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A Mathematical Analysis of Membrane Separation Parameters for Liquid/Liquid Dialysis in Single or Multiple Stages

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Abstract

The effects of membrane separation parameters using liquid/liquid dialysis under idealized conditions and using hollow fiber geometry were calculated with the aid of a computer. These calculations were carried out for both single stage and multiple stages. Membrane separation parameters include the intrinsic properties of the membrane, the nature of the dialysis solvents, the flow rates of both feed and solvent streams, and the dimension of the hollow fiber. It was concluded that an efficient process using liquid/liquid dialysis requires a membrane with a high intrinsic permeability constant and a reasonable separation factor, as small an inner radius of hollow fiber as is practical, and a dialysis solvent with an acceptable activity coefficient for the key species and a flow rate suitably coupled to that of the feed.

INTRODUCTION

It is known that liquid/liquid dialysis through selective membranes might be useful in industry and biomedicine. Purification, separation, and the artificial kidney are examples of those applications. The development of a liquid/liquid dialysis process requires a detailed knowledge of the relationship among the parameters affecting the operation of dialysis. Among these parameters are the intrinsic properties of the membrane, the nature of dialysis solvents, the flow pattern of both feed and solvent streams, and the geometry of membranes. An analysis of these parameters provides information about the range of these parameters which are desirable to achieve separation efficiently.

Walawender and Stern (*1*) have studied the membrane separation parameters for gas/gas permeation through a membrane in a single stage. For the multiple or cascade process of gas/gas permeation through the membrane, the principle of mathematical analysis were developed by Cohen (*2*) and a summary of the theory has been presented by Benedict and Pigford (*3*). However, no mathematical analysis of membrane separation parameters for liquid/liquid dialysis has ever been published. The present work deals with the mathematical analysis of some parameters which may have significant effects on liquid/liquid dialysis using the geometry of hollow fiber membranes. A numerical solution was developed for those nonlinear differential equations of dialysis through the hollow fiber membrane. A computer calculation based on the numerical solutions shows the effects of possible separation parameters on the operation of dialysis. Although this paper is limited to studies of the system of binary components in the feed stream, the principles can be extended to systems of multiple components.

DIFFERENTIAL EQUATIONS

Differential equations using countercurrent flow for dialysis through hollow fiber membranes have been proposed by J. J. Hermans (*4*)

$$\frac{d}{dx}[q(x)a(x)] = \frac{d}{dx}[Q(x)A(x)] = J_A(x) \tag{1}$$

$$\frac{d}{dx}[q(x)b(x)] = \frac{d}{dx}[Q(x)B(x)] = J_B(x) \tag{2}$$

$$\frac{d}{dx}\{Q(x)[1 - A(x) - B(x)]\} = 0 \tag{3}$$

$$a(x) + b(x) = 1 \tag{4}$$

where a(x) and b(x) are the volume fractions of Components A and B in the feed stream q(x) at position x in the hollow fiber membrane shown in Fig. 1. A(x) and B(x) are the volume fractions of Components A and B in the dialysis solvent stream Q(x) at position x in the membrane. Stream Q(x) flows on all sides of the hollow fiber. $J_A(x)$ and $J_B(x)$ are the permeation fluxes through the membrane for the Components A and B.

Equations (1) and (2) can be obtained from the principles of conservation of mass. Equation (3) is obtained by assuming that the membrane

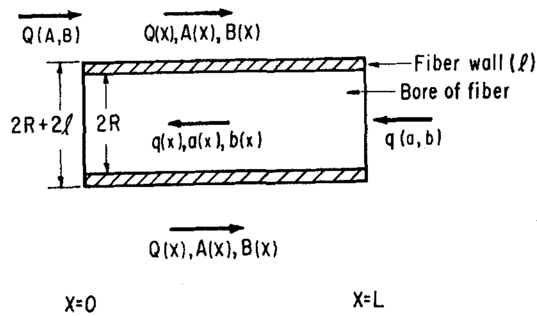

FIG. 1. Cross section of a length for a single hollow fiber (for meaning of symbols, see text).

is impermeable to the dialysis solvents. Equation (4) limits the feed stream to two components.

The above differential equations are valid only for the following conditions:

1. The flow pattern is countercurrent.
2. The partial specific volumes are constant.
3. The feed stream has only two components.
4. The membrane is impermeable to the solvents.

