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MEMBRANE ASSEMBLAGES FOR DIALYSIS SEPARATION OF SOLUTES

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ABSTRACT

This paper examines the performance of several configurations dialysis units for the separation of two solutes. Dialyzers arranged in series, in parallel and the continuous column in countercurrent flow are studied. The single dialysis unit is also included.

For the recovery of the less permeable solute, the series configuration can give a good performance. The parallel configuration favors the recovery of the more permeable component. The continuous column has better capabilities for the separation and recovery of both the more permeable component and the less permeable component.

1. Introduction

The separation and purification of substances to produce useful chemical products are critical steps in the manufacturing process. Hence the choice of the type and the economics of the separation are important considerations.

Some products are separated and purified using a single separation unit. Many products, however, are obtained by connecting together single separation units. There are many possible configurations and arrangements when single units are connected with each other. The performance of each assembly is considerably different from each other. Much time and effort are spent on the determination of performance of such assemblages.

Developments in membrane separation technology (hyperfiltration or reverse osmosis, ultrafiltration, microfiltration, dialysis, electrodialysis) have led to its evaluation and comparison

with the so-called conventional or traditional separation technology (distillation, absorption, stripping, adsorption, precipitation, ion exchange, crystallization, extraction, filtration). The main attraction of a membrane separator is still its low energy consumption. Its most successful high volume applications have been in the separation of gas stream components, desalination of seawater by reverse osmosis, and specialized membrane reactors for high value products. In areas where energy is expensive, membrane technology can provide the alternative for materials separation in industry.

This work aims to determine the performance of several configurations of dialysis units for the separation of two solutes. Dialyzers arranged in series, in parallel and the continuous column in countercurrent flow are studied. The single dialysis unit is also included.

II. Review of Related Literature

Dialysis is a selective transfer process that makes use of the difference in the diffusivity of the species. Solute molecules are transferred from one liquid to another through a membrane.

Of the many membrane separation processes, dialysis is one of the oldest in use in chemical technology. There have been, however, very few large scale applications. Among these are the dialysis of concentrated sodium hydroxide solutions containing hemicellulose and nickel recovery in the refining of copper [1]. The most important application of dialysis is the treatment of end-stage renal disease. A drawback may be the inherent slowness of the process. Also, the selectivity is low when the difference in the permeability of the solutes to be separated is not large, or when the molecules are structurally similar. Besides, good membranes which are economical have only recently become available.

These limitations of dialysis make it useful only when the solutes to be separated are present in high concentrations. If the concentrations of the solutes are low, the separation is practical only if the membrane area is increased, which would affect the economics of the process.

One advantage of dialysis over the other processes is simplicity, in which the driving force depends only on the solution concentrations. This advantage finds use in separating mixtures that are sensitive to temperature, or to mechanical degradation due to high pressure or high shear rates.

Separations by dialysis are improved under certain conditions by complexing one or more of the species to be separated, or by chemically converting the permeating solute, or by staging the dialysis cells.

Suehiro, Yamanaka and Mizoguchi [2] proposed a novel continuous column for separating solutes by dialysis. Their work followed an earlier study by Hwang and Thorman [3] who developed a continuous membrane column for the separation of gas mixtures. Noda and Gryte [4] analyzed the input-output response of various configurations of interconnected units using dialysis as the separation process.

The degree of separation of a single separation unit is limited. When units are connected to form assemblages, the degree of separation may be enhanced. There is the possible application of dialysis in the separation of solutes with relatively close permeabilities.

III. Mathematical Analyses

The configurations which are considered in this study are modeled as steady state systems. The configurations, as shown in Figure 1 to 5, are 1) the single dialysis unit, 2) two dialysis units arranged in series, 3) three dialysis units arranged in series, 4) two dialysis units in parallel configuration and 5) the continuous column in countercurrent flow.

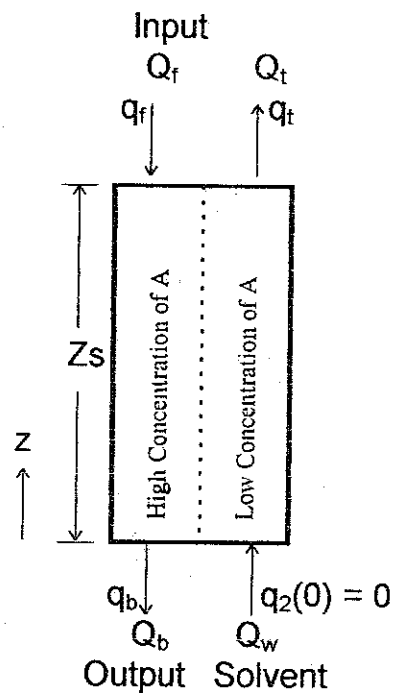

Figure 1. Single Unit Configuration

3.1 Single Unit Configuration

The single unit configuration (Figure 1) is divided into two sections, the high concentration side and the low concentration side. The feed solution enters the top of the high concentration side where the more permeable solute permeates to the low concentration side. The pure solvent enters the bottom of the low concentration side and carries upward the more permeable solute. The stream that leaves the top of the low concentration side is rich in the more permeable solute. The solution that leaves the bottom of the high concentration side is rich in the less permeable solute.

