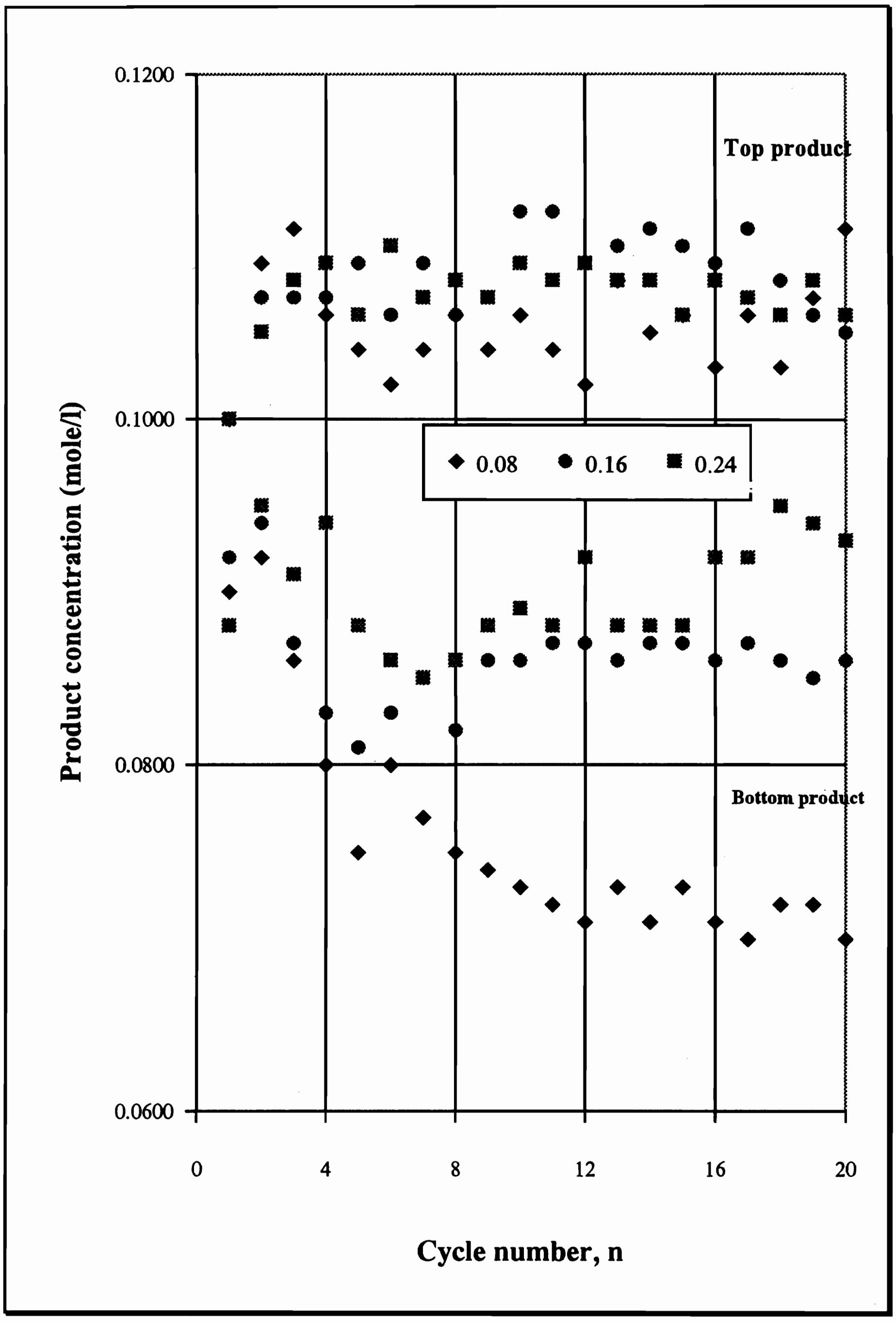


Figure 6 Effects of bottom-product withdrawal rate on separation, 30-cm column

Conclusion

This study examined the effects of cycle time and column length, the following effects are noted:

1. Better separation, i.e. leaner bottom product and more concentrated top product, is achieved at longer half-cycle times. However, for the experimental system under study, which is characterized by slow interphase mass-transfer rates, half-cycle times in excess of four hours would be required to achieve equilibrium operation and, hence, maximum separations. Gregory (1972) had previously established the beneficial effect of longer half-cycle times on separation in his work with batch and semi-continuous operations.