For the hollow fiber membrane, the permeation flux J_i can be shown to be (*4–6*)

$$J_i = \frac{2\pi P_i}{\ln\left(\frac{R+l}{R}\right)}[C_{i1} - \alpha_i C_{i2}] \tag{5}$$

where R is inside radius of hollow fiber and l is the effective thickness of membrane barrier. C_{i1} and C_{i2} are the concentrations of component i in the upstream and downstream, respectively. α_i is the partition coefficient between the phases on both sides of the membrane for the component i and is equal to the ratio of the activity coefficient of penetrant in the solvent stream over that in the feed stream.

Thus the permeation fluxes for Components A and B through the hollow fiber are given by

$$J_A(x) = \gamma_A[a(x) - \alpha A(x)] \tag{6}$$

$$J_B(x) = \gamma_B[b(x) - \beta B(x)] \tag{7}$$

where α and β are the partition coefficients for Components A and B, respectively, and where

$$\gamma_A = \frac{2\pi P_A}{\ln\left(\frac{R + l}{R}\right)}, \qquad \gamma_B = \frac{2\pi P_B}{\ln\left(\frac{R + l}{R}\right)} \tag{8}$$

If $R > l$ such that a first-order approximation via the Taylor expansion is used:

$$\gamma_A \approx \frac{2\pi R}{l} P_A, \qquad \gamma_B \approx \frac{2\pi R}{l} P_B \tag{9}$$

The above differential equations are nonlinear. Therefore, one can not solve them analytically. A numerical solution of those differential equations is possible because we have six differential equations and six unknowns [q(x), a(x), b(x), Q(x), A(x), B(x)].

COMPUTER PROGRAMS

Computer programs were written to solve differential equations for liquid/liquid dialysis through the hollow fiber. These programs were used for parametric studies of the assumed binary mixture separation under conditions outlined in the following sections. The computations were performed with the aid of a CDC 6600 computer using Fortran IV. A description of the programs follows.

Combining Eqs. (1) and (2) and substituting Eqs. (6) and (7), one can obtain

$$\frac{d\mathrm{q}(x)}{dx} = \gamma_A[\mathrm{a}(x) - \alpha \mathrm{A}(x)] + \gamma_B[\mathrm{b}(x) - \beta \mathrm{B}(x)] \tag{10}$$

Similarly, one can combine Eqs. (1), (2), and (3) to obtain

$$\frac{d\mathrm{Q}(x)}{dx} = \gamma_A[\mathrm{a}(x) - \alpha \mathrm{A}(x)] + \gamma_B[\mathrm{b}(x) - \beta \mathrm{B}(x)] \tag{11}$$

Equations (1) and (2) can be rewritten to be

$$\frac{d}{dx}[\mathrm{q}(x)\mathrm{a}(x)] = \gamma_A[\mathrm{a}(x) - \alpha \mathrm{A}(x)] \tag{12}$$

$$\frac{d}{dx}[\mathrm{Q}(x)\mathrm{A}(x)] = \gamma_A[\mathrm{a}(x) - \alpha \mathrm{A}(x)] \tag{13}$$

$$\frac{d}{dx}[\mathrm{q}(x)\mathrm{b}(x)] = \gamma_{\mathrm{B}}[\mathrm{b}(x) - \beta \mathrm{B}(x)] \tag{14}$$

$$\frac{d}{dx}[\mathrm{Q}(x)\mathrm{B}(x)] = \gamma_{\mathrm{B}}[\mathrm{b}(x) - \beta \mathrm{B}(x)] \tag{15}$$

The following computation procedure for countercurrent dialysis may be used if one knows the boundary conditions for the feed and solvent streams, i.e., q(L), a(L), b(L), A(o), B(o), Q(o), A(L)/[A(L) + B(L)] where the coordinate of the membrane is shown in Fig. 1.