Let

$$Q_t = Q_w = Q_2$$

$$Q_f = Q_b = Q_1$$

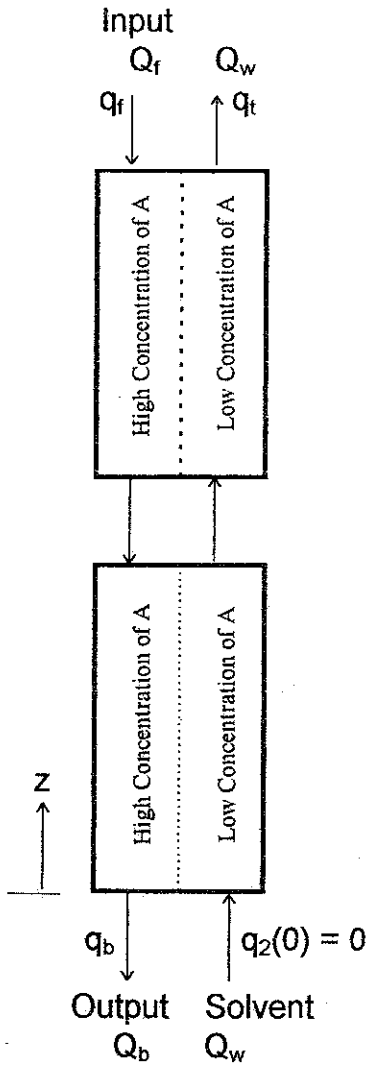

Figure 2. 2-in-Series Configuration

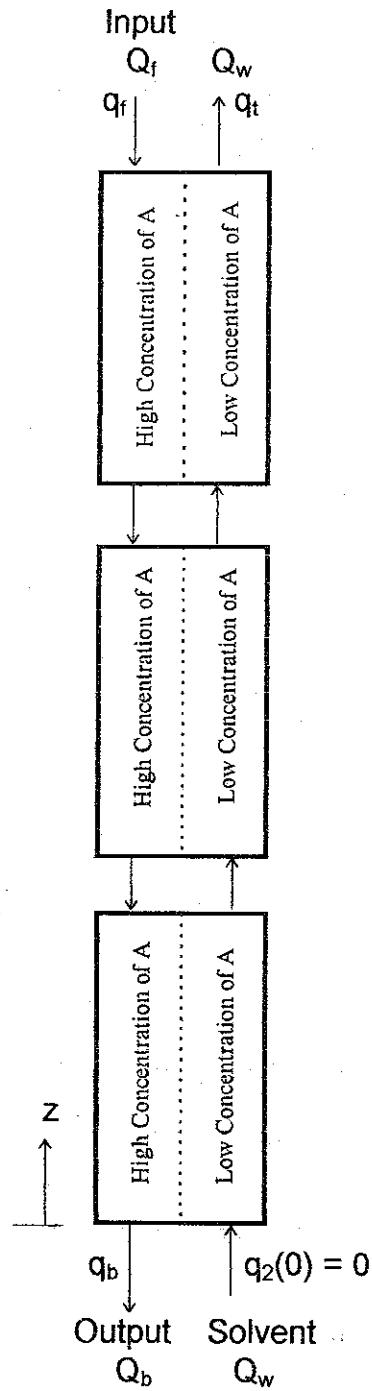

Figure 3. 3-in-Series Configuration

Overall mass balance

$$q_f = q_t + q_b$$

$$Q_f + Q_w = Q_h + Q_l$$

Side (1) mass balance

$$\frac{dq_1}{dz} = K\sigma\left(\frac{q_1}{Q_1} - \frac{q_2}{Q_2}\right) \tag{1}$$

Side (2) mass balance

$$\frac{dq_2}{dz} = K\sigma\left(\frac{q_1}{Q_1} - \frac{q_2}{Q_2}\right) \tag{2}$$

The boundary conditions are

$$q_2(0) = 0$$
$$q(z_s) = q_f$$

Solving equations (1) and (2) gives the result below.

$$\frac{q_t}{q_f} = \frac{\exp\left[\frac{1-\delta}{\delta} pz_s\right] - 1}{\exp\left[\frac{1-\delta}{\delta} pz_s\right] - \delta} = G(p) \tag{3}$$

where*

$$\delta = \frac{Q_f}{Q_w}$$

$$p = \frac{K_\sigma}{Q_w}$$

For a binary system

$$x_t = \frac{q_{At}}{q_{At} + q_{Bt}}, x_f = \frac{q_{Af}}{q_{Af} + q_{Bf}} \tag{4}$$

So

$$\frac{x_t}{x_f} = \left(\frac{q_{At}}{q_{Af}}\right)\left(\frac{q_{Af}+q_{Bf}}{q_{At}+q_{Bt}}\right) = G(p_A)\frac{q_{Af}+q_{Bf}}{q_{At}+q_{Bt}}$$

$$(1-x_t) = \frac{q_{Bt}}{q_{Bt}+q_{At}}, (1-x_f) = \frac{q_{Bf}}{q_{Bf}+q_{Af}}$$

$$\frac{1-x_t}{1-x_f} = \left(\frac{q_{Bt}}{q_{Bf}}\right)\left(\frac{q_{Af}+q_{Bf}}{q_{At}+q_{Bt}}\right) = G\left(P_B\right)\frac{q_{Af}+q_{Bf}}{q_{At}+q_{Bt}}$$

and

$$\frac{x_t}{x_f}\,\frac{1-x_f}{1-x_t} = \frac{G(p_A)}{G(p_B)} \tag{5}$$

The analysis for the 2-in-series (Figure 2) and the 3-in-series (Figure 3) are similar to the single unit configuration. The 2-in-series configuration has twice the membrane area of the single unit and the 3-in-series configuration has three times the membrane area of the single unit configuration.

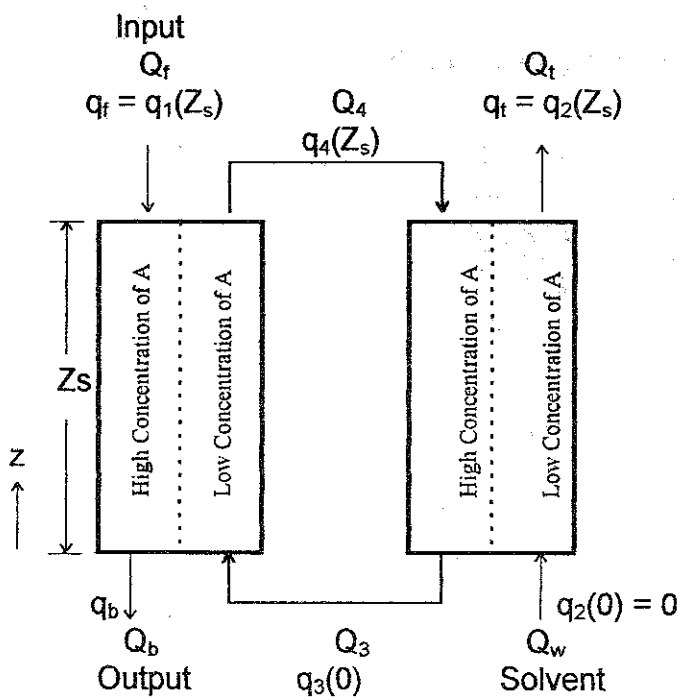

Figure 4. Parallel Configuration

3.2 Parallel Configuration

The parallel configuration consists of two columns as shown in Figure 4. There are three streams in this assembly. The feed solution enters the top of the high concentration side of the column on the left. The solvent enters the bottom of the low concentration side on the right. A middle stream circulates from the low concentration side on the left to the high concentration side on the right and back. As the feed stream enters the column, the more permeable component permeates preferentially through the membrane which will then be carried by the circulating stream to the high concentration side on the right column. Likewise, the more permeable component permeates again and is thus carried by the upward flow of the solvent stream.