2. Separation is greatly affected by the relative amounts of liquid fed to the adsorbent bed on the cold and hot half-cycles. This work establishes the fact that sufficient fluid must be fed to the bed on the hot half-cycles to remove all the solute adsorbed on the bed during the previous cold half-cycles. When the above is true, a steadily improving separation is achieved with increasing number of cycles of operation. When an insufficient amount of fluid is delivered to the column on the hot half-cycle, separation improves momentarily but then soon degenerates to a steadily worsening separation due to accumulation of solute in both the liquid and solid portions of the adsorbent bed. This effect is found to be depended on the relative amounts of hot and cold half-cycle displacement and not at all on total displacement relative to column liquid volume. This phenomenon is not treated in earlier works.

The nature of the parametric pumping process is such that no simple relation exists which predicts what the relative displacement of cold and hot half-cycle liquid must be to avoid the situation of worsening separation with time. The limiting lean-product withdrawal rate is a complex function of position of equilibrium (a function of temperature and fluid velocity), and the driving force interphase mass transfer (a function of half-cycle time and temperature), among other factors. Prediction of the operability of a particular parametric pumping application, if it is characterized by slow mass-transfer rates, must rely on evaluation of the individual mass-transfer relation, equilibrium isotherm, and concentration region.

This aspect of parametric pumping operation has not been treated by other workers in the field and provides fertile ground for future research efforts.

Acknowledgment

This work was supported through a grant from the Institute of Engineering Research and Development, Faculty of Engineering, Chulalongkorn University, grant No. 86-GER-2527 is appreciated

Reference

Camero, A.A. and Sweed, N.H. 1976. Separation of nonlinearly sorbing solutes by parametric pumping. *AIChE journal.* **22** : 369.

Chen, H.T. and Hill, F.B. 1971. Characteristics of batch, semicontinuous and continuous equilibrium parametric pumps. *Separation Science.* **6** : 411.

Chen, H.T., Hsieh, T.K., Lee, H.C. and Hill, F.B. 1977. Separation of proteins via semicontinuous pH-parametric pumping. *AIChE Journal.* **23** : 695.

Chen, H.T., Pancharoen, U., Yang, W.T., Kerobo, C.O. and Parisi, R.J. 1980. An equilibrium theory of the pH-parametric pump. *Separation Sciences.* **15** : 1377.

Gregory, R.A. and Sweed, N.H. 1972. Parametric pumping: behavior of open systems Part II: Experiment and computation. *Chemical Engineering Journal.* **4** : 139.

Pancharoen, U. 1981. *The batch equilibrium of the pH-parametric pumps: Applied graphical method for separation of proteins.* Master Thesis. Newark, N.J. : New Jersey Institute of Technology. (May).

Pancharoen, U. 1982. *Separation technique on proteins via a pH-parametric pump: A theoretical and experimental study.* Doctoral Dissertation. Newark, N.J. : New Jersey Institute of Technology. (May).

Sabadell, J.E. and Sweed, N.H. 1970. Parametric pumping with pH : *Separation Science.* **5** : 171.

Sweed, N.H. and Rigaudeau, J. 1975. Equilibrium theory and scale-up of parametric pumps. *AIChE Symposium Ser.* **152** : 1.

Weaver, K. and Hamrin, C.E. 1974. Separation of hydrogen isotopes by heatless adsorption. *Chemical Engineering Science.* **29** : 1873.

(Revised version accepted June 8, 1998.)