1. Specify P_A, P_B, R, l, α, β, q(L), a(L), b(L), Q(o), A(o), B(o), A(L)/[A(L)+B(L)]. (It is assumed that P_A, P_B, α, and β are independent of concentration.)
2. Assumed a(o), q(o), and L.
3. Calculate b(o) from Eq. (4).
4. Calculate dq(x)/dx at $x = 0$ using Eq. (10).
5. Partition L such that the following approximations hold for all x:

$$\mathrm{q}(x + \Delta L) \approx \mathrm{q}(x) + \frac{d\mathrm{q}(x)}{dx}\Delta L \tag{16}$$

6. Calculate q(ΔL) using Eqs. (10) and (16).
7. Calculate q(ΔL)a(ΔL) by using Eq. (12). Therefore, one can calculate a(ΔL). b(ΔL) is calculated similarly.
8. Calculate Q(ΔL), A(ΔL), and B(ΔL) similarly.
9. Procedures 4–8 give the values of q, a, b, Q, A, and B as a function of x.
10. Compare calculated a(L), q(L), and A(L)/ [A(L) + B(L)] with those values specified previously. Repeat the calculation with other values of a(o), q(o), and L until agreement is obtained.

The above procedure is used for a single stage of countercurrent dialysis with the boundary conditions specified by feed and solvent streams. For other cases such as multiple stages or cocurrent dialysis, the procedure is similar except for slight modifications.

PARAMETRIC STUDIES

The following conditions were assumed for the calculation of the effects of the parameters in countercurrent liquid/liquid dialysis.

1. The basic permeation unit was of 8 in. diameter, 10 ft long, with a packing density of 52%. Thus the number of hollow fibers in this unit, N, varies as a function of inner radius of hollow fiber:

$$N = 5.76 \times 10^8/R^2$$

   where R is the inside radius of hollow fiber in microns. The ratio of the outer to inner radius is assumed to be 3.
2. Poiseuille's equation was used to calculate the pressure drop through the length of hollow fiber (i.e., all flow was laminar). The pressure drop was calculated only in the bore streams. The viscosity of the feed stream was assumed to be 0.3 cP.
3. The desired product for the separation of mixtures of A/B is 90% A (A(L)/[A(L) + B(L)] = 0.9) with a total product rate of 2040 cc/sec (10^8 lb/year if the density is 0.72). The separation train was pictured schematically as:

```
                 ┌──→I II III --- m──┐
Feed solution →  │ →I II III --- m→  │ → Product
                 └──→I II III --- m──┘
```

Thus, in the calculation of the total number of permeation units needed, the number in series for a single train was multiplied by the number of trains.

Another design variable involves the feed concentration to the top stage as expressed by the arbitrarily defined selectivity limit (s.l.).

$$\text{s.l.} = [\mathrm{A}(L)/\mathrm{B}(L)]/[\mathrm{a}(L)/\mathrm{b}(L)]$$

The maximum value of s.l. is the $SF_B{}^A$ (the ratio of permeability constants of components A and B) and the s.l. is shown directly in each table or indirectly as a(L).

Single Stage

This is illustrated by the top stage in Fig. 2 and in the example in the next section. The following conclusions were drawn based on those calculations.

1. The permeation rate for a given 8 in. × 10 ft basic unit is inversely proportional to the inner radius of the hollow fiber (because N, the number of fibers per basic unit $\propto 1/R^2$, and the total permeation rate $\propto (N \times R)$, so that rate $\propto 1/R$). However, the pressure