Let

$$Q_t = Q_w = Q_2 \qquad Q_f = Q_b = Q_1 \qquad Q_3 = Q_4 = Q$$

Also, note that

$$q_3(0) = q_4(0)$$
$$q_3(z_s) = q_4(z_s)$$

Overall mass balance

$$q_f = q_1 + q_b$$
$$Q_f + Q_w = Q_b + Q_t$$

Side (1) mass balance

$$\frac{dq_1}{dz} = K\sigma\left(\frac{q_1}{Q_1} - \frac{q_3}{Q_3}\right) \tag{6}$$

Side (2) mass balance

$$\frac{dq_2}{dz} = K\sigma\left(\frac{q_4}{Q_4} - \frac{q_2}{Q_2}\right) \tag{7}$$

Side (3) mass balance

$$\frac{dq_3}{dz} = K\sigma\left(\frac{q_1}{Q_1} - \frac{q_3}{Q_3}\right) \tag{8}$$

Side (4) mass balance

$$\frac{dq_4}{dz} = K\sigma\left(\frac{q_4}{Q_4} - \frac{q_2}{Q_2}\right) \tag{9}$$

Applying the boundary conditions, the result is

$$\frac{q_f}{q_b} = \frac{\left\{\left(1+bQ_3\right)\left[\exp(K\sigma z_s b)-1\right]\right\}\left[\frac{\exp(K\sigma z_s a)-1}{\exp(K\sigma z_s b)-1}\right]\left(\frac{1}{aQ_4}\right)}{\left\{1+bQ_3\left[\frac{\exp(K\sigma z_s a)-1}{\exp(K\sigma z_s b)-1}\right]\left(\frac{1}{aQ_4}\right)\right\}} \tag{10}$$

and

$$\frac{q_f}{q_b} = \frac{\exp(K\sigma z_s b) + \left\{\left[\exp(K\sigma z_s a)-1\right]+aQ_4\right\}\left[\frac{\exp(K\sigma z_s b)-1}{\exp(K\sigma z_s a)-1}\right]\left(\frac{1}{bQ_3}\right)}{\left\{1+aQ_4\left[\frac{\exp(K\sigma z_s b)-1}{\exp(K\sigma z_s a)-1}\right]\left(\frac{1}{bQ_3}\right)\right\}} \tag{11}$$

where

$$\frac{1}{a} = \frac{Q_2 Q_4}{Q_2 - Q_4}$$

$$\frac{1}{b} = \frac{Q_1 Q_3}{Q_3 - Q_1}$$

3.3 Continuous Column Configuration

Figure 5 is a schematic representation of the continuous column configuration. It is composed of the membrane column and a solvent stripper. The membrane column is divided into two sections, namely the stripping section and the enriching section. Both sections have a high concentration side and a low concentration side.

The feed enters the top of the high concentration side of the stripping section while the solvent enters the bottom of the low concentration side in the stripping section. The more permeable solute permeates preferentially to the low concentration side where the solution flows upward to the enriching section. In the enriching section the same action takes place. This results in the accumulation of the more permeable component at the top and the accumulation of the less

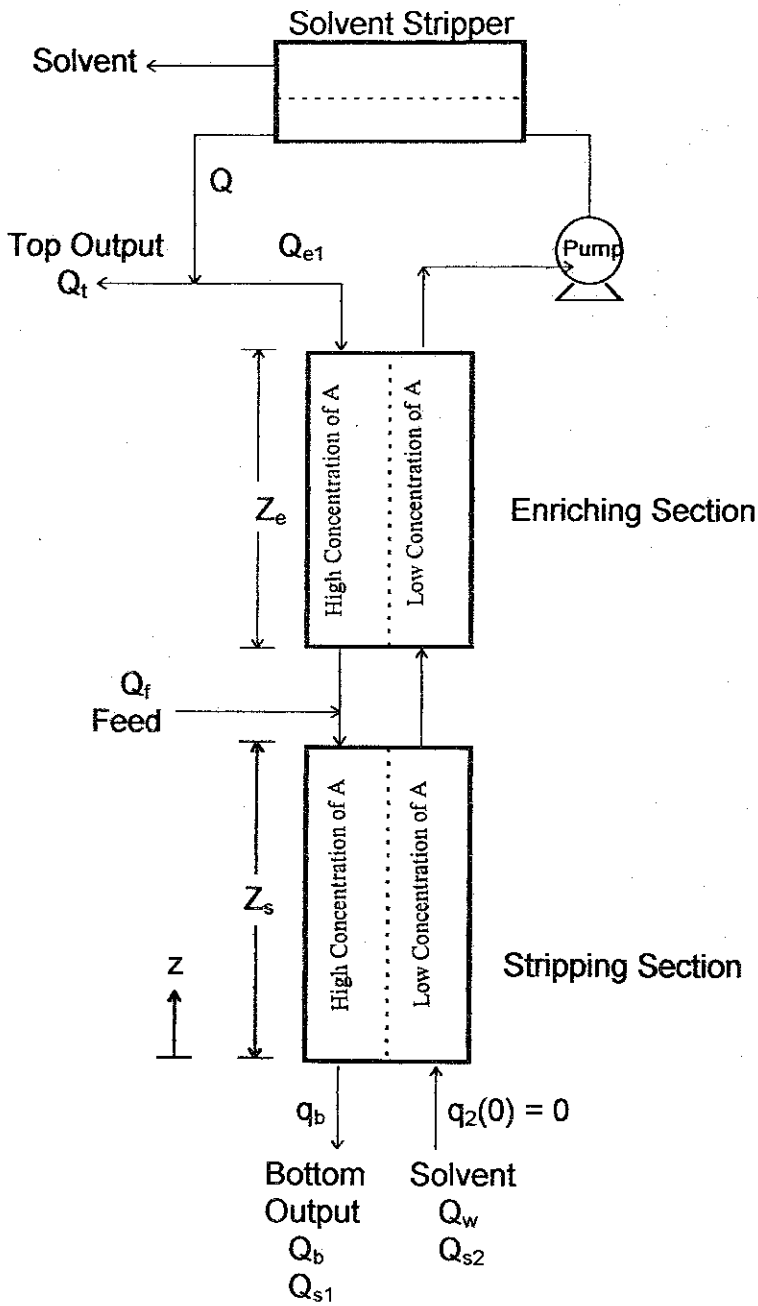

Figure 5. Continuous Column

permeable component at the bottom. In the solvent stripper the solution is concentrated without the loss of solute.

We have for the stripping section.

$$\frac{dq_1}{dz} = K\sigma\left(\frac{q_1}{Q_{s1}} - \frac{q_2}{Q_{s2}}\right) \tag{12}$$

$$\frac{dq_2}{dz} = K\sigma\left(\frac{q_1}{Q_{s1}} - \frac{q_2}{Q_{s2}}\right) \tag{13}$$

And for the enriching section, a similar derivation will yield

$$\frac{dq_1}{dz} = K\sigma\left(\frac{q_1}{Q_{e1}} - \frac{q_2}{Q_{e2}}\right) \tag{14}$$

$$\frac{dq_2}{dz} = K\sigma\left(\frac{q_1}{Q_{e1}} - \frac{q_2}{Q_{e2}}\right) \tag{15}$$

The boundary conditions are:

$$q_1\left(z_s^-\right) = q_f + q_1\left(z_s^+\right)$$
$$q_2\left(z_s^-\right) = q_2\left(z_s^+\right)$$
$$q_2(0) = 0$$
$$q_1\left(z_s + z_e\right) = Rq_2\left(z_s + z_e\right)$$

where $R = \dfrac{Q_{el}}{Q_t + Q_{el}}$

We get

$$\frac{q_t}{q_f} = \frac{\theta_s\left(1-\theta_e-\varepsilon R\theta_e\right)(1-R)(1-\varepsilon R)}{\left(1-\varepsilon R\left\{1+(1-R)\left(\theta_e+\theta_s\right)+(1-R)(1-\varepsilon R)\theta_s\theta_e\right\}\right)} \tag{16}$$

were

$$\varepsilon = \frac{Q}{Q_w}$$

$$\theta_s = \frac{\exp\left(pz_s \frac{1-\varepsilon R-\delta}{\varepsilon R+\delta} \right) - 1}{1-\varepsilon R-\delta}$$

$$\theta_e = \frac{\exp\left(pz_e \frac{1-\varepsilon R}{\varepsilon R} \right) - 1}{1-\varepsilon R}$$

IV. Results and Discussion

Some representative results for the various dialysis assemblies are given below.

1. Unit and Series Configuration
   It is observed in Figure 6 that a larger membrane area favors the bottom output, while a smaller area favors the top output.

2. Parallel Column
   Figure 7 is a graph in which the total membrane area is half that of Figure 8. In both cases, increasing the ratio Q/Q_w gives a better performance in the top output, while the bottom output shows little improvement.

3. 2-in-Series and Parallel Column Comparison
   Figure 9 shows that by increasing the ratio Q/Q_w the performance of the parallel configuration can match the 2-in-series configuration.

4. Series and Continuous Column Comparison
   Figure 10 shows a comparison of the series and the continuous column configurations. The top output is significantly better for the continuous column but the bottom output is slightly better for the 2-in-series and the 3-in-series.

5. Parallel Column and Continuous Column Comparison
   For the given set of conditions in Figure 11, the performance for the top and bottom output of the continuous column is better than the parallel configuration.

6. Continuous Column (Pilot Scale)
   A pilot scale continuous column can be approximated by choosing the solvent rate Q_w = 100 cu. cm. and the total membrane area = 200 sq. m. A very small Q_f/Q_w and a large reflux ratio gave a significantly better performance for both the top and the bottom output as shown in Figure 12.

V. Conclusion

The main objective of this study is the determination of the performance of the continuous column configuration, the parallel column configuration, the single unit and the series configuration of dialysis units.

For the recovery of the less permeable solute, the series configuration can give a good performance; for the recovery of the more permeable solute, the parallel column can be chosen; for the recovery of both the more permeable solute and the less permeable solute, the continuous column is a better choice.

A significant enhancement of both the more permeable solute in the top output stream Q_t and of the less permeable solute in the bottom stream Q_b is attainable in the continuous column when the ratio Q_f/Q_w is quite low and the reflux ratio r is very high.

The effect of a low feed to solvent flow ratio Q_f/Q_w in the continuous column is similar to that in the series configuration. With sufficient contact time, almost all the permeable solute can move across the membrane, leaving a high mole fraction value of the less permeable solute in the bottom stream Q_b.

The high reflux ratio r ensures that the membrane in the enriching section of the column is in contract with a stream that is already rich in the more permeable solute.

The combined effect of Q_f/Q_w and the reflux ratio r gives the continuous column better capabilities for separation.

References

1. Klein, Elias and Richard A. Ward (1987)."Membrane Processes - Dialysis and Electrodialysis." Handbook of Separation Technology. Edited by Ronald W. Rousseau.

2. Suehiro, Tetsuro, Tadae Yamanaka and Kensaku Mizoguchi (1990). "A Novel Continuous Membrane Column for Separating Solutes in Dialysis." Journal of Chemical Engineering of Japan, Vol. 23, No.1, pp.110 -112.

3. Hwang, Sun-Tak and John Thorman (1980). "The Continuous Membrane Column." AICHE Journal, Vol. 26, No. 4 (July 1980), pp. 558-560.

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Nomenclature

C	concentration, mole/m^3
K	mass transfer coefficient, m/s
Q	flow rate, m^3/s
q	molar flow rate, mole/s
r	reflux ratio Q_{el} / Q_t
x	mole fraction of solute
Z	column height, m
z	column axial distance, m

Symbols

ε	inverse of concentrating ratio by solvent stripper, Q / Q_w
σ	membrane area per unit length, m
δ	flow rate ratio of feed to pure solvent, Q_f / Q_w

Subscripts

1,4	high concentration side
2,3	low concentration side
A	more permeable solute
B	less permeable solute
b	bottom output
e	enriching section
f	feed
s	stripping section
t	top output
w	pure solvent

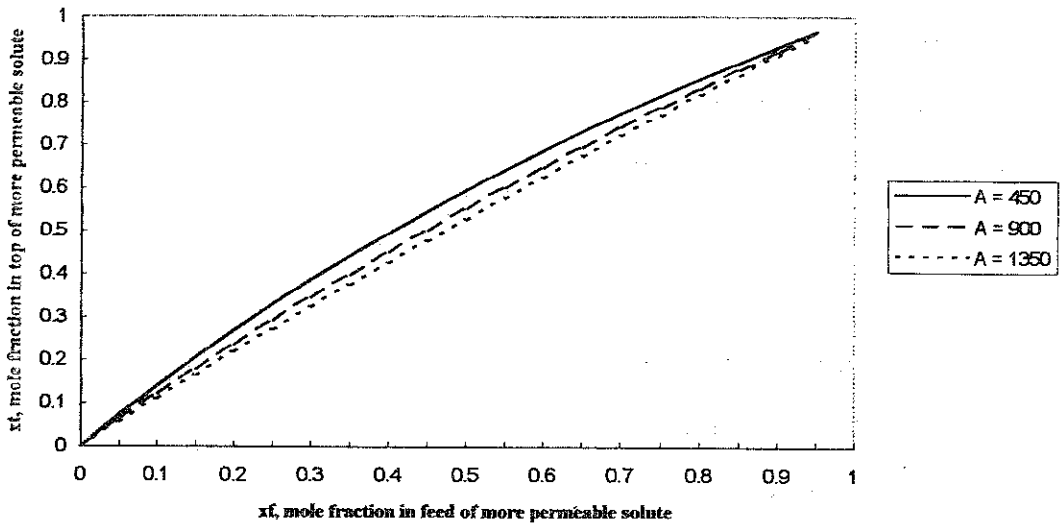

Figure 6A. Relationship Between Feed and Top Output
Single, 2-in-Series, 3-in-Series - Laboratory Scale