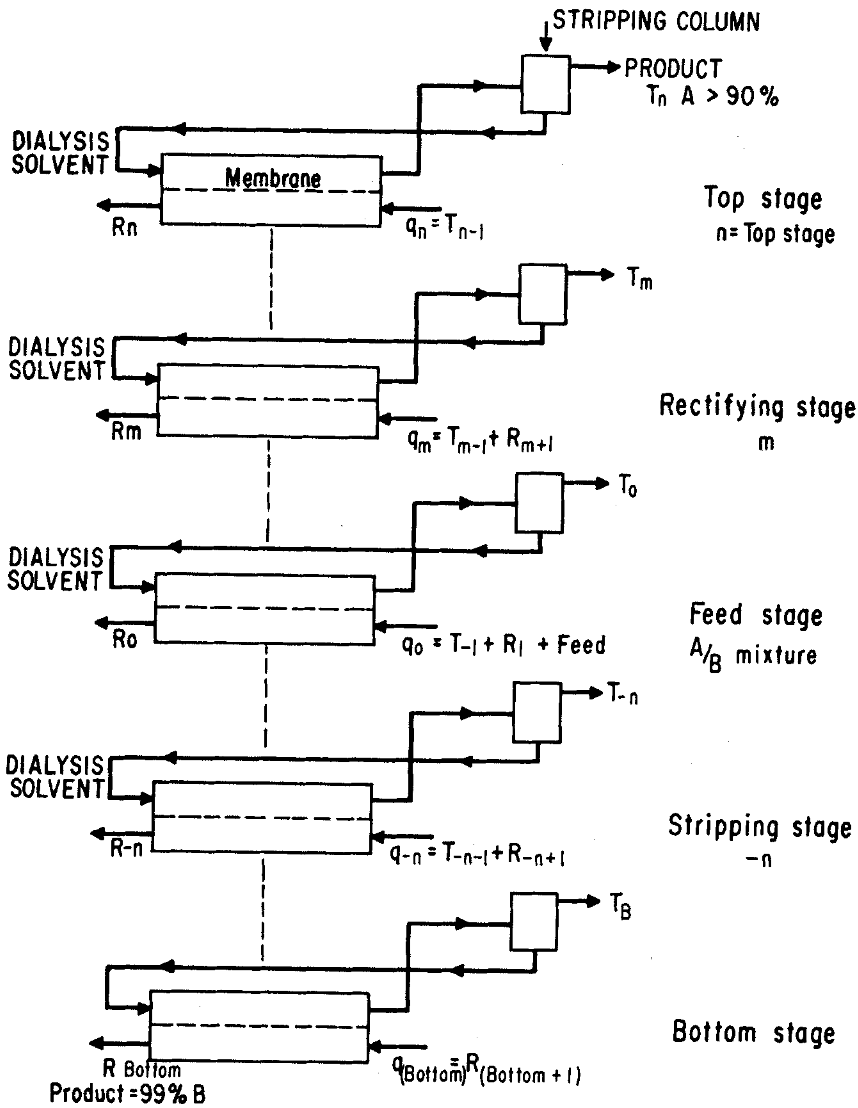

FIG 2. Staged process for the separation of mixture A/B via membranes using countercurrent liquid/liquid dialysis.

drop through the total length of a hollow fiber for a given degree of separation (where many basic units are arranged in series) will be inversely proportional to the fifth power of the inner radius [because $\Delta p \propto (\bar{q} \times L)/R^4$ while $\bar{q}$ is the same for the fibers in each case and $L \propto 1/R$ so that $\Delta p \propto 1/R^5$]. Table 1 shows the effect of varying the radius.

2. There is only a small effect of the s.l. on the required number of 8 in. × 10 ft hollow fiber units for the top stage (Table 2). However, there is an optimum value of the s.l. in considering the total number of stages required.
3. The permeation rate is obviously proportional to the membrane intrinsic permeability constant (P_A/l). Thus the required number of hollow fiber units will be cut in half if we can double the value of P_A/l. The pressure drop is inversely proportional to the values of P_A/l. [$L \propto 1/(P_A/l)$; pressure drop $\propto L \propto 1/(P_A/l)$]. Table 3 shows the effects of varying P_A/l.
4. If the values of q(L) and Q(o) are changed to kq(L) and kQ(o), the

TABLE 1

The Effects of Varying the Inner Radius of the Hollow Fiber (Top Stage)

R (μ)	a(o)	q(o)	Q(L)	A(L)	L (cm)	Δp (pressure drop) (psi)	No. of units required
150	0.68	0.0124	0.033	0.075	400	12	43
100	0.68	0.0124	0.033	0.075	600	92	28

[a]Conditions: a(L) = 0.72, q(L) = 0.0152, A(o) = B(o) = 0, Q(o) = 0.0304, $\alpha = \beta = 1.0$, $P_A/l = 0.25 \times 10^{-4}$, $SF_B^A = 4$, A(L)/[A(L) + B(L)] = 0.9. The units of P/l are cc/sec-cm^2-Δ (volume fraction), and q or Q is cc/sec/fiber. $SF_B^A = P_A/P_B$.