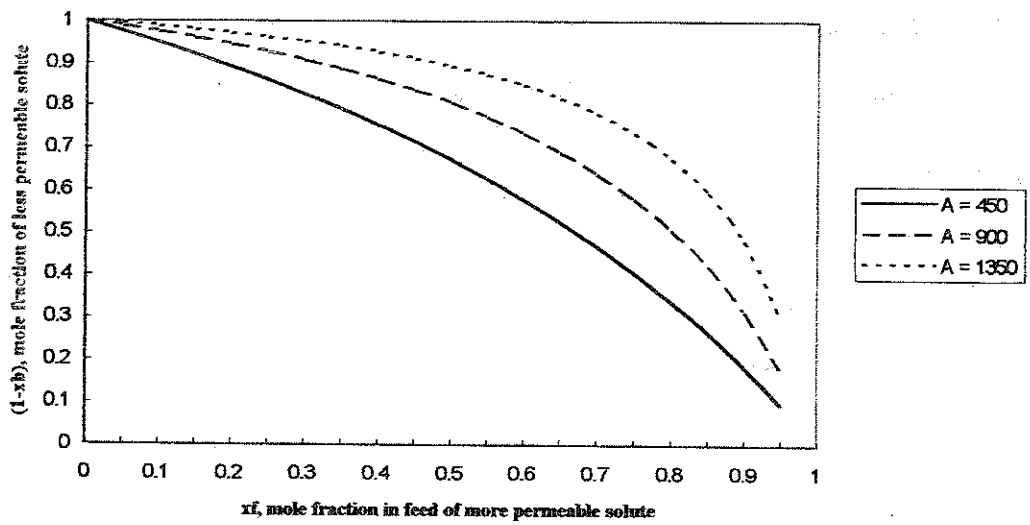

Figure 6B. Relationship Between Feed and Bottom Output
Single, 2-in-Series, 3-in-Series - Laboratory Scale

Flow Rate Parameters: Qw = 1.0 cu.cm/sec, Qf/Qw = 0.06

Permeability Parameters: mass transfer coeff. ratio, $(K_A/K_B) = 2$; $K_B = 0.0001$ cm/sec

A = membrane area in sq.cm.

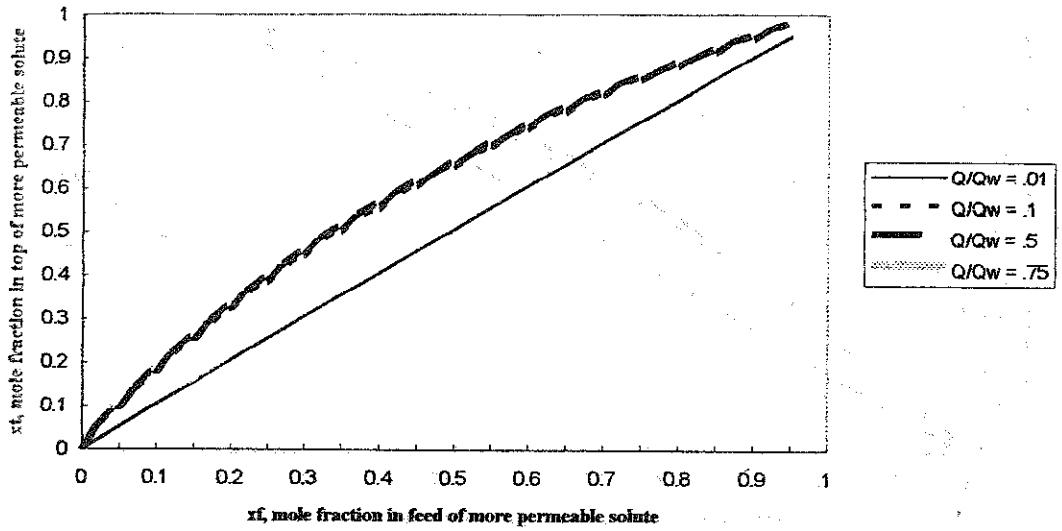

Figure 7A. Relationship Between Feed and Top Output
Parallel Column - Laboratory Scale

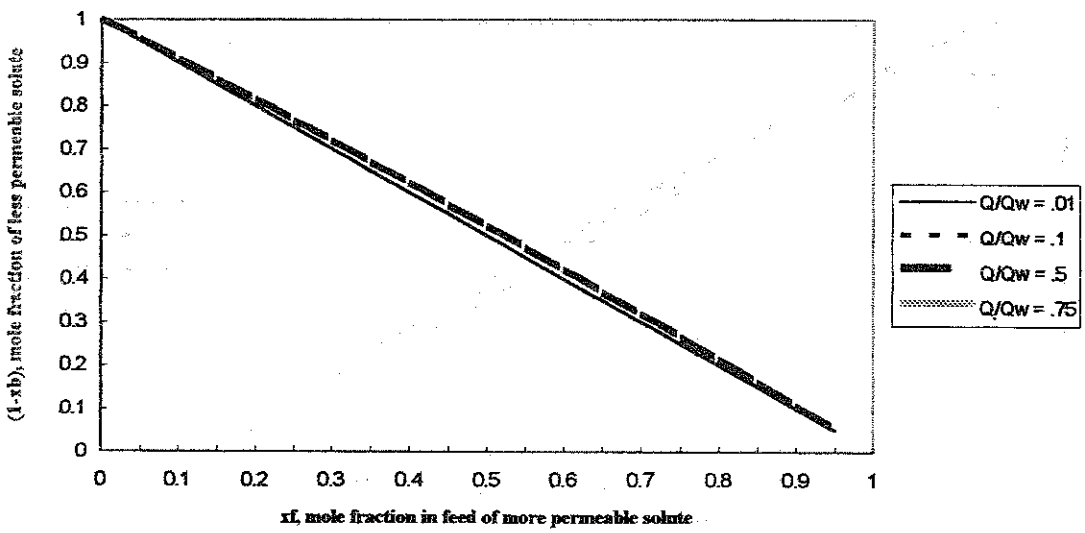

Figure 7B. Relationship Between Feed and Bottom Output
Parallel Column - Laboratory Scale

Flow Rate Parameters: Qw = 1.0 cu.cm/sec, Qf/Qw = 0.25
Permeability Parameters: mass transfer coeff. ratio, $(K_A/K_B) = 2$; $K_B = 0.0001$ cm/sec
Geometry Parameters: total membrane area = 900 sq.cm.

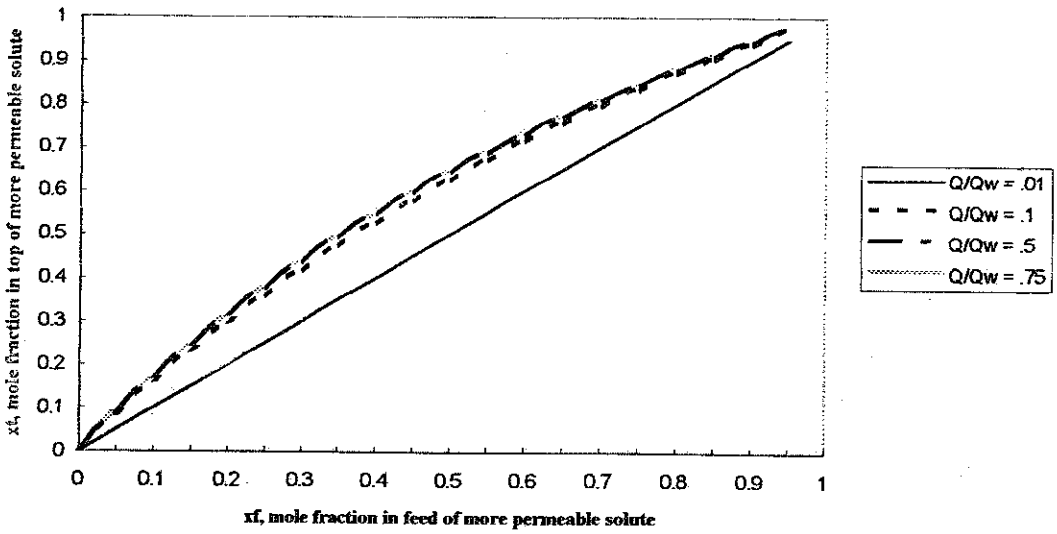

Figure 8A. Relationship Between Feed and Top Output
Parallel Column - Laboratory Scale

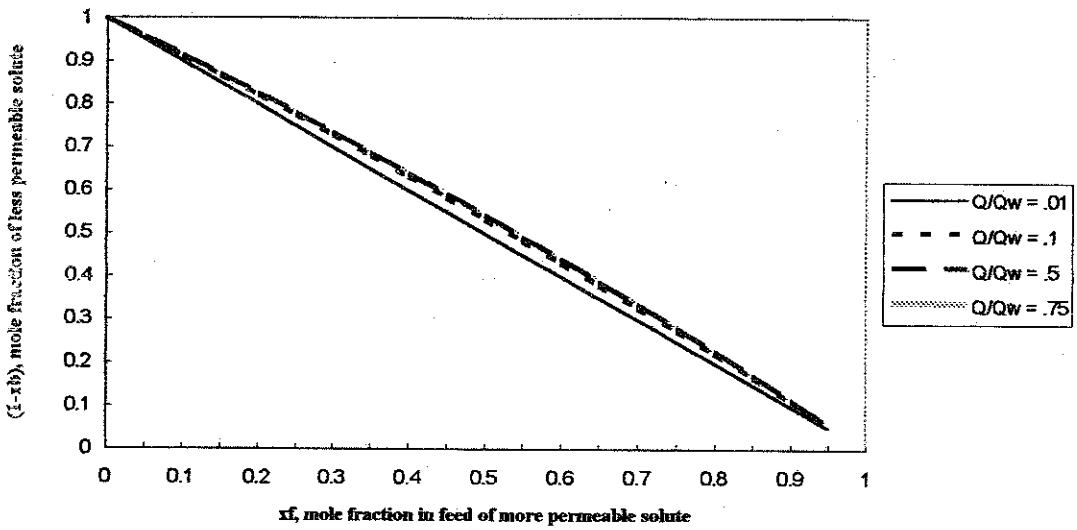

Figure 8B. Relationship Between Feed and Bottom Output
Parallel Column - Laboratory Scale

Flow Rate Parameters: Qw = 1.0 cu.cm/sec, Qf/Qw = 0.25
Permeability Parameters: mass transfer coeff. ratio, $(K_A/K_B) = 2$; $K_B = 0.0001$ cm/sec
Geometry Parameters: total membrane area = 1800 sq.cm.

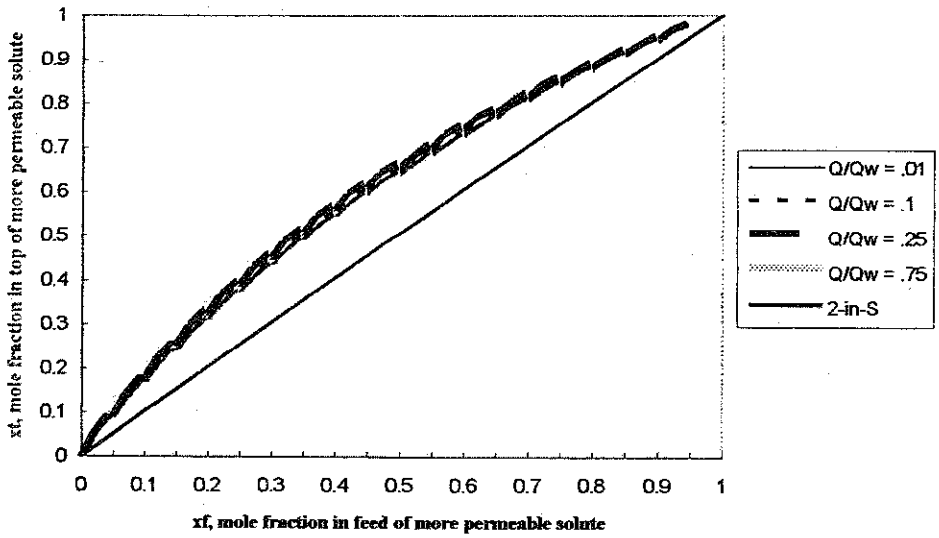

Figure 9A. Relationship Between Feed and Top Output
2-in-Series - Parallel Column Comparison

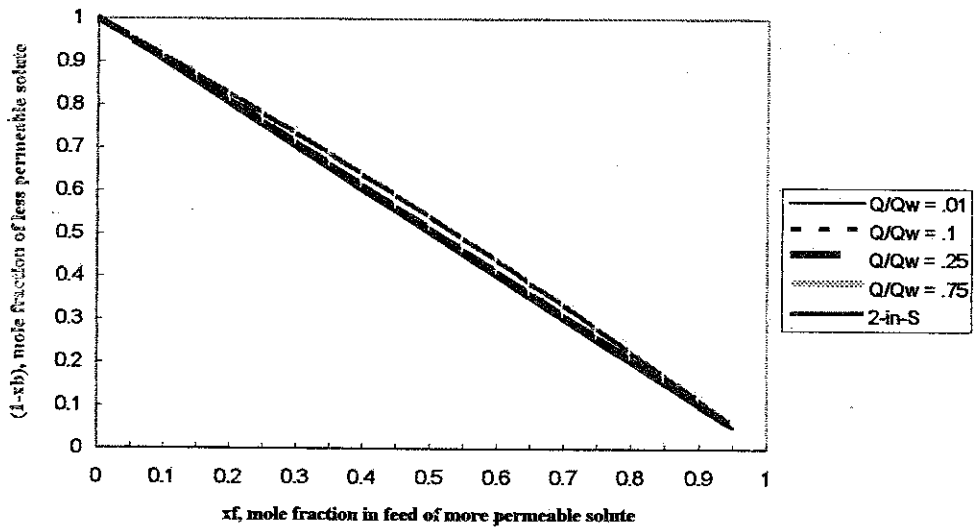

Figure 9B. Relationship Between Feed and Bottom Output
2-in-Series - Parallel Column Comparison

Flow Rate Parameters: Qw = 1.0 cu.cm/sec, Qf/Qw = 0.5
Permeability Parameters: mass transfer coeff. ratio, $(K_A/K_B) = 2$; $K_B = 0.0001$ cm/sec
Geometry Parameters: total membrane area = 900 sq.cm.