TABLE 2

The Effects of s.l. on the Number of Units Required (Top Stage)[a]

s.l.	a(L)	a(o)	q(o)	Q(L)	A(L)	L (cm)	Δp (psi)	No. of units required
2.5	0.78	0.61	0.0063	0.0393	0.203	1.4×10^3	33	47
3.0	0.75	0.655	0.0093	0.0363	0.146	888.9	23	45
3.5	0.72	0.68	0.68	0.0124	0.033	400	12	43

[a]Conditions: q(L) = 0.0152, A(o) = B(o) = 0, Q(o) = 0.0304, $P_B/l = 0.25 \times 10^{-4}$, $P_A/l = 10^{-4}$, $SF_B^A = 4$, R = 150 μ, $\alpha = \beta = 1.0$. A(L)/[A(L) + B(L)] = 0.9.

pressure drop is increased by a factor of k^2, while the required length of the hollow fiber is changed k times. However, the required number of units does not change. The advantage of varying q(L) and Q(o) is that one can control pressure drop without changing the number of hollow fiber units. Table 4 reflects those results.

5. The effect of changing the distribution coefficient (α) of the component A and the value of q(L)/Q(o) [Q(o) $\geqq$ q(L)] is not large in the top stage. However, small values of α still give some advantages as shown in Table 5.

TABLE 3

The Effects of Varying P_A/l of the Hollow Fiber Membrane (Top Stage)[a]

P_A/l	P_B/l	q(o)	a(o)	Q(L)	A(L)	L (cm)	Δp (psi)	No. of units required
5×10^{-4}	$\frac{1}{4} \times 5 \times 10^{-4}$	0.0124	0.68	0.033	0.0753	120	18	6
10^{-4}	$\frac{1}{4} \times 10^{-4}$	0.0124	0.68	0.033	0.0753	600	92	30

[a]Conditions: a(L) = 0.72, q(L) = 0.0152, A(o) = B(o) = 0, $\alpha = \beta = 1.0$, R = 100 μ, SF_B^A = 4. A(L)/[A(L) + B(L)] = 0.9.

TABLE 4

The Effect of Varying q(L) and Q(o) by the Same Factor k (Top Stage)[a]

q(L)	k	Q(o)	a(o)	q(o)	A(L)	Q(L)	L (cm)	Δp (psi)	No. of units required
0.076	5	0.152	0.68	0.062	0.0753	0.166	600	460	6
0.0152	1	0.0304	0.68	0.0124	0.0753	0.033	120	18	6

[a]Conditions: a(L) = 0.72, A(o) = B(o) = 0, $\alpha = \beta = 1.0$, $P_A/l = 5 \times 10^{-4}$, $P_B/l = \frac{1}{4} \times 5 \times 10^{-4}$, R = 100 μ, A(L)/[A(L) + B(L)] = 0.9.

TABLE 5

The Effect of Varying the Partition Coefficient (Top Stage)[a]

α	a(o)	q(o)	A(L)	Q(L)	L (cm)	No. of units required
1.0	0.804	0.0956	0.141	0.360	7.19×10^4	376
0.1	0.768	0.069	0.192	0.387	9.91×10^4	354

[a]Conditions: a(L) = 0.84, q(L) = 0.152, A(o) = B(o) = 0, Q(o) = 0.304, R = 150 μ, $P_A/l = 10^{-5}$, $P_B/l = \frac{1}{4} \times 10^{-5}$, β = 1.0. A(L)/[A(L) + B(L)] = 0.9.

Multiple Stages

The basic process scheme for separation of a A/B system is shown in Fig. 2. The feed stream is 114,200 lb/hr with 12% A and 88% B. The desired product streams are 99% B and >90% A. Based on these conditions, the results of a typical calculation are shown in Table 6. Based on a series of calculations, the following conclusions were reached.

1. An increase in the separation factor (with a constant P_A/l) decreases the number of stages and the total number of units required. An abrupt decrease in the number of hollow fiber units required was found as the values of SF were changed from 2 to 4. As the values of SF were made larger than 6, the number of stages and the number of hollow fiber units required did not change significantly (cf. Table 7).
2. The effect of the "partition coefficient" of A and B between the dialysis solvent and feed solution on the efficiency of hollow fiber dialysis depends greatly on the value of the membrane separation factor, SF. For high SF values the values of α, the "partition coefficient" of the A component, are more important than the selectivity ratio of the solvents (β/α, the ratio of partition coefficient of A divided by that of the B). For a low SF value ($1.0 < SF < 2.0$), the selectivity of the solvent becomes more important. Thus the separation of 114,200 lb/hr mixture of A/B (12% B) into 99% B

TABLE 6

Typical Results for the Calculation of the Separation of A/B via Hollow Fiber Countercurrent *l/l* Dialysis[a]