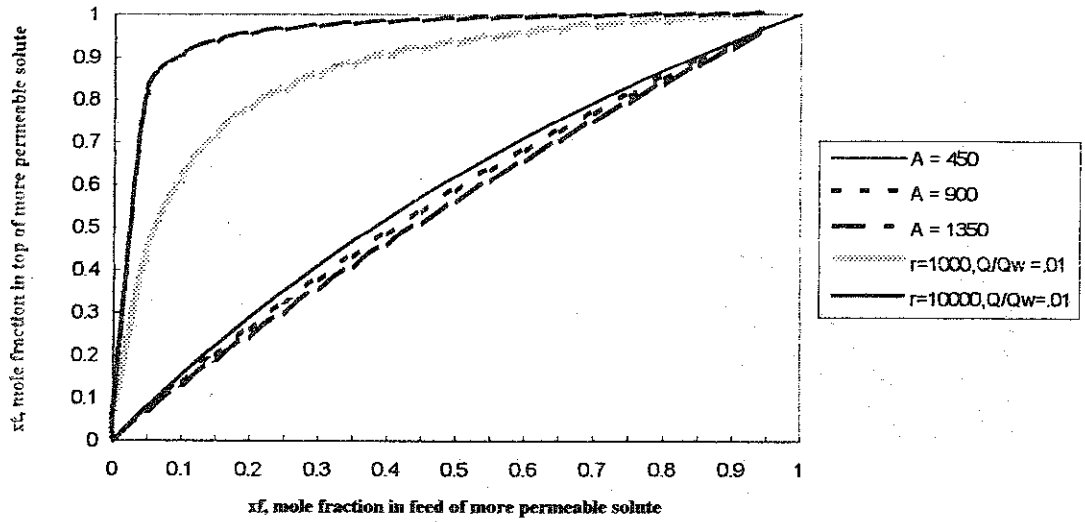

Figure 10A. Relationship Between Feed and Top Output
Single, 2-in-Series, 3-in-Series, Continuous Column Comparison

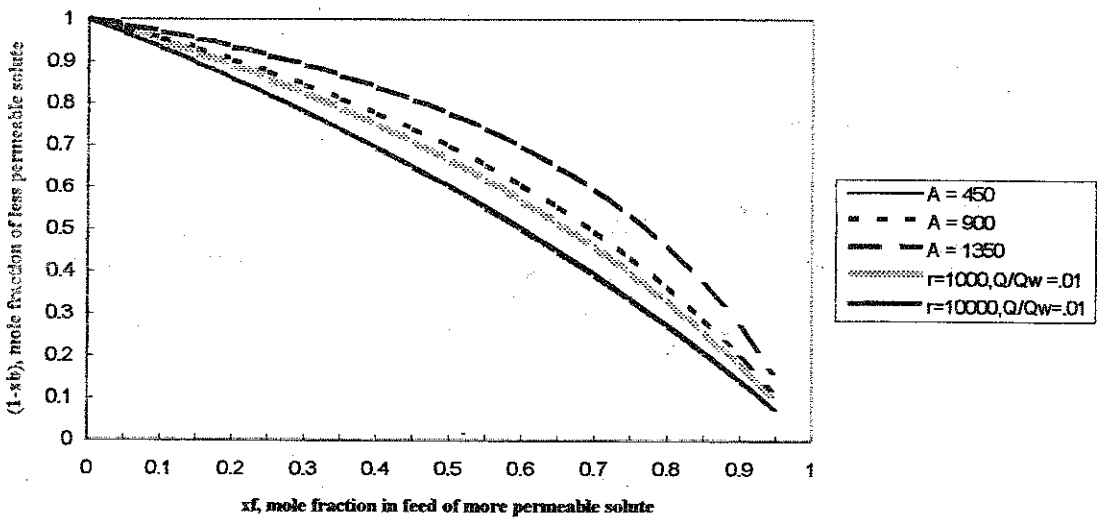

Figure 10B. Relationship Between Feed and Bottom Output
Single, 2-in-Series, 3-in-Series, Continuous Column Comparison

Flow Rate Parameters: Qw = 1.0 cu.cm/sec, Qf/Qw = 0.1

Permeability Parameters: mass transfer coeff. ratio, $(K_A/K_B) = 2$; $K_B = 0.0001$ cm/sec

A = membrane area in sq.cm.

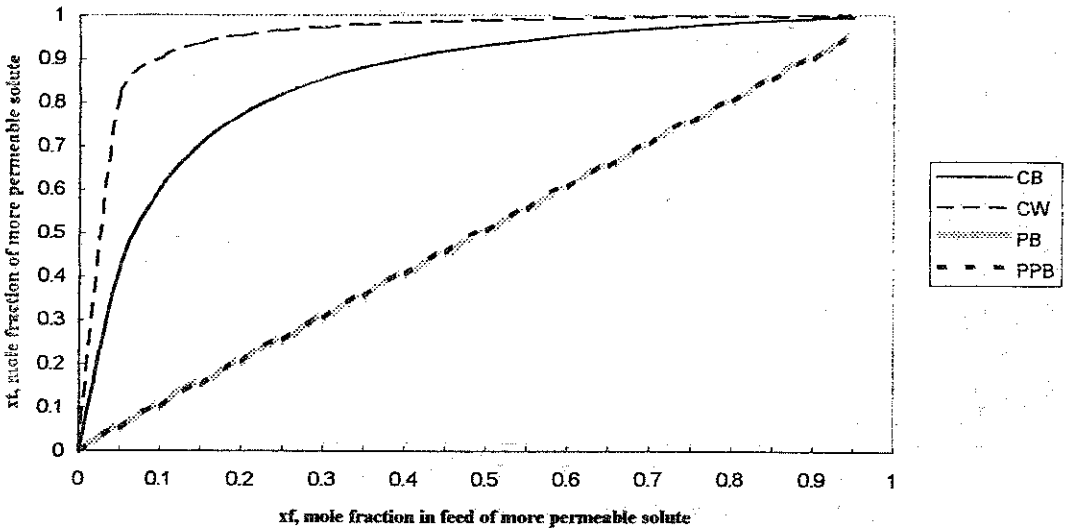

Figure 11A. Relationship Between Feed and Top Output
Parallel - Continuous Column Comparison

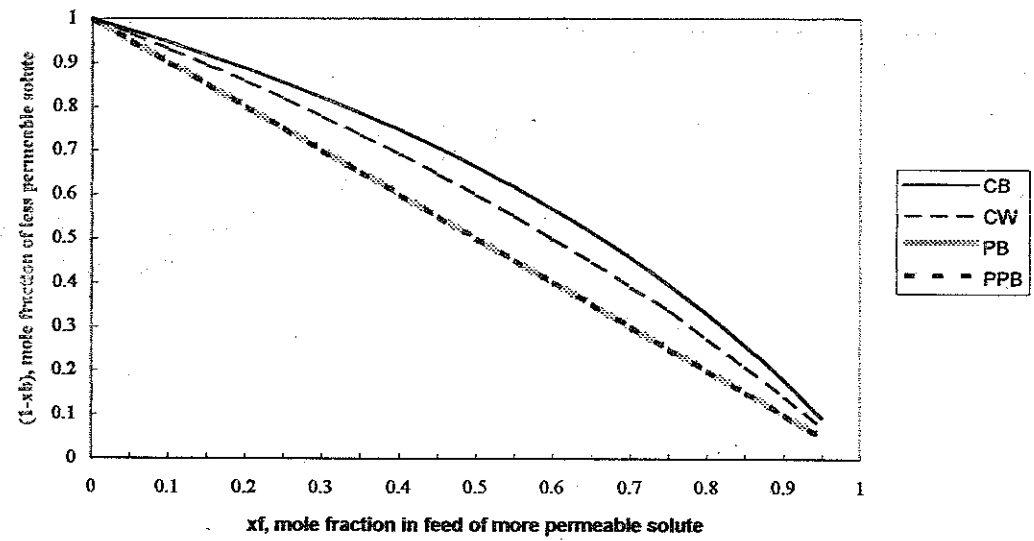

Figure 11B. Relationship Between Feed and Bottom Output
Parallel - Continuous Column Comparison

Flow Rate Parameters: Qw = 1.0 cu.cm/sec

Permeability Parameters: mass transfer coeff. ratio, $(K_A/K_B) = 2$; $K_B = 0.0001$ cm/sec

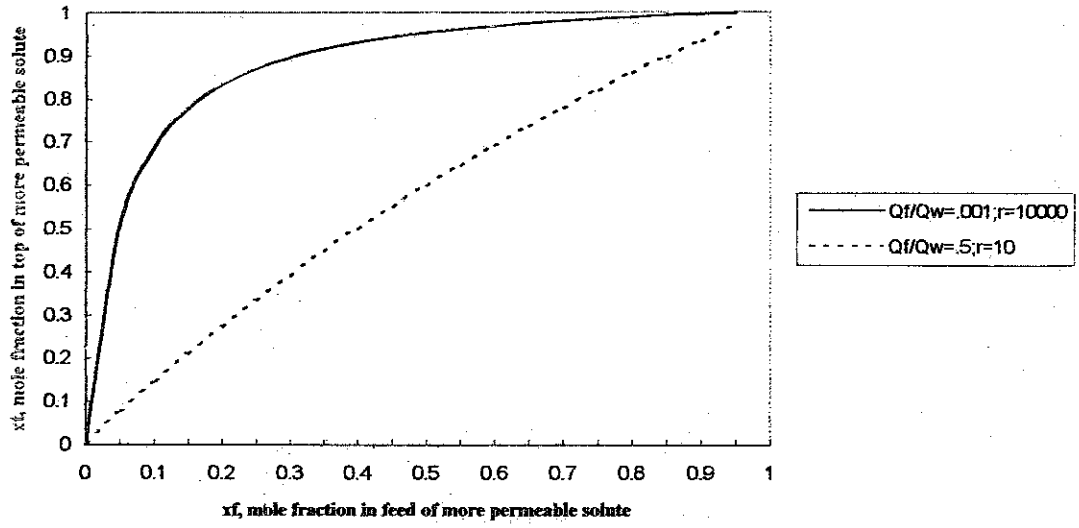

Figure 12A. Relationship Between Feed and Top Output
Continuous Column - Pilot Scale

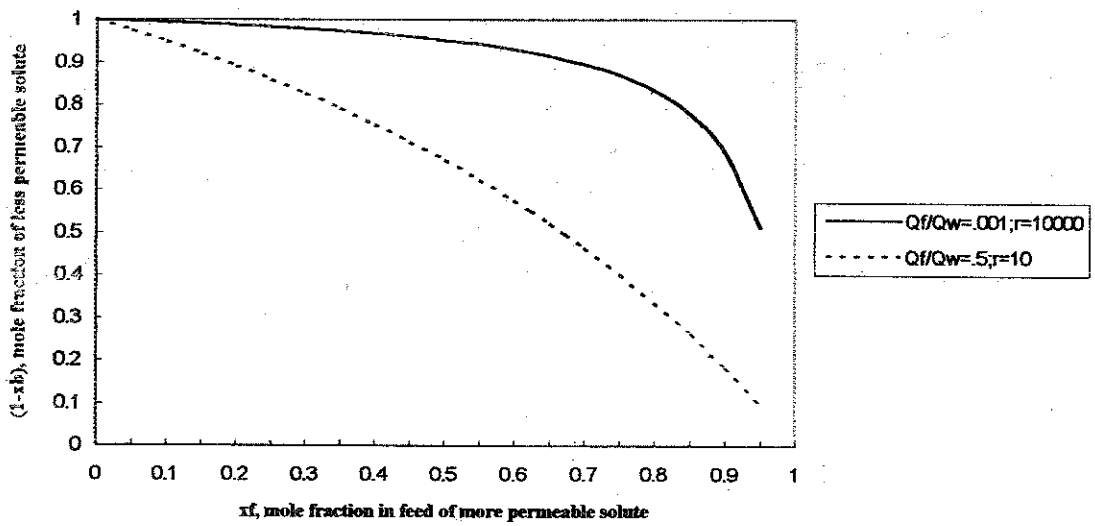

Figure 12B. Relationship Between Feed and Bottom Output
Continuous Column - Pilot Scale

Flow Rate Parameters: Qw = 100.0 cu.cm/sec, Qf/Qw = 0.25

Permeability Parameters: mass transfer coeff. ratio, $(K_A/K_B) = 2$; $K_B = 0.0001$ cm/sec

Geometry Parameters: enriching height/stripping height= 1, total membrane area= 2000000sq.cm.