Stage no.	q lb/hr	q %A	*R* lb/hr	*R* %A	*T* lb/hr	*T* %A	No. of units required (each in 8 × 10 ft)
3 (product)	20,180	82.18	6,632	58.66	13,550	93.697	31
2	37,800	58.66	17,620	31.72	20,180	82.18	65
1	73,740	31.72	42,580	12	31,170	58.66	158
0 (feed)	215,800	12	159,700	5.07	56,130	31.72	396
−1 (raffinate)	159,700	5.07	100,600	1	59,080	12	523
						Total =	1173

[a]Input: q(*L*) = 0.001 cc/sec/fiber, Q(o) = 0.002 cc/sec/fiber, $\alpha = \beta = 1.0$. Feed = 114,200 lb/hr with 12% A in the A/B mixture. $P_A/l = 5 \times 10^{-5}$, $P_B/l = 8.33 \times 10^{-6}$, ID = 100 μ. The units of P/l are cc/sec-cm^2-Δ(vol fraction).

and >90% A can be achieved either with a membrane with SF = 6.0, α = 1.0, β = 1.0 or with a membrane with SF = 1.0, α = 1.0, β = 10.0, with the total number of 8 in. × 10 ft hollow fiber units required being about 1000 in both cases. For a SF value of 6 with

TABLE 7

The Effects of the Separation Factor of the Membrane on the Number of Required Hollow Fiber Units for the Process of Separation of A/B Mixture (Countercurrent Dialysis)[a]

P_A/l	P_B/l	SF^A_B	No. of stages required	No. of units[b] required
5×10^{-5}	2.5×10^{-5}	2	11	6979
5×10^{-5}	1.25×10^{-5}	4	6	1651
5×10^{-5}	8.33×10^{-6}	6	5	1173
5×10^{-5}	6.25×10^{-6}	8	5	1011
5×10^{-5}	5×10^{-6}	10	4	894

[a]Input: Same as Table 6, except for P_B/l.
[b]The number of units required refers to a standard 8 in × 10 ft hollow fiber bundle.

TABLE 8

The Effects of the "Partition Coefficients" of A and B on the Number of Hollow Fiber Units (8 in. × 10 ft) Required for the Process of Separation of the Mixture via Hollow Fiber Countercurrent Dialysis[a]

α	β	q(L)	Q(o)	P_A/l	P_B/l	No. of stages	Total no. of units required
1	1	1×10^{-3}	1.5×10^{-3}	5×10^{-5}	8.33×10^{-6}	5	1327
1	3	〃	1.5×10^{-3}	〃	〃	5	1220
1	6	〃	1.5×10^{-3}	〃	〃	5	1010
1	1	〃	2×10^{-3}	〃	〃	5	1173
1	3	〃	2×10^{-3}	〃	〃	5	1104
1	6	〃	2×10^{-3}	〃	〃	5	1024
1	1	〃	4×10^{-3}	〃	〃	5	987
1	3	〃	4×10^{-3}	〃	〃	5	959
1	6	〃	4×10^{-3}	〃	〃	5	923
0.5	6	〃	2×10^{-3}	〃	〃	5	919
2	2	〃	1.5×10^{-3}	〃	〃	6	3190
2	4	〃	1.5×10^{-3}	〃	〃	6	3366
2	8	〃	1.5×10^{-3}	〃	〃	5	2515
1	1	〃	2×10^{-3}	〃	2.5×10^{-5}	11	6979
1	3	〃	2×10^{-3}	〃	〃	9	3014
1	6	〃	2×10^{-3}	〃	〃	7	1687
1	10	〃	2×10^{-3}	〃	〃	5	1136
1	10	〃	1×10^{-3}	〃	5×10^{-5}	5	1184

[a]The inputs are the same as those in Table 6, unless specified otherwise in Table 8.

$\alpha = 1.0$, a value of $Q(o)/q(L)$ of 4 will give the similar results as for the case where $\alpha = 0.5$ and the $Q(o)/q(L) = 2$. Some of these results are shown in Table 8.

CONCLUSIONS

We have discussed the differential equations for liquid/liquid dialysis through hollow fibers, the method of numerical solution of those differential equations, and the use of a computer to calculate the separation of typical A/B mixtures into a desired product either in a single stage or in multiple stages.

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